Exploring the Synergy of Functionalised Bio-carbons and their Performance in Supercapacitor Devices

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To my beloved mom Sophie, grandparents, Dan (d) and Oscar
Declaration

I, Dina Ibrahim Abouelamaiem, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

............................

Signature

............................

Date
Acknowledgements

I am not sure where to start as I can go forever in the only personal section (but also so close to my heart) in this thesis. It all started on the 19th of October, 2014 when I knew that Dan Brett will be my PhD supervisor, and I will never forget how I danced on my bed back in Lebanon that night. I was so scared the first time I met you, and wasn’t sure if I will fit in the EIL, but I have changed so much over the course of 4 years, hugely because of you. Dan, I can’t start to describe how much I love you and appreciate all your support for me throughout the years. I will always see a dad character in you that I never had, though you are not that old. The support, respect and appreciation you have shown me throughout the years, I will never forget. You have seen and treated me as a person, and not a number in your group, and that is quite rare these days. I look forward to all the coming meetings in your office, or most probably at the pub. I love you and I hope I will always be part of your family, or maybe work together one day if I ever reach half the figure you are to me. Thank you from the bottom of my heart for never giving up on me and accepting me as I am, Dan Brett.

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“Look deep into nature, and then you will understand everything better.” - Albert Einstein
Abstract

Supercapacitors have gained increasing interest due to their complementary performance to batteries and fuel cells. The electrochemical device has proven to provide exceptional performance through enhancing the electrode materials, exploration of potential electrolyte solutions, integration in new cell designs and therefore improving their performance to meet the needs of high energy and power requirements. However, there is little insight of the complex, multi-dimensional characterisation and correlation between the porous carbon structures generally exploited as electrode materials, and deviation-from-ideality performance in electrical double layer capacitors. The investigation from functionalisation of countless bio-carbons and their application in supercapacitor devices, to the prospective electrochemical dynamics in supercapacitors is not well established.

In this thesis, one-, two- and three-dimensional characterisation techniques, in combination with electrochemical quantification of activated cellulose carbons are used to tackle the effect of porous carbon structures on the behaviour of symmetric carbon supercapacitors. Non-ideal mechanisms were examined using the electrochemical impedance spectroscopy technique to quantify capacitances and relaxation times’ variation in wide frequency ranges across different carbonaceous morphologies. Extreme voltage conditions were employed and characterised with in-situ Raman spectroscopy to identify the electrode state-of-art and a critical reasoning for different performance rates. A printed circuit board design has been suggested as a promising device for the application of supercapacitors and possible integration with other electrochemical cells.

The experimental evaluations reported herein classify unreported affiliation between diversified architectural and electrochemical features. The interplay between structural dynamics and electrochemistry at standard and extreme conditions are described, highlighting the interpretation and importance of assessing non-ideal behaviour in supercapacitors. A new engineering approach for supercapacitor devices is revealed that opens a platform for hybridized systems in a well-known design. These perceptions are expected to be adapted for a better understanding of the framework of different supercapacitor devices and consideration of new design models.
Impact Statement

Communicating with Mother Nature: From green materials to green solutions.

A new approach utilises cellulose in trees and turns it into activated carbon, serving to meet environmental and sustainability requirements. The activated carbon is implemented as an electrode material for an electrochemical energy conversion and storage cell, which opens a platform for greener electronic and power applications.

“We shall need a substantially new way of thinking if humanity is to survive.” More than 60 years after Einstein immortalised these words, we are still facing ever growing problems of climate change, global warming and increased pollution levels. In addition, depletion of fossil fuels has also been identified as a future challenge, particularly when coupled with increasing energy demand and consumption. This drives the urge for alternative and renewable energy sources. The Electrochemical Innovation Lab (EIL) at UCL, led by Professor Dan Brett and Professor Paul Shearing, has been pioneering in the research field of electrochemical energy conversion and storage devices, including fuel cells, batteries, electrolyzers and supercapacitors. Each device is distinguished by its own unique advantageous characteristics, while all share the motivation of applying greener raw materials and/or the greener application of methods for final applications. In addition, the hybridization of these electrochemical cells has proven to have a great potential in replacing conventional energy sources to power devices such as phones, wearable and flexible electronics and electric vehicles.

Supercapacitors have been extensively studied in the literature and subsequently industrially commercialized, bridging the gap between fuel cells and batteries. They can be used as back-up power sources and/or for instant charging and discharging, having long shelf-lives.

In collaboration with Queen Mary University of London and the Chemistry department at UCL, and as part of the London Energy Materials and Devices Hub, the structure of different carbon materials has been characterised. Originating from Pinus Silvestris and Picea Abies trees, these materials have been further implemented in supercapacitors, where structural characterisations have been investigated and synergized with their electrochemical performance in the fabricated devices. The co-dependent relationship between microstructure, surface chemistry and electrochemistry is investigated, leading to a deep understanding of the different factors that influence capacitive performance. Ultimately, this provides information on how to optimize the micro-architecture for the final application as an electrochemical device.
Supercapacitors can also be hybridized with fuel cells, in a conventional and cost-effective design, which will accelerate the commercialization process and meets different energy and power demands. The integration of supercapacitors within engineered constructs has been successfully applied in different configurations and has proven to have great potential for meeting the ever-increasing energy and power demands.

The application of different electrochemical systems and the green future they promise are also a part of the mission statement of the non-profit public outreach group UCell, UCL Fuel Cells, initiated in the EIL. Engagement with the public at science festivals, school visits and social events raises awareness of the environmental concerns that everyone shares, and the drive towards, but also the possibility for, readily-available solutions: electrochemical systems.

“I did not know we still have time to save the world”.—7 year old at the Queen Elizabeth Olympic Park Bright Ideas Project.

The cross-disciplinary study of the materials chemistry and their microstructure, along with their electrochemistry and performance in supercapacitor applications has been peer reviewed and published, leading to increased investment in this research field, and paving the way for meeting energy and power demands of our day.
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<tbody>
<tr>
<td>$F_y$</td>
<td>Electrostatic Force [N]</td>
</tr>
<tr>
<td>$E$</td>
<td>Potential [V]</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Overpotential [V]</td>
</tr>
<tr>
<td>$E_e$</td>
<td>Electric Field [$N \ C^{-1}$]</td>
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<tr>
<td>$Q$</td>
<td>Charge [C]</td>
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<tr>
<td>$q$</td>
<td>Differential Charge [C]</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Dielectric Constant</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of Vacuum [$8.85 \times 10^{-12} \ C^2 N^{-1} m^{-2}$]</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Surface Charge Density [C m$^{-2}$]</td>
</tr>
<tr>
<td>$C$</td>
<td>Capacitance [F]</td>
</tr>
<tr>
<td>$C_s$</td>
<td>Specific Capacitance [F g$^{-1}$]</td>
</tr>
<tr>
<td>$C_{dl}$</td>
<td>Double-layer Capacitance [F]</td>
</tr>
<tr>
<td>$C_{diff}$</td>
<td>Diffusive Capacitance [F]</td>
</tr>
<tr>
<td>$C_H$</td>
<td>Helmholtz Double-layer Capacitance [F]</td>
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<tr>
<td>$C_{diff}$</td>
<td>Differential Capacitance [$\mu F \ cm^{-2}$]</td>
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<tr>
<td>$I$</td>
<td>Current [A]</td>
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<tr>
<td>$i$</td>
<td>Current Density [A g$^{-1}$]</td>
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<tr>
<td>$i_0$</td>
<td>Exchange Current Density [A]</td>
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<td>$i_{dl}$</td>
<td>Double-layer charging current [A]</td>
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<td>$i_F$</td>
<td>Faradaic leakage current [A]</td>
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<tr>
<td>$U_e$</td>
<td>Electrostatic Energy [J mol$^{-1}$]</td>
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<td>$U_c$</td>
<td>Chemisorption Energy [J mol$^{-1}$]</td>
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<td>$E_k$</td>
<td>Kinetic energy [J mol$^{-1}$]</td>
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<td>$P_m$</td>
<td>Gravimetric power Density [W kg$^{-1}$]</td>
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<td>$E_m$</td>
<td>Gravimetric energy density [Wh kg$^{-1}$]</td>
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<tr>
<td>$P_V$</td>
<td>Volumetric power density [mW cm$^3$]</td>
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<tr>
<td>$E_V$</td>
<td>Volumetric energy density [mWh cm$^3$]</td>
</tr>
<tr>
<td>$U_y$</td>
<td>Work [J]</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s Constant [$9.65 \times 10^4 \ C \ mol^{-1}$]</td>
</tr>
<tr>
<td>$V$</td>
<td>Rate of Reaction [units depend on order of reaction involved]</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of Electrons per mole product</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Change in Gibb's Free Energy [J mol$^{-1}$]</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Barrier Symmetry Factor</td>
</tr>
<tr>
<td>$K$</td>
<td>Rate Constant of Reaction at zero Potential [units depend on order of reaction involved]</td>
</tr>
<tr>
<td>$R$</td>
<td>Ideal Gas Constant [$J \ kmol^{-1}$]</td>
</tr>
<tr>
<td>$\theta_h$</td>
<td>electrode surface coverage by the product</td>
</tr>
<tr>
<td>$C_{H^+}$</td>
<td>Local concentration of reacting $H^+$ ions at the electrode surface [M]</td>
</tr>
<tr>
<td>$\alpha_t$</td>
<td>Transfer coefficient</td>
</tr>
<tr>
<td>$\tau_c$</td>
<td>Tortuosity factor</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro's number [$6.022 \times 10^{23} \ mol^{-1}$]</td>
</tr>
<tr>
<td>$A$</td>
<td>Area [$m^2$]</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass of active material [g]</td>
</tr>
<tr>
<td>$d$</td>
<td>Distance between two parallel plates of capacitor [m]</td>
</tr>
<tr>
<td>$SSA$</td>
<td>Specific surface area [$m^2 \ g^{-1}$]</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>Time for discharge half-cycle [s]</td>
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<tr>
<td>$\Delta V$</td>
<td>Voltage/potential window of cycling [V]</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure [bar]</td>
</tr>
<tr>
<td>$P_0$</td>
<td>Saturation pressure at 77 K [1 bar]</td>
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<tr>
<td>$A_m$</td>
<td>cross-sectional area of the adsorbed molecule [$m^2$]</td>
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<td>$n_m$</td>
<td>monolayer capacity</td>
</tr>
<tr>
<td>$S$-value</td>
<td>Stability value</td>
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<td>OCV</td>
<td>Open circuit voltage [V]</td>
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<td>$iR$</td>
<td>Ohmic drop [V]</td>
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<tr>
<td>$\varepsilon_p$</td>
<td>Porosity</td>
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<tr>
<td>$V_{Hg}$</td>
<td>Intruded mercury volume [$cm^3 \ g^{-1}$]</td>
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<tr>
<td>$E_{ref}$</td>
<td>Reference potential [V]</td>
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<tr>
<td>$Q_{ad}$</td>
<td>quantity adsorbed at a specified pressure [$cm^3$]</td>
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<tr>
<td>$\rho(r)$</td>
<td>equilibrium density profile [g cm$^{-3}$]</td>
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<tr>
<td>$\rho o(r)$</td>
<td>quantity of adsorptive, present in the absence of wall forces [g cm$^{-3}$]</td>
</tr>
<tr>
<td>$V_T$</td>
<td>Total pore volume [$cm^3 \ g^{-1}$]</td>
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<tr>
<td>$V_{N2}$</td>
<td>Total pore volume adsorbed with $N_2$ [$cm^3 \ g^{-1}$]</td>
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<td>$V_{CO2}$</td>
<td>Total pore volume adsorbed with $CO_2$ [$cm^3 \ g^{-1}$]</td>
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<tr>
<td>$I_D$</td>
<td>Intensity of D-band [a.u.]</td>
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<tr>
<td>$I_G$</td>
<td>Intensity of G-band [a.u.]</td>
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<tr>
<td>$L_a$</td>
<td>In-plane crystallite size [nm]</td>
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<tr>
<td>$\lambda_i$</td>
<td>Excitation wavelength in the Raman spectroscopy</td>
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<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$s$</td>
<td>Sweep rate of cyclic voltammogram [mV s$^{-1}$]</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature [K]</td>
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<tr>
<td>$L$</td>
<td>Inductance [H]</td>
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<tr>
<td>$T$</td>
<td>Relaxation time [s]</td>
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<tr>
<td>$f$</td>
<td>Frequency [Hz]</td>
</tr>
<tr>
<td>$f_{45}$</td>
<td>Knee frequency corresponding to 45° phase angle [Hz]</td>
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<tr>
<td>$Z_{\text{mod}}$</td>
<td>Impedance modulus [ohm]</td>
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<tr>
<td>$Z_{\phi}$</td>
<td>Phase angle [$^\circ$]</td>
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<tr>
<td>$Z'$</td>
<td>Impedance real part [ohm]</td>
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<tr>
<td>$Z''$</td>
<td>Impedance imaginary part [ohm]</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Angular frequency [radians s$^{-1}$]</td>
</tr>
<tr>
<td>$J$</td>
<td>Square root of negative 1</td>
</tr>
<tr>
<td>$A$</td>
<td>Non-ideality factor of capacitance</td>
</tr>
<tr>
<td>$R_F$</td>
<td>Faradaic resistance [ohm]</td>
</tr>
<tr>
<td>$R_{\text{PSD}}$</td>
<td>Resistance of electrolyte in corresponding PSD [ohm]</td>
</tr>
<tr>
<td>$R_{\text{CT}}$</td>
<td>Charge transfer resistance [ohm]</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Resistance of electrolyte inside the pores [ohm]</td>
</tr>
<tr>
<td>$ESR$</td>
<td>Equivalent series resistance [ohm]</td>
</tr>
<tr>
<td>$CPE$</td>
<td>Constant phase element [F]</td>
</tr>
<tr>
<td>$PZC$</td>
<td>Point of zero charge [V]</td>
</tr>
<tr>
<td>Abbreviations</td>
<td>Definition</td>
</tr>
<tr>
<td>---------------</td>
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</tr>
<tr>
<td>A-47N</td>
<td>Arlon-47N</td>
</tr>
<tr>
<td>AC</td>
<td>Activated carbons</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>AgCl</td>
<td>Silver chloride</td>
</tr>
<tr>
<td>BAC</td>
<td>Bead-shaped activated carbon</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmet-Teller</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CO2</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CP</td>
<td>Conducting polymer</td>
</tr>
<tr>
<td>CPE</td>
<td>Constant phase element [F]</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>EDLC</td>
<td>Electric double-layer capacitor</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>ESR</td>
<td>Equivalent series resistance [ohm]</td>
</tr>
<tr>
<td>FOV</td>
<td>Field of view</td>
</tr>
<tr>
<td>GCD</td>
<td>Galvanostatic charge discharge</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>H2</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>H2O</td>
<td>Water</td>
</tr>
<tr>
<td>H2SO4</td>
<td>Sulfuric Acid</td>
</tr>
<tr>
<td>H3PO4</td>
<td>Phosphoric acid</td>
</tr>
<tr>
<td>Hg</td>
<td>Mercury</td>
</tr>
<tr>
<td>IHP</td>
<td>Inner Helmholtz layer</td>
</tr>
<tr>
<td>KB</td>
<td>Ketjen Black</td>
</tr>
<tr>
<td>KCl</td>
<td>Potassium chloride</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium Hydroxide</td>
</tr>
<tr>
<td>MnO2</td>
<td>Manganese oxide</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
</tr>
<tr>
<td>N2</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Na2SO4</td>
<td>Sodium sulfate</td>
</tr>
<tr>
<td>NAC</td>
<td>Norit activated carbon</td>
</tr>
<tr>
<td>NH4Cl</td>
<td>Ammonium chloride</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>Abbreviations</td>
<td>Definition</td>
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</tr>
<tr>
<td>NiO</td>
<td>Nickel oxide</td>
</tr>
<tr>
<td>NLDFT</td>
<td>Non-local density functional theory</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>O₂</td>
<td>Oxygen</td>
</tr>
<tr>
<td>OHP</td>
<td>Outer Helmholtz layer</td>
</tr>
<tr>
<td>PANI</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PCB</td>
<td>Printed circuit board</td>
</tr>
<tr>
<td>Ppy</td>
<td>Polypyrrol</td>
</tr>
<tr>
<td>Pre-preg</td>
<td>Pre-impregnated composite fibres</td>
</tr>
<tr>
<td>PSD</td>
<td>Pore size distribution</td>
</tr>
<tr>
<td>PTFE</td>
<td>polytetrafluoroethylene</td>
</tr>
<tr>
<td>PTh</td>
<td>Polythiophene</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinylalcohol</td>
</tr>
<tr>
<td>PVDF</td>
<td>polyvinylidene fluoride</td>
</tr>
<tr>
<td>pzc</td>
<td>Point of zero charge [V]</td>
</tr>
<tr>
<td>RS</td>
<td>Raman spectroscopy</td>
</tr>
<tr>
<td>RSF</td>
<td>Relative sensitivity factor</td>
</tr>
<tr>
<td>RuOₓ</td>
<td>Ruthenium oxide</td>
</tr>
<tr>
<td>SC</td>
<td>Supercapacitor</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single-walled carbon nanotube</td>
</tr>
<tr>
<td>TEABF₄</td>
<td>Tetraethylammonium tetrafluoroborate</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TEMABF₄</td>
<td>triethylmethylammonium tetrafluoroborate</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>TLM</td>
<td>Transmission line model</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>Vanadium oxide</td>
</tr>
<tr>
<td>VSIA</td>
<td>Volume specific interfacial area [μm⁻¹]</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>X-ray CT</td>
<td>X-ray computed tomography</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>Zinc chloride</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

With the ever growing demand and consumption of energy by modern society, fossil fuels remain the major source of energy generation. In addition to the continuous greenhouse gas emissions and the threat of global warming, supplies of oil are increasingly dwindling and its extraction is becoming more costly. The rapidly developing global economy, depletion of fossil fuels and increasing environmental challenges, therefore call for alternative and more sustainable energy sources [1]. Electrochemical energy conversion and storage devices, in the form of batteries, fuel cells and supercapacitors, offer the benefits of high efficiency, flexibility and wide applicability, which can be partnered with intermittent renewable energy generation capacity to provide secure, low-carbon electricity supply [2]. Supercapacitors (SCs), also known as electrochemical capacitors or ultracapacitors, are charge-storage devices, consisting of two parallel electrodes, an electrolyte and usually a separator that electrically isolates the electrode compartments. These devices have the advantage of high power density, operation over a wide range of temperatures and long cycle lives [3, 4]. Recently, supercapacitors have been intensively investigated as they bridge the gap between conventional capacitors and batteries and fuel cells, with the ability to provide instant energy at short term pulses and high specific power rates [5-7]. However, these benefits are off-set by a number of drawbacks that include low energy densities, high self-discharge rates and low working potential window. Different electrode materials consisting of Faradaic and non-Faradaic capacitances as well as different electrolyte systems have been proposed to overcome these shortcomings [7, 8].

Carbon represents a very attractive candidate as an electrode material in electrochemical energy conversion and storage devices due to its versatile properties. These include its existence in various microstructures, different degrees of graphitization and easy manipulation [7, 9, 10]. More specifically, activated carbons have been the primary candidate for electrode materials in electrical double-layer capacitors (EDLCs). Their large specific surface area and hierarchical pore size distribution (PSD) with a high proportion of micropores are the primary factors that dictate their high performance in double-layer capacitors, and thus enable high capacitances and power densities [11]. However, there is still limited understanding of the structural and electrochemical interdependence of carbon electrode materials within supercapacitor devices. In this thesis, we focus on potassium
hydroxide (KOH)–activated carbon materials as model systems to specifically assess the role of the morphology/pore structure and surface functionalities in enhancing the electrochemical performance of double-layer capacitors. Successive characterisation techniques of the carbon structures were implemented and correlated with the electrochemical performance in EDLCs.

1.1. Research Objectives and Motivation

The operating principle of an EDLC is a charge separation process, in which capacitance arises from the accumulation of electrostatic charge at the electrode/electrolyte interface using two parallel electrodes and an ion-conducting electrolyte. The surface morphology and porous structure of an electrode are usually tailored for optimum access of the electrolyte to the available surface area, whilst allowing rapid ion transport throughout the pore network. Micropores are of great importance as they boost the charge storage capacity through the adsorption mechanism and hence improve the capacitance, while the meso- and macropores are regarded as the ‘accommodators’ for the ions’ kinetics [12].

In an EDLC, the capacitance ideally excludes any pseudocapacitive behaviour and the electrolyte ions are electrostatically and reversibly adsorbed in the double-layer of the porous networks of the carbon electrodes. However, in the case of surface functionalities on the carbon electrode, Faradaic processes may arise that comprise of reversible reactions between the functional groups at the accessible electrode surface and electrolyte ions. In addition, surface functional groups and wide PSDs can contribute to the hydrogen chemisorption process, delaying the hydrogen evolution reaction and consequently extending the operating potential windows of a supercapacitor device. Hence, the pore size distribution, porosity and functional groups content can be tuned to optimize the electrochemical performance of EDLCs within and beyond stable operating conditions. The non-ideal polarization of carbon surfaces, due to surface oxidation reactions and possible intercalation processes, makes fundamental understanding of the occurring electrochemical processes very challenging. [3]

As a result, the aim of this thesis is to extract the micro- and macro-structural properties and assess the role of each varying parameter in the electrochemistry of supercapacitors. A range of porous materials was investigated to study the form-function trend of activated carbons as electrodes in SCs. The reasons for non-ideal capacitive performances were explored, predominantly with electrochemical impedance and in-situ Raman spectroscopies when electrodes are exposed to nominal and extreme potential conditions. The electrochemical
results were synergized with the varying structural properties of multifarious carbons. The suite of structural, surface chemistry and electrochemical characterisation techniques allows obtaining thorough conclusions about the trade-off between various electrode structures and intended final applications in the supercapacitor field. Furthermore, the insights of new engineering designs of supercapacitor cells were found to play a crucial role towards their final energy and power capability and delivery.

1.2. Thesis Overview

This thesis starts with an introduction of the basic components of a supercapacitor device and a description of their operation principle. The main categories of supercapacitors and the main differences between their charge storage mechanisms are explored in Chapter 2. This is followed by descriptions of the conventional electrode materials and electrolytes used in the electrochemical storage device, with emphasis on carbon materials from bio-based origins. The electrochemical behaviour of porous carbon electrodes and functionalities on carbon surfaces are outlined.

Chapter 3 presents the characterisation techniques, structural and electrochemical, that are implemented throughout this work, with the aim of correlating the data obtained in the following chapters. A detailed description of the techniques alongside their strengths and disadvantages are explored to highlight the importance of congregating one, two and three-dimensional studies in attempt to understand the electrochemistry of porous carbon electrodes, which are examined in the various results chapters of this thesis.

In Chapter 4, the correlation between the morphology over multiple length scales, with the electrochemical performance of KOH-activated bio-carbon materials for supercapacitor devices is presented. The optimization of the KOH/cellulose ratio for supercapacitor electrode materials is found to be related to morphological characteristics and corresponding electrochemical performances, as described in terms of porosity, specific surface area, specific capacitance and electrochemical impedance. The microstructural information, including the narrow microporosity and oxygen functionalities, is examined. The results in this chapter demonstrate the structure-performance relationship observed in the KOH/cellulose model system, highlighting that the work can be extended to other similar systems. The importance of understanding the three-dimensional nanostructure of the electrode material in its entirety is emphasized in order to optimize the electrochemical performance.
Chapter 5 considers the relationship between the morphology of porous carbons used as electrode materials in supercapacitors and their electrochemical impedance spectroscopy responses. Impedance spectroscopy is explored as a powerful tool that can be used to acquire simulation models of experimental data and study the porous three-dimensional electrode behaviour in different electrochemical systems. The porous carbons with different KOH/cellulose compositions studied in Chapter 4 were used as model systems to investigate the structure-impedance correlation. A simple equivalent circuit was designed representing the electrochemical impedance behaviour over a wide range of frequencies at open circuit potential. The investigation of the bulk electrolyte resistance, Faradaic electrode processes and different pore size ranges contribution to the impedance response using a truncated version of the transmission line model was detailed. Thereafter, the suggested circuit was employed to investigate the shortcomings of porous materials as electrodes in supercapacitor applications and the reasons for their non-ideal performance. The concept of a specific relaxation time to a corresponding PSD and ‘best’ capacitive behaviour in different frequency ranges is introduced.

Chapter 6 extends the work presented in Chapter 5 by employing the curtailed version of the transmission line model and describing state-of-the-art porous carbon materials at different potentials and frequencies. Using the circuit suggested in the previous chapter (Chapter 5), the performance of the same KOH-activated model systems is predicted at different potentials over a wide frequency range. The relaxation times, specific capacitances and non-ideal performances were explored and presented in aqueous electrolyte. This is followed by introducing a correlation between the morphology and impedance behaviour of porous carbons at different potentials in a three-electrode system and within the potential stability windows. The impedance response was also evaluated beyond the thermodynamic operating potential conditions. The intrinsic dependence between the porous morphology and applied potential is highlighted and correlated to the optimized capacitive performance and promising application of porous carbons in aqueous supercapacitors beyond the stable operating conditions.

In Chapter 7, the different surface chemistry and porous textures of the KOH-activated model systems were investigated to study the mechanism of electrochemical hydrogen and oxygen evolution in supercapacitor devices. The structural changes of the activated carbons under severe electrochemical oxidation and reduction conditions were studied using in-situ Raman spectroscopy and correlated to the cyclic voltammograms obtained at extreme anodic and cathodic potentials. In an attempt to avoid nascent gas evolution in the supercapacitor device, the hydrogen chemisorption mechanism was detected for the range of different carbon powders, and the reversibility of the Faradaic reactions are investigated. Thereafter,
the influence of the specific surface area, narrow microporosity and functional groups on the chemical stability and hydrogen capture mechanism in the carbon electrodes is revealed. This chapter closes with describing the feasible application of aqueous supercapacitor devices beyond the electrolyte thermodynamic potential stability window as a result of the impact of the aforementioned factors on the electrochemistry of electrode materials.

Chapter 8 is the final chapter of results in this thesis, and explores the engineering of supercapacitors in a printed circuit board configuration. The integration of supercapacitors into a printed circuit board (PCB) construct is applied and its potential hybridization with fuel cells in the same cost-effective PCB composite is realized. A commercial activated carbon is used as an electrode material benchmark and is tested in aqueous and gel electrolytes. The work in this chapter provides a proof-of-concept study that paves the way for integrating supercapacitors into power electronics devices and their potential physical integration with PCB fuel cells. The electrochemical measurements of the supercapacitor-PCB device were also compared to standard two-electrode button-cell (coin cell) supercapacitors to reveal the advantages of supercapacitor-PCBs and their manufacturing feasibility for a broad range of applications.

Chapter 9 is the final chapter and includes a brief summary of the work presented in this thesis. Considerations for improved and optimized performances and designs of supercapacitors are outlined based on the results presented. The chapter concludes with an outlook on future work.
Chapter 2

Literature Review

This chapter outlines the fundamentals and the most recent advancements in the supercapacitor research area, markedly the ones associated with this work. The physics, chemistry and electrical engineering principles involved in the development of supercapacitors are summarized. In addition, the span of this project from the microstructural level to the cell design is introduced.

2.1. Historical Perspective of Supercapacitors

The concept of storing electrical charge on surfaces arose in the ancient times with the phenomena of rubbing amber. However, the origins of the effects of such a mechanism were not understood until the mid-1800’s, when the physical fundamentals of electrostatics were explored [3]. The comprehension of electricity at the molecular level began 140 years later with Michael Faraday [13, 14], followed by the study of the sub-atomic particle or corpuscle, now known as the electron, with Sir J.J. Thomson [15] and Millikan [16]. In regards to these historic investigations, the charge separation mechanism, by means of a layer of glass, was discovered in the Leyden jar by Dean Kleist and, independently, by Musschenbroek [17, 18]. The original setup constituted a glass compartment containing an acidic solution, and static electricity was stored between two electrodes, on the inside and outside of the phial. A metal foil was cemented on the outside surface, providing a dielectric medium in between, and thus creating a capacitor, which was known back then as a condenser. The improved version of the system comprises two metal foils or plates, on each side of the dielectric material (glass, vacuum or air).

The nature of electricity, however, remained uncertain until the discovery of J.J. Thomson with the charge-to-mass ratio, produced by the negative charge carriers that arose from the ionization of low-pressure gasses. This was followed by the works of Millikan [16] and Townsend [19] on the evaluation of the absolute values of these charges. The concept of electricity was then defined in terms of the accumulation or deficiency of the negative charges, and their corresponding dynamic motion. Around the same time, Johnstone Stoney [20] originated the name electron, from the Greek word for amber, for the negatively charged particles with an absolute charge of $4.8 \times 10^{-10}$ electrostatic units. Faraday’s laws
equally demonstrated the quantitative equivalence of the electrical charges to the produced chemical change extents, which is dependent on the chemical identity of the corresponding element and its oxidation state in a solution.

The aforementioned works, in addition to studies on the electron energy states in atoms and molecule through spectroscopy [21], reached the key conclusion that a fundamental unit of charge is universally equivalent, which announced the evolution of the science of electrochemistry. The electron theory of metals and the mechanism of current flow in the material were thereafter understood, which applied to the charging and discharging mechanisms in capacitors.

The charging of the two parallel metallic plates of a capacitor was understood to involve the generation of deficiency, constituting the positive plate, and excess, governing the negative plate, of the delocalized electron plasma density over a short distance, representing the Thomas-Fermi screening level. This will be discussed in more detail in the following section. In 1957, Becker [22] introduced the concept of storing electrical energy in a capacitor, by means of holding equally opposite charges at the interfacial double-layer of porous carbon electrodes in an aqueous electrolyte. This was followed by the manufacturing of double-layer capacitors using high surface-area carbons in non-aqueous electrolytes by Sohio Corporation in Ohio. The advantages of the latter included higher operating potential windows which enhanced the energy stored in the capacitors. In 1971, Nippon Electric Company took the technology’s license and was the first to produce commercial double-layer capacitors in the 1980s. During the same period of time in 1975, capacitors were developed based on the pseudo-capacitive mechanism using ruthenium oxide films [23-25]. Pinnacle Research Corporation then developed the first high-capacitance device by incorporating metal oxides in the electrode material. Due to the larger capacitances produced, in the order of several Farads or tens of Farads per gram of active material used, whether high surface area carbons or metal oxides, the term supercapacitor emerged.

20 years later, supercapacitors attracted significant attention in the power trains and electric vehicles industry, to complement the battery unit in such applications. These devices were also increasingly used due to the regulatory actions of the state of California, requiring a specific percentage of vehicles with zero toxic emissions. The hybridization of batteries with supercapacitors proved to provide level loading and therefore improving the batteries’ cycle lives and output voltages. Different classes of supercapacitors were then recognized, including carbon double-layer capacitors, pseudo-capacitors and hybrid capacitors in both aqueous and non-aqueous systems. The expanded utilisation of the different ranges of such devices encompassed hybrid power systems for electric vehicles [26, 27], military [28] and
medical [29] utilizations and applications in robotics [30]. Alongside the evolution of new electrode materials, there has been continuous improvement in the operating potentials of different electrolyte solutions, associated energy and power capabilities, practical design aspects including capacitor stacking and controlling the self-discharge mechanism. The requirements and advancements of each of the mentioned parameters will be discussed in the following sections of this chapter. Preliminary to that, an overview of the differences and similarities between supercapacitors and batteries, demonstrating the advantages of hybridizing the two devices into one compatible gear for power applications, will be described.

2.2. Brief Comparison of Supercapacitors with Batteries

As the amount of electricity generated from discontinuous renewable sources is increasing, the need for energy storage devices becomes more crucial. Electrochemical energy storage technology is already established for devices that are capable of demonstrating high energy density, such as batteries and high power density electrochemical capacitors. There is an emergent need, however, for near-future applications where high values for both energy and power densities are required [31].

As mentioned in the previous section, electrical energy can be stored via two different fundamental methods: i) in a direct electrostatic way with no Faradaic contribution, where negative and positive charges accumulate on the parallel plates of an electrical double-layer capacitor and ii) converting chemical energy through Faradaic oxidation and reduction processes of electrochemically active materials to release electrical energy via charges that can perform electric work across the potential difference between two electrodes, as in the case of batteries [32].

An important difference ensues between these two modes of electrical storage. Capacitors ideally only involve accumulation/deficiency in electron charges on its plates with no chemical changes of the materials; while the energy storage in batteries consists of chemical inter-conversions of the two electrodes (anode and cathode), which usually includes partial irreversibility in the conversion of the chemical reactants (reflected in the cyclic voltammograms). This leads to lower cycle lives in battery cells of several thousand cycles compared to capacitors with almost unlimited cyclability in the ideal state [33]. The same concept applies to the degree of recyclability, which reaches $10^6$ times in a capacitor. On a more microscopic level, the electrons involved in the double-layer charging are the conduction-band electrons, being in excess or deficit on the electrode plates. However, it is
the valence electrons of the reduction/oxidation processes that are involved in the Faradaic processes [3].

Both electrochemical systems require two electrodes and are usually accompanied by solution resistance as well as Faradaic impedance, even in the case of supercapacitors. The resulting impedances are due to the fact that EDLC devices in practice are not ideal, and Faradaic processes, of one type or more occur, including surface functional groups, impurities in the electrolyte solution and the presence of redox couples. This will be discussed in more detail in the following sections.

The problem of low local charge storage in capacitors has been overcome by using large surface area materials that can deliver high capacitances per physical surface area and mass of the electrode material, and hence the upgrade in name to supercapacitors. However, the energy densities of supercapacitors are substantially lower than those of batteries due to the low number of electrons per atom (~ 0.17 e\(^{-}\) per atom) stored at the double-layer, in contrast to one or two valence electrons involved in the Faradaic redox reactions in batteries [3]. Thus, supercapacitors with non-aqueous electrolytes have recently attracted significant attention due to the much further extended potential windows, where the decomposition of the electrolyte is delayed, compared to aqueous ones [34].

For a battery cell, the maximum Gibbs free energy can be determined as the product of the charge \( Q \), and potential difference \( E \) between the anode and the cathode. However, for a supercapacitor of the double-layer type, the Gibbs free energy is half that stored in a battery cell charging with the same charge \( Q \) to the same voltage \( E \). Conway [3] explained this difference by interpreting that every additional charge element that is added in the process of charging a capacitor has to do electrical work against the density that already accumulated on the capacitor plates, and therefore continuously increases the inter-electrode potential difference. In a battery, the potential difference would be ideally constant upon charging or discharging the device, independent of the charge \( Q \). The potential of a double-layer capacitor, however, has a linear relationship with the extent of charge/discharge, as demonstrated in Figure 2-1. It is noteworthy to mention that the two parallel lines of charge and discharge of a battery do not coincide, due to the polarization of the anode or cathode in a non-ideal case, in which ohmic potential drops arise from different resistive elements in the system. The same scenario applies for supercapacitors, in which the charge and discharge profiles will be separated due to ohmic drop; this will be demonstrated in the results chapters of this thesis.
Figure 2-1: Comparison of the charge and discharge mechanisms between an ideal capacitor and an ideal battery: the potential as a function of the state of charge.

The integration of the plots in Figure 2-1 corresponds to the energy of charging. Thus it can be seen that the energy stored in a supercapacitor is half that in a battery, functioning under the same conditions. With the similarities and differences in mind, both electrochemical systems can be hybridized to complement each other in pursuing high energy densities with no sacrifice of power densities in different technological applications, most interestingly a plug-in hybrid electric vehicle [35-37].

2.3. What is a Supercapacitor: An Overview

The ideal behaviour of a capacitive charge and energy storage device would constitute the involvement of only electrostatic processes and excluding any electrode kinetics of the Faradaic type, in which the electrode energetics would lead to deviations from ideality. However, this is rarely the case and electrode kinetics usually come into play regardless of the electrode material used, which will be classified in the following section [38]. This can occur due to an overcharge, inducing the electrolyte decomposition, and/or Faradaic reactions arising from impurities in the electrolyte, and/or reactive functional groups at the carbon surfaces [3].
Supercapacitors are therefore usually classified into two main categories; i) electrical double-layer capacitors (EDLCs), in which capacitance arises from the accumulation of electrostatic charge at the electrode/electrolyte interface; and ii) pseudo-capacitors, whereby reversible Faradaic processes governed by surface electro-active species provide the energy storage mechanism [39, 40]. Both types of supercapacitors have been intensively investigated as they bridge the gap between conventional capacitors and batteries, with the ability to provide instant energy for short periods with high specific power rates [5-7].

Upon applying a voltage and placing the resultant charged electrode interface in an ionic solution, accumulation of charges (of one sign) arises at each side, forming a double-layer and generating a dipole orientation in the solvent. Since the accumulated ions are usually existent in the liquid solvent in direct physical contact with the electrode, the polarization of the electrolyte media will also play a factor in determining the properties of the charges at or near the electrode/electrolyte interface.

The electric potential, $E$, for a charge $Q$, at a distance $d$ from the charge is defined as the work done to move a unit charge $q$ from charge-free medium (at infinity) to the distance $d$. At any distance $y$ from the total charge $Q$, the unit charge undergoes an electrostatic force, in a dielectric medium, of permittivity/dielectric constant $\varepsilon$, defined as:

$$-F_y = \frac{q}{\varepsilon y^2} \quad (2-1)$$

When the unit charge has moved from infinity to the point at distance $d$, work is done against this force so that the work/energy $U(y)$ is expressed as:

$$U(y) = \int_{\infty}^{d} F(y) dy = \frac{q}{\varepsilon d} \quad (2-2)$$

This is defined as the potential $E$ and the corresponding electric field $E_e$ is determined as the gradient of this potential:

$$E_e = \frac{dE}{dy} = -\frac{q}{\varepsilon y^2} \quad (2-3)$$

Using Coulomb’s law, $F_y = \frac{kq q'}{r^2}$, $F_y$ is identified as the attractive or repulsive force depending on the nature of the charges $q$ and $q'$, where $r$ is the distance between both charges and $k$ being a proportionality constant ($k = \frac{1}{4\pi\varepsilon_0}$) with $\varepsilon_0$ being the permittivity of vacuum. The force is then a product of the charge $q'$ multiplied by the field caused by another charge, $q$. 

39
The capacity, $C$, of a capacitor is then defined as follows:

$$C = \frac{dq}{dE} \quad (2-4)$$

If $\sigma$ is the surface charge density on the plates of a capacitor of area $A$, then $\sigma = \frac{q}{A}$, and the electric field $E_e = 4\pi \sigma$, with the charge referring to 1 cm$^2$ area and associated with $4\pi$ lines of force in the total cross section enclosed by the surface.

The capacity, when a dielectric is present, can then be expressed as:

$$C = \frac{A\varepsilon}{4\pi d} \quad (2-5)$$

or in a rationalized system to yield the capacitance in Farads as:

$$C = \frac{A\varepsilon\varepsilon_0}{d} \quad (2-6)$$

where the dielectric constant, $\varepsilon$, is a characteristic of the medium used and can be determined by the capacitance. It is also defined as the relative permittivity to free space. Figure 2-2 illustrates the accumulation of opposite charges at the electrode/electrolyte interfaces, with a separator arranged between the two electrodes, creating an electric field in the dielectric medium. The capacity is the ability of the capacitor to store charge, while the capacitance, usually reported in the literature, if the capacity to hold the same charge at a specified potential difference. The capacitance is defined as the ratio of the stored charge to the potential difference across the supercapacitor element.
In the case of supercapacitors, it is the microstructural properties of the dielectric that determine the double-layer capacitance rather than the bulk properties as in conventional capacitors. Additionally, the choice of electrode materials substantially influences the capacitive performance, and so to understand the whole body of a supercapacitor, an investigation on the different types of electrode materials and electrolyte media should be carried. However, and prior to that, the fundamentals of the two different classes of supercapacitors and the mechanism of charging in each are presented first.

2.4. The Energy Storage Mechanism: Classes of Supercapacitors

2.4.1. Electrical Double-Layer Capacitance

Electrical double-layer capacitors (EDLCs) store energy in a similar manner to that of conventional capacitors, by means of accumulation of opposite electrostatic charges at the electrode/electrolyte interface [7, 41, 42]. However, EDLCs can store higher amounts of
energy than a traditional capacitor due to smaller distances of charge separation and high surface areas of activated materials used as electrodes, which leads to increased sites for charge storage [43]. The principle of double-layer capacitance relies on the development of high surface area carbon powders or porous materials that are activated by physical and/or chemical pre-treatment.

It is essential to start by stating the fact that an electrochemical capacitor employing the double-layer capacitance mechanism is only possible when constructed with two interfaces of an electrode/electrolyte, which are worked against each other. One of the interfaces would be positively charged and the other is negatively charged against the electrolyte solutions, usually including a separator between the two electrodes [3]. Figure 2-2 demonstrates a single capacitor cell made of a two-electrode, two-interface configuration. The capacitive behaviour of an individual electrode can be studied independently, yet the presence of a second electrode, namely a counter electrode must be included in the electrical circuit. This device is known as a capacitor cell, also known as a two-electrode system. However, the presence of a third reference electrode, at which the potential measurements can be studied and controlled, is preferable to isolate any external factors influencing the working electrode. This setup is established as a three-electrode system and the difference between both configurations will be further described in later sections of this chapter.

The determination of the double-layer capacitance and its dependence on the potential of the electrode is necessary to provide detailed information on the electrode structure and behaviour in a supercapacitor device. This is mainly attributed to the fact that the charge, $Q$, held on each side of the electrode interface (electron density on the electrode side and ion density on the electrolyte side), is dependent on the potential of the electrode which corresponds to the Fermi level of electron energy states in this electrode. This prevails the differential quantity of capacitance, $C$, defined as $C = \frac{dQ}{dE}$. Different models have been suggested to describe the capacitive behaviour, all starting with the prototype consisting of two parallel plates, of opposite charges and separated by a small distance. The chronological models proposed are discussed herein, culminating with the correct description of the structure at electrode interfaces.

Hermann von Helmholtz described the concept of double layer capacitance in 1853, with the original perception of distribution of opposite charges at the interface of colloidal particles [44]. The charges on the colloid side of the double-layer arise from either acid or base ionization, or the adsorption of ions. Counter-ions of opposite charge on the electrolyte side accumulate to balance the charges formed on the colloid, constituting a double-layer bundle of opposite charges. The compact structure is referred to as the Helmholtz double-layer
model and is shown in Figure 2-3a. The model was later adapted for electrode interfaces, where a surface density of excess negative or positive charges can arise, corresponding to the excess or deficiency in the number of electrons of the delocalized electron plasma of the electrode. Since the electron density in a metal is quite high, the net charge density of the electrons at the metal surface is screened and therefore the gradient of the density at a charged surface is localized over a distance between 0.05−2 nm, also known as the Thomas-Fermi distance. An electron density spill-over occurs outside the electrode surface and into the electrolyte solution due to the decreasing magnitude of electrons, which is potential dependent.

Figure 2-3: Models of the electrical double layer at a negatively-charged surface: (a) Helmholtz model with the atomic distance \( d \) representing the double-layer, (b) Gouy point-charge model and (c) Stern model combining both models. \( \Psi \) and \( \Psi_0 \) are the potential and the electrode potential, respectively.

It was then realized that the proposed model by Helmholtz did not consider the thermal fluctuation effect according to the Boltzmann principle, which leads to the assumption that the ions in the solution remain stagnant. The thermal variation depends on the extent to which the electrostatic energy \( U_e \), along with any chemisorption energy \( U_c \) of the ions’ interaction with the electrode surface exceed the average thermal energy of the system, \( k_B T \) at a temperature \( T \) (with \( k_B \) being the Boltzmann constant), by a ratio of \( \frac{U_e + U_c}{k_B T} \) [45]. Gouy [46] introduced the thermal fluctuation factor into the modified version of the double-layer capacitance, in which the ions were assumed to be point charges, and were envisaged as a three-dimensional diffusive distribution of the ions of the electrolyte (Figure 2-3b). The latter has equal but opposite charges to the excess or deficit electron charge on the electrode.
surface. This model overestimated the total capacitance, calculated on account of an incorrect potential profile at the local region of the electrode/electrolyte interface. The mathematical treatment suggested by Gouy, calculates the diffusive double-layer capacitance and the overestimation problem was overcome by the model suggested by Stern in 1924 [47]. In his model, the combination of the two regions described by Helmholtz and Gouy-Chapman were recognized. In the inner region, the ions of finite size were distributed according to Langmuir’s adsorption isotherm; while the region beyond the inner one and into the electrolyte, was treated as a diffusive region of ionic charge distribution, as modelled by Gouy and Chapman (Figure 2-3c) [48]. The total size of the ions also included their hydration shells, as depicted by Helmholtz, to account for the geometrical limitations of the compact region of ion adsorption at the electrode surface. The total capacitance in the double-layer, \( C_{dl} \) can therefore be treated as a combination of two capacitances in series, the Helmholtz compact layer capacitance \( C_H \) and the diffusive capacitance \( C_{diff} \). Hence, \( C_{dl} \) can be expressed as follows:

\[
\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \quad (2-7)
\]

The distinction between the Helmholtz compact layer and diffusive layer can be inferred from the distance of closest approach of counter-ions in the solution to the electrode surface [49]. By introducing this distance, a good basis for the interpretation of electrode/electrolyte interface phenomena can be understood. However, Grahame afterwards emphasized the distinction of inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP), which correspond to the different distances of closest approach for cations and anions at the interface, as demonstrated in Figure 2-4 [50]. This categorization arises from the fact that cations are commonly smaller than anions, in which the former also retain solvation shells. This difference leads to the conclusion that anions have smaller distances of approach compared to hydrated cations and consequently inner-layer capacitances at positively charged electrodes are usually twice that of corresponding negatively charged electrodes. These aspects are of great significance to evaluate and understand the double-layer capacitance, taking into account the ions of the electrolyte, solvent and electrodes used [51, 52].
Figure 2-4: Representation of the structure of double-layer showing different adsorption regions of hydrated cations and less hydrated anions, according to Grahame’s model.

In practice, the diffusive layer in a capacitor is neglected compared to the inner compact layer, specifically in high concentrations of the electrolyte media. However, the diffusive-layer capacitance determines the overall double-layer capacitance, owing to the reciprocal sum relationship of the capacitances (Eqn. 2-7). The Stern treatment of the diffusive layer recognized that it is only applicable in dilute electrolyte solutions near the potential of zero charge (the potential at which the electrode has zero surface charge density). In the case of using porous electrode materials with high surface area, typically carbon, in a concentrated electrolyte solution, the distribution of the ions into the finest porous structures becomes more complex. The thickness of the diffusive part (i.e. Debye length) is accounted for in relation to the space inside the pores available for the ion distribution. Whereas in the case of dilute electrolyte concentrations, the diffusive layer can extend from the edge of one pore, overlapping with the ion distribution on the other side of the pore. The interpretation of the ion distribution, potentials across the double-layer and surface charge density then become more complex. In a real supercapacitor, the electrolyte is usually of few molar concentrations, and the overlapping situation does not occur. The charge density of the electrode surfaces will be completely screened with counter-ions on the compact layer and thus the overlap situation would no longer apply. However, it is noteworthy to mention that a different kind of problem might arise in porous structures, whereby capacitance might be
lost due to the incomplete electrolyte invasion of wetting of the finest pores. These phenomena will be further described and analysed in the different results chapters.

To this end, the fundamentals of electrostatic capacitors have been explored in this section, where the ideal mechanism of charging does not involve the applications of electrode kinetics with Faradaic processes of any kind. As mentioned earlier, this is barely the case, due to different factors, and the investigation of Faradaic mechanisms in supercapacitors will be discussed in the following section.

2.4.2. Faradaic Capacitance

Faradaic processes, if present, would lead to deviations from the ideal capacitive behaviour and the electrode ceases to be ideally polarizable. The charge storage is acquired via an electron transfer process which causes a change of state of the electroactive material. The electrode kinetics involving Faradaic processes would be due to one or a combination of different mechanisms:

1- Overcharge/overdischarge of the double-layer capacitance leading to decomposition of the electrolyte.

2- Charge/discharge of pseudocapacitive elements in EDLCs, mostly present on the carbon surfaces.

3- Charge/discharge of pseudo-capacitors, including oxides of conducting polymers of redox types.

The electron transfer process in an electrochemical manner is also called the radiationless transfer, whereby no photochemical emission or absorption takes place. The electrons adjust to selective energy levels in the electrode, which is relative to those of the reduced or oxidized reactants. The direction of electron transfer in the Faradaic process thus occurs to the Fermi level of delocalized conduction-band electrons at the electrode surface in an anodic process, or from the Fermi level, in a cathodic process. The maximum energy released and consumed during the charge or discharge process is given by the Gibbs free energy, $\Delta G$ of the electrochemical device as follows:

$$\Delta G = -nFE$$  \hspace{1cm} (2 - 8)

where $E$ is the potential difference between the electrodes (volts), $n$ is the number of electrons per mole product, and $F$ is Faraday’s constant ($96,485 \text{ C mol}^{-1}$).
The electrode kinetic rates are directly measured as current, $I$ or current density, $i$, which is expressed per accessible surface area of the electrode. The current density, in the case of 100% efficiency, can then be expressed as:

$$i = nFv$$  \hspace{1cm} (2 - 9)$$

where $v$ is the rate of reaction (mol s$^{-1}$ cm$^{-2}$).

The kinetics of electrode processes primarily depend on the potential, $V$, of a single electrode, usually measured against a reference electrode. This is due to the fact that the electron work function depends on the potential and a change in its energy as a reactant on the electrode surface would change the activation energy for the charge transfer mechanism and therefore the rate constant of the reaction. If the initial state energy of the reactants (ion and electron) is changed by $\pm VF$ per mole of electrons, the activation energy for the process will change by a fraction $\beta$ of $\pm VF$. $\beta$ is a measure of the asymmetry, known as the barrier symmetry factor, and commonly takes a value of 0.5 ± 0.1 in most electron charge transfer processes. The Gibbs free energy, $\Delta G$ is then expressed as:

$$\Delta G = \Delta G_{V=0} \pm \beta VF$$  \hspace{1cm} (2 - 10)$$

The current density, for example in the deposition of hydrogen ($H$) from water during discharge, can then be given by:

$$i = nFk\bar{c}_H^+ (1 - \theta_H)e^{-\frac{\beta VF}{RT}}$$  \hspace{1cm} (2 - 11)$$

where $k$ is the rate constant of the reaction at a potential of zero, $c_H^+$ is the local concentration of reacting $H^+$ ions at the electrode surface, $\theta_H$ is the electrode surface coverage by the product of the discharge process, $R$ is the molar gas constant and $T$ is the temperature. However, the potential of a single electrode cannot be measured, and therefore a reference electrode in the same electrolyte solution at reversible equilibrium ($V_{rev}$) for the same reaction is introduced. Applying a potential difference between the reactants and products is a source for activation overpotential $\eta$, the voltage needed to induce a net charge transfer from the dynamic equilibrium state.

$$\eta = V - V_{rev}$$  \hspace{1cm} (2 - 12)$$

Starting with Eqn. (2-11), the current density becomes:

$$i = nF\bar{k}c_H^+ (1 - \theta_H)e^{-\frac{\beta \eta F}{RT}}$$  \hspace{1cm} (2 - 13)$$
where $\bar{k} = ke^{-\frac{\beta \eta_F}{RT}}$, defined as an electrochemical rate constant, applicable to the reversible potential of the specific process under study. More generally, and in terms of the exchange current density, $i_o$, passing reversibly in a system at equilibrium potential, the current density can be expressed as the Butler-Volmer Eqn.:

$$i = i_0 \left( e^{-\frac{\beta \eta_F}{RT}} - e^{\frac{(1-\beta) \eta_F}{RT}} \right)$$  \hspace{1cm} (2 - 14)

The linearization of the Eqn. at near-equilibrium conditions yields:

$$i = \frac{i_0 \eta F}{RT}$$  \hspace{1cm} (2 - 15)

And differentiating the above Eqn. gives:

$$-\frac{di}{d\eta} = \frac{i_0 F}{RT}$$  \hspace{1cm} (2 - 16)

which can be rewritten to yield the variation of the overpotential with the current and therefore resistance according to Ohm’s law:

$$-\frac{d\eta}{di} = \frac{RT}{i_0 F}$$  \hspace{1cm} (2 - 17)

This Eqn. governs the Faradaic resistance, $R_F$, of the electrode reaction and therefore is of major importance to characterise the dynamics of the electrode reactions. At low overpotentials, micro-polarization occurs, whereby the current is linearly dependent on the overpotential. In addition, the impedance behaviour of the reaction with an alternating voltage signal can be characterised, and the Faradaic resistances alongside the double-layer capacitances can be determined.

