

# Improvement on performance and efficiency of direct methanol fuel cells using hydrocarbon-based membrane electrode assembly



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## HIGHLIGHTS

- Faradaic efficiency and water transfer coefficient (WTC) of DMFC MEAs are calculated based on mass balance measurements.
- Faradaic efficiency of the HC-based MEAs is generally improved over the Nafion-based MEAs.
- Nafion-based MEAs show a WTC of 3, whereas the HC-based MEAs show a very low WTC of -2.
- Low WTC of the HC-based MEAs indicates the back-diffusion of water from the cathode to the anode.
- Performance of HC-based MEAs is improved as the fuel stoichiometry increases, maintaining high Faradaic efficiency.

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## ABSTRACT

In order to improve the energy efficiency (fuel efficiency and electrical power) of direct methanol fuel cells (DMFCs), the hydrocarbon (HC) membrane-based membrane electrode assemblies (MEAs) are investigated under various operating conditions. The MEAs are then compared with the conventional Nafion-based MEA in terms of their efficiency and performance. The Faradaic efficiency and water transfer coefficient (WTC) are calculated based on mass balance measurements. The Faradaic efficiency of the HC-based MEAs is improved over the Nafion-based MEAs since methanol crossover decreased. The performance of HC-based MEAs shows strong dependency on the anode stoichiometry at high current densities probably because of the limited mass transport of fuel, which is not observed for the Nafion-based MEAs. The Nafion-based MEAs show a WTC of 3, whereas the HC-based MEAs show a very low WTC of -2, indicating the back-diffusion of water from the cathode to the anode. This may have limited mass transport by interrupting proton conduction at high current densities. The performance of HC-based MEAs at high current densities is improved as the fuel stoichiometry increases; High Faradaic efficiency is maintained by decreasing the cathode stoichiometry.

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## 1. Introduction

Over the past three decades, higher efficiencies and inexpensive membrane electrode assemblies (MEAs) of direct methanol fuel cells (DMFCs) have been achieved through decreasing methanol crossover and use of highly active catalysts in DMFCs [1]. Better construction, employing improved materials, stacks, and systems, has increased the efficiency, performance, and durability of DMFC systems [1–5]. In particular, higher efficiency would greatly aid the use of DMFC in portable electronic devices and decrease fuel costs per power output [6–8]. Commercialization, however, still requires advanced MEA components and operation logics to overcome the reduced energy efficiency resulting from the fuel crossover, which

is strongly dependent on MEA components (e.g. membrane, electrode design, and gas diffusion layers) and operating conditions (e.g. fuel concentration and flow rate, current density, and working temperature) [8].

Greater efficiency has been sought using highly efficient MEAs that consist of methanol-tolerant catalyst layers, hydrocarbon (HC) membranes, composite materials, and anodes with thicker microporous and gas diffusion layers (MPLs and GDLs) [9–12]. Many researchers have recently reported that more efficient use of methanol fuel can be achieved via developments of methanol-tolerant catalyst layers and anode MPLs [13–16]. In addition, methanol crossover from the anode to the cathode can be reduced by modifying existing Nafion-based membranes or by developing new composite or HC-based membranes [17,18]. MEAs compatible with high concentrations of methanol are also being sought. Among these technologies to improve energy efficiency, the

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polymer electrolyte membrane is the most important component in MEAs for fabricating the highly efficient DMFC system.

Fluorinated membrane materials such as Nafion are currently the most commonly used. Nafion-based MEAs contain hydrophilic sulfonic acid groups in Teflon, which give them high proton conductivity and chemical durability. However, they are hampered by high methanol crossover and their water permeability can cause cathode flooding [11,19]. Methanol that reaches the cathode can be converted into carbon dioxide, which decreases the cell efficiency. The resulting mixed potential at the cathode results in additional losses [12,15,20]. Such problems limit the operation of cells at high methanol concentrations; cathode catalyst poisoning can also occur during prolonged operation, which further decreases the performances of the cells. On the other hand, HC membranes are promising and less expensive alternatives to conventional fluorinated membranes. They are thermally stable and show high glass transition ( $T_g$ ) and melting ( $T_m$ ) temperatures ( $T_g$ :  $\sim 150$  °C for HC membrane and  $\sim 110$  °C for Nafion) [21,22]. Their narrow proton conduction channels can lead to greatly reduced methanol crossover [23–27]. Krivobokov et al. [25] tested the transport and sorption of water and methanol in membranes containing proton-conducting perfluorosulfonic acid and HCs. Lower power density was achieved than when using Nafion, though the membrane performed more reliably. Zhu et al. [26] prepared a sulfonated poly(ether ether ketone) membrane via crosslinking. It outperformed the Nafion 115 membrane, showing low water uptake and methanol crossover. However, HC membranes showed relatively low proton conductivity and high interfacial resistance with electrodes. Kim and Pivovar [27] suggested that HC-based membrane/electrode interfaces are caused by poor wetting, water transfer mismatch, and dimensional mismatch across the interface. Furthermore, HC-based MEAs for DMFCs are generally inferior to conventional fluorinated MEAs in terms of fabrication, performance, electrode interface adhesion, and durability.

