# Overcharge protection effect and reaction mechanism of cyclohexylbenzene for lithium ion batteries

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ABSTRACT

We studied the relationship between the structure of aromatic compounds and the overcharge protection effect, using cyclohexylbenzene, isopropylbenzene, and toluene as the overcharge protection agents. Cyclohexylbenzene proved to be the most effective overcharge protection agent among these aromatic compounds. The effect is enhanced using a higher concentration of cyclohexylbenzene and elevated temperatures. The reaction product of cyclohexylbenzene was analyzed using field desorption mass spectrometry to elucidate its reaction mechanism. The results suggested that some of the overcharge reaction products of CHB were more reactive than that of IPB, which is consistent with the better suppressing effect on overcharging of the active material in the positive electrode.

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## 1. Introduction

Lithium ion batteries (LIBs) are widely used in portable devices such as cellular phones and laptop computers because of their high energy density. The large LIBs for various kinds of industrial applications have recently attracted a lot of attention and their development is ongoing [1,2]. A LIB is comprised of a positive electrode such as $LiCoO_2$, $LiNi_{1-x-y}Mn_xCo_yO_2$ and $LiMn_2O_4$, a graphite negative electrode, and an electrolytic solution. The electrolytic solution for a LIB consists of a lithium salt and organic solvents, such as ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC). These organic solvents are flammable, for example, DMC spontaneously combusts above 465 °C. Under abuse conditions, such as for an overcharge, a LIB tends to burn under higher temperatures [3,4].

There are two strategies for protecting batteries from overcharging. One is to use external protection devices such as a positive temperature coefficient (PTC) element and an overcharge protecting circuit, and the other is to add something to the electrolytic solution such as a redox shuttle [5–7] and an overcharge protection agent (OPA) [8–12]. The redox shuttle additives are oxidized at the positive electrode when the positive electrode is overcharged to higher potentials. However, the diffusion rate of the oxidized

agent from the positive electrode to the negative electrode is not fast enough to protect from an overcharge except under low-rate charge conditions. An OPA, on the other hand, does not have the same recovery reactions as the redox shuttles, but reacts simply in one way. OPA, such as cyclohexylbenzene (CHB) and biphenyl (BP), is already used in commercial LIB [11].

Since an OPA does not react under the normal potential of the positive electrode but reacts under the overcharge potentials, the oxidation potential and the reaction rate for the OPA are the key parameters for evaluating their availability. But the reason why and the mechanism of why the OPA are effective have yet to be sufficiently elucidated [9,10]. As for the reaction rate, the OPA should react quickly to prevent positive electrodes from being overcharged by consuming an overcharge current during its oxidation. Shima et al. used matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) to analyze the reaction products [10]. However, MALDI-MS is intensively influenced by lithium salt, and the results were insufficient for presenting decisive data. Thus, the relationship between the overcharge protection effect and the chemical structure of the OPA has not been completely elucidated yet.

We studied the overcharge protection reaction of several aromatic compounds for this paper and chose CHB as the best one among them. Then, we studied the OPA effects of CHB as a function of the concentration or temperatures. We also attempted to elucidate the relationship between the functional groups of the aromatic compounds and their overcharge protection effect.

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## 2. Experimental

Three of the aromatic compounds, toluene (TOL), isopropylbenzene (IPB) and cyclohexylbenzene (CHB), were treated with molecular sieves 3A, and they were found to have a water content less than 10 ppm using Karl Fischer titration, and also showed no impurity signals when tested using $^1$H NMR. A 1.0 M LiPF$_6$ electrolytic solution with mixed solvents of EC/DMC/EMC at a 1/1/1 volume ratio, was used as a base solution, and TOL, IPB, or CHB were added to it at a content rate up to 4 wt%. A TOMCELL TJ-AC (TOMCELL JAPAN) was used as the testing cell. The cell contained a Li metal negative electrode, a micro porous polyolefin separator, and a positive electrode. The positive electrode active material was LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$, which is one of the most popular positive electrode materials and was used in some previous papers to study redox shuttle additives as the OPA [6,7]. The positive electrode consisted of the active material, a carbon conductive material and a polyvinylidene difluoride (PVDF) binder. They were mixed into a slurry using N-methylpyrrolidone (NMP) solvent and coated on a aluminum substrate to form a thin coated layer followed by drying, pressing, and cutting into the prescribed dimensions.

