A novel electrode formed with electrospun nano- and micro-scale carbon fibers for aqueous redox flow batteries

J. Sun a, H.R. Jiang a, M.C. Wu a, X.Z. Fan a, C.Y.H. Chao b, T.S. Zhao a,*

a Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China
b Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, China

HIGHLIGHTS

- Application of electrospun carbon electrodes in redox flow batteries is evaluated.
- Dual-diameter fibrous electrode is fabricated using electrospinning method.
- Dual-diameter electrodes show a large specific surface area and high permeability.
- The battery delivers a limiting current density of 1300 mA cm⁻².
- The battery achieves an energy efficiency of 79.43% at 150 mA cm⁻².

ARTICLE INFO

Keywords: Specific surface area Pore size Permeability Dual-diameter carbon fiber Electrospinning Aqueous redox flow battery

ABSTRACT

This work reports on a novel electrode prepared with electrospun nano- and micro-scale carbon fibers for aqueous redox flow batteries. Larger fibers, ~10 μm in diameter, form larger pores to provide pathways for electrolyte flow, while smaller fibers, ~1 μm in diameter, increase active surface area for redox reactions. Brunauer-Emmett-Teller and pressure drop tests show that the specific surface area of the prepared dual-diameter electrode is doubled as compared with the large-fiber electrode, while the estimated permeability is enhanced by 1.4 times as opposed to the small-fiber electrode. The application of the dual-diameter electrodes to a vanadium redox flow battery allows the battery to achieve an energy efficiency of 84.78% at the current density of 100 mA cm⁻², which is 13.57% higher than that with small-fiber electrodes, and 3.91% higher than that with large-fiber electrodes. Even at a high current density of 200 mA cm⁻², the battery with the prepared electrode can still maintain the energy efficiency of 74.18%, which is 5.5% higher than that with large-fiber electrodes, and the battery with small-fiber electrodes cannot be operated at such high current density. This dual-diameter fibrous structure provides inspirations for the future electrode design in aqueous redox flow batteries.

1. Introduction

In recent decades, renewable energies, such as wind and solar power, are broadly adopted as alternatives to fossil fuels, aiming to address the environmental pollution and energy shortage issues. However, the intermittent nature of these renewables makes them unreliable and unpredictable to be directly integrated into the grid. The redox flow battery represents a promising energy storage technology for the integration of renewable resources [1–4]. Among various types of flow battery systems like zinc/bromine [5], iron/chromium [6], and vanadium/bromine [7] redox flow batteries, the all-vanadium redox flow battery (VRFB) gains the most attention because the employment of the same electroactive element in both anolyte and catholyte can eliminate the cross-contamination issues [8–11]. Nevertheless, the broad market penetration of VRFBs is still hindered by the high capital cost arising from its high component cost (stack components and electroactive species) [12–14]. Improving the battery operating power density to reduce the stack size provides a straightforward approach to lower VRFB costs.

As one of the essential components in VRFBs, the electrode significantly influences the battery’s power density as it not only provides the active sites for redox reactions to take place but also decides the rate of...
To minimize the cell voltage losses and thus improve the battery performance, the electrode should possess a large reactive surface area to lower the activation overpotential [19–21], high electrical conductivity to reduce the ohmic loss [22,23], and high hydraulic permeability to obviate the concentration overpotential [24,25]. However, it is hard for a carbon fibrous material to simultaneously achieve the high permeability and large specific surface area, primarily due to the following reason. On the one hand, the specific surface area of fibrous material, \( a \) can be calculated by

\[
a = \frac{4(1 - \epsilon)}{d_f}
\]

where \( d_f \) and \( \epsilon \) are the bulk porosity and fiber diameter [26,27]. From this equation, it is inferred that, in order to achieve a large specific surface area, small fiber diameter and low porosity are preferred. On the other hand, the permeability can be calculated by the Carman-Kozeny equation [28–30].

\[
K = \frac{d^2_f \varepsilon^3}{16K_a(1 - \epsilon)}
\]

where \( K_a \) representing the tortuosity fitting parameter. It is clearly shown that small fiber diameter and low porosity will result in low permeability. Therefore, this contradiction between the specific surface area and permeability poses a great challenge in developing an optimal electrode with a balanced specific surface area and transport properties for aqueous redox flow batteries.

