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Characterization of PMMA based nanocomposite plasticized polymer electrolytes: Effect of plasticizer and fumed silica

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Abstract

Polymethylmethacrylate (PMMA) based polymer electrolytes containing ammonium trifluoromethane sulphonate ($NH_4CF_3SO_3$), have been synthesized by solution casting method. Ionic conductivity of polymer electrolytes has been measured and maximum conductivity of 2.05 $x10^4$ S/cm at room temperature has been observed at 10wt% $NH_4CF_3SO_3$. The conductivity of polymer electrolytes has been found to increase with the addition of plasticizers. The effect of dielectric constant of plasticizer has also been studied and found that the increase in ionic conductivity containing high dielectric constant plasticizer DMA (37.8) is more than that of electrolyte containing low dielectric constant plasticizer DEC (3.2). The conductivity of plasticized polymer electrolytes further increases by a factor with the addition of fumed silica (SiO_2) alongwith an increase in mechanical strength. The increase in ionic conductivity of polymer electrolytes with the addition of nano-filler has been explained by double threshold percolation model. Thermal stability of nano-composite plasticized polymer electrolytes has been checked by simultaneous measurement of DSC/TGA curves. The small change in ionic conductivity of nano-composite plasticized polymer electrolytes with temperature and time suggests that these electrolytes are thermally stable in 30-130°C temperature range, which is useful for their use in electrochemical device applications like fuel cells, supercapacitors, proton batteries etc.

Keywords: ionic conductivity; plasticizer; fumed silica; dielectric constant; nano-filler

1. Introduction

Polymer electrolytes are one of the most widely studied solid electrolytes due to its formation with desirable mechanical, thermal and electrochemical properties. A lot of work on different polymer electrolytes has been reported by various authors [1-10]. The ion transport mechanism in these polymer electrolytes has been explained by local relaxation as well as segmental motion of the polymer chains, which are favored by high degree of amorphicity of the polymers [11-12]. But, many host polymers used in the electrolytes are partially crystalline in nature, which shows low ionic conductivity. Plasticization is one of the methods to improve ionic conductivity by suppressing the crystallinity of polymer electrolytes. A substantial amount of a liquid plasticizer such as ethylene carbonate (EC), propylene carbonate (PC), diethylene carbonate (DEC), dimethylsulfoxide (DMSO), etc and low molecular weight poly(ethylene glycol) (PEG) or any aprotic organic solvent is added to the polymer electrolytes [13-17]. With the addition of the liquid phases in the polymer electrolytes, the crystallinity decreases or amorphicity increases, this decrease the glass transition temperature of the host polymer and promotes the segmental motion of the polymer chains. Hence, the ionic conductivity of the plasticized polymer electrolytes at ambient temperature increases. The high dielectric constant of the plasticizers like EC and PC also help in dissociation of ion aggregates, and produces more free ions, which further results into the higher ionic conductivity of the plasticized polymer electrolytes. Polymer gel electrolyte is another category of polymer electrolytes in which liquid phase is enclosed into a continuous solid skeleton of polymer. In polymer gel electrolytes, liquid phases are normally the organic liquids, which are obtained by dissolving ion donating salts or acids into the organic solvents, entrapped into the solid polymer network, which provides dimensional stability to the electrolytes [18-24]. It is observed that the larger amount of liquid electrolyte present in the polymer matrix gives rise to better ionic conductivity, but diminishes its mechanical integrity. Therefore, in order to improve the mechanical integrity, polymer electrolytes are dispersed with micro- and nano-sized fillers like silica (SiO_2), alumina (Al_2O_3), titanium oxide (TiO_2), barium titanate ($BaTiO_3$), zinc oxide (ZnO) etc. It is found that the dispersion of ceramic fillers not only improves mechanical strength, but also improves the ionic conductivity of polymer electrolytes [25 - 32]. This category of polymer electrolytes is named as composite polymer electrolytes or composite plasticized polymer electrolytes. A large number of polymer electrolytes with different salts have been developed in view of their various practical applications.

The proton conducting polymer electrolytes have their possible applications in the various electrochemical devices [33-40]. These electrolytes have largely been studied for their applications focused on development of low and moderate temperature fuel cells. Proton batteries are one of the other possible applications of these electrolytes, but this application has not yet widely studied. The literature reported on proton batteries indicate that these batteries may be considered as yet another potential alternative to the lithium ion batteries primarily because of small ionic radii of H^+ ions, like Li^+ ions, which makes them suitable for better intercalation into the layered structure of cathodes [31, 33-38]. Proton batteries have considered more attention in the recent years due to the important merits like low cost of electrodes and electrolyte materials, no safety issues.

