

Electrosynthesis and characterization of lead oxide thin films

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Abstract

Lead dioxide (PbO₂) is an important oxide material used extensively as anode material in batteries and fuel cells and its study has now taken new strides beyond the wide field of battery research. In the present study, lead dioxide films were electrodeposited onto precleaned copper substrate from nitrate baths. The film composition, morphology and structure were investigated using Energy Dispersive X-ray Analysis (EDX), scanning electron microscopy and X-ray diffraction techniques. The oxidation and reduction potential regions and the mechanism of lead dioxide film formation are discussed using cyclic voltammetry studies. X-ray diffraction results revealed tetragonal [α -PbO₂+ β -PbO₂] structures of the films which are influenced by bath temperature and solution pH value. EDAX studies show that the films deposited at higher bath temperatures and low solution pH values are rich in lead content and low in oxygen content. The effects of bath temperature and solution pH on the morphological features of lead dioxide films are also described.

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1. Introduction

During the past decade, lead dioxide (PbO₂) anodes have sparked a worldwide interest because of their structural, morphological, optical, and mechanical properties and their potential applications in waste water treatment [1,2], ozone generation[3], analytical

sensors [4], electro-winning of metals [5] and battery electrodes [6]. The substantial growth in new avenues such as telecommunication networks, electronics, computers etc., has raised new challenges for PbO₂ batteries. PbO₂ electrodes are also applied in industrial processes such as an energy conversion process, recycling and environmental treatment [7]. It is well known that PbO₂ exhibits excellent chemical stability, high conductivity, large over potential and chemical inertness for electrolysis in an acid medium. Recently, the deposition behavior of lead oxide thin films prepared by metal organic chemical vapor deposition was reported by Zhao et al. [8]. Eftekhari reported the

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fabrication of a pH sensor based on a lead oxide thin film prepared by chemical deposition [9]. The influence of ultrasonic frequency on the electrocrystallization of lead oxide was reported by Saez et al. [10]. Devilliers et al. [11] have studied the selective electrodeposition of PbO_2 on anodized titanium substrates. Shen and Wei [12] studied the morphological behavior of electrochemically grown PbO_2 thin films. In the present study, PbO_2 films have been prepared by electrodeposition techniques because of the following reasons: easy control of thickness and morphology of films, low cost, easily maintainable equipment, and relatively uniform film which can be formed on substrates of complex shapes, and the method is more environmentally friendly. Even though several reports are available in the literature of PbO_2 films, systematic studies of deposition parameters on the film properties are scarcely reported. In the present study, a systematic investigation of cyclic voltammetry and the effects of solution pH and bath temperature on the structural and morphological properties of PbO_2 thin films are given.

2. Experimental details

Lead dioxide thin films were prepared by potentiostatic electrodeposition using an aqueous electrolyte bath. The experiments were performed in a conventional three-compartment electrochemical cell and a potentiostat [EG&G, model 362, USA] with a Saturated Calomel Electrode (SCE) as the reference electrode, a graphite electrode as the counter electrode and copper substrate as the working electrode. We have used copper substrates for the preparation of lead dioxide films because of their low cost and high electrical conductivity suitable for electrodeposition of thin films. Prior to the deposition, the substrates were polished mechanically with silicon carbide emery paper and then chemically treated in 10% sulfuric acid for 1 min. After each of these pretreatment steps, the substrates were subjected to acetone cleaning in an ultrasonic bath to remove the chemical contaminants on the surface before subsequently rinsing in double distilled water. The substrates were immediately transferred to the deposition bath. Analytical grade chemicals and reagents (Merck) were used for all the experiments. PbO_2 films were prepared from a 0.1 M $\text{Pb}(\text{NO}_3)_2$ solution with triple distilled water and 1 M HNO_3 was used as the supporting electrolyte. The deposition cell consisted of a 100 ml beaker containing the deposition solution. The pH values of the electrolyte bath were adjusted from 2.0 ± 0.1 to $5.0 \pm$

0.1. The deposition potential and bath temperature during the depositions were maintained as -1100 mV vs. SCE and 32 °C to 80 °C ± 2 °C, respectively. During the depositions, the electrolyte was not agitated. The deposition time and scan rate were 20 min and 50 mV/s, respectively. In the present study, other methods to prepare lead dioxide thin films were not attempted.

