

Li⁺ conducting ‘fuzzy’ poly(ethylene oxide)–SiO₂ polymer composite electrolytes

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Abstract

Short and ‘fuzzy’ poly(ethylene) glycol chains with different molecule weights have been successfully grafted on to a pristine SiO₂ nanoparticle surface using toluene 2,4-diisocyanate as the bridging molecule. Solvent-free composite electrolytes based on poly(ethylene oxide), LiBF₄ and SiO₂ or modified SiO₂ particles have been prepared and compared. Composite electrolytes with modified SiO₂ show a noticeably smoother surface texture under scanning electron microscopy. This is attributed to improved compatibility between the ceramic particles and polymer. The increased amorphization of the polymer leads to increase in room-temperature ionic conductivity as more ion-conduction channels are created in close proximity to the modified silica particles. On the other hand, a lower transference number is the result of weakened Lewis acid–base interactions between the polymer backbone and a smaller number of OH groups on the silica surface.

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Keywords: Composite polymer electrolytes; Poly(ethylene oxide); Morphology; Rechargeable lithium battery; Conductivity; Transference number

1. Introduction

Poly(ethylene) oxide (PEO) is a semi-crystalline polymer at room temperature and is capable of ion conduction mostly in the amorphous regions [1]. Polymer electrolytes based on PEO alone often have inadequate room-temperature conductivity despite the high solvating power of the polymer for lithium ions. Composite electrolytes based on PEO and fine ceramic particles are therefore used to improve the performance of PEO electrolytes in rechargeable lithium batteries [2,3]. Various ceramic filler materials have been used, most notably TiO₂, SiO₂, Al₂O₃, and ZrO₂ [4–12], which also provide added benefits such as improved mechanical and interfacial properties. The presence of small inorganic particles in the polymer disrupts polymer crystallization, and lowers the glass-transition temperature of the polymer to maintain liquid-like characteristics at the microscopic level. Improvements in both ionic conductivity and mechanical properties have been shown and attributed to the enlargement of the amorphous domains in the PEO matrix. PEO and the ceramic

particles can be additionally chemically modified to enhance their compatibility, and achieve favorable structural adjustments in PEO that is otherwise not possible with mechanical blending of the two pristine constituents. For example, short PEO oligomers can be grafted on to inorganic scaffolds [13,14] or rigid macromolecules such as poly(*p*-phenylene) (PPP) to form ‘hairy-rod’ polymer structures [15–17].

The innate compatibility between the ceramic fillers and polymer is often not good. This has significant consequences in the thermal, mechanical and electrochemical properties of the composites. It is reasonable to assume that there will be phase separation gaps in the vicinities of the ceramic fillers due to the immiscibility of these rigid particles with the ethylene oxide units. Shrinkage normally occurs such that a continuous network is not formed and the mechanical properties of the composites are compromised. Hence, the addition of ceramic particles to amorphize the polymer is of limited practical effectiveness.

The substantial improvements in ionic conductivity still rely on novel designs of the Li⁺ conduction channels. It is believed that the sluggish creeping of PEO segments along each chain is the root cause of slow Li⁺ transport, despite the presence of large domains of amorphous PEO. One possible solution is to introduce chain-motion ‘lubricants’ into the

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PEO matrix, which is most conveniently done by grafting very short poly(ethylene) glycol (PEG) segments on to the surface of the particulate filler, to introduce an interfacial PEG/liquid layer between the ceramic filler and the PEO.

This study describes the design and preparation of ‘fuzzy’ SiO_2 particles using toluene 2,4-diisocyanate (TDI) as the bridging molecule to connect short PEG segments to SiO_2 nanoparticles. A very high degree of surface functionalization can be achieved without any hydrolytic process. The resulting fuzzy particles are then loaded into the PEO matrix to form a modified inorganic–organic hybrid electrolyte system with improved compatibility between the inorganic phase and the bulk polymer. These new solid polymer electrolytes are totally solid-state and mechanically superior to gel polymer electrolytes made with fused silica [10,17]. The electrolytes give the expected improvement in electrochemical properties and interfacial compatibility. Compared with previous work using sol–gel reactions for surface functionalizations [18], the new method delivers similar outcomes without the possibility of the presence of residual moisture in the polymer, which is undesirable for high-voltage applications such as Li-ion batteries.

