

Short communication

# Comparison of the electrochemical properties of LiBOB and LiPF<sub>6</sub> in electrolytes for LiMn<sub>2</sub>O<sub>4</sub>/Li cells

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## Abstract

The electrochemical stability and conductivity of LiPF<sub>6</sub> and lithium bis(oxalato)borate (LiBOB) in a ternary mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC) were compared. The discharge capacities of LiMn<sub>2</sub>O<sub>4</sub>/Li cells with the two electrolytes were measured at various current densities. At room temperature, LiMn<sub>2</sub>O<sub>4</sub>/Li cells with the electrolyte containing LiBOB cycled equally well with those using the electrolyte containing LiPF<sub>6</sub> when the discharge current rate was under 1 C. At 60 °C, the LiBOB-based electrolyte cycled better than the LiPF<sub>6</sub>-based electrolyte even when the discharge current rate was above 1 C. Compared with the electrolyte containing LiPF<sub>6</sub>, in LiMn<sub>2</sub>O<sub>4</sub>/Li cells the electrolyte containing LiBOB exhibited better capacity utilization and capacity retention at both room temperature and 60 °C. The scanning electron microscopy (SEM) images and the a.c. impedance measurements demonstrated that the electrode in the electrolyte containing LiBOB was more stable. In summary, LiBOB offered obvious advantages in LiMn<sub>2</sub>O<sub>4</sub>/Li cells.

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**Keywords:** Lithium bis(oxalato)borate; Electrolyte; Salt; LiMn<sub>2</sub>O<sub>4</sub>

## 1. Introduction

Spinel lithium manganese oxide (LiMn<sub>2</sub>O<sub>4</sub>) is considered a promising cathode material for lithium secondary batteries, but its poor cyclic ability, especially at high temperatures (above 55 °C), remains a problem [1]. One of the factors is related to spinel dissolution—the electrolyte salt LiPF<sub>6</sub> will decompose at elevated temperatures. HF is generated as a product of the decomposing reaction and will dissolve manganese [2]. As a lithium salt, lithium bis(oxalato)borate (LiBOB) has some unique properties that no other lithium salt possesses. It can effectively stabilize graphite structure in pure propylene carbonate (PC) [3]. The lithium-ion cells containing the LiBOB electrolyte exhibits excellent cycling capability even at 70 °C [4]. Moreover, the dissolution of Mn in a LiBOB electrolyte is far lower than in a LiPF<sub>6</sub> one [5]. Therefore, it appears that LiBOB is a superior candidate for use in lithium cells

with LiMn<sub>2</sub>O<sub>4</sub> cathodes than LiPF<sub>6</sub>. In order to investigate thoroughly the possibility of using LiBOB in LiMn<sub>2</sub>O<sub>4</sub> batteries, in this article, the electrochemical and thermal stability of LiBOB-based electrolytes, and the rate discharge performance and cyclic ability of LiMn<sub>2</sub>O<sub>4</sub>/Li cells with LiBOB-based electrolyte were studied. The results were compared with those of LiPF<sub>6</sub>.

## 2. Experimental

### 2.1. Preparation of the cells

LiBOB was synthesized and purified in our laboratory, then dissolved in mixed solvents EC/EMC/DEC (1:1:1 by volume) to get a 0.8 mol L<sup>-1</sup> electrolyte. LiPF<sub>6</sub> was dissolved in EC/EMC/DEC (1:1:1 by volume) to get a 1 mol L<sup>-1</sup> electrolyte. Lithium manganese oxide (LiMn<sub>2</sub>O<sub>4</sub>) was employed as the cathode active material. Celgard 2400 polyethylene/polypropylene acted as the separator. All reagents were battery grade. The test cells were assembled and sealed in an Ar-filled glove box.

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## 2.2. Measurements

A CH Instrumental Electrochemical Workstation (CHI660A) with a three-electrode system incorporating a planar Al working electrode, a planar Li auxiliary electrode, and a Li foil reference electrode was used for the cyclic voltammetry (CV) at the scanning rate of  $5 \text{ mV s}^{-1}$ .

