

Electrochemical properties of aryladamantanes as new overcharge protection compounds for lithium cells

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Abstract

The development of new overcharge protection compounds for 4 V-class lithium cells with LiCoO_2 cathodes was attempted in order to protect the cells from the hazards of ignition and/or explosion when overcharged. At least two requirements must be met as regards overcharge protection compounds. They must have an oxidation potential (E_{ox}) in the 4.6–4.8 V range versus Li/Li^+ and they must not adversely influence the lithium cycling efficiency (Eff). The overcharge protection compounds were used by adding them to the electrolyte solution, which was LiClO_4 /propylene carbonate. First, this study involved a basic examination of the relationships among the E_{ox} values of arenes including polyacenes, naphthalene derivatives and methylbenzenes, their chemical structure, the aromatic ring size and the effects of substituent functional groups. Next, the E_{ox} and Eff values of cycloalkanes including cyclohexane, decaline, adamantane and norbornane were examined. Based on these examination results, various adamantane derivatives were synthesized and their electrochemical properties were investigated. Finally, four aryladamantanes (1-(*p*-tolyl)adamantane, 1-(*m*-tolyl)adamantane, 1-(*o*-tolyl)adamantane, 1-(4-ethylphenyl)adamantane) were found to exhibit better E_{ox} and Eff values than those of biphenyl, which is already used in commercial cells as an overcharge protection additive.

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Keywords: Lithium cell; Safety; Overcharge; Electrolyte

1. Introduction

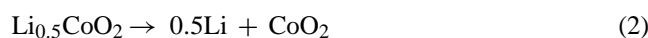
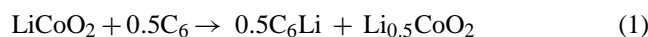
Many commercial lithium ion cells are composed of carbon anodes and lithium cobalt oxide (LiCoO_2) cathodes with organic electrolyte solutions. More than 100 million cells per year are used for a wide variety of applications including camcorders, cellular phones and note-type personal computers. However, the safety margin of these lithium ion cells is still small for practical use and they have two fundamental weaknesses: insufficient tolerance to overcharging and poor thermal stability. Lithium ion cells may be overcharged when the cell voltage is incorrectly

detected by the charging control system, when the charger breaks down, or when the wrong charger is used. Lithium ion cells are hazardous and have the potential to catch fire and/or explode when they are overcharged [1–3]. To protect them against overcharging, commercial cells have an electronic overcharge protection circuit. The circuit shuts off the current when it detects that the charging voltage has exceeded the normal full charging voltage (generally 4.2 V). However, it is desirable for the cell to be able to protect itself against overcharging.

When cells are overcharged [1], the lithium ions remaining in the lithium cobalt oxide cathode ($\text{Li}_{0.5}\text{CoO}_2$ after standard full charging) are removed at 4.3–4.7 V and more lithium ions are supplied to the carbon anode than under standard charging conditions [Eqs. (1) and (2)] [1,2]. If the lithium

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insertion ability of the carbon anode is small, lithium metal may be deposited on the carbon, and this causes a serious reduction in thermal stability. After lithium has been removed from the cathode, the electrolyte starts to be oxidized. This electrochemical electrolyte oxidation results in a distinct heat output. When the cell temperature increases the anode may simultaneously reduce the electrolyte. A severe case of cell overcharging occurs when a high rate overcharging current is applied or the thermal stability of the cell is extremely low. In this case, the cell may smoke, ignite or explode [1,2].



Biphenyl (BP) has already been used as an overcharge protection compound for commercial lithium ion cells [4,5]. This is because BP has a preferable E_{ox} value of 4.54 V versus Li/Li⁺ [3–5]. BP is used by adding it to the electrolyte. However, with a lithium metal anode, the lithium cycling efficiency decreases greatly when BP is added [3]. This is because biphenyl is easily reduced by alkali metals to form a one electron transferred stable reduction product, lithium biphenylide [6,7]. In addition, when a lithium ion cell is in a fully charged condition for a long period, there are concerns about the adverse influence of BP on cell storage life. This is because the E_{ox} of BP is close to the full charge/voltage and there is an oxidation shoulder even at 4.3 V versus Li/Li⁺ (approximately 4.2 V versus C₆Li). This means the oxidation of BP may proceed gradually when a fully charged cell is stored for a long period. Therefore, compounds are required that have a higher E_{ox} value than BP.

The overcharge protection compounds we are looking for must have at least the two properties described below. First, the oxidation potential must be between the final standard full charging voltage (4.2 V versus C₆Li, 4.3 V versus Li/Li⁺) and that of the complete removal of lithium from LiCoO₂ (4.3–4.7 V versus C₆Li, 4.4–4.8 V versus Li/Li⁺), which is lower than those of the electrolyte solutions generally used for lithium ion cells [3]. Specifically, compounds with a higher E_{ox} value than BP (4.54 V versus Li/Li⁺) are preferable. Second, the additives must not have a detrimental influence on the charge–discharge cycle life.

In this study, various aromatic compounds are tested for their applicability as overcharge protection additives. First, the relationship between the chemical structure of the aromatics and their oxidation behavior is systematically examined. In these basic examinations, we investigate polyacenes, naphthalene derivatives and methylbenzenes. We then attempt to design an appropriate chemical structure and to develop new overcharge protection additives that exhibit both an appropriate E_{ox} value (4.6–4.8 V versus Li/Li⁺) and a high lithium charge–discharge cycling efficiency. In this attempt, we examine cycloalkanes including cyclohexane, decaline, norbornane, adamantane and their derivatives.

