

Conductivity behaviour of polymer gel electrolytes: Role of polymer

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Abstract. Polymer is an important constituent of polymer gel electrolytes along with salt and solvent. The salt provides ions for conduction and the solvent helps in the dissolution of the salt and also provides the medium for ion conduction. Although the polymer added provides mechanical stability to the electrolytes yet its effect on the conductivity behaviour of gel electrolytes as well as the interaction of polymer with salt and solvent has not been conclusively established. The conductivity of lithium ion conducting polymer gel electrolytes decreases with the addition of polymer whereas in the case of proton conducting polymer gel electrolytes an increase in conductivity has been observed with polymer addition. This has been explained to be due to the role of polymer in increasing viscosity and carrier concentration in these gel electrolytes.

Keywords. Polymer gel electrolytes; carboxylic acids; conductivity; ion dissociation.

1. Introduction

Gels are generally defined as 'polymers and their swollen matters with three dimensional network structures that are insoluble in any solvents' and gels exist under special conditions not found in solids, liquids and gases (Osada and Kajiwara 2001). The swollen gels that have absorbed a large amount of solvent are in the states between solids and liquids and their properties vary from viscous liquids to hard solids according to the chemical composition and other factors.

Polymer gels consist of a polymer network and solvents in which the polymer network envelopes the liquid and prevents it from escaping or in other words plays the role of a container that can hold a large amount of solvent and as a result possesses the characteristics of both liquids and solids. The properties of polymer gels have been found to depend upon the structure of the polymer network that makes up the gel as well as on the interaction of the network and the solvent. As the polymer networks are solvated by a large amount of the trapped solvent so gels generally possess high mobility.

The replacement of the solvent by liquid electrolyte having high value of conductivity results in polymer gel electrolytes. They are generally salt–solvent–polymer hybrid systems in which first a salt solution is prepared and then it is immobilized with the help of a suitable polymer matrix. Since the first report of high conductivity in lithium ion conducting polymer gel electrolytes (Feuillade and Perche 1975), these materials are receiving much attention due to some of their unique properties like high value of conductivity at room temperature (10^{-2} – 10^{-4} S/cm), ease of preparation, wide range of composition and hence wider control of properties, good adhesive properties

suitable for lamination, good thermal/electrochemical stability etc. The interest in these materials is due to their potential applications in solid state batteries, electrochromic devices, fuel cells, supercapacitors etc (Abraham and Alamgir 1994).

Most of the work reported is on lithium ion conducting polymer gel electrolytes which is due to their use as electrolytes in high energy density lithium batteries (Scrosati 2000). In addition to that recently some work on proton conducting polymer gel electrolytes have also been reported due to their suitability as a proton conducting membrane in polymer electrolyte membrane fuel cells (PEMFC) and other devices (Colomban 1992).

In polymer gel electrolytes the salt generally provides free/mobile ions which take part in the conduction process and the solvent helps in solvating the salt and also acts as a conducting medium whereas the polymer is reported to provide mechanical stability by increasing the viscosity of electrolyte (Sekhon *et al* 1998). The possible interactions between the polymer and salt/solvent have not been clearly understood. The salt used should generally have large anions and low dissociation energy so that it easily dissociates whereas the solvent used should have high dielectric constant, low viscosity and high boiling point and low melting point. The addition of polymer to lithium ion conducting polymer gel electrolytes has been generally found (Bohnke *et al* 1993) to result in an increase in viscosity due to which mobility decreases and as a result conductivity also decreases ($\sigma = nq\mu$), whereas in the case of proton conducting polymer gel electrolytes containing weak acids the addition of polymer has been reported (Chandra *et al* 2000; Ericson *et al* 2000; Sekhon and Singh 2002; Sekhon *et al* 2002; Singh and Sekhon 2002) to result in an increase in conductivity.

In view of different effect of the polymer in lithium and proton conducting polymer gel electrolytes, detailed studies are required to understand the role of polymer on the conductivity behaviour of polymer gel electrolytes. In the present paper the role of different polymers viz. poly(methylmethacrylate) (PMMA), poly(acrylonitrile) (PAN), poly(ethylene oxide) (PEO), poly(vinylidene fluoride) (PVdF), poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) on the conductivity behaviour of polymer gel electrolytes containing various lithium salts and various carboxylic acids has been discussed. The variation of conductivity with polymer addition has been explained on the basis of changes in carrier concentration and viscosity. Different results obtained in lithium and proton-conducting gels have been discussed on the basis of the dissociation constant values.

2. Experimental

Liquid electrolytes are prepared by dissolving stoichiometric quantities of the salt/acid in a suitable solvent and concentration is generally expressed as molarity value (mol/l). Gel electrolytes are prepared by adding polymer in different concentrations (expressed as wt.% of liquid electrolyte) to the liquid electrolyte. The mixture is continuously stirred along with moderate heating so that uniform gel is formed. The conductivity of liquid electrolytes is measured by using WTW LF330 conductivity meter, which is regularly calibrated by using standard KCl solution whereas the conductivity of gel electrolytes is measured by a.c. impedance spectroscopy using HP4284A precision LCR meter in the 20 Hz–1 MHz frequency range. The details of the conductivity measurements have been described elsewhere (Sekhon *et al* 1998, 2002).

