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Direct Glucose Fuel Cell with the Anion Exchange Membrane in the Near-Neutral-State Electrolyte

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This paper deals with the direct glucose fuel cell with an electrolyte at near-neutral-state pH value at room temperature by incorporating an anion exchange membrane (AEM) that was directly attached to a cathode. The wetted surface of the cathode was exposed to the AEM without implementing hot-pressing. The current-voltage curves were measured and the specific energy values for glucose were calculated for every test. Different concentrations of glucose were used and the results show that the lower the concentration of glucose, the higher is the specific energy, apparently showing higher utilization of the fuel with high Coulombic efficiency.

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

1. INTRODUCTION

Monosaccharide glucose ($C_6H_{12}O_6$) is abundant and it can be produced from various sources like starch and cellulose. Therefore it is considered to be ideal and as an ecological fuel for application in direct bioorganic fuel cells (BioFCs). The use of glucose as a fuel in aqueous electrolytes for direct fuel cells has been reported in several studies in the temperature range of 20 to 60 ^{o}C in alkaline electrolytes, in which current densities up to 200 mA cm^{-2} [1-3] were achieved. On the other side in membraneless fuel cells with alkaline electrolytes, the current densities so far obtained were much smaller showing few mA cm^{-2} [3-6]. Usually the open-circuit voltages (OCV) for such systems varied from 0.8 to 0.9 V [1-6]. The advantages of the alkaline electrolyte having high conductivity has shown increased catalytic activity for both Pt-Pd at the anode as well as for the combination of CoTPP-

$MnCo_2O_4$ on the cathode [6,7]. The increase in the operation temperature from the room temperatures up to 60 °C has increased the oxidation rate of glucose on the anode due to the increased kinetics and conductivity of the electrolyte [6]. The number of extracted electrons per glucose molecule has been at maximum two of the 24 electrons available in an alkaline electrolyte due to formation of gluconic acid leading further to neutralization [5, 8, 9]. However, the target in the direct glucose fuel cells should be to produce a fuel cell with the near-neutral-state electrolytes, due to the following reasons: 1) the pH 7.4 is the pH values of living cells and therefore direct application without the need of highly acidic and alkaline electrolyte 2) Use of low-cost membranes for anion exchange and 3) The electrolyte should not lead to deactivation of the catalyst materials due to the severe conditions. The latter case is especially serious when Pt is used as the catalyst with surface deposition / redeposition (Ostwald ripening), corrosion of the carbon support with detachment of Pt nanoparticles and CO poisoning as a result leading to performance losses. The number of extracted electrons has been reported to reach up to 17.5 electrons per one glucose molecule in the direct fuel cell with the near-neutral-state electrolyte (pH 7.4) at temperature of 37 °C, when low current density has been used [10]. Unfortunately this impressive result with the near-neutral-state electrolyte has not been able to be verified, so the maximum number of the extracted electrons remains as two when the fuel cell is operated at the near-neutral-state electrolyte [11, 12]. The current densities of the fuel cells with the near-neutral-state electrolytes are much lower than those with the alkaline fuel cells. Some alloyed Pt-catalysts (Pt-Pb, Pt-Sn) and Raney-Ni has been considered to be potential anode electro catalysts in the near-neutral-state electrolytes, partly due to low tendency to be poisoned by glucose oxidation products [9, 11, 13]. At near-neutral-state electrolytes membraneless fuel cells do not perform well, because oxygen diffuses to the electrolyte from the cathode to the anode, where this oxidant is reduced to H_2O_2, lowering the OCV of the fuel cell [14]. Therefore, the OCV values of glucose in the near-neutral-state electrolytes are generally low. Because glucose hydrolyzes at temperatures $\geq$ 40 °C in a liquid phase, it should be preferably be applied low temperatures near room temperature for avoiding the losses of the fuel during fuel cell operation [7, 15].

