

Reaction mechanisms of aromatic compounds as an overcharge protection agent for 4 V class lithium-ion cells

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Abstract

Aromatic compounds such as biphenyl (BP), cyclohexylbenzene (CHB), and partially hydrogenated *m*-terphenyl (H-*m*TP) are used in commercial lithium-ion cells as a non-redox shuttle type overcharge protection agent, where they are electrochemically polymerized to form passive films on the positive electrode under overcharge conditions. The reaction mechanisms of these aromatic compounds were investigated. The oxidation products of these aromatic compounds on the positive electrode were identified by electrochemical and surface analysis techniques including SEM, TPD-MS and MALDI-TOF-MS. They were the oligomers having 6–12 benzene rings, where the bond formation occurs mainly at *ortho*-positions of phenyl group. Their formation was not dependent on the monomer structure (BP, CHB, or H-*m*TP) and temperature (25 or 60 °C). It was considered that the cyclohexane structure in CHB or H-*m*TP was converted to the benzene structure by dehydrogenation after the polymerization.

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1. Introduction

Lithium-ion cells are now widely used for portable PC, cellular phones, camcorders, etc., due to their high energy density. However, the cells have some safety problems. Particularly, the overcharge protection is an urgent problem to be solved, because the cells become thermally unstable at overcharged state, and sometimes smoke, ignite, or explode during overcharge [1]. The heat generation and the change in the cell voltage under the overcharge conditions were reported [2–4]. The main reasons of the thermally unstable state are Li metal deposition on the negative electrode and too much extraction of Li from the positive electrode. Thermal cut-off devices and overcharge protection circuits are used in commercially available cells to prevent the

abnormal situation. However, the overcharge protection is not sufficient.

Therefore, many fundamental researches are undertaken to protect overcharge situation. The redox shuttle approach to overcharge protection employs an electrolyte additive which acts as an internal current shunt when the positive electrode potential exceeds the oxidation potential of the additive [5]. Redox shuttle agents are oxidized on the positive electrode, and the oxidized products are reduced on the negative electrode to the initial compound. Recently, new redox shuttle compounds for 4 V class cells are reported [6–9]. The effectiveness of some aromatic compounds in electrolyte solutions such as 0.1 M (M = mol dm⁻³) 4-bromo-1,2-dimethoxybenzene in 1.0 M LiPF₆/PC + DMC [6] and 0.05 M 2,7-dibromothianthrene in 1.0 M LiPF₆/EC + PC + DMC + EMC [9] was demonstrated in a Li/LiCoO₂ 2025 coin cell and a C/LiCoO₂ prismatic cell, respectively.

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We have also proposed a new type of overcharge protection agent, where redox mediators such as *tert*-butylbenzene are oxidized on the positive electrode and reduced by the reaction with the electrolyte [10].

On the other hand, there is another type overcharge protection agent called a non-redox shuttle type. Aromatic compounds such as biphenyl (BP), cyclohexylbenzene (CHB), etc. are classified into this category [11–15]. In the cells containing these agents, they are electrochemically polymerized to form passive films on the positive electrode under the overcharge conditions. Liberated protons from these monomers migrate to the negative electrode, which results in hydrogen gas evolution on the negative electrode. In the case of cylindrical cells with pressure-activated current intermitted devices (CID), the internal pressure rise by hydrogen gas evolution helps to operate them. On the other hand, prismatic cells utilize the current shutdown mechanism by the increase in the internal resistance caused by the polymerized film as well as the meltdown of polyethylene-based separator derived by the generated heat [16].

In solutions of quaternary ammonium salts and acetonitrile solvent, it was reported that BP is electrooxidized to poly *p*-phenylene [17]. However, the reaction mechanisms of the non-redox shuttle type agents have not been clarified in an electrolyte used in lithium-ion cells. In this study, the reaction mechanisms of these non-redox shuttle type agents have been examined by electrochemical and surface analysis techniques [18,19].

2. Experimental

Biphenyl (BP) from Wako Pure Chemical Industries, Ltd., Japan was used as received. Cyclohexylbenzene (CHB) from Wako Pure Chemical Industries was purified to more than 99.9% in purity by distillation. Partially hydrogenated *m*-terphenyl (H-*m*TP) was prepared from *m*-terphenyl by hydrogenation. The obtained H-*m*TP is a mixture of nine compounds of *m*-terphenyl, 1,3-diphenylcyclohexane (*trans*- and *cis*-isomers), 3-cyclohexylbiphenyl, 3-phenylbicyclohexyl (*trans*- and *cis*-isomers), 1,3-dicyclohexylbenzene, and *m*-tricyclohexyl (*trans*- and *cis*-isomers) [20,21]. H-*m*TP of 42.8% in hydrogenation ratio was mainly used in this study.

Two weight percentage of BP, CHB, or H-*m*TP were added into a 1 M LiPF₆/ethylene carbonate (EC)–ethyl methyl carbonate (EMC) (30:70 in vol.%) electrolyte solution or a 1 M LiPF₆/EC–dimethyl carbonate (DMC)–EMC (30:35:35 in vol.%) electrolyte solution in an argon glove box, respectively.

Anodic cyclic voltammograms of the electrolyte were obtained at room temperature using a Pt working electrode (1.6 mm in diameter), a Li reference electrode, and a Li counter electrode in H-type glass cell in an argon glove box. The measurement was carried out over a potential range from open circuit voltage (OCV) to 5.0 V versus Li⁺/Li at a sweep rate of 5 mV s⁻¹. Analytical samples of the oxidation products were collected after anodic linear sweep voltammetry using a Pt plate (10 mm × 10 mm) as a working electrode at the same conditions except a sweep rate of 2 mV s⁻¹.

Overcharge tests of the electrolyte were undertaken at 25 and 60 °C using 2032-type coin cell (graphite as a negative electrode

and LiCoO₂ as a positive electrode, capacity; 3.7 mAh). The measurement was carried out over a voltage range from 4.2 to 5.0 V at ca. 2 mA cm⁻² (1 C rate).

Analyses of the oxidation products were performed by surface analysis techniques such as a scanning electron microscopy (SEM, JEOL JEM-6300F), a temperature programmed desorption (or decomposition)–mass spectrometry (TPD–MS, ANELVA AGS-7000), and matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF-MS, Applied Biosystem Voyager Elite).

