



Electrodeposition of lead dioxide from methanesulfonate solutions

A.B. Velichenko^{a,*}, R. Amadelli^b, E.V. Gruzdeva^a, T.V. Luk'yanenko^a, F.I. Danilov^a

^a Department of Physical Chemistry, Ukrainian State University of Chemical Technology, Gagarin Avenue 8, Dnipropetrovsk, 49005, Ukraine

^b ISOF-CNR, c/o Department of Chemistry, Università di Ferrara, via L. Borsari 46, 44100 Ferrara, Italy

ARTICLE INFO

Article history:

Received 24 September 2008

Received in revised form 11 October 2008

Accepted 15 October 2008

Available online 1 November 2008

Keywords:

Lead dioxide electrodeposition

Methanesulfonate

Physicochemical properties

ABSTRACT

Lead dioxide electrodeposition from methanesulfonic media and physicochemical properties of the resulting oxide were studied in this work to improve anodic process at PbO₂/Pb²⁺ electrode of flow battery. The presence of methanesulfonate ions in the electrodeposition solution causes only a quantitative difference in the PbO₂ electrodeposition process without apparently changing the reaction mechanism. In methanesulfonic media PbO₂ electrodeposition rate is higher than in nitrate solutions. Current efficiency of PbO₂ formation depends on electrode potential (or deposition current density), electrolyte composition (concentration of Pb²⁺ and methanesulfonate ions), hydrodynamic conditions, pH and temperature of the solution. It is important to note that thick PbO₂ coatings (up to 2 mm) with good mechanical properties and adhesion to the substrate can be deposited in a wide range of current density (2–100 mA cm⁻²).

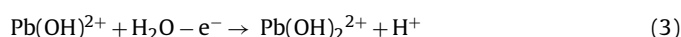
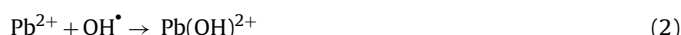
© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Flow battery is an attractive device for the energy storage thanks to its high energy efficiency (over 80%) [1]. Scale application depends on the volume of the electrolyte and the concentration of reactants. Recently, Pletcher et al. [2–7] proposed a new concept of flow liquid battery, based on the conventional lead acid cell. In this system, soluble Pb(II) (lead methanesulfonate), is oxidized to lead dioxide deposited on one electrode and reduced to lead deposited on the other electrode when the battery is charged, and the deposited PbO₂ and Pb turn back to the soluble salt when the battery is discharged. Only one reactant (lead methanesulfonate) exists in the electrolyte, thus no membrane is needed in this kind of flow liquid battery, and the cell can be built in a much simpler way than the conventional system. Any improvement of the process of PbO₂ formation necessarily requires a thorough understanding of lead dioxide electrodeposition from methanesulfonate media. Unfortunately, in most cases, details on the effect of methanesulfonate ions on the Pb(II) electrooxidation are not known [8], although there is a vast literature on lead dioxide electrodeposition from perchloric and nitric acid solutions [9–11].

According to [12] the presence of different ionic additives in the electrodeposition solution causes only a slight shift in the lead dioxide electrodeposition rate without seemingly changing the deposition mechanism, which was described by the following

scheme:



The first stage is the formation of oxygen-containing particles as OH_{ads}, chemisorbed on the electrode. In a subsequent chemical stage, these particles interact with lead species forming a soluble intermediate product, Pb(OH)²⁺ which is further oxidized electrochemically with transfer of the second electron forming a soluble oxygenated Pb(IV) compound. The latter is decomposed chemically to form hydrated Pb(IV) species in the electrolyte bulk that subsequently crystallize onto the surface. At low overpotential the rate-determining stage is the second electron transfer reaction (3) and at high overpotential the process is controlled by Pb²⁺ diffusion. According to the mechanism mentioned above the rate of lead dioxide growth depends on the amount of the intermediate product formed during reaction (2) at the electrode surface. In this case the adsorption of an ion should change the rate of PbO₂ electrodeposition due to an influence on the coverage by oxygen-containing particles [12]. In this connection, it appears very interesting to study the influence of methanesulfonate ions on the deposition process.

It has been previously reported [13] that variations of the conditions of PbO₂ electroplating cause changes in the oxide properties, such as the morphology and crystallographic nature, which result in a different electrochemical behaviour. In acidic solutions, electrodeposition of lead dioxide leads predominantly to the tetragonal

* Corresponding author. Tel.: +38 067 5635659; fax: +38 056 3772974.
E-mail address: velichenko@ukr.net (A.B. Velichenko).

β -form, although a small amount of the orthorhombic α -form is also present depending on the experimental conditions.

In the present work we report and discuss the results of a study of lead dioxide electrodeposition from methanesulfonate media and physicochemical properties of the resulting oxide with the aim to improve anodic process at $\text{PbO}_2/\text{Pb}^{2+}$ electrode in view of perspective application in flow batteries.

2. Experimental

Electrodeposition of lead dioxide was studied on a Pt electrode in methanesulfonic acid $\text{CH}_3\text{SO}_3\text{H}$ (MSA) and lead methanesulfonate $\text{Pb}(\text{CH}_3\text{SO}_3)_2$ solutions. Analytical grade reagents and double distilled water were used for all solutions. The solution temperature was maintained at $25 \pm 1^\circ\text{C}$ (in most cases). All potentials are given against $\text{Ag}|\text{AgCl}|\text{KCl}_{(\text{sat.})}$ electrode.

The Pt-RDE was prepared by pressing the metal rods into Teflon sleeves. The disk electrode surface area was 0.196 cm^2 . The electrode was polished with magnesium oxide ($3\ \mu\text{m}$) before each experiment. Then it was treated in a 1:1 mixture of concentrated H_2SO_4 and H_2O_2 during 2 min. The electrode potential was cycled within the range 0–1.60 V at 100 mV s^{-1} in the deposition solution until a reproducible background resulted (about 10 cycles).

The number of electrons at the elementary stage was calculated from the Delahay equation [14]:

$$i = 3.00 \times 10^5 n(\beta n_\beta)^{1/2} D^{1/2} C S V^{1/2} \quad (5)$$

The charge-transfer coefficient β was determined from the E_p vs. $\ln V$ dependence [14]:

$$E_p = E^0 - RT/\beta n_\beta F [0.78 - \ln k_s + \ln(D\beta n_\beta F V / RT)^{1/2}] \quad (6)$$

where n is the effective number of electrons exchanged in the reaction, β is the transfer coefficient, S is the electrode area, V is the potential sweep rate, D is the diffusion coefficient, k_s is the constant rate, C is the concentration of electroactive substance in the solution; all other terms have their usual electrochemical significance.

