



Ionic Transport and Material Properties Studies on Fumed Silica Dispersed Mg^{2+} -Conducting Nano Composite Polymer Electrolytes (NCPEs)

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Abstract— Present paper reports the fumed silica dispersed Mg^{2+} -conducting Nano Composite Polymer Electrolyte films: $[80PEO: 20Mg(CF_3SO_3)_2] + xSiO_2$, where $x = 0, 2, 4, 6, 8, 10, 12, \dots$ wt. (%), synthesized by solution cast technique. Solid Polymer Electrolyte composition: $[80PEO: 20Mg(CF_3SO_3)_2]$, identified as one of the high ion conducting film with better physical stability, used as I^{st} -phase host matrix and fumed nano-sized ($\sim 8nm$) silica SiO_2 used as II^{nd} -phase dispersoid. Dispersal of SiO_2 nano-particles resulted into ~ 4 -fold enhancement in room temperature ionic conductivity along with substantial improvement in mechanical/ thermal stability/ flexibility of film. The complexation of salt/ Dispersal of particles in PEO/ SPE have been confirmed by structural/ spectroscopic/ thermal analysis using XRD/ FTIR/ SEM/ DSC techniques. Ionic parameters were characterized in terms of ionic conductivity (σ), ionic/cationic (t_{ion}/t_+) transference number were evaluated experimentally employing different ac/dc methods. Temperature dependent conductivity measurements have also been carried out to compute activation energy (E_a) from linear fitting of 'log σ - $1/T$ ' Arrhenius plot.

Keywords— Nano-Composite Polymer Electrolyte, fumed silica particle, ionic conductivity, ionic/cationic transference number.

1. INTRODUCTION

Dry polymeric electrolytes, namely Solid Polymer Electrolytes (SPEs) and Nano-Composite Polymer Electrolytes (NCPEs) in thin flexible film form, attracted great deal of technological attentions primarily due to the fact that these films can be potentially employed as electrolytes to fabricate all-solid-state electrochemical power sources viz. batteries, fuel cells, supercaps etc. in any desired size/shape including mini/micro power devices [1-8]. Amongst variety of known polymer electrolytes reported so far, after the discovery of first SPE film in 1973 [1] and practical demonstration of first SPE based battery in 1979 [2], Li^+ -ion conducting polymer electrolytes remained most reliable/consistent as far as their battery applications are concerned. Majority of the batteries, used today in different portable/mobile applications, are Li^+ -ion batteries. However, despite impressive advancements in Li^+ -ion battery technology, there are many limitations and safety issues involved using Li -chemicals in these batteries [9-11]. To circumvent these problems, it is strongly felt that Li -chemicals be replaced by some non-lithium chemicals. Based on the survey of literature [8, 12], Mg^{2+} -ion salts/ Mg -metal can be considered as potential alternate to Li^+ -ion salt/ Li -metal electrode in all-solid-state battery applications. This is mainly due to the reasons that many of the prominent electrochemical characteristics viz. electrochemical equivalence ($Li^+ \sim 7g/eq$, $Mg^{2+} \sim 12.5$

g/eq), negative electrode potential ($Li^+ \sim 3.7V$, $Mg^{2+} \sim 2.36V$ w.r.t. SHE) etc. are almost comparable as well as the ionic radius is nearly same ($Li^+ \sim 0.68 \text{ \AA}$, $Mg^{2+} \sim 0.65 \text{ \AA}$). Moreover, as compared to Li -chemicals, Mg -chemicals are inexpensive, non-toxic, safe, environment friendly etc. However, the current status of all-solid-state batteries based on Mg^{2+} -ion salt complexed SPEs is not much pleasing due to the fact that these SPEs exhibit relatively poor room temperature conductivity (σ_{rt}). Nevertheless, σ_{rt} can be improved significantly by dispersing micro/nano filler particles as II^{nd} -phase dispersoid into SPE which acts as I^{st} -phase host-matrix. These systems are referred to as 2-phase micro/nano Composite Polymer Electrolytes (CPEs) [3]. Furthermore, σ_{rt} can also be alternatively improved by introducing nano-ionic effects [13-14].

