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INFLUENCE OF Ni CONTENT OF ELECTRODEPOSITED Pd-Ni ALLOY COATINGS ON THEIR ELECTROCATALYTIC ACTIVITY IN ALKALINE MEDIUM

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ABSTRACT

The influence of the Ni content (1.4 - 9.0 wt. %) in electrodeposited Pd-Ni alloy coatings on the rate of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in an alkaline media was investigated. Electrocatalytic activity of the electrodeposited layers towards methanol oxidation reaction (MOR) was also studied. The composition and surface morphology of the samples were characterized by energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM). The crystal structure of the Pd-Ni alloys was examined by X-ray diffraction (XRD). Electrochemical experiments were performed by cyclic voltammetry (CV). The presence of concentration ranges with respect to the Ni content is shown, wherein the electrocatalytic activity of the Pd-Ni alloy towards HER, OER and MOR is higher than that of pure Pd.

Keywords: electrocatalysis, electrodeposited Pd-Ni alloy coatings, cyclic voltammetry, HER, OER, MOR.

INTRODUCTION

Pd-based electrocatalysts are investigated as an alternative of Pt electrodes (anode or cathode) for low temperature fuel cells (PEMFCs, DAFCs, AMFCs) [1]. The addition of a transition metal element, such as Ni to Pd may significantly improve the overall catalytic activity of Pd due to the bimetallic promotional effect [2].

Both electrodeposited bimetallic Pd-Ni film [3] and Pd-Ni alloy [4] show an enhanced catalytic activity than pure Pd synthesized with the same processes. In addition, the combination of Pd with Ni is expected to further enhance the tolerance of Pd to poisoning as Ni is an oxophilic element [5].

Pd-Ni systems were obtained using different techniques - galvanic displacement [6, 7], electrodeposition [3, 8, 9], chemical reduction of the metal salts [8, 10], chemical precipitation [11], electroless co-plating [12], nanocapsule synthesis method [13]. The binary Pd-Ni catalysts were examined as electrodes for hydrogen oxidation reaction (HOR) [7, 14] and oxygen reduction reaction (ORR) [8, 10, 11]. Particular attention was devoted to the electrooxidation of alcohols - glycerol [15, 16], methanol [3, 6, 9, 17 - 19] and ethanol [3, 12, 13, 20]. Pd-Ni system was also investigated in respect to its applications as a catalyst for water splitting, HER or OER [21 - 23].

Literature data generally indicate that the presence of Ni increases the activity of the Pd alloy electrodes in respect to all the above-mentioned reactions, as well as improves the tolerance to the catalyst poisons. In many cases, however, one or two samples are a subject of the study, and in those with a larger number of samples, there is a contradiction: some papers have not shown a clear relationship between the alloys composition and the properties of the electrodeposited alloys as a catalyst for water splitting in alkaline solution [21]. According to others, when the Ni content is too high, the catalytic performance of Pd components in terms of oxidation of methanol and ethanol is greatly inhibited [3]. Investigating three samples with different contents of Ni, electrodeposited from ionic liquid, authors show that the bimetallic Pd-Ni coatings with atomic ratios of ~80/20 (about 12 wt. % Ni) possess the highest current for ethanol oxidation reaction (EOR) [24]. This is the sample with the lowest Ni content. This dependence was later confirmed for alloys obtained by other methods [20, 25, 26]. The question naturally arose of what is the electrocatalytic behavior of catalysts with even lower Ni content. Taking into account also the view of a number of authors that an improvement in the electrocatalytic properties of this system can be expected by an optimization of the Ni content in the Pd-Ni alloy coating, the present study aims to clarify the electrocatalytic activity of electrodeposited Pd-Ni alloy layers with a Ni content below 10 wt. % on the rate of HER, OER and MOR in alkaline media [8, 9, 20].

