The influence of formation conditions on the electrochemical behavior of lead oxide in sulfuric acid solution

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ABSTRACT

In course of anodic oxidation of lead in chloride–nitrate melt it has been formed β-PbO either in the form of nanopowder with the average size of the particles 20–70 nm or in the form of nanofibers with the thickness of 20 nanometers and length 500 nm. Synthesis is easily reproduced and can become a basis of industrial production lead nano-oxide. Lead oxide nanopowders and nanofibers tested in a course of potentiodynamic cycling in working conditions of a positive electrode of the acid lead battery, have shown good reproducibility of results and high values of currents density that can be unequivocally connected with increase in the true area of a surface of active mass of electrodes.

1. Introduction

A considerable amount of research has been conducted recently on the potential usage of nanopowders in lead-acid batteries [1–3]. Currently, the most developed methods of synthesis of lead oxides are the sol–gel and pyrochemical methods. However, in spite of a number of recent breakthroughs in this area, powders obtained by these methods are of spherical form, amorphous, and hence have no definite crystal structure. In addition, lead precursors which are used for preparing nano-oxides are expensive; the lead dioxide deposition is carried out from very diluted solutions, so it is possible to obtain only a very small amount of lead nano-oxide in a single experiment [3]. The above-mentioned techniques are still far from large-scale industrial production, which makes oxide nanopowders very expensive to fabricate.

One more disadvantage of the nanopowders obtained via chemical methods is the fact that they possess inferior electrochemical characteristics in sulfuric acid solutions, compared with the powders obtained by electrochemical methods [3,4].

Nevertheless, it is impossible to overlook a positive effect of the size reduction of lead oxide particles due to a substantial growth of the true surface area of electrodes. It can be speculated that the lead oxide, obtained in the form of nanopowder by the electrochemical oxidation of lead, can exhibit superior electrochemical characteristics.

During this study, it was decided to conduct the electrochemical oxidation of lead in the molten electrolyte. The decision was based on the fact that molten salts, as the reaction media, have a number of critical advantages over traditional water-based electrolytes, such as

- possibility to change the solubility and/or reactivity of the reactants;
- possibility to increase the reaction temperature;
- reactions are usually controlled by chemical equilibrium and proceed much faster than diffusion-controlled solid-state reactions;
- great variety of possible chemical reactions and products;
- possibility to form chemical compounds with the chosen crystallographic morphology.

Lead oxide nanopowder can be obtained by the direct electrochemical oxidation of lead in a nitrate or hydroxide melt. During the oxidation process, very dense and defect-free oxide layers are formed on the lead surface. Adding considerable amounts of halide ions into the melt weakens the adherence of lead oxide to the metallic electrode surface, and, as a result, a significant amount of the lead oxide nanopowder is formed in the bulk of the molten electrolyte [5].

The goal of present study was (1) to fabricate lead oxide nanopowders from the molten chloride–nitrate and chloride hydroxide mixtures in the temperature range of 673–813 K under an argon atmosphere by direct anodic oxidation of lead, and (2) to investigate characteristics of the resulting powders in the course of electrochemical cycling in sulfuric acid solutions.

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2. Experimental

2.1. Mechanism of synthesis of lead oxide nanopowder

Lead oxide powders were obtained by the direct anodic oxidation of lead in the molten mixture of chlorides and nitrates (or hydroxides) of alkaline metals in a temperature range of 673–813 K under an argon atmosphere. Anodic polarization of lead was carried out in a potentiostatic regime.