The present paper reports the investigations on Mg^{2+} -ion conducting 2-phase NCPE system based on Solid Polymer Electrolyte (SPE) composition: $[80PEO: 20 Mg (CF_3SO_3)_2]$ as I^{st} -phase host and nano particles ($\sim 8nm$) of an inert filler material SiO_2 as II^{nd} -phase dispersoid. In this study, SPE/NCPE films have been prepared by traditional solution cast method. However, similar films were prepared earlier by us using novel hot-press casting technique [12]. In this paper, a comparison has been made on the quality as well as ionic properties of SPE/NCPE films prepared by two casting procedures. From salt-concentration dependent conductivity study on different solution cast films, SPE film: $[80PEO: 20Mg(CF_3SO_3)_2]$ has been identified having relatively higher σ_{rt} -value a

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well as superior mechanical integrity as observed physically. Hence, it has been chosen as Ist-phase host. Dispersing fumed silica nano particles as IInd-phase dispersoid into Ist-phase SPE host, NCPE films have been solution cast. Further, from SiO₂ concentration dependent conductivity measurements NCPE film exhibiting highest room temperature conductivity was identified. This NCPE film has been referred to as Optimum Conducting Composition (OCC). These SPE host and NCPE films have been subjected to different characterization studies.

2. EXPERIMENTAL

To cast SPE/NCPE films by solution cast method, precursor chemicals: Poly(ethylene oxide) PEO (Mw ~6 x 10⁵), (Magnesium trifluoro-methane-sulphonate) Mg (CF₃SO₂)₂ (purity > 99%), fumed silica SiO₂ (> 99%, particle size ~8 nm, surface area ~325 m²/gm, density ~2.6 gm/ mL), procured from Sigma-Aldrich (USA), were used as supplied. Mg-metal to be used as non-blocking electrode in t₊-measurement, was pressed thin pellet of magnesium powder (>99% Sigma Aldrich). Salt and filler particle concentration dependent conductivity measurements were carried out using ac method to identify Ist-phase SPE host and NCPE OCC respectively, as mentioned. The structural/ spectroscopic properties were characterized using XRD (Model: 08 Discover, Bruker)/ FTIR (IR Affinity – 1, Shimadzu). SEM [model: JEOL – JXA 8100] has been used to study the surface morphology of newly synthesized optimum conducting magnesium SPE/ NCPE films. Thermal analysis have done by DSC (Model: Q 200 TA Instrument in static nitrogen atmosphere) techniques. The ion transport property was studied in terms of basic ionic parameters viz. conductivity (σ) and total ionic transference (t_{ion})/ cationic transference (t₊) numbers. These ionic parameters were measured experimentally using different ac/dc techniques e.g. ac Impedance Spectroscopy (IS), Transient Ionic Current (TIC) dc polarization [15] and combined ac/dc [16] techniques for σ, t_{ion}, and t₊ measurements respectively. These techniques have been discussed in previous papers [3, 12]. Temperature dependent conductivity study was also done and the activation energy (E_a) was computed by least square linear fitting of Arrhenius plot: 'log σ - 1/T'.

3. RESULTS AND DISCUSSION

3.1 Ion Transport Characterization Study

Fig. 1 shows salt concentration dependent conductivity variation of different solution cast SPE films. SPE composition: [80PEO: 20Mg(CF₃SO₃)₂], exhibiting relatively higher ionic conductivity as well as its physical overview shows its superior mechanical stability, hence forward selected as Ist-phase host for casting NCPE films. Similar plot for SPE film prepared earlier by hot-press method is redrawn in Fig. 1 for direct comparison [12]. SPE host film: [80PEO: 20 Mg (CF₃SO₃)₂] exhibited σ_r

~1.25 x 10⁻⁶ Scm⁻¹ (solution cast); ~2.77 x 10⁻⁶ Scm⁻¹ (hot-press).

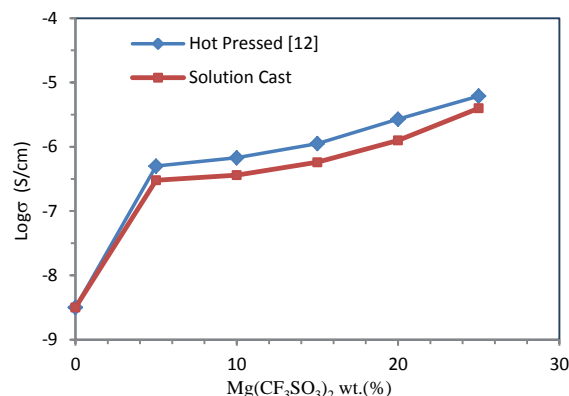


Fig. 1: Salt-concentration dependent conductivity variation for SPE films: [PEO: Mg (CF₃SO₃)₂].