2. Experimental

2.1. Materials

A 1 M (M: mole dm⁻¹) of commercially obtained LiClO₄/PC was used (Lithium Battery Grade, Tomiyama Pure Chemical Industries). Aryladamantane derivatives were synthesized by similar methods to that described in [8].

Nonvolatile solid additives were dried in vacuo for at least 3 h at room temperature. Test solutions were prepared by mixing the additives with electrolyte solution. Liquid or volatile solid additives were dissolved in electrolyte and the solutions were dried with type 4A molecular sieves. The additives were dissolved in the electrolyte at 2 wt% [3–5]. When the solubility of the additive was lower than 2 wt% at 25 °C, their saturated solutions were used.

2.2. Measurement of oxidation potential (E_{ox}) of electrolyte additives

All the test cells were prepared in an argon gas filled glove box. Measurements 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 cm² in area) as a working electrode, a lithium metal sheet (0.04 cm², 0.1 mm thick) pressed on nickel mesh (200 mesh, 0.05 mm thick, 15 mm² in area) as a counter electrode and a lithium metal reference electrode. These electrodes and the electrolyte solution were placed in a cylindrical glass test cell.

In this work, E_{ox} values were determined as the voltage at the intersection of the x -axis base line (voltage) and the tangent of the rapid increase in the current curve. The E_{ox} values determined by this method reflect the potential certainly starting oxidation, so from a practical viewpoint, the overcharge protection function can be guaranteed to work at this potential. Potential sweeping was performed from the open circuit voltage of the test cell to 10 V versus Li/Li⁺ at a scanning rate of 50 mV s⁻¹ by using a galvanopotentiostat (Hokuto Denko Co., HZ-3000). As an example, Fig. 1 shows the measured BP in 1 M LiClO₄/PC. It indicates that the E_{ox} of biphenyl is 4.54 V versus Li/Li⁺. The oxidation shoulder of biphenyl can be seen at 4.3 V versus Li/Li⁺.

2.3. Measurement of charge–discharge cycling efficiencies of lithium anodes

Lithium charge–discharge cycling tests were carried out galvanostatically at 25 °C with the same cell as that used for the E_{ox} measurements. The charge–discharge cycling efficiency (Eff) was obtained from the ratio of the stripping capacity (Q_s)/plating capacity (Q_p) on a Pt electrode using a 1.5 V potential cut-off as the stripping (discharging) end point. The charge–discharge current (I_{ps}) was 1.5 mA (10 mA cm⁻²) and the plating (charging) duration was

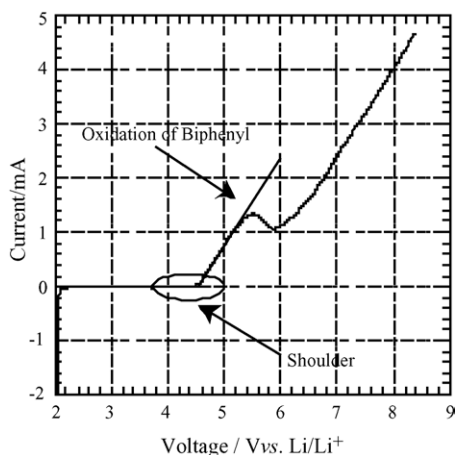


Fig. 1. I - V curve for 1 M LiClO_4/PC + biphenyl (2 wt%) at 25 °C.

1 min ($Q_p = 0.025$ mAh). Eff_{50} (%), namely the average Eff value from the first to the 50th cycle was calculated. Fig. 2 shows the lithium cycling efficiency of 1 M LiClO_4/PC alone. 1 M LiClO_4/PC alone shows an Eff_{50} of 64.5%. The ratio ($\text{Eff}_{\text{Add}}/\text{Eff}_{\text{PC}}$) of the Eff of 1 M LiClO_4/PC with additives to the Eff of 1 M LiClO_4/PC alone was used to compare the lithium cycling efficiencies of the electrolyte solutions with different additives (Eq. (3)). When Eff_{50} is used as the Eff in Eq. (3), the $\text{Eff}_{\text{Add}}/\text{Eff}_{\text{PC}}$ ratio is given as “(Eff_{Add})₅₀/ (Eff_{PC}) ₅₀”.

$$\frac{\text{Eff}_{\text{Add}}}{\text{Eff}_{\text{PC}}} = \frac{\text{Eff of 1 M LiClO}_4\text{-PC with additives}}{\text{Eff of 1 M LiClO}_4\text{-PC alone}} \quad (3)$$

We measured the cycling efficiencies of the lithium metal anodes rather than the carbon anodes for the following two reasons. First, it is difficult to draw general conclusions about the influence of additives on the cycling performance of carbon anodes, because too many types of carbon are known, and because of the influence of the electrolyte composition. Each type of carbon should be tested independently for the proposed electrolyte system when the cycle life of the specified carbon needs to be determined. Second, the present

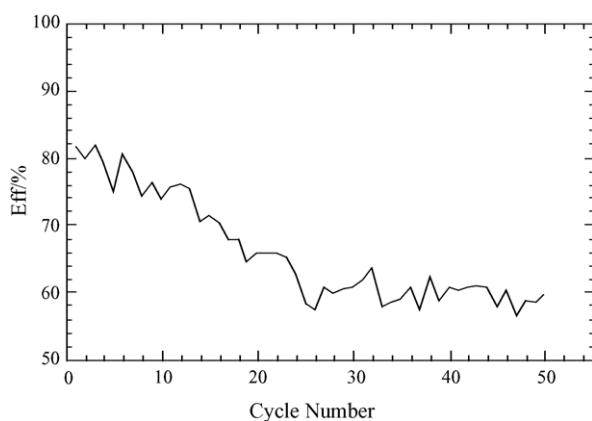


Fig. 2. Cycling efficiency of lithium (Eff) in 1 M LiClO_4/PC , $I_{\text{ps}} = 1.5$ mA (10 mA cm^{-2}), $Q_p = 0.025$ mAh (0.167 mAh cm^{-2}).

technology level makes it difficult to fabricate lithium metal anodes with sufficient practical cycle life. The influence of additives on cycle life should be determined more clearly for lithium metal anodes than for carbon anodes.