Conventionally, the commercial carbon materials such as carbon felt and carbon paper are used as electrodes in aqueous redox flow batteries [31,32]. Even though these carbon materials differ in their morphologies, they are all featured by good transport properties with high permeability. For example, carbon felts exhibit a filamentary microscopic morphology with the diameter of fibers ranging from 10 to 20 \( \mu \)m and high porosity of over 90% [33–35]. Carbon paper, which is much thinner in thickness compared with carbon felts, is also a carbon-fiber-based material with overlapping of binder residue, forming a porous structure with a pore diameter in the order of around 50 \( \mu \)m [36–38]. As discussed above, the high permeability of the commercial carbon electrodes is, however, sacrificed by the small specific surface area. For example, the specific surface area of carbon felt is as low as 1.0 \( \text{m}^2 \cdot \text{g}^{-1} \), resulting in the large activation overpotential when applied as electrodes in VRFBs [39,40]. To address this issue, in recent years, electrospinning methods are employed to fabricate carbon nanofiber electrodes, whose specific surface area can reach hundreds of square meters per gram [41,42]. However, the tightly packed arrays of nanofibers result in small permeability, making it hard for the electrolyte to transport in the flow battery system, which causes a large concentration overpotential in VRFBs [27,43]. Therefore, researchers are relentlessly seeking ways to improve the transport properties of the electrospin carbon nanofiber mat by increasing the fiber diameter or enlarging the pore sizes among the fibers [44,45].

In this work, we design and fabricate a novel dual-diameter carbon fibrous electrode 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. In this design, the efficient electrolyte pathways in the porous media are ensured by the large pores among the large fibers, while an increased specific surface area is achieved by abundant small fibers. The structural properties of the electrodes are adjusted by varying the ratio of the number of large-fibers to small-fiber while the surface properties are similar among these samples as the same peroxidization and carbonization methods were employed. The dual-diameter electrodes that adopted in the VRFB system enable the battery to deliver an energy efficiency of 79.43% at 150 mA cm\(^{-2}\), outperforming the battery with small-fiber electrodes and that with large-fiber electrodes.

## 2. Experimental

### 2.1. Synthesis of the dual-diameter electrode

The dual-diameter electrodes were fabricated using the electrospinning method. First, Polyacrylonitrile (PAN, MW = 150,000, Sigma-Aldrich) was dissolved in N, N-dimethylformamide (DMF, \( \geq 99\% \), Sigma-Aldrich) solvent to form a homogenous 15 wt% PAN solution. The resultant solution was then loaded at a constant feeding rate of 1 mL h\(^{-1}\) into a syringe equipped with a stainless-steel nozzle. A high voltage of 16 kV was applied between the tip of the nozzle and the collector (Fig. 1a). To obtain the dual-diameter fiber mat, the ambient air humidity inside the equipment chamber was adjusted from 35 to 65%, and the rotating rate of the collector was tuned from 30 to 500 rpm. Next, the freestanding fiber mat was preoxidized in the air at 250 °C for 2 h with a heating rate of 1 °C min\(^{-1}\) followed by a carbonization process under the nitrogen atmosphere at 1100 °C for 1 h. Fig. 1b shows the schematic illustration of the dual-diameter electrodes. The diameter of the large fiber bundles is around 10 \( \mu \)m, which is comparable to that of commercial fibers, while the diameter of the thin fibers is around 1 \( \mu \)m. A series of dual-diameter electrodes, namely ECF-x (\( x = 0, 30, 50, 60, 70, 90 \)), where ECF stands for electrospin carbon fiber and \( x \) represents the proportion of the large fibers are prepared and investigated to achieve the optimal structure. Commercial carbon paper (280 \( \mu \)m, SGL,39AA) was heat-treated in the air at 400 °C for 3 h.

