

Fumed silica-based composite polymer electrolytes: synthesis, rheology, and electrochemistry

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Abstract

An overview of our research is presented on developing composite polymer electrolytes (CPEs) based on low-molecular weight polyethylene oxide (PEO) (namely, poly(ethylene glycol) dimethyl ether), lithium salts (e.g. lithium triflate, lithium imide, etc.), and fumed silica. These CPEs demonstrate high room-temperature conductivities ($> 10^{-3}$ S/cm), mechanical strength, and form stable interfaces with lithium metal as a result of the fumed silica. The surface groups on the fumed silica determine the mechanical properties of the CPE while the low-molecular weight PEO and lithium salt determine the ionic transport properties. These CPEs show promise as electrolytes for the next generation of rechargeable lithium batteries. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

To date, the most common approaches to solid polymer electrolytes for lithium batteries have employed high-molecular weight ($M_n > 10^5$) polymers based on the polyethylene oxide (PEO) structure [1–3]. When combined with lithium salts, linear PEO forms poorly conductive crystalline complexes with room temperature conductivities $< 10^{-5}$ S/cm [1–3]. The use of random, graft, and block copolymers limits the crystallinity of the PEO segments, but the room-temperature conductivity of most of these polymers rarely exceeds 10^{-4} S/cm, a value too low for many applications [2,3]. To obtain high conductivities, the normal operating temperature for these systems must be $\geq 80^\circ\text{C}$ [1–3].

For more than a decade, researchers have recognized that adding inorganic fillers to PEO-based electrolytes improves the conductivity of the electrolytes Refs. [1,4–6]. Although initial attempts sought to improve the conductivity of electrolytes through the use of conductive particles,

the dominant effect of inorganic fillers is to decrease the crystallinity in samples prepared from high-molecular weight PEO, thus stabilizing the highly conductive amorphous phase. Reports show that smaller particles are the most effective, presumably because their high-surface area inhibits crystallinity [4–6], and that the conductivity of filled electrolytes decreases only slightly for particle contents below 30 wt.% Ref. [1 and references therein].

A fundamentally different approach to the use of fillers is exemplified by the addition of fumed silica [7] to low- and moderate-molecular weight PEOs to yield materials with the mechanical properties of solids, but having the processability of liquids [8–12]. The unique features of fumed silica are its branched, primary structure consisting of fused SiO_2 particles (Fig. 1) and the ability to tailor the surface functionalities of the fumed silica. In composite electrolytes formed by combining hydrophobic fumed silica, lithium salts and low-molecular weight PEO (Fig. 1), the filler and the electrolyte constitute separate phases, effectively decoupling the mechanical and conductive properties of the electrolyte [11]. In an extension of this approach, we showed that simple cross-linking reactions allow conversion of the electrolytes into rubbery materials with conductivities that rival liquid electrolytes [12]. In this communication, we provide an overview of fumed silica-

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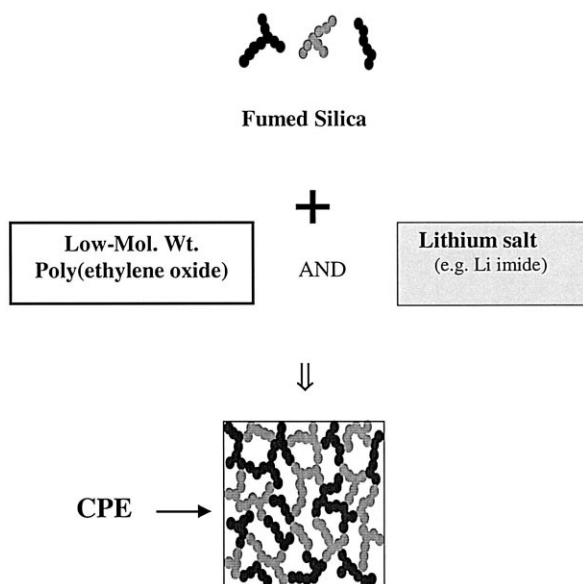


Fig. 1. Schematic route to CPE based on hydrophobic fumed silica (R805). The fumed silica particles are dispersed in a low-molecular weight PEO with a lithium salt. The fumed silica particles preferentially associate to generate an interconnecting network with open cells containing polymer electrolyte.

based composite polymer electrolytes (CPEs) for use in rechargeable lithium and lithium-ion batteries, emphasizing their mechanical and electrochemical properties.

