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Synergistic Gelation of Silica Nanoparticles and a Sorbitol-Based Molecular Gelator to Yield Highly-Conductive Free-Standing Gel Electrolytes

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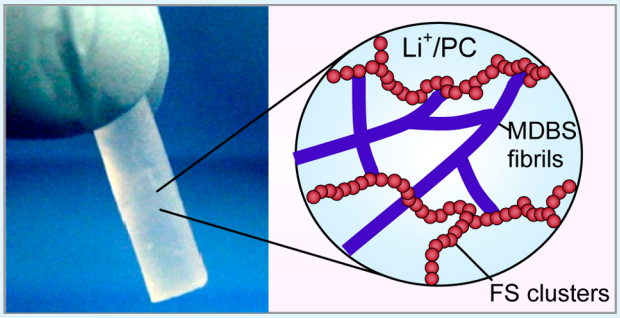
ABSTRACT: Lithium-ion batteries have emerged as the preferred type of rechargeable batteries, but there is a need to improve the performance of the electrolytes therein. Specifically, the challenge is to obtain electrolytes with the mechanical rigidity of solids but with liquid-like conductivities. In this study, we report a class of nanostructured gels that are able to offer this unique combination of properties. The gels are prepared by utilizing the synergistic interactions between a molecular gelator, 1,3:2,4-di-*O*-methyl-benzylidene-D-sorbitol (MDBS), and a nanoscale particulate material, fumed silica (FS). When MDBS and FS are combined in a liquid consisting of propylene carbonate with dissolved lithium perchlorate salt, the liquid electrolyte is converted into a free-standing gel due to the formation of a strong MDBS-FS network. The gels exhibit elastic shear moduli around 1000 kPa and yield stresses around 11 kPa—both values considerably exceed those obtainable by MDBS or FS alone in the same liquid. At the same time, the gel also exhibits electrochemical properties comparable to the parent liquid, including a high ionic conductivity (~5 × 10^{-3} S/cm at room temperature) and a wide electrochemical stability window (up to 4.5 V).



KEYWORDS: *dibenzylidene sorbitol, fumed silica, molecular gels, lithium-ion batteries, self-assembly, nanocomposite gels*

INTRODUCTION

Lithium-ion (Li-ion) batteries have emerged as the preferred type of rechargeable energy storage device.[1] Despite their popularity, these batteries have certain limitations because they mostly continue to use liquid electrolytes. The disadvantages with liquid electrolytes are well-known: these can leak out of the batteries, which is a particular concern because the pertinent liquids are typically flammable organic solvents.[2] Also, liquid electrolytes can interact adversely with the electrodes, leading to an electrolyte-solid interphase layer that adds a large electrical resistance.[1] In turn, these factors compromise the long-term stability and safety of liquid-based Li-ion batteries. It has long been recognized that solid polymer electrolytes (SPEs) could address many of the above concerns that exist with liquid electrolytes.[2−4] Solid polymers would not leak, and batteries with all solid-state components could be made in a variety of new geometries, including thin films, sheets, or rolls.[2] Accordingly, extensive research has been devoted to SPEs, especially those composed of high molecular-weight poly(ethylene oxide) (PEO) doped with Li salts.[2,3] However, these SPEs typically have low ionic conductivities, e.g., <10^{-5} S/cm at room-temperature.[2,3] For most practical applications at room temperature, an ionic conductivity >10^{-3} S/cm is essential.[1] Researchers have therefore been seeking ways to obtain electrolytes with solid-like mechanical character but with liquid-like ionic conductivities.

One way to achieve such desirable properties is to start with a liquid electrolyte and then convert it to a solid (gel) by adding appropriate gelling agents.[3−10] The use of the liquid solvent ensures a high ionic conductivity, provided the gel network has large enough pores to allow free diffusion of the solvent and Li^+ ions. Thus, the salient feature of gel-electrolytes is that ionic mobility (and hence conductivity) remain liquid-like while gelation imparts solid-like character.[4] This is unlike the SPEs wherein the ions have to hop along from one polymer chain to another, and therefore conductivity is determined by the flexibility and molecular weight of the polymer.[2,3]

