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Carbon felt supported carbon nanotubes catalysts composite electrode for vanadium redox flow battery application

Guanjie Wei [1], Chuankun Jia [1], Jianguo Liu, Chuanwei Yan*

State Key Laboratory for Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

HIGHLIGHTS

- A carbon felt (CF) supported carbon nanotubes (CNTs) catalysts composite electrode has been developed.
- The composite electrode improve the reversibility of the VO_2^+/VO^{2+} and V^{3+}/V^{2+} redox couples greatly.
- The CNTs can be stabilized on the CF evenly and strongly by Nafion which is stable in vanadium solution.
- The VRFB single cell with the modified CF with MWCNTs content of 0.94 wt.% exhibits excellent performance.

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ABSTRACT

A modified electrode for vanadium redox flow battery (VRFB) has been developed in this paper. The electrode is based on a traditional carbon felt (CF) grafted with the short-carboxylic multi-walled carbon nanotubes (MWCNTs). The microstructure and electrochemical property of the modified electrode as well as the performance of the VRFB single cell with it have been characterized. The results show that the MWCNTs are evenly dispersed and adhere to the surface of carbon fibres in the CF. The electrochemical activities of the modified CF electrode have been improved dramatically and the reversibility of the VO_2^+/VO^{2+} and V^{3+}/V^{2+} redox couples increased greatly. The VRFB single cell with the modified CF exhibits higher coulombic efficiency (93.9%) and energy efficiency (82.0%) than that with the pristine CF. The SEM analysis shows that the MWCNTs still cohere with carbon fibres after charge and discharge test, indicating the stability of the MWCNTs in flowing electrolyte. Therefore, the composite electrode presents considerable potential for the commercial application of CF in VRFB.

1. Introduction

In recent years vanadium redox flow battery has received great attention as one of important energy storage technologies due to its various advantages, such as long cycle life, high efficiency, flexible design, high reliability, low maintenance costs and environmental friendship [1–4]. As in other batteries, electrodes also play an important role in VRFB. The typical electrode materials for VRFB are metal and carbon materials. Metal materials such as noble metals and their oxides are not practical in VRFB because of their high cost and low specific area. Whereas, carbon materials, for example carbon felt, carbon paper and graphite powder, are widely used in VRFB, since they maintain remarkable advantages such as high specific surface area, wide operation potential range, stability and reasonable cost [5,6]. However, the poor kinetics and reversibility of the carbon materials restrict their applications in VRFB. Although plenty of efforts have been devoted to modify the materials to enhance their electrochemical properties [7–11], the modified electrodes are not used in VRFB practically or not show excellent performance in the battery.

It is reported that the activity of the VO_2^+/VO^{2+} and V^{3+}/V^{2+} redox couples on carbon electrodes are strongly influenced by the concentration and nature of the oxygen functional groups on the electrode surface [12–14]. Lu et al. reported that carbon fibres with high hydroxylation can provide more active sites for the vanadium redox reaction and make it more active [15]. Modifying CF with acidic oxygen functional groups such as hydroxyl, carbonyl and carboxyl groups seems to be a promising method to enhance their electrochemical activities. Due to the prominent physical and chemical properties, Carbon nanotubes (CNTs) are widely used in fuel cells as catalyst support [16–19]. It is also reported that the CNTs are used in VRFB as electrode catalysts ascribed to their high

* Corresponding author. Tel.: +86 24 2399 8320; fax: +86 24 2388 0201.
E-mail address: jck2003bx@yahoo.com.cn (C. Yan).
[1] These authors are contributed equally to this work.

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surface area and super electrical conductivity [20,21]. Especially, Li [22] explored the different catalytic properties of three kinds of MWCNTs (Pristine MWCNTs, hydroxyl MWCNTs and carboxyl MWCNTs) toward VO_2^+/VO^{2+} redox couples on a glassy carbon electrode by cyclic voltammetry and drew the conclusion that the catalytic property of the carboxyl MWCNTs is the best. However, because the carboxyl MWCNTs were loaded on the CF with no adhesion, and the loading of the carboxyl MWCNTs may not be stable enough to meet the challenge of washing out by flowing electrolyte in VRFB, the article only presented the performance of the modified CF as positive electrode in a static battery. The behavior of the modified CF in a flow battery had not been investigated.

In this regard, a new method is proposed to modify the CF electrode aiming at strengthening the stability of the carboxyl MWCNTs on the carbon fibres accompanied by obtaining excellent catalytic properties: the perfluorosulfonic acid polymer (Nafion) served as the agglomerant and attached the carboxyl MWCNTs onto the CF to form an integer composite electrode. In this way, the stability of the MWCNTs on the carbon fibres in flowing electrolyte is guaranteed by Nafion. The composite electrode was tested in VRFB practically and exhibited excellent electrochemical activity and durability. The method presented in this paper shows prospect to modify the CF electrode in VRFB for commercial application.