Cyclic-Voltammetry (CV) studies were carried out on well cleaned copper substrates in an aqueous bath potentiostatically in a conventional three compartment electrochemical cell. The deposited films were analyzed using an X-ray diffractometer (Philips Model PW 1710) using $\text{CuK}\alpha$ radiation with $\lambda = 0.1542$ nm. Surface morphological and compositional analyses were carried out using a scanning electron microscope and an energy dispersive X-ray analysis (EDAX) set up attached to an SEM (Philips, Model XL 30).

3. Results and discussion

3.1. Cyclic-Voltammetry studies

A typical cyclic voltammogram of electrodeposition of PbO_2 from 0.1 M $\text{Pb}(\text{NO}_3)_2$ solution onto copper substrate is shown in Fig. 1. During the CV studies, the scan rate was kept as 50 mV/s. Different cathodic and anodic peaks are observed on this cyclic voltammogram. The elucidation of the PbO_2 electrodeposition mechanism is very important for electrocatalytic activity applications. Cyclic voltammetric studies of PbO_2 material have been reported earlier on tin oxide (SnO_2) [13] and gold (Au) [14] electrodes.

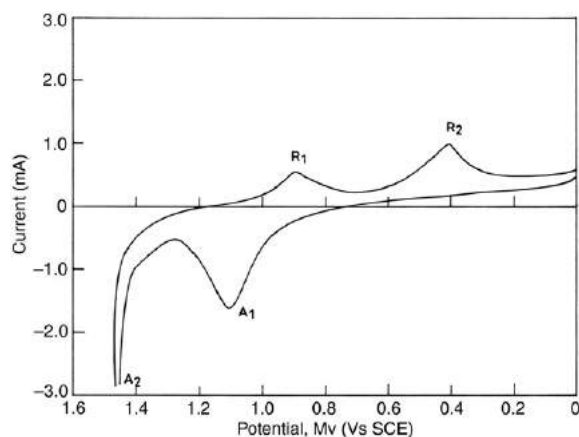
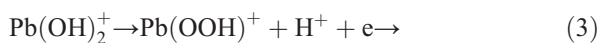
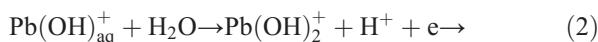
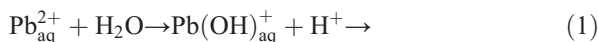


Fig. 1. A typical cyclic voltammogram of electrodeposition of PbO_2 from 0.1 M $\text{Pb}(\text{NO}_3)_2$ solution onto a copper substrate.

The oxidation mechanism of the Pb (II) ion may be expressed by the following equations:



In the above scheme, reaction (1) is an equilibrium reaction of hydration in an aqueous solution and reaction (2) leads towards a $\text{Pb}(\text{OH})_2$ intermediate phase on the substrate surface. Reaction (3) produces a $\text{Pb}(\text{OOH})^+$ intermediate product from the $\text{Pb}(\text{OH})_2^+$ and reaction (4) is a dehydration reaction. In Fig. 1, two cathodic current peaks at $E_{R_1} = 0.9$ V and $E_{R_2} = 0.41$ V are observed on the negative scan of the voltammogram, corresponding to Pb (III) and Pb (IV) species reduction. Here E_{R_1} and E_{R_2} refer to the reduction potentials. In the positive scan of the cyclic voltammogram, two anodic current peaks at $E_{A_1} = +1.1$ V and $E_{A_2} = +1.46$ V are observed. The dips A_1 and A_2 correspond to the oxidation potentials of Pb(II) species (reaction (1)) and Pb(III) species (reaction (3)), respectively. The over potential of oxygen evolution is higher than that of PbO_2 formation on a Pt substrate [15]. Hence, it can be suggested that the anodic process in the A_2 peak potential is mostly due to Pb (III) species oxidation. The reduction peak of PbO_2 on the copper (Cu) substrate was feeble but it is clearly observed in the reverse cycle.

3.2. Crystallographic analysis

The X-ray diffraction patterns recorded on PbO_2 films deposited onto copper substrates at various bath temperatures (32 °C, 55 °C and 80 °C) are shown in Fig. 2. The X-ray diffraction pattern for the film deposited at room temperature reveals a mixture of α - PbO_2 and β - PbO_2 phases with a tetragonal structure. The XRD pattern reveals several peaks corresponding to both α - PbO_2 and β - PbO_2 phases [9,16,17]. However, as the deposition temperature is increased to 55 and 80 °C, the number of peaks corresponding to the α - PbO_2 phase is reduced and most of the peaks correspond mainly to the β - PbO_2 phase. Moreover, the preferred orientation of the (110) peak corresponding to the β - PbO_2 phase is found to increase with the deposition temperature. The phase composition of PbO_2 depends upon parameters such as bath temper-

