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 $60\,^{\circ}$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. ^{1}H 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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Keywords: Lithium cell; Safety; Overcharge; Electrolyte

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 ^{1}H NMR and UV spectra.

2. Experimental

2.1. Material preparation

The 1 M (M, mol dm^{-1}) 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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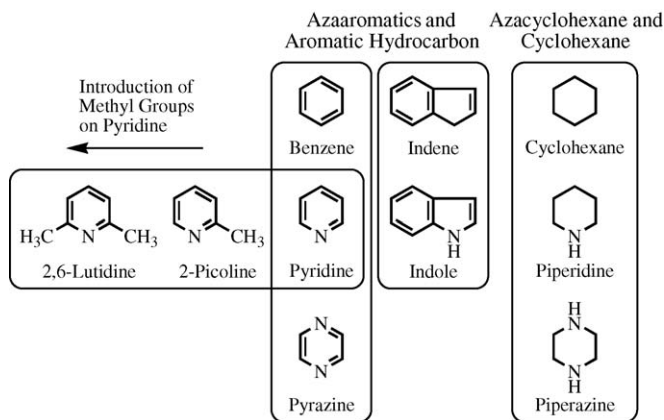*E-mail address:* tobi@chem.gunma-u.ac.jp (S.-I. Tobishima).

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. ^{1}H 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,
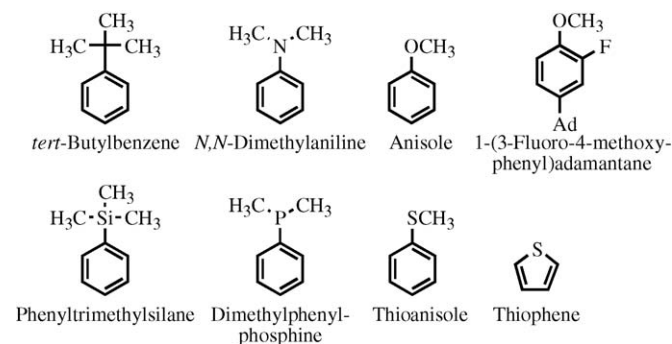

Fig. 2. Chemical structure of PhXMe$_n$-type compounds and other aromatics (Ad, 1-adamantyl).

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 (Eff$_{Add}$/Eff$_{PC}$)$_{50}$, which is the average of (Eff$_{Add}$/Eff$_{PC}$) value (Eq. (1)) from the first to the 50th cycle. Eff$_{Add}$ and Eff$_{PC}$ mean the Eff of 1 M LiClO$_4$-PC with additives and 1 M LiClO$_4$-PC alone, respectively:

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

^{1}H NMR spectra were obtained by JEOL α-300 (^{1}H at 300 MHz). UV spectra were obtained by a Shimazu 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

Table 1
E_{ox} and Eff of nitrogen compounds

Compound	E_{ox} (V) vs. Li/Li$^+$	$(Eff_{Add})_{50}/(Eff_{PC})_{50}$
Benzene	5.10	0.889
Pyridine	–[a]	0.561
2-Picoline	5.41	–[b]
2,6-Lutidine	4.87	0.661
Pyrazine	–[a]	–[b]
Indene	4.09	0.090
Indole	3.79	0.907
Cyclohexane	5.90[c]	0.875
Piperidine	4.87	0.332
Piperazine	–[a]	0.055

[a] Oxidation current was not observed in the region under 6 V, which is E_{ox} of electrolyte.

[b] Measurement was failed by large cell resistance.

[c] 1 M LiBF$_4$/PC was used for electrolyte.

in Table 1. Oxidation current was not observed under E_{ox} of electrolyte in pyridine and pyrazine because of the nitrogen atom which is higher electronegativity than carbon atom cause aromatic ring partially positive charge, whereas benzene is oxidized at 5.10 V. Similar to the relationship between benzene and methylbenzenes [7], E_{ox} value of 2-picoline (5.41 V) and 2,6-lutidine (4.87 V) that methyl groups are connected on pyridine, are lower than pyridine. According to Table 1, E_{ox} value of piperidine (4.87 V) is lower than cyclohexane (5.90 V) because of oxidation occurred at the nitrogen atom. E_{ox} values of piperidine and 2,6-lutidine are near to the region of 4.6–4.8 V, however, their Eff values are too low to apply to overcharge protection additives.

