

PREPARATION AND CHARACTERISATION OF TiO₂ NANOFILLER INCORPORATED POLYMER COMPOSITE FOR Li BATTERY APPLICATIONS

P. Pradeepa, M. Priya and M. Ramesh Prabhu

Department of Physics, Alagappa University, Karaikudi, Tamil Nadu, India.

Introduction

Solid polymer electrolytes have received a great deal of attention due to its rapid progress in the size reduction of electronic equipments and improvement of conductivity in electrochromic devices^[1]. Polymer electrolytes have many advantages such as flexibility, ease of processing into thin film of large surface area, electrochemical stability and leak-proof nature. These electrolytes are safe, flexible, mechanically stable and can offer higher energy density as compared to commercial liquid electrolytes^[2]. To date several polymer hosts have been investigated and developed among which the host polymer PEMA plays an important role in the ionic conductivity. The carboxylic (COOH) polymer can improve the interconnecting pathways which will ease ion movement through the polymer segments. However the large pendant groups limit the close packing of the chains in the PEMA polymer increasing the free volume. Furthermore, more separation of the chains increases the translational mobility of the polymer, which will lower the TG of the amorphous polymer^[3].

Poly (methyl methacrylate), PMMA & poly (ethyl methacrylate) PEMA are methacrylic ester polymers. PEMA has excellent chemical resistance, high surface tension and offers high optical transparency^[4]. PMMA electrolytes have

been widely investigated by researchers due to its high ambient temperature ionic conductivity. PEMA is reported^[5] to exhibit higher mechanical strength than PMMA. High transparency, sufficient mechanical strength, elasticity & good adhesion on to substrate make PEMA suitable for use as a host for ionic conduction in electrochromic devices. The elongation strength of PEMA (7%) is higher and its T_g (336K) is lower as compared to PMMA^[6]. Our preliminary tests indicated that the PEMA based electrolytes also exhibit greater mechanical strengths than their PMMA counterparts. For instance, the Generating Porous Electrodes (GPE) made from PEMA - PC - LiClO₄ - TiO₂ exhibited storage models of ~ 390 Mpa.

To the best of our knowledge PEMA - PC - LiClO₄ - TiO₂ based electrolyte for lithium battery applications has yet to be studied^[7]. In the present work, we attempt to investigate this new polymer electrolyte based on PEMA - TiO₂-PC - LiClO₄. It has been suggested that electrolytes with anion salts have higher ionic conductivity than other anion based systems. The prepared electrolytes were subjected to various characterisations such as XRD, TGDTA and a.c impedance analysis.

Experimental Procedure

All the samples were prepared by facile solution casting technique. The host polymer PEMA, the filler TiO₂ the

lithium salts (Sigma Aldrich, USA) heated to 100°C to remove moisture. The plasticizer Propylene Carbonate (PC) was used as received. The appropriate amounts of the selected polymer and Lithium salts were dissolved using a solvent, tetrahydrofuran (THF) with the help of continuous magnetic stirring to obtain a homogeneous mixture. The plasticizer was added with mixture & the stirring was continued for approximately 24 hours. The obtained slurry was degassed to remove air bubbles and then poured on a well cleaned Teflon covered glass plate to allow the solvent to evaporate at room temperature. The electrolyte films were heated at 60°C for 6 hours to remove any trace of the residual solvent. X-ray diffraction patterns of the samples were obtained using a computer controlled X'pert proanalytical diffractometer with cu-K α radiation (wavelength = 0.1541 nm) as the source at 40KV with a scanning range of 10-80. The AC impedance electrical conductivity study was carried out on the polymer electrolyte film with

stainless steel blocking electrodes using a computer controlled Micro-Autolab TYPE III potentiostat/galvanostat in the frequency range of 40 Hz-300 KHz for various temperatures ranging from 302 K to 363 K. TG-DTA thermal analysis of polymer electrolyte samples was performed using a Perkin Elmer pyris-6 TG/DTA with the scan rate of 10°C min⁻¹.

Results and Discussion

X-ray diffraction analysis

XRD patterns of pure PEMA, LiClO₄, TiO₂ and their complexes are shown in the Fig. 1. In order to investigate the complexation of lithium salt with the polymer, XRD studies were performed. The amorphous nature of the PEMA and crystalline nature of LiClO₄ salt are observed. The characteristic peaks at 18.6° for PEMA reveals the increasing nature in salt concentration. The intensity of PEMA peak decreases and leads, peak appears as single broad peak in the complexes.

