Aligned hierarchical electrodes for high-performance aqueous redox flow battery


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HIGHLIGHTS

- A hierarchical aligned carbon electrode was fabricated for aqueous flow batteries.
- The specific surface area and the transport properties are simultaneously enhanced.
- The as-prepared electrode enables 80.1% energy efficiency at 300 mA cm⁻².
- The battery with the prepared electrode exhibits favorable cycling stability.

ABSTRACT

Enhancing the transport properties and enlarging the surface area of electrodes are critical for achieving a high-power-density aqueous redox flow battery. In this work, we design and fabricate a hierarchical and ordered carbon fibrous (CNF-AECF) electrode by in-situ growing a layer of carbon nanofibers on the surface of aligned electrospun carbon fibers. The aligned macroscopic structure provides electrolytes transport pathways, while the highly porous carbon nanofiber layer offers a large specific surface area of up to 108 m² g⁻¹, enabling abundant active sites for redox reactions. Cyclic voltammetry tests show that the positive side peak potential separation is reduced from 92.77 mV to as low as 55.01 mV, while the negative side peak potential separation is reduced from 92.77 mV to 88.65 mV at the scan rate of 10 mV s⁻¹. The application of the as-prepared material to a vanadium redox flow battery as the positive electrode demonstrates an energy efficiency of 80.1% at the current density of 300 mA cm⁻², and 75.0% at the current density of 400 mA cm⁻², which is 5.0% and 6.6% higher than that with the pristine electrospun carbon fiber electrodes. All these results show that the custom-made carbon electrode with rationally designed geometric structures and surface properties offers the promise to achieve high power density for aqueous redox flow batteries.

1. Introduction

The rapid growth in the amount of energy collected from the renewables such as wind and solar necessitates the application of energy storage systems (ESS) due to their inherent intermittency nature, which causes unreliability and fluctuation when directly integrated into the grid [1,2]. The redox flow battery (RFB) presents a promising approach for the large-scale ESS [3,4]. Among all types of RFBs, the vanadium redox flow battery (VRFB), which was first proposed by Skylla-Kazacos and co-workers in 1985, gains the most attention primarily due to the employment of the same electrochemical element on both sides that can eliminate the cross-contamination issue existed in other RFBs [5-8]. However, the high capital cost arising from the stack components and the active materials has hindered the broad market penetration of VRFBs [9]. One of the widely recognized strategies to lower the capital cost is to reduce the stack size by enhancing the operating power density while maintaining high energy efficiency (EE).

Generally, the polarization becomes larger with the increased operating current density, leading to the decreased energy efficiency and electrolyte utilization. In addition to studies on fabricating highly selective and conductive membranes [10-13], considerable efforts have been taken to design, modify or fabricate the electrode to reduce the cell polarization which arises from activation, ohmic, and concentration losses, as the cell voltage can be expressed by

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The most commonly used carbon electrodes, such as carbon felt, carbon paper and carbon cloth, are respectively featured by a porous structure formed by needle-punched, binder-bonded, and woven carbon fibers [15,16]. Typically, electrode treatments can be classified into two categories based on the length scale. One is on the macroscopic scale, where treatments are conducted on the surface of fibers to enlarge the specific surface area and improve the electrochemical activity of the electrode to lower the activation polarization [17]. The other one is on the macroscopic scale, in which the size and shape of large pores among carbon fibers, fiber orientation and porosity of the electrode are adjusted to enhance the transport of the electrolyte, thereby reducing the ohmic loss and concentration loss.

