Effect of Nanoparticles on Electrical and Structural Properties of Magnesium Ion Conducting Polymer Electrolyte

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Abstract. In the present work, effect of nanoparticles (TiO\textsubscript{2}, MgO, ZnO or Al\textsubscript{2}O\textsubscript{3}) on solid polymer electrolyte (SPE) comprising polyvinyldienefluoride-co-hexafluoropropylene (PVDF-HFP) and magnesium chloride (MgCl\textsubscript{2}) has been explored. These films have been synthesized using the universal solution cast technique. Impedance Spectroscopy, X-ray Diffraction (XRD), Fourier transform infrared (FTIR) Spectroscopy and Differential scanning calorimetry-Thermogravimetric analysis (DSC-TGA) have been carried out to characterize transport, structural and thermal properties of these NCPE films. The highest conductivity value is 1.24\times10^{-4} \text{ S/cm} at 110 \degree \text{C} with activation energy \sim0.26eV for OCC of NCPE. The dielectric study was also done for OCC of NCPE in wide range of frequency and temperature. Electrochemical cell has been fabricated using cell configuration Mg|NCPE|C-cell and various cell parameters have been calculated from discharge characteristics.

INTRODUCION

Since 1991, Lithium ion conducting rechargeable batteries are gaining attention to fulfill energy requirements of our daily needs (hybrid electric vehicles, laptop, cell phones, and camera etc).[1] Li ion conducting polymer electrolytes used in battery device, studied by various researchers and faced problem like high cost and highly reactive nature so working with lithium is quite challenging. [2] This cause the search of other substitute like sodium, potassium and divalent ions (Mg\textsuperscript{2+} and Zn\textsuperscript{2+}) conducting polymer electrolytes for battery application. Rammohan et al. (2015) reported sodium ion conducting polymer electrolyte (PVA/PEG:NaClO\textsubscript{4} with ionic conductivity of \sim2.41\times10^{-6} \text{ S/cm}), prepared by solution casting method.[3] Potassium ion (K\textsuperscript{+}) conducting electrolyte reported by Murugendrappa et al. [4]with poly (ethylene glycol) (PEG) polymer as host with different salt (salt like KCl, KBr and KI ) complexation in it and effect of different salt on polymer with change in temperature from 299 to 331 K. They observed that when KCl and KBr mixed in PEG its conductivity value increased by about 2.5 times for KCl and about 6.25 times for KBr, while on mixing KI its conductivity reduced about 0.05 times its pure component value. Magnesium ion (Mg\textsuperscript{2+}) conducting polymer electrolyte reported by Ravindran et al. (2012) having composition: PEG-[Mg (CH\textsubscript{3}COO)\textsubscript{2}- Mg(NO\textsubscript{3})\textsubscript{2}]: [40-45-(7.5-7.5)] system, synthesized by solution casting method and have maximum ionic conductivity \sim9.852\times10^{-6} \text{ S/cm} at room temperature.[5] Noto et al. also reported Mg\textsuperscript{2+} ion conducting polymer electrolyte (PEG400/(MgCl\textsubscript{2})\textsubscript{2} (0.00329\leq x \leq0.7000) in eight different compositions). They studied the mechanism of ionic motion in polymer. [6] Now days PVDF based electrolyte gaining attention due to its high dielectric constant in place of PEG. Leons et al. (2013) reported PVDF based solid polymer electrolyte: \textit{PVDF-TrFE-NiTf\textsubscript{2}}, prepared by solvent casting method and they got maximum value of ionic conductivity i.e. 1.7x10^{-5} \text{ S/cm} for 32 wt% of ionic liquid at 110\degree\text{C}.[7] Rechargeable magnesium batteries with good efficiency using solid nanocomposite polymer electrolyte thin films are interesting area of research. By using thermally and mechanically stable electrolytes, desirable shape, size and low weight batteries can be developed. From literature survey, it reveals that nanoparticles (Al\textsubscript{2}O\textsubscript{3}, MgO, ZnO, TiO\textsubscript{2}, CuO and
SiO₂ etc.) dispersion in solid polymer electrolyte enhances its ionic conductivity in 2-3 order, mechanical, thermal and electrochemical stability. In our present study, PVDF-HFP as host polymer, MgCl₂ as ionic salt and MgO, ZnO, TiO₂ and Al₂O₃ nanoparticles as dispersoid are used and thin films of NCPE has been synthesized by solution casting method. [3-8]

