Short communication

Single-ion conductors for lithium batteries via silica surface modification

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Abstract

Single-ion conductors (SICs) have been prepared by free-radical polymerization of sulfonic acid-containing monomer on high-purity silica surface that was first tailored with unsaturated functionality using a silanation reaction. It was found that steric effects limited polyelectrolyte surface loading even when large amount of silane molecules were grafted by forming a cross-linked structure. The results indicate that large surface area is an important factor to achieve high-surface loading of ionic moieties. Composite electrolytes were prepared by dispersing these SICs in aprotic solvents. The effects of filler content and solvent on ionic conductivity were investigated.
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1. Introduction

Invented in the early 1990s and widely used as power sources for portable electronic devices such as laptops and cellular phones, rechargeable lithium ion batteries have attracted much attention and research; however, there remain deficiencies in lithium ion battery technology that need to be addressed, including unsolved drawbacks of electrolytes. Low lithium-ion transference number is an issue because of the resultant concentration polarization, especially when the local viscosity is high (such as in polymer electrolytes), and the impedance to ion transport that would occur as a consequence [1]. Advanced rechargeable lithium batteries are considered the most promising energy-storage devices for electric vehicles (EVs) and hybrid electric vehicles (HEVs) [2]; therefore, large lithium-ion transference number is desired since otherwise concentration polarization limits the value of the current and thus the power density of the battery [3]. Usually a large lithium-ion transference number can be achieved by immobilizing the anions, so-called single-ion conductors (SICs) [4], for example attaching those anions to polymer chains [5].

It is known that the addition of inorganic particles, e.g. $LiAlO_2$, Al_2O_3, TiO_2, and SiO_2, can improve the electrochemical and mechanical performance of electrolytes [6], such as increasing conductivity and lithium-ion transference number [3], depressing the crystallization of the polymer matrix [7], enhancing the cycle life and rate capability, helping form a passivation layer on lithium metal electrode [8], and inhibiting the growth of lithium dendrites [9].

In this work, high-purity silica particles, the precursor of Sumitomo Electric Industries (SEI) silica fiber, was employed as an inorganic matrix for preparation of SICs. As shown in Fig. 1, the silica surface was first tailored with methacryl groups using a silanation reaction, followed by free-radical polymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), and SICs are obtained after exchanging the acidic H^+ with Li^+. Since trichloro-silane was used as the silanation agent, after reaction with the silica surface two chloro-functionalities may remain that can be hydrolyzed to silanol and undergo

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Table 1
Sulfur analysis results of SICs prepared by different silanated silica

Entry	TGA weight loss (%)		Sulfur content (ppm)	Li$^+$ content[b] (mmol g^{-1} silica)
	Silanation	Polymerization[a]		
4-h	0.64	1.88	3505	0.109
15-h	0.96	2.54	4480	0.140
Cross-linked	7.92	3.92	5212	0.163

[a] Calculated by subtracting the weight loss of silanated silica from silica-pAMPS.
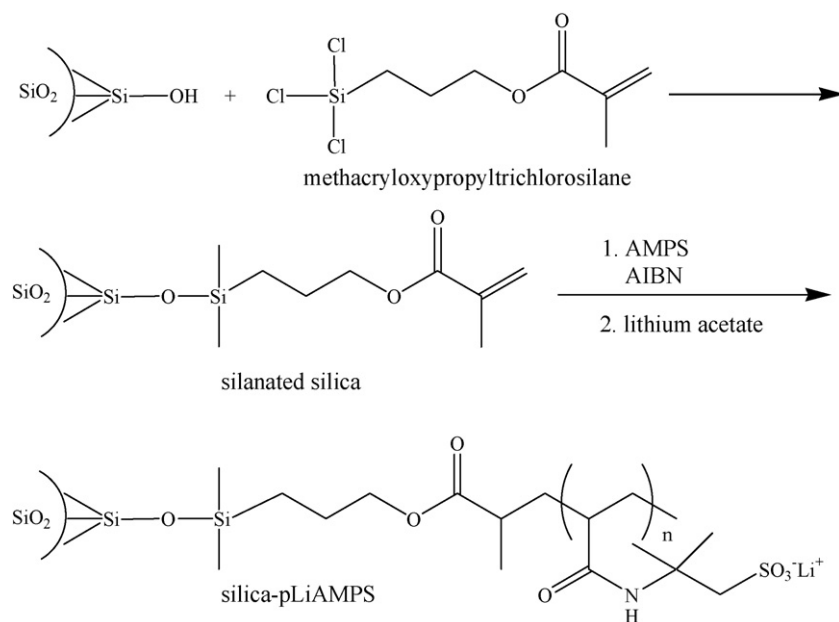[b] Calculated from sulfur content based on the stoichiometry of –SO$_3$Li.

