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ELECTROOXIDATION OF METHYL ALCOHOL WITH Ni-Co CATALYST

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Abstract

Due to development of the renewable energy sources, the powering of fuel cells (FCs) with bio-fuels is very important. The one of this fuel is methyl alcohol. The use of fuel cells on a large scale is mainly limited by the high cost of catalysts – mainly platinum. Elimination of Pt as catalyst would allow for wider commercial application of FCs. The paper presents a study of methyl alcohol electrooxidation on electrode with Ni-Co alloy catalyst. Researches were done by the method of polarizing curves of electrooxidation of methanol in glass vessel. Conducted measurements show that there is a possibility of electrooxidation of methanol with Ni-Co catalyst.

In any case, the process of electrooxidation of methanol occurs. A maximum current density was equal 50 mA/cm^2. So, the work shows possibility to use Ni-Co alloys as catalysts for fuel electrode to methyl alcohol electrooxidation.

Keywords: methanol, bio-fuel, Ni-Co catalyst, fuel cell, environment engineering

INTRODUCTION

Today's some alternative energy sources have been developing. One of these ecological sources of electric energy is fuel cell (FC). FC characterized by high efficiency and low influence on environment (Hoogers 2003, O'Hayre *et al.*

2005, Stolten 2010). The real efficiency of FCs reaches even 80% (O'Hayre *et al.* 2005, Stolten 2010). But, the real efficiency of entire fuel cell system is also very high (Gaines *et al.* 2008, Granovskii *et al.* 2006, Offer *et al.* 2006, Von Helmolt and Eberle 2007). Moreover, FCs has many other advantages: no moving parts and are noiseless (Larminie and Dicks 2003). FCs has been successfully used in spaceships, submarines, fuel cell vehicles (FCVs), portable power systems and other (Hoogers 2003, Larminie and Dicks 2005, Freeh *et al.* 2004, Barbira *et al*. 2005). But in aerospace solution, the costs of producing cells do not seem to be a limitation, whereas in case of mobile applications, e.g. FCVs or mobile energy sources for laptops and cell phones (Appleby and Foulkes 1988, Kakaç *et al.* 2007), the cost may be the deciding parameter. Wide use of FCs will allow improve air quality and influence the global warming reduction, because fuel cells transform the chemical fuel into electricity without intermediate stages (combustion). 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, e.g. the filling and storage of hydrogen (Furukawa and Yaghi 2009, Niaz *et al.* 2015, Sakintuna *et al.* 2007). For a long time, measurements of selection of fuels and catalysts for FCs have been conducted. New fuels allow to eliminate the need for using hydrogen (Włodarczyk and Włodarczyk 2016a, 2017b, 2017c, 2017d). For many years, measurements of selection of biofuels also have been conducted (Kelley *et al.* 2000, Papadias *et al.* 2012, Włodarczyk and Włodarczyk 2016a, 2016b, 2016c, 2017a, 2017b). Additionally, the new catalysts allow eliminating the costly platinum (Asazawa *et al.* 2007, Rolison *et al.* 1999, Steigerwalt *et al.* 2001, Włodarczyk and Włodarczyk 2016c). The catalyst for fuel cells should have high efficiency. In other case, expensive platinum will remain the main catalyst for fuel electrodes of fuel cell. So, search of new low cost catalysts is necessary for commercialization of fuel cells. 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. 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 fuel cells is hydrogen. However, problems with the storage of hydrogen necessitate the search for other fuels. One such fuel can be methyl alcohol. Methanol is the simplest alcohol, and is light, volatile, colorless, flammable liquid with a distinctive odor very similar to that of ethanol. It is also important that methanol is a biofuel. It can be produced in conventional steam reforming. It can be produced also from biomass (Dong and Steinberg 1997, Hiranoa *et al*. 1998, Wyman *et al.* 1993). The reactions in direct methanol fuel cell are represented by the equations (1), (2) and (3) (Hamnett 1997, Hoogers 2003, Kelley *et al.* 2000, Larminie and Dicks 2005).