2. Experimental

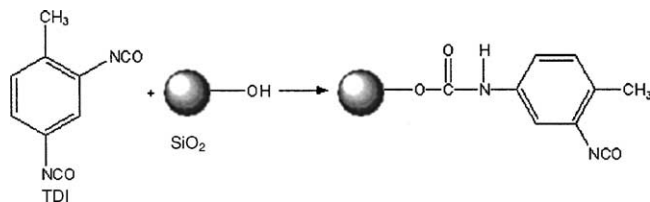
2.1. Materials

Polyethylene oxide (molecular weight = 900,000), high surface-area SiO_2 ($390 \text{ m}^2 \text{ g}^{-1}$, particle size = 7 nm), LiBF_4 , tetrahydrofuran (THF) and toluene 2,4-diisocyanate were purchased from Aldrich and used without further purification. Poly(ethylene glycol) methyl ethers with an average molecule weight of 350, 550 or 750 were also supplied by Sigma-Aldrich. Acetonitrile (gradient grade) from Merck was used as the solvent in casting polymer electrolyte membranes. Toluene (99.9% pure) was purchased from Baker. Dibutyltin dilaurate ($\text{C}_{32}\text{H}_{64}\text{O}_4\text{Sn}$) from Fluka served as the catalyst for the grafting reaction.

2.2. Modification of SiO_2

The anchoring of PEG segments on the SiO_2 particles comprised two sequential steps. First, 1 g SiO_2 was suspended in 20 ml toluene and de-flocculated by ultrasonic agitation for 2 h. An excess of TDI was then added to the dispersion (in a mole ratio of TDI to SiO_2 surface OH groups of 2:1, the density of hydroxyl groups on the SiO_2 surface was $7.1 \times 10^{-3} \text{ mol}^{-1} \text{ g}$). Several drops of dibutyltin dilaurate were introduced to the solution as the catalyst. The above procedure grafted the TDI on the SiO_2 surface according to the reaction shown in Scheme 1.

The resulting mixture was stirred at room temperature under an argon atmosphere for 24 h. The modified SiO_2 was recovered as a moist slurry after centrifugation at 15,000 rpm for 15 min. The slurry was washed with THF, re-dispersed



Scheme 1.

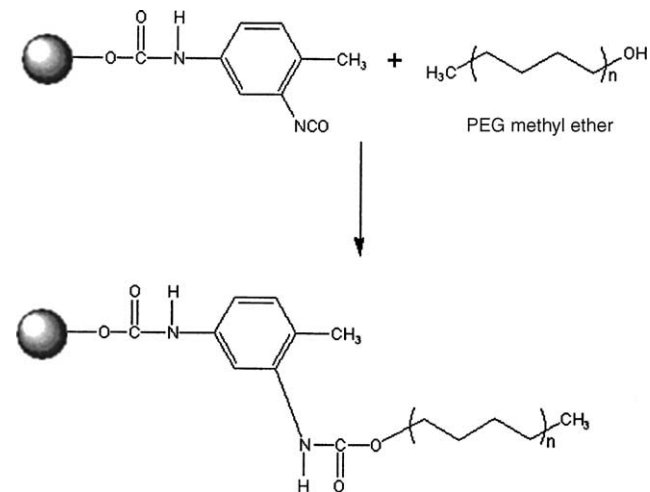
and re-centrifuged several times to remove the unused TDI. The slurry was dried to a powder in vacuum at 60°C for 72 h before characterization.

For step 2, the powder from step 1 was reacted with excess of PEG methyl ether of different molecule weight according to the reactions in Scheme 2.

The final product was also purified in THF through repeated re-dispersion and centrifugation; and was kept in vacuum at 60°C for 72 h before characterization and further use.

2.3. Characterization of modified SiO_2 powders

The modified SiO_2 particles were characterized by Fourier-transform infrared spectroscopy (FT-IR) using a Bio-Rad FTS 135 spectrometer. Each spectrum was the result of 16 scans in the range of $400\text{--}4000 \text{ cm}^{-1}$ and sampled at 8 cm^{-1} resolution. Thermogravimetric analysis (TGA) of the samples was performed on a TA Instruments TGA 2090 analyzer; the temperature was ramped from room temperature to 800°C at a rate of $10^\circ\text{C}/\text{min}$. A Perkin Elmer 2400 Series II CHN analyzer provided information on the carbon and hydrogen contents in the samples. Glass-transition temperatures were measured by differential scanning calorimetry (DSC) using a Mettler-Toledo analyzer that consisted of a DSC 822e main unit and STARe software. About 10 mg of sample was sealed in a standard aluminum pan inside a glove-box to prevent exposure of the sample to moisture.



Scheme 2.

The sample pan was then heated in a nitrogen atmosphere from -100 to 150 °C at a rate of 10 °C/min.

