한국신·재생에너지학회 2008년도 추계학술대회논문집 pp.40~43

고온/저가습 고분자전해질 연료전지를 위한 이온성 액체 기반 고분자 전해질막 개발

*새트팔 싱 세콘[1)], **박 진수[2)], 조 은경[3)], 박 구곤[4)], 김 창수[5)], 이 원용[6)]

Development of Polymer Electrolytes Based on Ionic Liquids for High Temperature/Low Humidity PEFC Applications

*Satpal Singh Sekhon, **Jin-Soo Park, EunKyung Cho, Gu-Gon Park, Chang-Soo Kim, Won-Yong Lee

Key words : Ionic liquid(이온성 액체), Polymer electrolyte fuel cell(고분자전해질 연료전지), High temperature(고온), Low humidity(저가습)

Abstract : High temperature polymer electrolyte membranes incorporating ionic liquids (ILs) in different polymers such as commercial fluorinated polymers, sulfonated polymers and recasted nafion have been developed. ILs based on imidazolium cation and different anions possess high ionic conductivity and good thermal stability and have been used in the present study. The membranes containing IL show conductivity ~10^{-2} S cm^{-1} above 100°C under anhydrous conditions and are thermally stable up to 250-300 °C. IL acts as a conducting medium in these electrolytes and plays the same role as played by water in fully hydrated nafion membranes. Due to high conductivity and good thermal stability, these membranes are promising materials for PEFCs at higher temperatures under anhydrous conditions.

1. Introduction

Fuel cells are important candidates for energy conversion system in the future and are expected to play an essential role in the resolution of emerging energy issue. Out of the different types of fuel cells, the polymer electrolyte fuel cells (PEFCs) are more suitable due to their low starting temperature, high energy conversion efficiency and ease of handling. However the present PEFCs use water swollen ion exchange (Nafion) membranes due to their excellent chemical, physical and electrical properties. But these membranes can be operated only below the water condensation temperature as their conductivity drops sharply at temperatures above 80°C due to the evaporation of water. The high cost, low thermal stability at higher temperatures and CO poisoning of platinum catalyst are some other drawbacks of such membranes. However the operation of PEFCs at higher temperatures (>120°C) can solve most of these problems and can also lead to an improved performance.[(1)] The replacement of water with other low volatile solvents like imidazole is another option which has been tried. ILs is another unique class of solvents that contain only charged species and have many interesting properties which make them

1) Department of Applied Physics, Guru Nanak Dev University
E-mail : sekhon_apd@yahoo.com
Tel : (91)183-225-8802 Fax : (91)183-225-8820
2) 한국에너지기술연구원, 연료전지연구단
E-mail : park@kier.re.kr
Tel : (042)860-3306 Fax : (042)860-3104
3) 한국과학기술원, 생명화학공학과
E-mail : euia7@yahoo.com
Tel : (042)860-3178 Fax : (042)860-3104
4) 한국에너지기술연구원, 연료전지연구단
E-mail : gugon@kier.re.kr
Tel : (042)860-3782 Fax : (042)860-3104
5) 한국에너지기술연구원, 연료전지연구단
E-mail : cskim@kier.re.kr
Tel : (042)860-3573 Fax : (042)860-3104
6) 한국에너지기술연구원, 연료전지연구단
E-mail : wy82lee@kier.re.kr
Tel : (042)860-3574 Fax : (042)860-3104

suitable for applications in polymer electrolytes. The aim of the present work is related to study the effect of replacement of water with IL and to develop polymer electrolytes based on ILs with high conductivity and good thermal stability.

2. Experimental

The ILs used in the present study have 2,3-dimethyl-1-alkyl imidazolium ($DMOIm^+$) cation and different anions (BF_4, PF_6, CF_3SO_3, $N(CF_3SO_2)_2$ etc) have been synthesized by the method reported in our earlier publications.[(2)] Some of the ILs ($EMIBF_4$, EMITf) have been purchased from TCI. Commercially available polymers such as PVdF-HFP has been purchased from Aldrich, whereas sulfonated poly(aryl ether ketone) (SPEAK-6F) and recasted Nafion have been synthesized.[(3,4)] Polymer electrolytes containing ILs have been prepared by solution casting method by using acetonitrile/methanol as the solvent. The details of measurements of conductivity, viscosity, TGA, AF-TEM are given in our earlier publications .[(2,4)]

