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ELECTROCATALYTICAL PROPERTIES OF PALLADIUM-DECORATED COBALT COATINGS OBTAINED BY ELECTRODEPOSITION AND GALVANIC DISPLACMENT

This work presents the studies on the electrochemical process of thin palladium layers formation onto electrodeposited cobalt coatings. The suggested methodology consists of the preparation of thick and smooth cobalt substrate via galvanostatic electrodeposition. Cobalt coatings were prepared under different cathodic current density conditions from acidic bath containing cobalt sulphate and addition of boric acid. Obtained cobalt layers were analyzed by x-ray diffraction to determine their phase composition. Freshly prepared cobalt coatings were modified by the galvanic displacement method in $PdCl_2$ solution, to obtain smooth and compact Pd layer. The comparison of electrocatalytic properties of Co coatings with Co/Pd ones enabled to determine the influence of Palladium presence in cathodic deposits on the hydrogen evolution process.

Keywords: linear voltammetry; electrodeposition; palladium; cobalt; galvanic displacement reaction, catalytic activity

1. Introduction

Hydrogen is one of the alternative and very promising carrier of energy. Electrochemical production of H_2 is getting less expensive among the years, waste-free and ecological. It is known that the best electrode materials for hydrogen evolution contains a lot of platinum group elements. However their use is difficult in an industrial scale because of their relatively high price. Cobalt and its alloys could replace platinum in the production of electrodes for hydrogen evolution process. In literature one can find several reports about electrodeposition of Co-Ru [1-4], Co-Mo [5-9] and Co-W [10] alloys and their catalytic activity. Electrochemical deposition of Co-Pd coatings was studied by K. Mech and co-workers [11,12]. They found that the ability of this alloy for the four-electron oxygen reduction reaction is similar to pure platinum and better than the pure palladium. Catalytic processes take place at the surface of the electrode which can be easily modified by formation of alloy to decrease of the hydrogen or oxygen evolution reaction overpotential.

Galvanic replacement method based on the spontaneous reaction of metallic surface layer M with a more noble metal, M_{noble}, when the metal surface is treated with a solution containing the other metal in ionic form [13,14]. This method allows to obtain bimetallic materials using a small amount of precious metal and to changing its properties by the substitution of underlying metal M using M_{noble} metal.

The aim of this work was the electrochemical synthesis of Co/Pd electrodes and measurement of their catalytic properties. The analyzed materials may find a potential application in industrial catalytic processes of hydrogen evolution, due to their efficiency and much lower price in comparison with pure noble metals.

2. Description of experiment

The plating bath was prepared by dissolving 0.9 M $CoSO_4$ H_2O (Acros Organics), 0.3 M H_3BO_3 (ChemPur) in demineralized water. The pH of electrolyte were adjust to pH = 2 by the addition of concentrated H_2SO_4 (POCH). All experiments were carried out at 55°C. All reagents were of analytical purity. The deposition process was carried out on formerly etched copper plates of 2.8 cm^2 area. Preparation of the working electrode consisted of chemical polishing in a mixture of H_3PO_4, HNO_3 and CH_3COOH concentrated acids at 1:1:1 volume ratio, in temperature 65°C for 45 seconds. The counter-electrode was a platinum foil (6 cm^2). The potential was determined with respect to the saturated calomel electrode. The phase composition was analysed with the XRD method (Rigaku MiniFlex II) with the use of a copper tube (λ = 1.54059).

The cathodic efficiency connected with the efficiency of electrodeposition process was calculated based on the Faraday's Law (Eq. 1), which can be expressed as:

$$\varphi = \frac{\Delta m}{m} \cdot 100\% \qquad (1)$$

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$$m = (J \cdot t) / F \left(\frac{2 \cdot m_{Co}}{M_{Co}} \right) \qquad (2)$$

where:

φ – cathodic efficiency [%],

Δm – mass of deposit [g],

m – theoretical mass, based on Faraday's Law [g],

J – current intensity [A],

t – time of electrodeposition [s],

F – Faraday's constant [C],

m_{Co} – mass of cobalt in coating [g],

M_{Co} – molar mass of cobalt [g/mol].

Average coating thickness can be expressed by the following equation:

$$\sigma = \frac{10000 \cdot \Delta m}{G \cdot 2.82} \qquad (3)$$

where:

σ – estimated coating thickness,

Δm – mass of deposit [g],

G – Cobalt density [g/cm^3].

