

Short communication

Ethanol crossover phenomena and its influence on the performance of DEFC

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Abstract

In the present work, Nafion[®] membrane porosity changes were determined in aqueous ethanol solutions with different concentrations by weighing vacuum-dried and ethanol aqueous solution equilibrated membranes at room temperature. The ethanol crossover rate through Nafion[®]-115 membrane at different temperatures and different concentrations had been investigated in a fuel cell test apparatus by using gas chromatography analysis. The experimental results show that the swelling degree of Nafion[®] membrane gets higher as ethanol solution concentration increases. The ethanol crossover rate increases with ethanol concentration and temperature increment. The single *direct ethanol fuel cell* (DEFC) tests were carried out to investigate the effect of ethanol concentration on ethanol crossover and consequently, on the open circuit voltage and the cell performance of DEFC. It can be found that ethanol crossover presented a negative effect on the OCV and the cell performance of DEFC. It can also be found that an improved DEFC performance was obtained as temperature increased although the ethanol crossover rate increased with temperature increment.

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1. Introduction

Direct ethanol fuel cells (DEFCs) have been paid more and more attention in recent years due to the natural availability of bioethanol and its low toxicity except for the advantages of direct methanol fuel cells [1–3]. Moreover, ethanol combustion produces just the products required by the nature to recompose ethanol molecules through photosynthesis, and therefore net CO₂ contribution in atmosphere can be negligible [4–6]. The DEFC system is still at its early development stage. The key considerations with respect to the DEFC development are large overpotentials at both the anode and the

cathode having a serious impact on the voltage efficiency of the DEFC and ethanol crossover that may also have a negative effect on the cathode performance and the electrode structure. As far as the large overpotential for ethanol electrooxidation is concerned, PtSn catalyst shows more efficiently electrocatalytic activity [7–10]. Increasing temperature can improve DEFC performance by taking advantage of the pronounced thermal activation of the electrochemical reactions. Aricò et al. [11] have reported higher single DEFC performances at 130 °C with a silica modified Nafion membrane as the electrolyte. However, increasing temperature is not an optimal choice to improve the cell performance due to the intrinsic limitations of the most commonly used Nafion[®] membranes. Nafion[®] membrane, a perfluorinated ionomer membrane manufactured by E. I. Du Pont de Nemours and Company is the most commonly and widely used polymer electrolyte in fuel cells to date. That is, because Nafion[®]

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membrane's conductivity is heavily dependent on the hydrate state of the membrane, this limits the working temperature is less than 100 °C. On the other hand, the investigation on direct ethanol electrooxidation by the single fuel cell test is mainly based on Nafion[®] membrane electrolyte [12,13].

Based on our previous work [14], in the present investigation, membrane porosity was determined in the ethanol aqueous solutions with different concentrations. The effects of temperature and aqueous ethanol concentrations on ethanol crossover rate through bare Nafion[®]-115 membrane had been investigated in a fuel cell test apparatus by a TCD gas chromatograph (Varian CP 3800) equipped with a packed Parapak Q column. The single DEFC tests were carried out to evaluate the effect of aqueous ethanol concentration and temperatures on single DEFC's open circuit voltage and performance.

2. Experimental

2.1. Nafion[®] membrane porosity

Nafion[®]-115 membranes were adequately cleaned and converted to the protonic form by successively slightly boiling the membranes in 3% H₂O₂ aqueous solution, deionized water, 0.5 mol L⁻¹ H₂SO₄ aqueous solution and then deionized water again for 1 h in each step [15,16]. In order to measure membrane porosity, Nafion[®]-115 membrane samples were immersed in the ethanol aqueous solution with different concentrations and equilibrated for 36 h. Then the membranes were removed from the ethanol solution and excess liquid was wiped from the membrane surface by using a filter paper. The weight of the swollen membranes was determined by accurate balance. Then the membranes were dried at 60 °C in vacuum for 24 h and their weight was also measured again. Each sample porosity measurement was re-

peated at least three times, and the results were within the experimental error.