3. Results and discussion

3.1. Basic examination

The E_{ox} values have been reported for a number of organic compounds. However, their values vary, due to variations in the experimental conditions and in the definitions of the E_{ox} values [9]. In this work, the E_{ox} values are measured and compared under the same experimental conditions using the same experimental cell, temperature, voltage scanning rate and the same electrolyte.

We examined the relationship between the E_{ox} values of aromatics and their chemical structure to design the overcharge protection additives. In this basic examination, we investigated the following three groups of aromatic compounds (Fig. 3): (i) benzene and fused ring aromatic compounds (polyacenes), (ii) naphthalene derivatives with substituents and (iii) various methylbenzenes with different numbers of methyl groups.

3.1.1. Polyacenes

First, the E_{ox} values of polyacenes (benzene, naphthalene, anthracene, tetracene) were measured as basic examinations. The solubility of tetracene was much lower (<0.1 wt%) than that of the other polyacenes. We then measured the E_{ox} value of tetracene by using its saturated solution. The E_{ox} values measured for these compounds are listed in Table 1. A decrease in the E_{ox} value was observed with an increase in the number of fused rings. This result shows that the cations generated by electrochemical oxidation are stabilized by a longer conjugation system (Fig. 4). Benzene has a higher E_{ox} value and the other three polyacenes exhibited lower E_{ox} values than the target E_{ox} value range of 4.6–4.8 V versus Li/Li^+ . That is, no compounds have a preferable E_{ox} value in terms of their use as overcharge protection additives.

3.1.2. Naphthalene derivatives

We measured the E_{ox} values of naphthalene derivatives, with various substituents that had electron-withdrawing or electron-releasing properties. The amino group, hydroxyl group, methoxyl group and methyl group were tested as

Table 1
 E_{ox} and Eff of benzene and polyacenes

Compound	E_{ox} (V) vs. Li/Li^+	$(\text{Eff}_{\text{Add}})_{50}/(\text{Eff}_{\text{PC}})_{50}$
Benzene	5.10	0.889
Naphthalene	4.36	0.481
Anthracene	4.03	0.590
Tetracene	3.76	1.07

