



Influence of surface modification of LiCoO₂ by organic compounds on electrochemical and thermal properties of Li/LiCoO₂ rechargeable cells

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ABSTRACT

LiCoO₂ is the most famous positive electrode (cathode) for lithium ion cells. When LiCoO₂ is charged at high charge voltages far from 4.2 V, cycleability of LiCoO₂ becomes worse. Causes for this deterioration are instability of pure LiCoO₂ crystalline structure and an oxidation of electrolyte solutions LiCoO₂ at higher charge voltages. This electrolyte oxidation accompanies with the partial reduction of LiCoO₂. We think more important factor is the oxidation of electrolyte solutions. In this work, influence of 10 organic compounds on electrochemical and thermal properties of LiCoO₂ cells was examined as electrolyte additives. As a base electrolyte solution, 1 M (M: mol L⁻¹) LiPF₆-ethylene carbonate (EC)/ethylmethyl carbonate (EMC) (mixing volume ratio = 3:7) was used. These compounds are *o*-terphenyl (*o*-TP), Ph-X (CH₃)_n (n = 1 or 2, X = N, O or S) compounds, adamantyl toluene compounds, furans and thiophenes. These additives had the oxidation potentials (E_{ox}) between 3.4 and 4.7 V vs. Li/Li⁺. These E_{ox} values were lower than that (6.30 V vs. Li/Li⁺) of the base electrolyte. These additives are oxidized on LiCoO₂ during charge of the LiCoO₂ cells. Oxidation products suppress the excess oxidation of electrolyte solutions on LiCoO₂. As a typical example of these organic compounds, *o*-TP (E_{ox}: 4.52 V) was used to check the fundamental properties of these organic additives. Charge–discharge cycling tests were carried out for the Li/LiCoO₂ cells with and without *o*-TP. Constant current charge at 4.5 V is mainly used as a charge method. Cells with 0.1 wt.% *o*-TP exhibited slightly better cycling performance and lower polarization than those without additives. Lower polarization arises from a decrease in a resistance of interface between electrolyte solutions and LiCoO₂ by surface film formation resulted from oxidation of *o*-TP. Oxidation products were found by mass spectroscopy analysis to be mixture of several polycondensation compounds made from two to four terphenyl monomers. Thermal stability of LiCoO₂ with electrolyte solutions did not improve by addition of *o*-TP. Slightly better charge–discharge cycling properties were obtained by using organic modifiers. However, when industrial applications were considered, drastic improvements have not been obtained yet. One of reasons may be too large influence of the deterioration of stability of pure LiCoO₂ structure at high voltage charging for industrial use. We hope to realize the tremendous improvements of high energy, long cycle life and safe lithium cells by the combination of both LiCoO₂ with more stable structure such as LiCoO₂ treated with MgO and new organic additives with molecular structure more carefully designed.

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1. Introduction

Lithium ion cells have been used for portable electronic devices such as cellular phones and note-type personal computers since these cells were commercialized in 1991. More increase in energy density is required for lithium ion cells because consuming power of these instruments is increasing. Also the new applications such as electric vehicles and power supplies need more energy density for these cells.

Many commercial lithium ion cells for mobile tools use LiCoO₂ as positive electrodes (cathodes). Standard charging voltage of LiCoO₂ cells is generally 4.2 V (constant voltage charge). When these cells are fully charged at 4.2 V, *x* value of Li_xCoO₂ is approximately 0.5. 4.2 V is set to ensure reliability of cycling performance and safety margin as the industrial products. Charge voltage of 4.35 V is applied for some commercial C/LiCoO₂ cells. In these 4.35 V charging cases, LiCoO₂ may be treated with some compounds such as MgO. The energy densities (Wh kg⁻¹ or Wh dm⁻³) of LiCoO₂ cells increase by simply raising charging voltage above 4.2 V since this operation provides these cells high energy by increasing both capacity and voltage. Fig. 1 shows the comparison of the first charge–discharge voltage curves of Li/LiCoO₂ cells galvanostatically charged at 4.2 and 4.5 V. However, charging exceeding 4.2 V for pure

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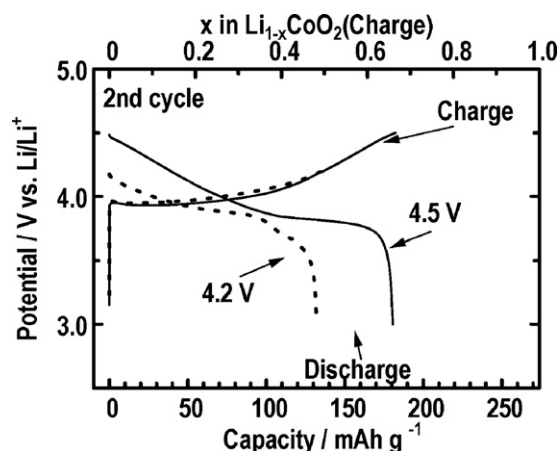


Fig. 1. Charge–discharge voltage curves of Li/LiCoO₂ cells at the first cycle, charge–discharge current density: 0.5 mA cm⁻², discharge cutoff voltage: 3.0 V.

LiCoO₂ causes several problems in related to cycleability and thermal stability (safety) of these commercial cells [1–4]. As the causes for these deteriorations of cell performance, two phenomena have been discussed. First is influence of the crystalline structure change of LiCoO₂ by excess lithium extraction at higher charging voltage far beyond 4.2 V. Second is the oxidation of nonaqueous electrolyte solutions on LiCoO₂ at high voltage charge state.

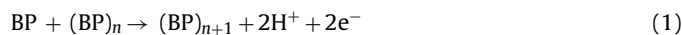
Crystalline structure of pure Li_xCoO₂ changes from hexagonal to monoclinic at higher voltage [3,4]. This complete phase transition occurs at $x < 0.2$ corresponding the charge voltage of 4.6 V [5]. Based on the report on the relation between charge voltage (constant voltage charge) and stability of crystalline structure of pure Li_xCoO₂ [5], the crystalline structure is judged to be stable at the charge voltages of 4.3 V ($x = 0.41$), 4.4 V ($x = 0.35$) and 4.5 V ($x = 0.28$). At 4.6 V charge ($x = 0.14$), the structure becomes unstable and the cycling performance drastically decreases. When 4.5 V charging, the electrolyte oxidation becomes vigor. The change in composition of electrolyte solutions is effective for the improvement of C/LiCoO₂ cells at 4.5 V charging. In case of LiPF₆-ethylene carbonate (EC)/diethyl carbonate (DEC) (1:9, volume mixing ratio), the decrease in EC content, exhibited better cycling performance than the cells with LiPF₆-EC/DEC (3:7). More improvement of cycling performance is obtained by modifying the surface of LiCoO₂ by ZrO₂ in addition to the use of the suitable electrolyte composition. Another report demonstrates even 4.6 V charge (constant current charge of 0.25 mA cm⁻²), LiCoO₂ has a possibility to cycle when the oxidation of the electrolyte is suppressed [6]. In this report, even at 4.6 V charge, electrolyte oxidation is a primary factor for cycling, not crystalline stability. In this report, surface of LiCoO₂ is coated with diamond-like carbon (DLC) to suppress the electrolyte oxidation. At 4.6 V charge, the discharge capacity of Li/pure LiCoO₂ cells with 1 M LiPF₆-propylene carbonate (PC)/1,2-dimethoxyethane (DME) (1:1) was 200 mAh g⁻¹ based on LiCoO₂ weight at 1st cycle. The discharge capacity drastically decreased to 120 mAh g⁻¹ at second cycle. However, in the Li/DLC-coated LiCoO₂ cells with the same electrolyte as above, LiPF₆-PC/DME, the discharge capacity of 1st cycle is 230 mAh g⁻¹ and second is 220 mAh g⁻¹. The cycleability improves by the suppression of electrolyte oxidation even at 4.6 V cycling. Based on these reports, for the study on the influence of surface treatment of LiCoO₂ to suppress the electrolyte oxidation, the challengeable critical target of highest charge voltage of LiCoO₂ resulted from the limit of phase transition (limit of stability) is considered to be 4.5 V. So, in this work, we used mainly 4.5 V as charge voltage for LiCoO₂ cells (constant current charge). The most important cause for these deteriorations of cell performance is suggested to be an oxidation of nonaqueous electrolyte solutions on

LiCoO₂ at high voltage charge state. When the charging temperature increases, the oxidation of electrolyte solutions more easily occurs at even at 4.2 V charge. The electrolyte oxidation products obstruct the uniform utilization and kinetics of electrode reaction. This electrolyte oxidation accompanies with the partial reduction of LiCoO₂.