In our earlier work, we have reported a series of 70PVDF-HFP: 30MgCl₂ solid polymer electrolyte system. [8] In the present work, we have reported the effect of various nanoparticles on temperature dependent conductivity, thermal and structural properties of 70PVDF-HFP:30MgCl₂ solid polymer electrolyte. Impedance Spectroscopy technique was employed to finding ionic conductivity and dielectric constant. XRD Analysis has done to find crystallinity and Differential scanning Calorimetry-Thermogravimetric analysis (DSC-TGA) to study thermal stability of the solid electrolytes. These NCPE films were also characterized by FTIR spectroscopy and battery discharge characteristics.

MATERIALS AND METHODS

Solution casting method used for synthesis of SPE and NCPE films using AR grade chemicals: PVDF-HFP with a purity of 99% (M.W. = 400000, Aldrich, USA), MgCl₂ (M.W. = 203.3) and various amount of Titania TiO₂, alumina Al₂O₃, MgO and ZnO nanoparticles (<50nm, M.W. = 79.82, 101.9, 40.30 and 81.38). MgCl₂ salt was dried in oven for 24 hrs to remove moisture then appropriate amount of PVDF-HFP and MgCl₂ were weighted and added into DMF and then stirred for ~24 hrs at 50 °C until homogeneous solution obtained this solution named as solid polymer electrolyte (SPE or S0 or 70PVDF-HFP:30MgCl₂), for preparing NCPE – add ceramic filler into SPE solution and stir again for 24 hrs then cast obtained solution in petri dish and dried for ~72hrs in oven maintained at 50 °C to obtain free standing film. Obtained films were named as S1, S2, S3 and S4 reported in Table 1 with composition. Carbon, Iodine and KI are used for preparing Carbon cell. Magnesium metal used for preparing test cell with cell configuration Mg|Polymer electrolyte|Carbon cell (C+I₂+ electrolyte in 5:5:1 ratio).

Structural characterization of solid polymer electrolyte and nanocomposite polymer electrolyte thin films were performed by XRD (Bruker, D8 Advance X-ray diffractometer with CuKα source having λ=1.54 Å), thermal study was done by DSC-TGA (Simultaneous Thermal Analyzer, 449F1 Jupiter NETZSCCH), and Impedance Spectroscopy (HIOKI, model no. 3532-50) by LCR Meter respectively. FTIR spectra were obtained (Bruker, alpha-II, FTIR spectrophotometer) in frequency range 500-4000 cm⁻¹. Battery testing of electrolytes were done by fabricating a cell with cell configuration Mg|Polymer electrolyte|Carbon cell (C+I₂+electrolyte in 5:5:1 ratio) and various parameters were also calculated from discharge characteristics.