Reaction on anode:

$$CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2 \tag{1}$$

Reaction on cathode:

$$\tfrac{3}{2}O_2 + \quad 6H^+ + 6e^- \rightarrow 3H_2O \tag{2}$$

Overall reaction:

$$CH_3OH + \tfrac{3}{2}O_2 \rightarrow 2H_2O + CO_2 \tag{3}$$

The electrochemical reactions in fuel cell 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). The correlation between current density and overpotential is described by the Butler-Volmer exponential function (Bockris and Reddy 2000). 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.

Previous, preliminary research of methanol electrooxidation with Ni-Co alloy showed that it is necessary to carry out wider scope of measurements in this area (Włodarczyk and Włodarczyk 2016d). The paper presents complementary research on the use of Ni-Co alloy as a catalyst for methyl alcohol electrooxidation. The scope of research concerns three alloys (with different concentrations of components – Ni and Co), nine methanol concentrations and two concentrations of alkaline electrolyte (KOH).

MATERIAL AND METHODS

Ni-Co alloy were obtained by the method of electrochemical deposition. The alloys were deposited on smooth copper electrode. The alloys were deposited from a mixture of $NiSO_4$ and $CoSO_4$. The alloys were obtained at temperature of 365K. Composition of mixture for alloy deposited shows Table 1.

Before the deposition of the alloy, copper electrode was prepared in several steps: surface was degreased in 25% aqueous solution of KOH (after degreasing, the surface shall be completely wettable with water); slectrode was digested in acetic acid; slectrode was washed with alcohol.

The chemical composition of Ni-Co alloys was determined with the XRD method. The alloys were obtained with different concentrations of Ni and Co (15, 25 and 50% of Co).

Table 1. Mixture composition for deposited Ni-Co alloy on copper electrode

component	volume [g/l]	pH	temperature [K]	current density [A/dm^2]	concentration of Co [%]
$NiSO_4 \cdot 7H_2O$ $CoCl_2 \cdot 6H_2O$ H_3BO_3	260 14 15	3.0	293	1.6	15
$NiSO_4 \cdot 7H_2O$ $CoSO_4 \cdot 7H_2O$ H_3BO_3 NaCl	200 20 30 15	5.5	293	1.0	25
$NiSO_4 \cdot 7H_2O$ $CoSO_4 \cdot 7H_2O$	195 35	2.0	293	3.0	50
$NiSO_4 \cdot 7H_2O$ $CoSO_4 \cdot 7H_2O$ H_3BO_3 KCl	140 120 30 15	4.0	323	1.0	75

Source: own compilation

Researches were done by the method of polarizing curves of electrooxidation of methyl alcohol 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 5000 potentiostat.

Researches on electrooxidation of methyl alcohol in alkaline electrolyte, for various concentrations of methanol (0.01, 0.1, 0.5, 1, 2, 3, 4, 5 and 6M) and for two concentrations (2M and 6M) of KOH, were carried out at a temperature of 313K.

RESULTS

Figures 1-3 show the polarization curves of electrooxidation of methyl alcohol with Ni-Co catalyst in alkaline electrolyte (2M KOH). Measurements were performed for methanol concentrations equal of 0.01, 0.1, 0.5, 1, 2, 3, 4, 5 and 6M.

Figures 4-6 show the polarization curves of electrooxidation of methyl alcohol with Ni-Co catalyst in alkaline electrolyte (6M KOH). Measurements were performed for methanol concentrations equal of 0.01, 0.1, 0.5, 1, 2, 3, 4, 5 and 6M.