On the macroscopic scale, depositing catalysts on the surface of carbon fibers can simultaneously improve the kinetics of the vanadium redox reactions and increase the active sites. The proposed catalysts include metal-based catalysts, such as Bi [18], Cu [19], Sn [20], Nb2O5 [21], Mn2O4 [22], and metal-free catalysts such as B4C [23], carbon nanotubes [24], carbon nanofibers [25], graphene nanowalls [26] etc. The effect of depositing various catalysts on enhancing the battery performances is closely related to their uniformity as the non-uniform deposition would lead to the accumulation of catalysts and thus decrease the active surface area [27]. Therefore, several pieces of research work suggested forming a catalytic layer on the surface of fibers to ensure uniform catalyst deposition. For example, Yang et al. developed a carbonized porous polymer skin layer deposited graphite felt electrode with large fibers of around 10 µm in diameter. Due to the reduced concentration polarization, the battery with aligned carbon fiber electrodes can enable an energy efficiency of 84.4% at the current density of 100 mA cm⁻², which is 13.2% higher than that with traditional electrospray electrodes [37]. However, the relatively small specific surface area of the aligned fibrous electrode with a large fiber diameter limits the battery to be operated at elevated current densities with high efficiencies. To further improve the battery performance, the specific area of the electrode needs to be enlarged based on the aligned fibrous structure.

In this work, a combined macroscopic and microscopic electrode architecture design was simultaneously realized by using the electrospraying method. The developed electrode structure is composed of well-aligned electrospray fibers (AE CF) in-situ grown with a porous carbon nanofibers (CNF) layer, forming a multiscale hierarchical structure. The aligned fibrous skeleton offers good transport properties, enabling a small flow resistance, while the carbon nanofiber layer acts as a uniform catalytic layer, providing abundant active sites for the redox reactions. As mentioned in previous studies, the performance of porous electrodes can be evaluated using the factor, k, which is the product of average mass transport coefficient, k, and volumetric electrochemical area, A, [38,39]. The enhanced transport properties of the electrode result in the increased velocity of the electrolyte; thus, k is larger in the aligned structure. Combined with the increase A, the value of k, in the aligned hierarchical electrode is greatly increased, leading to enhanced limiting current density. Battery performance with an energy efficiency of as high as 80.1% at 300 mA cm⁻² is achieved by applying this prepared electrode, indicating that the home-made carbon material can be a promising electrode candidate for VRFBs.

2. Experimental

2.1. Synthesis of CNF-AECF and ECF electrodes

Polyacrylonitrile (PAN, MW 150,000, CAS number: 25014-41-9), polyvinylpyrrolidone (PVP, MW 1300,000, CAS number: 9003-39-8) N, N-dimethylformamide (DMF, ≥99%, CAS number: 68-12-2), Nickel nitrate hexahydrate (Ni(NO3)2·6H2O, ≥99%, CAS number:13478-00-7), were obtained from Sigma-Aldrich. Nitric acid (HNO3,≥99%, CAS number: 7697-37-2) was obtained from Acros. All chemicals were used without any further refinement.

The synthetic procedure of the CNF-AECF electrode was illustrated in Fig. 1. Typically, a mixture of 2.4 g PAN and 2.4 g PVP was dissolved in 23.7 g DMF to form a homogenous solution, which was followed by adding 1.5 g Ni(NO3)2·6H2O. The weight percentage of the PAN, PVP and Ni(NO3)2 in the solution are 8 wt%, 8 wt% and 5 wt%. PVP can coordinate with metal ions and is incompatible with PAN in DMF solutions, which causes a phase separation and forms PVP and metal phase shell in the as-spun mat, leading to the formation of Ni on the fiber surface and catalyze the formation of CNF layer on the fiber surface [40,41]. Subsequently, the mixture was stirred vigorously overnight. The resultant solution was loaded to a stainless-needle-equipped syringe, which was pumped at a constant flow rate of 1.0 mL h⁻¹. A high voltage of 17 kV was applied between the tip of the nozzle and the collector. The rotating rate of the collector was set to be 200 rpm. During the electrospraying process, the PAN/PVP/Ni(NO3)2 blend polymer solution becomes conductive, which fosters the formation of aligned fibers. After electrospraying, the aligned fiber sheet was peeled off from the collector and was stabilized at 250 °C in air for 2 h. To grow carbon nanofibers on the fiber surface, the stabilized mat was placed in the middle of a tube furnace with PVP powder acting as the carbon source being placed on the upstream, and the mat was annealed at 1100 °C in the H2 (5%)/Ar (95%) atmosphere for 2 h. During the carbonization process, the Ni salts embedded in the fibers will be reduced to Ni metal, which is the catalyst for the growth of carbon nanofibers. The upstream PVP powder will decompose to short-chain hydrocarbons.
or carbon species, acting as the carbon source for the growth of CNFs. The as-obtained CNF-AECF fiber mat was washed with nitric acid to remove the Ni metal.