RESULTS AND DISCUSSIONS

XRD Study

X-ray diffraction patterns of OCC of SPE i.e. 70PVDF-HFP: 30MgCl₂ and NCPE thin films with various concentrations of nanoparticles dispersed in SPE are shown in Figure 1. From XRD patterns of different NCPE films, it was observed that a broad peak around 20.3° found to decrease in intensity and peaks at 31.73°, 34.4°, 36.2°, 46.4°, 57.8°, 62.7°, 66.7° and 69.4° appear in NCPE films with composition 70PVDF-HFP: 30MgCl₂:3ZnO due to dispersion of ZnO nanoparticles. Similarly peak at 42° in 70PVDF-HFP: 30MgCl₂:3MgO, peaks at 27°, 39° and 56° in 70PVDF-HFP: 30MgCl₂:3TiO₂ and peaks at 23°, 36.9°, 44.4° and 58.3° in 70PVDF-HFP: 30MgCl₂:2Al₂O₃ are appeared in NCPE films confirms formation of complex. The interaction of nano-sized filler particles with polymer matrix lead to decrease in intermolecular interactions among the polymer chain, this will increase in amorphous nature of polymer electrolyte. Average crystallite size(calculated from Scherer relation for studying reduction in crystallinity) of NCPEs is summarized in Table 1.
FIGURE 1. XRD patterns of SPE and NCPE films with various concentrations of nanoparticles dispersed in SPE.

FTIR

FTIR is an important technique which analyzes the chain structure of polymer and ion-polymer interactions at molecular level. The vibrational bands of FTIR spectra results from vibrational motion of individual bonds or group in a molecule. Any change occurring in bonding situation of molecule (polymer chain) results in change in vibrational frequency position of prominent characteristic bands appearing in the spectra. FTIR spectra of pure polymer, SPE and NCPE thin films with various nanoparticles dispersed in SPE are shown in Figure 2. Position of peaks present in PVDF-HFP are at 2358 cm\(^{-1}\), 1400.10 cm\(^{-1}\), 1175.78 cm\(^{-1}\), 874.30 and 774 cm\(^{-1}\) corresponding to CH\(_2\) symmetric stretching, CH\(_2\) wagging, symmetrical stretching of -CF\(_2\)- and alpha phase of PVDF-HFP respectively. It was observed from FTIR spectra of SPE peak shifted from 1386 to 1396 cm\(^{-1}\) due to C-F- Mg interaction, this shifting of peak may be due to addition of salt into pure PVDF-HFP, hence formation of complex confirmed or ion polymer interaction takes place. In case of FTIR spectra of NCPE peak intensity diminished at 1208 cm\(^{-1}\) due to –CF\(_2\)- Mg-nanoparticles interaction. On dispersing nanoparticles into SPE no significant changes were observed in terms of appearance of new peaks or absence of existing peaks, only intensity of peaks at 548, 970, 1208 and 2358 cm\(^{-1}\) got decreased confirm formation of complex.

FIGURE 2. FTIR patterns for pure PVDF-HFP, SPE i.e. 70PVDF-HFP:30MgCl\(_2\) and NCPE dispersed with various concentrations of nanoparticles.
DSC-TGA analysis

DSC curves of SPE and NCPE thin films dispersed with various concentrations of nanoparticles in SPE i.e. 70PVDF-HFP: 30MgCl₂ are displayed in Figure 3(a). It was observed from Figure 3(a) that melting temperature of NCPE (128°C) was lower than that of SPE (145°C), this indicates that there is decrease in melting temperature of polymer electrolyte on addition of nano-fillers resulting from micro-Brownian motion of main chain backbone (during formation of polymer electrolyte at high temperatures, interaction of polymer chain with ions and nano-filler particles takes place, which disturbs polymer backbone). Similarly degree of crystallinity was also decreases on increasing concentration of filler, indicates increase in amorphous phase as well as conductivity value of electrolyte. Figure 3(b) represents TGA curves of SPE and NCPE. It is clearly seen from figure that the polymer electrolyte films reveals two main weight loss regions. In the first region, 60-110 °C, mass loss (Δm₁ ~ 3 wt%) may be due to evaporation of water, in second region i.e. 311-385°C, mass loss (ΔmII ~20 wt%) may be due to degradation of C-F unit present in PVDF-HFP, indicates thermal stability of polymer material. OCC of NCPE has lowest mass loss i.e. 30wt%, this infers that this system is most stable and also has highest ionic conductivity and also confirmed by XRD studies.