There is another aspect for oxidation of electrolyte solutions on LiCoO₂ [6,7]. Based on this aspect, oxidation of electrolytes is accelerated mainly by the special active sites that may be scattered on the LiCoO₂ surface. These active sites arise from the impurities such as Li₂O, Li₂CO₃ or LiOH, lattice defects, deformation of microscopic shape or irregular chemical composition of the surface of LiCoO₂ [7]. These phenomena were resulted from the synthesis process of LiCoO₂, insufficient drying of cathodes or cathode handling atmosphere including small amount of H₂O.

One of the methods to suppress the oxidation of electrolyte solutions on the cathodes with higher voltage charging is the surface modification of inorganic compounds. General methods to suppress the oxidation of electrolyte solutions on the cathodes with higher voltage charging are the surface modification of LiCoO₂ by inorganic metal oxides. For instance, surface of LiCoO₂ is modified with ZrO₂, Al₂O₃ or B₂O₃ sintered at 550 °C for 3 h [7], at 300 °C for 4 h [8] or at 400 °C for 10 h [9], respectively after sol-gel liquid phase reaction. The adequate addition amount of these compounds to LiCoO₂ is small, such as 0.1 wt.%, in related to improving cycling performance of the LiCoO₂ cells. These additives are scattered as small particle on the surface of LiCoO₂ or covers surface of LiCoO₂ as thin film [7,10,11]. These surface modifications of LiCoO₂ are effective for suppression of the oxidation of organic electrolytes on LiCoO₂. LiCoO₂ modified with MgO is known to obtain considerably better cycling performance than other additives mentioned above at 4.2 V or 4.3 V charging [7,10,11]. This special effect of MgO is due to making the more stable crystalline structure of LiCoO₂ resulted from the formation of solid solution by the reaction between MgO and LiCoO₂ in addition to the effect of surface modification. These effects improve the tolerance of crystalline structure for higher voltage charging. This change of LiCoO₂ by MgO treatment also suppresses the oxidation of organic electrolytes on LiCoO₂.

Another method to suppress the electrolyte oxidation on LiCoO₂ is to use organic compounds as electrolyte additives [12–14]. These organic compounds are oxidized more quickly than base electrolyte solutions on the cathode surface and modify the cathode surface during charging cells. For instance, biphenyl (BP, oxidation potential is 4.54 V vs. Li/Li⁺) as electrolyte additive electrochemically oxidizes on the LiCoO₂ surface when the graphite/LiCoO₂ cells are cycled in the slight overcharge at charge voltage of 4.3 V (constant voltage charge) [12,13]. The oxidation of BP proceeds as shown in Eq. (1) and produces film made mainly of poly-*p*-phenylene [15]. This film makes the cycling performance of graphite/LiCoO₂ cells enhance at charge voltage of 4.3 V [12,13]. This film suppresses the direct contact of cathode and electrolyte solutions. Similar effects are reported for *o*-terpneyl, dibenzyl, diphenylether, *N*-methylpyrrole, furan, thiophene, 3,4-ethylenedioxythiophene, vinylacetate [12,13] and triple-bonded compounds [14]. This method is only to put additives into the electrolyte solutions and to make the cell cycle. Then, this is a technically effective and simple method and can be applied to the mass production of the cells in the manufacturing factory.



In this work, influence of 10 organic compounds with various chemical structures and oxidation potentials as 4V-class cathode modifying agents on electrochemical properties and thermal behaviors of LiCoO₂ cells were examined. Lithium metal is used as negative electrode (anode) for LiCoO₂ cells to avoid complicated influence of carbon anodes with variety of properties and

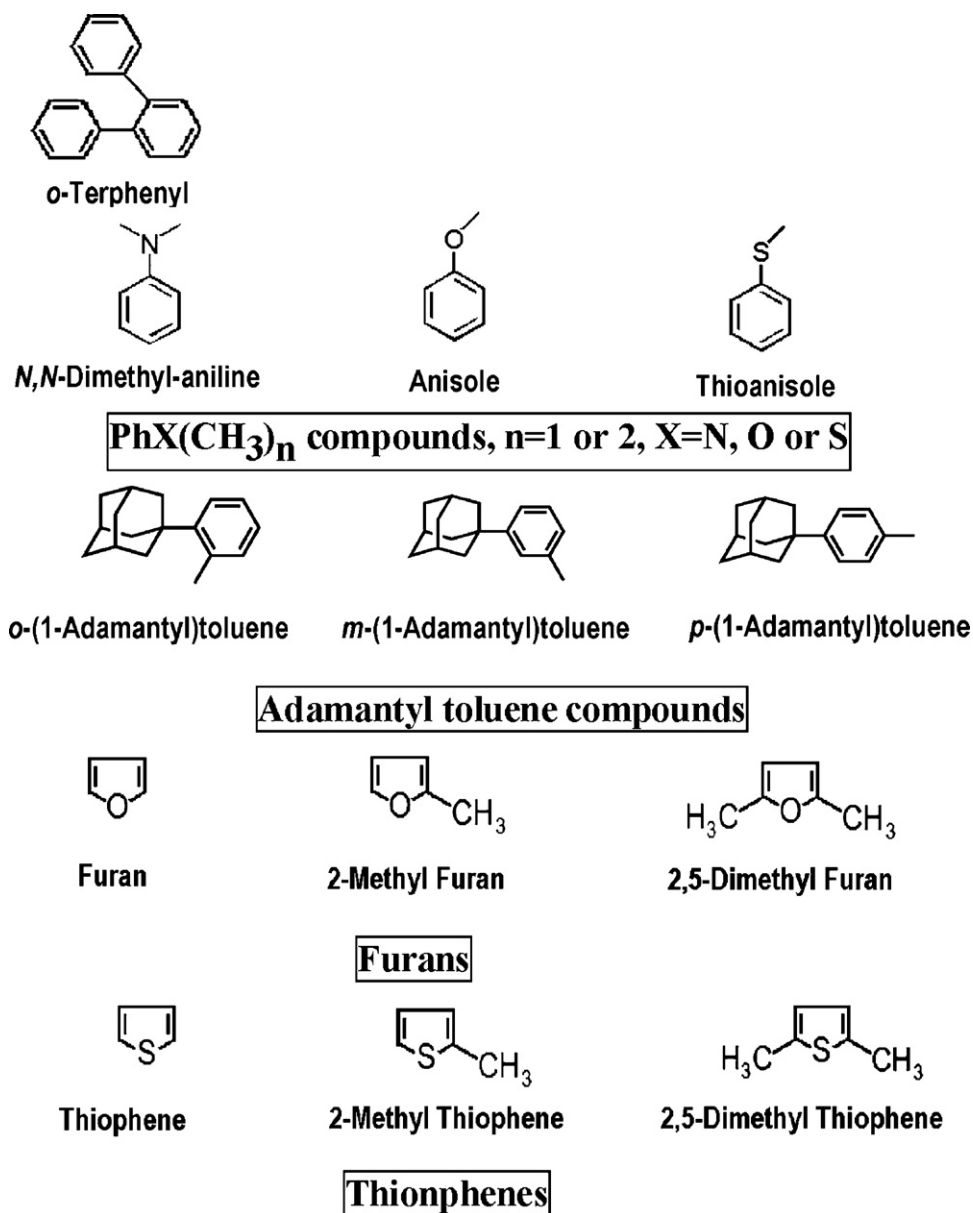


Fig. 2. Chemical structure of additives used in this work.

simply to discuss about the influence of additives on cathode properties. As the base electrolyte solution, 1 M (M: mol L⁻¹) LiPF₆-EC/ethylmethyl carbonate (EMC) (3:7 in volume mixing ratio) was used. These organic compounds are utilized as electrolyte additives. Chemical structure of organic compounds used here is shown in Fig. 2. Oxidation potentials (E_{ox}) of these compounds are shown Table 1. The method of definition of E_{ox} and experimental method for measuring E_{ox} were described later. These compounds are categorized roughly to five groups; (i) *o*-terphenyl (*o*-TP), (ii) Ph-X (CH₃)_n (*n* = 1 or 2) type-aromatic compounds containing heteroatoms of X = N, O or S, (iii) adamantyl toluene compounds, (iv) furans and (v) thiophenes. Many of these organic compounds have π-electron conjugated chemical bonds and have relatively low oxidation potentials of 3.4 and 4.7 V vs. Li/Li⁺ for 4V-class cathodes. These E_{ox} values were lower than that (4.63 V vs. Li/Li⁺) of base electrolyte solutions as shown later. These additives may more quickly oxidize than the base electrolyte solution. If LiCoO₂ has special active sites for oxidation of electrolytes, these additives may actively attack these sites and make these active sites inert for

Table 1
Oxidation potential (E_{ox}) of organic additives.

