



# Investigation of the synergetic effects of LiBF<sub>4</sub> and LiODFB as wide-temperature electrolyte salts in lithium-ion batteries

Lijuan Zhang<sup>1,2,3,4</sup> · Yanxia Sun<sup>1,2,3</sup> · Yuan Zhou<sup>1,2</sup> · Chunxi Hai<sup>1,2</sup> · Shuqing Hu<sup>4</sup> · Jinbo Zeng<sup>1,2</sup> · Yue Shen<sup>1,2</sup> · Shengde Dong<sup>1,2,3</sup> · Guicai Qi<sup>1,2,3</sup> · Faqiang Li<sup>1,2,5</sup>

Received: 8 November 2017 / Revised: 27 December 2017 / Accepted: 22 January 2018 / Published online: 2 February 2018  
© Springer-Verlag GmbH Germany, part of Springer Nature 2018

## Abstract

Herein, we present the use of lithium tetrafluoroborate (LiBF<sub>4</sub>) as an electrolyte salt for wide-temperature electrolytes in lithium-ion batteries. The research focused on the application of blend salts to exhibit their synergistic effect especially in a wide temperature range. In the study, LiCoO<sub>2</sub> was employed as the cathode material; LiBF<sub>4</sub> and lithium difluoro(oxalate)borate (LiODFB) were added to an electrolyte consisting of ethylene carbonate (EC), propylene carbonate (PC), and ethyl methyl carbonate (EMC). The electrochemical performance of the resulting electrolyte was evaluated through various analytical techniques. Analysis of the electrical conductivity showed the relationship among solution conductivity, the electrolyte composition, and temperature. Cyclic voltammetry (CV), charge-discharge cycling, and AC impedance measurements were used to investigate the capacity and cycling stability of the LiCoO<sub>2</sub> cathode in different electrolyte systems and at different temperatures. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were applied to analyze the surface properties of the LiCoO<sub>2</sub> cathode after cycling. The results indicated that the addition of a small amount of LiODFB into the LiBF<sub>4</sub>-based electrolyte system (LiBF<sub>4</sub>/LiODFB of 8:2) may enhance the electrochemical performance of the LiCoO<sub>2</sub> cell over a relatively wide temperature range and improve the cyclability of the LiCoO<sub>2</sub> cell at 60 °C.

**Keywords** Lithium-ion batteries · Lithium tetrafluoroborate · Lithium difluoro(oxalate)borate · Wide temperature · Blend salts

## Introduction

Lithium-ion batteries (LIBs) have advantages, such as a high discharging platform, large power and energy density, a long cycling life, no memory effect, and being environmentally

friendly [1, 2]. LIBs are widely used in small appliances, such as portable mobile devices and digital terminals, large power storage stations, space technologies, and in the area of traffic and transportation [3]. However, their utilization in electric automobiles has been hindered by the relatively narrow application temperature range [2]. Thus, in order for LIBs to be successfully applied in other fields of technology, the application temperature range of the LIBs must be broadened. A major contributor to this limitation is the electrolyte, which is one of the three essential elements of LIBs. LIB electrolytes currently available on the market have application temperature range of –20 and 60 °C and show a significantly lower capacity outside these temperatures [4, 5]. Ongoing attempts to broaden their working temperature range mostly focus on improvements of the solvent system [6, 7] and the use of lithium salts [7–10].

Currently, the most commonly used commercial electrolyte is a carbonate solvent system mixed with lithium hexafluorophosphate (LiPF<sub>6</sub>) salt. While the LiPF<sub>6</sub>-based electrolyte system has a relatively high conductivity and can form a stable solid electrolyte interface (SEI) [11], it is also moisture sensitive and thermally unstable.

✉ Yuan Zhou  
zhouyuan1613@163.com

<sup>1</sup> Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, 18th Xinning Road, Xining 810008, China

<sup>2</sup> Key Laboratory of Salt Lake Resources Chemistry of Qinghai Province, Qinghai, China

<sup>3</sup> University of Chinese Academy of Sciences, Beijing 100049, China

<sup>4</sup> College of Chemistry and Chemical Engineering, Qinghai University for Nationalities, Xining 810007, China

<sup>5</sup> Qinghai Research Center of Low-temperature Lithium-ion Battery Technology Engineering, Qinghai LCD New Energy Technology Co. Ltd., Xining 810000, China

When exposed to high temperature,  $\text{LiPF}_6$  decomposes into lithium fluoride ( $\text{LiF}$ ) and phosphorus pentafluoride ( $\text{PF}_5$ ) and  $\text{PF}_5$  readily hydrolyzes to form  $\text{HF}$  reacting with trace amount of water. The two products,  $\text{PF}_5$  and  $\text{HF}$ , can then react with the cathode and anode of the LIBs, leading to reduced cell performances [12, 13]. Thus, in order to circumvent these disadvantages, it is crucial that a new and optimized electrolyte system is invented.

