

Short communication

Optimum ionic conductivity and diffusion coefficient of ion-exchange membranes at high methanol feed concentrations in a direct methanol fuel cell

K. Lee, J.-D. Nam *

Department of Polymer Science & Engineering, Sungkyunkwan University, Suwon, Kyunggi 440-746, Republic of Korea

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Abstract

In direct methanol fuel cells (DMFCs), the optimum characteristics of ion-exchange membranes are investigated at high concentrations of methanol feed up to 7 M by modifying the diffusion coefficient and the ionic conductivity of the polyelectrolyte material. A Nafion membrane is modified by the incorporation of layered double hydroxide (LDH) nanoplatelets with different $Mg^{2+}:Al^{3+}$ ratios. When the feed concentration of methanol is lower than 3 M, the DMFC is controlled by the ionic conductivity of the polyelectrolyte membrane because methanol cross-over is not relatively significant. When the feed concentration is high, however, the diffusion coefficient of methanol is the key factor that determines the performance of the fuel cell. This is due to a high concentration gradient of methanol across the polyelectrolyte membrane. The open-circuit voltage is increased by the decreased diffusion coefficient in LDH/Nafion nanocomposite membranes at methanol feed concentrations up to 7 M; apparently because methanol cross-over is suppressed by the incorporation of LDH. The maximum power density of the DMFC is determined by the two competing transport processes of ion conduction and methanol diffusion, especially at a relatively high methanol concentration, that can provide optimum operating conditions in the membrane.

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Keywords: Direct methanol fuel cell; Layered double hydroxide; Diffusion coefficient; Ionic conductivity; Methanol cross-over

1. Introduction

Methanol cross-over in a direct methanol fuel cell (DMFC) results in direct oxidation of methanol at the cathode, and hence, in decreased fuel efficiency, reduced cathode voltage, fuel loss, CO corrosion, etc. Recently, layered double hydroxides (LDHs) have been incorporated into Nafion membranes, and both the diffusion coefficient and the ionic conductivity of the resulting membranes have been successfully adjusted to suit DMFC applications [1]. In LDHs, Mg^{2+} ions are replaced with Al^{3+} ions in a controlled manner and a charge deficiency is introduced in the layers to give positively charged LDH platelets at the nanoscale [2–6]. The positively charged LDH nanoplatelets are incorporated

into the negatively charged Nafion polymer chains through an ion-exchange process due to the sulfonic groups in Nafion polymer chains. The resulting nanocomposite membranes enhance the performance of DMFCs at limited feed concentrations of methanol due to decreased diffusion rates of methanol [1].

When small quantities of nano-sized entities like montmorillonite (MMT) or LDH particles are well dispersed in polymers, the diffusion rate of liquid or gas through the nanocomposites often decreases [7–14]. When LDH particles are dispersed in Nafion, the positively charged LDH nanoplatelets neutralize some of sulfonic groups in Nafion and this may well decrease the cation exchange capacity of Nafion. Accordingly, both the proton conductivity and the diffusion coefficient of the LDH/Nafion nanocomposite systems have been lowered depending on the Mg^{2+}/Al^{3+} ratio and the ion compositions [1]. These two counter effects are

* Corresponding author. Tel.: +82 31 290 7285; fax: +82 31 292 8790.
E-mail address: jdnam@skku.edu (J.-D. Nam).

a key issue in the development of DMFCs, especially when high operation temperatures or high feed concentrations are involved.

In DMFC development, a high methanol feed concentration is desired because the mass-transfer controlled region and methanol oxidation kinetics are directly related to the methanol concentration [15,16]. The onset of diffusion limitation occurs when the rate of reactant supply is lower than the rate of electro-chemical consumption. Thus, the limiting current density can be extended by using high feed concentrations. Although this desirable in theory, an increased methanol concentration results in a high concentration gradient across the membrane and, consequently, methanol cross-over is tremendously increased [16–18]. Operation of the DMFCs at high feed concentration requires the development of polyelectrolyte membranes with balanced material properties in methanol diffusion, oxidation kinetics and proton transport.

