Electrooxidation of canola oil with Pt catalyst in acid electrolyte

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Abstract

In recent decades the demand of energy has increased significantly. Providing more and more energy is an essential task of today's energetic industry. Energy production is based on crude oil, coal, natural gas and nuclear energy. Within the recent few years also alternative energy sources have been developing. One of these sources is fuel cell (FC), mainly due to their high efficiency. FC performs direct conversion of chemical fuel into electrical energy, without combustion. Generally FCs are powered by hydrogen. However, problems with the storage of hydrogen are the reason for the search of new fuels for FCs. Due to development of the renewable energy sources, the powering of high efficiency power sources with bio-fuels is very important. Vegetable oil is an alternative fuel for Diesel engines and for heating oil burners. Powering high efficiency power sources like fuel cells with renewable fuels (like vegetable oil) will allow development of renewable energy sources and elimination or reduce of toxic substances emissions. So, the paper presents the possibility of using canola oil as fuel for FCs. The work shows possible electrooxidation of canola oil emulsion prepared on the basis of a non ionic surfactant on a smooth platinum electrode in an aqueous solution of H_2SO_4. The resulting current density reached the level of 8 mA/cm^2, which means the possibility of using canola oil as fuel for FCs has been proved.

Keywords: renewable energy sources, fuel cell, environment protection, clean technology, canola oil, electrooxidation

Streszczenie

Elektoutlenianie oleju rzepakowego na katalizatorze platynowym w wodnym roztworze H_2SO_4

W ciągu ostatnich dziesięcioleci zapotrzebowanie na energię znacząco wzrosło. Dzisiejszy przemysł energetyczny zmaga się ze stale zwiększającym zapotrzebowaniem na energię. Do produkcji energii najczęściej wykorzystuje się węgiel, ropę naftową, gaz ziemny oraz energię atomową. W ostatnim czasie coraz silniej rozwija się energetyka niekonwencjonalna w tym czyste technologie. Jednym z takich rozwiązań są ogniwa paliwowe, głównie ze względu na ich wysoką sprawność. Ogniwa paliwowe przetwarzają energię chemiczną bezpośrednio na energię elektryczną, z pominięciem procesu spalania paliwa. Najczęściej zasilane są wodorem, jednak problemy z jego przechowywaniem wymuszają poszukiwanie innych paliw. Ze względu na rozwój odnawialnych źródeł energii koncepcję stanowi połączenie wysokosprawnych ogniw paliwowych z możliwością wykorzystania biopaliw do ich zasilania. Jedno z takich paliw może stanowić olej rzepakowy.
Praca przedstawia badania nad elektroutlenianiem emulsji oleju rzepakowego na elektrodzie platynowej w wodnym roztworze H_2SO_4. Uzyskana gęstość prądu wyniosła 8 mA/cm^2. Wykazano więc, że istnieje możliwość bezpośredniego zasilania ogniw paliwowych olejem rzepakowym.

Słowa kluczowe: odnawialne źródła energii, ogniwo paliwowe, ochrona środowiska, czyste technologie, olej rzepakowy, elektroutlenianie

1. 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, crude oil, natural gas, nuclear energy, 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 sources is also fuel cell (FC). Principle of operation of the FC is known from 1839 [1]. The theoretical efficiency of a reversible galvanic cell can be equal to 100%. In fact, the

real efficiency varies between 40-80% [2, 3]. In addition, zero or low negative influence on the environment and silent operation is what characterizes fuel cells. Generally, FCs are powered by hydrogen [4,5]. However, problems with storage of hydrogen are the reason for the search of new fuels for FCs [6-8], also using biofuels [9-13]. The search of new catalysts for FCs is also very important to lower costs of electrodes production [14, 15]. The paper presents the possibility of direct using canola oil as fuel for low temperature FCs.

2. Theory

2.1. Canola oil

Vegetable oil is an alternative fuel for Diesel engines and for heating oil burners. One of the vegetable oils is canola oil. The canola seed is 40% oil by weight. Potentially harmful gums and waxes, present in all oils seeds, are low in canola. Higher levels may require removal, which adds to the expense and complexity of obtaining a diesel fuel extender. This product is not hazardous, nor is it a controlled product. It is flammable upon open flame above the flash point and can be extinguished using foam, CO_2, dry chemical or water spray. Fumes may evolve upon burning [16, 17].

