

# LiBOB: Is it an alternative salt for lithium ion chemistry?

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## Abstract

In this paper, the perspective of lithium bis(oxalato)borate (LiBOB) as a possible candidate for the lithium ion batteries was evaluated on the basis of the knowledge accumulated thus far. Emphasis was placed on the electrochemistry of the BOB-anion on both graphitic anode and metal-oxide-based cathode surfaces. Certain issues associated with the impurity and safety of the salt in lithium ion systems were also discussed.

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## 1. Introduction

It has been well recognized that the basis for the reversible operation of lithium ion chemistry is the formation of electrode/electrolyte interfaces during the initial charge of the cell. Since the decomposition products of the electrolyte components constitute these interfaces, and hence, dictate their physicochemical properties, one could interpret that in a somewhat ironic way the electrochemical stability of the electrolytes is realized by how they decompose initially. To meet the stringent requirement of this electrochemical stability on the surfaces of both oxidizing cathode and reducing anode, majority of the state-of-the-art (SOA) electrolytes for lithium ion devices have two essential components: lithium hexafluorophosphate ( $\text{LiPF}_6$ ) as electrolyte solute and ethylene carbonate (EC) as co-solvent.

These key electrolyte components have made significant contributions to the commercialization of lithium ion technology; however, they also imparted their intrinsic thermal limitations to the SOA electrolytes and restricts their service temperature range in devices. In an over-simplified view, the high melting EC (mp  $36.4^\circ\text{C}$ ) is responsible for the reduced capacity and power capability at low temperatures, and the thermally unstable  $\text{LiPF}_6$  for the rapid deterioration of cell

performance at elevated temperatures. To expand the service temperature into sub-zero territories, a NASA group has reported impressive progress by displacing EC with lower melting solvents [1], while the efforts aiming at replacing  $\text{LiPF}_6$  with a more thermally stable salt have seen limited success so far. The main difficulty arises from the fact that  $\text{LiPF}_6$  possesses a host of physicochemical properties that are so well-balanced to meet the requirements from the lithium ion environment that any candidate replacing it will be accompanied with certain trade-offs. During the past decade, numerous new salts were proposed and tested despite the difficulty [2–14]. The family of boron-based salt anions with non-aromatic ligands, mainly synthesized by Xu and Angell, was one of the most recent advances in this area [12b,13], among which the title salt, lithium bis(oxalato)borate (LiBOB), is being evaluated at ARL as a potential candidate salt for use in lithium ion chemistry.

## 2. Experimental

The synthesis and preparation of electrolyte solutions have been described in our earlier publications [15–18]. Graphitic anode coated on Cu-foil- and  $\text{LiNiO}_2$ -based cathode coated on Al-foil were provided gratis by SAFT and cut into discs of  $0.97$  and  $1.27\text{ cm}^2$ , respectively. The assembly of the cells using stainless-steel coin cells (size CR2335) and the cycling

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of these have also been described [15–18]. For analytical purpose, some cells were opened at certain state-of-charge, and the subsequent procedures of sample preparation as well as the spectroscopic experiments and interpretation have also been described in these previous publications.

### 3. Results and discussion

#### 3.1. The highlights of LiBOB

During our early experiments with LiBOB, extensive tests with various graphitic anode and lithium nickel-based mixed metal oxide ( $\text{LiNi}_{1-x-y}\text{M}'_x\text{M}''_y\text{O}_2$ ) cathode materials were conducted, which showed that reversible lithium ion intercalation/de-intercalation could be supported after the initial “forming cycle”, and stable interfaces are formed and function as effective electronic barrier to prevent further electrolyte oxidation/reduction [15]. The Coulombic loss due to the formation of these interfaces (irreversible capacity) generally falls within the typical range where SOA electrolytes could achieve. As an example, Fig. 1 shows the slow scan cyclic voltammograms of graphitic anode and a  $\text{LiNiO}_2$ -based cathode in LiBOB/EC/EMC. Additional study showed that the electrolytes based on LiBOB can also effectively stabilize Al up to high potentials ( $>5.0$  V versus Li) in a similar manner with  $\text{LiPF}_6$ . Cycling of the full lithium ion cells using such electrolytes confirms their electrochemical stability with stable capacity performances at room temperature.

