

Functionalized SiO₂ in poly(ethylene oxide)-based polymer electrolytes

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Abstract

In this work, composite polymer electrolytes which consist of polyethylene oxide (PEO) as the polymer matrix, lithium tetrafluoroborate (LiBF₄) as the lithium salt and functionalized SiO₂ as the inert ceramic filler are prepared by a film-casting method. SiO₂ is functionalized by 2-[methoxy(polyethylenoxy)-propyl] trimethoxy silane. X-ray photoelectron spectroscopy (XPS) and thermal gravimetric analysis (TGA) are used to characterize the functionalized SiO₂. Compared with untreated SiO₂ as the ceramic filler there is noticeable improvement in ionic conductivity, stability of the Li/polymer electrolyte interface, and the mechanical properties when functionalized SiO₂ is used. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Battery; Composite polymer electrolyte; Polyethylene oxide; Silica; Ceramic filler

1. Introduction

Lithium batteries with polymer electrolytes have high specific energies that satisfy the needs of modern day portable electronic products. Moreover, the cost of manufacturing can be lowered to meet the demand for large-scale operations such as power sources for electric vehicles [1]. Compared with liquid electrolytes, polymer electrolytes could eradicate the problem of electrolyte leakage, inhibit reactions between electrode and electrolyte, and allow tremendous flexibility in cell design (various form factors are possible). Among a variety of polymers that can solvate Li salts [2], the polyethylene oxide (PEO)-based system is the most comprehensively investigated because of the unique properties of PEO to form ‘polymer solutions’ of good ionic conductivity. These systems, however, still suffer from inadequate room temperature ionic conductivity ($\sigma < 10^{-7}$ S/cm² at 25 °C) and poor mechanical properties.

One of the most promising ways to address the application deficiencies of PEO-based electrolytes is through the addition of ceramic fillers, as was first suggested by Weston and Steele [3]. The idea then was to use the ceramic filler to reduce the glass transition temperature and crystallinity of the polymer, and thus allow the amorphous polymer to

maintain liquid-like characteristics at the microscopic level. Various ceramic fillers, such as γ -LiAlO₂ [4], Al₂O₃ [5], and TiO₂/ZrO₂ [6] have been explored. The results generally showed improvements in both the ionic conductivity and mechanical properties. It is prevailing opinion that the increased ionic conductivity is due to an enlarged amorphous phase in the PEO matrix [4,7].

Recently, the particle size and the nature of ceramic fillers were found to have deterministic influence on the properties of the composite electrolytes [8–10]. The results of Krawiec et al. [5], who used both micron-size and nanometer-size Al₂O₃ in the PEO–LiBF₄ system, showed improved electrolyte mechanical and electrochemical performance with decreasing size of the ceramic fillers. The nanometer-size particles provided an order of magnitude increase in ionic conductivity over the micrometer-size particles. A substantial amount of work has been performed on SiO₂ [3,8,11,12]. The interest in using SiO₂ comes from several distinct advantages of this ceramic filler, namely: (1) its ‘starburst’ particulate shape enables it to effectively disturb the order packing tendency of the host polymer chains at low solid loadings; (2) its large surface area leads to an open network structure that supports high ionic mobility; (3) its surface groups can be modified to tailor the interfacial properties for a specific need.

Capiglia et al. [11] investigated the properties of composite electrolytes which consisted of SiO₂ powders with

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different surface features in a PEO–LiClO₄ system. They removed the hydroxyl groups on SiO₂ by calcination at 900 °C in order to reduce the hygroscopic properties of the particles. The absence of hydroxyl groups on the particle surface was found to increase ionic conductivity, which demonstrated the importance of the chemistry of the polymer–filler interface on the transport properties of the electrolytes. Matsuo and Kuwano [12] treated the SiO₂ powders with lithium dodecylsulfate (LDS), a surfactant, and introduced these powders into composite electrolytes based on PEG–LiCF₃SO₃. Their results showed a 5–10-fold increase in ionic conductivity [12] relative to untreated fillers. It was concluded that the conductivity enhancement was associated with the oriented absorption of surfactant molecules on the SiO₂ surface that facilitated the segmental motion of the PEG molecules. Walls et al. [8] prepared a series of SiO₂ materials with either hydrophilic or hydrophobic surface groups, and used them as ceramic fillers in PEGDM-based composite electrolytes. Their work showed clearly a cause and effect relationship between the observed properties and the surface chemistry. Fan et al. [13] attached different surface groups to the silica, and used the functionalized particles in PEGDM-based composite electrolytes. It was found that the silica surface chemistry affected mostly the rheological properties, but not the ionic conductivity.

