THE INFLUENCE OF ELECTROLYTE AND SUBSTRATE ON THE POTENTIAL AND CURRENT OF ELECTROCHEMICAL DEPOSITION OF PbO$_2$

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ABSTRACT
The surface treatment procedures include processes in which surface characteristics are modified, such as deposition of metal layers or formation of oxide layer. Novel technologies are focused towards the better corrosion characteristics, as well as physical and mechanical properties of the material

PbO$_2$ is very stabile in broad pH region at positive potentials, what enables its use as anode material. It appears in two crystal modifications α-PbO$_2$ and β-PbO$_2$, where the latter modification is more stabile and its standard potential value is 10-30 mV higher than standard potential of α-PbO$_2$. PbO$_2$ is non-stochiometric compound and with the decrease of oxygen content defect structure is more pronounced , and as a consequence, electronic conductance is higher. Anodes made of PbO$_2$ are the most frequently used, especially in industrial processes.

Experimental investigations were carried out to define the influence of electrolyte composition and substrate nature on the deposition potential and deposition current of PbO$_2$ formation. The results achieved showed that there is significant influence of electrolyte composition and pH value on the oxidation process of Pb^{2+} to Pb^{4+}, ie., on the formation of PbO$_2$. Beside that, the nature of the substrate for the electrochemical reaction of PbO$_2$ formation influences the deposition current and deposition potential.

Key words: Anode, lead dioxide, substrate, electrolyte

1. INTRODUCTION

The main problem in the electrochemical synthetic processes is the rational choice of electrode material. Their characteristics determine the direction, economy and the constructive solution of the process. Very demanding are choices of anode constructive material with respect to the catalytic activity, stability during the polarization in oxidizing environment, high electric conductivity, good mechanical properties and low price. Process characteristics of anodes should be stabile during the period of their usage. With these demands, except with the price, correspond the platinum group metal

anodes ,but the price of these metals and their deficiency necessitates the investigations with cheaper anode materials and improvement of their characteristics with different technological treatments.

In electrochemical industry it is possible to use less noble metals and their oxides in the production of stabile anodes. Also, it is possible to deposit the oxides of these metals on certain metal substrates in the plating procedure. These anodes have less noble metal as the base material and the active plating layer is deposited in the process of anodic polarization of the anode.

Lead dioxide is non stochiometric compound presented with formula $PbO_{1,95-1,98}$. Investigations have shown that after prolonged heating in the oxygen atmosphere and with permanent polarization, the oxygen content can not exceed 1,98.With the decrease of oxygen content defect structure of lead dioxide and electric conductivity is more pronounced [1].

PbO_2 is n-type semi-conductor with the electronic conductivity very close to metal conductivity. The oxygen evolution overvoltage is considerable on lead dioxide anodes. In accordance to the lierature data , tafel plots of polarization curves in acid solutions is 120-140 mV, and in alkaline solutions at lower exchange currents is 79 mV, but at higher exchange currents is 230 mV. Evolution of oxygen results in oxidation of water or OH^- ions with the formation of $OH^.$ radical and its recombination reaction at defined rate. Presence of active $OH^._{ads}$ particles on the surface of lead dioxide gives specific catalytic properties which enable the realization of many electrochemical reactions [2,3].

2. EXPERIMENTAL PART

The main objective of the experimental work was to examine the possibility of producing the PbO_2 on several substrates and in different electrolytes.

Electrochemical investigations of deposition of PbO_2 were carried in electrochemical micro cell M K0264 (EG&G PARC) with volume of 10 ml.

Having in mind the fact that substrate plays significant role in the electrochemical deposition process, as well as in the application of the developed electrode in electrochemical synthesis, the choice of substrate was considered as the most important factor.

The main feature of the materials used in electrochemical synthesis is their resistance in the given electrolyte with respect to the degradation of the deposit and in case of the break down of the electric supply, what could lead to the contamination of the product.

In the electrochemical deposition of PbO_2 , five different substrate materials were used: commercial gold microelectrode- GO227, platinum Go228; graphite GO229 (PAR) and specially constructed electrodes made of nickel and titan material.

