

# High-power nitrated TiO<sub>2</sub> carbon felt as the negative electrode for all-vanadium redox flow batteries

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**ABSTRACT.** This work describes the design of an electrode with enhanced performance applied to all-vanadium redox flow batteries (VRFBs). This new electrode consists of a structural porous carbon felt decorated with TiO<sub>2</sub> rutile nanoparticles, which has been nitrated using ammonolysis at 900 °C. An outstanding charge and mass transfer over the electrode-electrolyte interface was observed as a consequence of the synergetic effect of N- and O-functionalization over carbon felt (CF) and the partial formation of TiN (metallic conductor) phase. Moreover, this material has not only improved in terms of catalysis towards the V<sup>3+</sup>/V<sup>2+</sup> redox reaction ( $k_0 = 1.6 \times 10^{-3} \text{ cm s}^{-1}$ ), but also inhibited the hydrogen evolution reaction (HER), which is one of the main causes of imbalances that lead to battery failure. This led to an impressive high-power peak output value up to  $700 \text{ mW cm}^{-2}$ , as well as work at high current density in galvanostatic conditions (i.e.  $150 \text{ mA cm}^{-2}$ ), exhibiting low ohmic losses (overpotential) and great redox single cell reversibility, with a superior energy efficiency of 71%. An inexpensive, earth abundant and scalable synthesis method to boost VRFBs technology based on nitrated CF@TiO<sub>2</sub> is presented, being able to overcome certain constrains, and therefore to achieve high energy and power densities.

## INTRODUCTION

Stationary energy storage systems have increased in relevance over the past decade because of their important role in grid-scale applications, contributing to systems such as intermittent renewable power sources, smart-grid integration and energy self-consumption to guarantee the electrical supply in remote areas. In this framework, the important role of vanadium redox flow batteries (VRFBs) towards providing clean and affordable energy has been well-reported in the literature.[1–4] Nevertheless, the practical implementation of this mature technology has been hampered due to their high capital cost, proving to be a critical factor for the widespread commercialization. Recently, viability studies showed that the cost of VRFB for frequency regulation is about \$560 / *kWh*,[5] making VRFBs economically uncompetitive systems.[6,7]

The cost and performance of the stack is influenced by three components: 1) membrane[8–10]; 2) electrodes[11–18] and 3) bipolar plates[19–21]. Special attention should be paid to the electrodes since they support the electrode kinetics and determine the overpotential and, consequently, the efficiency of the entire system. In addition to this, the 3D porous structure of the electrodes determines the flow and permeability characteristics that influence the mass transport overpotential incurred during operation, as well as the pressure drop across the electrode[22]. It is well known that improvements in the electrochemical performance of the electrodes can be achieved by either increasing their surface area or their electrochemical activity. At this point, it should be considered that the reported values for the kinetic constant associated to  $V^{3+}/V^{2+}$  redox reaction,  $k_0$ , spread over three orders of magnitude, showing that the surface characteristics have a strong influence on the electrochemically active surface area, as well as the reaction rate

constant. Consequently, the study of the influence of functional groups over the surface properties and  $k_0$  values is still a fundamental open question[23]. Contrary to the initial expectations considering the simplicity of the reaction mechanisms[24], kinetics towards  $V^{2+}/V^{3+}$  are far less favoured comparatively to the  $VO^{2+}/VO_2^+$  redox reaction[25], limiting the cell performance. This is a particular problem due to the sluggish kinetics of the  $V^{2+}/V^{3+}$  redox couple at the negative electrode occurring at -0.26 V vs. SHE (1), more negative than the hydrogen evolution reaction (HER) (2) in highly acidic electrolyte[26–29].



Furthermore, this fact coupled with a high charge transfer resistance ( $R_{ct}$ ) of the carbon felt electrode leads to a large overpotential of the system, preventing the charge process achieving 100% state-of-charge (SoC) and lowering voltage and energy efficiency of the battery. We have previously demonstrated[29] improved performance by the implementation of hydrogen-treated  $TiO_2$  electrodes, which enhances the electrode's electrical conductivity, leading to a small overpotential and low charge transfer resistance.

In this context, recent research [30,31] have focused on the potential enhancement of performance due to the presence of oxygen and nitrogen-based functional groups at the surface of the electrodes, as a consequence of an increase of the electrochemical kinetics of the  $V^{2+}/V^{3+}$  redox reaction. Wei *et. al.* demonstrated that TiN bonds at the electrode/electrolyte interface are able to react with vanadium to form the stable V-N-Ti intermediate, necessary for the electron transfer process[30]. Additionally, TiN has also

received substantial attention, owing to its large electrical conductivity ( $10^{-4} S cm^{-1}$ )[32] and high stability in strong acid media[33], which in our case, coupled with the functionalization of the carbon structure, contributes to the enhancement of the electrocatalytic activity towards the  $V^{2+}/V^{3+}$  redox reaction. By growing  $TiO_2$  nanowires onto the surface of the graphite felt via a seed-assisted hydrothermal approach, that are then nitrified to TiN, we have obtain energy efficiency values above 70% at high current densities up to  $150 mA cm^{-2}$ , which evidences good stability and high capacity retention.

In parallel, other authors have reported on the significant role played by the C-N bonds in the interaction with the vanadium species [34]. Nitrogen-doped carbon samples have been widely investigated for electrochemical applications, especially for the oxygen reduction reaction in fuel cells, and it has been concluded that it is the facilitated adsorption of oxygen what improves the electrocatalytic activity of these carbon materials[35–38]. Moreover, it is known that after the mild oxidation of the carbon felt at  $500^{\circ}C$  for 5 h. the cell energy efficiency is improved, which is attributed to the formation of oxygen related functional groups[39]. The appropriate formation of C-OH, C=O, and C-O functionalities increases the standard heterogeneous electron transfer rate for  $V^{3+}/V^{2+}$ , from  $3.2 \times 10^{-7}$  to  $1 \times 10^{-3} cm s^{-1}$ , one of the highest values found in the literature[40]. These electrode modifications help to decrease the fraction of the current directed towards  $H_2$  evolution in the same way as reported in our previous paper on  $TiO_2:H$  graphite felt[29]. Therefore, nitrogen modified carbon-based surfaces show a similar improvement as increasing oxygen groups on the carbon-based surfaces, making it electrochemically more active as well. Among the four main types of nitrogen groups, the quaternary or graphitic-N has been found to be the more stable in the acidic environment[39]. However, pyrrolic-N has been proposed to be the most electrochemically active nitrogen site enhancing the catalytic activity in

these nitrogen-modified carbon-based electrode materials for VRFB[41]. Here, we discuss the synergetic effect of the oxygen and nitrogen groups' functionalization on the carbon-based surface, which is coupled with the nitrogen and oxygen (especially hydroxyl) group's formation from titanium-based coverage, when CF@TiO<sub>2</sub> is nitrated. Additionally, in the previous published paper on the role of TiN electrocatalyst in VRFB, their power-related application was not discussed and the performance evaluation being limited to the charge/discharge experiments as a proof-of-concept[30,31]. However, from the point of view of feasible applications, many efforts have been made to date to improve the peak power density as it constitutes a key parameter for the assessment of the battery power cost. For example, Aaron *et al.* demonstrated significant improvements using stacking sheets of carbon paper, achieving values up to 557  $mW\ cm^{-2}$  [1]. Liu *et al.* demonstrated a greatly improvement of this peak power values using no-gap architecture cell and thermal pre-treatment of the carbon paper electrodes, demonstrating a high-power density value of 540  $mW\ cm^{-2}$  [41]. Mayrhuber *et al.* also demonstrated an increased power density using carbon paper-based electrodes, attaining values up to 543  $mW\ cm^{-2}$  [42]. More recently, UTRC's cell technology enables substantially high power densities, where the peak power is around 1300  $mW\ cm^{-2}$  for UTRC's VRB cell [43]. In this context, due to the importance of the cell's power output, we have also analyzed the power peak density performance of the electrodes obtained applying our proposed nitride process of a carbon felt previously decorated with TiO<sub>2</sub>. Outstanding values of power density up to 700  $mW\ cm^{-2}$  have been measured, corroborating the relevance of the proposed procedure combining the synergetic effect produced by the nitride treatment over titanium dioxide and carbon felt. This presents a procedure for increasing the current density of the system with the concomitant

decrement of the stack size cost ( $\text{€ } m^{-2}$ ) and a route to lowering the large capital power-cost of VFRB ( $W m^{-2}$ ).



## EXPERIMENTAL SECTION

### *Nitrided CF@TiO<sub>2</sub> electrode synthesis.*

TiO<sub>2</sub> nanorods have been directly grown over a commercial carbon felt (CF, 4 cm<sup>2</sup> and 5 mm thickness from Mersen S.A., Spain) using a hydrothermal process reported in our previous studies[29]. Prior to this step, CF is plasma-treated in oxygen atmosphere for 10 minutes. Subsequently, an initial annealing at 500°C for 4 h in O<sub>2</sub> atmosphere is done in order to remove all the impurities, Afterwards, TiO<sub>2</sub>-based electrodes are nitrided by NH<sub>3</sub> gas at several temperatures 500 and 900°C for 14 hours. The samples are labelled as CF@TiO<sub>2</sub>N500 and CF@TiO<sub>2</sub>N900 electrode, respectively.

### *CF@N900 electrode synthesis.*

A commercial carbon felt (CF, 4 cm<sup>2</sup> and 5 mm thickness from Mersen S.A., Spain) has been modified using a hydrothermal process analogous to the nitrided CF@TiO<sub>2</sub> electrode synthesis but in absence on titanium precursor. Prior to this step, the CF was plasma treated in oxygen atmosphere for 10 minutes. Afterwards, the electrodes were nitrided by NH<sub>3</sub> gas at 900°C for 14 hours in order to study the structural changes on CF. The sample is labelled as CF@N900 electrode.

### *CF-HT electrode synthesis.*

A commercial carbon felt (CF, 4 cm<sup>2</sup> and 5 mm thickness from Mersen S.A., Spain) has been treated in a high vacuum plasma cleaner system (Plasma etch inc. PE-50) in oxygen atmosphere for 10 min.

### ***Morphological and structural characterization.***

The morphology and nanostructure of electrodes have been characterized with a Zeiss Serie Auriga field emission scanning electron microscope (FE-SEM). Structural characterization was carried out by X-Ray Diffraction (XRD) in a D8 Advance Bruker equipment with a Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation sources working at 40 kV and 40 mA. UV/Vis absorption spectra were recorded in the diffuse reflectance mode on a PerkinElmer Lambda 950 UV/Vis spectrometer equipped with a Praying-Mantis diffuse reflectance accessory. The chemical composition changes on the surface of the electrodes were analyzed by XPS using a PHI instrument model 5773 Multi-technique with Al K $\alpha$  radiation (1486.6 eV).

### ***Electrochemical characterization.***

A three-electrode glass cell was used to do fundamental electrochemical studies. As-prepared electrodes ( $0.25 \text{ cm}^2$ ) were used as working electrodes, platinum wire as counter electrode, and Hg/Hg<sub>2</sub>SO<sub>4</sub> as reference electrode. Nitrogen gas was used to deoxygenate the electrolyte. Electrochemical measurements are done with a Biologic® VMP-3 multi-potentiostat controlled by EC-lab® software. The electrocatalytic reaction of the studied electrodes towards negative reaction in VRFB was measured by cyclic voltammetry (CV) between cut-off voltages of 0.5 and -0.9 V vs. SHE at  $2 \text{ mV s}^{-1}$  scan rate in 0.05 M V<sup>3+</sup> and 1 M H<sub>2</sub>SO<sub>4</sub>, obtaining the fundamental parameters, detail as follow: i) Current density values for oxidation and reduction peaks ( $I_{pa}$ ,  $I_{pc}$ ); ii) Onset potential and peak potential ( $E_a$ ,  $E_c$ ); iii) The ratio of oxidation and reduction peak current densities ( $I_{pa}/I_{pc}$ ); and iv) and peak-to-peak potential separation. Moreover, the mass transfer negative electrode-electrolyte has been

obtained from CV at different scan rates, from 2 to 50  $\text{mV s}^{-1}$ . Electrochemical impedance spectroscopy (EIS) spectra containing 0.05 M vanadium species in 1 M sulfuric acid (PEIS - 0.26 V vs. SHE) was done at a frequency from 100  $\text{mHz}$  to 200  $\text{kHz}$ . The hydrogen-evolution reaction of all electrodes studied was evaluated using linear sweep voltammetry (LSV) at 2  $\text{mV s}^{-1}$  in 1M  $\text{H}_2\text{SO}_4$ . Tafel measurements were done under potentiostatic control in a 50% SoC  $\text{V}^{3+}/\text{V}^{2+}$  and 1 M  $\text{H}_2\text{SO}_4$  solution. In order to ensure it, potentiostatic -0.26 V was applied until the current is stable near 0  $\text{mA cm}^{-2}$ . Afterwards, differentials of potential were applied in a range of  $\pm 200$  mV from the equilibrium ( $E_{\text{ocv}} = -0.26$  V) to obtain  $j_0$  which is directly related to the kinetics of the reaction.