Even though the electrolyte system based on  $\text{LiBF}_4$  shows great potential, it is not widely applied because of its susceptibility to hydrolysis, relatively low conductivity, and hindered SEI formation [14]. However, compared to the currently used  $\text{LiPF}_6$  system,  $\text{LiBF}_4$  has several advantages. Zhang et al. reported that although  $\text{LiBF}_4$  has lower conductivity than  $\text{LiPF}_6$  at low temperature, it displays better performance because it has a lower electric charge transfer ( $R_{ct}$ ) than  $\text{LiPF}_6$ . In addition,  $\text{LiBF}_4$  is less moisture sensitive and has comparable cycling properties to  $\text{LiPF}_6$  at room temperature [11, 15]. All of these properties make  $\text{LiBF}_4$  a more suitable system for low-temperature applications. In contrast, the application of  $\text{LiBF}_4$  in high-temperature environments represents a challenge. Even though  $\text{LiBF}_4$  has better thermal stability than  $\text{LiPF}_6$  [16], which allows it to be applied in high-temperature environments, it exhibits poor film-forming performance. The increase in temperature of the  $\text{LiBF}_4$ -based electrolyte system causes a rapid decrease in the LIB capacity, which leads to a large reduction in the coulombic efficiency of the battery [11]. Thus, in order for  $\text{LiBF}_4$  to be applied to wide-temperature electrolytes, there are a few important changes that need to be made. First, the film-forming performance of  $\text{LiBF}_4$  needs to be improved, and second, the conductivity of the electrolyte should be increased so that its performance at high and low temperatures can be enhanced.

Lithium difluoro(oxalato)borate ( $\text{LiODFB}$ ) is a novel lithium salt, which has properties that are similar to both lithium bis(oxalato)borate ( $\text{LiBOB}$ ) and  $\text{LiBF}_4$ . It exhibits very good film-forming performance, which may lead to the inhibition of PC co-intercalation in graphite and the formation of a stable SEI at high temperature [17, 18]. Additionally,  $\text{LiODFB}$  electrolyte maintains high conductivity within a relatively wide temperature range. The novel lithium salt is compatible with nearly all common cathode materials, including  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiFePO}_4$ , and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ , and assembled cells can realize stable cycling without significant fade at 60 °C [8, 18–21].

Currently,  $\text{LiODFB}$  is used as a lithium salt additive that improves the performance of cells. A small addition of  $\text{LiODFB}$  into  $\text{LiPF}_6$  not only ensures the formation of an effective SEI but also greatly increases the capacity retention and life of the cell. Moreover, it leads to the significant decrease of the capacity fade of LIBs at high temperatures [8]. Monikowska et al. [15] pointed out that  $\text{LiODFB}/\text{LiBF}_4$ -based electrolytes display high conductivity in a solution of

$\text{EC}/\text{PC}/\text{DMC}$  (1:1:3,  $v/v/v$ ) at room temperature, which enhances the cycling performance of the cells. Based on these results, we propose the use of blend salts to employ their synergistic effects on the LIBs in an effort to broaden the application temperature range of the electrolyte. In this work, we attempted to extend the lower limit of the application temperature of the electrolyte. PC was the solvent of choice for this study, due to its low melting point (−48.8 °C). Additionally, fluoroethylene carbonate (FEC) [22, 23], a film-forming additive, was applied in combination with  $\text{LiODFB}$  in order to explore its synergistic effect in forming a stable interfacial protection film at the surface of the electrode.

## Experimental

### Preparation of the electrolyte

The battery grade  $\text{LiBF}_4$ ,  $\text{LiODFB}$ ,  $\text{LiPF}_6$ , PC, EC, EMC, and FEC were purchased from Guangzhou Tinci Materials Technology Co., Ltd., China. All electrolytes were prepared in an argon-filled glove box (LG1200/750TS, Vigor Gas Purification Technology (Suzhou Co., Ltd., China)) with water and oxygen content lower than 1 ppm. First, PC and EMC with a volume ratio of 1:3 were mixed. Since EC is a solid at room temperature, it was heated to dissolve. Part of the liquefied EC was added to PC/EMC solution, and the resulting solution had a volume ratio of 1:1:3 (PC/EC/EMC). The lithium salts,  $\text{LiBF}_4$  and  $\text{LiODFB}$ , were then added to the formed mixture. Add FEC, which accounts for 5% (weight ratio) of the above electrolyte to improve the cycling stability of the cell. The electrolyte consisted of 1 M (1-x)  $\text{LiBF}_4$ -x $\text{LiODFB}$  (x is the molar ratio of  $\text{LiODFB}$  in the  $\text{LiBF}_4$ - $\text{LiODFB}$  mixture). An electric conductivity meter (Smart tester CPC-505, Germany) was used to measure the electric conductivity of the prepared electrolyte system in the temperature range of −40 to 60 °C. The high- and low-temperature environments were controlled using a high-low temperature test box made by Shanghai Linpin Instrument Stock Co., Ltd., China.

