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A study incorporating nano-sized silica into PVC-blend-based polymer electrolytes for lithium batteries

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Abstract Blends of poly(vinyl chloride)-poly(methyl methacrylate) (PVC/PMMA) and poly(vinyl chloride)-poly (ethylene oxide) (PVC/PEO) with lithium triflate ($LiCF_3SO_3$) as salt, ethylene carbonate (EC), and dibuthyl phthalate (DBP) as plasticizers and nano-sized silica (SiO_2) as filler, the first of its kind in such a study, were prepared using the solution-cast technique. This study affirmed that SiO_2 added PVC-PMMA and PVC-PEO-blend-based polymer electrolytes have the ability to retain their ionic conductivity and integrity even after 60 days of storage time at room temperature. The reduction of ionic conductivity values in PVC-PMMA-$LiCF_3SO_3$-DBP-EC:SiO_2-based and SiO_2-free membranes are 9 and 30%, respectively. When PVC-PEO-blend was used, the reduction of ionic conductivity values in PVC-PEO-$LiCF_3SO_3$-DBP-EC:SiO_2-based and SiO_2-free system was 16 and 40%, respectively, after 60 days of storage also at room temperature. The SiO_2-based complexes were also found to maintain their conductivity at higher temperatures of 60 °C and 90 °C with progressive storage times. This clearly shows that the SiO_2-induced stabilizing effect is maintained even at higher temperatures. Silica has brought the conductivity of polymer electrolytes into the useful realm for materials in lithium polymer battery applications.

Introduction

The field of polymer engineering has become the driving force in the advances in battery technology with the emergence of the 21st century. This requires the availability of solid polymer electrolyte films with adequate conductivity, good mechanical property, electrochemical stability, and ease of processing [1, 2]. Typically, polymer electrolyte is prepared by dissolving lithium salt in a plasticizer and then adding them to a polymer network. Although this technique is the gold standard and widely used, the main disadvantage of this plasticized polymer electrolyte is the leakage of liquid from the films. This compromises not only the ionic conductivity of the whole system but also the battery reliability and safety as well. Moreover, most plasticizers are volatile at room temperature and as this study is carried out at room temperature, the possibility of the material reverting to its unplasticized, unenhanced state is high [3]. In order to further improve the desired properties of the electrolytes, inorganic fillers were added to these polymer electrolytes [4–10]. One such author, Scrosati et al. [11] reported that the addition of ceramic fillers, having the right particle size and composition, prevents crystallization and favors the amorphous, highly conducting structure of the polymer electrolyte.

In light of this, PVC was used as the host polymer in the present study. It is noteworthy that the incorporation of nano-sized silica into PVC-blend-based polymer electrolytes may give rise to new types of nanocomposite polymer electrolytes. These new types of nanocomposite polymer electrolytes are characterized by superior property in terms

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of ionic conductivity and more importantly, liquid retention capability.

Experimental

High molecular weight poly(vinyl chloride) (PVC) was obtained from Fluka, while poly(methyl methacrylate) (PMMA) with an average molecular weight of 350,000 and polyethylene oxide (PEO) with average molecular weight 200,000 were obtained from Aldrich. The PVC/PMMA-blends were prepared by dissolving in tetrahydrofuran (THF) that was obtained from J.T. Baker. Lithium triflate ($LiCF_3SO_3$), obtained from Aldrich, was used as the doping salt. The plasticizers, dibutyl phthalate (DBP) and ethylene carbonate (EC) were both procured from Aldrich and Fluka, respectively. Fumed silica (SiO_2) with particle size of 10–30 nm, which was supplied by Wacker Chemie was used as the nanocomposite filler.

$LiCF_3SO_3$ was dried at 100 °C for 1 h in order to eliminate trace amounts of water in the material. Desired amounts of PVC/PMMA-blend and $LiCF_3SO_3$ were dissolved separately in THF and the solutions were then mixed together and stirred. After incorporating the required amounts of plasticizers (DBP and EC), inorganic filler SiO_2 powder was suspended in the solution and stirred for 24 h to achieve a homogeneous solution. The solutions thus obtained were cast on a glass plate and allowed to evaporate slowly inside a desiccator. This procedure yields mechanically stable and free standing films. This is proven through the Young's Modulus value which was calculated to be in the range of $\sim 10^{-3}$ MPa.

