Effect of Recast Temperature on Diffusion and Dissolution of Oxygen and Morphological Properties in Recast Ion-exchange Polymer Membranes

Kunchan Lee, Akimitsu Ishihara*, Shigenori Mitsushima, Nobuyuki Kamiya and Ken-ichiro Ota Yokohama National University, * CREST · JST Department of Energy and Safety Engineering, Yokohama National University 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

Introduction

The polymer electrolyte fuel cells (PEFCs) are expected to be used for electric vehicle, portable power sources and co-generation systems for home use, owing to their high power density and energy efficiency. However, in order to obtain the higher performance than present level, the following problems should be solved; 1) the overvoltage of cathode reaction, 2) the Ohmic drop of electrolyte membrane, and 3) hydrogen crossover etc. In particular, the cell voltage loss due to the overvoltage of oxygen reduction reaction at the cathode should be lowered for practical commercialization¹⁾. Electrocatalyst particles are coated with recast ion-exchange polymer to form a three-phase boundary where catalyst, electrolyte and reactant gases get together at the gas diffusion electrode of PEFC. At the boundaries, the permeability and solubility of oxygen in the recast ion-exchange polymer affect the performance of cathode for $PEFC^{2}$.

In this study, we investigated the effect of the recast temperature, i.e. heat treatment, on the diffusion and solubility of oxygen and the morphological properties of recast ion-exchange membranes for the improvement of cathode in PEFC.

Experimental

The recast ion-exchange polymer membranes were prepared from 5wt% Nafion[®] solution(Aldrich chemical company, Inc., EW=1100) and Aciplex[®] solution (Asahi Kasei corporation, EW=1100) according to the following processes; 1) evaporation of solvent of Nafion[®] solution at 50 °C for 12 hours 2) heat treatment at 100°C, 120 °C, 135 °C, 150 °C or 180 °C for 1 hour.

A solid-state cell was used as an electrochemical cell. A working electrode, a reference electrode and a counter electrode were a disk-shaped platinum microelectrode with a diameter of 0.1mm, DHE and a platinum foil with Pt black, respectively. To obtain the diffusion coefficient and solubility of oxygen for recast ion-exchange polymer membranes, chronoamperometric measurements were performed in the temperature range from 30°C to 70°C under the humid oxygen at atmospheric pressure. Small-angle X-ray scattering (SAXS) measurements were used in order to obtain information about the morphological features of recast ion-exchange membranes³.

Results and discussion

Figure 1 shows the SAXS scans for recast Nafion[®] membranes. The Bragg spacing corresponding to ionic clusters increased with the decrease of the recast temperature. The recast Nafion[®] membranes of recast temperature range 135 to 180°C showed similar ionic cluster sizes. However, the cluster size increased with the decrease of the recast temperature below recast temperature 120 °C.

Figure 2 shows the diffusion coefficient(D) and

solubility(c) of oxygen in the recast Nafion[®] as a function of temperature. The diffusion coefficient of oxygen was different according to the recast temperature. Although the recast membranes between 135°C and 180°C showed almost the same D as Nafion[®] 117, the values increased with the decrease of recast temperature below 135°C. In the case of oxygen solubility(c), the recast temperature dependence of the c was opposite to that of the D.

It was found that the D and the c in the recast ionexchange polymer membrane were closely related to the recast temperature. In particular, the diffusion coefficient and permeability of oxygen showed linear relations with the ionic cluster size. Consequently, as the preparation of recast membrane at lower temperature allows the recast membranes to have larger ionic cluster and oxygen diffusion, it is thought that the recast ion-exchange polymer should be prepared at as low as possible the temperature in order to get the high diffusion coefficient and permeability of oxygen in gas diffusion electrode of PEFC.

Acknowledgements

The authors wish to thank Asahi Kasei corporation for providing samples.

Reference

- 1. K. Ota, Y. Inoue, N. Motohira, and N. Kamiya, J. New Mat. Electrochem. Systems, **3**, 193 (2000).
- F. N. Buchi, M. Wakizoe, and S. Srinivasan, J. *Electrochem. Soc.*, 143, 927 (1996).
- 3. T. D. Gierke, G. E. Munn, and F. C. Wilson, *J. Polym. Sci.*, *Polym. Phys. Ed.*, **32**, 5733 (1986).





Fig.2 Diffusion coefficient(D) and solubility(c) of oxygen in recast Nafion[®] at 50°C.