2.2. Ethanol crossover experiments

Ethanol crossover experiments were carried out in a single fuel cell test apparatus shown in Fig. 1. The above system has been previously described in details [2]. Nafion[®]-115 membrane was fixed by two polyester frames then clamped between two bipolar plates with silicone rubber gaskets to keep sealed. The effective area of each membrane sample was 3.4 cm × 3.4 cm. Ethanol aqueous solution was supplied through the anode compartment by a peristaltic pump at a flow rate of 1.0 mL min⁻¹. High-purity nitrogen at a pressure of 2 atm was supplied at a flow rate of 290 mL min⁻¹ to sweep off the permeated ethanol through Nafion[®] membrane and a cold trap collected the effluent mixture for 45 min. Finally, the amount of the permeated ethanol was determined by a TCD gas chromatograph (Varian CP 3800) equipped with a packed Parapak Q column.

2.3. MEA preparation and single fuel cell tests

The detailed preparation process of *membrane electrode assembly* (MEA) had been described in the literature [2]. The commercial PtRu/C (20Pt~10Ru wt.%) and Pt/C (20 wt.%) were used as the anode and cathode catalysts, respectively. The respective metal loadings were 2.0 mg (Pt + Ru) cm⁻² for the anode and 1.0 mg Pt cm⁻² for the cathode. The MEA was obtained by hot pressing at about 140 °C under a pressure of 100 kg cm⁻² for 90 s after spraying ca. 0.5 mg cm⁻² Nafion onto the surface of both anode and cathode catalyst layers.

Single DEFC tests were performed on the MEA with an active electrode area of 3 cm × 3 cm. The MEA was sandwiched between two stainless steel plates with dotted flow

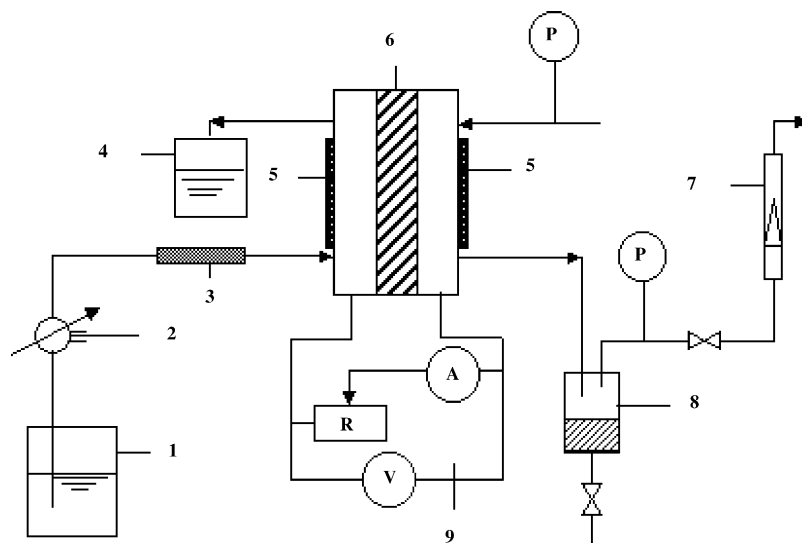


Fig. 1. Schematic diagram of a DEFC test apparatus: (1) ethanol aqueous solution tank, (2) pump, (3) heater, (4) ethanol aqueous solution recovery tank, (5) heating rod, (6) fuel cell, (7) flow meter, (8) Condenser and (9) external circuit.

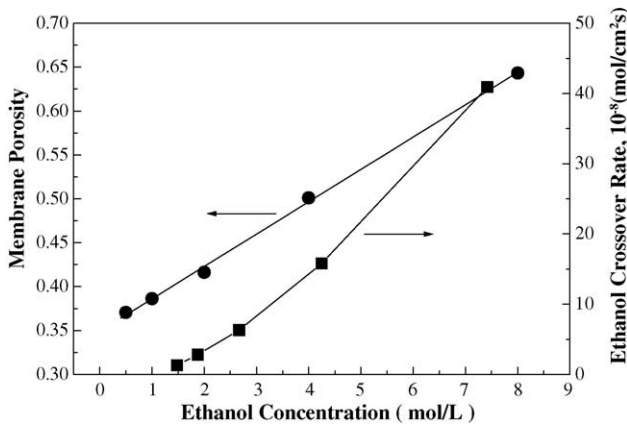


Fig. 2. The membrane porosity at room temperature and ethanol crossover rate at 75 °C vs. different ethanol concentration.

