A Sol-Gel Solid Electrolyte with High Lithium Ion Conductivity

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A new hybrid inorganic gel electrolyte has been synthesized by the sol−gel method. The inorganic gel electrolyte is based on the immobilization of a liquid electrolyte in an inorganic silica network. The former is responsible for ionic conduction, while the latter provides a three-dimensional microporous environment to support the liquid electrolyte. The synthesis involves mixing equal amounts by weight of a hydrolyzed silica precursor and a lithium ion conducting liquid electrolyte. The conductivity of the partially dried gel is 3.5×10^{-3} S cm^{-1} at room temperature and approaches 10^{-2} S cm^{-1} at 80 °C. The temperature dependence of the conductivity follows an Arrhenius relation with an activation energy of 0.15−0.17 eV over the temperature range 30−80 °C. NMR data confirm the lithium ion mobility and show its liquidlike behavior over this temperature range. TGA and DSC results indicate that the inorganic gel electrolyte is stable to 90 °C and that the thermal stability is simply limited by the liquid electrolyte. FT-IR and mass spectrometry establish that there is no water present in the dried material.

Introduction

Lithium ion conducting solid electrolytes continue to be an active area of research because of advances in several areas including lithium secondary batteries, electrochromic devices, and electrochemical sensors. Solid polymer electrolytes, in particular, have received considerable attention because of the desire for high energy density secondary batteries that can be used in a wide range of applications, from consumer electronics to electric vehicles. In addition to possessing high lithium ion conductivity and good electrochemical stability, these electrolytes must satisfy other requirements including chemical, thermal, and dimensional stability.[1] One of the serious limitations with polymer electrolytes is their low conductivity at or below room temperature. Two promising approaches developed to overcome this problem are plasticized polymer electrolytes and gelled liquid electrolytes.[1−5] The gel electrolyte approach consists of having a conductive and electrochemically stable liquid electrolyte contained within an organic polymer matrix. The liquid electrolyte is responsible for ionic conduction, while the polymer matrix provides an appropriate microstructure in which to immobilize the liquid electrolyte. Although ionic conductivity values close to those of liquid electrolytes have been reported, gel electrolytes have limitations associated with their poor mechanical strength and thermal stability.[6,7]

In this study we report on the properties of a highly conducting lithium solid electrolyte synthesized using the sol−gel process. The resulting hybrid material consists of a liquid electrolyte contained in an inorganic silicate matrix. The high ionic conductivity obtained with this material is due to the continuous liquid phase. The inorganic matrix provides chemical, thermal, and dimensional stability which is far better than that obtained with organic polymer matrixes. Our approach contrasts with that of composite polymer electrolytes where a polymer electrolyte is physically mixed with a finely dispersed oxide powder.[8,9] The inert filler is able to improve mechanical properties without compromising the conductivity of the polymer electrolyte.

The sol−gel process is a chemical synthetic technique for preparing inorganic gels, glasses, and ceramic powders through the hydrolysis and condensation of molecular precursors.[10−12] Previous attempts at using the sol−gel process to synthesize lithium ion conducting solid electrolytes were based on the preparation of xerogels where the solvent phase was removed during a drying treatment.[13,14] The resulting conductivities were in the range of values observed for inorganic oxide

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(1) Koksbang, R.; Olsen, I. I.; Shackle, D. *Solid State Ionics* 1**994**, *69*, 320.

(2) Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *Solid State Ionics* **1986**, *18*, 258.

(3) Huq, R.; Koksbang, R.; Tonder, P. E.; Farrington, G. C. *Electrochim. Acta* **1992**, *37*, 1681.

(4) Angell, C. A.; Liu, C.; Sanchez, E. *Nature* **1993**, *362*, 137.

(5) Maccallum, J. R.; Vincent, C. A. *Polymer Electrolyte Review*; Elsevier Applied Science: New York, 1987; Vol. 1.

(6) Olsen, I. I.; Koksbang, R. *J. Electrochem. Soc.* **1996**, *143*, 570.

(7) Croce, F.; Brown, S. D.; Breenbaum, S. G.; Slane, S. M.; Salomon, M. *Chem. Mater.* **1993**, *5*, 1268.

(8) Capuano, F.; Croce, F.; Scrosati, B. *J. Electrochem. Soc.* **1991**, *138*, 1918.

(9) Khan, S. A.; Baker, G. L.; Colson, S. *Chem. Mater.* **1994**, *6*, 2359.

(10) Hench, L. L.; West, J. K. *Chem. Rev. (Washington, D.C.)* **1990**, *90*, 33.

(11) Brinker, C. J.; Scherer, G. W. *Sol−Gel Science*; Academic Press: San Diego, 1990.

(12) Klein, L. C. *Annu. Rev. Mater. Sci.* **1985**, *15*, 227.

(13) Wang, B.; Szu, S.; Greenblatt, M.; Klein, L. C. *Chem. Mater.* **1992**, *4*, 191.

(14) Munro, B. Glastech. Ber. *Glass. Sci. Technol.* **1995**, *No. 4*, 68.

