



# High performance ceramic-coated separators prepared with lithium ion-containing SiO<sub>2</sub> particles for lithium-ion batteries

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## HIGHLIGHTS

- ▶ Core-shell SiO<sub>2</sub> particles are used as coating materials for ceramic-coated separators.
- ▶ The ceramic-coated separators exhibit good thermal stability and wettability.
- ▶ The cells assembled with ceramic-coated separators exhibit good cycling performance.

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## ABSTRACT

Sulfonated SiO<sub>2</sub> particles containing poly(lithium 4-styrenesulfonate) in their shell are synthesized and used as coating materials for the preparation of ceramic-coated separators for lithium-ion cells. The ceramic-coated separators exhibit good thermal stability and wettability for liquid electrolyte due to the presence of a heat-resistant silica with hydrophilic poly(lithium 4-styrenesulfonate). By using these ceramic-coated separators, lithium-ion cells composed of a carbon negative electrode and a LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> positive electrode are assembled and their cycling performances are evaluated. The cells assembled with the ceramic-coated separators demonstrate superior cycling performance compared to cell prepared with a polyethylene separator.

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## 1. Introduction

The use of lithium-ion batteries has been rapidly expanding in portable electronic devices, plug-in hybrid electric vehicles (PHEVs), HEVs, EVs and energy storage systems due to their high energy density and long cycle life. In lithium-ion batteries, a separator is a critical component which prevents physical contact of the positive and negative electrodes while permitting free ionic transport within the cell. Most of the separators currently used in lithium-ion batteries are based on microporous polyolefin membranes such as polyethylene (PE) and polypropylene (PP) as well as various combinations of the two [1–3]. Although these separators offer excellent mechanical strength and chemical stability, they shrink, soften and even melt at high temperatures [4–6], which cause short circuiting between electrodes in the case of unusual heat generation. Furthermore, without surface

treatment, the large difference in polarity between the non-polar polyolefin separator and the polar organic electrolyte leads to poor wettability [7,8]. As a result, there is a high resistance when the pores in the separator are not completely filled with liquid electrolyte. In order to solve these problems, ceramic-coated separators have been developed by combining the characteristics of a polymeric separator and ceramic materials [9–18]. In these separators, commercially available inorganic particles such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> have been coated with a polymer binder on a polyolefin separator. The coating of ceramic particles has been effective in improving the mechanical, thermal and electrical properties of separators only due to physical actions without directly contributing to the lithium ion transport process. In our previous studies, core-shell structured SiO<sub>2</sub> particles containing lithium ions in their shells were synthesized and used as functional fillers in Li<sup>+</sup>-conducting composite polymer electrolytes [19,20]. These fillers are unique because the SiO<sub>2</sub> core is covalently bonded to poly(lithium 4-styrenesulfonate) (PLSS) in the shell layer. Thus, it is of great interest to introduce the SiO<sub>2</sub>-based inorganic materials containing lithium ions to the ceramic-coated separator.

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With the goal of developing high performance separators with high thermal stability, good transport properties and enhanced wettability for non-aqueous liquid electrolytes, we prepared ceramic-coated separators based on a PE separator and core–shell structured SiO<sub>2</sub> particles containing lithium ions. Due to the presence of a heat-resistant silica core with a hydrophilic shell component, the ceramic-coated separator exhibited good thermal stability and wettability for liquid electrolyte. Using these ceramic-coated separators, we assembled lithium-ion cells composed of a carbon negative electrode and a LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> positive electrode. The cycling performances of the cells assembled with the ceramic-coated separator were evaluated as a function of the core–shell SiO<sub>2</sub> content and the results were compared to those obtained with a pristine PE separator.

## 2. Experimental

### 2.1. Synthesis of core–shell structured SiO<sub>2</sub> particles

The core–shell structured SiO<sub>2</sub>(Li<sup>+</sup>) particles were synthesized through three steps, as reported earlier [19]. Vinyltrimethoxysilane (VTMS) was added to double distilled water under stirring for 30 min until the VTMS droplets completely disappeared. A catalytic amount of NH<sub>4</sub>OH 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 was centrifuged and washed several times with ethanol. Core–shell SiO<sub>2</sub>(Na<sup>+</sup>) particles were synthesized by radical copolymerization of silica core particles with 4-styrenesulfonic acid sodium salt. The silica core particles were dispersed in *n*-methyl pyrrolidone (NMP) via ultrasonication for 30 min and a solution consisting of 4-styrenesulfonic acid sodium salt and azobisisobutyronitrile (AIBN) dissolved in NMP was added. To induce polymerization, the mixture was heated to 60 °C under stirring for 72 h. After polymerization, the solution was precipitated in excess diethyl ether under vigorous stirring. The precipitate was filtered and washed several times with methanol/ethanol. The Na<sup>+</sup> ions in the core–shell structured SiO<sub>2</sub>(Na<sup>+</sup>) particles were replaced by Li<sup>+</sup> ions by ionic exchange with LiOH·H<sub>2</sub>O [21]. The resulting core–shell SiO<sub>2</sub>(Li<sup>+</sup>) powders were washed with ethanol to remove any impurities and dried under vacuum at 110 °C for 12 h.