Canola oil is often used as additive for biodiesel fuel. Biodiesel is most commonly used as a blend with petroleum diesel fuel. All manufacturers of diesel vehicles and engines have approved the use of B5 (a blend containing 5% biodiesel and 95% petroleum diesel), and some approve the use of blends up to B20 (20% biodiesel and 80% petroleum diesel) or higher up to 100% biodiesel (B100) [17-19].

Canola seed oil has low energy content (39 MJ/kg) compared the diesel fuel (45 MJ/kg), but it is an environmentally friendly alternative to using diesel fuel. There has been an increasing demand for this type of fuel since it is ecologically safe for application in sensitive areas such as waterways, forestry or agriculture. This type of product is biodegradable, i.e. it can be broken down naturally [20, 21].

Due to the biofuels search for fuel cells we should pay attention on canola oil. Powering high efficiency power sources and renewable fuels will allow development of renewable energy sources and elimination or reduce of toxic substances emissions.

2.2. Efficiency of fuel cell

The efficiency of the fuel cell can be calculated from Equation 2.1 [22-24].

$$\eta = \frac{\Delta G}{\Delta H} = 1 - \frac{T \Delta S}{\Delta H} \qquad (2.1)$$

where ΔG is the change in Gibbs free energy [kJ/mol], ΔH is the change in enthalpy [J/kg], ΔS is the change in entropy [J/K] and T is the absolute temperature [K].

The equation (2.1) shows that the efficiency of the cell depends on the magnitude and sign of entropy. From the equation we see that if for the reaction in a fuel cell $\Delta H > 0$ and $\Delta S > 0$, then thermodynamic factor of efficiency $\eta < 1$ and it decreases with the increase of the temperature [25].

The maximum energy of chemical conversion of the energy into work is equal to the free energy reaction [24, 26]

$$\Delta G = \Delta H - T \Delta S \qquad (2.2)$$

Changing the Gibbs free energy ΔG associated with the cell electromotive force $E°$ is represented by the relation [24]

$$\Delta G = -nFE° \qquad (2.3)$$

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

By transforming Equation 2.3 we obtain

$$E° = \frac{-\Delta G}{n \cdot 96.4 \text{ kJ}} \text{ [V]} \qquad (2.4)$$

In a real cell the equation can be written as [2, 3, 27]

$$\Delta G' = -(nF)'E \qquad (2.5)$$

where $(nF)'$ is the real amount of energy obtained from one mole of fuel [kJ].

The relationship between Gibbs free energy in theoretical cell and in real cell shows that the Gibbs free energy in real is always lower in real cell:

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

The electrochemical reactions always involve the transfer of electrons between atoms or molecules. This transfer takes place on the electrode surface. The transfer rate is proportional to the surface on which the reaction is running because the resulting current determines the reaction. 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 [2, 27]

$$i = A \cdot i_0 \cdot \left(e^{\left[\frac{\alpha_a nF}{RT}(E - E_{eq})\right]} - e^{\left[-\frac{\alpha_c nF}{RT}(E - E_{eq})\right]} \right) \qquad (2.6)$$

where i is the electrode current density [A/m^2], A is the electrode active surface area [m^2], i_0 is the exchange current density [A/m^2], α_a is the so-called anodic charge transfer coefficient, α_c is the so-called cathodic charge transfer coefficient, E_{eq} is the equilibrium potential [V] and R is the universal gas constant

or in a more compact form

$$i = i_0 \cdot e^{K \cdot \eta_{act}} \qquad (2.7)$$

where η_{act} is the activation overpotential [V] and K is the factor of dependence of activation overpotential on reaction speed.

The Butler–Volmer exponential function is using to in the modelling of fuel cells [28]. Bockris and Reddy describe the Butler-Volmer equation as "central equation of electrode kinetics" [27].The current density is most important parameter obtained during electrooxidation of fuel in fuel cell. So, it is important to assurance high current density of canola oil electrooxidation. But first we must need to evaluate basic possibility of electrooxidation canola oil with reference (Pt) catalyst [29-31].