Most of the surface modifications cited above were based on PEG of low molecular weight, and only gel-like electrolytes were produced. The full extent for the surface modification of SiO₂ has yet to be explored: only small molecules and very simplified treatment methodologies have been employed this far. Furthermore, not all of the experimental results are unanimous about the extent and benefits of surface modification. Further investigations are definitely needed to inject additional experimental evidence, and examine the phenomenon from different perspectives in order to better understand the relationship between surface chemistry of the ceramic fillers and the properties of the composite electrolytes.

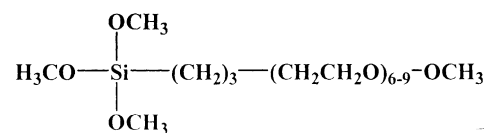
The purpose of the work presented here is to study the connection between the surface chemistry of ceramic fillers and the transport and mechanical properties of composite electrolytes, using nanometric SiO₂ functionalized by 2-[methoxy(polyethylenoxy)-propyl] trimethoxy silane as a test system. X-ray photoelectron spectroscopy (XPS) and thermal gravimetric analysis (TGA) measurements are used to characterize the surface after modification. Application of these functionalized SiO₂ particles as ceramic fillers in high molecular weight, PEO-based system is investigated. The mechanical and electrochemical properties of the composite electrolytes are compared with those of untreated SiO₂. The results show general improvements in various categories, which confirms that surface modification of ceramic fillers is an effective approach to prepare advanced composite electrolytes. The study also provides detailed information on the polymer functionalizing agent, and the sol–gel based treatment procedures, which could be

further extended and varied to provide a plethora of surface chemical effects.

2. Experimental

2.1. Materials

High molecular weight PEO, ($M_w = 900,000$) was obtained from Aldrich. Acetonitrile (gradient grade) from Merck was used as the solvent in the film-casting process. SiO₂ with a high surface area (255 m²/g, particle size = 11 nm) was also supplied by Aldrich. 2-[Methoxy(polyethylenoxy)-propyl] trimethoxy silane (90%) from Gelest was used to modify the SiO₂ surface. The chemical structure of the silane molecule is:



AR grade absolute alcohol was obtained from Hayman. Lithium tetrafluoroborate (LiBF₄) from Aldrich was used as received.

2.2. Functionalization of SiO₂ particles

The 0.5 ml of 2-[methoxy(polyethylenoxy)-propyl] trimethoxy silane was dissolved in 24.5 ml of absolute alcohol and 0.6 g of high surface area SiO₂ was added to form a suspension. The mixture was stirred at room temperature for 3 h. The resulting SiO₂ was then separated in a Jouan/BR4i centrifuge at 10,000 rpm for 10 min. To remove the unreacted silane in the SiO₂ surface, absolute alcohol was used to wash the product, and the slurry was centrifuged again. After the washing was repeated twice, the SiO₂ particles were dried in a SalvisLAB vacuum oven at 100 °C for 2 days and transferred to a M Braun glovebox in which the moisture content was kept below 1 ppm. Untreated SiO₂ was dried under the same conditions for comparative studies.

2.3. XPS and TGA measurements of SiO₂ powders

XPS measurements were made on a VG ESCALAB MkII spectrometer with a Mg K α X-ray source (1253.6 eV photons) and a constant retard ratio of 40. The powder sample was attached to a standard sample stud by means of double-sided adhesive tape. The X-ray source was run at a reduced power of 120 W. The pressure in the analysis chamber was maintained at 7.5×10^{-9} Torr or lower during each measurement. All binding energies (BE) were referenced to the C 1s hydrocarbon peak at 284.6 eV. A TA Instruments TGA 2050 analyzer was used for TGA. Samples were heated in N₂ atmosphere from room temperature to 450 °C at 10 °C/min.

2.4. Preparation of composite electrolyte membranes

The following procedures were carried out in a M Braun argon-filled glove-box in which the moisture content was below 1 ppm. PEO and a weighed amount of LiBF_4 and, whenever required, SiO_2 or functionalized SiO_2 were dissolved in acetonitrile. The mixture was kept at 40°C for 3 h with continuous stirring to obtain a homogeneous solution. The concentration of PEO in acetonitrile was maintained at 5 wt.% for all solutions. The ratio of PEO:Li was fixed at 20:1 for all samples. The solution was cast on to a polytetrafluoroethylene (PTFE) plate using a micrometer adjustable applicator from Sheen Instruments Ltd. The solvent was slowly evaporated, and the membrane was dried for 2–3 days until a constant weight was reached. The thickness of membranes prepared as such was in the range 50–150 μm .

