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ELECTROSYNTHESIS OF Ni-Co/HYDROXYAPATITE AS A CATALYST FOR HYDROGEN GENERATION *VIA* THE HYDROLYSIS OF AQUEOUS SODIUM BOROHYDRIDE ($NaBH_4$) SOLUTIONS

Adrian Nur[1,✉], *Anatta W. Budiman*[1], *Arif Jumari*[1], *Nazriati Nazriati*[2], *Fauziatul Fajaroh*[2]

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Abstract. To generate hydrogen from its storage as $NaBH_4$, a catalyst was synthesized *via* an electrochemical method. The catalyst, Ni-Co, had hydroxyapatite as a support catalyst. The electrochemical cell consisted of a DC power supply, a carbon anode and cathode, and a bipolar membrane to separate the cell into two chambers. The current density was adjusted to 61, 91, and 132 mA/cm^2. The electrolysis time was 30, 60, and 90 min. The particles produced were analyzed by XRD and SEM/EDX and tested in the hydrolysis of $NaBH_4$ for hydrogen generation. The Ni-Co/HA catalyst test concluded that the period of time used for electrolysis during catalyst formation was positively correlated with the rate of $NaBH_4$ hydrolysis in the production of hydrogen. The highest rate of hydrogen production was obtained using the synthesized catalyst with a current density of 92 mA/cm^2. The $NaBH_4$ hydrolysis reaction followed a first-order reaction with the rate constant of $(2.220–14.117)\cdot10^{-3}$ l/(g·min). The Arrhenius equation for hydrolysis reactions within the temperature range of 300–323 K is $k = 6.5\cdot10^{-6}\exp(-6000/T)$.

Keywords: Ni-Co/hydroxyapatite, hydrogen storage, synthesis, electrochemical method, bipolar membrane.

1. Introduction

Hydrogen is the fuel of the future for several advantageous reasons, chief among them being availability (obtainable from renewable sources), eco-friendliness, and efficiency [1-3]. One of the challenges of developing hydrogen as a future fuel relates to storage [4]. There are several hydrogen storage methods: high-pressure or cryogenic tanks, physical sorption methods, and as a chemical hybrid. Storage of hydrogen as a chemical hydride (liquid phase) is a promising alternative due to the ease of portability and safety under ambient conditions.

$NaBH_4$ has proven to be a useful hydrogen storage material due to its high storage capacity, high stability under ambient air, ability to be produced at low temperatures, and harmless reaction products [5, 6]. The catalyst for hydrogen production from a chemical hydride ($NaBH_4$) must possess high levels activity and durability under an alkaline atmosphere. Ni and Co are transition metals that have shown excellent catalyst properties [7-9]. Catalyst support is needed to increase the dispersion of the catalyst and to prevent it from escaping with hydrogen bubbles. Hydroxyapatite provides sufficient catalyst support [10, 11]. Electrochemical synthesis is effective for *in situ* metal-hydroxyapatite production which is easily controlled [12]. The Ni-Co/hydroxyapatite (HA) catalyst is used in hydride chemistry to produce hydrogen from storage as $NaBH_4$.

The novelty of this work involves the electrochemical synthesis of the Ni-Co/HA catalyst *in situ*, which is further used for hydrogen production. The purpose of this work was to synthesize an electrochemical Ni-Co/hydroxyapatite catalyst and its use in the $NaHB_4$ hydrolysis to generate hydrogen.

2. Experimental

The experimental setup used for the catalyst synthesis is represented in Fig. 1. The equipment consisted of an electrochemical cell, a DC power supply (Zhaoxin PS-3005D), and a 5×10×10 cm acrylic container with 250 ml of electrolyte solution. A bipolar membrane was used to divide the acrylic container into an anode chamber and a cathode chamber [12]. The bipolar membrane consisted of an anion exchange membrane that faced the anode chamber and a cation exchange

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[1] Department of Chemical Engineering, Sebelas Maret University, Jl. Ir. Sutami 36 A Jebres, 57126 Surakarta, Indonesia
[2] Department of Chemistry, Faculty of Mathematics and Science, State University of Malang, 65111 Malang, Indonesia
✉ *adriannur@staff.uns.ac.id*

