

Characteristics of Proton-Conducting Membrane Based on the Blended Matrix of PVdF Copolymer and Nafion

J.Y. EOM, K.Y. CHO, S.S. Shin, J.K. Park, J.H. Choi*, K.W. Park*, and Y.E.SUNG*KAIST,
*K-JIST

1. Introduction

Perfluorosulfonate ionomer membranes such as Nafion[®], Dow XUS[®], and Flemion[®] are used as SPE membrane for proton exchange membrane fuel cells (PEMFC) for their electrochemical stability, mechanical strength and high proton conductivity [1]. However, a situation called methanol crossover that occurs when methanol crosses through the SPE membrane rather than breaking up into electrons and protons has been seen during the operation of the DMFC. In our previous work [2], we reported a novel composite proton conducting membrane for DMFC. In this design, a blended matrix which consists of vinylidene fluoride - hexafluoropropylene copolymer (P(VdF-co-HFP)) matrix added with smaller amount of Nafion was coated with Nafion again. The novel composite membrane system showed a methanol permeability lowered by over one order of magnitude in comparison to pure Nafion membrane with a comparable proton conductivity to that. It showed the possibility of being used for the proton conducting membrane for DMFC with reduced methanol permeation and cost competitiveness. we did investigate on the relationship between blend morphology and electrochemical properties of the PVdF copolymer / Nafion blend, then. In all case of the blends, it is expected that the PVdF copolymer becomes a continuous phase and the Nafion forms a dispersed phase as we add the Nafion to the amount of 20 wt.-% of the blend.

2. Experimental

P(VdF-co-HFP) with a vinylidene fluoride content of 85 % and 88 wt.-% (Kynar Flex 2751, 2801, Mn=380,000) were supplied from Atofina Chemicals Inc.. Nafion 117 membrane (1100 E.W., sulfonic acid form) and Nafion (1100 E.W., sulfonic acid form) solutions, 5wt.-% and 20wt.-%, in isopropanol, n-propanol, and water mixture were purchased from E. I. Dupont de Nemours & Co.. Solution blends of P(VdF-co-HFP) with the ionomer were prepared in a following procedure. At first, P(VdF-co-HFP) powder was fully dissolved in acetone and the appropriate amount of Nafion solution was added to the dissolved solution. Then, the solution blend of P(VdF-co-HFP) and the ionomer was vigorously stirred to be a homoge neous

transparent solutions. The resulting solution was casted onto a flat glass surface with a doctor blade device gapped at 1 mm, then left in an oven at 25°C for about 5 hours to remove the solvents. The resultant dry, translucent, and flexible films were peeled from the glass plate in a diethyl ether bath. The notation of prepared samples with compositions and fabrication conditions is shown in Table 1.

Notation	PVdF-co-HFP		Nafion wt.-%	Solvent of PVdF copolymer	Casting temperature
	HFP content	wt.-%			
K12NA1000		100	0	Acetone	25°C
K12NA9505		95	5		
K12NA9010	12 wt.-%	90	10		
K12NA8515		85	15		
K12NA8020		80	20		
K15NA1000		100	0		
K15NA9505		95	5		
K15NA9010	15 wt.-%	90	10		
K15NA8515		85	15		
K15NA8020		80	20		

3. Results and discussion

We turn to proton conductivity of the blend film. Figure 1. compares typical complex-plane plots of Nafion 117, K15NA8020, and K12NA8020, where the intercepts of Z' axis exhibit bulk resistances of the film at room temperature. From these plots, proton conductivities of PVdF copolymer / Nafion blends (K15NA, and K12NA series) made of different fabrication conditions and HFP contents of PVdF copolymer with the variation of the Nafion content in blend was calculated and shown in Figure 2. The conductivity of these three types of blend increased roughly linearly with the increase of the Nafion content. Conductivity values of K15NA series were higher than that of the other types of the blends. Abrupt increase of the conductivity was also observed at the Nafion content around 5 wt.-% for K15NA series, and 10 wt.-% for K12NA series. That seems to be an indicative of difference in conductivity percolation threshold [3,4], which is thought to be generated by the difference in the blend morphology.