In the case of Faradaic decomposition of the electrolyte, the charging current can be maintained in the extreme potential ranges, and the double-layer will continue charging with the increase in the potential difference. However, the current would be divided into two components, the purely double-layer charging current $i_{dl}$, and the Faradaic current, $i_F$, that was shown to increase exponentially with the potential difference when the latter exceeds the thermodynamic potential difference. This increase follows the Tafel Eqn., and the total charging current, $i$, would be given by:

$$i = i_{dl} + i_F$$  \hspace{1cm} (2 - 18)
where $i_{dl} = C \frac{dv}{dt}$ and $i_F = e^{\frac{\alpha n F}{RT}}$, where $\alpha$ is the transfer coefficient.

Figure 2-5 shows schematically the relative changes in the current components as a function of increasing potential differences with time. The voltage-time demonstrates a linear relationship as the electrode is ideally polarizable and $i_{dl}$ is the only current component. However, the profile increasingly deviates from linearity as the Faradaic reactions and current leakage across the double layer come into play, corresponding to the decomposition of the electrolyte.

![Figure 2-5](image)

Figure 2-5: The double-layer interface changing from an ideal polarizable mode to non-ideal one when $i_F > 0$, charging at a constant current.

Pseudocapacitance is Faradaic in origin and involves the passage of a current through the double-layer interface. It charges and discharges like a battery, as conveyed in an earlier section, yet the capacitance arises on account of the charge change to the potential variation. The equations outlined in this section accommodate the pseudo-capacitive behaviour and show that such process involves chemical changes in the oxidized and reduced species through the electron transfer process, unlike the accumulation/deficiency of charge at the interfaces of a double-layer type of capacitor. It should be noted that the double-layer capacitance will always contribute to the total capacitance, even in the Faradaic-dominant regime, and can be generally separated from the pseudocapacitive mechanism.
2.5. Supercapacitor Components

The supercapacitor is typically composed of five main components, a positive electrode and a negative electrode, constituting the two parallel plates, each deposited on a current collector and separated by an electrolyte and a separator. The positive and negative electrodes can be identical or different to fabricate symmetric or asymmetric supercapacitors, respectively [53]. Most commonly, the electrode consists of a porous carbon material with high surface area, or a pseudo-capacitive element including metal oxides or conducting polymers. Hybrid capacitors have been also assembled, composed of EDLC materials and a pseudo-capacitive type of electrode, thus combining the properties of both systems [54]. The electrodes are immersed in the same electrolyte solution, which provides the means for either electrostatic charge storage mechanism or redox reactions, mentioned in the previous section. Different kinds of electrolytes have been investigated including aqueous and non-aqueous media, which determine the potential stability window of the supercapacitor cell and consequently the maximum energy that can be stored in the device. The electrically insulating, but ionically conducting separator is usually placed between the two electrodes to prevent short circuit. Figure 2-6 represents the primary components of the electrochemical cell. The charge storage then arises upon charging the capacitor, following either or both of the mechanisms previously described. The maximum energy stored in a supercapacitor is half that in a battery operating at the same conditions. Hence, the capacitive performance and energy delivery hugely depend on the choice of materials for each cell component, and the assessment of each of the electrode, electrolyte and separator options is crucial to understand the reasons for different electrochemical behaviours and respective potential optimization.
2.5.1. Electrode

2.5.1.1 Carbon-based Materials

Carbons are the most widely used materials for supercapacitor devices, in the form of activated carbon matrices, carbon aerogel or carbon nanotube forms [55]. The advantages of carbon include high specific surface area, easy tuning of its microstructural properties, good electronic conductivity, chemical stability, abundance and a wide operating temperature range [1]. The electrostatic charge storage mechanism in supercapacitor applications requires primarily high specific surface areas, wide pore size distributions and accessibility of the electrolyte into the finest pore structures. This would then allow for charge storage on porous plates upon the application of a potential difference between the two electrodes. Figure 2-7 presents the employment of activated carbon as an electrode material in a supercapacitor cell.

Activated carbons (ACs) have gained increasing interest in their application as electrode materials for double-layer capacitors [38]. They are generally produced via physical and/or
chemical activation of various types of carbonaceous precursors, including wood [56-58], cellulose [59-63], banana peels [64-67], coconut shells [68-70] and coal [71-73]. Physical activation constitutes a thermal treatment of the raw materials at high temperatures ranging between 700°C and 2500°C in an inert atmosphere or in the presence of oxidizing gases; while chemical activation corresponds to activating the carbon precursors with activating agents such as potassium hydroxide, zinc chloride, phosphoric acid and sodium hydroxide. The activation methods are usually combined to control the physicochemical properties of the fabricated carbons, yielding high specific surface materials (up to 3000 m² g⁻¹) with tuneable porosities and pore size distributions. However, it was demonstrated that very high surface areas are not favourable for the electrochemical performance in supercapacitors as the smallest pores are not accessible by the electrolyte ions, and therefore do not contribute to the total capacitance [74]. This leads to the conclusion that not all pores are effective for the charge accumulation and storage in an EDLC, and unless the electrolyte can penetrate the porous structures, the optimized capacitive performance cannot be reached. Therefore the electrochemically accessible surface area, rather than the apparent surface area accounts for the EDLC behaviour.

Figure 2-7: A close-up of the electrode material in an EDLC: a scanning electron micrograph of a KOH-activated carbon with mass ratio of 0.5:1 KOH/cellulose. Nickel foam is the choice of current collector here.

Bio-derived carbons present an alluring choice as raw materials for activated carbon in supercapacitor devices as they combine the characteristics of cost-effectiveness, abundance, environmental-friendliness and suitability in energy storage devices. Numerous studies have reported the fabrication of new emerging carbon materials as potential candidates for
supercapacitor devices, where the choice of the precursor along with the activation method determines their compatibility as electrodes for EDCLs. For example, activated carbon nanospheres with surface area of 2871 m² g⁻¹ were fabricated via the chemical activation of sugarcane bagasse with zinc chloride followed by air drying at 100 °C [75]. A specific capacitance of 300 F g⁻¹ at 0.25 A g⁻¹ current density in a three-electrode cell constituting H₂SO₄ electrolyte and 77% capacitance retention after 100,000 cycles were obtained when the zinc to raw material weight ratio was 3.5. The optimized performance was attributed to the microstructural properties constituting mesopores that aid the fast charge/discharge cycling at high current densities. However, a zinc chloride/sugar cane ratio of 1 showed the most stable performance at low current densities, proving that different pores come into play at different cycling conditions. Another study on the activation of macadamia nutshells with potassium hydroxide and zinc chloride, separately showed that different parameters affect the electrochemical performance, namely the activation temperature, the time for carbonisation and the activating agent to precursor material ratio [76]. It was found that both chemical agents share an optimized carbonisation time of 1 h and 1:1 agent to raw material ratio; yet the most favourable temperature was 500 °C for ZnCl₂ and 800 °C for KOH to produce a combined micro- and mesoporous structure. Ordered mesoporous carbons with controllable structures have then gained attention in the supercapacitor research field. The good capacitive behaviour was mainly attributed to the ordered mesopores (2-50 nm) as channels that facilitate the ion diffusion into the micropores (< 2nm) which provide adsorbing sites for ion storage [77]. Different raw materials were activated with chemical agents, or prepared with the templating procedure, to produce self-ordered mesoporous carbons and enhance the electrochemical performance in aqueous and non-aqueous supercapacitor systems [78-81]. However, it was then proven that the indicated advantages of ordered mesoporous carbons do not reflect an optimized performance of activated carbon electrodes in supercapacitors [82]. This is mainly attributed to the limited surface area of such carbons, ranging between 800 m² g⁻¹ and 1500 m² g⁻¹, and therefore low total microporous contribution to the structure. Efforts were then made to understand the relationship between the porous structure and electrochemistry, and it was a mutual conclusion that the accessible micropores by the electrolyte are essential for boosting the charge storage capacity. The role of the mesopores, typically between 2 nm and 8 nm, is to accelerate the ion transport from the electrolyte to the electrode microstructure, specifically at high current densities, thus enhancing the power capability of the device [10, 83]. Other studies have also concluded that the optimum pore size for the carbon electrodes in EDLCs is between 0.4-0.7 nm in aqueous media and 0.8 nm in organic electrolytes [11, 84]. More recent studies indicated that maximum capacitance can be achieved when the pore size is equal to the ion size in the electrolyte used, by minimizing the free space available [74].
However, there are different factors that also play an important role in favouring the electrochemical performance of EDLCs at specific conditions, and they will be further discussed in later sections.

In addition to the amorphous carbon materials, carbon nanotube (CNTs) and graphene have been widely explored as potential electrode materials for supercapacitor applications. Graphene sheets, with a two-dimensional structure and hexagonal network bring different advantages including high surface areas, high electron mobility and good thermal stability [85]. However, annealing graphene at high temperature is usually required to separate the sheets so as to optimize the surface area of these materials, and potentially producing reduced graphene oxide. The theoretical surface area of graphene is 2630 m$^2$ g$^{-1}$, yet the reported values of graphene sheets derived from graphene oxide (GO) have been well below that [86, 87]. Therefore, numerous studies have proposed the assembly of graphene sheets intro porous three-dimensional electrodes to create macropores (> 50 nm) that facilitate the ion transport to the electrodes, enhance the electrochemical surface area and boost the ionic conductivity [88-93]. Wang and co-workers prepared graphene by reducing GO with hydrazine in vacuum at room temperature [94]. Upon changing the reduction time, the highest specific capacitance and energy density obtained in KOH electrolyte in a two-electrode system were 205 F g$^{-1}$ and 28 Wh kg$^{-1}$, respectively at 0.1 A g$^{-1}$ current density when the reduction time was set to 72 h. These results were obtained due to the lowest degrees of agglomeration of the graphene sheets, compared to less-reduced samples and samples annealed at high temperatures. The pore accessibility and electrolyte transport in graphene sheets were enhanced in another work by three-dimensional porous graphene-based materials via a two-step process: i) hydrothermal carbonisation of sucrose with GO to attain a 3D structure and ii) chemical activation with KOH [88]. Ultra-high specific surface area of 3523 m$^2$ g$^{-1}$ and conductivity up to 3 S cm$^{-1}$ were achieved, yielding 281 F g$^{-1}$ specific capacitance and 98 Wh kg$^{-1}$ energy density values at 1 A g$^{-1}$ current density in an ionic liquid (tetraethylammonium tetrafluoroborate (TEABF$_4$) in acetonitrile) in a two-electrode cell. The study highlights the importance of optimizing the ratio of raw material to graphene oxide in the first preparation step, showing that a small amount of GO is favourable for better electrochemical performance, due to lower chances of graphene stacking. However, the pore size distribution of the fabricated materials was mainly in the mesopore range. In a similar study, microwave-exfoliated GO was chemically activated with KOH and carbonised at 800 °C under a pressure of 400 Torr [93]. The produced carbon had a wide pore size distribution, mainly constituting of micropores and mesopores with a total pore volume of 2.14 cm$^3$ g$^{-1}$ and 3100 m$^2$ g$^{-1}$ specific surface area. The microstructural properties of these carbons allowed obtaining a capacitive performance as high as 165 F g$^{-1}$
at a current density of 1.4 A g⁻¹ current density in 1-butyl-3-methyl-imidazolium tetrafluoroborate (BMIM BF₄)/acetonitrile electrolyte in a two-electrode configuration. Another approach is the in-situ deposition of reduced graphene oxide in the micropores of nickel foam to produce graphene hydrogel/nickel foam composites [85]. The latter composites are fabricated upon immersing the GO/nickel foam in a vitamin C solution followed by heating at 60 °C to reduce the graphene oxide [95]. This method allows the production of porous spongy structures with limited restacking of the graphene sheets, thus decreasing the pathway for ion and electron transport and consequently improving the capacitive behaviour and durability of the supercapacitor. Surface areas of 1260 m² g⁻¹ with outstanding capacitance retention (92%) upon increasing the current 100 folds were reported in a three-electrode system. Another study reported a similar binder-free procedure and obtaining a hierarchical porous structure after annealing at 400° in an inert argon atmosphere [96]. The porous carbons attained high specific capacitances of 366 F g⁻¹ at 2 A g⁻¹ current density in three-electrode compartments, yet a capacitance retention of 60% upon cycling the supercapacitor for 2000 cycles. This performance was attributed to residual and unstable oxygen functional groups.

CNTs are seamless cylinders formed by wrapping graphene sheets with carbons atoms, and based on the number of layers of the former, CNTs can be classified as single-walled CNTs (SWCNT) or multi-walled CNTs (MWCNTs) [55]. As mentioned previously, CNTs are candidate materials for the fabrication of composite electrodes for supercapacitors, due to their low gravimetric density, chemical stability and unique structure [97]. A wide variety of synthesis methods of CNTs have been explored, including arc discharge [98], laser ablation [99] and chemical vapour deposition [100]. The products of an arc discharge experiment on two graphitic rods results in impurities, and therefore should be followed by a purification step. The graphite is vaporized by a laser pulse in an inert atmosphere at high temperatures via the laser ablation process. As for the chemical vapour deposition technique, a catalyst precursor, typically ferrocene dissolved in toluene or xylene solutions, is sprayed into the first-stage furnace. The precursor decomposes at a temperature of 200 °C to provide the iron catalyst for the nucleation of nanotubes, while the solvent provides the carbon feed. The vapours are then swept into the second stage furnace where aligned nanotubes grow on a silica substrate and the walls of the furnace tube. However, this process is costly and therefore uncompetitive for scalability. The low volumetric and gravimetric capacitances of CNTs, compared to ACs, require combining them with active carbons to achieve high performances. Noked et. al [101] for example, incorporated CNTs with a high surface area carbon to attain a composite of surface area as high as 1429 m² g⁻¹. The amorphous carbons acted as the skeleton of the electrode material and the nanotubes provided mechanical
integrity, increased conductivity and enhancement in the porous structure. The electrodes with 20% CNT composition acquired a capacitance of 200 F g⁻¹ in KOH electrolyte with a stable behaviour over 50,000 cycles in three-electrode cells. A similar approach in another study demonstrated the excellent performances of CNT/AC composites in TEA-BF₄/acetonitrile organic electrolyte [102]. The mixture of polymeric species (polyvinyl dichloride) and CNT was carbonised in an inert atmosphere and further activated in a CO₂ atmosphere to attain a hierarchical porous structure of micro- and mesopores. The capacitance values achieved of the coin cells reached 171 F g⁻¹ at 0.12 A g⁻¹ with excellent capacitance retention of 93%. Different procedures have been more recently reported including the incorporation of CNTs with graphene; yet the preparation process is rather complicated. The nanotubes were attached to the surfaces and edges of the sheets, acting as spacers and preventing restacking, in an attempt to enhance the ionic transport pathways to the accessible surface areas. The performance of these materials in three-electrode systems was relatively modest, achieving capacitances of 151 F g⁻¹ at 0.5 A g⁻¹ current density and 86% capacitance retention, and the optimization of the process is still underway [103, 104].

Most recently, a new technique for the fabrication of CNT/carbon composites was suggested by Mazurenko et al [105]. The procedure was done stepwise as follows: i) electrophoretic deposition of the nanotubes/polystyrene in a beads assembly, ii) electro-polymerization of polypyrrole in the free spaces of the nanotubes followed by iii) template removal using toluene solution and finally iv) pyrolysis at high temperatures ranging between 650-950 °C. The superior performance (200 mF cm⁻² at 10 mV s⁻¹ scan rate) in 0.1 M potassium chloride in a conventional three-electrode cell achieved in this work, highlights the importance of compromise between the electron transfer kinetics and mechanical integrity of the electrode materials produced. In addition, these results confirm the necessity of robust matrices that support the activated carbon materials.

In summary, carbon materials, in various forms, can attain high specific surface areas and tuneable porous structures, which make them potential candidates for EDLCs. However, these materials still suffer from high resistivity values due to the contact internal resistances between the carbon particles, leading to deteriorated performances (described further in section 2.8). In addition, it was highlighted that the specific surface area that is not accessible by the electrolyte ions will impede the ion transport, resulting in lower capacitances in the real devices compared to theoretical values. Therefore, a balance between the porosity, specific surface area values, an optimum pore size distribution and surface functionalities (will be described in more detail in section 2.8) is needed to maximize the overall capacitance without compromising the stability of the system.
2.5.1.2. Faradaic-based Materials

Pseudocapacitors offer 10-100 folds higher capacitances than EDLC materials due to the charge storage mechanism using redox activated materials [106]. As mentioned in earlier sections of this chapter, a small percentage of the total capacitance is attributed to the double-layer mechanism; yet the dominating process is led by fast and reversible reactions on the surface of the electrodes. This leads to higher achieved capacitances and therefore increased energy densities. This is due to the fact that pseudocapacitive reactions occur throughout the bulk material where charge is stored in the entirety of the electrodes (as in the case of batteries), as opposed to the charge that is solely stored on the surface of the electrodes in the case of EDLCs. The word “pseudo” originates from the meaning of fake or false, whereby pseudocapacitors have the appearance of a conventional capacitor, whereby the properties of the electrode behave like the electrochemical capacitor [107]. However, the charge storage mechanism relies in the on the different redox reaction mechanisms rather than electrostatic non-Faradaic storage. Pseudocapacitance arises by the passage of charge across the double-layer through the whole bulk of the material, as a battery, but includes the capacitance term that thermodynamically originates from the relationship between extent of charge and the potential difference.

The Faradaic materials can be classified into two main types; electroactive metal oxides/hydroxides and conducting polymers (CPs). Figure 2-8 shows a scanning electron micrograph of a surface of fully oxidized carbon nitride material employed as an electrode of pseudocapacitive characteristic in a supercapacitor device.
Figure 2-8: A close-up of the electrode material in a pseudocapacitor: a scanning electron micrograph of fully composited graphene with carbon nitride with a mass ratio 3:1 graphene oxide/carbon nitride. Copper is the choice of current collector here.

Metal oxides and metal hydroxides can ideally achieve higher energy densities than carbon materials in EDLCs and better electrochemical stability compared to CPs. Within the nominal potential windows, these materials can store energy electrostatically and via electrochemical redox reactions [108]. The general requirements for metal oxides in the supercapacitor application comprise of i) electronic conductivity, ii) existence of the metal in at least two oxidation states that can coexist with no phase changes involving irreversible reactions and iii) free intercalation of ions into/out of the oxide lattice during reduction/oxidation respectively [3]. To date, the materials explored and that fulfil these requirements include manganese oxide, ruthenium oxide, nickel oxide, cobalt oxide and vanadium oxide.

Ruthenium oxide ($RuO_x$) is the most extensively investigated transition metal for its application as an electrode material for supercapacitors due to its high proton conductivity, remarkable specific capacitance, long cycle life, wide operating potential window and its existence in three different oxidation states within a voltage window of 1.2 V [109]. The mechanism of its charging involves different reactions in alkaline and acidic electrolytes. In an acidic media, a rapid electron transfer reaction occurs, accompanied by electro-sorption of protons on the surface of the metal oxide, whereby the oxidation state of ruthenium can change form $Ru^{2+}$ to $Ru^{4+}$ [110]. Contrarily, in a basic solution, it has been proposed that $RuO_2$ in a charged carbon/ruthenium electrode will be oxidized to $RuO_4^{2-}$, $RuO_4^-$ and $RuO_4$ [111]. Upon discharging the electrode, the high valence states will be reduced again to
RuO$_2$. The specific capacitances were determined by the anodic and cathodic currents at 0 V and the sweep rate of cyclic voltammetry. Maximum specific capacitances of 710 F g$^{-1}$ at 4 mV s$^{-1}$ sweep rate, and 720 F g$^{-1}$ at 2 mV s$^{-1}$ were obtained when ruthenium oxide was tested in KOH and H$_2$SO$_4$ electrolyte media, respectively [111, 112]. The pseudocapacitive mechanism is a consequence of the high specific surface areas that provide sites for multiple redox reactions and accordingly higher specific capacitances. Different approaches have thus been implemented to increase the specific surface area of RuO$_x$, including deposition of the metal oxide on substrates with rough surfaces, coating a thin film of RuO$_2$ on high surface area materials, and fabricating oxide electrodes of nanometer size. For example, thin-film electrodes of hydrous RuO$_x$ (RuO$_{x}$xH2O) were electrodeposited on titanium substrates, and the resulting electrode materials exhibited high specific capacitances of 786 F g$^{-1}$ at 100 μA cm$^{-2}$ with excellent cyclability and power density [113]. In another work, a gravimetric capacitance of 914 F g$^{-1}$ at 50 mV s$^{-1}$ scan rate was achieved in 1 M H$_2$SO$_4$ electrolyte solution by preparing the metal particles of uniform size using the polyl method and dispersing them on carbon surfaces [114]. It was also found that the effect of combined water in the metal oxide [115], its crystallinity [116] and size of the particles [117] all contribute to the capacitive mechanism in favourable or unfavourable attributes. The water content enhances the diffusion of cations into the electrode structure of amorphous form, whereby reactions can occur not only on the surface but also in the bulk of electrode. In addition, the smaller the particle size, the shorter the ion diffusion distance and therefore the higher the capacitive performance.

Recently, RuO$_2$.carbon composites have been investigated as potential electrode materials for SCs. Reduced amounts of ruthenium oxide were used, decreasing the costs of electrode fabrication without compromising the specific capacitances achievable in these materials [118-120]. The composites of 14 wt.% Ru/carbon aerogel [119], 9 wt.% RuO$_2$/activated carbon [121], and 60 wt.% RuO$_2$/Ketjen Black [122], have exhibited high specific capacitances of 256 F g$^{-1}$, 190 F g$^{-1}$ and 647 F g$^{-1}$, respectively in three-electrode compartments. The carbon support in the electrode composite would then serve the following purposes:

1- Prevent the agglomeration of the RuO$_2$ particles and contribute to their high dispersion, providing an interaction between RuO$_2$ and carbon surface functionalities.

2- Facilitate ion and electron transfer within its porous structure, therefore allowing the ease of access of the electrolyte ions into the oxide particles.

3- Enable the easy transport of solvated ions from the electrode to the electrode/electrolyte surface, hence increasing the Faradaic reaction sites.
However, it should be noted that the synthesis conditions for these composites require high annealing temperatures, which lead to higher crystallinity of the metal oxide and therefore compromise its utilisation efficiency [123].

The fabrication of ruthenium oxide/carbon composites has thus proven to enhance the homogeneity of the sites for the Faradaic reactions, increase the electrical conductivity and consequently improve the energy and power capabilities of a supercapacitor device. However, care must be taken in the relative ratios of the carbon to the metal oxide as carbons with different porosities, pore size distributions and specific surface areas impact the electrochemical behaviour of the metal oxide in various ways.

Despite the fact that amorphous RuO$_2$ provides very attractive properties for electrode materials in supercapacitors, substituting the metal oxide with other functional materials is necessary due the former’s toxicity to the environment and high cost. Alternative pseudocapacitive materials that have similar electrochemical properties to ruthenium oxide have thus been explored, namely manganese oxide (MnO$_2$) [124], vanadium oxide (V$_2$O$_5$) [125] and nickel oxides (NiO) [126]. The morphology of the manganese oxide primarily influences its capacitive behaviour alongside the valence and hydrous state of the oxide.

Different morphological structures of manganese oxide have been prepared, including nanorods [127], nanowires [128], nanobelts [129] and flower-like nanowhiskers [130]. Similar to RuO$_2$, manganese oxide favours the presence of water for the ease of electrolyte ion transport. In addition, the thickness of electrode plays a crucial role in the electrochemical performance. For instance, the specific capacitance of the electrode decreased from 400 F g$^{-1}$ to 177 F g$^{-1}$ upon increasing the MnO$_2$ loading from 50 μg cm$^{-2}$ to 200 μg cm$^{-2}$, due to the low conductivity of this material [131]. In addition, different challenges must still be addressed for enhancing the electrochemical performance of the metal oxide, including its dissolution problem dying cycling, low surface area and poor electronic and ionic conductivity. MnO$_2$/graphene and MnO$_2$/CNT have been investigated as potential composites that overcome the drawbacks of the metal oxide and optimize the electrochemical performance with effective utilisation of MnO$_2$ [132, 133].

CPs on the other hand, possess different advantages that make them potential materials for supercapacitor applications. These include their low cost, high conductivity in their doped state, wide operating potential windows, low environmental impact and chemical modification that allows redox activity [134, 135]. The Faradaic processes that occur in these candidate electrode materials are similar to that occurring in metal oxides, whereby fast and reversible redox reactions take place and ions are transferred to and from the polymer backbone during oxidation and reduction, respectively. The Faradaic reactions arise
not only on the surface but also throughout the bulk of the conducting polymer in a reversible manner with no alteration of the structures [136]. Electronic conductivity can be instigated with ion insertion in the polymer matrices, generating delocalized electrons on their corresponding chains. Positively-charged polymers, introduced by the oxidation of the repeating units are termed “p-doped” polymers and negatively-charged polymers introduced by reduction are designated as “n-doped” polymers [1]. The electronic state of the \( \pi \) electrons determines the potentials of the doping mechanisms. Commercial CPs employed as electrodes for supercapacitors include polyaniline (PANI) [137], polythiophene (PTh) [138] and polypyrrol (PPy) [139]. All polymers and their derivatives can be employed within a limited potential window, beyond which the polymers might degrade at more positive potentials or switch to an un-doped state and therefore become an insulating material.

Excellent electrochemical performances can be achieved with CPs as electrode materials; Kim et al. reported the fabrication of PPy/carbon fibres/carbon composites via in-situ polymerization with capacitances that reach 588 F g\(^{-1}\) and 550 F g\(^{-1}\) at 30 mV s\(^{-1}\) and 200 mV s\(^{-1}\) scan rates, respectively [140]. In another study, PANI electrode materials achieved a specific capacitance of 815 F g\(^{-1}\) [141]. However, the swelling and shrinking phenomena of CPS might occur during the intercalation and de-intercalation processes, which often deteriorate the electrode’s mechanical stability and subsequently its electrochemical performance. Additionally, CP-based electrodes generally degrade upon cyclability of less than 1000 cycles, specifically when a wide potential window is applied. A capacitance retention rate of 83.8% was reported in a supercapacitor with poly(3-methyl thiophene) after 200 cycles [142]. Another study showed a capacitance loss of 29.5% after cycling PANI nanorods for 100 cycles in the voltage window of 0.2-0.8 V [143]. Different suggestions have been investigated to mitigate the capacitance loss in CP-supercapacitors, including i) improving the materials’ structures and morphologies, such as fabrication of nanorods, nanotubes and nanowires [144], ii) hybridizing a CP electrode with a carbon electrode in asymmetric supercapacitors [145] and iii) manufacturing composite electrode materials, such as adding the conducting polymer with MnO\(_2\) and CNTs that enhance the conductivity and mechanical and cycling stabilities [146, 147].

In conclusion, pseudo-capacitive materials present attractive properties for their potential applications as electrodes in supercapacitors. The reported capacitances in the literature show great potential for improving the electrochemical performances of SCs and thereby increasing the capacitance values and energy delivery. However, the different electrode materials investigated still suffer from various drawbacks, such as low ionic conductivity, low electronic conductivity and difficulties in scalability due to environmental harmfulness and/or costliness. Hence, research is now focused on hybridizing the electrodes to fabricate
composites by combining different carbon-based and pseudocapacitive-based materials to feature the different advantages each offers for an optimized performance.

2.5.2. Electrolyte

The electrochemical performance of a supercapacitor device does not solely depend on the type of electrode materials used, but is also strongly determined by the electrolyte of choice. The electrolyte, of any kind, acts as an ion-conducting medium between the parallel electrode plates, preventing the transfer of electrons. As previously mentioned, the maximum energy that can be stored in electrochemical capacitors is determined by the capacitance and voltage window in which it operates, and therefore the higher the cell operating voltage, the better achieved energy and power densities. The nominal operating window, however, is limited by the stability of the electrolyte. Therefore, the trend in the supercapacitor fabrication is now shifting from an aqueous electrolyte, having a low operating window of 1 V and possibly 2 V, to non-aqueous electrolyte media that allow much higher operating condition up to 3.5-4 V [3]. The thermodynamic decomposition of water as a solvent for aqueous electrolytes, limits the maximum energy delivery in these systems; however, the decomposition voltages for many non-aqueous solvents are much higher. The requirements for the electrolyte in a supercapacitor for optimized capacitive performances include in addition to the wide operating potential windows, high ionic concentration, high conductivity, low toxicity, low cost and high electrochemical stability [1]. Typically, the most widely used electrolytes (electrolyte salt in solvent) in supercapacitors are aqueous, organic and ionic electrolytes.

Aqueous electrolytes, such as sulfuric acid (H₂SO₄), potassium hydroxide (KOH), sodium sulfate (Na₂SO₄) and ammonium chloride (NH₄Cl), provide higher ionic concentrations and lower resistances compared to organic electrolytes. Therefore, higher capacitances and power densities can be achieved, as the equivalent series resistance governing the bulk electrolyte resistance, is lower. Furthermore, aqueous media can be easily prepared and handled, in contrast to organic media that need strict conditions to obtain pure electrolytes. The voltage window of the aqueous electrolyte can be extended to 1.23 V (thermodynamic stability potential window of water), or even a bit higher (as will be demonstrated in the results chapters of this work); yet, it is still considerably low to achieve good energy densities. Generally, aqueous electrolytes exhibit excellent conductivities, as high as 0.8 S cm⁻¹ for 1 M H₂SO₄ at room temperature, which is one (or more) order of magnitude compared to ionic liquid and organic electrolytes [148]. This leads to lower equivalent series resistance values and thus better power delivery. Upon extending the potential windows
beyond the nominal range 0-1.23 V vs. the standard hydrogen electrode (SHE) to more anodic or cathodic conditions, hydrogen and/or oxygen evolution occurs, which consequently leads to deterioration of the capacitive performance. With that in mind, potentials might be extended beyond these values, due to the presence of surface functionalities on carbon surfaces in EDLCs and the structure of the carbon itself, as will be further explored in Chapters 6 and 7. Neutral aqueous electrolytes, generally give lower capacitances compared to alkaline and acidic media, due to the former’s lower conductivity [149, 150]. However, neutral electrolytes, Na₂SO₄ being most commonly used, can operate within extended potential windows in EDLCs of up to 2.3 V, since the concentrations of the H⁺ and OH⁻ ions are relatively lower to those present in basic and acidic electrolytes [151, 152]. This would lead to a delay in the hydrogen and oxygen evolution reactions at extreme potentials. These characteristics lead to increasing the energy densities attained; for example, an energy density as high as 29.1 Wh kg⁻¹ was achieved at a power density of 450 W kg⁻¹ in 1 M Na₂SO₄ for EDLCs in the potential range of 0-1.8 V [153].

Different organic electrolytes can operate within higher potential windows, with the favoured solvents being aprotic, i.e. those not containing electrochemically active hydrogen atoms, such as carboxyl and hydroxyl functional groups. This is a requirement for the operation of these electrolytes at high potentials to avoid the discharge of the hydrogen molecules from active protons in the solvent [3]. Carbonate-based solvents [such as propylene carbonate (PC)] and acetonitrile are the most commonly used solvents; PC offers the advantages of environmental-friendliness and operation within wide potential windows, yet cannot dissolve large amounts of salts that acetonitrile, of toxic nature, can. The organic salts usually employed for the operation of SCs include TEABF₄, tetraethylphosphonium tetrafluoroborate and triethylmethylammonium tetrafluoroborate (TEMABF₄). Generally, the organic electrolytes have lower dielectric constants and larger solvated ions, and consequently lower EDLC capacitance values [154, 155]. The larger organic ions cannot penetrate the finest pore structures of porous carbon electrode materials, which compromise the extensive use of the capacitive performance of the double-layer mechanism. Additionally, the pseudo-capacitive contribution of carbon-based electrodes is usually negligible in organic electrolytes, due to the un-favoured protonic participation on the carbon surface functionalities in aprotic electrolytes [155, 156]. Finally, it should be noted that a controlled environment is required for the preparation of the organic electrolytes, in addition to extensive purification processes to remove any residual impurities, such as water (below 3-5 ppm concentration) to avoid self-discharge mechanism and thus the fading of the electrochemical performance [1].
Ionic electrolytes are also known as low temperature or room temperature molten salts, whereby the salt is liquefied (melted) by providing heat to the system [157]. The ionic liquids present attractive candidates as electrolyte media in the supercapacitor application due to their high electrochemical stability over a wide potential window, high thermal stability and non-toxicity and non-flammability. The green electrolytes are in liquid state at ambient conditions or even at lower temperatures, and are composed solely of ions. The absence of solvents in these electrolytes allows the identification of the anion and cation sizes used, as there is no account for solvation shells. The most commonly used liquids for the supercapacitor application are imidazolium, pyrrolidinium, ammonium and sulfonium. The anions frequently employed include tetrafluoroborate, dicyanamide, bis(trifluoromethanesulfonyl)imide and hexafluorophosphate. It has been reported that pyrrolidinium-based ionic liquids provide wide potential windows while ionic liquids based on imidazolium can contribute to higher ionic conductivities [148, 158]. These ionic liquids can operate at higher potential windows compared to organic electrolytes without compromising the safety aspect and performance of the supercapacitor cell. However, these liquids still suffer from major drawbacks, mainly high viscosity, costliness, and low ionic conductivity. These characteristics affect the electrochemical behaviour of SCs as they lead to an increase in the bulk electrolyte resistances, thus diminishing the power performance of the device. One of the solutions suggested to overcome high resistances was operating the ionic liquids at higher-than-room temperature. The experiments conducted by Balducci et al. [159] demonstrated that an energy density of 31 Wh kg⁻¹ with a cell voltage of 3.5 V can be achieved at 60 °C. In another study, an asymmetric supercapacitor was fabricated using carbon of different loadings on each electrode in an ionic electrolyte with pyrrolidinium cations. Energy densities as high as 40 Wh kg⁻¹ within a 4 V voltage window in the temperature range of -30 °C to 60 °C with excellent cyclability of 98% were achieved, when the positive to negative electrode loading ratio was 1.49 [160]. However, due to their low ionic conductivity, power densities attained are still lower than those in aprotic electrolyte media (9.1 kW kg⁻¹). Hence, further investigations of fabricating ionic liquids with ions of high dissociation constants, giving rise to higher conductivities, and maintaining the electrochemical stability within wide potential windows are underway.

With the rapid development of flexible and wearable electronics, all-solid state electrochemical energy devices have been explored. Solid-state electrolytes have attracted significant attention as they can play the role of both the ionic conducting media and the separator, thus removing one of the bulky components in an SC device, and increasing their volumetric densities. The most commonly used solid-state electrolytes are polymer-based, whether in the solid state (solid polymer electrolytes), gel state (gel polymer electrolytes) or
polyelectrolytes. Gel electrolytes normally have the highest ionic conductivity due to the presence of a liquid phase that provides the means for ion transport; however, they still suffer from relatively narrow operating temperature windows and poor mechanical strength, leading to short-circuiting and thus safety concerns. On the other hand, solid-state electrolytes have the common disadvantages of limited contact area with the electrode materials, which increases the resistance values and limits the full accessibility of the electrolyte to the porous structure of the carbon electrodes [161]. This results in a reduced rate performance and low specific capacitances. Gel polymer electrolytes typically constitute a host polymer matrix (poly(acrylic acid), poly(vinyl alcohol), poly(ethyl oxide) etc.) and a liquid electrolyte which can be either in the form of aqueous or organic solvent. The organic solvent or water is used as the plasticizer, which traps the polymer chains through surface tension [162, 163]. As for the solid-state electrolytes, little research has been devoted in this area due to the electrolyte non-flexibility and non-bendability which leads to poor electrode/electrolyte contact areas and thus low specific capacitances [164]. For ease of fabrication and packaging, along with attaining the highest capacitance values, gel polymer electrolyte comprised of a polymer matrix (polyvinyl alcohol) and liquid electrolyte (Na2S04) have been used in this thesis for the fabrication of SCs in printed circuit board design (further described in Chapter 8).

2.5.3. Compatibility of Electrolytes with Inactive Components

Along with the considerations of the electrode materials and electrolyte media used for supercapacitor applications, it is also necessary to examine the possible interaction between the electrolyte with the bulky materials typically used in the SC. Predominantly, the current collectors, binders and separators, and their corresponding effect on the electrochemical performance need to be investigated prior to manufacturing the supercapacitor device.

2.5.3.1. Current Collector

The morphology and chemical and electrochemical stabilities of the current collectors can hugely influence the electrolyte’s performance as well as the utilisation of the active materials of the electrode. In the case of strong acid electrolytes, corrosion-resistant current collectors should be employed to avoid the degradation of the electrolyte of choice. Gold is the primary candidate for this application; yet to reduce the costs of the SC device, tin oxide [165], carbon-based materials (carbon cloth, carbon fabric, carbon paper etc.) [166] and electrically conductive polymers [167] can be used instead. Free-standing electrodes have also been fabricated to allow the possibility of removing the bulky current collector.
components and thus decrease the internal resistive elements in the system [168]. In alkaline media, the commonly used current collectors are nickel (Ni), due to their good chemical and electrochemical stability in strong basic solutions [169]. The Ni current collector is usually employed in the form of foam to increase the surface area with the electrode and therefore maximize the utilisation of the active materials. However, due to the possible oxidation of the nickel to nickel oxides/hydroxides [170] which might add a pseudocapacitive element in the total performance of the SC cell, stainless steel [171] and carbon-based materials, similar to the ones used in acidic media, can be implemented [172-174]. As for neutral electrolytes, the advantage of their less corrosive nature allows the utilisation of a wide choice of materials. These include titanium [175], nickel [176] and stainless steel [177]. In this thesis, most of the work was implemented in 6 M KOH and thus nickel foam was the current collector of choice. The cleaning process of the foam to avoid any oxidation was carried by washing it in a three-step method, twice with ethanol and once with deionized water, followed by sonication after every washing step. The current collectors were then vacuum-dried overnight and used directly for electrode preparation afterwards.

The current collector normally employed in organic electrolyte media is aluminium, though the solution might lead to its degradation at the highest operating potentials, depending on the type of salt used in the solvent [178]. The compatibility of current collectors with ionic liquids must be given more attention as aluminium can slowly corrode in certain molten salts but show excellent stability in others [179]. As for the polymer gel electrolytes, the choice of the current collector is usually optimized by checking the compatibility of the electrolyte and current collector, mainly considering the flexibility and bendability of the quasi-solid gel polymer [180]. In the SC-printed circuit boards constructed in this work, the pre-impregnated copper current collector showed slow degradation with Na$_2$SO$_4$/polyvinyl alcohol gel electrolyte employed. Further details are described in Chapter 8 and 9.

2.5.3.2. Binder

Binders are usually added to electrode materials composed of activated carbon powders or particles, in which they enhance the structural integrity of the electrodes and provide adhesion between the electrode and current collector. The most commonly used binders in SC cells are fluorinated polymers including, polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE). The properties and quantities of the binder added have proven to have a major influence on the electrochemical performance of the electrodes [181]. For example, increased amounts of PTFE can result in the fabrication of an electrode with hydrophobic nature, which impedes the electrolyte ion transport into the electrode
structure (in the case of using aqueous electrolytes) [182]. The addition of small amounts of polyvinylpyrrolidone into PTFE has shown to increase the electrode wettability, hence increasing the capacitive performance [183]. It is also important to note that the wettability of the electrodes in different electrolytes can vary depending on the choice of binder [184]. Recently, fluorine-free binders have been investigated to reduce the environmental impact, and different binders, such as polyvinylpyrrolidone [185], polyacrylic acid [186] and natural cellulose [187] have shown great potential for SC applications due to their electronic conductivity, in contrast to the fluorinated polymers. However, these binders might contribute to a pseudo-capacitive element to the total capacitance of the active material, thus not giving the corresponding real capacitance values of the electrodes. In this thesis, PTFE and PVDF have been used in different experiments carried, with weight percentages varying between 5% and 10% of the total electrode mass. Further explanation of the procedure can be found in section 3.3.2.1.

2.5.3.3. Separator

The separator layer is placed between the two electrodes of a supercapacitor device to prevent electrical contact between the electrodes, while transporting ions in the solution. The requirements for a separator include i) minimal resistance for ion transfer in the electrolyte, ii) strong electronic insulation, iii) chemical and electrochemical stability in the electrolyte and vi) good mechanical integrity. The separator materials are usually composed of thin, highly porous films such as cellulose, glass fibres and polymer membranes. The choice of the considered options depends on the electrolyte employed, working temperature and potential window. For example, cellulose separators are compatible with organic electrolytes, but might degrade in strong acidic media [188]. On the other hand, the conductivity of ionic liquids in the separator was found to vary and have an impact on the electrolyte resistance and capacitive performance in a supercapacitor [189]. The separator’s properties, including its porosity, pore size distribution, chemical composition and wettability were also found to have an appreciable influence on the bulk electrolyte resistance, time constants for charging/discharging and energy and power delivery. In this work, the separator materials used were glass fibres of 1.6 μm pore diameter in fabricating the different designs of supercapacitor cells.
2.6. Ideally Polarizable Electrode

In this thesis, the activation of cellulose-based materials was investigated, mainly in an alkaline medium. Different performances were achieved with varying the functionalisation conditions. However, the capacitive performance investigated in a range of materials, and at different conditions, leads to the conclusion that the electrodes’ behaviour was not ideal. Before exploring the different factors that might lead to a loss in the capacitance and energy and power densities, the concept of an ideally polarizable electrode is introduced in order to investigate the discrepancy between the theoretical and practical worlds.

In an ideally polarizable electrode, the application of a constant current (or current density) leads to the passage of charges into the double-layer interface without any Faradaic processes of charge transfer across the double layer. The current would remain purely capacitive and charge is stored solely by electrostatic mechanism [50]. The change in potential due to the application of a current to or from the electrode will only cause a change in the charge density on the electrode and associatively, a change in the ionic density on the solution side of the electrode/electrolyte interface, leading to the double-layer capacitive mechanism. The charged interface would then be at electrostatic equilibrium at a specified potential. Conway gave the example of charging a mercury (Hg) electrode in potassium chloride (KCl) aqueous solution where the electrode approaches the ideality state with no Faradaic reactions occurring in the system [3]. In the potential range -0.9–0.23 V vs. SHE, Hg is almost ideally polarizable. Beyond this operating potential window, Faradaic reactions are instigated due to the water electrolysis, leading to the production of nascent hydrogen or oxygen gases as follows:

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  \hspace{1cm} (2 - 19)  

\[ 2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^- \] \hspace{1cm} (2 - 20)

From a thermodynamic stance, the cathodic decomposition of water to give H+ ions would start at 0 V (or less); however in reality, the electrocatalysis for hydrogen evolution at the mercury electrode is very poor due to very small exchange current densities. Therefore, Faradaic processes corresponding to the leakage currents and therefore self-discharge do not commence until potentials less than -0.9 V or even -1 V are reached. The reactions governing the hydrogen evolution process are conveyed in the Eqns. below:

\[ H_2O + Hg \rightarrow HgH + OH^- \] \hspace{1cm} (2 - 21)  

\[ HgH + H_2O \rightarrow Hg + H_2 + OH^- \] \hspace{1cm} (2 - 22)
In the nominal potential window, purely double-layer capacitive currents pass at the electrode/electrolyte interface, which can be characterised with impedance spectroscopy or cyclic voltammetry. The extension of the potential window beyond this range will lead to the electrolyte decomposition, and the current will be a summation of the double-layer capacitive one and the Faradaic leakage one, as discussed in earlier sections.

In practice, the ideally polarizable electrode in supercapacitor application rarely exists, not only if extreme potential conditions were induced, but also due to the presence of impurities in the electrolyte or surface functionalities on the electrode surface. These factors will add a Faradaic element to the system and hence perturb the response of the electrode to a varying voltage or current. The detection of the surface functional groups and extreme potential conditions will be studied for different porous structures in this thesis, correlating the microstructure to the electrochemical performance. Therefore, it is necessary to investigate the underlying factors for non-ideality, such as microstructure and functional groups, and their co-dependence will be explored in the next section.

2.7. Activated Porous Carbon Electrodes

The focus of this thesis will be on activated carbons as electrode materials for supercapacitors, and the relationship between a different range of porous carbons and their electrochemical performance. Throughout the different results chapters, different characterisation techniques are employed and the correlation between the porous morphology, surface chemistry and electrochemistry is explored. Therefore, this section will highlight the findings in the literature of the optimized microstructural properties, surface functionalities and electrochemical performances of different activated and functionalised carbons.

Conway discussed the importance of implementation of porous electrodes with a three-dimensional structure, in the double-layer capacitive mode or pseudocapacitive charge mechanism for a maximized utilisation of the surface area so it renders as the electrochemical surface area [3]. However, the understanding of the trade-off between the pore size and porosity is necessary to implement the suitable carbon material to its corresponding supercapacitor application for maximum efficiency. The porosity usually diminishes with the decrease in the pore size, yet this relationship is also dependent on the pore size distribution and the class of carbonaceous precursor materials used. For optimized performance, the porous electrode should constitute sufficient volume for electrolyte accommodation, the means for electrolyte transport to all accessible surface area and
increasing the specific surface area for enhanced gravimetric and areal capacitances. However, the admission of the electrolyte into the porous matrix does not imply its efficient invasion in the finest porous networks. If this is the case, the finest pore fraction that constitutes most of the surface area of the carbon, would not be wetted by the electrolyte and capacitance loss occurs due to either ineffective electrolyte penetration or accumulation of electrolyte resistances. Pore sizes can be classified into: i) micropores (< 2 nm), ii) mesopores (2−50 nm) and iii) macropores (> 50 nm) [190]. Different pore sizes contribute to the capacitance in different ways; the micropores play a major role under slower kinetic regimes and formation of electrochemical double-layer at low current densities, whereas macropores ensure the wetting of the electrode and fast ion diffusion at higher current densities, which improves high rate performance. In addition, micropores of pore width less than 0.5 nm are too narrow for electrolyte access, whereas macropores of pore width greater than 50 nm do not contribute to the electrolyte adsorption, but can facilitate its diffusion and therefore electrode wettability during charge and discharge [190, 191]. Therefore, the surface morphology and carbon pore structure should be tailored for optimum access to the available surface area, whilst allowing rapid ion transport throughout the pore network. It is of major importance to realize that the porous structure will lead to a non-ideal performance, unlike a planar electrode of two-dimensional structure. Although the advantage of charging a porous electrode will lead to high specific capacitances due to the large specific surface areas, especially at low operating current densities or scan rates, disadvantages also accrue from the use of these materials. These are predominantly i) the difficulty of charge access into the finest elements of the porous structure due to the accumulation of the ohmic resistances associated with the electrolyte in the pores and ii) the internal contact resistances between the porous particles. Figure 2-9 shows a schematic of the charging and discharging mechanism of a porous activated carbon material soaked in an electrolyte solution, whereby double-layer interfaces arise in each of the porous elements of the whole electrode structure.
Figure 2-9: The double layer structure during (a) charging and (b) discharging mechanisms at the scale of a single pore in a porous electrode structure.

Soffer et al. showed that the conductivity of the electrolyte solution in the pores of diameters less than 0.37 nm was orders of magnitude smaller than the conductivity of 0.1 M NaCl electrolyte used in the bulk outside the porous matrix [192]. In addition, ultra-micropores in the oxidized state recorded much lower double-layer capacitances than non-porous electrodes. The study concluded that electrolyte ions invade the finest pores after depletion of their hydration shells. Thereafter, addressing such materials with a charging current or potentials that drive this current, the accessible surface area would not be charged or discharged simultaneously. This is reflected in the impedance spectrum, whereby charging a porous matrix with an alternating voltage or current will lead to non-uniform charge distribution and consequently different relaxation times of the different pore sizes represented by associated resistive and non-ideal capacitive elements. The interpretation of the frequency response of porous materials will be further discussed in Chapters 3, 5 and 6.

It must be noted that the pore size distributions along with the microporous structures hugely depend on the choice of the carbon raw materials and their activation procedure. Therefore, the comparisons of the performances reported in the literature must take this factor into account.

The surface functionalities on the carbon surface of a double-layer capacitor type are another major factor that affects the electrochemistry, in a favourable or unfavourable manner. The activation of carbon with thermal treatment in an inert atmosphere (nitrogen, argon),
hydrogen or vacuum at very high temperatures up to 2800 °C, can lead to micro-
graphitization of the structures with removal of any surface functional groups. In addition,
heat treatments at 1000 °C in carbon dioxide or steam can induce microporous structures and
removal of oxygen surface functionalities. However, due to the exposure to air and the
conditions of pretreatment and the resultant high surface area products, redox reactivity
might arise that contributes to a pseudocapacitive element of the total capacitive
performance. Oxygen complex formation at the carbon surfaces usually occurs initially with
physisorption on the surface, followed by chemical functionalisation and generation of
different functional groups, namely carboxylic, quinonoid, lactone, phenolic and ether
groups. Consequently, carbon materials are far from being inert which gives rise to
electrochemical reactivity upon oxidation or reduction of the different surface functionalities
at extended potential windows, upon overcharging/overdischarging. This can also cause the
introduction of additional oxygen functionalities at extreme anodic conditions or
electrochemical hydrogenations at cathodic polarizations, as will be further explored in
Chapter 7. The conductivity of carbon and surface conditioning are of substantial importance
for performance optimization and minimization of self-discharge rates, thus requiring a
lessening of surface functionalities. Albeit this fact, different acidic and basic groups can
enhance the wettability of the carbon electrodes, a favourable condition for improving the
electrolyte invasion into the porous structures. The presence of functional groups, mainly on
the edges of the planes in graphitic carbon for example, increases with the surface area. This
“addition” affects the contact angle between the electrode and electrolyte and thus can
influence the wetting behaviour of the porous matrices. It was reported that the oxidation of
carbons electrochemically increases their wettability, and thus electrochemical access of the
electrolyte into the pores, due to an increased number of oxygen functional groups,
associated with hydrophilic groups [193]. However, electrochemical reduction had the
opposite effect. The surface functionalities also influence the point of zero charge and
specific adsorption of ions to the electrode surface, making the distinction of the double-
layer capacitance and pseudo-capacitance much more complex in the case of a porous matrix
electrode [194]. Another study showed that the electrochemical oxidation of glassy carbon,
which generates an active surface region that is porous and permeable by the electrolyte,
decreases the internal resistance values and therefore makes these materials particularly
suitable for high power-density applications [195]. Therefore, the balance between different
factors that affect the pronounced performance, including the porosity, total pore volume,
pore size distribution, wettability and its relation to oxygen functionalities, and accessibility
of the electrolyte into the porous matrices needs to be assessed before announcing the best
capacitive performance. These aspects, combined will be further explored in the different
results chapters of this work.
Since most of the work in this thesis was conducted on activated cellulose materials with KOH, a brief review of the most relevant work is presented herein. The KOH activation procedure was first patented by Wenneberg and O’Grady in 1978. The activation mechanism with KOH is rather complex and comprises different chemical reactions. The products of melting KOH at 360 °C are potassium carbonate, potassium oxide, metallic potassium, hydrogen, carbon monoxide and carbon dioxide.