In this study, a polyelectrolyte membrane is modified by nano-sized LDH entities and its characteristics are investigated with respect to the methanol feed concentration. The concentration of methanol was increased up to 7 M to compare the competing electrochemical processes of methanol cross-over and proton transport in DMFC operation.

2. Experimental

For the synthesis of the LDHs, a stoichiometric amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in deionized water was slowly added to NaOH and Na_2CO_3 solution and the Mg^{2+} to Al^{3+} ratio was adjusted to 2:1, 4:1 and 6:1 [1–6,19]. The resulting gelatinous precipitate was aged at 65°C for 24 h, filtered and washed with water until the pH of the supernatant solution became neutral. The LDH powder was dried in air at room temperature for 24 h.

A SE-5112 polymer (Du Pont), containing 5 wt.% of Nafion NR50 resin (ion-exchange capacity of $>0.8 \text{ meq g}^{-1}$) in an acid (H^+) form, was evaporated and dried at room temperature. The dried Nafion polymer was then dissolved in a mixture of 1-propanol, isopropanol, methanol and deionized water. The prepared LDH powder was added to the Nafion solution, and then the LDH/Nafion nanocomposite film was prepared by casting the solution on a glass plate at room temperature. A colourless and slightly opaque membrane of LDH–Nafion nanocomposite membrane was obtained and subsequently heat-treated at 373 K in a vacuum oven [1,19].

The diffusion coefficients of the synthesized membranes were measured at room temperature by using two chambers separated by the polyelectrolyte membranes [20,21]. Each chamber was filled with a methanol aqueous solution (2 M) and distilled water, respectively, and 0.05 M of 1-butanol was used as a reference tracer for both chambers. The methanol concentration was measured by gas chromatography (M600D, YoungJin Co.). The ionic conductivity of the synthesized membranes was determined by the ac

impedance method using a SI 1269 impedance/gain-phase analyzer (Solatron Co.).

Catalyst powder was dispersed in a solvent mixture of 1-propanol, isopropanol, methanol and demineralized water. Johnson Matthey platinum black (fuel-cell grade) was used for the cathode. The anode catalyst was unsupported Pt–Ru (50:50 wt.%) from Johnson Matthey. Alcoholic Nafion solution was added to a content of 15 wt.% in the dry mixture for the anode and to a content of 10 wt.% for the cathode. The mixtures were sonicated for at least 30 min at room temperature.

The catalyst pastes were dispersed on carbon paper with an air gun. The membrane electrode assembly (MEA) was constructed by pressing the LDH–Nafion nanocomposite membranes, catalyst layer and carbon paper at 130°C under 100 bar for 3 min. The anode metal loading was 5 mg cm^{-2} of Pt–Ru, while the cathode loading was approximately 5 mg cm^{-2} of Pt. Single-cell tests were performed in a cell with a cross-sectional area of 9 cm^2 at room temperature.

3. Results and discussion

If the diffusion rate through the membrane complies with Fick's law, the following relation should be satisfied [1,20,21]:

$$\ln \left(\frac{C - C_R}{C_0 - C_R} \right) = \frac{DA}{lV} t \quad (1)$$

where C is the transient methanol concentration; C_R the methanol concentration of the water chamber; C_0 the initial concentration of the methanol chamber; D is the diffusion coefficient of methanol; A , l and V are the cross-sectional area of membrane, the thickness of membrane and the volume of the sample solution, respectively. The methanol concentration measured as a function of time through composite membranes containing different $\text{Mg}^{2+}/\text{Al}^{3+}$ ratios and LDH/Nafion compositions is shown in Fig. 1. As can be seen, the left-hand-side of Eq. (1) exhibits a linear relation

