

Sulfonated Poly(arylene perfluoroalkylene)s-based Proton Exchange Membranes in PEMFCs: a Perspective

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ABSTRACT

With the development of renewable energy, proton exchange membrane fuel cells (PEMFCs) are considered as a promising candidate of next-generation energy conversion. While the design of proton exchange membranes (PEMs) have been considerably investigated over the last decades, the performance and durability are still issues in PEMFCs. We have synthesized a series of sulfonated poly(arylene perfluoroalkylene)s with well-developed morphology, high proton conductivity, good fuel cell performance and excellent oxidative stability. The relationship among the chemical structures, bulk membrane properties and fuel cell performance is discussed and reviewed. The properties of those membranes are compared with the-state-of-the-art PEM (perfluorosulfonic acid).

Keywords: proton exchange membranes, sulfonated poly(arylene perfluoroalkylene)s, fuel cells

NONMENCLATURE

Abbreviations

PEM	Proton exchange membrane
PEMFCs	Proton exchange membrane fuel cells
PFSA	Perfluorosulfonic acid
SPAF	Sulfonated poly(arylene perfluoroalkylene)
IEC	Ion exchange capacity

OCV	Open circle voltage
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1. INTRODUCTION

As a promising energy-conversion devices, proton exchange membrane fuel cells (PEMFCs) have been paid much more attention because of their high efficiency, high power density and zero-pollution emission^[1,2]. Proton exchange membranes (PEMs) is a core to transport protons and water and prevent the crossover of hydrogen and oxygen gases^[3]. Up to now, the state-of-the-art PEMs are based on perfluorosulfonic acid (PFSA) ionomers such as Nafion from DuPont due to their high proton conductivity, mechanical properties, and fuel cell performance. Nevertheless, the issues from PFSA membranes can not be neglected, such as complicated and costly synthesis to increase the cost of PFSA, low glass transition temperature (90-100 °C) to limit the operable temperature of fuel cells, and high gas permeability to lower the efficiency and durability^[4-6].

To address the above-mentioned issues, a number of hydrocarbon PEMs with various structures have been investigated^[7], such as sulfonated poly(arylene ether sulfone)s^[8-9], sulfonated poly(arylene ether ether ketone)s^[10-11] and sulfonated polyphenylenes^[12-13]. However, none have successfully taken the place of PFSA because difficulties lie in the trade-off relation among proton conductivity, mechanical properties and chemical stability.

We have focused on the novel PEM materials over decades. Recently, much more attention was paid to the

PEMs containing no chemically vulnerable heteroatom linkages (for example, ether, sulfide, and sulfone groups) in the main chain and sulfonated poly(arylene perfluoroalkylene)s (SPAFs)-based PEMs were developed^[14-20].

2. RESULTS AND DISCUSSION

SPAFs is the combination of perfluoroalkylene, phenylene and sulfonated phenylene groups, where the strongly hydrophobic perfluoroalkylene makes the main chain flexible and the sulfonated phenylene is the functional groups for proton conduction.

2.1 Synthesis

The key monomer (PAF monomer) containing perfluoroalkylene was synthesized from perfluoro-1,6-diiodohexane and 1-chloro-3-iodobenzene by Cu-mediated Ullmann coupling reaction in high yield (>85%), as shown in Figure 1^[21].

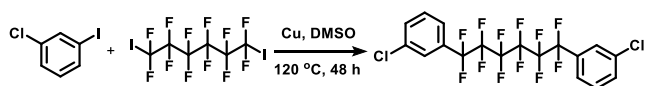


Fig. 1. Synthesis of PAF monomer

SPAF-based polymers were synthesized by direct polymerization from PAF monomer and sulfonated phenylene monomer (SP monomer) and post-sulfonation. Due to the lower polymerization activity between PAF monomer and SP monomer in the Ni-catalyzed polymerization, the obtained polymer with lower IEC (1.52 meq g^{-1}) possessed slightly high molecular weight ($M_w = 64 \text{ kDa}$, $M_n = 13 \text{ kDa}$) and provided a flexible membrane while the polymer with

