Ion transport property studies on PEO–PVP blended solid polymer electrolyte membranes

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Abstract

The ion transport property studies on Ag^+ ion conducting PEO–PVP blended solid polymer electrolyte (SPE) membranes, $(1 - x)[90PEO : 10AgNO_3] : xPVP$, where $x = 0, 1, 2, 3, 5, 7, 10 \, (wt\%)$, are reported. SPE films were caste using a novel hot-press technique instead of the traditional solution cast method. The conventional solid polymeric electrolyte (SPE) film, $(90PEO : 10AgNO_3)$, also prepared by the hot-press method and identified as the highest conducting composition at room temperature on the basis of PEO–$AgNO_3$-salt concentration dependent conductivity studies, was used as the first-phase polymer electrolyte host into which PVP were dispersed as second-phase dispersoid. A two-fold conductivity enhancement from that of the PEO host could be achieved at room temperature for PVP blended SPE film composition: $98(90PEO : 10AgNO_3) : 2PVP$. This has been referred to as optimum conducting composition (OCC). The formation of SPE membranes and material characterizations were done with the help of the XRD and DSC techniques. The ion transport mechanism in this SPE OCC has been characterized with the help of basic ionic parameters, namely ionic conductivity (σ), ionic mobility (μ), mobile ion concentration (n) and ionic transference number (t_{ion}). Solid-state polymeric batteries were fabricated using OCC as electrolyte and the cell-potential discharge characteristics were studied under different load conditions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Solid polymer electrolyte (SPE) systems have attracted widespread attention as the most appropriate choice to fabricate all-solid-state electrochemical devices, namely batteries, sensors, fuel cells, etc. The main advantages of SPEs are their high ionic conductivity, high mechanical strength, ease of fabrication of thin film form, etc. [1–5]. Polymer blending is among the methods used to enhance the ionic conductivity in polymeric electrolyte membranes. However, poor mechanical properties in SPEs were found at a high degree of polymeric blending [6]. Polymer electrolytes are prepared, in general, by conventional solution-cast and sol–gel techniques but recently a novel hot-press technique has been developed which shows several advantages

over the conventional techniques [7, 8]. With a view to fabricating an all-solid-state-electrochemical device, namely a battery, this investigation reports the ion transport property studies on hot-press synthesized Ag^+ ion conducting PEO–PVP blended solid polymer electrolyte (SPE) membranes: $(1 - x)[90PEO : 10AgNO_3] : xPVP$, where $x = 0, 1, 2, 3, 5, 7, 10 \, (wt\%)$. Solid-state polymeric batteries were also fabricated using the newly synthesized Ag^+ ion conducting PVP blended SPE OCC membrane as electrolyte. The cell potential discharge performances of batteries were studied under varying load conditions.

2. Experimental

Ag^+ ion conducting PEO–PVP blended solid polymer electrolyte (SPE) membranes: $(1-x)[90PEO : 10AgNO_3] : xPVP$,

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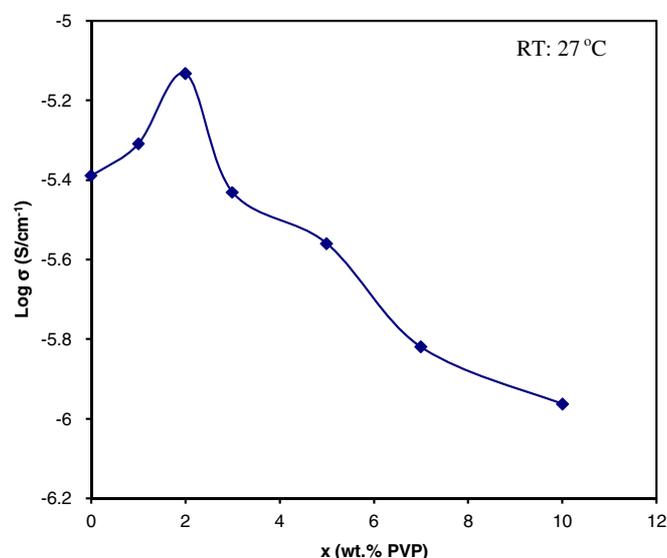[3] Author to whom any correspondence should be addressed.