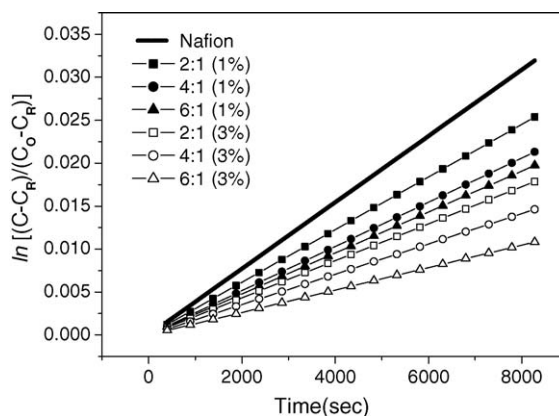


Fig. 1. Methanol concentration through LDH/Nafion membranes plotted as function of time.

Table 1
Summary of open-circuit voltage (OCV) of LDH/Nafion nanocomposite membranes at different methanol feed concentrations

Mg ²⁺ /Al ³⁺ ratios (LDH, %)	OCV (V) at 3 M	OCV (V) at 5 M	OCV (V) at 7 M	Ion conductivity (S cm ⁻¹) [1]	Diffusion coefficient (cm ² s ⁻¹) [1]
Nafion 115	0.65	0.63	0.61	0.027	4.47 × 10 ⁻⁷
2:1 (1%)	0.68	0.65	0.63	0.0187	3.54 × 10 ⁻⁷
4:1 (1%)	0.70	0.68	0.65	0.0156	2.94 × 10 ⁻⁷
6:1 (1%)	0.72	0.70	0.68	0.0125	2.45 × 10 ⁻⁷
2:1 (3%)	0.74	0.72	0.70	0.0094	2.03 × 10 ⁻⁷
4:1 (3%)	0.75	0.74	0.72	0.0080	1.75 × 10 ⁻⁷
6:1 (3%)	0.76	0.75	0.73	0.0067	1.51 × 10 ⁻⁷

with time, which validates the diffusion mechanism of Fick's law. Accordingly, the slope of the linear relation yields the diffusion coefficients of the synthesized membranes.

The diffusion coefficient and the open circuit voltage (OCV) of the synthesized LDH/Nafion nanocomposite membranes are summarized in Table 1 and plotted in Fig. 2. As can be seen, the diffusion coefficient of LDH/Nafion membranes decreases with the amount of LDH particles and with the Mg²⁺:Al³⁺ ratio. The ion conductivity exhibits a linear relation with the diffusion coefficient, which has been reported earlier [1]. Consequently, the LDH nanoparticles appear to suppress methanol cross-over to give a decreased diffusion coefficient, and neutralize the sulfonic groups in the Nafion polymer chains to decrease proton conductivity.

In a DMFC, direct oxidation of methanol at the cathode platinum catalyst leads to a mixed potential that results in a reduced electrode potential at high cell voltages to give a low OCV [22]. As can be seen from the data in Table 1 and Fig. 2, the OCV values of LHD/Nafion membrane systems decrease with increasing diffusion coefficient at 5 and 7 M of methanol feed concentration. In other words, the OCV is increased by decreasing methanol cross-over through the modified LDH/Nafion membranes at high feed concentrations. The OCV does, however, show a maximum at 3 M of feed concentration, where there is a region in which the OCV is not increased by simply decreasing the

