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TOPICAL REVIEW

A mini-review on decorating, templating of commercial and electrospinning of new porous carbon electrodes for vanadium redox flow batteries

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Abstract

Carbon-based materials have become indispensable in the field of electrochemical applications, especially for energy storage or conversion purposes. A large diversity of materials has been proposed and investigated in the last years. In this mini-review, we present recent advances in the design of carbon-based materials for application in vanadium redox flow batteries. As main part, different modification and fabrication methods for carbon-based electrodes are described. The decoration of carbon felts and graphite felts with metals or metal compounds to enhance mostly the electrocatalysis of the negative side is illustrated with examples. Furthermore, various options of synthesizing porous C–C composites are discussed, with specific emphasis on graphene-based composites as well as nitrogen doped composites and biomass-derived carbons. Apart from that the method of electrospinning is also examined in detail, a method which not only allows the production of nanofibrous high surface area electrodes, but also allows adaptation of fiber thickness and architecture. In this review the significant strengths of each method are pointed out, but also particular weaknesses are discussed with respect to the later battery performance. Finally, an outlook is given pointing to the remaining challenges that need to be overcome in the future.

1. Introduction

The significant imbalance between energy resources and energy consumption belongs to mankind's greatest concerns, in particular, since our civilization still relies to a considerable amount on fossil fuels 'grown' over millions of years. Fossil fuels, such as coal, petroleum and natural gas, are available only in finite quantities and, furthermore, causing excessive carbon dioxide emissions when being burnt. Directly linked to the latter is the observed global warming, which is also a consequence of our over-reliance on this limited fossil energy. In order to balance the challenge between industrial development and environmental needs, sustainable energy resources, such as wind, solar, wave, geothermal and tidal power, would be attractive alternative options. However, due to the intermittency and unpredictability of these so-called renewables, it is necessary to employ additional energy storage systems to create a more flexible and reliable smart-grid system shaving off peak times and striving for continuous and reliable power supply.

One of the most promising large-scale energy storage solutions in this context are redox flow batteries (RFBs) due to their durability (i.e. not depending on phase transitions as their competitor—the lithium ion battery) and decoupled energy and power density.

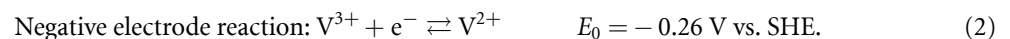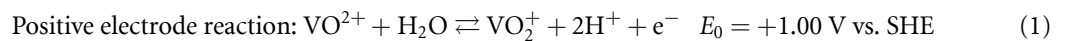During the last decades, a large variety of different all-liquid flow battery chemistries have been developed, which comprises the all VRFB, iron–chromium RFB, polysulfide–bromine RFB, all iron RFB etc. Among all these types, vanadium redox flow batteries (VRFB) invented at the University of New South Wales by Maria Skyllas-Kazacos *et al* have been widely studied and already achieved commercial fruition. One of

Figure 1. Working principle of a VRFB.
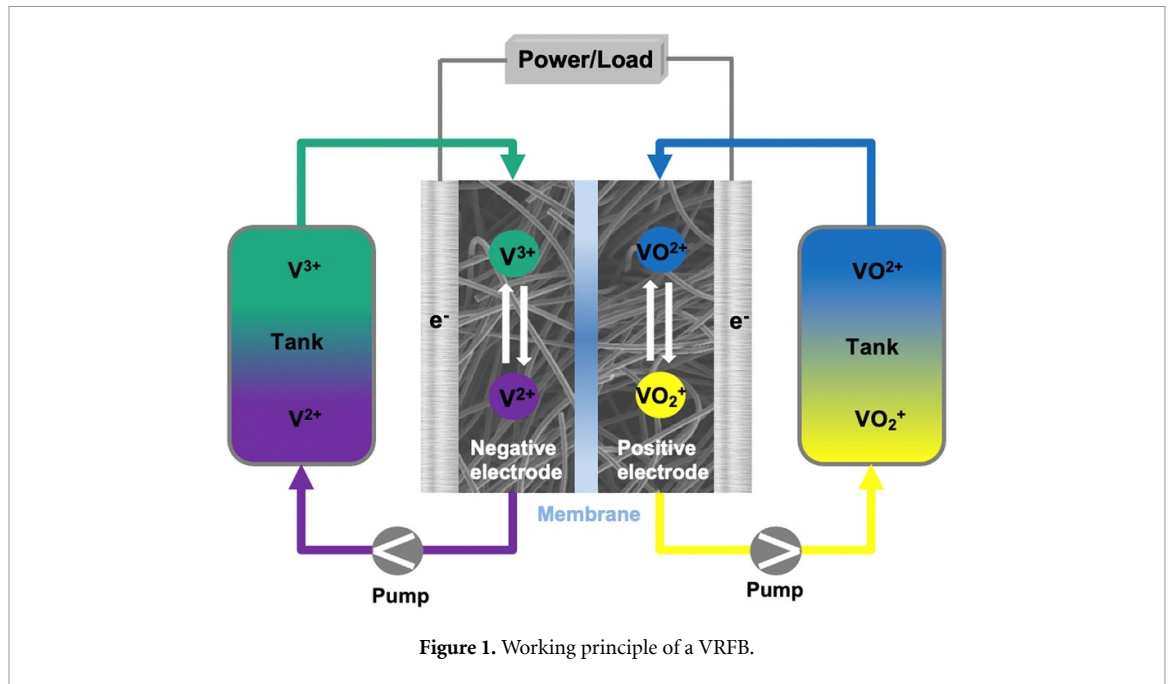
the most important advantages of RFB is that the energy is stored in solutions without solid phase changes which eliminates the possibility of short circuiting or loss of active material. On this premise, VRFB employ the same vanadium ions as active species in both catholyte (i.e. the electrolyte employed at the cathode side) and anolyte (i.e. the electrolyte employed at the negative side) to prevent undesirable performance fading due to contamination of the electrolyte solution by cross-over ions from the other half cell. Besides, in RFB the electrolyte solutions are kept separately from the stack, which is advantageous, as capacity and power can be adjusted independently and capacity fade with time will not be observed.

A VRFB consists of a stack of single cells. A single cell is composed of two electrodes separated by an ion exchange membrane, as schematically illustrated in figure 1. Both half cells are connected to additional electrolyte storage tanks, namely, VO^{2+}/VO_2^+ in the positive electrolyte and V^{2+}/V^{3+} in the negative electrolyte, where the energy is stored in the form of ions in the liquid electrolyte. The anolyte and catholyte are circulated and pumped through the porous carbon felts (CFs). A good balance should be found between contact time between electrode surface and electrolyte and pressure loss whilst pumping. The carbon surface enables the efficient electron transfer across the electrode–electrolyte interface thereby catalyzing the Vanadium redox reactions. The function of the membrane is to electrically separate both half cells, preventing short circuits and cross-over of ions from one half cell to the other. It also ensures exchange of selected ions (here: protons) for the sake of balancing the electrical charges of the anolyte and catholyte.

Equations (1) and (2) describe the redox reactions of VO^{2+}/VO_2^+ at the positive electrode and V^{2+}/V^{3+} at the negative electrode. During the charging process, VO^{2+} is oxidized to VO_2^+ at the positive side, while V^{3+} is reduced to V^{2+} at the negative side. Similarly, VO_2^+ is reduced to VO^{2+} and V^{2+} is oxidized to V^{3+} during the discharging process

$$\text{Positive electrode reaction: } VO^{2+} + H_2O \rightleftarrows VO_2^+ + 2H^+ + e^- \quad E_0 = +1.00 \text{ V vs. SHE} \tag{1}$$

$$\text{Negative electrode reaction: } V^{3+} + e^- \rightleftarrows V^{2+} \qquad E_0 = -0.26 \text{ V vs. SHE.} \tag{2}$$

The standard operation voltage of VRFB is 1.260 V at 25 °C, 1 atm.

The hydrogen evolution reaction (HER, $E_0 = 0.000$ V vs standard hydrogen electrode (SHE)) and oxygen evolution reaction (OER, $E_0 = +1.230$ V vs SHE) are possible parasitic reactions at the negative side and the positive side, respectively. Their occurrence as unwanted side reactions during battery operation has been described in various studies [1–3]. Wei *et al* even show *in-situ* results, in which the hydrogen bubbles produced during cell operation do not only block the active sites, but also suppress the desirable vanadium redox reaction and consume part of the charging current, which lowers the efficiency of the whole VRFB system [4]. In contrast, the evolution of oxygen in the presence of $VOSO_4$ was only observed at higher potentials, mostly above the voltage range of the operating battery [3, 5]. Besides OER, also carbon corrosion can be observed at higher potentials [6], where carbon is oxidized to carbon dioxide. While the reaction's

standard potential is comparatively low with $E_0 = 0.207$ V vs SHE, the oxidation is kinetically hindered up to >1.200 V vs SHE [7, 8].