The catalytic performance of the obtained coatings was estimated using linear scan voltammetry. All of the measurements were carried out in 1M NaOH solution in analogous experimental setup as for deposition of the cobalt coatings. All measured potentials for LSV experiments were converted to the reversible hydrogen electrode scale via Nernst equation:

$$E_{RHE} = E_{meas} + 0.059 pH + E^0_{SCE} \qquad (4)$$

Each of sample were immersed into NaOH solution directly after the deposition process and held in solution for 4 minutes to stabilize the OCP value, which was a starting point for LSV measurements. Sodium hydroxide solution were purged by argon gas to remove dissolved oxygen, which can interrupt the obtained results. Value of current density was calculated for the geometrical area of tested samples. Linear scans have been performed with a low scan speed 5 mV/s with non-stirred electrolyte. Moreover, cobalt and cobalt/palladium coatings were tested by chronopotentiometry measurements for 1800s at a constantly current density of –10 mA/cm^2.

3. Result and discussion

The electrodeposition of Co coatings have been performed under different current density. According to the obtained mass of coatings, using (Eq. 1 and 2.) the cathodic current efficiency have been estimated. From Fig. 1 it can be seen that the current efficiency increase from 80% for the lowest applied current density ($i = 5$ mA/cm^2) to 93% for 20 mA/cm^2. This parameter is stable in the range of i from 20 to 80 mA/cm^2 and oscillates around 92%. For higher than 80 mA/cm^2 current density, the efficiency of electrodeposition is diminished due to the hydrogen evolution process. Thickness of obtained coatings can be easily estimated according to (Eq. 3). Variation of thickness

as a function of current density is plotted on Figure 2. It is worth to note that, a compact continuous layer without cracks and holes can be obtained at 35 mA/cm^2 and higher current density.
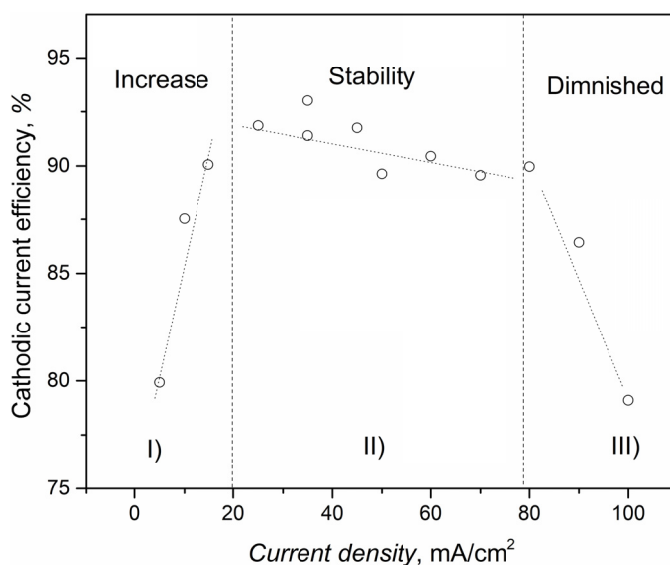

Fig. 1. Dependence of cathodic current efficiency for Co coatings obtained from different current density. Time of the electrolysis: 900s
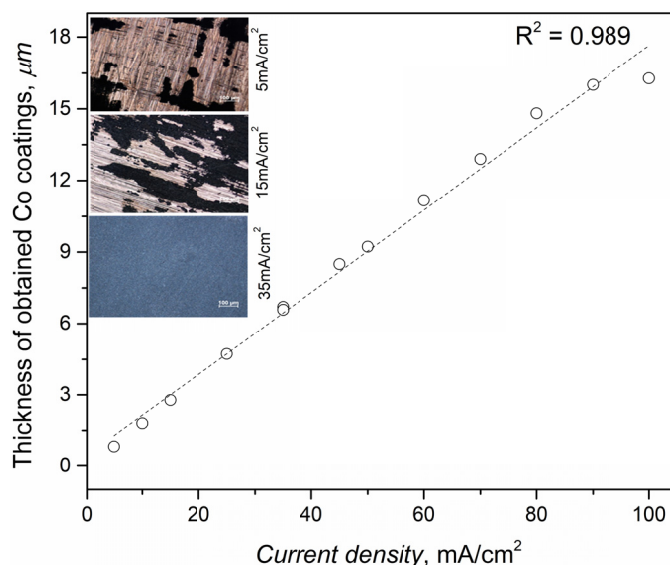

Fig. 2. Estimated thickness of cobalt coatings obtained from different current density. Time of the electrolysis: 900s

The change of crystal structure of Co layers was studied by XRD measurements. Fig. 3 shows that at current density $i = 5$-25 mA/cm^2 cobalt layers are a mixture of grains with different crystallographic orientation: (111), (200) and (220). At current density higher than 25 mA/cm^2 the peaks from (111) and (200) planes diminished and cobalt plane (220) is dominant.

