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Effect of Temperature on a Direct Glucose Anion Exchange Membrane Fuel Cell in a Near-Neutral-State Electrolyte

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A direct glucose anion exchange membrane fuel cell (AEMFC) with a near-neutral-state electrolyte was studied at varying temperatures of 20, 30 and 37 ^{o}C at two different concentrations of glucose of 0.1 and 0.3 M and with three concentrations of electrolyte of 0.1, 0.2 and 0.3 M $[PO_4]_{tot}$. The prime objective was to show how specific energy (W kg^{-1} glucose) of the direct glucose AEMFC is related to the operation temperature and concentrations of the species. Current and voltage values were measured together with the pHs and conductivities of the electrolytes. No component analysis of the final products after the fuel cell operation were done as the oxidation products of glucose is believed to be mainly gluconic acid and unreacted glucose as shown in the low Coulombic efficiency based on the exchange of 24 e$^-$. Temperature, electrolyte and glucose concentrations have shown to have pronounced effect for the achievement of the highest energy capacity of 5.15 Wh kg^{-1} glucose.

Keywords: Glucose, near-neutral-state electrolyte, direct bioorganic fuel cell, temperature, anion exchange membrane

1. INTRODUCTION

Glucose ($C_6H_{12}O_6$) has gained increased interest in recent years as a fuel for implementation directly as a fuel in bioorganic fuel cells (BioFCs) using aqueous alkaline or near-neutral-state electrolytes [1-7]. Recently, direct glucose fuel cells, employing anion exchange membranes (AEMs) instead of direct immersion of the fuel in an alkaline electrolyte in direct membraneless or proton exchange membrane (PEM) fuel cells, have resulted in harnessing higher energy output at a temperature range of 20 to 60 ^{o}C [1-6,8]. Theoretically the number of electrons to be exchanged is high, i.e. 24. However, the maximum number of extracted electrons per glucose molecule has been shown to be less than two [2, 9-10]. As the supposed oxidation pathways and reaction intermediates show that the oxidation of glucose mainly leads to the production of gluconic acid, which upon reaction with base electrolytes results not in the successive reactions but neutralization [11]. Glucose if mixed in alkaline electrolytes at temperatures beyond 40 ^{o}C might hydrolyze resulting in power losses [9,12]. AEM with bioorganic fuels have been reported to work effectively in an aqueous near-neutral-state and alkaline electrolytes with substantial ionic and electronic conductivities [13]. Thus, ideally a low-temperature bioorganic fuel cell using glucose as a fuel should have near-neutral-state electrolytes buffered in a pH around 7.4 and at temperature ranges below 40 ^{o}C. The use of near-neutral-state electrolyte has the following primary advantages such as living cells similar pH values for application of small devices, electrocatalysts are not corroded and the anion exchange membranes are usually low-cost compared to their counterparts of perfluorinated sulfonic polymers. Low heating demand by supply of heat to the fuel cell, makes these low temperature bioorganic fuel cells substantial for higher power output. In an earlier report an AEMFC type with the different glucose concentrations ranging from 0.1 to 0.5 M at temperature of 20 ^{o}C was studied, and stable current-voltage operations with high specific densities were recorded for low concentrations of glucose [8]. In this his work, we report a continuation of this direct glucose AEMFC in different concentrations of the near-neutral-state electrolytes by studying the effect of temperature and the concentrations of the fuel glucose

2. EXPERIMENTS

The fuel cell (FC) equipment included a direct fuel cell (developed from the commercial fuel cell model HC-100 of Oy Hydrocell Ltd.), an electric recirculation pump (capacity 100 cm^3 / min), and a bottle glass as a recirculation tank (0.4 dm^3) as reported in Ref. [8]. Equipment included also the electrically heated water bath for heating the fuel – electrolyte solution in the recirculation tank. The pipeline from the tank to the feed point in the AEMFC was insulated. Ref [8] gives the device of the test fuel cell equipment and the electrical connections. The pH values of the fuel-electrolyte solutions were measured by Eutech Instr pHTestr 30, and the conductivity values were measured by CyberScan 510 con.

The AEM (fumasep® FAA-3 by Fumatech GmbH) was installed as it on the wetted surface of the cathode as was told in Ref. [8]. Not any hot-pressing was used to adhere the AEM on the wetted surface of cathode and the details of prepared electrodes, assembly of the fuel cell and test procedures have been reported earlier in Ref. [8].

