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Journal

ACS applied materials & interfaces, 7(34)

ISSN

1944-8244

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Publication Date

2015-09-01

DOI

10.1021/acsami.5b06096

Peer reviewed

Plasticized Polymer Composite Single Ion Conductors for Lithium Batteries

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Abstract: Lithium bis(trifluoromethane) sulfonamide (TFSI) is a promising electrolyte salt in lithium batteries, due to its good conductivity and high dissociation between lithium cation and anion. N-pentane trifluoromethane sulfonamide (C₅NHTf), a TFSI analogue molecule, is tethered onto the surface of silica nanoparticle as monolayer coverage. Silica polymer composite has better mechanical property than that of the pure PEO. Anchoring anions on nanoparticles should increase the Li⁺ transference number to unity since anions bound to particles have reduced mobilities; trifluoromethane sulfonic aminoethylmethacrylate (TfMA), a TFSI analogue vinyl monomer is polymerized on silica nanoparticle surface as multilayer coverage. Polyelectrolytes anchored to particle surface offer multiple sites for anions, and in principle, the carrier concentration can be increased and approach the carrier concentration of the bulk polyelectrolyte. Monolayer grafted nanoparticle have lithium content of 1.2×10^{-3} g Li/g and multilayer grafted nanoparticle has lithium content over an order higher at 2×10^{-2} g Li/g. Electrolytes made from monolayer grafted particles exhibit a weak dependence of conductivity on temperature, ionic conductivity is still in the range of 10^{-6} S/cm when temperature increases to 80 °C; electrolytes made from multilayer grafted particles show a steep increase of conductivity with temperature, ionic conductivity with O/Li of 32 increases to 3×10^{-5} S/cm at 80 °C.

Keywords: lithium ion electrolyte, silica nanoparticle, TFSI

Introduction

Lithium Ion Batteries (LIBs) are the most popular type of rechargeable battery for portable electronics, they are featured for high energy density and no memory effect.¹ The electrolytes used for LIBs are normally composed of highly polar solvents such as carbonate derivatives or poly(ethylene oxide) (PEO) and lithium salts LiPF_6 , Lithium bis(oxalato)borate (LiBOB), LiCF_3SO_3 , $\text{Li}[\text{N}(\text{SO}_2\text{CF}_3)_2]$ (LiTFSI),² $\text{Li}[\text{N}(\text{SO}_2\text{C}_2\text{F}_5)_2]$ (LiBETI)³ etc. Lithium bis(trifluoromethane) sulfonamide (LiTFSI) was first brought to the application of lithium ion electrolytes by Armand.⁴ LiTFSI is less toxic and more stable than the widely used lithium hexafluorophosphate. There are two trifluoromethane sulfone groups attached to the nitrogen, the electron withdrawing group makes the negative charge delocalized to the big anion structure, this weakens the electrostatic interaction between anion and cation, enables a large dissociation degree. Ue and coworkers studied dissociation degree of common lithium salt followed this order: $\text{Li}[\text{N}(\text{SO}_2\text{CF}_3)_2]$, $\text{LiAsF}_6 > \text{LiPF}_6 > \text{LiClO}_4 > \text{LiBF}_4 > \text{LiC}_4\text{F}_9\text{SO}_3 > \text{LiCF}_3\text{SO}_3$.⁵

High molecular weight polyethylene oxide (PEO) mixed with lithium salt has been used as solid polymeric electrolytes.⁶ Use of this material could potentially avoid lithium dendrite formation in LIBs and address the safety issue. Both anions and cations contribute to the ionic conductivity, typically lithium cations only contribute to 10% to 20% of the whole conductivity, giving a lithium transference number (t_{Li^+}) of 0.1~0.3, anion mobility is the dominant species in the ionic conductivity of the electrolytes. This low t_{Li^+} leads to accumulation of ions close to the surface of one electrode and depletion of ions on the other, resulting in concentration polarization during the charging and discharging process. Clustering ions form a concentration gradient and limit power density; the resulting internal resistance generates heat and affects chemical stability

of the electrolyte. For high power LIBs for electric vehicles (EV), the concentration polarization caused by low lithium transference number of the electrolyte materials could be a serious problem.⁷