2. Experimental

2.1. Materials

The PAN-based CF (thickness: 4 mm) was produced by Shenhe Carbon Fibre Materials Co. Ltd. The MWCNTs (length: 0.5–2 μm, diameter: <8 nm, purity: >95%) were obtained from Nanjing XFNANO Materials Tech Co. Ltd and used as received. The 5 wt.% Nafion solution was got from DuPont and was diluted to 0.02 wt.% Nafion solution with ethanol.

2.2. Preparation of the composite electrode

The composite electrode was prepared as follows. Firstly, the pristine CF was washed in distilled water by ultrasonication for 30 min, and then dried at 100 °C for 2 h. Secondly, the carboxyl MWCNTs was added to 0.02 wt.% Nafion solution under agitation. Thirdly, the purified CF was immersed in the 0.02 wt.% Nafion solution after the carboxyl MWCNTs were well dispersed and suspended in the solution. Then the suspension with CF was treated by ultrasonication for 10 min. Finally, the modified CF was taken out of the suspension and was dried at 100 °C for 6 h. After the ethanol solvent vaporized, the carboxyl MWCNTs would be adhered onto the carbon fibres by Nafion.

The MWCNTs were mixed with the 0.02 wt.% Nafion solution as the ratios of 1 mg mL^{-1}, 2 mg mL^{-1} and 2.5 mg mL^{-1} to prepare the suspensions. In order to investigate the effect of the CFs size on its adsorption capacity, the CFs with different size were immersed in the suspension with the ratio of the MWCNTs to Nafion solution of 2.5 mg mL^{-1}. The related experiment parameters are listed in Table 1. In order to study the relationship between the loading of the MWCNTs on the CF and the quantity of them in the suspension, the CF with same size was immersed in the suspensions with three kinds of concentration mentioned above. The related experiment parameters are listed in Table 2. The content of the MWCNTs stabilized on the CF was calculated as the formula (because the quantity of Nafion cohering with the carbon fibres is quite small, the increase of CFs weight introduced by Nafion can be ignored):

Table 1
The parameters and research result for adsorption capacity of the CF with different size.

Parameters	1	2	3	4	5
Size of the CF/cm × cm	1.5 × 1.5	2.5 × 3.0	5.0 × 6.0	6.0 × 7.5	8.5 × 8.5
Volume of the CF/cm^3	0.9	3	12	18	28.9
Mass of the MWCNTs/mg	7.6	25	100	150	250
Volume of the Nafion solution/mL	3.0	10	40	60	100
Content of the MWCNTs/%	4.53	4.47	2.87	2.21	2.20

$$\text{Content} = \frac{W_{\text{after}} - W_{\text{before}}}{W_{\text{before}}} \times 100\%$$

where W_{before} is the weight of CF before modification; W_{after} is the weight of CF after modification.

2.3. Characterization of the composite electrode

The surface morphology and component of carbon fibres in the CF were analyzed by FEI INSPECT F scanning electron microscopy (SEM). The surface analysis was carried out by X-ray photoelectron spectroscopy (XPS).

2.4. Electrochemical tests

For cyclic voltammetry (CV) measurement, a three-electrode cell was used with the CF as the working electrode, a saturated calomel electrode as the reference electrode, and a Pt electrode as the counter electrode. The CF electrode was produced by sandwiching a piece of CF between two rubber sheets: the working area of one sheet was 1.286 cm^2, and on another sheet, a Pt thread was connected with the CF in order to collect the current. The analysis was performed in 0.1 M $VOSO_4$+2.0 M H_2SO_4 solution.

The charge and discharge test was carried out by using a VRFB single cell at a constant current density of 50 mA cm^{-2}. As for the cell, the conductive plastic plates were used as current collectors and a nafion 212 membrane (DuPont) served as a separator. The initial electrolytes for both positive electrode and negative electrode were 1.5 M $VOSO_4$+2 M H_2SO_4, and the volume of negative electrolyte was 80 mL while that of the positive one was 160 mL in order to avoid over-charging the positive electrolyte. The active area of each electrode was 28 cm^2. The upper and lower limit of the charge and discharge voltage was controlled to be 1.65 and 0.75 V, respectively. In order to reduce the experimental error, at least three different single cells with CFs (including pristine CF and modified CF) have been tested in the experiment and the related values were abstracted from these parallel tests' result.

3. Results and discussion

3.1. Adsorption rule of the MWCNTs

The modification of the CF is controlled by loading of the MWCNTs on it, and the loading of the MWCNTs is affected by the

Table 2
The parameters and research result for loading of the MWCNTs on the CF immersed in the suspensions with different ratio of the MWCNTs to Nafion solution.

Size of the CF/cm × cm	Content of the MWCNTs/%		
	Ratio of the MWCNTs to Nafion solution/mg mL^{-1}		
	1	2	2.5
2.5 × 3.0	1.50	3.27	4.47
8.5 × 8.5	0.94	1.68	2.20