INTRODUCTION

Polymer exchange membrane fuel cells (PEMFCs) are expected to be a key technology for solving the current problems with zero-emission vehicles. Perfluorosulfonic acid ionomers such as Nafion are the most promising ionomers for use in PEMFCs because of their high proton conductivities and chemical stabilities. However, the practical use of such polymers is limited by their high costs, relatively low glass transition temperatures, and high gas permeabilities. These issues have stimulated the development of alternative polymer electrolyte membranes over the past decade, with particular interest in hydrocarbon ionomers. Among the aromatic ionomers, poly(phenylene)s have been attractive candidates for polymer electrolyte membranes because of their high chemical stability due to the large aromatic C=C bond dissociation energy. Our previous studies demonstrated that sulfonated poly(4-phenoxynbenzoyl-1,4-phenylene) (SPP) exhibited excellent proton conductivity, chemical stability, and mechanical properties. On the other hand, the conductivities of these ionomers are lower than those of perfluorinated ionomers under high temperature and low humidity conditions because the aryl sulfonic acid groups have lower acidities than superacid groups such as perfluorosulfonic acid.

Recently, some groups have demonstrated that aromatic ionomers with perfluoroalkyl sulfonic acid groups can lead to improved proton conductivities under low humidity conditions without increasing the ion exchange capacity (IEC). These reports are limited to poly(arylene ether)s and there have been no reports on poly(phenylene)s with the exception of perfluoralkyl sulfonic acid-functionalized poly(phenylene)s with low levels of sulfonation, as prepared by the post-functionalization method. Because the post-functionalization of parent polymers is a complicated method for attaching superacid groups, it is poor at controlling the amount and position of the sulfonic acid groups. Use of monomers that have been prefunctionalized with superacid groups allows the synthesis of ionomers with well-controlled structures.

Here, we demonstrate the first direct synthesis of poly(phenylene)-based ionomers having perfluoroalkyl sulfonic acid groups from a functionalized monomer via a Ni(0)-catalyzed coupling polymerization. This process enables the synthesis of ionomers with aromatic backbones without other linkages and with a high density of superacid groups on the flexible side chains, which provides high chemical stability and high proton conductivity.

RESULTS AND DISCUSSION

The monomer used for the synthesis of the perfluoroalkyl sulfonic acid-functionalized poly(phenylene) ionomer was

Use of a High-Performance Poly(p-phenylene)-Based Aromatic Hydrocarbon Ionomer with Superacid Groups in Fuel Cells under Low Humidity Conditions

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 Supporting Information

ABSTRACT: Aromatic ionomers with perfluoroalkyl sulfonic acid groups for fuel cell applications have been prepared mostly by the post-functionalization method. Herein, we present a direct polymerization method using a novel monomer with a perfluorsulfonic acid group to control the amount and position of the sulfonic acid groups. A poly(p-phenylene)-based aromatic hydrocarbon ionomer bearing a pendant perfluorsulfonic acid group in a substituent at the 2-position is synthesized by Ni(0)-catalyzed coupling polymerization. The direct polymerization provides $M_n$ values of up to 169 000 with a highly controlled molecular structure and allows the formation of thin membranes. These ionomers were found to combine the positive features of perfluorinated and aromatic hydrocarbon ionomers, and these thin membranes with a relatively high ion exchange capacity showed high proton conductivity and excellent fuel cell performance (907 mW cm$^{-2}$ even at 80 °C and 30% RH) under low humidity conditions compared with other reported aromatic hydrocarbon ionomers.