A possible mechanism of the lead anodic oxidation in the chloride–nitrate melt is as follows:

$$Pb \rightarrow Pb^{2+} + 2\bar{e} \tag{1}$$

$$Pb^{2+} + 2NO_3^- \rightarrow Pb(NO_3)_2 \tag{2}$$

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2 \tag{3}$$
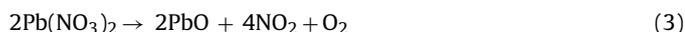
The net reaction can be expressed as

$$2Pb + 4NO_3^- - 4\bar{e} \rightarrow 2PbO + 4NO_2 + O_2 \tag{4}$$

A similar mechanism can be suggested for the anodic polarization of lead in the hydroxide–chloride melt:

$$Pb \rightarrow Pb^{2+} + 2\bar{e} \tag{5}$$

$$Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2 \tag{6}$$

$$Pb(OH)_2 \rightarrow PbO + H_2O \tag{7}$$

With the net reaction expressed as

$$Pb + 2OH^- - 2\bar{e} \rightarrow PbO + H_2O \tag{8}$$

Since all chlorides, nitrates, and hydroxides of alkaline metals are completely soluble in water, the lead oxide, being the only insoluble product of the reaction, can be easily separated by dissolving the molten electrolyte in water and filtering out the resulting sediment. In spite of very small size of the powder particles, washing the powder twice with distilled water resulted in a complete separation of the lead oxide from the cations and anions of the reaction medium. However, the amount of the powder formed in a single experiment by the anodic polarization of lead was found to be insignificant. In order to increase the rate of the electrochemical reaction and its output, small amounts (no more than 4 wt.%) of two water-soluble additives were added to the reaction mixture.

2.2. Synthesis of the lead oxide nanopowder

Synthesis of the lead oxide nanopowder in molten salts is simple and rather fast. The reaction itself is carried out above the melting point of a molten salts mixture. The synthesis reaction was conducted in a Quartz glass three-electrode electrochemical cell (Fig. 1) with the silver-chlorine reference electrode under an argon atmosphere in a temperature range of 673 K.

A control experiment was conducted to estimate the contamination of the reaction mixture by silicon. The CsCl–NaCl–30 wt.% NaNO_3 mixture was held for 100 h in a quartz cell under the conditions mimicking those of a typical synthesis experiment. After the cell was disassembled, the concentration of Si in the CsCl–NaCl–30 wt.% NaNO_3 mixture was found to be 3×10^{-4} wt.%, which is negligible, considering that the duration of a typical synthesis experiment was no longer than 3 h.

When the oxidation reaction was performed in the hydroxide–chloride melt, an alumina crucible placed inside the quartz cell was used to hold the melt in order to prevent quartz from reacting with the highly corrosive molten salts mixture.
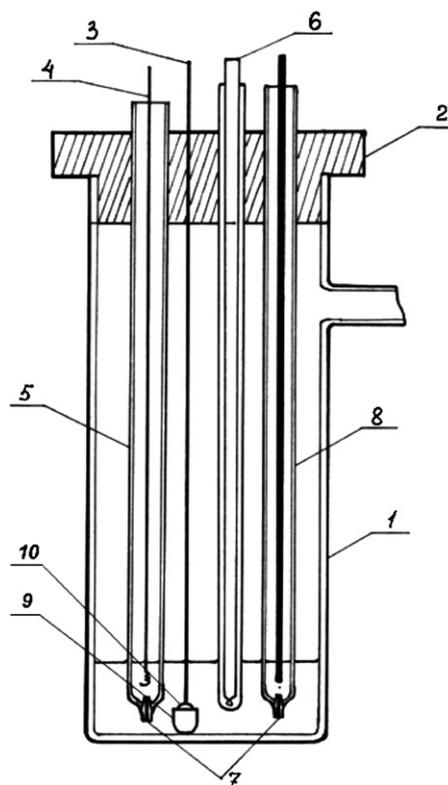
Fig. 1. High-temperature electrochemical cell: 1, quartz test-tube; 2, vacuum rubber tight fuse; 3, working electrode; 4, reference electrode; 5 and 8, covers of reference electrodes and counter-electrode; 6, thermocouple; 7, asbestoses diaphragm; 9, alumina crucible; 10, molten lead drop.

Lead (99.99% purity) was used in the form of platelets with the total area of 3.5 cm². Since the experiential temperature was significantly higher than the melting point of lead, a drop of molten lead lay on the bottom of the alumina crucible holding the molten electrolyte. Electric contact to the lead drop was established with a tungsten wire encased in an alumina tube in order to shield the wire from exposure to the hydroxide–nitrate melt. The electrolyte was prepared from salts with a total amount of impurities not exceeding 0.15 wt.%.

