



Can electrospun nanofibres replace traditional carbon felt electrodes in redox flow batteries?

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Electrospinning is fast finding its way as one of the preferred manufacturing techniques to process advanced materials for energy-storage applications. This is due to its remarkable advantages in terms of high versatility to produce free-standing nanofibre materials with controlled composition, porous microstructure and thickness. Among the different devices that can benefit from this technique, redox flow batteries are an emerging grid-scale energy-storage technology that uses electrodes consisting of commercially available carbon felts, cloths or papers. These materials exhibit relatively good stability and low cost. However, their activity towards relevant redox reactions is often poor, which leads to low-power densities and voltage efficiencies. Attempts to improve the electrochemical activity via thermal treatment or deposition of electrocatalytic species have produced mixed results. In addition, the microstructure and void volume are key properties that need optimisation to achieve effective mass transport. The electrodes act as porous media, providing heterogeneous interaction between the electrolyte and exposed catalytic sites. Therefore, the ability to control properties such as porous volume, specific surface area and tortuosity is highly desirable to minimise transport-limited inefficiencies and parasitic pumping losses. This opinion paper explores the potential of electrospun carbon materials to replace commercial carbons as electrodes for redox flow batteries, examining advantages, disadvantages and challenges.

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Introduction

Redox flow batteries (RFBs) have great potential for safe and effective medium–long-term energy storage, with a predicted market size expected to reach \$489 million by 2026 [1]. Some of the advantages of RFBs include depth of discharge, high round-trip efficiency, reduced environmental impact and decoupling of power and energy capacity [2•]. A typical RFB consists of two electrolyte tanks from which the dissolved electroactive species are circulated by pumping through two carbon-based electrodes, which provide catalytic active sites for the redox reactions, facilitating mass transport and charge transfer. It is obvious then that the RFB efficiency is highly dependent on the porous microstructure and surface chemistry of the electrode, electrolyte fluid dynamics and interaction membrane–electrode. Commercially available electrodes usually suffer from poor wettability and high pressure drop, leading to low electrochemical performance [3]. In order to achieve a wider commercialisation of RFBs, the design of high-performing electrodes obtained from sustainable and low-cost materials is crucial.

Researchers around the world have combined electrochemical methods, computational modelling and X-ray computed tomography to demonstrate that a porous structure with pore sizes of 10–20 μm in diameter and a smaller fraction of larger pores, is optimal for electrodes in RFBs. Nonetheless, recent studies suggest that the permeability of the electrodes seems to be intimately related with surface chemistry of the particular material, which leads to interesting correlations using L  v  que equation that links electrocatalytic activity, fluid dynamics and heterogeneous interactions between redox species and catalyst [4,5]. Also, by controlling the porosity and void structure of the electrodes can lead to a more effective operation in the mass transport-limited regime. Recently, it has been shown that a smaller fibre diameter improves the efficiency of the RFBs since the specific surface area of the electrode provides a higher exposure of catalytic active sites. A recent work by Forner-Cuenca et al. [6] presented a fascinating bottom-up computational approach that combined genetic algorithm and pore network models for the optimisation of the porous structure of RFB electrodes with notable results.

However, the range of modifications one can apply to the microstructure of commercial electrodes is very limited, with most cases only looking into tuning the surface chemistry of the electrode or decorating these carbonaceous electrodes with electrocatalytic species to enhance electrochemical kinetics. In this sense, electrospinning offers the opportunity to design truly bespoke free-standing microstructure materials. Standard electrospinning creates fibres derived from polymers, drawn out by applying a high-voltage bias ($\Delta\phi < 10$ kV) between a needle containing flowing polymeric solution and a metal plate collector where the fibres adhere. Additionally, via simple modifications of the electrospinning solution and set-up, this fabrication technique can achieve materials with controlled fibre size, void volume and alignment.