### 2.2. Material characterization

The path of the polymer jet under the high voltage between the tip of the nozzle and the collector was recorded using a high-speed camera (MotionXtra HG 100K) with 60 frames per second. The morphologies of the as-prepared dual-diameter electrodes were characterized by a field-emission scanning electron microscope (FESEM, JEOL 7100F) at a voltage of 10 kV. The X-ray photoelectron spectroscopy (XPS) was performed by a Physical Electronics PHI 5600 multi-technique system using an Al monochromatic X-ray with a power of 350 W. The C1s peak centered at 284.5 eV was used as the reference. Curve deconvolution of the spectra was performed following Shirley-type background subtraction. Raman spectra were collected with the InVia (Renishaw) Raman spectrometer with a 514 nm laser as the excitation source (Notch Filter). Nitrogen adsorption/desorption isotherms and Brunauer-Emmett-Teller (BET) surface area were measured with Beckman Coulter SA3100 surface area and a pore size analyzer. Mercury intrusion porosimetry (MIP) was examined with Micromeritics’ AutoPore IV 9500 Series.

### 2.3. Single flow cell tests

The as-prepared electrospin carbon fiber mats were cut into 2 x 2 cm\(^2\) per piece with a thickness of about 700 \( \mu \)m and applied as electrodes in a lab-made serpentine flow-by-cell [46]. The electrodes were compressed to about 500 \( \mu \)m with a compression ratio of 28%. 20 mL anolyte containing 1.0 M \( \text{VO}_2^+ + 3.0 \text{M H}_2\text{SO}_4 \) and 20 mL catholyte containing 1.0 M \( \text{V}_2\text{O}_5^2- + 3.0 \text{M H}_2\text{SO}_4 \) were pumped and circulated from the cell and external reservoirs at a constant flow rate of 20 mL min\(^{-1}\) (26 rpm). Nafion 212 (Dupont, USA) was used as the membrane. Both reservoirs were bubbled with nitrogen and sealed before the electrochemical test to avoid the oxidation of active species. The single-cell test was conducted using a potentiostat/galvanostat (Arbin Instrument). The cells were charged to a cut-off voltage of 1.65 V and discharged to the cut-off voltage of 0.9 V at the current densities ranging from 60–250 mA cm\(^{-2}\). The polarization curves were conducted from a full-charge state of the cells. The cells were then discharged at increasing current densities steps and lasted 10 s at each step until the voltage reached zero. In comparison, three layers of carbon paper were adopted as electrodes and compressed to 500 \( \mu \)m. The pressure drop tests were conducted using the pressure sensors (Asmik, MTK-P300) with water used as working fluid.
3. Results and discussions

3.1. Jet path characterization of the dual-diameter electrospun fibers

It was reported that the fiber morphologies in electrospinning technology were influenced by many factors, such as the concentration of the polymer solutions [47], applied voltage [48] and ambient humidity [49–52]. Here, to produce a polymer mat with both the large and small fibers (Fig. 1b), we electrospun from a viscous PAN solution and carefully adjusted the air humidity from 35 to 65% and the collector rotating rate from 30 to 500 rpm. Fig. 2a exhibits electrospun fibers with different proportions of small fibers formed under the “single fiber type” mode marked in blue (Fig. 2b) and large fibers formed under the “bundle type” jet mode marked in yellow (Fig. 2c) under varied humidity and rotation rate combinations. For example, the ECF-50 electrode which has 50% large fibers can be electrospun at a rotating rate of 50 rpm and the humidity in the range of 45–55%. The air humidity influences the evaporation of the solvent and the solidification rate of the polymer jet. Thin fibers prefer to form at low relative humidity, while large fiber bundles tend to form at high relative humidity. At low relative humidity, the fiber ejection mode is named as “single fiber type,” as shown in Fig. 2b, which agrees well with what has been reported in previous work [53]. Under this condition, when the charges imposed on the Taylor cone overcome the surface tension, the polymer jet is dispersed from the tip of the nozzle and solidifies into separate fibers and finally lands on the collector, forming a polymer mat with densely packed thin fibers. At high relative humidity, the mode of the jet path will transfer to “bundle type,” as shown in Fig. 2c, and the jet path goes through two stages. In the first stage, the polymer solution is ejected from the tip of the nozzle, forming a Taylor cone, which is stretched under the high voltage and the solvent starts to evaporate. In the second stage, the partially evaporated polymer fibers are twisted and form fiber bundles with the end sticking on the rotating collector. A large proportion of the fibers are twisted into fiber bundles at low rotation rates, while separate fibers are carried away by the collector before they are twisted to form bundles at high rotating rates. Thus, the increase in the relative humidity and the decrease in the rotating rate favor the formation of large fiber in the mixture. Transitional stages from the bundle type jet path to single fiber type are shown from Fig. 2d1-5, the longer duration time of the jet path in Fig. 2d1 results in the increased proportion of the large fibers in the mixture.

