



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 4.8M 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 -naphthoic 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.

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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 -naphthoic 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 m² 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-naphthol [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 $\text{Pb}(\text{NO}_3)_2$ 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 $\text{Pb}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 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 $\text{Pb}(\text{NO}_3)_2$ in HNO_3 .

The influence of the ultrasonic intensity on the electrocrystallization of lead dioxide on glassy carbon electrodes was reported by González-García 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]. Vastitas 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 $\beta\text{-PbO}_2$ 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 -naphthoic 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 its 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 $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) 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.

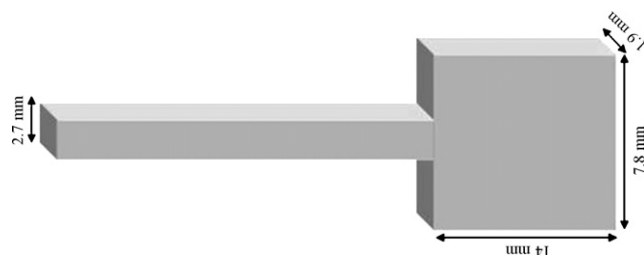


Fig. 1. Scheme and dimensions of the used electrode.

Table 1The effect of synthesis temperature on the phase composition of direct electrochemical oxidation of lead substrate^a.

Temperature (°C)	Frequency (Hz)	Component (wt%)					
		PbO	PbO·4H ₂ O	α-PbO ₂	β-PbO ₂	PbSO ₄	Pb ₄ O ₃ SO ₄ ·H ₂ O
0	12	30.5	14.15	33.96	0.0	0.0	21.38
20	12	41.16	23.49	0.0	0.0	0.0	35.34
45	12	55.70	0.0	0.0	8.10	36.21	0.0
70	12	52.98	10.28	10.27	4.02	0.0	16.37
100	12	45.58	10.46	6.43	24.13	0.0	13.40
45	6	36.98	0.0	0.0	32.50	30.52	0.0
45	0	0.0	0.0	1.12	88.67	10.21	0.0

^a All experiments were performed in 4.8 M sulfuric acid and pulse height of 33 mA cm⁻².

2.3.2. Lead dioxide synthesis

Before each deposition, the lead electrode was placed in the concentrated HNO₃ for 30 s and then rinsed with double-distilled water to remove any surface oxidized species in contact with air.

Two graphite electrodes coupled with the prepared lead electrode as anode of the electrochemical cell. The electrodes were put in 4.8 M sulfuric acid solution. Different rates of the pulsed current were applied for oxidizing of the lead substrate. For conversion of the different synthesized species (PbO, PbSO₄, PbO·4H₂O and Pb₄O₃SO₄·H₂O) to lead dioxide, one charge stage was used after pulse stage. The charge process was performed by constant voltage method (2.48 V) for at least 2 h. After performing charge process, all synthesized species at pulsed current stage were converted to lead dioxide. By applying pulse and charge steps, nanostructured lead dioxide was directly synthesized on the surface of the lead electrode (positive electrode) by oxidation of the lead substrate.

The effect of all parameters of the synthesis including H₂SO₄ concentration, synthesis temperature, pulse frequency and pulse current was optimized by a “one at a time” method.

For the investigation of cyclic voltammetric behavior of the nanostructured lead dioxide, the prepared electrode was used as a working electrode which coupled with a platinum counter electrode and an Ag/AgCl reference electrode equipped with 1 M H₂SO₄ solution in double-junction vessel. It should be mentioned that before the experiment, the reference electrode with sulfuric acid solution in double-junction vessel was kept in sulfuric acid for 24 h. At this step, Ag⁺ ions from the reference electrode with sulfate ions from double-junction vessel forms the hardly soluble compound Ag₂SO₄, which deposits on the silver electrode and forms a Ag/Ag₂SO₄ electrode system. Hence, the potential of the Ag/AgCl reference electrode will be varied [57]. Our initial cyclic voltammetry experiments showed that the formation of Ag₂SO₄ will be complete after 24 h so that, the reference electrode potential will be constant. The cyclic voltammetry behaviors of nanostructured positive electrodes were studied in 1 M sulfuric acid electrolyte containing different concentrations of humic acid, 1,2-acid and Vanillex.

