



Composite gel polymer electrolytes containing core-shell structured $\text{SiO}_2(\text{Li}^+)$ particles for lithium-ion polymer batteries

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ABSTRACT

In this work, we report novel composite gel polymer electrolyte for lithium-ion polymer batteries. As the lithium ion sources of single ion conductor, the core-shell structured $\text{SiO}_2(\text{Li}^+)$ particles with uniform spherical shape are synthesized and used as functional fillers in composite gel polymer electrolytes. We show that our material, based on the incorporation of core-shell structured $\text{SiO}_2(\text{Li}^+)$ particles into a gel polymer matrix, acts as a very effective polymer electrolyte for lithium-ion polymer batteries.

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1. Introduction

Due to their high energy density and long cycle life, lithium-ion batteries have rapidly become the dominant power sources for portable electronic devices, electric vehicles and energy storage systems. However, safety issues still prevent full utilization of these batteries. Therefore, the quest for safer and more reliable electrolyte systems is urgent and polymer electrolytes are promising candidates in this regard [1, 2]. Poly(ethylene oxide)-based solid polymer electrolytes are the most common examples; however, these electrolytes are affected by a low ionic conductivity ranging from only 10^{-8} to 10^{-5} S/cm at room temperature. Accordingly, consistent research has addressed the preparation and characterization of gel polymer electrolytes that exhibit higher ionic conductivity at ambient temperature. Polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVdF), poly(vinylidene fluoride-co-hexafluoropropylene) (P(VdF-co-HFP)) and poly(methyl methacrylate) (PMMA) are the most common host polymers used for preparing gel electrolytes [3]. Ceramic fillers such as SiO_2 , Al_2O_3 , TiO_2 and BaTiO_3 have also been incorporated along with the host polymer in order to obtain composite polymer electrolytes with improved electrical and mechanical properties [4–9]. The ceramic fillers promote electrochemical properties, but only by physical

action without directly contributing to the lithium ion transport process. By suitable surface modification of the ceramic particles, they can also act as the source of charge carriers [10–12]. It is of great interest to introduce inorganic materials containing dissociative lithium ions, which are based on core-shell structure with unique advantages in terms of control of the final morphology.

In this study, we synthesized monodisperse core-shell structured SiO_2 particles containing lithium ions in their shell. The $\text{SiO}_2(\text{Li}^+)$ particles were incorporated into a P(VdF-co-HFP) matrix polymer and were then activated by a liquid electrolyte to form a composite gel polymer electrolyte. We tested this unique composite polymer electrolyte in a lithium-ion polymer battery. The results reported in this work confirm the superior performance of our core-shell SiO_2 -based composite polymer electrolyte compared to conventional counterparts, e.g., plain fumed SiO_2 .

2. Experimental

2.1. Synthesis of core-shell structured silica particles

Fig. 1 illustrates the synthetic scheme of core-shell structured $\text{SiO}_2(\text{Li}^+)$ particles. Vinyltrimethoxysilane (VTMS) was added to water with stirring until the VTMS droplets completely disappeared. NH_4OH was then added to the solution and the reaction was continued for 12 h at room temperature. After completion of the reaction, the resulting precipitate (cored-silica) was centrifuged and washed with ethanol. The core-shell $\text{SiO}_2(\text{Na}^+)$ particles were synthesized by