3. Results and discussion

Lithium ion conducting polymer gel electrolytes were prepared by adding polymer (PMMA, PAN, PEO) to the 1 M solution of different lithium salts (LiClO_4 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$) in solvents based upon ethylene carbonate (EC), propylene carbonate (PC), dimethylformamide (DMF) and dimethyl sulphoxide (DMSO). The conductivity of these gel electrolytes was measured as a function of polymer concentration (expressed as wt.% of liquid electrolytes) and is given in figures 1, 2 and 3 for PMMA-, PAN- and PEO-based gel electrolytes. It has been observed that the conductivity of liquid electrolytes containing different lithium salts is in the range of 10^{-3} S/cm. The conductivity decreases with an increase in polymer content but the decrease in conductivity is small and is by a factor only and not by an order and the conductivity of gel electrolytes with high polymer content is also in the 10^{-3} S/cm range. The addition of polymer generally results in an increase in viscosity (h), which results in a

decrease in mobility (m) and as a result conductivity decreases. The measurement of viscosity as a function of polymer concentration shows an increase with polymer addition (Bohnke *et al* 1993). However, a distinction shall be made between microscopic and macroscopic viscosities. The experimentally measured viscosity is the macroscopic viscosity of the gel whereas the relation between carrier mobility (m) and viscosity (h) i.e. $m = q/6\pi r h$,

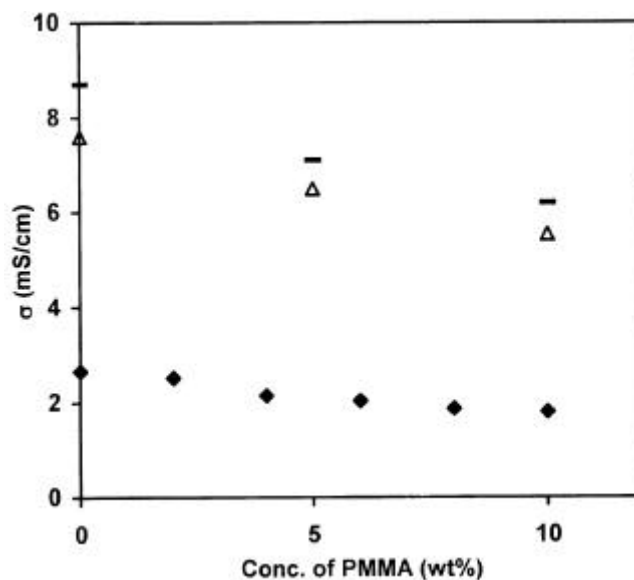


Figure 1. Variation of conductivity with PMMA concentration for gel electrolytes containing 1 M LiClO_4 (Δ), LiCF_3SO_3 (\blacklozenge) and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (—) in EC : PC.

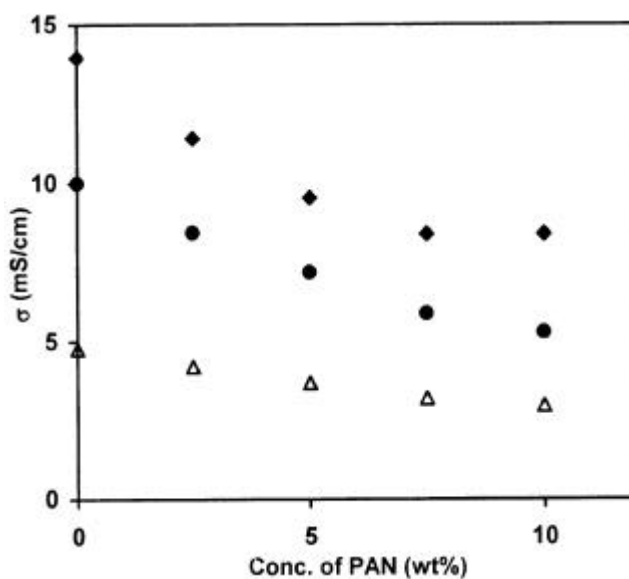


Figure 2. Variation of conductivity with PAN concentration for gel electrolytes containing liquid electrolytes of 1 M LiCF_3SO_3 (Δ) in EC and 1 M LiClO_4 in DMSO (\bullet) and EC : PC : DMF (\blacklozenge).

where q and r are the charge and radius of the mobile ion, involves microscopic viscosity. If a continuous path is available through the solvent for the ions to move in then the overall macroscopic viscosity is not related to the ion mobility. The small decrease in conductivity observed with polymer addition suggests that the polymer does not take part in the conduction process but simply acts as a stiffener only. Similar results have also been reported with other lithium salts and polymers (Weber 1991; Koksang *et al* 1994; Agnihotry *et al* 2000; Arora and Sekhon 2000; Sekhon 2000).

