Preparation and characterization of lead dioxide electrode with three-dimensional porous titanium substrate for electrochemical energy storage

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ABSTRACT

Lead dioxide electrodes with three-dimensional porous titanium as substrate (3D-Ti/PbO$_2$) were prepared by galvanostatic electrodeposition. The structure, morphology and electrochemical performances of 3D-Ti/PbO$_2$ were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), cyclic voltammetry and galvanostatic charge-discharge techniques. The electrochemical performances of 3D-Ti/PbO$_2$ were optimized by adjusting the applied deposition current density. Results reveal that the 3D-Ti/PbO$_2$ prepared at 1 mA cm^{-2} had nanoparticles on its surface with abundant crystal orientations. It had a high capacity of 132 mAh g^{-1} with an active material utilization of 57% at discharge current density of 0.9 A g^{-1}. With the same condition, the lead dioxide electrode with planar titanium substrate (Ti/PbO$_2$) only had a capacity of 20.8 mAh g^{-1}. The high electrochemical active surface area and small charge transfer resistance resulted in the high capacity of 3D-Ti/PbO$_2$. The possible factors, which affected the electrochemical performances of 3D-Ti/PbO$_2$, were interpreted in detail with voltammetric charge analysis and electrochemical impedance spectroscopy.

1. Introduction

Lead acid battery is a kind of important secondary battery with advantages of operational safety, high cost performance and well-established recycling system [1–3]. With the development of renewable energy storage and hybrid electrical vehicles (HEVs), it is crucial to improve the cycling stability and power performance of lead acid battery. In recent years, advanced lead acid batteries (PbO$_2$/AC asymmetric electrochemical capacitor [4], Ultra-battery [5] and lead-carbon battery [6]) have been fast developed. The addition of activated carbon in negative electrode improves the power performance and cycling stability of lead acid battery. Nevertheless, the pasted PbO$_2$ electrodes in lead acid batteries have not been improved effectively. The pasted PbO$_2$ electrodes fail prematurely due to active material softening and gird corrosion especially when discharged deeply or discharged at high current density [7,8]. The active material softening of the positive electrode can be eliminated to some extent by applying pressure to make the active material

compact [9], and grid corrosion can be suppressed by introducing extra additives [8]. Another method to eliminate active material softening and grid corrosion of pasted PbO$_2$ is to design novel PbO$_2$ electrodes.

The lead dioxide electrode with two-dimensional (2D) planar titanium substrate (2D-Ti/PbO$_2$, or Ti/PbO$_2$) prepared by electrode-position has compact structure, good stability [10]. Especially, Ti/PbO$_2$ with SnO$_2$-Sb$_2$O$_5$ intermediate layer is anticorrosive in concentrated sulfuric acid [11], leading to that Ti/PbO$_2$ becomes a significant candidate of positive electrode in lead acid batteries. Thus, the PbO$_2$/AC asymmetric electrochemical capacitor with Ti/PbO$_2$ obtains a service life of several thousand cycles without obvious capacitance decline [12–14], which demonstrates the suitability of Ti/PbO$_2$ in high power applications. Nevertheless, the disadvantage of Ti/PbO$_2$ is low capacity.

PbO$_2$ electrode with high capacity and good stability should satisfy the following two conditions: (i) high surface area facilitates the electrochemical reaction at electrode/solution interface; (ii) physical continuity of active material facilitates the electron conduction from electrode surface to current collector. It seems difficult to achieve the above-mentioned two goals simultaneously by direct electrodeposition on 2D planar titanium substrate due to the following reasons [15–18]. The Ti/PbO$_2$ prepared at low

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deposition current density has low surface area, and the deep discharge is impeded by the continuous $PbSO_4$ formed in discharge process resulting in low capacity. On the other hand, the Ti/PbO_2 prepared at high deposition current density has loose structure due to oxygen revolution reaction (OER), and electron conduction is impeded at high charge-discharge current density resulting in low cycling stability. Unlike 2D electrode, three-dimensional (3D) electrode can provide active material with large surface area and good continuity leading to enhanced capacity and power performance [19–21]. 3D PbO_2 electrode prepared by template method possesses higher surface area and capacity than Ti/PbO_2 [22,23]. However template method is complicated and expensive. Another method to prepare electrode with high surface area is using 3D substrates [24,25]. This method is facile and easy to realize real applications. For instance, the lead acid battery with carbon foam grid has the characteristics of high utilization of active material and good power performance [26]. However, carbon foam is unstable and will be oxidized at high potentials in concentrated sulfuric acid.

