Short communication

Application of cyclohexyl benzene as electrolyte additive for overcharge protection of lithium ion battery

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ABSTRACT

The electrochemical characterization and overcharge protection mechanism of cyclohexyl benzene as an additive in electrolyte for lithium ion battery was studied by microelectrode cyclic voltammetry, Galvanostatic charge–discharge measurements and SEM observation on both the cathode and separator of the overcharged cells. It was found that when the battery is overcharged, cyclohexyl benzene electrochemically polymerized to form polymer between separator and cathode at the potentials lower than that for electrolyte decomposition. The polymer blocks the overcharging process of the battery. The additive causes a small capacity loss and impedance increase in a real cell, but that can be mitigated if the operating voltage is much lower than the polymerization voltage.

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1. Introduction

Due to the high energy density, high discharge voltage, long cycle life, lithium ion batteries become more and more popular as a power source for advanced portable electronics [1,2]. A typical lithium ion battery system consists of a graphite anode, a cathode of transition metal oxide (such as $LiMn_2O_4$, $LiCoO_2$, $LiNiO_2$, etc.) and non-aqueous organic electrolyte, which acts as an ionic path between electrodes and separates them. The electrolytes used in commercial lithium ion batteries are prepared by dissolving $LiPF_6$ into binary or ternary solvents, which are of the mixtures of linear carbonates, including dimethyl carbonate (DMC), ethyl (methyl) carbonate (EMC) and diethyl carbonate (DEC), with cyclic carbonate ethylene carbonate (EC). It is well known that these organic solvents used for lithium ion battery electrolytes are flammable in ambient temperature [3]. If the battery is abused, a number of highly exothermic reactions of electrolyte decomposition may take place, accompanied by the decomposition of the cathode material and gas evolution, this certainly causes potential danger to society, especially in the application of large-scale lithium ion batteries [4].

The major abuse of the batteries is being overcharged. To prevent overcharge, commercial lithium ion batteries are equipped

with external protection devices, such as positive temperature coefficient (PCT) resistors or integrated circuits (ICs). However, both remedies add to the manufacturing cost and lead to a lower cell energy density. Most importantly, the safety of the external protection depends on the reliability of the electronic devices.

Therefore, it is essential to develop an internal overcharge protection for lithium ion batteries. Up to now, various internal methods of overcharge protective mechanisms have been developed for lithium ion batteries [5–7]. Redox shuttle additives were first reported to operate as a shuttle between the cathode and anode to shut charge currents [8–10]. However, few have been found to work effectively [11], because the additives reported so far are poorly soluble in the organic electrolyte, or their redox potentials are not appropriate for practical application (below 4.2 V), therefore they fail to operate effectively even at normal charge rates. In addition, most of these additives cause a severe capacity loss and self-discharge of the batteries. Another kind of additives for overcharge protection are polymerizable compounds, also called "shutdown additives", which can be electrochemically polymerized at an overcharged cathode. They are believed to be effective because the polymerization reaction can reduce the charging current and thus protect the batteries from hazardous explosion. For most commercial lithium ion batteries, the charge-cutoff potential reaches as high as 4.2 V and the oxidative decomposition of the electrolyte appears to be at about 5 V. Therefore, to avoid the decomposition of electrolyte,

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the overcharging protection additives should be polymerized at the potential region right above 4.2 V and below 5 V. If the kinetic effect is considered, the electro-oxidative polymerization of the additives should proceed at a sufficiently high rate to provide effective barrier to prevent cathodic materials and electrolyte from decomposition. On the other hand, the additives must have little negative effects on normal charge–discharge performance. The majorities of such additives belong to the aromatic compounds, such as biphenyl [5,12–15], xylene [16], cyclochexyl benzene [17,18]. The working mechanisms of biphenyl and xylene for the overcharging protection and their influences on the performance of lithium ion batteries have been reported in the literatures [5,12–16]. However, little knowledge about the working mechanism of cyclochexyl benzene and its effect on battery performance is available.

In this work, the electrochemical behavior of cyclohexyl benzene (CHB) and its effect on battery performance were studied.

