

Short communication

Thermal and electrochemical characterization of MCMB/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ using LiBoB as an electrolyte additive

Wenquan Lu^a, Zonghai Chen^a, H. Joachin^b, J. Prakash^b, J. Liu^a, K. Amine^{a,*}

^a Chemical Engineering Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439, United States

^b Chemical & Environmental Engineering Department, Illinois Institute of Technology, 10 W. 33rd Street, Chicago, IL 60616, United States

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Abstract

The gas generation associated with the use of the lithium bis(oxalate)borate—(LiBoB) based electrolyte at the elevated temperature were detected in the pouch cell (MCMB/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ with 10% excess Li), which might prevent the LiBoB usage as a salt. However, the cell capacity retention was improved significantly, from 87 to 96% at elevated temperature, when using LiBoB as an electrolyte additive. The capacity fade during cycling is discussed using dQ/dE , area specific impedance, and frequency response analysis results. Most of the capacity loss in the cell is associated with the rise in the cell impedance. Moreover, results from the differential scanning calorimetry indicate that the thermal stability of the negative electrode with the solid electrolyte interface (SEI) formed by the reduction of the LiBoB additive was greatly improved compared with that obtained from the reduction of LiPF₆-based electrolyte without additive. In this case, the onset temperature of the breakdown of the LiBoB-based SEI is 150 °C which is higher than that of the conventional electrolyte without additive. Furthermore, the total heat generated between 60 and 170 °C is reduced from 213 to 70 J g⁻¹ when using LiBoB as electrolyte additive compared to the one without additive. In addition, the thermal stability of the charged LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ with 10% excess Li was not affected when using LiBoB as an electrolyte additive.

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1. Introduction

Significant efforts have been made in the past to develop alternative salts, such as LiAsF₆, LiClO₄, LiBF₄, LiN(SO₂CF₃)₃, LiC(SO₂CF₃)₃, etc., in order to improve the cycle performance and the thermal stability of lithium-ion batteries [1]. However, none of these salts was able to replace LiPF₆ used in commercial lithium-ion cells presently due to their toxicity, explosive nature, high reactivity with the electrodes or corrosion of the current collector. The LiPF₆ salt itself is also very sensitive to moisture and can easily undergoes thermal decomposition to generate LiF and PF₅ or POF₃ [2]. Furthermore, the passivation film at the negative electrode resulting from the reduction of the LiPF₆ based electrolyte is not stable, and can lead to the cell capacity fade during cycling, especially, at elevated temperatures [3].

Recently, lithium bis(oxalate)borate (LiBoB) has drawn intensive attention since it was reported to be a potential salt for lithium-ion batteries [4–6]. This new salt has the ability of forming a new solid electrolyte interface (SEI) film at the surface of the carbon negative electrode. This film, usually thick, tends to prevent reactions between the electrolyte and electrodes at the interface and thus improves the cell's cycling stability. However, the LiBoB salt is not compatible with positive electrode material used in lithium-ion batteries, even though the salt itself has very good thermal stability compared with LiPF₆. For instance, the accelerating rate calorimetry (ARC) results show that cathode materials, such as LiCoO₂, in LiBoB-based electrolyte generate more heat and have less thermal stability when compared with LiPF₆-based electrolyte [7].

Therefore, it is rational to use LiBoB as an additive in order to stabilize the SEI film on the surface of anode and improve its cycling performance, as proposed by Jow's group and Amine's group [8–10]. Furthermore, Dahn's group has shown that cells having LiBoB as electrolyte exhibit significant improvement in their thermal abuse characteristics [11,12]. In this paper, we

* Corresponding author. Fax: +1 630 972 4451.

E-mail address: amine@cmt.anl.gov (K. Amine).

investigate the effect of LiBoB as an electrolyte additive on the thermal behavior and the cycle/calendar life at 55 °C of the $\text{Li}_{1.1}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{MCMB}$ full cell. Also, we discuss the gas issue of lithium-ion cell when using LiBoB as the only salt in the electrolyte.

