Materials Science and Engineering B 205 (2016) 6–17

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Optimization of hybrid polymer electrolytes with the effect of lithium salt concentration in PEO/PVdF-HFP blends

P. Pradeepa, S. Edwin raj, G. Sowmya, J. Kalaiselvimary, M. Ramesh Prabhu*

School of Physics, Alagappa University, Karaikudi 630004, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 17 August 2015
Received in revised form
17 November 2015
Accepted 28 November 2015
Available online 19 December 2015

Keywords:
Polymer blend
Salt concentration
AC-impedance spectroscopy
Cyclic voltammetry
Thermal stability

ABSTRACT

Poly(ethylene oxide) (PEO) 6.25 wt%/poly(vinylidene fluoride-co-hexafluoropropylene) [P(VdF-HFP)] 18.75 wt% blend based electrolyte films containing different concentrations (2–10) wt% of lithium salt were prepared. The miscibility studies have been performed by using X-ray diffraction and Fourier transform infrared spectroscopy. The role of interaction between polymer hosts on conductivity is discussed using the results of a.c. impedance studies. A room temperature conductivity of 2.3912×10^{-4} S cm^{-1} has been obtained for PEO (6.25)–PVdF-HFP (18.75)–$LiClO_4$ (8)–PC (67) polymer complex. The temperature dependence of the conductivity of polymer electrolyte seems to obey VTF relation. Electrochemical stability (3.3 V) was observed in the prepared polymer electrolyte. Reduction process and oxidation process of the prepared electrolyte system have also been evaluated by means of cyclic voltammetry. Thermogravimetric analysis results indicate thermal stability of PEO/PVdF-HFP lithium salt complexes. Roughness parameter of the sample having maximum ionic conductivity was studied by AFM. The morphology of the polymer complex is investigated by using SEM.

1. Introduction

An accumulator directly converts electrical energy and chemical energy reversibly by use of the active battery materials in a chemical redox reaction. One of the most promising classes of accumulators for today and future energy applications is lithium based battery systems because to their high energy density [1]. In solid state batteries, solid polymer electrolytes (SPE) are used as separators. It also functions as a electrolyte where they have to meet not only requirements such as high ionic conductivity, wide electrochemical stability windows, easy processability but also acceptable parameters determining the performance of SPE such as their thickness, permeability, porosity/pore size, wettability, electrolyte absorption and retention, chemical, dimensional and thermal stability [2]. A separator is considered as a key component to prevent battery safety failures, because its primary function is to secure electrical isolation between a cathode and an anode of a battery [3]. The commercial system nowadays usually uses organic carbonates based electrolytes, which are flammable and volatile. Heat evolved from the batteries at severe conditions, especially at short circuit or under abuse, may cause fire or explosions. In the case of lithium ion batteries, which contain large amount of liquid electrolytes, an appreciable amount of flammable gas evolves and subsequently leads the battery to poor safety hazards. This evolution of gas is attributed to the decomposition of a protective layer at the carbon surface. These problems could be solved if the nonaqueous electrolytes are replaced with solid polymer electrolytes [4]. Solid polymer electrolytes based on polyethylene oxide have been proposed as a valid alternative to increase the safety level of the battery and to allow the use of high capacity lithium metal as the anode. Furthermore the lithium polymer battery is considered, in principle, a versatile system that can be prepared by laminating thin film of plastic configuration using roll-to-roll techniques [5]. In practice, the choice of individual components in the electrolyte material is crucial. Polymer blending is one of the most important contemporary ways for the development of new polymeric materials and a useful technique for designing materials with a wide variety of properties [6]. Blending of two polymers not only results in improving the mechanical strength but also helps in increasing the conductivity by suppressing the crystallization of polymer chain in any one of the ways, i.e. co-polymerization, comb-formation and polymer alloying [7]. The manifestation of superior properties depends upon the miscibility of the blend. Furthermore, blending gives rise to a range of properties in the final product by changing the blend composition [8]. By careful selection of the support polymer, there may be the added advantage of lowering the degree of crystallinity. Combinations of proton-donating and proton-accepting polymers can

* Corresponding author. Tel.: +91 4565 223315; fax: +91 4565 225202.
E-mail address: mkram83@gmail.com (M. Ramesh Prabhu).

http://dx.doi.org/10.1016/j.mseb.2015.11.009
0921-5107/

form inter macromolecular complexes in aqueous or organic media. P(VdF-HFP) and PEO form one such complex. Among the various polymer blends poly(ethylene oxide) (PEO)/poly(vinylidene fluoride-co-hexafluropropylene) P(VdF-HFP) has attracted many researchers because of its good compatible nature, high mechanical stability and support to the ion transport [9]. Poly(ethylene oxide) (PEO) plays an important role in the development of SPE-based lithium ion batteries and solvates high concentration of ionic salts. Ionic salt with PEO has been the subject of interest in polymer electrolytes, where the transient cross-links between the cation and ether oxygen of PEO play the major role to facilitate ion dissociation [10]. However, PEO based systems tend to crystallize at ambient temperature, which limits the ionic transport. Poly(vinylidene fluoride-co-hexafluropropylene) (PVdF-co-HFP) possesses lower crystallinity and higher free volume due to the incorporation of an amorphous phase of HFP. It provides ionic pathway which will improve the overall ionic conductivity of the electrolyte system. Its high dielectric nature ($\varepsilon \sim 8.4$) helps in dissolving more ionic species in the polymer matrix. Apart from this, it has good electrochemical stability and resemblance to the electrolyte solutions [11]. Moreover the addition of a salt has a highly disturbing effect on the arrangement of the polymer chains and the ensuring conductivity. In order to realize a high lithium ion conduction: (i) a polymer should have compatibility with inorganic salts and their dissociate ions, (ii) a polymer should provide a connected polar domain as the conduction path and (iii) a polymer should not interact with carrier ions too strongly in order to avoid complete trapping of carrier ions.

