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Synthesis of Sub-Micro and Nanometer Sized Lead Oxide by Sol-Gel Pyrrolysis Method and Its Application as Cathode and Anode of Lead-Acid Batteries

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The overall goal of this program was to obtain an easy method for synthesizing more porous nano-structured lead oxide. Such structure probably can be useful as pigment and active material of lead-acid batteries. This paper discusses the results of a research aimed at investigating the synthesis of nanostructured lead oxide through sol-gel pyrrolysis method. In this method, the amount of $Pb(NO_3)_2$, PVA, the mixed solvent composition, and the pyrrolysis temperature have an affect on the composition, morphology, and particles sizes of the sample. The degree of these effects was optimized by the "one at a time" method. The prepared lead oxide powder was characterized by relative gravimetrical density (RGD), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Under optimum conditions, unformed nanostructured lead oxide powder with more spongy morphology and particle size 14-83 nm was obtained. The synthesized lead oxide was first used as anode of lead-acid battery which coupled with industrial positive plates. At the other stage, the proposed powder was used as cathode material which coupled with industrial negative plates to make lead-acid battery. All industrial production steps for the lead-acid batteries were performed to produce small-sized laboratorial lead-acid batteries by using the synthesized nanometer sized particles. The laboratory-made batteries showed high discharge capacity (230 mA.h/g) and long cycle life.

Keywords: PbO; Nanopowder; Sol-Gel Method; lead-acid batteries

1. INTRODUCTION

Lead oxide is widely used in different industries special in pigments and lead-acid batteries. In the industrial production of lead-acid batteries, lead oxide (PbO) is used as initial active material of both anode and cathode of the batteries. In formation process, lead oxide can be converted to spongy lead in anode and lead dioxide in cathode.

Lead-acid batteries developed as widespread articles of commerce in over a century. The concept of lead-acid batteries came into existence with the research and inventions of Raymond Gaston Plante in 1860, although batteries containing sulfuric acid or lead components were discussed earlier [1]. Some advantage of lead-acid batteries include: low cost of manufacture, simplicity of design, reliability and relative safety when compared to other electrochemical systems. Relatively good specific power has caused widespread use of lead-acid batteries in starting, lighting and ignition of engine (SLI) purposes for vehicular (e.g., automotive, marine and aviation) applications. The lead-acid system has also found widespread use in traction batteries in gulf carts and boats. However, the use of lead-acid batteries for electric cars as an alternative to fossil fuels has been limited by the need for better specific energy and deep discharge cycle life.

Because of the above-mentioned advantages of lead-acid batteries, there is a big interest to improve and develop lead oxide characteristics so that more discharge capacity and more cycle life can be obtained. Many researches are conducted to improve discharge capacity of lead oxide and lead dioxide [2-10]. In recent years, there has been an increase in the amount of trends focusing on the methods to prepare nanoparticles with extended advantages.

During the last few years, the synthesis of nano-structured oxide materials has attracted considerable attention [11–15]. The lead element has many oxide forms including PbO (α, β and amorphous), Pb_2O_3, Pb_3O_4, PbO_2 (α, β and amorphous). Among lead oxides, lead dioxide (PbO_2) has been studied more than any other forms. A number of electrochemical techniques have been used to prepare lead dioxide some of which are constant current and constant potential [16], cyclic voltammetry [17] and pulse current methods [18]. Shen and wei [16] deposited lead dioxide from a solution containing Pb^{2+} on there different substrates (i.e. Au, Pt and Ti) with different techniques.

We previously reported a new method for electrochemical synthesis of nanostructured PbO2 [19] and used the obtained PbO_2 as cathode of rechargeable lead-acid batteries [20]. Nevertheless, there are only few reports on the synthesis of lead oxide in nano-scale. Cruz et al. showed that the spray pyrrolysis method can be used for synthesis of lead oxide from lead salt solution; however, they did not focused on preparing nanostrures. They synthesized just a lead oxide thin film by spray pyrrolysis of lead salt solution on a preheated surface [21]. Konstantinov et al. used the spray pyrrolysis method for synthesis of nanostructured lead oxide. They had a systematic study of the effect of various spray pyrrolysis parameters such a temperature, solution concentration and solution flow rate on the morphology, crystallization process, crystal size and specific surface area. They synthesized globular shape lead oxide in the wide range of particle size of 20-127 nm [22]. We synthesized lead oxide nanoparticles by the sonochemical method from solution phase by two different precipitating agents and used it’s as cathode and anode of lead-acid batteries [23, 24].

Up to now there are few reports about the synthesizing of nanostructured materials by the sol-gel pyrrolysis method based on the polyvinyl alcohol (PVA) polymeric network. In the previous study, we fabricated CdO-ZnO nanocomposite by a new sol-gel pyrrolysis method based on the PVA network [25]. The obtained nanocomposite was used a sensing agent for the determination of CO [26].