Platinum wire was used as the counter electrode, and the Ag/AgCl electrode served as the reference electrode. The silver/silver chloride electrode represented a piece of Ag wire immersed into a molten chloride electrolyte (e.g. the eutectic mixture of NaCl and CsCl) containing 1 mol.% of AgCl.

The chloride–hydroxide or chloride–nitrate salt mixtures with small amounts of Additive 1 or Additive 2 were used as molten electrolytes. The freshly prepared salt mixture was crushed into small pieces and loaded into the quartz cell. The cell was vacuumed and then heated. Upon reaching the melting point of the salt mixture, the cell was filled with argon. The lead electrode was deoiled, dried, and placed into the reaction mixture only after the experimental temperature had been attained. Anodic polarization of lead was carried out in a potentiostatic regime at the potential of +1 V versus the Ag/AgCl reference electrode. After the oxidation experiment had been completed, the salt mixture was poured out from the cell into an alumina crucible, was let to cool down to room temperature, and then dissolved in distilled water. The resulting sediment was filtered out, washed twice with distilled water, and air-dried at 390 K. A typical experiment yielded on average about 30 g of lead oxide nanopowder. The obtained powder was analyzed by SEM device «GSM-5900 LV» and X-ray diffractometer «RIGAKU» DNAX 2200PC. The only phase present in the obtained nanopowder was shown to be β-PbO.

Table 1
Electrochemical and corrosion characteristics of positive electrodes which was made from different powders.

	E_{cor} (V)	$i_{discharge}$ (mA cm^{-2} 15th cycle)	$i_{discharge}$ (mA cm^{-2} 300th cycle)	[Pb^{2+}] (mg h^{-1} cm^{-2})
Powder 1	−0.486	12	12	0.012
Powder 2	−0.508	15	15	0.0086
Nanopowder 3	−0.247	51	120	0.0065
Nanofibers 4	−0.302	33	120	0.0056

2.3. Preparation of the working electrode and the electrochemical procedure in sulfuric acid

The working electrode was cut out of a pure (99.99% purity) lead plate of 5 mm thickness. The electrode was covered with a layer of an acid-resistant plastic, in which a hole was drilled of 3 mm in diameter and 3 mm deep.

The preparation procedure for the working electrode is as follows. Two drops of water were added to 400 mg of dry lead oxide nanopowder; the mixture was thoroughly homogenized, and then one drop of diluted sulfuric acid was added to it. The resulting paste was homogenized for 15 min and then used to fill the drilled hole in the acid-resistant plastic, thus forming the working electrode. The electrode was then dried for 2 h at 333 K.

In this study, the corrosion potential and discharge current density were chosen as main parameters that characterize the electrochemical activity of the obtained lead oxide nanopowders.

The electrochemical measurements in sulfuric acid solutions were conducted in a standard three-electrode cell in the potentiodynamic mode at a linear scanning rate of 10 mV s^{-1} and a holding time of 100 s at extreme potentials. In all experiments 4.57 M (32 wt.%) H$_2$SO$_4$ of extra pure grade was used as electrolyte.

The corrosion potential and the corrosion loss of the lead oxide electrode were determined in the same experiment.

Since it was impossible to determine the corrosion rate of lead oxide by gravimetry, it was measured analytically by monitoring the concentration of Pb^{2+} ions in sulfuric acid using an "Optima 4300 DV" spectrometer.

After 300 cycles, the working electrode was disassembled; the used lead oxide powder was washed in distilled water, dried, and then examined by SEM device «GSM-5900 LV».

3. Results and discussion

Lead oxide powders obtained by the anodic oxidation of lead in the hydroxide–chloride melt using various additives have different morphologies as depicted in Figs. 2 and 3. The powder obtained with Additive 1 consists of long (up to 150 μm) highly branched dendrites resembling a fish skeleton. However, under a higher magnification, it became evident that a single dendrite has a very large true surface area and consists of densely packed crystallites with an average size of 200 nm. It is obvious that during the anodic polarization self-assembling dendrites of lead oxide are formed, which later fall off from the electrode into the melt.

