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Improvement of lithium-ion battery performance at low temperature by adopting polydimethylsiloxane-based electrolyte additives

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ABSTRACT

Three kinds of polydimethylsiloxane (PDMS)-based grafted and ungrafted copolymers such as poly[dimethylsiloxane-*co*-(siloxane-*g*-acrylate)] (PDMS-A), poly(dimethylsiloxane-*co*-phenylsiloxane) (PDMS-P), and poly[dimethylsiloxane-*co*-(siloxane-*g*-ethylene oxide)] (PDMS-EO) are used as additives to standard liquid electrolyte solutions to enhance the lithium-ion battery performance at low temperatures. Liquid electrolyte solutions with PDMS-based additives are electrochemically stable under 5.0 V and have adequate ionic conductivities of 10^{-4} S cm^{-1} at -20 °C. Particularly, liquid electrolytes with PDMS-P and PDMS-EO exhibit higher ionic conductivities of around 5×10^{-4} S cm^{-1} at -20 °C, indicating a specific resisting property against the freezing of the liquid electrolyte components. As a result, the addition of PDMS-based additives to liquid electrolytes improves the capacity retention ratio and rate-capability of lithium-ion batteries at low temperatures.

1. Introduction

Nowadays, due to their long cycle life and high capacity, lithium-ion batteries have become the dominant power source for many portable devices such as laptop computers, electric vehicles, and energy storage systems. The typical electrolyte system of a conventional lithium-ion battery has been a solution of lithium salt dissolved in carbonate solvents such as ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and ethylmethyl carbonate (EMC), which worked stably under ambient temperature conditions [1]. At low temperatures, however, the power performance of lithium-ion batteries can be very low because a frozen state of the electrolyte solution can appear [2]. Among carbonate solvents used for liquid electrolytes, in particular, PC has a low melting point (-49 °C) and high dielectric index [3] that allows it to be used at low temperatures. Unfortunately, this material could cause surface exfoliation of the graphite anode, which would reduce the reversible capacity [3]. On the other hand, some optimization of the electrolyte components of lithium-ion batteries at low temperatures have also resulted in ternary and quaternary mixtures consisting of alkyl carbonates and alkyl carbonate esters [4], EC-DMC-methyl acetate [1], EC-PC-EMC-vinylene carbonate (VC) [2], and EC-DMC-EMC [5,6].

Using additives in a liquid electrolyte system has been considered a promising way to enhance the performance of lithium-ion batteries, due to the special services possible with such additives [7], including stabilizing and increasing of cycle life [8,9], film-forming and protecting of the anode or cathode [10–14], and flame-retarding during repeated charge-discharge processes [13,15]. Polysiloxanes-based copolymers have been used as suitable additives for electrolyte systems, and these materials have been previously reported by many authors [16–18]. In particular, polydimethylsiloxane (PDMS)-based additives or polymer electrolytes have high thermal and chemical stabilities that can allow them to be used over a wide temperature range [16,19–21]. Thus, it seems important to examine the low temperature performance of lithium-ion batteries by adopting PDMS-based additives in conventional liquid electrolyte systems.

Up to now, reports about the PDMS-based additives for the liquid electrolyte of lithium-ion batteries are very rare. The combinations between the liquid electrolyte and the PDMS-based additives can be enormously varied. The present combinations of this study are arbitrarily selected as preliminary examples. In this

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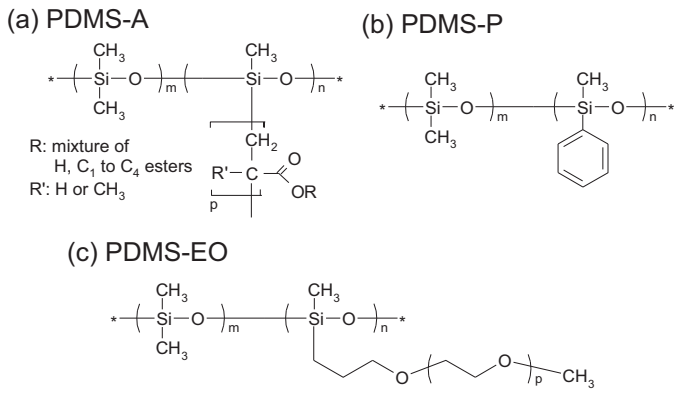

Fig. 1. Chemical structures of PDMS-based additives used in this study: (a) PDMS-A, (b) PDMS-P, and (c) PDMS-EO.

paper, three kinds of PDMS-derived grafted and ungrafted copolymers, such as poly[dimethylsiloxane-*co*-(siloxane-*g*-acrylate)] (PDMS-A), poly(dimethylsiloxane-*co*-phenylsiloxane) (PDMS-P or phenyl silicone oil), and poly[dimethylsiloxane-*co*-(siloxane-*g*-ethylene oxide)] (PDMS-EO or ether silicone oil) are examined as new additives for use in lithium-ion batteries at low temperatures. The chemical structures of these additives are shown in Fig. 1. Two liquid electrolyte solutions such as 1 M $LiPF_6$/EC-PC-DEC-EMC-VC-fluoroethylene carbonate (FEC) and 1 M $LiPF_6$/EC-DMC are examined as standard liquid electrolytes for the additives PDMS-A, and PDMS-P/PDMS-EO, respectively. A conventional lithium-ion battery consisting of $LiCoO_2$||polyethylene separator||graphite is used as a test vehicle. The low temperature of -20 °C is selected so that the additives can be dissolved easily in standard liquid electrolytes; also, at this temperature, the surface of the graphite anode will be protected. The room temperature performance of lithium-ion batteries containing the standard liquid electrolytes and PDMS-based additives is also evaluated for comparison.