The overall goal of this program was to obtain an easy method for synthesizing more porous nano-structured lead oxide. Such structure probably can be useful as pigment and active material of lead-acid batteries. In this work, we report a simple chemical method for synthesizing of lead oxide as positive and negative materials of lead-acid batteries.

2. EXPERIMENTAL

2.1. Chemicals and reagents

All materials and reagents used in these experiments were of reagent grade and were produced in the Loba Chemie Co. (India). Double-distilled water was used in all experiments. The calcium-tin-lead alloy was used for electrode making.

2.2. Instrumentals

A scanning electron microscope from Philips Co. (XL30) was used for the studying of the morphology and the particle size of the prepared lead oxide nanopowders. X-ray diffraction (XRD) studies were performed by a Decker D8 instrument.

2.3. Procedure

2.3.1. Synthesis of lead oxide nanopowder

Reagent grade lead acetate and polyvinyl alcohol (PVA) were used as the precursors. 200 ml mixture of lead acetate (2.5 wt %), PVA (8 wt %) and water/ethanol (40/60 V/V) was heated at 80 ºC to produce a transparent solution which called “sol”. The obtained sol was heated to evaporate major of its solvent and obtain a more viscous gel. The obtained gel was calcinated at 500 ºC for 5 h. At calcination process, nano-structured lead oxide was formed in nanopowder form. After milling, relative gravimetrical density (RGD) of the obtained powder was determined by a simple gravimetrical method. The morphology, particles sizes, and the composition of the obtained powder were studied by the scanning electron microscopy and XRD.

2.3.2. Battery construction and test

The scheme of the used electrode (grid) is shown in Fig. 1. Negative paste was prepared conventionally with the formulation which it is shown in Table 1. The required amounts of lead oxide nanopowder, carbon balk, barium sulfate, 1,2-acid (α-hydroxy β-naphtoic acid), Humic acid and polyacrylamide fibers were mixed together in a small paste mixer for 15 min. 0.5 ml water (per 1 g lead oxide) was added to above mixture and mixed for 5 min. Then, 1 ml sulfuric acid (1.25 g/cm^3) was gradually added. Paste was mixed for a period of time so that it becomes suitable for pasting.

Paste temperature was kept lower than 60 ºC. The prepared negative paste was pasted on the pasting hole of electrode (a one-hole plate, see Fig. 1).

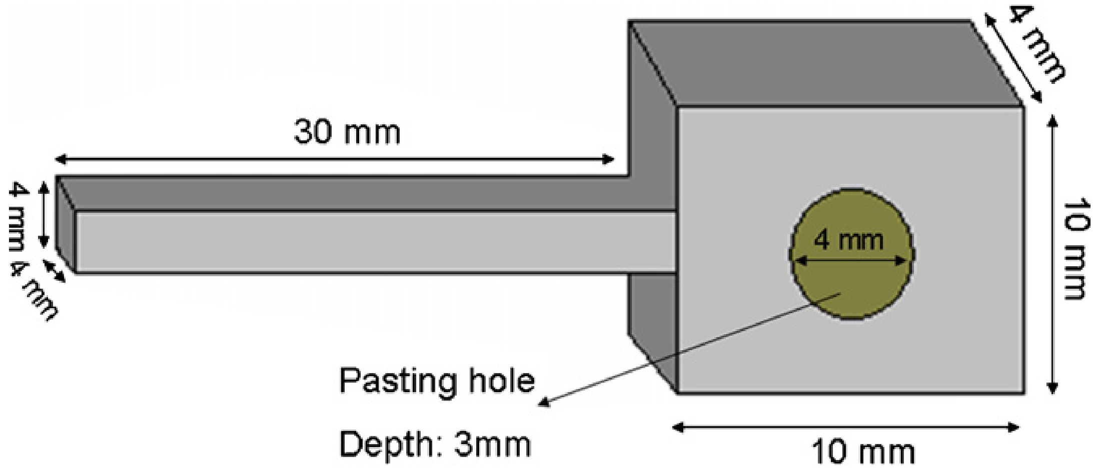

Figure 1. Scheme and dimensions of the used electrode

Table 1. The conventional formulation of negative paste for the used batteries

Compound	%wt
Lead oxide powder (or nanopowder)	99.27
Carbon black	0.15
Carboxy Methyl Cellulose	0.10
Humic acid	0.10
1,2-Acid	0.10
Barium Sulfate	0.20
Polyacrylamide Fiber	0.08

Positive paste was prepared conventionally and the process of preparation was exactly similar to that’s of negative paste. It should be mentioned that the positive paste includes only carbon black as additive. The positive paste was pasted on the one-hole electrode (Fig. 1) as negative pasted electrode.