high IEC (2.5 meq g^{-1}) showed low molecular weight ($M_w = 34 \text{ kDa}$, $M_n = 5 \text{ kDa}$) and provided a broken and rigid membrane.^[20] Therefore, the third components with better reactivity, such as alkylene^[20], phenylene^[17] and quinquenphenylene^[19], were introduced to improve the molecular weight and membrane-forming capability. The obtained terpolymers, as shown in Figure 2, proposed higher molecular weight ($M_w > 168 \text{ kDa}$, $M_n > 46 \text{ kDa}$) and excellent membrane forming capability, even for terpolymers with higher IEC than 2.5 meq g^{-1} , as shown in Table 1. Additionally, another preparation of SPAF-based polymers was post-sulfonation of precursor PAF polymers. The precursor PAF polymers were synthesized from PAF monomer and (multi)phenylene by Ni-catalyzed polymerization and then post-sulfonated by oleum to obtained SPAF polymers. SPAF-MM from PAF monomer and *meta/para*-phenylene monomer was easy one but its titrated IEC was only 1.59 meq g^{-1} while the theoretical IEC based on one substitution of sulfonic acid group per phenylene ring was 3.98 meq g^{-1} probably because of the strongly electron-withdrawing perfluoroalkylene groups^[14]. Therefore, SPAF-MM showed lower proton conductivity at low relative humidity. To increase proton conductivity, two strategies were carried out. One is the ordered morphology via highly sulfonated moieties. Therefore, the monophenylene monomer was replaced with quinquenphenylene monomer to obtain SPAF-QP containing densely sulfonic acid groups.^[16] Another is to increase phenylene amount via pendent phenyl, such as SPAF-BM^[14]. SPAF-QP and SPAF-BM both exhibited higher IEC than that of SPAF-MM probably because of the electronic (i.e., lack of the neighboring, electron-withdrawing perfluoroalkylene groups) and steric (i.e., less crowded) effects.