Gelling agents for gel electrolytes could be chosen from high-molecular-weight polymers,[3,4] nanoscale particles,[5,11−13] or small molecules.[14−17] Polymers such as PEO, poly(acrylonitrile) (PAN), and poly(vinylidene fluoride) (PVdF) are often combined with liquid electrolytes to create gel electrolytes (the polymers are said to be swollen with the liquid);[3,4] however, such systems often have poor interfacial stability with the electrodes in Li-ion batteries.[4,18] Among the nanoparticle-based gelling agents, one of the most used is fumed silica (FS), which is a form of silica with branched clusters of nanoscale primary particles.[5,11] By tuning the surface chemistry of fumed silica for a given solvent, it is possible to induce the particles to cluster into a three-dimensional fractal network.[5,11] The resulting gels have elastic shear moduli around 100 kPa, but they are thixotropic, i.e., the application of shear

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liquefies the gels, although the gel-like character is regained after shear is stopped.[11] Thus, the gels are not strong enough to be used as free-standing solids. To increase the mechanical strength of the gels, modified fumed silicas with polymerizable methacrylate groups have been developed.[12,13] Compositions with these modified silicas were cross-linked by ultraviolet (UV) light to give rubbery solids with improved mechanical properties (modulus of 200 kPa and yield stress of 7 kPa); however, the conductivity and interfacial stability with the electrolytes were somewhat lowered.[12,13]

Another class of gelling agents less commonly used for gel electrolytes are small-molecule organogelators, which form nanofibrillar networks in solvents by self-assembly.[14−17] A wide range of organogelators are known, and several of these are capable of gelling polar solvents of the kind used in Li-ion batteries.[19,20] Self-assembled organogels also tend to be mostly thixotropic or shear-degradable.[21] It is only in a few cases that self-assembled gels are rigid enough to form free-standing, shear-resistant solids.[22] The strength of these gels depends on the types of intermolecular interactions responsible for gelation; these are usually a combination of weak interaction forces such as van der Waals interactions, hydrogen-bonding, and $\pi-\pi$ interactions of aromatic units.[19,20] One well-known class of small-molecule gelators are the sorbitol derivatives, 1,3:2,4-di-*O*-benzylidene-D-sorbitol (DBS) and its variants, 1,3:2,4-di-*O*-methyl-benzylidene-D-sorbitol (MDBS) and 1,3:2,4-di-*O*-dimethyl-benzylidene-D-sorbitol (DMDBS). DBS is a "butterfly" shaped molecule derived from the sugar alcohol D-glucitol.[23−27] On dissolution in certain solvents, these molecules self-organize into a three-dimensional network of nanofibrils.[23−27] To our knowledge, few studies have been published on electrolytes gelled by DBS.[14,28]

In this study, we combine a small-molecule organogelator with a class of nanoparticles to produce a gel electrolyte that is strong enough to behave as a free-standing, dimensionally stable solid. The organogelator is MDBS (structure shown in Figure 1a), and the particles are the native FS (schematic in Figure 1b). The solvent in an electrolyte composed of lithium perchlorate ($LiClO_4$) salt in propylene carbonate (PC). The FS, which has silanol (Si−OH) groups on its particle surfaces, is not capable of gelling this solvent; instead it forms a weakly viscous paste. The MDBS, on the other hand, is able to gel the solvent on its own. The interesting result from our study is that the addition of the FS substantially increases the strength of the MDBS gel. The MDBS/FS gels have considerable yield stresses—around 11 kPa. At the same time, the ionic conductivities of the gels are very close to that of the parent liquid, i.e., well in excess of 10^{-3} S/cm. Thus, a synergistic effect is observed for mixtures of MDBS/FS with respect to the gelation of solvents like PC. We have probed the origins of this effect, and a tentative mechanism will be presented based on hydrogen-bonding between the FS nanoparticles and the MDBS nanofibrils.

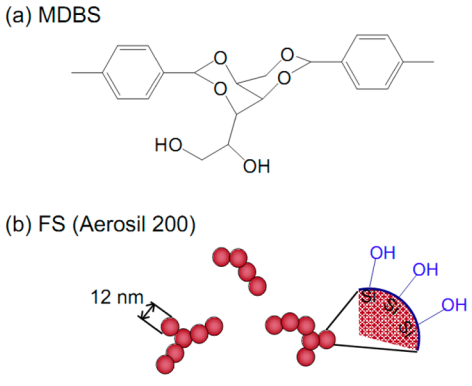

Figure 1. The main components of the gel electrolytes described in this paper (a): the sorbitol-derived organogelator, MDBS; and (b) fumed silica (FS), a class of nanoparticles that exist as submicrometer sized primary clusters. The clusters are composed of individual spherical particles, 12 nm in diameter. The silica surface is covered with silanol (Si−OH) groups. These two components are dispersed in a solution of $LiClO_4$ salt in propylene carbonate (PC).