Lead dioxide was deposited at potentiostatic (electrodeposition kinetic study) and galvanostatic (influence of electrodeposition conditions and electrolyte composition on current efficiency of PbO_2 , physicochemical properties of resulting oxide) conditions. The current efficiency of the lead dioxide (CE) and the PbO_2 electrodeposition current (I) was calculated from equations:

$$\text{CE} = \frac{Q_{\text{red}}}{Q} \quad (7)$$

$$I = \frac{Q_{\text{red}}}{t} \quad (8)$$

where Q is the total charge passed during the anodic polarization, Q_{red} is the charge passed on PbO_2 reduction at $E = 0.8\text{ V}$, t is the total time of an anodic polarization. In case of deposition of thick PbO_2 films at galvanostatic conditions CE calculated from gravimetric measurements.

XRD and SEM were used for the characterization of the deposited PbO_2 films.

3. Results and discussion

Typical cyclic voltammograms (CV) for a Pt electrode in the nitrate and methanesulfonate solutions are shown in Fig. 1a. The anodic branch of the curve, at potentials more positive than 1.4 V, features an important current growth that corresponds to the simultaneous reactions of $\text{Pb}(\text{II})$ oxidation and oxygen evolution [10–13]. In the cathodic branch of the curve, in the range 0.8–1.2 V, one can

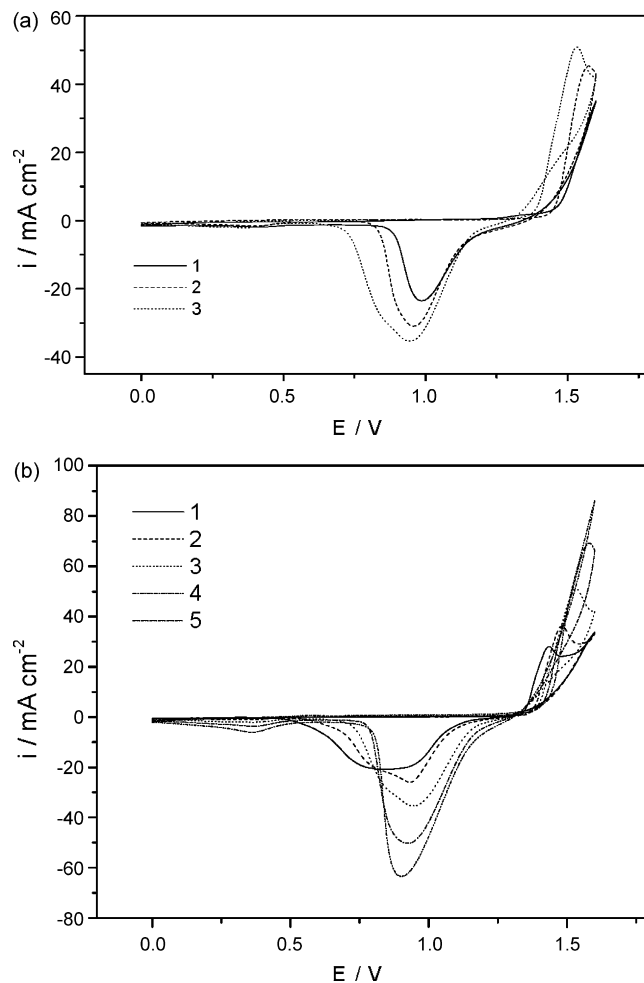


Fig. 1. (a) Cyclic voltammograms at the Pt-electrode in different solutions: 1, 0.1 M $\text{Pb}(\text{NO}_3)_2 + 0.1\text{ M HNO}_3$; 2, 0.1 M $\text{Pb}(\text{NO}_3)_2 + 0.1\text{ M CH}_3\text{SO}_3\text{H}$; 3, 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1\text{ M CH}_3\text{SO}_3\text{H}$. $v = 50\text{ mV s}^{-1}$. (b) Cyclic voltammograms at the Pt-electrode in 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1\text{ M CH}_3\text{SO}_3\text{H}$ at different potential sweep rate (mV s^{-1}): 1, 10; 2, 20; 3, 50; 4, 100; 5, 200.

observe a current peak due to reduction of lead dioxide. From gravimetric measurements, we established that the area and the magnitude (I_p) of the reduction peak are a good measure of the amount of lead dioxide deposited on the electrode surface [10–13]. The anodic overpotential decreases with increasing concentration of methanesulfonate ions in the electrolyte and both the anodic current and cathodic peak of lead dioxide dissolution increases (Fig. 1) indicating an increase in the PbO_2 deposition rate. The value of the current and the shape of CV in methanesulfonate solution strongly depend on potential sweep rate (V) (Fig. 1b). At high value of potential sweep rate ($100\text{--}200\text{ mV s}^{-1}$) one can observe an exponential dependence of the anodic current from the electrode potential both in the forward and in the reverse scan and sharp cathodic peak of PbO_2 reduction. A decrease of potential sweep rate ($V < 50\text{ mV s}^{-1}$) leads to appearance of an anodic peak and two cathodic peaks of PbO_2 reduction (Fig. 1b). This indicates a rather complex behaviour of the Pt electrode during PbO_2 electrodeposition from methanesulfonate electrolyte. Two cathodic peaks can result from the formation of two allotropic form of lead dioxide (α - and β -phases) in comparable amounts during initial PbO_2 deposition [15,16].

When the electrode potential was scanned to 1.6 V, the lead dioxide electrodeposition process occurred in conditions of practically complete kinetic control. We deem it necessary to state that

the current efficiency for lead dioxide amounted, in this case, to more than 90%. As the rotation rate of the electrode increases, there occurs a substantial decrease in the peak current of the cathodic process of PbO_2 reduction while the anodic current in the exponential portion of a cyclic voltammogram, specifically, at 1.5–1.6 V [10], remains practically invariant. The effect we observed can be explained in the framework of the mechanism described by equations (1)–(4). In this case, probably, mainly an intermediate product is removed from the electrode surface. The product, which is probably similar to $\text{Pb}(\text{OH})^{2+}$, takes part in the lead dioxide formation and is incapable of further electrochemical conversions. This implies that the stage described by reaction (3) is rate-determining. It should be noted that in these particular conditions, with the electrode potential scanned in the region from 0.0 to 1.6 V, the PbO_2 electrodeposition process proceeds each time on a freshly formed layer of oxide phases of platinum. The point is that after the reduction of lead dioxide in a cathodic cycle an ultrathin layer of low-valence phase oxides of lead remains on the electrode surface. The presence of this ultrathin layer drastically diminishes the overvoltage of the lead dioxide electrodeposition reaction on this surface [17]. A further shift of the electrode potential into the cathodic region leads to the reduction of the phase oxides of platinum with a simultaneous destruction of the ultrathin layer of lead oxides. This circumstance substantially hinders the process, in which a new phase of lead dioxide begins to form in an anodic cycle, and makes the stage, which is described by reaction (3), the rate-determining stage.

