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Fumed Silica-based Single-ion Nanocomposite Electrolyte

for Lithium Batteries

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Abstract: A composite lithium electrolyte composed of polyelectrolyte-grafted nanoparticles and polyethylene glycol dimethyl ether (PEGDME) is synthesized and characterized. Polyanions immobilized by the silica nanoparticles have reduced anion mobility. Composite nanoparticles grafted by poly(lithium 4-styrenesulfonate) only have moderate conductivity of at 60 $^{\circ}$C. Almost an order increase of the conductivity to ~10^{-6} S/cm is achieved by copolymerization of the poly(ethylene oxide) methacrylate with sodium 4-styrene sulfonate, which enhances dissociation between lithium cation and polyanion and facilitates lithium ion transfer from inner part of the polyelectrolyte layer. This composite electrolyte has the potential to suppress lithium dendrite growth and enable the use of lithium metal anode in rechargeable batteries.

Keywords: polymer-grafted silica nanoparticle, transference number, solid-state electrolyte, lithium battery, poly(ethylene oxide)

Introduction

Lithium ion batteries (LIBs) have enabled the development of a variety of portable electronic device, stationary grid-energy storage components, and hybrid/electric vehicles.[1,2] However, the low energy density of LIBs has been the bottleneck for the replacement of internal combustion vehicles by battery-powered electric vehicles.[3,4,5,6] Lithium metal is the most promising anode for a rechargeable battery, with a theoretical capacity of 3860 mAh/g, which 10 times larger than the state-of-art graphite anode (372 mAh/g).[7] The successful application of lithium metal anode will also open up the opportunities for other high-energy chemistries such as lithium air (O_2) and lithium sulfur batteries. Also, from the perspective of manufacturing, the ductile lithium metal is promising for a large scale production as battery anode materials.[8] Thus, a reliable rechargeable lithium metal battery has attracted attention from both academia and industry. However, the use of liquid electrolyte in contact with the lithium metal leads to irregular electrodeposition of metallic lithium, this causes serious hazardous issues.[9,10] Zhang *et al.* showed that the use of selected cations such as cesium or rubidium ions were able to force the deposition of lithium to adjacent regions of the lithium metal anode and eliminate dendrite formation.[11,12] Cui *et al.* deposited a monolayer of interconnected amorphous hollow carbon nanospheres, which isolated the lithium metal depositions and enabled the formation of a stable solid electrolyte interphase (SEI).[13]

Solid-state polymer electrolyte (SPE) with high mechanical modulus and high lithium transference number, on the other hand, proposes a promising solution to prevent the lithium dendrite formation and potentially address safety issues related to the use of liquid electrolytes.[14] Chazalviel proposed that electrolytes with high conductivity and reduced anion mobility could suppress the growth of lithium dendrite, which help avoid the decreased concentration gradient of

the electrolyte.[15] Polyethylene oxide (PEO) with dopant lithium salts, such as $LiPF_6$,[16] LiBOB,

$LiCF_3SO_3$ and $Li[N(SO_2CF_3)_2]$ (LiTFSI),[17] have been widely used as solid polymeric electrolytes.

Mobile ions generated from these dopant salts have typical lithium transference number (t_{Li+}) of

0.1~0.3, anion is the dominant species in the ionic conductivity of lithium electrolytes.[18] An

effective approach of increasing lithium transference number is to chemically attach the anions on

the polymer backbone and limit anion mobility. Structurally this material contains only one

mobile charge, which is the lithium cation dissociated from the anion.[19,20,21,22,23] Previously,

monolayer of anions were attached to the surface of silica nanoparticle.[24,25] Silica polymer

composite also has better mechanical property than that of the pure PEO.[26,27] However, decorating

particle surfaces with a monolayer of anions provides too few anions to support high conductivity

in a bulk electrolyte (O/Li ratio = 120).