The pasted negative and positive electrodes were cured in a small laboratory home-made curing vessel at relative humidity of 95% and temperature of 70 ºC. The cured pasted electrodes were dried at 80 ºC for 6 h. Each dried negative pasted electrode was coupled with a commercial positive plate (from Aranniru Co., Iran) and also each dried positive pasted electrode was coupled with a commercial negative plate (from Aranniru Co., Iran) to make the proposed batteries. It should be mentioned that the conventional pasted electrodes had electroactive materials more than the electrodes pasted with nanopowder materials. The electrochemical formation process of the constructed batteries was performed at sulfuric acid solution with density of 1.24 g/cm^3 using constant voltage method (2.48 V per cell) for 48 h. The discharge capacity and cycle life tests were done according to Iranian standards.

3. RESULTS AND DISCUSSION

3.1. Synthesis of PbO nanopowder

In this method, four factors including PVA and lead acetate amounts, solvent composition, and synthesis temperature can affect on the phase composition, particles sizes and morphology of samples. The effect of these parameters was studied by the "on at a time" method [26].

At the proposed method, the gel network rigidity controls the morphology and particle size of the synthesized sample to make uniform PbO nanoparticles. In the gel structure, lead acetate was homogeneously dispersed among polymeric network. Because of the gel network rigidity, the dispersed ions in the gel network can not alter their positions. Therefore, during the pyrrolysis of the gel's outer layers, the lead acetate molecules of the burnt layers connected together to form agglomerated particles. At pyrrolysis temperature, the agglomerated molecules are calcinated to lead oxide nanoparticles. The chemical reaction of the pyrrolysis process is as following:

$$Pb(CH_3COO)_2 + 2O_2 \xrightarrow{Heat} PbO + 3H_2O + 2CO_2$$

We previously reported that for an identified compound, by decreasing in relative grammatical density (RGD), porosity and effective area of the product can be increased [26]. It is obvious that, high surface area and high porosity of active materials of batteries can cause high performance for these materials. Therefore, RGD was used as optimizing parameters in all experiments. First, seven samples were synthesized at different PVA concentrations. Figure 2 shows the effect of PVA amount on the RGD of the samples.

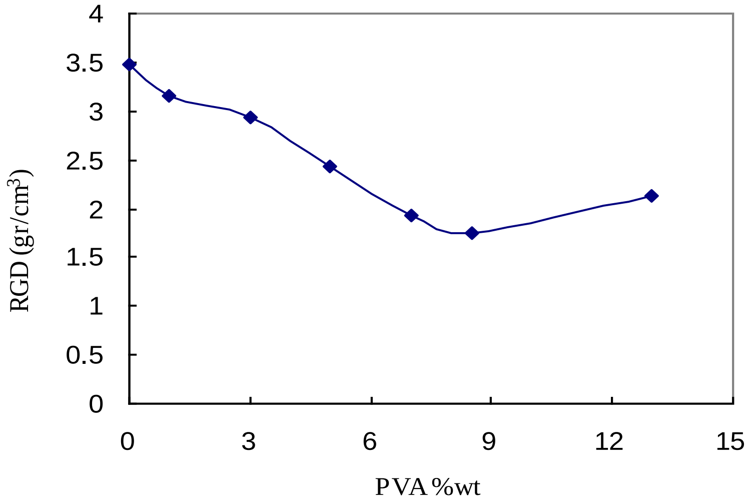

Figure 2. Effect of PVA concentration on the relative gravimetrical density (RGD) of PbO

Based on the shown data in Fig. 2, PVA content is an important factor which controls sample porosity. The gel network is completed when the PVA %wt is increased from 0 to 8.5 %wt. The lowest RGD can be obtained in the full completed gel network. At higher amounts (higher than 8.5 %wt), total amounts of the initial PVA can not dissolve in the used solvent so that, the obtained gel is not homogeneous.

Figure 3 shows the SEM image of the lead oxide sample that synthesized in PVA 8.5 wt%. As it is obvious in Fig. 3, the sample includes lead oxide particles with average size of 1000 nm.

