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Effects of Polymer Electrolyte Membrane's Property on Fuel Cell Performances

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SUMMARY: Platinum and/or metal-oxide nanocrystals (d = 1 - 2 nm) were highly dispersed in membranes such as a Nafion® commercially available (denoted as Pt-PEM or Pt-oxide-PEM) attempting to self-humidify the PEMs and/or to suppress the short-circuit reaction by a catalytic oxidation of the crossover hydrogen or methanol with oxygen on the Pt catalyst. High and stable performances under the suppressed crossover and lowered internal resistance are demonstrated at the H_2/O_2 fuel cells applied Pt-PEM or Pt-oxide-PEM without any external humidification. An appreciable increase of the cathode potential due to the reduced methanol crossover was clearly demonstrated at a direct methanol fuel cell (DMFC) with Pt-PEM. It also becomes clear that the development of new PEMs with lowered permeability against methanol is essential for DMFCs.

Introduction

Polymer electrolyte fuel cells (PEFCs) are now one of the most attractive candidates as a power source for zero-emission electric vehicles, due to the high efficiency and the low air-pollution in addition to the properties of lightweight and low-temperature operation. However, there are important subjects that must be overcome before the commercialization. Water management in polymer electrolyte membranes (PEMs) for the cell operation under sufficiently high proton conductivity is one of the subjects, since the water

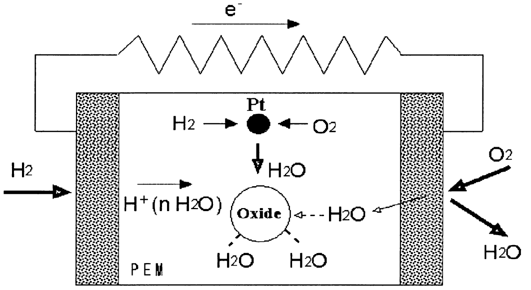

Fig. 1: Schematic explanation of a new self-humidifying PEM with highly dispersed nano-particles of Pt and oxides for H_2 PEFCs.

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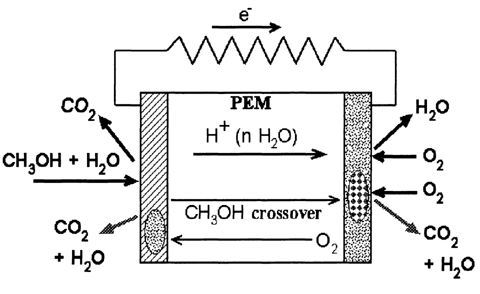
content is changed in the extremely complicated manner with the operating conditions[1-21]. In practical cells, so far, water content in PEMs has been managed indirectly by humidifying either the fuel gas or the fuel and oxygen. The reduction of PEM thickness reduces water management problems due to the water back-diffused from the cathode[11], resulting in not only the reduction of ohmic potential-drop in the cell but also the improvement of cathode performance[22]. However, this usually accelerates the crossover of H_2 and O_2 through the thin PEMs, which lowers the fuel utilization and the cell performance due to the chemical short-circuit reaction of the crossover H_2 with O_2 at the cathode. At direct methanol fuel cells (DMFCs), methanol (abbreviated as MeOH) dissolved in water is supplied to the anode in place of H_2. The suppression of MeOH crossover in the PEM is a key technology for the DMFCs, because the crossover is much serious compared with H_2 and lowers not only the fuel utilization but also does the cathode potential significantly, even if a thicker PEMs are used[23, 24].

(a) Conventional DMFC with normal-PEM



(b) New DMFC with Pt-PEM

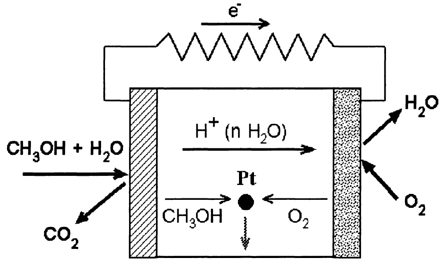


Fig. 2: Schematic explanation of the operation of DMFCs with a conventional PEM (a) and Pt-PEM (b).

