

Partially Perfluorinated Hydrocarbon Ionomer for Cathode Catalyst Layer of Polymer Electrolyte Membrane Fuel Cell



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ABSTRACT

Hydrocarbon ionomers have not been successfully employed in the cathode of polymer electrolyte fuel cell (PEFC)s due to their low oxygen permeabilities. In this work, we propose a partially fluorinated aromatic polyether with sulfonic acid groups (s-PFPE) as an ionomer for the cathode catalyst layer. Compared to sulfonated poly(ether ether ketone) (s-PEEK), it exhibited more than 1.5 times higher oxygen permeability at RH 40% and 1.3 times higher at RH 100%. The catalyst layer based on s-PFPE showed higher power performance than that based on s-PEEK owing to enhanced oxygen transport and fast proton conduction through the s-PFPE ionomer phase covering the catalyst layer. We demonstrate that the introduction of the perfluorinated moieties to the hydrocarbon backbone is an effective strategy for the use of hydrocarbon ionomer in the cathode of PEMFCs.

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1. Introduction

For decades, the use of hydrocarbon ionomers in PEMFCs has been constantly attempted as a membrane to replace the commonly used perfluorinated ionomers to lower costs, raise fuel efficiency, and enable easier manufacturing of membrane electrode assembly (MEA). Examples include sulfonated poly(arylene ether sulfone)(s-PAES), sulfonated poly(ether ether ketone) (s-PEEK), and sulfonated polyimide (s-PI) [1–3]. However, when a hydrocarbon membrane is assembled with catalyst layers (CLs) based on a perfluorinated ionomer, a problem of interfacial delamination between the membrane and the CL is often encountered [4,5]. To address this problem, hydrocarbon ionomers having chemical structures similar to those of the membrane have been introduced as proton conducting polymer electrolytes into CL [6–10]. However, due to the low oxygen permeability of the hydrocarbon ionomers, the corresponding CL showed a relatively low power performance;

compared to Nafion, a typical example of perfluorinated ionomer, hydrocarbon ionomers have gas permeability two orders of magnitude lower [11]. Very recently, it was reported that the ratio of oxygen diffusivity and the ratio of oxygen solubility at 80 °C and at RH 75% between s-PEEK and Nafion were 0.236 and 0.273, respectively, leading to the ratio of oxygen permeability of 0.064 [12]. Therefore, oxygen concentration at the catalyst surface is reduced for hydrocarbon-ionomer-based CL, resulting in a large voltage loss. Furthermore, recent investigations on the origin of mass transfer resistance have clarified that oxygen transfer resistance through ionomers covering catalysts dominates mass transfer resistance. In this regard, the molecular design of an ionomer for higher oxygen permeability is of great importance for the use in PEMFC cathode.

Here, we propose a sulfonated partially fluorinated aromatic polyether (s-PFPE) as a cathode ionomer which could mitigate a problem caused by low oxygen permeabilities of conventional hydrocarbon ionomers. We introduced fluorinated aromatic and aliphatic moieties to the sulfonated hydrocarbon backbone to enhance oxygen solubility (Fig. 1(b)) because the fluorine group has a high affinity to oxygen as exemplified by the high oxygen solubilities of Nafion ionomer and polytetrafluoroethylene (PTFE). We investigated the oxygen permeability of the s-PFPE ionomer under

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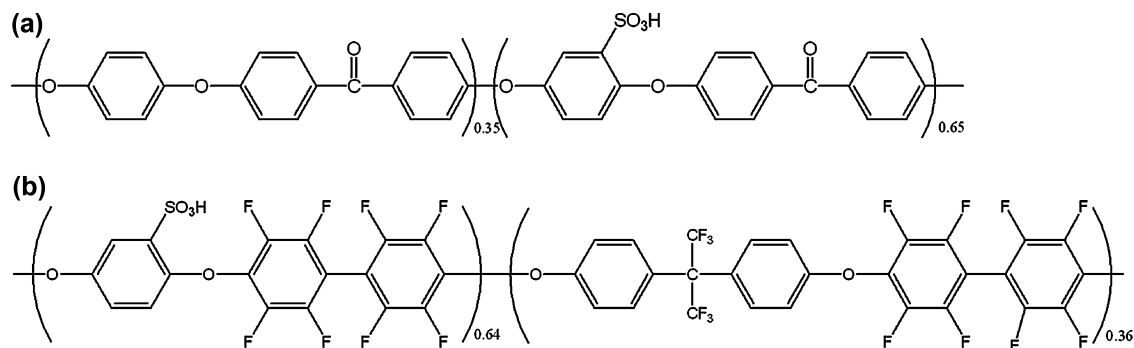


Fig. 1. Chemical structure of (a) s-PEEK, (b) s-PFPE.

both dry and humidified conditions as well as the electrochemical performance of the CL based on s-PFPE ionomer in comparison with a conventional hydrocarbon ionomer, s-PEEK (Fig. 1(a)). The influence of the s-PFPE ionomer on the power performance of cathode CL was analyzed by comparison of the exchange current density, limiting current density, and ion transport resistance of the s-PFPE based and s-PEEK based CL.