EXPERIMENTAL

In previous studies devoted to the internal stresses and to the degree of cathodic hydrogenation of Pd-Ni alloy coatings with a different ratio of the both elements, for electrodeposition of the alloy a basic electrolyte containing 33.3 g L^{-1} $PdCl_2$ and 100 g L^{-1} $(NH_4)_2SO_4$ was used to which $NiSO_4.7H_2O$ was added in portions [27]. In the present work, the same composition of the basic electrolyte and the same mode of preparation were applied. The pH of the electrolyte was adjusted at 9.2 by addition of ammonia. The coatings with a thickness of about 5 μm were electrodeposited onto copper substrates with dimensions 20 x 10 mm at room temperature and current density of 15 mA cm^{-2}. For comparison, plain Pd and Ni coatings were prepared at the same conditions from an electrolyte without $NiSO_4.7H_2O$ or $PdCl_2$, respectively. All used chemicals were of analytical grade.

The surface morphology and composition of the alloy coatings were analyzed using a scanning electron microscope JSM 6390 equipped with a system INCA Oxford Energy 350 (SEM, EDS).

X-ray powder diffraction patterns of the as deposited coatings were recorded in the angle interval 15 - 125^{o} (2θ) by Philips PW 1050 diffractometer, equipped with CuK_{α} tube and scintillation detector. Indexing, determination of unit cell parameters and evaluation of the volume fraction of phase constituents were carried out after least-squares procedure of profile fitting, performed by Powder Cell software package [28].

CV measurements were conducted in 1M KOH solution using an Autolab 30 (Eco Chemie) system. The investigations were performed in a three-electrode cell having a volume of 50 ml, a reference saturated calomel electrode (SCE), a working electrode with a surface area of 0.2 cm^2 and a Pt counter electrode. The electrolytes were deaerated with N_2 prior to each experiment.

The electroactive surface area (ECSA) of Pd in the Pd–Ni films was determined by CV measurements, performed between –0.75 V and +0.30 V (after repetitive scanning between hydrogen and oxygen evolution reactions in a supporting deaerated electrolyte of 1 M KOH) with a scan rate of 50 mV s^{-1}. The ECSA was calculated based on the PdO reduction peak, assuming a charge value of 420 C cm^{-2} for the reduction of the PdO monolayer [18, 29].

RESULTS AND DISCUSSION

Electrodeposition and crystallographic characterization of Pd-Ni alloys

Under the above operating conditions and by varying the concentration of $NiSO_4.7H_2O$ in the electrolyte, Pd-Ni alloy coatings were deposited containing up to about 9 wt. % Ni (Fig. 1).

The X-ray patterns of the corresponding coatings are presented in Fig. 2. Pd-Ni alloys form a continuous range of solid solutions with face-centered cubic lattices [30]. Thereby the increasing content of Ni in the alloy reduces the lattice parameter (Table 1). Increasing the amount of co-deposited Ni also changes the arrangement of crystallites. In the concentration range between 2.7 wt. % and 7.4 wt. % Ni, a change in the intensity of peaks with indexes (111) and (002) (Fig. 2) is registered on the diffractograms, and a transition from pyramidal to pseudo cubic microstructure is observed on the surface (Fig. 3). This is related to

Table 1**.** Lattice parameter and texture of Pd, Ni and Pd-Ni alloys with a different content of Ni.

Ni, wt.%	0.0	1.4	2.7	7.4	9.0	100
Parameter, Å	3.8701(1)	3.86(7)	3.85(1)	3.83(2)	3.82882(2)	3.516(6)
Texture	(022)	(022)	(022)	(020)	(020)	(111)

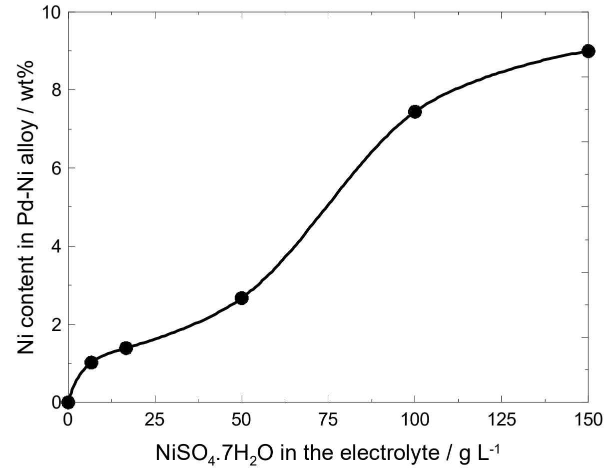

Fig. 1. Effect of the concentration of NiSO$_4$.7H$_2$O in the electrolyte for electrodeposition of Pd-Ni alloy on the Ni content in the alloy.