The interactions between alkaline hydroxides and carbon materials have been studied by Yamashita and Ouchi, who proposed the overall reaction that occurs at 597 °C and above, in the case of using KOH as the chemical agent [196]:

\[
4\text{KOH} + -\text{CH}_2 \rightarrow \text{K}_2\text{CO}_3 + \text{K}_2\text{O} + 3\text{H}_2 \quad (2 - 23)
\]

Otowa et. al later described the process with a set of reactions that happen beyond two temperatures onsets [197]. Below 700 °C, the dehydration of KOH into \( \text{K}_2\text{O} \) produces carbon, which evolves into carbon dioxide as follows:

\[
2\text{KOH} \rightarrow \text{K}_2\text{O} + \text{H}_2\text{O} \quad (2 - 24)
\]

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \quad (2 - 25)
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (2 - 26)
\]

\[
\text{CO}_2 + \text{K}_2\text{O} \rightarrow \text{K}_2\text{CO}_3 \quad (2 - 27)
\]

Beyond 700 °C, the formation of carbon monoxide (CO) occurs and its evolution occurs as follows:

\[
\text{K}_2\text{O} + \text{C} \rightarrow 2\text{K} + \text{CO} \quad (2 - 28)
\]

\[
\text{K}_2\text{CO}_3 + \text{C} \rightarrow 2\text{K} + \text{CO} \quad (2 - 29)
\]

The formation of metallic potassium occurs alongside the activation mechanism, which is directly related to the formation of the porous structures. The metal liberated at these reaction temperatures might intercalate and force the lamellae apart from each other in the crystallites. Washing the potassium salts away from the produced carbon creates the porous structure [198]. The dependence of the pore size distribution of the final product upon carbonisation on the weight ratio of activating agent to precursor material was also investigated, and it was illustrated that three different “zones” can be classified [199]. The first zone corresponds to agent/precursor ratio of less than 50%, whereby micropores are dominant in the structure. In the second zone, when the ratio ranges between 50% and 100%, a competition between the generation of micropores and their widening into
mesopores arises. As for the third zone, it constitutes the production of carbon materials that are mainly macroporous.

Different approaches of the activation and treatment methods and various choices of precursor materials have ever since been reported; however as mentioned earlier, the comparison between different capacitive performances should account for the variable conditions. Table 2-1 presents the specific surface areas (SSA) and specific capacitances ($C_s$) of different KOH-activated carbons from biomass in different electrolyte media reported recently in the literature.

Table 2-1: Most recent developments in the bio-based electrode materials and their properties in supercapacitors.

<table>
<thead>
<tr>
<th>Carbon Precursor</th>
<th>Electrolyte Media</th>
<th>Potential Window (V)</th>
<th>SSA (m$^2$ g$^{-1}$)</th>
<th>$C_s$ (F g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agar</td>
<td>6 M KOH</td>
<td>1</td>
<td>1672</td>
<td>226 at 1 A g$^{-1}$</td>
<td>[200]</td>
</tr>
<tr>
<td>Tobacco</td>
<td>6 M KOH</td>
<td>1</td>
<td>1297</td>
<td>148 at 0.5 A g$^{-1}$</td>
<td>[201]</td>
</tr>
<tr>
<td>Squid Gladius</td>
<td>1 M H2SO4</td>
<td>1.2</td>
<td>1129</td>
<td>204 at 05 A g$^{-1}$</td>
<td>[202]</td>
</tr>
<tr>
<td>Sugar Cane bagasse</td>
<td>1 M H2SO4</td>
<td>1</td>
<td>2904</td>
<td>350 at 1 A g$^{-1}$</td>
<td>[203]</td>
</tr>
<tr>
<td>Loofah Sponge</td>
<td>6 M KOH</td>
<td>1</td>
<td>2718</td>
<td>309 at 1 A g$^{-1}$</td>
<td>[204]</td>
</tr>
<tr>
<td>Bamboo Cellulose</td>
<td>6 M KOH</td>
<td>0.9</td>
<td>1085</td>
<td>381 at 5 mV s$^{-1}$</td>
<td>[205]</td>
</tr>
<tr>
<td>Rotten Carrot</td>
<td>6 M KOH</td>
<td>1</td>
<td>1253</td>
<td>135.5 at 10 mHz</td>
<td>[206]</td>
</tr>
<tr>
<td>Chitosan</td>
<td>0.5MLi2SO4</td>
<td>1.8</td>
<td>3312</td>
<td>264 at 10 mV s$^{-1}$</td>
<td>[207]</td>
</tr>
<tr>
<td>Aquatic Plant</td>
<td>6 M KOH</td>
<td>0.8</td>
<td>2895</td>
<td>275 at 0.5 A g$^{-1}$</td>
<td>[208]</td>
</tr>
<tr>
<td>Rice Straw</td>
<td>6 M KOH</td>
<td>1</td>
<td>3333</td>
<td>400 at 0.1 A g$^{-1}$</td>
<td>[209]</td>
</tr>
<tr>
<td>Osmanthus Flower</td>
<td>6 M KOH</td>
<td>1</td>
<td>2722</td>
<td>172 at 1 A g$^{-1}$</td>
<td>[210]</td>
</tr>
</tbody>
</table>

With the prospect of enhancing the surface area and the electrochemical performance of activated carbon, banana fibres were treated with different activating agents, namely zinc chloride ($\text{ZnCl}_2$) and KOH [211]. The activation with 10 wt.% ratio of either of the activating agents enhanced the surface area from 36 m$^2$ g$^{-1}$ in the untreated carbon to 1097 m$^2$ g$^{-1}$ and 686 m$^2$ g$^{-1}$ when activated with $\text{ZnCl}_2$ and KOH, respectively at 800 °C. In addition, it was found that pore generation was due to the presence of oxygen content in
KOH that results in the elimination of cross-linking and thus stabilization of carbon atoms in the crystallite. As for the metallic potassium, it intercalates in the pores during carbonisation and is afterwards removed in the washing process. However, ZnCl₂ acts as a dehydrating agent during pyrolysis, resulting in the carbon aromatization and consequently yielding the porous nature. In both cases, most pores were in the mesoporous range. This led to low capacitive performances of the KOH-activated and ZnCl₂-activated banana fibres in 1 M Na₂SO₄ neutral electrolyte of 66 F g⁻¹ and 86 F g⁻¹ at 5 mV s⁻¹ scan rate, respectively in a three-electrode system. In a more recent study, pomelo peels were activated with KOH to yield honeycomb-like porous carbons of 2725 m² g⁻¹ surface area and interconnected microporous structure [212]. The activation procedure comprised of carbonisation of the untreated pomelo at 400 °C, followed by activation with KOH and finally a second-step carbonisation process up to 800 °C. A ratio of 1.5:1 of KOH/pomelo yielded the highest specific capacitance of 342 F g⁻¹ at 0.2 A g⁻¹ current density and excellent cyclability of 98% after 1000 charge-discharge cycles. The assembly of a symmetric supercapacitor delivered an energy density of 9.4 Wh kg⁻¹ in the voltage range 0–1 V in 6 M KOH. These results were attributed to the domination of the microporous structure that boosted the charge storage capacity, with a small percentage of meso- and macropores that served as accommodators for the ions’ kinetics. In addition, a pseudo-capacitive element introduced by nitrogen and oxygen surface functionalities was demonstrated to contribute to the total capacitive performance. It was suggested that oxygen can contribute to redox reactions on the surface of porous matrices, while nitrogen can attract protons to the surface with their electron-rich nature. Similar conclusions were drawn in another study that constituted the same activation procedure of pomelo peels with KOH with weight ratio 4:1 KOH/pomelo [213]. A similar activation procedure was applied in this study by choosing 600 °C as the final temperature in the first-step carbonisation. However, the structures obtained were oxygen abundant, which led to the operation of the symmetric supercapacitors in a wide potential window of 0-1.7 V in 2 M KOH solution. The energy density was consequently hugely enhanced up to 17.1 Wh kg⁻¹ with a maximum capacitance of 43.5 F g⁻¹. The materials possessed a specific surface area of 2100 m² g⁻¹, lower than those obtained in a comparable study, highlighting that large specific surface areas are not the only factor that contributes to enhanced electrochemical performances. Another work highlighted similar conclusions to those of Reference [212], whereby oxygen and nitrogen functional groups contributed with a pseudocapacitive element to the total capacitance of microporous activated carbon electrodes from coconut shell [214]. However, it has shown that the functional groups, specifically quinone oxygen and pyrrolic and pyridinic nitrogen, reveal this role in pores of diameters larger than 1 nm. On the other hand, pores of smaller sizes (0.5-0.6 nm) showed most effectiveness in the formation of double-layers.
Different bio-derived materials were also activated with KOH of different mass loadings and their electrochemical performance in different electrolytes was investigated. The employed raw materials ranged between palm oil kernel shell [215], coconut shell [214], rice husk [216], palm oil fruit bunches [217], cotton [218] and tree bark [219]. Cellulose is also a widely used precursor material for electrode application in supercapacitors due to its versatile properties, including its eco-friendliness, abundance, biodegradability and cost-effectiveness. Different studies have investigated the activation of cellulose with KOH and its electrochemical performance in supercapacitor devices. Bacterial cellulose has been employed as the electrode material and electrolyte to fabricate symmetric supercapacitors [220]. The electrode material was prepared via activation of the cellulose with KOH (mass ratio 1:1) and carbonisation at 900 °C. As for the gel electrolyte, it was obtained by soaking bacterial cellulose in phosphoric acid. The electrode’s structure was dominated by micro- and mesopores and the specific surface area achieved was 491 m² g⁻¹. The maximum specific capacitance achieved was 242 F g⁻¹ at a current density of 0.1 A g⁻¹ with capacitance retention of 59% upon increasing the current density to 10 A g⁻¹ and, 93% cyclability after 10,000 cycles. The performance of bacterial cellulose was immensely improved in another study upon hybridizing the materials with graphene and N-doped activated carbon from shaddock peel [221]. The ultrafine three-dimensional structure showed an excellent capacitive performance of 2 F cm⁻² at a current density of 2 mA cm⁻², 82.3% capacitance retention upon increasing the current density to 40 mA cm⁻² and 97% cyclability over 10,000 cycles. The maximum energy and power densities achieved were 0.16 mWh cm⁻² and 28 mW cm⁻² in the voltage window of 0-1.4 V in Na₂SO₄ electrolyte. Upon controlling the nitrogen content in the electrode materials of cellulose origin, the specific capacitance was also enhanced to a value of 193 F g⁻¹ at 0.5 A g⁻¹ with 107% capacitance cyclability after 5000 cycles [222]. In addition, an energy density of 17.1 Wh kg⁻¹ was achieved at a power density of 400 W kg⁻¹ when the nitrogen content was optimized to 3.61 wt.% of the total cellulose aerogel mass. The good performances were attributed to the formation of interconnected channels of micro-, meso- and macropores in addition to the hydrophilic nitrogen content that increased the wettability of the electrodes and provided an additional pseudocapacitive contribution. Similar results were obtained in another study by carbonising nanocellulose aerogels in CO₂. The highly porous structure with a specific surface area of 1873 m² g⁻¹ and total pore volume of 2.65 cm³ g⁻¹ achieved specific capacitances of 30.2 F g⁻¹ and 205 F g⁻¹ at 20 A g⁻¹ and 0.5 A g⁻¹ current densities, respectively in 6 M KOH in a three-electrode setup. The work highlights the advantages of supercritical drying of carbon aerogels and further activation with CO₂ to obtain large specific surface areas and an interconnected porous structure [223].
Numerous techniques have been also employed to investigate and optimize the electrochemical behaviour of activated carbons as electrode materials in supercapacitors. One of these methods is electrochemical impedance spectroscopy, which is studied extensively in this thesis. The latter has proven to be a useful tool to evaluate the different resistive and capacitive components in different porous electrodes at variable conditions in attempt to decrease the total impedance values. Different studies included comparisons between different activated carbons [224, 225], different electrolyte solutions [226], various operating temperatures and voltages [227-230], before vs. after cycling the supercapacitor [231], and different contributions of pseudocapacitive elements added to the carbon surface [232, 233]. The modelling of the capacitance dependence on the frequency, thermal and voltage conditions of a Maxwell 2600F commercial supercapacitor has been also studied [234]. The proposed model included 14 equivalent circuit elements to mimic the frequency response over the temperature range of -20–60 °C and in the voltage range of 0–2.5 V. However, an in-depth study of the correlation between the microstructure, surface science and impedance behaviour in different frequency ranges is still lacking. In addition, the modelling of a porous carbon electrode with a simple and easily-applied equivalent circuit has not been explored. Therefore, in this work, we focus on KOH-activated carbons of different porous morphologies and surface chemistry, and investigate their impedance response at different frequencies and variable potentials. Further details on this work are described in Chapters 5 and 6. Studies in the literature have also reported the investigation and comparison of different amorphous structures of carbon electrodes in supercapacitors via in-situ Raman spectroscopy and X-ray diffraction techniques to adopt the best capacitive performance [133, 216, 235, 236]. Additionally, in-situ Raman spectroscopy was previously used in supercapacitor applications for studying the electrochemical polymerization of carbon nanotubes or graphene [237, 238], electrochemical tuning of the electronic structure of carbon nanotubes [239], demonstration of ion intercalation into microcrystalline graphite [240, 241] and electrochemical doping of carbon nanotubes [242]. In this work, in-situ Raman spectroscopy was employed to study the extreme anodic and cathodic conditions activated porous carbon electrodes can endure for supercapacitor applications, which is a function of the porous structure and oxygen content.

In conclusion, the focus of the different studies in this review on activated carbon materials is targeted towards the increase in specific capacitance values and the energy and power densities of the supercapacitor devices. All of the different aforementioned parameters in this section, including large specific surface areas, wide pore distributions and functional groups on the carbon surface are major factors that embellish the electrochemical performance. The achievements reported are of great value and importance; yet, the best
capacitive performance is typically determined at a specific condition, whether it is a constant scan rate, current density or a certain frequency in the impedance spectrum. Therefore, an evaluation of the electrochemistry at different conditions, be it potential, frequency or current density and understanding its synergy with the physical and chemical properties is still questionable. Applying different characterisation techniques of the carbon architecture, and correlating the results with electrochemical properties, investigated specifically with in-situ Raman and electrochemical impedance spectroscopies are the main aims of this work. This will allow the tailoring of the required properties of the electrode materials for their final application.

2.8. Insights into Fabricating New Supercapacitor Devices

Different approaches have been taken to optimize the capacitive performance and energy and power delivery of supercapacitors in recent years. Asymmetric supercapacitors have been predominantly fabricated for this purpose, by utilising the advantageous characteristics of both carbon-based and pseudocapacitive-based materials. For example, Chen et al. have shown that an asymmetric device based on an activated carbon from wood anode and MnO$_2$/wood carbon cathode separated by a wood membrane have shown excellent cyclability of 93% over 10,000 cycles in lithium chloride/PVA gel electrolyte [58]. In addition, a high energy density of 1.6 mWh cm$^{-2}$ and optimized power density of 24 W cm$^{-2}$ were achieved when the mass loadings of the active anode and cathode materials were increased up to 30 mg cm$^{-2}$ and 75 mg cm$^{-2}$, respectively. In another study, high specific capacitances of 276 F g$^{-1}$ at a current density of 2 A g$^{-1}$ with capacitance retention of 72% (current density of 20 A g$^{-1}$), were attained with porous polypyrrole nanowires/MnO$_2$ nanoflakes and activated carbon asymmetric supercapacitor [243]. An energy density of 25.8 Wh kg$^{-1}$ at a power density of 901 W kg$^{-1}$ was recorded in this work upon extending the potential window to 2 V in Na$_2$SO$_4$ electrolyte. Fibre-shaped flexible supercapacitors were also fabricated using molybdenum trioxide nanorods/reduce graphene oxide as the anode and MnO$_2$ nanorods/ reduce graphene oxide as the cathode in phosphoric acid/PVA polymer gel [244]. The superior performance was characterised with the cyclic reversibility of 97.6% after 500 cycles and 18.2 mWh cm$^{-3}$ energy density at a power density of 74.5 mW cm$^{-3}$. Many materials have been fabricated and investigated as candidate electrode materials for supercapacitors including, but not limited to functionalised carbon fibre fabrics with nitrogen and oxygen [245], holey-graphene niobia composites [246], three-dimensional vanadium nitride nanowires on CNT [247] and sulphur-doped graphene films [248].
The fabrication of micro-supercapacitors is another recent approach towards increasing the electrochemical performance of supercapacitors, as the ever-growing demand for flexible electronic devices requires highly compact energy storage. Extensive investigation has been carried on the manufacturing of micro-supercapacitors using different methods, namely printing [249], laser-assisted methods [250], and lithography [251]. Asymmetric micro-supercapacitors that were binder-free and without a current collector were assembled using a self-made mask and spray coating technique onto a transparent substrate [252]. The electrodes constituting reduced graphene oxide and titanium carbide achieved high electrochemical performance of 8.6 mW h cm$^{-3}$ energy density at 0.1 W cm$^{-3}$ power density within 1 V operating window. In addition, excellent cyclability of 97% was recorded after 10,000 cycles. Zhu et al., on the other hand used an electrochemical deposition technique of polypyrrole nanowires on fluorine-doped tin oxide glass [253]. The fabricated cells showed ultrahigh energy densities (15.25 mWh cm$^{-3}$) at a power density of 0.89 W cm$^{-3}$. Different flexible micro-supercapacitors have been fabricated since, using chemical vapour laser cutting [254], electrodeposition method in a three-electrode system [255], micro-plasma jet etching [256] and 3D printing [257].

As demonstrated in this section, the investigation of new materials as potential electrodes for supercapacitor devices and their compatibility with different electrolyte media has gained increasing interest. Extensive research has been carried out to overcome the unfavourable conditions of self-discharge, use of bulk inactive materials, and inefficient utilisation of the maximum capacitances, to increase the energy and power capabilities of these electrochemical devices. However, the packaging and scaling-up of supercapacitors for flexible and wearable electronics is still lacking. Therefore, it is suggested in this thesis the fabrication of supercapacitors in a printed circuit board (PCB) design. PCBs have been widely used in the fuel cell applications and have shown promising potential for commercialization at different scales for different devices [258-264]. The construct offers the mechanical integrity, cost-effectiveness, ability to produce different cell types, and the utilisation of a wide range of materials. In addition, its conventional application in the fuel cell industry offers the great potential of hybridization with different electrochemical devices, thus optimizing the performance of a combination of different energy conversion and storage systems. The demonstration of the feasibility of the integration of supercapacitors into PCBs is explored and its potential application in different electrolyte media is studied.
2.9. Conclusions

In this chapter, the basic operating principles of the two different classes of supercapacitors, as well as their essential components, are described. The double-layer capacitance based on the electrostatic charge mechanism and Faradaic processes arising from surface functionalities on carbon surfaces, pseudo-capacitive elements and electrolyte decomposition at extended potential windows are explored. The various electrolyte media and their compatibility with the inactive components in a supercapacitor have been also reviewed. The effects of surface functionalities on carbon electrode surfaces, surface areas of the carbon itself, alongside the tuning of the pore size distribution of the porous carbon electrode in double-layer type capacitors are portrayed as the primary factors that influence the capacitive mechanism in these devices. It was shown that the concept of an ideally-polarizable electrode cannot be achieved in practice and the reasons for non-ideality were explained. In addition, new insights into the fabrication of supercapacitor devices with high energy and power delivery are outlined.

Many materials have been investigated for their potential application as electrodes or electrolytes for EDLCs, pseudocapacitors and/or hybrid systems with great potential of enhancing the capacitive performance and energy delivery. However, a review of the literature reveals that there remains a lack of understanding of the correlation between the structural and surface-science properties of activated carbons and their electrochemical performance as electrodes in supercapacitor materials. In this thesis, the application of different characterisation techniques across multiple dimensions is carried out to present a comprehensive interdependence between the structure and function of conventional porous electrode materials in supercapacitors. This allows the determination of the reasoning of the capacitive behaviour of different employed electrodes at different operating conditions. Furthermore, the electrochemical impedance spectroscopy and \textit{in-situ} Raman spectroscopy techniques are explored at different potentials, providing insight on the electrochemistry synergized with the microstructural properties of activated carbons for favourable coordination of the suitable electrode material with its final application. The optimization of energy and power density was investigated by introducing a conventional, but new to supercapacitor, design.
Chapter 3

Methodology

As demonstrated in the literature review, different parameters play a major role in the optimization of supercapacitor devices. The synergy between structural and electrochemical conditions is therefore emphasised in this thesis, applying a suite of characterisation techniques that analyse porous carbon materials as potential electrodes for supercapacitors. The focus of this project was aimed at understanding the various essential (macroscopic and microscopic) specifications of electrical double-layer capacitors to promote the coordination between the starting point of choosing the suitable electrode materials and the demands of the specific final designated use. This study also covered the scope of the potential application of a new layout of supercapacitor devices to optimize the conditions of its hybridisation with other electrochemical storage devices and its suitable packaging for real-world applications. Therefore, the electrode criteria and overall device performance were evaluated as illustrated in Figure 3-1, by the joint application of the following methods:

- Fabrication of porous electrodes via chemical activation of biomass cellulose followed by carbonisation to optimize the materials’ nominal specification.
- Utilisation of one-, two- and three-dimension structural characterisation techniques that allow the investigation of the surface morphology, pore size distribution, porous structure and associated surface functionalities.
- Electrochemical testing of different porous structures and uncovering its interrelationship with the structural characteristics. More specifically, we will focus on the electrochemical impedance spectroscopy technique.
- Engineering new supercapacitor design based on the conventional and cost-effective construct of a printed circuit board.

The results of each experimental method in the subset of the corresponding techniques used will be validated throughout the following chapters of this thesis. In this chapter, these tools will be introduced to allow the analysis of the complex interplay between structural and electrochemical parameters throughout this project.
3.1. Carbon Materials Overview

For electrochemical double-layer capacitor applications, the chemical activation pre-treatment of raw carbon materials followed by thermal carbonisation is the preferred route to achieve high surface areas and optimum pore accessibility by the electrolyte ions. This allows attaining high volumetric and/or gravimetric capacitances, best stability rates, minimal self-discharge rates upon cycling and therefore highest energy and power delivery [3]. The activation procedure often comprises heat treatments between 800°C and 2800°C in inert atmospheres (Nitrogen, Argon) or in vacuum [265-269]. An alternative method of treatment is possible through carbon dioxide or hydrothermal carbonisation in steam [270-273]. At high temperatures, micro-graphitisation and removal of oxygen surface functionalities alongside the evolution of microporous structures occur. As previously mentioned in Chapters 1 and 2, bio-derived materials have gained increasing interest in the energy conversion and storage devices field due to their abundance, sustainability and reproducibility [220]. Different precursor materials, including coconut shells [69], banana peels [67] and chicken feather [274] have been functionalised and employed as electrode materials in EDLCs. These materials have been established as model systems and are easily tuned to achieve porous carbons of high specific surface areas that enhance the electrochemical performance of supercapacitors. The use of cellulose nanocrystals and nanofibres including both natural and bacterial types, has established a remarkable
revolution of being used as electrode materials for supercapacitor devices owing to their abundance, low cost and eco-friendliness [59-62, 275]. The flexibility in tuning the structure of cellulose and its incorporation with other materials to form composites of attractive specifications has a promising potential application in energy storage devices, both on academic research and industrial production levels [276-281]. Cellulose was the raw material of choice throughout the experiments conducted in this project and the preparation and characterisation techniques used will be discussed in the following sections of this chapter.

3.2. Raw Materials, Functionalisation and Carbonisation

All experiments in this thesis were conducted on cellulose precursor materials from softwood Kraft pulp origin as model systems for porous carbon electrodes in supercapacitor devices. The pulp constituted of α-cellulose (> 85 %), from Pinus Silvestris and Picea Abies and was provided by UPM-Kymmene Corporation (Finland). The mean fibre length the raw material, as provided by the manufacturer’s specifications, is 1 mm and the grammage of the sheets is 1000 g m\(^{-2}\). The native cellulose was first cut into 1 cm\(^2\) pieces and dispersed in deionised water to produce 1 wt.% cellulose solution of grammage 500 g m\(^{-2}\). The mixture was kept under ambient conditions for 24 hours to ensure the softening of the cellulose material and was then stirred for 2 minutes in a 400 W plug blender (Lloytron, UK). Once homogenised, the mixture was vacuum filtrated through a 9 cm diameter Buchner funnel (Appleton Woods Ltd, UK) using filtration and blotting papers of 9 cm (with 5−13 µm particle retention) and 15 cm diameters, respectively (VWR, UK). This procedure was followed by a two-stage press (Carver Inc., USA) process: (i) wet-pressing at room temperature for 5 mins and (ii) hot-pressing for 25 mins at a pressure of 5000 lbs and 120 °C to guarantee a flat and homogeneous sample throughout.

The chemical activation process involved dipping the cellulose filter cakes in different molar concentrations of potassium hydroxide (KOH) solutions supplied by Fisher Scientific (UK). More precisely, 10 g of raw paper was impregnated in 50 mL solution of KOH with KOH / cellulose ratios of 0.005, 0.01, 0.1, 0.5, 1, 2 and 3 (wt.%) and soaked for 4 h at 60 °C in air. The samples were then dried overnight in a vacuum oven at 110 °C and carbonised at 850 °C with a heating ramp of 20 °C min\(^{-1}\) for 2 h, under an inert atmosphere of dry nitrogen in a tubular furnace (Vecstar, UK). Similar activation procedures using KOH, as a chemical activating agent and starting with biomass materials have been described elsewhere [191, 272, 282-285].
The ‘chalky’ carbonised samples were washed with deionised water and hydrochloric acid and filtrated several times to remove any potassium carbonate residues, and dried overnight at 80 °C. Hereafter, the obtained carbonised samples with KOH activation will be denoted as KOH-$n$ throughout the different chapters of this thesis, where $n$ refers to the KOH / cellulose weight ratio. The yield was calculated according to Eqn. (3-1) and the values for each sample are reported in Table 3-1 below:

$$\text{% yield} = \frac{\text{mass after carbonization}}{\text{initial mass before carbonization}} \times 100 \text{ (%) \hspace{1cm} (3 - 1)}$$

Table 3-1: Summarization of the yield of each experiment using different KOH loadings.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH-0</td>
<td>10.0</td>
</tr>
<tr>
<td>KOH-0.005</td>
<td>12.7</td>
</tr>
<tr>
<td>KOH-0.01</td>
<td>13.2</td>
</tr>
<tr>
<td>KOH-0.1</td>
<td>12.0</td>
</tr>
<tr>
<td>KOH-0.5</td>
<td>10.9</td>
</tr>
<tr>
<td>KOH-1</td>
<td>4.1</td>
</tr>
<tr>
<td>KOH-2</td>
<td>4.7</td>
</tr>
<tr>
<td>KOH-3</td>
<td>1.2</td>
</tr>
</tbody>
</table>

It should be noted that the carbonisation temperature was chosen to be 850 °C as lower temperatures proved to yield amorphous structures, while higher temperatures resulted in products containing graphitic fringes with interlayer spacing approaching that of graphite which lead to a decrease in the specific surface area [190]. Figure 3-2 describes the synthesis steps starting with the raw pulp materials onto the fabrication of the final carbonised samples used in the electrode preparation step.
Figure 3-2: Schematic illustration of the synthetic procedure of activation and carbonisation of precursor cellulose materials.

The prepared carbons were compared against a baseline of commercial benchmarks, Ketjen Black 600 (KB), Norit activated carbon (NAC), and bead-shaped activated carbon (BAC). KB (AkzoNobel, UK) is a pure conductive carbon black, BAC (Kureha America Inc., USA) is a conductive carbon with petroleum pitch as raw material, and NAC (CABOT Corporation, USA) is an activated carbon with < 15 wt.% KOH composition.

3.3. Characterisation Techniques

As will be elucidated in the different chapters of this work, different characterisation techniques were used to analyse the chemically activated and commercial carbons in one-, two- and three-dimensional analyses. As a big portion of this thesis is focused on the correlation between form and function of carbons as electrode materials in supercapacitors, the depictions formed by a suite of characterisation techniques of the surface structure, pore size distribution, surface chemistry and electronic structuring are described in this section.

3.3.1. Imaging

3.3.1.1. Scanning Electron Microscopy

Scanning electron microscopy (SEM) is used to capture the surface structure of a sample with a resolution in the range of micrometers to nanometers. The sample is irradiated with a focused beam of electrons at a specified voltage, resulting in interactions between the atoms of the sample at various depths and the electrons [286]. Signals including back-scattered
electrons, secondary electrons and characteristic X-rays are produced, and the topographic images of the sample are collected on the detector, from the back-scattered or secondary electrons, depending on the type of detector used in the machine. In this thesis, the surface morphology of the different carbons described in the earlier section was detected using the Zeiss EVA MA 10 (Germany) scanning electron microscope, operating at 10 kV in the secondary electron imaging mode to achieve high-resolution capture of the topography of different samples. The samples were mounted on a carbon-coated stub in the SEM. Since the samples in this work are conductive, the use of a gold coater was not necessary. Figure 3-3 shows an example of the surface morphology of Ketjen Black, one of the carbon materials used as a benchmark electrode in this work. The porous structure at a micrometer resolution can be observed using this technique.

![SEM image of KB carbon showing the surface structure in the micrometer range.](image)

Figure 3-3: SEM image of KB carbon showing the surface structure in the micrometer range.

### 3.3.1.2. Transmission Electron microscopy

To achieve higher resolutions of the surface structure of a material in the nanometer range, transmission electron microscopy (TEM) can be used to complement the images obtained with an SEM to cover a big range of sizes of the parameter of interest (particles, fibres, pores, etc.). The beam of electrons used in this microscopy technique is transmitted (and hence the name) through the sample which causes an interaction between the sample and the beam [287]. Different types of electrons would then be projected from the surface of the specimen, un-scattered and scattered electrons of different wavelengths. Imaging methods (imaging and diffractions modes) modify the wave distribution and the selected signal is magnified and focused onto an imaging device with the help of a projector lens. In this work, the JEOL JEM-2100 (UK) TEM was used to capture the pores of nanometer range of the different carbon samples, operating at an accelerating voltage of 200 kV. For the sample
preparation, it is necessary to have the specimens of less than 100 nm thicknesses or diluted in a solution on a grid to avoid artefacts from scattering cross-section of the atoms of the materials of interest. In this work, a small amount of each of the carbon powders was diluted in isopropanol and sonicated for 1 h to ensure good dispersion. Using a micropipette and under an optical microscope, a few drops of the suspension were applied to a carbon mesh TEM grid (Agar Scientific) and allowed to dry. The grid was then fixed on the sample holder and positioned in the TEM. Figure 3-4 presents one of the TEM images collected for KOH-0.1 sample showing the microporous structure (pores of diameter < 2 nm) and almost-graphitic plane structures.

Figure 3-4: TEM image of KOH-0.01 showing curved graphene planes (with interlayer spacing higher than that of pristine graphite (0.335 nm)) and formation of micropores due to the carbonisation process. Graphitization level depends on precursor carbon material, temperature and heating program during the carbonisation process.

3.3.1.3. X-ray Computed Tomography

A beam of X-rays is incident upon an object from an X-ray source, in which they get absorbed, transmitted and/or scattered using the X-ray computed tomography (X-ray CT) technique [288, 289]. The projected 2-dimensional images would then be obtained progressively as the specimen is rotated 180° at specified angular increments. The transmitted X-rays would then be recorded by a detection instrument and the image collected is digitised for further processing. The two imaging modes of an X-ray CT constitute the absorption-contrast and phase contrast modes. The former detects the X-ray radiation attenuated by an object; i.e. the extent to which the radiations are lost in the material. The phase-contrast mode comprises increasing the contrast between different objects of similar
attenuation and poor X-ray absorption contrast. Zernike phase contrast is of most relevance in this work as this technique emphasizes the material edges of the weakly attenuating carbons by using phase shifts across the incident beam.

In this work, the ZEISS Xradia 810 Ultra (USA) was used in the Zernike phase-contrast mode to collect nano-CT 3D datasets of three samples, with the beam energy set to 5.4 keV. For the tomographic scans of KOH–0.1, KOH–1 and KOH–2, 1901, 1801 and 1401 images were acquired respectively, with an exposure time of 24, 40 and 70 s for each projection image, over 180° rotation of each sample and a camera binning setting of 1. This yielded an effective voxel size of 63.1 nm for all scanned materials. The tomographic scan details of the imaged samples are shown in Table 3-2.

Table 3-2: Tomography scan details of the three imaged samples.

<table>
<thead>
<tr>
<th>Scan Parameter</th>
<th>KOH-0.1</th>
<th>KOH-0.5</th>
<th>KOH-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contrast Mode</td>
<td>Phase</td>
<td>Phase</td>
<td>Phase</td>
</tr>
<tr>
<td>X-ray Energy (keV)</td>
<td>5.4</td>
<td>5.4</td>
<td>5.4</td>
</tr>
<tr>
<td>Field of View (FOV)</td>
<td>Large FOV</td>
<td>Large FOV</td>
<td>Large FOV</td>
</tr>
<tr>
<td>Number of Projections</td>
<td>1901</td>
<td>1801</td>
<td>1401</td>
</tr>
<tr>
<td>Radiograph Exposure Time (s)</td>
<td>28</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>Camera Binning</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The transmission images for all scans were reconstructed using XMReconstructor, employing a proprietary parallel beam filtered back-projection algorithm. The segmentation of porous and carbon phases and volume visualisation were obtained using Avizo software package (Avizo, version 9.2 FEIO, VSG). The carbon phase was segmented based on its higher grey-scale value and saved as a binary TIFF file, and the pore phase was separated from the solid phase using non-local means filtration and threshold segmentation [290, 291]. 3D reconstructed images and their corresponding grey-scale and binary ortho-slices of each sample were created, along with segmented 3D TIFF image files. The images were processed for quantification and characterisation of the continuous PSD method, as developed by Munch and Holzer [292] and the mercury intrusion porosimetry PSD method (results described in Chapter 4). The algorithm is provided via an open-source plugin in ImageJ for the image processing package. The volume fraction of the porous phase can be filled with spheres of different radii that can be calculated by determining a distance map in which voxels are allocated a value matching the shortest distance, as starting from the binary pore mask to the boundary separating pores and carbon material [290]. In addition, the
porosity and volume specific interfacial area (VSIA) between the cellulosic fibres and porous media were evaluated \([293, 294]\). A binarised 2D slice taken from a 3D reconstruction of KOH-0.1 sample and the corresponding color-coded image based on the PSD algorithm developed by Munch and Holzer is shown in Figure 3-5.

**Figure 3-5**: 2D reconstructed slices from the X-ray nano CT in the XY Plane for KOH–0 in binary where light grey represents the carbon phase and dark grey represents the pore phase (left) and with the color coding of the radius of largest possible sphere fitted in the pore (right), based on the continuous PSD algorithm developed by Munch and Holzer.

The TauFactor software plug-in for MATLAB was applied directly on the resulting voxel grid to calculate the tortuosity factors of the activated samples based on a uniform shrink representative volume analysis \([295]\).

The directional tortuosity \(\tau\) in each of the three planes was calculated feeding the segmented voxel data and reconstructed by Avizo XLab into TauFactor as follows:

\[
\tau = \varepsilon \frac{Q_{\text{cv}}}{Q_{\text{pore}}} \quad (3-2)
\]

where \(\varepsilon\) is the porosity, \(Q_{\text{cv}}\) is the flow rate through the fully porous control volume and \(Q_{\text{pore}}\) is the simulated flow rate through the porous network \([290]\).

Representative volume analysis with uniform shrinkage (between 10\% and 100\% of the total volume element) was then implemented to calculate the characteristic tortuosity factor, \(\tau_c\), from the tortuosity factors in the three principle directions, due to the anisotropy of each of the samples:

\[
\tau_c = 3 \left(\tau_x^{-1} + \tau_y^{-1} + \tau_z^{-1}\right)^{-1} \quad (3-3)
\]
where $\tau_x^{-1}$, $\tau_y^{-1}$ and $\tau_z^{-1}$ are the tortuosity factors in the X, Y and Z principal planes, respectively.

3.3.2. Pore Size Distribution

3.3.2.1. Nitrogen Isotherms and Specific Surface Area Evaluation

Porous carbon materials usually exhibit an appreciable apparent surface area and a microporous volume, and access to these pores is critical in the selection criteria of the materials for the associated research and industrial applications of supercapacitors [4]. The analysis of the different sizes and shapes of pores, alongside the pore size distribution (PSD) is therefore important for a complete characterisation of the porous carbons [296].

The adsorption mechanism takes place when a degassed solid sample is in a confined space followed by exposure to an adsorptive (gas or liquid). The pressure stabilises and thermodynamic equilibrium is reached after the transfer and accumulation of the adsorptive molecules in the adsorbate/adsorbent interfacial layer. Physical adsorption and chemisorption are the two types of adsorption, depending on the interaction achieved between the adsorbent and adsorptive. Physical adsorption is distinguished by the reversible attractive and dispersive forces in addition to repulsive, polarization and electrostatic forces. As for the chemisorption mechanism, the process is irreversible and comprises chemical interactions between the different molecules.

Physical adsorption of nitrogen ($N_2$) gas is one of the most widely used techniques for the analysis of the porous structure. However, due to the sensitivity of the isotherms in the micro- and mesoporous ranges, measurements are usually conducted at 77 K in the subcritical phase of $N_2$. The measurements are usually evaluated on a volumetric or gravimetric basis to obtain the porous characteristics of the material of interest. The representation of the amount of adsorbed gas as a function of the pressure (absolute or relative) yields the adsorption isotherm. Six general groups have been classified to characterise different physical adsorption isotherms, that give necessary information on the porosity and size range of the pores in the solid material tested. $N_2$ adsorption covers a wide range of relative pressures ($10^{-8}$–1); however, due to diffusion limitations into the narrowest micropores (diameter < 0.7 nm), the kinetics are slow and equilibrium might not be reached [297]. This results in a source of error in the evaluation of total microporosity and the use of other adsorptive to complete the analysis is necessary (discussed in the following section).
Different theories can be used for the analysis of the isotherm data of physical adsorption accompanied with their own assumptions, including the Langmuir, BET, t-plot method and Dubinin theories. The BET theory, proposed by Brunauer, Emmet and Teller, was the method of choice in this thesis to evaluate the specific surface areas and analyse the physical adsorption isotherms of the different carbonaceous samples recorded. The method is based on the kinetic model developed by Langmuir [298], but was extended to describe a multilayer adsorption mechanism, as opposed to one adsorbed molecule per free site of adsorbent. The different assumptions made in this model include i) the first adsorbed layer follows the Langmuir model, ii) in all layers, with the exception of the first one, the heat of adsorption has the same value as the molar heat of liquefaction of the adsorptive at adsorption temperature, iii) evaporation and condensation have identical conditions, except in the first layer and vi) the number of layers reaches infinity when the relative pressure is equal to 1. The fitting of the experimental isotherm data using the BET theory can then be obtained according to the following Eqn. [299]:

\[
\frac{P}{n(P_0 - P)} = \frac{1}{n_mC} + \frac{C - 1}{n_mC P_0} \frac{P}{P_0} \quad (3 - 4)
\]

where \( n \) is the adsorbed amount at a pressure \( P \), \( n_m \) is the adsorbed amount per gram of the solid material to complete one monolayer of adsorbent, \( C \) is a constant exponentially related to the heat of adsorption in the first layer and \( P_0 \) is the saturation pressure at 77 K; i.e. \( P_0 = 1 \) bar.

The specific surface area can then be obtained, if the cross-sectional area of the adsorbed molecule (\( A_m \)) and monolayer capacity (\( n_m \)) are known. The specific surface area (SSA) of the adsorbent solid is given by Eqn. (3-5) [299]:

\[
SSA = (n_mA_mN_A)10^{-18} \quad (3 - 5)
\]

Where \( N_A \) is Avogadro’s number.

The pore size distribution is another major factor in completing the characterisation of a porous texture. As in the case of determining the surface area and isotherm data, various theories and models govern the evaluation of the PSD with their assumptions and limitations. All computational methods share the assumptions of well-defined pore shape (parallel slits or perfect cylinders) and rigidity of the pores with no interconnection; both of which are not true in almost all microporous solids. The PSD can be evaluated based on different methods including the Kelvin Eqn., Horvath-Kawazoe method, Dubinin Eqn. and density functional theory (DFT) [300]. The latter approach has been developed into the nonlocal DFT (NLDFT) by adding nonlocal corrections in an inhomogeneous system of
spheres. The modern version of the theory (NLDFT) allows obtaining local isotherms for pores of different diameters \( \text{via} \) the general adsorption isotherm Eqn. starting with the grand potential function of an average density to obtain an equilibrium density profile \([301]\). The quantity adsorbed \( (Q_{ad}) \) at a specified pressure can then be obtained \( \text{via} \) the integration of the equilibrium density profile \( \rho(r) \) and subtracting the quantity of adsorptive, present in the absence of wall forces \( \rho_o(r) \). In the case of slit pores, the densities are only a function of the normal distance \( (z) \) from the pore wall and therefore the quantity adsorbed can be expressed according to Eqn. (3-6):

\[
Q_{ad} = \int_0^H \left( \rho(z) - \rho_o(z) \right) dz \quad (3-6)
\]

where \( H \) is the upper limit of the integration, chosen as a large value to ensure that the quantity adsorbed is constant upon further extension of the upper limit.

In this work, the \( \text{N}_2 \) adsorption-desorption isotherms were carried out in a 3Flex Surface and Catalyst Characterisation System (Micromeritics, USA) to determine the BET SSA and PSD in the microporous (> 0.7 nm) and mesoporous size ranges as well as the total pore volume in these pore size ranges of all prepared and commercial carbon samples. The SSA was calculated at a relative pressure range between 0.001 and 0.2. The volume was evaluated at a relative pressure \( (P/P_o) \) of 0.99, and the PSD was evaluated by NLDFT. All samples were degassed for 24 hours at 300 °C using a VacPrep 061 Sample degas system (Micrometrics, USA) prior to experimental analysis. To study the effect of adding booster carbon (super C65) and binder (PVDF) in the preparation of the electrode materials (discussed later in this chapter) on the nano-porosity of the activated carbons, nitrogen sorption isotherms were also performed on KOH-0.005 and KOH-0.5 sample. Figure 3-6 shows the isotherm and corresponding PSD, reflecting the incremental pore volume at different pore sizes, as evaluated by NLDFT method of KB activated carbon. The isotherm can be classified as Type IV hysteresis loop, a characteristic of a mesoporous carbon.
3.3.2.2. Carbon Dioxide Isotherms

As discussed in the previous section, N\textsubscript{2} physical adsorption can be limited in quantifying micropores of pore sizes less than 0.7 nm and the use of alternative adsorbents becomes necessary. Carbon dioxide (CO\textsubscript{2}) adsorption, at 273 K or 298 K, can therefore be used as a promising method for the assessment of narrow microporous structures, also known as ultra-micropores [302, 303]. Although the critical dimensions of CO\textsubscript{2} and N\textsubscript{2} molecules are similar, the high temperatures used for CO\textsubscript{2} adsorption leads to higher kinetic energy of the adsorbent molecules, which enables them to enter the ultra-micropores [4]. CO\textsubscript{2} adsorption data can therefore provide complementary adsorptive analysis of the ultra-micropores to the bigger pores analysed by N\textsubscript{2} adsorption. It is noteworthy mentioning that this technique suffers from the drawback of carrying out the experiment at high pressures to cover the whole range of ultra-microporosity since CO\textsubscript{2} at these temperatures has a high saturation pressure.

The same methods mentioned in the earlier section for the analysis of the porous texture and physical N\textsubscript{2} adsorption isotherms can be used for the interpretation of the CO\textsubscript{2} data. Dubinin Radushkevich (DR) method was used for the assessment of the CO\textsubscript{2} isotherms and ultra-microporosity herein. The theory, using numerous experimental data, correlates the degree of micropore filling with the differential molar work function of adsorption according to the following Eqn.:

\[
\frac{V}{V_0} = \exp\left(-\frac{K}{\beta^2} \left(\frac{RT\ln P_0}{P}\right)^2\right) \quad (3 - 7)
\]
where $V$ is the adsorbed volume at a pressure $P$, $V_o$ is the microporous volume, $K$ is a dependant constant on the pore structure and $\beta$ is the affinity coefficient, characteristic of the adsorptive, CO$_2$ in this case.

In this work, the carbon powders were characterised by CO$_2$ isotherms at 273 K using an Autosorb-6 (Quantachrome, USA) that followed sample degassing at 200°C overnight. The narrow micropore volume with pore diameter $< 0.7$ nm were calculated using the DR method at relative pressures between 0.0001 and 0.25 from the CO$_2$ adsorption isotherms. The density of the adsorbed phase, CO$_2$ used was 1.023 g cm$^{-3}$. Using Eqn. (3-7), the characteristic curve of KOH-1 sample using CO$_2$ as an adsorptive at 273 K yields the plot in Figure 3-7.

![Figure 3-7: Characteristic CO$_2$ curve at 273 K of KOH-1 sample. The y-intercept of the plot corresponds to ln($V_o$), which from the volume of the micropores can be deduced.](image)

### 3.3.2.3. Mercury Intrusion Porosimetry

The non-wetting behaviour of mercury (Hg), alongside its high surface tension, makes it a unique substance for probing macroporous spaces (0.005-100 μm) employing the mercury intrusion porosimetry (MIP) technique. The surface tension at the liquid/material of interest interface is defined as the force per unit length along the surface of the mercury at right angles to the line separating both phases [304]. The mercury would only intrude the capillaries (pores) under pressure and the relationship governing the mechanism is described in Eqn. (3-8) below:

$$P = -\frac{4\gamma \cos \theta}{d}$$  \hspace{1cm} (3 - 8)
where $P$ is the pressure, $\gamma$ is the surface tension, $\theta$ is the contact angle between mercury and the material, and $d$ is the diameter of the pore. The PSD of macropores can therefore be determined from the volume intruded at specified pressure increments. However, the MIP technique has a number of limitations, including the ink-bottle effect, whereupon the intruding mercury enters a pore at a pressure relative to the size of the pore entrance, rather than the pore itself. Therefore, the analysis of the intruded volumes can underestimate the big pores and/or overestimate the smaller pores [305]. It is also necessary to deconvolute the data obtained as not all peaks refer to the volume intruded in the pores, but might be due to the interparticle porosity [306]. The deconvolution process thus allows a more accurate representation of the PSD of the macropores and total pore volume intruded.

In this work, MIP Poremaster (Quantachrome, USA) was used to detect the pore size distribution and the total pore volume of the carbonised samples in the macropore region. The total pore volume of each carbon sample was consequently evaluated as the sum of pore volumes in all PSD ranges obtained by the $\text{N}_2$ and $\text{CO}_2$ adsorption techniques and MIP to draw a direct correlation between the PSDs, pore volumes and electrochemical performance (as will be described in the different chapters of this thesis). Figure 3-8 shows the macrop-PSD of KOH-0.1 sample with the incremental pore volume and corresponding cumulative pore volume.

![Figure 3-8](image_url)

Figure 3-8: (a) Incremental and (b) cumulative pore volumes of KOH-0.1 samples as obtained by MIP.
3.3.3. Surface Chemistry

3.3.3.1. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), also known as electro-spectroscopy for chemical analysis (ESCA), is a widely used technique for the analysis of the surface chemistry of materials, due to its relative simplicity and data interpretation. The sample of interest is irradiated with photons of known energy from an X-ray source. The excitation source can be i) a monochromatic aluminium, Al Kα source of 1486.6 eV and linewidth of 0.85 eV, monochromatic magnesium, ii) Mg Kα excitation source of 1253.6 eV and linewidth of 0.7 eV, or iii) synchrotron sources of variable photon energies [307]. The photon of energy \((h\nu)\) penetrates the surface of the specimen, absorbed by an electron of binding energy \((E_B)\) at a condition below vacuum level, and consequently emerges from the surface with a kinetic energy \((E_K)\) [308]. The photo-emitted electrons generated on the sample surface are then detected by an energy analyser that scans a specific range of energies, and produce a spectrum of intensities (counts per second) as a function of the binding energy. The peaks generated are visible in this spectrum and can be classified as i) Auger emission peaks, ii) core level photoemissions and iii) valence band emissions. The narrowest and most intense peaks correspond to the core levels and represent the sample’s electronic structure, namely “1s” peaks. The intensity of valence bands is usually much lower (0–20 eV) compared to that of the core levels, and is a characteristic of electrons in de-localised or binding orbitals. This band is usually studied by lower energy excitation sources than XPS. The Auger electron spectroscopy governs the process of the ionisation of an atom in a core hole by an excitation source, whereupon the ion loses some of its potential energy when filling the core hole with an electron on a shallower level with the energy being emitted. This energy can appear as a kinetic energy given to another shallow bound-electron, giving rise to “KLL” peaks. This analysis gives valuable information on the chemical composition of the surface. Fitting of the XPS spectra requires the deconvolution of the raw data sets with a Lorentzian or Gaussian functions, alongside background subtraction, using a linear, Tougaard or Shirley models [309-311]. A typical XPS spectrum of a carbon material with oxygen functional groups is shown in Figure 3-9.
The surface chemistry of the carbonised powders in this thesis was detected using a K-ALPHA Surface Analysis XPS (Thermo Scientific) with monochromatic Al Kα radiation of 1486.6 eV as an excitation source to detect the oxygen and carbon content. The Lorentzian curve fitting and Shirley background correction were done using Casa XPS software. Detailed information on the changes in the binding energy of C\textsubscript{1s} peaks corresponding to different activated carbons and the surface functionalities and individual carbon peaks was analysed in this work (described in more detail in Chapters 4 and 7). The oxygen/carbon ratios (O:C) were determined from the C\textsubscript{1s} and O\textsubscript{1s} peaks using the following Eqn.[312]:

\[
\frac{A_{O1s}}{RSF_{O1s}} = \frac{A_{C1s}}{RSF_{C1s}} \tag{3 - 9}
\]

where \(A_{O1s}\) and \(A_{C1s}\) are the areas obtained from the O\textsubscript{1s} and C\textsubscript{1s} peaks in the XPS spectra, respectively, and \(RSF_{O1s}\) and \(RSF_{C1s}\) are the relative sensitivity factors of O\textsubscript{1s} and C\textsubscript{1s}, respectively. The \(RSF\) is used to scale the measured areas of the peaks so that the variations in the areas can be representatives of the amount of material on the sample surface. An elemental library is compiled for \(RSF\) values of different peaks. In this case, \(RSF_{O1s}\) and \(RSF_{C1s}\) have the values of 2.93 and 1, respectively.