Fig. 1. (a) Schematic of the electrospinning process and the recording of the jet path with a charge-coupled device (CCD) camera. (b) Schematic of the single nano-scale fiber, micro-scale fiber, and the dual-diameter fiber structure.

Fig. 2. (a) Statistics of jet path modes under different electrospinning conditions (relative humidity and rotating rate of the collector). (b) Image of the jet path of single fiber mode, (c) image of the jet path of fiber bundle mode. (d1) - (d5) Images of the transition of the jet path from the “bundle type” mode to “single fiber type” mode.
mixture, which corresponds to the larger yellow area in Fig. 2a and vice versa.

3.2. Characterizations of dual-diameter carbon fibers

Fig. 3 displays the microscopic structures of as-prepared six samples. As shown in Fig. 3a, the ECF-0 is mainly composed of thin fibers with the diameter of around 1 μm (inset in Fig. 3a), offering a large specific surface area, which is the typical structure of electrospun PAN polymers [27]. On the contrary, the ECF-90 sample is featured with large fibers with only a small portion of thin fibers sparsely dispersed among the skeleton of the large fibers. The size of large fibers in these samples is comparable to that of commercial graphite felt or carbon paper with a diameter of 10 μm (inset in Fig. 3f). The dual-diameter samples with gradually increased proportions of large fibers and decreased proportions of small fibers are displayed in Fig. 3b–f, showing gradually expanded pores among interconnected fibers.

The structural properties of these six samples are characterized by the BET, MIP, and pressure drop tests. Fig. 4a displays the adsorption-desorption isotherms of all the samples. Differed from the isotherm of ECF-0, distinct loops are observed at the high relative pressure (>0.8 $P/P_0$) in the isotherms of the other samples, indicating the presence of macropores. The BET specific surface area (SSA) of all the samples is listed in Table 1. The ECF-0 sample, which is composed of small fibers, shows the largest SSA of 10.50 m$^2$ g$^{-1}$. When part of small fibers is replaced by the large fibers, the SSA is decreased accordingly. The SSAs of ECF-30, ECF-50, ECF-60, ECF-70, and ECF-90 are 7.35, 5.44, 4.62, 3.89, and 2.20 m$^2$ g$^{-1}$, respectively. Based on the measured SSA of each sample, the proportion of large fibers in the dual-diameter fibers can be proximately calculated based on several assumptions: i) solid fibers in the given volume can be assumed as cylinders; ii) the dual-diameter sample is composed of small fibers with the diameter of 1 μm and large fibers with the diameter of 10 μm; iii) the ECF-0 sample is assumed to be composed of 100% small fibers. The SSA in the unit of m$^2$ g$^{-1}$ of fibrous material with uniform diameter can be calculated as

$$\text{SSA} = \frac{\pi d_f L_f}{m_f} = \frac{\pi d_f \sqrt{V_f/m_f}}{V_f/\rho_f} = 4 \frac{d_f}{\rho_f}$$  \hspace{1cm} (3)

where $d_f$ and $L_f$ represent the diameter and length of fibers, respectively; $V_f$ and $m_f$ are the volume and mass of cylindrical fibers, and $\rho_f$ is the density of the material. It is seen from the above equation that SSA is inversely proportional to the fiber diameter. Since the measured SSA of ECF-0 sample which is composed of fibers with the diameter of around 1 μm is 10.50 m$^2$ g$^{-1}$, it can be induced that SSA of the fibrous material with a fiber diameter of 10 μm is around 1.05 m$^2$ g$^{-1}$, which is consistent with that of commercial carbon felt [54]. Based on the above assumptions and calculations, the proportion of the thin and large fibers in the dual-diameter mixture can be calculated and listed in Table 1.