Electrochemical impedance spectroscopy (EIS) measurements were performed with a CH Instrumental Electrochemical Workstation (CHI660A) to study the impedance of the interface film between the electrolyte and the electrode. The working frequency was from 0.001 Hz to 100 kHz.

Thermogravimetric/differential thermal analysis (TG/DTA) of the electrolytes was performed on a Setaram Labsys TG/DTA Analyzer (France). The electrolytes were heated at  $5^\circ\text{C min}^{-1}$  from 25 to  $400^\circ\text{C}$  in a  $\text{N}_2$  atmosphere.

The test cells were cycled on a Land BT-10 Tester (Wuhan, China) between 3.3 and 4.35 V. The test cells all were  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells.

The test cells were dissected after testing, and their positive electrodes were taken out. The electrodes were soaked in and then rinsed with pure DEC repeatedly to remove the electrolyte. The washed electrodes were dried at room temperature, after which they were carefully transferred from the glove box to a vacuum chamber for SEM with a JSM-5600LV scanning electron microscope, JEOL.

## 3. Results and discussion

The electrochemical stabilities of the two electrolytes –  $0.8 \text{ mol L}^{-1}$  LiBOB EC/EMC/DEC (1:1:1) electrolyte and  $1 \text{ mol L}^{-1}$  LiPF<sub>6</sub> EC/EMC/DEC (1:1:1) – were investigated by cyclic voltammetry. The results were shown in Fig. 1. The result indicated that the electrochemical stability of the  $0.8 \text{ mol L}^{-1}$  LiBOB EC/EMC/DEC (1:1:1) electrolyte was higher than that of the  $1 \text{ mol L}^{-1}$  LiPF<sub>6</sub> EC/EMC/DEC (1:1:1). The current of both plots began emergent at 3.0 V versus Li/Li<sup>+</sup>. The current density of  $1 \text{ mol L}^{-1}$  LiPF<sub>6</sub> EC/EMC/DEC (1:1:1) electrolyte started to increase dramatically when the potential was higher

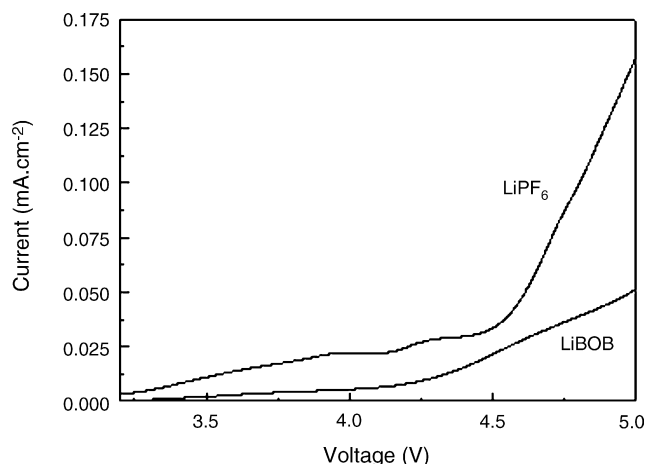


Fig. 1. Current–potential curves of different electrolytes at a scan rate of  $5 \text{ mV s}^{-1}$  at  $25^\circ\text{C}$ .

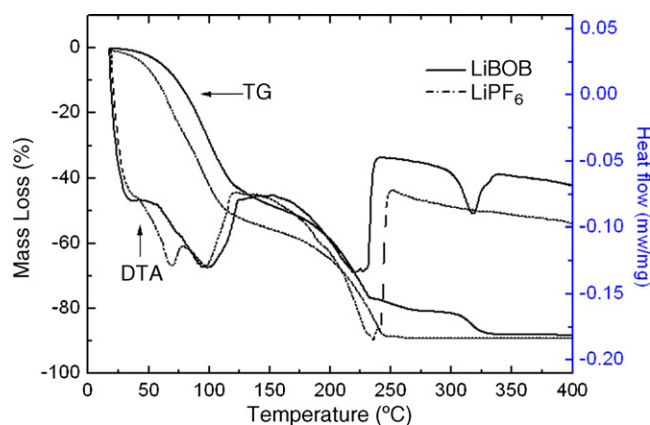


Fig. 2. The TG/DTA plots of LiBOB and LiPF<sub>6</sub> electrolyte.

than 4.5 V, while the current density of the  $0.8 \text{ mol L}^{-1}$  LiBOB EC/EMC/DEC (1:1:1) electrolyte grew more slowly and was always lower than that of the LiPF<sub>6</sub> electrolyte. The oxidation potential of the LiBOB-based electrolyte was higher than 4.3 V, the operating potential window of lithium-ion batteries. It is evident that the LiBOB-based electrolyte was quite suitable for use in lithium-ion batteries.

