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Communication and Perspective

Sucrose pyrolysis assembling carbon nanotubes on graphite felt using for vanadium redox flow battery positive electrode

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ABSTRACT

In the present paper, multi-walled carbon nanotubes (MWCNTs) are successfully assembled on graphite felt (GF) using sucrose pyrolysis method for the first time. The in situ formed pyrolytic carbon is chosen as the binder because it is essentially carbon materials as well as CNTs and GF which has a natural tendency to achieve high bonding strength and low contact resistance. The MWCNTs/GF electrode is demonstrated to increase surface area, reduce polarization, lower charge transfer resistance and improve energy conversion efficiency comparing with GF. This excellent electrochemical performance is mainly ascribed to the high electro-catalytic activity of MWCNTs and increasing surface area.

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1 VRFBs have attracted much attention due to their remarkable
2 properties such as fast response time, flexible design, long cycle
3 life and environmental friendship [1,2]. As one of the key parts of
4 VRFB, the electrode provides the place for redox reaction and fa-
5 cilitates the reaction. The electrochemical property of an electrode
6 material directly affects energy utilization efficiency for a VRFB [3].
7 Up to now, the PAN-based graphite felt (GF) and carbon felt (CF)
8 are the most common electrode material for a VRFB. Even though
9 they have large porosity, high electrical conductivity, and low cost,
10 the GF and CF still have serious drawbacks, such as low electro-
11 catalytic activity (poor kinetics and reversibility) [4]. In particu-
12 lar, the positive redox reaction ($\text{VO}^{2+} + \text{H}_2\text{O} - e^- = \text{VO}_2^+ + 2\text{H}^+$) is
13 less reversible and slower than the negative one ($\text{V}^{3+} + e^- = \text{V}^{2+}$),
14 because the former involves at least three elementary steps [5].
15 Therefore, it is significant to enhance the electro-catalytic activity
16 of GF toward positive $\text{VO}^{2+}/\text{VO}_2^+$ redox reaction [6].

17 The carbon nanotubes (CNTs) with unique bamboo-shaped
18 structure possess large surface areas, high density of defects and
19 active sites, which represent a great electro-catalytic activity ma-
20 terial [7]. Recently some researchers have attempted to introduce
21 CNTs on the surface of GF/CF for VRFBs [8]. Wang et al. [9] synthe-
22 sized carbon nanotubes on GF by using toluene as carbon source
23 via a chemical vapor deposition method. The results showed that
24 the CNT/CF electrode gave improving electrochemical activity. Li
25 et al. [10] employed dimethyl formamide to combine CNTs with

the glassy carbon electrode. And the accelerated charge transfer
processes were obtained [10]. Wei et al. [11] adopted the Nafion
solution to bond the carboxylic carbon nanotubes on the CF. The
obtained composite electrode improves the electrochemical re-
versibility of the $\text{VO}^{2+}/\text{VO}_2^+$ redox couples. However, the process
to directly grow CNTs on the CF/GF via a chemical vapor deposition
method is complicated and difficult to implement. Furthermore,
the catalyst such as ferrocene may not be removed completely in
the acid washing process, which will lead to harmful metal ions
pollution in VRFB. The organic solvent volatilization method usu-
ally realizes bonding at low temperatures ($\leq 150^\circ\text{C}$), which may
cause a weak adhesion strength and high contact resistance. And
most of the conductive organic binders are high cost, such as
Nafion. Moreover, it may also lead to organic residues pollution for
VRFBs if the organic solvents were not entirely volatilization.

The sucrose pyrolysis carbon-coated method was widely used in
lithium-ion battery cathode materials due to its good distribution
uniformity, the simplicity of operation, low cost and high electrical
conductivity [12]. Furthermore, the pyrolytic carbon, CNTs, and GF
are essentially carbon materials. And the in situ formed pyrolytic
carbon has a natural tendency to possess high bonding strength
and low contact resistance. To the best of our knowledge, immobi-
lizing CNTs on the GF/CF using pyrolytic carbon from sucrose has
not been reported for the positive electrode applications of the
VRFBs. In the present paper, MWCNTs were simply and efficiently
assembled on the surface of GF by the sucrose pyrolysis method for
the first time. The MWCNTs/GF composite electrode was demon-
strated to be an advanced electrode material in the VRFB.

