Ionic Liquids—New Materials for Fuel Cells

S.S.Sekhon, C.S. Kim*
Department of Applied Physics, Guru Nanak Dev University, Amritsar-143 005, India, *Polymer Electrolyte Fuel Cell Research Department, Korea Institute of Energy Research, Daejeon 305-343, Korea

Ionic liquids due to their high conductivity, good chemical and electrochemical stability, negligible vapour pressure and green nature are finding applications in various electrochemical devices. The prospects of the use of ionic liquids and membranes based on ionic liquids in fuel cells will be discussed.

Ionic liquids also known as ambient temperature salts or room temperature molten salts are finding wide use as potentially safe electrolytes in various electrochemical devices due to their unique properties such as wide liquid range, non-flammability, high thermal stability , wide electrochemical stability window, high ionic conductivity and unmeasureable vapour pressure[1]. Due to their environment friendly green nature, they are being used in many diverse fields including as reaction solvents, in separation process etc. [2]. Ethylammonium nitrate was the first ionic liquid reported in 1914 [3] and later ionic liquids based on chloroaluminates were reported in 1951 [4]. Despite having high conductivity as they consist of ions only, they could not be used in many applications due to their high sensitivity to moisture and the decomposed product upon hydrolysis was HCl which is highly corrosive.However the report of air and moisture stable non-chloroaluminate ionic liquids in 1992 [5] changed it and generated a renewed interest in these materials. Due to their high conductivity, ionic liquids have been proposed as suitable electrolytes for various electrochemical devices including batteries, supercapacitors, fuel cells, electrochromic display devices etc. Most of the ionic liquids reported are based on organic cations such as quaternary ammonium, pyridinium, pyrrolidinium, pyrazolium, triazolium, phosphonium and particularly imidazolium and bulky and soft fluoroanions like BF^{4-}, PF^{6-}, CF_3SO^{3-}, $N(CF_3SO_2)^{2-}$, etc. [6]. Although ionic liquids can maintain high conductivity over a wide temperature range yet most of the small and portable electronic devices require membrane like electrolytes. As ionic liquids can dissolve a wide variety of organic and inorganic compounds to very high concentrations so polymer electrolytes obtained by incorporating suitable polymers in ionic liquids will be suitable for applications in devices as their safety, stability and good mechanical properties will also be advantageous. Although initially these electrolytes containing ionic liquids were studied for their use in solid state lithium batteries [7-8] yet recently they are being proposed as potential materials for use in supercapacitors, alkaline fuel cells, polymer electrolyte fuel cells, in the synthesis of catalysts for fuel cells etc. [9-17]. In the present presentation, the applications of ionic liquids and of polymer electrolytes based on ionic liquids in fuel cells, supercapacitors and fuel cell catalysts will be presented.

Supercapacitors are generally used in combination with fuel cells in fuel cell powered electric vehicles and provide power peaks during acceleration especially with fuel cells which have low performance power. A hybrid supercapacitor using ionic liquid: 1-buthyl-3-methyl imidazolium hexafluoro- phosphate as electrolyte in an activated carbon and poly(3- methylthiophene)has been reported [9]. It was tested at 60°C which is normally the temperature required for use in fuel cell

powered vehicles and showed a capacitance of 0.23 F/cm^2 corresponding to a specific capacitance of 19 F/g and a specific capacity of 7 mAh/g. Similarly an electrochemical double-layer capacitor (EDLC) based on polymer electrolytes containing ionic liquid: 1-ethyl-3-methyl imidazolium phosphate $(EMIm)_3PO_4$ in a polymer has also been reported to have a capacity of 0.25 F which leads to a specific capacity of 236 F/g and 90 F/g for an activated carbon powder with a specific surface area of 2600 and 870 m^2/g respectively [10]. The high conductivity (~ mS/cm), wide electrochemical stability (> 4.0 V)and very high specific capacity (~230 F/g) suggests that these polymer electrolytes containing ionic liquids are good candidates for applications in double layer capacitors.

Ionic liquids has also been reported to be used in the preparation of Pt-Ru /C catalyst which is presently used in direct methanol fuel cell and this catalyst such prepared show high electroactive activity for the methanol oxidation [11]. The preparation of the catalyst is very simple and secondly the ionic liquid can be recycled. Nanoparticle catalysts for biphasic hydrogenation reactions can also be prepared by using ionic liquids as the solvent as the ionic liquids can provide a polar environment for chemical synthesis alongwith their green nature. The choice of a suitable ionic liquid is important as it can affect the relative crystallinity and the chemical state of the metal particles in the catalyst.