2.4. Preparation of composite electrolyte membranes

The following procedure was carried out in a M Braun, recirculating, argon-filled glove-box in which the moisture and oxygen contents were both below 1 ppm. Calculated amounts (for a ceramic loading of 10 wt.%) of PEO, LiBF_4 and SiO_2 (or modified SiO_2) were dispersed in acetonitrile at 40 °C and stirred continuously for 12 h to obtain a homogeneous suspension. The mole ratio of EO to Li was fixed at 8:1 for all samples. The solution was poured over a flat polytetrafluoroethylene (PTFE) Petri dish and covered. The solvent was allowed to evaporate slowly and the membrane so obtained was dried at 40 °C for 2–3 days until a constant weight was reached. Visibly homogeneous, translucent and mechanically stable membranes with a thickness in the range of 60 – 80 μm could be obtained in this way.

2.5. Morphology examination of composite electrolyte membranes

A JSM-5600LV scanning electron microscope (SEM) operating at 15 kV was used for morphological examination and microstructural characterization of the composite polymer electrolyte membranes.

2.6. Measurements of electrochemical properties

Electrochemical measurements were performed with blocking SS|composite electrolyte|SS cells, where SS represents stainless-steel. An Eco Chemie PGSTAT 30 potentiostat/galvanostat equipped with a frequency response analyzer module was used to obtain sample electrochemical impedance responses between 30 and 90 °C. Ionic conductivity was calculated from the impedance response using a widely accepted equivalent circuit model and extracting the bulk resistance of the electrolyte from the high frequency response [19–21].

For measurement of Li^+ transference numbers, lithium metal was used for both electrodes to constitute a symmetric test cell with a Li|electrolyte|Li configuration. The electrochemical impedance was measured before a dc bias of 10 mV was applied to the cell. The current response of the cell was monitored over time until a steady-state was reached. Another measurement of the cell impedance was then made to complete the procedure. The resulting data were analyzed by the method developed by Evans et al. [22].

3. Results and discussion

3.1. Characterization of modified SiO_2

As shown in Scheme 1, the NCO groups at the *para*-position of the TDI molecules are primarily involved

in the reaction when TDI is present in excess (i.e., in a mole ratio of 2:1). The remaining *meta*-NCO groups will then react with the OH ends of PEG–methyl ether in the second step. Excess of the ether was used to completely remove all the remaining –NCO functionality. The stepwise reactions were confirmed by FT-IR and TGA measurements of the SiO_2 particles before reaction, and at the conclusion of each modification step. The modified SiO_2 is differentiated using acronyms to indicate the molecule weight of the PEG group attached to the nanoparticle surface. Thus, S2-350, S2-550 and S2-750 represent samples obtained in step 2 using PEG of molecule weight 350, 550 and 750, respectively. In addition, S1-TDI denotes the sample obtained from the first step (S1) of attaching TDI to the SiO_2 surface.

FT-IR spectra for (a) pristine SiO_2 and (b) S1-TDI, obtained by grafting TDI only on SiO_2 are shown in Fig. 1, together with those for (c) S2-350, (d) S2-550 and (e) S2-750 obtained after reaction of the pendant TDI on SiO_2 with PEG–methyl ether molecules of different molecular weight. The IR spectrum of unmodified SiO_2 is characterized by strong IR absorption at 3436 cm^{-1} due to the surface –OH groups and Si–O vibrations in the region of 1100 – 850 cm^{-1} . A peak at round 2270 cm^{-1} is present in spectrum (b). This agrees well with the characteristic frequency of the NCO group [23] and hence could be used to indicate the success of –NCO grafting on the SiO_2 particles in the first step. The fingerprint vibration of the NCO groups is dramatically reduced in spectra (c)–(e) after the second reaction step; concurrent with the emergence of new C–H vibrations at 2900 cm^{-1} , which are a property of the PEG segment. This spectral evolution is most easily understood by the successful anchoring of PEG–methyl ether to the pendant TDI groups which, thereby removes the free NCO functionality. Successful modification is also shown by the peak around 1522 cm^{-1} in Fig. 1(b)–(e) that arises from H–N–C=O vibration of the urethane groups.