2.5. Measurement of electrochemical properties

The membrane was cut into circular discs and a sample membrane disc was sandwiched between two stainless-steel electrodes and assembled into a tightly sealed test cell. The cell was thermostated so that its temperature could be varied between 30 and 80°C . The electrochemical impedance of the cell between 1 Hz and 1 MHz was measured by means of an Eco Chemie PGSTAT 30 potentiostat/galvanostat equipped with a frequency-response analyzer module. Ionic conductivity was calculated from the impedance response according to a widely used method [14–16]. The experimental data were analyzed in terms of equivalent-circuit models, from which the bulk resistances of the electrolyte were deduced.

The stability of the polymer electrolyte/Li metal interface was evaluated using by a symmetric Li/composite electrolyte/Li test cell kept at the open-circuit condition, and by monitoring the change in impedance with time.

2.6. Measurements of mechanical properties of composite electrolytes

The tensile strength of composite electrolyte membranes was measured by an Instron Model 5544 materials tester. The composite electrolytes membranes were cut into rectangular strips, and their widths and thicknesses were measured by a micrometer before taking measurements. All measurements were carried out at a crosshead speed of 5 mm/min. Each tensile strength reported is the average value of three consecutive measurements.

3. Results and discussions

3.1. Characterization of Functionalized SiO_2

During the treatment by 2-[methoxy(polyethylenoxy)-propyl] trimethoxy silane, the OH^- groups on the surface

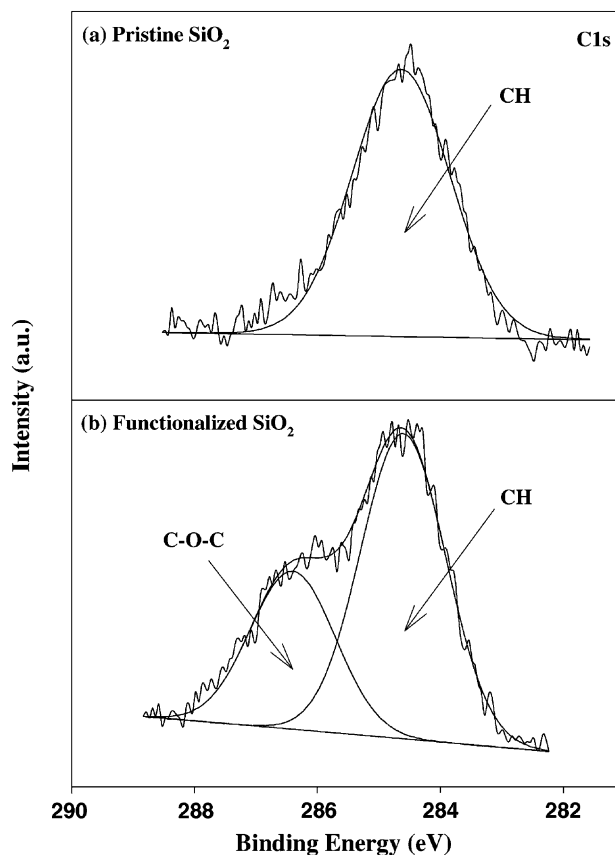


Fig. 1. XPS C 1s core-level spectra of SiO_2 surface: (a) pristine SiO_2 ; (b) functionalized SiO_2 .

of SiO_2 react with partially hydrolyzed silane. XPS measurements confirmed that reaction had taken place. The C 1s core-level spectra in Fig. 1 highlight the difference between functionalized SiO_2 and untreated SiO_2 . For untreated SiO_2 in Fig. 1(a), the XPS data can be fitted by band centring at an energy of 284.6 eV, which is often the characteristics of adventitious CH_2 species in the measurement chamber. By contrast, the data in Fig. 1(b) have to be fitted by two peaks at 284.6 and 286.2 eV, respectively. The former is due to the adventitious CH_2 species while the later is the C–O–C group signature [17]. The appearance of the C–O–C group is the result of the functionalization reaction. The reactions between active silane and silica [18] are believed to commence with the hydrolysis of three Si-O-CH_3 groups in the silane molecule, which produces three Si-OH groups. These OH^- groups then react with the OH^- groups on the surface of SiO_2 to form Si-O-Si bonds and release H_2O as the condensation product. The silane molecules that were attached to the SiO_2 surface might further link together through unused Si-OH groups to generate a cross-linking structure which surrounds the silica particles.

