



Alkaline direct oxidation fuel cell with non-platinum catalysts capable of converting glucose to electricity at high power output

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ABSTRACT

Glucose is a potential fuel for fuel cells because it is renewable, abundant, non-toxic, and easy in handle and store. Conventional glucose fuel cells that use enzymes and micro-organisms as the catalyst are limited by their extremely low power output and rather short durability. In this work, a direct glucose fuel cell that uses an anion-exchange membrane and in-house non-platinum electrocatalysts is developed. It is shown that this type of direct glucose fuel cell with a relatively cheap membrane and catalysts can result in a maximum power density as high as 38 mW cm^{-2} at 60°C . The high performance is attributed mainly to the increased kinetics of both the glucose oxidation reaction and the oxygen reduction reaction rendered by the alkaline medium with the anion-exchange membrane.

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1. Introduction

Glucose is a renewable and abundant energy as it can be derived from a large amount of waste biomass that is generated by agricultural activities and from dedicated energy crops, such as corn and other grains [1,2]. Potential approaches for deriving energy from glucose include production of ethanol and conversion to hydrogen, but these approaches are hindered by technical and economic problems [3,4]. An alternative approach to deriving energy from glucose is to feed it to a fuel cell that directly oxidizes the fuel to generate electricity. Over the past decades, extensive efforts have been made to study glucose as a fuel for both enzymatic and microbial fuel cells.

Typically, enzymatic glucose fuel cells employ glucose oxidase and laccase for the glucose oxidation reaction (GOR) and oxygen reduction reaction (ORR). Nevertheless, the most critical technical hurdle for this type of fuel cell is its extremely low performance; the state-of-the-art power density is only 0.43 mW cm^{-2} at the voltage of 0.52 V [5]. Furthermore, the limited stability of enzymes results in rather poor fuel cell durability. In this regard, microbial fuel cells are better than enzymatic fuel cells because they can be less susceptible to poisoning and loss of activity under normal operating conditions, and this leads to relatively long-term durability. Nevertheless, the most critical problem of microbial fuel cells is the

difficulty in transferring the electrons from the microbe to the electrode [6]. For this reason, the performance of microbial glucose fuel cells is also extremely low; the state-of-the-art power density is 0.431 mW cm^{-2} at a voltage of 0.664 V [7]. As both enzymatic and microbial fuel cells face the above-mentioned technical hurdles, direct glucose fuel cells (DGFCs) that use a membrane electrolyte and metal catalysts have been receiving attention.

In a direct oxidation fuel cell, the membrane can be either an acid type (e.g., Nafion) [8,9] or an alkaline type [10,11]. It has recently been demonstrated that when the electrolyte is changed from acidic to alkaline, i.e., an anion-exchange membrane (AEM), the performance is substantially improved [10,11]. This behaviour can be attributed mainly to the enhanced kinetics of the GOR and ORR in alkaline media compared with those in acid media [12]. Moreover, in an AEM-DGFC the direction of the electro-osmotic drag is from the cathode to the anode, which can reduce the rate of fuel crossover from the anode to cathode and thereby improve cell performance [13,14]. In addition, the cost of AEMs is much lower than that of PEMs (typically Nafion®).

The above advantages make AEM-DGFCs more appealing than PEM-DGFCs. Chan et al. [15] measured the cell performance of a glucose–air fuel cell with PtCo and Pt as the anode and the cathode catalysts. The maximum power density and open-circuit voltage (OCV) is 3.0 mW cm^{-2} and 1.08 V with 1.85 M glucose and 7.0 M potassium hydroxide (KOH). Recently, Fujiwara et al. [10] compared the cell performance of an AEM-DGFC and a PEM-DGFC using the PtRu black and Pt black as the anode and cathode catalysts. The cell performance significantly increased from 1.5 to 20 mW cm^{-2}

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when the electrolyte membrane was changed from a PEM to an AEM.

