Application of HTO as radioactive tracer to investigate water transport properties of fluoropolymer-based fuel-cell electrolyte membranes

T. Sekine[a, b], S. Sawada[b], T. Yamaki[b,*], M. Asano[b], A. Suzuki[a], T. Terai[c], Y. Maekawa[b]

[a] *Department of Nuclear Engineering and Management, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
[b] *Quantum Beam Science Directorate, Japan Atomic Energy Agency (JAEA), 1233 Watanuki, Takasaki, Gunma 370-1292, Japan*
[c] *Institute of Engineering Innovation, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

The major problem in the development of direct methanol fuel cells is a large methanol crossover through a polymer electrolyte membrane (PEM). As alternatives to a currently-used Nafion membrane, we recently developed the novel fluoropolymer-based PEMs by a radiation-induced grafting method [1] and then showed their lower methanol permeability, P_M, compared to that of Nafion using an aqueous methanol solution at concentrations of 2-10 M [2]. As the next step, we have been interested in the transport of water in the PEMs swollen by the water-methanol mixture because the P_M value is affected by a simultaneous collective interaction among methanol and water molecules. In this study, therefore, tritiated water (HTO) was used as radioactive tracer [3] to measure the permeability coefficient of water, P_W, for our grafted PEMs.

The HTO permeation experiment was performed by a home-made cell, which was separated into two compartments by a PEM. At the beginning, the donor and receptor compartments were filled with a 2 M methanol aqueous solution containing HTO at an activity of 300 Bq/mL and with pure water, respectively. The HTO concentration in the receptor compartment was measured by a liquid scintillation technique. The P_W was estimated from the slope of the HTO concentration *vs.* time straight line according to the Fick's diffusion theory. The P_W of our PEMs was dependent on their ion exchange capacity (*IEC*) and exhibited 0.46×10^{-10} m^2/s at an *IEC* of 1.2 meq/g, being lower than that of Nafion (1.5×10^{-10} m^2/s). The permeation selective factor for methanol, calculated as the ratio of P_M to P_W, P_M/P_W, was 1.2 for Nafion, indicating preferential permeation of methanol. On the contrary, the grafted PEM showed the P_M/P_W of 0.78. This lower P_M/P_W suggests poorer methanol selectivity, which would be one of the origins of the previously observed high methanol barrier property [2]. We discussed the above difference in water/methanol selectivity between the two types of PEMs in terms of chemical affinity between the permeant and polymer matrix predicted by a mathematical model of the thermodynamics of polymer solutions (the so-called Flory-Huggins theory) [4].

[1] T. Yamaki et al., *Radiat. Phys. Chem.*, 67, 403 (2003).
[2] T. Sekine et al., *Trans. Mater. Res. Soc. Jpn.*, 31, 871 (2006).
[3] Lopez et al., *Anal. Chem.*, 49, 629 (1997).
[4] J.P.G. Villaluenga et al., *J. Membr. Sci.*, 323, 421 (2008).