The two unique properties of LiBOB, although probably with a common origin, were identified at ARL: (1) the abil-

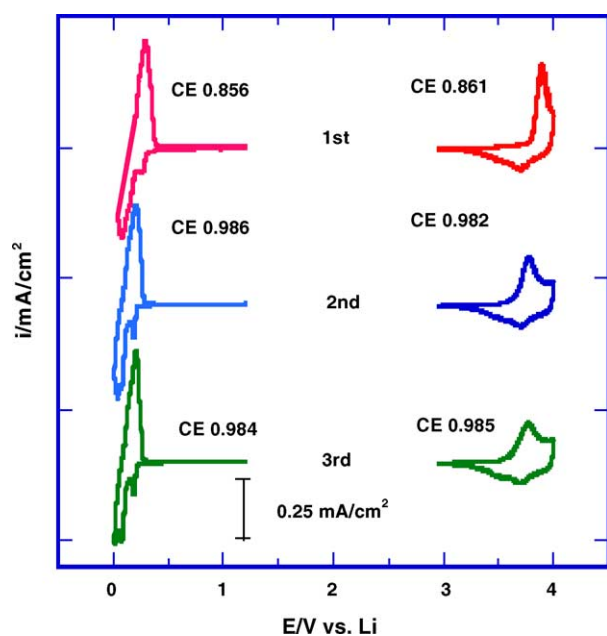


Fig. 1. The cycling of graphitic anode and  $\text{LiNiO}_2$ -based cathode in LiBOB/EC/EMC at  $0.01 \text{ mV s}^{-1}$ . The first three cycles were shown with Coulombic efficiency indicated (reproduced with the permission of Electrochemical Society).

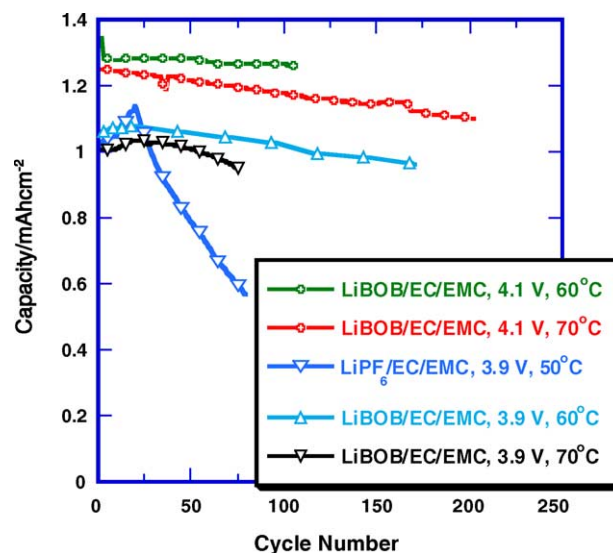


Fig. 2. The performance of lithium ion cells containing LiBOB/EC/EMC at elevated temperatures.

ity of the LiBOB-containing lithium ion cells with lithium nickel-based mixed metal oxide cathode to cycle at elevated temperatures (Fig. 2) [15] and (2) the ability of LiBOB to effectively stabilize the graphene structure even in neat PC solution (Fig. 3) [16]. While the LiBOB salt starts thermal decomposition (shown by TGA) at above  $300^\circ\text{C}$  (versus  $80^\circ\text{C}$  for  $\text{LiPF}_6$ ) [19], we believe that the thermal stability of the lithium ion cell at these temperatures is determined by more than just bulk thermal stability; instead surface chemistry, especially the SEI layer on graphitic anode, should have played a role. A deep involvement of BOB-anion in the surface chemistry during the formation of the so-called solid electrolyte interface (SEI) is highlighted by the reversible cycling of SEI is highlighted by the reversible cycling of graphitic anode in neat PC solution (Fig. 3). It was these

