



# Improvement of low-temperature performance by adopting polydimethylsiloxane-g-polyacrylate and lithium-modified silica nanosalt as electrolyte additives in lithium-ion batteries



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## ABSTRACT

In this work, poly[dimethylsiloxane-co-(siloxane-g-acrylate)] (PDMS-A) and lithium-modified silica nanosalt (Li2O2) are used together as low-temperature electrolyte additives in lithium-ion batteries (LIBs), taking advantage of the electrochemical and interfacial stabilities due to their surface functional groups. Using these additives together improves the electrochemical stability and ionic conductivity of liquid electrolyte solution to over 5.5 V and  $4 \times 10^{-4} \text{ S cm}^{-1}$  at  $-20^\circ\text{C}$ , respectively. The room-temperature electrochemical performance of a conventional LIB (LiCoO<sub>2</sub>/graphite) is improved by the addition (e.g., initial discharge capacity of  $95.9 \text{ mAh g}^{-1}$  obtained after charging at 1.0 C-rate and consequent discharging at 5.0 C-rate). The low-temperature performance is also enhanced, achieving a capacity retention ratio of 63.4% after 50 cycles at  $-20^\circ\text{C}$ , compared to 38.7% without the additives. It is also notable that the PDMS unit commonly existing in both additives may be the main cause of the synergistic effects on the electrochemical performance due to the compatibility between PDMS-A and Li2O2.

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## Introduction

As we know, conventional lithium-ion batteries (LIBs) contain a liquid electrolyte solution composed of lithium ionic salt dissolved in non-aqueous carbonate solvents, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylmethyl carbonate (EMC). Putting the organic solvents aside, the electrolyte additives for LIB have been studied to overcome the safety problems that can occur due to the flammable, volatile, and corrosive properties of the solvent components. There have been attempts to improve performance by using additives to overcome thermal and interfacial instability over the prolonged cycling of charging and discharging at high current rates under various thermal environments. Low-temperature performance of LIBs has become a major challenge to be

solved because some conventional electrolyte components of LIBs can freeze at low temperatures, due to the melting point at ambient temperature (e.g.,  $37^\circ\text{C}$  for EC). To lessen this problem, the optimization of LIB electrolyte components has been studied and resulted in ternary and quaternary mixtures consisting of alkyl carbonates and alkyl carbonate esters [1], EC-DMC-methyl acetate [2], EC-DMC-EMC [3,4], and EC-PC-EMC-vinylene carbonate (VC) [5].

Recently, polysiloxane-based copolymers [6–8], more precisely, polydimethylsiloxane (PDMS)-based copolymer additives, or polymer electrolytes [6,9–11], have been shown to have high thermal and chemical stabilities that can be utilized over a wide temperature range. In particular, a previous report [12] on a PDMS-based electrolyte additive revealed that 1 wt% addition of poly[dimethylsiloxane-co-(siloxane-g-acrylate)] (PDMS-A) to an electrolyte solution of 1.0 M LiPF<sub>6</sub> dissolved in EC/PC/EMC/DEC/VC/fluoroethylene carbonate (FEC) (20:5:55:20:2:5 by volume) achieved a higher ionic conductivity of  $2.5 \times 10^{-4} \text{ S cm}^{-1}$  and an improved cycle performance of LiCoO<sub>2</sub>/graphite at  $-20^\circ\text{C}$  due to avoidance of electrolyte degradation and protection of the graphite

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anode surface. However, the low-temperature performance of PDMS-A was slightly inferior to that of other PDMS-based additives (e.g., phenyl and ether silicone oils) [12].

On the other hand, the use of lithium-modified nanosalts from hydrophilic [13,14] and hydrophobic fumed silica nanoparticles [15,16] has been suggested as additives in conventional electrolyte solutions. In particular, the 2.5 wt% addition of lithium-modified silica nanosalt ( $\text{Li}_2\text{O}_2$ ) in an electrolyte solution of 1.0 M  $\text{LiPF}_6$  dissolved in EC/PC/EMC/DEC (20:5:55:20 vol%) + VC (2 wt%) enhanced the cycle performance of a  $\text{LiCoO}_2$ /graphite cell at both room temperature (RT) and  $-20^\circ\text{C}$  due to the stabilized surface groups of the  $\text{Li}_2\text{O}_2$  [15].

Combining the concepts of the PDMS-based and the lithium-modified nanosalt-based electrolyte additives, the effects of using both PDMS-A and  $\text{Li}_2\text{O}_2$  on the electrochemical properties of an electrolyte solution to which they are added are investigated in this study. Moreover, the capacity and cycle performance of  $\text{LiCoO}_2$ /graphite cell adopting the electrolyte solution with the additives are also examined at RT and  $-20^\circ\text{C}$ .

## Experimental

A standard commercial liquid electrolyte (PanaX Etec) consisting of 1.0 M  $\text{LiPF}_6$  dissolved in EC/PC/EMC/DEC (20:5:55:20 vol%) + VC (2 wt%) + FEC (5 wt%) was used. The PDMS-A ( $M_w = 26,000$ ) used was purchased from Sigma-Aldrich and was dried in a vacuum chamber for at least 12 h prior to use. The  $\text{Li}_2\text{O}_2$  nanosalt was obtained by modifying hydrophobic fumed silica (R202, Aerosil<sup>®</sup>, Evonik) to give surface groups of PDMS [ $-\text{OSi}(\text{CH}_3)_2$ ] $_n$ - and end-capped propane lithium sulfonate ( $-(\text{CH}_2)_3\text{SO}_3\text{Li}$ ). The detailed procedure of synthesizing  $\text{Li}_2\text{O}_2$  can be found in previous reports [15,16]. The chemical structures of PDMS-A and  $\text{Li}_2\text{O}_2$  are shown in Fig. 1.

