Short communication

The effect of nanosized TiO₂ addition on poly(methylmethacrylate) based polymer electrolytes

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Abstract

The electrochemical, X-ray diffraction, thermal, rheological and spectroscopic studies have been carried out to examine the effect of nanosized TiO₂ addition in different concentration to polymethylmethacrylate (PMMA) based gel polymer electrolytes (GPE). This work demonstrates that with optimum concentration of TiO₂ loadings in GPE, the ionic conductivity enhances with negligible effect on other electrochemical properties. The obtained ionic conductivity value is $>10^{-3}$ S cm^{-1}. An increase in viscosity by an order of magnitude is obtained which also restricts the flow property of GPE. The addition of TiO₂ retains the amorphicity of the GPE while the T_g increases. Enhanced mechanical stability of these composite polymer electrolytes (CPEs) with solid-like behavior is evident from their appearance. The activation energy has been calculated by fitting the conductivity profile in VTF equation, which decreases on the addition of fillers. FTIR characterization also confirms the interaction of filler with C=O of PMMA. The capabilities and properties exhibited by these CPEs will be of immense interest for electrochemists to use them in solid-state devices.
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1. Introduction

The societal needs towards self-dependable and greener energy sources, lead to profound interest to material scientists and engineers for the development of high performance energy sources. Among theses energy sources much attention has been focused on Li ion secondary battery, which is a potential power source in all the diverse range of "all solid-state" devices such as hybrid electric vehicles, modern hi-tech gadgets and electrooptical devices [1–3].

Gel polymer electrolytes (GPE), which have recently attracted an immense interest in several solid-state devices due to their high ionic conductivity combined with a tailor made mechanical stability [4]. GPEs consist of a lithium salt dissolved in an aprotic solvent encaged in a preferable non-interactive polymer such as polymethylmethacrylate (PMMA), polyacrylonitrile (PAN) and polyvinylidene fluoride (PVDF). PMMA is of special interest due to its amorphous nature and wider choice of solvents. GPEs are highly viscous gels but they still have flow properties, which is a major hindrance in their application. An intriguing and facile approach to overcome this shortcoming is the addition of inert ceramic filler like SiO₂, TiO₂, Al₂O₃, ZrO₂ and MgO to obtain composite polymer electrolytes (CPEs) [5–8]. In our earlier communication [9] we have demonstrated the effect of SiO₂ on the properties of GPE and elaborated the passive nature of PMMA with an increment in conductivity by a small factor. Unlike other nanoparticles, TiO₂ has a very complex surface and is available in three crystalline forms (anatase, rutile and brookite). Anatase is the stable form at low temperature and can be obtained as high surface area material. Depending on the matrix in which TiO₂ is dispersed, an increase or decrease in the conductivity can be obtained. In an article by Scrosati and co-workers [6], ionic conductivity enhancement by an order of magnitude has been reported in a PEO matrix at its melting point. Similar increase has been put forward recently [10] along with an increased value of transference number of 0.51 for composite polymer electrolyte in comparison with 0.21 for GPE, with 5 wt.% of TiO₂ addition in PEO matrix. Adebahr et al. [11] reported a decrease in conductivity with the addition of TiO₂ in a PMMA matrix though an enhancement in diffusion of the cations has been observed which was attributed to anion

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filler interaction. Johansson and Jacobsson [12] based on their computational studies established the improved properties of TiO_2 based nanocomposite polymer electrolytes to specific surface interaction. In this communication, we present our findings on the effect of nanosized TiO_2 addition in a system consisting of $LiCF_3SO_3$ (LiTf) dissolved in PC or in a mixture of EC/DMC encaged in a PMMA matrix, by studying structural, thermal, electrochemical and rheological properties of the resultant CPEs.

