Short communication

Effect of mixed LiBOB and LiPF$_6$ salts on electrochemical and thermal properties in LiMn$_2$O$_4$ batteries

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Abstract

The effects of mixed LiBOB and LiPF$_6$ salts as electrolyte for lithium ion batteries are investigated by electrochemical testing and thermal stability analysis. Elevated temperature cycle, specific power, DCIR and EIS tests reveal that mixed salts electrolyte has a distinct effect on cycle life and effectively stabilize impedance increase, as optimum concentration of LiBOB is between 0.1 and 0.25 M. Fading mechanism analyses demonstrate that the mixed salts system could decrease Mn dissolution and LiBOB decomposition at elevated temperature application. Accelerating rate calorimetry (ARC) shows that the thermal stability of mixed salts electrolyte is also acceptable. In short, the mixed salts of LiBOB and LiPF$_6$ provide a possible solution to improve the instability of LiMn$_2$O$_4$ as cathode in lithium ion batteries at elevated temperature conditions and show a promising capability in high current discharge for high power application such as hybrid electrical vehicles.
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Keywords: LiBOB; LiPF$_6$; Mixed salt; LiMn$_2$O$_4$; ARC; Fading mechanism

1. Introduction

Meanwhile, the demands for lithium ion batteries with high power performance have increased for use in wireless power tools or hybrid electrical vehicles. With the advantages of low cost, safety, high potential and high specific power, LiMn$_2$O$_4$, is one of potential cathode materials for this application. However, the battery is easy to operate at elevated temperature for such heavy duty application conditions will accelerate Mn dissolution from the LiMn$_2$O$_4$ electrode then deposit on the graphite anode and has been resulted in the severe capacity fading [1–4]. HF formation from the decomposition of LiPF$_6$ salt in the presence of trace of water is believed in accelerating the Mn dissolution.

Recently, a fluorine-free lithium salt, lithium bis (oxalate)borate (LiBOB), was developed as a potential replacement salt for LiPF$_6$ to avoid the above issue [5–10]. However, lower conductivity by the limited solubility is an issue in LiBOB system. Besides the difference between LiBOB and LiPF$_6$ in physical properties, LiBOB electrolytes also present different reactivity to electrodes, such as different mechanism in forming SEI. That is, different electrochemical

characteristics and thermal behavior were affected by the electrolyte composition of salts.

In order to compromise the issues from LiPF$_6$ and LiBOB, a mixed salt system has been investigated in this study. Optimizing the LiBOB/LiPF$_6$ ratio is expected to improve the performance of LiMn$_2$O$_4$ cells especially at elevated temperature environments.

2. Experimental

An 18650-type cell was introduced for this study. Cathode electrode was prepared by combining, by mass, 85% LiMn$_2$O$_4$ (from Nikki Chemical Co. Ltd.), 5% conductive carbon, and 10% poly-vinylidene fluoride (PVDF, from Kuraha Chemical). Anode electrode was prepared by mixing 90% MCMB (mesophase carbon microbead, from Osaka Gas) and 10% PVDF. The electrodes were preserved after coating and then assembled into the cell in the dry room (dew point below −40 °C). Celgard 2400 was used as separator. One molar of LiPF$_6$ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (1:2, v/v) was obtained from Mitsubishi Chemicals. LiBOB (from Chemetall) was dissolved to 0.8 M concentration in EC/EMC (1/2) solvent. Mixed salts electrolytes whose concentration are 0.1 M LiBOB/0.9 M LiPF$_6$, 0.25 M LiBOB/0.75 M LiPF$_6$ and 0.5 M LiBOB/0.5 M LiPF$_6$, as well as pure LiPF$_6$ and

LiBOB salt electrolytes were prepared for studying the effects of salts on electrochemical and thermal performances of $LiMn_2O_4$-based 18650 cells. The capacity design for 18650-type cell was 500 mAh due to the facilitation of jerry roll preparation in winding process.

Cycle performance tests in charge–discharge were performed at $1C$ rate current (500 mA) at 55 °C with the Bitrode BT-2040 battery testing instrument. The voltage range was 4.2–2.8 V. Before measuring the electrochemical impedance, batteries were charged to 4.2 V and placed at room temperature for at least 2 h. A potentiostat/galvanostat instrument (model series 1287, Solartron) and a frequency response analyzer (model series 1255, Solartron) were used for measuring electrochemical impedance spectrum (EIS). Scanning frequencies were from 10 kHz to 0.01 Hz, and the perturbation amplitude was 2 mV.