LiBOB possesses much better thermal stability than LiPF<sub>6</sub>, which starts to decompose at  $80^\circ\text{C}$  [5]. LiBOB would not decompose until  $300^\circ\text{C}$ . Obviously, LiBOB would have an advantage over LiPF<sub>6</sub> at high temperatures. The thermal stabilities of the two electrolytes were compared in our laboratory and the result was showed in Fig. 2. Both electrolytes have three endothermic peaks at the DTA plots. The three endothermic peaks of the LiBOB electrolyte were at 100, 230, and  $310^\circ\text{C}$ , respectively; while those of the LiPF<sub>6</sub> electrolyte were at 70, 100, and  $230^\circ\text{C}$ . The peaks at  $100^\circ\text{C}$  (of both electrolytes) were caused by the evaporation of the volatile solvents DEC and EMC, and the peaks at  $230^\circ\text{C}$  were caused by the evaporation of EC. The peak at  $310^\circ\text{C}$  corresponded to the decomposing of LiBOB, while the peak at  $70^\circ\text{C}$  corresponded to the decomposing of LiPF<sub>6</sub>. The weight loss of the LiBOB electrolyte started later than that of the LiPF<sub>6</sub> electrolyte. According to the TG and DTA analyses, the thermal stability of  $0.8 \text{ mol L}^{-1}$  LiBOB EC/EMC/DEC (1:1:1) was higher than that of  $1 \text{ mol L}^{-1}$  LiPF<sub>6</sub> EC/EMC/DEC (1:1:1).

The discharge capacities of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells with the two electrolytes were compared at various current densities. Fig. 3a shows the comparison of the discharge capacities at room temperature. The discharge capacity of the cells containing the LiBOB electrolyte was lower than that of the cell containing the LiPF<sub>6</sub> electrolyte. However, when the ambient temperature was  $60^\circ\text{C}$ , the discharge capacity of the cell with the LiBOB-based electrolyte improved greatly (Fig. 3b). At lower current densities the discharge capacity of the cell containing the LiBOB-based electrolyte was as good as the LiPF<sub>6</sub> one. At higher current densities the discharge capacity of the cell containing the LiBOB-based electrolyte was higher than that of the LiPF<sub>6</sub> one. The  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells were able to maintained the discharge capacity at  $110 \text{ mA h g}^{-1}$  even when the current density was 2C. After 25 cycles, the discharge capac-

