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Investigations on PVC/PAN composite polymer electrolytes

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Abstract

Composite electrolyte films consisting of poly(vinylchloride), poly(acrylonitrile), ethylene carbonate, $LiClO_4$ and also TiO_2 particles have been prepared by solution casting technique. The effect of inorganic filler on the conductivity of the blended polymer electrolyte was studied. A conductivity of ($7.57 \times 10^{-5}\,S\,cm^{-1}$) is achieved at room temperature for the composition PVC–PAN–$LiClO_4$–EC (4.8–19.2–8–68), whereas it improves two orders of magnitude ($4.46 \times 10^{-3}\,S\,cm^{-1}$) upon dispersing fine particles of TiO_2 as inert filler. The role of ceramic phase is to reduce the melting temperature which is ascertained from the thermogravimetric/differential thermal analysis.

Keywords: Polymer electrolyte; Composite; Inert filler; Plasticizer; Impedance studies

1. Introduction

The interest in the study of polymer electrolyte system is continually growing, because of the potential application of these materials in a great variety of electrochemical devices such as high energy density batteries, fuel cells, sensors and electrochromic devices [1]. The development of polymer system with high ionic conductivity is one of the main objectives in polymer research. Various approaches have been made to modify the structure of polymer electrolytes in order to improve their electrical, electrochemical and mechanical properties. These approaches include: synthesizing new polymers [2]; cross-linking two polymers [3]; blending of two polymers [4]; adding plasticizers to polymer electrolytes [5]; adding inorganic inert fillers [6] to make composite polymer electrolytes. Among these approaches, polymer blending is a useful technique for designing materials with a wide variety of properties by changing the composition of blend matrix. The effect of various PVC/PMMA blend ratio on the ionic conductivity has been studied by Rhoo et al. [7].

A material, containing polymer and ceramic phases is called as a polymer–ceramic composite in this paper, and composite materials comprise an intimate mixture of lithium-ion conducting solid electrolyte and insulating ceramic powder. The first such a system studied was LiI–Al_2O_3 and it was found that the conductivity was enhanced significantly with respect to LiI [8].

Further studies reported that the addition of Al_2O_3 [9,10], TiO_2 [11], $BaTiO_3$ [12] and other fillers such as SiO_2 and related oxides [13] to polyethyleneoxide (PEO)-based polymeric electrolytes improved the ionic conductivity. Mechanisms of such conductivity enhancement have also been studied by impedance spectroscopy and NMR measurements [14,15]. In these cases, the ceramic filler may act as a solid plasticizer [9] or a dissociation promoter due to its high ferroelectricity. The addition of ceramic fillers results in an increase in the conductivity value by one to three orders of magnitude. The increase in conductivity has been found to depend upon the concentration and the particle size of the inert phase. The increase in conductivity is generally attributed either to the formation of a new kinetic path via a thin layer along the interphase itself, or to a concentration enhancement due to phase change in the sub-interphase region [16] and enlargement of the amorphous phase in the polymer matrix [17]. From a microscopic point of view, it has been suggested that ionic transport may benefit from the existence of a space charge layer at the polymer–filler interphase. Croce et al. [18] have developed models to explain the enhanced ionic transport

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properties in polymer–inorganic composite electrolytes in which acid, normal and basic surface functional groups are attached on nano-sized fillers. Kumar et al. [19] have advanced a theory which is based on the dielectric property of the filler and thermal history of the polymer.

In a blend-based polymer electrolytes [20], one conductive component acts as a plasticizer to reduce the non-conducting phase leading to an increase in the ionic conductivity at low temperatures. Therefore, it is expected that the combination of the composite polymer electrolyte system with the blend-based polymer electrolyte system would provide an interesting polymer electrolyte for all solid-state lithium-ion batteries. Though the system is fairly complex, the polymer electrolyte would become one of the most promising ones.

In our earlier works [21–23] we have dealt with the preparation of polymer blend electrolytes with PVC–PAN and the suitable plasticizer and the salt concentration are discussed. In the present paper in order to increase both the ionic conductivity and thermal stability of PVC–PAN blended polymer electrolytes, TiO_2 was added in different concentration (5, 10, 15 and 20 wt%). The effect of an addition of TiO_2 on the conductivity value and thermal stability is discussed in detail.

