

수소이온 전도성 부분불소계 가지형 공중합체 전해질막 제조 및 분석

김용우, 최진규, 노동규, 김종학*

120-749 서울시 서대문구 신촌동 134 연세대학교 화학공학과

jonghak@yonsei.ac.kr*

Synthesis and Analysis of Proton Conductive Partially Fluorinated Graft Copolymer Electrolyte Membranes for Fuel Cells

Yong Woo Kim, Jin Kyu Choi, Dong Kyu Roh, Jong Hak Kim*

Department of Chemical Engineering, Yonsei University, 134

Shinchon-dong, Seodaemun-gu, Seoul 120-749, South Korea

jonghak@yonsei.ac.kr*

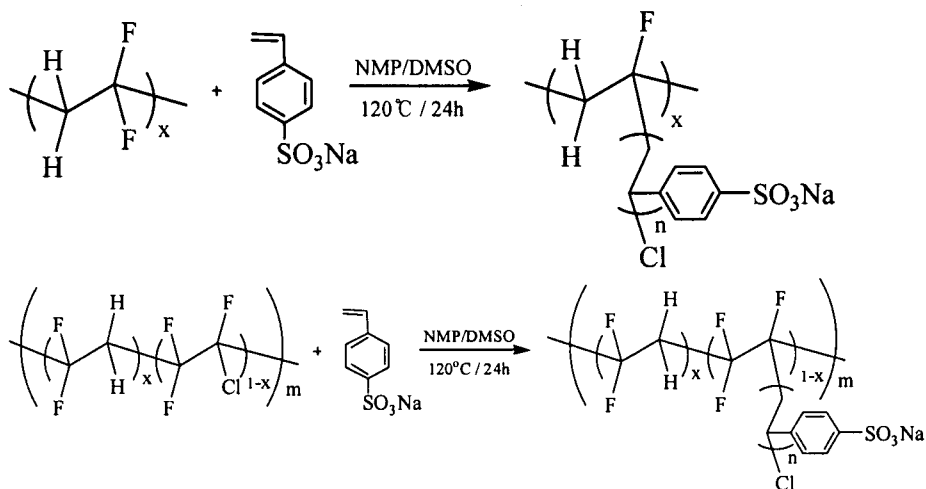
1. Introduction

Proton conducting polymer electrolyte membranes have been extensively investigated for the applications to fuel cells during the last decade. The most common polymer electrolyte membranes used in fuel cells applications are perfluorinated polymer membranes, e.g. the Nafion series from DuPont, and the Aciplex series from Asahi Chemical. poly(vinylidene fluoride) (PVDF) and P(VDF-co-CTFE) were directly grafted with a sulfonated monomer, i.e. styrene sulfonic acid (SSA) using ATRP from secondary chlorines on the main chain backbone. The membranes were further crosslinked by converting terminated chlorine atoms to end-functional azide group, followed by UV irradiation.

2. Experimental

1.0g of P(VDF) and P(VDF-co-CTFE) were dissolved in 25ml NMP in a round flask at 80°C. Separately, the different amounts of SSA were dissolved in 20ml DMSO at 80°C and added to P(VDF) and P(VDF-co-CTFE) solution. After producing homogeneous solution, 0.08g of CuCl and 0.2ml of HMTETA were added and the reaction flask was

sealed with a rubber septum. After N₂ purging for 30min, the reaction vessel was immersed in an oil bath at 120°C. The reaction was allowed to proceed for 24h. After polymerization, the resultant polymer precipitated into methanol. The polymer was purified by redissolving in DMSO and reprecipitating in methanol. Finally, the polymer was dried in a vacuum oven overnight at room temperature.

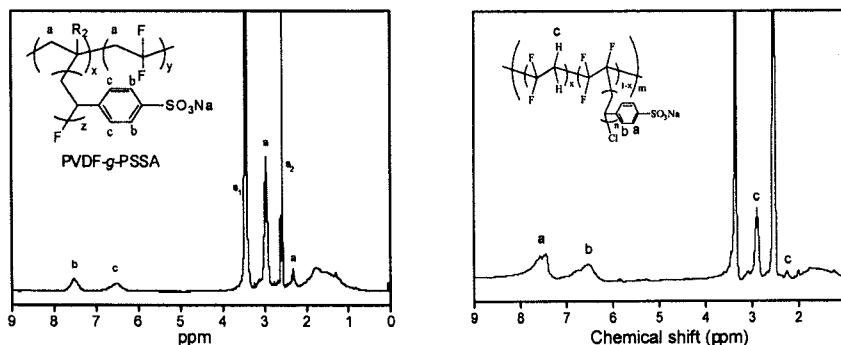


P(VDF-*co*-CTFE)-*g*-PSSA was dissolved in DMSO and added to 10-folded NaN₃ solution in DMF. The solution was stirred and allowed to react at 25°C for 24h. The product was precipitated into methanol and the precipitate was washed several times to remove the unreacted NaN₃. The product was dried under vacuum at 25°C.

