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Electrospun carbon nanofibers/electrocatalyst hybrids as asymmetric electrodes for vanadium redox flow battery

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HIGHLIGHTS

- Composite electrodes have been made by electrospinning technique.
- CNTs/ECNFs show best electrocatalytic activity to VO^{2+}/VO_2^+ redox couple.
- Bi/ECNFs present best electrocatalytic activity to V^{2+}/V^{3+} redox couple.
- Hydrogen evolution on the Bi/ECNFs composite electrode is suppressed.
- CNTs/ECNFs and Bi/ECNFs are used as asymmetric electrodes for VRFB.

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ABSTRACT

To improve the electrochemical activity of polyacrylonitrile (PAN)-based electrospun carbon nanofibers (ECNFs) toward vanadium redox couples, the multi-wall carbon nanotubes (CNTs) and Bi-based compound as electrocatalyst have been embedded in the ECNFs to make composite electrode, respectively. The morphology and electrochemical properties of pristine ECNFs, CNTs/ECNFs and Bi/ECNFs have been characterized. Among the three kinds of electrodes, the CNTs/ECNFs show best electrochemical activity toward VO^{2+}/VO_2^+ redox couple, while the Bi/ECNFs present the best electrochemical activity toward V^{2+}/V^{3+} redox couple. Furthermore, the high overpotential of hydrogen evolution on Bi/ECNFs makes the side-reaction suppressed. Because of the large property difference between the two composite electrodes, the CNTs/ECNFs and Bi/ECNFs are designed to act as positive and negative electrode for vanadium redox flow battery (VRFB), respectively. It not only does improve the kinetics of two electrode reactions at the same time, but also reduce the kinetics difference between them. Due to the application of asymmetric electrodes, performance of the cell is improved greatly.

1. Introduction

VRFB has attracted a great deal of interests as a large-scale energy storage device due to its outstanding advantages such as long cycle life, large capacities, flexible design and no cross-contamination [1,2]. Because of the high surface area and low electrical resistivity, the carbon felt (CF) is widely used as electrode material for VRFB. However, the electrochemical reversibility of vanadium redox couples on the CF is very poor. In addition, some previous literature report the reaction kinetics of V^{2+}/V^{3+} redox couple is much slower than that of VO^{2+}/VO_2^+ redox couple on carbon electrodes [3,4]. The hydrogen evolution also happens easily on carbon electrodes in the acid solution [5]. All of these negative effects limit the energy efficiency of VRFB seriously. Therefore, a lot of electrocatalysts such as Ir, Bi, $CuPt_3$, Nb_2O_5, Mn_3O_4, WO_3, CNTs, graphene, and reduced graphite oxide have been developed to modify the CF and enhance its electrochemical activity [6–16]. Although some electrocatalysts present good electrocatalytic activity toward vanadium redox couples, they can not still solve the problems mentioned above efficiently. Besides, the adhesion of electrocatalysts on the CF is low with current loading methods, thus, the electrocatalysts may meet the challenge of washing out by flowing electrolyte in VRFB.

Therefore, a new composite electrode is developed in this paper. Applying the electrospinning technique and subsequent carbonization process, PAN polymer with electrocatalysts can be made into composite carbon nanofibers easily. With this method, the

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electrocatalyst will be embedded in the carbon nanofibers and not be washed out by flowing electrolyte. Among the numerous electrocatalysts, CNTs shows high electrocatalytic activity toward VO^{2+}/VO_2^+ redox couple while the hydrogen evolution on it is easy to happen; Bi metal or its trivalent ion presents high electrocatalytic activity toward V^{2+}/V^{3+} redox couple and the overpotential of hydrogen evolution on Bi metal is quite large [17–19]. Therefore, CNTs and Bi-based compound are used as electrocatalyst for positive and negative electrode in the paper, respectively. In this way, the reaction kinetics on two electrodes will be improved at the same time, and the hydrogen evolution on the negative electrode will be also suppressed.

2. Experimental

2.1. Preparation of composite electrodes

12 wt.% of PAN was dissolved in N,N-dimethylformamide (DMF) by stirring at 60 °C for 4 h firstly. Then the CNTs and bismuth nitrate were added into the PAN solution, mixing with PAN polymer by mass ratios of 1: 100 and 1: 10 by stirring at room temperature for 1 h to prepare the precursor solution for electrospinning, respectively. The two kinds of precursor solution were made into electrospun nonwoven web consisting of nanofibers by process reported in the previous work, respectively [20]. Then the electrospun nanofibers were pre-oxidized at 280 °C for 30 min in air. After that, the stabilized nanofibers were carbonized by heating them to 1000 °C at a rate of 5 °C min^{-1} and holding for 90 min in nitrogen flow. After this procedure, the CNTs/ECNFs and Bi/ECNFs composite electrode were obtained. For comparison, the pristine ECNFs without electrocatalyst were also prepared.

