Journal of Energy Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

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Ultrathin free-standing electrospun carbon nanofibers web as the electrode of the vanadium flow batteries

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ARTICLE INFO

Article history:
Received 4 November 2016
Revised 27 February 2017
Accepted 28 February 2017
Available online xxx

Keywords:
Vanadium flow battery
Electrode material
Carbon nanofiber
Electrospinning

ABSTRACT

Ultrathin free-standing electrospun carbon nanofiber web (ECNFW) used for the electrodes of the vanadium flow battery (VFB) has been fabricated by the electrospinning technique followed by the carbonization process in this study to reduce the ohmic polarization of the VFB. The microstructure, surface chemistry and electrochemical performance of ECNFW carbonized at various temperatures from 800 to 1400 °C have been investigated. The results show that ECNFW carbonized at 1100 °C exhibits the highest electrocatalytic activity toward the V^{2+}/V^{3+} redox reaction, and its electrocatalytic activity decreases along with the increase of carbonization temperature due to the drooping of the surface functional groups. While for the VO^{2+}/VO_2^+ redox couple, the electrocatalytic activity of ECNFW carbonized above 1100 °C barely changes as the carbonization temperature rises. It indicates that the surface functional groups could function as the reaction sites for the V^{2+}/V^{3+} redox couple, but have not any catalytic effect for the VO^{2+}/VO_2^+ redox couple. And the single cell test result suggests that ECNFW carbonized at 1100 °C is a promising material as the VFB electrode and the VFB with ECNFW electrodes obtains a super low internal resistance of 250 mΩ cm^2.

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1. Introduction

Renewable energies have attracted unprecedented global attention in the recent decades. However, renewable energies from sources such as solar and wind bear the nature of randomness and intermittence that can affect the final quality, especially the stability of the power output [1–3]. Therefore, large-scale energy storage techniques are inevitably needed for load leveling and peak shaving. Among those techniques, the vanadium flow battery (VFB), first proposed by Skyllas-Kazacos, has the unique benefits for its long cycle life, high reliability, outstanding energy conversion efficiency, instant response, flexible design, economical operation and maintenance costs [4–7]. A VFB employs VO^{2+}/VO_2^+ and V^{2+}/V^{3+} redox couples in the positive and negative half-cell, respectively, whose open circuit voltage is approximately 1.26 V [8]. And the supreme advantage of VFB is that the common cross contamination between the negative and positive electrolytes can be eliminated by applying the same element [9,10]. Due to these features, the VFB, as a burgeoning battery, is anticipated to boost its share in the market of energy storage. Nevertheless, there are still some hindrances hampering the wider commercialization application of a VFB, such as the electrolyte stability [11,12], membrane selectivity [13,14], and electrode activity [15–19].

Electrode, as one of the key composition parts in a VFB, has an important impact on the power density and energy efficiency (EE) of a VFB. It provides the sites for redox reactions [20]. Therefore, its physicochemical properties are significant to the VFB performance. An ideal electrode material of a VFB should possess the following features: large surface area, high electrochemical activity, excellent conductivity, reliable stability in the electrolyte and favorable structure for mass transfer [21]. As yet, carbon materials, especially Polyacrylonitrile (PAN) based carbon materials, have been widely used as electrodes for VFB [22]. Among them, carbon felt (CF) and graphite felt (GF) are the common electrode materials for their high conductivity, good stability and low cost [23]. However, their kinetics reversibility and electrochemical activity on vanadium redox reactions are thought not very satisfactory [15,23]. Accordingly, some modification methods, like thermal treatment, acid oxidation and electrodeposition of metals, have been extensively investigated to improve their electrochemical activity [24–27]. The introduction of nitrogen and oxygen functional groups onto the surface of carbon-based materials could remarkably improve their electrochemical activity [28]. For oxygenic groups, the C–OH and COOH

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http://dx.doi.org/10.1016/j.jechem.2017.03.005
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groups are speculated to play important roles on catalyzing the VO^{2+}/VO_2^+redox reaction. While among various nitrogen species, the quaternary nitrogen is much more stable and acts as the active site for the VO^{2+}/VO_2^+ reaction [29]. However, Friedl et al. found that there was a decrease in activity of the VO^{2+}/VO_2^+ reaction with the increasing amount of the surface functional groups on the multiwall carbon nanotubes (MWCNTs), further concluded that polar molecules would play not any role in the VO^{2+}/VO_2^+ reaction, and meanwhile, such polar molecules actually would decelerate the reaction by decreasing the mobility of the vanadium ions [20]. Furthermore, the previous research mostly focused on the VO^{2+}/VO_2^+ reaction, ignoring the V^{2+}/V^{3+} reaction. Therefore, a comprehensive investigation on the electrocatalytic effect of the surface functional groups of carbon materials toward VO^{2+}/VO_2^+ and V^{2+}/V^{3+} redox reactions is necessary.

In addition, a variety of carbon nanomaterials have been developed and investigated for VFB due to their great specific surface areas, high electrochemical activity and good conductivity. Both graphene oxide and multi-walled carbon nanotubes exhibit the high electrocatalytic activity towards vanadium redox couples [30,31]. However, those nanomaterials are complicated and costly to synthesize, whose existing form of powder is not suitable for VFB. Recently, electrospun carbon nanofibers (ECNFW) in the form of electro-conducting non-woven webs, have been introduced into the VFB [32,33]. Yan et al. did plenty of work on ECNFW for VFB and they investigated the effect of carbonization temperature, carbonization time and the conversion of carbon structure on the electrochemical activity of ECNFW toward VO^{2+}/VO_2^+ reaction [33,34]. Subsequently, they introduced ECNFW as the elctrocatalytic layer of carbon felt electrodes of VFB and obtained the improved battery performance [36,37]. Fetyan et al. used 5 layers of ECNFW as negative electrode and carbon felt as the positive electrode to assemble a VFB single cell, and obtained an energy efficiency of 59% at the current density of 15 mA/cm^2 [38]. However, their usages of ECNFW are all combined with carbon felt. While the currents used commercial carbon felts are too thick, which lead to a large ohmic polarization of the VFB, so that it is difficult to improve the VFB's power density. Since the ohmic resistance of the VFB can be dramatically decreased via decreasing the electrode thickness, ECNFW with the ultrathin thickness is used as both positive and negative electrodes of the VFB independently in this paper to minimize the distance between negative and positiveelectrodes to reduce the ohmic polarization of the VFB.