3. Material and Methods

Canola oil is a hydrophobic substance and does not conduct the electric current. To cause the conduction an intermediate agent to solve canola oil in water was used. Due to excellent emulsification properties SYNTANOL DS-10 was used as a detergent [32, 33]. SYNTANOL DS-10 is a mixture of primary oxygen-ethylene-glycol ethers of fatty alcohol of C$_{10}$-C$_{18}$ fraction, and is characterized by high superficial activity, emulgation, dispersion, solubilization capabilities [34, 35].After electrooxidation of emulsion SYNTANOL DS-10 can be degraded e.g. promoted by energy transfer reactions or by bacteria [36, 37].
Investigated emulsion was obtained by mixing, in various ratios of canola oil, detergent and water, using a mixer with the speed of 1200 rpm [32]. Stabilization time was 8 hours.
Researches were done by the method of polarizing curves of electrooxidation of canola oil emulsion in glass vessel, on a smooth platinum electrode. Platinum was used as a catalyst due to excellent catalytic properties [27]. Calomel electrode was used as a reference electrode. Researches were done in a glass cell with potentiostat AMEL System 5000.
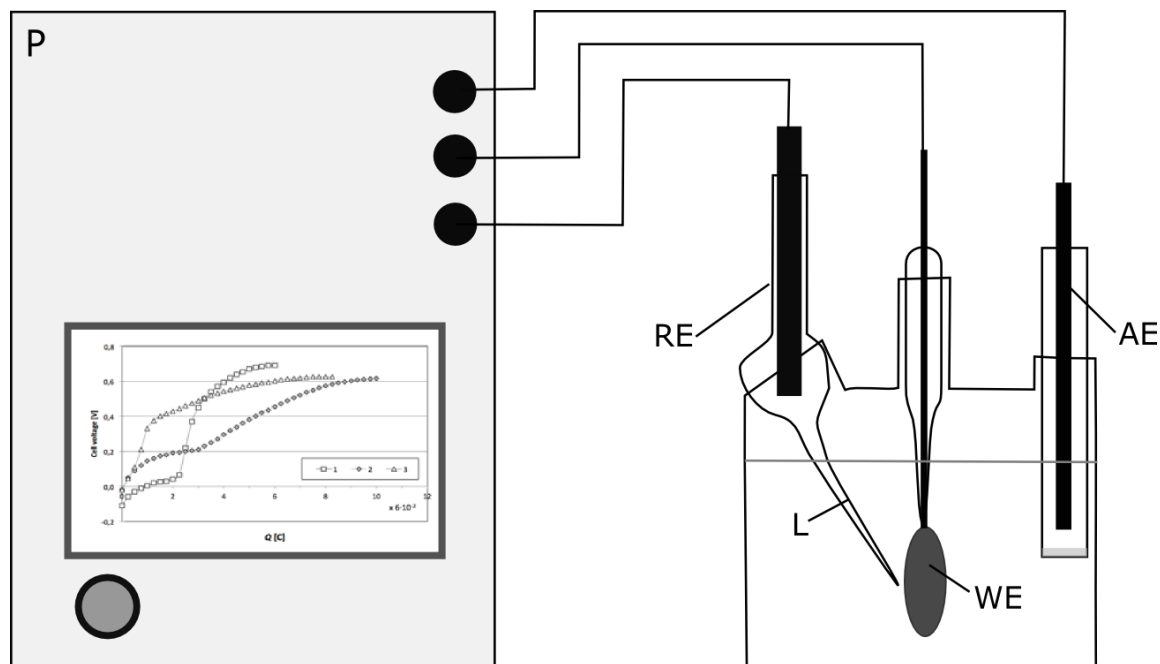
Fig. 3.1.Scheme of research position for research of canola oil emulsion electrooxidation with Pt catalyst. RE - reference electrode (saturated calomel electrode), P – potentiostat, L - Luggin capillary, WE - working electrode (platinum electrode), AE - auxiliary electrode

Researches on electrooxidation of the emulsion based on canola oil in acid electrolyte, for various concentrations of canola oil and detergent, and at various temperatures (20-60°C) are presented in this paper.

4. Results

First was carried researches on electrooxidation of SYNTANOL DS-10 in acid electrolyte, for various concentrations detergent at temperatures 20-60°C.