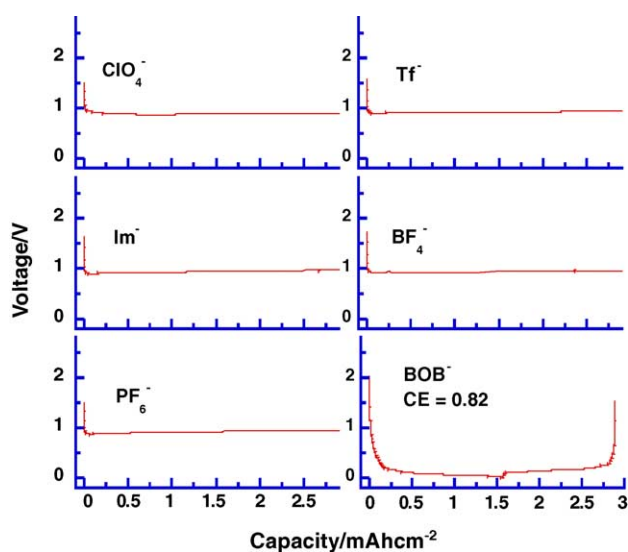


Fig. 3. The stabilization of graphene structure by LiBOB in neat PC solutions. Also shown are PC solutions of other lithium salts as comparison (reproduced with the permission of Electrochemical Society).

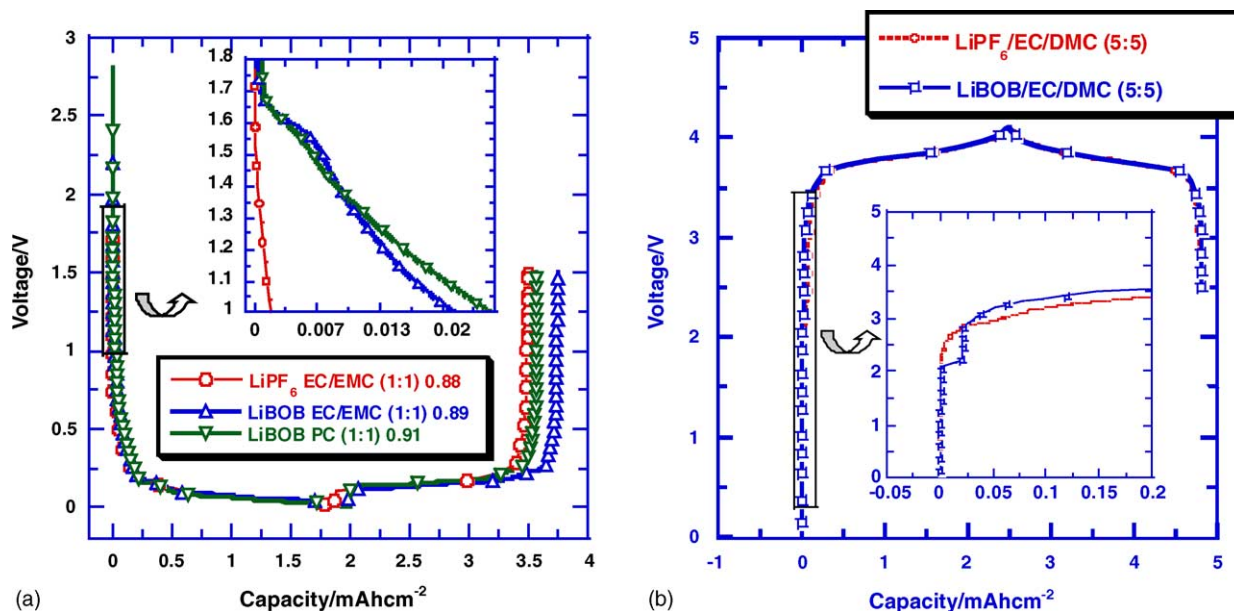


Fig. 4. (a) The characteristic reduction process of BOB-anion at 1.70 V on graphitic anode surface (reproduced with the permission of Electrochemical Society). (b) The same reduction process appears at ca. 2.0 V in full lithium ion cell.

two preliminary observations that initiated our detailed characterization of this new lithium salt because we believe that these merits will probably enable LiBOB to find an application niche in lithium ion chemistry.