Electrochemical characterization of the powder in sulfuric acid solution brought somewhat unsatisfactory results. Electrochemical activity of the powder obtained from the hydroxide–chloride melt is low; the current density measured during cycling does not exceed 2.2 mA cm^{-2}. The corrosion potential on this electrode reached a stable value during 120–140 min from the moment when the electrode was immersed into the sulfuric acid electrolyte. During this time, the potential shifted by ca. 50 mV to the positive direction. Besides, this dendrite powder possesses the lowest corrosion resistance compared to all other examined powders in this study. Values of the corrosion potential and lead solubility in sulfuric acid are presented in Table 1.
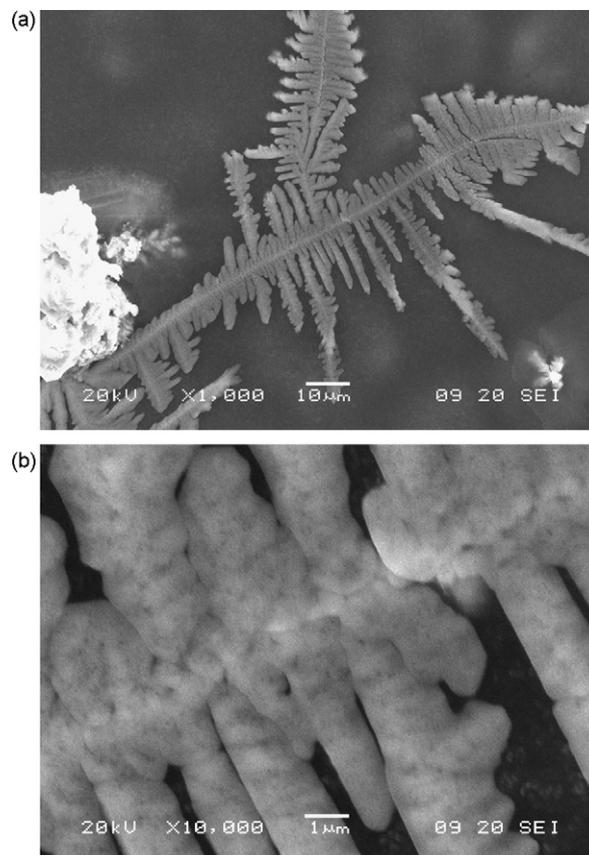
Fig. 2. SEM picture of PbO powder obtained by electrochemical oxidation of lead in NaCl–CsCl–NaOH + Additive 1.

The powder obtained by the anodic oxidation of lead in the hydroxide–chloride melt with Additive 2 consists of agglomerates of particles 100–500 nm in diameter. Due to a high degree of particles agglomeration, the powder's true surface area is also low as in the case of Additive 1.

The corrosion potential values were measured to be more negative than those for Powder 1. The current density values measured during electrochemical cycling of the electrode in a sulfuric acid solution were found to be low, not exceeding 1.2–1.5 mA cm^{-2}. Long-term corrosion testing of Powder 2 showed a decrease in its corrosion losses compared to powder 1.

Next two powders were synthesized in the chloride–nitrate melt using Additives 1 and 2.

Average size of lead oxide particles obtained from the chloride–nitrate melt (Powder 3) was found to be between 50 and 70 nm (Fig. 4). The corrosion potential value for Powder 3 is much more positive than those for the both powders obtained from the hydroxide–chloride melt, and it was measured to be −0.247 V. Besides, corrosion losses after a long-term testing of Powder 3 was found to be much lower compared with the powders synthesized from the hydroxide–chloride melt. Solubility of lead oxide was measured to be 0.0065 mg cm^{-2} h^{-1}.