#### ***Flow-Cell Test.***

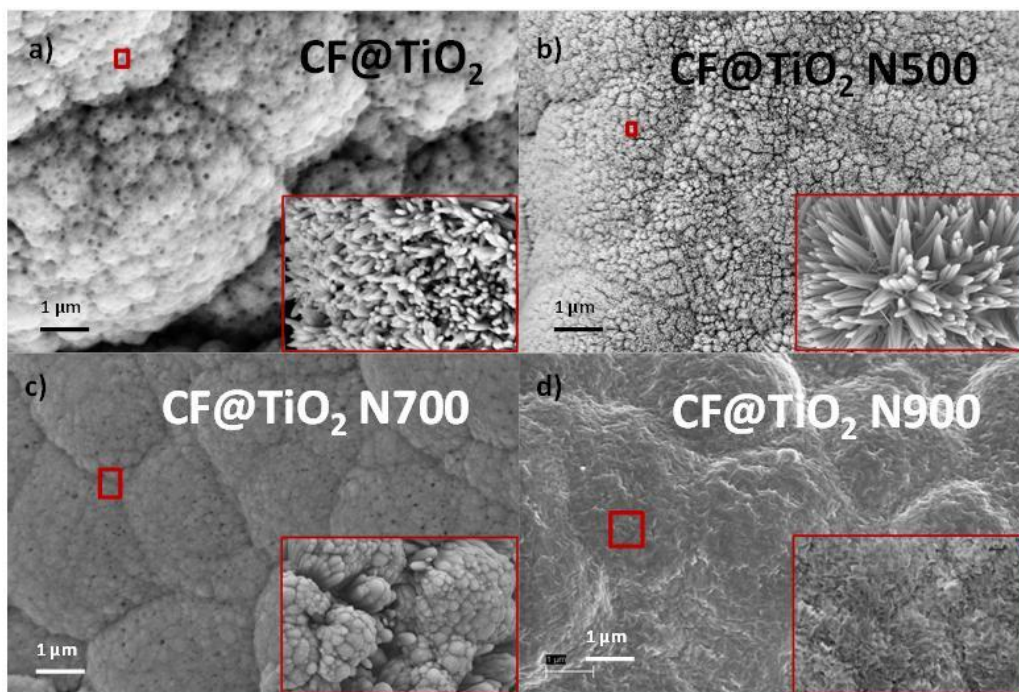
The electrolytes were prepared dissolving 1 M vanadium ions (Alfa Aesar) in 3 M  $\text{H}_2\text{SO}_4$  (Aldrich, 98%) solutions. The corresponding anolytes and catholytes can be prepared through an electrochemical process[12]. The VRFB single-cell performance was measured using an in-house designed flow cell system, which has been described in our previous work [12]. The single-cell was assembled sandwiching the membrane (Nafion® 117, 6 cm  $\times$  6 cm) between two pieces of working electrodes with an area of 4  $\text{cm}^2$ , approximately compressed a 30%. The graphite bipolar plates which are composed of 3 serpentine flow fields with diameter of 2 mm. The outer faces of the bipolar plate were coated with a sputtered layer of copper to act as a current collector. Viton® gasket was used to seal the cell. Metallic aluminium end-plates were used to close the cell. In order to investigate the effect of the different materials, nitrided  $\text{TiO}_2$  nanorods have been used as negative electrodes, while CF-HT was used as positive electrode. The single-cell was connected to two glass reservoirs containing 20 mL catholytes and anolytes, respectively.

The flow rate at each side was  $10 \text{ mL min}^{-1}$  and the negative reservoir was continuously purged with nitrogen to avoid any oxidation of the active species. The flow cell was charged up to 1.8 V and then discharged to 0.8 V, at different current densities, from 25 to  $150 \text{ mA cm}^{-2}$ . The performance evaluation method for the VRFB single cell was mainly determined by the following efficiencies: 1) Coulombic efficiency (CE), the ratio of the average discharging capacity to the average charging capacity, 2) Voltage efficiency (VE), the ratio of the average discharging voltage to the average charging voltage, (3) Energy efficiency (EE), VE multiplied by CE/100. According to Faraday's law, the theoretical capacity in VRFB was calculated to be 536 mAh ( $13.4 \text{ Ah L}^{-1}$ ) or  $18.8 \text{ WhL}^{-1}$  for 1 M vanadium ions concentration, respectively. The theoretical capacity expressed in  $\text{AhL}^{-1}$  has been calculated taking into account the total volume of the tanks (i.e. 40 mL). Additionally, to study the battery response to pulsed current and therefore plot the polarization curve, the battery was discharged at a specified current density, from 0 to  $1900 \text{ mA cm}^{-2}$ , for 60s. After, a rest period of 2 min to a steady state at OCP was measured. The power density curves were obtained from the product of output voltage at the voltage applied and the corresponding current density. These measurements were performed at a 100% state of charge (SoC) as a starting point for each one of the current densities applied.

## RESULTS AND DISCUSSION

### MORPHOLOGICAL AND STRUCTURAL CHARACTERIZATION

The morphological structures of the as-prepared electrode were characterized by FE-SEM. TiO<sub>2</sub> nanowire coverage directly growth into the surface of carbon felt with a rod morphology by hydrothermal process (**Figure 1a**). Some changes can be appreciated after the NH<sub>3</sub> thermal treatment, which forms local agglomerations of TiO<sub>2</sub>-nanorods in the case of the CF@TiO<sub>2</sub> N500 sample (**Figure 1b**), due to the reductive conditions of the ammonia gas[44]. In the case of higher annealing temperatures, the rods became more compact and decrease their length (**Figure 1c and d**) with a well-dispersed rods decoration over the carbon felt surface after NH<sub>3</sub> treatment.



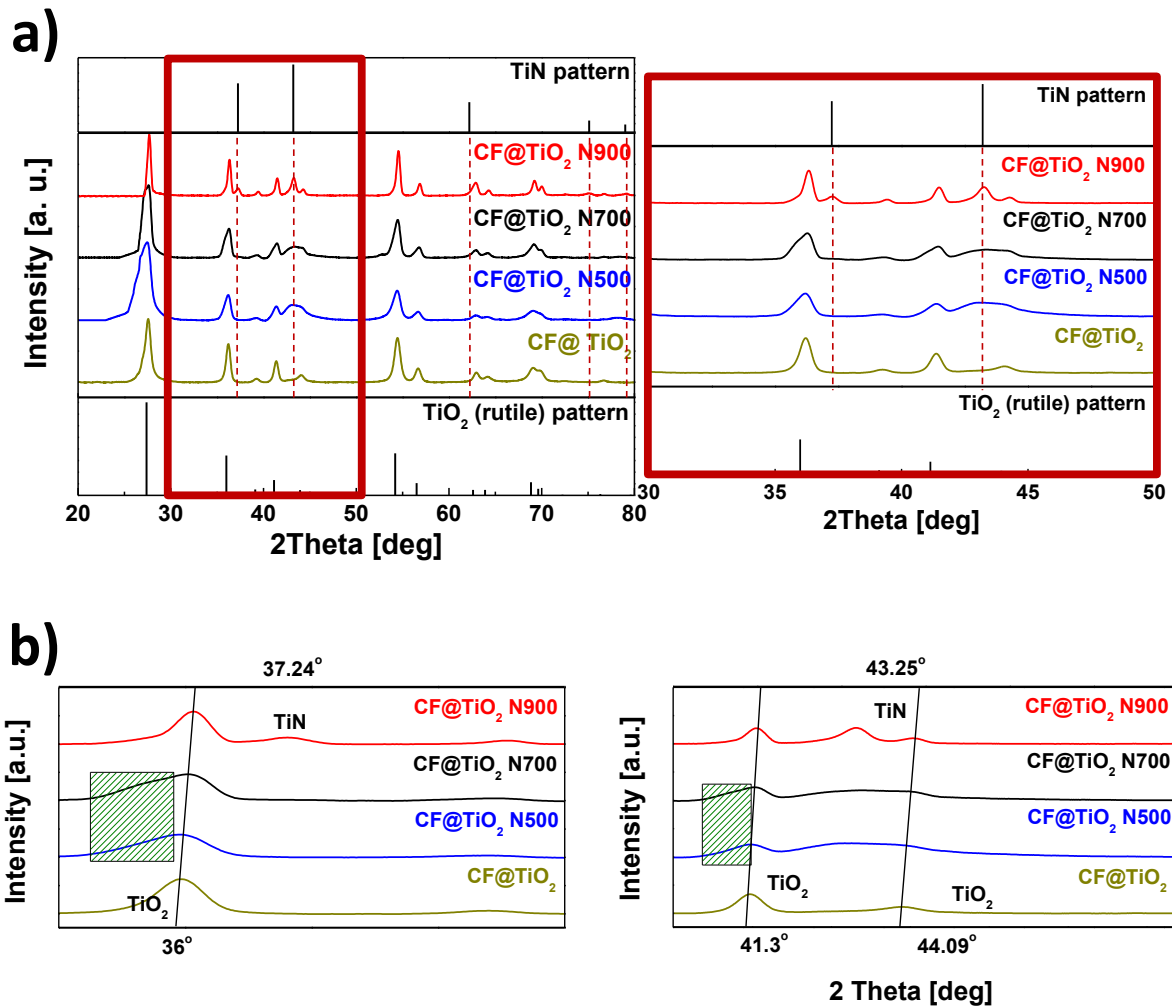
**Figure 1-** FE-SEM images of the: **a)** CF@TiO<sub>2</sub>; **b)** CF@TiO<sub>2</sub> N500; **c)** CF@TiO<sub>2</sub> N700  
**d)** CF@TiO<sub>2</sub> N900.

Subsequently, the XRD spectra of the samples annealed at different temperatures (**Figure 2c**) showed an initial rutile ( $\text{TiO}_2$ ) structure of the deposit over carbon felt with the diffraction peaks at 27.4, 35.8, and 54.38  $\theta$ , consistent with the rutile  $\text{TiO}_2$  (110), (101), and (211) crystalline planes, respectively. All peaks were in line with the standard pattern (JCPDS no.:21-1276). After the  $\text{NH}_3$ -treatment at 900°C, three diffraction peaks appear at 61.8; 42.7 and, 37.2  $2\theta$ , which correspond to the (111), (200) and (220) planes of the cubic TiN phase (JCPDS: 65-0714). Below 900°C as a temperature annealing, it can only be observed a broad peak due to the nitride process at 42.7 corresponding to (210) for the rutile phase. A more detailed analysis (**Figure 2b**) of the diffraction peaks associated with the rutile phase showed a distortion of the peak profile produced by the incorporation of nitrogen into the interstitial sites of rutile phase.

- i) The rutile peaks show an asymmetrical shape indicated by the area patterned with a sparse green square, as **Figure 2b** shows around 36°. This corroborates that nitridation process due to the chemical interaction at the surface level is producing the breakage of the bonds in the  $\text{TiO}_2$ , producing a lattice weakness that leads to the generation of defects and vacancies and gives rise to a damaged outermost  $\text{TiO}_2$  layer, which justifies the asymmetrical shape of the peaks, as the damaged area contributes essentially with larger interatomic distances, i.e. to the left area of the peaks[45]. The optical absorption capability of these defects with localized energy state in the bandgap of the material explains the color change revealed in the optical absorption spectra (**Figure 2a**).
- ii) Secondly, the  $\text{TiO}_2$  rutile structure remains even after the appearance of a cubic TiN phase around 900 °C pointing out that only a TiN formation. However, the position of

the XRD pattern of the rutile peaks shifts towards higher  $2\theta$  values as the temperature is increased from 500 to 900°C, i.e. from 27,58° to 27,71° showing that rutile had undergone a nitrogen doping over titanium dioxide nanorods as temperature was increased achieving strain values ( $\Delta d/d$ ) around +1%, where “d” is the inter-planar spacing. The crystalline domain size from these XRD spectra considering Debye-Scherrer formula is around 50 *nm*.

- iii) Thirdly, as the nitrated treatment reaches 900 °C, there is an overall modification of the sample structure. The broad peaks presented in the green area, observed in **Figure 2b**, disappear, showing that the stoichiometry of TiO<sub>2</sub> is recovered and TiN phase formed. Therefore, it is plausible to assume that TiN is localized at the outermost zone of the remain unaffected TiO<sub>2</sub>, exactly where TiN stress phase formation can be relaxed. For this phase, the crystalline domain from the Debye-Scherrer formula is around around 30 *nm*. Additionally, the XRD of CF@TiO<sub>2</sub>N500 and CF@TiO<sub>2</sub>N700 does not show any peak related to TiN. In consequence, at this stage, TiN phase is not yet segregated from the TiO<sub>2</sub> and nitrogen is only present inside of the TiO<sub>2</sub> lattice such as the peak deformation corroborates. It is also worth consider such high temperatures could also functionalize the carbon felt surface.



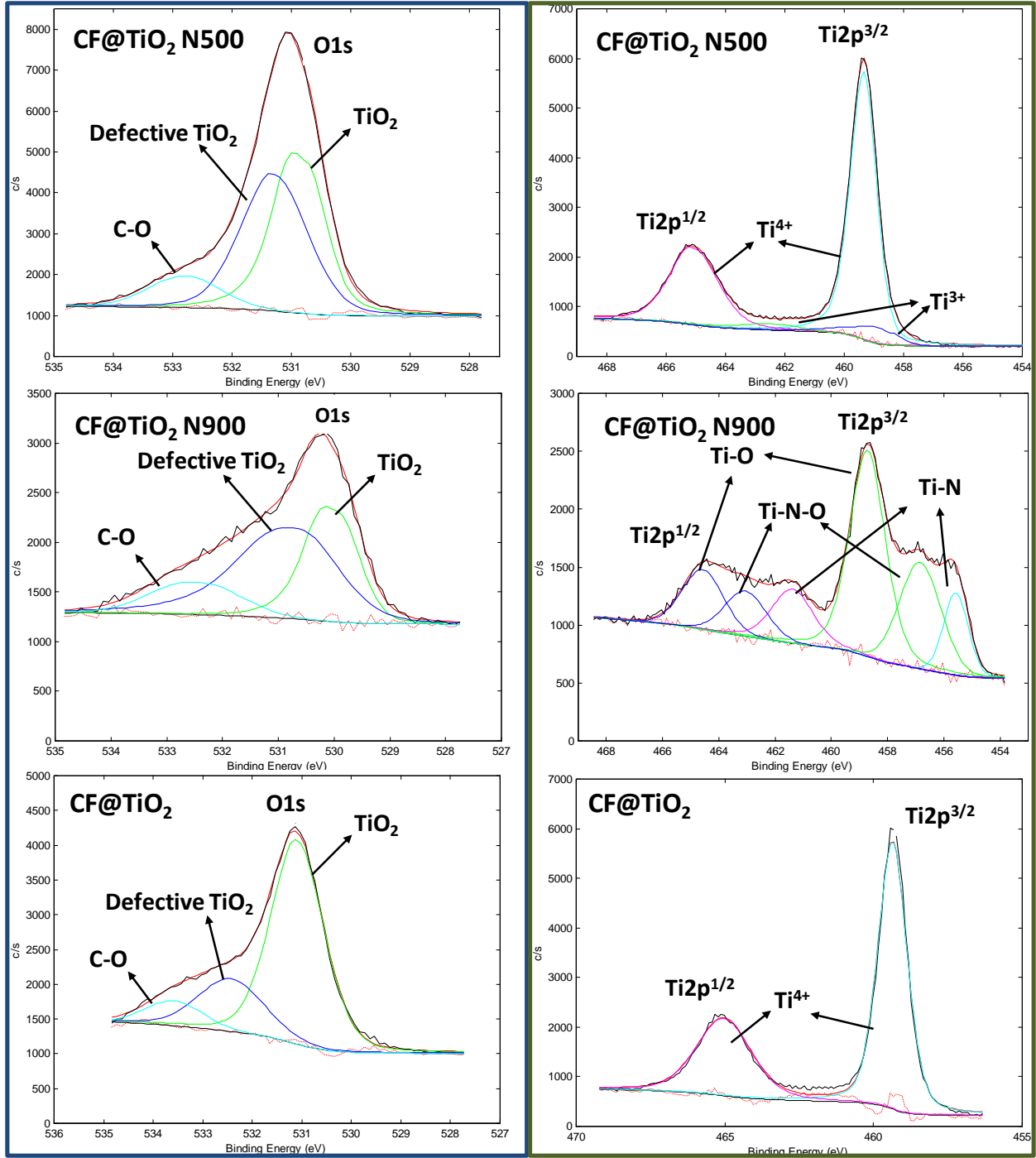
**Figure 2-** a) X-ray diffractogram of CF@TiO<sub>2</sub>, CF@TiO<sub>2</sub> N500, CF@TiO<sub>2</sub> N700 and CF@TiO<sub>2</sub> N900 electrodes, showing characteristic TiN (top) and TiO<sub>2</sub> (rutile, bottom) patterns. b) Detailed analysis of the XRD peaks showing the asymmetrical shape due to the nitrided process as well as the appearance of the new TiN phase at 900°C.



