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The catalytic effect of bismuth for VO_2^+/VO^{2+} and V^{3+}/V^{2+} redox couples in vanadium flow batteries

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ABSTRACT

The effect of bismuth (Bi) for both VO_2^+/VO^{2+} and V^{3+}/V^{2+} redox couples in vanadium flow batteries (VFBs) has been investigated by directly introducing Bi on the surface of carbon felt (CF). The results show that Bi has no catalytic effect for VO_2^+/VO^{2+} redox couple. During the first charge process, Bi is oxidized to Bi^{3+} (never return back to Bi metal in the subsequent cycles) due to the low standard redox potential of 0.308 V (vs. SHE) for Bi^{3+}/Bi redox couple compared with VO_2^+/VO^{2+} redox couple and Bi^{3+} exhibit no (or neglectable) electro-catalytic activity. Additionally, the relationship between Bi loading and electrochemical activity for V^{3+}/V^{2+} redox couple was studied in detail. 2 wt% Bi-modified carbon felt (2%-BiCF) exhibits the highest electrochemical activity. Using it as negative electrode, a high energy efficiency (EE) of 79.0% can be achieved at a high current density of 160 mA/cm^2, which is 5.5% higher than the pristine one. Moreover, the electrolyte utilization ratio is also increased by more than 30%. Even the cell operated at 140 mA/cm^2 for over 300 cycles, the EE can reach 80.9% without obvious fluctuation and attenuation, suggesting excellent catalytic activity and electrochemical stability in VFBs.

1. Introduction

Recently, energy storage technologies have been playing increasingly important roles in meeting the growing demands of such renewable clean energy as wind power and solar energy for the unsteady and intermittent behavior exhibited during the process of power generation [1–3]. Among them, vanadium flow batteries (VFBs) are considered to be one of the most promising candidates for the merits in decreasing contamination of metal cation by employing same element in both half-cells, where VO_2^+/VO^{2+} and V^{3+}/V^{2+} serve as the positive electrolyte and the negative electrolyte, as well as it's long life, active thermal management and independence from energy and power ratings [4,5]. Despite the considerable merits, the commercial application process of VFBs, to some extent, is still slowed down by the high material cost of stacks ($/kW). Hence, to search an economic and efficient way to decrease the material cost is the first imperative. Among tremendous methods, to increase the material utilization of VFB stack per kilowatt shows most effective, especially by increasing the operation current (charge and discharge) density on electrodes [6]. By doing this, however, the voltage efficiency of VFB stack is prone to drop sharply, due to the obviously increased electrochemical polarization of the VO_2^+/VO^{2+} and V^{3+}/V^{2+} redox couples on pristine commercial carbon electrodes. The situation will be worse at even higher current densities, leading to an overall inferior electrochemical performance [7].

As a result, how to improve the electrochemical activity of vanadium redox couples on the electrodes has attracted great attention. For one thing, catalytic activity of the pure carbon fiber electrodes could be enhanced by many methods, such as thermal activation [8,9], acid treatment [10,11], nitrogen-doping [12–15], and electrochemical oxidation [16]. The similar contributions described for these methods are the improvement of hydrophilicity of carbon materials, by introducing oxygenated or nitrogenous groups onto the carbon surface, as well as the increase of active sites for redox reaction of VO_2^+/VO^{2+} and V^{3+}/V^{2+} [17]. For another thing, to modify the carbon materials with metal and metallic derivation is also an efficient and promising way to enhance electrochemical activity. Wang and Wang [18], have reported that the resistance of the cell assembled with Ir-modified graphite felt as positive electrode was 25% decrease compared with the cell using non-modified one. Meanwhile, a high voltage efficiency of 87.5% was achieved under a current density of 20 mA/cm^2. However, the high cost is still an obstacle which remains for such

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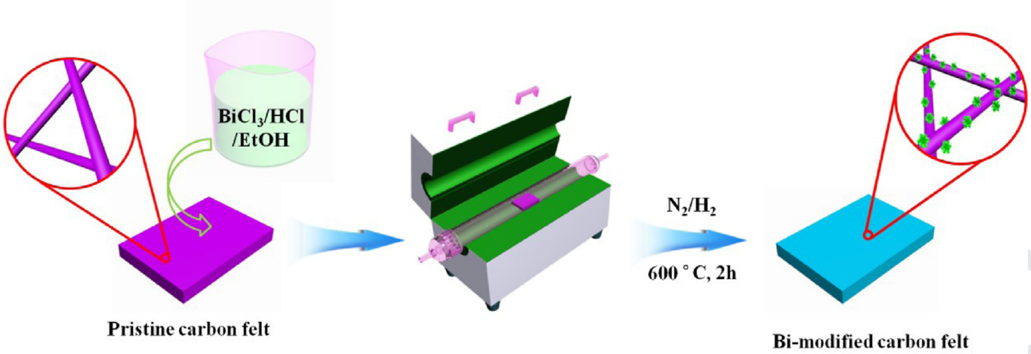

Scheme 1. Schematic illustration of the *x*-BiCF preparation.

noble metals. After that, Tungsten oxide (WO_3) was proposed as an alternative for both $VO_2{}^+/VO^{2+}$ and V^{3+}/V^{2+} redox couples [19]. Unfortunately, low conductivity evidently exhibited for this kind of material as one of important semiconductor materials.