To characterize pore size distributions, the mercury intrusion porosimetry was applied and the corresponding results were given in Fig. 4b. The pore size exhibits a wide distribution range for all these samples, which extends from several micrometers to tens of micrometers, owing to the coexistence of thin fibers and large fibers. The majority size of pores is around 6, 11, 20, 22, 24, and 33 μm in ECF-0, ECF-30, ECF-50, ECF-60, ECF-70, and ECF-90, respectively, representing the increased average pore size as the increased proportion of large fibers. The relation between the pore size and fiber diameter of the randomly arranged fiber mat can be explained as follows. Smaller fibers always translate to a longer fiber length inside a fixed volume, which increases the probability of fiber intersecting (packing density), hence reduces the average distance between these fiber intersections and leads to the small average pore sizes. When part of the small fibers is replaced by large fibers, the packing density is reduced, resulting in the increased average pore size [28,55]. Such a trend is always observed in the single-diameter fibrous material and is also detected in our dual-diameter electrodes. In addition, it is expected that the permeability also increases with the increased proportion of large fibers due to the expanded pore sizes. To verify the enhanced permeability of the electrode with increased proportions of large fibers, the pressure drop of water flowing through the material is measured. It is seen in Fig. 4c that the pressure drop augmented with the increased flow rate. The pressure drop of water flowing by the ECF-0 sample was the largest, indicating the highest flow resistance for the electrolyte to transport through it. In addition, the gradually decreasing trend of the pressure drop from ECF-0 to ECF-90 samples proves that the increased pore size can effectively enhance the hydraulic permeability, thus reducing the flow resistance. Specifically, the pressure drop of the water flow by the ECF-60 electrode is reduced by 30% compared with that of the ECF-0 electrode. According to Darcy’s law, under a constant flow rate, the permeability is inversely proportional to the pressure drop, indicating that the permeability of the ECF-60 electrode is about 1.4 times that of ECF-0 electrode.

Fig. 5a shows the Raman spectra of the as-obtained six ECF samples, in which two typical bands located at 1350 and 1590 cm$^{-1}$ can be ascribed to the D and G bands [56]. The D-band corresponds to the defect-induced mode while the G-band relates to the $E_{2g}$ graphitic mode, and the relative intensity of $I_D/I_G$ is used to reflect the disorder degree of carbon. The value of $I_D/I_G$ is 0.895, 0.901, 0.908, 0.893, 0.905 and 0.885 for ECF-0, ECF-30, ECF-50, ECF-60, ECF-70, and ECF-90 respectively, suggesting the similar graphitization degree in these samples.
Furthermore, XPS was conducted to gain insights into the chemical composition and configurations of these samples. Fig. 5b reveals that the ECF samples are mainly composed of C, N, O elements, indicating that the samples are functionalized with nitrogen-containing and oxygen-containing groups. The high-resolution N1s spectrum can be deconvoluted into four characteristic peaks at the binding energies of 398.0, 399.8, 401.0, and 403.2 eV, corresponding to pyridinic N, pyrrolic N, quaternary N and N oxide, respectively [57], whilst the O 1s spectrum shows three fitting peaks (Fig. 5d) located at 531.5 (C–O), 532.5 (C–OH) and 533.8 eV (COOH) [58, 59]. A summary of the content of N and O of all the samples are plotted in Fig. 5e, showing that the content of O and N for all the samples varied slightly. The content of each component of the N element is summarized in Fig. 5f, which displays that quaternary N is the main composition while pyrrolic N is

Table 1

BET surface area data of the as-prepared electrodes.

