

UDC 544.653.2

*T. Luk'yanenko, A. Velichenko, V. Knysh, O. Shmychkova***INFLUENCE OF METHANESULFONATE IONS ON ELECTROOXIDATION OF Pb(II)****Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

It is shown that the process of lead dioxide electrodeposition can be described by a four-stage kinetic scheme in which the electroactive particles are methanesulfonate complexes of lead with different composition. The initial stage of the process is the electrooxidation of water with the formation of oxygen-containing particles of radical type OH'_{ads} on the electrode surface. Considering the water concentration in aqueous solutions and the fact that the hydroxylation of the electrode surface occurs at much lower potentials than the processes of oxygen evolution and oxidation of lead compounds, this stage is fast. Then the chemical stage of oxidation of $[\text{Pb}(\text{CH}_3\text{SO}_3)]_n^{(2n)+}$ by oxygen-containing radicals OH'_{ads} occurs with the formation of the unfixed on the electrode surface Pb(III) hydroxo complexes $[\text{Pb}(\text{CH}_3\text{SO}_3)_n(\text{OH})]^{(2-n)+}$, which are subsequently oxidized in the electrochemical stage of charge transfer. At low polarization, this stage is rate-determining. The extremal dependence of the reaction rate on the concentration of methanesulfonate ions observed in this case is due to the simultaneous action of two oppositely directed factors: a decrease in the charge of electroactive particles and the surface of the electrode on the one hand, and the effect of inhibition by specifically adsorbed methanesulfonate ions, on the other. In the last stage of the process, the hydroxo complexes of tetravalent lead decay by chemical mechanism with the formation of lead dioxide. At high polarization, the rate-determining step of the process is the delivery of lead complex ions to the electrode.

Keywords: methanesulfonic acid, lead dioxide, electrodeposition, hydroxo complex, voltammogram.

Introduction

Dimensionally stable lead dioxide anodes are recognized to have a number of advantages over other electrode materials. They are characterized by high electrical conductivity, ease of production and low cost, as well as electrochemical and chemical stability in various solutions. It is noteworthy that the base oxide displays enhanced electrocatalytic activity in reactions occurring at high anode potentials (oxidation of toxic organic substances, ozone evolution) [1,2].

Among all electrolytes, methanesulfonate one is known to attract great attention [3,4], since materials obtained from such solutions have high electrochemical stability and better mechanical properties than coatings deposited from other electrolytes [5–7].

It is recognized that methanesulfonic acid affects the water structure [8] forming $\text{CH}_3\text{SO}_3\text{H}-(\text{H}_2\text{O})_n$ clusters. It should be noted that all water molecules in the $\text{CH}_3\text{SO}_3\text{H}-(\text{H}_2\text{O})_n$ cluster tend to accumulate on the hydrophilic side of methanesulfonic acid

($-\text{SO}_3\text{H}$ group), which is favorable for electrostatic interactions or the interaction of hydrogen bonds and also agrees with the fact that $\text{CH}_3\text{SO}_3\text{H}$ has a preferred orientation relative to the surface of the liquid, thereby changing the relationship between labile and inert oxygen-containing particles in the near-electrode layer [9]. Thus, the amount of inert (strongly bound) oxygen-containing particles in electrolytes based on methanesulfonic acid increases in the near-electrode layer which should obviously lead to an increase in the deposition rate of lead dioxide [7] from the methanesulfonate electrolyte.

At the same time, there is a lack of information regarding the effect of methanesulfonate ions on the characteristics of electrodeposition of materials based on lead dioxide, especially the physicochemical properties of the obtained oxides and their electrocatalytic activity. In this connection, the effect of methanesulfonate ions on the Pb(II) electrooxidation process was investigated in this paper.

Material and methods

All chemicals were reagent grade. Electrodeposition regularities of doped lead dioxide were studied on a Pt rotating disk electrode (Pt-RDE, 0.19 cm²) by steady-state voltammetry and chronoamperometry in electrolyte containing 0.1 M Pb(NO₃)₂+1.0 M HNO₃+(0.1÷1.2) M NaCH₃SO₃. The Pt-RDE surface was treated before use in freshly prepared mixture (1:1) of concentrated H₂SO₄ and H₂O₂. Such preliminary treatment permits stabilizing the surface of the electrode and obtaining reproducible results. Voltammetry measurements were carried out in a standard temperature-controlled three-electrode cell. All potentials were recorded and reported vs. Ag/AgCl/KCl (sat.). The temperature was 25±1°C.

The number of electrons that take part in the kinetic stage was determined from linear potential sweep voltammetry measurements. The characteristic value in this method is the peak of the anode current on the potentiodynamic polarization curve, the magnitude of which depends on the sweep rate of the potential.

For an irreversible process, the charge transfer coefficient (α_n) was calculated from the dependence of the peak potential on the sweep rate [7]:

$$E_p = E^0 - \frac{RT}{\alpha n_\alpha F} \left[0,78 - \ln k_s + \ln \left(\frac{D \alpha n_\alpha F V}{RT} \right)^{\frac{1}{2}} \right] \cdot (1)$$

The number of electrons was calculated according to Delahay equation [7]:

$$i = 3,00 \cdot 10^5 \cdot n \cdot (\alpha n_\alpha)^{1/2} \cdot D^{1/2} \cdot C \cdot S \cdot V^{1/2}, \quad (2)$$

where n is the number of electrons; D is the diffusion coefficient (cm² s⁻¹); C is the concentration of lead ions (mol dm⁻³); S is the electrode surface (cm²); and V is the sweep rate (V s⁻¹).