The capacity of the cell was 2.4 mAh based on the charge/discharge of between 3.0 V and 4.3 V at 0.8 mA. The state of charge (SOC) for the cell was defined according to this capacity. Overcharge tests were conducted at a 4.8 mA (2CA) constant current from 100 to 200% SOC. The open circuit voltages (OCV) of the TOMCELL after overcharging were defined by those after 12 h rest at 25 °C. The purpose to measure OCV is to quantify the degree of overcharge suppression. Namely, a good OPA reduces overcharge reactions effectively and suppresses the OCV after charging definitely.

In order to separate the electrochemical reactions of the electrolytic solutions itself from that of the positive electrode active materials, we also applied linear sweep voltammetry with a platinum wire working electrode along with a counter and a reference electrode of lithium metal. The sweep range was 3.5–6.3 V vs. Li/Li$^+$ with 5 mV s$^{-1}$ sweep rate.

FT-IR spectroscopy (VARIAN 3100) and field desorption mass spectrometry (FD-MS, JEOL JMS-700) were used to analyze the overcharge reaction product of CHB prepared in the TOMCELL by overcharging up to 200% SOC in the same way as described above. The measurement range for FT-IR was from 4000 to 680 cm$^{-1}$. As for FD-MS, the CHB reaction product deposited around the positive electrode was washed with chloroform, methanol and ion-exchanged water, and transferred to the tungsten electrode, then, an ionization voltage as high as 8 kV was applied to the electrode under a vacuum. The measurement range of $m/z$ was from 10 to 2000.

## 3. Results and discussion

### 3.1. Overcharge protection effect

Fig. 1 shows the $Q$–$E$ curves for the overcharge test at 25 °C containing 2 wt% of OPA. Table 1 lists the chemical structure of the OPA and a summary of the overcharge test results. In the no additive cell of Fig. 1, there are two voltage plateaus at 5.8 V and 5.1 V. Fig. 2 shows the liner sweep voltammetry of the electrolytic solution using platinum working electrode. The oxidation current increased above 5.8 V drastically, which is consistent with the plateau at 5.8 V of the no additive curve in Fig. 1. However, there is no abrupt current increase around 5.1 V in Fig. 2, while there is a voltage plateau at 5.1 V in Fig. 1. This inconsistency suggests that the reaction at 5.1 V in Fig. 1 is caused not by the electrolytic solution but by the positive electrode. Presumably, the reaction is related to the over-
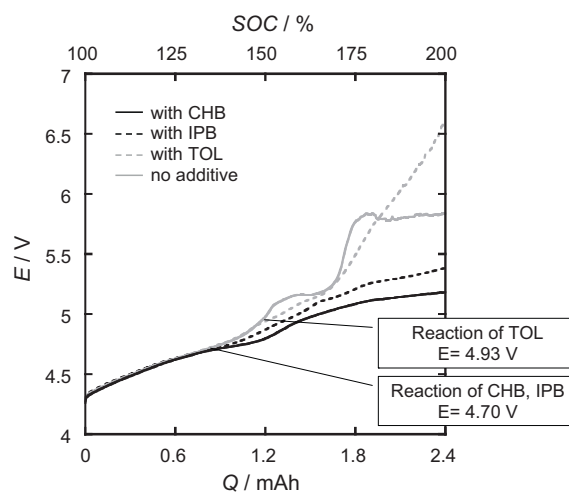