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membrane that faced the cathode chamber. The bipolar membrane was a Fumasep FBM that was acquired from FUMATECH BWT GmbH. The electrolyte solution consisted of 0.1M Ni^{2+}, 0.1M Co^{2+}, 0.25M Ca^{2+}, 0.15M PO_4^{3-}, and 0.25M EDTA. For this solution, we dissolved $NiCl_2$, $CoCl_2$, $CaCl_2$, KH_2PO_4, and $Na_2H_2EDTA{\cdot}2H_2O$. All chemicals were of analytical grade and were purchased from Merck. There was no treatment before use. The anode and cathode electrodes were formed from 5.2×2 cm plate-shaped carbon with a thickness of 0.4 cm. The DC power supply provided the potential difference between two electrodes with current density that could be adjusted to 61, 92, and 132 mA/cm^2. During the electrolysis process, the pH of the solution was measured using a portable pH meter (Ohaus ST300). In addition to current density, the electrolysis time was also varied (30, 60, and 90 min). The electrochemical cell was placed in an ultrasonic cleaner acquired from Elmasonic. Electrolysis was conducted at room temperature. Furthermore, filter paper was used to separate the resultant particles from the solution, and the particles were then washed with demineralized water, and dried in an oven at 313 K overnight. The particles produced were analyzed by XRD and SEM/EDX. XRD analysis was carried out using a Shimadzu 6000 X-ray diffractometer (XRD) with CuKα (λ = 1.5406 nm) radiation with a step size of $0.7°{\cdot}s^{-1}$ over angular ranges (2θ) from 20 to 60°. SEM/EDX analysis was accomplished by scanning electron microscopy (Inspect S40, FEI) using an acceleration voltage of 20 kV.

The viability of the Ni-Co/HA catalyst was tested in the hydrolysis of $NaBH_4$ for hydrogen production. The hydrolysis reaction was carried out in a batch reactor (Fig. 2). A 0.1M sample from 150 ml of a $NaBH_4$ solution was placed in a water bath to maintain a reaction temperature that could be duplicated under various conditions that could reasonably be encountered using other catalysts and temperatures. The catalyst tested was subjected to electrolysis for 60 min under current densities of 61 mA/cm^2 (cat61mA/cm^{2}60min), 92 mA/cm^2 (cat92mA/cm^{2}60min), and 123 mA/cm^2 (cat123mA/cm^{2}60min). The reaction occurred at various temperatures: 300, 313 and 323 K. The formed hydrogen gas was drained into a closed tube filled with water. The water was pushed into an Erlenmeyer flask to allow measurement of its weight and volume.

3. Results and Discussion

The pH values of the solution during electrolysis in the both anode and cathode chambers are shown in Fig. 3. The solution pH in the anode chamber decreased from an initial value of 3.0 to near zero. The decrease in pH in the anode chamber occurred during the oxidation of water via electrolysis, which resulted in H^+ ions. The resultant H^+ ions were held in the anode chamber of the bipolar membrane and caused a drop in the pH of the solution. An increase in the current density accelerated the decrease in the pH of the solution. A higher current density resulted in a faster oxidation reaction, faster production of H^+ ions, and a faster decrease in the pH of the solution. The pH of the solution in the cathode chamber was increased from 3 to 12 with an increase in the electrolysis time. The increase in pH in the cathode chamber also happened during the electrolysis process, where there was a reduction in water and OH^- ions were produced. The bipolar membrane in the cathode chamber trapped the OH^- ions so that the solution pH in the cathode chamber increased. Higher current density accelerated the increase in pH. The larger current density accelerated the reduction reaction at the cathode, which in turn accelerated the production of OH^- ions. The rapid production of OH^- ions also accelerated the increase in the solution pH.