2. Experimental

2.1. Materials

PMMA (molecular weight 996,000) and lithium triflate (LiTf) were supplied by Aldrich and used after drying at $100\,^{\circ}C$ in a vacuum oven overnight. Synthesis grade propylene carbonate and dimethyl carbonate (DMC; Merck, Germany) were used after drying over 4 Å molecular sieves while ethylene carbonate (EC) was obtained from Aldrich. TiO_2 (anatase, size 15 nm) from Nanostructured & Amorphous Materials Inc., USA, was used after drying in a vacuum oven for 24 h at $120\,^{\circ}C$. XRD investigations have confirmed anatase phase of TiO_2 having a space group 141 and amorphous nature of the prepared CPEs.

2.2. Sample preparation

An appropriate amount of LiTf was first dissolved in PC or in a 1:1 mixture of EC and DMC to obtain a 1 M liquid electrolytes. To prepare CPEs TiO_2 nanoparticles were then dispersed in different weight percentage upto 10 wt.% with respect to liquid electrolyte weight, under continuous stirring. After observing a homogenous mixing, 15 wt.% PMMA was added slowly while heating at $55\,^{\circ}C$ for 2 h until homogenous CPEs were obtained. GPEs were prepared similarly, but without adding TiO_2 nanoparticles. The five CPEs thus prepared with different concentrations of TiO_2 particles were identified as CPE-2, CPE-4, CPE-6, CPE-8 and CPE-10 the numbers indicating the weight percentage of added TiO_2 in GPE. With EC–DMC based liquid electrolyte totally four samples were prepared: (1) 1 M liquid electrolyte, (2) 1 M liquid electrolyte + 2 wt.% TiO_2, (3) GPE and (4) CPE-2.

2.3. Instrumentation

Electrolyte conductivities were measured using Metrohm 712 conductometer, having a cell constant, K, $0.89\,cm^{-1}$ and controlled by a Paar Physica circulating water bath. Rheological measurements were carried out on Anton-Paar DV2P digital viscometer equipped with a temperature controlled circulating water bath at a shear rate $0.17–68\,s^{-1}$. XRD measurements carried out on Philips PW3710 diffractometer confirmed anatase phase of TiO_2 and amorphous nature of all CPEs. Differential scanning calorimetry (DSC) was performed with a Mettler Toledo analyzer that consists of a DSC 851 main unit and STARe software equipped with a low temperature cell under nitrogen purge and the samples were heated to $400\,^{\circ}C$ at a rate of $10\,^{\circ}C\,min^{-1}$. Infrared absorption spectra were recorded by

sandwiching the electrolyte between NaCl windows in the region of $4000–400\,cm^{-1}$ on a computer interfaced Perkin-Elmer FX-RX1. The current versus voltage (I–V) plots of these CPEs were determined with the help of Keithley current source 2400 with a computer controlled software in a custom made cell encapsulated in a teflon ring having a configuration of Li/sample/Li at room temperature at an interval of $1\,mV\,s^{-1}$.

3. Results and discussion

3.1. Thermal properties

Fig. 1 illustrates the calorimetry studies of the PC based GPE as well as CPE-2. A single glass transition temperature (T_g) appear for both the samples much below $-100\,^{\circ}C$ without any feature up to a temperature much above $200\,^{\circ}C$ is an evidence of homogeneous and amorphous nature of the samples over a wide temperature range. The experimentally observed T_g value for GPE is $-119\,^{\circ}C$, far below the T_g value of PMMA ($125\,^{\circ}C$). Bohnke et al. [13] have reported the T_g value at $-94\,^{\circ}C$ using 10 wt.% of PMMA in a $LiClO_4$ based liquid electrolyte. Such a large difference in T_g values is ascribable to difference in salts.

The addition of 2 wt.% of TiO_2 has increased the T_g value to $-103.4\,^{\circ}C$. In a report by Best et al. [14] no change in the T_g value has been reported due to addition of fillers but the changes occurred due to the addition of different salts. However, we observed that the addition [15] of filler in different amount brings changes in the T_g value but T_g almost remains unchanged with different type of fillers.