To understand better some detail of PbO_2 nucleation under initial electrodeposition conditions, we performed chronoamperometric measurements at Pt electrode. Two markedly different models for nucleation and growth processes can be found in the literature [18]: the rate-determining step is identified as the incorporation of ions into the growing lattice (kinetic control); the limiting step is the mass transport from the solution to the growing nucleus (diffusion control). Fig. 2 presents a series of potential step experiments obtained for the Pt electrode in different potentials and solutions. Under our experimental conditions, the i vs. t transients are characterized by several features. After the onset of the potential step, a sharp decrease of the current density occurs until a minimum value i_0 is reached, the time involved being much higher than expected for double layer charging; the current remains at i_0 during an induction time t_0 after which the current rises up to a steady-state value (i_{ss}) at long times (kinetic control). This behaviour we observe at low deposition potential. At high deposition potential steady-state current plateau (i_{ss}) value is observed after passing through a maximum (diffusion control). The values of t_0 and i_{ss} depend on the applied step potential and methanesulfonate concentration. Increase in deposition potential and methanesulfonate concentration lead to a decrease of the induction time and to an increase of the steady-state current. This indicates an acceleration of PbO_2 crystallization in the presence of methanesulfonate ions.

To determine the number of electrons involved in the kinetic stage of the PbO_2 deposition, voltammetry with linear potential scan was used [14]. An increase in the anodic peak potential in the voltammetric curve with increasing potential scan rate ν points to irreversible electron transfer kinetics (Fig. 3). In all cases, the number of electrons involved in the elementary stage, which is calculated by the Delahay equation, is unity. This indicates that the charge-transfer proceeds in stages, i.e. two single-electron stages (1) and (3) of the PbO_2 formation reaction exist, and the deposition regularities in the methanesulfonate solutions is adequately described by mechanism (1)–(4). The transfer coefficient (β), which is determined from the E_p vs. $\ln \nu$ [14], depends on content of methanesulfonate ions in the solution. For instance, an increase in

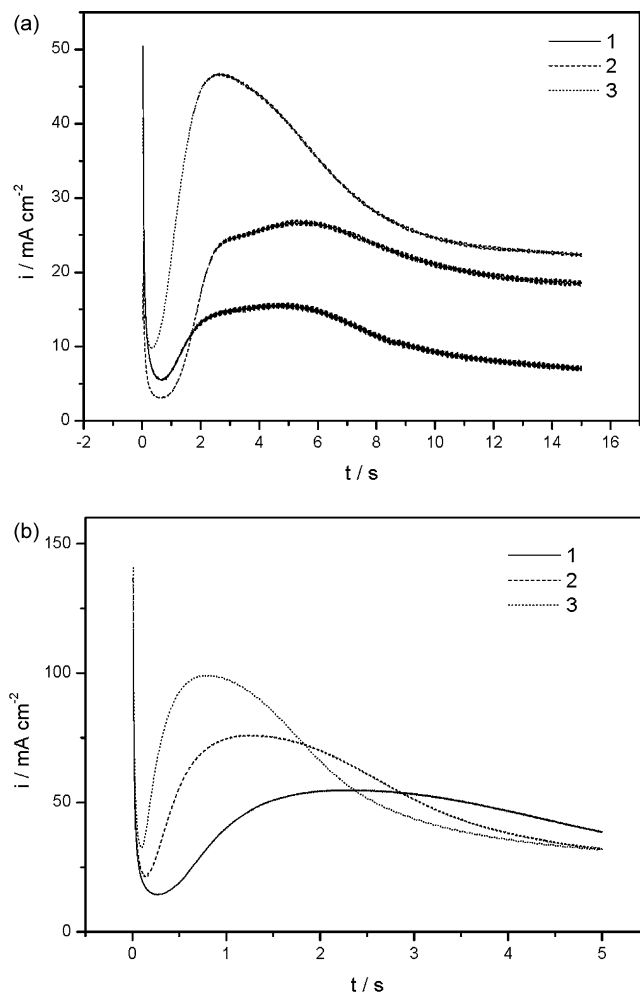


Fig. 2. (a) i - t curves at the Pt-electrode in different electrolytes: 1, 0.1 M $\text{Pb}(\text{NO}_3)_2 + 0.1$ M HNO_3 ; 2, 0.1 M $\text{Pb}(\text{NO}_3)_2 + 0.1$ M $\text{CH}_3\text{SO}_3\text{H}$; 3, 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1$ M $\text{CH}_3\text{SO}_3\text{H}$. $E = 1.5$ V. (b) i - t curves at the Pt-electrode in 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1$ M $\text{CH}_3\text{SO}_3\text{H}$ at different electrode potential (V): 1, 1.50; 2, 1.55; 3, 1.60.

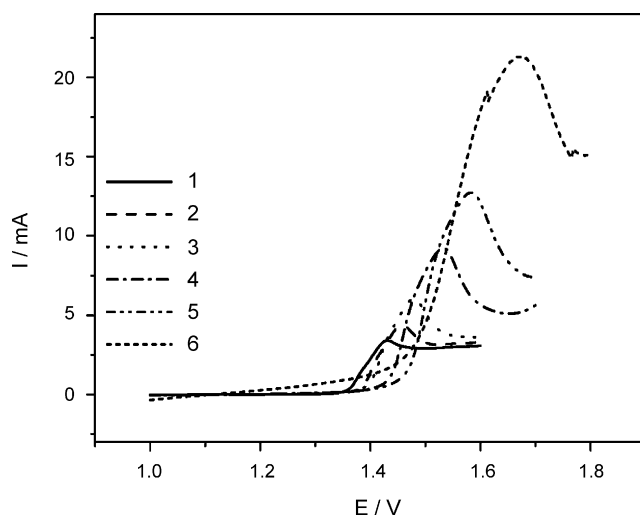


Fig. 3. Linear sweep voltammograms in 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1$ M $\text{CH}_3\text{SO}_3\text{H}$ at different potential sweep rate (mV s^{-1}): 1, 5; 2, 10; 3, 20; 4, 50; 5, 100; 6, 200.

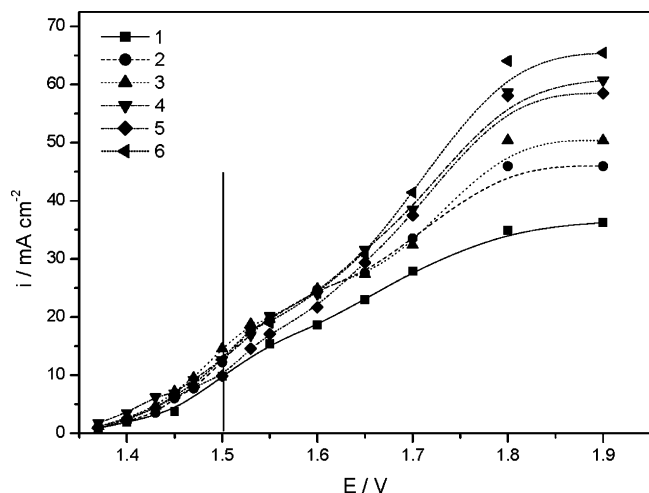


Fig. 4. Steady-state polarization curves of Pt-electrode for partial current of PbO_2 electrodeposition in solutions: 1, 0.1 M HNO_3 + 0.1 M $\text{Pb}(\text{NO}_3)_2$; 2, 0.1 M $\text{CH}_3\text{SO}_3\text{H}$ + 0.1 M $\text{Pb}(\text{NO}_3)_2$; 3, 0.1 M HNO_3 + 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2$; 4, 0.1 M $\text{CH}_3\text{SO}_3\text{H}$ + 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2$; 5, 0.1 M $\text{CH}_3\text{SO}_3\text{H}$ + 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2$ + 0.2 M $\text{CH}_3\text{SO}_3\text{Na}$; 6, 0.1 M $\text{CH}_3\text{SO}_3\text{H}$ + 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2$ + 0.7 M $\text{CH}_3\text{SO}_3\text{Na}$.

concentration from 0.1 to 0.3 M leads to decrease β from 0.51 to 0.40. This indicates a possible adsorption of methanesulfonate ions on the growing lead dioxide.