| Additive | E _{ox} /V vs. Li/Li ⁺ |
|-------------------------------------|---|
| <i>o</i> -Terphenyl (<i>o</i> -TP) | 4.52 |
| <i>N,N</i> -dimethyl aniline | 3.49 |
| Anisole | 4.43 |
| Thioanisole | 4.09 |
| <i>o</i> -(1-Adamantyl) toluene | 4.68 |
| <i>m</i> -(1-Adamantyl) toluene | 4.65 |
| <i>p</i> -(1-Adamantyl) toluene | 4.54 |
| Furan | 4.38 |
| 2-Methylfuran | 4.23 |
| 2,5-Dimethylfuran | 4.09 |
| Thiophene | 4.50 |
| 2-Methylthiophene | 4.39 |
| 2,5-Dimethylthiophene | 4.26 |
| 1 M LiPF ₆ -EC/EMC (3:7) | 6.30 |

* E_{ox} values were obtained by linear scanning of voltage method with Li/Pt cells, scan rate: 5 mV s⁻¹. Details of the experiments and definition of E_{ox} were described Section 2.2.

subsequent oxidation. As a typical example of these compounds, *o*-TP with the Eox value of 4.52 V vs. Li/Li⁺ was used to check the various fundamental properties of these organic additives and various experiments were carried out for *o*-TP. 4.5 V was mainly used as the target of charging voltage in this work for Li/LiCoO₂ cells (constant current charge). Charging at 4.5 V is an overcharge based on general thinking. However, as mentioned above, the influence of surface modification of LiCoO₂ on the cell performance must be more clearly evaluated and discussed by using 4.5 V charging (constant current charge) than that by 4.2 V charging.

2. Experimental

2.1. Preparation of electrolyte solutions

Electrolyte solutions were prepared by mixing additives (Nippon Steel Chemicals Co.), which had been pre-dried in a vacuum oven, and 1 M LiPF₆-EC/EMC (3:7 in volume mixing ratio) (Tomiya Pure Chemicals Co.) in an argon gas filled dry box. Hereafter, "EM" represents 1 M LiPF₆-EC/EMC (3:7).

2.2. Oxidation potential measurements

Eox values of electrolyte solutions were measured by a linear sweep of voltage (LSV) using three kinds of working electrodes (WE) of Pt, glassy carbon (GC) and LiCoO₂ at 25 °C. A cylindrical glass test cell was used with a Li metal sheet counter electrode (0.1 mm thick) pressed on a Ni net (200 mesh, 15 mm long, 6 mm wide, and 0.05 mm thick), a lithium reference electrode and a Pt sheet WE (4.5 mm long, 6 mm wide, 0.05 mm thick, and 0.27 cm² in area) or a GC WE (3 mm diameter). LiCoO₂ WE was prepared as a printed sheet (approximately 150 μm thick) on an aluminum sheet (20 μm thick) by using poly(vinylidene fluoride) (PVDF) binder and conductive graphite carbon. In this work, Eox values were determined as voltage at the intersection of *x*-axis base line (voltages) and a tangent of the rapid increase in the current curve [16].

2.3. Charge–discharge cycling tests of Li/LiCoO₂ cells

The charge–discharge tests of Li/LiCoO₂ cells were galvanostatically carried out. In these tests, the coin cells (20 mm in diameter, 3.2 mm in thickness) were used with a lithium metal sheet anode (0.1 mm thickness, 15 mm diameter). For these experiments, the printed LiCoO₂ electrodes (15 mm in diameter and 0.15 mm in thickness) were prepared by coating an Al sheet with a mixture of LiCoO₂, acetylene black (AB, conductive carbon) and PVDF (weight ratio of LiCoO₂:AB:PVDF = 85:5:10) in *N*-methylpyrrolidinone. We then evacuated the solvent and dried the electrodes. All the electrochemical measurements were carried out at 25 °C.

2.4. AC impedance and conductivity measurements

AC impedance measurements of electrode/electrolyte interface were carried out at 25 °C by using Li/LiCoO₂ coin cells with an impedance analyzer (Iviumstat, Hokuto Denko Co.). AC frequency range was 100 mHz ~ 20 kHz and amplitude of vibration was 20 mV.

2.5. Thermal stability tests of electrolyte solutions

Thermal behavior of electrolyte solutions or solvents toward LiCoO₂ was evaluated with a differential scanning calorimeter (DSC, Rigaku Co., model DSC 8320). Before DSC measurements, Li/LiCoO₂ coin cells were charged at 4.5 V in EM with or without *o*-TP (0.1 and 2 wt.%). Cells after charging were disassembled in a dry box. Cathodes were washed with mixed solvents of EC/EMC (3:7) and solvents were evaporated in vacuum at 25 °C. Dried cathodes were

transferred to the DSC sample pan made of stainless steel. Solvents or electrolyte solutions were put into these pans. Solvents or electrolyte solutions of 3 μl were used for 7 mg cathodes. Sample pans were crimp-sealed. All the DSC experiments were carried out at the heating rate of 10 °C min⁻¹ from room temperature to 450 °C.

2.6. Analysis of oxidation products

Analysis of oxidation products were carried out with matrix-assisted laser desorption ionization–time flight mass spectroscopy (MALDI-TOF-MS, Applied Biosystem Voyager Elite).

3. Results and discussion

Influences of *o*-TP on electrochemical and thermal properties of Li/LiCoO₂ cells were investigated as a typical example of organic modifiers for LiCoO₂.

3.1. Oxidation potential of *o*-terphenyl

Electrochemical oxidation behaviors of EM with and without *o*-TP were examined by LSV. Fig. 3(a) shows the results of LSV for EM with and without *o*-TP by using Pt WE. In EM alone, large oxidation current peak around 6.5 V was observed. This peak corresponds to an electrochemical oxidation of EM. In EM with *o*-TP, new current peak around 4.5 V was observed in addition to the oxidation current peak of EM around 6.5 V. Then current peak around 4.5 V corresponds to an electrochemical oxidation of *o*-TP. *o*-TP is oxidized at lower voltage than that of EM. Eox values of EM and *o*-TP defined in this work are 6.30 V and 4.52 V vs. Li/Li⁺, respectively. In case of EM with *o*-TP, small current starts to flow from 3.8 V. When Li/LiCoO₂ cells are charged even at 4.2 V, oxidation of *o*-TP may gradually proceed inside the cells because small current flows under its Eox value. Fig. 3(b) shows the results of LSV with GC WE. The same Eox values of EM and *o*-TP were obtained as those obtained with Pt WE. Fig. 4 shows the photographs of surface of Pt working electrodes after LSV measurements for EM with and without *o*-TP. In EM with *o*-TP, black solid compounds were obtained. These black compounds (oxidation products of *o*-TP) are oligomers as discussed in Section 3.2.

Eox values depend on various experimental factors. One of the important factors is chemical material of working electrode. In fundamental and standard measurements of Eox values, pseudo-inert electrodes such as glassy carbon are generally used. Pt is often used as working electrode although strictly speaking there is a possibility of partial oxidation of Pt around 4.25 V vs. Li/Li⁺ based on the equilibrium electrode potential value (1.20 V vs. normal hydrogen electrode) described generally in the textbooks of electrochemistry [17]. In potential sweep experiments, current values reflect the kinetics of electrode reaction. Current values depend on chemical materials of working electrodes. The working electrodes sometimes work as catalysts and sometimes provide large polarization for electrochemical reaction and oxidation of the highlighted sample. From a technical view about batteries, the measurements of Eox values are preferable to carry out on the actual electrode as the working electrode. We used LiCoO₂ as main cathode in this paper. So, Eox values were measured also by using LiCoO₂ as the working electrode.