3. Results and discussion

Biphenyl (BP) is the first proposed compound for non-redox shuttle type overcharge protection agents [11,12]. Since BP has an disadvantage that it deteriorates the cell performances during full charge storage at elevated temperatures, partially hydrogenated compounds such as cyclohexylbenzene (CHB), hydrogenated terphenyl (H-TP), hydrogenated dibenzofuran (H-DBF), and tetralin were proposed [13,14]. Partial hydrogenation shortens π -electron conjugated systems in aromatic compounds, and leads to higher oxidation potentials, more resistant to the full charge storage at elevated temperatures. We have found a possibility that partial hydrogenation of *m*-terphenyl (*m*TP) gives rise to the compounds having appropriate oxidation potentials by molecular orbital calculations [18,19]. Partially hydrogenated *m*-terphenyl (H-*m*TP) consists of nine components, *m*-terphenyl, 1,3-diphenylcyclohexane (*trans*- and *cis*-isomers), 3-cyclohexylbiphenyl, 3-phenylbicyclohexyl (*trans*- and *cis*-isomers), 1,3-dicyclohexylbenzene, and *m*-tricyclohexyl (*trans*- and *cis*-isomers) [20,21]. Fig. 1 shows the highest occupied molecular orbital (HOMO) energy of each component, BP, and CHB, calculated by *ab initio* molecular calculations, HF/6-

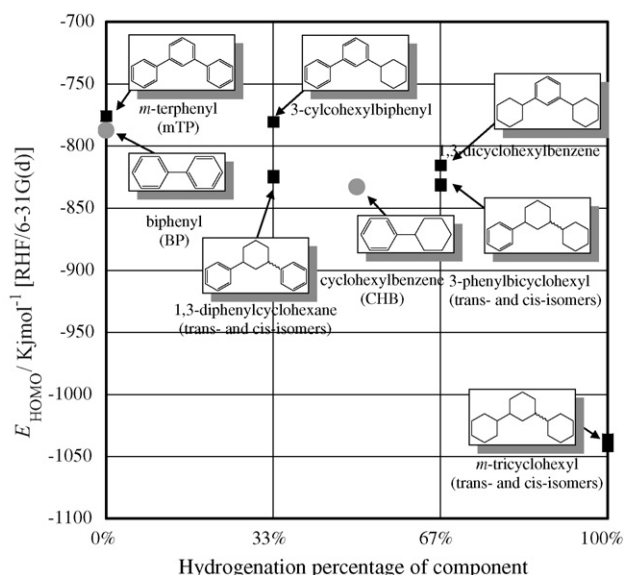


Fig. 1. Calculated HOMO energies of H-*m*TP components, BP, and CHB [H-*m*TP components are *m*-terphenyl, 1,3-diphenylcyclohexane (*trans*- and *cis*-isomers), 3-cyclohexylbiphenyl, 3-phenylbicyclohexyl (*trans*- and *cis*-isomers), 1,3-dicyclohexylbenzene, and *m*-tricyclohexyl (*trans*- and *cis*-isomers)].

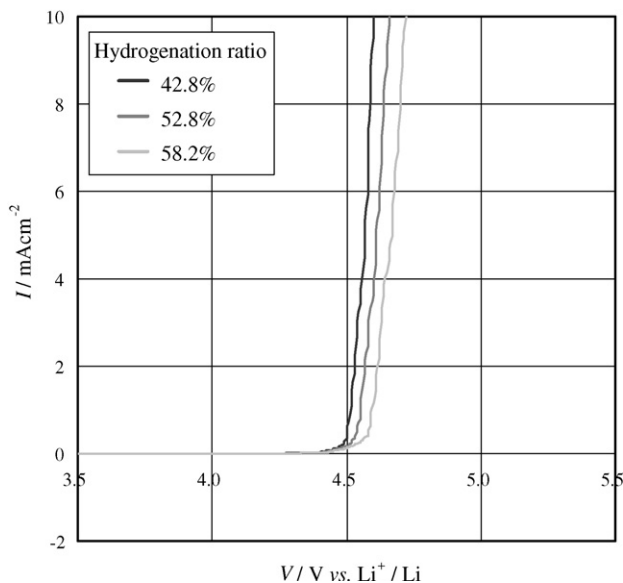


Fig. 2. Linear sweep voltammograms of H-*m*TP (2 wt.%) in 1 M LiPF₆/EC–EMC (30:70) (WE: Pt, RE: Li, sweep rate: 5 mV s⁻¹).

31G(d) [22]. If we ignore the solvation energy and entropy change by the oxidation, the internal energy change of additives is “HOMO energy”. Therefore, the oxidation potential (E) versus Li⁺/Li is expressed by the following equation using thermodynamics:

$$E = -(\text{“HOMO energy”} + \Delta U)/F,$$

where F is the Faraday constant ($9.6485 \times 10^4 \text{ C mol}^{-1}$) and ΔU is the internal energy change of electrolyte and Li electrode by the oxidation. The sign of HOMO energy is minus. Therefore, the oxidation potential increases with decreasing the HOMO energy (with increasing the absolute value of the HOMO energy).

The calculation results of H-*m*TPs indicate that HOMO energy depends on hydrogenation percentage of each component, and it is predicted that the oxidation potential of H-*m*TP depends on the hydrogenation ratio (the average value of the hydrogenation percentage). In the case of the components on 33% in hydrogenation, we also found that 1,3-diphenylcyclohexane without a biphenyl structure is less oxidizable than its isomer, 3-cylcohexylbiphenyl with a biphenyl structure. This is because the conjugated-benzenes such as a biphenyl structure have more π electrons than the simple phenyl group.

Fig. 2 shows anodic linear sweep voltammograms of H-*m*TP (hydrogenation ratio; 42.8, 52.8, and 58.2%). It was observed that the oxidation potential depends on the hydrogenation ratio as predicted by the HOMO calculation. Detailed experiments have proved that the oxidation potential of H-*m*TP (various mixtures containing nine compounds) was continuously controlled by changing the hydrogenation ratio of *m*TP.