Partial steady-state polarization curves (PbO_2 electrodeposition only) for Pt are shown in Fig. 4. In the potential range 1.30–1.50 V, the current increases according to an exponential law and the Tafel plot of E vs. $\log(i)$, obtained from partial steady-state polarization curve has a slope of about 120 mV/dec. At low polarization, the anodic current decreases with increasing electrode rotation rate (Fig. 5a) due to the removal of soluble intermediate product $\text{Pb}(\text{III})$ (which forms at chemical stage (2)) from the reaction zone [10]. The observed effect indicates that, in this case, reaction (3) of the second electron transfer is rate-determining.

It is important to note the rather complex influence of methanesulfonate concentration on steady-state partial current of PbO_2 electrodeposition is observed in kinetic zone of the polarization curve (Fig. 5b). The methanesulfonate ions influence on the deposition kinetics can be caused by both bulk and surface effects. The bulk effects are determined by the interaction of Pb^{2+} with methanesulfonate ions in the bulk electrolyte, yielding complex compounds or strong ionic associates. As is shown by the potentiometric measurements on the lead electrode, adding methanesulfonate does not lead to a considerable change in the potential and, consequently, in the composition of potential-determining ions.

The surface nature of these kinetic effects is a result of methanesulfonate ions adsorption on lead dioxide. The influence of adsorption on the electron transfer stage can be described by following equation [19,20]:

$$\frac{i_\theta}{i_{\theta=0}} = (1 - \theta) \exp(-A\theta) \exp\left[-\frac{(z + \beta n)F\Delta\psi'(\theta)}{RT}\right] \quad (9)$$

where θ is the electrode coverage by additives, A is the inhibition parameter, z is the charging number of the electroactive particle, n is the effective number of electrons exchanged in the reaction, β is the transfer coefficient, $\Delta\psi'(\theta)$ is dependence of the ψ' -potential on electrode coverage by additives.

According to equation (9), the adsorption of substances at an electrode profoundly affects the rate of discharge–ionization stage. This effect is due to several factors that change the concentration of reacting species in the surface layer and the activation

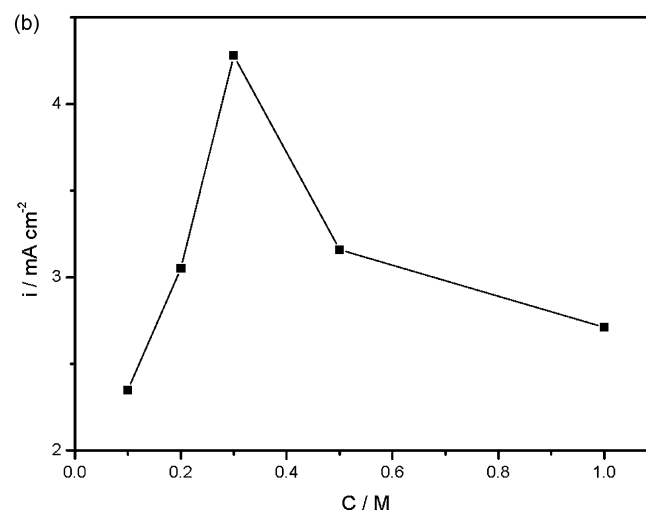
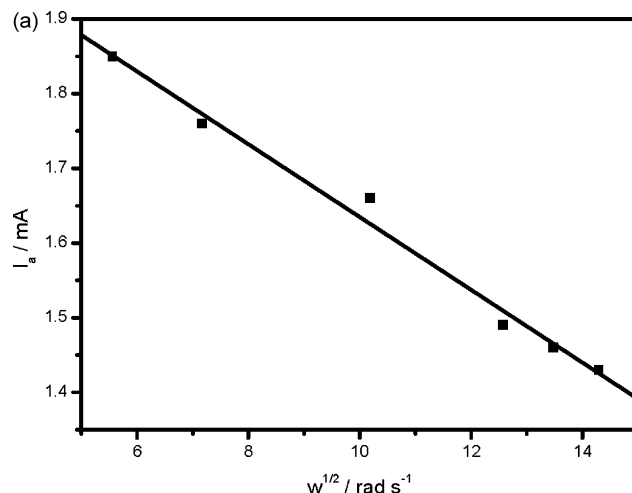


Fig. 5. (a) Effect of rotation rate of Pt-RDE ($E = 1.5$ V) on current of PbO_2 deposition in 0.1 M $\text{CH}_3\text{SO}_3\text{H}$ + 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2$. (b) Effect of methanesulfonate ions concentration in the electrolyte on current of PbO_2 deposition at Pt-electrode ($E = 1.4$ V).

energy for the electrode process. A decrease of potential ψ' in the active-complex localization plane accelerates the charge-transfer stage. This was observed at low methanesulfonate concentrations (Fig. 5b). When the anion is adsorbed at the electrode surface, ψ' can not only significantly decrease, but even become negative due to the recharge of the electrical double layer. The inhibition parameter A in (9) reflects both electrostatic and chemical interactions of the activated complex with the adsorbed layer, leading to an increase in the activation energy for the charge-transfer stage. A further increase in the bulk concentration of methanesulfonate in electrolyte leads to an increase in the electrode surface coverage θ with adsorbed anions. This slows down the charge-transfer stage (Fig. 5b) due to the blocking of active centers on the electrode surface [12,19,21,22].

At higher anodic polarization (Fig. 4, $E \geq 1.6$ V), a limiting current of the lead dioxide deposition is observed in the steady-state polarization curve. The magnitude of the partial current in this region strongly depends on the rotation speed of the electrode; the dependence of the current on the square root of electrode rotation speed is linear (Fig. 6a), indicating that, in this potential region, lead dioxide deposition occurs under diffusion control. An increase of the limiting current in the polarization curve with increasing methanesulfonate concentration can also be caused by ion adsorption.