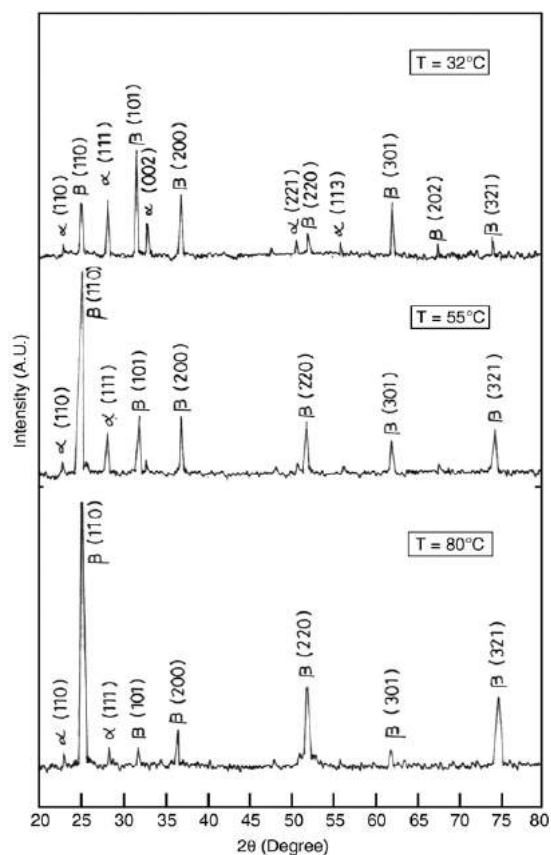


Fig. 2. X-ray diffraction patterns recorded on PbO_2 films deposited onto copper substrates at various bath temperatures (32 °C, 55 °C and 80 °C).

ature, current density, mass transport conditions etc. During the rise in bath temperature, the mass transport increases. Consequently, recrystallization to the more stable β - PbO_2 takes place from the metastable α - PbO_2 [18]. It has been reported earlier that PbO_2 films which were electrodeposited at higher bath temperature consist mainly of β - PbO_2 [19]. Although several peaks of α - PbO_2 and β - PbO_2 are significant, essentially two distinct preferred orientation peaks of α - PbO_2 and β - PbO_2 are α (111) and β (110), respectively. As observed in Fig. 2, the locations of the measured diffraction peaks do not change significantly by increasing the bath temperature of the PbO_2 electrolyte. However, with an increase in bath temperature, the intensities of the β - PbO_2 peaks become more intense whereas the intensities of the α - PbO_2 peaks are diminished. At a higher bath temperature (80 °C), especially the (111) peak corresponding to α - PbO_2 diminishes whereas the (110) peak of β - PbO_2 is sharply enhanced.

X-ray diffraction spectra of the films deposited at a bath temperature of 80 °C at various pH values (2, 3

and 5) are shown in Fig. 3. It is observed that the films deposited at various solution pH values are polycrystalline in nature with a tetragonal structure and also with a preferential orientation along β (110). The film deposited at a solution pH 2.0 ± 0.1 reveals a mixture of α -PbO₂ and β -PbO₂ phases with a preferred orientation along β (110). As the solution pH increases to 3.0 ± 0.1 , the film exhibited predominantly β -PbO₂ peaks with only one peak corresponding to α -PbO₂. As the pH is further increased to 5.0 ± 0.1 , the deposited film reveals only peaks for β -PbO₂ and the peaks corresponding to α -PbO₂ disappeared. The increase in pH value alters the conductivity of the electrolyte and seems to result in the growth of a PbO₂ film with mainly the β phase. The disappearance of the α -PbO₂ phase at a relatively higher pH (5.0 ± 0.1) value may be partly attributed to the higher deposition temperature (80 °C). By the proper choice of the pH value, a mixture of α and β -PbO₂ or a single phase β -PbO₂ could be achieved.