The energy efficiency of the DMFC is also strongly dependent on the operating conditions of the system such as fuel concentration and flow rate, current density, and working temperature [8,10]. In general, the fuel efficiency of the DMFC obviously increases due to the reduced methanol crossover through the membrane, as the temperature and methanol concentration decreases and the current density increases. Determining the optimal operating conditions in the DMFC is therefore an important factor in the design of highly efficient FC systems.

Hence, this work seeks to prepare HC-based MEAs that are less expensive and more fuel efficient than fluorinated Nafion-based MEAs. The performance of MEAs with respect to operating parameters is tested to minimize methanol and water crossover, while they maintain high power output. Polarization curves are measured under various flow rates at both the anode and cathode, and the performance of MEAs is assessed by calculating the Faradaic efficiency and water transfer coefficient (WTC) via a mass balance study [13,10,28]. With respect to the Nafion-based MEAs, the comparable performance of HC-based MEAs, while maintaining the higher efficiency, could be achieved by optimizing the operating conditions involving anode stoichiometry.

## 2. Experimental

### 2.1. MEA fabrication

A commercial Nafion-based MEA was employed with a Nafion115 (Dupont, USA) membrane with an anode of  $6 \text{ mgPtRu cm}^{-2}$  (Johnson Matthey, UK) and a cathode of  $2 \text{ mgPt cm}^{-2}$  (Johnson Matthey, UK) catalysts. A similar HC-based MEA was prepared using a Toyobo membrane (DM-102, Japan). The catalyst ink was

mixed by catalysts, Nafion ionomer solution, and polytetrafluoroethylene (PTFE) in isopropanol alcohol solution to ensure a homogeneous suspension. The catalyst inks were coated uniformly onto polyethylene terephthalate (PET) blank films and the catalyst layers of both electrodes were then transferred from the PET films to the membrane by hot pressing at  $0.3 \text{ tonf cm}^{-2}$  for 10 min. The MEA was fabricated by placing gas diffusion layers (GDLs, TGP-H-060, Toray Carbon, Japan) on either side of the catalyst coated membrane by hot pressing at  $125$  °C and  $0.1 \text{ tonf cm}^{-2}$  for 3 min. The active area of both MEAs was  $25 \text{ cm}^2$ .

The operation characteristics of the DMFC MEA were automatically controlled by a Fuel Cell Test Station (Sci-Tech, Korea). Current–voltage polarization curves were measured in galvanostatic mode ( $0.1 \text{ A}$  per step and  $10 \text{ s}$  per step) with a  $0.5 \text{ M}$  methanol and compressed dry air at various flow rates (stoichiometry  $\lambda = 2.0$ – $4.0$  with the criterion of  $0.5 \text{ M}$  MeOH solution and  $130 \text{ mA cm}^{-2}$ ). Methanol and air were fed into the single DMFC MEA by a FMI pump (ISMATEC, Switzerland) and a mass flow controller under ambient conditions. The power density was obtained from current–voltage polarization curves at  $65$  °C.

### 2.2. Measurements of Faradaic efficiency and WTC

Faradaic efficiency describes the transfer of charge in a system that facilitates an electrochemical reaction. It can be measured in two ways (Fig. 1). Kang et al. [28] reported Faradaic efficiency measurement by assessing the change of methanol concentration before and after contact with the anode, as shown in Fig. 1a. The mass difference between the anode feed ( $F_{\text{MeOHin}}$ ) and effluent ( $F_{\text{MeOHout}}$ ) allows calculation of the methanol concentration change and Faradaic efficiency ( $\eta_f^*$ ) at a given time.



$$\eta_f^* = \frac{F_{\text{MOR}}}{F_{\text{MeOHin}} - F_{\text{MeOHout}}} \times 100 \quad (2)$$