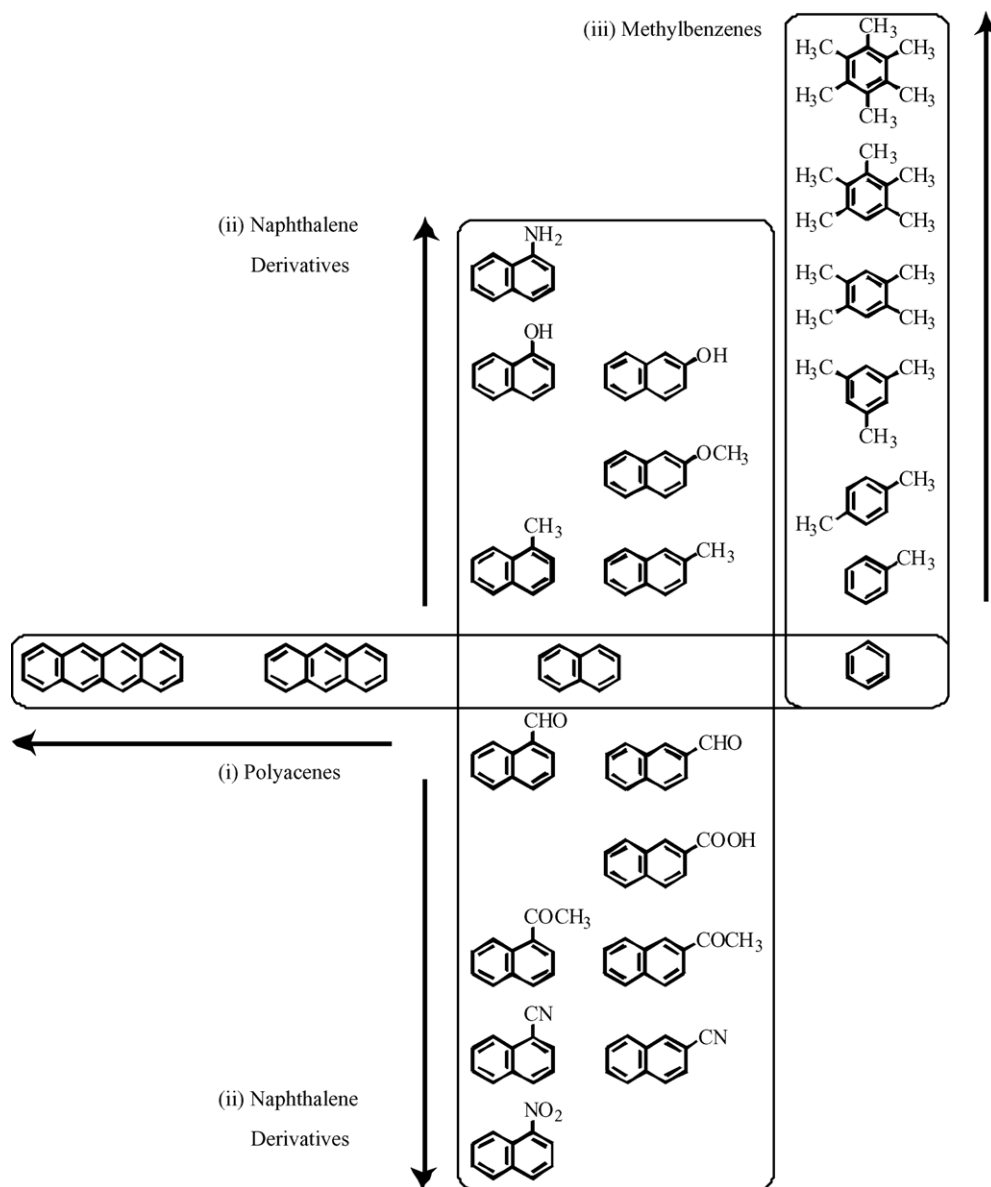



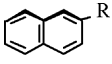
Fig. 3. Aromatics tested as basic examination.

the electron-releasing groups. The aldehyde group, carboxyl group, acetyl group, cyano group and nitro group were examined as the electron-withdrawing groups. These results are summarized in Table 2. These E_{ox} values are plotted against their *para*-substitution constants (σ_p), which represent the electron-releasing or electron-withdrawing strength in terms of the Hammett law [10] (Fig. 5). σ_p was used because its approximation was preferable to that of σ_o or σ_m [10]. Fig. 5 indicates that the increase in the σ_p value of 1.0 causes an increase in the E_{ox} value of 1.0 V in naphthalene derivatives. Naphthaldehyde, acetylnaphthalene, naphthoic acid, naphthonitrile and nitronaphthalene exhibit appropriate E_{ox} values as overcharge protection additives (Fig. 5). However, the Eff values in the electrolytes with these compounds were too low for practical applications (Table 2).

3.1.3. Methylbenzenes

The E_{ox} values of methylbenzenes were measured to confirm the influence on these values of the substituent constant. These results are summarized in Table 3. Fig. 6 represents the relationship between the number of methyl groups of methylbenzenes and the E_{ox} values. These results indicate that an increase of one methyl group results in a 0.1 V decrease in the E_{ox} . These results coincide with the discussion in the previous section. Hence, we confirmed the influence of the electron-releasing property of methyl groups on the E_{ox} values. *p*-Xylene exhibits a preferable E_{ox} value (4.68 V versus Li/Li⁺) as an overcharge protection additive. However, Eff_{Add}/Eff_{PC} in the electrolytes with *p*-xylene had a much lower value (0.64) than that of the base electrolyte (Table 3). We then began to look for compounds that exhibited a high Eff.

Table 2
 E_{ox} and Eff of naphthalene derivatives

R					σ_p of R
	E_{ox} (V) vs. Li/Li ⁺	(Eff _{Add}) ₂₀ /(Eff _{PC}) ₂₀ ^a	E_{ox} (V) vs. Li/Li ⁺	(Eff _{Add}) ₂₀ /(Eff _{PC}) ₂₀ ^a	
NH ₂	3.40	0.832	–	–	–0.66
OH	3.87	0.429	4.00	0.566	–0.37
OCH ₃	–	–	4.09	0.502	–0.28
CH ₃	4.29	0.875	4.27	0.572	–0.14
H	4.36	0.543	4.36	0.543	0
CHO	4.58	0.809	4.57	0.624	0.43
COOH	–	–	4.59	0.379	0.45
COCH ₃	4.57	0.481	4.59	0.651	0.47
CN	4.70	0.169	4.72	0.385	0.71
NO ₂	4.77	0.699	–	–	0.81

^a Average of 1–20 cycles of Eff used for Eff_{Add}/Eff_{PC} evaluation.

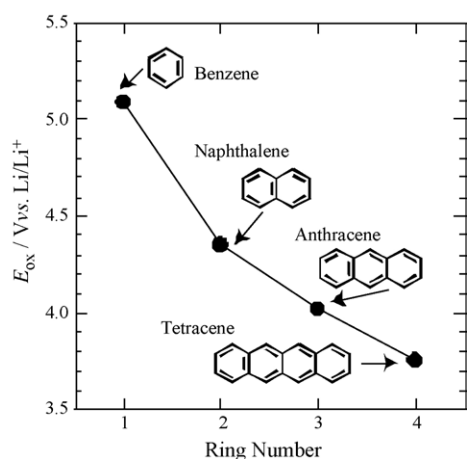


Fig. 4. Relationship between aromatic ring number and E_{ox} for fused ring aromatic compounds.

3.2. Development of new additives

Some compounds shown in the previous section show preferable E_{ox} values. However, these compounds exhibit

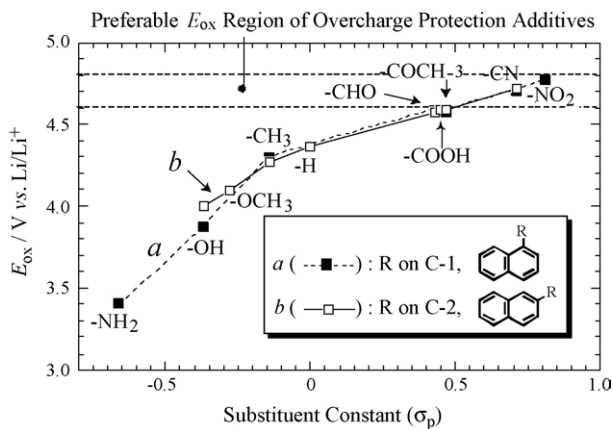


Fig. 5. Relationship between E_{ox} and Hammett sigma constant of substitution (σ_p) for naphthalene derivatives.

