

Preparation and Characterization of Single Ion Conductors from High Surface Area Fumed Silica

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Abstract

Anions that can form dissociative salts with Li⁺ have been prepared and covalently attached to high surface area fumed silica. When blended with polyethylene oxide (PEO), the functionalized fumed silica suppresses the crystallization of the PEO, provides dimensional stability, and serves as a single ion conductor. Since functionalized fumed silica is easily dispersed in common polar solvents, it can be incorporated in both the polymer electrolyte and the electrodes.

Introduction

The development of a solid polymer electrolyte with high ionic conductivity as well as the requisite electrochemical stability, has been the subject of extensive recent research. Since in a rechargeable lithium battery only the lithium ions are electroactive towards the electrodes, the critical transport property is the lithium ion transference number (t°_{+})¹. If the anions are immobile, then t°_{+} should approach unity and DC polarization effects, attributed to the localization of counterions near the anode, which inhibits the supply of alkali-cations from it², can be avoided. There has therefore been a thrust towards the development of so-called single ion conductors (SICs). Preparation of SICs has focused on the synthesis of polymers in which the anion is covalently attached to the polymer backbone. The ion conductivities of alkali metal salts of polyelectrolytes such as poly(methacrylic acid), poly(styrenesulfonic acid), modified poly(phosphazene)³, and poly(tetraalkoxyaluminate)⁴ are low, presumably due to factors such as ion pairing or clustering⁵ and high glass transition temperatures. Solvents or plasticizers increase polymer chain flexibility and ionic conductivity⁶.

In PEO based systems, the Li ion is solvated by the ether oxygens of the PEO.

The interest in an all solid state polymer electrolyte, as well as the relative insolubility of many polyanions has motivated the synthesis of materials in which flexible groups are incorporated covalently into SICs. PEO oligomers used in the main chain⁷, as side chains^{3,8-11}, or as crosslinking agents¹², solvate the lithium ion; side chain PEO lengths of $n \sim 7$ were observed to optimize the conductivity¹³. Blends of PEO and SICs achieve similar results¹⁴.

Ion conductivity also depends on the dissociation energy of the anion. For PEO oligomers with charge groups at their ends, trifluoromethyl sulfonamide had the highest ionic conductivity¹⁵ followed by methyl- or benzene-sulfonamide, and then benzenesulfonate or carboxylate¹⁶. Similarly, in PEO comb-branched copolymer electrolytes, the conductivities were in the order trifluorobutane sulfonate > butane sulfonate > carboxylate¹⁷. Siloxyaluminate polymers were specifically designed to delocalize the anion charge and sterically inhibit close approach of the Li⁺^{11,13}.

To date, ionic conductivities in these systems have been low. Room temperature ionic conductivities of 1×10^{-7} S cm⁻¹ have been obtained for carboxylate systems¹⁸⁻²⁰, 2×10^{-6} - 6×10^{-7} S cm⁻¹ for sulfonate systems^{10,21}, 10^{-5} for fluorosulfanate systems¹⁷, 1.2×10^{-6} S cm⁻¹ for trifluoromethylsulfonamide²², and 2×10^{-5} S cm⁻¹ with a siloxy aluminate system¹¹.

Another consideration in cells prepared using SICs is that the composite electrodes must contain the single-ion conducting species. This is necessary in order for the Li⁺ to penetrate into the porous electrode structure, to avoid high electrode-

electrolyte impedance. However, polymer electrolytes are often difficult to dissolve in aprotic polar solvents, and therefore are difficult to incorporate into the electrodes.

Recently, inorganic-organic hybrids of PEO, lithium salts and ceramics such as TiO_2 , Al_2O_3 , and SiO_2 have been prepared as solid state electrolytes (SSEs) with reasonable mechanical properties and conductivities $\sim 10^{-5}$ S/cm. The inorganic particles suppress crystallization of the PEO, which enhances the RT conductivity.

In the present work, anions have been attached to fumed silica, with the purpose of forming SICs with blends of PEO. The functionalized fumed silica suppresses crystallization of the PEO. In addition, fumed silica readily disperses in solvents used to cast both PEO and PVDF-HFP, and therefore can be incorporated into both the electrolyte and electrode materials.

