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Broad temperature adaptability of vanadium redox flow battery–Part 4: Unraveling wide temperature promotion mechanism of bismuth for V^{2+}/V^{3+} couple

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ABSTRACT

Vanadium flow battery (VFB) is a fast going and promising system for large-scale stationary energy storage. However, drawbacks such as low power density and narrow temperature window caused by poor catalytic activity of graphite felt (GF) electrodes limit its worldwide application. In this paper, bismuth, as a low-cost, no-toxic and high- activity electrocatalyst, is used to modify the thermal activated GF (TGF) *via* a facile hydrothermal method. Bismuth can effectively inhibit the side reaction of hydrogen evolution in wide temperature range, while promoting the V^{2+}/V^{3+} redox reaction. As a result, the VFB assembled with Bi/TGF as negative electrode demonstrates outstanding rate performance under the current density up to 400 mA cm^{-2}, as well as a long-term stability over 600 charging/discharging cycles at a high current density of 150 mA cm^{-2}. Moreover, it also shows excellent temperature adaptability from -10 °C to 50 °C and high durability for life test at the temperature of 50 °C.

1. Introduction

Renewable energy sources such as solar and wind have been deployed and integrated with global environmental pollution and energy shortages becoming increasingly prominent [1,2]. However, these renewable energies are unstable and intermittent due to the process of power generation [3]. So energy storage techniques especially the large-scale energy storage systems are in critical need. Among them, vanadium flow battery (VFB), which is a new type of secondary battery for electric power storage, was first successfully demonstrated and developed by Skyllas-Kazacos and co-workers in the 1980s [4,5]. Its key advantages includes independence of power and capacity, fast response time, long cycle life, low maintenance cost and high safety [6]. In the VFB, energy is stored in the electrolyte via four different oxidation states of vanadium ions (V^{2+}/V^{3+} and VO^{2+}/VO_2^{+}) which are separated by the membrane during charging and discharging [7]. The vanadium redox reactions mainly occur on the electrode surface, whereas the electrochemical activity of the electrode such as graphite felt (GF) and carbon felt (CF) is low [8].

Over the past decades, intensive efforts have been devoted to treating or modifying the electrode surface to introduce more active sites and enhance their catalytic activities. Some intrinsic treatments such as thermal treatment [9], acid activation [10] and electrochemical oxidation [11] are used to improve the electrochemical activity of GF. The electrocatalysts applied in modifying the electrode for VFB can be categorized into carbon-based and metal-based nanocatalysts. Carbon-based catalysts mainly include carbon nanotubes or nanofibers [12–15], graphene [16–19] and nitrogen-doped carbon materials [20–22]. However, they are tedious to fabricate and easy to peel off from the surface after long cycling. By contrast, metal-based catalysts such as Au, Pt, Ir [23–25] and some metallic oxides [26–28] have been deposited on the GF electrodes and exhibited highly improved catalytic activities. However, this approach is not really practical because of the high cost of these noble metals and sensitivity of gas evolution. Recently, it is reported that some cheap metals such as copper and tin deposited on the GF show excellent electrocatalytic effects on the performance of the VFB [25,29].

Bismuth is a non-toxic, cheap and safe metal and has been used for catalytic applications in the energy storage systems and

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Table 1. Comparison of various bismuth modified GF or CF electrodes for VFB application.

Materials	Reagent and treatment conditions	Promotive effect		Rate performance				Cycling performance		Test temperature	Ref.
		P	N	Electrode size (cm^{-2})	Membrane	j (mA cm^{-2})	EE (%)	j (mA cm^{-2})	Cycle number		
GF	Bi_2O_3, ethylene glycol and ethanol, hydrothermal reaction		√	25	Nafion 115	50	85.8	150	600	−10–50 °C	This work
						150	78.9				
						400	58.6				
	Bi_2O_3 in 0.01 M HCl, 450 °C in air, 3 h	√		–	–	–	–	–	–	R.T.	32
	$BiCl_3$ in electrolyte		√	10	Nafion 115	50	90.1	50	50	R.T.	33
						150	78.1				
	$BiCl_3$ electro-deposited onto GF		√	–	–	–	–	–	–	R.T.	34
	$BiCl_3$, HCl, ethanol, hydrogen reduction		√	48	Nafion 115	80	85.3	–	–	R.T.	35
						160	75.8				
CF	$BiCl_3$, HCl, ethanol, hydrogen reduction		√	48	Nafion 115	80	84.8	–	–	R.T.	
						160	79.4				
	$BiCl_3$, HCl, ethanol, hydrogen reduction		√	48	Nafion 115	80	85.5	140	300	R.T.	36
						160	78.8				
	KOH etching, $Bi(NO)_3$ deposited onto CF		√	4	Nafion 212	60	88.1	80	100	R.T.	37
						200	74.5				