3.3.3.2. Temperature Programmed Desorption

Heating a specimen surface would lead to an increase in the desorption rate of the adsorbed species bound to the surface with a specific amount of energy. The desorbed species can be
detected in the gaseous state by a mass spectrometer coupled with the temperature programmed desorption (TPD) technique that allows the application of a specific heating rate at a slow ramp [308]. The rate of gas evolution of different species changes with the temperature, whereby the rate can go through a maximum at different temperatures. This results in a rise in the instantaneous gas density, which allows the assessment of the nature and quantity of adsorbed species present at the surface of the sample. However, the gas density is a function of desorption and adsorption rate laws, the heating plot of the sample and the pumping speed out of the cell as the evolution of the gasses progresses [313]. It should be noted that the assumption of different peaks corresponding to species already present at the surface of the material is not always valid. This is due to the fact that the vacuum chamber wall effects may introduce contributions of the material already adsorbed on the chamber walls. Hence the necessity of coupling a TPD instrument with a mass spectrometer. In addition, temperature inhomogeneity across the sample and the presence of adsorbate species in both atomic and molecular states on the surface must be taken into account. The thermogravimetric analysis (TGA) provides valuable data on the variation of the mass of the sample with temperature, coupled with the data analysed by the mass spectrometer of the masses of different species desorbed from the sample surface [314]. The integration of the mass values of distinct species at different temperatures yields the total amount of desorbed species and their molar fraction at different temperatures. A typical thermogravimetric plot coupled with the molar fraction of calcium oxalate monohydrate (usually used for calibration before analysing any sample in the TPD technique) is shown in Figure 3-10.

![Figure 3-10: (a) Thermal decomposition of oxalate showing the different mass losses, using the molar masses of each of the corresponding species and (b) molar fractions of each of the species desorbed, evaluated using the data obtained by the mass spectrometer.](image-url)
In this work, the surface chemistry of the carbon materials was assessed using TPD conducted in a DSC (differential scanning calorimetry) -TGA instrument (TA Instruments, SDT Q600 Simultaneous) coupled with a mass spectrometer (Thermostar, Balzers, GSD 300 T3). 5 mg of each sample were heated up to 950 °C at a heating ramp of 20 °C min$^{-1}$ under a helium flow rate of 100 ml min$^{-1}$. Calibration of the instrument using calcium oxalate monohydrate was conducted prior to analysing the samples. Care must be taken in the analysis of the results obtained since CO and CO$_2$ as disproportionation, and CO peaks might be observed during the CO$_2$ decomposition process and vice versa. Therefore, integration of the mass spectrometer data must be done in each temperature range to deduce the total amount of each of the desorbed species as follows: i) entire temperature range for water, ii) 350 °C to 550 °C for CO alongside > 550 °C for CO evolving from CO$_2$ and iii) 350 °C to 550 °C for CO$_2$ evolving from CO and > 550 °C for CO$_2$ originally desorbed from the species. The results obtained by XPS and TPD will be further compared and described in Chapter 7.

3.3.3.3. In-situ Raman Spectroscopy

Molecular chemistry can be determined using Raman spectroscopy (RS), which is a vibrational technique involving high energy photons that are based on the inelastic scattering of radiation in the visible and/or near-infrared regions of the sample [315]. Inelastic scattering constitutes the shifting in the photon frequency or changes in its wavelength by molecules having a different frequency than the incident beam. The shift in the wavelength hence occurs due to deactivation or excitation of the molecular vibrations. The shift in photon frequency is a function of the chemical structure of the molecules, and therefore RS can provide valuable information regarding the electronic structure and surface chemistry, along with the bonding and symmetry of the molecules. The molecules are irradiated with an incident beam of monochromatic light whereupon the net energy exchange might be positive or negative, i.e. the light photon will either gain vibrational energy from the molecule, or vice versa [316].

The Raman spectrometer constitutes a light source, monochromator, a detector and sample holder. Different types of lasers are used as the excitation source, including argon ion, helium: neon and diode laser, each operating at a specific excitation line, usually close to the electronic absorption band. The basic requirement for a molecule to be Raman active is the change in polarizability during the vibration, where symmetry of a molecule gives the most intense Raman spectra [317].
The ratio of the sp$^2$ (graphite-like) to sp$^3$ (diamond-like) bonds affects the Raman spectra obtained of amorphous, crystalline and nano-crystalline carbons. The spectra of amorphous carbons are dominated by sharp G and D bands; the G peak represents the graphitic mode, is assigned to the stretching of the C-C bonds and always lies in the range of wavenumbers 1500-1630 cm$^{-1}$. The D band is characteristic of the disorder-induced mode in the carbon materials and occurs at ~1360 cm$^{-1}$. The quantification of disorder is usually analysed by the ratio of the D band intensity ($I_D$) to the G band intensity ($I_G$), which varies upon changing the electrochemical conditions, and therefore surface chemistry of a carbon material (as will be discussed in Chapter 7).

*In-situ* RS is also used to study the hydrogenation of carbon materials in different electrochemical devices to evaluate the hydrogen uptake and storage in porous carbon materials [318, 319]. This technique has also been used to modify the electronic structures of carbon nanotubes and graphene oxide films at different redox potentials [239, 320]. The cell would constitute of the working electrolyte with the different electrodes, and tuning the potential can alter the surface chemistry via reversible or irreversible processes. The porosity, PSD and initial surface chemistry of the materials have proven to be of major factors in determining the final state of the sample. A typical full spectrum of an amorphous carbon material is shown in Figure 3-11 using KOH electrolyte in a three-electrode system at a potential of -1 V.

![Raman spectra](image)

Figure 3-11: *In-situ* Raman spectra of KOH-0 sample as the working electrode in 6 M KOH at -1 V. Ag/AgCl and platinum mesh were used as the reference and counter electrodes, respectively.

In this thesis, the carbon materials were prepared as electrode pastes with the same composition as those used for electrochemical testing, described in the following section.
In-situ RS was employed to detect the hydrogen evolution and oxygen evolution reactions for different carbon electrodes in a wide potential range to further understand the possible mechanisms in a supercapacitor arising at extreme potentials. A more detailed description of the procedure and corresponding conditions used in this work are found in Chapter 7.

3.4. Electrochemical Measurements

3.4.1. Preparation of Electrode Materials

The preparation of the electrode materials for supercapacitors in two- and three-electrode systems was carried in a similar manner for all experiments, unless indicated otherwise in the experimental section of the corresponding chapter.

Prior to electrode fabrication, the carbonised materials (described in section 3.2) were vacuum-dried in the oven overnight at 110 °C to ensure the powders are free of moisture content. The electrodes were then assembled by mixing 85% of the prepared or commercial activated carbon, 5% booster carbon (C65) and 10% polyvinylidene fluoride (PVDF) acting as a binder. C65 and PVDF were used as supplied by PIKEM Ltd (UK). The binder was premixed in N-methyl-2-pyrrolidone (NMP) solvent (Sigma Aldrich) in a 5 wt.% solution to ensure the fine mixing of the binder with the carbons. A few drops of NMP were consequently added to the electrode paste and mixed using mortar and pestle to reach a honey-like consistency for better control of the total loading of the active material per specific physical surface area. The booster carbon C65 was used in the experiments to increase the conductivity of the electrode materials and thus their electrochemical performance [321], in addition to maintaining the structural integrity of the electrodes [322].

For the three-electrode setup, the paste was coated on nickel foam current collectors (Suzhou JSD Co. Ltd., China), having a total physical surface area of 1 cm$^2$ and a mass loading of 1-2 mg, followed by drying the composites at 80 °C under vacuum overnight to ensure complete removal of NMP solution. The mass of dried nickel foam was measured prior to and after electrode deposition to evaluate the total mass of the active material for further analysis of the electrochemical results of the working electrode. The mass of electrode active material (85% of total mass added) after vacuum drying was calculated as follows:

$$mass_{active\ material} = 0.85 \times (mass_{Ni\ after\ deposition} - mass_{Ni\ before\ deposition}) (3 - 10)$$
In all three-electrode measurements, silver/silver chloride (Ag/AgCl) in 3 M KCL solution was used as the reference electrode. A platinum (Pt) mesh of 1 cm$^2$ geometrical surface area was used as the counter electrode. Both electrodes were washed with ethanol and deionised water prior to any electrochemical testing. The counter electrode is employed to pass the current to ensure accurate measurements by maintaining the reference electrode at equilibrium. The nickel foam tip of the prepared working electrode was connected to stainless steel rod to ensure good contact with the potentiostat connections. 6 M KOH solution was the electrolyte of choice throughout all experiments in this setup and was filled in a three-electrode configuration of three beakers connected by glass tubes as shown in Figure 3-12. The counter and reference electrodes and the three-electrode setups were supplied by Tianjin AiDaHengSheng Technology Development Co. Ltd. (China). All electrochemical measurements were controlled and recorded using the same model of potentiostats (Interface 1000, Gamry Instruments, USA).

Figure 3-12: Schematic diagram of the three-electrode testing system with the working, counter and reference electrodes, all dipped in 6 M KOH solution and connected to the potentiostat.
3.4.2. Cyclic Voltammetry

Linear sweep voltammetry, or when applied repetitively, cyclic voltammetry (CV) is a common procedure for the evaluation of the electrochemical performance of supercapacitors. Upon applying a linear modulation of the potential ($E$) with time ($t$) at a constant rate, a potential-dependant current arises and is recorded [3]. The resulting current-potential plot is called a cyclic voltammogram. In alkaline electrolyte media, the three-electrode system is usually cycled between -1 V and 0 V vs. Ag/AgCl to obtain a characteristic profile of an EDLC. More specifically, the potential stability window was established to be within $-0.872 - 0.072$ V vs. SHE in 6 M KOH, and therefore $-1.077$ V $-$ 0.072 V vs. Ag/AgCl, where the potential different of Ag/AgCl reference electrode vs. SHE is 0.205 V in 3 M KCl solution at standard conditions [39]. Upon extending the potential windows beyond these limits, water electrolysis can occur and the evolution of nascent hydrogen gas at extreme anodic conditions and oxygen gas at extreme cathodic conditions can occur. The study of the electrochemical behaviour of the different porous carbon materials within and beyond the nominal windows will be studied throughout the different chapters of this thesis. Cyclic voltammetry was applied at scan rates of 1, 2, 5, 10, 20, 50, 100 and 200 mV s$^{-1}$ in three-electrode setups on all electrode materials, unless specified otherwise in the following chapters of this work.

The gravimetric capacitance, $C_s$ (F g$^{-1}$) can be inferred from the CV plots using Eqn. (3-11):

$$C_s = \frac{1}{2} \frac{\int I(V) dV}{s \Delta V m} \quad (3 - 11)$$

where $I$ is the current (A), $V$ is the voltage (V), $s$ is the sweep rate of the cyclic voltammogram (V s$^{-1}$), $\Delta V$ is the voltage range the sweep is carried within (V), and $m$ is the mass of the electrode materials (g).

Normalized CV plots by the scan rate are also reported to realize the real capacitance values of the electrode [323]. The slower the scan rate, the higher the amount of electrolyte ions diffusing into the porous networks of an EDLC. Figure 3-13 shows a typical CV profile of an EDLC at different scan rates and the corresponding normalized plot (in Farads).
Figure 3-13: (a) CV plot and (b) corresponding normalized CV plot of KOH-3 sample at different scan rates. The highest capacitance is achieved at the slowest sweep rates.

As mentioned herein, the electrode stability in a specific electrolyte solution is defined by a stability potential window. Anodic and cathodic currents can be applied at the extreme potentials prior to the pronunciation of hydrogen or oxygen gases by employing the CV method [324]. The window opening experiment, introduced by Xu et al., comprises of applying anodic and/or cathodic conditions in a separate setup, determining vertex potentials via small potential steps until surface oxidative or reductive decomposition of the electrolyte is pronounced [325]. This would result in the formation of a Faradaic current ($i_F$) in addition to the capacitive response current ($i_{nF}$) that is proportional to the scan rate. Consequently, during an anodic part of a scan to extreme negative potentials, the total anodic current ($i_A$) is:

\[ i_A = i_{nF} + i_F \]  \hspace{1cm} (3 - 12)

And the total anodic charge ($Q_A$) would be expressed as:

\[ Q_A = \int i_{nF} \, dt + \int i_F \, dt = Q_{nF} + Q_F \]  \hspace{1cm} (3 - 13)

where $Q_{nF}$ and $Q_F$ are the charges associated with reversible capacitive and irreversible electrolyte decomposition. The cathodic charge ($Q_C$) corresponds to the non-Faradaic capacitive mechanism within the cathodic potential limit and therefore is equal to $Q_{nF}$. Therefore, the ratio ($S$-value) of Faradaic to non-Faradaic charges in a cyclic scan at an anodic decomposition limit of the electrolyte can be expressed as [325]:

\[ S_{value} = \frac{|Q_A|}{|Q_C|} - 1 \]  \hspace{1cm} (3 - 14)
The ratio can be also applied for cathodic decomposition limits and should ideally give a value of zero when the Faradaic irreversible processes are negligible. The Faradaic fraction (S-value) therefore serves as a stability indicator of the system. A value of 0.1 (10% of the total charge infused in an electrode accounts for electrolyte decomposition) was arbitrarily chosen as a reversibility limit value for determining the electrochemical stability window of the employed electrolyte. The stability values (S-value) of the prepared carbon materials will be further analysed in Chapter 4.

3.4.3. Galvanostatic Charge-Discharge Cycling

Cyclic charge-discharge is a complementary standard method to CV, used to test the electrochemical performance of batteries and supercapacitors (EDLCs or pseudo-capacitors). One cycle constitutes the repetitive loop of charging and discharging between two potential limits, and if conducted at a constant current, would render the Galvanostatic charge-discharge (GCD) type. Upon applying a constant current (I), the potential difference (ΔV) developed across the electrodes varies linearly with time (t), as the charge (ΔQ) delivered by the current builds up. The capacitance (C) can then be evaluated as follows:

\[ C = \frac{\Delta Q}{\Delta V} \quad (3 - 15) \]

and the charge is:

\[ \Delta Q = \int I dt \quad (3 - 16) \]

Therefore the capacitance is:

\[ C = I \frac{\Delta t}{\Delta V} \quad (3 - 17) \]

Eqn. (3-17) applies if the capacitance is constant with the potential, and often this is not the case and the capacitance can be evaluated from the reciprocal of the slope of the discharge curve. These equations apply for ideally-polarizable electrodes within the potential limits of the electrolyte (i.e. no Faradaic decomposition of the solution occurs at the electrode), as previously discussed in Chapter 2. A conventional symmetrical GCD curve of an electrode for EDLC application with three cycles is shown in Figure 3-14.
Increasing the current density will decrease the time needed for the potential difference to develop across the electrodes between the two set potential limits; i.e. the higher the current (or current density), the lower the time for charge and discharge half-cycles and therefore the lower the capacitance (and specific capacitance) values. Knowing the mass of the electrode active material, the currents were set in this thesis to perform GCD cycles at current densities of 0.5, 1, 2, 5, 10 and 20 A g\(^{-1}\). Three cycles were performed on each of the carbon materials and the specific capacitance \(C_s\) was obtained from the 2\(^{nd}\) discharge half-cycles, according to Eqn. (3-15):

\[
C_s = \frac{It}{mV}
\]

(3 – 18)

where \(I\) is the discharge current, \(t\) is the time take by the electrode to discharge, \(m\) is the total active mass of the electrode material and \(V\) is the potential window used during the discharge time. Stability tests of 5000 cycles were also performed in the three-electrode systems at a specified current density (mentioned in each chapter) to test the electrochemical performance of the electrode materials for real applications. The stability tests constitute the same procedure used in the GCD experiments but for a larger number of cycles.

### 3.4.4. Voltage Hold

The cycling test mentioned in the previous section is complemented with a float test in which the potential of the electrode in the three-electrode configuration is held at a nominal
voltage value and the capacitance is determined by occasional charge/discharge cycles. The float test, also known as the voltage hold, confirms the lifetime stability and duty cycles for the feasibility of these materials in real-life applications, whereby a charged capacitor might be needed as a back-up device in an emergency event [326, 327]. The rate of degradation of the electrode (or whole supercapacitor device) at elevated potentials has been proven to be a result of the gas evolution caused by the decomposition of the electrolyte at extreme potentials, which results in an increased pressure [328], leading to a loss of the electrode cohesion and loss of electrolyte ions [329]. However, increasing the number of oxygen functionalities at the carbon surface can enhance the ageing mechanism of the supercapacitor [330]. This experiment is usually conducted to confirm that real-life conditions are more demanding than respective cycling tests with identical upper potential limits, as the cycling test takes longer before a clear result about the electrochemical performance of a supercapacitor can be drawn.

In this work, the voltage hold test has been conducted by applying a critical potential to the best performing electrodes in a three-electrode setup for 10 h, followed by occasional cycling (3 cycles) at a current density of 0.5 A g⁻¹. The experiment was iterated for 100 times and the respective capacitance, from the 2nd discharge-half cycle of GCD experiments, was evaluated every 10 h as follows [327]:

$$C_s = \frac{It}{m(V - V_{drop})} \quad (3 - 19)$$

where $V_{drop}$ accounts for the voltage drop (ohmic resistance) at the beginning of the discharge cycle.

A demonstration of a conventional ageing experiment is shown in Figure 3-15.
3.4.5. Electrochemical Impedance Spectroscopy

The current response behaviour to time-dependent potentials or complementarily, the changes in potential across a capacitor in response to perturbing the current amplitude govern the method of electrochemical impedance spectroscopy (EIS) [3]. The response is usually presented in a complex plane plot, representing i) the impedance magnitude (|Z|) as a function of the logarithmic frequency (f) or what is known as the Bode plot; ii) the phase angle (Z\_phi) vs. the logarithmic frequency; or iii) the imaginary part of the impedance (Z\'' ) as function of the real component of the impedance (Z\'), also known as the Nyquist plot. The latter is usually used to identify the different ohmic and Faradaic resistances of the system and is fitted with a number of equivalent circuit elements representing the equivalent circuit model. The elements commonly employed are the resistance (R), capacitance (C) and inductance (L). The Warburg impedance element (W) is also included in the equivalent circuit if diffusional impedances arise in the system under study.

Taking the example of potentiostatic impedance (alternating the voltage and recoding the current response), a sinusoidal perturbation in the time-variant voltage (V(t)) applied to a capacitor over a wide range of frequencies and response current (I(t)) can be given by:

\[ V(t) = V_0 \sin(\omega t) \]  \hspace{1cm} (3 - 20)

where \( V_0 \) is the maximum amplitude of the signal and \( \omega \) is the angular frequency.

and

\[ I = \frac{dQ}{dt} = \omega C V_0 \cos(\omega t) \]  \hspace{1cm} (3 - 21)
The current hence is out of phase with the voltage by -90° in an ideal capacitor element as shown in Figure 3-16.

Figure 3-16: Applied sinusoidal voltage and resulting current response in an ideal capacitive system with 90° phase shift.

The impedance of the capacitor ($Z_c$) can be expressed as its equivalent resistor, and since the current and voltage are out of phase, $Z_c$ can therefore be written as:

$$Z_c = -\frac{j}{\omega C}$$

where $j = \sqrt{-1}$.

Similarly, the impedance of a resistor ($Z_R$) is the resistance $R$, and that of the inductor ($Z_L$) is $j\omega L$. In the case of equivalent circuits involving more than one equivalent circuit element, mathematical separation of the real and imaginary parts is required [331].

If the more general case is considered, where different elements contribute to the total impedance behaviour, the voltage and current in polar forms using Euler’s relationship can be expressed as:

$$V(t) = V_0e^{j\omega t}$$

$$I(t) = I_0e^{j(\omega t - \phi)}$$
And therefore, the total impedance can be expressed in Cartesian or polar coordinates, defined in an analogous way to Ohm’s law for resistance, as:

\[
Z = Re\{Z\} + Im\{Z\} \quad (3 - 25)
\]

\[
Z = |Z|e^{j\phi} \quad (3 - 26)
\]

where \(Re\) represents the real part of the impedance (i.e. the resistance) and \(Im\) corresponds to the imaginary part, including the inductive and capacitive elements. The magnitude and phase shift are therefore given by:

\[
|Z| = \sqrt{Re\{Z\}^2 + Im\{Z\}^2} \quad (3 - 27)
\]

\[
\phi = \tan^{-1}\left(\frac{Im\{Z\}}{Re\{Z\}}\right) \quad (3 - 28)
\]

From the interpretation of the EIS measurements, a purely capacitive behaviour will correspond to \(-90^\circ\) phase angle at low frequency, in addition to Nyquist plots of vertical lines, parallel to the imaginary-axis with the absence of any resistive components. However, in real cases, capacitive elements are accompanied by resistive and inductive elements, that make the equivalent circuit more complex and the performance far from ideal. Nyquist plots and Bode plots, as previously mentioned can be analysed to deduce the different parameters of the impedance at different frequencies. In addition, the time constants (relaxation times), equivalent series resistances and charge transfer resistances can be inferred. Typical complex plane plots of an almost-ideal capacitive system (discussed in more detail in Chapters 5 and 6) are shown in Figure 3-17.
Figure 3-17: (a) Bode and (b) Nyquist plots of KOH-1 carbon in a three-electrode system in 6 M KOH electrolyte. A phase shift of almost -90° is associated with an almost ideal capacitive behaviour at very low frequencies. Corresponding Nyquist plot with a very small resistance value at high frequency and almost-parallel line behaviour to the y-axis confirms ideality.

In an ideally polarizable electrode, the charge passes into the electrode/electrolyte interface without any Faradaic processes of charge transfer across the double layer, and therefore the surface chemistry of the electrode remains unchanged. However in practice, this is rarely the case due to the presence of functional groups on the electrode surfaces or the Faradaic decomposition of the electrolyte at extreme anodic and/or cathodic conditions. The current would then be a summation of the Faradaic current and the capacitive charging current (detailed in Chapter 2).

EIS measurements and corresponding computational simulations and theoretical equivalent circuits for EDLCs have been extensively reported in the literature [226-229, 234]. However, there is a small amount of work reported on the analysis of a non-deal performance of a porous electrode in a supercapacitor device [332-335]. In chapter 4, EIS measurements were recorded for different porous electrodes and the electrochemical behaviour in correlation with the porous morphology was further analysed in Chapter 5. The different circuit models reported in the literature for these systems are mentioned, and a new suggested equivalent circuit that governs the behaviour of porous materials at open circuit potential is explored. The extension of the work in Chapter 5 will be discussed in Chapter 6, using the EIS tool to interpret the electrochemical performance of the supercapacitor at different potentials. Throughout all experiments conducted in this work, EIS was performed in the frequency range of 0.01 Hz and 1 MHz at open circuit potential (unless specified otherwise) with a sinusoidal voltage signal of 5 mV amplitude. The variation in the
equivalent series resistances, charge transfer resistances, time constants and impedance magnitude is correlated to the PSD, pore volume and surface functionalities of the KOH-activated carbons, used as model porous systems.

3.4.6. Two-electrode Devices

The two-electrode setup employed in this work comprises a standard supercapacitor cell of CR2032 geometry. The coin cell parts (electrodes, spring, gasket and coin cell testing box) were supplied by Hohsen Corporation (Japan). All coin cell parts were washed with ethanol and deionised water followed by vacuum-drying at 80 °C overnight to ensure no encounter with any impurities. Whatman glass microfibre filter papers, used as electrical separator materials, were purchased from Sigma-Aldrich Ltd (UK). The electrode pastes for the coin cell setup were prepared in a similar manner to that of the three-electrode system and were coated on 2.01 cm² nickel foam current collectors. The cells were fabricated and crimped afterwards using CR2032 crimper (Hohsen Corporation, Japan) to ensure the insulation of the cell components. CV and GCD cycling in the voltage range 0−1 V, and EIS tests were performed in the two-electrode configuration in 6 M KOH solution of the best performing samples in the three-electrode setup. The cycling performance of these samples was also recorded at a current density of 10 A g⁻¹. A voltage hold test of the best performing carbon material was conducted in the two-electrode cell at which a critical voltage (1 V) was applied to the full cell. A similar procedure to the three-electrode float test was followed and the capacitance of the whole system was evaluated every 10 h by the occasional cycling at a constant current density of 0.5 A g⁻¹.

The electrochemical behaviour of the best-performing carbon materials was also tested in an organic electrolyte (1 M tetraethylammonium tetrafluoroborate, TEA-BF₄ in acetonitrile) in a two-electrode configuration to detect the redox-enabling effect of the carbon materials in 6 M KOH solution. CVs at different scan rates and GCD cycling at different current densities between 0 V and 3 V have been performed. This allows the determination of the pseudocapacitive contribution of the carbon electrodes to the total supercapacitor performance in KOH solution. The capacitance was evaluated from the GCD and CV plots using the same equations employed for the three-electrode compartments, but with the total mass of active carbon material of both electrodes. This allows the determination of the specific capacitance of the whole device. Evaluating the specific capacitances at different current densities, the Ragone plot of the two-electrode systems can be inferred. A Ragone plot represents the amount of energy available in an electrochemical device vs. the rate of delivering this energy (power) or vice versa on a logarithmic scale to allow the comparison
between the performances of different energy conversion and storage devices (Figure 3-18). It is demonstrated that supercapacitors bridge the energy-power gap between conventional capacitors and batteries and fuels, as previously explained.

The energy density ($E_m$) and power density ($P_m$) (gravimetric unless otherwise specified in the corresponding chapters of results) can be calculated as follows.

$$E_m = \frac{1}{2} C_s V^2 \quad (3 - 29)$$

$$P_m = \frac{E}{\Delta t} \quad (3 - 30)$$

where $V$ is the two-electrode cell voltage.

Figure 3-18: Generic Ragone plot representing the energy and power density ranges of different electrochemical devices.

3.5. Integration of a Supercapacitor within a Printed Circuit Board

The proof-of-concept study integrates supercapacitors in a printed circuit board (PCB) design. Norit activated carbon (NAC) was the electrode material used throughout the
experiments conducted for this work. The choice of the electrode material was based on testing a benchmark commercial material with known electrochemical behaviour.

Sodium sulphate (Na$_2$SO$_4$) and Na$_2$SO$_4$/polyvinyl alcohol (PVA) were used as electrolytes in the PCBs and were supplied by Fisher Scientific (UK) and Tokyo Chemical Industry Co. Ltd (Japan), respectively. All prepared electrodes were manually cast on an Arlon DiClad PCB configuration manufactured by Arlon Electronic Materials (UK) and supplied by ZOT Engineering Limited (UK). The pre-impregnated (prepreg) composite bonding fibres, (Arlon-47N) were also manufactured by Arlon Electronic Materials (UK) and supplied by ZOT Engineering Limited (UK). The supercapacitor-PCB configuration was compared against the standard two-electrode systems (coin cells). The layout of the PCB device is presented in Figure 3-19.

![Figure 3-19: Photograph of (a) the PCB prior to assembly showing the different layers of DiClad, copper coating and carbon ink on which the carbon electrode was coated and (b) assembled SC-PCB.](image)

The morphology and PSD of NAC material are discussed in Chapter 4. Electrochemical measurements of the supercapacitor-PCB devices and coin cells in aqueous and solid electrolytes are conducted using CV, GCD, cycling stability tests and EIS. The volumetric and gravimetric energy and power capabilities were inferred at different cycling current densities. The description of different procedures is detailed in Chapter 8.
3.6. Summary of Experimental Procedure

In this chapter, an overview of the basic theories of the different characterisation and electrochemical techniques that are employed in this thesis was presented. For the full characterisation of electrode materials for EDLC applications, the porous structure, PSD and surface chemistry need to be assessed to understand the relationship between the form of the porous carbons and their function as electrode materials in two and three-electrode supercapacitor devices. The different experiments conducted in this thesis were conducted on cellulose precursor materials that were KOH-functionalised and carbonised. The fine-tuning of the morphology and PSD of the porous electrodes is highlighted and correlated with the electrochemical performance in Chapter 4. This allows conducting in-depth studies of the electrochemical impedance behaviour and in-situ Raman spectra on the different porous carbons, detailed in Chapters 5-7. The engineering of new supercapacitor devices using the PCB design will be described in Chapter 8, employing the different techniques described herein.
Chapter 4

Properties of Functionalised Carbons


Scope of this chapter: Application of different characterisation techniques in multidimensional scales of KOH-activated carbons, and the investigation of the synergy between their morphology and electrochemical performance as porous electrode materials for supercapacitors.
4.1. Introduction

Activation of carbon, including biocarbon-based materials, with KOH at high temperatures, is one of the most explored methods in the supercapacitor field [93, 211, 336-338]. The process allows the formation of porous carbons with high electrical conductivities and specific capacitances whereby the ratio of activating agent to precursor material is known to affect the electrochemical performance and specific capacitance of the carbon materials. In this chapter, the manufacturing of porous carbons from softwood Kraft pulp for supercapacitor electrodes is considered in the context of the effect of KOH/cellulose ratio on the porous structure and consequently the electrochemical behaviour. An approach is taken that relates form and function, using techniques such as transmission electron microscopy, nitrogen adsorption-desorption isotherms and X-ray tomography to capture the pore network characteristics at different length scales and establish a correlation to the electrochemical performance.

One of the biggest challenges in developing ECs is the compromise between the use of low-cost and readily-available materials and the prominent requirements for delivering high performance and durability [272]. Activated carbons have been extensively used as supercapacitor electrode materials and can be complemented with pseudocapacitive materials (ruthenium oxide and manganese oxide being the most popular) to achieve high specific power and energy. The majority of available carbon materials are chemically and/or physically activated, starting with carbonaceous organic precursors and ‘engineered’ to exhibit different attributes [282-285, 339, 340]. The physical activation constitutes the pre-treatment of raw carbon materials at high temperatures ranging between 700°C and 1200°C under oxidizing conditions like air, steam or CO₂. As for chemical activation, the process is generally carried out at lower temperatures (400-700 °C) using an activating agent (potassium hydroxide, phosphoric acid, and sodium hydroxide), that tunes the morphology of the carbonised samples. For supercapacitors, desirable properties include high surface area and electrical conductivity as well as an optimised pore network structure that can enhance access of ions to the electrode surface and boost the charge storage capacity at the electrode/electrolyte interface. Certain biocarbon-based materials have shown promise for supercapacitor applications in aqueous electrolytes and have the advantage of low cost and abundance. For example, wood-based raw material was activated in an N₂ atmosphere at 1000 °C, followed by a CO₂ activation step at 900 °C yielded a maximum specific capacitance value of 72.4 F g⁻¹ at a scan rate of 20 mV s⁻¹ [341]. In another study, coconut shells were treated in a one-step thermal process, combining pyrolysis at 400 °C and steam activation at different temperatures. It was found that an increase in the activation time and
temperature increased the mesoporous contribution in the total pore volume and hence an increase in the specific capacitance values (228 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$) [70]. Bamboo-based carbons activated with KOH were reported to achieve a specific capacitance of 258 F g$^{-1}$ at a current density of 0.1 A g$^{-1}$ with 36% retention rate as the current density increased to 5 A g$^{-1}$ [285]. As another example, highly porous carbon materials originating from waste coffee beans and treated with ZnCl$_2$ have been reported to achieve a specific capacitance of 368 F g$^{-1}$ and energy density of 20 W h kg$^{-1}$ at a current density of 0.05 A g$^{-1}$ [342]. Wei et al. used cellulose, potato starch and eucalyptus wood as raw materials to produce microporous carbons that achieved a capacitance of 236 F g$^{-1}$ at a sweep rate of 1 mV s$^{-1}$ in symmetric supercapacitor configurations [273]. Many activated carbons from biomass have been used in supercapacitor applications yielding different capacitance values in different electrolytes and system configurations [270, 281, 343-348], but a clear understanding between their multiscale porosity-electrochemical performance is still missing. In this study, we address this gap in the XYZ dimensional analysis. Herein, the morphology was studied using different multiscale characterisation techniques to investigate the effect of all structural parameters on the electrochemistry in supercapacitor devices [349].

4.2. Experimental

4.2.1. Porous Texture

This study focuses on activated cellulose pulp with different KOH mass loadings. The different porous morphologies of the carbonised carbons and the effect on their performances at various electrochemical conditions are investigated. The results in this chapter highlight the necessity of studying the structure of electrode materials at multidimensional scales for the optimization of the supercapacitor behaviour. As described in section 3.2, the KOH-$n$ electrode materials were obtained starting with the dry cellulose filter “cakes” mixed with different KOH concentrations and their structural-performance relationship was studied and benchmarked with commercial activated carbons, KB, NAC and BAC.

Different characterisation techniques constituting the study of the pore size distribution, specific surface area, and elemental content and electronic structure of the prepared samples are presented. Imaging of the samples was carried using SEM, TEM, and X-ray CT techniques, and nitrogen sorption isotherms and carbon dioxide adsorption isotherms along
with MIP were used to characterise the specific surface area and pore size ranges. In addition, XPS and elemental analysis confirmed the carbon, hydrogen and oxygen content and chemical structure of the analysed samples. Details on each of the employed techniques can be found in Chapter 3.

4.2.2. Electrochemistry

Electrochemical measurements were carried out in three-electrode systems and coin cells connected to a potentiostat. The three-electrode measurements were performed in 6 M KOH electrolyte solution using a platinum mesh counter electrode and silver/silver chloride (Ag/AgCl) reference. The working electrodes were prepared with 85% activated carbon, 5% SuperC65 and 10% PVDF. The mixture was then mixed and drop-casted on nickel foam to give a final mass between 2 and 3 mg of activated carbon across a physical surface area of 1 cm$^2$. Cyclic voltammetry (CV) at scan rates between 1 and 200 mV s$^{-1}$ were performed along with galvanostatic charge-discharge (GCD) at current densities of 0.5–20 A g$^{-1}$. Cyclic voltammetry in the three-electrode configurations was used to infer the positive and negative potential limits to determine the stability (S-value) as follows:

$$S_{\text{pos}} = \frac{q_{\text{pos}}}{q_{\text{neg}}} - 1 \quad (4-1)$$
$$S_{\text{neg}} = \frac{q_{\text{neg}}}{q_{\text{pos}}} - 1 \quad (4-2)$$

The Q-value corresponds to the charge and discharge from negative and positive current incurred by one separate polarization, respectively [324, 325]. The quantification of the stability of the supercapacitor, determined by the electrolyte stability and hence removing any irreversible Faradaic contributions to the total capacitance is discussed in further details in section 3.4.2. The cycling test was complimented with a float test, described in more detail in Chapter 3.

Potentiostatic Electrochemical Impedance Spectroscopy (EIS) was performed in a frequency range between 0.1 Hz and 1 MHz at open circuit voltage (OCV) with sinusoidal signal of 5 mV amplitude. The specific capacitances were calculated from the GCD curves and the resistances were inferred from the impedance curves. iR drop, product of current ($i$) and resistance ($R$), is defined as the potential difference between two conducting phases during a current flow and can be also inferred from GCD curves. Electrode materials in coin cells were prepared in a similar manner to that of the three-electrode system and glassy fibres
were used as separators between the electrodes/current collectors. CV, GCD and EIS tests were performed in the two-electrode configuration in 6 M KOH solution. A voltage hold test of the best performing carbon material was conducted in the two-electrode cell at which a critical voltage was applied to the full cell. The details of the procedure are described in section 3.4.4.

The electrochemical behaviour of the best-performing carbon materials was also tested in an organic electrolyte (1 M tetraethylammonium tetrafluoroborate, TEA-BF$_4$ in acetonitrile) in a two-electrode configuration to detect the redox-enabling effect of the carbon materials in 6 M KOH solution. CV at different scan rates and GCD at different current densities between 0 V and 3 V have been performed. This allows the determination of the pseudocapacitive contribution of the carbon electrodes to the total supercapacitor performance.

4.3. Results

4.3.1. Morphological Characterisation and Porous Texture

To investigate the pore morphology and size distribution among the different commercial activated carbons and prepared samples, different characterisation techniques were exploited. SEM and TEM images of the carbonised samples with different KOH / cellulose ratios and commercial carbons can be compared in Figure 4-1 and Figure 4-2, and further images are provided in section 10.1 of Appendices (Figure 10-1). Ketjen Black is a mesoporous activated carbon with low microporosity of a sponge-like structure. Compared to NAC and BAC commercial carbons of disordered morphology, the KOH / cellulose materials showed a fibrous structure that evolved to a ‘spongy’ morphology with increasing KOH content. The fibrous structure of KOH-0, KOH-0.005 and KOH-0.01, constitutes of micro- and mesopores that can be detected with TEM only. However, the higher activated samples show a porous structure of pore sizes that can be detected by both SEM and TEM techniques. At KOH / cellulose ratios of 0.5 and 1, the KOH etching process resulted in a hierarchal porous network structure. The fibrous structure of un-activated carbonised cellulose (KOH-0) gradually transforms into microporous etched fibres upon increasing the KOH loading to 0.005, 0.01 and 0.1. As the KOH proportion is further increased, the fibrous texture converts into a more porous form. A wide pore size distribution across the micro-, meso- and macropore size ranges was attained once the KOH / cellulose ratio was set at 0.5 and 1. The combination of the SEM and TEM images show that the different ranges of pore sizes have been achieved at the 0.5:1 and 1:1 KOH / cellulose samples.
Figure 4-1: SEM images of (a) KOH-0.01, (b) KOH-0.1, (c) KOH-0.5, (d) KOH-1, (e) KOH-2 and (f) KOH-3.

Figure 4-2: TEM images of (a) KOH-0.01, (b) KOH-0.05, (c) KOH-0.1, (d) KOH-0.5, (e) KOH-1 and (f) KOH-3.

The N\textsubscript{2} adsorption-desorption isotherms of activated carbons are shown in Figure 4-3a,b in which all samples (excluding KB) display a Type I isotherm characteristic of a microporous
solid. Both BAC and NAC samples show equal microporous volumes, with a higher mesoporous contribution in the NAC sample, yielding a higher SSA in the latter commercial carbon. It is clear that increasing the KOH ratio increases the total pore volume until the optimum is reached, after which it decreases due to the formation of macropores. The samples KOH-0.5, KOH-1 and KOH-2 display the highest total pore volume composed of very similar micro- and mesopore volume fractions (Figure 4-3d). All carbons contain a mesoporous structure (pore diameter > 2 nm) which is clearly shown in Figure 4-3c,d. The total pore volume decreased upon increasing the KOH/cellulose ratio beyond 2:1. This is due to the fact of not only the domination of macroporous structures but also a highly disordered structure conveyed in TEM for KOH-3 sample. KB sample displays a Type IV isotherm with a hysteresis loop which is a characteristic feature of capillary condensation on the mesopores (Figure 4-3b).

![Image](https://via.placeholder.com/150)

**Figure 4-3:** Pore size characterisation of commercial and KOH-activated carbonised samples. (a) Nitrogen adsorption/desorption isotherms at 77 K of BAC, NAC and KOH-n carbons, (b) nitrogen sorption isotherms of KB, (c) cumulative pore size distribution using DFT and (d) incremental pore size distribution of commercial and activated carbons using DFT method.
BET surface area and total pore volume were obtained using the isotherm data and those of pore size, pore size distribution and micropore volume were calculated using the NLDFT data evaluation method. The hierarchical porous network structure gave rise to a substantial increase in the BET specific surface area but decrease in the micropore volume fraction as more meso- and macropores were formed. At higher KOH/cellulose ratios, the macropores dominated and the ‘spongy’ nature of the material evolved. There was a decrease in the specific surface area at the highest KOH loading (3:1 KOH / cellulose ratio). The bulk densities, BET SSA, total pore volume determined by N₂ sorption isotherms and the contribution of the micro- and mesopores are reported in the table below. It is worth noting that the bulk density of the carbonised samples decreased with increasing the chemical activation conditions in which the KOH etching effect and porosity are expected to increase with macropore domination at high activation conditions.

Table 4-1: Comparison of bulk densities, BET specific surface areas, pore volumes determined by NLDFT on N₂ isotherms and pore size distribution of different commercial and activated carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk Density (g cm⁻³)</th>
<th>BET (m² g⁻¹)</th>
<th>Total Pore Volume (N₂) (cm³ g⁻¹)</th>
<th>Micropore Volume (cm³ g⁻¹)</th>
<th>Mesopore Volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAC</td>
<td>0.33</td>
<td>1140</td>
<td>0.44</td>
<td>0.2</td>
<td>0.24</td>
</tr>
<tr>
<td>NAC</td>
<td>0.19</td>
<td>1466</td>
<td>0.74</td>
<td>0.2</td>
<td>0.54</td>
</tr>
<tr>
<td>KB</td>
<td>0.12</td>
<td>1396</td>
<td>1.39</td>
<td>0.09</td>
<td>1.3</td>
</tr>
<tr>
<td>KOH-0</td>
<td>0.38</td>
<td>11</td>
<td>0.008</td>
<td>0</td>
<td>0.008</td>
</tr>
<tr>
<td>KOH-0.005</td>
<td>0.32</td>
<td>252</td>
<td>0.16</td>
<td>0.05</td>
<td>0.11</td>
</tr>
<tr>
<td>KOH-0.01</td>
<td>0.21</td>
<td>598</td>
<td>0.28</td>
<td>0.17</td>
<td>0.11</td>
</tr>
<tr>
<td>KOH-0.1</td>
<td>0.25</td>
<td>717</td>
<td>0.34</td>
<td>0.18</td>
<td>0.16</td>
</tr>
<tr>
<td>KOH-0.5</td>
<td>0.13</td>
<td>1351</td>
<td>0.55</td>
<td>0.34</td>
<td>0.21</td>
</tr>
<tr>
<td>KOH-1</td>
<td>0.06</td>
<td>1306</td>
<td>0.47</td>
<td>0.3</td>
<td>0.17</td>
</tr>
<tr>
<td>KOH-2</td>
<td>0.05</td>
<td>1579</td>
<td>0.59</td>
<td>0.39</td>
<td>0.2</td>
</tr>
<tr>
<td>KOH-3</td>
<td>0.03</td>
<td>785</td>
<td>0.43</td>
<td>0.07</td>
<td>0.36</td>
</tr>
</tbody>
</table>

It has now become accepted that specific surface area is not the only factor that governs a good electrochemical performance but the surface morphology and pore size distribution also play an important role. Hence, ultra micropores (< 0.7 nm) in the different porous structure must be determined to fully analyse the structure of the different activated carbons and determine the underlying reasons for optimized performance in the following section.
The samples were analysed with CO$_2$ physical adsorption to further target the narrow micropore volume with pore sizes smaller than 0.7 nm. However, in-depth studies proved that micropores that accommodate nitrogen adsorption at 77 K can also be available for electro-sorption of hydrated ions such as K$^+$ or OH$^-$ at low concentrations due to the similar sizes of the individual atoms and therefore pores with sizes larger than 0.5 nm can be easily accessed by electrolytic solutions [40, 350]. The CO$_2$ adsorption isotherms are shown in Figure 4-4 indicating the total volume of CO$_2$ adsorbed in the different activated samples. It is clear that an increase in the micropore volume occurs with an increase in KOH activation. However, since the macroporous volumes also increase with further activation, the total contribution of the micropores decreases as the KOH loading is increased. It is worth noting that the total adsorbed CO$_2$ has drastically dropped in KOH-3 sample which might be attributed to extreme activation conditions of the precursor materials.

Figure 4-4: CO$_2$ adsorption isotherms at 273 K of all activated samples, with the numbers indicating the total pore volume adsorbed corresponding to each sample.

As for the determination of the macropore size distribution of the activated carbons, the two techniques involved in the evaluation of the macropores used were X-ray CT and MIP.

X-ray CT technique provides data on the pore size distribution, porosity and tortuosity factor, which are three major characteristics of electrode materials in supercapacitor devices. A wide average pore size, high porosity and low tortuosity enhance capacitance retention, cyclability with low impedance at low frequencies and enhance electrolyte diffusion in different pore sizes. 3D images of KOH-0.1, KOH-0.5 and KOH-2 samples and associated grey-scale and binary ortho-slices have been reconstructed and are shown in Figure 4-5. The
volume visualization and image processing performed using Avizo software package show that the segmented images correlate well to the greyscale images. The samples analysed are a representation of low, intermediate and high levels of KOH-activation and show the macroporosity distribution along with porosity and tortuosity factor changes in different morphologies of representative activated samples. The porosity ($\epsilon_p$) and volume specific interfacial area between carbon and pores (VSIA) of the binary images of the segmented volumes were obtained. To assess the directional uniformity of the pore, the porosity was calculated in the three principal planes on a slice-by-slice basis from the 3D volume, whereby each slice thickness is a single voxel thick (63.1 nm). The same representative volume element was also used for determining the tortuosity factors in the three planes and the corresponding calculated characteristic tortuosity $\tau_c$ (refer to section 3.3.1.3 for further details of the calculation) [295]. Table 4-2, Figures 4-6 and 10-2 in Appendix 10.1 show that the porosity and tortuosity factor values determined by the representative volume element analysis used for each of the samples did not significantly change with sample size and is therefore representative of each of the bulk materials. However, the parameters are independent of the KOH loading and do not correlate with the specific surface area values reported in the previous section. It should be noted that these values hugely depend on the measurement technique used whereby all herein are carried out on segmented volumes of the microstructures and hence would not capture the nanostructured details below the scan resolution [293].
Figure 4-5: Volume rendering and associated grey-scale (left) and binary (right) slices in the XY plane of (a) KOH-0.1, (b) KOH-0.5 and (c) KOH-2 activated samples. White is carbon phase and black is pore phase in the binary images.

Table 4-2: Summary of the activated carbons properties as determined with X-ray CT, Avizo XLab and TauFactor code.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varepsilon_p$ (%)</th>
<th>VSIA (µm$^{-1}$)</th>
<th>$\tau_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH-0.1</td>
<td>77</td>
<td>0.60</td>
<td>1.67</td>
</tr>
<tr>
<td>KOH-0.5</td>
<td>49</td>
<td>0.56</td>
<td>4.62</td>
</tr>
<tr>
<td>KOH-2</td>
<td>79</td>
<td>0.91</td>
<td>1.48</td>
</tr>
</tbody>
</table>
According to the data above, the porosity and VSIA of the KOH-0.5 sample are the lowest, while the tortuosity factor is the highest amongst the three samples. This can be explained by the fact that KOH-0.5 sample has a wide pore size distribution between micro-, meso- and macropores in which not all pores can be detected in the X-ray CT as the micro- and mesopores might be overshadowed/ integrated within the macropores. This is not the case for KOH-0.1 sample as most pores are in the micro- and mesopore range while the macropores dominate in the KOH-2 sample. Hence, the higher porosity and VSIA values and lower tortuosity factors values for KOH-0.1 and KOH-2 samples. However, the porosity and VSIA values are considered relatively high for all samples, whereas those of tortuosity to be low which enhanced the electrolyte movement within the porous structure. The interconnection with smaller pores if detected is suggested to increase the porosity and VSIA values and decrease the tortuosity factor values. The carbon atoms were etched at higher levels with increasing the KOH / cellulose ratio, placing them in an “intermediate” state in KOH-0.5 sample that consists of a porous network structure covering different pore size distributions. Further increase of the activating agent amount transfers the carbon state towards wider pores which results in a decrease in surface area as larger pores form on the expense of the smaller micropores. These results of evaluation of the porosity, tortuosity and VSIA corroborate with the characterisation techniques already mentioned in this chapter, including SEM, TEM and BET.
Figure 4-6: Representative volume element analysis in the three principal planes (X, Y, Z) for KOH-2 showing that the segmented volumes are considered to be representative volumes for porosity and tortuosity factors of the bulk materials. The directional tortuosities of the sample upon applying the uniform shrinkage analysis confirm that the chosen volume is a representative one as all values converge upon increasing the volume fraction. The porosity evaluated in each of the three planes is of similar value to the calculated one for the segmented volume in Avizo.

Figure 4-7: Pore size distribution of different KOH-activated cellulose samples obtained from all image slices with X-ray tomography technique and determined by (a) the Munch and Holzer 3D method and (b) MIP simulation method.

X-ray CT was also used to determine the pore size distribution (PSD) using two different methods: i) the Munch and Holzer continuous PSD method and ii) MIP simulation, both of which discussed in section 3.3.1.3 [292]. Figure 4-7 shows that the majority of the pore
volume consists of the detected pore radii within the range of 0.09-5 μm for the different samples using the two different methods. The X-ray CT resolution provides larger volume analysis compared to that of BET technique whereby macropores are suggested to overshadow micro- and mesopores in all samples imaged in addition to the limitation of this tool to a minimum voxel size of 63.1 nm. The two methods exhibit very clear different averages of the pore sizes with different volume fractions, which are also different to the distribution evaluated by MIP technique, discussed next. The MIP simulation shows that most macropore radii lie within the range of 0.09-1.5 μm, above which the volume fractions of bigger pores are almost zero for samples KOH-0.5 and KOH-2. As for the continuous pore size distribution method, it extends the pore size distribution to the range of 0.09-5 μm, hence arising different PSDs and average pore sizes. This reflects the shortcomings of X-ray CT to a pixel resolution of 63.1 nm and a maximum quantified pore size between 0.06 and 5 μm for different porous samples; any smaller pores would not be identified and are hence neglected. Also, any pore sizes bigger than 4 μm would need to be further analysed using the Zeiss Xradia Versa 520 (Carl Zeiss Microscopy, Pleasanton, CA, USA), which quantifies bigger pores. In addition, the pores in the smaller size ranges of 0.6-2 um might not all be detected in the case of interconnected pores of any of the samples; which is the case in the three analysed samples here as shown by SEM and TEM images. The total pore volume attained by X-ray CT per unit mass of the activated carbons yielded the same values using both PSD evaluation techniques of 1.83, 1.08 and 1.6 cm"3 g"1 for samples KOH-0.1, KOH-0.5 and KOH-2 samples, respectively. The PSD evaluation and total pore volume analysed by MIP technique will be discussed next.

As previously mentioned, MIP has limitations in estimating the size of the pores and might underestimate the smaller pores or overestimate the larger pores; however, this technique not only complements but rather is a more reliable tool than X-ray CT in the case of carbons with low attenuation to X-rays. MIP is hence used to confirm the pore size distribution of the macropores and extends the macropore distribution in the range between 0.1-1000 μm. It should be noted that the calculation of the total mercury intrusion volume requires the deconvolution of the plots obtained, as mentioned in 3.3.2.3 [306]. This allows a more accurate evaluation of total macropore volume and hence drawing the correlation between the morphological structure and its effect on the electrochemical performance. The mercury cumulative intrusion profiles and interparticle macroporosity were studied. As shown in Figure 4-8, the higher KOH/cellulose ratios displayed sharper peaks at different pore sizes in the macropore region and attained higher cumulative intrusion volumes. KOH-0.1 and KOH-0.5 samples had similar profiles whereby both samples exhibited a porous network structure encompassing the different pore size ranges while KOH-2 sample had a wide
macropore size distribution with little micro- and mesopore contribution. Total macropore volumes of all activated samples are reported in Table 4-3.