Incorporating electrospun electrodes into redox flow batteries

The use of electrospun fibres as electrodes in redox flow batteries was demonstrated for the first time in 2013 by Wei et al., who employed polyacrylonitrile (PAN) as carbon source, obtaining fibres with diameters between 100 and 200 nm, an order of magnitude smaller than commercial carbon electrodes [7]. Although the fibres produced via electrospinning display high surface area for the studied redox reactions, the mass transport was impeded due to the more dense structure of the electrospun electrodes [8,9]. One approach to overcome this consists in enlarging the void volume of the obtained materials through customised electrospinning processes, such as the horizontally opposed blending electrospinning method [10]. A pioneering study by Flox et al. investigated the

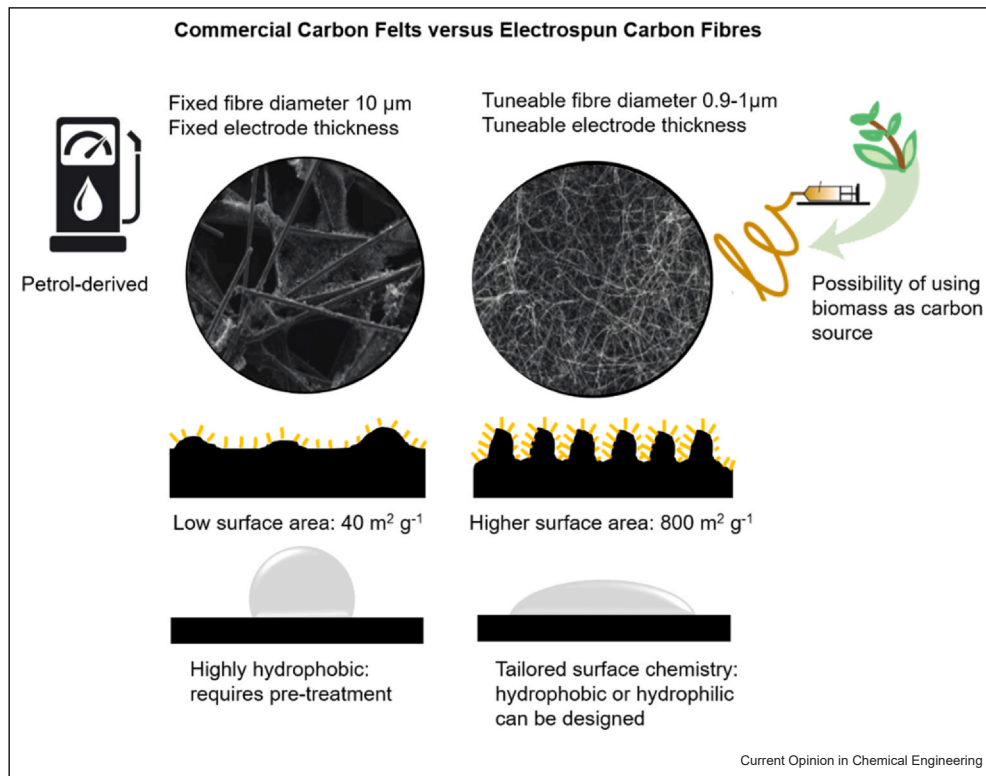
effect of fibre alignment in electrospun RFB electrodes by using different collectors [11]. Their findings showed that the use of a rotating drum collector enabled the alignment of the fibres producing a directional anisotropy. These electrospun fabrics exhibited more homogeneous fibre-size distribution and larger diameter than the ones produced using a static collector, which translated into an enhanced conductivity, particularly in the aligned direction. The resulting nanofibrous electrode exhibited an enhanced charge-transfer process and electrocatalytic performance (Figure 1).

The fibre morphology can also have a large impact on the kinetics of the system [12]. In general, the smaller the fibre size, the greater the available electrochemical active surface area (ECSA). However, this reduction in fibre diameter leads to a lower permeability of the electrolyte, increasing mass transport resistance. On the other hand, the carbonisation temperature governs the degree of graphitisation and therefore the electrical conductivity of the electrospun fibres. Hence, a compromise between the degree of graphitisation, surface chemistry and specific surface area needs to be reached to achieve highly efficient electrodes [13,14].