In this paper anion exchange membrane (AEM) was applied in a direct fuel cell with glucose as a fuel at near-neutral-state electrolyte and a temperature of 20 °C by loading different concentrations of glucose (in the range of 0.1 to 0.5 M). The main objective was to combine the good operation characteristics of both the alkaline and near-neutral-state electrolytes by implementing anion exchange membrane in between anode and cathode. The effects of concentration and current-voltages on the Coulombic efficiency (CE) and specific energy are reported.

2. EXPERIMENTAL

2.1 The test equipment

The test fuel cell equipment included a direct fuel cell (developed from the commercial fuel cell model HC-100 of Oy Hydrocell Ltd.), a recirculation pump (capacity 100 cm^3 / min) and a glass bottle as a recirculation tank. The test fuel cell equipment and the electrical connections are shown in

Fig. 1 (a & b). 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.

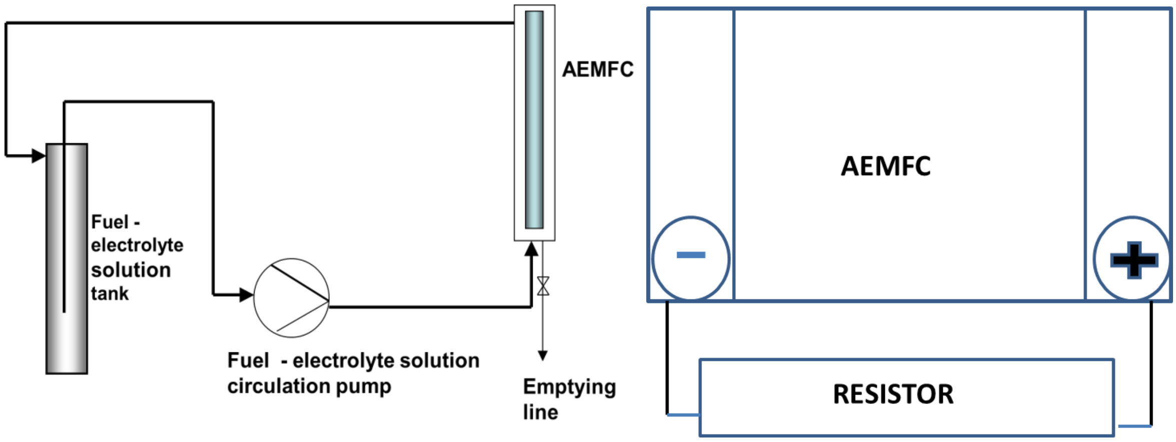


Figure 1. The test fuel cell equipment (on the left, a.) and the electrical connection (on the right, b.).

The fuel cell electrodes in Fig. 1a consisted of a two-cylinder structure, where the inner cylinder was an anode and the outer electrode was a cathode. The anode was wetted on all sides of the catalyst/carbon electrode materials. The AEM (fumasep® FAA-3, Fumatech GmbH) was installed on the wetted surface of the cathode. Hot-pressing was not used to adhere the AEM on the cathode in order to establish a membrane electrode assembly (MEA) as is usual in polymer electrolyte membrane fuel cells (PEMFC) or anion exchange membrane fuel cells (AEMFC). The AEM (FAA-3) delivered in bromide form was converted to OH-form by immersing it in 0.6 M potassium hydroxide (KOH) for 24 hours prior to the fuel cell operation. After emptying the alkaline solution and filling the fuel cell with distilled water at 20 ^{o}C for one hour and repeating this procedure, the AEM was ready to be used in the fuel cell. The distance between the anode and the cathode was 0.8 mm. The thickness of the AEM was 0.13 – 0.15 mm in wet form according to the data by the supplier. The catalyst loadings of the anode were 4.5 mg cm^{-2} for both the Pt and Pd in the bimetallic combination (in a weight ratio of 1:1) with the catalyst composition of 10 wt-% on carbon. The cathode contained a combined catalyst loading of 3.15 mg cm^{-2} of CoTPP with a concentration of 18 wt-% on carbon and 17.5 mg cm^{-2} of $MnCo_2O_4$ respectively. The anode was composed of a single-layer structure without any diffusion material. The cathode was of the double-layer type containing both the active (catalyst) and the diffusion layer. The diffusion layer contained 60% carbon (Vulcan XC-72) and 40% PTFE. The electrodes were compressed at 100 bar and then sintered at a temperature of 250 ^{o}C. The geometrical areas of both electrodes were 200 cm^{2}. The Pt-Pd catalyst was a commercial grade purchased from Johnson -Matthey. The CoTPP and $MnCo_2O_4$ catalysts were commercial products obtained from Oy Hydrocell Ltd.