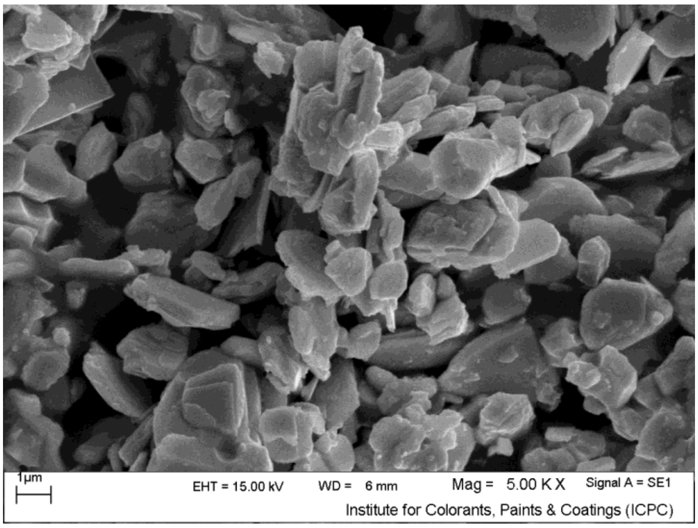

Figure 3. SEM image of PbO sample synthesized at PVA concentration of 8.5 %

As it was mentioned, it is expected that the synthesis performance depends on lead acetate concentration. To evaluation of this factor, five samples were synthesized in different lead acetate concentrations. The effect of lead acetate concentration on the RGD was shown in Fig. 4. As it can be seen in Fig. 4, lead acetate concentration can strongly change the sample RGD. At lower concentrations, the synthesized sample includes particles with low specific surface area and high density. At 2.5 %wt lead acetate, the synthesized sample has the lowest RGD. At this level, the ratio of PVA to lead salt is suitable to make a rigid and uniform gel network. At higher concentrations, the excess amount of lead salt disturbs the gel network.

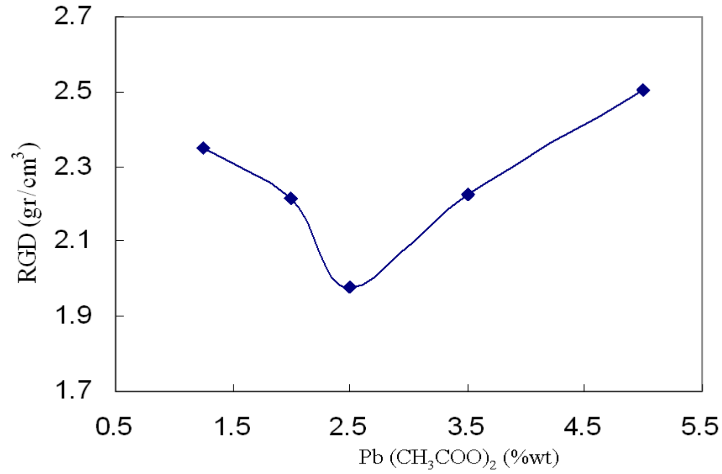

Figure 4. Effect of lead acetate concentration on RGD of PbO samples

Figure 5 shows the SEM image of the sample synthesized at 2.5 %wt lead acetate. As it is obvious in Fig. 5, the sample includes non-uniform sub-micro lead oxide particles.