2.3.3. Battery production and test

Commercial negative and positive pasted electrodes were obtained from Aranniru battery manufacturing Co. and used without any improvement. The prepared nanostructured positive electrode (lead dioxide) by the suggested pulse method was coupled to the industrial negative electrode to form a lead-acid battery with nominal voltage of 2 V. To compare, a battery with two commercial negative plate and one positive plate was constructed and separately tested its performance in the presence of different concentrations of humic acid, 1,2-acid and Vanillex. In the all batteries, the used negative plates had more electroactive material and more effective surface area than the positive plates to limit the battery performance by positive active material. The battery charge process

was performed at sulfuric acid solution with density of 1.24 g cm⁻³ using constant voltage method (2.48 V per cell) for 24 h. Determination of discharge capacity for the constructed batteries were carried out by the constant resistance method [58]. The effect of humic acid, 1,2-acid and Vanillex on the electrochemical behaviors of the synthesized nanostructured lead dioxide and the discharge capacity and cycle life of the prepared and commercial positive plates of lead-acid batteries was tested.

3. Results and discussion

3.1. Synthesis of nanostructured lead dioxide positive electrode

Nanostructured lead dioxide was directly synthesized by the pulsed current method on the lead electrode in 4.8 M sulfuric acid solution. In the current study, a direct current with constant amplitude was supplied by a common power supply instrument. The output of the power supply system (DC current) was connected to a home-made pulse maker apparatus. The current output of the pulse system is a pulsed direct current as it is shown in Fig. 2. According to Fig. 2, there are 4 variable parameters for pulse system including pulse height, pulse time, relaxation time and pulse frequency. The results of our initial experiments indicated the desirability of relaxation time/pulse time ratio of 3 for majority of syntheses; therefore, the ratio of 3 was selected for further experiments. At a constant ratio of relaxation time to pulse time, a pulse system has 3 variable parameters including pulse height, pulse time and pulse frequency.

X-ray diffraction patterns were used for investigating the phase compositions of the prepared samples. The effect of different

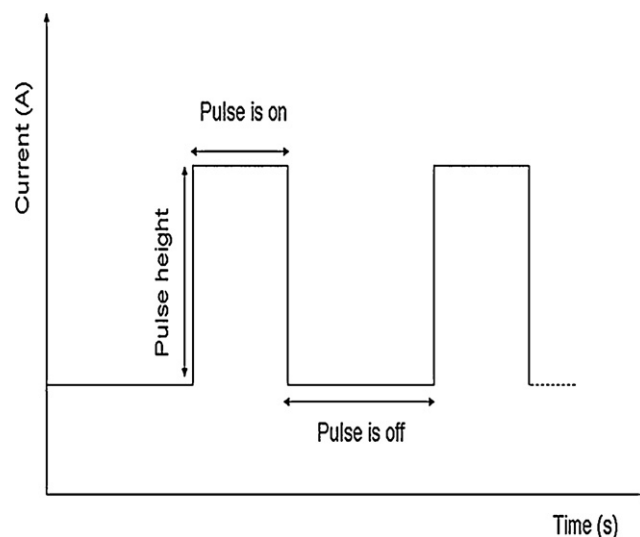


Fig. 2. Pulsed current diagram including pulse time, relaxation time and pulse height.

Table 2The effect of pulse frequency on the phase composition of direct electrochemical oxidation of lead substrate^a.

Temperature (°C)	Frequency (Hz)	Component (wt%)					
		PbO	PbO·4H ₂ O	α-PbO ₂	β-PbO ₂	PbSO ₄	Pb ₄ O ₃ SO ₄ ·H ₂ O
45	12	55.70	0.0	0.0	8.10	36.21	0.0
45	6	36.98	0.0	0.0	32.50	30.52	0.0
45	0	0.0	0.0	1.12	88.67	10.21	0.0

^a All experiments were performed in 4.8 M sulfuric and pulse height of 33 mA cm⁻².

parameters including pulse height, pulse frequency, sulfuric acid concentration and temperature of synthesis solution were optimized by the “one at a time” method.

