

Low methanol permeable and high proton-conducting Calcium phosphate/Nafion composite membrane for DMFC

직접메탄올연료전지용 저메탄올 투과성 및 고프로톤
전도성을 가진 칼슘포스페이트/나피온 복합막

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1. Introduction

Fuel cells are promising as the alternative power source to the conventional fossil fuels in relation to the environmental pollution and the decrease of oil deposits. In particular, the direct-methanol fuel cells (DMFCs) are receiving significant attention in the portable power source and electric vehicular transportation because of its high-energy efficiency as a liquid fuel, low cost, and no requirement of fuel reforming process. Nafion[®] has been used as a proton-exchange membrane in DMFC, owing to excellent electro-chemical and mechanical stability and high ionic conductivity. However, methanol supplied at the anode as fuel passes through the Nafion[®] membrane to the cathode, i.e methanol crossover, resulting in the energy efficiency loss. Furthermore, the conductivity of Nafion[®] tends to decrease at the high temperature due to the dehydration phenomena and low thermal stability in the main backbone.

In this study, we present here new composite membrane using inorganic calcium phosphate (CP, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) as a suppressant of methanol crossover and conductivity promoter simultaneously. We are interested in its high crystallinity and proton exchange reaction between Ca ion and other cations and proton-conducting property through hydroxyl ion channel. This shows good compatibility with various

polymers expecting the increase in crystallinity owing to strong interface adhesion between inorganic CP and organic Nafion structure. It is therefore expected that some structural alternation, produced by incorporation of CP into the native Nafion, make methanol crossover low and proton conductivity high.

2. Experimental

CP/Nafion composite membrane was prepared through intensive dispersing process using an ultra-sonicator and solvent drying process. We have performed structural analysis with X-ray, FT-IR, SEM, TEM, TGA and Focused Ion Beam (FIB). In addition to proton conductivity using a AC impedance technique, methanol permeability in 1.5, 3, and 5 M methanol solutions were measured using methanol sorption/desorption and methanol permeation tests.

3. Results and Discussions

TEM shows well-distributed CP particles and moreover strong interfacial adhesion between Nafion matrix and CP domains, indicating no de-lamination between two structures. X-ray analysis indicates that new crystalline peaks, caused by the dispersed CP and structural modification, can be created in the original amorphous region of Nafion. Crystallinity, analyzed by Gaussian peak deconvolution technique, increases with increasing CP amounts while crystalline sizes, calculated by Scherrer equation, decreases. Composite membranes also showed higher thermal stability in the sulfonic acid bridge shown at 2360 cm^{-1} detected by FTIR. In thermogravimetry (TGA) curve, composite membranes exhibit the higher thermal stability than that in cast Nafion and Nafion[®]117. In FIB micrographs, many channels are shown in the cross-section and surface regions of the composite membrane, implying the existence of three-dimensionally connecting proton tunnels.

The composite membranes, containing 2.5 (C1) and 5 wt% (C2) of CP, showed higher proton conductivity than in cast Nafion (Fig. 1). It is thought that the ion exchange reaction occurs between calcium ions in CP structure and protons, expecting to form new proton conducting paths and thus to increase proton conductivity in the composite membranes.

In the 2M water/methanol sorption-desorption tests, composite membranes showed a lower methanol permeability than in the cast Nafion and Nafion[®]117 (Fig. 2). Moreover also in the methanol crossover test, using a diffusion cell from 18 to 60 °C, methanol permeability through the composite membrane decreased compared to the cast Nafion and Nafion[®]117 (Fig. 3).

4. Conclusion

We 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 the incorporation of CP allow lower water uptake, lower methanol crossover, and higher proton conductivity in the CP/Nafion composite membranes.

Reference

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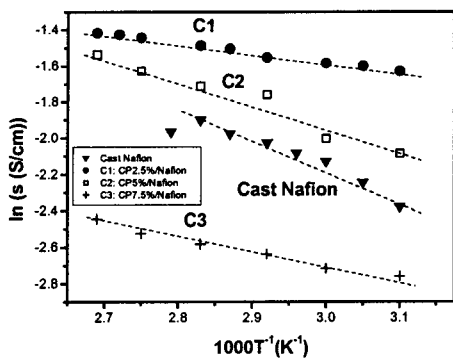


Fig. 1. Arrhenius plot of the proton conductivity for the cast Nafion.

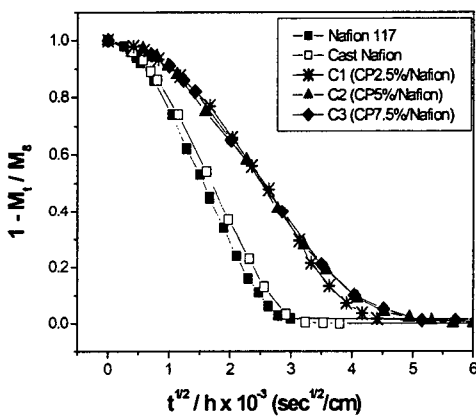


Fig. 2. Methanol desorption curves at room temperature.

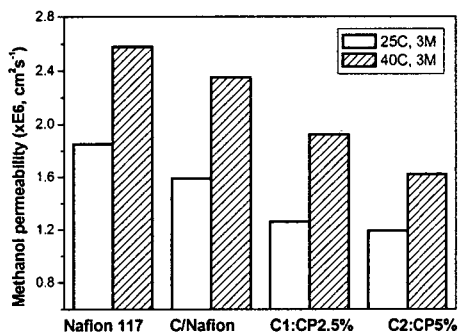


Fig. 3. Methanol permeability at 25 and 40°C in 3M water/methanol binary mixture.