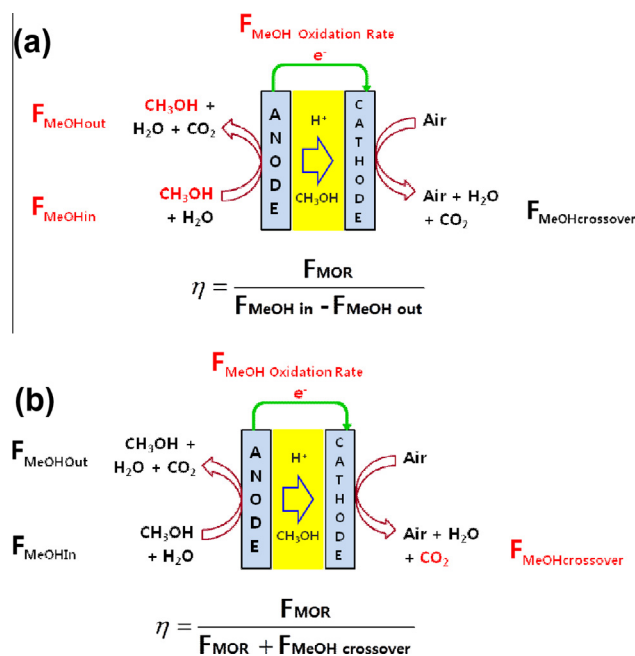


Fig. 1. Calculations of Faradaic efficiency and water transfer coefficient (WTC) via (a) assessment of the change of methanol concentration before and after contact with the anode and (b) measurement of the cathode exhaust's carbon dioxide concentration.

where  $F_{MOR}$  is the amount of fuel used to generate a current by the oxidation of methanol. The efficiency was obtained in this work by calculation from the measurement of the cathode exhaust's carbon dioxide concentration, assuming full oxidation of the methanol that crosses the membrane to the cathode, as shown in Fig. 1b [8,13]. For this method, Faradaic efficiency ( $\eta_f$ ) is defined as the proportion of the methanol flux consumed by oxidation at the anode out of the total amount of methanol consumed.

$$\eta_f = \frac{F_{MOR}}{F_{MOR} + F_{MeOHcrossover}} \times 100 \quad (3)$$

where  $F_{MeOHcrossover}$  is the amount of fuel consumed by methanol crossover.  $CO_2$  in the cathode exhaust gas was measured *in situ* using a sensor (Valsaia, Finland) and was used to calculate the corresponding amount of methanol that passed through the membrane. The water transport coefficient (WTC) indicates the movement of water through the membrane from the cathode to the anode, which occurs through electro-osmotic drag and diffusion or permeation, due to the hydraulic pressure gradient [19,23,29]. The electro-osmotic drag coefficient represents the number of water molecules transported across the membrane per proton during the passage of current in the absence of activity gradients. Diffusion occurs through water activity gradients in the membrane. WTC can thus be calculated as follows:

$$WTC = N_{H_2O} \frac{F}{i} \quad (4)$$

where  $N_{H_2O}$ ,  $i$ , and  $F$  are the water crossover flux, current density, and Faraday constant, respectively. Details on experimental procedures are described in previous works [8,13,28].

### 3. Results and discussion

#### 3.1. MEA performances

The physical–chemical characteristics of the Toyobo HC membrane (DM-102) are summarized in Table 1 and are compared with those of Nafion115 [30–35]. The Nafion membrane is comprised of a perfluorinated backbone with side chains that are terminated by strongly acid  $-SO_3H$  groups [36,37], whereas DM-102 HC membrane consists of a poly (arylene ethers) (PAEs) group [38]. The proton conductivity and MeOH permeation rate (in 5 M MeOH) of the HC membrane are  $0.06 \text{ S cm}^{-1}$  and  $6.9 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ , respectively, of  $30 \mu\text{m}$  thickness, whereas those of the Nafion115 are  $0.012 \text{ S cm}^{-1}$  and  $2.8 \times 10^{-5} \text{ mol cm}^{-2} \text{ s}^{-1}$ , respectively, of  $127 \mu\text{m}$  thickness. The low methanol permeability of the HC membrane could be related to the high Faradaic efficiency with low methanol crossover through the membrane from the anode to the cathode. Selectivity is also a crucial parameter for comparing membranes in DMFCs and defining the ratio of proton conductivity

to methanol permeability [35]. HC membrane shows higher selectivity than that of Nafion115 under a 5 M MeOH solution at  $25^\circ\text{C}$ , suggesting that HC membrane may be the better membrane with respect to application for high efficiency DMFCs.

