

Lithium-silica nanosalt as a low-temperature electrolyte additive for lithium-ion batteries



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ABSTRACT

A lithium-modified silica nanosalt (Li–SiO₂, coded Li202) of hydrophobic fumed silica (R202) is synthesized to use as an electrolyte additive for lithium-ion batteries (LIBs) under low temperature conditions. The synthesis method consists of reacting the silica nanoparticles with LiH and consequently quickly reacting the conjugate silicate ions with 1,3-propanesultone as a surface stabilizer. The obtained Li202 nanosalt (2.5 wt%) is added into an electrolyte solution of 1.0 M LiPF₆ dissolved in ethylene carbonate/propylene carbonate/ethylmethyl carbonate/diethyl carbonate (20:5:55:20 vol%) + 2 wt% vinylene carbonate. The electrolyte solution including the Li202 nanosalt shows higher ionic conductivity and superior electrochemical stability over 5 V, which is due to the stabilized surface group. The high-rate capability at –20 °C of the LiCoO₂/graphite cell is particularly enhanced by adding Li202 nanosalt. In addition, excellent cycle performance at –20 °C endorses the use of Li202 nanosalt as a low-temperature electrolyte additive for LIBs.

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1. Introduction

Lithium-ion battery (LIB) performance at low temperatures offers huge challenges that have to be solved. Knowledge of electrolyte solvents is crucial to the understanding of low-temperature battery performance [1–6]. LIB electrolyte solvents are usually composed of alkyl carbonate mixtures in a distinct wide range of temperatures [3–5,7]. Despite the use of solvents with a low freezing point, such as ethylmethyl carbonate and diethyl carbonate, a sizable bulk of the LIB capacity remains unutilized at low temperatures of about –20 °C. Moreover, several limitations introduced by electrode-separator-electrolyte combinations, such as the issue around solid electrolyte interphase (SEI), have suggested the use of additives. There has been a wide range of additives targeted at achieving a number of functions including enhanced SEI stability, of which thermal stability [8–14] is only improved. Electrolyte additives have been considered as an effective and

economically viable way of boosting battery performance when they were used in minute amounts of not more than 5% [7,9,10,15–18]. Notable among the additives are the inorganic nanoparticles such as fumed silica, alumina, and their derivatives [15,18–21].

It is well known that OH groups are commonly distributed on the surfaces of hydrophilic fumed silica and they connect with each other in liquid media through hydrogen interactions to form gels [19,22,23]. The porous networks of the gel make lithium ions move across the electrolyte medium, resulting in an increase in the ionic conductivity of LIB electrolytes [19,23–25]. The surface OH groups often interact with the electrolyte components to result in decomposition, which may influence the formation of an SEI layer and thereby affect the overall LIB performance including the cycle life. For instance, Choi et al. [26] and Sun et al. [27] successfully modified the surface of hydrophilic fumed silica A200 (Aerosil[®]) by interacting the surface protons with lithium *tert*-butoxide (LiOtBu) and fixing them with the addition of 1,3-propanesultone. However, this study deals with a hydrophobic fumed silica (R202, Aerosil[®]), rather than a hydrophilic silica, and uses a sonicated mixture of

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lithium hydride (LiH) and LiOtBu. According to Evonik's supplemental information, the Aerosil® R202 is a product made after treatment with a polydimethylsiloxane to create a hydrophobic surface. In this study, LiH is also used as a starting material to minimize base contamination by the other lithium sources because the generated by-product (H_2) is easier to handle. The obtained lithium nanosalt (Li–SiO₂, coded Li202) is also tested as an electrolyte additive for LIB applications. In particular, the use of Li202 as an additive is examined in LIB performance at low temperature. We make this study expecting promising results from the interactions with silica nanosalt components similar to our previous report using some polydimethylsiloxane-based electrolyte additives to enhance the LIB performance at low temperature [14].

2. Experimental

The hydrophobic fumed silica R202 (particle size 18–22 nm, surface area $100 \pm 20 \text{ m}^2 \text{ g}^{-1}$, Aerosil®, Evonik) was preheated at 320 °C in a vacuum oven for 48 h before use. First, 9 g of R202 was suspended in 300 mL of tetrahydrofuran (Duksan Chemicals) and stirred for 1 h. To the suspension, 50 mL of 1.0 M LiOtBu (>99.9%, Aldrich)/tetrahydrofuran solution and 0.05 g of LiH (>99.9%, Aldrich) were added and stirred for 2 h at ambient temperature. Then, 9 g of 1,3-propanesultone (>99%, Aldrich) was added to stabilize the nanoparticle surfaces by sulfonation, stirred for 6 h at ambient temperature, and finally sonicated for 1 h at 60 °C. Centrifugation, washing with excess tetrahydrofuran, and drying in a vacuum at 70 °C for 3 days were followed for purification. This procedure of synthesizing the Li–SiO₂ nanosalt (Li202) is summarized in Fig. 1. The obtained Li202 was characterized using Fourier-transform infrared spectroscopy (Bomem MB100) and X-ray photoelectron spectroscopy.

