

Quaternary electrodeposits on nickel-foam for application in a hybrid direct borohydride fuel cell - hydrogen-on-demand system

M. Y. Mitov¹, G. Y. Hristov¹, R. S. Rashkov², Y. V. Hubenova³

¹Department of Chemistry, South-West University "Neofit Rilski", Blagoevgrad, Bulgaria,

²Institute of Physical Chemistry "Acad. Rostislav Kaishev", Bulgarian Academy of Sciences, Sofia, Bulgaria

³Department of Biochemistry and Microbiology, Plovdiv University "Paisii Hilendarski", Plovdiv, Bulgaria

Received June 26, 2014, Revised September 10, 2014

In this study, CoNiMoW electrodeposits produced under different galvanostatic conditions were investigated as anode materials in a Direct Borohydride Fuel Cell. As a tendency, higher generated power was obtained with electrodeposited anodes produced at lower currents. Maximum power of 250 mW was achieved by using CoNiMoW-anode electrodeposited at the lowest current density (15 mA cm⁻²) and two air gas-diffusion cathodes. This value exceeds 2.5 times that obtained with the same anode and one gas-diffusion electrode, which indicates that the oxygen reduction on the cathode is the rate-limiting step of the overall process. In addition, the catalytic properties of the CoNiMoW electrodeposits towards the "non-productive" borohydride hydrolysis reaction were also examined. The highest hydrogen generation rate of 15.0 ml min⁻¹ was achieved with CoNiMoW electrodeposits produced at the lowest current. Activation energy of the order of 36.5±2.7 kJ mol⁻¹ was obtained for all materials studied. Summarizing the results from the fuel cell and catalytic tests, we propose the CoNiMoW electrodeposits as potential candidates for application in a hybrid Direct Borohydride Fuel Cell – Hydrogen-on-demand system.

Keywords: Electrodeposition, CoNiMoW anodes, Direct Borohydride Fuel Cell, catalyst, borohydride hydrolysis.

INTRODUCTION

Fuel cells have attracted increasing attention as alternative power sources as they generate electricity with higher efficiency and lower pollution than the conventional combustion technologies and batteries. Currently, the proton exchange membrane fuel cells (PEMFCs), utilizing hydrogen as a fuel, represent the most advanced fuel cell technology and are promising for transportation, as well as stationary applications [1]. However, the storage and transportation of hydrogen is still a problem as both classical methods with an industrial impact - high pressurized gas and cryogenic liquid, are highly energy-consuming and keep risk for a wide application [2].

Since 1990's, hydrogen-rich compounds such as alkaline hydrides, borohydrides and alanates are intensively studied as safe hydrogen storage materials [3-5]. Sodium borohydride (NaBH₄) is one of the most attractive candidates for this purpose. In addition to its high hydrogen content (10.6 wt.%), exceeding that of most hydrogen storage alloys, sodium borohydride is chemically stable, non-combustible, easily stored and distributed.

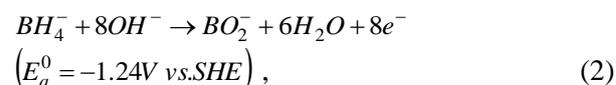
In the presence of a proper catalyst, sodium

borohydride reacts with water to produce hydrogen gas and sodium metaborate according to the following reaction:



The generated H₂ is highly pure and humidified, which makes it suitable for direct use in PEMFCs. In addition, the resulting borate may be recycled back to borohydride [6, 7]. Based on catalyzed borohydride hydrolysis, various hydrogen-on-demand (HOD) systems were recently developed as a promising way to overcome disadvantages with existing hydrogen storage and transportation methods [8, 9].