2. Experimental

2.1. Preparation of CPEs

Lithium bis(trifluoromethanesulfonyl)imide [$\text{LiN}(\text{CF}_3\text{SO}_2)_2$], lithium triflate [LiCF_3SO_3], and lithium tris(trifluoromethanesulfonyl)methide [$\text{LiC}(\text{SO}_2\text{CF}_3)_3$] were gifts from 3M. The Aerosil fumed silicas were gifts from Degussa. All other chemicals were obtained from Aldrich. The lithium salts were dried at 80°C under vacuum overnight before use. Poly(ethylene glycol) dimethyl ether (PEGdm, M_n 250 and 500) was dried over 4 Å molecular sieves for 1 week. All fumed silicas were dried at 120°C under vacuum for 3 days before use in making CPEs. Table 1 shows the various fumed silicas used for making CPEs.

The CPEs were prepared from PEGdm solutions of the desired lithium salt (0.3–1.2 M) in an argon-filled glove box (moisture content < 5 ppm). The fumed silica was then added to the PEGdm and dispersed into the electrolyte by use of a high shear mixer (Fig. 1). The moisture content of the CPEs was < 50 ppm, as determined by Karl–Fischer titration. The preparation of cross-linked CPEs are detailed elsewhere [12]. Briefly, fumed silicas modified to contain surface-bound methacrylates (or similar polymerizable groups) are combined with PEGdm,

lithium salt, AIBN, and butyl methacrylate (used as a tie molecule). This uncured CPE is then cross-linked thermally, or via UV radiation from a mercury lamp to form rubbery or hard solids.

2.2. Methods and measurements

Rheological measurements were done using either a Rheometrics Dynamic Stress Rheometer (DSR-II) or a Rheometrics mechanical spectrometer (RMS 800; a strain controlled rheometer). Details of the dynamic and steady shear rheology are given elsewhere [11,13]. Here we briefly present the two parameters that are most useful for describing the physical properties of the CPEs. Dynamic rheology involves applying a low-amplitude sinusoidal deformation (γ) to the sample at some frequency (ω) and maximum strain amplitude (γ_0):

$$\gamma = \gamma_0 \sin(\omega t). \quad (1)$$

The sinusoidal-stress response (τ) of the sample may be written as an in-phase and out-of-phase component as shown in:

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

The in-phase component is attributed to energy stored in the sample and thus defines the elastic modulus G' . The out-of-phase component is attributed to energy dissipated and thus defines the viscous modulus G'' . In short, for a liquid sample G'' dominates, and for a solid sample G' dominates. The values of these moduli as a function of frequency are used to characterize materials [13,14].

Conductivity was measured using ac impedance spectroscopy. Two different impedance spectroscopy setups were used. One was an EG&G Princeton Applied Research 263A potentiostat and an EG&G Princeton Applied Research frequency response detector controlled by the PAR 398 impedance software. The second setup was an

Table 1

Fumed silicas used to prepare CPEs. Designation is the name in the literature or specified by us for the particular fumed silica. Note that the Degussa trade name for fumed silica is Aerosil and that Si–OH is the “native” surface group. For the modified fumed silicas (those containing surface groups other than Si–OH), about 50% of the surface coverage is Si–OH and 50% is covered by the designated group(s)

Designation	Surface group(s)	Type of surface	Source
A200	100% Si–OH	hydrophilic	Degussa
R805	50% Si– C_8H_{17}	hydrophobic	Degussa
R974	50% Si– $(\text{CH}_3)_2$	hydrophobic	Degussa
R711	methacrylate	cross-linkable	Degussa
TOM	Si– C_8H_{17} + Si– $(\text{CH}_2)_3\text{CO}_2$ -	hydrophobic cross-linkable	in-house synthesis
FS-C8	CCH_2CH_3 Si– C_8H_{17}	hydrophobic	in-house synthesis
FS-C3EG3ME	Si– $(\text{CH}_2)_3$ – $(\text{CH}_2\text{O})_3$ – OCH_3	hydrophilic	in-house synthesis