An alternative approach to increasing anion concentrations is to move from monolayer coverage

of particles to polyelectrolytes anchored to the fumed silica particle surfaces (Figure 1). In

principle, growing polymers from particle surfaces, especially by controlled polymerization

methods, such as Atom Transfer Radical Polymerization (ATRP), will increase the carrier

concentration near the carrier concentration of the bulk polyelectrolyte. The research described in

this manuscript focuses on nanoparticle systems where lithium counter anions are immobilized on

polyelectrolytes grown from nanoparticles. A low-molecular weight (M_w=500 g/mol) polyethylene

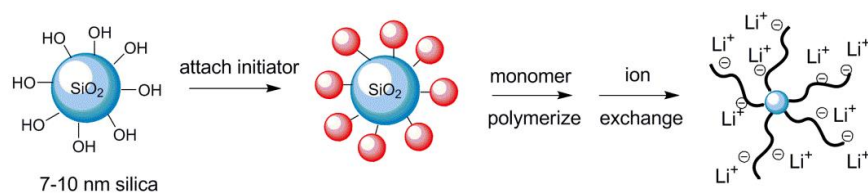glycol dimethyl ether (PEGDME) is used for lithium ion transport.

Figure 1. Synthetic approach for polyelectrolyte-decorated nanoparticles.

Results and discussion

Silica nanoparticles modified with lithium 4-styrenesulfonate (Si-PSSLi) The synthetic route to initiator-decorated nanoparticles (Si-I) is shown in Figure 2a. Synthesis of the attachable 11-(2-Bromo-2-methyl)propionyloxyundecenyltrichlorosilane followed the procedure of Matyjaszewski *et al*.[28] The bromoisobutyryl structure is chemically bounded to the surface of silica particles, which is a very good initiating structure to trigger surface ATRP.[29,30,31]
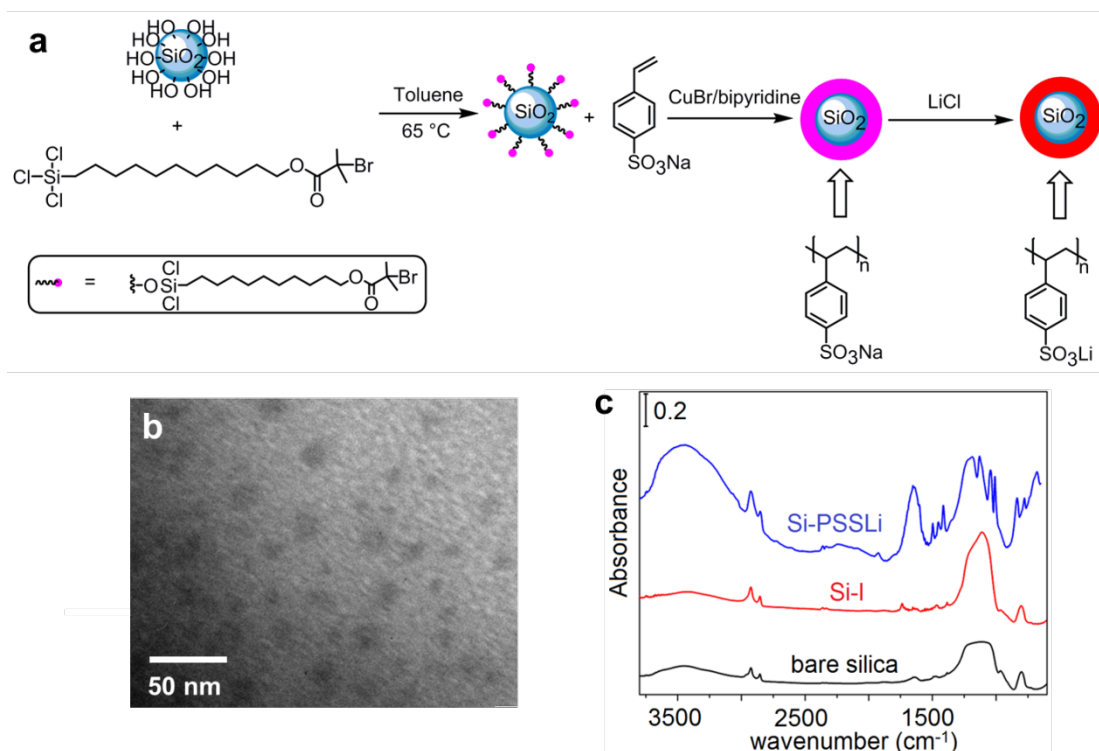

