Ni-Co Alloy as Catalyst for Fuel Electrode of Hydrazine Fuel Cell

Paweł Piotr Włodarczyk, Barbara Włodarczyk

Opole University, Opole, Poland

Recent times have shown significant development of non-conventional and renewable sources of energy. Much attention has been paid to increase the use of fuel cells (FCs). However, the use of FCs on a large scale is mainly limited by the high cost of catalysts. Due to its excellent catalytic properties, platinum is most commonly used as the catalyst. However, due to the high price of platinum, other high efficiency catalysts should be researched. Elimination of platinum as catalyst would allow for wider commercial application of FCs. This will contribute to the development of high efficiency green energy sources. The paper presents a study of hydrazine electro-oxidation on electrode with Ni-Co alloy catalyst. The work shows a possibility of use of Ni-Co alloys as catalysts for electro-oxidation of hydrazine. Researches were done by the method of polarizing curves of electro-oxidation of hydrazine in glass vessel, on a copper electrode with Ni-Co alloy as a catalyst. An aqueous solution of KOH was used as the electrolyte. Measurements were done with the use of potentiostat. Conducted measurements show that there is a possibility of electro-oxidation of hydrazine on Ni-Co electrode. In any case, the process of electro-oxidation of hydrazine occurs. A current density of about 40-60 mA/cm^2 has been obtained for all concentrations of hydrazine and electrolyte. The current density is low, but the price of the catalyst is much lower than platinum. At 75% of Co, there is a sudden fall of current density. So, the work shows possibility to use Ni-Co alloys as catalysts for fuel electrode of hydrazine FCs.

Keywords: fuel cell (FC), catalyst, electro-oxidation, Ni-Co alloy, hydrazine

Introduction

There are many solutions that are used to achieve "clean" energy sources, such as photovoltaic cells, solar panels, wind turbines, heat pumps, and etc. One of the ecological sources of electric energy is fuel cell (FC), mainly due to high efficiency and low influence on environment. Although the operation principle of a FC has been known since 1939 (Grove, 1839), they still are not widely used. FCs have been successfully used in aerospace (Hoogers, 2003; Nowicki & Zięcina, 1989). However, in this case, the costs of producing cells do not seem to be a limitation, whereas in case of mobile applications, e.g. FC vehicles (FCVs) or mobile energy sources for laptops and cell phones (Kakaç, Pramuanjaroenkij, & Vasilev, 2007), the cost may be the

Paweł Piotr Włodarczyk, Ph.D., Faculty of Natural Sciences and Technology, Department of Process Engineering, Opole University, Opole, Poland.

Barbara Włodarczyk, Ph.D., Faculty of Natural Sciences and Technology, Department of Process Engineering, Opole University, Opole, Poland.

Correspondence concerning this article should be addressed to Paweł Piotr Włodarczyk, Department of Process Engineering, Opole University, Dmowskiego Street 7-9, 45-365 Opole, Poland. E-mail: pawel.wlodarczyk@uni.opole.pl.

deciding parameter. Wide use of FCs may improve air quality and influence the global warming reduction. The FCs transform the chemical fuel into electricity without intermediate stages. Therefore, the real efficiency reaches even 80% (O'Hayre, Cha, Colella, & Prinz, 2005; Stolten, 2010). Moreover, FCs have many other advantages. They also have no moving parts and are noiseless (Redey, 1970). There are, however, two major barriers regarding the use of FCs: the expenses associated with the cost of platinum catalysts and many restrictions associated with fuels (the filling and storage of hydrogen). For a long time, measurements of selection of fuels and catalysts for FCs have been conducted (Asazawa et al., 2007). New fuels allow to eliminate the need for using hydrogen (P. P. Włodarczyk & B. Włodarczyk, 2013; Gawdzik, Gajda, Włodarczyk, & Sofronkow, 2002; Milewski & Lewandowski, 2013; Milewski, Michalska, & Kacprzak, 2013). Additionally, the new catalysts allow to eliminate the costly platinum (Gawdzik, Gajda, Włodarczyk, Sofronkow, & Kurmaszev, 2003; Gajda et al., 2002; Rolison, Hagans, Swider, & Long, 1999; Steigerwalt, Deluga, Cliffel, & Lukehart, 2001; Twigg, 1989; P. P. Włodarczyk & B. Włodarczyk, 2015). However, these catalysts must have high efficiency, comparable to that of platinum. In other case, the platinum will remain the main catalyst for fuel electrodes of FC. So, search of new low cost catalysts is essential for commercialization of FCs.

Theory

Development of platinum substitutes has been studied intensely, but further improvement of output performance is still required for practical use (Matsumoto, Nagashima, Yamazaki, & Nakamura, 2006; Bashyam & Zelenay, 2006). For realization of the Pt-free FC with the potential of practical use, it is also required to examine the fuel (Asazawa et al., 2007). The most commonly used fuel for FCs is hydrogen. One main advantage of FCs is that the only by-product is water. Nevertheless, problems with the storage of hydrogen necessitate the search for other fuels. One such fuel is hydrazine. Hydrazine is an inorganic compound with the formula N_2H_4. It is a colourless flammable liquid with an ammonia-like odor. Hydrazine is highly toxic and dangerously unstable unless handled in solution.
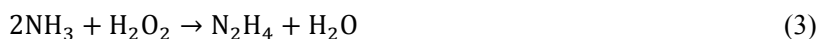
Hydrazine Production