The apparent heterogeneous rate constants, K_s , for anodic Pb(II) oxidation were calculated according to the Koutecky-Levich equation [7] from $1/I$ vs. $1/\omega^{1/2}$ plot:

$$\frac{1}{I} = \frac{1}{nkFSC_0} + \frac{1}{0.62nFSD^{2/3}v^{-1/6}C_0} \cdot \frac{1}{\omega^{1/2}}, \quad (3)$$

where n is the number of electrons transferred in the half reaction; S is the electrode area (cm²); ω is the angular velocity of electrode rotation (rad s⁻¹); v is the solution viscosity (Pa·s) and other terms have their conventional electrochemical significance.

Diffusion coefficient was calculated according to Levich equation:

$$I = 0.62 \cdot n \cdot F \cdot D^{2/3} \cdot \omega^{1/2} \cdot v^{-1/6} C_0. \quad (4)$$

Results and discussion

First of all, let us consider the state of lead ions in methanesulfonate solutions, in which, according to the literature data [10], the formation of complex compounds of different stoichiometry, such as [PbCH₃SO₃]⁺, [Pb(CH₃SO₃)₂] and [Pb(CH₃SO₃)₃]⁻, is possible. Based on the stability constants of lead complex compounds in which the methanesulfonate ion serves as the ligand, a distribution diagram of complex compounds was

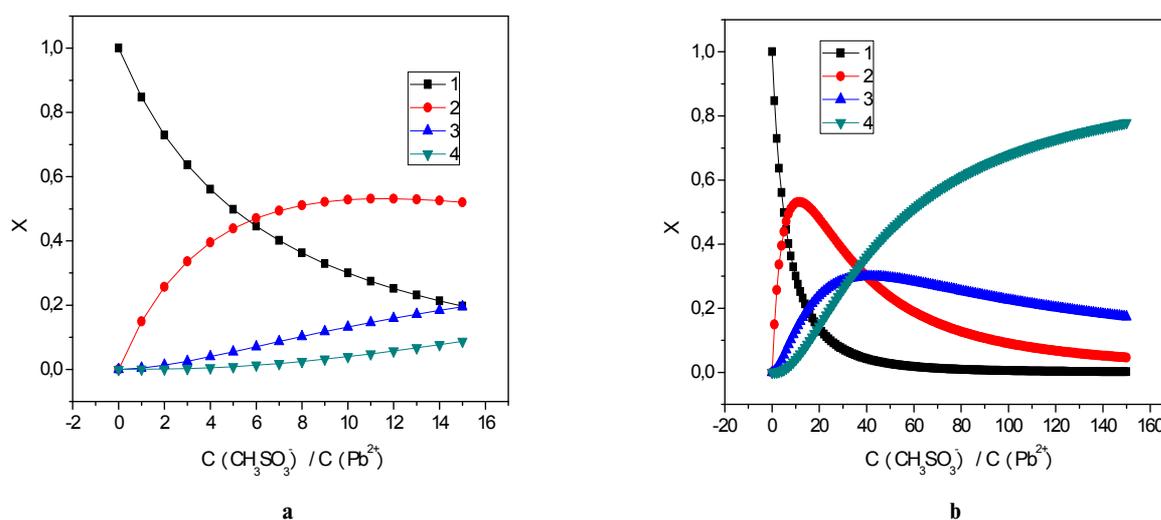


Fig. 1. A distribution of lead complex compounds at different ratios of the concentrations CH₃SO₃⁻/Pb²⁺:

1 – Pb²⁺; 2 – [Pb(CH₃SO₃)⁺]; 3 – [Pb(CH₃SO₃)₂]; 4 – [Pb(CH₃SO₃)₃]⁻

constructed at different ratios of the concentrations of $\text{CH}_3\text{SO}_3^-/\text{Pb}^{2+}$ (Fig. 1).

As follows from the obtained results (Fig. 1,a), at least half of the Pb^{2+} ions is in free form and the rest forms a positively charged complex $[\text{Pb}(\text{CH}_3\text{SO}_3^-)]^+$ in concentrated lead electrolytes which are preferred for use in flowing energy storage or asymmetric supercapacitors (the content of lead methanesulfonate is 1.0–1.2 M with a concentration of methanesulfonic acid in the range of 0.1–1.0 M). Similar in composition will also be observed in electrolytes containing 0.1 M lead methanesulfonate and 0.1 M methanesulfonic acid which are used to produce electrocatalysts based on lead dioxide in lieu of similar nitrate solutions.

However, the oxide deposition is often carried out at higher acidity when the acid concentration is 1 M. In this case, at an unchanged concentration of lead methanesulfonate, the ratio between methanesulfonate ions and lead ions reaches 12, this leads to a significant change in the composition of the solution. The fraction of Pb^{2+} in free form is only 25% while the complex forms $[\text{Pb}(\text{CH}_3\text{SO}_3^-)]^+$, $[\text{Pb}(\text{CH}_3\text{SO}_3)_2]$ and $[\text{Pb}(\text{CH}_3\text{SO}_3)_3]^-$ are 53, 16 and 6%, respectively, i.e. complex ions with the predominance of a cationic form are mainly represented in the solution.

Another extreme case is a solution with a low concentration of lead (0.01 M) with high acidity, when the ratio of methanesulfonate ions to lead ions can reach 100–150. In this case, free Pb^{2+} ions are practically absent and the predominant form of complex ions is anion $[\text{Pb}(\text{CH}_3\text{SO}_3)_3]^-$ (from 68 to 78%).

Thus, the observed significant change in the composition of the solution, even with a fixed initial concentration of lead compounds, can lead to changes in both qualitative and quantitative characteristics of lead dioxide electrodeposition. Since the formation of PbO_2 proceeds on a constantly renewable surface, complex particles can be adsorbed from the solution bulk on the surface of the growing oxide. These particles are probably involved in the oxidation of bivalent lead and the differences in their adsorption on the electrode surface lead to different effects.