Nafion- and HC-based MEAs were analyzed through polarization curve measurements at  $65^\circ\text{C}$  and are shown in Fig. 2. Fuel and air flow rates were controlled within a stoichiometric range of 2.0–4.0. The Nafion-based MEA achieved  $0.515 \text{ V}$  at  $130 \text{ mA cm}^{-2}$ , and showed no significant changes at different air and fuel stoichiometries ( $\lambda$ ). The observed power densities were 67.9, 68.3, and  $67.8 \text{ mW cm}^{-2}$  in the current density of  $130 \text{ mA cm}^{-2}$  as air flow increased at the cathode stoichiometries ratios ( $\lambda$ ) of 2.0, 3.0, and 4.0, respectively (Fig. 2a). In addition, the power densities were 67.5, 67.7, and  $67.1 \text{ mW cm}^{-2}$  at  $130 \text{ mA cm}^{-2}$  when the MeOH flow rate was increased to 2.0, 3.0, and 4.0 stoichiometry, indicating a slight increase in cell performance (Fig. 2b). That is, the Nafion-based MEA was slightly influenced by the anode stoichiometry but not by air flux at the cathode, and therefore maintained a stable output.

On the other hand, the performance of the HC-based MEA greatly improved as anode stoichiometry increased from 2.0 to 4.0 at fixed cathode stoichiometry (Fig. 3a): the operation voltage increased from  $0.396 \text{ V}$  to  $0.462 \text{ V}$  at a current density of  $130 \text{ mA cm}^{-2}$ . Performance was increasingly reduced by limited mass transport at high current densities with increasing anode stoichiometry, indicating that the fuel was not adequately supplied at high current densities. Similar performance loss has been reported for anode gas diffusion layers with thick anode MPLs [13,14,39]. This suggests that dense anode electrode layers, formed to reduce methanol crossover, lead to increased Faradaic efficiency at the cost of performance. At fixed anode stoichiometry and variable cathode stoichiometry, performance was not greatly influenced by the cathode flow rate, similar to the Nafion-based MEA (Fig. 3b). The performance of the HC-based MEAs depended on the anode stoichiometry, which needs to be optimized for improved performance and efficiency. The ionomer for the HC-based MEAs also needs additional development to reduce cathode water flooding, improve  $CO_2$  elimination in the anode, and improve the interfacial adhesion between the electrode and the membrane [40,41].

#### 3.2. Comparison of properties of MEAs

##### 3.2.1. Faradaic efficiency under various operating conditions

Mass balance was studied to analyze the cause of the different responses of MEAs to fuel flow rate. HC-based MEAs show low methanol permeability so that the advantage of low fuel consumption can be maximized by reducing the volume of the system or by extending the duration of operation. Faradaic efficiencies of MEAs were assessed at different fuel and air stoichiometries and current

**Table 1**  
Comparison of physical–chemical characteristics of the Toyobo HC membrane (DM-102) and Nafion115.

Properties	Unit	Toray DM-102	Nafion115 (Refs. [30–35])
Normal thickness	$\mu\text{m}$	30	127
Proton conductivity <sup>a</sup>	$\text{S cm}^{-1}$	0.06	0.012
Methanol permeation rate <sup>b</sup>	$\text{mol cm}^{-2} \text{ s}^{-1}$	$6.9 \times 10^{-7}$	$2.8 \times 10^{-5}$
Selectivity <sup>c</sup>	$\text{S mol}^{-1} \text{ cm}^{-3} \text{ s}^{-1}$	$8.70 \times 10^4$	$4.29 \times 10^3$
IEC (available acid capacity)	$\text{meq g}^{-1}$	1.56	0.9
Water content <sup>d</sup>	%water	13.9	5
Water uptake <sup>e</sup>	%water	44.5	38