Fig. 2 shows SiO₂ nano-particle concentration dependent conductivity variation for solution cast NCPE films: [80PEO: 20Mg (CF₃SO₃)₂] + x SiO₂, where x = 2,4,6,8,10,12,15 wt. (%). Similar plot for hot-press NCPE films has also been redrawn for direct comparison [12]. One can notice the existence of two σ-maxima at x = 2 & 10 wt. (%) SiO₂ in 'log σ - x' plot for both solution and hot-press cast films. Majority of NCPE films investigated in the past reported the existence of two σ-peaks in their respective 'log σ - x' plot and has been attributed to two kinds of conduction processes operative in this system [17]. Accordingly, first σ-peak (x = 2 wt.%) is due to the increase in mobile ion concentration as a result of dissociation of the salt/ ion aggregates and second σ-peak (x = 10 wt.%) can be related to the formation of space charge double layer region around the insulating filler nano-particles where mobile ions get accumulated at the interfacial boundaries. These boundaries may also get interconnected to form high conducting paths for easy ion migration and resulting into an overall increase in the conductivity. Addition of more filler particles beyond second percolation threshold subsequently decreases the conductivity due to possible blocking effect. One can note, as a consequence of dispersal of nano filler material, an enhancement of more than 2-fold in the room temperature conductivity could be achieved in NCPE OCC film: [80PEO: 20Mg (CF₃SO₃)₂] + 2 SiO₂ with σ_r ~5.81 x 10⁻⁶ S/cm (solution cast); ~5.86 x 10⁻⁶ S/cm (hot pressed) [12]. Table 1 lists σ_r-values for SPE host and NCPE OCC films (prepared by both the casting procedures) along with that of pure PEO film.

Fig. 3 shows 'log σ - 1/T' plot for solution cast and hot press NCPE OCC film. Both plots look almost alike except that σ-values of hot-press cast NCPE OCC film are relatively higher in the high temperature region. It can be noticed that as temperature increased, the conductivity increased gradually upto ~60 °C, followed by an upward jump in the slope ~60–70 °C then increased gradually

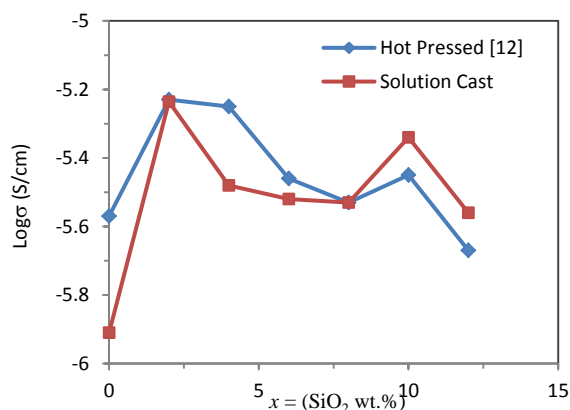


Fig. 2: ‘Logσ – x’ plots for NCPE films: [80PEO: 20Mg (CF₃SO₃)₂] + x SiO₂.

again with temperature. The upward jump in the conductivity is due to well-known semi-crystalline to amorphous phase transition of polymer PEO which occurs at ~65 °C. The activation energy (E_a) values computed for SPE host and NCPE OCC films in the lower temperature region are listed in Table 1. t_{ion} -value for solution cast SPE host/ NCPE OCC films, evaluated by Transient Ionic Current (TIC) technique [15] as mentioned, was found to be ~0.98, also listed in Table 1 along with those for hot-press SPE host/ NCPE OCC films [12]. However, the cations should be significantly high for battery application [3, 18]. t_+ value (i.e. cationic (Mg²⁺) transport number) for both solution cast (present study) and hot-press [12] NCPE OCC films evaluated using combined ac/dc technique [16], were ~0.30 and ~0.31 respectively and listed in Table 1. On comparing these ionic parameter values listed in Table 1, one can clearly note that they are almost comparable to each other. However, on comparing merits/demerits of the two film casting procedures, the solution cast method is a wet/relatively more lengthy procedure and involves high consumption of chemicals while, hot-press method is dry/solution free, quicker and low chemical consumption procedure, hence, can be preferred over traditional method [12].

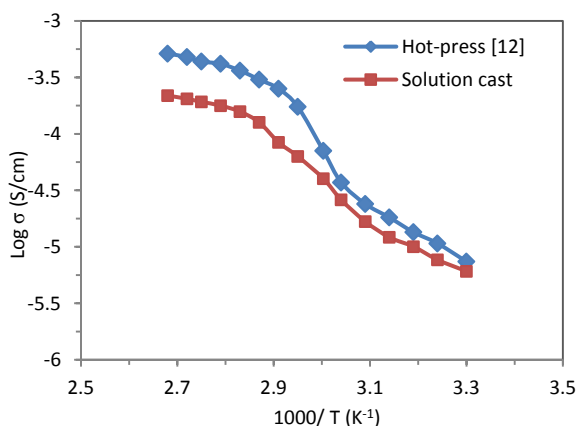


Fig. 3: ‘Logσ – 1/T’ plot for NCPE host film: [80PEO: 20 Mg(CF₃SO₃)₂] + 2SiO₂.