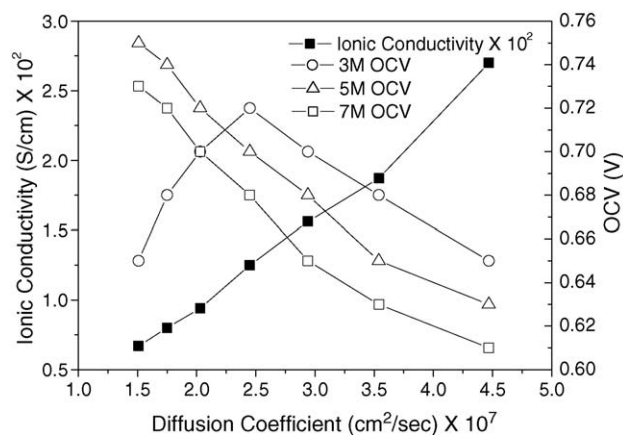


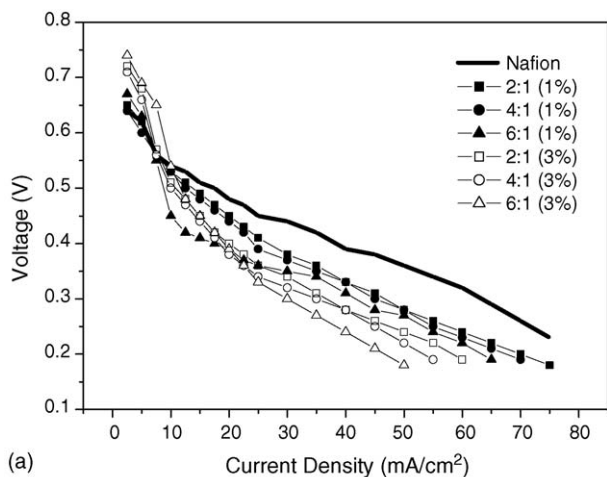
Fig. 2. Open-circuit voltage of LDH/Nafion composite membranes measured at 3, 5 and 7 M methanol feed concentrations plotted as function of diffusion coefficient and ionic conductivity.

diffusion coefficient. In this region, it is possible that the ionic conductivity exerts an important influence on the OCV at a relatively low value of methanol feed concentration.

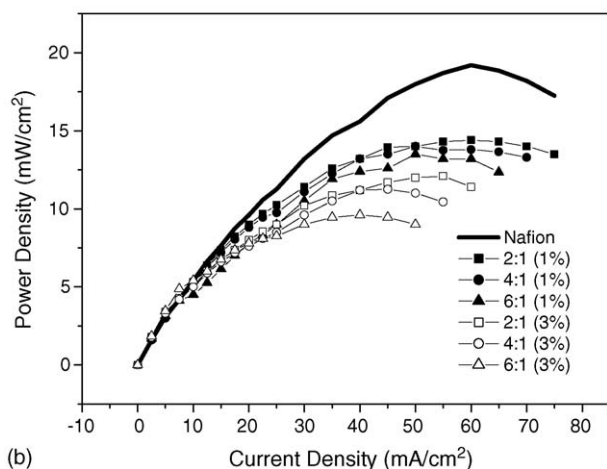
In the region of low current densities and at high cell potential, methanol dehydrogenation and water discharging takes place at a slow rate. This is often referred as a kinetic-controlled region, and potential drop is ascribed to methanol oxidation and methanol cross-over [15,16]. In an intermediate region between the kinetic-controlled region and the mass-transport controlled region in polarization curves, ionic or ohmic resistance is represented by the slope of the *I*-*V* and proton transport takes place through the membrane electrolyte and the catalyst layers in the fuel-cell stack [22]. At feed concentration of 3 M in Fig. 3(a), the slope in the pseudo-linear region of the pristine Nafion membrane is lower than the LDH/Nafion composite membranes. This indicates that the ionic resistance or ohmic resistance of the pristine Nafion film is lower than those the LDH composite membranes. As discussed above (Table 1 and Fig. 2), this feature is ascribed to the fact that the ionic conductivity of pristine Nafion membranes is higher than the LDH/Nafion composite membranes.

In the kinetic-controlled region in Fig. 3(a), the two competing transport processes of methanol cross-over and proton conduction result in complex *I*-*V* characteristics at a feed concentration of 3 M for different LDH membrane systems. When the feed concentration is relatively low, i.e., <3 M, the pristine Nafion membrane gives a higher overpotential and a higher power density than all the composite films reported in Fig. 3(a and b). This is because pristine Nafion film has the lowest ohmic resistance. In this case, the concentration gradient of methanol across the membrane is relatively low and thus the diffusion coefficient of the membrane does not appear to be a dominating factor; the *I*-*V* characteristics of the DMFC are controlled by the ionic conductivity. The resulting power density is shown in Fig. 3(b). The DMFC performance clearly decreases with decreasing proton conductivity of the LDH/Nafion membranes, even with decreasing diffusion coefficient.

