Composite Polymer Electrolytes Based on Poly(ethylene glycol) and Hydrophobic Fumed Silica: Dynamic Rheology and Microstructure

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Dynamic rheological techniques are used to probe the microstructures present in fumed silica-based *composite polymer electrolytes*. These electrolytes are obtained by dispersing hydrophobic fumed silica in a poly(ethylene glycol)−lithium salt solution and display high conductivities ($\sigma_{298K} > 10^{-3}$ S/cm), mechanical stability, and easy processability. The materials behave as soft solids (gels) under ambient conditions due to the presence of a three-dimensional network of silica entities. Network formation occurs as a result of van der Waals (dispersion) forces between the nonpolar surface layers on silica units. Factors which affect the van der Waals interaction, and hence the gel network density, include the nature of the PEG end group, the presence of ionic species, and the size of the hydrophobic surface group on the silica. The composites also exhibit shear-thinning behavior due to the shear-induced disruption of network bonds, and this behavior can be advantageously utilized in electrolyte processing.

Introduction

Rechargeable lithium batteries employing solid electrolyte materials have been envisaged for the last two decades ever since the discovery of polymer electrolytes based on poly(ethylene oxide) (PEO).[1] Solid polymer electrolytes can potentially eliminate battery leakage, negate the need for a separator, and, moreover, be amenable to low-cost manufacturing technologies that are well-established in the polymer industry. Notwithstanding these obvious advantages, there are serious impediments to commercialization of the above technology. The most significant drawback of conventional PEO-based electrolytes is their low conductivity ($\sigma < 10^{-5}$ S/cm) at ambient temperatures, which is mainly due to the presence of a nonconductive crystalline phase under these conditions.[2]

At temperatures above 60 °C, PEO-based polymer electrolytes show appreciable conductivities ($\sigma > 10^{-4}$ S/cm) as the crystalline phase in PEO melts; however, under these conditions the materials lose their dimensional stability and behave like extremely viscous liquids. Weston and Steele[3] hence proposed that particulate fillers could be introduced into the polymer matrix to improve its mechanical stability at high temperatures. Materials thus formed are called *composite polymer electrolytes* (CPE). The fillers not only contribute to enhanced mechanical properties but also

lead to superior interfacial stability for the electrolyte in contact with lithium metal, by a mechanism not yet understood.[4] In some cases, increases in conductivity have also been observed on addition of filler and have been attributed to a decreased level of polymer crystallinity.[4,5] The conductivity increase is not related to the ion-conducting abilities of the filler particles, and in fact, electrochemically inert fillers are found to be as effective as conducting fillers.[7]

Several alternative approaches to electrolyte design have also been examined in the past decade. However, problems persist with each new approach, as pointed out recently by Fauteux et al.[2] Many of the electrolyte designs suggested so far have been based on high-molecular-weight polymers; for these systems the low room-temperature conductivity continues to be a limiting factor. Thus, the goal of developing solidlike electrolyte materials with stable mechanical properties and high conductivities at ambient temperature still remains a technological challenge.

In recent years, our group has investigated an alternate class of composite polymer electrolytes which use low-molecular-weight polymers as the conducting medium.[8,9] These electrolytes are obtained by dispersing *fumed silica* particulates[10] in a matrix consisting of poly-

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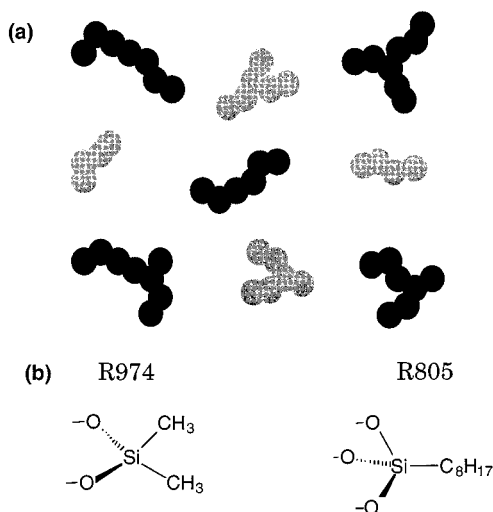
Figure 1. (a) Aggregated structure of fumed silica. Each aggregate is formed by the irreversible fusion of primary spherical silicas. (b) Surface chemistries of hydrophobic fumed silicas. In each case, 50% of surface groups are hydroxyls (OH, not shown) while the remaining 50% are the hydrophobic groups shown.

(ethylene glycol) (PEG) and lithium salt. The electrochemical characteristics of these materials have been the subject of earlier publications.[8,9] To summarize the findings, we have obtained conductivities exceeding 10^{-3} S/cm (at room temperature), a wide potential window (5.5 V) of operability, and a stable interface toward lithium metal. The detection of a stable interface is particularly noteworthy, and can be contrasted with the resistive interfaces observed with rival systems such as gel electrolytes.

In this paper, we focus on the rheological behavior of our composite polymer electrolytes. These materials behave like soft solids under ambient conditions due to the reinforcing action of the fumed silica fillers. In other words, the silica acts as a "gelling agent" which immobilizes the liquid medium to produce a quasi-solid electrolyte. Fumed silica is an amorphous, nonporous type of silica (SiO_2) and is an electrochemically inert material. The primary structure of fumed silica consists of branched aggregates formed by the fusion of primary spherical particles (Figure 1a). This complex-aggregated structure is responsible for the unique properties of this material, in particular, its ability to impart high viscosities to liquids.[10,11] The silicas used in our study are hydrophobic varieties having nonpolar surface groups. When dispersed in PEG–lithium salt solutions, silica aggregates interact to form characteristic microstructures which in turn determine the mechanical response of the electrolyte. The goal of this paper will be to elucidate the microstructural features of our CPE systems using dynamic rheological techniques and then correlate the microstructures with the colloidal interactions existing in each system.