2. Experimental

To investigate the gas generation associated with the use of LiBoB electrolyte, we selected a cell configuration on using $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with 10% excess Li (denoted as “NCM”) as the positive electrode, MCMB 10-28 graphite as the negative electrode, Celgard 3501 as a separator, and either 1.2 M LiPF_6 in EC/PC/DMC (1/1/3) or 0.7 M LiBoB in EC/PC/DMC (1/1/3) as electrolytes. Several pouch cells with 40 cm² areas were fabricated in a glove box with two different electrolytes—1.2 M LiPF_6 in EC/PC/DMC (1/1/3) and 0.7 M LiBoB in EC/PC/DMC (1/1/3). These cells were subjected to three formation cycles at a C/10 rate, followed by extensive cycling at a 1 C rate (at 55 °C). At the end of 500 cycles, the pouch cells that showed signs of gassing were taken into the glove box, and the gases were analyzed using an Agilent Technologies’ 6890 gas chromatograph with a 5973 mass selective detector (Wasson ECE instrumentation), which is highly modified GC–MS/TCD system using packed columns for fixed gases and capillary columns for hydrocarbons. This multi-column/multi-detector system uses heart-cutting and column back flushing techniques to separate the interested gases.

To investigate the impact of LiBoB additive on cycling performance, we used MCMB 10-28/NCM cell systems in 1.2 M $\text{LiPF}_6/\text{EC}/\text{PC}/\text{DMC}$ (1/1/3) electrolyte with 0, 1, and 2 wt.% LiBoB as electrolyte additive. The cells were initially cycled between 4.0 and 3.0 V at a 1 C rate at room temperature (25 °C), then at elevated temperature (55 °C). The cells area specific impedances (ASIs) were collected every 10 cycles using 30-s current interrupt. After each 100 cycles, the cells were taken out of the heating oven, and ac impedance measurements were carried out on these cells using the BAS-Zahner IM6 Impedance Analyzer (Zahner Electric) at room temperature. The frequency window was between 1 MHz and 20 mHz, with an amplitude of 5 mV.

To study the impact of LiBoB as an electrolyte additive on the cell thermal behavior, several MCMB 10-28/NCM cells in 1.2 M $\text{LiPF}_6/\text{EC}/\text{PC}/\text{DMC}$ (1/1/3) electrolyte with 0, 1, and 2 wt.% LiBoB as additive were fabricated, subjected to three formation cycles at the C/10 rate, and then charged to 4.3 V. The cells were disassembled in the glove box, and both positive and negative electrode materials were recovered for differential scanning calorimetry (Perkin-Elmer, Pyrix 1) studies. DSC tests were carried out using high-pressure, gold-plated stainless crucibles in the temperature range of 50–375 °C at a scanning rate of 10 °C min⁻¹.

3. Results and discussion

Fig. 1a shows the gas composition from gas chromatography/mass spectrometry (GC–MS) of cells based on MCMB/NCM in

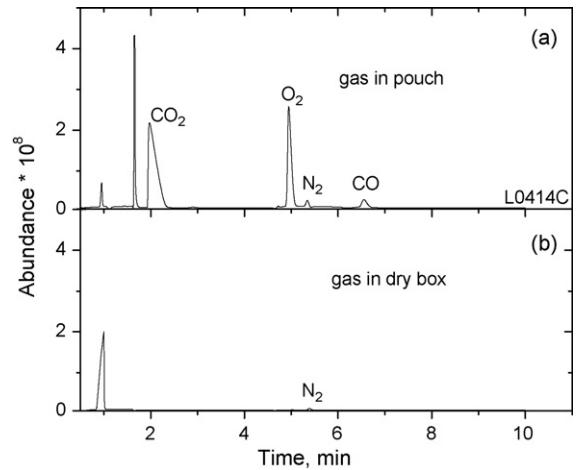


Fig. 1. GC–MS analysis of gas from pouch cell (NCM/MCMB 10-28) after 500 cycles at 55 °C using 0.7 M LiBoB EC/PC/DMC (1/1/3) electrolyte.

