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Composite electrolytes from self-assembled colloidal networks

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Abstract

In this study, we present two approaches to developing composite electrolytes exploiting the self-assembling nature of colloidal fillers. The first system comprises of oligomers of poly(ethylene glycol) dimethyl ether, branched fumed silica particulates and lithium salt. The fumed silica forms a three-dimensional, self-supporting network that provides mechanical stability. The large pores of the network has little effect on diffusivity of ions and oligomers, lithium transference number and ionic conductivity, with the latter showing values $> 10^{-3}$ S/cm at ambient conditions. The second system consists of Li exchanged hectorite clay in a mixture of low molar mass carbonates. Similar to the fumed silica, the clay provides mechanical stability through formation of a three-dimensional network. In addition, the immobile clay platelets also serve as the anion rendering the system to be a single ion conductor. Near-unity transference number is observed in this case. However, the room temperature conductivity of the clay composite is lower than the fumed silica, revealing a value of about 10^{-4} S/cm. The lower conductivity can be attributed to the clay not being in a fully exfoliated form as evident from morphological analysis.

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1. Introduction

The poor room-temperature conductivity and low lithium transference numbers of electrolytes based on high-molecular weight (M_n 10^5) polyethylene oxide (PEO) have impeded development of lithium and lithium-ion batteries with solid electrolytes [1–4]. Electrolytes based on low molecular weight solvents such as oligoethers, propylene carbonate (PC) and ethylene carbonate (EC) have high room-temperature ionic conductivities ($\sigma > 10^{-3}$ S/cm), but lack the mechanical stability of a solid. One approach to resolving this issue involves utilizing colloidal particles with tailored surface characteristics, which when dispersed in these solvents can associate to form a volume spanning network structure, thus converting the material from a free flowing liquid to a mechanically stable solid—a physical gel. Our scheme to the designing of electrolytes that

simultaneously have high ionic conductivities and good mechanical properties, therefore, involve preparing ion-conducting gels with two different colloidal particles, synthetic clays and fumed silica (Fig. 1). These two gel systems are complementary, and both that have high room-temperature ionic conductivities, are mechanically stable yet processable, and can be tailored to meet various applications.

The fumed silica based gels are typically composed of poly(ethylene glycol) dimethyl ether (PEG_{dm}, 250 M_n), a lithium salt (e.g. Li(CF₃SO₂)₂N, LiTFSI), and hydrophobic fumed silica. Fumed silica is formed through a flame hydrolysis process that irreversibly fuses 10 nm diameter spheres of SiO₂ into branched structures about 100 nm in size [5,6]. The native surface is Si–OH, which can be readily modified by simple chemical reactions to place alkyl, ether, methacrylate and other functional groups on the surface of the silica. About half of the surface Si–OH groups can be modified; the remainder are trapped within the fumed silica particles and are inaccessible to chemical reagents. This current research emphasizes the use of hydrophobic fumed silica with a surface terminated in alkyl (C₈H₁₇) groups. When