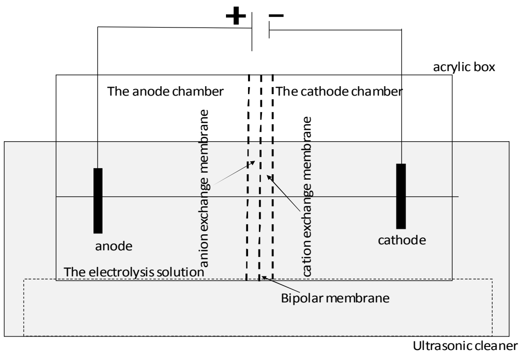

Fig. 1. Experimental setup for the catalyst synthesis

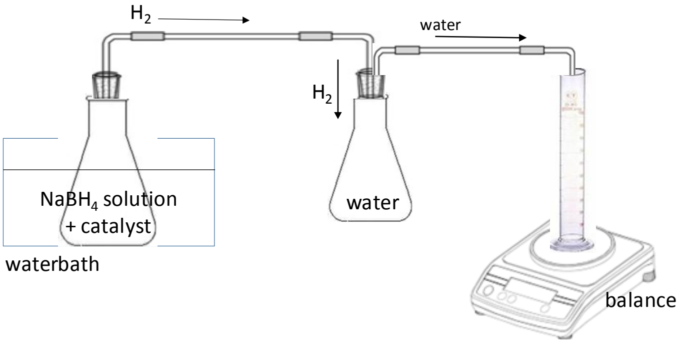

Fig. 2. Equipment for the $NaBH_4$ hydrolysis in the production of hydrogen

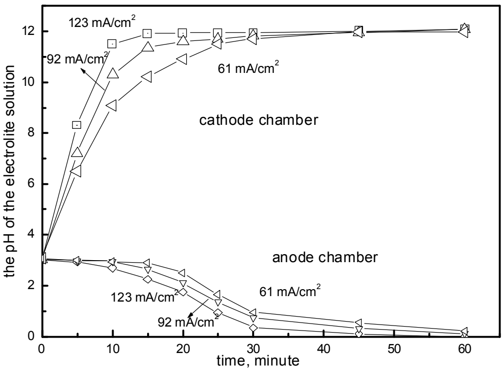

Fig. 3. The solution pH during electrolysis in the anode and cathode chambers

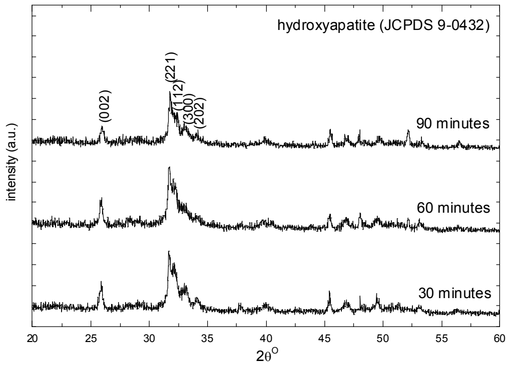

Fig. 4. XRD patterns of the particles as a result of electrolysis in the anode chamber

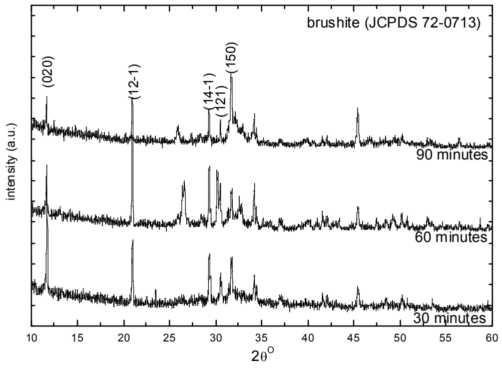

Fig. 5. XRD patterns of the particles as a result of electrolysis in the cathode chamber

Particles obtained in the anode and cathode chambers were analyzed using an X-ray diffractometer. The resultant diffraction patterns appear in Figs. 4 and 5. Fig. 4 shows the particle diffraction patterns produced by the anode chamber for electrolysis times of 30, 60, and 90 min. The particles produced in the anode chamber at electrolysis times of 30, 60 and 90 min corresponded to the brushite diffraction pattern. Brushite diffraction patterns are characterized by peaks at 11.71° (020), 20.99° (12-1), 29.35° (14-1), 30.53° (121), and 34.21° (150). The calcium phosphate that formed in the anode chamber was brushite. Brushite forms in solutions with low pH. Based on the patterns shown in Fig. 3, the pH of the calcium phospate particle solution is approximated to 0.