Figure 2. (a) Surface ATRP of sodium 4-styrenesulfonate on silica particle (Si-PSSNa) and lithiation to Si-PSSLi. (b) TEM image of Si-PSSLi, (c) FTIR spectra of bare silica nanoparticles, Si-Initiator and Si-PSSLi.

Surface ATRP uses CuBr/bipyridine catalyst, poly(sodium 4-styrenesulfonate) brushes are grown from nanoparticles at room temperature. The poly(sodium 4-styrenesulfonate) modified particles (Si-PSSNa) are converted to the corresponding Li^+ salt (Si-PSSLi) by reaction with lithium chloride solution (Figure 2a). TEM image of Si-PSSLi (Figure 2b) shows that the particle diameter increases to 15~20 nm, compared to bare silica particles with 7~10 nm diameter. TEM characterization also shows that there is no significant aggregation of the particles.

Figure 2c shows FTIR spectra of the synthesized materials at different stages. The IR spectrum of bare silica particle 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}. In addition, there are C-H stretching bands at 2800~3000 cm^{-1} associated with cetyltrimethyl ammonium bromide (CTAB).[32,33] 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 displaced the CTAB. The silica nanoparticles are received as well dispersed in water solution, a surfactant such as CTAB is necessary to precipitate the silica particles, thus a monolayer of CTAB might cover the particle surface, which is difficult to wash off. The IR spectrum of the poly(lithium 4-styrenesulfonate) brushes showed strong bands associated with the sulfonate group (S=O stretching, 1250, 1125 cm^{-1}) overtone/combination bands (1920 cm^{-1}) consistent with a 1,4-disubstituted aromatic ring, and a significant increase in the C-H stretching bands (2800~3200 cm^{-1}). These data confirm successful growth of the polyelectrolyte from the surface.
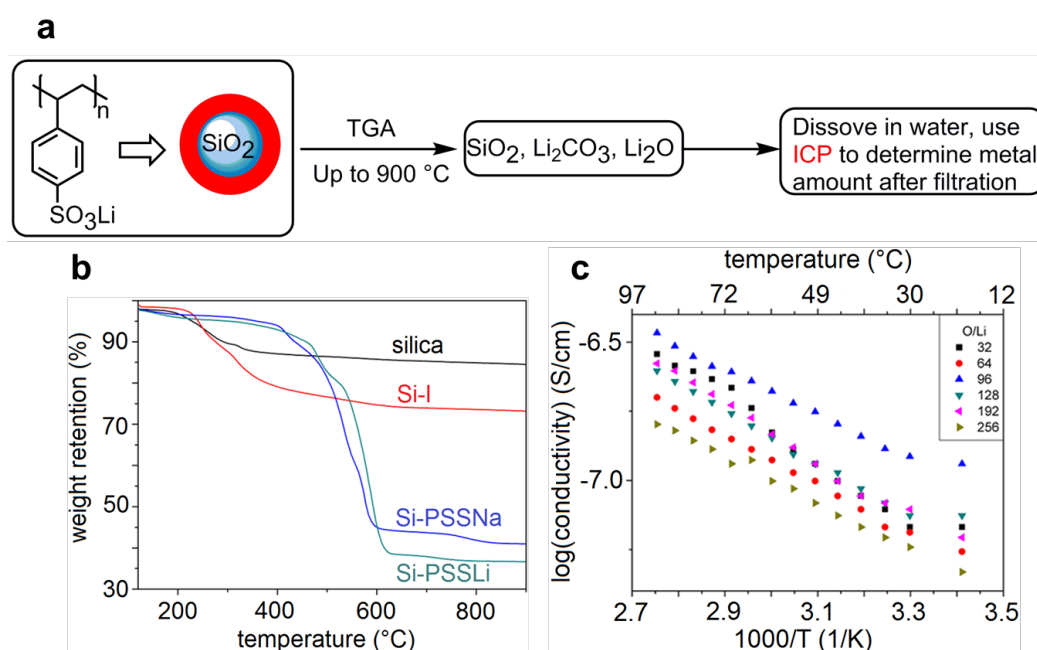
Figure 3. (a) Schematic description of the combined TGA and ICP technique to quantitatively characterize the lithium content in the polyelectrolyte-modified silica nanoparticles, (b) TGA of bare silica nanoparticles,