3. Results and discussion

Fig.1 shows the variation of conductivity and viscosity of a representative ionic liquid (DMOImTFSI) with temperature. With an increase in temperature, the decrease in viscosity has been found to be accompanied by an increase in conductivity. The decrease in viscosity leads to higher mobility, as viscosity and mobility are inversely related to each other, which increases conductivity and conductivity higher than 10^{-2} S cm^{-1}has been observed above 70°C. As the IL comprise entirely of ions, so ions are in contact with each other in the IL and are not separated by solvent molecules as in a salt solution. The addition of a suitable solvent, with higher dielectric constant and low viscosity, has been observed to result in an increase in conductivity. The higher conductivity of binary mixture of IL and solvent as compared with the IL is due to (i) a decrease in viscosity, as viscosity of solvent is lower than that of the IL, which leads to higher mobility and (ii) making ions present in IL free from each other and hence these ions can contribute to conductivity. However the boiling point of the solvent should be higher than 200°C, so that it does not evaporate when the membrane containing IL and solvent is operated at higher temperatures (100-200°C). The conductivity of the binary mixture of IL and solvent has been found to be higher than that of the IL at all temperatures.

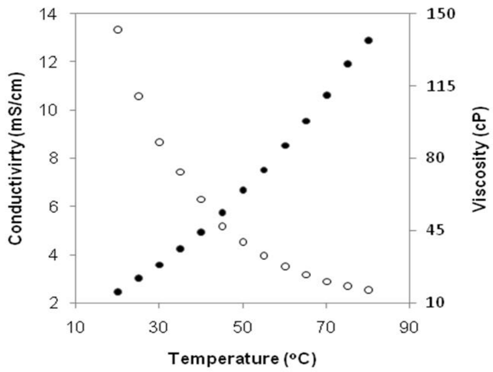

Fig. 1 Ionic conductivity and viscosity of the ionic liquid, DMOImTFSI

Polymer electrolyte membranes containing ILs were prepared by using three different types of polymers as discussed below:

3.1 Polymer electrolytes containing commercial polymers:

Polymer electrolytes based on various ILs and different commercially available polymers namely PEO, PAN, PVdF, PVdF-HFP have been synthesized and studied. For the same IL, polymer electrolytes containing PVdF-HFP have been found to show maximum conductivity[(2)] as well as good mechanical and thermal properties, which may be due to the presence of fluorine in the polymer, as C-F bonds have higher strength than C-H bonds. However the conductivity of polymer electrolytes is lower than that of the neat IL, which is due to the addition of inert polymer. Although these polymer electrolytes show higher conductivity at temperatures above 100°C, yet it is lower than for Nafion membranes at 80°C under fully hydrated conditions.

The thermal stability of the IL and of polymer electrolytes containing IL has been checked by TGA/DSC measurements. The IL containing imide anion has been found to be thermally stable up to 400°C, whereas the polymer electrolytes containing the IL are thermally stable up to 300°C. Weight loss by less than 5 % only has been observed up to 300°C, which suggests that these membranes can be used at temperatures up to 200°C in different devices. However the lower conductivity of these polymer electrolytes containing commercial polymer as compared to Nafion needs improvement by at least one order of magnitude so as to get higher value of current density in PEFCs.

3.2 Polymer electrolytes containing recasted Nafion:

In order to check whether water being used in Nafion membranes can be replaced by the IL or not, nafion membranes fully hydrated with water and those containing IL were studied under similar conditions. The ionic conductivity of Nafion membranes swollen with IL(EMITf) and with water was measured at different temperatures and the variation of conductivity with temperature is shown in Fig.2. Although the conductivity of fully hydrated Nafion membranes is relatively higher than for membranes containing IL, yet it has been observed that membranes containing IL also show conductivity of the same order under non-humid conditions. This indicates that IL can be used as the conducting medium in place of water in Nafion membranes and secondly these membranes can be operated at temperatures higher than 100°C and under non-humid conditions. However the retention of IL by the membranes at higher temperatures over extended periodsof time and its mechanical properties has to be studied in detail. Work is in progress to understand the conduction mechanism in such polymer electrolytes containing ILs.

