

Organic compounds with heteroatoms as overcharge protection additives for lithium cells

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Abstract

Various organic compounds with heteroatoms (N, O, F, Si, P, S) were tested as overcharge protection additives for 4-V class lithium cells. It was found that trimethyl-3,5-xylylsilane exhibited preferable oxidation potential (E_{ox}) as overcharge protection additive, and charge–discharge cycling efficiency (Eff) of lithium anode in electrolyte with arylsilanes was as high as tolyladamantanes, reported previously by us. From room temperature to 60 °C, E_{ox} of trimethyl-3,5-xylylsilane decreased only 0.07 V. Difference in E_{ox} among regioisomers of tolyltrimethylsilanes is smaller than that among tolyladamantanes. ^1H NMR and UV spectra suggest the steric repulsion between tolyl group and trimethylsilyl group in *o*-tolyltrimethylsilane is smaller than that of the related substituents of *o*-tolyladamantane.

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1. Introduction

Lithium ion cells are hazardous if they undergo overcharge. To protect cells from overcharge, electrolyte additives (overcharge protection additives) have been utilized. When the cell is overcharged, current is consumed by electrochemical oxidation of the overcharge protection additive. As the overcharge protection additive, various compounds were tested to protect the cell by irreversible electrochemical polymerization such as biphenyl [1,2] or redox shuttles [3–5] reported that they consume current by reversible redox reaction occurred between anode and cathode. Biphenyl was well known additive, however, its low oxidation potential (E_{ox} , 4.54 V versus Li/Li^+) brings deterioration of the storage property of cell when the cell is fully charged. For the lithium cells with LiCoO_2 cathode, compounds oxidized in the region of 4.6–4.8 V are preferred as overcharge protection additives. At the same time, it is also required that notable worth effects for lithium cycling efficiencies is not observed when overcharge protection additives is used. With lithium metal anode, Eff was considerably decreased by addition of biphenyl [6]. Recently, we suggested several aryladamantanes as new over-

charge protection additives, which show preferable oxidation potentials and charge–discharge cycling efficiencies [7].

Almost additives reported previously are aromatic compounds composed of carbon, hydrogen and oxygen atoms. In this study, we investigated nitrogen compounds (Fig. 1) and aromatic compounds containing heteroatoms, i.e. N, O, F, Si, P, or S (Fig. 2) to find new additives. These compounds have not been investigated in detail for overcharge protection additives, and their electrochemical behavior, especially the effects on Eff, has not been clear.

We attempt to develop new overcharge protection additives with heteroatoms (N, O, F, Si, P, or S) for 4-V class lithium cells. We discuss about the difference of E_{ox} values of organosilicon regioisomers by measurements of ^1H NMR and UV spectra.

2. Experimental

2.1. Material preparation

The 1 M (M , mol dm^{-3}) LiClO_4 /propylene carbonate (PC) (Lithium Battery Grade, Tomiyama Pure Chemical Industries) was used as an electrolyte solution. Test solutions were prepared by mixing the additives with electrolyte solution. Liquid additives were dissolved in electrolyte and the solutions

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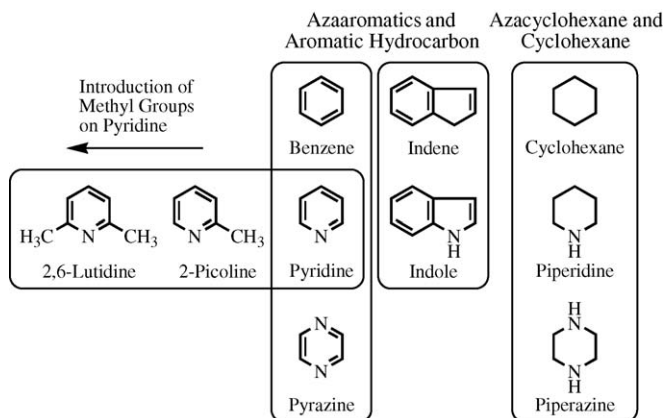


Fig. 1. Chemical structure of nitrogen compounds examined in this study.

were dried with type 4A molecular sieves. Solid samples were dried in vacuo for at least 3 h at 25 °C. The additives were dissolved in the electrolyte at 2 wt.%. When the solubility of the additive was lower than 2 wt.% at 25 °C, their saturated solutions were used. Aryltrimethylsilanes were prepared by similar method as described in literature [8,9]. 1-(3-Fluoro-4-methoxyphenyl)adamantane was prepared by following procedure referred to the literature [10].