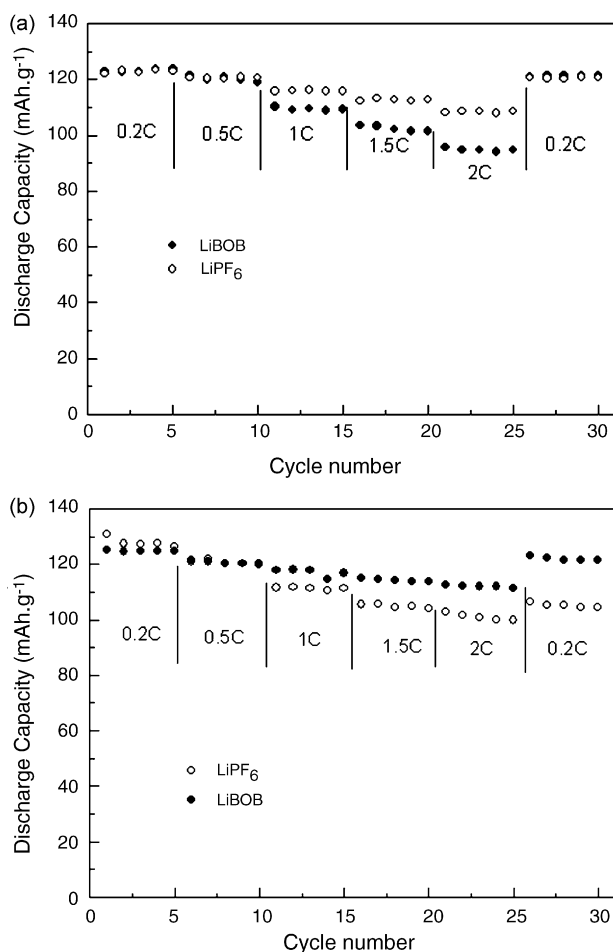


Fig. 3. (a) The discharge capacity of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells at different discharge rates at room temperature. (b) The discharge capacity of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells at different discharge rates at  $60^\circ\text{C}$ .

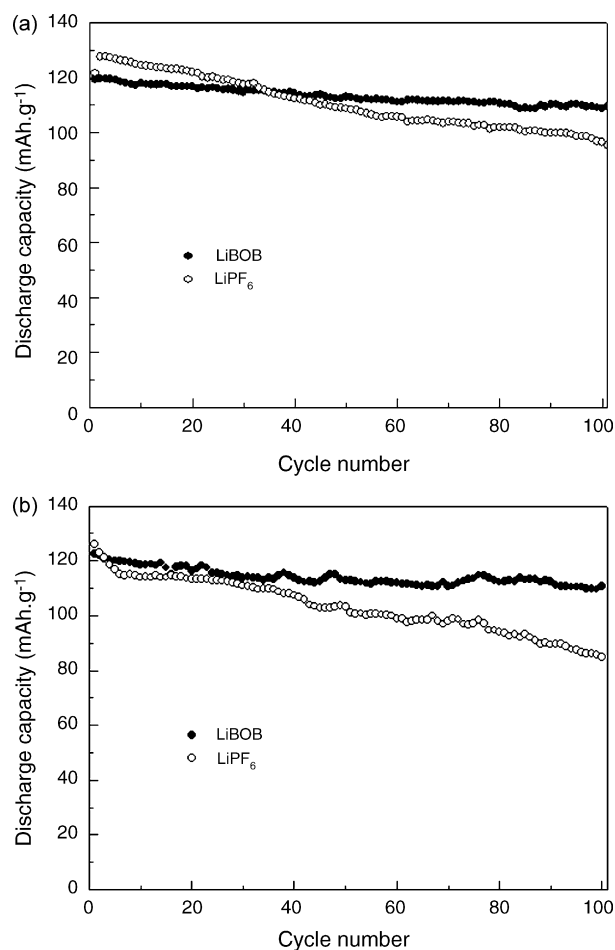


Fig. 4. (a) The discharge capacity retention of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells at 0.5 C discharge rate at room temperature. (b) The discharge capacity retention of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells at 0.5 C discharge rate at  $60^\circ\text{C}$ .

ity came back to the initial discharge capacity when the current density became 0.2 C. But the discharge capacity of the cell with the  $\text{LiPF}_6$ -based electrolyte could not maintain well. After 25 cycles, the discharge capacity was lower than that of the initial one.

Fig. 4a summarizes the capacity versus cycle number for the cells containing  $\text{LiBOB}$  and  $\text{LiPF}_6$  as electrolyte salts at room temperature. Each cell was tested for 100 cycles in order to observe the capacity fade clearly. In the first 30 cycles or so, the electrolyte with  $\text{LiPF}_6$  showed better electrode utilization. Between the 30th and the 100th cycle, the cell containing  $\text{LiPF}_6$  started to show fading capacity, while the  $\text{LiBOB}$ -based electrolyte maintained constant capacity up to 100 cycles, and the gap between the two widened as the cycle number increased. After 100 cycles the capacity retention efficiencies were 91.7% and 79.3% for  $\text{LiBOB}$  and  $\text{LiPF}_6$ , respectively. The difference in the performance of the two cells with the two electrolytes was more pronounced when the cells were placed into the elevated temperature of  $60^\circ\text{C}$ , as shown in Fig. 4b. The  $\text{LiPF}_6$ -based cell experienced a rapid deterioration. (The same phenomenon can be observed for almost any cells with  $\text{LiPF}_6$  cycled at elevated temperatures.) For the cell containing  $\text{LiBOB}$ , a rather encour-

aging result emerged: the fading rate in the capacity for the  $\text{LiBOB}$ -based cell was very low. After 100 cycles, the capacity retention was 90.5%, which was much higher than the 67.3% of the cell containing  $\text{LiPF}_6$ .

