High proton conducting and low methanol permeable Nafion/Hydroxyapatite (HA) composite membrane

Y. S. Park, Y. Yamazaki
Department of Innovative and Engineered Materials
Tokyo Institute of Technology
4259, Nagatudacho, Yokohama, Kanagawaken, Japan

Novel Nafion/HA composite membranes have been developed for direct methanol fuel cells (DMFCs). The purpose of this work is to increase proton conductivity and to decrease methanol crossover, which are known to be important issues in DMFCs. The Nafion has been modified utilizing a high crystalline inorganic material, i.e., hydroxyapatite (HA). We have performed structural analyses with X-ray, FT-IR, SEM, TEM, TGA and Focused Ion Beam (FIB). In addition to proton conductivity, methanol permeability in 1.5 M, 3 M and 5 M methanol aqueous solutions was measured using a permeation cell in the range 18-60 ℃ .

The X-ray analyses indicate that new crystalline peaks, formed by the dispersed HA and structural modification, were found in the original amorphous region of Nafion. Crystallinity, obtained by peak deconvolution technique, increased whereas crystalline sizes, calculated by Scherrer equation, decreased with the HA amounts. FTIR shows the absorbance of non-hydrogen bonding modes at 3,570 cm^{-1} increased while the absorbance of water bending at 3,470 cm^{-1} and water stretching vibrations and 1,670 cm^{-1} decreased, suggesting that composites have lower water uptake. This result is similar to the water uptake test where the amount of water decreased gradually as the HA increase in the composites.
Also the disappearance of bending vibration of hydrated proton at 1,730 cm^{-1} in composites suggests that proton can transport in a simple hydrated form. Composites also showed higher thermal stability in sulfonic acid bridge shown at 2,300 cm^{-1}. In the TGA curve composites exhibit the higher degradation temperature than cast Nafion and Nafion® 117. In FIB, many channels are shown in the cross-section and surface of the membrane, implying the existence of three-dimensionally inter-connecting proton tunnels.

The composites, containing 2.5 and 5 % of HA, showed higher proton conductivity and lower activation energy than in cast Nafion (Fig. 1). Furthermore the decrease in conductivity, shown in the cast Nafion at over 80 ℃, was not shown in the composite membranes. We examined an ion exchange reaction occurs between calcium ions in HA and protons in the HCl solution. We expect that it help to form new proton paths and thus proton conductivity increases in the composite membranes.

In the methanol sorption/desorption test, the Nafion/HA composites showed a lower methanol permeability than in the cast Nafion and Nafion® 117 (Fig. 2). Moreover in the methanol crossover test, using a diffusion cell from 18 to 60 ℃, the methanol crossover through the composite membrane decreased by 25-50% relative to the Nafion® 117 and cast Nafion (Fig. 3)

We may conclude that the structural modification such as the increase in crystallinity, the decrease in crystalline size and the formation of new proton channels due to ion exchange allows lower water uptake, lower methanol crossover and higher proton conductivity in the Nafion/HA composite membranes.

References

1. P. Dimitrova, K.A. Friedrich, B. Vogt, and U. Stimming, J. Electroanal. Chem., 532, 75 (2002)
2. M. Ludvigsson, J. Lindgren and J. Tegenfeldt, Electrochimica Acta., 47, 1023, (2002)
3. B. Bae, D. Kim, J. Membr. Sci., 220, 75 (2003)

This work was supported by a Grant-in-aid for Scientific Research (No. 13134101) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

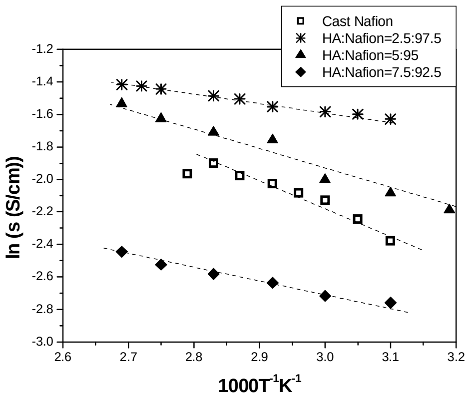

Fig. 1 Proton conductivity for cast Nafion and composite membranes.

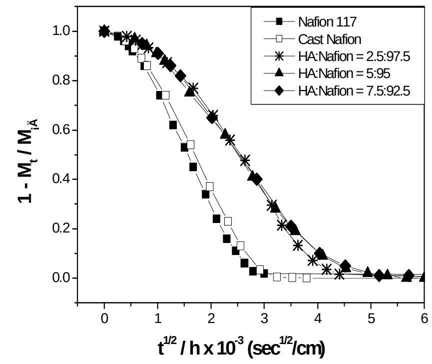

Fig. 2 Methanol desorption curves for Nafion® 117, cast Nafion and composite membranes.

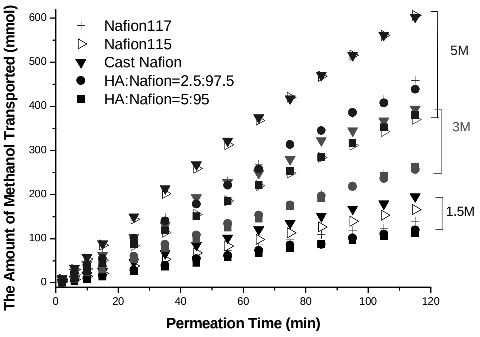

Fig. 3 The amount of transported methanol in 1.5 M, 3 M and 5 M methanol solutions at 18 ℃ in Nafion® 117, cast Nafion and composite membranes.