An effective approach of increasing lithium transference number is to chemically attach the anions on the polymer chains, limit anion mobility and build up single ion conductor.^{8,9,10,11} A good anion structure should enable the dissociation between lithium cation and counterion, which could increase the mobile lithium cation concentration in the electrolyte. This requirement makes TFSI an interesting structure to be used in the construction of single ion conductors. In this study, we tethered two TFSI analogue structures on silica nanoparticle surface to achieve a polymer composite single-ion conducting electrolyte. Silica particles also increase the mechanical stability and processibility of the electrolyte. Polyethylene glycol dimethyl ether with a molecular weight of 500 (PEGDME500) is used as plasticizer solvent for lithium transport. Anchoring anions on nanoparticles should increase the Li^+ transference number to unity since anions bound to particles have minimal mobility.

Results and Discussion

Figure 1. Synthetic route for Si-C5NHTf and lithiation to Si-C5NTfLi.

Silica nanoparticle has surface area of $200 \pm 25 \text{ m}^2/\text{g}$ and average particle size of 10 nm. The synthetic sequence shown in Figure 1 is used to anchor the salts to silica nanoparticle. A five carbon tether places the salt a reasonable distance from the surface. 1-Pentenyl amine is synthesized following a literature procedure.¹² Formation of the trifluoromethylsulfonimide uses triflic anhydride, and hydrosilylation of the resulting alkene with triethoxysilane uses Karstedt's catalyst.

Figure 2. (a) FTIR and (b) TGA of the bare silica nanoparticles, Si-C5NHTf, and Si-C5NTfLi. (c) Temperature dependent conductivity for the Si-C5NTfLi mixed with PEGDME500.

IR spectra of the modified silica demonstrate successful anchoring of the sulfonimide (Figure 2a). The IR spectrum of silica nanoparticle exhibits a sharp peak at 3750 cm^{-1} corresponding to the free Si-OH stretching. Near-complete loss of the O-H band and the appearance of bands for the imide at $2800\text{-}3000 \text{ cm}^{-1}$ (CH stretching) and at 1443 and 1369 cm^{-1} (sulfonyl asymmetric and symmetric stretching) confirm attachment of the imide. The expected

CF₃ band was obscured by intense bands from the fumed silica. We are unable to observe the N-H stretch of the sulfonimide, a problem previously reported by others for similar systems. Jezorek et al. characterized alkyl amines bound to silica surfaces and they found it difficult to observe the amine stretch.¹³ Only after the amine was chemically modified did evidence of the amine become apparent. In a similar manner, the existence of the amine is supported by the appearance of a broad peak at 1470 cm⁻¹ after lithiation, which is attributed to the SO₂ asymmetric and symmetric stretches of the sulfonimide salt.^{14,15} We use a small molecule model, *N*-pentenylsulfonimide, to explore the deprotonation conditions. *N*-pentenylsulfonimide is reacted with *n*-butyllithium in toluene. As shown in Supporting Figure 2, the NH stretch at 3250 cm⁻¹ is lost upon reaction with *n*-butyllithium under these conditions. The ease in the formation of the bound sulfonimide salt assures the conditions we use here for deprotonation, we propose this same condition should also work well for the sulfonimide structure on particle surface.

Figure 2b shows TGA data for silica bare nanoparticles and Si-C5NHTf. The surface coverage of silanol groups on the silica nanoparticle is ~1.0 mmol/g.¹⁶ Assuming the alkyl sulfonimide is attached to the silica through each of the alkoxy groups, complete coverage of the nanoparticles with 0.33 mmol of imide (81 mg), would give modified silica with 7.9% of the mass as the bound imide. The extent of surface coverage can be probed by TGA experiments run in air. Assuming all decomposition products of the imide are volatile, the resulting weight loss should be at most 7.9%. The measured weight loss for the functionalized silica was 2.6 % corresponding to 36 % surface coverage, or 0.12 mmol/g silica (Figure 3). If each sulfonimide is converted to the corresponding lithium salt upon reaction with butyl lithium, then the maximum lithium carrier concentration in an electrolyte would be 7.2×10^{-4} g Li/g sample.