Table 1: Room temperature (27°C) conductivity (σ_{rt}) values for SPE host/ NCPE OCC along with that of pure PEO films. The values of E_a , t_{ion} & t_+ are also listed.

Film	Casting Method	σ_{rt} (S/cm)	E_a (eV)	t_{ion}	t_+
Pure PEO		3.32×10^{-9}	-	-	-
SPE host: [80PEO: 20Mg (CF ₃ SO ₃) ₂]	Solution cast	1.25×10^{-6}	0.58	0.98	-
	Hot-press	2.27×10^{-6}	0.40	0.98	-
NCPE OCC: [80PEO: 20Mg (CF ₃ SO ₃) ₂] + x SiO ₂	Solution cast	6.81×10^{-6}	0.42	0.98	0.30
	Hot-press	6.86×10^{-6}	0.36	0.98	0.31

3.2 Material Characterization Study

Fig. 4 shows XRD patterns for SPE host/ NCPE OCC films prepared by solution cast method along with that of pure PEO film. It can be clearly noted that the intensity of some prominent peaks of PEO decreased significantly. On a closer inspection, one can also note the broadening of the peaks in the XRD patterns of SPE host (b) and NCPE OCC (c). It is noticed that the crystalline peaks have been observed at 19° and 23° for the pure PEO. Comparison of these peak patterns clearly confirmed the complexation of salt in the polymeric host, as many of the peaks related to the salt appeared along with PEO peaks, although slightly displaced with decreased intensity. The positions of two main peaks of PEO remained almost intact even after complexation of salt in PEO in SPE and dispersal of SiO₂ (in NCPE). However, the intensity of PEO main peaks has been decreased substantially specially in NCPE film. This is indicative of decrease in degree of crystallinity and/ or increase of amorphousity in PEO.

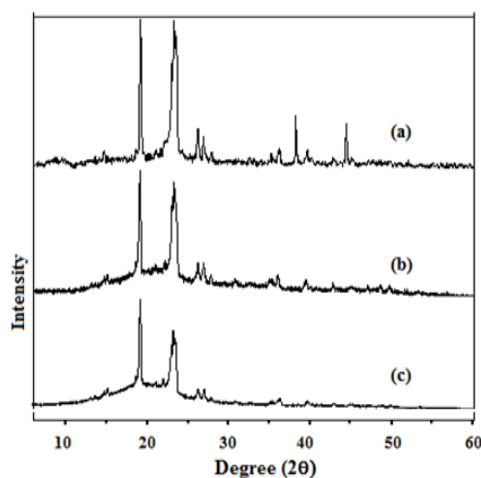


Fig. 4: XRD patterns for films: (a) Pure PEO, (b) SPE host: [80PEO: 20Mg (CF₃SO₃)₂], (c) NCPE OCC: [80PEO: 20Mg (CF₃SO₃)₂] + x SiO₂

Complexation of salt in PEO/dispersal of IInd-phase filler particles in Ist-phase SPE host have further been confirmed by FTIR spectroscopy. FTIR spectra for different NCPE OCC films and those of pure PEO/ SPE host are shown in Fig. 5 for solution cast films. The existence of characteristic vibrational responses of pure PEO at wavenumber (cm^{-1}) at 2238, 2163 and 1963 indicates PEO uniqueness in all films. However, peak intensity at $\sim 525\text{--}530$ and ~ 1200 cm^{-1} related to C-O-C bending and stretching respectively in pure PEO, decreased after salt complexation in SPE host and/or dispersal of filler particles in NCPE OCC films. Some other indicative bands in the range 750–950, ~ 1820 , $\sim 2900\text{--}3000$, ~ 1475 , ~ 845 cm^{-1} which correspond to symmetrical/ asymmetrical stretching/ vibration of CH_2 group, CH_2 bending, CH_2 rocking etc. in PEO have also changed after salt- complexation. The changes in the spectral responses were akin to those as already reported earlier [12].