Experimental Section

Materials. The hydrophobic surface groups on the fumed silicas (Degussa Corp., Akron, OH) are shown in Figure 1b.

Most of our studies were done with the "R805" silica which has native hydroxyl (OH) and octyl (C_8H_{17}) groups in equal (50%) proportions on its surface.[10] To probe the effects of silica surface chemistry, we studied a second variety of hydrophobic silica (R974) which has dimethyl groups instead of octyl groups, again at 50% coverage.[10] Poly(ethylene glycols) with different end groups were purchased from Aldrich Chemicals. The unmodified glycol (henceforth called PEG) with hydroxyl end groups has a molecular weight of 300 (number of $-CH_2-CH_2O-$ repeat units $n = 6$). The glycol with one of its ends capped by a methyl group (PEG-m) has a molecular weight of 350, and the glycol with both of its ends capped by methyl groups (PEG-dm) has a molecular weight of 250. All the liquids were dried using 4 Å molecular sieves. Three lithium salts were used in our study, viz. lithium perchlorate ($LiClO_4$), lithium triflate ($LiCF_3SO_3$) (both from Aldrich Chemicals), and lithium imide ($LiN(CF_3SO_2)_2$) (from 3M Specialty Chemicals).

Electrolyte Preparation. The solution of lithium salt in polymeric glycol was prepared by continuously stirring the mixture at an elevated temperature (90 °C). Conductivity measurements on pure solutions (with no silica filler) indicated that a mole ratio of 1:20 for Li:O yielded the highest conductivity.[9] This solution composition was therefore used for the rheological studies. The composite polymer electrolytes were prepared by adding the fumed silica to the previously prepared solution of lithium salt in glycol. The mixture was stirred intensely in a Silverson SL2T mixer (Silverson machines, Chesham, U.K.) till homogeneity was reached. The resulting composite was exposed to vacuum (≈ 1 kPa) at room temperature for several hours to remove entrained bubbles.

Rheological Experiments. The rheological behavior of our materials was determined under both steady and oscillatory shear.[12] In steady-shear experiments, the viscosity of the sample is measured as a function of shear stress or shear rate. However, steady-shear measurements are not very sensitive to the microstructure present in the system. Dynamic rheology, performed under oscillatory shear, is the preferred technique for detecting microstructural features.[12,13] In dynamic experiments, a low-amplitude sinusoidal deformation γ is imposed on the sample at a fixed frequency ω and maximum strain amplitude γ_0:

$$\gamma = \gamma_0 \sin \omega t \qquad (1)$$

Within the region of linear viscoelasticity, the resulting stress is also sinusoidal and can be decomposed into an in-phase and an out-of-phase component:[13]

$$\tau = G'\gamma_0 \sin \omega t + G''\gamma_0 \cos \omega t \qquad (2)$$

The stress component in-phase with the deformation defines the *elastic* (or storage) modulus G' and is related to the elastic energy stored in the system on deformation. The component out-of-phase with the strain gives 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. 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.[13] The elastic modulus G', in particular, is an important indicator of the degree of structuring in a disperse system.[12]

Rheological experiments were performed on a Rheometrics Dynamic Stress Rheometer (DSR). Dynamic experiments were conducted in either the constant stress or constant strain mode, with the latter mode being used for frequency sweeps due to its superior strain resolution. All experiments were done at ambient temperature (25 °C) in a cone-and-plate

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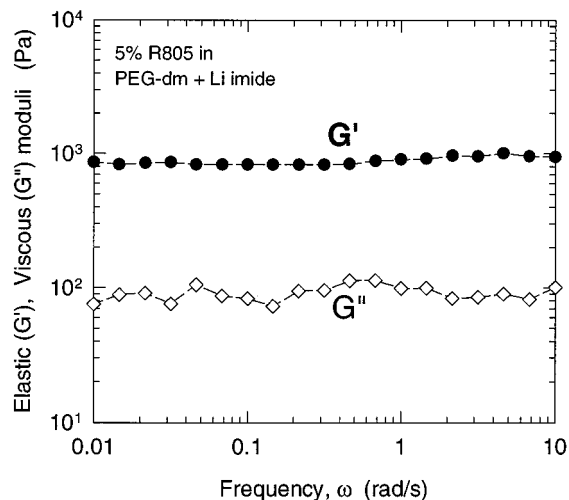
Figure 2. Elastic (G') and viscous (G'') moduli as a function of frequency for a composite electrolyte containing 5% R805 fumed silica in PEG-dm + lithium imide. The strain amplitude was held constant at a value within the linear viscoelastic regime of the material.

geometry. Before each dynamic experiment, a steady preshear was performed at a shear rate of 0.5 s^{-1} for 60 s, followed by a 120 s rest period. This procedure was necessary to erase any previous shear histories and to ensure that the material establishes its equilibrium structure.[14] Two different cone-and-plate fixtures were used, the larger fixture having a diameter of 40 mm and a cone angle of 0.04 radians and the smaller fixture having a diameter of 25 mm and a cone angle of 0.1 radian. Experiments were done using both fixtures to ensure that instrumental artifacts such as wall slip were absent.

