Highly conductive non aqueous polymer gel electrolytes containing ammonium hexafluorophosphate (NH$_4$PF$_6$)

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Non aqueous polymer gel electrolytes based on polyethylene oxide (PEO) and ammonium hexafluorophosphate (NH$_4$PF$_6$) show high conductivity above 10^{-2} S/cm at 25°C. The addition of PEO to liquid electrolytes has been found to result in an increase in free ion concentration by dissociating ion aggregates present in these electrolytes at higher concentrations (≥ 0.4 M) of NH$_4$PF$_6$ alongwith an increase in viscosity. The free ion concentration and viscosity play a dominant role on the conductivity behaviour of these polymer gel electrolytes at low and high concentrations of PEO respectively. The presence of ion aggregates and their dissociation with the addition of PEO has also been checked by FTIR and the results are in agreement with the conductivity behaviour. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Polymer gel electrolytes obtained by immobilizing the salt solution with the addition of a suitable polymer matrix are important materials due to their high conductivity (10^{-2}–10^{-4} S/cm), good chemical and thermal stability, ease of preparation, wide range of compositions allowing a wider control of properties etc. [1, 2]. Although initial work concentrated mainly on gel electrolytes containing various lithium salts [3–5] yet proton conducting polymer gel electrolytes are also being studied [6–9] to explore their possible use in devices including proton exchange membrane fuel cells. The addition of different polymers enhances the viscosity (η) of the electrolytes which will lower ionic mobility ($\mu = q/6\pi\eta r$) resulting in a decrease in conductivity ($\sigma = nq\mu$) [10] which is generally small and is by a factor only not by an order which suggests that the polymer plays the role of a stiffener only [4, 10–12]. However it has recently been reported [13–16] that polymer addition can also result in an increase in conductivity and gels have conductivity higher than the corresponding liquid electrolytes. This is generally explained to be due to an increase in free ion concentration with the addition of polymer but the exact mechanism is not clearly understood. Recently "breathing polymeric chain model" has been proposed to explain this conductivity behaviour in non aqueous proton conducting polymer gel electrolytes containing different aromatic carboxylic acids and aliphatic dicarboxylic acids [13]. Polyethylene oxide (PEO) which is widely used in polymer salt complexes type polymer electrolytes has been reported to result in conductivity enhancement in lithium ion conducting polymer gel electrolytes [15]. However the role of PEO on the conductivity behaviour of proton conducting polymer gel electrolytes has not been studied in detail.

In present study, PEO based non aqueous polymer gel electrolytes containing ammonium hexafluorophosphate (NH$_4$PF$_6$) have been synthesized and the role of PEO in conductivity modification has been investigated. The variation of viscosity and pH of gel electrolytes as a function of PEO concentration has been correlated with the conductivity results and the presence of free ions and ion aggregates has been analysed by FTIR studies.

2. Experimental

Ammonium hexafluorophosphate (NH_4PF_6) (Aldrich), polyethylene oxide (PEO) (Aldrich, $M_w = 5 \times 10^6$) and propylene carbonate (PC) (Merck) were used as the starting materials in the preparation of various liquid and gel electrolytes. Polymer gel electrolytes containing NH_4PF_6 and PEO in different concentrations were prepared by adding PEO to the solutions of NH_4PF_6 in PC alongwith continuous stirring [9, 13]. The conductivity was measured by complex impedance spectroscopy with computer interfaced Hioki 3532-50 Hi Tester and HP 4284A precision LCR meter using a cell with platinum electrodes. pH of electrolytes was measured by Systronics 335 pH meter and viscosity was measured by Fungilab rotating viscometer (Visco Basic L) and temperature of samples was maintained by Julabo water circulator (F-12EC) with an accuracy of $\pm 0.1°C$. FTIR spectra of all samples was recorded at 25°C with a computer interfaced Shimadzu FTIR 8400S spectrometer.

3. Results and discussion

The conductivity (σ) of liquid electrolytes due to the motion of ions is related to the diffusion coefficient (D) of the mobile species through the Nernst-Einstein relation [17]

$$\sigma = ne^2D/kT \qquad (1)$$

where 'n' is the number density of charge carriers, k Boltzmann constant, T absolute temperature and e is the electronic charge. The diffusion coefficient (D) is related to the viscosity (η) of the electrolyte through the Stokes-Einstein equation

$$D = kT/6\pi r\eta \qquad (2)$$

where r is the effective radius of the diffusing species.

