Suppression of Methanol Crossover in Pt-Dispersed Polymer Electrolyte Membrane for Direct Methanol Fuel Cells

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Suppression of methanol crossover in polymer electrolyte membranes is a key technology for direct methanol fuel cells (DMFCs). We have prepared a Nafion® 117 wherein platinum nanocrystals are highly dispersed and subsequently used it in a DMFC. This is expected to suppress the short-circuit reaction by oxidizing methanol at the Pt catalysts. Indeed, this is observed by the appreciable increase in the cathode potential, resulting from the reduced amount of methanol reaching the cathode.

Polymer electrolyte fuel cells (PEFCs) have attracted enormous interest as a primary power source for electric vehicles (EVs). Compared with PEFCs operating with an on-board methanol reformer, the major advantages of a direct methanol fuel cell (DMFC) include simplicity in the total system, quick start-up, and easy maintenance, etc. However, there are two main points that should be addressed to achieve high efficiency with DMFCs. First is the development of highly active anode catalysts coupled with suitable anode structure for the direct methanol oxidation.[1–8] Second is the prevention of crossover of methanol from the anode to cathode through the polymer electrolyte membrane (PEM). Methanol crossover has deleterious effects on the performance of DMFCs. A significant reduction of the cathode potential due to a chemical short-circuit reaction of the crossed over CH_3OH with O_2 at the cathode occurs. This is shown in Figure 1a ($CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$). Another obvious effect is the reduction in fuel utilization efficiency.

In this direction, methanol crossover in Nafion® membranes has been studied to optimize operation conditions for obtaining improved performance.[9,10] Efforts to develop new PEMs to reduce the crossover effects are also pursued.[11] Although the effect of methanol crossover on the cathode performance has been focused on in the literatures, it is also noted that a crossover of O_2 through PEM from the cathode to anode may lower the anode performance (see Figure 1a). Hence, the suppression of crossover of both reactants in a PEM is essential for high-performance DMFCs.

We have recently proposed new PEMs with highly dispersed nanometer-size Pt and/or metal-oxides for PEFCs.[12–15] These PEFCs utilize hydrogen and oxygen as reactants. The nm-sized Pt particles (d. = 1–2 nm) in a thin Nafion® film are found to catalyze the recombination of the crossed over H_2 with O_2. The product of this recombination reaction, water, is used to humidify the PEM directly, thus obliterating the need for any external humidification.

It may be expected that this Pt-dispersed PEM, when applied to a DMFC, would result in the effective recombination of the crossed over CH_3OH and O_2 at the catalytic platinum sites. This is schematically shown in Figure 1b. This would lead to a significantly improved performance of both electrodes, particularly the cathode. This is due to the reduced amount of reactants arriving at the counter electrode, as compared to that occurring in the normal-PEM cell. The PEM used here is a strong acid and hence it is conceivable that the CO_2 produced as a result of methanol oxidation in the Pt-PEM is not present in the ionized form. This is probably exhausted through the hydrophobic backbone to the anode and the cathode.

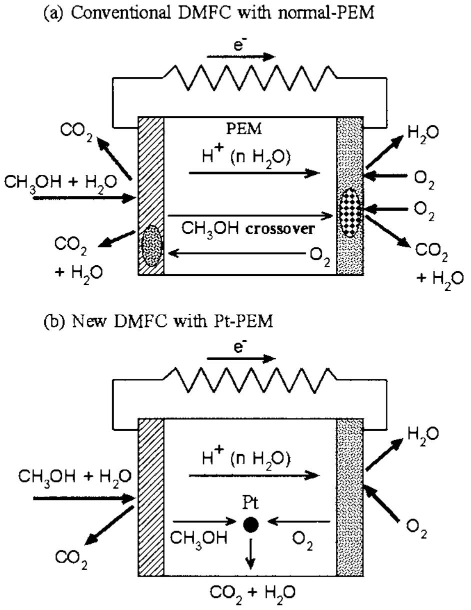

Figure 1. Schematic diagram of a conventional DMFC with normal-PEM (a) and a DMFC with Pt-PEM (b).

In this paper, we demonstrate an appreciable increase of the cathode potential due to reduced amount of methanol crossover by using the Pt-PEM in DMFCs.

PEM used was Nafion® 117 (thickness = 180 μm) dispersed with Pt nanocrystals.[16] A pure Nafion® 117 without any metal loading was also used for comparison. These are denoted as Pt-PEM and normal-PEM, respectively. The main objective of this research is to measure the amount of methanol crossover to the cathode and the resulting cathode potential in two types of cells (normal-PEM cell and Pt-PEM cell). Hence, we intentionally used pure Pt electrocatalysts of high-loading (2 mg/cm^2) for both the cathode and the anode. The electrodes with an active area of 3 cm^2 were attached to the PEM and subsequently assembled into a circular test cell housing equipped with a reversible hydrogen reference electrode (RHE).

