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Synthesis of Lead Dioxide Nanoparticles by the Pulsed Current Electrochemical Method

Hassan Karami[*], *Mahboobeh Alipour*

Nano Research Laboratory, Department of Chemistry, Payame Noor Unirvesity (PNU), Abhar, Iran
[*]E-mail: karami_h@yahoo.com

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In this paper, lead dioxide nanoparticles were directly synthesized by pulsed current electrochemical method on the lead substrate in 4.8 M sulfuric acid solution. In order to obatin uniform morphology , narrowest size distribution and best composition of lead dioxide nanoparticles, the effect of experimental variables such as concentration of sulfuric acid, bath temperature, pulse frequency and pulse height (current amount), have been investigated. For conversion of all synthesized species to lead dioxide, each prepared sample was oxidized by low voltage method. The composition, morphology and structure were investigated using Energy Dispersive X-ray Analysis (EDX), scanning electron microscopy (SEM) and X-ray diffraction techniques (XRD). XRD results revealed lead dioxide samples, prepared under optimized experimental conditions, contain only PbO_2 in the range of 24-32 nm. Electrochemical behavior of the prepared electrodes was studied by cyclic voltammetry. The obtained results indicate that pulsed current electrochemical method can be used as a confident and controllable method for direct preparation of the lead dioxide nanoparticles on lead substrate. The lead dioxide synthesized in the optimum conditions showed an excellent discharge capacity (230 mA.h/g) when it was used as the cathode of lead-acid batteries.

Keywords: Lead dioxide; Nanoparticles; Pulsed current; Direct oxidation

1. INTRODUCTION

Nanostructured materials have received increasing attention in various fields of science and technology [1-3]. A variety of physicochemical methods, including metal evaporation [4], spray pyrolysis [5], sol-gel [6] and electrochemical methods [7], have been used to produce nanometer-sized materials.

Electrochemical synthesis was widely used to prepare different nanostructured materials such as nickel hydroxide [8], polyaniline [9], nickel [10], iron [11].

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 [12-14], in the oxidation of organic compounds [15-17], oxidation of phenol [18], Cr^{3+} [19], and glucose [20], and evolution of ozone [21] and as an electrocatalyst for salicylic acid [22], 2-naphtol [23], and trans-3,4-dihydroxycinnamic acid [24].

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 [21], the presence of forming agents such as F^- and Nafion [26], as well as the type of preparation techniques, such as pulse current [27] and cyclic voltammetry [28-29].

In the recent years, increased attentions have been focused on the synthesis of nanostructured lead dioxide. Cao et al. [30] 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 [31]. 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- 400nm with a wall thickness of about 30-50nm.

Shen and Wie [32] 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.

Sateralay et al. [33] 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 electrocrystallisation of lead dioxide on glassy carbon electrodes was reported by Gonzalez-Garcia et al. [34]. 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 [35].

M.F. Mousavi et al. prepared lead dioxide in nano-sized dimension on a Pt wire electrode applied as a suitable fiber in solid phase micro extraction (SPME) process [36]. Vatistas and Cristofaro [37] 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 [38]. In the other work, we studied the effect of particle size on the electrochemical behaviors of lead dioxide nanoparticles [39].

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. Finally, the optimized lead dioxide was used as the cathode of lead-acid batteries.

2. EXPERIMENTAL PART

2.1. Materials

Analytical grade sulfuric acid, HNO_3 (Merck) was used without any purification. In all of the experiments, double - distilled water was used. Pure lead substrate was purchased from the National Iranian Lead-Zinc Company (NILZ Co., Zanjan, Iran).

2.2. Instrumentals

The morphology and diameter of lead dioxide nanoparticles were studied by a Philips scanning electron microscopy (XL30 model). X-ray powder diffraction (Philips X'pert diffractometer) and 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. Figure 1 shows the used laboratory systems including power supply, pulse apparatus and electrochemical cell. Electrochemical behavior of the synthesized lead dioxide nanoparticles was studied by an electrochemical apparatus known as Auto Lab (model 102). The temperature of the synthesis solution was kept constant by water bath (Optima, Tokyo, Japan).

Figure 1. Laboratory systems used to syntheses the lead dioxide nanoparticles including power supply, pulse maker apparatus and electrochemical cell.

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.2.

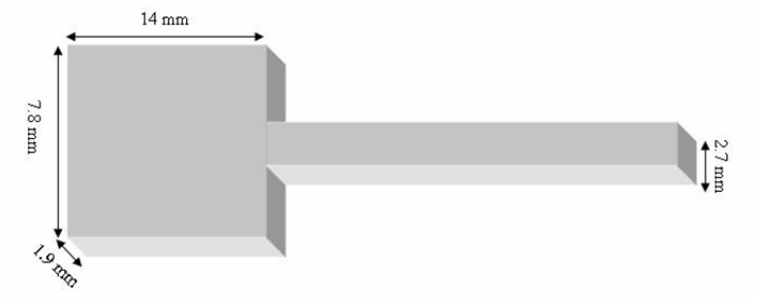

Figure 2. Scheme and dimensions of the used electrode

2.3.2. Lead dioxide synthesis

Before each deposition, the lead electrode was placed in the concentrated HNO_3 for 30s and then rinsed with double-distillated water to remove any surface oxidized species in contact with air.