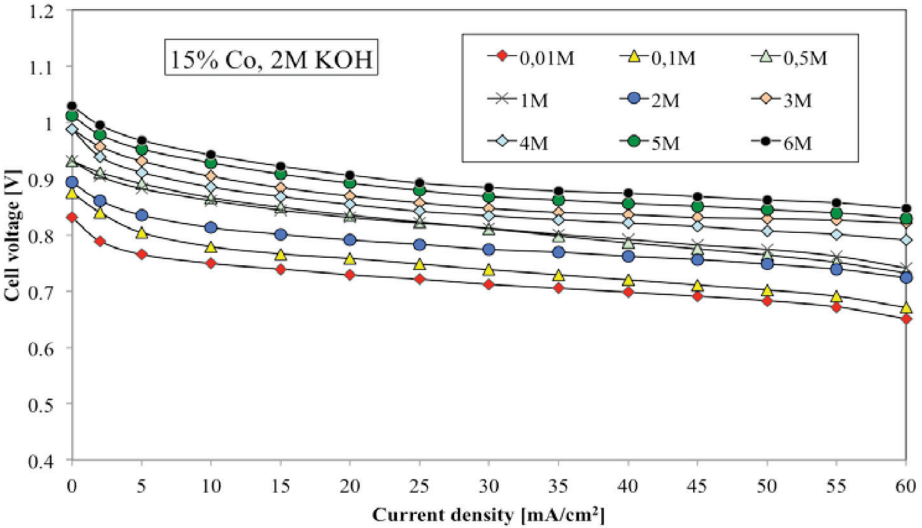

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Figure 1. The polarization curves of electrooxidation of methyl alcohol with Ni-Co catalyst in alkaline electrolyte (2M KOH), Ni-Co alloy contained 15% of Co

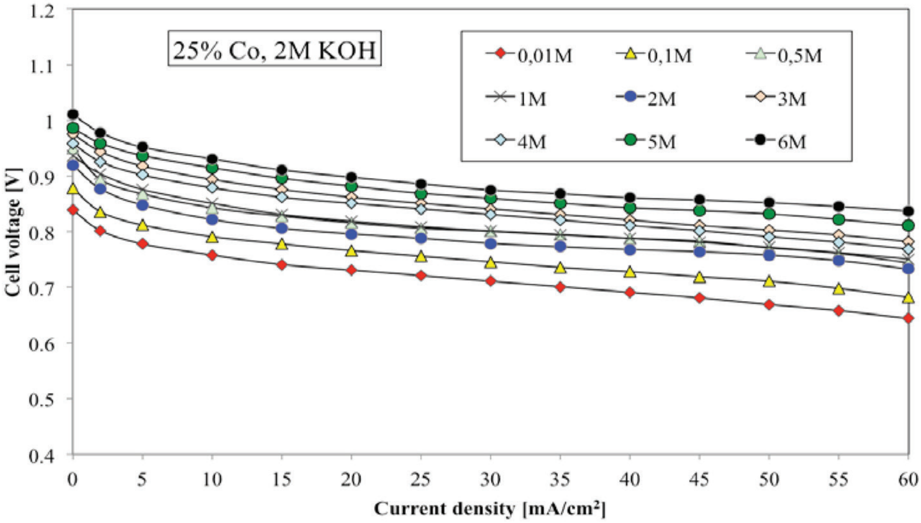

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Figure 2. The polarization curves of electrooxidation of methyl alcohol with Ni-Co catalyst in alkaline electrolyte (2M KOH), Ni-Co alloy contained 25% of Co

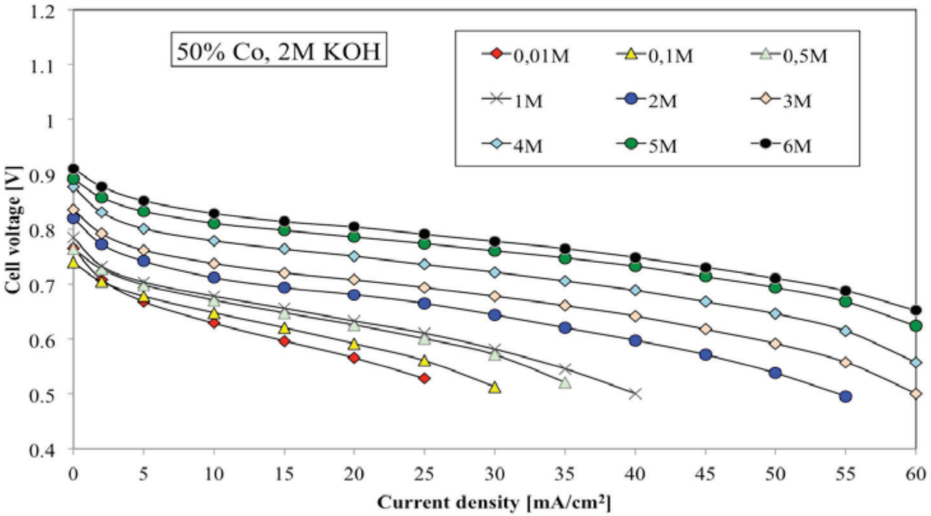

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Figure 3. The polarization curves of electrooxidation of methyl alcohol with Ni-Co catalyst in alkaline electrolyte (2M KOH), Ni-Co alloy contained 50% of Co