0.7 M LiBoB/EC/PC/DMC (1:1:3) after 500 cycles at 55 °C. At the end of the cycling, a volume expansion of the pouch cell was observed, indicating a significant release of gases during cycling. Only GC result is shown in Fig. 1 and a large amount of CO_2 , O_2 , and some CO gases were observed. The hydrocarbon gases peaks – methane, ethylene, propylene, etc. – appear together just before CO_2 peak, because they cannot be separated by the packed columns designed for fixed gases. The issue of gas generation in the lithium-ion battery during formation and cycling is very complicated and difficult to explain. Nevertheless, we believe that these gases likely result from the oxidation of the LiBoB salt and/or the reaction between the oxide and the salt at high voltage and elevated temperatures, since very little gas generation was observed when using LiPF_6 -based electrolyte. It is known that CO and CO_2 can be generated from the thermal decomposition of LiBoB [4,13]. However, this thermal decomposition usually takes place at temperatures higher than 300 °C. CO_2 gas can be generated from the reduction of carbonate solvent at the surface of the negative electrode during the formation process [14]. However, the amount of gases generated during the formation process is too small to account for the large amount of gases observed during cycling in the pouch cell with LiBoB-based electrolyte. Furthermore, a large oxygen-gas peak was also observed using GC–MS. Initially, we thought that the source of oxygen gas could be from the dry box that we used for disassembling the cells and collecting gases. However, GC–MS of gases from the dry box showed no sign of oxygen (see Fig. 1b). The source of oxygen gas could be related to the partial decomposition of the charged oxide at the elevated temperature. Further study is on going to clarify this issue.

Fig. 2a and b shows the voltage profiles and dQ/dE plot of MCMB 10-28/NCM cells in 1.2 M LiPF_6 -based electrolyte having 0, 1 and 2 wt.% LiBoB as additive during the formation process. The voltage plateaus in Fig. 2a and corresponding dQ/dE peaks in Fig. 2b are observed at around 2.0 V, indicating SEI film formation due to the reduction of LiBoB additive at the surface of the carbon negative electrode. Both the length of the plateau observed from the voltage curve and the peak intensity

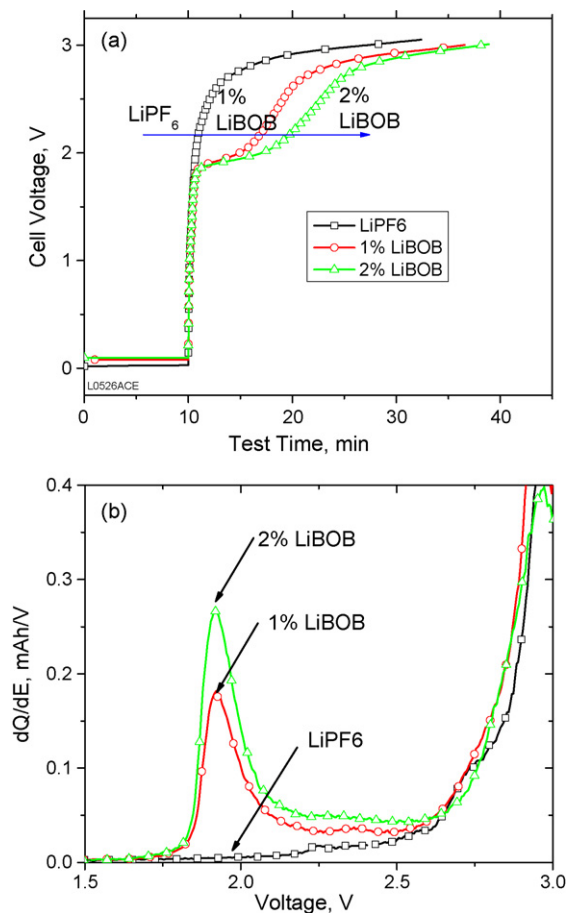


Fig. 2. (a) Voltage profiles and (b) dQ/dE plot of NCM/MCMB 10-28 in 1.2 M LiPF₆ EC/PC/DMC (1/1/3) electrolyte with 0, 1, and 2 wt.% LiBoB during first formation cycle.

observed from the dQ/dE increase with increasing concentration of the LiBoB additive. This result indicates that the thickness of the SEI film formed at the negative electrode depends on the concentration of LiBoB additive used in the electrolyte. The advantage of having a thick SEI film is its ability to provide better protection against electrode/electrolyte reactivity at the interface, resulting in better cyclability even at high temperature. However, the LiBoB reduction on the surface of the anode will cease when the SEI film is thick enough to prevent further reduction [10].