TGA analysis also confirmed the successful functionalization of the SiO_2 powder. TGA traces of both pristine and functionalized SiO_2 are shown in Fig. 2. At temperatures below 180 – 200°C both samples experience only a small

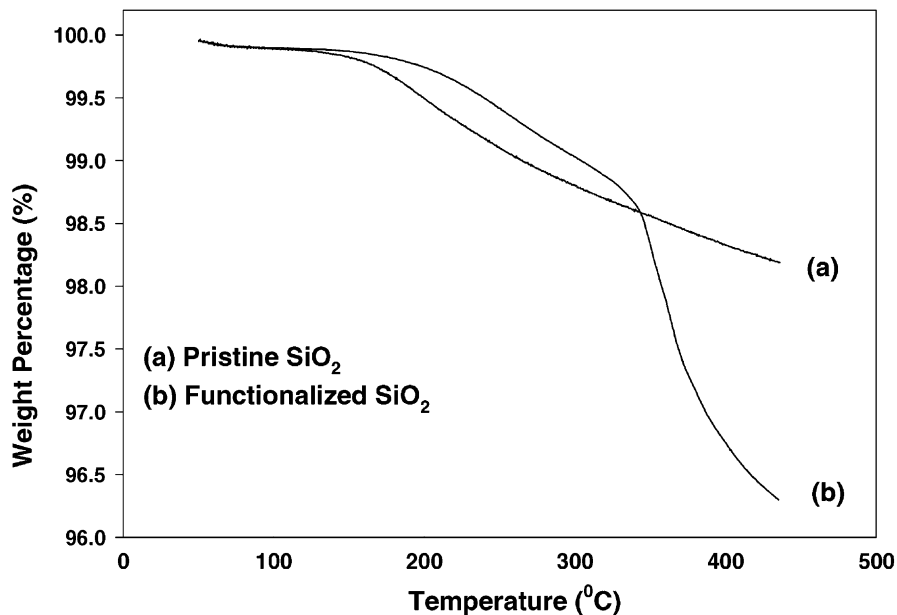


Fig. 2. TGA measurements of: (a) pristine SiO₂; (b) functionalized SiO₂.

weight loss (<0.2%), due to the removal of residual water on the SiO₂ surface. At increasing temperatures, the OH-groups on the surface of SiO₂ powder begin to decompose, to give rise to slight increases in the weight loss. For pristine SiO₂ in Fig. 2(a), the total weight loss up to 450 °C is 1.6%. While for the functionalized SiO₂ in Fig. 2(b), addition to the decomposition of the OH- groups, another weight loss event takes place at about 350 °C. This apparent weight loss can be attributed to the decomposition of the silane molecule chains that are bonded on the SiO₂ surface. According to TGA measurements, approximately 2 wt.% silane is grafted on to the surface of SiO₂. The amount of silane that can be attached to the surface depends on a number of factors such as the concentration of the silane solution, the reactivity of silane, and the effects of solvent. In comparison with published data on silane adsorption [19], our results suggest that the adsorption of 2-[methoxy(polyethylenoxy)-propyl] trimethoxy silane on SiO₂ is likely to give a sub-monolayer coverage.

3.2. Ionic conductivity of composite electrolytes

The beneficial effect of ceramic filler addition on the ionic conductivities of the composite electrolytes is demonstrated in Fig. 3. An order of magnitude increase in ionic conductivity is obtained with 15–20 wt.% of SiO₂ addition. Functionalization introduces small but noticeable improvements over untreated SiO₂, particularly at low loading levels (<15 wt.%). The enhancement in ionic conductivity after the addition of ceramic fillers is generally explained by the effective media theory (EMT) [20–22]. From a microscopic perspective, the composite electrolyte can be treated as a quasi two-phase system which consists of a polymeric ion-conducting matrix with

dispersed composite units. The ionic conductivity could benefit from the existence of a highly ionic conducting layer at the polymer–filler interface. It is speculated that the surface modified SiO₂ powder is more compatible with the PEO–LiBF₄ solution because the silane molecule carries a short PEO block. The subsequent increase in the polymer–ceramic filler interfaces raises the proportion of effective media for ion conduction in the electrolyte.

For functionalized SiO₂, the silane moieties attached on the SiO₂ surface can effectively prevent coagulation among the SiO₂ particles during blending because of steric repulsive actions. This increases the dispersability of SiO₂ powders in a PEO matrix. Compared with the use of unmodified SiO₂ powder, a higher interfacial area between polymer and filler can be obtained, which therefore brings about a further increase in the ionic conductivity.

