



Structural, morphological, electrical and electrochemical study on plasticized PVdF-HFP/PEMA blended polymer electrolyte for lithium polymer battery application



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ABSTRACT

The compositional effect of blending plasticized poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) with different wt% of poly(ethyl methacrylate) (PEMA) on its electrical properties was studied through AC impedance analysis. The maximum ionic conductivity of 2.14×10^{-2} S/cm at 303 K was found for 5 wt% of PEMA blended film which almost one order higher than the plasticized PVdF-HFP film with no blending (3.15×10^{-3} S/cm). However, blending of 10 wt% of PEMA dropped the conductivity to (5.12×10^{-4} S/cm). This drastic change in conductivity was explained in detail by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM) analysis. The dielectric studies showed increase in side chain movements of the host polymer PVdF-HFP for 5 wt% of PEMA blending. However, this segmental motion was found hindered for 10 wt% of PEMA due to steric effect. TG-DTA shows the thermal stability of the plasticized polymer membrane to be increased for the addition of 5 wt% PEMA. Lithium metal polymer cell was made using the optimized blend membrane as an electrolyte with LiV_3O_8 as cathode and Li metal as anode. The lithium metal polymer cell was found to deliver the specific discharge capacity of 223 mAh/g at the second cycle.

1. Introduction

In recent years, there has been a great attention on gel polymer membranes for high energy density rechargeable solid state batteries used in portable electronic devices owing to their high ionic conductivity, safe, low cost and design flexibility [1]. To date, several polymer hosts like poly(vinylidene fluoride) (PVdF), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), etc. were investigated and developed to prepare gel polymer electrolytes. Among those, fluoropolymers have received remarkable attention as polymer electrolytes in lithium metal/lithium ion polymer battery (PIB) applications owing to their good electrochemical stability and affinity toward electrolyte solutions [2,3]. Among various fluoro polymers like poly(vinylidene fluoride) (PVdF), poly(vinyl fluoride) (PVF), poly(tetrafluoro ethylene) (PTFE), etc., the copolymer PVdF-HFP is considered as a potential candidate for PIB because of its high dielectric constant, low crystallinity and low glass transition temperature which helps to provide high dissolution of the salt in the polymer matrix [4,5].

High ionic conductivity, mechanical stability, thermal stability and electrochemical compatibility are the expected outcome of a good polymer electrolyte and polymer blending is one among the ways to achieve it. Though many studies were reported on plasticized electrolytes based on PVdF-HFP blended with polymers like poly(methyl methacrylate) (PMMA) [6], poly(vinyl chloride) (PVC) [7] and poly(vinyl acetate) (PVAc) [8], to the best of our knowledge there are trivial articles based on the plasticized PVdF-HFP polymer electrolyte blended with PEMA for electrochromic device and PIB applications [9–12]. The systematic study on compositional effect of blending PEMA with PVdF-HFP is not reported so far and is the focus of the present work. The porosity of the blended films was found to vary greatly depending on the type of polymer chosen for blending, solvent used and preparation methods. In the present work, porous films were produced by blending PVdF-HFP with different wt% of PEMA, by simple solution casting technique. Blending of different wt% of PEMA with plasticized PVdF-HFP was found to give interesting results in terms of porosity and ionic conductivity. The blend systems were explored in depth by means of the

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structural, vibrational, morphological, thermal and the electrical analysis. Lithium metal polymer cell was made with optimized blend film and the electrochemical studies were carried out.

2. Experimental procedure

2.1. Preparation of polymer electrolyte films

The polymer electrolytes were prepared by simple solution casting technique. All the chemicals were purchased with high purity grade from Sigma-Aldrich/Himedia. PVdF-HFP [$M_w = 400,000$], PEMA [$M_w = 515,000$], and lithium perchlorate (LiClO_4) were purchased from Sigma-Aldrich. The plasticizer ethylene carbonate (EC) and solvent acetone were purchased from Himedia. PVdF-HFP (85 wt%) and LiClO_4 (15 wt%) was dissolved in 30 ml of acetone and stirred well for 24 h. The obtained solution was poured in a petri dish and evaporated in air oven at 303 K for about 48 h to get the polymer electrolyte film. Before subjecting to further studies, electrolyte film was dried again for 5 h at 323 K under reduced pressures of 400 mbar. The thickness of all the prepared membranes was found to be in the range of 1–2 mm. Plasticized polymer films were prepared by the same procedure as above by adding various weight percentages of EC. The composition, 50 wt% PVdF-HFP + 35 wt% EC + 15 wt% LiClO_4 was taken as the optimized plasticized electrolyte film, based on the conductivity which are to be discussed later. The polymer PEMA was blended in different wt% (5, 10, 15, 20, 25 and 40), to study its implications on the structural, vibrational, morphological, thermal and electrical properties. The sample codes are as assigned as in Table 1. The reproducibility of the polymer membranes (PL-35, PL-40 (45 wt% PVdF-HFP + 40 wt% EC + 15 wt% LiClO_4), PE-5 and PE-10) were checked twice.