2. Experimental

The standard liquid electrolytes used were commercial products (PanaX Etec) of 1 M $LiPF_6$ dissolved in EC/PC/EMC/DEC/VC/FEC (20:5:55:20:2:5 by volume, coded as (A)) and 1 M $LiPF_6$ in EC/DMC (1:1 by volume, coded as (B)). All additives, PDMS-A (M_w = 26,000), PDMS-P, and PDMS-EO were purchased from Sigma-Aldrich; these materials were dried in a vacuum chamber for 12 h prior to use. The additive PDMS-A was used for liquid electrolyte (A) only, whereas the other additives, PDMS-P and PDMS-EO, were used for liquid electrolyte (B). The electrochemical stabilities of the liquid electrolytes with and without the additives (0-5 wt.% for PDMS-A and 5 wt.% for PDMS-P and PDMS-EO, based on the content of standard liquid electrolyte solution) were measured using the linear sweep voltammetry technique. The 5 wt.% value for PDMS-P and PDMS-EO was arbitrarily selected as a representative composition that can be examined for the effect of addition. 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 2-6 V. The ionic conductivities of the electrolytes containing different amounts of additives were examined in the temperatures range of -20 to 80 °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 liquid electrolytes with and without the additives between two Ni electrodes (1 cm × 1 cm) in an Al-pouch.

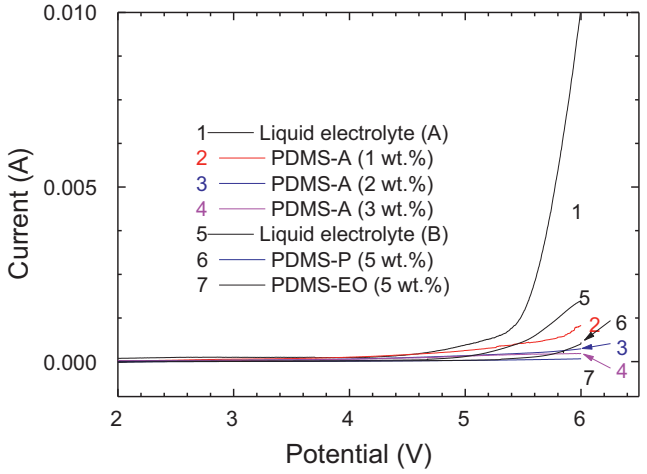

Fig. 2. Electrochemical stabilities of electrolyte solutions adopting the additives: liquid electrolyte (A) with 0-3 wt.% of PDMS-A and liquid electrolyte (B) with PDMS-P and PDMS-EO (0 and 5 wt.% each).

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 lithium-ion batteries ($LiCoO_2$||polyethylene separator||graphite) at room temperature and at -20 °C. The cathode and anode (92 wt.% each) were composed of poly(vinylidene fluoride) (5 wt.%) as a binder and carbon black (Super P, Timcal Graphite & Carbon, 3 wt.%) as a conductive agent. The porous polyethylene separator used was provided by Celgard (Model 2045). PDMS-based additives were injected into the standard liquid electrolytes before sealing the coin cells. Charge-discharge cycling tests of the lithium-ion batteries were carried out in constant-current mode in the range of 3.0-4.2 V at 0.1-2.0 C-rate using a 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 mAh g^{-1} of Li_xCoO_2 (x = 0.5). Room temperature cycling was performed under conditions of charging at 0.1 C-rate and discharging at 0.5 C-rate, whereas the low temperature cycling was carried out under conditions of charging at 0.1 C-rate (25 °C) and discharging at 0.1 C-rate (-20 °C). The electrochemical impedance spectra were also obtained after the initial discharge 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, using

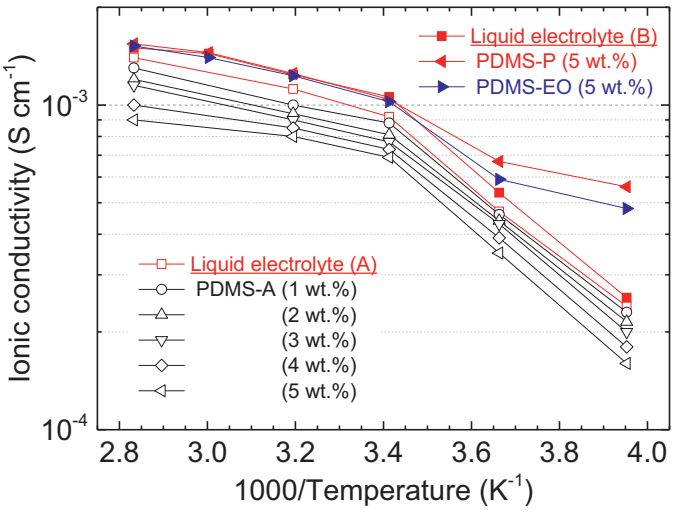

Fig. 3. Temperature dependence of ionic conductivities of electrolyte solutions adopting the additives.