The TGA curves of SiO_2 , TDI-modified SiO_2 , and PEG-modified SiO_2 are presented in Fig. 2. For pristine SiO_2 , the 3% weight loss between 30 and 250 °C is most likely due to the desorption of physically held water. In the case of modified SiO_2 , the weight loss between 250 and 800 °C is significantly higher at 14 wt.%, as expected from the thermal decomposition of the organic moieties. For SiO_2 modified with different molecular weights of PEG (curves (c)–(e) in Fig. 2), the increasing weight loss from 19.1 to 22.9 and to 24.4 wt.%, respectively, appears to scale with the molecular weight. Compared with previous work [18], the extent of grating has been successfully improved (2 wt.% in [18]), which should result in more extensive amorphization of the polymer in the composite polymer electrolytes. The more effective modification is attributed to a facile hydrogen-shift reaction between the NCO and OH functional groups using TDI as the bridging molecule. This facilitates a more uniform and greater number of NCO groups becoming attached to the SiO_2 surface for subsequent reaction with the short PEG chains

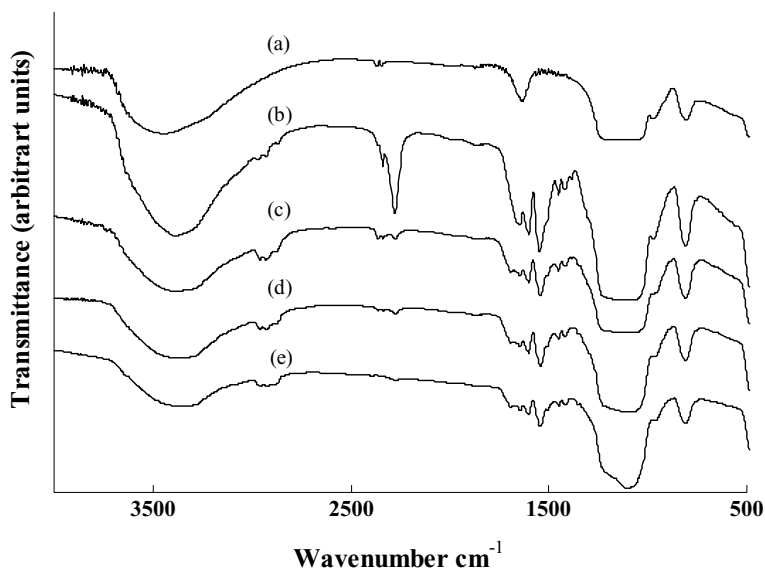


Fig. 1. FT-IR spectra of: (a) precursor SiO₂; (b) S1-TDI; (c) S2-350; (d) S2-550; (e) S2-750.

in the second step, so as to give a greater extent of grafting modification.

3.2. Morphology of composite electrolyte films

A similar acronym system was used for the polymer composite electrolytes, i.e., PEO-350, PEO-550 and PEO-750 correspond to composite polymer electrolytes prepared from SiO₂ particles that are surface modified with PEG of molecule weight 350, 550 and 750, respectively.

It is well known that PEO-based composite electrolytes have multiphase features when they are prepared by film casting, and that the compatibility between the polymer and the ceramic fillers has great impact on the thermal, mechanical and optical properties of the polymer electrolytes. Normally, three-to-four phases co-exist in PEO-based electrolytes namely, a crystalline PEO phase, a crystalline PEO–lithium salt complex phase, an amorphous PEO phase and a ceramic phase. Scanning electron microscopy is often used to assess the compatibility between the various phases

through the detection of phase separations and interfaces [24–29].

Electron micrographs of the five samples reveal large differences in surface morphology. The typical rough microstructure of pristine PEO under high magnification is shown in Fig. 3(a). Several crystalline domains and many microcracks and spherulitic structures are evident. After blending with pristine SiO₂, the surface texture becomes somewhat smoothed, but the same corrugated appearance can still be observed (Fig. 3(b)); a smooth appearance is generally associated with the lowering of PEO crystallinity, e.g., in the presence of salts [25]. The presence of SiO₂ particles has therefore caused a lowering of the polymer crystallization, but to a limited extent. Further and more dramatic refinements of the surface morphology are achieved with incorporation of modified SiO₂, as shown in Fig. 3(c)–(e). On comparing these images with those in Fig. 3(a) and (b), it is evident that PEG-modified SiO₂ is much more effective in suppressing the formation of microcracks within the composite polymer electrolyte. It is reasonable to assume that modified SiO₂ with short PEG chains is more comparable with PEO, and improves the compatibility between the inorganic particles and the polymer such that miscibility between the materials is increased. This proposition is confirmed by the DSC investigation described in the next section. In addition, the more even distribution of the modified SiO₂ also enhances the opportunity for a continuous network through cross-linking, with an expected increase in mechanical properties. Consequently, the interfacial gaps between differently oriented crystal phases are replaced by flexible amorphous coils. This effect is crucial for practical applications in lithium batteries since micro-structural discontinuity could easily result in short-circuiting of the positive and negative electrodes and thus curtail cycle life.