EG&G 273 potentiostat and an EG&G 5210 lock-in amplifier controlled by the EG&G PAR M398 impedance software. The temperature was controlled to $\pm 0.5^\circ\text{C}$ using an Associated Environmental Systems environmental chamber or a circulating water bath (Isotemp 1016 S, Fisher). Details of the platinum electrode conductivity cell and the measurements are described in Ref. [12]. Pulse-field gradient NMR (pfg-NMR) was used to measure cation and anion self-diffusion coefficients [15,16]. Transference numbers were measured using the electrophoretic NMR (ENMR) method of Dai and Zawodzinski [16,17] and Walls and Zawodzinski [18].

The lithium metal–CPE interface was studied via constant-current cell cycling and electrochemical impedance spectroscopy (EIS) in a symmetrical Li/CPE/Li cell. An Arbin battery cycler (Model BT2042) and a Zahner impedance analyzer IM6e were used to run cell cycling and impedance tests, respectively. Constant-current densities of 1.0 mA/cm^2 with fixed charge density of 120 mC/cm^2 were applied in the cell cycling. Cell cycling tests were terminated either by reaching the prefixed maximum cycle number of 584 or by reaching the voltage safety limit of 10 V. Open-circuit impedance data were collected during cell cycling in a frequency range of 100 kHz to 100 mHz with a voltage amplitude of 10 mV. The interfacial resistance (R_{int}) between the lithium metal and the electrolyte was determined according to the method of Fauteux [19]. All experiments were carried out at room-temperature using symmetrical Li/CPE/Li button cells (diameter = 1.27 cm) with Celgard 2400 as separator.

3. Results and discussion

3.1. Physical gels based on hydrophobic fumed silica

CPEs are formed by combining lithium salt, fumed silica, and PEGdm (a low-molecular weight PEO end-capped with methyl groups) as shown in Fig. 1. The properties of the CPEs strongly depend on the type and density of groups attached to the surface of the fumed silica. For example, a physical gel forms when R805, a hydrophobic fumed silica with 50% surface coverage by octyl chains, is dispersed in PEGdm at a concentration of $\geq 5\text{ wt.}\%$ [11,20]. The fumed silica flocculates into an inter-connecting network structure (Fig. 1), which is driven by the mismatch in solubility parameters between the hydrophobic chains attached to the silica surface and the surrounding PEGdm solvent [20]. If A200, a hydrophilic silica with silanol surface groups, is used, a gel does not form [21] because the solubility parameters of PEGdm and silica surface are similar.

The strength of the fumed silica network may be characterized using dynamic rheology. The elastic modulus (G') gives an indication of the density and association strength of the network. The scaling relationship of gel

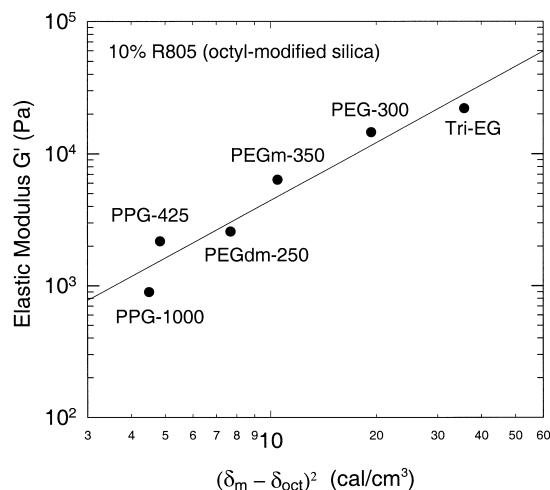


Fig. 2. Scaling relationship between the elastic modulus (G') and the difference in the solubility parameters of the silica surface group and solvent. R805 (hydrophobic fumed silica) dispersed in various media: PPG — poly(propylene glycol) 1000 and 425 M_n , PEG — poly(ethylene glycol) 350 M_n , PEGm — PEG methyl ether 350 M_n , PEGdm — PEG dimethyl ether 250 M_n , Tri-EG — Triethylene glycol. δ_m is the solubility parameter of the medium (solvent) and δ_{oct} is the solubility parameter of the octyl group on the R805 fumed silica surface.