<table>
<thead>
<tr>
<th></th>
<th>ECF-0</th>
<th>ECF-30</th>
<th>ECF-50</th>
<th>ECF-60</th>
<th>ECF-70</th>
<th>ECF-90</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m² g⁻¹)</td>
<td>10.50</td>
<td>7.35</td>
<td>5.44</td>
<td>4.62</td>
<td>3.89</td>
<td>2.20</td>
</tr>
<tr>
<td>1 μm thin fiber proportion</td>
<td>1.00</td>
<td>0.67</td>
<td>0.46</td>
<td>0.38</td>
<td>0.30</td>
<td>0.12</td>
</tr>
<tr>
<td>10 μm large fiber proportion</td>
<td>0</td>
<td>0.33</td>
<td>0.54</td>
<td>0.62</td>
<td>0.70</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Furthermore, XPS was conducted to gain insights into the chemical composition and configurations of these samples. Fig. 5b reveals that the ECF samples are mainly composed of C, N, O elements, indicating that the samples are functionalized with nitrogen-containing and oxygen-containing groups. The high-resolution N1s spectrum can be deconvoluted into four characteristic peaks at the binding energies of 398.0, 399.8, 401.0, and 403.2 eV, corresponding to pyridinic N, pyrrolic N, quaternary N and N oxide, respectively [57], whilst the O 1s spectrum shows three fitting peaks (Fig. 5d) located at 531.5 (C–O), 532.5 (C–OH) and 533.8 eV (COOH) [58, 59]. A summary of the content of N and O of all the samples are plotted in Fig. 5e, showing that the content of O and N for all the samples varied slightly. The content of each component of the N element is summarized in Fig. 5f, which displays that quaternary N is the main composition while pyrrolic N is
barely detected in all the samples. In addition, the content of the oxygen functional group of each sample is given in Fig. 5f. As revealed in Fig. 5e and f, the composition of the six samples are similar, which indicates there is little difference in the chemical states of the elements in the ECFs. Therefore, the surface properties of the six materials can be regarded as the same, which is understandable since all the samples are treated under the same conditions, ensuring the differences in the battery performances in the following tests mainly result from the electrode structure.

3.3. Single-cell performance of the dual-diameter electrodes

To gain insights into the influence of electrode geometric structure on the battery performances, single-cell tests based on the vanadium redox couples were conducted. For convenient comparison, the six samples were divided into two groups: the first group is from ECF-0 to ECF-60, and the second group is from ECF-60 to ECF-90. The charge-discharge profiles of the ECF-0 to ECF-60 at current densities from 60 to 200 mA cm⁻² are depicted in Fig. 5a–e. It is shown that the battery assembled with ECF-0 electrodes delivers the largest overpotential and can only be charged and discharged at small current densities of lower than 100 mA cm⁻². Even worse, there are fluctuations at the final stages of discharge, indicating the battery performance is deteriorated by the poor electrolyte transport inside the dense electrode. When the pores of the samples are expanded from ECF-0 to ECF-60, obvious improvements in battery performances are observed since the electrolyte can access the surface of the fibers much easier, and more surface area of the electrodes can be utilized. The polarization curves, which can give detailed voltage loss analysis, are plotted in Fig. 6f. Voltage losses from activation overpotential at small current densities, ohmic overpotential at linear reduction part, and concentration overpotential at final stages are observed. Results show that the cell with ECF-0 electrodes entered the mass transport limit region at around 200 mA cm⁻² and delivered a limiting current density of 400 mA cm⁻². With the gradually enlarged pores from ECF-0 to ECF-60, the batteries entered the mass transfer dominant region at much higher current densities, resulting in the increased limiting current densities. More remarkably, the cell with ECF-60 electrodes can reach a high limiting current density of 1300 mA cm⁻². Therefore, replacing the small fibers with large fibers to form the dual-diameter structure is an efficient approach to improving the transport properties of the electrode.

In the second group, the battery performances of cells equipped with ECF-60, ECF-70, and ECF-90 electrodes are summarized in Fig. 7. Contrary to the rising trend of battery performances observed from ECF-0 to ECF-60, the batteries assembled with ECF-70 and ECF-90 electrodes exhibit inferior performance to that with the ECF-60 electrodes. As shown in Fig. 7a–e, the electrochemical overpotentials of the cell with ECF-70 and ECF-90 electrodes are larger than that with ECF-60 electrodes at all investigated current densities. To get a better understanding of origins of the difference in battery performances, the polarization tests were conducted. As shown in Fig. 7f, when the portion of large fibers further increased from 60% to 70% and then to 90%, the batteries suffer from increased polarization, resulting from the reduced active surface area. As a result, the battery with the ECF-60 electrode presents the highest performance among samples tested, attributable to its well-balanced specific surface area and transport properties.