The polymer-salt, solvent interactions in lithium ion conducting polymer gel electrolytes have also been studied by using FTIR (Wang *et al* 1999), Raman (Cazzanelli *et al* 1995; Ostrovskii *et al* 1998), NMR/PFG NMR (Saito *et al* 2000), ESR (Qureshi *et al* 1998) and photon correlation spectroscopy (Svanberg *et al* 2000) techniques. In the widely studied PMMA-PC-LiClO₄ gel electrolytes, the polymer matrix has been reported to play a passive role at low (0–35 wt.%) PMMA concentrations and gel electrolytes has been considered as a liquid electrolyte encaged in a polymer matrix (Bohnke *et al* 1993). However, ESR studies on this gel system shows that the direct interactions of cations (Li⁺) with PMMA are largely responsible for increase in viscosity with salt addition. Similarly in PMMA/PAN-EC/PC-LiClO₄ gel electrolytes the influence of polymer on ion-solvent interactions has been found to depend upon the nature of the polymer used. PMMA based gel electrolytes do not show any strong interaction between various components whereas PAN based gel electrolytes show strong electrolyte-polymer interactions, which may be due to the presence of polar C≡N group in the monomer of PAN (-CH₂CHC≡N-). The addition of PAN to PC-LiClO₄ has

been reported to suppress Li⁺-PC interaction and Li⁺-PAN interaction is observed which depends upon the content of PAN in gel electrolytes.

Similarly detailed investigation on LiN(CF₃SO₂)₂-EC/DEC-PVdF, PVdF-HFP gel electrolytes by pulsed field gradient NMR shows that the diffusion coefficient of cation (Li⁺) and anion (F⁻) approach a common value with an increase in polymer concentration. The polymer chains act on ion pairs to effect dissociation and the dissociated ions in the solvent are further solvated by the polymer chains which results in a change in carrier concentration (n) and mobility (m). Thus the addition of polymer has been found to affect the carrier concentration value.

In PEO based polymer gel electrolytes, the addition of PEO to the 1 M solution of LiCF₃SO₃ in EC/PC has been reported (Kim *et al* 2000) to result in an increase in conductivity at low polymer concentrations which has been explained to be due to a steady build up of free ions with an increase in PEO content. However, at higher PEO concentrations conductivity of gel electrolytes decreases due to an increase in local viscosity. The ion solvating ability of the polymer has been reported to be strongly correlated with the donor number of the polymer functional group and the ionic conductivity and cation transference number in gel electrolytes can be controlled by the donor number of the polymer component/solvent.

However, in the case of PEO based gel electrolytes with salicylic acid it has recently been found (Sekhon *et al* 2003) that the change in conductivity with polymer addition also depends upon the donor numbers of the solvent used. Solvent with high and low donor number show different conductivity behaviour in polymer gel electrolytes. On the basis of different experimental studies, it has been observed that increasing polymer concentration results in an increase in the mechanical stability of polymer gel electrolytes. It also results in a decrease in the ionic conductivity as it is governed by the mobility of the solvents. The existence of any interaction between polymer and liquid electrolyte does not modify the conductivity by a large amount. Gel electrolytes containing some other metal salts also show similar conductivity behaviour with the addition of polymer (Upadhyaya *et al* 2001).

Proton conducting polymer gel electrolytes is another promising category of gels with potential applications in fuel cells, electrochromic devices, supercapacitors, batteries etc. The high cost of Nafion membrane used in fuel cells has renewed interest in the search for an alternative proton conducting membranes with high value of conductivity suitable for fuel cell applications. Initial work on these materials was mainly with strong acids like H₂SO₄, HCl (Lassegeus *et al* 1989; Vaiars *et al* 1997). Due to high value of dissociation constant, these acids are fully dissociated in the electrolyte and hence provide large number of H⁺ ions for conduction. However, the strong acids are likely to degrade the polymer used and

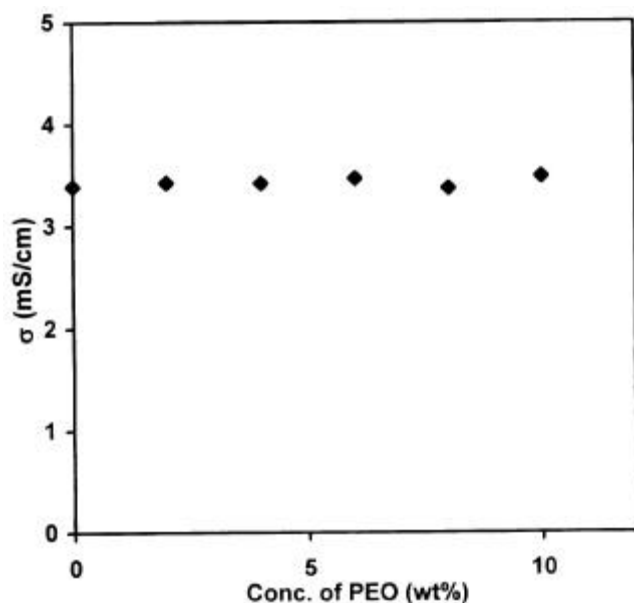


Figure 3. Variation of conductivity with PEO concentration for gel electrolytes containing 1 M LiCF₃SO₃ in EC : PC.

as a result may not be suitable for practical applications.

