

The Electrodeposition Kinetics of Modified Lead Dioxide

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Abstract – The influence of complex ions on kinetics of lead dioxide electrodeposition from methanesulfonate electrolytes was studied. Experimental results are consistent with a mechanism previously proposed in literature for lead dioxide electrodeposition. The presence of ions involved in the electrodeposition solution causes a decrease of rate constants of lead dioxide formation due to co-adsorption phenomena. Oxygen evolution was investigated to test electrocatalytic activity. It is shown, that oxygen overpotential on modified electrodes is significantly higher than on non-modified PbO₂-electrode.

Key words – lead dioxide, methanesulfonate electrolyte, electrodeposition kinetics, complex ions, oxygen evolution.

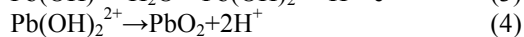
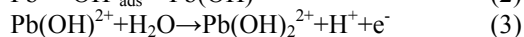
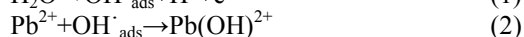
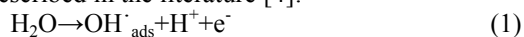
I. Introduction

Lead dioxide is known to be promising as an anodic material owing to its well-proven advantages, including good chemical stability in corrosive media, low cost compared to noble metals and high electrocatalytic reactivity in respect to reactions proceeding at high anodic potentials with oxygen containing particles participation. PbO₂ is widely used in the electroplating, hydrometallurgy, electrosynthesis processes of strong oxidizing agents, organic and inorganic compounds, reagent methods of destruction of various toxicants [1]. As it is known [1-3], the introduction of ion additives or surfactants in the PbO₂ deposition electrolyte leads to changing in electrodeposition regularities. Additives can incorporate in the growing deposit producing lead dioxide micromodified electrodes. At that physico-chemical properties of obtained materials significantly differ from PbO₂. Thus, PbO₂ modification is one of the most promising ways of tailoring its solid state properties as well as its electrocatalytic activity.

In the present work we examine the electrodeposition kinetics of PbO₂ from methanesulfonate electrolytes, that additionally contain complex [SnF₆]²⁻ and [NiF₆]²⁻ ions.

II. Experimental

We carry out an analysis of mechanism of lead dioxide electrodeposition according to the following reaction scheme described in the literature [4]:



The electrode surface state, deposition potential, lead ions concentration and hydrodynamic conditions are known to be substantially determining the nature of limiting stage of the lead dioxide electrodeposition. As a rule, at the low anodic polarizations ($E < 1,6$ V) reactions

will be under the kinetic control, whereas at the high polarizations a Pb²⁺ ions transport to the electrode surface will be the rate-determining stage.

All chemicals were reagent grade. Electrodeposition kinetics of the doped lead dioxide was studied on a Pt disk electrode (Pt-DE, 0.19 cm²) by cyclic and steady-state voltammetry. The Pt-DE surface was treated, before use, by the procedure described in [5]. Such preliminary treatment permits to achieve 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.).

Apparent heterogeneous rate constants were determined with rotating disc electrode (RDE). For the RDE experiments the voltammetry system SVA-1BM was used. The potential scan rate was varied within 1÷100 mVs⁻¹ depending on purposes of the experiments.

Oxygen evolution reaction was investigated by steady-state polarization and impedance spectroscopy on computer controlled EG & G Princeton Applied Research potentiostat model 273A and lock-in Amplifier model 5210. PbO₂ was deposited on Pt wire (0.13 cm²) at 10 mAcm⁻².

The determination of current efficiency and partial current of lead dioxide deposition ($I_{\text{Pb(II)}}$) was done by polarizing the electrode at a chosen potential above 1.4 V for 30 s ÷ 5 min (depending on potential value) and measuring coulometrically the total charge passed during electrolysis (Q). Subsequently, the charge (Q_{red}) passed for the cathodic reduction of the pre-formed PbO₂ was also measured coulometrically, in the background electrolyte, in the potential range from established potential to 0.9 V. As shown earlier [5], at slow sweep rates, quantitative reduction of PbO₂ takes place for thin oxide films. For relatively thick films, the adequacy of this method was confirmed by gravimetric experiments that show a direct proportionality between charge and amount of deposited PbO₂, as reported in the above cited publication. Then, in all cases, the data enable one to evaluate current efficiency and partial current for PbO₂ electrodeposition.

The partial Pb²⁺ oxidation current ($I_{\text{Pb(II)}}$) is determined from the relationship:

$$I_{\text{Pb(II)}} = Q_{\text{red}} / \tau \quad (5)$$

where Q_{red} is the PbO₂ reduction charge passed and τ is electrolysis time at an established anodic potential. The current efficiency for PbO₂ formation was calculated from the reduction charge divided by the total charge.