In this paper, a direct glucose fuel cell that uses an anion-exchange membrane and in-house non-platinum electrocatalysts is developed. It is shown that this type of fuel cell with a relatively cheap membrane and catalysts can result in a maximum power density as high as 38 mW cm^{-2} at 60°C .

2. Experimental

2.1. Membrane electrode assembly

A membrane electrode assembly (MEA), with an active area of $1.0 \text{ cm} \times 1.0 \text{ cm}$, was comprised of an AEM sandwiched between an anode and a cathode electrode. The AEM, with a thickness of $28 \mu\text{m}$ (A201), was provided by Tokuyama. The cathode electrode was a single-sided electrode consisting of a non-platinum HYPERMEC™ catalyst (Acta) with a loading of 1.0 mg cm^{-2} , which was attached to a backing layer made of carbon cloth (E TEK). On the anode, the catalyst layer (CL) was fabricated in-house via an anode catalyst coated substrate (CCS) method [16]. The anode catalyst ink was prepared by mixing a home-made carbon-supported PdNi catalyst [17] with a loading of 2.0 mg cm^{-2} and ethanol as the solvent and 5 wt% PTFE as the binder [18]. Subsequently, the anode catalyst ink was stirred continuously in an ultrasonic bath for 20 min such that it was well dispersed. The anode catalyst ink was then brushed on a piece of nickel foam (Hohsen Corp., Japan) that served as the backing layer to form an anode electrode.

2.2. Fuel cell set-up and instrumentation

As shown in Fig. 1, the prepared MEA was fixed between the anode and cathode flow-fields. Both flow-fields were made from 316 L stainless-steel plate, in which a single serpentine flow channel, 1.0 mm wide, 0.5 mm deep, and 1.0 mm wide, was grooved by the wire-cut technique. A fuel solution containing glucose and KOH was fed into the anode flow channel by a peristaltic pump, while pure oxygen was fed to the cathode without humidification. The flow rate of the oxygen was controlled and measured by a mass flow controller (Omega FMA-7105E). Additionally, the cell temperature was measured with a thermocouple located at the anode current-collector, and two electrical heating rods were installed in the cell fixtures to control the operating temperature. An Arbin BT2000 system (Arbin Instrument Inc.) was employed to measure polar-

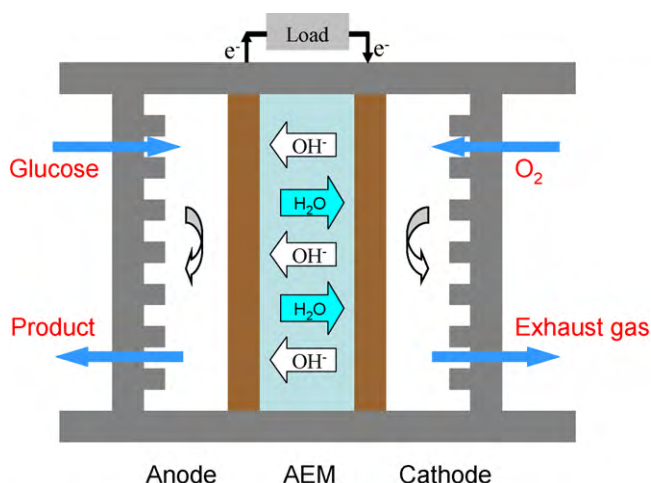


Fig. 1. Schematic representation of the AEM-DGFC.