Catalytic tests were performed by LV scans in 1 M NaOH solution. The hydrogen desorption peak and the value of current density obtained for specific, arbitral selected potential can be used to compare the electrochemical activity of tested materials.
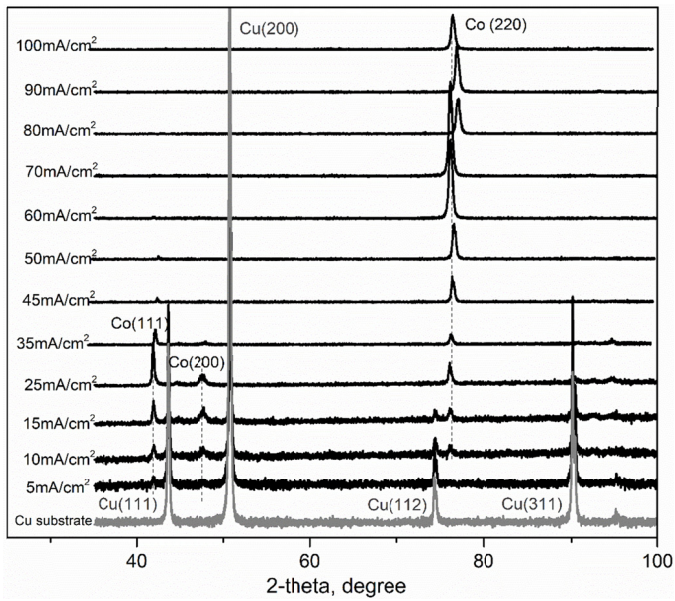
Fig. 3. XRD patterns of cobalt coatings electrodeposited on copper electrode for different current density. Time of electrodeposition: 900 s

The LV curves was employed in a range from Open Circuit value, to –0.9 V vs SHE. Fig. 4 shows, that the sample electrodeposited at 50 mA/cm^2 shows lowest potential, where the formation of H$_2$ bubbles have been created onto a Co surface. This effect can be attributed to high active surface area of sample obtained under this conditions.
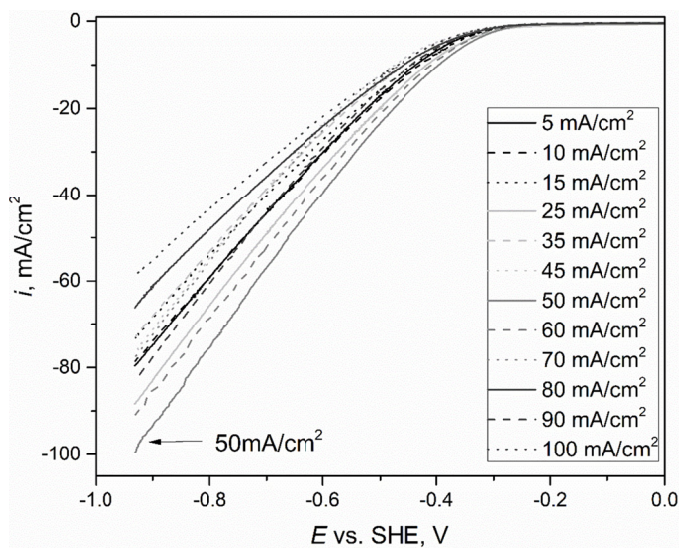

Fig. 4. CV responses of the cobalt coatings in 1 M NaOH solution. Scan speed: 5 mV/s, from E$_{OCP}$ to –1.0 V vs SHE

The electro-activity of cobalt samples were increased by a surface modification in PdCl$_2$ solution. The noble metal ions were reacting with a cobalt surface and galvanic displacement reaction takes place. For these tests 5 identically cobalt samples were selected which were electrodeposited at 50 mA/cm^2 and immersed into palladium chloride solution (PdCl$_2$, Cl$^-$ = 1 M/dm^2, pH = 1) for different time.