Fig. 1. Scheme of the preparation procedure of single-ion conductors (SICs).

further silanation reaction. This results in a cross-linked structure of silanation moieties on the silica surface, depicted in Fig. 2, that provides an increased surface loading of methacryl groups. In this work, monolayer and cross-linked surface silanated silica samples were prepared and used to carry out the follow-on free-radical polymerization. It was found that the resulting polymer chain growth did not increase proportionally to the surface methacryl group loading due to steric effects.

2. Experimental

The silica used in this work was ultra-high purity silica powder obtained from SEI, which is prepared by reacting SiCl$_4$ in an oxy-hydrogen flame and has a typical particle surface area of 20 m^2 g^{-1}.

The SEI silica was washed with 1.8 M H$_2$SO$_4$, dried under vacuum overnight, and dispersed in anhydrous pentane in the presence of triethylamine followed by the addition of methacryloxypropyltrichlorosilane (Gelest). To obtain monolayer coverage silanated silica, the dispersion was reacted under stirring for 4 or 15 h, and centrifuged to remove the pentane solution. The solid was rinsed with methanol/pentane = 1/1 (v/v) mixture four times, and dried under vacuum overnight at room temperature. The two silanation reaction times provided different surface grafting of silane. To obtain cross-linked surface silanated silica, the dispersion was reacted overnight, centrifuged to remove the pentane solution, and dried under vacuum at 120 °C for two days to cure the surface cross-linking process. The solid was then rinsed with methanol/pentane = 1/1 (v/v) mixture four times, and dried under vacuum overnight. The
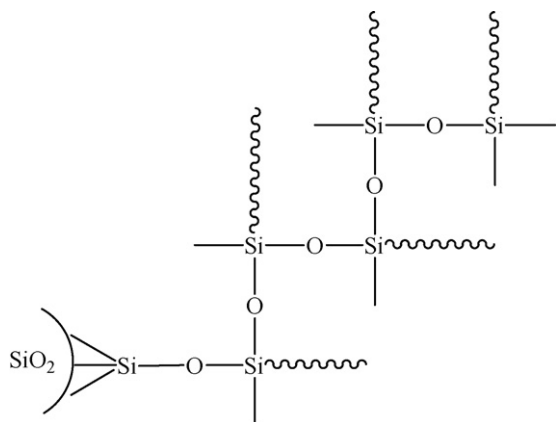

Fig. 2. The cross-linked structure formed by trichloro-silane.

surface-grafted amounts were characterized by thermogravimetric analysis (TGA).

Free-radical polymerization of silanated silica with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, Aldrich) was carried out in *N,N*-dimethylformamide (DMF, Aldrich) at 65–70 °C overnight in the presence of the initiator 2,2′-azobis(2-methylpropionitrile) (AIBN, Aldrich). Weight ratio of silica:AMPS was 15, and the AIBN content was 0.5 wt% of AMPS. After completion of reaction, the solid product was washed with deionzed water three times to remove the unattached polymer, polyAMPS, and unreacted AMPS to yield polyAMPS-grafted silica particles (silica-pAMPS). Finally, poly(AMPS, lithium salt)-grafted silica (silica-pLiAMPS) as SICs were obtained by dispersing silica-pAMPS in 0.1 M lithium acetate (Aldrich) aqueous solution, followed by washing with methanol three times and drying under vacuum at 100 °C for at least 3 days. TGA determined the surface grafting after polymerization, and elemental analysis of sulfur, using inductively coupled plasma (ICP) emission spectroscopy, determined the content of $-SO_3^-$ moieties, and thus Li^+ content.

FTIR spectra were recorded using a Nicolett Magna-IR 750 spectrometer under dry air purge (DGTS detector, 4 cm^{-1} resolution, 254 scans); a thin layer of silica sample was sandwiched between two KBr windows.

Polyethylene glycol dimethyl ether (PEGdm, MW 250, Aldrich), polyethylene oxide (PEO, MW 20k, Aldrich), and propylene carbonate (PC, Aldrich) were used as solvents for electrolyte preparation. Before use, PEGdm and PC were dried over 4 Å molecular sieves for at least 1 week, and PEO was dried under vacuum at 60 °C for 1 week. When PEGdm or PEGdm/PEO (3:1 w/w) blend was used as solvent, silica-pLiAMPS particles were ultrasonically dispersed in a 10 wt% anhydrous acetonitrile (Acros) solution of PEGdm and/or PEO, and dried under vacuum at 90 °C for 1 week to remove acetonitrile. When PC was used as solvent, silica-pLiAMPS particles were directly dispersed in PC.

