Preparation and surface modification of PVDF-carbon felt composite bipolar plates for vanadium flow battery

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ABSTRACT

The performance of vanadium flow batteries (VFBs) is closely related to the materials used in the bipolar plates. Carbon-based composite bipolar plates are particularly suitable for VFB applications. However, most original preparation methods cannot simultaneously achieve good electrical conductivity and mechanical performance. In this paper, we propose a novel approach to fabricating bipolar plates with carbon plastic materials, including four steps, namely coating a poly (vinylidene fluoride) (PVDF) solution onto carbon felt, solvent evaporation, hot-pressing, and surface modification. The resulting bipolar plates showed high conductivity, good mechanical strength, and corrosion resistance. Surface modification by coating with carbon nanotubes (CNTs) removed the PVDF-rich layer from the surface of the carbon fibers. The high surface area of the CNT withdrew PVDF resin from the carbon fiber surface, and promoted the formation of a conductive network. The flexibility and battery charge-discharge cycle measurements showed that the composite bipolar plates can meet requirements for VFB applications.

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1. Introduction

Bipolar plate (BP) is an important part of vanadium flow batteries, by which single cells connected in series can generate high voltages to meet the power output needs of grid-scale energy conversion and storage [1–3]. Bipolar plate is generally required with excellent electrical conductivity, adequate mechanical stability, good corrosion resistance, and low permeability to the electrolyte [4–6]. Furthermore, bipolar plates must be amenable to rapid, low-cost processing methods if they are to be widely used in large scale electricity systems.

Generally, bipolar plates (BPs) are made of sintered graphite, metals, and carbon plastics [7,8]. Graphite materials have high electrical conductivity, excellent corrosion resistance, and can be mechanically processed easily to produce a specific channel structure on their surface, which is used to confine the hydrodynamic field and improve electrolyte flow distribution. To date graphite bipolar plates have been widely applied in the development of fuel cells [9]. However, owing to brittleness of graphite, graphite bipolar plates are unyielding and it is difficult to prepare bipolar plates over large areas (e.g., a length and width of ~600 mm) [10]. Unlike fuel cells, vanadium flow batteries provide low current densities, typically below 150 mA/cm², because of slow mass transport and charge transfer in the electrolyte. Thus, a battery stack and bipolar plates with a large area are needed to meet performance requirements [11–13]. Currently, few makers use graphite bipolar plates to assemble flow batteries. Compared with graphite bipolar plates, metal bipolar plates have better mechanical properties and conductivity, which are beneficial for stack assembly and reducing the internal resistance of the battery. Molding processes can be used to make the surface channel structure efficiently. However, corrosion resistance issues seriously restrict the practical applications of metal bipolar plates. Researchers have sought to address these issues, with the use of surface coatings and electroplating to form protective layers on metal surfaces. Although these methods show some effectiveness, metal bipolar plates cannot yet be used for long-term operations [14,15].

To meet the needs of both conductivity and mechanical performance for bipolar plates in flow battery applications, an alternative approach involves the use of plastic bipolar plates, composed of graphite or other carbon materials and polymers. The carbon materials provide high electrical conductivity, corrosion resistance; the polymeric materials are responsibility for flexibility and strength [16]. Moreover, carbon plastic composites can be made by molding processes, enabling simple manufacturing and scale-up. In recent decades, investigations have been performed into various carbon black, nanotube, and graphite materials to understand the relationship between the carbon content and conductivity [17–20].

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The conductive agent in the bipolar plate needs to be present in a proportion higher than a certain threshold value, to ensure the conductive agent is connected in the polymer matrix and forms a continuous conductive path. To improve the conductivity of bipolar plates, an high content of the conductive agent is usually necessary [21]. However, excess carbon reduces the flexibility and also increases the viscosity of the polymer melt, leading to small residual gas bubbles in a bipolar plate, which increase the permeability to the electrolyte. Major challenges remain in improving the conductivity of bipolar plates, while maintaining acceptable synthetic properties.