Figure 4-8: (a) Log differential of cumulative intrusion profiles specifying the pore size distributions and (b) mercury cumulative intrusion porosimetry profiles of KOH-n samples (with n = 0, 0.005, 0.01, .0.1, 0.5, 1, 2 and 3).

Hence, SEM images were used to determine the maximum pore size detected in different micrographs and an X-ray CT technique was employed to complement these results and confirm the pore size distribution that refers to the size of the cavity rather than the size of the cavity entrance that might be included in the evaluation of MIP. The deconvoluted pore volumes obtained by MIP are reported below.

Table 4-3: Porous texture identified by mercury (Hg) intrusion experiments reporting the macropore volumes determined by MIP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>V(Hg) (cm$^{-3}$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH-0</td>
<td>0.015</td>
</tr>
<tr>
<td>KOH-0.005</td>
<td>0.028</td>
</tr>
<tr>
<td>KOH-0.01</td>
<td>0.015</td>
</tr>
<tr>
<td>KOH-0.1</td>
<td>0.781</td>
</tr>
<tr>
<td>KOH-0.5</td>
<td>1.976</td>
</tr>
<tr>
<td>KOH-1</td>
<td>3.824</td>
</tr>
<tr>
<td>KOH-2</td>
<td>5.244</td>
</tr>
<tr>
<td>KOH-3</td>
<td>2.225</td>
</tr>
</tbody>
</table>
All of the above analysed carbons, prepared and commercial, have been used as electrode materials in two- and three-electrode systems. However, the activated carbons are mixed with PVDF binder and conductive carbon C65, following the procedure mentioned in section 3.4.1. The two additives might change the structural composition of the electrodes and hence the investigation potential change of the pore size distribution is necessary. In order to study the effect of the binder and booster carbon in the preparation of the electrode materials, nitrogen sorption isotherms were performed as this technique provides the evaluation of micro- and mesoporous changes in the structure. A low activated sample (KOH-0.005) and a higher activated one (KOH-0.5) were tested for comparing the variation in the changes the additives might have in the case of a carbon with limited pore size distribution to micropores and another carbon that constitutes a hierarchical porous structure.

The BET specific surface area and PSD of the activated samples KOH-0.005 and KOH-0.5 with the same PVDF binder and super C65 compositions for EDLC testing are shown in Figure 4-9. The effect of adding 10 wt.% binder and 5 wt.% super C65 has different effects on the nano-porosity of each of the activated carbons. A significant difference in the total pore volume and the PSD of KOH-0.005 sample upon the addition of a binder is detected. This shows that the micropores in the low-activated samples might have been blocked whereby the total pore volume drops from 0.16 cm$^3$ g$^{-1}$ to 0.03 cm$^3$ g$^{-1}$ upon the addition of the booster carbon and binder, as shown in Figure 10-3. However, a smaller contribution in blocking the micro- and mesopores is illustrated in the PSD of the KOH-0.5 sample when mixed with PVDF and super C65. The incremental pore volume of both samples show the same PSD profiles with insignificant change in the pore volume of different micro- and mesopore diameters. These results could be attributed to the introduction of macropores in the higher activated samples that prevent the additives of blocking most microporous structures. In addition, the total micropore volume detected by N$_2$ isotherms has drastically increased with increasing the KOH loading whereby the pores blocked by the additives might have constituted a smaller percentage of the total number of pores in higher activated samples. The BET SSA of KOH-0.005 sample dropped from 252 m$^2$ g$^{-1}$ to 52 m$^2$ g$^{-1}$ (79% decrease) upon the addition of C65 and PVDF. Contrarily, the SSA of KOH-0.5 sample decreased to 1063 m$^2$ g$^{-1}$ from an initial value of 1351 m$^2$ g$^{-1}$ upon mixing the sample with the additives (21% decrease).

This proves that the specific surface area values and PSD recorded for the prepared activated samples are not the only factors to be considered when studying the electrochemistry of these materials. However, the correlation of the surface pore structure and porosity to the electrochemical behaviour of the carbons also depends on the additives to the electrode
materials for supercapacitor applications and hence should always be taken into consideration prior to electrochemical testing.

Figure 4-9: Incremental pore volume of (a) KOH-0.005 sample in comparison with KOH-0.005 sample mixed with PVDF and super C 65 and (b) KOH-0.5 sample in comparison with KOH-0.5 sample mixed with PVDF and super C65.

Elemental analysis was conducted to further study the surface chemistry and impurity of all carbonised samples and chemical compositions are reported in Table 4-4. The carbon and hydrogen content were evaluated and show a consistent decrease in the carbon percentage of the materials as the KOH loading was increased; this is attributed to the increasing “etching” effect of the KOH and production of more impurities during the carbonisation process.

Table 4-4: Elemental analysis of all samples with different KOH loadings showing carbon and hydrogen contents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon %</th>
<th>Hydrogen %</th>
<th>Other %</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH−0</td>
<td>90.45</td>
<td>0.63</td>
<td>8.91</td>
</tr>
<tr>
<td>KOH−0.005</td>
<td>89.14</td>
<td>0.77</td>
<td>10.10</td>
</tr>
<tr>
<td>KOH−0.01</td>
<td>86.94</td>
<td>0.90</td>
<td>12.16</td>
</tr>
<tr>
<td>KOH−0.1</td>
<td>79.95</td>
<td>0.80</td>
<td>19.25</td>
</tr>
<tr>
<td>KOH−0.5</td>
<td>72.42</td>
<td>0.87</td>
<td>26.70</td>
</tr>
<tr>
<td>KOH−1</td>
<td>79.62</td>
<td>1.08</td>
<td>19.30</td>
</tr>
<tr>
<td>KOH−2</td>
<td>73.25</td>
<td>1.33</td>
<td>25.42</td>
</tr>
<tr>
<td>KOH−3</td>
<td>71.81</td>
<td>1.15</td>
<td>27.04</td>
</tr>
</tbody>
</table>
To confirm the elemental oxygen presence in all activated samples, XPS was employed on three different sites of each sample. The results obtained confirm the presence of the peaks C$_{1s}$, O$_{1s}$, oxygen Auger (O$_{KLL}$) and carbon Auger (C$_{KLL}$) at binding energies of 284 eV, 532 eV and 983.68 eV, 1223.68 eV respectively in all spectra, as shown in Figure 4-10. The carbon content decreased with increasing the KOH activation loading, while the hydrogen content slightly increased and that of oxygen was increased up to KOH-0.1 sample, beyond which it decreases again. Further analysis and deconvolution of the XPS data and corresponding contribution of different chemical bonds will be discussed in more detail in Chapter 7.

![XPS spectra of all activated samples, showing the different carbon and oxygen peaks.](image)

**Figure 4-10**: XPS spectra of all activated samples, showing the different carbon and oxygen peaks.

### 4.3.2. Electrochemical Performance

#### 4.3.2.1. Three-electrode Systems

The electrochemical performance was first investigated in a three-electrode system to isolate the performance of the active materials. The un-chemically activated sample, KOH-0 presents a narrow CV profile and asymmetrical GCD curve, as shown in Figure 4-11a,b. The poor electrochemical performance is attributed to the relatively low surface area and lack of interconnected porous network in addition to the blocking of the micropores upon the addition of the binder and booster carbon to the low-activated samples. KOH-activated
Materials exhibit improved performance with quasi-rectangular CV profiles in the potential window of -1–0 V vs. Ag/AgCl at a scan rate of 200 mV s\(^{-1}\) which is a characteristic profile of porous carbons in EDLCs [3]. The normalized CV profiles of KOH-1 sample over different scan rates (1-200 mV s\(^{-1}\)) confirm these results (Figure 4-12a). The highest capacitance is achieved at the lowest sweep rate, which gives the electrolyte ions enough time to percolate into the smaller pores and therefore allow the maximum separation of charges and energy storage mechanisms to take place in. In addition, comparing the performance of the activated carbons to each other and to the commercial carbons, it was found that KOH-0.5 and KOH-1 samples have the highest capacitances, reflects in the highest current ranges for both activated carbons in the same potential window than the rest of the electrode materials including the commercial carbons, the latter shown in Figure 4-12b.

![Image](image1.png)

**Figure 4-11:** (a) Cyclic voltammetry of activated carbons with different KOH loadings at 200 mV s\(^{-1}\) in three-electrode systems, (b) galvanostatic charge-discharge at 1 A g\(^{-1}\), (c) influence of KOH/cellulose ratio on the specific capacitance at different current densities and (d) relation between specific capacitance at different current densities and total pore volume determined from N\(_2\) and CO\(_2\) adsorption isotherms, and corresponding BET specific surface area values.
The GCD curves at a current density of 1 A g\(^{-1}\) are presented in Figure 4-11b. Commercial activated carbons (BAC, NAC and KB) display symmetrical and triangular GCD curves with low iR drop (0.006-0.02 V), as inferred from the discharge half-cycles, which is a characteristic of an EDLC. In contrast, the un-activated KOH-0 samples exhibited an asymmetrical GCD profile with high iR drop, lower specific capacitances at higher current loads and a poor retention capability of 18% at a current density of 20 A g\(^{-1}\). This is attributed to the morphology of the sample that is constituted of a limited number of micropores within the fibrous structure of the carbonised cellulose. The ultra-micropores detected by CO\(_2\) adsorption isotherms might have been too small for the sorption of the electrolyte ions and therefore do not hugely contribute to the total capacitance of the electrode materials. All KOH-activated carbons display symmetrical charge-discharge profiles with low iR drops (0.01-0.04 V), even at very low KOH/cellulose ratios. These results show excellent potential for employing the KOH-activated carbons as supercapacitor electrodes with high power densities due to the very low ohmic drops, specifically at high current densities. The KOH-0.5 and KOH-1 samples show the best performance, having specific capacitances of 162 F g\(^{-1}\) and 161 F g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\), respectively. The latter samples possess a charge retention capability of 73% and 78%, respectively upon increasing the current density to 20 A g\(^{-1}\), as shown in Figures 4-11c and 10-4. This is comparable to commercial activated carbons but with much higher specific capacities at different current loads. This might be attributed to the morphology of the KOH-0.5 and KOH-1 samples which consist of a porous network structure among the different pore size ranges.

Figure 4-12: (a) Normalized cyclic voltammograms KOH-1 sample in a three-electrode system in 6 M KOH at different scan rates ranging from 1 mV s\(^{-1}\) to 200 mV s\(^{-1}\) and (b) cyclic voltammograms of commercial materials in three-electrode systems in 6 M KOH at a scan rate of 200 mV s\(^{-1}\).
The improved supercapacitor performance detected in 1-, 2- and 3-dimensional analyses for the first time yields insight into the importance of the hierarchy of micro-, meso-, and macropores for obtaining high specific capacitance and maintaining a stable behaviour at high current rates. As the amount of KOH activating agent was increased, the specific capacitance increased until reaching an optimum value, beyond which it drastically decreased again. It is evident from different pore size distributions, detected by N₂ and CO₂ isotherms, MIP and X-ray CT, that the average pore sizes of both samples KOH-0.5 and KOH-1 are much smaller (~1.7 nm) than the samples with high KOH loading (in the macroporous range of 0.1-5 μm); yet much higher than those with low KOH / cellulose ratios in which the micropores might not be accessible by the electrolyte. The non-accessible pores do not contribute to the total capacitance of the electrode material. This behaviour has been reported as the ion-sieving effect [11, 191, 351]. The total micropore volume has also increased with the KOH loading, providing more energy storage potential in the three-electrode supercapacitor. Furthermore, BET and PSD analyses, as previously shown, demonstrate that the micropores are blocked by the PVDF and super C65 addition to the active carbon materials in the low-activated sample KOH-0.005. However, a small decrease in the specific surface area and negligible changes in the PSD are depicted for the KOH-0.5 sample upon adding the same loadings of the binder and booster carbon materials. These results confirm the importance of the accessibility of the micropores by the electrolyte solution and the selectivity of a suitable precursor material depending on the electrolytic solution.

Figure 4-11c shows the change in the specific capacitances with increased KOH amount at different current densities. At low current densities, the specific capacitance reaches a maximum with KOH-0.1 sample due to the major role that micropores play at slow kinetics. The KOH-0.5 and KOH-1 samples have similar specific capacitances in the chosen range of current densities. The microporous properties of the structure accommodate the charges and meso- and macroporous features determine transport of ions within the structure as previously mentioned [12]. At higher current densities, the performance of the KOH / cellulose samples with low KOH loading drastically decays as the micropores cannot accommodate the fast ion transport kinetics, whereas the macroporous networks can still play the role of adsorption and transportation. This shows that the absence of a microporous surface area leads to a decrease in the gravimetric capacitance in KOH electrolyte, which corroborates the results of previous works [37, 187]. Figure 4-11d confirms that a ‘balanced’ micro- and macropore distribution of total pore volume maintains high specific surface area values along with highest capacitance, especially at rapid charge-discharge cycling.
The stability value was recorded using CV tests at a sweep rate of 50 mV s\(^{-1}\). Single cell potential window opening experiments were conducted to study the stability criterion of the different carbon samples in three-electrode arrangements \([325, 326]\). Figure 4-13 shows the S-values at different vertex potentials in the potential range -1.5—1.5 V vs. \(E_{\text{ref}}\) (Ag/AgCl).

![Graph showing S-value vs. vertex potential for different carbon samples](image)

Figure 4-13: S-value vs. vertex potential plot for all carbonised samples. Positive/negative polarization was conducted in separate cells. Dashed dark grey line represents the stability criterion introduced by Xu. \textit{et al.}\[325\].

The S-values and hence the electrochemical stability for the different carbon samples show a clear dependence on the morphology in both anodic and cathodic conditions. KOH-0 sample, in particular demonstrates good stability in a wide potential window of -1.3—0.4 V, beyond which the magnitude of the S-value drastically increased above the stability limit. The stability criterion is determined by the dark grey dashed-line at a value of 0.1 and shows the critical dependence of the electrochemical stability not only on the electrolyte anions and cations, but also the porous structure of the different carbonised samples. The most activated sample (KOH-3) shows instability at cathodic conditions, while the rest of the samples have an S-value < 0.1 in the normal potential window -1—0 V at which they are usually electrochemically tested. Using this criterion, it is clear that the low- and intermediate-activated KOH samples constitute a more stable system than the high-activated samples. This can be again attributed to the morphology of the carbons, whereby a hierarchical porous network structure is vital for not only good performance, but also stability at extreme potentials.
The stability of the carbons was also detected via the stability test upon cycling the electrode materials for 5000 cycles. The cycling stability of activated carbons at 10 A g⁻¹ is shown in Figure 4-14a. KOH-1 sample exhibits the best stability with 98.5% capacitance retention after 5000 cycles. The cycling stability is better than or comparable to those of biomass carbon electrodes reported in the literature [75, 272, 342] but this study presents the performance at a much higher current loading of 10 A g⁻¹, which proves excellent performance rate. The non-activated samples showed more than 100% capacitance retentions and these results will be further explained in Chapter 5.

Figure 4-14: (a) Galvanostatic charge-discharge stability of KOH-activated carbons with different KOH loadings at 10 A g⁻¹, and Nyquist plots of KOH-n activated carbon electrode materials with different KOH loadings (b) across a range of frequencies and (c) in high frequency region.
Figure 4-14b presents the electrochemical impedance spectra of the different samples at 0 V vs. the open circuit voltage in the frequency range of 0.1 Hz to 1 MHz. All impedance curves show a depressed semicircle in the high frequency region (Figure 4-14c) with different x-intercepts and diameters of the semicircle, corresponding to different electrolyte/electrode contact resistances, electronic resistances of the electrode materials and the ionic resistance of the electrolyte ions [352]. Similar results were obtained with the commercial benchmark carbons (Figure 10-5a). As the KOH loading is increased, a more ideal capacitive behaviour is reached with a more vertical line in the low frequency region with KOH-0.5, KOH-1 and KOH-2 samples. However, an almost-vertical asymptote, reflecting an ideal behaviour was not observed in the impedance curves of any of the samples. An in-depth investigation of these values governed by an electric series model suggested in this thesis will be further discussed in Chapters 5 and 6.

4.3.2.2. Two-electrode Systems

To investigate the performance of the materials in practical cells, symmetric coin cells were fabricated in a CR2032 geometry. Based on the findings from the 3-electrode study, the performance of the two best performing samples, KOH-0.5 and KOH-0.1, was investigated in a two-electrode system. The cyclic voltammograms at a scan rate of 50 mV s⁻¹ scan in the potential window of 0–1 V and GCD cycling tests at different current densities are shown in Figure 4-15a-c. Both samples show quasi-rectangular CV curves in the potential window of 0–0.8 V where a small hump at 0.85 V in the KOH-1 sample occurs, above which a rapid increase in the current takes place. This is attributed to possible irreversible reactions above this potential due to oxygen evolution at a potential of 0.8 V. The average specific capacitance values of 5 cells of the same sample were found to be 39 F g⁻¹ and 47 F g⁻¹ at a current density of 0.05 A g⁻¹ for KOH-0.5 and KOH-1 samples, respectively. The specific capacitance values are dictated by a number of factors including the total mass of activated carbon materials in both electrodes, the amount of electrolyte added and separator thickness. Among all samples, the KOH/cellulose ratio of 0.5:1 and 1:1 displayed the best performances and are comparable to commercially available activated carbons. Upon increasing the current density form 0.05 A g⁻¹ to 10 A g⁻¹, the capacitance retention of KOH-0.5 and KOH-1 symmetric supercapacitors achieved was 38% and 62%, respectively (Figure 4-15d).
Figure 4-15: Two-electrode measurements of symmetrical coin cells in 6 M KOH electrolyte. Galvanostatic charge-discharge cycles of (a) KOH-0.5 sample and (b) KOH-1 sample at different current densities, (c) cyclic voltammogram of the two coin cells in the potential window 0–1 V at 50 mV s⁻¹ scan rate and (d) capacitance as a function of current density between 0.05 A g⁻¹ and 20 A g⁻¹.

The capacitance retention of both activated samples was recorded to be 99.8% upon 5000 cycles for both KOH-0.5 and KOH-1 coin cells, as demonstrated in Figure 4-16a. In addition, the EIS behaviour was similar to that obtained in the three-electrode system (Figure 10-5b). To further evaluate the supercapacitor performance, the average energy and power densities of the whole cell were represented in a Ragone plot (Figure 4-16b). The densities were inferred from the specific capacitance and discharge times corresponding to different current densities of cycling the full cell, as described in section 3.4.6. The KOH-1 device exhibits an energy density of 6.6 W h kg⁻¹ and power density of 25 W kg⁻¹ at a current density of 0.05 A g⁻¹. At a higher current density of 10 A g⁻¹, the power density increases to 5332 W kg⁻¹, with corresponding energy density of 4.1 W h kg⁻¹. These results
show that a simple two-step procedure yields good preliminary results and may be improved further by incorporating pseudocapacitive materials into the porous structure, in addition to optimizing the coin cell fabrication. These results prove that the real application of supercapacitors to complement batteries at such high power densities can be employed in different application requiring quick adaptation in charging and discharging.

Figure 4-16: (a) Galvanostatic charge-discharge stability test of KOH-0.5 and KOH-1 samples at 10 A g$^{-1}$ current density in 6 M KOH. The specific capacitance is calculated from discharge half-cycles during galvanostatic cycling in coin cell systems, and (b) Ragone plot summarising specific energy and power densities of the devices.

To investigate the electrochemical stability in a real-life application at extreme conditions and test the actual ageing of the electrochemical performance of the carbon materials, the voltage hold test was performed for commercial applications in two- and three- electrode configurations. The conditions at which the voltage hold was done are as follows: i) -1 V for KOH-0.5 and KOH-1 samples in the three electrode configuration with occasional cycling between -1 and 0 V every 10 h and ii) 1 V for the KOH-1 coin cell and the respective upper cell voltage with the same occasional charge/discharge cycling [326, 327]. Both tests were conducted at a current density of 0.5 A g$^{-1}$. The three cycling tests were performed every 10 h for 100 h Potentiostatic hold, yielding 1000 h for the voltage hold procedure and Figure 4-17 shows the respective voltage hold experiments.
Figure 4-17: Cycle test for (a) a three-electrode arrangement utilising KOH-0.5 and KOH-1 electrode samples in 6 M KOH solution and (b) KOH-1 coin cell in 6 M KOH solution. Upper voltage limit used is -1 V vs. Ag/AgCl for the three-electrode arrangement and 1 V for the full cell. Lower/upper limit is 0 V during cycling.

The initial capacitance values for the KOH-1 three-electrode system and KOH-1 full cell was 140 F g⁻¹ at -1 V vs. Ag/AgCl and 42 F g⁻¹ at 1 V, respectively with insignificant capacitance loss over 1000 h. In addition to the almost constant capacitance value observed over the 1000 h test, insignificant capacitance fluctuations were observed during the voltage hold in both configurations whereby the capacitance value decreases by less than 1% after 500 h for the full cell test and 4% of its initial value after 1000h. The ageing of the electrode materials in two- and three-electrode systems proves that these materials do not significantly degrade at extreme conditions for a long period of time. For the voltage limits indicated in the cycling experiment, the capacitance retention was above 99% for KOH-1 sample as illustrated previously. The voltage hold test after 1000 h and cycling test, therefore, both suggest a stable full cell system and no significant loss in the capacitance values. The capacitance loss for the voltage hold test attains similar results to those obtained by cycling of ~1% for the KOH-1 coin cell and 1.5% for the KOH-1 three-electrode configuration. This proves that the chemical and structural integrity of the electrode materials and supercapacitor device have not been altered upon applying long voltage hold tests.

The same electrochemical tests reported above have been conducted in the same coin cell system but with the organic electrolyte 1 M TEA-BF₄ in acetonitrile and are presented in Figure 4-18. Herein, KOH-1 carbon was used as the electrode material for the fabrication of a symmetric supercapacitor to detect the redox capacitive mechanisms in 6 M KOH electrolyte solution. The cyclic voltammograms at different scan rates show that there is no pseudocapacitive contribution to the total capacitance of the carbon materials in the organic
electrolyte (Figure 4-18a). The CVs illustrate quasi-rectangular profiles similar to that of KOH-1 sample in 6 M KOH solution in the voltage range of 0−3 V. This proves that these materials have a typical profile of porous carbons in EDLCs in organic electrolytes with no redox behaviour, due to the absence of necessary protons, unlike the redox-enabling effect witnessed in 6 M KOH aqueous electrolyte [226, 353]. GCD curves at different current densities ranging between 0.5 A g\(^{-1}\) and 20 A g\(^{-1}\) and in the voltage range 0−3 V, were also performed in which all profiles at different current densities exhibit almost symmetrical and triangular curves, which is also a property of EDLC behaviour. However, the iR drop was much higher (~0.1 V at a current density of 1 A g\(^{-1}\)) compared to the same carbon electrodes in KOH aqueous electrolyte. In addition, the KOH-1 carbon sample, one of the best performing materials in an alkaline solution, attained an average specific capacitance value of 13 F g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\) (Figure 4-18b) and a capacitance retention of 91% of its initial value after 5000 cycles at a current density of 10 A g\(^{-1}\) (Figure 4-18c). Compared to the same carbon sample in aqueous electrolyte, the specific capacitance achieved in the two-electrode system was 39 F g\(^{-1}\) at 0.5 A g\(^{-1}\) current density, confirming that the redox reactions involving KOH ions were present in the aqueous system. These results agree with the shape of the cyclic voltammograms in aqueous electrolyte with the humps at different potentials in the three-electrode setup, which are attributed to the oxygen content in the carbon materials, as detected by elemental analysis and XPS techniques, and therefore the pseudocapacitance effect in the aqueous electrolyte. The effect of oxygen functionalities on the electrochemical performance in an aqueous electrolyte will be further explored in Chapters 5, 6 and 7. In addition, the capacitance values in organic electrolytes prove that the electrolyte ions in such systems cannot penetrate the smallest pores of the hierarchical morphology of KOH-1 sample, in which the smaller anions and cations of the aqueous electrolyte can, thus giving rise to higher capacitances in the latter cells. These results highlight the advantages of aqueous systems, specifically at low current densities or scan rates, in which the porous structures are utilized more efficiently for attaining maximum capacitances.

The Ragone plot displaying the energy and power densities of the full cell is shown in Figure 4-18d. The activated carbon sample in 1 M TEA-BF\(_4\) in acetonitrile solution achieves an average energy density of 19.78 W h kg\(^{-1}\) at an average power density of 150 W kg\(^{-1}\) at a current density of 0.1 A g\(^{-1}\). As the current density was increased to 10 A g\(^{-1}\), the energy density decreases but maintains a value of 6.4 W h kg\(^{-1}\) at a corresponding power density of 15 kW kg\(^{-1}\), which is a typical behaviour of carbon materials in organic electrolyte solutions that operate in wide voltage windows [354]. Using a voltage window of 3 V in organic electrolyte solutions can therefore, and despite the fact of achieving lower capacitance...
values due to the absence of Faradaic reactions, enhance the amount of energy stored without compromising the stability of these systems or their power efficiency. These results are due to the fact that the energy density is proportional to the capacitance, but increases with the square of the voltage or charge, and thus the substantial improvement in the energy densities of non-aqueous supercapacitor systems.

Figure 4-18: Electrochemical behaviour of KOH-1 sample 1 M TEA-BF₄ in acetonitrile solution in a full cell configuration. (a) Cyclic voltammetry at different scan rates 1-200 mV s⁻¹, (b) galvanostatic charge-discharge at different current densities 0.5-20 A g⁻¹, (c) galvanostatic charge-discharge stability at 10 A g⁻¹ current density upon 5000 cycles and (d) Ragone plot summarising specific energy and power densities of the coin cell.
4.4. Conclusions

In this chapter, different interconnected porous carbons with high surface areas and total pore volumes were prepared via activation of cellulose with different potassium hydroxide loadings followed by a direct carbonisation process. The results reported in this chapter form a model system with which to explore how different morphological factors directly influence the electrochemical system of the electrodes in supercapacitor applications. It was found that optimum KOH / cellulose ratios of 0.5:1 and 1:1 yielded high surface areas, crucially with a hierarchical pore size distribution, both of which that give rise to the best electrochemical performance in supercapacitor devices. This study reveals that the electrochemical performance does not solely depend on high surface areas but also on an optimum pore size distribution, specifically at low current densities. For the first time, X-ray CT was coupled with different characterisation techniques to study the effect of three-dimensional structure on electrochemical performance in supercapacitor applications. Further study on the interconnectivity of the pores via TEM tomography is needed to provide a complete determination of these parameter groups and provide significantly smaller analysis volumes compared to X-ray CT used herein. The characterisation techniques presented herein are discussed and the limitations of each are presented. However, there is a clear correlation between the morphological properties of porous electrode materials and their electrochemical capacitive performance. The KOH-0.1 sample displayed best electrochemical performance at very low current densities due to the domination of microporous networks. However, KOH-0.5 and KOH-1 carbons exhibited good electrochemical performances with superior stability at different current densities with specific capacitances of 162 F g\(^{-1}\) in 6 M KOH. These findings demonstrate the contribution of interplaying morphological factors to double-layer capacitance and high performance rates over a variety of length scales, and open new pathways for the optimization of supercapacitor materials starting with activated carbons. An in-depth study of the electrochemical impedance behaviour and its direct synergy with the morphology of the same activated carbons will follow in Chapters 5 and 6 that will allow a more crucial understanding of the supercapacitor performance at different frequencies and voltage ranges.
Chapter 5

Correlating Electrochemical Impedance with Hierarchical Structure for Porous Carbon-based Supercapacitors Using a Truncated Transmission Line Model


Scope of this chapter: Starting with the transmission line model, an equivalent circuit has been developed to characterise the effect of pore size distribution and total pore volume on the electrochemical impedance spectra. KOH-activated carbons were used as model systems to study the frequency response at open circuit potential. The EIS spectra represent the electrolyte ions passing from macropores into mesopores and finally reaching the micropores, showing the capacitance as a function of frequency and total pore volume of the porous structure.
5.1. Introduction

Electrochemical impedance spectroscopy (EIS) is a powerful diagnostic tool used to deconvolute the various frequency dependent impedances in electrochemical systems. The method of alternating current impedance spectroscopy, whereby an alternating potential (usually 5 mV) is applied over a wide frequency range, allows the determination of the kinetic and electrical responses of an electrochemical system under study [3]. When evaluating the capacitive behaviour of one electrode (or more) in a supercapacitor with EIS, the method enables the quantitative analysis of: i) the capacitance as a function of frequency, ii) phase relation between the real and imaginary components of the overall impedance and distinguishing the i) the equivalent series resistance of the whole device and ii) double-layer and pseudo-capacitances in different frequency ranges. Thus, there is a wide scope for applying EIS to supercapacitors to understand the frequency response of porous carbon materials and their corresponding capacitive behaviour.

Electrode materials exhibiting porous and high-surface area structures are commonly used in electrochemical energy storage devices [355-358]. Carbon is extensively used as one of these electrode materials or catalyst support in electrochemical energy conversion and storage devices due to its versatile properties. This includes its existence in various microstructures, different degrees of graphitization and ease of manipulation [7, 9, 10]. More specifically, activated carbons have been the primary candidate for electrode materials in electrical double-layer capacitors (EDLCs). Large specific surface area, a hierarchically structured pore size distribution (PSD) and a high proportion of micropores, are the primary factors that dictate the high performance of double-layer capacitors [11]. However, the trade-off between the porosity and pore size in addition to the accessibility of the electrolyte into the porous structure and therefore wetting the pore matrix are critical factors for the optimization of the electrode performance. Therefore, the porous structure displays a complex impedance response, far from the one of an ideally polarizable electrode. For these electrode-electrolyte systems, the impedance response would be associated with the bulk solution resistance, electrode/electrolyte interphasial impedance, charge transfer resistance and the double layer capacitance. Pseudocapacitance might also have a contribution in the total impedance behaviour if Faradaic reactions were involved. In this case, addressing an electrode as such with an alternating current or potential that drives this current, the electrode would not charge (or discharge) uniformly due to the mentioned inhomogeneities outside and throughout the electrode matrix. The EIS technique can be used to examine the underlying electrochemical behaviour of different porous electrode materials to further assess their suitability for different devices requirements.
As previously mentioned, supercapacitor electrode materials composed of porous carbon materials, whether in an activated carbon matrix, carbon aerogel or carbon nanotube forms, exhibit various internal resistances that contribute to the total equivalent resistance of the equivalent resistance circuit [359]. More precisely, the electronic resistance element is comprised of the electrode material resistance (interparticle and intraparticle resistances), electrode/current collector contact resistance and the electrode/separatotr resistance. As for the ionic resistance, this comprises the bulk electrolyte resistance, the electrode/electrolyte ‘external’ surface resistance and the ‘internal’ electrolyte resistance within the different sized pores [360-362]. The charge transfer resistance governs the Faradaic processes, commonly induced in carbon electrodes due to i) redox reactions with surface functionalities or pseudocapacitive elements, and/or ii) overcharge/overdischarge leakage resistance Each of the individual resistances contributes to the EIS profile and can be modelled using an equivalent circuit.

Ion transport in three-dimensional porous electrodes must be considered differently to ‘two-dimensional’ electrochemical processes on the ‘flat’ surface of planar electrodes where semi-infinite diffusion can generally be assumed [3]. Hence, ‘ideal’ finite-length Warburg impedance elements cannot be applied to the porous electrodes used in supercapacitors in the same way as planar electrodes. The phase angle between the applied potential at the pore orifice and the charging current at low frequency has a similar behaviour to that of the Warburg diffusion impedance of a planar electrode in solutions of low concentrations. However, the distribution of resistances originating from various pore channel sizes can be used to model the non-uniform current distribution, and to classify the dispersion of capacitance in the porous matrix over a wide range of frequencies. A ‘universal’ equivalent circuit based on a transmission line model (TLM), has been suggested to represent the electrochemical impedance behaviour of porous materials [3]. In this arrangement, a network of parallel resistance (R) and capacitance (C) elements, each with its own time constant, combine to represent the impedance behaviour of a porous electrode. Fletcher et. al then developed a family of “Pascal” equivalent circuits through software and hardware realizations of their model. The suggested circuit proved to reproduce the overall impedance response of real carbon-based supercapacitors [363, 364]. It was proposed that the equivalent circuit theory can be complemented with molecular dynamics simulations to determine the exact distributions of the RC time constants and corresponding complex processes in porous electrode structures [365, 366].

A limitation of the use of complex equivalent circuits is that plausible fits can be achieved to EIS data using a range of different circuit element values. Such ‘degenerate networks’ can establish identical impedance values over an entire range of frequencies and therefore
identifying the behaviour of a specific complex system is not trivial. While the likes of Fletcher has derived transformation formulas for common ‘degenerate networks’ to solve the ambiguity of different electrical models [333], the more complicated the equivalent circuit the greater the inherent uncertainty in the determination of fitted parameters. Thus it is normally preferable to apply the simplest equivalent circuit possible with an adequate and reasonable number of components.

An equivalent circuit for a single pore was first proposed by de Levie, in which an ideal pore has a solution resistance $R$, and a double-layer capacitance $C$ that behaves equivalently to the TLM [335]. Modifications and simplifications of the TLM followed; these methods have used different assumptions based on the precursor materials and corresponding morphological structures [367, 368]. Table 5-1 summarizes the suggested equivalent circuit models for EDLCs, along with the assumptions made and elements governing the models.
Table 5-1: Summary of equivalent circuits suggested in the literature showing the different model elements and different assumptions made, with resistance ($R$), capacitance ($C$) and frequency ($f$).

<table>
<thead>
<tr>
<th>Equivalent series circuit suggested</th>
<th>Elements</th>
<th>Assumptions</th>
</tr>
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<tbody>
<tr>
<td>$dz$: section of equivalent circuit of single pore; $R$: solution $R$; $C$: double-layer $C$ inside the pore; $V$: voltage; $i$: current.</td>
<td>De-Levie: A model of an element of a single pore; cylindrical with uniform radius; $R$ &amp; $C$ uniformly distributed down the pore, both expressed per unit length; current conducting matrix of negligible $R$. [335]</td>
<td></td>
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<tr>
<td>$R_s$: electrolyte $R$ outside pores; $R$: electrolyte $R$ inside pores; $C$: double-layer.</td>
<td>TLM: $RC$-parallel elements with well-chosen numbers of ‘values’; Faradaic reactions are absent; cylindrically porous carbons; curvature is neglected; uniform pores; frequency-response exhibits $-45^\circ$ phase angle; behaviour is ideal capacitor at low $f$. [3]</td>
<td></td>
</tr>
<tr>
<td>$R_i$, $C_i$: vertical ladder network of $RC$-series components of electrolyte $R$ inside pores and $C$ at patch of pore walls; $R$ &amp; $C$: bulk solution $R$ and dielectric polarization $C$ of solution.</td>
<td>Any set of non-uniform pores in parallel; correspondence is not one-to-one with physical values; proposed circuit is degenerate with another random set of parallel $RC$-elements; electrolyte $R$ in pores is higher than $R$ of solid carbons; asynchronous charging. [332]</td>
<td></td>
</tr>
</tbody>
</table>
$R_A$: $R$ of electron flow in porous carbons of electrode 1; $R_C$: $R$ of ion flow in pore solution in electrode 1; $C$: double-layer $C$; $R_B$: $R_D$: same as $R_A$ and $R_C$ on electrode 2; $V$: voltage of power source; $i$: current; $R_E$: separator $R$.

No direct flow of charges from carbon into electrolyte; electrode/electrolyte interface is similar to plane-electrodes; electrolyte flows between particles but not through them; micropore surface accessible at any rate; effect of concentration on $V$ and charge is neglected; double-layer at local equilibrium; charge transfer ignored; concentration and $V$ of electrolyte are uniform across pore cross-section. [369]

$2$ $RC$ parallel branches; $C_1$: capacitor; $ESR$: equivalent series resistance (small $\tau$); $EPR$: equivalent parallel resistor (high $\tau$ ≠ constant) accounts for long-term self-discharge; $C_2$: capacitor and $R_2$: ($R_2$ $>>$ $ESR$).

Intermediate $\tau$ omitted; specific for cases when $V$ rebounds due to charge redistribution after discharging fully charged $C$; based on TLM; $\tau$ in each branch is average of $\tau$'s for all pore systems; independent of size of $C$; $RC$ values in each branch depend on amount of porous materials and physical arrangement in electrode. [43]
\( R_s \): high frequency resistance; \( R_i \): active material/current collector interface resistance; \( C_i \): interface capacitance with dispersion parameter \( \alpha_i \); \( R(\omega) \): partial resistance depending on frequency \( f \); \( C(\omega) \): supercapacitor capacitance.

At high frequency, the cell behaves on the loop represented by parallel RC circuit with \( R_s \) delaying or blocking capacitive behaviour; at low frequency, the cell is represented by \( R(\omega) \) having total resistance \( R \); continuation of de Levie’s work. [370]

2 RC branches; \( C_1 \): voltage-dependent capacitance; \( R_1 \): equivalent series resistance; \( C_2 \): charge transfer capacitance; \( R_2 \): charge transfer resistance; \( R_p \): equivalent parallel resistance.

Models different charge transfers; \( C_1 \) varies linearly with voltage \( V \); \( R_1C_1 \) dominates response (\( \tau \) in seconds); \( R_1C_1 \) determines energy evolution during half-cycles in power electronics; \( R_2C_2 \) governs slow responses and compliments \( R_1C_1 \) in minutes; \( R_2C_2 \) governs internal energy distribution at the end of half-cycles; \( R_p \) only in long-term storage that governs leakage effect and neglected during fast half-cycles; inductance is neglected; process of each branch observed separately by measuring voltage \( V \). [371]
EIS using such equivalent circuits has not been used to examine the correlation between morphology and electrochemistry across a range of porous electrode structures. To this end, the effect of different porous networks and PSDs on the capacitive behaviour over a wide frequency range has been studied for the first time herein. The focus of this chapter is divided into two main scopes: i) developing a simple equivalent circuit that describes the performance of porous electrodes in supercapacitors using KOH-activated carbon materials as model systems and ii) assessing the role of the morphology/pore structure in determining non-ideal performances and enhancing the electrochemical performance of double-layer capacitors. Different PSDs and micropore volume fractions are investigated, in favour of how this affects the electrochemical impedance behaviour and the relaxation times in different porous carbon networks are evaluated. A truncated version of the universal equivalent circuit was proposed for porous electrodes, wherein non-branching pores are assumed throughout the porous matrix [332]. This study resolves the issue of selecting the “best” fitting circuit, regardless of the number and relevance of the elements in the candidate models considered, where the number $n$ and values of the “RC” vertical ladder is chosen arbitrarily [372]. However, it might not represent all the different PSDs in the porous electrode and therefore not have a direct correspondence with the real physical values of the modelled circuit. In addition, this work addresses the critical importance of finding the trade-off between minimization of pore resistance and maximizing pore capacitance based on the use of model systems composed of different relaxation times ($\tau$). The average pore sizes were identified, categorized as being in the order: i) micropore range ($< 2$ nm), ii) mesopore range ($2−50$ nm) or iii) macropore range ($> 50$ nm), and the corresponding relaxation times are all expressed by Eqn. (5-1):

$$\tau = RC \quad (5-1)$$

where $R$ and $C$ describe the resistances and capacitances, respectively, associated with the different aspects of the occurring processes, as will be detailed throughout this work.

5.2. Experimental

5.2.1. Synthesis and Characterisation

In this study, KOH-activated cellulose of softwood pulp origin, previously analysed via a suite of characterisation techniques (Chapter 4), were used as the electrode material. All KOH / cellulose samples are denoted as KOH-$n$ where $n$ represents the KOH / cellulose
mass ratio. The characterisation techniques used in the previous work (Chapter 4) have been used to complement the electrochemical analysis of the different electrode materials. This would allow a full understanding of the morphology, surface chemistry and porous texture of the carbon materials. It is worth mentioning that KOH-3 sample has been excluded from this study and the reason for that will be explained later in this chapter.

5.2.2. Electrochemical Testing

6 M KOH was the electrolyte of choice throughout all electrochemical measurements in three-electrode configurations using a Gamry potentiostat. The working electrodes were prepared as follows: 85 % activated carbon, 5 % Super C65 as a booster carbon and 10 % polyvinylidene fluoride (PVDF) as a binder were first mixed in N-methyl-2-pyrrolidone (NMP) solvent. The mixture was then coated on 1 cm² nickel foam to form a final active material mass loading of 1-3 mg. The counter electrode used was a 1 cm² platinum mesh and the reference electrode was Ag/AgCl. Galvanostatic charge-discharge (GCD) cycling stability test was performed on all samples at a current density of 20 A g⁻¹ over 5000 cycles. Electrochemical impedance spectroscopy was performed over a frequency range of 10 mHz to 1 MHz with a voltage amplitude of 5 mV, all performed at open circuit potential after an initial conditioning of cycling the electrodes at 50 mV s⁻¹ scan rate for 20 cycles. The equivalent series resistance, different electronic and ionic contributions of resistive components, constant phase elements and relaxation times of different porous structures were successively determined as average values of 5 measurements of the same sample. The synergy between different morphologies, total pore volume and pore size distribution and the electrochemical performance was inferred for different porous electrode materials by employing the equivalent circuit model suggested in this study (Echem Analyst software, Gamry Instruments). The variation in specific capacitance before vs. after cycling was also studied.

5.3. Results

5.3.1. Surface Morphology, Pore Volume and Pore Size Distribution

SEM and TEM characterisation techniques illustrate the etching effect of KOH on the carbon precursors, as shown in Chapter 4. The morphology dramatically changes from a
fibrous structure with micropores at low KOH / cellulose ratios to a hierarchical porous network of micro-, meso- and macropores at medium loadings (KOH−0.5 and KOH−1). Further increase in the KOH loading enhances the formation of meso- and macropores that dominated at the highest KOH / cellulose mass ratios. Figures 4-1, 4-2, 10-1 and 5-1 show that this change is attributed to the expulsion of the more volatile matter as the KOH mass was increased, leaving behind a diverse range of pore diameters. The selection of activation conditions of the carbon precursor with different KOH loadings determined the width of the PSD in the micro-, meso- and macroporous regions.

Figure 5-1: SEM images of four representative activated KOH-n samples with increasing n; (a) KOH-0.01, (b) KOH-0.1, (c) KOH-0.5 and (d) KOH-2.

The dominance of micropores at low or zero chemical activation, and that of macropores at high KOH concentrations is shown in Figure 5-2. The total pore volume of the samples was determined by combining the macropore volumes calculated using MIP, and micro- and mesopore volumes extracted from N₂ and CO₂ isotherms. The total pore volume increased with the KOH/cellulose ratio, which was attributed to the formation of a macroporous structure and a decrease in the micropore volume fraction and therefore, contribution to a wider PSD. The pore volume in the range of 0.7−50 nm displayed sharp peaks in the micro- and mesoporous ranges at different KOH activation ratios, in addition to the dominance of macropore peaks, whilst still maintaining a mesoporous structure for higher
activation ratios (depicted from MIP, DFT and DR, as described in Chapter 4). The volume of CO₂ adsorbed also confirms an increase in the total microporous volume (micropores of diameter < 0.7 nm) with the increasing KOH loading. The total pore volume, constituting micro-, meso- and macropores increased with increasing KOH loading. However, the micropore fraction decreased with higher KOH etching due to the formation of more macropores.

Figure 5.2: Total pore volume and volume percentage contributions of each of the pore size ranges in different KOH-activated carbons.

5.3.2. Frequency-dependent Impedance Characteristics

The modelling of the frequency response of porous materials using an equivalent circuit has been discussed in the literature, so as to understand and distinguish the different elements that contribute to the total resistance and capacitance values of the whole device [332, 333, 369, 373-375]. However, it is normally assumed that the electrode is ideally polarizable. According to Grahame’s definition in an ideally polarizable electrode, a change in potential causes solely a flow of charge from the external circuit to the electrode/electrolyte interface, with no charge flow across the double-layer [50]. The double-layer is then at electrostatic equilibrium at a specified potential and no Faradaic processes that lead to a change of the surface chemistry of the electrode occur. The ideal polarizability is detected by a 90° phase angle (current and voltage are out of phase by 90°). This performance is demonstrated by a vertical line, parallel to the imaginary part of impedance (Z’’), on the y-axis of the Nyquist
complex plot. In the case of porous materials, and unlike planar electrodes, non-ideal and incompletely polarizable behaviour occurs that is frequency-dependant and is distributed over a porous electrode surface in a non-uniform current distribution mode across the porous matrix. Hence, when a small alternating current or voltage signal is imposed to a porous matrix electrode, the behaviour is far from ideal, and the double-layer capacitance is dispersed over the wide range of frequencies whereby different pore sizes ‘tune in’ after different lapses of time. This means that the narrower the pore, the longer the time or the lower the frequency at which the pore pronounces its relaxation time, due to the large inner electrode surface area compared to the outer surface area [334, 335, 376].

In the case of the porous KOH-activated carbons studied in this work, the morphologies with different PSDs and oxygen functionalities determine the capacitive behaviour in different frequency regions. EIS was applied at the open circuit potential, and the different complex plane plots; Nyquist, modulus of impedance ($Z_{\text{mod}}$), phase angle ($Z_{\text{phi}}$), and equivalent series resistance are presented in Figure 5-3.
Figure 5-3: Impedance plots of KOH-activated samples showing: (a) Nyquist plot, (b) ESR as a function the micropore volume fraction, and Bode plots showing the variation of (c) impedance modulus ($Z_{\text{mod}}$) with frequency and (d) phase angle ($Z_{\phi}$) with frequency.

The particular features in order of the speed of processes governing the different resistive and capacitive elements contributing to the electrochemical performance are investigated using the impedance data. As mentioned earlier, the capacitive response is distributed over a wide frequency range, and the examination of the various bulk electrolyte, surface and different pore sizes elements within the carbon electrodes is necessary to understand the impedance behaviour. The impedance response will be considered below starting at the highest frequencies employed and onto the more complex behaviour of the carbon model systems at lower frequencies.

The equivalent series resistance (ESR) represents the impedance behaviour at very high frequency ($f \to \infty$) and is evaluated at the intercept on the real axis ($Z'$) of the Nyquist plot (Figure 5-3a). This resistance governs the bulk electrolyte ionic resistance and interparticle and intraparticle electrical resistances originating from the porous nature of the electrode materials. The resistance of the bulk electrolyte is the only common component of the ESR
in this system where the same electrolyte (6 M KOH) is employed throughout all experiments. Therefore, the different values of the $ESR$ attained in the porous carbons reflect the relative change in the internal electrical resistances of the carbon particulates. The $ESR$ value decreased with an increased total pore volume and decrease in the microporous contribution (i.e. with the KOH loading), where the $ESR$ reached a minimum in KOH-0.1 and KOH-0.5 samples, beyond which the values increase again (Figure 5-3b). These results might be attributed to the combination of two different factors. i) A hierarchical porous structure and a balance between the micro- and macropores achieved in KOH-0.1 and KOH-0.5 samples where the micro- and macroporous volume contributions were almost identical, as shown in Figure 5-2. ii) The increase in the oxygen content in the latter two carbons that optimizes the wettability of these carbons (as will be detailed in Chapter 7). An increase in oxygenated functional groups of hydrophilic nature can enhance the admittance of electrolyte ions into the smallest pores of the carbon materials.

In the intermediate frequency range, the charge transfer resistance is indicated by the high-frequency semicircle in the Nyquist plots (inset of Figure 5-3a). It is clear that not all samples exhibit a distinct semicircle, indicating very low charge transfer resistance due to the lack of a Faradaic contribution associated with redox reactions at the electrode surface. The values slightly decreased with the KOH loading, which is attributed to the increased accessible electrode surface area and hierarchical porous structure that boost the electron/ion transfer in the carbons, despite the increase in their total oxygen content [7, 377].

At the lowest frequency of 0.01 Hz, the impedance magnitude ($Z_{mod}$) decreased from the non-activated sample to activated ones, as the morphology evolved from a fibrous structure to a more porous one (Figure 5-3c). All of the porous carbons demonstrated a non-ideal performance (phase angle $Z_{phi} < 90^\circ$), as shown in the Nyquist plot and Bode plot of the phase angle. The deviation from ideality at low frequencies decreases with the increase in the total pore volume with an increased macroporous contribution (increased KOH / cellulose mass ratio). This behaviour might be associated with the porous network structure comprised of micro-, meso- and macropores that play a major role in determining the response at low frequencies, in which different pore size ranges participate in the impedance response. The wide PSD, dominated by macropores with a high total pore volume, leads to a high diffusion rate of the ions into the pores. Consequently, the formation of macropores eases the access of electrolyte ions into the meso- and micropores, thus constituting a more ideal performance and the phase angles approaching $90^\circ$. Whereas the total ultra-micropore volume (<0.7 nm) was dominant in the low activated samples (KOH-0, KOH-0.005 and KOH-0.01), hence impeding the wetting of the finest porous matrices that might not occur even at the lowest frequencies used, leading to non-ideal impedance response [3].
results will be further investigated in the next section through the evaluation of the specific capacitances using EIS.

The frequency where the phase angle is closest to 45°, \( f_{45} \) (the frequency that represents the transition of predominantly resistive to predominantly capacitive behaviour) also decreases as the total pore volume, with different pore size ranges, is increased with the KOH loading (Figure 5-3d). A wider PSD and larger total pore volume at high activation ratios requires longer relaxation times to allow the accessibility of the electrolyte ions into different pore features, starting from macro-, passing into meso- and finally reaching micropores (Figure 5-4). Therefore, the capacitive character of the electrode will only dominate once the pores are ‘tuned in’, such that the electrolyte ions can invade the smallest pore sizes.

![Figure 5-4: A schematic representation of electrolyte ions transport into the porous electrode, starting with macropores, diffusing into the mesopores and finally reaching the micropores.](image)

5.3.3. Equivalent Circuit of Porous Carbons

Based on the different porous structure models characterised above and the different circuit elements that contribute to the impedance response previously discussed in the chapter, and using the TLM model, a simple equivalent circuit is devised and illustrated in Figure 5-5. The first part of the circuit consists of i) an inductive element \( (L) \) associated with electrical connections, ii) an equivalent series resistance \( (ESR) \) of the bulk electrolytic ohmic resistance and interparticle and intraparticle resistances arising from the porous nature of the electrodes, iii) charge transfer resistance \( (R_{CT}) \) and accompanying constant phase element.
(\textit{CPE}_{CT}) of surface functionalities at the electrode/electrolyte interface. The latter two elements combine to form the semi-circle in the Nyquist plot and model the parallel combination of Faradaic charge transfer resistance and double-layer capacitance at the surface within the porous matrix. A truncated version of the transmission line is employed using three different time constants (\textit{RCPE}) that govern the microporous (\textit{R}_{micro}CPE_{micro}), mesoporous (\textit{R}_{meso}CPE_{meso}) and macroporous (\textit{R}_{macro}CPE_{macro}) impedance contributions. These series \textit{RC} combinations represent the migration of ions through the hierarchy of pore sizes that contribute to the total impedance response with different time constants. The resistances described in the transmission line primarily represent the electrolyte resistance in the different pore hierarchies. The capacitance is evaluated inside the pores, effectively modelling the capacitive contribution of each PSD, with corresponding uniform pore size.