### 3.2. Understanding the electrochemistry of LiBOB

#### 3.2.1. The reduction process at 1.70 V on graphitic anode

When graphitic anodes were cycled in LiBOB-based electrolytes, a characteristic reduction process was always observed at 1.70 V versus Li (Fig. 4a) [17]. The Coulombic capacity of this process varies with the graphite material type, solvent composition and the rate of lithiation. In full cell, this process would appear in the neighborhood of 2.0 V depending on the relative polarization of cathode and anode (Fig. 4b); however, there is no doubt that it is uniquely associated with the presence of BOB-anion in the electrolyte solutions. Considering the conventional wisdom guiding the selection of SEI additives [20], we were initially tempted to attribute this process to the formation of a protective SEI layer on graphitic anode.

To support the above hypothesis, we assembled a series of anode half cells loaded with LiBOB/PC, and lithiated the cells down to a series of potentials at C/10 rate followed by switching the electrolyte to LiPF<sub>6</sub>/PC. Since the later electrolyte cannot form protective SEI, the surface deposition from LiBOB/PC should be responsible for any form of graphite stabilization. Fig. 5 shows selected voltage profiles for these pre-formed anode half cells at different cell potentials, and an interim conclusion is that the reduction process at 1.7 V versus Li appears to be not directly linked to an effective SEI. In other words, down to 0.6 V versus Li the graphite in Li-

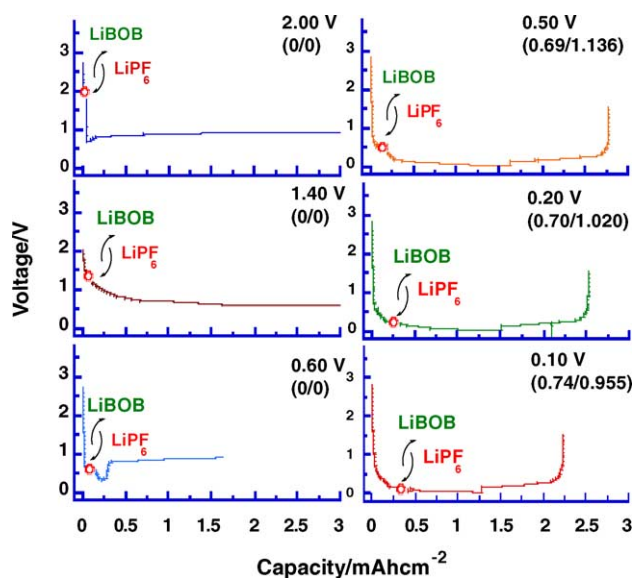
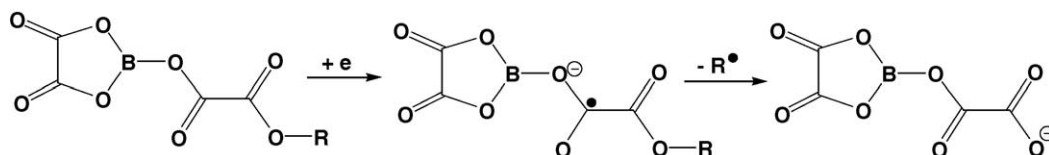


Fig. 5. The dependence of anode surface chemistry on forming potential (reproduced with the permission of Electrochemical Society).

BOB/PC was still not covered with a sufficiently protective interface, hence whatever the process at 1.7 V is, it does not provide the necessary chemical species for the unique SEI that LiBOB is known to provide.

On the other hand, it has been known that the reductive cleavage of oxalate esters occurs at approximately  $-1020$  mV versus Ag/AgI (which translates to  $\sim 1.65$  V versus Li) [21]. If similar oxalate esters exist as impurity in LiBOB salt, then the following reductive process will very likely occur at the characteristic potential of 1.70 V:



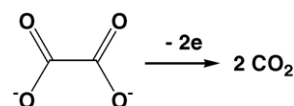
These oxalate esters could be generated as the result of solvents used during the synthesis or even the trans-esterification between the salt anion and the solvents used to prepare the electrolyte solutions.