field for reactants and products to enter and exit the cell respectively. The insulation rubber gaskets were used to prevent the cell from leaking. The fuel cell was heated to the desired temperature by using an electrical heater placed in the middle of the stainless steel bipolar plates and a thermocouple to monitor the temperature. Aqueous ethanol solution preheated at the same temperature as the fuel cell was pumped through the anode compartment at a flow rate of 1.0 mL min^{-1} . Unhumidified oxygen was supplied to the cathode compartment from the cylinder at ambient temperature and a backpressure regulator controlled the desired gas pressure. During the operation of single DEFC test, the dilute ethanol aqueous solution was supplied to an inlet located at the bottom of the anode, and oxygen was fed into an inlet located at the top of the cathode. The polarization curves of DEFC were obtained using a Fuel Cell Test System (Arbin Instrument Corp.) in a galvanodynamic polarization mode.

3. Results and discussion

The effect of different ethanol concentrations in aqueous solutions both on Nafion[®] membrane porosity and on ethanol crossover rate is shown in Fig. 2. In the present work, wet membrane porosity (ε) was determined at room temperature by weighing vacuum-dried and ethanol aqueous solution equilibrated membranes and was calculated by using the following equation [17,18]:

$$\varepsilon = \frac{\text{fluid uptake volume}}{\text{total volume}} = \frac{(W_{\text{wet}} - W_{\text{dry}})\rho_{\text{dry}}}{(W_{\text{wet}} - W_{\text{dry}})\rho_{\text{dry}} + W_{\text{dry}}\rho_{\text{sol}}} \quad (1)$$

where ρ_{dry} is the dry membrane density (2.075 g cm^{-3} , for dry proton-form Nafion[®] membrane), ρ_{sol} is the aqueous solution density and W_{wet} and W_{dry} are the wet membrane density and the dry membrane density, respectively.

It can be clearly seen from Fig. 2 that the swelling degree of Nafion[®] membrane gets higher with ethanol solution concentration increment. There exit microscopic and macroscopic or bulk swelling for Nafion[®] membranes in aqueous ethanol solutions [19]. The microscopic swelling is related to the amount of water adsorbed by the ionic clusters while the macroscopic swelling is related to ethanol which can penetrate and plasticize the fluorocarbon matrix, resulting in an increase in the number density of clusters and producing an enhanced macroscopic swelling. This phenomenon can be explained also by considering electrostatic interactions in the polymer. According to Hsu and Gierke [20], the Nafion[®] membrane is described as a series of clusters interconnected by narrow pores. In each cluster, the fixed membrane charges must create an electrostatic field which extends inward the center of each sphere. Within this region, the size of the ionic atmosphere can thus be described by the Debye length defined as

$$\lambda = \left[\frac{\varepsilon RT}{2F^2 \bar{c}} \right]^{1/2} \quad (2)$$

where ε is the relative permittivity of water, F the Faraday constant and \bar{c} the ionic concentration in the cluster. Ethanol is less polar than water. Therefore when the aqueous ethanol concentration is increased, \bar{c} becomes smaller, and thus the size of the ionic atmosphere becomes larger and we can assume that the cluster size is increase as well. In other words, the membrane porosity gets higher with ethanol concentration increment.

From Fig. 2, the ethanol crossover rate changes are also plotted against ethanol concentration at 75 °C. Obviously, the ethanol crossover rate increases as ethanol concentration increases. For bare Nafion[®] membranes, the permeation of water and ethanol through the membrane will take place under the driving forces of concentration and pressure gradients. Considering the similar molecular structure of methanol and ethanol, we assume the methanol permeation model shown in Eq. (3) [21] is also suitable for ethanol.

$$j = \frac{C_1}{\left(\frac{l}{D} + \frac{1}{k} \right) + \frac{K}{kD} \Delta P} \quad (3)$$

where j is the ethanol permeation. L and D are the thickness of membrane and the effective diffusivity, respectively. K is a constant related to the effective hydraulic permeability and the constant k is a mass transfer coefficient for the cathode. C_1 is the feed side ethanol concentration.