For understanding the interactions of ions and nanoparticles with polymer matrix in nanocomposite polymer electrolytes, we proposed a phenomenological model as shown in Scheme 1. Scheme 1 shows i) pure polymer matrix with line Structure of PVDF, ii) polymer electrolyte complex having polymer + ionic salt, iii) Nanocomposite polymer electrolyte having low concentration of nanoparticles in polymer electrolyte and iv) aggregation of nanoparticles in polymer electrolyte when nanoparticles present in large amount. This scheme also explains about conductivity behavior of electrolytes i.e. on addition of salt and nano-filler in the polymer, ionic conductivity value increases.

**FIGURE 3(a).** DSC curves of SPE with composition 70PVDF-HFP: 30MgCl₂ and NCPE with various concentrations of nanoparticles in SPE and (b). TGA curve of SPE and NCPE with various concentrations of nanoparticles in SPE.

**SCHEME 1.** Possible interactions of ions and nanoparticles with polymer matrix within nanocomposite polymer electrolyte.
Conductivity Analysis

Figure 4 shows Log $\sigma$ vs. $1/T$ (Arrhenius) plot of SPE and NCPE films with various concentrations of nanoparticles in SPE and it was observed that as temperature of polymer electrolyte increase polymer get expand and produce free volume which enhance ion transport and increases in conductivity. Nature of curve of electrolyte films were explained by Arrhenius equation i.e. $\sigma=\sigma_0 \exp(E_a/k_B T)$ where $\sigma$- ionic conductivity, $\sigma_0$-pre-exponential factor, $E_a$ - activation energy, $k_B$- Boltzmann constant and $T$- temperature respectively. Table 1 summarizes ionic conductivity value and activation value.

**TABLE 1.** Ionic conductivity, Activation energy and Crystallites size of NCPEs-

<table>
<thead>
<tr>
<th>Polymer electrolyte</th>
<th>Sample No.</th>
<th>Ionic conductivity ($\sigma$) (S/cm)</th>
<th>Activation energy ($E_a$) (eV)</th>
<th>Crystallite Size L (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70PVDF-HFP:30MgCl$_2$</td>
<td>S0</td>
<td>4.62x10$^{-7}$</td>
<td>0.45</td>
<td>86.00</td>
</tr>
<tr>
<td>70PVDF-HFP:30MgCl$_2$ : 3 MgO</td>
<td>S1</td>
<td>1.01x10$^{-5}$</td>
<td>0.30</td>
<td>44.45</td>
</tr>
<tr>
<td>70PVDF-HFP:30MgCl$_2$ : 3 ZnO</td>
<td>S2</td>
<td>7.25x10$^{-5}$</td>
<td>0.26</td>
<td>29.90</td>
</tr>
<tr>
<td>70PVDF-HFP:30MgCl$_2$ : 3 TiO$_2$</td>
<td>S3</td>
<td>3.01x10$^{-5}$</td>
<td>0.27</td>
<td>34.32</td>
</tr>
<tr>
<td>70PVDF-HFP:30MgCl$_2$ : 2 Al$_2$O$_3$</td>
<td>S4</td>
<td>7.90x10$^{-6}$</td>
<td>0.31</td>
<td>38.51</td>
</tr>
</tbody>
</table>

Dielectric analysis

Dielectric behavior of material is expressed by the equation i.e. $\varepsilon =\varepsilon' + j\varepsilon''$ where, $\varepsilon'$ is real part (dielectric constant) and $\varepsilon''$ is imaginary part (dielectric loss) of dielectric constant, $Z$ is complex impedance, $C$ is capacitance of a material, $C_p$ is parallel capacitance, $t$ is distance between the electrodes and $A$ is area of sample, $\sigma$ is ionic conductivity and $w$ represents angular frequency. Figure 5(a) shows variation of real part of dielectric constant with frequency and Figure 5(b) shows variation of imaginary part of dielectric constant with frequency at different temperatures for OCC of NCPE 70PVDF-HFP: 30MgCl$_2$ :3ZnO. As frequency increase dielectric constant decreases and got saturated at higher frequencies, this may be due to inability of dipoles rotate rapidly or electrical relaxation.
Discharge Studies