Two graphite cathodes 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, $PbSO_4$, $PbO.4H_2O$ and $Pb_4O_3SO_4{\cdot}H_2O$) 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, lead dioxide nanoparticles were directly synthesized on the surface of the lead electrode (anode) by oxidation of the lead substrate.

The effect of all parameters of the synthesis including H_2SO_4 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 H_2SO_4 solution in double-junction vessel.

2.3.3. Battery production and test

Negative pasted electrode was obtained from Aranniru battery manufacturing Co. and used without any improvement. The prepared 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. The battery charge process was performed at sulfuric acid solution with density of 1.24 $g.cm^{-3}$ using constant voltage method (2.48V per cell) for 24 h. Determination of discharge capacity for the constructed battery was carried out by constant resistance method [40].

3. RESULTS AND DISCUSSION

3.1. Pulse specifications

Lead dioxide nanoparticles were directly synthesized by 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. 3. According to Fig. 3, 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.

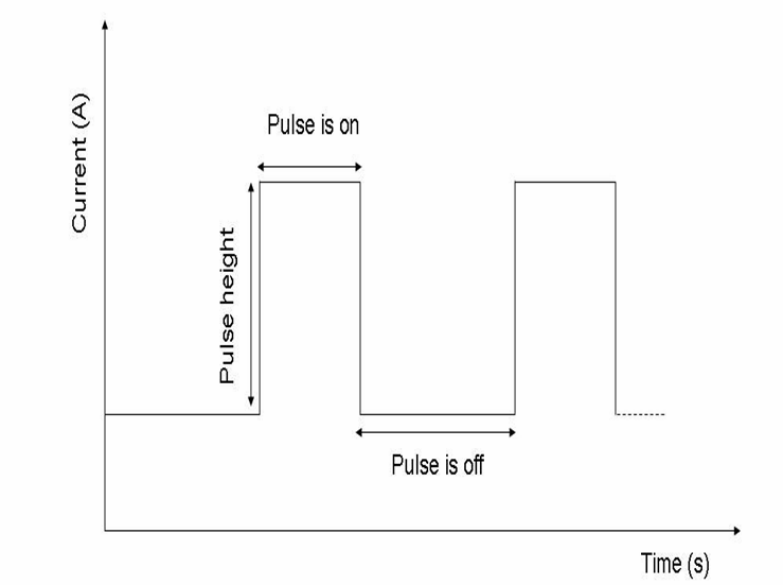

Figure 3. Pulsed current applied mode including pulse time, relaxation time and pulse height.

X-ray diffraction patterns were used for investigating the phase compositions of the prepared samples. The effect of different parameters including pulse height, pulse frequency, sulfuric acid concentration and temperature of synthesis solution were optimized by a "one at a time" method.