Fig. 5 shows the LSV results of EM with and without *o*-TP by using LiCoO₂ as the WE. In EM alone, distinct two current peaks around 4.4 V and 6.2 V were observed. The first peak around 4.4 V corresponds to the charge of Li_xCoO₂, i.e., deintercalation of lithium from Li_xCoO₂. The second peak around 6.2 V corresponds to the electrochemical oxidation of EM. On the LiCoO₂, EM is oxidized at similar Eox value to that on Pt and GC electrodes. In EM with *o*-TP, the third new current peak around 4.65 V was observed in addition

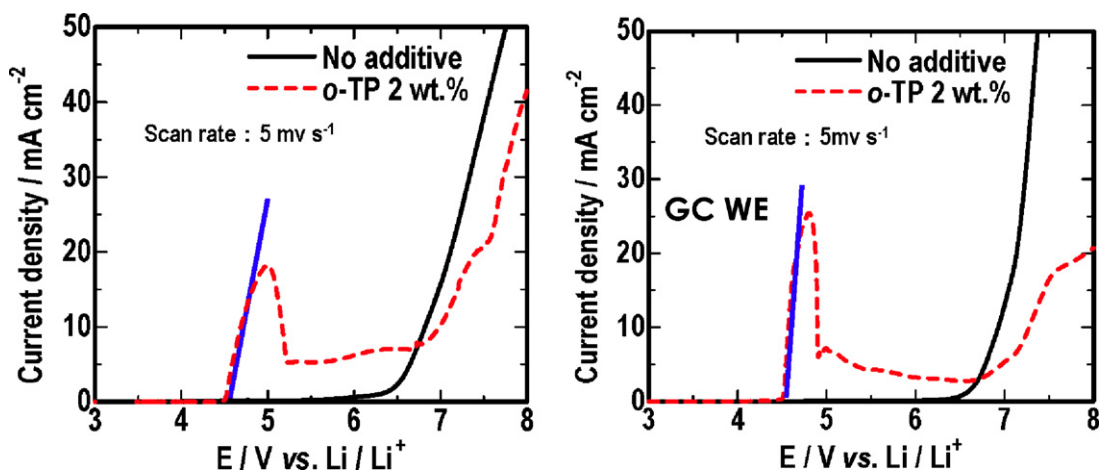


Fig. 3. Oxidation behavior of 1 M LiPF₆-EC/EMC (3:7) with and without *o*-TP, (a) Pt working electrode, (b) GC working electrode.

to two current peaks observed in EM. E_{ox} value of *o*-TP defined from the peak around 4.65 V is the same (4.52 V) as those obtained with Pt and GC working electrodes. So, oxidation of *o*-TP should proceed on LiCoO₂ at 4.5 V charging and the black oxidation products may remain on LiCoO₂ surface.

3.2. Chemical composition of oxidation products of *o*-TP

Chemical composition of oxidation products of *o*-TP by LSV using Pt WE and EM with *o*-TP (2.0 wt.%) was analyzed by MALDI-TOF-MS. Fig. 6 shows results of mass spectra. Several polycondensation compounds were detected. Oxidation products are a mixture of oligomers made of two, three and four terphenyl monomers. Reaction scheme of *o*-TP is predicted as shown in Fig. 7. Polymerization begins by the formation of chemical bond between *o*-position of benzene rings of monomers [18]. Two electrons per *o*-TP were released by its oxidation. At the largest, eight electrons per an *o*-TP are consumed during its oxidation. When 0.1 wt.% *o*-TP is applied to Li/LiCoO₂ coin cells used in this work, the elec-

trochemical reaction of *o*-TP by eight electrons corresponds to approximately 1% capacity of that of LiCoO₂.

3.3. Charge–discharge cycling tests of Li/LiCoO₂ cells with and without *o*-TP at various charge voltages

Charge–discharge cycling tests were galvanostatically carried out for Li/LiCoO₂ coin cells with and without *o*-TP (2.0 wt.%). Charge cutoff voltage varied at 4.2, 4.3, 4.4 and 4.5 V. Fig. 8 shows the first charge and discharge voltage curves for Li/LiCoO₂ cells. Charge–discharge voltage curves between the cells with and without *o*-TP were similar among the cells charged at 4.2, 4.3 and 4.4 V. However, at 4.5 V charge, the voltage plateau around 4.45 V appeared for cells with *o*-TP at the end of charge. Without *o*-TP, this plateau did not exist. This voltage plateau is close to the E_{ox} of *o*-TP and suggested to correspond to the oxidation of *o*-TP. In the following discharge, discharge voltages of the cells with *o*-TP were lower than that with EM alone. Discharge capacities with *o*-TP decreased by approximately 20 mAh g⁻¹ to that of the cell with-

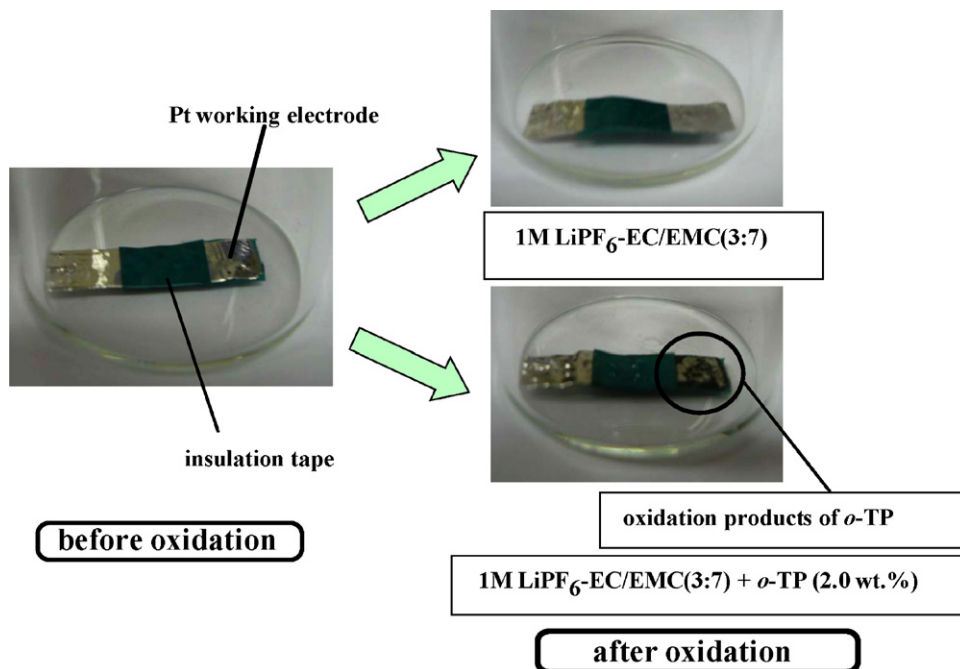


Fig. 4. Photographs of Pt working electrodes before and after LSV measurements, scan rate: 5 mV s⁻¹.

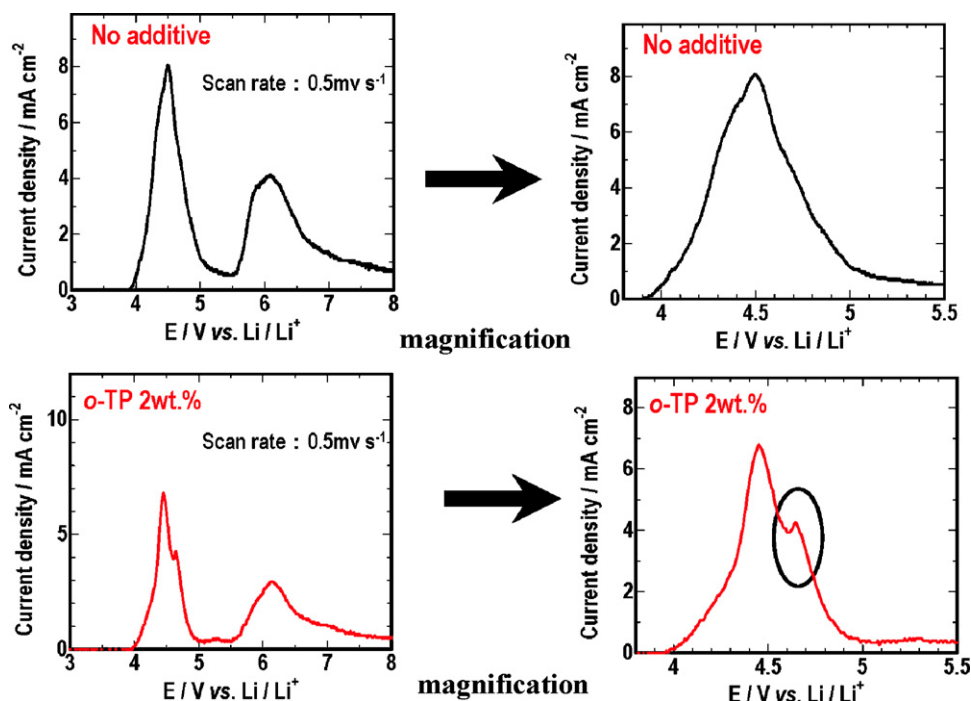


Fig. 5. LSV measurements for 1 M LiPF₆-EC/EMC(3:7) without and with *o*-TP, working electrode: LiCoO₂.

out *o*-TP. This drop of discharge voltage with *o*-TP may result from an increase in resistivity of the interface between electrolyte solutions and LiCoO₂ surface modified by oxidation products of *o*-TP. Fig. 9 shows coulombic efficiencies of Li/LiCoO₂ cells. Coulombic efficiency is a ratio of discharge capacity/charge capacity. For the first cycle charged at 4.2, 4.3 and 4.4 V, difference of coulombic efficiencies between cells with and without *o*-TP were almost the same. Small capacities of excess charge result from oxidation of *o*-TP. However, at 4.5 V charge, large excess charge capacity appeared at the first cycle. This large excess charge capacity is due to the start of vigorous oxidation of *o*-TP. At the second cycle, similar tendencies were observed. At the second cycle, the oxi-

dation of *o*-TP at the end of charge occurred with the a little bit lower excess capacities than those at the first cycle. At the third cycle, similar tendencies were observed. However, the amount of *o*-TP oxidation was getting considerably smaller for 4.5 V charging. These results are considered to make the surface film thick enough to protect the oxidation on the LiCoO₂ by three cycles.