(a)

(b)
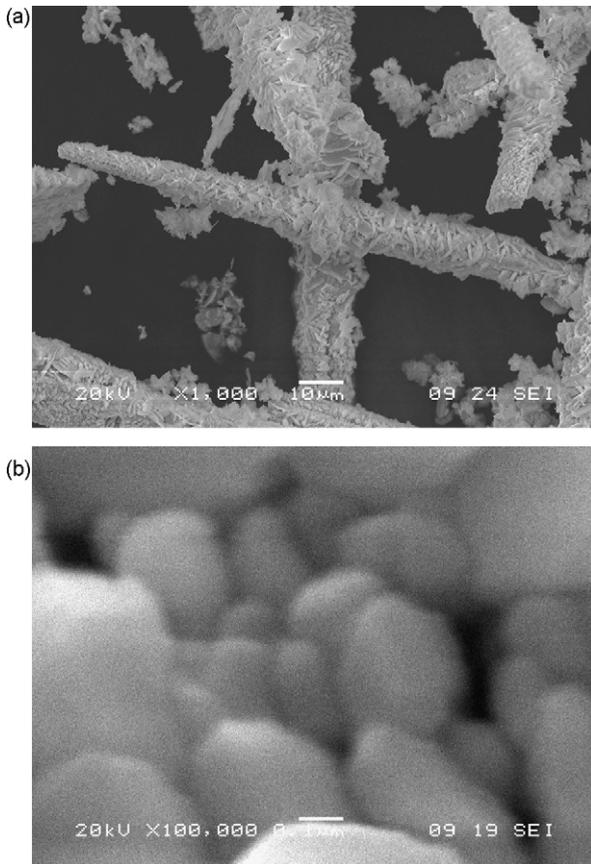
Fig. 3. SEM picture of PbO powder obtained from electrochemical oxidation of lead in NaCl–CsCl–NaOH + Additive 2.

(a)

(b)
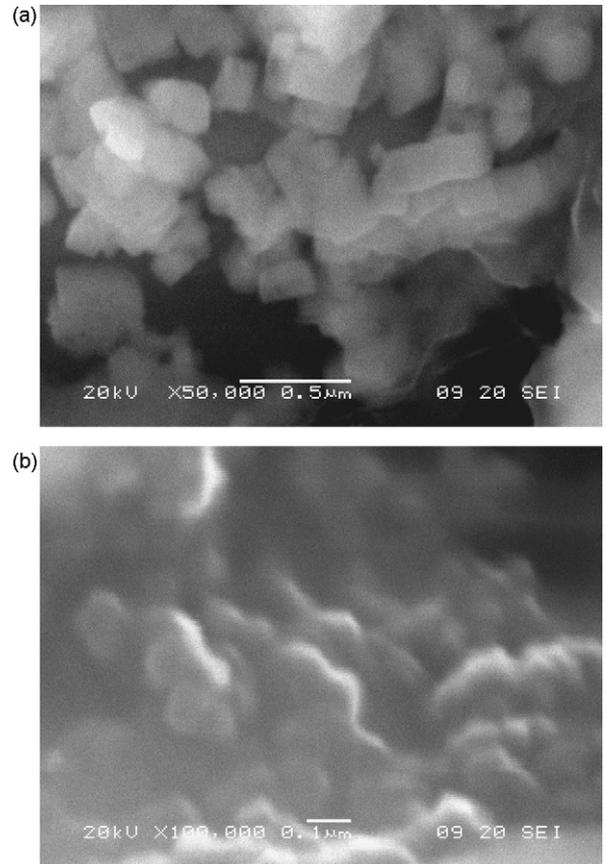
Fig. 4. SEM picture of PbO powder obtained from electrochemical oxidation of lead in CsCl–NaCl–NaNO3 + Additive 1.