Carboxylic acids which also provide H^+ ions upon dissociation and are relatively weak acids with varying values of dissociation constant (less than one in aqueous solution) may prove to be a better alternative. Keeping this in view, a program to develop non aqueous proton conducting polymer gel electrolytes containing different carboxylic acids was undertaken in our research group. Under this project, the following carboxylic acids have been chosen for study:

(A) Aromatic carboxylic acids: (i) benzoic acid, (ii) ortho-, meta- and para-hydroxybenzoic acids, (iii) ortho-, meta- and para-nitrobenzoic acids, and (iv) ortho-, meta- and para-chlorobenzoic acids.

(B) Aliphatic dicarboxylic acids: $COOH-(CH_2)_n-COOH$: (i) oxalic acid ($n = 0$), (ii) malonic acid ($n = 1$), and (iii) succinic acid ($n = 2$).

The dissociation constant and other properties of these carboxylic acids are given in table 1. Solvents based upon ethylene carbonate (EC), propylene carbonate (PC), dimethylacetamide (DMA) and dimethylformamide (DMF) with high dielectric constant and low viscosity as given in table 2 were used in the preparation of gel electrolytes. Gel electrolytes were prepared by using different polymers viz. polymethylmethacrylate (PMMA), polyvinylidene fluoride (PVdF), polyvinylidene fluoride-co-hexafluoropropylene (PVdF-HFP) and polyethyleneoxide (PEO).

The conductivity of liquid electrolytes prepared by dissolving different carboxylic acids was studied as a function of acid concentration and representative results are given in figure 4 for electrolytes containing different aromatic carboxylic acids (a) and dicarboxylic acids (b). The results of figure 4 can be explained as follows:

– The conductivity of solvent ($\sim 10^{-6}$ S/cm) increases by two to three orders of magnitude to 10^{-4} – 10^{-3} S/cm with the addition of different carboxylic acids.

– At low concentrations of acid, conductivity increases linearly with an increase in acid concentration due to the availability of free ions provided by the acid. It generally reaches a maximum value at moderate acid concentrations and then shows a saturation or even a small decrease at high acid concentrations which is due to the formation of ion aggregates which do not contribute to conductivity. However, the acid concentration at which the maximum conductivity or saturation is reached has been found to depend upon the nature of the acid used and its dissociation constant.

– The conductivity of different substituted (chloro (Cl^-), nitro (NO_2^-), hydroxy (OH^-) and benzoic acid (BA)) carboxylic acids has been found to depend upon the nature of the substituted group and varies as:

$$s(Cl^-) > s(NO_2^-) > s(OH^-) > s(BA).$$

This trend is in the order of the electron withdrawing power of the substituted group.

– The conductivity of electrolytes with different (ortho-, meta- and para-) hydroxy-, nitro- and chloro-benzoic acids varies as:

$$s(o-) > s(m-) > s(p-),$$

and this variation follows the dissociation constant values of the acid, which also varies as:

$$K(o-) > K(m-) > K(p-),$$

and is known as 'ortho effect'.

Table 1. Some physical properties of different (*o*-, *m*- and *p*-) hydroxy, chloro and nitro substituted benzoic acids and simple aliphatic dicarboxylic acids.

Acid	MP (°C)	Dissociation constant (K_a)
Benzoic acid	122	6.5×10^{-5}
<i>o</i> -Hydroxybenzoic acid	158	105×10^{-5}
<i>m</i> -Hydroxybenzoic acid	202	8.3×10^{-5}
<i>p</i> -Hydroxybenzoic acid	214	2.6×10^{-5}
<i>o</i> -Chlorobenzoic acid	141	120×10^{-5}
<i>m</i> -Chlorobenzoic acid	154	15.1×10^{-5}
<i>p</i> -Chlorobenzoic acid	242	10.3×10^{-5}
<i>o</i> -Nitrobenzoic acid	147	670×10^{-5}
<i>m</i> -Nitrobenzoic acid	141	32×10^{-5}
<i>p</i> -Nitrobenzoic acid	242	36×10^{-5}
Oxalic acid	189	5400×10^{-5} (K_1) 5.2×10^{-5} (K_2)
Malonic acid	136	140×10^{-5} (K_1) 0.20×10^{-5} (K_2)
Succinic acid	185	6.4×10^{-5} (K_1) 0.23×10^{-5} (K_2)

Table 2. Some important physical properties of the solvents.