Three electrolyte solution samples termed 'Electrolyte' (1.0 M LiPF₆ dissolved in a mixture of ethylene carbonate, propylene carbonate, ethylmethyl carbonate, and diethyl carbonate (20:5:55:20 vol%) plus vinylene carbonate (2 wt%), PanaX eTec), 'Electrolyte' + R202 (2.5 wt%), and 'Electrolyte' + Li202 (2.5 wt%) were also prepared to compare the electrochemical properties of electrolyte systems with different R202-based additives. The ionic conductivities of the electrolyte samples were examined in the

temperatures range of –20 to 70 °C by complex impedance spectroscopy using an Autolab instrument (PGstat 100, Eco Chemie). The test cells for ionic conductivity measurement were assembled by sandwiching the electrolyte samples on a polypropylene separator (Celgard) between two Pt electrodes (1 cm × 1 cm) in an Al-pouch. The coin-type (2032) half-cells for linear sweep voltammetry were composed of stainless steel plates as working electrodes, liquid electrolytes with and without additives, and lithium metal foil as counter and reference electrodes. Linear sweep voltammetry was also carried out using an Autolab instrument (PGstat 100, Eco Chemie) in a range of 2.0–7.0 V at 1 mV s^{-1} .

Coin-type (2032) full-cells were fabricated in an Ar-filled glove box to investigate the effect of the additives on the performance of conventional LIBs (LiCoO₂||polyethylene separator ||graphite) at room temperature and at –20 °C. The positive and negative electrodes were composed of LiCoO₂ and graphite (87 wt% each) as the cathode and anode active materials, respectively, poly(vinylidene fluoride) (6 wt%) as a binder, and carbon black (Super P, Timcal Graphite & Carbon, 7 wt%) as a conductive agent. The electroactive material loadings of the electrodes utilized in the coin cell testing were evaluated to be $50.3 \pm 0.5 \text{ mg}$ and $42.1 \pm 0.5 \text{ mg}$ for LiCoO₂ and graphite, respectively, which were already adjusted to be comparable for all cells tested because the low-temperature performance could be significantly affected by the electrode loadings. The porous polyethylene separator used was provided by Celgard (Model 2045). The liquid electrolytes with and without the additives (R202 and Li202, 2.5 wt% each) were injected just before sealing the coin cells.

Charge-discharge cycling tests of the LIBs were carried out under constant-current and subsequent constant-voltage modes in the range of 3.0–4.2 V at 0.1–2.0 C-rate using a battery cycler (Toscat 3000, Toyo Systems) which was equipped with a temperature-controlled chamber. As a reference, the 1.0 C-rate was set to correspond to 140 mAh g^{-1} of Li_xCoO₂ ($x = 0.5$). The anode/cathode (N/P) ratio may be determined to be $(42.1 \times 320)/(50.3 \times 140) = 1.91$ if assuming the practical capacity of graphite to be 320 mAh g^{-1} . Room-temperature cycling was performed under conditions of charging-discharging at 1.0 C-rate, whereas the low-temperature cycling was carried out under conditions of charging at 1.0 C-rate (25 °C), resting (cooling) for 10 min, and discharging at 0.1 C-rate (–20 °C). The electrochemical impedance spectra were also obtained after the initial and 50th cycles at –20 °C using an Autolab instrument (PGstat 100, Eco Chemie) in a frequency range of 10^{-2} – 10^5 Hz and an excitation voltage of 10 mV. In particular, the surface image of the graphite anode was observed after the initial discharge at –20 °C using a field-emission scanning electron microscope (Hitachi S-4800), which was equipped with an energy dispersive X-ray spectroscope. All synthesis and cell preparations were done in an Ar environment in a glove box to maintain moisture-free conditions.

3. Results and discussion

Unlike the previous lithium-modified silica nanoparticles [26,27], this study i) deals with a surface modification of hydrophobic fumed silica R202, ii) starts with LiH to reduce waste contamination by generating H_2 gas, and iii) uses a sonication solution method to improve yield efficiency. The previous studies succeed in fast ion conduction [26] and high lithium cycling efficiency [27], whereas the present study mainly aims at the enhancement of low-temperature performance of LIBs by using the R202-modified nanosalt to attach the surface functional groups. Fig. 2 shows Fourier-transform infrared spectra of the R202 as an original silica nanoparticle and the Li202 as the surface-modified nanosalt. In the R202 spectra, the absorption bands at 1000–1300

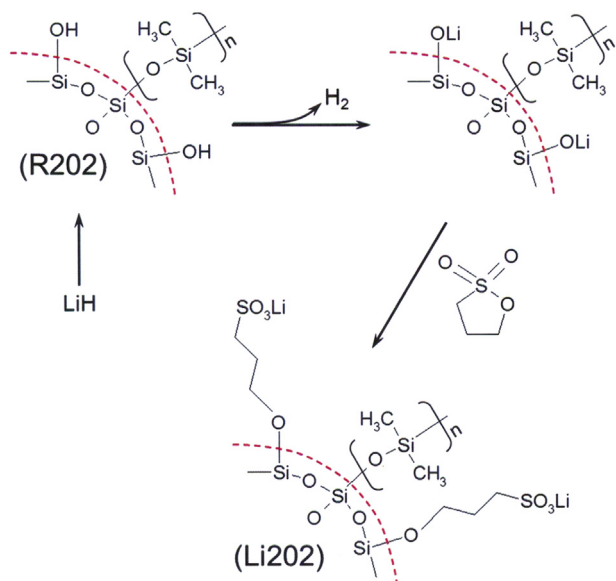


Fig. 1. Schematic diagram of the synthesis procedure of Li202 from R202.

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