Preparation of Organic-Inorganic Nano-Composite Electrolyte Membrane for Intermediate-Temperature PEFCs

Shintaro Aono*1, Hirotoshi Yamada2 and Isamu Moriguchi2

1 Graduate School of Science and Technology,
2 Faculty of Engineering,
Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan
*Tel/Fax: +81-95-819-2669, E-mail: mrgch@nagasaki-u.ac.jp

Abstract
Proton conducting membranes were prepared by using an epoxy-resin-silica hybrid polymer as a flexible matrix and Cs doped phosphotungstic acid or phosphoric acid as proton conductors. The siloxane part of the resin exhibited good affinity to the inorganic proton conductors, resulting in a uniform membranes.

Introduction
In many researches on polymer electrolyte membrane fuel cells (PEMFCs), protonic conducting membranes that work above 100°C have been strongly required in order to solve the inactivation of Pt catalyst by CO, to reduce the amount of Pt, and to improve the quality of exhaust gas as heat sources. Protonic conducting membranes consisting of organic-inorganic composites are attractive because of their flexibility of organic matrices and high protonic conductivity at elevated temperatures of inorganic materials. In this study, we employed an organic-inorganic compound “Compoceran® E201” consisting of epoxy monomer and siloxane (E201, Arakawa Chemical Industries, LTD.) as a matrix. With E201, better dispersion of inorganic materials in the matrix is expected because siloxane part exhibits affinity to inorganic materials. We report the preparation and characterization of protonic conducting membranes consisting of E201 and Cs doped phosphotungstic acid (Cs-PWA) or phosphoric acid (H3PO4) as inorganic proton conductors.

Experimental
Cs-PWA was synthesized by mecahnochemical reaction of Cs2SO4 and PWA by using a ball-mill.1) Cs-PWA was dispersed and well stirred in an acetone solution of E201. After 2-ethyl-4-methylimidazol was added as a hardener of epoxy parts of E201, the solution was spread on a PTFE dish and heated at 60°C for 4 hours and consecutively at 150°C for 2 hours under vacuum to form a membrane. For comparison, we also prepared a membrane in the same way using epoxy monomer without siloxane (Epicoat 828®, Japan Epoxy Resins Co.,Ltd.) as a matrix. The dispersion of Cs-PWA was observed using SEM.
The well-known proton conductor, Nafion®, is composed of a hydrophobic organic matrix and hydrophilic functional groups that form nanosized domains, which leads the high conductivity of Nafion®. To fabricated Nafion-like membranes, H₃PO₄ was dispersed in an E201 matrix as follows. First, H₃PO₄ and succinic anhydride as a hardener of epoxy were added to an acetone solution of E201. Then, the solution was stirred for 30 minutes and spread on a PTFE dish. After three-step consecutive heat treatments at 30°C for 4 hours, at 60°C for 4 hours and 150°C for 2 hours under vacuum, finally a membrane was obtained. Local structure of E201 and H₃PO₄ in the obtained membranes was investigated using FT-IR spectra.

Results and Discussions

Fig. 1 shows cross-section SEM images of Cs-PWA-dispersed membranes. For the membrane using Epicoat 828 (Fig. 1a), the Cs-PWA particles were observed to precipitate in the membrane due to the higher density than the matrix. On the other hand, Cs-PWA particles was well dispersed in the E201 matrix. It is considered that siloxane parts of E201 surrounds Cs-PWA forming a homogeneous membrane.

Fig. 2 shows FT-IR spectra of H₃PO₄:E201 membranes with different P/Si ratio. With increasing H₃PO₄, the bands around 1010 and 1160 cm⁻¹ are clearly observed to increase, which are attributed to the TO and LO modes of asymmetric stretching of Si-O-P bonds, respectively. It is considered that H₃PO₄ disperses uniformly by forming Si-O-P bonds to siloxane part of E201. And the bands of free PO₄³⁻ (940 cm⁻¹) and P-O-P bond (890 cm⁻¹) were not observed. The results suggest that all H₃PO₄ are chemically bound to siloxane, and thus Nafion-like local structure is expected.

Conclusions

New protonic conducting membranes were prepared using an organic-inorganic hybrid material. The hybrid precursor lead homogeneous dispersion of Cs-PWA in the membranes. For H₃PO₄:E201 membrane, H₃PO₄ was dispersed by forming the chemical bonds between siloxane and PO₄³⁻.

References