**Fig. 1.** $Q$–$E$ curves in overcharge test.

charge reaction of the active material or insertion reaction of PF$_6^-$ into the conductive material carbon. In Fig. 1, the voltages of all the cells increased with the increase of the SOC, but the shape of the $Q$–$E$ curves were different in the higher SOC region over 140%. The voltage increase of the "with IPB" and "with CHB" cells began to be suppressed at 4.70 V compared with that with no additive cell, and the voltage increase for "with TOL" also began to be suppressed at 4.93 V. This suppression implied that the electric current supplied by an external power source is consumed by overcharge reactions of the positive electrode active material under lower cell voltages. However, the OPA consumes the current instead of the active material under higher cell voltages, suppressing the overcharging of the material. This is the very mechanism and effect of the OPA, which we may call a dummy active material or overcharge retardant.

The difference in the cell voltages among the OPA can be understood as follows. The electrochemical oxidation of these three aromatic compounds seems to occur at the relevant voltages discussed above, and the oxidation voltages of the aromatic compounds are influenced by the substituent group of the benzene ring. TOL contains a substituent of a methyl group. The carbon atom of a methyl group has only one chemical bond with another carbon atom, and is called as a primary carbon, while the carbon atoms bonding with the benzene ring of IPB and CHB are called ternary carbons, as indicated in Table 1. The π electron density of the benzene ring in the aromatic compounds is dependent on its substituent groups. Methyl and methylene groups are electron-donating groups, and the electron donating force of the alkyl groups
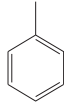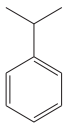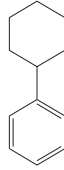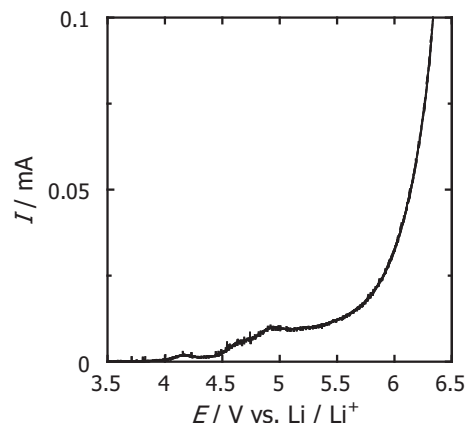


**Fig. 2.** Liner sweep voltammetry of the electrolytic solution.

**Table 1**
Chemical structure of aromatic compounds and results of overcharge test.

| Chemical structure | | | | No additive |
|---|---|---|---|---|
| Abbreviation of aromatic compound | TOL | IPB | CHB | – |
| Class of central carbon of substituent group | Primary | Ternary | Ternary | – |
| Oxidation voltage/V | 4.93 | 4.70 | 4.70 | – |
| OCV of positive electrode after overcharge test/V vs. Li/Li$^+$ | 4.51 | 4.45 | 4.34 | 4.65 |

increases with the class of the carbon atoms, called as either primary, secondary, or tertiary, bonding to the benzene ring. The electrochemical oxidation of the aromatic compounds is initiated by pulling the $\pi$ electron out of the ring. Thus, similar $\pi$ electron densities of the benzene rings of CHB and IPB cause their oxidation voltages to be equal as shown in Fig. 1. Similarly, the $\pi$ electron density of TOL is lower than those of CHB and IPB, and the oxidation voltage of TOL is higher than those of CHB and IPB, as shown in Fig. 1 and Table 1.

Table 1 also lists the open circuit voltages (OCV) after the overcharge tests. The OCV of the no additive cell was 4.65 V vs. Li/Li$^+$, which is the highest voltage in the table. In other words, the addition of TOL, IPB, or CHB suppressed the overcharging. TOL had the highest OCV after the overcharge test among the aromatic compounds. It must be oxidized in the latter stage of the overcharge because of its high oxidation voltage. Although the oxidation voltage of IPB and CHB is the same, the OCV of CHB is lower than that of IPB. The OCV after overcharging is an equilibrium voltage and can be used as an indication to show the degree of overcharging for the active material of the positive electrode. Therefore, the OCV values listed in Table 1 seem to suggest that the reaction rate of CHB is faster than that of IPB, which means CHB suppresses the positive electrode reaction better than IPB; CHB is the best OPA among these aromatic compounds.

