Hot-pressed nano-composite polymer electrolytes: (1-x) [70PEO:30KBrO₃]:xSiO₂

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Received 28 February 2011; revised 22 July 2011; accepted 11 August 2011

The electrical and electrochemical properties of PEO-based hot-pressed nano-composite polymer electrolyte (NCPE) membranes: (1-x) [70PEO:30KBrO₃]:xSiO₂, where x = 0-20 wt. (%), have been studied. NCPE membranes have been casted using a novel hot-press technique in place of the traditional solution cast method. The conventional Solid Polymer Electrolyte (SPE) composition: (70PEO: 30KBrO₃), identified as the highest conducting film at room temperature, has been used as 1ˢᵗ-phase host matrix and nano-size (~8 nm) particles of SiO₂ as 2ⁿᵈ-phase dispersoid. As a consequence of dispersal of SiO₂ in SPE host, a conductivity enhancement of an order of magnitude was achieved in NCPE film: [95(70PEO:30KBrO₃):5SiO₂]. This composition has been referred to as Optimum Conducting Composition (OCC). Materials characterization has been done with the help of SEM and DSC techniques. The ion transport behaviour in NCPE membranes have been discussed on the basis of conductivity (σ), mobility (µ), mobile ion concentration (n) and ionic transference number (tᵢₒᵣ) studies. The temperature dependent conductivity studies have also been done to compute the activation energy (Eₐ) values by least square linear fitting of ‘logσ=1/T’ Arrhenius plots. Thin film solid-state polymeric batteries were fabricated using NCPE OCC as electrolyte and the cell-potential discharge characteristics were studied under different load conditions.

Keywords: Hot-pressed polymer electrolytes, ionic conductivity, Scanning electron microscope, Differential scanning calorimetry

1 Introduction

The ion conducting Solid Polymer Electrolytes (SPEs) show tremendous technological promises to develop all-solid state electrochemical power sources viz. flexible/compact/light-weight/leak-proof thin film micro-batteries of desirable shapes/sizes. The conduction mechanism in polymer electrolytes was reported for the first time in 1973⁵, while, the first practical SPE battery based on ‘Poly (ethylene oxide) (PEO)-Li’-ion salt complex’ was demonstrated in 1979⁶. Since then, a wide variety of SPEs, involving different kinds of mobile ions viz. Li⁺, H⁺, Na⁺, K⁺, Ag⁺ etc. as principle charge carriers, has been reported. PEO-based polymer electrolytes are one of the most promising materials due to their good mechanical and electrochemical properties. SPEs are prepared usually by solution-cast method. It has been observed in general that the existence of high degree of amorphousity in polymer host (viz. PEO) supports high ionic mobility and hence, high ionic conduction in SPEs. However, the SPE films, prepared conventionally by complexing the salts in the polymeric host, are found to be less stable mechanically. In a recent investigation, it has been observed that the mechanical strength of the polymer electrolyte membranes as well as the degree of amorphousity in polymer host could be enhanced substantially by dispersing nano-size particles of an inert/insulating material such as Al₂O₃ or SiO₂ or TiO₂ etc.⁷-¹². Such systems are referred to as nano-composite polymer electrolytes (NCPEs). The size of the filler particles plays a significant role in improving these physical properties of SPEs. Very recently, in place of the traditional solution casting method, a novel hot-press technique has been developed to prepare SPE membranes¹⁰-¹⁴. The present paper reports the some electrical viz. ionic conductivity (σ), mobility (µ), mobile ion concentration (n), ionic transference number (tᵢₒᵣ) and electrochemical properties of hot-press synthesized a new K⁺ ion conducting nano-composite polymer electrolyte (NCPE) membranes:(1-x) [70PEO: 30KBrO₃]:xSiO₂, where x = 0-20 wt. (%), using different experimental techniques.

2 Experimental Details

The AR grade precursor chemicals: poly (ethylene oxide) PEO (10³ Mw, Aldrich, USA), KBrO₃ (purity > 98%, Merck, India) and SiO₂ (> 99.8%, size ~8 nm, Sigma, USA) were used for synthesis of hot-pressed
CHANDRA et al.: HOT-PRESSED NANO-COMPOSITE POLYMER ELECTROLYTES

NCPEs:(1-x) [70PEO:30KBrO₃]:xSiO₂, where x = 0-20 wt. (%). The details related to hot-press casting of SPEs/NCPEs have been given elsewhere in our earlier communications. To identify the highest ionic conducting I₄-phase conventional solid polymer electrolyte (SPE):(PEO:KBrO₃) was also prepared by hot-press technique. The polymer-salt complexation were done with the help of SEM (model:JEOL, JXA-8100, Japan) and DSC (model: Perkin-Elmer) techniques. The conductivity (σ)-measurements were carried out on different samples at a fixed frequency (i.e. 5 kHz) using an LCR-bridge (model: HIOKI 3520-01, Japan). Ionic mobility (μ) and ionic transference number (t_ion) were determined directly employing dc polarization Transient Ionic Current (TIC) technique using an x-y-t recorder (model: Graphtec WX 2300-1L, Japan). The mobile ion concentration (n) was evaluated from σ and μ data. The activation energy (E_a) values were also determined by temperature dependent conductivity studies. Thin film solid state batteries were fabricated in the following cell configuration:

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Anode</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-metal</td>
<td>95[70PEO:30KBrO₃] + 5SiO₂</td>
<td>(C+I₂+Electrolyte)</td>
</tr>
</tbody>
</table>

The cathode in the film form has been prepared by hot-pressing the slurry of the physical mixture of elemental iodine (I₂), the conducting graphite (C) and NCPE in 1:1:1 weight ratios at ~ 70°C. The cell performances were studied under 100 and 50 kΩ load condition at room temperature. The cell potential discharge profiles were drawn as a function of time and some important cell parameters were calculated from the plateau of the discharge curves.

3 Results and Discussion

3.1 Electrical Properties

Figure 1 shows the room temperature conductivity (σ) variation as a function of salt KBrO₃ concentration for the hot-pressed solid polymer electrolyte (SPE): (PEO:KBrO₃). The maximum conductivity was observed at 30 wt. % of KBrO₃ (i.e. for the composition 70PEO:30KBrO₃) with conductivity (σ~4.36x10⁻⁷ S.cm⁻¹) and this composition has been used as a host for the formation of nano-composite polymer electrolytes (NCPEs). The increase in conductivity is due to increase in the degree of amorphicity in this composition, such type of behaviour were also reported in our earlier communications. The filler (SiO₂) concentration dependent conductivity variation at room temperature for the hot-press nano-composite polymer electrolyte (NCPE) membranes:(1-x)[70PEO:30KBrO₃]:xSiO₂, where x = 0-20 wt. (%), is shown in Fig. 2. The room temperature conductivity increased initially with the increase in the nano-size filler concentration in the SPE host:(70PEO:30KBrO₃). The conductivity (σ) maxima were observed at 5 wt. % of SiO₂ and then decreased gradually. The increase in conductivity is due to the increase in degree of amorphicity and creation of additional hopping sites as well as available of more conducting pathways for migration.

Fig. 1—Compositional dependent conductivity plot of hot-pressed SPEs: (PEO: KBrO₃)

Fig. 2—‘logσ – x’ plot of hot-pressed NCPEs: (1-x) [70PEO:30KBrO₃]: xSiO₂.
of ionic species through Lewis acid-base interactions between ionic species and O/OH sites on the filler SiO₂ grain surface. The decrease in the ionic conductivity for higher SiO₂ concentrations can be attributed to the usual blocking effect by the filler particles. The ionic mobility (µ), ionic transference number (tₗion), mobile ion concentration (n) of SPE host and NCPE OCC were determined directly at room temperature using dc polarization TIC technique. The room temperature values of all these ionic parameters: σ, µ, n, tₗion are listed in Table 1 along with the activation energy (Eₐ). One can obviously note from the table that the reason for the overall increase in conductivity of NCPE OCC has been predominantly due to the increase in both µ and n which can be attributed as a consequence availability of relatively larger number of mobile ions at this composition. The ionic transference number (tₗion) ~ 0.95, was obtained for both the SPE host and OCC NCPE which is very close to unity. This, in turn, indicated the fact that the hot-press synthesized both the electrolytes are an ion conducting system with K⁺ ions as the sole charge carriers and small contribution of electrons.

Table 1 — Some important electrical parameters of the hot-pressed SPE host and NCPE OCC at room temperature