The DCIR and specific power of cells are calculated as follows. The fully charged cells are discharged by $1C$ current with 2 s period. The voltage drop within 2 s divided by the applied current is the index of DCIR. The charged cells discharged by $0.2C$, $1C$ and $3C$ current for 30 s. The end potential of 30 s discharge at $0.2C$, $1C$ and $3C$ current are plotted as V–I curve and extrapolate to peak current at 2.8 V. The peak current multiplied by 2.8 and divided by cell weight is the index of specific power.

The fading mechanism analysis of cycled batteries was performed by two ways. In the first way, new electrolyte was injected into the cycled battery to study the effect of electrolyte decomposition for capacity fading. The discharged 18650 cells were drilled a hole, injected 2 ml new electrolyte and sealed by UV curing resin. In the second way, capacity fading from cathode electrode was checked by CR2032 coin cells. After dismantled batteries, the cathode electrodes were punched and soaked in new electrolyte for cleaning, and then assembled coin cells with Li metal. The cells were charged and discharged between 4.2 and 3.0 V versus Li/Li^+ with $0.1C$ current for capacity evaluation. In this study, all the process was done in dry room to avoid the water contamination.

In the accelerating rate calorimeter (ARC, from Thermal Hazard Technology EV-ARC) tests, the cells were put in a closed holder connected with pressure sensor for pressure monitoring. The cells were heated between 60 and 200 °C with 5 °C increments in the search for reaction between active materials and electrolyte at the sensitivity threshold of $0.02\,°C\,min^{-1}$. The controller was programmed to wait for 15 min for equilibrium between the sample and calorimeter temperatures, and then to search 20 min for a temperature increase of $0.02\,°C\,min^{-1}$.

3. Results and discussion

3.1. Electrochemical performance

Fig. 1 shows the cycling performances at 55 °C for cells containing 0.8 M LiBOB, 1 M $LiPF_6$ and mixed LiBOB and $LiPF_6$ (0.25 M and 0.5 M LiBOB, respectively) as electrolytes. After the first 100 cycles, there is no obvious difference in the capacity fading of the pure 0.8 M LiBOB and pure 1 M $LiPF_6$ salt electrolytes. Specifically, the cycle performance is markedly improved by introducing the mixed salt of LiBOB and $LiPF_6$.
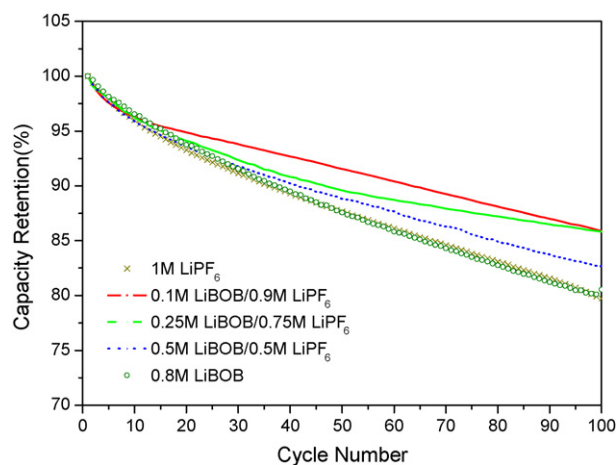

Fig. 1. The battery cycle performance with different salt composition in EC/EMC (1/2, v/v) solvents at 55 °C. Salt composition is 0.8 M LiBOB, 1 M $LiPF_6$, 0.1 M LiBOB/0.9 M $LiPF_6$, and 0.25 M LiBOB/0.75 M $LiPF_6$ and 0.5 M LiBOB/0.5 M $LiPF_6$.

For the 0.25 M LiBOB/0.75 M $LiPF_6$ system, 86% capacity is retained after 100 cycles, as compared to 79% of capacity retained in both pure salt systems. Also, 86% capacity retention (82%) is observed in 0.5 M LiBOB/0.5 M $LiPF_6$ system after 100 cycles.

