

## EARLY STAGES OF NUCLEATION AND GROWTH OF LEAD DIOXIDE

Ukrainian State University of Chemical Technology, Dnepropetrovsk

The coatings obtained from a methanesulfonate bath are shown to be almost entirely composed of  $\alpha$ -phase. The temperature of deposition influences on the phase composition of  $\text{PbO}_2$  coatings. Thus, an increase in temperature leads to the growth of  $\beta$ -phase content in the coating. At the same time, the rising of temperature also increases the peaks intensity on the diffractogram. The latter, probably, indicates an increase in the crystal size. The differences in the phase composition of obtained materials have been also detected as changing pH of the solution. Thus, pH growth leads to an increase in the  $\beta$ -phase content in the coating. The electrocrystallization of  $\text{PbO}_2$  begins with the formation of a monolayer on the electrode surface, and then the formation and growth of three-dimensional nuclei take place. The simultaneous formation of  $\alpha$ - and  $\beta$ -phases results in the presence of two linear areas on the plot of  $(j-j_1)^{1/3}$  vs. time for the progressive growth of crystals. The formation of one phase is noticeably lagged behind the other. At layer-by-layer crystallization and significant lagging of one of phases, the ingesting of growing centres of one phase by another may occur. The type of lagging phase depends on the nature of electrolyte: it is  $\beta$ -phase for the nitrate bath, and  $\alpha$ -phase for the methanesulfonate one.

**Keywords:** lead dioxide, methanesulfonate electrolyte, nucleation and growth, phase composition.

### Introduction

Lead dioxide is a promising anodic material owing to corrosive resistivity, low cost and high electrocatalytic activity in respect to reactions proceeding at high anodic potentials with oxygen containing radicals' participation. Lead dioxide is extensively employed in electroplating, hydrometallurgy, processes of electrosynthesis of strong oxidative agents, organic and inorganic compounds, in reactions of the electrochemical combustion of various organic pollutants [1–5].

In the present work, we examine early stages of electrocrystallization of  $\text{PbO}_2$  from methanesulfonate electrolytes and identify correlations between the deposition conditions and phase composition of coatings. It should be pointed out that such data is currently absent in the literature.

### Experimental

All chemicals were reagent grade. Electrodeposition regularities of doped lead dioxide were studied on a Pt disk electrode (Pt-DE,  $0.19 \text{ cm}^2$ ) by steady-state voltammetry and chronoamperometry. The Pt-DE surface was treated, before use, by the procedure described in [6]. Such a preliminary treatment permits achieving a reproducible surface. 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 inversion voltamperometry was used for estimation of the deposition regularities of lead

dioxide both in nitrate and methanesulfonate electrolytes. The method consisted in the accumulation of pre-analyzed oxide on the working electrode by the electrolysis at a controlled potential and its subsequent electrochemical dissolving under the linearly changing potential.

Electrodeposition of lead dioxide was studied in the methanesulfonate/nitrate electrolytes that contained 1 M  $\text{CH}_3\text{SO}_3\text{H}/\text{HNO}_3$ , 0.01 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2/\text{Pb}(\text{NO}_3)_2$  depending on purposes of the experiments.

### Results and Discussion

Current transients for  $\text{PbO}_2$  deposition on Pt disk electrode were obtained for investigation of initial stages lead dioxide electrodeposition from methanesulfonate electrolytes. A typical  $j-t$  curve of  $\text{PbO}_2$  deposition is shown in Fig. 1. Observed transient can be divided on several characteristic regions [7]: the current density step in the initial period of electrode polarization corresponding to charging of the double electrical layer; induction period corresponding to the time required for beginning of the phase formation; maximum current density due to a decrease in the concentration of electroactive species in the near electrode space and the achievement of a quasi-stationary current density. The type of transient is determined by the electrode potential. At low polarizations ( $E=1.55 \text{ V}$ ) the biggest induction period with a further stretched maximum of current is observed. Increasing an anodic polarization leads to substantial decreasing the induction period and

to increasing the current maximum.