The power density of VRFB depends predominantly on the cell stack, of which the porous electrodes are essential components. Consequently, it is essential to improve the performance of the electrodes, since they provide active sites for the redox reactions and influence the kinetics and reversibility of the redox couples significantly. Besides, the structure of the electrodes impacts seriously on the activation and concentration overpotentials, which should be overall as low as possible. Hence, a great amount of attention has been focused on the development of novel electrode materials for RFB.

With this mini-review we provide an overview of recent developments in materials and electrode design for application in VRFB. We will focus specifically on (a) the decoration of carbon and graphite felts (GFs) with metals and metal compounds to catalyze the redox reactions, (b) the synthesis of C–C composites to enhance surface area and for heteroatom doping, as well as (c) electrospinning (ES) for producing high surface area fibrous electrode mats. Besides the synthesis pathways and detailed materials characterization, comparisons of electrode performance in three-electrode model cells, half and full cells will be shown. Recommendations for further reading with respect to these topics are provided throughout the text.

2. Electrodes for VRFB

The vanadium redox reactions take place on the surface of the porous electrodes in the flow battery, when the V-containing electrolytes are brought into contact with and flown through the fibrous material. Carbon-based materials are favored for such electrochemical energy applications due to their many inherent advantages, such as low cost, high stability, and good electrical conductivity. But while carbon materials are already commercially applied in electronic, electromagnetic and biomedical applications, their utilization in energy conversion or storage is comparatively new. In VRFB, the electrodes—besides other components—play a key role, when it comes to capacity and long-term stability of the battery system.

Because of their stability over a wide potential range, even in highly acidic media, carbon-based materials are the perfect candidate for use as electrode materials. Various types of carbon materials, like carbon paper [9] or carbon foam [10], have been investigated for their later implementation in VRFBs, while carbonaceous and graphitic felts [11, 12] turned out to be the most suitable, meeting above requirements best. Such fibrous mats, non-wovens or felts are characterized in particular by their three-dimensional (3D) structure and their high electrical conductivity in plane, resulting from the delocalized π-electrons. Apart from that they are stable in highly acidic media, possess high corrosion resistance and low flow resistance (i.e. pressure drop) [13, 14]. Although carbon corrosion to CO_2 should already thermodynamically occur at potentials as low as 0.207 V vs saturated calomel electrode (SCE), it is kinetically hindered up to much higher potentials [7, 8]. Nowadays, GF and CF based on polyacrylonitrile (PAN) or rayon (cellulose) fibers are the most common, commercially available electrode materials. Using PAN as precursor has also the advantage that nitrogen can be retained in the structure. N-doped carbons have been reported to improve electrochemical performance, e.g. in fuel-cell relevant reactions such as the ORR.

Despite these clear advantages and excellent prerequisites for serving as electrode material in VRFB, there is still need for improving the performance of those electrodes. The inherent electrochemical activity of the carbon materials is comparatively low and in particular a lack of reversibility has been observed especially for the negative reaction. Pristine GF and CF are both severely hydrophobic and cannot provide a sufficient number of active sites, therefore their electrochemical activity is quite poor.

A common and prominent way to increase the electrochemical activity of the carbon electrodes is the introduction of functional oxygen groups, such as hydroxyl and carboxyl groups. It is assumed, that these groups attract more positively charged vanadium ions increasing the wettability, and therefore also enhance the electrocatalytic activity of the electrode surface [15].

Since the 1990s commercial felts have been treated by heating them in concentrated acids like sulfuric acid or nitric acid [16]. Later on also plasma treatments were presented to increase the number of surface groups [17, 18]. However, the thermal treatment [13], where the felts were heated up to 400° under air atmosphere, turned out to be both simple and effective. Depending on the material type or the thickness of the electrode, the duration of the activation step has to be adapted. The thermal oxidation of the felts has been considered as the state-of-the-art for a long time, also because it is easy to implement by companies and battery manufacturers.

However, there is a huge disadvantage concerning the long-term stability of such activated electrodes. Up to now no reliable information can be found in the literature, about how long this increase of activity will last or whether it is permanent. Additionally, still details of the activation mechanisms are lacking and contradictory suggestions can be found in the literature regarding this topic. A few groups propose that

oxygen-containing surface groups only increase the wetting with electrolyte, but do not help with or even impede the vanadium redox reactions [19–22].

Moreover, the enhanced activity of the electrodes is often accompanied by the parallel activation of the undesired side reaction in the negative half cell, the HER. Accordingly, it becomes a necessary prerequisite of optimized electrodes that their overpotential for the parasitic reactions is high.

Therefore, one important aspect in recent research was to find alternative strategies for electrode activation and to combine all positive properties in one single electrode material. The development of new approaches aims at an increase of the specific surface area of the electrodes on the one hand, controlled doping of heteroatoms, such as N, P, B [23–26] and on the other hand they focus on the decoration of CFs or GFs with metals or metal compounds.

It is supposed that higher specific surface areas are beneficial for facilitating the vanadium redox reactions as well as the electron transfer [27]. By introducing heteroatoms into the carbon structure, active centers seem to be created, where the redox reactions preferentially could take place.

And the decorating methods are presumably not only capable of creating reactive sites, but also lead to less corrosion and degradation of the electrode [10, 28, 29].

Unfortunately, clear structure–activity correlations, as well-known for other materials, still do not yet exist for the porous carbon electrodes. On the one hand side, this is due to the not yet established catalytically active site. On the other hand, while carbonization, heteroatom doping and higher surface areas have all been reported to positively affect the electrode's activity, the individual effects cannot be disentangled easily. For instance, a four times higher surface area is not necessarily reflected in a four times higher activity.

In the following, we will review three very specific approaches decorating, templating of commercial and ES of new porous carbon electrodes for VRFB.

2.1. Decorating with metals and metal compounds

Metal decoration of the felts was reported to increase the redox reactions at the carbon surface. A good catalyst should thereby make the following contributions: increase the electrode's conductivity, lower its charge transfer resistance, enhance electrolyte accessibility and reduce the parasitic reactions (as mentioned above, HER and OER). The enhancement should be stable with time and also available at low cost. At the early stages, noble metals, such as Pt, Au, Ir, Pd, etc were reported being decorated onto the carbon electrode as electrocatalysts. However, considering their high cost, low abundance and susceptibility to the described parasitic reactions, precious metals do not seem to be viable options in VRFB [14, 30]. In the past few years, oxides, nitrides and carbides of low cost metals, e.g. Bi [28, 29, 31–39], Ti [40–47], Nd [48], Pb [49], Co [50], W [51], Ta [52], Mo [10], Nb [53] have gradually emerged and are being investigated as electrocatalysts in VRFB.
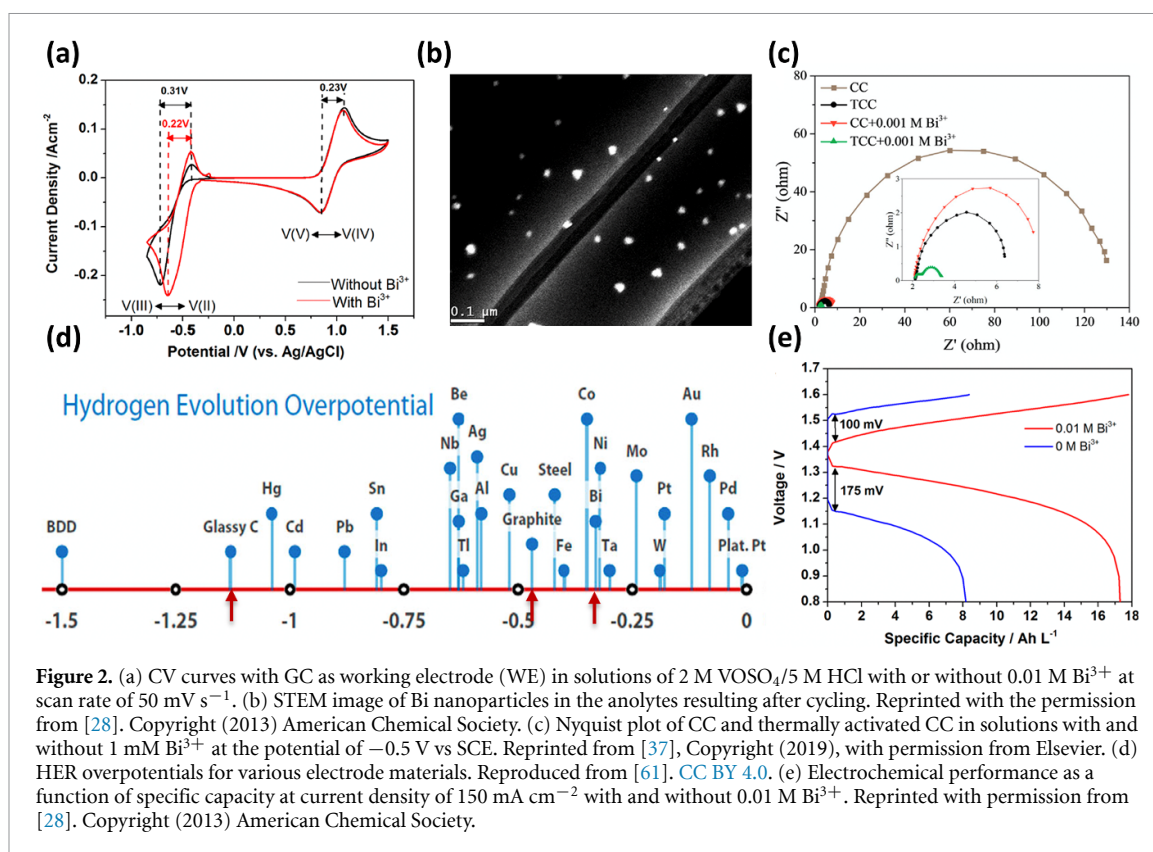
According to the literature, it is still under debate which half-cell reaction, VO^{2+}/VO_2^+ or V^{2+}/V^{3+}, is the rate determining one [22, 54]. Earlier studies found that the VO^{2+}/VO_2^+ redox reaction has a lower rate constant compared to the V^{2+}/V^{3+} reaction by means of cyclic voltammetry and Tafel analysis, both indicating that VO^{2+}/VO_2^+ limits the battery performance [55–57]. However, recent reports by Sun *et al* investigating electrode losses in VRFB with impedance spectroscopy reported that the negative electrode comprising the V^{2+}/V^{3+} redox couple contributes approximately 80% of the cell overpotential during discharge [58, 59]. Langner *et al* has also shown that the negative side is more impeded by employing reference electrodes in RFB set-up [2, 60]. Nevertheless, numerous studies on improving the kinetics of both vanadium redox reactions have been carried out for both the positive and negative side and reported in the recent literature. Among them, bismuth and titanium-based compounds were reported as very effective catalysts for the V^{2+}/V^{3+} redox reaction in anolyte, which we will introduce in detail in the following part. The others, namely, Nd, Pd, Pb, Co, W and the like, are mainly explored for the enhancement of the VO^{2+}/VO_2^+ redox reaction in the catholyte.