Discharge characteristics of an electrochemical device gives information about cell parameters so we have fabricated a battery of our material in cell configuration Mg|NCPE|C-cell (C+I₂+electrolyte, 5:5:1) and discharge it at 100kΩ. It was observed from Figure 6 that initial sharp decrease in voltage with time may be due to polarization or formation of thin layer of magnesium salt at electrode electrolyte interface. Cell parameters such as an open circuit voltage (OCV), current density, energy and power density etc. were calculated and are reported in Table 2. For all the samples area of cell is constant i.e. 1.33cm². From the table it is clear that the parameters of the cell for the system 70PVDF-HFP: 30MgCl₂:3ZnO was seems to be better in comparison with all others.
**TABLE 2.** Cell parameters of Mg|NCPE|C cell at 100kΩ-

<table>
<thead>
<tr>
<th>Cell Parameters</th>
<th>OCV (V)</th>
<th>Cell Weight (gm)</th>
<th>Current density (μA/cm(^2))</th>
<th>Discharge time (h)</th>
<th>Discharge Capacity (mAh)</th>
<th>Power density (W/Kg)</th>
<th>Energy Density (Wh/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>1.7</td>
<td>0.62</td>
<td>38.84</td>
<td>75</td>
<td>3.79</td>
<td>0.10</td>
<td>11.9</td>
</tr>
<tr>
<td>S1</td>
<td>1.79</td>
<td>0.64</td>
<td>77.8</td>
<td>96</td>
<td>9.25</td>
<td>0.25</td>
<td>27.01</td>
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<tr>
<td>S2</td>
<td>1.85</td>
<td>0.65</td>
<td>81.01</td>
<td>122</td>
<td>10.9</td>
<td>0.31</td>
<td>32.3</td>
</tr>
<tr>
<td>S3</td>
<td>1.8</td>
<td>0.66</td>
<td>73.01</td>
<td>99</td>
<td>8.01</td>
<td>0.22</td>
<td>22.9</td>
</tr>
<tr>
<td>S4</td>
<td>1.74</td>
<td>0.63</td>
<td>59.9</td>
<td>94</td>
<td>8.0</td>
<td>0.19</td>
<td>18</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

Nanocomposite polymer electrolytes dispersed with various concentrations of ZnO, MgO, TiO\(_2\) and Al\(_2\)O\(_3\) nanoparticles in SPE 70PVDF-HFP: 30MgCl\(_2\) have been synthesized by using solution cast technique. The XRD and FTIR analysis confirms the nanocomposite polymer electrolyte formation. Composition and temperature dependant ionic conductivity studies give highest ionic conductivity for 70PVDF-HFP: 30MgCl\(_2\): 3ZnO system i.e. $\sigma$~7.25x10\(^{-5}\) S/cm at room temperature and 1.24x10\(^{-4}\) S/cm at 110 °C with lowest activation energy ~0.26eV. DSC-TGA curves of the NCPE- 70PVDF-HFP: 30MgCl\(_2\):3ZnO system is most stable in nature with lowest melting point~128 °C and lowest mass loss of ~30%. 70PVDF-HFP:30MgCl\(_2\):3ZnO NCPE system has maximum dielectric constant observed from temperature dependant dielectric studies. From battery performance of all electrolytes, 70PVDF-HFP:30MgCl\(_2\):3ZnO system has highest OCV~ 1.85V, suggests this systems can be suitable candidate for fabrication of Electrochemical Devices in near future.

**ACKNOWLEDGMENTS**

We gratefully acknowledge the kind support of Dept. of Chemistry of Dr. Harisingh Gour Vishwavidyalaya for providing the facility of Impedance analyzer and FTIR spectrophotometer. Authors also thanks to the DST-(PURSE)-II phase programme for extending the facility of Simultaneous Thermal Analyzer.

**REFERENCES**