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glasses (10^{-3} S cm^{-1} at 300 °C). The present study is based on the use of aged gels rather than xerogels. In our prior work, the sol−gel approach was shown to lead to high ionic conductivity provided that the solvent phase was not removed.[15] Experiments with sol−gel derived silica demonstrated that the high proton conductivity of the sol was retained during gelation and aging because the continuous pore network was filled with an aqueous solvent phase. Ion transport occurred within the solvent phase, and the addition of an acid catalyst during synthesis provided protons. The present paper follows a similar approach except that in these materials the interconnected porous network of the inorganic phase is filled with a low vapor pressure nonaqueous liquid electrolyte in which a lithium salt is dissolved. In this study the synthesis and characterization of a lithium ion conducting inorganic gel electrolyte are described. Fourier transform infrared (FT-IR) spectroscopy and mass spectrometry (MS) are used to monitor the chemical changes that occur as the material evolves from a sol to a gel to a (partially) dried gel. Complex impedance measurements are made to determine the transport properties of the material during this evolution and ^{7}Li NMR is used to confirm the high mobility of the Li^+ ions. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are used to characterize thermal stability.

Experimental Section

Synthesis. The lithium conductive gel was synthesized by mixing various amounts of a hydrolyzed silicate precursor with a liquid lithium electrolyte. The hydrolyzed silicate precursor was prepared in air under ambient temperature and pressure by mixing TMOS (tetramethyl orthosilicate, $Si(OCH_3)_4$) with deionized water in a 1:2 molar ratio. Two drops of acid (0.04 N HCl) were used to catalyze the hydrolysis reaction. The solution underwent ultrasonic mixing for 15 min, transforming the alkoxy ligands to Si−OH groups. The sonicated mixture is a homogeneous solution consisting mostly of hydroxy silicates and methanol. The hydrolysis reaction is described by the following equation:

$$Si(OCH_3)_4 + 4H_2O \rightarrow Si(OH)_4 + 4CH_3OH \qquad (1)$$

The liquid lithium electrolyte was prepared by dissolving ethylene carbonate (EC, 15.8034 g) and lithium tetrafluoroborate ($LiBF_4$, 4.6033 g) in propylene carbonate (PC, 21.086 g) in an Ar-filled glovebox. The EC/PC ratio was 2:3 (vol). Ethylene carbonate was used as a cosolvent to increase the concentration of the lithium salt. The resulting molarity of the lithium liquid electrolyte was 1.65 M. All the chemicals were obtained from Aldrich and used as received.

The hydrolyzed silica precursor and the liquid electrolyte were mixed in the glovebox at room temperature to form a lithium ion conducting sol. The two components formed homogeneous solutions easily without any observable phase segregation. This behavior was expected since alkoxide-based precursors tend to dissolve well in polar solvents, and the liquid electrolyte is rather polar in this respect.[16,17] The lithium ion conducting sol was then poured into polystyrene cuvettes and covered by parafilm. A small hole in the parafilm was used to control the drying rate. The condensation reaction of the lithium conductive sol proceeds with the release of water by combining two hydroxylated groups into a siloxane Si−O−Si group as described by the following equation:

$$Si(OH)_4 + Si(OH)_4 \rightarrow 2SiO_2 + 4H_2O \qquad (2)$$

The presence of the salt ($LiBF_4$) results in a basic environment, which is expected to catalyze the condensation reaction.[11] As the condensation reactions proceed, the solution becomes viscous and transforms into a free-standing lithium ion conducting gel. The compositions prepared in this study ranged from a ratio of 3:1 to 1:3 (liquid lithium electrolyte: hydrolyzed silicate precursor, by weight). All lithium ion conducting sol compositions gelled within 1 h. After gelation, the samples were kept in a glovebox for 1 month for drying. Slight amounts of shrinkage of the gel occurred as methanol and water evaporated during the drying process. As discussed later, the liquid lithium electrolyte does not evaporate and remains in the porous network. The capillary forces that develop from the receding liquid cause the silicate network structure to contract. After 1 month, samples were removed from the cuvettes and their dimensions recorded prior to conductivity measurements. The sample monoliths were typically 1 × 1 × 1 (cm), and the amount of shrinkage ranged from 5 to 15%. The samples with 3:1 composition have a light yellowish color; the color becomes more pale for samples containing a higher ratio of hydrolyzed silicate precursors. The gel samples with 1:3 composition are transparent.

Conductivity Measurements. Conductivity measurements were performed on both the lithium ion conducting sol and the resulting inorganic gel during several stages of the synthesis process. In the liquid state, the ionic conductivity of the hydrolyzed silicate precursors, the liquid lithium electrolyte, and a series of lithium ion conducting sols with various ratios of each starting material were measured. After 1 month of drying, conductivity measurements of the inorganic gel electrolytes were made at 25 °C. The temperature dependence of the conductivity between 30 and 80 °C was also measured. The ionic conductivity was determined by measuring the impedance response of the test cell using an LCR meter (Hewlett-Packard 4284A) over the frequency range 20 Hz to 1 MHz.

The test cell for the liquid samples was constructed from polystyrene cuvettes with a square cross section of 1 cm^2. The cuvette was cut to 1.2 cm in length and the two opposite side walls (both interior and exterior) were sputtered with gold in order to serve as electrodes. The two side walls were carefully masked by adhesive tape to produce a well-defined surface area. Copper wire was attached to both sputtered exterior walls for electrical contact to the LCR meter. The test cell was calibrated by using 1 wt % KCl solution. Impedance measurements were taken using 1 mL of the liquid sample within the test cell.

The volume shrinkage upon drying causes the gel to detach itself from the side walls, resulting in loss of electrical contact. The loss of contact and change in dimensions restrict the use of the gold-sputtered cuvette cell for continuous conductivity measurements during drying. Therefore, a different test cell was used for the inorganic lithium conductive gel. The test cell consisted of two brass bolts as electrodes. The head of each bolt was polished to a flat surface for contacting the gel samples. One of the brass electrodes was spring loaded to maintain firm electrical contact while further shrinkage of the gel was occurring. Silver paste was applied to the sample surface in order to minimize the interfacial resistance. The test cell was inserted into a glass tube so that all measurements were made in an atmosphere of flowing argon. The cell was connected to the LCR meter by copper wire. The temperature of the test cell was varied between 30 and 80 °C. The sample was heated to 80 °C initially, and impedance measurements were taken upon cooling in 5 °C increments to 30 °C. Since all dimensional changes occurred upon heating to 80 °C, this ensured that all measurements were taken on dimensionally stable samples. After the measurements, the samples were removed from the test cell and their dimensions measured to compute the ionic conductivity.