2.1.1. Bismuth-based catalysts

Bismuth used as electrocatalyst at the negative side of VRFB was first reported by Li *et al* [28], and has drawn significant attention from then. As shown in figure 2(a), additions of Bi^{3+} ions decrease the peak separation for the V^{2+}/V^{3+} redox reaction, while Bi^{3+} has hardly any effects on the positive side.

There have been mainly three approaches reported for Bi modification. For the first method, commercial GFs have been straightforwardly impregnated or soaked with aqueous bismuth solutions and then dried in air at around 80 °C [29, 36, 38, 55, 58]. Another alternative strategy is by adding bismuth ion solutions directly into the vanadium electrolyte and setting a potential range which includes both the V^{2+}/V^{3+} ($E_0 = -0.26$ V vs SHE) and Bi/Bi^{3+} ($E_0 = +0.308$ V vs SHE) reactions to achieve bismuth nanoparticles or coated thin films electrodeposited onto the surface of the electrodes [28, 31]. The STEM image in figure 2(b) demonstrates the uniform distribution of electrodeposited Bi on a mirror-finish glassy

Figure 2. (a) CV curves with GC as working electrode (WE) in solutions of 2 M VOSO$_4$/5 M HCl with or without 0.01 M Bi^{3+} at scan rate of 50 mV s^{-1}. (b) STEM image of Bi nanoparticles in the anolytes resulting after cycling. Reprinted with the permission from [28]. Copyright (2013) American Chemical Society. (c) Nyquist plot of CC and thermally activated CC in solutions with and without 1 mM Bi^{3+} at the potential of -0.5 V vs SCE. Reprinted from [37], Copyright (2019), with permission from Elsevier. (d) HER overpotentials for various electrode materials. Reproduced from [61]. CC BY 4.0. (e) Electrochemical performance as a function of specific capacity at current density of 150 mA cm^{-2} with and without 0.01 M Bi^{3+}. Reprinted with permission from [28]. Copyright (2013) American Chemical Society.
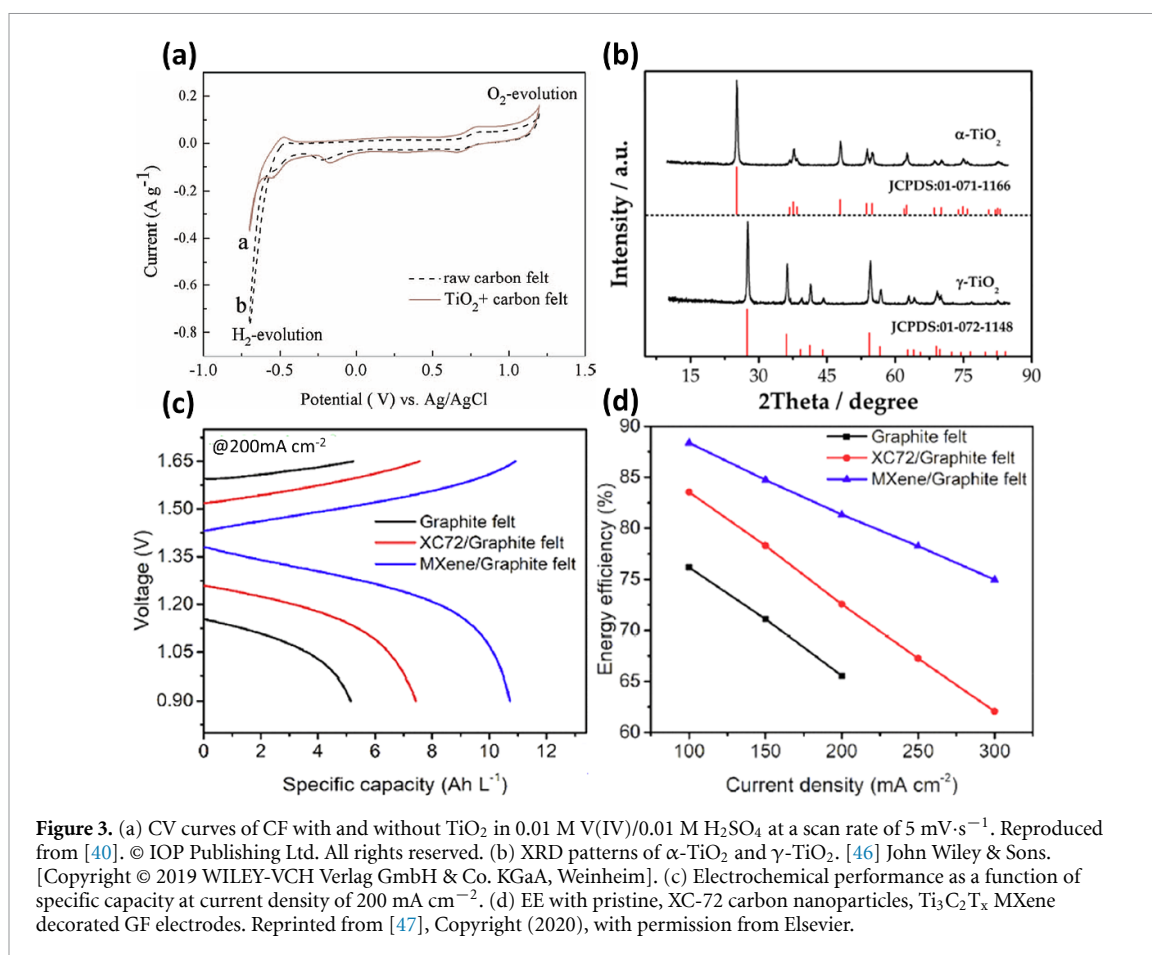
carbon (GC) model surface. It is noteworthy that for this approach to work, only those metals can be used as catalyst, which have a redox potential that allows them to be deposited on the surface of the electrode before the vanadium redox reaction sets in. The third practice is by combining pretreatment for pristine electrode material, such as thermal activation (which introduces more surface functional groups) or acid/base etching (which develops more well-defined pore sizes for later uniform particle distribution) with Bi electrodeposition on the electrode [32–34, 37].

The most well-known explanation for the catalytic effect of bismuth in VRFB is that it suppresses the HER and thus enhances the reversibility of V^{2+}/V^{3+}. Some researchers attribute the suppression of hydrogen evolution to the subsequent increase in the HER overpotential [34]. However, the hydrogen evolution overpotential on bismuth compared to GC and GF, as illustrated in figure 2(d), is actually lower and the corresponding current response is higher [31, 61]. Another assumption proposed by Suarez suggests that an intermediate BiH$_x$ is formed, which acts as a competitor to the undesirable irreversible HER. More hydrogen combines with bismuth and there will be less hydrogen ions left for H$_2$ formation [31].