EXPERIMENTAL SECTION

Materials. The fumed silica (FS) used in this study was supplied by Evonik Degussa Corporation and is available under the trade name Aerosil 200. This is the native, unmodified fumed silica with its surface covered with silanol (Si−OH) groups (Figure 1b). The primary particles of this silica are 12 nm in diameter, and the BET surface area is 200 m^2/g. Prior to use in dispersions, the silica was dried for 24 h in a vacuum oven at 120 °C and transferred immediately to an argon-filled glovebox. The MDBS was from Milliken Chemicals and were used as received. PC (anhydrous, 99.7%) and $LiClO_4$ (battery grade, dry, 99.99%) were purchased from Sigma-Aldrich. The PC and the $LiClO_4$ were also vacuum-dried for 24 h to remove any adsorbed moisture before being transferred to the glovebox.

Gel Electrolyte Preparation. The gel electrolyte samples were prepared in the argon-filled glovebox. The parent electrolyte solution was made by dissolving $LiClO_4$ in PC in the molar ratio of 1:16. A measured amount of MDBS was added to this electrolyte and heated with constant stirring on a hot plate till the MDBS dissolved, indicated by the formation of a transparent and homogeneous sample. The required amount of FS was then added to this solution and dispersed using a high-shear mixer (TissueTearor, BioSpec Products). The vial was then taken off the hot-plate and allowed to cool down to room temperature, whereupon the sample turned into a gel. The gels were stored in vials at room temperature in the glovebox.

Rheological Studies. Dynamic rheological experiments were performed on an AR2000 stress controlled rheometer (TA Instruments). Samples were run on a parallel plate geometry (20 mm diameter). A solvent trap was used to minimize contact of the sample with air and moisture. Dynamic frequency spectra were conducted in the linear viscoelastic regime of the samples, as determined from dynamic stress sweep measurements. Dynamic stress sweeps were conducted at a constant frequency of 1 Hz.

Electrochemical Properties. Conductivity measurements were performed using a stainless steel (SS)/gel/SS cell by ac impedance spectroscopy over the frequency range 1 Hz to 1 MHz using a Reference 3000 Potentiostat from Gamry Instruments. An ac signal with an amplitude of 10 mV was used. The instrument was calibrated at 25 °C using a standard KCl solution (conductivity of 1409 μS/cm at 25 °C). Linear sweep voltammetry was used to determine the electrochemical stability window of the sample in an Al/gel/Li cell with an Al disk as the working electrode and an Li foil as the counter electrode. A voltage sweep between 2.5 and 6 V was carried out on the sample at a constant scan rate of 1 mV/s. Interfacial stability of the gel electrolyte with lithium metal electrode was studied using an Arbin battery test station. This was used to conduct cycling of a Li/gel/Li cell at a constant current of 0.1 mA/cm^2. The direction of the current was reversed every hour and the test was run for 100 cycles. Impedance spectroscopy was carried out at the end of various cycles.

Transmission Electron Microscopy (TEM). TEM was conducted on a Jeol JEM 2100 microscope at 80 keV. The staining agent, uranyl acetate (UA) (from Sigma-Aldrich), was dissolved in water to form a 1 wt % solution. A hot composite of MDBS/FS/PC (without the lithium salt) was dropped on carbon/Formvar-coated copper grids immediately after the MDBS had dissolved and before the gelation. After standing for 2−3 min, the excess gel was carefully wiped off and the