### 2.2. Preparation of the ceramic-coated separator

Ceramic-coated separators were prepared from the core–shell SiO<sub>2</sub>(Li<sup>+</sup>) particles and poly(vinylidene fluoride-co-hexafluoropropylene) (P(VdF-co-HFP), Kynar 2801) as a polymer binder. P(VdF-co-HFP) was dissolved in an acetone/butanol solvent mixture (90/10 by volume), and the core–shell SiO<sub>2</sub>(Li<sup>+</sup>) particles were directly added to the polymer solution at concentrations of 0, 10, 20, and 30 wt.%. The slurry was uniformly mixed by ball milling for 24 h. Using a dip coating method, the resulting slurry was then coated onto both sides of a microporous PE separator (Asahi-Kasei Co.) with a thickness of 20 μm and a porosity of 40%. Next, the separator was dried at room temperature for 10 min to allow the solvent to evaporate, followed by additional drying in a vacuum oven at 60 °C for 24 h. The coating thickness was adjusted by changing the content of the SiO<sub>2</sub>(Li<sup>+</sup>) particles and P(VdF-co-HFP) in the slurry so that the total thickness of the ceramic-coated separator was kept to be about 29 μm.

### 2.3. Electrode preparation and cell assembly

The positive electrode was prepared by coating the *N*-methyl pyrrolidone (NMP)-based slurry containing 85 wt.% LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (3 M), 7.5 wt.% poly(vinylidene fluoride)(PVdF), and

7.5 wt.% super-P carbon (MMM Co.) on an aluminum foil. After vacuum drying, the electrode was punched into a disk. A geometrical area of the positive electrode was 1.54 cm<sup>2</sup>, and its active mass loading corresponded to a capacity of about 2.0 mAh cm<sup>-2</sup>. The negative electrode was prepared similarly by coating the NMP-based slurry of mesocarbon microbeads (MCMB, Osaka gas), PVdF and super-P carbon at a weight ratio of 85/7.5/7.5 on a copper foil. The negative electrode was also cut into a disk with a geometric area of 2.01 cm<sup>2</sup>. Lithium-ion cells were assembled by sandwiching the ceramic-coated separator between the carbon electrode and the LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> electrode. The cell was then enclosed in a 2032 coin cell and injected with the same amount of electrolyte solution, which consisted of 1.15 M LiPF<sub>6</sub> in ethylene carbonate (EC)/diethyl carbonate (DEC) (3:7 by volume, Soulbrain Co. Ltd.). The nominal capacity of coin cell was about 3.1 mAh, and thus 1C rate corresponded to 3.1 mA. All cells were assembled in a dry box filled with argon gas.

### 2.4. Measurements

The morphologies of the materials were examined using a field emission scanning electron microscope (FE-SEM, JEOL JSM-6330F) and a field emission transmission electron microscope (FE-TEM, FEI, Tecnai G2 F30). Fourier transform infrared (FT-IR) spectra were recorded on a Magna IR 760 spectrometer in the range of 400–4000 cm<sup>-1</sup> with KBr powder-pressed pellets. The presence of lithium ions in the core–shell structured SiO<sub>2</sub> particles was confirmed by Auger Electron Spectroscopy (AES, ULVAC-PHI, PHI 700). The thermal shrinkage of the ceramic-coated separators in the form of their dimensional change was measured before and after being held at 130 °C for 30 min. The internal short circuit temperature of the cell was determined as the temperature which showed a sudden voltage drop, as the temperature of the cell was increased. In order to measure the electrolyte uptake and ionic conductivity, the ceramic-coated separator was immersed in the 1.15 M LiPF<sub>6</sub> in EC/DEC solution for 1 h. Afterward, the separator was taken out from the electrolyte solution and the excess electrolyte solution on the surface of separator was removed by wiping with filter paper. The uptake of the electrolyte solution was then determined by using equation (1),

$$\text{uptake (\%)} = (W - W_0)/W_0 \times 100 \quad (1)$$

where  $W_0$  and  $W$  are the weights of the separator before and after soaking in the liquid electrolyte, respectively [22–24]. The wetted separator was sandwiched between two stainless steel electrodes for conductivity measurements. AC impedance measurements were performed to measure the ionic conductivity using an impedance analyzer over the frequency range of 10 Hz–100 kHz with amplitude of 10 mV. Charge and discharge cycling tests of the lithium-ion cells were conducted at a current of 1.55 mA (0.5 C rate) over a voltage range of 3.0–4.5 V using battery test equipment.

## 3. Results and discussion

Fig. 1(a) shows an FE-SEM image of the silica core particles. The particles have a uniform spherical shape with particle size ranging from 790 to 830 nm. From the FT-IR spectra of the silica core particles, peaks corresponding to the siloxane (Si–O–Si) group (766, 1000–1200 cm<sup>-1</sup>) and C=C double bonds (1410, 1603 cm<sup>-1</sup>) were observed [19]. These results imply that the silica core particles contain reactive vinyl groups which permit the growth of silica particles by radical polymerization with 4-styrenesulfonic acid sodium salt. Core-shell structured SiO<sub>2</sub> particles were obtained by

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