Besides the influence of bismuth on the HER, also the charge transfer resistance derived from impedance spectroscopy has been reported to decrease dramatically after adding Bi^{3+} ions at the negative side. This beneficial effect also reflects in the lower overpotential in the full cell measurement, as shown in figures 2(c) and (e).

2.1.2. Titanium-based catalysts

In addition to extensive research on bismuth in recent years, titanium-based compounds, such as TiO$_2$, TiN and TiC, have also been comprehensively investigated as electrocatalysts at the negative side of VRFB. TiO$_2$ was proposed by Tseng *et al* in 2014; contact angle measurements indicated significantly improved wettability of the electrode upon TiO$_2$ addition. It is furthermore observed that TiO$_2$ contributes to suppress the parasitic HER, as illustrated in figure 3(a) [40]. Cheng *et al* investigated two structural modifications, anatase (α-TiO$_2$) and rutile (γ-TiO$_2$), whose x-ray diffraction (XRD) patterns are displayed in figure 3(b) [46]. Both of them were found to catalyse the V^{2+}/V^{3+} redox reaction. However, α-TiO$_2$ demonstrated better electrochemical activity and kinetic reversibility towards V^{2+}/V^{3+} reaction as its γ-TiO$_2$ counterpart. Wei *et al* reported excellent performances for GFs decorated with titanium nitride nanowire arrays and hollow Ti$_3$C$_2$T$_x$ MXene [45, 47]. Such modifications served to enhance electrochemical surface area and hydrophilicity and successfully lowered the kinetic activation energy in corresponding charge and discharge

Figure 3. (a) CV curves of CF with and without TiO_2 in 0.01 M V(IV)/0.01 M H_2SO_4 at a scan rate of 5 mV·s^{-1}. Reproduced from [40]. © IOP Publishing Ltd. All rights reserved. (b) XRD patterns of α-TiO_2 and γ-TiO_2. [46] John Wiley & Sons. [Copyright © 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]. (c) Electrochemical performance as a function of specific capacity at current density of 200 mA cm^{-2}. (d) EE with pristine, XC-72 carbon nanoparticles, $Ti_3C_2T_x$ MXene decorated GF electrodes. Reprinted from [47], Copyright (2020), with permission from Elsevier.

Table 1. Comparison of different carbon and GF electrodes decorated with various metals or metal compounds.

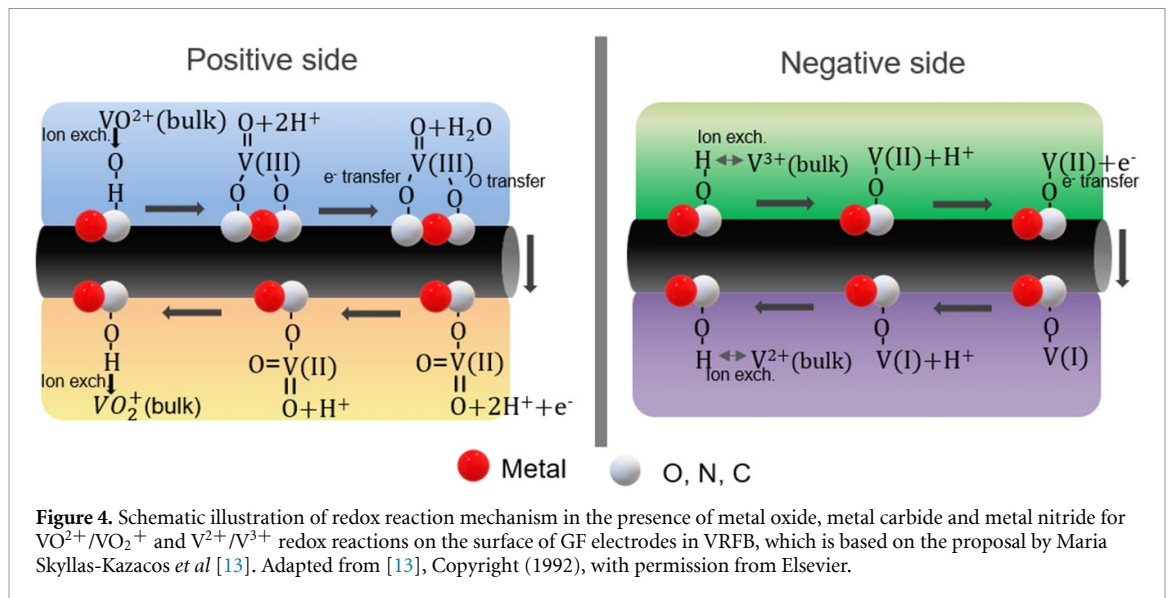| Catalyst	Electrode	Catalyzing which half cell	Current density (mA cm^{-2})	EE (%)	Reference
Bi nanoparticles	GF	Neg	100	84	[28]
Bi (HEDTA)	CF	Neg	80	80	[36]
TiO_2	GF	Neg	80	77	[46]
TiN nanowires	GF	Neg	100	88.5	[45]
Nd_2O_3	CF	Pos, neg	100	70	[48]
PbO_2	GF	Pos	80	78.1	[49]
CoO	GF	Pos	100	72.1	[50]
WON	GF	Neg	80	81.6	[51]
Ta_2O_5	GF	Pos	80	73.7	[52]
MoO_2	GF	Pos	80	73	[10]
Nb_2O_5	GF	Pos, neg	150	74	[53]

processes. Figures 3(c) and (d) exhibit significantly improved specific capacity of GF electrode modified with $Ti_3C_2T_x$ Mxene and higher EE of about 81.3% at 200 mA cm^{-2} in full cell test.

2.1.3. Summary of different metal-based electrocatalysts

Table 1 summarizes results reported in the time period from 2013 until 2020 for an intuitive comparison. Energy efficiency (EE) is the combination of coulombic efficiency (CE) and voltage efficiency (VE) as a function of current density and reflects the overall cell performance [62].

Consequently, EE at the current density of 80 mA cm^{-2} or 100 mA cm^{-2} is chosen as an indicator for the electrocatalytic effect of different metal and metal compound catalysts. However, there are still many other factors influencing the overall cell performance, such as catholyte and anolyte concentrations, electrolyte volumes, flow rate etc. As shown in table 1, Bi, Ti, W based materials show an electrocatalytic effect for V^{2+}/V^{3+} redox reactions [28, 29, 31–38, 40–47, 51], while Pb, Co, Ta and Mo based materials demonstrate an electrocatalytic effect for VO^{2+}/VO_2^{+} redox reactions [10, 49, 50, 52]. Nd and Nb were found having an electrocatalytic effect on both half cells [48, 53]. However, detailed studies on the catalytic mechanisms and its stability over time are scarce.

Figure 4. Schematic illustration of redox reaction mechanism in the presence of metal oxide, metal carbide and metal nitride for VO^{2+}/VO_2^+ and V^{2+}/V^{3+} redox reactions on the surface of GF electrodes in VRFB, which is based on the proposal by Maria Skyllas-Kazacos *et al* [13]. Adapted from [13], Copyright (1992), with permission from Elsevier.

2.1.4. General reaction mechanism of VRFB with metal or metal compounds decoration

Taking the whole picture of the recent publications on metal-decorated electrodes for VRFB into account, the exact catalytic mechanism is either not discussed at all or mostly attributed to more functional groups involved, which serve as electrocatalytically active sites for both VO^{2+}/VO_2^+ and V^{2+}/V^{3+} redox reactions. On a second glance, the improved performance of the metal-decorated electrodes is linked to the modified surface morphology, which enhances the wettability of the felt electrode and therefore increases the electrolyte accessibility and electrode/electrolyte interaction.

The mechanism proposed here is based on the early study by Maria Skyllas-Kazacos [63]. It is proposed that the metal oxide [35, 41, 44, 48, 52], metal carbide [43, 47] or metal nitride [41, 45] form hydroxyl functional groups more easily on the electrode surface. In a first step, an ion exchange process takes place between VO^{2+} transported from the bulk of catholyte and the H^+ ions of the hydroxyl group. Then, one oxygen atom from the functional group is transferred to VO^{2+} to form VO_2^+, with an electron transfer along the bond in parallel. Finally, newly formed VO_2^+ ions exchange with the H^+ ions in the electrolyte and diffuse back into the bulk solution. The steps are summarized in figure 4 accordingly. The redox reaction occurs in reverse during the discharge process. A similar reaction mechanism applies for the negative side. Ion exchange occurs initially between V^{3+} from the bulk of the anolyte and H^+ ions of the hydroxyl group combined with the catalytic metal. After that, an electron transfer takes place and therefore V^{3+} ions are reduced to V^{2+} ions. Finally, a simultaneous ion exchange and desorption process occur between V(I) and H^+ ions, which leads to V^{2+} ions diffusing back into the bulk solution. It is expected that by using sophisticated operando characterization and unraveling mechanistic details during operation rather than just proposing them, catalysts can be found and materials tailored in the future, which are specifically adapted to the requirements.