Fig. 10 shows cycling performance of Li/LiCoO₂ cells with and without *o*-TP. The relation between discharge capacity and cycle number was similar between the cells charged at 4.2, 4.3 and 4.4 V. At 4.2 and 4.3 V charge, addition of *o*-TP exhibited a little bit higher capacities than that EM alone. At 4.4 V charge, addition of *o*-TP exhibited a little bit lower capacities than that EM alone. However,

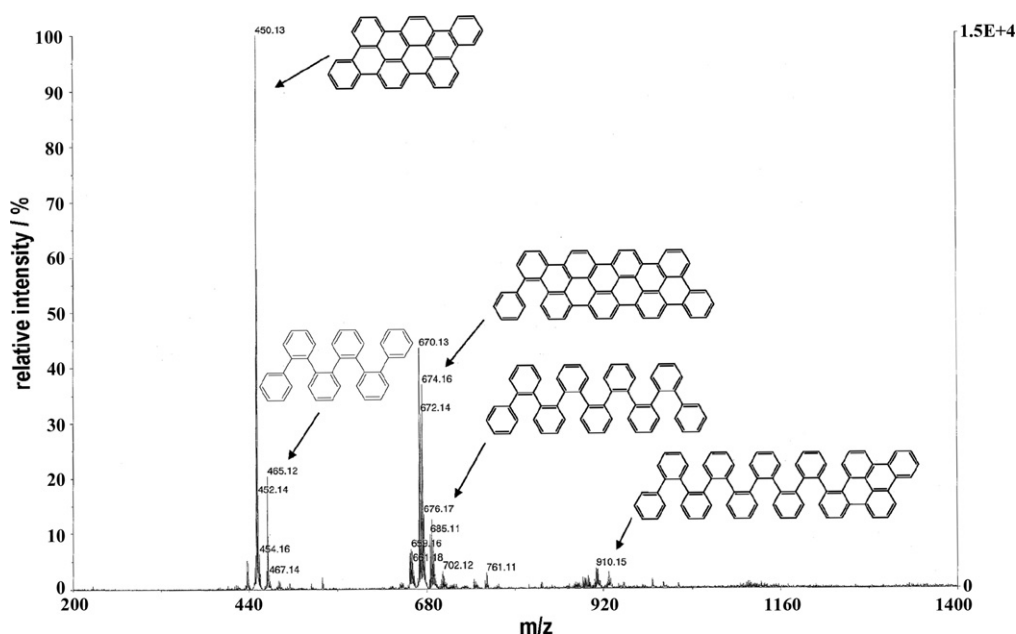


Fig. 6. Identification of oxidation products of *o*-TP by MALDI-TOF-MS after LSV measurements with Pt working electrode for 1 M LiPF₆-EC/EMC (3:7) + *o*-TP (2.0 wt.%).

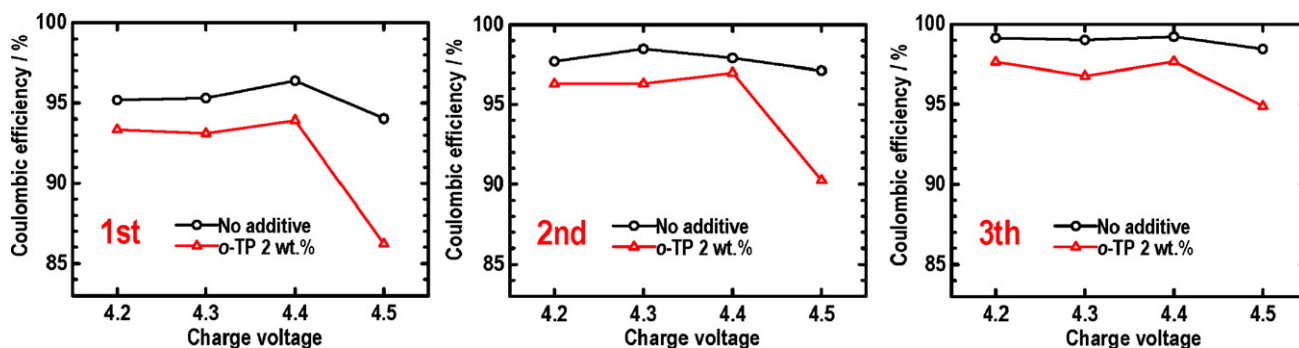


Fig. 9. Coulombic efficiencies of Li/LiCoO₂ cells with EM with and without *o*-TP, discharge cutoff voltage: 3.0 V, charge–discharge current density: 0.2 mA cm⁻² at first cycle and 0.5 mA cm⁻² at second and third cycles.

the discharge capacity drastically decreased at 4.5 V charging, compared with those at 4.2, 4.3 and 4.4 V. At 4.5 V charge, oxidation of *o*-TP showed bad influence on cycleability when 2.0 wt.% *o*-TP was added. In case of graphite/LiCoO₂ cells with BP at 4.3 V constant voltage charge [12,13], small amount of 0.1 wt.% showed better cycleability than that without additives. However, it is impossible to predict the suitable addition amounts of *o*-TP for our cases of Li/LiCoO₂ cells at higher 4.5 V constant current charge because the degree of both the deterioration of LiCoO₂ and the degree of oxidation of electrolyte solutions is unknown. So, influence of *o*-TP addition amount on cycleability of Li/LiCoO₂ cells was experimentally examined.

3.4. Charge–discharge cycling tests of Li/LiCoO₂ cells with various amounts of *o*-TP

Influence of addition amount of *o*-TP on charge–discharge cycling properties of Li/LiCoO₂ cells was examined. Addition amounts of *o*-TP varied at 0.1, 0.3, 0.5 and 2.0 wt.%. 4.5 V was

chosen as the charge cutoff voltage because oxidation of *o*-TP vigorously occurred at 4.5 V. Fig. 11 shows discharge and charge voltage curves of Li/LiCoO₂ cells with various amounts of *o*-TP at first, 10th, 30th and 50th cycles. Fig. 12(a) shows relation between discharge capacity and cycle number of Li/LiCoO₂ cells with various amounts of *o*-TP. Fig. 12(b) shows relation between coulombic efficiency and cycle number of Li/LiCoO₂ cells. All the cells with *o*-TP showed lower coulombic efficiencies than those of the cells without *o*-TP from first to third cycle. With an increase in *o*-TP amount, coulombic efficiency at first cycle became low. These results indicate that oxidation of *o*-TP proceeds during charge process even at 0.1 wt.%. Coulombic efficiencies of cells with *o*-TP were getting closer to those without *o*-TP with an increase in cycle number. With an increase in *o*-TP amount, cycle number making coulombic efficiencies saturate to constant values increases. During several cycles, oxidation of *o*-TP might almost complete and modify LiCoO₂ surface. Up to the 50th cycle, cells with smaller amount of *o*-TP showed a little bit higher discharge capacities than those without *o*-TP. However, discharge–charge voltage curve profiles of cells