In the present study, PAN nanofibers were synthesized by the electrospinning method firstly. After peroxidation, PAN nanofibers were carbonized from 800 °C to 1400 °C to prepare ECNFW. The microstructures were studied through the test of scanning electron microscope (SEM), and the surface chemistry was studied by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). And then the electrochemical performance of various ECNFW was investigated by the test of electrochemical impedance spectroscopy (EIS) and the cyclic voltammetry (CV). The influence of the carbonization temperature on the electrocatalytic activity of ECNFW toward VO^{2+}/VO_2^+ and V^{2+}/V^{3+}redox reactions was comprehensively studied. The VFB single cell performance was also tested when ECNFW was used as the electrodes independently. These results are constructive to improve the power density of the VFB.

2. Experimental

2.1. Electrode preparation

2.1.1. Preparation of carbon nanofiber (ECNFW) by electrospinning

The ECNFW was manufactured through electrospinning method and following preoxidation and carbonization. Electrospinning precursor solution was prepared by dissolving 10 wt% PAN in N, N-dimethylformamide (DMF) followed by stirring at 70 °C for 8 h. Afterwards, a positive direct current voltage which is about 15 kV was applied by a voltage regulated DC power that can produce the polymer jet. The precursor-feeding rate was 1 mL/h with a copper needle of 0.8 mm diameter as the spinneret. PAN nanofibers were collected by a roller collector at a speed of 150 r/min. The distance between the copper needle and the metal collector was fixed at 10 cm. After PAN nanofibers were preoxidized at 250 °C for 1 h under air atmosphere, the stabilized nanofibers were carbonized by heating to 800 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C, 1300 °C and 1400 °C, respectively, at a heating rate of 5 °C/min and holding for 1 h in Ar atmosphere.

2.2. Material characterization

The surface morphology of ECNFW carbonized at various temperatures was observed with a scanning electron microscopy (SEM, JEOL/EO, JCM-6000 Instrument, Japan) at an accelerating voltage of 15 kV. The hydrophilicity was evaluated by the contact angle measurement on the instrument of JC2000A (Shanghai Zhongchen Digital Technic Apparatus Co. Ltd, China). The crystal structures of various ECNFW were characterized by a DX-2700 diffractometer (Dandong Haoyuan Instrument Co., China) using Cu-K_α radiation ($\lambda = 0.1541$ nm). The electrical conductivity was tested by the four-probe method. The elements and the functional groups on the surface of various ECNFW were detected by XPS (ESCALAB250 system) which utilizes Al $K\alpha$ monochromatic (1486.6 eV). The result was calibrated by the C 1s (284.7 eV) peak.

2.3. Electrochemical tests

The electrochemical performances of as-prepared ECNFW electrodes were evaluated by the cyclic voltammetry (CV) and the electrochemical impedance spectroscopy (EIS) measurements. For the electrochemical tests, a three-electrode system was used with ECNFW as the working electrode, the reference electrode employs a saturated calomel electrode (SCE) and the counter electrode is the graphite plate. The working electrode was prepared by sandwiching a piece of ECNFW between two plastic flakes; one of them has an open circular hole of 0.385 cm^2 which is used as the working area. A piece of Cu foil contacted to the ECNFW served as the current collector. The investigations for VO^{2+}/VO_2^+ and V^{2+}/V^{3+} redox reactions were carried out in the same electrolyte solution as published [18]. CV results were recorded on the CHI604E workstation (CH Instruments, USA). EIS investigations were also carried on the CHI604E by exerting an AC voltage of 5 mV on a constant DC voltage over the frequency range from10^{-1} to 10^5 Hz.

2.4. Single cell performance

The ECNFW with an area of 9 cm^2 (3.0 × 3.0 cm), a thickness of ca. 50 μm and a porosity of ca. 80%, was used as positive and negative electrodes, respectively. A Nafion 115 membrane (DuPont, USA) was used as the ion exchange membrane. A graphite plate which had serpentine channels on it served as the current collector. The cell was sealed with rubber washers. And the flow rate is about 15 mL/min. Charge–discharge test was measured on Arbin-BT 2000 instrument battery test system (Arbin Co., USA) under a constant current density of 40 mA/cm^2. The charge/discharge cut-off voltage was set as 1.65 V and 1.0 V, respectively. The negative electrolyte was 30 mL (1.5 M V^{3+} in 3.0 M H_2SO_4 solution) and the positive electrolyte is 30 mL (1.5 M VO^{2+} in 3.0 M H_2SO_4 solution), respectively.

The VFB single cell's EIS test was carried out by KFM2030 impedance meter (Kikusui electronics Co., Japan) in a frequency

Please cite this article as: C. Xu et al., Ultrathin free-standing electrospun carbon nanofibers web as the electrode of the vanadium flow batteries, Journal of Energy Chemistry (2017), http://dx.doi.org/10.1016/j.jechem.2017.03.005

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