Physical Measurements. Variable-temperature ^{7}Li NMR spectra were collected on a Bruker ARX 500 equipped with a 5 mm broad-band probe operating at 194.364 MHz with a field

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(15) Durakpasa, H.; Breiter, M. W.; Dunn, B. *Electrochim. Acta* **1993**, *38*, 371.

(16) Dunn, B.; Zink, J. I. *J. Mater. Chem.* **1991**, *1*, 903.

(17) Nishida, F.; Dunn, B.; Knobbe, E. T.; Fuqua, P. D.; Kaner, R. B.; Mattes, B. R. *Mater. Res. Soc. Symp. Proc.* **1990**, *180*, 747.

Table 1. Physical and Electrical Properties of Inorganic Gel Electrolytes

composition/ratio[a]		liquid electrolyte	3:1	2:1	1:1	1:2	1:3	silica sol
conductivity[b]	liquid	3.9×10^{-3}	1.03×10^{-2}	1.12×10^{-2}	9.9×10^{-3}	7.6×10^{-3}	6.0×10^{-3}	9.8×10^{-5}
	aged gel				3.5×10^{-3}			
mechanical behavior	aged gel		← soft and easily deformed wet surface, nonuniform shape		rigid, dimensionally stable, slight flexibility	brittle, rigid → easily fractured		
appearance	aged gel		light yellow		less pale yellow color →	transparent		

[a] Ratio of liquid electrolyte to silica sol (by weight). [b] In S cm^{-1}.

strength of 11.7 T. Samples of the lithium conductive gel were ground to a fine powder with an agate mortar and pestle and loaded into NMR tubes. The experiments were performed using 11 μs 90° pulses. Data were acquired for 0.1 s with a delay time of 0.4 s to avoid saturation. A typical experiment involved 132 scans. Temperature was varied between −70 and 80 °C in increments of 10 °C. Spin−lattice relaxation (T_1) measurements were conducted using an inversion recovery method (180°−τ−90°).

Infrared spectra were obtained on a Nicolet 510P FT-IR spectrometer. The samples were ground into a powder in an agate mortar and pestle and mixed with NUJOL oil and spread onto KBr windows for analysis.

Mass spectrometry data were acquired using a quadrupole mass spectrometer (Hewlett-Packard 5985B) using a low-resolution solid probe with a 70 eV electron ionization source. Each sample was prepared by breaking off a small piece of the inorganic gel electrolyte and inserting it into the solid probe. The sample was then heated at 10 °C/min while scanning between 14 and 200 amu.

Thermogravimetric analysis (TGA) was performed on a TA instruments Model 910 TGA. Approximately 25−30 mg of the inorganic gel electrolyte was placed in an aluminum pan and heated at 10 °C/min to 400 °C in a nitrogen atmosphere. Differential scanning calorimetry was performed on a modulated DSC (TA instruments Model 2100). DSC spectra were obtained by placing 17−20 mg of the sample into a sealed aluminum pan under an inert nitrogen atmosphere. The sample was heated to 400 °C at 10 °C/min.

Results

Synthesis and Physical Properties. The synthetic approach was designed to produce a porous SiO_2 network whose interconnected pores contain the lithium ion conducting solvent phase. The first step of the synthesis was to hydrolyze the TMOS sol. Acid catalysis in combination with sonication has established that the resulting sol is fully hydrolyzed.[18] Condensation of this sol proceeds quite slowly because of its low pH; at least 4 days are required for gelation to occur. The addition of the liquid lithium electrolyte, however, raises the pH and accelerates condensation. As the Si−O−Si linkages start to form within the sol, the viscosity increases dramatically and the gelation time for the lithium ion conducting sol is less than 1 h. The resulting lithium ion conducting inorganic gel electrolyte consists of a three-dimensional silicate network with an encapsulated liquid phase. The encapsulated liquid is composed of the liquid lithium electrolyte, the reaction product of hydrolysis (methanol) and a small amount of unreacted water. Further condensation of hydroxyl ligands and evaporation of the methanol and unreacted water during the drying process result in a slight shrinkage of the gel (less than 15%). After 1 month of ambient temperature drying, only the liquid lithium electrolyte remains in the interconnected porous network.

It is important to emphasize that the effects of drying the inorganic gel electrolyte are substantially different from those which occur when the sol−gel process uses aqueous solvents. Silica xerogels prepared with alcohol/water commonly shrink to 15−20% of their initial sol volume during ambient temperature drying and lose some 70−80% of their weight. The inorganic gel electrolytes are purposely dried so that the low vapor pressure pore liquid does not volatilize. As a result these materials shrink only 5−15% and lose only 25% of their weight. Thus, after the ambient temperature drying treatment, the material is more accurately described as an "aged" gel because it consists of solvent-filled pores. In contrast, "dried" gels have the connotation of being xerogels.