To confirm the possible involvement of the oxalate ester in the 1.70 V reduction, we deliberately added diethyloxalate (DEO) as a model impurity to a baseline electrolyte, LiPF<sub>6</sub>/EC/DMC, which does not have any detectable event at the questioned potential range (Fig. 4a and b). The presence of this “authentic impurity” does reproduce the reduction process at 1.70 V in an anode half cell (Fig. 6a) and the corresponding 2.0 V process in a full lithium ion cell (Fig. 6b). Beside the location of the reduction potential, there also seems to be a very certain, if not linear, relation between the amounts of DEO and the irreversible capacity associated with the reduction process, in well accord with our observation about the 1.70 V when LiBOB was used. At this point, a more definite conclusion would be that there seems to be no direct connection between the unique SEI chemistry formed by LiBOB and the characteristic reduction at 1.70 V.

### 3.2.2. The anodic stability on various cathodes

A legitimate concern over the anodic stability of BOB-anion occurred to us based on the common knowledge that the oxidation potential of oxalate anion lies somewhat 3.5–4.0 V versus Li on inert electrode surfaces, which is below or near

the operation range of the SOA cathode materials: [22].



Considering that the porous surface structure of the composite cathode with various transition metal sites might be catalytic for the above oxidation, the anodic stability of the oxalate anion should be even lower. However, it should also be considered that there is no free oxalate anion moiety in BOB-anion, and the chelation with the electron-deficient center (boron) should reduce the anodic reactivity of the oxalate ligand, thus stabilizing the BOB entity. The question remains: is the extent of this stabilization sufficient for the long term application of BOB in the presence of those cathode materials? Preliminary cycling data of LiBOB-based electrolytes (Fig. 1; Ref. [15]) seems to provide positive answer to the above question under the condition the tests were done.

In a closer examination, LiCoO<sub>2</sub> cathode half cells with LiBOB-and LiPF<sub>6</sub> in EC/EMC solutions were cycled up to 4.2 V, and the differential capacities of the first cycle were compared in Fig. 7. Except for the slightly higher polarization of LiBOB-electrolyte due to the more resistive cathode/electrolyte interface, there is essentially no differ-