Solvent	MP (°C)	BP (°C)	Viscosity (η)	Dielectric constant (ϵ)
Ethylene carbonate (EC)	38	244	1.90	89
Propylene carbonate (PC)	– 55	240	2.53	64.6
Dimethylacetamide (DMA)	– 20	165	1.93	37.8
Dimethylformamide (DMF)	– 61	153	0.80	36.7
Dimethylsulphoxide (DMSO)	18.4	189	1.1	45

– The conductivity of electrolytes containing aliphatic dicarboxylic acids varies as:

$$s(OA) > s(MA) > s(SA),$$

which also follows the first dissociation constant values of these dicarboxylic acids

$$K_1(OA) > K_1(MA) > K_1(SA),$$

and is known as ‘inductive effect’.

– Some undissociated acid shall also be present in all the electrolytes as the dissociation constant of these weak carboxylic acids is less than one. The percentage of undissociated acid shall however depend upon the dissociation constant of the acid and nature of the solvent used.

Gel electrolytes were prepared by adding different polymers (PMMA, PVdF, PVdF–HFP, PEO) to the solutions of different carboxylic acids in the ternary solvent mixture and containing different concentrations (in mola-

rity value) of the acids. The variation of conductivity of gel electrolytes as a function of PMMA, PVdF, PVdF–HFP and PEO content are given in figures 5–8, respectively. The conductivity of liquid electrolytes has been observed to increase with the addition of polymer i.e.

$$s(\text{gel}) > s(\text{liquid}).$$

Such behaviour has been observed with electrolytes containing different carboxylic acids as well as with different polymers used in the present study. These results are contrary to the results of lithium ion conducting polymer gel electrolytes in which the addition of polymer results in a decrease in conductivity as already shown in figures 1–3.

The conductivity (s) of an electrolyte given by $s = nq\mathbf{m}$ depends upon the carrier concentration (n) and mobility (\mathbf{m}). The mobility is inversely related to the viscosity (\mathbf{h}) of the electrolyte as $\mathbf{m} = q/6\pi r\mathbf{h}$. The addition of polymer to the liquid electrolyte results in an increase in the viscosity, which decreases mobility, and hence conductivity also decreases. The decrease in conductivity with polymer addition in the case of lithium ion conducting polymer gel electrolytes is generally explained on the basis of this reasoning. However, the conductivity can show an increase if with the addition of polymer, carrier concentration (n) also increases and secondly the increase in ‘ n ’ is more than the decrease in ‘ \mathbf{m} ’ observed with polymer addition. The increase in ‘ n ’ with polymer addition can be explained as follows:

The carboxylic acids used in the present study are weak acids with dissociation constant (in aqueous solution) less than one as given in table 1. Thus these acids

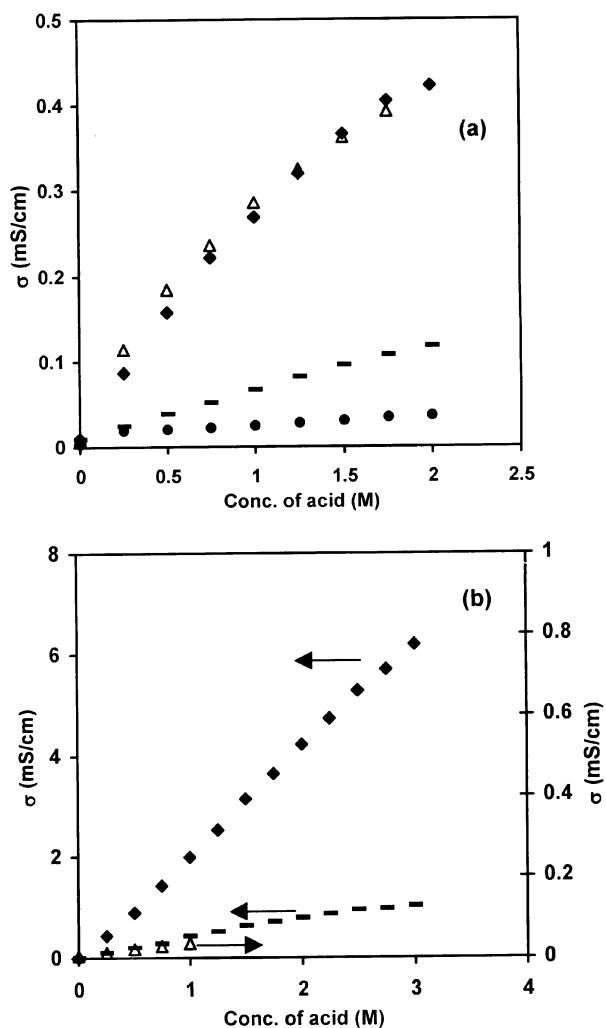


Figure 4. Variation of conductivity with acid concentration for liquid electrolytes containing (a) benzoic acid (●), chloro benzoic acid (–), hydroxy benzoic acid (◆) and nitro benzoic acid (Δ) and (b) containing oxalic acid (◆), malonic acid (–) and succinic acid (Δ) in EC : PC : DMA.