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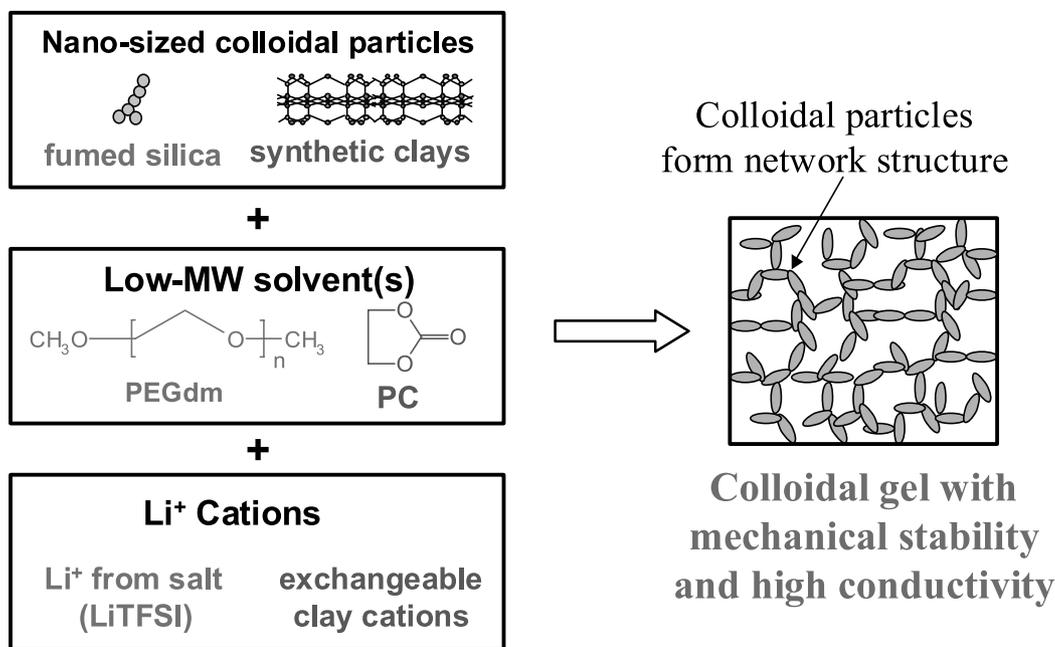


Fig. 1. Schematic representation of the formation of ion conducting physical gels using silica or clay filters.

dispersed in the polar PEGdm/Li salt liquid the hydrophobic fumed silica forms a 3-D network structure, giving rise to a gel electrolyte where the mechanical properties are primarily determined by the fumed silica and the ion transport is primarily determined by the PEGdm/salt liquid electrolyte.

The synthetic clay electrolytes, on the other hand, are composed of lithium exchanged hectorite or laponite dispersed in a high dielectric solvent such as pure PC, mixtures of carbonates, or a mixture of PEGdm and carbonate. Ideally, the clay exfoliates to provide a mechanically stable structure, while the lithium cations associated with the large anionic clay platelet become highly mobile. This results in a single ion conductor (i.e. lithium transference number of unity) that requires no additional salt to be added to the system.

In this paper, we review our recent findings for these two ion-conducting gels. The fumed silica system allows independent tailoring of mechanical and electrochemical properties, and forms a stable interface with lithium metal. The synthetic clay system is a single-ion lithium conductor where the ion transport and mechanical properties are coupled to the amount of clay added.

2. Experimental

2.1. Electrolyte preparation

The lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 3 M) salt was dried under vacuum at 80 °C for 48 h before use. PEGdm (250 M_n, Aldrich) was dried over 4 Å molecular sieves for 1 week. Hydrophobic

fumed silica (Aerosil R805, Degussa) was dried at 120 °C under vacuum for 5 days. These compounds were stored and used in an Ar-filled glove box maintained at a moisture level of < 5 ppm.

The fumed silica nanocomposite electrolytes were prepared by first dissolving a predetermined quantity of Li salt in PEGdm. The fumed silica particles were then added to the salt solution and dispersed with a high-shear BioSpec mixer (Biospec Products) equipped with a 7-mm diameter probe. The nanocomposite electrolyte was subsequently degassed under vacuum for 1 h to remove bubbles. The maximum moisture content in the material was < 50 ppm, according to a Karl–Fischer titration.

Two synthetic clays were used: Na-hectorite (SKS-21, ~ 88 meq/100 g, ~ 250 nm size, platelet anionic charge of ~ 65 000) was provided by Hoechst, and Laponite (Laponite B, sodium form, ~ 78 meq/100 g, ~ 25 nm size, platelet anionic charge of ~ 850) was provided by Southern Clay Products. EC (Aldrich) and PC (Aldrich) were dried in similar fashion as the PEGdm. The procedures for generating Li-exchanged hectorite and preparing nanocomposite electrolytes with exfoliated Li-hectorite involved converting native hectorite to Li-hectorite via serial mixing with LiCl in deionized water, followed by centrifugation and drying in a conventional oven [7]. The resultant dry Li-hectorite powder was then dispersed in a high-dielectric solvent by a Silverson high-shear mixer. Solvents used were PC, a mixture of PC and EC (1:1 v:v) and, a mixture of EC and PEGdm (1:1 v:v). The final Li-hectorite nanocomposites retained a water content of ca. 200–300 ppm.