Electrochemical cycling of the positive paste electrode in the course of first nine cycles also exhibited small current density values, which can be attributed to the oxidation of lead from oxide to dioxide. However, beginning from cycle 10, the voltammogram started to exhibit a cathodic peak at 1.45 V relative to the Ag/AgCl reference electrode (Fig. 5), which is attributed to the reduction of PbO_2 to $PbSO_4$. The current density discharge increases from 16 to

125 mA cm^{-2} between cycles 10 and 35. After that the current density discharge stays constant up to cycle 300. However, in the course of cycling, beginning from cycle 20, a shift of the cathodic peak was observed to the potential of 1.42 V, with the peak becoming asymmetrical. Even an insignificant shift of the cathodic peak potential can be caused by changes in chemical composition, structure, or water content of the lead oxide paste during cycling. In order to
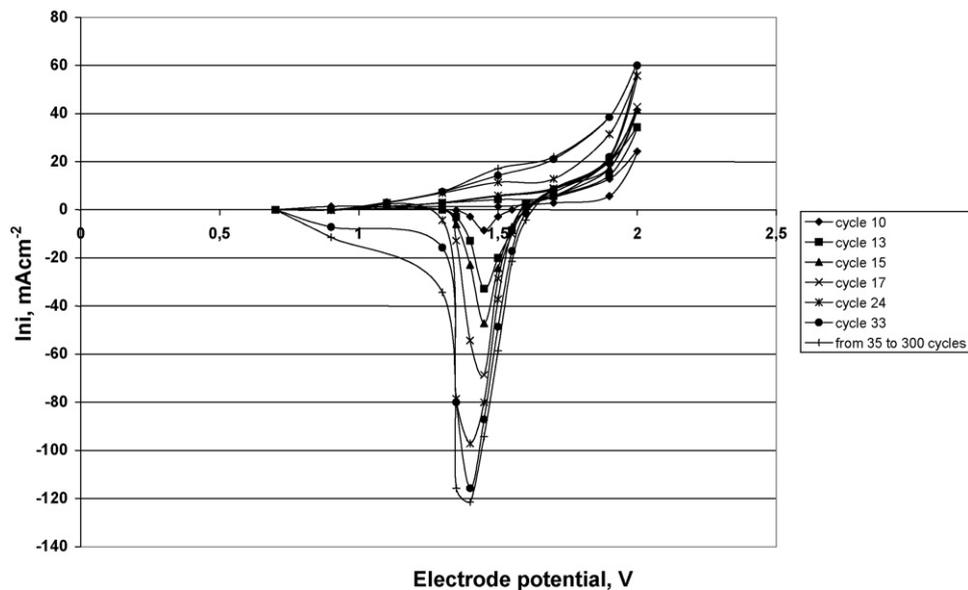
Fig. 5. Cyclic voltammograms of PbO nanopowder electrode in 4.57 M sulfuric acid solution (vs. silver-chlorine reference electrode).
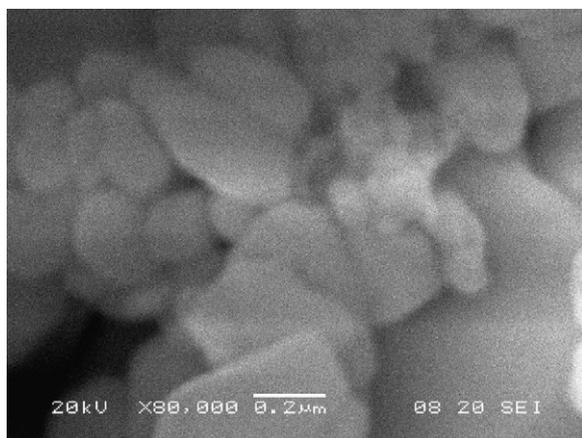
Fig. 6. SEM picture of positive paste with the nanopowder 3 after 300 cycles in H_2SO_4.

confirm possible changes in the composition and morphology of the powder, it was re-examined after cycle 300 using SEM and XRD. As depicted in Fig. 6, the powder consists of both large (100–500 nm) and small (5–20 nm) $PbSO_4$ crystals. Apparently, even after long-term cycling in sulfuric acid solution, a considerable amount of positive active mass remains in the form of nanopowder, which allows for high discharge current density values.