In this study, we propose a novel strategy that involves filling polymer resins into a conductive network carbon conductive fibers, such as graphite felt, to prepare bipolar plates for vanadium flow batteries. Owing to the high length - diameter ratio of carbon fiber, these fibers contact each other to form a network and provide excellent conductivity. The filling polymer can effectively prevent electrolyte from entering the plate. Compared with previously reported bipolar plates made of mixtures of plastic resin and carbon materials [22, 23], the composition of carbon in these bipolar plates was considerably lower and the content of the polymer resin content was higher. This composition improved the flexibility, bending strength, and processability, which can all benefit practical applications. Furthermore, this method is relative easy to scale-up for manufacture on a production line and is no longer limited to the molding processes, enabling us to greatly reduce processing costs. We investigated methods for preparing bipolar plates for vanadium flow batteries. In particular, we examined reducing the surface resistance, and highlighted a mechanism for the removal of polymer adhered to the fiber surface. We also show the results of bipolar plate measurements in vanadium flow battery charge-discharge processes.

2. Experimental

2.1. Materials

Polyvinyl fluoride (PVDF FR904) was purchased from 3F-Wanhao Fluorine Chemical Co., Ltd., and dimethyl sulfoxide (DMSO AR) was purchased from Beijing Modern Oriental Fine Chemistry Co., Ltd. Both materials were used without further purification. Carbon felt (thicknesses of 2 and 5 mm) was purchased from Sichuan Rui-Sheng Carbon Felt Co., Ltd. Carbon nanotubes (CNTs) were purchased from C-Nano technology Ltd. and Beijing DK S&T Ltd. The flaked graphite (diameter of 1 µm) was purchased from Qingdao TianYuanDa graphite Co., Ltd. The SGL bipolar plate TP6 was purchased from SGL Technic Int, which was composed of 6% (wt) polymer resin, 150 ppm metallic contaminants and about 94% (wt) carbon composition.

2.2. Preparation of bipolar plates and surface treatments

Fig. 1 shows a schematic of the PVDF-carbon composite bipolar plate fabrication. PVDF and DMSO were mixed in a 3:16 mass ratio, heated to 80 °C and stirred for 5 h continuously until the mixture became a clear solution. The solution was allowed to stand for some time to remove air bubbles. Carbon felt was soaked into the solution until it became completely saturated. The carbon felt was removed with tweezers, and excess liquid on the surface of the carbon felt was gently wiped off. The carbon felt was placed in an air-circulating oven and dried for 8 h at 80°C to ensure that the DMSO was completely removed. The dried samples were hot-pressed by an open mill at 175°C. The roll spacing and speed were adjusted to ensure that the sample was fully hot-pressed to the thickness of 0.75 mm, apparent density of 1.23 g/cm³.

The hot-pressed samples were modified in various ways. Flaked graphite or CNTs was coated onto the sample surfaces and then hot-pressed again. Plasma processing (700 W, 5–10 min, atmosphere condition) was also used to modify the sample surfaces.

2.3. Characterization of bipolar plates

2.3.1. Conduction performance

The bipolar plate is located between two carbon felts in the cell, thus, it is necessary to measure not only the resistance of the bipolar plate itself, but also the contact resistance between the bipolar plate and the carbon felt. Fig. 2 shows the method used to evaluate the resistance of the bipolar plate.

The electrical resistance was measured with a micro resistance tester (Nanjing Daming Instrument Co., Ltd. DME-20). As shown in Fig. 2, the composite bipolar plates and carbon felts were placed between two copper end plates, and a pressure was applied with a universal material experiment machine (Shanghai Hengzhun Instrument Technology Co., Ltd. HZ-1003A). The pressure was varied in the range of 15–90 kPa.