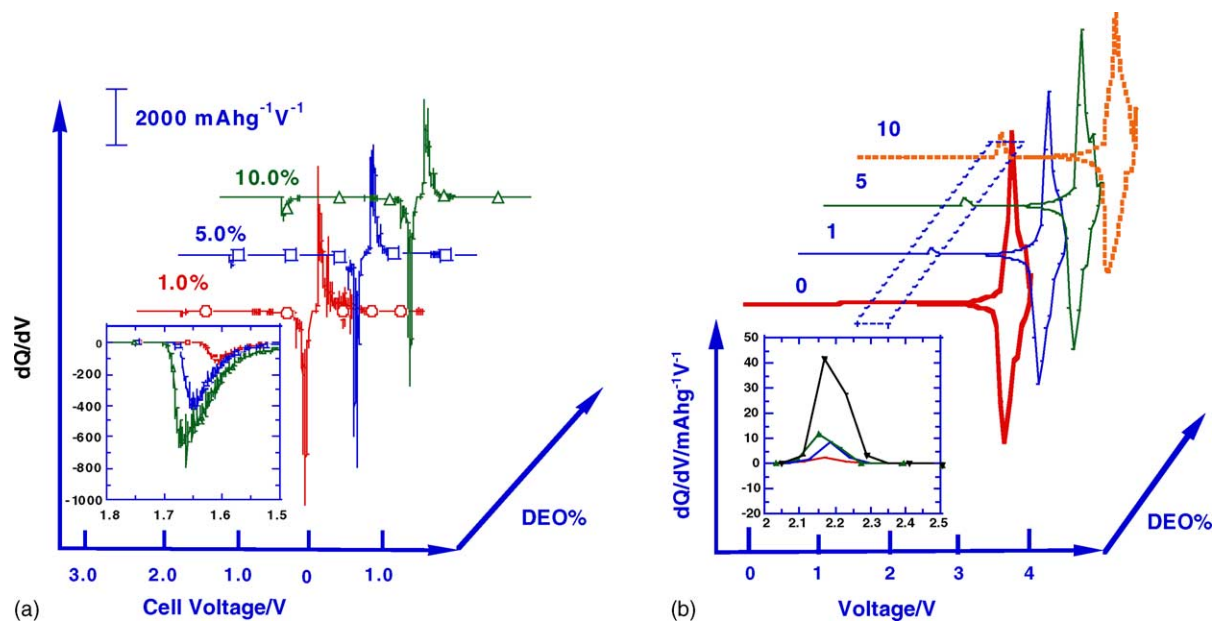


Fig. 6. (a) The plots of differential capacity vs. cell voltage for graphite/Li half cell containing LiPF<sub>6</sub>/EC/DMC with various content of DEO. (b) The plots of differential capacity vs. cell voltage for LiNiO<sub>2</sub>/Li half cell containing LiPF<sub>6</sub>/EC/DMC with various content of DEO.

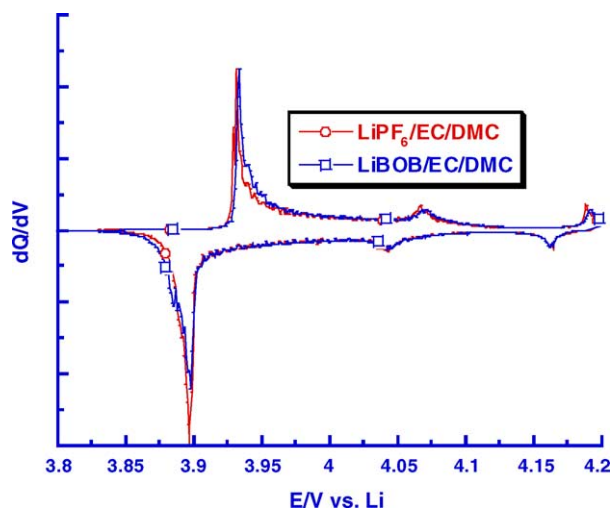


Fig. 7. The plots of differential capacity vs. cell voltage for  $\text{LiCoO}_2/\text{Li}$  cells containing LiBOB or  $\text{LiPF}_6$  in EC/DMC as electrolytes.

ence between these two cells, indicating that BOB-anion remains non-reactive against oxidation till 4.20 V at room temperature. Similar results were obtained with other cathode materials (spinel,  $\text{LiNiO}_2$ -based cathode, etc.) when the cells were charged up to 4.3 V, as Fig. 8 showed for such a cell built with  $\text{LiNiO}_2$ -based cathode. While our stainless-steel cell hardware prevented us from carrying on the tests to higher potentials, the results from Chen and Dahn proved that BOB could maintain this stability up to 4.5 V on  $\text{LiCoO}_2$  cathode surface [23]. Therefore, an interim conclusion would be drawn that LiBOB has comparable anodic stability with  $\text{LiPF}_6$  on various cathode surfaces under normal conditions.