<table>
<thead>
<tr>
<th>Film</th>
<th>σ (S/cm)</th>
<th>µ (cm² V⁻¹ s⁻¹)</th>
<th>n (cm⁻³)</th>
<th>tₗion</th>
<th>Eₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPE host: 70PEO: 30KBrO₃</td>
<td>4.36 × 10⁻⁷</td>
<td>2.12 × 10⁻³</td>
<td>1.28 × 10¹⁵</td>
<td>0.95</td>
<td>0.35</td>
</tr>
<tr>
<td>NCPE OCC: 95[70PEO: 30KBrO₃]: 5 SiO₂</td>
<td>2.13 × 10⁻⁶</td>
<td>1.58 × 10⁻²</td>
<td>7.9 × 10¹⁵</td>
<td>0.95</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Figure 3 shows the surface morphology of SPE host and NCPE OCC were observed by scanning electron micrograph (SEM). It can be clearly seen from the figures that the smooth surface morphology as well as amorphism increased (as indicated by the white portion of the micrograph) by the addition of nano-sized SiO₂. It is due to the filler SiO₂ occupied the pores and fillers also break the grain boundaries of SPE host which helped the transport of K⁺ ions in a faster way. Figure 4 shows the DSC thermograms for the pure PEO, SPE host and NCPE OCC. The broad endothermic peak was observed in polymeric films at ~ 60-70°C and it is corresponding to the melting point temperature of pure PEO. It is clearly shown from the figure that the melting temperature (Tₘ) of pure PEO decreased from 64° to 62°C, due to the increase in degree of amorphicity in SPE host and again decreased the Tₘ in NCPE OCC up to 58°C. It is due to the interaction between the PEO backbone and the filler SiO₂ have affected the main chain dynamics of the SPE host. A possible mechanism for this behavior...
could be the creation of additional hopping sites and favorable conducting pathways for ionic migration. Figure 5 shows the temperature dependant conductivity variations for hot-pressed NCPE membranes: (1-x)[70PEO:30KBrO₃]:xSiO₂ as well as SPE host: (70PEO:30KBrO₃). ‘logσ–1/T’ plots exhibited straight line behavior with an upward change in slope at ~70°C which is due to the well-known semi-crystalline to amorphous phase transition. The activation energy (Eₐ) values computed from the linear portion of all the plots (below the ~70°C) by using the following Arrhenius equation:

\[ \sigma(T) = \sigma_0 \exp(-E_a/kT) \]  

where \( \sigma_0 \) is the pre-exponential factor, Eₐ is the activation energy in eV and k is the Boltzmann constant. Figure 6 shows the ‘Eₐ–x’ plots of hot-pressed NCPE membranes: (1-x)[70PEO:30KBrO₃]:xSiO₂. The low activation energy for NCPE OCC indicative of relatively easier ion transport in the newly synthesized system and hence can be potentially used for electrochemical device applications.

### 3.2 Electrochemical Property

The electrochemical cell potential discharge profiles for a polymeric cell under different loads viz. 100 kΩ, 50 kΩ at room temperature is shown in Fig. 7. The Open Circuit Voltage (OCV) ~2.75 V obtained for the cell. It can be clearly noticed that except for the initial potential drop, OCV value remained practically stable for ~80 and ~27 hrs when discharged through 100 and 50 kΩ, respectively (i.e. during a low current drain state). However, the cell potential decreased relatively faster when discharge through 50 kΩ load (i.e. during higher current drain states). Table 2 lists some important cell parameters for polymeric cell, calculated in the plateau regions of the discharge profiles. On the basis of these studies, it can be observed that the above cell, based on the this newly synthesized K⁺ ion conducting NCPE, performed fairly satisfactorily especially during low current drains. The ionic transference number (\( t_{\text{ion}} \)) for the newly synthesized NCPE OCC was also determined employing electrochemical cell potential method using following equation 17:

\[ t_{\text{ion}} = E'/E \]
where $E'$ and $E$ are the measured and theoretical values of OCV respectively. On substituting $E$ and $E'$ values in the above equation, $t_{\text{ion}} \sim 0.95$ observed for the NCPE electrolyte system which is exactly similar to what was obtained earlier using dc polarization method. $t_{\text{ion}} = 0.95$ is indicative of the fact that K$^+$ ions are the sole charge carriers in the solid electrolyte system with negligibly small electronic contribution to the total conductivity.

4 Conclusions

A new hot-pressed nano-composite polymer electrolyte (NCPE) membrane: 95 [70PEO:30KBrO$_3$]:5SiO$_2$ has been synthesized. Materials characterization have been done with the help of SEM and DSC techniques. The filler particles play the important role of enhancement in the electrical and mechanical properties of polymer electrolytes. Ionic mobility ($\mu$) and mobile ion concentration ($n$) studies on NCPEs indicated clearly that the increase in room temperature conductivity is predominantly due to the increase in $n$ and $\mu$ both. A new polymeric battery has been fabricated and their discharge characteristics were studied under varying load conditions. The cell performed quit satisfactorily under low current drains.

Acknowledgement

We gratefully acknowledge DST, New Delhi for providing financial assistance through the ‘Fast Track Young Scientist Research Project’ (No. SR/FTP/PS-23/2009).

<table>
<thead>
<tr>
<th>Load (kΩ)</th>
<th>Working Voltage (V)</th>
<th>Current Density (µA.cm$^{-2}$)</th>
<th>Discharge Capacity (µA.h)</th>
<th>Power Density (mW.kg$^{-1}$)</th>
<th>Energy Density (mWh.kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2.3</td>
<td>1.8</td>
<td>184</td>
<td>33.06</td>
<td>2645</td>
</tr>
<tr>
<td>50</td>
<td>1.0</td>
<td>0.8</td>
<td>27</td>
<td>6.25</td>
<td>168.7</td>
</tr>
</tbody>
</table>

Table 2 — Some important cell parameters calculated from the plateau region of discharge profiles

References