Setting the number of bipolar plates and carbon felts between the copper plates to be X and X + 1, respectively, the total resistance of this system could be calculated from the following formula:

\[ R_X = 2R_{Cu} + X R_{BP} + (X + 1) R_f + 2R_{Cu-f} + 2X R_{BP-f} \] (1)
where $R_k$ is the total resistance of this system, $R_{Cu}$, $R_{BP}$, and $R_t$ are the bulk resistance values of the Cu end plates, bipolar plates, and carbon felts, $R_{Cu-f}$ is the contact resistance between the copper plate and carbon felt, and $R_{BP-f}$ is the contact resistance between the bipolar plate and carbon felt.

When the number of bipolar plates and carbon felt between the Cu end plates was increased by one, the total resistance increment could be calculated by the following formula:

$$R_{\Delta} = R_{X+1} - R_X = R_{BP} + R_t + 2R_{BP-f}$$  (2)

Where $R_{X+1}$ is the total resistant when the amount of bipolar plates and carbon felts in the Cu end plate were $X+1$ and $X+2$ and $R_X$ is the resistance increment of this system.

The value of $R_t$ can be measured simply by a four-probe method, the resistance of the bipolar plate $R_{BP} + 2R_{BP-f}$ can then be calculated from the following difference:

$$R_{BP} + 2R_{BP-f} = R_{\Delta} - R_t$$  (3)

2.3.2. Morphology observation

The surface morphology of the bipolar plate was observed by a MERLIN Compact scanning electron microscope.

2.3.3. Mechanical performance

A universal material experiment machine was used to measure the bending and tensile strength of the bipolar plates based on ISO 527-2:2012 and GB/T 13465.2:2002 standards. For measurement of the tensile strength of the bipolar plate, the bipolar plate was made into a dumb bell shape with dimensions of 150 × 20 mm. The distance between the two clamps was 120 mm, the narrow part was 65 × 10 mm, the tensile speed was set to be 1 mm/min. For measurement of the bending strength a 3-point method was used and the bipolar plate was made into a rectangle shape with dimensions of 80 × 20 mm. Testing was performed at a span length of 40 mm and at a bending speed of 1 mm/min.

2.3.4. Battery measurements

The performance of the bipolar plates in vanadium flow batteries was tested in a 24 cm$^2$ cell with carbon felt as the electrode. Nafion 115 membrane was used as separator, and a platinum plate as the current collector. A bipolar plate was placed between the current collector and carbon felt, in a configuration similar to that of a real battery. A 150-ml portion of electrolyte was used in both sides of the half-cell with 1.5 M vanadium sulfide in 1.5 M H$_2$SO$_4$. For the first charge, the cell was charged to 1.55 V at a constant current density of 50 mA/cm$^2$ and the cell polarization curve was measured. A current density of 40 mA/cm$^2$ was used in the charge/discharge cycle testing, with the conditions of charging/discharge ending at 1.55 and 1 V, respectively.

3. Results and discussion

3.1. Fabrication of PVDF-carbon felt composite bipolar plates

To obtain both high electrical conductivity, corrosion resistance of the carbon materials, and good mechanical strength of thermoplastic polymers with the necessary flexibility for flow battery assembly, the framework of a carbon plastic composite material was used for the bipolar plates. PVDF resin was used to fill in spaces in the conductive network of a commercial carbon felt. This approach achieved good electrical conductivity from the inner carbon network and the polymer resin matrix prevented permeation by the vanadium electrolyte. As shown in Fig. 1, the preparation of the bipolar plate featured the following steps.

Solution coating: all the pores in carbon felt were filled by immersion in the PVDF solution. For this purpose, PVDF resin was first dissolved into DMSO to prepare a homogeneous solution, so that PVDF molecules could move inside the carbon felt easily and thus achieve a uniform distribution of PVDF in the carbon felt.

Solvent evaporation: the volatile organic solvent DMSO was removed completely by a heating processes. In the process of solvent evaporation, the PVDF concentration increased gradually over time, enabling the PVDF molecules to become evenly distributed within the carbon felt, and wrap tightly around the carbon fibers, thus leading to some porous structures inside the carbon felt.