2.2. *Porous carbon–carbon composites*

Carbon–carbon composites have been synthesized for many years. However, their advantages in the field of energy storage, especially for the application as electrode material in RFBs, were only discovered a few years ago.

In 2008 for the first time, Zhu *et al* used two different carbons in order to combine their respective positive properties with regard to the application in RFBs [64]. They combined graphite with carbon nanotubes (CNTs) in order to have a higher electrical conductivity, than for the conductivity of the individual components. The authors varied the amount of the CNTs from 1 wt% to 9 wt% trying to find the optimum ratio. They concluded that a content of 5 wt% of CNTs enhances the activity of the electrode most and attributed the observed improvement to the high electrical conductivity of the CNTs.

Since then, various other composites have been developed by other researchers. These differ from one another not only in their individual components, but also in the choice of the manufacturing method. Herein, we provide a summary of the obtained results by various researchers. This may provide a strategy for future work in manufacturing of effective VRFB electrodes.

2.2.1. Graphene-based composites—conductivity

From the beginning of the 2010s, graphene oxide (GO) [65], carbon nanowalls [66, 67], reduced GO (rGO) [68–70] as well as carbon nanorods [71], have been investigated extensively for VRFB applications. In a nutshell, the aim of this strategy was to create new active centers for the vanadium redox couples as well as larger specific surface areas introduced by the graphene-based structures. On the other hand, their electrical conductivities should be improved by the addition of graphene-based materials. The enhanced conductivity of the material was expected to further increase the electrochemical activity and therefore positively affect the overall performance of the VRFB.

As a specific example, Nia *et al* grew reduced graphene sheets on the surface of a CF in a simple one-step electrodeposition process, to employ the resulting composite material as electrode for the positive half-cell reaction [72]. A significant decrease of the overpotential during the charge–discharge cycles could be noticed and was ascribed to the positive effect of rGO, which provides a high amount of active sites for the vanadium ions to react. The approach is characterized by the fact that it is particularly cost-effective and also scalable in view of later industrially sized applications.

However, severe agglomeration in the case of the two-dimensional (2D) GO was identified as a significant drawback. The agglomerates resulted in a lower specific surface area and limited ion diffusion, both of which reduced the efficiency of the VRFB [73]. Based on that issue, Park *et al* developed a hierarchical electronic and ionic mixed conducting network consisting of carbon nanofibers and nanotubes (CNFs/CNTs) [74]. They observed that due to the formation of large edge-plane defects of the CNF combined with fast electron transfer rate of the in-plane side wall of the CNT walls, an excellent performance could be achieved.

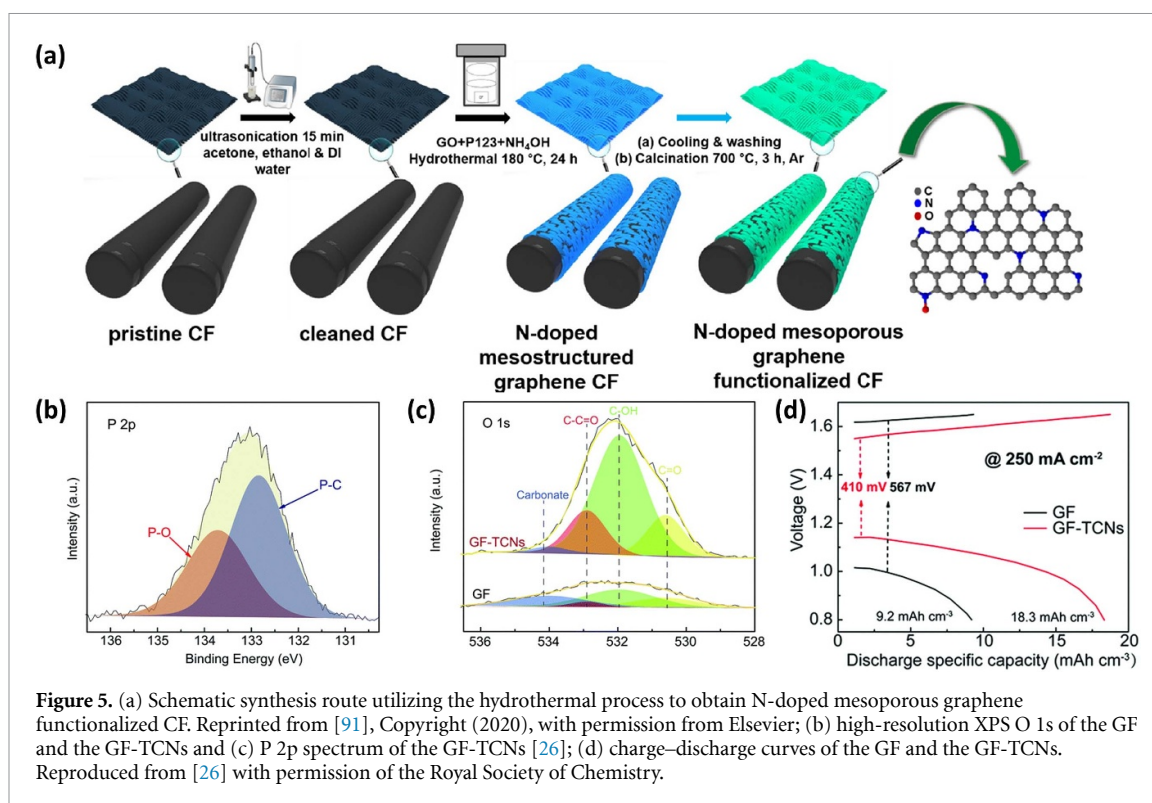### 2.2.2. Nitrogen-doped composites—heteroatoms

Further experimental studies showed that doping the CFs' surface with heteroatoms is a promising way to increase the activity of the CF electrodes [18, 24]. Additional heteroatoms introduced into the carbon structure resulted in increased electronegativity between carbon and the heteroatom (e.g. N, P, O, S), which modifies the electronic properties of the carbon material [25, 75, 76]. Oftentimes it is assumed that the number of active sites can be increased by doping the surface of the carbon materials [77] leading to an accelerated adsorption of vanadium-ions. Consequently, C–C composites having a heteroatom-doped surface combined with a higher specific surface area, could in principle be promising candidates with outstanding electrochemical activity for RFB applications.

Accordingly, Wang *et al* [78] grew nitrogen-doped CNTs on a common GF for the first time by using chemical vapor deposition. They reported that due to the innovative porous structure of the CNTs the diffusion of the vanadium electrolyte could be facilitated, while the additional doping of nitrogen changes the electronic properties of the CNTs resulting in an improved chemisorption of the vanadium-ions. This strategy combining heteroatoms-doping and surface increase might be one way to increase the performance of the battery with respect to capacity and EE.

In another very promising approach, Yang *et al* [79] synthesized nitrogen-doped CNTs on GF using metal phthalocyanines as precursors. These macrocles own an alternating nitrogen–carbon ring structure and already serve as catalysts for application in fuel cells [80–84]. Due to the high amount of nitrogen bound within the molecular structure the macrocycle can react as nitrogen and carbon precursor at the same time. Depending on the metal center, different amounts of CNTs could be deposited on the surface of the felts, which means that the metal center has an influence on the deposition process during the carbonization step. Very good activities could be achieved when iron was utilized as metal center. Yang attributed the enhanced activity to an increased active surface area, higher conductivity and wettability improving the contact between electrode and liquid electrolyte.

2.2.3. Templating approach—porosity

The presence of meso- and micro-pores in the material is an important aspect for an efficient VRFB electrode, since it increases the contact between the electrode and the electrolyte and determines the pressure drop, when the liquid electrolyte is flown through the porous electrode in a real device. In general, there are different ways to incorporate porosity into carbon-based electrodes in a controlled fashion. Due to pyrolysis and subsequent physical or chemical activation of organic precursors, like wood or polymers, porous carbons could be traditionally synthesized [85]. The porous structure of the organic precursor material would then prevail in the final product, i.e. a favorable hierarchical structure could be replicated in the carbonaceous electrode [86]. Nowadays, the application of templates is a commonly used strategy to introduce porosity into carbon materials, as it offers many ways to control the synthesis. The template acts as a structure-directing agent forming an inverse copy of the template morphology. This method generates highly ordered nanostructures with large surface areas, which offers many benefits in the later application. As mentioned above, a higher surface area leads to a better electrocatalytic activity of the electrode material,

Figure 5. (a) Schematic synthesis route utilizing the hydrothermal process to obtain N-doped mesoporous graphene functionalized CF. Reprinted from [91], Copyright (2020), with permission from Elsevier; (b) high-resolution XPS O 1s of the GF and the GF-TCNs and (c) P 2p spectrum of the GF-TCNs [26]; (d) charge–discharge curves of the GF and the GF-TCNs. Reproduced from [26] with permission of the Royal Society of Chemistry.

because more active sites are exposed for the reaction even though it is still debated whether the increase in surface area is directly linked to an increase in performance.