A decrease in ionic conductivity was observed at high loadings of ceramic fillers. The appearance of a maximum in ionic conductivity for both the treated and untreated SiO₂ indicates that there are two competing effects at play. At low ceramic filler loadings, the conductivity increases with SiO₂ content basically due to the increase in the amount of conductive layers. At higher ceramic filler concentrations, phase discontinuities and dilution effects will predominate instead and result in low conductivities. Because of increased dispersability, composite electrolytes with surface modified SiO₂ can reach the same maximum conductivity at lower filler loadings than that of untreated counterparts. The similar maximum conductivity value indicates that there are no fundamental changes in the conduction mechanism caused by introducing the silane monolayer on to SiO₂. The modification layer simply generates a more effective form of the untreated interface to deliver the same effects at lower loadings.

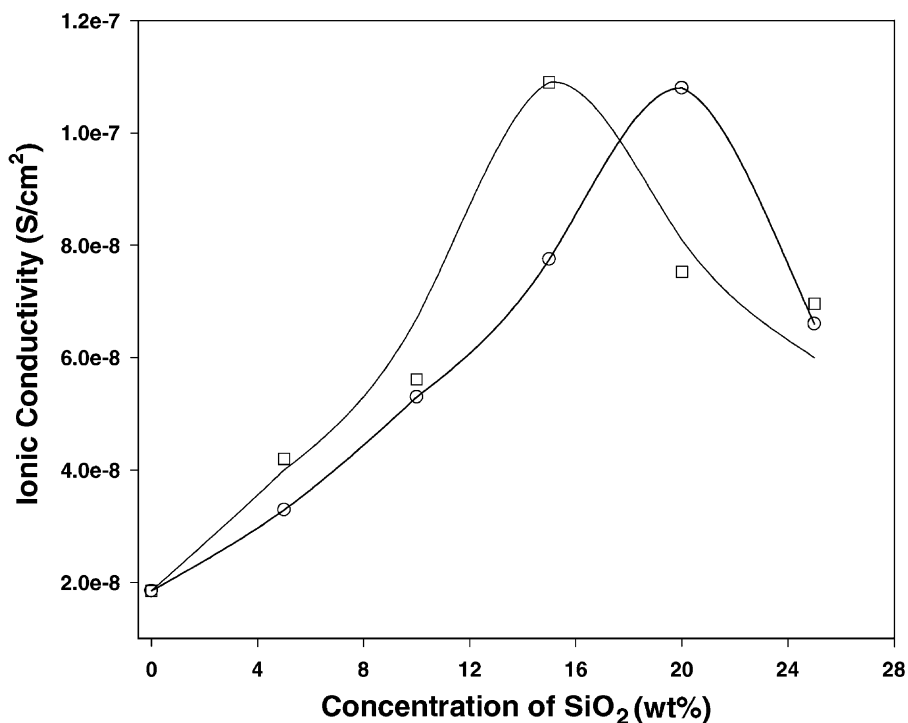


Fig. 3. Ionic conductivities of PEO composites at various SiO₂ concentrations: (○) pristine SiO₂ and (□) functionalized SiO₂ as ceramic filler.

The temperature dependence of ionic conductivity is shown in Fig. 4. Regression of experimental data according to the Arrhenius equation $\sigma = \sigma_0 T \exp(-E_0/RT)$ results in a similar activation energy of about 78 kJ/mol for all three cases. This suggests that the local dynamics of lithium-ion transport is not changed. The addition of ceramic fillers (both untreated and functionalized SiO₂) did not alter the

mechanism for ion conduction in the PEO system. In all of them, the ionic conductivity was imparted by the segmental motion of the polymer chains [2,10]. The order of magnitude increase in ionic conductivity upon the addition of ceramic fillers, is due to the increase in the amount of amorphous phase in the system. Because the segmental mobility of polymer chains is much higher in amorphous regions than in