biomedical field [30,31]. It was first proposed for the application in VFB in 2011 and the decorated GF was used as a positive electrode material [32]. The results indicated that bismuth nanoparticles acted as active sites for $VO^{2+}/VO_2{}^+$ couple, and thereby promoted the electrochemical reaction to occur. Then Li et al. have reported low cost Bi had great catalytic effect on the negative electrode reaction but little effect on the reaction of the positive electrode [33]. Some researchers explained that bismuth forms an intermediate to promote the reduction of V^{3+} into V^{2+}, and inhibit the hydrogen evolution reaction [34]. Other researchers confirmed a VFB with GF electrode has been improved significantly by modification with Bi due to the largely reduced electrochemical polarization [35–37]. To better understand the development of bismuth as electrocatalysts in VFB systems, recent studies are summarized in Table 1, presenting the performance of VFB with various current densities and cycling numbers. However, the data are still short of wide temperature adaptability of electrodes with bismuth under VFB operation.

Wide temperature endurance of the VFB is very essential to its practical application. In our previous work, we have carried out a series of fundamental research, including electrolyte analysis [38], single cell research [39], membrane evaluation [40] and effects study of total vanadium concentration and sulfuric acid concentration [41], to expand the temperature windows of the VFB. In this work, the promotion mechanism of bismuth on the performance of VFB in wide temperature range is comprehensively studied. Comparing with the works in Table 1, the electrochemical performances of TGF electrode with Bi were measured under the temperature ranging from −10 °C to 50 °C. The rate performance under current density up to 400 mA cm^{-2} and the power density of the VFB with the modified electrode were tested. In addition, long life testing of VFB over 600 charging/discharging cycles and high temperature durability testing at 50 °C were also conducted.

2. Experimental

2.1. Materials

The thickness of GF (Gansu Haoshi Carbon Fiber Co., Ltd.) is 5 mm and the pretreatment of GF was washing with ethanol and deionized water, respectively. Then they were thermally treated at 420 °C for 10 h in air and denoted as TGF. Other chemicals were of analytical grade and used without further purification.

2.2. Electrode preparation and characterization

0.466 g Bi_2O_3 (Sigma-Aldrich, 99.9%) was added into a solution of 78 mL ethylene glycol and 22 mL ethanol. The suspension was transferred into a 200 mL autoclave liner after sonication for 30 min. Then a piece of TGF (5 cm × 5 cm) was placed into the autoclave and heated at 200 °C for 6 h in an oven. After naturally cooling down to ambient temperature, the sample was washed several times with ethanol and distilled water, and dried at 60 °C to obtain the Bi/TGF.

The morphology of the samples was obtained through field emission scanning electron microscopy (SEM, ZEISS SUPRA®55) at 5 kV, and energy dispersive X-ray spectroscopy (EDX) was recorded at an acceleration voltage of 20 kV. Wide-angle X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance with a Cu Kα radiation (40 kV, 40 mA, 10° min^{-1} from 10 to 70°).

2.3. Electrochemical measurement

Electrochemical measurements were carried out using a three-electrode system on a PARSTST 2273 electrochemical workstation using a three-electrode system [42]. A working electrode with a geometric area of 1 cm^2 was clamped by an electrode holder where only a small part of the GF was contacted with the platinum current collector. And the system was also equipped with a platinum plate counter electrode and a saturated calomel electrode (SCE) reference electrode. A solution of 0.1 M V^{3+} in 2 M H_2SO_4 was used for negative tests as well as a solution of 0.1 M VO^{2+} in 2 M H_2SO_4 for positive tests in cyclic voltammograms (CV) test. Electrochemical impedance spectroscopy (EIS) measurements were performed by applying a polarization potential of −0.4 V with 5 mV amplitude in the frequency range from 100 kHz to 10 mHz for the negative reaction. Linear sweep voltammetry (LSV) experiments were performed in a 2 M H_2SO_4 solution. Wide temperature (−10–50 °C) tests of CV and LSV were performed in a thermostat (PU-80, Guangdong Hongzhan).

2.4. VFB single cell test

The configuration of the VFB is an improved version of the single cell we reported previously [43], as shown in Fig. S1. The TGF and Bi/TGF with an active area of 25 cm^2 (5 × 5 cm) were used as the positive and negative electrode, respectively. The Nafion 115 membrane (7 cm × 7 cm) used as separator was pretreated by boiling in 1 M H_2SO_4 solution for 1 h and then in deionized water for

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