### 3.2. Overcharge protection by CHB

#### 3.2.1. Effect of concentration

Since CHB proved to be the best OPA as described above, we studied its OPA effect in more detail as a function of the concentration and the temperature.

Fig. 3 shows the $Q$–$E$ curves of the cells with different CHB concentrations. The cells of 2 and 4 wt% started to suppress the voltage increase at 4.7 V, which indicated that CHB began to react at this voltage. However, a 1 wt% cell did not show this phenomenon, and followed the voltage profile of the 0 wt% cell up to 5.15 V. The traces of the $Q$–$E$ curves above 4.7 V for 2 and 4 wt% were different. Fig. 4 shows the relationship between the CHB concentration and the OCV after overcharging. Although the voltages rose in rather complicated traces as shown in Fig. 3, the overcharge protection effect was explicitly and monotonously enhanced with the concentration of CHB. The 1 wt% cell showed a lower OCV than the no additive cell, which implies that it has an overcharge protection effect, even though the cell did not reveal an explicit CHB reaction at 4.7 V, as shown in Fig. 3.

#### 3.2.2. Effect of overcharge temperatures

Fig. 5 shows the $Q$–$E$ curves at different temperatures, 25, 60, and 80 °C, when containing a 2 wt% CHB. The $Q$–$E$ curves at higher temperatures showed significantly lower voltages than that at 25 °C. There is a large voltage jump between 25 °C and 60 °C, while the voltage difference between 60 °C and 80 °C is very small. Two rea-
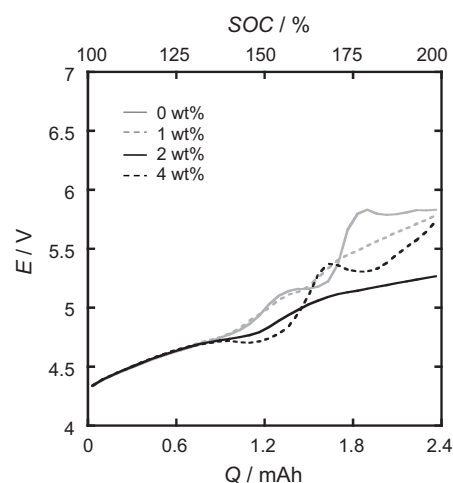


**Fig. 3.** $Q$–$E$ curves with different CHB concentrations.

sons are supposed for these lowered voltages at high temperatures. One is the decrease in internal resistance particularly that for the electrolytic solution due to the rise in temperature, the other is the superiority of the overcharge protection reactions on the positive electrode charging reaction because of the enhanced reactivity of CHB at high temperatures. Besides, the gap between the first and the second step at around 150% SOC, which appeared at 25 °C clearly, also reduced drastically at higher temperatures. The reason why the gap became minimized is supposed to be caused by the considerable decrease of the whole resistance of the test cell system at elevated temperatures. Fig. 6 shows the relationship between the overcharge temperature and the OCV. The OCV lowered as the tem-
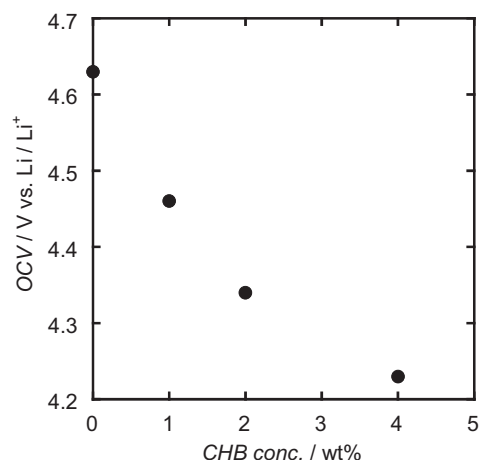