Solving Equations 1 and 2, we get

$$\sigma = e^2n/6\pi r\eta \qquad (3)$$

which shows the dependence of conductivity (σ) on the concentration of charge carriers (n) and viscosity (η) of the electrolytes [18 , 19]. The variation of conductivity as a function of reciprocal viscosity ($1/\eta$), also known as fluidity, for electrolytes containing different concentrations of NH_4PF_6 in PC is given in Fig. 1a. With an increase in salt concentration from 0 to 1 M, the viscosity of electrolytes increases marginally from 3.8 to 5.1 cP whereas the free ion concentration will increase by a large amount. The increase in 'n' will increase the conductivity of electrolytes whereas increase in viscosity will decrease conductivity. As the increase in 'n' is much more than the increase in viscosity, so there will be a net increase in conductivity with an increase in salt concentration. However at medium salt concentrations, the presence of a large number of ions may also lead to the formation of ion aggregates which do
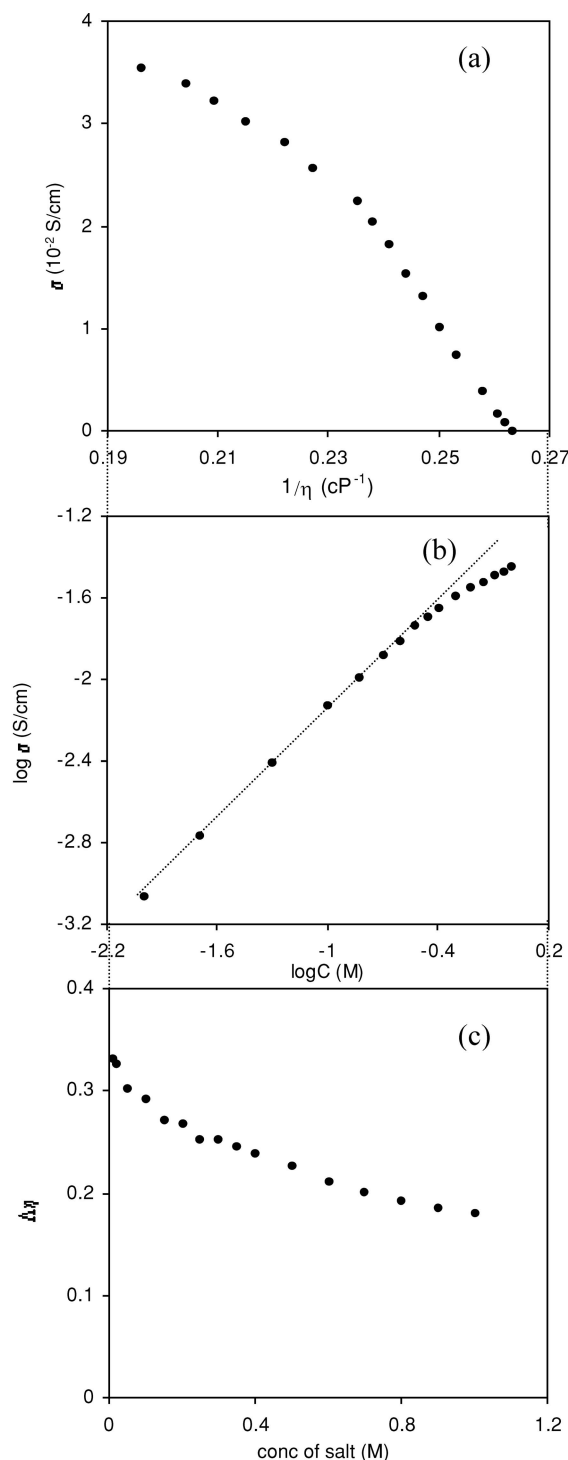

Figure 1 Variation of (a) conductivity (σ) with reciprocal viscosity ($1/\eta$), (b) log conductivity with log concentration and (c) Walden product ($\Lambda\eta$) with salt concentration, for electrolytes containing NH_4PF_6 in PC.