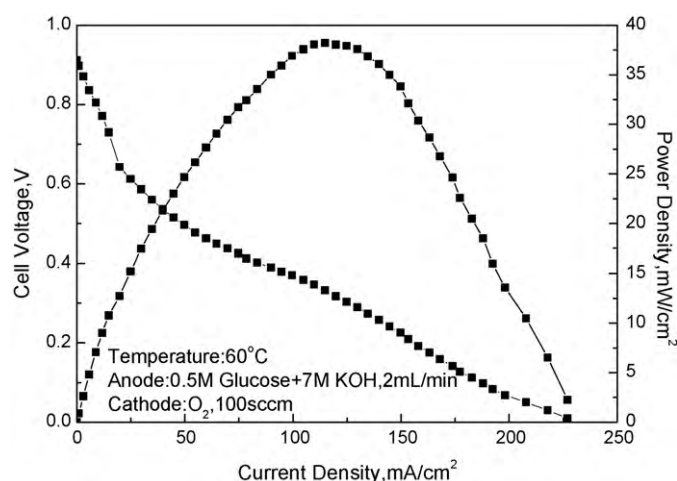


Fig. 2. Polarization and power density curves of AEM-DGFC. Anode: 0.5 M glucose + 7.0 M KOH concentration aqueous solutions, 2.0 mL min^{-1} . Cathode: pure oxygen, 100 sccm . Temperature: 60°C .

ization curves. The internal resistance of the cell was measured by the built-in function of Arbin BT2000.

3. Results and discussion

3.1. General performance

The polarization and power density curves of the AEM-DGFC with non-platinum catalysts both at the anode and the cathode are presented in Fig. 2. The experiment was performed at 60°C with an aqueous solution of 0.5 M glucose mixed with 7.0 M KOH pumped into the anode at a rate of 2.0 mL min^{-1} and with dry pure oxygen at a flow rate of 100 standard cubic centimeter per minute (sccm) fed to the cathode. A maximum power density of 38 mW cm^{-2} is achieved at a current density of 115 mA cm^{-2} . It was reported earlier [8] that a PEM-DGFC which consisted of more expensive PtRu and Pt as the anode and cathode catalysts, respectively, could yield a power density of 2.0 mW cm^{-2} . It was also found [10] that an AEM-DGFC with PtRu black and Pt black as the anode and cathode catalysts, respectively, could achieve a maximum power density of 20 mW cm^{-2} . In this study, the substantially high performance achieved with the present AEM-DGFC is attributed to the superior electrocatalytic activity of the home-made Pd-based catalyst for the GOR and the HYPERMEC™ catalyst for the ORR in the alkaline medium.

3.2. Effect of glucose concentration

The cell performance with different glucose concentrations at a KOH concentration of 1.0 M is shown in Fig. 3. The performance increases with glucose concentration from 0.1 to 0.5 M, and the limiting current density is increased from 120 to 200 mA cm^{-2} . Further increase in glucose concentration degrades the cell performance. Hence, there exists an optimum glucose concentration of 0.5 M that yields a maximum power density of 23 mW cm^{-2} , as shown in Fig. 3. The explanation of these phenomena is as follows. For a given anode catalyst, the anode potential depends on the local concentrations of both glucose and hydroxyl ions in the anode CL. A change in either one of these concentrations leads to a change in the other. Increasing the glucose concentration from 0.1 to 0.5 M causes to an increase in the glucose concentration and a reduction in the hydroxyl ions concentration at the anode CL. The concentration of hydroxyl ions, however, can still be maintained at an appropriate level for GOR. As such, the increased glucose con-

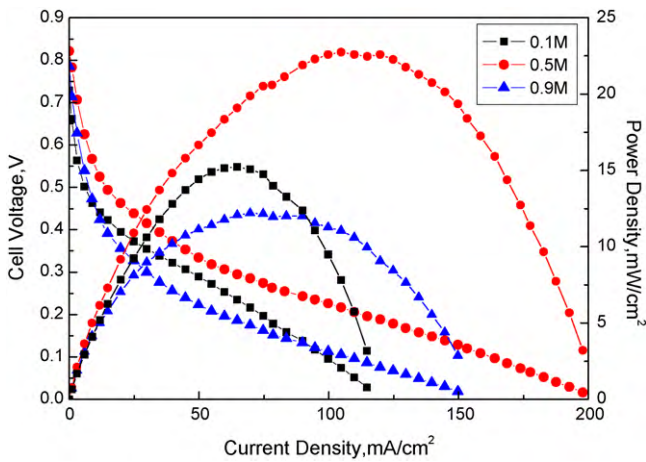


Fig. 3. Effect of glucose concentrations on cell performance. Anode: 1.0 M KOH containing various glucose concentration aqueous solutions, 2.0 mL min⁻¹. Cathode: pure oxygen, 100 sccm. Temperature: 60 °C.