The test procedure in the entire test was as follows: glucose and potassium dihydrogenphosphate (KH_2PO_4 by Sigma-Aldrich or Fluke) were dissolved in the distilled water. The concentrations of glucose were 0.1 and 0.3 M. The concentrations of KH_2PO_4 were 0.1, 0.2 and 0.3 M in the tests. The pH value of the each solution was set at a value of 7.4 by adding potassium hydroxide (KOH by Algol) in the aqueous solution of both glucose and KH_2PO_4. It was assumed that the aqueous solutions at pH 7.4 had properties of the buffered solutions due to the formations of both KH_2PO_4 and dipotassium hydrogen phosphate (K_2HPO_4) after adding of KOH in the aqueous solution of both glucose and KH_2PO_4. In fact, the added amounts of KOH (g dm^{-3}) in the solutions in each test corresponded well with the estimated values, which were calculated by Henderson-Hasselbach Equation.

The electrolyte-fuel solution was added to the fuel cell at temperatures of 20, 30 and 37 ^{o}C in each test. After 5 minutes the fuel cell was loaded by current density of 0.1 mA cm^{-2} for a short period (i.e. 10 s) in order to activate the electrodes. The open circuit voltage (OCV) was recorded until a stable value with minimum value of 1-2 mV min^{-1} was obtained. The polarization curve was recorded until a current density of 1 mA cm^{-2} (200 mA) was attained.. After five minutes the current-voltage voltage values (i.e. the stability tests) were recorded as follows: 1. During 60 minutes the current density from 0.3 to 0.4 mA cm^{-2} was applied and 2. During the last 60 minutes the current density was kept relatively equal or increased in the range of 0.5 to 1.1 mA cm^{2} (at 30 and 37 ^{o}C) until the voltage of the test fuel cell decreased to 0.1 V. In each test the electrically controlled resistor was operated within equal control area. The values of 1 mA cm $^{-2}$ (for measuring the current density) and of 0.1 V (for measuring the final voltage) were selected to prevent the possible damages of the fuel cell electrodes as in Ref [8].The Coulombic Efficiencies were calculated as reported in our earlier papers [8-9,12].

3. RESULTS AND DISCUSSION

The conductivity and pH values of the fuel-electrolyte solutions before the feed to the test fuel cell are listed in Table 1. The values for 0.1 and 0.3 M glucose in 0.1 M KH_2PO_4 buffer solutions are obtained from [8].

Table 1. The pH and conductivity values of the fuel-electrolyte solutions before the each test.

Fuel-Electrolyte Glucose / $[PO_4]_{tot}$ [M]	Temperature [^{o}C]	pH value	Conductivity value [mS cm^{-1}]
0.1 / 0.1	20	7.4	9.81 [8]
0.1 / 0.2	20	7.4	17.40
0.1 / 0.3	20	7.4	24.60
0.3 / 0.1	20	7.4	9.38 [8]
0.3 / 0.2	20	7.4	16.10
0.3 / 0.3	20	7.4	22.80

As Table 1 shows the conductivities increase with the increasing the concentration of the buffered KH_2PO_4 – KOH electrolyte, while it decreases slightly when the concentration of glucose increases from 0.1 to 0.3 M. The specific energy curves of the direct glucose AEMFC at three different temperatures and with the concentrations of 0.1 and 0.3 M glucose in three concentrations of 0.1 to 0.3 M buffered electrolytes are shown in Figures 1 and 2. The values for 0.1 and 0.3 M glucose in 0.1 M

KH_2PO_4 are from our previous work [8]. In [8] the length of the test for 0.3 M glucose in 0.1 M KH_2PO_4 buffer electrolyte exceeded 120 min, so the specific energy value was reduced by multiplying this value by a factor of (120 min / 153 min ~) 0.78. This was regarded as appropriate for the estimation of the comparative study as the test procedure was identical as the procedure used in this study.