The diffraction patterns of the particles formed in the cathode chamber are shown in Fig. 5. HA particles formed in the cathode chamber showed the highest peaks for HA: 25.99° (002), 28.37° (210), 31.73° (211), and 33.23° (300). HA has a tendency to be formed when the solution pH exceeds 8. Fig. 3 shows that the solution pH in the cathode chamber achieved 12 after 30 min of electrolysis. HA was formed in the cathode chamber due to the high pH of the solution.

Fig. 6 shows the reactions occurred in the anode chamber when water oxidation produced H^+ ions. The H^+ ions lowered the solution pH in the anode chamber. At low pH, calcium and phosphate reacted and formed brushite. The reactions occurred in the cathode chamber, where a water reduction reaction produced OH^- ions were observed as well. The OH^- ions raised the pH of the solution. The OH^- ions shifted the chemical equilibrium of some reactions to form HA.

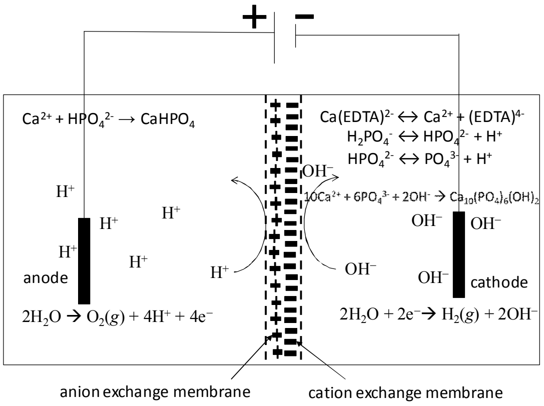

Fig. 6. Reactions that form brushite and hydroxyapatite

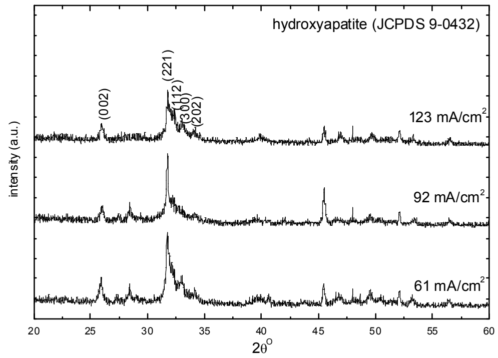

Fig. 7. XRD patterns of the particles caused by electrolysis at various current densities

The effect of current density on the calcium phosphate phase that formed is shown in Fig. 7. There were no significant differences in the calcium phosphate phases formed at current densities of 61, 92, and 123 mA/cm^2. All three of the current densities tested produced HA. The pH of the solution at the cathode was quite high (approximately 12). Because of the high pH, all the calcium phosphate that formed was HA.

The SEM image (Fig. 8) shows that the particles that were formed consisted of smaller particles forming agglomerations. These small particles had irregular shapes, and particle density increased with the increase in current density.

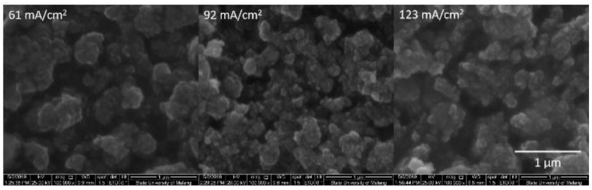

Fig. 8. Morphology of the particles produced by electrosynthesis of the Ni-Co/HA catalyst

The results of EDX analysis of particles in the anode and cathode chambers are shown in Figs. 9 and 10.

The mole ratio of Ca/P particles in the anode chamber ranged from 1 to 1.15, which agreed with the results of XRD analysis showing that the calcium phosphate phase formed brushite. A longer electrolysis time resulted in a higher mole ratio of Ca/P. The amount of Ni in the particles formed in the anode chamber ranged from 0.69 to 1.14 wt % while Co ranged from 0.75 to 1.17 wt %. A longer electrolysis time resulted in a higher weight for Ni and Co in the particles formed in the anode chamber. Particles containing Ni and Co formed in the anode chamber even though the pH in the anode chamber was very low. Particles likely formed from the oxidation of nickel and cobalt which then resulted in formation of nickel oxide and cobalt oxide.