However, until now only a very small number of publications has been dedicated to templated electrode materials and their specific use in RFBs [25, 87–89]. Schnucklake *et al* [90] reported a salt-templating approach, where they embedded a pristine PAN-based CF into a eutectic salt mixture combined with an ionic liquid. The eutectic salt mixture acted as suitable porogen, while the ionic liquid provided the carbon source. With this simple method, they could increase the specific surface area up to a 100 times compared to a pristine felt with a literature value of <0.5 $m^2 g^{-1}$. The composite material showed promising activities for both vanadium redox couples and demonstrated electrochemical performances comparable to the typical state-of-the-art heat-treated felt electrodes.

They also presented an alternative and more environmentally friendly strategy by a so-called soft-templating approach for designing highly active carbon–carbon composite electrodes [87]. They figured out, that co-doping with nitrogen and sulfur could introduce a substantial number of functional groups that raised the number of active sites for the VO^{2+}/VO_2^+ redox reaction and significantly improved the current density indicated from model CV studies. Moreover, the carbon substrate with fiber structure could deliver high electron conductivity, while the amorphous carbon 'coating' on top of the fibers provided the catalytic functionality.

Recently, Opar *et al* modified commercial PAN-based CFs with nitrogen-doped mesoporous graphene by using the hydrothermal process [91]. The hydrothermal carbonization is a cost-effective, environmentally friendly and innovative method to produce functionalized carbon materials. Ammonium hydroxide was suggested as nitrogen source, whereas Pluronic® P-123 was utilized as template. The applied synthesis route is depicted in figure 5(a). They analyzed the XPS detail spectra of the N 1s and the C 1s region, to find out that due to doping some carbon atoms are replaced by nitrogen in the graphitic structure, which generates defect sites. Because of the negative charge of the nitrogen those generated defects in the lattice act as active sites for the positively charged vanadium redox species.

2.2.4. Composites based on biomass and bioprecursors

With the current societies' inclination towards more sustainability, innovative methods for the production of porous carbons, which are cheap and environmentally friendly, are gaining significant momentum [92]. For this reason, different biomass precursors, such as coconut shells [93], fish scales [88], and corn protein [94], are of interest.

Also recently discussed is the use of bioprecursors such as guanosine, which is part of the human ribonucleicacid [95]. It is comprised of the nucleobase guanine and the sugar D-ribose. Guanosin owns a

Table 2. Summary of the influence of electrode synthesis pathway and atom doping on CE, VE and EE of various electrocatalysts for VRFB application.

Precursors	Synthesis pathway	Atom doping	Current density (mA cm^{-2})	CE (%)	VE (%)	EE (%)	Reference
MWCNT, CF	Infiltration	—	50	93.9	87.3	82.0	[67]
CNF, CNT, CF	Chemical vapor deposition	—	40	96.8	87.5	85.0	[74]
Carbon black particles, corn protein 'zein', CF	Evaporation-induced self-assembly	N	50	97.5	—	87.0	[94]
GO, GF	Hydrothermal reaction	O	200	—	74.5	72.0	[68]
Phthalocyanine, GF	Infiltration	N	50			88.0	[79]
Phytic acid, aniline, GF	Hydrothermal reaction	N, P	100	—	87.1	84.5	[98]
Phytic acid, GO, GF	Hydrothermal reaction	P, O	150	—	78.9	76.6	[26]
Phytic acid, urea, carbon sheets, GF	*In-situ* polymerization	O, N, P	150	—	—	74.8	[97]
Fish scales	Hydrothermal reaction	O, N	150	—	64.9	63.4	[88]
GO, NH$_4$OH, CF	Hydrothermal reaction	N	100	95.2	84.8	80.7	[91]
Dopamine, MWCNT, CF	Infiltration	O, N	80	95.6	84.3	80.5	[92]

unique structure, has low cost and can be considered as a resource with sustainability. The ribose molecule within guanosin leads to the formation of microspheres, while guanine is responsible for the formation of the carbon nanosheets and thereby acts as the template and structure-directing agent.

Employing this approach enables the simultaneous formation of two different carbon morphologies on the GF, which may lead to a hierarchically mesoporous structure that has a large specific surface area. Furthermore, it contains a high fraction of nitrogen heteroatoms, associated with moderate numbers of additional defect sites. At current densities between 100 and 500 mA cm^{-2} high EEs can be achieved when using this excellent electrode [95].

Recently, phytic acid was utilized as a precursor to dope the CFs' surface with phosphorus atoms [26]. This acid is indeed able to link several GO units between the fibers of the felt, whereby the electron conductivity and the ion diffusion between the fibers is enhanced. Both properties lead to an enhanced EE for the VRFB. The high-resolution XPS O 1s and P 2p spectra of the GF could be seen in figures 5(b) and (c), showing that in addition to the successful doping of phosphorus, the amount of hydroxyl-groups could be also increased, which might promote the electrocatalytic activity of the electrode material even more. Furthermore, this electrode possesses very good cycling stability, in contrast to many other sophisticated strategies reported in the literature, where the obtained electrodes survived only a few charge–discharge cycles. The charge–discharge curves of the GF in comparison with the GF-TCNs are displayed in figure 5(d). It is demonstrated manifold in the literature that the introduction of a higher number of heteroatom-sites due to co-doping enhances the kinetics of both half-cell reactions of the VRFB [24, 75, 96]. Combining phytic acid with urea [97] makes it possible to dope the electrode surface with additional nitrogen atoms. Ling *et al* presented a hierarchical carbon micro/nanonetwork prepared by cross-linking polymerization of aniline and phytic acid on a GF [98]. This composite electrode seems to provide more active sites for the vanadium-ions due to a so-called synergistic catalytic effect of P-, O- and N-doping. Additionally, due to the specific structure the electron transport channels accelerate the transport properties of the electrode, resulting in a uniform distribution of electrons and ions within the whole electrode.

In table 2 an overview of different synthesis pathways in conjunction with the respective electrochemical activity indicators is shown. The synthetic pathways have a large impact on the size-/surface-dependent properties like the mechanical or electrical properties, which will furthermore have a significant effect on the efficiency. It is worth mentioning here that a direct comparison between different synthesis approaches is mostly neither convincing, nor useful, whereas it is quite possible to consider individual trends. This is in line with our general observation that a straightforward structure–activity correlation has not yet been established for these kinds of carbonaceous materials as it is a rather complex adventure to separate the individual effects of conductivity, porosity, doping, and dominant surface functional groups.

2.3. Electrospinning (ES)

The ES is one of the most efficient procedures to prepare nanostructures to be utilized as high performance materials for multifarious applications. Its low cost, versatility and simplicity make this technique very appealing [99–101]. Electrospun nanofibers as well as freestanding nanofibrous mats are considered to be promising candidates to address critical issues in VRFB electrodes, as they possess excellent characteristics, such as large specific surface area, good flexibility and high porosity and multiple functionalities [102–105]. Therefore, electrospun fibrous nonwovens have been intensively explored recently as alternative VRFB electrode materials, since fiber diameter, architecture, and surface area can be adjusted over a wide range depending on the selected parameters [106, 107].

2.3.1. Electrospun materials as VRFB electrode

PAN is the most popular host polymer precursor for producing free-standing electrospun CNFs for VRFBs [106, 108]. The common practice is to electrospin PAN-based solutions to provide a robust free-standing nanofibrous polymeric construct. Then, this porous electrospun mat is post-treated by carbonization using widely reported treatment protocols to obtain electronically conductive CNFs for an improved electrochemical performance. However, completely homogeneous electrospun products should not be expected. Since ES is a dynamic process, the diameter of the fibers can change during the spinning process, in particular, during start and end of the spinning procedure. Furthermore, upon carbonization the fiber size at the surface (near ES collector) becomes significantly lower due to the compression and/or temperature gradients created at the boundary with the metallic collector. This usually results in an electrospun mat which has smaller fibers towards the edges and larger fibers in the middle of the fibrous mat. These structure specifics were already demonstrated and discussed using computational methods on 3D tomographical images. Therefore, the realistic 3D structure of the porous spun mat has to be carefully evaluated and taken into account for a given application. Especially, since the lattice Boltzmann method showed that the most dominant determining factor for the permeability of the electrode was its porosity demonstrating the direct link between 3D porous architecture and pressure drop as well as flow characteristics [109].