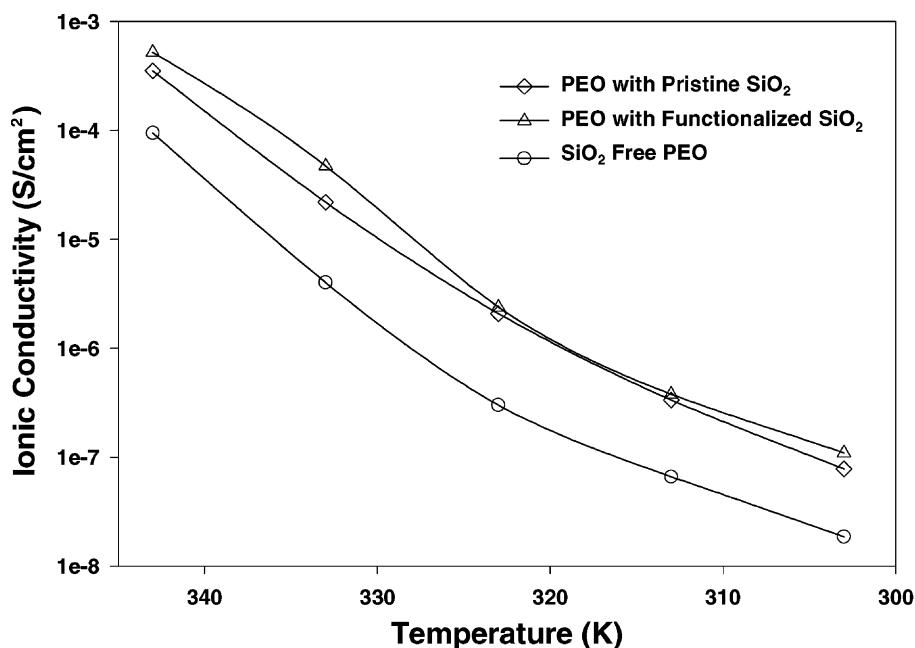


Fig. 4. Temperature-dependent ionic conductivities of PEO–SiO₂ composite electrolyte systems.

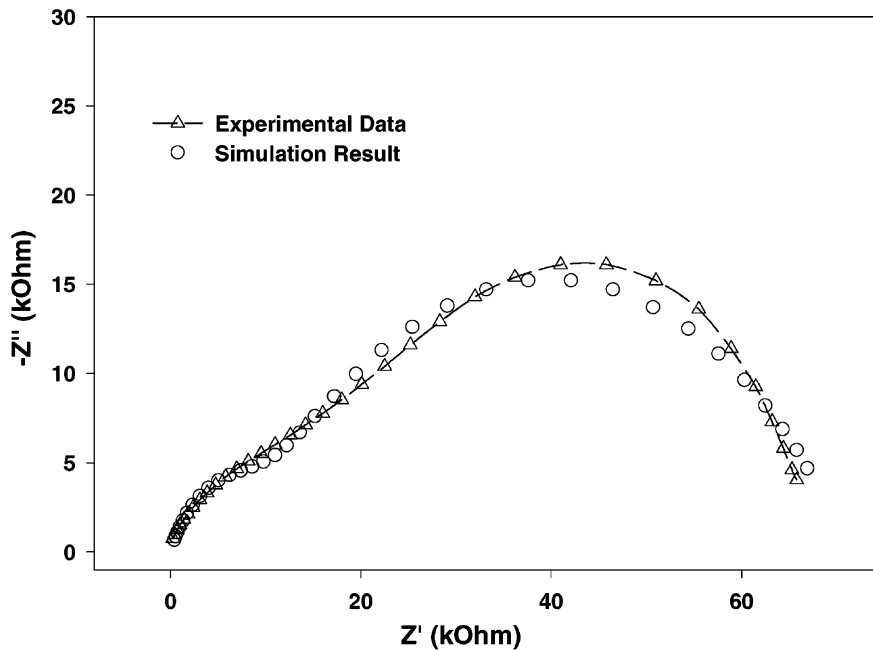
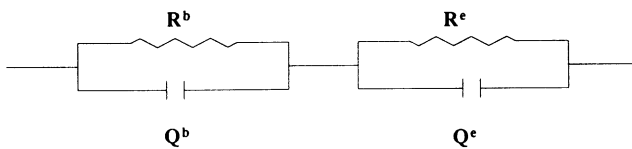


Fig. 5. Typical Nyquist plot for Li/PEO–SiO₂ composite electrolyte/Li assembly.

crystalline regions, a decrease in crystallinity will lead to an increased number of “active” charge carriers, which have high mobility for ionic conduction. On the other hand, in PEO-based electrolytes, Li⁺ ions are coordinated to oxygen atoms in the polymer chains. The movement of dissociated Li⁺ ions can be constrained by multiple oxygen atoms coordinated to the same central Li ions. Upon the addition of functionalized SiO₂, the oxygen atoms from the short polyether units on the SiO₂ surface can also compete with oxygen atoms in the PEO backbone for complexation with Li⁺ ions. The result is a more relaxed coordination between oxygen atoms and Li⁺ ions which in turn, facilitates the transport of Li⁺ ions through the polymer.

3.3. Stability of the Li-composite electrolyte interface

The stability of the Li/polymer electrolyte interface was assessed in a symmetric Li/composite electrolyte/Li test cell. The impedance of the cell was monitored as a function of time. The following equivalent-circuit model was found to describe adequately the measured impedance response, as shown by the good fit of experimental data in Fig. 5.