Results and Discussion

Our approach is to probe the microstructures present in our composite polymer electrolytes using rheology. Thereafter we will interpret the observed microstructures in terms of the colloidal interactions prevailing in each system. Note that our composites are three-component systems, where the continuous phase is a solution of lithium salt in polymeric glycol, and the disperse phase is a particular type of fumed silica.

We first describe the rheology and microstructure of a typical composite polymer electrolyte formed by dispersing 5% R805 (octyl-terminated) fumed silica in a lithium imide—PEG-dm solution. From dynamic rheology, we obtain the characteristic frequency spectrum of the sample showing the elastic (G') and viscous (G'') moduli as a function of frequency (Figure 2). Two important features of the rheological response are apparent from this plot: first, the moduli are both independent of frequency and, second, the elastic modulus G' significantly exceeds the viscous modulus G''. The dominance of G' indicates that the material behaves primarily in an elastic manner, while the frequency independence of the moduli shows that the system behavior is unchanged over a range of time scales. Such behavior is characteristic of a physical gel consisting of a three-dimensional network of physical bonds.[12] The network responds elastically at small deformations and the stresses generated do not relax over the time period of the experiment. The magnitude of G' ($\approx 10^3$ Pa for

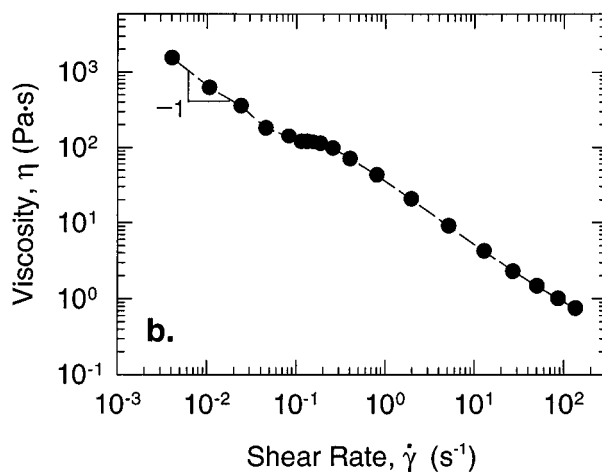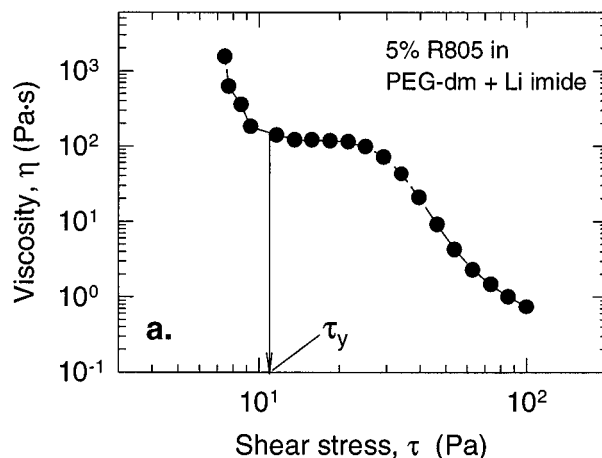(14) Raghavan, S. R.; Khan, S. A. *J. Rheol.* **1995**, *39*, 1311.

Figure 3. Steady-shear viscosity as a function of (a) shear stress and (b) shear rate for the same composite as in Figure 2 (i.e., 5% R805 in PEG-dm + Li imide).

this system) is an indication of the density of network bonds in the system.[13] Note that the dynamic response is consistent with visual observations on the material, both of which indicate that it is a soft elastic solid under ambient conditions.

The composite electrolytes also exhibit a variety of other complex rheological phenomena. Under steady shear, they show a yield stress as well as shear-thinning, both of which can be seen in Figure 3. The yield stress τ_y is a manifestation of the network structure present in the system and signifies the minimum stress required to induce sample flow. This can be observed from Figure 3a, where the viscosity is plotted as a function of shear stress. For low stresses, the material shows considerable resistance to flow (plastic response) and the corresponding viscosities are very large (>10^5 Pa·s). At a stress of ≈ 10 Pa (i.e., τ_y), the material abruptly yields and a viscosity plateau is observed. For even higher stresses, the viscosity continues to drop with increasing stress.

The same data is plotted in Figure 3b as a function of shear rate to better indicate the shear-thinning response. Here, the plot of viscosity vs shear rate is approximately linear, corresponding to power-law behavior. The existence of a yield stress is reflected as a slope of -1 at low shear rates.[12] Shear thinning occurs because the bonds composing the network structure are weak, physical bonds that can be disrupted by shear.

