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Li-ion conduction on nanofiller incorporated PVdF-co-HFP based composite polymer blend electrolytes for flexible battery applications

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ABSTRACT

Composite polymer electrolytes (CPE) composed of Poly (vinyl acetate) (PVAc), poly (vinylidenefluoride-co-hexafluoropropylene) (PVdF-co-HFP), barium titanate ($BaTiO_3$) nanofiller, lithium tetrafluroborate ($LiBF_4$), ethylene carbonate (EC) and propylene carbonate (PC) were prepared using simple solution casting method. The $BaTiO_3$ nanofillers were homogeneously dispersed in the polymer electrolyte matrix and exhibited excellent interconnection with PVAc/PVdF-co-HFP/EC/PC/$LiBF_4$ polymer electrolyte. The addition of $BaTiO_3$ nanofillers improved the ionic conductivity of the polymer electrolytes to some extent when the content of the $BaTiO_3$ is 8 wt.%. The addition of $BaTiO_3$ also enhanced the thermal stability of the electrolyte. The structural and complex formations of the composite electrolyte membranes were confirmed by X-ray diffraction and FTIR analysis, respectively. Surface morphology of the samples was depicted using scanning electron microscope and atomic force microscope studies.

1. Introduction

In recent years, rechargeable Li-ion batteries (LIBs) have been widely used as power sources in modern portable electric devices such as laptop computers, video cameras, electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1–3]. However, the electrolytes which are used in the LIBs still need improvement especially in terms of ionic conductivity at room temperature, thermal stability and mechanical stability.

To accomplish these requirements, extensive research has been conducted on several polymer hosts namely poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVdF), poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP), etc. [4,5]. Among the various polymers, the PVdF-co-HFP based electrolyte has received much attention due to its unique properties i.e. the host polymer possesses both amorphous and crystalline phases in which the crystalline VdF phase acts as a mechanical stiffer and the amorphous HFP phase helps in improving the ionic conductivity [6,7].

According to Ratner and Shriver [8] the conduction of ions in the polymer electrolyte takes place mainly in the amorphous region. PVAc has an amorphous nature and the addition of a small amount of PVAc will reduce the crystalline nature of the host polymer since it helps to improve the ionic conductivity. The possibility of using PVAc/PVdF-co-HFP based polymer blend electrolytes for rechargeable lithium batteries has been investigated by Choi et al. [9]. In order to enhance the conductivity at room temperature, considerable research has been carried out on various polymers using different approaches, such as blending of two polymers [10,11], addition of plasticizers to get gel polymer electrolytes [12] and addition of fillers to get composite electrolytes [13]. The above studies reveal that using composite polymer electrolytes is the best solution to make a lithium battery with high reliability, good interfacial stability and improved safety [14]. Polymer electrolytes with a variety of ceramic particles such as TiO_2, SiO_2, Al_2O_3 and $BaTiO_3$ [15,16] incorporated were prepared and they showed remarkable conductivity at room temperature with good mechanical stability. Karmarkar and Ghosh [17] studied the ionic conductivity of the PEO based electrolytes with different anions. The effect of different organic fillers ZnO and CdO on the PEO based electrolyte matrix was studied and reported by Karmarkar and Ghosh [18,19] and Bhattacharya and Ghosh [20]. Park et al. [21] obtained the ionic conductivity of the order of 3.81×10^{-4} S cm^{-1} for PEO-$LiClO_4$ system with 20 wt.% of Al_2O_3 nanofiller. In the case of composite polymer electrolytes, the particle size and the filler concentrations play an important role because the addition of a small amount of inert filler will collapse the chain-organization of the polymers which in turn facilitates higher ionic conduction [22]. Very recently Ragavan et al. [23] reported that the nano sized $BaTiO_3$ incorporated P(VdF-co-HFP) membrane is suitable for battery application and they found that the $BaTiO_3$ added membrane exhibited better mechanical strength than the other composite electrolytes

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that contained Al_2O_3 and SiO_2 fillers. Though a number of composite polymer electrolyte membranes have been studied over the years, their performance falls short to fulfill the requirements. In order to develop and improve the performance of the polymer electrolyte, an attempt was made in the preparation of PVAc/PVdF-co-HFP/EC/PC/$LiBF_4$ based electrolytes with varying the concentrations of $BaTiO_3$.

2. Experimental

2.1. Materials and methods

PVAc, P(VdF-co-HFP), the nano sized $BaTiO_3$ (99%) and the salt $LiBF_4$ (98%) were purchased from Aldrich chemicals (USA) and they were dried under vaccum at 100 °C about 12 h. The plasticizers ethylene carbonate (EC) (Alfa aesar, 99%) and propylene carbonate (PC) (Aldrich, USA, 99%) were used as received. All the composite polymer electrolytes were prepared using a simple solvent casting technique. The salt $LiBF_4$ and the polymers were first dissolved in tetrahydrofuran (THF) separately and then mixed together. The given amounts of plasticizers were also added into the above polymer-salt mixtures. Finally, the nanofiller $BaTiO_3$ was incorporated into the complex mixture and was stirred continuously about 24 h for avoiding the fillers aggregation and to ensure the fine mixing. The obtained homogenous viscous slurry was degassed to remove air bubbles and was poured into the Petri dish. The solvent was allowed to evaporate slowly from the complex at 60 °C for 6 h. The composite polymer electrolyte films were harvested and stored in an evacuated desiccator.