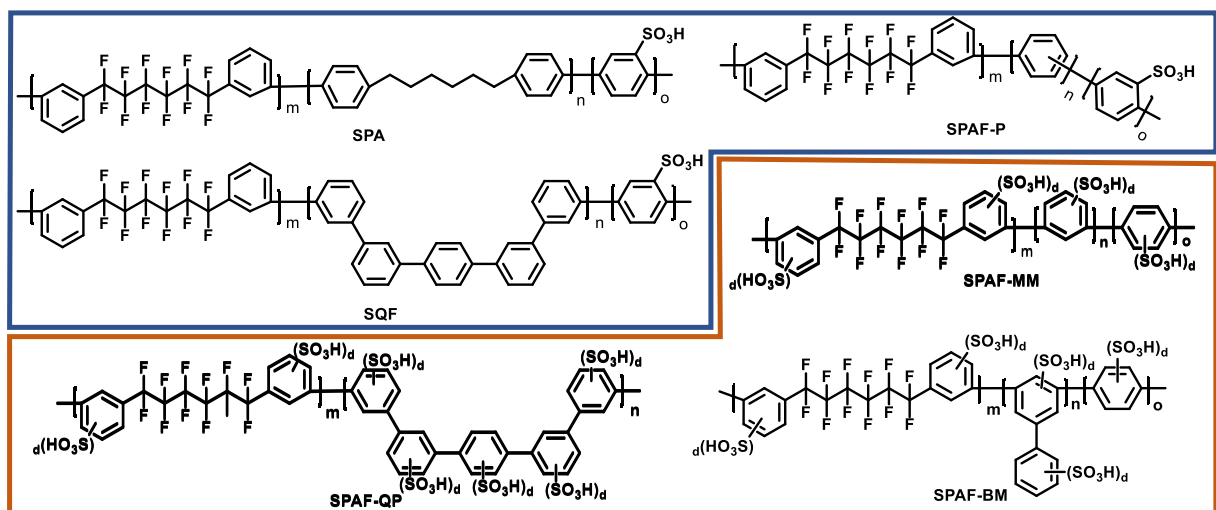


Fig. 2. Chemical structures of SPAF-based membranes

Table 1. Composition, molecular weight, IEC of SPAF-based membranes

Polymer	m:n:o	Mn (kDa) ^a	Mw (kDa) ^a	Mw/Mn ^a	Membrane forming capability	IEC Titration (meq g ⁻¹) ^b
SPA ^[14]	1:0:1.1	13	64	4.92	O	1.52
SPA ^[14]	1:0:1.85	5	34	6.8	x	-
SPA-B ^[14]	0.65:0.35:2.14	88	168	1.91	O	2.51
SQF ^[13]	1:1:4.7	46	194	4.22	O	2.56
SPAF-pP 1.85 ^[11]	1:1:1.71	79	172	2.18	O	1.85
SPAF-MM ^[12]	1:0.48:0.62	96	856	8.92	O	1.59
SPAF-QP ^[10]	1:0.22	164	431	2.62	O	1.97
SPAF-BM ^[8]	1:0.48:0.62	216	744	3.44	O	2.07

^a Determined by GPC; ^b Obtained by acid-base titration.

2.2 Morphology

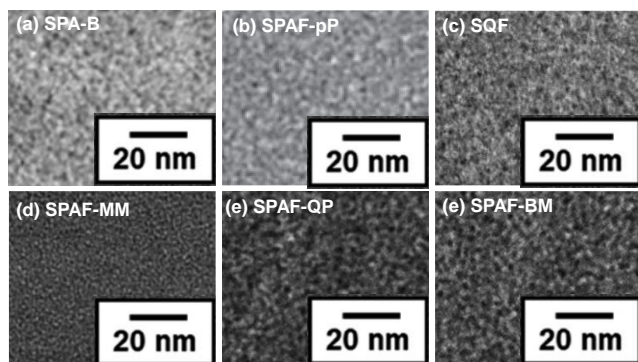


Fig. 3. Morphology of SPAF-based membranes stained with Pb²⁺ ions.

The morphology of SPAF-based membranes was analyzed by cross-sectional transmission electron microscopic images in Fig. 3, where the dark areas show hydrophilic domains containing stained sulfonic acid ($-\text{SO}_4^-(\text{Pb}^{2+})_{1/2}$) groups and their aggregates and the bright areas represent the hydrophobic domains. All SPAF-based membranes exhibited well-developed phase-separation because of difference of hydrophilia between perfluoroalkylene and sulfonated phenylene. Compared with the direct-polymerization-polymers, the post-sulfonated polymers showed more distinct interface between hydrophilic and hydrophobic domain, indicating well-developed phase-separation of post-sulfonated polymers and the third component with moderate hydrophilia (phenylene, quinquenphenylene or alkylene) in the direct polymerization make the interface vague. The hydrophilic domain size was 3.0 nm for SPA-B (2.51 meq g⁻¹), 1.9 nm for SPAF-pP (1.85 meq g⁻¹), 3.2 nm for SQF (2.56 meq g⁻¹), 1.6-2.0 nm for SPAF-MM (1.59 meq g⁻¹), 2.6 nm for SPAF-QP (1.97 meq g⁻¹) and 2.1 nm

for SPAF-BM (2.01 meq g⁻¹), corresponding to the IEC value of membranes.

