Electrocatalytic activity of Pd-Au co-deposits on Ni-foam towards hydrogen evolution reaction

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Pd-Au coatings were electrodeposited on Ni-foam from electrolytes with different contents of both metals. The morphology of the produced co-deposits was analyzed by scanning electron microscopy. Their electrocatalytic activity towards hydrogen evolution reaction from neutral phosphate buffer solution was explored by means of linear voltammetry. In addition, the current was monitored under potentiostatic polarization from -0.6 to -1.2 V (vs. Ag/AgCl) and the quantities of the produced hydrogen gas with the electrocatalysts were calculated. The highest hydrogen evolution rate was achieved with the electrocatalysts produced from an electrolyte with equal Pd and Au contents.

Keywords: Pd-Au electrocatalysts, hydrogen evolution reaction, neutral electrolyte, linear voltammetry, chronoamperometry.

INTRODUCTION

Hydrogen evolution reaction (HER) takes place at the cathode in many industrial electrolysis processes with aqueous electrolytes, as well as in bioelectrochemical systems, in particular – microbial electrolysis cells (MECs), where the production of hydrogen is the main target [1,2]. The development of MECs represents an exciting new area of the environmental biotechnological research. The MECs, commonly exploiting wastewater as a fuel source to produce hydrogen while accomplishing wastewater treatment, are closely related to two intensively developing technologies - microbial fuel cells (MFCs) and water electrolysis. As far as the anodic reactions, as well as the operational conditions in MECs are the same as those in MFCs, the achievements concerning development of the bioanodes could be directly transferred from the one technology to the other one. Although HER is the common cathodic reaction in MECs and water electrolyzers, the operating conditions in both systems are quite different. The use of microorganisms as biocatalysts in MECs requires mild conditions such as near neutral electrolytes and ambient temperatures, while most industrial water electrolyzers operate with acidic or alkaline electrolytes at elevated temperatures. By these reasons, the crucial point for the practical application of MECs as a feasible hydrogen production technology is to find cost effective and high catalytically active cathodes for near-neutral pH and moderate temperatures.

Platinum is well-known as the best electrocatalyst for HER, but it is too expensive [1, 2-6]. Partial substitution of Pt and decrease of catalyst amount are among the main strategies for cost reduction [7-9]. Kye et al. [10] have demonstrated that the Pt-Au electrocatalyst shows higher area-specific activity than platinum nanoparticles alone. Huang et al. [11] reported that Pd nanoparticles coated carbon cloth was almost 50 times more effective than Pt as cathode catalyst for HER in MEC. In our previous study [12], it was established that Pd-Au co-deposits, produced by electrodeposition on carbon felt, display electrocatalytic activity for HER in neutral electrolyte, increasing with augmentation of the gold content.

Ni-foam has been widely used as an electrocatalyst supporting material due to its well-developed porous structure, high conductivity, corrosion resistivity and good mechanical properties [13-16].

In this study, Pd-Au composites were synthesized by electrodeposition on Ni-foam and

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their electrocatalytic activity towards HER was investigated in neutral phosphate buffer solution with a view to their possible application as cathodes in MECs.

EXPERIMENTAL

Electrodes were prepared by electrochemical co-deposition of Pd and Au on Ni-foam (RCM-Ni-4753.016). The electrodeposition was carried out in a three-electrode cell and the potential was controlled by PalmSens handheld potentiostat/galvanostat. A round-shaped sample of Ni-foam with geometric area of 1.6 cm^2 was connected as a working electrode, platinum-titanium mesh was used as a counter electrode and the potential was measured against Ag/AgCl reference electrode. The electrolyte was a mixture of 2% PdCl$_2$ in 0.1M HCl and 2% HAuCl$_4$ in 0.1M HCl in different ratios (w/w %): 9:1, 7:3 and 1:1 [17]. The electrodeposition was performed in potentiostatic regime at E$_{deposit}$ = -500 mV (vs. Ag/AgCl) for 10 s.

The morphology of the produced electrodeposits, further denoted in the text as Pd$_{50}$Au$_{50}$/Ni-foam, Pd$_{70}$Au$_{30}$/Ni-foam and Pd$_{90}$Au$_{10}$/Ni-foam, was analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) using JEOL 6300 microscope.