For comparison, the pure ECF electrode was fabricated under the same conditions without adding the nickel salt in the polymer solution and carbon source (PVP powder) in the annealing process.

### 2.2. Material characterizations

The morphologies of the as-prepared electrodes were characterized by a field-emission scanning electron microscope with energy dispersive X-ray (EDX) micro-analysis (FESEM, JEOL 7100F) and a transmission electron microscope (TEM, JEOL 2010) with energy dispersive x-ray (EDX) micro-analysis. 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 100 K) with 60 frames per second. The crystal structure was analyzed by X-ray diffraction (XRD, PW1825) analysis with Cu Kα radiation from 10° to 90° at a scan rate of 5° min⁻¹. 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. The pressure drop tests were conducted with the pressure sensor (Asmik, MIK-P300), and water is the working fluid.

### 2.3. Electrochemical measurements

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted on the Autolab (PGSTAT30) workstation. A typical three-electrode cell was employed with the as-prepared electrodes attached to the glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and the platinum mesh as the counter electrode. To quantify the assessable surface area of the prepared CNF-AECF and ECF electrodes, CV tests were conducted in 3.0 M H₂SO₄ electrolyte with the scanning voltage ranging from 0.5 to 0.9 V (vs. SCE) with the scan rate of 100 mV s⁻¹. To characterize the electrochemical behavior of the positive and negative redox towards different electrodes, CV tests were further carried out. The scanning voltage window for the VO²⁺/VO₃⁻ redox reaction was from 0.6 to 1.1 V (vs. SCE) in 0.1 M VO²⁺ + 3.0 M H₂SO₄ electrolyte, while that was scanned from −0.2 to −0.7 V (vs. SCE) in 0.1 M V³⁺ + 3.0 M H₂SO₄ electrolyte for the V²⁺/V³⁺ redox reaction. In the EIS tests, fixed voltages of 0.9 and −0.5 V (vs. SCE) were applied for the positive and negative redox reactions, respectively. A frequency ranges from 100 kHz to 0.01 Hz with a wave amplitude of 10 mV was applied to obtain the AC impedance spectra.

### 2.4. Single flow cell tests

The as-prepared CNF-AECF mats were cut into pieces of 2 × 2 cm² as the electrodes. With the uncompressed thickness of 700 ± 10 µm, the electrodes were assembled to the cell with interdigitated flow-by configuration [40] and compressed to about 500 µm. Nafion 212 (DuPont, USA) was used as the membrane. 20 mL 1.0 M V³⁺ + 3.0 M H₂SO₄ anolyte and 20 mL 1.0 M VO²⁺ + 3.0 M H₂SO₄ catholyte were stored in external reservoirs and pumped to the cell with a constant flow rate of 77 mL min⁻¹ (100 rpm); the mean linear flow rate is approximated as 0.86 cm s⁻¹. Both reservoirs were bubbled with nitrogen and sealed before the battery test to avoid the oxidation of the 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 a cut-off voltage of 0.9 V at the current densities ranging from 100 to 400 mA cm⁻². The contrast group was applied with the ECF electrodes under the same test conditions.