It was assumed that the difference in the behavior of the two electrolytes at room temperature and  $60^\circ\text{C}$  was due to the difference in the stability of the cathode material in the electrolytes. Amine et al. [5] has demonstrated that the concentration of Mn dissolved from  $\text{LiMn}_2\text{O}_4$  powders stored in a  $\text{LiPF}_6$ -based electrolyte at  $55^\circ\text{C}$  for 4 weeks was 64 ppm, while it was only 0.05 ppm in a  $\text{LiBOB}$ -based electrolyte. The result of SEM also showed that the  $\text{LiMn}_2\text{O}_4$  electrode was more stable in the  $\text{LiBOB}$  electrolyte than in the  $\text{LiPF}_6$  electrolyte. Fig. 5 shows the SEM images of the  $\text{LiMn}_2\text{O}_4$  electrode in the  $\text{LiBOB}$ -based electrolyte and the  $\text{LiPF}_6$ -based electrolyte after 30 cycles at  $60^\circ\text{C}$ . The SEM image of the  $\text{LiMn}_2\text{O}_4$  electrode in the  $\text{LiBOB}$ -based electrolyte showed a smooth surface, accompanied by fine particles. In contrast, on the surface of the electrode in the  $\text{LiPF}_6$ -based electrolyte, there were large particles and large gaps among them. This indicated that the  $\text{LiBOB}$  electrolyte was not able to erode the electrode, thus allowing cells containing  $\text{LiBOB}$  salt to work satisfactorily at elevated

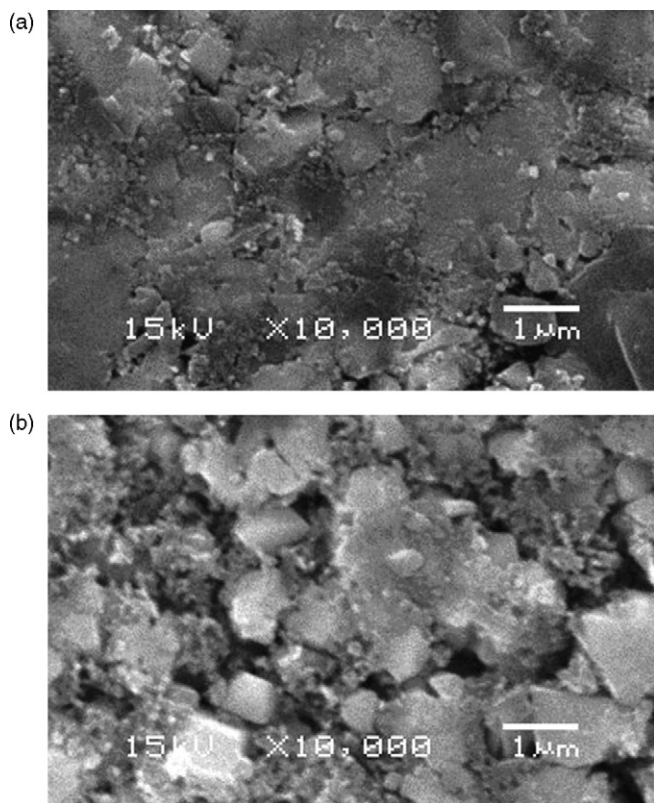


Fig. 5. SEM images of the  $\text{LiMn}_2\text{O}_4$  electrode in two electrolytes (a) in LiBOB-based electrolyte (b) in  $\text{LiPF}_6$ -based electrolyte.

temperatures; whereas, the electrode would be dissolved in the  $\text{LiPF}_6$  electrolyte in the same temperature range.