As indicated above, ES is a versatile, rapid, and flexible method for the fabrication of 3D interconnected porous electrodes suited for VRFBs. However, to significantly improve the performance of VRFBs, the exploitation of new materials to adjust the structure and properties of the porous carbonaceous electrode is of particular importance. In recent years, advances have been made towards new manufacturing strategies to optimize electrospun-based nanofibers as potential VRFB electrodes and the conventional ES method developed further to fabricate more reproducable and tunable electrodes in the several manners that will be discussed below.
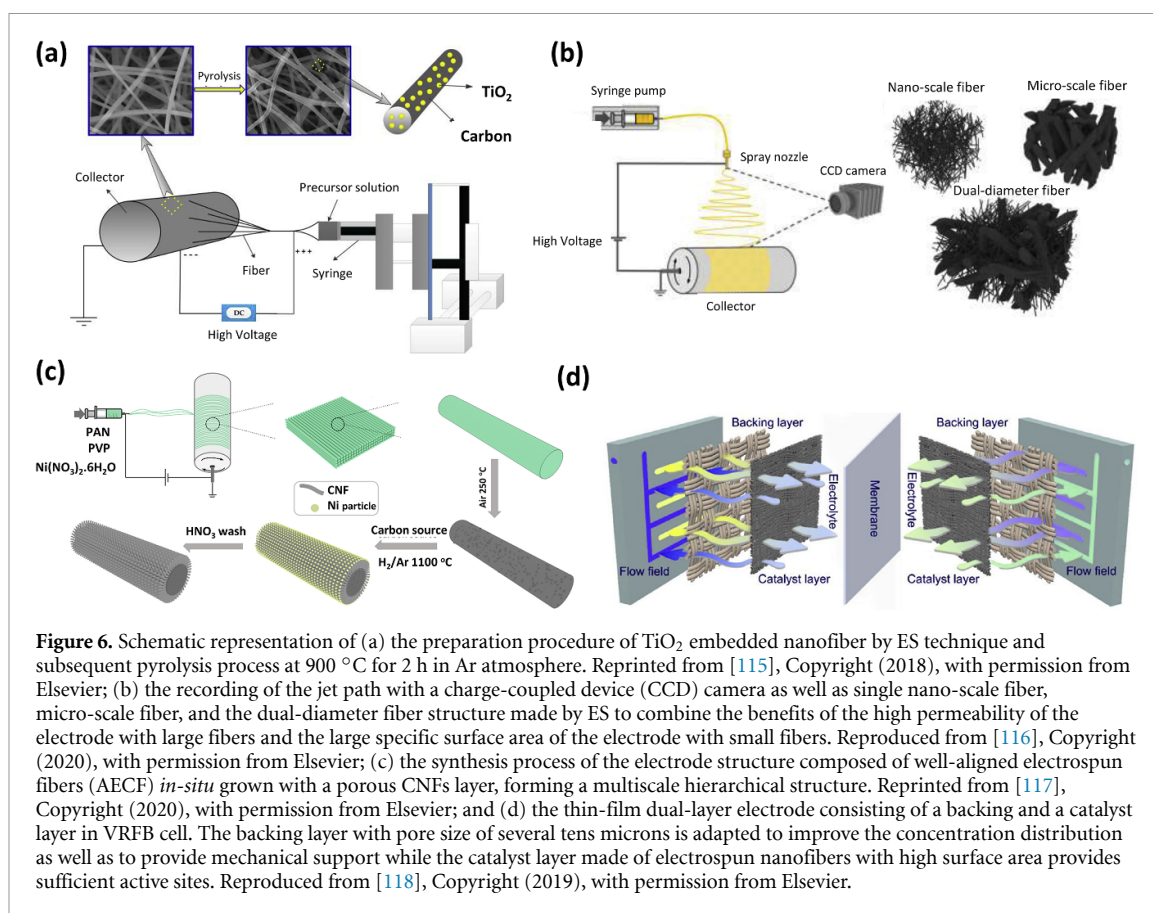
2.3.2. Fabrication of electrospun electrodes with nanoparticles embedded in the fibers

Although pristine electrospun CNFs possess excellent conductivity, high surface area and good electrochemical activity toward catalysis of the vanadium redox reactions, other dopants or agents such as carbon blacks (CBs), CNTs, elemental/metallic Bi, graphite nanoparticles, CeO_2, V_2O_3, TiO_2, ZrO_2, Mn_3O_4 and Ni may be utilized in order to improve their electrode performance (see also section 3.1 and table 1). Embedding these materials with catalytic functionality into the 3D interconnected porous structure of the electrospun electrodes, oftentimes a more graphitic structure of the carbon is obtained within the carbonization process (i.e. catalyzed by these additives). Consequently, these fiber mats with embedded nanoparticles demonstrate improved electrical conductivity, often also enhanced wettability resulting in their overall better electrochemical performance. In our work, we demonstrated that utilization of CB loaded electrospun electrodes could improve the electrochemical activity towards VO^{2+}/VO_2^+ and V^{2+}/V^{3+} redox reactions compared to the commercial CF and CB-free fibers. This was shown by as a higher reversibility, a lower anodic potential peak value and a higher current for the reactions [110, 111]. Moreover, utilization of polyaniline to this CB-loaded electrospun composite ensured that the interior of the utilized polymers and CB particle was electronically addressable, and provided alternative reaction sites for the redox reaction at the surface of the fibers. Our theoretical model underlined the exceptional importance of the electrode conductivity and furthermore demonstrated that the electrode area is not necessarily correlated with electrochemically active electrode area [112].

Furthermore, CeO_2 nanoparticles as hydrophilic agent were embedded in PAN fibers via ES. Introduction of CeO_2 nanoparticles resulted in improved wettability (i.e. contact angle of 27° for CeO_2-loaded fibers vs 102.3° for the pristine carbon fibers), four times higher electrochemical surface area (i.e. 312.3 $m^2 g^{-1}$ for CeO_2-loaded fibers vs 72.5 $m^2 g^{-1}$ pristine carbon fibers), improved electrocatalytic activity toward the negative reaction and enhanced discharge capacity at current density of 100 mA cm^{-2} and EE [113].

ES technique was also used to synthesize electrospun vanadium trioxide carbon composite nanofibers (V_2O_3-CNF) from a solution containing vanadium (V) oxytriisopropoxide VO-(OiPr)$_3$ as metal oxide

Figure 6. Schematic representation of (a) the preparation procedure of TiO$_2$ embedded nanofiber by ES technique and subsequent pyrolysis process at 900 °C for 2 h in Ar atmosphere. Reprinted from [115], Copyright (2018), with permission from Elsevier; (b) the recording of the jet path with a charge-coupled device (CCD) camera as well as single nano-scale fiber, micro-scale fiber, and the dual-diameter fiber structure made by ES to combine the benefits of the high permeability of the electrode with large fibers and the large specific surface area of the electrode with small fibers. Reproduced from [116], Copyright (2020), with permission from Elsevier; (c) the synthesis process of the electrode structure composed of well-aligned electrospun fibers (AECF) *in-situ* grown with a porous CNFs layer, forming a multiscale hierarchical structure. Reprinted from [117], Copyright (2020), with permission from Elsevier; and (d) the thin-film dual-layer electrode consisting of a backing and a catalyst layer in VRFB cell. The backing layer with pore size of several tens microns is adapted to improve the concentration distribution as well as to provide mechanical support while the catalyst layer made of electrospun nanofibers with high surface area provides sufficient active sites. Reproduced from [118], Copyright (2019), with permission from Elsevier.

Table 3. Summary of the influence of the decorated fibers of PAN-based electrospun electrode on CE, VE and EE for VRFB applications.

Method	Current density (mA cm^{-2})	CE (%)	VE (%)	EE (%)	Reference
Mn$_3$O$_4$/CNF	80	97	86	83.4	[120]
ZrO$_2$/CNF	60	98	83.9	81.4	[119]
ZrO$_2$/CNF	80	98	78.8	77.2	[119]
ZrO$_2$/CNF	100	98	74	73.3	[119]
CeO$_2$/CNF	60	—	—	83	[113]
CeO$_2$/CNF	80	—	—	78	[113]
CeO$_2$/CNF	100	—	—	73	[113]
TiO$_2$/CNF	50	98	82	80	[115]
TiO$_2$/CNF	70	99	77	76	[115]
TiO$_2$/CNF	90	99	74	73	[115]

precursor and polyvinylpyrrolidone as carbon source. The better electrocatalytic activity (in terms of less peak separation and lower charge transfer resistance) for the urchin-like V$_2$O$_3$-CNF composite compared to pristine CNF was attributed to its higher surface area due to the presence of the oxygen functional groups that could act as active sites for the VO^{2+}/VO$_2$$^+$ reaction at the electrode/electrolyte interface [114].

TiO$_2$-CNF composites fabricated using ES shown in figure 6(a) exhibited superior electrochemical activity towards V^{2+}/V^{3+} redox reaction compared with pristine CNF. A possible synergistic effect between electrospun CNFs with high electrical conductivity and rutile TiO$_2$ with high electrocatalytic properties, was held responsible for the observed increased performance [115].

On the other hand, ES was employed to load ZrO$_2$ nanoparticles in the CNF. This ZrO$_2$-CNF composite utilized as negative electrode resulted in good electrochemical activity due to the increased hydrophilicity of ZrO$_2$-CNF composite and good electrocatalytic properties of ZrO$_2$ thanks to the presence of plenty unsaturated Lewis acid-base Zr^{4+}–O^{2-} pairs and oxygen-containing functional groups [119].