2.2. Characterization techniques

X-ray diffraction pattern of the samples was obtained using SHIMADZU-XRD-6000 diffractometer with $\text{Cu-K}\alpha$ radiation (wavelength = 0.1541 nm) as the source at 40 kV and having a scanning range between 10° and 80° . FTIR spectroscopy studies were carried out using a BRUKER-FTIR-ATR spectrometer in the range of $400\text{--}4000\text{ cm}^{-1}$ with the spectral resolution of 4 cm^{-1} . Morphology analysis was done using JEOL-JSM 6000 scanning electron microscope. Thermo gravimetric and differential thermal analysis (TG-DTA) studies were performed with the aid of NETSZCH Thermogravimetric analyzer at a scan rate of 283 K/min in the temperature range of room temperature to 873 K. The AC impedance studies were carried out for the as prepared polymer electrolyte films with stainless steel as the blocking electrodes, using a computer-controlled electrochemical analyzer (Model: CHI-600E, Make: CH-instrument) in the frequency range of

Table 1
Sample codes.

Sample code	Composition
PP	Pure PVdF-HFP
PE	Pure PEMA
PS	85 wt% PVdF-HFP + 15 wt% LiClO_4
PL-35	50 wt% PVdF-HFP + 35 wt% EC + 15 wt% LiClO_4
PE-5	45 wt% PVdF-HFP + 5 wt% PEMA + 35 wt% EC + 15 wt% LiClO_4
PE-10	40 wt% PVdF-HFP + 10 wt% PEMA + 35 wt% EC + 15 wt% LiClO_4
PE-15	35 wt% PVdF-HFP + 15 wt% PEMA + 35 wt% EC + 15 wt% LiClO_4
PE-20	30 wt% PVdF-HFP + 20 wt% PEMA + 35 wt% EC + 15 wt% LiClO_4
PE-25	25 wt% PVdF-HFP + 25 wt% PEMA + 35 wt% EC + 15 wt% LiClO_4
PE-40	10 wt% PVdF-HFP + 40 wt% PEMA + 35 wt% EC + 15 wt% LiClO_4

40 Hz–1 MHz at room temperature to 353 K.

2.3. Lithium metal polymer cell construction

Lithium trivanadate (LiV_3O_8) was prepared by poly(ethylene glycol)-*block*-poly (propylene glycol)-*block*-poly (ethylene glycol) (Pluoronic P123) assisted reflux method and the phase pure structure was confirmed by XRD analysis [data yet to be reported]. The active material LiV_3O_8 (70 wt%) was mixed with super P carbon black (15 wt%) and poly(vinylidene fluoride) (PVdF: Kynar 2801) binder (15 wt%) using the solvent *N*-methyl pyrrolidone (NMP). Then the obtained electrode paste was coated on aluminium foil of 20 μm thickness and dried at 353 K for 24 h in oven to remove the solvent NMP. Lithium metal foil (Kyokuto metal Co., Japan) was used as the counter and reference electrode. The optimized polymer film (PE-5) was immersed in a solution of 1 M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) (Merck) for 10 s, and used as the electrolyte. The 2016 size coin cells were assembled in an Ar-filled glove-box (MBraun, Germany) which was maintained at O_2 and H_2O level of less than 2 ppm. The cells were aged for 12 h before measurement. Galvanostatic charge-discharge cycling was carried out at room temperature by using a computer-controlled Bitrode multiple battery testers (Model SCN, Bitrode, USA) in the voltage range of 2–4 V for a current density of 30 mA/g.

3. Results and discussion

3.1. XRD analysis

XRD patterns of films PP, PS, PL-35 and PE-5 are shown in Fig. 1(a). The XRD pattern of PP shows the characteristic peaks at $2\theta \sim 18^\circ$ and 21° . This belongs to the planes (020) and (110) respectively, of the VdF γ -phase crystals. The peaks at $2\theta \sim 27^\circ$ and 39° belongs to planes (021) and (131) respectively, of the VdF α -phase crystals [12–16]. Similar observation of mixture of phases was observed by Aravindhan et al. [16], when acetone was used as the solvent. An increase in the amorphous nature was observed for PS, with no characteristic peak for the salt which would otherwise occur at $2\theta = 20.9^\circ, 22.92^\circ, 26.56^\circ, 32.75^\circ$ and 35.4° (JCPDS No: 30-0751), indicating complete miscibility. For PL-35, the (021) plane at $2\theta \sim 27^\circ$ corresponding to the VdF α -phase of PVdF-HFP was found to be completely suppressed. This suggests that the plasticizer EC interacts well with the VdF- α -phase, and increases the amorphous nature of the film. For PE-5, the XRD shows an increase in overall broadness of the peaks, thereby indicating the increase in amorphous nature of the film. The total area under the peaks corresponding to (020) and (110) planes of VdF γ -phase was found to be 4152 for PE-5, whereas it was only 1665 in the case of PL-35. Due to the increase in amorphous nature, higher ionic conductivity is expected for

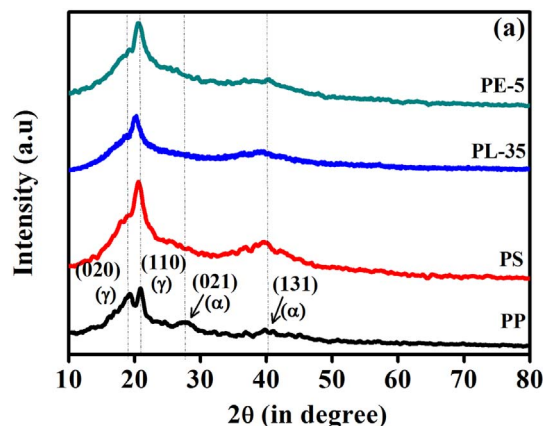


Fig. 1(a). XRD pattern for (range $2\theta = 10$ to 80°) PP, PS, PL-35 and PE-5.

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