Micro-Raman Study of Water Distribution inside Electrolyte Membrane in Operating PEFC

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Proton exchange membrane (PEM) is one of the key materials for PEFC, and fundamental understanding of PEM during the cell operation is required to improve the cell performance. In particular, the investigation of water transport across PEM during operation is one of the most important topics to be studied for optimizing the cell operating conditions and improving the cell performance. The back-diffusion and electro-osmotic drag of water, as well as the water transport at the membrane/catalyst layer (CL) interface, have considerable impact on the proton conductivity of the membrane, and hence, the cell performance.¹ Therefore, the precise water managements in the cell are required to ensure the proper operation of PEFCs. In this study, an in-situ micro-Raman spectroscopic method combining a specially designed PEFC was applied to investigating the water distributions in the PEM during the cell operation under various $\frac{1}{2}$ operating conditions.

The membrane electrode assembly (MEA) for the micro-Raman cell was composed of the commercial Nafion membrane and gas diffusion electrodes prepared by pulse-swirl-spray of a Pt/C catalyst paste containing Nafion ionomer as a binder on a gas diffusion layer. The Pt loading of all electrodes were 0.5 ± 0.1 mg cm⁻². The MEA was assembled into a square test cell designed in our laboratory.² The confocal micro-Raman spectroscopy (LabRAM HR-800, HORIBA Jobin Yvon Ltd) was employed to obtain spectra of PEM in the MEA. The Raman spectra were obtained by excitation with the radiation from an He–Ne laser (632.8 nm) or Ar laser (514.5 nm).

A set of micro-Raman spectra across the Nafion membrane were obtained at 80 °C and 50% RH, either under an N₂ atmosphere or under cell operating conditions purged with H₂ at the anode and O₂ or N₂ at the cathode. The water distribution in Nafion was estimated from band intensity of the sulfonic acid groups in the spectra during the depth scan through the electrolyte membrane. The measurement procedure in the depth direction was reported in our papers.^{2,3}

Figure 1 shows the distribution profiles of λ_R (number of water molecules per sulfonic acid group) calculated as a function of the distance from the anode at 100–250 mA cm⁻². λ_R measured under a 50%-RH N₂purging condition, obtained without current flow, is shown as a dashed line, which was constant across the membrane. The values of λ_R obtained in the operating cell were higher than that in the membrane purged with 50% RH N₂, which gradually increased from the anode to the cathode. The λ_R profiles indicate the presence of the water flux from the cathode to the anode due to the back diffusion of product water at the cathode. λ_R , especially at the cathode side, increased with increasing the current density. On the other hand, the water content gradient was smaller at the anode side. The higher amount of water caused a larger water flux at the PEM/CL interface, resulting in increased levels of water content near the cathode and presumably increased the flux by a back-diffusion of water to the anode side.

In order to investigate electro-osmotic drag of water further, the water content profile was measured in the configuration of a proton-pump cell purged with 50% RH H₂ and N₂. Figure 2 shows the profiles of the λ_R distribution at 50–200 mA cm⁻². The λ_R values obtained under current applying condition were lower than that for the zero-current condition (measured under 50%-RH N_2 condition, as shown by a dashed line in Fig. 2). The amount of water in the PEM was found to be lower than that under the equilibrium condition based on the humidity of the feed gases, especially at the anode side. Such λ_R profiles clearly imply the water transport due to the electro-osmotic drag accompanying the proton transfer from the anode to the cathode. Hence, the in-situ micro-Raman spectroscopy is very powerful to clarify the water transport behavior in the PEM under an actual fuelcell operating condition.

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Fig. 1 Plot of λ_R distribution inside Nafion in operating cell at 50% RH and 80 °C. Feed gas: anode H₂, cathode O₂.



Fig. 2 Plot of λ_R distribution inside Nafion in proton pump cell at 50% RH and 80 °C. Feed gas: anode H₂, cathode N₂.

References

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