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ELECTROOXIDATION OF DIESEL FUEL IN ALKALINE 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. In the last few years, addition to traditional methods of energy production, alternative energy sources have been developing fast. One of these sources is fuel cell, mainly due to their high efficiency. Generally fuel cells are powered by hydrogen. However, problems with the storage of hydrogen are the reason for the search of new fuels for fuel cells. Moreover, fuel cells can provide an additional/emergency electricity source in energy systems using combustion engines. So, it is important using the main fuel for powering the fuel cell. One of the fuels used for powering the fuel cells could be diesel fuel. Diesel engines drive cars, trucks, boats, tanks and also agricultural machinery e.g. tractors or harvesters. So, there are a lot the possibilities of using this solution. The paper presents results of measurements of electrooxidation of diesel fuel emulsion prepared on the basis of a nonionic surfactant on a smooth platinum electrode in an aqueous solution of KOH. The resulting current density reached the level of 25 mA/cm^2. So, the possibility of using diesel as the fuel for emergency of the fuel cells has been proved.

Keywords: fuel cell, diesel fuel, electrooxidation, additional electricity source, renewable energy sources, environment engineering

INTRODUCTION

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. But in the last few years some alternative energy sources also have been developing fast. There are used heat pumps, solar collectors, photovoltaic cells, with wind turbines and more. One of these sources is a fuel cell (FC). Principle of operation of the FC is known from 1839 (Grove, 1839). The real efficiency of fuel cells varies between 40-80% (O'Hayre at al., 2005; Stolten, 2010). In addition, zero or low negative influence on the environment and quiet operation is what characterizes the fuel cells (Larminie & Dicks, 2003). Generally, FCs are powered by hydrogen (Hoogers, 2003; O'Hayre at al., 2005; Stolten, 2010). However, problems with storage of hydrogen are the reason for the search of new fuels for FCs (Gawdzik at al., 2002; Harrison & Khan, 1970; Redey, 1970; Larminie & Dicks, 2003; Włodarczyk & Włodarczyk, 2013) or also biofuels (Hamnett, 1997; Milewski & Lewandowski, 2013; Włodarczyk & Włodarczyk, 2015b; Włodarczyk & Włodarczyk, 2015c; Włodarczyk & Włodarczyk, 2016). The search of new catalysts for FCs is also very important to obtain high current density and to lower costs of electrodes production (Twigg, 1989; Włodarczyk & Włodarczyk, 2015c; Włodarczyk & Włodarczyk, 2015d), but first there is the need to evaluate a basic possibility of new fuels electrooxidation with reference (Pt) catalyst (Twigg, 1989; Bockris & Reddy, 2000).

Fuel cells can be used as emergency electricity sources (Vielstich, 1965; Vielstich, 1969; Vielstich at al., 2003; Redey, 1970; Stolten, 2010). It is important to use a fuel in vehicles which use internal combustion engines for powering emergency fuel cells. These fuel cells could be used during the vehicles layover, when combustion engines are stopped. One of fuels for powering the fuel cells could be diesel fuel. Diesel engines drive cars, trucks, boats, tanks and also agricultural machinery e.g. tractors or harvesters. So, there is a lot the possibilities of using this solution.

Diesel fuel, in general, is any liquid fuel used in diesel engines, where a fuel ignition takes place, without spark as a result of compression of the inlet air mixture and then injection of a fuel. Diesel fuel is produced from various sources from which the most common is petroleum. Other sources include biomass, animal fat, biogas, natural gas, and coal liquefaction. Petroleum diesel (fossil diesel) is the most common type of diesel fuel. It is produced from the fractional distillation of crude oil in temperature between 200°C (473K) and 350°C (623K) at atmospheric pressure which results in a mixture of carbon chains that typically contain between 8 and 21 carbon atoms per molecule (Collins, 2007).

The current density is most important parameter of a fuel cell (Bockris & Reddy, 2000; Liebhafsky & Cairns, 1968; Vielstich, 1965; Vielstich at al., 2003). Thus, it is important to assure an adequate current density of diesel fuel electrooxidation. The correlation between current density and overpotential is described by the Butler-Volmer exponential function (Bockris & 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. The paper presents the electrooxidation of diesel fuel with Pt catalyst in alkaline electrolyte (KOH) in various temperatures, and various concentration of oil. So, the paper presents the possibility of direct use of diesel fuel as the fuel for low temperature alkaline FCs.