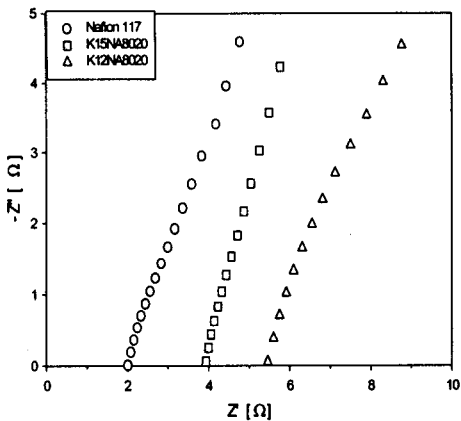


Figure 1. impedance spectroscopy

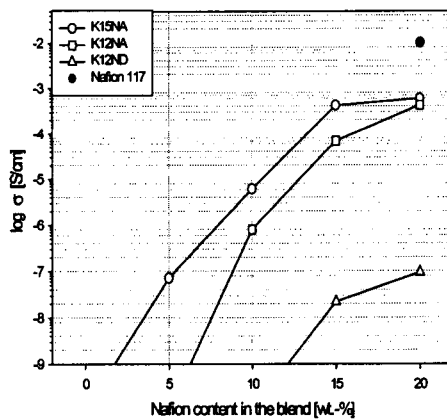


Figure 2. Proton conductivities

Figure 3 reports the methanol permeabilities for K15NA, and K12NA series. The permeability varied approximately linearly with the increase of the Nafion content, and showed the difference for the three types of blends. It is notable that the methanol permeability of the blend membrane was suppressed remarkably by around 2 orders, being compared with that of the Nafion 117 membrane.

It is doubtful that the methanol permeability (Figure 3) was quite suppressed in the PVdF copolymer / Nafion blends. Tricoli *et. al.* reported that the polar methanol molecules permeate through hydrated ion-rich domains which are interconnected in the Nafion membrane [5]. If such a process can be applied to this system, the remarkable suppression of methanol permeation through the blends in comparison with the Nafion 117 membrane might be originated from the modulation of ionic pathway, and it can be attributed to the control of the blend morphology of PVdF copolymer / Nafion.

4. Conclusion

In this study, blends of P(VdF-co-HFP) with Nafion were prepared with a variation of blend ratio, fabrication condition, and HFP content in the PVdF copolymer. It was found that the blend morphology could be controlled by the variation of fabrication condition, blend ratio, and HFP content in the PVdF copolymer. Proton conductivity and methanol crossover of the blend showed a strong dependence on the blend morphology.

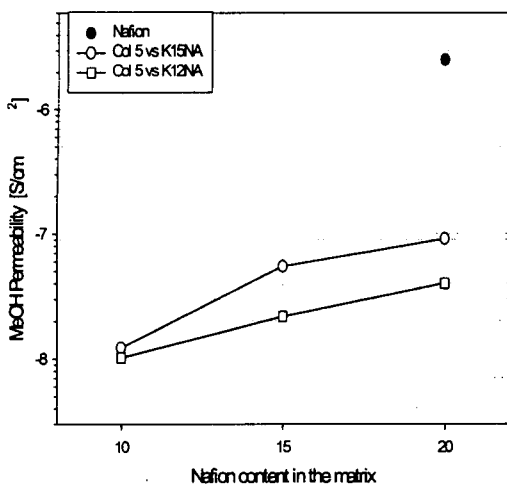


Figure 3. Methanol permeabilities

5. Reference

- [1] O. Savadogo, " Emerging membranes for electrochemical systems : (I) solid polymer electrolyte membranes for fuel cell systems ", *J. New Mat. Electrochem. Systems*, Vol.1, pp47-66, 1998
- [2] Y. G. Lee, J. Y. Eom, and J. K. Park, " Novel proton conducting membrane for DMFCs based on PVdF copolymers ", submitted, 2001
- [3] N. Carretta, V. Tricoli, and F. Picchioni, " Ionomeric membranes based on partially sulfonated poly(styrene) : synthesis, proton conduction and methanol permeation", *J. Membrane. Sci.*, Vol.166, pp189-197, 2000
- [4] K. A. Mauritz, " Dielectric Relaxation Studies of Ion Motions in Electrolyte-Containing Perfluorosulfonate Ionomers. 4. Long-Range Ion Transport ", *Macromolecules*, Vol.22, pp4483-4488, 1989
- [5] V. Tricoli, *J. Electrochem. Soc.*, "Proton and Methanol Transport in Poly (perfluorosulfonate) Membranes Containing Cs⁺ and H⁺ Cations", Vol.145, pp3798-3800, 1998