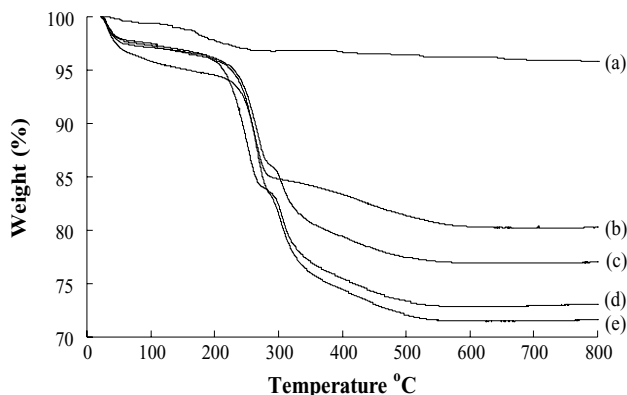


Fig. 2. TGA curves for pristine and modified SiO₂.

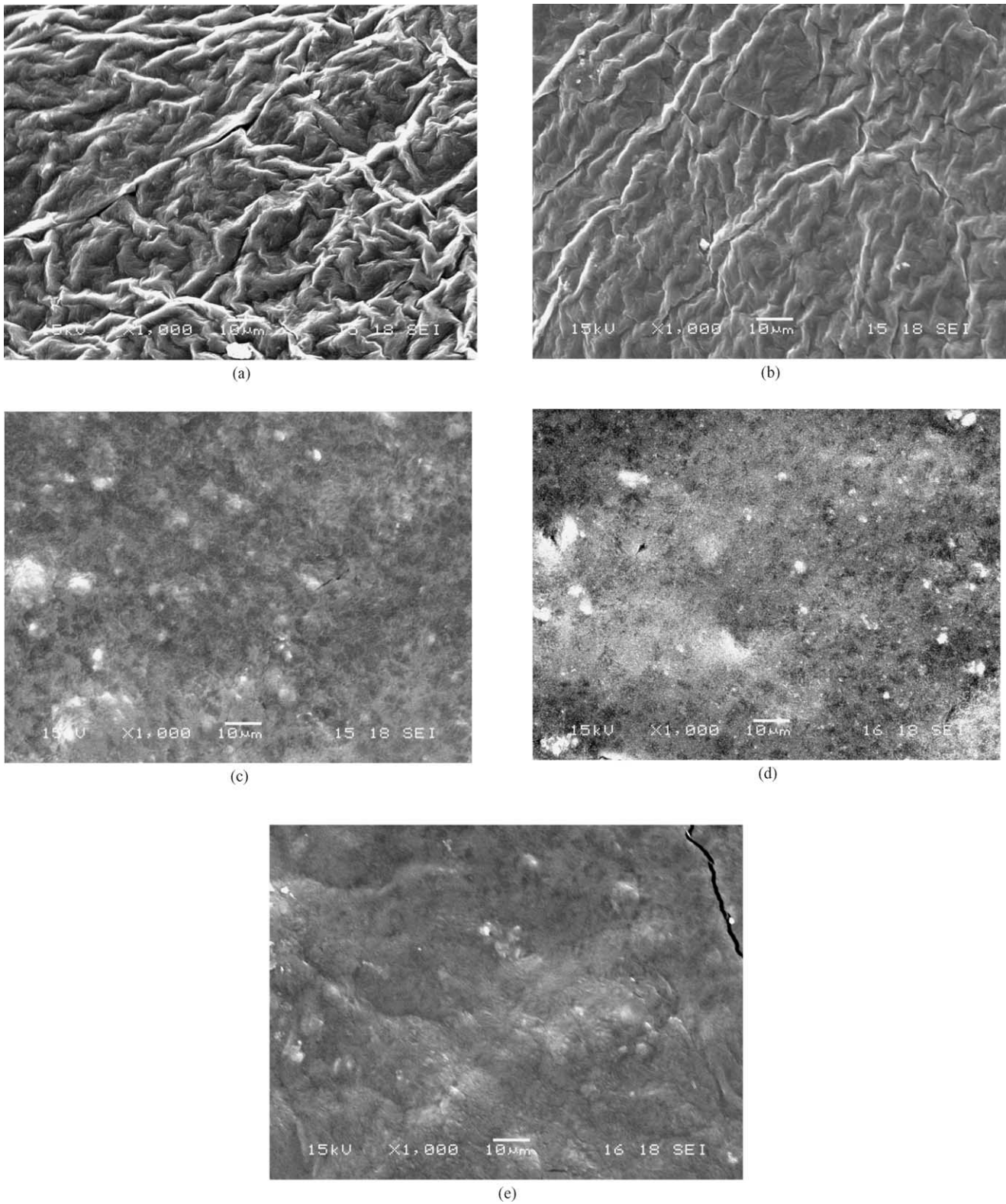


Fig. 3. Scanning electron micrographs of: (a) PEO alone; (b) PEO-SiO₂; (c) PEO-350; (d) PEO-550; (e) PEO-750.