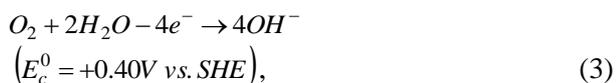
Except as a hydrogen source, alkaline borohydrides can be directly used as a fuel in power sources referred to as direct borohydride fuel cells (DBFCs). In aqueous alkaline medium borohydride ions can undergo electrochemical oxidation on a variety of electrode materials liberating a maximum of eight electrons. The reaction of direct borohydride electrooxidation is as follows:



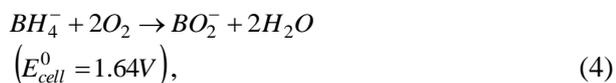
Besides the great number of participating electrons, the direct anodic oxidation of borohydrides provides more negative potential compared to the case when hydrogen is used. In

* To whom all correspondence should be sent:
E-mail: mitovmario@mail.bg

DBFCs, most commonly the anode oxidation of borohydride is coupled to the reduction of oxygen on an air cathode:



The net cell reaction in this system is represented as:

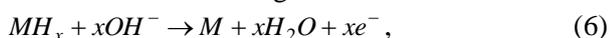


The high electromotive force, exceeding those of hydrogen and direct methanol fuel cells, makes DBFCs attractive energy suppliers, especially for portable applications [10]. The major research on DBFC development is focused on the efficiency of borohydride fuel utilization, which strongly depends on the anode material. Usually, the electrochemical oxidation reaction (2) is accompanied by a parallel hydrolysis reaction (1) due to the high catalytic activity of the electrocatalysts used towards both reactions. Thus, the actual anodic reaction should be described as:



where x is the number of electrons that are generated during electrooxidation of 1 mol BH_4^- . It has been demonstrated that among the commonly studied metallic catalysts – Pt, Pd, Ni, Au and Ag, gold is the most effective and nickel is the least effective electrocatalyst towards borohydride oxidation [10-12]. High coulombic numbers near the theoretical $8e^-$ have been obtained by using Au-electrodes [13-15] and associated with its inactivity towards the hydrolysis reaction. The slow kinetics of gold towards borohydride electrooxidation, however, restricts its practical application. Participation of 4 and 6 electrons has been reported for BH_4^- oxidation on Pt- and Pd-electrodes, respectively [15, 16].

Various AB_5 and AB_2 -type hydrogen storage alloys have been also explored as anode materials in DBFCs [17-20]. On the metal hydride surface, electrooxidation of borohydrides takes place through a sequence of steps with concomitant atomic hydrogen generation [21]. The released hydrogen (H) is stored in the hydrogen storage alloy anode as a metal hydride (MH_x), which is involved in the discharge reaction as follows:



It has been established that the coulombic efficiency of borohydride electrooxidation depends not only on the anode material properties but also on a variety of other experimental factors such as

the method of the electrode preparation, the catalyst support, the use of membrane, etc. [10, 22].

Novel multicomponent Co-based electrodeposits containing large amounts of hydrogen (up to 9 at.%), have been recently synthesized by us and investigated as catalysts for different applications [23-25].

In this study, quaternary CoNiMoW alloys, electrodeposited on nickel foam under different galvanostatic conditions, were investigated as anode materials in DBFC. In parallel, the catalytic properties of the obtained CoNiMoW electrodeposits towards the “non-productive” borohydride hydrolysis reaction were also examined.

EXPERIMENTAL

Quaternary CoNiMoW coatings were electrodeposited from alkaline electrolyte (pH 10 adjusted by addition of NH_4OH), containing sodium citrate (72 g L^{-1}), $Na_2WO_4 \cdot 2H_2O$ (24 g L^{-1}), Na_2MoO_4 (6 g L^{-1}), $Ni(SO_3NH_2)_2$ (16 g L^{-1}), $Co(SO_3NH_2)_2$ (16 g L^{-1}), on nickel foam (RECEMAT, RCM-Ni-2733.03, pore diameter $d=0.6 \text{ mm}$, $SSA=2500 \text{ m}^2/\text{m}^3$) under different galvanostatic regimes for 30 min and electrolyte stirring at 250 min^{-1} . Round shaped samples of Ni-foam with diameter 3 cm were used as electrodes. The applied current density was estimated and presented in respect to the real surface (64 cm^2) of the electrodes.