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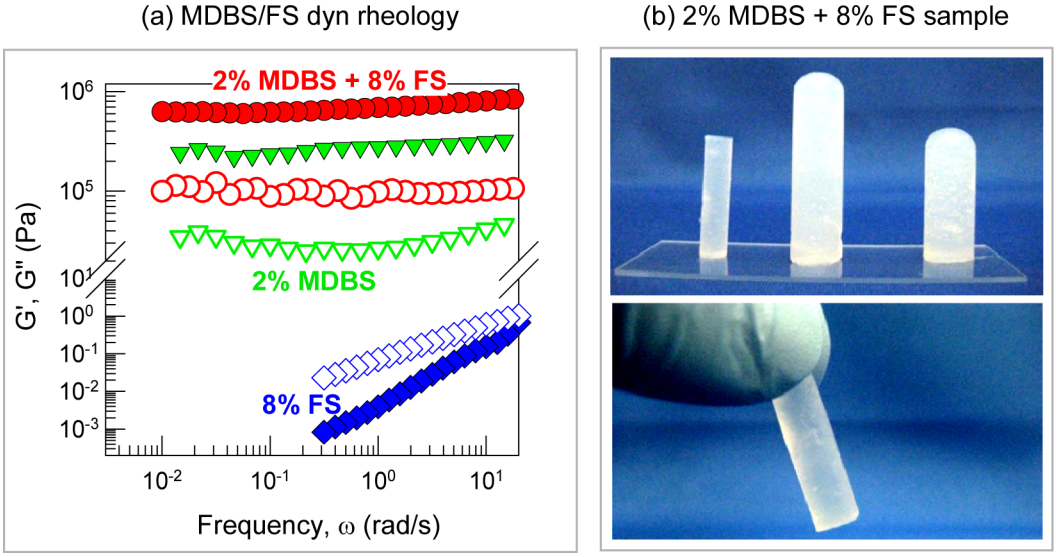

Figure 2. (a) Dynamic rheology of three samples in a PC/$LiClO_4$ matrix: 2% MDBS + 8% FS (red symbols); 2% MDBS (green symbols); and 8% FS (blue symbols). In all cases, the elastic modulus G' (filled symbols) and the viscous modulus G'' (open symbols) are shown as functions of frequency. The data reveal a synergistic enhancement in the gel stiffness for the MDBS/FS mixture. (b) Photographs of 2% MDBS + 8% FS gels showing that the samples are free-standing solids that can be placed on a surface or held between one's fingers.

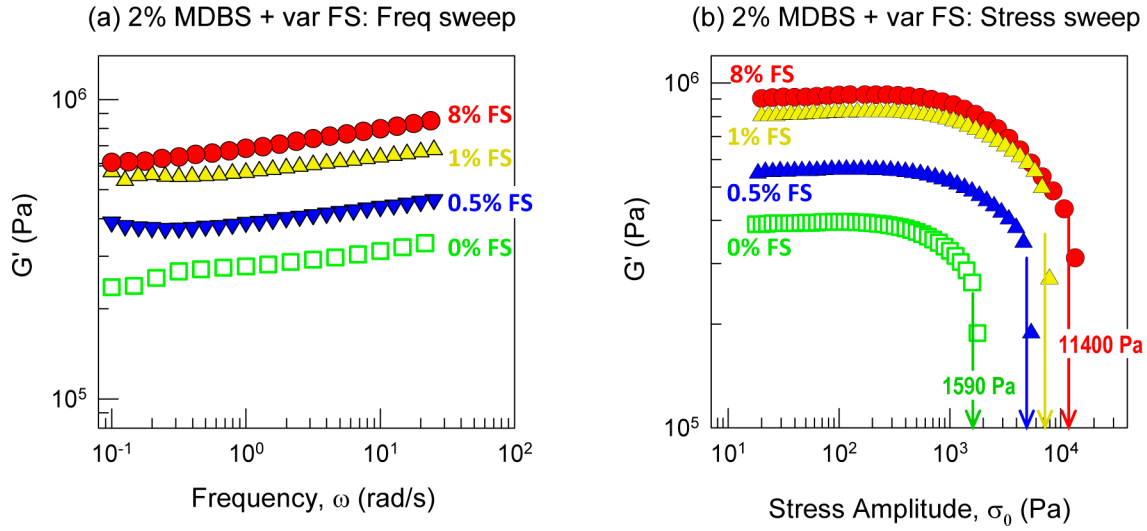

Figure 3. Dynamic rheology of samples in a PC/$LiClO_4$ matrix containing 2% MDBS and varying concentrations of FS. All samples were gels, and so for clarity only the elastic modulus G' is shown. (a) Frequency sweeps and (b) stress sweeps at a constant frequency of 1 Hz. In part b, the stress at which G' rapidly plummets is the yield stress σ_y and it is marked by arrows.

grids were then dried at room temperature. The dried TEM grids were then stained with a drop of the 1 wt % UA solution and air-dried before imaging.