Table 3 compares the cell performance when using differently decorated electrospun nanofibrous electrodes for VRFBs applications. These studies clearly demonstrate that electrospun fibrous mats embedded with nanoparticles are promising electrode materials for VRFB application.

2.3.3. Effect of graphitization on the performance of electrospun electrodes

Higher graphitization temperatures (900 °C and above) will improve the graphitization degree of the carbon-based fibers greatly influencing the surface and structure characteristics of the fibers simultaneously, with a direct effect on electrical conductivity and VRFB performance. For the electrospun carbon material made of PAN with a lower graphitization degree at 1000 °C, the fraction of edge-planes and the heteroatoms (i.e. N) retained at these comparatively low temperatures are enough to catalyse the electrode reaction. However, higher performances have been observed for a sample heat-treated under inert gas at 1200 °C, as the conductivity of the electrode increases with the increasing graphitization degree because of the increasing quantity and completeness of the graphite layers. However, as the graphitization degree increases even further at 1300 °C, the graphitic layers will interconnect with each other and form a long-range ordered structure containing fewer edge-plane sites and heteroatoms, so that the electrochemical activity will decrease in spite of the structure's increasing conductivity [121].

Furthermore, PAN-based electrodes showed an improved electrochemical reversibility for the vanadium redox reactions, when the carbonization time was increased from 60 min to 90 min at 1000 °C. The higher electrochemical activity could be attributed to the promoted electron transfer rate and enhanced mass transport process, which resulted from higher conversion of carbon structure by increasing the stacks of the graphitic layers. Forming more 2D graphitic lattices not only helped to improve the electrical conductivity of the electrospun fibers, but also contributed to accelerate the mass transport [122].

2.3.4. Electrospun electrode having different composite structures

Enhancing the transport properties and enlarging the surface area of electrodes are two main goals for achieving a high power density in VRFBs. Therefore, the continuous development of fabrication and modification strategies for multifunctional electrospun electrodes was only possible having these important aims in mind.

Sun *et al* [116] fabricated a novel dual-diameter electrode prepared with electrospun nano- and micro-scale carbon fibers varying the relative humidity and rotation rates of the drum collector (figure 6(b)). Interestingly, the application of this dual-diameter electrode (i.e. consisting of 60% microfibers and 40% nanofibers) resulted in an EE of 84.78% at the current density of 100 mA cm^{-2}, which was 13.6% higher than that with small-fiber electrodes, and 3.9% higher than that with large-fiber electrodes. The authors propose that the larger fibers of about 10 μm in diameter can accommodate more electrolyte and provide larger pathways for electrolyte flow at reduced pressure drop, while smaller fibers (approx. 1 μm in diameter) offer more active surface sites for the respective redox reactions. Hence, a mixture with an optimized ratio between larger and smaller fibers seems to be the best compromise with the highest performance.

Moreover, a hierarchical and ordered carbon fibrous electrode was constructed by *in-situ* growing a layer of CFNs on the surface of aligned electrospun carbon fibers as shown in figure 6(c). In this manner, the aligned macroscopic structure provides distinctive pathways for electrolyte transport with only small flow resistance, while the highly porous CNF layer provides abundant active sites for redox reactions. The application of this multiscale hierarchical electrospun structure as the positive electrode in a full cell set-up demonstrated an EE of 80.1% at the current density of 300 mA cm^{-2} which was 5.0% higher than that with the conventional electrospun electrodes [117].

In another study by Wu *et al*, a dual-layer thin-film electrode, consisting of a backing layer and a catalyst layer was proposed as illustrated in figure 6(d). The electrospun fiber mat with smaller pores to provide a sufficient number of active sites was used as the catalyst layer, while the backing layer with several tens microns pore size to improve the concentration distribution and to provide mechanical support was made from a commercial CC. Using this dual-layer structured electrode created an additional interfacial resistance. However, the battery could reach EEs as high as 80.2% at a current density of 240 mA cm^{-2} which was much higher than the one achieved by conventional electrospun fiber mat electrodes (61.9%). Furthermore, the battery could operate stably over 800 cycles at 240 mA cm^{-2} [118].

In the light of recent literature, ES is an interesting technology to manufacture porous carbonaceous fibrous electrodes with excellent electrochemical performance in VRFB. In particular, its versatility allows a wide variety of different structures to be obtained in a controlled fashion ranging from plain carbon fibrous nonwovens over nanoparticle loaded felts towards dual structure and hierarchical composite architectures. Moreover, ES offers the potential to implement both the decoration and templating approach described before, by this procedure positively addressing conductivity—carbonization, porosity—flow features, surface—catalysis all at once. All of these strategies offer promising ways to improve VRFB electrodes in the immediate future.

3. Conclusion

The VRFB as one of the most reliable and promising energy storage systems has drawn significant attention in recent years. In order to improve the power output of the system, fabricating high performance electrode materials is one of the most pressing needs. Improving the transport properties, long-term stability and surface characteristics of the electrodes are very important issues for developing a high performance electrode for VRFBs.

Electrode decoration with different metals and metal compounds, such as metal oxide or metal carbide, has been investigated to increase the kinetics of the vanadium redox reactions. Bismuth and titanium-based compounds have shown great potential to catalyze the vanadium redox reaction at the negative side, whereas neodymium, cobalt or lead have been found capable of facilitating the redox reaction at the positive side. Operando measurements should help to unravel mechanistic details in order to forecast efficient catalyst combinations in the future.

C–C composites made from different carbon materials are a hot topic and offer tremendous potentials as innovative electrodes for RFBs. The focus of this approach is to combine beneficial properties of the individual components into a composite material that offers an enlarged reactive surface for the vanadium redox reactions. Initially, C–C composites were proposed, in which the carbon coating strongly enhances the electrical conductivity of the commercial CF. Subsequently, an additional doping with heteroatoms was suggested to obtain a material that exhibits even more reaction sites. In this context, the co-doping with N, S heteroatoms turned out to be a very useful strategy, having a synergistic effect, which leads to an outstanding performance.

Requirements of high-performing electrodes were also successfully met by means of ES, due to nano-scale fiber diameter and the reduction in thickness of the electrode. A hydrophobic electrode may not only lead to a relatively high transfer resistance for electrolyte transport, but also decrease the available active sites for vanadium redox reactions. Commercial carbon electrodes (e.g. CC, GF and carbon paper) are mostly hydrophobic towards the electrolyte probably due to their lack of functional groups and high degree of graphitization. Hence, electrospun fiber mats offer highly desirable properties which can be tailored over a wide range to e.g. facilitate the filling with electrolyte.

4. Future outlook

A deeper understanding of the role of the catalyst for enhancing the kinetics of the respective redox reaction is strongly advocated in the future. Hence, systematic investigations on both pure metal and metal compounds should be taken into consideration in order to pave the way for a knowledge-based rather than empirical approach. Besides, while investigating the catalytic effect of metal or metal compound decoration on the electrode, both desirable vanadium redox reactions and parasitic reactions should be taken into consideration. An ideal decoration material should be catalyzing the vanadium redox reactions and suppress parasitic reactions at the same time.

Related to the C–C composites particular attention should be paid to the long-term stability of the electrodes in the future. Moreover the relationship between the surface area and the electrochemical activity of the electrode as well as the role of the heteroatom doping associated with the overall performance of the battery should be examined in detail. Due to deeper insights into the redox reactions on the electrolyte–electrode interface new materials could be developed, as well as the properties tailored as desired. With regard to the electrochemical characterization of porous, 3D felt electrodes, new methods of evaluation are desirable [21]. The simplified analysis of the cyclic voltammograms, such as the typical determination of the peak separation, is only useful to a limited extent and does not provide sufficient information [123], which necessitates us to rethink the quantitative analysis of the electrochemical data.

Most of the thin-film electrodes developed to date using ES suffer from high mass transport resistance and deliver unsatisfactory performance. This high resistance is most probably related to small fiber diameters which result in small pore sizes that cannot accommodate large amounts of electrolyte in their extended void space. Moreover, electrical connectivity (i.e. percolation) might be impeded due to the fibrous structure and heat-treatment at too low temperatures. Therefore, to further improve the flow cell performance, future efforts on the electrospun-based electrodes may include: (a) developing novel structures with highly interconnected pores for ease of electrolyte flow; (b) employing composites with reduced interfacial resistance; (c) decorating the electrospun fibers/mat with functional groups and/or efficient nanocatalysts to accelerate the kinetics of redox reactions; and (d) improved wettability and electrolyte penetration into electrospun fibers by modifying the fibrous web structure and use of pore forming agents (i.e. surface and bulk properties).

We propose to tackle the remaining challenges in electrode design and manufacturing for VRFB electrodes jointly across the different disciplines benefitting from materials, electrochemical and engineering background and encourage fellow scientists to contribute their expertise to the development of highly active, low cost and long-living energy storage systems for a sustainable future.

Data availability statement

No new data were created or analyzed in this study.

Acknowledgments

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