## CHEMICAL CHARACTERIZATION

XPS spectra analysis (**Figure S2**) shows the surface effects of the nitride process. The influence of nitrogen incorporation on the state of titanium was probed through the Ti2p spectra (**Figure 3**). Significant differences can be distinguished for the CF@TiO<sub>2</sub> N900 sample, it can be seen that 3 doublets are needed to fit the titanium signal corresponding to the different expected bonds Ti-O (458.5 eV), Ti-N-O (456.8 eV) and Ti-N (455.9 eV) in a relative percentage of 50%, 29% and 21%, respectively. Comparatively the typical TiO<sub>2</sub> doublet related to titanium (IV) at 458.5 eV is seen in CF@TiO<sub>2</sub> and CF@TiO<sub>2</sub> N500, with a small additional doublet contribution from Ti (III) in the lattice structure in case of CF@TiO<sub>2</sub> N500 at 458.9 eV.

Furthermore, the O1s spectra in **Figure 3** shows an increasing surface defect formation over the metal oxide lattice by oxygen deficient groups, Ti-O (dark blue peaks) at 531.5 eV, following the relative area percentage: CF@TiO<sub>2</sub> (22%) < CF@TiO<sub>2</sub> N500 (45%) < CF@TiO<sub>2</sub> N900 (51%). There is also the existence of small contributions related to different oxygen bonds over the carbon surface centered at higher energy values (533 eV) (light blue peaks). Oxygen XPS band for CF@N900 (**Figure S3**) gives evidence for the oxygen groups formed on the carbon felt surface, as three deconvolution peaks related to C=O (rel. 2%) at 530.8 eV, C-O (rel. 69%) at 532.1 eV and C-O-H (rel. 29%) at 534.2 eV



**Figure 3-** O1s and Ti2p XPS spectra for CF@TiO<sub>2</sub>, CF@TiO<sub>2</sub> N500 and CF@TiO<sub>2</sub> N900.

Hence, bearing in mind that XPS signal is accurate for a few nanometers thickness (about 10 nm)[46,47], the crystalline domain determined from the XRD spectra the surface of CF@TiO<sub>2</sub> N900 electrode could be described as a TiO<sub>2</sub> surface with numerous zones of TiN (21%) surrounded by Ti-O-N transition areas between TiN and TiO<sub>2</sub> at surface level (29%). It is confirmed by the N1s XPS band spectra (**Figure S4**) that CF@TiO<sub>2</sub> N900 shows as main contributions the N-Ti (4% at.) bonding at 396 eV, as well as Ti-N-O (4% at.) at 398 eV, both centered at 396.1eV. Moreover, there is a 2% contribution of the spectra coming from pyridinic, pyrrolic and graphitic nitrogen groups formed at the carbon felt surface uncovered , which are centered at 400.2 eV. A 55% corresponds to pyridinic-N (399.7 eV), 31% to pyrrolic-N (400.3 eV) and 13% to graphitic-N (401.3 eV). The nitrogen functionalization is confirmed for CF@N900, as the deconvolution of the high resolution N1s spectra reveals the presence of the peaks related to: pyridine-N (399.7 eV), pyrrole-N (400.3 eV) and graphitic-N (401.3 eV).

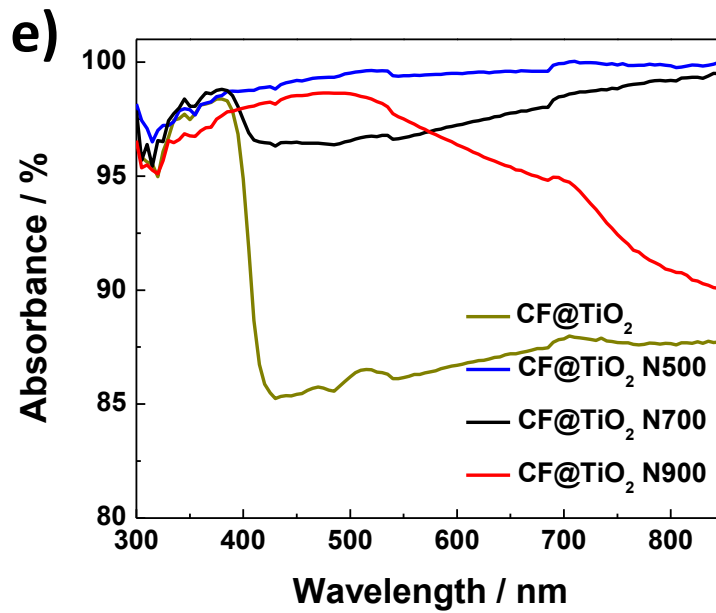
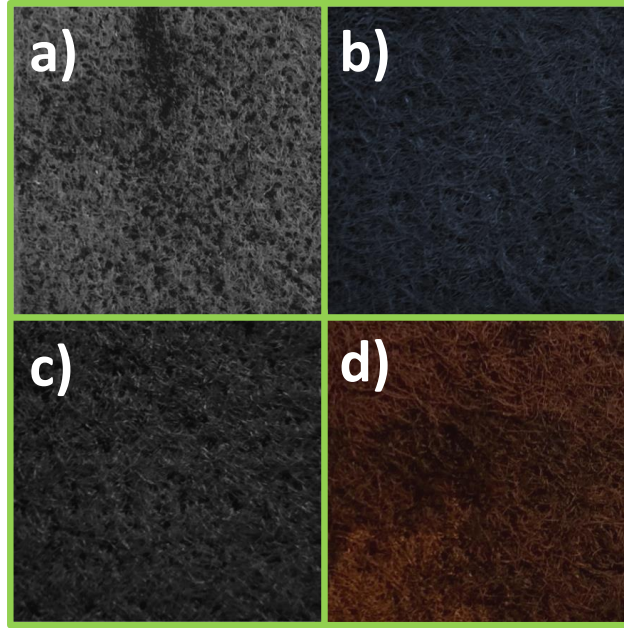
The NH<sub>3</sub>-treatment notably modifies the surface chemical states and, consequently, the optical properties of the TiO<sub>2</sub>. For example, the color of the rutile's deposit, which is completely white in the case of the initial TiO<sub>2</sub> sample, (**Figure 4a**) turns bluish on the deposit after NH<sub>3</sub>-treatment at 500°C (**Figure 4b**), due to defect formation on the rutile[48]·[49] caused by the reducing effects produced by the presence of ammonia. The annealed sample at 700°C (**Figure 4c**) is changed to black due to a deeper defect formation. Finally, the case of 900°C (**Figure 4d**) turns to a brown color as a result of the titanium nitride (TiN) formation. The following reactions explain the annealing processes that the electrodes are subjected to in the presence of ammonia at temperatures above .....[50]:





Initially, when ammonia gas is heated, it decomposes to hydrogen and nitrogen gas (4). Hydrogen partially reduces the titanium dioxide phase to titanium monoxide (5) which in the presence of the acidic electrolyte will form the oxyhydroxide. However, in order to produce titanium nitride, the heating temperature should reach at least 800 °C. Below that temperature, reaction (6) will not take place; therefore TiN will not be formed. Intermediate reactions (7) and (8) take place from 700°C to form the oxynitride phase[51].

In order to confirm these findings, the UV-vis spectra (**Figure 4e**), was performed in the as-prepared electrodes. Considering the CF@TiO<sub>2</sub> electrode as the initial spectra, there is broad absorbance decay, from 400 to 850 nm wavelength, corresponding with the visible and Near-IR region. It increases to maximum absorbance when the sample is annealed in ammonia at 500°C. When annealed at 700°C, the absorbance is lowered around 5% relative to the CF@TiO<sub>2</sub> N500 sample, from 400 to around 700 nm. Finally, the absorption after nitride formation appears to be stronger in the visible range (400-550 nm) for the sample annealed at 900°C in presence of ammonia (CF@TiO<sub>2</sub> N900). Afterwards we can observe a linear decreasing absorbance, from 550 to 850 nm, as the color of our electrode's deposit turns from black to dark brown[52]·[53].



**Figure 4-** Images, taken from Carl-Zeiss optical lens, of the electrodes after their respectively treatment: **a)** CF@TiO<sub>2</sub>; **b)** CF@TiO<sub>2</sub> N500; **c)** CF@TiO<sub>2</sub> N700 **d)** CF@TiO<sub>2</sub> N900 **e)** UV-vis Absorption spectra for CF@TiO<sub>2</sub>, CF@TiO<sub>2</sub> N500, CF@TiO<sub>2</sub> N700 and CF@TiO<sub>2</sub> N900.

## ELECTROCHEMICAL CHARACTERIZATION

After studying the chemical modification of the different electrodes, cyclic voltammetry (CV) was conducted to analyze the electrochemical performance of our electrodes towards  $V^{2+}/V^{3+}$  redox reaction (**Table 1**). Several electrochemical observations can be made from the CV (**Figure 5a**). It is clearly evidenced the poor electrocatalytic activity of the CF towards the negative reaction in VRFB, as large differential peak potential corresponding to the  $V^{3+}/V^{2+}$  redox reaction is observed. This irreversibility is due to the fact that the CF electrode promotes the HER over the  $V^{3+}/V^{2+}$  redox reaction. The presence of the  $TiO_2$  electrocatalyst over the surface of the CF electrode largely prevented the HER and the oxidation and reduction peaks corresponding to the  $V^{3+}/V^{2+}$  redox reaction could be clearly observed. However, none of these peaks are no symmetrical and the obtained current density values are the lowest for all modified electrodes tested. Further differences can be observed, when compare  $CF@TiO_2$  N500 and  $CF@TiO_2$  N900 electrodes, and are summarized below:

- 1) The highest current densities for both processes, oxidation and reduction, is displayed by  $CF@TiO_2$  N900 electrode (i.e.  $I_{ox} = 24.01 \text{ mA/cm}^2$  and  $I_{red} = -27.67 \text{ mA/cm}^2$ ), which evidences the greater electrochemical conversion of the active species on its surface due to a larger electrochemical active surface area towards the  $V^{3+}/V^{2+}$  redox reaction.
- 2) The peak-to-peak potential separation ( $\Delta E$ ) and the ratio of the reduction peak and the oxidation peak current ( $I_{red}/I_{ox}$ ) provide information about the reversibility of the redox process. For one-electron transfer reaction, the values for a reversible redox reaction are  $\Delta E = 0.059 \text{ V}$  and  $I_{red}/I_{ox} = 1$  at 298 K. A slight difference of the  $\Delta E$  values between both electrodes,  $CF@TiO_2$  N500 and  $CF@TiO_2$  N900, can be observed 0.24 and 0.22 V

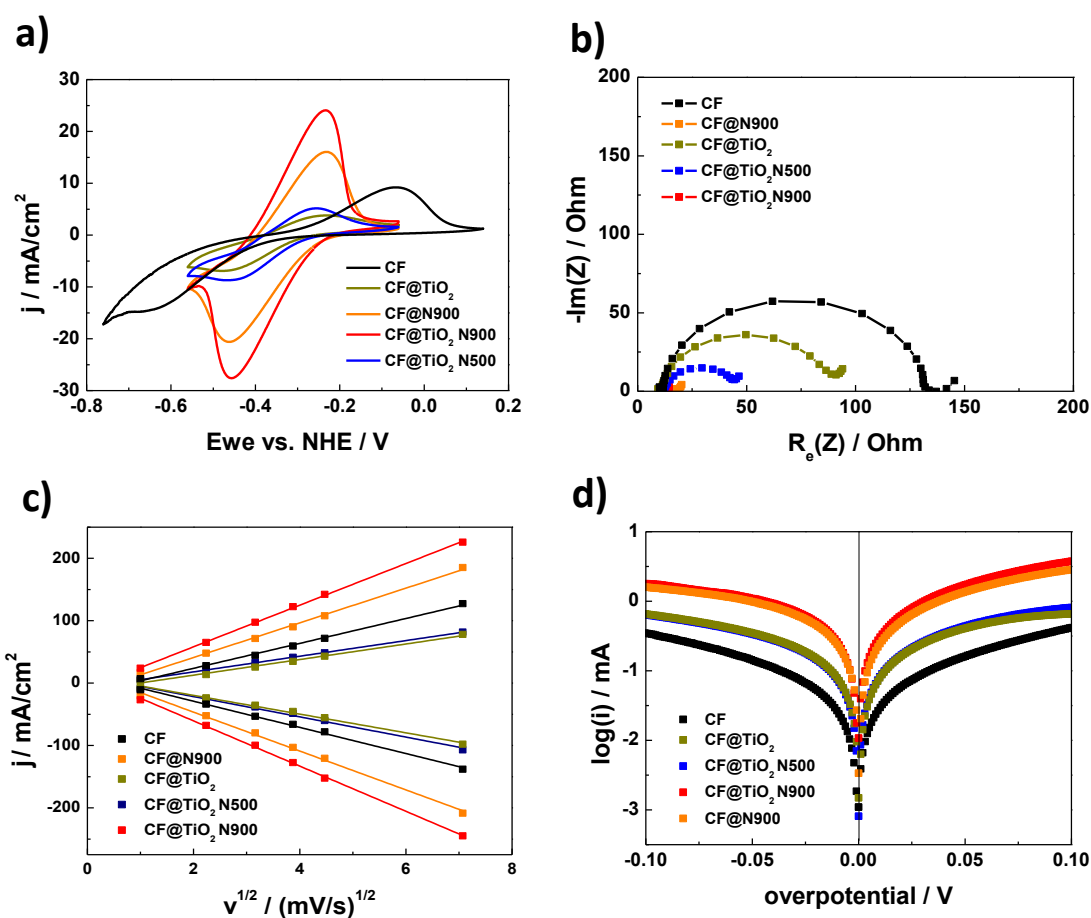
respectively. However, a significant increase from 0.60 to 0.87 for  $I_{red}/I_{ox}$  can be observed, showing a higher symmetry for CF@TiO<sub>2</sub> N900 electrode towards the reaction. Thus, in terms of electrochemical reversibility, the CF@TiO<sub>2</sub> N900 electrode presents better features, achieving values for a quasi-reversible reaction towards V<sup>2+</sup>/V<sup>3+</sup>.

