



Ionic conductivity, FTIR and thermal studies of nano-composite plasticized proton conducting polymer electrolytes

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ABSTRACT

Ionic conductivity of polymer electrolytes obtained by complexation of trifluoromethanesulfonic acid (HCF_3SO_3) (triflic acid) with polyethylene oxide (PEO) has been found to increase with the addition of dimethylacetamide (DMA) as plasticizer. The increase in conductivity has been explained to be due to dissociation of ion aggregates with the addition of plasticizer, which has also been supported by FTIR studies. Plasticized polymer electrolytes have high ionic conductivity but not show better mechanical properties. Nano-sized fumed silica (SiO_2) is added to improve its mechanical strength alongwith an increase the ionic conductivity of plasticized polymer electrolytes. Maximum ionic conductivity of plasticized nano-composite polymer electrolytes of $8.14 \times 10^{-3} \text{ Scm}^{-1}$ at room temperature has been observed for the composition $\text{PEO} + 8 \text{ wt\% HCF}_3\text{SO}_3 + 50 \text{ wt\% DMA} + 3 \text{ wt\% SiO}_2$. X-ray diffraction studies of polymer electrolytes suggests that the amorphous content increases with the addition of plasticizer and nano-filler, which is in agreement with the conductivity results. The small change in conductivity over 30–130 °C temperature range suggests that these electrolytes are suitable for their use in device applications like fuel cells, supercapacitors, sensors, separators and other electrochromic devices. DSC/TGA studies show that these nano-composite plasticized polymer electrolytes possess good thermal properties alongwith high conductivity.

1. Introduction

In the present time, polymer electrolytes become important materials due to extraordinary development in lithium ion batteries, which have nearly replaced all existing battery systems based on liquid electrolytes in electronic market [1–4]. The research on polymer electrolytes has started by a Sheffield Polymer Chemist P. V. Wright in 1975 by studying complexation of polyethylene oxide (PEO) polymer with sodium and potassium salts [5]. After then large number of polymer electrolytes with different polymers and salts have been reported [6–8]. Proton conducting polymer electrolytes have also become of great interest due to their potential applications in various electrochemical devices like fuel cells, sensors, supercapacitors and other electrochromic display devices [9–13]. Proton conducting polymer electrolytes containing different acids/salts and polymers have been reported by various authors [14–21]. Poly(ethylene oxide) based polymer electrolytes have several advantages such as high safety, ease of fabrication, low cost, high energy density, good electrochemical stability, and excellent compatibility with salts/acids, but possess low ionic conductivity at moderate temperatures, which restrict their use in

potential applications [22]. Numerous attempts have been made to increase the ionic conductivity of polymer electrolytes to a reasonable value suitable for applications, which includes the use of copolymers, use of salt with large anions, use of polyelectrolytes and the addition of plasticizers [23–29]. The addition of plasticizer enhances the dissociation of ion aggregates/undissociated salt/acid present in the electrolytes at high concentration and enhance the amorphous content alongwith lowering of glass transition temperature (T_g). But the conductivity has also been increased by adding inert insulating matrix like Al_2O_3 , SiO_2 , ZnO , TiO_2 etc. in polymer electrolytes alongwith an improvement in mechanical properties of electrolytes [30–40]. The interaction between constituents of these polymer electrolytes has been studied by using FTIR studies [18,26,41].

In the present study, trifluoromethanesulfonic acid (HCF_3SO_3), also known as triflic acid, has been used to prepare polymer electrolytes because it is a super acid provides free H^+ ions easily to the electrolytes for conduction and having high thermal stability. Triflic acid is a functional group of perfluorosulfonated polymer electrolyte membranes where the sulfonate group is responsible for proton conduction. However, even at extremely low hydration, triflic acid exists as a

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triflate ion. The conductivity of immobilized imidazole doped with various proportions of triflic acid was studied by various authors and found that the doping of triflic acid results in the increase of conductivity [42–45].

Poly(ethylene oxide) based nano-composite plasticized polymer electrolytes containing triflic acid have been prepared and the effect of addition of acid, plasticizer and nano-sized fumed silica on ionic conductivity of polymer electrolytes has been studied. FTIR studies have been carried out to check the formation of ion aggregates at higher acid concentration and its dissociation with the addition of plasticizer, which leads to increase in conductivity. Polymer electrolytes have also been characterized by XRD studies to check their crystallinity or amorphousness. DSC/TGA studies have been carried out to study thermal stability of nano-composite plasticized polymer electrolytes.

2. Experimental details

The commercially available polyethylene oxide (PEO) (Aldrich, average molecular weight $\sim 5,000,000$; 99%), trifluoromethanesulfonic acid (triflic acid) (HCF_3SO_3) (Aldrich, 98%), *N,N*-dimethylacetamide (DMA) (Merck, 99%) and nano-sized fumed silica (SiO_2) (Aldrich, average particle size ~ 7 nm and surface area $380 \text{ m}^2/\text{g}$, 99.8%) were used as starting materials for preparation of plasticized nano-composite polymer electrolytes. Polymer electrolytes have been prepared by solution casting method [21,24] in which acid and polymer were dissolved in acetonitrile and stirred continuously until a homogeneous solution was obtained. Nano-composite plasticized polymer electrolytes have been prepared by adding nano-sized fumed silica to the plasticized polymer electrolytes. The solution obtained is then poured in polypropylene dishes and the solvent is allowed to evaporate slowly. The free standing films having thickness $\sim 100 \mu\text{m}$ so obtained are used for different experimental studies. The ionic conductivity of the films was measured by using a computer-interfaced impedance analyzer HIOKI 3532-50 LCR Hi TESTER Meter operating in the 50 Hz to 1 MHz frequency range using a sample holder with silver electrodes [46–49]. Impedance spectroscopy refers to the measurement of real and imaginary part of impedance/admittance over a wide range of frequencies. It is based upon simple principle, when a sinusoidal potential is applied across the sample whose impedance is to be measured, a current flows through it. In the present work, bulk conductivity of polymer electrolytes was measured using impedance spectroscopy, which is the most widely used method to measure conductivity in fast ion conductors. X-ray diffraction (XRD) pattern of polymer electrolyte films was recorded by PANalytical (Philips analytical) x-ray powder diffractometer with copper K_α radiation having wavelength 1.54 \AA in a wide range of Bragg angles (2θ) at a scan speed of 0.50 min^{-1} [21]. The thermal properties of the polymer electrolytes were studied by differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) (Mettler Toledo Star System) in the $25\text{--}300^\circ\text{C}$ temperature range at the heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. FTIR spectra of the samples were recorded by Perkin Elmer FTIR spectrometer at room temperature.