2.2. Characterization

Ionic conductivity of the polymer composite electrolytes was estimated with the help of stainless steel blocking electrodes using a computer controlled micro-Autolab Type III Potentiostat/Galvanostat electrochemical work station of frequency range 1 Hz–300 kHz. The ionic conductivity (σ) of the composite electrolytes was calculated using the following equation: $\sigma = l/R_bA$, where l, R_b and A are the thickness (cm), the bulk resistance (Ω) and the surface area (cm^2) of the membrane, respectively. The conductivity values were found at different temperature.

The XRD equipment used in this study is X'pert PROPANalytical diffractometer using Cu-K_α radiation as source and operated at 40 kV. The sample was scanned from 10 to 80º for 2 sec in the 2θ step scan mode. FTIR spectra of the electrolytes were recorded using SPECTRA RXI, Perkin Elmer spectro-photometer in the spectral range of 400–4000 cm^{-1}. TG/DTA thermal analysis study of the membrane having maximum ionic conductivity was performed using Perkin Elmer Pyris-6 TG/DTA in an atmosphere containing nitrogen from ambient temperature to 865 °C with the heating rate of 10 °C min^{-1}.

Surface morphology of the samples was examined using a JEOL, JSM-840A scanning electron microscope (SEM). The electrolyte exhibiting maximum ionic conductivity was also subjected to atomic force microscopy (AFM) study and the image over the scanned area of 1 μm × 1 μm was depicted using the Veeco-diCP-II microscope model. The pore size and the rms roughness of the film were estimated from the topographic image.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the XRD pattern of $BaTiO_3$, $LiBF_4$, PVdF-co-HFP, PVAc, and PVAc/P(VdF-co-HFP)/EC + PC/$LiBF_4$/$BaTiO_3$ based composite polymer electrolytes at different $BaTiO_3$ concentrations. The high crystalline nature of $BaTiO_3$ has been confirmed from Fig. 1($BaTiO_3$). Using Debye–Scherrer equation, particle size of $BaTiO_3$ was calculated for every θ (sharp peaks) values and the average particle size is found to be 55 nm. Diffraction pattern of $LiBF_4$ showed high intense characteristic peaks which revealed the crystalline nature of the salt. The XRD pattern of the P(VdF-co-HFP) polymer confirmed its semicrytalline nature [24]. Two broad humps have been observed for PVAc which confirm the amorphous nature of the polymer. The absence of crystalline peaks pertaining to $LiBF_4$ in the polymer complexes (Fig. 1(N0-N6)) confirms the complex formation which seems to occur only in the amorphous phase [25]. It is noted that some of the crystalline peaks corresponding to $BaTiO_3$ are absent and some of them have been slightly shifted in the complexes. This confirms that interaction takes place between the constituents that are involved in the preparation of the composite electrolytes. It is evident from Fig. 1(N1-N6) that the amorphous phase is maintained up to 8 wt.% of $BaTiO_3$ and on further addition, the crystallinity of the complex is found to increase, which could be the reason for lower conductivity of the films N5 and N6. This result is also in accordance with the earlier reports for TiO_2 incorporated PAN/PVC and PMMA/PEDGA blend [26,27] and PAN-$LiClO_4$-alpha-Al_2O_3 composite systems [28].

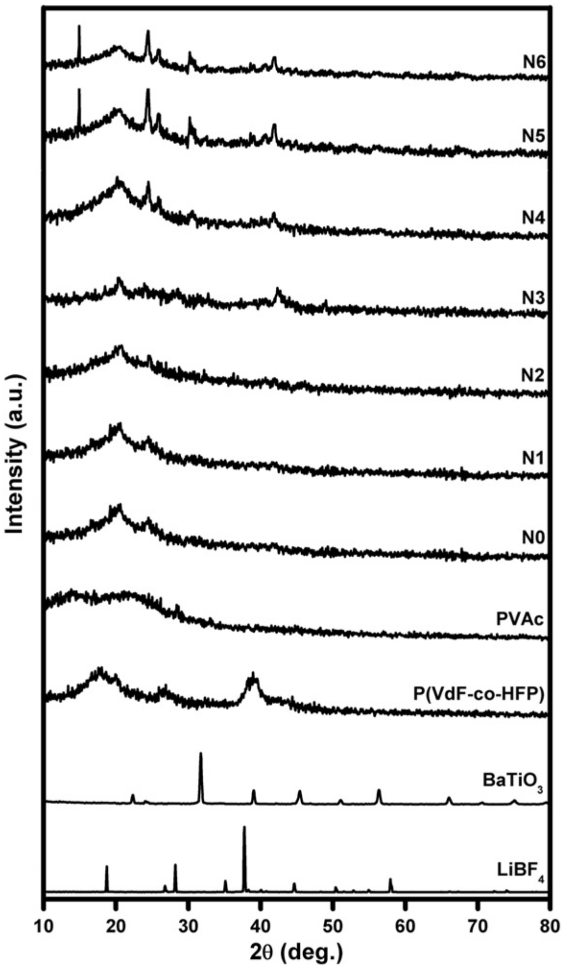

Fig. 1. XRD patterns of pure and prepared electrolyte membranes.

3.2. FTIR analysis

FTIR spectroscopy is an important tool for identification and characterization of various substances. In the present work, the spectra of the prepared complexes vary depending on their composition and are able to show the interaction between the polymers and the filler which accounts for the change in the vibrational modes of atoms or