On the other hand, at a high methanol concentration, i.e., 7 M in Fig. 4(a and b), the overpotential and the power density of 2:1 (1%), 4:1 (1%), 6:1 (1%) and 2:1 (3%) systems shift upward as a function of decreasing diffusion coefficient and thereby provides a higher overpotential and power density. The slopes of the four curves in the pseudo-linear region of



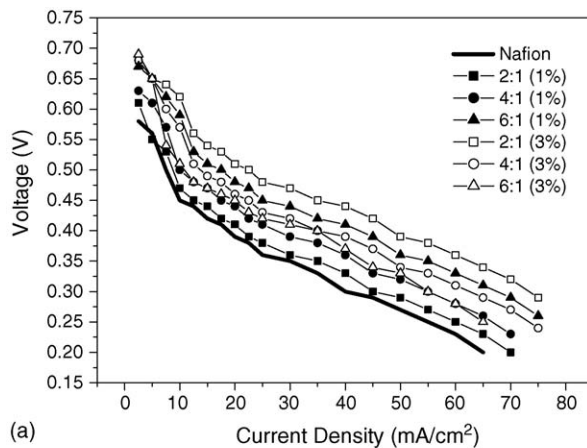
(a)



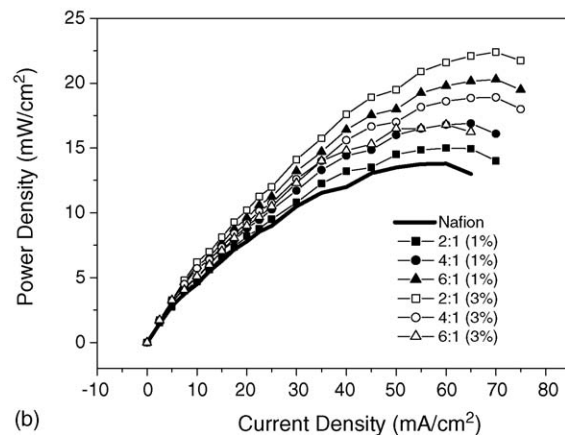
(b)

Fig. 3. (a) I - V polarization and (b) power density curves of LDH/Nafion nanocomposite membranes containing different $Mg^{2+}:Al^{3+}$ ratios and compositions at 3 M methanol feed concentration measured at room temperature.

I - V curves give the ohmic resistance of membranes. As can be seen in Fig. 4(a), the slopes of all the membrane systems are similar at 7 M of feed concentration, although the ionic conductivities shown in Table 1 are different. It is considered that any effect of the difference in ionic conductivity of these membrane systems is rendered insignificant by the critical difference in diffusion coefficients of methanol at such a high concentration. Accordingly, it is reasonable to mention that the DMFC performance of 2:1 (1%), 4:1 (1%), 6:1 (1%) and 2:1 (3%) systems is enhanced due to the decreased diffusion coefficient even with decreasing ionic conductivity of the LDH/Nafion nanocomposite membranes. When the diffusion coefficient is further decreased in 4:1 (3%) and 6:1 (3%) systems, however, the DMFC performance declines accordingly. Apparently, this is because the ionic conductivity is decreased to such an extent that it becomes the critical factor in determining DMFC performance. Overall, it should be mentioned that there are optimum conditions of the diffusion coefficient and the ionic conductivity for the attainment of improved DMFC performance at high feed concentrations.



(a)



(b)

Fig. 4. (a) I - V polarization and (b) power density curves of LDH/Nafion nanocomposite membranes containing different $Mg^{2+}:Al^{3+}$ ratios and compositions at 7 M methanol feed concentration measured at room temperature.