centration enhances the kinetics of GOR, which lowers the anode activation loss, so that the cell voltages are improved, as evidenced by OCV in Fig. 4. On the other hand, the increased glucose concentration can also reduce the mass transport polarization, which further improves the cell performance. It should be noted that increasing the glucose concentration will increase the internal cell resistance as a result of the increased mass transport resistance of hydroxyl ions, increasing the ohmic loss. The reduced activation and mass transport losses due to the increased glucose concentration, however, not only compensate the increased ohmic loss but also improve the cell performance. Therefore, the performance of the AEM-DGFC upgrades with increase in glucose concentration from 0.1 to 0.5 M.

When the glucose concentration is raised further to 0.9 M, however, the cell performance is lowered. This is because the glucose concentration will be too high at the active surfaces corresponding to the hydroxyl ions concentration rendered by 1.0 M KOH, and thereby lead to difficulty in the adsorption of hydroxyl on the active site. Hence the electrochemical kinetics is lowered, as shown in Fig. 4, and the cell performance is reduced [19]. On the other hand, the solution with too high a glucose concentration may create a barrier to the transfer of hydroxyl ions and therefore give rise to an

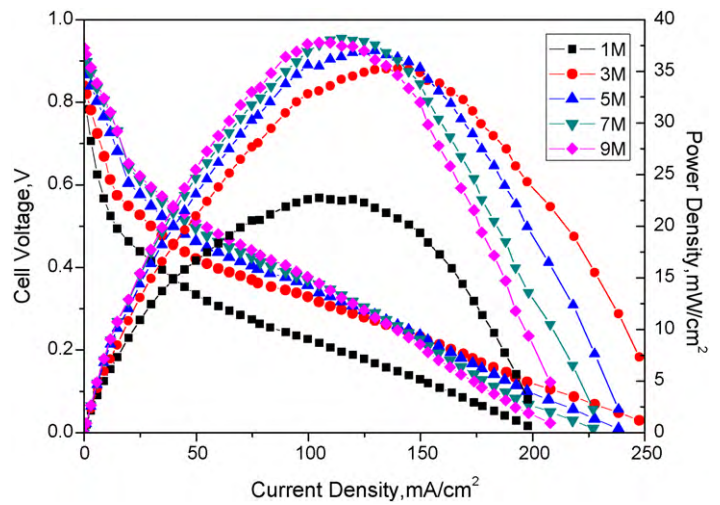


Fig. 5. Effect of KOH concentrations on cell performance. Anode: 0.5 M glucose containing various KOH concentration aqueous solutions, 2.0 mL min⁻¹. Cathode: pure oxygen, 100 sccm. Temperature: 60 °C.

increase in internal cell resistance (shown in Fig. 4) and a lowering of cell performance. As a result, the cell performance decreases with further increase in glucose concentration from 0.5 to 0.9 M, due to the lowered electrochemical kinetics and the increased ohmic loss.

3.3. Effect of KOH concentration

The effect of the KOH concentration on cell performance at a fixed glucose concentration of 0.5 M is presented in Fig. 5. In the low current density region (below 100 mA cm⁻²), it can be seen that the cell voltage increases with KOH concentration. This is because a higher KOH concentration can enhance the GOR kinetics, as shown in Fig. 6. In the meantime, the higher KOH concentration in the anode CL will increase the internal cell resistance from 419 to 537 mohm as a result of the increased mass transport resistance of hydroxyl ions from the cathode to anode, causing the larger ohmic loss, but the voltage loss is predominated by the activation polarization at low current densities. As a result, the cell voltage monotonously increases with KOH concentration due to the enhanced electrochemical kinetics, as demonstrated in Fig. 5.