Fig. 3a and b shows the normalized capacity retention and the area specific impedance as a function of cycle numbers of MCMB10-28/NCM cells having LiPF₆-based electrolyte, with or without LiBoB additive. All of the cells were tested at a 1 C rate for 60 cycles at room temperature and then continued cycling at 55 °C. At room temperature, the cells cycle very well with no capacity fade (Fig. 3a). However, the cells with LiBoB additives show much better capacity retention after extensive cycling when the cycling temperature is raised to 55 °C. In this case, the cycling performance of cells with 1 wt.% LiBoB is similar to that with 2 wt.%, indicating that the optimal amount of LiBoB additive in the electrolyte should be (at most) 1 wt.%.

Fig. 3b shows that the cell ASIs are 18, 25, and 30 $\Omega \text{ cm}^2$ for cells in LiPF₆-based electrolyte with 0, 1, and 2 wt.% LiBoB,

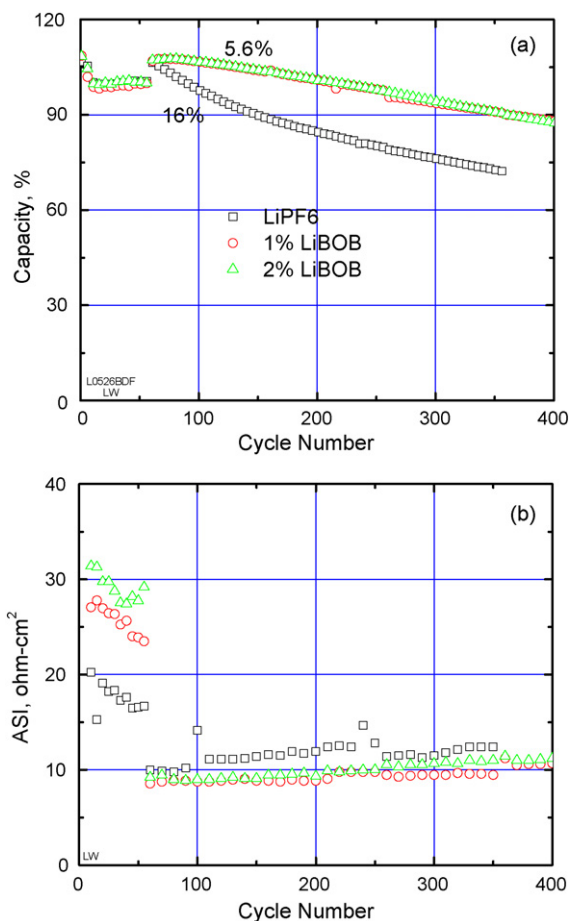


Fig. 3. (a) Capacity retention and (b) ASI plots of MCMB 10-28/NCM cells at 55 °C in 1.2 M LiPF₆ EC/PC/DMC (1/1/3) electrolyte with 0, 1, and 2 wt.% LiBoB.

respectively, at room temperature. Obviously, the impedance increase is caused by the increased thickness of SEI films on the anode electrode when more LiBoB is added to the electrolyte system. However, the cells initial ASIs were very similar when cycling at high temperature, regardless of whether additives were used. The ASI value includes contact resistance, charge resistance, and part of the diffusion resistance (when 30-s current interruption was applied). It is very likely that the impedance caused by lithium-ion diffusion in the interface can be neglected at elevated temperature. Therefore, the impedance at 55 °C may be attributed solely to the lithium intercalation in the bulk electrodes, which should be the same regardless of SEI film thickness. In addition, the conductivity of the electrolyte at 55 °C is very high, which could explain the low impedance value observed at high temperature. It can also be seen (Fig. 3b) that the impedance of cells without additive increases linearly during the cycling process at 55 °C, while the cells with additives show no noticeable impedance increase. This result was correlated with the ac impedance study of cells with and without additive, as shown in Fig. 4. In this case, the ac impedance was taken at room temperature after 259 and 359 cycles. The cell with no additive shows a significant increase in the interfacial impedance with cycling, while the cell with 1 or 2 wt.% LiBoB additive shows no interfacial impedance increase after exten-

