



CeO₂ embedded electrospun carbon nanofibers as the advanced electrode with high effective surface area for vanadium flow battery



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ARTICLE INFO

Article history:

Received 11 May 2016

Received in revised form 18 August 2016

Accepted 20 August 2016

Available online 21 August 2016

Keywords:

Vanadium flow battery

Cerium oxide nanoparticles

Wettability

Electrochemical surface area

Electrochemical performance

ABSTRACT

Although electrospun carbon nanofibers (ECNFs) possess excellent conductivity, high surface area and good electrochemical activity toward vanadium redox couples, much surface area of ECNFs was still unutilized because of its poor hydrophilicity. CeO₂ nanoparticles as an excellent hydrophilic agent are embedded in polyacrylonitrile (PAN) based carbon nanofibers by a simple electrospinning and subsequent carbonization process. The physicochemical characterizations show that the introduction of CeO₂ nanoparticles slightly changes the structure and compositions of ECNFs, while the corresponding wettability is greatly improved. It is worth noting that the electrochemical surface area (ECSA) of CeO₂/ECNFs is more than four times of that for ECNFs. According to the cyclic voltammograms (CV) and electrochemical impedance spectra (EIS) results, the addition of CeO₂ improves the electrocatalytic activity toward the negative reaction of vanadium flow battery (VFB) to some extent while has less effect on that toward the positive reaction, the significant improvement in the electrochemical performance of CeO₂/ECNFs might be mostly ascribed to the remarkable enhancement in ECSA. In addition, the charge/discharge tests further verify that CeO₂/ECNFs with high ECSA could significantly reduces the electrochemical polarization during the discharging process and results in an enhanced discharge capacity and energy efficiency. The accomplishment of this work provides a new concept that it might be more convenient and effective to improve the electrochemical performance of the electrode materials for VFB by increasing their ECSA.

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1. Introduction

With the continuous development of the renewable energy, increasing attentions have been provided to the large scale energy storage system and conversion technologies in recent years [1,2]. Among the promising advanced energy storage technologies, vanadium flow battery (VFB) plays an important role in the development of sustainable energy storage last decades due to its outstanding properties such as the long cycle life, high reliability, flexible design and no cross-contamination [3,4]. As the platform on which the electrochemical reactions take place, the electrodes affect the electrochemical performance of VFB to a great extent [5]. Because of the low cost, good conductivity, wide potential window range and high stability in the harsh environment,

carbon felt (CF) and graphite felt (GF) are mostly used as the electrode materials in the engineering application of VFB. However, the lower electrochemical activity of CF and GF toward the vanadium redox couples restricts the battery performance of VFB and its energy storage cost. Therefore, plenty of researchers have been devoted to improve their electrochemical activity such as the activation treatment and electrocatalysts modification [6–11]. Indeed, the above-mentioned modifications improve the electrocatalytic activity of these carbon materials toward vanadium redox couples in some extent, however, none of them demonstrate their superiorities in commercial applications because of the tedious treatment procedures, the unstable functional groups decorated at the surface of them, in addition to the limited improvement of electrochemical performance for VFB [12,13].

In general, there are mainly two approaches to improve the electrochemical performance of the electrode materials for VFB, the first one is the improvement in their electrocatalytic activity,

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which has been studied repeatedly just as the above-mentioned literatures. The other one is the enhancement of the corresponding effective surface area, by which the discharge current density will be significantly decreased with the same discharge current and the electrochemical performance of VFB will be greatly improved. Herein, the effective surface area, which is also named electrochemical surface area (ECSA), means the surface area of the electrode which is infiltrated by the electrolyte, and the surface area which is not infiltrated is no use for the electrochemical reaction. Generally, the decoration of the nano-scale particles [14,15], decrease of the wire diameter [16], as well as improvement of the wettability [17,18] will result in the increase of the ECSA for the electrodes. Compared with the first approach, the latter could be carried out during the preparation process of the precursors, the pre-oxidation and carbonization process of CF or GF, and it is more suitable for the mass production of the surface-enhanced electrodes. Indeed, the improved performance of electrode immobilized carbon nanotubes, nanofibers, and metal oxide nanoparticles might be ascribed to the coupling effect of the enhancement of electrocatalytic activity and the increase of ECSA. However, the role of the former was emphasized and that of the latter was weakened in the reports [10,11,14], even though the surface area of some electrodes increased to hundreds of times. For instance, the BET area of the modified GF electrode increases drastically from $0.33 \text{ m}^2 \text{ g}^{-1}$ to $32.4 \text{ m}^2 \text{ g}^{-1}$ after the in-situ growth of carbon nanofibers by Liu et al. [19], while the effect of the enhanced surface area (almost 100 times) was seldom discussed and the newly generated C=C bonds on the carbon nanofibers were considered as the main reason for the improved electrochemical performance. Until recently, Flox et al. [20] firstly proposed to use the flexible nanofiber (NF)-based electrodes with a doubled electroactive surface area as the electrodes for VFB, and this is the first report in which the role of the surface area of the electrode in its electrochemical activity for VFB is emphasized. In addition, a latest article has showed that many oxidation treatments are observed to have a significant effect on the CV response for the carbon-based materials, while these changes are shown to be due almost entirely to the effective wetting of the porous carbon paper rather than any electroactivation effect of surface functional groups on the intrinsic kinetics of the $\text{V}^{3+}/\text{V}^{2+}$ reaction [21], and the importance of wetting in carbon paper electrodes for vanadium redox reactions was highlighted. Up to now, little attention has been given to the ECSA of the electrodes for VFB, despite the enhancement of the effective surface area might be more feasible and effective.