Hot-pressing: a rolling press process at elevated temperature was used to eliminate macrovoids inside the carbon felt. The PVDF molecules that were wrapped around the carbon fibers were heated and melted, before reconnecting with each other under the pressure of the two hot rollers. In this way, the macrovoids inside the carbon felt were eliminated, reducing the permeability of the bipolar plates to the electrolyte.

Surface modification: the surfaces of these bipolar plates became covered by PVDF owing to its low surface energy. This surface-coating effect seriously affected the conductivity. In this study, we modified the bipolar plate surface by a plasma treatment, flake graphite coating, and CNT coating. These approaches removed the PVDF from the carbon fiber surface, and promoted the formation of a conductive network. These effects in turn decreased the surface resistance of the carbon plastic composite bipolar plates.

Fig. 3 shows the morphology changes before and after filling the polymer resin into the carbon felt. The original carbon felt had a porosity of more than 90%, and the internal space was enclosed by a large number of carbon fibers in contact with each other. Each carbon fiber had a smooth surface and was made up of graphitized carbon and amorphous carbon. The PVDF resin was filled into the inner space of the carbon felt, covering the carbon fiber surface to form a tight matrix, which could prevent permeation of the vanadium electrolyte. Considering that over higher concentrations of PVDF often made it difficult to get well immersion and distribution of PVDF in carbon felt, so that some defect could be formed to affect its rejection behaviors to vanadium electrolyte. On contrary, much low PVDF concentration could not cover all gaps in carbon felt, which also produced defect in BPs. After some primary test and measurement, the weight ratio of PVDF:DMSO was set to within the range of 3:16–1:4 to prepare polymer solution. The composition was kept as given range in later study, thus resulting in the bipolar plate composted of approximately 70%(wt) PVDF resin and 30%(wt) carbon. Owing to the close combination of PVDF and the carbon fiber surface, ion penetration through the bipolar plate could be effectively prevented. However, the PVDF layer covering the carbon fibers was harmful for the formation of a conductive network inside the bipolar plate. Because of its low surface energy, the PVDF resin tended to concentrate on the plate surface near to air. This effect increased the polymer concentration of the outer surface of the bipolar plate, and decreased the bipolar plate conductivity. Therefore, it became necessary to modify the surface of the bipolar plate after the hot-pressing process.

3.2. Conductivity improvement with various surface modification approaches

The conductivity of the bipolar plates could be improved effectively by the surface treatments. Fig. 4 shows SEM images of the structure after plasma irradiation, coating with flake graphite or CNTs, and are compared with the original sample (Fig 4a). The carbon fiber and polymer on the surface adsorbed energy from the plasma irradiation. The elevated temperature led to the polymer melting on the surface and increased the connection points where the polymer adhered (Fig 4b). This resulted in an increase of the electrical resistance and the bipolar plate conductivity was
Fig. 3. Morphology change during bipolar plate fabrication: (a) original carbon felt; (b) composite plate before hot-pressing; (c) composite plate after hot-pressing.

Fig. 4. Bipolar plate surface morphology from SEM images: (a) no surface treatment; (b) plasma treatment; (c) crystalline flaked graphite (1 μm) coating; and (d) CNT coating.

The flaked graphite could squeeze into the polymer resin and neatly arrange on the bipolar plate surface (Fig 4c), leading to a partial increase in the conductivity of the bipolar plate. After the CNT coating was applied to the surface of the bipolar plate, the CNTs were completely mixed with the PVDF resin owing to their small diameter, and high length–diameter ratio and specific surface area. Owing to contraction of the CNTs, the PVDF resin peeled away from the carbon fiber surface and formed PVDF/CNTs particles, which exposed the carbon fiber at the surface (Fig 4d). Fig. 5 compares the conductivity of the bipolar plates subjected to different surface treatments. The conductivity decreased in the order: CNT coating > flaked-graphite coating > untreated > plasma irradiation. The effect of resin moving from the carbon felt to the CNTs indicated a general tendency for the polymer to redistribute depending on the specific surface area. This process effectively increased the conductive area and facilitated the formation of the electronic network. As shown in Fig. 5, the resistivity of the surface of the bipolar plate was gradually reduced and stabilized as the pressure applied to the sample was increased. The samples treated

Fig. 5. Comparison of bipolar plate conductivity of samples subjected to different surface treatments.
by CNTs showed the lowest surface resistance of 0.125 $\Omega$ $\text{cm}^2$, which was close to that of the commercial SGL-bipolar plate.

