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Effects of addition of $BaTiO_3$ Nano particles on the conductivity of PVdF/PMMA based polymer blend electrolytes

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Abstract: *Composite polymer electrolyte (CPE) membranes, comprising poly (vinylidene fluoride) (PVdF)/poly (methyl methacrylate) (PMMA),* $BaTiO_3$ *as ceramic filler and* $LiBF_4$ *as the lithium salt were prepared using a solution casting technique. The prepared membranes were subjected to XRD, FT-IR, impedance spectroscopy and thermal stability studies. The incorporation of nanofiller greatly enhanced the ionic conductivity and the thermal stability of the composite polymer electrolyte. Polymer blend electrolyte with 15 wt% of* $BaTiO_3$ *ceramic powder exhibited higher ionic conductivity (1.335 x* 10^{-3} *S/cm) compared to the other ratios.*

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

I. Introduction

In recent years, there has been a growing demand for high-energy density rechargeable batteries for portable electronic products. The science of polymer electrolytes is a highly specialized interdisciplinary field which encompasses the disciplines of electrochemistry, polymer science, organic chemistry, and inorganic chemistry. The field has attracted ever-increasing interest both in academia and industry [1, 2]. Since Wright et al. [3] found out in 1973 that the complex of poly (ethylene oxide) (PEO) and alkaline salts have the ability of ionic conductivity. Solid polymer electrolytes (SPEs) have drawn significant interest for the possible replacement of liquid electrolytes in secondary lithium batteries due to the advantages of SPE-based lithium batteries considering safety, weight and size [4]. The main reason in choosing these polymers the host is that it forms more stable complexes and possesses higher ionic conductivities than any other group of solvating polymers without the addition of organic solvents [5].

Thus, several approaches have been applied to enhance the properties of polymer electrolytes. One of the most effective approaches has been the addition of inorganic fillers, such as ceramic fillers [6], as well as syntheses of organic/inorganic hybrid materials [7]. The results showed that the addition of the inorganic fillers has improved many properties of the polymer electrolytes, such as ionic conductivity, lithium ion transference number ($t+$), mechanical properties, and the stability of electrolyte–electrode interface [8]. These improvements have been ascribed to fillers that (1) acted as the plasticizers and lowered the crystallinity of the polymer matrix [9], (2) increased ion mobility by providing additional conductive pathway due to formation of the Lewis acid–base interactions [10], and (3) increased the number of charge carriers due to enhancement of the salt dissociation [11] .

In this work, we investigated preparation of PVdF/PMMA based composite polymer blend electrolytes composed of $LiBF_4$ as a salt and $BaTiO_3$ as a ceramic filler. This study focuses on improvement of the ionic conductivities of polymer electrolytes by the addition of $BaTiO_3$ nanoparticles. The effects of the $BaTiO_3$ nanoparticles on the performance of polymer electrolytes are presented and discussed.

II. Materials and Methods

PVdF and PMMA (both from Aldrich) were dried under vacuum at 80°C for 24 hours. Reagent grade anhydrous lithium tetraflouro borate was used after drying in vacuum at 110°C for 24 hours. The plasticizer propylene carbonate (PC) (from Aldrich) was used as supplied. The nano sized $BaTiO_3$ (Aldrich) was used as a ceramic filler. All the electrolytes have been prepared by the solvent casting technique. Appropriate quantities of PVdF, PMMA and $LiBF_4$ are dissolved by adding in sequence to tetrahydrofuran (THF) and stirred for 24h. The resulting solution is poured on to a glass plate and the THF is allowed to evaporate in air at room temperature for several hours. The films are further dried at 60º C for 24 hours in vacuum to remove any traces of THF.

Thin films thus obtained were subjected to XRD and FTIR studies to investigate the complexation behaviour and the nature of crystallinity of the polymer electrolytes using Bruker (D8 Advance) diffractometer and Perkin-Elmer (Paragon 500 grating) IR spectrophotometer respectively. Thermal stability of the film was also characterized by TG/DTA at a heating rate of 10°C per minute from room temperature. The electrical conductivity of polymer complexes was measured from impedance plots at different temperatures using Keithley 3330 LCZ meter. The impedance measurement was recorded in the frequency range 40Hz-100 KHz with signal amplitude of 10mV.