Scanning electron microscopy (SEM) using Leo 1455VP and Leo Supra 55VP microscopes with energy dispersive X-ray (EDX, Oxford Inca 200 instrument, Software INCA-Version 4) was applied for examination of the surface morphology and elemental analysis of the electrodeposited coatings.

XRD spectra for structure identification of layers was recorded in the angle interval $10-100^\circ$ (2θ) by using Philips PW 1050 diffractometer, equipped with $Cu K\alpha$ tube and scintillation detector.

The produced CoNiMoW/Ni-foam samples were applied as anodes in DBFC. Air gas-diffusion electrodes (GDE) developed for metal-air systems [26] were used as cathodes. Stabilized 5% (w/v) $NaBH_4/6M KOH$ solution served as borohydride fuel and liquid electrolyte. The investigations were performed in single-chamber DBFCs (10 ml working volume) with one or two air gas-diffusion cathodes and one anode. Polarization measurements at variable load resistances in a borohydride-containing electrolyte were carried out. The power output was calculated from the recorded values of voltage, U , and current,

I , by the equation $P=U \times I$ and the polarization and corresponding power curves were plotted. Long-term discharge measurements in galvanostatic mode were performed and the discharge capacity was estimated.

In parallel, the catalytic properties of the CoNiMoW electrodeposits towards borohydride hydrolysis were also explored. The examined sample was placed into a reaction vessel, which was then hermetically closed. 10 ml of

5% (w/v) $\text{NaBH}_4/6\text{M KOH}$ solution was injected into the vessel and the volume of the generated hydrogen was measured over time by means of the water-displacement method [23, 24]. The reaction temperature was kept constant by thermostat in the range from 288 to 315 K. The rate constants at different temperatures were estimated from the obtained kinetic curves and the activation energy was calculated from the constructed Arrhenius plots.