2. Experimental

Poly(vinylchloride) (PVC) (average molecular weight 1.5×10^5) and poly(acrylonitrile) (PAN) (average molecular weight: 94,000) bought from Aldrich, USA were dried at 373 K under vacuum for 10 h; $LiClO_4$ (Aldrich) was dried at 343 K under vacuum for 24 h. Plasticizer ethylene carbonate (EC) (Aldrich) was used without further purification.

TiO_2 procured from Aldrich, USA of particle size <5 μm was used after annealing at 373 K for 10 h. All the electrolytes were prepared by solution casting technique. Appropriate quantities of PVC, PAN, $LiClO_4$ (Table 1) were dissolved by adding in sequence to pre-distilled DMF (di methylformamide. E. Merck, Germany). After incorporating the required amount of plasticizer EC, inorganic filler TiO_2 (titanium di oxide) was suspended in the solution and stirred for about 48 h at room temperature and then at 333 K for 4 h before the electrolytes were cast on finely polished Teflon supports or Teflon covered glass plates. The films were dried in vacuum oven at 333 K at a pressure of 10^{-3} Torr for 24 h. The thus obtained film was visually examined for its dryness and free-standing nature. The phase analysis of the polymer was performed with X-ray diffractometer (XRD) [Bruker (D8 Advance)] at room temperature. The Fourier transform infrared (FTIR) spectrum in the range 4000–400 cm^{-1} was recorded using Jasco FTIR 460 plus (Japan) spectrophotometer.

The conductivity measurements were carried out with a circular film thus obtained by the casting technique. The electrolyte film was placed between the stainless steel electrodes with a spring load arrangement to ensure proper contact between the electrolyte and electrode. This specially designed conductivity jig was used for electrical measurements. For electrical conductivity measurement, a LCZ (inductance capacitance and impedance analyzer) meter model 3330 Keithley was used with a signal amplitude of 10 mV in the frequency range 40–100 kHz. Variation in conductivity with increase of temperature is recorded in the range 302–373 K.

The films were subjected to thermogravimetry and differential thermal analysis (TG/DTA) using PerkinElmer (pyres diamond) TG/DTA with a heating rate of 10 °C/min.

Table 1
Conductivity values of PVC–PAN–$LiClO_4$–EC (4.8–19.2–8–68)–TiO_2 polymer complexes

Sample	TiO_2 wt%	σ ($\times 10^{-2}$ S cm^{-1})				
		302	318	333	353	373
T_0	0	0.008	0.010	0.034	0.057	0.073
T_1	5	0.020	0.055	0.132	0.209	0.427
T_2	10	0.446	0.741	1.380	1.860	5.012
T_3	15	0.225	0.433	0.568	0.817	1.362
T_4	20	0.126	0.167	0.284	0.418	0.818

3. Results and discussion

3.1. X-ray diffraction studies

X-ray diffraction (XRD) studies can provide a wide range of information on crystal structure, crystal orientation, crystallinity, crystallite size and phase changes of materials which are characterized by the presence of sharp diffraction rings or peaks. In amorphous materials, there is no long-range order present, however, the non-crystalline samples are characterized by one or two broad “halos”. For the present case, the X-ray diffraction method has been used only in a limited perspective to identify the following:

(a) Amorphous, crystalline or semicrystalline nature of material.
(b) Complex formation.
(c) Relative amorphicity of the composite films.

The X-ray diffraction patterns of pure PVC, PAN, $LiClO_4$, TiO_2 and the complexes are shown in Fig. 1(a–d and e–i), respectively. The complexes contain 0, 5, 10, 15 and 20 wt% of the total polymer content of the electrolyte. It is evident from the Fig. 1(a and b) that pristine PVC and PAN exhibit an amorphous phase. The presence of sharp diffraction peaks in Fig. 1(c and d) indicates the crystalline nature of $LiClO_4$ and TiO_2, respectively. The absence of sharp peaks pertaining to $LiClO_4$ in the polymer complexes (Fig. 1(e–i)) shows that the complexation has taken place in the amorphous phase [24]. The XRD patterns obtained for the electrolyte films PVC–PAN–EC–$LiClO_4$ with different concentration of TiO_2 exhibit crystalline peaks at 2θ values 32°, 41° and 48°, etc. indicating the presence of undissolved TiO_2 in the polymer matrix. Some of the crystalline peaks corresponding to TiO_2 at 2θ values 37°, 38°, 62°, 68°, 70° and 75° are found absent and some shifted in the complex indicating the interaction between the constituents of the complex. It is evident from the Fig. 1(f–i) the crystalline peaks are few and the amorphicity is maintained till 10 wt% of TiO_2 and on further addition the