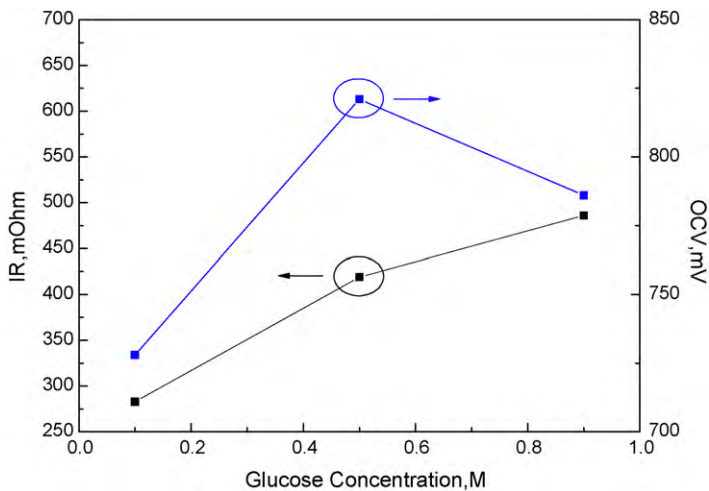


Fig. 4. Effect of glucose concentrations on open-circuit voltage and internal resistance. Anode: 1.0 M KOH containing various glucose concentration aqueous solutions, 2.0 mL min⁻¹. Cathode: pure oxygen, 100 sccm. Temperature: 60 °C.

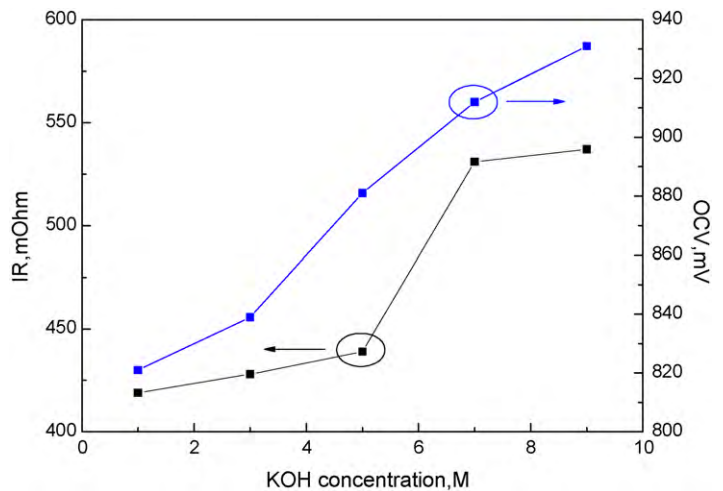


Fig. 6. Effect of KOH concentrations on open-circuit voltage and internal resistance. Anode: 0.5 M glucose containing various KOH concentration aqueous solutions, 2.0 mL min⁻¹. Cathode: pure oxygen, 100 sccm. Temperature: 60 °C.

At moderate and high current densities, it is seen that there exist different optimum KOH concentrations. With increase in current density, the optimum KOH concentration is gradually decreased from 7.0 to 3.0 M. The reason for this phenomenon is as follows. For a fixed current density region, e.g., from 100 to 130 mA cm⁻², there is an optimum KOH concentration (7.0 M). The increase in the KOH concentration from 1.0 to 7.0 M can provide faster kinetics of GOR, which is indicated by the OCV behaviour in Fig. 6. In general, the alkalinity of the anode environment significantly affects not only the electrochemical kinetics, but also the transfer of species to the anode [19,20]. As shown in Fig. 6, the high KOH concentration leads to an increase in internal cell resistance. The reason for this phenomenon is as follows. In the AEM-DGFC, the net transport of the hydroxyl ion is from the cathode to the anode. Increasing the KOH concentration at the anode causes a higher hydroxyl ion concentration in the anode CL and this impedes the hydroxyl ion transport from the cathode to the anode and thereby increases the transport resistance. The improved electrochemical kinetics of GOR as a result of the high KOH concentration, however, not only compensates the increased ohmic loss, but also improves the cell performance in this current density range. Therefore, the cell performance of this AEM-DGFC increases with KOH concentration from 1.0 to 7.0 M in this current density region. Nevertheless, when the KOH concentration further increases from 7.0 to 9.0 M, the cell performance is reduced. This is because too high a KOH concentration leads to an excessive coverage of hydroxyl ions that decreases the number of sites available for glucose adsorption in the anode CL [21] and this causes the cell performance to decline. In the meantime, the internal cell resistance continues to increase with the KOH concentration, as shown in Fig. 6, leading to a larger ohmic loss and thus a lowered cell performance. Therefore, 7.0 M can yield the highest power density of 38 mW cm⁻² in this current density region.