**Table 1** – Electrochemical values obtained from the cyclic voltammetry plots.

<b>Sample</b>	<b>E<sub>ox</sub> / V</b>	<b>E<sub>red</sub> / V</b>	<b>ΔE / V</b>	<b>I<sub>ox</sub> / mAcm<sup>-2</sup></b>	<b>I<sub>red</sub> / mAcm<sup>-2</sup></b>	<b>I<sub>red</sub>/I<sub>ox</sub></b>
<b>CF</b>	<b>-0.066</b>	<b>-0.625</b>	<b>0.69</b>	<b>9.21</b>	<b>-13.98</b>	<b>0.66</b>
<b>CF@TiO<sub>2</sub></b>	<b>-0.228</b>	<b>-0.469</b>	<b>0.24</b>	<b>3.67</b>	<b>-6.84</b>	<b>0.54</b>
<b>CF@TiO<sub>2</sub> N500</b>	<b>-0.233</b>	<b>-0.468</b>	<b>0.24</b>	<b>5.28</b>	<b>-8.77</b>	<b>0.60</b>
<b>CF@TiO<sub>2</sub> N900</b>	<b>-0.232</b>	<b>-0.456</b>	<b>0.22</b>	<b>24.01</b>	<b>-27.67</b>	<b>0.87</b>
<b>CF@N900</b>	<b>-0.230</b>	<b>-0.463</b>	<b>0.23</b>	<b>15.95</b>	<b>-20.56</b>	<b>0.78</b>

Additionally, in order to elucidate the electrochemical influence of the nitrated process onto TiO<sub>2</sub> layer, as well as on the carbon felt, samples without TiO<sub>2</sub> layer were also prepared and analyzed, labeled as CF@N900. As observed in **Table 1**, the main differences between these two electrodes are observed in the current density values, the lower current density, from 33% for reduction to 25% for oxidation reactions, slightly smaller ΔE (0.23 V) and reduced  $I_{red}/I_{ox}$  (0.78)

displayed by CF@N900 comparatively to CF@TiO<sub>2</sub> N900 electrode. It points out the positive benefit of the proposed technological route to enhance the VRFB negative redox reaction. Accordingly, the experimental data showed a synergetic effect between the nitrated process effect over the CF and on TiO<sub>2</sub> structure, coupling the better electron transfer towards V<sup>3+</sup>/V<sup>2+</sup> redox reaction due to functionalization over the carbon electrode's surface and over the TiN nanocatalyst formed.



**Figure 5** – a) Cyclic Voltammetry of the electrodes in 0.05 M V<sup>3+</sup> and 1 M H<sub>2</sub>SO<sub>4</sub> solution. The voltage was scanned negatively from  $E_{ocv}$  at 50% SoC (V<sup>3+</sup>/V<sup>2+</sup>) at a scan rate of 1 mV s<sup>-1</sup>, to -0.56 V vs. SHE and after reversing the direction to an oxidative potential up to -0.06 V vs.



SHE. **b)** Potentiostatic electrochemical impedance spectroscopy (PEIS) done at -0.26 V vs. SHE. **c)** Randles-Sevcik plot of  $j$  vs.  $v^{1/2}$ . **d)** Tafel plot  $\log i$  vs.  $\eta$  (overpotential) for the different electrodes used in a 0.05 M 50% SoC  $V^{2+}/V^{3+}$  in 1 M  $H_2SO_4$  solution.

Electrochemical impedance spectroscopy (PEIS) measurements were conducted for all the electrodes at -0.26 V vs. SHE, in order to establish the difference in the electrochemical behavior of the prepared electrodes. Nyquist plots (**Figure 5b**) of all electrodes a semi-circle at high frequency region and a sloped line at the low frequency region ascribed to charge transfer process and the diffusion process, respectively. The data were fitted using Randles equivalent circuit (**Figure 5b** onset). The following elements can be ascribed to the fitting: i) the  $R_s$  element represents the ohmic resistant, combining the electrolyte resistance, connection resistance, and the electrode resistance; ii) CPE-1 has a Faradic component ( $Y_1$ ), which is a double layer capacitance ( $C_{dl}$ ) of the interface between the electrode and the electrolyte, and a no-Faradic component ( $n_1$ ), iii) charge transfer resistance ( $R_{ct}$ ), and iv) CPE-2 has a Faradic component ( $Y_2$ ), which represents the diffusion capacitance in pores of the electrodes, and a no-Faradic component ( $n_2$ ). The data parameters obtained are listed in **Table 2** with an error less than 10%.

**Table 2** – Parameters obtained from fitting the Nyquits plots with the equivalent circuit model of **Figure 5b**.

Sample	$R_s$ / Ohm	CPE-1		$R_{ct}$ / Ohm	CPE-2	
		$Y_1$ ( $C_{dl}$ )	$n_1$		$Y_2$	$n_2$
CF@TiO <sub>2</sub>	10.4	0.004451	0.92136	80.5	0.77467	0.81453

<b>CF@TiO<sub>2</sub> N500</b>	11.7	0.020095	0.89663	34.4	1.589	0.91352
<b>CF@TiO<sub>2</sub> N900</b>	12.3	0.084218	0.76553	1.25	2.781	0.6693
<b>CF@N900</b>	13.9	0.034198	0.61148	4.79	1.83	0.75279
<b>CF</b>	11.4	0.000322	0.97239	122	0.96348	0.58562

Consequently, CF@TiO<sub>2</sub> N900 sample has an electrochemical charge transfer resistance undeniably low (1.25 Ω) compared to the rest of electrodes. The formation of TiN phase highly improves the charge transfer processes between the negative electrode and the vanadium ions, especially for CF@TiO<sub>2</sub> N900, as well as the presence of nitrogen groups at the surface of the carbon felt, as supported by XPS data (Figure S4). This makes CF@TiO<sub>2</sub> N900 the best performing electrode in this study, exhibiting a charge transfer resistance almost two orders of magnitude lower than CF@TiO<sub>2</sub>[54]. It was also found that CF@N900 performed second best, due to the presence of N and O-groups over the carbonaceous surface, with an R<sub>ct</sub> of 4.79 Ω. Moreover, C<sub>dl</sub> values were found to follow the same trend as the R<sub>ct</sub>, obtaining the larger value for CF@TiO<sub>2</sub> N900 (8.4 x 10<sup>-2</sup> F) electrode due to higher amount of the active sites available for the reaction, which also agrees well with the CV analysis.

Besides, in cyclic voltammetry, the peak current,  $i_p$ , depends not only on the concentration and diffusion properties of the electroactive species, but also on the scan rate, as described by the Randles-Sevcik equation:

$$i_p = 0.4463nFAC \left( \frac{nFvD}{RT} \right)^{1/2}$$

Where  $i_p$  is the current maximum in Amps,  $n$  is the number of electrons transferred in the redox event (usually 1),  $A$  is the electrode area in [cm<sup>2</sup>],  $F$  is the Faraday constant in [C mol<sup>-1</sup>],  $D$  is the diffusion coefficient in [cm<sup>2</sup>/s],  $C$  is the concentration in [mol/cm<sup>3</sup>],  $v$  is the scan rate in [V/s],  $R$

is the gas constant in [ $\text{J K}^{-1} \text{mol}^{-1}$ ] and  $T$  is the temperature in [K]. When a linear behavior is observed between the scan rate and the peak current for the redox couple  $\text{V}^{3+}/\text{V}^{2+}$ , the reaction is diffusion controlled. Prior to use this equation it is worth mention it is applied just as a qualitative approximation because it applies to reversible reactions and planar electrodes while the studied electrodes are porous and quasi-reversible reactions. In order to estimate the mass transfer the Randles-Sevcik equation is used [55]. The equation's plot (**Figure 5c**) gives us a relationship where the slope is directly related to the associated mass transfer, which follows the trend:  $\text{CF@TiO}_2 \text{ N900} > \text{CF@N900} > \text{CF} > \text{CF@TiO}_2 \text{ N500} > \text{CF@TiO}_2$ . These values evidence the higher mass transfer on the  $\text{CF@TiO}_2 \text{ N900}$  electrode towards the negative reaction, which is directly a consequence of a larger active area of the vanadium ions over the electrode and therefore being less diffusive limited. Moreover, the close value of  $\text{CF@N900}$  to  $\text{CF@TiO}_2 \text{ N900}$  also evidences a facilitated mass transfer attributed to larger active area on the electrode's surface.

The Tafel equation was applied in order to confirm the catalytic properties of the different carbon felt modified electrodes (**Figure 5d**), which was mathematically treated and their values disclosed in **Table 3**. As seen, the exchange current density follows the trend ( $mA$ ):  $\text{CF@TiO}_2 \text{ N900} (9.58 \times 10^{-1}) > \text{CF@N900} (6.87 \times 10^{-1}) > \text{CF@TiO}_2 \text{ N500} (3.51 \times 10^{-1}) > \text{CF@TiO}_2 (2.38 \times 10^{-1}) > \text{CF} (6.6 \times 10^{-2})$ . This is directly related to the equilibrium exchange current on the electrode towards the negative VRFB reaction. Therefore, the material prepared at the highest temperature ( $900 \text{ }^\circ\text{C}$ ) shows a superior electron exchange current with the electrolyte towards the redox reaction ( $\text{V}^{3+}/\text{V}^{2+}$ ), which implies good catalytic behavior of highly nitrated electrodes. The heterogeneous rate constant was also determined, see **Table 3**, obtaining  $1.6 \times 10^{-3} \text{ cm s}^{-1}$  for

CF@TiO<sub>2</sub> N900 electrode one order of magnitude larger than CF@TiO<sub>2</sub> N500 electrode ( $5.8 \times 10^{-4} \text{ cm s}^{-1}$ ). CF@TiO<sub>2</sub> N900 rate constant value is among the best values in the literature[23].

**Table 3** – Exchange current density ( $i_0$ ) values and heterogeneous kinetic rate constant obtained from the Tafel plot in 0.05 M V<sup>3+</sup> in 1 M H<sub>2</sub>SO<sub>4</sub> at 50% SoC (V<sup>2+</sup>/V<sup>3+</sup>) for the electrodes CF, CF@TiO<sub>2</sub> and CF@TiO<sub>2</sub> N500, CF@TiO<sub>2</sub> N900 and CF@N900.

Electrode	I <sub>0</sub> / mA	k <sup>0</sup> / cm s <sup>-1</sup>
CF	0.066	$1.1 \times 10^{-4}$
CF@TiO <sub>2</sub>	0.238	$3.9 \times 10^{-4}$
CF@TiO <sub>2</sub> N500	0.351	$5.8 \times 10^{-4}$
CF@TiO <sub>2</sub> N900	0.958	$1.6 \times 10^{-3}$
CF@N900	0.687	$1.1 \times 10^{-3}$

Comparatively, **Figure S5** shows at -0.26 V vs. SHE, the different slopes associated to the response time according to the proposed method by Fink *et al*[23] to determine the kinetic information for rough and non-planar electrode structures using a straightforward linear-relationship between the  $1/R_{ct}$  and Cdl, both parameters obtained from EIS analysis (Figure 5b).

According to this model, charge transfer resistance and double layer capacitance are related by the following equation:

$$1/R_{ct} = \frac{nFt_{dl}}{RT\varepsilon_r\varepsilon_0}j_0C_{dl}$$

Where the variables correspond to the exchange current density  $j_0$ , the gas constant  $R$ , the absolute temperature  $T$ , number of transferred electrons  $n$ , Faraday constant  $F$ , relative dielectric permeability  $\varepsilon_r$ , permittivity of free space  $\varepsilon_0$ , and the thickness of the double layer  $t_{dl}$ . This indicates that  $R_{ct}$  decreases inversely with  $C_{dl}$  and that the slope of this equation yields the kinetic information  $j_0$  (which is directly proportional to  $k^0$ ).

Consequently, from the data shown in **Figure S5**, it can be observed CF@TiO<sub>2</sub> N900 possesses slightly faster kinetics than CF@N900, and significantly more than CF@TiO<sub>2</sub> 500. Although the slope value is also included, the values referred to CF and CF@TiO<sub>2</sub> electrodes have a large error. The larger slope means a faster transition frequency towards the vanadium negative redox reaction, which is related to the kinetic constant ( $k^0$ ), as the formula shown above. Therefore, the electrodes follow a kinetically favored trend as: CF@TiO<sub>2</sub>N900 > CF@N900 > CF@TiO<sub>2</sub>N500 > CF@TiO<sub>2</sub> > CF. The slope obtained by Fink's method (**Figure S5**) follows a linear relationship with the previously obtained values of  $k^0$  by Tafel, evidencing the good behavior of the method.