Ionic conductivity was measured using electrochemical impedance spectroscopy (EIS). An EG&G Princeton Applied Research 273 potentiostat and an EG&G 5210 lock-in amplifier were used and controlled by the EG&G PowerSuite software. The conductivity cell with two platinum electrodes is described elsewhere [10].

3. Results and discussion

Typical TGA results for the methacryl-functionalized silica (silanated silica) and polyelectrolyte-grafted silica (silica-pAMPS) are given in Fig. 3. Organic moieties on the silanated silica started decomposing above 400 °C; whereas the polyelectrolyte moities on the silica-pAMPS samples decomposed in a lower temperature range (200–350 °C), and the weight loss above 400 °C was nearly identical to their silanated silica precursors. Based on the TGA weight loss and the assumptions that the surface area of SEI silica is 20 m^2 g^{-1} and the weight loss is from the decomposition of the organic moiety of the silane, the grafted silane number density of the three silanated silica samples, 4-h, 15-h and cross-linked, were 1.5, 2.3, and 20 silane nm^{-2},
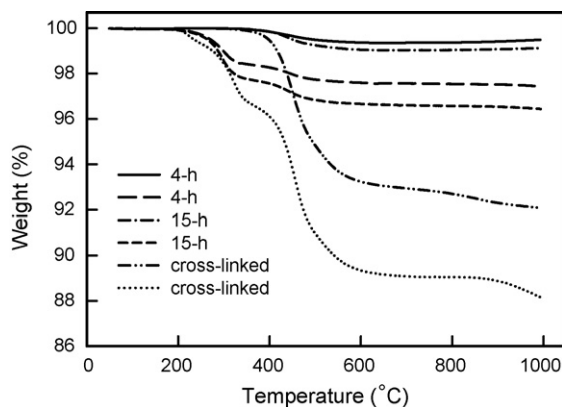

Fig. 3. TGA curves of silanated silica and silica-pAMPS samples. The silanation reaction time is indicated for the non-cross-linked samples. For each similarily labeled pair, the top line represents data for silanated silica and the bottom represents data for silica-pAMPS.

respectively. These results agree with our monolayer coverage and cross-linked structure hypothesis, as the silanol density of amorphous silica, when the surface is fully hydroxylated, is about 4–5 OH nm^{-2} [11]. If the silane-modified silica surface formed as a monolayer, the follow-on polymerization-produced surface loading of polyelectrolyte is proportional to the starting silane coverage, as indicated by the TGA results of 4- and 15-h silanation reactions. However, if the silane molecules formed a cross-linked structure on the surface, the silane surface loading would be approximately 10 times as much, compared with the 15-h monolayer silanation. But the polymerization only produced about 1.5 times as much polyelectrolyte, which is not a proportional increment. A reason for this lower-than-expected loading can be attributed to steric effects that limit the accessibility of grafted methacryl groups in the cross-linked structure and the growth of polymer chains. Elemental analysis (Table 1) shows that the sulfur content of samples is related to their TGA weight losses: the sulfur content for the monolayer coverage samples 4- and 15-h is proportional to the weight losses contributed by polymerization.

FTIR spectra (Fig. 4) of SEI silica, silanated silica, and silica-pAMPS provide evidence for successful surface modification. The 1717 and 1636 cm^{-1} vibrations of silanated silica are due to C—O and C—C, respectively, in methacryl groups. After poly-
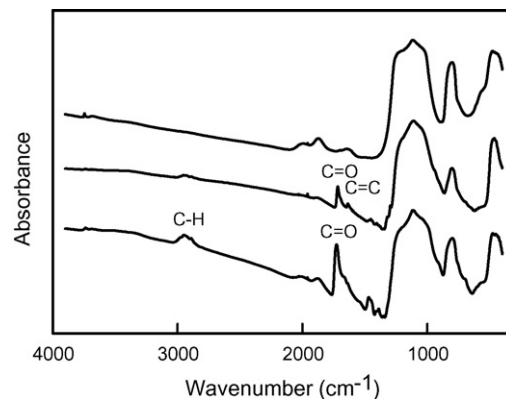