The weight of the co-deposits was estimated from the current transients, obtained during electrodeposition, by using the Faraday's law and data for the molar percentage, determined in a previous study [12].

The electrocatalytic activity of the obtained materials towards HER was investigated in 67 mM phosphate buffer solution (pH 7.0) by means of linear voltammetry (LV). The experiments were carried out in a three-electrode cell. The explored sample was connected as a working electrode and a platinum-titanium mesh (10 cm^2) and Ag/AgCl (3 M KCl) were used as a counter and a reference electrode, respectively. The potential was swept from 0 to -1.2 V (vs. Ag/AgCl) with a scan rate of 2 mV.s^{-1}. Three subsequent scans were performed for each sample and the third scan was used for data analysis.

In parallel, chronoamperometric measurements were carried out under the same conditions. The working electrode was polarized from −0.6 to −1.2 V (vs. Ag/AgCl) with a voltage step of 0.1 V for 10 min at each step and the current was monitored. The quantity of the produced hydrogen was calculated by integration of the areas under the chronoamperometric curves at each potential and applying Faraday's law.

The voltammetric and chronoamperometric studies were performed by using potentiostat/galvanostat PJT 35-2 with IMT-101 electrochemical interface.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM) observations show that the obtained Pd-Au electrodeposits are irregularly distributed over the Ni-foam, forming islands with varying size (Fig. 1). In all cases the distribution of the particles is not uniform. The bigger magnifications of the co-deposits reveal that the islands consist of nearly spherical complex structures sized up to 2.5 μm. The recorded EDS spectra confirm the co-presence of Pd and Au in the deposits (Fig. 2).
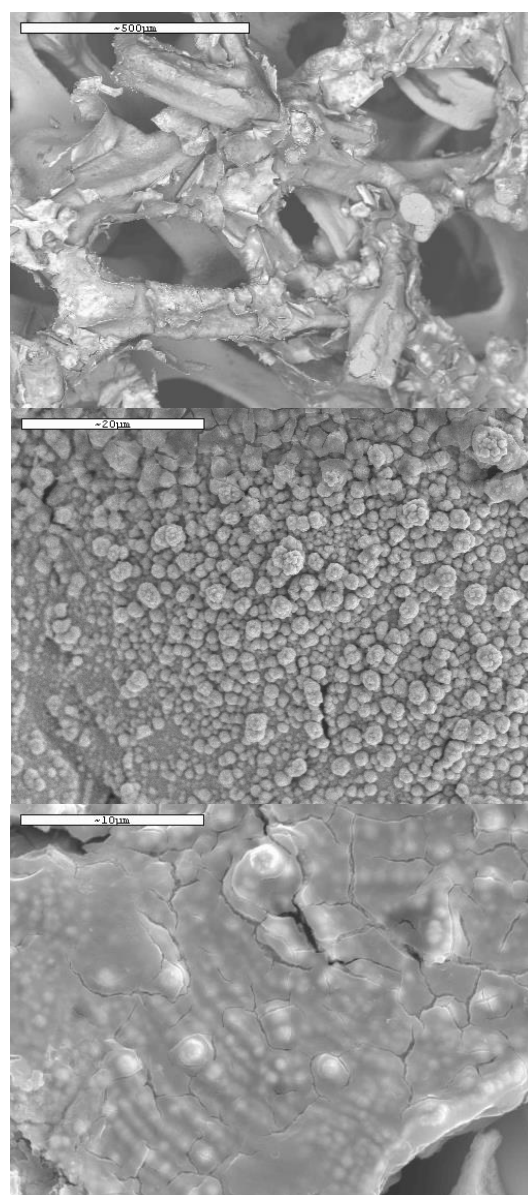

Fig. 1. SEM images of Pd-Au electrodeposits on Ni-foam, taken at different magnifications.

Earlier studies [18] have proved that each globular structure is formed by a large number of nanosized particles, whose shape is strongly affected by the percentage of gold in the deposit and changes from needle-like crystallites (as with the co-deposits with high Pd content) to cauliflower-like shape, observed with Au-enriched crystallites. In the same paper [18], the XRD spectra of Pd-Au co-deposits, produced in varied proportions of both metals, were compared with those of the pure Au and Pd electrodeposits. The 2Θ values of the deposits indicate the availability of fcc crystalline metal phases corresponding to (111), (200), and (220) facets. The diffraction peaks of the co-deposited metal phases were shifted to the lower 2Θ values as compared to that of the pure Pd. The lattice expansion caused by the inclusion of Au atoms into the Pd fcc structure is indicative for alloy formation.

