Composite polymer electrolytes using surface-modified fumed silicas: conductivity and rheology

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Abstract

We report results from our studies on composite polymer electrolytes based on novel surface-modified fumed silicas. The electrolytes were prepared by dispersing fumed silica in a matrix formed by methyl-capped polyethylene glycol and lithium salt. Silicas with widely different surface chemistries were synthesized in order to study the effects of surface modification, with the attached surface groups ranging from non-polar alkyl moieties (C_1 or C_8) to polar polyethylene oxide (PEO) oligomers (MW ~ 200). We find, rather surprisingly, that the conductivity is independent of the type of surface group present on the silica. Moreover, the conductivity decreases only slightly on addition of fumed silica, even at high weight fraction of solids. In contrast, the rheological properties of the composites are strongly affected by both the silica surface chemistry and weight fraction. Dynamic rheology measurements reveal that fumed silicas with silanol and octyl coverage both flocculate into gels (networks). The resulting materials are mechanically stable, with the elastic modulus of the gel being strongly dependent upon weight fraction of solids. The PEO-modified silica, in contrast, gives rise to a low-viscosity suspension where the silica units exist as distinct, non-interacting species. The findings of this study have significant implications for future work on composite electrolytes, in that we can tailor the mechanical properties of the system without affecting the electrochemical behavior. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Surface-modified fumed silicas; Composite polymer electrolytes; Conductivity; Rheology

1. Introduction

Composite polymer electrolytes are among the most promising candidate materials for use in rechargeable lithium batteries [1–7]. These electrolytes are obtained by dispersing inorganic particles (e.g., SiO_2, Al_2O_3) in a polymer electrolyte. Generally, the composite electrolyte shows better conductivity,

mechanical stability, and compatibility with lithium metal in comparison to the parent electrolyte [2–4].

Several groups, including Scrosati and co-workers [2,3] have been focusing on a high molecular-weight polymeric matrix for their composite electrolytes. In our laboratories, we have pioneered an alternate concept, where we use a low molecular-weight oligomeric polyether as the continuous phase, to which we add fumed silica particles. Results from our studies on fumed silica-based composite elec-

trolytes in methyl-capped poly(ethylene glycol) oligomers have been reported recently [6,7]. We have shown that the corresponding composites exhibit both high conductivity ($> 10^{-3}$ S/cm) as well as mechanical stability (gel-like behavior). Additionally, we have found that the interfacial resistance between lithium metal and electrolyte is lowered in the presence of fumed silica, thereby indicating a more stable interface. The latter phenomenon has been the subject of much discussion in the literature, and its precise mechanism is yet to be understood.

Our previous studies exclusively dealt with either the electrochemical [6] or the rheological [7] characteristics of these electrolytes. Moreover, we focused our attention only on two commercially available fumed silicas in each study. One advantage of fumed silica over competing fillers is that its surface can be chemically modified quite readily. Thus, by attaching appropriately selected ligands to the silica surface, we may arrive at a combination of desirable properties not otherwise obtainable. A particularly interesting approach is to make the filler surface conductive by attaching moieties capable of complexing with Li^+ cations. This can be accomplished, for example, by tethering short, oligomeric poly(ethylene oxide) (PEO) chains to fumed silica particles. The corresponding composites could potentially show a higher conductivity due to the provision of additional conductive pathways.

Our objective in this study, therefore, is to determine whether the fumed silica surface chemistry has an effect on the conductivity of composite electrolytes. Simultaneously, we also examine the rheological properties of the resulting composites to ascertain whether there exists a link between conductivity and rheology. We extend our studies to cover a broad variety of fumed silicas, some of which are obtained from commercial sources, and some of which we have synthesized ourselves. The silica surfaces range from non-polar (alkyl-terminated) to highly polar (native fumed silica, OH-terminated) to potentially conductive (PEO-modified). To the best of our knowledge, no investigations have been performed previously using fillers with a range of tailored surface chemistries in composite electrolytes.

Procedures for modifying the fumed silica surface are relatively straightforward in the case of alkyl-terminated surfaces [8,9]. The synthesis of PEO-
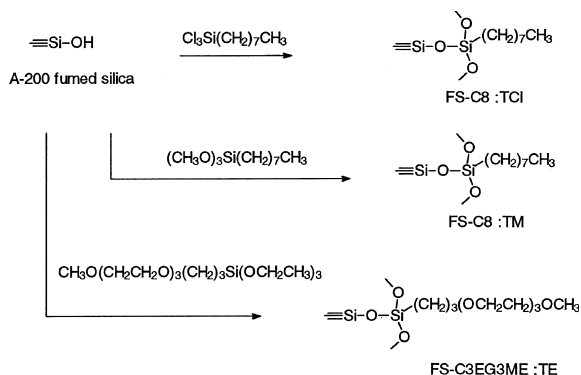
modified silicas has never been attempted before, and for this, we resort to some novel chemistry as described in further detail in the experimental section.