3.3. Structural studies

The compositional analyses of the PbO₂ electro-deposits were performed at various bath temperatures

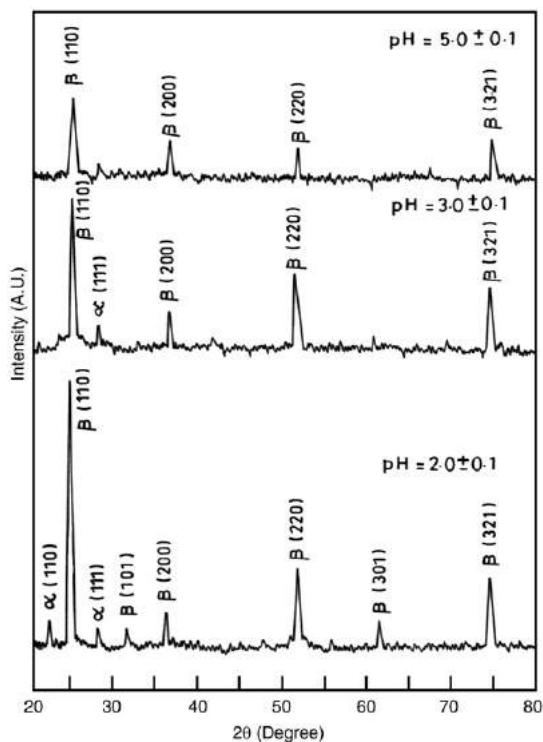


Fig. 3. X-ray diffraction spectra of the films deposited at a bath temperature of 80 °C at various pH values (2, 3 and 5).

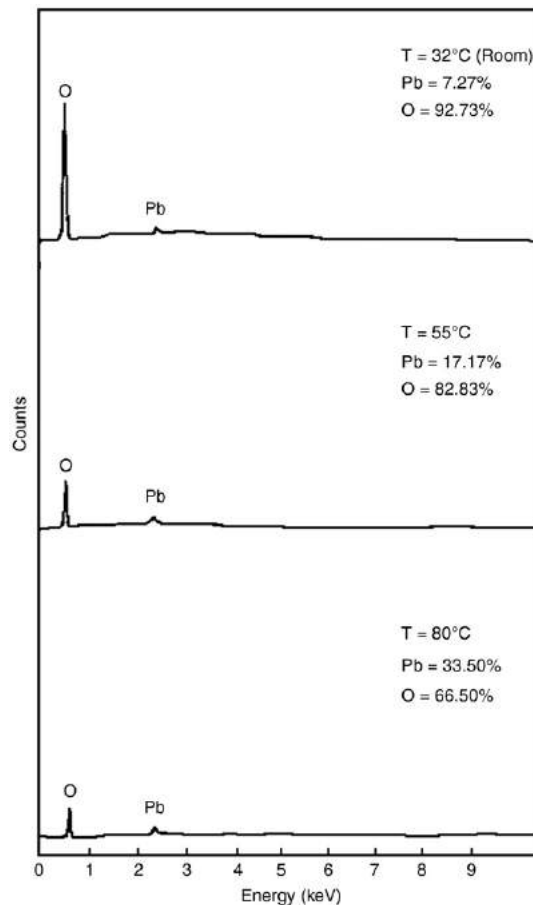


Fig. 4. EDAX spectra of PbO₂ films deposited at various bath temperatures.

and solution pH values using Energy Dispersive X-ray Analysis (EDAX). EDAX spectra of PbO₂ films deposited at various bath temperatures are shown in Fig. 4. It is found from the figure that as the bath temperature increases, the Pb content also is found to increase. The compositional variation of PbO₂ films with solution pH was also estimated and shown in Table 1. It is found from the table that as the solution pH in the bath is increased from 2.0 to 5.0, the lead (Pb) content decreases and consequently, the oxygen (O) content increases.

Table 1
Compositional analysis of PbO₂ films deposited at various solution pH

S. no	Solution pH	Atomic percentage	
		Pb	O
1	2.0 ± 0.1	33.50	66.50
2	3.0 ± 0.1	32.08	67.92
3	5.0 ± 0.1	05.87	94.13

3.4. Surface morphological studies

Fig. 5 shows scanning electron micrographs of PbO_2 electrodeposited onto copper substrates at a solution pH 2.0 ± 0.1 and at various bath temperatures (32 and 80 °C) at different magnifications (A) 32 °C (B) 80 °C and (C) 80 °C. PbO_2 electrodeposited at a low bath temperature (32 °C) exhibited irregular-shaped morphology as shown in Fig. 5A. At a higher bath temperature (80 °C), the morphology of electrodeposited PbO_2 films was characterized by cubic-shaped grains as shown in Fig. 5B and C. However, some flaws are observed between grains in the SEM. The change of morphologies of the deposits with bath temperature is interesting and may be explained as follows: the deposition process of PbO_2 film occurs in two phases. The first phase is the formation of nuclei and the second phase is their growth into crystals. Once the electrode is fully covered by a few PbO_2 layers, cubic-shaped macroscopic deposits begin to grow. The mechanism of the oxide growth process is quite different from that of the metal deposit. At a low bath temperature (32 °C), the mass transport process is quite low and the deposited structure could not be formed well. Hence, the deposit

