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Solid state polymeric battery fabrication of hot-pressed nanocomposite polymer electrolyte

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Solid state polymeric battery based on newly synthesized Na^+ ion conducting nano- composite polymer electrolyte (NCPE): 93 (70PEO: $30NaClO_4$) + 7 SiO_2, has been fabricated in the cell configuration: Na-metal 93 (70PEO: $30NaClO_4$) + 7 SiO_2 (C + I_2+NCPE). Na-metal and (C + I_2 + NCPE) in 1: 1:1 wt % ratios have been used as anode and cathode, respectively. The cell-potential discharge performances have been studied at different temperatures under different load conditions. To explain the ionic nature of the present NCPE, ionic transference number (t_{ion}) has also been calculated with the help of electrochemical cell-potential method.

Keywords: Nano-composite polymer electrolyte, Polymer battery, Ionic transference number, Electrochemical cell potential method

1 Introduction

Some new class of PEO-based superionic polymeric electrolytes (SPE) shows great technological promises as potential electrolyte systems to fabricate all solid-state electrochemical devices viz. batteries, fuel cells, super-capacitors, memories electrochromic displays, etc[1-7]. Polymer electrolytes are prepared, in general, by complexing/ dissolving ionic salts in variety of polymeric hosts. The SPE films are casted usually by solution-cast technique in which both the salt and polymer host are dissolved in a common solvent, mixed in appropriate proportions, stirred for sufficient time then poured into a petri dish for drying. Majority of the polymer electrolyte films reported so far, are either alkali ion or proton conducting systems. Very few nanocomposite polymer electrolytes (NCPEs) involving other mobile ions such as Na^+, Cu^+, etc could be prepared by this technique. This is probably due to the experimental limitation of the solution-cast technique. However, very recently, a novel hot-press method has been developed which can be potentially used for casting SPE films of any kind. This technique is more rapid and least expensive as well as solvent-free procedure to form completely dry polymer electrolyte membranes complexed with variety of ionic salts[8-11].

To understand the electrochemical properties of PEO-based NCPEs, the present paper, reports the fabrication and characterization of thin film solid state polymeric batteries using hot-press synthesized Na^+ ion conducting nano-composite polymer electrolyte (NCPE): 93 (70PEO: $30NaClO_4$) + 7 SiO_2, as an electrolyte.

2 Experimental

A nano-composite polymer electrolyte (NCPE): (1-x) [70PEO: $30NaClO_4$] + x SiO_2, where $0 < x < 20$ wt %, were synthesized by hot-press technique. The composition: 93 (70PEO: $30NaClO_4$) + 7 SiO_2 with conductivity ~ 7.6×10^{-6} $S.cm^{-1}$, has been identified as highest conducting composition and this has been used as an electrolyte for synthesis of polymeric batteries[9]. Thin film solid state polymeric battery was fabricated in the following cell configuration:

Na (Anode)	93 (70PEO: $30NaClO_4$) + 7 SiO_2 (NCPE)	C+I_2+NCPE (Cathode)

Na-metal was used as anode while cathode film was prepared by hot-pressing the homogeneous physical mixture of elemental iodine (I_2), conducting graphite (C) and NCPE in 1:1:1 weight ratios at 50 °C. The thickness of the anode, electrolyte and cathode are 0.124 cm, 0.012 cm, 0.045 cm, respectively. The area of all the components is 1.25 cm^2 and the total weight of the polymeric cell is 0.189 g. The cell potential discharge profiles were drawn as a function of time and some important cell parameters were calculated. The ionic transference number (t_{ion}) in NCPEs was measured using electrochemical cell potential method.

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3 Results and Discussion

A new nanocomposite polymer electrolyte (NCPE): 93 (70PEO: 30$NaClO_4$) + 7 SiO_2 with ionic conductivity (σ) ~ 7.6×10^{-6} $S.cm^{-1}$ has been synthesized and the ion conduction mechanism has been explained with the help of various ionic parameters viz ionic conductivity, mobility, ionic transference number, FTIR, DSC, TGA etc., in previous communication[9]. To study the electrochemical properties of newly synthesized NCPE, a solid state polymeric battery was fabricated, as mentioned in experimental section. Figure 1 shows the cell potential discharge profiles under 50 and 100 kΩ loads at different temperatures. A solid state battery shows the better performance when it discharged through 50 kΩ or above loads and we can easily find the comparative study of the solid state batteries, as reported in the literature[12,13]. The Open Circuit Voltage (OCV) ~ 2.7 V obtained for the polymeric cells. The initial sharp decrease in voltage of these thin film solid-state batteries may be due to the initial cell polarization effect and/or the formation of a thin layer of salt at the electrode/electrolyte interface[14,15]. It can be clearly noticed that except for the initial potential drop, OCV value remains practically stable for ~ 90 and ~ 30 when discharged through 100 and 50 kΩ, respectively (i.e., during a low current drain state). However, the cell potential decreases relatively faster when discharged through 50 kΩ load (i.e., during higher current drain states). Table 1 lists some important cell parameters for the present polymeric cell, calculated in the plateau regions of the discharge profiles. On the basis of these studies, it can be observed that the newly investigated hot-pressed NCPE, performed relatively superior at higher temperature and during low current drains. The present solid state battery shows the superior results as compared to previously reported other PEO-based Na^+ ion batteries[16,17]. The nanofiller SiO_2 plays an important role for improvement in electrical as well as electrochemical properties of the present solid state batteries.