The cycling performance of pure LiBOB electrolyte at elevated temperature in $LiMn_2O_4$ cells is not as expected from our result, even though it has been reported that LiBOB has the advantages of high thermal stability and non-HF system to prevent Mn dissolution from $LiMn_2O_4$ cells. The shortcomings of LiBOB such as low solubility, low ion conductivity and decomposition, as discussed in the next section, may decrease its performance in cycleability. This trade-off characteristic is optimized by mixing it with $LiPF_6$ salt, which combines the advantages of thermal stability of LiBOB and conductivity of $LiPF_6$. The mixed salts show synergetic effects on the long-term cycle performance at elevated temperature.

The DCIR and specific power characteristics of mixed salt electrolyte dependence of different LiBOB concentration are shown in Fig. 2. When cells are at fresh state (after formation), the increase in LiBOB concentration is observed with increasing impedance (DCIR) and with decreasing specific powder. It may be due to LiBOB decomposition and this formed a resistive SEI. After 100 cycles; however, careful inspection of the specific power and DCIR discover that the increase in impedance of mixed salt electrolyte is smaller than pure salt systems, as shown in Table 1. In specific power performance, the variation

Table 1
The variation of the ratio of specific power and DCIR of cells after 100 cycles at 55 °C

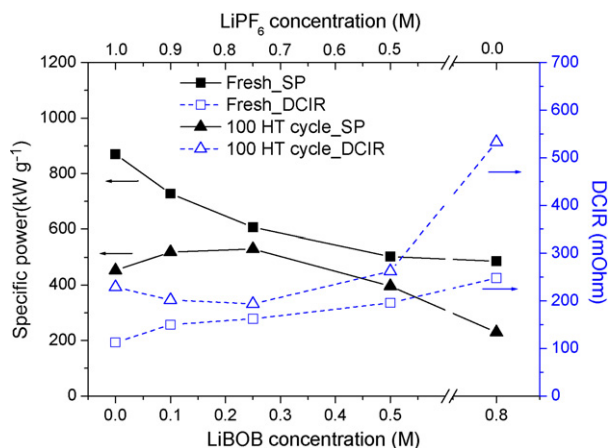| LiBOB concentration	SP ratio	DCIR ratio
0	0.52	2.04
0.1	0.71	1.35
0.25	0.87	1.19
0.5	0.79	1.34
0.8	0.47	2.15

Fig. 2. Specific power and DCIR performances of fully charged cells before and after 100 cycles at 55 °C. (0 M represents pure LiPF$_6$ salt as 0.8 M stands for pure LiBOB salt.)

Fig. 3. Electrochemical impedance spectrum of 18650 cells with 1 M LiPF$_6$; 0.8 M LiBOB; 0.25 M LiBOB/0.75 M LiPF$_6$ in EC/EMC solvent after 100 cycles at 55 °C.

ratio after 100 cycles decreases to 0.52 and 0.47 for pure LiPF$_6$ and pure LiBOB cells, respectively. However, it keeps at 0.87 for 0.25 M LiBOB/0.75 M LiPF$_6$ mixed salt cell. The variation ratio for DCIR increase of 0.25 M LiBOB/0.75 M LiPF$_6$ mixed salt cell also shows a lower value at 1.19 when compared to pure LiPF$_6$ and LiBOB cells at 2.04 and 2.15, respectively. Consequently, the performance of specific power and DCIR shows an optimum result at 0.1–0.25 M LiBOB mixed with LiPF$_6$ electrolytes.
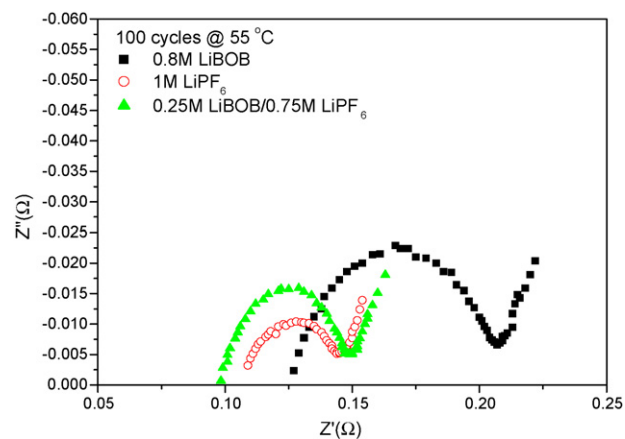
The impedance variation was also investigated by electrochemical impedance spectrum (EIS) analysis. Fig. 3 shows the EIS of cells with different salts electrolyte after 100 cycles. The impedance of pure LiBOB cell is larger than that of pure LiPF$_6$. It is conducted that LiBOB is involved in the SEI formation [7,10], which is contributed to higher SEI impedance. By mixing LiBOB and LiPF$_6$ salts could effectively control the impedance rise.

