Dissertation Abstract

Understanding the relationships between nanostructure, and ion-transport properties are critical to the design of PEM. However, it should be difficult to directly evaluate the relationship between the structure and proton conductivity because of less structural nature in the high proton conductive PEMs. In this thesis, the author paid attention to understanding of the relationship between the proton transport property and polymer nanostructure.

Nafion membrane is one of the most promising PEM for PEFC because of their high proton conductivity. Recently, several studies of Nafion thin films have reported the structure, proton conductivity and water uptake and diffusion coefficient. However, for use in fuel cell operations, the structure and proton conductivity of Nafion thin films on a Pt surface have not been investigated systematically. By considering the above points, I focused on the development of proton conductivity measurement and analysis method of molecular structure of the Nafion thin films on Pt-deposited surface. I found that the Nafion has an orientation structure at the Pt-deposited surface. The degree of orientation on the Pt-deposited surface depends on the thickness. A different dissociation state of sulfonic acid groups was also observed. At the low-RH region, proton conductivity depends on the Pt-deposited and SiO_2 surfaces. Proton conductivity on the Pt-deposited surface was 1 order of magnitude higher than that on SiO_2 substrate, but its conductivity remained lower than that of the bulk membrane. This difference might derive from the different thin film structure and/or the dissociation state of the protons at the sulfonic acid groups.

In the second part of this article, I demonstrated the importance of higher-order structure for achieving high proton conductivity. Sulfonated polyimides of planar and nonplanar polymer backbone were synthesized to investigate the relationship between the proton transport property and organized polymer nanostructure. These highly oriented ASPI thin films with organized lamellar structure achieved high proton conductivity (above 10-2 S/ cm). For the investigation of the water uptake of ASPI thin films, I developed the in-situ QCM system. The water uptake almost followed the order of the IEC values. The thresholds of the proton conductivity was observed at the c.a. $\lambda = 5$-6.5. This result was consistent with dissociation state of the sulfonic acid groups. All ASPI films exhibited strong birefringenceand LC like morphology with large domain. The results of GI-SAXS revealed that all ASPI thin films formed highly in-plane ordered structure, in which lamellar distance expands to the out-of-plane direction and a degree of molecular ordering improves by water uptake. I propose that the proton conductivity depends on not only the water uptake but also degree of the molecular ordering.The highly in-plane orderings of the ASPI thin films are significantly influenced by molecular structure of diamine moiety with alkyl sulfonated side chains. The degree of the molecular ordering of those hydrated domains increased with proton conductivity.

Keywords: Proton conductivity, Nafion, Fuel cell, Lyotropic liquid crystalline, Thin film