With an increase in potential, the surface of the electrode will have a more positive charge, which should also facilitate fixing negative and neutral charged particles on the surface. Subsequently, complex compounds on the surface most likely undergo electrochemical transformations with the formation of PbO_2 .

Regardless of the solution composition, cyclic

voltammograms (CVA) obtained in solutions with different concentrations of methanesulfonate ions are described by the presence of a number of characteristic sites (Fig. 2). The anodic branch of the curve features an exponential current growth corresponding to the simultaneous reactions of lead (II) oxidation and oxygen evolution. In the cathodic branch of the curve, a current peak can be observed due to lead dioxide electrochemical reduction. The area of this peak (the charge consumed in reduction of deposited lead dioxide) can be used as a convenient criterion reflecting the integral rate of the PbO_2 formation process. This criterion is especially useful for a small amount of PbO_2 under conditions of parallel evolution of oxygen at the electrode, when the current is distributed among several processes [7].

As follows from the obtained data (Fig. 2,a), the formation of lead dioxide is accelerated in the presence of methanesulfonate ions in the solution, but the obtained dependence has an extremal character with a maximum at 0.4 M concentration of sodium methanesulfonate. Further increase in its concentration from 0.5 to 1.2 M leads both to the drop of the anode current and the amount of formed lead dioxide characterized by the cathode peak (Fig. 2,b). It should also be noted that the forward and reverse scans of the anode sections of the CVA do not coincide indicating a significant effect of the phase formation stage on the characteristics of deposition of lead dioxide on a foreign substrate.

The differences in the rate of lead dioxide formation in the presence of methanesulfonate ions are probably associated with the formation of lead complex compounds with methanesulfonate ions and their adsorption on the electrode surface which leads to the inhibition of PbO_2 electrodeposition process.

Steady state polarization curves obtained in nitrate and methanesulfonate electrolytes are shown in Fig. 3. These curves reflect both the total (oxygen evolution and lead ions oxidation) and the partial Pb (II) electrooxidation processes. As one can see from figure, there is a similarity of their character in both electrolytes. At the same time, there is some increase in the partial current of Pb(II) oxidation at potentials higher than 1.60 V in methanesulfonate bath, an expansion of the range of high current outputs is observed too, compared with nitrate bath (a decrease of the difference between the partial and total current).

It is noteworthy that the observed rise in the partial current in both electrolytes at potentials higher than 1.75 V is caused by the mixing of the near-electrode layer by evolved oxygen. At the same time,