2.3 Water uptake and proton conductivity

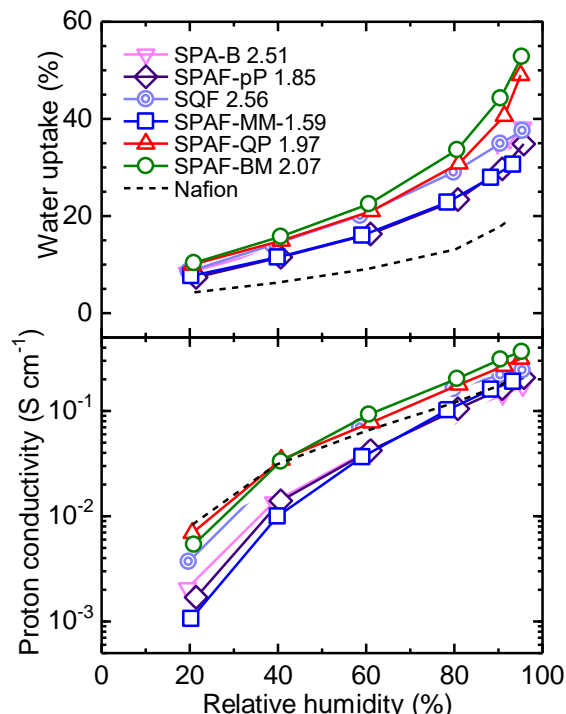


Fig. 4. Water uptake and proton conductivity of SPAF-based membranes as a function of RH at 80 °C.

Water uptake and proton conductivity were conducted at 80 °C, as shown in Fig.4. It is reasonable that as increasing humidity, the water uptake and proton conductivity were increased. Among the direct-polymerization polymers, SQF exhibited higher water uptake and proton conductivity while their IEC was similar in comparison with SPAF-B, indicating π - π conjunction phenylene-based main chain was more

hydrophilic and therefore beneficial to the proton conductivity, compared with alkylene-contained backbone for sulfonated aromatic polymers. It is worth noting that SPAF-BM and SPAF-QP showed higher water uptake and proton conductivity than those of SQF (2.56 meq g⁻¹) even though the IEC (1.97-2.07 meq g⁻¹) was lower. Probably because the intrapolymer ladderization reaction proceeded in the post-sulfonation to introduce the sulfone-bonded ladder structure^[15], which could improve the hydrophilization and conjunction of backbone and is responsible to the higher proton conductivity.

2.4 Fuel cell performance

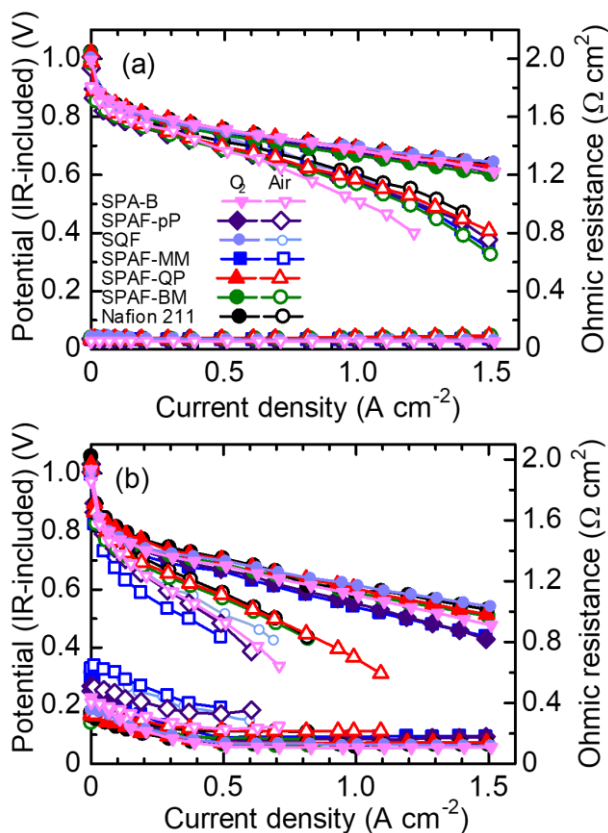


Fig. 5. Fuel cell performance of SPAF-based membranes at (a) 80 °C and 100% RH and (b) 80 °C and 30% RH.