Si-Initiator and Si-PSSLi, and (c) plots of conductivity as a function of inverse temperature for Si-PSSLi/PEGDME electrolytes at various O/Li ratios.

Figure 3b shows TGA curves for the synthesized composite material at different stages from 100 °C to 900 °C. Since the data are obtained in air, all organic components of the samples are oxidized to CO_2 and H_2O, the residual components are silica particles and other nonvolatile inorganic species. The bare silica particles have a weight loss of 15 wt% at 800 °C, which includes the loss of the CTAB surfactant residue, adsorbed water, and water formed by condensation of surface bound silanol groups. Assuming 10 nm diameter spherical SiO_2 particles (ρ=2.6 g/cm^3) with a surface area of 300 m^2/g, a close packed monolayer of CTAB (cross section of 0.8 nm^2) the expected mass loss due to CTAB is 16.5 wt%. A similar calculation for the initiator-modified particles predicts a weight loss of 15.1 wt%, assuming 0.6 nm^2/initiator chain,[17] although the actual weight loss for Si-initiator is higher at 27 wt%. After growing poly(sodium 4-styrenesulfonate) from the particles, the weight loss increases to 64 wt%. After lithium exchange, the weight loss increase to 72 wt%, consistent with the lower atomic weight of lithium.

Quantitative analysis of the TGA residue for lithium content provides an estimate of the number of anions bound to the nanoparticles (Figure 3a). Lithium in the TGA residue should be in the form of salts or metal oxides (Li_2O, Li_2O_2, etc.), which 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 DI water for 12 hours, and filtered prior to the analysis. ICP analysis of the TGA residue from a 6.6 mg Si-PSSLi sample give 0.16 mg lithium, which corresponds to 2.4×10^{-2} g Li/g sample. The data indicate that more than 95% of the Na ions are exchanged with Li ions, this enables formation of electrolytes with lithium content as high as 32/1 without excessive amount of the inorganic particles in the Si-PSSLi/PEGDME composite. This lithium content is

one to two orders higher than previous work with monolayer of anions on the nanoparticles surface. By grafting polyanions on the nanoparticles, the samples contain high lithium content, we expect a good conductivity from this system. This combined TGA-ICP characterization method enables us to quantitatively characterize the lithium content of polyelectrolyte grafted nanoparticles.

Homogeneous electrolytes with various O/Li ratios are prepared by dispersing polyelectrolyte-grafted silica nanoparticles in PEGDME. Figure 3c shows the Arrhenius plot of conductivities for the electrolytes at different O/Li ratios. With the initial addition of polyelectrolyte-modified silica nanoparticles into PEGDME, the conductivity is limited by the concentration of Li^+, thus the conductivity increases with the increase of Si-PSSLi. However, when the Si-PSSLi exceeded particular amount, there are too much inorganic particles in the polymer matrix, not all the lithium sources can be fully used, the composite also starts losing continuity. That causes the decrease of the conductivity. The conductivities extracted from the impedance spectroscopy data are roughly linear, consistent with thermal activated transport. 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[34,35,36]

$$\sigma = \sigma_0 \exp\text{-}E_a(T\text{-}T_0)$$

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. Typically lithium transport is only limited to the amorphous regions. PEO, as most widely used polymer electrolyte host, is featured for its high crystallization degree in solid state.[37] To avoid the influence of the PEO crystalline and facilitate study of polyelectrolyte-grafted silica nanoparticle/PEO system, we