As a result of ion-exchange adsorption, the association of surface Pb^{2+} ions with anions decreases the free charge. The involvement of

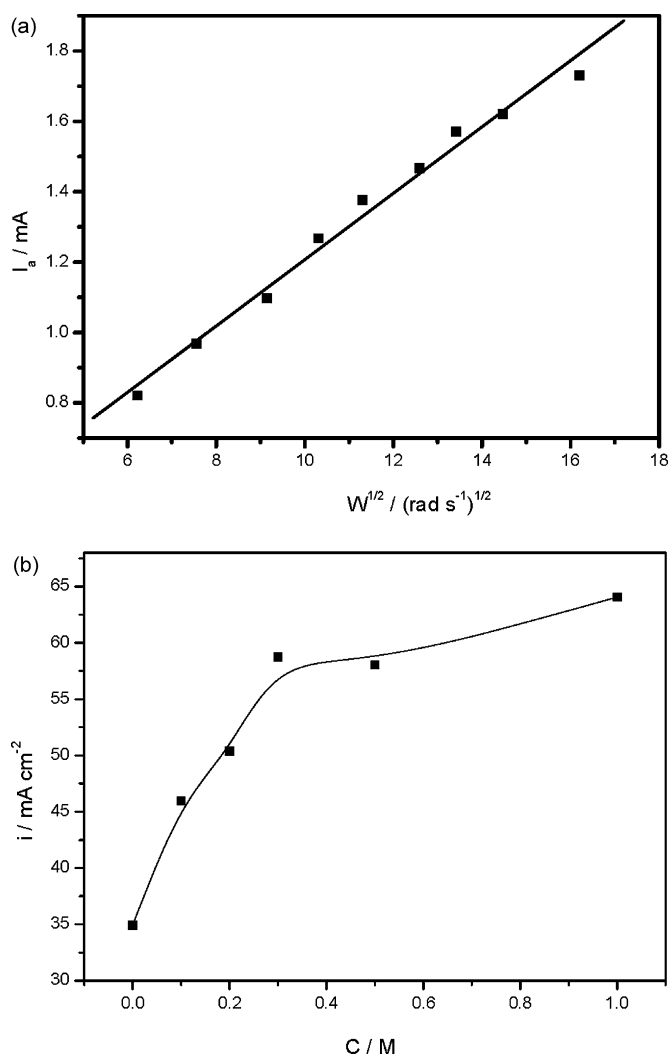


Fig. 6. (a) Effect of rotation rate of Pt-RDE ($E = 1.7$ V) on current of PbO_2 deposition in 0.1 M $\text{CH}_3\text{SO}_3\text{H} + 0.1$ M $\text{Pb}(\text{CH}_3\text{SO}_3)_2$. (b) Effect of methanesulfonate ions concentration in the electrolyte on limiting current of PbO_2 deposition at Pt-electrode ($E = 1.8$ V).

lead ions in the electrochemical reaction brings about the appearance of an excess negative charge on the electrode surface. This, in turn, accelerates the migration of positively charged lead ions to the electrode. Similar cases for the processes proceeding at a limiting current were described in [12,19,21–23]. Thus, an increase in the limiting current with increasing methanesulfonate concentration is most probably associated with an increase in the contribution of the migration component.

Thus in all cases the electrodeposition process obeys the basic relationship mentioned previously for Pt electrodes in HClO_4 and HNO_3 solutions, and it is described satisfactorily by the kinetic scheme given in (1)–(4). The important conclusion is that the presence of methanesulfonate ions in the electrodeposition solution causes only a quantitative difference in the PbO_2 electrodeposition process without apparently changing the qualitative relationships. In methanesulfonic media PbO_2 electrodeposition rate is higher than in nitrate solutions.

The polarization curve at high anodic overpotential features an exponential current growth [13] that corresponds to the simultaneous reactions of Pb^{2+} oxidation and oxygen evolution. In this potential region, oxygen evolution contributes significantly to the total current thus decreasing the current efficiency of lead dioxide

formation with deposition potential or current density. For application of $\text{Pb}^{2+}/\text{PbO}_2$ system as positive electrode (in charge mode) of flow Red-Ox battery, the current density window where PbO_2 formation takes place with 100% current efficiency (CE) has to be as wide as possible. In this connection we studied effects of electrode potential (or deposition current density), electrolyte composition (concentration of Pb^{2+} and methanesulfonate ions), hydrodynamic conditions, pH and temperature of the solution on current efficiency of PbO_2 formation. In case of fresh Pt electrode, not covered by PbO_2 (initial oxide electrodeposition), one can observe a rather complex influence of electrodeposition potential on PbO_2 CE. At low overpotential CE increases due to increasing oxide electrodeposition current and overpotential of oxygen evolution on porous lead dioxide coating to reach maximum at 100% surface coverage by PbO_2 . At potential higher than 1.55 V oxygen evolution contributes significantly to the total current thus, decreasing the current efficiency of lead dioxide formation.

It is important to note that in most cases an electrode is already covered by thin PbO_2 film after 5–30 s of electrolysis. So the nature of electrode material hardly influences lead dioxide electrodeposition at relatively long electrolysis times [12]. At steady-state conditions we deposit PbO_2 on lead dioxide electrode. A typical dependence of CE PbO_2 from current density is shown in Fig. 7a. At low current density one can observe a plateau of 100% CE until beginning oxygen evolution process when current efficiency decreases. To increase the 100% CE window we need to accelerate PbO_2 electrodeposition or/and to inhibit oxygen evolution reaction. Taking into account that at high overpotential lead dioxide electrodeposition is controlled by diffusion stage we can increase deposition rate at higher Pb^{2+} concentration and temperature, stirring of the solution. According to the data presented in Fig. 7a, increasing the concentration of Pb^{2+} from 0.1 to 1.0 M leads to an increase of the maximum deposition current density (at 100% CE) from 12 to 120 mA cm^{-2} . It is important to note that concentration of methanesulfonate ions is hardly influenced to current efficiency of lead dioxide probably due to its influence both PbO_2 electrodeposition and oxygen evolution rates. In the case of a 1.0 M solution of Pb^{2+} the maximum deposition current density can be increased from 120 to 140 mA cm^{-2} by solution stirring (Fig. 7a). Temperature increases CE PbO_2 too (Fig. 7b) due to acceleration of diffusion rate of Pb^{2+} ions. For instance, at temperature range 25 – 80 °C CE increases from 82 to 100% (1.0 M Pb^{2+} , 300 mA cm^{-2}). Conversely, an increase in the methanesulfonic acid concentration acid leads to a decrease of PbO_2 CE (Fig. 7c) due to inhibition of lead dioxide electrodeposition.

It is important to note that at 25 °C we deposited thick PbO_2 coating (up to 2 mm) in wide range of current density (2 – 100 mA cm^{-2}) with good mechanical properties and adhesion to the substrate even on smooth Pt plate ($S = 4$ cm^2 , electrolyte— 1.0 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1$ M $\text{CH}_3\text{SO}_3\text{H}$).