In the present work, polymethylmethacrylate (PMMA) based nano-composite plasticized polymer electrolytes containing ammonium trifluoromethanesulfonate ($NH_4CF_3SO_3$), dimethyl acetamide (DMA), diethylene carbonate (DEC) and nano-sized fumed silica (SiO_2) have been prepared and characterized by different techniques. The effect of plasticizer and dielectric constant of plasticizers on the variation of ionic conductivity has been studied. The role of nano-sized fumed silica in enhancing the ionic conductivity and mechanical properties of nano-composite plasticized polymer electrolytes has also been discussed. FTIR studies have been carried out to check the role of plasticizer in the dissociation of undissociated salt/ion aggregates present at higher concentration of salt. Thermal stability of nano-composite plasticized polymer electrolytes has been checked by simultaneous measurement of DSC/TGA curves.

2. Materials and Methods

Polymethylmethacrylate (PMMA) (Aldrich, average MW = 996,000), Ammonium trifluoromethanesulfonate or ammonium triflate ($NH_4CF_3SO_3$) (Aldrich), dimethylacetamide (DMA) (Aldrich), diethylcarbonate (DEC) (Lancaster) and fumed silica (SiO_2) (Aldrich, with surface area 380 m^2/g, average grain size 7nm) were used as received.

3. Experimental

Polymer electrolytes were prepared by solution casting method [16-17] in which $NH_4CF_3SO_3$ and PMMA are dissolved in a solvent (methanol or acetonitrile) and stirred continuously until a uniform solution is obtained. The homogeneous solution is then poured in polypropylene dishes and the solvent is allowed to evaporate slowly. The free standing films so obtained are removed from the dishes, dried and then used for different experimental studies. Plasticized (polymer-salt-plasticizer) polymer electrolytes were prepared by adding stoichiometric quantities of plasticizer to the starting solution of polymer and salt. Plasticized nano composite (polymer-salt-plasticizer-insulating matrix) polymer electrolytes have been prepared after adding nano size fumed silica to the plasticized polymer electrolytes.

The ionic conductivity was measured by complex impedance spectroscopy with HP4284 A precision LCR meter operating in the 20Hz– 1MHz frequency range with conductivity cell having pressure contacts with stainless steel electrodes [39-42]. A graphite paste was applied on both sides of the film sample and it was placed between two electrodes of the sample holder by pressure contacts. For the measurement of conductivity at different temperatures, the sample holder containing sample is placed in a temperature controlled furnace and ionic conductivity measurements were carried out at different temperatures. True bulk conductivity of nano-composite polymer electrolytes was measured by using the relation given below $\sigma = Gl/A = l/RA$, where G is the conductance which is inverse of resistance R [16] and is determined from admittance plots, R is the resistance which is determined from the impedance plots, is the distance between the electrodes and A is the area of cross section of each electrode. Differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) (Mettler Toledo Star System) studies were carried out to study the thermal properties of the nano-composite polymer electrolytes in the 25–300 °C temperature range at the heating rate of 10 °C/min under nitrogen atmosphere.

4. Results and Discussion

The variation of log conductivity of polymer electrolytes containing PMMA as a function of $NH_4CF_3SO_3$ concentration is shown in Fig. 1. From Fig. 1, it has been observed that the ionic conductivity increases linearly initially with an increase in salt concentration, then reaches a saturation value.

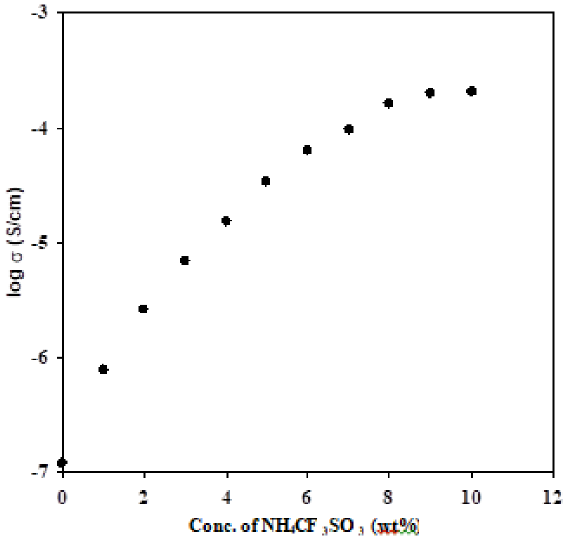

Figure 1. Variation of log conductivity (log σ) for $PMMA+NH_4CF_3SO_3$ polymer electrolytes with $NH_4CF_3SO_3$ concentration