Thus, it is easily inferred from Eq. (3) that, increasing the feed side ethanol concentration C_1 will lead to the bigger ethanol permeation with the pressure gradient kept constant. On the other hand, there is a linear relation between ethanol crossover rate and ethanol concentration. However, the observed behavior of ethanol crossover rate versus ethanol concentration in Fig. 2 is not exactly linear, which could be probably due to the following reasons: (1) ΔP could not be controlled constant; (2) there is a coupling effect between

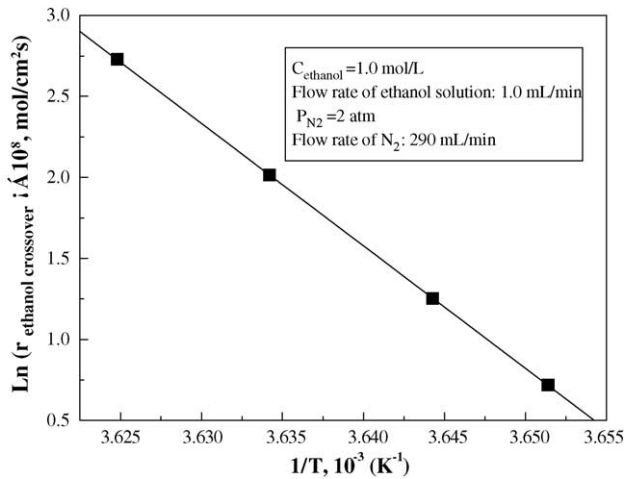


Fig. 3. The effect of the temperature on ethanol crossover rate through Nafion[®]-115 membrane. $C_{\text{ethanol}} = 1.0 \text{ mol L}^{-1}$, flow rate of ethanol aqueous solutions: 1.0 mL min^{-1} , $P_{\text{N}_2} = 2 \text{ atm}$, flow rate of nitrogen: 290 mL min^{-1} .

ethanol and water molecules, which influences the independent transportation of ethanol and water molecules through Nafion[®] membrane [22].

The effect of temperature on ethanol crossover rate through Nafion[®]-115 membrane is presented in Fig. 3. It can be distinguished from Fig. 3 that ethanol crossover rate increases as the temperature increases. The increased ethanol crossover rate with temperature increment may be attributed to the fact that at higher temperature the polymer backbone expands due to softening of the fluorinated chain [23], leading to increased permeation of ethanol as well as to a higher a water transport rate. On the other hand, the enhanced temperature also accelerates ethanol molecules thermodynamic motion, which facilitates to transport ethanol molecules through Nafion[®] membrane and consequently leading to a higher ethanol crossover rate. The ethanol crossover through Nafion[®] membranes will restrict the ethanol aqueous solutions feed concentration. Furthermore, increasing temperature can accelerate the ethanol oxidation kinetics and result in an improved single DEFC performance, at the same time, increasing temperature can also lead to a higher ethanol permeation rate, having a negative effect on the single DEFC performance, which will counteract the positive effect of temperature on the direct ethanol fuel cell performance to some extent.