Since the lower contribution of the parasitic reactions must be settled in order to assess a high Coulombic efficiency, as well as long lifespan of the electrodes performance, CV were performed in absence of any vanadium ion to study the HER on the surface of the different studied electrodes (**Figure S6**). The maximum current density values for the as prepared

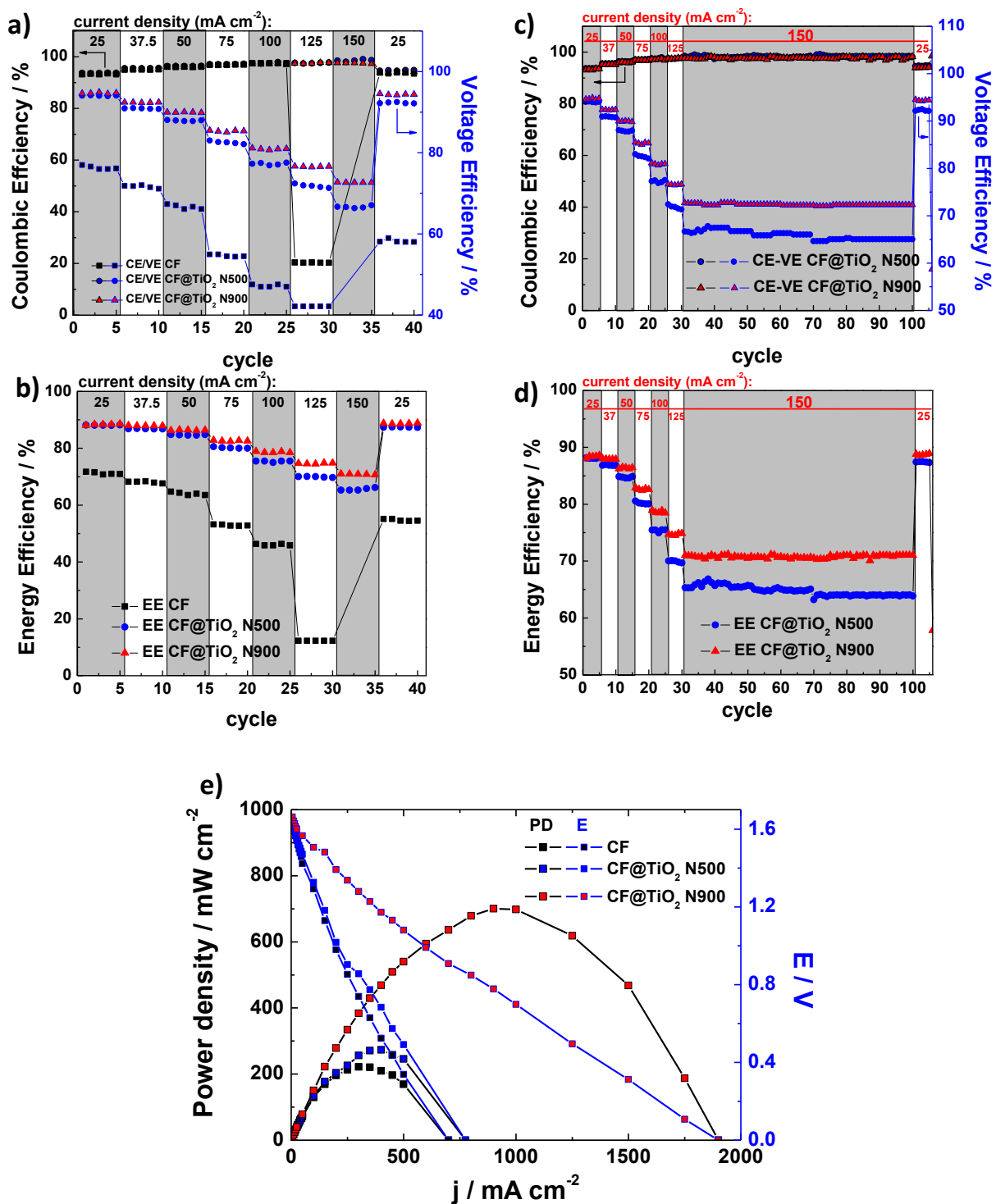
electrodes towards HER increases in the following order ( $\text{mA cm}^{-2}$ ):  $\text{CF@TiO}_2$  (89) <  $\text{CF@TiO}_2$  N900 (150) <  $\text{CF@TiO}_2$  N500 (180) <<  $\text{CF@N900}$  (248) < CF (258). There is a large inhibition of hydrogen evolution on the carbon felt covered by titanium dioxide as rutile phase, leading to a shift of the onset potential of HER, from -0.024 to -0.49 V vs. SHE[56]. The nitrated samples,  $\text{CF@TiO}_2$  N500 and  $\text{CF@TiO}_2$  N900, also inhibited the HER compared to bare carbon felt, though not as strongly as before the nitridation treatment, -0.15 and -0.30 V vs. SHE onset potential for annealing at 500 and 900°C, respectively. The inhibition of HER in this case was not as noticeable as in the case of pure titanium dioxide, due to the presence of fewer oxygen C-O centers, as demonstrated by XPS for  $\text{TiO}_2$  and  $\text{CF@TiO}_2$  N500 [29]. Moreover,  $\text{CF@TiO}_2$  N900 exhibited a more negative onset potential compared to  $\text{CF@TiO}_2$  N500 as the activation energy towards HER is comparatively larger. Last but not less important,  $\text{CF@N900}$  increases the kinetics towards HER, in spite the fact that postpones the onset potential compared to CF. This result showed that the presence of  $\text{TiO}_2$  does not inhibit  $\text{H}_2$  formation and therefore,  $\text{CF@N900}$  was not studied into a single cell.

## SINGLE CELL PERFORMANCE

In order to assess the performance of the modified electrodes in a single cell, the carbon felt electrode incorporated with the nitrated titanium dioxide catalyst is used as the negative electrode in an all-vanadium redox flow cell, while for all the experiments treated carbon felt (CF-HT) was used as positive electrode. Several cell cycles at different current densities from 25 to 150  $\text{mA cm}^{-2}$  (**Figure S7**) were conducted in order to observe the effect of the current density on the cell capacity. Our carbon felt capacity drops dramatically from 12.6  $\text{Ah L}^{-1}$  at 25  $\text{mA cm}^{-2}$  current density to 3.3  $\text{Ah L}^{-1}$  at 100  $\text{mA cm}^{-2}$ . However, it partially recovers its capacity when it is returned to the initial current density applied (10.9  $\text{Ah L}^{-1}$ ). On the contrary, the nitrated  $\text{TiO}_2$

electrode retains the majority of their charge capacity from 13.1 and 13.6  $Ah L^{-1}$  at 25  $mA cm^{-2}$  to 9.8 and 10.1  $Ah L^{-1}$  at 150  $mA cm^{-2}$ . This outstanding performance is a consequence of the synergetic catalytic effect of the oxygen and nitrogen sites on the carbon nitrated CF@TiO<sub>2</sub> over the adsorption, redox reaction and later desorption of V<sup>2+</sup>/V<sup>3+</sup> redox pair [34]·[57].

Furthermore, the sample treated at 500 °C displays low voltage losses over the charge and discharge compared to the CF. However, this value was still higher than the cell with the nitrated electrode prepared at 900 °C. One of the main reasons for this result is the presence of TiN, coupled with the nitrogen and oxygen group formation on the carbon felt, which allows a reduced charge transfer resistance. As a consequence of this, during the charge-discharge at 150  $mA cm^{-2}$ , the ohmic drop decreases, from CF@TiO<sub>2</sub> N500 to CF@TiO<sub>2</sub> N900 by 104  $mV$  and 56  $mV$  for charge and discharge respectively (**Figure S8**). As all components remained constant between tests, any differences on the system are due to the negative electrode. Therefore, the surface properties of the electrodes have a critical influence not only over the redox reaction kinetics, as previously shown, but also its ohmic resistance.



**Figure 6** – a) CE and VE b) EE dependency with the applied current density (from 12.5 to 150  $\text{mA cm}^{-2}$ ) of CF, CF@TiO<sub>2</sub> N500 and CF@TiO<sub>2</sub> N900 as electrodes, for 1M of initial



vanadium ions and 3 M H<sub>2</sub>SO<sub>4</sub> as electrolyte. Single cell long-term cycling of the CF@TiO<sub>2</sub> N500 and N900 electrodes for 1M vanadium ions and 3 M H<sub>2</sub>SO<sub>4</sub>. **c)** Coulombic Efficiency (CE) and Voltage Efficiency (VE) ; **d)** Energy Efficiency (EE). **e)** Power density plot vs. current density for the electrodes CF, CF@TiO<sub>2</sub> N500 and CF@TiO<sub>2</sub> N900.

Subsequently, **Figure 6a and b** presents the Coulombic, Voltage and Energy efficiency for the electrodes CF, CF@TiO<sub>2</sub> N500 and CF@TiO<sub>2</sub> N900 respectively, as we cycle with current densities from 25 to 150 mA cm<sup>-2</sup>. The sample annealed at 900°C shows smaller losses as the current density is increased, and therefore a higher efficiency. A maximum energy efficiency of 86.5% is seen at the lowest current density (25 mA cm<sup>-2</sup>), dropping to 71% at 150 mA cm<sup>-2</sup>. We attribute the lower values compared to the state of the art in the literature[30] to the difference in cell set-up design and conditions. Nevertheless, it is clear that the coating of nitride TiO<sub>2</sub> on the surface of the graphite felts has a drastic improvement on performance of the cell compared to bare CF, under the same experimental conditions. Similarly, the decrease in energy efficiency for CF@TiO<sub>2</sub> N500 is markedly less than for the CF, where the efficiency decays abruptly when the current density applied increases. Especially up to 100 mA cm<sup>-2</sup>, where the value collapses due to large overpotential, as seen in **Figure S10d**. The voltage efficiency, which is the ratio of charge and discharge voltage, follows the same trend as the Energy efficiency, a consequence of being the limiting factor of the battery performance. The Coulombic efficiency shows similar values for all samples (**Figure S9**), of above 95% for all current densities, except for the bare CF, due to an enormous overpotential at current densities above 100 mA cm<sup>-2</sup> that causes a Coulombic efficiency drop approximately 20%. As HER increases, the overpotential also increases (**Figure**

**S10d**), causing critical imbalances between charge and discharge process. This provokes the system to fail when bare CF is used as negative electrode. Moreover, **Figure S10** shows the voltage profiles between 0.8 and 1.8 V for carbon felt, CF@TiO<sub>2</sub> nitrided at 500 °C and 900 °C, applying increasing current densities. It is obvious that the bare CF exhibited a larger ohmic drop than the nitrided electrodes, especially when compared to CF@TiO<sub>2</sub> N900, exhibiting remarkably low polarization at high currents densities. There is a clear logarithmic tendency of the overpotential with increasing the current density (**Figure S10d**).

Thus, the nitrided catalysts annealed at 500 and 900°C exhibited a stable cycling performance above 100 cycles at different current densities with more than 50 cycles at high-current (150 mA cm<sup>-2</sup>). Nitrided CF@TiO<sub>2</sub> displays an initial Energy efficiency of 88.9% and 87.2%, for 900 and 500°C annealing temperature, respectively. After 100 cycles, which is the largest stability reported up to date for these materials, corresponding to 2-3 weeks of cycling, the enhancement of CF@TiO<sub>2</sub> N900 achieved a stable cycling energy efficiency of 71.2% at 150 mA cm<sup>-2</sup> compared to 63.9% energy efficiency for CF@TiO<sub>2</sub> N500. Therefore, we have demonstrated that there is a significant enhancement in the electrode performance, especially at high current densities, due to the significantly reduced polarization by increased redox active sites towards vanadium ions for the fast charge and mass transfer, which is consistent with all the electrochemical data previously shown. Following cycling at increased current densities, the system was returned to a charge-discharge rate of 25 mA cm<sup>-2</sup>, in order to evaluate the catalyst stability (**Figure 6c and d**). Remarkably, the initial energy efficiency was recovered after cycling at high current densities, indicating an electrochemical and chemical robustness of nitrided CF@TiO<sub>2</sub> catalyst in concentrated acidic and high current conditions. Moreover, Coulombic efficiency and voltage efficiency values were the highest for CF@TiO<sub>2</sub> N900

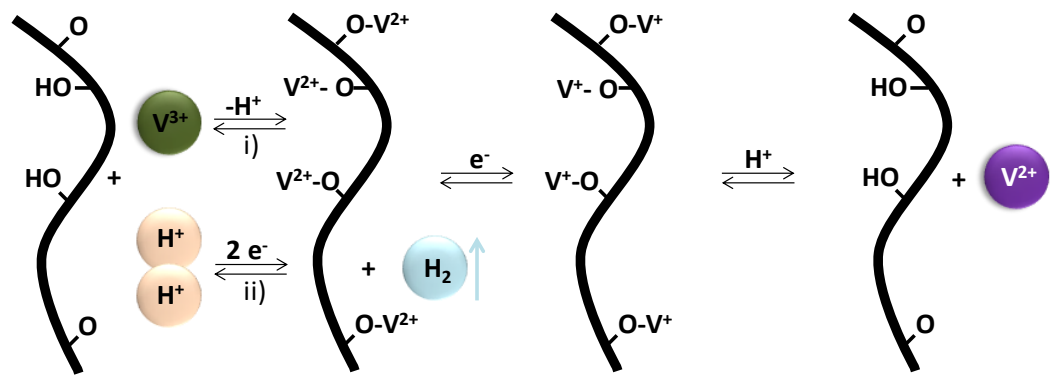
samples. Nitrided CF@TiO<sub>2</sub> catalyst was shown to exceptionally enhance the electrochemical performance of the VRFB system. In fact, CF@TiO<sub>2</sub> N900 induces a fast charge transfer and vanadium ion adsorption, resulting in a high rate capability at 150 mA cm<sup>-2</sup> and excellent capacity retention. This outstanding performance is a consequence of the synergetic catalytic effect of the oxygen and nitrogen sites on the nitrided carbon felt and TiO<sub>2</sub> over the adsorption, redox reaction and later desorption of V<sup>2+</sup>/V<sup>3+</sup> redox pair [34][57].

In fact, the observed improved performance in the electrode's mass and charge transfer, low ohmic resistance, as well as, limiting current density enables CF@TiO<sub>2</sub> N900 material to reach a superior power density, which is coherent with the electrode reaching a superior current values in the CV, previously shown in **Figure 5a**. The value of power density obtained, 700 mW cm<sup>-2</sup>, is two and a half times higher than when annealed at 500°C and three times more than carbon felt electrode. The shape of the polarization curves (**Figure 6e**) shows that the maximum current density supply by the device is increased by two effects: i) a low ohmic drop as the current density is increased and ii) faster vanadium mass transfer, allowing larger amounts of vanadium to be polarized over the electrode surface as the power density increases. The voltage decay is much smoother in the case of CF@TiO<sub>2</sub> N900 electrode. It reaches a greater maximum power, while the other samples show abrupt voltage decay and significantly lower maximum power density. Therefore, the modified carbon felts (CF@TiO<sub>2</sub> N900) have enhanced the electrochemical performance of the negative electrode in all-vanadium redox flow batteries and, more importantly, the power density, which is usually insufficient in flow batteries technology.