3.3. Thermal properties

Phase changes in the modified and unmodified systems were investigated by means of DSC studies. It was expected

that a uniform dispersion of ceramic particles would be more successful in retarding the tendency for PEO to crystallize. The amorphization effect of ceramic fillers on PEO has been reported by other workers [30].

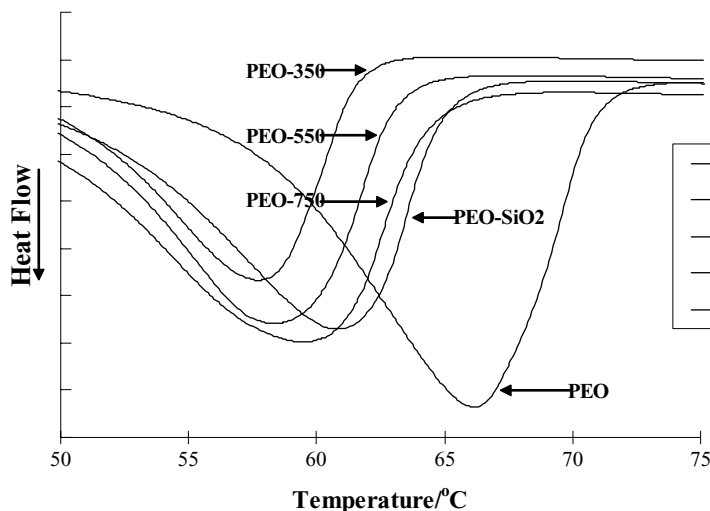


Fig. 4. DSC curves of modified and unmodified systems.

The DSC traces given in Fig. 4 show that the crystallization temperature, T_c , is lower in the composite electrolytes. This is an expected response from the hypothesis presented in Fig. 5, which suggests that modified SiO_2 particles kinetically inhibit the ordered packing of PEO chains around the particles to result in a relatively slack crystalline phase. In fact, since the PEG chains attached to the SiO_2 particles are very short, this organic modification layer is actually in the liquid form at room temperature. It can therefore function as a ‘lubricant’ to the segmental motion of the PEO chains, and provide more conduction channels for ion transport. Besides, these particles also retard the crystallization tendency of the PEO main chains. Li ion conductivity is expected to increase as a result, as will be shown in the following section.

3.4. Electrochemical properties of composite polymer electrolytes

For conductivity measurements using two blocking electrodes, the following equation may be used:

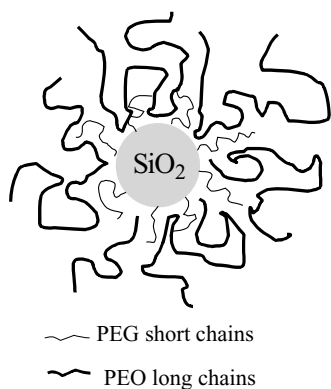


Fig. 5. Hypothesized interactions between short PEG chains on modified SiO_2 and PEO main chains.

$$\sigma = \frac{d}{R_b r^2 \pi} \quad (1)$$

where d and r are the thickness and radius of a sample membrane disc, respectively; R_b the bulk resistance of the polymer electrolyte obtained from complex impedance measurements. It is widely accepted that R_b can be obtained from the intercept on the real axis at the high frequency end of the Nyquist plot of complex impedance [19,20].

The difference between the temperature dependence of the ionic conductivity of composite polymer electrolytes with 10 wt.% SiO_2 or modified SiO_2 systems, as shown in Fig. 6, is within expectation. The increase in ionic conductivity with temperature up to the melting point of PEO is a well-understood phenomenon. When SiO_2 is added to PEO, the Lewis acid–base interactions between PEO and SiO_2 will amorphize the polymer locally around the ceramic particles. This will create more effective conduction pathways for the lithium ions and thus result in higher conductivity at lower temperatures, as shown in Fig. 6. It is important to note that