The linear increase in ionic conductivity at low salt concentration is due to complete dissociation of salt and nearly all ions are available for conduction. At higher salt concentrations, the deviation in linearity is observed that can be explained to be due to the formation of ion aggregates, which do not take part in the conduction process and hence the concentration of free ions decreases, which increases the viscosity and reduces the ionic mobility [43]. The maximum ionic conductivity of 2.05 x 10^{-4} S/cm at room temperature has been obtained at 10wt% $NH_4CF_3SO_3$ concentration. This ionic conductivity is quite small, which restrict its use in device applications. To increase the ionic conductivity, the plasticizers of different dielectric constants DMA (37.8) and DEC (3.2) have been added in unplasticized polymer electrolytes.

Ionic conductivity of plasticized polymer electrolytes containing PMMA+10wt% $NH_4CF_3SO_3$ was measured as a function of concentration of plasticizers (DMA and DEC) and the results obtained are shown in Fig. 2. In plasticized polymer electrolytes containing DMA, the conductivity increases by two orders of magnitude from 10^{-4} to 10^{-2} S/cm and a maximum conductivity of 6.12x10^{-2} S/cm at 50 wt% DMA in PMMA+10M $NH_4CF_3SO_3$ polymer electrolytes has been observed at room temperature. Initially, the increase in ionic conductivity is large, which could be explained to be due to the dissociation of ion aggregates/undissociated salt present in the unplasticized polymer electrolyte. As the salt concentration in the electrolyte is kept constant (10 wt%), but with an increase in DMA concentration, the amount of undissociated salt/ion aggregates decreases and hence the rate of increase in conductivity is not same at higher salt concentrations.

In the case of plasticized polymer electrolytes containing DEC, the conductivity of unplasticized polymer electrolyte also increases with the addition of plasticizer, but the increase in conductivity is quite small as compare to electrolyte containing DMA. The lower value of ionic conductivity of electrolytes containing DEC is due to the relatively lower value of the dielectric constant (3.2) of the solvent as the ion aggregates/undissociated salt is not fully dissociated. The maximum ionic conductivity of 5.63x10^{-3} S/cm has been obtained for PMMA+ 10wt% $NH_4CF_3SO_3$+ 50wt% DEC electrolyte at room temperature. Overall it has been observed that higher the dielectric constant of plasticizer leads to higher ionic conductivity and vice versa.

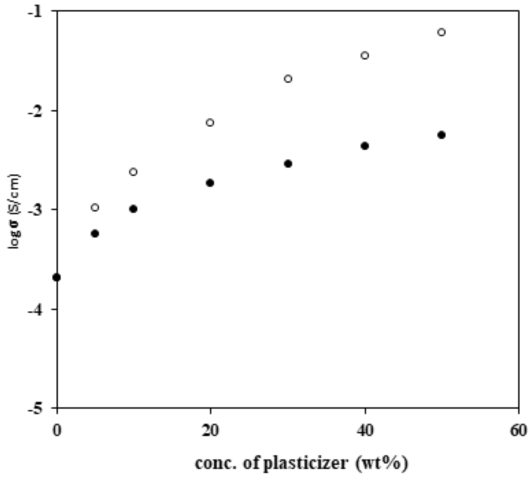

Figure 2. Variation of log conductivity (log σ) as a function of concentration of plasticizers DEC (●) and DMA (o) for plasticized polymer electrolytes 10wt% $NH_4CF_3SO_3$ in PMMA

The effect of nano size fumed silica on ionic conductivity of nano-composite plasticized polymer electrolytes has also been studied. The variation of ionic conductivity of plasticized (PMMA+10wt%NH_4CF3SO_3 +50wt%DMA) polymer electrolyte with the concentration of fumed silica has been given in Fig. 3 (a). From Fig. 3(a), it has been observed that with an increase in fumed silica concentration, the conductivity of plasticized polymer electrolytes increases, which is possibly due to enhanced dissociation of undissociated salt/ion aggregates with the addition of fumed silica. Due to the charged surface of fumed silica particles, the NH_4^+/H^+ ion of $NH_4CF_3SO_3$ will be attracted towards the oxygen of fumed silica, which shall result in an increase in the dissociation constant of salt. So, the free ion concentration is increased by dissociation of salt present in the electrolyte and as a result the conductivity increases. The rate of increase in conductivity becomes small at higher concentration of fumed silica, which is due to the blocking effect that hinders the motion of ions [16, 44-45].