In order to understand the resistance of the interface film formed on the cathode surface in the LiBOB electrolyte, the impedances of the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells were measured. Fig. 6 gives the Cole–Cole plots of the cells containing the two different electrolytes. The locus of each of the Cole–Cole plots of the freshly assembled cells consisted of two distinct regions, i.e., a semi-arc in the high frequency region and a sloping line in the low frequency region. The locus of each of the

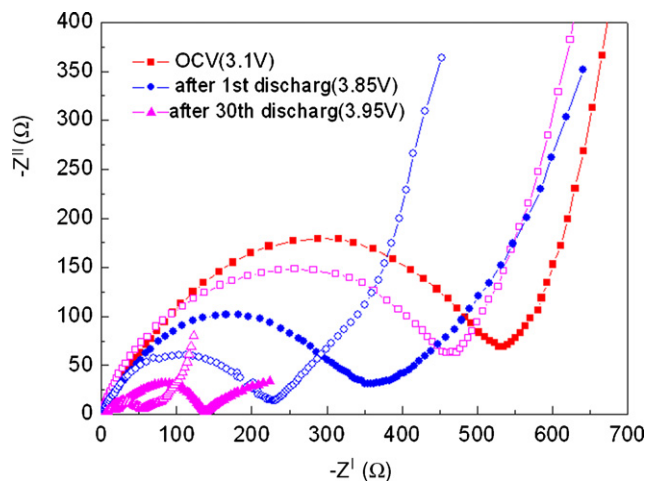


Fig. 6. The a.c. impedance spectra for  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells at 0.5 C discharge rate at 30 °C. LiBOB (solid)  $\text{LiPF}_6$  (hollow).

Cole–Cole plots of the cells after one cycle (and those after 30 cycles) consisted of two overlapping semicircles at the high and medium frequency ranges, and a sloping line at the low frequency range. These represented, respectively: the resistance and capacitance of the interface film formed on the cathode surface, the charge-transfer resistance, the double-layer capacitance and the Warburg impedance arising from the semi-infinite diffusion of the lithium ions in the electrode. One can easily see that the radius of the first semicircle of the cell containing the LiBOB electrolyte was bigger than that of the cell containing the  $\text{LiPF}_6$  electrolyte at either open circuit voltage or later cycles. This indicated that the resistance of the interface film of the cell containing the LiBOB electrolyte was higher than that of the cell containing the  $\text{LiPF}_6$  electrolyte. This further implied that the surface film in the LiBOB electrolyte was thicker and more stable than that in the  $\text{LiPF}_6$  electrolyte. This may be the reason why the  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells containing LiBOB had better capacity retention and performance at lower discharge rates. In short, the poor performance of the cell containing the LiBOB electrolyte at high discharge rates was closely related to two factors. One was the low conductivity of the LiBOB electrolyte and the other was the high resistance of the interface film in the LiBOB electrolyte.

#### 4. Conclusions

The electrochemical stability and thermal stability of the 0.8 mol  $\text{L}^{-1}$  LiBOB EC/EMC/DEC (1:1:1 by volume) electrolyte was higher than that of the 1 mol  $\text{L}^{-1}$   $\text{LiPF}_6$  EC/EMC/DEC (1:1:1 by volume) electrolyte. When used in  $\text{LiMn}_2\text{O}_4/\text{Li}$  cells, the rate capability of the LiBOB-based electrolyte was lower than that of the  $\text{LiPF}_6$ -based electrolyte at room temperature. However, at 60 °C the LiBOB-based electrolyte cycled better than the  $\text{LiPF}_6$ -based electrolyte even when the current density was higher than 1 C, due to the good thermal stability of LiBOB. The LiBOB-based cell maintained stable performance at both room temperature and 60 °C. The SEM result and the a.c. impedance analysis indicated that the  $\text{LiMn}_2\text{O}_4$  electrode was more stable in the LiBOB-based electrolyte than in the  $\text{LiPF}_6$ -based electrolyte. Overall, LiBOB was more suitable than  $\text{LiPF}_6$  as electrolyte salts that are used with  $\text{LiMn}_2\text{O}_4$  electrodes, especially at elevated temperatures.

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