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METHANOL ELECTROOXIDATION WITH Cu-B CATALYST

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Abstract

In the last few years alternative energy sources have been fast developing. One of these sources is fuel cell. Due to development of the renewable energy sources, the powering of fuel cells with bio-fuels is very important. The one of this fuel is methanol. 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 fuel cells. The paper presents a study of methanol electrooxidation on electrode with Cu-B alloy catalyst. Researches were done by the method of polarizing curves of electrooxidation of methanol in glass vessel. An aqueous solution of KOH was used as the electrolyte. Conducted measurements show that there is a possibility of electrooxidation of methanol on Cu-B catalyst. In any case, the process of electrooxidation of methanol occurs. A current density of about 10-20 mA/cm2 has been obtained for all concentrations of methanol and B in alloy. So, the work shows possibility to use Cu-B alloys as catalysts for fuel electrode of DMFC.

Keywords: fuel cell, methanol, bio-fuel, electrooxidation, Cu-B catalyst, renewable energy sources, environment engineering

INTRODUCTION

In recent decades the energy consumption has increased very much due to the increase of the standard of living. Energy production is generally based on coal, nuclear energy, natural gas, crude oil, etc. Currently also some alternative energy sources have been developing. They are used with wind turbines, heat

pumps, solar collectors, photovoltaic cells and more. One of these ecological sources of electric energy is also fuel cell (FC), mainly due to high efficiency and low influence on environment (Redey 1970; Hoogers 2003; O'Hayre *et al*. 2005; Stolten 2010). Although the operation principle of a FC has been known nearly 180 years (Grove, 1839), they still are not widely used. Fuel cells have been successfully used in aerospace (Nowicki and Zięcina 1989; Hoogers 2003; Freeh *et al*. 2004; Barbira *et al*. 2005). But 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 (Appleby and Foulkes 1988; Kakaç *et al*. 2007), the cost may be the deciding parameter. Wide use of FCs may improve air quality and influence the global warming reduction, because fuel cells transform the chemical fuel into electricity without intermediate stages (combustion). Therefore, the real efficiency reaches even 80% (Hoogers 2003; O'Hayre *et al*. 2005; Stolten 2010). Moreover, FCs have many other advantages, e.g. they have no moving parts and are noiseless (Redey 1970; Larminie and Dicks 2003). 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). 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 (Vielstich 1969; Harrison and Khan 1970; Włodarczyk and Włodarczyk 2013). For many years, measurements of selection of biofuels also have been conducted (Hamnett 1997; Kelley *et al*. 2000; Milewski and Lewandowski 2013; Włodarczyk and Włodarczyk 2015b; Włodarczyk and Włodarczyk 2015d; Włodarczyk and Włodarczyk, 2016). Additionally, the new catalysts allow eliminating the costly platinum (Asazawa *et al*., 2007; Rolison at al., 1999; Steigerwalt at al., 2001; Włodarczyk and Włodarczyk 2015b; Włodarczyk and Włodarczyk, 2015e; Włodarczyk and Włodarczyk 2015f). 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 fuel cell. So, search of new low cost catalysts is essential for commercialization of FCs. Development of platinum substitutes has been studied intensely, but further improvement of output performance is still required for practical use (Bashyam and Zelenay 2006; Matsumoto *et al*. 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 methanol. Methanol is the simplest alcohol, being only a methyl group linked to a hydroxyl group. Methanol is a light, volatile, colorless, flammable liquid with a distinctive odor very similar to that of ethanol. Moreover, methanol is a biofuel. Moreover, methanol is a biofuel. So, developing of direct methanol fuel cells (DMFCs)

will allow develop a renewable energy sources. Methanol can be produced in conventional steam reforming. It is the simplest and most widely practiced route to synthesis gas production (Cheng and Kung 1994). Methanol can be produced also from biomass (Dong and Steinberg 1997; Hiranoa *et al*. 1998; Wyman *et al*. 1993). This solution is a future solution, due to obtaining energy from renewable sources (Hamelinck and Faaij 2002).