The electrical equipment in Fig. 1 b includes the electrodes, current/voltage measurements and a resistor. To operate the fuel cell, an auxiliary device (Velleman, PS 613, and DC) was used as a resistor. The voltage values were measured by Fluke 73. The current and voltage values were recorded with an Agilent 34970A data logger. The current was determined indirectly from the voltage loss over the shunt with known voltage loss and current values (60 mV, 5 A).

2.2. The test procedure

The procedure in the entire test was as follows: glucose (anhydrous, Oriola) and potassium dihydrogenphosphate (KH_2PO_4, Sigma-Aldrich) were dissolved in the distilled water. The glucose concentrations used were 0.1, 0.3 and 0.5 M. The concentration of KH_2PO_4 was kept constant 0.1 M in all the tests. The pH value of each solution was set at 7.4 by adding potassium hydroxide (KOH, Algol). It was assumed the aqueous solutions at pH 7.4 had certain properties of the buffered solutions due to the formations of both KH_2PO_4 and dipotassium hydrogen phosphate (K_2HPO_4) after addition of KOH in the aqueous solution of both glucose and KH_2PO_4.

The electrolyte-fuel solution was added to the fuel cell at a temperature of 20 ^oC. After 5 minutes small current was loaded for a short period (i.e. 10 s) in order to secure that the electrodes were activated. The fuel cell was left idle so that the OCV generation was recorded until a steady-state or minimum variation of 1 - 2 mV min^{-1} was attained. The polarization curve was then recorded where a current density as high as 1 mA cm^{-2} (200 mA) was applied. The current-voltage voltage performances (i.e. the stability tests) were recorded until the voltage of the test fuel cell reached a value of 0.1 V. The current density of 1 mA cm^{-2} and voltage of 0.1 V were chosen in order to prevent any possible damage to the fuel cell electrodes. The Coulombic Efficiencies were calculated based on the theoretical 24 electrons according to the following Equation [16]:

$$CE = \frac{(Mw \int I\, dt) 100\ \%}{F\ ne\ V\ an\ \Delta C} \qquad (1)$$

In equation 1 M_w is the molecular weight of glucose (180 g mol^{-1}), n_e is the number of the transferred electrons, V_{an} is the volume of liquid in the anode (0.4 dm^3), F is Faradays constant (96487 As mol^{-1}) and ΔC is the change in the substrate mass concentration (C= C_o the start concentration of glucose). The term $(\int I\, dt)$ corresponds to the recorded Coulombs (As) in each test.

3. RESULTS AND DISCUSSIONS

The main focus for this work was based on our earlier membaraneless fuel cell as in Ref. [6]. At first the fuel cell was tested without installation of any AEM in between the electrodes with 1 M glucose as a fuel in near-neutral-state electrolyte (at pH 7.4) The polarization curve in near-neutral-state electrolyte is shown in Fig. 2.

Fig. 2 shows a substantially lower the OCV value of the membraneless direct glucose fuel cell when compared to the OCV of 0.8 V in alkaline electrolytes [6]. The low OCV values are mostly due to the dissolved oxygen, diffusing to the anode compartment resulting in a competitive reaction and surface oxide formations on the electrocatalyst of Pt-Pd.