Recently, ionic liquid : 1-n-buthyl-3- methyl imidazolium tetrafluoroborate (BMImBF4) which is liquid down to 80°C has been used as an electrolyte in commercial alkaline fuel cell at room temperature with air and hydrogen at atmospheric pressure [12]. A commercial single cell fuel cell with a Pt-based anode and Ag-based cathode with electrode area 5 cm^2, cell volume 7.5 cm^2 and total volume 200 cm^2 was used. The open circuit voltage of the cell was 1.0 V which is less than the theoretical value of 1.22V due to the gas diffusion through the media. The overall efficiency of the cell using ionic liquid was reported to be 67% at 27°C which decreased to 29% at 60°C. However a change in the n-alkyl group as well as of the anion can be used to change the physico-chemical properties of the ionic liquid suitable for such applications.

Polymer electrolyte membrane fuel cell (PEMFC) use Nafion perfluorinated ionomer membrane and are generally operated at 80°C under fully hydrated (100% RH) conditions. However the poisoning of the platinum catalyst by carbon monoxide in the reform gas requires very pure hydrogen fuel which increases the operational cost and it can be avoided if the fuel cell is operated at higher temperatures generally above 140°C. But the conductivity of Nafion membrane which is dependent on humidity level falls drastically above 100°C due to the loss of water. Although a number of alternative membranes are being studied which have been reviewed recently [18] yet there is no report on the demonstration of positive fuel cell tests using these electrolytes. High conductivity obtained in some cases is accompanied by relatively poor thermal and electrochemical stability. Modified Nafion membranes either recast or those containing various additives including ionic liquids are also being studied. In this context perfluorinated ionomer membranes with different equivalent weights were swollen with ionic liquid: 1-butyl,3-methyl imidazolium trifluoromethanesulfonate has been reported to give composite free standing membranes with good stability and show high conductivity of 0.1 S/cm at 180°C although fuel cell testing results are not available [13]. The conductivity has been found to depend upon the EW of the ionomer membrane and those with low EW show higher conductivity some even more than the neat ionic liquid also.

Similarly ion gels prepared by in-situ polymerization of vinyl monomers in ionic liquids and ion gels containing polyvinylidenefluoride (PVdF) in 1,2,4-triazole and bis trifluoromethanesulfonyl imide has been tested in a single cell H_2/O_2 fuel cell at 130°C to demonstrate the use of an ion gel as a proton conducting non aqueous electrolyte under non- humidifying conditions [14]. The same group has recently reported Bronsted acid-base complexes prepared by the combination of 2,5-diphenyl-1,3,4-oxadiazole with bis trifluoromethanesulfonyl imide are electroactive for hydrogen oxidation and oxygen reduction at a platinum electrode and hence can be used as fuel cell electrolyte under anhydrous conditions [15]. The performance of the electrolyte has been found to improve with an increase in temperature from 130 to 150°C. Hagiwara et al have also recently shown the possibility of using a room temperature ionic liquid: 1-ethyl-3-methyl imidazolium fluorohydro-genate in a fuel cell without humidification and obtained an open circuit voltage of ~1.1 V under the flow of H_2 and O_2 gas at 298 K [16]. However due to the liberation of HF from the salts they can not use these electrolytes in actual fuel cell. Due to their liquid nature such ionic liquids may not be suitable for use in PEMFCs. Angell et al. have recently reported the use of ethyl ammonium nitrate- which was the first ionic liquid reported in 1914 along with a number of other ionic liquids as solvent free fuel cell electrolytes and compared their performance with 85% aqueous H_3PO_4 electrolyte at temperatures above 100°C [17]. High temperature polymer electrolytes containing ionic liquids with dihydrogen phosphate and bisulphate anions are also being actively studied for their use in polymer electrolyte fuel cells at higher temperatures.