strength based on mismatch of the fumed silica surface groups and solvent solubility parameter is described by Eq. (3) and shown in Fig. 2 [20].

$$G' \propto (\delta_m - \delta_{\text{sur}})^2. \quad (3)$$

In Eq. (3), G' is the elastic modulus, δ_{sur} is the solubility parameter of the surface groups, and δ_m is the solubility parameter of the solvent (the surrounding medium). Fig. 2, generated by measuring G' for R805 dispersed in a variety of solvents [20], shows that the dominant driving force for gel formation is the mismatch in the solubility parameters. Thus, Eq. (3) provides a predictive tool for designing CPEs based on different fumed silica surface chemistries and solvent systems.

The effects of fumed silica concentration on mechanical stability is illustrated in Fig. 3 which shows the elastic modulus (G') as a function of hydrophobic R805 fumed silica content. Increasing the concentration of the fumed silica generates a stronger network structure with the modulus increasing by more than two orders of magnitude [11]. Also included in Fig. 3 is the room-temperature conductivity of the CPE as a function of R805 fumed silica content. The data shows that the increase in the mechanical strength of the CPE is obtained with only minor decreases in conductivity, with the conductivity remaining above 10^{-3} S/cm in all cases.

Conductivity measurement is only one method to characterize the ionic transport in a polymer electrolyte, and independent measurements of the transference numbers of the ions are needed to completely describe the system [22,23]. We have used pfg-NMR to measure the self-diffusion coefficient of the lithium cation (D_{Li}) and the fluo-

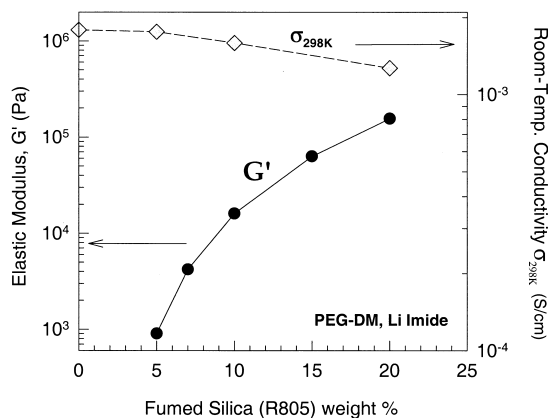


Fig. 3. Effect of fumed silica content on the mechanical stability and room-temperature conductivity of the composite polymer electrolyte [11]. The sample is PEGdm (250 M_n), Li imide (O/Li = 20), and R805.

rine-containing anion (D_F) for the R805-based CPE, as shown in Fig. 4 [15]. ENMR was used to determine the lithium transference number (T_{Li}) for the same CPE systems (Fig. 4) [15]. The data confirm that the mechanical and conductive properties of the CPEs are decoupled, i.e. the fumed silica network has negligible effect on ionic transport through the electrolyte. The decoupling of transport properties from fumed silica content (and mechanical strength) can be explained from the fact that the fumed silica network occurs at a microscopic level, unlike cross-linked polymers where the molecular level network hampers ion mobility.

The interactions of the lithium cations with the fumed silica can be detected by comparing the spin-lattice relaxation times (T_1) for lithium cations in silica-based CPEs and in PEGdm electrolytes without fumed silica [15,24]. The surface coverage of R805 is roughly 50% Si–OH groups and 50% octyl groups. Since lithium ions are known to strongly interact with OH groups a decrease in the T_1 relaxation time is expected if the cations can access

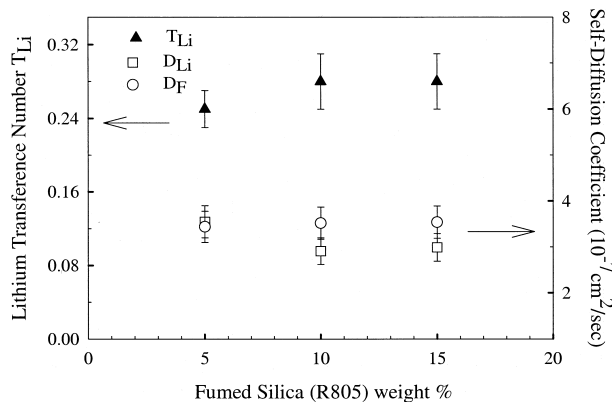


Fig. 4. Transport properties as a function of R805 fumed silica. Self-diffusion coefficients were measured using pfg-NMR and lithium transference number via ENMR. The sample is PEGdm ($M_n = 250$), Li imide (O/Li = 20), and R805 fumed silica.