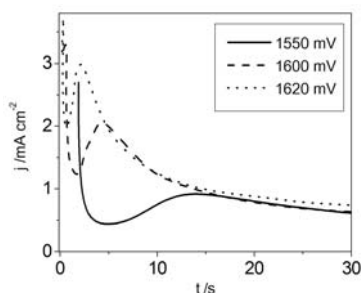


Fig. 1. Current transients for  $\text{PbO}_2$  deposition on Pt disk electrode from 0.01 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1$  M  $\text{CH}_3\text{SO}_3\text{H}$  at different deposition potentials

A linear relationship between the natural logarithm of the induction time of crystallization and the applied potential with negative slope is observed both for nitrate and methanesulfonate electrolytes (Fig. 2). Such dependence shows that the electrocrystallization of  $\text{PbO}_2$  begins with the formation of a monolayer on the entire surface of the electrode, and then the formation and growth of nuclei occurs. Growth of lead dioxide occurs through layer-by-layer crystallization, so each following layer is formed on the renewed surface.

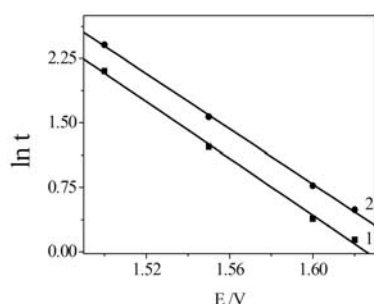


Fig. 2. Plot of the natural logarithm of the induction period of crystallization vs. potential for methanesulfonate (1) and nitrate (2) electrolytes

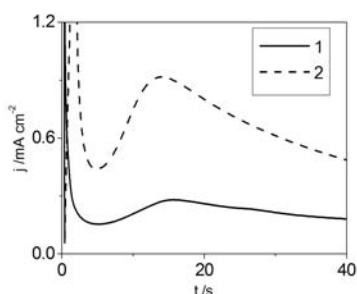


Fig. 3. Current transients for  $\text{PbO}_2$  deposition on Pt disk electrode from different electrolytes: (1) 0.01 M  $\text{Pb}(\text{NO}_3)_2 + 1$  M  $\text{HNO}_3$ ; (2) 0.01 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1$  M  $\text{CH}_3\text{SO}_3\text{H}$

According to transients obtained from nitrate and methanesulfonate electrolytes (Fig. 3), one can

conclude that despite the same concentration of lead ions in solution, there are significant differences in currents of the deposition that is an unusual effect caused, probably, by adsorption of negatively charged lead methanesulfonate complexes on positively charged electrode [8].

Lead dioxide formation takes place at constantly renewed surface. Particles like  $\text{Pb}(\text{CH}_3\text{SO}_3)_2$ ,  $\text{Pb}(\text{CH}_3\text{SO}_3)^+$  or  $\text{Pb}(\text{CH}_3\text{SO}_3)_3^-$  can be adsorbed on the growing oxide surface from the bulk. According to [8] data, three lead(II)-methanesulfonate complexes are characterized as being the predominant species, thus particles like  $\text{Pb}(\text{CH}_3\text{SO}_3)_2$  and  $\text{Pb}(\text{CH}_3\text{SO}_3)_3^-$  can be in the surface layer. With the potential growth, the electrode surface will become redundant positively charged, that would promote the binding of particles with the opposite sign on the surface. Complex compounds with a neutral or negative charge, adsorbed on the surface, would facilitate the lead dioxide crystallization on a positively charged electrode surface. Similar phenomena for the processes occurring in the limiting current region have been described in work [9].

For the analysis of obtained transients, we used the model, described in [7], and calculated current densities for instantaneous and progressive nucleation. Fig. 4 represents the plots of  $(j-j_1)^{1/3}$  and  $(j-j_1)^{1/2}$  vs. time for a transient obtained at 1.62 V.