not contribute to the conduction process [18] and as a result conductivity does not increase at the same rate as has been observed at low salt concentrations. This is reflected in a change in slope in σ vs. $1/\eta$ plot in Fig. 1a. Similar behaviour has also been reported [18] for electrolytes containing lithium salts.
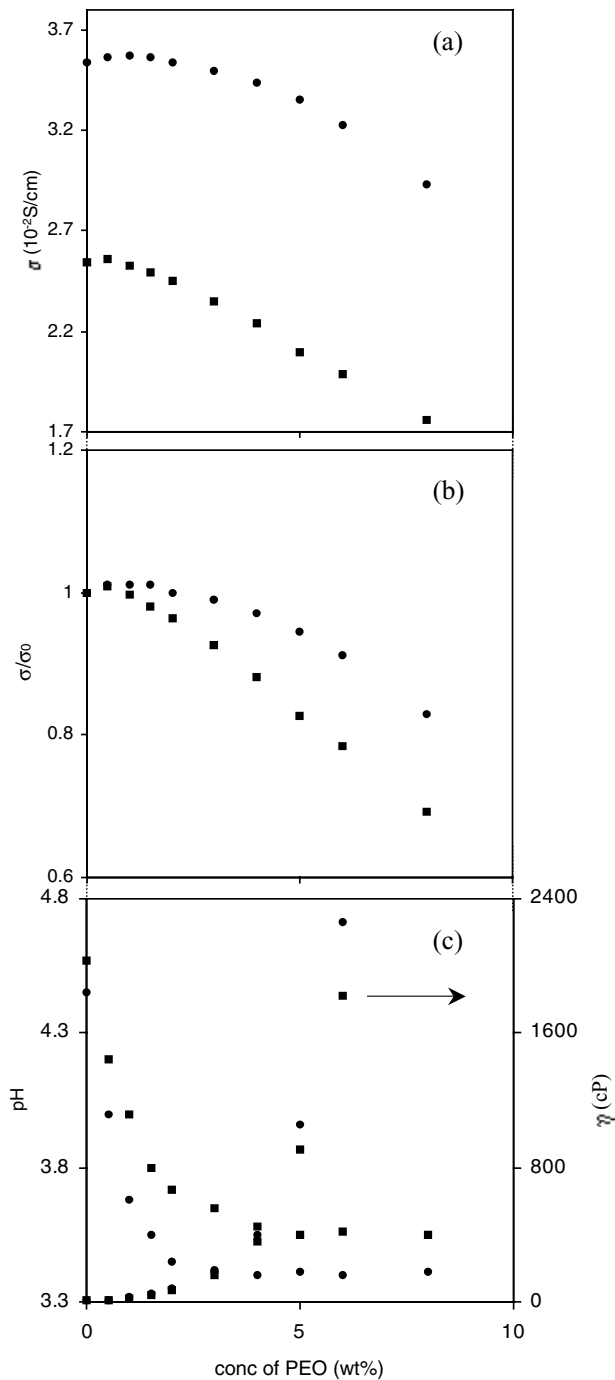
Figure 2 Dependence of (a) conductivity (σ), (b) fractional change in conductivity(σ/σ_o) where σ and σ_o are the conductivity of gel and liquid electrolytes respectively and (c) pH and viscosity (η) with the concentration of PEO, for electrolytes containing 0.5 (■) and 1.0 M (●) NH_4PF_6 in PC.