Fig. 4 is shown the SEM investigation of cathode electrode after 250 cycles at 55 °C. It reveals a clean surface on LiMn$_2$O$_4$ particles both in pure LiBOB and mixed of LiBOB and LiPF$_6$
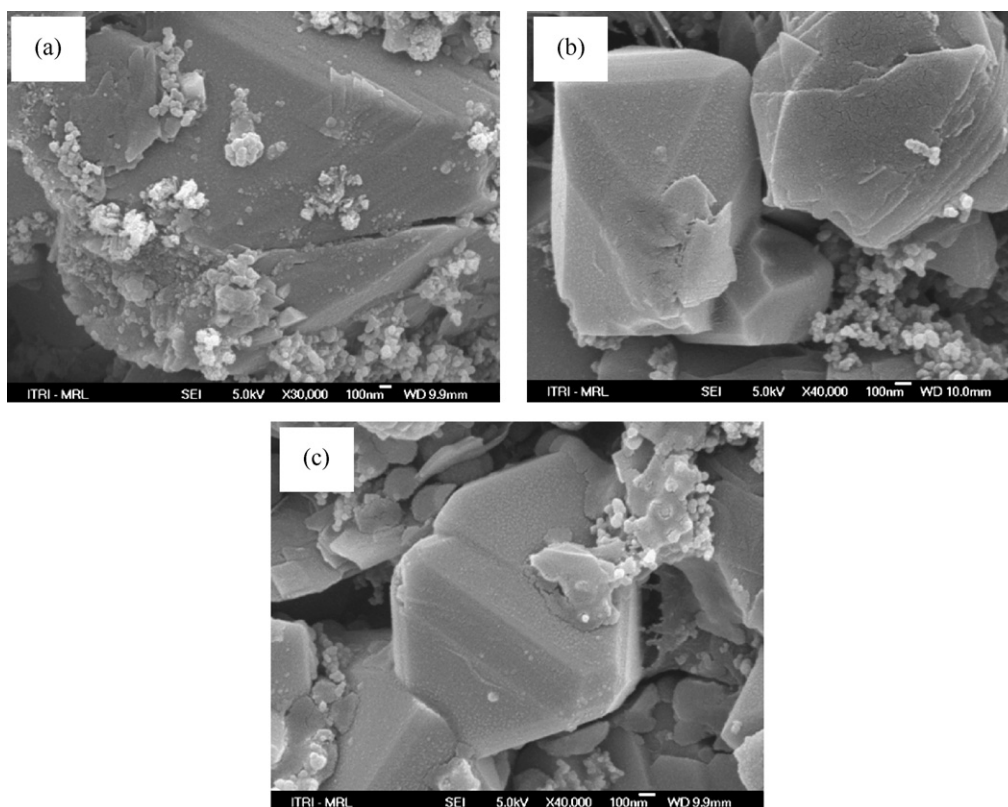