Currently, bismuth (Bi) was proposed as the catalyst of VFBs, with combined merits of low cost, higher electrical conductivity and stiff stability in sulfuric acid solution, compared with Ir [18], $CuPt_3$ [20], WO_3 [19], Mn_3O_4 [21], Nb_2O_5 [22], and CeO_2 [23]. In a recent study, Gonzalez and his co-workers have shown that using Bi-modified graphite felt as the positive electrode presented quite excellent electro-catalytic activity [24]. Nevertheless, after that, more and more reports show the trend that no electrocatalytic activity exhibited for Bi as the positive electrode catalyst [6,25]. Hence, the real role of Bi for the reaction of $VO_2{}^+/VO^{2+}$ is still uncertain.

On the contrary, unlike the competing explanations of the role of Bi for $VO_2{}^+/VO^{2+}$ redox couple, nearly all of the reports show that Bi can improve the electrochemical activity of negative electrode [6,25,26]. In other words, Bi is a well-suited negative electrode catalyst in VFBs application, especially for the electrode with relatively low electrochemical activity. Hence, further figuring out the relationship between Bi loading and electrochemical activity for V^{3+}/V^{2+} redox couple is significant.

Along this line, a relatively systemic investigation of role of Bi for $VO_2{}^+/VO^{2+}$ and V^{3+}/V^{2+} redox couples by introducing Bi on the surface of carbon felt (CF) with traditional high-temperature H_2 reduction, is presented in this study. The surface morphology and microstructure of CF and Bi modified carbon felt (BiCF) were investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM). The relationship between Bi loading and electrochemical activity for V^{3+}/V^{2+} redox couple was discussed by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Ultimately, the effect of Bi on the final battery performance was checked by the charge/discharge cycling test.

2. Experimental

2.1. Synthesis of Bi-modified electrodes

CFs with different Bi loadings were labeled as *x*-BiCF ($x = 0\%$, 0.5%, 1%, 2%, 3% and 5%, all of value are on the basis of weight), which were obtained by traditional high-temperature H_2 reduction method, as illustrated in Scheme 1. In brief, 0.038 g $BiCl_3$ (Sinopharm Chemical Reagent Co., Ltd.) was dissolved in a mixture of 20 mL 5 wt% HCl and 5 mL ethanol; afterward, the mixed solution was impregnated into a piece of prepared CF (Yongdeng industrial felt factory) with a geometrical area of 48 cm^2. After that, the semi-finished product was dried at 100 °C for 8 h and thermal treated at 600 °C for 2 h in a mixture of N_2 and H_2 ($V/V = 5/3$). After cooling to room temperature, the obtained product is 1%-BiCF.

2.2. Characterization of Bi-modified electrodes

X-ray diffraction (XRD, DX-2700) with Cu K_a radiation ($\lambda = 0.154$ nm) operated at 40 kV and 30 mA was used for crystal structure analysis and the XRD dates were collected from 10° to 90° in 2θ at a scanning rate of 1 °/min. Scanning electron microscopy (SEM, JSM-6360LV) using secondary electron (SE) and backscattered electron (BSE) detectors was employed for morphology inspection.

Cyclic voltammetry (CV) tests and electrochemical impedance spectroscopy (EIS) were provided even better insight into the electrochemical activity of *x*-BiCF. All the tests were operated on a three-electrode system on a CHI604e (CHI instruments, USA) workstation, where *x*-BiCF filled in a glass carbon electrode with 0.28 cm^2 effective active area; an area of 12 cm^2 graphite plate and a saturated calomel electrode (SCE) work as the working electrode, the counter electrode, and the conference electrode, respectively. The solution for positive and negative reactions study consists of 0.05 M $VO_2{}^+$ + 0.05 M VO^{2+} + 3 M H_2SO_4 solution and 0.05 M V^{3+} + 0.05 M V^{2+} + 3 M H_2SO_4 solution, respectively. EIS curves were obtained by applying an alternating voltage of 5 mV over the frequency varying from 10^6 to 10^{-2} Hz.

The charge/discharge tests were measured on Arbin-BT 2000 instrument (Arbin Co., USA) with a constant current density of 80, 100, 120, 140 and 160 mA/cm^2. Two pieces of *x*-BiCF (thickness: 6 mm; geometrical area: 48 cm^2), separated with a piece of Nafion 115 ion exchange membrane (Dupont) were used as the negative and positive electrode. 60 mL 1.5 M V^{3+} in 3.0 M H_2SO_4 solution and 60 mL 1.5 M VO^{2+} in 3.0 M H_2SO_4 solution, working as negative and positive electrolytes, respectively, were circulated in both sides by two magnetic pumps with a flow rate of 40 mL/min. The charge/discharge cutoff voltage was set as 1.55 V and 1 V.

3. Results and discussion

3.1. SEM survey of Bi-modified electrodes

The catalytic effect of Bi for $VO_2{}^+/VO^{2+}$ and V^{3+}/V^{2+} redox couples were investigated. Fig. 1 shows the surface morphology of *x*-BiCF ($x = 0\%$, 2%) at different charge/discharge periods. As shown in Fig. 1(a) and (b), 0%-BiCF is fabricated with large number of carbon fibers with a diameter of nearly 200 μm. After 2 wt% Bi modified (2%-BiCF), the overall morphology shows no change but some particles whose average size are nearly 50 nm except a handful of large particles around 200 nm uniformly distributed on the surface of CF, which can be attributed to Bi^{3+} reduced to Bi under Ar/H_2 atmosphere (Fig. 1(c) and (d)). Interestingly, when the 2%-BiCF worked as the positive electrode, during the first charge process, all of the particles disappeared, which can be owed to the low standard redox potential of 0.308 V for Bi^{3+}/Bi redox

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