The mechanical integrity of the inorganic gel electrolyte was dependent upon composition. Samples prepared with a high ratio of the liquid lithium electrolyte to hydrolyzed silica precursor sol (3:1 or 2:1) tended to be structurally unstable after drying. They exhibited nonuniform shrinkage and a constantly wet surface. One possible explanation for the latter effect was that the amount of remaining liquid after the sol-to-gel transition exceeded the available space (i.e., pore volume) provided by the inorganic component. In these cases, the silicate network falls short of containing or even supporting the remaining encapsulated liquid. Samples prepared with a high content of the hydrolyzed silica precursor (1:2 or 1:3) exhibited mechanical properties similar to those of a typical acid-catalyzed silicate xerogel, i.e., brittle and rigid. In the sol state, they were also less conductive compared to samples containing a higher ratio of liquid lithium electrolyte (Table 1). The optimum mechanical integrity was achieved by mixing equal weights of the liquid lithium electrolyte and the hydrolyzed silica precursor. The resulting gels exhibited relatively little shrinkage (less than 10%) during the drying. The materials were rigid and dimensionally stable and exhibited slight flexibility. Furthermore, the ionic conductivity of these materials was comparable to the highest ionic conductivity achieved. As a result, the experimental work described in this paper emphasized conducting gels with a 1:1 composition. The effects of composition on the electrical conductivity, mechanical integrity, and physical appearance are summarized in Table 1.

Thermal Stability. The thermal stability of the inorganic gel electrolyte (1:1 composition) was investigated by DSC and TGA methods. The sharp decrease at 30 °C and the sharp rise at 400 °C shown in the DSC plot in Figure 1 are due to the DSC furnace turning on and off, respectively, and should be ignored. The DSC plot indicates that the inorganic gel electrolyte is stable to 240 °C, at which point a large endothermic event begins. This endotherm is likely due to the boiling of

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(18) Fuqua, P. D. Ph.D. Thesis, University of California, Los Angeles, 1995.

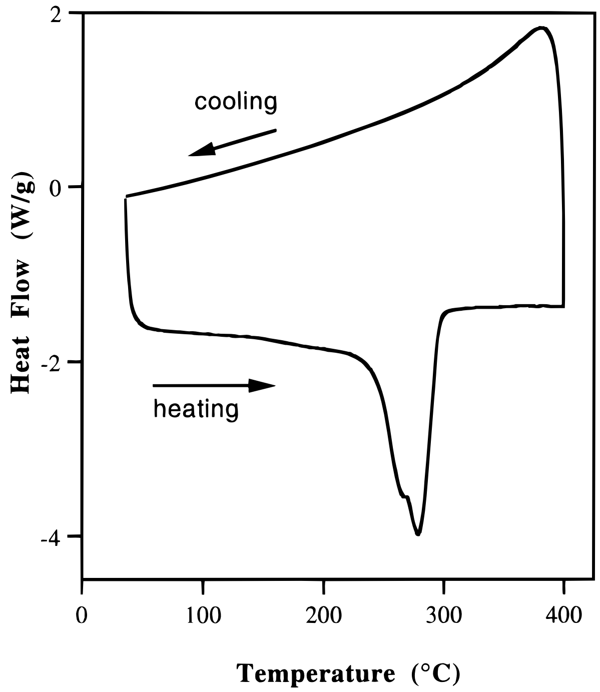

Figure 1. Differential scanning calorimetry of an inorganic gel electrolyte being heated (bottom curve) and then cooled (top curve).

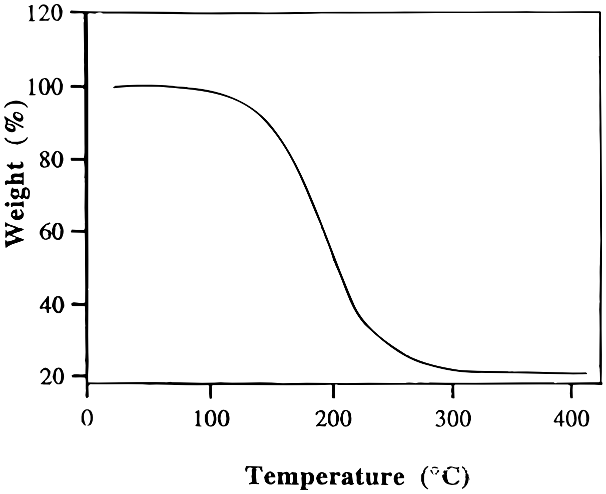

Figure 2. Thermogravimetric analysis of an inorganic gel electrolyte showing a weight loss of 1.1% at 100 °C and 76.6% at 300 °C.

the ethylene carbonate/propylene carbonate solvent since it closely corresponds to the boiling points of the pure materials; ethylene carbonate boils at 243 °C, and propylene carbonate boils at 240 °C. The absence of a corresponding exotherm in the cooling curve is consistent with the boiling of the solvent which then escapes from the sample pan and is therefore not observed on cooling. There is no evidence of any glass transition phenomenon which is consistent with the high T_g for SiO_2.

The TGA plot shown in Figure 2 indicates that the sample does not start losing mass appreciably until 100 °C. Above this temperature, the liquid electrolyte remaining in the pore network evaporates. The sample loses 76.6% of its weight by 300 °C, leaving behind only the $LiBF_4$ and the silica network. This is in excellent agreement with a theoretical weight loss of 75% assuming that only the ethylene carbonate and propylene carbonate are lost. It is worth noting that the DSC experiment takes place in a “sealed” pan, whereas the TGA sample is simply open and exposed to flowing dry nitrogen which removes any volatile material such as the PC and EC. This explains why the DSC curve is flat until the boiling point of the electrolyte is reached, while in the TGA experiment weight loss occurs at a much lower temperature because the sample is uncovered and therefore solvent volatilizes well below its boiling point. These results suggest that the inorganic gel electrolyte could be used up to at least 100 °C in an open system and to temperatures approaching the boiling point of the electrolyte (~240 °C) in a sealed system.