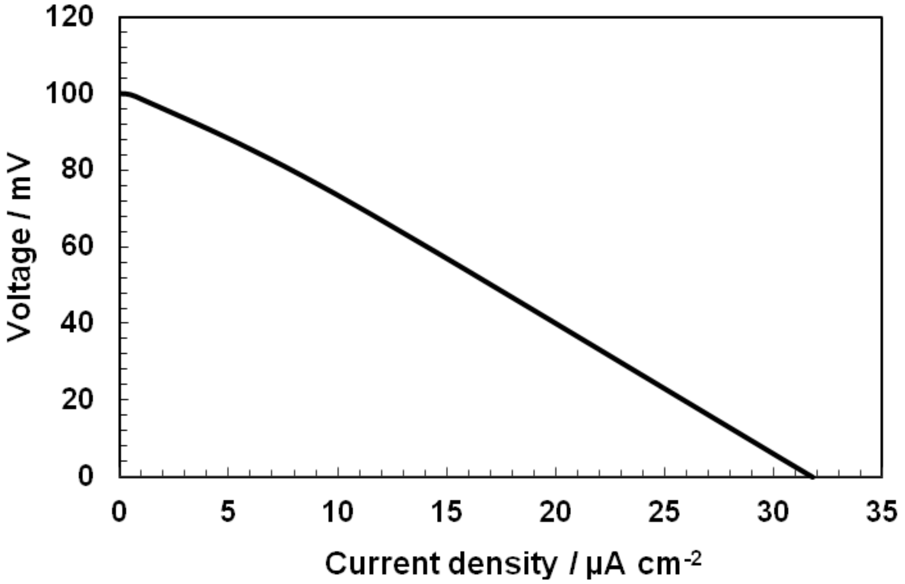


Figure 2. The current density-voltage curves of the membraneless direct-mode fuel cell with 1 M glucose in near-neutral-state electrolyte (KH_2PO_4-KOH, [PO_4] =0.1 M, pH 7.4) at 20 °C.

Therefore, in order to increase the electrode kinetics without interference of intermediate products due to both glucose and surface oxidations in a membraneless configuration of the electrodes without direct mixture of the fuel-electrolyte, a MEA where the cathode was wrapped in AEM was installed.

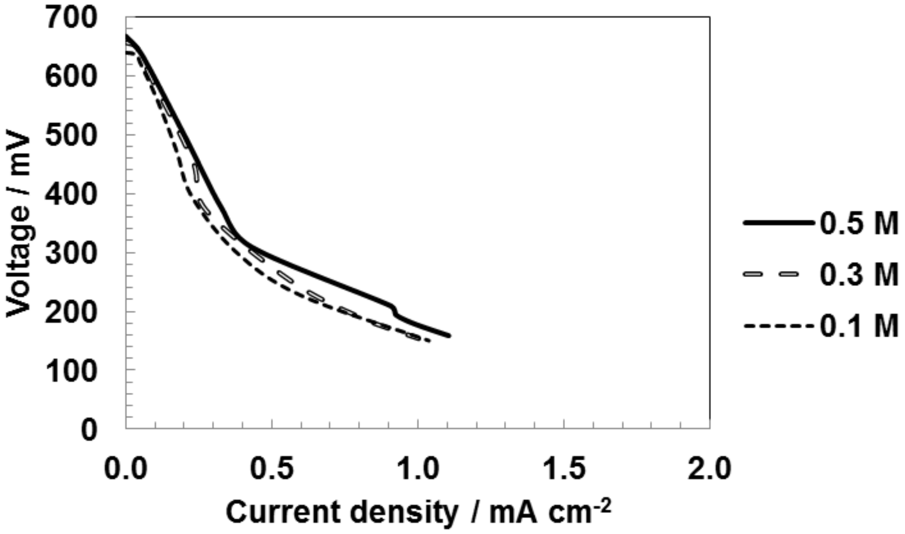


Figure 3. The current density-voltage curves of the direct glucose AEMFC with three different glucose concentrations at a temperature of 20 °C.