The use of sacrificial agents has also proven to be an effective approach to enhance the efficiency of RFB electrospun electrodes by introducing mesopores. This approach leads to high wettability and electrocatalytic activity towards the redox processes happening on the surface of the nanofibres. Zhao et al. [15] used iron (III) acetylacetonate as sacrificial agent, and PAN as carbon source to produce highly conductive, mesoporous free-standing carbon electrodes (Figure 2a–d). In their work, they achieved a greater specific surface area of 348.88 $\text{m}^2 \text{g}^{-1}$, compared with commercial carbon felt ($\sim 8 \text{m}^2 \text{g}^{-1}$ on average). The produced electrodes exhibited faradaic efficiencies of 91.4% and 79.3% at current densities of 20 and 100 mA cm^{-2} , respectively. An average coulombic efficiency of $\sim 100\%$ was determined for both current densities. Sun et al. reported electrospun free-standing electrodes for vanadium redox flow batteries (VRFB), derived from PAN and polystyrene. The method employed produced self-assembly of individual fibres into fibre bundles by varying the viscosity of the precursor spinning solution [16]. This strategy led to an increased void volume, while maintaining high specific surface area, deriving into faradaic efficiency of 87.7% at a current density of 100 mA cm^{-2} , which is 12.5% higher than conventional electrospun fibres (Figure 2e–h).

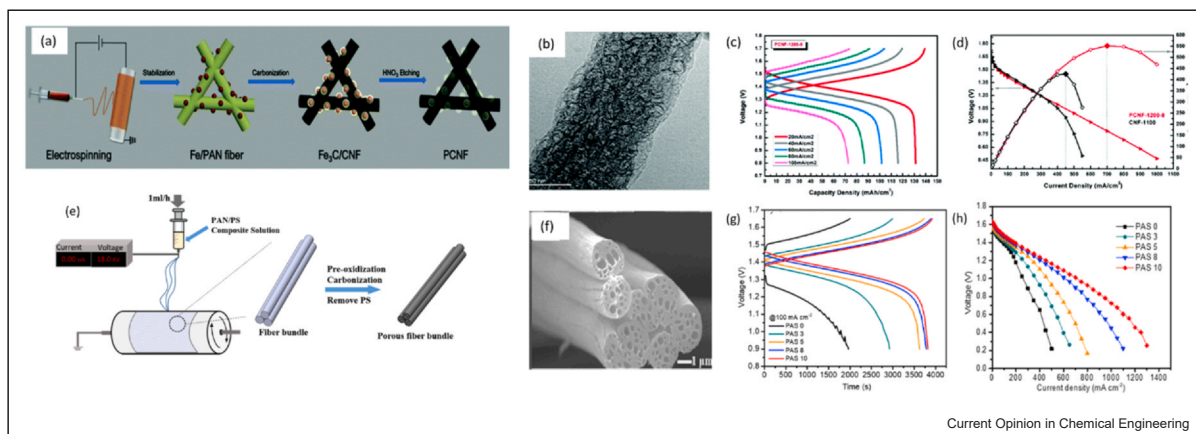
Jervis et al. explored for the first time the relationships between permeability, fibre diameter, pore-size distribution and tortuosity factor in electrospun carbon electrodes using nano X-ray computed tomography [17]. This work compared fibres with uncontrolled, controlled and aligned configurations, showing that the

Figure 1



Schematic representation of carbon felt versus electrospun materials as electrodes for redox flow batteries. Carbon felts exhibit fibre diameters in the range of 10 μm and low surface areas of $\sim 30\text{--}40\text{ m}^2\text{ g}^{-1}$. In contrast, the diameter of electrospun fibres can achieve lower values, $\sim 0.9\text{--}1\text{ }\mu\text{m}$, and surface areas of $\sim 800\text{ m}^2\text{ g}^{-1}$.