Hydrazine is produced in the Olin Raschig process from sodium hypochloride and ammonia. This method relies on the reaction of chloramine with ammonia:

$$NH_2Cl + NH_3 \rightarrow N_2H_4 + HCl \tag{1}$$

Another route of hydrazine synthesis involves oxidation of urea with sodium hypochloride:

$$(H_2N)_2CO + NaOCl + NaOH \rightarrow N_2N_4 + H_2O + NaOCl + Na_2CO_3 \tag{2}$$
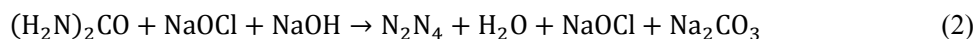
Hydrazine can be synthesized also from ammonia and hydrogen peroxide, according to the following formula (in the Pechiney-Ugine-Kuhlmann process) (Hayashi, Kainoh, Katayama, Kawasaki, & Okazaki, 1976):

$$2NH_3 + H_2O_2 \rightarrow N_2H_4 + H_2O \tag{3}$$

Hydrazine can also be produced via the so-called ketazine. It is a variation of the Olin Raschig process (1), in which ammonia is oxidized by chlorine or chloramine in the presence of aliphatic ketones, usually acetone. The resulting ketazine process is then hydrolyzed to hydrazine (Matar & Hatch, 2001).

Hydrazine can also be produced the following way:

$$2NH_3 + NaClO \rightarrow N_2H_4 + NaCl + H_2O \tag{4}$$
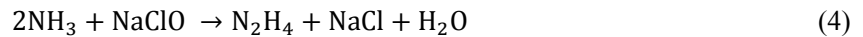
Hydrazine Application

Fuel hydrazine is used as a propellant onboard space vehicles (e.g. as a component of aerozine fuel in moon missions), and both to reduce the concentration of dissolved oxygen and to control PH of water used in large industrial boilers. It is often used as unsymmetrical dimethyl hydrazine in hypergolic rocket fuels as a bipropellant in combination with the oxidizer nitrogen tetroxide and less frequently with liquid oxygen. The hydrazine can also be a fuel for high efficiency FCs (Asazawa et al., 2007; Serov & Kwak, 2010; Kobayashi et al., 2003; Yamada et al., 2003).

Reactions in FC

The reaction of oxidation of the hydrazine in FC is represented by the relation (5) (Vielstich, 1970; Harrison & Khan, 1970):

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e \tag{5}$$
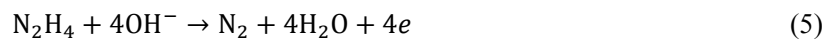
This reaction is subdivided into partial reaction (6) and (7) (Vielstich, 1970):

$$N_2H_4 \rightarrow N_2 + 4H \tag{6}$$

$$4H + 4OH^- \rightarrow 4H_2O + 4e \tag{7}$$

As shown in the above equations, the by-products are water and nitrogen. Nitrogen at normal pressure is indifferent to living organisms. Therefore, the direct hydrazine FC is as safe as hydrogen FC.

The operation of the direct hydrazine FC (Yamada et al., 2003) is shown in Figure 1.
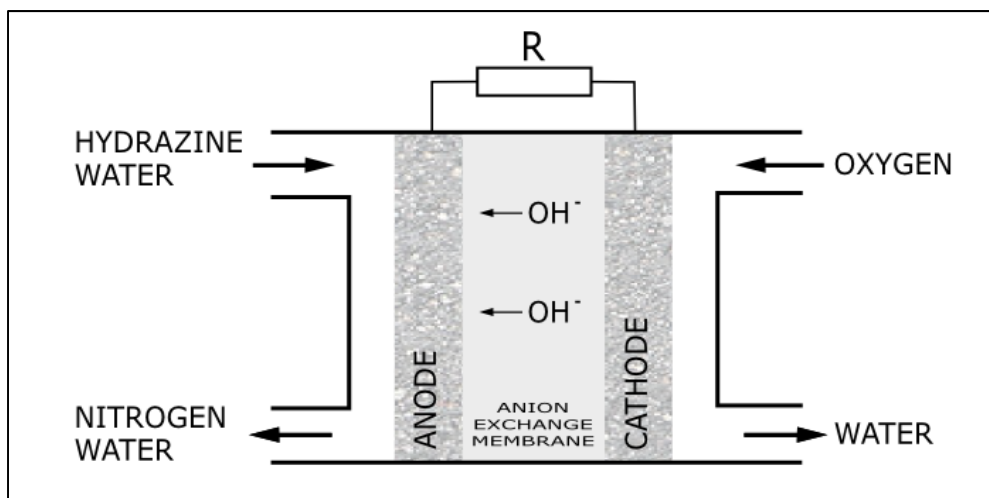

Figure1. Schematic diagram of the hydrazine cell reaction.

In direct hydrazine FC, the waste products are just water and nitrogen. Moreover, the great advantage of hydrazine is that it can be stored in simple lightweight containers. Since hydrazine is a liquid fuel, it is easy to handle during filling and its energy density is also high. However, high-concentration hydrazine is designated as a poisonous substance and it must be handled with the same safety standards applicable to gasoline and most industrial chemicals. Moreover, hydrazine vapor when mixed with air can explode. Therefore, as a fuel, it uses a mixture of hydrazine and water. Then water vapor fills empty spaces above the liquid surface during storage.