3.2. PhXMe$_n$ (X = C, N, O, Si, P and S) type compounds

Results of E_{ox} and Eff measurement of PhXMe$_n$-type compounds are described in Table 2. E_{ox} of N,N-dimethylaniline was unusually lower than other samples because of the effect of electron-releasing of dimethylamino group. Anisol was already examined in our previous report [7]; its E_{ox} value is 4.38 V. Although thiophene is also too low E_{ox} to use as overcharge protection additive, this E_{ox} value seems inconsistent with electronegativity of O and S atom. This phenomenon may relate the

Table 2
E_{ox} and Eff of PhXMe$_n$ (X = C, N, O, Si, P and S) and other aromatics

Compound	E_{ox} (V) vs. Li/Li$^+$	$(Eff_{Add})_{50}/(Eff_{PC})_{50}$
$tert$-Butylbenzene	5.00	0.899
N,N-Dimethylaniline	3.59	0.730
Anisole	4.38	0.626
1-(3-Fluoro-4-methoxyphenyl) adamantane	4.46	0.924
Phenyltrimethylsilane	5.01	0.894
Dimethylphenylphosphine	–[a]	–[a]
Thioanisole	4.07	1.00
Thiophene	4.49	0.769

[a] Electrolyte became slightly cloudy by addition of sample, and oxidation current was not observed in the region under 6 V which is E_{ox} of electrolyte.

Table 3
Solubility of aryladamantanes in 1 M LiClO$_4$/PC electrolyte at 25 °C

Compound	Solubility (10^{-2} M)
Phenyladamantane	5.2
p-Tolyladamantane	2.3
1-(4-Methoxyphenyl)adamantine	7.0
1-(3-Fluoro-4-methoxyphenyl)adamantane	4.9

difference of steric interaction between methoxyl or methylthio group and benzene ring [11].

Fluorine atom on aromatic ring affects as electron-withdrawing. So, it was expected that E_{ox} of fluorobenzene is higher than that of benzene. When fluorobenzene is used as overcharge protection additives, it requires preferable electron-releasing group on the benzene ring to show E_{ox} value in the region of 4.6–4.8 V. Methyl group, methoxyl group or adamantyl group on benzene ring affect as electron-releasing groups, more or less. 1-(4-Methoxyphenyl)adamantane shows low E_{ox} and high Eff (E_{ox} = 4.22 V; $(Eff_{Add})_{50}/(Eff_{PC})_{50} = 1.01$) [7]. If E_{ox} of it increase 0.4 V by fluorination, then it is expected to show preferable E_{ox}. Therefore, 1-(3-fluoro-4-methoxyphenyl)adamantane was synthesized and examined.

E_{ox} and Eff values of 1-(3-fluoro-4-methoxyphenyl)-adamantane are shown in Table 2. Its E_{ox} is only 4.46 V. It is not enough value. On the other hand, halogenation of organic compound generally causes increase of its lipophilicity, therefore the solubility in electrolyte may be influenced. Table 3 shows solubility of aryladamantanes and 1-(3-fluoro-4-methoxyphenyl)adamantane for 1 M LiClO$_4$/PC electrolyte. Solubility of 1-(3-fluoro-4-methoxyphenyl)adamantane is lower than phenyladamantane whereas solubility of aryladamantane with a methoxyl group is higher than phenyladamantane. It is presumed that further fluorination of methoxyphenyladamantane cause increasing its E_{ox} nearer to 4.6 V. At the same time, its solubility in electrolyte may more decrease.