2. Experimental

2.1. Preparation of s-PFPE and s-PEEK

Potassium 2,5-dihydroxybenzenesulfonate (SHQ), 4,4'-(hexafluoroisopropylidene)-diphenol (6F-BPA), decafluorobiphenyl (DFBP), poly(ether ether ketone) (PEEK), potassium carbonate, benzene, and dimethylsulfoxide (DMSO) were supplied by Aldrich Chemical Co. The potassium carbonate was dried at 120 °C before use.

A 250 ml round-bottom flask was equipped with a Dean-Stark trap, a condenser, and a nitrogen gas inlet. To the round-bottom flask was added SHQ (9.54 g, 41.8 mmol), 6F-BPA (0.8 g, 2.5 mmol), DMSO (90 ml), benzene (30 ml), and potassium carbonate (6.99 g, 50.55 mmol). The contents of the flask were then heated at reflux for 6 h at 150 °C. After the 6 h, water was evaporated as an azeotrope with benzene and was removed in the Dean-Stark trap, and the remaining benzene was distilled from the flask. A solution of DFBP (7.52 g, 22.5 mmol) in 10 ml of DMSO was added to the flask, and the mixture was stirred for 20 h at 110 °C. The mixture was precipitated into 800 ml of ethanol. The precipitated polymer was filtered and successively washed with deionized water. Drying of the polymer at 60 °C under vacuum gave a solid brown product [13]. The density and equivalent weight (EW) of s-PFPE was 1.56 and 550, respectively. s-PEEK was prepared by sulfonation of PEEK supplied from Aldrich Chemical Co. The detailed procedure for sulfonation can be found elsewhere [9]. The degree of sulfonation of s-PEEK used in this work was 65% which is equivalent to EW of 560, and the density of s-PEEK is 1.21.

2.2. Measurements of oxygen permeabilities of ionomers

To measure the oxygen permeability of the ionomer film under various relative humidities (RHs), planar cells comprising of an IrO_x/C counter electrode, s-PFPE or s-PEEK membrane, and a Pt/C working electrode were constructed; the limiting current of oxygen reduction reaction at the working electrode in a N₂/O₂ (working/counter) configuration was then recorded [14]. The IrO_x/C consisted of 40 wt.% of 3.2 nm IrO_x and 60 wt.% of a graphitized carbon. The IrO_x/C electrode, where water or carbon oxidation happens, acts as both the reference and counter electrode in these cells. The loading level of IrO_x and Pt was 0.4 mg cm⁻², respectively. The

RH of the N₂ and the O₂ feed was varied to 40%, 70%, and 100%. The water content of the membranes at the various RHs was also determined by measuring the weight gain.

2.3. Preparation and characterization of s-PFPE and s-PEEK based CL

s-PFPE or s-PEEK ionomer was completely dissolved in N,N-dimethylacetamide (DMAc), and then a carbon-supported catalyst consisting of 60 wt.% Pt and 40 wt.% of activated carbon (AC01) (HIS-PEC 9100, Johnson-Matthey) was added to the ionomer solution to form ink for CL. The resultant catalyst inks were sonicated for 6 h and then cast onto a Kapton film supported on a glass plate using a doctor blade with a gap of 300 μm. The coats of the inks were first dried at 50 °C for 24 h and further dried at 100 °C for 24 h. For the anode CLs, the same procedure was applied except for the use of a sulfonic acid form of Nafion (SE-5112, DuPont) as an ionomer. The size of the catalyst layers was 5 × 5 cm². The weight ratio of ionomer to the carbon-supported Pt was controlled to be 3:7 for both the s-PFPE and s-PEEK CL. The Pt loading level of CL (L_{Pt}) was carefully controlled to be within 0.3 ± 0.03 mg cm⁻² for the cathode and the anode CLs.

The pore size distributions of the CLs were obtained by a mercury porosimetry (Autopore IV 9500, Micrometrics), and the morphologies of the CLs were investigated by scanning electron microscopy (SEM) (Sirion, FEI).

2.4. Fabrication, electrochemical performance, and electrochemical analysis of MEAs

MEAs were fabricated by transfer of the anode and the cathode CLs coated on Kapton film to each side of a Nafion membrane (NR-212, Dupont) at a pressure of 10.3 MPa and at 130 °C for 3 min. At room temperature, the Kapton films were peeled off from the laminate.

A single cell was assembled with the MEA of 25 cm², a pair of gas diffusion media (TGPH 090, Toray), a pair of Teflon gaskets, and a pair of graphite blocks with triple serpentine flow field for the reactants. The flow fields for the anode and cathode reactants were mirror images. The IV polarization curves of the single cells were obtained with a fuel cell test station (SMART II, Won-A tech, Korea). We tried to exclude the influence of water flooding by operating the cells at a high flow rate of 500 sccm for a humidified hydrogen (RH 100%) and of 1500 sccm for a humidified air (RH 100%), which correspond to the stoichiometry of H₂/Air = 14.3/18.0 at 0.2 A cm⁻². The IV polarization curve of each cell was obtained at 65 °C without any back pressures after daily measurements of three IV curves for successive three days as a break-in. The IV curves were not varied after the second day.

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