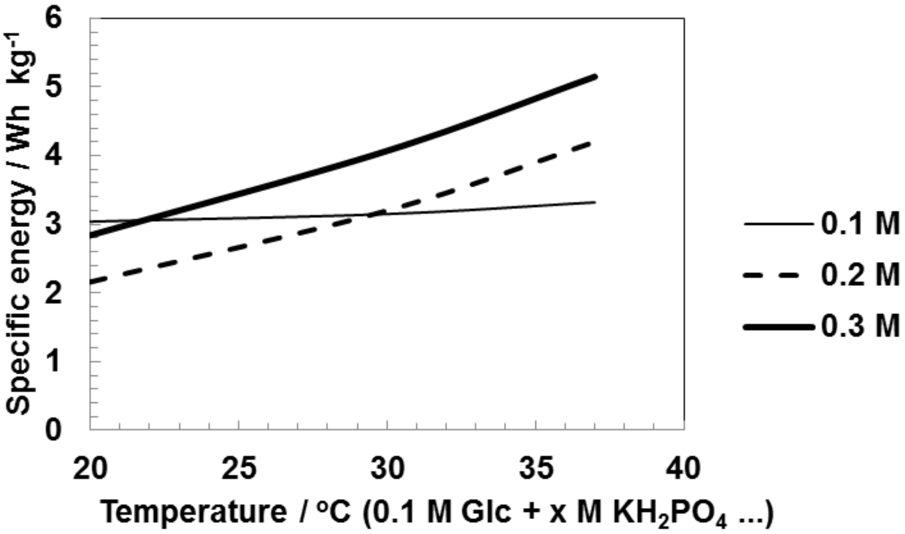

Figure 1. Specific energy as function of the near-neutral-state electrolytes at 0.1 – 0.3 M $[PO_4]_{tot}$ at three temperatures for 0.1 M glucose. The value for 0.1 M glucose in 0.1 M $[PO_4]\}_{tot}$ at 20 ^oC was taken from [8].

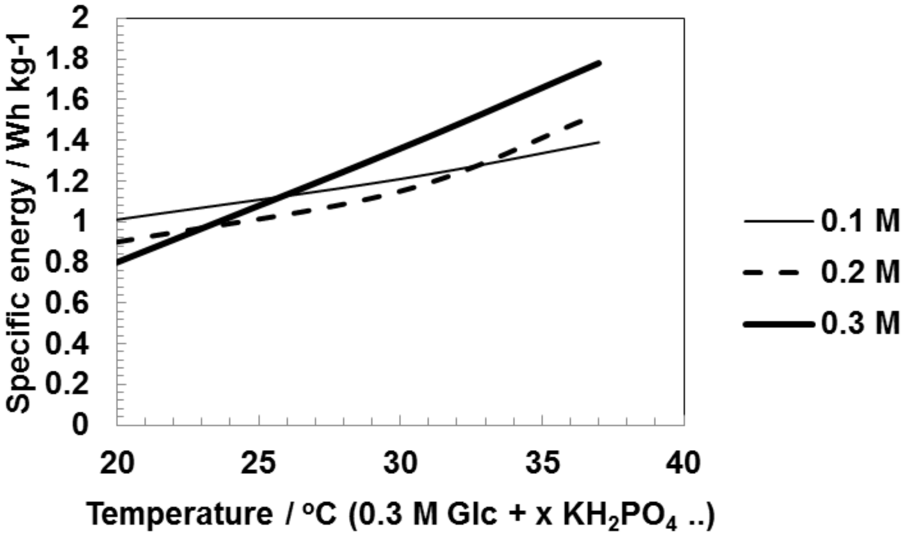

Figure 2. The specific energy as function of the near-neutral-state electrolytes at 0.1 – 0.3 M $[PO_4]_{tot}$ at three temperatures for 0.3 M glucose. The value for 0.3 M glucose in 0.1 M $[PO_4]_{tot}$ at 20 ^oC was taken from [8].

The highest specific energy values of 4.20 and 5.15 Wh kg^{-1} glucose in Fig. 1 correspond to the Coulombic efficiency values 0.65 % (24 e$^-$) and 0.70 % (24 e$^-$), respectively. The highest specific energy values 1.53 and 1.78 Wh kg^{-1} glucose in Fig. 2 correspond to the Coulombic efficiency values 0.22 % (24e$^-$) and 0.23 % (24 e$^-$), respectively. These CE values are of equal order of magnitudes than it was reported earlier in [8]. The higher specific energy values (Figs. 1-2), as compared to [8], are due to the higher average voltage due to the increase in temperature, the electrolyte concentration and the increased electric conductivities of the fuel-electrolyte solutions (see Table 1). It should be noted that at a temperature of 20 °C the glucose AEMFC has the best operating values at 0.1 and 0.3 M glucose with 0.1 M a $[PO4^-]_{tot}$ respectively, indicating that the ionic diffusivities are decreasing as the concentrations of each electrolyte component increases at room temperature. However, the increase in temperature from 20 °C to 37 °C implies the highest specific energy with both concentrations of glucose and the electrolytes. It is also possible that glucose starts to activate near 40 °C due to the initialization of hydrolyses [8] and the electrocatalytic activity for both cathode and anode is enhanced. Therefore temperatures near 40 °C enable the highest performances for operation of such fuel cells , especially for higher concentrations of the buffered solutions.

