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Flexible electrospun carbon nanofiber embedded with TiO_2 as excellent negative electrode for vanadium redox flow battery

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ABSTRACT

In this paper, flexible carbon nanofiber embedded with TiO_2 (CNF/TiO_2) was prepared by electrospinning technique, and used as negative electrode for vanadium redox flow battery (VRFB). CNF/TiO_2 composites were synthesized from solution consisting of $Ti(OC_4H_9)_4$ as TiO_2 precursor and polyacrilonitrile (PAN) as carbon precursor. High-purity rutile TiO_2 can be dispersed evenly in CNF with the diameter of 100–200 nm. CNF/TiO_2 composites exhibited superior electrochemical activity towards V^{2+}/V^{3+} redox reaction compared with pristine CNF. The excellent energy storage performances of VRFB were achieved via using CNF/TiO_2 as negative electrode, with larger capacity and efficiency. At a current density of 90 mA cm^{-2}, the discharge capacity of the cell using CNF/TiO_2 electrode reached 84.0 mA h, 48.5 mA h higher than that of pristine cell. The energy efficiency of the cell based on CNF/TiO_2 increased by 8.7% compared with pristine cell. The excellent electrochemical performance of CNF/TiO_2 composite towards V^{2+}/V^{3+} redox reaction was attributed to the synergistic effect between carbon nanofiber networks with high conductivity and rutile TiO_2 with high electrocatalytic properties.

1. Introduction

Vigorously developing new energy sources such as wind, solar, and nuclear energy is an important way to solve the problems including the lack of conventional energy and environmental pollution [1–5]. With rapid development of new energy, especially for wind power and nuclear energy, increasing notices have been paid to large-scale energy storage system and supporting equipment in the last few years [6–10]. VRFB has been focused extensively in most prospective energy storage systems thanks to its excellent performances such as high efficiency, long cycle life, and environmental friendliness [11–14].

VRFB can convert chemical energy into electricity by the oxidation-reduction reactions of positive and negative reactants. In VRFB system as illustrated in Fig. 1, the energy is stored in electrolytes, consisting of the positive side corresponding to VO^{2+}/VO_2^+ sulfate electrolyte and the negative side ascribed to V^{2+}/V^{3+} sulfate electrolyte [15]. The electrolytes in two compartments are separated by proton-exchange membrane. The standard voltage of 1.26 V is formed in VRFB through following reactions [15,16]. Generally, graphite felt (GF) is widely used electrode materials in the practical application of VRFB [17,18]. However, the poor electrochemical activity of GF limits the further development of VRFB. Therefore, many researchers have paid much attention on the improvement of the electrochemical activity: activation treatment and electrocatalyst modification, for instance.

$$\text{Cathode}: VO^{2+} + H_2O \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2^+ + 2H^+ + e \qquad E^0 = 1.00V \tag{1}$$

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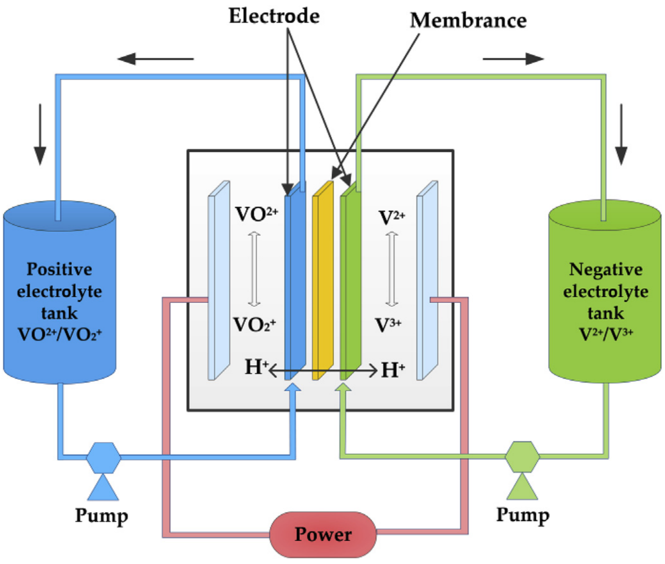

Fig. 1. The schematic representation of VRFB.

$$\text{Anode}: V^{3+} + e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} V^{2+} \qquad E^0 = -0.26V \tag{2}$$

$$\text{Cell}: VO^{2+} + H_2O + V^{3+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} VO_2^+ + 2H^+ + V^{2+} \qquad E^0 = 1.26V \tag{3}$$

