

## ANODIC DEPOSITIONS OF COMPOSITE ELECTRODE PbO<sub>2</sub>/CoO<sub>x</sub> ON SUBSTRATE OF TITANIUM

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### ABSTRACT

*In order to obtain a new anodic materials having catalytic properties for reaction of oxygen releasing, but also for another electrochemical oxidation processes, in this work composite deposition has been investigated comprising of lead and cobalt oxides. In this composite, PbO<sub>2</sub> has role of a good conductor of electricity, and CoO<sub>x</sub> has role of electrocatalysator, which results in stable anode with good properties.*

*Thorough experimental investigations have been made with aim of studying the electrolyte composition as well as substrate influence of electrochemical deposition of lead and cobalt oxides. PbO<sub>2</sub>/CoO<sub>x</sub> anodes with good properties have been obtained from sulphamate solution as well as from acid and alkali suspension with Co<sub>3</sub>O<sub>4</sub> particles.*

*For electrochemical deposition of the composite, nickel as substrate exhibited good results, and alkali suspension was proved as good electrolyte.*

*The composite electrode was tried for reaction of oxygen release from NaOH solution with aim of studying electro-catalytic properties, stability, and economic aspects.*

**Key words:** Anode, composite electrode, PbO<sub>2</sub>/CoO<sub>x</sub>, electrochemical deposition, titan.

### 1. INTRODUCTION

During exploitation, in electrolytic process, the electrodes are using and on that way, disturbing working condition. Also, this process increasing distance between electrodes and electrical resistance which influence to change voltage in cell. This change of working condition significantly effects on electrical balance of cell, temperature and optimal condition of process.

Products of corrosion of electrodes causing the uncleaning of electrolyte and products of electrolytic process, so that the separate treatment is indispensable.

There are no completely undissolving anode. Anode can be stable in once conditions work, while in second conditions are less stable or they are completely unstable.

For each kind of anodic materials existing the conditions in which disturbance of their stability appeared, and, in which start their intensive destructions. These conditions called „critical“ conditions for this process and this anodic material. Changing the composition, pH of electrolytes, density of current, temperature, anodic potential, in relation to proper conditions the unwanted effects could appear and came the rapid destroy of anode. Therefore, if we wanted to keep stability of anode, their working conditions mustn't be nearly critical conditions.

The complexity problem of anodic materials lay in the facts that during anodic polarization anodic surface are significantly change in medium which contain oxygen. In presence of oxygen, all metals, except gold, are thermodynamically unstable. Stability of anode is directly depends of nature and state of surface of oxide membrane.

Excludy, alkali, alkali – earth and metals of III – group periodic system, all other metals to present potential anodic materials .

The main aim of this study is getting the composites of anode with electrocatalytic properties for the reactions of oxigen separation and possibly some other electrochemical process. In this work we also examine the anodic deposition the composites wich consits of  $PbO_2/CoO_x$  [1].

## 2. EXPERIMENTAL

Examination of the influence of electrolytic composition, pH, as well as of the nature of metallic matrix - substrate were done by linear voltametric chronopotenciometric and chronamperometric methods.

For examination electrochemical depositions of composites plate, potenciostat / galvanostat M263 are used, with electrochemical microcell M K0264 (EG & GPARC).

In cells for voltametric examination as reference electrode Ag/AgCl electrode type K0265 is used. Additional electrode is platinum.

For depositions composites plate  $PbO_2/CoO_x$ , with current control, as working electrodes is used tile from titanium, bigger surface.

Electrode is first polished with abrasion paper after that the grease is removed from electrode in ethanol.

Finaly, electrodes are threating with solutions for microdamage.