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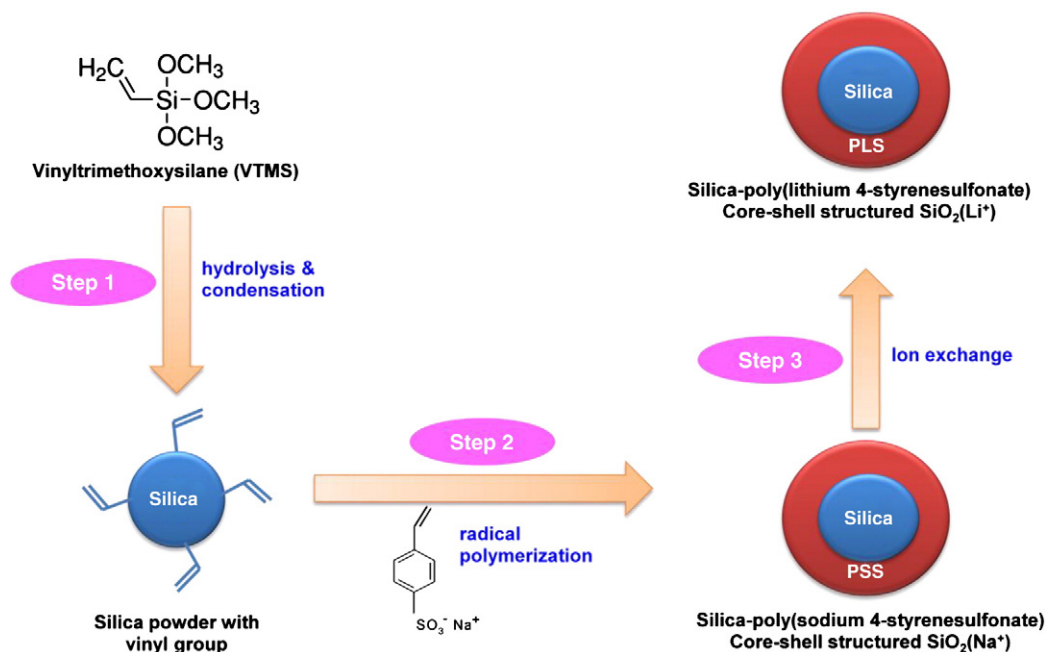


Fig. 1. Reaction scheme for synthesis of core-shell structured $\text{SiO}_2(\text{Li}^+)$ particles.

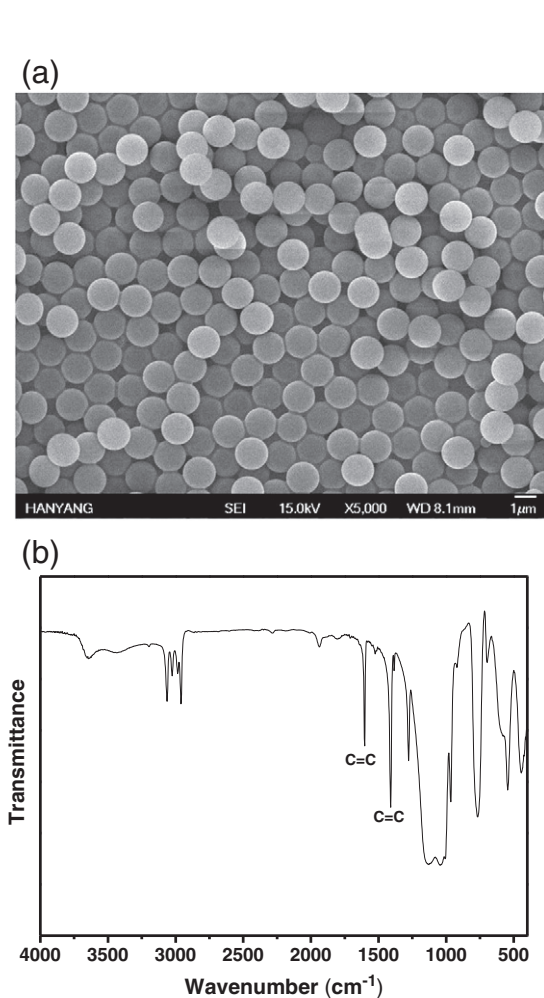


Fig. 2. (a) SEM image and (b) FT-IR spectrum of SiO_2 core particles.