Figure 2



Examples of electrospun fibres used as electrodes for redox flow batteries. **(a)** Schematic representation of the porous carbon electrospun nanofibres (PCNF). **(b)** TEM image of the fibres after FeC_3 etching by HNO_3 . **(c)** Charge/discharge voltage-capacity curves of the mesoporous electrode at different current densities. **(d)** Polarisation curves as a function of current density in the range $0\text{--}1.1\text{ A cm}^{-2}$. **(e)** Illustration of synthesis process of the electrospun porous carbon fibre bundle structure. **(f)** SEM image of the carbonised fibre bundles. **(g)** Charge/discharge curves at current density of 100 mA cm^{-2} . **(h)** Polarisation curve of single VRFB with different electrospun bundle electrodes. **(a–d)** Adapted from Ref. [15]. **(e–h)** Adapted from Ref. [16].

aligned electrospun fibres exhibited significantly higher permeability in the direction of alignment. This was further studied by Kok et al., who concluded that a deep analysis and microstructure optimisation followed by *operando* characterisation of the battery was always required to realise the ideal electrospun fibre electrode permeability and mass transfer coefficient [18••]. Another interesting example of electrospun electrodes was published by Sun et al. [19•] In their work, they used an alternative electrospinning technique, achieving uniaxially aligned electrospun electrodes with an average fibre diameter of $9 \pm 2 \mu\text{m}$, showing an enhanced permeability compared with nonaligned electrospun fibres. When assembled into an all-vanadium RFB, this device exhibited a faradaic efficiency of $\sim 84.4\%$ at a current density of 100 mA cm^{-2} , 13.2% higher than the observed values for conventional electrospun fibre electrodes. Additionally, by adjusting the orientation of the electrospun-aligned fibres perpendicular to the flow channels of the battery, the device delivered the largest discharge capacity at a current density of 900 mA cm^{-2} .

Wu et al. studied the effect of combining different carbon supports (graphite felt, carbon cloth and carbon paper) with PAN-derived electrospun fibre electrodes [20]. According to their findings, electrospun PAN fibres supported on carbon cloth showed the highest faradaic efficiency, $\sim 80\%$ at a current density value of 240 mA cm^{-2} and good stability after 800 cycles.

Another interesting approach of tailoring electrospun free-standing electrodes was provided by Fetyan et al. [21] In their work, they reported a full carbon-based composite by electrospinning a mixture of PAN, carbon black (CB) and polyacrylic acid supported onto commercial carbon felts. These materials exhibited promising performance at current densities below 60 mA cm^{-2} , with faradaic efficiencies above 80%. However, the efficiency of the RFB decreased significantly at higher current densities. This is due to the smaller void volume provided by the electrospun fibres, translating into lower permeability. Maleki et al. also explored the incorporation of CB to the electrospinning solution, deriving into rougher surface and larger fibre diameter. These electrodes exhibited higher catalytic activity compared with commercial carbon felts, displaying a prominent anodic peak value for the $\text{V}^{4+}/\text{V}^{5+}$ redox pair [22].

With an interesting approach, Sun et al. studied the effect of fibre diameter in electrospun PAN-derived electrodes [23]. In their work, they produced dual-diameter electrodes, where larger fibres provided microchannels for the electrolyte flow, whilst the smaller fibres enabled a greater ECSA for redox reactions. Consequentially, their electrodes were able to reach a faradaic efficiency of 84.78% at a current density of 100 mA cm^{-2} , 13.57%

higher than nanofibrous electrodes, and 3.91% higher than commercial electrodes. The electrocatalytic efficiency of these electrodes was maintained at current densities of up to 200 mA cm^{-2} .

Additional modification of electrospun fibres to optimise their performance has been explored widely in the literature. These additional steps imply wet chemistry, thermal and electrochemical surface modification of the electrospun mats, resulting in a significant enhancement towards the reversibility of redox processes [9,24]. For example, Xu et al. used a postfunctionalisation approach to tailor the micro- and nanoscale-structured electrodes [9]. The electrodes exhibited 80.28% faradaic efficiency at a current density of 250 mA cm^{-2} , showing stability for more than 1000 cycles. The electrospun micro- and nanostructured electrodes delivered a peak power density of $702.98 \text{ mW cm}^{-2}$, 69.45% greater than commercial carbon felts.