Composite Polymer Electrolytes Based on PEG

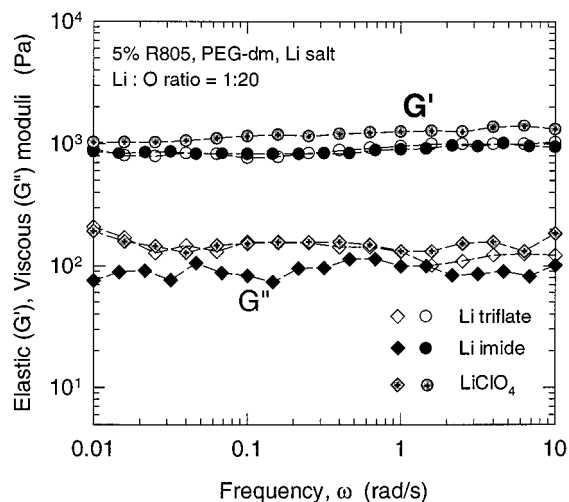*Chem. Mater., Vol. 10, No. 1, 1998* **247**

Figure 4. Effect of lithium salt type on the dynamic moduli (G', G'') of composite electrolytes. Each composite contained 5% R805 fumed silica dispersed in a solution of lithium salt in PEG-dm.

We thus find from rheology that the composite electrolytes are physical gels due to the formation of a three-dimensional particulate network. The nature of the network bonds between individual silica units will be discussed at a later point in this paper. As we shall see, network formation is intimately related to the fumed-silica surface chemistry and the nature of the liquid. Note that the silica used here is a hydrophobic type (R805), having a surface covered by octyl chains. Gel formation by the R805 silica has been observed previously in polar polymeric liquids such as poly-(propylene glycols) (PPGs).[15]

Effect of Lithium Salt Variety. We show dynamic rheological data (frequency spectra) in Figure 4 for composites containing 5% R805 fumed silica in a matrix formed by various lithium salts and PEG-dm. In each case the sample is a physical gel, since G' is significantly larger than G'' with both moduli being frequency-independent. Moreover, we find that the moduli are largely insensitive to the type of lithium salt. We can therefore conclude that the network density in our composites (which is proportional to G') is independent of the lithium salt anion. This may work advantageously in designing composite electrolytes in that one can independently tailor the electrochemical response by using different salts without affecting the mechanical properties of the composite.

Effect of PEG End Group. In our studies we have evaluated three different poly(ethylene glycols) each having different end groups. The PEG having both its ends capped by methyl groups (i.e., PEG-dm) is best suited for battery applications as it provides the highest conductivity and the best interfacial stability.[8,9] (In fact, the conductivity decreased in the order PEG-dm > PEG-m > PEG for the three liquids studied.) The rheology of the composite electrolytes is also influenced by the nature of the PEG end groups. Figure 5 shows the frequency spectrum for composites containing 5% R805 in glycol−lithium triflate solutions. The composites show a gel-like microstructure ($G' > G''$, moduli independent of frequency) regardless of glycol type. (In
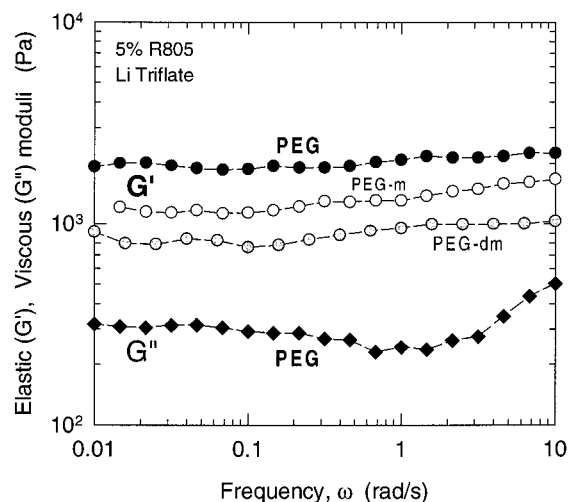
(15) Khan, S. A.; Zoeller, N. J. *J. Rheol.* **1993**, *37*, 1225.

Figure 5. Effect of PEG end group on dynamic moduli (G', G''). The same silica concentration (5% R805) and lithium salt (triflate) were used in all cases. For the sake of clarity, the viscous modulus, G'' is shown only for the composite based on PEG (i.e., having OH end groups).
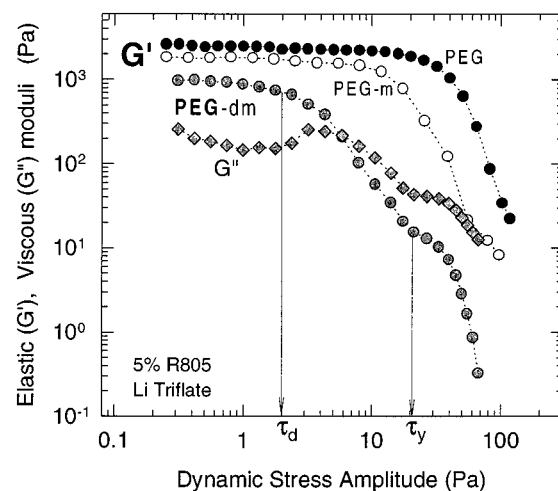

Figure 6. Effect of PEG end group on dynamic rheological properties. The plot shows the moduli (G', G'') as a function of dynamic stress amplitude for the same composites as in Figure 5. The experiment was conducted at a constant frequency of 5 rad/s. Both G' and G'' are shown for the composite based on PEG-dm.

the figure, the viscous modulus G'' is shown only for the PEG-based composite for the sake of clarity.) However, the magnitude of the elastic modulus (G') for the gels is dependent on PEG end group, with G' decreasing in the order PEG > PEG-m > PEG-dm. This trend is also observed at higher fumed silica weight fractions (cf. 10%). A higher value of G' indicates a denser network and thereby a more rigid gel structure. Thus, we find that the density of the network structure is dictated by the glycol end groups.