Table 2 shows the R^2 values for the each test. The R^2 values show that the measured values in Figs. 1 and 2 fit well with the linear regression of the observed data. Thus, the previously mentioned estimation value for 0.3 M glucose in 0.1 M $(PO_4)_{tot}$ is valid at temperature of 20 °C [8].

Table 2. The R^2 values for the each tests.

Fuel –Electrolyte [M]	Temperatures [°C]	R^2
0.1 – 0.1	20 - 30 - 37	0.9778
0.1 – 0.2	20 - 30 - 37	0.9919
0.1 – 0.3	20 - 30 - 37	0.9959
0.3 – 0.1	20 - 30 - 37	0.9986
0.3 - 0.2	20 - 30 - 37	0.9523
0.3 - 0.3	20 - 30 - 37	0.9996

Due to the fact that 0.1 and 0.3 M glucose in the near-neutral-state electrolyte of 0.3 M KH_2PO_4 produced the highest specific energy values at 37 °C in Figs. 1-2 , these concentrations are selected when the polarization curves for the various temperatures and concentrations are shown in Figs. 3 and 4. The Figs.3-4 show that the polarization curves have increased voltages at the current density of 1 mA cm^{-2} as the temperatures increase from 20 °C to 37 °C. The polarization curves at the temperature of 20 °C were stable with glucose concentrations of 0.1 and 0.3 M in aqueous 0.1 M $(PO_4)_{tot}$ electrolyte [8]. When higher electrolyte concentrations (0.3 M) were used, higher performances were obtained as shown in the polarization curves at the temperatures of 30 and 37 °C.

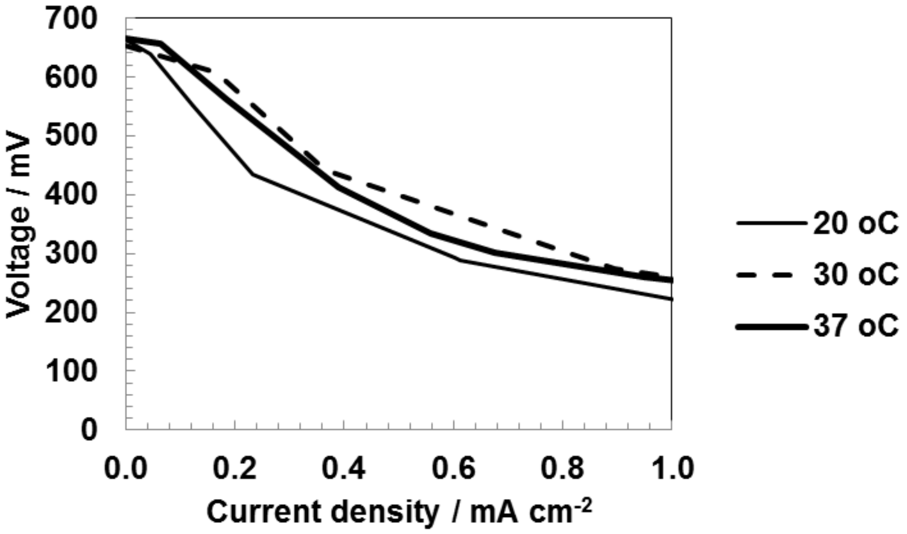

Figure 3. The polarization curves of the direct glucose AEMFC with 0.1 M glucose in the near-neutral-state electrolyte 0.3 M $[PO_4]_{tot}$ at three temperatures.