the Si–OH groups. For a solution composed of PEGdm (250 M_n) and 1.2 M Li imide (no fumed silica), the lithium T_1 relaxation is 400 ms. For the same solution containing 15% R805, the lithium T_1 is 350 ms, which is not statistically different from the 400 ms T_1 . In contrast, for an identical solution containing only 5% A200 (100% coverage by Si–OH groups) a 25% decrease in T_1 is observed. Thus, for R805 fumed silica, the Si–OH groups are effectively shielded by the large octyl groups preventing any significant interaction between the lithium cations and fumed silica network.

The conductivities of CPEs prepared from various surface-modified fumed silicas are shown in Fig. 5 [10]. Despite the large variation in the type of groups anchored to the surface, we observe no discernable change on the conductivity of the different CPEs. This result together with those of Figs. 2–4 and Eq. (3) show that the mechanical properties of this class of CPEs can be tuned in a predictive manner without compromising their transport properties and high room-temperature conductivity of $\geq 10^{-3}$ S/cm.

3.2. Effect of fumed silica on the interfacial stability of CPE with lithium metal

Notwithstanding the high conductivity obtainable with liquid electrolytes, a major drawback is their reactivity with lithium. It has been reported, however, that ceramic fillers such as γ -LiAlO₂ and zeolites stabilize the interface between high-molecular weight PEO and lithium Ref. [25

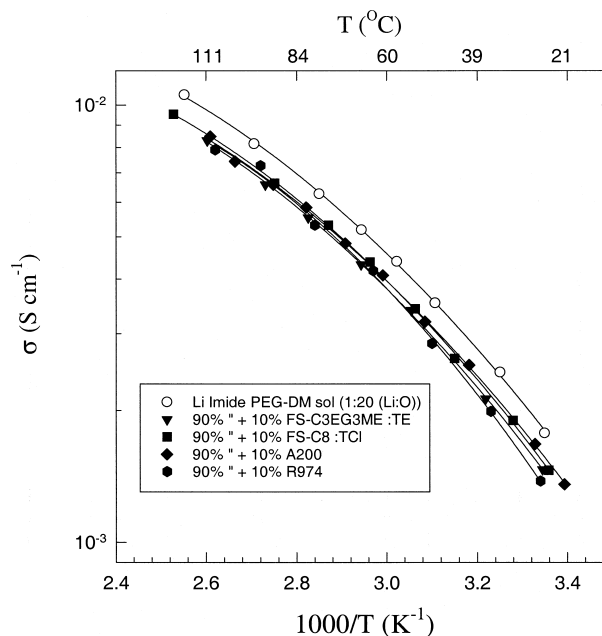


Fig. 5. Effect of fumed silica surface chemistry on the conductivities (σ) of CPEs [10]. The CPEs were prepared from various surface functionalized fumed silicas (Table 1), PEGdm and lithium imide salt (O/Li = 20).

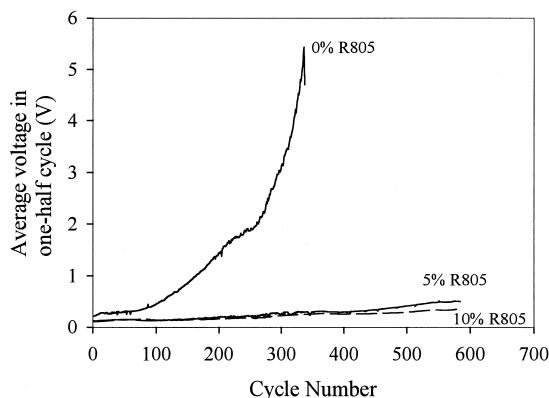


Fig. 6. Effect of fumed silica on average voltage required for a 120-mC/cm^2 half cycle. The 0% R805 sample was stopped after 336 cycles because the instrument's safety limit was reached. The CPE was PEGdm ($250 M_n$), Li imide ($O/Li = 20$), and R805 fumed silica.