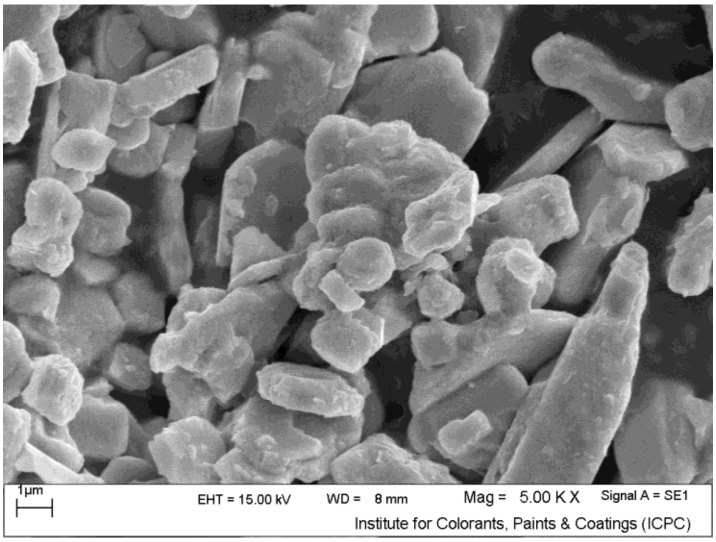

Figure 5. SEM image of PbO sample synthesized at 2.5 %wt lead acetate

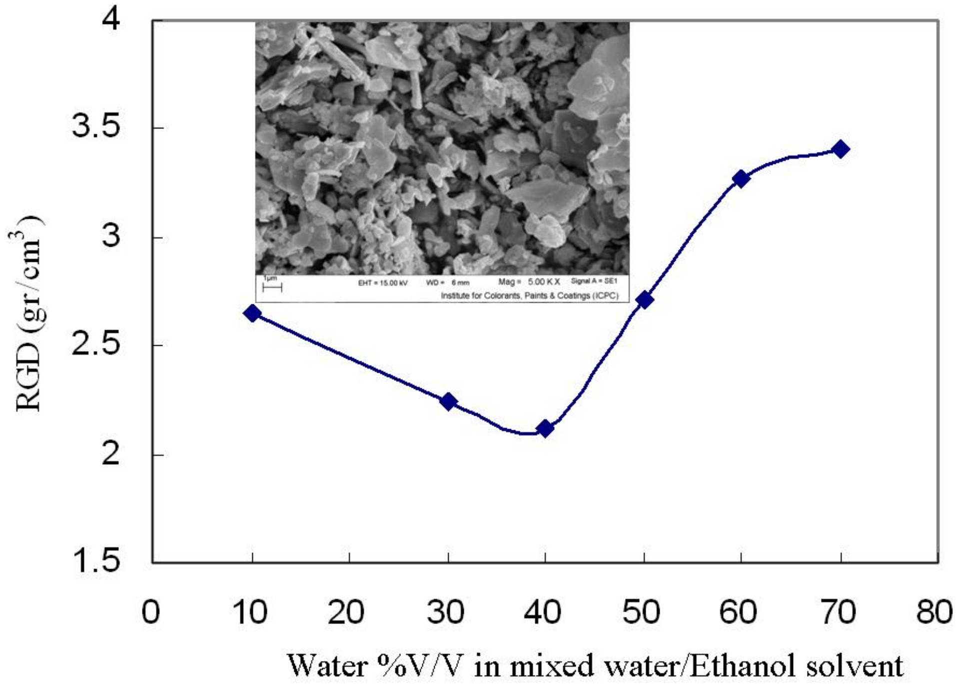

Figure 6. Effect of ethanol/water ratio in the mixed solvent on the RGD of PbO samples and the SEM image of PbO sample synthesized at water/ethanol 40:60 ratios as inserted picture.

Third factor that can affect on the synthesis is the solvent composition. To evaluate the effect of this factor, six synthesizes were performed in different compositions of mixed water/ethanol solvent.