2.2. Electrochemistry

An EG&G Princeton Applied Research (PAR) 273 potentiostat and PAR 5210 lock-in amplifier controlled by the PAR M398 impedance software was used to measure electrolyte conductivity by ac impedance spectroscopy. The temperature was controlled to within ± 0.5 °C using a Fisher Isotemp 1016S circulating water bath. Conductivity cells with Pt wire electrodes were used [7,8]. Lithium-ion transference numbers were measured by two different methods. Electrophoretic nuclear magnetic resonance (ENMR) spectroscopy was performed on the fumed silica nanocomposite electrolytes according to the methodology prescribed by Dai and Zawodzinski [9] and Walls and Zawodzinski [10]. In this analysis, a sample was placed in an electric field during pulse field gradient NMR (pfg-NMR) so that the migration of cations or anions (depending on the nucleus of interest) could be probed and related to the transference number. This ENMR method is preferred given that no assumptions are needed about the extent of dissociation of the electrolyte [10,12]. The steady-state current method of Bruce and Vincent [11] was used to examine the Li-hectorite nanocomposite electrolytes [7]. ENMR was not practical for the Li-clay systems given the presence of paramagnetics in the clays, which lead to T_1 relaxations that are too short to meet the experimental conditions needed to perform ENMR.

2.3. Rheology

Rheological properties of LiTFSI-fumed silica electrolytes were measured on a Rheometrics Dynamic Stress Rheometer (DSR II) in which the test geometry temperature was controlled by a Polyscience recirculating water bath. Several different test geometries were used according to sample and test requirements: Couette, 40 mm cone and plate (cone angle of 0.05 rad), 40 mm parallel plates with a ridged (serrated) surface, 25 mm cone and plate (cone angle of 0.1 rad), and 25 mm serrated plates. A Rheometrics RMS 800 strain-controlled rheometer was used to measure the dynamic rheology of the Li-hectorite electrolytes. In this case, a single test geometry consisting of 25 mm parallel plates with a 1 mm sample gap was used. All measurements were acquired at ambient temperature (~ 20 °C).

2.4. Microscopy

Gel electrolytes consisting of either clay or silica were not compatible with typical sample preparation techniques for transmission electron microscopy. Therefore, a homologous series of samples was prepared by partially or completely replacing PEGdm with PEG diacrylate (PEGda) from Aldrich Chemicals. The PEGda was chemically crosslinked in the presence of AIBN (Aldrich

Chemicals) at 80 °C to form a more rigid solid. Fumed silica nanocomposites were produced with 10 wt.% Aerosil R711 (Degussa), which possesses crosslinkable methacrylate surface groups but the same primary particle size and surface area as R805, in various PEDdm/PEGda solutions. The Li-hectorite nanocomposite electrolytes were prepared over a concentration range of 0.25–1.00 M Li^+ (approximately 20–50 wt.% Li-hectorite) in a 1:1 v:v mixture of EC and PEGda. In all cases, the crosslinked materials were sectioned at -100 °C in a Reichert–Jung cryo-ultramicrotome, and the electron-transparent sections were imaged at 80 kV and various energy-loss (ΔE) settings with a Zeiss EM902 electron spectroscopic microscope.

3. Results and discussion

3.1. Fumed silica gel electrolytes

The effect of fumed silica concentration on various ion transport properties is shown in Fig. 2. The addition of the silica causes only a minor attenuation of diffusivity of PEGdm, diffusivity of the cation and the ionic conductivity. In the latter case, the room temperature conductivity remains larger than 10^{-3} S/cm regardless of silica concentration. Essentially, we observe little direct interaction between the charge carrying liquid electrolyte and the mechanically supportive fumed silica network. A more detailed discussion of these results is given elsewhere [12]. The morphology of the fumed silica network is shown in Fig. 3. The TEM image of a cross-linked silica (Aerosil R711) shows aggregation and network formation by the silica particles (shown in white); the large dark regions are liquid electrolyte that provides the favorable ion transport properties. We find