![Diagram](image)

Figure 5-5: Equivalent circuit of carbon-based electrode employed in a supercapacitor.

The elements of least resistive nature (i.e. macropores) of the porous matrix are accessed first and hence have the fastest response times at high frequency alternating current or potential step, followed by mesopores, and finally micropores. The parallel (\textit{RCPE}) network representing the pore contribution to impedance, dominates at low frequencies, whereas the \textit{ESR} and charge transfer elements govern the EIS behaviour at the high frequency limit. This model demonstrates that the current distribution is dispersed non-uniformly (temporally and spatially) in the electrode structure, owing to the inhomogeneities of the porous channels.

The circuit model suggested herein suffices to model and fit the impedance responses of the different samples over a wide frequency range, whereby the maximum chi-square goodness of fit for different impedance behaviours among all the samples is $5.6 \times 10^{-2}$, as presented in Figure 5-6. The fitting of the data for KOH-3 sample was also reported (Figure 10-6); however, KOH-3 had a disordered morphology whereby the porous structure was analysed.
by SEM, TEM and N\textsubscript{2} and CO\textsubscript{2} sorption isotherms (reported in Chapter 4). Therefore, this carbon sample did not follow the impedance and relaxation time trends of the rest of the carbon samples and the data was omitted from this study for the sake of clarity.

Figure 5-6: Nyquist plots of all KOH-activated samples with fitting curves according to the truncated TLM equivalent circuit suggested in this study.

5.3.4. Specific Capacitance in Different Frequency Ranges

The “best performance” of electrodes with the highest capacitance values is usually evaluated from CV measurements at a specific scan rate, or by galvanostatic charge-discharge cycles, at a specific current density. However, the capacitance values for porous electrodes are usually frequency-dependant, and the determination of capacitive behaviour must be demonstrated in a specific frequency range. The change in specific capacitance as a function of frequency for all samples is shown in Figure 5-7 and 10-7, and is calculated as follows [360, 378]:

\[
C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2} \quad (5 - 2)
\]

\[
C^*(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|^2} \quad (5 - 3)
\]

\[
C(\omega) = C'(\omega) - jC^*(\omega) \quad (5 - 4)
\]
where $Z', Z''$ and $Z$ are the real, imaginary and total impedance values, respectively in ohms, with $j = \sqrt{-1}$. $C', C''$ and $C$ represent the real part, imaginary part and total capacitance, respectively, at a specified frequency, all in Farads. The total capacitance, $C$ is also known as the equivalent series capacitance and the term does not have a physical correspondence to the system, where its sole purpose is to replicate the frequency response of the system under study [332]. The imaginary part of the capacitance corresponds to the energy dissipation by irreversible processes [379, 380]. The maximum in the imaginary capacitance-frequency plot corresponds to the dielectric relaxation time of the whole system, in which the frequency response transforms form a resistive to a capacitive one. The results obtained, shown in Figure 10-8 are consistent with the Bode phase plot values presented in Figure 5-3d. The real capacitance part represents the characteristic behaviour of the capacitance of the electrode structure and the electrode/electrolyte interface, and is referred to as the gravimetric or volumetric capacitance in the literature [381]. To obtain the corresponding real specific capacitances in this instance as a function of frequency, the $C'(\omega)$ values were divided by the mass of active material in each of the samples. The values calculated, at the lowest frequency, show that the capacitance increases with the activation ratio to an optimum in KOH-0.1 sample, beyond which the capacitance decreases for KOH-0.5 and KOH-1 sample and then again increases with further activation.

As the fibrous structure evolves into a microporous matrix among the fibres in the low-activated samples, the capacitive element, of the cumulative number of pores with higher total pore volume increases. However further increase of the porous surface area at a fixed volume causes an increase in the internal pore resistance, which might lead to the observed decrease in total capacitance. The carbon matrices composed of micro-, meso- and macropores in KOH-0.5 and KOH-1 samples do not exhibit the “best performance” at low frequency, in which the capacitance is lost due to ineffective electrolyte invasion of the finest pore fraction which itself accounts for most of the specific surface area of these materials. However, for the most activated sample KOH-2, the macropores dominate the porous network and the ease of accessibility of the electrolyte ions into the different pore sizes leads to an increase in the specific capacitance values again. Thus, it is established that there is a trade-off between the total pore volume, nature and width of the PSD, the specific surface area and the associated impedances within the porous structures.
Figure 5-7: Real part of the specific capacitance of all activated samples in the frequency range of 0.01-10 Hz demonstrated in (a) a Bode plot and (b) as a function of frequency and total pore volume determined by N\textsubscript{2} and CO\textsubscript{2} isotherms and MIP data.

The capacitive behaviour in the low-frequency region of 0.01-1 Hz adopts two different trends amongst the carbons employed as electrode materials: i) a rapid decrease in the low frequency for low-activated samples and ii) a plateau of almost constant capacitance for higher activated samples after which the capacitance declines at higher frequency. These observations suggest that the complete wetting of the finest pore structures has not been reached in the low activated samples and that the capacitance values of these carbons are yet still to increase upon employing frequencies \( f < 0.01 \) Hz. This proves that the micropores play a major role in the impedance behaviour only at very low frequencies and the performance decays drastically as the time needed for adequate ingress of electrolyte ions inside the fine pores is not sufficient. This is not the case for high-activated samples with high pore volumes, whereby meso- and macropores accommodate a quicker frequency response of the electrolyte solution invasion into bigger pores. The total pore volume increase was accompanied by an increase in the macroporous contribution to the total capacitance value, which enhances the performance and quick adaptation of these carbon electrodes at higher frequency responses. These observations confirm that the determination of the ‘best’ capacitive behaviour of porous carbon electrodes in supercapacitors is arbitrary unless evaluated at a specific frequency. Upon applying lower frequency ranges to the low activated samples, the capacitances will further increase to reach a plateau profile similar to that of the high activated samples, indicating maximum utilisation of the accessible pores by the electrolyte ions.

These results do not imply that the wettability of the finest pore structures (i.e. ultramicropores) is achieved, which consequently might impede the response behaviour and lead
to loss of the total capacitances. However, the maximum capacitance values in the low activated samples (KOH-0.01 and KOH-0.1) would be even higher than those achieved with the carbons of high KOH loading that have already reached their maximum values (plateau profile), indicating that the low activated materials might be more suitable for applications with very low-frequency responses.

It should be also noted that the capacitance values obtained are a function of the mass loading of the active material used. An increase in the electrode mass can either lead to higher or lower capacitance values (depending on the optimized amount of electrode mass used) and in some cases, longer relaxation times, as will be elaborated in the following section [246, 382]. However, an increase in the mass loading would also lead to an increase in the equivalent series resistance and electrolyte resistances within an increased number of pores, which will consequently deteriorate the electrochemical performance [83]. Thus, the mass loading also plays an important role in analysing the impedance response, and the intrinsic specific capacitance values obtained should be defined at the applied conditions to analyse the behaviour of supercapacitor electrode materials. In this work, the mass of deposited electrode material was kept constant amongst the different KOH activated samples, and the preparation method was consistent throughout all experiments to evaluate the materials’ characteristics, independent of different parameters in the preparation process. In addition, all electrode materials were deposited on porous nickel foam, acting as a current collector, in which the capacitance and resistance values, deduced from EIS method, would vary when using different current collectors and/or electrolyte media [34, 229, 370, 383].

5.3.5. Determination of Circuit Elements and Relaxation Times

The model components discussed in the previous section can reproduce, with high precision, the small voltage amplitude impedance response of the KOH-activated porous carbons over a wide frequency range. Pores in the same size range are assumed to be identical with a uniform cross-section and the curvature and surface roughness of pores are neglected. Furthermore, in each of the RCPE-parallel elements in the truncated transmission line, the capacitance and electrolyte resistance inside the pores is considered to be independent of the distance down the length of the pore from its orifice. It is worth mentioning that other equivalent circuits can be proposed with random sets and different values of RCPE elements, which can generate similar fittings, yet have no correspondence to the real physical values of the different element components [332].
The time constant of each RCPE series combination is calculated as the product of the non-ideal capacitance (constant phase element) and the sum of resistances from the element being evaluated inward to the pore surfaces and channels from the outer electrode/bulk solution interface, as follows:

\[
\tau_{macro} = CPE_{macro} (ESR + R_t + R_{macro}) \tag{5 - 5}
\]

\[
\tau_{meso} = CPE_{meso} (ESR + R_t + R_{macro} + R_{meso}) \tag{5 - 6}
\]

and \[
\tau_{micro} = CPE_{micro} (ESR + R_t + R_{macro} + R_{meso} + R_{micro}) \tag{5 - 7}
\]

where \[CPE_i = C^a\] with \(a\) accounting for non-ideality (5 – 8)

The capacitive elements of the smallest pore size i.e. the micropores, have the highest time constants and therefore the slowest response rate at low frequencies (<0.1 Hz), followed by mesopores and finally macropores [3]. Consequently, the change in the imposed electrode potential does not charge or discharge the different areas of the matrix at a uniform rate; in reality, the time constants can vary by orders of magnitude [3, 332]. The asynchronous charging at different rates (or discharging behaviour) of a porous electrode hence constitutes a far more complex impedance behaviour than for planar electrodes. This leads to the conclusion that the concept of a “best capacitive” behaviour cannot be inferred unless specified at a certain frequency, whereupon different pore sizes “participate” at different time constants and contribute to the total capacitance only if adequate time for the ingress of the electrolyte into porous matrix is provided. The relationship between the morphology of the KOH-activated porous carbons and the relaxation times at the lowest frequency (0.1 Hz) to show the total contribution of the entire spectrum of pore sizes is presented in Figure 5-8.

Figure 5-8: Variation of the relaxation times in all activated carbons as a function (a) the micropore volume percentage and (b) with the KOH loading with different total pore volumes in each PSD.
It is clear that the micro- and mesoporous volume fractions decrease, while that of macropores increases with KOH/cellulose ratio, as shown in previous sections and Chapter 4. Furthermore, the total pore volume increases with the increasing macropore volume contribution. The results obtained demonstrate a co-dependence between the nature of the PSD, the total pore volume and the total relaxation times evaluated for the different porous carbons.

Upon increasing the KOH activation loading from the non-activated sample with a dominant ultra-microporous structure (KOH-0) to the lowest activated one (KOH-0.005), an increase in the total relaxation time, as well as the relaxation times of each of the porous structures, occur. This is due to the introduction of chemical activation that leaves behind a limited porous structure upon carbonisation in inert atmospheres. However, a further increase in the activation ratio, and thus an increase in the total pore volume with macroporous morphologies, leads to a decrease in the total and PSD-specific relaxation times, whereby meso- and macro-pores have a lower resistive component compared to micropores in the transmission line. These values are also corroborated by the decreasing impedance magnitude upon increasing the KOH loading. Beyond an optimum activation loading in sample KOH-1, in which the micro- and macro-pores both contribute to the frequency response, the impedance magnitude increases again in KOH-2 sample (Figure 5-3a). This is attributed to the further increase in total pore volume, wherein although the micropore fraction has decreased, the total number of the pores in different size ranges has drastically increased. This leads to the increase in the total relaxation charging/discharging times of KOH-2 electrode. The formation of more meso- and macroporous structure in a high total pore volume serves to increase the total relaxation times that are needed for adequate access of the electrolyte ions into the increased number of micropores. This is demonstrated in Figure 5-8b which shows the different relaxation times in each pore size range of the carbonaceous samples.

The difference in order of magnitudes between the different PSD relaxation times at low or no activation for the same sample diminishes as the activation is further increased, whereby all PSDs contribute significantly to the total time periods needed to charge or discharge the supercapacitor. The frequency response of different pores thus becomes more homogenous as a balance between the micro- and macroporous contributions to the total pore volume is achieved. The employment of lower frequencies for the low activated samples will further increase the total relaxation times with the increase of the microporous relaxation times with the micropores requiring the longest periods of time to charge/discharge. Consequently, the difference in order of magnitudes of the PSD-specific relaxation times will further escalate due to the employment of the meso- and macropores at higher frequencies. This is not the
case for high activated samples, as the capacitances have reached their maximum values with the plateau character, as previously shown, implying the full utilisation of the porous matrices upon applying frequencies as low as 0.01 Hz.

These realizations are also validated through observation of the values of the imaginary part of the specific capacitances at low frequency, analysed in the previous section. The imaginary capacitance, $C''(\omega)$ is ascribed to the energy losses in the supercapacitor, and its value increases with the KOH loading to a maximum in KOH-0.01 and KOH-0.1 samples, beyond which it decreases again (Figure 10-8). The energy loss, dissipated as heat via the electric current distribution in the electrode, has thus increased, as evidenced by the aforementioned increase in the imaginary capacitance values in the low activated samples, which are dominated by a microporous morphology. This increase is due to a redistribution of the charges within the pores in non-uniformly charged porous electrodes. The low-activated samples are dominated primarily by micropores and thus require lower frequencies and longer relaxation times to realize complete charging of the electrode. By way of explanation, a porous electrode exhibiting transmission line model behaviour (or truncated behaviour) that is subjected to a charging regime of period shorter than the $RCPE$ time constant, will be incompletely charged, wherein the smaller micro- and mesopores will be less charged than the macropores. Upon terminating the charging period, the redistribution of the charges in the porous matrix acts to achieve a uniform voltage across the matrix, causing a potential decay and consequently an apparent energy loss with higher values of $C''(\omega)$ [3]. The adsorbed electrolyte ions migrate across different $RCPE$ time constants to achieve full electrical relaxation, whereby no Faradaic reactions occur, nor is any charge lost [332]. A fraction of the ions redistribute from the easily accessible macropores into the meso- and micropores characterised by slower response times, higher internal resistances and lower ionic concentration. The extension of the impedance measurement (or charging period) to lower frequencies will demonstrate higher relaxation times for the low activated samples, more homogenous charge distribution and suppressed ion migration processes. This behaviour will consequently exhibit lower $C''(\omega)$ and apparent energy dissipation values associated with the electrical relaxation process and charge redistribution, as described herein [43, 384]. This is not the case for higher activated samples, which are dominated by macropores, as these have demonstrated full utilisation of the pores (capacitance profiles and PSD relaxation times) and thus have attained a complete charging process at the lowest frequencies applied in this work. These results confirm that an energy loss associated with a voltage drop in these carbon-based electrodes is due to the wider distribution of $RCPE$ time constants over a wide pore size distribution, as opposed to unfavourable electrochemical reactions. The apparent energy loss and self-discharge
mechanism can thus be avoided by charging carbon electrodes dominated by a microporous nature for longer periods of time (or \( f < 0.01 \) Hz). These assumptions also confirm that a substantial proportion of the total capacitance is contributed by the microporous structures.

These observations thus dictate the accommodation of different carbon materials for designated power applications. Porous structures that can quickly accommodate the charging/discharging behaviour, similar to the high activated KOH sample models, can be employed in applications that require high-frequency responses without major losses in the capacitive mechanism. Whereas carbon materials that are capable of delivering high capacitances but require slow charging/discharging rates, such as the low activated carbons used herein, can be employed in applications of low-frequency response demands.

The suggested model and extracted values of impedance and relaxation times confirm that when addressing a porous matrix with a small alternating voltage signal, the impedance behaviour is far from ideal, and is not uniformly accessible by the electrolyte solution.

5.3.6. Comparison with Uniform PSD Electrode Equivalent Circuit

The equivalent circuit suggested in this study takes into account three discrete PSDs (micro-, meso- and macro-pores), to which an average pore size range can be assigned to each. The different elements, as discussed earlier, represent different resistive and capacitive components in the circuit. However, if it was assumed that the porous matrices were homogenous in the carbonised samples and composed of one uniform pore size, a more simplified circuit can be used to describe the impedance behaviour. This circuit is composed of the inductive \( L \), equivalent series resistance \( ESR \), constant phase element \( CPE_1 \) and charge transfer resistance \( R_{CT} \) elements, similar to the previously suggested circuit. However, only one capacitive constant phase element \( (CPE_2) \) describes the non-ideal capacitance inside the pores (Figure 5-9a). The relaxation time for \( CPE_2 \) would then be calculated as:

\[
\tau_{CPE_2} = CPE_2 (ESR + R_t) \quad (5 - 9)
\]

The relaxation time for the uniform PSD model was compared to the total relaxation time of the curtailed version of the TLM proposed in this work (Figure 5-9b). The difference between the relaxation times evaluated by the two circuits is significant for the low- and non-activated samples, where the total pore volume is a minimum. At low pore volumes, the matrices were mainly composed of ultra-micropores and/or micropores and the relaxation times, evaluated by the suggested equivalent circuit, varied between different PSD by an order of magnitude. In this case, one capacitive element cannot govern the impedance
behaviour of such PSD. Further activation of the carbon materials leads to a decrease in the percentage difference of the time constants for the carbon sample, wherein the porous structure is composed of more macropores and attains a greater porous structure. As the microporous structure develops to a more meso- and macroporous matrix, the variance between both models was still high, yet decreased by an order of magnitude on account of the similarity in frequency response (and relaxation times) of the pores at high activation ratios.

Figure 5-9: (a) Equivalent circuit of porous materials with one PSD and (b) the difference between the one PSD model and suggested model as a function of the total pore volume determined by BET.
5.3.7. Effect of Cycling on EIS and Specific Capacitance

GCD cycling experiments were applied for 5000 cycles at 20 A g\(^{-1}\) current density on the different porous carbons and the effect of PSD on the capacitance values at low frequency was studied before and after cycling. The specific capacitance values obtained from EIS measurements at 0.01 Hz, before and after cycling, are shown in Figure 5-10. The lowest frequency was chosen to evaluate the capacitance values to include the contribution of the different capacitive elements to the total electrochemical behaviour. The capacitance retention rates are usually reported to be less than 100 % upon cycling in which indicated values do not correspond to the frequency-dependant region [385-387]. However, depending on the porous structure tested, different results can be obtained. For low-activated materials, the specific capacitance increased upon cycling, also in agreement with the results obtained in the cycling experiments performed in Chapter 4. This is due to the high volume fractions of micropores that dominate the porous network. Upon cycling, the electrolyte can invade parts of the porous matrices that were not accessible by electrolyte ions prior to cycling. The finest pore fractions in the porous matrix can then be slowly wetted by the electrolyte, whereby the smallest pores account for the highest capacitance values, and hence the increase in overall specific capacitance after 5000 cycles [388-390]. This is not the case for the KOH-0.5, KOH-1 and KOH-2 samples where the meso- and macropores were accessed by electrolyte ions when recording impedance measurements prior to cycling, and hence a decay in their performance after 5000 cycles is realized. The full utilisation of the pores as capacitive components hence comes into effect at different rates depending on the PSD of the electrode material. These results also agree with the trends of the specific capacitances demonstrated in Figure 5-7, where the rapid decrease in the specific capacitance for low-activated samples was dissimilar to the plateau capacitive behaviour for high activated carbons. This was also demonstrated in the phase angle values, whereby the rapid capacitive-to-resistive transition for the low-activated samples before pore exhaustion is opposed to extended capacitive performance for higher activated samples in which the pores are more easily accessed through the hierarchical structure. This behaviour is accompanied by an increase in the impedance in the low frequency region for high-activated samples and vice-versa for the low-activated ones, noting that both samples had smaller deviation from ideality upon cycling (Figure 10-9).
Figure 5-10: Specific capacitances for all activated carbon materials before vs. after cycling as a function of the microporous volume fraction determined by BET.

The specific capacitance values reported in this Chapter reflect the electrode materials properties on the microscopic level to further understand and enhance the behavior of porous carbon materials in supercapacitors. However, this is the first step in the optimization process from a form-function perspective of the materials, and complementing these realizations with device optimization should be considered for industrial and scale-up applications. In Chapter 8, the volumetric capacitance values based on the entire device configuration were evaluated to highlight the major importance of supercapacitor design and packaging. Different device properties can hugely influence the energy and power delivery of supercapacitors when employing the same carbon electrodes [391]. Therefore, the understanding and optimization of the synergy between microscopic materials properties and macroscopic device architecture should be implemented for optimized performances of real supercapacitor devices.

5.4. Conclusions

In this chapter, electrochemical impedance responses of different porous carbons for supercapacitor application were described and analysed using a designed equivalent circuit based on the transmission line model. The simplified model of an equivalent circuit is suggested for porous network structures, compared to the equivalent circuit governing the behaviour of planar electrodes. Cellulose precursors activated with different KOH loadings were used as the model systems in this work and the various porous structures attained with
different KOH/cellulose ratios were analysed with different characterisation techniques, and their corresponding effect on the impedance spectra is reported. This work can be extended to different porous materials acquiring different pore size distributions and morphologies that are used in supercapacitors, as the range of materials used herein covers different porous structures from narrow to wide PSD profiles.

The suggested circuit explains the different capacitive and resistive elements over a wide frequency response, namely the inductive element, bulk electrolyte resistance, charge transfer resistance and capacitance, and porous matrix resistive and capacitive contributions. The bulk electrolyte resistance outside the porous matrix, the charge transfer elements governing surface functionalities on the carbon electrodes, can be separated from the impedance behaviour of a multifarious system of a porous electrode of three main PSDs, using the EIS technique. The effect of a wide pore size distribution on the impedance behaviour is studied and introduced in the equivalent circuit for the first time in this study. A ‘best’ performing supercapacitor device cannot be quantified without specifying the nature of the capacitance reported and its frequency dependency-or independency. The amount of micropores plays a vital role in the specific surface area and total capacitance, but unless effectively entered by electrolyte ions, a loss in capacitance occurs after long-term cycles. Meso- and macropores accommodate the change in an alternating voltage signal more quickly, and hence such porous structures can be implemented in applications that require a high response rate. The present work demonstrates that an assessment of the relaxation times is essential to demonstrate the trade-off and possible optimization of porosity, pore size distribution, internal pore resistance and capacitance. The evaluation of these parameters of different porous structures at different rates of frequency response for a supercapacitor device can then be studied to assess power capabilities in charging and discharging and thereby its application for real-world utilisations. This would allow “matching” the right materials for the corresponding device of predetermined conditions. In this chapter, all electrochemical impedance responses were recorded vs. the open circuit potential in a three-electrode system. The frequency response of the same porous carbons at different potentials vs. the reference potential, and consequently the determination of a supercapacitor electrochemical behaviour within and beyond the potential limits will be the focus of the following chapter.
Chapter 6

Investigating the Operating Potential Window of Aqueous Supercapacitors with Varying Electrode Microstructure; An Electrochemical Impedance Spectroscopy Study

Scope of this chapter: The equivalent circuit suggested in the previous chapter was used to extend the analysis of the electrochemical impedance spectra of various KOH-activated porous carbons at different potentials. Relaxation times and specific capacitances were evaluated using the truncated version of the transmission line model, and the capacitance dependence on the applied potential and frequency is investigated using the EIS tool.
6.1. Introduction

The design of a successful electrochemical capacitor, EDLC and/or pseudo-capacitor, relies in the essence of engineering electrode materials that constitute a large surface area that is electrochemically accessible by the electrolyte ions in a small mass/volume of the material [3]. Carbon materials, in their various forms, offer an attractive range of properties in the supercapacitor industry as explained throughout the different chapters of this thesis. The optimization of the carbon morphology, porosity and electrochemical performance has always been a hot research area [34, 392-394]. Different electrolyte solvents and salts have been investigated as potential candidates for supercapacitor devices, including aqueous and non-aqueous media [180]. A wider operating potential window can be achieved with non-aqueous solvents due to the higher decomposition potential of the solvent, thus enhancing energy storage. However, with these advantages, some drawbacks arise, including extensive purification processes and practical challenges, low ionic conductivities and costliness [54].

Powdered or fibrous carbon materials provide a substantial increase in specific capacitance and conductivity values. This is as a result of high specific surface areas, enhanced electrolyte accessibility to porous networks, and good conductivity and wettability within the porous matrices [7, 93]. “Real” electrochemical surface areas and optimum pore accessibility can hence be achieved. However, the trade-off between pore size and porosity, and therefore the total capacitance of the whole system and the resistance of individual pores, is still to be considered [332]. For porous carbon electrodes in supercapacitor devices, the requirements include i) adequate pore volume for electrolyte compliance, ii) facile electrolyte movement into the porous matrices and iii) development of the highest realizable specific and volumetric capacitances, via the optimization of electrochemical surface areas. These parameters highlight the importance of assessing the limitations of the electrical accessibility of the electrolyte into the porous matrices, whereby the high-area materials might not be fully realized by the electrolyte solution. This is due to the cumulative resistances of the bulk solution and porous particles and to a bigger extent, the accumulating resistances of the electrolyte ions in the pores of the electrode material which are all factors that impede the electrolyte transport pathways and therefore wetting the pores. Consequently, the resistances associated with the electrolyte ions in the pores have to be taken into account, as well as the contact resistances in the pores that form the matrix. The improvement of the specific capacitances and power and energy densities can consequently be addressed at a specified frequency, that is correlated with the impedance components [5].

In the previous chapter (Chapter 5), we have demonstrated the impedance response of porous electrodes at open circuit potential using KOH-activated carbons as model systems.
We illustrated that EIS is a powerful tool that enables the understanding and separation of the distributed resistive and non-ideal capacitive elements in the bulk solution, at the electrode/electrolyte interface and inside the multi-porous matrix [333, 369, 395]. In addition, the interdependence between the morphology of different porous structures and the frequency response was highlighted. The extension of the impedance interpretation of the same porous carbons at different potentials vs. the reference electrode will be discussed in this chapter.

An EDLC is expected to have an ideally and purely capacitive behaviour, whereby ideally polarizable electrodes are in a state of electrostatic equilibrium. This behaviour would exhibit itself in the Nyquist plot in which the slope of the curve would approach infinity. Nonetheless, in practice, the distribution of double layer capacitance in a porous matrix, Faradaic processes and finite ionic and electrical resistances in the porous framework create energy dissipation in the cycling process of supercapacitors and thus lead to non-ideal performances [334, 335, 376]. The “porous electrode” effect, as introduced by de Levie in addition to the equivalent series resistance comprising the bulk solution and porous particles resistances in the entire system, contribute as a source of non-ideality, leading to complex frequency-dependent behaviour of the overall capacitance, as demonstrated in Chapter 5 [3, 335]. Based on the transmission line model, a curtailed version was used to analyse the behaviour of different porous electrode materials and so as to understand the underlying mechanisms in the capacitive system. This model correlates Faradaic leakage resistances with surface impurities and the non-ideal capacitance defined by the constant phase element (CPE), over different pore size ranges can be evaluated as follows[396]:

\[ CPE = C^\alpha \]  

where \( C \) is the ideal capacitance in Farads and \( \alpha \) is the non-ideality factor between 0 and 1; with 1 corresponding to ideal capacitor behaviour.

The series combinations of resistances (\( R \)) and non-ideal capacitances (CPE) governing the curtailed transmission line model represent the electrolyte ions migration through the different PSDs, contributing to the impedance response at lower frequencies. The corresponding PSD relaxation time (\( \tau_{PSD} \)) of each RCPE combination can be defined as:

\[ \tau_{PSD} = CPE_{PSD} (ESR + R_{CT} + R_{PSD} + R_{>PSD}) \]  

where \( CPE_{PSD} \) and \( R_{PSD} \) are PSD-specific, representing the capacitance inside the pores of each discrete PSD range, and electrolyte resistances inside the corresponding pores, respectively. From Eqn. (6-2), it is demonstrated that another resistive term exists (\( R_{>PSD} \)).
reflecting the resistances accumulated in PSDs larger than those specifically assigned. The electrolyte resistances in the macropores are consolidated into the total value of the resistance in the mesopores; \emph{i.e.} as the pores progressively get smaller, the total resistance value is a summation of those pores larger than it plus its own. Therefore the electrolyte resistance in the macropores is defined by its own resistance, whereas a mesopore total resistance is an accumulative value consisting of both macro- and mesoporous ranges. The total electrolyte resistance in the micropores is the summation of macro-, meso- and micropore resistances. This is due to the electrolyte pathway from the bulk solution penetrating the macropores, into the mesopores and finally reaching the micropores. A more detailed analysis and evaluation of the PSD relaxation times can be found in Chapter 5 [372].

Impedance spectroscopy of carbon-based supercapacitors has been extensively studied and used to evaluate the capacitance of the entire system [360, 361]. However, the impedance measurements are usually (except for some studies) recorded at the rest potential (open circuit potential) of the system to evaluate the capacitance and resistive elements of the device. Rafik \emph{et al.} found that the capacitance increases non-linearly with the applied potential within the specified potential limits [234]. In addition, they found that changing the temperature would not affect the capacitive performance at low frequency, but would increase the capacitance with the temperature in the middle-frequency range due to reduced ion mobility in the viscous electrolyte at low temperature. In another study, the dependence of the differential capacitance on temperature and its correspondence with the point of zero charge are discussed [397]. The capacitance was found to increase with the temperature and the trend was attributed to ‘weakening’ of the ions’ association in the double layer. However, and to our best knowledge, using the EIS technique and mathematically analysing the frequency response of different porous electrode materials at different potentials has not been addressed yet. For the full investigation of different capacitive and resistive mechanisms the supercapacitor undergoes within and beyond the potential limits of the device, impedance spectra can be analysed at different potentials \emph{vs.} the reference electrode. This allows a better understanding of the electrochemical properties of different porous materials when subject to different potentials, as in real-world applications. In order to ascertain the effect of electrode porous structure on performance, it is desirable to have a means of selectively controlling the electrode structure, and ideally, this analysis should be performed in the three-electrode setup to isolate the response of an individual electrode material.

In this work, the frequency- and potential-dependence of non-ideal capacitive behaviour at the interface and in the porous carbons is studied through the application of a small
alternating voltage signal. Factors affecting electrolyte ion ingress, specific capacitance, electrode resistance and electrolyte degradation (electrolysis) are examined. The contribution of each resistive and capacitive component can be separated and studied using the EIS technique and by applying the equivalent model for porous materials (suggested in the previous chapter) over a wide range of frequencies. The reasons for inefficient invasion of the electrolyte ions into the finest pore fraction of carbon materials are also investigated, alongside trends in relaxation times of different pore structures in the same aqueous electrolyte. This study highlights the application of aqueous supercapacitor devices within and beyond thermodynamic stability limits employing a suitable porous structure, and thus achieving better performances without compromising the chemical stability of the electrolyte and carbon electrodes. In addition, it gives insight about the ageing and failure mode of EDLCs due to overpotentials that can affect different porous electrodes in distinct manners. To investigate the effect of porous structure on electrode capacitance, a means of systematically fabricating electrodes with different microstructures is required. KOH-activated carbons were used in this study as the model system to further complement the results obtained in Chapters 4 and 5, which can consequently be extended to different porous systems.

6.2. Experimental

This work is an extension of the studies conducted in Chapters 4 and 5 whereby all KOH-\(n\) activated samples were previously characterised, structurally and electrochemically. The electrode materials in this work were prepared by mixing 85\% of the activated carbon, 5\% booster carbon (C65) and 10\% PVDF. The paste was coated on nickel foam current collectors, having a total physical surface area of 1 cm\(^2\) and a mass loading of 1-2 mg. Electrochemical impedance measurements were conducted using a Gamry potentiostat and performed in 6 M KOH solution with a platinum mesh counter electrode and a silver/silver chloride (Ag/AgCl) reference electrode. All measurements were performed in the frequency range of 10 mHz to 1 MHz with a voltage amplitude of 5 mV, for voltages between -1.3 V and 0.4 V vs. the reference potential after 20 voltammetric cycles at 50 mV s\(^{-1}\) scan rate. The evaluation of the impedance magnitude, phase angles at different frequencies and specific capacitances were deduced from the impedance response of 5 measurements of the same sample. The relaxation times of the series resistance-constant phase elements in different pore size distributions (PSDs) were determined from the experimental data fitting (Echem Analyst software) at low frequency, using the suggested equivalent circuit in Chapter 5. A correlation between different morphological structures and the impedance behaviour of
porous carbon electrodes was established at different potentials, specifically with regards to the microporous volume contribution.

6.3. Results

6.3.1. Electrochemical Impedance Response at Different Potentials

The suitability of carbon materials as supercapacitor electrodes is determined by its capacitance, stability and electrochemical properties across the available potential window. In addition to the bulk electrolyte resistance, the electrode electrical resistance and surface area, and the mobility of ions within the electrode porous matrix, the available potential window determines the nominal power density and maximum specific capacitance of a supercapacitor. The maximum operational potential window of a supercapacitor is usually determined by i) the electrolyte (1.23 V vs. the SHE in case of aqueous electrolytes due to water electrolysis), ii) the active electrode material and iii) the current collector material and geometry [5]. Despite the fact that the thermodynamic potential window of water is 1.23 V vs. SHE, different studies have been focused on extending the stability potential window of aqueous electrolytes in order to increase the energy storage of EDLCs [398]. These attempts included using different electrolyte media, different electrode materials and fabricating asymmetric supercapacitor devices [399-403]. In the case of 6 M KOH electrolyte, the potential stability window was established to be within the limits of -0.9 – 0.1 V vs. SHE, and therefore -1 – 0 V vs. Ag/AgCl electrode [39, 77, 404]. The extreme potential conditions will be further analysed using CV and in-situ Raman spectroscopy and are described in Chapter 7. The optimum potential window determined by the aforementioned parameters can determine the nominal power density and maximum specific capacitance values, when studied in conjunction with the series resistive components associated with the equivalent series resistance outside the surface of the porous matrix and the solution resistance inside the pores.

It should be noted that the lowest (KOH-0) and highest (KOH-3) samples were analysed with EIS at different potentials; however, the data of both carbon samples were not included in this study to simplify the trends obtained with the different calculated parameters and avoid anomaly.
6.3.1.1. The Double-layer Region

The double-layer capacitance at the electrode/electrolyte interface is dictated by the charge separation accumulated at the electrode/electrolyte interface. An ideally polarizable electrode constitutes a double-layer at electrostatic equilibrium, in which no charge transfer occurs and charges only flow from the electrolyte solution to the electrode/electrolyte interface (described in more details in section 2.6) [50]. The latter would then be represented by a simple capacitance element where no Faradaic processes or leakage currents are considered. This ideal behaviour is detected by a 90° phase angle between the current and voltage, and a vertical line parallel to the imaginary part of the impedance (y-axis) in a Nyquist plot. However, porous structures constituting different PSDs and oxygen surface species do not follow an ideal behaviour and the double-layer capacitance is distributed throughout the porous network. Therefore, the EIS performance is far from ideal and is represented by a more complex equivalent circuit exhibiting the different resistive and capacitive components.

In the previous chapter, it was demonstrated that the different morphologies of the KOH-activated samples determined the recorded frequency response at open circuit potential. The carbon electrodes displayed different equivalent series resistances, the relaxations times in each of the PSDs, and the double layer capacitances at low frequencies. The impedance response of different activated samples in 6 M KOH solution, was measured in a three-electrode system at different potentials in this work and the Nyquist plots in the potential window -1–0 V vs. Ag/AgCl are presented in Figures 6-1 and 10-10. The Nyquist plots, which represent the imaginary component of the impedance (Z") vs. its real part (Z'), show that the low and intermediate-activated samples (KOH−0.005, KOH−0.01, KOH−0.1 and KOH−0.5) exhibit most-ideal capacitive behaviour at potentials between -0.6 – -0.8 V. The non-ideality is detected by a non-parallel line to the imaginary (Z") axis and a phase angle < 90°. The impedance magnitude |Z| at lowest frequency (10 mHz), significantly decreases with increasing the potential difference across the electrodes to reach a minimum at -1 V (Figure 6-2). The |Z| value at lowest frequency is of interest as this frequency represents the maximum utilisation of the porous structures that can be wetted by the electrolyte (theoretically) and therefore includes their contribution to the total capacitive mechanism. In the case of high-activated samples (KOH−1 and KOH−2), the deviation from ideal capacitive behaviour is least at an applied potential of -0.2 V, whereupon the most ideal response diminishes again when applying higher absolute potential differences. The impedance magnitude has the largest values at 0 V for these samples, decreasing with increasing the applied potential. The same trend of decreasing |Z| with increasing potential is observed for all samples due to the increased driving force for ion penetration into the
narrower pores and thus decreasing electrolyte resistances in these pores in the lowest frequency range and increasing the porous contribution to the total capacitance [405].

The increase in the KOH loading enhances the etching of the carbon surface and creates micropores in the fibrous cellulose structure, whereby the micropores and mesopores dominate the fibrous/porous morphology with limited macropore contribution (detailed analysis in Chapter 4) [349]. Further increase in the KOH loading increases the 'sponginess' effect and introduces macropores to form a hierarchical porous network of micro-, meso- and macropores in the KOH-0.5 and KOH-1 samples. The highest activation ratio of 2:1 KOH/cellulose herein further increases the growth of macropores, which dominate the matrices with little contribution from micropore regions (Figures 4-3, 4-4 and 4-7).

Figure 6-1: EIS Nyquist plots in the frequency range of 10 mHz-1 MHz at potentials between -1–0 V of the samples: (a) KOH-0.005, (b) KOH-0.1, (c) KOH-0.5 and (d) KOH-2.

At low activation, the microporous structures demonstrate the most ideal capacitive performance as the applied potential difference was increased. Higher potentials - away from
the potential of zero charge (PZC) - help the electrolyte ions to migrate into the narrow structures with a higher driving force, which improves capacitance. The impedance hence decreases as the electrolyte ions effectively invade the fine pore structure, allowing utilisation of a larger portion of the pore matrix for charge storage. It is worth noting that the finest pores may not be entirely wetted by the electrolyte ions, being smaller than the size of solvated electrolyte ions, even at the highest potential differences applied.

More effective ionic migration is achieved at lower potentials for high-activated samples due to the predominance of macropores, wherein the larger pores can be easily wetted by the electrolyte ions at different potentials, serving as an “electrolyte reservoir” that reduces the diffusion distance of the ions into the smaller pores. [5, 406-409]. The impedance magnitude still decreases upon applying higher potential differences due to the faster ion diffusion rate into the pores. This reveals the importance of macroporous structures at low potentials or equivalently, high scan rates and/or cycling current densities.

![Figure 6-2: Impedance magnitude of all activated carbons at 10 mHz frequency as a function of potential.](image)

The equivalent series resistance (ESR), evaluated at the high-frequency intercept with the real axis (Z’), represents the summation of bulk electrolyte resistance and inter- / intra-particle resistances of the porous electrode matrix (Figures 10-11 and 10-12). Given that the bulk electrolyte resistance is constant amongst all samples tested, changes in ESR values can be attributed to the electrode structure. The intermediate activated samples (KOH−0.1 and
KOH–0.5) show the lowest ESRs, due to a decrease in the interparticle and intraparticle porous matrix resistance. This is attributed to the increase in the total pore volume with hierarchical porous structures of balanced micropore-macropore proportions in these samples of high specific surface area, and the increase in the oxygen content that enhances the wettability of the carbon matrices and thus the electrolyte admittance into the porous networks, as previously detected by XPS. These results dictate the maximum power densities for different microstructures that are limited by the ESR value at rapid responses [377].

A similar variation in ESR is reported at OCP for the same KOH activated carbons in Chapter 5 [372], and is consistent throughout different applied potentials, whereby the ESR values stay almost constant for the sample at different potentials, as shown in Fig 6-3. It was previously reported that impedance (and therefore resistance) at high frequency is independent of the potential in the high frequency range in porous electrode materials [410, 411].

Figure 6-3: Variation of the ESR values of activated carbon samples at different potential differences.

The diameter of the depressed semi-circles in the intermediate frequency range reflects the charge transfer resistance (R<sub>CT</sub>), of Faradaic redox reactions associated with the likes of surface oxygen-containing functional groups [133]. The R<sub>CT</sub> values increase with the KOH loading at low potential differences (0 V and -0.2 V), which might be due to the increased oxygen content with the KOH loading. However, as the potential difference is further increased, the charge transfer resistance decreases to a minimum in KOH-0.1 and KOH-0.5 samples, which can be attributed to the increased electrolyte access into the hierarchical electrode porous structures at higher absolute potential differences, boosting the ions transfer into the electrodes, despite the increased amount of oxygen functional groups (Figures 10-11.
and 10-12) [7, 377]. The hierarchical porous frameworks of high specific surface areas might have enhanced the charge transfer at the electrode/electrolyte interface and thus the surface adsorption of the electrolyte ions and their diffusion into the pores from the surface at higher potential differences, causing a decrease in $R_{CT}$ values with intermediate activation conditions [377].

While the Nyquist plot representation lends itself more to comparison with equivalent circuit features, the Bode plot allows for a better appreciation of the frequency-dependent nature of the impedance response (Figures 6-4 and 10-13). The phase angle ($Z_{\phi_b}$) response for low-activated samples significantly shifts to lower frequencies as the absolute potential difference is increased from 0 to -1 V. The frequency shift decreases as the KOH loading is increased up to the maximum KOH loading, whereby the phase angle response is almost constant at different potentials for the same sample. The frequency at which the phase angle reaches a value of 45° ($f_{45}$) represents the transition between primarily resistive behaviour (frequencies higher than $f_{45}$) and primarily capacitive behaviour (frequencies lower than $f_{45}$), also known as the ‘knee’ frequency [360]. The variation of the transition frequency with potential is shown in Figure 6-4d. The $f_{45}$ values decrease dramatically for the KOH-0.005 sample as the potential difference is increased. The change in resistive-to-capacitive performance decreases with increasing the macroporous morphology dominance and decreasing the micropore volume percentage, i.e. upon increasing the KOH / cellulose ratio. The trend in the frequency response is attributed to increased penetration of the electrolyte ions into the macroporous structures reaching the meso- and micropores of the high-activated samples at low potentials in contrast to the need for higher potentials to drive the electrolyte ions into microporous matrices, which are more prevalent in the low-activated samples. Therefore, when applying a higher potential, the rapid decrease in phase angle response for low-activated samples and the relatively constant frequency responses for higher activated samples is expected. These results highlight the initiation of the capacitive mechanism in different porous structures, studied with the EIS tool, and thus the importance of hierarchical porous structures of different PSDs for supercapacitor electrodes. This electrochemical behaviour dictates the determination of relaxation times in the porous morphologies and changes in the capacitive behaviour in the capacitive regime, which will be discussed further in the following sections of this chapter.
Figure 6-4: EIS Bode plots over the frequency range of 10 mHz-10 KHz at potentials between -1 V and 0 V of (a) KOH-0.005, (b) KOH-0.1 and (c) KOH-2. (d) The change in frequency that corresponds to a phase angle of 45° for all samples at different potentials.

6.3.1.2. Limits of Stability Potential Window

While the theoretical potential window for a given solvent/electrolyte system is dictated by thermodynamics, the practical potential window is also determined by the electrode material, its structure and surface functionalities. Extending the potential window and/or being able to operate closer to the potential limit have important implications for the energy storage properties of a supercapacitor. EIS technique was employed to study the effect of the micro-architecture and surface functionality of the different porous carbons on the kinetics of hydrogen and oxygen evolution reactions to define and understand the potential limits. The results give an insight into the promising applications of different types of porous materials in aqueous electrolytes at specific conditions and therefore understanding the form-function synergy for capacitance optimization.
Electrocatalysis for hydrogen and oxygen evolution ideally commences between -1.23 V and 0 V respectively, vs. SHE [3]. In practice, however, the evolution of gases is kinetically limited and therefore Faradaic charge transfer currents across the electrode/electrolyte interface do not commence until potentials that are lower or higher than the thermodynamic limits are applied. In the case of 6 M KOH electrolyte, the stable potential window is established within -1 – 0 V vs. Ag/AgCl, in which the impedance behaviour of the different carbon electrodes was studied in the previous section.

To explore the overpotential limitations for different electrode activations (microstructures), EIS measurements were conducted beyond the -1–0 V range, into the expected hydrogen and oxygen evolution regimes. The recorded data is presented in Figures 6-5, 6-6, 10-14 and 10-15. The Nyquist plots of the different activated carbons reveal non-ideal capacitive behaviour with a non-parallel line to the imaginary part of the impedance upon increasing the potential difference to -1.1 V. The Faradaic hydrogen evolution reaction leads to a significant increase in $R_{CT}$ at a potential of -1.3 V (Figure 10-16). Upon applying the negative potentials beyond the stability window and up to -1.1 V and -1.2 V, all activated samples showed an insignificant change in the charge transfer resistance value at high frequencies. Specifically, there was a decrease in $R_{CT}$ for the intermediate-activated samples at -1.1 V, whereby the charge transfer increased as the potential approached the redox potential of faster charge transfer processes (Figure 10-17) [410]. This can be attributed to the hierarchical porous structure with the KOH loading in the intermediate range, which plays a major role in enhancing the Faradaic charge transfer processes across the double-layer, as previously mentioned. These results highlight that the ion diffusion can be enhanced for the intermediate-activated samples at high frequencies, yielding better capacitance values for applications requiring rapid response. These results are further corroborated with in-situ Raman spectra experiments of the carbons at extreme potentials, discussed in detail in Chapter 7.
Figure 6-5: EIS Nyquist plots in the frequency range of 10 mHz-1 MHz at potentials between -1.3 — -1 V of the samples: (a) KOH-0.005, (b) KOH-0.1, (c) KOH-0.5 and (d) KOH-2.

Upon applying overpotentials at more anodic conditions, all activated samples showed a non-ideal behaviour at 0.1 V, 0.2 V and 0.3 V vs. Ag/AgCl. In addition, the $R_{CT}$ values exhibited a similar trend to that obtained at more cathodic conditions, whereby a significant increase in the resistances was observed at 0.4 V (Figure 10-17), confirming that the electrode microstructure does not affect the Faradaic charge transfer reactions at the electrode/electrolyte interface at high frequency and extreme anodic potentials. However, at lower frequencies, the increased number of oxygen functional groups in high-activated samples deteriorated the capacitive performance at low frequency, as detected from the Nyquist plots at $\geq$ 0.1 V. The increased amount of oxygen functionalities with the KOH loading, offering less unsaturated active sites on the carbon surface demonstrated an oxygen evolution profile, and thus the impedance behaviour changed into an almost two depressed
semit circles profile beyond 0.1 V in the high-activated samples. The hierarchical porous structure of high total pore volume aided the transport of the electrolyte at anodic conditions from the bulk into the porous matrix, and consequently the evolution of oxygen in the porous matrix. This deteriorated the capacitive performance at low frequency [412, 413]. However, the low-activated samples with a limited number of oxygenated groups had a typical non-ideal capacitive performance at applied potentials up to 0.3 V. It is proposed that the delay in the detection of the oxygen evolution reaction is due to the number of active free sites on the carbon surface and the ultra-microporosity (with limited macroporosity) whereupon the evolution of oxygen gas has not occurred in the finest structures at the applied potentials within the frequency range used [414, 415].

These results highlight the importance of each of the PSDs and oxygen functionalities in contributing to the extension of the potential window of aqueous supercapacitors and therefore achieving higher energy and power capabilities. Based on the results obtained, a combination of a hierarchical porous structure and a limited number of stable oxygen functional groups might lead to widening the stable potential range, both at the anodic and cathodic limits [151, 416]. The effect of specific surface areas, pore size distribution and oxygen functional groups on the carbon surface of the potential-dependent performance of the supercapacitor all play a major role in determining the crucial synergy between morphology and electrochemical function and thus dictating the application of aqueous supercapacitors with enhanced performances. The investigation of the resistive elements at high frequency and capacitive elements at low frequency using the EIS technique demonstrates that a trade-off exists between high specific surface areas, micro- and macroporous contributions and oxygen functionalities. The EIS analysis of the carbon electrodes allows the selection of the potentials needed for demanding voltage float tests in real-world supercapacitors of different porous electrodes without detrimental ageing, and therefore enhancing the energy and power delivery at anodic/cathodic conditions [324, 326].
Figure 6-6: EIS Nyquist plots in the frequency range of 10 mHz-1 MHz at potentials between 0.1 - 0.4 V of the samples: (a) KOH-0.005, (b) KOH-0.1, (c) KOH-0.5 and (d) KOH-2.

### 6.3.2. Specific Capacitance Evaluation

The capacitive behaviour was evaluated using the impedance data collected, and using the active carbon mass added in each sample. The capacitance was determined at a frequency of 10 mHz, at which the electrolyte ions have wetted (ideally) all accessible pores to give the best specific capacitance \( C_S \), which would include the contribution of different PSD capacitive elements. The described ‘real’ capacitance \( C \) was determined using the EIS technique at a specific angular frequency \( \omega \) as follows [360, 378]:

\[
C'(\omega) = \frac{-Z''}{\omega |Z|^2} \quad (6-3)
\]

and

\[
C_S = \frac{C}{m} \quad (6-4)
\]

where \( C \) is in Farads and \( m \) is the mass (g) of active electrode material.
Figure 6-7 shows the capacitance as a function of potential for the different electrode structures. The specific capacitances decrease as the potential difference is decreased from -1.1 V to 0 V reaching a minimum at between 0 and 0.2 V, before increasing again at more positive potential. The minimum corresponds to the potential of zero charge (PZC), where the charge density at the electrode surface has a value of zero and the electrode reaches electrostatic equilibrium [3]. On both sides of the PZC, the displacement of the ions at positive or negative potentials decreases the double-layer dielectric thickness and therefore increases the capacitance values [397, 417].

The samples with low KOH loading, and specifically KOH−0.1, demonstrated higher capacitance values across the potential range. This is attributed to the microporous structures that are dominant in these samples, thus requiring high potential differences for the effective electrolyte invasion into the finest pores. This implies that low-activated samples establish higher capacitance values than high-activated ones at the potential limits or beyond, prior to the evolution of hydrogen gas. Further increases in KOH loading result in smaller increases in the capacitance values, which are attributed to the introduction of more surface functional groups and hierarchical structures that manifest good performances at low potential differences. The surface functionalities enhance the wettability of the electrodes alongside the macroporous contribution that enhances the ingress of electrolyte ions into the smaller pores at any chosen potential within the potential stability window. However, these samples have lower capacitance values compared to the low-activated ones at any specific potential and frequency of 10 mHz, which is due to the ‘tuning’ of the different micropores dominating the structures in the low-activated samples in the lowest frequency range. These results highlight that the hierarchical structures are not favourable for attaining the best capacitances when applications require low frequency, or equivalently low scan rates/current densities.

This trend also extends beyond the stability window, i.e. between -1.1 – 0.3 V, to further confirm the results described in the previous section, where Faradaic and double-layer capacitive mechanisms both govern the electrochemical behaviour. Potentials outside the aforementioned window lead to the pronounced cathodic/anodic electrochemical evolution of gases (hydrogen or oxygen) displacing the electrolyte out of a fraction of the pores, as previously demonstrated. This explains the decrease in capacitance values at more negative (< -1.1 V) and positive polarizations (> 0.3 V), as Faradaic reactions dominate.
Figure 6-7: Specific capacitance values of all samples at different potentials evaluated at 10 mHz, with a potential range -1.1—0.3 V double-layer region with Faradaic contribution and the green shaded area demonstrating the overpotential kinetics dominance.

