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Energy storage capacity investigation of pulsed current formed nano-structured lead dioxide

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Abstract

An electro-deposition method was used for the preparation of nano-structured lead dioxide. The lead dioxide films prepared were used as positive electrodes of lead acid batteries. Different parameters such as pulse time (t_{on}), pulse height, and relaxation time (t_{off}) were optimized to obtain higher capacity. Depend on the pulse conditions, a range of different morphologies of various porosities and connectivity was obtained. The resulting batteries were discharged to a cut off voltage of 1.75 V by a pulsed current method. The energy storage ability of the prepared lead acid batteries shows a close relation with the morphology of cathode materials. Maximum capacity was observed when pulse and relaxation time was equal to 0.1 and 5 s, respectively, at a current density of 25 mA cm^{-2}. A change in morphology of lead dioxide from aggregated globular structure to nanofiber was occurred. It was found that the high surface area as well as high connectivity between particles resulted in increased discharge capacity. Analysis of electrochemical impedance spectroscopy (EIS) data revealed that the charge transfer resistance is decreased by a change in morphology from bulk globular to nanofiber as the energy storage test showed. The time dependence of impedance behavior of a sample prepared at $t_{on} = 0.1$ s and $t_{off} = 5$ s at 25 mA cm^{-2} was investigated and the results are discussed.

Keywords: Lead dioxide; Pulsed current; Lead acid battery; Nanofiber; Capacity

1. Introduction

Due to their low cost, rechargeability and easy construction lead acid batteries have attracted great interest for use in motorcycles, electrical vehicles, and communication equipments. There are increased studies devoted to improvement of efficiency of these batteries. A major part of efforts to improve the performance of lead acid batteries has been focused on the improvement of cathode properties including capacity, life cycle, and rechargeability [1–8].

Lead dioxide (PbO_2) is active material for storage of chemical energy in lead acid batteries. Because of non-stoichiometry of lead dioxide, it has electrochemical activity. Electrochemically prepared lead dioxide has higher electrochemical activity compared to the chemically prepared one. The electrodeposition of PbO_2 achieved on various substrates including glassy carbon [9], gold [10], platinum [11], Ebonex [13,14] and lead or lead alloy [12] by means of various electrochemical methods such as cyclic voltammetry [14,15], constant current and constant voltage [15] approaches.

Shen et al. deposited lead dioxide from a solution containing Pb^{2+} on three different substrates (i.e., Au, Pt and Ti) with different techniques [15]. At constant current and at lower current densities, a uniform crystal grain was synthesized on the Pt substrate. With increasing current density, a rice-shape crystal was observed. In fact, at low current densities, the mass transport process is fast compared with the electron transfer resulted in the formation of a well-formed structured lead dioxide.

Vatistas et al. [16] used a pulse method for anodic deposition of PbO_2 from solutions containing HNO_3 and NaF, on a Ti/SnO_2 substrate. The mass transfer limitation of pulse current coating was avoided by using a pulse step of 2.71 $mCcm^{-2}$ and a 0.1 s relaxation time. The pulse height was between 3.43

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and 68.2 mA cm^{-2}. The SEM of surface showed heterogeneous nucleation of lead dioxide. The dimension of lead dioxide was decreased, with increasing of pulse current.

Das and Mondal [17] prepared electrodeposited lead and lead dioxide on carbon electrode and evaluated its capacity and performance during cycle life. They observed that capacity was increased during the initial steps, probably due to the increased effective surface area of deposited PbO_2 layers.

In this work, we studied the energy storage capacity of pulse current formed lead dioxide under various preparation conditions. It was found that the capacity of the resulting lead dioxide was dependent on the morphology of the electrode prepared. The highest capacity was increased when the morphology of the prepared electrode changed from globular to nanofibriliar. Variation in the structure of the nano-structured lead dioxide, from globular to nanofibriliar form, resulted in increased active surface area and, consequently, in improved energy storage capacity. The EIS technique was used to investigate the electrochemical properties of the prepared electrode.

2. Experimental

The procedure for the preparation of nano-structured lead dioxide by an anodic pulse current has been explained in detail in our previous work [18]. A battery was constructed with the prepared lead dioxide electrode as cathode and a commercial charged negative plate of motorcycle battery (2 cm × 4 cm) as anode, without using any separator. A solution containing 4.8 M sulfuric acid was used as battery electrolyte.