Figure 4.1 shows the polarization curves of electrooxidation of detergent SYNTANOL DS-10 in 0,1n concentration of electrolyte H_2SO_4 and figure 4.2 shows the polarization curves of electrooxidation of emulsion of canola oil in various concentration of canola oil. The electrooxidation was carried out at a temperature of 20°C.
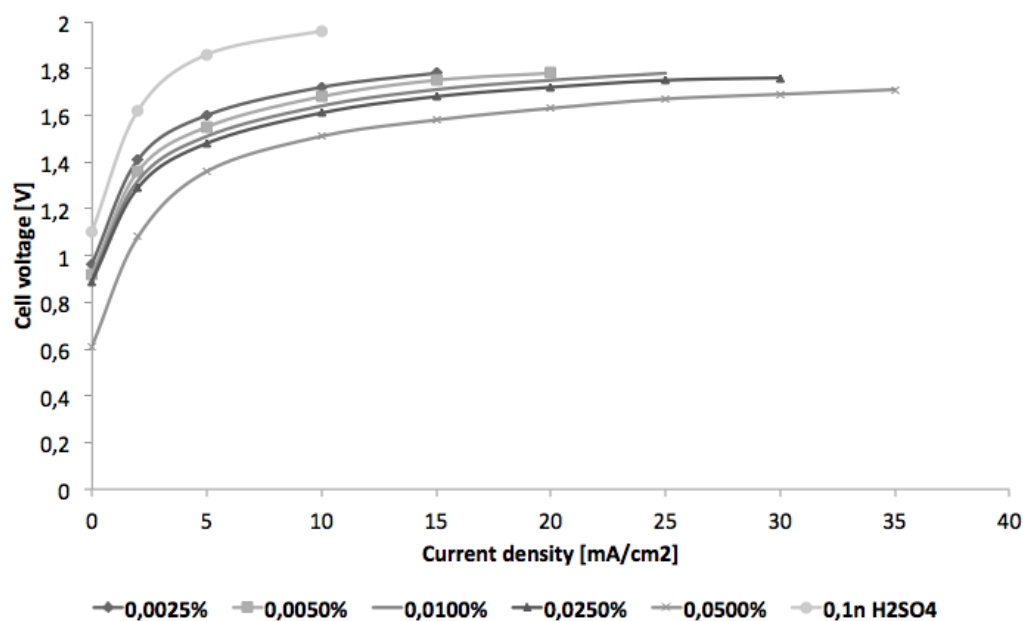
Fig. 4.1. Polarization curves of electrooxidation of detergent SYNTANOL DS-10 in 0,1n concentration of electrolyte H_2SO_4 (at 20°C). Concentration of detergent was equal 0,0025%; 0,0050%; 0,0100%; 0,025% and 0,0500%.
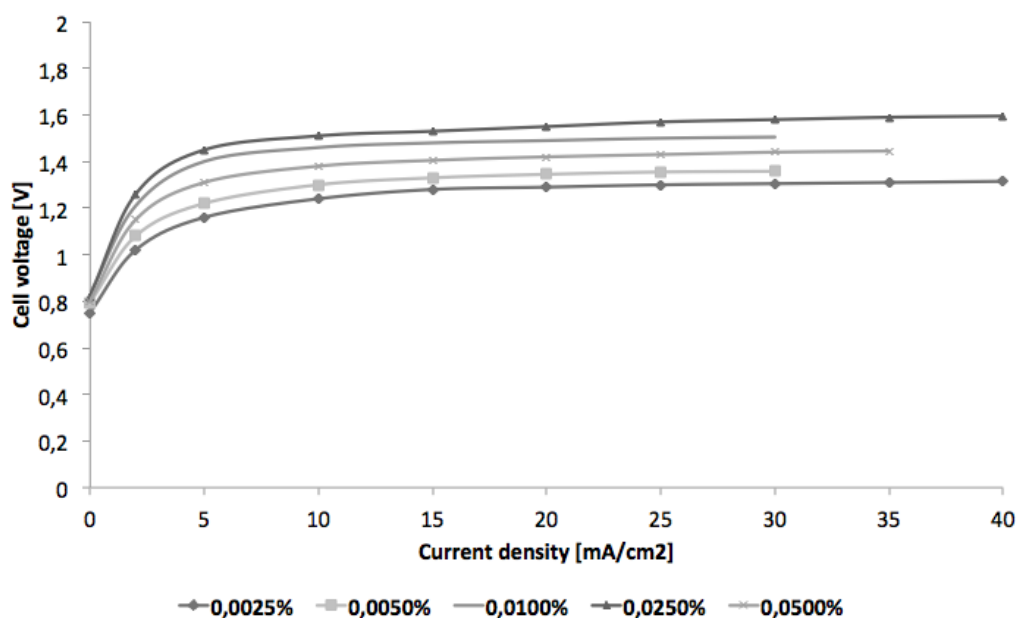