The electrochemical reactions involve the transfer of electrons. This transfer takes place on the electrode surface. The resulting current determines the reaction and thus the transfer rate is proportional to the surface on which the reaction is running, hence, the concept of current density (A/m^2). Activation barriers impede the conversion of reactants to products. So, part of the cell voltage is used for the reduction in the activation barrier. These losses are called the overpotential η_{act}. The correlation between current density and overpotential is described by the Butler-Volmer exponential function (Bockris & Reddy, 2000):

$$i = A \cdot i_0 \cdot \left(e^{\left[\frac{\alpha_a nF}{RT}(E - E_{eq}) \right]} - e^{\left[-\frac{\alpha_c nF}{RT}(E - E_{eq}) \right]} \right) \qquad (8)$$

where i is electrode current density (A/m^2); i_0 is exchange current density (A/m^2); R is universal gas constant; E is electromotive force at the terminals of the real cell (V); E_{eq} is equilibrium potential (V); α_a is the so-called anodic charge transfer coefficient; α_c is the so-called cathodic charge transfer coefficient; A is electrode active surface area (m^2); n is number of electrons involved in the electrode reaction; F is faraday constant per volt gram equivalent (kJ); or in a more compact form:

$$i = i_0 \cdot e^{K \cdot \eta_{act}} \qquad (9)$$

where η_{act} is activation overpotential (V); K is the factor of dependence of activation overpotential on reaction speed; Bockris and Reddy (2000) described the Butler-Volmer equation as central equation of electrode kinetics. In equilibrium, the adsorption and desorption fluxes of changes at the interface are equal (Bockris & Reddy, 2000).

Energy Conversion in FC

Direct methanol FC (DMFC) is characterized by easy handling, storage of fuel, and powering. However, compared to the DHFC and hydrazine FC, DMFC has a lower output current density. As shown in Figure 2, the current density of the hydrazine FC is slightly lower compared to DMFC, in particular, comparing the current density of the Pt-free DMFC and hydrazine FC with Ni catalyst.
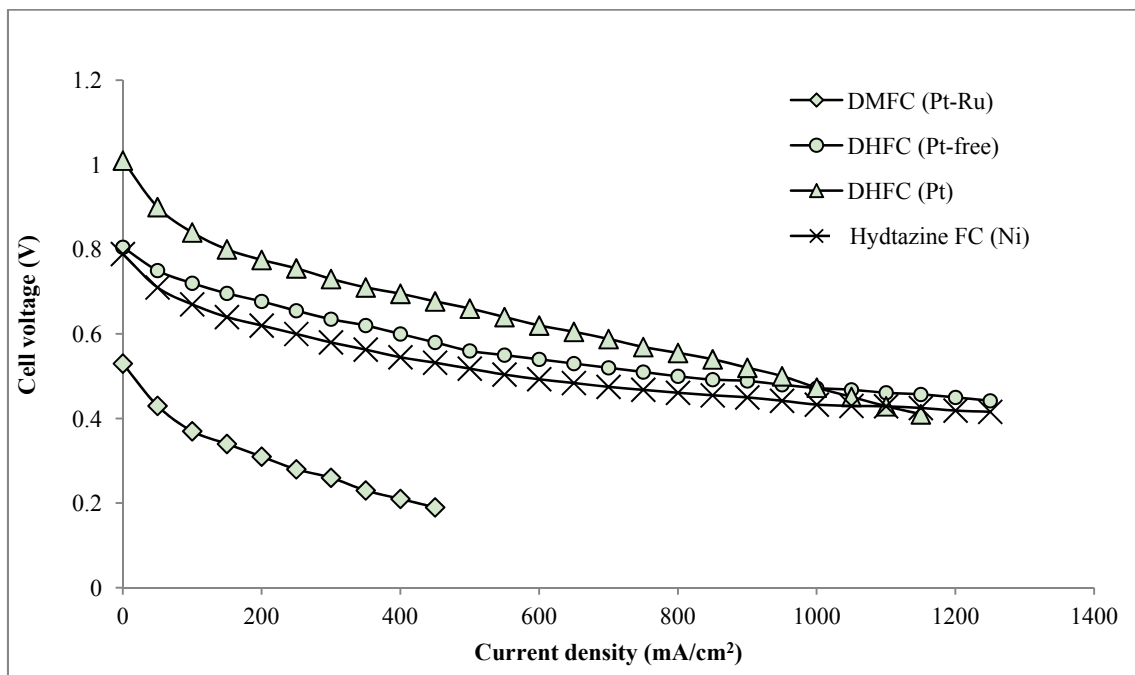

Figure 2. The polarization curves of electro-oxidation of fuels in aqueous solution of KOH.

Figure 2 shows the polarization curves of electro-oxidation of different fuels in aqueous solution of KOH (Asazawa et al., 2007).

The maximum energy of chemical conversion of the energy into work is equal to the free energy reaction (10) (Vielstich, 1970; Bockris & Reddy, 2000):

$$\Delta G = \Delta H - T\Delta S \tag{10}$$

where ΔG is change in Gibbs free energy (kJ/mol); ΔH is change in enthalpy (J/kg); T is absolute temperature (K); and ΔS is change in entropy (J/K).

Changing the Gibbs free energy ΔG associated with the cell electromotive force $E°$ is represented by the relation (11):

$$\Delta G = -nFE° \tag{11}$$

where n is number of electrons involved in the electrode reaction; F is Faraday constant per volt gram equivalent (kJ); and $E°$ is electromotive force (V).