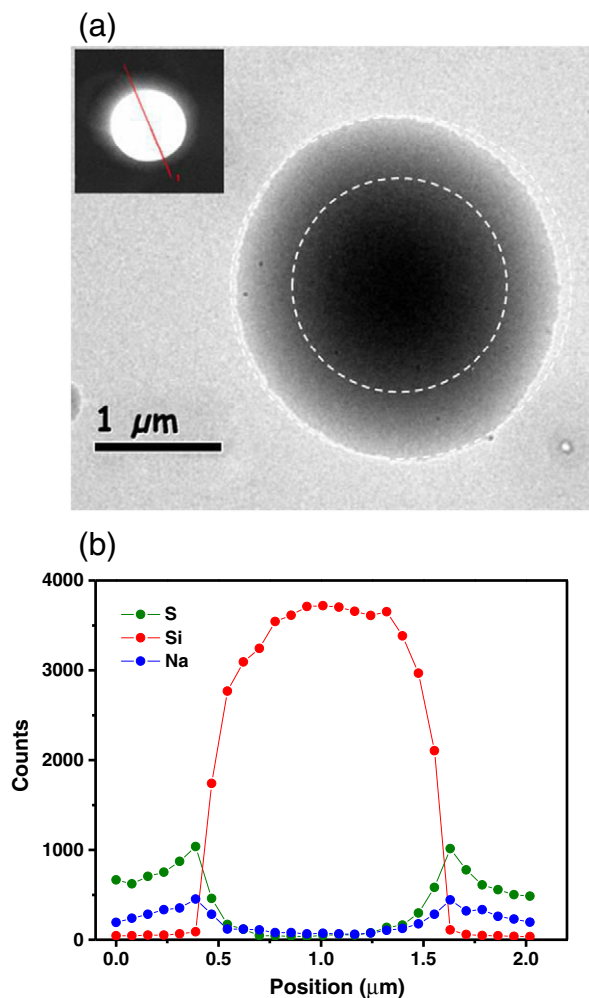


Fig. 3. (a) TEM image and (b) EDAX profile of core-shell structured $\text{SiO}_2(\text{Na}^+)$ particle.

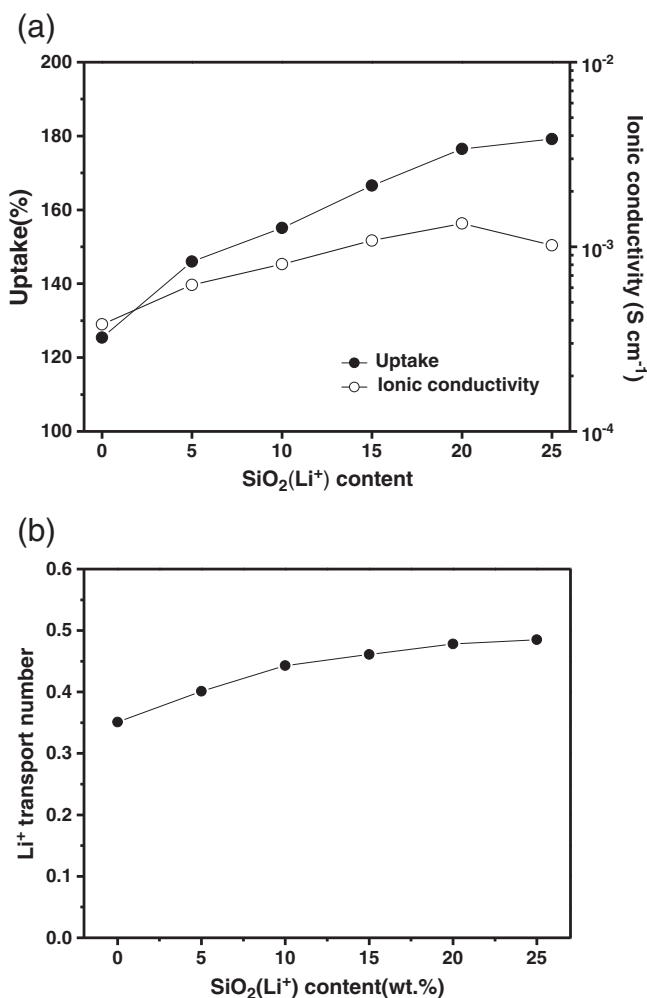


Fig. 4. (a) Ionic conductivities and (b) Li⁺ transport number of composite gel polymer electrolytes, as a function of the content of core-shell structured SiO₂(Li⁺) particles.

radical copolymerization of cored-silica particles and 4-styrenesulfonic acid sodium salt with azobisisobutyronitrile in *n*-methyl pyrrolidone (NMP) at 60 °C for 72 h. After polymerization, the solution was precipitated into a large excess of diethyl ether. The precipitate was filtered and washed with methanol/ethanol several times. The Na⁺ ions in the core-shell structured SiO₂(Na⁺) particles were replaced by Li⁺ ions by ionic exchange with LiOH·H₂O [13].