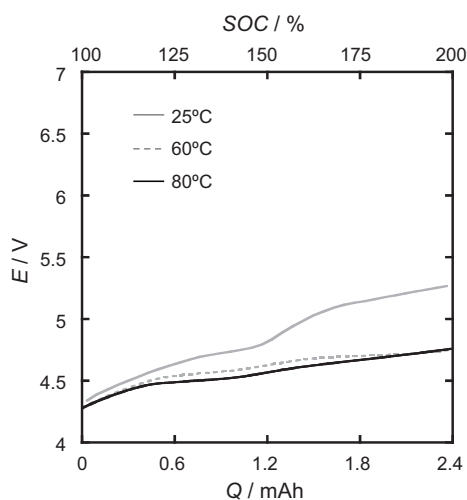**Fig. 4.** CHB concentration and OCV after overcharge test.

**Fig. 5.** Q–E curves at different temperatures (2 wt% CHB).



**Fig. 7.** Microscopic FT-IR spectrum of reaction product of CHB produced by the overcharge test using the electrolytic solution containing 2 wt% CHB.



**Fig. 8.** FD-MS spectrum of reaction product of CHB produced by the overcharge test using the electrolytic solution containing 2 wt% CHB.

perature increased, implying an enhanced reactivity of the CHB. The difference in OCV between 60 °C and 80 °C is very small the same as that for Q–E curves in Fig. 5. These two results imply that higher cell temperatures, which is usual in overcharging, are favorable for the overcharge protection effect by CHB. On the other hands, increased temperatures may also accelerate other electrochemical reactions such as the oxidation of the electrolytic solution and the overcharge reaction of the positive electrode active materials which are not advantageous for the OPA effect. We should clarify the temperature dependence of these reactions and select the best temperature to be controlled. Therefore, the thermal management of the battery will be an essential technology for using CHB in practical batteries.