3. Results and discussion

The conductivity of PEO + HCF_3SO_3 polymer electrolytes as a function of acid concentration has been measured and the results obtained are shown in Fig. 1. The conductivity of pure polymer has been found to increase with the addition of acid and reaches a maximum value of $3.74 \times 10^{-5} \text{ S/cm}$ for electrolytes containing 8 wt % HCF_3SO_3 in PEO. The conductivity measurements have been taken only upto 8 wt% HCF_3SO_3 , because after this concentration the films started to deteriorate. An increase in conductivity with the addition of acid concentration is due to an increase in concentration of free charge carriers by dissociation of acid due to its high dissociation constant value of strong acid [17]. The conductivity of the polymer electrolytes

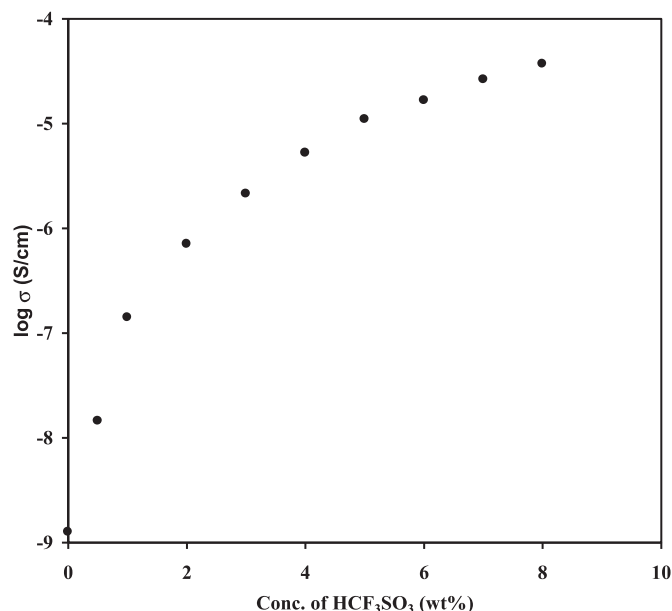


Fig. 1. Variation of log conductivity of polymer electrolytes with HCF_3SO_3 concentration.

is quite low for their use in potential applications. So, a high dielectric constant solvent dimethylacetamide (DMA) ($\epsilon = 37.8$) is added as plasticizer in the polymer electrolytes to increase its conductivity. The conductivity of polymer electrolytes has been increased by two orders of magnitude (10^{-5} S/cm to 10^{-3} S/cm) with the addition of plasticizer (DMA).

The effect of addition of plasticizer on the conductivity behavior of PEO + HCF_3SO_3 polymer electrolytes has been studied. Variation of room temperature conductivity of polymer electrolytes with the concentration of plasticizer (DMA) is given in Fig. 2. From Fig. 2, it has been observed that the conductivity of polymer electrolytes increases with the addition of plasticizer at all concentrations. The increase in conductivity is due to increase in segmental mobility of the charge carriers. Net dielectric constant of the polymer electrolytes increases with the addition of high dielectric constant plasticizer, which helps in increasing the amorphous content of the polymer electrolytes and

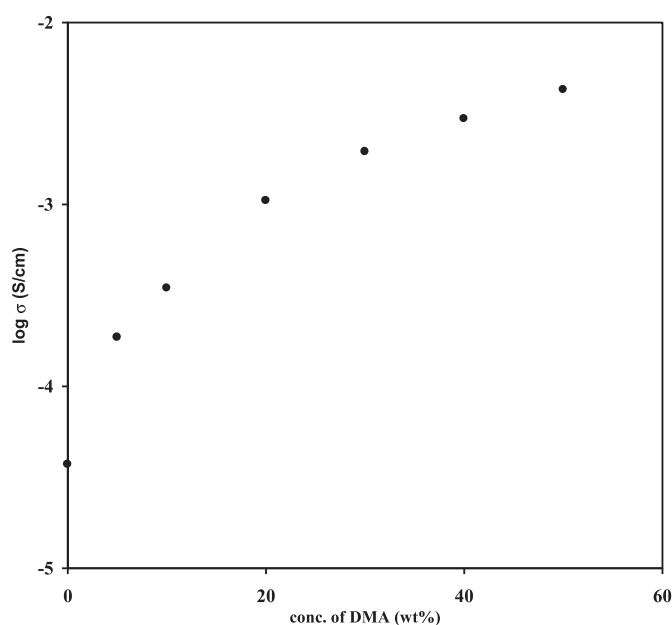


Fig. 2. Variation of log conductivity of plasticized polymer electrolytes as a function of DMA concentration.