2. Experimental

2.1. Fumed silicas – synthesis and characterization

Fumed silica is an amorphous, non-porous form of silicon dioxide (SiO_2), and is electrochemically inert. Its primary structure consists of branched aggregates (~ 0.1 μm) formed by the fusion of spherical primary particles (~ 10 nm) [8]. Three commercially available fumed silicas (Degussa Corp., Akron, OH) were used in this study. These are the native A200 fumed silica which has a hydroxyl (silanol) terminated surface; the R974 silica which has a methylated surface; and the R805 silica which has octyl chains attached to the surface. Both R974 and R805 are prepared by modifying A200: the R974 silica is obtained by reacting A200 with dimethyldichlorosilane (DMDCS), while the R805 is generated by reacting A200 with octyltrimethoxysilane (OTMS). In both R974 and R805, approximately 50% of the surface silanol groups are replaced by alkyl groups [8,10].

Fumed silicas with appropriately tailored surfaces were synthesized from native hydroxyl-terminated fumed silica (A200) through the following schemes [10]. Note that all the modified silicas in this study (commercial and in-house synthesized) are made from the same starting material, and therefore have identical particle size (12 nm) and surface area (200 m^2/g).

The acronyms for the modified fumed silica (FS) are chosen to indicate, in order, the group attached to the surface and the reagent used in the synthesis scheme. Thus FS–C_8:TCl and FS–C_8:TM are octyl (C_8)-terminated silicas, synthesized using different reagents, viz. octyl trichlorosilane (OTCS) and octyl trimethoxy silane (OTMS), respectively. FS–C_3EG-3ME:TE is a PEO-modified silica where the triethylene glycol monomethyl ether moiety (EG3ME) is attached to the surface through a propyl (C_3) spacer. In order to make this silica, a chlorodimethylsilane precursor containing the above ether moiety needed to be synthesized. For this purpose, triethylene glycol allyl methyl ether was first prepared, and was reacted with chlorodimethylsilane to yield chlorodimethyl(4,7,10,13-tetraoxatetradecyl)silane. A solution of this silane was added in the presence of dry toluene and Speier's catalyst to fumed silica which had previously been silylated using triethoxysilane. This procedure yielded the final PEO-modified product.

In order to verify the success of the synthesis schemes, FT–IR and TGA were performed on the modified silicas. FT–IR spectra were obtained using a Nicolet IR/42 spectrometer purged with dry nitrogen. Samples used were 1 cm^2 pressed pellets prepared from approximately 10 mg of silica. TGA was performed under a helium atmosphere at a heating rate of 10°C/min on a Perkin Elmer TGA 7 instrument. Further experimental details as well as additional details on the synthesis are given in [10].

2.2. Composite preparation

Two lithium salts were used in this study: lithium imide (LiN(CF_3SO_3)$_2$) (from 3M Specialty Chemicals) and lithium triflate (LiCF$_3$SO$_3$) (from Aldrich). Polyethylene glycol dimethyl ether (MW 250, Aldrich) (PEG–DM) was selected as the parent liquid. A solution of lithium salt in PEG–DM was prepared at a salt content yielding maximum conductivity, i.e., a 1:20 mole ratio for Li:O [6]. Composites were made by dispersing the fumed silica in this solution. The resulting composite was exposed to vacuum for several hours to remove entrained bubbles. Handling of all components as well as sample preparation were done in an Argon-filled glove box.

2.3. Conductivity measurements

The conductivity of electrolytes was measured using AC Impedance Spectroscopy on an EG&G Princeton Applied Research potentiostat (273) and lock-in amplifier (5210) using the M398 software. The conductivity cell consisted of a sealable vial into which two platinum wires and a thermocouple are arranged. The sample vial was placed in a temperature bath thus allowing measurements to be conducted over a range of temperatures. Further details on sample preparation and the conductivity measurements are provided in [6].