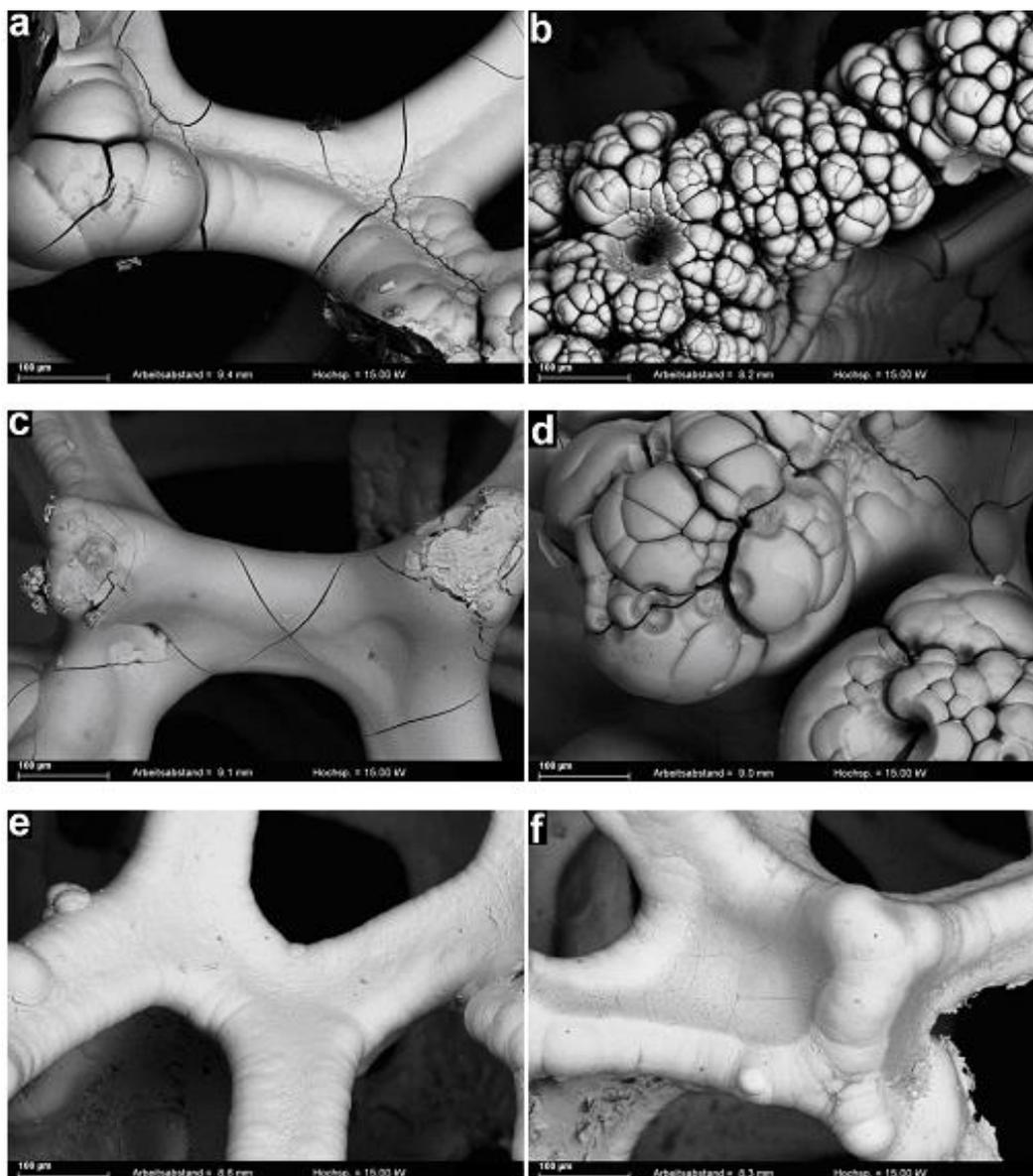


Fig. 1. Morphology of CoNiMoW-coatings on nickel foam at different electrodeposition regimes: (a,b) 75 mA cm^{-2} – center (a), edge (b) of the sample; (c,d) 30 mA cm^{-2} – center (c), edge (d) of the sample; (e,f) 15 mA cm^{-2} – center (e), edge (f) of the sample.

RESULTS AND DISCUSSION

Characterization of CoNiMoW electrodeposits

The SEM images presented in Fig. 1 show that the variation of the current regimes during electrodeposition affects the morphology of the obtained CoNiMoW coatings. The morphology significantly changes from the center to the edge of the samples, especially for those produced at the highest current density applied. The coating turns from nearly smooth with rounded parts on the Ni-support swellings (Fig. 1a) into dendrite-type on the edges (Fig. 1b). More uniform coatings without cracks were obtained at the lowest current density (Fig. 1e).

The results from the elemental analysis, presented in Table 1, show a varying distribution of the elements depending on the applied current, as well as on the different zones of the sample surface. The current increase leads to enrichment of Co, Mo and W and decrease of Ni content in the middle parts of the samples.

Table 1. Elemental content of CoNiMoW-coatings obtained at different current regimes.

Sample zone	$i_{\text{deposit.}}$ mA cm ⁻²	Co, wt. %	Ni, wt. %	Mo, wt. %	W, wt. %	O, wt. %
Center	75	67.4	9.0	7.5	9.9	6.2
	30	61.8	4.9	8.8	7.8	16.7
	15	48.4	39.9	3.0	0.6	8.1
Edge	75	56.8	21.1	5.5	9.8	6.8
	30	44.2	9.7	9.6	10.2	26.3
	15	50.9	8.9	11.5	6.4	22.3

Because of the edge effects and complex morphology of the support, the composition of the coatings at the edges significantly differs from that in the central parts of the samples at the same current densities applied.

The XRD study of the electrodeposited CoNiMoW coatings indicates that all of them, except those obtained at 15 mA cm⁻², possess amorphous structure - Fig. 2. We suppose that the observed exception is due to deposition of thin layers at the lowest current and appearance of characteristic peaks of Ni from the support.

Fuel cell studies

Polarization and power curves, obtained with DBFC by using the studied CoNiMoW/Ni-foam samples as anodes and one GDE as a cathode are plotted in Fig. 3. Despite the observed variation of

anode morphology, composition and structure, the obtained fuel cell outputs do not differ significantly.