The effect of PEG end group can also be observed in stress sweeps conducted on each composite. In a stress-sweep experiment, the frequency is held constant and the stress amplitude is varied in increasing steps. Figure 6 shows a plot of the moduli (G' and G'') as a function of dynamic stress amplitude τ for the three composites indicated in Figure 5. Attention should be focused on the elastic modulus G' for each composite and its variation with stress amplitude. For each
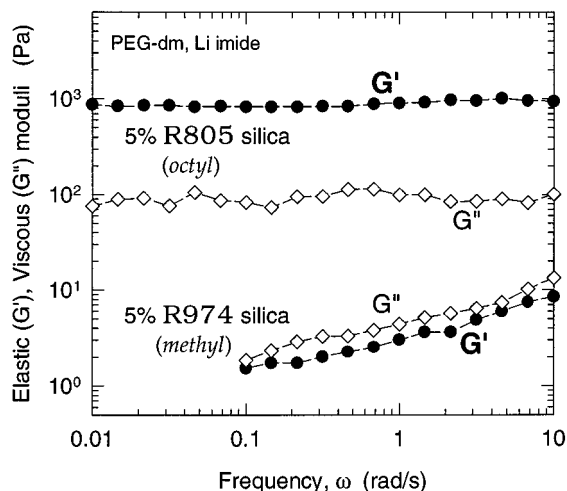
Figure 7. Dynamic moduli (G', G'') as a function of frequency for composite electrolytes based on two types of hydrophobic silica: R805 (octyl-terminated) and R974 (methyl-terminated). Each composite contains 5% silica in a PEG-dm−Li imide matrix.
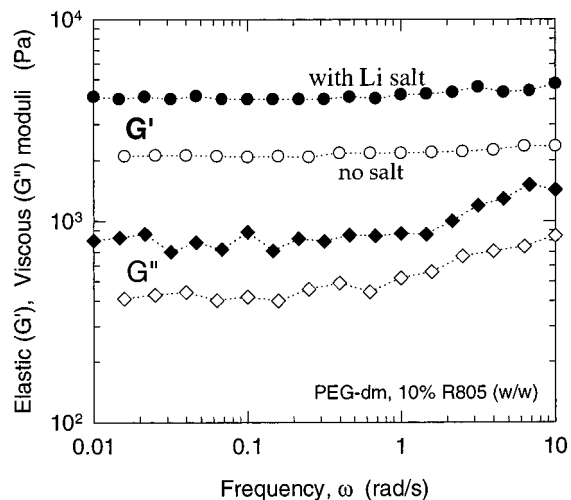

Figure 8. Effect of ionic species on the rheology of R805 silica-based composites. Both samples contain 10% R805 fumed silica (w/w) in PEG-dm. One of the samples is a composite electrolyte having lithium imide dissolved in the PEG-dm, while the other sample contains no salt or other additional components.

sample, G' shows a plateau at low stresses and decreases with stress amplitude beyond a critical stress τ_d (illustrated on the figure for PEG-dm only). The decrease of G' with stress indicates disruption of network bonds at large deformations. The critical stress τ_d marking the linear viscoelastic (LVE) limit for the sample can be considered a dynamic yield stress. The value of G' in the plateau region corresponds to the modulus in the frequency-sweep plots (Figure 5). Both the plateau modulus as well as the dynamic yield stress τ_d decrease in the order PEG > PEG-m > PEG-dm.

A second interesting feature apparent from the plot for the R805−PEG-dm/ Li triflate sample is the existence of a subsequent plateau (denoted by τ_y) at intermediate stresses. This plateau is observed at about the same stress level as was the yield stress from steady shear, indicating a correspondence between the two parameters (compare Figures 3 and 6). Thus, the second yield stress under dynamic shear (τ_y) indicates the minimum stress needed to cause sample flow. In contrast, the first dynamic yield stress τ_d represents the stress required to barely disrupt the network, thereby signifying the limit of elastic behavior. The existence of two distinct yield stresses has been reported before for dispersions of interacting particles in liquids.[16,17]

Effect of Silica Surface Chemistry. In Figure 7 we show the frequency spectrum for a composite containing 5% R974 (methyl-terminated) silica in lithium imide−PEG-dm. Data for the corresponding composite with R805 (octyl-functionalized) silica is also shown for comparison. The R974-based system shows a significantly different rheological response, with the viscous modulus G'' dominating the elastic modulus G' over the entire frequency range. Moreover, both moduli vary significantly with frequency and are considerably lower than the moduli obtained with the R805 silica. Thus, while the R805 silica forms a physical gel, the R974 (methyl-terminated) silica gives rise to a "sol-like" microstructure with little or no interconnections between
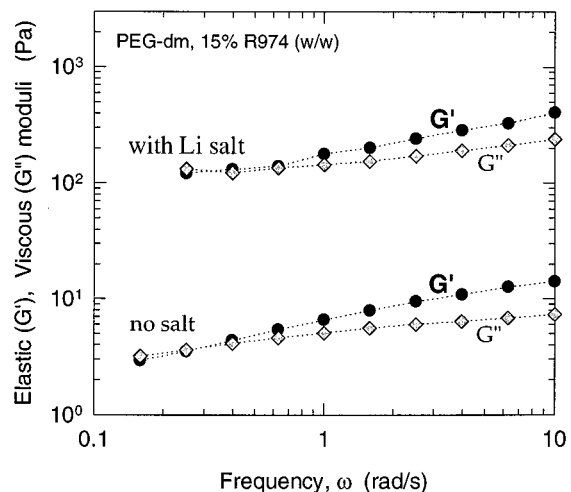
Figure 9. Effect of ionic species on the rheology of R974 silica-based composites. Both samples contain 15% R974 fumed silica (w/w) in PEG-dm. As in Figure 8, one sample is a composite electrolyte containing lithium imide, while the other sample does not contain any salt.

silica units. (At higher silica concentrations, a limited degree of flocculation occurs and the moduli exhibit a crossover, as depicted later in Figure 9).