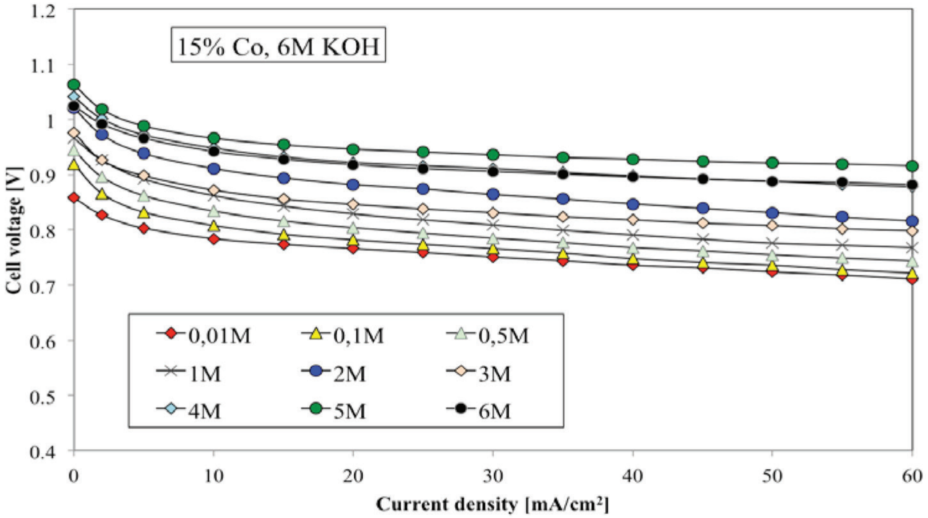

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Figure 4. The polarization curves of electrooxidation of methyl alcohol with Ni-Co catalyst in alkaline electrolyte (6M KOH), Ni-Co alloy contained 15% of Co

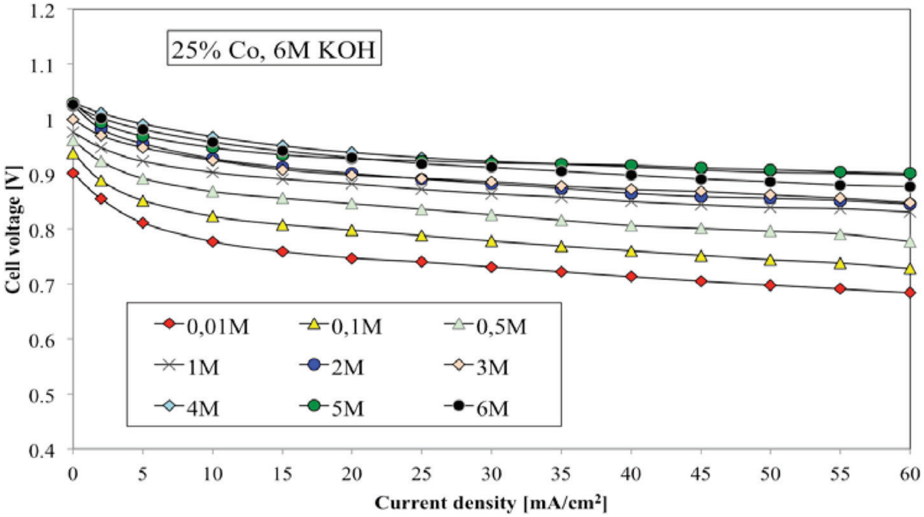

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Figure 5. The polarization curves of electrooxidation of methyl alcohol with Ni-Co catalyst in alkaline electrolyte (6M KOH), Ni-Co alloy contained 25% of Co