Figure 1. Room temperature conductivity of hot-pressed PVP blended SPE membranes: $(1 - x)[90\text{PEO} : 10\text{AgNO}_3] : x\text{PVP}$, where $x = 0, 1, 2, 3, 5, 7, 10$ (wt%).

where $x = 0, 2, 3, 5, 7, 10$ (wt%), were prepared using the hot-press procedure in place of the conventional solution-cast technique. The details of the hot-press procedure have been reported elsewhere [8]. The formation of the solid polymer electrolyte and thermal behaviour were explained on the basis of XRD and DSC results. The basic ion transport parameters, namely ionic conductivity (σ), ionic mobility (μ), mobile ion concentration (n) and ionic transference number (t_{ion}), have been measured employing different experimental techniques, as reported in our earlier communications [9, 10]. Solid-state polymeric batteries were fabricated in the following cell configuration:

Ag-metal foil (Anode)	98[90PEO : 10AgNO$_3$] + 2PVP (SPE OCC membrane)	(C+I$_2$+Electrolyte) (Hot-pressed cathode film)

The cell performances were studied under different load conditions and the cell-potential discharge profiles were drawn as a function of time and the important cell parameters were calculated from the plateau of the profiles.

3. Results and discussion

The room temperature conductivity variation of hot-pressed SPE membranes: [PEO : AgNO$_3$] indicated that the conductivity (σ) increased abruptly ($> 10^3$ times) as AgNO$_3$ concentration increased initially, then remained almost unaltered on further addition of the salt and a moderate-sized σ-maxima was observed at 10 wt% of AgNO$_3$ (i.e. for the composition 90PEO : 10AgNO$_3$), as reported in our previous communication [11]. Figure 1 shows the conductivity plot of hot-pressed PEO–PVP based SPE membranes: $(1 - x)[90\text{PEO} : 10\text{AgNO}_3] : x\text{PVP}$, where $x = 0, 1, 2, 3, 5, 7, 10$ (wt%). One can clearly note from the figure that the conductivity increased rapidly as the PVP ratio increased up to 2 wt%, then decreased on further addition of the PVP.
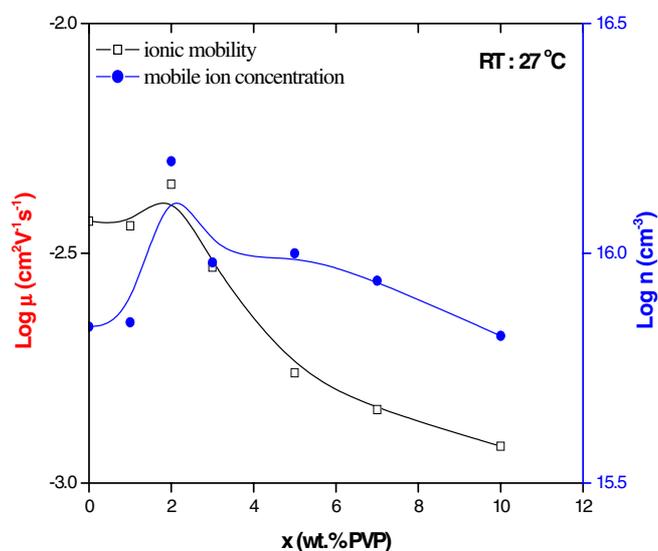

Figure 2. Log μ–x and log n–x plots for PVP blended SPE membranes: $(1 - x)[90\text{PEO} : 10\text{AgNO}_3] : x\text{PVP}$.

A two-fold conductivity enhancement was achieved at room temperature for PEO host complexes with 2 wt% of PVP. This blended SPE film composition: 98[90PEO : 10AgNO$_3$] : 2PVP has been referred to as the optimum conducting composition (OCC). The conductivity increase in OCC SPE membrane may be probably due to the increase in n or μ or both. The increase in ionic mobility (μ) is due to the increase in the degree of amorphousness and the increase in mobile ion concentration (n) would be due to the availability of loosely entangled Ag$^+$ ions with the polymer chains after blending with PVP. Figure 2 shows log μ–x and log n–x plots for SPE blended membranes: $(1 - x)[90\text{PEO} : 10\text{AgNO}_3] : x\text{PVP}$. It is obvious from the figure that both the variations are almost analogous to log σ–x. These results clearly indicated the fact that the increase in room temperature conductivity of the OCC SPE film is due to the increase in both μ and n. The ionic transference number (t_{ion}) of SPE OCC was determined using the transient ionic current (TIC) technique [12]. $t_{\text{ion}} \sim 0.95$ was obtained for PVP blended SPE OCC film, which is very close to unity and indicated the fact that the newly synthesized SPE OCC film is purely an ion conducting system with Ag$^+$ ions as the sole charge carriers.