We have synthesized a number of ionic liquids containing 2,3-dimethyl-1-octyl imidazolium cation ($DMOIm^+$) and different fluoroanions such as BF^{4-}, PF6-, CF_3SO^{3-}, $N(CF_3SO_2)^{2-}$ etc. [19-20]. All the ionic liquids have been found to be liquid at room temperature (25°C). The viscosity and conductivity of these ionic liquids has been measured at different temperatures and with an increase in temperature, the decrease in viscosity has been found to be accompanied by an increase in conductivity and maximum conductivity greater than 0.01 S/cm has been obtained for some ionic liquids. Polymer electrolytes in the membrane form has also been prepared by incorporating different polymers (PEO, PAN, PMA, PMMA, PVdF, PVdF-HFP etc.) in these ionic liquids by the solution casting technique. These membranes show maximum conductivity of the order of 0.001 S/cm along with good thermal and mechanical properties. As generally both cations and anions are reported to be mobile in these polymer electrolytes but for their applications in fuel cells only proton conductivity is important so this was checked in the present case by solid state NMR studies. 1H solid state NMR spectra of these membranes was recorded at different temperatures and line narrowing observed in the variation of line width with temperature shows that proton diffusional motion takes place above 200°C in these electrolytes. Such membranes in which protons have been found to be mobile were tested in fuel cell studies. Preliminary results obtained with using these polymer electrolytes membranes containing ionic liquids in actual fuel cell under non –humidifying conditions show that these membranes are electroactive for hydrogen oxidation and oxygen reduction [21]. The potential drop observed with an increase in current density is possibly due to the electrode polarization and IR drop which is a clear indication of electric power generation by a H_2/O_2 fuel cell using an electrolyte containing ionic liquids. Due to their non aqueous nature, these membranes could be used at elevated temperatures under non-humidifying conditions. The current and power density obtained is although

comparable with the value reported for similar electrolytes yet it is quite low as compared with PEMFCs using Nafion membranes. This was expected as the single cell test station used in the present study has been optimized for Nafion membranes under completely hydrated conditions. Further work is in progress to improve the conductivity and thermal as well as mechanical properties of these membranes. This along with an optimization of fuel cell conditions suitable for such membranes containing ionic liquids will be helpful in improving the performance of these membranes in actual fuel cell conditions.

ACKNOWLEDGEMENTS

This work was supported by Ministry of Science and Technology and by Ministry of Commerce, Industry and Energy, Republic of Korea.

REFERENCES

1.R.D.Rogers, K.R.Seddon (Eds.), Ionic Liquids: Industrial Applications to Green Chemistry, ACS Symposium Series 818 (American Chemical Society,Washington,DC,2002).
2. T. Welton, Chem. Rev. 99 (1999) 2071.
3. P.Waldon, Bull. Acad. Imper. Sci. (St, Petersburg) 1914,1800.
4. F.H.Hurley, T.P. Wier, J. Electrochem. Soc. 98 (1951) 203.
5. J.S.Wilkes,M.J.Zaworotko J Chem Soc., Chem. Commun. (1992) 965.
6. Bonhote, AP.Dias, M.Armand, N.Papageorgiou, K.Kalyanasundram, M.Gratzel, Inorg. Chem. 35 (19960 1168.
7. B.Garcia, S.Lavallee, G.Perron, C.Michot, M.Armand, Electrochim. Acta 49 (2004) 4583.
8. Y.Hu, H.Li, X.Huang, L.Chen, Electrochem. Commun. 6 (2004) 28.
9. A.Balducci, U.Bardi, S.Caporali, M.Mastragostino, Electrochem. Commun. 6 (2004) 566.
10. A.Lewandowski, A.Swiderska, Polish J. Chem. 78 (2004) 1371.
11. X.Xue, T.Lu, C.Liu, W.Xu, Y.Su, Y.Lv, W.Xing, Electrochim. Acta 50 (2005) 3470.
12.R.F.deSouza, J.C.Padilha, R.S.Goncalves, J.Dupont, Electrochem .Commun. 5 (2003) 728.
13. M.Doyle, S.K.Choi, G.Proulx, J. Electrochem. Soc. 147 (2000) 34.
14. M.A.B.H.Susan, A.Noda, N.Ishibashi, M.Watanabe in Solid State Ionics: The Science and Technology of Ions in Motion, V.R.Chowdari, H.I.Yoo, G.M.Choi, J.H.Lee (Editors),World Scientific, Singapore (2004) 899.
15. H.Matsuoka, H.Nakamoto, M.A.B.H.Susan, M.Watanabe, Electrochim.Acta 50 (2005) 4015.
16. R.Hagiwara, T.Nohira, K.Matsumoto, Y.Tamba, Electrochem. and Solid State Lett. 8 (2005) A231.
17. C.A.Angell, W.Xu, J.P.Belieres, M.Yoshizawa, Patent WO 2004 / 114445.
18. W.H.J.Hogarth, J.C.D.Costa, G.Q.(Max)Lu, J.Power Sources 142 (2005) 223.
19.B.Singh, S.S.Sekhon, J. Phys.Chem. B (2005).
20. B.Singh, S.S.Sekhon, Chem. Phys. Lett. (2005) communicated.
21. S.S.Sekhon et. al. unpublished results.