In paper are used four different electrolytes wich differs by the nature and pH:

- $0,12 \text{ moldm}^{-3} Pb(CH_3COO)_2 + 0,8 \text{ moldm}^{-3} Pb(NO_3)_2 + 0,1 \text{ moldm}^{-3} Co(NO_3)_2$
- sulfamatic solution  $Pb(II)$  and  $Co(II)$  ions. In prepared solution  $Pb(II)$  sulfamat is added  $0,1 \text{ moldm}^{-3}$  solution of  $Co(II)$  nitrats.
- acid suspension :  $0,12 \text{ moldm}^{-3} Pb(CH_3COO)_2 + 0,8 \text{ mol/dm}^3 Pb(NO_3)_2 + \text{particles } Co_3O_4$ , wich are wide  $< 1 \mu\text{m}$ . Volume percent of particles was:  $\varphi=0,03; \varphi=0,1; \varphi=1,0$
- alkali suspension :  $0,1 \text{ mol/dm}^3 Pb(CH_3COO)_2 + 3 \text{ mol/dm}^3 NaOH + \text{particles } Co_3O_4$ , wich are wide  $< 1 \mu\text{m}$ . Volume percent of particles  $Co_3O_4$  in suspenzion was :  $\varphi=0,03; \varphi=0,1; \varphi=1,0$ .

## 3. RESULTS AND DISSCUSIONS

Influence of the electrolytic composites on anodic reaction of simultaneouns rising composites of  $PbO_2/CoO_x$  is showed on figure 3.1.

Based on eksperimental research and literature data, the most appropriate current density for simultaneous deposition  $PbO_2$  and  $CoO_x$  is determinated . For composites deposits of that oxid from sulfamatic electrolyt, as well as for the suspension, we used current density from  $3,0 \text{ mA/cm}^2$ . Changing the concetration ratio  $Pb^{2+}$  and  $Co^{2+}$  ions, hronopotenciometric depositions on substract of titanium were done (figure 3.2.).

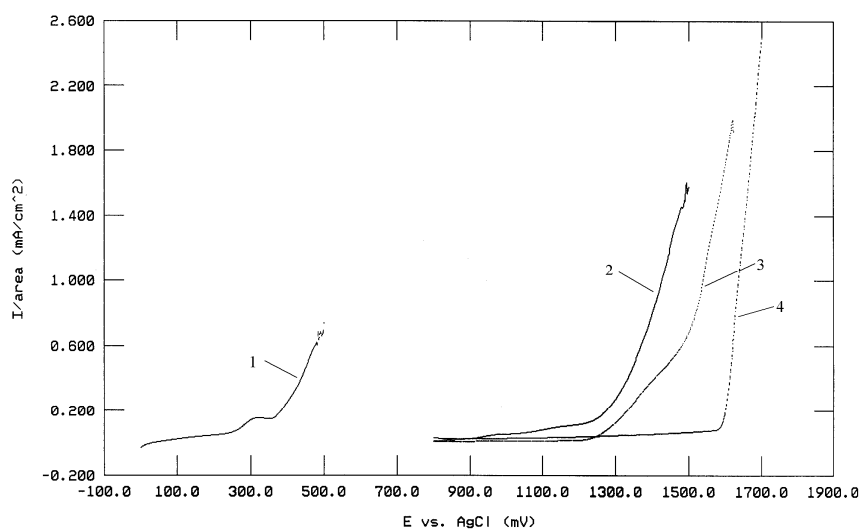


Figure 3.1.  $I-E$  voltamogram of reaction rise  $PbO_2/CoO_x$  on substrat of titanium, electrolyt: 1- $0,1 \text{ moldm}^{-3} Pb(CH_3COO)_2 + 0,02 \text{ volume } Co_3O_4 + 3,0 \text{ moldm}^{-3} NaOH$ ; 2- $0,13 \text{ moldm}^{-3} Pb(CH_3COO)_2 + 0,9 \text{ moldm}^{-3} Pb(NO_3)_2 + 0,03 \text{ volume } Co_3O_4$ ; 3- $0,13 \text{ moldm}^{-3} Pb(CH_3COO)_2 + 0,9 \text{ moldm}^{-3} Pb(NO_3)_2 + 0,1 \text{ moldm}^{-3} Co(NO_3)_2$ ; 4- $0,1 \text{ moldm}^{-3} Pb(SO_3NH_2)_2 + 0,1 \text{ moldm}^{-3} Co(NO_3)_2$ .