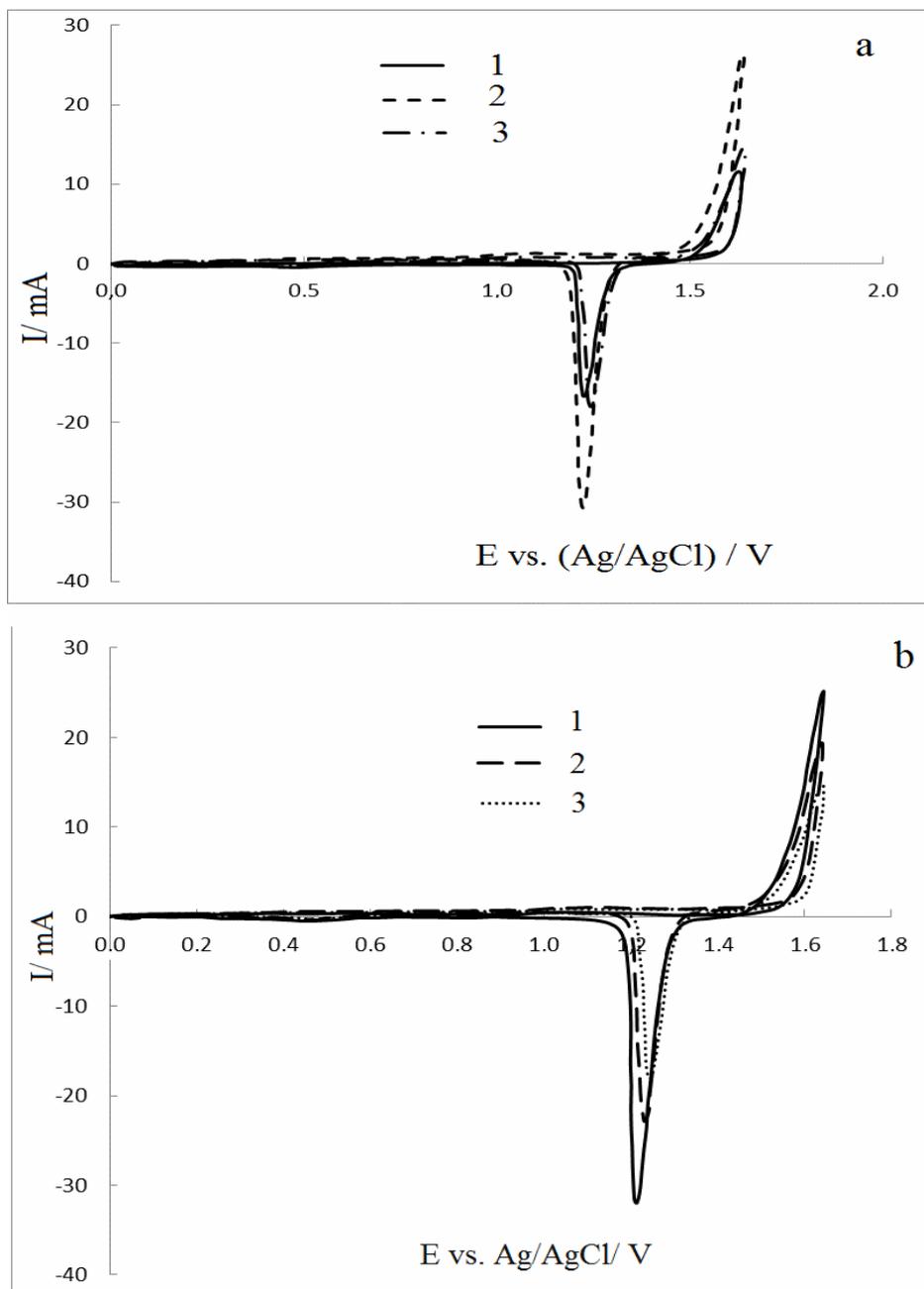


Fig. 2. CVA recorded on Pt disk electrode in electrolytes containing: 0.1 M $\text{Pb}(\text{NO}_3)_2$ +1.0 M HNO_3 +X M $\text{CH}_3\text{SO}_3\text{Na}$, where X is 0 (1), 0.4 (2), 1.2 (3) (a), and 0.5 (1), 1.0 (2), 1.2 (3) (b). Sweep rate was 100 mV s^{-1} , scan area was in the range of 0 to 1.65 V

the oxygen evolution causing the exponential growth of the current at potentials more positive than 1.70 V is observed in methanesulfonate electrolyte at lower polarizations than in the nitrate electrolyte.

The polarization curves of partial lead dioxide deposition obtained both in the nitrate and methanesulfonate electrolyte can be divided into two regions (see Fig. 3): (i) low polarizations, $E < 1.6 \text{ V}$, and (ii) high polarizations, $E > 1.75 \text{ V}$. The visually

perceptible formation of the PbO_2 deposit on platinum electrode begins at potentials higher than 1.25 V. In the low polarization region, the deposition current of lead dioxide increases with exponential growth of the potential which indicates the kinetic control of the process. It should be assumed that the current should not depend on the angular velocity of electrode rotation. However, this is not so, and in this range of potentials, the anode current decreases

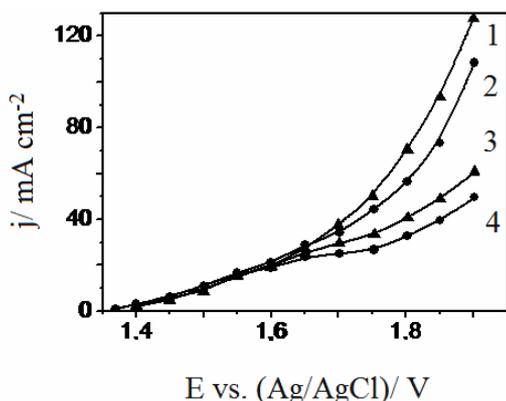


Fig. 3. Steady state polarization curves for total (1,2) and partial (3,4) PbO_2 electrodeposition current on Pt disk electrode in solutions containing: 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1$ M $\text{CH}_3\text{SO}_3\text{H}$ (1,3) and 0.1 M $\text{Pb}(\text{NO}_3)_2 + 0.1$ M HNO_3 (2,4)

with increasing of velocity as the angular velocity of disk electrode rotation increases, both on platinum and on the previously obtained PbO_2 electrode.

A similar anomalous phenomenon was observed earlier in case of the PbO_2 electrodeposition from nitrate and perchlorate solutions [5-6,11-12]. The drop in the currents of $\text{Pb}(\text{II})$ ions oxidation with an increase in the angular velocity of disk electrode rotation or under conditions of electrolyte mixing is explained by the presence of $\text{Pb}(\text{III})$ intermediates that are not fixed on the electrode and capable of further electrochemical conversions with the formation of PbO_2 . Intermediate electroactive particles are removed from the surface of the electrode under mixing conditions thereby inhibited the deposition rate of lead dioxide. Along with the described drop in current, the amount of lead dioxide formed on the electrode decreases, as evidenced by a decrease in cathodic peaks area of PbO_2 reduction on CVA. The obtained data allow suggesting that the formation of surface-free electroactive particles in methanesulfonate electrolytes as well as in nitrate solutions occurs in the chemical stage of the interaction of divalent lead compounds with hydroxyl radicals formed as a result of anodic oxidation of water. Subsequently, the resulting compounds are electrochemically oxidized to $\text{Pb}(\text{IV})$. Having in mind the dependence of the reaction current on the angular velocity of the electrode rotation, the charge transfer in the low polarizations region is a rate-determining step.

To get further insight in the kinetic characteristics of process (namely the number of electrons participating in the kinetic stage of PbO_2 electrodeposition), linear voltammetry measurements were performed. With an increase in the potential

sweep rate, the anode peak shifts toward an increase in electrode potentials, this indicates an irreversible transfer of the electron in the kinetic stage. The calculated number of electrons in the elementary stage was one confirming that PbO_2 formation is a multistep charge transfer and also additionally evidencing the formation of trivalent lead intermediate product in the preceding chemical stage.

To establish the mechanism of the reaction, the data on the order of the reaction with respect to Pb^{2+} ions are of considerable interest. As one can see from Fig. 4, the limiting current of lead dioxide deposition is observed in steady state polarization curves of PbO_2 electrodeposition from methanesulfonate electrolytes, the limiting current increases linearly with increasing concentration of Pb^{2+} in the deposition electrolyte.

