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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.

Keywords: Single-ion conductors; Silanation; Free-radical polymerization; Electrolytes; Conductivity; Lithium batteries

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 $–SO_3Li$.

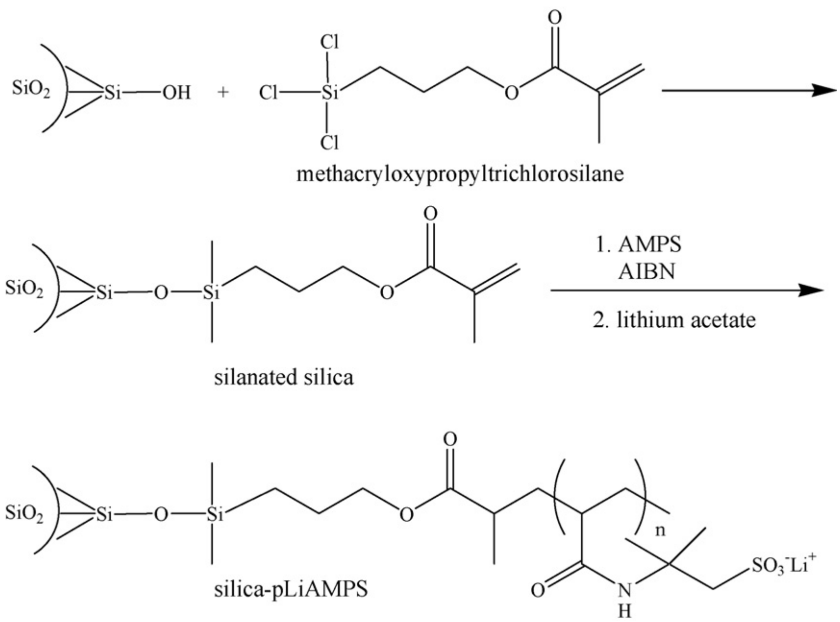

Fig. 1. Scheme of the preparation procedure of single-ion conductors (SICs).

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.

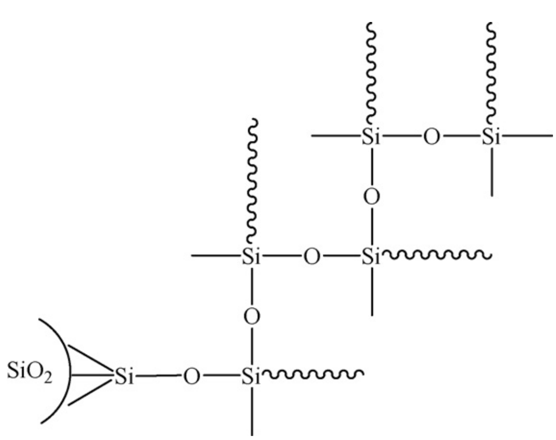

Fig. 2. The cross-linked structure formed by trichloro-silane.

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_2SO_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