Fig. 4.2. Polarization curves of electrooxidation emulsion of canola oil in 0,1n concentration of electrolyte H_2SO_4 (at 20°C).Concentration of canola oil was equal 0,0025%; 0,0050%; 0,0100%; 0,025% and 0,0500%.

Figure 4.3 shows the polarization curves of electrooxidation of detergent SYNTANOL DS-10 in 0,1n concentration of electrolyte H_2SO_4 and figure 4.4 shows the polarization curves of electrooxidation of emulsion of canola oil in various concentration of canola oil. The electrooxidation was carried out at a temperature of 40°C.
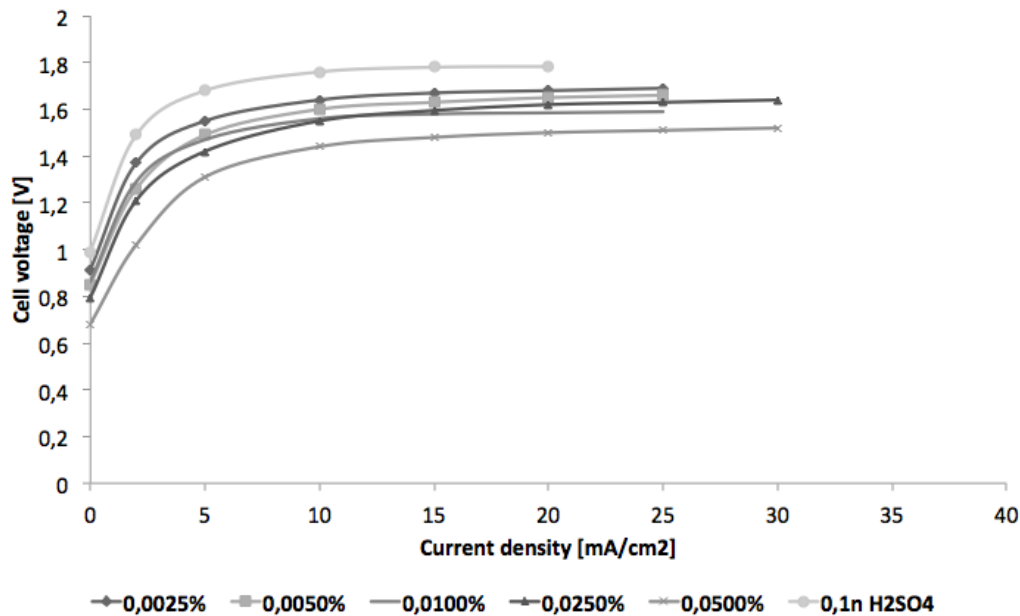

Fig. 4.3. Polarization curves of electrooxidation of detergent SYNTANOL DS-10 in 0,1n concentration of electrolyte H_2SO_4 (at 40°C). Concentration of detergent was equal 0,0025%; 0,0050%; 0,0100%; 0,025% and 0,0500%.