In recent years, the 3D porous titanium has been used as the electrode substrate material, owing to its good electrical conductivity, high surface area and corrosion resistance. The results show that the boron-doped diamond electrode with 3D porous titanium substrate (3D-Ti/BDD) has high roughness, large porosity and high surface area [25,27]. Compared with 2D-Ti/BDD, 3D-Ti/BDD has outstanding electrochemical performance.

In this paper, we have tried to electrodeposit PbO_2 on 3D porous titanium to prepare 3D-Ti/PbO_2. The 3D-Ti/PbO_2 had a much higher capacity than traditional Ti/PbO_2. The applied deposition current density had obvious effects on the morphology, structure and electrochemical performance of 3D-Ti/PbO_2. The associated factors, which influenced the electrochemical performance of 3D-Ti/PbO_2, were interpreted in detail with voltammetric charge analysis and electrochemical impedance spectroscopy (EIS). The obtained results are helpful for the performance improvement of positive electrodes in advanced lead acid batteries.

2. Experimental

2.1. preparation of 3D-Ti/PbO$_2$ and Ti/PbO$_2$

Planar titanium plates and 3D porous titanium plates with average pore size of 60 μm (TA1, Baoji Titanium Industry Co., Ltd, China) were polished with emery paper firstly and degreased with 10 wt% NaOH. Then, they were etched in an aqueous solution of HCl (30 wt%) at 100 °C for 1 h. Afterwards, they were rinsed with deionized water and reserved in deionized water. Finally, SnO_2-Sb_2O_5 intermediate layer was prepared on titanium substrates by thermal decomposition described in reference [28]. The purpose of the preparation of SnO_2-Sb_2O_5 intermediate layer is to increase the conductivity of electrodes and prevent the formation of TiO_2 both in deposition process and in charge-discharge process.

The preparation of Ti/PbO_2 and 3D-Ti/PbO_2 were performed on a potentiostat-galvanostat (HYL-A, Yanbian Yongheng Co., China) by galvanostatic electrodeposition in electrolytic cell with single compartment. Planar titanium substrates with SnO_2-Sb_2O_5 intermediate layer ($Ti/SnO_2 + Sb_2O_5$) and 3D porous titanium substrates with SnO_2-Sb_2O_5 intermediate layer (3D-$Ti/SnO_2 + Sb_2O_5$) were used as anodes. Titanium mesh (2.5 cm × 2.5 cm) was used as cathode. The plating solution was 100 mL aqueous solution of 0.5 mol L^{-1} $Pb(NO_3)_2$ and 1.0 mol L^{-1} HNO_3. The applied current densities were 1, 10 and 50 mA cm^{-2}, respectively. The deposition charge was 9.0 C cm^{-2}. After electrodeposition, the PbO_2 electrodes obtained were rinsed with deionized water. Analytical grade reagents and deionized water (the resistivity was 18.25 MΩ cm) were used in all experiments.
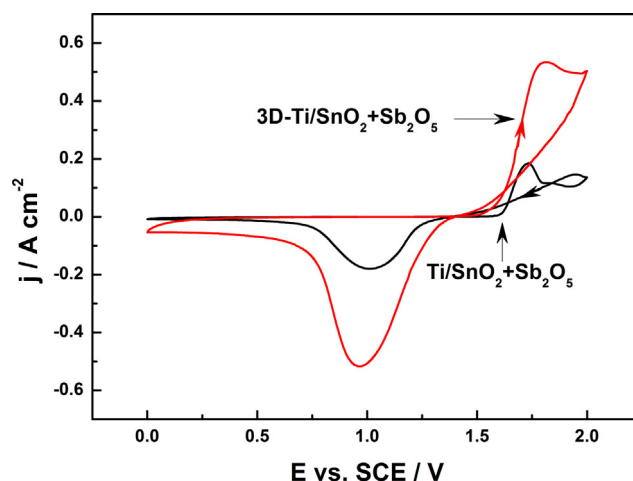