and references therein]. It was proposed that these ceramic fillers trap trace impurities such as water and oxygen and protect the electrode surface from corrosion [25]. We discovered that fumed silica in low-molecular weight PEOs also appears to stabilize the interface between the CPE and lithium [10]. As an illustration of this phenomena, Fig. 6 shows the average voltage required to move 120 mC/cm^2 of lithium from one electrode to the other during cell cycling for electrolytes containing 0%, 5%, and 10% fumed-silica. The average voltage required in the absence of fumed silica increases dramatically after 100 cycles to the extent that the test must be stopped due safety limits. When fumed silica is present, however, the average voltage required stays about a factor of 10 lower, even after more than 550 cycles. Further evidence of the stabilizing effect of fumed silica is shown in Fig. 7 which illustrates the interfacial resistance before and after the cell cycling shown in Fig. 6. The interfacial resistance is significantly lower when R805 is present, and increasing concentration

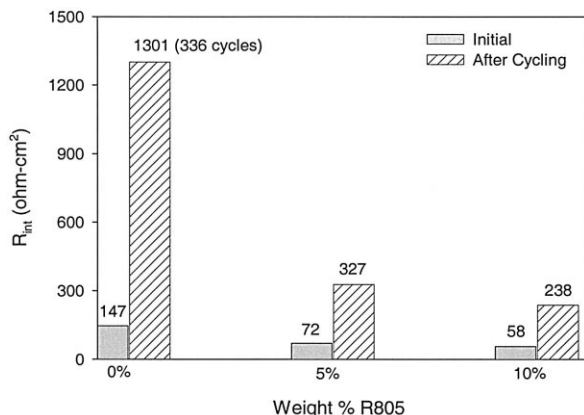


Fig. 7. Interfacial resistance of cells before and after cell cycling according to Fig. 6.

of R805 improves the interfacial stability. A more detailed discussion of the effect of fumed silica on the interfacial stability will appear in a future publication.

3.3. Chemically cross-linked CPEs

The motivation behind our development of chemically cross-linked fumed silica networks was to increase the mechanical stability of the CPE by locking the network in place via covalent bonds. The physical gels discussed above [8–11] showed promising mechanical characteristics in terms of high modulus (G') values of $\sim 10^5$ Pa, and processability with shear thinning viscosity [11]. However, these CPEs typically showed yield stresses of 1–10 Pa suggesting that a separator may be required in order to construct a battery using these CPEs. Construction of a lithium secondary battery using polymer electrolytes, ideally, would not require the use of a separator and mechanical destruction of the battery would not result in release of electrolyte or fire due to exposure of the lithium metal [2,3]. Therefore, both high modulus and high yield stress are desired of CPEs.

Fumed silica with surfaces functionalized by cross-linkable groups, such as Degussa's R711 or our custom synthesized TOM silica (methacrylate functionalized) [26] (Table 1), can be chemically linked to form a permanent network of fumed silica. Butyl methacrylate can be added to the uncured CPE to serve as tie molecules that enhance the formation of the cross-linked fumed silica network. Fig. 8 shows the elastic and viscous moduli as a function of strain amplitude of two cross-linkable fumed silica systems that contain different amounts of added butyl methacrylate. From this figure a measure of yield stress

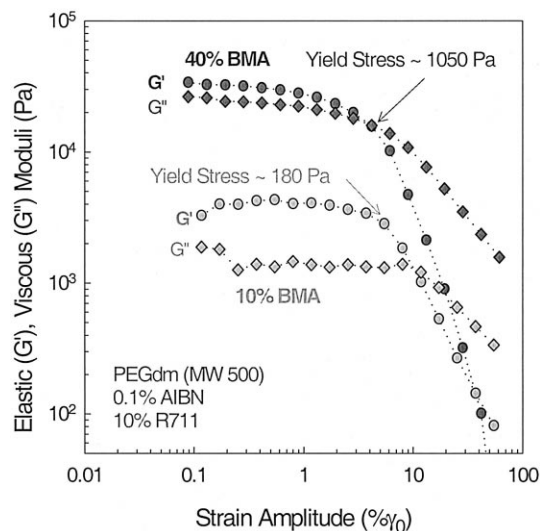


Fig. 8. Effect of cross-linking and composition (butyl methacrylate concentration) on the dynamic moduli vs. strain behavior of CPEs prepared from R711 fumed silica in PEGdm.

