

Synthesis and characterization of dip-coated CoB-, NiB- and CoNiB-carbon felt catalysts

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Received June 21, 2014, Revised September 10, 2014

In the present study, CoB, NiB and CoNiB catalysts were dip-coated on carbon felt by borohydride reduction. The morphology and the elemental composition of the synthesized coatings were characterized by scanning electron microscopy and energy-dispersive X-ray spectroscopy. The electrocatalytic activity of the produced materials towards hydrogen evolution reaction in neutral electrolyte was investigated by means of linear voltammetry and chronoamperometry. The highest intrinsic activity was evaluated for the NiB catalysts.

Keywords: dip-coated catalysts, borohydride reduction, electrocatalytic activity, hydrogen evolution reaction, neutral electrolyte.

INTRODUCTION

Over the past few years, bioelectrochemical systems (BESs), such as microbial fuel cells (MFCs) and microbial electrolysis cells (MECs), have attracted an increasing attention as a novel and promising approach for utilization of organic materials in wastewaters for production of electrical energy or valuable chemicals [1-3]. Hydrogen production in MECs is considered as a main goal of this strategy. Although laboratory-scale MECs operate with high electrical energy efficiency at applied voltages even below the theoretical electromotive force of water electrolysis (1.23 V), numerous challenges need to be faced before the microbial electrolysis can achieve practical implementation as a feasible hydrogen production technology. Because all types of BESs are based on the same microbial-assisted anodic reactions, the major task for improving the MECs performance is connected with a development of high catalytically active and cost-effective cathodes [3,4]. The replacement of the expensive platinum-catalyzed cathodes with alternative precious-metal free catalysts is one of the main strategies in the field.

Nickel-based materials have been extensively studied as cost-effective cathodes for hydrogen production in MECs [1,3,4]. Promising results have been reported for the use of different stainless steel and nickel alloys [5], commercially available nickel

and stainless steel powder supported on carbon cloth [6], NiMo and NiW electrodeposited onto a carbon cloth [7] or carbon felt [8]. Recently, we have demonstrated that carbon supported NiFe-, NiFeP- and NiFeCoP-nanocomposites possess high catalytic activity towards HER in neutral and weak acidic solutions and could be applied as cathodes in MECs [9]. Jeremiasse et al. [10] reported NiFeMo and CoMo alloys as possible HER catalysts in an MEC around neutral and mild alkaline pH.

Nanofabrication is considered as a perspective approach for producing efficient electrocatalysts due to the fact that nanomaterials possess unique chemical, structural and electrical properties [11]. In our previous studies [12, 13], it was established that CoB nanoparticles, produced by borohydride reduction, could be applied as an electrode material in alkaline batteries due to their ability for electrochemically reversible hydrogen absorption/desorption. An electrocatalytic activity of electrodes prepared from NiB nanosized powders towards HER and hydrogenation of some organic compounds was also found [14-16].

In the present study, CoB, NiB and CoNiB catalysts were dip-coated on carbon felt by borohydride reduction. The morphology and the elemental composition of the produced coatings were characterized and their electrocatalytic activity towards HER in neutral electrolyte was evaluated and compared.

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EXPERIMENTAL

Cobalt- and nickel-containing coatings were deposited on carbon felt (SPC-7011, 30 g/m², Weibgerber GmbH & Co. KG) by borohydride reduction. 10% Co(NO₃)₂ and 10% Ni(NO₃)₂ or a mixture of both solutions in a volume ratio of 1:1 were used as a metallic precursor, and 5% NaBH₄ in 1% NaOH was the reducing agent. Prior to use the carbon felt samples (round-shaped with geometric area of 1.4 cm²) were sonicated in ethanol:acetone 1:1 (v/v) mixture for 10 min and then rinsed with DI water. The carbon felt was subsequently immersed into the precursor and the reducing solutions for 10 s and finally washed with DI water. The dip-coating procedure was repeated several times in order to produce substantial catalyst loading. The prepared catalysts were heated at 100 °C for 2 h to enhance the adhesion between the coatings and the support [17]. The weight difference before and after the deposition was used to calculate the catalyst loading.

