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

Dinesh K. Sahu$^{1}$, Y.K. Mahipal$^{2}$, Ram K. Gupta$^{3}$ and R.C. Agrawal$^{2}$

$^{1}$State Forensic Science Laboratory, Raipur, India.
$^{2}$SoS in Physics & Astrophysics, Pt. R. S. University, Raipur.
$^{3}$Govt. Engineering College, Raipur

Abstract—Present paper reports the fumed silica dispersed Mg$^{2+}$-conducting Nano Composite Polymer Electrolyte films: [80PEO: 20Mg(CF$_3$SO$_2$)$_2$] + xSiO$_2$, where $x = 0, 2, 4, 6, 8, 10, 12$....wt.%, synthesized by solution cast technique. Solid Polymer Electrolyte composition: [80PEO: 20Mg(CF$_3$SO$_2$)$_2$], identified as one of the high ion conducting film with better physical stability, used as 1$^{st}$-phase host matrix and fumed nano-sized (~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 complexity 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 ($\sigma$), ionic/cationic ($t_{\text{ion}}/t_{\text{cat}}$) 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$\sigma$ - 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$^+$ ~7g/eq, Mg$^{2+}$ ~12.5 g/eq), negative electrode potential (Li$^+$ ~3.7V, Mg$^{2+}$ ~2.36V w.r.t. SHE) etc. are almost comparable as well as the ionic radius is nearly same (Li$^+$ ~0.68 Å, Mg$^{2+}$ ~0.65 Å). Moreover, as compared to Li$^+$-chemicals, Mg$^{2+}$-chemicals are inexpensive, non-toxic, safe, environment friendly etc. However, the current status of all-solid-state batteries based on Mg$^{2+}$-ion salt complexes SPEs is not much pleasing due to the fact that these SPEs exhibit relatively poor room temperature conductivity ($\sigma_n$). Nevertheless, $\sigma_n$ 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, $\sigma_n$ 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$_3$SO$_2$)$_2$] as I$^{st}$-phase host and nano particles (~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$_3$SO$_2$)$_2$] has been identified having relatively higher $\sigma_t$-value a
well as superior mechanical integrity as observed physically. Hence, it has been chosen as \( 1^\text{st} \) phase host. Dispersing fumed silica nano particles as \( 2^\text{nd} \) phase dispersed into \( 1^\text{st} \) phase SPE host, NCPE films have been solution cast. Further, from \( \text{SiO}_2 \) 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 \( \sim 6 \times 10^4 \)), (Magnesium trifluoro-methane-sulphonate) \( \text{Mg} (\text{CF}_3\text{SO}_3)_2 \) (purity > 99%), fumed silica \( \text{SiO}_2 \) (> 99%, particle size \( \sim 8 \text{ nm} \)), were used as supplied. \( \text{Mg} \)-metal to be used as non-blocking electrode in \( t_e \), -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 \( 1^\text{st} \) 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 (\( \sigma \)) and total ionic transference (\( t_{\text{ion}} \))/ 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 \( \sigma \), \( t_{\text{ion}} \) 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: ‘\( \log \sigma - 1/T \)’.

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(\( \text{CF}_3\text{SO}_3 \))_2], exhibiting relatively higher ionic conductivity as well as its physical overview shows its superior mechanical stability, hence forward selected as \( 1^\text{st} \) 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 (\( \text{CF}_3\text{SO}_3 \))_2] exhibited \( \sigma_{\text{rt}} \sim 1.25 \times 10^{-6} \text{ S/cm} \) (solution cast); \( \sim 2.77 \times 10^{-6} \text{ S/cm} \) (hot-press).