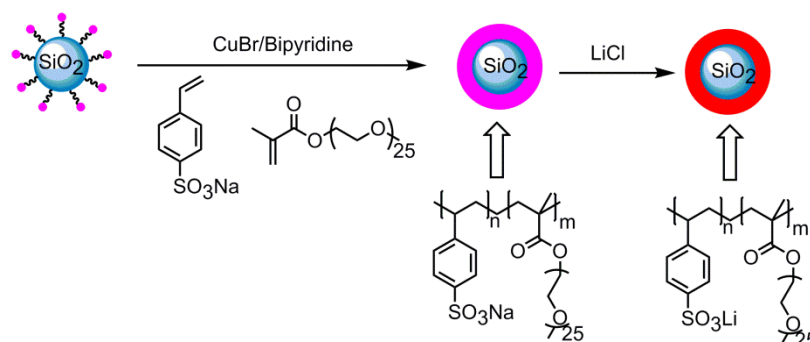use PEO oligomer, which is in liquid state and does not have any crystallization region in the material.

Figure 4. Copolymerization of sodium 4-styrenesulfonate and PEGMA from silica nanoparticles (Si-PSSNa- PEGMA) and lithiation to Si-PSSLi-PEGMA.

Silica nanoparticles modified with lithium 4-styrenesulfonate and PEGMA (Si-PSSLi-PEGMA) Conductivities of the composite electrolyte based on Si-PSSLi at 60 ^{o}C are in the range of 10^{-7} S/cm, the highest value is 2.2×10^{-7} S/cm with O/Li of 96. The ionic conductivity of the composite electrolyte is much lower than expected. It is proposed that with a dense polyelectrolyte brush on the nanoparticles surface, most of the lithium ions are trapped in the inner part of the polyelectrolyte and not contribute to the overall conductivity. Yameen et al. grew brushes from a mixture of oligo(ethylene glycol) and 2-sulfoethyl methacrylate,[21] they obtained a 10^{5} increase of the proton conductivity, which was ascribed to the hygroscopic oligo(ethylene glycol) chains. In a similar study, Schaefer et al. functionalized silica nanoparticle with polyethylene glycol (PEG) and sulfonate groups.[15] It is proposed that the tethered PEG functionalities could increase dissociation between lithium cation and sulfonate anion and improve solubility of the functionalized nanoparticles in tetraglyme solvent. In our study, diluting the sodium 4-styrenesulfonate phase with poly(ethylene glycol) methyl ether methacrylate (PEGMA) facilitates lithium ion transport, adding PEG chains to the particles could also improve the interface between the particles and the PEGDME host. To test these hypothesis and increase the