The morphology of the developed materials was analyzed by scanning electron microscopy (SEM) using JEOL 6300 microscope. In addition, the elemental content of the coatings was analyzed by energy-dispersive X-ray spectroscopy (EDS).

The electrocatalytic activity of the produced materials towards hydrogen evolution reaction (HER) in phosphate buffer solution (PBS, pH 7.0) was explored by means of linear voltammetry (LV) and chronoamperometry (CA). The electrochemical examinations were performed in a three-electrode cell by using PJT 35-2 potentiostat/galvanostat (Radiometer-Tacussel) by automatic data acquisition via IMT-101 electrochemical interface. The investigated material was connected as a

working electrode; a platinum wire was used as a counter electrode and Ag/AgCl (3 M KCl) as a reference electrode.

The LV was carried out in a negative direction with a scan rate of 2 mV/s. Three subsequent scans were performed for each sample and the third scan was used for data analysis. During chronoamperometric measurements, the working electrode was polarized from -0.6 V to -1.2 V (vs. Ag/AgCl) for 10 min at each potential step and the current response was recorded. The hydrogen generation rate at each potential was calculated from the coulombs, determined by integration of areas under CA curves, applying the Faraday's law.

RESULTS AND DISCUSSION

Production and characterization of CoB-, NiB- and CoNiB-coated carbon felt

Preliminary experiments have shown that a single dip-coating cycle with the Co-containing precursor results in approximately double catalyst loading in comparison with the use of Ni-containing solution. The results reported hereafter in the paper are obtained with catalysts produced by 20 repetitions of the dip-coating process with the Ni precursor and 10 repetitions with the Co and mixed Co-Ni solution. The estimated loadings of the coatings, obtained as a result of the described procedure, are 9.6, 9.7 and 5.8 mg/cm² for the Ni-, Co- and CoNi-containing catalysts, respectively. These results indicate that the presence of Ni in the precursor solutions suppresses the coating deposition on the carbon felt, probably due to more favorable implementation of the reduction process in the solution volume than on the support surface.