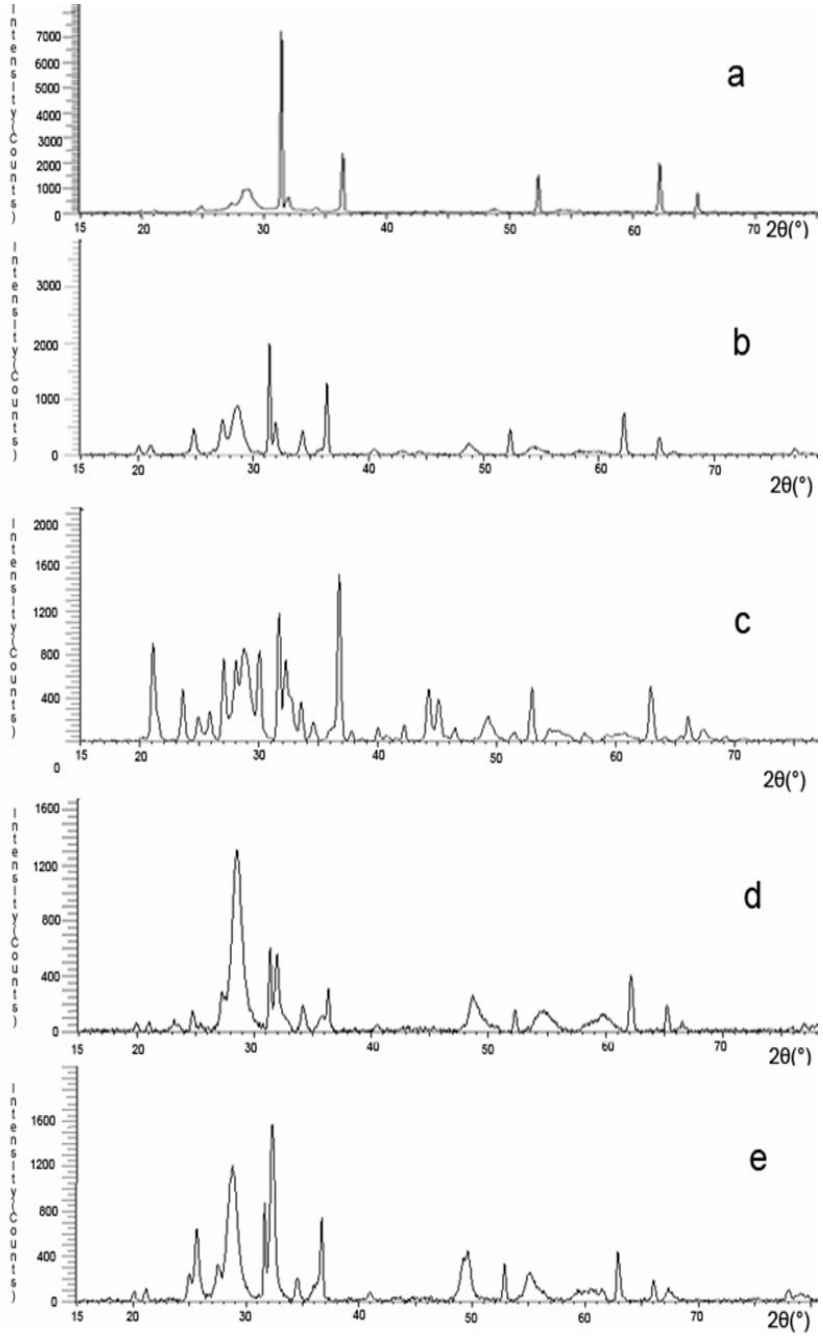

Figure 4. XRD patterns for the samples which synthesized at different temperature of 0ºC (a), 20ºC (b), 45 ºC (c), 70ºC (d) and 100ºC (e)

3.1. Effect of synthesis temperature

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

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

Temperature	Component %wt					
(ºC)	PbO	$PbO{\cdot}4H_2O$	α-PbO_2	β-PbO_2	$PbSO_4$	$Pb_4O_3SO_4{\cdot}H_2O$
0	30.5	14.15	33.96	0.0	0.0	21.38
20	41.16	23.49	0.0	0.0	0.0	35.34
45	55.70	0.0	0.0	8.10	36.21	0.0
70	52.98	10.28	10.27	4.02	0.0	16.37
100	45.58	10.46	6.43	24.13	0.0	13.40

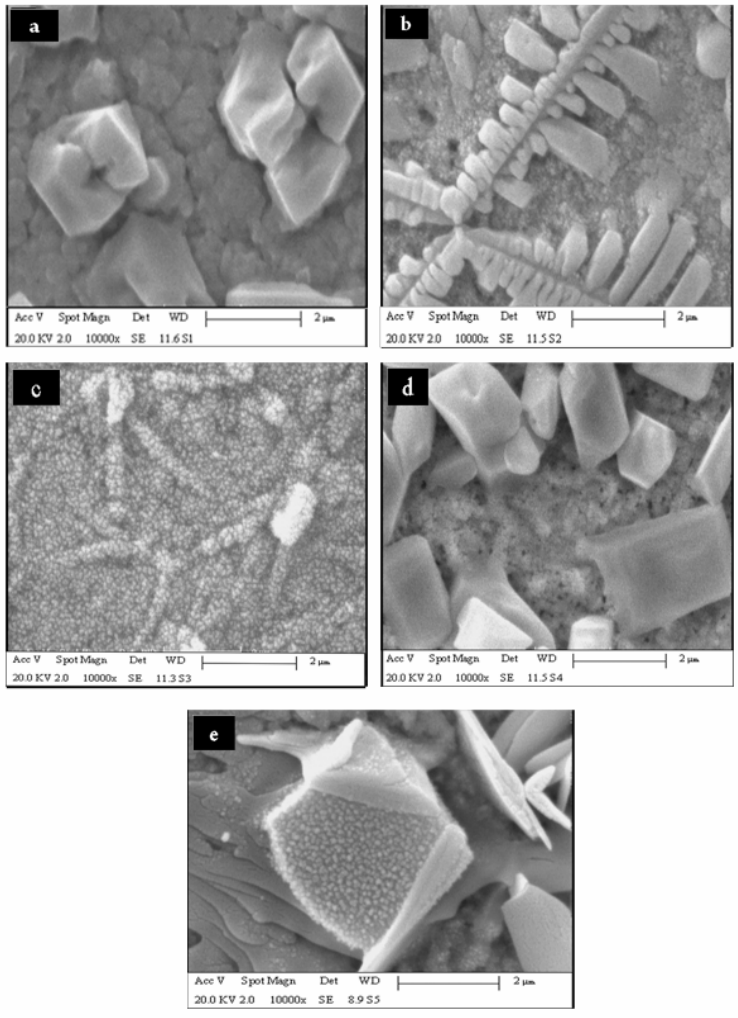

Figure 5. SEM images of lead dioxide samples synthesized at temperatures of 0ºC (a), 20ºC (b), 45 ºC (c), 70ºC (d) and 100ºC (e), (the other experiment conditions including pulse height, pulse frequency and sulfuric acid concentration were kept constant).

