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Study on Morphological Properties and Mass Transport Parameters of ORR in Recast Ion-exchange Polymer Electrolyte Membranes

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ABSTRACT

We have investigated the effect of the recast temperature, i.e., heat treatment of a polymer electrolyte, on the diffusion coefficient and solubility of oxygen in the electrolyte and also on the morphological properties of recast ion-exchange membranes for improving the cathode activity in PEFCs. The recast membranes were prepared at different recast temperatures from Nafion® and Aciplex® solutions. Based on the chronoamperometric measurements, it was found that the diffusion coefficient and solubility of oxygen were deeply affected by the recast temperature. The diffusion coefficient increased with the decreasing recast temperature while the solubility had the opposite tendency. The water uptakes and ionic cluster size also varied with the recast temperature. Based on the X-ray measurements, it is considered that the differences in the mass transport parameters, the cluster sizes and water uptakes are due to the growth of clusters and crystallinity in the electrolyte.

INTRODUCTION

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

In this study, we investigated the effect of the recast temperature, i.e., heat treatment of the polymer electrolyte, on the diffusion coefficient and solubility of oxygen and also on the morphological properties of recast ion-exchange membranes for improving the cathode activity in the PEFCs.

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=1025) according to the following processes; 1) evaporation of solvent at 50 °C for 12 hours, and 2) heat-treatment at 100°C, 120 °C, and 150 °C for 1 hour. In this study, the notation “recast100” means that the recast temperature is 100°C.

In order to obtain the diffusion coefficient and solubility, an electrolyte technique with an electrochemical cell was used. 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. In order to obtain the diffusion coefficient and solubility of oxygen for the recast membranes, the chronoamperometric measurements were performed in the temperature range from 30°C to 60°C in humid oxygen at atmospheric pressure.

The water uptake of the recast membrane was determined from the weight difference between the wet and dry membranes by Eq. 1,

$$W = 100(W_s - W_d)/W_d \qquad (1)$$

where W, W_s and W_d are the water uptake(wt%), weight of wet and dry membranes, respectively. After the membranes were allowed to equilibrate in pure water for over 1 or 2 days, the excess water on the surface of the membrane was removed and the weight of the wet membranes was obtained. In order to determine the weight of the dry membranes, the wet membranes were dried in a vacuum oven at 80°C for over 24 h. All of the measurements were performed at 20°C under atmospheric pressure.

Small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements were used in order to obtain information about the morphological features of the recast ion-exchange membranes. The SAXS and the WAXS were performed on the wet and dry membranes with the H^+ form at room temperature, respectively.

RESULTS AND DISCUSSION

Nafion® and Aciplex®, which are expected to be used in PEFCs are both perfluorosulfonic acid membranes. These membranes have almost the same chemical structures, that is, a polytetrafluoroethylene backbone and pendant side chains terminated by a sulfonate ionic group. It is known that the difference between these membranes is just the length of the side chain. In this study, Nafion® recast and Aciplex® recast membranes were used to investigate the diffusion coefficient and solubility of oxygen. Figure 1 shows the diffusion coefficient of oxygen for the Nafion® and Aciplex® recast membranes. The diffusion coefficients increase with the increase in the temperature of all the membranes. The diffusion coefficients of the Nafion®117 and Aciplex® S1104 membranes are almost the same. For the recast membranes, the Nafion® and Aciplex® recast membranes, which were prepared at 100°C, show the highest diffusion coefficient. The diffusion coefficient decreases at the higher recast temperatures. This tendency is almost the same for both Nafion® and Aciplex®. On the other hand, the solubility of oxygen shows the opposite tendency versus the recast temperature when compared to the diffusion coefficient as shown in Fig. 2. The recast membranes prepared at the higher recast temperature shows the higher solubility of oxygen.

The diffusion coefficient and the solubility of oxygen in the recast membranes are deeply affected by the recast temperature. Based on these results, we have concluded that the morphological properties of the membranes might be affected by the recast temperature.

In order to investigate the changes in the morphological properties between the different recast membranes, we measured the water uptake and ionic clusters which consist of ionic groups. Table 1 shows the water uptakes on the Nafion® recast membranes. In agreement with a previous study, the water uptake of Nafion®117 is 32wt.% and the ionic cluster size is 5nm. However, Nafion® recast100 and 120 show higher water uptakes than that of Nafion®117. As already described, since the equivalent weights of all the recast membranes are 1100 geq^{-1} and fracture of the ionic group may not occur during a 1 hour heat-treatment, we consider that all the recast membranes have the same equivalent weight. The differences in the water uptakes indicate that the hydrophilic phases might vary with the recast temperature. It is well known that the hydrophilic phases consist of ionic clusters. Therefore, the changes in the hydrophilic phases mean changes in the size of the ionic clusters. As shown in Table 1, the ionic cluster size increases with a decrease in the recast temperature. For the Nafion® recast100, the water uptake and the ionic cluster size are about 2.5 times and 1.5 times larger than those of Nafion® recast150, respectively. Because of the large cluster size, the recast100 membrane can contain more water molecules.