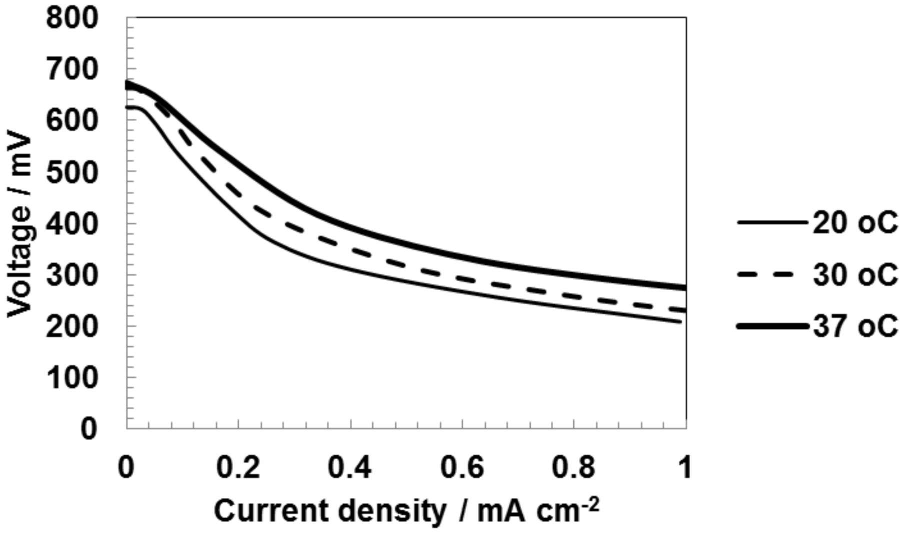

Figure 4. The polarization curves of the direct glucose AEMFC with 0.3 M glucose in the near-neutral-state electrolyte 0.3 M $[PO_4]_{tot}$ at three temperatures

The current-voltage values as function of time are shown in Figures 5 to 8 at three different temperatures for glucose concentrations of 0.1 and 0.3 M in 0.3 M $[PO_4]_{tot}$ electrolytes.

The Figs. 5-8 show that the effect of temperature remarkably enhances the current-voltage characteristics of the fuel cell. With glucose concentration of 0.1 and 0.3 M respectively the highest current values 215 mA and 170 mA were recorded at a temperature of 37 ^{o}C (Figs 5 and 7). While a temperature of 20 ^{o}C shows in both cases a constant current with time, there is a clear substantiation that the increase in temperature increases the oxidation of glucose significantly.

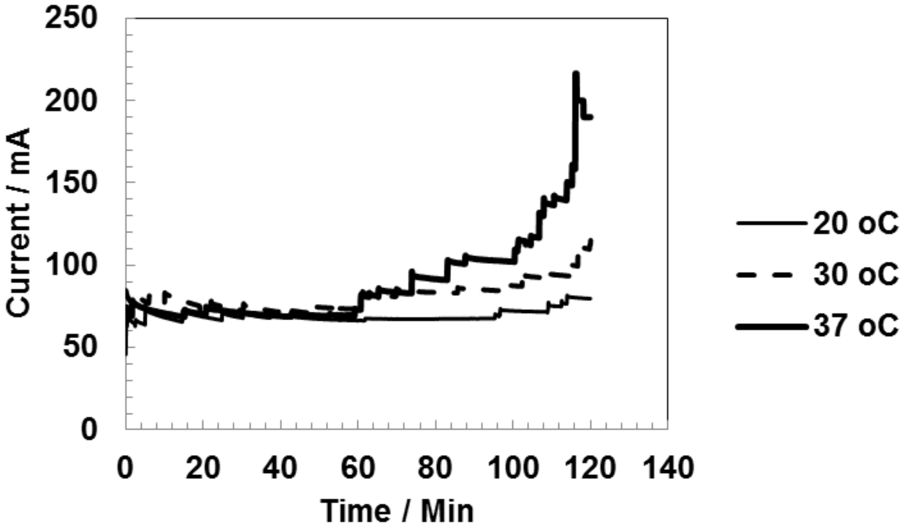

Figure 5. The current values of the direct glucose AEMFC with 0.1 M glucose as a fuel in the buffered 0.3 M $[PO_4]_{tot}$ electrolyte versus time at three different temperatures.