Chemical Composition Analysis. FT-IR spectroscopy provides considerable insight concerning the nature of the dried inorganic gel electrolyte. The solid line in Figure 3 is a representative spectrum of the dried inorganic gel electrolyte, and the spectrum plotted as a dashed line is for the liquid lithium electrolyte (i.e., 1.65 M $LiBF_4$ in EC/PC). The two marked peaks (●) indicate the presence of some water in the starting electrolyte. However, this amount is small compared to the peaks for ethylene and propylene carbonate (1740−1830, 1030−1220 cm^{-1}), which are off scale. It is important to note the absence of OH stretches in the region of 3200−3800 cm^{-1} for the inorganic gel electrolyte. Both water and methanol have a very strong O−H absorption in the 3200−3800 cm^{-1} region, and the absence of any peak indicates that the amount of water and methanol left in the inorganic gel electrolyte after the drying treatment is negligible. This indicates that the small amount of water present in the liquid electrolyte is either consumed in the hydrolysis reaction with the TMOS or leaves as an azeotrope with methanol during the drying stage. The other peaks in the spectrum can be attributed to ethylene carbonate, propylene carbonate, and Nujol (which was used to prepare the samples and has an intense absorption at 2800−3000 cm^{-1}). Fabricating IR samples by pressing pellets with KBr was not feasible since the application of sufficient pressure to form a pellet extrudes the encapsulated liquid from the sample.

In addition to the FT-IR, mass spectrometry was used to qualitatively identify the encapsulated materials in the inorganic gel electrolyte. The results are shown in Table 2 and compared to EC and PC reference samples. The peak (104 amu) is present in both the PC and the dried gel and should be treated as impurities from the PC. The rest of the peaks can be attributed to either EC (88 amu), PC (102 amu), or fragments for both of these molecules as listed in Table 2. Mass spectrometry cannot be used to detect residual water or methanol since their atomic masses (18 and 29 amu) are the same as fragments of the parent molecules. However, the relative abundance of the peaks at 18 and 29 amu are consistent with the premise that the liquid phase is the EC/PC lithium electrolyte encapsulated in the silica framework and the FT-IR results, which show the aged gel contains no water or methanol.

Ionic Conductivity. Table 1 lists the ionic conductivities (25 °C) for the liquid lithium electrolyte, the hydrolyzed silica precursor, and various compositions of the lithium ion conducting sols. The ionic conductivity of the liquid lithium electrolyte and the hydrolyzed

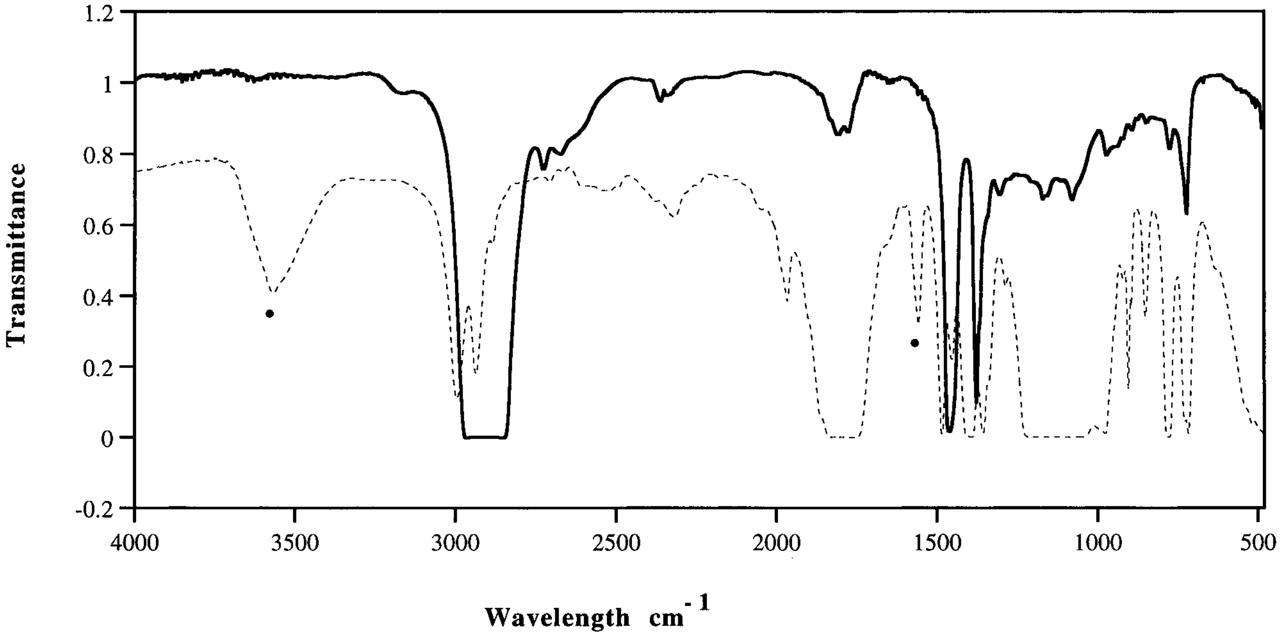

Figure 3. FT-IR spectra for an inorganic gel electrolyte (solid line) and the EC/PC−$LiBF_4$ liquid electrolyte (dashed line). The dots (●) indicate absorption due to water.