3.1.1. Temperature effect

Among the synthesis parameters, solution temperature had more effect on the phase composition of the produced lead dioxide. As a result, temperature studies of lead dioxide synthesis were carried out by X-ray diffraction. Our initial studies showed that the synthesis temperature had an important role on the morphology and particles sizes of the oxidation products. Therefore, some syntheses were carried out at different temperatures of solution including 0, 20, 45, 70 and 100 °C. To highlight the results, the information of XRD studies has been summarized numerically in Table 1. As it is obvious from Table 1, at 45 °C lead substrate oxidized to PbO (55.7 wt%), PbSO₄ (36.21 wt%) and β-PbO₂, while it can be produced as α-PbO₂ and some other species can be produced at other temperatures. The obtained data (Table 1) are different from previous reports [59–61]. For insurance about accuracy of this data, the experiments were repeated two times. The obtained results were same. This difference is probably related to oxidation method. In the previous reports, oxidation has been performed by constant current and or constant voltage methods. In the pulse method, the mechanism of oxidation can be different with other method so that the oxidation products are different. All of these experiments were performed under pulsed current amplitude of 33 mA cm⁻² and pulse frequency of 12 Hz. By use of this current, cell voltage was increased up to 2.8 V. This voltage in double-electrode system is enough for oxidation of lead to lead dioxide. Oxidation of the lead electrode during the pulse current stage results in formation of mostly bivalent lead compounds (Table 1). Cell voltage measurements showed that the voltage amplitude is enough for oxidation of lead to lead dioxide. This indicates that the oxidation potential is enough but, oxidation time at the used pulse was not enough for complete oxidation of lead. Two experiments were done at temperature of 45 °C and pulse frequency of 0 and 6 Hz and, the obtained samples analyzed by XRD. The obtained results were shown in Table 2. Investigating of these results shows that oxidation degree is increased when the pulse frequency is decreased (this means pulse time is increased). Phase composition for the sample synthesized by simple constant current (without pulse; 0 Hz) is same with those previously reported [59–61]. More evaluation of pulse frequency was shown in Section 3.1.3. To select an optimum temperature value, SEM was used to study the morphology and particle size of the samples prepared at different temperatures. The SEM images of the synthesized particles showed that 45 °C is the most optimum temperature to yield the smallest size and most uniform particles. The obtained results are probably related to the fact that at this temperature (45 °C), growth rate, nucleation rate and agglomeration rate are suitable for forming more uniform and smaller particles. Based upon the obtained information from SEM studies, the temperature of 45 °C is the optimum value for the synthesis of the uniform nanostructures, but the data of Table 1 (XRD results) shows that at this temperature, lead substrate can be oxidized to lead dioxide at low yield percent (8.1 wt%). Our studies showed that in the pulse method the lead dioxide could not be synthesized in more per-

centages by varying of synthesis parameters. Therefore, to convert the other synthesized species to lead dioxide, a charge stage after synthesizing the sample was added. Comparing the SEM images of the sample before and after charge process indicated that charge step could not considerably affect on the morphology and particle size (Fig. 3). XRD studies for the sample after the charge process showed that there was only lead dioxide species (β-PbO₂). Therefore, in all the following experiments, charge process was carried out after synthesis processes.

3.1.2. Effect of pulse height

The effect of pulse height (current amplitude) on the particle size of the synthesized lead dioxide was investigated. The pulse height was varied from 33 to 202 mA cm⁻² while the other parameters were kept constant (temperature of 45 °C, pulse frequency of 12 Hz and sulfuric acid concentration of 4.8 M). The morphology and particle size of produced lead dioxide was studied by SEM. Five different current amplitudes were used in this series of optimization experiments. The morphology and particle size of the obtained lead dioxides are shown in Fig. 4. As it is seen in

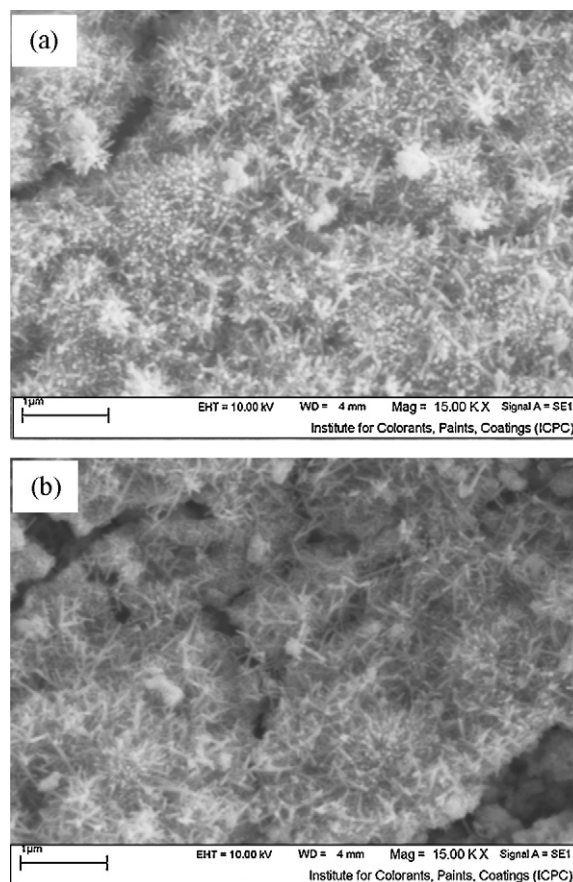


Fig. 3. SEM images of the synthesized nanostructured positive plate before (a) and after charge process (b).