The following four electrolyte samples were prepared: (i) 'Electrolyte' as the standard liquid electrolyte, (ii) 'Electrolyte' + PDMS-A (1 wt%), (iii) 'Electrolyte' +  $\text{Li}_2\text{O}_2$  (1 wt%), and (iv) 'Electrolyte' + PDMS-A (1 wt%) +  $\text{Li}_2\text{O}_2$  (1 wt%). The ionic conductivities of the electrolyte samples were examined in the temperature range of  $-20$  to  $70^\circ\text{C}$  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 between two Pt electrodes ( $1 \times 0.5 \text{ cm}^2$ ) with a distance of 0.3 cm in an Al-pouch. The coin-type half-cells (2032) for linear sweep voltammetry were fabricated from stainless steel plates as working electrodes, liquid electrolyte with and without additives, and lithium metal foil as counter and reference electrodes. Linear sweep voltammetry was carried out using an Autolab instrument (PGstat 100, Eco Chemie) in a range of 2.0–6.0 V at  $2 \text{ mV s}^{-1}$ .

Coin-type full-cells (2032) were fabricated in an Ar-filled glove box to investigate the effect of the additives on the performance of conventional LIB cells ( $\text{LiCoO}_2$ ||polyethylene separator||graphite) at RT and  $-20^\circ\text{C}$ . The loadings of electroactive materials in the positive and negative electrodes were determined to be  $52.1 \pm 0.5 \text{ mg}$  and  $40.5 \pm 0.5 \text{ mg}$  for  $\text{LiCoO}_2$  and graphite, respectively. A porous polyethylene separator (W-Scope,  $20 \mu\text{m}$  thick) was inserted between the positive and negative electrodes. The liquid electrolytes with and without the additives (PDMS-A and  $\text{Li}_2\text{O}_2$ , 1 wt% each) were injected just before the coin cells were sealed. The fabricated LIB cells were aged for at least 24 h at ambient temperature to ensure that sufficient amounts of the liquid samples were absorbed in the electrodes and separator within the cell. The electrochemical impedance spectra for the LIB cells were obtained before initial charging at RT and  $-20^\circ\text{C}$  using an Autolab instrument (PGstat 100, Eco Chemie) in a frequency range of  $10^{-2}$  to  $10^5 \text{ Hz}$ .

Initial charging-discharging tests of the LIB cells were carried out under constant-current and consequent constant-voltage modes in the range of 3.0–4.2 V using a battery cycler (Toscat 3000, Toyo Systems) equipped with a temperature-controlled chamber. As a reference, the 1.0 C-rate was set to correspond to  $140 \text{ mAh g}^{-1}$  of  $\text{Li}_x\text{CoO}_2$  ( $x = 0.5$ ). In the initial charging-discharging tests at RT, charging was performed at a 1.0 C-rate, and discharging was performed at 0.1–10.0 C-rates. In the low-temperature initial charging-discharging tests, charging was carried out at a 1.0 C-rate ( $25^\circ\text{C}$ ), followed by resting (cooling) for 10 min, and finally discharging at 0.1 C-rate ( $-20^\circ\text{C}$ ). Also, room-temperature cycling for 50 cycles was performed under conditions of charging-discharging at a 1.0 C-rate, whereas low-temperature cycling for 50 cycles was carried out under conditions of charging at a 1.0 C-rate ( $25^\circ\text{C}$ ), resting (cooling) for 10 min, and finally discharging at a 0.1 C-rate ( $-20^\circ\text{C}$ ).

## Results and discussion

The effects of adding PDMS-A and  $\text{Li}_2\text{O}_2$  have been individually described in previous reports [12,15]. In summary, PDMS-A in liquid electrolyte solution shows good electrochemical stability imparted by the PDMS main chain and by the grafted functional group of acrylate, which protects the liquid electrolyte components from degradation and/or freezing to improve the capacity retention and enhance the rate-capability of LIBs at low temperatures [12]. Meanwhile,  $\text{Li}_2\text{O}_2$  plays the role of stabilizing the liquid electrolyte against oxidation at higher voltages to give better cycle performance at  $-20^\circ\text{C}$  due to the PDMS surface groups within  $\text{Li}_2\text{O}_2$  and extra lithium ions from the end-capped- $(\text{CH}_2)_3\text{SO}_3\text{Li}$  functional groups on the  $\text{Li}_2\text{O}_2$  surface. That is, PDMS-A can be used as an electrolyte additive because the acrylate species in the chemical structure of PDMS-A is soluble in a

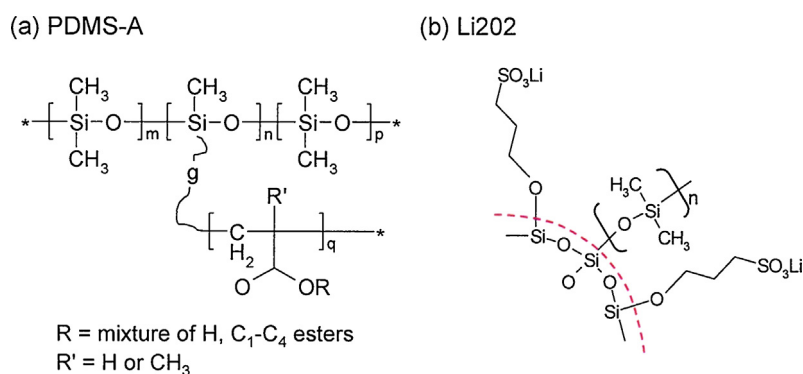


Fig. 1. Chemical structures of the additives used in this study.

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