The lowest maximum power (81 mW) was obtained with the electrodes deposited at 75 mA cm⁻² and the highest power (94 mW) was achieved with those obtained at 15 mA cm⁻², which shows a slight tendency to increase of the fuel cell power outputs by using CoNiMoW/Ni-foam anodes produced at lower current density of electrodeposition.

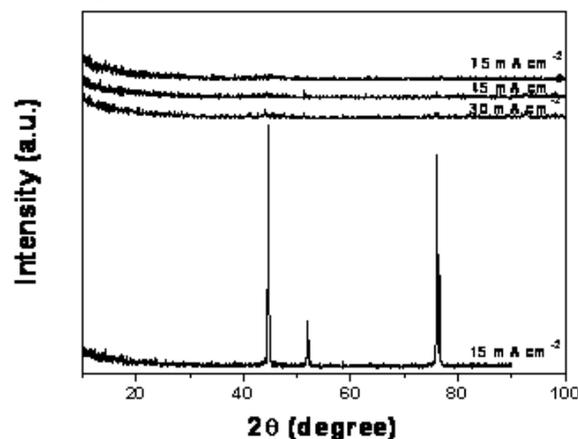


Fig. 2. XRD of CoNiMoW-coatings electrodeposited on nickel foam at different current regimes.

In many cases, when GDEs are used as air cathodes in electrochemical power sources, the kinetics of the overall process is limited by transportation hindrances connected with the delivery of oxygen to the cathode [27]. To facilitate the oxygen supply and reduce the limitation effect of the cathodic reaction, usually the cathode area is enlarged.

The polarization experiments carried out with a fuel cell using two air cathodes confirmed this suggestion. The obtained polarization curves are characterized by quite smaller slope, resp. internal cell resistance, in comparison with that in the case of DBFC with one air cathode and even at very low load resistances (<1 Ω) no drop of the voltage occurs, while at the same time the power curve does not pass through a maximum. As a result, much higher power of 250 mW compared to that obtained with DBFC using one GDE was achieved - Fig. 4.

The measurements at constant load show that the fuel cell could be used as a power source for over five hours in batch mode - Fig. 5. The estimated discharge capacity of 300 mAh g⁻¹ NaBH₄, however, is rather below the theoretical one. Based on the observed noticeable hydrogen evolution when the anode was put in contact with the borohydride electrolyte, we supposed that the

obtained low discharge capacity is mainly due to the fuel depletion, connected with “non-productive” catalytic hydrolysis of sodium borohydride.

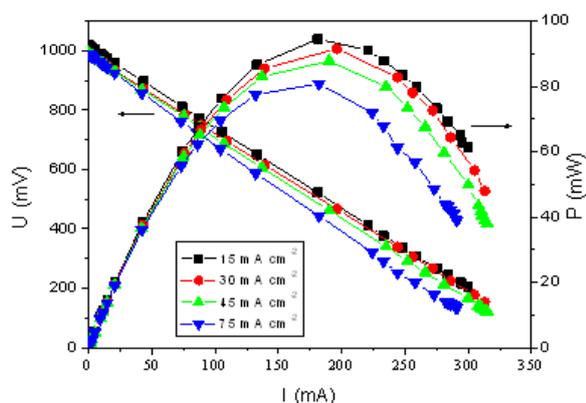


Fig. 3. Polarization and power curves obtained with DBFC by using CoNiMoW/Ni-foam anode and GDE cathode.

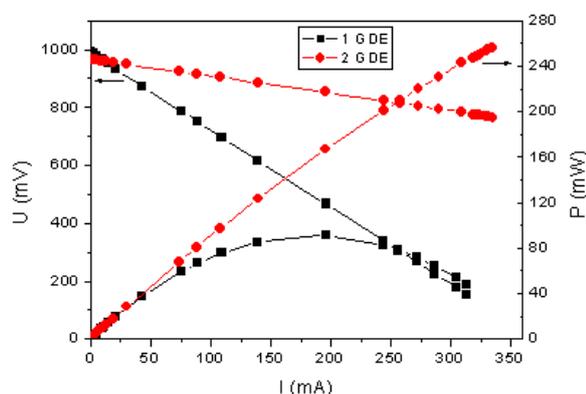


Fig. 4. Comparison of polarization and power curves obtained with DBFC by using CoNiMoW/Ni-foam anode and one or two air-cathodes.