As an alternative, changing the geometry and morphology of the electrospun fibres, for instance from cylindrical to flat, can also impact the efficiency of electrospun electrodes in RFB. In this context, Yadav et al. [25•] used a coaxial electrospinning set-up delivering electrospun fibres comprised by PAN shell and polystyrene core. As a sacrificial element, polystyrene was removed after spinning, deriving into the collapse of the fibres to ribbons. The obtained flat ribbons exhibited higher power density at low current densities, compared with commercial electrodes. These findings reasonably attributed to the obtained higher surface area and permeability. However, these electrodes suffered from significant electrochemical potential loss at a high current density region, due to poor mass transfer.

Although there are still not many examples in the literature for flow batteries, the amount of research towards the application of sustainable materials has increased dramatically over the last few years and it is expected that redox flow batteries will follow a similar trend [26•,27•]. One exciting approach depicting electrospinning as a feasible method to produce free-standing electrodes using biomass as the carbon source was shown by Vilvo-Vilches et al. [28•] In their work, they demonstrated the potential application of lignin-derived electrospun fibres for VRFB, comparing the electrocatalytic activity amongst different types of lignin. Specifically, the electrospun fibres derived from kraft lignin showed enhanced charge transfer and towards the oxidation of $\text{V}^{3+}-\text{V}^{4+}$ and reduction of $\text{V}^{4+}-\text{V}^{5+}$. Subsequently, with a very interesting approach, Ribadeneyra et al. manufactured and tested lignin-derived P-doped electrospun electrodes for all-vanadium RFB for the first time, exhibiting an initial capacity of 790 mAh at a current density of 40 mA cm^{-2} , deriving into a faradaic efficiency of $\sim 84\%$ [29••].

Decorating commercial and electrospun carbon electrodes to boost their electrochemical performance

Computational studies have predicted that the introduction of heteroatoms can have a positive impact on the electrochemical performance of RFB electrodes [30]. The introduction of heteroatom functionalities and halogens (N, O, P, B, F, Cl, and Br) increases the number of surface-active sites available to catalyse the redox processes [31–36]. The presence of surface functionalities also enhances the hydrophilicity of the electrode, promoting and improving accessibility of electrolyte, founding tremendous attention in the past to improve the reaction rate towards the vanadium redox couples [37]. Electrografting has been recently employed to successfully attach taurine to carbon cloth through an amine group via covalent bond [38]. The hydrophilic sulphonic acid tail of the taurine enables better wettability and promotes faster reduction-reaction kinetics for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox pair and demonstrates electrografting as an effective approach to customise the surface chemistry of commercial carbon electrodes.

The introduction of heteroatom functionalities in commercial electrodes inevitably requires the use of post-treatments. Since carbon felts are highly hydrophobic, a thermal, chemical or plasma treatment must be applied to introduce oxygen functionalities, mainly hydroxy and carbonyl (-OH, -COOH), adding extra steps to the electrode fabrication [39,40]. A better understanding of the benefit of a particular heteroatom versus another is still needed, as well as the stability of these surface functionalities over time under electrochemical redox flow conditions. For instance, galvanostatic charge–discharge experiments have shown to deplete the surface oxygen groups over time [41]. The addition of heteroatoms can often promote structural and morphological changes in the electrodes, too, and the effect caused by these changes should be separated from the ones due to the mere heteroatom [42].