2.2. Preparation of composite gel polymer electrolytes

A porous composite polymer membrane consisting of P(VdF-co-HFP) and core-shell structured SiO₂(Li⁺) powders was prepared by mixing P(VdF-co-HFP), SiO₂(Li⁺) powders and dibutyl phthalate (DBP) in acetone by ball milling, and casting to a thickness of 500 μm using a doctor blade. The membrane was immersed in methanol to remove DBP and then vacuum dried at 70 °C for 12 h. SiO₂(Li⁺) powder content in the prepared composite polymer membranes varied from 0 to 25 wt.%. Free-standing composite gel polymer electrolyte films were finally obtained by soaking the membrane in a 1.15 M LiPF₆-ethylene carbonate/diethyl carbonate (3:7 by volume, battery grade, Techno Semichem Co.) for enough time (1 h) so as to facilitate the membrane imbued effectively with the electrolyte solution. Accordingly, the aging effect on ionic conductivity after soaking can be neglected.

2.3. Electrode preparation and cell assembly

LiCoO₂ electrode was prepared by coating a NMP-based slurry containing LiCoO₂, PVdF and super-P carbon on an Al foil. The graphite electrode was similarly prepared by coating a NMP-based slurry of mesocarbon microbeads, PVdF and super-P carbon on a copper foil. Lithium-ion polymer batteries were assembled by sandwiching the composite gel polymer electrolyte between the carbon anode and the LiCoO₂ cathode. Charge and discharge cycling tests of the lithium-ion polymer batteries were conducted over a voltage range of 3.0–4.2 V with a battery cycler.

3. Results and discussion

Fig. 2-(a) shows the FE-SEM image of silica core particles. The particles had a uniform spherical shape with average diameter of 1.2 μm. To confirm the presence of C=C double bonds in the silica core particles, FT-IR measurements were performed, and the resulting spectrum is shown in Fig. 2-(b). The symmetric stretching vibrations of the siloxane (Si–O–Si) group appeared at 766 cm⁻¹, while the asymmetric stretching vibrations of siloxane were observed between 1200 and 1000 cm⁻¹. The spectrum also reveals two sharp peaks at 1603 and 1410 cm⁻¹, which are characteristic of the C=C double bond [14, 15], indicating that the silica core particles do contain vinyl groups.

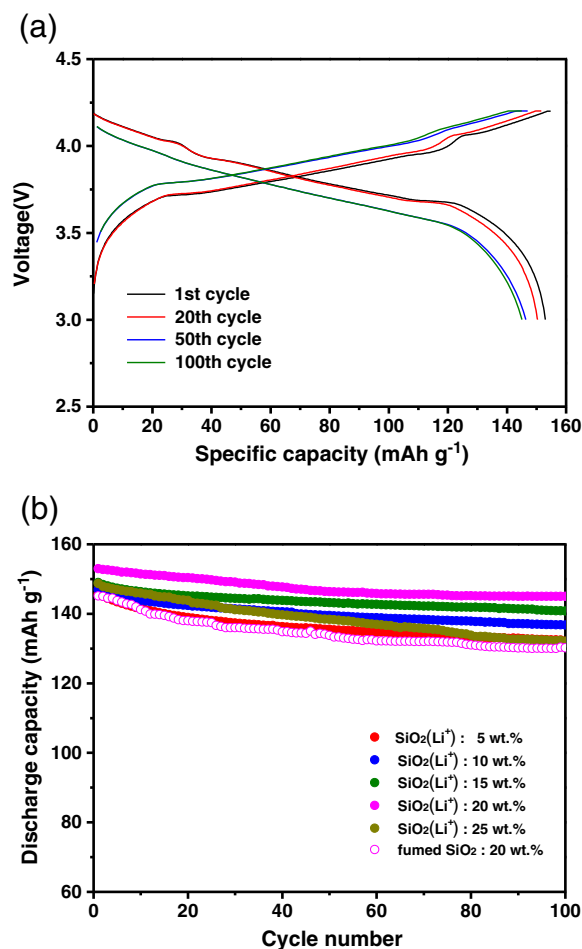


Fig. 5. (a) Charge and discharge curves of the lithium-ion polymer battery assembled with the composite gel polymer electrolyte containing 20 wt.% SiO₂(Li⁺) particles (0.5 C CC and CV charge; 0.5 C CC discharge; cut-off, 3.0–4.2 V) and (b) discharge capacities of the lithium-ion polymer batteries assembled with the composite gel polymer electrolyte containing different contents of SiO₂(Li⁺) particles.