According to Nernst Eq. (4), it can be theoretically obtained that at the given

$$U_{\text{cell}} = U_{\text{cell}}^0 + \frac{RT}{12F} \ln \left\{ \left(\frac{\alpha_{\text{C}_2\text{H}_5\text{OH},\text{a}} \alpha_{\text{H}_2\text{O},\text{a}}^3}{\alpha_{\text{H}_2\text{O},\text{c}}^6} \right) \times \left(\frac{P_{\text{CO}_2,\text{a}}}{P^\theta} \right)^{-2} \left(\frac{P_{\text{O}_2,\text{c}}}{P^\theta} \right)^3 \right\} \quad (4)$$

(where a and c denote anode and cathode, respectively) operating conditions, the *open circuit voltage* (OCV) of single DEFC will be increased as the ethanol solution feed concen-

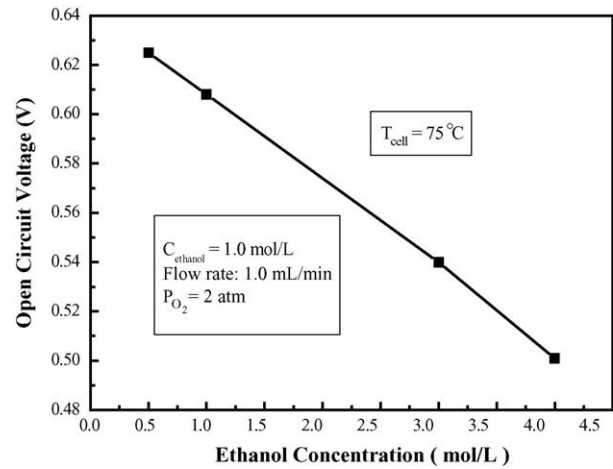


Fig. 4. Effect of the concentrations of ethanol aqueous solutions on the open circuit voltage of DEFC: $T_{\text{cell}} = 75 \text{ }^\circ\text{C}$; anode: PtRu/C (20Pt~10Ru wt.%, Johnson Matthey Corp.), $2.0 \text{ mg (Pt + Ru) cm}^{-2}$, $C_{\text{ethanol}} = 1.0 \text{ mol L}^{-1}$; flow rate: 1.0 mL min^{-1} ; cathode: Pt/C (20 wt.%, Johnson Matthey Corp.); $1.0 \text{ mg Pt cm}^{-2}$, $P_{\text{O}_2} = 2 \text{ atm}$; electrolyte: Nafion[®]-115 membrane.

tration at the anode increases. Nevertheless, it can be clearly seen from Fig. 4 that the OCV of single DEFC decreases with ethanol aqueous solution concentration increment; moreover, these corresponding values are far away from the theoretical value 1.145 V [24]. This great difference between the experimental and theoretical values may be mainly attributed to the lower anode catalytic activity and the ethanol crossover. In the present work, the anode catalytic activity effect is just considered identical because of the use of the same MEA to investigate the effect of ethanol solution concentration on DEFC's OCVs. Then considering from another point of view, the overall cell voltage for a DEFC can be written as

$$V_{\text{cell}} = E_{\text{cell}} - \eta_{\text{a}} - \eta_{\text{c}} - \eta_{\text{ohmic}} - \eta_{\text{xover}} \quad (5)$$

where E_{cell} is the difference between the half-cell potentials of the anode and the cathode. η_{a} and η_{b} are the anode and the cathode overpotentials, respectively, η_{ohmic} is the overpotential due to the ohmic drop in the system and η_{xover} the overpotential due to the ethanol crossover through the membrane. Eq. (5) does not take into account the mass transport limitation at the electrocatalyst surfaces, which would produce an additional mass transport overpotential due to limitations in the diffusion rate through the porous electrode structures. When there is no current through the cell circuit, the overpotential due to the ohmic drop and the anode and cathode overpotentials do not exist, and Eq. (5) is reduced to the OCV. One can conclude that the open circuit voltage of the cell has a

$$(V_{\text{cell}})_{I=0} = \text{OCV} = E_{\text{cell}} - \eta_{\text{xover}} \quad (6)$$

direct relationship to the ethanol crossover rate. When the ethanol aqueous solution concentration supplied to the anode is increased, the ethanol crossover through Nafion[®] membrane will be increased, just as observed in Fig. 2. Consequently, this could result in a more negative effect on the open