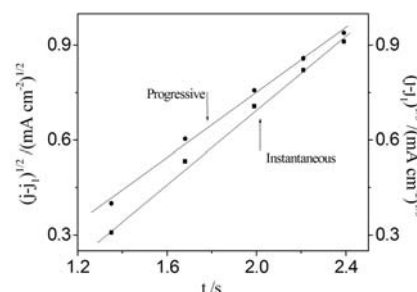


Fig. 4. Plots of  $(j-j_1)^{1/3}$  and  $(j-j_1)^{1/2}$  vs. time for a transient recorded during the electrocrystallization of  $\text{PbO}_2$  from a solution of 0.01 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1$  M  $\text{CH}_3\text{SO}_3\text{H}$  at an applied potential of 1.62 V

At this potential, a difference between instantaneous and progressive nucleation is not apparent. Plot of  $(j-j_1)^{1/2}$  vs.  $t$  deviates from linearity and curve downwards indicating that  $(j-j_1)$  is proportional to  $t$  to the powers smaller than 2, and the plot of  $(j-j_1)^{1/3}$  vs.  $t$  has a slight tendency to curve downwards indicating that  $(j-j_1)$  is proportional to  $t$  to the powers slightly less than 3. However, in accordance with results obtained for nitrate bath in [7], it may be assumed that our experimental data also follows more closely the plot of  $(j-j_1)^{1/3}$  vs.  $t$ .

The existence of two linear parts in the plot of  $(j-j_1)^{1/3}$  vs.  $t$  (Fig. 5) indicates the simultaneous deposition of two phases of  $\text{PbO}_2$ , and the formation of one phase is noticeably lagged behind the other.

The type of lagging phase depends on the nature of electrolyte: it is  $\beta$ -phase for nitrate bath, and it is  $\alpha$ -phase for methanesulfonate one.

Moreover, as has been shown by investigations using inversion voltamperometry, the reduction of deposits obtained from the methanesulfonate bath ( $\alpha$ -phase) occurs at a lower potential than such for coatings deposited from nitrate bath ( $\beta$ -phase).

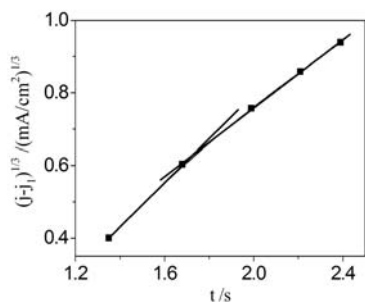


Fig. 5. Analysis of plot of  $(j-j_1)^{1/3}$  vs. time for a transient recorded during the electrocrystallization of  $\text{PbO}_2$  from a solution of 0.01 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1$  M  $\text{CH}_3\text{SO}_3\text{H}$  at an applied potential of 1.62 V

According to data obtained by X-Ray diffraction, one can conclude that the nature of depositing electrolyte considerably influences on the phase composition of lead dioxide coatings and on crystallographic orientations of individual faces [10–12].

Thus, lead dioxide deposited from nitrate bath is mainly composed of  $\beta$ -phase [1,4], whereas coatings obtained from methanesulfonate bath are almost entirely composed of  $\alpha$ -phase.

The temperature of deposition influences on the phase composition of  $\text{PbO}_2$ -coatings. Thus, an increase of temperature leads to the growth of  $\beta$ -phase in the coating. At the same time, the rising of temperature also increases the peaks intensity on the diffractogram. The latter, probably, indicates an increase in crystal size. The differences in the phase composition of obtained materials have been also detected as changing pH of the solution. Thus, pH growth leads to an increase in the  $\beta$ -phase content in the coating.

It should be pointed out that in the line involved, values of  $(j-j_1)^{1/3}$  for progressive nucleation increase, the induction time decrease and the content of  $\beta$ -phase in the deposit grows. At layer-by-layer crystallization and significant lagging of one of phases, the ingesting of growing centres of one phase by another may occur.