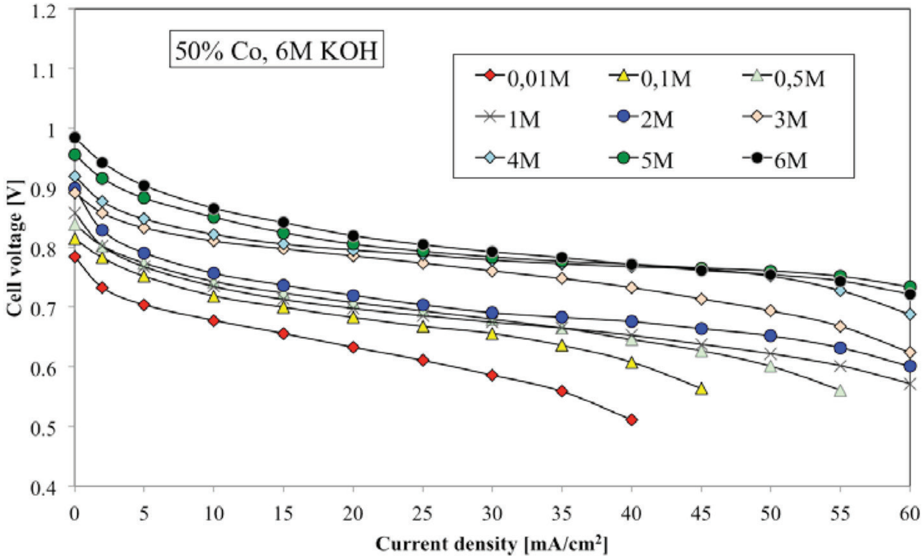

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Figure 6. The polarization curves of electrooxidation of methyl alcohol with Ni-Co catalyst in alkaline electrolyte (6M KOH), Ni-Co alloy contained 50% of Co

In any case, the process of electrooxidation of methanol occurs. A current density of about 10-20 mA/cm^2 has been obtained for all concentrations of methyl alcohol (Fig. 1-6). Maximum current density (50 mA/cm^2) was obtained for 15% of Co in alloy (Fig. 1 and Fig.4). It should be noted that at 50% of Co, there is a sudden fall of current density.

CONCLUSIONS

Measurements were conducted for concentration of methyl alcohol in range from 0.01 to 6M (0.01, 0.1, 0.5, 1, 2, 3, 4, 5 and 6M) and for two concentrations of KOH (2M and 6M). All measurements were carried out at a temperature of 313K. The electrooxidation of methanol took place for each alloy (15, 25 and 50% of Co). Moreover, in any case, for all concentration of methanol and for two concentrations of electrolyte, the process of methanol electrooxidation with Ni-Co alloy as catalyst occurred. A current density of half-cell with Ni-Co electrode with 15 and 25% of Co of about 23-35mA/cm^2 was obtained for all concentrations of methyl alcohol. For Ni-Co electrode with 50% of Co, a current density of about 9-21mA/cm^2 was obtained. A maximum current density of methanol electrooxidation with Ni-Co alloy as catalyst was equal 50 mA/cm^2. This value was obtained for Ni-Co alloy with 15% of Co, and for concentration of KOH equals 6M. Conducted measurements show that there is a possibility of electrooxidation of methyl alcohol with Ni-Co catalyst.

Platinum and Pt/Ru electrodes are the basic catalysts for obtaining high current density of cell (Chung *et al.* 2016; Tripković *et al.* 2002). Certainly, electrooxidation with Pt or Pt/Ru electrode allows to obtain a higher current density than with Ni-Co alloy (Li and Xing 2009; Steigerwalt *et al.* 2001), but the price of Ni-Co catalyst is much smaller than price of Pt. Also 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). For this reason nickel is more difficulty for use than Ni-Co alloy.

The fundamental possibility of methyl alcohol electrooxidation with Ni-Co electrode in alkaline electrolyte (aqueous solution of KOH) was presented in this paper. The obtained current density and power of glass fuel cell is low, but it was demonstrated a fundamental possibility of using Ni-Co alloy (mainly with high concentration of Ni = 15%) as catalyst for methanol electrooxidation.

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