MATERIAL AND METHODS

Summer diesel fuel (B), with the Cold Filter Plugging Point (CFPP) not higher than 0°C, was used as the fuel in measurements. This fuel is used in the moderate climate, during the summer period, i.e. from mid-April to the end of September. Parameters of fuel are shown in table 1.

Table 1. Parameters of diesel fuel

Parameter	Value
Density in temp. 15 ^{o}C [kg/m^3]	820.0-845.0
Concentration of polycyclic aromatic hydrocarbons, max. [%]	7.0
Content of sulphur, max. [mg/kg]	10.0
Content of water, max. [mg/kg]	200.0
Content of solid pollutants, max. [mg/kg]	24.0
Kinematic viscosity in temp. 40^{o}C [mm^2/s]	2.0-4.5
Temperature of Cold Filter Plugging Point (CFPP) [K]	not plugging

Source: own compilation based on data fuel producers and Polish standards for liquid fuels

In the case of using any fuel as the fuel for a fuel cell, conducting the electric current is very important (Bockris & Reddy, 2000). Diesel fuel is a hydrophobic substance and does not conduct the electric current. To cause the conduction there was used an intermediate agent to solve diesel fuel in water. Due to excellent emulsification properties of Syntanol DS-10 it was used as a detergent (Sakharov at al., 1975; Włodarczyk & Włodarczyk, 2013; Włodarczyk & Włodarczyk, 2015a; Włodarczyk & Włodarczyk, 2015b; Włodarczyk & Włodarczyk, 2016). DS-10 is characterized by high superficial activity, emulgation, dispersion and solubilisation capabilities (Survila at al., 2005; Paraska & Karvan, 2010). After electrooxidation of emulsion, Syntanol DS-10 can be degraded e.g. promoted by energy transfer reactions or by bacteria (Ignatov at al., 1995; Kravchenko at al., 1994).

Investigated emulsion of diesel fuel (EDF) was obtained by mixing in various ratios of diesel fuel detergent and water using a mechanical stirrer with the speed of about 1200 rpm (Włodarczyk & Włodarczyk, 2013; Włodarczyk & Włodarczyk, 2015a; Włodarczyk & Włodarczyk, 2015b; Włodarczyk & Włodarczyk, 2016). Emulsion stabilization time was about 8 hours. Before obtaining an emulsion of diesel, the fuel was filtered in a standard automotive fuel filter.

Measurements were done by the method of polarizing curves of electrooxidation of EDF in glass vessel, on a smooth platinum electrode in KOH electrolyte. Figure 1 shows the scheme of the research position for measurements of EDF electrooxidation.

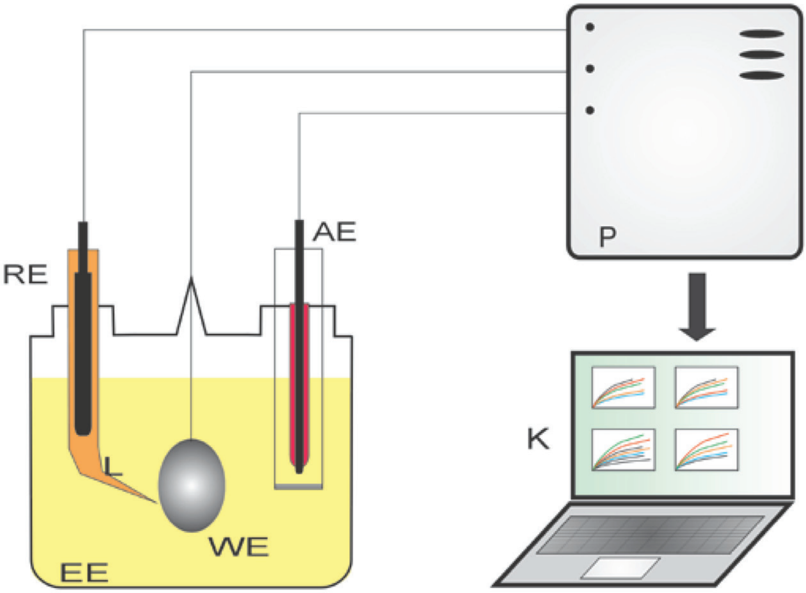

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Figure 1. Scheme of apparatus for EDF electrooxidation (P – potentiostat, WE – working electrode (Pt electrode), L – Luggin capillary, AE – auxiliary electrode, RE – reference electrode (SCE), EE – electrolyte (2M KOH) with EDF, K – computer)

Platinum was used as a catalyst of working electrode due to excellent catalytic properties (Bockris & Reddy, 2000; Twigg, 1989), while saturated calomel electrode (SCE) was used as a reference electrode. In this paper are presented researches on electrooxidation of the emulsion based on diesel fuel in alkaline electrolyte (aqueous solution of KOH) for various concentrations of diesel fuel and detergent and in various temperatures (293-333K). Electrochemical measurements were performed in a glass cell with potentiostat (AMEL System 5000 apparatus connected with computer).

