Electrocatalytic activity of Ni- and Co-modified graphitized paper towards hydrogen evolution reaction in neutral electrolyte

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The choice of highly effective cathode materials for microbial electrolysis cell (MEC) is the main challenge for the practical implementation of this innovative technology for hydrogen generation. In this study, nickel and cobalt catalysts, synthesized by direct selective grafting from acetylacetonate precursors, were deposited on graphitized paper with microspores sublayer (GP with MPL). The electrocatalytic activity of the produced modified electrodes towards hydrogen evolution reaction (HER) in neutral electrolyte was examined by linear voltammetry, chronoamperometry, and electrochemical impedance spectroscopy. Both types of modified materials exhibit much higher electrocatalytic activity towards HER than the unmodified graphitized paper. The highest electrocatalytic activity was achieved with 0.5 mg.cm^{-2} loading of nickel and cobalt catalysts.

INTRODUCTION

The opinion of most scientists is that the hydrogen will be the main energy source in the near future [1-4]. Currently, about 95% of the industrial hydrogen production worldwide is based on steam reforming of natural gas and other light hydrocarbons, partial oxidation of heavier hydrocarbons, and coal gasification, which is not perspective in terms of the recently proclaimed "circular" economy. In this regard, new alternative methods for hydrogen production have been intensively researched and developed in recent decades. One of the newest methods in this direction is the microbial electrolysis cell (MEC) - an electrochemical device that uses microorganisms to oxidize organic substrates at the anode and generate hydrogen at the cathode. The use of exoelectrogenic microorganisms requires mild experimental conditions such as neutral medium and ambient temperature [5].

The main challenge for the practical implementation of MEC for hydrogen production is the choice of effective cathode electrocatalysts with high electocatalytic activity in neutral medium. Platinum is the best catalyst for the electrochemical generation of hydrogen by water electrolysis. It possesses high electrocatalytic activity and low hydrogen overpotential [6], but its high cost, scarcity and propensity to poisoning limit the wide

application in MEC [7]. The development of efficient and cost-effective cathodes as an alternative to Pt has provoked intensive research over the last decade. Partial replacement or reduction of the platinum load are among the main strategies applied [8-10]. Kye *et al.* [11] showed that Pt-Au electrocatalysts have a larger active surface area than Pt nanoparticles alone. Palladium, with its high electrical conductivity and excellent catalytic properties, is closest to platinum. Huang *et al.* [12] reported that deposited palladium nanoparticles on carbon cloth are 50 times more efficient than platinum catalyst. In our previous studies [13-15], it was established that the electrocatalytic activity of Pd-Au co-deposits for HER increases with the augmentation of the gold content. Nickel is widely used as electrode material in industry due to its low cost and good catalytic properties in highly advanced alkaline water electrolysis [16]. To enhance the catalytic activity of Ni-based materials, various methods have been applied, such as alloying with other metals, incorporation of particles, as well as production of electrodes with a well-developed, rough or porous surface. For example, the alloying of nickel with transition metals (Fe, Mo, W, Co), as well as with P significantly improves the catalytic activity for HER compared to that of the pure metals [17]. Selembo *et al.* [18] deposited nickel oxide on a thin layer of metal and thus obtained an effective cathode for MEC. Hu *et al.* [19] demonstrated

comparable MEC performances in terms of hydrogen production rate using NiMo and NiW catalysts electrodeposited on carbon cloth with those achieved with Pt cathodes. Investigating NiW and NiMo electrodeposited on Ni-foam as cathodes in MEC, Mitov *et al.* [20] achieved a hydrogen production rate in the range from $0.04 \div 0.14$ $m^3(H_2)$ m^{-3} d^{-1} at an applied voltage of 0.6 V. Cobalt-based composites have also shown relatively high catalytic activity for HER [21] and other related reactions [22, 23] with practical importance.

Despite the high cathodic efficiency achieved with some of the materials studied in MEC, their productivity is still relatively low and has not been confirmed in large-scale reactors. This necessitates the creation and research of new highly efficient catalysts as one of the priority tasks for turning MEC into a technology of industrial importance.

In this study, nickel and cobalt catalysts dispersed over non-stoichiometric titanium oxides, synthesized by direct selective grafting from acetylacetonate precursors, were deposited on graphitized paper (GP) and the electrocatalytic activity of the produced modified electrodes towards HER in neutral electrolyte was examined. The results obtained with different electrodes were compared and discussed.