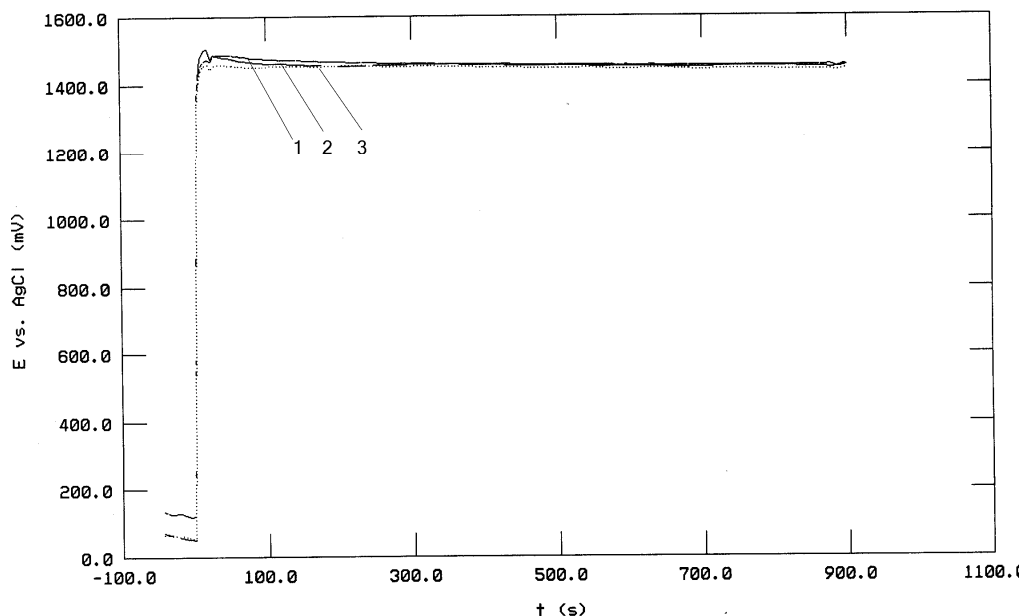


Figure 3.2. Hronopotenciometric diagram; substrat titan. (1)- $0,5 \text{ moldm}^{-3} \text{Pb}(\text{SO}_3\text{NH}_2)_2 + 0,5 \text{ moldm}^{-3} \text{Co}(\text{NO}_3)_2$ ; (2)- $0,3 \text{ moldm}^{-3} \text{Pb}(\text{SO}_3\text{NH}_2)_2 + 0,7 \text{ moldm}^{-3} \text{Co}(\text{NO}_3)_2$ ; (3)-  $0,1 \text{ moldm}^{-3} \text{Pb}(\text{SO}_3\text{NH}_2)_2 + 0,9 \text{ moldm}^{-3} \text{Co}(\text{NO}_3)_2$ .

We supposed that composites obtained by hronoampermetryc methods from solution of Pb(II) and Co(II) ions and Co particles gives the plate with in own composition except,  $\text{PbO}_2$  has  $\text{CoO}_x$ . This hypothesis we confirmed by testing anode on reaction of oxygen separating from solution of 1M NaOH.

The obtained composites electrodes  $\text{PbO}_2 / \text{CoO}_x$ , were applied as anode for reaction of oxygen separating, in purpose of examine their characteristic.

At figure 3.3 is showed voltamogram of reaction separate oxygen :

- at anode from substrate of titanium
- at anode from same substrate with plate from  $\text{PbO}_2$  obtained from solution lead –sulfamat.
- at anode from same substrate with composites  $\text{PbO}_2/\text{CoO}_x$  obtained from acid suspension, with different volume percent  $\text{Co}_3\text{O}_4$ .