The cyclic voltammograms of the electrolytes with BP, CHB, and H-*m*TP (hydrogenation ratio; 42.8%) are shown in Fig. 3. It was observed that the onset oxidation potentials of the 2nd and 3rd cycles were lower than that of the 1st cycle in all

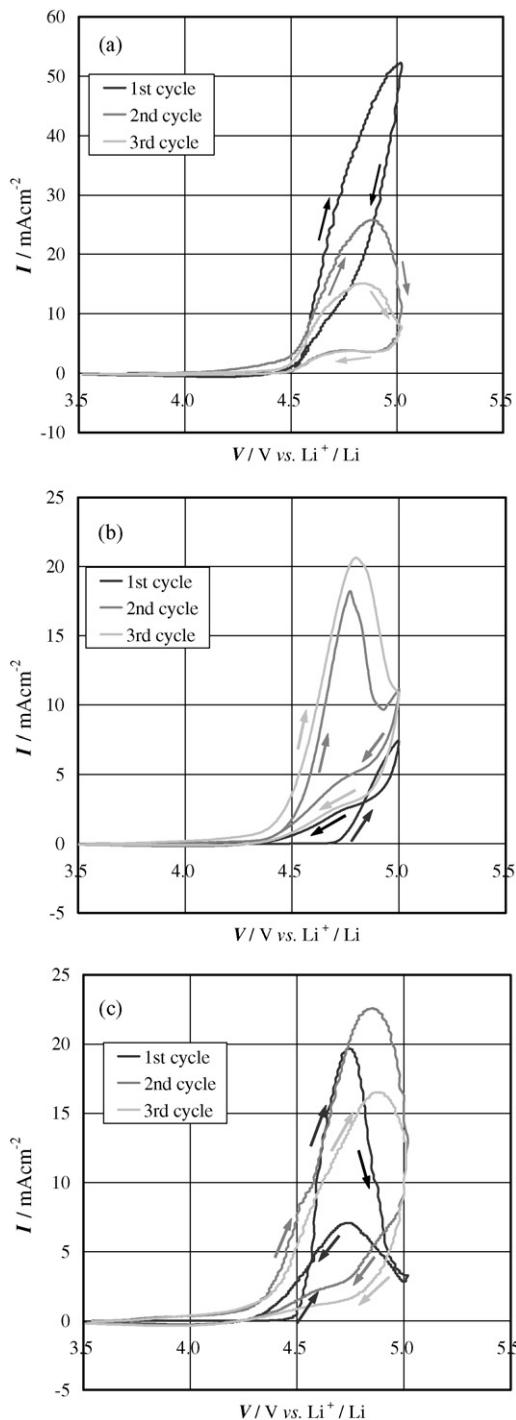


Fig. 3. Cyclic voltammograms of agent (2 wt.%) in 1 M LiPF₆/EC–EMC (30:70): (a) BP, (b) CHB and (c) H-*m*TP (WE: Pt, RE: Li, sweep rate: 5 mV s⁻¹).

voltammograms. This result suggests a possibility that the oxidation product by electrochemical reaction reacts chemically, and the compound by the chemical reaction has a lower oxidation potential than that of original BP, CHB, or H-*m*TP. This story is supported by the fact that the oxidized compound by electrochemical reaction is a radical cation, and the cation cannot be oxidized electrochemically further at the same conditions. A plenty of black precipitates were observed on the surface of the working electrodes after the cyclic sweep voltammetry

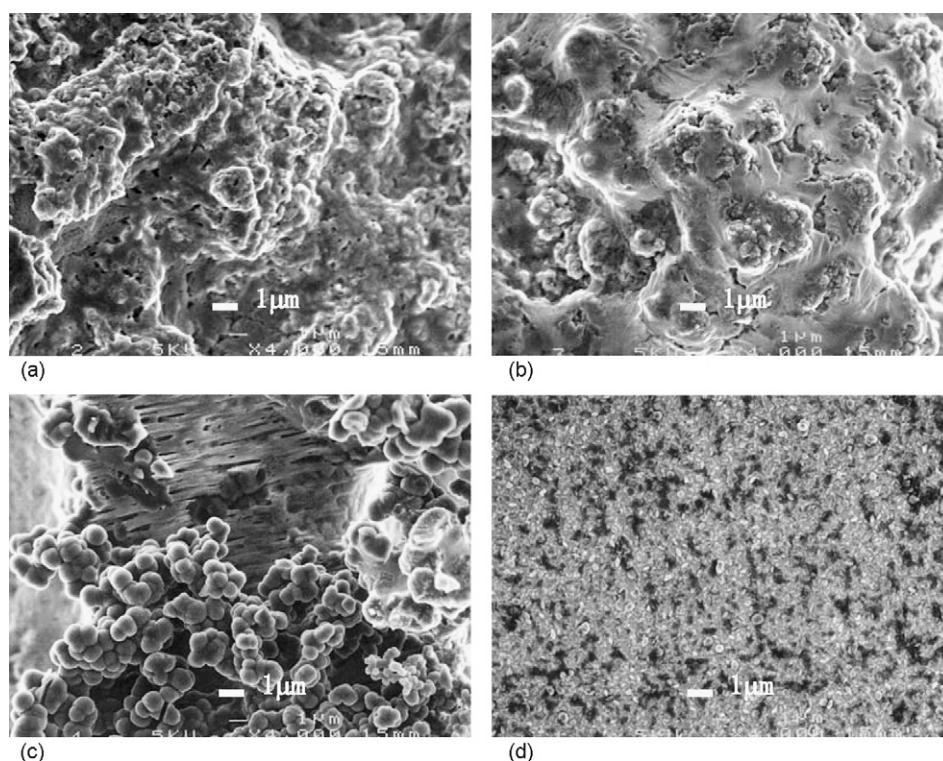


Fig. 4. SEM images of the black precipitates after the linear sweep voltammetry tests. Agent (2 wt.%) in 1 M LiPF₆/EC–EMC (30:70): (a) BP, (b) CHB, (c) H-*m*TP and (d) none.

tests. This result indicates that the precipitates have a certain electronic conductivity at least during the voltammetry test. If the precipitates do not have an enough electronic conductivity, the oxidation current is reduced by the compound on the electrode. This was the case when BP was used, where the current decreased with cycling. On the other hand, the current increased with cycling in the case of CHB. H-*m*TP showed the current increase at the 2nd cycle and decrease at the 3rd cycle.

In order to clarify the structure of the black precipitates, the anodic linear sweep voltammetry of the electrolytes were carried out to collect the sample using a Pt plate. Fig. 4 shows the SEM images of the black precipitates. The morphology of the precipitates of BP and CHB were almost the same and they were uneven and dense. In the case of H-*m*TP, the morphology consists of uneven and flat places. This may be caused by the difference in the reactivity of the components, because H-*m*TP is a mixture of more than one component.