Two endothermic peaks appear in the thermograms, which have already been assigned, in our most recent communication [15], the one at lower temperature $234\,^{\circ}C$ in GPE is due to the evaporation of PC. The addition of filler has increased
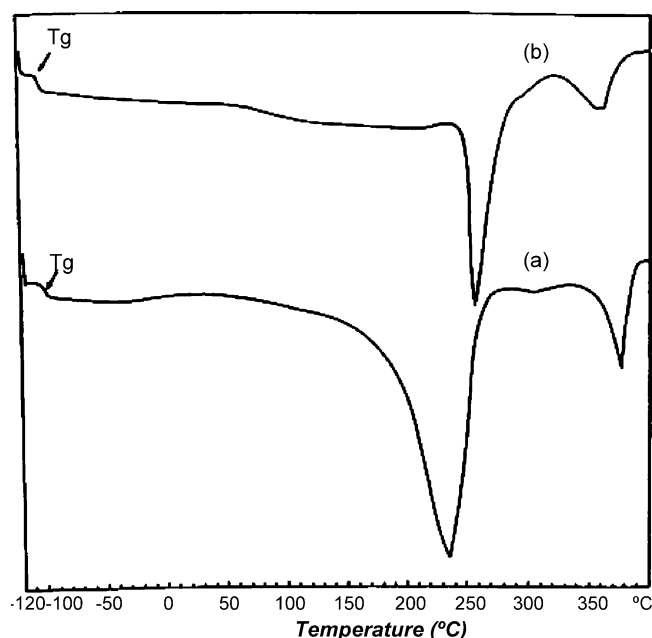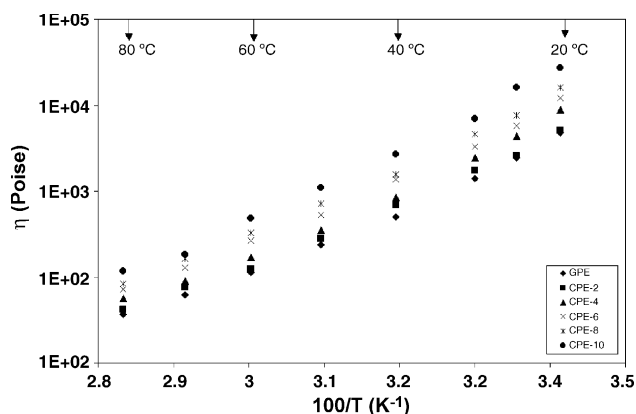

Fig. 1. DSC thermogram of: (a) GPE and (b) CPE-2.

Fig. 2. Arrhenius plot of viscosity for GPE and CPEs in PC.

Fig. 3. Arrhenius plot of conductivity for liquid electrolytes, GPE and CPEs in PC.

remarkably this temperature to 250.9 °C. This demonstrates the capability of CPEs to enhance thermal stability. The peak at higher temperature is due to the degradation of unsaturated groups of PMMA [9,16], while in PMMA it occurs at 387.5 °C and is decreasing from GPE (375 °C) to CPE-2 (356.4 °C).

3.2. Rheological properties

Fig. 2 illustrates the plot of logarithm of viscosity as a function of absolute temperature, for different CPEs and GPE, which follow typical characteristic of highly amorphous materials that can be described by a VTF relationship [13,17]. The viscosity increases monotonically with the filler content in the GPE, which is due to increase in the volume percentage of TiO_2 in the matrix. As the wt.% of filler increases it becomes more viscous and more pronounced effect can be seen for CPE-4 and thereafter, while for GPE and CPE-2 the values are comparable. For CPE-10 there is abrupt increase in the viscosity value by an order of magnitude with almost solid-like behavior.

All these CPEs are shear sensitive and at high shear rate they exhibit comparable viscosity, which mainly occurs due to the presence of weak physical bonds between the TiO_2 particles.

