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Investigation of organic expanders effects on the electrochemical behaviors of new synthesized nanostructured lead dioxide and commercial positive plates of lead-acid batteries

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ABSTRACT

Positive electrode with uniform lead dioxide nanostructures was directly synthesized by pulsed current electrochemical method on the lead substrate in 4.8 M sulfuric acid solution. The effect of synthesis parameters were studied by the "one at a time" method on the morphology and particle size of lead dioxide. The composition, morphology and structure were investigated using energy dispersive X-ray analysis (EDX), scanning electron microscopy (SEM) and X-ray diffraction techniques (XRD). The effect of conventional organic expanders including humic acid, 1,2-acid (α-hydroxy β-naphtoic acid) and Vanillex was studied on the electrochemical behaviors of the prepared positive electrodes by cyclic voltammetry and on the discharge capacity and cyclelife of commercial positive plates. The used organic expanders improve the performance of negative plates but, they have not positive effects on the performance of positive electrodes of lead-acid batteries.

1. Introduction

It is well known that the performance of the negative plates of lead-acid batteries is strongly influenced by the presence of some substances such as expanders, conductive additives and others which are added to the negative active material during paste making. Additives are added to the negative pastes of lead-acid batteries to improve their performance in cycle life. Two types of additives were used in negative paste of lead-acid batteries including organic and inorganic additives. For example, barium sulfate as a common inorganic expander provides nucleation sites of lead sulfate during discharge process. Barium sulfate has similar unit cell dimensions to lead sulfate during battery discharge. This similarity of structures facilitates the formation of small crystals of lead sulfate in the negative active material in preference to the formation of large crystals that are difficult to recharge.

Organic additives such as humic acid, 1,2-acid (α-hydroxy β-naphtoic acid), Vanillex are strongly adsorbed on the surface of the active material and induce fine, porous crystal structure and increase the specific surface area from 0.2 to 0.8 $m^2\,g^{-1}$ [1–3]. Increasing surface area reduces the effective current density during discharge and thereby, increases utilization of the active material. This effect is particularly important at low temperatures and at high rates of discharge and is the principle reason why automotive battery expanders use high dosage of lignin sulfonate. Additives in the negative electrode of lead-acid batteries promote the development of fine crystal sponge lead upon formation and preserve the high surface area structure upon cycling [2,4–7]. The effects of such additives mainly concern the performance at high rates of discharge and cyclic performance, but they also exert other beneficial actions on the overall behavior of the negative plate [8–12]. Although the mechanism of action of the additives is very complex and not yet completely understood, it is commonly accepted that adsorption of such substances on the crystals is of fundamental importance for their behavior [13–18]. In fact, the expanders adsorbed on lead seem to facilitate a dissolution precipitation mechanism for lead sulfate formation, thus preventing passivity by a solid-state reaction [19–23].

According to the previous reports [14,16], the effects of additives are simply explained by considering that a porous lead sulfate is formed during discharge as a consequence of the partial coverage of the lead surface by adsorption of the additive substances, while a limitation of the size of lead crystals occurs during charging. As already mentioned, the presence of additives can also affect other aspects of the negative plate behavior. In fact, the adsorption of such substances on lead modifies the electrochemical cathodic behavior of lead by affecting the hydrogen evolution reaction, and thus yields a possible inhibiting action on the effects of impurities [24–31].

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Lead dioxide is an attractive material, which has been used in variety of electrochemical and industrial applications, including its use as a positive active material in lead-acid batteries [32–41], as an electrocatalyst for salicylic acid [42], 2-naphtol [43], and trans-3,4-dihydroxycinnamic acid [44], in the oxidation of organic compounds [35–37], oxidation of phenol [37,38], Cr^{3+} [39], and glucose [40], and evolution of ozone [41].

Lead dioxide has been prepared by the chemical and electrochemical methods. The previous reports showed that the morphology and the structure of PbO_2 could be readily controlled by electrochemical technique conditioned, deposition conditions including pH of the solution [45], the presence of forming agents such as F^- and Nafion [46], as well as the type of preparation techniques, such as pulse current [47] and cyclic voltammetry [48,49].

In the recent years, increased attentions have been focused on the synthesis of nanostructured lead dioxide. Cao et al. [50] successfully synthesized single-crystalline PbO_2 nanorods with less than 100 nm in diameter and 500 nm to 1 μm in length from a basic solution containing $Pb(NO_3)_2$ and cetyltrimethyl ammonium bromide (CTAB) upon the addition of $NaClO_4$ while maintaining the temperature at 85 °C for 3 h.

Xi et al. prepared sub-micrometer-sized PbO_2 hollow spheres using a new synthetic route [51]. Lead dioxide was prepared from a basic solution of $Pb(NO_3)_2$ and $(NH_4)_2S_2O_8$ in the presence of poly(vinyl pyrrolidone) as a morphology controlling agent. The diameter of the resulting PbO_2 hollow spheres was about 200–400 nm with a wall thickness of about 30–50 nm.

Shen and Wei [52] deposited uniformly distributed high porous structured lead dioxide with various shapes and size on Ti, Pt and Au substrates by constant current density, constant potential and potential cycling methods in an alcohol containing solution.