### 3.3. Reaction mechanism of OPA and overcharge protection effect

The CHB reaction product was analyzed to elucidate the reaction mechanism. The electrolytic solution for the overcharge test contained 2 wt% CHB. The reaction product was a black precipitate deposited around the positive electrode. It was washed for three times with three different solvents. They were chloroform, methanol and ion-exchanged water, and were used in this order separately to make them free from lithium salts without losing the reaction product so that they would not interfere in the following measurements. Fig. 7 is a microscopic FT-IR spectrum of the CHB reaction product. The signals at 1807 cm$^{-1}$ (C=O stretch-
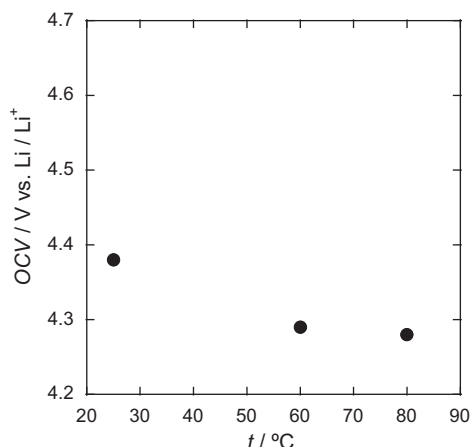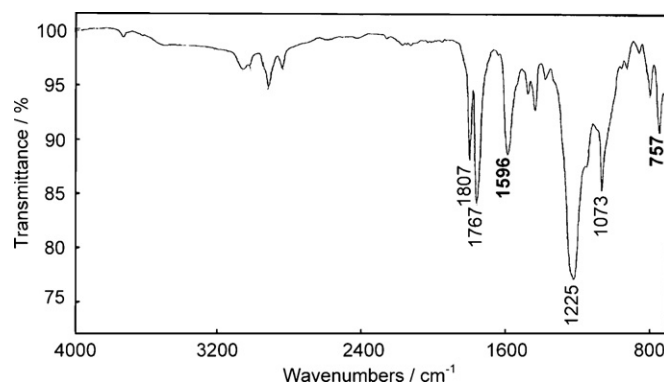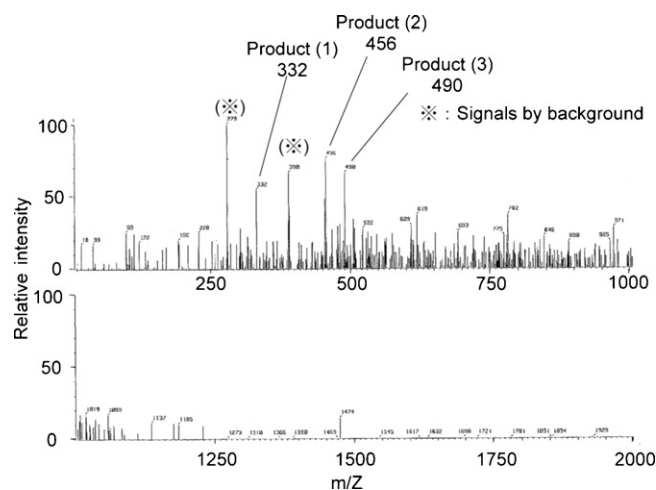
ing), 1767 cm$^{-1}$ (C=O stretching), 1225 cm$^{-1}$ (C–O–C stretching) and 1073 cm$^{-1}$ (C–O stretching) are the typical absorption lines of the carbonate compounds contained in the electrolytic solution. However, the LiPF$_6$ signals at 1018 cm$^{-1}$ (P–F stretching) and the decomposed product of it, POF$_3$, at 989 cm$^{-1}$ (P–F asymmetric stretching) were not observed [13]. The absorption lines at 1596 cm$^{-1}$ (C=C stretching) and 757 cm$^{-1}$ (C–H angle bending) are typical of aromatic compounds. Therefore, the product proved to have an aromatic structure as its component.

The reaction product was further analyzed using field desorption mass spectrometry (FD-MS). Fig. 8 presents the results, and three principal signals (m/z = 332, 456, and 490) were observed in it.
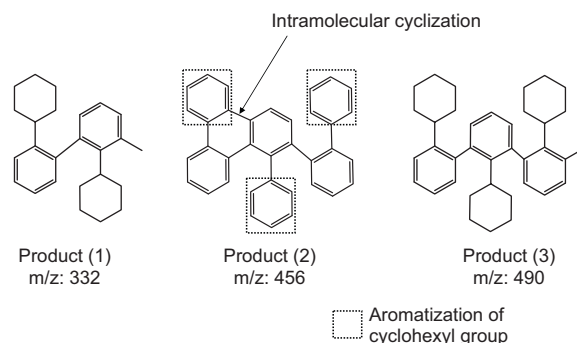


**Fig. 6.** Temperature dependency of OCV after overcharge test (2 wt% CHB).



**Fig. 9.** Chemical structure presumed for principal signals in FD-MS spectrum.

**Table 2**
Intermediates and their properties.

| | CHB | IPB |
|---|---|---|
| Unit structure of Reaction (3) reactant | | |
| Side chain | Phenyl | 2-Propenyl |
| Electronic property of side chain | Electron donative | Electron withdrawing |
| Oxidation potential | Low | High |
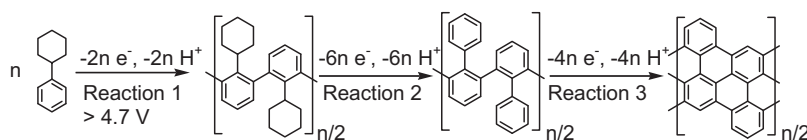