circuit voltage of the direct ethanol fuel cell, with a decrease in DEFC's OCV from 0.62 to 0.497 V when the ethanol solution concentration increases from 0.5 to 4.0 mol L⁻¹, which one can distinguish from Fig. 4. Considering only from the point of the open circuit voltage of the cell, it appears that the lower the ethanol aqueous solution concentration is the more desirable the situation becomes. Nevertheless, from the practical considerations, one should take into account the comprehensive factors affecting the single direct ethanol fuel cell performance, such as concentration polarization. On the other hand, according to the energy conservation law, only when there is enough energy input, is there enough energy output. As an integrated result of these considerations, there is an optimum ethanol aqueous solution feed concentration, which is shown in Fig. 5. As one can distinguish from Fig. 5, the concentration of ethanol significantly affects the DEFC performance. By comparing the peak power densities with different ethanol concentration solution supplied to the anode shown in Fig. 5(b), it can be distinguished that there is a volcano-type behavior presenting a maximum 19.4 mW cm⁻² when

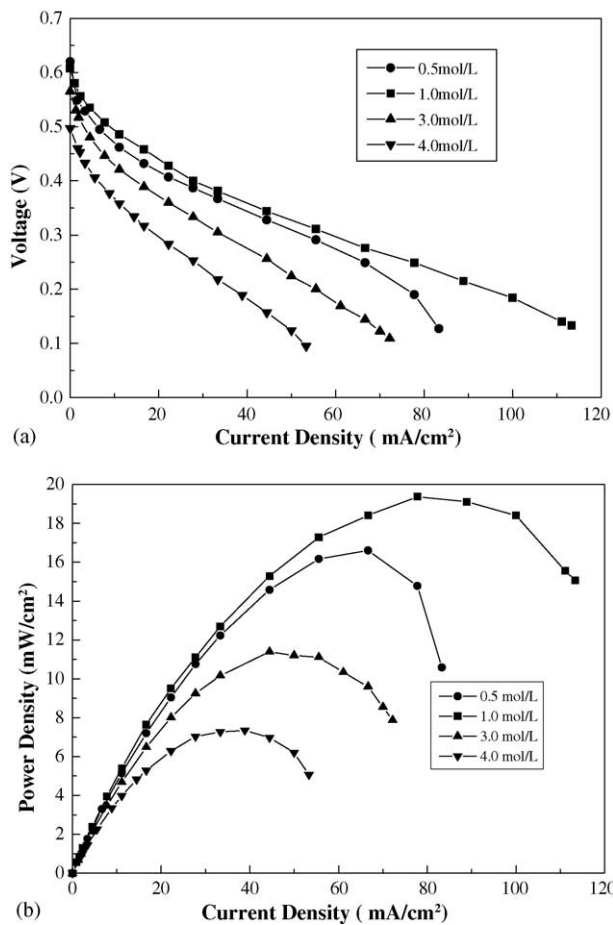


Fig. 5. Effect of the concentration of ethanol aqueous solutions on the single DEFC performance: $T_{\text{cell}} = 75^\circ\text{C}$; anode: PtRu/C (20Pt~10Ru wt.%, Johnson Matthey Corp.), 2.0 mg (Pt + Ru) cm⁻², $C_{\text{ethanol}} = 1.0 \text{ mol L}^{-1}$; flow rate: 1.0 mL min⁻¹; cathode: Pt/C (20 wt.%, Johnson Matthey Corp.), 1.0 mg Pt cm⁻², $P_{\text{O}_2} = 2 \text{ atm}$; electrolyte: Nafion[®]-115 membrane.

ethanol concentration is 1.0 mol L⁻¹. It is worth noticing that in Fig. 5(a) that there is a more rapid voltage drop during the ohmic polarization region. This may be caused by the broken electrode structure due to the delamination of catalyst layer from the electrolyte membrane resulting from a higher Nafion[®] membrane swelling degree in ethanol solution of higher concentrations which is mentioned above in Fig. 2. The cell internal resistance will get higher when the electrode delamination occurs which will lead to the rapid voltage drop in the ohmic polarization region. It can also be seen from Fig. 5(a) that when the ethanol solution is 0.5 mol L⁻¹, there is the mass transportation limitation at higher current density. So in order to maximize the direct ethanol fuel cell performance, it is very important to optimize and regulate the ethanol feed concentration with respect to current density.