In the model, R_b and Q_b are elements that account for the ionic conductivity in the bulk of the electrolyte (R_b = bulk ionic resistance and Q_b = geometrical capacitance), and R_e and Q_e are elements that are due to the passivation film at the electrode–electrolyte interface (R_e = interfacial resistance;

Q_e = interfacial double-layer capacitance). The values of R_b and R_e were obtained from non-linear fitting of the experimental data to above equivalent-circuit. The evolution of the interfacial resistance R_e with time for the three systems is shown in Fig. 6. Although the interfacial resistance for all samples increases with storage time, the polymer electrolyte without any ceramic filler displays the highest rate of increase in resistance. The addition of SiO₂ significantly lowers the rate of increase of the interfacial resistance, which results in a flatter response curve with time. Functionalized SiO₂ shows the most remarkable interfacial control; after 2 days of initial passivation of the Li/polymer interface, only a slight increase in the R_e value is observed. Since it is reasonable to assume that the increase in the interfacial resistance is due to the progressive growth of the passivation film, a slower growth in R_e after the addition of ceramic fillers is indicative of a stabilized Li/electrolyte interface. Functionalized SiO₂, in particular, has provided a low interfacial resistance that increase only slowly during storage. Interfacial stabilization is believed to derive from the adsorptive removal of soluble impurities such as residual solvent, water and other small molecules by the ceramic fillers [23,24]. The greater dispersability of the functionalized SiO₂ particles in the polymer matrix provides more active surface area for such scavenging action.

3.4. Mechanical properties of composite electrolytes

It has been generally observed that addition of ceramic fillers can improve substantially the mechanical properties of polymer electrolytes. As early as 1982, Weston and Steele [3] used ceramic fillers to improve the mechanical properties of PEO films. The mechanism of the reinforcing action is

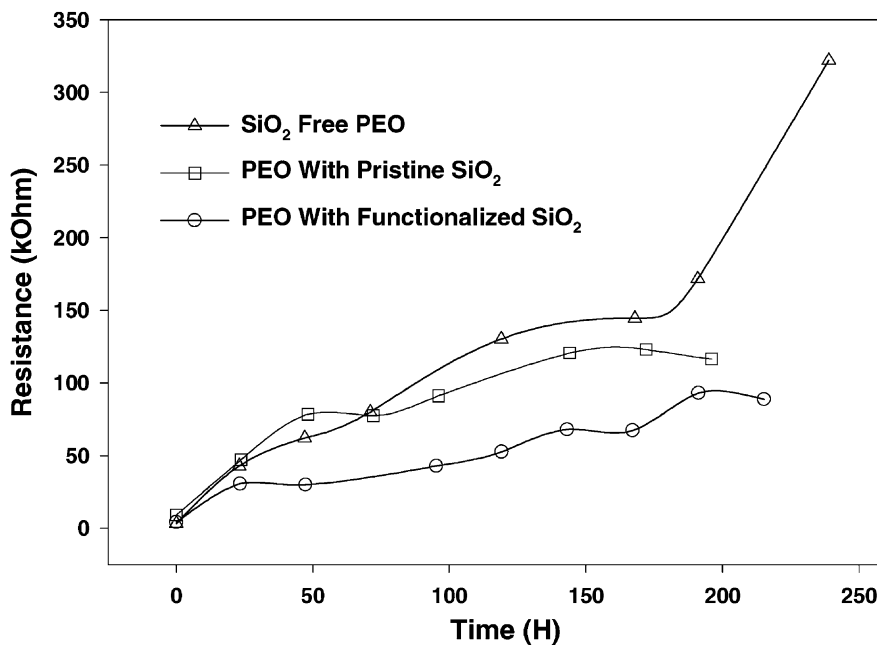


Fig. 6. Evolution of Li/PEO–SiO₂ composite interfacial resistance at prolonged storage time (stored under OCP).

fairly well understood [25]. Inorganic fillers are actually bonded to the macromolecular chains and thereby, immobilize the polymer chains. The degree of adhesion between the polymer matrix and fillers, the surface area of the filler, and the packing characteristics of the filler particles are important factors that determine the mechanical properties of the composites [25–27].