E_{ox} values of $tert$-butylbenzene and phenyltrimethylsilane are both ca. 5.0 V. E_{ox} of phenyltrimethylsilane is slightly higher than $tert$-butylbenzene because of electronegativity of silicon atom is lower than carbon atom. Investigation of organosilicon compounds are not satisfactorily. So examination of phenyltrimethylsilane was carried prior to the carbon analog whereas its Eff value is similar to $tert$-butylbenzene. If the E_{ox} value of phenyltrimethylsilane was decreased 0.2–0.4 V without notable decreasing in Eff, it may be satisfactory additive in the point of the oxidative property. Decrease of its E_{ox} was attempted by synthesis of derivatives with electron-releasing groups on their benzene ring (Fig. 3). E_{ox} and Eff values of these derivatives are summarized in Table 4. E_{ox} of these derivatives reflect Hammett σ_p value of their substituent (Fig. 4) and λ_{max} of UV spectra (Fig. 5). Electron density of benzene ring influence on E_{ox}, so it is suggested that electrochemical oxidation is occurred at benzene ring. As a result, trimethyl-3,5-xylylsilane exhibits preferable E_{ox}. Temperature dependency of trimethyl-3,5-xylylsilane is shown in Fig. 6. From room temperature to 60 °C, E_{ox} is kept in the region of 4.6–4.8 V whereas E_{ox} of biphenyl is decreased at higher temperature.
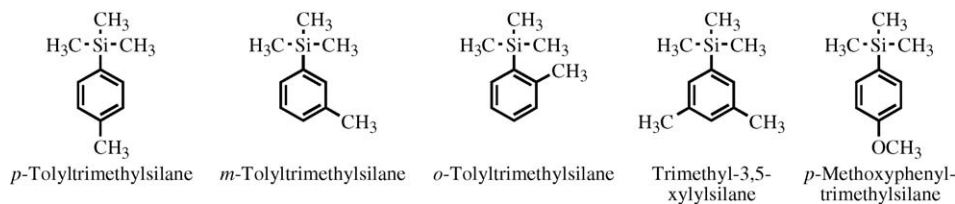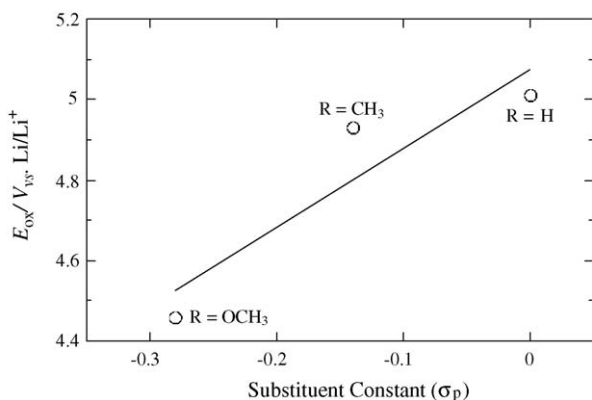
Fig. 3. Chemical structure of phenyltrimethylsilane derivatives.

Table 4
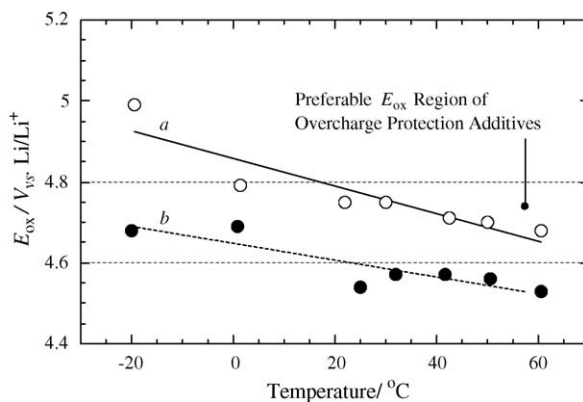E_{ox} and Eff of phenyltrimethylsilane derivatives