Ionic conductivity of the polymer electrolytes was determined by ac-impedance measurements using HIOKI 3531 Z bridge interfaced with a computer for data acquisition over a frequency range between 50 Hz and 1 MHz. The thin film polymer electrolyte films were sandwiched between two stainless disk electrodes, which acted as a blocking electrode for ions.

Results and discussion

In order to study the aging effect of silica-based composite polymer electrolytes in the present study, we monitored the room temperature ionic conductivity of the silica-based membrane (PVC-blend-$LiCF_3SO_3$-DBP-EC-SiO_2) and of an analogous, silica-free membrane (PVC-blend-$LiCF_3SO_3$-DBP-EC) for a period of 60 days.

Figure 1 shows the variation of ionic conductivity values as a function of storage time in PVC-PMMA-$LiCF_3SO_3$-DBP-EC:SiO_2 (95:5) complex and of an analogous, SiO_2-free complex, at room temperature. The reduction of conductivity values in silica-based and silica-free membranes after 60 days of storage time is 9 and 30%, respectively. Figure 2 illustrates the impedance responses obtained for PVC-PMMA-$LiCF_3SO_3$-DBP-EC:SiO_2 (95:5) complex at progressive storage times.

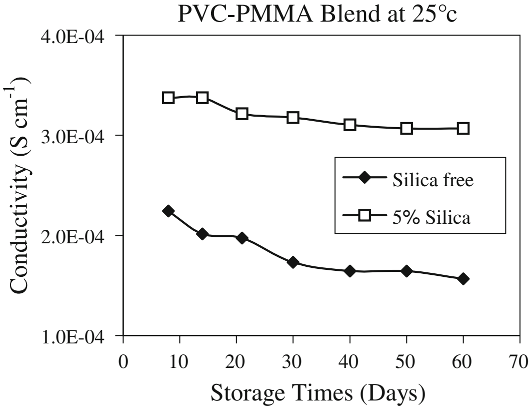

Fig. 1 Time evolution of the ionic conductivity of a PVC-PMMA-$LiCF_3SO_3$-DBP-EC:SiO_2 (95:5) membrane and of an analogous, SiO_2-free membrane at room temperature

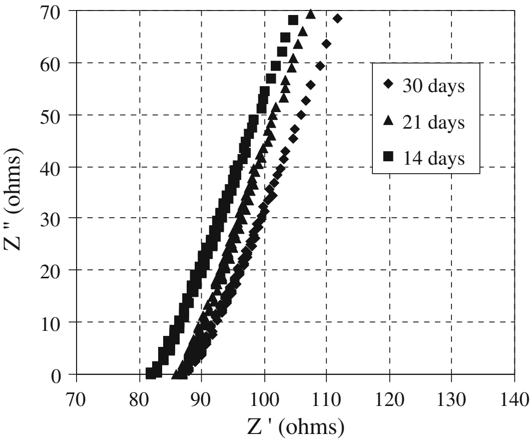

Fig. 2 Impedance responses of a PVC-PMMA-$LiCF_3SO_3$-DBP-EC:SiO_2 (95:5) membrane at room temperature. The measurements were performed at various progressive storage times

Upon analysis of PVC-PEO-blend system, the reduction of ionic conductivity for PVC-PEO-$LiCF_3SO_3$-DBP-EC: iO_2 (95:5) complex and of an analogous, SiO_2-free complex at room temperature was found to be 16 and 40%, respectively. Figure 3 clearly illustrates this. The impedance responses obtained for PVC-PEO-$LiCF_3SO_3$-DBP-EC:SiO_2 (95:5) complex at progressive storage times are depicted in Fig. 4.

Figures 1 and 3, which show the time evolution at room temperature of the silica-based membrane in comparison with that of an analogous, silica-free membrane, clearly evidences the superior behavior of the former over the latter. The ionic conductivity of the silica-based membranes does

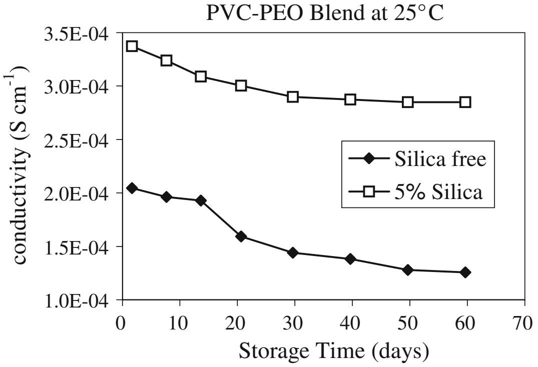

Fig. 3 Time evolution of the ionic conductivity of a PVC-PEO-$LiCF_3SO_3$-DBP-EC:SiO_2 (95:5) membrane and of an analogous, SiO_2-free membrane at room temperature