In most cases the PbO_2 films were a mixture of the α - and β -phases, the latter being more prevalent (Fig. 8). There is a good agreement with the data reported in [13] for nitrate solutions. Interestingly, we note a sensible change of the crystalline orientation for both the α - and β -phase depending on the electrodeposition conditions (Fig. 8). For instance, intensity of peaks 110 and 301 of β - PbO_2 decreases with increasing electrodeposition current density. A different dependence of the relative peak intensities on the electrodeposition was observed in the kinetic and diffusion controlled regions, respectively. The dependence of intensity of peaks 111 of α - PbO_2 and 211 of β - PbO_2 from the electrodeposition current density has a volcanic shape. At the same time plots for 200 , 411 of β - PbO_2 and 222 of α - PbO_2 pass through a minimum at 8 mA cm^{-2} . It is important to note that at higher current density preferred crystallographic orientations appear.

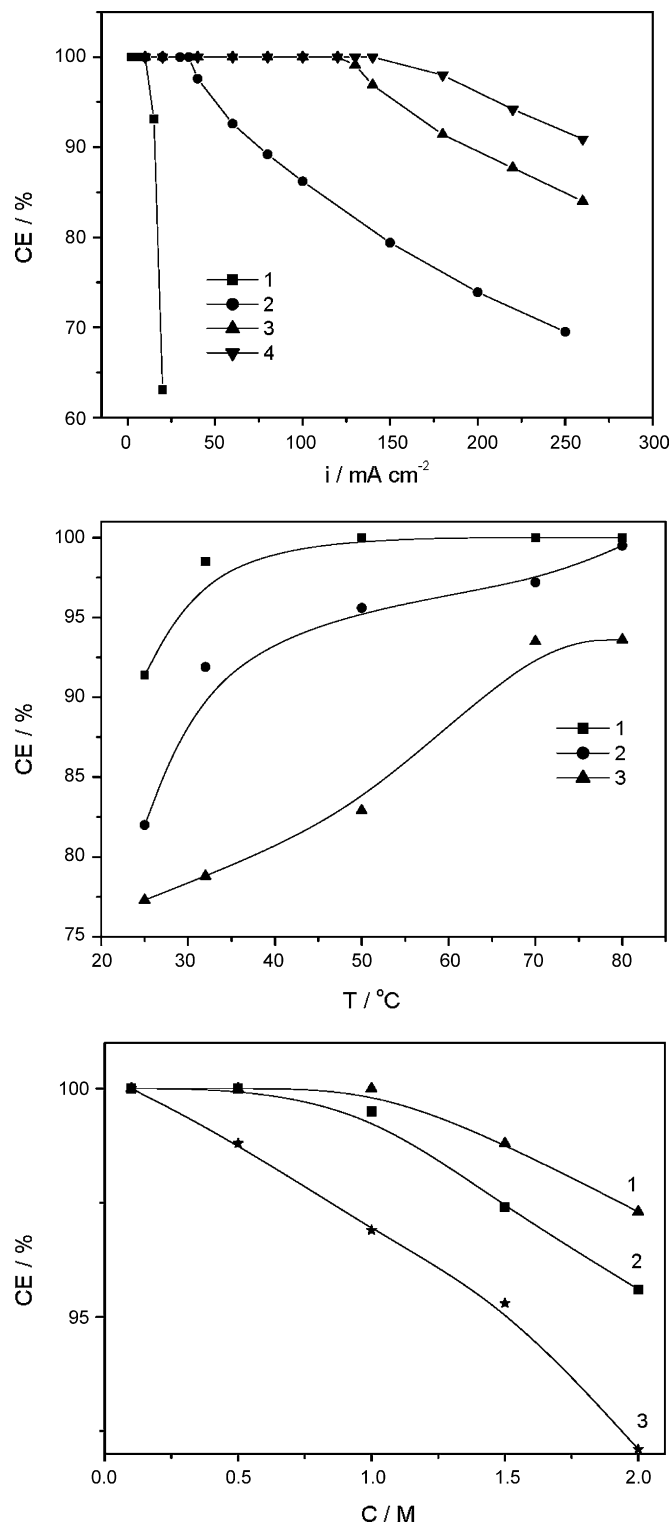


Fig. 7. (a) Effect of deposition current density on CE PbO₂: 1, 0.1 M CH₃SO₃H + 0.1 M Pb(CH₃SO₃)₂; 2, 0.1 M CH₃SO₃H + 0.2 M Pb(CH₃SO₃)₂; 3, 0.1 M CH₃SO₃H + 1.0 M Pb(CH₃SO₃)₂; 4, 0.1 M CH₃SO₃H + 1.0 M Pb(CH₃SO₃)₂, stirring. (b) Effect of temperature on CE PbO₂ at different current density (mA cm⁻²): 1, 180; 2, 300; 3, 650. Electrolyte—0.1 M CH₃SO₃H + 1.0 M Pb(CH₃SO₃)₂. (c) Effect of MSA concentration on CE PbO₂ at different current density (mA cm⁻²): 1, 40; 2, 60; 3, 100. Electrolyte—x M CH₃SO₃H + 1.0 M Pb(CH₃SO₃)₂.

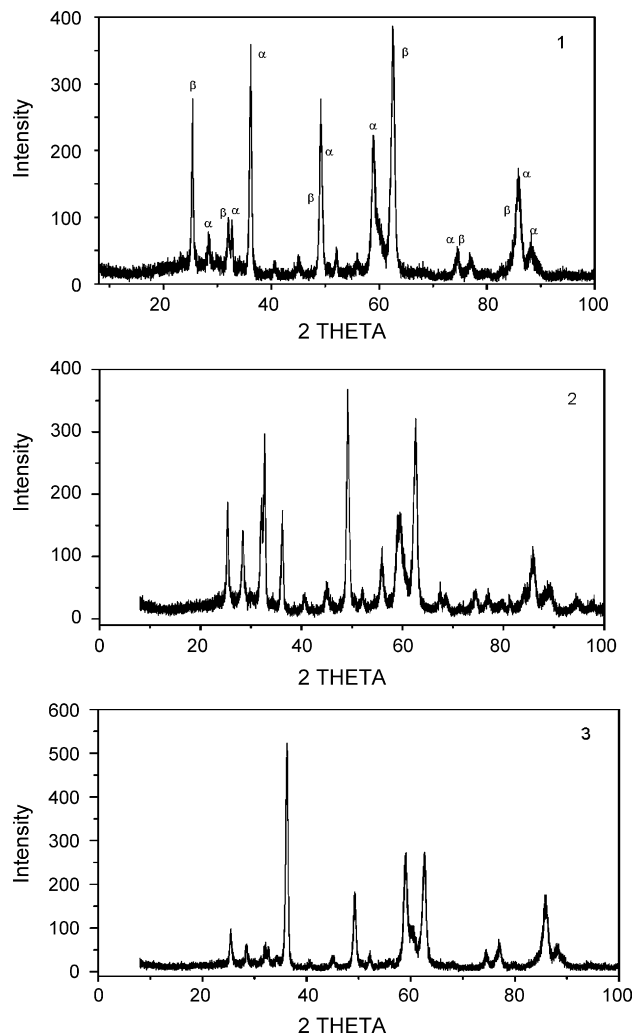


Fig. 8. X-ray diffractograms of PbO₂ films deposited in 0.1 M CH₃SO₃H + 0.1 M Pb(CH₃SO₃)₂ at different current density (mA cm⁻²): 1, 4; 2, 8; 3, 12.