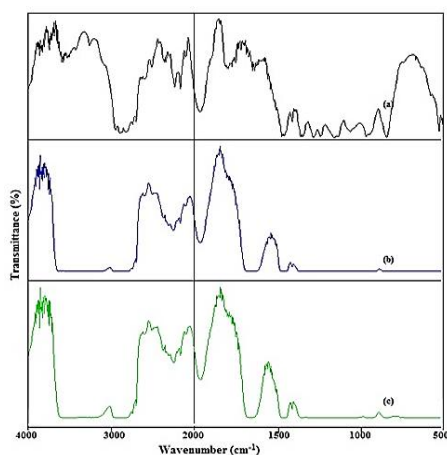


Fig. 5: FTIR spectra for films: (a) Pure PEO, (b) SPE host: [80PEO: 20Mg (CF_3SO_3) $_2$], (c) NCPE OCC: [80PEO: 20Mg (CF_3SO_3) $_2$] + x SiO_2

The surface morphology of solution cast SPE host and NCPE OCC films are shown in Fig. 6. In SEM images, there exists distinct spherulites texture separated by boundary regions. This is indicative of crystalline lamellar structure while the amorphousity of the polymer is shown by boundary regions. Different textures have been observed due to dispersal of different active/ passive filler material particles as well as film casting procedures.

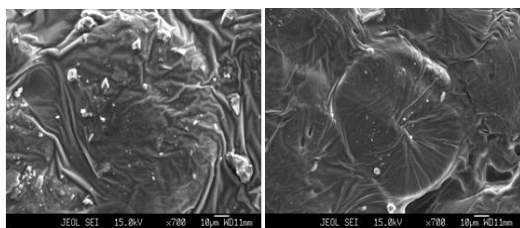


Fig. 6: SEM for solution cast: (a) SPE host: [80PEO: 20 Mg (CF_3SO_3) $_2$]; (b) NCPE OCC film: [80PEO: 20 Mg (CF_3SO_3) $_2$] + 2 SiO_2

Fig. 7 shows DSC thermal spectra for solution cast SPE host/ NCPE OCC along with that of pure PEO films. The endothermic peak $\sim 69^\circ\text{C}$ in DSC thermogram corresponds to usual semi-crystalline to amorphous phase transition temperature of pure PEO. These endothermic peaks shifted towards the lower temperature region $\sim 57^\circ\text{C}$ for curve b & c respectively. An arrow marked shallow endothermic peak in temperature region ~ -60 to -50°C is related to glass transition temperature (T_g). It is well reported in the literature that as a result of complexation of salt in PEO and/or dispersal of filler particles in SPE host, these peaks usually shift. We observed that the peak $\sim 60\text{--}70$ $^\circ\text{C}$ shifted towards lower temperature while T_g shifted towards higher temperature region. A broad endothermic hump just after melting temperature of SPE/ NCPE films is indicative of increased degree of amorphousity in PEO.

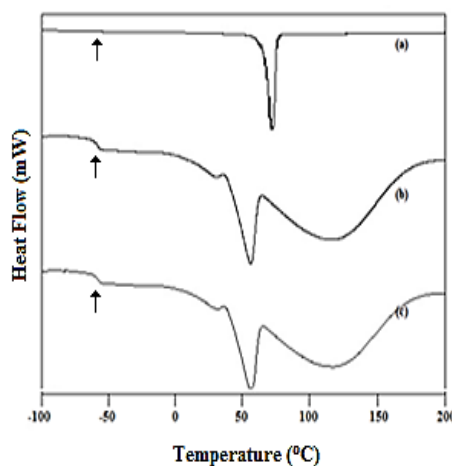


Fig. 7: DSC thermogram for films: (a) Pure PEO, (b) SPE host: [80PEO: 20Mg (CF_3SO_3) $_2$], (c) NCPE OCC: [80PEO: 20Mg (CF_3SO_3) $_2$] + x SiO_2

4. CONCLUSIONS

Mg^{2+} -ion conducting NCPE film has been synthesized by solution cast method. The ion transport/materials properties have been characterized and compared with those of similar NCPE film prepared by hot-press technique. It has been found that ion transport parameters of NCPE films prepared by two different casting procedures are quite comparable to each other. However, on the basis of comparing merits/demerits of two casting procedures, it can be concluded that hot-press method can be preferred over solution cast method for casting SPE/NCPE films. The complexation of salt/ dispersal of filler in PEO/ SPE host have been confirmed by XRD/FTIR/DSC analysis. The total ionic (t_{ion}) and cationic (t_+) transport numbers have been evaluated independently using dc polarization and combined ac/dc techniques. Newly synthesized Mg^{2+} -ion conducting NCPE film can be used as non-lithium polymer electrolyte for the fabrication of all-solid-state batteries.

ACKNOWLEDGEMENT

One of the author Dr. Dinesh K Sahu sincerely thanks to Director, State Forensic Science Laboratory, Raipur, India. for financial/ technical support.

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