Effect of Ionic Species. One aspect of interest is to examine the rheology of systems containing no lithium salt. These would be two-component materials (fumed silica, PEG) in contrast to the three-component electrolytes discussed earlier. We have studied a series of such systems to help clarify the effects of ionic species on the rheology. For accurate comparison of samples with and without salt, it is necessary to hold the total amount of solids (i.e. the *volume fraction* of silica) constant. We have therefore compared samples with equal concentrations on a w/w (silica/liquid) basis rather than a w/w (silica/total) basis.

In Figure 8 we indicate the frequency spectra for two samples containing 10% w/w of the R805 silica in PEG-dm. In one sample no additional components are present, while the other sample contains lithium imide dissolved in the PEG-dm liquid. (The overall silica

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(17) Bonnecaze, R. T.; Brady, J. F. *J. Rheol.* **1992**, *36*, 73.

weight fractions are correspondingly 9.07% and 7.03%.) Both composites are gels, but the composite prepared using the PEG−lithium salt solution exhibits a higher elastic modulus G'. We find that G' approximately doubles in the presence of salt ions, a finding which has been corroborated at other silica concentrations (cf. 10%) as well. Thus, with the R805 (octyl-modified) silica, the addition of ions tends to increase the network density in the system.

In the case of the R974 (methylated) silica, the effect of salt is even more dramatic. Samples at 15% w/w (silica/ PEG-dm liquid) are shown in Figure 9, both in the presence and absence of salt (lithium imide). We find that the moduli are increased by an order of magnitude in the presence of salt ions. Note, however, that there is no qualitative change in the response: in each case, the two moduli are approximately equal over the frequency range and show a crossover. Similar results were obtained for other R974 silica concentrations (cf. 10%) as well. Thus, the presence of ionic species significantly enhances the flocculation of R974 silica units; nevertheless, the attractive forces are not strong enough to enable the formation of a network structure.

Colloidal Interactions and Microstructure. So far, we have elucidated the microstructural features of our composite electrolytes using dynamic rheology. We will now try to unravel the colloidal interactions responsible for the microstructures. In the process we will address two issues: (a) what are the governing interaction forces in our system and (b) can we correlate the trends in rheological (microstructural) data with changes in the intensity of these forces?

A typical composite electrolyte consists of silica (SiO_2) aggregates bearing hydrophobic surface groups suspended in a polyether glycol liquid. Since the glycols are weakly polar media (dielectric constant ϵ ranging from 8 to 13), we can rule out the existence of any significant electrostatic interactions between silica aggregates. This point may seem surprising at first glance because our systems are *electrolytes* with lithium salt dissolved in the matrix. However, it is highly unlikely that the silica units in our composites show any appreciable surface charge, especially because of their nonpolar nature. In this regard, our interpretation is fully consistent with the silica literature[11,18] and also with studies conducted on dispersions in nonaqueous electrolytes.[19]

We then have to consider two contributions to the net interaction force between silica units: (i) specific interactions arising due to the acid−base character of the particles and (ii) van der Waals dispersive forces. Specific interactions can occur primarily through hydrogen bonding between residual surface hydroxyls (Si−OH) situated on adjacent silica aggregates. Note that both the R805 (octyl-terminated) and the R974 (methylated) silicas have similar densities of residual hydroxyls (approximately 50% coverage). Nevertheless, the two silicas lead to widely different microstructures, as shown by Figure 7, with a network structure being observed

for the R805 silica and a nonflocculated structure for the R974 silica. Hence, interactions between the hydroxyl groups alone cannot explain the behavior of these systems, and the van der Waals (vdW) dispersive forces between hydrophobic silica units must play a significant role in structuring.

We now consider the magnitude of vdW interaction forces in such a system, as derived by Israelachvili.[20] For this, we will treat the various components as continuous media, ignoring for a moment the details of their molecular structure. The van der Waals forces are normally expressed in terms of the Hamaker constant A. For example, in the case of two identical spheres of radius a, at a distance of closest approach H (where $H \ll a$), the vdW energy of attraction V (i.e., the pair potential) is given by[19,20]

$$V = -A_{eff} \frac{a}{12H} \quad (3)$$

The force of attraction between the spheres can be obtained from the first derivative of the pair potential, as given below

$$F = -\frac{dV}{dH} = A_{eff} \frac{a}{12H^2} \quad (4)$$

In our system, the silica aggregates (Figure 1a) have a complex geometry and can neither be approximated as a sphere or as a flat plate. However, in our analysis, the geometrical details are not important. What is significant is that the intensity of the vdW forces is controlled by an effective Hamaker constant (A_{eff}) for interaction of particles across the liquid.