2.4. Rheological measurements

Dynamic rheological measurements were conducted at ambient temperature (25°C) on a Rheometrics Dynamic Stress Rheometer (DSR-II) using a cone-and-plate apparatus. The dynamic response can be deconvoluted into two components: the elastic (or storage) modulus G' which is related to the elastic energy stored in the system on deformation, and the viscous (or loss) modulus G'' which is linked to the viscous dissipation of energy in the system. The moduli G' and G'' are functions only of the oscillation frequency ω for low deformations confined within the region of linear viscoelasticity. In order to evaluate the characteristics of a viscoelastic material, it is customary to examine the frequency spectrum showing G' and G'' as a function of ω. The relative magnitudes and shapes of the G' and G'' curves indicate the type and extent of microstructure present [11]. Additional details on rheological experimentation can be found in [7].

3. Results and discussion

We first report upon the surface chemistry of the modified fumed silicas using FT–IR to verify that the chemical reactions occurred as planned. Fig. 1 illustrates the FT–IR spectra for each of the surface-modified fumed silicas, together with that of the starting material (A200). The resonance peak characterizing the Si–OH group ($\sim$3744 cm^{-1}) [10] is observed to decrease as the silanols on A200 are replaced. At the same time, both octyl-modified silicas (i.e., FS–C_8:TCl and FS–C_8:TM) show the
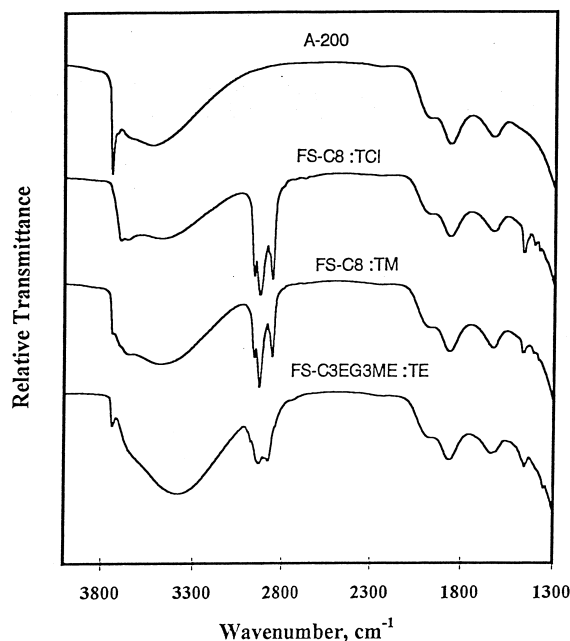
Fig. 1. IR spectra of fumed silicas: A200 (native silanol surface); FS–C$_8$:TCl (octyl-modified surface); FS–C$_8$:TM (octyl-modified surface); and FS–C3EG3ME:TE (PEO-modified surface).

Fig. 2. Effect of PEO-modified fumed silica (FS–C3EG3ME:TE) on conductivity. Data for conductivity as a function of temperature is shown for a solution (Li:O = 1:20) of lithium imide in PEG–DM (MW 250), and its corresponding composites containing 10% and 20% by weight of fumed silica.

expected C–H stretching bands at ~2800–2900 cm^{-1}. The PEO-modified fumed silicas (FS–C3EG-3ME:TE) also shows a similar band at 2900 cm^{-1} corresponding to the C–H absorption of ethylene oxide units.

Additional data obtained from TGA studies (not shown here) indicate significant weight loss when the modified silicas are heated, corresponding to the removal of tethered organic chains from the silica surface. Furthermore, titration studies on the modified silicas, using LiAlH$_4$ in diglyme, indicate the expected decrease in residual Si–OH density upon modification. Thus, the data from FT–IR, TGA, and titration taken together confirm that the surface-modification reactions have occurred successfully. From titration studies, we estimate that the surface coverage of attached groups is approximately 50% in each of the modified silicas [10].