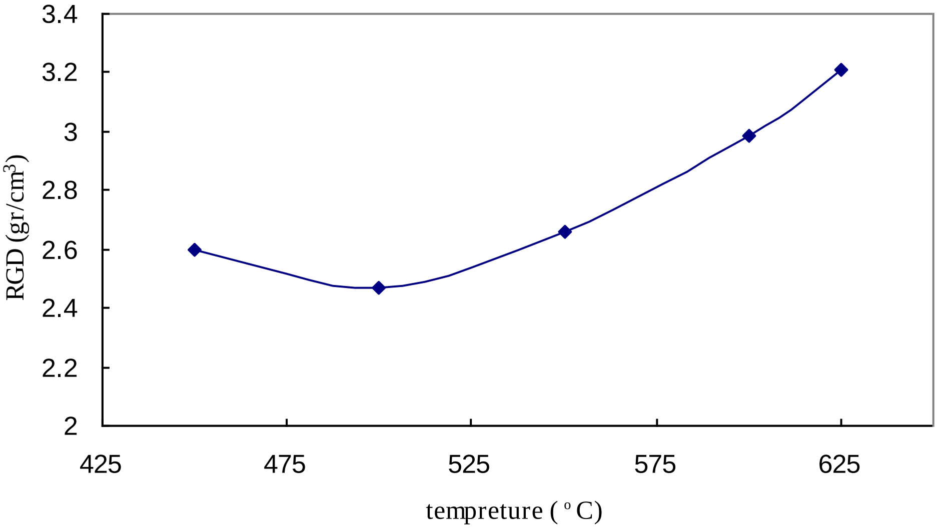

Figure 8. Effect of pyrrolysis temperature on the RGD of PbO samples

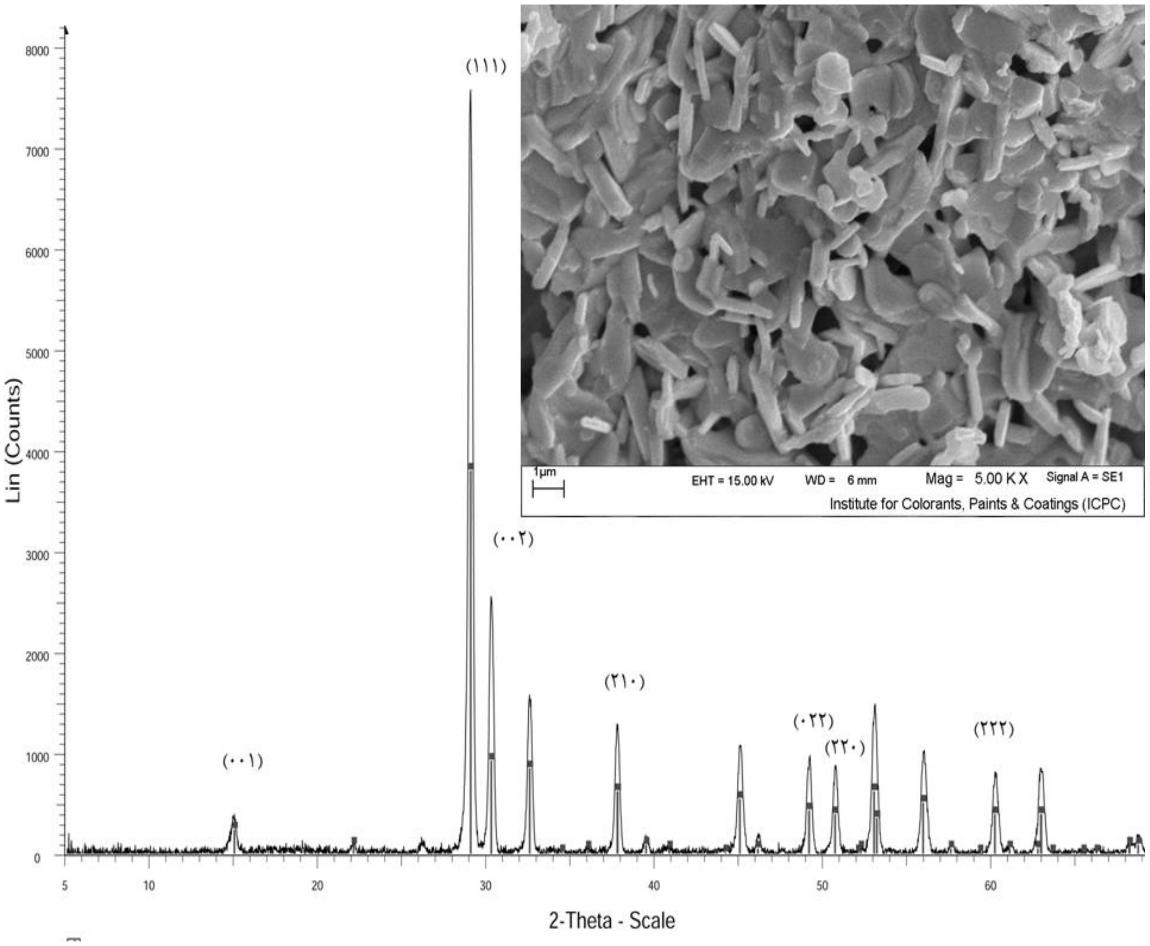

Figure 9. XRD patterns and SEM image of the PbO sample synthesized at 8.5 5wt PVA, 2.5 %wt lead acetate, 40:60 water/ethanol mixed solvent and 500 °C.

The effect of water/ethanol ratio on the RGD of the samples and SEM image of the optimum sample as inserted was shown in Fig. 6. The ethanol content in mixed solvent controls its polarity, consequently the solubility of PVA and lead salt. At 40:60 water/ethanol, solvent polarity is the best to dissolve completely PVA and lead salt. The inserted SEM image in Fig. 6 shows that this sample has smaller particles with respect to the previous samples which shown in Figs 3 and 5.

Based on the previous reports [23, 24], the pyrrolysis temperature is more important parameter which can affect on the morphology, particles sizes and the phase composition of samples. Therefore, 5 samples were pyrrolysis at different temperature in the range 450 to 650 °C. Figure 7 shows the effect of pyrrolysis temperature on the RGD of the synthesized samples. Nucleation and particle growth rates can be adjusted by variation of pyrrolysis temperature. In pyrrolysis temperature of 500 °C, these two kinetic rates are suitable to form a low density and more porous nanopowder. At higher temperature, PbO decomposed to melted lead and oxygen. Figure 8 shows the XRD patterns and SEM image of the sample synthesized with solution temperature 500 °C. Based on XRD patterns, the sample had only PbO. As it can be seen in Fig. 9, the synthesized sample includes nanometer sized and sub-micro sized PbO particles.