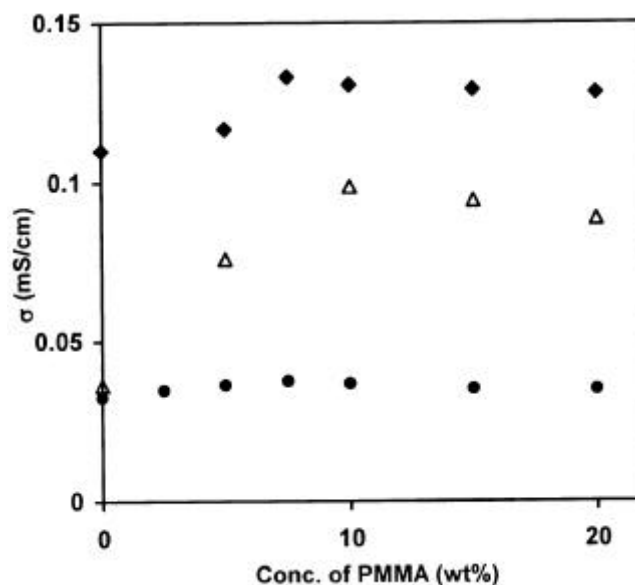


Figure 5. Variation of conductivity with PMMA concentration for gel electrolytes containing 1 M succinic acid (●), hydroxy benzoic acid (Δ) and nitro benzoic acid (◆) in EC : PC : DMF.

shall not be fully dissociated in the electrolyte and some undissociated acid shall also be present. The fraction/quantity of undissociated acid shall further depend upon the dissociation constant of the acid used and the nature of the solvent. If the addition of polymer results in the dissociation of undissociated acid, then 'n' shall increase and as a result increase in conductivity will be observed. The polymer can also help in the dissociation of ion

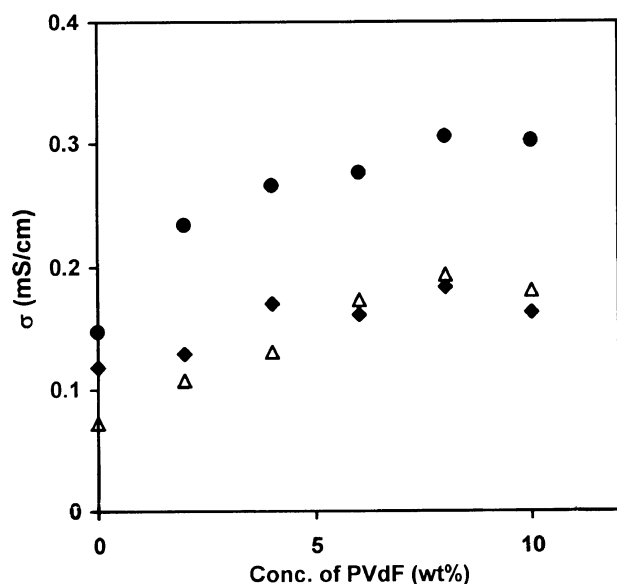


Figure 6. Variation of conductivity with PVdF concentration for gel electrolytes containing 1 M succinic acid (◆), chloro benzoic acid (Δ) and 0.5 M hydroxy benzoic acid (●) in EC : PC : DMA.

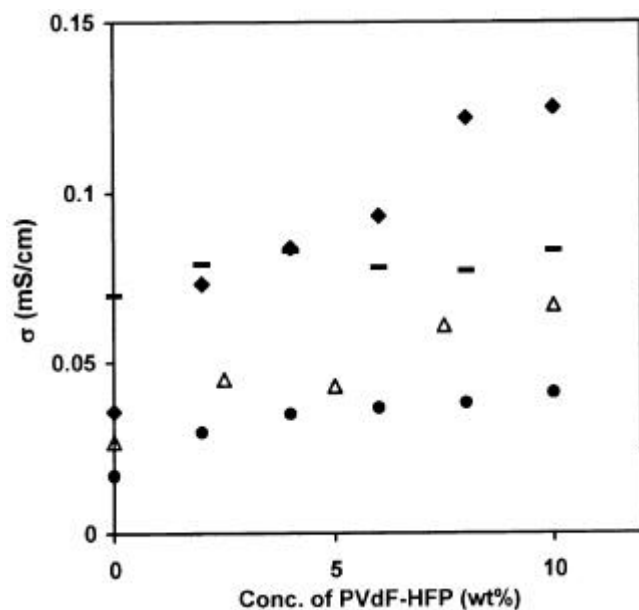


Figure 7. Variation of conductivity with PVdF-HFP concentration for gel electrolytes containing 1 M succinic acid (◆), benzoic acid (●), hydroxy benzoic acid (Δ) and chloro benzoic acid (—) in EC : PC : DMA.