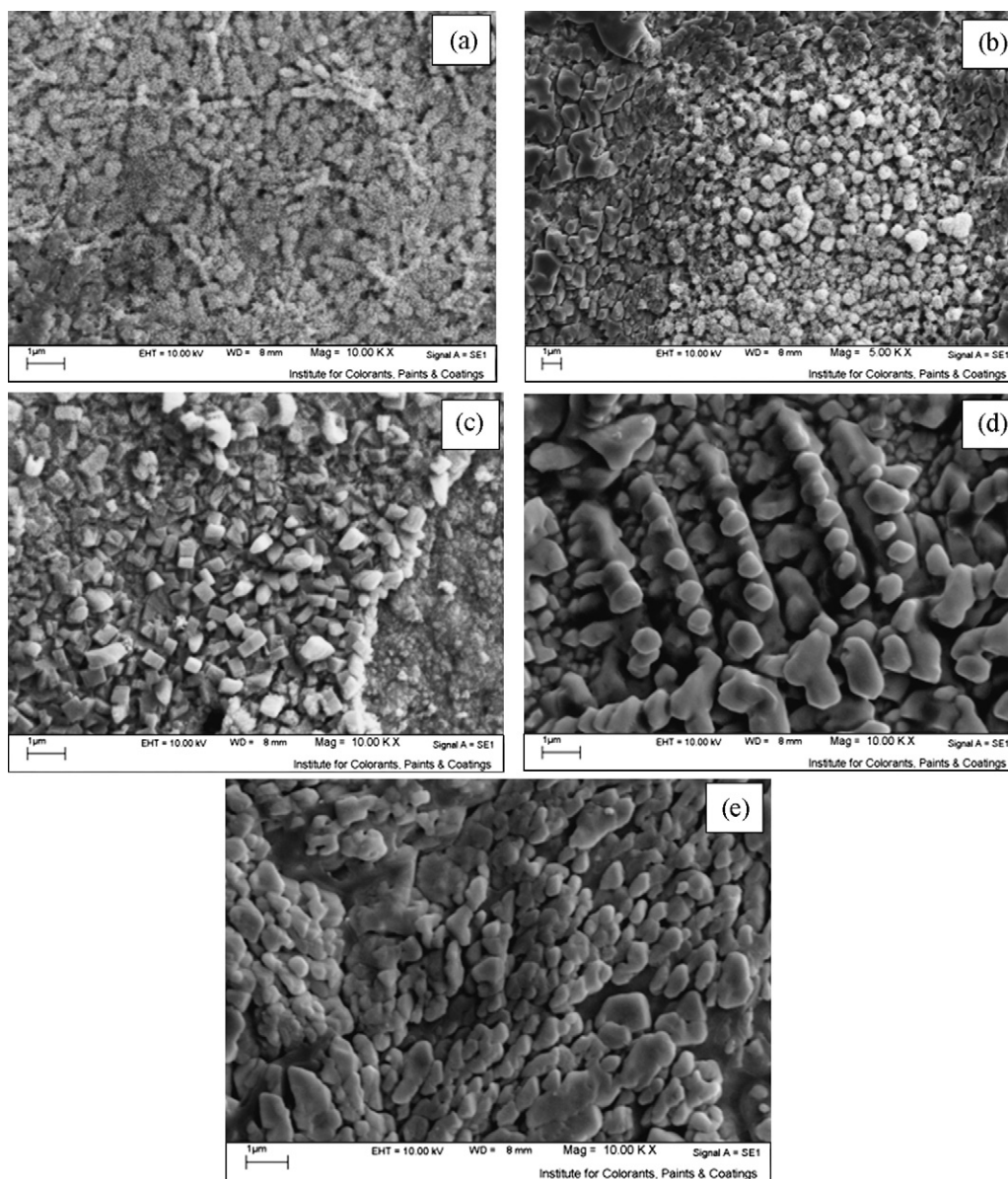


Fig. 4. SEM images of lead dioxide samples synthesized at different pulse heights; 33 mA cm^{-2} (a), 50 mA cm^{-2} (b), 67 mA cm^{-2} (c), 135 mA cm^{-2} (d) and 202 mA cm^{-2} (e) (the other experiment conditions including pulse frequency, temperature and sulfuric acid concentration were kept constant).

Fig. 4, the pulse height (current amplitude) of 33 mA cm^{-2} makes more uniform and smaller particles than the others. At lower pulse heights, the synthesis rate is very slow therefore the synthesis time will be very long. Based on this concept, the pulse heights lower than 33 mA cm^{-2} were not studied. The large crystalline lead dioxide is appeared as the pulse height is increased. It can be related to this fact that the higher currents make higher rates for the nuclear growth. At pulse height of 67 mA cm^{-2} and more, the more nuclear growth rate provides large crystals of lead dioxide. The more pulse heights (more than 135 mA cm^{-2}) make very high nuclear growth thus the produced lead dioxide will be amorphous (Fig. 4e).