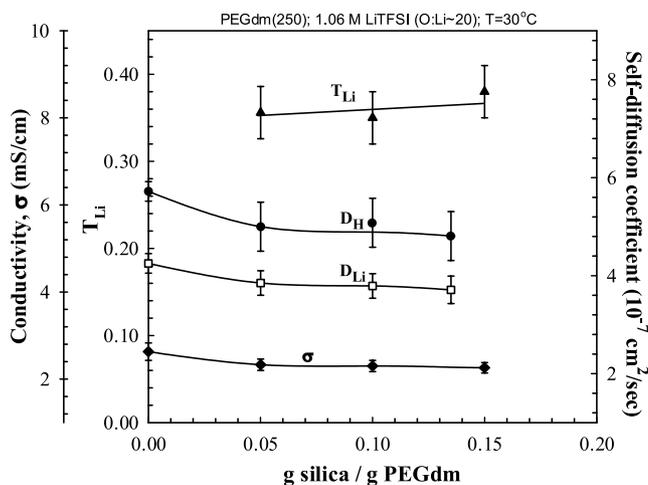


Fig. 2. Effect of fumed silica concentration on transport properties of a 1.06 M LiTFSI gel electrolyte [12]. D_{H} and D_{Li} refer to diffusion coefficients of the polymer and lithium cation, respectively.

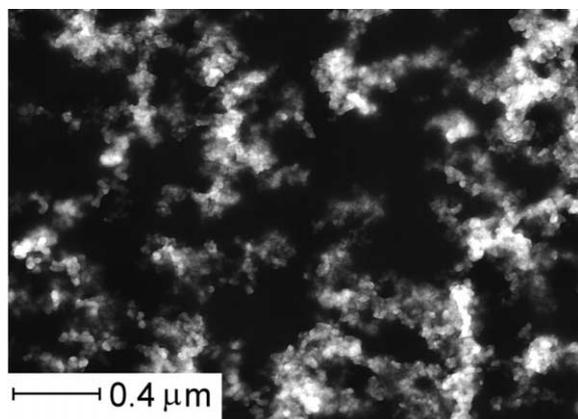


Fig. 3. TEM micrograph of a typical fumed silica gel electrolyte. An inverse image is shown such that white represents the fumed silica and dark the polymer. The sample comprises methacrylate terminated fumed silica (Aerosil R711) in crosslinked polyethylene diacrylate.

the nanoscopic hydrophobic fumed silica particles aggregate to form an open three-dimensional network structure which provide for the minimally impeded ion transport properties observed in Fig. 2.

Given the minimal effect of fumed silica on ion transport, we have examined the effect of salt using a liquid electrolyte (without fumed silica), as displayed in Fig. 4. The electrolyte viscosity and the diffusivity of cation and solvent are inversely related, with the diffusivity monotonically decreasing as the viscosity increases. As seen in other lithium ion electrolytes, the ionic conductivity passes through a maximum (at 1.06 M, O:Li ~ 20:1) which reflects the trade off of adding more charge carriers to the system against the deleter-

ious effects of decreased mobility and increased ion–ion interactions [12].

Fig. 5a displays the rheological behavior of a typical fumed silica sample plotted in terms of the elastic (G') and loss (G'') moduli as a function of frequency. We find both moduli to be essentially independent of frequency and G' to be substantially larger than G'' , features characteristic of an elastic gel [13]. The effects of fumed silica volume fraction (ϕ) and salt concentration on the gel modulus (G') is illustrated in Fig. 5b. In this figure, we observe that addition of salt increases the gel modulus but to a much lesser extent than when silica is added. Thus, the gel properties are primarily a function of fumed silica volume fraction, with a secondary increase in gel strength from the salt. We postulate that addition of salt increases G' and yield stress (data not shown) as a result of increasing the polarity of the bulk solvent phase. This in turn increases the attraction amongst the C_8H_{17} groups attached to the silica surface. In other words, the pair potential of two particles is increased while making no significant change to the overall morphology of the fumed silica network. The gel property dependence on salt and filler volume fraction along with the mechanism of network formation detailed elsewhere [14].