aggregates present in electrolytes at higher acid concentrations as mentioned in the variation of conductivity with acid concentration given in figure 4. However, this net increase in conductivity observed is despite the increase in viscosity with polymer addition which lowers mobility and hence conductivity. Secondly the addition of polymer also results in a decrease in molarity of acid in the gel electrolytes as no acid is added and low acid concentration should also decrease conductivity. The increase in conductivity of electrolytes containing different (*o*-, *m*- and *p*-) hydroxy benzoic acids and aliphatic dicarboxylic acids with the addition of PMMA has earlier been explained by 'Breathing polymeric chain model' proposed by us (Chandra *et al* 2000). According to this model polymer gel electrolytes generally consist of free ions, ion aggregates and polymer chains dispersed in the gel matrix. The breathing of the polymer by folding/unfolding up of its chains results in density/pressure fluctuations at the microscopic level which assist the motion of ions alongwith the dissociation of ion aggregates/undissociated acid which results in an increase in conductivity. Similar results have been obtained with proton conducting polymer gel electrolytes containing other carboxylic acids, dicarboxylic acids and different polymers like PVdF, PVdF-HFP, PEO and PMMA (Ericson *et al* 2000; Wieczorek *et al* 2001; Sekhon *et al* 2002; Singh and Sekhon 2002).

These results are in agreement with similar studies on PMMA based proton conducting polymer gel electrolytes containing salicylic acid in which gel electrolytes have been reported to have higher conductivity than the corresponding liquid electrolyte (Grillone *et al* 1999). This has been attributed to a specific interaction between the poly-

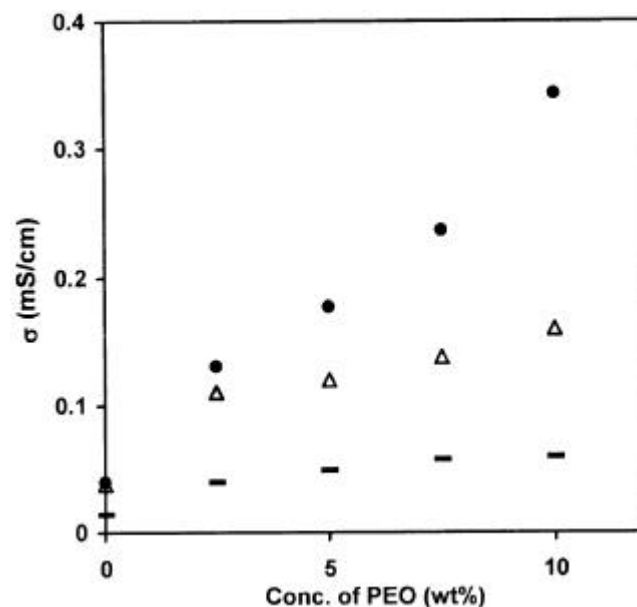


Figure 8. Variation of room temperature conductivity with PEO concentration for gel electrolytes containing 1 M hydroxy benzoic acid in DMF (●), EC : PC (—) and EC : PC : DMF (Δ).

mer and the non-polar segment of the acid molecule and as a result more charge carriers are expected to be active in the gel than in the solution electrolyte. The presence of undissociated acid in gel electrolytes containing benzoic acid and salicylic acid has also been studied by Raman spectroscopy (Ericson *et al* 2000) and the fraction of dissociated acid in these gels has been reported to be in the 0.1–0.6 range which proves the presence of undissociated acids in these electrolytes. Similar results have also been reported for H_3PO_4 containing gel electrolytes having composition GMA–DMF– H_3PO_4 (Wieczorek *et al* 2001). The gel electrolytes containing 23 and 7.4 mass% H_3PO_4 have been found to have higher conductivity than the corresponding liquid electrolytes. It has been reported that the use of glycidyl methacrylate (GMA) (Wieczorek *et al* 2001) as a part of the polymer matrix enhances the ionic conductivity due to the reaction between GMA and H_3PO_4 .

Why such an increase in conductivity has not been observed in lithium ion conducting polymer gel electrolytes? The answer to this question is that in the case of lithium ion conducting polymer gel electrolytes, lithium salts used with bigger anions have very low dissociation energy and are nearly fully dissociated in the electrolytes. The study of variation of conductivity with lithium salt concentration always shows the presence of ion aggregates at higher salt concentration values. The presence of large salt concentration also leads to an increase in viscosity and as a result the viscosity is the dominant factor in those electrolytes. As the salts are fully dissociated, so a large number of free ions shall be present and the dissociation of ion aggregates by polymer addition

(if any) shall be negligible in comparison with total ion concentration and as a result net increase in conductivity is not observed.

However, in the case of proton conducting polymer gel electrolytes containing weak acids, although the addition of polymer:

- increases viscosity which lowers mobility and hence conductivity;
- lowers net concentration of acid in the electrolyte and hence conductivity shall be lower;
- increases acid dissociation which increases ‘ n ’ and hence conductivity shall increase.