All the studies were carried out at a constant cell temperature (T_{cell}) of 80 °C under ambient pressure. 1 M (M = mol dm^{-3}) CH_3OH aqueous solution was pumped through the anode flow field and dry oxygen was supplied to the cathode.[17] The amount of crossed over CH_3OH at the cathode was followed by determining the steady-state concentration of CO_2 in the cath-

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ode exhaust (after trapping water with an ice trap), by gas chromatography. The oxidation current density equivalent to the crossed over CH_3OH, $j(CH_3OH)$, is calculated based on the CO_2 production.[18] All steady-state *I–E* curves reported here are referred to RHE with a correction of IR-drop in the PEM.

Figure 2a shows the variation of the crossover rate (given as $j(CH_3OH)$), as a function of the current drawn from the DMFCs at T_{cell} = 80 °C for three methanol feed rates. The variation in cathode potentials, $E_{cathode}$, simultaneously measured, is also shown in Figure 2b. It is clear that the $j(CH_3OH)$ is reduced by the presence of dispersed Pt in PEM, leading to a higher cathode potential than that of normal-PEM cell, at all feed rates. For example, at a feed rate of 0.11 mL/min and at a current density of 100 mA/cm^2, the $j(CH_3OH)$ in Pt-PEM cell is about 2/3 of that in normal-PEM cell, and the potential gain is about 50 mV. This indicates that Pt particles in PEM reduce the deleterious effects of crossover by the catalytic recombination of the crossed over CH_3OH with O_2, as expected, in the schematic diagram shown in Figure 1b.

It is observed that the value of $j(CH_3OH)$ monotonically decreases with increasing output current density. A decrease in CH_3OH feed rate also causes a reduction in $j(CH_3OH)$. It is already reported that the crossover in DMFCs is caused by both diffusion and the electro-osmotic-drag of methanol.[9,10] In Nafion®117 based membranes, at low feed concentrations of CH_3OH ($\leq$ 1 M), the predominant contribution to the crossover is reported to be from the diffusion part.[9] The present results are consistent with these literatures.[9,10] A change in CH_3OH concentration at the anode/membrane interface can rationally explain the observed results. Methanol concentration at the interface decreases with increasing Faradaic consumption of CH_3OH and consequent production of CO_2 at the anode. Hence, the CH_3OH crossover rate due to diffusion through PEM decreases. Secondly, the lower feed rate of CH_3OH also results in a reduced concentration at the interface, leading to a reduced crossover rate. It is noted, however, that the advantages brought about, by the presence of Pt particles in PEM, i.e., the reduced $j(CH_3OH)$ and enhanced $E_{cathode}$, are not significant at the high CH_3OH feed rate of 0.21 mL/min. This may probably be due to a higher CH_3OH crossover rate than the rate of catalytic oxidation in Pt-PEM. Thus, at a given current density and operation temperature, several parameters such as the CH_3OH feed concentration, the feed rate, the thickness of anode catalyst layer, and the flow field structure, which control the CH_3OH concentration at the anode/membrane interface, should be optimized for a "lean feed" of CH_3OH. This, of course, is true as long as the concentration polarization at the anode does not overweigh the improved cathode performance by the suppressed crossover.

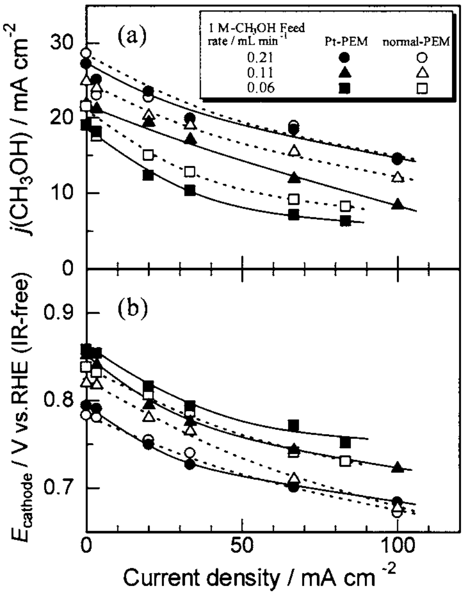

Figure 2. (a) Plots of the equivalent current density for the oxidation of crossed over methanol, $j(CH_3OH)$, in normal-PEM cell (open symbols) and Pt-PEM cell (closed symbols) as a function of output current density in DMFCs operated at 80 °C and ambient pressure. (b) Plots of the steady-state cathode potential, $E_{cathode}$, as a function of output current density.

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16 The preparation procedure of Pt-PEM was similar to that described previously..[13] Platinum-complex cations were impregnated in the normal-PEM by an ion-exchanging reaction with $[Pt(NH_3)_4]Cl_2$ solution, followed by a reduction by hydrazine. After washing with water, all the PEMs prepared were acid-treated and then washed thoroughly with water. The amount of Pt in the film was about 0.1 mg/cm^2, and the mean diameter of Pt particles observed by TEM ranged from 1 to 2 nm.
17 The solution flow rate was 0.06, 0.11 and 0.21 mL/min, corresponding to the utilization of methanol of 51.8, 28.3 and 14.8% at 0.1 A/cm^2, respectively. The oxygen flow rate was 20 mL/min.
18 Some fraction of CO_2 produced in the Pt-PEM was probably exhausted in the cathode air. Hence, the actual $j(CH_3OH)$ in the Pt-PEM cell must be smaller than that shown in Figure 2a.