The presence of ion aggregates was also studied (qualitatively) by mass action considerations [20] according to which the plot between $\log \sigma$ and $\log C$ (C is salt concentration) should be a straight line if all the ions are present as free ions and a deviation from straight line will indicate the presence of ion aggregates which do not contribute to conductivity. The plot between $\log \sigma$ and $\log C$ for PC-NH_4PF_6 electrolytes as given in Fig. 1b shows a deviation from straight line behaviour above 0.4 M NH_4PF_6, which
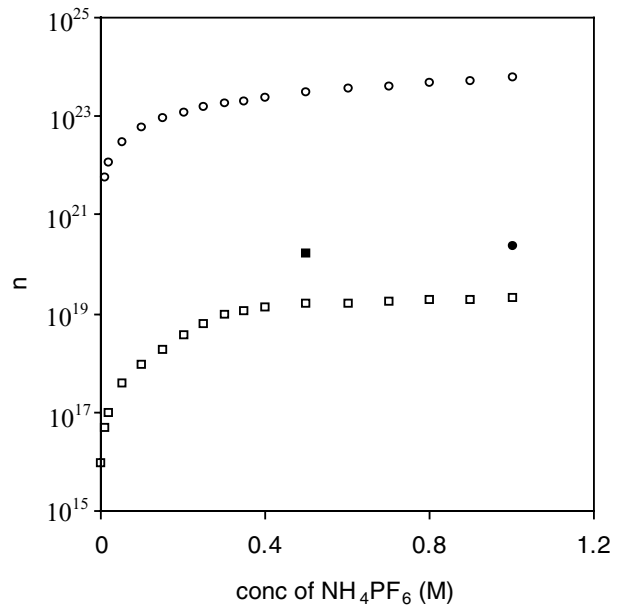

Figure 3 Variation of concentration of charge carriers (*n*) with salt concentration by assuming the salt to be fully dissociated (○) and calculated from pH data (□). ■, ●-show the charge carrier concentration for gel electrolytes containing 0.5, 1 M NH_4PF_6 respectively.

suggests the presence of ion aggregates above this salt concentration and this is in agreement with the conductivity results discussed above.

If the effect of salt concentration '*C*' is compensated by calculating equivalent conductivity ($\Lambda = \sigma/C$), then the Walden product ($\Lambda\eta$)should remain constant. However the plot of $\Lambda\eta$ with salt concentration in Fig. 1c shows a small decrease which suggests that all ions are not free and hence do not contribute to conductivity, possibly due to the formation of ion aggregates as proposed above [19].
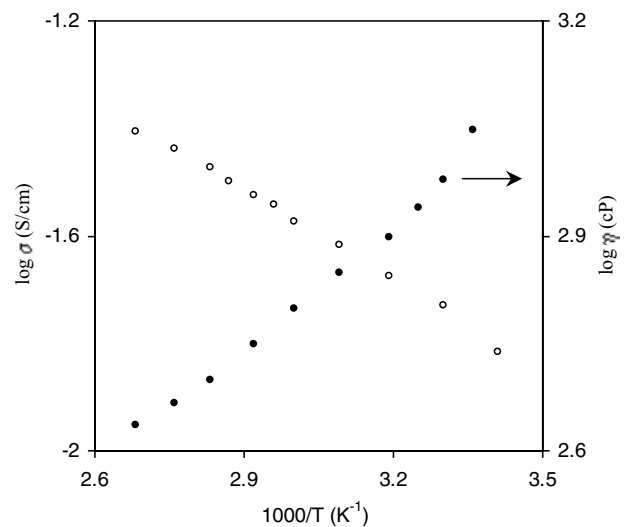

Figure 4 Dependence of log conductivity and log viscosity on reciprocal temperature for polymer gel electrolytes having composition PC $+$ 0.5 M NH_4PF_6 $+$ 6 wt.% PEO.

The variation of conductivity of polymer gel electrolytes containing 0.5 and 1 M NH_4PF_6 in PC as a function of PEO concentration is given in Fig. 2a. The conductivity does not decrease with the addition of PEO but shows a marginal increase at very low concentrations (~ 1 wt.%) of PEO and then decreases by a small factor at higher concentrations of PEO but still gels have conductivity of the same order (10^{-2} S/cm) as observed for liquid electrolytes. Due to the high molecular weight of PEO used in the present study, the viscosity of gel electrolytes is large and as a result PEO upto only 8 wt.% of liquid electrolytes could be added. The variation of fractional change in conductivity σ/σ_o (where σ and σ_o are the conductivity of gel and liquid electrolytes respectively) with PEO concentration as given in Fig. 2b shows that the conductivity of gel electrolytes containing 0.5 and 1 M NH_4PF_6 decreases by ~ 30 and $\sim 18\%$ of the conductivity of starting liquid electrolytes. The small increase in conductivity (Fig. 2a) at very low concentrations of polymer is not generally observed as observations are normally taken at 0, 5, 10, ...wt.% of polymer concentration only.