Fig. 1. Cyclic voltammagrams of $Ti/SnO_2 + Sb_2O_5$ and 3D-$Ti/SnO_2 + Sb_2O_5$ in an aqueous solution of 0.5 mol L^{-1} $Pb(NO_3)_2$ and 1.0 mol L^{-1} HNO_3 at scan rate of 50 mV s^{-1}.

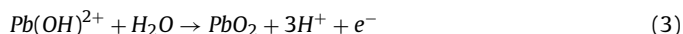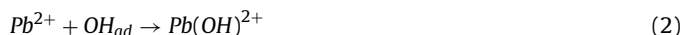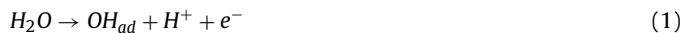### 2.2. characterization of 3D-Ti/PbO$_2$ and Ti/PbO$_2$

SU8020 SEM (HITACHI, Japan) was employed to characterize the surface morphology of the PbO_2 electrodes. The microstructure of the PbO_2 was detected with XRD on a D/max diffractometer (Ragaku, Japan) with Cu-Kα radiation source (λ=1.541874 Å) operating at 50.0 kV and 200.0 mA. The electrochemical performances of PbO_2 electrodes were tested on PARSTAT 2273 electrochemical work station (Princeton Applied Research, USA) in a conventional three electrode cell with single compartment. A Ti/RuO_2-TiO_2 electrode was used as the counter electrode. A KCl-saturated calomel electrode (SCE) was used as the reference electrode. All the potentials were quoted with respect to SCE. EIS was tested in the frequency range of 100 kHz-100 mHz with voltage amplitude of 10 mV.

3. Results and discussions

3.1. Electrodeposition of 3D-Ti/PbO$_2$

Cyclic voltammetry was used to characterize the electrodepositon behavior of PbO_2 at $Ti/SnO_2 + Sb_2O_5$ and 3D-$Ti/SnO_2 + Sb_2O_5$ (Fig. 1). The peak current of PbO_2 electrodeposition at $Ti/SnO_2 + Sb_2O_5$ was 186 mA cm^{-2}, and the peak current of PbO_2 electrodeposition at 3D-$Ti/SnO_2 + Sb_2O_5$ was as high as 534 mA cm^{-2}. The high peak current density of 3D-$Ti/SnO_2 + Sb_2O_5$ indicates a smaller resistance of electrodeposition at 3D-$Ti/SnO_2 + Sb_2O_5$ than that at $Ti/SnO_2 + Sb_2O_5$, which is related to the mechanism of PbO_2 electrodeposition.

PbO_2 electrodeposition is a multistep reaction. It can be illustrated as follows [29–31]:

$$H_2O \rightarrow OH_{ad} + H^+ + e^- \tag{1}$$

$$Pb^{2+} + OH_{ad} \rightarrow Pb(OH)^{2+} \tag{2}$$

$$Pb(OH)^{2+} + H_2O \rightarrow PbO_2 + 3H^+ + e^- \tag{3}$$

The first step is forming oxygen-containing species (Eq. (1)), denoted as OH_{ad}. The subsequent step is the reaction between Pb^{2+} and OH_{ad}, forming $Pb(OH)^{2+}$. Herein, Pb^{2+} is chemically oxidized to $Pb(OH)^{2+}$ by OH_{ad} (Eq. (2)). Finally, the $Pb(OH)^{2+}$ is electrochemically oxidized to Pb(IV), which is chemically transformed to PbO_2 colloid (Eq. (3)). The second charge transfer step (Eq. (3)) is the rate-determining step at low potentials, while the diffusion of Pb^{2+} ion is the rate-determining step at high potentials [29].