MATERIALS AND METHODS

Nickel and cobalt catalysts were synthesized from an acetylacetonate precursor $(M[(C_5H_7O_2)_n]_m,$ M = Ni, Co) by direct selective grafting following the procedure previously described by Maksimova *et al.* [24]. Magneli-phase titanium sub-oxide (MPT) powder with particle size of 60 to 100 nm was used as a catalytic carrier for the samples. The metallic part in each of the catalysts was 40 wt.%, denoted Ni40/MPT and Co40/MPT. The prepared catalysts were deposited on round-shaped samples of graphitized paper (GP provided by Freudenberg, Germany (H2315)) with geometric area of 1.0 cm^2 by airbrush technique with purified air gas carrier. The catalytic loading of all developed electrodes variates in the range of 0.25 to 1 $mg.cm^{-2}$. The modified electrodes were dried at room temperature for 6 h before electrochemical characterization.

The phase composition, surface morphology and structure of the catalysts were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The XRD patterns were recorded on a X-ray diffractometer Philips APD15 with Cu K_α radiation at constant rate of 0.02° over an angle range $2\theta = 10 \div 90°$.

The electrochemical performance of the produced electrodes in neutral phosphate buffer solution (PBS) was investigated by linear voltammetry (LV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS).

LV was performed with a scan rate of 0.01V/s over the potential range from 0 to −2.0 V (*vs.* Ag/AgCl) in 67 mM PBS (pH 7.0). The evaluation of the 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.

Chronoamperometric measurements were carried out in the same electrolyte at -0.9;-1.0 and -1.2 V (*vs.* Ag/AgCl) for 10 min at each potential. The quantity of the produced hydrogen was calculated by integration of the areas under the obtained chronoamperograms and applying Faraday's law.

The EIS measurements were performed at applied AC with an amplitude of the signal of 0.01V and E_{dc} = -1.2V (*vs.* Ag/AgCl) in the frequency range from 100 kHz to 0.1Hz.

All electrochemical experiments were carried out in a three-electrode cell with an electrolyte volume of 30 cm^3 by using a potentiostat-galvanostat AUTOLAB PGSTAT 204. The electrode samples were connected as a working electrode and a platinum wire was used as counter electrode, the potential was measured against Ag/AgCl (3.5 M KCl) reference electrode.

RESULTS AND DISCUSSION

The phase composition of the MPT support and of the monometallic catalysts was studied by XRD. The diffraction patterns are presented in Fig. 1. The reflections show that both Ni and Co are in the crystal state and the crystallographic orientation of Ni particles is mainly in (111) and (200), while the Co particles are in (100) and (002) crystallographic planes. The calculated crystallite average size by Sherrer equation [25] is 22 nm for Ni40/MPT and 26 nm for the Co40/MPT.
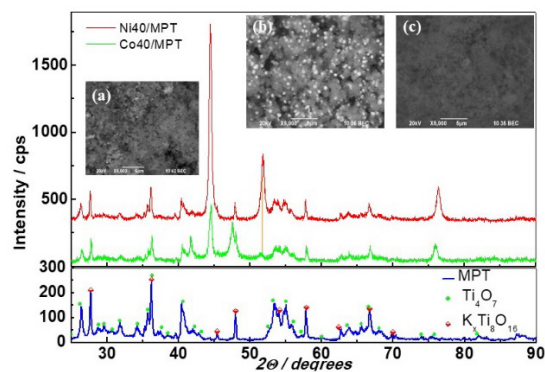

Fig. 1. XRD patterns of the MPT support and the Ni40/MPT and Co40/MPT catalysts; SEM images of the MPT (a) support, Co40/MPT (b), and Ni40/MPT (c).

In addition, the SEM images, presented in Fig. 1 b, c show fine dispersion of the catalytic particles over the whole surface of the support (a).