We first illustrate the effects of adding the PEO-modified fumed silica (FS–C3EG3ME:TE) to a lithium imide–PEG–DM solution. In Fig. 2, the conductivity is shown as a function of temperature for the base solution (Li:O = 1:20) and for compos-
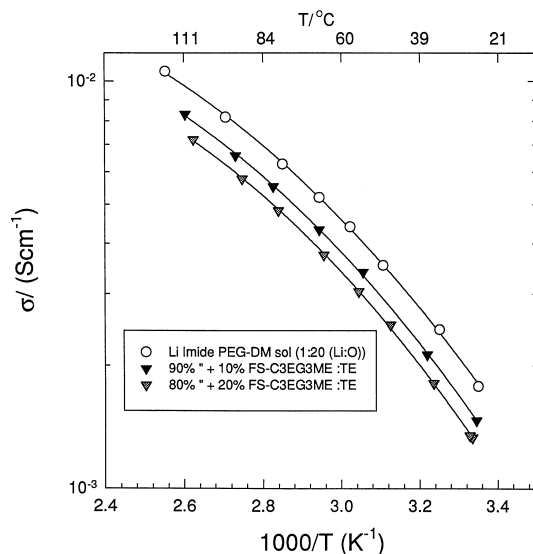
ites containing 10% and 20% by weight of FS–C$_3$EG3ME:TE. We find the conductivity to be lowered by a small, finite amount on adding the silica, with a greater decrease at a higher fumed silica content.

The effects of fumed silica surface chemistry on conductivity are illustrated in Figs. 3 and 4. In Fig. 3 the conductivity as a function of temperature for a lithium imide solution (Li:O = 1:20) in PEG–DM and the corresponding composites prepared using various fumed silicas is shown. The silica surface groups range from methyl (R974) to octyl (FS–C$_8$:TCl) to hydroxyl (A200) to oligoether (FS–C$_3$EG3ME:TE). In Fig. 3a data for composites of 10% weight fraction are shown, and Fig. 3b for composites of 20% weight fraction. Likewise, Fig. 4 shows the conductivity of composites containing three varieties of octyl-modified silica: (the in-house synthesized FS–C$_8$:TCl and FS–C$_8$:TM, and the commercial R805).

Figs. 3 and 4 demonstrate that at a given weight fraction of solid, the conductivity is nearly independent of surface chemistry. This observation appears to hold regardless of the nature of the lithium salt as

Fig. 4. Conductivity of composites containing three varieties of octyl-modified fumed silica: R805, FS–C$_8$:TCl, and FS–C$_8$:TM. Data is shown for the base solution (PEG–DM–Lithium imide) and for composites containing 10% (filled symbols) and 20% (open symbols) by weight of silica.
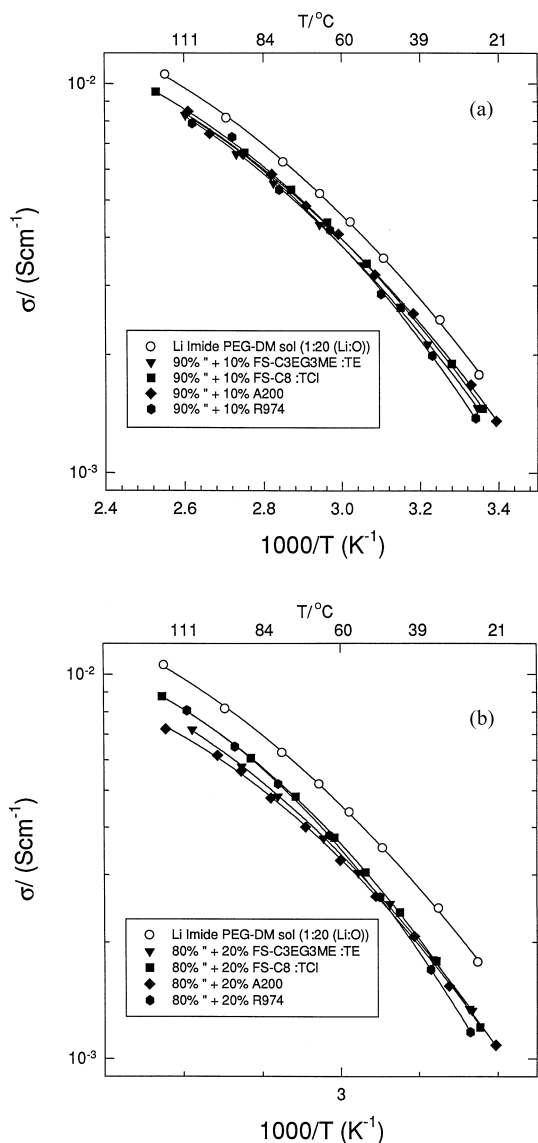

Fig. 3. Effect of fumed silica surface chemistry on conductivity. Data for conductivity as a function of temperature is shown for the base lithium imide–PEG–DM solution and for composites containing 10% (a) and 20% (b) by weight of the following fumed silicas: A200 (native, silanol); R974 (methyl); FS–C$_8$:TCl (octyl); FS–C3EG3ME:TE (ethylene oxide oligomers).