Customarily, there are mainly two techniques to advance the electrochemical activity of electrode materials for VRFB. The first one is raising the efficacious surface area, and the other one is improving the electrocatalytic activity. Therefore, the raise of efficacious surface area can be achieved by the introduction of nanoscale materials, decrease of fiber diameter, and improvement of wettability. For instance, Sahin et al. [19] prepared graphene layer coated graphite electrode by cyclic voltammetry in HNO_3 solution, which exhibited excellent electrochemical activity for VO^{2+}/VO_2^+ redox reaction and good cycling stability. Wang et al. [14] developed carbon layer-exfoliated and SO_3H-functionalized carbon paper as superior positive electrode for VRFB by ultrasonication-assisted sulfonation reaction, resulting in larger surface area and more active sites. Recently, electrospinning technique has been applied to prepare carbon-based fibers as the electrode for VRFB [20–23]. Flox et al. [24] firstly exploited electrospinning technique to prepare carbon nanofiber applied in VRFB. After that, many researchers further developed this technique by changing calcination parameters and composite technology. Yan et al. [25] studied the relationship of carbonization temperature and electrochemical activity of PAN-derived carbon nanofiber by electrospinning technique, and verified the highest performance at 1000 °C due to inner-structure of fiber and improved electrical conductivity. Fetyan et al. [23] produced non-woven carbon nanofiber networks as alternative electrode for VRFB by electrospinning technique, with energy efficiency increase of 10% compared with commercial carbon felt. Zhang et al. [26] developed ultrathin free-standing electrospun carbon nanofiber web electrode for VRFB, which led to reduction of ohmic polarization of the cell. As reported by Blasi et al. [20], flexible carbon nanofiber incorporated with Mn_3O_4 (Mn_3O_4/CNF) as electrode for VRFB was prepared by electrospinning method, and Mn_3O_4/CNF electrode show outstanding electrocatalytic activity towards both positive and negative redox couples. Based on reported work about electrospun carbon nanofiber, it is generally believed that the electrospun carbon nanofiber shows excellent electrical conductivity, large specific surface area, and good electrochemical activity toward vanadium redox couples. Many reports reveal the potential use of nano-scale fiber by electrospinning method as electrode in VRFB.

Compared with VO^{2+}/VO_2^+ reaction, V^{2+}/V^{3+} reaction demonstrates larger voltage loss in VRFB due to its slower heterogeneous electron transfer rate [27–29]. And there is so much literature reporting electrode modification and novel electrocatalysts to raise electrochemical kinetics for VO^{2+}/VO_2^+ reaction [30–32]. Therefore, enhancing electrochemical kinetics for V^{2+}/V^{3+} redox reaction is an efficient way to boost VRFB comprehensive performance. Recently, titanium-based compounds (e.g. TiC, TiO_2, TiN) have been proved to exhibit excellent electrocatalytic performance towards V^{2+}/V^{3+} redox couple for VRFB. Yan et al. [33] prepared NiC nanoparticle-decorated graphite felt by hydrothermal synthesis and subsequent carbothermal reaction, and employed as negative electrode for VRFB with high performance. Flox et al. [34] used hydrogen-treated TiO_2 as electrocatalyst for V^{2+}/V^{3+} reaction for VRFB with excellent catalytic properties, coming from the formation of oxygen functional groups and oxygen vacancies in the lattice structure. Xiang et al. [35] developed TiN nanoparticle coated carbon paper composite as negative electrode, which demonstrated superior electrochemical activity and reversibility resulting from the facilitated charge transfer in negative reaction. Considering these advantages of electrospun carbon nanofiber and high electrocatalytic performance of titanium-based compounds, in this paper, TiO_2 nanoparticles were introduced in the carbon nanofiber (CNF/TiO_2) by electrospinning technology and subsequent pyrolysis process, as shown in Fig. 2. A series of CNF/TiO_2 electrode with flexible characteristic (see Fig. 4i) were produced, and the electrochemical performance of CNF/TiO_2 electrode towards V^{2+}/V^{3+} redox reaction was investigated systematically.

2. Experimental

2.1. Preparation of materials

TiO_2 embedded carbon nanofiber was prepared via electrospinning technique. The technology includes following parts: electrospinning, preoxidation, and pyrolysis. Firstly, polyacrylonitrile (PAN) was dissolved in N,N-dimethylformamide (DMF) to form 10 mL of 10 wt% PAN/DMF solution, followed by agitating for 10 min. Then $Ti(OC_4H_9)_4$ (TnBT) as titanium dioxide (TiO_2) source was dissolved in PAN/DMF solution, and kept constant magnetic stirring at 70 °C for 4 h. TiO_2 content was controlled by adding 0.4, 1.0, and 2.0 mL of TnBT, respectively. As comparison, the pristine carbon nanofiber was derived from PAN/DMF solution without TnBT. The precursor solution was suctioned into a syringe, in which the model of stainless steel needle is 21 G. The whole process was maintained with the speed of 0.1 mm min^{-1} at the positive voltage of 10 kV and negative voltage of 3.5 kV. The electrospun nanofibers were gathered on a roller, and the distance from the roller to the syringe was 17 cm. After that, electrospun nanofibers were pre-oxidized at 270 °C for 1 h in air. Finally, the pre-oxidized nanofiber was calcined at 900 °C for 2 h in Ar atmosphere.

2.2. Characterizations of materials

The crystalline structure of samples was investigated by X-ray diffraction (X-pert 3710 XRD) with Cu-Kα radiation. The morphology and microstructure of electrospun carbon nanofiber