III. Results and Discussion

3.1 X-ray diffraction

X-ray diffraction patterns of pure PVdF, PMMA, $LiBF_4$ and PVdF(17.5)- PMMA(7.5)- PC(67)- $LiBF_4$(8) with X % of $BaTiO_3$ (where X= 0,5,10,15,20) in the total polymer weight are shown in the figure 1. The nano sized $BaTiO_3$ dispersed emulsion can penetrate the space between the polymer chains and consequently, the homogeneously dispersed ceramic filler in the matrix prevents or retards crystallization of the polymers due to its large surface area. The intensity of the peaks abruptly decreases in the composite electrolytes. No peaks have appeared corresponding to the salt in the complexes, which confirms the amorphicity of the electrolytes. These observations illustrate that the polymer electrolytes have turned to an amorphous phase.

3.2 FT-IR analysis

FT-IR studies were carried out using FTIR ABB BOMEN MB104 IR spectrophotometer at 0.9 cm^{-1} resolution. The characteristic vibrational frequencies at 3010 and 2951 cm^{-1} are assigned to O–CH_2 asymmetric stretching and CH_3 asymmetric stretching of PMMA, which are displaced to 2995 and 2947 cm^{-1} in the complexes. The vibrational peaks appearing at 1389 and 1280 cm^{-1} are assigned to O–CH_3 deformation and C–O stretching of PMMA. They are shifted to 1392 and 1276 cm^{-1} in the complexes. The C=O stretching, CH_2 scissoring, twisting, wagging modes of PMMA at 1736, 1483, 1173 and 947 cm^{-1} are found to be absent in the complexes.

The vibrational bands at 1263 and 1186 cm^{-1} are ascribed to the stretching frequencies of C–F and CF_2, respectively, in pure PVdF. Also the peaks at 1070 and 533 cm^{-1} are ascribed to symmetric C–C stretching and CF_2 bending vibrations of pure PVdF, respectively. In the blended polymer complexes, the vibrational band observed at 875–870 cm^{-1} is ascribed to the combinations of symmetric C–C stretching and skeletal CF–CH–CH bending of PVdF. The peaks observed at 1268 cm^{-1} is ascribed to C–F stretching vibrations of PVdF, respectively.

It is also found that some of the peaks disappear in the complexes such as (976, 1185, 1724, 2645, 3435 cm^{-1}). In addition to this, few new peaks are observed at (489, 881, 1800, 2085 cm^{-1}) in the polymer complexes. The above analysis confirms the complex formation.

3.3 Conductivity studies

Figure 3 shows the complex impedance plot of PVdF(17.5)- PMMA(7.5)- PC(67)- $LiBF_4$(8) with 15 wt % of $BaTiO_3$ of the total polymer weight at various temperatures. This plot shows linear spikes. The disappearance of the high frequency semicircular portion in the polymer complex impedance plot indicates that the current carriers are ions and the total conductivity is the result of ion conduction. The bulk resistance of the electrolyte was measured by extrapolating an intercept of this plot on the real axis. The electrical conductivity of the electrolyte was calculated for the known values of bulk resistance (R_b), area (A) and the thickness (l) of the film using the formula $\sigma = l/R_bA$.

It has been seen that the addition of inorganic fillers leads to an increase in the ambient temperature conductivity upto 15 wt% of $BaTiO_3$ in the total polymer weight and then the ionic conductivity decreases due to higher concentration of ceramic fillers. Indeed, one may surmise that the presence of high dispersed particles in the polymer matrix may affect the crystallization rate by preventing the agglomeration of the polymer chains. Further, the particle size and content of the ceramic additive appear to be a critical factor. It is also seen that a reasonably high concentration of the filler is also necessary to affect the recrystallization rate of the polymer host.

The temperature dependence of the ionic conductivity of PVdF(17.5)- PMMA(7.5)- PC(67)- $LiBF_4$(8)- X% of $BaTiO_3$ (where X= 0,5,10,15,20) in the total polymer electrolyte is shown in the figure 4. From the plot it has been observed that as temperature increases the conductivity values also increase for all the compositions. The non-linearity in Arrhenius plots indicates that ion transport in polymer electrolytes is dependent on polymer segmental motion. The curvature behaviour of the plots suggests that the data can be better described by the Vogel–Tamman–Fulcher (VTF) relation, which described the transport properties in a viscous matrix. It supports the idea that the ion moves through the plasticizer-rich phase.

3.4 Thermal analysis

Figure 5 shows the TG/DTA traces of PVdF (17.5)-PMMA (7.5)-PC (67)-$LiBF_4$ (8)- $BaTiO_3$ (15 wt%) polymer composite which shows maximum conductivity value. An endothermic peak was observed at 35°C and corresponding about 2% of weight loss is attributed to the presence of moisture in the samples. The film starts decomposing at 251°C followed by an endothermic peak, which indicates that the film is stable up to 251°C.