Fig. 3 shows the TEM image and EDAX profile of particles containing poly(sodium 4-styrenesulfonate) (henceforth referred to as PSS) in their shell. Clearly, the particle has a core-shell morphology with a 350–450-nm-thick shell layer of PSS (in gray) surrounding a SiO₂ core particle (in dark). The EDAX profile reveals that the silicon atoms are positioned at the particle core (~1.2 μm), while sulfur and sodium atoms arising from the PSS appear in the shell (~400 nm). These findings are well consistent with the TEM image, confirming that the SiO₂ particles were encapsulated by PSS with a uniform thickness and thus the core-shell structured SiO₂(Na⁺) particles with spherical shape were successfully synthesized. We then proceeded by replacing the sodium ions with lithium ions. XPS analysis on the particles revealed a 57.4 eV characteristic peak corresponding to lithium [16], confirming that the SiO₂(Na⁺) particles were converted to SiO₂(Li⁺) particles.

Fig. 4-(a) shows the ionic conductivity of composite gel polymer electrolyte as a function of the content of SiO₂(Li⁺) particles, demonstrating that the conductivity increases with increasing SiO₂(Li⁺) content, up to a maximum at 20 wt.%. We postulate that the increase in ionic conductivity promoted by the SiO₂(Li⁺) particles is associated with the electrolyte uptake, as well as with an increase in mobile lithium ions dissociating out of the shell of the SiO₂(Li⁺) particles. Indeed, it is confirmed that the lithium transport number measured by combination of AC impedance and DC polarization [17] increases with increasing SiO₂(Li⁺) particle in the composite gel polymer electrolytes. As shown in Fig. 4-(b), the transport number increased from 0.35 for the polymer electrolyte without SiO₂(Li⁺) to 0.48 when 25 wt.% SiO₂(Li⁺) was added. This result is due to the fact that the SiO₂(Li⁺) particle is intrinsically single ion conductor and the lithium ions dissociated from the SiO₂(Li⁺) particles contribute to the ionic conductivity. The generation of free volume at the interface of the dispersed SiO₂(Li⁺) particles may also have contributed to the improved ionic conductivity. The decrease in ionic conductivity beyond 20 wt.% SiO₂(Li⁺) may be attributed to a blocking effect on charge carrier transport since the core of SiO₂(Li⁺) powder is an insulator by nature. As a result, the connectivity of ion conducting phase becomes more tortuous at high content of SiO₂(Li⁺) particles.

Fig. 5-(a) shows typical charge-discharge profiles of the lithium-ion polymer battery assembled with the composite gel polymer electrolyte containing 20 wt.% SiO₂(Li⁺). The battery initially delivers an initial discharge capacity of 153 mAh g⁻¹ based on the LiCoO₂ active material in the cathode. It should be noted that the capacity recovered during the constant voltage charging step is very small, which suggests that the battery has very low internal cell resistance and is capable of delivering high capacity. Fig. 5-(b) shows the discharge capacity versus cycle number of lithium-ion polymer batteries containing different amounts of SiO₂(Li⁺) particles. The initial discharge capacity slightly increased with the addition of SiO₂(Li⁺) up to 20 wt.% in accordance with the associated increase in ionic conductivity. The capacity retention was also improved by increasing the SiO₂

(Li⁺) content in the composite gel polymer electrolyte. It was assumed that the ability to retain the electrolyte solution in the composite gel polymer electrolyte was favored by the addition of SiO₂(Li⁺) powder, which helped to prevent release of electrolyte solution during cycling. The stable interfacial characteristics promoted by the SiO₂(Li⁺) powder may also have contributed to the improved capacity retention [4–6]. The cell assembled with the composite gel polymer electrolyte containing 20 wt.% SiO₂(Li⁺) powder exhibited a higher initial discharge capacity and better capacity retention than did the battery with a composite gel polymer electrolyte containing the same amount of fumed SiO₂; this finding is additional evidence of the superior performance of our core-shell material.

4. Conclusions

The core-shell structured SiO₂ particles are successfully synthesized by radical polymerization of 4-styrenesulfonic acid sodium salt with SiO₂ core materials containing vinyl groups. We demonstrate that composite gel polymer electrolytes with core-shell structured SiO₂(Li⁺) particles as fillers have unique transport and mechanical properties. We show that these materials are very promising polymer electrolytes for use in rechargeable lithium-ion polymer batteries.

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