The results for the fumed silica gels thus far indicate that ion transport in this system depends primarily on the salt and PEGdm while the fumed silica filler dictates the mechanical stability. This decoupling of electrochemistry from rheology is further illustrated in Fig. 6 which plots G' and G'' of three PEGdm-based gels containing different salts but prepared with similar silica

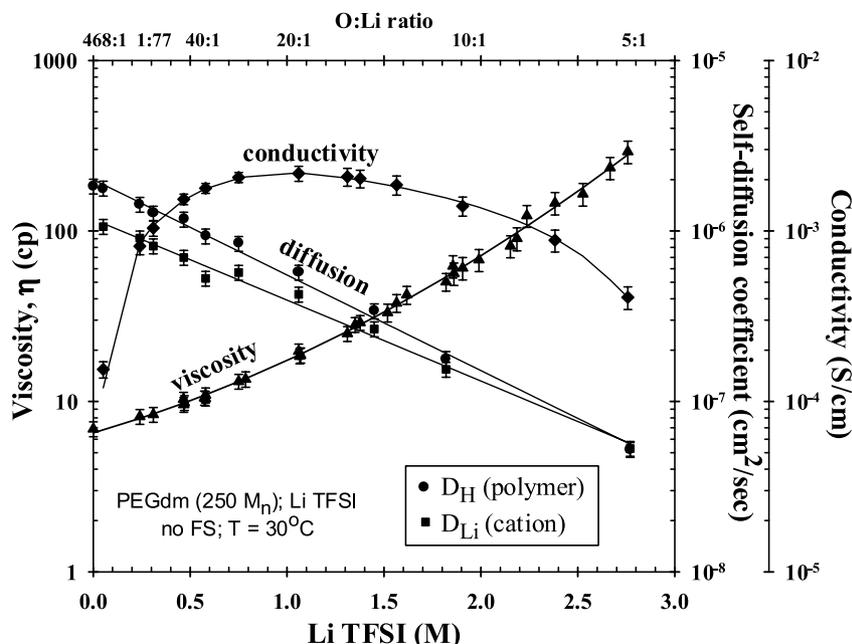


Fig. 4. Effect of salt concentration on ion transport properties of a liquid PEGdm electrolyte. D_H and D_{Li} refer to diffusion coefficients of the polymer and lithium cation, respectively.

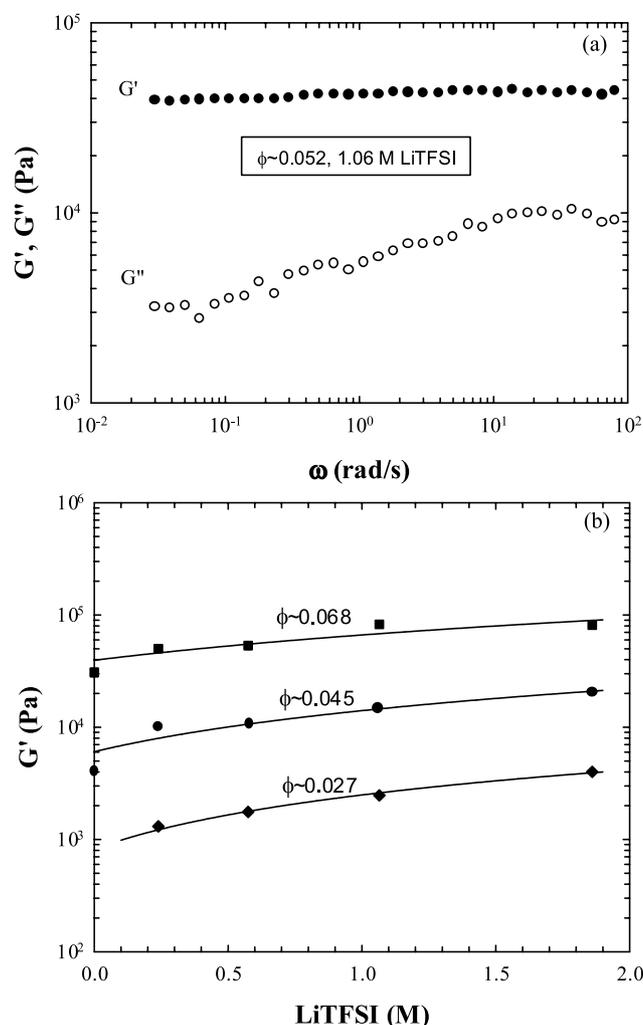


Fig. 5. Rheology of fumed silica gels: (a) dynamic frequency test, (b) Gel modulus (G') as a function of salt concentration and silica volume fraction (ϕ). Experiments were conducted at 30 °C.