In the case of a real cell the equation can be written as (O'Hayre et al., 2005; Stolten, 2010; Bockris & Reddy, 2000):

$$\Delta G' = -(nF)'E \tag{12}$$

where $\Delta G'$ is change in Gibbs free energy in real cell (kJ/mol); $(nF)'$ is real amount of energy obtained from one mole of fuel (kJ); and E is electromotive force at the terminals of the real cell (V).

Under real conditions the following relationship always occurs:

$$\Delta G' < \Delta G$$

However, due to the high price of platinum, other catalysts should be researched. Elimination of platinum as catalyst would allow for wider commercial application of FCs. This will contribute to the development of high efficiency green energy sources. Unfortunately, despite extensive knowledge in the field of solid-state physics and kinetics of catalytic reactions, the implementation of the catalysts is carried out mainly experimentally.

Material and Methods

Ni-Co alloy was obtained by the method of electrochemical deposition. The alloy was deposited on smooth surface of copper electrode. The alloys were deposited on copper electrode from a mixture of $NiSO_4 \times 7H_2O$, $CoSO_4 \times 7H_2O$, $CoCl_2 \times 6H_2O$, H_3BO_3, NaCl, and KCl. The alloys were obtained with different concentrations of Ni and Co. The chemical composition of Ni-Co alloys was determined with the XRD (X-ray diffraction) method. Those alloys contained 15%, 25%, 50%, and 75% of Co.

Researches were done by the method of polarizing curves of electro-oxidation of hydrazine in glass vessel, on a copper electrode with Ni-Co alloy as a catalyst. An aqueous solution of KOH was used as the electrolyte. Measurements were done in a glass cell with the use of AMEL system 5,000 potentiostat. Researches on electro-oxidation of hydrazine in alkaline electrolyte, for various concentrations of hydrazine (0.01, 0.1, 0.5, 1, 2, 3, 4, 5, and 6M) and for two concentrations (2M and 6M) of KOH, are presented in this paper.

Results

Figures 3-6 show the polarization curves of electro-oxidation of hydrazine with Ni-Co catalyst in alkaline electrolyte (2M KOH).

Figures 7-10 show the polarization curves of electro-oxidation of hydrazine with Ni-Co catalyst in alkaline electrolyte (6M KOH). Similarly to the results illustrated in Figures 3-6, measurements were performed for concentrations of hydrazine 0.01, 0.1, 0.5, 1, 2, 3, 4, 5, and 6M.
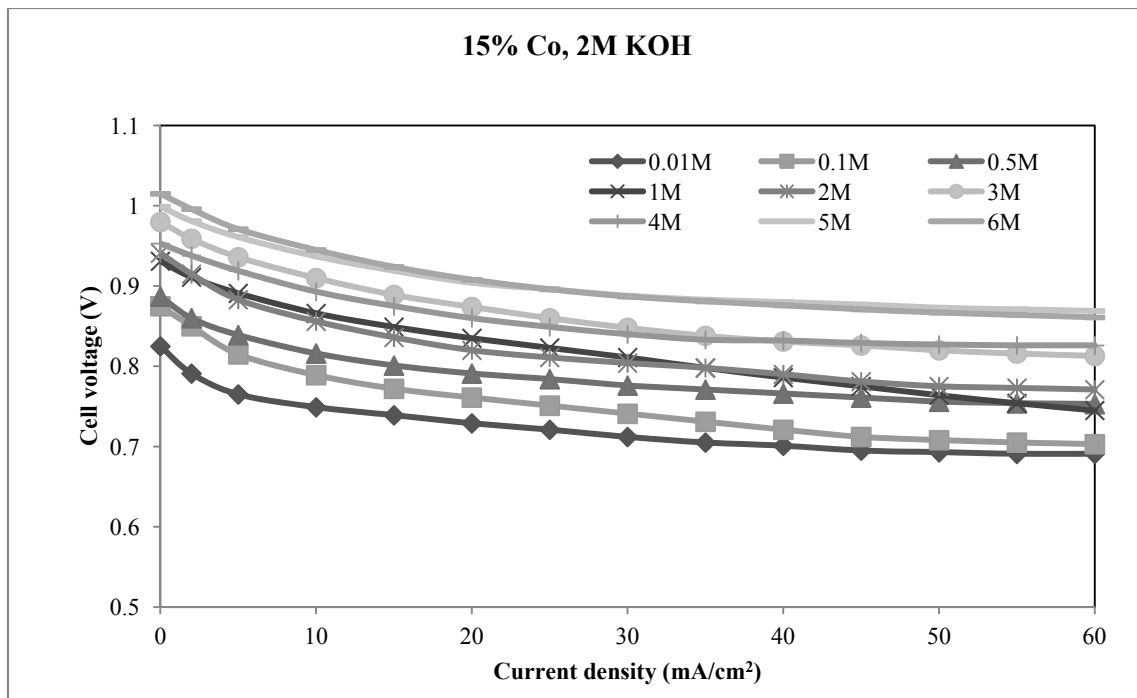