Figure 5. shows X-Ray diffraction patterns of cobalt after modification. Increase of immersion time clearly show that the peaks corresponding from Pd reflexes gradually increase. This confirms that process of galvanic replacement of cobalt by palladium is under diffusion control of palladium spices close to the cobalt surface.
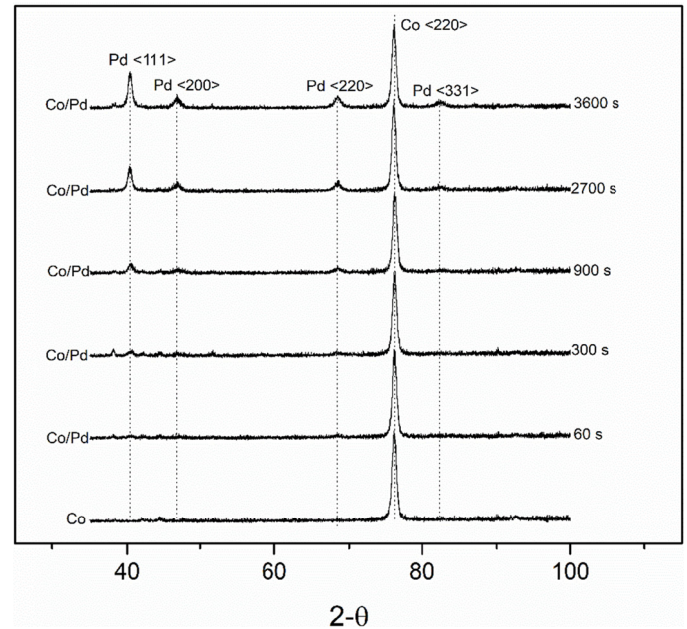

Fig. 5. XRD patterns of cobalt coatings after galvanic displacement surface modification for different time in palladium chloride solution

SEM micrographs of Co and Co/Pd coatings have been presented in Table 1. Morphology of cobalt coatings is regular, without any cracks and irregularities. Nodules shape is uniform and size varied from 3-10 µm. Palladium modification change the size of grains and the visibility of grain boundaries, hence the effective surface of catalytically active material increases.

Modification of cobalt surface significantly increase the catalytic activity of samples. Value of onset potential for hydrogen evolution reaction is lower than the cobalt coating. It may be noted that the catalytic activity also increases with time of surface modification. It is clearly visible on Fig. 6, where the lower current density has been observed for sample after 1 h of galvanic displacement. It can be attributed with gradual increase of the surface area of sample and number of active sites, where overpotential for reduction reaction is lower.

CP study also allows to determine the impact of palladium modification on the catalytic performance. Application of a constant current cause the voltage response, which can be connected with the water splitting reaction overpotential. Fig. 7 present the values of potentials obtained for cobalt and cobalt/palladium coatings after applying the constant current. For cobalt deposit the value was close –395 mV vs SHE. Palladium addition will decrease the overpotential to –329 mV for sample with 60 s of modification. Increase of time of galvanic replacemenetement reaction gradually increase the catalytic activity, by diminished the overpotential value to -318 mV.