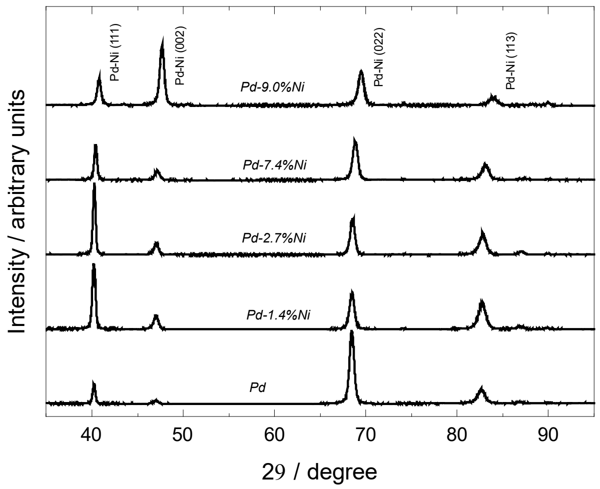

Fig. 2. X-ray diffraction patterns of Pd and Pd-Ni alloys with different content of Ni.

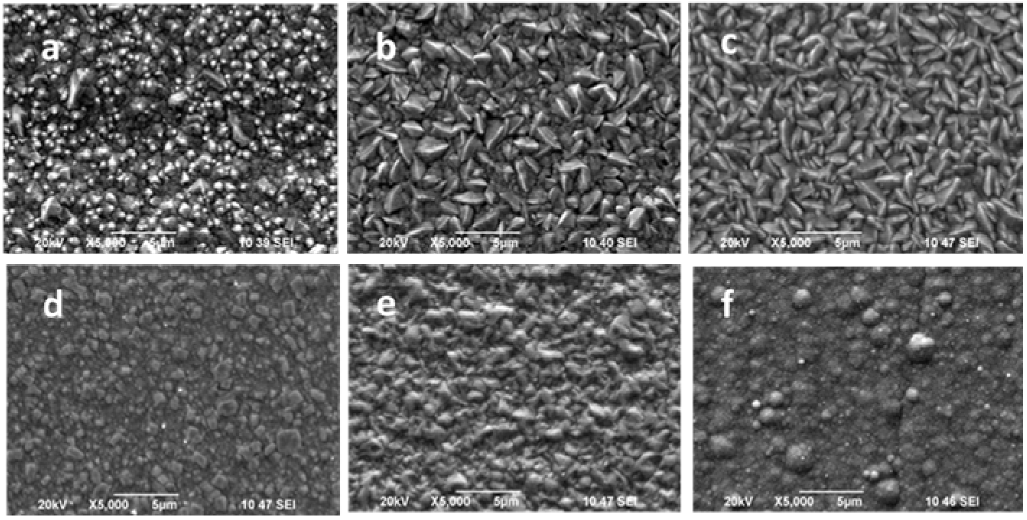

Fig. 3. Morphology of Pd, Ni and Pd-Ni coatings with different content of Ni. a - Pd, b - Pd-1.4 wt. % Ni, c - Pd-2.7 wt. % Ni, d - Pd-7.4 wt. % Ni, e - Pd-9.0 wt. % Ni, f - Ni.

a change in the growth direction of the crystals (the predominant orientation changes).

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Electrochemical characterization of the Pd-Ni layers

Effect of the Ni content in the Pd-Ni alloys on the rate of HER

Fig. 4a shows the effect of the Ni content in Pd-Ni alloys on the CV curves in the area of HER in a supporting deaerated electrolyte of 1 M KOH with a scan rate of 50 mV s^{-1}. The rate of HER on Pd is an order of magnitude higher than that on Ni. The co-deposition of small amounts of Ni (1.4 wt. %) with Pd leads to a slight increase of the rate of HER as compared to that of Pd, but further increase of Ni content, especially above 7.4 wt. %, decreases the rate of HER on Pd-Ni alloy. According to several authors, the high activity of Ni-based electrodes is caused by the ability of these electrodes to adsorb and absorb great amounts of hydrogen, which changes the electron structure of the basic metal [31 - 33]. In this regard, the following comparison is interesting. When studying the change in internal stresses of electrodeposited Pd-Ni alloys under cathodic polarization in a sulfuric acid medium, it was shown that at low Ni content, the change in internal stresses due to the hydrogenation of the alloy coatings increases, then sharply decreases [27].