According to obtained results, one can conclude that investigated factors (temperature, pH, current density and the presence of dopants in the electro-deposition solutions) lead to changes in the surface charge; namely, they make its charge more positive, which, in turn, leads to an increase in the content of  $\beta$ -phase in the coating.

## Conclusions

The nature of depositing electrolyte considerably influences on the phase composition of lead dioxide coatings and on crystallographic orientations of individual faces. Thus, lead dioxide deposited from nitrate bath is mainly composed of  $\beta$ -phase, whereas coatings obtained from methanesulfonate bath are almost entirely composed of  $\alpha$ -phase. The simultaneous deposition of two phases of  $\text{PbO}_2$  occurs, but the formation of one phase is noticeably lagged behind the other. The type of lagging phase depends on the nature of electrolyte: it is  $\beta$ -phase for nitrate bath, and it is  $\alpha$ -phase for methanesulfonate one.

## REFERENCES

1. Li X., Pletcher D., Walsh F.C. Electrodeposited lead dioxide coatings // *Chem. Soc. Rev.* – 2001. – Vol.40. – P.3879-3894.
2. Oury A., Kirchev A., Bultel Y. Potential response of lead dioxide/lead(II) galvanostatic cycling in methanesulfonic acid: a morphologico-kinetics interpretation // *J. Electrochem. Soc.* – 2013. – Vol.160. – P.A148-A154.
3. Achieving high efficiency and cyclability in inexpensive soluble lead flow batteries / Verde M.G., Carroll K.J., Wang Z. et al. // *Energy Environ. Sci.* – 2013. – Vol.6. – P.1573-1581.
4. Low C.T.J., Pletcher D., Walsh F.C. The electrodeposition of highly reflective lead dioxide coatings, *Electrochem. Commun.* – 2009. – Vol.11. – P.1301-1304.
5. Liu Y., Liu H. Comparative studies on the electrocatalytic properties of modified  $\text{PbO}_2$  anodes, *Electrochim. Acta.* – 2008. – Vol.53. – P.5077-5083.
6. Lead dioxide electrodeposition and its application: influence of fluoride and iron ions / Velichenko A.B., Girenko D.V., Kovalyov S.V. et al. // *J. Electroanal. Chem.* – 1998. – Vol.454. – P.203-208.
7. Electrocrystallization of lead dioxide: Analysis of the early stages of nucleation and growth / Abyaneh M.Y., Saez V. et al. // *Electrochim. Acta.* – 2010. – Vol.55. – P.3572-3579.
8. 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.
9. Nafion effect on the lead dioxide electrodeposition kinetics / Velichenko A.B., Luk'yanenko T.V., Nikolenko N.V. et al. // *Russ. J. Electrochem.* – 2007. – Vol.43. – P.118-120.
10. Bi-doped  $\text{PbO}_2$  anodes: electrodeposition and physico-chemical properties / Shmychkova O., Luk'yanenko T., Velichenko A. et al. // *Electrochim. Acta.* – 2013. – Vol.111. – P.332-338.
11. Electrodeposition of Ce-doped  $\text{PbO}_2$  / Shmychkova O., Luk'yanenko T., Velichenko A. et al. // *J. Electroanal. Chem.* – 2013. – Vol.706. – P.86-92.
12. Physico-chemical properties of  $\text{PbO}_2$ -anodes doped with  $\text{Sn}^{4+}$  and complex ions / Shmychkova O., Luk'yanenko T., Amadelli R. et al. // *J. Electroanal. Chem.* 2014. – Vol.717-718. – P.196-201.