CNTs have characteristics including a high specific surface area and high length-diameter ratio, which have a considerable influence on the effectiveness of the surface modification. In this study, the treatment effects of various CNTs were investigated systematically to highlight the mechanism of the surface modification process. Unlike modification with flaked graphite, the CNTs played roles in inducing surface detachment and enhancing the electrical conductivity. SEM images in Fig. 6 show the morphology change through coating with different CNTs. As shown in Table 1, the conductivity of the bipolar plates gradually increased together with the CNTs specific surface area, as well as the length–diameter ratio. The greater surface area of the CNTs could absorb more of the PVDF resin that would otherwise cover the surface of the carbon fiber. This effect enhanced electron conduction through the bipolar plate because more of the carbon fibers became exposed at the surface, thus promoting the formation of a conductive network. As shown in Fig. 6, owing to the large surface area of the CNTs, the PVDF covering on the surface of the carbon fibers was transferred to the surface of the CNTs. After the high temperature melting process, blended particles of CNTs and PVDF were formed. Compared with the previous CNTs, the CNTs absorbed PVDF to form a clustered structure (Fig. 6b). During a surface treatment with carbon materials, the PVDF resin transferred from the surface with a low specific area to areas of high specific area.

### 3.3. Characterization of mechanical performance

Fig. 7 shows the mechanical properties of the carbon plastic bipolar plates, characterized by bending strength and tensile strength, compared with those features of the commercial SGL bipolar plates. The flexibility of the bipolar plates was characterized by bending experiments (Fig. 7a). The deformation of the bipolar plate in the vertical direction increased gradually under the deformation force from a steel indenter, a turn platform appeared and kept some time at 2 N, and then the resilience force was measured after the indenter approached to the position of 15 mm. The flexibility of the SGL bipolar plate was determined by the same method, a similar curve of deformation to force was measured; however, the SGL bipolar plate showed a greater force slope during the deformation increasing process, and a lower resilience force than that of the home-made bipolar plate in the loosing process. The extension behaviors of bipolar plate was measured by applying a tensile force on it. When the extension rate exceeded 20%, the tensile force decreased rapidly at a maximum value of 60 N (Fig. 7b). In contrast, the SGL bipolar plate cracked when the extension rate reached 15% due to its higher stiffness. Fig. 7(c) shows photographs taken after the bending experiments. The elastic deformation in our bipolar plate was recovered immediately, when the imposed force was removed. Although the SGL bipolar plate showed a similar curve of deformation to force, its deformation could not be recovered owing to irreversible damage to its inner structure. Therefore, our bipolar plate showed better flexibility, which is important characteristic for vanadium battery assembly to prevent mechanical damage. This result is attributed to the internal structure of the carbon plastic plate and the high PVDF resin composition of 70% (wt), which can provide good flexibility. To obtain the same conductivity as that of the SGL bipolar plate, we were able to use a lower carbon content of only 30% (wt) in our bipolar plate due to the preformed conductive network of the carbon felt. Hence, the content of the PVDF resin in the bipolar plate could be increased, thus allowing for better flexibility of the carbon plastic bipolar plate.

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**Fig. 6.** Surface morphology of BPs with (a) no CNTs, (b) CNT102, (c) CNT104, (d) CNT105, (e) CNT106, and (f) CNT107.