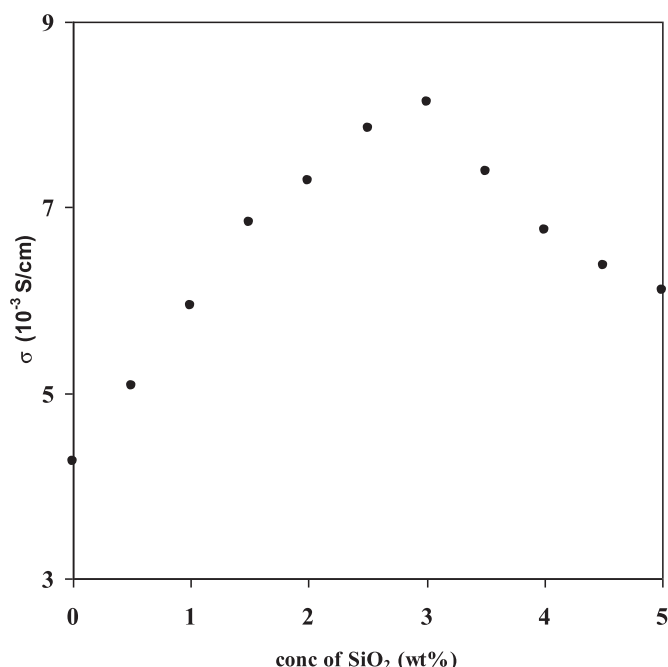


Fig. 3. Conductivity variation of PEO + 8 wt% HCF₃SO₃ + 50 wt% DMA polymer electrolytes as a function of SiO₂ concentration.

hence conductivity. Several theories like Lubricity Theory, Gel Theory, Free Volume Theory etc. have been reported/used to explain the increase in conductivity of polymer electrolytes with the addition of plasticizers [50–51]. Maximum conductivity of 4.26×10^{-3} S/cm has been observed for plasticized polymer electrolytes at 50 wt% DMA. The films become unstable at higher plasticizer concentrations, so the plasticizer (DMA) was not added further after 50 wt% concentration. Although the conductivity increases with the addition of plasticizer, but it deteriorate its mechanical properties. The mechanical properties of plasticized polymer electrolytes have been improved by adding nano-sized fumed silica alongwith an enhancement in ionic conductivity.

The variation of conductivity of plasticized polymer electrolytes containing PEO + 8 wt% HCF₃SO₃ + 50 wt% DMA with nano-sized fumed silica concentration is shown in Fig. 3. It has been observed that, the ionic conductivity of plasticized polymer electrolytes increases with the addition of fumed silica and the maximum conductivity of 8.14×10^{-3} S/cm has been obtained at 3 wt% fumed silica. After that the conductivity decreases with an increase in SiO₂ concentration. The increase in conductivity with the addition of fumed silica has been explained on the basis of space charge-model by various authors. According to this model, the high conducting interfacial layers on the surface of grains overlaps on each other which provides high conducting pathways for free ions. These highly conducting pathways are expected to increase with an increase in concentration of fumed silica. However at higher concentration of fumed silica, the conductivity become small due to the blocking effect, which hinders the motion of ions leading to lower conductivity value [21,52–54]. Overall the conductivity of nano-composite plasticized polymer electrolytes has been increased by nearly two orders of magnitude with the addition of fumed silica. The plasticizer mainly increases the ionic conductivity, whereas nano-filler improves the mechanical strength, resulting in nano-composite plasticized polymer electrolyte films with high ionic conductivity and better mechanical properties. On the basis of above studies it could be inferred that although the addition of plasticizer and fumed silica to PEO + HCF₃SO₃ polymer electrolytes results in an increase in conductivity yet the mechanical properties have also been improved. The presence of both DMA and fumed silica in polymer electrolytes results in an increase in conductivity by nearly two order of

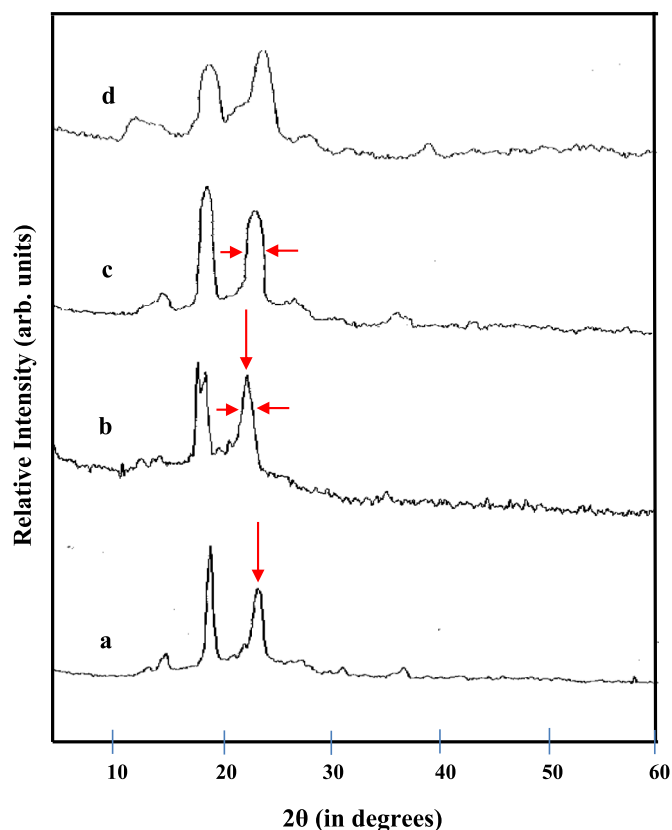


Fig. 4. XRD spectra of pure PEO (a); PEO + 8 wt% HCF₃SO₃ (b); PEO + 8 wt% HCF₃SO₃ + 50 wt% DMA (c) and PEO + 8 wt% HCF₃SO₃ + 50 wt% DMA + 3 wt% SiO₂ (d).

magnitude with improved mechanical strength (no measurement, only by visual observations).