The fuel cell based on the SPAF-based membranes was evaluated at 80 °C under humidity of 100% RH and 30% RH with 70% and 40% utilization for H₂ and O₂, respectively, as shown in Fig.5. At 80 °C and 100% RH, the fuel cell performance of SPAF-based membranes was similar to Nafion NRE 211 with supplying O₂ while it was lower with supplying air even though the ohmic resistance of all cells was similar (0.05-0.08 Ω cm²), suggesting the issue of compatibility between SPAF-based membranes and Nafion-based catalyst layers. At

30% RH, SPAF-MM and SPAF-pP membranes showed lower fuel cell performance than others because of the higher ohmic resistance (lower proton conductivity at low humidity). In addition, interfacial issue was more obvious for SPAF-B membrane at 30% RH. SPAF-B exhibited obviously lower ohmic resistance than that of SPAF-pP while the fuel cell performance was similar, further suggesting of the inferior compatibility with Nafion-based catalyst layer, indicating the alkylene in the main chain lower the interfacial compatibility. Among the new designed SPAF-based membranes, SPAF-QP and SPAF-BM are more promising because of comparable fuel cell performance to that of Nafion NRE 211 at wide range of humidity (30-100% RH) because of high proton conductivity and fluorine amount to enhance the interfacial compatibility with Nafion-based catalyst layer.

The oxidative stability of those SPAF-based membranes was evaluated by OCV hold test at 80 °C and 30% RH. The lifetime of Nafion NRE 211 membrane was lower than 250 h because of high gas permeability. All SPAF-based membranes showed excellent durability and withstood the OCV hold test for 1000 h with low OCV decay. The average decay was in order, 40 μV h⁻¹ for SPAF-BM < 50 μV h⁻¹ for SPAF-QP = 50 μV h⁻¹ for SPAF-MM < 60 μV h⁻¹ for SPAF-pP < 90 μV h⁻¹ for SQF < 120 μV h⁻¹ for SPA-B. Among the polymers from direct polymerization, SPA-B and SQP exhibited the apparent degradation of fuel cell performance in the post analysis, compared with SPAF-pP, indicating that 1) the alkylene in SPA-B membrane went against the oxidative stability of SPAF-based membranes and 2) higher IEC SPAF-based membranes (i.e. high amount of sulfonic acid groups) were more easily attacked by the free radical, resulting in falling sulfonic acid groups off. The post-sulfonated SPAF-based membranes all possessed excellently oxidative stability, only 40-50 μV h⁻¹ of average decay during OCV hold test for 1000 h. The post-mortem results showed that three post-sulfonated polymers exhibited excellent reproducibility of fuel cell performance after OCV hold test for 1000 h. Therefore, the post-sulfonated SPAF membrane showed better oxidative stability than those from direct polymerization, probably because ladderization structure in the post-sulfonated SPAF membranes could make the membrane dense and lower the gas permeability.

CONCLUSION

A series of SPAF-based membranes containing no chemically vulnerable heteroatom linkages in the main chain have been developed and therefore exhibited excellently oxidative stability under OCV condition. SPAF-

based membranes possessed well-developed morphology on account of the great difference of water affinity between perfluoroalkylene and sulfonated phenylene. The SPAF-based membranes were prepared by direct polymerization from sulfonated phenylene monomer or post-sulfonation and herein made a comparison. Compared with direct-polymerization polymers, the post-sulfonated SPAF-based membranes possessed higher molecular weight, water uptake, proton conductivity, fuel cell performance and durability, probably because of the generation of sulfone-bonded ladder structure during post-sulfonation, which improved the hydrophilization and conjunction of backbone. The average decay of post-sulfonated SPAF-based membranes was only 40-50 $\mu\text{V h}^{-1}$ after OCV hold test for 1000 h and the fuel cell performance was easily reproduced. Therefore, such a series of post-sulfonated SPAF membranes was promising to take the place of PFSA because of similar fuel cell performance at wide range of humidity and much more superior oxidative stability.

ACKNOWLEDGEMENT

This work was partly supported by the New Energy and Industrial Technology Development Organization (NEDO), the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, through Grants-in-Aid for Scientific Research (18H05515), Japan Science and Technology (JST) through SICORP (JPMJSC18H8), JKA promotion funds from AUTORACE, the thermal and electric energy technology foundation.

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