Fig. 5 shows the oxidation products and its molecular distribution by MALDI-TOF-MS. All products were condensed aromatic compounds and had similar structures. It was found that the bond formation between monomers occurs mainly at *ortho*-positions of the phenyl groups. These condensed aromatic compounds have the extensive conjugated system with π electrons. Probably, BP, CHB, or H-*m*TP reacts with these condensed aromatic compounds at lower oxidation potentials than those of BP, CHB, or H-*m*TP on Pt electrode. Therefore, the cyclic voltammograms showed the negative shift of the oxidation potentials in the 2nd and 3rd cycles. In the case of the electrolyte with BP, poly *p*-phenylene was not detected under our conditions.

In order to analyze the oxidation products on the surface of the positive electrode more precisely, the overcharge tests at ca. 2 mA cm⁻² (1 C rate) were carried out by adding 2 wt.% of each agent in C/LiCoO₂ 2032 coin cells (3.7 mAh) using 1 M LiPF₆/EC + DMC + EMC (30:35:35 in vol.%). The results of overcharge tests of the electrolytes with BP, CHB, and H-*m*TP are shown in Fig. 6. Unstable voltage profiles are observed at 25 °C, because of a breakdown of insulation film (the black precipitates) on the positive electrode or the internal shorting between the electrodes by lithium dendrites. In contrast, very smooth voltage profile was obtained at 60 °C. This difference may be caused by the resistance reduction of the insulation film by temperature rise in the cell. The reaction potential of each agent can be estimated from the OCV after the overcharge tests.

Figs. 7–9 show the gas chromatograms of the oxidation products after the overcharge tests at 25 and 60 °C in TPD–MS analysis. Long chain alkanes were observed in some samples. Table 1 summarizes the existence of long chain alkanes in each sample. These results clearly indicate that the agents including

Table 1
Existence of long chain alkanes in oxidation products by TPD–MS analysis

Additive	Cyclohexane structure	Overcharge temperature	
		25 °C	60 °C
BP	No	None	None
CHB	Yes	Detected	None
H- <i>m</i> TP	Yes	Detected	None

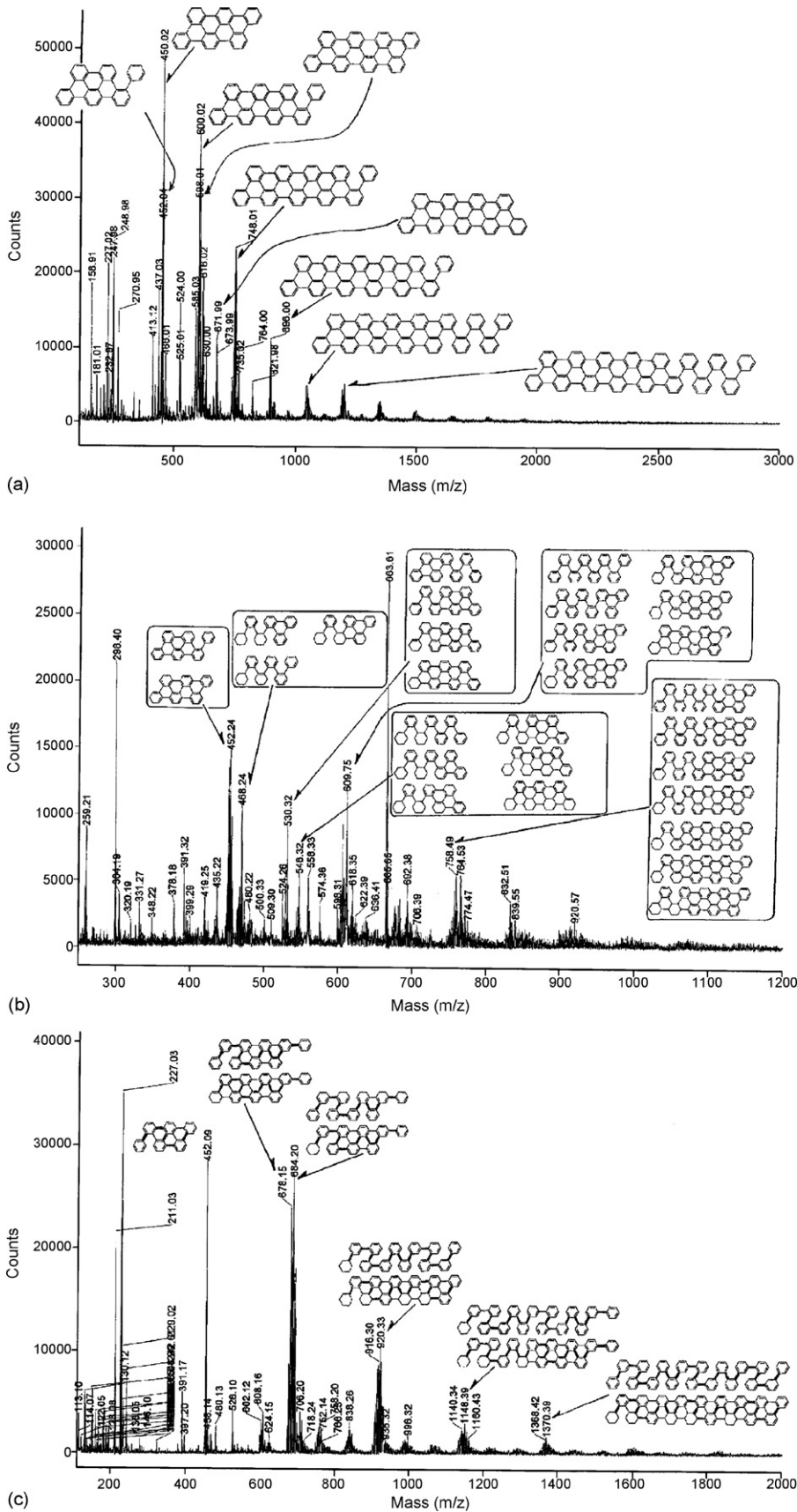


Fig. 5. Identification of the oxidation products by MALDI-TOF-MS after the linear sweep voltammetry tests. Agent (2 wt.%) in 1 M LiPF₆/EC–EMC (30:70): (a) BP, (b) CHB and (c) H-mTP.