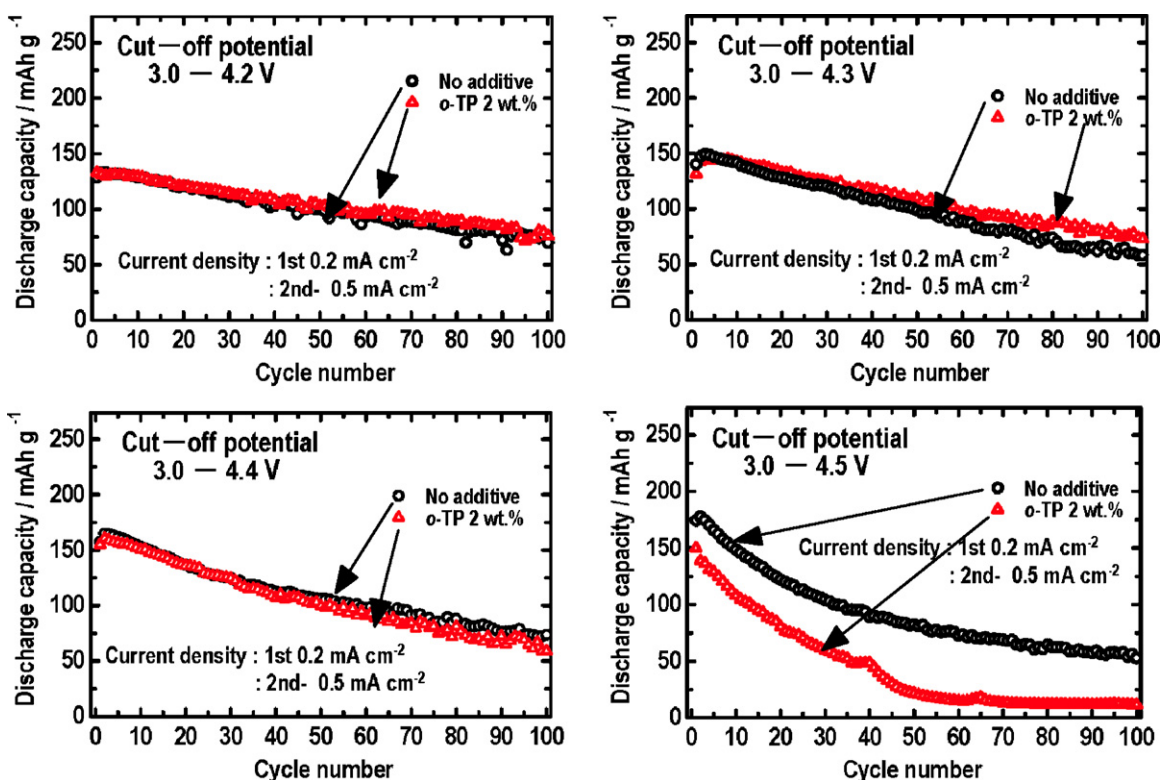


Fig. 10. Results of charge–discharge cycling tests of Li/LiCoO₂ cells with various charge voltages, EM with and without *o*-TP.

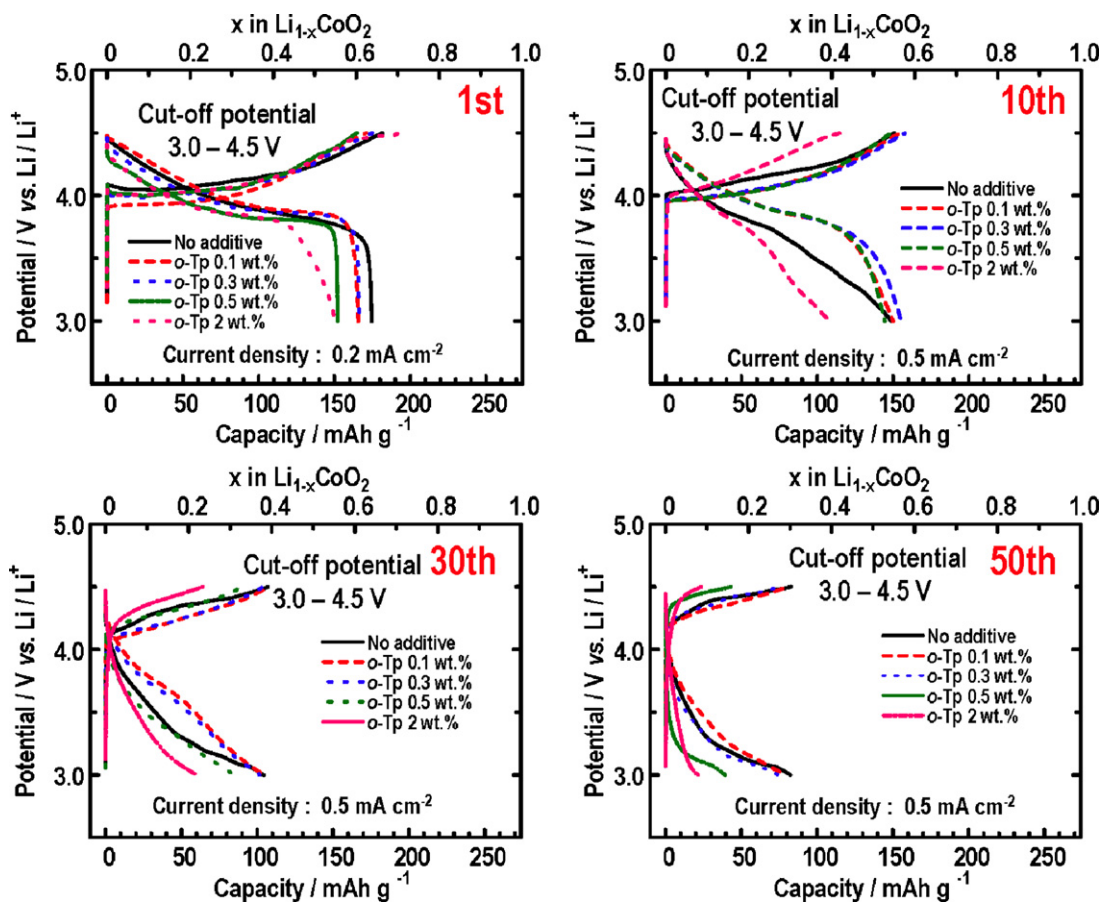


Fig. 11. Charge–discharge voltage profile for Li/LiCoO₂ cells, EM with and without *o*-TP.

with *o*-TP were different from those without *o*-TP. Deterioration of plateau region in discharge voltage curves of cells without *o*-TP more quickly occurred than those of cells with 0.1 and 0.3 wt.% *o*-TP. These phenomena are considered to result from smaller polarization of cells with 0.1 and 0.3 wt.% *o*-TP by change in interface state between electrolytes and LiCoO₂ whose surface was modified with oxidation products of *o*-TP. Discharge energy densities (Wh kg⁻¹) per cycle of cells with 0.1 and 0.3 wt.% *o*-TP were higher than those without *o*-TP even though discharge capacity densities (Ah kg⁻¹) per cycle did not differ so much. Higher addition exceeding 0.5 wt.% *o*-TP, degree of degradation of discharge capacities was obviously larger than that of EM.

Fig. 13 shows results of rate capabilities of Li/LiCoO₂ cells with and without *o*-TP. In the range of discharge current densities from 0.5 to 5.0 mA cm⁻², cells with 0.1 wt.% showed similar rate capability to that without *o*-TP. So, small amount addition of *o*-TP improved the cycleability without sacrificing rate capability of Li/LiCoO₂ cells.

3.5. Resistance of interface between electrode and electrolytes by AC impedance measurements

To discuss about influence of *o*-TP on surface modification of LiCoO₂, AC impedance measurements for electrode/electrolyte interface were carried out.

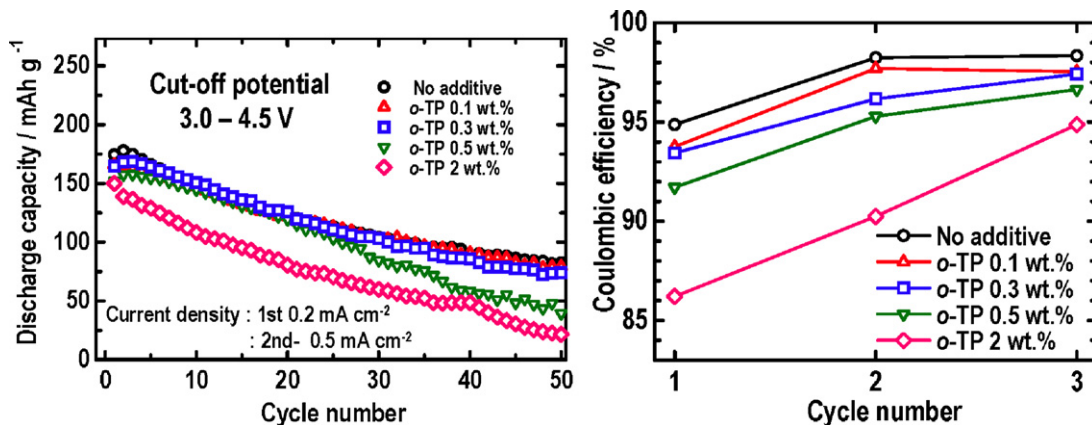


Fig. 12. (a) Results of charge–discharge cycling tests of Li/LiCoO₂ cells with various *o*-TP content, EM with and without *o*-TP, (b) coulombic efficiencies of Li/LiCoO₂ cells with EM with and without *o*-TP.