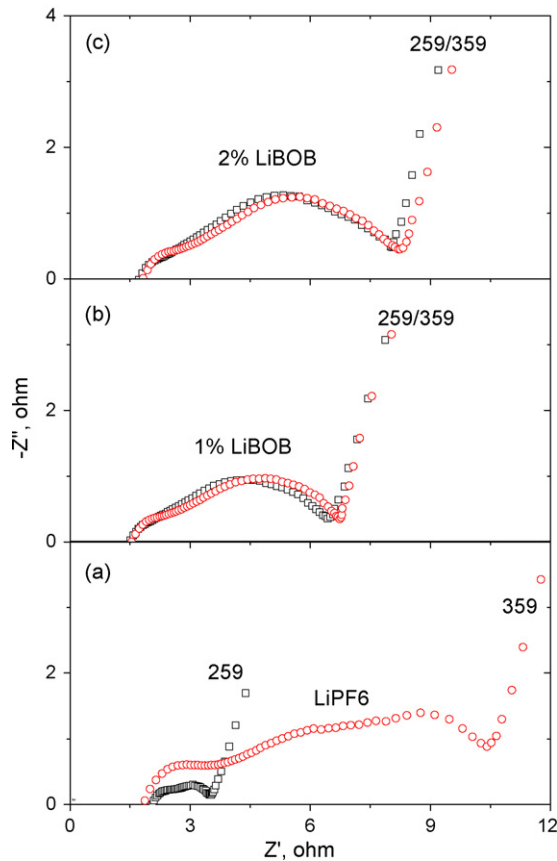


Fig. 4. ac impedance as a function of cycle number of MCMB 10-28/NCM cell in 1.2 M LiPF₆ EC/PC/DMC (1/1/3) electrolyte with (a) 0 wt.%, (b) 1 wt.%, and (c) 2 wt.% LiBOB.

sive cycling. This occurs because the SEI film formed by the reduction of LiBOB additive is very stable and tends to prevent surface reactivity between the electrode and electrolyte during the cycling process.

More information on capacity fade can be obtained from dQ/dE plots as a function of the cycle numbers. Fig. 5a shows a dQ/dE plot of a MCMB 10-28/NCM cell in LiPF₆-based electrolyte from 69 to 349 cycles at 55 °C. It is well known that the NCM has one redox peak around 3.9 V and graphite has three major peaks at 0.2, 0.1, and 0.07 V versus lithium during lithium-ion intercalation [15,16]. Thus, the three peaks observed in the dQ/dE plot (Fig. 5a) are due to the combination of cathode and anode electrodes. The first peak during the charging process (3.55 V) can be attributed to the first lithium-ion intercalation into graphite, which occurs at around 0.2 V versus Li/Li⁺. This peak tends to shift toward high potential with cycling because of interfacial impedance growth due to the continuous growth of SEI film, caused by the electrode/electrolyte reactivity during cycling. Also, the intensity of the two additional major peaks (2nd and 3rd peaks) in Fig. 5a, corresponding to the redox reactions of NCM, decreases with cycling. This decrease is attributed to the decreasing number of lithium ions removed from the NCM cathode because of the increase of the overpotential of the anode caused by the resistance increase. The increase in the overpotential of the anode can lead to an early cut-off voltage of the full