The methanol can be use as fuel for fuel cell. The DMFC relies upon the oxidation of methanol on a catalyst layer to form carbon dioxide. Water is consumed at the anode and is produced at the cathode. Protons (H^+) are transported across the proton exchange membrane (most often Nafion) to the cathode where they react with oxygen to produce water. Electrons are transported through an external circuit from anode to cathode, providing power to connected devices. The reactions in DMFC are represented by the equations (1), (2) and (3) (Hamnett 1997; Hoogers 2003; Kelley *et al*. 2000; Larminie and Dicks 2005).

ANODE $$CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2 \quad (1)$$

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

OVERALL REACTION $$CH_3OH + \tfrac{3}{2}O_2 \rightarrow 2H_2O + CO_2 \quad (3)$$

The operation of the DMFC (Hoogers, 2003; Kelley at al., 2000; Larminie and Dicks, 2005) is shown in Figure 1.

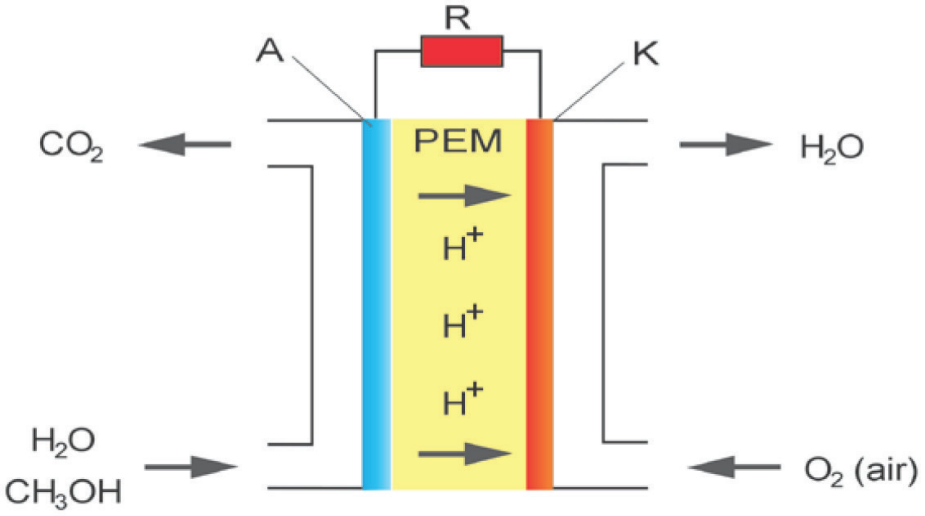

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Figure 1. Direct methanol fuel cell with PEM (proton exchange membrane) A – anode, K – cathode, R – electricity receiver, PEM – proton exchange membrane

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). 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 and Reddy 2000). 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

The Cu-B alloy was used as catalysts for fuel electrode. Cu-B alloys were obtained by the method of electrochemical deposition. The alloys were deposited on smooth surface of titanium electrode. The alloys were deposited from a mixture of mainly $NaBH_4$ and $CuSO_4$ (Włodarczyk and Włodarczyk 2014b; Włodarczyk and Włodarczyk 2014c; Włodarczyk and Włodarczyk 2015a). The alloys were obtained at temperature of 365K.

Table 1. Mixture composition for deposited Cu-B alloy on copper electrode

Component	Concentration [mol/l]
$CuSO_4 \cdot 7H_2O$	0,05
$NaBH_4$	0,02
NaOH	1,00
Trilon B	0,12

Source: Own compilation

Before the deposition of the alloy, copper electrode was prepared in several steps:

- surface was mechanically purified to a shine,
- surface was degreased in 25% aqueous solution of KOH (after the degreasing the surface shall be completely wettable with water),
- electrode was digested in acetic acid,
- electrode was washed with alcohol.

The chemical composition of Cu-B alloys was determined with the X-ray diffraction method (XRD). The alloy selected for measurements was Cu-B alloy with 3, 9 and 15% of B. Researches were done by the method of polarizing curves of electrooxidation of methanol in glass vessel, on Cu-B 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 of methanol electrooxidation in alkaline electrolyte, for various concentrations of methanol (0.1, 0.2, 0.3, 0.4, and 0.5M) and for concentrations 2M of KOH, were carried out at a temperature of 313K.

RESULTS

Figure 2 shows dependence of deposition time on percentage of B.