Compounds	E_{ox} (V) vs. Li/Li$^+$	(Eff$_{Add}$)$_{50}$/(Eff$_{PC}$)$_{50}$
Phenyltrimethylsilane	5.01	0.894
p-Tolyltrimethylsilane	4.93	0.945
m-Tolyltrimethylsilane	4.92	0.754
o-Tolyltrimethylsilane	4.91	0.923
Trimethyl-3,5-xylylsilane	4.75	0.902
4-Methoxyphenyltrimethylsilane	4.46	0.783
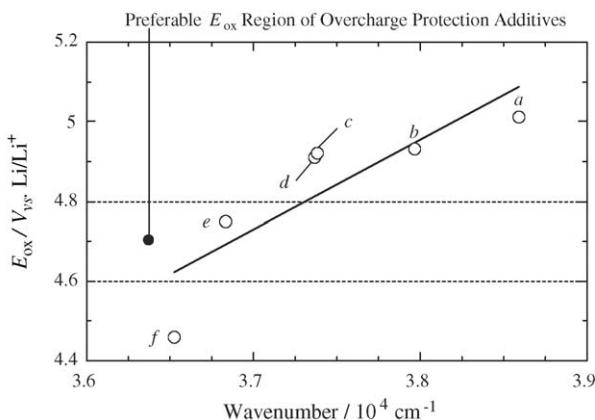
Trimethyl-3,5-xylylsilane is more preferable than biphenyl in the point of the property of the cell storage at high temperature.

Tolyltrimethylsilanes and tolyladamantanes have similar moiety of structure on the benzene ring, each other. By the steric repulsion between methyl group on benzene ring and adamantyl group, E_{ox} of o-tolyladamantane is 0.15 V higher than *para*-isomer. In contrast, difference of E_{ox} between their *para*- and *ortho*-isomers of tolyltrimethylsilanes is only 0.02 V. The deference of their steric effects clearly appears in ^{1}H NMR spectra. Chemical shifts of protons affected by bulky substituent are shifted to lower magnetic field [12]. Fig. 7 shows difference of chemical shifts among each regioisomers. Hydrogen signal of methyl groups on benzene ring of o-tolyltrimethylsilane appears 0.137 ppm deshielded than *para*-isomer whereas the case of tolyladamantane is 0.305 ppm. Difference in hydrogen signals of trimethylsilyl group among regioisomers of tolyltrimethyl-silanes is also smaller than that of adamantyl group of toly-ladamantanes. These behaviors reflect the smaller steric effect of tolyltrimethylsilanes than tolyladamantanes. In both series, signals of hydrogen atom of methyl group, adamantyl group or trimethylsilyl group of *meta*-isomer were in the middle of between *para*- and *ortho*-isomers. E_{ox} value of *meta*-isomer agrees to the relationship between their chemical sifts.

Steric effect also influences λ_{max} and absorbance of UV spectra of tolyltrimethylsilane and tolyladamantanes (Table 5). Absorbance of p-tolyladamantane is about 2.7 times as large as *ortho*-isomer because of hindrance of hyperconjugation between methyl group and benzene ring by the steric repulsion in *ortho*-isomer. However, among isomers of tolyltrimethylsi-lanes, absorbance of *ortho*-isomer is higher than *para*-isomer.

Fig. 4. Substituent effect to E_{ox} of phenyltrimethylsilane derivatives.

Fig. 5. Relationship between wavenumber at the absorption maximum of aryltrimethylsilane and their E_{ox} values: scan range, 240–400 nm; 25 °C in ethanol solvent. *a*, Phenyltrimethylsilane; *b*, p-tolyltrimethylsilane; *c*, m-tolyltrimethylsilane; *d*, o-tolyltrimethylsilane; *e*, trimethyl-3,5-xylylsilane; *f*, 4-methoxyphenyltrimethylsilane.