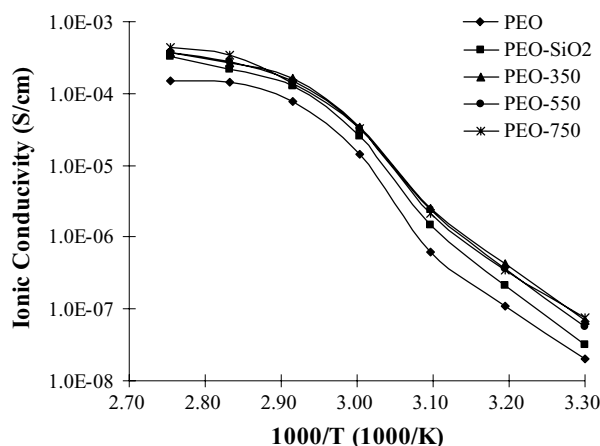


Fig. 6. Temperature-dependence of ionic conductivity.

with modified SiO₂, there is a small, but noticeable, further upward adjustment in ionic conductivity at temperatures below the melting point of PEO. Since ion conduction occurs predominantly in the amorphous phase [1], any inducement to increase the proportion of the amorphous phase below the melting point of PEO is expected to increase the conductivity at room temperature. Grafting short PEO segments (which are totally liquid-like at room temperature) on the SiO₂ surface is therefore effective in increasing the amorphous phase in the composite electrolytes to support more ion-conduction channels. Above the melting point of PEO, all systems are amorphous with or without SiO₂, and the advantage of SiO₂ understandably disappears (Fig. 5).

The lithium transference numbers in the SiO₂ and modified-SiO₂ systems were also measured to determine the relative contributions of cations and anions to the overall conductivity. The transference numbers were calculated by the method of Evans et al. [22]. The decrease in current from $t = 0$ to the steady-state after the potential of the symmetric test cell was stepped up is the result of two concurrent processes namely, the growth of passivation layers on the lithium electrode to a limiting thickness and the establishment of a concentration gradient in the electrolyte that affects ionic movement. The following equation can be used to calculate the transfer numbers after taking these two effects into consideration:

$$T_+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \quad (2)$$

where ΔV is the value of the applied dc bias (10 mV); R_0 and R_s the initial and steady-state resistances of the passivation layer obtained from complex impedance measurements; I_0 and I_s the initial and steady-state currents, respectively.

The transference number for the pristine SiO₂-PEO system is 0.25. The transference number for the modified-SiO₂-PEO systems is lower, viz., 0.22, and shows negligible variation between the different modified systems. These numbers fall within the range common for PEO-based polymer electrolytes ($T_+ = 0.1$ – 0.3 , approximately) [31].

The Li transference number in composite electrolytes is an indication of the cationic mobility, which is influenced by the interactions between lithium ions, anions, ether oxygen atoms and the functional groups on the ceramic particle surface. The hydrogen bonding between the hydroxyl groups of the ceramic particles and the BF₄[−] anions or the ether oxygen atoms of PEO is expected to constraint the movement of BF₄[−] anions, even though such interactions might be relatively weak and subtle. The competition between the hydroxyl groups and lithium ions for binding with ether oxygen atoms of PEO, on the other hand, should promote the transport of lithium ions [4,11]. When considered collectively, these mechanisms predict a higher Li transference number for systems with high OH densities. For the modified SiO₂ system, the particles contribute primarily to the amorphization of the polymer with weaken acid–base interactions since part of the OH groups are replaced by

short polymer chains. The interactions between ceramic particles, lithium salt and PEO chains may not be comparable to pristine SiO₂, which has a high concentration of hydroxyl groups on its surface. The modification also brings about reformative compatibility between the ceramic particles and the polymer so that the former may be considered as an extension of the polymer phase, as well as an increase in amorphization. The increased compatibility between the inorganic and the polymer phases is therefore derived at the expense of weakened Lewis acid–base interactions.

4. Conclusions

In an attempt to increase the amorphous content of PEO as a means to improve ionic conductivity at room temperature, short PEG chains with different molecule weights have been grafted on to the surfaces of SiO₂ particles using toluene 2,4-diisocyanate as the bridging molecule. The use of TDI also significantly increases the extent of grafting compared with earlier work using a sol–gel process [18]. There is a smoother texture and a more continuous polymer network after the modification, which indicates enhanced compatibility between the two, basically immiscible, components (polymer and ceramic filler). The modified systems have higher room-temperature conductivities but lower transference numbers. The increase in ionic conductivity is caused by an increase in the number of ion-conduction channels in close proximity to the modified SiO₂ particles. The decrease in transference number is due to the weakened Lewis acid–base interactions between the PEO backbone and the reduced number of surface OH groups on the modified SiO₂.