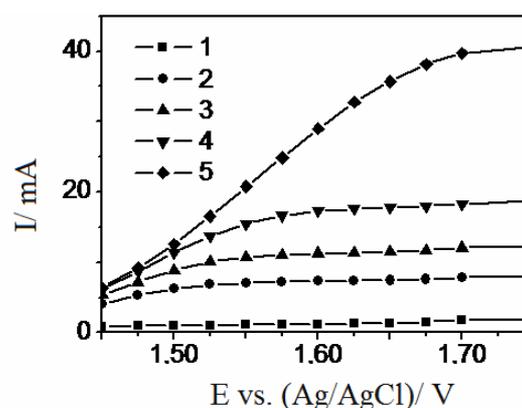


Fig. 4. Steady state polarization curves for partial PbO_2 electrodeposition recorded at various concentrations of lead ions in solution containing: 0.1 M $\text{CH}_3\text{SO}_3\text{H} + 0.2$ M $\text{CH}_3\text{SO}_3\text{Na} + X$ M $\text{Pb}(\text{NO}_3)_2$, where X is 0.01 (1); 0.05 (2); 0.07 (3); 0.1 (4); 0.2 (5)

The order of the reaction was calculated from the steady state i - E plots of the partial lead dioxide electrodeposition process at different contents of lead ions in solution. Its value was determined from the slopes on $\lg(I_{\text{part}})$ vs. $\lg(C_{\text{Pb(II)}})$ dependences. According to the obtained data, the reaction order with respect to lead ions is one in the low polarizations region.

In the region of kinetic control of the process ($E < 1.40$ V), an extremal dependence of the steady state partial current of lead dioxide deposition is observed with an increase in the amount of methanesulfonate ions in the deposition electrolyte (Fig. 5).

This dependence is most likely due to the influence of methanesulfonate ions on the water

structure in the near-electrode layer [8]. As has been shown by Feliu et al. [8], the amount of inert oxygen-containing particles increases in the presence of methanesulfonate ions. This, in turn, contributes to an increase in the rate of lead dioxide formation. This fact explains the increase in the steady state partial current.

On the other hand, with an increase in the content of $\text{CH}_3\text{SO}_3\text{Na}$, the inhibition of the charge transfer stage should appear due to the adsorption of methanesulfonate ions on lead dioxide. The possibility of this, in contrast to platinum, is indicated by the displacement of pH_0 of PbO_2 in the presence of $\text{CH}_3\text{SO}_3\text{Na}$ by 0.3 units. The result of the simultaneous action of two opposite factors is the extremal dependence which is observed in Fig. 5.

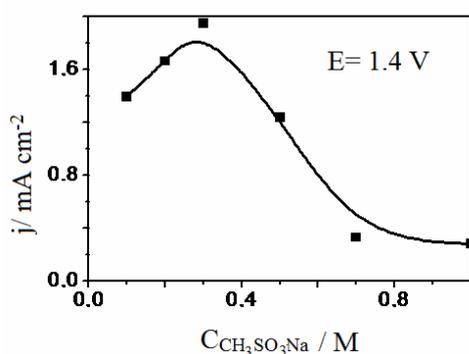


Fig. 5. Current density vs. concentration of methanesulfonate ions in solution containing 0.1 M $\text{Pb}(\text{NO}_3)_2 + X$ M $\text{CH}_3\text{SO}_3\text{H}$ on Pt electrode

Apparent heterogeneous rate constants were calculated according to the Koutecky-Levich equation from intercepts of $1/I$ vs. $1/w^{1/2}$ plots at 1.7 V. The dependence shown in Fig. 6 has an extremal character with a maximum at a ratio of 3, which is typical of methanesulfonate electrolytes containing 0.1 M Pb^{2+} and methanesulfonic acid in the deposition electrolyte. It should be noted that the increase in the content of methanesulfonate ions to the ratio of 12 does not practically affect the value of the rate constant, in contrast to the effects obtained at 1.4 V (Fig. 5). A strong inhibition of lead dioxide electrodeposition is observed only when the ratio of concentrations exceeds 100 (Fig. 6), when free Pb^{2+} ions are practically absent, and the anions $[\text{Pb}(\text{CH}_3\text{SO}_3)_3]^-$ are the predominant form of complex ions (from 68 to 78%) (Fig. 1).

At high polarizations, the limiting current is observed on the partial polarization curves, the magnitude of which increases with the growth of angular velocity of electrode rotation. The linear dependence of the current value on $w^{1/2}$ (Fig. 7)

indicates the diffusion limitations of the deposition process of lead dioxide. This is also confirmed by the pseudo-first order of the reaction with respect to Pb^{2+} ions calculated at high polarizations from the experimental data shown in Fig. 4.

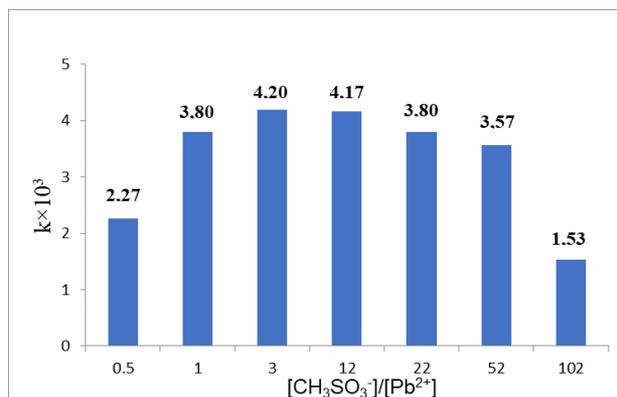


Fig. 6. Apparent heterogeneous rate constants of Pb (II) electrooxidation vs. $[\text{CH}_3\text{SO}_3^-]/[\text{Pb}^{2+}]$ ratio in the deposition electrolyte at 1.7 V

As the content of CH_3SO_3^- ions in the solution increases, a certain decrease in the slope is observed (see Fig. 7), which is largely due to the decrease in the diffusion coefficient of the discharging Pb^{2+} ions because of the increase in the size of the electroactive particles due to complexation (see Fig. 1). However, the viscosity of the solution increased insignificantly. The diffusion coefficients for the lead compounds in electrolytes with different contents of methanesulfonate ions were calculated according to Levich equation, they are summarized in Table.