The capacitive behaviour of low-activated samples at low frequencies (10 mHz) have recorded better performances than higher-activated ones, despite lower specific surface areas and smaller total pore volumes (described in Chapter 4). This performance arises from the dominance of microporous matrices that constitute a major component for charging/discharging sites for electrolyte ions, and therefore govern the excellent capacitive performance at very low frequency values at the extreme potential limits. These results are corroborated with cycling tests of the samples performed in Chapter 5, demonstrating higher capacitances for the low activated samples upon cycling, in contrast to decay in the capacitance values for higher activated ones [372]. In addition, the cyclic voltammetry profiles and respective ratios of the cathodic ($I_{ca}$) to anodic currents ($I_{an}$) at -1.1 V for the carbon electrodes confirm that low-activated samples have significant increases in the capacitances at negative potentials with high current leaps, while those of high-activated carbons are more stable and show ‘flat’ capacitive values with extending the potential window at cathodic conditions (Figure 6-8). These observations show that a decrease in the current ratios with high KOH loadings is due to the hierarchical porous that govern a good capacitive behaviour at any applied potential. Similar experiments are demonstrated in Chapter 7, with in-situ Raman spectroscopy measurements to further confirm these observations.
Figure 6-8: Cyclic voltammograms of different activated carbons in the potential window -1.1 V -0.2 V and b) corresponding $I_{ca}/I_{an}$ ratio at this potential with varying the microporous architecture.

The EIS experiments highlight the possible application of microporous structures in low frequency domains at extreme potential holds for excellent capacitance and energy delivery, vs. the suitability of hierarchical porous structures in applications requiring quick responses at different potential conditions. These results, along with the non-ideality detected with the Nyquist and Bode plots, show that an almost ideally polarizable performance of a porous electrode for a supercapacitor device might not entail the full utilisation of the accessible surface area by the electrolyte and consequently the highest capacitance values that can be achieved in the porous electrodes. Contrarily, a non-ideal capacitive performance detected by EIS constitutes the tuning of the different pores in the electrochemical performance and thus obtaining higher capacitances.

6.3.3. Relaxation Times of Porous Structures

A porous electrode cannot be accurately represented with a simple double-layer capacitance element, due to different factors including resistive components associated with the electrolyte in the bulk and inside the pores, charge transfer resistances due to surface species and complex electrode structures of different pore sizes. The electrochemical response of a supercapacitor dictates the power capabilities upon discharging and recharging it, and thus its potential application for practical utilisations. The determination of the accessibility of electrolyte ions into the different PSDs allows the evaluation of a best capacitive performance under specific conditions, in this case, frequency. At high frequencies, or equivalently high scan rates and current densities, the electrochemical performance does not include the contribution of the pores to the total capacitance, as different pore sizes might
not tune in to follow the variations in the current or potential sufficiently quickly. The increase and dispersion of the capacitance at low frequency is due to the 'tuning of' different pore sizes with a non-uniform charging/discharging rate of a porous matrix with a complex impedance response. The relaxation times ($\tau$) reflecting the time constants needed for charging/discharging a capacitor, were calculated based on an extended equivalent circuit of the transmission line model, as described in Chapter 5 [372]. Briefly, this simple porous electrode model assumes three pore size distributions (PSDs) and provides good fitting of all experimental EIS data, with a maximum chi-square goodness of fit of $1.38 \times 10^{-2}$ (Figure 10-18). The time constants were calculated for three different PSDs; micropores, mesopores and macropores, assuming an average circular pore of each of the PSDs. The relaxation time henceforth represents the product of the non-ideal capacitive element of the pore ($CPE$), and a summation of the bulk electrolyte resistance, inter- and intra-particle resistances of the porous matrix and electrolyte resistance inward from the bulk electrolyte to the corresponding PSD, as previously mentioned.

The PSD relaxation times reveal that the pores of smaller diameter, i.e. micropores, usually have the highest time constant, followed by mesopores and finally macropores, due to the lower resistive component in larger pores, and the pathway the electrolyte ions follow in the porous matrices [3, 332, 363]. The accumulation of resistances associated with macropores is added to that in the mesopores and finally into the micropores, as the trajectory of electrolyte ions starts from the bulk and into the biggest pores to reach the smallest ones. The sum of relaxations times in the three PSDs was calculated for each of the samples at different potentials and two trends were observed for the: i) low- and intermediate-activated samples, and ii) high-activated samples (Figure 6-9).

![Figure 6-9: Total relaxation times of micro-, meso- and macropore size distributions at different potentials against Ag/AgCl of a) KOH-0.005, KOH-0.01, KOH-0.1 and KOH-0.5 samples and b) KOH-1 and KOH-2 samples.](image-url)
The time constants for low-activated samples decrease by at least one order of magnitude upon increasing the applied potential difference; in contrast, the higher activated samples increase with applied potential difference. These trends are attributed to the different porous morphologies. Low-activated samples have a low total pore volume, dominated by micropores within the fibrous structure. Higher potential differences facilitate the electrolyte ion access into the low total porous volume, thus significantly increasing the specific capacitance values alongside the decrease in impedance magnitude values, as previously demonstrated. This trend in the total relaxation times for these carbons confirms that, with the decrease in the magnitude of the impedance at low frequency, the necessity of applying high potential differences for a narrow microporous structure so as the cumulative ohmic resistances decrease and the electrolyte can penetrate the finest structures. The same trend was also obtained for the intermediate-activated carbons (KOH−0.1 and KOH−0.5), having a hierarchical micro- and macroporous structure. The diversion from ideality as the potential is increased to -1 V in the Nyquist plots (Figure 6-2) corroborates with these results. The difference in the relaxation times for different samples at the same potential is governed by both the ultra-microporous percentage of the total volume and the total pore volume accessible by the electrolyte.

Contrarily, in a macropore-dominant network structure (KOH−1 and KOH−2 samples), applying higher potential differences enhances the ingress of ions into the larger pores, which facilitates the ion transport into the mesopores and finally reaching the micropores. A slight increase in the total relaxation time occurs is accompanied with the deviation from ideality increase and the impedance magnitude decrease (Figure 6-1), whereby the tuning of different pore sizes in the high total pore volume is boosted at high potential differences. The tuning of the different ultra-micropores in the capacitive performance occurs at low frequency, despite the hierarchical morphology of the sample as the wetting of the micropores requires higher driving force, i.e. higher potentials. This highlights the fact that the wetting of the porous matrices with a high total pore volume, even in a hierarchical porous structure, is not fully accomplished unless the ultra-micropores partake in the total electrochemical capacitance behaviour. This did not occur unless more cathodic potentials were applied.

6.4. Conclusions

In this chapter, the extension of the previous work on the electrochemical impedance spectroscopy at different potentials has been carried. KOH-activated carbons, studied in the
previous chapters have been used as model systems to correlate the effect of pore size distribution on the electrochemical impedance behaviour at different potentials in three-electrode systems. The porous carbon materials with different morphological structures have been electrochemically tested within the potential stability windows of the electrolyte and active material, as well as beyond the potential limits where water electro-reduction and electro-oxidation occur. It was found that the potential dependence of capacitance should be taken into account, as the application of different potentials can enhance the capacitive performance at low frequency for various porous matrices. In addition, different capacitance-potential trends were demonstrated for the porous matrices, revealing the importance of the nature of the electrode when tested in an aqueous supercapacitor. The investigation of possible extension of anodic and cathodic potentials beyond theoretical stability window for aqueous media was also investigated using the EIS tool. It was found that each of the pore size distribution, oxygen content and total pore volume has an influence on the resistive and capacitive elements of the equivalent circuit and can aid or impede the electrolyte penetration into the finest pores, which will be discussed further in Chapter 7. The total pore volume is also coupled with available high surface area material for wetting by the electrolyte which can only be realized upon applying high potential differences. The combination of stable oxygen functionalities and a hierarchical porous structure is suggested for an optimized capacitive performance that takes advantage of both delaying the nascent hydrogen gas at extreme anodic conditions and evolution of oxygen gas that can occur in the finest porous matrices at extreme cathodic conditions. The magnitudes of impedance, total relaxation times for wetting porous matrices with electrolyte ions, and specific capacitances have been evaluated. The rate of electrical response was evaluated using different relaxation times in wide PSDs using the suggested equivalent circuit in Chapter 5. It remains a question whether almost ideally polarizable porous electrodes at specific conditions are the right choice for optimizing the capacitive behaviour. We reported that this can dictate the application of suitable materials in corresponding applications, depending on the power capabilities upon the discharge and recharge of electrode materials. The observations in this work can be extended to different porous electrode structures, which can dictate the application of suitable materials in corresponding real-world supercapacitors, depending on the ageing and power capabilities upon the discharge and recharge of porous carbon electrodes. In the next chapter, the electrochemical behaviour of the different porous carbons is studied via in-situ Raman spectroscopy to complement the results obtained herein, on a surface science level.
Chapter 7

Insights into the electrochemical behaviour of porous carbon electrodes using \textit{in-situ} Raman spectroscopy


Scope of this chapter: Effects of surface chemistry and porous morphologies of KOH-activated carbons on the extension of operating potential window and the electro-reduction and oxidation of water using TPD, XPS and \textit{in-situ} Raman spectroscopy are investigated. The corroboration of this work with the results obtained in Chapter 6 is explored.
7.1. Introduction

Porous carbons have been extensively exploited in electrochemical applications including gas storage and separation, catalyst supports and energy conversion and storage electrodes [418, 419]. Carbon is the most versatile element on earth with the highest catenation power and when combined with other atoms leads to materials with unique properties including high specific surface area, tuneable chemical structure/functional groups, electronic and ionic conductivity, lightweight and more. Due to all these unique features, carbon materials are ideal candidates for energy conversion and storage devices [420]. Activated carbons, a special class of amorphous microporous carbons, have been intensively used as supercapacitor electrode materials, as well as to store hydrogen by controlling the resulting microporosity and surface chemistry [93, 159, 392, 421, 422]. The role of the factors above and their importance in the electrochemical hydrogen storage mechanism have been previously discussed [423-425]. KOH-activated carbons with different KOH loadings have been produced and the role of morphology, porosity and surface chemistry and its correlation with electrochemical performance, and more specifically EIS, has been explained in Chapter 4, 5 and 6.

Nanostructured carbons have gained increasing interest as a promising alternative for electrochemical energy storage systems in aqueous media; however, the fine-tuning of the pore structure and surface functionality is yet to be fully addressed [424]. It was found that the hydrogen uptake increases with narrow microporosity and an increase in unsaturated carbon atoms, i.e. low content in surface oxygen functionalities, favours electrochemical storage of hydrogen via the electroreduction of water in basic media [318]. Ultra-microporosity also plays an important role in hydrogen uptake and storage, whereby a hierarchical porous structure consisting of meso- and micro-pores can provide the mass transport channels to the smaller pores and therefore provide excellent capacity retention and promising features for electrochemical hydrogen storage applications [426].

Carbon/carbon supercapacitors belong to the class of EDLCs, as mentioned and explained in previous chapters, where energy is stored via charge separation at the electrode/electrolyte interface [393]. In brief, the charge storage mechanism excludes any pseudocapacitive behaviour, and the electrolyte ions are electrostatically and reversibly adsorbed in the double-layer of the porous networks of the carbon electrodes. However, in the case of surface functionalities, Faradaic processes may arise that comprise of reversible reactions between the functional groups at the accessible electrode surface and electrolyte ions. Hence, the pore size distribution, porosity and functional groups content can be tuned to optimize the electrochemical performance of supercapacitors. Nanostructured electrodes have gained
increasing popularity as the manipulation of narrow microporosity and surface functional groups leads to an enhancement in the gravimetric capacitance, as well as the self-discharge mechanism (the relaxation of potentials across the elements of the porous electrodes) in supercapacitors, hence increasing the energy and power densities of carbon materials [3, 427]. The non-ideal polarization of carbon surfaces, due to surface oxidation reactions and possible intercalation processes, specifically upon cathodic polarization, makes fundamental understanding of the electrochemical processes occurring very challenging [3]. The behaviour of EDLCs is surface specific, whereby adsorption interactions between oxygen species on the carbon surface and electrolyte ions occur. The identification of surface functionalities on carbon surfaces and their effect on potential-of-zero-charge, the contact angle between electrode/electrolyte interface and wettability of electrode materials, have been studied previously via in-situ XPS, Raman spectroscopy and Fourier transform infrared (FTIR) techniques [193, 428-430]. However, a full chemical and structural characterisation of different porous carbon electrodes, and the link between structure and electrochemical performance as electrodes in supercapacitors have not been established yet. In this chapter, a continuation on the previous works on KOH-activated samples, as model systems will be explored to further assess the role of morphology and surface chemistry, but this time to fully investigate the extreme conditions different porous structural electrodes can withstand. TPD, XPS, and in-situ Raman spectroscopy techniques have been mainly employed, in aid with the characterisation techniques previously described (SEM, TEM, CO₂ and N₂ sorption) to determine the surface changes at different electrochemical behaviour of porous carbons. This study opens a platform to i) understand the behaviour of different carbon electrodes at extreme conditions and ii) correlate the surface and morphological effects of different porous structures to the electrochemistry in order to avoid the electro-reduction and/or electro-oxidation processes.

Levya-Garcia et al. reported that carbon-hydrogen bonds form reversibly when using KOH–activated carbon materials from anthracite and commercial activated carbons in different aqueous media under cathodic conditions [319]. In-situ Raman spectroscopy and surface chemistry characterisation via temperature programmed desorption (TPD) technique were employed in this study and it was found that the surface functionality and porous texture play a major role in determining the electrochemical hydrogen storage process [318]. The efficient process of hydrogen storage in activated carbons has proven to be more efficient than in carbon nanotubes or other methods, including pressure and cryogenic conditions, due to the easy penetration of nascent hydrogen produced in the electrolyte into the porous carbon network [431, 432]. However, a direct correlation between the structural properties, presence of functional groups, pore size distribution and wettability of
nanocarbons and reversible hydrogen chemisorption and storage has not yet been identified [418]. The process of electrochemical decomposition of water in different media leads to the formation of nascent hydrogen atoms that readily diffuse in the electrolyte solution and penetrate into the porous structures of carbons. Upon decreasing the potential of the electrode below the equilibrium potential, hydrogen is produced via the reduction of water in basic media, opposed to its formation via the reduction of hydronium ions in acidic media [432]. Consequently, and via producing and storing charges through the water electrolysis, the formation of weak carbon-hydrogen chemical bonds is obtained [431]. It has been established that the hydrogen storage capability in carbons mainly depends on the porous nature and chemical structure of the materials. Different studies have proven that microporous carbons constituting pore sizes in the range of 0.5-0.7 nm demonstrate the most efficient methods the storage mechanism. However, the presence of meso- and macro-pores, comprising a “reservoir” of the produced hydrogen ad-atoms, facilitate the diffusion process of the nascent hydrogen into the smaller pores, whereby a double-layer capacitance is created on the carbon electrode surface [433].

In addition, the presence of functional groups has previously been proven to affect the hydrogen adsorption mechanism negatively, whereby the trapping of the nascent hydrogen atoms decreases upon increasing the amount of surface oxygen groups. It was suggested that active sites that are saturated with oxygen groups cannot contribute to the hydrogen trapping mechanism, given that the porosity is kept constant [318]. The presence of the same functional groups can induce the wettability and pseudocapacitive mechanism in EDLCs giving rise to the capacitance of the carbon electrode, yet might lead to the supercapacitor instability due to leakage currents and electrochemical oxidation/reduction of the carbons [434, 435].

Theoretically, and from a thermodynamic point of view, cathodic decomposition of water can commence at a potential of, or lower to, 0 V vs. SHE. However, the electrocatalysis for hydrogen evolution has a poor exchange current density ($\sim 10^{-13}$ A cm$^{-2}$), and therefore Faradaic charge transfer is not pronounced until potentials more negative than -1 V vs. SHE are applied [3]. The electrode/electrolyte interface would be theoretically close to ideality within the potential limits of water electrocatalysis, and the porous structure has a huge impact on the electrode behaviour in aqueous solutions within and beyond these limits. Hence, there is a vital need to better understand the hydrogen production/energy storage in supercapacitor devices in order to specify the extreme conditions different porous carbons can withstand in order to avoid the production of nascent gases at cathodic and anodic conditions and improve their performance in terms of reversibility of the porous electrode material. The porosity, pore size distribution and oxygen are all taken into account as major
factors in providing a necessary understanding of the different electrochemical performances of different carbon electrode materials.

In this chapter, a fundamental study on the role of surface chemistry has been performed and techniques including pore size distribution and specific surface area on the electrochemical performance of KOH–activated carbons using cyclic voltammetry (CV), \textit{in-situ} Raman spectroscopy and temperature programmed desorption (TPD) were applied. We have revealed the role of different percentages of narrow micropores, the amount and type of oxygen functionalities and the corresponding hydrogenation and oxygenation of the carbons during cathodic and anodic processes, along with the limits of potential windows on their energy storage ability and avoiding the evolution of gases, when used as electrodes in supercapacitors. The reversibility of the different redox pseudocapacitive reactions at different voltages under different activation conditions, which is a prerequisite for attaining a good capacitance and energy density, has also been examined.

7.2. Experimental

7.2.1. Carbon Activation

Chemical activation of softwood Kraft cellulosic pulp (UPM-Kymmene Corporation, Finland) with different KOH loadings was conducted under a nitrogen atmosphere at a flow rate of 1 L min\(^{-1}\) heating ramp of 20 °C min\(^{-1}\) up to 850 °C with a dwell time of 1 h, as detailed in section 3.2. Briefly, the cellulose of 500 g m\(^{-2}\) and 1 wt.% consistency was soaked in different concentrations of KOH solutions and dried in a vacuum oven overnight prior to the carbonisation process. The KOH / cellulose weight ratios used were: 0.005, 0.01, 0.1, 0.5, 1, 2 and 3 wt. %. All samples are denoted as KOH–\(n\), with \(n\) representing the weight ratio of KOH/cellulose.

7.2.2. Characterisation of Porous Texture and Surface Chemistry

The techniques used in this work constituted TPD coupled with a mass spectrometer and XPS with the aid of all the techniques previously discussed in Chapter 4. The suite of characterisations allows the full investigation of the morphology, surface chemistry and functionalities and PSDs. In addition, the wettability behaviour of the various activated carbons has been determined by measuring the contact angle between water and the surface
of the prepared carbon electrodes (95:5 wt.% carbon: polytetrafluoroethylene) using First Ten Angstroms (FTA) 1000 B Drop Shape Analyser (First Ten Angstroms Inc., USA). The contact angle was measured using the software FTA32 Video 2.1. A detailed description of each of the characterisation techniques can be found in Chapter 3.

7.2.3. Electrochemical Characterisation

Activated carbons in this work were prepared as electrode pastes by mixing 95 wt. % of the synthesized carbons and 5 wt.% polytetrafluoroethylene (PTFE) binder solution without any booster carbon. The carbon slurry was manually pasted on nickel foam acting as a current collector. All samples had a final weight of 5-6 mg of activated carbon. Platinum and saturated Ag/AgCl electrodes were used as counter and reference electrodes, respectively, throughout all electrochemical measurements. Further details can be found in [349].

The resistivity of the prepared electrodes was measured using the Ecopia HMS-3000 Hall Measurement System (Four-Point-Probes, USA) after pressing all electrodes in sheets of 30 μm thicknesses. Three measurements were taken at different points of the samples and an average of four measurements was calculated.

All experiments run in this work were in three-electrode configurations. The electrochemical performance of the three-electrode systems was studied by cyclic voltammetry (CV) in 6 M KOH electrolyte solution using a Gamry potentiostat. The electrodes were soaked for 24 h in the electrolyte solution prior to electrochemical tests. CVs were conducted at a scan rate of 5 mV s\(^{-1}\) at different potential ranges until extreme cathodic and anodic polarizations are reached, for separate samples.

7.2.4. In-situ Raman Spectroscopy Characterisation

The activated carbon pastes were prepared by mixing the carbon powder and 60 wt. % PTFE solution in a ratio of 95:5; the slurry was then vacuum-dried at 80 °C for 2 h and soaked in 6 M KOH solution overnight. The activated carbon sample was then deposited on a glassy carbon disc of 3 mm diameter acting as the electrical contact and enveloped by a polytetrafluoroethylene (PTFE) piece. The working electrode was fitted into a spectroelectrochemical PTFE cell, covered with a quartz window to form a closed system and to separate the microscopic lens from the electrolytic solution while acquiring Raman spectra. A three-electrode system was implemented with a platinum wire as the counter
electrode and saturated Ag/AgCl as the reference electrode, placed through a Luggin capillary to ensure contact with the 6 M KOH electrolyte solution. A schematic of the cell for the Raman acquisition data can be found in [436].

*In-situ* Raman characterisation was conducted using a LabRam spectrometer (Jobin-Yvon Horiba, UK) coupled with a microscope Olympus BX30 (UK). All presented spectra are deconvoluted using the Lorentz function to separate multiple components from different bands in the same spectrum [437]. All data acquired correspond to an average of four measurements with an acquisition time varying between 40 s and 100 s per measurement upon an excitation line provided by 17 mW He-Ne laser at 632.8 nm. A slice of silicon (521 ± 2 cm⁻¹) was used for the calibration of the spectrometer prior to experiments. The laser beam was focused into a 2 μm spot at the electrode surface through a 50 × long-working objective (0.5 NA). The viewing system comprised of a television camera coupled with the microscope. The resolution of the spectrometer was better than 3 cm⁻¹ throughout all measurements and the detector used was a Peltier cooled charge-coupled device (1064 × 256 pixels). The confocal pinhole employed was set to 600 μm and a 600 lines mm⁻¹ diffraction grating was used with an aperture slit of 200 μm. The spectra were collected at each potential once a steady-state current was reached upon applying chronoamperometry [319, 438, 439] by using a DropSens portable bipotentiostat/galvanostat μstat 400. In the case of water electrocatalysis and the evolution of hydrogen or oxygen gas bubbles, loss of contact with the current collector occurs and the data, if acquired is very noisy. Therefore, we have not reported these data in this work (Figure 10-19).

7.3. Results

7.3.1. Porous Texture and Surface Chemistry

The porous texture and surface chemistry of all activated carbons were previously characterised by SEM and TEM techniques (Figures 4-1, 4-2 and 10-1). Briefly, the fibrous structure of the non-activated sample (KOH-0) showed a limited amount of micropores that evolved into a more porous structure upon increasing the KOH loading. The KOH activation process resulted in a hierarchical porous structure in samples KOH-0.5 and KOH-1 having a wide pore size distribution. Further increase in the KOH/cellulose ratio reveals the domination of macropores in the porous networks. These results were confirmed with sorption isotherms and MIP measurements. The total pore volume ($V_p$) and specific surface area values are enhanced by increasing the KOH loading until they reach a maximum in the
KOH−1 and KOH−2 samples (Table 4-1); beyond which the values decrease again [349]. The macropores contribution was determined by MIP and found to increase with KOH loading, indicating most macropore diameters were in the range of 50 nm- 100 μm (Table 4-3). The narrow micropore volume, detected by CO₂ adsorption, increased with the KOH / cellulose ratio, yet the microporous contribution to the total porosity decreased. The fraction of ultra-micropores (V_Co2/V_N2) decreased from 97% in the non-activated sample (KOH-0) to 27% with the highest activation (KOH−3). If the micropores (< 2 nm) measured by N₂ physical adsorption were taken into account in the total micropore volume value in addition to the macropore volume determined by MIP, the micropore fraction of the total porous network is observed to decrease from 97% in the KOH-0 sample to a minimum of 8% in the KOH-3 sample. Figure 4-3a presents the isotherms and pore size distribution of all KOH-n activated and non-activated samples. All samples characterised with N₂ adsorption display a Type I isotherm [440], which is a characteristic of a microporous solid and shows a shift from a narrow microporous structure at low activation ratios, to a wider micro- and macropore size distribution and a hierarchical porous network at intermediate KOH loadings and finally a macroporous structure at high activation ratios.

The TPD data presents the evolution of carbon monoxide (CO) and carbon dioxide (CO₂) gases through the decomposition of oxygen surface functionalities upon heating the samples up to 950 °C. The data is presented in Table 7-1 and Figure 7-1.

Table 7-1: Porous texture and surface chemistry characterisation of all activated carbon samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SBET (m²/g)</th>
<th>V(CO₂) (cm³/g)</th>
<th>V(N₂) (cm³/g)</th>
<th>μmol CO/g</th>
<th>μmol CO₂/g</th>
<th>μmol O/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH-0</td>
<td>11</td>
<td>0.23</td>
<td>0.008</td>
<td>699</td>
<td>292</td>
<td>1283</td>
</tr>
<tr>
<td>KOH-0.005</td>
<td>252</td>
<td>0.22</td>
<td>0.16</td>
<td>786</td>
<td>324</td>
<td>1435</td>
</tr>
<tr>
<td>KOH-0.01</td>
<td>598</td>
<td>0.22</td>
<td>0.28</td>
<td>836</td>
<td>366</td>
<td>1570</td>
</tr>
<tr>
<td>KOH-0.1</td>
<td>717</td>
<td>0.28</td>
<td>0.34</td>
<td>1599</td>
<td>990</td>
<td>3581</td>
</tr>
<tr>
<td>KOH-0.5</td>
<td>1351</td>
<td>0.42</td>
<td>0.55</td>
<td>1828</td>
<td>937</td>
<td>3702</td>
</tr>
<tr>
<td>KOH-1</td>
<td>1063</td>
<td>0.54</td>
<td>0.47</td>
<td>1911</td>
<td>976</td>
<td>3862</td>
</tr>
<tr>
<td>KOH-2</td>
<td>1579</td>
<td>0.6</td>
<td>0.59</td>
<td>2178</td>
<td>1399</td>
<td>4976</td>
</tr>
<tr>
<td>KOH-3</td>
<td>785</td>
<td>0.16</td>
<td>0.43</td>
<td>1633</td>
<td>1258</td>
<td>4150</td>
</tr>
</tbody>
</table>

CO evolves at high temperatures, mainly due to the decomposition of basic and neutral functional groups, such as phenols, carbonyls, ethers and quinones. However, the
decomposition of lactones and carboxylic groups occurs at a lower temperature, giving rise to the evolution of CO$_2$. Anhydride groups decompose to give CO and CO$_2$. The desorbed amounts from the TPD profiles show that the content of surface oxygen groups increases with the activation of the cellulose precursor materials with KOH until a maximum is reached at KOH-2. The amount of total oxygen desorption can be deduced as follows:

$$\mu \text{mol } O \text{ g}^{-1} = \mu \text{mol } CO \text{ g}^{-1} + 2 \times \mu \text{mol } CO_2 \text{ g}^{-1} \quad (7 - 1)$$

Figure 7-1: TPD profiles of activated carbon materials showing the: (a) CO and (b) CO$_2$ profiles.

The TPD profiles consist of different peaks for the CO and CO$_2$ profiles, which reveal the presence of different functional oxygen groups in the KOH-activated samples. Several peaks in the CO spectra show that carboxylic anhydrides are decomposed at 500 °C and carbonyl, phenol, ether and quinone groups are decomposed at higher temperatures for all samples [441, 442]. In the CO$_2$ spectra, three peaks are detected: i) a peak at 300 °C related to the decomposition of carboxyl groups, ii) a peak at 500 °C corresponding to carboxylic anhydrides and iii) peaks beyond 500 °C related to the decomposition of lactones or CO$_2$ via secondary reactions that are boosted in porous carbon structures [443]. All samples present a diversity in oxygen functionalities on the carbon surface; however, larger amounts of CO and CO$_2$ desorption occur at higher KOH loadings, with the maximum reached in the KOH–2 sample. The oxygen wt. % increased from 2.1 % in KOH-0 to a maximum of 8 % in KOH-2, decreasing again to 6.6 % in KOH-3, evaluated from TPD experiments.
Figure 7-2: C1S XPS deconvolution of (a) KOH-0, (b) KOH-0.01, (c) KOH-1 and (d) KOH-2 with Shirley background subtraction (in green).

XPS data of all activated and non-activated samples were investigated. Figure 7-2 and 10-20 show the C$_{1s}$ spectra with a broad oxygenated carbon spectrum in a binding energy (BE) range of ~284.1–288.8 eV with KOH loading. The carbon peak corresponding to the C-C, C=O and C-H bonds at a binding energy of 284.1–284.2 eV, exhibited the highest intensity in the non-activated sample (KOH-0) with a small shoulder representing the carbon-oxygen bonds. The shoulder percentage increased to a maximum in KOH-2, as indicated in Table 7-2. The detailed deconvoluted information of the variation in surface chemistry shows that the oxygenated carbon percentage and oxygen/carbon atomic ratio has increased with the activation. The intensities of C$_{1s}$ signal corresponding to C−O, C=O, and O-C=O bonds show pronounced peaks at ~285.8 eV, ~287.1 eV and ~288.6 eV, respectively. They increased in relative abundance from 22.5 % in KOH−0 to 36.7 % in KOH−2, showing more oxygen surface functionalities with increased activation. The decrease in oxygen content upon further activation in KOH-3 could be attributed to the dominant macroporous morphology and decrease in the specific surface area of the materials which also decreased the total CO and CO$_2$ desorption in TPD experiments. These results are confirmed with XPS
data, despite the fact that XPS is not directly/qualitatively comparable with TPD, as the former provides information at the most external surface of the sample. The discrepancy in oxygen percentages between XPS and TPD techniques is because TPD analysis usually underestimates the oxygen content as some oxygen functionalities can be decomposed into water or decompose at higher temperatures than those reached by TPD, and hence are not quantified [439]. However, the trends obtained by both experiments and presented in Figure 7-3 are very similar and the peaks corresponding to different oxygen functional groups detected by TPD correspond to the intensities of C–O (ether groups), C=O (carbonyl groups) peaks and O-C=O (carboxyl groups) peaks obtained by XPS.

Table 7-2: Fitted results of percentages of oxygen to carbon content and C1S XPS data of all samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>O:C Ratio (%</th>
<th>C-C, C=C, C-H (284.1-284.2 eV)</th>
<th>C-O (285.7-285.9 eV)</th>
<th>C=O (287.1 eV)</th>
<th>O-C=O (288.4-288.8 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH-0</td>
<td>7.78</td>
<td>77.6</td>
<td>12.7</td>
<td>5.1</td>
<td>4.7</td>
</tr>
<tr>
<td>KOH-0.005</td>
<td>9.6</td>
<td>77.0</td>
<td>12.7</td>
<td>5.6</td>
<td>4.7</td>
</tr>
<tr>
<td>KOH-0.01</td>
<td>14.1</td>
<td>75.5</td>
<td>14.6</td>
<td>5.4</td>
<td>4.5</td>
</tr>
<tr>
<td>KOH-0.1</td>
<td>21.11</td>
<td>70.3</td>
<td>20.5</td>
<td>2.7</td>
<td>6.4</td>
</tr>
<tr>
<td>KOH-0.5</td>
<td>21.01</td>
<td>67.9</td>
<td>21.1</td>
<td>5.8</td>
<td>5.1</td>
</tr>
<tr>
<td>KOH-1</td>
<td>18.06</td>
<td>65.2</td>
<td>21.2</td>
<td>7.6</td>
<td>6.0</td>
</tr>
<tr>
<td>KOH-2</td>
<td>22.7</td>
<td>63.3</td>
<td>21.5</td>
<td>7.8</td>
<td>7.4</td>
</tr>
<tr>
<td>KOH-3</td>
<td>13.87</td>
<td>71.6</td>
<td>16.5</td>
<td>6.6</td>
<td>5.3</td>
</tr>
</tbody>
</table>

The amount of oxygen functional groups on the surface as determined by XPS directly correlates to the total amount of oxygen evolved in the TPD experiment. The desorbed oxygen content by the TPD experiment and that analysed by XPS were compared with the microporous volume contribution to the samples’ structure. It is evident that the oxygen desorbed at the carbon surfaces raises by at least two-folds with the activation of the carbon atoms with higher KOH concentrations (decrease in total micropore contribution); yet, there is no direct correlation between both parameters. The high values of specific surface area (high microporous content) provide sites for oxygen functional groups; however, the samples exhibit different porous textures and surface chemistry as determined by the physical adsorption isotherms, TPD and XPS data. Hence, the total oxygen content does not rely solely on the level of activation of the precursor material, but also on the porosity, pore size distribution and surface chemistry, in which each plays a critical factor in the
electrochemical performance of these materials and which will be discussed in the following sections of this chapter.

Figure 7-3: Oxygen content inferred from TPD (red line) and XPS (black line) analyses as a function of micropore contribution to the structure of activated carbon materials. A similar trend by both techniques is clearly observed.

The increase in the oxygen content played a major role in determining the wettability of the different carbon electrodes. The water droplets in the un-activated and low-activated samples (KOH=0, KOH=0.005 and KOH=0.01) stayed floated on top of the carbon pastes, showing a relatively large contact angle of more than 90°, proving the hydrophobic nature of these carbons, shown in Figure 10-21. However, the wetting behaviour of higher activated samples showed immediate dispersion/spreading of the water droplets on top of the samples and therefore their hydrophilic nature. The contact angle increases again in KOH-3 sample due to the decrease in the oxygen content, as shown by XPS measurements. The different wettability characteristics of the KOH-n activated carbons along with the contact angle between water and the carbon surface are attributed to the different extent of the amounts of polar oxygenated groups generated by the KOH activation on the amorphous carbons. These results confirm that the presence of hydrophilic surface oxygen groups can immensely affect the contact angle value and wettability of the electrodes, and their absence or low content might lead to incomplete wetting of the pores of the electrodes, regardless of high specific surface area values achieved.
7.3.2. Electrochemical Performance

It is well established that the surface oxygen groups increase the resistivity of carbon materials in which they increase the barrier for electron transfer from one microcrystalline carbon element to the other [444]. However, the conductivity values also depend on the porosity and surface-area values [7]. The presence of hierarchical porous networks enhances the movement of electrons from one microcrystalline to another and therefore induces the conductivity of the carbons. The conductivity of the KOH-\(n\) activated electrodes, presented in Figure 7-4 in combination with Figure 7-3, showed a correlation between the oxygen content, total pore volume and pore size distribution. It was found that KOH-0 sample with the limited microporosity had a conductivity value of 0.03 S cm\(^{-1}\), that increased dramatically upon increasing the KOH loading content. KOH-0.5 and KOH-1 samples recorded values of 3.8 S cm\(^{-1}\) and 5 S cm\(^{-1}\), similar to the values obtained for these activated carbons in the literature [445, 446]. These results confirm that different factors play a role in determining the resistivity of the carbon materials, and a balance between the porosity and conductivity of carbons is needed to achieve optimized electrochemical performance rates [447].

![Figure 7-4: Conductivity measurements of all KOH-\(n\) activated samples showing the similar trend to the total pore volume](image)

The electrochemical characterisation of all carbon samples was obtained by applying a CV at a sweep rate of 5 mV s\(^{-1}\). It was intended to check the behaviour of the different porous carbons within the potential stability limits and beyond to investigate the “tolerance” of
different porous structures to extreme anodic and cathodic conditions. The effect of morphology and surface chemistry on the limitation of the different carbons was followed.

Figures 7-5, 10-22 and 10-23 present the voltammograms of all KOH-n activated samples and the profiles show a quasi-rectangular shape in the voltage range of -0.9-0.1 V vs. Ag/AgCl, a typical behaviour for EDLCs. However, for the low activated samples (KOH-0, KOH-0.005, KOH-0.05, KOH-0.1), the voltammetric charge is smaller at higher potentials compared to the higher activated samples, indicating the hindrance of the ions in the ultramicroporous structures dominating the structure of the former samples. The KOH-3 sample shows similar performance to the low-activated samples, which can be attributed to the drastic decrease in the total pore volume and decrease in the specific surface area upon extreme activation conditions, leading to a highly disordered morphology examined in Chapter 4. Moreover, this behaviour could be associated with a decrease in the electrical conductivity of the samples, as previously shown. These results are corroborated by the cyclic charge-discharge behaviour detected for all samples and shown in Figures 4-11b and 10-4. The electrochemical performance of the carbons was enhanced upon increasing the KOH loading; the poor performance of the non-activated sample (KOH-0) is attributed to the low specific surface area and very narrow microporosity. Upon increasing the KOH/cellulose ratio, the specific capacitance increases to 161 F g\(^{-1}\) for KOH-0.5 and KOH-1 samples and 0.5 A g\(^{-1}\) current density, owing to the hierarchical porous morphology and relatively high specific surface areas. In addition, a capacitance retention of 78% at 20 A g\(^{-1}\) current density is achieved in KOH-1 sample, compared to 18% in the non-activated sample and 48% for KOH-3 sample. The ohmic drop (iR), inferred from the discharge curve, also reflects the conductivity of the different samples, whereby the most conductive samples (KOH-0.5 and KOH-1) established the lowest iR drop, compared to the non-activated sample or the highest activated one. These results confirm that the accessibility of the electrolyte ions into the pores, at low and high current densities plays a major role in the electrochemical performance of the porous carbons. Specifically, an optimized electrode porous network for supercapacitor applications should be composed of i) micro- and mesopores that improve the charge storage mechanism and ii) macropores that facilitate the ion transport of the electrolyte at the electrode surface [12]. More details on the electrochemical characterisation can be found in Chapters 4, 5 and 6.
Figure 7-5: Cyclic voltammograms of (a) and (b) KOH-0, (c) and (d) KOH-1 and (e) and (f) KOH-2 at different potential ranges towards hydrogen evolution reaction (right) and oxygen evolution reaction (left).

When the negative cut-off potential is extended towards more cathodic conditions to more negative values for all samples, a reduction current is generated at \(-1.3\) V vs. Ag/AgCl, corresponding to the decomposition of water and nascent hydrogen evolution and its adsorption to the carbon electrodes. It should be noted that this reduction current is lower than the theoretical value of the equilibrium potential in 6 M KOH solution which is \(-0.872\)
V vs. the standard hydrogen electrode, and hence -1.077 vs. Ag/AgCl reference electrode (the potential of Ag/AgCl vs. SHE is 0.205 V in 3 M KCl solution at 25°C) [39]. As this reduction occurs at voltages below -1.3 V vs. Ag/AgCl, an oxidation current of the hydrogen is present during the anodic scan at potentials around -0.7 V for low activated samples (KOH−0, KOH-0.005, and KOH-0.01). This indicates that the hydrogen is weakly chemisorbed during the negative scan at lowest potential conditions in the low activated samples [319]. The noticeable hump due to the hydrogen oxidation starts broadening as the activation level further increases in KOH-0.1 and KOH-0.5 samples, and reappears once the activation level is further increased in the KOH-1 and KOH−2 samples. This is clearly illustrated upon extending the cut-off potential value to -1.5 V, shown in Figure 10-24. This behaviour is attributed to two main factors: i) the variation of the pore size distribution and contribution of ultra-micropores to the morphology of the carbons analysed by N2 and CO2 isotherms and MIP [424] and ii) the oxygen content in the different materials as detected by TPD and XPS techniques [318]. The lowest activated carbons show the largest contribution of ultra-micropores in their structure; these micropores have proven to be effective for hydrogen adsorption and trapping [448]. In addition, these samples recorded the lowest oxygen content and thereby they constitute unsaturated sites in the porous structure, readily reactive in alkaline media at extreme cathodic conditions. However, the small anodic humps recorded for these samples are attributed to irreversible trapping of hydrogen in these structures. As for KOH−1 and KOH−2 samples, the high oxygen content offering less unsaturated sites for water reduction and interaction with nascent hydrogen, is mitigated by the fact that the oxygenated groups are associated with the hydrophilic surface functionalities that increase the wettability of the carbons and hence permit an easier admittance of the atoms/ions into the narrowest pores [3]. Furthermore, and despite the decrease in the total pore volume fraction detected by CO2 adsorption isotherms, the total ultra-microporous volume has drastically increased in these samples, in which the high specific surface area generates more active sites for the formation of hydrogen and its chemisorption to the carbon materials. The process can also be enhanced by the meso- and macroporous networks in these samples that ease the transport of the atoms/ions into the smaller pores [424]. These results confirm that there is not only one factor that dictates the hydrogen chemisorption mechanism and stability of porous carbon materials for electrochemical conversion and storage applications, but rather a balance between the chemistry and the porous texture.

The evaluation of the ratios of the cathodic current (Ica) to anodic current (Ian) at an extreme cathodic condition of -1.3 V vs. Ag/AgCl for the different carbon electrodes confirms that
hydrogen evolution is least pronounced with i) increasing the oxygen content to an optimum along with ii) creating a hierarchical porous morphology in the carbon structure (Figure 7-6).

The decrease in the ratio of the current leap at extreme negative potentials to the nominal current range with increasing the KOH loading proves that the evolution of nascent hydrogen is more pronounced with low total pore volumes of dominant microporous morphology and a small proportion of surface oxygen functionalities. The data point that does not follow the trend in Figure 7-6b corresponds to KOH-3 sample that was characterised with a sudden decrease in the specific surface area and total pore volume as previously mentioned. These observations establish that there is not one factor that determines the optimum performance of carbon electrodes; it is rather the co-dependence of various parameters that embellish a superlative electrochemical cell.

If the potential window is extended beyond -1.3 V to more negative values, the hydrogen oxidation hump during the positive scan increases, indicating higher amounts of chemisorbed hydrogen during the negative scan, presented in Figure 7-7. The decrease in the negative cut-off potential value, in the case of both KOH-0 and KOH-1 samples, increases the anodic peak of hydrogen oxidation and hence a more positive current and a more visible hump are recorded. In addition, the hump slightly shifts towards more positive values of potential as the negative potential window is further extended. At extreme cut-off potentials (as low as -2 V), the hydrogen is more strongly adsorbed to the porous carbon structure [432]. This implies that the different carbon electrodes possess the ability to store hydrogen in energetically different sites and that lower negative cut-off potential values reached, the higher the energy values of adsorption sites [425].

Figure 7-6: $I_c/I_{an}$ ratio at extreme cathodic conditions of -1.3 V of the different activated samples with (a) micropore volume contribution and (b) oxygen content.
Figure 7-7: Cyclic voltammograms at a scan rate of 5 mV s⁻¹ of (a) KOH-0 and (b) KOH-0.1, shifting the cut-off potentials to more negative values; -1.3 V (black), -1.4 V (red) and -1.5 V (blue).

Upon expanding the potential window to more anodic conditions at more positive currents, an oxidation peak is evident at a voltage ~ 0.3–0.35 V in the CVs of low activated samples. A reduction peak occurs at ~ 0.2 V and -0.3 V during the cathodic scan in KOH-0 and at ~ 0.2 V for all other activated carbons, which could be related to the reduction of the samples. The oxidation of the low activated samples exhibit a clear oxidation peak during the positive scan and the reverse processes did not occur at the same potential. This is attributed to the oxidation of the surface functionalities that are initially present in these samples, and further introduction of oxygen-containing functional groups when overcharging the electrode materials [429]. Hence, the electroactive redox species are introduced during the voltammetric cycles when the positive cut-off potential is extended to 0.4 V and 0.5 V with noticeable oxidation and reduction peaks. This indicates an increase in the surface oxygen groups during the positive scan that cannot be completely reversibly reduced during the cathodic scan. For the higher activated samples, KOH-0.1, KOH-1, KOH-2 and KOH-3, the oxidation reaction process occurs when the potential window is extended beyond 0.3 V, and a small hump is observed at 0.2 V during the negative scan. However, a clear but broad hump during the cathodic scan around a voltage of ~ 0.35–0.4 V is observed when the applied potential was extended towards 0.4 V and 0.5 V, with an irreversible reduction peak occurring during the negative scan. This could be attributed to the presence of high oxygen content in the samples before electro-oxidation of water in an alkaline medium. The introduction of redox pairs in the high activated carbons have restricted electrochemical reactivity compared to the primary functionalities already present in the structure and hence smaller reduction peaks are observed in these samples due to high irreversibility [151].
To check whether external factors have affected the CV profiles of the different carbon electrodes, the nickel foam used as the current collector throughout all experiments was cycled at extreme potentials. Figure 10-25 shows that the nickel foam possesses a similar trend at very positive/negative cut-off potentials; yet, the current values recorded are very low, and hence the nickel had an insignificant contribution to the electrochemical behaviour of the different activated samples.

7.3.3. *In-situ* Raman Spectroscopy Characterisation

To complement the CV measurements and investigate the underlying reason of different behaviour different porous carbon electrodes, *in-situ* Raman spectroscopy was employed to gain a better understanding of the mechanism of the hydrogen evolution and adsorption mechanisms in the porous carbons. This technique allows the structural characterisation of carbon materials at different potentials and identifies changes at the carbon surfaces upon their electrochemical oxidation or reduction. The potentials applied to collect the Raman spectra was done following chronoamperometry to ensure stable potentials and was based on the potentials previously used in the cyclic voltammetry experiments. A spectrum was first collected at -0.5 V and was further decreased to more negative potentials where electrochemical reduction occurs and then returning to more positive potentials. The Raman spectra of the different activated carbons recorded in three-electrode systems in 6 M KOH are presented in Figures 7-8 and 10-26.
The D (~1330 cm\(^{-1}\)) and G (~1580 cm\(^{-1}\)) bands are observed in all experiments, a characteristic of graphene-based carbons. The D-band corresponds to the presence of defects in the carbon structure, and the G-band is related to the graphitic lattice vibration mode. Upon decreasing the potential, different spectra were obtained in different porous carbon samples. KOH-0 spectra reveal that the D-band’s shift is insignificant, while the G-band position was shifted by almost 10 cm\(^{-1}\) Raman shifts in the negative direction upon decreasing the potential to -1.1 V. This can be attributed to a change in the hydrogen content in the carbon bulk and/or a slight change in the sp\(^2\) domain size. In addition, the G-band broadened upon decreasing the applied potential, illustrating that a higher degree-of-disorder is introduced into the structure upon applying extreme potentials. The change in the bands’ positions and widths are shown in Figure 7-9. These results are also confirmed with the increase of relative intensity ratio of the D-band (\(I_D\)) to the G-band (\(I_G\)) (Figure 10-27). Applying potentials more negative than -1.1 V to this sample caused the evolution of hydrogen bubbles and hence the contact with the current collector is lost and the spectra cannot be recorded. The hydrogen evolution occurred in these samples as indicated.
by CV and *in-situ* Raman spectroscopy experiments, yet the chemisorption of the hydrogen gas was too weak to be recorded before the bubbling process. This is attributed to two factors: i) the narrow microporous morphology in these samples, which enhances the hydrogen chemisorption and trapping in the ultra-porous structures, and ii) low oxygen content, that impedes the electrolyte wettability on the carbon surfaces. Similar behaviour was recorded for KOH−0.005, KOH−0.01 and KOH−0.1 samples. Hence, the hydrogen gas evolution in these samples, as shown in the CV curves, is detected before recording the hydrogen chemisorption, regardless of the facile formation of the weak carbon-hydrogen bonds in unsaturated sites in the carbon bulk.

Figure 7-9: Variation of (a) width and (b) position of D- and G-bands with the potential vs. Ag/AgCl of KOH-1 activated carbon electrode

When the KOH activation ratio was further increased, a different behaviour was observed. Decreasing the applied potential introduced two bands at ~1110 cm⁻¹ (D4) and 1500 cm⁻¹ (D3), which both correspond to the electrochemical hydrogen storage, and are assigned to C(sp²)-H and C=C stretching vibrations, respectively [452]. This suggests that the bands observed are a consequence of the formation of carbon-hydrogen bonds and a structural change on the carbon surface occurs when the potential is decreased to -0.8 V in KOH-0.5 and KOH-1 samples, and at -0.9 V for KOH-2 and KOH-3 samples. The D and G bands are both narrowed upon the introduction of D3 and D4 bands, which have been suggested previously as a direct consequence of the hydrogenation of carbon [318]. The bands appear and disappear simultaneously, which indicates the reversibility of hydrogen chemisorption. However, these bands appear at -0.8 V for KOH-1 sample and at -0.9 V for KOH-2 sample, showing that hydrogenation is easier in the former sample. In addition, D3 and D4 bands disappear when increasing the potential for the different activated carbons. The potential corresponding to complete reversibility of the hydrogen reduction is -0.2 V for KOH-0.5, -0.6 V for KOH-1 and -0.5 V for KOH-2 sample. This is due to the different trends obtained
in total pore volume, specific surface area and oxygen content, in which the increase in oxygen surface functionalities, along with the specific surface area and wide pore size distribution, does not only enhance the adsorption of hydrogen onto the porous media, but also improves the reversibility of the reduction reaction that occurs at negative potentials. The different oxygen functionalities enhance the wettability of the ultra-microporous carbons and therefore the chemisorption of the hydrogen to the carbons. The increase in pore volume improves the transport of the hydrogen ions/atoms in and out of the porous networks and permits more active sites for the nascent hydrogen [425]. All of the mentioned factors are deduced to affect the rate of hydrogenation of the carbon atoms and finding the right configuration of all key factors plays an important role in optimizing the porous carbons for the required application and preventing hydrogen evolution for supercapacitor devices at extreme conditions. These results substantiate the impedance spectra analysed at different potentials vs. the reference electrode in Chapter 6 whereby different potential limits were realized for different porous matrices.

The $I_D/I_G$ ratio (Figures 7-8d and 10-27) followed a similar trend in all high activated samples upon decreasing the potential, whereby the degree-of-disorder in the graphitic structure increased once the carbon-hydrogen bonds formed at -0.8 V or -0.9 V for different samples, and then decreased upon further decrease in the potential. This could be attributed to the introduction of the D3 and D4 bands when carbon hydrogenation occurs, whereby the intensity and the width of the first order D-band decrease, hence decreasing the $I_D/I_G$ ratio. The position of both first-order bands shift by almost 10 Raman shifts, the D-band to lower frequency, and that of G-band to a higher frequency, confirming the transition from a graphitic to more amorphous carbon [453].

Going to more positive potentials and starting from -0.5 V, no changes in the bands have been observed in the low activated carbons, as shown in Figure 7-10a. On the contrary, the recorded spectra show very similar behaviour to that obtained when the electrodes were negatively polarized before going to more positive potentials. This confirms that applying potentials close to the electrolysis of water would not affect the surface chemistry of these carbons and hence their durability is promising as electrode materials for supercapacitor devices. The width of both first-order bands and their respective positions insignificantly changed upon increasing the positive cut-off potential to 0.5 V. The ratio between the D and G band intensities ($I_D/I_G$) stays almost constant with the electrochemical processes, shown in Figure 10-27. This indicates that the electrochemical oxidation treatment does not degrade these samples and the degree-of-disorder of the graphitic structure stays constant, and hence the carbon surface is not modified. This can be attributed to the porous structure that is dominated by ultra-micropores in the samples and hence the evolution of oxygen, and as
detected by the CV curves at low scan rates, cannot reach the smallest pores and the number of unsaturated active sites in these samples within the short Raman spectra scan. This is also confirmed by CV profiles at higher scan rates of 50 mV s$^{-1}$, whereby the cathodic humps at 0.2 V are less pronounced since the carbons electrodes are cycled at high scan rates and the evolution of oxygen gas would not invade the narrowest microporous structures in the specified time lapse (Figure 10-28).