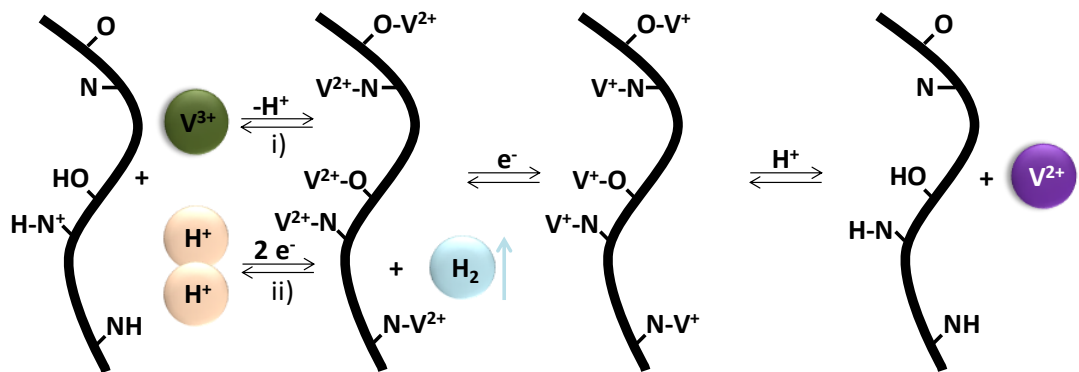
## MECHANISM PROPOSED

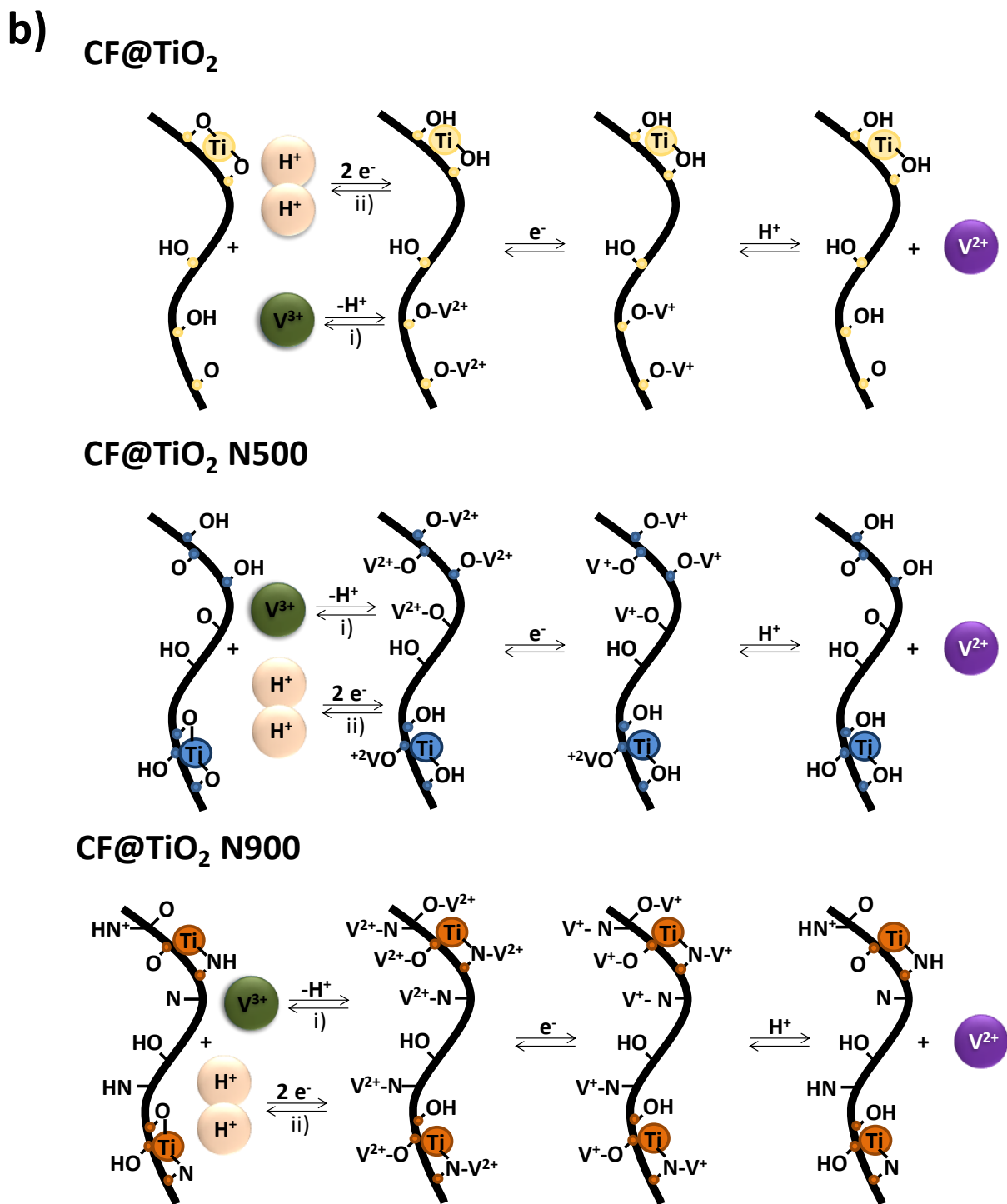
Based on previous research[58] and implementing the presented results, the mechanism proposed for the electrodes used is shown in **Figure 7a and b**. Firstly on bare CF,  $V^{3+}$  ions are adsorbed over the oxygen groups, -OH and C-O, on the carbon felt surface, generating O-V bonds, which breaks a O-H bond in the case where it is adsorbed on the hydroxyl group and releases a proton to the solution. Consequently, an electron is donated to the  $V^{3+}$  reducing it to  $V^{2+}$  and breaking the previously formed bond (O-V) and taking the proton again from the solution to re-form the hydroxyl groups. In this case, this redox reaction competes with the hydrogen evolution reaction as the protons are easily adsorbed to the C surface to form an H-H bond and subsequently desorbed as  $H_2$ . The former reaction is kinetically more favourable, causing electrolyte imbalance and low performance. The inhibition of the HER is therefore an important factor in catalyst performance, as well as the enhancement of the  $V^{3+}/V^{2+}$  redox reaction.

a) CF



CF@N900





**Figure 7.** – a) Mechanism interpretation, based on published results[58], for the negative reaction of VRFBs using CF and CF@N900 electrodes. b) Mechanism interpretation,

based on published results[58], for the negative reaction of VRFBs using CF@TiO<sub>2</sub>, and nitrated CF@TiO<sub>2</sub> as electrodes.

In the case of CF@N900, V<sup>3+</sup> ions are adsorbed over the oxygen (-OH and C-O) and nitrogen (pyridinic, pyrrolic and graphitic-N) groups on the carbon felt surface, generating O-V and N-V bonds, which breaks a O-H, N-H, +N-H bond in the case where it is adsorbed on the hydroxyl, pyrrolic or graphitic group, respectively, releasing a proton to the solution. Consequently, an electron is donated to the V<sup>3+</sup> reducing it to V<sup>2+</sup> and breaking the previously formed bond and taking the proton again from the solution. This redox reaction also competes with the hydrogen evolution reaction for the same reasons as with the[59].

Thirdly, after the TiO<sub>2</sub> is deposited there are two conditions that favour the V<sup>3+</sup> reduction:

- i) Increase of -OH groups and less importantly -O groups, as XPS data shows, due to the presence of titanium dioxide itself that promote the number of active sites per area for the reaction to happen, enhancing the electron charge transfer at the electrode/vanadium interface.
- ii) Highly stable proton absorption over the Ti-O bond inhibiting the HER side reaction. However, large electrode polarization is dominant at high rate capability leading to a limited specific capacity and a modest electrolyte-utilization ratio (SoC).

Consequently, the partially reduced sample (CF@TiO<sub>2</sub> N500) favours the V<sup>3+</sup>/V<sup>2+</sup> due to a reduced charge transfer resistance as an increased number of oxygen active sites (-OH and -O), especially hydroxyl groups, are present on the surface (**Figure 3**), and therefore, more vanadium ions are capable of reaction simultaneously.

Finally, for the sample where TiN is partially formed (CF@TiO<sub>2</sub> N900) there are two conditions that favour the V<sup>3+</sup> reduction[60]: i) Increase of –N groups on the carbon felt and over the TiO<sub>2</sub> surface forming TiN, due to the nitride process that promotes the number of active sites, enhancing the electron charge transfer at the interface electrode/vanadium. ii) Increase of oxygen groups, especially hydroxyl electroactive sites (-OH) over the electrode surface, for which electron charge transfer is facilitated by the nitrogen groups, most favoured by pyrrolic-N[61,62].

## CONCLUSIONS

We have demonstrated that a novel negative electrode material, CF@TiO<sub>2</sub> N900, exhibited significantly enhanced performance for VRFB applications, with power density values of up to 700 *mW cm*<sup>-2</sup> based on nitrated TiO<sub>2</sub> decorated carbon felt. Samples were prepared by a simple and scalable two-step approach based on a first hydrothermal step for TiO<sub>2</sub> carbon felt decoration, followed by a high temperature nitriding step of 4 hours at 900°C (after 4 hours at 500°C under oxygen).

Furthermore, the reaction kinetics and reversibility of the negative electrode, V<sup>3+</sup>/V<sup>2+</sup> redox couple, showed an outstanding improvement when the nitridation treatment is conducted at 900°C, CF@TiO<sub>2</sub> N900. the electrode CF@TiO<sub>2</sub> N900 showed an improvement of more than 310% in its associated kinetic constant rate, *k*<sub>0</sub>, compared to carbon felt decorated with TiO<sub>2</sub>, and an increase of 176% in relation to the TiO<sub>2</sub> decorated carbon felt nitrated at 500°C. The partial transformation of TiO<sub>2</sub> to TiN takes place at the same time than the nitridation of the carbon felt itself occurs. From the potential catalytic properties of the three types of nitrogen groups (quaternary, pyrrolic and pyridinic), graphitic-N or quaternary-N is considered to be the more



stable in the acidic environment. However, it is the pyrrolic-N group that is responsible for the enhancement of the catalytic activity. These effects are coupled to the presence of oxygen groups, especially hydroxyl active sites. The incorporation of O and N-containing groups has been determined to be a key step due to substantial improvement of the electrochemical activity (i.e., higher current density, low oxidation-reduction differential of potential and higher reversibility).

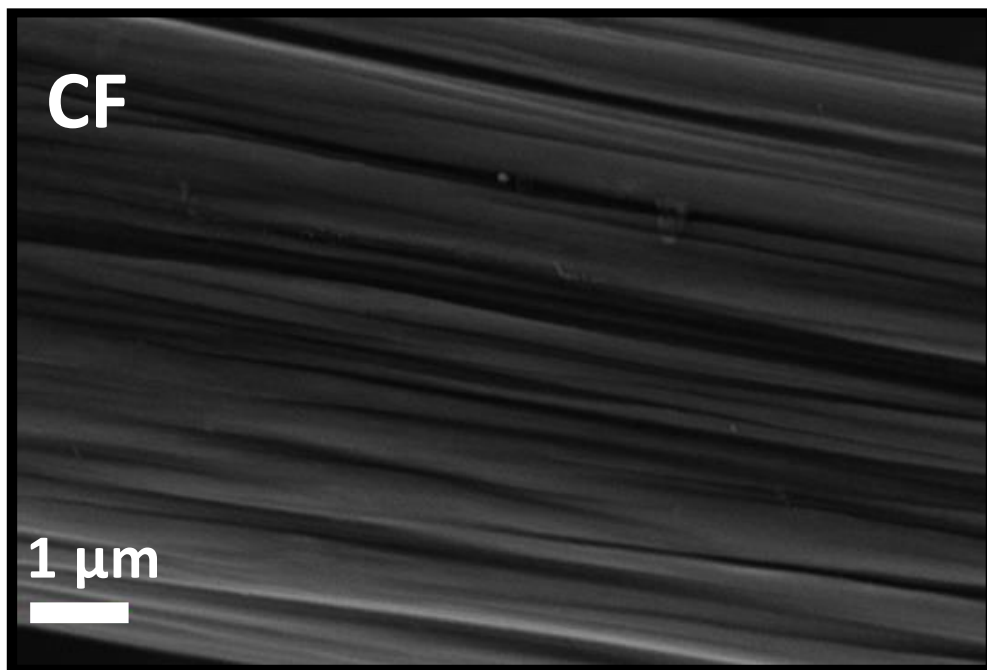
Additionally, it enhances catalytic activity at the surface which makes both, the electrochemical  $V^{2+}$  oxidation and  $V^{3+}$  reduction reactions more favorable and faster on these electrodes for which apparent kinetic constant rates as high as  $10^{-3} \text{ cm s}^{-1}$  have been observed. These kinetic characteristics have also been corroborated by analyzing the electrochemical impedance spectra from where the deduced charge transfer resistance values decrease almost two orders of magnitude between the reference CF@TiO<sub>2</sub> and the sample treated at 900 °C, corroborating the suitability of these electrodes for working stably at high density currents. These effects on the electrode behavior have also been shown with a reduction of the overpotential when large current densities are applied according to the Tafel plots. Likewise, this enhancement of the heterogeneous electron transfer kinetics, for  $V^{3+}/V^{2+}$ , has a significant impact on the current lost due to the parasitic HER, greatly decreasing it and contributing to an increase of the faradic efficiency.

Finally, the tested cell exhibits high coulombic, voltage, and energy efficiencies at different charge-discharge current densities, achieving more than 70% energy efficiency at 150mA cm<sup>-2</sup>. Consequently, the reported procedure gives rise to electrodes with a large active surface area due to abundant oxygen functional groups and N-modified surface for vanadium active sites, which also reduces the charge transfer resistance. Compared with the electrode surface in absence of