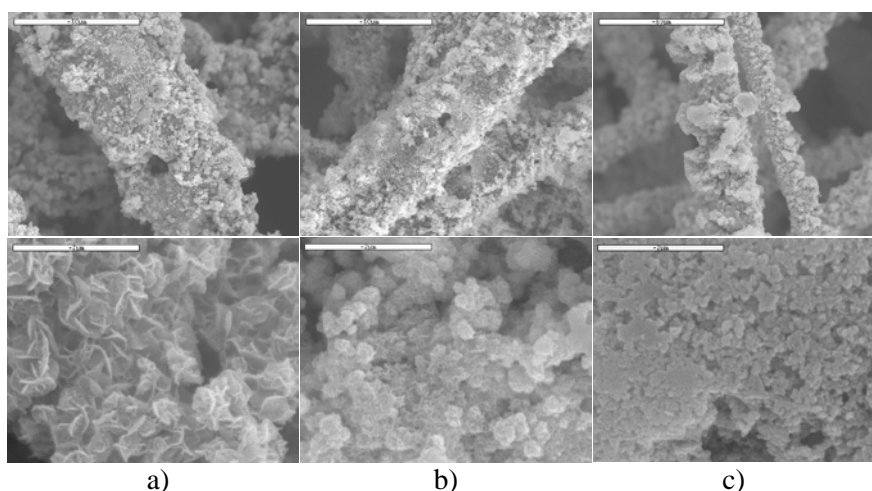
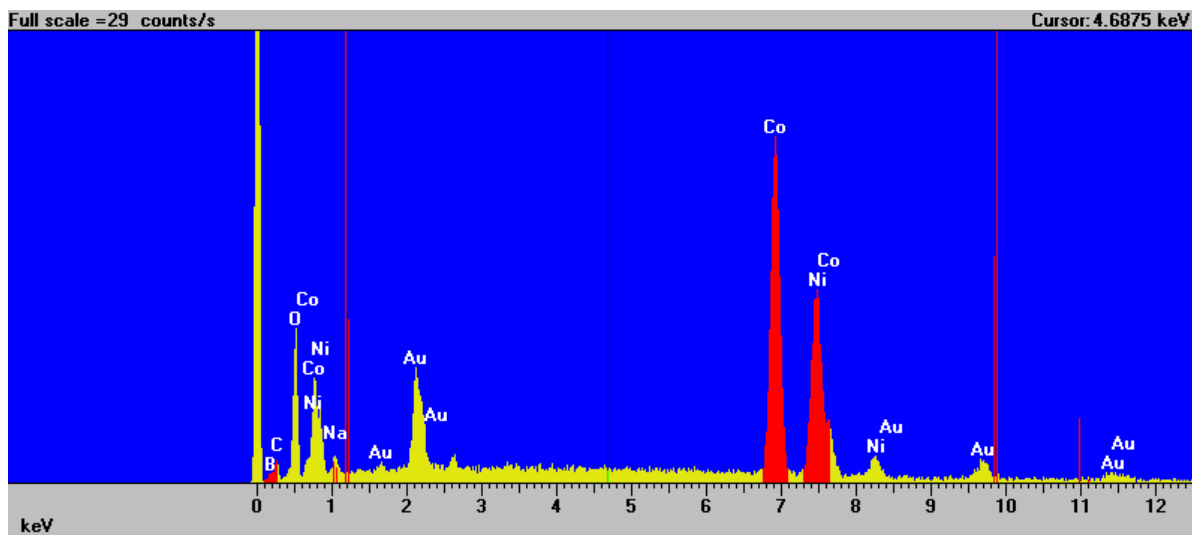


Fig. 1. SEM images of the investigated materials: a) CoB; b) CoNiB; c) NiB. Magnification: $\times 1000$ (top) and $\times 25000$ (down).



SEM images of the developed materials taken at different magnifications are presented in Fig. 1. The carbon felt used consists of randomly dispersed fibres with a diameter between 8 and 10 μm [18, 19], which provides a large surface area. The SEM observations show that rugged coatings are formed from all applied precursors, which cover not only the surface, but also the fibres in a depth of the carbon felt. The thickness of the coated fibres increases from ca. 15 μm for the deposits produced from Ni precursor to over 50 μm for those prepared from Co-containing solution, suggesting a preferential reduction of Co(II) on the carbon surface. The developed CoNi-coatings enlarge the fibres' diameter to ca. 30 μm . The higher magnification reveals that the Co-containing deposits possess a flakes-like shape, while the Ni-based ones have a more dense cauliflower-like structure. The CoNi-coating structure resembles that of Co-deposits, however, the inclusion of nickel results in a decrease of the flakes size.

The obtained EDS-spectra of the investigated materials confirm the presence of cobalt and nickel, and also indicate an existence of boron in the deposits (Fig. 2). These findings suggest that the produced coatings consist of CoB and NiB (nano)particles, as previously described [12,13,20]. Assuming this, the coatings obtained in this study will be further denoted as CoB, NiB and CoNiB. Besides the close molar percentages of Co and Ni in the mixed precursor solution, the atomic ratio of both metals in the produced CoNiB-deposits was determined as 61.7:38.3. The enriched Co content supports the supposition for preferential deposition of Co(II) on the carbon felt surface.

Electrocatalytic properties for HER in neutral electrolyte

The electrochemical behavior of the produced coated carbon felt samples in neutral PBS was investigated by means of LV. Linear voltammograms, presenting the performance of the studied electrodes in the cathodic region of potentials, are plotted on Fig. 3. The electrocatalytic activity in respect to HER was evaluated by the onset potential (V_e) needed to initiate hydrogen production as a measure of the relative overpotential [21] and the current density obtained at -1.0 V (vs. Ag/AgCl). The values of both quantities, derived from LVs, are summarized in Table 1.