RESULTS AND DISCUSSION

Rheological Properties. The gels under inspection here are four-component systems, where the continuous phase is a solution of $LiClO_4$ in PC and the dispersed phases are the MDBS and FS. Figure 2a illustrates that the MDBS and FS synergistically interact to form a stronger gel than is possible by either one of these components alone. The data shown are dynamic frequency spectra, i.e., plots of the elastic (G') and viscous (G'') moduli as functions of frequency ω. The frequency spectra of three electrolyte samples are compared in this plot. In the case of the sample containing 8% FS, the viscous modulus G'' exceeds the elastic modulus G' over most of the frequency range; moreover, both moduli are strong functions of frequency. Such a response indicates that the electrolyte containing 8% FS is a viscous liquid, not a gel,[29] and indeed the sample was visually observed to be a free-flowing material as well. In comparison, the two MDBS-containing samples both show a gel-like frequency response: i.e., their $G' > G''$ over the range of frequencies, indicating elastic behavior and, moreover, their moduli are relatively independent of frequency, reflecting the presence of a network structure that is invariant (nonrelaxing) over long time scales.[29] For a given gel, the value of its G' reflects the stiffness of the gel and can be termed the gel modulus.[29] Figure 2a shows that the modulus of the gel with 2% MDBS + 8% FS is about twice that of the gel with 2% MDBS alone. Thus, despite the fact that the FS by itself is not a gelator of PC, it appears to synergistically strengthen the MDBS network. The photographs in Figure 2b

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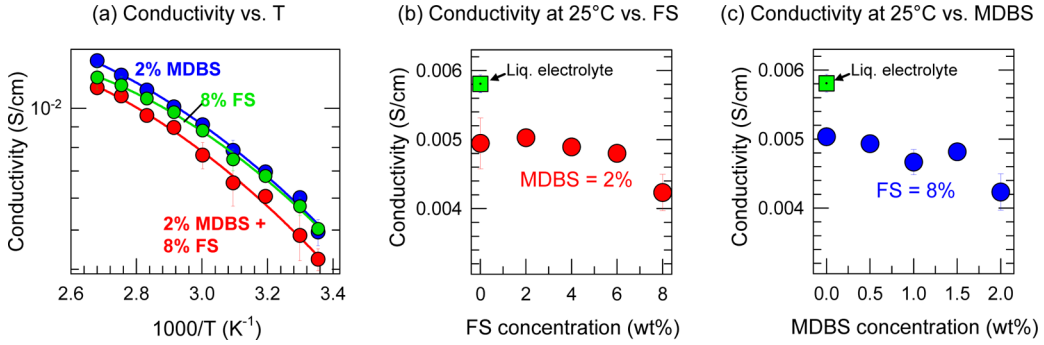

Figure 4. Conductivity of PC/$LiClO_4$ electrolytes containing MDBS and FS. (a) Conductivity as a function of temperature for selected samples. Data are shown as Arrhenius plots of log (conductivity) vs $1/T$, where T is the absolute temperature. (b) Conductivity at 25 °C as a function of FS concentration at a constant MDBS of 2%; (c) conductivity at 25 °C as a function of MDBS concentration at a constant FS of 8%. The conductivity of the liquid electrolyte (no MDBS or FS) is shown in parts b and c as a single point (green square).

show that the MDBS/FS gels are translucent solids that are strong enough to be placed on a surface as free-standing objects and robust enough to be held between a person's fingers or between laboratory forceps.

The synergy between MDBS and FS was studied further by varying the FS content for a fixed MDBS content of 2% (Figure 3a). All the samples were gels, i.e., their G' far exceeded their G'', and so for clarity, only the G' for each sample is shown in the figure. We note that even addition of 0.5% FS enhances the modulus of the 2% MDBS gel by an appreciable amount. A further increase in G' occurs when the FS is raised to 1%, and then the effect more or less saturates, with only a small further enhancement in G' found on increasing the FS content to 8%. Note again that the gel modulus, i.e., the magnitude of G', correlates with the density of cross-links in the gel network and thereby with the stiffness of the gel.