Such a formulation of AEM in an abiotic cell with inorganic catalysts and glucose as fuel in a near-neutral-state electrolyte at pH 7.4 as in Fig 1 has not been tested earlier. The concentrations of glucose were varied between 0.1 to 0.5 M. The maximum concentration of glucose was held at 0.5 M as this concentration was supposed to show higher performances compared to low and high concentrations [1].

The current density-voltage curves for the three glucose concentrations (0.1, 0.3 and 0.5 M) at a temperature of 20 ^{o}C are shown in Fig. 3.

The OCVs are improved to significant level as shown in Fig. 3 and lie between 0.62 and 0.68 V for all the concentrations of glucose when compared with the OCV of 0.1 V in Fig 2. The current densities were more than three orders of magnitudes better due to the incorporation of AEM in the cell configuration, in contrast to the membraneless fuel cell. This has mainly to do with the dissolution and transport of the oxygen species to the anode, whereby further reactions and interference with the oxidation and intermediate reaction products may take place on the surface of the anode. Thus, the AEM serves as impermeable matrix between the anode and cathode and thereby increase the electrode kinetics for both the oxygen reduction reaction and glucose oxidation reaction. Both at low and high current densities, no significant differences in voltages are observed, as the readily oxidizable concentration of glucose by the active sites of the electro catalyst do not vary substantially, taking into account the total electrode area. However, on long-term operation of the fuel cell and at similar currents, the lower glucose concentrations are depleted faster than those with higher concentration according to Faraday’s law of the amount of the substances oxidized. The activation overpotential of more than 0.4 V up to a current density of 0.5 mA cm^{-2} (in Fig. 3) is high and therefore work on active catalysts to suppress this huge loss in potential is considered to be important for glucose oxidation.

The current-voltage curves as a function of reaction time for the three different concentration of 0.1 to 0.5 M glucose at 20 ^{o}C are shown in Fig. 4. The current outputs were taken at current densities in between 0.3 and 0.4 mA cm^{-2} until the voltage of the AEMFC decreased down to a voltage of 0.1 V. Table 1 shows the total recorded Coulombs along with the Coulombic efficiency based on 24 electrons and the specific energy values for each of the glucose concentrations of Fig. 4. The pH and the conductivity values for each fuel-electrolyte solution before and after the tests are also shown in Table 2.

High CE was obtained for the glucose concentration of 0.1 M due to the successive hydroxyl ion transport through the membrane to the anode, albeit for the 2 electron transfer. The anode electrocatalyst is accessible to the lower concentration of glucose without too high a concentration gradient. There is a mass transport hindrance and ohmic loss due to the increased concentration of glucose, exacerbating the total cell performance [1]. Furthermore, due to the lower concentration of glucose the conductivity is high and decreases with the increase of the concentration of glucose together in the electrolyte. Likewise, the pH of the solution decreases more in the 0.1M glucose, showing a substantial reaction of this fuel, while the pH for the 0.5 M is unchanged. It is interesting, however to note that the relationship between the specific energy obtained as a function of the glucose concentration. Fig. 5 shows higher Wh kg^{-1} is achieved for the lower concentration and shows an exponential dependence. The R^2 fits well the regression line in the observed data.

Table 1. The total Coulombs and the Coulombic Efficiencies (24 e$^-$) for AEMFC with different glucose concentration at 20 ^{o}C.