Table 1. Values of V_e and current density at -1.0 V (vs. Ag/AgCl), derived from LVs.

Material	V_e , V (vs. Ag/AgCl)	Current density, mA cm^{-2}
NiB/C-felt	-0.467	1.53
CoNiB/C-felt	-0.551	1.40
CoB/C-felt	-0.695	1.34
C-felt	-0.762	0.14

The obtained results indicate that CoB possesses the highest overpotential for HER among the explored modified electrodes. The increase of the Ni content in the deposits shifts the V_e values in positive direction, thus, the hydrogen production on NiB electrodes starts at the lowest onset potential -0.467 V (vs. Ag/AgCl). The augmentation of nickel also results in enhancing the hydrogen current production rate, evaluated by the current density at -1.0 V (vs. Ag/AgCl). All dip-coated electrodes exhibit lower overpotentials and HER

rates with an order of magnitude higher than the bare carbon felt.

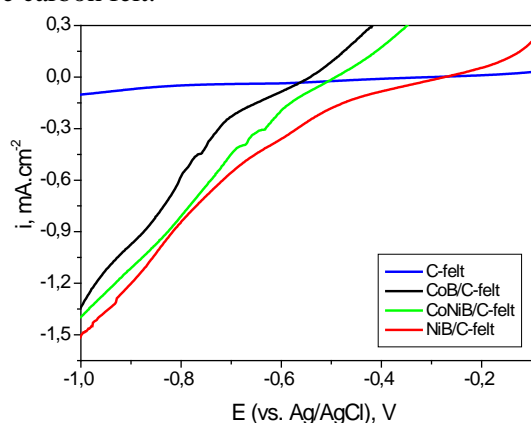


Fig. 3. Linear voltammograms obtained with investigated materials in PBS, scan rate 2 mV/s.

The catalytic properties of the studied materials towards HER were more precisely evaluated by chronoamperometric measurements [22], performed in the potential range from -0.6 to -1.2 V (vs. Ag/AgCl). The chronoamperograms recorded at the highest cathodic potential applied are presented in Fig. 4. The electric charge values, obtained by integration of the areas under the current-time plots, were used for estimation of the hydrogen production rates at different potentials, shown in Fig. 5a. In general, the obtained results confirm the findings from the LV-studies that the electrocatalytic activity of the dip-coated electrodes surpasses that of the non-modified carbon felt. The highest hydrogen production rates at all applied potentials were achieved with the NiB/carbon felt electrodes, exceeding over twice those obtained

with the CoB- and CoNiB-catalysts. In order to evaluate the intrinsic electrocatalytic activity of the explored materials, the hydrogen production rates were normalized to catalyst loadings. The results, presented in Fig. 5b, show that the co-deposition of Co and Ni enhances the intrinsic activity in comparison to that of CoB, however, the highest values were achieved with NiB catalysts. Although these values are lower than those previously reported for Pd-Au/carbon felt electrodes [22], the absence of precious metals and the easy production by the dip-coating method supposes the NiB/carbon felt as a promising cost-effective cathode material for hydrogen production from neutral electrolytes, i.e. in microbial electrolysis cells.