X-ray diffraction studies have been carried out for different polymer electrolyte systems. Fig. 4 shows the X-ray diffraction pattern of (a) pure polymer (PEO), (b) polymer electrolytes (PEO + 8 wt% HCF₃SO₃), (c) plasticized polymer electrolytes (PEO + 8 wt% HCF₃SO₃ + 50 wt% DMA) and (d) plasticized nano-composite polymer electrolytes (PEO + 8 wt% HCF₃SO₃ + 50 wt% DMA + 3 wt% SiO₂). PEO based polymer electrolytes have generally crystalline as well as amorphous phases [55] and amorphous phase is high conducting phase. The sharp peaks are due to crystalline phase and broad peaks are due to amorphous phase. In the spectra of PEO (a), two main diffraction peaks at $2\theta \approx 18.7^\circ$ and $\approx 23.0^\circ$ corresponding to the partial crystalline nature of the polymer [56–57] has been observed. On complexation of polymer with HCF₃SO₃ (Fig. 4(b)), the characteristic peaks of PEO are slightly shifted to 18.1° , 22.1° signifying the interaction between polymer and acid. These peaks become broadened with the addition of plasticizer (DMA) as shown in Fig. 4(c), which is due to an increase in amorphous content of polymer electrolytes [58]. This increase in amorphous content is also accompanied by an increase in conductivity of these polymer electrolytes as explained in conductivity results. When nano-sized fumed silica is added to plasticized polymer electrolytes, the peaks get broadened and a small decrease in intensity of peaks has been observed in Fig. 4(d). The broadening of peaks suggests the increase in amorphous content and decrease in intensity shows the decrease in crystallinity in polymer electrolytes containing both DMA and SiO₂ simultaneously. On the basis of above X-ray diffraction results, it has been observed that the crystallinity/amorphicity of the electrolytes has been changed due to change in intensity and broadening of peaks, with the addition of plasticizer and fumed silica. The amorphous content has been found to increase due to broadening of peaks, while the crystalline phase decreases due to decrease in intensity of the peaks in plasticized

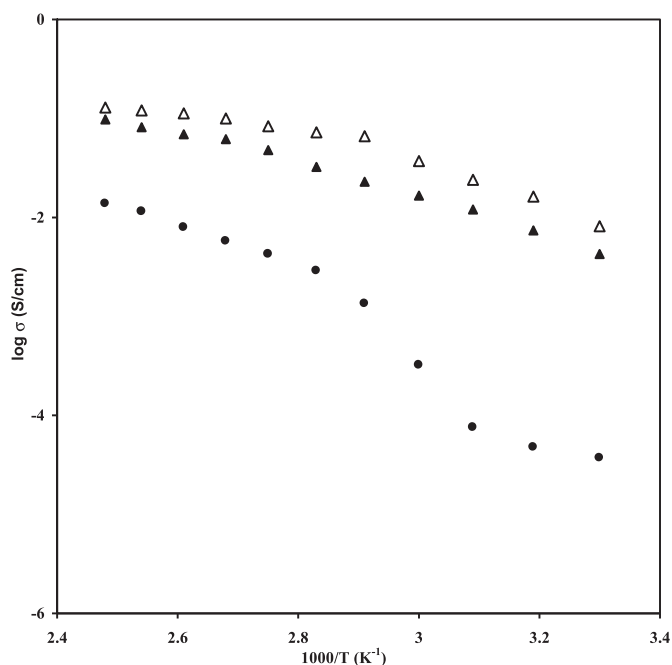


Fig. 5. Variation of log conductivity with reciprocal temperature for unplasticized {PEO + 8 wt% HCF₃SO₃ (●)}; plasticized {PEO + 8 wt% HCF₃SO₃ + 50 wt% DMA (▲)} and nano-composite plasticized {PEO + 8 wt% HCF₃SO₃ + 50 wt% DMA + 3 wt% SiO₂ (Δ)} polymer electrolytes.

nano-composite polymer electrolytes, which is clearly reflected in the conductivity behavior.

The conductivity of unplasticized (PEO + 8 wt% HCF₃SO₃), plasticized (PEO + 8 wt% HCF₃SO₃ + 50 wt% DMA) and nano-composite plasticized (PEO + 8 wt% HCF₃SO₃ + 50 wt% DMA + 3 wt% SiO₂) polymer electrolytes has been measured as a function of temperature and the variations of log conductivity with reciprocal temperature in the 30–130 °C temperature range are shown in Fig. 5. In case of unplasticized polymer electrolytes, a sharp change in conductivity has been observed nearly at 65 °C (melting point of PEO), which is due to transition from semicrystalline to amorphous phase of polymer. Similar results have been reported earlier by different authors [21,58]. In case of plasticized polymer electrolytes, no sharp change in conductivity has been observed, which suggests that the electrolytes become more amorphous with the addition of plasticizer (DMA). The transition in the conductivity is almost absent in case of plasticized nano-composite polymer electrolytes (containing both plasticizer and fumed silica), which confirms that the electrolyte become amorphous. The curved nature of log conductivity versus reciprocal temperature plot for electrolytes containing plasticizer and both plasticizer & fumed silica indicates the amorphous nature of these electrolytes. The activation energies were also calculated from log σ versus 1000/T plots by a given formula:

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

where σ_0 is constant, E_a the activation energy, k the Boltzmann constant and T is the absolute temperature [59]. The conductivity and activation energy values of polymer electrolytes are given in the Table 1. Joykumar and Bhat reported the increased lithium ion conductivity in PEG-LiClO₄ polymer electrolytes with the addition of δ -Al₂O₃ nanoparticles is due to decrease in crystallinity & activation energy and increase in effective mobility in lithium ions [60].