important role on the morphology and particles sizes of the oxidation products. Therefore, many syntheses were carried out at different temperatures of solution including 0, 20, 45, 70 and 100°C. Figure 4 shows the effect of synthesis temperature on the phase composition of lead dioxide. To highlight the results, the information in Fig. 4 has been summarized numerically in Table 1. As it is obvious from Table 1, lead substrate oxidized to PbO (55.7%wt), PbSO4 (36.21%wt) and β-PbO_2, while it can be produced as α-PbO_2 and some other species can be produced at other temperatures. To select an optimum temperature value, SEM was used to study the morphology and particle size of the samples prepared at different temperatures. Figure 5 shows the effect of the temperature of synthesis solution on the morphology and particle size of the samples. 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 effect of temperature on the average particle size and the range of particles sizes are shown in Fig. 6. As it is seen from Fig. 6, the sample which synthesized at solution temperature of 45ºC has the lowest average size and also the narrowest range of particles sizes. The obtained results are probably related to the fact that at this temperature (45ºC), growth rate, nucleation rate and agglomeration rate are suitable for forming more uniform and smaller particles. Based upon the obtained information from Figs 5 and 6, the temperature of 45ºC is the optimum value for the synthesis of the uniform nanostructures, but the data of the Table 1 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 percentages by varying the 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 the morphology and particle size. XRD studies for the sample after the charge process showed that there was only lead dioxide species (β-PbO_2). Therefore, in all the following experiments, charge process was carried out after synthesis processes.

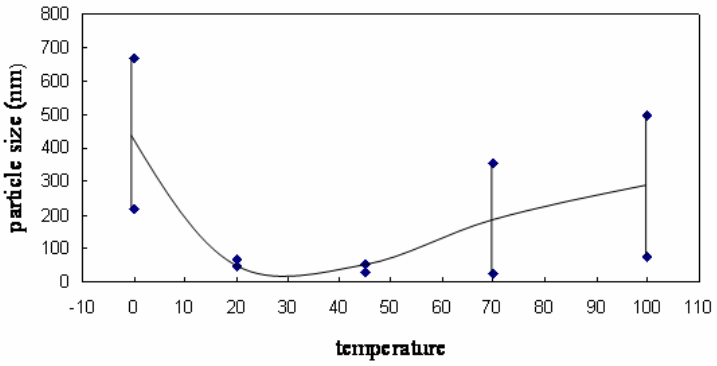

Figure 6. Effect of solution temperature on the range of lead dioxide particles size; 0ºC (a), 20ºC (b), 45 ºC (c), 70ºC (d) and 100ºC (e), (the other experiment conditions including pulse height, pulse frequency and acid concentration were kept constant).

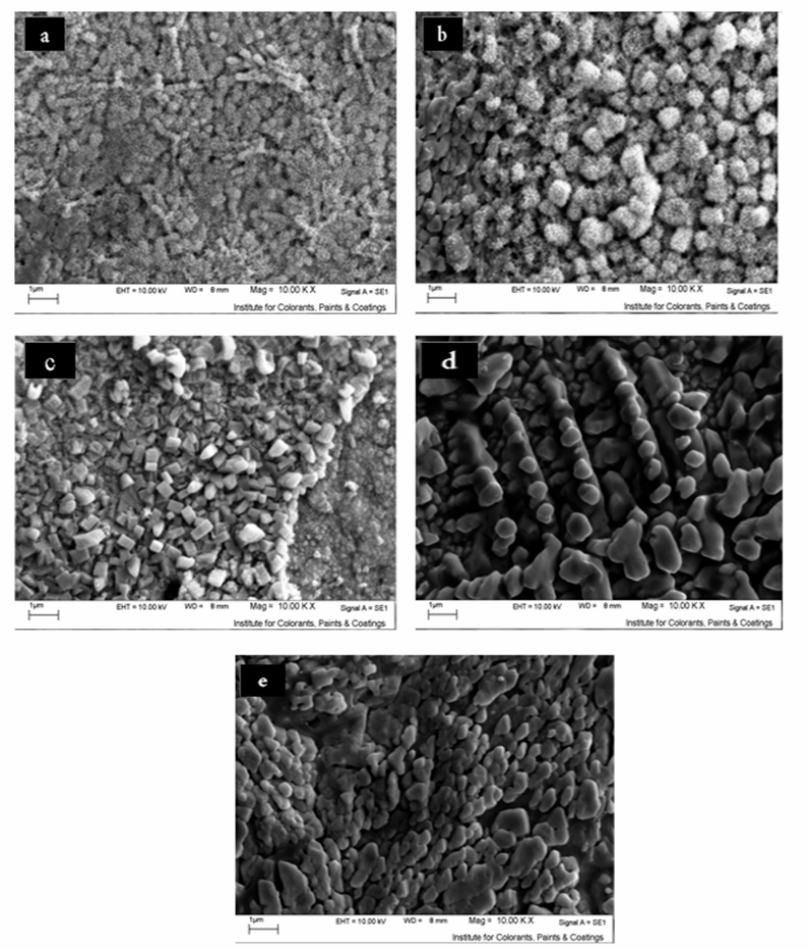

Figure 7. SEM images of lead dioxide samples synthesized at different pulse heights; 33 mA.Cm^{-2} (a), 50 mA.Cm^{-2} (b), 67 mA.Cm^{-2} (c), 135 mA.Cm^{-2} (d) and 202 mA.Cm^{-2} (e); (the other experiment conditions including pulse frequency, temperature and sulfuric acid concentration were kept constant).