Based on the charge-discharge profiles of the as-prepared samples under different current densities, the coulombic efficiency (CE), voltage efficiency (VE), energy efficiency (EE), and discharge capacity, are summarized in Fig. 8. It is found that CE increases with the increased operating current density, which can be attributed to fewer reactants across the membrane due to the decreased charge-discharge time at higher current densities. Compared to the cell assembled with ECF-0, the cells with dual-diameter electrodes (ECF-30–ECF-90) all delivered higher VE and EE, among which the cell with ECF-60 achieves the highest value. To be specific, VE of 86.92% and EE of 84.78% are achieved for the battery with ECF-60 electrodes, compared with 72.59% VE and 71.21% EE for that with ECF-0, and 82.63% VE and 80.87% EE for that with ECF-90, at the current density of 100 mA cm⁻². Consistent with the charge-discharge profile, the cell with ECF-60 electrodes

![Fig. 6. (a)–(e) Charge-discharge profiles of the VRFBs using ECF0–ECF-60 samples as electrodes at current densities of 60, 80, 100, 150 and 200 mA cm⁻². (f) Polarization curves of the VRFBs using ECF0–ECF-60 electrodes.](image)
deliver the largest discharge capacity, reaching about 9.55 Ah L\(^{-1}\) at the current density of 100 mA cm\(^{-2}\). In addition, the cycling performance of the dual-diameter electrodes (ECF-60) is shown in Fig. 8d, which displays that the battery can be cycled for around 200 cycles with no obvious decay in energy efficiency and voltage efficiency, indicating that the VRFB with the as-prepared electrodes can be stably cycled over long terms in practical operation. In addition, the as-prepared electrodes were compared with commercial carbon paper. As shown in Fig. S1, the battery with the as-prepared dual-diameter electrodes outperforms that with the as-prepared commercial carbon paper electrodes, evidenced from the smaller polarizations in the charge/discharge curves at 60–150 current densities (Figs. S1a–c). The battery with ECF-60 electrodes
delivers a VE of 80.50% and EE of 79.43%, compared with 65.54% VE and 64.48% EE of the battery with carbon paper electrodes. The polarization curves of the battery with carbon paper electrodes show a larger activation and concentration voltage loss compared with that adopted ECF-60 electrodes, demonstrating the as-prepared electrodes exhibit better electrochemical activity and transport properties.

In addition to the electrode composed of 10 μm large fibers and 1 μm small fibers, varied combinations of fiber diameter can be explored, e.g., the diameter of small fibers can be reduced to several hundreds of nanometers, or the diameter of large fibers be reduced to several microns. To effectively tune the dual-diameter structure, the multi-nozzle electrospinning method needs to be adopted in the future with different nozzles supplied with different precursor solutions. Then, based on the macroscopic structure design, surface modification methods can be employed to further improve the electrochemical activity of the electrodes. With all these efforts done to design the electrode structure, the electrode can be scaled-up by adopting industrial-scale electrospinning equipment for practical applications of redox flow batteries.

4. Conclusions

In this work, a novel dual-diameter fibrous electrode is designed and fabricated by electrospinning a high concentration PAN polymer solution under the varied relative humidity and rotating rate conditions. The dual-diameter carbon fibrous structure offers efficient electrolyte pathways due to the formation of large pores among the large fibers and abundant surface area. The ECF-60 electrode which consists of 60% large fibers and 40% small fibers offers a doubled specific surface area compared with the ECF-90 electrode and 1.4 times higher tested permeability compared to the ECF-0 electrode. It is found that VRFB assembled with ECF-60 electrodes shows an EE of 84.78%, which is 13.57% higher than that with ECF-0 electrodes, and 3.91% higher than that with ECF-90 electrodes at the current density 100 mA cm−2. All the results suggest that the dual-diameter electrode is a promising electrode structure with balanced transport properties and specific surface area, providing guidance for the future electrode structure design in aqueous redox flow batteries.

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.

CRediT authorship contribution statement

J. Sun: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Writing - review & editing. H.R. Jiang: Methodology, Writing - original draft, Writing - review & editing. M.C. Wu: Methodology, Writing - review & editing. C.X. Fan: Methodology, Writing - review & editing. C.Y.H. Chao: Writing - review & editing, Supervision. T.S. Zhao: Resources, Writing - review & editing, Supervision, Project administration.

Acknowledgements

The work described in this paper was supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. T23-601/17-R) and HKUST fund of Nanhai (Grant No. NSN1-18PYR01).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2020.228441.