Table 2. Mass Spectrometry for Inorganic Gel Electrolyte, Ethylene Carbonate (EC), and Propylene Carbonate (PC) Standards

	dried gel	relative abundance	
M/E	relative abundance	EC standard	PC standard
18	1.2	2.5	
25	1.7		12.5
26	12.5	2.4	1.2
27	20.2	2.4	30.7
28	100.0	100.0	58.0
29	63.5	79.9	64.3
30	21.4	18.8	26.7
31	2.4	1.2	4.9
32	26.1	34.5	7.1
37	2.5		2.9
38	4.8		5.5
39	14.9		17.9
40	4.6	3.6	3.6
41	6.7	1.2	7.4
42	21.2	12.1	15.6
43	54.9	72.6	81.2
44	28.6	26.8	13.0
45	7.4	6.0	6.2
53	0.6		0.6
55	2.4		2.0
56	0.8	0.4	
57	36.0		100.0
58	9.3	9.5	123.7
59	0.6		3.6
73	1.1	2.4	1.8
87	11.5	1.2	16.7
88	31.3	91.7	0.8
89	1.2	3.6	
102	5.4		6.0
104	0.6		1.5

silica precursor were 3.9 × 10^{-3} and 9.8 × 10^{-5} S cm^{-1}, respectively. It should be emphasized that the mobile cationic species, Li^+ and H^+, are different for these two constituents. The measured conductivity of the liquid lithium electrolyte is in good agreement with the value reported (3.5 × 10^{-3} S cm^{-1}) for a similar electrolyte consisting of 1 M $LiBF_4$ in 1:1 (vol ratio) of EC/PC.[19] Interestingly, certain lithium ion conducting sol compositions exhibited ionic conductivities in the range of 10^{-2} S cm^{-1}, i.e., a higher conductivity than the pure liquid lithium electrolyte. Possible explanations for the increased ionic conductivity are (1) dilution of the concentrated liquid electrolyte by the addition of hydrolyzed silica precursor (leading to more dissociation of associated ionic pairs) and (2) higher mobility of cations and anions in the lithium conductive sol. The latter can occur because addition of the hydrolyzed silica precursor significantly reduces the viscosity of the lithium conductive sol as compared to the lithium liquid electrolyte, resulting in higher ionic mobility (Walden's rule).[20]

Also shown in Table 1 is the ionic conductivity of the inorganic gel electrolyte (1:1 composition) after drying for 1 month. The ionic conductivity of this hybrid material is 3.5 × 10^{-3} S cm^{-1}, which is comparable to that observed for the liquid electrolyte (3.9 × 10^{-3} S cm^{-1}). Although this value is less than that of the corresponding lithium ion conducting sol (1 × 10^{-2} S cm^{-1}), this behavior is consistent with the chemical changes occurring during the sol−gel transition. During drying, methanol and residual water decreased continually until the only remaining solvent in the pores consisted of the EC/PC component. Thus, it is not surprising that the conductivity of the inorganic gel electrolyte decreases to a value comparable to that of the liquid lithium electrolyte.

Figure 4 compares the complex impedance response from both the inorganic gel electrolyte and the liquid electrolyte. The complex impedance spectra exhibit the characteristic behaviors of a liquid electrolyte with two mobile ionic species. The higher frequencies give the resistive contribution while the lower frequencies exhibit approximately a 45° line indicative of a Warburg-like impedance. The Warburg impedance is due to the coupled diffusion of both species (cations and anions) upon the applied sinusoidal voltage.[21] These measurements clearly show that despite the solid-state appear-

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(19) Dudley, J. T.; Wilkinson, D. P.; Thomas, G.; Levae, R.; Woo, S.; Blom, H.; Horvath, C.; Juzkow, M. W.; Denis, B.; Juric, P.; Aghakian, P.; Dahn, J. R. *J. Power Sources* **1991**, *35*, 59.

(20) Adamczewski, I. *Ionization, Conductivity, and Breakdown in Dielectric Liquids*; Tayor and Francis: New York, 1969.

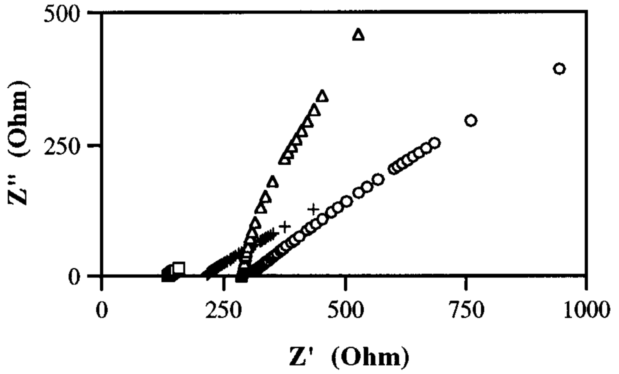

Figure 4. Complex impedance for an inorganic gel electrolyte at different temperatures compared to the EC/PC–$LiBF_4$ liquid electrolyte. Liquid electrolyte at 25 °C (△); inorganic gel electrolyte at 30 °C (○), 50 °C (★) and 80 °C (□).