The effect of the cell temperature on the single DEFC performance is presented in Fig. 6 (a) and (b). It can be clearly seen from Fig. 6 that the cell performance was improved with the cell temperature increment. The enhanced cell performance could be attributed to the accelerated electrode reaction kinetics of both ethanol electro-oxidation at the anode and oxygen electro-reduction at the cathode resulting from

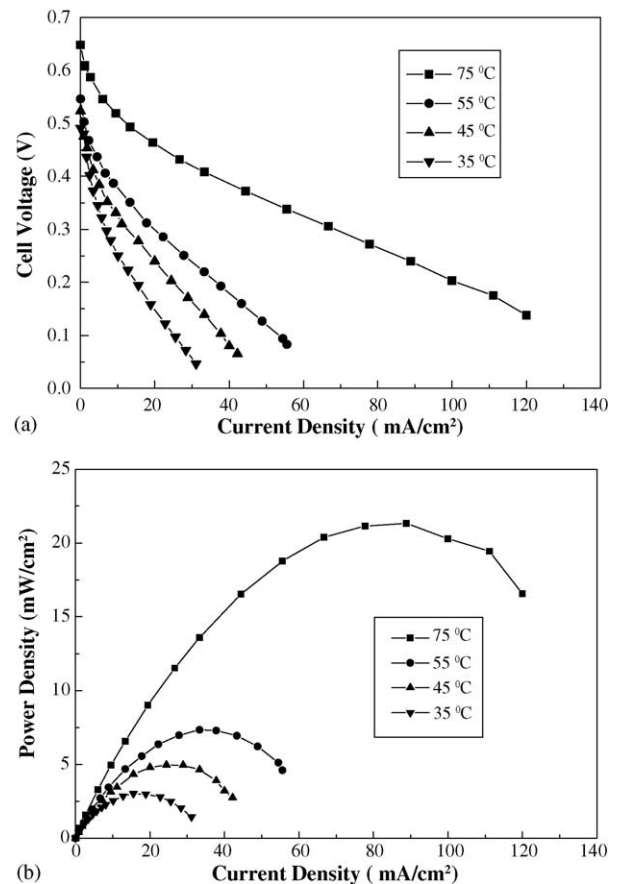


Fig. 6. Effect of temperature on the single DEFC performance: anode: PtRu/C (20Pt~10Ru wt.%, Johnson Matthey Corp.), 2.0 mg (Pt + Ru) cm⁻², $C_{\text{ethanol}} = 1.0 \text{ mol L}^{-1}$; flow rate: 1.0 mL min⁻¹; cathode: Pt/C (20 wt.%, Johnson Matthey Corp.), 1.0 mg Pt cm⁻², $P_{\text{O}_2} = 2 \text{ atm}$; electrolyte: Nafion[®]-115 membrane.

the more facile transportation of electrons and protons because of the increased temperature. On the other hand, when the cell temperature is increased, the ethanol crossover rate will accordingly be increased which can also be observed in Fig. 3. Consequently, the incremental ethanol crossover rate could lead to a more negative effect on the open circuit voltage and the DEFC performance. This will counteract the positive effect of the increased temperature on the cell performance to some extent. Ethanol crossover will limit the feed concentration and the cell temperature. So, it is necessary and important to eliminate, or reduce to some degree, the ethanol crossover through the electrolyte membrane from the anode to the cathode. The ultimate solution to this problem is to research and develop a novel electrolyte membrane with higher proton conductivity and no or much lower ethanol permeability. Furthermore, it is desirable that this novel electrolyte membrane can also sustain higher temperatures since the ethanol electro-oxidation kinetics is sluggish at lower temperatures and this is one of the main factors resulting in the lower DEFC performance.

4. Conclusion

Nafion[®] membrane presents a higher swelling degree in ethanol aqueous solutions with a higher concentration. Ethanol crossover through Nafion[®] membrane increases with ethanol aqueous solution concentration and temperature increment. At a given working temperature, ethanol solution feed concentration has an obvious effect on the open circuit voltage and the performance of the single direct ethanol fuel cell. The increased cell temperature can significantly improve the single DEFC performance even if the incremental ethanol crossover with temperature increment counteracts the positive effect of the temperature on the DEFC's performance to some extent.