3.1.3. Effect of pulse frequency

In the present method, each pulse cycle consists of one pulse time and one relaxation time, and the pulse frequency (f) includes numbers of pulse cycles in the time unit (s). In the current work, the ratio of relaxation time to pulse time is kept constant of 3 therefore, the pulse time (t_{on}) and relaxation time (t_{off}) can be easily calculated

from pulse frequency (Eqs. (1) and (2)):

$$t_{\text{on(s)}} = \frac{1}{4f} \quad (1)$$

$$t_{\text{off(s)}} = \frac{3}{4f} \quad (2)$$

In order to investigate the effect of pulse frequency on the morphology and particles size of the produced lead dioxide, the pulse frequency was varied from 0 to 18 Hz at temperature of 45°C , sulfuric acid concentration of 4.8 M and pulse height of 33 mA cm^{-2} . Fig. 5 shows the SEM images of lead dioxide samples of this experimental series. As it is seen from Fig. 5, at simple DC current (frequency of 0), lead dioxide particles make more agglomerations. At the frequency of 6 Hz, the agglomerations of lead dioxide are decreased, but the nanoparticles are less uniform. At the frequency of 12 Hz (Fig. 5c), it can be seen that the nanoparticles are smaller and more uniform. The lead dioxide nanoparticles are changed to short nanorods. As it is seen from Fig. 5d, the uniform nanorods are slowly transformed to large crystalline lead dioxide. Fig. 5e

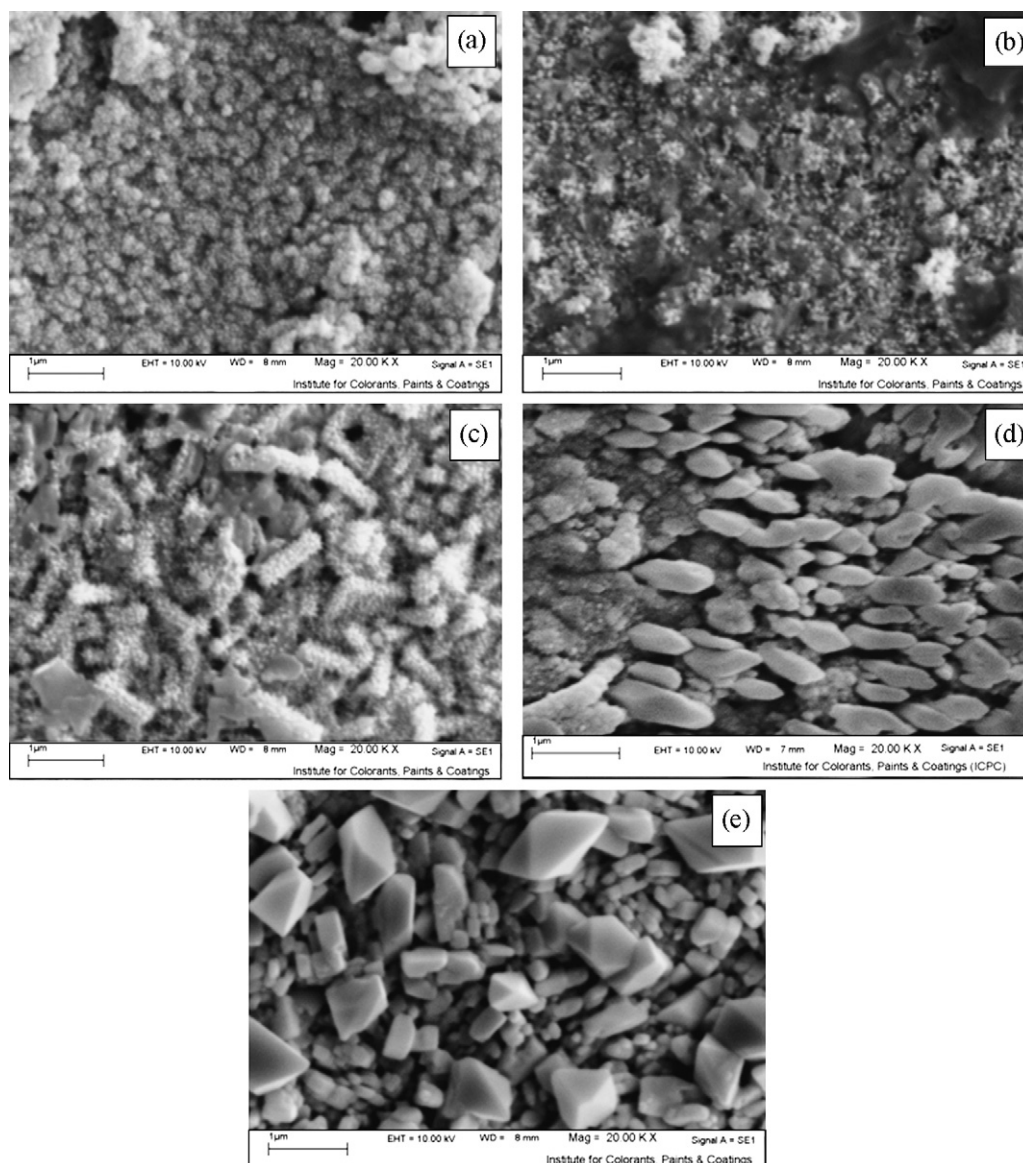


Fig. 5. SEM images of lead dioxide samples synthesized at different pulse frequencies of 0 Hz (a), 6 Hz (b), 12 Hz (c), 18 Hz (d) and 24 Hz (e).