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prepared by the reaction of sodium 2-(4-(4′,2,5-
dichlorobenzoyl)phenoxophenoxy) tetrafluoroethane sulfinate with N-chlorosuccinimide to form the sulfonyl chloride, followed by esterification. Because the acidic protons and even caiton salt forms of the perfluorosulfonic acid groups inhibit the polymerization, the sulfonic acid groups of the monomers required protection to produce high molecular weight polymers. The esterification reaction was carried out using 3,5-dimethylphenol, phenol, or 2,2,2-trifluoroethanol as protecting groups for the perfluoroalkyl sulfonic acid but not using 2,2-dimethyl-1-propanol, which is the appropriate protecting group used for SPP. The chosen alcohols and phenols have relatively high acidities, making them suitable protecting agents. Ni(0)-catalyzed coupling polymerization was carried out using 2,2-dimethyl-1-propanol, which is the appropriate protecting group for the per sulfonic acid group (Scheme 1). After the deprotection and subsequent acidification, as shown in Scheme 1. After the Ni(0)-catalyzed coupling polymerization, around 20% of the protecting groups were detached from FPP, as determined using 1H NMR spectroscopy. The 3,5-dimethylphenyl groups of FPP were fully cleaved using sodium hydroxide and subsequent acidic hydrolysis to afford SFPP. The deprotection was also confirmed using 19F NMR of SFPP, which showed that chemical shifts related to the polyether backbone peak at –83.3 ppm and –115 ppm were eliminated (Figure S8). SFPP was soluble in aprotic polar solvents such as dimethylformamide (DMF), dimethylsulfoxide (DMSO), and N-methylpyrrolidone (NMP). For comparison, SPP was also prepared by the Ni(0)-catalyzed coupling polymerization. The Mn values of SPP and SFPP as estimated by gel permeation chromatography based on polystyrene standards using DMF as an eluant were 169 000 and 180 000 g mol⁻¹, respectively (Figure S9). Polymer membranes were prepared using a solution casting method from DMSO solutions. The weight-based IEC (IECw) values, as determined by back-titration, for the SPP and SFPP membranes were 2.13 and 2.86 meq g⁻¹, respectively, which were consistent with the theoretical values. It is noteworthy that SFPP and SPP have higher water resistance even with relatively high IECw than other aromatic hydrocarbon ionomers with superacid groups.

The humidity dependence of the number of water molecules per sulfonic acid group (λ: [H2O][SO3H]⁻¹) and the in-plane proton conductivities of SFPP, SPP, and Nafion membranes at 80 °C are shown in Figure 1. The λ values of all of the polymer membranes increased with increasing relative humidity (RH).

The IECw values of the membranes, 2.13 and 2.86 meq g⁻¹, were measured as a function of RH at 80 °C (Figure 2). The gas permeability coefficients of the SFPP, SPP, and Nafion membranes increased with increasing RH. This was possibly due to the plasticizing effect of water, which caused H2 and O2 to pass easily through the membranes. While poly(arylene ether)s containing perfluoroalkyl sulfonic acid groups showed almost the same gas permeability coefficients as Nafion at 80 °C under dry conditions, the gas permeability coefficients of SFPP and SPP were lower than that of Nafion between 10 and 90% RH. The gas permeability coefficient of the SFPP membrane was higher than that of the SPP membrane. This could be related to the strong interactions between the poly(p-phenylene) backbones, which would reduce the gas diffusivity, and reduced interactions between

![Figure 1](https://example.com/figure1.png)  
**Figure 1.** Humidity dependences of the number of absorbed water molecules per sulfonic acid group (left) and in-plane conductivities (right) of SFPP, SPP, and Nafion NR-211 membranes at 80 °C.

The λvalue of SFPP was 3.7 at 30% RH and 11.2 at 90% RH, both of which were higher than those of SPP (λ = 3.0 at 30% RH and 10.3 at 90% RH). Above 60% RH, the in-plane conductivities of the SFPP and SPP membranes were higher than that of the Nafion NR-211 membrane (IECw = 0.91 meq g⁻¹). At 30% RH, SFPP membranes exhibited a conductivity of 7.95 mS cm⁻¹, which was higher than that of the SPP membrane (4.50 mS cm⁻¹) but comparable to that of Nafion NR-211. Although the IECw values of the membranes affected the conductivities under high humidity conditions, the degree of acidity had a larger effect on the proton transport under low humidity conditions. In addition, the diffusion coefficient of water in these membranes (D(NMR)) was determined by pulsed field gradient NMR at 30 °C. These data also showed similar humidity dependences, indicating that SFPP had a high carrier density and/or a more effective structure for proton and water transport under a wide range of humidity conditions.