Figure 3. The polarization curves of electro-oxidation of hydrazine with Ni-Co catalyst in alkaline electrolyte (2M KOH) (Ni-Co alloy contained 15% of Co).
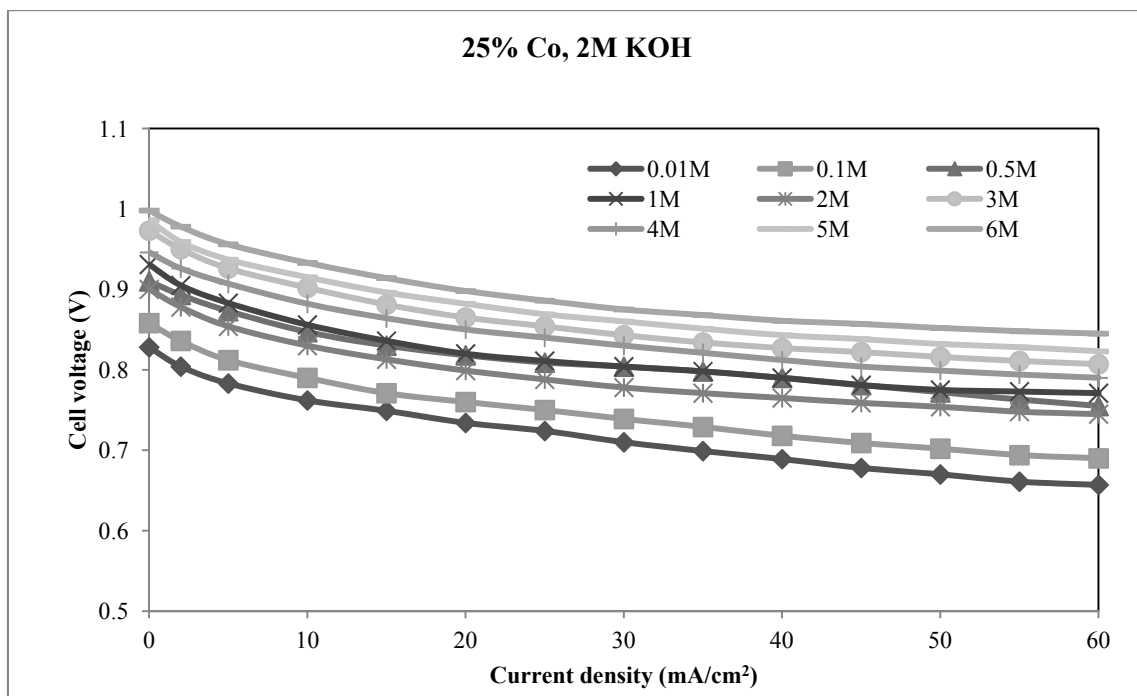

Figure 4. The polarization curves of electro-oxidation of hydrazine with Ni-Co catalyst in alkaline electrolyte (2M KOH) (Ni-Co alloy contained 25% of Co).
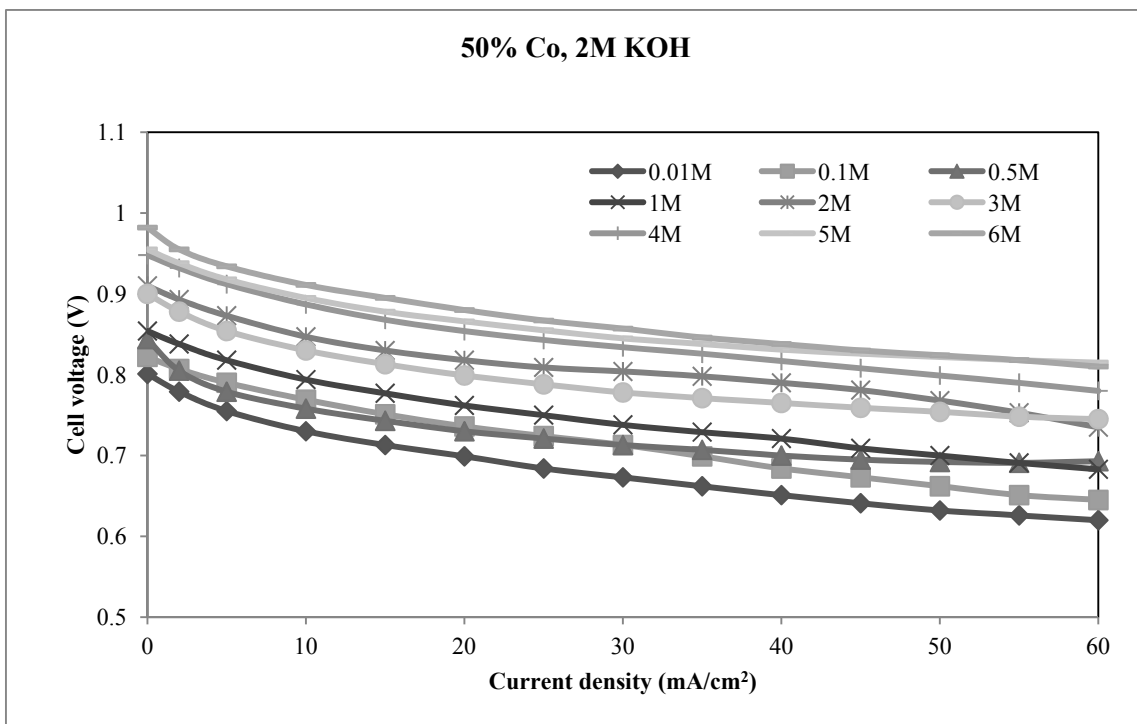
Figure 5. The polarization curves of electro-oxidation of hydrazine with Ni-Co catalyst in aqueous solution of KOH (2M) (Ni-Co alloy contained 50% of Co).
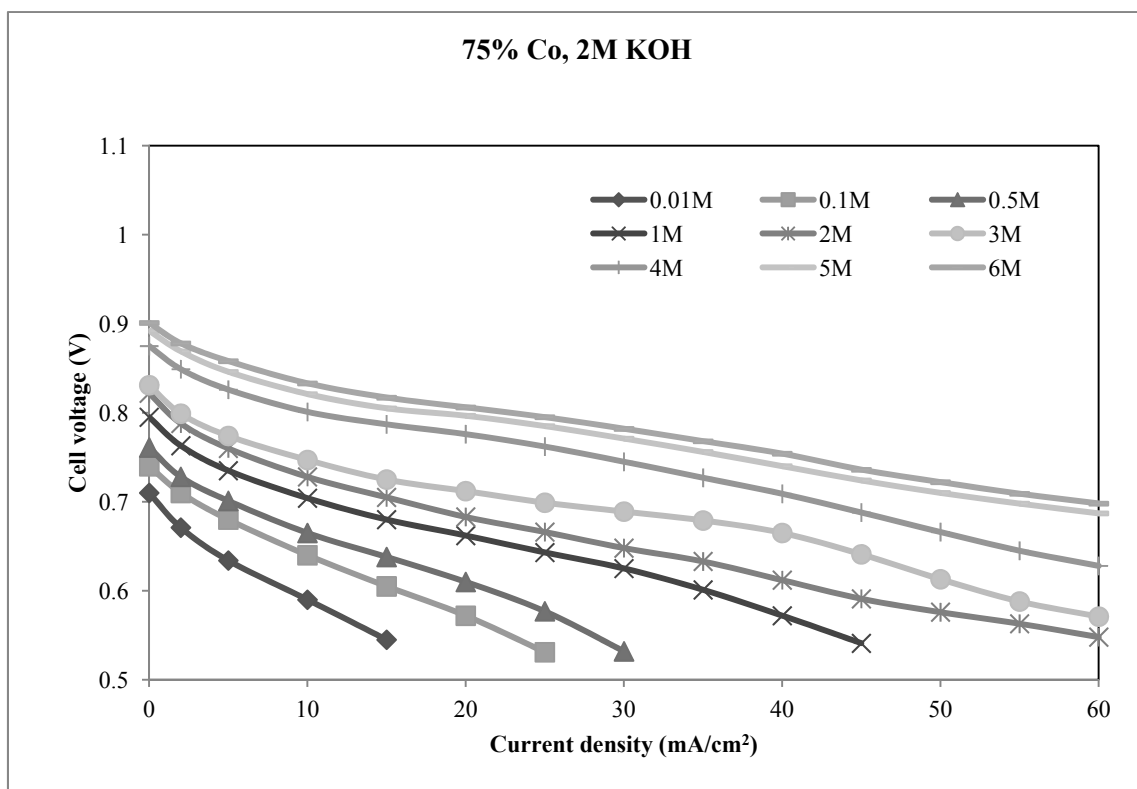