In voltammetric investigations , the reference electrode Ag/AgCl electrode was used (KO265; EG&G PARC) and the reference potentials were expressed with respect to it. Counter electrode was platinum electrode wire (KO266, EG&G PARC).

Electrochemical deposition of PbO_2 was performed in four different electrolytes at different pH values:

$$- 0,1 \ moldm^{-3} \ Pb(NO_3)_2 + 1,0 \ moldm^{-3} \ HClO_4 \qquad pH = 1,0$$
$$- 0,1 \ moldm^{-3} \ Pb(SO_3NH_2)_2 \qquad pH = 2,0$$
$$- 0,13 \ moldm^{-3} \ Pb(CH_3COO)_2 + 0,9 \ moldm^{-3} \ Pb(NO_3)_2 \quad pH = 4,5$$
$$- 0,1 \ moldm^{-3} \ Pb(CH_3COO)_2 + moldm^{-3} \ NaOH \qquad pH = 13,7$$

Voltammetric technique with linear potential change was applied in the polarization process of the working electrode in electrochemical cell and the current respond was registered. Deposition potentials and values of deposition currents were determined from the voltammograms of deposition of lead dioxide from different electrolytes and at different substrates of working electrodes.

3. RESULTS AND DISCUSSION

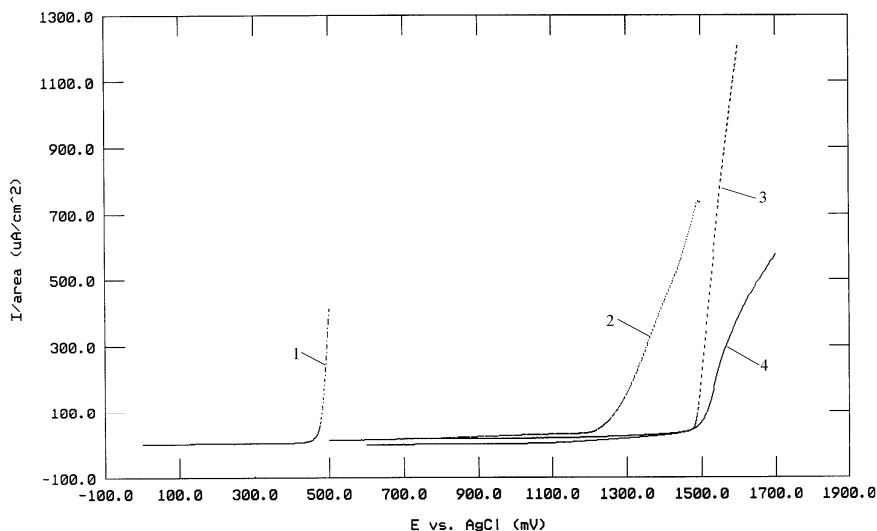Figure 1 presents the voltammogram curve for the electrochemical deposition of PbO_2 on titan substrate.

Figure 1. i-E voltammogram for PbO₂ deposition on titan substrate. (1)- 0,1 moldm⁻³ Pb(CH₃COO)₂ + 3,0 moldm⁻³ NaOH ; (2)- 0,13 moldm⁻³ Pb(CH₃COO)₂ + 0,9 moldm⁻³ Pb(NO₃)₂; (3)- 0,1 moldm⁻³ Pb(SO₃NH₂)₂; (4)- 0,1 moldm⁻³ Pb(NO₃)₂ + 1,0 moldm⁻³ HClO₄.

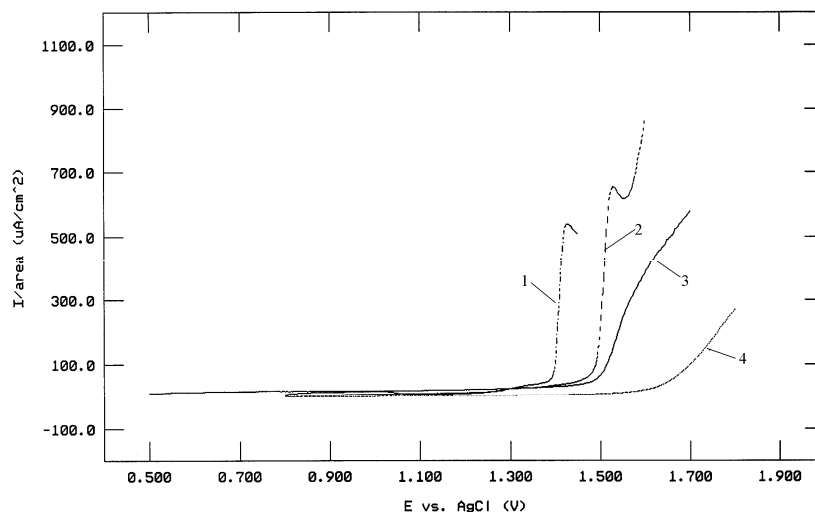The deposition of PbO₂ from nitrate electrolyte is presented on voltammogram on Figure 2.

