

The Simultaneous Uses of the Direct-Mode Bioorganic Fuel Cell and the Function Generator for the Enhancement of the Glucose Electro-chemical Oxidation

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In this study a test of the direct-mode bioorganic fuel cell (DMBFC) in which the fuel and the alkaline electrolyte are mixed with each other at two temperatures of 20 and 35 °C are carried out. The direct-mode bioorganic fuel cell is exposed to an externally generated electromagnetic field with simultaneous discharging in order to split the fuel molecule before the electrochemical oxidation at the two operation temperatures. The current-voltage characteristics are measured and analyzed. The liquid phase of the fuel-electrolyte concentration of the glucose was analysed both before and after the electrochemical tests at the operation temperature 20 °C. The aim is to continue with the development of the direct-mode glucose fuel cell by increasing the power density range by several mWcm^{-2} . This type of the fuel cell with glucose as a fuel has increased to the specific capacity levels of 120.8 and 132.7 Ah / kg glucose at the temperatures of 20 °C and 35 °C, respectively.

Keywords: direct-mode bioorganic fuel cell, catalyst materials, glucose, electrochemical reforming, function generator

1. INTRODUCTION

The ideal fuel for fuel cells in power generation systems is the direct use of a fuel like glucose, which is produced from cellulose by hydrolysis, in the form of a liquid phase [1-6]. In direct-mode bioorganic fuel cells (DMBFC) in which the fuel glucose and an aqueous electrolyte are mixed with each other the current densities have been very low. Depending on the pH value of the electrolytes, the

current densities have ranged at the temperature of 20 °C from 0.8 to 11 mAcm⁻² with or without the use of the function generators before the discharging of the DMBFC [1-4]. The corresponding capacities have ranged from 470 As to 7321 As [3-4]. The operating capacities of the anode and cathode catalysts have been found to increase as a result of the use of the function generator before the discharging of the DMBFC [4]. As far as glucose is concerned, the total yield of electrons from the molecule in the electro chemical reactions has been two electrons from 24 available electrons [3, 4, 5, 6]. In the DMBFCs the current densities are very low in comparison to current densities of several hundred mAcm⁻² in the direct fuel cells, which are supplied with either hydrogen or alcohols [7, 8]. However, the DMFC is simple to use and provides good application potentials for both small portable equipment and large systems.

In this study a function generator (FG), which produces the high frequency signals, is used simultaneously with the discharging of the DMBFC at two different operation temperatures of 20 °C and 35 °C. The idea is to use the FG for producing an alternating electromagnetic field between the electrodes [4]. The aim is to find out if the electrochemical reforming of glucose molecule could be enhanced more as a result of the simultaneous operations of the DMBFC and FG. Starch and cellulose (polysaccharides) are known to be the main sources for the production of the monosaccharide glucose (C₆H₁₂O₆) by catalytic hydrolysis at elevated temperatures between 150 and 250 °C [9, 10]. The main aspect of this work is to continue with the development of a direct-mode bioorganic fuel cell with an alkaline electrolyte and with a higher power density production through the use of an effective and simple cell configuration. The concentration in the electrochemical oxidation of glucose at 20 °C was obtained with liquid phase component analysis of the samples from the fuel-electrolyte solution mixture before and after use in the DMBFC. The anode catalyst consisted of the bimetallic mixtures of platinum and palladium (Pt-Pd) and the cathode was a combined catalyst of pyrolyzed cobalt porphyrin complex (CoTPP) on carbon together with a spinel (MnCo₂O₄).

2. EXPERIMENTAL PART

The test fuel cell (FC) equipment included as in the earlier tests a direct-mode fuel cell (developed from the commercial fuel cell model HC-100 of Oy Hydrocell Ltd), a recirculation pump (capacity 100 ml / min), an air fan (i.e. a PC cooling fan) and a recirculation tank (a glass bottle) for the fuel-electrolyte solution [2, 3, 4]. The recirculation tank had an electrically controlled heating system (a resistor). The test fuel cell equipment and the electrical connections are shown in Fig. 1.