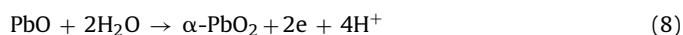
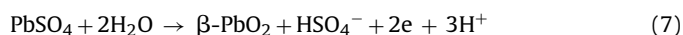
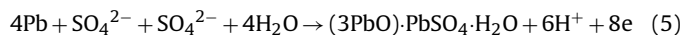
shows that higher frequencies make lead dioxide in large crystalline forms.

At lower frequencies (0 and 6 Hz), nucleation rate is high and the lead dioxide crystals grow irregularly and are connected to each other to make agglomeration bulks. At the frequency of 12 Hz, nucleation rate and nuclear growth rate are suitable so that the nanoparticles are synthesized in uniform nanorods. At higher frequencies, nuclear growth rate of lead dioxide crystals is more than nucleation rate so that the large crystalline particles are synthesized. Therefore, the frequency of 12 Hz was selected as an optimum pulse frequency for electrochemical syntheses of nanometric lead dioxide.

3.1.4. Effect of sulfuric acid concentration

Sulfuric acid solution is used as an electrolyte for all lead-acid batteries. Pavlov et al. have studied the effect of sulfuric acid on lead-acid performance, phase composition of PbO_2 and other properties of lead-acid batteries [62]. They showed that lead sulfate solubility depends strongly on sulfuric acid concentration. Phase type of PbO_2 also depended on pH of the synthesis electrolyte. When the current pulse is applied to the electro-synthesis cell, the

pure lead is oxidized to various forms of lead sulfate (such as PbSO_4 , $\text{PbO}\cdot\text{PbSO}_4$, $2\text{PbO}\cdot\text{PbSO}_4$, $3\text{PbO}\cdot\text{PbSO}_4$ and $4\text{PbO}\cdot\text{PbSO}_4$) then, all forms of lead sulfate are oxidized to PbO_2 . Peterson et al. [32] proposed the overall reaction for the preparation of PbO_2 as follows:



As it is obvious, $\alpha\text{-PbO}_2$ is produced by oxidation of PbO (Eq. (8)), while $\beta\text{-PbO}_2$ is formed by oxidation of PbSO_4 (Eq. (7)). Based on the type of the applied electrochemical technique and the experimental conditions, different proportions of $\alpha\text{-PbO}_2$, $\beta\text{-PbO}_2$ and PbSO_4 are synthesized.

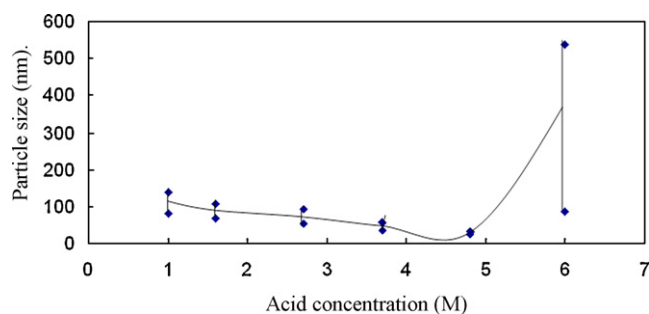


Fig. 6. Effect of sulfuric acid concentration on the range of lead dioxide particles size.

Regarding the important role of acid concentration on lead dioxide synthesis, the effect of sulfuric acid concentration on particles size was investigated. The concentration of sulfuric acid solution was varied from 1 to 6 M (at temperature of 45 °C, pulse frequency of 12 Hz and pulse height of 33 mA cm⁻²).

Morphology and particles size of each sample were studied by SEM. The data obtained from SEM studies was used to sketch (Fig. 6). The presented diagram in Fig. 6 shows that the acid concentration of 4.8 M makes the most uniform and the smallest nanoparticles. The results of this experiment reveal that acid concentration of 4.8 M can be used as a suitable electrolyte for lead-acid batteries. The obtained results are exactly in accordance with the previous reports about the acid concentration for lead-acid batteries [62]. At lower concentration of sulfuric acid, the solubility of lead sulfate, as an intermediate of lead dioxide synthesis, is different so that the morphology and particles size of the lead dioxide will be different. Therefore, at major applications of the lead-acid batteries, sulfuric acid of 4.8 M is used as an electrolyte.