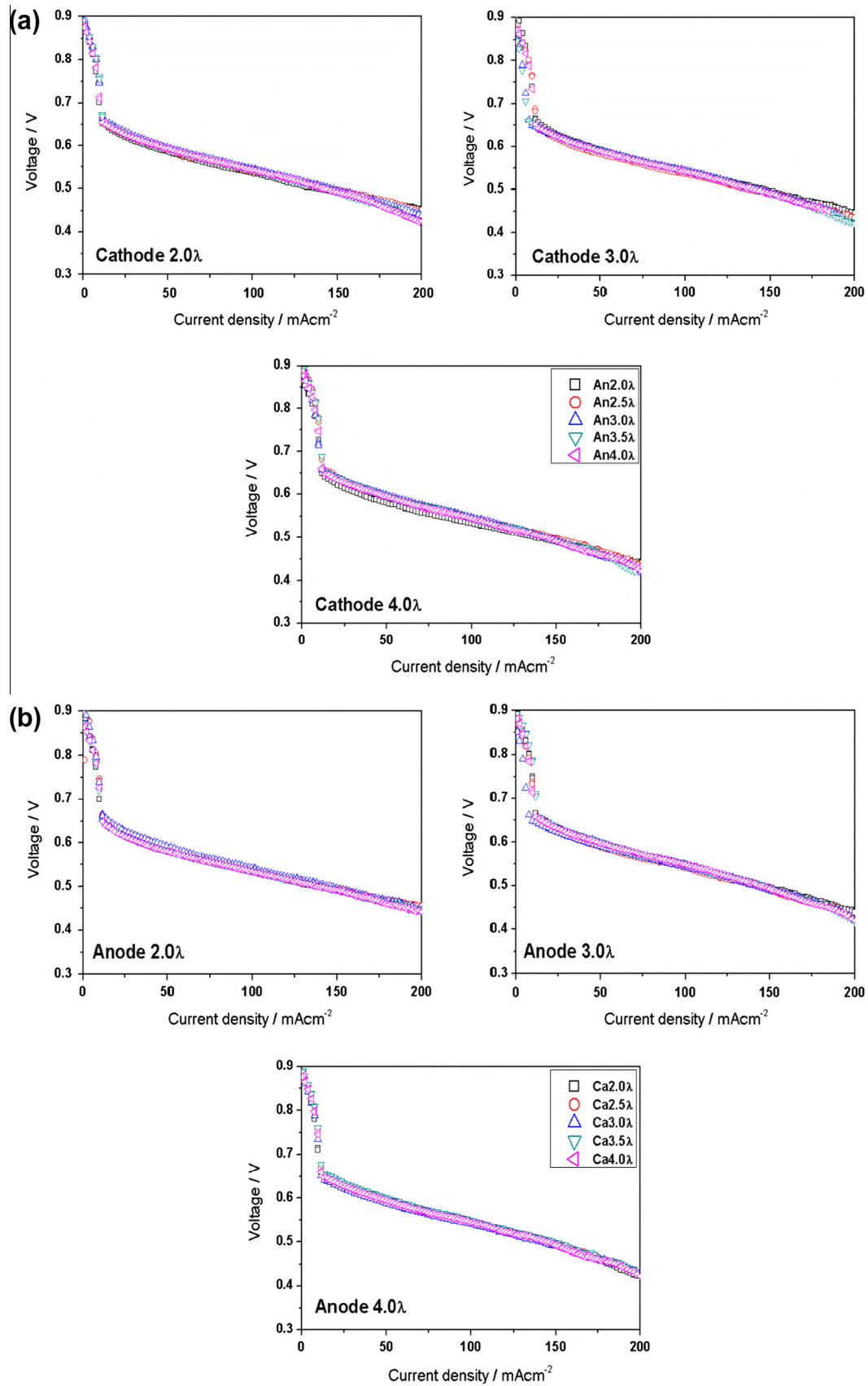
<sup>a</sup> Measured by an electrochemical impedance spectroscopy at  $30^\circ\text{C}$  and 95% RH.

<sup>b</sup> Measured under a 5 M MeOH solution at  $25^\circ\text{C}$ .

<sup>c</sup> Ratio of conductivity to methanol permeation rate.

<sup>d</sup> Measured at  $25^\circ\text{C}$ .

<sup>e</sup> Measured after soaked in  $100^\circ\text{C}$  water.



**Fig. 2.** Performance of Nafion-based MEAs with respect to (a) cathode (Ca) air and (b) anode (An) fuel stoichiometries ( $\lambda$ ).