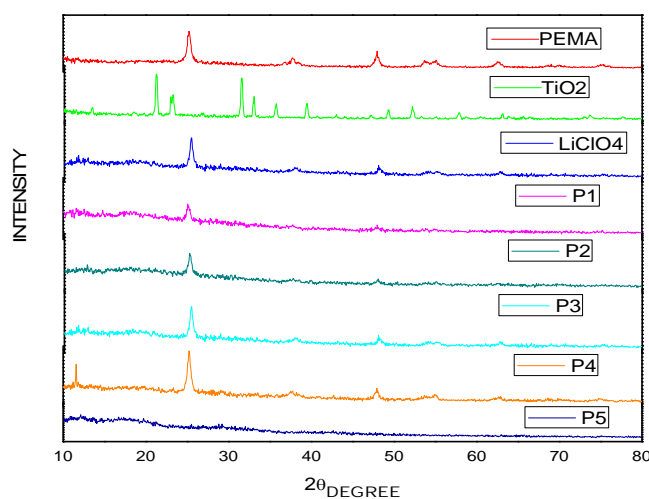


Fig. 1: XRD- Patterns of pure PEMA, LiClO₄, TiO₂, and prepared electrolyte membranes

The crystallinity of the electrolytes is greatly reduced by the addition of salt and plasticiser. The addition of PC induces significant disorder in the polymer structure, resulting in lower crystallinity. The nanosized TiO₂ emulsion can penetrate the space between the polymer chains and consequently the homogenously dispersed ceramic filler in the matrix prevents and retards crystallisation of the polymers. Due its large surface area the intensity of the peak abruptly increases in the composite electrolytes. No peak have appeared corresponding to the salt in the complexes, which confirms the amorphicity of the electrolytes. It illustrates that the polymer electrolytes have tend to be in amorphous phase.

Ionic Conductivity

Electrochemical impedance spectroscopy is an excellent tool for characterising

many of the electrical properties of materials and their interfaces with electronically conducting electrodes^[8]. A temperature dependent complex impedance plot of the electrolyte membrane with higher ionic conductivity is shown in the Fig. 2. The measurements were done in the frequency range from 40HZ to 300KHZ at ambient temperature. The impedance studies were carried out by sandwiching the polymer electrolyte film between two stainless steel (SS) electrodes under spring pressure. The thickness of each sample was measured using a micrometer screw gauge. The ionic conductivity of each sample was calculated using the following equations. $\sigma = t / R_b A$ Where t is the thickness of the film, R_b is the bulk resistance and A is the area of electrolyte electrode contact^[9].

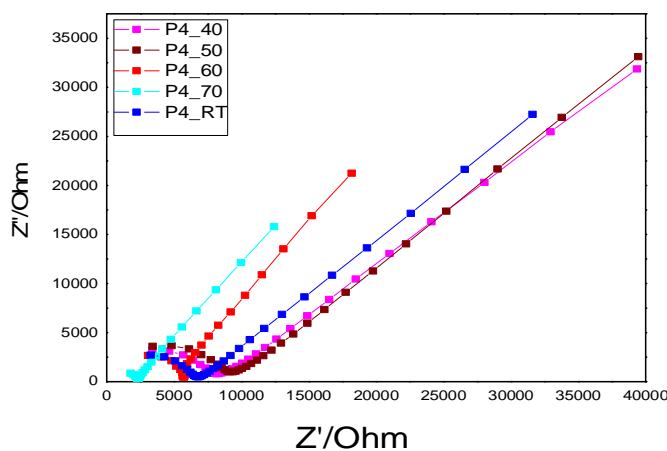


Fig. 2. Room temperature complex impedance plot of the prepared samples.