References

- [1] C. Berthier, W. Gorechi, M. Mivier, et al., *Solid State Ion.* 11 (1983) 91.
- [2] F.M. Gray, *Solid Polymer Electrolytes*, VCH, Weinheim, 1991.
- [3] M. Gauthier, A. Belanger, B. Kapfer, G. Vassort, M. Armand, in: J.R. MacCallum, C. Vincent (Eds.), *Polymer Electrolyte Reviews*, vol. 1, 1987, vol. 2, 1989, Elsevier, London.
- [4] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, *Nature* 394 (1998) 456.
- [5] F. Croce, R. Curini, A. Martinelli, L. Peris, F. Ronci, B. Scrosati, R. Caminiti, *J. Phys. Chem. B* 103 (1999) 10632.
- [6] B. Scrosati, F. Crose, L. Persi, *J. Electrochem. Soc.* 147 (5) (2000) 1718.
- [7] F. Croce, L. Persi, B. Scrosati, F. Serraino-Fiory, E. Plichta, M.A. Hendrickson, *Electrochem. Acta* 46 (2001) 2457.
- [8] W. Wiczorek, J.R. Stevens, Z. Florjanczyk, *Solid State Ion.* 85 (1996) 67.
- [9] C. Capiglia, P. Mustarelli, E. Quartarone, C. Tomasi, A. Magistris, *Solid State Ion.* 118 (1999) 73.
- [10] H.J. Walls, J. Zhou, J.A. Yarian, P.S. Fedkiw, S.A. Khan, M.K. Stowe, G.L. Baker, *J. Power Sources* 89 (2000) 156.
- [11] S.H. Chung, Y. Wang, L. Persi, F. Croce, S.G. Greenbaum, B. Scrosati, E. Plichta, *J. Power Sources* 97–98 (2001) 644.
- [12] B. Kumar, L.G. Scanlon, *Solid State Ion.* 124 (1999) 239.

- [13] M. Anne Mehta, T. Fujinami, S. Inoue, K. Matsushita, T. Miwa, T. Inoue, *Electrochim. Acta* 45 (2000) 1175.
- [14] J. Fan, S.R. Raghavan, X.Y. Yu, S.A. Khan, P.S. Fedkiw, J. Hou, G.L. Baker, *Solid State Ion.* 111 (1998) 117.
- [15] L. Marchese, M. Andrei, A. Roggero, S. Passerini, P. Prospero, B. Scrosati, *Electrochim. Acta* 37 (1992) 1559.
- [16] M. Watanabe, A. Nishimoto, *Solid State Ion.* 79 (1995) 306–312.
- [17] U. Lauter, W.H. Meyer, G. Wegner, *Macromolecules* 30 (1997) 2092.
- [18] Y. Liu, J.Y. Lee, L. Hong, *J. Power Sources* 109 (2002) 507.
- [19] K.M. Abraham, Z. Jiang, B. Carroll, *Chem. Mater.* 9 (1997) 1978.
- [20] M. Watanabe, K. Sanui, N. Ogata, T. Kobayashi, Z. Ohtaki, *J. Appl. Phys.* 57 (1) (1985) 123.
- [21] B.A. Boukamp, *Solid State Ion.* 20 (1986) 31.
- [22] J. Evans, C.A. Vincent, P.G. Bruce, *Polymer* 28 (1987) 2324.
- [23] C. Wu, T.W. Xu, W.H. Yang, *J. Membr. Sci.* 216 (2003) 269.
- [24] G. Hsiue, W. Kuo, Y. Huang, R. Jeng, *Polymer* 41 (2000) 2813.
- [25] P.P. Chu, M.J. Reddy, *J. Power Sources* 115 (2003) 288.
- [26] Z. Wen, M. Wu, T. Itoh, M. Kubo, Z. Lin, O. Yamamoto, *Solid State Ion.* 148 (2002) 185.
- [27] L. Fan, Z. Dang, C.W. Nan, M. Li, *Electrochim. Acta* 48 (2002) 205.
- [28] P.P. Chu, M.J. Reddy, H.M. Kao, *Solid State Ion.* 156 (2003) 141.
- [29] S. Mitra, A.R. Kulkarni, *Solid State Ion.* 154–155 (2002) 37.
- [30] G.B. Appetecchi, F. Croce, B. Scrosati, *Electrochim. Acta* 45 (2000) 1481.
- [31] G.B. Appetecchi, G. Dautzenberg, B. Scrosati, *J. Electrochem. Soc.* 443 (1996) 6.