To account for the hydrophobic nature of the silicas, we can consider that the nonpolar surface groups form a "grafted layer" on the silica aggregates. Furthermore, for simplicity, we can assume that the thickness of this grafted layer δ is constant for all aggregates. In such cases, it has been shown that, at close approach, the vdW interaction between hydrophobic silica entities is dominated by the properties of the grafted layers covering the substrate.[20] Thus, A_{eff} can be related to bulk properties such as the dielectric constant (ϵ) and refractive index (n), using the following equation:

$$A_{eff} = \frac{3}{4}kT \frac{(\epsilon_m - \epsilon_\delta)^2}{(\epsilon_m + \epsilon_\delta)^2} + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_m^2 - n_\delta^2)^2}{(n_m^2 + n_\delta^2)^{3/2}} \quad (5)$$

Here, the subscript δ refers to the surface layer and the subscript m refers to the continuous medium. Note that the properties of the bare, unmodified silica particles do not enter into the above relation. The parameter ν_e refers to the main electronic absorption frequency for the dielectric permittivity and can be taken to be 3×10^{15} s^{-1} (assumed to be the same for both media).[20] The other parameters have their usual meanings: h is the Planck's constant, k is the Boltzmann constant, and T is the absolute temperature.

Let us now calculate the effective Hamaker constant A_{eff} for interaction of R805 (octyl-terminated) silica in PEG. For the grafted layer we use values tabulated for

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(19) van der Hoeven, P. H. C.; Lyklema, J. *Adv. Colloid Interface Sci.* **1992**, *42*, 205.

(20) Israelachvili, J. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: San Diego, 1991.

n-octane ($\epsilon = 1.95$; $n = 1.3870$ at 20 °C).[20] For the PEG continuous phase we use a dielectric constant of 13.4 (at 25 °C) which was reported for a PEG of molecular weight 400 by Salomon et al.[21] The refractive index of PEG at 20 °C is $n = 1.4630$, as supplied by the manufacturer. On the basis of these values, we compute A_{eff} at ≈298 K to be 3.3×10^{-21} J. Our value for A_{eff} matches well with literature estimates for the vdW interaction of a nonpolar medium across a polar solvent.[20] Translating the A_{eff} into an effective vdW potential (eq 3) is not straightforward because of the complicated fumed silica geometry. However, it is entirely reasonable for the potential to be ~20 times A_{eff} at short interaggregate distances (0.1–0.5 nm).[18] For our system, this implies an attractive potential exceeding $15kT$ at these distances, at room temperature.

We have thus shown that the flocculation of R805 silica in PEG-type liquids is due to the vdW attraction between octyl surface layers on silica units. The effective Hamaker constant has two contributions emanating due to the differences in dielectric constants (first term in eq 5) and the disparities in the refractive indices (second term in eq 5). In our case, both terms make approximately equal contributions to the overall A_{eff}. The net result is that the octyl moieties prefer to associate with each other, rather than with the PEG phase. Thus, the R805 silica units will have an inherent tendency to flocculate into a network.

One of the main assumptions we have made is that a continuous grafted layer of nonpolar groups extends across each silica aggregate. This assumption is reasonable for the R805 silica, since the octyl groups are relatively large and can effectively cover the whole surface.[11] In alternate terms, the octyl chains on R805 present a steric barrier, preventing the liquid molecules from accessing the bare (unmodified) silica surface which is covered with polar hydroxyls.

However, the above reasoning cannot be extended to the R974 silica, which has methyl groups on its surface at 50% coverage. The smaller methyl groups will be incapable of presenting an effective steric barrier for access to the remaining 50% surface hydroxyls. In that case, vdW interactions cease to be the exclusive mode and hydrogen-bonding interactions between the Si–OH groups and the liquid molecules become possible. The site for H-bonding on the polyether chain would preferentially be at the OH end groups but could also occur at the ether oxygens. The formation of H-bonds between the glycol and silica would reduce the tendency of the silica to flocculate. This explains why the R974 silica displays a nonflocculated microstructure (Figure 7), in comparison to the network formed by R805. Note also that at high silica concentrations a limited degree of flocculation does occur with the R974 (Figure 9), but even then the silica flocs are not linked into a network. Similar differences between the behavior of R974 and R805 silicas have been observed in other polyethers, such as poly(propylene glcyols) as well.[15]

We now turn our attention to some of our other results. In Figures 5 and 6, we showed that the network density due to R805 silica was highest in PEG and progressively reduced as the glycol was end-capped.

These results are due to the differences in polarity (i.e., dielectric constant ϵ) and refractive index (n) between the PEGs. The uncapped PEG has the highest polarity among the glycols studied due to the presence of two OH groups on its ends. As the end groups on the glycol are capped by methyl groups, the polarity of the glycol decreases. For example, Salomon et al.[21] report that for an identical molecular-weight of 400, ϵ for PEG is 13.4, while ϵ for PEG-dm is 7.9. Similarly, the refractive index drops from 1.4630 for PEG to 1.4410 for PEG-dm. Using these values in eq 5, we find that the effective Hamaker constant A_{eff} for R805 silica drops from 3.3×10^{-21} J in PEG to 1.9×10^{-21} J in PEG-dm. This shows that the vdW interactions between R805 silica aggregates are weakened by ~40% in the end-capped glycol, thus explaining the lower network density.