The data of the present work concerning the α -phase impurities in the deposits (Fig. 8) are in good agreement with those of Campbell and Peter [24] who reported that the preferred orientation of the α -phase planes strongly depends on the electrodeposition current density. Specifically, at low current densities, α -PbO₂ deposits were highly oriented, and an increase of the current density led to randomly oriented films.

An examination of the XRD spectra shows that peak intensities generally decrease in comparison with nitrate solution. This indicates that the grain size is smaller for the lead dioxide films formed in the presence of methanesulfonate ions probably due its adsorption on lead dioxide. However, a difference in intensity does not provide sufficient evidence of the existence of an amorphous phase. It is noteworthy that the same effect can result if water is trapped in a porous lead dioxide structure [25].

The SEM micrographs show that morphology of PbO₂ strongly depends on electrodeposition conditions and electrolyte composition. Mainly it is more regular, with better-oriented crystals of smaller size in comparison with PbO₂ deposited from nitrate solutions. It is important to note that in the presence of MS ions in the electrolyte, submicro- and nano-crystalline coatings are formed (Fig. 9). So difference in intensity provides sufficient evidence of the existence of low crystalline phase and it is in good agreement with SEM data.

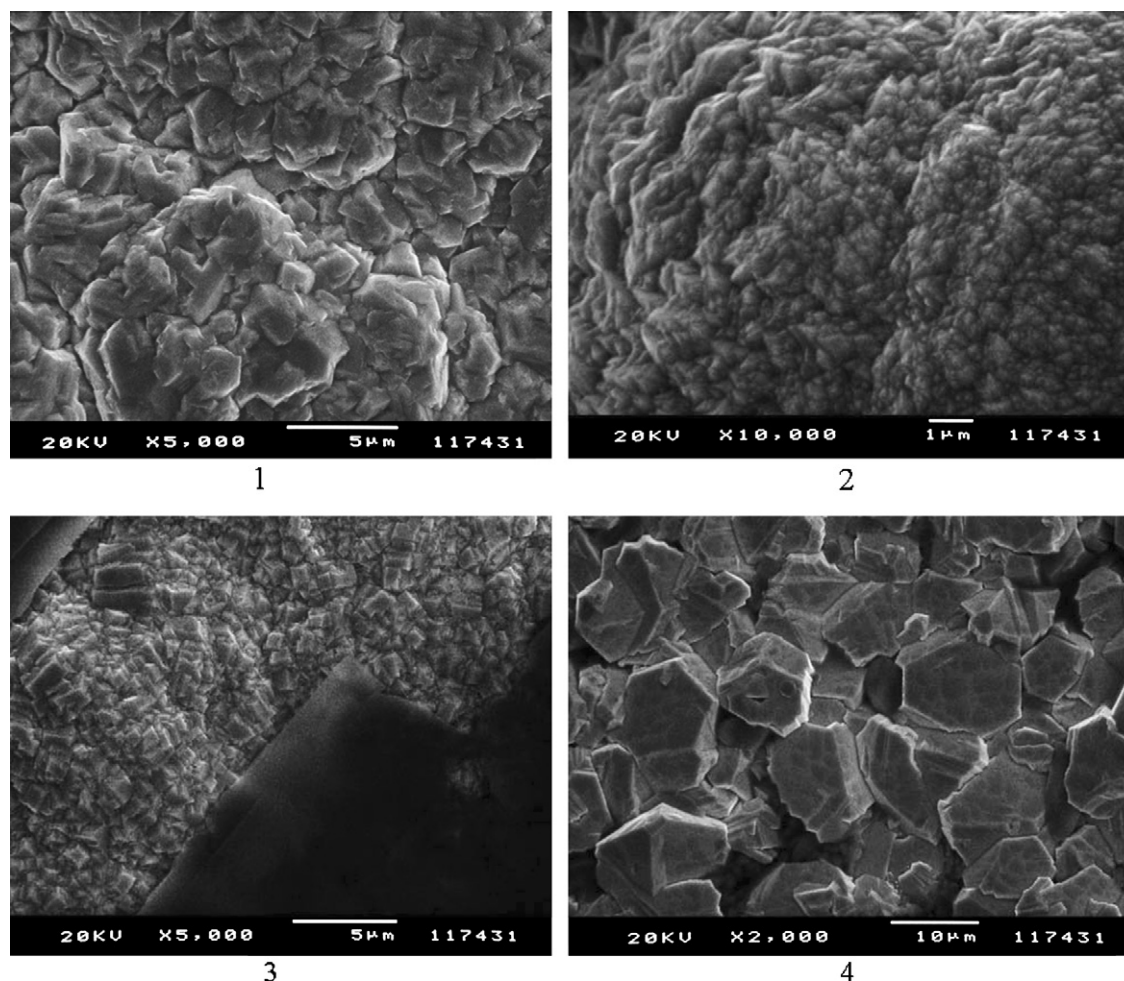
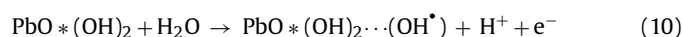


Fig. 9. SEM micrographs of PbO_2 deposited at different conditions: 1, 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1$ M $\text{CH}_3\text{SO}_3\text{H}$, $i_{\text{dep.}} = 5 \text{ mA cm}^{-2}$; 2, 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1$ M $\text{CH}_3\text{SO}_3\text{H}$, $i_{\text{dep.}} = 12 \text{ mA cm}^{-2}$; 3, 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1.0$ M $\text{CH}_3\text{SO}_3\text{H}$, $i_{\text{dep.}} = 5 \text{ mA cm}^{-2}$; 4, 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1$ M $\text{CH}_3\text{SO}_3\text{H}$, $i_{\text{dep.}} = 5 \text{ mA cm}^{-2}$, 60°C .

We next report on the electrocatalytic activity of oxygen evolution reaction at PbO_2 electrodes deposited from nitrate and methanesulfonate electrolytes. It was shown that electrodes prepared in nitrate electrolyte and used in HClO_4 are more active than electrodes in methanesulfonic acid medium (this means both electrodes prepared from the MS solution and electrodes prepared in nitrate media and used in methanesulfonic acid). Our view on a possible mechanism is that the model of O_2 evolution on Pb/PbO_2 electrodes proposed by Pavlov and co-workers [26–28] can provide a reasonable explanation for the present data. According to that mechanism, O_2 evolution occurs at active sites located in a hydrous layer on PbO_2 whose structure and characteristics have been examined in detail in a series of papers by Pavlov and co-workers [29–31]. According to their description, the surface consists of crystal line (PbO_2) or hydrated [$\text{PbO}(\text{OH})_2$] zones which are in equilibrium, and the latter is a rather open structure which can exchange cations and anions. Oxygen evolution proceeds through the following elementary steps:



It is important to point out that, from preliminary data, there is evident flaking and shedding during O_2 evolution [32] in the case of electrodes prepared in nitrate media/perchloric

acid. Electrodes prepared from methanesulfonic medium or electrodes used in methanesulfonic acid are sensibly more resistant. Accelerated test of PbO_2 electrodes ($\text{Ti}/\text{Pt}/\text{PbO}_2$; 1 M sulphuric acid; $i = 200 \text{ mA cm}^{-2}$; 20°C) shows that service life of anodes deposited from methanesulfonate electrolytes in three times higher than ones from nitrate solutions. It indicates better mechanical properties of lead dioxide formed in methanesulfonate media.