The lead dioxide formed on lead substrate can be removed from the surface with a 10% (wt/wt) solution of mannitol ($C_6H_{14}O_6$) in 1:1 methanol and acetic acid. The amount of lead dioxide was formed on lead substrate was the measured gravimetrically from the difference between lead weight before and after lead dioxide formation.

2.1. Impedance spectroscopy

The AC impedance measurements were made as a function of frequency using an AUTOLAB system with PGSTAT30 and FRA2 boards (Eco Chemie, Utrecht, and The Netherlands). The system is run by a PC through FRA and GPES 4.9 software. The working electrode was prepared from lead dioxide. A Pt wire was used as a counter electrode. The reference electrode was a double junction Ag/AgCl reference electrode (KCl, saturated) and the cell electrolyte was 0.05 M sulfuric acid. At open circuit voltage (OCV), the frequencies were swept between 1 Hz and 100 kHz with amplitude of applied sine wave of 5 mV rms.

2.2. Cell capacity test

The cells were charged at a pulsed current mode having a pulse time and a relaxation time of 1 s and a pulse height of 12.5 mA cm^{-2} to reach a voltage of about 2.35 V for 2 h, and were discharged to a cut-off voltage of 1.75 V at a current density of 12.5 mA cm^{-2}. Charge and discharge experiments of the batteries were carried out with an automatic battery test unit (BPT Co., Tehran, Iran) and a PC computer with an A/C interface. All experiments were performed at room temperature.

3. Result and discussion

3.1. Discharge capacity

We have recently reported on the synthesis and morphological investigation of pulsed current formed nano-structured lead dioxide [18]. It was found that different experimental conditions including pulse height, pulse time, relaxation time and ratio of pulse time to relaxation time significantly affected the morphology of the anodic films prepared. In this work, we used different batches of the prepared lead dioxide films as the cathode of lead acid batteries and investigated the influence of the morphology of the nano-structured film electrodes on the performance characteristics of the resulting batteries. The experimental conditions used for the preparation of 13 different cathode electrodes were summarized in Table 1. The prepared electrodes were used as cathode of the lead acid batteries.

The effect of discharge current density on the capacity of the battery prepared with sample S_8 was tested (Fig. 1). Maximum capacity was achieved when a current density of 12.5 mA cm^{-2} was used for discharge of the battery. At higher current densities, however, only the outer layer of the electroactive material can contribute to the discharge process and a lower capacity was observed. This current density was selected for charge and discharge of the batteries. The batteries with different positive electrodes were discharged at constant current of 12.5 mA cm^{-2}.

The time-voltage behaviors of some of the batteries during discharge process were shown at Fig. 2. As it could be seen from Fig. 2, the discharge time for the battery assembled with cathode of S_8 is more than others. Therefore, this battery has the highest capacity, energy density and power. Comparing of the sample S_8 with the sample S_1 (which prepared at an approximately constant current mode $t_{on} = 10$ s and $t_{off} = 0.01$ s) shows that the discharge capacity could be considerably increased by using of pulse current formation technique.

Table 1
Synthetic conditions of different pulse current formed lead dioxide electrodes and discharge capacity of the corresponding lead acid batteries

Synthesis number	Pulse height (mA cm^{-2})	Pulse-time (s) (t_{on})	Relaxation time (s) (t_{off})	Capacity (mA hg^{-1})
S_1	25.00	10.00	0.01	81.3
S_2	25.00	0. 10	0.10	145.2
S_3	25.00	0.01	1.00	181.7
S_4	25.00	0.10	1.00	159.0
S_5	25.00	1.00	1.00	141.7
S_6	25.00	5.00	1.00	118.0
S_7	25.00	0.01	5.00	97.2
S_8	25.00	0.10	5.00	223.2
S_9	25.00	1.00	5.00	151.4
S_{10}	25.00	5.00	5.00	138.4
S_{11}	12.50	0.10	5.00	186.1
S_{12}	18.75	0.10	5.00	207.3
S_{13}	50.00	0.10	5.00	146.1