Attempting to overcome these problems at PEMs commercially available, we have proposed new PEMs dispersed nm-size Pt and/or metal-oxides, as shown schematically in Fig. 1 [25-28] and Fig. 2(b)[29]. The Pt particles were expected to inhibit the crossover by the catalytic recombination of crossover H_2 or MeOH and O_2. On the other hand, the oxide particles that have hygroscopic property were expected to adsorb the water produced at Pt particles together with that produced at the cathode reaction and to release the water once the PEM needs water. The Pt-PEM in DMFCs is expected to suppress MeOH reaching to the cathode by the catalytic oxidation by O_2 unlike the conventional PEMs. The PEFCs with these new PEMs demonstrated the superior performances and suppression of the crossover of H_2 and O_2 even under externally non-humidified condition. The proton conductivity was comparable to that of the conventional PEM fully humidified. It is very much important to clarify the self-humidifying mechanism and the suppression mechanism of the crossover from the viewpoints not only of the practical application but also the basic science on PEMs.

Experimental

PEMs of different thickness (50 or 20 μm) recasted from Nafion® solution or Nafion® 112 or 117 were used for the preparation of PEMs containing uniformly dispersed Pt (0.09 mg/cm^2) and/or TiO_2 (3 wt.%) or having Pt-probes.[26, 29] The mean diameter of Pt particles observed by a transmission electron microscopy ranged from 1 to 2 nm and that of TiO_2 was ca. 5 nm. Both the anode and cathode in PEFCs or DMFCs contained Pt electrocatalysts of 0.37 or 2.0 mg/cm^2, respectively. All H_2/O_2 PEFCs with these PEMs were operated first with the dry reactants at a constant cell temperature T_{cell} = 80°C. DMFCs were operated at T_{cell} = 80°C by supplying 1M MeOH to the anode. In order to evaluate the mass balance among H_2 or MeOH, O_2 and H_2O under the cell operation, the amounts of H_2 and O_2 consumptions and humidity or CO_2 contents in the exhaust gases were measured. Distribution profiles of the specific resistances (ρ) in thickness direction were measured with monitoring Pt-probes inserted into the PEMs[17, 28]. The experimental detail was described elsewhere[28, 29].

Results

H_2/O_2 PEFC Properties: Figure 3(a) shows I-V curves for PEFCs with normal-PEM, TiO_2-PEM, Pt-PEM and Pt-TiO_2-PEM under non-humidified condition [29]. The normal-PEM cell shows the poor I-V curve, resulting in the poor output performance, e.g., 0.2 W/cm^2 at 0.6 A/cm^2 and 0.33 V. Compared with this normal-PEM cell, it is

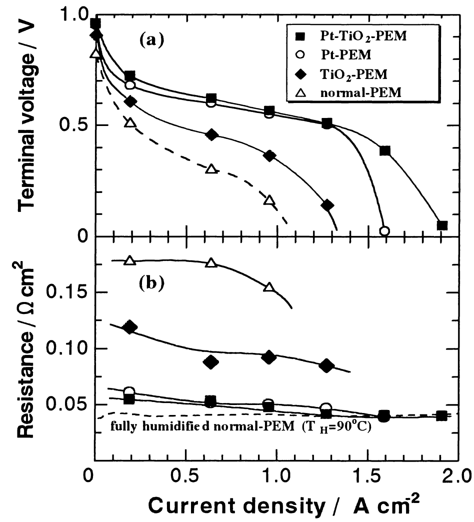


Fig.3: Performances of PEFCs using various PEMs operated at 80°C and ambient pressure without any external humidification. Utilization; H_2=70%, O_2=40%.

found that by using the new PEMs the cell performances are dramatically improved in the cell voltages and the current densities. Order of the improvement is, TiO_2-PEM < Pt-PEM < Pt-TiO_2-PEM, as expected from our design concept. The cell voltage gains of ca. 0.2 V and 0.4 V were achieved at 0.6 A/cm^2 by using TiO_2-PEM and Pt-PEM or Pt-TiO_2-PEM, respectively, compared with that of normal-PEM. Particularly, the combination of Pt and TiO_2 showed the superiority in the maximum output, i.e., ca. 0.7 W/cm^2 at 1.6 A/cm^2 and about 0.50 V. The extreme improvement of the performance will be ascribed to a self-humidification at the new PEMs, i.e., ca. 0.4 V gain in the cell voltage.