Thermal stability of nano-composite polymer electrolytes having composition PEO + 8 wt% HCF₃SO₃ + 50 wt% DMA + 3 wt% SiO₂ has been studied by simultaneous DSC/TGA measurement in 25–300 °C temperature range at a heating rate of 10 °C/min under nitrogen atmosphere and the results are given in Fig. 6. The DSC

Table 1

Conductivity and activation energy values of polymer electrolytes at 303 K and 353 K.

Sample (composition)	Conductivity at 303 K (S/cm)	Activation energy at 303 K (eV)	Conductivity at 353 K (S/cm)	Activation energy at 353 K (eV)
PEO + 8 wt% HCF ₃ SO ₃	3.72×10^{-5}	1.15	2.92×10^{-3}	0.77
PEO + 8 wt% HCF ₃ SO ₃ + 50 wt% DMA	4.26×10^{-3}	0.62	3.25×10^{-2}	0.45
PEO + 8 wt% HCF ₃ SO ₃ + 50 wt% DMA + 3 wt% SiO ₂	7.38×10^{-3}	0.54	7.35×10^{-2}	0.34

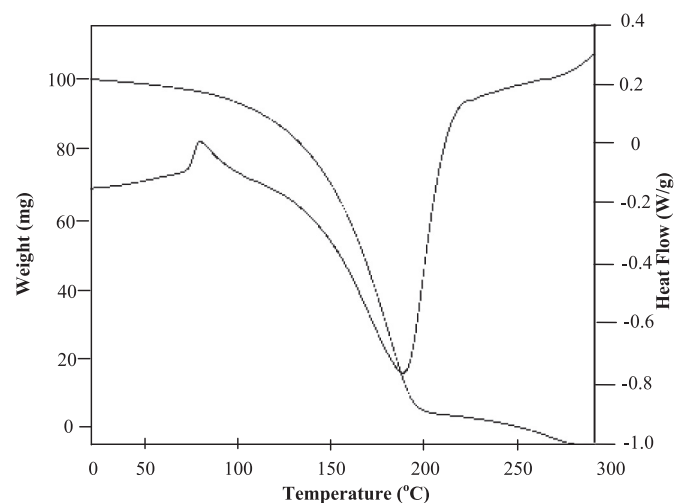


Fig. 6. DSC and TGA plots for nano-composite plasticized polymer electrolytes having composition PEO + 8 wt% HCF₃SO₃ + 50 wt% DMA + 3 wt% SiO₂.

thermogram of nano-composite polymer electrolytes shows an endothermic peak at ~190 °C (150–200 °C temperature range) which is corresponding to the boiling temperature of solvent (DMA, B.P. ~165 °C) and melting point of HCF₃SO₃ (162 °C) for this electrolyte. TGA plots for the same nano-composite polymer electrolytes show weight loss by 1.2% upto 200 °C, which is corresponding to the temperatures at which endothermic peak has been observed in the DSC thermogram. The weight loss is quite small, which shows that the fumed silica improves the thermal stability of polymer electrolytes [61]. The fumed silica helps in preventing the loss of plasticizer from the polymer electrolytes. Thus nano-composite plasticized polymer electrolytes are thermally stable upto 150 °C alongwith higher value of conductivity.

The formation of ion aggregates in unplasticized polymer electrolytes at higher HCF₃SO₃ concentrations and dissociation of ion aggregates in plasticized polymer electrolytes with the addition of DMA as proposed above while explaining conductivity results, has been studied by FTIR spectroscopy. Room temperature FTIR spectra of unplasticized, plasticized and nano-composite electrolytes are recorded. Fig. 7 shows the FTIR spectra of unplasticized polymer electrolytes containing 8 wt% HCF₃SO₃ (a); plasticized polymer electrolytes containing 50 wt% DMA (b) and corresponding nano-composite plasticized polymer electrolytes containing 3 wt% SiO₂ (c) in 1000–1500 cm⁻¹ region. In the spectra of unplasticized polymer electrolyte (a), the peak observed at 1087 cm⁻¹ is attributed due to $\nu_{s,a}$ (C–O–C) - symmetric & asymmetric stretching of C–O–C group in PEO. The peak observed at 1057 cm⁻¹ has been assigned to be due to overlapping of ν_s (SO₃⁻) - symmetric stretching of SO₃⁻ in triflate anion and $\nu_{s,a}$ (C–O–C) - symmetric & asymmetric stretching of C–O–C group in PEO [26,62–63]. The peaks observed at

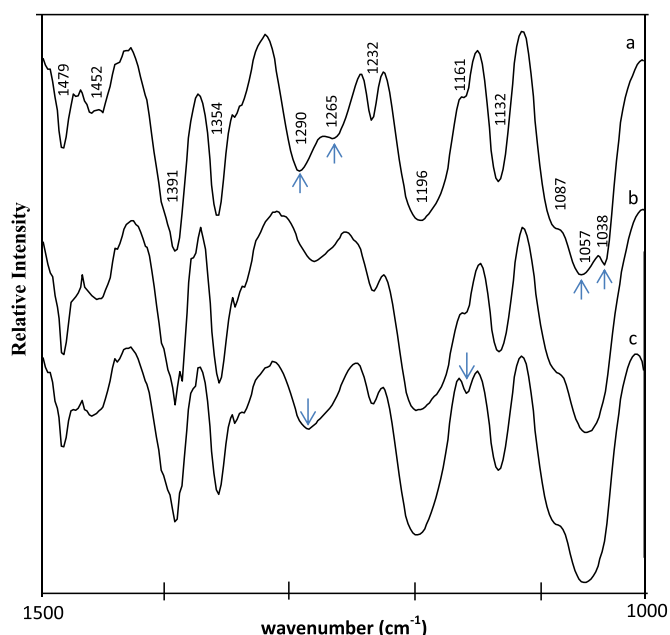


Fig. 7. FTIR spectra of unplasticized (PEO + 8 wt% HCF_3SO_3) (a); plasticized (PEO + 8 wt% HCF_3SO_3 + 50 wt% DMA) (b) and nano-composite plasticized (PEO + 8 wt% HCF_3SO_3 + 50 wt% DMA + 3 wt% SiO_2) (c) polymer electrolytes in 1000–1500 cm^{-1} region.