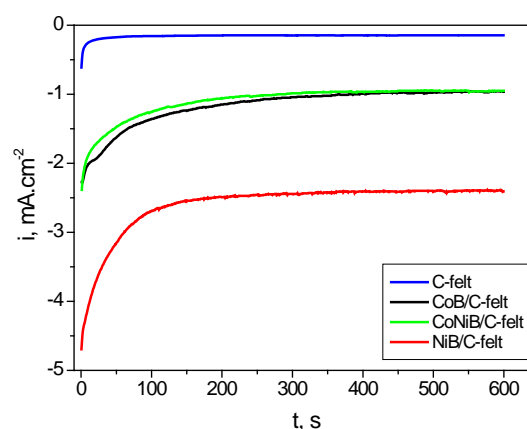
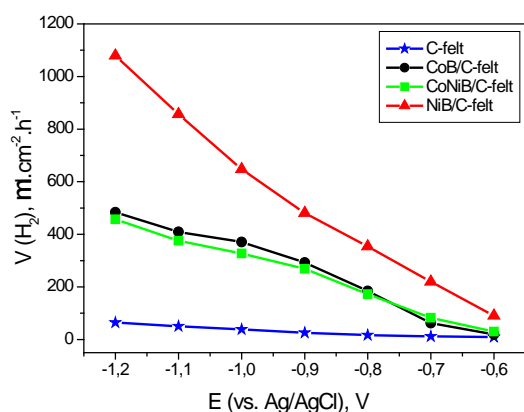
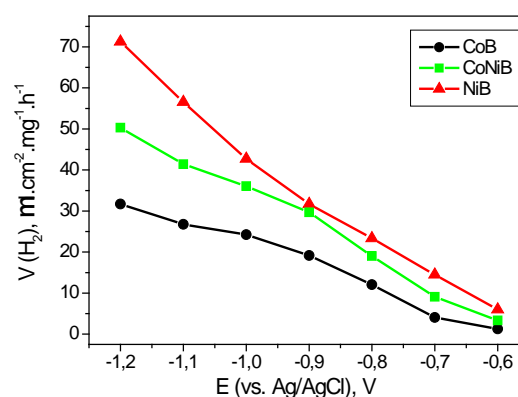


Fig. 4. Chronoamperograms obtained with different materials at a potential of -1.2 V (vs. Ag/AgCl) in PBS.



a)



b)

Fig. 5. a) Hydrogen evolution rates at different applied potentials, estimated from chronoamperometric measurements; b) Intrinsic electrocatalytic activity of the investigated dip-coated catalysts towards HER, expressed as a volume of generated hydrogen per hour normalized to the weight of the deposits and geometric area of the support.

CONCLUSION

Carbon supported CoB, CoNiB and NiB catalysts can be produced by borohydride reduction applying a dip-coating procedure. The catalyst loading increases with augmentation of Co in the precursor solution. The intrinsic electrocatalytic activity of the synthesized catalysts towards HER in neutral electrolyte increases in the order CoB < CoNiB < NiB. The achieved hydrogen production rates suggest the NiB/carbon felt as a promising cost-effective cathode material for hydrogen production from neutral electrolytes.

Acknowledgements: *This study was funded by the program "Hydrogen Economy Cooperation Network for Research - Public Awareness - Business Opportunities across Greek-Bulgarian borders – HYDECON". The Project is co-funded by the European Regional Development Fund and by national funds of the countries participating in the ETCP "Greece-Bulgaria 2007-2013" through contract B1.33.01.*

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СИНТЕЗ И ОХАРАКТЕРИЗИРАНЕ НА CoB-, NiB- И CoNiB- КАТАЛИЗАТОРИ ОТЛОЖЕНИ ВЪРХУ ВЪГЛЕРОДНО КЕЧЕ

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Получена на 21 юни 2014 г.; коригирана на 10 септември 2014 г.

(Резюме)

В настоящата разработка, CoB, NiB и CoNiB катализатори са отложени върху въглеродно кечче чрез борхидридна редукция. Морфологията и елементният състав на синтезираните покрития са охарактеризирани чрез сканираща електронна микроскопия и енергийно-дисперсионна рентгенова спектроскопия. Електрохимичната активност на произведените материали по отношение катодното отделяне на водород в неутрален електролит е изследвана чрез линейна волтаперометрия и хроноамперометрия. Най-голяма специфична активност е установена за NiB катализатори.