Changes of over-all resistances in PEMs without any external humidification are shown in Fig. 3(b) as a function of current density$^{28)}$. The resistance of the normal-PEM (Nafion® 112) is large, i.e., ca. 0.18 Ωcm^2 at the current density less than 0.6 A/cm^2, and decreases slightly at a higher current density due to the humidification by back-diffused water from the cathode. The Pt-PEM or Pt-TiO_2-PEM showed a small resistance of ca. 0.06 Ωcm^2 even at a low current density. Adding to this effect of Pt and/or TiO_2, the resistance decreased further with an increase in current density due to the back-diffused water, finally to the value of 0.04 Ωcm^2 (or 8 Ωcm) at around 1.6 A/cm^2. This value coincides with that of the normal-PEMs fully humidified by supplying H_2 gas saturated with water vapor at T_H = 90°C (shown by dotted line). But, this over-all reduction in the electrolyte resistance corresponds to the IR-drop of ca. 0.06 V at 0.6 A/cm^2, so that can not explain fully such a large cell voltage gain of 0.4 V for the I-V curves at PEFCs with Pt-PEM or Pt-TiO_2-PEM. Therefore, it is essential to see the humidification behavior in more details.

Figure 4 shows the change of specific resistances of different parts in Pt-TiO_2-PEM with the drawing current densities in comparison with normal-PEM. At the normal-PEM, the specific resistance increases with increasing the current density at the anode side

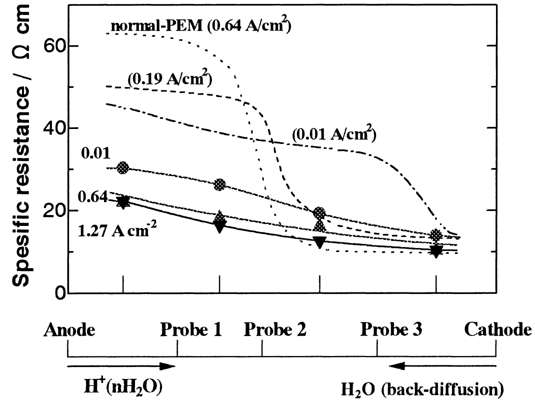


Fig. 4: Changes in the specific resistances as a function of the different portion of Pt-TiO_2-PEM at various current densities in comparison with those of normal-PEM (without data points). The operation conditions are the same as those of Fig. 3.

and vise versa, as predicted in literatures as the result of the electro-osmotic drag. But, this is the first experimental evidence of it. A great difference was found at the Pt-TiO_2-PEM from the normal-PEM that the specific resistance never increases over the entire parts of the PEM and shows the monotonous reduction with the increase of the current density, which could not be predicted just by the measurement of the over-all resistances. The uniform and small resistance in Pt-TiO_2-PEM makes the PEFC operation without any serious performance-loss possible under either a completely dried or slightly humidified reactant-gases. Such a water distribution is brought by the complement to the water transferred by electroosmotic drag with that formed inside of the PEM by the recombination of crossover gases and that back-diffused from the cathode. This is confirmed by the measurement of water balance at the anode and cathode.

The amounts of H_2 and O_2 consumed by the non-Faradic process in the normal-PEM or Pt and/or TiO_2 dispersed PEMs were estimated by subtracting the amounts of consumption calculated by Faraday's law from those of the total consumption measured. The results are shown in Figure 5(a) with the equivalent current density $J(H_2)$ (right axis) based on the H_2 consumption as a function of the faradic current density under constant utilization of H_2 and O_2[28)]. The results for the O_2 consumption are also shown in Figure 5(b). In every cell, the non-Faradic consumption resulting from the crossover clearly increases with increasing current density. Amounts of the consumption at high current density at the normal-PEM using Nafion® 112 is the largest, although the consumption at zero-current density was sufficiently small, i.e., nearly zero. $J(H_2)$ = 0.28 A/cm^2, namely, more than 20 % of the total H_2 consumption is still lost at the normal-PEM by the useless recombination reaction at the current drawing of 1.0 A/cm^2. It is