3. Result and discussion

The successful graft copolymerization of P(VDF-*co*-CTFE) has been confirmed using ¹H NMR spectroscopy. A representative ¹H-NMR spectrum for P(VDF-*co*-CTFE)-*g*-PSSA with 1:7 wt ratio of added P(VDF-*co*-CTFE):SSA amounts is presented in Figure 1. The strong peaks at 2.6 and 3.5 ppm are due to DMSO and water, respectively. The two peaks at 2.9 and 2.3 ppm are attributed to the head-to-tail (ht) and head-to-head (hh) bonding arrangements of vinylidene fluoride units, respectively. Grafting of PSSA to P(VDF-*co*-CTFE) produced additional new peaks at 7.5 and 6.5 ppm corresponding to the aromatic

bonding environments in the styrene sulfonic acid.



(a) P(VDF)-g-PSSA

(b) P(VDF-co-CTFE)-g-PSSA

Figure 1. ^1H NMR spectra of (a) P(VDF) and (b) P(VDF-co-CTFE)-g-PSSA copolymer.

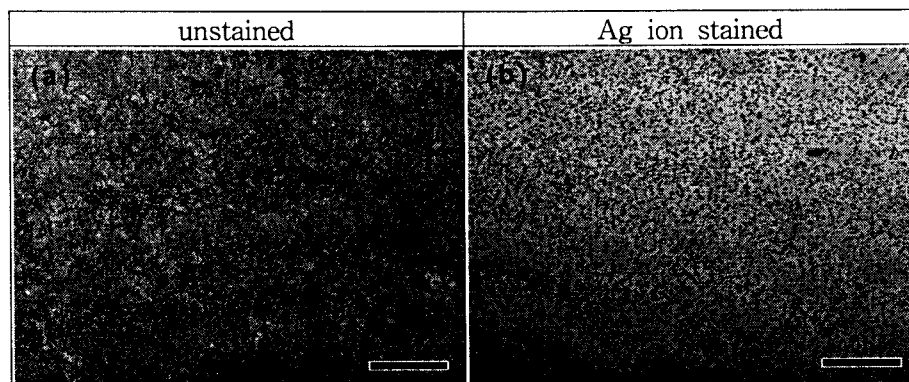


Figure 2. TEM images of P(VDF-co-CTFE)-g-PSSA copolymer with 47w% of PSSA content.

TEM analysis was carried out to characterize the morphology of graft copolymer. Figure 2 presents the TEM images of unstained and Ag^+ stained P(VDF-co-CTFE)-g-PSSA membrane with 47w% of PSSA content. Crystalline domains were observed in the unstained TEM image of the membranes. More clear microphase-separated morphology was observed in the silver ion stained sample, where dark regions represent

the localization of ionic SO₃Ag domains of PSSA side chains whereas lighter regions do hydrophobic domains of P(VDF-co-CTFE) main chains. Ionic channels with a nanometer wide are seen to be visibly connected to yield a continuous ionic network.

The proton conductivities increased with the increase of temperature for all the membranes. The elevation of temperature favors both the dynamics of proton transport and the structural reorganization of polymeric chains, resulting in the increased proton conductivity at high temperatures.

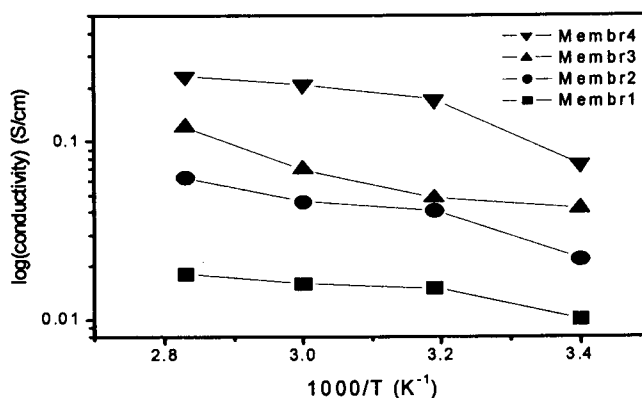


Figure 3. Temperature dependent proton conductivities of P(VDF-co-CTFE)-*g*-PSSA copolymer membranes with various amounts of PSSA.

4. References

- [1]. C. Y. Chiu, W. H. Hsu, Y. J. Yen, S. W. Kuo, F. C. Chang, *Macromolecules*, 38, 6640, (2005).
- [2]. J. H. Kim, M. S. Kang, Y. J. Kim, J. Won, N.G. Park, Y.S. Kang, *Chem Commun*, 14, 1662, (2004).
- [3]. S.D. Mikhailenko, K.P. Wang, S. Kaliaguine, P.X. Xing, G.P. Robertson, M.D. Guiver, *J. Membr. Sci.*, 233, 93, (2004).
- [4]. D. S. Kim, G. P. Robertson, M. D. Guiver, Y. M. Lee, *J. Membr. Sci.*, 281, 111, (2006).