![Fig. 1: Salt-concentration dependent conductivity variation for SPE films: [PEO: Mg (\( \text{CF}_3\text{SO}_3 \))_2].](image)

Fig. 2 shows \( \text{SiO}_2 \) nano-particle concentration dependent conductivity variation for solution cast NCPE films: [80PEO: 20Mg(\( \text{CF}_3\text{SO}_3 \))_2] + \( x \) \( \text{SiO}_2 \), where \( x = 2, 4, 6, 8, 10, 12, 15 \text{ wt. }\% \). Similar plot for hot-press NCPE films has also been redrawn for direct comparison [12]. One can notice the existence of two \( \sigma \)–maxima at \( x = 2 \& 10 \text{ wt. }\% \) \( \text{SiO}_2 \) in ‘\( \log \sigma - x \)’ plot for both solution and hot-press cast films. Majority of NCPE films investigated in the past reported the existence of two \( \sigma \)–peaks in their respective ‘\( \log \sigma - x \)’ plot and has been attributed to two kinds of conduction processes operative in this system [17]. Accordingly, first \( \sigma \)–peak (\( x = 2 \text{ wt.}\% \)) is due to the increase in mobile ion concentration as a result of dissociation of the salt/ ion aggregates and second \( \sigma \)–peak (\( x = 10 \text{ wt.}\% \)) 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(\( \text{CF}_3\text{SO}_3 \))_2] + 2 \( \text{SiO}_2 \) with \( \sigma_{\text{rt}} \sim 5.81 \times 10^{-6} \text{ S/cm} \) (solution cast); \( \sim 5.86 \times 10^{-6} \text{ S/cm} \) (hot pressed) [12]. Table 1 lists \( \sigma_{\text{rt}} \) values for SPE host and NCPE OCC films (prepared by both the casting procedures) along with that of pure PEO film.

Fig. 3 shows ‘\( \log \sigma - 1/T \)’ plot for solution cast and hot press NCPE OCC film. Both plots look almost alike except that \( \sigma \)-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 up to ~60 °C, followed by an upward jump in the slope ~60–70 °C then increased gradually.
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].

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 19º and 23º 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 SiO_2 (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 amorphosity in PEO.

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

<table>
<thead>
<tr>
<th>Film</th>
<th>Casting Method</th>
<th>σ_r (S/cm)</th>
<th>E_a (eV)</th>
<th>t_ion</th>
<th>t_+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PEO</td>
<td></td>
<td>3.32 x 10^{-9}</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SPE host: [80PEO: 20Mg (CF_3SO_3)_2]</td>
<td>Solution cast</td>
<td>1.25 x 10^{-6}</td>
<td>0.58</td>
<td>0.98</td>
<td>-</td>
</tr>
<tr>
<td>Hot-press [12]</td>
<td></td>
<td>2.27 x 10^{-6}</td>
<td>0.40</td>
<td>0.98</td>
<td>-</td>
</tr>
<tr>
<td>NCPE OCC: [80PEO: 20Mg (CF_3SO_3)_2] + x SiO_2</td>
<td>Solution cast</td>
<td>6.81 x 10^{-6}</td>
<td>0.42</td>
<td>0.98</td>
<td>0.30</td>
</tr>
<tr>
<td>Hot-press [12]</td>
<td></td>
<td>6.86 x 10^{-6}</td>
<td>0.36</td>
<td>0.98</td>
<td>0.31</td>
</tr>
</tbody>
</table>
Complexation of salt in PEO/dispersal of 1nnd-phase filler particles in 1st-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 \(\sim 525–530\) and \(\sim 1200\) 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, \(\sim 1820\), \(\sim 2900–3000\), \(\sim 1475\), \(\sim 845\) 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\(_3\)SO\(_3\))]\(_2\), (c) NCPE OCC: [80PEO: 20Mg (CF\(_3\)SO\(_3\))]\(_2\) + 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 amorphosity 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\(_3\)SO\(_3\))]\(_2\); (b) NCPE OCC film: [80PEO: 20 Mg (CF\(_3\)SO\(_3\))]\(_2\) + 2SiO\(_2\)

Fig. 7: DSC thermogram for films: (a) Pure PEO, (b) SPE host: [80PEO: 20Mg (CF\(_3\)SO\(_3\))]\(_2\), (c) NCPE OCC: [80PEO: 20Mg (CF\(_3\)SO\(_3\))]\(_2\) + 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/DIR/SC analysis. The total ionic (\(t_{\text{ion}}\)) 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.

REFERENCES