

Ion Exchange Behavior of Polymer Electrolyte Membranes with Metal Cations and the Influence on the Characteristics of the Membranes

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In application of metal materials to polymer electrolyte membrane fuel cell (PEMFC), there is a possibility that perfluorosulfonic polymer electrolyte membranes are contaminated by ion exchange with metal cations (M^{n+}) eluted by metal corrosion. It has been predicted that this might cause to lower performance of PEMFC mainly due to deterioration of H^+ transport in the membranes. Extensive studies on the M^{n+} exchange of the membranes, focusing on ion exchange isotherms and cation uptakes etc., have been performed, however, there are few reports regarding ion exchange in the simulated environments. In this study, we investigate the ion exchange behavior of Nafion 117 membranes with Cr^{3+} , $Fe^{2+(3+)}$ and Ni^{2+} at the wide range experimental condition (0.1-1000 ppm, pH 1-3, and 298-363 K), and the effects on the characteristics of the membranes.

The ion exchange of Nafion 117 (H^+ form) membranes with M^{n+} was carried out by batch-equilibrium method. In order to suppress decrease in pH after ion exchange, the amount of use of the membrane was controlled so that the ion exchange amount in the used membrane might become 1/100 or less of the amount of H^+ contained in the M^{n+}/H_2SO_4 aqueous solution. Thus the ion exchange was achieved within 0.5 % of change in pH.

The membranes undergo ion exchange at 343 K, near the PEMFC operation temperature, more easily than at 298K. The membranes are equilibrated with large extent of ion exchange either at higher concentration of M^{n+} or at higher pH (Fig.1). In the PEMFC, it is supposed that the membrane located at the catalyst neighborhood is exposed to strong acid condition. Assuming the internal pH is plausible 3, it is implied that membranes would undergo ion exchange with the extent of ~ 100% in the contaminated water of ~ 10 ppm for Fe^{2+} and Ni^{2+} , and ~ 2 ppm for Cr^{3+} . In the case of Cr^{3+} , it is apparent that the extent of ion exchange exceeds 100 % at high concentration in pH 3 at 298 K- 363 K, as is also the case for pH 2 at 298 K. This is due to the formation of hydroxyl compounds such as $Cr(OH)_{3-x}^{x+}$ in the membrane, revealed by UV-Vis spectra of the Cr^{3+} exchanged membranes (Fig.2).

The water content (λ) and the specific conductivity (κ) of M^{n+} exchanged membranes were studied. The water content decreases by about 10% on fully M^{n+} exchanged membranes, and there is no obvious difference in influence of M^{n+} on λ among M^{n+} tested. As shown in Fig. 3, the peculiar influence on κ is seen by the kind of M^{n+} . For divalent cations, κ decreases almost linearly with the extent of ion exchange. For trivalent cations, the decrease of κ is nonlinear throughout, and sharp in the range of low content of ion exchange. In particular, Cr^{3+} exchange of membranes results in marked decrease of κ .

The results explored in the simulated conditions will offer a convenient method for predicting the extent of lowering performance of PEMFC based on deterioration of membrane characteristics, by the concentration of M^{n+} (contained in the water exhausted from PEMFC) using the extent of ion exchange as an interface. It is noted that ion exchange by Cr^{3+} at specific conditions brings about excess exchange, unlike the cases of Ni^{2+} and Fe^{2+} .

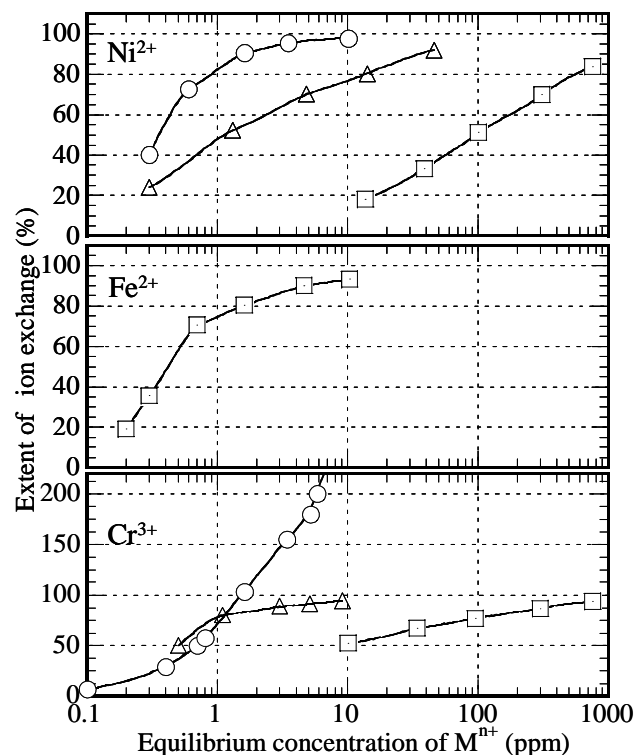


Figure 1. Plots of the extent of ion exchange by M^{n+} on membranes versus equilibrium concentration of M^{n+} . The ion exchange was carried out at 343 K in pH 3 (○), pH 2 (△), and pH 1 (□). The extent of ion exchange was calculated by assuming that one divalent or trivalent cation can be exchanged for two or three protons.

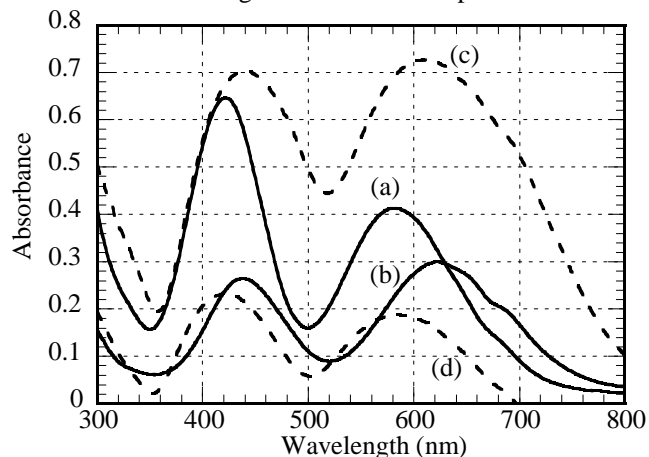


Figure 2. UV-Vis spectra of Cr^{3+} exchanged membranes at pH3/343K (216) (a) and pH1/298K (98) (b), $Cr_2SO_4 \cdot nH_2O$ powder (c), and $Cr(OH)_3$ powder (d); samples were dried *in vacuo*. (The number indicates the % exchange.)

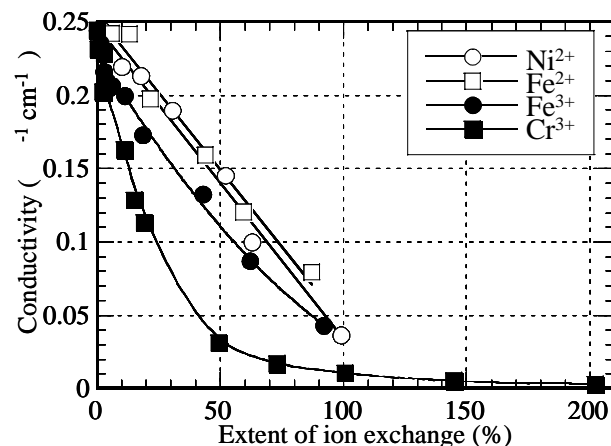


Figure 3. Plots of the specific membrane conductivity versus the extent of ion exchange. The conductivity was measured at 353 K and 95% RH.