The DTA trace shows an endothermic peak around 360°C, which corresponds to the melting point of PMMA polymer host.

It is clear from these observations, that the PMMA based hybrid polymer electrolytes, which contain $LiClO_4$ as salt can be operated up to 251°C.

IV. Conclusion

The salt-in-polymer electrolytes prepared from the PVdF/PMMA show a strong enhancement of the ionic conductivity by the addition of $BaTiO_3$ nanoparticles. The ionic conductivity of the resulting composite polymer electrolyte is better than the blend polymer electrolyte. The temperature dependent ionic conductivity plot of the composite films seems to obey the VTF relation.

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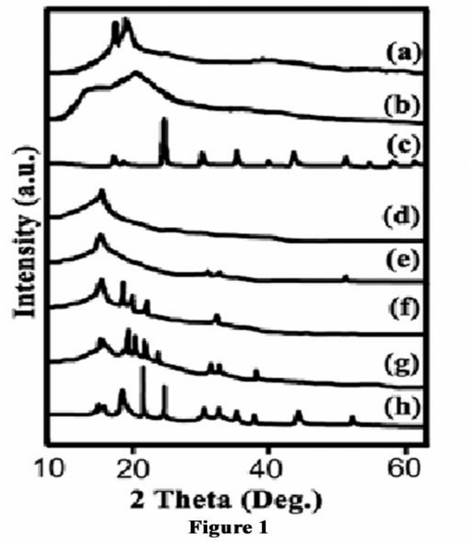

Figure 1. X-ray diffraction patterns of (a) Pure PVdF (b) Pure PMMA (c) $BaTiO_3$

(d) PVdF (17.5)-PMMA (7.5)-$LiBF_4$ (8)-PC (67)-$BaTiO_3$ (0)
(e) PVdF (17.5)-PMMA (7.5)-$LiBF_4$ (8)-PC (67)-$BaTiO_3$ (5)
(f) PVdF (17.5)-PMMA (7.5)-$LiBF_4$ (8)-PC (67)-$BaTiO_3$ (10)
(g) PVdF(17.5)-PMMA(7.5)-$LiBF_4$(8)-PC(67)-$BaTiO_3$(15)
(h) PVdF(17.5)-PMMA(7.5)-$LiBF_4$(8)-PC(67)-$BaTiO_3$(20)

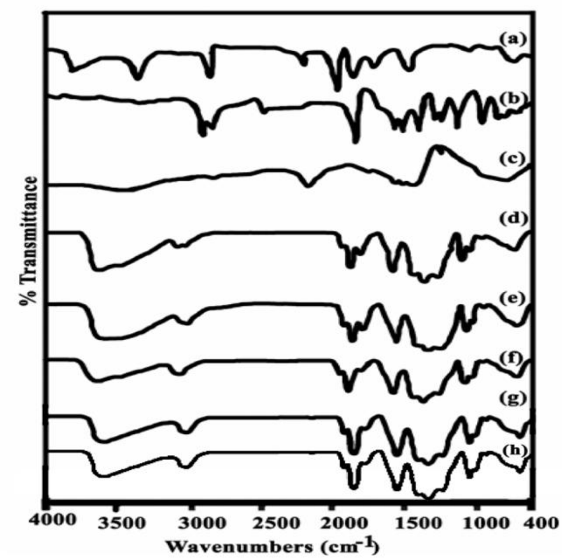

Figure 2

Figure 2. FTIR Spectra of (a) Pure PVdF (b) Pure PMMA (c) $LiBF_4$

(d) PVdF (17.5)-PMMA (7.5)-$LiBF_4$ (8)-PC (67)-$BaTiO_3$(0)
(e) PVdF (17.5)-PMMA (7.5)-$LiBF_4$ (8)-PC (67)-$BaTiO_3$(5)
(f) PVdF (17.5)-PMMA (7.5)-$LiBF_4$ (8)-PC (67)-$BaTiO_3$(10)
(g) PVdF(17.5)-PMMA(7.5)-$LiBF_4$(8)-PC(67)-$BaTiO_3$(15)
(h) PVdF(17.5)-PMMA(7.5)-$LiBF_4$(8)-PC(67)-$BaTiO_3$(20)