Fig. 6. Temperature dependency of the E_{ox}. Potential scan rate, 5 mV s^{-1} at −20 and 0 °C; 50 mV s^{-1} at 20, 30, 40, 50 and 60 °C. *a* (−○−), Trimethyl-3,5-xylylsilane; *b* (··●··), biphenyl.
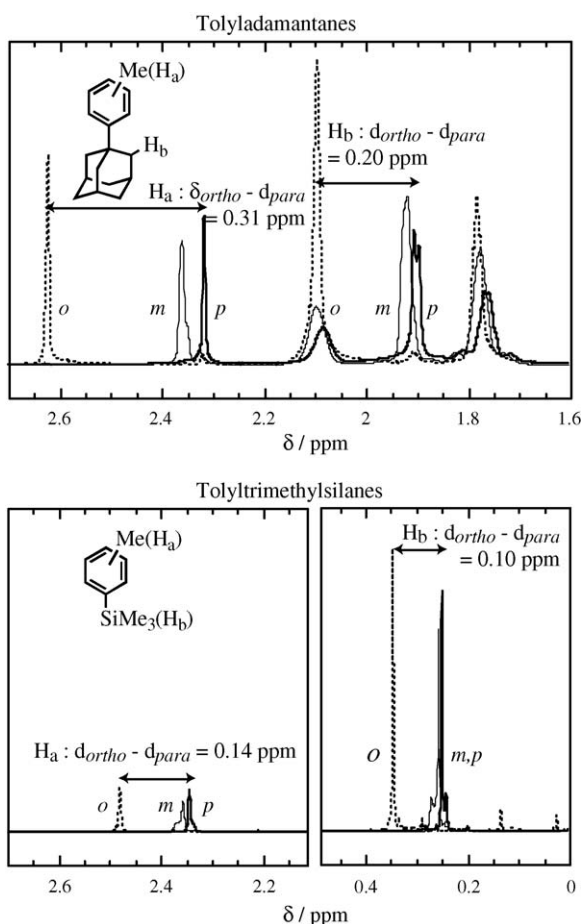
Fig. 7. ^{1}H NMR spectra of regioisomers of tolyltrimethylsilane and tolyladamantane: p (——), *para*-isomer; m (—), *meta*-isomer; o (···), *ortho*-isomer.
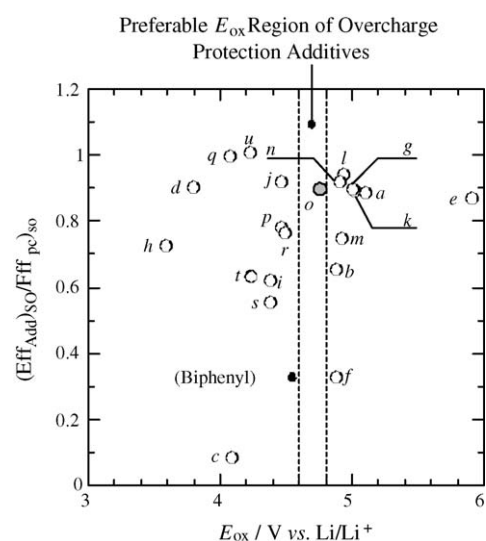

Fig. 8. Relationship between E_{ox} and Eff of compounds examined in this study.

4. Conclusion

Through this work, nitrogen compounds, PhXMe$_n$-type compounds were examined as overcharge protection additives for 4-V class lithium cells. Trimethyl-3,5-xylylsilane demonstrates possibility of application to overcharge protection additive because of its preferable E_{ox} (around 4.7 V) and higher charge–discharge cycling efficiencies of lithium anode. It is expected that other organosilicons with 3,5-xylyl groups such as 3,5-xylyltrialkylsilane and di(3,5-xylyl)dialkylsilane show similar E_{ox} value to trimethyl-3,5-xylylsilane.

–R effect of the trimethylsilyl group in p-tolyltrimethylsilane [13,14] may influence this phenomenon. This effect is not apparently observed in their E_{ox} values.

As discussed above, any regioisomers of tolyltrimethylsilanes show similar E_{ox} among regioisomers. Hence, there is a possibility of that they can be used as overcharge protection additives without separation of isomers. It is an advantageous point for industrial application. On the other hand, E_{ox} of tolyladamantane series easily changes by appropriate selection of isomers because of their large steric effect.

Relationships between E_{ox} and (Eff$_{Add}$)$_{50}$/(Eff$_{PC}$)$_{50}$ was plotted in Fig. 8. Among these compounds, trimethyl-3,5-xylylsilane exhibit both preferable E_{ox} and higher Eff than biphenyl.

Table 5
The λ_{max} and absorbance of tolyltrimethylsilanes and tolyladamantanes

Compound	λ_{max} (nm) (Absorbance)
p-Tolyltrimethylsilane	263 (260)
m-Tolyltrimethylsilane	268 (450)
o-Tolyltrimethylsilane	268 (410)
p-Tolyladamantane	265 (400)
m-Tolyladamantane	264 (300)
o-Tolyladamantane	261 (150)

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