

Highly Durable Cross-linked Hydroxide Ion Conducting Pore-filling Membrane

Mi-Soon Lee, Taeyoung Kim, ** Seok-Hee Park, Chang-Soo Kim, Young-Woo Choi*

Fuel Cell Research Center, New and Renewable Energy Research Division, Korea Institute of Energy Research (KIER), 102 Gajeong-ro, Yuseong-gu, Daejeon, 305-343.

**Corresponding author. E-mail: cozmoz67@kier.re.kr (Y. Choi); Tel: +82-42-860-3306; Fax: +82-42-860-3104*

*** Co-corresponding author. E-mail: abc@kier.re.kr (T. Kim); Tel: +82-42-860-3007; Fax: +82-42-860-3104*

These authors contributed equally to this work.

Materials

The host microporous substrate, which consisted of polyolefin and was to be used for the preparation of a pore-filling, anion-exchange membrane, was purchased from Asahi Kasei. According to detailed information provided by Asahi Kasei, the pores made up 45% of the volume of the substrate. The average pore diameter and the thickness of substrate were 70 nm and 22 µm, respectively. The (vinylbenzyl) trimethylammonium chloride and *N,N'*-bis(acryloyl)piperazine were purchased from Aldrich and used without further purification. The used surfactant is a sodium dodecyl sulphate.

Fabrication of anion exchange membrane

The monomers, which consisted of (vinylbenzyl) trimethylammonium chloride with functionalized ammonium groups and *N,N'*-bis(acryloyl)piperazine used as the cross-linker, were dissolved in water to prepare a homogenous solution. The (vinylbenzyl) trimethylammonium chloride in aqueous solution was added in various concentrations with respect to the weight of the *N,N'*-bis(acryloyl)piperazine monomer to increase the ion exchange capacity (IEC). The porous substrate was treated with a surfactant to make the substrate hydrophilic rather than hydrophobic. The porous substrate was immersed in the aqueous monomer solution to allow the monomer to fill the pores, and, then, the monomer-impregnated substrate was sandwiched between two polyethylene terephthalate (PET) films. To polymerize the monomer, the assembly was placed in a UV reactor with a power density that ranged from 30 to 150 mJ cm⁻². The by-products that accumulated on the surface of the membrane were removed to make the surface uniform, and, then, the membrane was washed thoroughly with deionized water several times to remove any water-soluble compounds. Finally, the resulting membranes were soaked in 2 N NaOH solutions for 24 h to convert the chloride to the OH⁻ form.

Conductivity of anion exchange membrane

A rectangular piece of the membranes that we prepared was immersed in deionized water for 1 h. Then, the membrane was removed from the water and, without removing the water from the surface of the membrane, the membrane was sandwiched between two glass plates. The ionic conductivities of the membranes were obtained by impedance spectroscopy using a Solartron Frequency Response Analyzer at room temperature. A two-point probe conductivity cell was used to measure the ionic conductivities of the membranes. The measurements were conducted in potentiostatic mode in the frequency range from 4 MHz to 100 Hz with an oscillating voltage of 5 mV. The ionic resistance (*R*) in the membrane is defined as the value at which the high-frequency arc passes through the real axis in the high-frequency arc. The ionic conductivity (σ) of the membrane can be calculated by using the formula $\sigma = L/RWd$, where *L* is the distance between the two-point probes, *W* is the width of the membrane, and *d* is the thickness of the membrane.

Ion exchange capacity and water uptake

The anion exchange membranes were prepared as previously stated. The prepared membranes in the OH⁻ form were immersed in 50 mL of 3 N NaCl for 24 h. The solutions were then titrated with 0.01 N HCl solution using 848 Titrino plus. Water uptake was determined from the mass difference between the dried and the fully hydrated membrane. The membrane was dried at 80 °C for 24 h until constant weight to obtain the dry material. This membrane was then immersed in deionized water at room temperature for 24 h. The membrane was taken out, wiped with paper towel, and quickly weighted on the microbalance.