2. Experimental

Carbonate solvents, EC, DMC and EMC, were purified by distilling and soaked in 4 Å molecular sieves till the purity was higher than 99.95% (GC-14C, SHIMADZU). The electrolytes were prepared by dissolving $1 \, mol \, L^{-1}$ $LiPF_6$ (Stella Chemical, Japan) in 1:1:1 mixture (by weight ratio) of EC, DMC and EMC. The preparation of the electrolyte was carried out in a dry glove box (Mikrouna, $H_2O < 1$ ppm) filled with high purity argon. Water and free acid (HF) contents in the electrolyte were controlled to be less than 20 ppm, determined by Karl–Fisher 831 Coulometer (Metrohm) and Karl–Fisher 798 GPT Titrino (Metrohm).

The electrochemical behaviors of cyclohexyl benzene (Fujian Chuangxin Science and Technology Develops Co. Ltd, China) were examined by cyclic voltammetry (CV) on Pt microelectrode and $LiMn_2O_4$ powder microelectrode. The Pt microelectrode was made directly by sealing a Pt (wt% > 99.9%) wire of 100 μm diameter in a glass tube. The $LiMn_2O_4$ powder microelectrode was prepared by corroding Pt microelectrode in acid, and then filled the $LiMn_2O_4$ powders (Hunan Reshine New Material Co. Ltd, China) into the microcravity [19,20]. The cyclic voltammetric measurements were carried out in a three-electrode cell on a Solartron 1480 potentiostat (England), with a large lithium sheet served as both counter electrode and reference electrode.

2016 coin cells were set up to determine the charge–discharge behavior and the cells were composed of two electrodes with $LiMn_2O_4$ as positive electrode and lithium foil as negative electrode. The coin cells were charged and discharged at 1/3 C rate in the potential range of 3.6–4.2 V, and then overcharged to 5.5 V at 2/3 C rate.

063048-size batteries were fabricated to determine electrochemical performance of batteries with and without CHB. The charge–discharge performances of the lithium ion batteries were tested by using BS-9300R type battery charger (Guangzhou, China). The batteries were charged to 4.2 V at a constant current of 1 C rate, followed by a constant potential of 4.2 V until the current reached C/20, and then discharge to 3.0 V at a constant current of 1 C rate. To evaluate overcharge performance of CHB, the batteries were charged to 4.2 V at a constant current of 1 C rate, followed by a constant potential of 4.2 V until the current reached C/20, and then overcharged at a constant current of 2 C for about 35 min.

The morphological changes on both $LiMn_2O_4$ electrodes and separators after overcharged were examined by scanning electron microscope (JEOL, Hitachi).
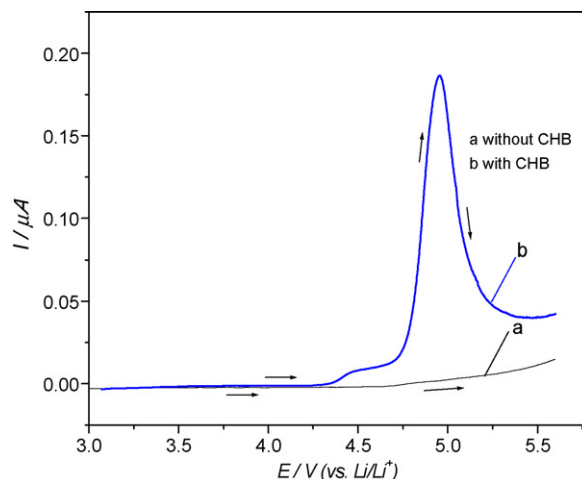

Fig. 1. Linear sweep voltammograms of Pt microelectrde in $1 \, mol \, L^{-1}$ $LiPF_6$/EC–EMC–DMC (1:1:1 by weight) without (a) and with (b) 5 wt% CHB additive, scan rate of $10 \, mV \, s^{-1}$.

3. Results and discussion

### 3.1. Electrochemical behavior of cyclohexyl benzene on Pt electrode

Fig. 1 shows the linear sweep curves of Pt microelectrodes in $1 \, mol \, L^{-1}$ $LiPF_6$/EC–EMC–DMC (1:1:1 by weight) without (a) and with (b) 5 wt% CHB additive at a scan rate of $10 \, mV \, s^{-1}$. In the electrolyte without CHB, oxidation current appears when the potential is swept to 4.7 V, which is attributed to the oxidation of electrolyte on Pt electrode. Different curve can be obtained in the electrolyte with CHB. Small oxidation current appears at 4.3 V and the oxidation current increase quickly as the potential becomes more positive, reaching a maximum at 4.9 V. The small oxidation current can be ascribed to the electro-oxidation of the adsorbed CHB on the Pt electrode, and the large current can be ascribed to the oxidation of CHB in the electrolyte, which is controlled by diffusion. It is obvious that cyclohexyl benzene has suitable polymerization potential as overcharge protection additive.