volume fractions ($\phi \sim 0.045$) and at the same oxygen to lithium ratio (O:Li = 10:1). From an electrochemical standpoint, Li triflate [LiCF_3SO_3] is known to form ion complexes at modest concentrations and has the lowest conductivity [1] while Li methide [$\text{Li}-\text{C}(\text{SO}_2\text{CF}_3)_3$] has the largest anion, dissociates the best, and has the highest conductivity [15,16]. However, despite these differences in electrochemistry, the gel moduli are same for all three samples. This independence of mechanical and electrochemical characteristics can be exploited to design materials with specific properties for a particular application.

3.2. Synthetic clay ionic gels

While fumed silica based gels provide a system with high room-temperature conductivity ($\sigma > 10^{-3}$ S/cm) and allow independent tailoring of rheology and ion transport, the lithium transference numbers are modest ($T_{\text{Li}} \sim 0.35$). Several researchers have pointed out the

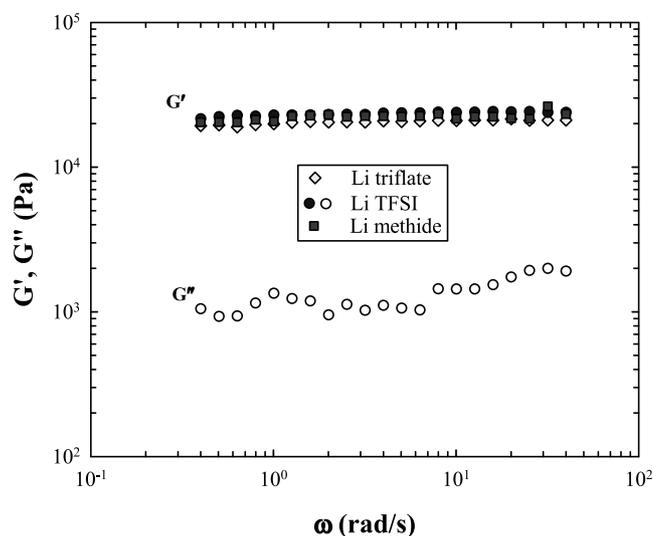


Fig. 6. Effect of salt anion type on fumed silica gel elastic modulus G' . Salt concentration is ten PEGdm oxygens to one Li with a fumed silica volume fraction of ~ 0.045 . Temperature is 30 °C. The viscous modulus G'' is shown for only LiTFSI for the sake of clarity (data for the remaining samples exhibit same behavior).

importance of the lithium transference number [17–20] and theoretical studies have shown that conductivities as low as 10^{-4} S/cm may be acceptable if unity transference numbers could be achieved [21,22]. The motivation for the development of synthetic clay gels was to achieve single ion conductors where the large anionic platelet would be relatively immobile. If lithium ion-exchanged clays were exfoliated, the cations located between the galleries could be solvated by low molecular weight solvents and then both high ionic conductivity and unity transference numbers could, in principle, be achieved [23].

Fig. 7 displays ionic conductivity at two temperatures for Li exchanged hectorite in a 1:1 (v:v) mix of PEGdm