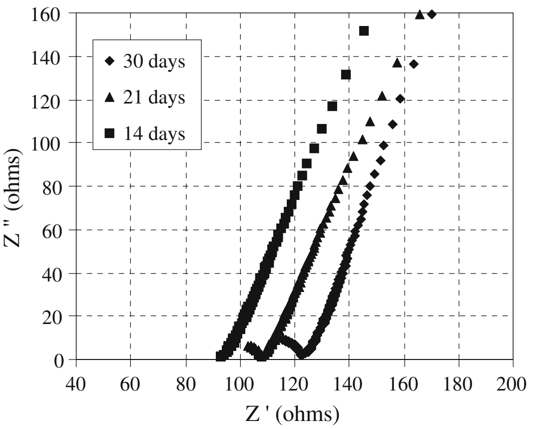

Fig. 4 Impedance responses of a PVC-PEO-$LiCF_3SO_3$-DBP-EC:SiO_2 (95:5) membrane at room temperature. The measurements were performed at various progressive storage times

not appreciably change upon long storage time. From Figs. 2 and 4, two important features are noted. The first being the high value of conductivity of the order of 10^{-4} S cm^{-1} and secondly, the intercepts exhibiting only a minor shift even after 30 days of storage.

It is noteworthy that addition of SiO_2 enhances the ionic conductivity of both PVC-PMMA and PVC-PEO-blend-based polymer electrolytes. This could be attributed to the increase in mobility and number of charge carriers upon addition of SiO_2.

The features noted in Figs. 2 and 4, concur to demonstrate that the addition of silica considerably contributes to enhance the stability of both the PVC-PMMA and PVC-PEO-blend-based polymer electrolyte membranes without affecting their conductivity. The results evidently clearly show that the membranes have retained their conductivity and thus, their integrity over the entire storage time [12, 13]. When compared, PVC-PMMA-blend systems were found to retain their conductivity and integrity better than PVC-PEO-blend system over the entire storage time. This is due to the presence of polar functional groups in PMMA that have higher solvent retention capability. The slightly lower solvent retention ability of PEO than PMMA may be ascribed to the higher crystallinity of the former [14].

The test has been extended to temperatures higher than ambient (i.e., 60 and 90 °C) in order to approach critical conditions where liquid release is expected to occur more easily. Thermal stability studies show that the films are thermally stable up to 110 ° C. This is clearly seen as the first weight loss of the films occurred only above 110 °C. Figure 5 shows the time evolution of PVC-PMMA-$LiCF_3SO_3$-DBP-EC:SiO_2 (95:5) complex at high temperatures (60 and 90 °C). The impedance responses obtained for this complex at progressive storage times at 90 °C are depicted in Fig. 6.

The time evolution of the PVC-PEO-$LiCF_3SO_3$-DBP-EC:SiO_2 (95:5) complex at 60 and 90 °C and the impedance responses obtained for this complex at progressive storage times at 90 °C are depicted in Figs. 7 and 8, respectively.

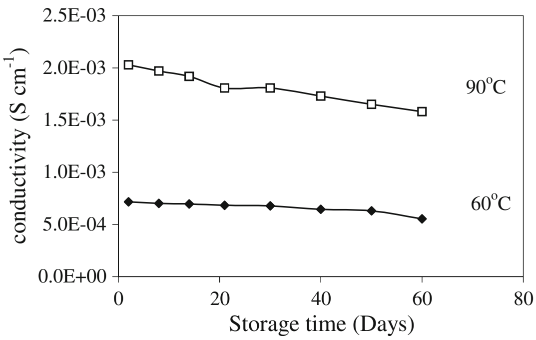

Fig. 5 Time evolution of a PVC-PMMA-$LiCF_3SO_3$-DBP-EC:SiO_2 (95:5) complex at 60 and 90 °C