Table 1. Values of V_e, V_h and current density at -1.2 V (vs. Ag/AgCl), estimated from LVs.

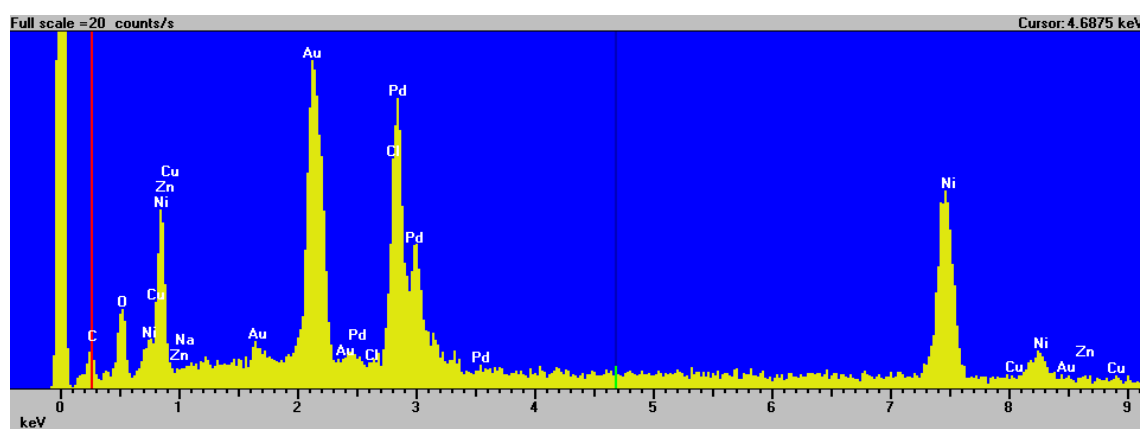| Material	V_e, V (vs. Ag/AgCl)	V_h, $A.V^{-1} \times 10^{-3}$	Current density, $mA.cm^{-2}$
Ni-foam	-0.63	3.42	1.32
$Pd_{90}Au_{10}$ / Ni-foam	-0.52	4.30	1.91
$Pd_{70}Au_{30}$ / Ni-foam	-0.48	5.25	2.47
$Pd_{50}Au_{50}$ / Ni-foam	-0.41	10.40	5.29

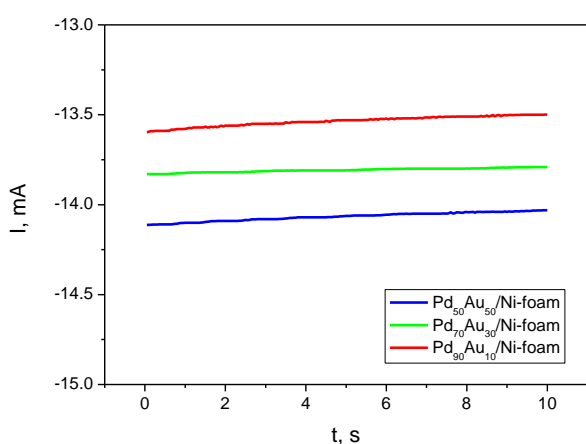**Fig. 2.** EDS-spectrum of $Pd_{50}Au_{50}$/Ni-foam.

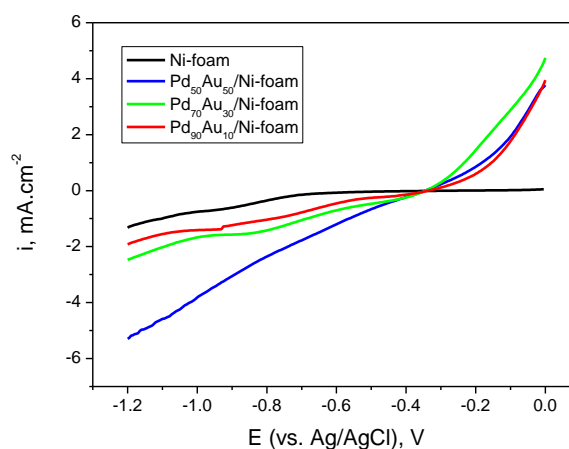**Fig. 3.** Chronoamperograms obtained during co-electrodeposition of Pd and Au

Fig. 4. Linear voltammograms obtained with Pd-Au in different ratios on Ni-foam in phosphate buffer (pH 7).