Figure 2. i-E voltammogram for deposition of PbO₂ from 0,1 moldm⁻³ Pb(NO₃)₂ + 1,0 moldm⁻³ HClO₄ electrolyte, pH = 1,0 on different substrates: (1) Pt ; (2) Au (3) Ti (4) graphite.

The results of investigations of deposition process of PbO₂ from different electrolytes and on different substrates showed voltammograms with marked influence of pH value of the electrolyte on the oxidation process of Pb²⁺ to Pb⁴⁺, ie.the formation of PbO₂. With the increase of pH value, potential of electrochemical reaction is decreased , what is expected from the thermodynamic data for system lead-water [4]. The potential of lead-dioxide formation has the lowest value in case of alkaline acetate electrolyte (0,1 moldm⁻³)
Pb(CH₃COO)₂ + 3,0 moldm⁻³ NaOH, pH= 13,7) on all electrode substrates, while in nitrate electrolyte   (0,1 moldm⁻³ Pb(NO₃)₂ + 1,0 moldm⁻³ HClO₄, pH= 1,0) more positive values of deposition of PbO₂ were achieved, as it is illustrated in Table 1.
Figure 3.2. illustrates the significant influence of the substrate nature. In nitrate electrolyte (0,1 moldm⁻³ Pb(NO₃)₂ + 1,0 moldm⁻³ HClO₄, pH= 1,0) the lowest deposition potential is observed at platinum substrate (1410 mV), and the highest values is observed at graphite substrates (1728 mV).

Table 1. Deposition potentials of the formation of PbO$_2$

Electrolyte	pH	Deposition potential PbO$_2$ mV, en substrate:				
		Au	Pt	Grafit	Ti	Ni
0,1 moldm^{-3} Pb(NO$_3$)$_2$ + 1,0 moldm^{-3} HClO$_4$	1,0	1690	1528	1728	1582	1642
0,1 moldm^{-3} Pb(SO$_3$NH$_2$)$_2$	2,0	1540	1440	1544	1534	1564
0,13 moldm^{-3} Pb(CH$_3$COO)$_2$ + 0,9 moldm^{-3} Pb(NO$_3$)$_2$	4,5	1452	1410	1528	1388	1518
0,1 moldm^{-3} Pb(CH$_3$COO)$_2$ + 3,0 moldm^{-3} NaOH	13,7	424	410	431	498	400

4. CONCLUSION

The results of the investigations showed that the values of the deposition potentials of formation of PbO$_2$ depends on pH value of the electrolyte, and with the increase of pH value, deposition potential is changed towards less positive values.

In accordance to the values of deposition potentials of the PbO$_2$ formation in alkaline electrolytes (0,1 moldm^{-3} Pb(CH$_3$COO)$_2$ + 3,0 moldm^{-3} NaOH; pH 13,7) , deposition of PbO$_2$ on all electrode substrates is taking place in the potential range where there is no oxygen evolution, but in other investigated electrolytes (0,1 moldm^{-3} Pb(NO$_3$)$_2$ + 1,0 moldm^{-3} HClO$_4$, pH = 1,0; 0,1 moldm^{-3} Pb(SO$_3$NH$_2$)$_2$, pH=2 and 0,13 moldm^{-3} Pb(CH$_3$COO)$_2$ + 0,9 moldm^{-3} Pb(NO$_3$)$_2$, pH=4,5) simultaneously with the deposition of PbO$_2$, the evolution of oxygen is taking place.

5. REFERENCES

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