

Poly-ether modified siloxanes as electrolyte additives for rechargeable lithium cells

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Abstract

Influence of four poly-ether modified siloxanes as electrolyte additives on charge–discharge cycling properties of lithium was examined. As siloxanes, diethylene glycol methyl-(3-dimethyl(trimethylsiloxy)silyl propyl)ether (sample A), diethylene glycol methyl-(3-dinethyl(trimethylsiloxy)silyl propyl)-2-methylpropyl ether (sample B), diethylene glycol methyl-(3-bis(trimethylsiloxy)silyl propyl)ether (sample C) and diethylene glycol-(3-methyl-bis(trimethylsiloxy)silyl-2-methylpropyl)ether (sample D) were investigated. As a base electrolyte solution, 1 M ($M, \text{mol L}^{-1}$) LiPF_6 -ethylene carbonate (EC)/methyl ethyl carbonate (MEC) (mixing volume ratio = 3:7) was used. As the anodes, lithium metal, natural graphite carbon and silicon– SiO_2 –carbon (Si–C) composite electrodes were used. Lithium cycling efficiencies of these three anodes improved and an impedance of anode/electrolyte interface decreased by adding poly-ether modified siloxanes. Graphite/ LiCoO_2 and Si–C/ LiCoO_2 cells exhibited better anode utilization and good cycling performance by using 1 M LiPF_6 -EC/MEC + siloxane electrolytes. It was also found that thermal stability of the electrolyte solutions improved by adding siloxanes. Thermal decomposition temperature of 1 M LiPF_6 -EC/MEC shifted to higher temperature by adding siloxanes. Amount of heat-output of graphite–lithium anodes with M LiPF_6 -EC/MEC electrolyte solutions decreased and the temperature starting the heat-output shifted to higher temperature by adding siloxanes. Among siloxanes examined here, samples B and D exhibited much better performance.

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1. Introduction

Many of commercial lithium ion cells are composed of carbon anode and LiCoO_2 cathode with nonaqueous electrolyte solutions. Typical example of nonaqueous electrolyte solutions is LiPF_6 -ethylene carbonate (EC)/methyl ethyl carbonate (MEC). The improvement of energy density of lithium ion cells has been required every year. However, now the capacity of carbon anodes is getting closer to the theoretical value (372 mA h g^{-1}). Then, new anode materials having higher energy density than carbon have been studied. Examples of these materials are lithium metal, various Si- and Sn-based compounds [1]. At this stage, the cycleability of these materials is not sufficient for commercial use. The choice of the electrolyte materials (solvents and solutes) is one of the most important factors for

the charge–discharge cycling performance of lithium cells with various anodes.

Many researches on the electrolyte solutions have been carried out for improving lithium cycleability [2]. One of these researches is an addition of surfactants (surface active agents) to electrolyte solutions such as poly-ethyleneglycol dimethyl ethers [3]. The mechanism of lithium cycling efficiency enhancement by the addition of these compounds is explained as follows. These compounds are less reactive toward lithium and adsorbed on the lithium anode surface. This adsorption layer suppresses the lithium dendrite formation and the reduction of electrolyte solutions by lithium [3].

In this study, influence of poly-ether modified siloxanes as electrolyte additives on lithium cycling efficiency was examined. As siloxanes, diethylene glycol methyl-(3-dimethyl(trimethylsiloxy)silyl propyl)ether (sample A), diethylene glycol methyl-(3-dinethyl(trimethylsiloxy)silyl propyl)-2-methylpropyl ether (sample B), diethylene glycol methyl-(3-bis(trimethylsiloxy)silyl propyl)ether (sample C) and diethylene glycol-(3-methyl-

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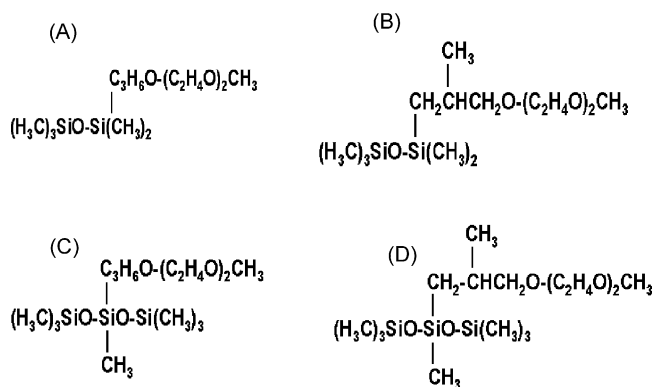


Fig. 1. Chemical structure of poly-ether modified siloxanes. Sample A, diethylene glycol methyl-(3-dimethyl(trimethylsiloxy)silyl propyl)ether; sample B, diethylene glycol methyl-(3-dinethyl(trimethylsiloxy)silyl propyl)-2-methylpropyl ether; sample C, diethylene glycol methyl-(3-bis(trimethylsiloxy)silyl propyl)ether and sample D, diethylene glycol-(3-methyl-bis(trimethylsiloxy)silyl-2-methylpropyl)ether.