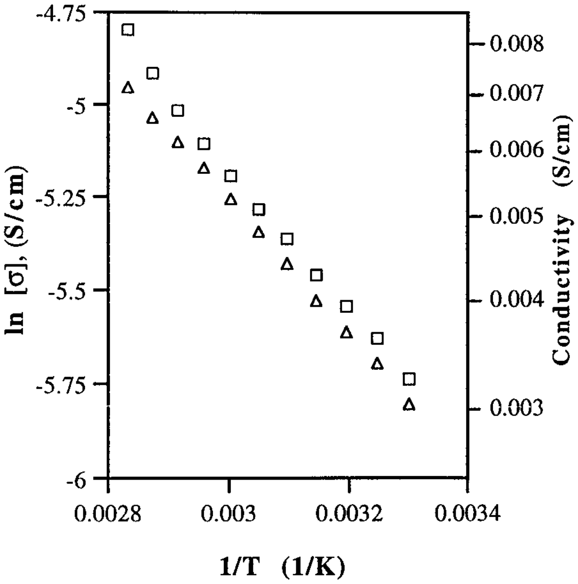

Figure 5. Ionic conductivity vs inverse temperature for an inorganic gel electrolyte. (△) First measurement after 1 month drying; (□) second measurement, 1 day after first measurement).

ance of the inorganic gel electrolyte, its impedance spectra are similar to the spectra obtained for the liquid electrolyte system. This response indicates that the conduction mechanism of the inorganic gel electrolyte can be attributed to the presence of a continuous liquid phase. The solid silicate network provides the necessary porous structure which encapsulates the liquid but does not contribute to the ion conduction process. In this way, impedance spectroscopy provides insights into the conduction process.

Figure 5 shows the temperature dependence of the ionic conductivity for the inorganic gel electrolyte. Over the temperature range 30–80 °C, the samples follow a well-behaved Arrhenius relation of the form

$$\sigma = \sigma_0 \exp(-E_a/kT) \tag{3}$$

where σ_0 is a preexponential factor and E_a is the activation energy. Ion transport in the inorganic gel electrolyte is thermally activated. The activation energy, E_a calculated from the Arrhenius relation, is 0.16 eV. Figure 5 also demonstrates that there is no conductivity change after the first measurement. That is, the hybrid material can be reheated to 80 °C without affecting transport properties. This behavior is consistent with the TGA and DSC results. Conductivity measurements made at temperatures above 90 °C exhibited an irreversible conductivity loss arising from volatilization of the liquid electrolyte.

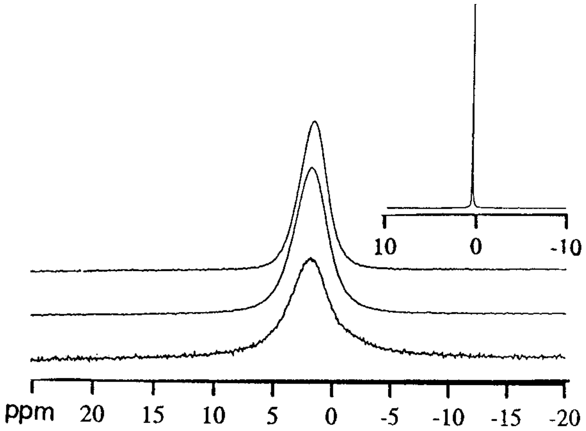

Figure 6. ^7Li NMR spectra of a dried inorganic gel electrolyte showing line narrowing at different temperatures. From top to bottom the spectra are as follows; 355 K (fwhm 413 Hz), 255 K (fwhm 506 Hz), and 205 K (fwhm 670 Hz). Inset is the spectrum of the liquid electrolyte at 298 K.

NMR. To establish whether the ionic conductivity of the inorganic gel electrolyte was due to the mobility of the Li^+ ions, ^7Li NMR measurements were made. The line narrowing of the ^7Li signal over the temperature range 205–355 K is shown in Figure 6 and confirms the presence of Li^+ ion motion on a time scale comparable to the reciprocal of the line width.

Note that although the inorganic gel electrolyte appears as a solid macroscopically, it was not necessary to use solid-state NMR techniques such as magic angle spinning to obtain a signal. The acquisition parameters for the inorganic gel electrolyte were identical with the liquid electrolyte itself (shown as an inset in Figure 6). A single relaxation time (T_1) of 0.68 s was measured for the inorganic gel, indicating only one type of ^7Li is present in the sample. The relaxation time is in the range of values reported for lithium in a liquid[22] and suggests that all the lithium remains in the mobile liquid phase and none has incorporated itself into the solid silica framework. The fact that the NMR of ^7Li was obtained so easily without the use of magic angle spinning is another strong indication that the Li^+ ions are dissolved in a liquid matrix and not trapped in a solid silicate network.

Discussion

Synthesis Considerations. We have successfully demonstrated a new approach for synthesizing high-conductivity solid electrolytes using sol–gel methods. The approach involves polymerizing the inorganic silicate network in the presence of a liquid electrolyte, leading to encapsulation of the liquid electrolyte within the microporous inorganic network. The synthesis was investigated only for bulk materials; however, the

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(21) Macdonald, J. R. *Impednce Spectroscopy*; Wiley: New York, 1987.

(22) Harris, P. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: New York, 1978.

gelation time is sufficiently long (1 h) that this method will be readily adaptable to the preparation of thin films by dipping or spinning techniques.