Similar electrochemical behavior was observed for Powder 4 that was synthesized in the chloride–nitrate melt using Additive 2. The lead oxide powder consists of nanofibers 20 nm thick and 500 nm long (Fig. 7). The corrosion potential value for such electrode is slightly more negative than that of Powder 3, but much more positive than that of the lead oxide powders obtained in the hydroxide–chloride melt. Besides, the powder consisting of nanofibers possesses the lowest solubility of all powders examined in this study.

During cycling of the paste electrode prepared from Powder 4 it was observed that after only five cycles the voltammograms began to look very similar to those obtained for Powder 3. All voltammograms exhibit a cathodic peak at a potential of 1.45 V between cycles 6 and 300, and no shift in the potential was observed during these cycles (Fig. 8). The discharge current density values are close to those for Powder 3, however the form of the voltammogram
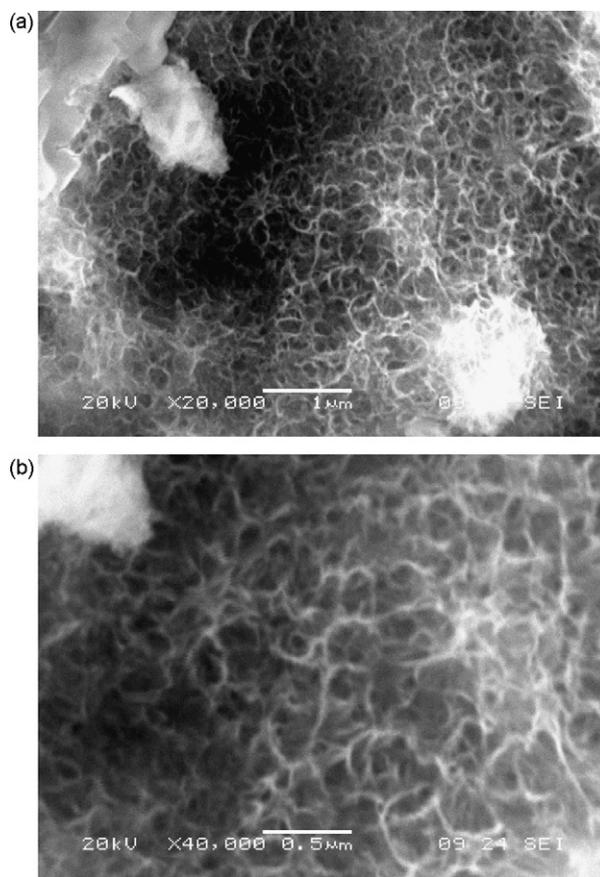
Fig. 7. SEM picture of lead oxide fibers obtained from electrochemical oxidation in NaCl–KCl–NaNO3 + additive 2.