Figure 6. The polarization curves of electro-oxidation of hydrazine with Ni-Co catalyst in alkaline electrolyte (2M KOH) (Ni-Co alloy contained 75% of Co).
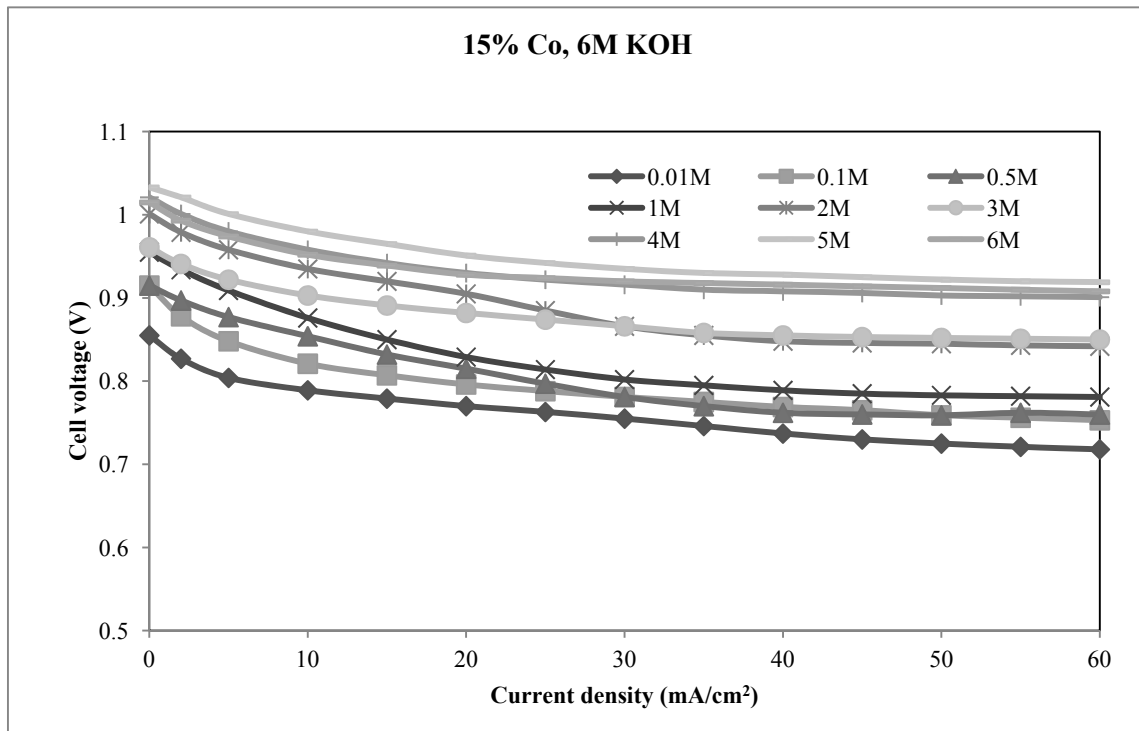
Figure 7. The polarization curves of electro-oxidation of hydrazine with Ni-Co catalyst in alkaline electrolyte (6M KOH) (Ni-Co alloy contained 15% of Co).