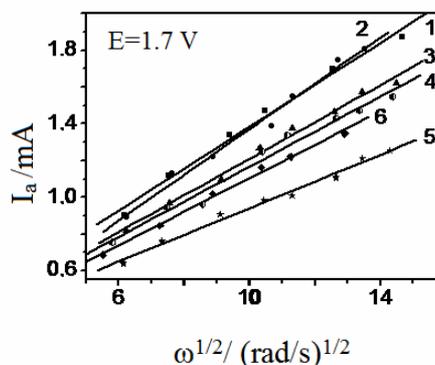


Fig. 7. Anode current vs. angular velocity of Pt electrode rotation at 1.7 V in solutions containing:
 1 – 0.1 M $\text{Pb}(\text{NO}_3)_2 + 0.1$ M $\text{CH}_3\text{SO}_3\text{H}$;
 2 – 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1$ M HNO_3 ;
 3 – 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1$ M $\text{CH}_3\text{SO}_3\text{H}$ (1);
 4 – (1) + 0.2 M $\text{CH}_3\text{SO}_3\text{Na}$; 5 – (1) + 0.4 M $\text{CH}_3\text{SO}_3\text{Na}$;
 6 – (1) + 0.7 M $\text{CH}_3\text{SO}_3\text{Na}$

The diffusion coefficients of lead compounds at 25°C

Electrolyte	$D \cdot 10^6, \text{cm}^2 \text{s}^{-1}$
0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.5 \text{ M } \text{CH}_3\text{SO}_3\text{H} + 0.5 \text{ M } \text{HNO}_3$	7.43
0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M } \text{CH}_3\text{SO}_3\text{H}$	6.87
0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M } \text{CH}_3\text{SO}_3\text{H} + 0.2 \text{ M } \text{NaCH}_3\text{SO}_3$	6.39
0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M } \text{CH}_3\text{SO}_3\text{H} + 0.5 \text{ M } \text{NaCH}_3\text{SO}_3$	5.18

An unusual effect is the extremal dependence of the limiting current on the content of methanesulfonate ions, presented in Fig. 8. The increase in the limiting current in the polarization curve with increasing the concentration of methanesulfonate ions in the electrolyte is associated with complexation and adsorption of anions on the electrode surface, which leads to a decrease in its positive charge. The participation of complex lead ions in the electrochemical reaction leads to the appearance of excessive negative charges on the electrode surface, which, in turn, increases the migration rate of positively charged free and complex lead ions to the electrode. Similar cases for the processes occurring in the region of limiting current were described in works [3,5]. Thus, the observed increase in the limiting current with increasing concentration of methanesulfonate ions in the electrolyte is most likely due to an increase in the contribution of the migration component.

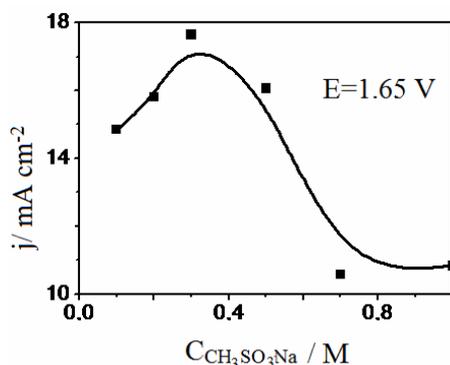


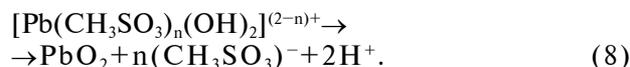
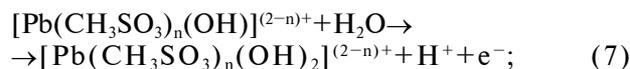
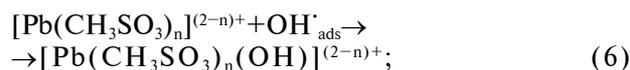
Fig. 8. Current density vs. concentration of methanesulfonate ions in solution containing 0.1 M $\text{Pb}(\text{NO}_3)_2 + X \text{ M } \text{CH}_3\text{SO}_3\text{H}$ on Pt electrode

At the same time, with an increase in the concentration of methanesulfonate ions of more than 0.3 M, the limiting current falls both as a result of a decrease in the diffusion coefficient of lead complex ions and inhibition of the process by specifically adsorbed methanesulfonate ions.

It should also be noted that when the disk electrode rotates, lead dioxide particles appear outside the platinum disc (on Teflon), indicating the

existence of lead (IV) compounds loose on the surface. These compounds are able to crystallize both in the bulk and at the electrode-electrolyte interface. Moreover, the inclusion of methanesulfonate ions in the Pb (IV) compounds as well as the adsorption of the latter on colloidal PbO_2 particles in the bulk facilitates their delivery to the electrode surface due to electrophoretic forces.

