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FORMATION AND PHYSICOCHEMICAL PROPERTIES OF COMPOSITE PbO$_2$ MATERIALS

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There is a great interest in the improvement of lead dioxide based materials for use in different applications. Some metal ions present in the Pb(II) deposition solution are well incorporated into the PbO$_2$ matrix during electrodeposition (for example Bi$^{3+}$, Fe$^{3+}$, F$^-$) to produce a doped oxide with improved reactivity and stability in comparison with pure PbO$_2$ [1-3]. In comparison, there is much less information on effects of polyelectrolytes and surfactants additives on the process of oxide electrodeposition and the physicochemical properties of the resulting materials [4-6]. In the present work we used some polyelectrolytes (Nafion®, Drimax 1235, Magnafloc, gelatin, polyamino guanidinehydrochloride) and surfactants (potassium salt of nonafluoro-1-butanesulfonic acid, sodium dodecylsulphate, sodium lauretsulphate) as electrolyte additives for electrosynthesis of composite materials oxide-polyelectrolyte and oxide-surfactant.

It is shown that both polyelectrolytes and anionic surfactants are adsorbed on PbO$_2$. Despite additives adsorption on the oxide surface the mechanism of lead dioxide electrodeposition does not depend on the nature of polyelectrolyte or surfactant and it can be described by following scheme:

\[
\begin{align*}
H_2O - e^{-} & \rightarrow OH^\bullet + H^+ \quad (1) \\
Pb^{2+} + OH^\bullet & \rightarrow Pb(OH)^{2+} \quad (2) \\
Pb(OH)^{2+} + H_2O - e^{-} & \rightarrow Pb(OH)_2^{2+} + H^+ \quad (3) \\
Pb(OH)_2^{2+} & \rightarrow PbO_2 + 2H^+ \quad (4)
\end{align*}
\]

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)$_2^{2+}$ 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 colloidal PbO$_2$ particles in the electrolyte volume that then crystallize on the surface. At low overpotential the rate-determining stage is the second electron transfer reaction and at high overpotential the process is controlled by Pb$^{2+}$ diffusion.

Some surfactants and polyelectrolytes, especially anionic ones, can adsorb on the positively charged PbO$_2$ particles (Fig. 1). At low overpotentials the influence of adsorption on the electron-transfer stage can be described by following equation [7-9]:

\[
\frac{i_{\theta}}{i_{\theta=0}} = (1 - \theta) \exp(-S\theta) \exp[-(z + \beta n)F\Delta\psi'(\theta)/RT] \quad (5)
\]

Polyelectrolytes inhibit lead dioxide electrodeposition mainly due to their adsorption on the PbO$_2$ coating that blocks some active centers on the electrode surface where further reaction takes place. Rarely anionic polyelectrolytes can accelerate the deposition process. For instance, the dependence of the constant rate for PbO$_2$ electrodeposition on the concentration of Nafion$^\circledR$ added to the deposition solution has a volcano shape (Fig. 1). At low content of Nafion$^\circledR$ in the solution the constant rate of the process increases with increasing the additive concentration, probably due to \psi’
effect. At higher Nafion® contents in the solution, the process is inhibited due to the site blocking effect.

Fig. 1. Effect of the content of Nafion® polymeric additive in the electrolyte (0.1M HNO₃ + 0.1M Pb(NO₃)₂) on the constant rate of the second electron transfer stage (3). Adsorption isotherm on PbO₂ powder.

It was shown that the nature of additives strongly influences on the PbO₂ formation rate on Pb anode in sulfuric acid. Some additives, for instance F⁻, accelerate formation of PbO₂ and other ones (ions of iron group, surfactants and polyelectrolytes) inhibit oxide formation on the lead anode.

Table 1. Effect of nitric acid concentration on the Nafion® content in the composite material (i = 4 mA/cm²).

<table>
<thead>
<tr>
<th>№</th>
<th>Electrolyte composition</th>
<th>Nafion® in PbO₂, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1 M HNO₃ + 0.1 M Pb(NO₃)₂ + 0.05 % wt. Nafion®</td>
<td>7.0</td>
</tr>
<tr>
<td>2</td>
<td>0.5 M HNO₃ + 0.1 M Pb(NO₃)₂ + 0.05 % wt. Nafion®</td>
<td>8.7</td>
</tr>
<tr>
<td>3</td>
<td>1.0 M HNO₃ + 0.1 M Pb(NO₃)₂ + 0.05 % wt. Nafion®</td>
<td>10.2</td>
</tr>
<tr>
<td>4</td>
<td>2.0 M HNO₃ + 0.1 M Pb(NO₃)₂ + 0.05 % wt. Nafion®</td>
<td>13.1</td>
</tr>
<tr>
<td>5</td>
<td>3.0 M HNO₃ + 0.1 M Pb(NO₃)₂ + 0.05 % wt. Nafion®</td>
<td>17.0</td>
</tr>
</tbody>
</table>

It is interesting to note that both polyelectrolytes and surfactants are incorporated into the deposited lead dioxide forming a composite material. The additive content in the lead dioxide can change from 1 wt. % to 20 wt. % depending from the electrodeposition conditions and the
The colloidal-electrochemical mechanism of the composite formation was proposed, which include electrochemical formation of oxide particles in the solutions volume (6), adsorption of polyelectrolyte and surfactants on the oxide particles (7), their electrophoresis to the electrode (for particles with negative $\xi$-potential) with further crystallization on the anode surface (8):

$$\text{Pb}^{2+} + 2\text{H}_2\text{O} - 2e \rightarrow \text{PbO}_2(\text{vol.}) + 2\text{H}^+ \quad (6)$$
$$\text{PbO}_2(\text{vol.}) + R \leftrightarrow \text{PbO}_2-R_{\text{ads.}}(\text{vol.}) \quad (7)$$
$$\text{PbO}_2-R_{\text{ads.}}(\text{vol.}) \rightarrow \text{PbO}_2-R_{\text{ads.}}(\text{sur.}) \quad (8)$$

![Graph showing the effect of deposition current density (i) and concentration polymeric additive (C Nafion) on the Nafion® content in the composite material.](image)

**Fig. 2.** Effect deposition current density (i) and concentration polymeric additive (C Nafion) on the Nafion® content in the composite material.

It is important to note that in the presence of polyelectrolytes and surfactants submicro- and nano-crystalline coatings are formed (Fig. 3). In most cases the PbO$_2$ films were a mixture of the $\alpha$- and $\beta$-phases, the latter being prevalent. An examination of the XRD spectra shows that peak intensities generally decrease with increasing surfactants and polyelectrolytes content in the composite. This indicates that the grain size is smaller for the lead dioxide films in the composite materials. Difference in intensity provides sufficient evidence of the existence of an amorphous phase and it is a good agreement with SEM data.
It was shown that physicochemical properties of the materials and their electrochemical behaviour strongly depend from nature and content of additive in the composites.

Fig 3. SEM images of lead dioxide (a) and composite material oxide-polymer with different content of Nafion® (wt. %): b – 3.5; c – 7.0; d – 17.0 %.

References
7. A. N. Frumkin, Doklady AN SSSR 85 (1952) 373.