Figure 8. The polarization curves of electro-oxidation of hydrazine with Ni-Co catalyst in alkaline electrolyte (6M KOH) (Ni-Co alloy contained 25% of Co).
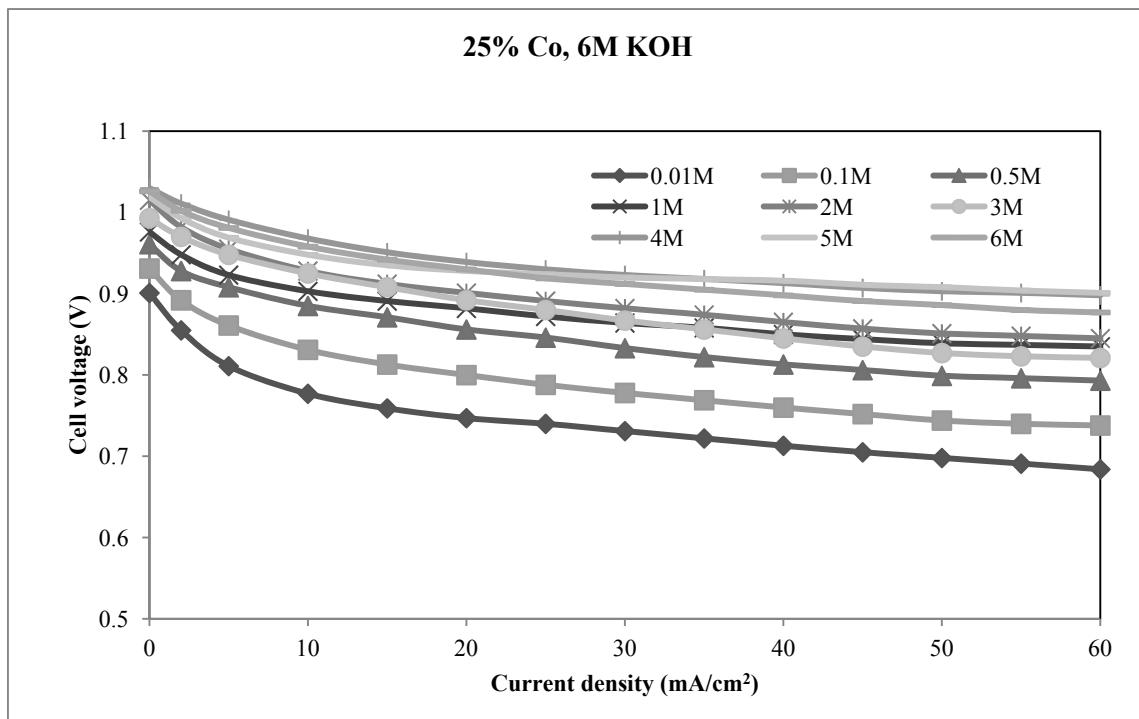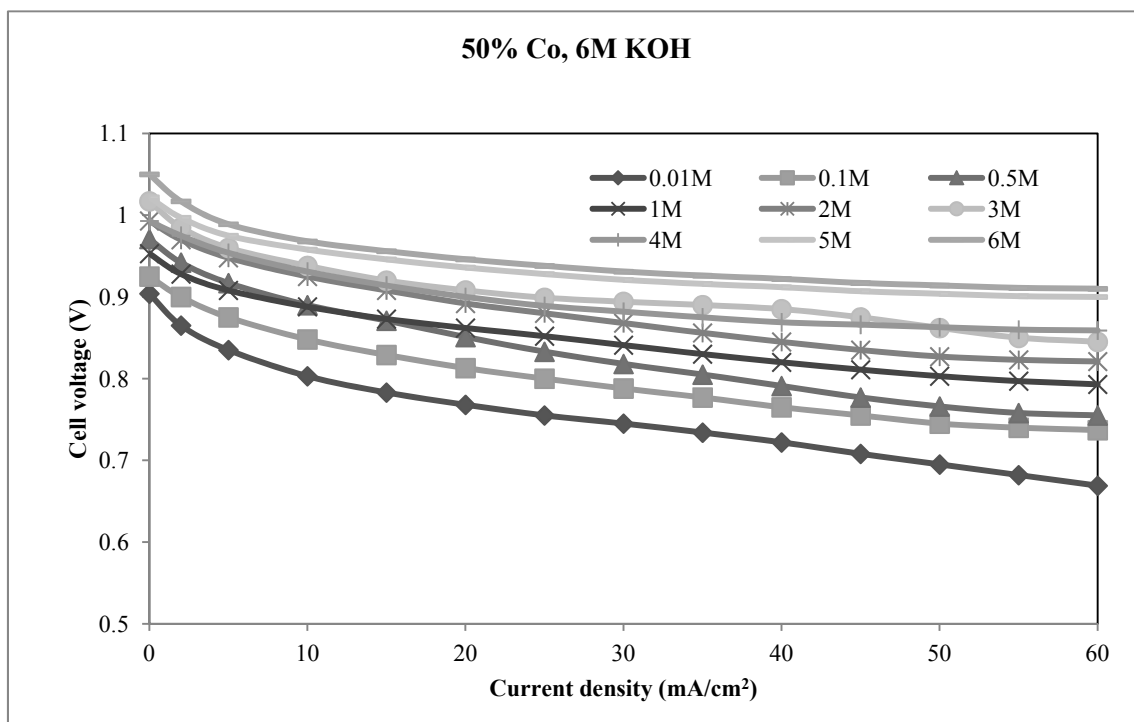
Figure 9. The polarization curves of electro-oxidation of hydrazine with Ni-Co catalyst in aqueous solution of KOH (6M) (Ni-Co alloy contained 50% of Co).
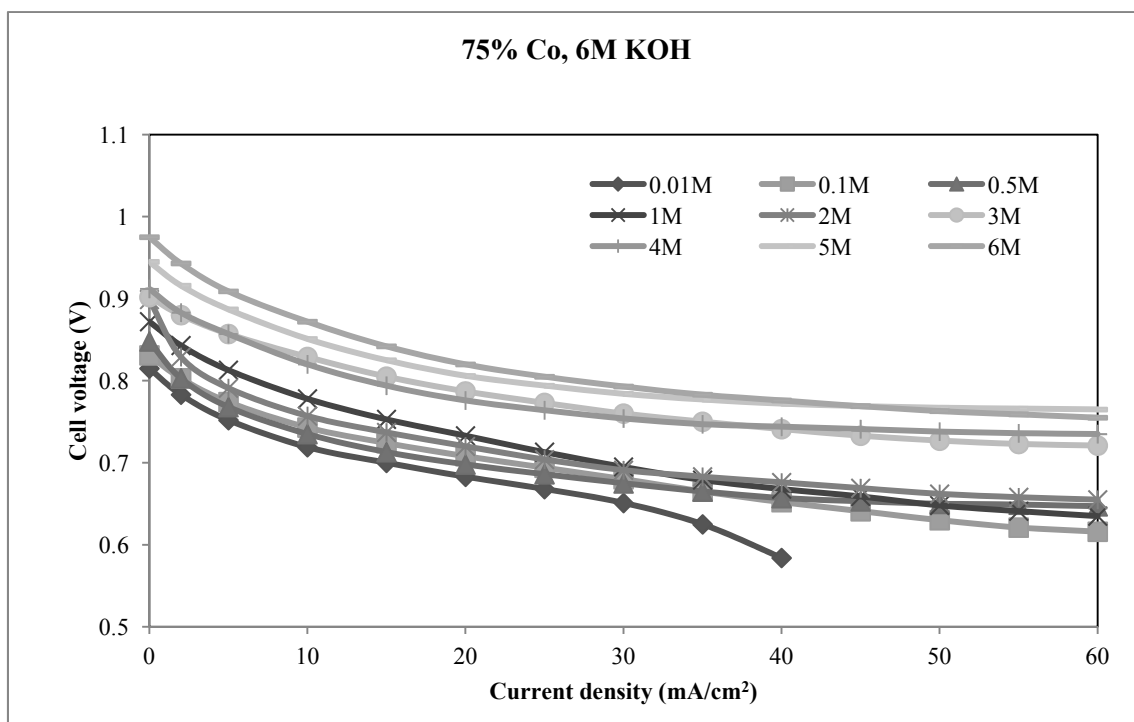