1132, 1161, 1195 and 1232 cm^{-1} have been assigned to be due to $\nu_{s,a}$ (C–O–C) - symmetric & asymmetric stretching of C–O–C in PEO, ν_a (CF_3^-) - asymmetric stretching of CF_3^- , ν_a (C–H) - symmetric stretching of C–H in PEO and ν_a (SO_3^-) - asymmetric stretching of SO_3^- respectively [26,62–63]. Two shoulders at 1038 cm^{-1} and 1265 cm^{-1} appeared in the spectra of unplasticized polymer electrolyte (a) near the peaks of free triflate ions are due to coordinated triflate ion/ion aggregates of triflate anion (CF_3SO_3^- anion and H^+ cations). Similar results regarding formation of ion aggregates have already been reported by various authors (Battisti et al., Bernson et al., Geji et al. and Huang et al.) for lithium triflate salt in their findings [62–65]. Bernson et al. observed that the triflate ion is assumed to have a point group symmetry. An asymmetric SO_3^- stretching mode ν_a (SO_3^-) with E symmetry is doubly degenerate, while the symmetric mode ν_s (SO_3^-), with A_1 symmetry is non-degenerate and both modes are infrared active [63]. When the triflate ion is coordinated to a cation (H^+), then degenerate ν_a (SO_3^-) band split into two bands. This is evidenced from the spectra (a), as two free triflate ion bands are seen at 1232 cm^{-1} and 1057 cm^{-1} which are attributable to ν_a (SO_3^-) and ν_s (SO_3^-) as discussed above.

The shoulders at 1038 cm^{-1} and 1265 cm^{-1} have been found to disappear with the addition of DMA (b) which is possibly due to the dissociation of ion aggregates as proposed above while explaining conductivity results in Fig. 2. The peak observed at 1290 cm^{-1} has been assigned to be due to stretching of C–O group in PEO [66]. This peak gets broadened with the addition of DMA (b), which is possibly due to the overlap of the carbonyl group peak of PEO with DMA. The broadening in peak at 1290 cm^{-1} (c) has also been observed after the addition of fumed silica to plasticized polymer electrolytes, which indicates that fumed silica also affects C=O stretching vibration mode of DMA. Also this peak (at 1290 cm^{-1}) shift towards higher wavenumber side, which indicates the interactions of fumed silica with H^+ ion of the acid [32,67] as discussed in the conductivity results. The peaks observed at 1354, 1391 cm^{-1} in the spectra of unplasticized and plasticized polymer electrolytes has been assigned to be due to the overlapping of symmetric deformation mode of C–H in PEO and DMA bands [26,68]. The other strong peaks in 1400–1500 cm^{-1} region (1452 and 1479 cm^{-1}) have also been assigned to C–O stretching

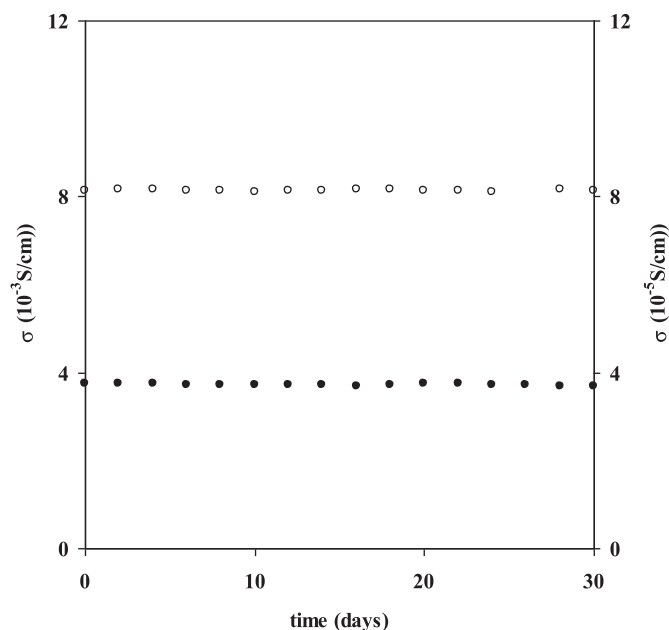


Fig. 8. Variation of conductivity with time of nano-composite plasticized polymer electrolytes (PEO + 8 wt% HCF_3SO_3 + 50 wt% DMA + 3 wt% SiO_2).

vibrations in PEO [26].

Thus FTIR results indicate that ion aggregates are present in unplasticized polymer electrolytes at high acid concentrations (8 wt %) along with the presence of free ions. The addition of plasticizer (DMA) results in the dissociation of ion aggregates leading to an increase in free ion concentration, which enhances ionic conductivity of the electrolytes. The shifting of peak towards higher wavenumber side with the addition of fumed silica indicates the interactions of fumed silica with H^+ ion of the acid. These results are in agreement with the conductivity results discussed in plasticized and nano-composite plasticized polymer electrolytes.

The conductivity of unplasticized (PEO + 8wt% HCF_3SO_3) and nano-composite plasticized (PEO + 8wt% HCF_3SO_3 + 50 wt% DMA + 3wt% SiO_2) polymer electrolytes as a function of time has also been measured and results are given in Fig. 8. From Fig. 8, it has been observed that the conductivity of unplasticized and nano-composite plasticized polymer electrolytes nearly remains constant for a period of 30 days, which is desirable for their use in device applications.