To experimentally quantify the lithium content in the synthesized Si-C5NTfLi, after TGA under air, lithium content in the TGA residue should be in the form of salts or metal oxides; both are water soluble and can be analyzed by Inductive Coupled Plasma (ICP) optical emission spectrometry. For the ICP analysis, the TGA residue are stirred in water for 12 hours, and filtered prior to the analysis, this combined TGA-ICP characterization gives lithium content of 1.2×10^{-3} g Li/g sample. This measured value is 1.7 times higher than the calculated lithium content. Presumably because there are three alkoxide groups in each alkyl sulfonimide molecule, we assumed all three alkoxide groups react with the silanol group on silica nanoparticle surface. In reality, as long as one or two alkoxide groups react with silanol, the alkyl sulfonimide molecule is already tethered on the particle surface.

O/Li ratio	425	320	230	185
Particle content (wt%)	18.5	23.6	30.0	35.0
Conductivity at 30 °C (S/cm)	1.3×10^{-6}	8.4×10^{-7}	1.2×10^{-6}	5.31×10^{-7}

Table 1. Particle weight content for electrolytes prepared from Si-C5NTfLi dispersed in PEGDME500.

Homogeneous electrolytes with various particle contents are prepared by vigorously stirring Si-C5NTfLi and PEGDME500. The movement of ions is directly coupled to polymer chain mobility, this behavior is thermally activated and is often described by Vogel-Tammann-Fulcher (VTF) equation (equation 1)^{17,18,19}

$$\sigma = \sigma_0 \exp(-E_a(T - T_0)) \quad (1)$$

Where is where σ_0 is the pre-exponential factor related to number of charge carriers, E_a is the apparent activation energy for ion transport, and T_0 is a parameter related to chain mobility of the polymer. For polymers, low T_g should correlate to fast relaxation and high conductivity. polyethylene glycol dimethyl ether (PEGDME500) is used as solvent to disperse the modified

silica particles. Electrolytes with low silica loadings (10 – 25 wt%) are pastes while higher loadings (30 – 50 wt%) are powders that become pastes upon shearing. The conductivity data for the samples appear in Table 1 and Figure 2c. The conductivities at 30 °C for the 19, 24, 30 and 35 wt% composites were $\sim 10^{-6}$ S/cm. The conductivities of the 10, 15, and 50 wt% composites could not be determined due to the low concentration of charge carriers (Li^+) in the case of the first two samples. For samples >45 wt%, the low conductivity stems from poor connectivity, i.e. the volume fraction of PEGDME500 is too low to be continuous throughout the electrolyte.

Lithium concentrations in polyether electrolytes are often expressed as the ratio of ether oxygen to lithium ion. For electrolytes prepared from binary lithium salts, the conductivity usually increases with decreases in the O/Li ratio, reaching a maximum at ~ 20 . For the current system, the O/Li ratios reported in Table 1 are an order of magnitude lower than the optimum O/Li ratio of 20. One concern with the measured conductivities is a potential contribution to the conductivity from residual silanols on the surface of the silica particle. These groups also should be lithiated under the conditions used to deprotonate the sulfonimide. To test for conductivity due to the silanols, silica bare particles are treated with *n*-butyllithium using the same protocol for the synthesis of Si-C5NTfLi. 30 wt% composite prepared from the lithiated silica and PEGDME500 is analyzed by impedance spectroscopy. The conductivity of the composite was $< 10^{-8}$ S/cm, the detection limit of the AC impedance analyzer. Thus we conclude that the contribution from lithiated silanols can be neglected. Electrolytes containing 19-35 wt% silica had conductivities of $\sim 10^{-6}$ S/cm. The ionic conductivity of each complex is similar and exhibited a weak dependence on temperature. The conductivities of the 10, 15 and 50 wt% composites were $< 10^{-8}$ S/cm, presumably due to

insufficient carriers in the case of the first 10 and 15 wt% composites, and discontinuity in the PEGDME500 polymer phase for the 50 wt% composite.

The ionic conductivity (σ) at a specific temperature is often expressed as

$$\sigma = n * q * \mu \quad (2)$$

Where n is the number of charge carriers per unit volume, q is charge of the carrier and μ is the mobility of the ions. At a specific temperature, the ionic conductivity of a polymer electrolyte is directly related to the number of charge carriers, the charge of the carrier, and mobility of the carrier (equation 1). Since the mobility of Li^+ should be constant in a homogeneous medium such as PEGDME500, we attempt to increase the conductivity by increasing the number of carriers. Increasing particle content causes discontinuity of the electrolyte materials without attaining high lithium content, because of this low lithium content conductivity data could not improve even at high temperature (Figure 2c). As for the particle system studied in this research, use the silica nanoparticles to carry more lithium content is important to improve the electrolyte conductivity.