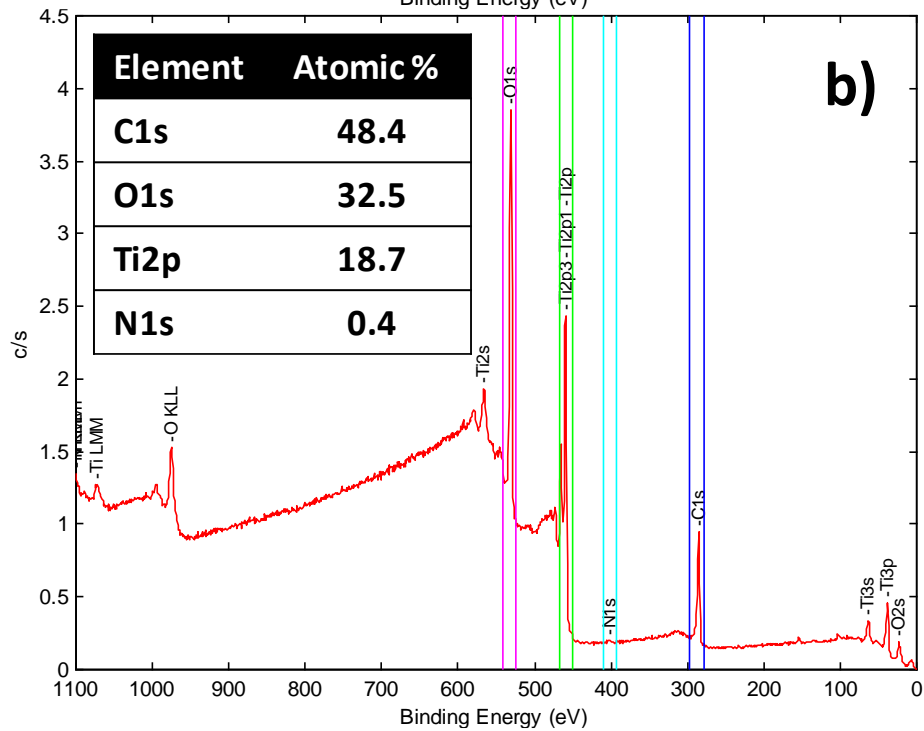
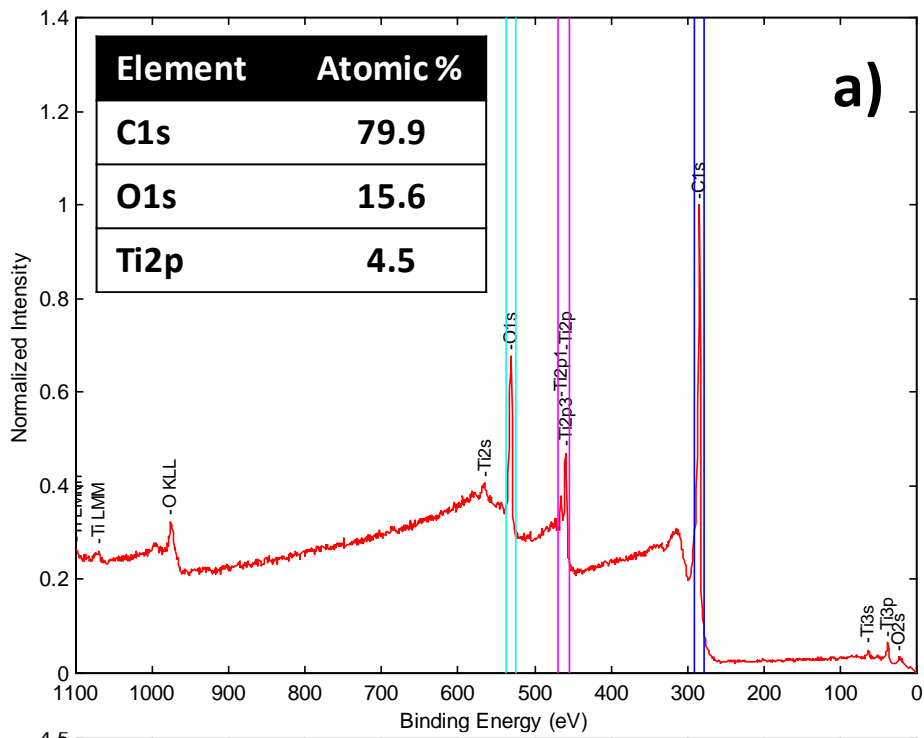
nitrogen, or a low concentration of it, the treated electrodes exhibit excellent catalytic activity towards vanadium redox reactions also due to the enhanced rate of electron transfer through the nitrogen groups producing fast kinetics for vanadium ion transfer. Moreover, the battery with the proposed electrode has demonstrated an excellent stability and high capacity retention during the cycling test. Herein, the proposed energy storage system is capable of an improvement, supplying around 250% higher power compared to non-treated CF.

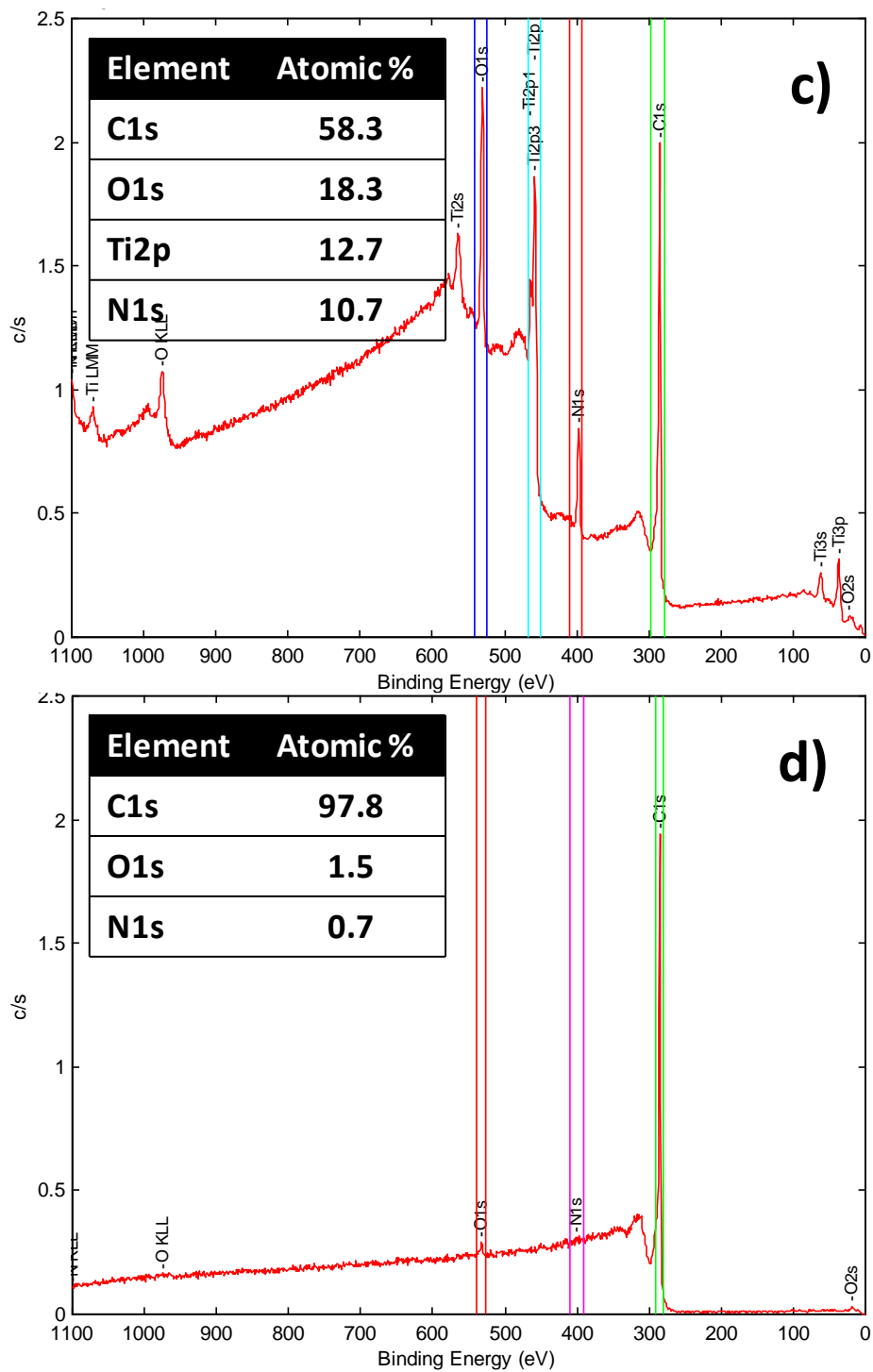
In summary, this work shows for the development and study of the electrocatalytic properties of highly active and stable nitrogen-modified carbon-based materials for VRFB applications, showing a synergetic effect of O- and N- functional groups at the surface of the carbon felt and the presence of  $\text{TiO}_2$  /  $\text{TiN}$  .

ASSOCIATED CONTENT

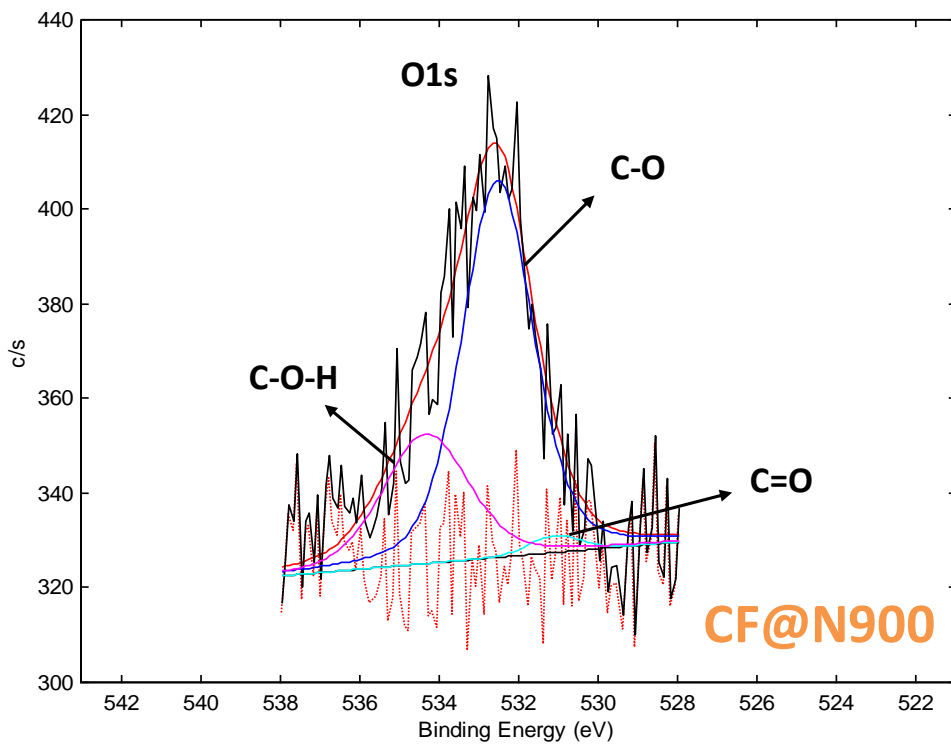


**Figure S1.** SEM image of carbon felt used as electrode, which has been treated.

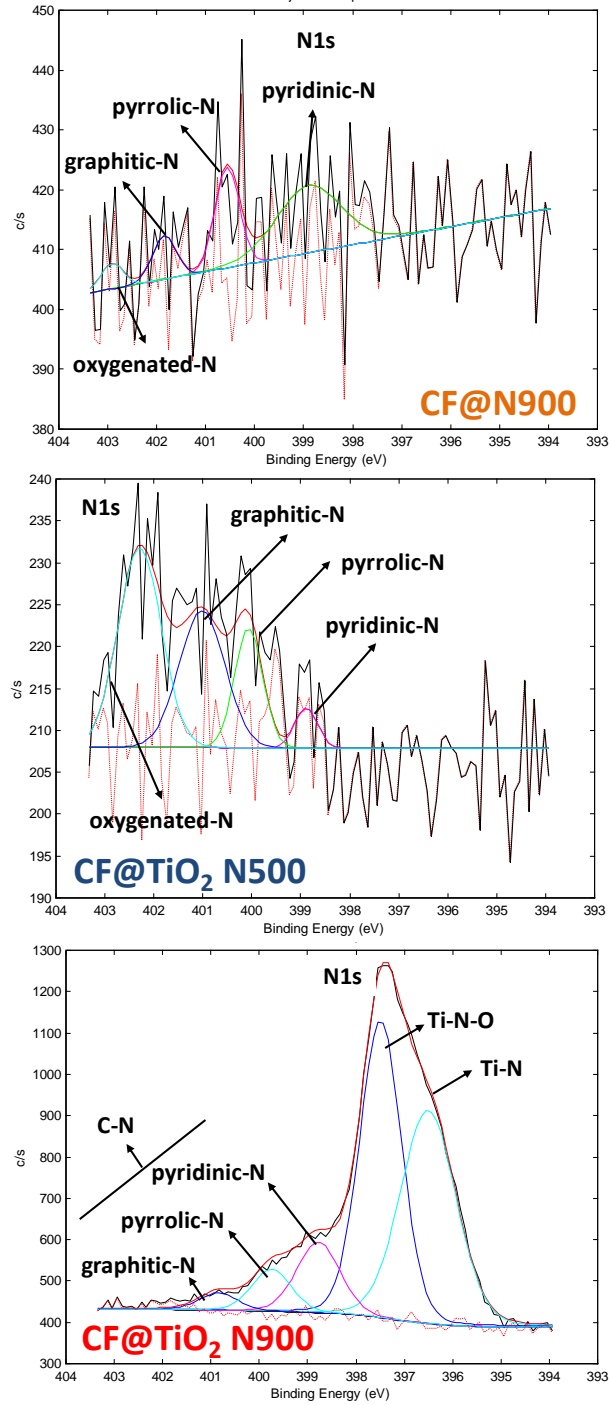




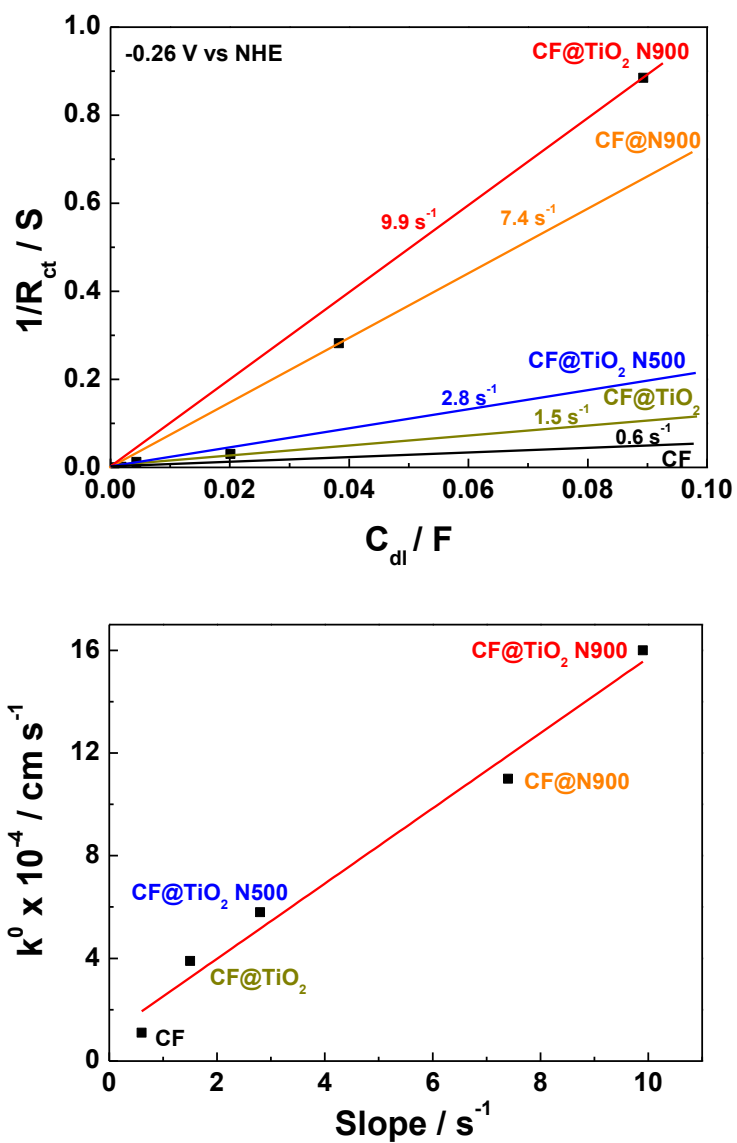
**Figure S2.** XPS general spectra **a)** CF@TiO<sub>2</sub> **b)** CF@TiO<sub>2</sub> N500 **c)** CF@TiO<sub>2</sub> N900 and **d)** CF@N900.