The decrease in conductivity at higher concentrations of PEO is due to the dominant role of viscosity which shows an exponential increase at higher PEO concentrations as given in Fig. 2c. The large viscosity lowers ionic mobility and as a result conductivity decreases. However the small increase in conductivity at very low concentrations of PEO is possibly due to the role of PEO in enhancing free ion concentration by dissociating ion aggregates/undissociated salt present in these electrolytes and the change in free ion concentration was calculated from pH of gel electrolytes. Fig. 3 gives the variation of free ion concentration (n) with NH_4PF_6 concentration for electrolytes: (a) assuming the salt to be fully dissociated and all ions are present as free ions and (b) actual variation of 'n' determined from pH of electrolytes containing NH_4PF_6 in PC. An increase in free ion concentration with the addition of PEO to electrolytes containing 0.5 and 1 M NH_4PF_6 has been observed and the results are in agreement with similar results reported for lithium gels [15]. From above, it appears that both free ion concentration as well as viscosity affects the conductivity behaviour of polymer gel electrolytes. The free
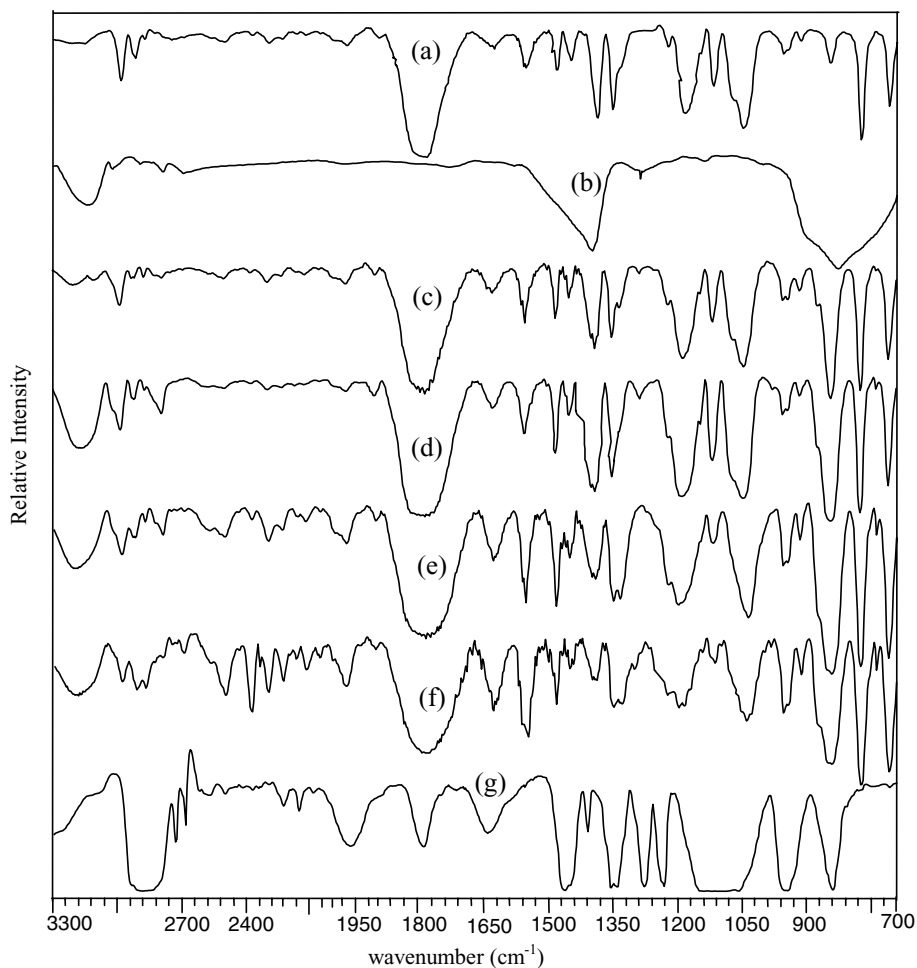

Figure 5 FTIR spectra of PC (a), NH_4PF_6 (b), liquid electrolytes containing 0.5 M (c) and 1 M (d) NH_4PF_6 and polymer gel electrolytes containing 1 (e), 5 (f) wt.% PEO and of PEO (g).

ion concentration plays a dominant role at low concentrations of PEO whereas viscosity plays a dominant role at higher concentrations of PEO. Similar behaviour has also been reported for PMMA based polymer gel electrolytes containing different nitrobenzoic acids [9].