Thus, the obtained data allows one to propose a following multi-stage kinetic scheme for the electrodeposition of lead dioxide from methanesulfonate electrolytes:



The initial stage of the process is the electrooxidation of water with the formation of oxygen-containing particles of radical type OH'_{ads} on the electrode surface (5). Considering the water concentration in aqueous solutions and the fact that the hydroxylation of the electrode surface occurs at much lower potentials than the processes of oxygen evolution and oxidation of lead compounds, this stage is fast. Then the chemical stage of oxidation of $[\text{Pb}(\text{CH}_3\text{SO}_3)_n]^{(2n)+}$ by oxygen-containing radicals OH'_{ads} (6) occurs with the formation of the unfixed on the electrode surface Pb (III) hydroxo complex $[\text{Pb}(\text{CH}_3\text{SO}_3)_n(\text{OH})]^{(2-n)+}$ which is subsequently (7) oxidized in the electrochemical stage of charge transfer. At low polarization, this stage is a rate-determining step. The extremal dependence of the reaction rate on the concentration of methanesulfonate ions observed in this case is due to the simultaneous action of two oppositely directed factors: a decrease in the charge of electroactive particles and the surface of the electrode, on the one hand, and the effect of inhibition by specifically

adsorbed methanesulfonate ions, on the other hand. In the last stage of the process, the hydroxo complexes of tetravalent lead decay by chemical mechanism with the formation of lead dioxide (8). At high polarization, the rate-determining step of the process is the delivery of lead complex ions to the electrode.

Conclusions

The process of lead dioxide electrodeposition can be described by a four-stage kinetic scheme in which the electroactive particles are methanesulfonate complexes of lead with different composition. The initial stage of the process is the electrooxidation of water with the formation of oxygen-containing particles of radical type $\text{OH}_{\text{ads}}^{\cdot}$ on the electrode surface. At low polarization the electrochemical stage of oxidation of Pb(III) hydroxo complex $[\text{Pb}(\text{CH}_3\text{SO}_3)_n(\text{OH})]^{(2-n)+}$ is a rate-determining step. The extremal dependence of the reaction rate on the concentration of methanesulfonate ions is observed in this case, it is due to the simultaneous action of two oppositely directed factors: a decrease in the charge of electroactive particles and the surface of the electrode and the effect of inhibition by specifically adsorbed methanesulfonate ions. At high polarization, the rate-determining step of the process is the delivery of lead complex ions to the electrode.

REFERENCES

1. Li X., Pletcher D., Walsh F.C. Electrodeposited lead dioxide coatings // *Chem. Soc. Rev.* – 2011. – Vol. 40. – P.3879-3894.
2. Liu Y., Liu H. Comparative studies on the electrocatalytic properties of modified PbO_2 anodes // *Electrochim. Acta.* – 2008. – Vol. 53. – P.5077-5083.
3. *Electrodeposition* of lead dioxide from methanesulfonate solutions / A.B. Velichenko, R. Amadelli, E.V. Gruzdeva et al. // *J. Power Sources.* – 2009. – Vol. 191. – P.103-110.
4. Walsh F.C., Ponce de Leon C. Versatile electrochemical coatings and surface layers from aqueous methanesulfonic acid // *Surf. Coat. Technol.* – 2014. – Vol. 259. – P.676-697.
5. *Mechanism* of electrodeposition of lead dioxide from nitrate solutions / A.B. Velichenko, E.A. Baranova, D.V. Girenko et al. // *Russ. J. Electrochem.* – 2003. – Vol. 39. – P.615-621.
6. *Electrosynthesis* and physicochemical properties of PbO_2 films / A. B. Velichenko, R. Amadelli, A. Benedetti et al. // *J. Electrochem. Soc.* – 2002. – Vol. 149. – P.C445-C449.
7. Velichenko A.B., Girenko D.V., Danilov F.I. Mechanism of lead dioxide electrodeposition // *J. Electroanal. Chem.* – 1996. – Vol. 405. – P.127-132.
8. *Interaction* of water with methanesulfonic acid on Pt single crystal electrodes / A.P. Sandoval, M.F. Suarez-Herrera, V. Climent et al. // *Electrochem. Commun.* – 2015. – Vol. 50. – P.47-50.
9. Li S., Qian W., Tao F.-M. Ionic dissociation of methanesulfonic acid in small water clusters // *Chem. Phys. Lett.* – 2007. – Vol. 438. – P.190-195.
10. Capelato M.D., Nobrega J.A., Neves E.F.A. Complexing power of alkanesulfonate ions: the lead-methanesulfonate system // *J. Appl. Electrochem.* – 1995. – Vol. 25. – P.408-411.
11. *Electrodeposition* of Ni^{2+} -doped PbO_2 and physicochemical properties of the coating / O. Shmychkova, T. Luk'yanenko, R. Amadelli et al. // *J. Electroanal. Chem.* – 2016. – Vol. 774. – P.88-94.
12. *Electrodeposition* of Ce-doped PbO_2 / Shmychkova O., Luk'yanenko T., Amadelli R., Velichenko A. // *J. Electroanal. Chem.* – 2013. – Vol. 706. – P.86-92.

Received 27.03.2018

ВПЛИВ МЕТАНСУЛЬФОНАТ-ІОНІВ НА ЕЛЕКТРООКИСНЕННЯ РВ(ІІ)