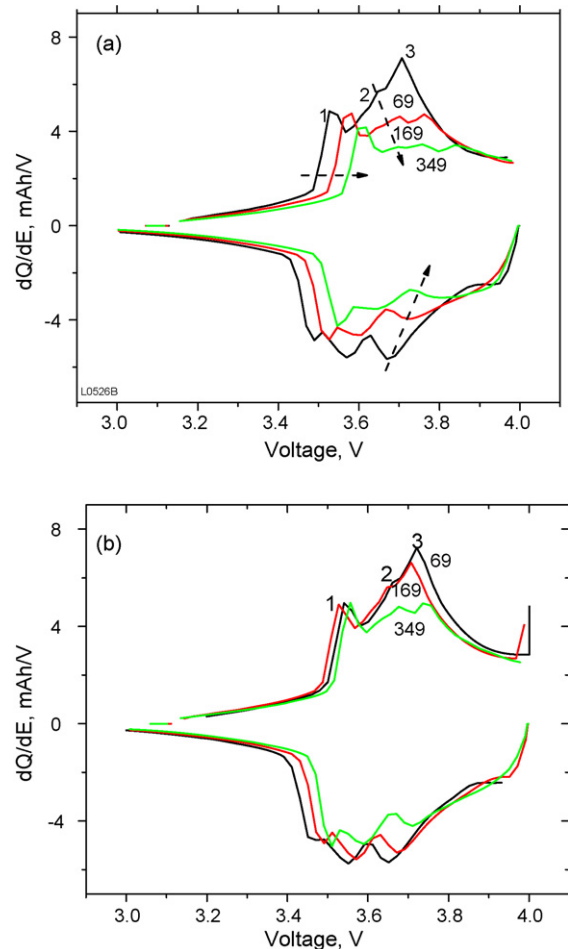


Fig. 5. dQ/dE plots of cells in 1.2 M LiPF₆ EC/PC/DMC (1/1/3) electrolyte as a function of cycle numbers at 55 °C: (a) without LiBOB and (b) with 1 wt.% LiBOB from 69 to 349 cycles.

cell at 3 V during the discharge process, resulting in less lithium being removed from cathode material. Fig. 5b shows the dQ/dE plots at the 69th, 169th, and 349th cycles of the cells having 1 wt.% LiBOB additive at 55 °C. Unlike the cell without additive, which has seen a continuous shift toward high potential of the first dQ/dE peak (Fig. 5a), the cells with LiBOB additive show a very limited shift of the first dQ/dE peak (especially from 69 to 169 cycles), indicating limited interfacial resistance growth because of the stability of the SEI film, as observed previously from ac impedance studies (Fig. 4). Furthermore, the decrease in the intensity of the two major peaks related to the NCM cathode is smaller compared with that for the cell without additive.

Fig. 6a shows the DSC results of the fully charged MCMB 10-28 in 1.2 M LiPF₆ EC/PC/DMC (1/1/3) electrolyte, with and without LiBOB additive. Without additive, the onset of the SEI breakdown takes place at 80 °C. However, the breakdown of the SEI film takes place at around 130 and 150 °C for 1 and 2 wt.% LiBOB, respectively. This result clearly shows that the LiBOB-based SEI film is more stable and requires higher energy to be broken down, which is consistent with the ARC results for LiPF₆ and LiBOB-based electrolytes [11,12]. One of the main contributors to the safety of lithiated carbon is the amount of heat genera-