The power density of Nafion and LDH/Nafion membrane systems at different feed concentrations is presented in Fig. 5(a and b), respectively. For the pristine Nafion membrane, the power density at 3 M is higher than that at 1, 5 and 7 M. When the feed concentration is 1 M, the reaction rate of methanol oxidation is low and thus DMFC performance is also low. When the feed concentration is increased to 5 and 7 M, methanol cross-over deteriorates DMFC performance to a large extent, as has been reported in previous studies [16–18]. By contrast, the LDH/Nafion membrane system with a Mg^{2+} to Al^{3+} ratio of 2:1 (3%) exhibits higher performance at 7 M than at 3 or 5 M of methanol feed concentration. In this nanocomposite membrane system, the diffusion coefficient and ionic conductivity are well balanced by the incorporation of LDH entities and thus the DMFC performance is enhanced at a high feed concentration. Furthermore, it can be seen that the limiting current density is desirably increased at higher feed concentrations.

The maximum power densities of the various LDH/Nafion membrane systems are compared in Fig. 6 as a function of diffusion coefficient and ionic conductivity at different feed concentrations. At 3 M of methanol feed concentration, the maximum power density increases as a

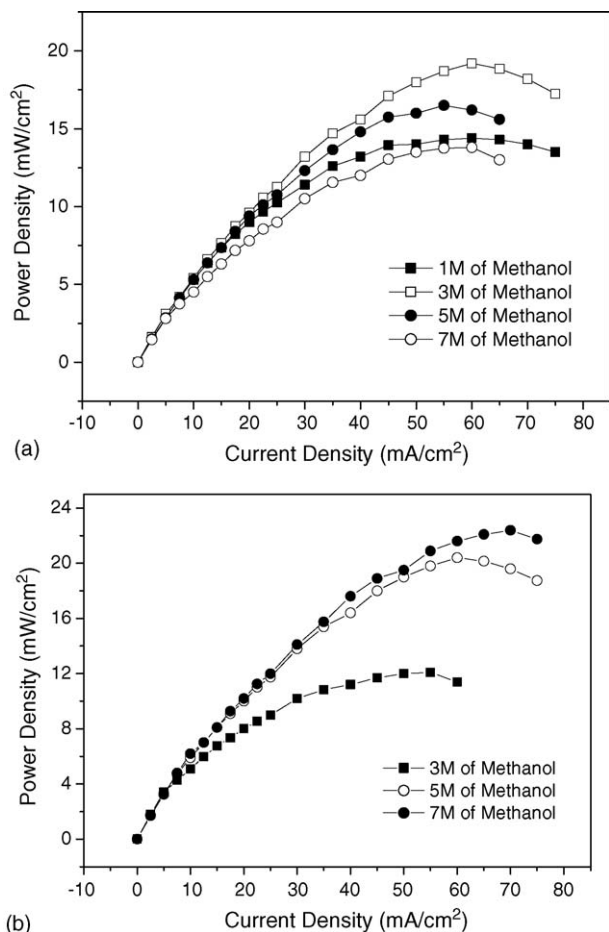


Fig. 5. Power density curves of (a) pristine Nafion and (b) LDH/Nafion nanocomposite membranes (3% with 2:1 Mg²⁺:Al³⁺ ratio) at different methanol feed concentrations measured at room temperature.

function of both diffusion coefficient and ionic conductivity. Thus, it can be concluded that high ionic conductivity is desirable at a relatively low feed concentration because the methanol cross-over is not significant due to a low