Table 3
 E_{ox} and Eff of methylbenzenes

Compound	E_{ox} (V) vs. Li/Li ⁺	(Eff _{Add}) ₅₀ /(Eff _{PC}) ₅₀
Benzene	5.10	0.889
Toluene	4.83	0.943
<i>p</i> -Xylene	4.68	0.644
Mesitylene	4.59	0.721
1,2,4,5-Tetramethylbenzene	4.45	0.871
Pentamethylbenzene	4.35	0.839
Hexamethylbenzene	4.31	0.985

very low Eff values. Then, We attempted to develop electrolyte additives that exhibit a preferable E_{ox} for overcharge protection and provide the cell with the high Eff of lithium. The results described in previous Section 3.1, were used for this trial. We propose a procedure for this development as follows. First, a compound providing a relatively high Eff value was selected as a starting material. Besenhard et al. reported [11] that saturated hydrocarbons work as a surfactant to delay the irreversible reduction of organic electrolyte by lithium and reduce the growth of lithium dendrites, and polycyclic hydrocarbons such as *cis*-decalin are more soluble than chain-type

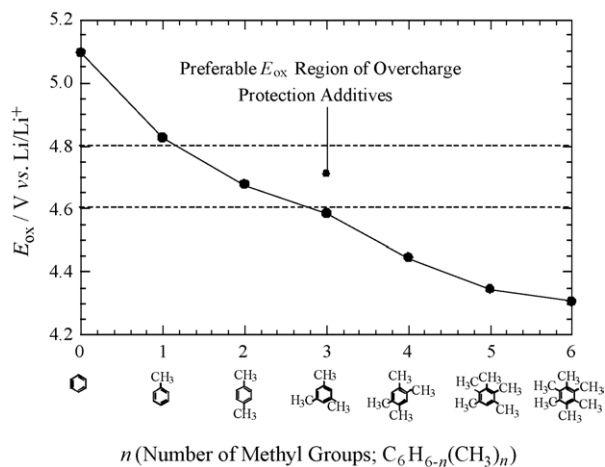


Fig. 6. E_{ox} of methylbenzenes.

Table 4
 E_{ox} and Eff of cycloalkanes

Compound	E_{ox} (V) vs. Li/Li ⁺	(Eff _{Add}) ₅₀ /(Eff _{PC}) ₅₀
Cyclohexane	5.90 ^a	0.875
Decalin	5.42	1.00
Adamantane	5.17	1.08
Norbornane	5.55	0.963

^a 1 M LiBF₄/PC was used as electrolyte.

hydrocarbons. So, cycloalkanes are potential additives for the improvement of lithium cycling efficiency. On the other hand, it has been reported that adamantane is expected to exhibit the property of *cis*-decalin in nonaqueous electrolytes [12]. According to these reports, it is expected that cycloalkanes will provide lithium with a high cycling efficiency. However, the E_{ox} values of saturated hydrocarbons are too high for them to be used as overcharge protection additives for lithium ion cells (Table 4). Hence, we attempted to introduce aromatic rings into cycloalkanes in order to decrease their E_{ox} values. We also expect to be able to control E_{ox} by the appropriate selection of the aromatic ring and its substituents. As a goal of this trial, we expected to obtain compounds that provided both high lithium cycling efficiencies and preferable E_{ox} values.

This attempt to design overcharge protection additives involved the following three steps. Step 1: a specific cycloalkane was selected from several cycloalkanes as a basic structure that provides a high Eff. Step 2: an aromatic ring was connected to the cycloalkane in order to adjust the E_{ox} of the cycloalkane selected in step 1. Step 3: substituents on the aromatic ring of the cycloalkane selected in step 2 were chosen to control the E_{ox} value, and thus realize an overcharge protection additive.

3.2.1. Step 1

Four kinds of cycloalkanes (cyclohexane, decalin, adamantane, norbornane) were tested as compounds having basic chemical structure. The solubility of these cycloalkanes in an electrolyte solution is lower than aromatic compounds such as biphenyl. This low solubility may be caused by the difference between the polarities of the electrolyte and the cycloalkanes. Cycloalkanes do not have double bonding and are expected to be more tolerant to reduction by lithium than an electrolyte solvent with double bonding such as PC. In addition, cycloalkanes act as surfactants on lithium metal, which delay the reaction between the lithium and the electrolytes and make the deposition morphology smoother, and finally improve the lithium cycling efficiency.

Table 4 gives the E_{ox} and Eff values for these hydrocarbons. The E_{ox} of cyclohexane is too high to be measured in 1 M LiClO₄/PC. Therefore, the E_{ox} of cyclohexane was measured by using 1 M LiBF₄/PC, which has a higher E_{ox} value than 1 M LiClO₄/PC. The E_{ox} values of all cycloalkanes exceed 5.0 V, which is higher than the target E_{ox} value. Of the four cycloalkanes examined here, adamantane exhibited

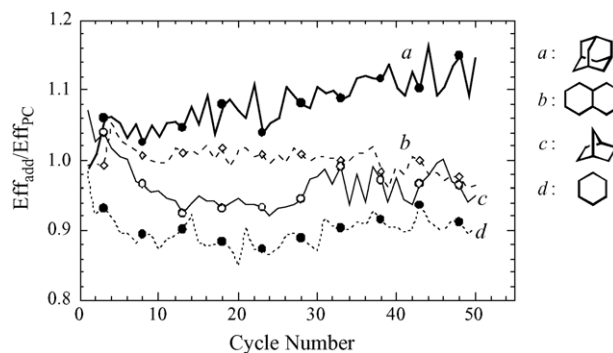


Fig. 7. Eff in 1 M LiClO₄/PC + additives, $I_{ps} = 1.5$ mA, $Q_p = 0.025$ mAh. a (●): adamantane, b (◇): decalin, c (○): norbornane and d (●): cyclohexane.

the highest Eff value (Fig. 7). Adamantane was selected as the basic compound for the next stage of the examination, because of its high lithium cycling efficiency. In the next stage, we attempted to modify the chemical structure of adamantane by introducing aromatic rings, and thus reduce the E_{ox} value and move closer to the target value.