Figure 3. Synthetic approach for silica nanoparticles grafted by lithiated poly(trifluoromethane sulfonic aminoethyl-methacrylate) (Si-TfMALi).

We move to a multilayer grafted silica nanoparticle, surface atom transfer radical polymerization (ATRP) could give a dense layer of polymer structures on surface. Figure 3 shows the proposed monomer structure trifluoromethane sulfonic aminoethylmethacrylate (TfMA) for a surface ATRP on the silica nanoparticles. Methacrylate structure of TfMA enables the monomer to be polymerized, the sulfoimide tail structure is a mimic of TFSI, upon polymerization and lithiation the polyelectrolyte on particle surface should be able to give high concentration of lithium cations. Polyelectrolytes anchored to particle surface offer multiple sites for anions, and in principle, the carrier concentration can be increased arbitrarily and approach the carrier concentration of the bulk polyelectrolyte. The synthetic route to initiator-decorated nanoparticles is shown in Scheme 5. Synthesis of the attachable 11-(2-Bromo-2-methyl)propionyloxy undecenyltrichlorosilane followed the procedure of Matyjaszewski et al.²⁰ One end of the organosilane is chemically bounded to the surface of silica particles as a monolayer through the reaction between the Si-Cl and surface silanol groups; the other end of organosilane works as initiator to trigger surface ATRP. *n*-Butyl lithium in dry toluene is used to lithiate the Si-TfMA to Si-TfMALi.

Figure 4. (a) TGA and (b) FTIR of the bare silica nanoparticles, Si-initiator, Si-TfMA, and Si-TfMALi. (c) Temperature dependent conductivity and (d) Conductivity at 20 °C for the Si-TfMALi mixed with PEGDME500 at various O/Li ratios.

Figure 4a shows TGA curves of TfMA monomer grafted silica particles from 120 °C to 900 °C. The samples are dried at 90 °C under vacuum before characterization. Since the data are obtained in air, all organic components of the samples are oxidized to CO₂ and H₂O, the residue components are silica particles and other nonvolatile inorganic species. The silica particles have a weight loss of 15 wt% at 800 °C, which includes adsorbed water, and water formed by condensation of surface bound silanols. After surface polymerization, the large weight loss of sample (62% for Si-TfMA) and (57% for Si-TfMALi) proved that surface polymerization was successfully conducted.

Figure 4b shows FT-IR spectra of the polyTfMA grafted particles at different stages. The IR spectrum of silica particles shows a characteristic broad band centered at ~790 cm⁻¹ associated with Si-O, and a strong and broad absorption band at 1150 cm⁻¹. After anchoring the ATRP initiator (11-(2-bromo-2-methyl) propionyloxy)undecyltrichlorosilane) to the nanoparticle surface,

a new band appeared at 1730 cm^{-1} (C=O) as the initiator. Further development of the peak at $980\text{-}1300\text{ cm}^{-1}$ and split of the peak from FT-IR spectra corresponds to S=O stretching, the sharp peak at $680\text{-}780\text{ cm}^{-1}$ was assigned to CF_3 stretching, both proved the polymer content on particle surface.

O/Li ratio	16	32	64	96	128
Particle content (wt%)	33.2	19.9	11.1	7.7	5.8

Table 2. Particle weight content for electrolytes prepared from Si-TfMALi (2.0×10^{-2} g Li/g sample) dispersed in PEGDME500.

Combined TGA-ICP characterization gives 2×10^{-2} g Li/g sample, this method enables us to quantitatively obtain the lithium content of polyelectrolyte grafted nanoparticles. Based on weight retention data from TGA, polyTfMA content on the silica nanoparticle could be obtained, lithiation efficiency is calculated based on the lithium content, which gives a value of around 80%. Table 2 shows particle weight content of Si-TfMALi for different O/Li ratios. With this high lithium content (2×10^{-2} g Li/g sample), we are able to get O/Li ratio to 32 and 16 without losing the continuity of the composite materials. This lithium cation concentration approaches the concentration in the bulk polyelectrolyte. Homogeneous electrolytes with various O/Li ratios are prepared by mixing polymer-grafted silica particles and PEGDME500. Figure 4c shows the temperature-dependent conductivity for electrolytes at different O/Li ratios. The conductivities extracted from the impedance spectroscopy data are roughly linear, consistent with thermally activated transport. Compared to Si-C5NTfLi (Figure 2c), conductivities for the multilayer grafted Si-TfMALi show a steep increase with temperature, from ambient temperature to around $90\text{ }^{\circ}\text{C}$, there is an increase of over an order. The room temperature conductivities of Si-TfMALi at different O/Li ratios plot in Figure 4d shows an increase in conductivity with the increase of O/Li ratio. After reaching a peak value of 10^{-6} S/cm at an O/Li of 32, the conductivity decreases. As the

