Comparison of sodium borohydride hydrolysis kinetics on Co-based nanocomposite catalysts

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***Abstract**: In this study, we compared the results, obtained with several Co-based nanocomposites (CoMnB, CoNiMnB and CoNiMoW) produced by electrodeposition on Ni-foam, as catalysts for the sodium borohydride hydrolysis reaction. Based on the comparative analyses, we propose CoNiMnB electrodeposits as most proper catalysts for development of Hydrogen-on-Demand (HOD) system, while CoNiMoW ones as potential anodes for Direct Borohydride Fuel Cells (DBFCs).*

***Keywords:** Hydrogen-on-Demand (HOD), Nanocomposites, Hydrolysis, Catalyst, Kinetic.*

1. INTRODUCTION

The prospect of peaking world-wide oil production has motivated the development of alternative energy sources and energy carriers. Hydrogen has been claimed as a likely replacement energy carrier and renewable energy source [1]. A hydrogen energy economy would be less dependent on limited fossil fuel supplies. Nevertheless, many critical technical challenges remain to be addressed before hydrogen-based energy can become widely available and economical [2]. The main problems of using hydrogen as a fuel are connected with its storage and transportation [3]. Two promising hydrogen storage material categories are metal hydrides and chemical hydrides, both of which rely on catalysis to improve kinetics. Chemical hydride systems always involve reactions between the storage medium and a solvent, in most cases water. The reaction can be catalyzed by solid catalysts. At room temperature, the reaction between sodium borohydride and water is very slow [1]. For sodium borohydride systems, the chemical hydride is dissolved in alkaline solution. A pH level of 14 is the most likely for practical applications involving stabilized solutions [4].

Ruthenium and rhodium salts showed the best catalytic activity. Chloride salts of manganese, iron, cobalt, nickel and copper were also exhibited good catalytic properties for hydrolysis of sodium borohydride to

produce hydrogen gas at room temperature [5,6]. Although these homogeneous catalysts are active, the metal ions dissolved in aqueous solution cause serious contamination concerns for discharged fuel recycling or disposal. In this regard, heterogeneous catalysts offer distinct advantages of ease separation of catalyst from discharge fuel and for controllable generation and delivery of hydrogen on demand [4]. Cobalt and nickel metals, and also metal oxide supported Pt, Pd, Rh, Ru, Ir, Os, Au, Ag catalysts were reported to be active for catalytic hydrolysis of sodium borohydride in an aqueous alkaline solution at near room temperature conditions [7].

In the present study, three different types of newly synthesized Co-based nanocomposites: CoMnB, CoNiMnB and CoNiMoW, produced by electrodeposition on nickel foam, were investigated as potential catalysts for borohydride hydrolysis reaction. The hydrogen generation rates and activation energy values, obtained with the examined nanocomposite materials, were compared and discussed.

2. EXPERIMENTAL

Composite CoMnB coatings were obtained by potentiostatic electrodeposition from electrolyte, containing 5 g/l Co^{2+}, 5 g/l Mn^{2+}, 5 g/l Ni^{2+} and 35 g/l boric acid. The CoNiMnB nanocomposites were obtained from similar electrolyte, but with different amounts of Co^{2+} and Ni^{2+}. The electrolysis continued 30 min at 40 ^{o}C. Co-electrode was used as an anode and Ni-foam (RECEMAT, RCM-Ni-4753.016 pore diameter d=0.4 mm, SSA=5800m^2/m^3 and RCM-Ni-2733.03, pore diameter d=0.6 mm, SSA=2500m^2/m^3) as a cathode.

Composite CoNiMoW coatings were obtained by galvanostatic electrodeposition from alkaline electrolyte, containing 72g/l sodium citrate, 24g/l $Na_2WO_4.2H_2O$, 6g/l Na_2MoO_4, 16g/l $Ni(SO_3NH_2)_2$, 16g/l $Co(SO_3NH_2)_2$. pH 10 was fixed by addition of NH_4OH. The composites were electrodeposited on nickel foam under different galvanostatic regimes (1A, 2A, 3A, 4.8A) for 30 min and electrolyte stirring at 250 min^{-1}.

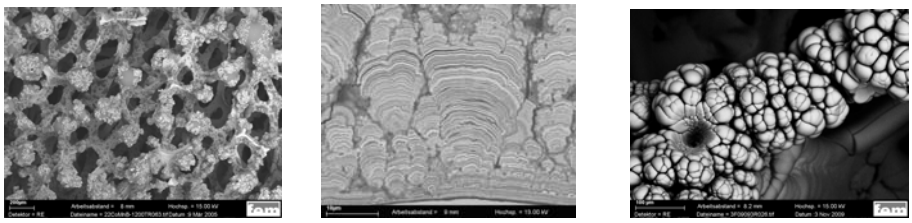
Varying the electrolysis conditions nanocomposites with different content, structure and morphology have been produced. Scanning electron microscopy (SEM) using Leo 1455VP and Leo Supra 55VP microscopes with Energy dispersion X-ray (EDX, Oxford Inca 200 instrument, Software INCA-Vers.4) was applied for 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° (2θ) by using Philips PW 1050 diffractometer, equipped with Cu Kα tube and scintillation detector.