Experimental

Aerosil 380 (A380) fumed silica, with a primary particle size of 7nm and a surface area of $380\text{m}^2/\text{g}$, was obtained from DeGussa. The silanes 2-(4-chlorosulfonylphenyl) ethyl trichloro (or trimethoxy) silane [referred to as R- SO_2Cl silane] and dimethylchlorosilane [referred to as R-SiH], whose structures are shown in Figure 1, were obtained from Gelest. Allyl bromide, Pt(dvs) catalyst and all other chemicals and solvents were obtained from Aldrich.

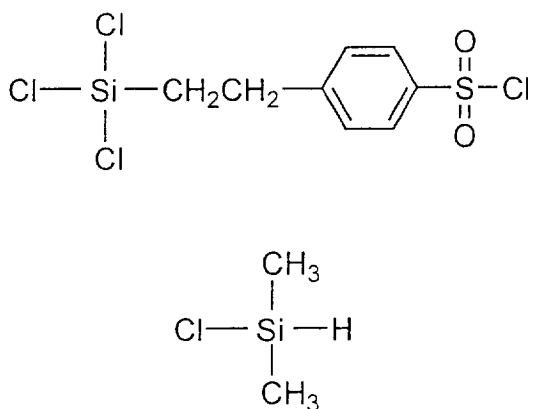


Figure 1. (top) 2-(4-chlorosulfonylphenyl) ethyl trichlorosilane; (bottom) dimethylchlorosilane

Two methods were used to attach anions to fumed silica. In one, surface silanols, Si_sOH , where Si_s is a surface silicon atom, are reacted with trichloro or trimethoxysilanes, to produce the structure shown in Figure 2.

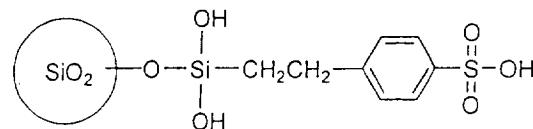


Figure 2. $-\text{RSO}_3\text{H}$ silanated silica

RSO_3Cl is the only commercially available silane that contains a useful anion.

In order to attach anions with lower lattice energies and higher resonance stabilization energies, a second method was used in which RSiH silane was first attached to the fumed silica, to produce the structure shown in Figure 3, followed by a hydrosilylation reaction with an allyl or vinyl compound containing an anion.

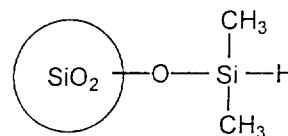


Figure 3. RSiH silanated silica

Since silica is unstable to HF and to base hydrolysis, the Li salts of styrene sulfonic acid, 2-allyloxy-1,1,2,2-tetrafluoroethanesulfonic acid, and allyltrifluoromethylsulfonamide, shown in Figure 4, were prepared before the hydrosilylation reaction.

The Li salt of styrene sulfonic acid was prepared using the commercially available sodium salt, dissolving it in 10% HCl, followed by removal of water, redissolution in ethanol, filtration (to remove NaCl), evaporation of ethanol, and passing the product through a silica gel column to remove residual NaCl and other impurities. Ethanol was evaporated and a viscous liquid was obtained, which was redissolved in water and titrated with LiOH, followed by removal of water, redissolution in ethanol and filtration to remove excess LiOH. After solvent evaporation, solid crystals of the lithium salt were obtained. The lithium salt of allyltrifluoromethylsulfonamide was prepared according to reference 22. The lithium salt of 2-

allyloxy-1,1,2,2-tetrafluoroethanesulfonic acid was prepared from 2-allyloxy-1,1,2,2-tetrafluoroethanesulfonyl fluoride (allyl-OCF₂CF₂SO₂F) by mixing 1 equivalent of allyl SO₂F with 2 equivalents of LiOH in 2M aqueous solution and ethanol (~1 H₂O/2 EtOH) at RT. Allyl SO₂F was soluble in EtOH but not in H₂O. The solvent was evaporated and the allyl SO₃Li was obtained (in addition to LiF). ¹H and ¹⁹F NMR indicated that the double bond was not affected under these reaction conditions, and the SO₂F was hydrolyzed. The structures and lithium ion exchange for the other salts were confirmed by ¹H and ¹⁹F NMR, and atomic absorption spectroscopy.