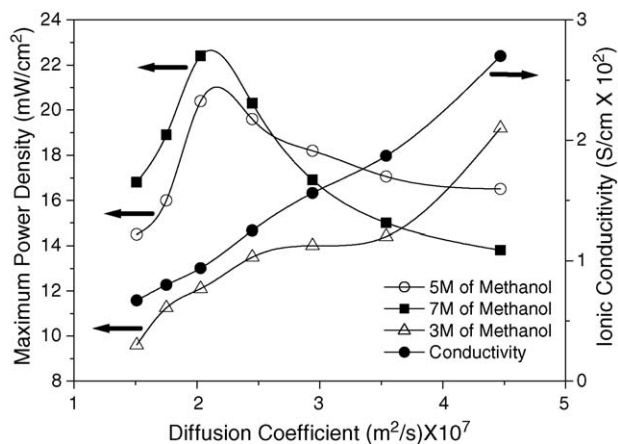


Fig. 6. Maximum power density of LDH/Nafion membrane systems plotted as function of diffusion coefficient and ionic conductivity at different methanol feed concentrations.

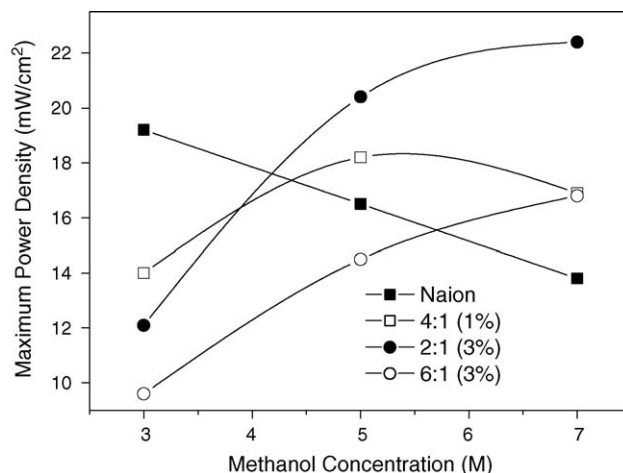


Fig. 7. Maximum power density of LDH/Nafion membrane systems plotted as a function at different methanol feed concentrations for different Mg²⁺:Al³⁺ ratios and compositions of LDH.

concentration gradient across the membrane. On the other hand, the maximum power density at 5 and 7 M displays a maximum as a function of diffusion coefficient and ionic conductivity. When the feed concentration is high, the methanol cross-over becomes significant and thus the two transport processes of methanol diffusion and ion conduction compete in a contrary way and, consequently, an optimum membrane property exists in the DMFC operation window.

Finally, the maximum power densities of the different membrane systems are compared as a function of methanol feed concentration in Fig. 7. The maximum power density of the pristine Nafion membrane decreases between 3 and 7 M of methanol feed due to cross-over. When the diffusion coefficient is decreased by the incorporation of LDH particles with Mg²⁺ to Al³⁺ ratios at 2:1 (3%) and 6:1 (3%), the maximum power density increases as a function of feed concentration, which can be attributed to the decreased diffusion coefficients of the membranes. In the case of the 4:1 (3%) Mg²⁺/Al³⁺ ratio, the highest power density appears at a 5 M feed concentration.

Overall, it should be mentioned that the membrane characteristics should be optimized by a fundamental understanding of electrochemical kinetics and transport phenomena of ions and methanol in DMFC development. The ionic conductivity and the diffusion coefficient of ion-exchange membranes appear to be the controlling factors of DMFC performance in relation to feed concentration and, possibly, operating temperature. The developed LDH/Nafion nanocomposite technique can be further used to investigate the competing processes of the electrochemical reaction and the diffusion of methanol for the development of DMFC membranes.

4. Conclusions

LDH nanoparticles have been incorporated into a Nafion membrane in order to investigate DMFC performance at

high feed concentrations of methanol up to 7 M. The OCV is increased by virtue of a decrease in methanol cross-over through the modified LDH/Nafion membranes at high feed concentrations, viz. 5 and 7 M. At low concentrations of methanol, methanol cross-over is so important that the OCV and the power density are strongly affected by the ionic conductivity of the membrane. At high concentrations of methanol feed, on the other hand, there exists an optimum balance between the diffusion coefficient and the ionic conductivity that yields the highest performance from the DMFC.

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