3.3. Conductivity

The Arrhenius plots (Fig. 3) illustrating the temperature dependent conductivity of the PC based liquid electrolyte, GPE and CPEs follow a trend as demonstrated by viscosity in Fig. 2. The overall increase in conductivity due to the addition of fillers is not as much as obtained for GPEs with other polymers such as PEO and PAN [18,19].

All the CPEs demonstrated improved ionic conductivity value except CPE-10, which exhibits slightly lower value than that of GPE. This states that the addition of fillers up to an optimum amount does not impede the mobility of Li^+ ions in the GPE. Much higher dielectric constant of TiO_2 ($\varepsilon = 180$) than PC ($\varepsilon = 64.5$) assists the lithium salts to dissociate more easily than in GPE matrix. However, for CPE-10, the effect induced by filler does not seem to dominate over dissociation of salt. Increase in its viscosity by an order seems to be lowering the chain mobility resulting in decreased conductivity. The addition
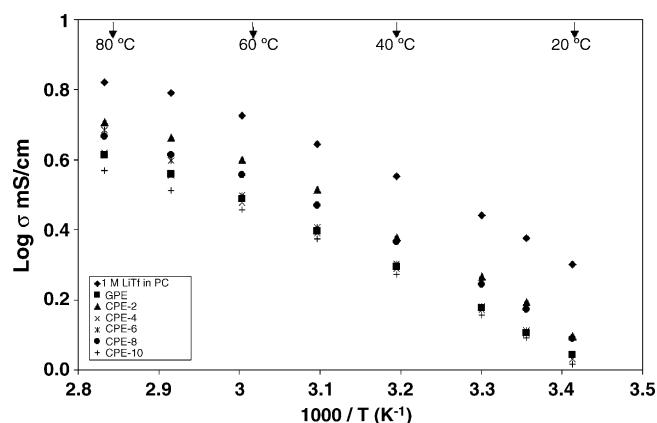
of optimum amount, inducing most favorable environment for Li^+ ions helps to attain higher conductivity value than the rest of the CPEs. In our earlier communication with SiO_2 fillers [9] we have obtained maximum conductivity for only 2 wt.% of fillers, not for all loadings of SiO_2, as it has much lower dielectric constant ($\varepsilon = 4.1$). In order to further investigate the conduction mechanism the activation energy (E_a) was calculated in a similar fashion as by other workers [13,20] by fitting the conductivity in the following VTF equation.

$$\sigma T^{1/2} = A \exp(-B/T - T_o) \qquad (1)$$

Here, A is related to charge concentration, T_o the ideal glass transition temperature and here taken as T_g in Kelvin, while B is proportional to activation energy of conduction and its multiplication with gas constant, R gives E_a. Both the parameters were obtained by best fitting the curve and were found to be better than 0.05.

The obtained E_a value for GPE is 5.36 kJ mol^{-1} that is similar to report by Best et al. [14] and for CPE-2 the calculated E_a is 4.4 kJ mol^{-1} indicating a decrease by 18% from GPE to CPE-2, nearly close to the increase in conductivity value. So as discussed, the presence of TiO_2 fillers helps to dissociate the salt more easily. However, this leads to interaction of the cations with the C=O groups of PMMA and increase in anions as reported by Chen et al. [21] and supported by FTIR results discussed further in Section 3.4.

Fig. 4 represents conductivity and viscosity plots for EC/DMC system. It may be noticed that unlike PC based system, the addition of 2 wt.% TiO_2 does not increase the conductivity at all temperatures but only at lower temperature. Though the addition of TiO_2 in liquid electrolyte increases the conductivity, but further PMMA addition lowers it and it is less than that of pristine GPE.