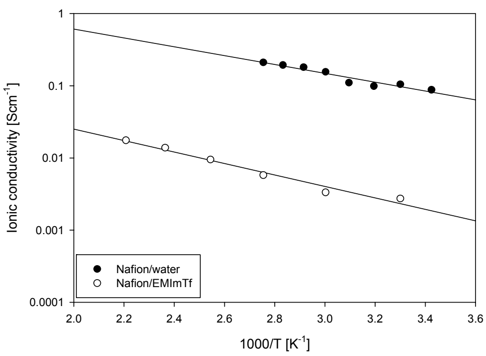

Fig. 2 Variation of ionic conductivity of water swelled Nafion and EMImTf-based Nafion with temperature

3.3 Polymer electrolytes containing sulfonated polymers:

Sufonated poly aryl ether ketone (SPAEK-6F) random copolymers with different degrees of sulfonation have been synthesized in our group via nucleophilic aromatic substitution.[3,4] Sulfonation of different polymers provides $-SO_3H$ groups on the backbone / side chains of the polymer, which helps the conduction by protons in the membranes based on such polymers. The conductivity of sulfonated polymers containing ILs has been found to depend upon (i) the concentration of IL present in the membrane, (ii) the degree of sulfonation of the polymer and (iii) temperature. Although the conductivity of membranes has been found to be higher at large concentrations of the IL and at higher DS, yet they can not be increased beyond a certain limit as it leads to a deterioration of mechanical properties of polymer electrolytes. For applications of these membranes in PEFCs, the concentration of IL and DS has to be adjusted in such a way that we obtain polymer electrolytes having optimum properties-high conductivity and good mechanical strength. The conductivity of polymer electrolytes containing IL (EMITf) in SPAEK-6F was also measured at different temperatures. For comparison purposes, the conductivity of sulfonated polymers under fully hydrated conditions was also measured and the variation of conductivity with temperature for both the membranes is given in Fig.3. In this case also the polymer electrolytes containing sulfonated polymer have higher conductivity under fully hydrated conditions than for polymer electrolytes containing IL, yet the sulfonated polymers containing IL also show high conductivity at temperatures above 120°C under non-humid conditions. These results suggest that IL can act as a conducting medium instead of water in these sulfonated polymers and can replace water in such polymer electrolytes which can thus be used at temperatures higher than 100°C under non- humid conditions. However the mechanical stability, ability to retain IL for long periods of operation and compatibility with electrodes has to be checked before their actual application in devices.

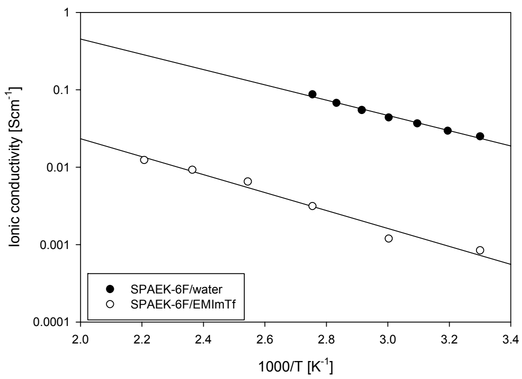

Fig. 3 Variation of ionic conductivity of water swelled SPAEK-6F and EMImTf-based SPEAK-6F with temperature

4. Conclusion

Ionic liquids can be used to replace water in polymer electrolyte membranes based on nafion and sulfonated polymers. The conductivity of polymer electrolytes containing ionic liquid is however slightly lower than for membranes swelled with water. The polymer electrolytes containing ionic liquids can be used at higher temperatures (>80°C) and under anhydrous conditions, which is required for their applications in PEFCs.

References

[1] Li Q., He R., Jensen J.O., Bjerrum J., 2003, Approaches and recent development of polymer electrolyte membranes for fuel cells operating above 100℃, Chem. Mater., Vol.15, No.26, pp 4896-4915.
[2] Singh B., Sekhon S.S., 2005, Ion conducting behaviour of polymer electrolytes containing ionic liquids, Chem. Phys. Lett., Vol.414, Issue 1-3, pp 34-39.
[3] Park S.H., Park J.S., Yim S.D., Park S.H., Lee Y.M., Kim C.S., 2008, Preparation of organic/inorganic composite membranes using two types of polymer matrix via a sol-gel process, J. Power Sources, Vol.181, Issue 2, pp 259-266.
[4] Cho E., Park J.S., Sekhon S.S., Park, G.G., Yang T.H., Lee W. Y., Kim C.S., Park S.B., 2008, A study on composite membranes based on ionic liquid/ sulfonated polymer for high temperature anhydrous polymer electrolyte fuel cells, communicated -unpublished results.