Non-Crosslinked Perfluoro-polymer Electrolytes with Two Acid Groups and Their Properties

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"Ionomers", the electrolytes contained in catalyst layers, have very important functions in the fuel cell system. First, they bind the catalyst powder to form a catalyst layer and attach the catalyst layer to an electrolyte membrane. Second, they carry proton to/from the membrane from/to reaction sites, Pt catalysts. Third, since ionomers cover the catalyst surface and hinder transportation of a reactant (H_2 or O_2) from the gas phase to the catalyst, ionomers should allow the reactants to permeate smoothly. To realize PEFCs that are operable under a high-temperature low-humidity condition with a reduced amount of Pt, an ionomer with both high proton conductivity and high oxygen permeability is highly required [1]

For achieving high proton conductivity for the membrane, we had synthesized crosslinked perfluoro polymers having two acid groups, bissulfonyl imide acid and sulfonic acid, partially on their branches, from the Nafion membrane.[2] These polymers, however, are insoluble in solvents because of the crosslinking and lacks the first function of an ionomer as a binder.

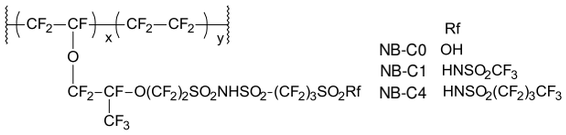

Figure 1. Structures of NB-Cn

To obtain a solvent-soluble high-conductivity polymer with two acid groups in a branch for an ionomer, we synthesized non-crosslinked bifunctional perfluoro-polymer electrolytes, NB-Cn (n = 0, 1, 4) (Figure 1). In this paper, the synthesis of these polymers and their properties such as proton conductivity and oxygen permeability are discribed.[3]

$FO_2S(CF_2)_3.SO_2Rf$ (C3Sn) were generated from the condensation reaction of $FO_2S(CF_2)_3SO_2F$ and HRf (Rf = OH, $NHSO_2CF_3$, and $NHSO_2(CF_2)_3CF_3$) with diisopropyl ethyl amine in MeCN at 0 °C. Then, sulfonamidated Nafion polymers ending in SO_2NH_2 group were added to the solution, and the mixture was stirred for 1 week at 80 °C. After removing solvents, polymers were washed by NaOH aq., H_2O_2 aq., and HNO_3 aq. at 80 °C successively in this order to give the non-crosslinked bifunctional perfluoro-polymers, NB-Cn (n = 0, 1, 4).

NB-Cn were soluble in the mixture of water and ethanol at 180 ºC by autoclave treatments. The ^{19}F NMR spectrum in solution of NB-C0 shows 3 characteristic peaks from -110 to -120 ppm belonging to the 3 CF_2 groups on their branches. Solutions of these polymers were cast into thin films, and then they were annealed above 120 ºC to make the films insoluble in hot water. IEC and water uptakes of cast films are listed in table 1.

Cast films of NB-Cn show higher proton conductivity than Nafion membrane (Figure 2). The proton conductivity of NB-C0 under 20%RH at 25 ºC is $4.3x10^{-3}$ S/cm, which is about 3 times as high as that of Nafion ($1.3x10^{-3}$ S/cm). The proton conductivity of NB-C4 at 100%RH is higher than that of NB-C0 despite smaller IEC. While the oxygen permeabilities of NB-C0 and Nafion are almost the same, that of NB-C4 shows 1.5 times as high as that of NB-C0 (Figure 3).

In conclusion, we synthesized bifunctional perfluoro-polymer electrolytes from Nafion. These polymers showed high proton conductivity. NB-C4, with perfluorobutyl group on its terminal, had higher oxygen permeability than other electrolytes with $-SO_3H$ or $-CF_3$ group on their terminals.

References

[1] Tabe, Y.; Nishino, M.; Takamatsu, H.; Chikahisa, T. J. Soc. Mech. Eng. B, 2011, **77**, 301-312.
[2] Hasegawa, N.; Tanaka, H.; Nakano, M.; Usuki, A.; Kawasumi, M.: Morimoto, Y. JP PAT., 2005, No. 3630306.
[3] Shinohara et al., Japanese Patent, JP 2011- 40363.

Table 1. Properties of NB-Cn

Name	Calculated IEC (meq/g)	measured IEC (meq/g)	Conv. (%)	water uptake (%)
Nafion	-	1.01	-	24
NB-C0	1.56	1.37	82	119
NB-C1	1.41	1.32	89	110
NB-C4	1.28	1.18	93	119

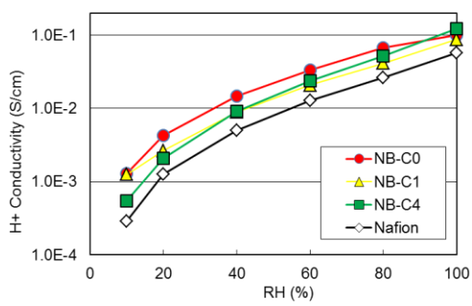

Figure 2. Proton Conductivity vs. RH(%)

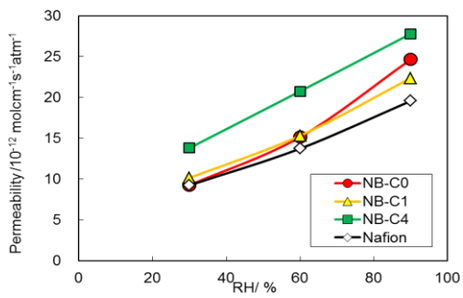

Figure 3. Oxygen Permeability vs. RH(%)