Fig. 4. FTIR spectra (top to bottom) of silica, silanated silica, and silica-pAMPS.
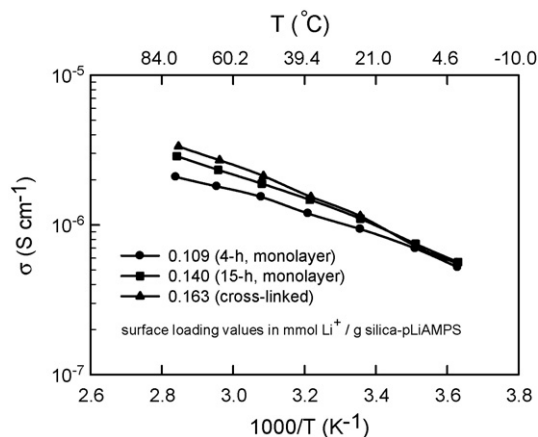
Fig. 5. Effect of surface Li$^+$ content on the conductivity of composite electrolytes. All electrolytes were 7.5 wt% silica-pLiAMPS in PEGdm.
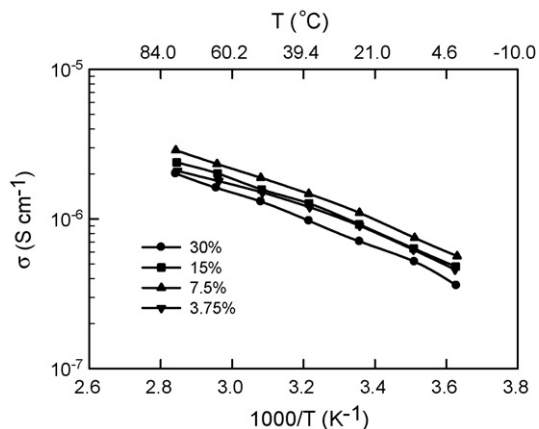

Fig. 6. Temperature dependence of ionic conductivity of composite electrolytes with various filler content of 15-h silica-pLiAMPS in PEGdm.

merization of AMPS on the surface, the C—C band disappears and subsequently a strong C—O vibration at 1727 cm^{-1} is evident.

Fig. 5 shows the temperature dependence of ionic conductivity of three different polyelectrolyte surface loadings. All electrolytes were prepared by dispersing 7.5 wt% of silica-pLiAMPS particles in PEGdm. The 15-h silanation reaction achieved higher silane coverage than the 4-h reaction and produced higher pLiAMPS loading. Consequently, the ionic conductivity of the higher Li$^+$ content electrolyte was greater than that of the lower one. The cross-linked surface had higher Li$^+$ content compared with monolayer coverage silanated samples; however, the conductivity did not demonstrate a significant increment, as might be anticipated, which may be attributed to the cross-linked structure hindering Li$^+$ diffusion and transport. At temperatures below 20 °C, the conductivity of cross-linked sample was even lower than the15-h sample, and only at higher temperatures did the conductivity become slightly greater of the two. These temperature dependencies agree with a previous study [12], i.e., only with increasing temperature does the number of charge carriers play a more important role.

Composite electrolytes are prepared by dispersing silica-pLiAMPS particles in a solvent. The filler (i.e., particles) content will affect the following factors: (i) the number of charge carriers; (ii) the volume fraction of the ionically conductive domain (the dilution effect of non-conductive silica) [12,13]; (iii) the viscosity of the resultant electrolyte. Ion conduction in the composite electrolyte is comprehensively affected by all three factors. Fig. 6 shows the temperature dependence of ionic conductivity of 15-h silica-pLiAMPS + PEGdm composite electrolytes at various filler content. The ionic conductivity increases with filler content as more lithium ion are added up to 7.5 wt% but the conductivity decreases at greater filler content. The decrease of conductivity may be ascribed to poor particle dispersion or formation of an overly tortuous path because of high particle loading. The highest room-temperature conductivity, 1.1×10^{-6} S cm^{-1}, was obtained at the filler content of 7.5 wt%.