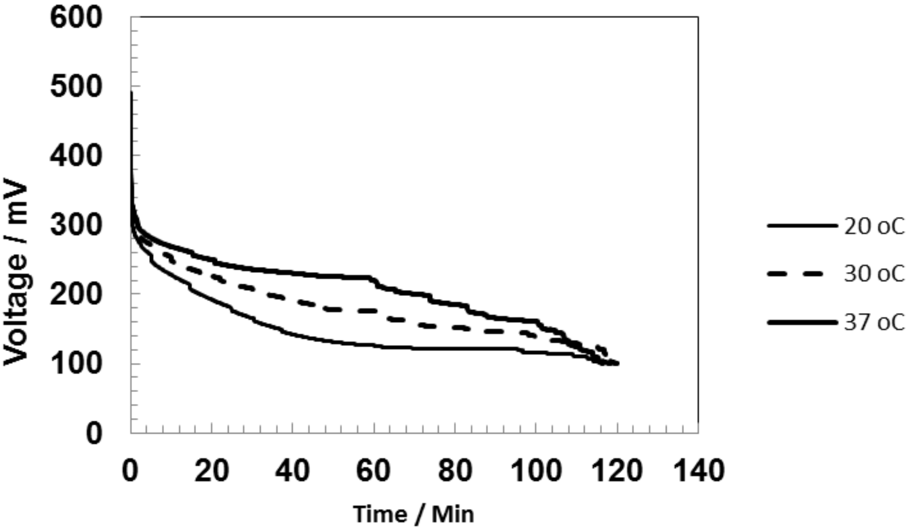

Figure 6. The voltage values of the direct glucose AEMFC with 0.1 M glucose as a fuel in the buffered 0.3 M $[PO_4]_{tot}$ electrolyte versus time at three different temperatures.

Figs. 1 and 2 showed that high specific energy values (Wh kg^{-1}) are achieved with the increased temperatures both at 30 and 37 ^{o}C. For both concentrations of glucose (0.1 and 0.3 M) the specific energy values show an exponential dependence on the temperature between 20 to 37 ^{o}C. The direct glucose AEMFC operates better with lower 0.1 M glucose concentration than with higher 0.3.M glucose (Figs. 1-2). However at temperature of 37 ^{o}C occurs a highest decrease in the pH value of fuel-electrolyte solution as a result from the formation of acidic the oxidation products of glucose (gluconic acid) due to a poor buffering capacity of the used near-neutral-state electrolyte that may inhibit the glucose electrochemical oxidation. In Figure 9 are shown the final pH values of the fuel-electrolyte solutions after the current vs. voltage tests with 0.1 M glucose (Figs. 5-6) were carried out.

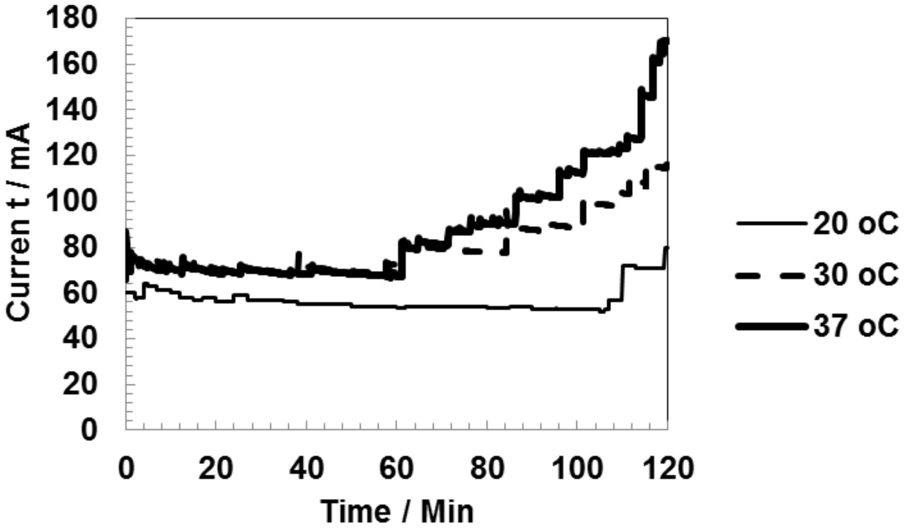

Figure 7. The current values of the direct glucose AEMFC with 0.3 M glucose as a fuel in the buffered 0.3 M $[PO_4]_{tot}$ electrolyte versus time at three different temperatures.