3.2. Electrochemical behavior of cyclohexyl benzene on $LiMn_2O_4$ powder microelectrode

Fig. 2 presents the cyclic voltammograms of $LiMn_2O_4$ powder microelectrode in $1 \, mol \, L^{-1}$ $LiPF_6$/EC–EMC–DMC (1:1:1 by weight) without (a) and with (b) 5% CHB. It can be seen from Fig. 2 that the intercalation and de-intercalation of lithium ion in $LiMn_2O_4$ electrode take place at the potentials between 3.75 and 4.25 V [21]. Comparing the curves a and b of Fig. 2, it can be found that the oxidation peak for the electro-polymerization of CHB on $LiMn_2O_4$ electrode appears at about 4.8 V. When the scan is reversed, no reduction peak according to the reduction of polymerized product can be found and the cathodic peak current related to lithium ion intercalation into $LiMn_2O_4$ electrode is significantly decreased. This indicates that the electro-polymerization of CHB blocks the electrode process on $LiMn_2O_4$ electrode.
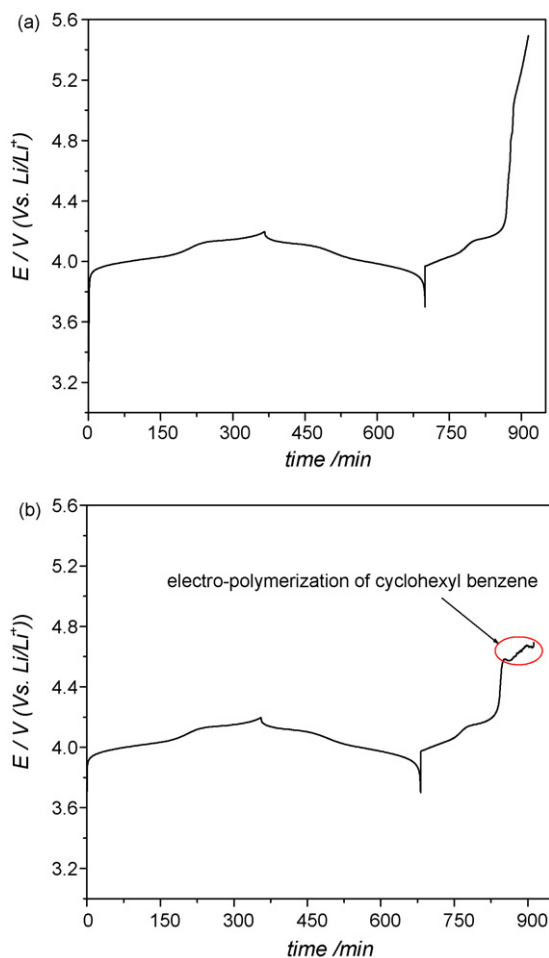
3.3. Effects of cyclohexyl benzene on overcharged $Li/LiMn_2O_4$ cells

Galvanostatic charge–discharge tests were carried out to evaluate the effects of CHB on the overcharge behavior of $Li/LiMn_2O_4$ coin cells. The coin cells were firstly cycled at 1/3 C rate in the
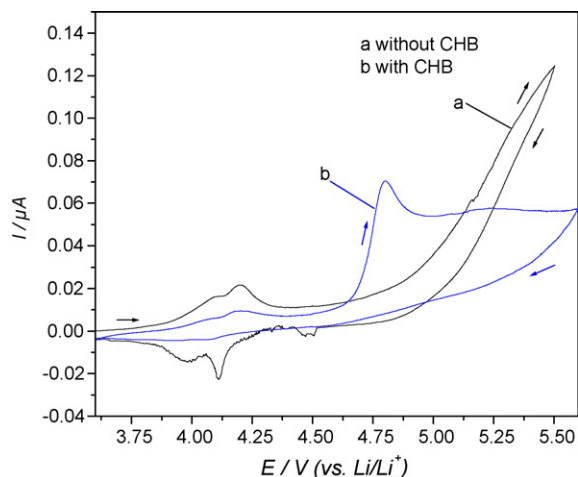
Fig. 2. Cyclic voltammograms of LiMn$_2$O$_4$ powder microelectrode in 1 mol L^{-1} LiPF$_6$/EC–EMC–DMC (1:1:1 by weight) without (a) and with (b) 5% CHB, scan rate of 0.5 mV s^{-1}.