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References

- [1] F. Delime, Ph.D. thesis, University of Poitiers, 1997.
- [2] S. Song, L. Chen, J. Liu, Z. Wei, Q. Xin, *Chin. Electrochem.* 8 (1) (2002) 105.
- [3] J. Wang, S. Wasmus, R.F. Savinell, *J. Electrochem. Soc.* 142 (1995) 4218.
- [4] S.L. Douvartzides, Ph.D. thesis, University of Thessaly, 2003.
- [5] S.L. Douvartzides, F.A. Coutelieris, A.K. Demin, P.E. Tsiakaras, *Int. J. Hydrogen Energy* 29 (4) (2004) 375.
- [6] M.A. Goula, S.K. Kontou, P.E. Tsiakaras, *Appl. Catal. B* 49 (2) (2004) 135.
- [7] W. Zhou, Z. Zhou, S. Song, W. Li, G. Sun, Q. Xin, P. Tsiakaras, *Appl. Catal. B* 46 (2) (2003) 273.
- [8] W.J. Zhou, B. Zhou, W.Z. Li, Z.H. Zhou, S.Q. Song, G.Q. Sun, Q. Xin, S. Douvartzides, M. Goula, P. Tsiakaras, *J. Power Sources* 126 (2004) 16.
- [9] F. Delmine, J.-M. Léger, C. Lamy, *J. Appl. Electrochem.* 29 (1999) 1249.
- [10] W.J. Zhou, S.Q. Song, W.Z. Li, Z.H. Zhou, G.Q. Sun, Q. Xin, S. Douvartzides, P. Tsiakaras, *J. Power Sources* 140 (2005) 50.
- [11] A.S. Aricò, P. Cretì, P.L. Antonucci, V. Antonucci, *Electrochem. Solid-State Lett.* 1 (2) (1998) 66.
- [12] F. Vigier, C. Coutanceau, A. Perrard, E.M. Belgsir, C. Lamy, *J. Appl. Electrochem.* 34 (2004) 439.
- [13] W.J. Zhou, W.Z. Li, S.Q. Song, Z.H. Zhou, L.H. Jiang, G.Q. Sun, Q. Xin, K. Poulianitis, S. Kontou, P. Tsiakaras, *J. Power Sources* 131 (2004) 217.
- [14] S. Song, W. Zhou, Z. Liang, R. Cai, G. Sun, Q. Xin, V. Stergiopoulos, P. Tsiakaras, *Appl. Catal. B* 55 (2005) 65.
- [15] K. Scott, W.M. Taama, P. Argyropoulos, *J. Power Sources* 79 (1) (1999) 43.
- [16] X. Ren, M.S. Wilson, S. Gottesfeld, *J. Electrochem. Soc.* 143 (1996) L12.
- [17] T.E. Springer, E.W. Schneider, R.S. Conell, R.F. Hill, *J. Electrochem. Soc.* 139 (12) (1992) 3421.
- [18] M.W. Verbrugge, *J. Electrochem. Soc.* 136 (1989) 417.
- [19] J.A. Elliott, S. Hanna, A.M.S. Elliott, G.E. Cooley, *Polymer* 42 (2001) 251.
- [20] W.Y. Hsu, T.D. Gierke, *J. Membr. Sci.* 13 (3) (1983) 307.
- [21] J. Cruickshank, K. Scott, *J. Power Sources* 70 (1998) 40.
- [22] M. Mulder (Ed.), *Basic Principles of Membrane Technology*, 2nd ed., Twente University, 1996.
- [23] V. Gogel, T. Frey, Y. Zhu, K.A. Friedrich, L. Jörissen, J. Garche, *J. Power Sources* 127 (2004) 172.
- [24] C. Lamy, E.M. Belgsir, J.-M. Leger, *J. Appl. Electrochem.* 31 (2001) 799.