formed will be less ordered with unshaped grains leading to the outward growth of the PbO_2 layer. At a higher bath temperature (80 °C), the mass transport process is fast compared with electron transfer and well-developed cubic-shaped crystals are formed. The average grain size of the PbO_2 film deposited at 80 °C is in the range between 1.1 and 1.3 μm . Fig. 5D shows a scanning electron micrograph of a typical PbO_2 film deposited at a solution pH 5.0 ± 0 and at a bath temperature of 80 °C. The grains appeared to be cloudy and spongy shaped.

This may be due to the increased pH in the solution bath which leads to reduced mass transport resulting in spongy shaped grains. The surface morphology is found to be not as good as in the films deposited at pH = 2.0 ± 0.1 . It is also to be noted that the preferential orientation of PbO_2 films along the β (110) orientation is larger for films deposited at a solution pH = 2.0 ± 0.1 at various temperatures (Fig. 3).

4. Conclusions

Lead dioxide thin films were electrodeposited from an aqueous bath of lead nitrate electrolyte to

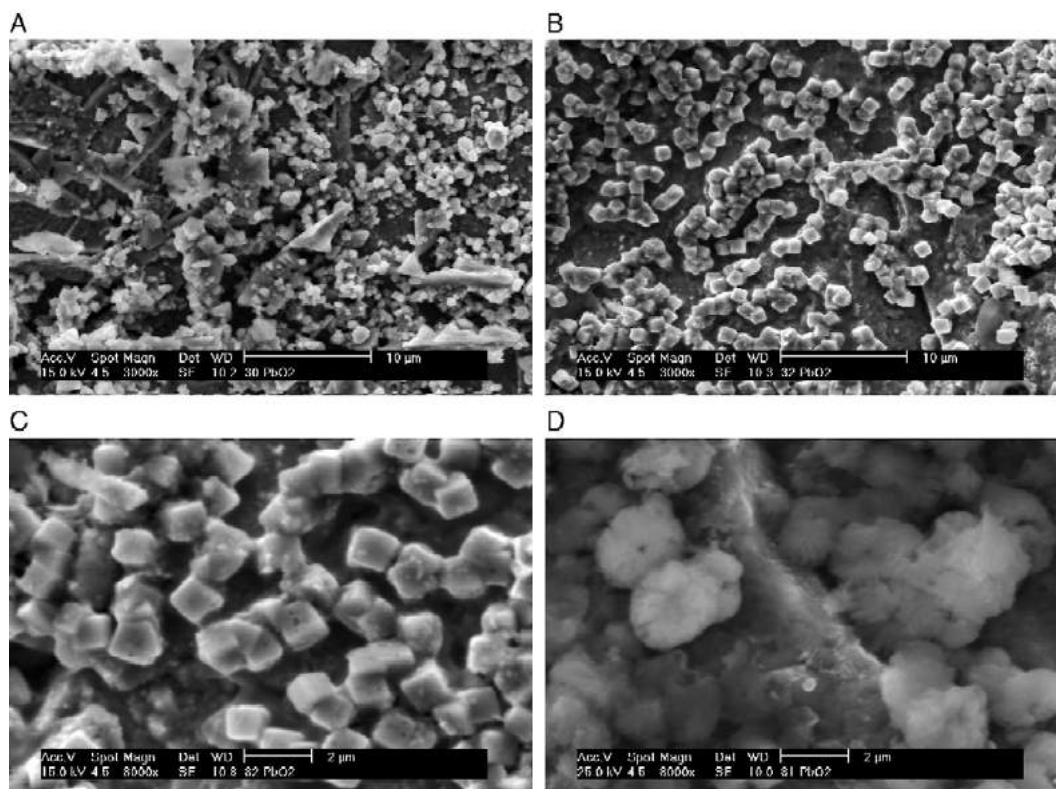


Fig. 5. Scanning electron micrographs of PbO_2 thin films electrodeposited onto copper substrates at various bath temperatures (32 and 80 °C) at different magnifications (A) 32 °C (B) 80 °C, (C) 80 °C and (D) 80 °C.

investigate the dependence of the structural, compositional and morphological properties at various bath temperature and solution pH values. The properties of PbO₂ films are found to be influenced by the bath temperature and solution pH. CV studies revealed the oxidation and reduction potential regions and also the mechanism for the formation of PbO₂ films. X-ray diffraction results of PbO₂ electrodeposits exhibited a mixture of α and β -PbO₂ phases at room temperature deposition and at higher bath temperatures the contribution of β -PbO₂ phase increases. The bath temperature and the solution pH are found to influence the composition of the deposited films. Surface morphological studies exhibited irregular-shaped features at a low temperature deposition and at higher bath temperatures and a low solution pH a cubic-shaped morphology is observed. The studies carried out here suggest that thin films of lead dioxide may be considered for the fabrication of stable β -PbO₂ anodes.