3.4. Spectroscopy

For the PC based samples, in going from GPE to CPEs the viscosity increases monotonically while the conductivity values follow the order as:
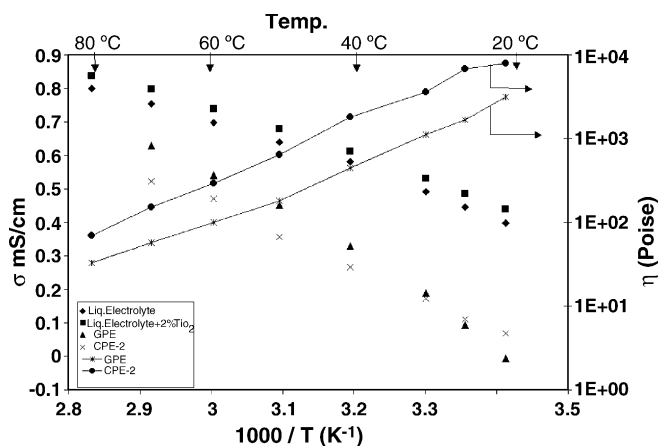
Fig. 4. Arrhenius plots of conductivity and viscosity in a 1:1 EC/DMC system of liquid electrolytes, GPE and CPE-2.

CPE-2 > CPE-8 > CPE-4 > GPE > CPE-10. Though the variations in the conductivity values are much smaller and are not in any systematic order, CPE-2 exhibits maximum conductivity value among them, while CPE-10 shows minimum, both these results are well explained by FTIR investigations.

An intense ν(C=O) of PMMA which appears at 1728 cm^{-1} in the spectrum of GPE has almost disappeared for 2 wt.% of TiO$_2$ and is present as only a weak shoulder for higher TiO$_2$ content, while for the maximum content, i.e. CPE-10, it has transformed into a doublet as shown in Fig. 5. Such a doublet was ascribed to coordination of the Li$^+$ ions with carbonyl oxygen on the ester side of PMMA along with the CF$_3$SO$_3^-$ ions acting as a transient cross-links [22]. This leads to insufficient amount of solvent to satisfy the solvation requirement, there by decreasing the conductivity. Also, contribution of highly enhanced viscosity of CPE by an order of magnitude cannot be overlooked for the observed decrease in its conductivity.

There are sufficient evidences pointing towards increase in conductivity of CPE-2. Firstly, the almost disappearance of the ν(C=O) band of PMMA as described earlier points towards complete dissolution of the salt. Secondly, the band at 1052.4 cm^{-1} in GPE, due to symmetric SO$_3$ stretching mode ν_s (SO$_3^-$) of the CF$_3$SO$_3$ anion of LiTf characterizing highly aggregated anions, is shifted to lower frequency at 1050.1 cm^{-1}. This is suggestive of the least agglomeration in CPE-2 which and is responsible for increase in conductivity.

Two bands appear due to −CH$_2$ stretching modes of PMMA, The asymmetric stretching mode appearing at 2990 cm^{-1} shows no change in its position while its intensity varies with the filler content. The symmetric stretching mode at 2900 cm^{-1} though exhibits noticeable changes in position as well as intensity. It shifts at 2925 and 2951 cm^{-1}, respectively, for CPE-2 and CPE-6. These changes are also indicative of PMMA's interactive role with the fillers.