The catalytic properties of the investigated nanocomposites towards the borohydride hydrolysis were also studied. The examined sample was placed into a reaction vessel, which was then hermetically closed. 10 ml of 5% (w/v) $NaBH_4$/6M KOH solution was injected in the vessel and the volume of the generated hydrogen was measured with time by means of water-displacement method [8]. The reaction temperature was kept constant by thermostat in the range from 15 ^oC to 45 ^oC. The rate constants at different temperatures were estimated from the slopes of the obtained kinetic curves and the activation energy was calculated from constructed Arrhenius plots.

3. RESULTS AND DISSCUSION

3.1. SEM investigation of the Co-based electrodeposits

SEM images of the investigated nanocomposites are shown on Fig. 1. All of the three types of the Co-based electrodeposits have a dendrite structure. The bright spots on the SEM image were mainly Co.



CoMnB CoNiMnB CoNiMoW

Fig. 1: SEM images of the CoMnB, CoNiMnB, CoNiMoW nanocomposites.

Detailed SEM investigations proved that there was different elemental distribution on the Ni-foam surface. For example, significant amount of Co (70%) was found in the center than on the edge of the electrode (50%). Also the amount of Co enriched, but that of Ni decreased with increasing the current applied under galvanostatic deposition regimes.

3.2. Catalytic hydrolysis of sodium borohydride

A gaseous bubbling started immediately after immersion of investigated sample (CoMnB, CoNiMnB or CoNiMoW) into sodium borohydride solution, which proved that the examined materials catalyzes the sodium borohydride hydrolysis process [9]:

(1) $$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$$

The hydrolysis followed an apparent zero order kinetics with all studied materials. The estimated from kinetic curves rate constants and activation energy values, obtained with the examined nanocomposite materials, are presented in Table 1.

Two types of Ni-foam with different pore diameter were used as a pad for the CoMnB deposits. The hydrogen generation rate was about 4 times higher on the nanocomposites, electrodeposited on Ni-foam with bigger pore diameter. That can be explained with better mass transfer through the catalysts pores and easy diffusion of the reagents and the obtained products. That is why all of the other nanocomposites were electrodeposited on the Ni-foam pad with bigger pores.

Two types CoNiMnB electrodeposits were prepared under potentiostatic conditions (-1.5V and -1.8V) and the samples were also investigated as catalysts for the sodium borohydride hydrolysis. For the both types of CoNiMnB electrodeposits, the examined hydrogen generation rates and the calculated activation energy were the same in practice, which indicated that the potential regime did not exert any influence on the catalytic properties of these nanocomposites.

Four types CoNiMoW electrodeposits were prepared under galvanostatic conditions (1.0A, 2.0A, 3.0A and 4.8A). The bigger current in the galvanostatic regime applied, the less catalytic activity showed the examined CoNiMoW nanocomposite. The best catalyst for the sodium borohydride reaction was the CoNiMoW electrodeposit, produced under 1.0A galvanostatic regime.

All of the examined nanocomposites exhibited lower activation energy than Ru (56,0 kJ/mol), which is known as one of the best catalysts for sodium borohydride hydrolysis process [9]. Including Ni in the nanocomposite increased sufficiently the activity of the catalyst. Comparing the results from the Ni-foam as a catalyst with those obtained with CoMnB and CoNiMnB, we can purposed that the size of the composite is in a correlation with the activity – the smaller composite, the higher activity.

Table 1: The hydrogen generation rate using different Co-based catalysts, ml/s.

Temperature, °C / Sample	**15**	**25**	**30**	**40**	**E_a, kJ/mol**
CoMnB small pores	0,06	0,16	0,21	0,28	54,5

CoMnB big pores	0,37	0,68	0,80	1,34	54,9
CoNiMnB -1,5V	0,86	1,24	1,50	2,20	35,7
CoNiMnB -1,8V	0,90	1,30	1,47	2,12	36,9
CoNiMoW 1,0A	0,06	0,08	0,12	0,25	37,8
CoNiMoW 2,0A	0,04	0,05	0,07	0,12	33,8
CoNiMoW 3,0A	0,02	0,03	0,05	0,09	38,9
CoNiMoW 4,8A	0,02	0,02	0,04	0,07	35,6

Although the calculated activation energy for the sodium borohydride reaction catalyzed by CoNiMoW had the lowest value, the hydrogen was generated with the slowest rate, which indicated that there were other factors that limited the reaction, for example, diffusion. Additional experiments are needed to prove such hypotheses.

4. CONCLUSIONS

The catalytic properties of three different types newly synthesized Co-based nanocomposites towards sodium borohydride hydrolysis reaction were studied. The obtained order of descending catalytic activity is CoNiMnB>CoMnB>CoNiMoW. The best catalyst among the examined nanocomposites is CoNiMnB (1.8 V) with 1.3 ml/s generated hydrogen (at 25 ^{o}C). Besides the elemental composition, the catalytic activity of the investigated nanocomposites also depends on the applied deposition regime as well as pore size of Ni-foam used as a support. The galvanostatic regime used influences more significantly the catalytic properties of the examined materials, while those obtained under potentiostatic regime exhibit almost the same activity. The bigger pore sized Ni-foam improves the catalytic activity of investigated electrodeposits, probably due to facilitated mass transport of reagents and products through the catalysts. Based on the comparison of results, we consider that CoNiMnB nanocomposites can be used in newly designed Hydrogen-on-Demand generators, while CoNiMoW electrodeposits, exhibited the lowest catalytic activity towards sodium borohydride hydrolysis, can be potentially applied as anodes in Direct Borohydride Fuel Cells.

5. REFERENCES

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