The ionic cluster size of the polymer membrane can be determined by the counterbalance between the electrostatic energy of the cluster formation and the elastic free energy of the PTFE matrix. In order to investigate why the ionic

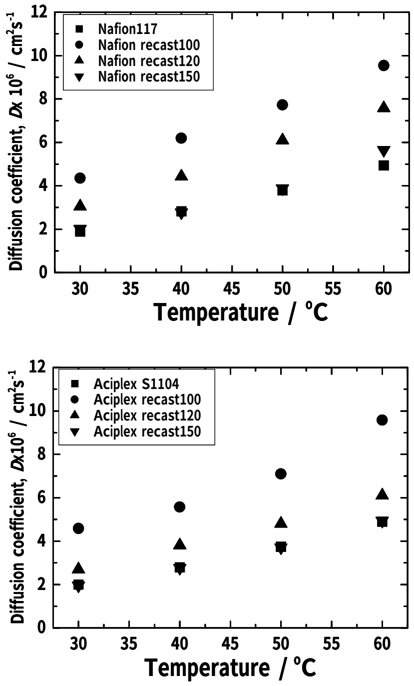

Fig. 1. Oxygen diffusion coefficient for Nafion® and Aciplex® recast membranes.

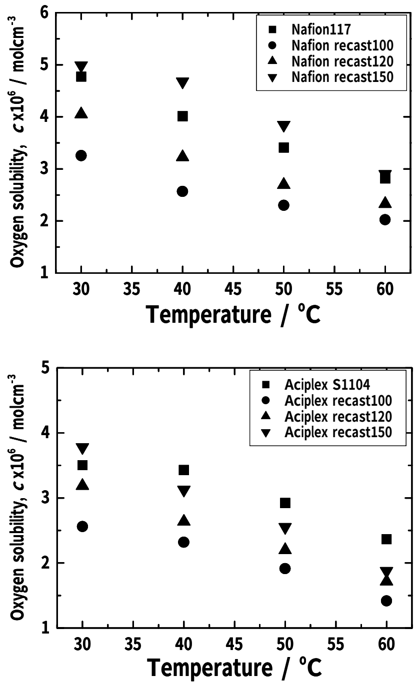

Fig. 2. Oxygen solubility for Nafion® and Aciplex® recast membranes.

cluster sizes are different between the recast membranes, we measured the crystallinity of the recast membranes.

Figure 3 shows the WAXS (wide-angle X-ray scattering) results for the recast membranes. All of the recast membranes showed crystalline peaks for the perfluorocarbon backbone at 2 θ =17.5°. This value is consistent with that of PTFE. Since the crystalline peaks are superimposed on the amorphous halo, most of the recast membranes consist of an amorphous phase. Although most of the recast membrane is amorphous, the full width of half maximum (FWHM) of the peaks decreases with the increasing recast temperature. This means an increase in the crystallinity in accordance with the recast temperature. Since the changes in the crystallinity produces changes in the elastic energy in the PTFE matrix, the ionic cluster size may be determined by the changed elastic energy of the PTFE matrix. Consequently, since the recast membranes prepared at 100°C have a lower crystallinity and elastic energy in the PTFE matrix, the ionic clusters in these membranes might grow to a large size. The ionic clusters in the membranes prepared at a lower recast temperature have more fixed charges. This means that the process of cluster growth is not simple and the growth might take place through the combination of small clusters.

Table 1. Water uptake and ionic cluster size for Nafion® recast membranes.

Membranes	Recast temp. (°C)	Water uptake (wt%)	Ionic cluster diameter (nm)	Fixed charge/cluster	H_2O / cluster
Nafion recast100	100	79	7.9	172	8700
Nafion recast120	120	48	6.4	146	4516
Nafion recast150	150	40	5.4	101	2600
Nafion117	-	32	5.0	99	2060

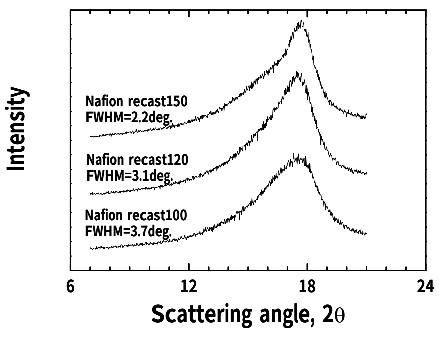

Fig. 3. WAXS scans for Nafion® recast membranes.

CONCLUSIONS

The characteristics of the diffusion coefficient and the solubility for the recast polymer electrolyte have been investigated as a basic study to improve the performance of the cathode in a PEFC. Based on the chronoamperometric measurements, we found that the diffusion coefficient and solubility of oxygen in the recast membranes depended on the recast temperature. The recast temperature also affected not only the mass transport parameters but also the water uptake and morphological properties. The recast membranes showed higher water uptakes with a decrease in the recast temperature. From the X-ray measurements, it was found that the ionic cluster size increased with the decreasing recast temperature. Therefore, it is considered that the diffusion coefficient, solubility and water uptake in the recast membranes are affected by the relationship between the growth of the clusters and the crystallinity in accordance with the recast temperature. Although, the recast100 and 120 membranes are more brittle than the other recast membranes, these recast membranes are expected to have sufficient stability in the gas diffusion electrode during operation of the PEFC.

In order to obtain a higher performing PEFC, it is necessary to investigate the optimum conditions relating to the recast temperature for the preparation of the cathode gas-diffusion electrode.

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