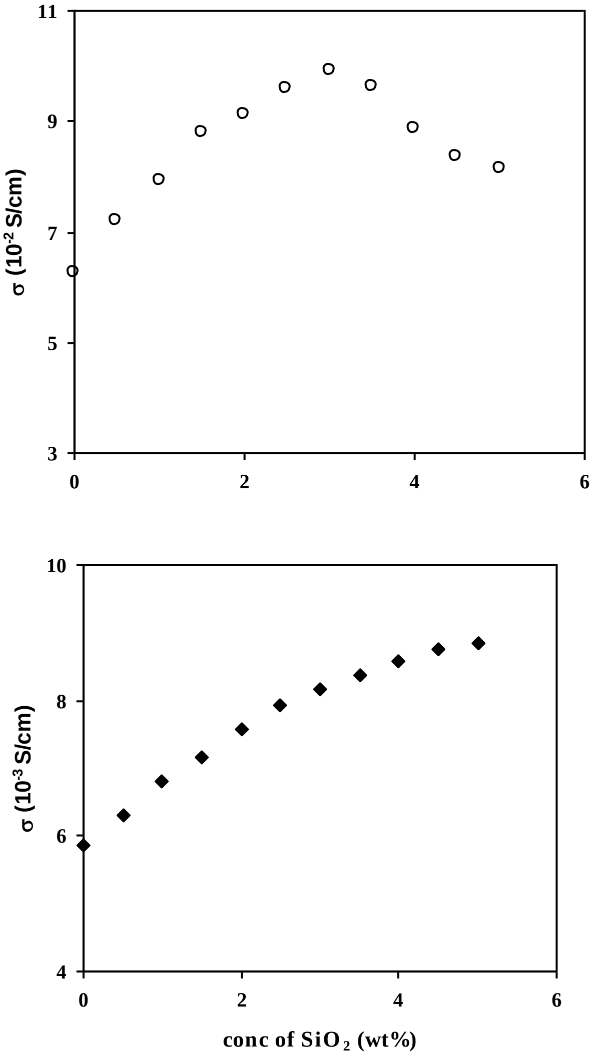

Figure 3. Variation in conductivity of nanocomposite plasticized polymer electrolytes containing PMMA+10wt% $NH_4CF_3SO_3$+50wt% DEC (●) and DMA (o) as a function of SiO_2concentration

The presence of plasticizer mainly enhances the ionic conductivity as explained in Fig. 2, whereas fumed silica improves the mechanical properties of polymer electrolytes alongwith an increase in ionic conductivity. As the salt has fully dissociated in plasticized polymer electrolytes due to high dielectric constant of DMA, so undissociated salt/ion aggregates were not present in these electrolytes. But the increase in conductivity with the addition of fumed silica has been observed, which can be explained due to the formation of high conducting interfacial layer between fumed silica and polymer [44-53]. The grain size of fumed silica is quite small (~7 nm), so maximum conductivity (9.92x10^{-2} S/cm) is observed at low concentration (3wt%) of fumed silica. It has been observed that the conductivity of plasticized nano-composite (presence of both DMA and fumed silica) polymer electrolytes increases by nearly three orders of magnitude than unplasticized nano-composite polymer electrolytes.

The variation of ionic conductivity of plasticized polymer electrolyte (PMMA+ 10wt% $NH_4CF_3SO_3$+50wt%DEC) with the concentration of fumed silica has been given in Fig. 3 (b). From Fig. 3(b), it has been observed that with an increase in fumed silica concentration, the ionic conductivity of plasticized polymer electrolytes also increases and maximum room temperature conductivity of 8.86x10^{-3} S/cm has been observed at 5wt% concentration of SiO_2 for nanocomposite plasticized polymer electrolyte. The increase in ionic conductivity is possibly due to enhanced dissociation of undissociated salt/ion aggregates with the addition of fumed silica due to attraction between oxygen of the charged surface of fumed silica particles, the NH_4^+/H^+ ion of $NH_4CF_3SO_3$, which shall result in an increase in the dissociation constant of salt. So, the free ion concentration is increased by dissociation of salt present in the electrolyte and as a result the conductivity is increased. The rate of increase in conductivity becomes small at higher concentration of fumed silica, which is due to the blocking effect that hinders the motion of ions. Similar results for different polymer electrolytes have been reported by various authors [39, 45-48].