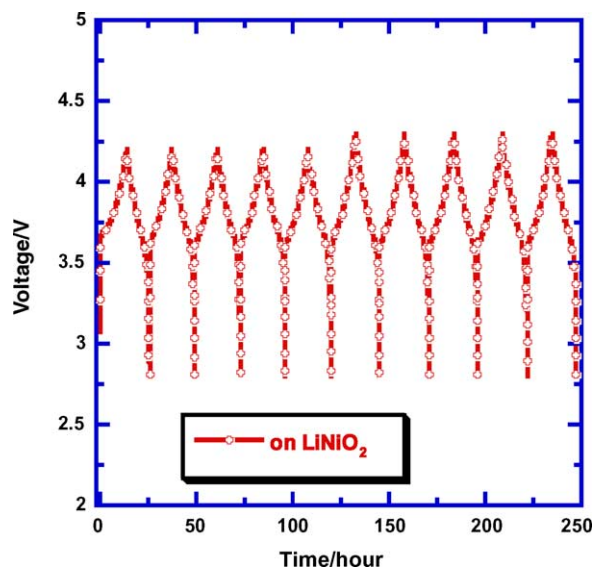
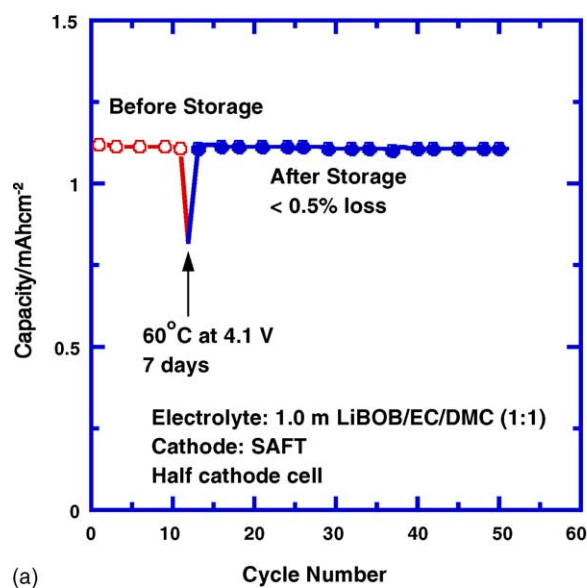
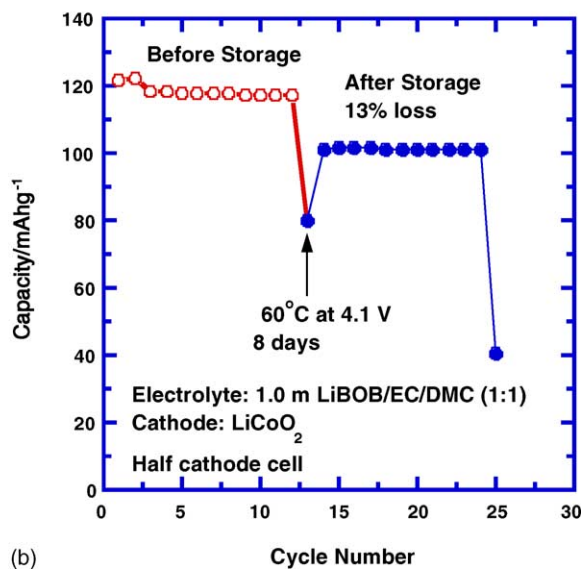


Fig. 8. The cycling of  $\text{LiNiO}_2/\text{Li}$  cell containing LiBOB/EC/DMC at constant drain rate with various high voltage cut-offs.

To further evaluate the anodic stability of LiBOB on these cathode materials in longer terms or under the conditions of accelerated aging, we stored the cycled lithium ion cells at 4.1 V under  $60^\circ\text{C}$  for a week and compare the capacity loss. Our preliminary results suggested that the retention of the post-storage capacity might be cathode-specific, as Fig. 9a and b showed [24]. Meanwhile, Ue and co-workers reported serious capacity loss of LiBOB-electrolyte in  $\text{LiCoO}_2$ -cells upon  $60^\circ\text{C}$  storage [25]. Whether the oxidative decomposition of BOB-anion is specifically catalyzed by  $\text{LiCoO}_2$ , or a combined effect of both cathode potential and tempera-



(a)



(b)

Fig. 9. (a) The effect of HT storage on the capacity retention of cathode half cell using  $\text{LiNiO}_2$ -based cathode and LiBOB/EC/DMC. (b) The effect of HT storage on the capacity retention of cathode half cell using  $\text{LiCoO}_2$  cathode and LiBOB/EC/DMC.

ture accelerates this decomposition will require additional studies.

#### 4. The disadvantages and concerns

As a new candidate for lithium ion chemistry, many key properties of LiBOB remain unknown, as the efforts of the researchers continue to accumulate knowledge about it in an attempt to comprehensively evaluate its perspective future in the application. Besides the above-discussed advantages, it has been found that LiBOB also has the following disadvantages/concerns.