### 3. Results and discussions

#### 3.1. Material characterizations

For the formation of the hierarchical aligned electrode structure, the electrosprinning process needs to be judiciously tailored. A homogeneous PAN/PVP/Ni(NO₃)₂ blend was prepared as the precursor solution, which is more electrically conductive than the PAN/PVP solution due to the addition of nickel salts, leading to the change in the jet path under high voltage and leading to the formation of the aligned fibrous structure. In addition, the nickel salts inside the as-spun fibers will reduce to evenly-distributed catalysts (metal nickel nanoparticles) for the formation of carbon nanofibers during the carbonization
The as-prepared mat. With randomly packed thin precursor solution, as shown in Fig. 2b, which has a dense morphology around 3.0 ± 0.5 µm, as shown in Fig. 3d, and a porous layer of carbon becomes conductive, and the jet path becomes similar to the so-called bending instabilities with the spread of the polymer jets, the fibers solidify and randomly land on the collector. A white polymer mat can be peeled off from the collector after electrospinning a 10 mL precursor solution, as shown in Fig. 2b, which has a dense morphology with randomly packed thin fibers, as evidenced by the SEM micrograph (Fig. 2c).

When the nickel salt is added to the solution, the precursor solution becomes conductive, and the jet path becomes similar to the so-called "standing fiber" [41–44]. As shown in Fig. 2d, instead of forming bending instabilities with the spread of the polymer jets, the "standing fiber" tends to stick with each other due to the strong electrostatic force between them and is stretched between the spinneret and the collector. As a result, the well-stretched fibers land on the collector with a fixed anchoring position, forming aligned fibers under the rotation of the collector and scanning of the spinneret. As shown in Fig. 2e, the aqua as-spun mat exhibits an obvious orientated direction, which is even visible with naked eyes. The SEM image in Fig. 2f further confirms the well-oriented filaments in the as-spun mat (Fig. 2f).

The morphologies of the as-prepared ECF and CNF-AECF samples are shown in Fig. 3. Fig. 3a–c displays the PAN/PVP derived ECF under different magnifications, which is composed of randomly packed smooth fibers with diameters of about 500 ± 50 nm. In contrast, the carbon fibers in the CNF-AECF are well-aligned with a diameter of around 3.0 ± 0.5 µm, as shown in Fig. 3d, and a porous layer of carbon nanofibers (CNF) is grown on the surface of each electrospun fiber (Fig. 3e). The high-resolution TEM image (Fig. 3f) shows that the CNF layer is highly porous, and the thickness of the CNF layer reaches 350 ± 10 nm, o

Fig. 2. (a) Jet path of the PAN/PVP polymer solution, (b) digital photo of the as-spun PAN/PVP mat, (c) SEM image of the macroscopic structure of the PAN/PVP fiber, (d) jet path of the PAN/PVP/Ni(NO₃)₂ solution, (e) digital photo of the as-spun PAN/PVP/Ni(NO₃)₂ mat, (f) macroscopic structure of the aligned structure of the as-prepared mat.
two orders of magnitude larger than that of the ECF sample, indicating the increased electrochemical accessible surface area in the CNF-AECF sample. The capacitance of the tested double-layer capacitance can be calculated by the equation $C_p = \frac{i dV}{v \Delta E}$, where $i$ is the current, $V$ is voltage, $v$ is scan rate, and $\Delta E$ is the voltage window (0.4 V) [47]. With the specific capacitance assumed to be 0.081 F m$^{-2}$ [48], the electrochemical active surface area can be calculated to be 1.2 m$^2$ g$^{-1}$ for the ECF electrode and 154.3 m$^2$ g$^{-1}$ for the CNF-AECF electrodes. The ratio between the electrochemical active area of CNF-AECF electrode and that of ECF electrode is 128:1. The transport properties of the as-prepared electrodes can be measured through the pressure-drop test [49]. As plotted in Fig. S3, the pressure drop of water flowing through the CNF-AECF electrode is smaller than that through the ECF electrodes, which demonstrates that the CNF-AECF electrode exhibits improved mass transport properties and increased specific surface area simultaneously.

Fig. 3. (a)–(c) SEM images of the ECF electrode, (d)–(f) SEM images of the CNF-AECF electrode, and (g) SEM image of CNF-AECF filament after acid wash. (h) TEM image of the CNF-AECF filament. (i) High-resolution TEM image of the CNF after acid wash.