The dependence of conductivity and viscosity on temperature was also studied for polymer gel electrolytes and the variation of log conductivity and log viscosity with reciprocal temperature is given in Fig. 4. A decrease in viscosity observed with an increase in temperature results in an increase in conductivity.

Interactions between the salt, solvent and polymer; the presence of ion aggregates and their dissociation with the addition of polymer were also studied by FTIR and spectra of some selected samples are given in Fig. 5. The assignment of some important peaks is also given in Table I.

The spectra of solvent (PC) shows a doublet due to Fermi resonance at 1800 cm^{-1} (due to $\upsilon_{C=O}$) and 1896 cm^{-1} (due to overtone of ring breathing mode at 950 cm^{-1}) [18, 21, 22] and their positions shifts to 1789 cm^{-1} and 1903 cm^{-1} respectively with the addition of NH$_4$PF$_6$ which suggests the interaction of NH$_4^+$ with the electronegative oxygen of C=O group of PC. It has been reported [23] that at low salt concentrations, the salt is dissociated and the cations are solvated by the solvent molecules via strong interactions between the cation of the

salt and the oxygens of the carbonate solvent. The broadening of the 1789 cm^{-1} peak with the addition of PEO is due to its overlapping with the peak due to the ether oxygen of PEO at 1793 cm^{-1} [24] which suggests that PEO chains also affect the Fermi resonance doublet of PC. An increase in salt concentration from 0.5 to 1 M in PC also results in an increase in intensity of peaks of PC at 711, 777 and 846 cm^{-1} due to the interactions of NH$_4^+$ with solvent molecules [18]. The appearance of new peak at 742 cm^{-1} with the addition of salt is due to the stretching vibrations of PF$_6^-$ [25]. The peaks at 1290 cm^{-1} alongwith a shoulder at 1073 cm^{-1} at high salt concentrations is due to the presence of NH$_4$PF$_6$ in these electrolytes. However these peaks disappear with the addition of PEO due to their overlapping with the peaks of PEO present in this region. The peak at 1402 cm^{-1} due to the asymmetric H-N-H bending [26] interacts with the 1388 cm^{-1} peak of PC and shifts to 1392 cm^{-1} in liquid electrolytes alongwith the appearance of a shoulder at 1428 cm^{-1} which has been assigned to be due to ion aggregates [18, 27]. The disappearance of this shoulder with the addition of PEO due to their overlapping with the peaks of PEO is possibly due to the dissociation of ion aggregates as proposed above while explaining conductivity results. Similarly a shoulder at 3029 cm^{-1} due to the presence of salt in electrolytes containing 1 M NH$_4$PF$_6$ is also not present in the spectra of gel electrolytes. The peak at 3190 cm^{-1} due to NH$_4$PF$_6$

TABLE I Group frequencies and possible assignments of PC-(0.5, 1 M) NH$_4$PF$_6$-(1, 5 wt.%) PEO