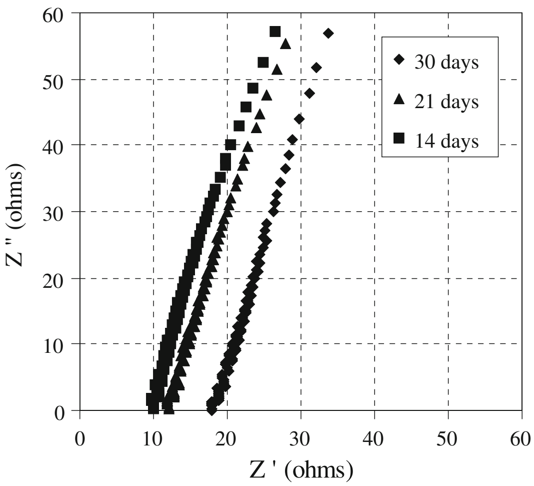

Fig. 6 Impedance responses of a PVC-PMMA-$LiCF_3SO_3$-DBP-EC:SiO_2 (95:5) at 90 °C. Measurements were performed at various progressive storage times

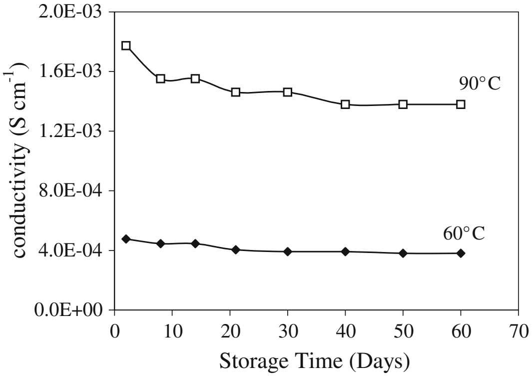

Fig. 7 Time evolution of a PVC-PEO-LiCF$_3$SO$_3$-DBP-EC:SiO$_2$ complex at 60 and 90 °C

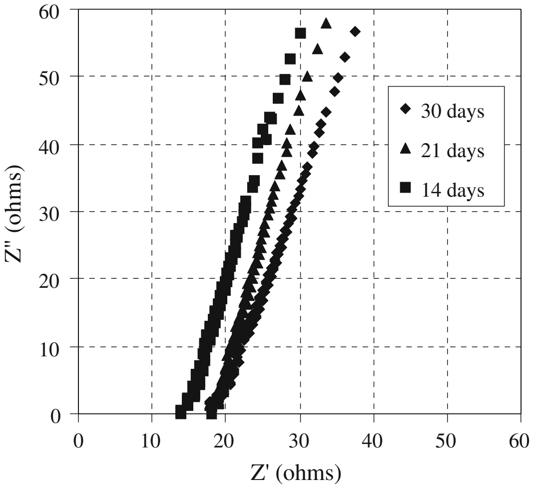

Fig. 8 Impedance responses of a PVC-PEO-LiCF$_3$SO$_3$-DBP-EC:SiO$_2$ (95:5) complex at 90 °C. Measurements were performed at various progressive storage times

From the impedance spectra, it is noted that the intercepts exhibit only a minor shift even after 30 days of storage and no evidence of deviation from linearity. In fact, should liquid losses, phase separation and/or crystallization occur, these would have been evidenced by shifts at the real axis intercept and deviation from linearity in the high frequency region of the impedance spectra. This clearly demonstrates that the ceramic-induced stabilizing effect is maintained even at higher than ambient temperatures.

It has been shown that silica, when properly selected in terms of nature and particle size, may greatly influence the characteristics and the properties of polymer electrolytes. In the present study, it may be suggested that the enhancement of the mechanical stability is associated with the ability of the polymer chains to entangle with the ceramic particles, while it is the liquid-phylic tendency of these particles that help in holding the liquid component within the membrane structure [12, 13].

Conclusions

Novel nanocomposite polymer electrolytes have been synthesized by dispersing nano-sized silica (SiO$_2$) in PVC-blend-based polymer electrolytes (PVC-PMMA-LiCF$_3$SO$_3$-DBP-EC and PVC-PEO-LiCF$_3$SO$_3$-DBP-EC). These new types of nanocomposite polymer electrolytes have been found to be homogeneous with high ionic conductivity. In addition to that, these silica-based polymer electrolytes also retain their high ionic conductivity and high chemical integrity (no liquid leakage) over the entire storage time at room temperature, 60 and 90 °C. The results achieved propose that nanocomposite PVC-blend-based polymer electrolyte may be a potential candidate for all solid lithium rechargeable batteries.

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