The amounts of the electrodeposits were calculated from the coulombs, obtained by integration of the current passed through the system during deposition (Fig. 3), applying the Faraday's law. The obtained values are of the order of 0.080 ± 0.004 mg, slightly increasing with augmentation of gold content in the electrodeposition bath.

Linear voltammograms (LVs) obtained with a Ni-foam and with the newly produced Pd-Au modified electrodes are plotted in Fig. 4. The evaluation of the electrocatalytic performance was based on the voltage needed to initiate hydrogen production (V_e) and the slope (V_h) of the first linear region in the voltammogram. The value of V_e indicates the relative overpotential, while V_h reflects the current production rate at an applied voltage. Better catalytic performance is achieved by a lower V_e and higher V_h [19]. The values of V_e and V_h estimated from LVs are summarized in Table 1. In addition, the current density values, derived from Fig. 3 at a potential of -1.20 V (vs. Ag/AgCl), are also presented.

The obtained results indicate that the bare Ni-foam possesses a higher overpotential in respect to HER than the electrodeposited electrodes. The increase of gold content in the electroplating bath, resp. in the co-deposits [12], diminishes the overpotential; thus, the hydrogen production on $Pd_{50}Au_{50}$/Ni-foam begins at the lowest potential - 0.41V (vs. Ag/AgCl). In the same direction, a tendency for increase in both V_h and current density values is observed, showing that the augmentation of gold content improves the cathodic reaction. The quantitative deviations between the ratios of V_h and current density at -1.20 V (vs. Ag/AgCl) for the different materials studied are due to the appearance of a cathodic hump in the LVs of deposited $Pd_{90}Au_{10}$ and $Pd_{70}Au_{30}$ electrodes, which could be assigned to possible hydrogen absorption and/or hydride formation in these samples [20]. We suppose that the decrease of palladium in the deposit lowers its capability for hydrogen absorption, thus making the competitive hydrogen evolution reaction more favourable.
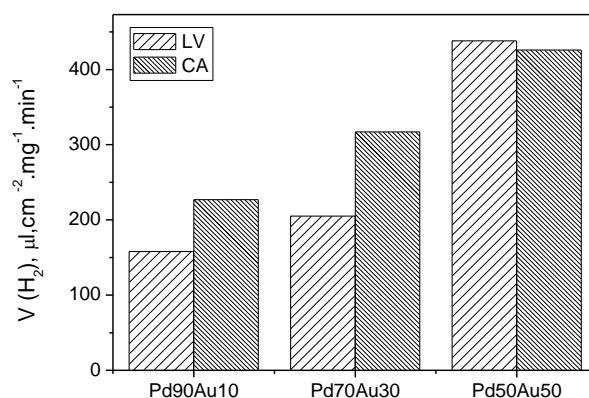
Fig. 6. Intrinsic electrocatalytic activity of the investigated Pd-Au electrodeposits towards HER, expressed as a volume of generated hydrogen per min normalized to the weight of the co-deposits and the geometric area of the support. The estimations were performed by using current density values from the linear voltammograms (LV) and chronoamperograms (CA) at potential -1.2 V (vs. Ag/AgCl).