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The MWCNTs (length: 3 ~ 12 μm, diameter: 8 ~ 15 nm) were got from Suzhou Carbon Abundance Science and Technology Co. Ltd. (Suzhou, China). And the PAN-based GF (3 mm) was purchased from Shenhe Carbon Fiber Materials Co., Ltd. (Tieling, China). All chemicals were analytical reagent grade.

The GF sample was obtained from as-received GF that was first cleaned in 5% H₂O₂ solution at 40 °C for 30 min to remove organic compounds, followed by washing with pure water and drying in an oven at 90 °C for 6 h.

The MWCNTs/GF sample was prepared using the following process steps. Firstly, the GF was treated in H₂O₂ solution using the above-mentioned approach. Secondly, the impregnating solution was prepared. And it was composed of 10 g/L MWCNTs, 20 g/L sucrose, and 2 g/L sodium dodecyl benzene sulfonate. The impregnating solution should be treated with ultrasonic dispersion and magnetic stirrer before dipping experiment. Thirdly, the GF was immersed into the impregnating solution for 20 min, and then dried in an oven at 90 °C for 6 h. Finally, the MWCNTs/GF was assembled in a controlled atmosphere furnace at 900 °C for 20 min with 1 L/min nitrogen and then cooled down to room temperature under the protection of nitrogen. The loading amount of MWCNTs on the GF was 2.50% (weight ratio) that was tested via weight increase method [11].

The surface morphologies of GF and MWCNTs/GF were investigated by a field-emission scanning electron microscope (FESEM, JSM-7001F). Nitrogen adsorption isotherms of GF and MWCNTs/GF were measured using a Quantachome NOVA 2000e at 77 K. Total specific surface areas were tested using multi-point Brunauer–Emmett–Teller (BET) methods. The surface chemistry information of GF and MWCNTs/GF was obtained via an X-ray photoelectron spectroscopy surface analysis system (Escalab 250Xi, Thermo Fisher Scientific).

The cyclic voltammograms (CV) and electrochemical impedance spectra (EIS) were tested on an IM6ex (Zahner-Elektrik GmbH & Co. KG, Germany) electrochemical workstation, respectively. A standard three-electrode system was employed. The working electrodes were GF and MWCNTs/GF. The working electrode was clamped by an electrode holder with an exposed geometric area of 1 cm². A mercurous sulfate electrode containing saturated potassium sulphate (INESA, Shanghai, China) was used as the reference electrode. The potentials reported in this paper were referred to the standard hydrogen electrode (SHE). A platinum plate (15 mm × 15 mm) was used as the auxiliary electrode. The electrolyte was agitated with bubbling nitrogen during CV tests. The CV and EIS measurements were conducted in 0.1 M VOSO₄ + 2.0 M H₂SO₄ solutions at 25 °C. The scanning range of CV was limited from 0 V to 1.6 V, and the scanning rate was 2 mV s⁻¹. The EIS tests were performed with an alternating voltage of 5 mV over the frequency range from 10⁵ to 10⁻² Hz. The potential was 1.05 V (SHE) during the EIS tests. The impedance spectra was simulated with the ZSimpwin software.

The VRFB cell was prepared via sandwiching the proton exchange membrane (Nafion 115) between two pieces of the electrode placed in polytetrafluoroethylene frames. The compression ratio of electrode is about 70%. The main objective of this research is to improve the electrochemical activity of positive electrode. So both of the negative electrodes in the single cell test are graphite felt. The proton exchange membrane was treated according to standard acid boiling procedure before use [13,14]. The bipolar plate was carbon paper and the current collector was gold-coated copper sheet. The effective areas of the membrane and the electrode both were 9 cm² (3.0 cm × 3.0 cm). The cycling performance of the VRFB cell was assessed using a battery tester (Wuhan LAND electronics Co., Ltd., Wuhan, China). The flow rate was fixed at 20 mL/min, which was controlled by a peristaltic pump (Baoding Chuang Rui Precision Pump Co., Ltd., Baoding, China). The anolyte

and catholyte both were 20 mL and contained 1.5 M vanadium ions [V(III):V(IV) = 1:1] and 5.0 M sulfate ions. The cell was charged to 1.7 V and discharged to 0.8 V with a current density of 80 mA/cm² at 25 °C.