In the next step there was built a prototype fuel cell powered by EDF. Platinum was used as a catalyst of anode and Ni-Co alloy was used as a catalyst of cathode (Włodarczyk & Włodarczyk, 2015d). The anode was used in the mesh form with dimensions 4x1.5 cm. The cathode was also used in the mesh form with dimensions 3x2 cm and it was immersed in aqueous solution of KOH. Ni-Co cathode during the fuel cell working was aerated. Nafion 117 (thickness 183 μm) was used as a proton exchange membrane (PEM), which separates the cathode area (with aerated electrolyte) and anode area. The perforated ABS plastic cover was used as PEM casing. This part was printed on 3D printer (Włodarczyk & Włodarczyk, 2015b). Figure 2 shows the scheme of prototype fuel cell powering of EDF.

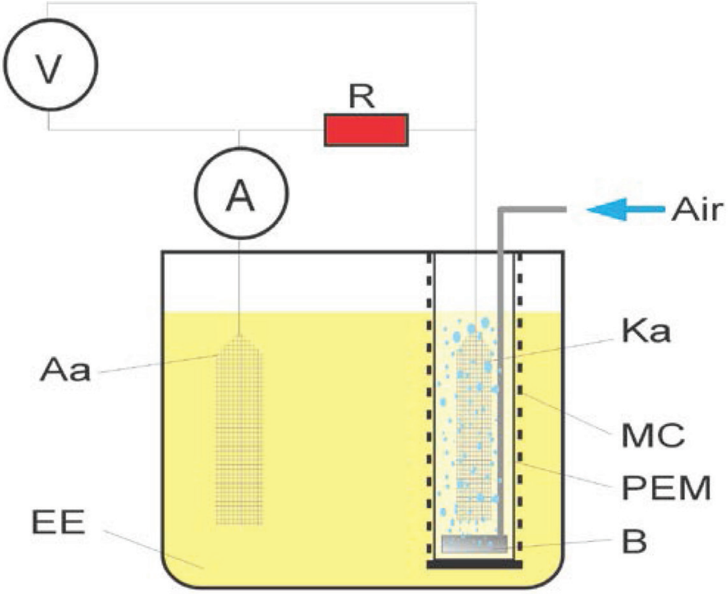

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Figure 2. Scheme of prototype fuel cell powering of EDF (V – voltmeter, A – amperemeter, R – electricity receiver, PEM – proton exchange membrane, MC – membrane cover, An – Pt anode, Ka – Ni-Co cathode, B – bubbler, EE – electrolyte with EDF, Air – air)

RESULTS

First, there were carried measurements on electrooxidation of Syntanol DS-10 in alkaline electrolyte (aqueous solution of KOH). This measurement was allowed to assess whether the current density was formed from the electrooxidation of diesel fuel or only from detergent. Figures 3-5 show the polarization curves of electrooxidation of EDF in various concentration of fuel. The electrooxidation was carried out at temperature of 293-333K.

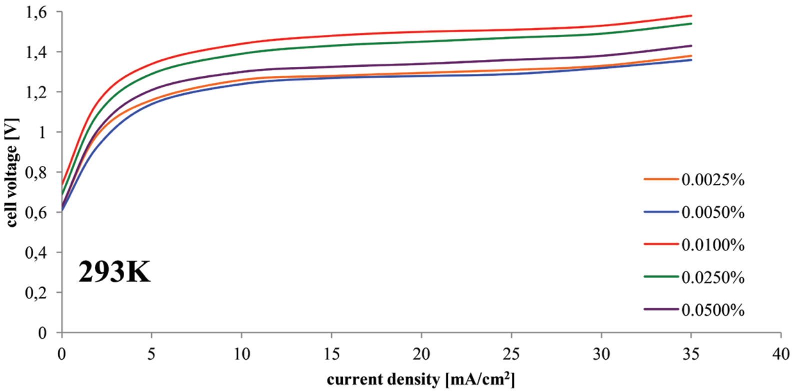

Figure 3. Polarization curves of EDF electrooxidation in 0.1n concentration of electrolyte KOH at temperature 293K; Concentration of diesel fuel was equal 0.0025%; 0.0050%; 0.0100%; 0.025% and 0.0500%