In the previous work, the as-prepared electrospun carbon nanofibers (ECNFs) with the wire diameter of 200 nm presented excellent conductivity, high surface area and good electrochemical activity toward vanadium redox couples [12,16,22,23]. Even so, much surface area of ECNFs was still unutilized because of the poor hydrophilicity. The modification of the oxygen and nitrogen containing functional groups is helpful to improve the hydrophilicity, while the increasing resistance obsessed with the modification is unwanted. CeO_2 nanoparticles with large surface area, excellent wettability, high chemical stability, high catalytic efficiency, strong adsorption ability and high oxygen ionic conductivity [24–26] make it to be a potential catalyst material to construct an effective electrode in a VRB. With the consideration of improving the wettability and conductivity, CeO_2 nanoparticles was introduced in the carbon nanofibers by electrospinning technique and subsequent carbonization process. With this method, CeO_2 was embedded in the ECNFs uniformly and the corresponding wettability was greatly improved, the improved electrochemical performance of VFB with $\text{CeO}_2/\text{ECNFs}$ electrode might be attributed to the increasing ECSA.

2. Experimental

2.1. Preparation of composite electrodes

Firstly, polyacrylonitrile (PAN) of 12 wt.% was dissolved in N, N-dimethylformamide (DMF) and kept stirring at 80°C for 6 h. Then $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ as the Cerium source with mass ratio of 1:10 ($\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$: PAN) was added into the PAN/DMF solution, and the blended solutions were kept stirring at room temperature for another 10 h. After the above-mentioned preparatory work, the electrospinning was carried out at a positive direct voltage of 20 kV. A 10 mL syringe with a metal needle of 0.84 mm diameter was used for holding the precursor solution. The electrospun nanofibers were collected on a roller with aluminum foil at a rotating speed of 250 r min^{-1} and the collection distance was about 17 cm. The delivery rate was controlled at 1.5 mL h^{-1} . Afterwards the electrospun nanofibers were pre-oxidized at 280°C for 30 min in air, and then the stabilized nanofibers were carbonized by heating them to 1000°C with the heating rate of 5°C min^{-1} and holding them for 90 min in nitrogen flow. For comparison, the pristine ECNFs were also prepared.

2.2. Physicochemical characterization

The morphology and diameter distribution of ECNFs and $\text{CeO}_2/\text{ECNFs}$ were examined by scanning electron microscopy (SEM, FEI INSPECT-F) and transmission electron microscopy (TEM, JEOL JEM-2100F) respectively. Energy Dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250) using Mg-K α radiation (1253 eV, 250 W) under a pressure of ca. 10^{-7} Pa were constructed to analyze the surface elements of the as-prepared samples. All binding energy values were calibrated to the C1s graphitic peak at 284.7 eV. The crystallographic structure of the samples were determined by X-ray diffraction (XRD, X'Pert PRO) under a voltage of 40 kV and a current of 40 mA with Cu K α ($\lambda = 0.154 \text{ nm}$) radiation between 10° and 80° with a scan rate of 4° min^{-1} . In addition, the hydrophilicity and electrical conductivity of ECNFs and $\text{CeO}_2/\text{ECNFs}$ were measured by contact angle test (JYPHb, CHENGDE JINHE INSTRUMENT MANUFACTURING Co., Ltd.) and the four-probe method (RTS-8, 4 PROBES TECH) respectively.

For electrochemical measurement, a three-electrode cell was used as reported in the previous work [16]. ECNFs and $\text{CeO}_2/\text{ECNFs}$ with the thickness of about $20 \mu\text{m}$ (0.385 cm^2) were used as the work electrodes, a saturated calomel electrode along with a salt bridge full of saturated potassium chloride solution in addition to a 1 cm^2 platinum sheet acted as the reference electrode and counter electrode respectively. ECSA of the as-prepared samples was measured by a small amplitude potential step with the potential of 5 mV. The powders of GF, ECNFs and $\text{CeO}_2/\text{ECNFs}$ were added into the nafion solution with the ultrasonic agitation for 0.5 h, then the uniformly dispersed lactescence was dropped on to the glass carbon electrode (GCE). GCE is 0.385 cm^2 and the mass of the additive amount for all the samples were 0.4 mg which could be controlled by adjusting the additive volume of the lactescence. Furthermore, the electrochemical performances of pristine ECNFs and $\text{CeO}_2/\text{ECNFs}$ were tested by cyclic voltammograms (CV) and electrochemical impedance spectra (EIS). CV curves were recorded at 2 mV s^{-1} scan rate in 0.1 M VOSO_4 and 2.0 M H_2SO_4 solution and EIS was measured by applying an alternating voltage of 5 mV over the frequency ranging from 10^5 to 10^{-2} Hz.

With the consideration of the previous cell structure [16], a VFB single cell was assembled by sandwiching the Nafion212 (DuPont) ion exchange membrane ($5 \text{ cm} \times 10 \text{ cm}$) between two pieces of GF (Liao Yang JinGu Carbon Fibre Sci-Tech Co., Ltd.) ($4 \text{ cm} \times 7 \text{ cm}$). In special, the pristine ECNFs and $\text{CeO}_2/\text{ECNFs}$ were sandwiched between GF and ion exchange membrane in both half cells. The

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