3.2. Pulsed current amplitude optimization

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 weres 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 Fig7. As it is seen in Fig. 7, the pulse height (current amplitude) of 33 mA.cm^{-2} makes more uniform and smaller particles than the others. To shed more light on the results, Fig. 8 shows the effect of pulse height on the range of lead dioxide particles sizes. As Fig. 8 shows, the lower pulse heights not only make small particles but also narrow range of particle sizes.

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 than135 mA.cm^{-2}) make very high nuclear growth thus the produced lead dioxide will be amorphous (Fig. 7e).

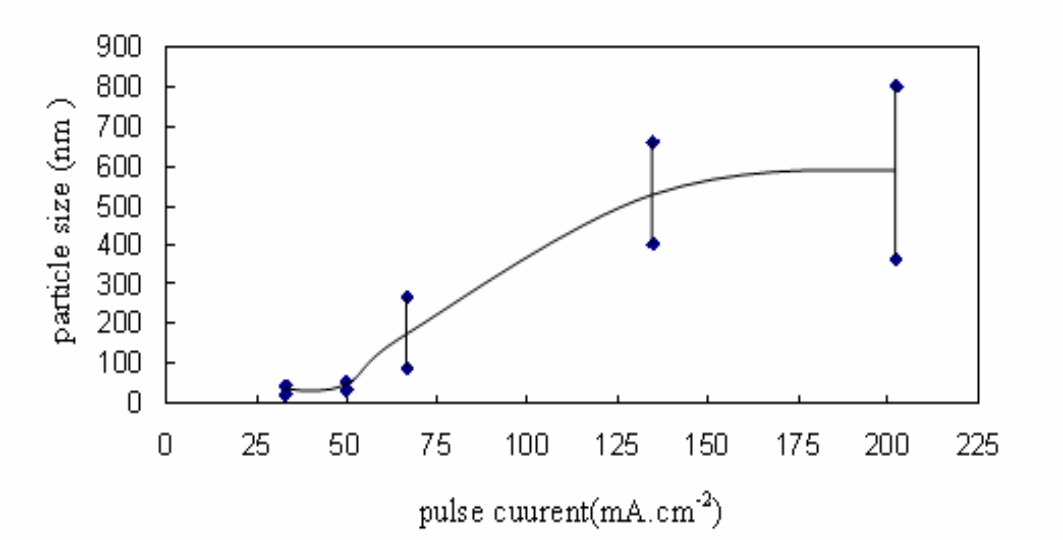

Figure 8. Effect of pulse height on the range of lead dioxide particle size; 33 mA.Cm^{-2} (a), 50 mA.Cm^{-2} (b), 67 mA.Cm^{-2} (c), 135 mA.Cm^{-2} (d) and 202 mA.Cm^{-2} (e); (the other experiment conditions including pulse frequency, temperature and sulfuric acid concentration were kept constant).

3.2. Optimization 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 (1 and 2 equations):

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

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

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}. Figure 9 shows the SEM images of lead dioxide samples of this experimental series. As it is seen from Fig. 9, 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 9c), 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. 9d, the uniform nanorods are slowly transformed to large crystalline lead dioxide. Figure 9e shows that higher frequencies make lead dioxide in large crystalline forms.

