한국신·재생에너지학회 2009년도 추계학술대회논문집 pp.147~148

고온 PEFCs를 위한 탄화수소계열 고분자와 이온성 액체를 함유하는 복합막에 관한 연구

*백 지숙[1),2)], **박 진수[3)], 김 경현[4)], 문 기영[4)], 김 혜경[4)], 최 영우[2)], 박 구곤[2)], 양 태현[2)], 김 창수[2)], 설 용건[1)]

A study on composite membranes based on hydrocarbon polymers and ionic liquids for high temperature PEFCs

*Ji-Suk Baek, **Jin-Soo Park, Kyung-Hyun Kim, Gi-Young Moon, Hye-Kyung Kim, Young-Woo Choi, Go-Gun Park, Tae-Hyun Yang, Chang-Soo Kim, Young-Gun Shul

Abstract : The water-like ionic liquids have been widely used to enable the proton conduction in ionic liquid based membranes at high temperature and anhydrous PEFCs. In this study, we synthesized various kinds of composite membranes based on hydrocarbon polymers having good thermal and mechanical stabilities at high temperatures and ionic liquids. The composite membrane consisting of hydrocarbon polymer and ionic liquid was characterized by thermogravimetric analyzer (TGA) and impedance spectroscopy. Consequently the non-aqueous composite membranes of a variety of hydrocarbon polymer and ionic liquids have good conductivity and thermal stability at high temperature conditions.

Key words : Ionic liquid(이온성 액체), hydrocarbon polymer(하이드로카본계열 고분자), composite membrane(복합막), high temperature fuel cells(고온용 연료전지)

1. Introduction

Recently, many research efforts have been focused on new membranes suitable for high temperature polymer electrolyte fuel cells (HT-PEFCs). Among those, the hydrocarbon membranes have been intensively investigated as an alternating membrane due to their having better thermal and mechanical stabilities compared with the perfluorosulfonic acid membranes under water free and high temperature condition.

Under this circumstance, this work aims at elucidating the relationship between the type of copolymers and membrane properties. [(1)]

And the ionic liquid is a liquid that contains essentially only ions. In particular, the salts that are liquid at room temperature are called room-temperature ionic liquids, or RTILs. Unlike conventional molten salts, ionic liquids (ILs) are salts with low melting points (<100 ^{o}C) and, most importantly, often are hydrolytically stable. Since ionic liquids exhibit extremely low vapor pressures and wide liquid ranges, and are highly polar yet non-coordinating, they are good solvents for a wide range of organic and inorganic materials. These liquids have been utilized not only as clean solvents, but also as catalysts for green chemistry and electrolytes for batteries, photochemistry and electrosynthesis and even as advanced heat transfer fluids and lubricants. Many of these types of ionic liquids are available commercially.[(1)] Ionic liquids (ILs) have also shown much promise as

1) Department of Chemical & Biomolecular Engineering, Yonsei University
E-mail : pseungr@yonsei.ac.kr
Tel : (02)2123-3554(#34) Fax : (02)312-6507
2) Fuel Cell Research Center, Korea Institute of Energy Research (KIER)
E-mail : gogun@kier.re.kr
Tel : (042)860-3782 Fax : (042)860-3104
3) Department of Environmental Engineering, Sangmyung University
E-mail : energy@smu.ac.kr
Tel : (041)550-5315
4) Department of New Materials, Youngnam University
E-mail : hkkim@ynu.ac.kr
Tel : (053)810-2536

replacement for water as they are non-volatile and also have a larger electrochemical stability window than water. Membranes based on different polymers (commercial polymers, recast Nafion, sulfonated copolymers etc.) containing ILs have been also reported[1,2,3] for use in PEFCs at higher temperatures and under anhydrous conditions.

For this purpose, we synthesized various composite membranes by adding ionic liquids to hydrocarbon copolymers with different structures. From the analyses of the ac-impedance spectra and thermogravimetric analyzer (TGA) curves, the composite membranes containing ionic liquids were investigated on electrochemical and thermal properties at high temperature and anhydrous condition.

2. Experimental

We used various hydrocarbon polymers and ionic liquids. The electrochemical properties of the composite membranes were investigated at elevated temperatures under anhydrous conditions. The ionic conductivity of the composite membranes was measured by a.c. impedance spectroscopy using a four-point-probe conductivity cell with platinum electrodes. The measurements were carried out under a potentiostatic mode in the frequency range of 100 mHz to 10 MHz with 5mV oscillating voltage. Ionic conductivity of the samples was calculated from the following equation:

$$\sigma = \frac{L}{RWd}$$

here σ is the ionic conductivity, L the distance between two potential sensing platinum wires, R the membrane resistance derived from the impedance value at zero phase angle, Wthewidthofthepotentialsensingplatinumwire, and d the membrane thickness. Each electrochemical data was averaged by three measurements, and the standard deviation of all data was below 1%. And heat scans were carried out in the temperature range of 50 to 600 ^{o}C with 10 ^{o}C min^{-1} of a heating rate under nitrogen.

3. Summary

The sulfonated aromatic polymers are widely investigated as candidate PEM materials due to their high chemical and thermo oxidative stability, good mechanical properties. As a results, the composite membranes of hydrocarbon copolymers and ionic liquids have good conductivity at high temperature and anhydrous condition. Furthermore, the composite membranes have good thermal and mechanical stabilities.

Acknowledgement : This work is supported in part by Basic Research Program (Grant No. GP2009-0003) of Korea Institute of Energy Research and the outcome of a Manpower Development Project of the Specialized Graduate School of hydrogen & Fuel Cell supported financially by the Ministry of Commerce, Industry, and Energy (MOCIE).

References

[1] E. K. Cho, J. S. Park, S. S. Sekhon, G. G. Park, T. H. Yang, W. Y. Lee and C. S. Kim, 2009, "A study on composite membranes based on ionic liquid/sulfonated polymer for high temperature anhydrous polymer electrolyte fuel cells" Journal of the Electrochemical Society, 156, B197.

[2] Sekhon, S. S., Lalia, B. S., Park, J. S., Kim, C. S. Yamada, K., 2006, "Physicochemical properties of proton conducting membranes based on ionicliquid impregnated polymer for fuel cells" Journal of Materials Chemistry, 16, 2256.

[3] Sekhon, S. S., Krishnan, P., Singh, B., Yamada, K., Kim, C. S., 2006 "Proton conducting membrane containing room temperature ionic liquid" Electrochimica Acta 52,1639.