3.2. Battery construction and test

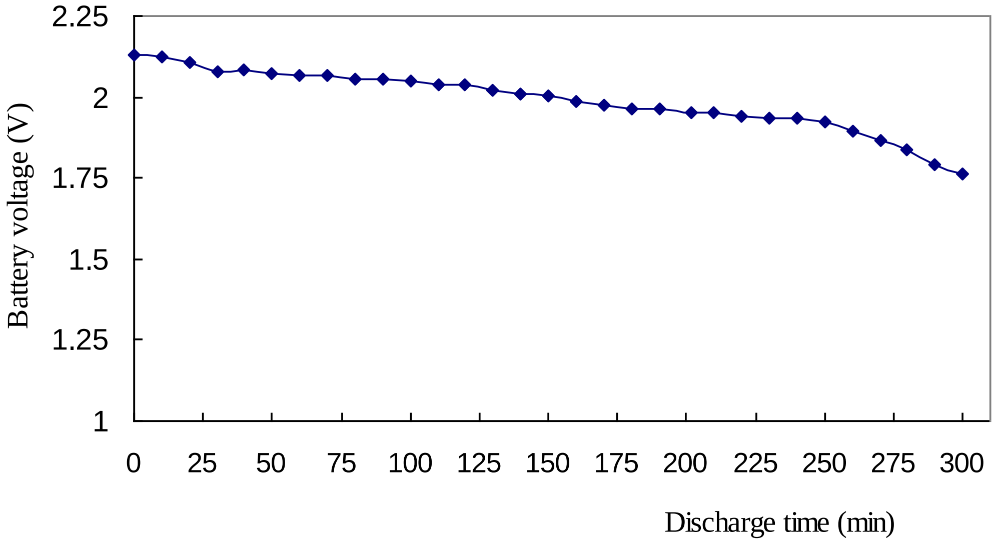

Figure 10. Time-voltage behavior for the lead-acid battery constructed with nanostructured lead oxide as anode (coupled with a larger industrial cathode)

The optimized sample (according to section 3.1), was used as anode and cathode of laboratory-made lead-acid batteries. For this propose, PbO nanopowder was mixed with conventional additives to make negative paste (according to Table 1). The prepared negative paste was pasted on the hole of the designed electrode (Fig. 1). The PbO nanopowder was mixed with carbon black and sulfuric acid exactly according to the industrial method to make positive paste. The positive paste was also pasted on the hole of the electrode (similar with negative electrode). The pasted negative and positive electrodes was cured and dried. Each final negative electrode was coupled with larger industrial positive plate to construct a single unit lead-acid battery. Each final positive electrode was coupled with larger negative industrial plate to obtain a single unite battery. The designed batteries were filled with sulfuric acid and initially charged to form electroactive materials. The formed batteries were tested by constant resistance method to determine their discharge capacities. Figure 10 shows the time-voltage behavior of the battery including nanostructured negative electrode.

As it can be seen in Fig. 10, the battery with nanostructured PbO as anode electroactive material has a high discharge capacity. For more clarification of this concept, time-current density of the discharge curve based on the presented data in Fig. was shown in Fig. 11.

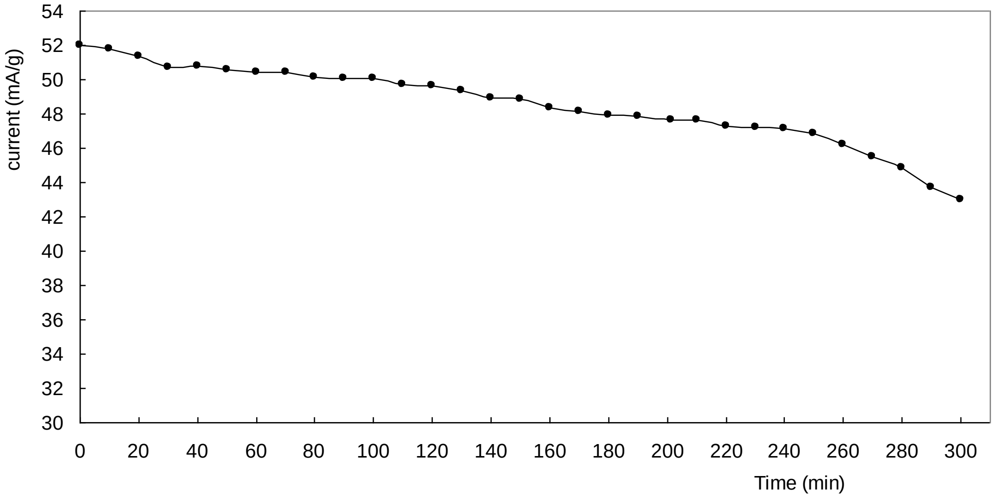

Figure 11. Time-current curve for discharge of the battery constructed with industrial cathode and nanostructured anode.

Based on the data presented in fig. 11, the battery reveals the highest discharge capacity (230 mA.h/g) exactly same with its theoretical capacity.