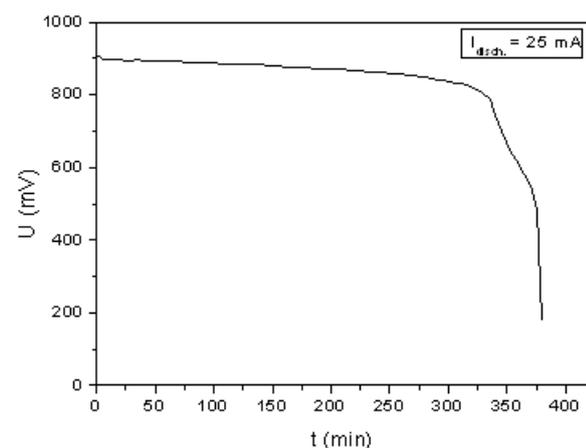


Fig. 5. Discharge curve obtained with the studied DBFC.

Catalytic studies

To evaluate the catalytic activity of the investigated CoNiMoW electrodeposits towards borohydride hydrolysis reaction, kinetic

experiments for determination of the hydrogen generation rate and activation energy of the process were carried out at different temperatures. The catalytic studies were performed in the temperature range from 288 to 315 K, where the alkaline sodium borohydride solution is relatively stable in the absence of catalyst. Typically, as seen from Fig. 6, the reaction starts instantly after the catalyst comes into contact with the solution and a constant-rate hydrogen evolution is observed during the whole experimental window.

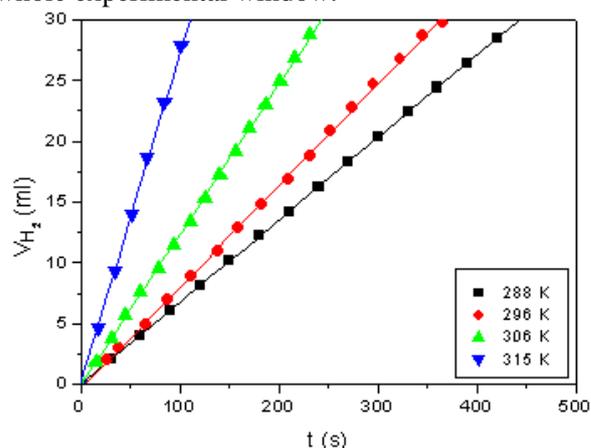


Fig. 6. Kinetic curves of catalyzed borohydride hydrolysis using CoNiMoW/Ni-foam (15 mA cm^{-2}) as catalyst and 5% (w/v) $\text{NaBH}_4/6 \text{ M KOH}$ solution.

From the slopes of the kinetic curves obtained at different temperatures the hydrogen evolution rate values were calculated and presented as Arrhenius plots ($\ln k$ vs. $1/T$) – Fig. 7. The values of the activation energy, E_a , estimated from the slope of the Arrhenius plots, are shown in Table 2.

Table 2. Activation energy, E_a , of catalyzed borohydride hydrolysis depending on the current density, $i_{\text{deposit.}}$, applied during CoNiMoW catalyst preparation.

$i_{\text{deposit.}}$, mA cm^{-2}	E_a , kJ mol^{-1}
15	37.8
30	33.8
45	38.9
75	35.6

The analysis of the results obtained by the catalytic studies show that the rate of hydrogen evolution, as a product of borohydride hydrolysis, increases when CoNiMoW obtained at lower currents are applied as catalysts. The highest hydrogen generation rate of 15.0 ml min^{-1} (at 315 K) was achieved with CoNiMoW electrodeposited at 15 mA cm^{-2} . The close values of the activation energy indicate that the process takes

place via identical mechanism on all examined catalysts.