Fig. 4. (a) N$_2$ adsorption/desorption isotherms, (b) pore size distribution and (c) double-layer capacitance of CNF-AECF and ECF samples.
The crystal structures of the ECF and CNF-AECF samples are characterized by X-ray diffraction (XRD). As shown in Fig. 5a, diffraction peaks indexed to Ni metal are observed in the CNF-AECF sample, indicating the existence of Ni residues inside the CNF-AECF fiber even after acid wash [50]. Two diffraction peaks at 26.5° and 44° can be assigned to the (0 0 2) and the (1 0 0) planes of graphite [26]. It is shown that the graphite peak intensity of the CNF-AECF sample is much stronger than that of the ECF sample, implying the well-ordered structure of the graphite walls in CNF, which is ascribed to the catalytic effect of Ni particles during the carbonization process. Additionally, the Raman spectra of the two samples are compared in Fig. 5b. Here, the D-band located at 1360 cm⁻¹ corresponds to defects or lattice disorders in the graphene structure, while the peak at around 1590 cm⁻¹ is indexed to the G-band, which relates to the sp² carbon [51]. The relative intensity of D band to G band (ID/IG) can be used to reflect the disorder degree of the graphite. Results show that the ID/IG value of the CNF-AECF sample is 0.59, which is much smaller than that of ECF sample (0.84), indicating the enhancement in graphitization. More importantly, the existence of 2D-band at around 2700 cm⁻¹ in the CNF-AECF sample further confirms the layered structure of graphitic walls, which agrees with the high-resolution TEM images in Fig. 3i.

To characterize the composition and chemical states of the elements, the XPS tests were conducted. The full spectra of ECF and CNF-AECF show the presence of C, N, O elements (Fig. 5c). As summarized in Table 1, the contents of N and O are 4.56 and 4.97 wt% for the CNF-AECF electrode, and 4.04 and 4.98 wt% for the ECF electrode. The Ni element is not detected in the CNF-AECF sample from the XPS survey, indicating that the Ni metal on the surface of the fibers is totally removed by acid wash, with some residues remaining inside of the fiber, which has been stated in the XRD analysis (Fig. 5a). The high-resolution C1s spectrum can be divided into five characteristic peaks located at 284.6, 285.2, 285.9, 287.2, and 289.8 eV, which correspond to C=C, C–C, C–N or C–OH, C=O, and COO–, respectively (Fig. 5d) [52]. It is found that the content of the C–C bond in the CNF-AECF decreases, and part of it is incorporated into the sp² carbon [51]. The relative intensity of D band to G band (ID/IG) value of the CNF-AECF sample is 0.59, which is much smaller than that of ECF sample (0.84), indicating the enhancement in graphitization. More importantly, the existence of 2D-band at around 2700 cm⁻¹ in the CNF-AECF sample further confirms the layered structure of graphitic walls, which agrees with the high-resolution TEM images in Fig. 3i.

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<th>Composition (wt%)</th>
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<td>4.05</td>
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3.2. Electrochemical measurements