4. Conclusions

In all cases the PbO_2 electrodeposition process obeys the basic relationship mentioned previously for Pt electrodes in HClO_4 and HNO_3 solutions, and is described satisfactorily by the kinetic scheme given in (1)–(4). The important conclusion is that the composition of the electrodeposition solution causes only a quantitative difference in the PbO_2 electrodeposition process without apparently changing the qualitative relationships.

Results show that in methanesulfonic media the rate of PbO_2 electrodeposition is higher than in nitrate solutions. At low overpotential the rate-determining stage is the second electron transfer reaction (3) and at high overpotential the process is controlled by Pb^{2+} diffusion. It is important to note the rather complex influence of methanesulfonate concentration on steady-state partial current of PbO_2 electrodeposition, both in the kinetic and the diffusion zones of the polarization curve due to change of ψ' potential and

migration. All effects are a result of adsorption of methanesulfonate ions on PbO_2 .

The current efficiency of PbO_2 formation depends from electrode potential (or deposition current density), electrolyte composition (concentration of Pb^{2+} and MS ions), hydrodynamic conditions, pH and temperature of the solution. It is important to note that thick PbO_2 coatings (up to 2 mm) with good mechanical properties and adhesion to the substrate were deposited in wide range of current density ($2\text{--}100\text{ mA cm}^{-2}$).

According to XRD and SEM data crystallinity of the PbO_2 materials deposited from methanesulfonate electrolytes decreases in comparison with nitrate medium probably due to adsorption of methanesulfonate on the electrode surface. Difference in intensity provides sufficient evidence of the existence of low crystalline phase and it is in good agreement with SEM data. Morphology of PbO_2 strongly depends on electrodeposition conditions and electrolyte composition. Mainly it is more regular, with better-oriented crystals of smaller size in comparison with PbO_2 deposited from nitrate solutions. It is important to note that in the presence of MS ions in the electrolyte, submicro- and nano-crystalline coatings are formed.

References

- [1] C. Ponce de Leon, A. Frias-Ferrer, J. Gonzalez-Garcia, D.A. Szanto, F.C. Walsh, J. Power Sources 160 (2006) 716.
- [2] A. Hazza, D. Pletcher, R. Wills, Phys. Chem. Chem. Phys. 6 (2004) 1773.
- [3] D. Pletcher, R. Wills, Phys. Chem. Chem. Phys. 6 (2004) 1779.
- [4] D. Pletcher, R. Wills, J. Power Sources 149 (2005) 96.
- [5] A. Hazza, D. Pletcher, R. Wills, J. Power Sources 149 (2005) 103.
- [6] D. Pletcher, H. Zhou, G. Kear, J. Low, F.C. Walsh, R. Wills, J. Power Sources 180 (2008) 621.
- [7] D. Pletcher, H. Zhou, G. Kear, J. Low, F.C. Walsh, R. Wills, J. Power Sources 180 (2008) 630.
- [8] H.Y. Peng, H.Y. Chen, W.S. Li, S.J. Hu, H. Li, J.M. Nan, Z.H. Xu, J. Power Sources 168 (2007) 105.
- [9] H. Chang, D.C. Johnson, J. Electrochem. Soc. 139 (1989) 23.
- [10] A.B. Velichenko, D.V. Girenko, F.I. Danilov, J. Electroanal. Chem. 405 (1996) 127.
- [11] A.B. Velichenko, E.A. Baranova, D.V. Girenko, R. Amadelli, F.I. Danilov, Russ. J. Electrochem. 39 (2003) 615.
- [12] A.B. Velichenko, D. Devilliers, J. Fluorine Chem. 128 (2007) 269.
- [13] A.B. Velichenko, R. Amadelli, A. Benedetti, D.V. Girenko, S.V. Kovalyov, F.I. Danilov, J. Electrochem. Soc. 149 (2002) C445.
- [14] Z. Galus, Fundamentals of Electrochemical Analysis, Ellis Horwood, Chichester, 1976.
- [15] D. Devilliers, M.T. Dinh Thi, E. Mahé, V. Dauriac, N. Lequeux, J. Electroanal. Chem. 573 (2004) 227.
- [16] A.B. Velichenko, D.V. Girenko, S.V. Kovalyov, F.I. Danilov, Russ. J. Electrochem. 35 (1999) 1250.
- [17] H. Chang, D.C. Johnson, J. Electrochem. Soc. 136 (1989) 17.
- [18] M.V. Mirkin, A.P. Nilov, J. Electroanal. Chem. 283 (1990) 35.
- [19] A.N. Frumkin, Dokl. AN SSSR 85 (1952) 373.
- [20] B.B. Damaskin, Electrode Processes in Solutions of Organic Compounds, MSU, Moscow, 1985.
- [21] M.A. Loshkarev, F.I. Danilov, G.E. Bol', L.G. Sechin, Elektrokhemia 13 (1977) 593.
- [22] A.B. Velichenko, T.V. Luk'yanenko, N.V. Nikolenko, R. Amadelli, F.I. Danilov, Russ. J. Electrochem. 43 (2007) 118.
- [23] R.Yu. Bek, T.E. Tsupak, L.I. Shuraeva, G.V. Kosolanov, Elektrokhemia 23 (1987) 1618.
- [24] S.A. Campbell, L.M. Peter, Electrochim. Acta 34 (1989) 943.
- [25] I. Petersson, E. Ahlberg, B. Berghult, J. Power Sources 76 (1998) 98.
- [26] D. Pavlov, B. Monahov, J. Electrochem. Soc. 143 (1996) 3616.
- [27] D. Pavlov, B. Monahov, J. Electrochem. Soc. 145 (1998) 70.
- [28] B. Monahov, D. Pavlov, D. Petrov, J. Power Sources 85 (2000).
- [29] D. Pavlov, I. Balkanov, T. Halachev, P. Rachev, J. Electrochem. Soc. 136 (1989) 3189.
- [30] D. Pavlov, I. Balkanov, J. Electrochem. Soc. 139 (1992) 1830.
- [31] D. Pavlov, J. Electrochem. Soc. 139 (1992) 3075.
- [32] R. Amadelli, A. Maldotti, A. Molinari, F.I. Danilov, A.B. Velichenko, J. Electroanal. Chem. 534 (2002) 1.