potential range of 3.6–4.2 V at the same rate and followed by over-charging to 5.5 V at 2/3 C rate. The results for the cells with and without CHB are shown in Fig. 3. It can be seen from Fig. 3 that two typical redox platforms relating to de-intercalation/intercalation
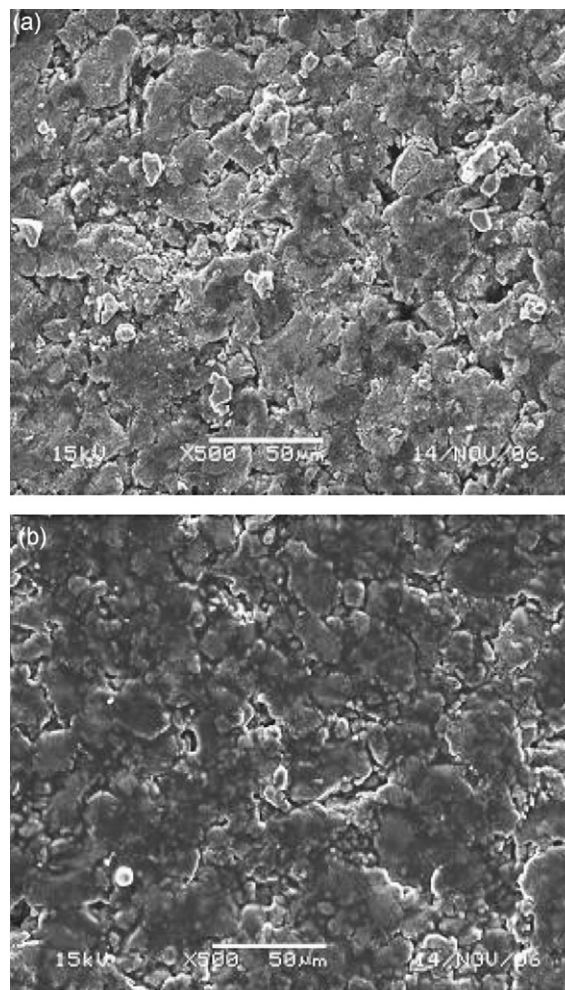
of lithium ions appear in both of the electrolytes with and without CHB during the first normal charge–discharge process, and the initial charge–discharge capacity of the LiMn$_2$O$_4$ electrode in the electrolyte with 5% CHB is 105.4 mAh g^{-1}, which approximates to that of the LiMn$_2$O$_4$ electrode with base electrolyte (111.2 mAh g^{-1}). This indicates that CHB has slightly negative effects on LiMn$_2$O$_4$ electrodes during normal charge–discharge process.

However, different voltage behaviors appear when the cells are overcharged, as seen from Fig. 3. The voltage at overcharged stage of the cell without CHB rises up very quickly to 5.5 V. But for the cell with 5% CHB, a charging voltage plateau at 4.5–4.7 V can be found, which can be ascribed to the electro-polymerization of CHB on LiMn$_2$O$_4$ electrode.

3.4. SEM observation

Fig. 4 presents the SEM images of the LiMn$_2$O$_4$ electrodes from the coin cells after overcharged to 5.5 V. As can be seen from Fig. 4a, the electrode is rough with primary particles ranges from 1 to 20 μm. And some amorphous materials can be detected on the electrode surface, observed as white regions in the SEM image. However, the SEM image of the LiMn$_2$O$_4$ electrode from the over-charged cell in the electrolyte with 5% CHB is very different, as shown in Fig. 4b. The surface of LiMn$_2$O$_4$ electrode is found to be

Fig. 3. V–t curves of Li/LiMn$_2$O$_4$ cells during normal charge–discharge and over-charge. The electrolyte is 1 mol L^{-1} LiPF$_6$/EC–DMC–EMC without (a) and with 5% CHB (b).