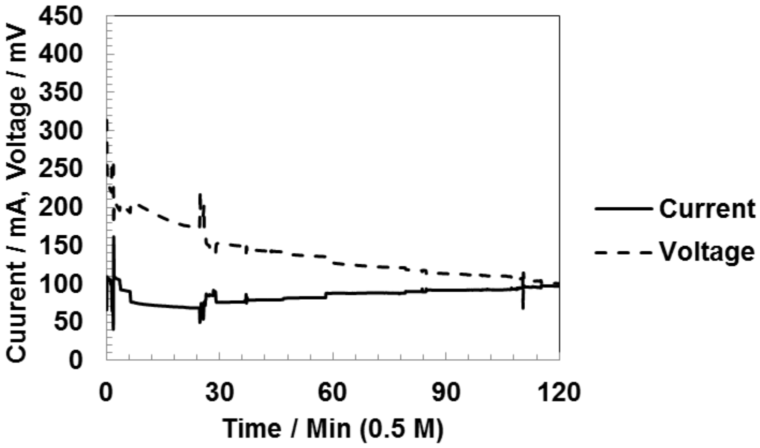
Concentration [M]	Recorded Coulombs [As]	The Coulombic Efficiency CE [%]	Specific energy [Wh kg^{-1} glucose]
0.1	613	0.66 (24 e-)	3.04
0.3	769	0.28 (24 e-)	1.35
0.5	626	0.14 (24 e-)	0.67

Table 2. The detected pH-values and the conductivity values of the fuel-electrolyte solutions before and after the tests in the direct glucose AEMFC at the temperature 20 ^{o}C.

Concentration [M]	pH before test	pH after test	Conductivity before [mS cm-^{1}]	Conductivity after [mS cm^{-1}]
0.1	7.40	7.26	9.81	9.76
0.3	7.40	7.30	9.38	9.34
0.5	7.40	7.40	8.39	8.36

The specific energy value with 100 % Coulombic efficiency (24 e$^-$ per one molecule) would be 482 Wh kg^{-1} glucose (for a concentration corresponding to 0.3 M) that is much more than the values of the energy densities of the Li-ion batteries (from 120 to 200 Wh kg^{-1}) [17]. During a lengthy operation of the fuel cell from 120 to 150 minutes, a complete oxidation of glucose did not take place. The CE varies from 0.14 to 0.66 % based on 24 e$^-$, which is improbable due to the various steps in the oxidation pathways and intermediate reaction products in glucose [9].

Compared to those reported results either with abiotically catalyzed, enzymatic or microbial fuel cells [12, 18-21], the results so far obtained through a combination abiotic electrode materials, near-neutral-state electrolyte and AEM, are encouraging. The simpler construction of the cell and easy operation makes this type of direct glucose AEMFC preferable, though efforts are needed to circumvent the sluggish kinetics of the glucose oxidation.