3.5. Electrochemical stability

Finally, we address the most important part for the CPEs, the electrochemical stability. Fig. 6 depicts the variation of the
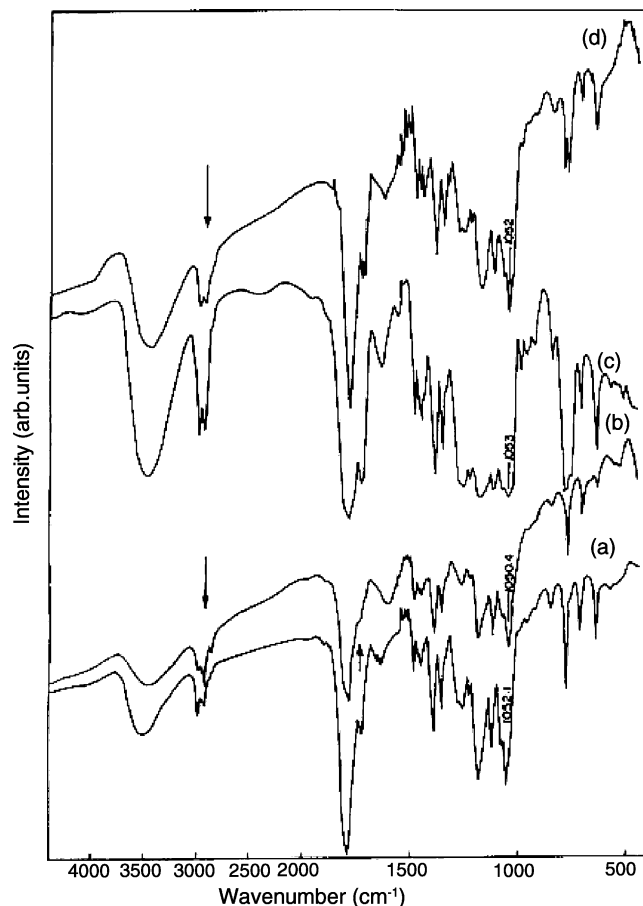

Fig. 5. FTIR spectra of: (a) GPE, (b) CPE-2, (c) CPE-6 and (d) CPE-10 in PC.

residual electronic current of the CPE in a non-blocking electrode as a function of applied voltage. The current voltage curve is used to determine the maximum working voltage (V_{max}) of the CPE [23]. The abrupt increase in the current is the indication of crossing the safe value of these electrolytes. The value of V_{max} for GPE is at 3.86 V, while CPE-2 somehow exhibits lower V_{max} value. It can be clearly seen from the figure that CPE-2 shows higher value of current than GPE, which is an indication of
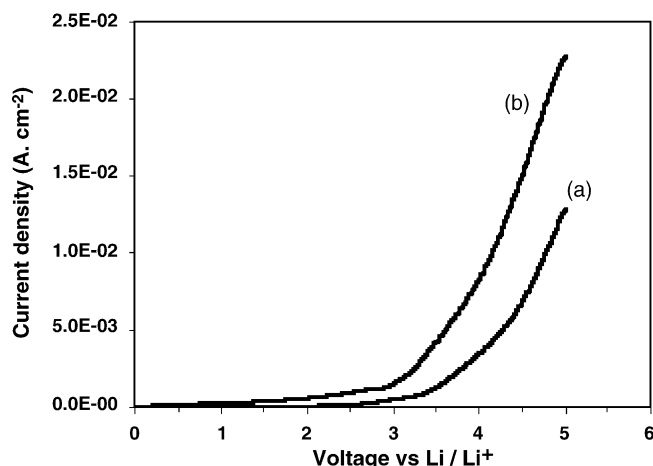

Fig. 6. Current density vs. voltage curve for: (a) GPE and (b) CPE-2 in PC.

greater mobility, thus exhibiting maximum conductivity at this concentration.

These results indicate that though conductivity increases but the electrochemical stability mostly remains unchanged with the addition of TiO_2 particles.

4. Conclusion

Thermal, electrochemical, X-ray diffraction and rheological studies with TiO_2 fillers have been carried out as a function of filler concentration and temperature. Addition of fillers in a PMMA based GPE did not show any changes in X-ray diffraction pattern, but changes are observed in the T_g of the electrolytes, which increases on the addition of fillers. The addition of different wt.% of fillers does not bring any remarkable changes in the conductivity, which increases by 18% for CPE-2 at room temperature while the viscosity value changes by an order or more. FTIR results indicate specific interaction between PMMA, LiTf and TiO_2. The maximum conductivity value in a PC based system exhibits by CPE-2 among all CPEs is due to having least aggregated ion pairs formation as shown by FTIR spectroscopic studies.

We believe that the ease of synthesis, stability and more importantly the electrochemical properties of thus synthesized nanocomposite polymer electrolytes will enable us to use them in future electrochemical devices.

Acknowledgments

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