Figure 5. (a) Temperature dependent conductivity for Si-C5NTfLi at O/Li 425 and Si-TfMALi at O/Li 32, both samples have particle weight fraction of around 19 wt%. (b) Proposed structural changes of monolayer Si-C5NTfLi (top) and multilayer Si-TfMALi (bottom) from room temperature to 80 °C.

Monolayer system has ambient temperature conductivity of around 10^{-6} S/cm, this value is in the same level upon increase of temperature to around 80 °C, since the monolayer structure only gives low lithium content, temperature increase does not help improve the conductivity based on this low lithium content. PolyTfMALi does not have a good solubility in PEGDME500, the multilayer system only has the outer layer of lithium ions accessible to the PEGDME500 solvent at room temperature and result in a similar conductivity data as the monolayer system. Increase of the temperature increases solubility of polyelectrolyte on particle surface, the inner part of the ionic species are able to enter the solution and contribute to conductivity, which give an order increase of conductivity to around 3×10^{-5} S/cm.

Conclusions

Two types of plasticized fume silica based polymer composite single ion conductors were successfully developed. Lithium bis(trifluoromethane) sulfonamide (TFSI) analogue structures are grafted on to silica nanoparticles as monolayer and multilayer structures. Electrolytes are prepared from the purified particles and polyethylene glycol dimethyl ether (PEGDME500). Optimum room temperature conductivities of both systems are around 10^{-6} S/cm, however, electrolytes made from monolayer grafted particles exhibit a weak dependence on temperature, ionic conductivity is still in the range of 10^{-6} S/cm when temperature increases to 80 °C; electrolytes made from multilayer grafted particles show a steep increase of conductivity with temperature. Increase of the temperature increases solubility of polyelectrolyte on particle surface, the inner part of the ionic species are able to enter the solution and contribute to conductivity, which give an order increase of conductivity to around 3×10^{-5} S/cm at 80 °C. The key to improve ion conducting

in a composite system is to improve the ion concentration and polymer chain flexibility next to the particles. The synthetic strategies can be used to improve conductivity in other polymer based electrolyte system.

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ABBREVIATIONS

C5NHTf, *N*-pentenyl trifluoromethane sulfonamide; Si-C5NHTf, silica nanoparticle grafted by *N*-pentenyltrifluoromethane sulfonamide; Si-C5NTfLi, silica nanoparticle grafted by lithiated *N*-pentenyltrifluoromethane sulfonamide; TfMA, trifluoromethanesulfonic aminoethylmethacrylate; Si-TfMA, silica nanoparticles grafted by poly(trifluoromethane sulfonic aminoethylmethacrylate); Si-TfMALi, silica nanoparticles grafted by lithiated poly(trifluoromethanesulfonic aminoethylmethacrylate); PEGDME500, polyethylene glycol dimethyl ether with Mw of 500 g/mol.

ASSOCIATED CONTENT

Supplementary Information

Detail about material synthesis and electrochemical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGEMENTS

This work was funded by the Assistant Secretary for Energy Efficiency, Vehicle Technologies Office of the U.S. Department of Energy (U.S. DOE) under the Advanced Battery

Materials Research (BMR) and Applied Battery Research (ABR) Programs, supported by the U.S. Department of Energy under Contract # DE-AC02-05 CH11231. Transmission electron microscopy was performed at the National Center for Electron Microscopy (NCEM), Soft X-ray scattering and analysis at the Advanced Light Source (ALS), and nuclear magnetic resonance spectroscopy (NMR) analyses at the Molecular Foundry—all located at Lawrence Berkeley National Laboratory and supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under contract no. DE-AC02-05CH11231.