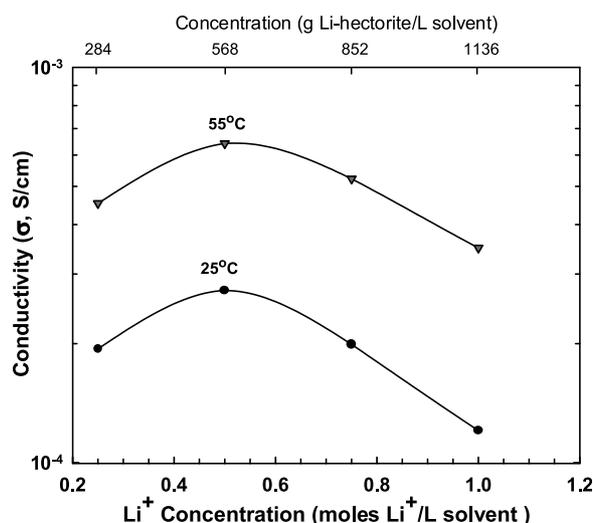


Fig. 7. Conductivity of Li exchanged hectorite as a function of concentration. The solvent is a 1:1 (v:v) mix of EC and PEGdm.

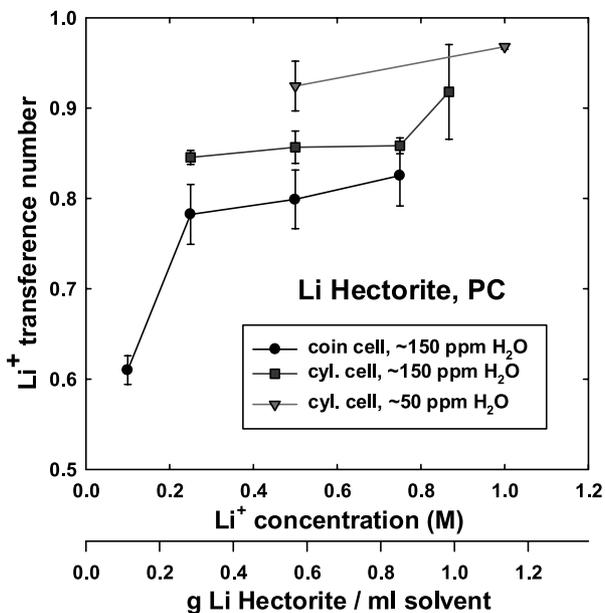


Fig. 8. Lithium transference number as a function of clay concentration showing how factors such as cell volume and water content influence transference numbers [7].

and EC, which shows that conductivities $> 10^{-4}$ S/cm are obtainable. The maximum in the conductivity is attributed to a balance between the increase in the number of carriers with clay content offset by the decrease in the volume fraction of the PEGdm/EC solvent. High clay loadings are thought to result in an overly tortuous path for the cations to travel through the clay network. Similar results are observed when the Li hectorite is dispersed in a solvent of EC:PC (1:1 v:v).

Li hectorite dispersed in a variety of solvents was tested in a coin cell architecture with lithium electrodes and evaluated using the steady-state current method of Bruce and Vincent [11]. Our initial results were disappointing, with the lithium transference numbers measured typically between 0.6 and 0.8 [7]. Although significantly better than the $T_{Li} \sim 0.2$ for $LiPF_6$ in PC:EC [7], it is still short of the expected value of 1. To further explore this issue, a cylindrical test cell was developed that significantly increased the volume of electrolyte studied, and efforts were made to reduce residual water in the electrolyte. As shown in Fig. 8, lithium transference numbers values approaching unity are obtained using this improved protocol. A more detailed investigation of the electrochemistry of these hectorite electrolytes appears elsewhere [7].

Rheological investigation of synthetic clay gels was done on the native sodium clays for simplicity. The frequency spectrum of the elastic and loss moduli of a typical hectorite sample is shown in Fig. 9. As with the fumed silica gels, we observe that $G' > G''$ and moduli are independent of frequency, indicative of an elastic network. However, the critical volume fraction to form