Fig. 4. SEM images of the LiMn$_2$O$_4$ electrodes from the coin cells after overcharged with the electrolyte 1 mol L^{-1} LiPF$_6$/EC–DMC–EMC without (a) and with 5% CHB (b).
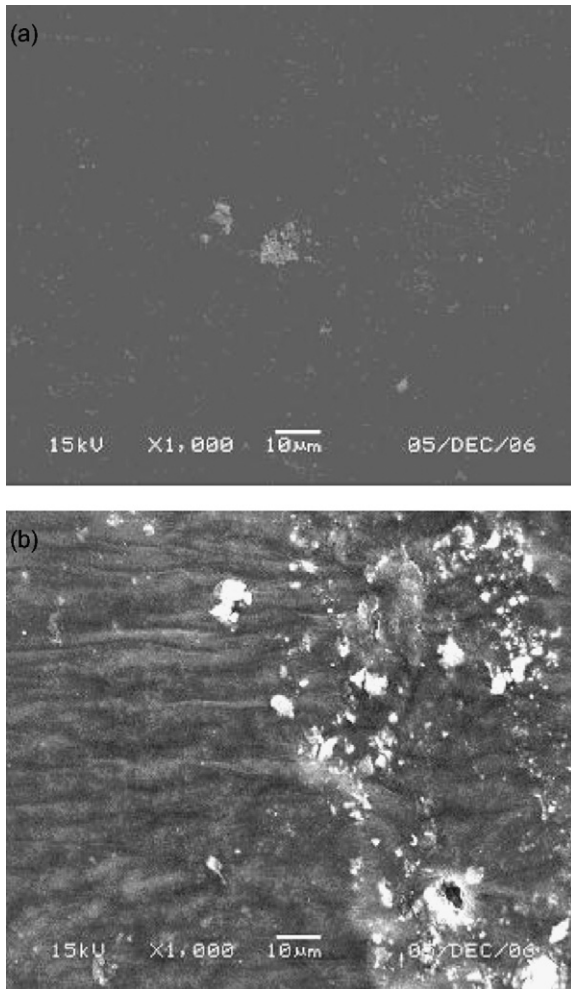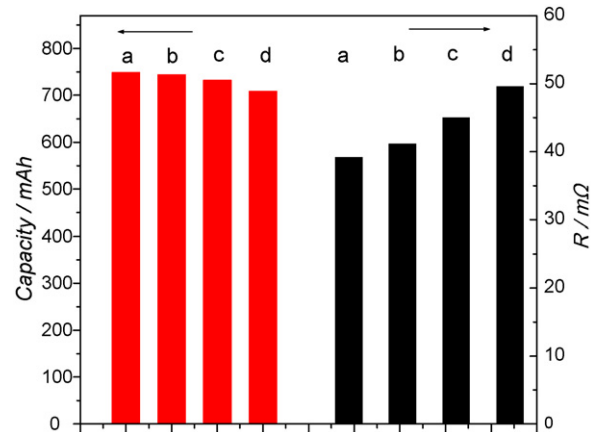
Fig. 5. SEM images of the separators from the coin cells after overcharged with the electrolyte 1 mol L^{-1} LiPF$_6$/EC–DMC–EMC without (a) and with 5% CHB (b).

coated by a thin film of polymer layer. Obviously, this deposited film is ascribed to the polymerization of CHB.

Fig. 5 shows the SEM images of the separators disassembled from the coin cells after overcharged to 5.5 V. It can be seen from Fig. 5a that the surface of the separator is very clear and smooth
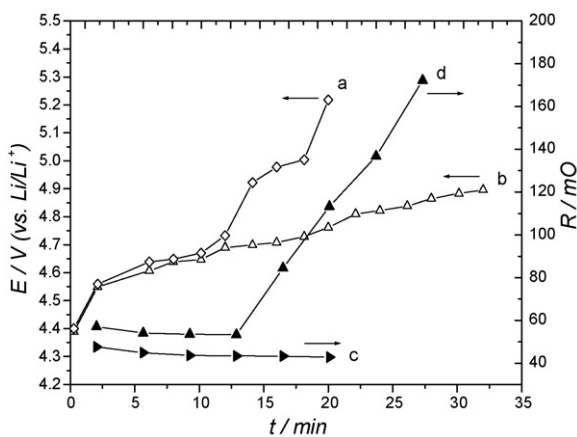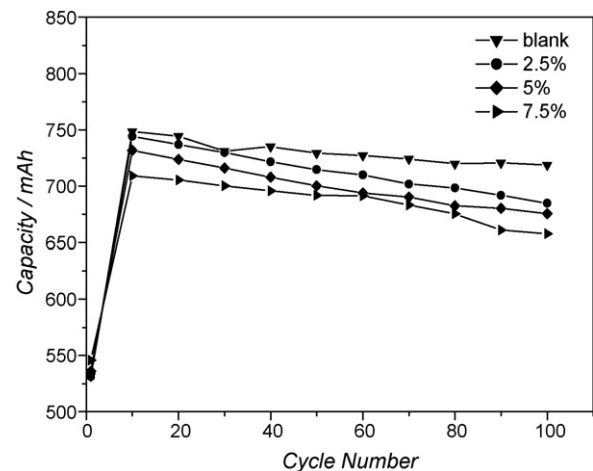