Received 10.09.2014

## EARLY STAGES OF NUCLEATION AND GROWTH OF LEAD DIOXIDE

O. Shmychkova, T. Luk'yanenko, A. Piletska, A. Velichenko  
Ukrainian State University of Chemical Technology, Dnepropetrovsk, Ukraine

The coatings obtained from a methanesulfonate bath are shown to be almost entirely composed of  $\delta$ -phase. The temperature of deposition influences on the phase composition of  $PbO_2$  coatings. Thus, an increase in temperature leads to the growth of  $\delta$ -phase content in the coating. At the same time, the rising of temperature also increases the peaks intensity on the diffractogram. The latter, probably, indicates an increase in the crystal size. The differences in the phase composition of obtained materials have been also detected as changing pH of the solution. Thus, pH growth leads to an increase in the  $\delta$ -phase content in the coating. The electrocrystallization of  $PbO_2$  begins with the formation of a monolayer on the electrode surface, and then the formation and growth of three-dimensional nuclei take place. The simultaneous formation of  $\delta$ - and  $\epsilon$ -phases results in the presence of two linear areas on the plot of  $(j-j_0)^{1/3}$  vs. time for the progressive growth of crystals. The formation of one phase is noticeably lagged behind the other. At layer-by-layer crystallization and significant lagging of one of phases, the ingesting of growing centres of one phase by another may occur. The type of lagging phase depends on the nature of electrolyte: it is  $\epsilon$ -phase for the nitrate bath, and  $\delta$ -phase for the methanesulfonate one.

**Keywords:** lead dioxide; methanesulfonate electrolyte; nucleation and growth; phase composition.

## REFERENCES

1. Li X., Pletcher D., Walsh F.C. Electrodeposited lead dioxide coatings. *Chem. Soc. Rev.*, 2001, vol. 40, pp. 3879-3894.
2. Oury A., Kirchev A., Bultel Y. Potential response of lead dioxide/lead(II) galvanostatic cycling in methanesulfonic acid: a morphologico-kinetics interpretation. *J. Electrochem. Soc.*, 2013, vol. 160, pp. A148-A154.
3. Verde M.G., Carroll K.J., Wang Z., Sathrum A., Meng Y.S. Achieving high efficiency and cyclability in inexpensive soluble lead flow batteries. *Energy Environ. Sci.*, 2013, vol. 6, pp. 1573-1581.
4. Low C.T.J., Pletcher D., Walsh F.C. The electrodeposition of highly reflective lead dioxide coatings. *Electrochem. Commun.*, 2009, vol. 11, pp. 1301-1304.
5. Liu Y., Liu H. Comparative studies on the electrocatalytic properties of modified  $PbO_2$  anodes. *Electrochim. Acta*, 2008, vol. 53, pp. 5077-5083.
6. Velichenko A.B., Girenko D.V., Kovalyov S.V., Gnatenko A.N., Amadelli R., Danilov F.I. Lead dioxide electrodeposition and its application: influence of fluoride and iron ions. *J. Electroanal. Chem.*, 1998, vol. 454, pp. 203-208.
7. Abyaneh M.Y., Saez V., Gonzales-Garcia J., Mason T.J. Electrocrystallization of lead dioxide: Analysis of the early stages of nucleation and growth. *Electrochim. Acta*, 2010, vol. 55, pp. 3572-3579.
8. 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, pp. 408-411.
9. Velichenko A.B., Luk'yanenko T.V., Nikolenko N.V. Nafion effect on the lead dioxide electrodeposition kinetics. *Russ. J. Electrochem.*, 2007, vol. 43, pp. 118-120.
10. Shmychkova O., Luk'yanenko T., Velichenko A., Meda L., Amadelli R. Bi-doped  $PbO_2$  anodes: electrodeposition and physico-chemical properties. *Electrochim. Acta*, 2013, vol. 111, pp. 332-338.
11. Shmychkova O., Luk'yanenko T., Velichenko A., Amadelli R. Electrodeposition of Ce-doped  $PbO_2$ . *J. Electroanal. Chem.*, 2013, vol. 706, pp. 86-92.
12. Shmychkova O., Luk'yanenko T., Velichenko A., Amadelli R. Physico-chemical properties of  $PbO_2$ -anodes doped with  $Sn^{4+}$  and complex ions. *J. Electroanal. Chem.*, 2014, vol. 717-718, pp. 196-201.