As for the higher activated samples, significant changes in the surface chemistry of the porous carbons occurred upon applying more positive potentials. The D-band and G-band widths decreased by almost 25% and 10%, respectively, and the D-band was shifted to lower frequencies when the potential was increased, shown in Figures 7-10b and 10-29. The intensity ratio between both bands ($I_D/I_G$) also increased when the potential window was extended beyond 0 V, confirming the modification in the carbon structure and an increase in the degree-of-disorder of these carbons. The initial composition of these samples with high oxygen content, hence Faradaic contribution, as previously shown, might have had a contribution in the oxygen evolution at these potentials. In addition, the meso- and macropores ease the transport of the oxygen ions/atoms into the carbon bulk, which modifies the surface chemistry of the materials. All of the aforementioned factors play a role in determining the stability of the multifarious porous carbons at extreme conditions. Despite the fact that oxygen evolution in the three-electrode systems employing low-activated porous carbons as electrode materials did not show significant changes, the latter conveyed poor electrochemical behaviour at high current densities (Chapter 4). On the other hand, high-activated samples showed a significant change in the surface structure at the extreme potentials and yet, their electrochemical performance was recorded to be excellent at different conditions within the potential limits. These results emphasize the importance of the advantage and drawbacks of different carbon materials with varying different parameters, and the necessity of an in-depth investigation of the different characteristics of porous structures for their intended final application.
Figure 7-10: Raman spectra for (a) KOH−0 and (b) KOH−1 samples at different potentials going to more positive potentials.

7.4. Conclusions

In this chapter, porous carbons with different pore structures and surface chemistries have been investigated to identify the effect of oxygenated functional groups on their performance as supercapacitor electrode materials. The combination of chemical and electrochemical characterisation methods was used to determine the electrochemical surface properties of KOH−activated carbons. The results in this work convey the importance of entwining a whole suite of characterisation techniques to fully explore the nature of porous materials and their electrochemical behaviour in supercapacitors. Measurements at extreme cathodic and anodic conditions of different porous structures revealed that the porosity, PSD and surface functionalities play an important role in delaying the electro-reduction and/or oxidation of water solvent in aqueous electrolytes, and therefore nascent gas formation. This allows the application of aqueous electrolytes beyond the thermodynamic potential limits and therefore opens a platform to delivering higher energy and power densities. The techniques used herein, including in-situ Raman spectroscopy, CV, XPS and TPD coupled with mass spectrometry confirmed that the increase in oxygen surface functionalities, together with a sufficiently wide PSD, allow an easy wettability of electrodes and hence reversible hydrogen chemisorption. The hydrogenation of carbon atoms can hence be delayed to occur, highlighting the importance of surface chemistry and porous texture of the carbon materials. The reversible hydrogen oxidation process is further delayed at high activation conditions due to the combination of high oxygen content and ultra-microporous structures which give rise to strong hydrogen adsorption and trapping in the porous media and hydrogen storage at energetically different carbon sites. The results show that most of the active sites for hydrogen chemisorption are located in the microporosity and if it is not accessible by the...
electrolyte, no hydrogen storage occurs. Furthermore, the extreme anodic and cathodic conditions modified the surface chemistry of the carbons at different conditions, which indicates that all factors that affect the hydrogenation of carbon and its stability at extreme electrochemical conditions have to be considered for optimized processes in supercapacitor applications. This study, along with the previous concatenation of techniques employed on KOH-activated carbons as model systems suggest the prominence of understanding the co-dependence of various chemical, structural and electrochemical properties of the materials under investigation. Only this would allow the depiction of the portrait of a “best” performing material for a designated final purpose.
Chapter 8

Integration of Supercapacitors into Printed Circuit Boards


Scope of this chapter: Fabrication of supercapacitor-printed circuit boards in aqueous and all-solid state systems: opening a manifesto for the hybridization of fuel cells and supercapacitors in a well-known and cost-effective design.
8.1. Introduction

Physically integrated energy storage devices are gaining increasing interest due to the rapid development of flexible, wearable and portable electronics technology [8, 454-457]. Hence, new versatile, flexible, environmental-friendly and lightweight materials with specific electrochemical properties are in high demand to meet the various energy and power needs for energy storage devices [458, 459]. Electrical energy storage systems combining two or more storage devices, including fuel cells, supercapacitors and/or batteries have been previously addressed and shown a great potential in utilising the advantages of each device and complementing its drawbacks [460, 461]. Supercapacitors acquire high power densities and fast response times while fuel cells use a clean energy source and can recover most of the wasted heat, yet are limited with their long time constants. Batteries, on the other hand, exhibit high energy densities but are still limited with low power delivery and cycle life. As a result, all the mentioned energy storage devices offer, when hybridized, a great technology for the integration of renewable sources that meet the necessary requirements of different applications and provide the benefits of peaking power, standby and load following modes [462, 463].

Supercapacitors have gained increasing interest in a range of applications including automotive and hybrid electrochemical systems due to their long cycle life, rapid charging-discharging and high power density compared to batteries [54, 464]. However, the major drawback of supercapacitors is their low energy density, and hence the development of new electrode materials to meet the requirements of both high energy and power densities is gaining increasing interest [465]. Hybrid SCs with asymmetrical configurations have recently gained increasing interest, offering higher energy and power densities, whereby Faradaic and electrostatic processes are both used as means for the storage mechanism [244, 466, 467]. While extensive research has been, and continues to be, dedicated to developing improved materials for supercapacitors, much less attention has gone into looking at how they are packaged and physically integrated with other power sources to form unitised hybrid systems.

On the other hand, the advantages associated with integrating fuel cells into PCBs are well known. Polymer electrolyte membrane fuel cells (PEMFC), direct formic acid fuel cells (DFAFC) and direct ethanol fuel cells have been fabricated using the printed circuit board (PCB) technology [259, 263, 264, 468], and the approach is being commercialized by the likes of Bramble Energy in the UK [469]. Printed circuit boards typically consist of fibreglass/epoxy composites, coated with a thin layer of conductive copper [262]. The flow-field can be constructed from the insulating composite and the conducting layer (typically
protected with an anti-corrosive layer) can act as the current collector. The PCB approach to constructing fuel cells provides a range of advantages, including robustness, rapid manufacture times, low cost and design flexibility [259]. The PCB technology has been scaled-up to develop an array of functional miniature fuel cell devices, providing power of several hundred watts[259]. It has also been used as a tool for the analysis of current distribution in fuel cells [258, 470], and as design for both flow fields and current collector simultaneously [260]. With its flexibility, ease-of-design and scalability, adopting the printed circuit board as a thin current collector for supercapacitors would ideally allow the reduction of a number of bulky materials used for a supercapacitor and provide isolation of the two electrode compartments without using a separator.

The scope of integrating fuel cell and supercapacitor technology into a single integrated construct would therefore offer the opportunity to i) improve fuel cell performance with only marginal increases in cost, weight and volume and ii) increase the volumetric capacitance and energy and power density values in supercapacitors. While the concept of PCB encapsulated capacitors has been asserted in the patent literature [471, 472], to our knowledge this is the first time that a supercapacitor PCB has been demonstrated.

This proof-of-concept study shows how supercapacitors can be integrated into printed circuit board structures [391]. The PCB construct offers a low-cost easily manufactured means of making supercapacitors and can directly integrate supercapacitors with PCB fuel cells to make for a highly flexible hybrid power source. Supercapacitors using commercially available carbon electrodes have demonstrated good specific capacitance up to 120 F g⁻¹, and power density ranging between 10 kW kg⁻¹ and 20 kW kg⁻¹ [473, 474]; such standard materials have therefore been used for integration into PCB composites using neutral electrolyte without a separator. In addition, an all-solid-state supercapacitor PCB has been fabricated using a gel electrolyte. Results are compared using the same materials in standard coin cells.

8.2. Experimental

8.2.1. Preparation of Electrode Materials and Gel Electrolyte

Commercial carbon, NAC, was used as the electrode material and was mixed with PVDF binder with 95:5 wt.% composition in NMP solvent. The carbon pastes were manually cast onto the Arlon DiClad PCB, and on nickel foam current collector for the coin cell devices, to
obtain a constant mass loading of 2 mg cm$^2$ of active electrode materials. Whatman glass microfibre filter papers were used as electrical separator materials where indicated.

The flexible gel electrolyte was prepared by mixing 6 g PVA powder in 60 ml deionised water using magnetic stirring at 90°C. 6 g of 0.5 M Na$_2$SO$_4$ was subsequently added to the mixture and stirred until the solution became clear. It is worth noting that the choice of electrolyte in this chapter differs from the rest of the thesis, as neutral electrolytes were favoured in the PCB construct due to the presence of copper as a current collector, already impregnated in the as-received DiClad laminates. The application of alkaline or acidic electrolyte media would have caused the rapid deterioration of the supercapacitor performance due to the reaction between copper and the non-neutral media.

8.2.2. PCB Properties and Assembly of the Supercapacitor-PCBs

The 0.42 mm thick DiClad PCBs (85 mm $\times$ 70 mm circuit size) were used as supplied. The DiClad laminates, composed of woven fibreglass/polytetrafluoroethylene (PTFE) composites were used as the substrate for the PCB devices. A thin copper film (38 μm) was electrodeposited on one side of each of the laminates, to provide electrical conductivity, and a conductive carbon ink, which acts as a current collector for the supercapacitor PCBs (SC-PCBs), was coated on top of the copper with a thickness of 35.5 μm and 4 cm diameter circle. The prepared carbon electrode pastes were cast on the conductive ink area and vacuum dried overnight to give a final total mass of 2 mg cm$^{-2}$ of physical surface area. Figures 8-1 and 3-16 illustrate the PCB design used prior to assembly.

![PCB layout](image)

Figure 8-1: PCB layout constituting the base of fibreglass/PTFE composite, a thin layer of copper coating along with another layer of carbon ink on which the activated carbon is deposited on.
For the PCB device in aqueous electrolyte medium, the electrode-coated DiClads were separated by two pre-impregnated (prepreg) composite bonding fibres, (Arlon-47N), each of 80 μm thickness, prior to hot pressing. The prepregs were laser-cut to the same dimensions of the PCBs using a CO₂ laser cutter/engraver LS3020 (HPC Laser Ltd, UK) and pre-vacuumed at room temperature for 2 h. The whole device, composed of the PCB and two prepregs, was then hot pressed at 140°C (curing temperature of prepregs) at a pressure of 2 bar for 1 hr in a multilayer press (RMP 210, Bungard, Germany). The final thickness of each of the prepregs ranged between 40 μm and 50 μm after the curing process in the hot press. The SC-PCB device was then irrigated with 0.5 M Na₂SO₄ solution via an access hole in the PCB which was subsequently taped to prevent any electrolyte loss.

The all-solid-state PCB was prepared using the same procedure as the aqueous one without using the prepregs material. The Na₂SO₄-PVA gel electrolyte was placed between both electrodes along with Whatman filter papers, acting as a separator and gently pressed. Figure 8-2a,b demonstrates the layering of the two different configurations of the supercapacitor PCB assemblies, with gel and aqueous electrolytes, respectively.

Figure 8-2: Schematic of the SC-PCBs, (a) as an all-solid-state PCB using a gel electrolyte and (b) in aqueous media.

8.2.3. Characterisation of Porous Texture

Suitable characterisation of the electrode materials used in the SC-PCB was necessary in order to make a fair comparison with other systems reported in the literature. The surface morphology of the activated carbon was examined using SEM operating at 10 kV. Degassing of the carbon sample at 300°C using a sample degas system was followed by a collection of nitrogen sorption isotherms. The total pore volume of the activated carbon was
calculated at a relative pressure ($P/P_0$) of 0.99 and specific surface areas (SSA) were obtained using Brunauer-Emmet-Teller (BET) method at a relative pressure range between 0.001 and 0.2. Non-local density functional theory (NLDFT) was used to determine the micropore volume [475].

8.2.4. Electrochemical Characterisation

Cyclic voltammetry (CV) at scan rates of 1, 2, 5, 10, 50, 100 and 200 mV s$^{-1}$ were performed in the voltage range 0–2 V in the aqueous and all-solid-state coin cell configurations and SC-PCBs using a potentiostat.

Recalling the Eqns. derived in Chapter 3, the specific capacitance was evaluated from the CV curves using Eqn. (8-1):

$$C_s = \frac{1}{2} \int \frac{I(V) dV}{s \Delta V \ m} \quad (8 - 1)$$

where $I$ is the current (A), $V$ is the voltage (V), $s$ is the sweep rate of the cyclic voltammogram (V s$^{-1}$), $\Delta V$ is the voltage range the sweep is carried within (V), and $m$ is the mass of the electrode materials (g).

Galvanostatic charge-discharge cycles (GCD) at current densities ranging between 1 A g$^{-1}$ and 20 A g$^{-1}$ (when possible) were conducted, and the specific capacitances ($C_s$) were calculated from the GCD curves for comparison to the values attained by CV measurements using Eqn. (8-2):

$$C_s = \frac{i \ t}{\Delta V} \quad (8 - 2)$$

where $i$ is the current density (A g$^{-1}$), $t$ is the time (s) needed for the discharge half-cycle, and $\Delta V$ is the voltage range (V) in which the cycling is applied.

The energy density ($E_v$) and power density ($P_v$) based on the area-specific volume of the device (SC-PCB or coin cell) on which the carbon electrodes have been coated (without including the edge material) were obtained from Eqn. (8-3) and (8-4):

$$E_v = \frac{1}{2} C \frac{v^2}{3600 \ v} \quad (8 - 3)$$

$$P_v = \frac{E}{t} \quad (8 - 4)$$

where $C$ is the capacitance (F) and $v$ is the volume of the device (cm$^3$).
The energy density \( (E_m) \) and power density \( (P_m) \) based on the total mass of the active materials used in the device were calculated following Eqn. (8-5) and (8-6):

\[
E_m = \frac{1}{2} C_s V^2 \quad (8-5)
\]

\[
P_m = \frac{E_m}{\Delta t} \quad (8-6)
\]

Potentiostatic electrochemical impedance spectroscopy (EIS) was performed in a frequency range between 0.1 Hz and 1 MHz vs. open circuit voltage with an AC perturbation of 10 mV; the different resistances were inferred from the impedance curves.

8.3. Results

8.3.1. Porous Texture and Surface Morphology Characterisation

The pore morphology and pore size distribution (PSD) of the commercial carbon NAC was characterised using SEM and nitrogen sorption isotherms, respectively. Table 8-1 and Figures 10-30 and 10-31 summarize the properties of the activated carbon. It is clear that NAC has a disordered morphology with relatively high SSA and bulk density, yet lower compared to functionalised carbons with KOH, H₃PO₄ and other activating chemical agents, reaching 3200 m² g⁻¹ SSA and 0.91 g cm⁻³ bulk densities \[421, 476-479\]. The sorption isotherm and NAC exhibit a Type I isotherm, characteristic of microporous solids (described in more detail in Chapter 4).

The major parameters that enhance the electrochemical behaviour of electrode materials in supercapacitor applications include high surface areas, a wide pore size distribution and an interconnected porous structure. In addition, low values of packing density can affect the volumetric energy and power densities of the supercapacitor devices \[480\]. The effect of these parameters on the electrochemical performance in the coin cells and SC-PCBs is highlighted in the following section.

Table 8-1: Structural properties, including bulk density, SSA determined by BET and total pore volume determined by NLDFT method commercial carbon NAC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk Density (cm³ g⁻¹)</th>
<th>SSA (m² g⁻¹)</th>
<th>Total Pore Volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAC</td>
<td>0.19</td>
<td>1466</td>
<td>0.74</td>
</tr>
</tbody>
</table>
8.3.2. Electrochemical Characterisation in Coin Cells

Electrochemical measurements were first conducted in coin cell devices using aqueous and gel electrolytes to assess the performance of the activated carbons in standard operating cells. The coin cells were fabricated in aqueous 0.5 M Na$_2$SO$_4$ electrolyte solution and as a solid-state coin cell with Na$_2$SO$_4$-PVA gel electrolyte. The total mass loading of the active material was similar to that used in the SC-PCBs to ensure relative comparisons between both configurations. The electrochemical performance of both NAC coin cells is presented in Figures 8-3 and 8-4. NAC exhibited a stable performance in the voltage range of 0−2 V in the aqueous electrolyte with a CV profile approaching a rectangular shape, in comparison with the activated carbon in the gel electrolyte, which presented a quasi-rectangular profile (Figure 8-3). The performance of both of the symmetric devices exhibits a profile characteristic of electrical double-layer capacitors [34].

![Normalized cyclic voltammograms of NAC coin cells in (a) Na$_2$SO$_4$ electrolyte and (b) Na$_2$SO$_4$-PVA electrolyte at different sweep rates increasing from 1 mV s$^{-1}$ to 200 mV s$^{-1}$.](image)

Figure 8-3: Normalized cyclic voltammograms of NAC coin cells in (a) Na$_2$SO$_4$ electrolyte and (b) Na$_2$SO$_4$-PVA electrolyte at different sweep rates increasing from 1 mV s$^{-1}$ to 200 mV s$^{-1}$.

The specific capacitance at different sweep rates was evaluated and is reported in Figure 8-4a. Both NAC coin cells achieve specific capacitance values of 91 F g$^{-1}$ and 81 F g$^{-1}$ in aqueous and solid systems, respectively, at a scan rate of 1 mV s$^{-1}$. However, the capacitance maintained was 38% in the aqueous Na$_2$SO$_4$ electrolyte and 17% in Na$_2$SO$_4$-PVA electrolyte of initial capacitance values upon increasing the sweep rate to 200 mV s$^{-1}$. The performances in both cells are attributed to the disordered morphology of the activated carbon that does not facilitate the electrolyte diffusion into the micropores and hence the decreased performance at high sweep rates [481]. In addition, the poorer performance of the supercapacitor cell in the gel electrolyte is due to the lower ionic conductivity of the gel and
the lower wettability at the electrode/electrolyte interface. These results corroborate the GCD experiments conducted at different current densities, as shown in Figure 8-4c,d. The coin cell configurations recorded almost symmetrical charge-discharge curves with an ohmic drop of 63 mV and 312 mV at 2 A g\(^{-1}\) current density in the aqueous and gel electrolytes, respectively showing that the charge transfer resistances in the gel electrolyte are more than 5 times higher than the aqueous solvent. The EIS data confirmed that the impedance values at high frequency are higher for the all-solid-state cell (8.9 Ω cm\(^2\)), compared to the coin cell in 0.5 M Na\(_2\)SO\(_4\) (1.3 Ω cm\(^2\)), shown in Figure 8-4b. Since the interparticle and intraparticle resistances of NAC electrode materials are the same for both systems, the higher equivalent series resistance in the solid-state coin cell has a higher ohmic bulk electrolyte resistance due to the relatively low conductivity of the gel electrolyte and poor wettability of the electrode [482]. This is also reflected in the charge transfer resistance values, inferred from the semicircle in the complex plane plots. The EIS analysis of different resistive and capacitive elements is described in more detail in Chapters 5 and 6.

Figure 8-4: Electrochemical characterisation of NAC coin cells: (a) variation of specific capacitance in aqueous Na\(_2\)SO\(_4\) and Na\(_2\)SO\(_4\)-PVA electrolyte with the sweep rate, (b) normalized Nyquist plots with the coated surface area of the electrodes comparing two different electrolytes in the frequency range 0.01 Hz-1 MHz and GCD cycles at different
current densities in (c) Na$_2$SO$_4$ aqueous electrolyte solution and (d) Na$_2$SO$_4$-PVA gel electrolyte.

Upon cycling the coin cells for 5000 charge-discharge cycles, the capacitance retention was found to be 44% for the coin cell in an aqueous medium, and 70% for the solid-state coin cell at 2 A g$^{-1}$ current density, shown in Figure 8-5a. The limited electrochemical stability is attributed to the disordered structure of the commercial carbons that does not consist of hierarchical porous structures, compared to fabricated carbon materials reported in the literature [77, 392, 483]. In addition, the extended potential window up to 2 V might lead to the evolution of nascent gases that abrupt the electrolyte ion diffusion, and therefore diminishes the capacitive performance; although different studies have demonstrated good stability in aqueous Na$_2$SO$_4$ up to 2 V [232, 484-487]. A current leap usually occurs when the cell voltage is extended to 2 V in these electrolytes, demonstrating the gas evolution at the anode and/or cathode, thus implicating lower potential limits to ensure excellent stability and cyclability of the supercapacitor device [488]. This may be extensively enhanced if carbons with an optimised hierarchical porous network were used as the electrode materials and decreasing the potential window to 1.8 V in the electrolyte media used herein [489-491]. The reason for choosing NAC as an electrode material in this study was to confirm the potential application of SCs in PCB construct, which can then be extended to a whole range of different carbon materials along with pseudocapacitive materials in aqueous or solid electrolyte systems.

The Ragone plot presented in Figure 8-5b of the coin cells in different electrolytes demonstrates that a volumetric energy density of 0.27 mWh cm$^{-3}$ and 0.2 mWh cm$^{-3}$ are achieved at power densities of 8.8 mW cm$^{-3}$ and 9.8 mW cm$^{-3}$, in the aqueous and solid-state full cells, respectively. The volumetric densities can be further boosted with higher mass loadings of electrode materials whilst maintaining a good capacitive performance [83]. In this instance, using NAC as the electrode material would result in sluggish electrochemical behaviour if we were to increase the mass loading. This is due to the disordered morphology, low total pore volume and packing density of the electrode material. This would consequently lead to extended electron/ion transport pathways to the pores and therefore loss of the initial capacitance value upon increasing the sweep rate of CV or current density of GCD.
Figure 8-5: (a) Cycling stability test of NAC coin cells in Na$_2$SO$_4$ and Na$_2$SO$_4$-PVA electrolytes and (b) Ragone plot of the volumetric energy and power densities of the activated carbons in the coin cell configuration in both electrolytes.

If the volumetric energy and power densities were calculated based on the volume of the carbon electrode only, energy densities 17.3 mWh cm$^{-3}$ at a power density of 554 mW cm$^{-3}$ for the aqueous system and 12.6 mWh cm$^{-3}$ at 620 mW cm$^{-3}$ in the gel electrolyte are recorded (Figure 8-6a). The corresponding gravimetric energy densities (based on the mass of active carbon in both electrodes) achieved were 31.2 Wh kg$^{-1}$ and 20.3 Wh kg$^{-1}$ at a power density of 1 kW kg$^{-1}$ in the aqueous and all-state coin cells, respectively which are similar to those achieved in the literature for the same activated carbon [492, 493]. Both gravimetric and volumetric Ragone plots show the same trend of energy density upon increasing the power density, as shown in Figure 8-6b.
8.3.3. Electrochemical Characterisation in SC-PCBs

These results set the baseline for coin cell supercapacitor performance using an established carbon electrode material operating in aqueous and solid-state electrolyte systems. The electrochemical behaviour of SC-PCBs was tested in both aqueous 0.5 M Na$_2$SO$_4$ and Na$_2$SO$_4$-PVA gel electrolytes. Cyclic voltammograms of the NAC in both electrolyte solutions were performed at a range of scan rates from 1 mV s$^{-1}$ to 200 mV s$^{-1}$, presented in Figure 8-7. NAC exhibited a stable performance in the voltage range of 0−2 V in the aqueous electrolyte with a CV profile of almost rectangular shape, in comparison with the activated carbon in gel electrolyte, which presented a quasi-rectangular profile. The performances of both flexible symmetric devices are characteristic of electrical double-layer capacitors, which is similar to the behaviour obtained in the coin cells. The specific capacitance at a scan rate of 1 mV s$^{-1}$ recorded values of 93 F g$^{-1}$ and 84 F g$^{-1}$ in aqueous and all-solid-state devices, respectively. The results obtained demonstrate that the SC-PCBs can deliver the capacitance achieved in coin cell systems with the same active material and can be optimized with a smaller coating surface area for the carbon electrodes along with optimization of the fabrication of the PCBs. These results highlight the advantageous application of supercapacitors to complement batteries and/or fuel cells in real-life application, which require high power densities, specifically at abrupt acceleration or braking; i.e. at very high frequencies.

Figure 8-6: Ragone plots of (a) volumetric energy and power densities of NAC coin cells based on the volume of carbon electrode only and (b) the gravimetric energy and power densities of NAC coin cells in aqueous and gel electrolytes.
Figure 8-7: Normalized cyclic voltammograms of NAC SC-PCBs at different sweep rates increasing from 1 mV s\(^{-1}\) to 200 mV s\(^{-1}\) in the voltage range of 0–2 V in (a) Na\(_2\)SO\(_4\) electrolyte solution and (b) Na\(_2\)SO\(_4\)-PVA electrolyte

Figure 8-8a shows that the capacitive performance quickly diminished upon increasing the sweep rate to 5 mV s\(^{-1}\) in both electrolytes; however, the values of the specific capacitance decreased gradually with a further increase of the scan rate to 200 mV s\(^{-1}\). This is due to the morphological structure of the activated carbon used as electrode material, previously shown in the coin cell performance.

The GCD curves at different current densities demonstrated almost symmetrical and triangular charge/discharge curves, shown in Figure 8-8c,d. A smaller voltage drop (iR drop) of 7 mV at the start point of the discharge curve was obtained in the aqueous system at 2 A g\(^{-1}\) current density, compared to 186 mV in the gel electrolyte. EIS plots of the SC-PCB devices, illustrated in Figure 8-8b, showed a similar trend for the electrolytes obtained with the GCD curves, with a higher impedance value in the all-solid-state system at high-frequency (10 kHz–1 MHz). This is usually attributed to the lower conductivity of the gel electrolyte caused by the addition of a polymer and therefore the difference in the bulk electrolyte resistance and electrode/electrolyte resistances between Na\(_2\)SO\(_4\) and Na\(_2\)SO\(_4\)-PVA [494]. The high-frequency impedance governing the bulk electrolyte and interparticle and intraparticle resistances of the NAC electrode material was \(\sim2.6\ \Omega\ \text{cm}^2\) in the aqueous electrolyte; a similar value to that achieved in the coin cell. However, the high-frequency impedance in the all-solid state device of 21.7 \(\Omega\ \text{cm}^2\) was much higher in the SC-PCB device compared to the coin cell with the same electrolyte. These results indicate that the bulk ionic resistance of the electrolyte is higher in the all-solid state SC-PCB, possibly due to the loss of water content upon exposure to air in the SC-PCB and therefore decrease in the ionic mobility and conductivity of the gel electrolyte [495]. This also led to impeding the electron/ion diffusion at the electrode surface and therefore an increase in the charge transfer...
resistance, whereupon the electrolyte resistance at the electrode/electrolyte interface has also increased due to the loss of gel conductivity.

Figure 8-8: Electrochemical characterisation of NAC SC-PCBs (a) variation of specific capacitance in aqueous Na$_2$SO$_4$ and Na$_2$SO$_4$-PVA electrolyte with the sweep rate, (b) normalized Nyquist plots with the physical coated surface area of the electrodes comparing two different electrolytes in the frequency range 0.01 Hz-1 MHz and GCD cycles at different current densities in (c) Na$_2$SO$_4$ aqueous electrolyte solution and (d) Na$_2$SO$_4$-PVA gel electrolyte.

Figure 8-9a shows that the SC-PCB with the NAC electrodes retained 76% of the initial capacitance in the Na$_2$SO$_4$ electrolyte after 5000 charge-discharge cycles at a current density of 2 A g$^{-1}$. However, SC-PCB in gel electrolyte showed a capacitance retention of 42% of its initial value after the cycling test. The stability of the aqueous system was higher than that acquired in the coin cell, which is likely due to the undesirable evolution of gases in the sealed coin cell system occurring at the upper voltage limit. This causes the rapid degradation of the coin cell performance. On the other hand, the SC-PCB device incorporates drill holes that allow evolved gas to be released from the setup, hence delaying the deterioration of the capacitive performance upon repetitive cycling [151, 152, 496]. As for the all-solid state devices, the fully sealed design of the coin cell system ensures that the water content of the gel electrolyte is maintained throughout the cycling test; whereas the
ventilated SC-PCB device can lead to electrolyte dehydration, and thus diminished wettability and ionic conductivity of the gel upon its complete solidification. The stability of the all-solid-state SC-PCB can be improved by sealing the device and hence maintaining the water content of the gel electrolyte. This boosts the ion mobility by enhancing the conductivity of the gel [495, 497]. It is also worth mentioning that the decomposition of the electrolytes were witnessed in both systems with different media due to the chosen voltage range, in which Na2SO4 starts decomposing around 1.6 V, and thus the deteriorated performance after a few thousand cycles in the coin cells and PCBs.

The Ragone plot, shown in Figure 8-9b demonstrates the volumetric energy density at different power densities of the whole PCB construct. In both electrolyte media, higher volumetric energy densities are achieved in the SC-PCBs compared to the coin cell devices. The aqueous and all-solid-state SC-PCBs achieved an energy density of 0.69 mWh cm$^{-3}$ and 0.56 mWh cm$^{-3}$ at a power density of 37 mW cm$^{-3}$ and 26 mW cm$^{-3}$, respectively. The energy density values do not decrease significantly upon increasing the power density, especially for the SC-PCB in an aqueous electrolyte, where an energy density of 0.35 mWh cm$^{-3}$ is maintained at 555 mW cm$^{-3}$ power density. Since the specific capacitance is an intrinsic value and the voltage range used throughout all experiments was constant, the volumetric densities were enhanced upon eliminating bulky materials (separators, coin cell casing) to enhance the power and energy delivery. However, these values are lower than those of the micro-supercapacitor devices reported in the literature [498, 499]. Hence, increasing the mass loading per geometric surface area and using electrode materials with higher performance rates (including pseudocapacitive materials) would be the next step in fabricating SC-PCBs with higher performance [500-502].

![Figure 8-9: (a) Cycling stability test up to 5000 cycles of NAC SC-PCBs in Na$_2$SO$_4$ and Na$_2$SO$_4$-PVA electrolytes and (b) Ragone plot of the volumetric energy and power densities of the activated carbons in the SC-PCBs in both electrolytes.](image)
8.4. Conclusions

In this chapter, new insights on the fabrication of an engineered supercapacitor device were studied. Supercapacitor materials have been integrated and tested in a composite printed circuit board construct for the first time. A commercial activated carbon was used as the electrode material and its electrochemical performance in aqueous and gel electrolytes has been compared with that of a conventional coin cell configuration. The results of this work show that the approach of a supercapacitor-PCB is feasible and can deliver promising performance. The specific capacitances, and gravimetric and volumetric energy densities were compared in both configurations; it was found that a volumetric energy density of 0.56 mWh cm\(^{-3}\) at a power density of 26 mW cm\(^{-3}\) was obtained in the solid-state SC-PCB system, which is over twice the values acquired in the standard cell configuration. Similar results were obtained in the aqueous system, whereby an energy density of 0.69 mWh cm\(^{-3}\) was obtained at a power density of 37 mW cm\(^{-3}\) in the all-solid state SC-PCB, double the quantities obtained in the aqueous coin cell configuration.

While a variety of materials have been investigated to be employed as electrodes in supercapacitors, its packaging and incorporation with other electrochemical devices are still to be addressed. Fuel cell-PCBs have proven to have the potential commercialization due to the versatile benefits of the construct and therefore the PCB design was implemented in this study on supercapacitors. Building on this proof-of-concept study, higher performing, state-of-the-art materials, such as pseudocapacitive electrode materials, can be used to improve performance and act as a ‘drop-in’ to the PCB structural hardware. The approach also offers the possibility of integrating both supercapacitor and polymer electrolyte fuel cell into an established single and flexible design package to bring the best of both power and energy density to a hybridised system.
Chapter 9

Conclusions and Future Work

This thesis described the use of different characterisation techniques in attempt to understand the reasons for different electrochemical performances of electrical double-layer capacitors. The exploration of micro- and macroscopic properties of carbon electrode materials in three-dimensional scales has proven to be of eminent value for the optimisation of the capacitive behaviour of supercapacitors, tailored for the end use. The thesis starts with an in-depth analysis of the structural properties and surface chemistry of a range of KOH-activated cellulose precursors with different KOH loadings and their correlation with the electrochemical performance in a three-electrode system, independent of external factors. The surface morphology, pore size distribution, total pore volume and chemical content of the multifarious carbon powders are analysed and it is revealed that each of the mentioned factors contributes to the capacitance performance and energy and power delivery.

The range of architectural arrangements of the porous carbons is then analysed using the electrochemical impedance spectroscopy tool, investigating the capacitive performance within the nominal potential conditions and beyond. An equivalent series circuit based on the transmission line model, and using equivalent circuit elements corresponding to the real behaviour of the electrode, has been also suggested and proven to mimic the impedance spectra. Henceforth, the structural characteristics and impedance response over a wide frequency range were correlated to uncover a trend between the microporous volume and proportion with the capacitive performance at a specific frequency and applied potential.

\textit{In-situ} Raman spectroscopy was also implemented as a tool to explore the structural changes of the electrodes at extreme anodic and cathodic conditions to investigate the possibility of extending potential windows in aqueous electrolyte media with the benefit of delaying the hydrogen and/or oxygen evolution reactions. This technique paves the way for the enhancement of the energy and power delivery of supercapacitor devices, conditional to avoiding detrimental alterations to the surface chemistry of electrode materials.

Finally, the supercapacitor device was integrated within a printed circuit board design, a well-known and cost-effective construct used in the fuel cell application, showing the potential fabrication of new supercapacitor designs and the feasibility of hybridizing them with other electrochemical devices.
The key observations of this work along with insights into extending the techniques used for examining different materials and different designs are outlined in this chapter.

9.1. Insights for Improving Capacitive Performance

9.1.1. Considerations for Microstructural Design

The microstructure of electrode materials was analysed using different characterisation techniques and the relative structural impact on the overall performance of a supercapacitor was revealed in Chapter 4. The etching effect of KOH was analysed and deduced to create porous structures, which evolve from micro- to macropore dominant as the KOH loading is increased. Optimized KOH/cellulose ratios of 0.5:1 and 1:1 were found to have the highest capacitance values in three-electrode systems with excellent stability and voltage hold profiles over several thousand cycles. It was attributed to the interconnected porous structure constituting ultra-micro, micro-, meso- and macropores of a high total pore volume. Different pore sizes have been established to influence the capacitance in different ways; micropores play a major role under slower kinetic regimes and formation of electrochemical double-layer at low current densities, whereas macropores ensure the wetting of the electrode and fast ion diffusion at higher current densities, ensuring high rate performance. The interconnection between the porous structure and the electrochemical performance at different current densities or sweep rates have shown to be of great importance in tailoring the best material for the intended supercapacitor application. The relationship between form and function of porous electrodes can be extended beyond the KOH-activated carbon model systems to exploit the optimization of charging and storage mechanism in EDLCs.

By studying the electrochemical impedance spectra of the carbon electrodes, the assessment of the optimum structure becomes more challenging. Using a curtailed version of the transmission line model, the suggested equivalent circuit in Chapter 5 has proven to govern the behaviour of different porous models as electrodes in EDLCs. The different resistive and capacitive equivalent circuit elements including the bulk electrolyte resistance, double-layer capacitance, and porous matrices contribution to the frequency response are described. The evaluation of the electrical relaxation times of different PSDs calls for a trade-off between the wide PSDs and associated internal resistances inside the pores. The term of best capacitive performance can therefore be only quantified when specifying if it is frequency-dependant, and if so, the frequency it is being measured at. The non-ideal performance of the electrodes arise with the porous structure and surface functionalities, and the role of each
PSD, assuming an average pore size in each size range, is revealed. The extension of the use of the equivalent circuit model is explored in Chapter 6 by employing the impedance spectroscopy at different potentials within and beyond the normal operating conditions. The outcomes in this study confirm the conclusions of Chapter 7 and the feasibility of extending the potential windows of aqueous electrolytes, which is interrelated to the surface structure and chemistry of the electrode materials used. Thereafter, the impedance behaviour can be predicted for different porous electrodes in EDLCs. This is discussed further in the future work section. Since some applications require low-frequency electrical filtering, while other uses are in electric vehicles, the results outlined can be used to assess the energy and power delivery of a supercapacitor with the electrode material of choice for applications of specific requirements.

In Chapter 7, the study of the surface chemistry of the same carbon powders with the aid of the results outlined in Chapter 4, reveal the importance of oxygen functionalities on the carbon surface in optimizing the energy and power capabilities of an EDLC. This can be achieved by extending the potential windows of an aqueous system beyond the thermodynamic stability window of the electrolyte solution and taking advantage of the hydrogen chemisorption process on the carbon electrodes. The presence of oxygen functional groups and ultra-micropores enhance the carbon-hydrogen bonding and consequently alleviate the delay of the hydrogen evolution reaction at extreme anodic conditions. Contrarily, the oxygen evolution reaction was not pronounced in different porous structures even beyond the nominal cathodic potential values. It was revealed that applying higher potentials did not affect the surface chemistry of the carbons with low oxygen content and total pore volume. This was not the case for the activated samples with the desirable properties. The results in this work raise the question of the trade-off between different surface and structural parameters and the necessity of evaluation of the different characteristics of an optimum structure for determined applications.

9.1.2. Considerations for Supercapacitor Cell Design

One of the major drawbacks of supercapacitor devices is their low volumetric energy and power densities. This is due to the number of bulky materials used, such as the separator and the casing to insulate the device. Whilst different electrode and electrolyte materials have been intensively explored for supercapacitor applications, the encasing, commercialisation and integration with other devices is still needed and thereafter addressed in Chapter 8. Engineering new lightweight and cost-effective designs have gained increasing interest. In Chapter 8, fabrication of supercapacitors using the known printed circuit board design was investigated. A commercial activated carbon was used as a benchmark and SC-PCB devices
in solid and aqueous electrolytes were compared to standard SC coin cells. The outcomes of this chapter highlight the potential application of this construct and open the platform to its hybridisation with other electrochemical devices, already manufactured within a PCB design. The energy and power densities evaluated for both systems show that much higher values can be obtained using the SC-PCB device in both electrolytes, due to the elimination of different bulky materials and lower thickness of commercialised PCBs, yet still maintaining their structural integrity. The optimization of the SC-PCB construct using different materials will be further discussed in the future work.

9.2. Future Work

This section outlines the future experiments to be carried along with the analyses to complement the work presented in this thesis.

9.2.1. Effect of Ageing and Degradation on Microstructure

The ageing of the non-ideally polarizable electrode materials and their degradation are among the primary factors of diminishing the capacitive behaviour of an EDLC. Upon cycling the supercapacitor and/or carrying voltage hold tests, as presented primarily in Chapter 4, the electrochemical performance might degrade and a self-discharge mechanism may arise. This is due to i) the pseudocapacitive driving force governed by surface functionalities on the electrode surface, ii) extending the potential windows to extreme anodic and/or cathodic conditions leading to the decomposition of the electrolyte, and/or iii) the impurities (redox couples) in the electrolyte itself. The unreliability factor in energy storage in a supercapacitor is consequently introduced and the understanding of the self-discharge mechanism and mitigation control is necessary to improve the commercial performance. Figure 9-1 presents the surface-capacitive and pseudo-capacitive elements constituting the total capacitance, among the range of different KOH-activated carbons prior to cycling experiments. The different contributions were calculated according to the different capacitances evaluated in aqueous and non-aqueous systems, in which the latter does not include any pseudocapacitive contributions to the electrochemical performance.

It is clear that the porous structure is a major factor in dictating the percentage of diffusion-controlled processes and hence the total capacitive performance. However, studying the microstructure when the electrode is cycled or held at an extreme potential, is especially important to understand the correlation between the structural characteristics and shelf-life
of the device. The changes in the microstructures and their surface chemistry can be detected using different techniques including XPS, \textit{in-situ} Raman and EIS before and after the cycling and float tests. The self-discharge rate can be measured prior to and after the cycling experiments \textit{via} i) recording the potential difference between the two electrodes in a supercapacitor device at open circuit voltage, following charging over long periods of time or ii) employing the same procedure but in a three-electrode system and measuring the change in potential of the separate working electrode \textit{vs.} the reference electrode. The latter is usually conducted first to realize the self-discharge mechanism of the electrode itself, independent of any external factors.

The aim of this experiment is to understand the reasons for the self-discharge mechanism in different porous materials. This will allow for the optimization of the electrode material for a better shelf-life and energy and power capabilities over longer periods of time.

![Figure 9-1: (a) Kinetic analysis of KOH-1 sample from CV curve at 50 mV s\(^{-1}\) scan rate and (b) variation of the different capacitive contributions with the porous structure of KOH-\(n\) activated carbons.](image)

9.2.2. \textbf{Application of EIS as a Diagnostic Tool for Different Classes of Supercapacitors}

Most capacitors, whether EDLCs, pseudo-capacitors or hybrid capacitors, do not exhibit an ideal capacitive performance, as detected by the EIS tool (more elaborated in Chapters 5 and 6). This is due to limitations set by i) the equivalent series resistance (\textit{ESR}), representing the kinetic limitations at high frequencies and ii) less-than-90° out of phase behaviour in the complex plane plots at low frequencies due to the Warburg element in pseudo-capacitors and combination of \textit{RCPE} elements in porous matrices.
The ESR value sets restrictions on the rate at which the capacitor can be charged/discharged and therefore leads to energy dissipation and power loss in the device. Therefore, its minimization is desirable for applications at elevated power levels. On the other hand, the behaviour at lower frequencies of porous high-surface area matrices approximates the Warburg impedance, giving rise to a 45° phase angle. Therefore, applying the impedance tool to analyse the ESR variation with different materials in attempt to minimize the values in addition to distinguishing the transmission line behaviour from a pseudo-capacitance one in a hybrid system is of major importance. Figure 9-2 demonstrates the EIS profiles of a porous carbon electrode and a graphitic carbon nitride/graphene hybrid electrode. The complex plots exhibit different ESR and charge transfer resistance values. However, the impedance response at low frequencies is somehow similar and the non-ideal phase angle can be attributed to different elements in each system. The combination of a series of resistive and capacitive elements govern the response behaviour in porous EDLCs, while the Warburg element represents the diffusional limitations of Faradaic charge transfer processes and redox reactions. Therefore, the aim of this future experiment is to discern the various impedance elements in different types of capacitors and extend the EIS model developed in Chapter 5 with adding/removing/replacing circuit elements to represent a new family of universal equivalent circuits for different classes of supercapacitors. The development of these circuits would allow the identification of the elements dictating the non-ideal behaviour in different systems, optimization of the capacitive response with understanding its correlation with the microstructural properties and therefore accommodating the best-performing material for the commercial specifications of such devices.

Figure 9-2: Complex plane Nyquist plots of (a) KOH-0.01 activated carbon and (b) reduced graphene oxide-carbon nitride.
9.2.3. Optimization of Supercapacitor-PCB Design

The SC-PCBs fabricated in this work have shown great potential in delivering high volumetric energy and power densities, as discussed in Chapter 8. The configurations had comparable or even higher performances to standard coin cell supercapacitors in aqueous and solid electrolytes. However, the specific capacitance retention attained with the commercial benchmark carbon are still lower than the nominal values. This might be attributed to the incomplete utilisation of the active material in the PCB construct. Thereafter, the next step in optimising the device performances is ensuring adequate contact between the electrode material, current collector and the electrolyte. The aqueous system has shown great stability upon cycling, compared to the coin cells, which leads to the conclusion of enhancing the performance by keeping the configuration constituting drill holes. The latter provides means for the nascent gases produced at extreme anodic/cathodic conditions to exit the system, without perturbing the electrochemical performance. However, establishing the full utilisation of the electrolyte ions would constitute maintaining the aqueous solution in the device and therefore repositioning the drill holes where the gas can escape the device while keeping the solution intact inside the SC-PCB.

Contrarily, the all-solid state device has demonstrated deteriorated performance with cycling. This was explained in Chapter 8 by the drying mechanism of the water content in the electrolyte, lessening the ion mobility and conductivity and therefore dwindling the capacitive performance. Figure 9-3 shows the “depletion effect” of the PCB with gel electrolyte upon cycling. This performance can be rectified by sealing the device, and therefore eliminating any drill holes in the all-solid PCB construct in addition to insulating the device from external exposure to air. This might also open the platform for fabricating the SC-PCBs without the use of separator bulky materials to increase the energy and power delivery.

Finally, the electrode materials used in the fabrication of the SC-PCB were commercial carbons, with limited interconnected porous structure and low total pore volume. The electrochemistry can be exceedingly improved with using electrode materials with much higher specific surface area and desirable properties, the ones that the KOH-activated materials possess. The incorporation of pseudo-capacitive elements can be the next step in assembling hybrid SC-PCB devices for higher capacitances and energy and power densities. All of the aforementioned further explorations can be implemented into looking at hybridised SC-PCB devices with fuel cells in the same commercialized architecture.
Figure 9-3: (a) PCB as supplied, prior to carbon coating and (b) all-solid state SC-PCB device after cycling, showing the deteriorated structure due to dehydration of the gel electrolyte.
Publications and Conferences

Primary Publications


Secondary Publications


Conferences Attended

Talks

- 2016 STFC Early Careers Research Conference, Abingdon, UK, 2016
  Title: Functionalised Cellulose-based Nanocomposite ‘Papers’ for Electrochemical Energy Conversion and Storage
  Title: The Application of Functionalised Cellulose-based ‘Papers’ in Electrochemical Conversion and Storage Devices
  Title: The Optimization of Functionalised Cellulosic ‘Papers’ for Supercapacitor Electrode Applications
- 9th International Conference on Advanced Materials (ROCAM 2017), Bucharest, Romania, 2017
  Title: The Correlation between Porous Morphology of KOH-Activated Carbons & EIS in Supercapacitor Applications
- Modelling of Energy Materials Workshop, University of Surrey, UK, 2018
  Title: Establishing an Equivalent Series Circuit for Carbon-based Supercapacitors

Poster Presentations

- 21st Topical International Society of Electrochemistry Meeting, Szeged, Hungary, 2017
  Title: The Correlation between Electrochemical Impedance Spectra and Morphology of KOH-functionalised "Papers" in Supercapacitors
  Title: Activated KOH–Biocarbons for Supercapacitor Electrode Materials
Chapter 10

Appendices

10.1. Chapter 4 Appendix

Figure 10-1: SEM images of (a) BAC, (b) NAC, (c) KB, (d) KOH-0 and (e) KOH-0.005.
Figure 10-2: Representative volume element analysis in the three principal planes (X, Y, Z) for (a) KOH-0.1 and (b) KOH-0.5 showing that the segmented volumes are considered to be representative volumes for porosity and tortuosity factors of the bulk materials above a 0.3 fraction of the total volume. The directional tortuosities of the sample upon applying the uniform shrinkage analysis confirm that the chosen volume is a representative one as all values converge upon increasing the volume fraction. The porosity evaluated in each of the three planes is of similar value to the calculated one for the segmented volume in Avizo.
Figure 10-3: (a) Nitrogen sorption isotherms of KOH-0.005 and KOH-0.5 comparing the total pore volume of activated carbons with and without the adding a binder and conductive carbon, and cumulative pore size volume comparing activated carbon (b) KOH-0.005 and (c) KOH-0.5 with and without additives.
Figure 10-4: Capacitance retention of all activated carbons.

Figure 10-5: Nyquist plots in the frequency range of 0.1 Hz to 100 kHz at 0 V vs. open circuit voltage of (a) commercial activated carbons and (b) KOH-0.5 and KOH-1 coin cells.
10.2. Chapter 5 Appendix

Figure 10-6: Nyquist plot of KOH-3 carbon sample with the fitting of the suggested equivalent circuit in Chapter 5.

Figure 10-7: Bode plots of real specific capacitance values of all samples in the frequency range of (a) 10-1000 Hz and (b) 1000 Hz-1 MHz.
Figure 10-8: Imaginary part of the specific imaginary capacitance over the studied frequency range.

Figure 10-9: Nyquist plots showing the difference in impedance behaviour before cycling and after 5000 cycles for (a) KOH-0.005 and (b) KOH-1 samples.
10.3. Chapter 6 Appendix

Figure 10-10: EIS Nyquist plots in the frequency range of 10 mHz–1 MHz at potentials between -1–0 V of the samples: (a) KOH-0.01 and (b) KOH-1.
Figure 10-11: Nyquist plot in the high frequency range to detect any changes in the ESR and $R_{CT}$ of the samples at different potentials (a) KOH-0.005, (b) KOH-0.1, (c) KOH-0.5 and (d) KOH-2.
Figure 10-12: a) EIS Nyquist plots in the high frequency range of all samples at 0 V vs. Ag/AgCl, showing the x-intercept corresponding to ESR, and the depressed semi-circular region that corresponds to the $R_{CT}$ values and b) deduced $R_{CT}$ values of the different activated samples with varying the potential difference.

Figure 10-13: Complex Bode plots of (a) KOH-0.01 and (b) KOH-0.5.
Figure 10-14: EIS Nyquist plots in the frequency range of 10 mHz−1 MHz at potentials between -1.3−-1 V of the samples: (a) KOH-0.01 and (b) KOH-1.

Figure 10-15: EIS Nyquist plots in the frequency range of 10 mHz−1 MHz at potentials between 0.1−0.4 V of the samples: (a) KOH-0.01 and (b) KOH-1.
Figure 10-16: $R_{CT}$ values at a) cathodic and b) anodic overpotentials of the different activated samples; evaluated from the diameter of the depressed semicircle of the Nyquist plot at high frequency.

Figure 10-17: Nyquist plots in the high frequency range of (a) KOH-0 and (b) KOH-0.5. The potential (-0.4 V) was chosen randomly as all the EIS plots in the nominal potential window of every sample have a similar trend in the high frequency region. Therefore the comparison will also apply for another potential within the nominal window for comparison reasons with the extreme potentials applied.
Figure 10-18: EIS Nyquist plots of KOH-0.5 sample at different potentials, with fittings given by the suggested porous electrode model.
10.4. Chapter 7 Appendix

Figure 10-19: Raman spectra acquired for KOH-0.5 sample at 1.4 V showing a noisy signal due to oxygen gas bubbling.
Figure 10-20: C\textsubscript{1s} deconvolution XPS of (a) KOH-0.005, (b) KOH-0.1, (c) KOH-0.5 and (d) KOH-3.

Figure 10-21: Water/carbon surface contact angle of KOH-$n$ activated samples with $n =$ (a) 0, (b) 0.1, (c) 0.5 and (d) 3. The different contact angles reflect the wetting behaviour of different carbon samples with different oxygen content.
Figure 10-22: Cyclic voltammograms of (a) KOH-0.005, (b) KOH-0.01, (c) KOH-0.1 and (d) KOH-3 at different voltage ranges towards hydrogen evolution reaction.
Figure 10.23: Cyclic voltammograms of (a) KOH-0.005, (b) KOH-0.01, (c) KOH-0.1 and (d) KOH-3 at different voltage ranges towards oxygen evolution reaction.
Figure 10-24: Cyclic voltammograms of all activated carbons at a negative cut-off potential of -1.5 V and a scan rate of 5 mV s\(^{-1}\).

Figure 10-25: Cyclic voltammograms of nickel foam current collector towards more (a) negative potentials and (b) positive potentials.
Figure 10-26: Raman spectra for samples (a) KOH-0.1 and (b) KOH-0.5 at different potentials in 6 M KOH.

Figure 10-27: $I_D/I_G$ for He-Ne laser of samples (a) KOH-0 and (b) KOH-2.
Figure 10-28: Cyclic voltammograms of KOH-0 towards more positive potentials at a scan rate of 50 mV s$^{-1}$.

Figure 10-29: Variation of (a) width and (b) position of D- and G-bands with the potential vs. Ag/AgCl of KOH-1 activated carbon electrode.
10.5. Chapter 8 Appendix

Figure 10-30: SEM images of the activated carbon (NAC) showing a disordered morphology.

**Figure 10-31:** (a) Nitrogen sorption isotherms and (b) cumulative pore size distribution of NAC determined by NLDFT method.
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