Table 1
Viscosities of siloxanes

Siloxanes	Kinematic viscosity at 20 °C ($\times 10^{-4} \text{ m}^2 \text{ s}^{-1}$)
Sample A	3.3
Sample B	3.7
Sample C	4.0
Sample D	4.3

bis(trimethylsiloxy)silyl-2-methylpropyl)ether (sample D) were investigated. As the base electrolyte solution, 1 M (M , mol L^{-1}) $\text{LiPF}_6\text{-EC/MEC}$ (3:7 in volume mixing ratio) was used. As the anodes, lithium metal, natural graphite carbon and Si-SiO₂-carbon composite (Si-C) anodes were investigated. Fig. 1 shows the chemical structure of four siloxanes used in this work. Chemical bonding of Si-O is stronger and more stable than that of C-O. The siloxanes shown in Fig. 1 have ether groups as hydrophilic groups and they work as the surfactants. They are colorless and clear liquid at room temperature. Their kinematic viscosities are less than $5 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ at 20 °C (Table 1).

2. Experimental

2.1. Preparation of electrolyte solutions

Siloxanes were obtained from Shin-Etsu Chemical Co. Electrolyte solutions were prepared by mixing siloxanes and 1 M $\text{LiPF}_6\text{-EC/MEC}$ (3:7 in volume ratio) (Tomiya Pure Chemicals Co., Lithium Battery Grade). Before mixing, siloxanes were dried over molecular sieves 3A (Kanto Chemicals Co.). Water content of electrolyte solutions was less than 20 ppm as determined by the Karl-Fisher titration method. Hereafter, “EM” represents 1 M $\text{LiPF}_6\text{-EC/MEC}$ (3:7).

2.2. Charge-discharge cycling tests of lithium anodes and LiCoO_2 cells

Cyclic voltammetry was performed, using a glass cylindrical test cell with a lithium metal sheet counter electrode

(0.1 mm thickness) pressed on a Ni net (200 mesh, 15 mm length, 4 mm width, 0.05 mm thickness) and a Pt working electrode (4 mm length, 4 mm width and 0.05 mm thickness, 0.09 cm^2). Lithium charge-discharge cycling tests were carried out galvanostatically, using a coin cell (coin type 2032, diameter 20 mm in diameter, 3.2 mm in thickness) with a lithium metal sheet counter electrode (0.1 mm thickness, 15 mm diameter) and a stainless steel (SUS 316) cathode case of the coin cell as the working electrode. The charge-discharge cycling efficiency (Eff) was obtained from the ratio of the stripping charge (Q_s)/plating charge (Q_p) on the stainless steel electrode with a charge-discharge voltage range of -2.0 to 1.0 V . The charge-discharge current density (I_p) was 0.5 mA cm^{-2} . The Q_p had a constant value of 0.5 mA h cm^{-2} .

In cases of Si-SiO₂-carbon composite (Si-C) and natural graphite electrodes, the charge-discharge tests were carried out by the charge-discharge voltage cut-off (0 and 1.5 V versus Li/Li^+) with a constant current density of 0.5 mA cm^{-2} by using the 2032 coin cells. These cells have a lithium metal counter electrode and the working electrode of Si-C or graphite. Using the 2032 coin cells carried out the charge-discharge test of LiCoO_2/C and $\text{LiCoO}_2/\text{Si-C}$ cells.

For these experiments, we prepared the printed carbon electrodes by coating a Ni sheet with a mixture of carbon powder (around 18 mg) and poly(vinylidene fluoride) (PVDF) (weight ratio of carbon:PVDF = 9:1) in *N*-methyl pyrrolidinone (NMP). We then evacuated the solvent and dried the electrodes. The printed carbon electrodes are 15 mm in diameter and 0.15 mm in thickness. Natural graphite powder used here has an average particle size of $10.7 \mu\text{m}$ in diameter, a surface area of $10.3 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ and a density of 0.21 kg m^{-3} . The printed LiCoO_2 electrodes were prepared by coating an Al sheet with a mixture of carbon powder (around 18 mg) and poly(vinylidene fluoride) (PVDF) (weight ratio of carbon:PVDF = 9:1) in *N*-methyl pyrrolidinone (NMP). We then evacuated the solvent and dried the electrodes.

The printed Si-C electrodes (15 mm in diameter and 0.15 mm in thickness) were prepared by similar method as natural carbon electrodes by using Si-C powder and polymer binder. Si-C material was prepared according to the papers [4–6] by methane-argon gas mixture-chemical vapor deposition (CVD) with $1100 \text{ }^\circ\text{C}$ heat treatment. Image of this final product of Si-C material is shown in Fig. 2. Fine silicon crystal was distributed in the SiO₂. The surface of the final product was covered with double layers composed of thin inside layer of SiC (silicon carbide) and thick outside layer of carbon.

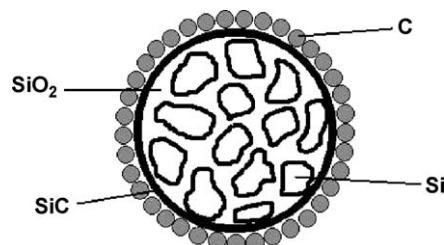


Fig. 2. Image of Si-SiO₂-carbon composite (Si-C).

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