3.2. Electrochemical studies of the synthesized nanostructured lead dioxide

The electrochemical behavior of the nanostructured lead dioxide in the presence of humic acid, 1,2-acid and Vanillex was studied by the cyclic voltammetry technique. The electrochemical processes of forward and backward scans of cyclic voltammetry are exactly similar with those carried out in charge/discharge processes of lead-acid batteries. Therefore, for investigating the cycle-life of the synthesized lead dioxide, the cyclic voltammetric behavior was studied during 45 cycles under 10 mV s⁻¹ potential scan rate and in 1 M sulfuric acid (Fig. 7). As it is seen from Fig. 7, lead dioxide is reduced to lead sulfate at the potential of 1.2 V (vs. Ag/AgCl), and lead sulfate is

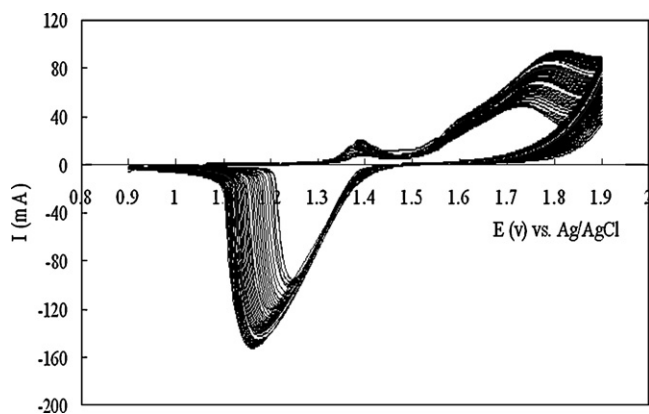


Fig. 7. Cyclic voltammograms of the synthesized lead dioxide vs. Ag/AgCl reference electrode under potential scan rate of 10 mV s⁻¹ and in 1 M sulfuric acid solution during 45 cycles.

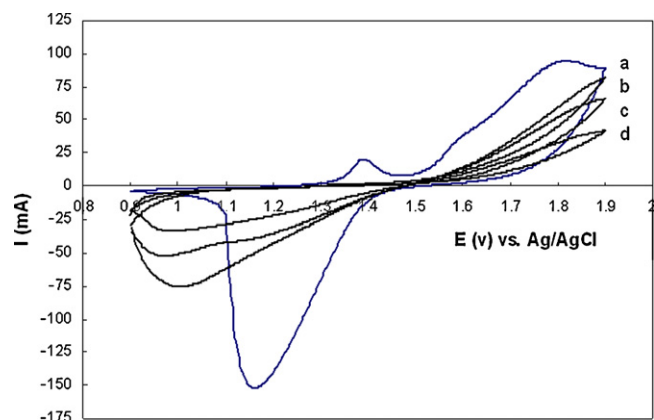


Fig. 8. Cyclic voltammograms of the synthesized lead dioxide vs. Ag/AgCl reference electrode under potential scan rate of 10 mV s⁻¹ and in 1 M sulfuric acid solution in the absence of any organic additive (a), saturated with 1,2-acid (b), humic acid (c) and Vanillex (d) at 45th cycle.

oxidized to lead dioxide at 1.75 V. The obtained results showed that there was not any considerable decreasing for peak currents during 45 cycles. It can be concluded that the synthesized lead dioxide will have good cyclic life when it is used as a positive electrode for lead-acid batteries.

The effect of humic acid, 1,2-acid and Vanillex on the cyclic voltammetric behavior of the nanostructured lead dioxide during 45th cycle were shown in Fig. 8. As it is obvious in Fig. 8, reduction and oxidation peaks currents of lead dioxide reduce in the presence of organic expanders. This concept means that the organic expanders cause to reduce the kinetic rate of reduction and oxidation reactions. The kinetic rate drop can make a considerable drop in cyclife of positive plates.

The obtained results reveal the following order for the cyclife of the nanostructured positive electrode:

Pure sulfuric acid > 1, 2-acid > humic acid > Vanillex

3.3. The effect of organic expanders on the discharge capacity and cyclife of the nanostructured lead dioxide

The final electrode coated by nanostructured lead dioxide was used as positive electrode of lead-acid batteries. Each prepared positive electrode was coupled with a commercial negative plate for construction of four single unit batteries. The electrolyte (1.28 g cm⁻³ sulfuric acid solution) of the first, second and third battery was saturated with humic acid, 1,2-acid and Vanillex, respectively. One another battery was filled with the same sulfuric acid electrolyte without any expander. Four batteries were fully charged by constant voltage of 2.48 V for 24 h. Discharge capacities of the batteries were determined during 100 cycles. The obtained results were shown in Fig. 9. As it is seen in Fig. 9, the organic expanders including humic acid, 1,2-acid and Vanillex has not positive effect on the cyclic discharge capacities of the nanostructured lead dioxide. Based on the obtained results, organic expanders reduce the cyclife of positive pastes as above-mentioned order.