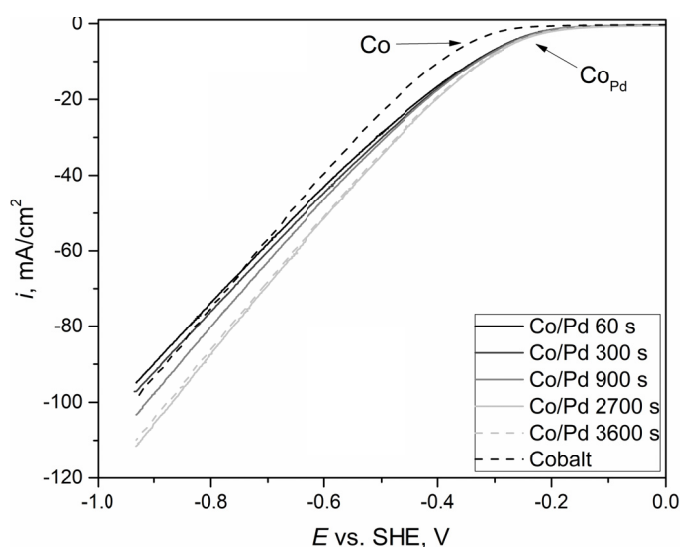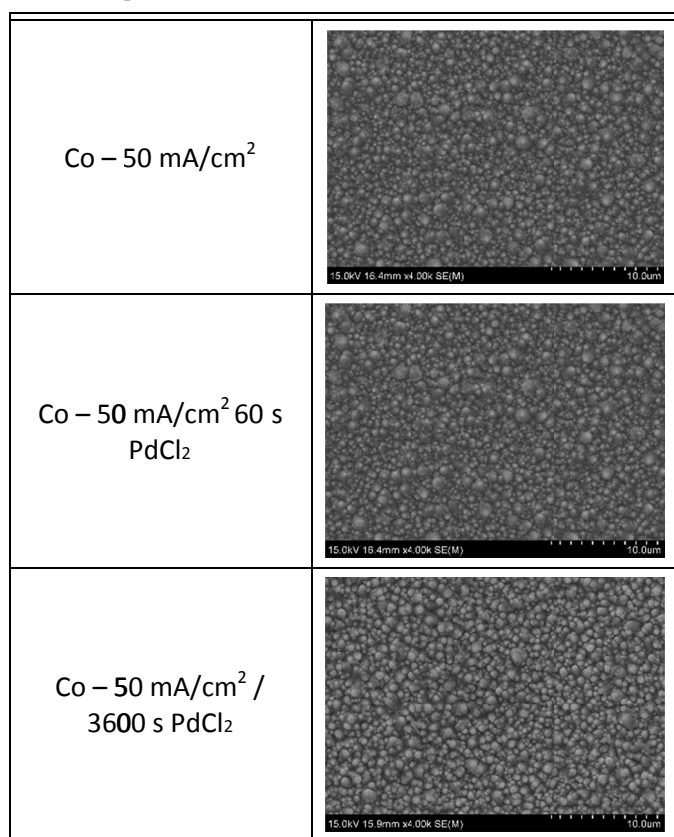SEM micrographs of Cobalt coatings before and after immersion in palladium chloride solution for 60 and 3600 s

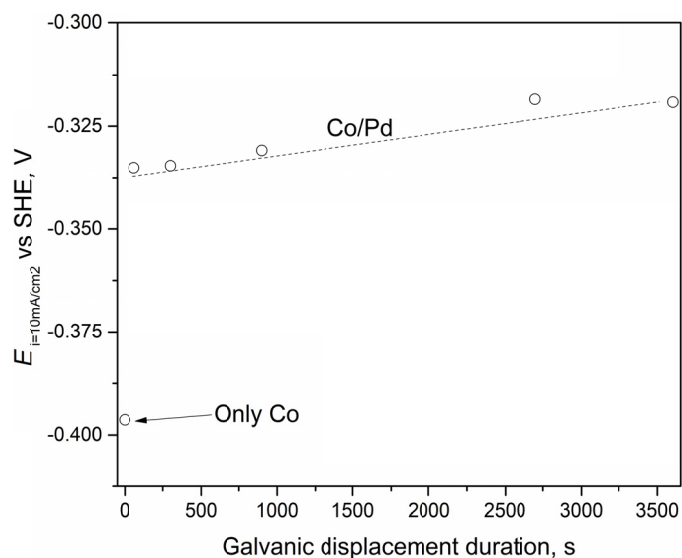|	
Co – 50 mA/cm^2	
Co – 50 mA/cm^2 60 s PdCl$_2$	
Co – 50 mA/cm^2 / 3600 s PdCl$_2$	

Fig. 7. Potential values obtained from chronopotentiometry measurements performed for the cobalt and Co-Pd coatings in 1 M NaOH solution. Applied current density: -10 mA/cm^2, time of polarization: 1800 s

3. The best catalytic activity has been obtained for sample obtained at 50 mA/cm^2.

4. Modification of cobalt coatings by galvanic replacement is very easy and low cost method to improve their catalytic activity for water splitting reaction. Presence of Pd on the surface of cobalt decrease the overpotential of hydrogen evolution reaction.

Fig. 6. CV responses of the cobalt and Co-Pd coatings in 1 M NaOH solution. Scan speed: 5 mV/s, from E_{OCP} to -1.0V vs SHE

4. Conclusions

1. Efficiency of cobalt coatings deposition can be modified by variation of applied current density.

2. Deposits synthesized below 25 mA/cm^2 are not compact. Obtained coatings in higher current density are smooth, uniform and consist of only one phase Co (220).

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