Figure 3 shows the x-ray diffraction patterns for the pure PEO, SPE host: [90PEO : 10AgNO$_3$] and PVP blended SPE OCC membrane: 98[90PEO : 10AgNO$_3$] : 2PVP. On closer inspection of XRD patterns, one can clearly note that some of the PEO peaks became relatively broader as well as less prominent/feeble after salt complexation and this is indicative of complexation of salts with PEO. Figure 4 shows DSC thermograms for the pure PEO and a newly synthesized PVP blended SPE OCC. The broad endothermic peak ~68 °C– 70 °C corresponds to the melting point temperature of pure PEO. The slight shift in the melting point temperature towards the higher side has also been observed due to the PEO–PVP blending.

Figure 5 shows 'log σ – $1/T$' plots for the SPE host: [90PEO : 10AgNO$_3$] and PVP blended SPE OCC:

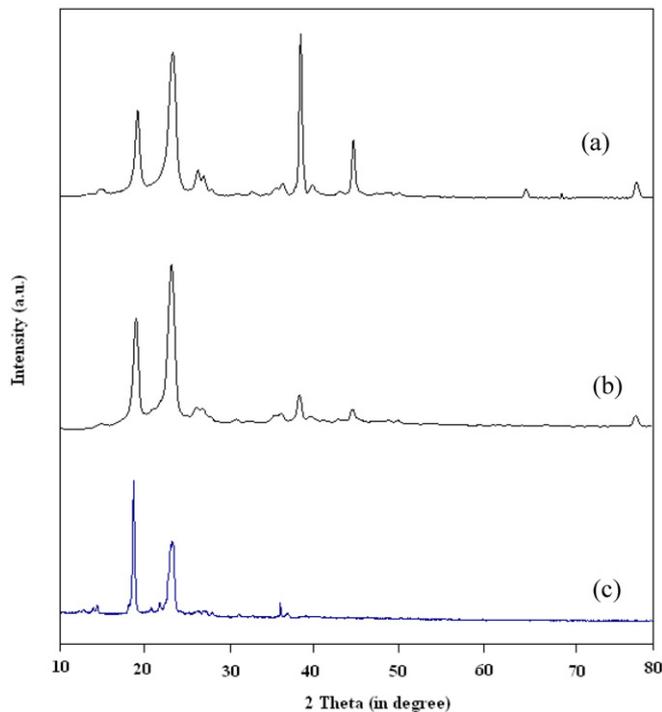J. Phys. D: Appl. Phys. **42** (2009) 135107

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Figure 3. XRD patterns: (a) pure PEO, (b) SPE host: (90PEO : 10AgNO₃), (c) PVP blended SPE OCC: [98(90PEO : 10AgNO₃) : 2PVP].
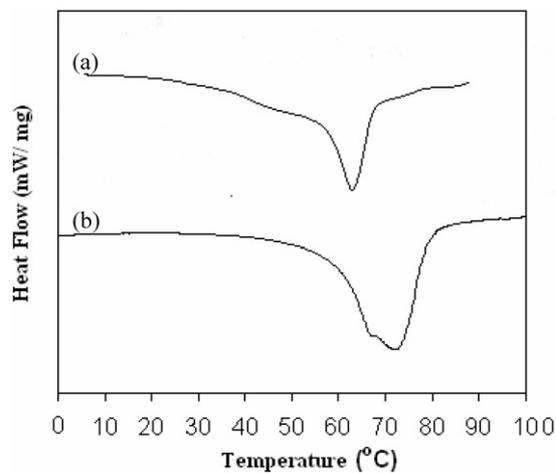

Figure 4. DSC thermograms: (a) Pure PEO, (b) PVP blended SPE OCC: [98(90PEO : 10AgNO₃) : 2PVP].

98[90PEO : 10AgNO₃] : 2PVP. The conductivity increased linearly with temperature, except for an upward change in the slope at ∼70 °C which corresponds to a semi-crystalline to amorphous phase transition temperature of PEO. The linear portion below this transition temperature exhibited Arrhenius type equations and can be expressed as:

SPE host: $\sigma(T) = 2.01 \times 10^1 \exp(-0.40/KT)$ (S cm⁻¹), (1)