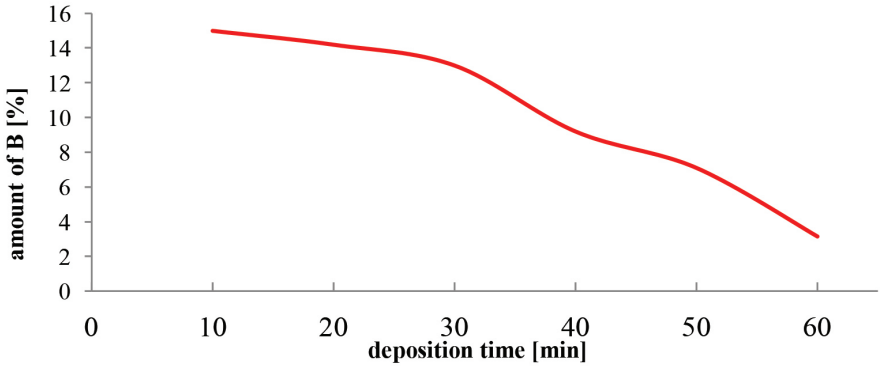

Figure 2. Dependence of deposition time on percentage of B

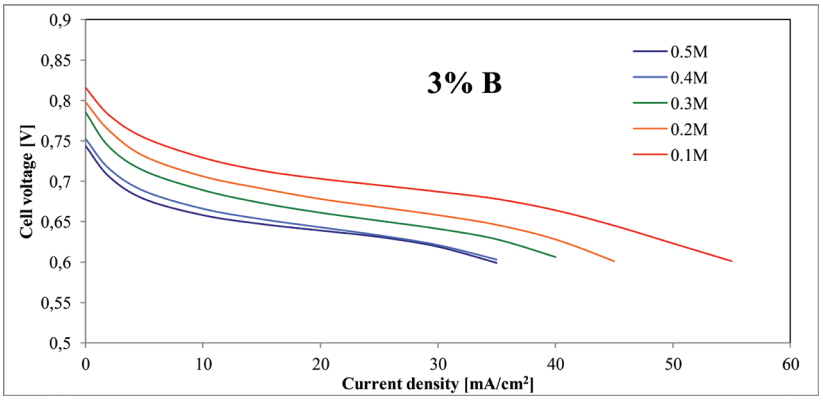

Figure 3. The polarization curves of electrooxidation of methanol with Cu-B catalyst in alkaline electrolyte (2M KOH) (Cu-B alloy contained 3% of B)

Figures 3-5 show the polarization curves of electrooxidation of methanol with Cu-B catalyst in alkaline electrolyte (2M KOH). Measurements were performed for methanol concentrations equal of 0.1, 0.2, 0.3, 0.4, and 0.5M.

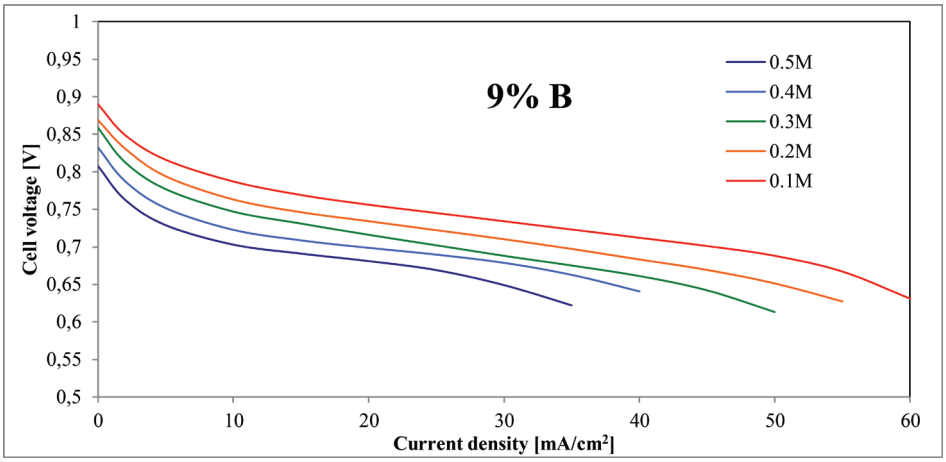

Figure 4. The polarization curves of electrooxidation of methanol with Cu-B catalyst in alkaline electrolyte (2M KOH) (Cu-B alloy contained 9% of B)