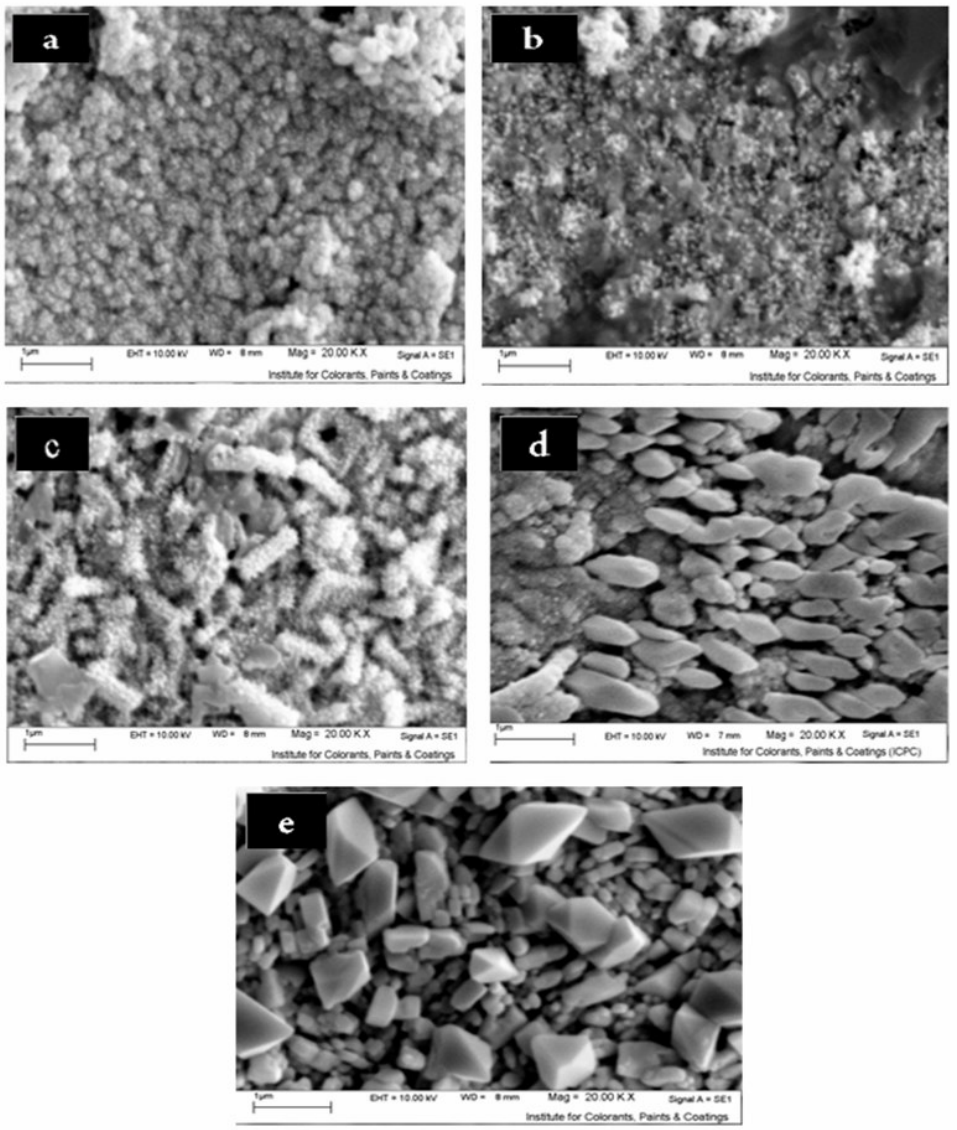

Figure 9. SEM images of lead dioxide samples synthesized at different pulse frequencies of 0Hz (a), 6 Hz (b), 12 Hz (c), 18 Hz (d) and 24 Hz (e).

Figure 10 shows the effect of pulse frequency on the range of particles size of the synthesized lead dioxide. The original data in Fig. 10 are based on the measurements of the particle size of lead dioxide in SEM images. As it is seen from Fig. 10, the pulse frequency of 12 Hz has resulted in the smallest particle size and the narrowest range of particle size.

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.

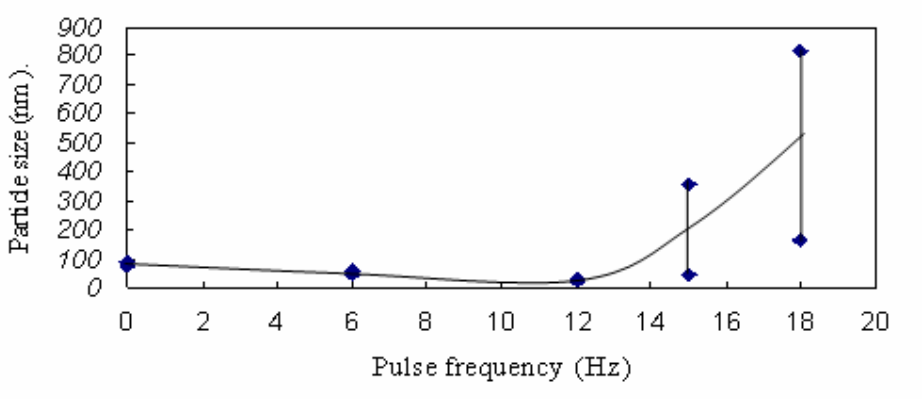

Figure 10. Effect of pulse frequency on the range of lead dioxide particle size; 0 Hz (a), 6 Hz (b), 12 Hz (c), 18 Hz (d) and 24 Hz (e); (the other experiment conditions including pulse height, temperature and sulfuric acid concentration were kept constant).

3.3. 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 [41-44]. 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 electrosynthesis cell, the pure lead is oxidized to various forms of lead sulfate (such as $PbSO_4$, $PbO.PbSO_4$, $2PbO.PbSO_4$, $3PbO.PbSO_4$ and $4PbO.PbSO_4$) then, all forms of lead sulfate are oxidized to PbO_2. Peterson et al. [12] proposed the overall reaction for the preparation of PbO_2 as follows:

(1) $$Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e$$

(2) $$2Pb + SO_4^{2-} + H_2O \rightarrow PbO.PbSO_4 + 2H^+ + 4e$$

(3) $$4Pb + SO_4^{2-} + 4H_2O \rightarrow (3PbO).PbSO_4.H_2O + 6H^+ + 8e$$

(4) $$Pb + H_2O \rightarrow PbO + 2H^+ + 2e$$

(5) $$PbSO_4 + 2H_2O \rightarrow \beta - PbO_2 + HSO_4^- + 2e + 3H^+$$

(6) $$PbO + 2H_2O \rightarrow \alpha - PbO_2 + 2e + 4H^+$$

(7) $$\alpha - PbO_2 \rightarrow \beta - PbO_2$$

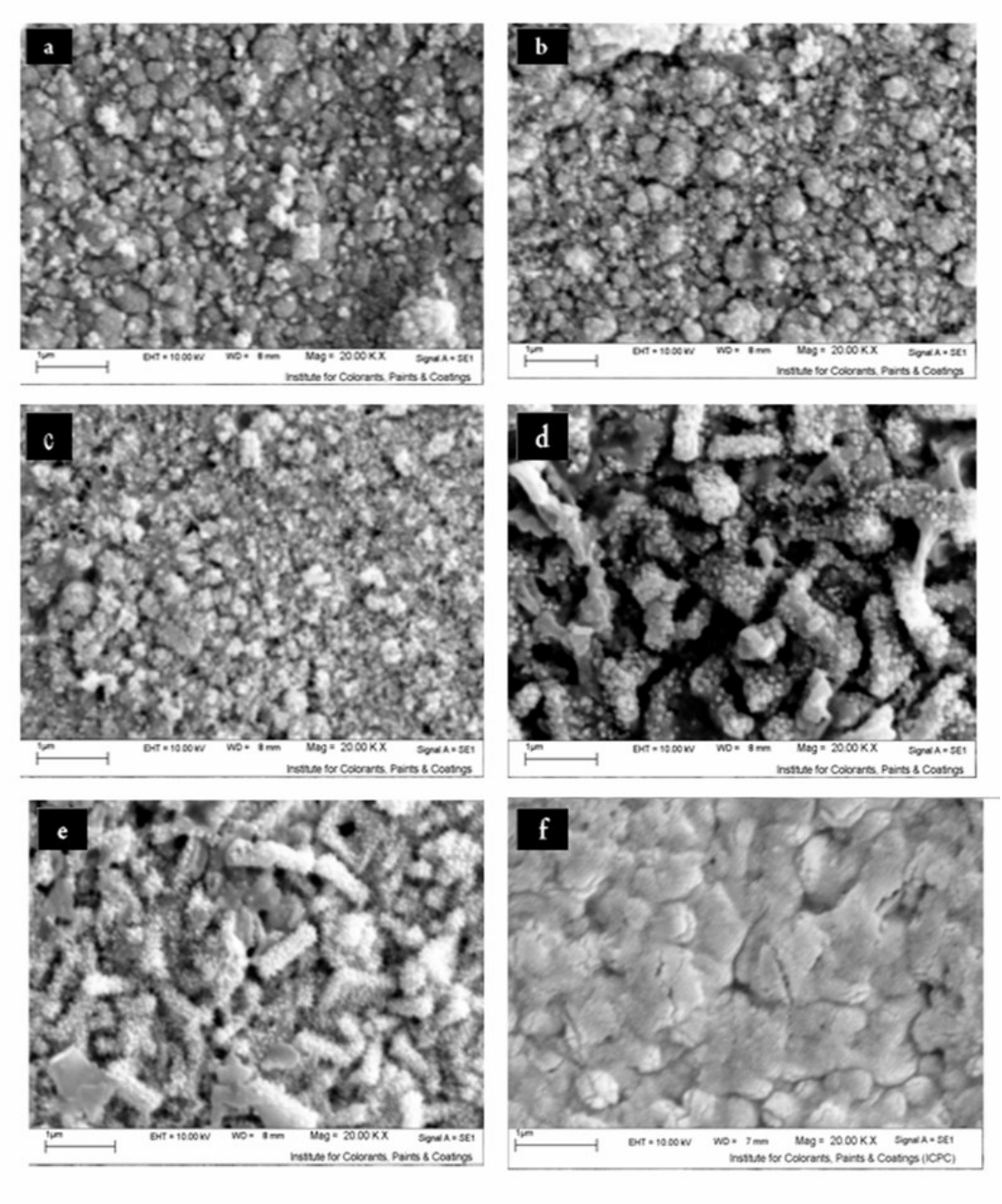

Figure 11. SEM images of lead dioxide samples synthesized at sulfuric acid concentrations of 1 M (a), 1.6 M (b), 2.7 M (c), 3.7 M (d), 4.8 M (e) and 6 M (f); (the other experiment conditions including pulse height, pulse frequency and temperature were kept constant).

As it is obvious, α-PbO_2 is produced by oxidation of PbO (Eq. 6), while β-PbO_2 is formed by oxidation of $PbSO_4$ (Eq. 5). Based on the type of the applied electrochemical technique and the experimental conditions, different proportions of α-PbO_2, β-PbO_2 and $PbSO_4$ are synthesized.

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 obtained results are shown in Fig. 11. As it is seen from Fig. 11, the sulfuric acid concentration of 4.8 M produces more uniform and smaller particles. The data obtained from Fig. 11 was used to sketch Fig. 12. The presented diagram in Fig. 12 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 [41-44]. 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.