2.2. Material characterization

The morphology of ECNFs and electrocatalysts were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

For electrochemical measurement, a three-electrode cell was used as reported in the previous work [21]. The electrochemical properties of pristine ECNFs, CNTs/ECNFs and Bi/ECNFs composite electrode were tested by cyclic voltammograms (CV) and electrochemical impedance spectra (EIS). The CV curves were recorded at 2 mV s^{-1} scan rate in 0.1 M $VOSO_4$ + 2.0 M H_2SO_4 solution. The EIS was measured by applying an alternating voltage of 5 mV over the frequency ranging from 10^5 to 10^{-2} Hz in 0.1 M $VOSO_4$ + 2.0 M H_2SO_4 solution at different potentials.

The VRFB single cell performance was tested in the cell structure described in the previous work [21]. The asymmetric electrodes were used by sandwiching them between pristine CF and ion exchange membrane in both half cells. The CNTs/ECNFs acted as positive electrode while the Bi/ECNFs acted as negative electrode. For comparison, the cell just with pristine CF was also tested.

3. Results and discussion

3.1. Morphology of ECNFs

Surface morphology of the pre-oxidized nanofibers with Bi-based compound is presented in Fig. 1a and b. Comparing the SEM image and Z-contrast image obtained by a backscattering

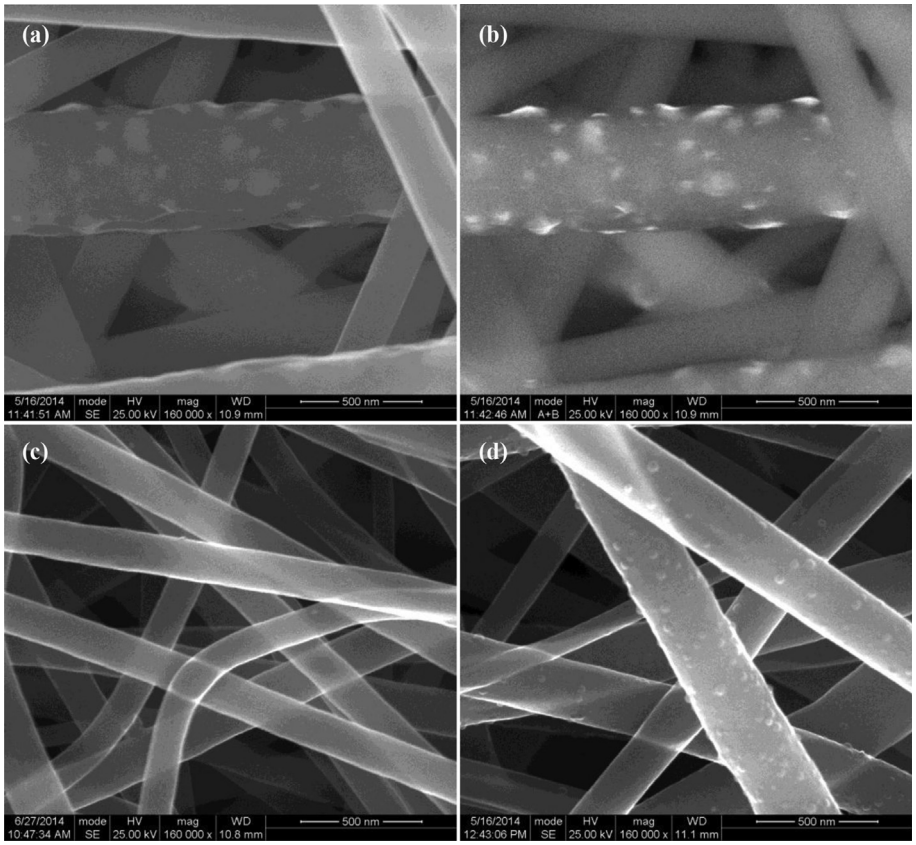

Fig. 1. Surface morphology of PAN-based nanofibers: SEM image (a) and Z-contrast image (b) of the pre-oxidized nanofibers with Bi-based compound; SEM image of the pristine ECNFs (c) and Bi/ECNFs (d).