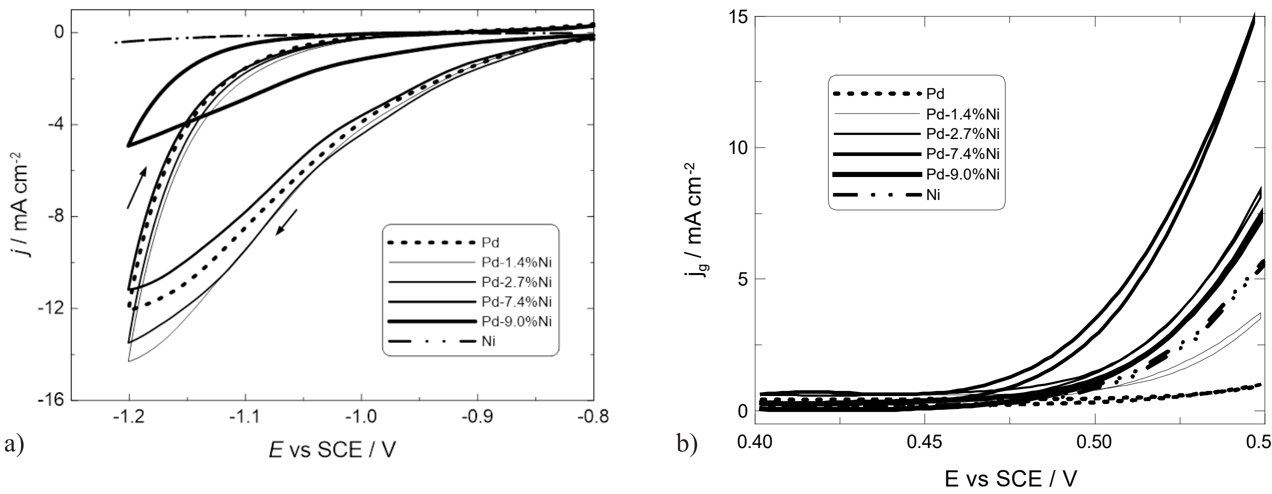

Fig. 4. CV curves in 1M KOH of Pd, Ni and Pd-Ni alloys with different content of Ni (a) – cathodic reaction, (b) – anodic reaction.