is different, with the cathodic discharge peak being symmetrical. Characterization of the composition and structure of the powder after 300 cycles revealed that it consisted mostly of small (20 nm) crystals and relatively small number of large crystals of ca. 200 nm in size. Apparently, the long-term cycling of Powder 4 transforms its nanofibers to nanopowder with an average crystal's size of no more than 20 nm (Fig. 9).
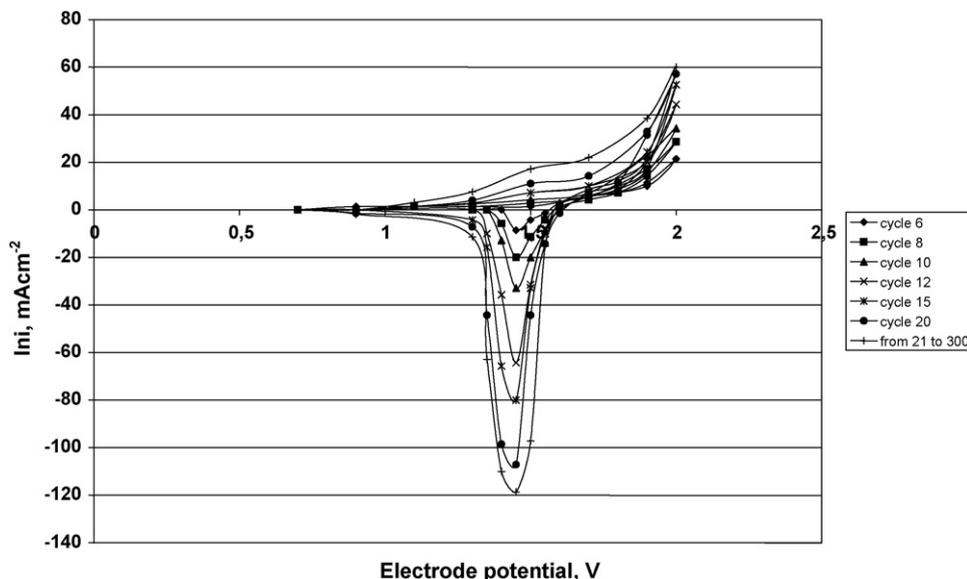
Fig. 8. Cyclic voltammograms of PbO fibers electrode in 4.57 M sulfuric acid solution (vs. silver-chlorine reference electrode).
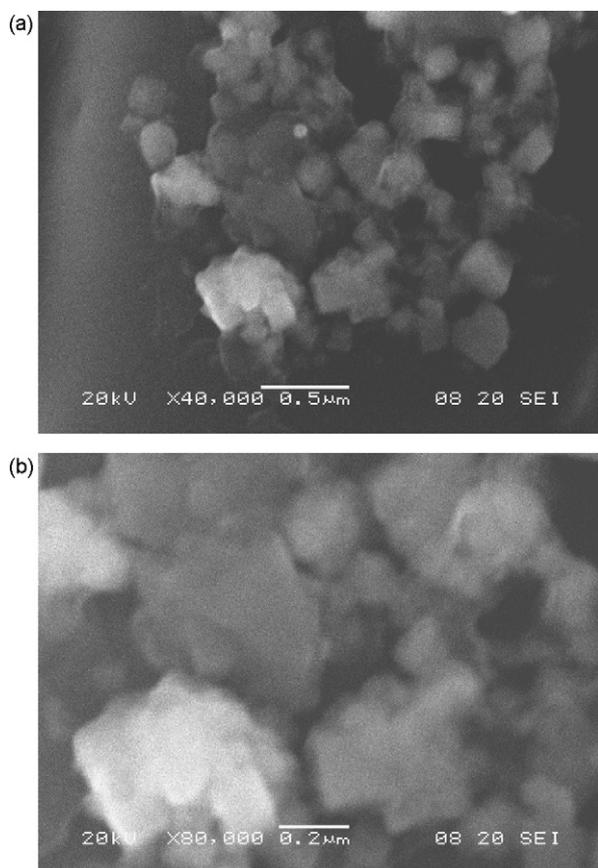
Fig. 9. SEM picture of positive paste with the nanofibers 4 after 300 cycles in sulfuric acid.

It was anticipated that such a drastic change in the powder texture should affect the potentials and discharge current density values. However, it is possible that the formation of large amount of the nanopowder of 20 nm particles is responsible for high true sur-face area of the positive electrode and its superior electrochemical activity.

4. Conclusions

By means of the high-temperature anodic oxidation in the chloride–nitrate melt, lead oxide was synthesized in the form of (1) nanopowder with an average particle size of 50–70 nm or (2) nanofibers of 20 nm thick and 500 nm long. The synthesis proce-dure is simple, cheap, highly reproducible, and potentially can be a basis for producing lead oxide on an industrial scale.

The lead oxide nanopowder and nanofibers were tested under potentiostatic cycling condition as materials of the positive elec-trode of the lead-acid battery (LAB). Both materials showed low corrosion losses, high discharge current densities, and excel-lent reproducibility of their electrochemical characteristics, which undoubtedly can be attributed to their highly increased true surface area.

Lead oxide nanopowders and nanofibers obtained by anodic oxi-dation of lead in chloride–nitrate melt can be used for preparing the positive electrode paste of LAB after an additional oxidation to lead dioxide in sulfuric acid solution in the course of electrochemical cycling.

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