Composite electrolytes were also prepared incorporating 15-h silica-pLiAMPS particles in PEGdm/PEO, PEGdm, and PC, and the temperature dependence of the ionic conductivity in different solvents is presented in Fig. 7. PC has a high-dielectric constant, ~65 [14], and as a small molecule solvent, a relatively low viscosity, whereas the dielectric constant of PEGdm oligomers typically range from 8 to 13 [15]; high-Mw PEO has dielectric constant of about only 5 [16]. In addition, PEO is a high-MW polymer and semicrystalline at room temperature. Therefore, among these three solvents, PC has the highest dielectric constant and the lowest viscosity. In contrast, the PEGdm/PEO blend has the lowest dielectric constant and the highest viscosity. It is known that a solvent with high-dielectric constant and low viscosity will intrinsically produce high-ionic conductivity, which is also demonstrated by our results: electrolytes in PC solvent had the highest conductivity, 3.0×10^{-6} S cm^{-1} at room temperature, and PEGdm/PEO solvent had the lowest, where the abrupt change in conductivity at 40–50 °C was caused by melting of crystalline domains. Nevertheless, high-Mw PEO is the most widely studied candidate to solid polymer electrolytes due to its significant advantages including good dimensional and thermal stability, wide potential stability window, and processability.
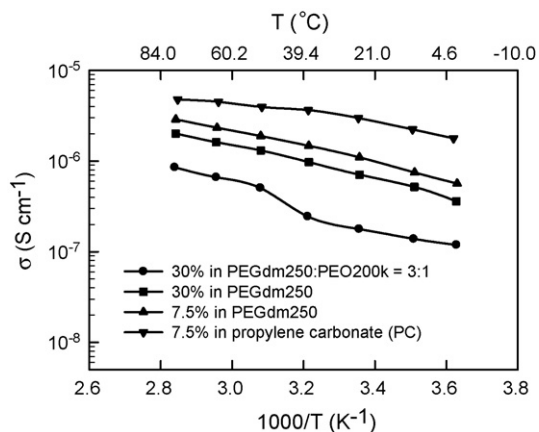

Fig. 7. Effect of solvent on the conductivity of composite electrolytes. The filler was 15-h silica-pLiAMPS particles at the indicated wt%.

4. Conclusion

This work presents a procedure to prepare SICs for lithium batteries: modification with unsaturated functionality on the tailorable surface of ceramic particles, silica in this work, followed by the growth of polymer chains containing anionic moieties, such as sulfonate, with Li$^+$ counter ion. TGA results and elemental analyses of silanated silica and the silica-pAMPS indicate that surface area plays a crucial role of surface loading due to steric effect. That is, the formation of cross-linked structure permits grafting onto the surface more silane molecules, but the follow-on polymerization is sterically constrained.

The effects of polyelectrolyte surface loading, filler content and solvent on ionic conductivity of composite electrolytes were studied. The highest room-temperature conductivity, $3.0 \times 10^{-6}\,\mathrm{S\,cm^{-1}}$, was obtained by dispersing 7.5 wt% filler in PC. The conductivity can be further improved by employing larger surface area material, and hence higher polyelectrolyte surface loading. A solvent with high-dielectric constant and low viscosity will produce high conductivity; however, the filler content affects conductivity comprehensively. The optimal filler content value will be determined by the nature of filler particles and the solvent, the rheological properties of the resultant dispersion, etc.

Acknowledgements

References

[1] K. Xu, Chem. Rev. 104 (2004) 4303.
[2] G.-A. Nazri, MRS Bull. 27 (2002) 628.
[3] S. Panero, B. Scrosati, H.H. Sumathipala, W. Wieczorek, J. Power Sources 167 (2007) 510.
[4] P.V. Wright, MRS Bull. 27 (2002) 597.
[5] D.J. Bannister, G.R. Davis, I.M. Ward, J.E. McIntyre, Polymer 25 (1984) 1291.
[6] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, Nature 394 (1998) 456.
[7] J.-H. Ahn, G.X. Wang, H.K. Liu, S.X. Dou, J. Power Sources 119–121 (2003) 422.
[8] B. Scrosati, F. Croce, S. Panero, J. Power Sources 100 (2001) 93.
[9] X.-W. Zhang, Y. Li, S.A. Khan, P.S. Fedkiw, J. Electrochem. Soc. 151 (2004) A1257.
[10] J. Fan, P.S. Fedkiw, J. Electrochem. Soc. 144 (1997) 399.
[11] L.T. Zhuravlev, Colloids Surf. A: Physicochem. Eng. Aspects 173 (2000) 1.
[12] H. Zhang, S. Kulkarni, S.L. Wunder, J. Electrochem. Soc. 153 (2006) A239.
[13] P. Johansson, M.A. Ratner, D.F. Shriver, J. Phys. Chem. B 105 (2001) 9016.
[14] L. Simeral, R.J. Amey, J. Phys. Chem. 74 (1970) 1443.
[15] S.R. Raghavan, M.W. Riley, P.S. Fedkiw, S.A. Khan, Chem. Mater. 10 (1998) 244.
[16] C.H. Porter, R.H. Boyd, Macromolecules 5 (1971) 589.