Wavenumber (cm^{-1})	Group/species/molecular ions with their possible assignments	References
711	sym. ring (deformation + breathing) in PC (in liquid and gel electrolytes)	18
742	stretching vibrations of PF$_6^-$ (in PC-NH$_4$PF$_6$ interaction)	25
777	ring deformation mode in PC (in liquid and gel electrolytes)	18
840	PC-NH$_4$PF$_6$ interaction	
842	CH$_2$ asymm. rocking in PEO	24
845	free PF$_6^-$ anions	30
846	vibration of methyl group of PC molecules	25
950	ring stretching and breathing modes in PC	18, 21
957	CH$_2$ rocking sym., C–O–C asymm. stretching in PEO	24
1100	C–O–C (sym. + asymm.) stretching in PEO	24
1190	CH wagging and sym. stretching (υCO) in PC	28
1224	CH wagging and sym. stretching (υCO) in PC (in liquid and gel electrolytes)	18
1236	CH$_2$ twisting sym. in PEO	24
1280	CH$_2$ twisting (asymm. + sym.) in PEO	24
1290	NH$_4$PF$_6$	31
1291	υ(C–O) of –COO– in PC	28
1344	CH$_2$ asymm. wagging in PEO	32
1353	CH sym. bending in PC	32
1357	CH$_2$ sym. wagging, CC stretching in PEO	32
1388	CH wagging (out of plane) in PC	33
1392	asymm. H–N–H deformation in liquid and gel electrolytes	
1402	asymm. H–N–H bending	26
1428	PC-1M NH$_4$PF$_6$ (ion aggregates)	18, 27
1789	υ_s (C=O) in PC (in liquid and gel electrolytes)	18, 21
1793	(C–O) group in PEO	24
1903	2 × ring breathing mode of PC ($\sim$950 cm^{-1}) (in liquid and gel electrolytes)	18, 21
2798	NH$_4$PF$_6$	
3029	PC-1M NH$_4$PF$_6$ (ion aggregates/undissociated salt)	
3120	PC-0.5 M NH$_4$PF$_6$ (free ions)	
3190	NH$_4$PF$_6$	
3210	PC-0.5 M NH$_4$PF$_6$ (ion aggregates/undissociated salt)	

changes into the doublet (3120 cm^{-1} and 3210 cm^{-1}) in liquid electrolytes containing 0.5 M NH$_4$PF$_6$ which indicates the presence of two different kinds of environment for PF$_6^-$ anions [28] in these electrolytes and splitting of some bands of solvent may be due to the solvation of salt. Similar behaviour has earlier been reported for electrolytes containing LiPF$_6$ [29]. The formation of doublets near 1200 cm^{-1} and 1350 cm^{-1} after the addition of polymer is due to the strong electrostatic attraction between the cation and ether oxygen of PEO.

Thus FTIR results also indicate that ion aggregates are present in liquid electrolytes at high salt concentrations alongwith the presence of free ions and some undissociated salt. The addition of PEO results in the dissociation of some ion aggregates/undissociated salt leading to an increase in free ion concentration which enhances conductivity of the electrolytes. However due to the large molecular weight of PEO, there is a large increase in viscosity also which plays a dominant role and results in lower mobility and hence conductivity decreases at higher concentrations of PEO. These results are in agreement with the conductivity, viscosity and pH results discussed above for these gel electrolytes.

4. Conclusions

PEO based non aqueous polymer gel electrolytes containing NH$_4$PF$_6$ possess high conductivity $\sim 10^{-2}$ S/cm at 25°C. Ion aggregates present in these electrolytes at high concentrations of salt gets dissociated with the addition of PEO and as a result a small increase in conductivity is observed. The conductivity of polymer gel electrolytes depends upon the free ion concentration and viscosity which play a dominant role at low and high concentrations of PEO respectively. A decrease in viscosity with an increase in temperature is accompanied by an increase in the conductivity of gel electrolytes. The presence of ion aggregates and their dissociation with the addition of PEO is also supported by FTIR results. Due to high conductivity, these polymer gel electrolytes are potential materials for different devices.