The tensile strength of the composite electrolytes as a function of SiO₂ content is given in Fig. 7. Although the pristine PEO–LiBF₄ system can form free-standing films, the films are mechanically weak and sticky, which makes it difficult to measure their mechanical properties. After addition of SiO₂, with or without functionalization, non-sticky films are produced. The stickiness of the polymer

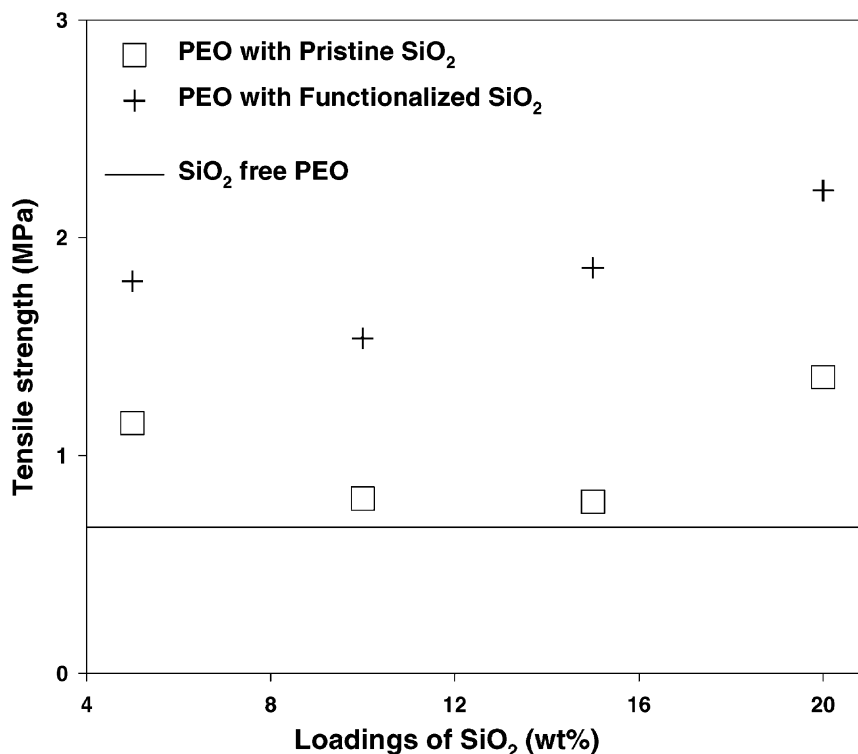


Fig. 7. Tensile strength of various PEO–SiO₂ composite electrolytes.

films is mostly due to adsorption of atmospheric moisture, which can occur when the films are exposed to air during mechanical testing. The addition of SiO₂ powder, both with and without functionalization, apparently decreases the hygroscopic character of the polymer film and thus reduces the propensity of the polymer films for moisture uptake.

Untreated SiO₂ serves primarily as a non-reactive filler, giving some but limited improvement in the mechanical properties. The reinforcement effect from functionalized SiO₂ is more significant (Fig. 7). In some aspects, functionalized SiO₂ can be considered as a fillers which carries a pendant coupling agent. The coupling agent, which is 2-[methoxy(polyethylenoxy)-propyl] trimethoxy silane in this case, has two types of functional groups, namely, one capable of forming a chemical bond with the surface of the filler and the other capable of entangling with the PEO chains [27]. Because the repeat unit (EO) in 2-[methoxy-(polyethylenoxy)-propyl] trimethoxy silane molecule is the same as that in the polymer matrix, the oligomeric moieties that are attached to the SiO₂ surface have no difficulty in entangling with the PEO main chains to form pseudo-interpenetrating polymer networks (IPN) at the polymer–filler interface and hence provide improved adhesion between the polymer matrix and the filler.

4. Conclusions

Previous work on the use of SiO₂ fillers in PEO-based composite electrolytes has highlighted the importance of SiO₂ surface features in determining the properties of the composite electrolytes. Enhanced conductive and mechanical properties can be expected through proper treatment of the SiO₂ surface, as shown by the results of this investigation.

2-[Methoxy(polyethylenoxy)-propyl] trimethoxy silane is used in this work to functionalize SiO₂. Compared with untreated SiO₂ as ceramic filler in PEO-based electrolytes, functionalized SiO₂ further improves the Li/polymer interface stability, as well as the mechanical properties and ionic conductivity of composite electrolytes. Good dispersability of functionalized SiO₂ particles in the PEO matrix is thought to result in an increase in the number of charge carrier and, hence, to improve ionic conductivity. In addition, the presence of polymeric moieties on the SiO₂ surface gives rise to improved interfacial stability through perhaps better scavenging of impurities molecules in the system. The polymeric fragments on the SiO₂ can also form chain entanglements with the PEO matrix with resulting increase in mechanical performance. This investigation is limited to the use of 2-[methoxy(polyethylenoxy)-propyl] trimethoxy silane as a

surface modifier, and only a small amount of polymer chains has been grafted on to the SiO₂ surface. It is perceivable that such approach is generic, and different polymer types and extents of functionalization may be used to vary the end properties of the composite electrolytes. Our on-going work is, therefore, focusing on the effects of different polymeric functionalizing agents with different chain lengths on the SiO₂ surface, and the methodologies to effect such modification in practice.

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