

Fabrication of Highly Anion Conductive Membranes by Positive Charge Delocalization and Assembly of Nitrogen-Containing Polycyclic Aromatic Cations

Yuki Motoishi

Graduate School of Engineering, Kyushu University,
World Premier International (WPI), International Institute for Carbon-Neutral Energy Research

The achievement of a sustainable society through the resolution of global energy and environmental issues requires the realization of a hydrogen-based society in which hydrogen is the energy carrier. Anion exchange membranes (AEMs) are a type of electrolyte essential for hydrogen production and power generation, and their replacement with the widely used proton exchange membranes (PEMs) will reduce the overall cost of hydrogen technology. However, OH⁻ is a relatively poorly mobile ionic species and absorbs carbon dioxide from the air to form carbonate ions, which are less conductive than those of PEM.

Ion conductivity is expressed as the product of ion concentration and mobility, and is generally improved by increasing the amount of ionic groups, or ion exchange capacity (IEC), which is generally proportional to IEC and conductivity. Although high IEC membranes increase conductivity, the increase in hydrophilic ionic groups causes excessive water absorption in the operating environment, leading to swelling, softening, and dissolution of the membrane. Focusing on ion concentration, delocalized cationic species such as guanidinium and imidazolium are often used as cationic species to resolve the low dissociation between ammonium ions and OH⁻. The cationic species exhibit properties as soft acids in the Hard Soft Acid Base (HSAB) rule, and their interaction with the hard base OH⁻ decreases, resulting in increased dissociation and thus increased ion concentration. Furthermore, ion mobility reflects the motion of ions in a restricted region within a nano-sized conduction channel, and mobility has been improved by phase separating ionic and hydrophobic domains to form ionic conduction paths, which are paths for ions. In recent years, there have been reports of covalent bonding or intermolecular interactions between cationic groups to increase the density of cationic groups and improve mobility.

Based on the above, we considered that by assembling cationic species with delocalized positive charges, higher ionic conductivity could be obtained by increasing both ion concentration and mobility. We considered that fused expanded pyridinium (FEP), which has a wide π -plane and assembles by π -stacking, would be useful as a cation that can achieve high ion conductivity by increasing both ionic concentration and mobility. In this study, we prepared AEMs in which FEPs were introduced into the polymer side chains to (1) improve mobility and ion concentration by decreasing the interaction with OH⁻ due to delocalization of positive charge, and (2) obtain high ion conductivity by increasing mobility due to the assembly of cation groups by the intermolecular interaction between FEPs.