An increase in gel modulus does not necessarily imply an increase in gel strength. The key parameter that distinguishes a "strong" gel (e.g., one that can be held between forceps) from a "weak" gel (e.g., one that is a thixotropic, paste) is the magnitude of the yield stress σ_y. This is a measure of the stress it would take to "break" the gel. One way to determine σ_y is from a dynamic stress sweep test, where G' is measured as a function of the stress-amplitude at constant ω. This test was conducted for all the samples from Figure 3a, and indeed the synergistic interaction of MDBS and FS becomes more evident from these data, as shown in Figure 3b. For each sample, G' follows a plateau at low stresses and then decreases rapidly beyond a certain value of the stress, which is the yield stress σ_y. We estimate σ_y by drawing tangents at the point of rapid decrease in G', as shown by the arrows in Figure 3b. The results show that σ_y increases almost 10-fold when FS is added to MDBS gels. Note that the 2% MDBS + 8% FS sample has a yield stress σ_y of ~11 kPa. This is considerably higher than the σ_y of 7 kPa reported for gel electrolytes made from cross-linkable fumed silica.[12,13] In fact, to our knowledge, the above values are the highest yield stresses that have been reported for self-assembled (nonpolymeric) gel electrolytes.

Electrochemical Properties. Next, we studied the electrochemical properties of MDBS/FS-based gel electrolytes. Note that the parent liquid electrolyte consists of $LiClO_4$ in PC at a molar ratio of 1:16. First, we focused on the ionic conductivities of these electrolytes. As shown by the representative plots in Figure 4a, all electrolytes showed a non-Arrhenius dependence of their conductivity as a function of temperature, similar to previous observations with FS-based gel electrolytes.[5] From these plots, we focus on the conductivity values at a specific temperature, viz. 25 °C (room temperature). In the case of the parent PC/$LiClO_4$ electrolyte, the conductivity is 5.8×10^{-3} S/cm at 25 °C. The conductivity at 25 °C is shown as a function of FS content at constant MDBS in Figure 4b and as a function of MDBS content at constant FS in Figure 4c. The data indicate that neither MDBS nor FS reduce the conductivity by much: both additives cause the conductivity to decrease slightly to about 5.0×10^{-3} S/cm. Thus, it is clear from the data that the gels still show liquid-like conductivities even though their rheological properties are solid-like. As mentioned in the Introduction, the reason for this is that the gels have a network structure with large pores, which allows for free diffusion of solvent molecules and ions. The above result also holds regardless of salt type, i.e., for lithium salts other than $LiClO_4$.[5,11]

It is also important for the gel electrolytes to have an electrochemical stability window that is wide enough to encompass the operating potential.[1] Figure 5 shows the results

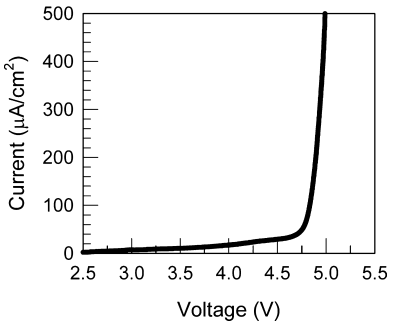

Figure 5. Linear sweep voltammetry of a 2% MDBS + 8% FS gel in PC/$LiClO_4$. The voltage at which the current undergoes a sharp increase defines the electrochemical stability window.

of a linear voltammetry scan on a 2% MDBS + 8% FS gel electrolyte sandwiched between an aluminum (Al) working electrode and an Li foil. The point where the current rapidly increases in the plot defines the above window.[1] Thus, the gel is seen to have an electrochemical stability window >4.5 V at room-temperature.

The interfacial stability of the gel electrolyte against lithium was monitored by measuring the overpotentials of Li/gel-electrolyte/Li cell at different lithium plating/stripping cycles. The electrolyte sample was loaded between two lithium metal