Linear voltammograms obtained with the newly produced Ni and Co modified GP with different loading of catalysts and non-modified GP are compared in Fig. 2. The LVs indicated that by sweeping the potential more negative than −0.3 V (*vs.* Ag/AgCl) for Ni modified materials and -0.6 V (*vs.* Ag/AgCl) for Co modified materials, respectively, the cathodic current for all modified GP electrodes gradually increased. The values of current density at −2.0 V (*vs.* Ag/AgCl) are given in Table 1. The obtained values are by an order of magnitude higher than those reported for PdAu electrodeposits [15] and those for NiFeCoP/carbon felt examined under the same conditions [26]. In addition, the estimated values of the voltage needed to initiate hydrogen production, V_e, and the slope in the voltammogram, V_h, which corresponds to the rate of the HER are also presented in Table 1. The minimum voltage needed to initiate substantial current (V_e) was in the range between -0.3 ÷ -0.7 V *vs.* Ag/AgCl (-0.1÷ - 0.5 V *vs.* SHE) for all studied electrodes, which is comparable to that reported for Pt/carbon cloth in PBS [21]. The obtained results indicate that the bare GP possesses a higher overpotential (V_e = -0.82 V *vs.* Ag/AgCl) in respect to HER than the modified electrodes. V_e for Ni-modified electrodes is about two times lower than bare GP. The values of the V_h of the Ni modified materials are twice higher than GP and for the Co-modified materials – four times, respectively. The combination of lowest overpotential and highest hydrogen production rate determines 0.50 mg.cm^{-2} Co/GP and 0.50 mg.cm^{-2} Ni/GP as the best electrocatalysts for HER among all modified materials. Probably, the increasing of the catalyst loading on the GP clogs the electrode material and reduces its electrocatalytic properties.

A deeper insight into the electrochemical kinetics of the electrodes was obtained by electrochemical impedance spectroscopy (EIS). Nyquist plots of the graphitized paper and modified materials recorded at -1.2V (vs. Ag/AgCl) are presented in Fig. 3. The obtained results show that the polarization resistance of all modified electrode materials is with an order of magnitude lower than that of the non-modified graphitized paper. The lowest polarization resistance for both types of catalysts is exhibited by the samples with catalytic loading of 0.5 mg.cm^{-2}, which explains their highest electrocatalytic activity.
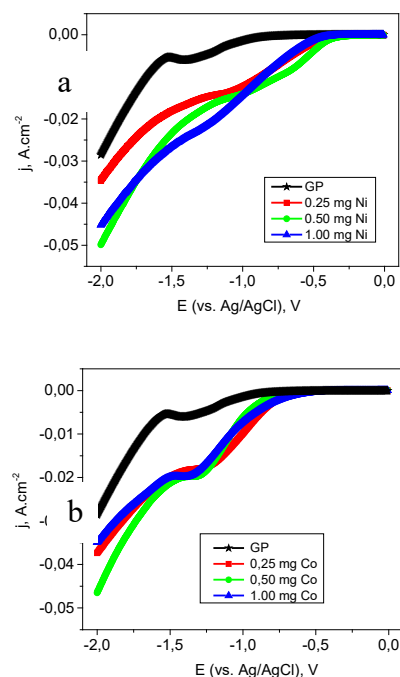

Fig. 2. Linear voltammetry obtained with non-modified GP and modified GP with: a) nickel catalyst/GP; b) cobalt catalyst/GP

Table 1. Summarized table of the estimated values of the voltage needed to initiate hydrogen production, V_e, and the slope in the voltammogram, V_h, which corresponds to the rate of HER.

Material	j (−2.0V), A.cm^{-2}	V_e, V (*vs.* Ag/AgCl)	V_h, A/V
GP	0.029	-0.82	0.011
0.25 Ni	0.035	-0.35	0.020
0.50 Ni	0.050	-0.31	0.024
1.00 Ni	0.045	-0.40	0.027
0.25 Co	0.037	-0.65	0.032
0.50 Co	0.046	-0.67	0.041
1.00 Co	0.035	-0.57	0.028

Chronoamperograms obtained with non-modified GP and with the investigated materials at -1.2V (*vs.* Ag/AgCl) in PBS are presented in Fig. 4 a, b.