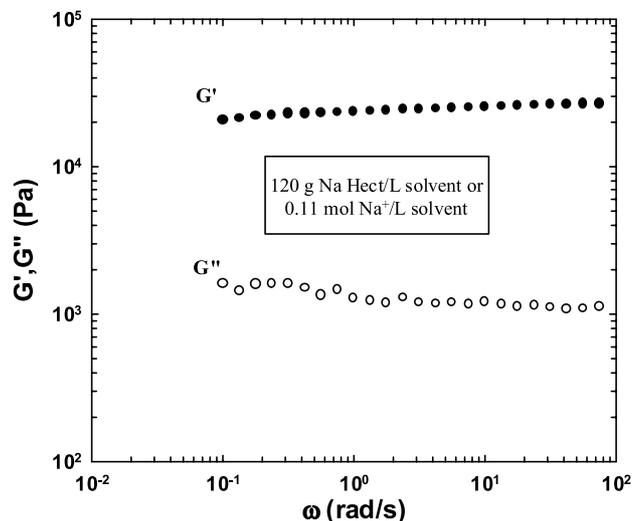


Fig. 9. Dynamic frequency test of a hectorite gel at ambient temperature. Solvent is a 1:1 (v:v) mix of EC and PEGdm.

a gel is much higher in the clay systems and a stronger dependence of G' on ϕ is observed (data not shown) [23]. These differences between the two systems can be attributed to the difference in the primary particles and morphology of the network formed particularly the very high aspect ratio of clay particles (250:1 for hectorite).

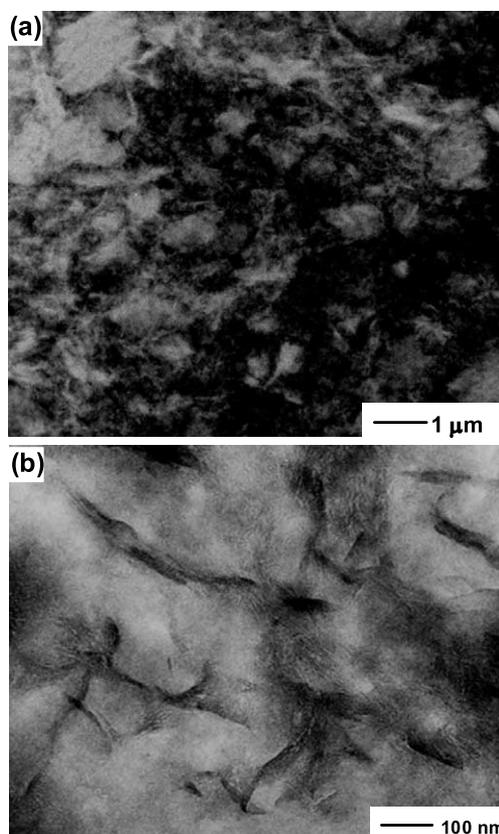


Fig. 10. TEMs of Li-hectorite in cross-linked EC:PEGda (1:1 v:v). (a) Energy-filtered TEM with $\Delta E = 200$ eV for 0.5 M Li hectorite. (b) High magnification, zero-loss TEM of 1.00 M Li hectorite to observe some platelets edge on [26].

The morphology of the Li hectorite is further explored in Fig. 10. Energy-filtered transmission electron microscopy allows viewing of noncarbonaceous features (i.e. the silicate clays) [24,25] and clearly shows the spatial distribution of the platelets in Fig. 10a. Considering the rather high concentration (1.00 M Li or 1136 g hectorite/l solvent) a reasonably good dispersion of clay platelets was achieved. However, the dispersion is less uniform than that of the fumed silica (Fig. 3). The orientation of the platelets is random, which should yield isotropic mechanical and conductivity properties. Fig. 10b displays a high magnification non-energy filtered TEM to aid in assessing exfoliation. In order to observe intercalation, the platelets must be oriented edge-on to the electron beam. We are able to observe several stacks of individual platelets, with each bundle containing two to four platelets. It appears that intercalation instead of full exfoliation is the norm for these dispersions. This could explain the lower conductivity of this system compared with the fumed silica, as complete exfoliation would have enhanced conductivity.

4. Summary

In this paper we gave an overview of our efforts to generate nano-structured ion conducting gels with favorable mechanical and ion transport properties. Two approaches are taken: (i) a decoupled system employing hydrophobic fumed silica as a gelling agent and low-molecular weight PEO and LiTFSI for favorable ion transport, (ii) a single ion conductor from lithium exchanged clays (e.g. Li hectorite) dispersed in low-molecular weight solvents (e.g. EC:PC) such that rheology and ion transport are both controlled by filler (clay) concentration.

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