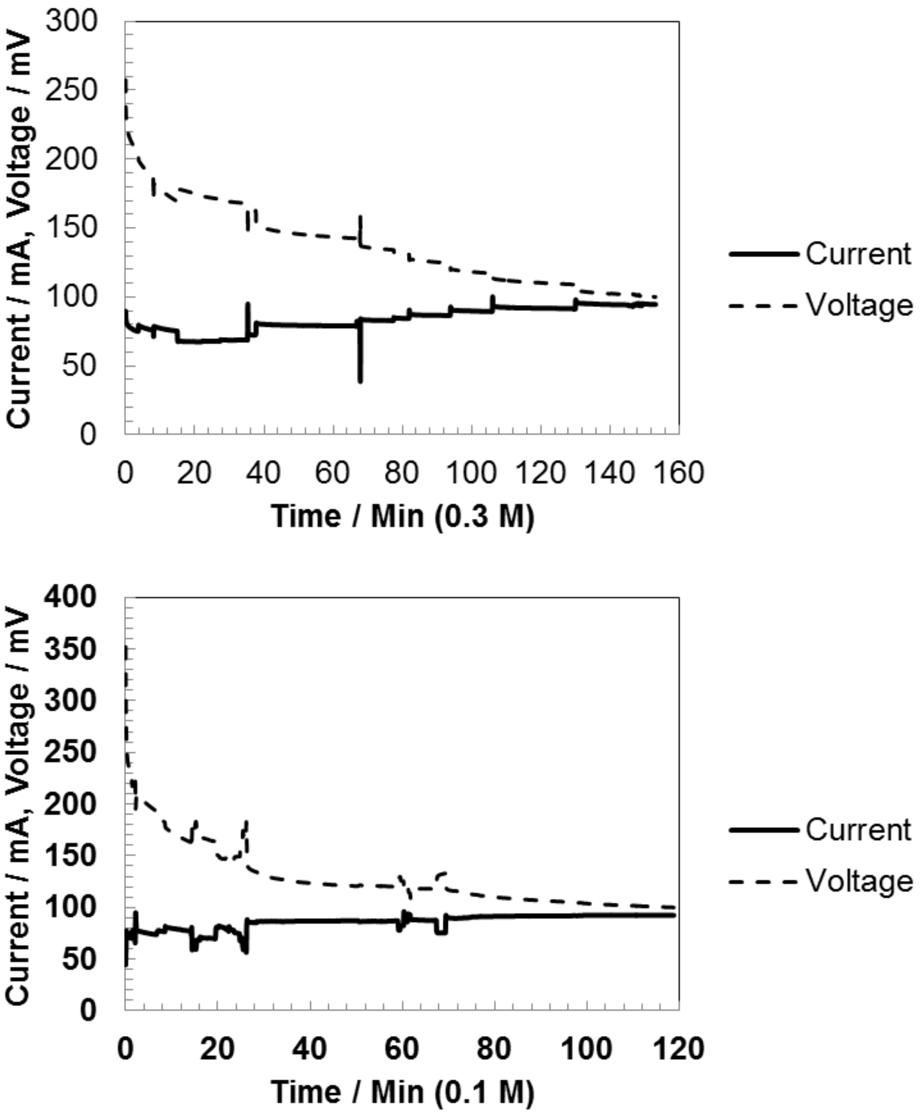


Figure 4. The current-voltage curves of the direct glucose AEEFC with three different glucose concentration 0.1, 0.3 and 0.5 M at 20 °C.

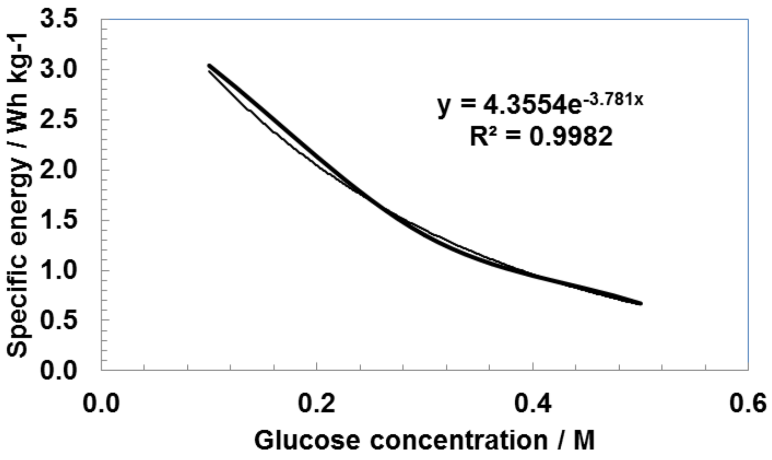


Figure 5. Effect on glucose concentration on specific energy.

Effective direct glucose fuel cell has a potential application for small power supply in portable electric devices and/or as an electric charger for batteries due to the abundance of glucose as a fuel in nature. Therefore, work for this type of fuel cell should be directed to research on active catalysts with high selectivity for the oxidation of glucose, electrolyte (conductive and nor reactive with the reaction products and intermediates), anion exchange materials together with low resistances and a temperature regime for high power density.

4. CONCLUSIONS

The introduction of AEM in the glucose fuel cell has shown to result in improved specific energy, where the membrane impedes the transport of dissolved oxygen to the anode compared to a direct glucose fuel cell. The specific energy depends on the concentration of the glucose used showing better utilization of the fuel for 0.1 M. The low concentration facilitates oxidation of glucose to take place on the Pt-Pd. However, work has to be directed to prepare active electrocatalysts in order to increase the overall power density effectively in the near-neutral-state electrolytes and at temperatures under 40 ^{o}C.

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