The inorganic gel electrolyte consists of two continuous phases. The liquid electrolyte phase provides ionic conduction, while the solid inorganic phase offers a continuous porous matrix with dimensional stability and mechanical integrity. The synthetic approach represents a variation on the acid–base catalysis method developed previously.[11] The silicate precursor, which is acid catalyzed to promote hydrolysis, is combined with the liquid electrolyte which serves to catalyze condensation of the silanol groups. In this way, the inorganic gel network develops and grows within the liquid electrolyte. Upon completion of the condensation reactions, the resulting gel appears to be a solid material as it exhibits macroscopic rigidity. However, since the silicate network is immersed in a liquid phase, the aged gel will possess its characteristic viscoelastic behavior microscopically.[11] The continuous inorganic network is the reason aged gels are substantially more rigid ($G > 10^7$ Pa) than composite polymer electrolyte ($G \sim 10^4$ Pa).[9]

The conduction process is not affected by the sol–gel transition because the liquid electrolyte represents a continuous phase within the aged gel. The drying process causes relatively little change in conductivity; there is only a small chemical change during drying, and the continuous microporosity of the inorganic phase is essentially unaffected. The liquid electrolyte in the inorganic silica network is stable from room temperature to at least 90 °C with a relatively low vapor pressure. From the FT-IR and MS measurements, it is reasonable to conclude that neither water nor methanol remain in the gel after drying. The high conductivity of the continuous liquid electrolyte phase ensures that the final material exhibits a high conductivity. The measured conductivity of the ambient dried inorganic gel electrolyte (3.5×10^{-3} S cm^{-1} at 25 °C) is comparable to the value exhibited by the pure liquid electrolyte (3.9×10^{-3} S cm^{-1}). This conductivity level is greater than that reported for composite polymer electrolytes (1×10^{-4} S cm^{-1}).[9]

Proton Conduction. Despite the presence of protons, their contribution to the conductivity is expected to be negligible. Previous results showed that the proton conductivity of sol–gel derived silica (aqueous solvent) decreased substantially once solvent loss began to occur.[14] This response is expected since high proton conductivity in solids requires a more or less continuous water-rich path to promote the proton-transport process.[23] Another means of decreasing proton conductivity in sol–gel materials is to replace the aqueous solvent in the pore network with a nonaqueous solvent. Solvents such as dimethyl formamide and DMSO, for example, reduce the conductivity of aged gels by 1–2 orders of magnitude when they replace the initial aqueous solvent phase.[24,25] In light of this behavior, there is little likelihood that proton conduction contributes to the values observed for the inorganic gel electrolytes. The conductivity value of the inorganic gel electrolyte after the ambient drying treatment was some forty times greater than the hydrolyzed sol, i.e., when an aqueous phase was present. There is no evidence whatsoever of an aqueous phase in the inorganic gel electrolyte. The mass spectrometry and FT-IR experiments indicate that after the drying treatment, no water was present in the material. Moreover, residual protons present in the liquid phase will be complexed by the nonaqueous solvent and are not likely to enhance protonic conduction.

Comparison with Gel Electrolytes. The solid electrolytes reported in this paper may be generally considered as inorganic analogues of gel electrolytes which are based on the use of organic polymers. A variety of gel electrolyte systems have been explored as these materials are of considerable interest as separators for secondary lithium batteries. The most conductive gel electrolytes reach conductivity values on the order of 10^{-2} S cm^{-1} at 60 °C.[7] The temperature dependence of the conductivity is better approximated by the Vogel–Tamman–Fulcher (VTF) equation than by an Arrhenius equation as the ionic conductivity of gel electrolytes is influenced by the glass transition temperature of the polymer matrix.[26] There are indications that matrix interactions with the ionic species occur and serve to decrease the conductivity of the gel electrolytes below that of the corresponding liquid electrolyte.

The inorganic gel electrolytes prepared in this study use a sol–gel derived silica matrix to contain the liquid electrolyte. The initial results are very promising for separator applications. Ionic conductivities comparable to liquid electrolyte have been achieved, with values reaching 10^{-2} S cm^{-1} at 80 °C. The temperature dependence of the conductivity was well fit by an Arrhenius relation, although it is possible that not a wide enough temperature range was investigated to determine whether the VTF equation is more appropriate. It is difficult to compare the activation energy determined for these inorganic gel electrolytes, 0.15–0.17 eV, with those reported for organic gel electrolytes because the activation energy from the VTF equation is generally lower than that of the Arrhenius equation. Nonetheless, the values seem to fit within the range of activation energies reported for gel electrolytes. Perhaps the most significant aspect of the inorganic gel electrolytes is that they offer superior thermal and mechanical properties as compared to gel electrolytes without sacrificing ionic conductivity or electrochemical stability. The materials are rigid and dimensionally stable, and their thermal stability is limited only by the boiling point of the encapsulated liquid electrolyte.

Conclusions

The sol–gel process has been used to prepare a new type of solid electrolyte in which a lithium ion conducting liquid electrolyte is encapsulated within a porous inorganic network. The continuous liquid phase gives the material its ionic conductivity while the inorganic matrix provides excellent thermal, chemical, and mechanical stability. The resulting materials are as

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(23) Colomban, P.; Novak, A. *J. Mol. Struct.* **1988**, *177*, 277.

(24) Durakpasa, H.; Breiter, M. W.; Dunn, B. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 251.

(25) A similar solvent-exchange approach was recently reported to produce lithium ion conduction in silicate gel: Wasincionek, M.,Breiter, M. W. *J. Appl. Electrochem.*, in press.

(26) Bruce, P. G. *Solid State Electrochemistry*; Cambridge University Press: Cambridge, 1995.

conductive as gel electrolytes with far greater rigidity. The optimum composition consists of a EC/PC−$LiBF_4$ electrolyte added to a hydrolyzed TMOS sol in the ratio of 1:1 (by weight). The conductivity of the resulting inorganic gel electrolyte is 3.5×10^{-3} S cm^{-1} at 25 °C, which increases to 10^{-2} S cm^{-1} at 80 °C. ^7Li NMR studies indicate that Li^+ ions are mobile in this material, and the synthesis is developed so that protonic conduction is negligible. The inorganic matrix used in this study is SiO_2, and thus the thermal stability of the inorganic gel electrolyte is determined by the liquid electrolyte phase.

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