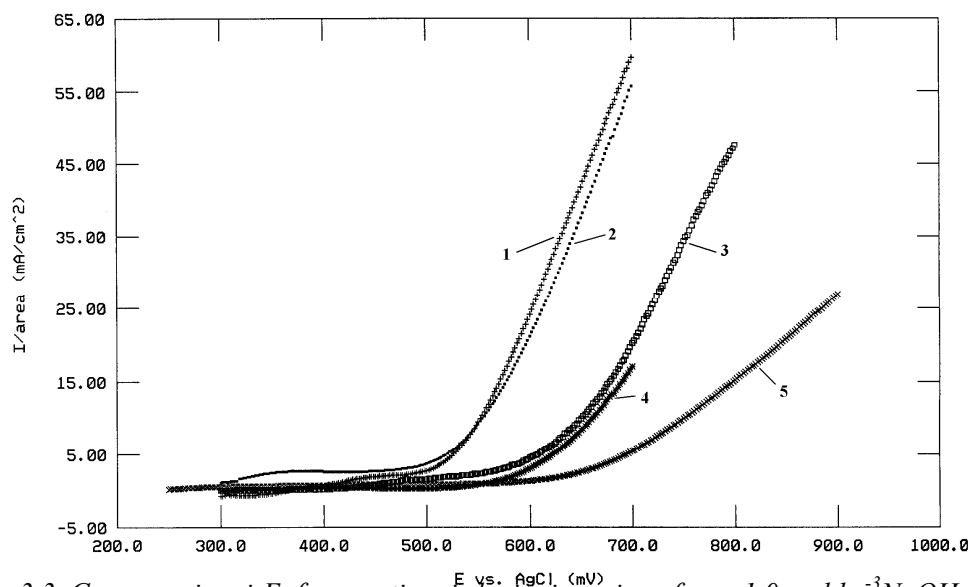


Figure 3.3. Comparasion  $i-E$  for reaction  $\text{izdvajanja}$  oxygen from  $1,0 \text{ moldm}^{-3} \text{NaOH}$ ; composites  $\text{PbO}_2/\text{Co}_3\text{O}_4$ , on substratat of titanium, (acid suspension):(1)- $\varphi=0,1 \text{ Co}_3\text{O}_4$ ; (2)- $\varphi=1,0 \text{ Co}_3\text{O}_4$ ; (3)- $\varphi=0,03 \text{ Co}_3\text{O}_4$ ; (4) -  $\text{PbO}_2$  on substrat of titanium

#### 4. CONCLUSION

Experimentally obtained voltamograms of electrochemic reactions to rise of composites lead dioxide and oxides of cobalt, are showed dependences of potentials of reactions from pH of electrolytes. Lowest valuable the potential of reaction to rise of composites, were done for the alkali suspension of composition:  $0,1\text{mol/dm}^3 \text{Pb}(\text{CH}_3\text{COO})_2 + 3,0\text{ mol/dm}^3\text{NaOH} + \text{particles } \text{Co}_3\text{O}_4$ , with volume part,  $\varphi = 0,02$ ; Potentials for the sulfamic electrolyte of composition:  $0,1\text{mol/dm}^3 \text{Pb}(\text{CO}_3\text{NH}_2)_2 + 0,1\text{mol/dm}^3 \text{Co}(\text{NO}_3)_2$ , were done more positively.

Comparison i-E (fig.3.3.), to discern of significant changes of potential for the reaction of separatings of oxygen all tested composites anodes obtained on the substrat of titanium (line 1,2,3) in the comparison with the lead dioxide anode and alone substrats (line 4 and 5). Obtained composites electrode has catalytic effects. Biggest the moving potential towards smaller positive values, reactions separatings of oxygens, to descerned for the composites  $\text{PbO}_2/\text{Co}_3\text{O}_4$ , wich obtained from suspension with volume part of  $\text{Co}_3\text{O}_4$  particles,  $\varphi = 0,1$  (line 1), [2,3].

#### 5. REFERENCES

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