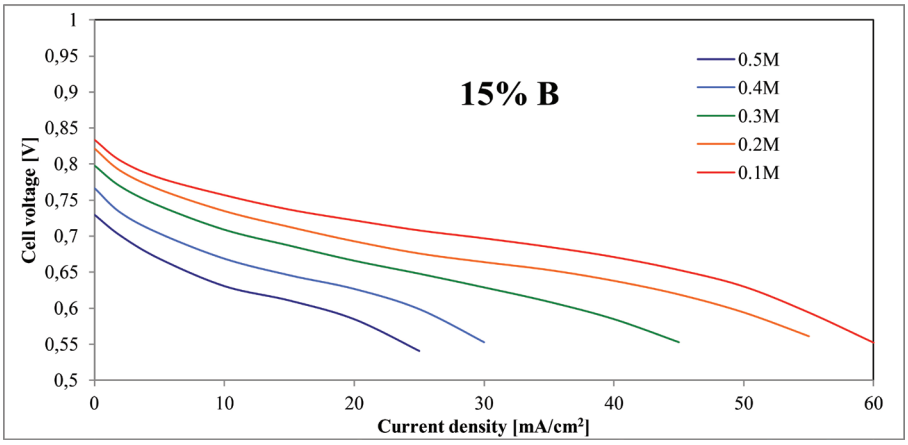

Figure 5. The polarization curves of electrooxidation of methanol with Cu-B catalyst in alkaline electrolyte (2M KOH) (Cu-B alloy contained 15% of B)

During the measurements the deposition time was analysed in the range of 10-60 min (fig. 2). It should be noted that along with increasing time of deposition, the percentage of boron in the alloy decreases. At 10 min the boron part

was over 15%. While at 60 minutes, the B part was only 3% (fig. 2). Carried out measurements indicate that the methanol electrooxidation on the Cu-B catalytic converter Cu-B occurs for all concentrations of B (3, 9, and 15%) in the catalyst and for all the methanol concentrations (0.1, 0.2, 0.3, 0.4, and 0.5 M) (figs. 3-5). However, while the B concentration increases, the current density decreases. And with the increase in the concentration of boron to 15% a sudden drop in current density occurs (fig. 5). This sudden drop in current density (for 15% B) occurs (in 2M aqueous solution of KOH) for all concentrations of methanol. In this case (15% B) for 0.5M concentration of methanol the current density of about 20 mA/cm^2 was obtained. And for 0.1M concentration of methanol the current density of about 35 mA/cm^2 was obtained. But for 9% of boride and for 0.5M concentration of methanol the current density of about 25 mA/cm^2, and for 0.1M of about 50 mA/cm^2 was obtained. The highest current density during electrooxidation of methanol in 2M KOH was obtained for 9% of boride in catalyst. For 9% concentration of B in catalyst occurs for all concentrations of methanol (0.1, 0.2, 0.3, 0.4, and 0.5 M) (fig. 4). Maximum current density of about 50 mA/cm^2 was obtained for 0.1M concentration of methanol (fig. 4).

CONCLUSIONS

Measurements were conducted for concentration of methanol in range from 0.1 to 0.5M and for one concentrations of KOH (2M). Conducted measurements show that there is a possibility of electrooxidation of methanol on Cu-B catalyst. 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 methanol (fig. 3-5). Maximum current density (50 mA/cm^2) was obtained for 9% of B in alloy (fig. 4). The current density is low, but the price of Cu-B catalyst is about 5000-6000 times smaller than price of Pt.

A possibility of methanol electrooxidation with Cu-B catalyst in alkaline electrolyte was presented in this paper. So, it is possible to use Cu-B alloy as catalyst of fuel electrode for fuel cells powering with bio-fuel. But this alloy as catalyst has a too low current density to build an efficient DMFC. However, the main advantage compared to platinum is the price. Moreover, compared to e.g. Raney Ni, the Cu-B alloy is easier to use (Armour, 2003). Due to the low current density but also low cost in comparison to platinum, Cu-B alloy can be used mainly as a catalyst for stationary DMFC.

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