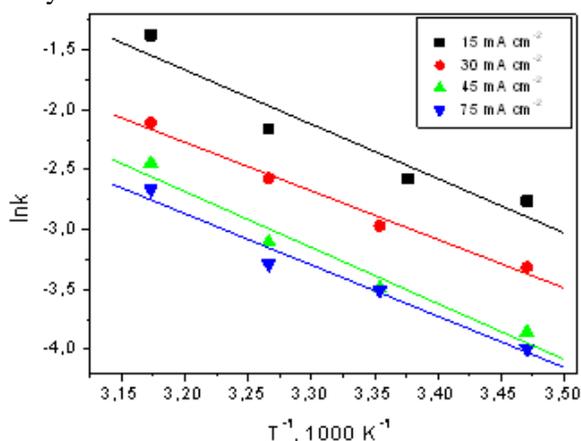


Fig. 7. Arrhenius plots of borohydride hydrolysis catalyzed by CoNiMoW electrodeposited on Ni-foam at different galvanostatic regimes.

CONCLUSION

The quaternary CoNiMoW alloys electrodeposited on nickel foam exhibit a promising performance as anodes in DBFC. A power of 250 mW was achieved by using two air cathodes. This value exceeds 2.5 times the maximum power obtained with one air cathode, which supposes that the overall electrochemical reaction is limited by hindrances connected with oxygen delivery to the cathode. The anode performance is improved by decrease of the current applied for electrocatalyst deposition. The same tendency was also observed when the studied materials have been investigated as catalysts for borohydride hydrolysis. Based on the results from both electrochemical and catalytic studies it can be concluded that the CoNiMoW electrodeposits are suitable for application in hybrid systems combining DBFC and Hydrogen-on-demand generator, which may further supply a low-power hydrogen fuel cell.

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.

REFERENCES

1. S.J.C. Cleghorn, X. Ren, T.E. Springer, M.S. Wilson, C. Zawodzinski, T.A. Zawodzinski, S. Gottesfeld, *Int. J. Hydrogen Energy*, **22**, 1137 (1997).

2. A. Zuttel, *Naturwissenschaften*, **91**, 157 (2004).
3. B. Sundqvist, *Solid-State Phenom.*, **150**, 175 (2009).
4. F. Agresti, A. Khandelwal, A. Maddalena, G. Principi, S. Russo, *Int. J. Nucl. Hydrogen Prod. Appl.*, **2**, 122 (2009).
5. E.Y. Marrero-Alfonso, A.M. Beaird, T.A. Davis, M.A. Matthews, *Ind. Eng. Chem. Res.*, **48**, 3703 (2009).
6. Y. Kojima, T. Haga, *Int. J. Hydrogen Energy*, **28**, 989 (2003).
7. T. Kemmitta, G.J. Gainsford, *Int. J. Hydrogen Energy*, **34**, 5726 (2009).
8. S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, M.T. Kelly, P.J. Petillo, M. Binder, *J. Power Sources*, **85**, 186 (2000).
9. S.U. Jeong, R.K. Kim, E.A. Cho, H.J. Kim, S.W. Nam, I.H. Oh, S.A. Hong, S.H. Kim, *J. Power Sources*, **144**, 129 (2005).
10. J. Ma, N. Choudhury, Y. Sahai, *Renew. Sust. Energ. Rev.*, **14**, 183 (2010).
11. H. Dong, R. Feng, X. Ai, Y. Cao, H. Yang, C. Cha, *J. Phys. Chem. B*, **109**, 10896 (2005).
12. H. Celikkan, M. Sahin, M.L. Aksu, T.N. Veziroglu, *Int. J. Hydrogen Energy*, **32**, 588 (2007).
13. E. Gyenge, *Electrochim. Acta*, **49**, 965 (2004).
14. H. Cheng, K. Scott, *Electrochim. Acta*, **51**, 3429 (2006).
15. M. Chatenet, F. Micouda, I. Roche, E. Chainet, *Electrochim. Acta*, **51**, 5459 (2006).
16. M. Simoes, S. Baranton, C. Coutanceau, *J. Phys. Chem. C*, **113**, 13369 (2009).
17. L. Wang, C. Ma, Y. Sun, S. Suda, *J. Alloys Compd.*, **391**, 318 (2005).
18. Y.P. Petrov, M.Y. Mitov, A.K. Popov, *Bulg. Chem. Commun.*, **38**, 217 (2006).
19. Z.P. Li, B.H. Liu, K. Arai, S. Suda, *J. Electrochem. Soc.*, **150**, A868 (2003).
20. S.M. Lee, J.H. Kim, H.H. Lee, P.S. Lee, J.Y. Lee, *J. Electrochem. Soc.*, **149**, A603 (2002).
21. J.Y. Lee, H.H. Lee, J.H. Lee, D.M. Kim, US Patent 5599640 (1997).
22. V. Kiran, S. Srinivasan, *J. Indian Inst. Sci.*, **89**, 447 (2009).
23. M. Mitov, R. Rashkov, N. Atanassov, A. Zielonka, *J. Mater. Sci.*, **42**, 3367 (2007).
24. M. Mitov, G. Hristov, E. Hristova, R. Rashkov, M. Arnaudova, A. Zielonka, *Environm. Chem. Lett.*, **7**, 167 (2009).
25. R. Rashkov, G. Hodjaoglu, N. Atanassov, A. Zielonka, in: Nanostructured Materials in Electroplating, D. Stoychev, E. Valova, I. Krastev, N. Atanassov (eds.), St. Kliment Ohridski University Press, Sofia, 2006, p. 190.
26. A. Kaisheva, I. Iliev, S. Gamburzev, *J. Power Sources*, **13**, 181 (1984).
27. E. Budevski, *J. Optoelectron. Adv. Mater.*, **5**, 1319 (2003).