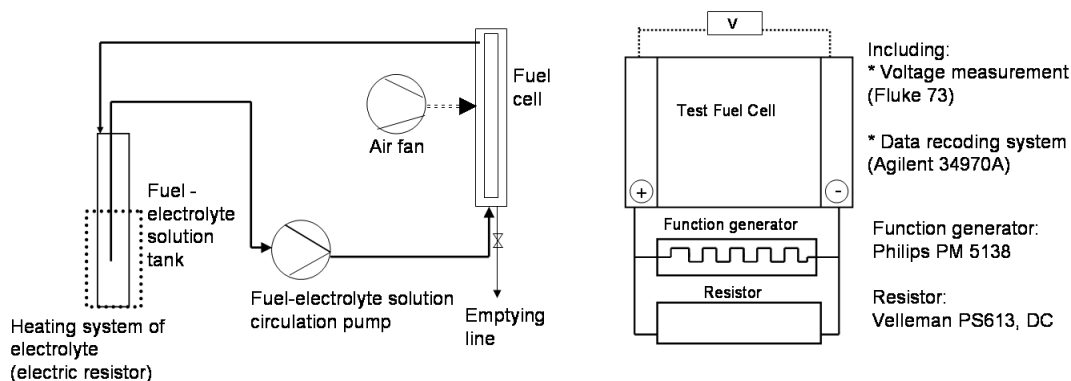


Figure 1. The test fuel cell equipment (on the left) and the electrical connection (on the right).

A FG of Philips PM 5136 was used to create a change in the electro-magnetic field over the electrolyte space in the fuel cell during the discharge of the DMBFC. In the test one type of electromagnetic signal (square) was used. In the tests a square signal with an alternating current (AC) of 0.6 V (+/-20 %) with 5 MHz was used. The current output of the FG was measured to be 30 mA, which corresponds to the electric power of 18 mW_e. The reason for using the low-voltage values of the signals was to prevent the electrochemical decomposition of the water in the test fuel cell under 1 V. Also the lower limit for the voltage of the signals from the FG had to be very near the value of 0.5 V to prevent the possible damage of the cathode electrode of the DMFC.

The progress in the electrochemical oxidation of glucose with preset concentration (C_0) of 1 mol dm⁻³ (M) in an aqueous 2 M potassium hydroxide (KOH) electrolyte is analysed also by liquid analysis from samples from fuel-electrolyte solution before and after use in the DMBFC. The glucose content was determined by using an Aminex HPX-87P column (Bio-Rad) at 70 °C with distilled water as the mobile phase at an elution rate of 0.6 ml min⁻¹. All components were analysed with a refractive index (RI) detector.

The Coulombic efficiency (CE) values of each test were calculated using the recorded current and time values according to Eq. 1 [11]:

$$CE = \frac{(M_w \int I dt) \cdot 100\%}{F n_e V_{an} \Delta C} \quad (1)$$

In Eq. (1) M_w is the molecular weight of glucose, n_e is the number of electrons transferred, V_{an} is the volume of liquid in the anode (0.3 dm⁻³), F is the Faraday constant (96500 As mol⁻¹), and ΔC is a change in the substrate mass concentration ($C_0 - C$). $\Delta C = C_0$ is often used. In Eq. (1) the term $(\int I dt)$ corresponds to the integration of the recorded Coulombs, and the denominator corresponds to the maximum available Coulombs from the initial glucose molar amount in the aqueous electrolyte.

The progress in the electrochemical oxidation of glucose was analysed at the operation temperature of 20 °C also by liquid analysis of samples from fuel-electrolyte solution before and after use in the DMBFC.

3. RESULTS AND DISCUSSION

The current capacity tests of the DMBFC with the simultaneous use of the FG at two temperatures are shown in Fig. 2. The voltage values of the fuel cell were recorded in combination of both with changing current intervals at the beginning and at the end of the test and with relatively constant current value in the middle stage of the test until a decrease in voltage from the OCV to value of 0.5 V was noticed (Fig. 2). After the test runs the function generator was switched off and the OCV of the DMBFC achieved the voltage values of 0.71 V (at 20 °C) and 0.67 V (at 35 °C), indicating that there were still capacity levels left in the fuel to be utilized further.

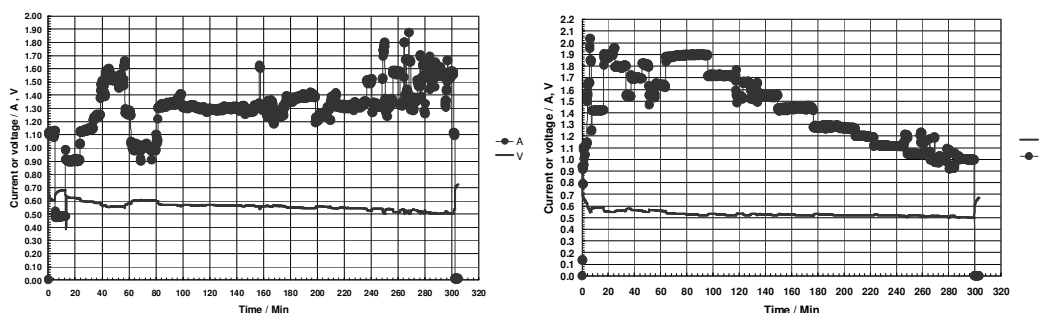


Figure 2. The capacity test of the direct-mode fuel cell at 20 °C (A) and at 35 °C (B) after the simultaneous use of the function signal generator with AC square signals.