**Table 1.** Influence of CNT properties used for surface coating on bipolar plate conductivity.

<table>
<thead>
<tr>
<th>CNTs number</th>
<th>Diameter (μm)</th>
<th>Length (μm)</th>
<th>Length-diameter ratio</th>
<th>Specific surface area (m²/g)</th>
<th>Surface resistance under pressure (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30 kPa</td>
</tr>
<tr>
<td>CNT102</td>
<td>&lt;8</td>
<td>10-30</td>
<td>≈2500</td>
<td>350</td>
<td>0.201</td>
</tr>
<tr>
<td>CNT104</td>
<td>10-20</td>
<td>10-30</td>
<td>≈1300</td>
<td>200</td>
<td>0.210</td>
</tr>
<tr>
<td>CNT105</td>
<td>20-30</td>
<td>10-20</td>
<td>≈600</td>
<td>110</td>
<td>0.225</td>
</tr>
<tr>
<td>CNT106</td>
<td>30-50</td>
<td>10-20</td>
<td>≈400</td>
<td>60</td>
<td>0.281</td>
</tr>
<tr>
<td>CNT107</td>
<td>&gt;50</td>
<td>10-20-50</td>
<td>≈300</td>
<td>40</td>
<td>0.343</td>
</tr>
</tbody>
</table>
3.4. Electrochemical behaviors in vanadium flow battery charge/discharge cycles

Charge-discharging cycle testing of a single vanadium flow battery cell was used to characterize the bipolar plate properties. Fig. 8 shows the polarization characteristics of this battery, which directly reflect the conductivity of the bipolar plate. As the current density increased, the charge voltage increased and the discharge voltage decreased gradually. The variation of the current showed an almost linear relationship with the voltage, which is typical of vanadium flow batteries. Our bipolar plate showed similar electrochemical polarization properties to those of the commercial SGL bipolar plate. Moreover, Fig. 9 shows the results of voltage efficiency measurements performed during vanadium flow battery charge/discharge cycles. The voltage efficiency remained over 80% which was a little higher than that of the SGL bipolar plates, due to the addition of CNT to generate rough surface which somewhat benefits for redox reaction. This result shows that the conductivity of our bipolar plates can meet the requirements of vanadium flow batteries.

In order to obtain enough resistance against both chemical and electrochemical corrosion, PVDF and carbon felt were selected to prepare composite plastic BP, these materials have been employed in VFB as electrode and membrane composition. Moreover, we measured the corrosion current with home-made PB and SGL BP. Based on the comparison of the corrosion performance in 1 M acid at room temperature, both of the composite BPs has almost same corrosion current, meaning that the home-made BP is of good corrosion resistance like the commercial sample.

In addition, static diffusion measurements were used to indicate the crossover behaviors of the electrolyte by observing the concentration increase in the permeate chamber, which was filled with deionized water. Over 72 h, the concentration of protons in the permeate chamber showed no notable increase, indicating that our bipolar plate effectively isolates the electrolytes.

4. Conclusions

To develop vanadium flow batteries for electricity energy storage, in this study we propose a novel approach to fabricating car-
bon plastic bipolar plates, which show high conductivity and good mechanical strength and corrosion resistance. The four fabrication steps for our bipolar plates included solution coating, solvent evaporation, hot-pressing, and surface modification. This process enabled full use of the inherent characteristics of both carbon felt, which has good conductivity and corrosion resistance, and PVDF resin, which is flexible and provides bending capacity. After the PVDF resin was filled into the porous carbon felt, hot-pressing helped to form a dense composite layer that could block the electrolyte. Surface modification with CNTs removed PVDF from the surface of the carbon fibers, leading to a clear improvement in conductivity, reducing the area resistance of the bipolar plate to 0.125 Ω cm². Because carbon felt has a high length - diameter ratio and forms a conductive network, the carbon content in the bipolar plate could be considerably reduced to 30%(wt), compared with that of present SGL products with 94%(wt) carbon composition; hence, the content of the PVDF resin could be increased up to 70%. The flexibility of our bipolar plate was thus markedly improved. This new approach is suitable for scale-up and continuous manufacturing of bipolar plates. We expected that this method could be applied for future manufacture as a fundamental technology in flow battery development.

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Supplementary materials

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References