In production process of lead-acid batteries, humic acid, 1,2-acid and Vanillex were used as effective expanders for negative pastes in weight percentage of 0.1–0.5% in the different factories. These amounts can make saturated concentrations for the expanders in battery electrolyte. As the obtained results showed, expander-saturated electrolyte is a drop agent for the cyclife of positive paste so that, it can be suggested to replace these expanders with other compounds or use these expanders in low levels in the negative paste formulations.

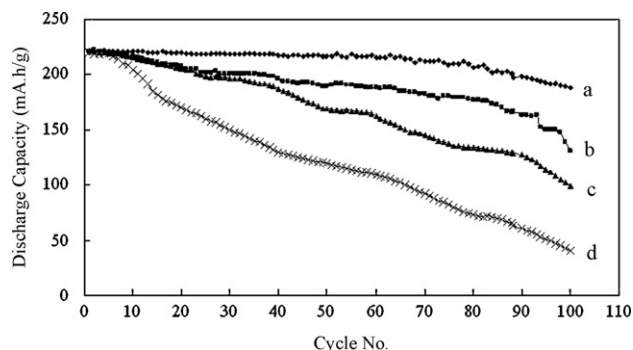


Fig. 9. Variation of discharge capacity of the nanostructured lead-dioxide vs. charge/discharge cycles in the absence of any organic additive (a), saturated with 1,2-acid (b), humic acid (c) and Vanillex (d).

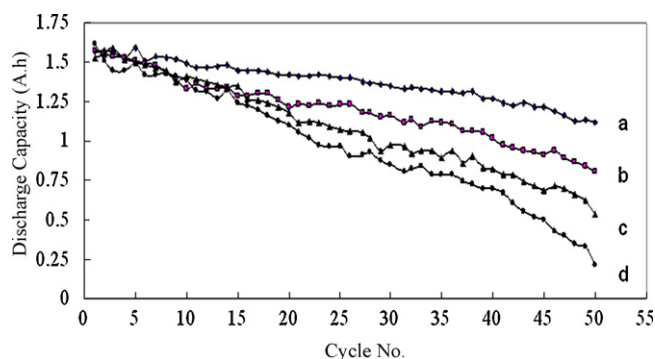


Fig. 10. Variation of discharge capacity of the commercial positive plates vs. charge/discharge cycles in the absence of any organic additive (a), saturated with 1,2-acid (b), humic acid (c) and Vanillex (d).

3.3.1. The effect of organic expanders on the commercial positive plates

One commercial positive small plate was coupled to two commercial negative small plates to make a single unite lead-acid battery with limited positive paste. Four batteries were constructed in this manner. The prepared batteries were filled with pure sulfuric acid ($d = 1.28 \text{ g cm}^{-3}$), sulfuric acid saturated with humic acid, 1,2-acid and Vanillex, respectively. All batteries were fully charged by constant voltage of 2.48 V for 24 h. Discharge capacities of the batteries were determined during 50 cycles. Fig. 10 shows the effects of humic acid, 1,2-acid and Vanillex on the consecutive discharge capacities of commercial positive plates. The obtained results confirmed the previous results of nanostructured lead dioxide so that the following order for the effect of organic expanders was again obtained (cyclelife order):

Pure sulfuric acid > 1,2-acid > humic acid > Vanillex

The obtained results from cyclic voltammetric studies, cyclelife studies for nanostructured lead dioxide and also for commercial positive plates showed that the organic expanders of humic acid, 1,2-acid and Vanillex reduce the kinetic rate of lead dioxide reactions so that it cause to drop discharge capacity of lead-acid battery during consecutive discharges.

4. Conclusions

The results indicated which pulsed current electrochemical method could be used as a confident and controllable method for preparation of nanostructured lead dioxide. These optimum conditions include sulfuric acid concentration of 4.8 M, pulse frequency of 12 Hz, pulse height of 33 mA cm^{-2} and solution temperature of

45°C has excellent uniform and the smallest particles. Lead dioxide sample prepared under optimized experimental conditions has particles in the dimensions range of 24–32 nm as shown by SEM. The synthesized lead dioxide in the optimum conditions can be used as positive electrode of the lead-acid batteries with the highest discharge capacity (220 mA h g^{-1}).

Cyclic voltammetry and cyclelife tests showed that the presence of humic acid, 1,2-acid and Vanillex in the battery electrolyte cause a considerable drop in discharge capacity during consecutive charge/discharge processes. Charge/discharge experimental data were in good agreement with cyclic voltammetry data.

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