Fig. 4. SEM image of cathode electrodes after 250 cycles at 55 °C with different salts: (a) 1 M LiPF$_6$; (b) 0.8 M LiBOB; (c) 0.25 M LiBOB mixed with 0.75 M LiPF$_6$.
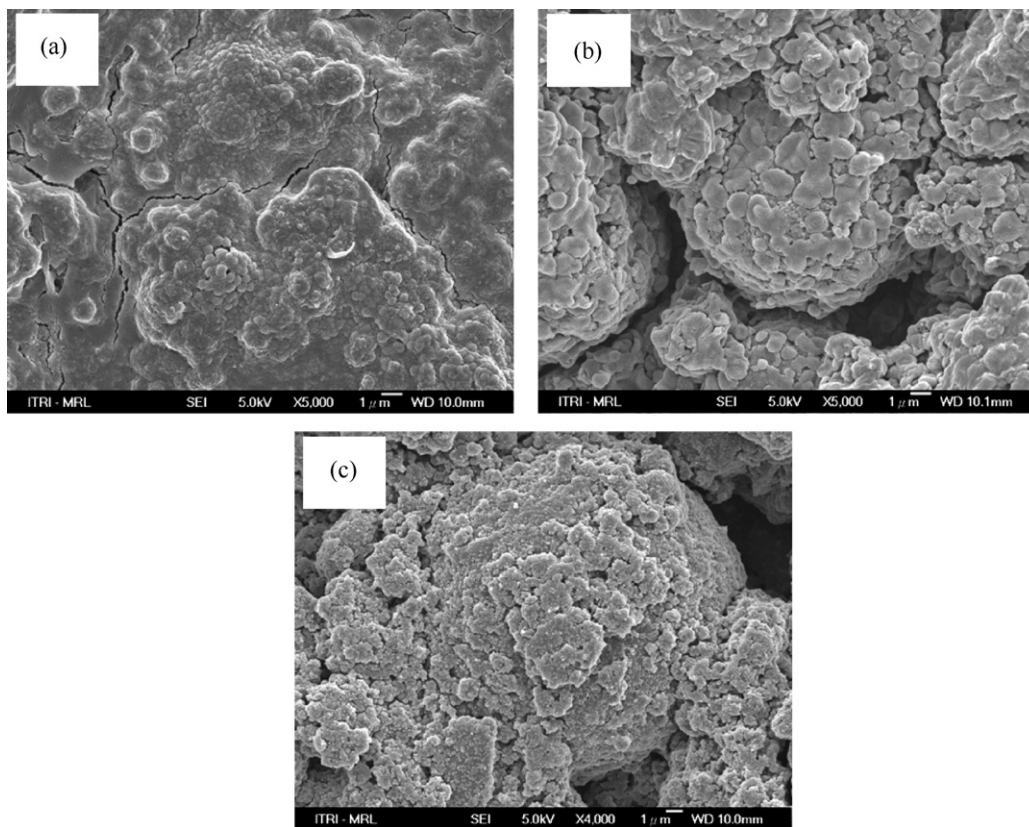
Fig. 5. SEM image of anode electrodes after 250 cycles at 55 °C with different salts: (a) 1 M LiPF$_6$; (b) 0.8 M LiBOB; (c) 0.25 M LiBOB mixed with 0.75 M LiPF$_6$.

electrolyte systems (Fig. 4(b) and (c)). For pure LiPF$_6$ electrolyte, some deposits are observed on the surface of LiMn$_2$O$_4$ (Fig. 4(a)). Similarly, a large amount of mud-like SEI was found on the anode surface in pure LiPF$_6$ electrolyte system (Fig. 5(a)), which is different in LiBOB-contained systems (Fig. 5(b) and (c)). The morphology indicates the different formation and decomposition mechanisms of passive film on electrodes in different electrolyte systems, which are contributed to the different electrochemical performance.

3.2. Fading mechanism

Since excess electrolyte has been injected in the investigated cells, pure LiBOB salt with 0.6 and 0.8 M concentration are tested to check the effect of LiBOB salt decomposition during cycling at elevated temperature. After 100 cycles at 55 °C, there is no obvious difference that can be observed in capacity retention for 0.8 and 0.6 M pure LiBOB cells. However, the capacity retention decreases to around 74% and 14% for 0.8 and 0.6 M LiBOB cells, respectively, after 250 cycles. In order to under-

stand the different fading rate after 250 cycles, the cells were discharged and adding a new electrolyte into the cells. Then the cells are performed 0.2C charge and discharge current to check the capacity recovery. Table 2 shows the capacity variation after cycles and after refilling the fresh electrolyte. There is no obvious capacity recovered after refilling the fresh electrolyte except 0.6 M pure LiBOB cell. For 0.6 M LiBOB cell, the capacity was dramatically recovered from 70 to 220 mAh. It indicates that salt decomposition plays an important role in pure LiBOB electrolyte during cycling at elevated temperature. The presence of LiPF$_6$ can inhibit the decomposition of LiBOB.

In addition, for studying the major factors of capacity fading in elevated temperature cycling, the cells were disassembled after 250 cycles and took the cathode electrode out to fabricate CR2032 coin cells for capacity check. From the results listed in Table 3, it is clear that the capacity losing is directly related to the amount of LiPF$_6$. The results confirm that the pure LiPF$_6$ salt form HF in the presence of trace of water lead to Mn dissolution and result in capacity fading in LiMn$_2$O$_4$ cells. In contrast, capacity fading of cathode electrode in pure LiBOB electrolyte

Table 2
Electrolyte effect in capacity fading (C/D current: 0.2C)