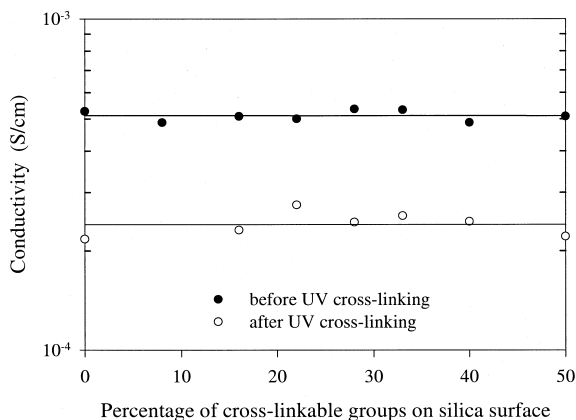


Fig. 9. Effect of cross-linkable methacrylate groups and curing on room-temperature conductivity. UV curing used on a sample of lithium perchlorate ($O/Li = 20$), PEGdm ($500 M_n$), TOM fumed silica, and butyl methacrylate. Note that 50% cross-linkable groups on the silica surface is the maximum coverage (i.e. 50% of the surface is methacrylates and 50% is Si-OH). At 0% coverage, the surface is composed of 50% octyl groups and 50% Si-OH.

can be obtained from the product of G' and the strain at which G' starts to decrease. We observe that the sample cross-linked with 10% BMA gives a yield stress of approximately 180 Pa, which is more than an order of magnitude higher than that obtained in physical gels. Increasing the BMA content to 40 wt.% further increases the yield stresses to ~ 1000 Pa. Thus, robust network structures, in terms of both modulus and yield stress, can be achieved by varying the fumed silica composition and covalently bonding the fumed silica particles to form a dimensionally stable network.

We have begun to explore the effect of cross-linking and fumed silica surface chemistry on conductivity. Fig. 9 shows data from CPEs made from TOM fumed silica, PEGdm ($500 M_n$), butyl methacrylate, and lithium perchlorate. The surface fractions of the methacrylate and octyl groups were varied and the conductivities of the cured and uncured sample are reported. The significant increase in the mechanical strength of the network (data not shown) upon curing of the CPE, is bought with only a small decrease in the room-temperature conductivity. The ratio of the methacrylate to the octyl groups on the fumed silica surface also exhibit no noticeable effect on the conductivity. Note that use of lithium imide salt would result in a conductivity of greater than 10^{-3} S/cm vs. the 10^{-4} S/cm conductivity reported for the lithium perchlorate salt.

4. Summary

We have developed a class of CPEs based on a low-molecular weight PEO (namely poly(ethylene glycol) dimethyl ether), lithium salt, and surface functionalized fumed silica. The surface chemistry and amount of fumed

silica determines the mechanical properties of the gel. On the other hand, the low-molecular weight polymer and lithium salt determine the ionic transport properties and yield conductivity greater than 10^{-3} S/cm. This means that the mechanical and electrochemical properties of our CPEs are effectively decoupled. Furthermore, we can tune and predict the mechanical properties of our CPE by modifying the surface chemistry of the fumed silica.

Continued investigations on our CPE systems are currently underway from many standpoints. We are delving into several fundamental aspects including: (a) the mechanisms for ion conduction and lithium transference; (b) the reasons for improved interfacial stability in the presence of fumed silica; and (c) the molecular pathways for chemical cross-linking. Our long-standing scientific goals are to develop a comprehensive understanding of our electrolytes at the molecular/microstructural level.

An improved understanding of the various fundamental issues should in turn enable us to develop a series of structure–property correlations for our system. This should provide the rationale for designing a range of appropriately tailored fumed silicas, and for optimizing the composition of each system. Thus, we hope to play a major role in developing the next generation of rechargeable lithium batteries.

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