To investigate the morphology of the SFPP membranes, small-angle X-ray scattering (SAXS) was performed using a synchrotron beam line in Photon Factory of KEK. The SAXS profile of a dry SFPP membrane showed a diffraction peak at q = 1.9 nm⁻¹, corresponding to a d-spacing of 3.3 nm. Yoshimura and Iwasaki reported that a dry Nafion membrane showed a diffraction peak that indicated the size of the ion cluster channel as 3.3 nm. On the other hand, no peak was observed for most poly(arylene ether sulfone)s with perfluoroalkyl sulfonic acid and SPP membranes due to a lower level of phase-separation. In the case of the SFPP membrane, the high density of the acid groups could produce distinct ion channels, resulting in high proton conductivities under low humidity conditions.

The H2 and O2 permeability coefficients of the polymer membranes were measured as a function of RH at 80 °C (Figure 2). The gas permeability coefficients of the SFPP, SPP, and Nafion membranes increased with increasing RH. This was possibly due to the plasticizing effect of water, which caused H2 and O2 to pass easily through the membranes. While poly(arylene ether)s containing perfluoroalkyl sulfonic acid groups showed almost the same gas permeability coefficients as Nafion at 80 °C under dry conditions, the gas permeability coefficients of SFPP and SPP were lower than that of Nafion between 10 and 90% RH. The gas permeability coefficient of the SFPP membrane was higher than that of the SPP membrane. This could be related to the strong interactions between the poly(p-phenylene) backbones, which would reduce the gas diffusivity, and reduced interactions between

![Scheme 1](https://example.com/scheme1.png)  
**Scheme 1.** Synthesis of Poly(phenylene) with Perfluoroalkyl Sulfonic Acid Group, SFPP.
the linear fluoroalkyl chains of SFPP, which could enhance the gas diffusivity.

We investigated the fuel cell performances of SFPP membranes that were thinner than previously reported aromatic ionomer membranes with perfluoroalkyl sulfonic acid groups (thicknesses of 18 μm and 40–125 μm, respectively)\(^2\) to show the effects of the superacidic groups on fuel cell performance. In other words, the SFPP membranes had good mechanical properties to allow fabrication of thin membranes and fuel cell performance tests. Indeed, the tensile strength and elongation break values of SFPP at 30 °C and 90% RH were 10 MPa and 11%, respectively, which were higher than those of SPP (tensile strength = 4 MPa, elongation break = 5%). Figure 3 shows the fuel cell polarization and power density curves of a SFPP membrane electrode assembly (MEA) at 80 °C, 90% RH or 30% RH, and 0.1 MPa G for both electrodes. The SFPP MEA showed high open circuit voltages of 0.98 V at 90% RH and 0.99 V at 30% RH because of the low gas permeability of SFPP. The maximum power density (\(W_{\text{max}}\)) was 976 mW cm\(^{-2}\) at 90% RH and remained at 907 mW cm\(^{-2}\) even at 30% RH, showing superior performance to that of Nafion NR-211 (\(W_{\text{max}} = 803\) mW cm\(^{-2}\) at 80 °C and 30% RH, thickness 25 μm). The excellent performance and low humidity dependence were due not only to the high proton conductivity but also to the relatively good mechanical properties.

### CONCLUSIONS

We have designed and synthesized a novel poly(phenylene) with perfluoroalkyl sulfonic acid groups via a Ni(0)-catalyzed coupling polymerization. The SFPP membranes showed high proton conductivity under low humidity conditions that was comparable to Nafion 211 membranes. Although the \(H_2\) and \(O_2\) permeability coefficients of SFPP and SPP were lower than that of Nafion 211 membranes between 10 and 90% RH, SFPP membranes showed relatively higher gas permeability than SPP membranes. We demonstrated that SFPP MEAs displayed an excellent performance with low humidity dependence. The introduction of perfluoroalkyl sulfonic acid groups and synthetic strategies without post functionalization provided positive effects on the poly(p-phenylene)-based aromatic hydrocarbon ionomer. Further investigations of the block copolymers are underway to provide improvements to the polymer morphology, proton transport, mechanical properties, and stability.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00313.

Synthetic procedures, characterization of polymers, and other experimental data (PDF)

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**Notes**

The authors declare no competing financial interest.

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