In our previous study [12], it was verified that the estimations based on chronoamperometric measurements are related to the quantities of the evolved hydrogen detected by mass spectrometry. These findings allowed evaluation of the hydrogen production by monitoring the current response at different potentials. Considering the results from LVs, chronoamperometric experiments with the investigated materials were performed at potentials from -0.6 to -1.2 V (vs. Ag/AgCl). Chronoamperograms obtained with Pd-Au electrodeposits and Ni-foam at -1.2 V (vs.
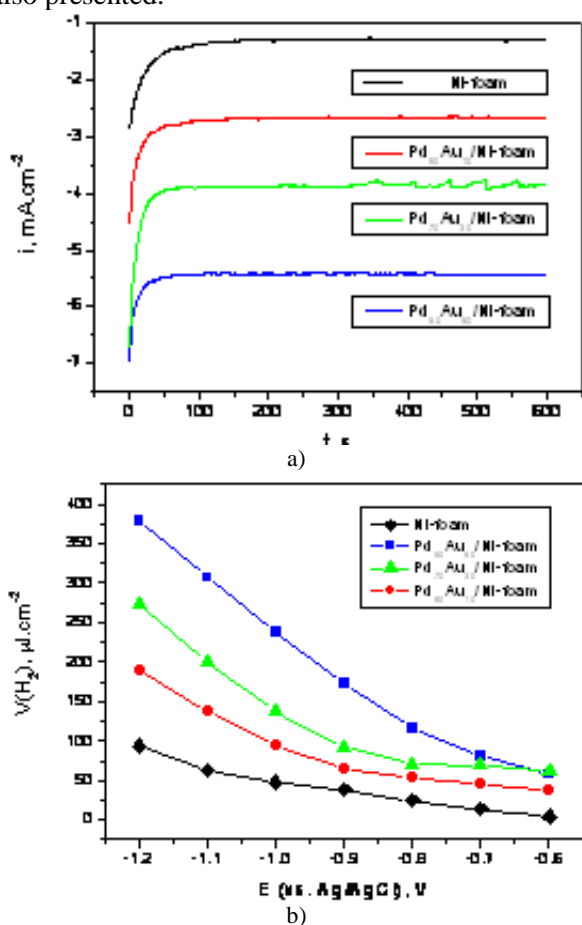

Fig. 5. a) Chronoamperograms obtained with Ni-foam and Pd-Au electrodeposits at potential -1.2 V (vs. Ag/AgCl); b) Quantities of evolved hydrogen at different applied potentials estimated from chronoamperometric measurements.

Ag/AgCl) are presented in Fig. 5a. The estimated quantities of the produced hydrogen at different applied potentials are plotted on Fig. 5b.

In general, the results from chronoamperometric measurements confirm those obtained by LV. The hydrogen production rates on all electrodeposited electrodes are higher than those on the non-modified Ni-foam and a tendency for increasing the amount of generated hydrogen with the increase of gold content in the electrodeposited catalysts is observed.

To evaluate the intrinsic electrocatalytic activity of the explored Pd-Au electrodeposits, the quantities of generated hydrogen were normalized to the weight of the co-deposits. The estimations were done by using current density values at -1.2 V (vs. Ag/AgCl), derived from the corresponding LVs and chronoamperograms, and summarized in Fig. 6. The slight increase of the deposits' weight with the rise in the gold amount does not significantly influence the estimated intrinsic activity values, which enhance in the order $Pd_{90}Au_{10} < Pd_{70}Au_{30} < Pd_{50}Au_{50}$.

CONCLUSION

Palladium and gold could be co-deposited on Ni-foam by electrodeposition at -0.5 V (vs. Ag/AgCl). The increase of the gold content in the electrolyte bath enhances the electrocatalytic activity of the obtained Pd-Au electrodeposits towards HER in neutral phosphate buffer solution. The highest intrinsic electrocatalytic activity was achieved with $Pd_{50}Au_{50}$ electrodeposits. Based on the results obtained in this study we consider that Pd-Au co-deposits are promising electrocatalysts for hydrogen generation in microbial electrolysis cells.

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ЕЛЕКТРОКАТАЛИТИЧНА АКТИВНОСТ НА Pd-Au КО-ДЕПОЗИТИ ВЪРХУ ПЕНООБРАЗЕН НИКЕЛ ПО ОТНОШЕНИЕ ЕЛЕКТРОХИМИЧНОТО ОТДЕЛЯНЕ НА ВОДОРОД

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(Резюме)

Тънки слоеве от Pd-Au са отложени върху пенообразен никел от електролити с различно съдържание на двата метала. Морфологията на получените електроотложения е анализирана чрез сканираща електронна микроскопия. Чрез линейна волтамперометрия е изследвана електрокаталитичната активност на материалите по отношение електрохимичното отделяне на водород от неутрален фосфатен буферен разтвор. Паралелно са проведени потенциостатични измервания в интервала от -0.6 до -1.2 V (vs. Ag/AgCl), от които е изчислено количеството водород, получавано с различните депозити. Най-висока скорост на отделяне на водород е постигната с електрокатализаторите, отложени от електролит с еднакво съдържание на Pd и Au.