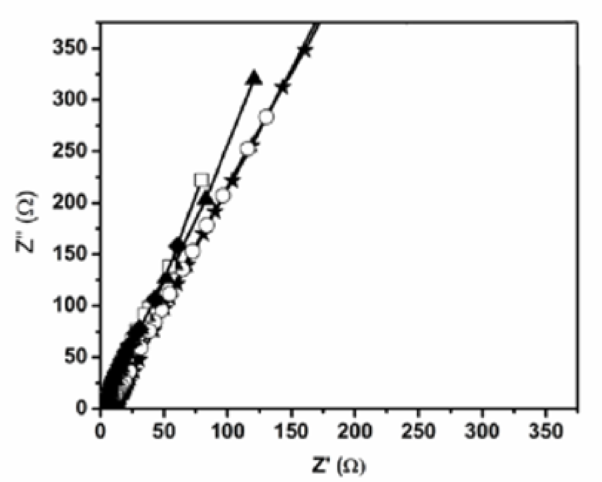

Figure 3

Figure 3. Impedance diagram for PVdF(17.5)-PMMA(7.5)-$LiBF_4$(8) -PC(67)-$BaTiO_3$(10) wt% at various temperatures.

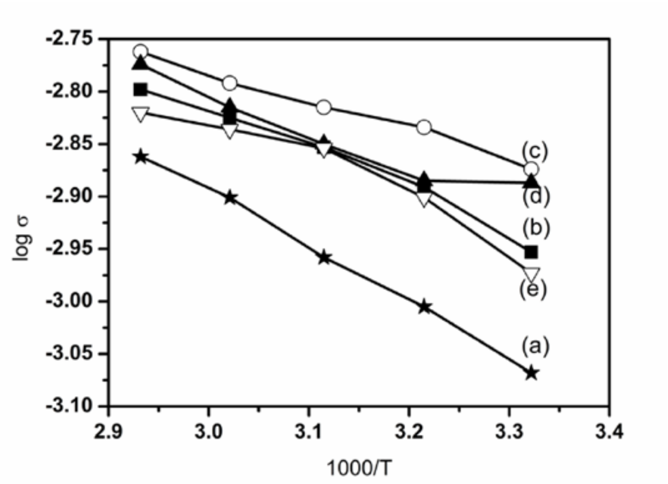

Figure 4

Figure 4. Arrhenius plot of PVdF(17.5)-PMMA(7.5)-$LiBF_4$(8)-PC(67)- $BaTiO_3$(X wt %) (where X= 0, 5, 10, 15, 20) composites.

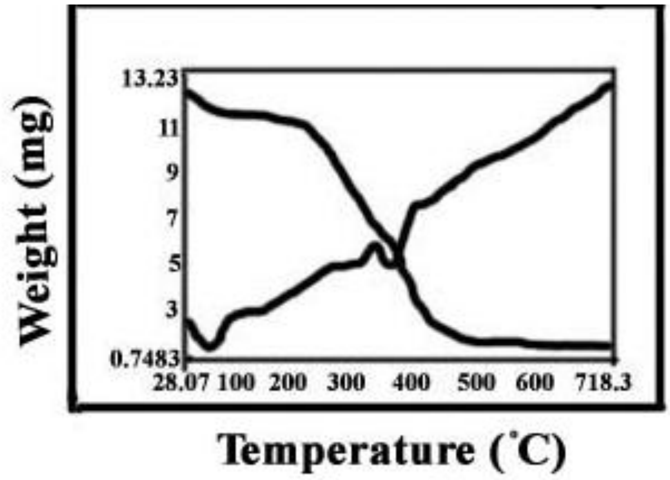

Figure 5

Figure 5. TG/DTA curves of PVdF(17.5)-PMMA(7.5)-$LiBF_4$(8)-PC(67)- $BaTiO_3$(15 wt %) composite.

Table 1

Ionic conductivity values for PVdF (17.5)-PMMA (7.5) -PC (67) - $LiBF_4$ (8) – $BaTiO_3$(X wt %) (where X= 0, 5, 10, 15, 20) system

Film	**$BaTiO_3$ ratio**	**Ionic conductivity x 10^{-3} S cm^{-1}**				
		301K	**311K**	**321K**	**331K**	**341K**
V1	0	0.854	0.988	1.101	1.256	1.372
V2	5	1.113	1.283	1.401	1.493	1.591
V3	10	1.335	1.463	1.531	1.611	1.726
V4	15	1.297	1.303	1.412	1.528	1.679
V5	20	1.064	1.256	1.397	1.456	1.512