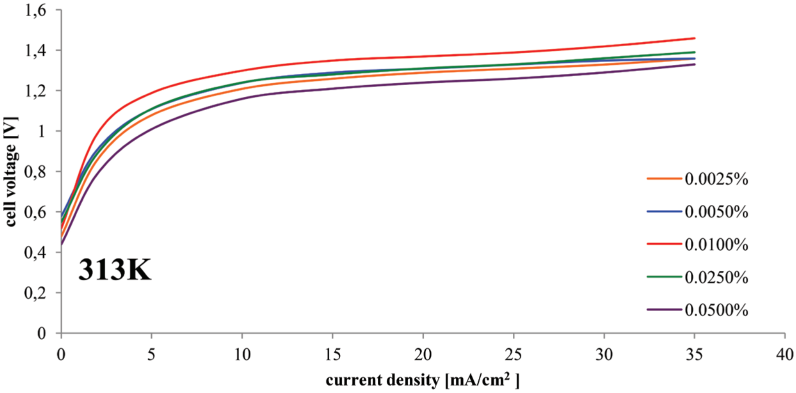

Figure 4. Polarization curves of EDF electrooxidation in 0.1n concentration of electrolyte KOH at temperature 313K; Concentration of diesel fuel was equal 0.0025%; 0.0050%; 0.0100%; 0.025% and 0.0500%

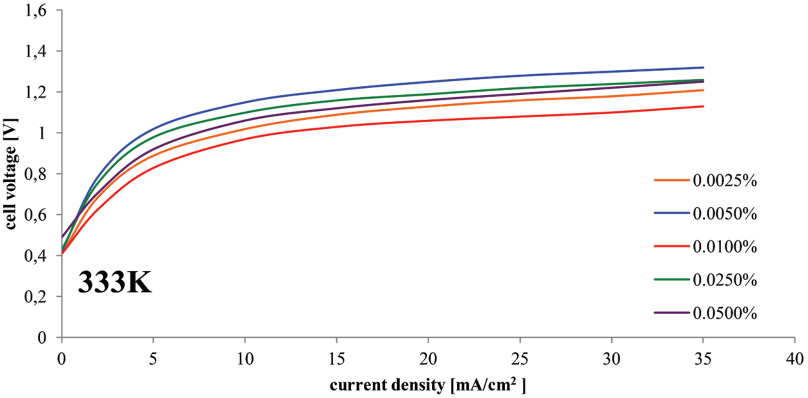

Figure 5. Polarization curves of EDF electrooxidation in 0.1n concentration of electrolyte KOH at temperature 333K; Concentration of diesel fuel was equal 0.0025%; 0.0050%; 0.0100%; 0.025% and 0.0500%

CONCLUSIONS

The potential of the working electrode was establishing in time of about 20 minutes and was badly reproducible. Stationary, current-free real potential depends on diesel fuel concentration and is included in potentials range from 0.63-1.28 V. To ascertain that the emulsion and not the detergent was electrooxidated, measurements of electrooxidation process run in the scope of kinetics but the potential of the electrode is low and establishes in a long period of time. The highest results of the potential were obtained at temperature of 313K. In any case, the process of electrooxidation of EDF occurred. A current density of about 10-20 mA/cm^2 was obtained for all concentrations of diesel fuel. With the increase in temperature to 333K the first electrooxidation of Syntanol DS-10 took place, and only then of EDF.

A fundamental possibility of electrooxidation of diesel fuel on platinum catalyst in alkaline electrolyte (aqueous solution of potassium hydroxide) was presented in this paper. It was demonstrated that use of the detergent Syntanol DS-10 to prepare the EDF allows the electrooxidation of this fuel in aqueous solution of potassium hydroxide, and thus a permits a direct conversion of diesel fuel into electrical energy with alkaline medium. Measurements showed maximum current density of 25 mA from 1 cm^2 of smooth surface platinum electrode in temperature of 333K. The prototype fuel cell (fig. 2) was characterized by power of about 50 mW. The current density and power is low, but it was demonstrated a fundamental possibility of powering alkaline FC with diesel fuel. So, there was also demonstrated a possible construction of direct powering the fuel cell with diesel fuel. However, the current density is low. So, it is necessary to conduct research for increase of current density e.g. with another detergent. The increase of current density will allow to power the emergency fuel cell with diesel fuel. This solution will allow equipping cars, trucks, boats, tanks, tractors or harvesters with an emergency source, powered by the fuel from a main tank.

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