The mole ratio of Ca/P particles in the cathode chamber ranged from 1.61 to 1.64, which agrees with the results of XRD analysis showing that the calcium phosphate phase that formed in the cathode chamber was HA. A longer electrolysis time produced higher Ca/P molar ratios. Ni content in particles formed in the cathode chamber ranged from 1.93 to 6.63 wt % while Co content ranged from 2.92 to 11.91 wt %. A longer electrolysis time produced a higher content of Ni and Co in the particles.

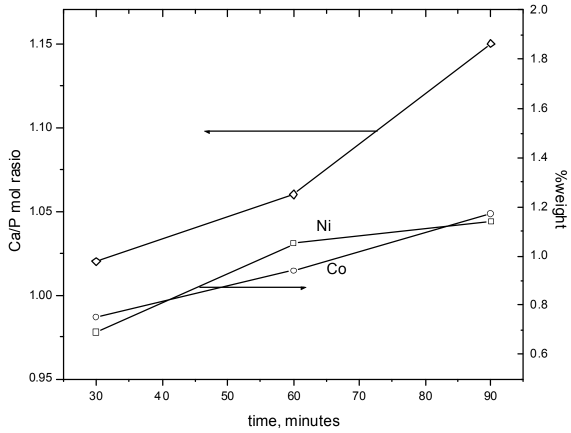

Fig. 9. Mole ratio of Ca/P particles and Ni-Co content in particles formed in the anode chamber

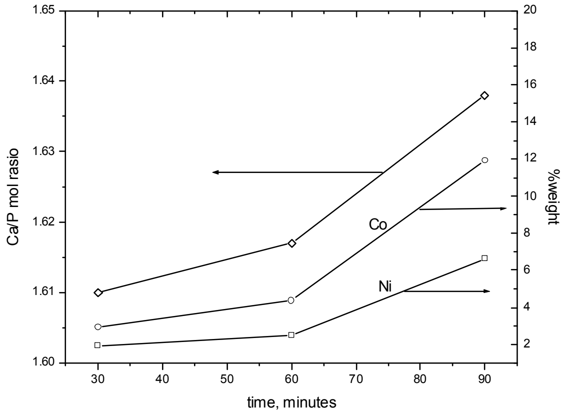

Fig. 10. Mole ratio of Ca/P particles and Ni-Co content in particles formed in the cathode chamber

The Ni-Co/HA catalyst was used in the hydrolysis reaction of $NaBH_4$ as a test for hydrogen production in a batch reactor. The volumes of hydrogen produced appear in Figs. 11, 12, and 13. Fig. 11 shows the volume of hydrogen generated during electrolysis for 30 and 60 min. The volume of hydrogen produced was always increased with the increase in the reaction time. The hydrolysis reaction using a catalyst produced during 60 min of electrolysis was faster than that using a catalyst produced after 30 min of electrolysis. The catalyst produced by 60 min of electrolysis had higher contents of both Ni and Co compared with that of the catalyst produced after 30 min of electrolysis. Higher contents of Ni and Co in the catalyst accelerated the hydrolysis of $NaBH_4$ for hydrogen production. Comparisons of hydrogen production as a result of hydrolysis with and without catalyst appear in Fig. 11, and demonstrate that the rate of hydrogen production with a catalyst can increase 3-fold in 80 min compared with the rate of hydrogen production without a catalyst.

Fig. 12 shows the volume of hydrogen produced using a catalyst under current densities 61, 92, and 123 mA/cm^2. The fastest production of hydrogen occurred using a catalyst synthesized at a current density of 92 mA/cm^2, followed by a catalyst synthesized with a current density of 123 mA/cm^2, while the slowest production used a the current density of 61 mA/cm^2. In general, a higher current density during catalyst synthesis equated to a greater content of Ni and Co, which accelerated the hydrolysis reaction that produced hydrogen. The catalyst produced with a current density of 92 mA/cm^2 produced hydrogen faster than the catalyst with a current density of 123 mA/cm^2, because the latter example resulted in a catalyst amount that was so high it interfered with reactant transfer, which lowered the rate of hydrogen production.