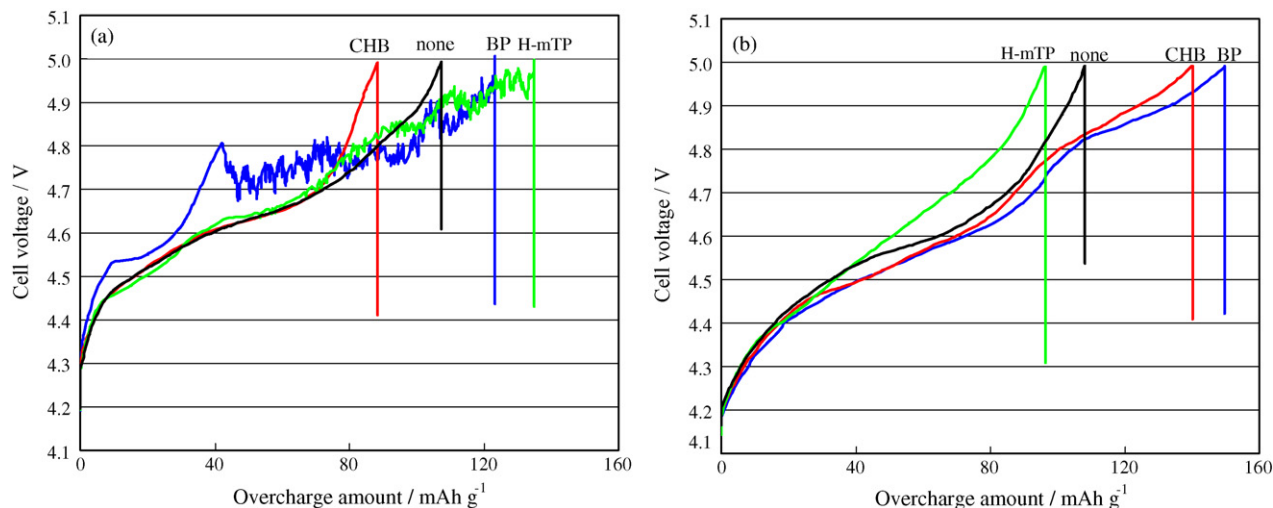


Fig. 6. Voltage profile of overcharge tests of agent (2 wt.%) in 1 M LiPF₆/EC–DMC–EMC (30:35:35): (a) 25 °C and (b) 60 °C.

the cyclohexane structure produce long chain alkanes at 25 °C. However, long chain alkanes were not observed at 60 °C. The results indicate that conversion of the cyclohexyl group into the phenyl group requires a higher temperature (60 °C). The unstable voltage profile (Fig. 6) can be explained by the existence of the long chain alkanes as an insulator, except for the sample with BP at 25 °C.

Figs. 10 and 11 show the oxidation products and its molecular distribution by MALDI-TOF-MS. All products were condensed aromatic compounds and had similar structures. The bonds formed between monomers mainly at *ortho*-positions of the phenyl groups. This result agrees with that of the anodic linear sweep voltammetry test (Fig. 5), however, the products on the positive electrode (Li_xCoO₂) have lower molecular weight than

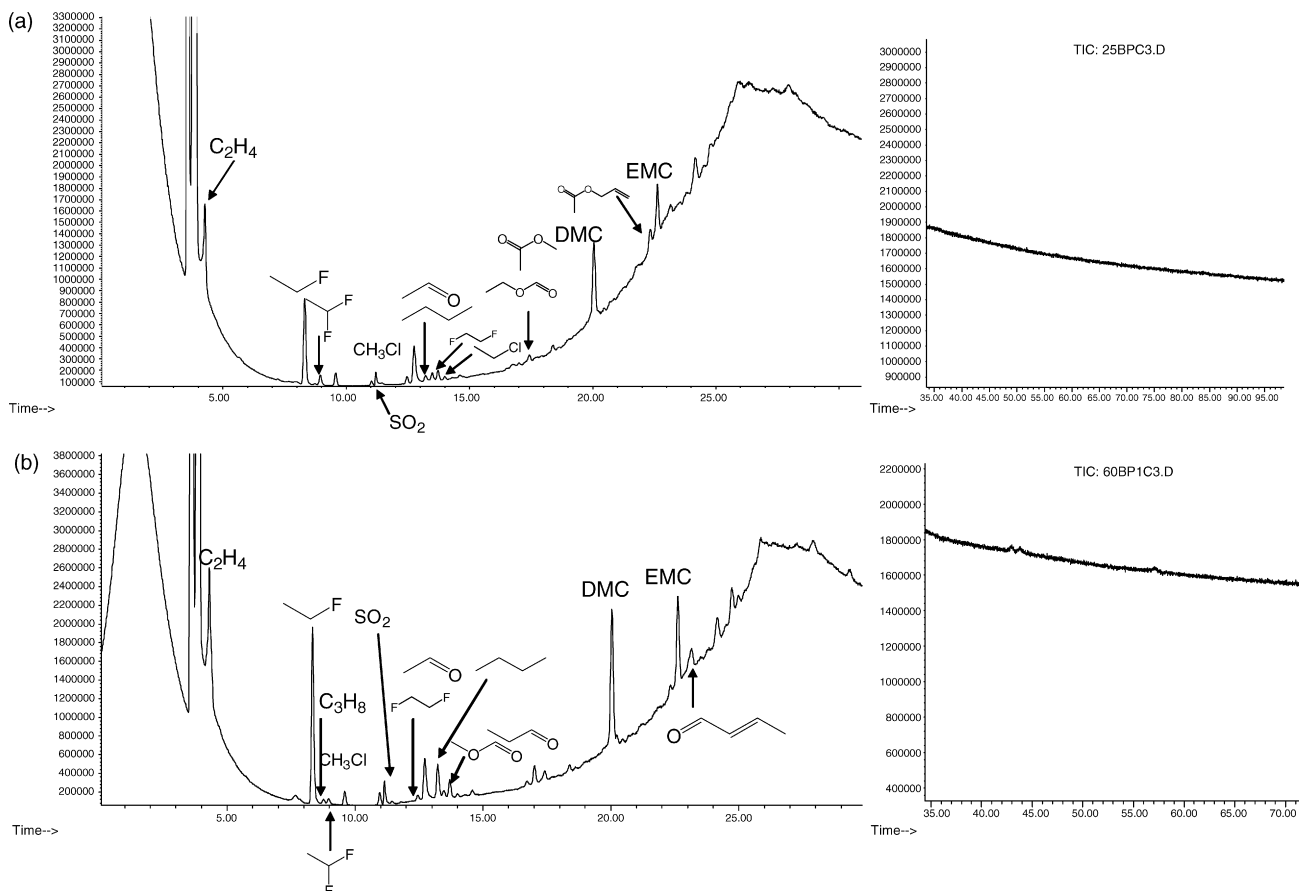


Fig. 7. Identification of oxidation products using gas chromatography, BP (2 wt.%) in 1 M LiPF₆/EC–DMC–EMC (30:35:35): (a) 25 °C and (b) 60 °C.