**Figure S3.** - XPS O1s band spectra deconvolution for the sample CF@N900.

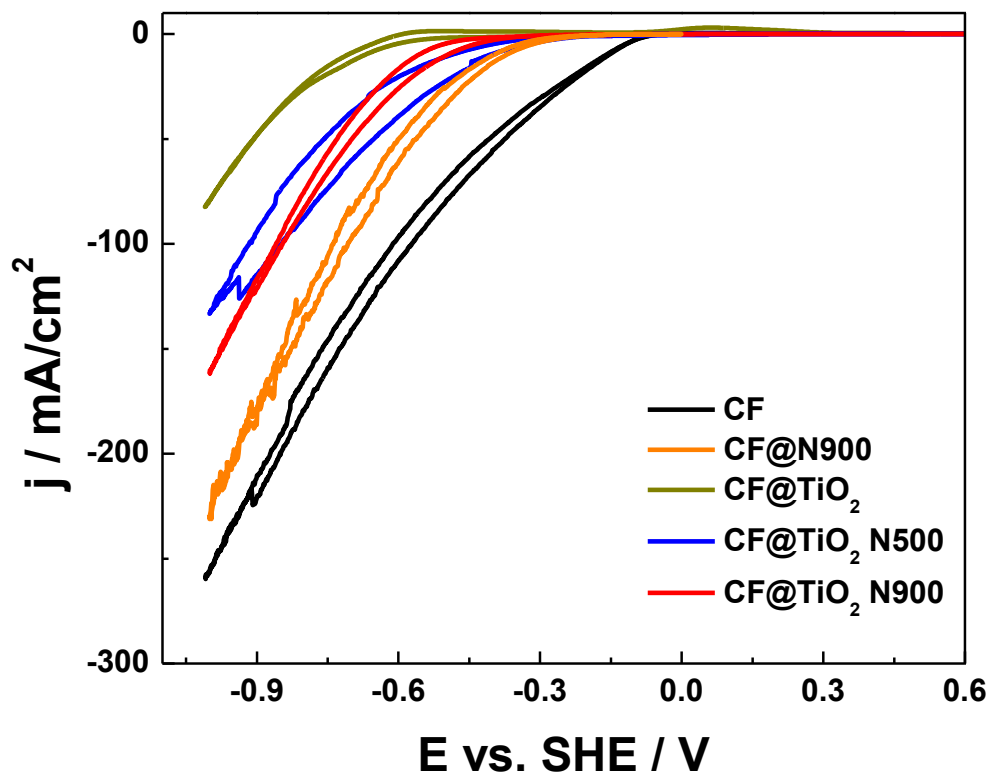


**Figure S4.** - XPS N1s band spectra for the samples CF@N900, CF@TiO<sub>2</sub>N500 and CF@TiO<sub>2</sub> N900.

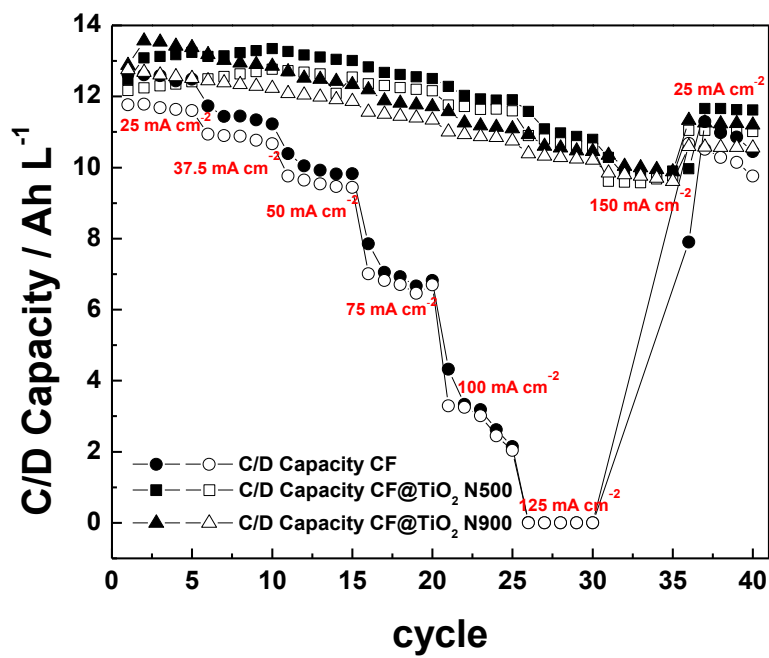


**Figure S5 – Top.** Plot of inverse of the charge transfer resistance ( $1/R_{ct}$ ) vs. Capacitance of the double layer on the electrode surface ( $C_{dl}$ ) for the different electrodes used at -0.26 V vs. SHE. **Bottom.** Linear relationship between  $k^0$  Tafel values and slope obtained by Fink method.

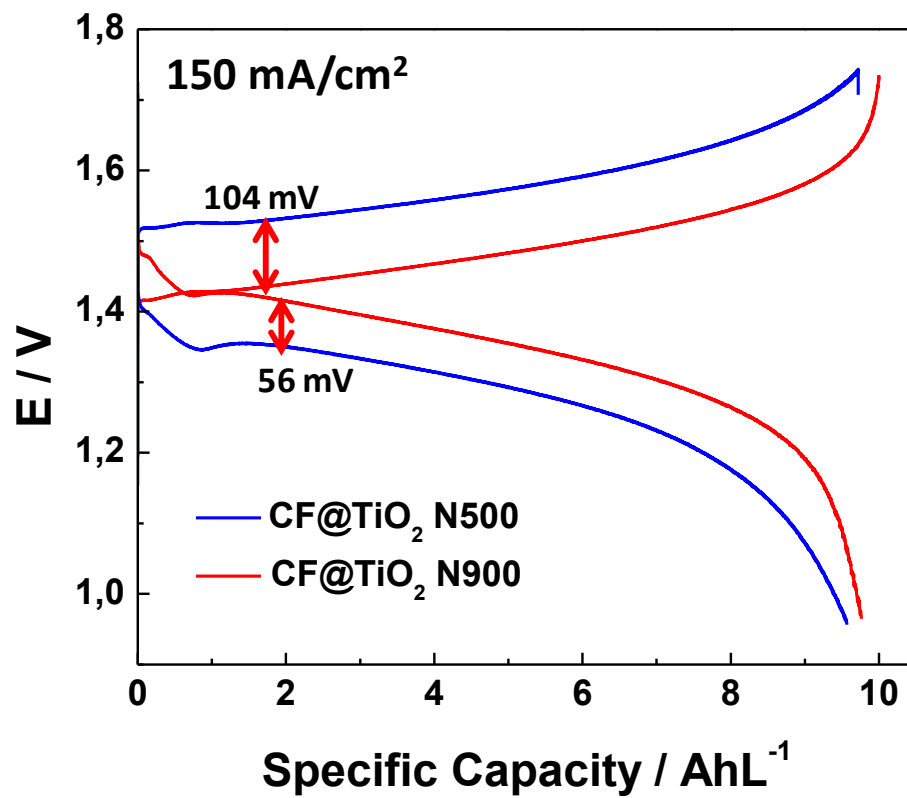




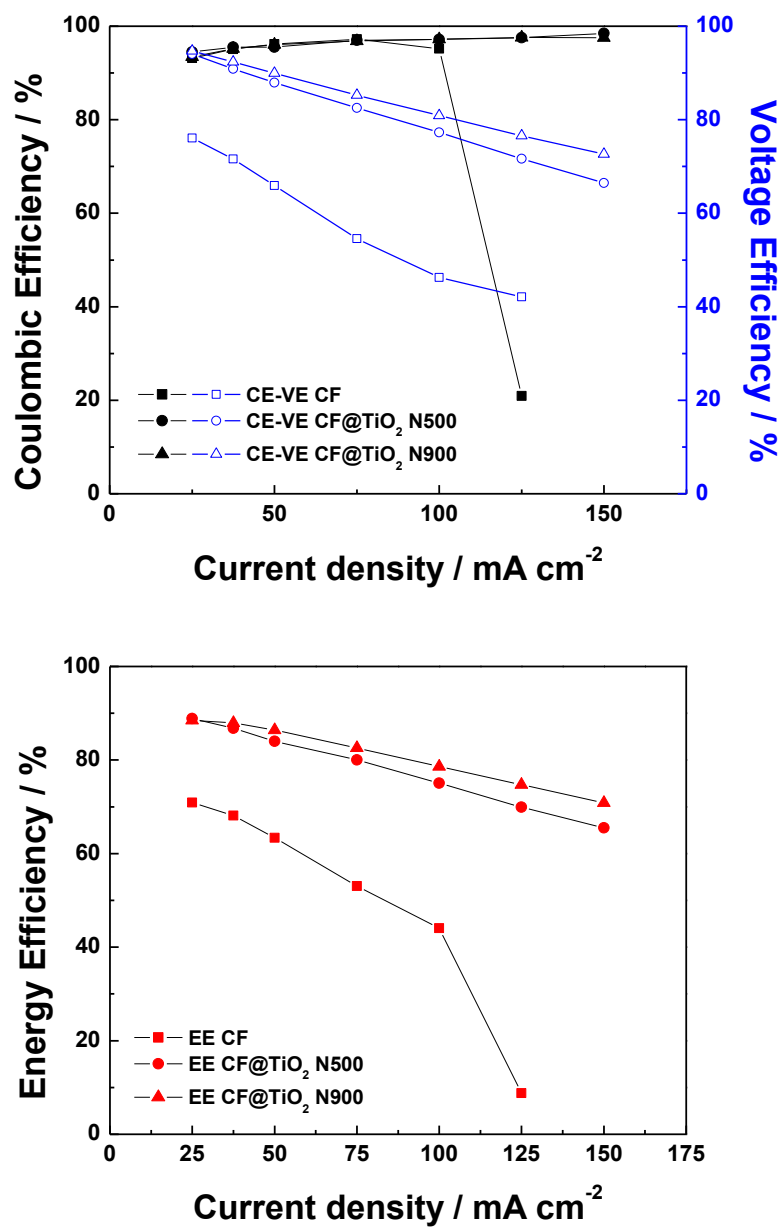
**Figure S6** - Cyclic voltammetry (CV) of carbon felt, CF@TiO<sub>2</sub> and CF@TiO<sub>2</sub> N500 and N900 electrodes using a 1M sulphuric media at  $2 \text{ mV s}^{-1}$ , with potential window of 0.6 to -1 V vs. SHE.



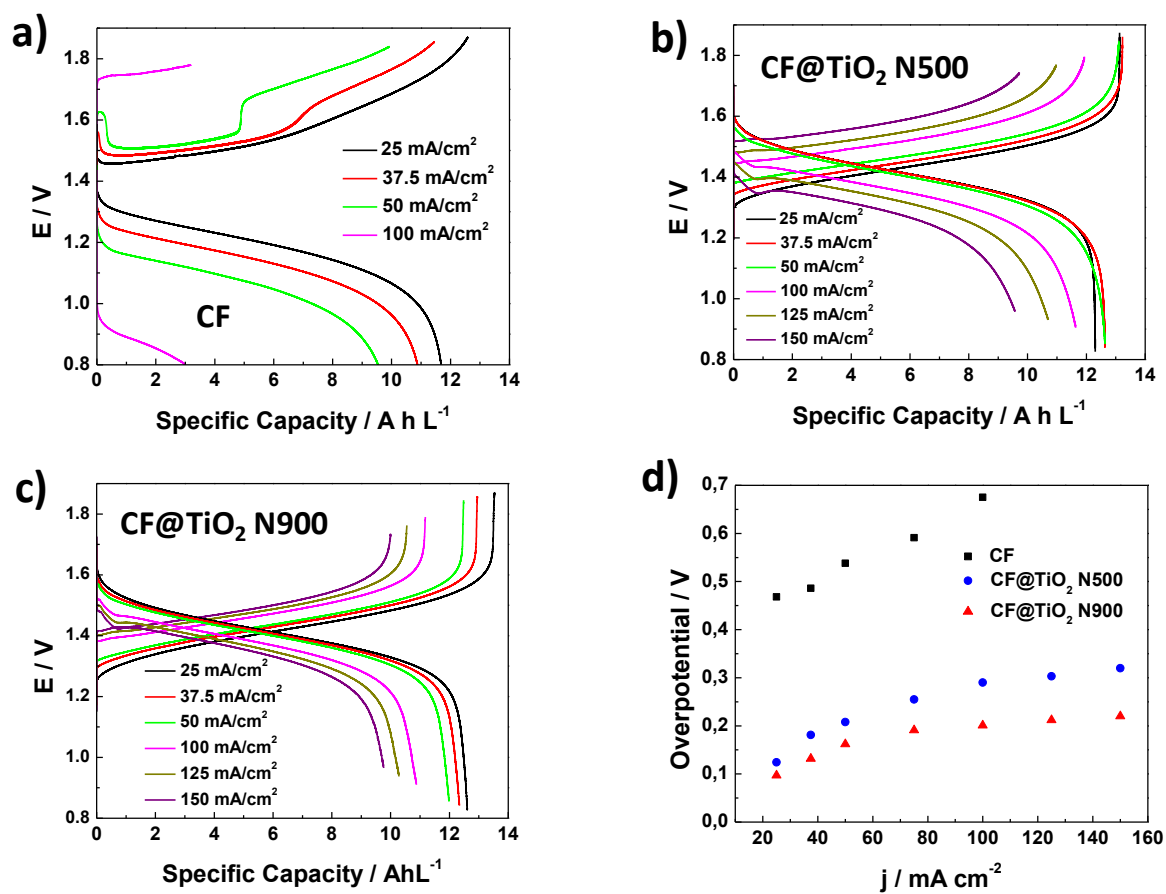
**Figure S7.** Battery's capacity as a function of the current density for different modified electrode used as, CF-HT, CF@TiO<sub>2</sub> N500 and CF@TiO<sub>2</sub> N900.



**Figure S8** – Comparative between voltage profiles for CF@TiO<sub>2</sub> N500 and CF@TiO<sub>2</sub> N900 for current density applied of 150 mA cm<sup>-2</sup>.



**Figure S9.** Average efficiencies (CE, VE and EE) as a function of the current density applied for different electrodes in galvanostatic single cell conditions.



**Figure S10** – Charge-discharge voltage profiles between 1.8 and 0.8 V at different current densities (25 to 150 mA cm<sup>-2</sup>) for **a)** CF, **b)** CF@TiO<sub>2</sub> N500 and **c)** CF@TiO<sub>2</sub> N900. **d)** Overvoltage during charge period comparatively to E<sub>ocv</sub>

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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