4. Conclusions

The conductivity of polymer has been increased by four orders of magnitude from 10^{-9} S/cm to 10^{-5} S/cm with the addition of triflic acid. The conductivity of polymer electrolytes has been further increased by two orders (10^{-5} S/cm to 10^{-3} S/cm) with the addition of plasticizer and maximum conductivity of 4.26×10^{-3} S/cm has been obtained at 50 wt% DMA in PEO + 8 wt% HCF_3SO_3 at room temperature. The mechanical strength of plasticized polymer electrolytes has also been improved with the addition of nano-sized fumed silica (SiO_2) along with an increase in ionic conductivity. Maximum ionic conductivity of 8.14×10^{-3} S/cm at room temperature has been observed for nano-composite plasticized polymer electrolytes at 3 wt% SiO_2 in PEO + 8 wt% HCF_3SO_3 + 50 wt% DMA. On the basis of above studies it could be inferred that although the addition of plasticizer and fumed silica to PEO + HCF_3SO_3 polymer electrolytes results in an increase in conductivity yet the mechanical strength of the films have also been improved. The increase in conductivity with the addition of plasticizer has been explained due to dissociation of ion aggregates, which has also been supported by FTIR studies. The decrease in crystallinity and increase in amorphicity of polymer electrolytes has

been observed by XRD studies, which is responsible for increase in conductivity. DSC/TGA studies show that these electrolytes are thermally stable upto 150 °C temperature. The small change in conductivity observed over the 30–130 °C temperature range and nearly shows constant value of conductivity for a period of 30 days for nano-composite polymer electrolytes suggest that these electrolytes are suitable for their use in different devices like fuel cells, supercapacitors, sensors, separators and other electrochromic devices.