Fig. 7. Influence of CHB on the discharge capacity and internal impedance of batteries, the CHB content in electrolyte is (a) 0 wt%, (b) 2.5 wt%, (c) 5 wt%, and (d) 7.5 wt%.

from the cell without CHB. However, a thin film can be clearly seen on the surface of the separator from the cell with 5% CHB, as seen from Fig. 5b. This indicates that the electro-polymerization product exists not only on the cathode but also on the separator.

3.5. Overcharge tests on lithium ion batteries

Fig. 6 shows the voltage curves and internal impedance curves with the electrolytes 1 mol L^{-1} LiPF$_6$/EC–DMC–EMC without and with 5% CHB at overcharging state. The batteries with and without CHB were charged at a constant current of 1 C rate to 4.2 V, followed by a constant potential of 4.2 V until the current reached C/20, and then overcharged at a constant current of 2 C for about 35 min. It can be seen from Fig. 6a and c that with the increasing of overcharging time, the voltage of the battery without CHB rises up quickly, but the internal impedance of the battery decreases. The decrease of the internal impedance can be ascribed to the increase of conductivity of the materials and the internal temperature of the battery during overcharging state [5]. However, it can be seen from Fig. 6b that voltage of the battery with 5% CHB rises up slowly and is much lower than that of the battery without CHB. Fig. 6d shows that the internal impedance of the battery with 5% CHB is slightly larger than that without CHB at the initial stage of overcharging and increases sharply during the late stage. This indicates that the

Fig. 6. Variation of voltage and internal impedance of the C/LiMn$_2$O$_4$ cells with time during overcharge at 2 C rate with the electrolyte 1 mol L^{-1} LiPF$_6$/EC–DMC–EMC without (a and c) and with 5% CHB (b and d), respectively.

Fig. 8. Effect of CHB on cycling performance of batteries, the CHB content in electrolyte is (a) 0 wt%, (b) 2.5 wt%, (c) 5 wt%, and (d) 7.5 wt%.

electro-polymerization of CHB results in the increase of internal impedance.

3.6. Effects of cyclohexyl benzene on the capacity and internal impedance of lithium ion batteries

Fig. 7 displays the influence of CHB on the discharge capacity and internal impedance of the batteries. It can be seen that the discharge capacities of the batteries decrease slightly with increasing the content of CHB in electrolyte. For instance, the discharge capacity of the battery without CHB is 748.5 mAh and is reduced to 709.1 mAh for the battery with addition of 7.5% CHB. The internal impedance of the battery increases distinctly with increasing CHB. As can be seen from Fig. 7, the internal impedance of the battery without CHB is 39.17 mΩ and increases to 49.61 mΩ for the battery with the addition of 7.5% CHB.

In order to evaluate the influence of CHB on the cycling performance of the batteries, cycling tests were carried out by charging the batteries at a constant current of 1 C rate to 4.2 V, followed by a constant potential of 4.2 V until the current reached C/20, then discharged at constant current of 1 C rate to 3.0 V for each cycle. Fig. 8 shows the obtained results. From Fig. 8, we can see that although the fading rate of capacity increases with increasing CHB in the electrolyte, this increase is not so significant. For instance, the battery without CHB has a capacity loss of 5.7% after 100 cycles, while the battery with 7.5% CHB has a capacity loss of 10.3% after 100 cycles. This suggests that CHB causes a small capacity loss and impedance increase in a real cell, but that can be mitigated if the operating voltage is much lower than the polymerization voltage of CHB.

4. Conclusion

Cyclohexyl benzene can be used as an additive for effective overcharging protection of lithium ion battery. It electro-polmerizes on cathode when the battery is under overcharging, forming a polymer film between the cathode and separator. Its application in the battery reduces the discharge capacity and cycling stability and increases the internal impedance of the battery, but these negative effects can be mitigated if the operating voltage is much lower than the polymerization voltage.

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