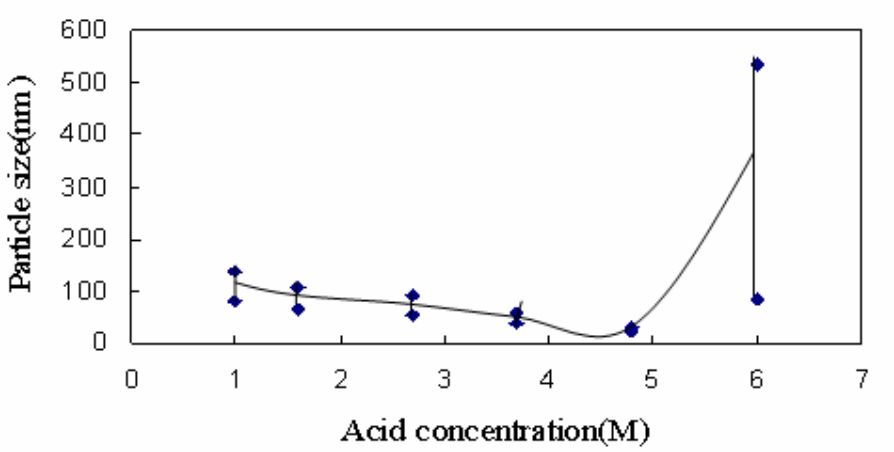

Figure 12. Effect of sulfuric acid concentration on the range of lead dioxide particles size; 1 M (a), 1.6 M (b), 2.7 M (c), 3.7 M (d) and 4.8 M (e), (the other experiment conditions including pulse height, pulse frequency and temperature were kept constant).

3.6. Electrochemical studies

The electrochemical behavior of the lead dioxide obtained in the optimum conditions was studied by cyclic voltammetry. As it is seen from Fig. 13, lead dioxide is reduced to spongy lead at the potential of 1.2 V (vs. Ag/AgCl), and lead is oxidized to lead sulfate at 1.35 V. The obtained lead

sulfate is oxidized to lead dioxide at 1.75 V. These processes are exactly similar with those carried out in charge/discharge processes of lead-acid batteries. Therefore, for investigating the cyclelife of the synthesized lead dioxide, the cyclic voltammetric behavior was studied during 45 cycles under potential scan rate of 10 mV/s. 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 has very excellent cyclic life when it is used as a cathode for lead-acid batteries.

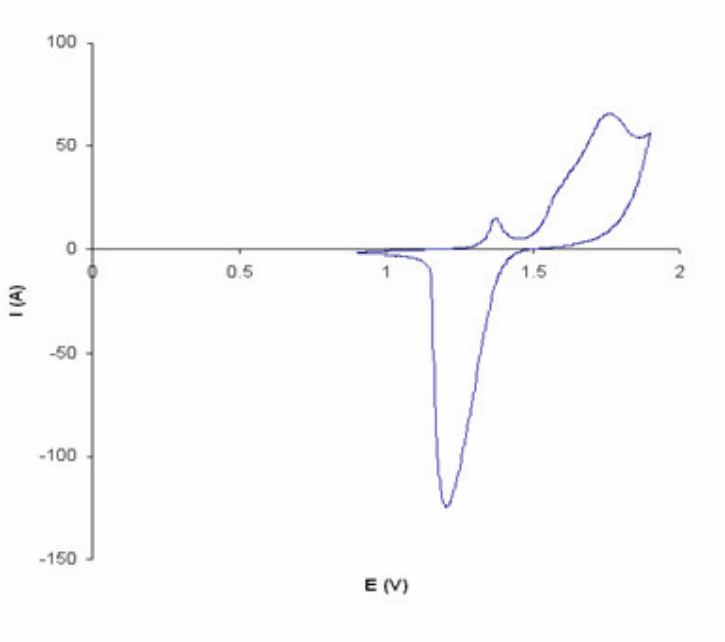

Figure 13. Cyclic voltammogram for the synthesized lead dioxide in 1.0 M sulfuric acid solution vs. Ag/AgCl reference electrode under potential scan rate of 10 mV/s.

3.7. Battery making and tests

The final electrode coated by lead dioxide nanoparticles was used as cathode of lead-acid batteries. Each prepared positive electrode was coupled with commercial negative plate for construction of single unit battery. Each experimental battery was charged by constant voltage of 2.48V for 24 h. Discharge capacity of the battery made of the proposed cathode was obtained 230 mA.h g^{-1}. The obtained results for the constructed batteries shows that the lead dioxide nanoparticle can be deliver the practical discharge capacity equal to the theoretical capacity of lead dioxide.

4. CONCLUSIONS

Results indicated which pulsed current electrochemical method could be used as a confident and controllable method for preparation of lead dioxide nanoparticles. Lead dioxide is

formed on lead substrate from a H_2SO_4 solution by use of pulsed current electrochemical method. Pulse time, relaxation time, pulse height and synthesis temperature are among the most important parameters affecting the morphology of anodic products. The lead dioxide was synthesized under the optimum conditions in which particles were the most uniform and the smallest. 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 45º 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 cathode of the lead-acid batteries with the highest discharge capacity (230 $mA.h.g^{-1}$).

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