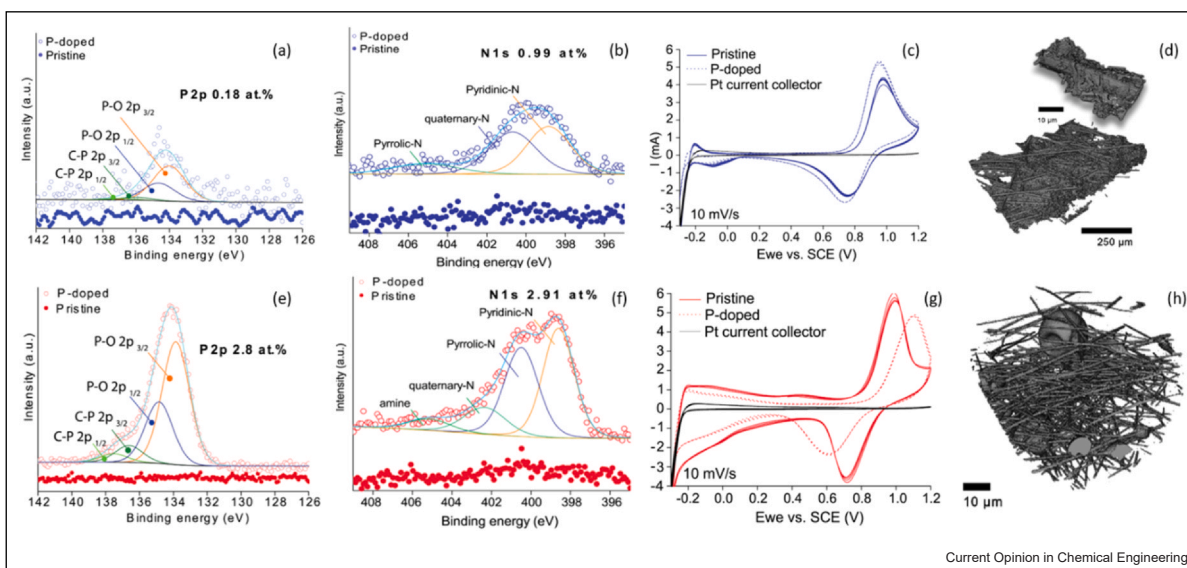
The introduction of heteroatoms in electrospun fibres can be achieved either during the electrospinning process by introducing the heteroatom precursor in the spinning solution, enabling also the introduction of more than one heteroatom at the same time, or via post-treatment, for example, using wet chemistry procedures, electrochemical-induced doping and thermal treatments [42,43]. The surface chemistry of the electrospun fibres can be easily tuned to promote electrocatalytic activity via the introduction of redox-active sites. Depending on the precursor polymer used for spinning, inherent residual heteroatom functionalities are maintained to some extent after the carbonisation step of the electrospun fabric. He et al. reported the use of N-doped electrospun fibres for VRFB applications, showing the improvement of the electrocatalytic properties because of the presence

of surface defects and hydrophilicity [43]. This led to remarkable values of energy-storage capacity of 98.0 mA h, 30.0 mA h higher than the values obtained with a carbon felt electrode. However, the use of heteroatoms different from O using electrospinning has not yet been extensively explored in the literature. Moreover, comparative studies on the effect of heteroatoms as dopants to enhance the electrocatalytic activity of the commercial and electrospun electrodes would be extremely beneficial to understand structure–composition property relationships in these systems. Figure 3 shows one of the few examples that compares P doping in commercial carbon felts and electrospun electrodes [29], where P was introduced in the form of PO_4^{2-} to enhance the electrochemical activity towards the V(IV)/V(V) redox pair. These findings showed opposite trend for commercial carbon and electrospun lignin. In the case of the electrospun lignin-derived carbon electrodes, the introduction of P had a negative effect on the performance of the electrode (Figure 3c). Comparatively, the lignin-derived electrospun fibres suffered a decrease in current density and an increase of the vanadium oxidation overpotential, when using a half-cell electrochemical configuration (Figure 3g). The negative effect was attributed to the smaller fibre diameter in the electrospun fibres and higher PO_4^{2-} content that could block the access to additional functional groups, decreasing the number of active sites and surface area.

Another alternative widely investigated to boost the electrocatalytic activity of carbon electrodes in RFBs consists in decorating carbonaceous materials with electrocatalytic species. Specifically, transition metal compounds, which exhibit partially filled *d*-orbitals, that can easily donate or accept electrons during redox processes [44]. Some of the transition metals investigated include Bi, Sb, Cu, Ni, Mo, Co, and Ta [36,45,46]. Metal oxides have also been demonstrated to be a viable option towards boosting the electrocatalytic properties of the electrodes with a much higher selectivity towards either one side of the vanadium reaction or towards both, without promoting parasitic reactions [36,47,48].