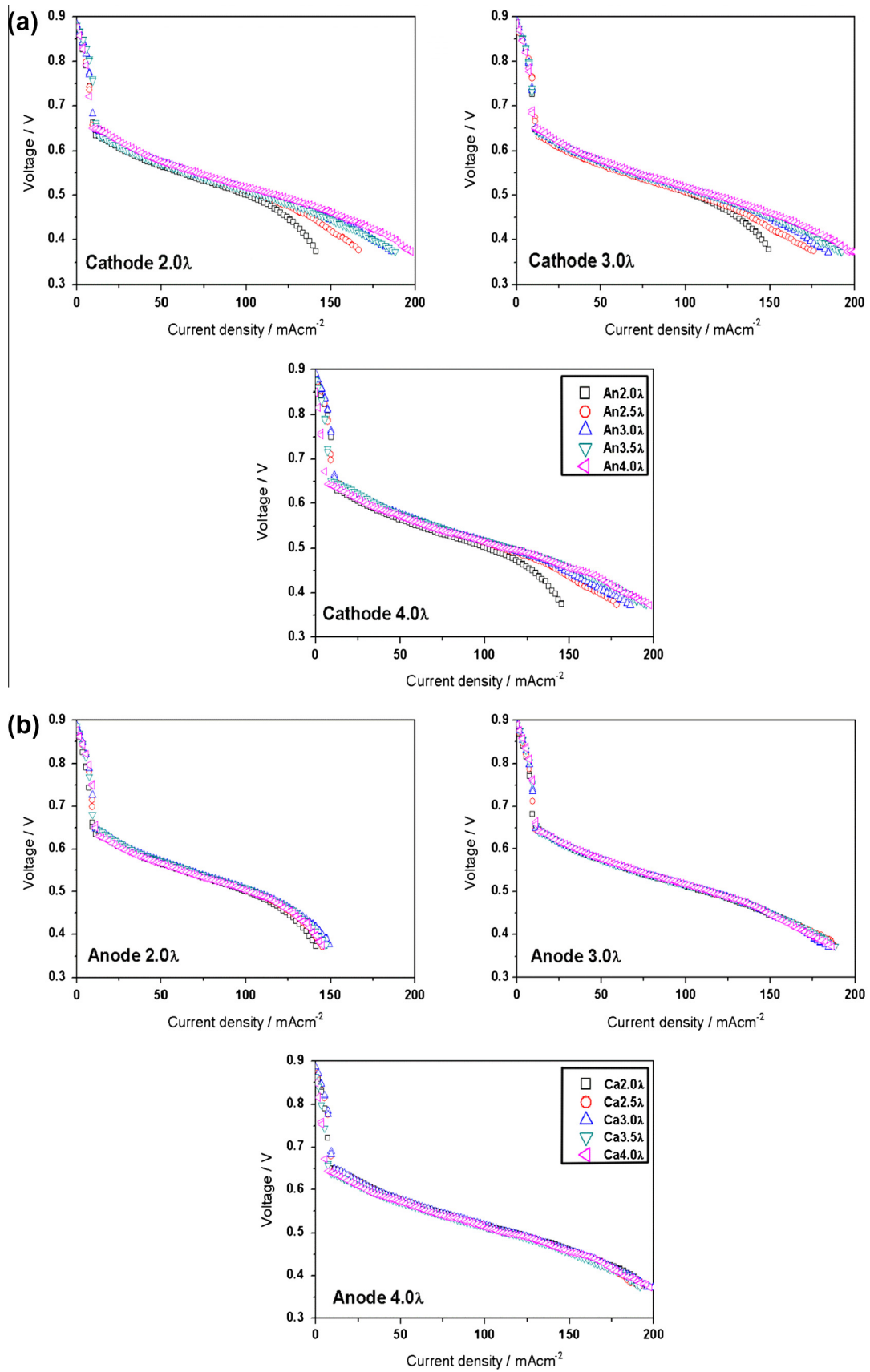


Fig. 3. Performance of HC-based MEA with respect to (a) cathode (Ca) air and (b) anode (An) fuel stoichiometries ( $\lambda$ ).



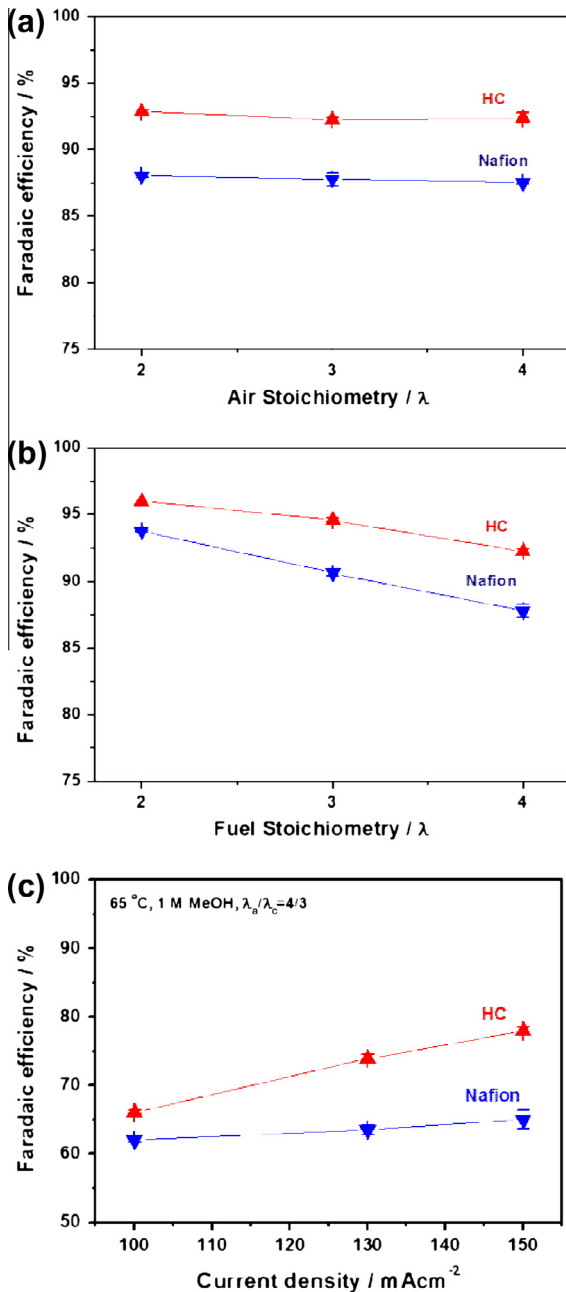


Fig. 4. Faradaic efficiency of Nafion- and HC-based MEAs with varying (a) air stoichiometry, (b) fuel stoichiometry, and (c) current density.