Figure 10. The polarization curves of electro-oxidation of hydrazine with Ni-Co catalyst in alkaline electrolyte (6M KOH) (Ni-Co alloy contained 75% of Co).

Conclusions

Ni-Co alloy was obtained by the method of electrochemical deposition. The alloy was deposited on a smooth surface of copper electrode.

Measurements were conducted for concentration of hydrazine in range from 0.01 to 6M and for two concentrations of KOH. Conducted measurements show that there is a possibility of electro-oxidation of hydrazine on Ni-Co electrode. In any case, the process of electro-oxidation of hydrazine occurs. A current density of about 40-60 mA/cm^2 has been obtained for all concentrations of hydrazine and electrolyte. The current density is low, but the price of the catalyst is much lower than platinum. It should be noted that at 75% of Co, there is a sudden fall of current density. This fall is particularly noticeable at a concentration of KOH equal to 2M (Figure 6). However, at a concentration of KOH equal to 6M, there is also a significant decrease in the current density (Figure 10). This fall is smaller compared to the measurements at a concentration 2M of KOH.

A possibility of electro-oxidation of hydrazine on electrode with Ni-Co catalyst in alkaline electrolyte was presented in this paper. It is possible to use Ni-Co alloy for electro-oxidation of hydrazine. So, it is possible to use Ni-Co alloy as catalyst of fuel electrode for hydrazine FC. But this alloy as catalyst has a too low current density to build an efficient FC. However, the main advantage compared to platinum is the price. Compared to nickel, e.g. Raney Ni, Ni-Co alloy is not too easily oxidizable and thus it is easier to use. Raney nickel is typically supplied as 50% slurry in water. It should never be exposed to air. Even after reaction, Raney nickel contains significant amounts of hydrogen gas, and may spontaneously ignite when exposed to air (Armour, 2003).

Due to the low current density but also low cost in comparison to platinum, Ni-Co alloy can be used mainly as a catalyst for stationary FC. But along with the catalyst researches, some measurements should be performed for selection of anion exchange membrane for hydrazine FC. So, search of new low cost and high efficiency catalysts is very important for development and commercialization of mobile FCs, e.g., for FCVs.

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