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References

- [1] Ph. Colomban (Ed.), *Proton Conductors: Solids, Membranes and Gels – Materials and Devices*, Cambridge University Press, 1992.
- [2] B. Scrosati, B. Scrosati (Ed.), *Applications of Electroactive Polymers*, Chapman and Hall, London, 1993, p. 354.
- [3] B. Scrosati, *Nature* 573 (1995) 557–558.
- [4] L. Porcarelli, C. Garbaldi, F. Bella, J.R. Nair, *Sci. Rep.* 6 (2016), <http://dx.doi.org/10.1038/srep19892>.
- [5] P.V. Wright, *Br. Polym. J.* 7 (1975) 319–324.
- [6] M.B. Armand, J.M. Chabagno, M.J. Duclot, Extended Abstract on Second International Meeting on Solid Electrolytes, St. Andrews, Scotland (1978).
- [7] S. Chandra, *Superionic Solids—Principles and Applications*, Amsterdam, North Holland (1987).
- [8] B.B. Owens, *J. Power Sources* 90 (2000) 2–8.
- [9] M. Stainer, L.C. Hardy, D.H. Whitmore, D.F. Shriver, *J. Electrochem. Soc.* 131 (1984) 784–790.
- [10] S. Chandra, M.Z.A. Munshi (Ed.), *Handbook of Solid State Batteries and Capacitors*, World Scientific, Singapore, 1995, p. 579.
- [11] A.M.M. Ali, N.S. Mohamed, A.K. Arof, *J. Power Sources* 74 (1998) 135–141.
- [12] Ph. Colomban, *Ann. Chim. Sci. Mater.* 24 (1999) 1–18.
- [13] S.R. Narayanan, S.P. Yen, L. Liu, S.G. Greenbaum, *J. Phys. Chem. B* 110 (2006) 3942–3948.
- [14] W. Wiczkorek, Z. Florjanczyk, J.R. Stevens, *Electrochim. Acta* 40 (1995) 2327–2330.
- [15] H. Ericson, C. Svanberg, A. Brodin, A.M. Grillone, S. Panero, B. Scrosati, P. Jacobsson, *Electrochim. Acta* 45 (2000) 1409–1414.
- [16] S. Chandra, S.S. Sekhon, R. Srivastava, N. Arora, *Solid State Ionics* 154–155 (2002) 609–619.
- [17] R. Kumar, S.S. Sekhon, *Ionics* 10 (2004) 436–442.
- [18] R. Kumar, S.S. Sekhon, *Ionics* 14 (2008) 509–514.
- [19] M. Morita, T. Shirai, N. Yoshimoto, M. Ishikawa, *J. Power Sources* 139 (2005) 351–355.
- [20] L.E. Shmukler, N.V. Thuc, Y.A. Fadeeva, L.P. Safonova, *J. Polym. Res.* 19 (2012) 9770–9777.
- [21] S. Sharma, N. Dhiman, D. Pathak, R. Kumar, *Ionics* 22 (2016) 1865–1872.
- [22] G. MacGlashan, Y.G. Andreev, P.G. Bruce, *Nature* 398 (1999) 792–794.
- [23] W.T. Whang, C.L. Lu, *J. Appl. Polym. Sci.* 56 (1995) 1635–1643.
- [24] S.S. Sekhon, M. Kumar, *Proceedings of 8th Asian Conference on Solid State Ionics*, (2002), pp. 377–384.
- [25] P.P. Chu, M.J. Reddy, H.M. Kao, *Solid State Ionics* 156 (2003) 141–153.
- [26] R. Kumar, J.P. Sharma, S.S. Sekhon, *Eur. Polym. J.* 41 (2005) 2718–2725.
- [27] T. Kuila, H. Achaya, S.K. Srivastava, B.K. Samantaray, S. Kureti, *Mater. Sci. Eng. B* 137 (2007) 217–224.
- [28] S. Sharma, N. Dhiman, D. Pathak, R. Kumar, *i-Manager's, J. Mater. Sci.* 3 (2016) 28–34.
- [29] A. Kumar, S.V. Murugadoss, S. Angaiah, *J. Appl. Polym. Sci.* (2017), <http://dx.doi.org/10.1002/APP.45177>.
- [30] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, *Nature* 394 (1998) 456–458.
- [31] B. Singh, R. Kumar, S.S. Sekhon, *Solid State Ionics* 176 (2005) 1577–1583.
- [32] J.P. Sharma, S.S. Sekhon, *Ind. J. Engg. & Mater. Sci.* 12 (2005) 557–562.
- [33] R. Kumar, S.S. Sekhon, *J. Appl. Electrochem.* 39 (2009) 439–445.
- [34] T. Hanemann, D.V. Szaba, *Materials* 3 (2010) 3468–3517.
- [35] R. Kumar, *i-manager's, J. Mater. Sci.* 2 (2014) 12–17.
- [36] R. Kumar, *Ind. J. Phys.* 89 (2015) 241–248.
- [37] R. Kumar, N. Arora, S. Sharma, N. Dhiman, D. Pathak, *Ionics* (2016), <http://dx.doi.org/10.1002/s11581-016-1845-4>.
- [38] S. Gomari, M. Esfandeh, I. Ghasemi, *Solid State Ionics* 303 (2017) 37–46.
- [39] R. Kumar, *Int. J. ChemTech Res.* 10 (2017) 289–295.
- [40] M.L. Verma, H.D. Sahu, *Ionics* (2017), <http://dx.doi.org/10.1007/s11581-017-2063-4>.
- [41] S.S. Sekhon, J.P. Sharma, J.S. Park, *Macromol. Symp.* 249–250 (2007) 209–215.
- [42] M.F.H. Schuster, W.H. Meyer, M. Schuster, K.D. Kreuer, *Chem. Mater.* 16 (2004) 329–337.
- [43] S.S. Sekhon, B.S. Lalia, J.-S. Park, C.-S. Kim, K. Yamada, *J. Mater. Chem.* 16 (2006) 2256–2265.
- [44] A.P. Sunda, A. Venkatnathan, *J. Comput. Chem.* 32 (2011) 3319–3328.
- [45] A.P. Sunda, M. More, A. Venkatnathan, *Soft Matter* 9 (2013) 1122–1132.
- [46] R. Kumar, B. Singh, S.S. Sekhon, *J. Mater. Sci.* 40 (2005) 1273–1275.
- [47] H.P. Singh, R. Kumar, S.S. Sekhon, *Bull. Mater. Sci.* 28 (2005) 467–472.
- [48] R. Kumar, S.S. Sekhon, *Ionics* 19 (2013) 1627–1635.
- [49] R. Kumar, *Curr. Smart Mater.* 1 (2016) 63–67.
- [50] J.K. Sears, J.R. Darby, *Mechanism of Plasticizer Action in the Technology of Plasticizers*, Wiley-Interscience, New York, NY, USA, 1982, pp. 35–77.
- [51] W. Barends, V.M. Litvinov, F. Socren, R.L. Scherreenberg, C. Gondard, C. Colemonts, *Macromolecules* 32 (1999) 167–180.
- [52] K.L. Kliewer, *J. Phys. Chem. Solids* 27 (1966) 705–717.
- [53] R.C. Agrawal, R.K. Gupta, *Solid State Ionics* 72 (1994) 314–317.
- [54] Y. Shekibi, A. Gray-Weale, D.R. MacFarlane, A.J. Hill, M. Forsyth, *J. Phys. Chem. C* 111 (2007) 11463–11468.
- [55] A.J. Bhattacharya, J. Maier, *Adv. Mater.* 16 (2004) 811–814.
- [56] N.S. Mohamed, M.Z. Zakaria, A.M.M. Ali, A.K. Arof, *J. Power Sources* 66 (1997) 169–172.
- [57] D.K. Pradhan, B.K. Samantaray, R.N.P. Choudhary, A.K. Thakur, *J. Power Sources* 139 (2005) 384–393.
- [58] K. Ragavendran, P. Kalyani, A. Veluchamy, S. Banumathi, R. Thirunakaran, T.J. Benedict, *Port. Electrochim. Acta* 22 (2004) 149–159.
- [59] C.W. Kuo, C.W. Huang, B.K. Chen, W.B. Li, P.R. Chen, T.H. Ho, C.G. Tseng, T.Y. Wu, *Int. J. Electrochem. Sci.* 8 (2013) 3834–3850.
- [60] T. Joykumar, S.V. Bhat, *J. Power Sources* 129 (2004) 280–287.
- [61] J. Zhou, P.S. Fedkiw, *Solid State Ionics* 166 (2004) 275–293.
- [62] D. Battisti, G.A. Nazri, B. Klassen, R. Aroca, *J. Phys. Chem.* 97 (1993) 5826–5830.
- [63] A. Bernson, J. Lindgren, *Solid State Ionics* 60 (1993) 37–41.
- [64] S.P. Gejji, K. Hermansson, J. Tegenfeldt, J. Lindgren, *J. Phys. Chem.* 97 (1993) 11402–11407.
- [65] W. Huang, R. Frech, R.A. Wheeler, *J. Phys. Chem.* 98 (1994) 100–110.
- [66] B.L. Papke, M.A. Ratner, D.F. Shriver, *J. Phys. Chem. Solids* 42 (1981) 493–500.
- [67] D.O. Hummel, Wiley, New York, 1966.
- [68] R.M. Silverstein, F.X. Webster, 6th edition, Wiley, New York, 1997.