densities (Fig. 4). Typical measurement conditions included anode stoichiometry of 4.0, cathode stoichiometry of 3.0, 0.5 M MeOH, operation at 65 °C, and 130  $\text{mA cm}^{-2}$  current density. The fuel used at each stoichiometry was assessed to allow calculation of the Faradaic efficiencies.

Faradaic efficiency did not change significantly when the anode stoichiometry was 4.0 and the air flux was adjusted (Fig. 4a), indicating that fuel consumption was not influenced by the air supply to the cathode. The Nafion-based MEA showed approximately 5% lower Faradaic efficiency than the HC-based MEA (88.0% vs. 92.8%) due to higher methanol crossover [8,13,10]. At a fixed air stoichiometry of 3.0, Faradaic efficiency decreased in both MEAs as the fuel stoichiometry increased from 2.0 to 4.0 (Fig. 4b). The Nafion-based MEA showed a greater decrease (93.8% to 87.8%) than the HC-based MEA (96.0–92.3%) due to increasing methanol crossover with increasing fuel flow, indicating that the lower

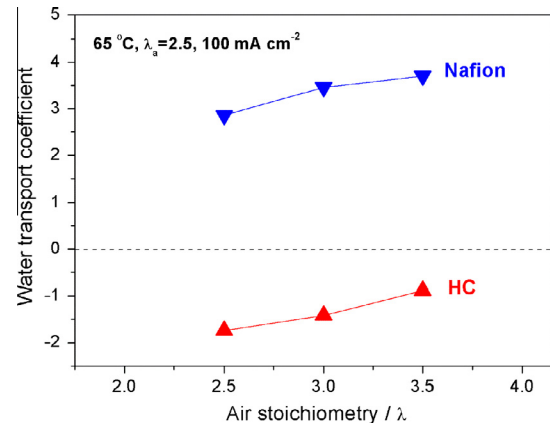


Fig. 5. WTCs of Nafion- and HC-based MEAs with respect to air stoichiometry at 100  $\text{mA cm}^{-2}$ , 65 °C and 2.5 anode fuel stoichiometry ( $\lambda_a = 2.5$ ).

methanol permeability of HC-based MEA prevented methanol crossover. Faradaic efficiency increased as the fuel stoichiometry and the methanol concentration decreased because of decreased methanol crossover under such conditions.

The Faradic efficiencies of MEAs increased as current density increased from 100 to 150  $\text{mA cm}^{-2}$  under similar stoichiometry conditions of 4.0, 0.5 M MeOH, and 65 °C (Fig. 4c) due to reduced methanol crossover. However, the Nafion-based MEA showed smaller increases (62.0–65.0%) than the HC-based MEA (66.1–78.0%). The electrochemical reactions – methanol oxidation at the anode and oxygen reduction at the cathode – occurred more frequently at higher current densities, leading to greater fuel efficiency. The increased oxidation reaction at the anode meant that less methanol being available to diffuse across the membrane to the cathode. The HC-based MEA was considered more effective as it showed lower methanol crossover at high current densities than the Nafion-based MEA.

### 3.2.2. WTC under various operating conditions

The water generated at the cathode affects the cell efficiency as power consumption can be saved by reducing the burden of an air blower and recycling the methanol fuel. Water can be generated at the cathode due to factors such as proton crossover by electro-osmotic drag, oxygen reduction reaction, and hydraulic permeation, as mentioned earlier. WTCs of MEAs were calculated by measuring cathodic water production. Since the performance of the HC-based MEA strongly depended on anode stoichiometry, the WTC measurement focused on the effects of anode stoichiometry.

WTCs were measured at different stoichiometries at 100  $\text{mA cm}^{-2}$ , 2.5 fuel stoichiometry, 1 M MeOH, and 65 °C and the results are shown in Fig. 5. As the anode fuel flux in the Nafion-based MEA increases from 2.5 to 3.5, WTC increases from 2.85 to 3.70, similar to the previous results [6,13], and for the same reason; the Nafion membrane allowed higher methanol crossover. Methanol oxidation at the cathode resulted in water formation. Furthermore, the methanol was crossovered with water molecules through the membrane to the cathode. This water crossover contributed to the high WTC.