PVP blended SPE OCC : $\sigma(T)$
$= 1.05 \times 10^1 \exp(-0.36/KT)$ (S cm⁻¹), (2)

where the numbers 0.40 and 0.36 are the activation energies (E_a) in (eV) computed by least square linear fitting of the
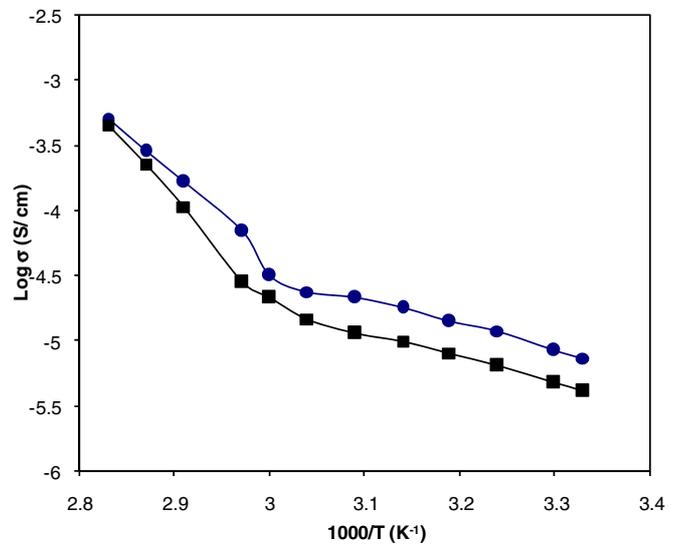

Figure 5. Log σ–1/T plots: PVP blended SPE OCC: [98(90PEO : 10AgNO₃) : 2PVP] (●) and SPE host: [90PEO : 10AgNO₃] (■).
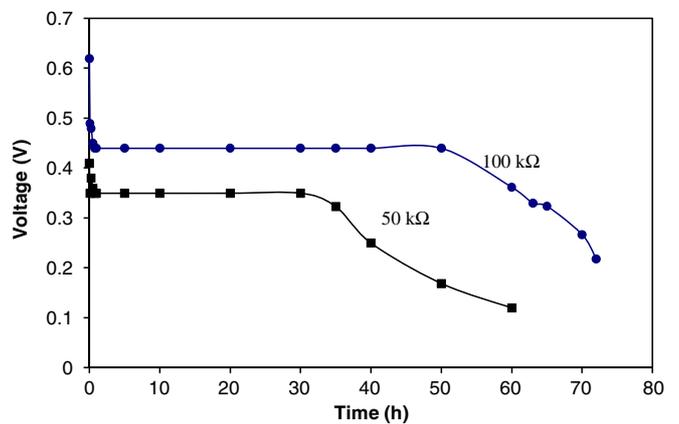

Figure 6. Cell-potential discharge profiles for the thin film solid state battery: Ag/[98(90PEO : 10AgNO₃) : 2 PVP]/ (C + I₂ + Electolyte) under 100 kΩ (●) and 50 kΩ (■).

data. It can be clearly noticed that the activation energy for PVP blended SPE OCC has been substantially decreased. Low activation energy is indicative of an easy ion transport in the newly synthesized PVP blended solid polymer electrolyte system.

Figure 6 shows the cell-potential decay profiles for the solid-state polymeric batteries, when discharged through 100 kΩ and 50 kΩ loads, respectively. An open circuit voltage (OCV) ∼0.61 V, obtained for all the batteries, decreased sharply in the beginning due to the initial cell polarization effect, then remained almost stable at: ∼0.44 V ∼55 h (100 kΩ); ∼0.35 V for ∼30 h (50 kΩ). One can clearly note that the performance of the batteries has been relatively superior during low current drain states. Table 1 lists some important cell parameters calculated in the plateau region of the discharge profiles of figure 6. OCV ∼0.62 V is fairly low as compared with the theoretical OCV ∼0.687 V obtained usually for Ag/I₂ electrode couple [13]. Hence, low OCV of the present battery may be due to the addition of SPE OCC in the cathode

Table 1. Some important cell parameters obtained from the plateau region of the discharge profiles of figure 6.

Load (kΩ)	Working voltage (V)	Current density (μA cm^{-2})	Discharge capacity (μA h)	Power density (mW kg^{-1})	Energy density (mWh kg^{-1})
100	0.44	0.35	22	0.387	19.36
50	0.35	0.28	12.25	0.245	8.57

(C + I$_2$) and/or probably the fact that all the Ag$^+$ ions in SPE are not mobile.

4. Conclusion

A new Ag$^+$ ion conducting PEO–PVP blended solid polymer electrolyte membrane: 98[90PEO : 10AgNO$_3$] : 2PVP (wt%) has been synthesized. On the basis of ion transport parameter studies it has been proved that polymer blending is one of the important techniques for enhancement in the room temperature conductivity, mobility, mobile ion concentration and mechanical stability of the solid polymer electrolyte membranes. The ionic transference number measurements indicated that the newly synthesized blended solid polymer electrolyte membrane is an ionic conductor and the charge transport is due to Ag$^+$ ions. The cell-potential discharge characteristics have been studied under varying load conditions and the cell performed quite satisfactorily especially under low current drain states.

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