Saterlay et al. [48] have used a powerful ultrasound to enhance PbO_2 deposition efficiency on a Born-doped diamond (BDD) from a solution containing $Pb(NO_3)_2$ in HNO_3.

The influence of the ultrasonic intensity on the electrocrystallization of lead dioxide on glassy carbon electrodes was reported by Gonzàlez-Garcìa et al. [53]. They show that the ultrasonic intensity strongly affects the lead dioxide electrodeposition kinetics on glassy carbon electrodes. The concentration of hydroxyl radical produced during water sonolysis increasing ultrasonic intensity, which resulted in the formation of more nucleation centers [54].

Mousavi and co-workers prepared lead dioxide in nano-sized dimension on a Pt wire electrode applied as a suitable fiber in solid phase microextraction (SPME) process [55]. Vatistas and Cristofaro [47] used a pulse method for anodic deposition of PbO_2 from solutions containing HNO_3 and NaF, on a Ti/SnO_2 substrate.

Recently we chemically prepared the lead dioxide nanoparticles by the ultrasonication of a lead oxide solution at 60 °C, followed by oxidation with the addition of ammonium peroxydisulfate as an oxidizing agent. By the proposed method, lead dioxide nanoparticles with diameter of 50–100 nm were obtained only in β-PbO_2 form [56].

As it was mentioned, there are many reports about investigation of organic expanders on the capacity and cyclic behaviors of negative paste of lead-acid batteries. Based on our knowledge, there are not any reports about the effect of organic expanders on the positive plates of lead-acid batteries. It should be mentioned that the used organic additives in negative paste can be dissolved in the electrolyte and diffuse into positive paste of lead-acid batteries so that, it is expected that the organic expanders of negative paste affect on the positive paste behaviors.

In this work, we have tried to present a reliable method for direct oxidation of lead substrate to synthesize nanostructure lead dioxide in order to use in laboratory and industrial applications. We have applied a pulsed current method for the direct synthesis of nanostructured lead dioxide in 4.8 M sulfuric acid solution without any additives. A series of experiments were conducted to establish the optimum conditions for obtain uniform morphology, narrowest size distribution and best composition of lead dioxide nanoparticles by the "one at a time" method. The effect of commercial organic expanders including humic acid, 1,2-acid (α-hydroxy β-naphtoic acid) and Vanillex was studied on the electrochemical behaviors of the prepared nanostructured positive electrodes by cyclic voltammetry. After electrochemical studies, the optimized nanostructured lead dioxide was used as the positive electrode of lead-acid batteries and the constructed battery was used for investigating of the expanders effects on the it's discharge capacity and cyclelife. Finally, the obtained results were checked in the lead-acid batteries constructed by commercial positive and negative plates.

2. Experimental

2.1. Materials

Analytical grade sulfuric acid, HNO_3 (Merck) was used without any purification. Pure lead substrate was purchased from the National Iranian Lead-Zinc Company (NILZ Co., Zanjan, Iran). Humic acid, 1,2-acid and Vanillex were industrial grade and obtained from chine's companies. In all of the experiments, double-distilled water was used. Commercial positive and negative plates of motorcycle batteries (12 V to 3 Ah) were obtained from Aranniru Battery Manufacturing Company.

2.2. Instrumentals

The morphology and particle diameter of lead dioxide samples were studied by a Philips scanning electron microscopy (XL30 model). X-ray powder diffraction (Philips X'pert diffractometer) with Cu Kα radiation (λ = 0.15418 nm) were used to study the phase composition of the prepared samples. MPS-3010L model of a power source, made by the Taiwan Matrix Company was used for making a constant current. A home-made electrical pulse apparatus was applied to make the reproducible current pulses. Electrochemical behavior of the synthesized lead dioxide nanoparticles was studied by an electrochemical apparatus known as Auto Lab (model 102). Ag/AgCl reference electrode equipped with 1 M H_2SO_4 solution in double-junction vessel was used in the electrochemical test.

The temperature of the synthesis solution was kept constant by water bath (Optima, Tokyo, Japan). Capacity and cyclelife tests of the constructed batteries were performed by multi-channel battery tester (CEMT Co., China).

2.3. Procedure

2.3.1. Electrode preparation

In order to make leaden electrodes, pure lead was melted in 400 °C and was cast in a home-made steel mould. The structure and dimensions of the electrode which obtained by the casting method is shown in Fig. 1.

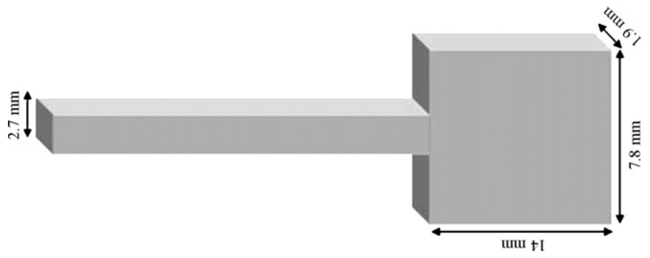

Fig. 1. Scheme and dimensions of the used electrode.