In order to focus on the above parameters, an appropriate amount of salt is necessary to achieve a favourable conductivity in lithium ion battery electrolytes. In order to facilitate the higher degree of ionization of the salt, low lattice energy is considered as an important criterion. Hence lithium perchlorate ($LiClO_4$) has been chosen as the ionic salt because of its low lattice energy of 723 kJ mol^{-1}, high thermal stability and less hygroscopicity which facilitate for increasing charge carriers [12]. During oxidation the formation of a positive cation whose charge is counterbalanced by the electrolyte doping anion (ClO_4^-) diffuses into the polymer matrix. The oxidation at the positive electrode is accompanied at the negative electrode by the reduction of lithium ions which deposit as lithium metal. This electrochemical process drives the Li/polymer batteries which involves the insertion–deinsertion of ionic species ClO_4^-. The small size of cation and large size of anion have dictated the choice of the metal salts. Due to the larger size of anion of $LiClO_4$ compared to the other lithium salts $LiClO_4$ was chosen which exhibits higher conductivity. The plasticizer, propylene carbonate has a dielectric constant of 64.4 and its addition to PEO leads to a significant increase of the ionic charge carriers along with a gain in ionic mobility [13]. In the present study polymer film consisting of PEO (6.25)–PVdF-HFP (18.75) with the different weight ratios of salt $LiClO_4$ and plasticizer propylene carbonate (PC) was prepared to optimize the salt concentration and achieve the highest conductivity.

2. Experimental

2.1. Materials used

The polymers poly(ethylene oxide) (PEO) of an average molecular weight Mw ~ 8000, poly(vinylidene fluoride-co-hexafluropropylene) (PVdF-co-HFP) of an average molecular weight Mw ~ 110,000, plasticizer propylene carbonate (PC) and the salt lithium perchlorate ($LiClO_4$) were procured from Sigma–Aldrich Chemicals Limited, USA. These were used as starting material for the polymer electrolyte preparation.

2.2. Preparation

The obtained PEO, PVdF-co-HFP and $LiClO_4$ were dried in vacuum oven at 55 °C for 4 h to remove moisture. The reason for choosing this blend ratio is that, among the different (PEO), (PVdF-HFP) compositions examined, PEO (6.25), PVdf-HFP (18.75) exhibited the highest ionic conductivity. This blend yields mechanically stable and free standing films. This composition of polymers was fixed as PEO (6.25 wt%) and PVdf-HFP (18.75 wt%) as it was found to be an optimized composition. Solid polymer electrolyte with blend ratio of 8 wt% of lithium salt to PEO/PVdF-HFP has been reported to have the highest ionic conductivity, because the electrolyte with highest Li salt concentration was not physically stable. Cracks were seen in the electrolytes film once the sample was subjected to high humidity levels. This was due to the crystallization of the excessive Li salt in the dry environment which formed phase separation with the polymer matrix. As a result, the formation of Li salt with 8 wt% was chosen. The ratios of PEO (6.25) wt% and PVdF-HFP (18.75) wt% with various concentrations (2–10) wt% of $LiClO_4$ and PC (67) wt% based electrolytes were prepared by solution casting technique with acetone as a solvent. The polymers PEO and PVdF-HFP were dissolved in room temperature respectively. After that, the polymer solution was slowly evaporated at 40 °C for obtaining a homogeneous solution, poured on a well cleaned petri dish. The residual solvent was allowed to evaporate slowly 40 °C in a vacuum oven for 48 h. The free standing films were obtained. The films are harvested and stored in highly evacuated desiccators to avoid the moisture absorptions. Flexible thin films with thickness of about 0.22 mm were obtained.

2.3. Characterization techniques

The prepared films were subjected to a.c. impedance analysis, in order to calculate the ionic conductivity. This was carried out with the help of stainless steel blocking electrodes using a computer controlled micro auto lab type III potentiostat/galvanostat in the frequency range of 10 Hz–300 kHz over the temperature range of 303–353 K. To investigate the cyclability and reversibility of the electrolyte films, cyclic voltammetry and linear sweep voltammetry studies have been performed using computer controlled micro auto lab type III potentiostat/galvanostat. The amorphousness of the polymer electrolytes has been investigated by XRD analysis with the help of X'pert PROPAN analytical X-ray diffractometer. The data were collected in the range of diffraction angle 2θ from 10° to 80° at the rate 0.05° s^{-1} at room temperature. The complex formation between the polymer and the salt has been confirmed by FTIR spectra using SPECTRA RXI, PerkinElmer spectrophotometer in the range of 400–4000 cm^{-1}. Thermal stability of the polymer electrolyte was carried out by thermogravimetric and differential analysis (TG/DTA) by using PYRIS DIAMOND from room temperature to 700 °C with the scan rate of 10 °C min^{-1} with nitrogen atmosphere. The surface morphology of the electrolyte film was examined by Hitachi S3000H scanning electron microscope. Roughness parameter was observed by AFM with the help of AFM (A100SGS).

3. Results and discussion

3.1. X-ray diffraction studies

In order to investigate the influence of the concentration of lithium salt, XRD studies were performed for PEO, PVdF-HFP, $LiClO_4$ and complexes are shown in Fig. 1. Two broad peaks are found at $2\theta = 19.2°$ and 23.15° corresponding to the reflection of (120) and (010) plane respectively which confirms the semi-crystalline