3.2.2. Step 2

We selected the aromatic rings for connection with adamantane to reduce its E_{ox} value. Two compounds with an aromatic ring, such as 1-phenyladamantane and 1-(2-naphthyl)adamantane were examined. 1-Phenyladamantane and 1-(2-naphthyl)adamantane were synthesized from the reactions of 1-bromoadamantane with corresponding aryl Grignard reagents [8]. Fig. 8 shows the reactions and the yields of the target compounds. The product was identified from ¹H NMR and ¹³C NMR spectra, which were in agreement with previously reported results [13]. The compounds were purified and then electrochemical measurements were carried out.

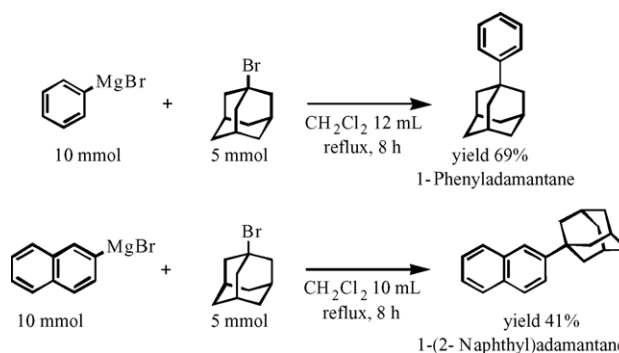


Fig. 8. Synthesis of aryladamantanes.

Table 5
 E_{ox} and Eff of aryladamantanes

Compound	E_{ox} (V) vs. Li/Li ⁺	(Eff _{Add}) ₅₀ /(Eff _{PC}) ₅₀
Adamantane	5.17	1.08
1-Phenyladamantane	4.88	0.936
1-(2-Naphthyl)adamantane	4.33	0.636

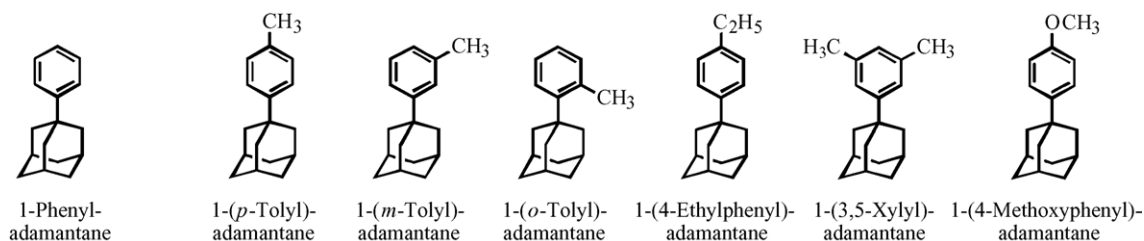


Fig. 9. Chemical structures of phenyladamantane derivatives.

Table 5 shows the measured E_{ox} and Eff values for these aryladamantanes. It is clear that the E_{ox} values of the aryladamantanes are lower than that of adamantane, due to the π -electron conjugation of the aromatic ring. 1-Phenyladamantane is superior to the other aryladamantanes, because of its higher solubility and ease of synthesis. However, its E_{ox} value was still higher than the desired potential. In the next step, the chemical structure of 1-phenyladamantane was further modified to adjust the E_{ox} value.

3.2.3. Step 3

In order to reduce the E_{ox} value of 1-phenyladamantane slightly, six phenyladamantane derivatives (Fig. 9) with electron-releasing substituents on their phenyl group, namely 1-(*p*-tolyl)adamantane, 1-(*m*-tolyl)adamantane, 1-(*o*-tolyl)adamantane, 1-(3,5-xylyl)adamantane, 1-(*p*-methoxyphenyl)adamantane and 1-(4-ethylphenyl)adamantane, were synthesized by the reaction described in Fig. 10. The reaction times and the product yields are shown in Table 6. The solubility with 1-(*p*-methoxyphenyl)adamantane electrolyte was higher than with the other derivatives. The high polarity of the methoxyl group may be the reason for this result. The E_{ox} and Eff values of these derivatives were measured using their saturated solution (Table 7).

From Table 7 and Fig. 11, four aryladamantanes (1-(*p*-tolyl)adamantane, 1-(*m*-tolyl)adamantane, 1-(*o*-tolyl)ada-

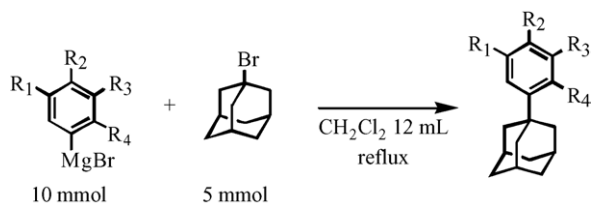


Fig. 10. Synthesis of phenyladamantane derivatives.