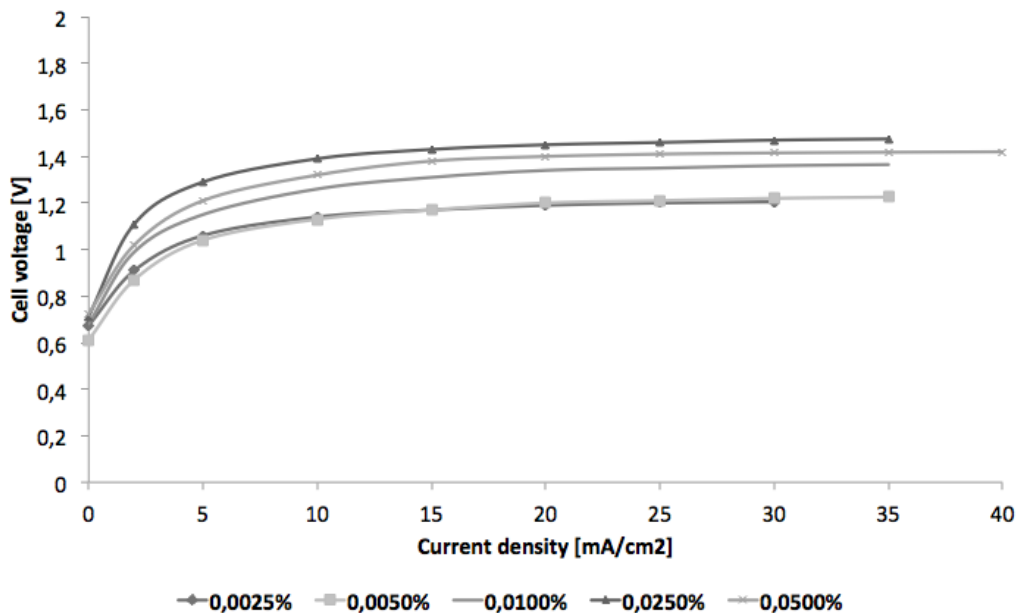Fig. 4.4. Polarization curves of electrooxidation emulsion of canola oil in 0,1n concentration of electrolyte H_2SO_4 (at 40°C).Concentration of canola oil was equal 0,0025%; 0,0050%; 0,0100%; 0,025% and 0,0500%.

Figure 4.5 shows the polarization curves of electrooxidation of detergent SYNTANOL DS-10 in 0,1n concentration of electrolyte H_2SO_4 and figure 4.6 shows the polarization curves of electrooxidation of emulsion of canola oil in various concentration of canola oil. The electrooxidation was carried out at a temperature of 60°C.
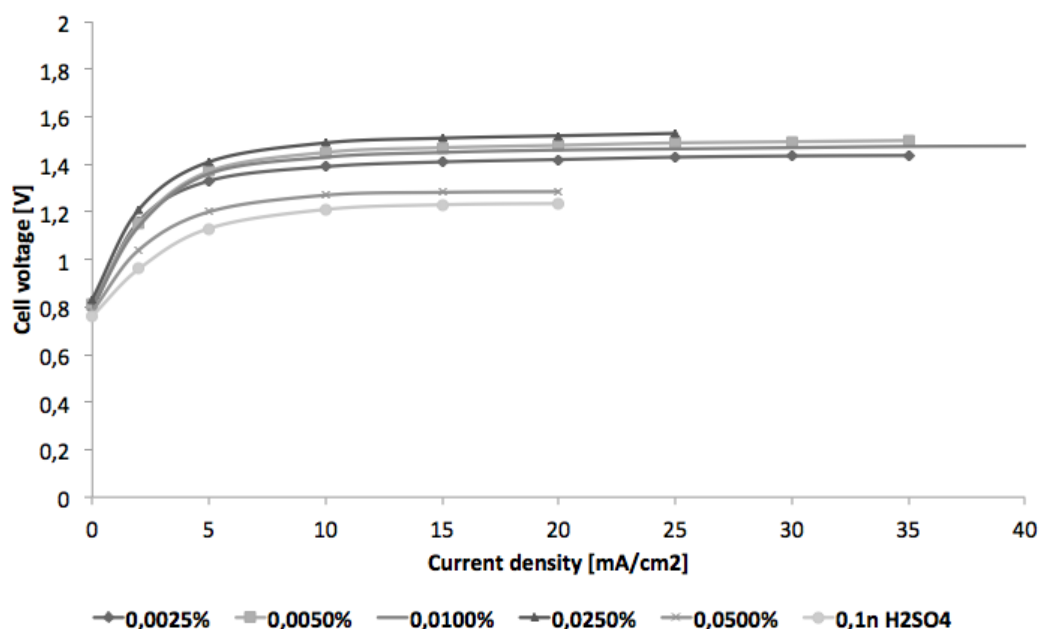

Fig. 4.5. Polarization curves of electrooxidation of detergent SYNTANOL DS-10 in 0,1n concentration of electrolyte H_2SO_4 (at 60°C). Concentration of detergent was equal 0,0025%; 0,0050%; 0,0100%; 0,025% and 0,0500%.