**Fig. 10.** CHB reaction mechanism.
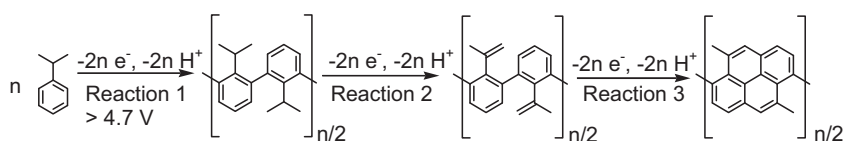


**Fig. 11.** IPB reaction mechanism.

Product 1 seems to correspond to a dimer and Product 3 to a trimer of CHB which has a molecular weight of 160. These products must be formed simply by way of the electrochemical polymerization of CHB. However, Product 2 should not be a simple origomerization product of CHB, but a product formed by the polymerization and dehydrogenation of the cyclohexyl groups into phenyl groups accompanying an intramolecular cyclization because of its lower $m/z$ than that for three times of CHB. According to this discussion, we propose the molecular structures for these three products. Fig. 9 shows the presumable products that can be formed as the overcharge products of CHB and can meet the principal signals of the FD-MS spectrum.

Fig. 10 is the proposed reaction mechanism of CHB, based on the results and discussion from Figs. 7–9. Reaction (1) is an oxidative polymerization of CHB molecules by dehydrogenation, and it is the reaction between two CHB molecules although the polymerization must occur simultaneously among the CHB molecules in order to form an oligomer or a polymer. Thus, a fragment of the product will cause the signals for products 1 and 3 shown in Fig. 8. Reaction (2) is a process for producing the biphenyl groups through the electrochemical dehydrogenation of the cyclohexyl groups. Reaction (3) is an intramolecular cyclization between the biphenyl groups. Thus, similarly, a fragment of the product from Reaction (3) will create the signal of Product 2 in Fig. 8. The formation point of Product 2 in Fig. 1 is not clear yet. We should elaborate quantitative and stepwise experiments so as to elucidate the complete scheme of the overcharge reaction of CHB.

Fig. 11 is the presumed reaction mechanism of IPB from the analogy with that for CHB shown in Fig. 10. Both Reactions (1) and (2) for IPB and CHB are supposed to be similar. Reaction (1) for IPB is an oxidative polymerization, and Reaction (2) for IPB is an electrochemical dehydrogenation. Therefore, their reaction rates are expected to be similar to those for CHB. However, Reaction (3) for CHB and that for IPB seem to differ. Table 2 lists the comparison between the intermediates of CHB and IPB. The reactant of Reaction (3) for CHB is polyphenylene with phenyl groups as the side chain. On the other hand, the reactant of Reaction (3) for IPB is polyphenylene with 2-propenyl groups as the side chain. Phenyl groups are electron-donating groups, while the 2-propenyl groups are electron-withdrawing groups. The electrochemical oxidation of aromatic compounds with a high density of π electrons occurs at lower potentials, and therefore, the reactant for Reaction (3) of CHB is oxidized more easily than that of IPB. The difference in the overcharge protection effect between CHB and IPB seems to be caused by the difference in the reaction rates of Reaction (3) in Figs. 10 and 11.

## 4. Conclusion

We compared the overcharge protection agent (OPA) performances of cyclohexylbenzene (CHB), isopropyl benzene (IPB), and toluene (TOL). CHB proved to be the most effective OPA among these three aromatic compounds. We also studied the relationship between the CHB concentration and the overcharge protection effect, and also that between the temperatures and the effect. It proved that the overcharge protection was enhanced at a higher concentration or temperatures. The CHB reaction product was analyzed using FD-MS to elucidate the CHB reaction mechanism. The overcharge reaction products of CHB seemed to be more reactive than that of IPB, which is consistent with the better suppressing effect on overcharging of the active material in the positive electrode.

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