References

- [1] Polarco AM, Palmas S, Renoldi F, Mascia M. On the performance of Ti/SnO₂ and Ti/PbO₂ anodes in electrochemical degradation of 2-chlorophenol for waste water management. *J Appl Electrochem* 1999;29:147–51.
- [2] Johnson DC, Feng J, Houk LL. Direct electrochemical degradation of organic wastes in aqueous media. *Electrochim Acta* 2000;46:323–30.
- [3] Stucki S, Theis G, Kolz R, Devantay H, Christen HJ. Ozone in water using a membral electrolyzer. *J Electrochem Soc* 1985;132:367–71.
- [4] Velayuthan D, Noel M. Preparation of a polypyrrole-lead dioxide composite electrode for electrochemical applications. *Talanta* 1992;39:481–6.
- [5] Beck F. In: Kuhn AT, editor. *Electrochemistry of Lead*. New York: Academic Press; 1979.
- [6] Grugeon-Dewaele S, Laruelle L, Torcheux L, Tarascon J-M, Delahaye-Vidal A. Optimization of the positive anode material capacity in lead-acid cells through control of the basic lead sulfate precursor. *J Electrochem Soc* 1998;145:3358–65.
- [7] Kuhn AT, editor. *The Electrochemistry of Lead*. London: Academic Press; 1979.
- [8] Zhao JS, Sim JS, Lee HJ, Park DY, Hwang CS. Investigation of the deposition behavior of a lead oxide thin film on Ir substrate by liquid delivery metallorganic chemical vapor deposition. *Electrochem Solid-State Lett* 2006;9:C29–31.
- [9] Eftekhari Ali. pH sensor based on deposited film of lead oxide on aluminium substrate electrode. *Sens Actuators B Chem* 2003;88:234–8.
- [10] Saez V, Garcia JG, Iniesta J, Ferrer AF, Aldaz A. Electrodeposition of PbO₂ on glassy carbon electrodes: influence of ultrasound frequency. *Electrochem Commun* 2004;6:757–61.
- [11] Devilliers D, Baudin T, Din Thi MT, Mahe E. Selective electrodeposition of PbO₂ on anodized-polycrystalline titanium. *Electrochim Acta* 2004;49:2369–77.
- [12] Shen PK, Wei XL. Morphologic study of electrochemically formed lead oxide. *Electrochim Acta* 2003;48:1743–7.
- [13] Ho CN, Hwang BJ. Effects of copper cation and acetate anion on the growth of PbO₂ on a SnO₂/Ti substrate. *Electrochim Acta* 1993;38:2749–57.
- [14] Chang H, Johnson DC. Electrocatalysis of anodic oxygen-transfer reactions; Chrono amperometric and voltammetric studies of the nucleation and electrodeposition of β -lead oxide at a rotated gold disc electrode in acidic media. *J Electrochem Soc* 1989;136:17–22.
- [15] Fleischmann M, Liler M. The anodic oxidation of solutions of plumbous salts. Part 1.-The kinetics of deposition of α -lead oxide from acetate solutions. *Trans Faraday Soc* 1958;54:1370–81.
- [16] Lee J, Varela H, Uhm S, Tak Y. Electrodeposition of PbO₂ onto Au and Ti. *Electrochem Commun* 2000;2:646–52.
- [17] I. Petersson, E. Ahlberg, B. Berghult: Parameters influencing the ratio between electrochemically formed α and β -PbO₂ 1998; 76: 98–105.
- [18] Abaci S, Pekmez K, Hokelek T, Yildiz A. Investigations of some parameters influencing electrocrystallization of PbO₂. *J Power Sources* 2000;88:232–6.
- [19] Velichenko AB, Amadelli R, Benedetti A, Girenko DV, Kovalyov SV, Danilov FI. Electrosynthesis and physicochemical properties of PbO₂ films. *J Electrochem Soc* 2002;149:C445–9.