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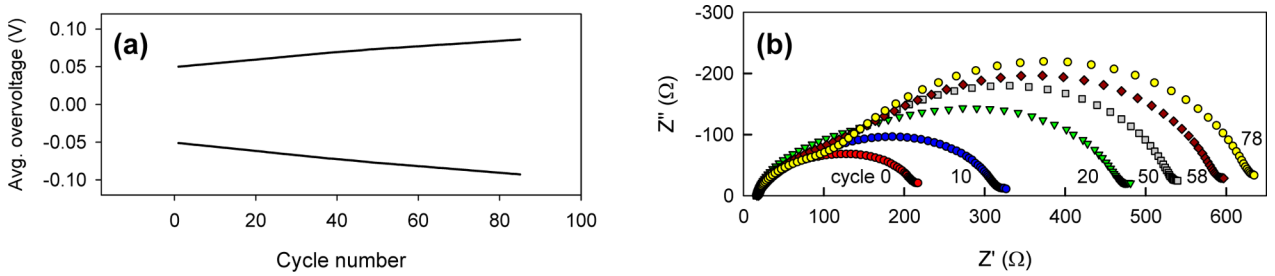

Figure 6. Average overvoltage of Li/gel-electrolyte/Li cell vs cycle number at a current of 0.1 mA/cm^2 (a) and impedance responses of the cell at different cycles (b).

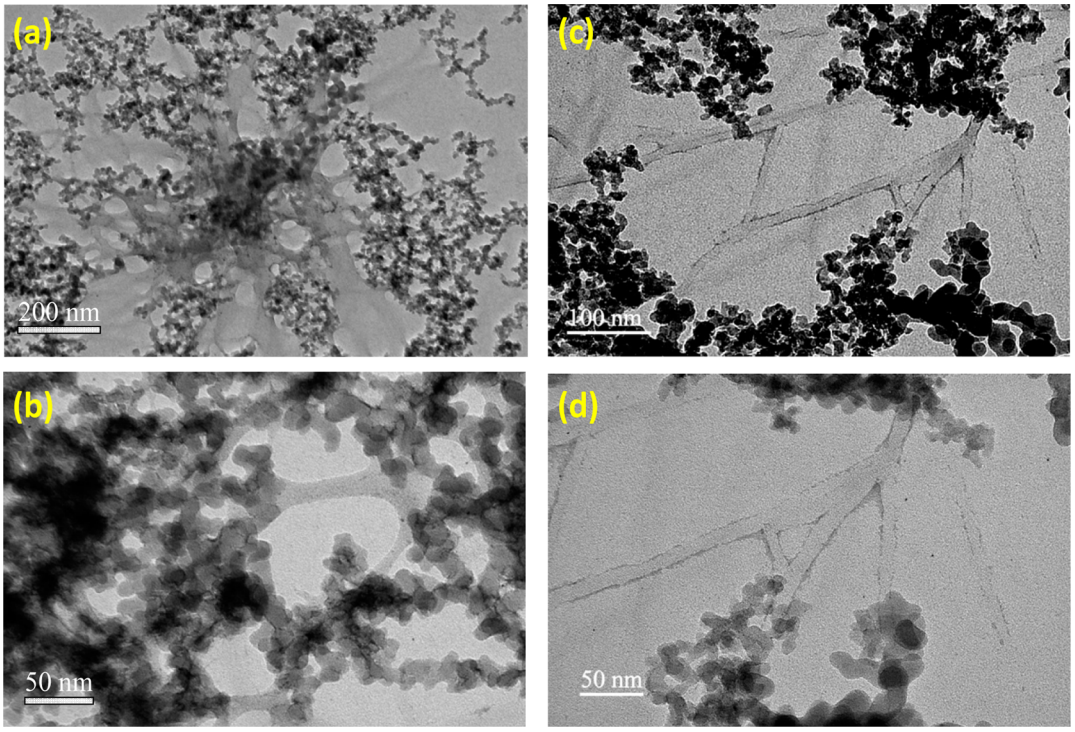

Figure 7. TEM images of MDBS-FS gels in PC. Branched clusters of FS and nanofibrils of DBS can both be seen in the images. Moreover, some of the FS appears to be bound to the MDBS nanofibrils.

electrodes separated by Teflon O-rings to maintain the thickness of the gel-electrolyte. The plating/stripping current density of 0.1 mA cm^{-2} and plating electricity of 0.36 C/cm^2 in each direction were used. The average overvoltage at different lithium plating/stripping cycles is shown in Figure 6a, and scans from electrochemical impedance spectroscopy (EIS) at corresponding cycles are shown in Figure 6b. The overvoltage of the gel-electrolyte very slowly increased with charge/discharge cycles, demonstrating the good stability of the gel against the lithium electrode. The slow increase in interfacial impedance is mainly attributed to the gradual growth of charge transfer resistance that appeared at the low frequency of EIS while the resistance of the solid electrolyte interphase in high frequency EIS is relatively stable with cycles. Similar behavior was also reported for fumed silica[30] and block copolymer electrolytes.[31]