We also observe an increase in network density in R805-based systems in the presence of cations and anions from the lithium salt (Figure 8). Likewise, the presence of ions leads to more flocculation in the R974 silica-based composites (Figure 9). These results can be interpreted to be due to the polarizing effect of the ions in the electrolyte, as they cause a separation of charge centers on the glycol molecules.[9,22] Thus, the dielectric constant (ϵ_m) and the refractive index (n_m) of the medium are expected to be altered in the presence of ions.[21,22] An enhancement in ϵ_m has been reported by other workers for PEG–salt complexes: for example, Firman et al.[22] found that adding 0.1 M LiClO$_4$ to tetraglyme (a lower molecular weight analogue of PEG-dm) increased the dielectric constant from 7.70 to 10.90. By eq 5, this increase in dielectric constant would lead to a modest enhancement in the intensity of vdW interactions between R805 silica units, and thereby to a denser R805 network structure (Figure 8). In the case of the R974 silica, it is also possible that, in the presence of salt, the tendency for H-bonding between surface hydroxyls and polyether chains would be reduced, owing to the stronger affinity of the polyether toward the salt ions. This can explain why the rheological properties of R974-based composites show a large enhancement in the presence of ionic species (Figure 9).

Silica Concentration Effects. We believe that the R805 fumed-silica-based composite electrolytes are promising candidates for rechargeable lithium batteries. The silica enhances the mechanical properties of the electrolyte due to its ability to form network structures. Concomitant effects of fumed silica on the rheology and conductivity of the electrolytes are shown in Figure 10. We find that the addition of silica leads to large increases in the elastic modulus G'. An addition of 20 wt % of R805 silica to a PEG-dm/Li$^+$ solution leads to a G' of ~10^5 Pa, a value comparable to many rubbery polymeric materials. Moreover, the enhanced mechanical stability is accompanied by a small loss in conductivity. For example, the conductivity of the same 20% silica composite is only 15% lower than that of the pure PEG-dm/Li$^+$ solution.

The drop in conductivity is much smaller than would be expected on the basis of a volume-filling effect.[9] The reason for this lies in the open, branched nature of the

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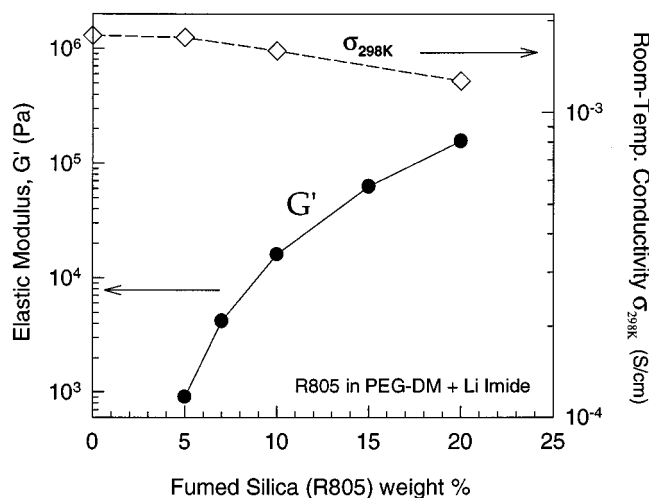(22) Firman, P.; Xu, M.; Eyring, E. M.; Petrucci, S. *J. Phys. Chem.* **1993**, *97*, 3606.

Figure 10. Variation of elastic modulus (G') and room-temperature conductivity (σ_{298K}) with silica (R805) weight fraction for the composite polymer electrolytes under study.

fumed-silica network. It has been shown that fumed silica is a self-similar material, showing fractal behavior (fractal dimension, $d_f = 1.75$) over a range of size scales.[23] As a result, the motion of Li^+ ions in the composite, under the influence of an electric field, is not hindered by the network structure.

Processability of Electrolytes. We would also like to draw specific attention to the processability of our composite electrolytes. As mentioned earlier, these materials are shear-sensitive and yield when large stresses are applied. This is because the bonds comprising the silica network are physical bonds (H-bonds or vdW bonds) which are weak and susceptible to shear. In practice, the shear-thinning behavior can be advantageously utilized in processing these electrolytes as thin-film materials. At high stresses or shear rates,

such as those typically encountered in industrial processing operations, the network structure is disrupted and the viscosity drops by several orders of magnitude (the yield stress for the 20% R805 composite is about 10^2 Pa). This allows the material to be processed easily into desired configurations. On cessation of shear, the network structure recovers to its initial state. Studies on shear effects in silica-filled materials have shown that structural recovery is instantaneous and almost complete, provided the shear rates employed are high.[14]

Conclusions

In this study, we focused our attention on composite polymer electrolytes prepared by dispersing fumed silica fillers in a PEG−lithium salt matrix. We have demonstrated the utility of rheological techniques in probing microstructures in such disperse systems. Dynamic rheological behavior indicates that the composite electrolytes are physical gels due to the presence of a three-dimensional, sample-spanning network. The network is formed by silica aggregates interacting through van der Waals forces between their nonpolar surface layers.

The use of R805 (octyl-modified) silica leads to high modulus composite electrolytes ($G' > 10^5$ Pa) which at the same time have room-temperature conductivities exceeding 10^{-3} S/cm. Additionally, the electrolytes can be easily processed at high shear rates into desired configurations. Thus, our composite polymer electrolytes show promise as viable candidates for the next generation of rechargeable batteries.

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