The conductivity of nanocomposite plasticized polymer electrolytes having composition PMMA+10wt%$NH_4CF_3SO_3$+50wt%DMA+3wt%SiO_2 and PMMA+10wt%$NH_4CF_3SO_3$+50wt% DEC+5wt%SiO_2 have been measured as a function of reciprocal temperature in the 30-130°C temperature range and results obtained are shown in Fig. 4. It has been observed that the ionic conductivity of nanocomposite plasticized polymer electrolytes containing DMA and DEC plasticizers increases with an increase in temperature. The curved nature of the plot between log conductivity and reciprocal temperature for the electrolytes indicates the amorphous nature of these electrolytes. A small change in conductivity of the electrolytes with temperature has been observed, which shows that these polymer electrolytes are thermally stable in the 30-130°C temperature range.

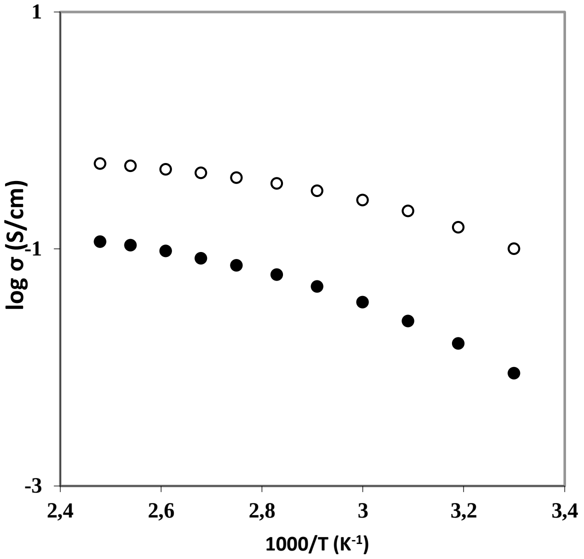

Figure 4. Variation of log conductivity with reciprocal temperature for nanocomposite plasticized polymer electrolytes containing PMMA+10wt% $NH_4CF_3SO_3$+50wt% DEC (●) +5wt% SiO_2 and PMMA+10wt% $NH_4CF_3SO_3$+50wt% DMA (o) + 3wt% SiO_2

The variation of ionic conductivity of plasticized nanocomposite polymer electrolytes containing DMA and DEC plasticizers as a function of time for the period of 30 days has also been measured and results are given in Fig. 5. No appreciable change in conductivity with time as well as temperature has been observed, which is desirable for their use in practical applications.

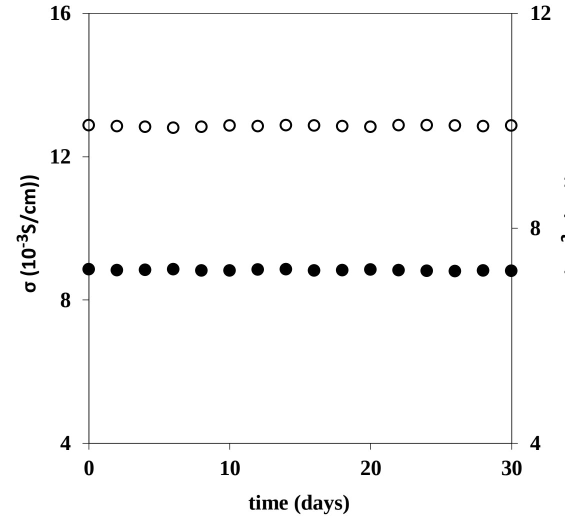

Figure 5. Variation of ionic conductivity with time for nanocomposite plasticized polymer electrolytes containing PMMA+10wt% $NH_4CF_3SO_3$+50wt% DEC (●)+5wt% SiO_2 and PMMA+ 10wt% $NH_4CF_3SO_3$+50wt% DMA (o) + 3wt% SiO_2