The above finding is not the case in the current density region from 130 to 160 mA cm⁻². The optimum KOH concentration is lowered to 5.0 M. For a fixed KOH concentration, the ohmic loss is more marked in the higher current density region. Hence, when the KOH concentration is over 5.0 M, the negative effect of the ohmic loss has exceeded the positive effect of the improved electrochemical kinetics and thereby decreased cell performance. Similarly, in the higher current density region, the optimum KOH concentration is gradually decreased to 3.0 M.

In summary, the optimum KOH concentration is dependent on the current density. At low current densities, the cell performance is predominated by the KOH concentration, due to the faster kinetics of the GOR with higher KOH concentration. In moderate and high current density regions, however, cell performance depends on adequate KOH concentrations in the anode CL for different current density regions. For a fixed current density region, too high a KOH concentration resists the transport of hydroxyl ions from the cathode to the anode and this results in a large ohmic loss and thus poor cell performance; too low KOH concentration lowers GOR kinetics that causes high activation polarization and thus poor cell performance.

3.4. Effect of anode and cathode flow rates

The effect of the anode flow rate on cell performance from 2.0 to 8.0 mL min⁻¹ at 60 °C is presented in Fig. 7. This variation in virtually does flow rate not change the cell performance. Similarly, Fig. 8 shows that the polarization curves corresponding to the different oxygen flow rates are also almost the same. In conclusion, the effects of the anode and cathode flow rate on cell performance are rather small for the present MEA.

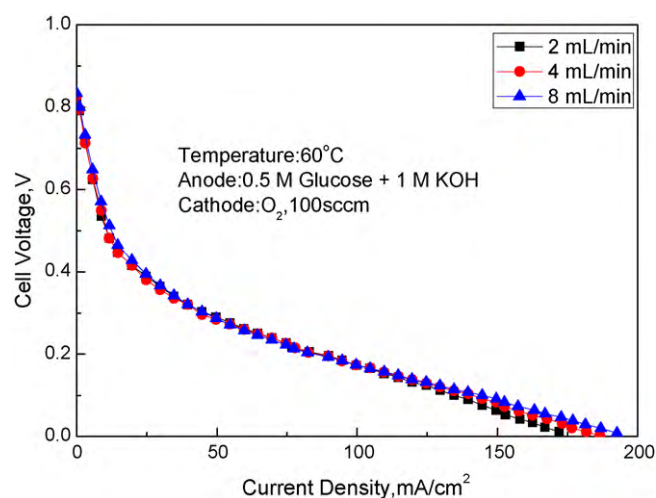


Fig. 7. Cell polarization at different anode flow rates. Anode: 0.5 M glucose + 1.0 M KOH aqueous solution, 2.0–8.0 mL min⁻¹. Cathode: pure oxygen, 100 sccm. Temperature: 60 °C.