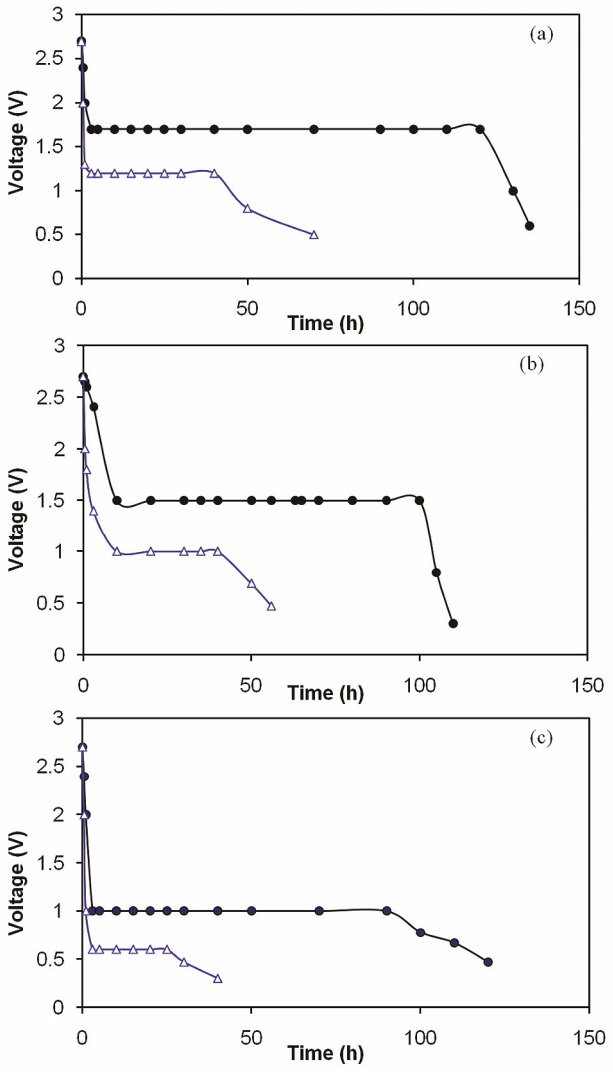

Fig. 1 – Cell potential discharge profiles for the solid state polymeric batteries under 100 kΩ (●) and 50 kΩ (Δ) load resistances at different temperatures: (a) 40 °C, (b) 27 °C and (c) 15 °C

Figure 2 shows the schematic representation of solid state polymeric cell. The ionic transference number (t_{ion}) can be evaluated by the electrochemical cell potential method, using the following equation[14,15]:

$$t_{ion} = E`/E \quad \ldots (1)$$

Table1 – Some important cell parameters at various temperatures and load conditions

Cell parameters	Loads (kΩ)	Temperature (°C) 40	27	15
Working voltage (V)	100	1.7	1.4	1.0
	50	1.2	1.0	0.6
Current density (μA.cm^{-2})	100	1.36	1.2	0.8
	50	0.8	0.8	0.48
Discharge capacity (μA.h)	100	204	150	90
	50	36	30	15
Power density (mW.kg^{-1})	100	17.7	13.8	6.13
	50	8.83	6.1	2.20
Energy density (mWh.kg^{-1})	100	2127	1380	552
	50	265	184	55.2

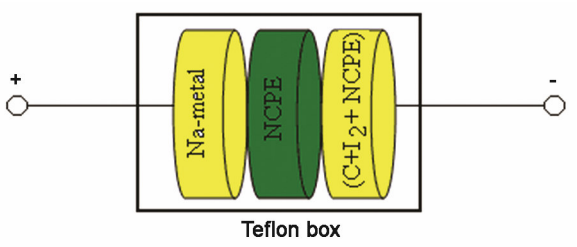

Fig. 2 – Schematic structure of solid state polymeric cell

where $E`$ and $E$ are measured and theoretical open circuit (OCV) values, respectively. Substituting the values of $E`$ and E in above equation, we obtain ionic transference number (t_{ion}) ~ 0.95 for the present polymeric cell. These results clearly indicate the fact that majority of Na^+ ions (~ 95 %) in NCPE are mobile. However, a small fraction of Na^+ ions (~ 5 %) are not free in the polymeric network. This has also been confirmed by DSC, TGA and dc polarization t_{ion} studies, as reported in previous communication[9].

4 Conclusions

A new thin film solid state polymeric battery has been fabricated using the newly synthesized hot-pressed Na^+ ion conducting nano-composite polymer electrolyte. The cell potential discharge characteristics have been studied under varying load conditions at different temperatures. The cell performed fairly satisfactorily under low current drain states at all the temperatures. The ionic transference number (t_{ion}), evaluated by electrochemical cell potential method, indicated that majority of Na^+ ions (~ 95 %) in NCPE are mobile and a small fraction of Na^+ ions (~ 5 %) are not free in the polymeric network.

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