КВАТЕРНЕРНИ ЕЛЕКТРОДЕПОЗИТИ ВЪРХУ ПЕНООБРАЗЕН НИКЕЛ ЗА ПРИЛОЖЕНИЕ В ХИБРИДНА СИСТЕМА ГОРИВЕН ЕЛЕМЕНТ С ДИРЕКТНО ЕЛЕКТРООКИСЛЕНИЕ НА БОРХИДРИД – ГЕНЕРАТОР НА ВОДОРОД

М. Й. Митов¹, Г. Й. Христов¹, Р. С. Рашков², Й. В. Хубенова³

¹Катедра Химия, Югозападен университет „Неофит Рилски“, Благоевград, България

²Институт по Физикохимия „Акад. Ростислав Каишев“, Българска Академия на Науките, България

³Катедра Биохимия и Микробиология, Пловдивски Университет, Пловдив, България

Постъпила на 26 юни 2014 г.; коригирана на 10 септември 2014 г.

(Резюме)

В настоящата разработка, CoNiMoW електроотложения, получени при различни галваностатични условия, са изследвани като анодни материали в Горивен елемент с директно електроокисление на борхидрид. Като тенденция, по-голяма мощност е получена с аноди, електроотложени при по-ниски плътности на тока. Максимална мощност от 250 mW е достигната с използването на CoNiMoW-анод, електроотложен при най-ниската плътност на тока (15 mA cm^{-2}) и два въздушни газо-дифузионни катода. Тази стойност надвишава 2.5 пъти достигнатата мощност със същия анод и един газо-дифузионен катод, което е указание, че редукцията на кислорода върху катода е скоростоопределяща за цялостния процес. Паралелно са изследвани каталитичните свойства на CoNiMoW електродепозити по отношение на „непроизводителната“ борхидридна хидролиза. Най-голяма скорост на генериране на водород (15.0 ml min^{-1}) е постигната с CoNiMoW-електроотложения, получени при най-малката приложена плътност на тока. Близки стойности на активиращата енергия ($36.5 \pm 2.7 \text{ kJ mol}^{-1}$) са получени с всички изследвани материали. Обобщавайки резултатите от проведените изследвания, електроотложените CoNiMoW материали се предлагат като потенциални кандидати за приложение в хибридна система Горивен елемент с директно електроокисление на борхидрид – Генератор на водород.