Fig. 13 shows the volume of hydrogen produced at hydrolysis reaction temperatures of 300, 313, and 323 K using a catalyst produced under a current density of 92 mA/cm^2 for 60 min. A higher temperature for hydrolysis reaction equaled at faster hydrolysis reaction for hydrogen production. This result agrees with the Arrhenius equation.

The volume of hydrogen that was generated was used to determine the reaction rate equation that determine the moles of $NaBH_4$ that had reacted. The first-order reaction assumption was used to develop the reaction rate equation. Fig. 14 shows the relationship of the initial natural logarithmic of $NaBH_4$ moles per mole of $NaBH_4$ ($\ln(N_{NaBH4,o}/N_{NaBH4})$) used *versus* the hydrolysis reaction time on various catalysts with different current densities. The relationship shows a straight-line equation with $R^2 > 0.99$. This relationship shows that the first-order reaction assumption was accurate for the hydrolysis reaction equation. The reaction rate constants obtained ranged from $2.220 \cdot 10^{-3}$ to $3.864 \cdot 10^{-3}$ l/(g·min).

Fig. 15 shows the relationship of $\ln(N_{NaBH4,o}/N_{NaBH4})$ *versus* the hydrolysis reaction time at various temperatures. The relationship also shows a straight-line equation with R^2 approaching 1, so the assumption of the order of the reaction was correct. The reaction rate constant ranged from $3.175 \cdot 10^{-3}$ to $14.117 \cdot 10^{-3}$ l/(g·min).

The reaction rate constants at various temperatures were used to determine the Arrhenius equation. Fig. 16 shows the relationship of $\ln(k)$ *versus* $1/T$ that was used to determine the Arrhenius equation. Based on this picture, the Arrhenius equation for this hydrolysis reaction is $k = 6.5 \cdot 10^{-6} \cdot \exp(-6000/T)$.

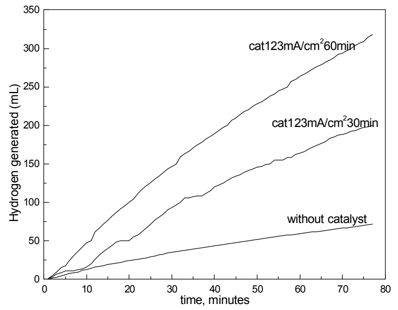

Fig. 11. The volume of hydrogen generated by electrolysis times of 30 and 60 minutes

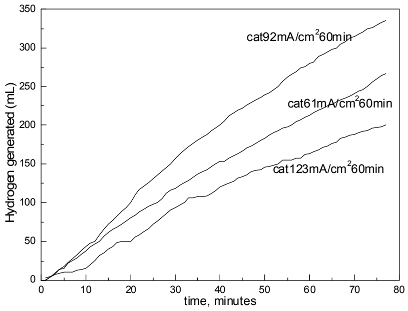

Fig. 12. Volume of hydrogen generated using a catalyst produced at various current densities

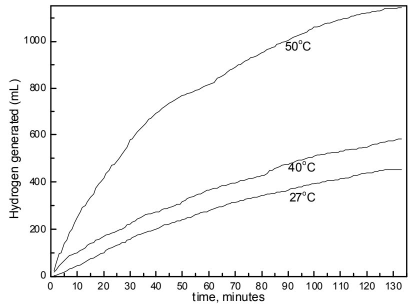

Fig. 13. Volume of hydrogen generated at various hydrolysis reaction temperatures using a catalyst produced under a current density of 92 mA/cm^2 for 60 minutes

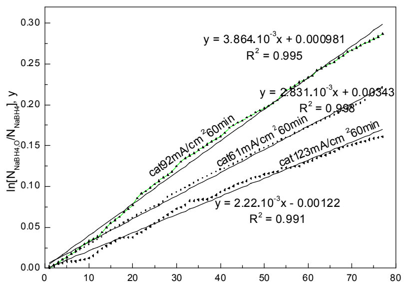

Fig. 14. Relationship of $\ln(N_{NaBH4,o}/N_{NaBH4})$ *vs.* the hydrolysis reaction time on various catalysts with different current densities