CV and EIS tests were conducted to study the electrochemical behavior of the VO²⁺/VO₃⁻ and V²⁺/V³⁺ redox couples on the ECF and
CNF-AECF electrodes. Fig. 6a compares the CV curves of VO$_2^+$/VO$_2^{2+}$ redox couple on the two electrodes at the scan rate of 10 mV s$^{-1}$. It is seen that the peak potential separation for VO$_2^+$/VO$_2^{2+}$ is reduced from 92.77 mV with the ECF electrode to only 55.01 mV with the CNF-AECF electrode, indicating the improved reversibility of the positive redox couple on the CNF-AECF electrode. Fig. 6b and c shows the CV plots of the VO$_2^+$/VO$_2^{2+}$ redox couple on the CNF-AECF and ECF electrodes at different scan rates (10–40 mV s$^{-1}$). Notably, the CNF-AECF electrode exhibits larger double-layer capacitance behavior, which is due to the enhanced surface area provided by the CNF layer. Based on the statics of the CV curves under different scan rates, the ratio between peak reduction current and oxidation current ($I_{pc}/I_{pa}$) were summarized in Fig. 6d. The enhanced reversibility of VO$_2^+$/VO$_2^{2+}$ on the CNF-AECF electrodes is further confirmed, which is reflected from the value of $I_{pc}/I_{pa}$: 0.93, 0.92, 0.92, and 0.92 for the VO$_2^+$/VO$_2^{2+}$ redox on the CNF-AECF electrode, which are much closer to the ideal value of 1.00, compared to 0.75, 0.74, 0.74 and 0.74 on ECF electrode at the scan rates of 10, 20, 30 and 40 mV s$^{-1}$. Moreover, the peak current is in linear relation to the square root of the scan rate, as plotted in Fig. 6e, indicating that the peak currents in CV tests are controlled by mass transport rather than kinetics. In addition, the larger slope of the CNF-AECF electrode potential demonstrates the increased electrochemical surface area of the material. Finally, the charge transfer resistance, which is reflected by the diameter of the semicircle in the high-frequency region, is greatly decreased from around 0.7 Ω cm$^2$ for the VO$_2^+$/VO$_2^{2+}$ redox reaction with ECF electrodes to around 0.2 Ω cm$^2$ with CNF-AECF electrodes as displayed in Fig. 6f, confirming the improved catalytic properties of the CNF-AECF electrode. In addition, the electrochemical performance of the negative side redox couple (V$^{2+}$/V$^{3+}$) on the two electrodes are also evaluated under the scan rates ranging from 10 mV s$^{-1}$ to 40 mV s$^{-1}$, as shown in Fig. S4a and b. The peak potential separation of the V$^{2+}$/V$^{3+}$ redox couple was reduced from 92.77 mV on the CNF-AECF electrode to 88.65 mV on the ECF electrode, at the scan rate of 10 mV s$^{-1}$ (Fig. S4c) and the charge transfer resistance in the EIS tests was reduced from around 0.6 Ω cm$^2$ to about 0.2 Ω cm$^2$ (Fig. S4d), both of which indicate that the kinetics of V$^{2+}$/V$^{3+}$ redox reaction can also be improved by applying CNF-AECF electrode. However, it is worth noting that the side reaction of the hydrogen evolution is detected at the negative scanning voltage range for the CNF-AECF electrode, which caused the increase of cathodic peak current, implying that the reversibility of the negative redox reaction is deteriorated. The improved kinetics of the vanadium redox reactions are due to the catalytic effects of the highly graphitized CNF layer as well as the enhanced active surface area of the hierarchical electrodes.