Table 6
Preparation of phenyladamantane derivatives shown in Fig. 10

R ₁	R ₂	R ₃	R ₄	Time (h)	Yield (%)
CH ₃	H	H	H	10	27
H	CH ₃	H	H	7	60
H	C ₂ H ₅	H	H	8	29
H	H	H	CH ₃	10	22
CH ₃	H	CH ₃	H	16	23
H	OCH ₃	H	H	8	13

Table 7
 E_{ox} and Eff of 1-phenyladamantane derivatives

Compound	E_{ox} (V) vs. Li/Li ⁺	(Eff _{Add}) ₅₀ /(Eff _{PC}) ₅₀
1-Phenyladamantane	4.88	0.936
1-(<i>p</i> -Tolyl)adamantane	4.65	0.960
1-(<i>m</i> -Tolyl)adamantane	4.75	0.909
1-(<i>o</i> -Tolyl)adamantane	4.80	0.973
1-(4-Ethylphenyl)adamantane	4.63	1.05
1-(3,5-Xylyl)adamantane	4.57	0.838
1-(<i>p</i> -Methoxyphenyl)adamantane	4.22	1.01

mantane and 1-(4-ethylphenyl)adamantane exhibit the best performance in that they achieve the target E_{ox} values (4.6–4.8 V versus Li/Li⁺) and have preferable relative Eff values (0.909–1.05) among the phenyladamantane derivatives, thus allowing them to be employed as overcharge protection additives in lithium cells.

The E_{ox} values of the phenyladamantane derivatives, benzene derivatives and naphthalene derivatives are plotted against the substituent constant (σ_p) of these aromatic rings in Fig. 12. The E_{ox} values of the phenyladamantane derivatives and benzene derivatives increased by 0.2 V when their σ_p value increased by 0.1 as average value (Fig. 12).

The π -electron of aromatic compounds is excited to the antibonding orbital from the bonding orbital by the absorption of ultraviolet light (UV). The wavenumber,

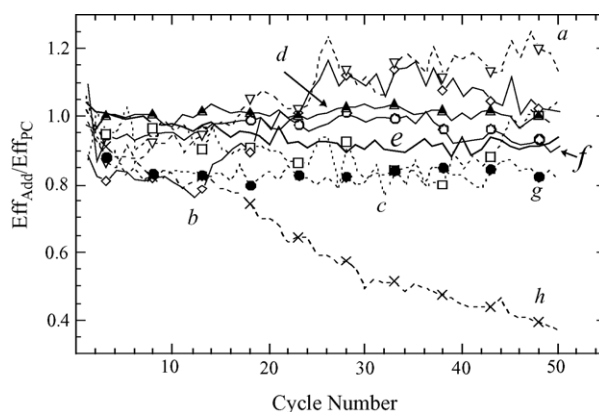


Fig. 11. Eff in 1 M LiClO₄/PC + aryladamantanes, $I_{\text{ps}} = 1.5$ mA, $Q_p = 0.025$ mAh. a: 1-(4-ethylphenyl)adamantane, b: 1-(*o*-tolyl)adamantane, c: 1-(*m*-tolyl)adamantane, d: 1-(4-methoxyphenyl)adamantane, e: 1-phenyladamantane, f: 1-(*p*-tolyl)adamantane, g: 1-(3,5-xylyl)adamantane and h: 1-(2-naphthyl)adamantane.

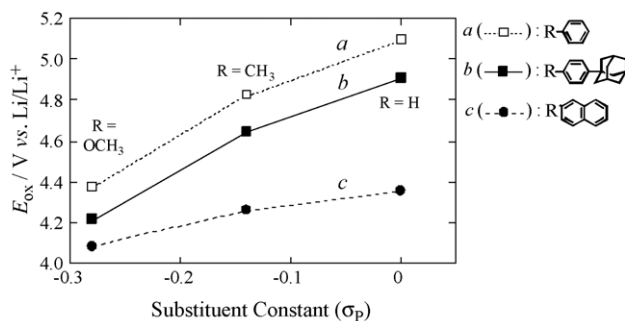


Fig. 12. Comparison of the substituent effect difference among aromatic ring systems.

obtained from λ_{\max} values for aromatic compounds, reflects the energy of the $\pi-\pi^*$ transition. The energy level of the highest occupied molecular orbital (HOMO) determines the oxidation potential. Hence, the UV absorption spectra of the aryladamantanes and some alkylbenzenes were measured to allow us to compare the λ_{\max} values with the E_{ox} values. The λ_{\max} of 1-(*p*-tolyl)adamantane and 1-(3,5-xylyl)adamantane are shifted to a longer wavelength region than that of 1-phenyladamantane, because of the bathochromic effect of alkyl groups on these derivatives. Fig. 13 shows the relationship between the wavenumber and E_{ox} . There is an apparent correlation between the excitation energy and E_{ox} . We confirmed the obtained E_{ox} values for these compounds. The approximation line in Fig. 13 also indicates that the compounds that exhibit λ_{\max} values of 260–265 nm can be expected to oxidize at 4.6–4.8 V.