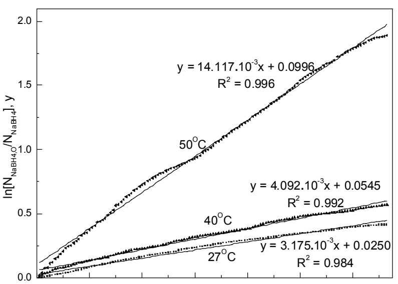

Fig. 15. Relationship of $\ln(N_{NaBH4,o}/N_{NaBH4})$ *vs.* the hydrolysis reaction time at various temperatures

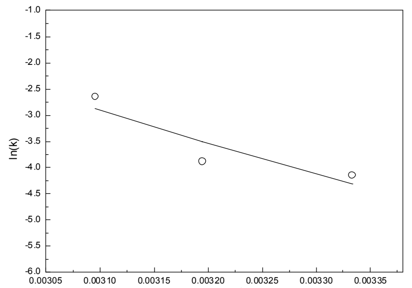

Fig. 16. Relationship of $\ln(k)$ *vs.* $1/T$

4. Conclusions

An electrochemical synthesis of Ni-Co/hydroxyapatite catalyst was accomplished. The catalyst was tested for application to the hydrolysis of NaHB$_4$, which generates hydrogen. The Ni-Co/hydroxyapatite catalyst synthesis was carried out in electrochemical cells that were separated into two chambers *via* the use of a bipolar membrane. The pH of the solution in the anode chamber dropped rapidly to zero while the pH of the solution in the cathode chamber rose rapidly to 12. Higher levels of current density resulted in faster decreases in the pH of the anode chamber, while in the cathode chamber the pH was increased at an accelerated rate. A low solution pH supported the formation of brushite in the anode chamber while a high pH solution resulted in the formation of HA in the cathode chamber. Testing of the Ni-Co/HA catalyst showed that longer durations of electrolysis of during catalyst formation resulted in an acceleration of the hydrolysis reaction with NaBH$_4$ in the production of hydrogen. The highest rate of hydrogen production was obtained from the catalyst synthesized with the current density of 92 mA/cm^2. The NaBH$_4$ hydrolysis reaction followed a first-order reaction with a reaction rate constant of $2.220\cdot10^{-3}$ to $14.117\cdot10^{-3}$ l/(g·min). The Arrhenius equation for hydrolysis reactions at the temperatures from 300 to 323 K is $k = 6.5\cdot10^{-6}\cdot\exp(-6000/T)$.

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ЕЛЕКТРОСИНТЕЗ Ni-Co/ГІДРОКСИАПАТИТУ – КАТАЛІЗАТОРА ДЛЯ ВИРОБНИЦТВА ВОДНЮ – ГІДРОЛІЗОМ ВОДНОГО РОЗЧИНУ БОРОГІДРІДУ НАТРІЮ (NABH$_4$)

Анотація. *Електрохімічним методом синтезований каталізатор Ni-Co на основі гідроксиапатиту для виробництва водню з NaBH$_4$. Показано, що електрохімічна комірка складається з джерела живлення постійного струму, карбонового анода і катода, і біполярної мембрани для розділення комірки на дві камери. Процес проводили за густини струму 61, 91 та 132 мА/см^2 та тривалості електролізу 30, 60 та 90 хвилин. Проведено аналіз отриманих частинок за допомогою рентгенівської дифракції та скануючої електронної мікроскопії. Встановлено, що збільшення тривалості електролізу для утворення каталізатора Ni-Co/HA позитивно корелюється зі швидкістю реакції гідролізу NaBH$_4$ для виробництва водню. Встановлено, що найбільший вихід водню досягається за щільності струму 92 мА/см^2. Визначено, що реакція гідролізу NaBH$_4$ є реакцією першого порядку з постійною швидкістю реакції (2,220–14,117)·10^{-3} л/(г·хв). Показано, що рівняння Арреніуса для реакцій гідролізу за температури від 300до 323 К має вигляд k = 6,5·10^{-6}·exp(-6000/T).*

Ключові слова: *Ni-Co/гідроксиапатит, накопичення водню, синтез, електрохімічний метод, біполярна мембрана.*