	1 M LiPF$_6$	0.1 M LiBOB/0.9 M LiPF$_6$	0.5 M LiBOB/0.5 M LiPF$_6$	0.6 M LiBOB
Old cell (mAh)	203	306	320	70
After adding new electrolyte (mAh)	203	296	313	220
Capacity recovery (%)	0	−3.3	−2.2	214.3

Table 3
Capacity check of cathode electrode after 250 cycles at 55 °C

	1 M LiPF$_6$	0.25 M LiBOB/0.75 M LiPF$_6$	0.8 M LiBOB
Capacity (mAh/electrode)	1.279	1.406	1.436
Capacity losing[*] (%)	23	16	14

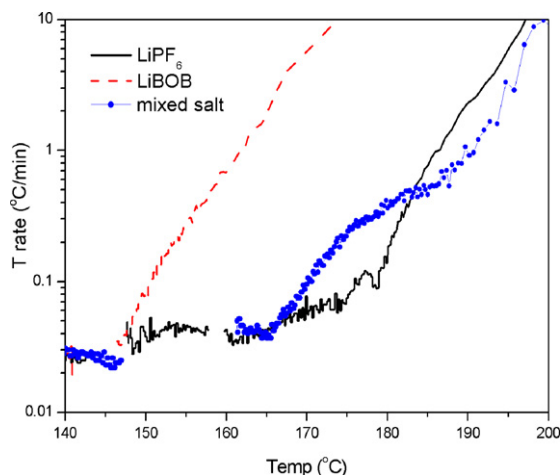[*] Originally designed capacity: 1.48 mAh/electrode.

Fig. 6. Self-heating rate vs. temperature for fully charged 18650 cells with 1 M LiPF$_6$, 0.8 M LiBOB, and 0.5 M LiBOB/0.5 M LiPF$_6$ electrolyte system.

is light after 250 cycles. And by mixing LiBOB with LiPF$_6$ as salt could effectively improve the capacity fading from cathode electrode.

In mixed LiBOB and LiPF$_6$ salts system, it could combine the advantages of decreasing Mn dissolution from LiMn$_2$O$_4$ cathode and stabilizing the LiBOB salt decomposition during elevated temperature cycling, and then enhancing the electrochemical performance.

3.3. ARC study

Accelerating rate calorimetry (ARC) has used to study the reaction between LiMn$_2$O$_4$ and 1 M LiPF$_6$, mixed 0.5 M LiBOB/0.5 M LiPF$_6$ as well as 0.8 M LiBOB electrolyte with EC/EMC solvent as electrolyte systems. The result was shown in Fig. 6. Compared to pure LiPF$_6$ electrolyte system, pure LiBOB electrolyte system shows poor thermal stability. The onset temperature of exothermic reaction in pure LiBOB electrolyte system is approximate at 145 °C, which is about 30 °C lower than that in pure LiPF$_6$ electrolyte system. This result is similar to the reaction between LiCoO$_2$ and LiPF$_6$ as well as LiCoO$_2$ and LiBOB electrolyte systems [11]. According to Dahn's study, LiBOB salt can decrease the reactivity on anode but not on cathode. It may suggest the reduction of reactivity on anode is due to a stable SEI formed on anode by LiBOB, how-

ever, no stable passive layer formed on cathode. The different morphologies on cathode and anode showed in SEM pictures also could support this explication. As mentioned above, the electrolyte component or decomposition products formed on LiMn$_2$O$_4$ surface are different in LiPF$_6$ and LiBOB electrolyte systems, such passive film interface may lead to different thermal stability against the reaction between electrolyte and electrode surface. Besides pure salt electrolytes, most importantly, the effect of mixed LiBOB and LiPF$_6$ salts on its thermal stability is significant. The onset temperature of exothermic reaction in mixed salt electrolyte system is higher than that in pure LiBOB electrolyte system, but close to pure LiPF$_6$ electrolyte system.

4. Conclusion

In this work, mixed LiBOB and LiPF$_6$ salts as electrolyte system are performed to enhance the cycleability in LiMn$_2$O$_4$ cell at elevated temperature. Effective control of the impedance increase, minimizing Mn dissolution and reducing LiBOB salt decomposition during cycling are characterized for improving the cell performance. Besides, mixed salts apparently have effect on the reactivity between LiMn$_2$O$_4$ and LiBOB electrolyte system. With the restrictions of pure LiPF$_6$ and LiBOB, the approach of mixed salt potentially enables the application of LiMn$_2$O$_4$ at high temperature environments.

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