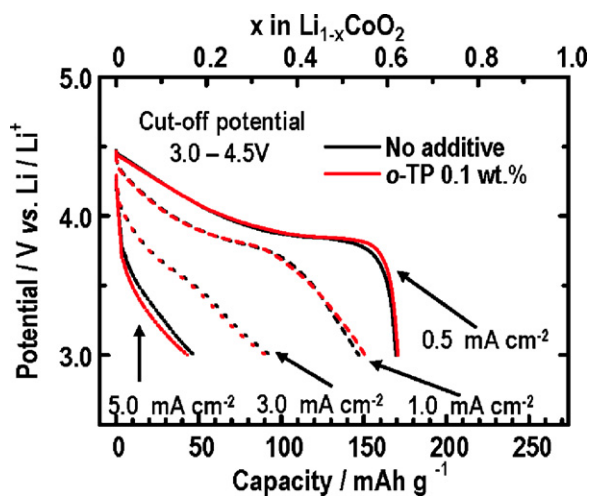


Fig. 13. Rate capability of Li/LiCoO₂ cells, discharge cutoff voltage: 3.0 V, charged at 4.5 V.

Resistance of interface between electrode and electrolyte in Li/LiCoO₂ cells with and without *o*-TP was examined by AC impedance measurements. Charge voltage was 4.5 V. Fig. 14(a) shows the results of AC impedance measurements for Li/LiCoO₂ cells with EM alone after 5th and 10th charge. Two semicircles were observed. Diameter of a semicircle in higher frequency region corresponds to resistance of interface between electrolyte solutions and Li. Diameter of a semicircle in lower frequency region corresponds to resistance of interface between electrolyte solutions and LiCoO₂. With an increase in cycle number, resistance of interface between electrolyte solutions and LiCoO₂ increased drastically. Resistance of interface of electrolyte/Li did not increase so much. Table 2 shows change in resistance with a change in cycle number and in addition amount of *o*-TP. Fig. 14(b) and (c) shows results of AC impedance measurements for Li/LiCoO₂ cells after 5th and 10th charge with 0.1 and 2.0 wt.% *o*-TP, respectively. In case of 0.1 wt.% *o*-TP addition, two semicircles similar to those with EM

alone were observed. With an increase in cycle number, resistance of interface of electrolyte/LiCoO₂ increased as in case of EM alone. Degree of increase in resistance with an increase in cycle number for cells with 0.1 wt.% *o*-TP was smaller than that of EM. In case of 2.0 wt.% *o*-TP addition, there was one semi-circle in high frequency region and a part of large semicircle in low frequency region. Large one in lower frequency region is not a straight line by the Warburg diffusion. A semicircle in the higher frequency region is due to interface between Li and electrolytes. Large one at lower frequencies is due to LiCoO₂/electrolyte interface. Excess formation of surface film by oxidation of *o*-TP on LiCoO₂ at 2.0 wt.% *o*-TP made resistance of interface between electrolyte and LiCoO₂ increase drastically. These results reflect large resistance (polarization) with high amount of surface film due to *o*-TP for kinetics of electrode reaction. This is a reason for the worse cycleability of Li/LiCoO₂ cells with higher amounts of *o*-TP. As shown in Table 2, change in resistance of Li/electrolyte with a change in amount of *o*-TP was not large for all the cells without and with *o*-TP. In Li/LiCoO₂ full cells, *o*-TP interacts more strongly with LiCoO₂ than that with Li.

So, summarizing the results of AC impedance and charge–discharge cycling tests of Li/LiCoO₂ cells with and without *o*-TP, the cycleability of Li/LiCoO₂ cells are mainly controlled by the cathode modification resulted from the oxidation of *o*-TP on LiCoO₂, not by Li anodes.

3.6. Thermal behavior of LiCoO₂ with and without *o*-TP addition

Thermal behaviors of LiCoO₂ charged at 4.5 V without and with *o*-TP (0.1 and 2.0 wt.%) were examined by DSC measurements. DSC was carried out for two kinds of DSC samples. First samples were the combination of LiCoO₂ charged at 4.5 V and three kinds of electrolyte solutions, i.e., EM, EM with 0.1 wt.% *o*-TP and EM with 2 wt.% *o*-TP (Fig. 15(a)). Second samples were the combination of LiCoO₂ charged at 4.5 V and three kinds of solvents without LiPF₆ (Fig. 15(b)). Fig. 16 shows thermal gravity (TG) results of dry LiCoO₂ cathode alone after charged at 4.5 V without any components of electrolyte solutions. Before this TG measurement, Li/LiCoO₂ cell

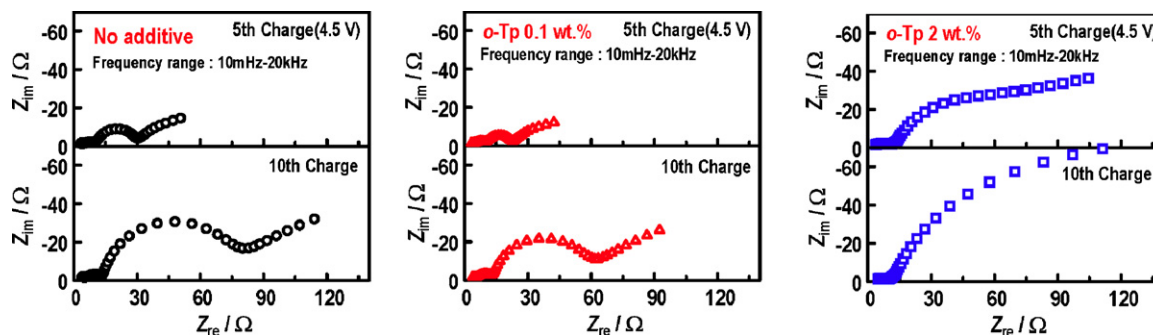


Fig. 14. Results of AC impedance measurements for Li/LiCoO₂ cells, charge voltage: 4.5 V, (a) EM, (b) *o*-TP (0.1 wt.%), (c) EM with *o*-TP (2.0 wt.%).

Table 2

Resistance of interface between electrolyte solutions and LiCoO₂ cathodes and lithium anodes after charged at 4.5 V, cycling condition: charge cutoff voltage: 4.5 V, discharge cutoff voltage: 3.0 V, charge–discharge cycling current density: 0.2 mA cm⁻² at first cycle, 0.5 mA cm⁻² after first cycle.

| Amount of <i>o</i> -TP | Electrodes | Resistance (Ω) | | Difference of resistance values between 5th and 10th cycle (resistance at 10th – resistance at 5th) |
|------------------------|------------|----------------|-------|---|
| | | Cycle number | | |
| | | 5th | 10th | |
| No addition | Cathode | 22.2 | 69.3 | 47.1 |
| | Cathode | 11.6 | 52.3 | 40.7 |
| | Cathode | 65.7 | 140.8 | 75.1 |
| No addition | Anode | 4.2 | 6.1 | 1.9 |
| | Anode | 4.2 | 5.9 | 1.7 |

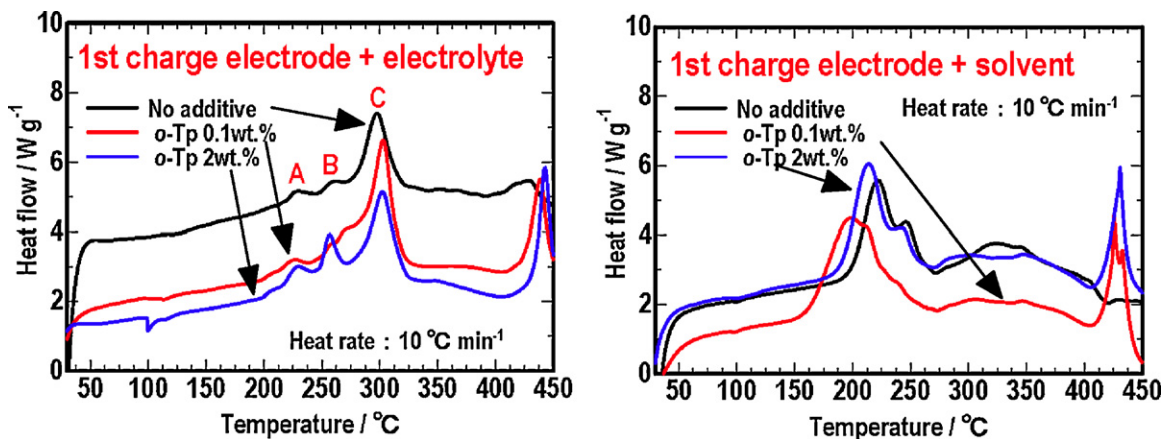


Fig. 15. DSC results for LiCoO₂ charged at 4.5 V, (a) EM + o-TP, (b) EC/EMC (3/7, v/v) + o-TP.