Fig. 2 shows the complex impedance plot of PEMA (19)-PC (67) - LiClO₄(8) with 6 wt % of TiO₂ 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 ionic conduction. The bulk resistance of the electrolyte was measured by

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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 (t) of the film using the formula:

$$\sigma = t/R_b A$$

Table 1
Ionic conductivity values of PEMA (19) + PC (67) + LiClO₄(8), X wt.% of TiO₂ in the total polymer weight

Sample coding	PEMA(25)-TiO ₂ (X)-LiClO ₄ (8)_PC(67) Wt %	Ionic conductivity values (σ) $\times 10^{-3}$ Scm ⁻¹ at different temperatures (K)				
		303	313	323	333	343
P1	X=0	2.016	2.713	3.426	4.012	4.913
P2	X=2	2.312	3.026	3.812	4.423	5.162
P3	X=4	2.613	3.253	4.007	4.926	5.346
P4	X=6	2.903	3.621	4.287	5.396	6.102
P5	X=8	2.788	3.438	4.110	5.167	5.998

It has been seen that the addition of inorganic fillers leads to an increase in the ambient temperature conductivity upto 6 wt% of TiO₂ in the total polymer weight and then the ionic conductivity decreases due to higher concentration of ceramic fillers. Indeed, one may summarise that the presence of high dispersed particles in the polymer matrix may affect the crystallization rate by preventing the agglomeration of the polymer chains^[10]. 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-PEMA(19)- PC(67)-LiClO₄(8)- X% of TiO₂ (where X= 0,2,4,6,8) in the total polymer electrolyte is shown in the figure 3. 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.

TG-DTA Analysis

Thermal stability is an important parameter for acceptable performance during high temperature operation, which is related to safety concerns^[11]. In this work, the thermal stability of the polymer electrolytes was observed using thermo gravimetric analysis (TGA).

The TGA curves indicates that the films of various ratio of filler TiO₂ exhibit weight loss and is mainly due to the presence of moisture which may be acquired during the loading of the sample or the evaporation of residual solvent^[12].

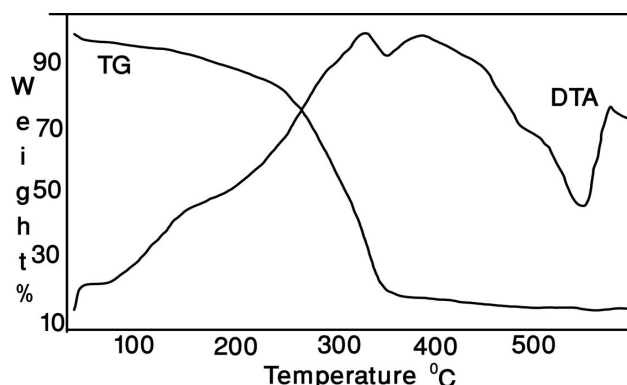


Fig. 3: TG/DTA analysis of TG/DTA traces of PEMA (19)-PC (67)-LiClO₄ (8) - TiO₂ (6 wt %)

Figure shows the TG/DTA traces of PEMA (19)-PC (67)-LiClO₄ (8)-TiO₂ (6 wt %). The weight loss is also confirmed from the endothermic peaks observed at 120°C in almost all the samples. All the prepared samples show appreciable weight losses of approximately 13, 23, 24 & 9% respectively at 250°C-300°C is primarily due to the degradation of Propylene Carbonate (PC) because of the boiling point of the PC (242°C). It may also be due to the blended polymer degradation.

An endothermic peak was observed at 65°C and corresponding 7% of weight loss is attributed to the presence of moisture in the samples. The film starts decomposing at 222°C followed by an endothermic peak, which indicates that the film is stable up to 222°C. The DTA trace shows an endothermic peak around 416°C, which corresponds to the melting point of PEMA polymer host.

It is clear from these observations, that the PEMA based hybrid polymer electrolytes, which contain LiClO₄ as salt can be operated up to 222°C.

Conclusions

PEMA based single polymer electrolyte have been investigated with the addition of PC as a plasticizer and TiO₂ as filler. The complexation of the prepared electrolyte systems was confirmed from XRD and FTIR analysis. X-Ray diffraction analysis revealed the semi crystalline nature of all the polymer electrolytes, which improves ionic conduction. All the electrolytes show appreciable conductivity at room temperature. Maximum conductivity $2.903 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature with good mechanical stability has been observed for PEMA (19)-PC (67)-LiClO₄ (8)-TiO₂ (6 wt%). At 303K free standing nature was observed for PEMA/TiO₂/PC/LiClO₄ electrolyte film. From the TG-DTA observations it was noted that the electrolyte exhibited a maximum thermal stability of approximately 222°C.

In summary, polymer blend electrolytes with possible applications in high-energy density batteries have been identified in terms of such parameters as conductivity and thermal stability.

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