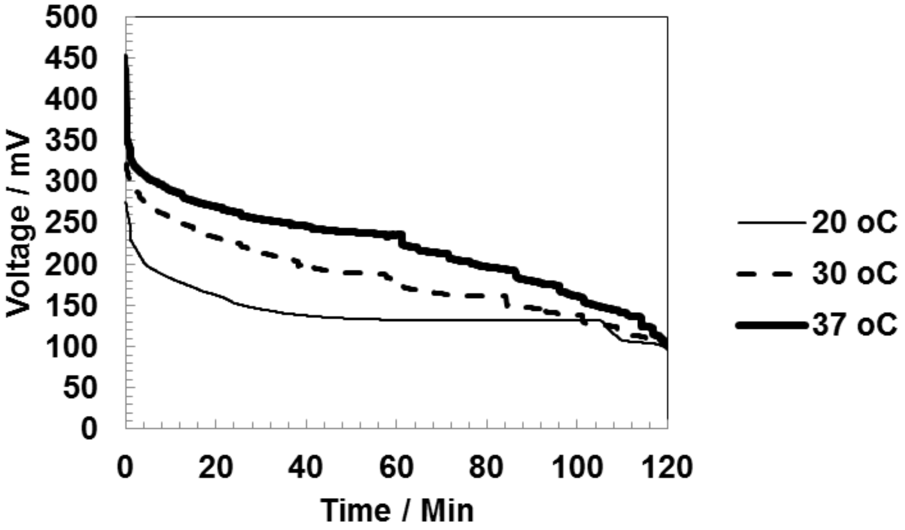

Figure 8. The voltage values of the direct glucose AEMFC with 0.3 M glucose as a fuel in the buffered 0.3 M $[PO_4]_{tot}$ electrolyte versus time at three different temperatures.

The higher concentrated electrolytes (0.2 - 0.3 M $[PO_{4]tot})$ have stronger buffering capacities than 0.1 M $[PO_4]_{tot}$, so the pH value of the fuel-electrolyte solution decrease less than when operating with the buffer 0.1 M $[PO_4]_{tot}$. The corresponding changes with 0.3 M glucose are similar but the differences are smaller than with 0.1 M glucose.

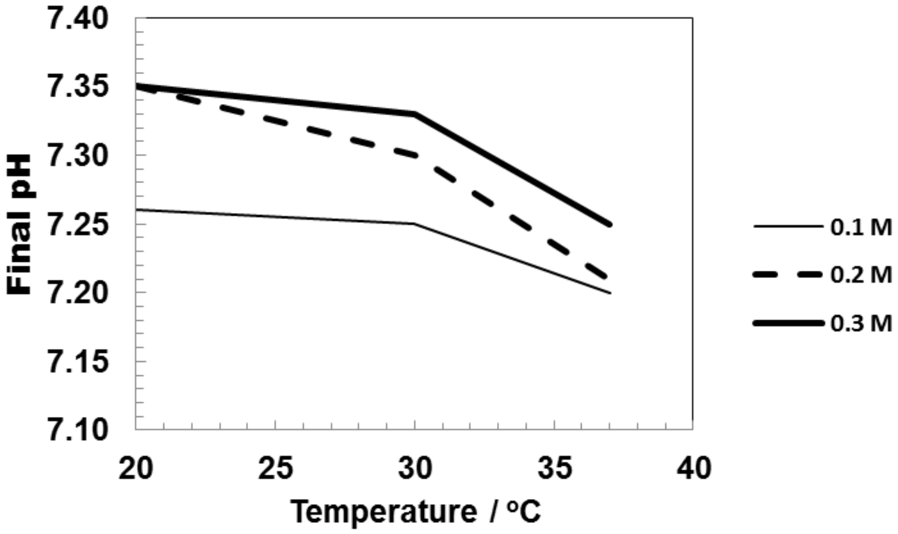

Figure 9. The final pH values of the fuel-electrolyte solutions after the current-voltage tests with 0.1M glucose in 0.1 to 0.3 M $[PO_4]_{tot}$ buffered aqueous solution.

Based on our earlier reported studies [8] on glucose oxidation it could be claimed that the decrease in pH value results also from several side reactions (in addition to glucose electrochemical oxidation) between glucose, acidic oxidation products of glucose and electrolyte components in the liquid phase at temperatures of 30 ^{o}C and above and especially when lower glucose concentration is used. These side reactions could lead to formations of e.g. enediol ions ($C_6H_{11}O_6^-$) even in slightly alkaline solutions, which could be further catalyzed by some liquid phase ionic components in intermediate reactions into many organic acids like formic acid [14,15]. As the acidic components from glucose electrochemical oxidation and subsequent side reactions are reacting with components in the buffer solution,this would lead to the lowering of the pH value of the electrolyte.