III. Results and Discussion

In typical cyclic voltammograms, the anodic branch of the curve (Fig. 1), at potentials higher than 1.55 V, 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 due to lead dioxide reduction can be observed at potentials between 1.1 and 1.3 V. The reaction proceeds according to the following scheme:

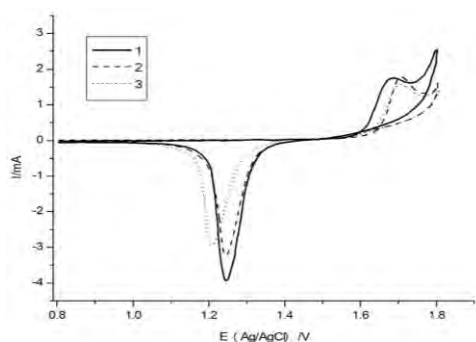
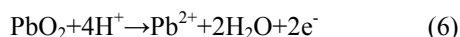


Fig. 1. Cyclic voltammograms (scan range 0.8 to 1.8 V) on Pt-DE in solutions containing 0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M CH}_3\text{SO}_3\text{H}$ (1), 0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M CH}_3\text{SO}_3\text{H} + 0.01 \text{ M } [\text{NiF}_6]^{2-}$ (2) and 0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M CH}_3\text{SO}_3\text{H} + 0.01 \text{ M } [\text{SnF}_6]^{2-}$ (3). $v = 100 \text{ mVs}^{-1}$



We observed that upon increasing the concentration of complex ions in the deposition solution, the charge decreases. Since it is established [4] that the cathodic peak charge (integrated area) is proportional to the amount of electrodeposited PbO_2 , this behaviour indicates that the lead dioxide electrodeposition process is inhibited. In the case of $[\text{SnF}_6]^{2-}$ the cathodic current peak position is shifted to more negative potentials probably as a result of changes in phase composition of the oxide deposits.

Steady state polarization curves shown in Fig. 2. These curves take into account both the total (oxygen evolution and lead ions oxidation) and the partial Pb (II) electrooxidation processes, in the absence and in the presence of additive [4].

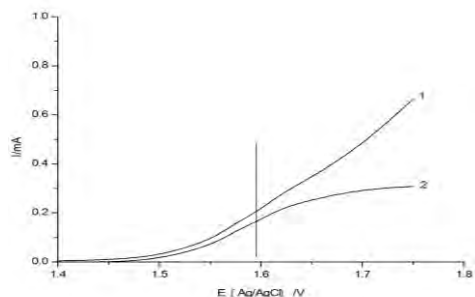


Fig. 2. Steady state polarization curves for total (1) and partial (2) PbO_2 electrodeposition current on Pt-DE for lead dioxide deposition in 0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M CH}_3\text{SO}_3\text{H} + 0.01 \text{ M } [\text{SnF}_6]^{2-}$.

The number of electrons that take part in the kinetic stage was determined from linear potential sweep voltammetry measurements according to Delahay equation, as described in the literature for analogous conditions [4]. The calculated number of electrons in the elementary stage was one, confirming that PbO_2 formation is a multistep charge transfer which involves consecutive two one-electron stages, as outlined in the kinetic scheme reported above (reactions 1-4), both in the absence and in the presence of added ions.

Apparent heterogeneous rate constants were calculated according to the Koutecky-Levich equation from inter-

cepts of $1/I$ vs. $1/\omega^{1/2}$ plots. Results show that the presence of dopants in the deposition solution causes the apparent heterogeneous rate constant to decrease from $15 \times 10^{-4} \text{ ms}^{-1}$ to $13.6 \times 10^{-4} \text{ ms}^{-1}$. These results are in agreement with the voltammetry data (Fig. 2) presented above.

Electrocatalytic properties of obtained materials were studied in respect to oxygen evolution reaction. The rate of oxygen evolution process can change in relation to nature and amount of foreign additive. The change of composite materials properties in relation to oxygen evolution reaction mainly depends on changes in chemical properties of oxide surface that, in turn, leads to bond strength change of oxygen-containing particles chemisorbed on the electrode surface.

According to obtained results, oxygen overpotential on micromodified electrodes is sensibly higher than on non-modified PbO_2 -electrode which depends on dopant nature in deposit. Results showed that oxygen evolution potential increases in line $\text{PbO}_2 > \text{PbO}_2 - [\text{NiF}_6]^{2-} > \text{PbO}_2 - [\text{SnF}_6]^{2-}$.

Conclusion

According to experimental data discussed in present work, one can conclude that the presence in the deposition electrolyte of complex ions influences on kinetics of lead dioxide electrodeposition without process mechanism changing. In this way, at low anodic polarizations second electron transfer stage is rate determining, whereas at high anodic polarizations such stage is diffusion transport of the lead ions to the electrode surface. Presence of additives in the deposition solution leads to the inhibition of PbO_2 electrodeposition process due to ions adsorption on the electrode surface. The apparent heterogeneous rate constant for anodic Pb(II) oxidation decreases in line $\text{PbO}_2 > \text{PbO}_2 - [\text{NiF}_6]^{2-} > \text{PbO}_2 - [\text{SnF}_6]^{2-}$, also in this line increase an oxygen evolution potential.

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