In other experiment, discharge capacity of the battery constructed with industrial negative plate and nanostructured positive electrode was studied. Figure 12 shows the time-voltage behavior of the assembled battery. Based on these data, time-current data was calculated point by point. Figure 13 shows the time-current curve for the discharge process. Based on Figs. 12 and 13, the discharge capacity is 120 mA.h/g. This capacity is normal value for lead-acid batteries. Comparing of the results of anode and cathode studies shows that the synthesized nanostructured lead oxide acts successfully as anode of lead-acid batteries. This concept can be related to the special morphology of the synthesized nanoparticles. The synthesized nanoparticles in oxidation process (in charge step) are converted into lead dioxide. It should be mentioned that special volume of lead dioxide is more than lead oxide so that, in charge process, nanoparticles connected together to make good electrical conductivity. On the other hands, lead oxide has more volume with respect to metal lead. Therefore, when lead oxide converts to metallic lead, some connectivity of the particles are probably broken. The lose of electrical connectivity cause to obtain low discharge capacity.

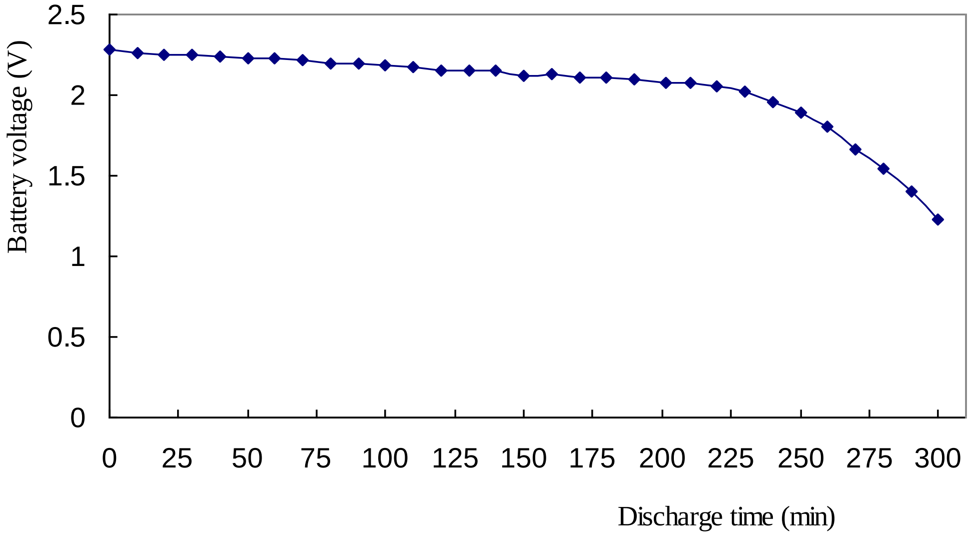

Figure 12. Time-voltage curve of lead-acid battery constructed with industrial anode and nanostructured cathode

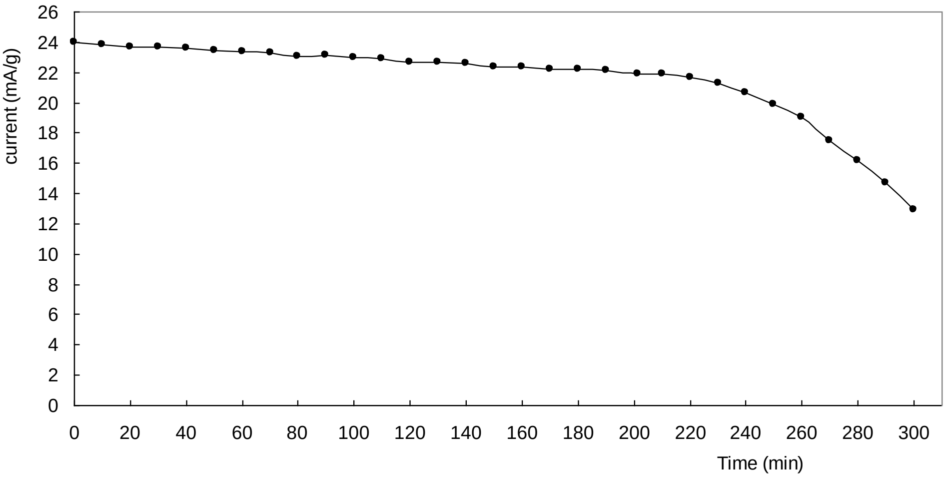

Figure 13. Discharge time-current of lead-acid battery constructed with industrial anode and nanostructured cathode

4. CONCLUSIONS

Sol-gel method can be used as a powerful method to synthesize uniform nanopowder of PbO. The more porous and uniform lead oxide nanopowder can be used as cathode and anode electroactive material in lead-acid batteries. The anodes prepared by lead oxide nanoparticles show very excellent discharge capacity. Lead oxide nanoparticles are better anodic material that cathode material.

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