Overall the tests show improvements in the kinetics of the oxidation reactions and in the activities of the electrocatalysts in the AEMFCs due to the increase in the operation temperature as was also earlier noticed in tests with glucose mixed with the alkaline electrolyte in the direct glucose fuel cells [8-9, 12,16]. The specific energy values (in Figs. 1-2) increase with the increase of the conductivity of the electrolyte concentration, although the CE values are higher when concentration of the fuel is low. However the OCV values in Figs. 3 and 4 are still far away from the theoretical value of 1.24 V, which is the value for the Gibbs free energy for glucose oxidation with maximum yield of 24 electrons per molecule [17]. Also the average voltage values (Figs. 6 and 8) of the output currents together with the durations of each test are very small when compared to the earlier reported values with the membraneless alkaline fuel cell [4,9]. The pH values of the fuel-electrolyte solutions after each tests show that the pH value of the fuel-electrolyte will decrease more due to enchanced reaction at higher temperature resulting in acidic compounds, which are present in the fuel-electrolyte and the plausible side reactions of the glucose and the electrolyte components. The Coulombic efficiency values indicate the low yield of electrons. The CE value of 0.70 % (24 e^-) for 0.1 M glucose at temperature of 37 ^{o}C corresponds to CE 8.4 % ($2e^-$), so the oxidation of glucose occurs mainly for the two electrons transferred per glucose molecule, which essentially needs to be addressed using different kinds of electrocatalyst materials. That is why not any component analysis were conducted, because it was assumed that the fuel-electrolyte solutions contained mostly unreacted glucose in addition to gluconic acid ($C_6H_{12}O_7$). The clear indication for the low degree of the oxidation of the glucose molecules was also that not any visual signs of the change in color of the fuel-electrolyte solutions were noticed as in the previous tests with the direct glucose alkaline fuel cell [4,9,12]. The solutions from the AEMFC remained clearly transparent in each test during this study. However, the liquid sample analyses have to be done in future test after to find out different possible side reactions between glucose and electrolyte components when the concentrations of each component and temperatures are changed. The acidic oxidation products in the liquid phase have an influence on the glucose electrochemical oxidation.

Although the Coulombic efficiencies are low, the current outputs are remarkably high when compared to some earlier reported results with different direct and microbial glucose fuel cells in near-neutral-state and alkaline electrolytes in Refs [17-21]. In our work we used low concentrations of the electrolytes, but it may be expected that the current density may increase if the concentration of the electrolyte is adjusted upward the 0.3 M $[PO4]_{tot}$ used, or by replacing the aqueous buffered phosphate electrolyte with more effective near-neutral-state electrolyte with higher electric conductivity value. The near-neutral state electrolyte should have a good buffering capacity for preventing the high drop in pH value due to the formation of acidic components in the electrolytes at the high temperatures near 40 ^{o}C. The current output values in this work are especially encouraging when one takes into account how the AEM was installed in the cathode electrode without application of high adhesion by hot-pressing technology. The OCV and the current output values may increase if other highly active electrocatalysts such as Ni and other alloyed materials are used instead of Pt-Pd/C [18, 21-22]. The used anion exchange material FAA-3 (Fumatech) is specially intended for alkaline fuel cells. Thus, the AEMs should be developed especially for operation in the near-neutral-state electrolytes limiting the crossover of the acidic oxidation products in the electrolytes. When glucose and electrolyte concentrations, electrocatalysts, operation temperatures and effective near-neutral-state electrolytes are optimized, it is possible to produce effective direct glucose AEMFC, in which the current-voltage values might increase substantially.

4. CONCLUSIONS

In this work the direct glucose anion exchange membrane fuel cell in a near-neutral-state electrolyte was studied. The current output values in the test fuel cell with 0.1 and 0.3 M glucose as a fuel in the buffered 0.1- 0.3 M KH_2PO_4 electrolytes at pH value of 7.4 at low temperatures between 20 to 40 ^{o}C were satisfactory and promising when compared to those reported results with other direct and microbial fuel cell types. Specific energy as high as 5.15 Wh kg^{-1} at 37 ^{o}C was achieved showing the effect of temperature and electrolyte concentration as important parameters for this type of fuel cells. Although not significant change in pH was shown, its constant value changes abruptly with increase in temperature beyond 30 ^{o}C. Low fuel concentration implies better utilization of the oxidation products of glucose compared to higher concentrations.

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