Thermal stability of nanocomposite plasticized polymer electrolyte has been checked by simultaneous DSC/TGA measurements. DSC/TGA studies have been carried out for nanocomposite plasticized polymer electrolyte (PMMA+10wt% $NH_4CF_3SO_3$+50wt% DMA+5 wt% SiO_2 in the 25–300 °C temperature range at a heating rate of 10 °C/min under nitrogen atmosphere and the results are given in Fig. 6. In DSC thermogram (Fig. 6 a), an endothermic peak between 130 and 220°C has been observed, which could be due to the glass transition temperature of polymer PMMA [54-58]. The actual glass transition temperature of pure PMMA is 105°C, but it is slightly shifted from its actual value due to complexations with salt, plasticizer and silica in nanocomposite plasticized polymer electrolytes. The TGA plot of nanocomposite plasticized polymer electrolyte (Fig. 6 b) does not show any weight loss up to 130°C and the weight loss of about 92% has been observed between 130-220°C temperature range due to the evaporation of electrolyte solution or residual solvent. So, DSC/TGA results show that these nanocomposite plasticized polymer electrolytes are thermally stable only up to 130 °C.

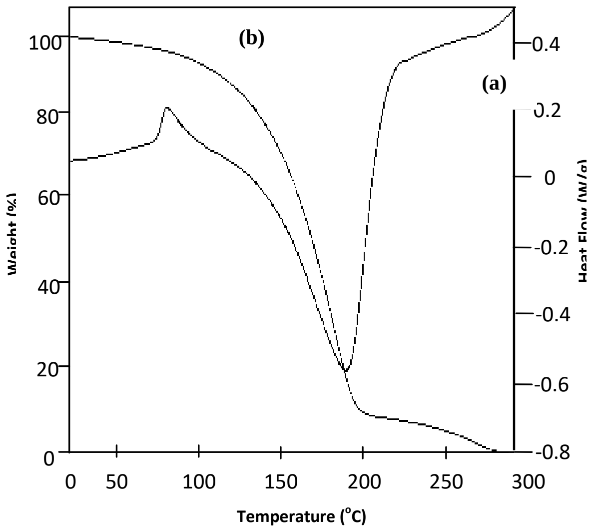

Figure 6. DSC (a) and TGA (b) plots for nanocomposite plasticized polymer electrolyte containing PMMA+ 10wt% $NH_4CF_3SO_3$+50wt% DMA (o) + 5wt% SiO_2

5. Conclusion

The ionic conductivity of the polymer (10^{-7} S/cm) has been found to increase by three orders of magnitude (10^{-4} S/cm) with the addition of $NH_4CF_3SO_3$. Maximum room temperature ionic conductivity of 2.05×10^{-4} S/cm has been obtained for polymer electrolyte at 10 wt% ammonium trifluoromethanesulfonate. The increase in ionic conductivity of polymer electrolytes with the addition of plasticizers has been explained to be due to the dissociation of ion aggregates/undissociated salt present in the electrolytes. The effect of dielectric constant of plasticizer on ionic conductivity of plasticizer polymer electrolytes has been discussed and it has been observed that higher the dielectric constant of plasticizer leads to higher ionic conductivity. The maximum ionic conductivities of $6.12x10^{-2}$ S/cm and $5.63x10^{-3}$ S/cm have been obtained for plasticized polymer electrolytes containing DMA (37.8) and DEC (3.2) plasticizer respectively. Further an increase in ionic conductivity alongwith an improvement in mechanical strength of polymer electrolytes has been observed by adding nano sized fumed silica. Maximum ionic conductivities of $9.92x10^{-2}$ S/cm and $8{\cdot}86 \times 10^{-3}$ S/cm have been obtained for nanocomposite plasticized polymer electrolytes containing PMMA + 10 wt% $NH_4CF_3SO_3$ + 50 wt% DMA + 3 wt% silica and PMMA + 10 wt% $NH_4CF_3SO_3$ + 50 wt% DEC + 5 wt% silica respectively. The thermal properties of these polymer electrolytes have been checked by simultaneous DSC/TGA studies and found to thermally stable only up to 130°C. The variation in ionic conductivity with temperature over the 30–130°C temperature range and time for a period of 30 days has also been studied, and a small change in conductivity has been observed, which is suitable for their use in device applications such as fuel cells, supercapacitors, solid state batteries etc.

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