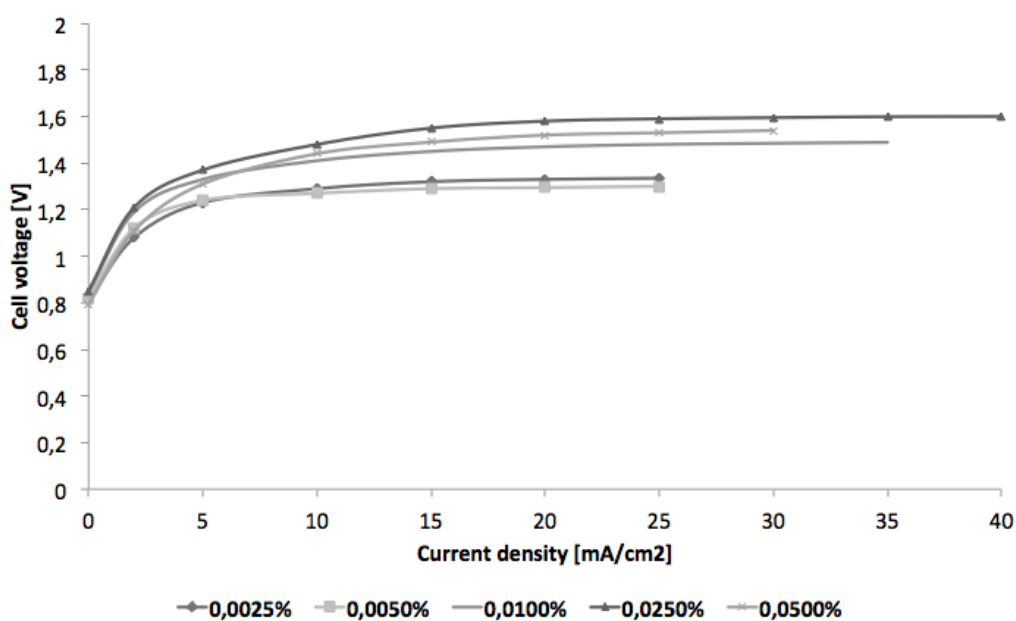

Fig. 4.6. Polarization curves of electrooxidation emulsion of canola oil in 0,1n concentration of electrolyte H_2SO_4 (at 60°C). Concentration of canola oil was equal 0,0025%; 0,0050%; 0,0100%; 0,025% and 0,0500%.

Potential of examined electrode was establishing in time from 15 to 20 minutes and was badly reproducible. Stationary, current-free real potential depends on canola oil concentration and is included in potentials range from 0,62-1,29 V.

To ascertain that the emulsion and not the detergent was electrooxidated, researches of electrooxidation process run in the scope of kinetics, but the potential on electrode is low and establishes in a long period of time. The highest results of potential were obtained for acid electrolyte at the temperature of 40ºC. At 40°C the rate of electrooxidation of canola emulsion is greater than the rate of electrooxidation SYNTANOL DS-10. With the increase in temperature to 60°C first electrooxidation of SYNTANOL takes place, and only then of canola oil emulsion.

5. Conclusions

A fundamental possibility of electrooxidation of canola oil on smooth platinum electrode in acid electrolyte was obtained in this paper. It has been demonstrated that using the detergent to prepare the emulsion of canola oil allows for the electrooxidation of canola oil, and thus a possibility of direct conversion of canola oil into electrical energy. Measurements showed current intensity I of 8 mA from 1 cm^2 of smooth surface platinum electrode at the temperature of 40ºC. Further studies will allow to identify the substances that were left after canola oil electrooxidation.

A fundamental possibility of powering FC with canola oil has been demonstrated (with acid electrolyte). Also, a possible construction of direct powering the fuel cell with canola oil (DCO-FC – direct canola oil fuel cell). It is necessary to undertake studies with a selection of catalysts for DCO-FC and with a selection of proton exchange membranes (PEM) cooperating with emulsion of canola oil. The use the canola oil in FCs will contribute to the fast development of high efficiency green energy sources. This solution will allow to significantly reducing of pollutant emissions in electricity production process. However, the current density is low, so this solution is a suitable for stationary units only.

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