conductivity, we copolymerize PEGMA (M_n=1,100) with sodium 4-styrenesulfonate from the particle surface (Figure 4). The procedure for the surface-initiated copolymerization is similar to those used for the homo-polymerization of sodium 4-styrenesulfonate. The molar ratio of sodium 4-styrene sulfonate to PEGMA monomers is 3/1, which corresponds to a polyelectrolyte with an O/Li ratio of 8/1. The ratio of the two monomers added to the particles can be calculated, since TGA provides the mass fraction of the organic phase on the particles, and ICP allows an estimate of the number of styrene sulfonate groups. The calculated value, 3.45/1, is close to the 3/1 feed ratio. Compared to styrene derivatives, methacrylate monomers have higher reactivity towards radical polymerization. However, the long PEG chain in PEGMA reduces the reactivity, thus we are able to obtain a copolymer structure on the nanoparticle surface. Lithium exchange of Si-PSSNa-PEGMA was carried out using the same procedure as Si-PSSNa (Figure 4). The combined TGA-ICP analysis shows that lithiation efficiency is higher than 90% for different batches of materials. The Si-PSSLi-PEGMA sample used for making electrolytes has a lithium content of 1.6×10^{-2} g Li/g sample.
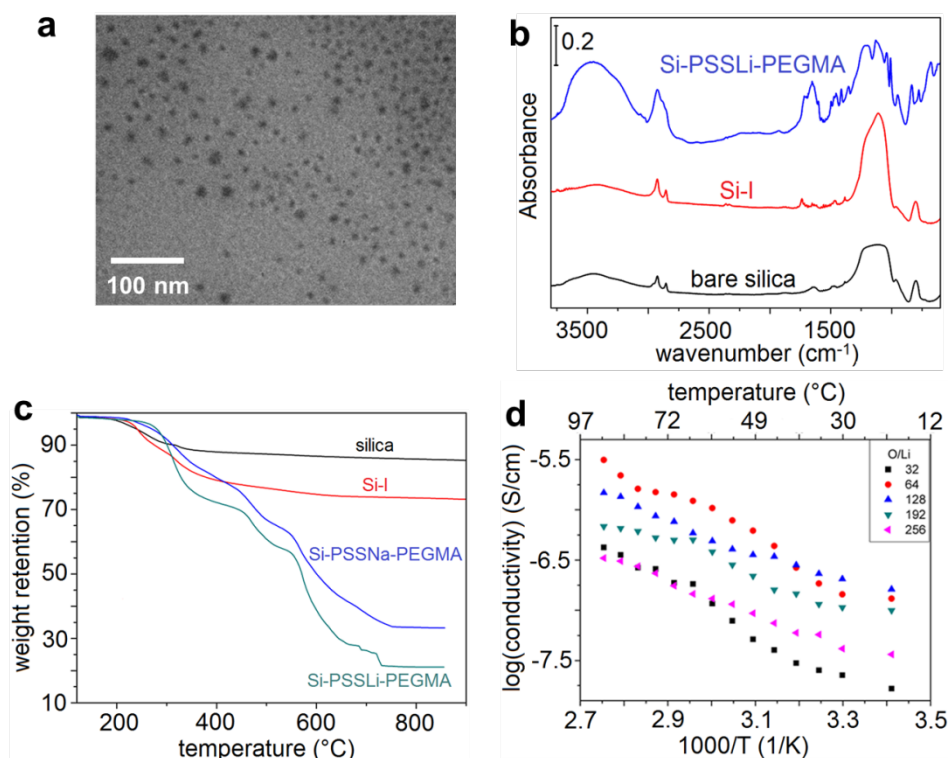
Figure 5. (a) TEM image of Si-PSSLi-PEGMA, (b) FTIR spectra and (c) TGA of bare silica nanoparticles, Si-Initiator and Si-PSSLi-PEGMA, (d) plots of conductivity as a function of inverse temperature for Si-PSSLi-PEGMA/PEGDME electrolytes at various O/Li ratios.

The TEM shows particles with ~15 nm diameter (Figure 5a). IR spectrum of Si-PSSLi-PEGMA is shown in Figure 5b, signals correspond to PEG side structure are in the range of 1000~1200 cm^{-1}, which overlap with PSSLi signals. Figure 5c clearly shows that polyelectrolytes are grown from nanoparticle surface, based on the considerable increase of weight loss. Since the PEGMA monomer used here has a molecular weight of ~1,100, after copolymerization the composite nanoparticles have an increased organic component. TGA curves in Figure 5c shows that Si-PSSNa-PEGMA has a weight loss of around 67% and Si-PSSLi-PEGMA has a weight loss of around 80%, compared to weigh loss of 64% for Si-PSSNa and 72% for Si-PSSLi. Figure 5d shows that the conductivities of the composite electrolytes based on Si-PSSLi-PEGMA increase with temperature. For Si-PSSLi-PEGMA, the highest conductivity at 60 $^{\circ}$C is 1.3×10^{-6} S/cm at O/Li = 64, this value is almost an order higher than the composite electrolytes prepared from pure

Si-PSSLi particles (2.2×10^{-7} S/cm). A proposed model in Figure 6 is used to explain the difference between Si-PSSLi and Si-PSSLi-PEGMA.