As shown in Fig. 1(a), the surface of the GF is relatively smooth and ridged. While for the MWCNTs/GF electrode, as shown in the Fig. 1(b), the MWCNTs were evenly and densely immobilized to GF surface. Besides, the MWCNTs networks have been successfully formed and possess a very porous structure (Fig. 1(c)). The Fig. 1(c) was obtained by enlarging the blue area in the Fig. 1(b). The in situ formed pyrolytic carbon presented excellent bond quality, as it is essentially carbon materials as well as CNTs and GF. And the good adhesion of MWCNTs/GF is helpful to improve its conductivity. The MWCNTs/GF has plenty of defect sites, which should enhance electrode performance (electrochemical reversibility/catalytic activity).

The BET surface area of GF and MWCNTs/GF is 6.3 m² g⁻¹ and 35.9 m² g⁻¹, respectively. The increasing surface area should be ascribed to the introduction of MWCNTs. A higher surface area of the MWCNTs/GF electrode will result in a lower actual current density, which is beneficial to reduce electrochemical polarization [15]. The surface chemistry information of GF and MWCNTs/GF was studied using XPS wide scan spectra, and the results were shown in Fig. 1(d). The oxygen content of MWCNTs/GF is 8.1%, that is obviously higher than the value (4.9 %) of GF. The oxygen-containing functional group is usually considered as active site for VO²⁺/VO₂⁺ redox reactions [14]. The higher oxygen content of the MWCNTs/GF is beneficial to improve its electrochemical activity.

Fig. 2(a) presents the CV curves of the GF and MWCNTs/GF electrode materials. The corresponding electrochemical parameters are listed in the inset of Fig. 2(a). It can be found that the oxidation peak potential of MWCNTs/GF appears at 1.166 V, which is lower than that of the GF (1.294 V). And the reduction peak of MWCNTs/GF is positioned at 0.900 V, which is higher than that of GF (0.724 V). The reduced oxidation potential and increasing reduction potential of MWCNTs/GF represents electrode depolarization behavior, reflecting high electrochemical reactive activity. The ΔE_p of GF is 570 mV. As for the MWCNTs/GF, the ΔE_p is only 266 mV. The decreased ΔE_p represents the improving reversibility of electrode materials [16].

Redox peak current also is a key factor corresponding to the electro-catalytic activity of electrode materials [17]. As shown in Fig. 2(a), the oxidation peak current of MWCNTs/GF (51.2 mA) is slightly higher than that of GF (48.7 mA). However, the reduction peak current of MWCNTs/GF (43.7 mA) is conspicuously higher than that of GF (29.5 mA). The raised redox peak current of MWCNTs/GF represents high reaction velocity and electro-catalytic activity [17]. Another important parameter of reversibility is the ration of the redox peak current (*I*_{pa}/*I*_{pc}) [18]. The ration (*I*_{pa}/*I*_{pc}) of the MWCNTs/GF is 1.11, which is prominently smaller than that of GF (1.73). The value (*I*_{pa}/*I*_{pc}) of the MWCNTs/GF is much more closer to 1.0 (theoretical reversibility value) than that of GF, reflecting high electrochemical reversibility [19].

Fig. 2(b) shows the Nyquist complex plane impedance plots of GF and MWCNTs/GF electrode materials. It can be found that the reaction toward VO²⁺/VO₂⁺ is mixed and controlled by the charge transport and diffusion step [20,21]. The equivalent circuit (the inset of Fig. 2(b)) was proposed to simulate the mixed controlled electrochemical process [22]. For the equivalent circuit, *R*₁ represents the ohmic resistance caused by the electrode, electrolyte, and the connection. *R*₂ stands for charge transport resistance. *Q*₁ is the constant phase element (CPE) which is related to the electric double layer capacitor. *Q*₂ is the CPE related to vanadium ion diffusion capacitance [23,24].

As shown in the inset of Fig. 2(b), the *R*₁ of MWCNTs/GF is 1.0 Ω, which is slightly lower than that of GF (1.17 Ω). The

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