The net increase in conductivity observed with polymer addition as shown in figures 5–8 for different gel systems suggests that the increase in carrier concentration is dominant factor in these gel electrolytes. This is very advantageous for device applications. We have liquid electrolyte with certain value of conductivity. The polymer is added to increase its mechanical stability and it also results in an increase in conductivity. Thus in comparison to liquid electrolytes, we have polymer gel electrolytes with higher conductivity and higher mechanical stability. Thus polymer used in proton conducting polymer gel electrolytes does not act as a stiffener only but also helps in acid dissociation, which increases carrier concentration and as a result conductivity increases.

The variation of conductivity has also been studied as a function of temperature and the results are given in figure 9 for lithium ion conducting and in figure 10 for proton conducting liquid and gel electrolytes. It has been observed that the conductivity of lithium ion conducting gel electrolytes is lower than the conductivity of liquid

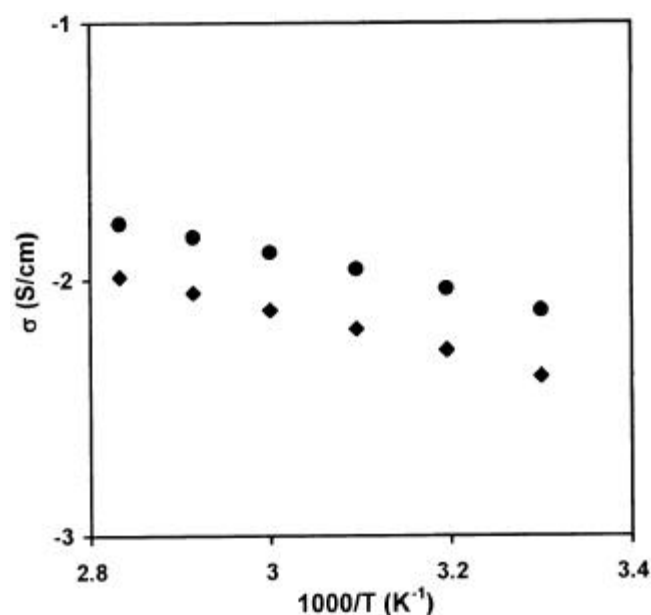


Figure 9. Variation of conductivity with temperature for liquid and gel electrolytes containing 1 M LiClO_4 with 0 (●) and 20 (◆) wt.% PMMA.

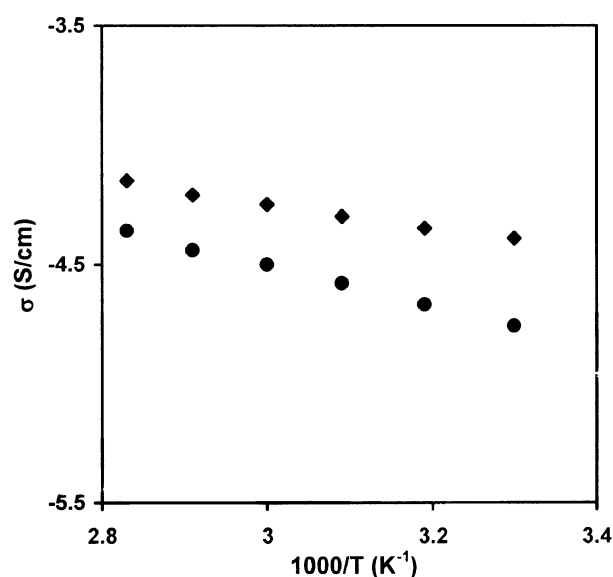


Figure 10. Variation of conductivity with temperature for liquid and gel electrolytes containing 1 M benzoic acid with 0 (●) and 10 (◆) wt.% PVdF-HFP.

electrolytes at different temperatures whereas in the case of proton conducting polymer gel electrolytes the conductivity of gel electrolytes is higher than the conductivity of liquid electrolytes at all temperatures studied and secondly the variation of conductivity with temperature for gel electrolytes is similar to that for liquid electrolytes which shows the liquid like behaviour of these gel electrolytes.

4. Conclusions

The role of polymer in gel electrolytes has been found to depend upon the nature of salt used. In the case of lithium ion conducting polymer gel electrolytes containing various lithium salts—which are nearly fully dissociated—the addition of polymer results in an increase in viscosity which lowers mobility and conductivity decreases. Whereas in the case of proton conducting polymer gel electrolytes containing weak carboxylic acids, the acids are not fully dissociated in the electrolytes. The addition of polymer in addition to an increase in viscosity also helps in increasing carrier concentration by dissociating undissociated acid/ion aggregates present in these gel electrolytes and gel electrolytes with net conductivity higher than the corresponding liquid electrolytes has been observed. The variation of conductivity of gel electrolytes with temperature shows liquid like behaviour.

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