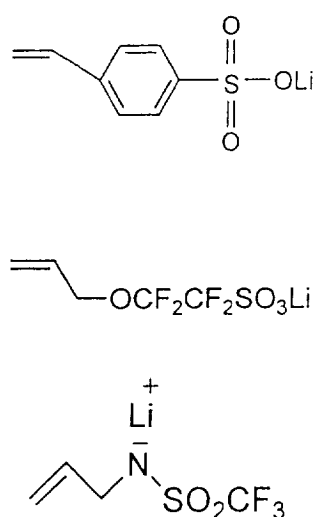


Figure 4: Li salts of: (top)styrene sulfonic acid; (middle)2-allyloxy-1,1,2,2 tetrafluoroethanesulfonic acid; and (bottom) allyltrifluoromethylsulfonamide

The silanated silicas were characterized by thermogravimetric analysis (TGA) weight loss measurements, elemental analysis and atomic absorption in order to determine the amount of silane on the silica and the degree of lithium ion exchange.

Results and Discussion

In order to demonstrate that anions could be covalently attached to fumed silica, the commercially available -RSO₃H silane was first used, although its anion was expected to result in

the least favorable conductivity and transport number for Li⁺. Our initial approach was to determine silanization conditions that optimized the amount of covalently bound silane. A typical procedure (carried out in a glove box purged with argon) consisted of dispersing 0.4g A380 (previously heated in oven at 120-130°C overnight) in 40mL anhydrous pentane, followed by addition of 0.1mL R-SO₃Cl. The reaction mixture was stirred for 1h, centrifuged, rinsed 3x with toluene (to remove unreacted silane); in the last rinse 0.5mL water was added, to ensure the hydrolysis of sulfonyl chloride that was attached to the silica. The silanated silica was then rinsed 4x with methanol (by centrifugation at 8000-10,000rpm), and evaluated at RT overnight.

Typical TGA data for both the silane and the silanated silica are shown in Figure 5. For silanes that are completely removed by 800°C, the TGA weight loss between 100 and 800°C is used to quantify the amount of adsorbed silane. However, the heteronuclear aromatic silane does not completely decompose by 800°C. In order to determine whether the amount of adsorbed silane could be obtained by normalizing for the TGA weight loss of the pure silane, this method of calculation was compared with the results of elemental analysis, shown in Table I, and found to be in agreement. Typical TGA weight losses of ~50% were obtained for the silane.

Table I. Comparison of TGA and elemental analysis data for -RSO₃H silanated silica

Analysis	C	H	Si	S
Result %	20.6	2.5	25.6	6.6
	Calculated from TGA or formula		Element Analysis Measurement	
Si%	29.8		25.6	
C: S ratio	3.0		3.12	

Ion exchange was carried out using 0.7g silanated silica mixed with 40 mL 0.1M Libenzoate in 95% EtOH for 10min in a sonicator bath. The material was centrifuged at 10,000rpm, decanted, and rinsed with 95% EtOH 1x, and MeOH 3x (by centrifugation), then dried in a vacuum oven at RT overnight.

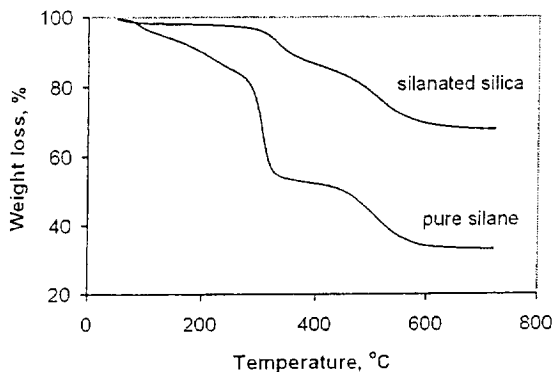


Figure 5. TGA data for 2-(4-chlorosulfonylphenyl) ethyl trichlorosilane and this silane covalently attached to fumed silica.

Films prepared from silanated silica and PEO of molar mass 600,000 were strong and self-supporting, and had no PEO crystallization. Conductivity data will be presented for these films.

Acknowledgements

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