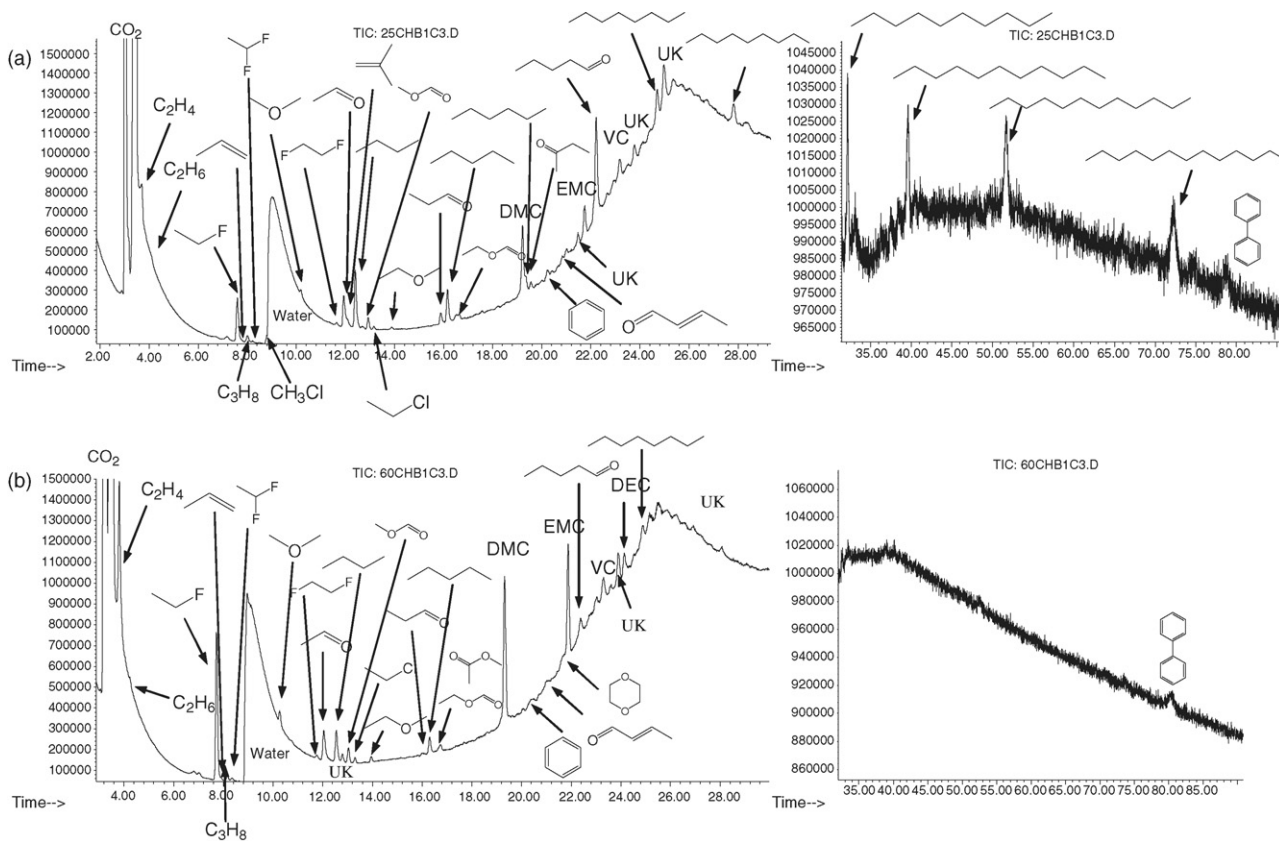


Fig. 8. Identification of oxidation products using gas chromatography. CHB (2 wt.%) 1 M LiPF₆/EC–DMC–EMC (30:35:35): (a) 25 °C and (b) 60 °C.