The newly produced materials exhibit higher electrocatalytic activity than non-modified GP. The quantities of evolved hydrogen, estimated from chronoamperometric measurements, are compared in Fig. 3c. The hydrogen evolution rates achieved with modified materials are several times higher than those obtained with GP.
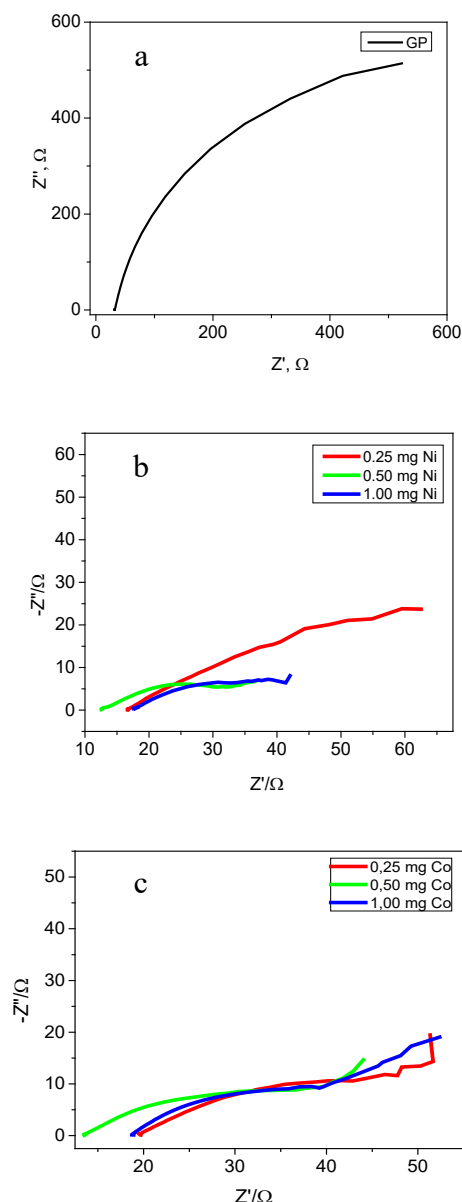
Fig. 3. Nyquist plots of the EIS of the: a) Graphitized paper; b) Nickel catalysts/GP; c) Cobalt catalyst/GP

CONCLUSIONS

Nickel and cobalt catalysts were deposited on graphitized paper (GP). The electrocatalytic activity of the newly synthesized materials towards HER was investigated in neutral phosphate buffer solution with respect to their potential application as cathodes in microbial electrolysis cells. Despite different catalyst loadings, the estimated current production rates indicate that the developed Ni- and Co-modified electrodes exhibit much higher electrocatalytic activity compared to the non-modified GP. The obtained electrochemical results determined as optimal the catalytic loading of 0.50 mg.cm^{-2}.
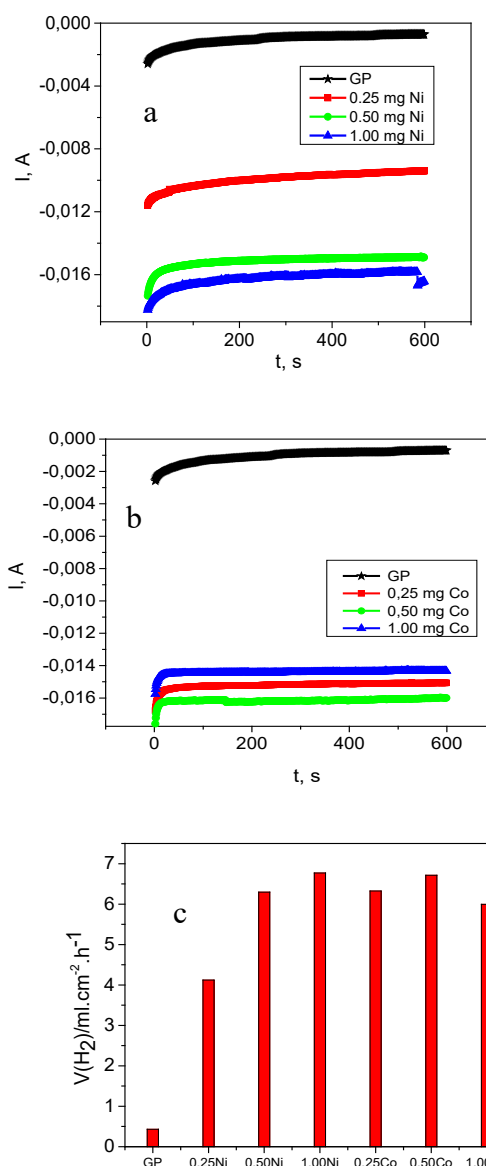
Fig. 4. Chronoamperometric curves obtained at a potential of -1.2V with investigated materials: a) Ni/GP; b) Co/GP; c) Quantity of the produced hydrogen, calculated by integration of areas under chronoamperometric curves obtained at a potential of -1.2V.

The highest current density of 0.05A.cm^{-2} (at -2.0V *vs*. Ag/AgCl) was achieved with 0.50 mg Ni/GP. The obtained values of the quantities of the produced hydrogen, calculated by integration of areas under the chronoamperometric curves obtained at potential -1.2V (*vs*. Ag/AgCl), for the examined materials are ranged in 6.0 ÷ 6.8 ml.cm^{-2}.h^{-1}, except for 0.25 mg Ni/GP – 4.1 ml.cm^{-2}.h^{-1}. Further evaluation of the produced materials as cathodes in MEC is in progress.

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