well. For example, we have found in earlier studies with lithium triflate, that the conductivity of a PEG–DM–based composite electrolyte containing 10% R805 was practically identical to the conductivity obta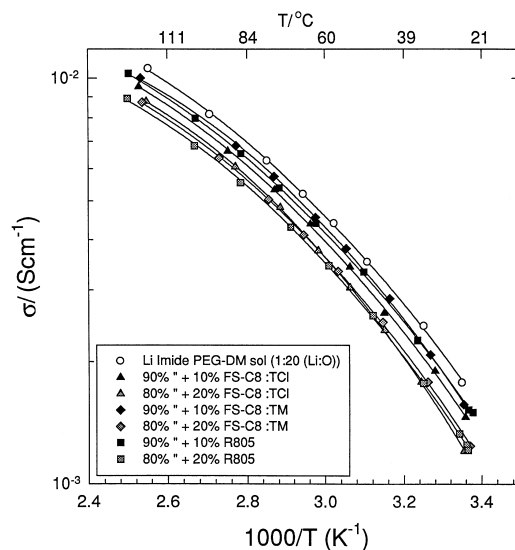ined using 10% A200 instead [6]. It seems clear that the dominant factor affecting the conductivity of the composites is the action of fumed silica as a volume-filling insulator, regardless of the nature of the surface groups. The conductivity decrease is determined primarily by the weight fraction of fumed silica present in the composite.

In contrast to conductivity, the rheological properties of the composite depend strongly on the type of surface group. We illustrate this in Fig. 5 where we compare the dynamic rheological response of composite electrolytes containing 20% of native (A200), octyl-modified (FS–C$_8$:TCl), or PEO-modified (FS–C$_3$EG3ME:TE) fumed silica. In the case of the FS–C$_8$:TCl and A200 composites, the response is highly elastic and solid-like, as in each case the elastic modulus (G') significantly exceeds the viscous modulus (G'') with both G' and G'' being frequency independent. This behavior indicates the presence of a three-dimensional network structure in the two composites, whereby the materials exhibit gel-like behavior and good mechanical stability [11]. The FS–C3EG3ME:TE fumed silica, in contrast, gives rise to a predominantly viscous response, as both moduli, G' and G'' show frequency-dependent
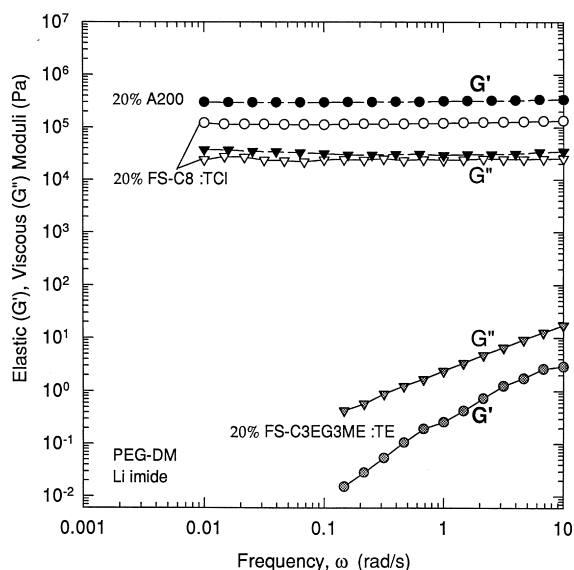
Fig. 5. Dynamic rheology of composite electrolytes. The elastic (G') and viscous (G'') moduli are shown as a function of frequency for composite electrolytes prepared using the following fumed silicas: A200 (native), FS–C_8:TCl (octyl), and FS–C3EG-3ME:TE (ethylene oxide chains). In each case, the base solution is lithium imide in PEG–DM (MW 250) (Li:O = 1:20), and the silica weight fraction is 20%.

behavior with the viscous modulus (G'') exceeding the elastic modulus (G'). This behavior indicates that the FS–C3EG3ME:TE composite is a non-flocculated suspension of low viscosity, and therefore behaves like a liquid rather than a stable solid [11]. In an earlier communication [7], we have also shown that there is a dramatic difference in rheological behavior between the R974 silica (methyl groups) and the R805 silica (octyl groups). The R974 silica weakly flocculates to give a viscoelastic response (refer Fig.7 in [7]) in contrast to the elastic, gel-like response observed with the R805 silica.