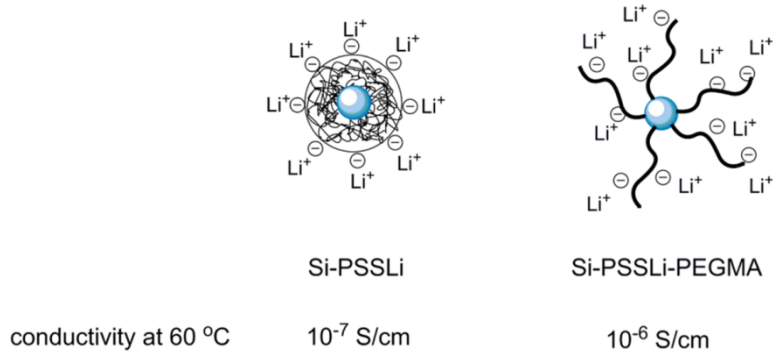|	Si-PSSLi	Si-PSSLi-PEGMA
conductivity at 60 °C	10^{-7} S/cm	10^{-6} S/cm

Figure 6. A proposed model for structural difference of Si-PSSLi and Si-PSSLi-PEGMA dispersed in PEGDME.

In the case of Si-PSSLi, polyelectrolyte itself does not have a good solubility in oligomer PEO, most of the polymer chains are collapsed on the nanoparticle surface, only the lithium cations in the outmost part could access the solvent and contribute to the conductivity, that is why conductivity of Si-PSSLi is very low. PEGMA, on the other hand, has a long side chain with 25 repeating units of PEO, the bulky side group are solvated by the solvent, which is oligomer PEO. The function of this structure is two-fold, first, it helps to expand the dense polyelectrolyte brush on the nanoparticle surface, lithium ions inside the polyelectrolyte layer gain excess to the oligomer PEO solvent and contribute to the conductivity. Second, this long side chain on PEGMA also facilitates lithium ion mobility. We use AC Impedance Spectroscopy to measure the ionic conductivity of synthesized electrolyte materials, thus the reported conductivity data here are contributed by all the ions in the electrolyte material. Previous model study indicates a polymer electrolyte with high lithium transference number holds great promise in preventing lithium dendrite formation.[38,39] The polyelectrolyte-grafted silica nanoparticles synthesized in this work represents a potential candidate that could enable the use of lithium metal in the rechargeable batteries.

Conclusions

Nanocomposite lithium electrolytes are obtained by dispersing polyelectrolyte-grafted silica nanoparticles in oligomer PEO. A combined TGA-ICP characterization method enables us to quantitatively obtain the lithium content of polyelectrolyte-grafted nanoparticles, this lithium value is much higher compared to previous study with monolayer anion-grafted nanoparticles. Si-PSSLi gives moderate conductivity at 60 ^{o}C because of the poor solubility of polyanions in the solvent. Si-PSSLi-PEGMA has PEGMA, with a long PEO side chain in the polymer backbone, there is an order increase of the conductivity to ~ 10^{-6} S/cm. Other polyelectrolyte and anion structures that give better dissociation of ions could potentially improve the conductivity. Also, the use of other solvents with high dielectric constants, such as ethylene carbonate ($\varepsilon \approx 90$), propylene carbonates ($\varepsilon \approx 65$) and ionic liquids, should further improve the conductivity.

Abbreviations

PEGDME, polyethylene glycol dimethyl ether with M_w of 500 g/mol; PEGMA, poly(ethyleneoxide) methacrylate; Si-PSSLi, silica nanoparticles grafted with poly(lithium 4-styrenesulfonate); Si-PSSLi-PEGMA, silica nanoparticles grafted with co-poly(lithium 4-styrenesulfonate)-PEGMA.

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Notes

The authors declare no competing financial interests.

Acknowledgement

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TOC

7-10 nm silica

attach initiator

monomer polymerize

ion exchange