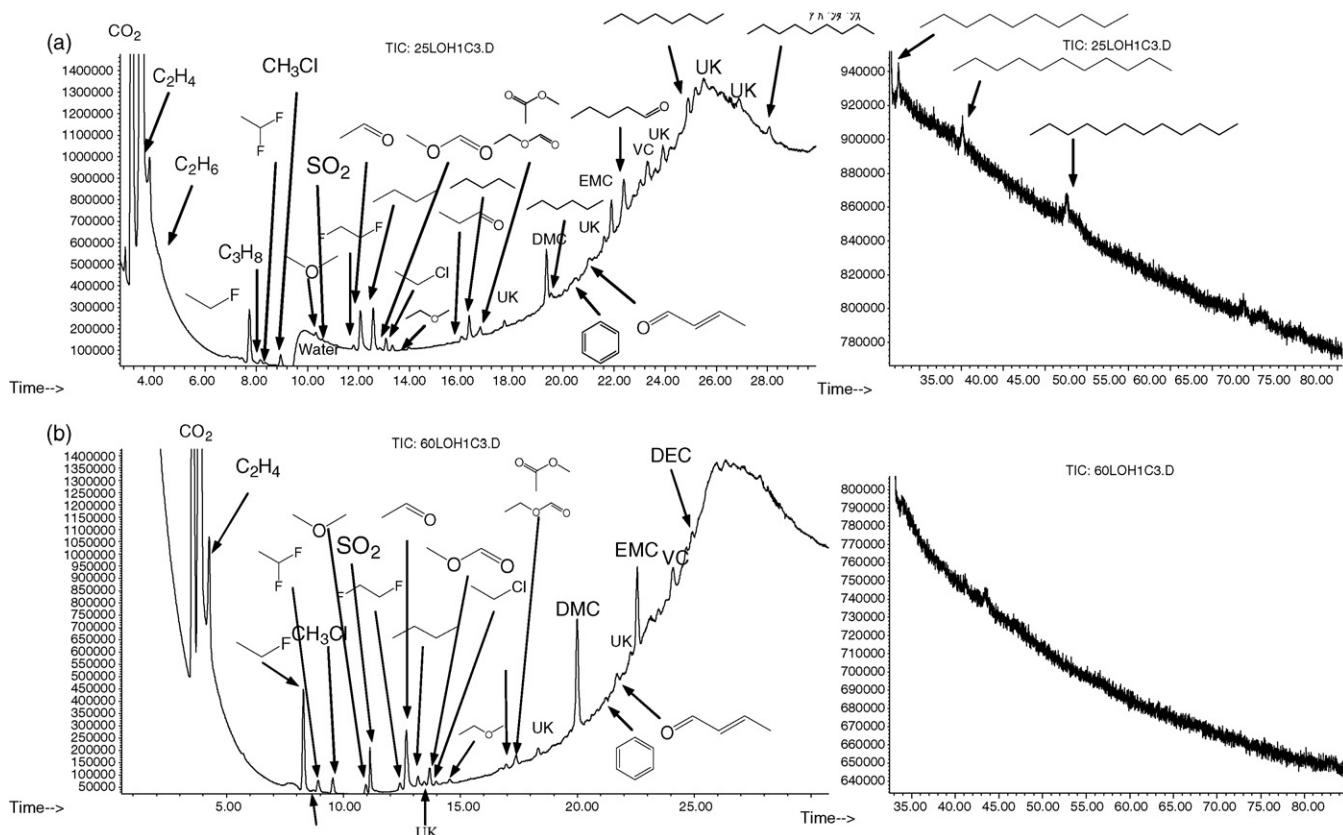


Fig. 9. Identification of oxidation products using gas chromatography. H-mTP (2 wt.%) in 1 M LiPF₆/EC–DMC–EMC (30:35:35): (a) 25 °C and (b) 60 °C.

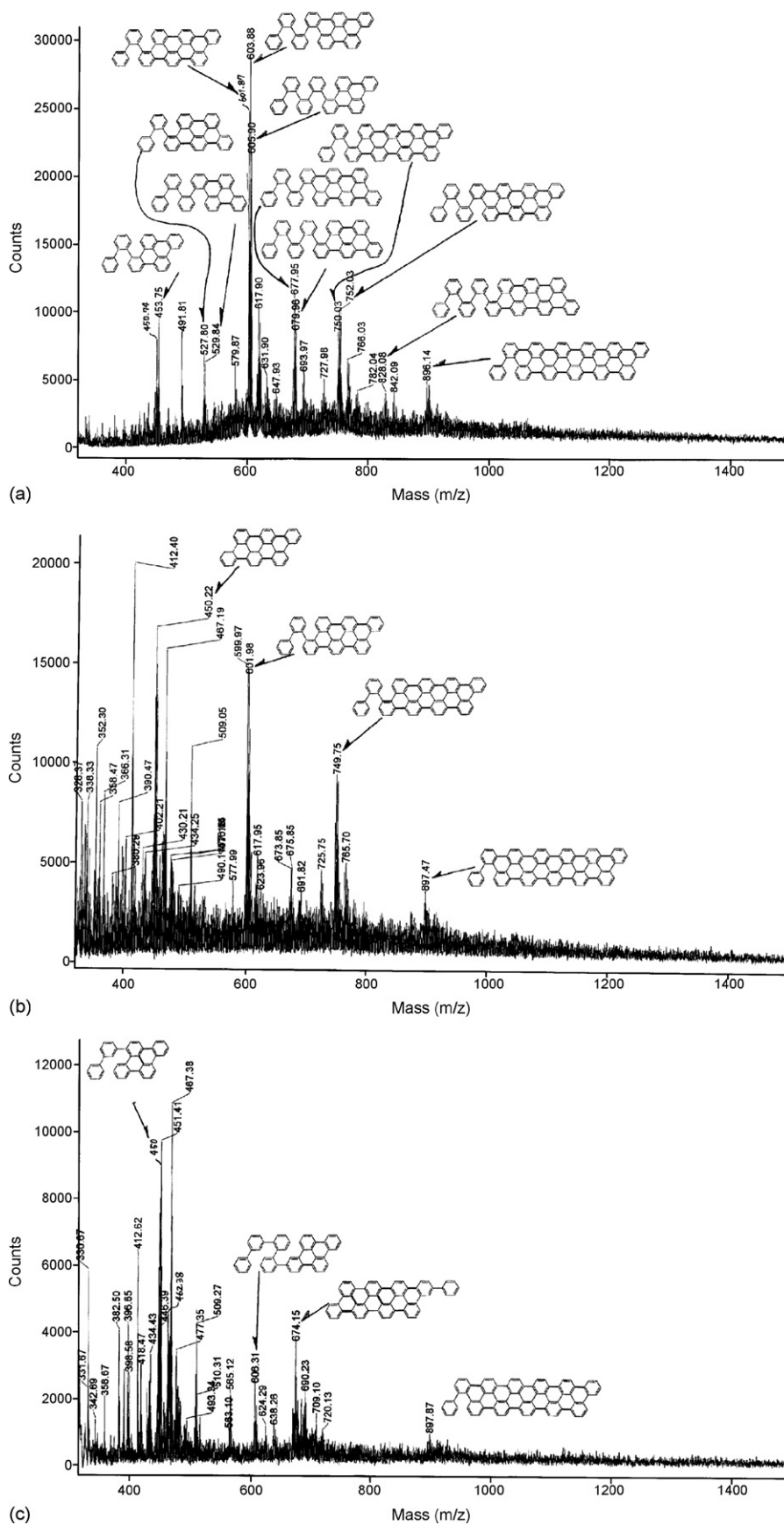


Fig. 10. Identification of the oxidation products by MALDI-TOF-MS after overcharge tests at 25 °C. Agent (2 wt.%) in 1 M LiPF₆/EC–DMC–EMC (30:35:35): (a) BP, (b) CHB and (c) H-mTP.