The decoration of commercial carbon felts with electrocatalysts mainly involves impregnation by submerging the electrode in the precursor solution and a subsequent thermal treatment to enhance the adhesion of the catalytic particles onto the fibre surface [49,50]. Alternatively, metals can also be deposited via electrodeposition. One of the advantages electrospinning can offer in this sense is that the electrocatalytic transition metals and metal oxide species can be effectively included as nanoparticles or precursors in the electrospinning solution. This procedure enables a homogeneous distribution of the electrocatalyst particles throughout the nanofibrous mat, increasing the anchoring of the particles and maximising their use as

Figure 3



Comparison of the effect of P-surface doping in commercial carbon paper versus electrospun fibres. *Carbon paper*: (a) P 2p high-resolution XPS(X-ray Photoelectron Spectroscopy). (b) N1s high-resolution XPS(X-ray Photoelectron Spectroscopy). (c) Cyclic voltammograms in V(IV)/V(V) electrolyte. (d) X-ray computed tomography image. *Electrospun fibre electrode*: (e) P 2p high-resolution XPS(X-ray Photoelectron Spectroscopy). (f) N1s high-resolution XPS(X-ray Photoelectron Spectroscopy). (g) Cyclic voltammograms in V(IV)/V(V) electrolyte. (h) X-ray computed tomography image. Adapted from Ref. [29].

active sites. Several examples in the literature compare the decoration with electrocatalysts of electrospun electrodes versus commercial carbon electrodes. TiO_2 , CeO_2 , Mn_3O_4 and ZrO_2 are among the metal oxide electrocatalysts explored for electrospun electrodes in VRFBs, resulting in increase of the electrochemical activity [36,47–50]. This approach still needs further development, including *operando* characterisation techniques that enable a greater understanding on the synergetic effect between transition metal oxide species and the electrospun carbonaceous support [51].

Conclusions and perspective

There is a clear potential of electrospun fibres for commercial application as free-standing electrodes for RFBs. A fine control of structural features, including fibre diameter, void volume and hierarchical porosity, along with the easy incorporation of surface functional groups and electrocatalyst nanoparticles, makes electrospinning an ideal technique for tailor-made electrodes. Furthermore, the electrocatalytic properties of each electrode can be optimised, depending on the redox chemistries of the RFB. The role of the electrode is to provide active sites for heterogeneous electrocatalysis of redox reactions, providing efficient mass transport and charge transfer. Because of this, the efficiency of a RFB is highly

dependent on the porous structure of the electrodes. For instance, commercial electrodes suffer from poor wettability and high pressure drop, whilst electrospun electrodes provide enhanced wettability with a nonideal permeability for the redox electrolyte. Extensive efforts have focused on tuning the surface chemistry of the electrode to enhance electrocatalytic properties. However, more research is needed to understand the role of the porous structure on the RFB performance, specifically from an experimental point of view. A few numerical models have been developed as tools to help design electrodes and to gain fundamental understanding of mass transport and electron-transfer processes within these electrodes. However, these models require experimental validation, for which the development of experimental approaches that can provide tailored microstructure is of great importance, making electrospinning an ideal candidate for this purpose.

There are certainly some limitations to overcome, mainly related to the fibre and pore size of electrospun fibres, which tend to be an order of magnitude smaller than commercial felts. Therefore, this fact leads to higher ECSA for redox reactions. Yet, mass transport properties can suffer, causing parasitic pumping power losses and inhomogeneity of reaction across the

electrode. More comparative studies between surface modification and use of heteroatoms between commercial and electrospun electrodes are needed to understand the effect of those also related to the fibrous microstructure. Furthermore, the addition of catalytic species for boosting the electrochemical activity has showed great potential and has shown considerable enhancement of performance. However, so far, increase in the cell efficiency following this approach has demonstrated to be more dramatic in commercial felts than electrospun electrodes, suggesting more research should be conducted towards tailoring fibre diameter, alignment, surface chemistry and void volume to be an effective contender to substitute commercial carbons in RFBs.

Data Availability

No data were used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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