Nanostructure. Finally, the nanostructure of the gels was studied by TEM to probe the origin of the synergistic gelling behavior. Figure 7 shows TEM images of MDBS/FS gels stained by uranyl acetate. Numerous branched clusters of FS nanoparticles can be seen, as well as MDBS nanofibrils with diameters in the range of 10−100 nm. The nanofibrillar structure in TEM is as expected for gels of DBS and its derivatives.[23,26,27] The self-assembly of MDBS molecules into such fibrils is expected to occur by a combination of hydrogen-bonds between the hydroxyls and $\pi-\pi$ stacking of the aromatic rings.[24−27] Gelation occurs when the fibrils form an entangled network that extends across the sample volume.

A key finding from these images is that the FS nanoparticles are not uniformly distributed across the sample; rather, the nanoparticles are localized right next to the MDBS fibrils. For example, in Figure 7c,d, the FS nanoparticles appear to be enveloping the MDBS fibrils. This finding suggests that there is an attractive interaction between the FS nanoparticles and the MDBS nanofibrils, which may occur through hydrogen-bonding of surface silanols from the FS with the free hydroxyls on MDBS, as suggested by Figure 8. Indeed, similar binding of colloidal silica particles to DBS nanofibrils has been observed in one previous study, where the two materials were combined in poly(ethyl methacrylate).[32] The above interaction is evidently the cause of the synergistic gelation observed in MDBS/FS mixtures. Presumably, one effect of these interactions is to introduce additional bonds or cross-links in the overall network, which can explain the increase in gel modulus (stiffness) for

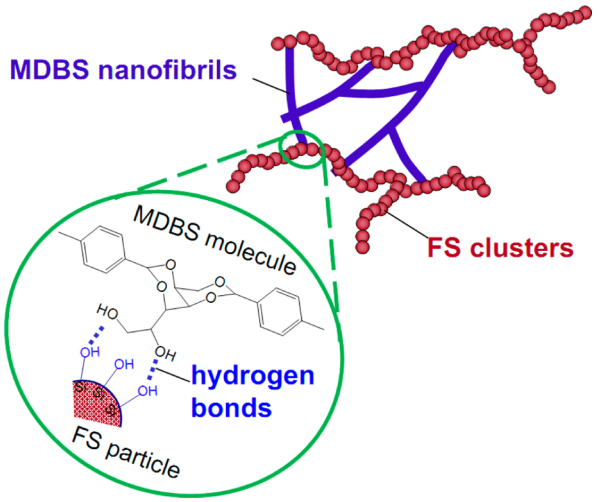

Figure 8. Schematic depicting the synergistic interaction between FS and MDBS. The FS clusters are shown to envelop portions of the MDBS nanofibrils and thus strengthen the composite network. The binding of FS to MDBS is hypothesized to occur through hydrogen-bonding of surface silanols on FS to hydroxyls on MDBS.

MDBS/FS mixtures compared to that for MDBS alone. Moreover, it is possible that when MDBS nanofibrils are enveloped by FS nanoparticles, the composite fibril structures become harder to disrupt via shear. This may explain the increase in the yield stress, i.e., the fact that MDBS/FS mixed networks are stronger than with either component alone.

CONCLUSIONS

We have demonstrated gel electrolytes self-assembled from MDBS molecules and FS nanoparticles in a PC/$LiClO_4$ matrix. The synergistic interaction between the two additives leads to a mechanically robust electrolyte with a yield stress of ~11 kPa and a modulus of ~1000 kPa. We believe these are the highest values reported for a self-assembled (nonpolymeric) gel electrolyte. At the same time, this electrolyte shows a high ionic conductivity at room temperature (>10^{-3} S/cm), a wide electrochemical stability window (>4.5 V), and good interfacial stability aginst Li. We hypothesize that the synergy between MDBS and FS arises as a result of hydrogen bonding between the polar groups on the two sets of structures. The combination of desirable properties make this new electrolyte an attractive material for use in Li-ion batteries.

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Notes

The authors declare no competing financial interest.

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