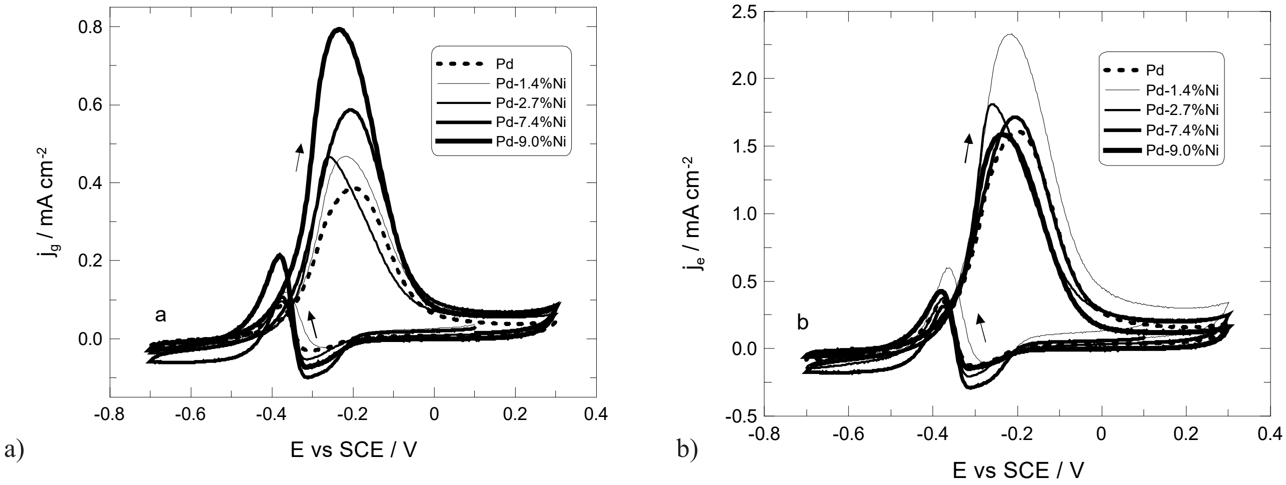

Fig. 5. Cyclic voltammograms of the catalysts in deaerated 1 M KOH + 0.5 M CH_3OH solutions (a). The same CVs corrected for the ECSA (b). Scan rate 10 mV s^{-1}.

Effect of the Ni content in the Pd-Ni alloys on the rate of OER

In the case of the oxygen evolution reaction, the dependence is different. Part of the anodic CV curves is given in Fig. 4b. On the Ni electrode, reaction starts at more negative potentials than on Pd and at a potential of 0.55 V the rate of OER on Ni is significantly higher compared to that on Pd. All tested Pd-Ni alloys show better electrocatalytic activity towards OER than Pd. When the content of Ni in the Pd-Ni alloy exceeds 2.7 wt. %, the electrocatalytic activity of Pd-Ni alloy towards OER becomes better than that of Ni. Increasing the content of Ni to 7.4 wt. %, the OER rate increases, then decreases, but is still higher than that on pure Pd.

Electrocatalytic activity of the deposited layers towards MOR

A stronger interest in the Pd-Ni alloy systems is observed in relation to the electrooxidation of alcohols. The role of Ni is to enhance the catalytic performance of the bimetallic catalysts through assisting Pd to oxidize the CO-like adsorbed species on the film surfaces. The combined action of Pd and Ni compositions make the bimetallic Pd–Ni electrocatalysts generate the higher catalytic activity and the stronger tolerance to the catalyst poisons [3].

Fig. 5a presents the voltammograms of Pd and Pd-Ni electrodes in deaerated 0.1M KOH + 0.5M CH_3OH solution after repetitive scanning between

-0.70 V and +0.30 V vs. SCE until steady state is achieved. Increasing the Ni content in the alloys leads to an increase in their electrocatalytic activity. This dependence can be explained by modification of the electronic properties of Pd by Ni, and with the change in the morphology of the coatings, respective of their actual area. The currents, normalized by Pd electroactive surface areas (j_e), calculated from the PdO reduction peak are compared in Fig. 5b. The more pronounced intrinsic electrocatalytic activity possesses the Pd-Ni alloy, containing 1.4 wt. % Ni. The further increase of the Ni content leads to a reduction of this effect. The Pd-Ni alloy containing 9.0 wt. % Ni displays a comparable electrocatalytic activity to that of plain Pd. This shows that the morphology, respectively the real area of the electrocatalysts play an essential role in their electrocatalytic activity.

CONCLUSIONS

Pd-Ni alloy coatings containing from 1.4 wt. % to 9.0 wt. % Ni were electrodeposited by increasing the concentration of $NiSO_4.7H_2O$ in basic electrolyte containing $PdCl_2$ and $(NH_4)_2SO_4$.

The electrochemical studies conducted in 1 M KOH show that the Ni content in the alloy coatings affects the rate of all three investigated reactions - HER, OER and MOR. The Pd-Ni alloys with 1.4 wt. % Ni display higher electrocatalytic activity as regards HER compared to that of Pd. Further increase of Ni content in the alloy leads to decrease in the activity. All investigated Pd-Ni alloys have better electrocatalytic activity towards OER than plain Pd. The dependence has a maximum at 7.4 wt. % Ni. The Pd-Ni catalyst with 1.4 wt. % Ni shows the best intrinsic catalytic activity towards the MOR. With increasing Ni content in the alloy, theirs intrinsic electrocatalytic activity decreases. Due to the developed surface, alloy coatings with higher Ni content (9.0 wt. %) have better electrocatalytic properties.

The results obtained in the present work show, that the low Ni alloys deserve further investigation. In a more distant perspective, the results can serve as a prerequisite to load with Pd-Ni alloy high surface area support materials (TiO_2 or WO_3 powders), alternative to carbon-based substrates and use them as catalysts in fuel cell technology.

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