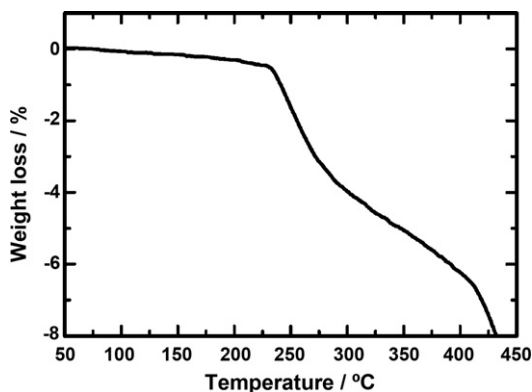


Fig. 16. TG result of dry LiCoO₂ charged at 4.5 V.

was charged at 4.5 V with EM. As shown in Fig. 15(a), three distinct exothermic peaks (peak A around 220 °C, peak B around 250 °C and peak C around 290 °C) were observed for LiCoO₂ charged at 4.5 V and electrolyte solutions. Peaks A and B were also observed in Fig. 15(b). Peak A around 220 °C corresponds to reaction of LiCoO₂ and the solvents. Reaction between LiCoO₂ and EC is shown in Eq. (2) [19]. Heat output of peak A for EM with o-TP was smaller than that for EM alone. Peak B around 250 °C corresponds to thermal decomposition of LiCoO₂ (Eq. (3)) [19,20]. As shown in Fig. 16, weight loss accompanied with this heat output (peak B) because oxygen gas was released from LiCoO₂. This oxygen accelerates the oxidation of the electrolyte solutions at high temperature such as 250 °C. Peak C around 290 °C corresponds to thermal decomposition of LiPF₆ (Eq. (4)) [21]. Table 3 shows total heat output obtained from these DSC results between 50 and 450 °C. Unfortunately, distinct effects for decreasing amount of heat output and shifting

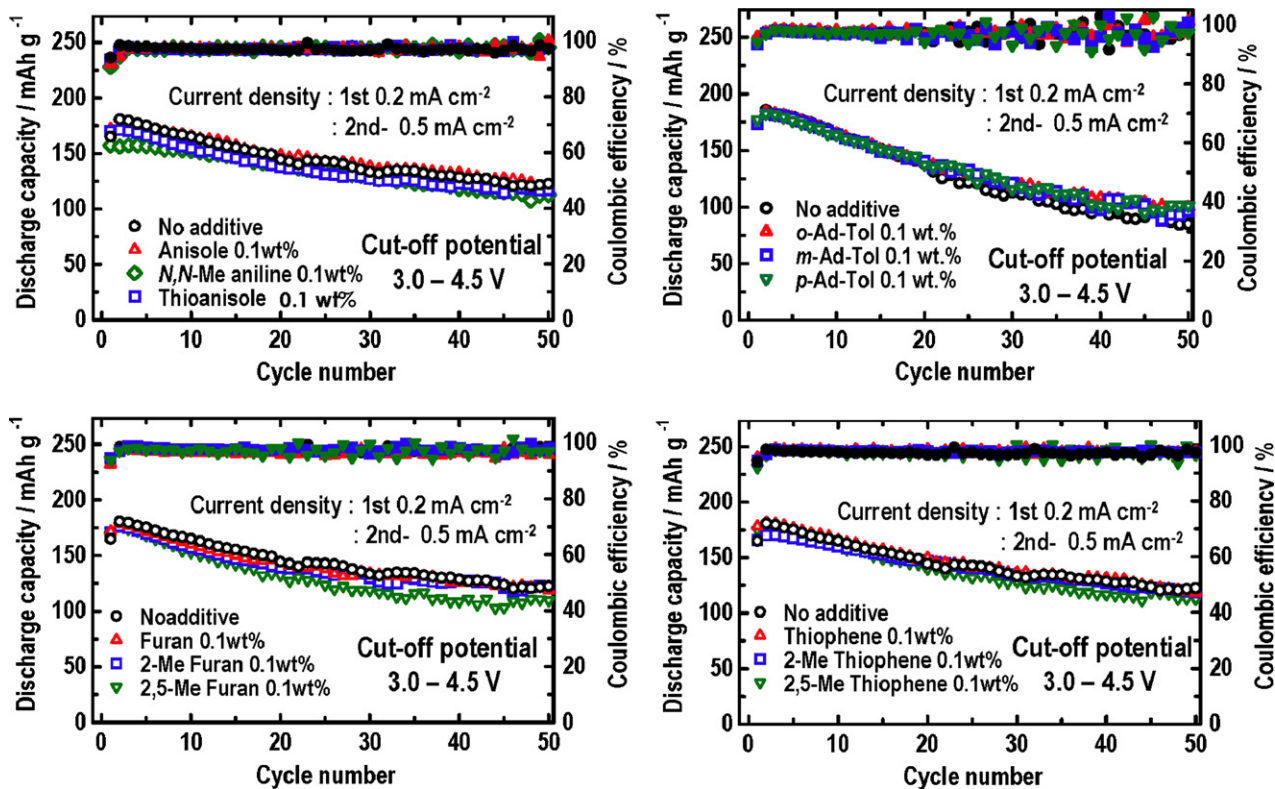


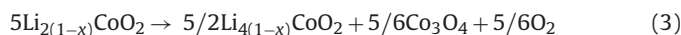
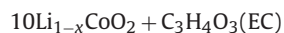
Fig. 17. Results of charge-discharge cycling tests of Li/LiCoO₂ cells with EM + additives, (a) PhX(CH₃)₃ compounds, (b) adamantyl toluene (Ad-Tol) compounds, (c) furans, (d) thiophenes.

Table 3

Heat output based on LiCoO₂ weight (J g⁻¹) between 50 and 450 °C for the DSC samples of LiCoO₂ charged at 4.5 V and solvents or electrolyte solutions, charge current density: 0.2 mA cm⁻², scan rate: 10 °C min⁻¹.

| Solute | Solvents | <i>o</i> -TP, wt.% | Heat output, J g ⁻¹ |
|-----------------------|----------------|--------------------|--------------------------------|
| 1 M LiPF ₆ | EC/EMC (30:70) | – | 395.5 |
| 1 M LiPF ₆ | EC/EMC (30:70) | 0.1 | 680.9 |
| 1 M LiPF ₆ | EC/EMC (30:70) | 2.0 | 591.6 |
| – | EC/EMC (30:70) | – | 586.5 |
| – | EC/EMC (30:70) | 0.1 | 794.1 |
| – | EC/EMC (30:70) | 2.0 | 604.5 |

exothermic temperature peaks to higher temperatures were not obtained by surface modification of LiCoO₂ by *o*-TP.



From a technical point of view, cycling performance of Li/LiCoO₂ cells at 4.5 V charge did not improve drastically by *o*-TP addition. To find better additives making the cycleability improve drastically, various organic compounds with different oxidation potentials and chemical structure were examined as electrolyte additives.

3.7. Charge–discharge cycling tests of Li/LiCoO₂ cells with various LiCoO₂ surface modification additives

Chemical structure and Eox of organic additives as LiCoO₂ surface modifier examined here were already shown in Fig. 2. These compounds have the Eox values between 3.4 and 4.7 V vs. Li/Li⁺. These Eox values were lower than that of EM. Charge voltage of 4.5 V was between the Eox values of these compounds. These compounds are categorized roughly to four groups according to their chemical structures; (i) Ph-X(CH₃)_n (*n* = 1 and 2) compounds containing heteroatoms of X = N, O or S, (ii) adamantyl toluene compounds, (iii) furans and (iv) thiophenes. Fig. 17(a–d) shows charge–discharge cycling results of Li/LiCoO₂ cells with 0.1 wt.% additives. Cells with adamantane derivatives showed a little bit higher discharge capacities during cycles than that with EM alone. However, these additives did not show large difference in cycling performance. Eox values, heteroatoms or molecular structures did not matter and did not exhibit any significant effects on charge–discharge cycling properties from a technical point of view.

4. Conclusion

Influence of organic compounds as cathode surface modifier on electrochemical and thermal properties of Li/LiCoO₂ cells was examined. How the addition of organic compounds affects LiCoO₂ properties was found. Slightly better charge–discharge cycling properties were obtained. However, when industrial applications were considered, drastic improvements have not been obtained yet. One of reasons should be that the influence of the deterioration of stability of pure LiCoO₂ structure at high voltage charge is still too large for industrial use. In order to utilize the effects of organic surface modifiers, we may have to use more stable LiCoO₂ such as LiCoO₂ treated with MgO in the next step of research. We hope to realize the tremendous improvements of high energy, long cycle life and safe lithium cells by the combination of both LiCoO₂ with more stable structure and new organic additives with molecular structure more carefully designed.

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