The HC-based MEA showed lower WTCs: –1.73 to –0.88 at fuel stoichiometries of 2.5–3.5. Negative WTC indicates that less water was generated at the cathode than was produced through the reduction of oxygen; this is a significant property that could affect the development of portable fuel cells. The water that passed from the anode to the cathode was back-diffused to the anode. The low WTC of HC-based MEA reduced the flooding in the cathode, which would be expected to contribute to its durability. However, the

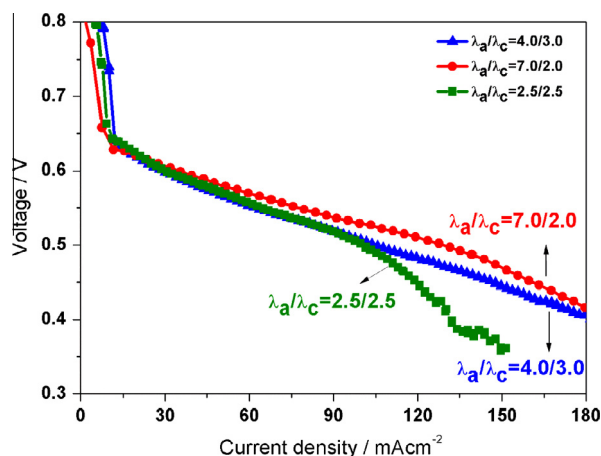


Fig. 6. Performance of HC-based MEA under various anode fuel ( $\lambda_a$ ) and cathode air stoichiometries ( $\lambda_c$ ).

water diffusive flux of HC-based MEA was so small that electroosmotic drag was the dominant driving force of water transfer to the cathode. Therefore, the water content of HC-based MEA was never adequate to allow sufficient proton conductivity. Therefore, the negative WTC probably contributed to the poorer performance of HC-based MEA than that of the Nafion-based MEA.

### 3.3. Improvement of the HC-based MEA's performance

The mass-balance analyses of Faradaic efficiency and WTC allowed the optimization of the performance of HC-based MEAs by increasing the anode stoichiometry and decreasing the cathode stoichiometry. Performance was measured based on the polarization curves shown in Fig. 6. The optimized conditions allowed increased water content of the membrane and the MEA, which would prevent dehydration of the membrane; proton conductivity also improved. At a cathode stoichiometry of 2.0, increasing the anode stoichiometry from 2.5 to 7.0 increased the voltage performance of the HC-based MEA from 0.414 to 0.496 V at  $130 \text{ mA cm}^{-2}$ , an increase of about 20%. Maximum performance increased 1.47 times from  $54.46$  to  $80.25 \text{ mW cm}^{-2}$  at  $65^\circ\text{C}$ .

Under optimal conditions, mass transport limitation was reduced and sufficient methanol fuel could be supplied for oxidation at high current densities. As the anode stoichiometry increased, the amount of methanol participating in the reaction also increased and the number of protons passing through the membrane increased, leading to greatly increased performance. Faradaic efficiency was inversely dependent on the amount of fuel; it decreased with increasing anode stoichiometry. Despite Faradaic efficiency decreasing gradually ( $96.0\% \rightarrow 94.6\% \rightarrow 92.3\%$ ), it remained higher than that shown by the Nafion-based MEA ( $87.8\%$ ). Overall, the HC-based MEA operated more efficiently at higher anode stoichiometries.

## 4. Conclusions

The performance of a HC-based MEA for use in DMFCs was compared with a Nafion-based MEA via a polarization curve measurement and mass balance study. It showed high Faradaic efficiency due to low methanol crossover. Performances and efficiencies of both MEAs were not affected by cathode stoichiometry. Both performed better, though less efficiently, with increasing anode stoichiometry. The Faradaic efficiency of the Nafion-based MEA decreased greatly from  $93.8\%$  to  $87.8\%$  as the fuel stoichiometry increased from 2.0 to 4.0. The HC-based MEA exhibited higher

Faradaic efficiency that decreased less (from  $96.0\%$  to  $92.3\%$ ); this showed a small efficiency loss due to its relatively low methanol permeability. However, its performance was undermined through limited mass transport at high current densities. The mass balance study showed that the Nafion-based MEA exhibited a WTC of 3 compared to the negative WTC shown by the HC-based MEA, which was attributed to low water crossover and also back diffusion. Low WTC can decrease power consumption by the cell through lessening the need for an air blower. It can also aid fuel recycling and reduce cathode flooding for a more durable sustained operation. However, low WTC and back diffusion may also decrease the conductivity of methanol or protons passing from the anode to the cathode. This was resolved by increasing the anode stoichiometry from 2.5 to 7.0, based on the observed Faradaic efficiency and WTC. Although this decreased the efficiency of the HC-based MEA by  $3.7\%$ , it increased voltage performance by approximately 20%.

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