##### 4.1. Solubility

LiBOB is essentially insoluble in solvents of low dielectric constants such as linear carbonates. For example, its maximum solubility in a mixture of EC/DMC (3:7) is only 0.80 M, thus restricting the formulation of the solvents to be EC- or PC-rich. However, the high content of these cyclic carbonates in an electrolyte formulation tends to reduce its wettability toward the separator/electrode as well as to increase the viscosity of the resultant electrolyte. The latter could render the electrolyte with poor low temperature performance and rate capability. To solve this problem, a proper solvent mixture that is tailored for LiBOB needs to be formulated.

##### 4.2. Ion conductivity

Compared with LiPF<sub>6</sub>, LiBOB is less conductive in typical carbonate mixtures [26]. This sacrifice in bulk ion conductivity will usually be reflected in the cell impedance when passivation films (such as SEI) are formed, and in turn affect the low *T* performance and power rate of the lithium ion cell.

##### 4.3. Ambient-sensitivity

Contrary to a general misunderstanding that LiBOB is more ambient-stable than LiPF<sub>6</sub>, this new salt can be readily hydrolyzed by ambient moisture, although experimental results have shown that monohydrate of LiBOB can remain stable [19]. Prolonged exposure to air/moisture results in the precipitation in electrolyte solutions, probably in the form of boric acid and oxalate esters or acids.

##### 4.4. Safety

The series of work by Jiang and Dahn systematically investigated the safety feature of LiBOB with various electrode materials by means of accelerated rate calorimetry (ARC) [27–30]. It was known that, while enhanced safety can be obtained with fully lithiated graphitic anode and LiBOB-electrolytes, the safety concern rises when most of the tested cathode materials showed higher self-heating rate, indicating

higher reactivity between LiBOB and these metal oxides. The only exception in this sense is LiFePO<sub>4</sub> [29], which showed much higher onset temperature in the presence of LiBOB. Thus, Dahn and co-workers proposed a so-called “thermally stable lithium ion cell” with the configuration of graphite/LiBOB/EC/DEC/LiFePO<sub>4</sub> [30].

##### 4.5. Gassing in lithium ion cell

As reported by Wietlemann et al. recently, gas production was observed in lithium ion cells based on LiCoO<sub>2</sub> cathode. A connection was established by them between the gas amount as measured by cell swelling and the impurities in LiBOB salt [19]. Specifically, a solvent that has been used during the processing of LiBOB, ethyl acetate, has been identified as the culprit. However, more work is needed to determine if this gassing phenomenon is caused by the presence of impurity, or rather by the intrinsic chemical structure of LiBOB. After all, oxalate moiety is a functionality that has the potential to release CO<sub>2</sub>. Whether it remains stable at high potentials or at elevated temperatures will depend on how effectively the cathode surfaces are passivated.

##### 4.6. Impurity

The production of high purity LiBOB at industrial scale remains a challenge, and this appears to be a reminiscence of the early days of LiPF<sub>6</sub> when its potential application in the emerging lithium rechargeable batteries was incessantly plagued by the impurities (HF or LiF) present in the commercial product from most of the manufacturers [31]. It was the successful commercialization of high purity LiPF<sub>6</sub> that ensured the success of lithium ion chemistry, and a brand name “Hashimoto LiPF<sub>6</sub>” was thus made in the early 1990s. We expect to see the quality improvement with LiBOB in a much shorter time frame due to the active efforts of Chemetall [19,32].

While the methods used to monitor the quality are also being actively explored by Chemetall Co., the reactivity of LiBOB toward the common Karl-Fischer reagents certainly complicates the effort to find a facile determination of moisture level of the electrolytes [31]. Considering that LiBOB is still a young salt (~5 years), we believe that, while much has been accomplished, much more still needs to be done.

## 5. Conclusion

Although much has been accomplished to understand the physicochemical properties, electrochemistry, surface chemistry as well as thermal safety of LiBOB, the title question still remains to be answered. With more efforts made by both the research community and the manufacturer, we believe that whether LiBOB, with its unique properties, would find applications in lithium ion batteries will become clear.

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