References

1. G. FEUILLADE and PH. PERCHE, *J. Appl. Electrochem.* **5** (1975) 63.
2. Z. JIANG, B. CARROL and K. M. ABRAHAM, *Electrochim. Acta* **42** (1997) 2667.
3. K. M. ABRAHAM, in "Applications of Electroactive Polymers", edited by B. Scrosati (Chapman and Hall, London, 1994) p. 75.
4. R. KOKSBANG, I. I. OLSEN and D. SHACKLE, *Solid State Ionics* **69** (1994) 320.
5. J. Y. SONG, Y. Y. WANG and C. C. WAN, *J. Power Sources* **77** (1999) 183.
6. D. RADUCHA, W. WIECZOREK, Z. FLORJANCZYK and J. R. STEVENS, *J. Phys. Chem.* **100** (1996) 20126.
7. K. D. KREUER, *Solid State Ionics* **97** (1997) 1.
8. J. PRZYLUSKI and W. WIECZOREK, *Synth. Met.* **45** (1991) 323.
9. S. S. SEKHON, N. ARORA and S. CHANDRA, *Eur. Polym. J.* **39** (2003) 915.
10. O. BOHNKE, G. FRAND, M. REZRAZI, C. ROUSSELOT and C. TRUCHE, *Solid State Ionics* **66** (1993) 97, 105.
11. A. WEBBER, *J. Electrochem. Soc.* **138** (1991) 2586.
12. S. S. SEKHON, N. ARORA and S. A. AGNIHOTRY, *Solid State Ionics* **136/137** (2000) 1201.
13. S. CHANDRA, S. S. SEKHON and N. ARORA, *Ionics* **6** (2000) 112.
14. A. M. GRILLONE, S. PANERO, B. A. RETAMAL and B. SCROSATI, *J. Electrochem. Soc.* **146** (1999) 27.
15. C. S. KIM and S. M. OH, *Electrochim. Acta* **45** (2000) 2101.
16. W. WIECZOREK, G. ZUKOWSKA, R. BORKOWSKA, S. H. CHUNG and S. GREENBAUM, *Electrochim. Acta* **46** (2001) 1427.
17. I. M. WARD, N. BODEN, J. CRUICKSHANK and S. A. LENG, *ibid.* **40** (1995) 2071.
18. D. BATTISTI, G. A. NAZRI, B. KLASSEN and R. AROCA, *J. Phys Chem.* **97** (1993) 5826.
19. J. P. SOUTHALL, H. V. ST. A. HUBBARD, S. F. JOHNSTON, V. ROGERS, G. R. DAVIES, J. E. MCINTYRE and I. M. WARD, *Solid State Ionics* **85** (1996) 51.
20. M. A. RATNER, in "Polymer Electrolyte Reviews-I", edited by J. R. Maccallum and C. A. Vincent (Elsevier, London, 1987) p. 173.
21. S. A. HYODO and K. OKABAYASHI, *Electrochim. Acta* **34** (1989) 1551.
22. Z. WANG, M. IKEDA, N. HIRATA, M. KUBO, T. ITOH and O. YAMAMOTO, *J. Electrochem. Soc.* **146** (1999) 2209.
23. E. CAZZANELLI, F. CROCE, G. B. APPETECCHI, F. BENEVELLI and P. MUSTARELLI, *J. Chem. Phys.* **107** (1997) 5740.
24. B. L. PAPKE, M. A. RATNER and D. F. SHRIVER, *J. Phys. Chem. Solids* **42** (1981) 493.
25. K. KONDO, M. SANO, A. HIWARA, T. OMI, M. FUJITA, A. KUWAE, M. IIDA, K. MOGI and H. YOKOYAMA, *J. Phys. Chem. B* **104** (2000) 5040.
26. S. A. HASHMI, A. KUMAR, K. K. MAURYA and S. CHANDRA, *J. Phys. D: Appl. Phys.* **23** (1990) 1307.
27. A. BERNSON and J. LINDGREN, *Polymer* **35** (1994) 4842.
28. M. DEEPA, S. A. AGNIHOTRY, D. GUPTA and R. CHANDRA, *Electrochim. Acta* **49** (2004) 373.
29. D. AURBACH, K. GAMOLSKY, B. MARKOVSKY, G. SALITRA, Y. GOFER, U. HEIDER, R. OESTEN and M. SCHMIDT, *J. Electrochem. Soc.* **147** (2000) 1322.
30. R. AROCA, M. NAZRI, G. A. NAZRI, A. J. CAMARGO and M. TRSIC, *J. Solution Chem.* **29** (2000) 1047.
31. D. OSTROVSKII, F. RONCI, B. SCROSATI and P. JACOBSSON, *J. Power Sources* **103** (2001) 10.
32. R. FRECH and S. CHINTAPALLI, *Solid State Ionics* **85** (1996) 61.
33. L. DOUCEY, M. REVAULT, A. LAUTIE, A. CHAUSSE and R. MESSINA, *Electrochim. Acta* **44** (1999) 2371.