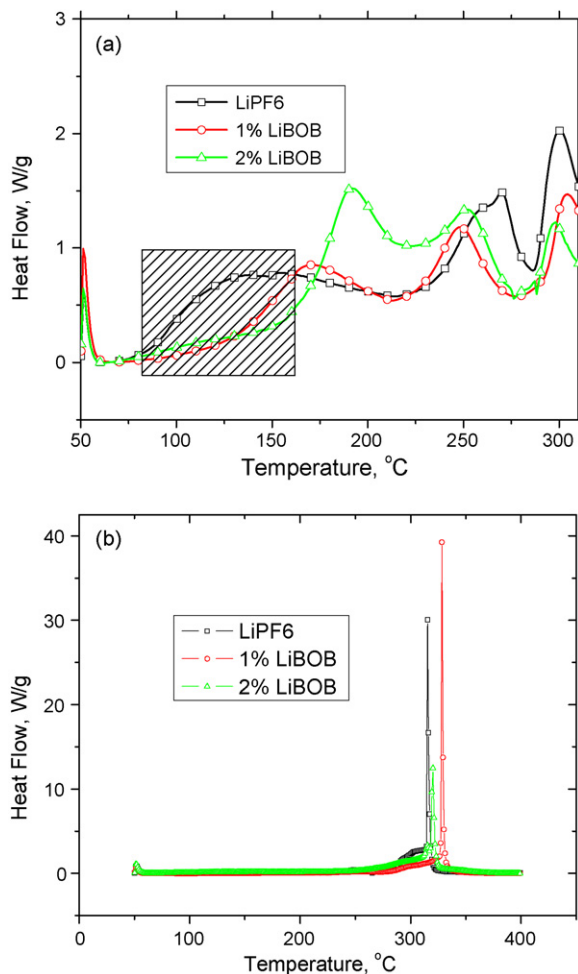


Fig. 6. DSC results of fully charged (a) MCMB 10-28 and (b) NCM in 1.2 M LiPF₆ EC/PC/DMC (1/1/3) electrolyte with 0, 1, and 2 wt.% LiBoB.

tion during the continuous reaction between the SEI breakdown temperature and 170 °C. Beyond 170 °C, the cathode decomposes, and the main reaction responsible for the thermal runaway is the reaction between the cathode and the electrolyte. In order to reduce the effect of the carbon anode on the safety of the cell, it is important to limit the amount of heat generation after the SEI breakdown. When using LiPF₆-based electrolyte without additive, the amount of heat generated from DSC after the SEI breakdown was 213 J g⁻¹. However, the amount of heat generated dropped significantly, to 70 J g⁻¹, with only 2 wt.% LiBoB additive present in the electrolyte. DSC results also demonstrate that the charged MCMB material with 1 wt.% LiBoB in LiPF₆-based electrolyte has nearly the same thermal characteristics as the charged MCMB anode in the electrolyte with 2 wt.% LiBoB. From these results, one can conclude that a stable SEI film at the anode, as is attained with LiBoB-based electrolyte, can improve not only the electrochemical performance, but also the safety characteristics, of the cell. In LiPF₆-based electrolyte, the SEI film is made of lithium alkyl carbonates (semicarboxylate: ROCO₂Li) as reduction products of EC and DEC during the first charge cycle [17,18]. However, the SEI film may have a very different chemical nature where LiBoB additive is used [4,19]. Fig. 6b shows the DSC results for the charged cathode material,

with and without LiBoB additive. No significant difference in the thermal signature or the onset temperature of the thermal peaks is observed with or without LiBoB additive. This result is different from that in the safety test carried out on nickel-based layered oxide, where LiBoB is used as a full salt in the electrolyte. In this case, the cathode shows significant reactivity at a much lower onset temperature because of the heat generation from the decomposition of the salt [7]. However, when LiBoB is used as an additive, most of it will be consumed during the passivation of carbon, and no effect on the thermal safety of the cathode is observed.

4. Conclusions

The issue of gas generation with LiBoB-based electrolyte in cells of MCMB 10-28/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ with 10% excess lithium was investigated. Significant amounts of gases, including CO₂, CO, and O₂, were detected from cells that were subjected to 500 cycles at 55 °C. These gases may have originated from the oxidation of the LiBoB salt at the positive electrode, which could result in poor cell performance. Studies using LiBoB as an additive in LiPF₆-based electrolyte indicate that much better cell capacity retention can be achieved at 55 °C during cycling. This improvement is caused by the formation of a stable SEI film during the reduction of the LiBoB additive at the surface of the negative electrode. Furthermore, the DSC results show that the onset temperature for SEI film breakdown when using LiBoB as electrolyte additive is much higher than that for the conventional SEI film obtained by electrolyte reduction. The increase in the onset temperature for the SEI breakdown can result in much lower heat generation from the carbon electrode between 70 and 170 °C.

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