3.3. Single flow cell performances

The as-prepared ECF and CNF-AECF electrodes were then tested in the home-made VRFB setup. Since the parasitic reaction of hydrogen evolution is enhanced when applying the CNF-AECF electrode on the negative side, as seen from the CV results (Fig. S4c), we firstly tested the battery assembled the CNF-AECF mat as the positive electrode and ECF mat as the negative electrode, and compare it with the cell constructed with ECF electrodes on both sides. As shown in Fig. 7a–c, the battery with CNF-AECF electrodes shows a reduced polarization, evidenced by the lower charge plateau and higher discharge plateau in the charge–discharge profiles, resulting in the prolonged charge and discharge capacities. The reduced polarization can be attributed to three parts: (i) reduced activation loss due to the improved VO$_2^+$/VO$_2^{2+}$ redox kinetics on the CNF-AECF electrode; (ii) reduced ohmic loss arising from the enhancement in the electrical conductivity of CNF-AECF electrode; (iii) reduced concentration loss owing to the enhanced electrolyte transport enabled by the well-aligned structure. To quantitatively compare the cell performance, the coulombic efficiency (CE), VE, and EE were calculated and compared in Fig. 7d and e. As shown in Fig. 7d, CE increases with the increase of the current density due to the reduced operating time in each cycle. It is found that the cell with CNF-AECF positive electrode can be operated with a higher VE at all current densities than that with the ECF electrodes, resulting in the increased EE. Specifically, an EE of 80.1% is achieved by using the CNF-AECF electrode as the positive electrode at the current density of 300 mA cm$^{-2}$, while EE of the cell with the ECF electrode on both sides
shows an EE of 75.1%. Even at a high current density of 400 mA cm\(^{-2}\), the cell with the CNF-AECF positive electrode can still deliver an EE of 75.0%, which is 6.6% higher than the cell with the ECF electrodes. Meanwhile, the discharge capacities of the two cells at different operating current densities are summarized in Fig. 7f, which was calculated by referring to the total volume of anolyte and catholyte. The value of specific capacity doubles if only half-cell electrolyte was considered. Prominent enhancement in the discharge capacity is achieved in the cell with the CNF-AECF electrode as the positive electrode material, compared with 67.0% VE and 65.9% EE for the cell with AECF electrodes. The improvement in the cell performance of the battery adopting CNF-AECF electrodes can be ascribed to the increased specific surface area of the electrodes. However, the side reactions on the negative side are boosted when adopting CNF-AECF electrode, resulting in a lower CE and smaller discharge capacity. The polarization curve was measured at the full-charged state (Fig. S8c). It is shown that the voltage loss is dominated by the ohmic loss, and the cell can reach a peak power density of as high as 1.5 W cm\(^{-2}\) with CNF-AECF electrodes on both sides, compared to 1.1 W cm\(^{-2}\) for the electrode with both AECF electrodes. The side reactions on the negative side will cause a fast decay in the discharge capacity, seen from the cycling tests in Fig. S9.

Hence, it can be concluded that the CNF-AECF electrode is effective to be applied as the electrode materials on both sides if the side reaction can be successfully suppressed.

From the above discussions, it is concluded that the CNF-AECF electrodes show a large specific surface area and good transport properties, which leads to reduced activation and concentration polarizations, thus enabling the VRFB to be operated at high current densities of about 300-400 mA cm\(^{-2}\) with an energy efficiency of 80%. However, in the acidic aqueous redox flow batteries, the hydrogen evolution is enhanced when adopting the CNF-AECF electrodes on the negative side, which causes a relatively low coulombic efficiency at small current densities and capacity decay over the repeated cycles. It is expected that the electrodes are suitable for the positive electrodes in aqueous redox flow batteries and can be applied as negative electrodes in organic electrolytes. In addition, this method of fabricating CNF-AECF electrodes can be scaled-up by adopting industrial-scale electrospinning equipment [61], the materials for the fabrication of the electrode include PAN, PVP, DMF, and Ni salts, which are widely available and safe. The cost of the as-prepared electrode is estimated to be comparable to the industrial graphite felts as similar materials and thermal treatments were employed.
4. Conclusion

In summary, a home-made electrode with a rationally designed macroscopic and microscopic architecture is successfully fabricated using the electrospinning method. Free of excess treatment, the aligned structure is formed during the electrospinning process, which is beneficial to the electrolyte transport, and the CNF layer in situ grew on the surface of the film during the carbonization process of the electrospun polymer fiber, providing abundant active surface area for the redox reactions. It is demonstrated that the VRFB assembled with the as-developed CNF-AECF positive electrode is capable of delivering an EE of 80.1% at the current density of 300 mA cm\(^{-2}\) and 75.0% at the current density of 400 mA cm\(^{-2}\). By contrast, the battery with the ECF electrode can only achieve an EE of 75.1% at the current density of 300 mA cm\(^{-2}\) and 68.4% at the current density of 400 mA cm\(^{-2}\). This study proves that the performance of VRFBs can be greatly boosted by simultaneously enhancing the transport properties and the specific surface area of the electrode, which will pave the way for the development of high-power-density aqueous redox flow batteries.

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. X.Z. Fan: Methodology, Writing - review & editing. C.Y.H. Chao: Writing - review & editing, Supervision. T.S. Zhao: Resources, Writing - review & editing, Supervision, Project administration.

Declaration of Competing Interest

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

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Appendix A. Supplementary material

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References