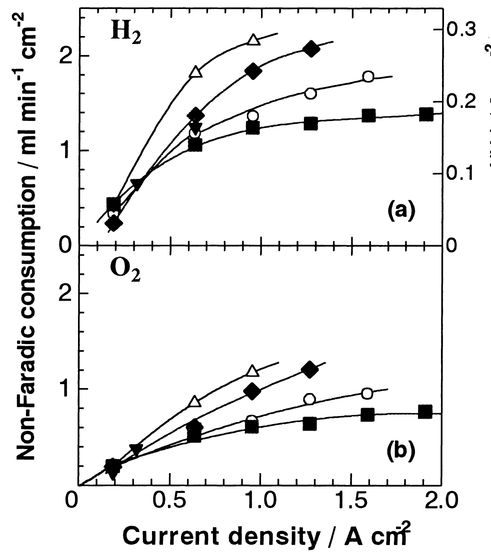


Fig. 5: The change of non-faradic consumption of H_2 and O_2 at the cathode and anode, respectively in the PEFCs with various PEMs as a function of current density. The operation conditions and symbols are the same as those of Fig. 3.

evident that the crossover is greatly suppressed at Pt and/or TiO_2-PEMs, in the order of TiO_2-PEM, Pt-PEM and Pt-TiO_2-PEM. The loss at 1.0 A/cm^2 can be reduced up to 2/3 and a half of that of normal-PEM for the Pt-PEM and Pt-TiO_2-PEM, respectively. This is probably brought by the increased and uniform humidity throughout the new PEMs as seen above.

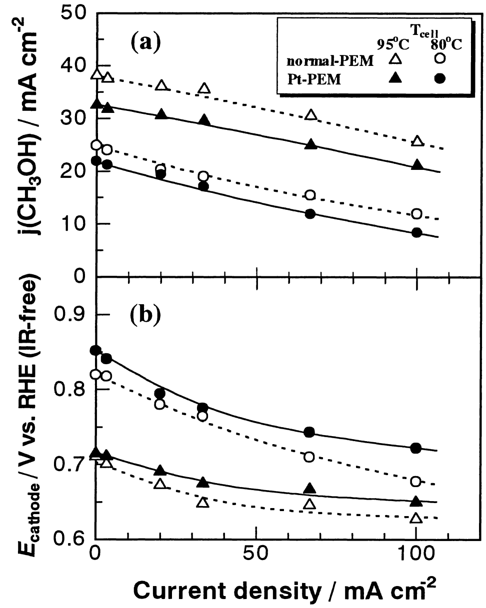


Fig. 6: The suppression of MeOH crossover and the improvement of cathode performance at 100 mA/cm^2 by the use of Pt-PEM in comparison with those of Nafion® 117.

DMFC Properties: Figure 4 shows $j(CH_3OH)$ and Ecathode as a function of the output current density at T_{cell} of 80 and 95°C in the cell with Pt-PEM in comparison with those of the normal cell [29]. It is clear that the crossover amount was suppressed by the presence of Pt catalyst in the PEM. Because of the increase of the MeOH diffusion coefficient in Nafion® by elevating the cell temperature[23], however, $j(CH_3OH)$ at 95°C is 2.5 times higher than that at 80°C even in the Pt-PEM cell. Therefore it is essential to develop new PEMs that have an order of magnitude lower permeability against the MeOH crossover. With increasing the drawing current density, the amount of crossover decreased probably due to the reduction of MeOH concentration at the interface of the anode catalyst layer and the PEMs. Reflecting the degree of the crossover, the cathode potentials were changed, i.e., $E_{cathode}$ significantly declines by the high temperature operation in spite of the reduction of the real overpotential for the O_2 reduction reaction [30,31].

Conclusion

Even the conventional PEMs, the dispersion of small amounts of nano-sized Pt and/or oxides such as TiO_2 or SiO_2 into them makes PEMs water-management free, as demonstrated above by the operation with dry reactant gases. The new PEMs may bring lots of advantages, e.g., the simplification of the PEFC control system, the reduction of the cell or system size and the cold start even under freezing condition and the quick response to the load change. The application of Pt-PEM to DMFCs showed the reduction of MeOH crossover, resulting in the improvement of the cathode performance. However, it was found that the concept may demonstrate it's usefulness more clearly when some new PEMs that have less MeOH permeability than that of the convenient ones will be developed.

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