Т. Лук'яненко, О. Веліченко, В. Книш, О. Шмичкова

Показано, що процес електроосадження плюмбум діоксиду можна описати чотирьохстадійною кінетичною схемою, в якій електроактивними частинками являються метансульфонатні комплекси плюмбуму різного складу. Початковою стадією процесу є електроокиснення води з утворенням на поверхні електрода оксигеновмісних частинок радикального типу $\text{OH}_{\text{адс}}^{\cdot}$. З огляду на концентрацію води в водних розчинах і той факт, що гідроксилування поверхні електрода проходить за значно менших потенціалів, ніж процеси виділення кисню та окиснення сполук плюмбуму, вона являється швидкою. Наступна стадія – хімічна стадія окиснення $[\text{Pb}(\text{CH}_3\text{SO}_3)_n]^{(2n)+}$ оксигеновмісними радикалами $\text{OH}_{\text{адс}}^{\cdot}$ з утворенням незакріпленого на поверхні електрода гідроксокомплексу Рв(ІІІ) типу $[\text{Pb}(\text{CH}_3\text{SO}_3)_n(\text{OH})]^{(2-n)+}$, який в подальшому окиснюється в електрохімічній стадії перенесення заряду. За низьких поляризацій дана стадія являється лімітувальною. Спостережувана в цьому випадку екстремальна залежність швидкості реакції від концентрації метансульфонат-іонів обумовлена одночасною дією двох протилежно спрямованих факторів: зменшенням заряду електроактивних частинок і поверхні електрода, з одного боку, і ефектом інгібування специфічно адсорбованими метансульфонат-іонами, з іншого. В останній стадії процесу являється доставка комплексних іонів плюмбуму до електрода.

Ключові слова: метансульфонова кислота, плюмбум діоксид, електроосадження, гідроксокомплекс, вольтамперограма.

INFLUENCE OF METHANESULFONATE IONS ON ELECTROOXIDATION OF Pb(II)

T. Luk'yanenko, A. Velichenko, V. Knys, O. Shmychkova
Ukrainian State University of Chemical Technology, Dnipro, Ukraine

It is shown that the process of lead dioxide electrodeposition can be described by a four-stage kinetic scheme in which the electroactive particles are methanesulfonate complexes of lead with different composition. The initial stage of the process is the electrooxidation of water with the formation of oxygen-containing particles of radical type OH_{ads} on the electrode surface. Considering the water concentration in aqueous solutions and the fact that the hydroxylation of the electrode surface occurs at much lower potentials than the processes of oxygen evolution and oxidation of lead compounds, this stage is fast. Then the chemical stage of oxidation of $[Pb(CH_3SO_3)]_n^{(2n)+}$ by oxygen-containing radicals OH_{ads} occurs with the formation of the unfixed on the electrode surface Pb(III) hydroxo complexes $[Pb(CH_3SO_3)_n(OH)]^{(2-n)+}$, which are subsequently oxidized in the electrochemical stage of charge transfer. At low polarization, this stage is rate-determining. The extremal dependence of the reaction rate on the concentration of methanesulfonate ions observed in this case is due to the simultaneous action of two oppositely directed factors: a decrease in the charge of electroactive particles and the surface of the electrode on the one hand, and the effect of inhibition by specifically adsorbed methanesulfonate ions, on the other. In the last stage of the process, the hydroxo complexes of tetravalent lead decay by chemical mechanism with the formation of lead dioxide. At high polarization, the rate-determining step of the process is the delivery of lead complex ions to the electrode.

Keywords: methanesulfonic acid; lead dioxide; electrodeposition; hydroxo complex; voltammogram.

REFERENCES

1. Li X., Pletcher D., Walsh F.C. Electrodeposited lead dioxide coatings. *Chemical Society Reviews*, 2011, vol. 40, pp. 3879-3894.
2. Liu Y., Liu H. Comparative studies on the electrocatalytic properties of modified PbO_2 anodes. *Electrochimica Acta*, 2008, vol. 53, pp. 5077-5083.
3. Velichenko A.B., Amadelli R., Gruzdeva E.V., Luk'yanenko T.V., Danilov F.I. Electrodeposition of lead dioxide from methanesulfonate solutions. *Journal of Power Sources*, 2009, vol. 191, pp. 103-110.
4. Walsh F.C., Ponce de Leon C. Versatile electrochemical coatings and surface layers from aqueous methanesulfonic acid. *Surface and Coatings Technology*, 2014, vol. 259, pp. 676-697.
5. Velichenko A.B., Baranova E.A., Girenko D.V., Amadelli R., Kovalev S.V., Danilov F.I. Mechanism of electrodeposition of lead dioxide from nitrate solutions. *Russian Journal of Electrochemistry*, 2003, vol. 39, pp. 615-621.
6. Velichenko A.B., Amadelli R., Benedetti A., Girenko D.V., Kovalyov S.V., Danilov F.I. Electrosynthesis and physicochemical properties of PbO_2 films. *Journal of the Electrochemical Society*, 2002, vol. 149, pp. C445-C449.
7. Velichenko A.B., Girenko D.V., Danilov F.I. Mechanism of lead dioxide electrodeposition. *Journal of Electroanalytical Chemistry*, 1996, vol. 405, pp. 127-132.
8. Sandoval A.P., Suarez-Herrera M.F., Climent V., Feliu J.M. Interaction of water with methanesulfonic acid on Pt single crystal electrodes. *Electrochemistry Communications*, 2015, vol. 50, pp. 47-50.
9. Li S., Qian W., Tao F.-M. Ionic dissociation of methanesulfonic acid in small water clusters. *Chemical Physics Letters*, 2007, vol. 438, pp. 190-195.
10. Capelato M.D., Nobrega J.A., Neves E.F.A. Complexing power of alkanesulfonate ions: the lead-methanesulfonate system. *Journal of Applied Electrochemistry*, 1995, vol. 25, pp. 408-411.
11. Shmychkova O., Luk'yanenko T., Amadelli R., Velichenko A. Electrodeposition of Ni^{2+} -doped PbO_2 and physicochemical properties of the coating. *Journal of Electroanalytical Chemistry*, 2016, vol. 774, pp. 88-94.
12. Shmychkova O., Luk'yanenko T., Amadelli R., Velichenko A. Electrodeposition of Ce-doped PbO_2 . *Journal of Electroanalytical Chemistry*, 2013, vol. 706, pp. 86-92.