The rheological behavior of a composite is determined by the colloidal interactions prevalent in the system, which in turn are controlled by the fumed silica surface chemistry. In a given system, there will be competitive interactions between the surface groups and the liquid continuous phase. A mismatch in chemical nature (e.g., polarity) between the surface layer and surrounding liquid will lead to strong interactions between surface groups on adjacent particles [12]. Thus, for octyl-modified fumed silica

in PEG-DM, the non-polar octyl groups prefer to interact with other octyls rather than with the more polar PEG-DM. This preferential interaction leads to the formation of a three-dimensional network of particulates and thus to a gel. Also, as the weight fraction of R805 silica is increased, the density of crosslinks in the gel increases, and therefore the gel modulus G' also increases. The difference in behavior between the R974 (methylated) and the R805 (octyl-modified) silicas can be attributed to a lack of steric barrier in the case of R974 due to the smaller CH_3 groups, as has been discussed earlier [7].

In the case of the FS-C_3EG3ME:TE-based composites, the surface-bound PEO chains interact with similar molecules present in the PEG–DM continuous phase. This precludes flocculation of fumed silica units, and consequently, a suspension of distinct entities is formed. Gel formation by the native (A200) fumed silica in PEG–DM likely occurs because the silanol groups on A200 fumed silica preferentially form hydrogen bonds with each other, rather than with the ether oxygens on PEG–DM. This 'gelling' ability of the A200 silica has been observed in a series of end-capped polyethers [13].

An important conclusion from our data is that the conductivity and mechanical strength of fumed silica-based composite electrolytes are essentially decoupled, and can therefore be optimized independently. This presents a significant advantage over conventional polymer electrolytes, where an enhancement in mechanical stability is inevitably accompanied by a loss in conductivity. This decoupling is further illustrated in Fig. 6 which simultaneously shows the effects of silica weight fraction (octyl-modified, R805) on the elastic modulus and room-temperature conductivity. The elastic modulus is increased by orders of magnitude upon addition of R805 while the conductivity decreases by less than 30% for up to 20% solids content.

The presence of conductive PEO chains on the fumed-silica surface did not contribute to an enhancement in conductivity, as might be anticipated. Apparently, the behavior of fumed silica as a volume-filling insulator dominates any possible enhanced surface-conductivity effects. Otherwise, an increase in conductivity should be seen upon addition of fumed silica, such as that which occurs with $LiAlO_2$ and other fillers in high molecular-weight
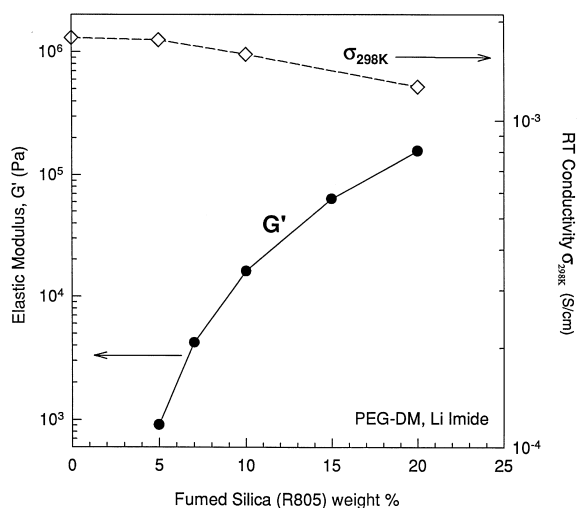
Fig. 6. Variation of elastic modulus (G') and room-temperature conductivity (σ_{298}) with weight fraction of R805 (octyl-modified) fumed silica. The base solution is lithium imide in PEG–DM (MW 250) (Li:O = 1:20).

PEO-based composites [2,4]. However, note that the conductivity decrease on adding fumed silica is quite modest; for example, a ~30% decrease in conductivity is observed on adding 20% solids. This decrease is even lower than might be anticipated based purely on volume-filling effects using the approximate theory of Maxwell [6], thereby suggesting that surface effects may not be totally absent in our system.

4. Conclusions

Fumed silica-based composite polymer electrolytes show almost complete decoupling between conductivity and rheology. The conductivity shows negligible dependence on the type of fumed silica

surface group (silanol, alkyl, or PEO), and moreover, decreases only marginally even at high-solids content. In contrast, rheological properties are strongly affected by the surface chemistry; in particular, mechanically stable composites (gels) are formed by fumed silicas with silanol or octyl surfaces dispersed in PEG–DM.

Acknowledgements

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