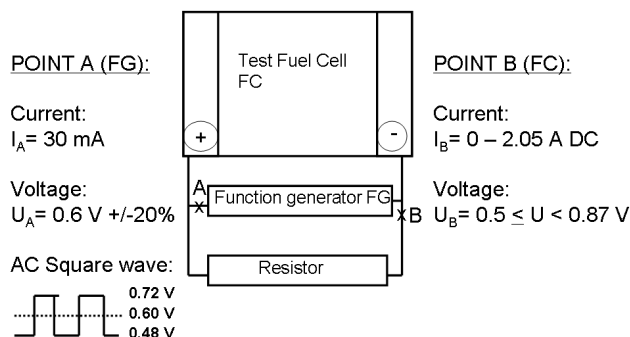


Figure 3. The properties of and flows of the currents from the DMBFC and the FG.

The properties and flows of the current from the DMBFC and the FG in the tests are shown in the Fig. 3.

It can be read from the Fig. 3 that the relative proportion of the current flow from the FG (30 mA) was very small when compared to the extracted current flow (at maximum 2.05 A) from the DMBFC. Therefore the current output from the DMBFC is suggested to be mainly from the electro-chemical oxidation of the fuel glucose.

From the results shown in Fig. 2 it can be concluded that when the electro-magnetic field with a high frequency value is used simultaneously with the discharging of the DMBFC, the capacity of the DMBFC is increased strongly as compared to earlier results when the function generator was used only in OCV state before the discharging [4]. The recorded Coulombs for the experimental tests are shown in Table 1 and the evaluation of the CE value for the fuel cell according to Eq. (1) is shown in Table 2. The CE value was calculated as a ratio to theoretical value when two and at maximum 24 electrons are supposed to be released from one glucose molecule in the electro-chemical oxidation.

Table 1. Recorded Coulombs from the experimental test.

Temperature (°C) / Signal	Coulombs (As) / (Ah)
20 / Square	23490 / 6.50
35 / Square	25836 / 7.20

Table 2. The CE values as ratio to theoretical value with the release of two and 24 electrons per molecule.

Temperature / Signal type (°C)	CE (%)
20 / Square AC	40.6 (2 e- per molecule) 3.4 (24 e- per molecule)
35 / Square AC	44.6 (2e- per molecule) 3.7 (24 e- per molecule)

The recorded Coulombs in Table 1 and Coulombic efficiency values (CE) in Table 2 were shown to be much higher than it was reported earlier, when function generator was used before the discharging of the DMFC with the frequencies of the sine or square AC signals between 20 kHz to 5 MHz at 20 °C (i.e. recorded Coulombs varied from 2778 to 7321 As, CE (2 e- per molecule) values varied from 4.8 % to 12.6 %, respectively [4]). Thus high increases in the recorded Coulombs are detected when the FG is used simultaneously with the operation of the DMFC. The absolute recorded Coulombs (As) correspond the Coulombs per mole glucose (C_o) as 78300 As/mol (21.75 Ah/mol) at 20 °C and 86121 As (23.90 Ah/mol) at 35 °C, which correspond to specific energies of 78.5 Wh/kg (at

20 °C) and 86.3 Wh/kg (at 35 °C) with average voltage of 0.65 V. The concentrations of the glucose samples from fuel – electrolyte solution mixture both before and after the electro-chemical oxidation in the DMBFC at temperature of 20 °C are shown in Table 3.

Table 3. The analysis results for the glucose in liquid samples before and after the electrochemical oxidation in the DMBFC at 20 °C.

The aqueous alkaline fuel - electrolyte solution before the electrochemical oxidation at 20 °C	
Glucose	91.9 g dm⁻³ (0.51 M)
Standard deviation	5.6 %
The aqueous alkaline fuel – electrolyte solution after the electrochemical oxidation at 20 °C	
Glucose	35.2 g dm⁻³ (0.20 M)
Standard deviation	0.5 %
Total reduction rate of glucose	61.7 %