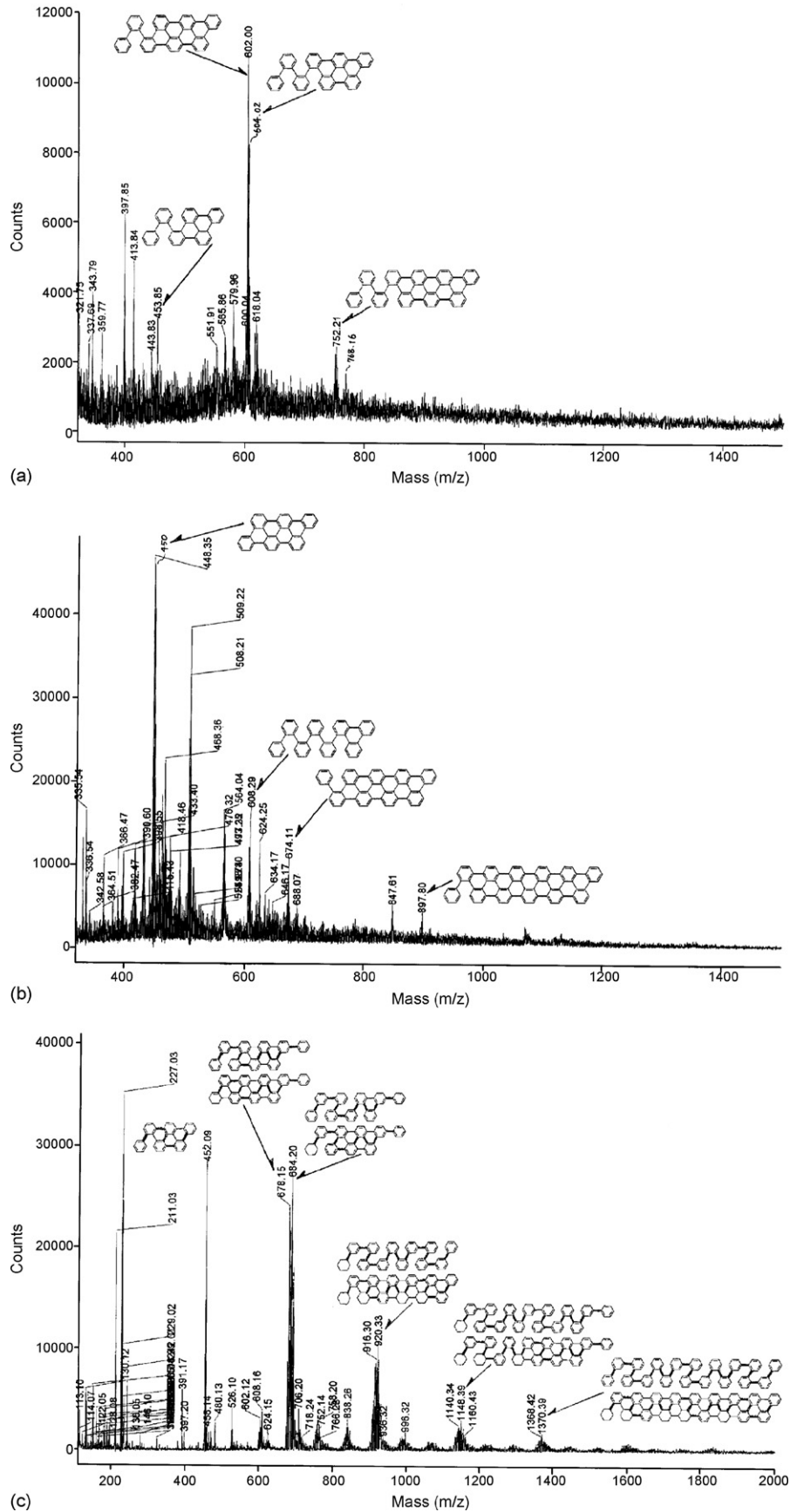


Fig. 11. Identification of the oxidation products by MALDI-TOF-MS after overcharge tests at 60 °C. Agent (2 wt.%) in 1 M LiPF₆/EC–DMC–EMC (30:35:35): (a) BP, (b) CHB and (c) H-mTP.

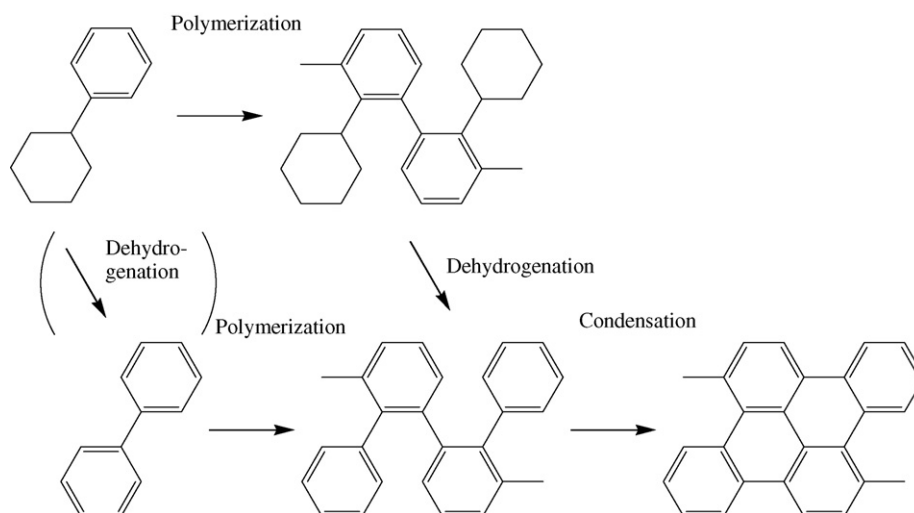


Fig. 12. Proposed reaction mechanisms of BP and CHB.

Table 2
Degree of oligomerization (benzene unit)

Additive	Overcharge temperature	
	25 °C	60 °C
BP	6–12	6–10
CHB	6–12	6–12
H- <i>m</i> TP	6–12	6–12

those on the Pt electrode. Table 2 shows the degree of oligomerization of benzene unit. The oligomers have 6–12 benzene rings, and their formation was not dependent on the monomer structure and temperature.

Fig. 12 shows a possible reaction mechanism of BP and CHB. In the case of CHB or H-*m*TP, it is considered that the cyclohexane structure was converted to the benzene structure after the polymerization.

4. Conclusions

Reaction mechanisms of the non-redox shuttle type overcharge protection agents (BP, CHB, and H-*m*TP) were investigated. A plenty of black precipitates were observed on the surface of the Pt working electrodes after the cyclic sweep voltammetry tests. All these oxidation products were the condensed aromatic compounds with extensive π -electron conjugated systems, where the bond formation between monomers was found to occur mainly at *ortho*-positions of the phenyl groups by MALDI-TOF-MS. BP, CHB, or H-*m*TP reacted with these condensed aromatic compounds at lower oxidation potentials than those of BP, CHB, or H-*m*TP, because the cyclic voltammograms showed the negative shift of the oxidation potentials in the 2nd and 3rd cycles. On the other hand, the oxidation products on the surface of the positive electrode (Li_xCoO_2) after overcharge tests were the similar oligomers having 6–12 benzene rings, and their formation was not dependent on the monomer structure (BP, CHB, or H-*m*TP) and temperature (25 or 60 °C). Long

chain alkanes were observed in TPD-MS analysis, when CHB or H-*m*TP was used at 25 °C. However, there was no long chain alkane at 60 °C. It was considered that the cyclohexane structure in CHB or H-*m*TP was converted to the benzene structure at 60 °C by dehydrogenation after the polymerization.

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