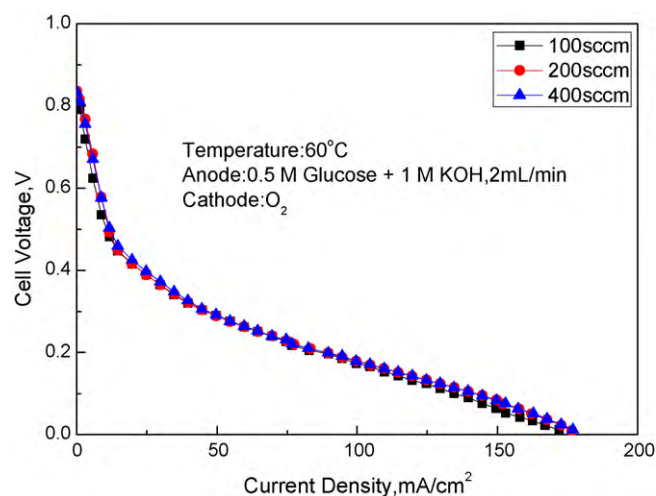


Fig. 8. Cell polarization at different cathode flow rates. Anode: 0.5 M glucose + 1.0 M KOH aqueous solution, 2.0 mL min⁻¹. Cathode: pure oxygen, 100–400 sccm. Temperature: 60 °C.

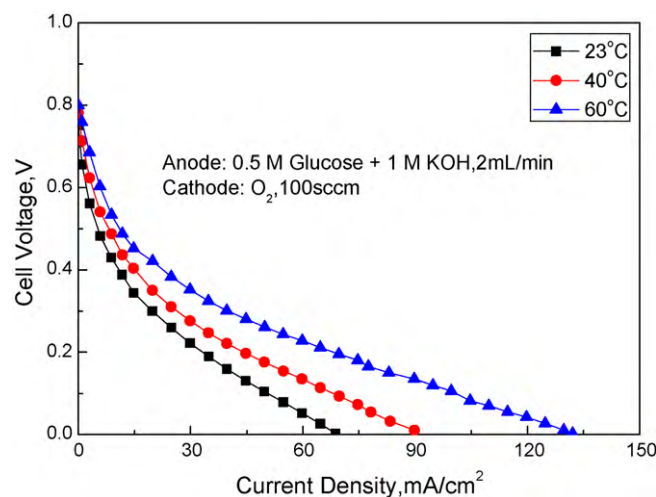


Fig. 9. Effect of temperature on cell performance. Anode: 0.5 M glucose + 1.0 M KOH aqueous solution, 2.0 mL min⁻¹. Cathode: pure oxygen, 100 sccm.

3.5. Effect of cell operating temperature

The influence of cell operating temperature on cell performance is shown in Fig. 9. It is seen that cell performance increases with temperature. In particular, the limiting current density increases from 70 to 130 mA cm⁻² when the temperature is raised from 23 to 60 °C. The improvement in cell performance with increasing operating temperature is due to faster electrochemical kinetics, increased conductivity of the hydroxyl ions, and enhanced mass transfer [11]. An increase in the operating temperature can enhance the kinetics of both the GOR and ORR. Increased hydroxyl ion conductivity will reduce ohmic polarization. In addition, increasing the operating temperature will increase the glucose and oxygen diffusivities, resulting in the low mass transport polarization due to higher reactant concentration in the anode and the cathode CLs. Consequently, the temperature is an important determinant of cell performance.

4. Concluding remarks

An alkaline direct glucose fuel cell with non-platinum catalysts has been developed and tested. When compared with conventional glucose fuel cells, such as enzymatic fuel cells and microbial fuel cells, this type of fuel cell can yield a much higher power output (38 mW cm⁻² at 60 °C) and longer durability. The high performance is attributed mainly to the increased kinetics of both the glucose oxidation reaction and the oxygen reduction reaction rendered by the alkaline medium with the anion-exchange membrane. It has been also shown that operating parameters such as glucose concentration, KOH concentration and operating temperature can significantly influence the cell performance. It should be also mentioned that although the fuel cell system developed in this work is promising in terms of its higher performance with cheaper electrolyte and catalyst materials than all other reported glucose fuel cells, some fundamental issues, such as the mechanism and the

product of glucose oxidation on the present non-platinum catalyst in alkaline media, merit extensive research.

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