Three-necked-flask with condenser was placed with magnesium (253 mg, 10.4 mmol) and dry diethyl ether (4 mL). 4-Bromo-2-fluoroanisole (2.14 g, 10.4 mmol) in diethyl ether (4 mL) was added dropwise, the reaction mixture was stirred at refluxed for 1 h. The ether was evaporated, filled with argon gas again, dichloromethane (12 mL) and 1-bromoadamantane (1.07 g, 4.97 mmol) was added. This mixture was stirred at reflux temperature for 9 h. The mixture was pored into ice-water and extracted with dichloromethane for three times, dried over sodium sulfate. After evaporation of the solvent, product was separated by silica gel column chromatography (hexane/ethyl acetate = 1/1). Further purification was achieved by recrystallization from methanol. The final product (752 mg of colorless crystal) was obtained in 58% yield. Melting point: 110–111 °C. ^1H NMR (CDCl_3 ppm), δ : 1.70–1.81 (m, 6H), 1.857 (d, 6H, $J = 2.4$ Hz), 2.086 (s, 3H), 3.868 (s, 3H), 6.87–6.93 (m, 1H), 7.01–7.11 (m, 2H). ^{13}C NMR (CDCl_3 ppm), δ : 28.88, 35.68, 36.68, 43.25, 112.88, 113.12, 120.15, 145.04, 150.59, 153.82. IR (KBr cm^{-1}), ν : 2912, 2848, 1518, 1268, 1130,

1022, 798. Mass (m/z (%)): 260 (M^+ , 100), 203 (89), 166 (23), 139 (18).

2.2. Measurement of electrochemical and physical properties

2.2.1. Electrochemical properties and spectral measurement

All the test cells were prepared in argon gas filled glove box. Measurements of E_{ox} were carried out at 25 °C unless otherwise noted. Test cells were assembled by using a platinum sheet electrode (0.1 mm thick, 0.15 cm^2 in area) as a working electrode, a lithium metal sheet (0.04 cm^2 , 0.1 mm thick) pressed on nickel mesh (200 mesh, 0.05 mm thick, 15 mm^2 in area) as a counter electrode and a lithium metal as reference electrode. These electrodes and the electrolyte solution were placed in a cylindrical glass test cell. Additives were dissolved into 1 M LiClO_4/PC electrolyte by 2 wt.%. If the solubility of additives was less than 2 wt.%, saturated solution was used for measurement. E_{ox} was measured by liner sweep voltammetry at 50 mV s^{-1} with platinum sheet electrode (0.1 mm thick, 0.15 cm^2 in area). Lithium charge–discharge cycling tests were carried out galvanostatically at 25 °C with the same cell as that used for the E_{ox} measurements with lithium metal anode. Evaluation of E_{ox} and lithium cycling efficiency (Eff) were performed same as already described [7]. In this report, lithium cycling efficiency was evaluated by using the ratio of $(\text{Eff}_{\text{Add}}/\text{Eff}_{\text{PC}})_{50}$, which is the average of $(\text{Eff}_{\text{Add}}/\text{Eff}_{\text{PC}})$ value (Eq. (1)) from the first to the 50th cycle. Eff_{Add} and Eff_{PC} mean the Eff of 1 M $\text{LiClO}_4\text{-PC}$ with additives and 1 M $\text{LiClO}_4\text{-PC}$ alone, respectively:

$$\frac{\text{Eff}_{\text{Add}}}{\text{Eff}_{\text{PC}}} = \frac{[\text{Eff of 1 M LiClO}_4\text{-PC with additives}]}{[\text{Eff of 1 M LiClO}_4\text{-PC alone}]} \quad (1)$$

^1H NMR spectra were obtained by JEOL α -300 (^1H at 300 MHz). UV spectra were obtained by a Shimadzu UV-3000PC spectrometer.

2.2.2. Evaluation of solubility of additives in electrolyte solution

Additives were dissolved in 1 M LiClO_4/PC electrolyte respectively, with stirring for 24 h at 25 °C. Saturated solution were filtrated and diluted in ethanol. These samples were measured UV absorption spectra at 25 °C, solubility of additives were evaluated from absorbance at the wavelength of absorption maximum (λ_{max}).

3. Results and discussion

3.1. Nitrogen compounds

As azaaromatics and cycloamines, pyridine and their methyl derivatives, pyrazine, indole, piperidine and piperazine were examined for the overcharge protection additive. Their E_{ox} and Eff values were compared with those of the related aromatic hydrocarbons. Their E_{ox} and Eff values are summarized

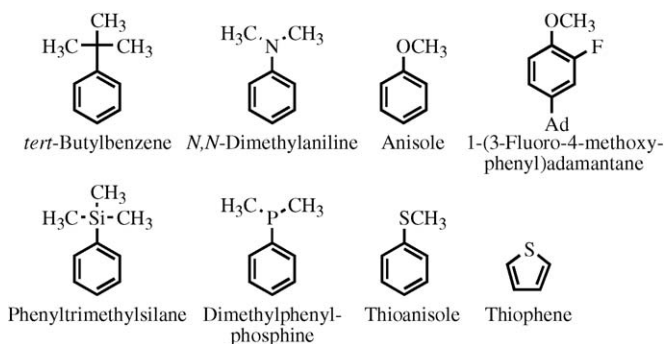


Fig. 2. Chemical structure of PhXMe_n-type compounds and other aromatics (Ad, 1-adamantyl).

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