3.3. Temperature dependence of E_{ox} of additives

Overcharge protection additives are required to retain their E_{ox} value in the operating temperature range of the cell. The temperature range for the discharge mode of commercial

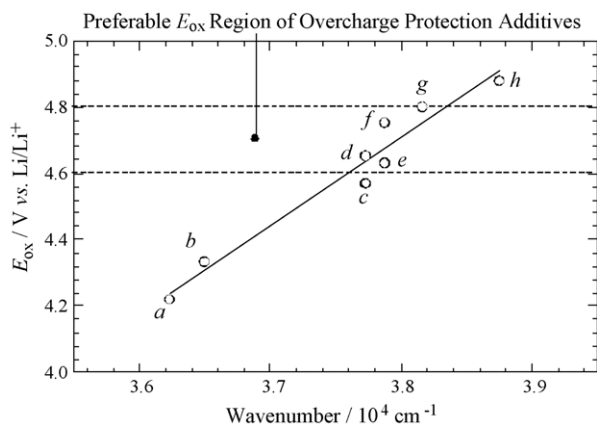


Fig. 13. Relationship between wavenumber at the absorption maximum of aromatics and their E_{ox} values, scan range 240–400 nm, 25 °C in ethanol solvent. a: 1-(methoxyphenyl)adamantane, b: 1-(2-naphthyl)adamantane, c: 1-(3,5-xylyl)adamantane, d: 1-(*p*-tolyl)adamantane, e: 1-(4-ethylphenyl)adamantane f: 1-(*m*-tolyl)adamantane, g: 1-(*o*-tolyl)adamantane and h: 1-phenyladamantane.

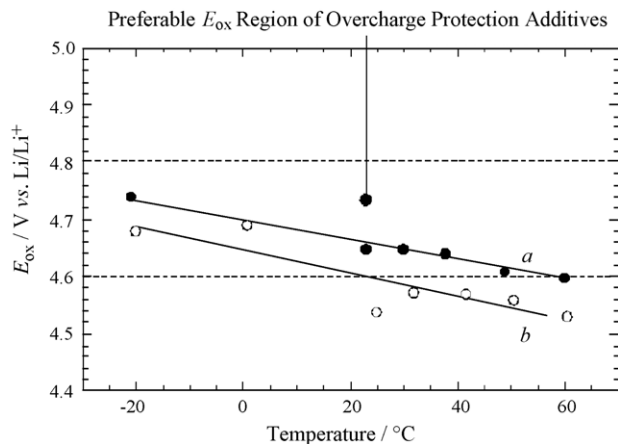


Fig. 14. Temperature dependence of E_{ox} , potential scan rate: 5 mV s⁻¹ at –20 and 0 °C, 50 mV s⁻¹ at 20, 30, 40, 50 and 60 °C. a (●): 1-(*p*-tolyl)adamantane and b (○): biphenyl.

lithium ion cells is generally –20 to 60 °C and the charging temperature range is slightly narrower, for example, 0–40 °C. The electronic device that controls the 4.2 V charging voltage is designed to provide 4.2 V even at 60 °C. There are concerns about the adverse influence of biphenyl on high temperature charging or on cell storage life when a lithium ion cell is in a fully charged condition for a long period at a high temperature such as 60 °C. This is because the E_{ox} value of biphenyl is close to the full charge voltage and there is an oxidation shoulder even at 4.3 V versus Li/Li⁺ (about 4.2 V versus C₆Li). This means the biphenyl gradually oxidizes when a fully charged cell is stored for a long time. The change in the E_{ox} value with changes in temperature is important for overcharge protection compounds from a practical point of view. From the Nernst equation, the E_{ox} decreases with an increase in temperature. However, the way in which

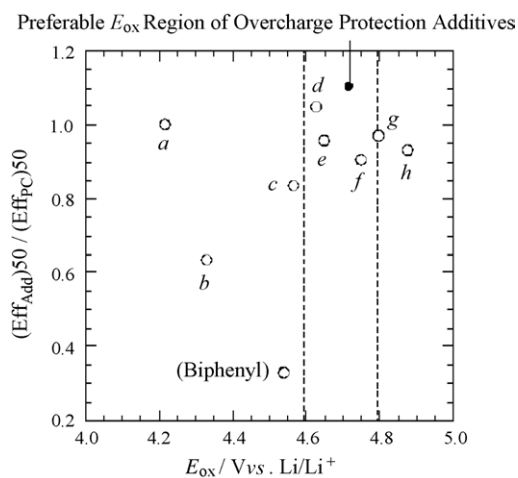


Fig. 15. Relationship between E_{ox} and Eff of aryladamantanes. a: 1-(4-methoxyphenyl)adamantane, b: 1-(2-naphthyl)adamantane, c: 1-(3,5-xylyl)adamantane, d: 1-(4-methoxyphenyl)adamantane, e: 1-(*p*-tolyl)adamantane, f: 1-(*m*-tolyl)adamantane, g: 1-(*o*-tolyl)adamantane and h: 1-phenyladamantane.

the E_{ox} really changes with a change in temperature must be measured, because the absolute value of the activity coefficient changes and this depends on how the oxidation proceeds with specific electrolytes.

The E_{ox} values of 1-(*p*-tolyl)adamantane and biphenyl were measured between -20 and 60°C (Fig. 14). In this temperature range, 1-(*p*-tolyl)adamantane exhibits E_{ox} values of more than 4.6 V, which are preferable for overcharge protection additives, while the degree of the decrease in the E_{ox} value of biphenyl is larger (Fig. 14).

4. Conclusion

The influence of the chemical structure and substituents in aromatic compounds on their oxidation behavior has been clarified. A molecular method for designing aromatic compounds to control the E_{ox} value is described. The results are summarized in Fig. 15. Of the compounds examined here, four aryladamantanes (1-(*p*-tolyl)adamantane, 1-(*m*-tolyl)adamantane, 1-(*o*-tolyl)adamantane, 1-(4-ethylphenyl)adamantane) exhibited the best performance as new overcharge protection additives for lithium cells with LiCoO_2 cathodes in terms of both oxidation potential and lithium cycling efficiency.

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