It can be read from Table 3 the analysed concentrations of glucose in the fuel-electrolyte solution before and after the electrochemical oxidation reactions in the DMBFC. The calculated compositions of glucose and KOH were 1 M and 2 M in the aqueous solution, respectively. Therefore, it is assumed that glucose concentration has decreased as a result from reaction with KOH. It is reported earlier that endiolate ions ($C_6H_{11}O_6^-$) are generated from glucose in the strong alkaline solutions [12]. Thus, the reaction products which were not detected by the used analysis method were formed. Also, it is assumed that the oxidation products of glucose might have reacted further with glucose in the DMBFC. There was noticeable change in colour of the used fuel-electrolyte solution: before the electrochemical reactions the colour was yellow and after the electrochemical oxidation in the DMBFC the colour was violet (at 20 °C) and it turned into black (at 35 °C). By using the relative change in the COD value of the fuel-electrolyte solution in our earlier studies, the number of transferred electrons per glucose molecule was approximated to be as two [4]. Based on the analysis results in Tables 3, on the calculated CE value in Table 2, and on the literature [13], the previous assumption is also valid for this study. The CE value of 40.6 % at 20 °C in Table 3 could be included in the total oxidation rate (61.7 %) of glucose. Glucose is mostly oxidised to gluconic acid $C_6H_{12}O_7$ with release of two electrons per one glucose molecule [13]. However, the increased CE values in Table 2 may indicate that the total activity of both the anode and cathode catalysts together with the function generator has increased significantly compared to the previous results [4] when the FG and DMBFC were operated separately. However, further work is needed to assess the oxidation reactions by cyclic voltammetry and rotating ring electrode measurements together with life tests as to the content of the various reaction products in the electrolyte. Also ultimate optimisation of various temperatures higher than 20 °C should be used as increased temperature shows improved electrode kinetics as well

as the diffusivities of the ions. Sugars do not withstand higher temperatures than 40 °C due to decomposition [4] and therefore the temperature has to lie lower than this value.

The polarisation curves of the DMBFC were not measured in these tests, because it was assumed that the FG could not stand the high power loads without malfunction. However it is supposed that the maximum current density value of the DMFC at the voltage of 0.5 V has increased together with the recorded Coulombs from the values between 11 to 13 mA cm⁻² (at voltage of 0.5 V), which were measured in the earlier tests, when the FG was used before the discharge of the FC [4]. Current density of the DMBFC is still lower when compared to those observed in direct fuel cells (hydrogen- or alcohol-fed) with membranes [7, 8], but are much higher than the current density values for microbial and enzymatic biofuel cells [14]. However, when compared to the direct fuel cells the DMFC is simple to use and provides good application potentials for both small portable equipment and larger systems. The DMBFC with high power density could be used for short-term power supply or as a battery charger for small electric equipment. The glucose fuel, which is produced from cellulose materials, provides a good alternative to alcohols (methanol and ethanol) thanks to its renewable and sustainable nature and development. Furthermore, direct use of methanol and ethanol in alkaline electrolytes causes carbonisation of the electrolyte, due to the electrochemical reactions [15, 16].

Based on the results both from our earlier tests and from this test it is assumed that the use of FG or signal generator SG with higher signal frequencies than 5 MHz [4] will cause the release of more than two electrons per glucose molecule in electro-chemical oxidation reactions of the DMBFC. Earlier studies on the near-infrared spectroscopy analysing glucose from aqueous solutions (i.e. from the absorbance bands) [17] show that the required frequencies of the signals from the signal generator have to be increased to higher frequencies in order of magnitudes of THz to cause resonance vibrating, which could break the bonds in glucose molecule. The required frequency of the AC signals from the signal generator has to be confirmed in future tests. If the electron yield from one molecule of glucose increases from 2 towards the 24 available electrons, glucose will be considered better fuel for low-temperature direct fuel cells than liquid alcohols [4].

The AC signals from the FG or SG with the actually much higher frequency values than 5 MHz are important for providing higher current densities in the direct-mode fuel cells. Also the search for more active catalyst materials for both the anode and cathode electrodes could also improve the operating capacities of bioorganic fuel cells. When the concentrations of fuel electrolyte, the frequencies of the function or signal generator and electro catalysts are optimised, higher current densities would be expected and as a result the number of Coulombs extracted from the bioorganic fuel would even increase in this type of direct-mode fuel cells.

4. CONCLUSIONS

An electrochemical test, in which a direct-mode glucose fuel cell FC was connected to a function generator FG at temperatures of 20 °C and 35 °C, has shown promising results in using glucose as a fuel in the fuel cell. Using glucose in an aqueous alkaline electrolyte in the FC together

with the operation of the FG simultaneously, it has attained current capacities of 21349 As (6.50 Ah) at temperature 20 °C and 25836 As (7.20 Ah) at temperature of 35 °C, which correspond to the specific energies of 78.5 Wh/kg glucose (at 20 °C) and 86.3 Wh / kg glucose (at 35 °C). The frequency of the signals has to be increased even more from the value of 5 MHz in order to cause a noticeable increase in both the current density and the specific energy values of the direct-mode fuel cell. The influence of the function or signal generator on the operation of the direct-mode fuel cell has to be optimised in order to further increase the overall current-voltage characteristics by varying the different parameters (the form, the voltage, and the frequency of the electromagnetic signals) together with the higher operation temperature, the concentrations of the fuel and the electrolyte as well as the activity of the catalysts. The extended yield of the electrons from one glucose molecule would make it as an important fuel for the bioorganic fuel cells.

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