### Cell assembly

The cathode material  $\text{LiCoO}_2$ , Super P, and the adhesive (polyvinylidene fluoride, PVDF) were mixed in a weight ratio of 8:1:1. A solution of N-methylpyrrolidone (NMP) was added, and the mixture was ball milled. The slurry was spread out on aluminum foil and dried at 120 °C under vacuum for 12 h. After being pressed at 10 MPa, the aluminum foil coated with the slurry was cut into cathode plates with a 12 mm diameter. The  $\text{LiCoO}_2$  cathodes were assembled in CR2025-type coin cells with lithium metal as a counter electrode

separated by a Celgard 2400 separator. The prepared electrolytes were injected in cells accordingly.

## Electrochemical performance

CV and electrochemical impedance spectroscopy (EIS) measurements were performed in order to evaluate the electrochemical stability of the electrode. CV and EIS were carried out in cells with three electrodes: LiCoO<sub>2</sub> electrode served as the working electrode and a lithium metal disk was applied as a counter and reference electrode. CV test was performed with a scan rate of 0.1 mV s<sup>-1</sup> and scanning voltage ranging from 2.5 to 5.0 V, and EIS was performed at a frequency range from 0.1 to 10<sup>5</sup> Hz and amplitude of 5 mV using an electrochemical workstation (Princeton, PARSTAT MC). The LAND CT2001A battery test system (Wuhan, China) was applied to test the charge-discharge performance of the LiCoO<sub>2</sub>/Li half cells at 25, -20, and 60 °C, between 3 and 4.2 V (vs. Li/Li<sup>+</sup>). The button cells were cycled twice at the rate of 0.1 C, and then, cycling tests were carried out at the rate of 1 C.

## Characterization of the electrode/electrolyte Interface

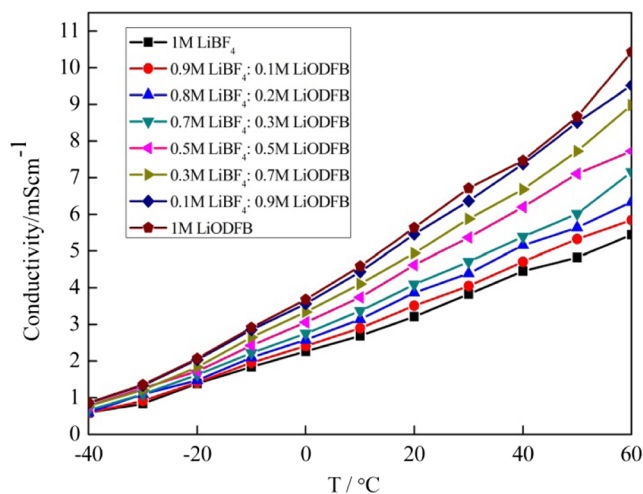
The morphology and composition of the film on the cathode surface were investigated by cycling it in different electrolytes. The cycled cells were disassembled in the glove box, and the residual electrolyte on the cathode surface was washed off repeatedly with dimethyl carbonate (DMC). The cathodes were dried at 50 °C under vacuum for 2 h, and their morphology was examined with a field emission scanning electron microscopy (FESEM, Hitachi SU8010, Japan). X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos Analytical Ltd.) was used to analyze the composition of the film on the cathode surface.

## Results and discussions

### Ionic conductivity

Conductivity is an important parameter to measure the performance of an electrolyte, and it determines the internal resistance and rate of an electrode. Figure 1 shows the ionic conductivity of the electrolytes at different concentrations of blended salts in a temperature range of -40 to 60 °C.

The results showed temperature- and concentration-dependent conductivity of different electrolyte systems. It is evident that the conductivity of the electrolyte increased significantly proportional to the rising temperature. This was due to the decreased viscosity of the electrolyte and increased transfer rate of Li<sup>+</sup> [24]. Meanwhile, the conductivity of the electrolyte increased proportionally to the rising LiODFB concentration causing the pure LiODFB-based electrolyte to have

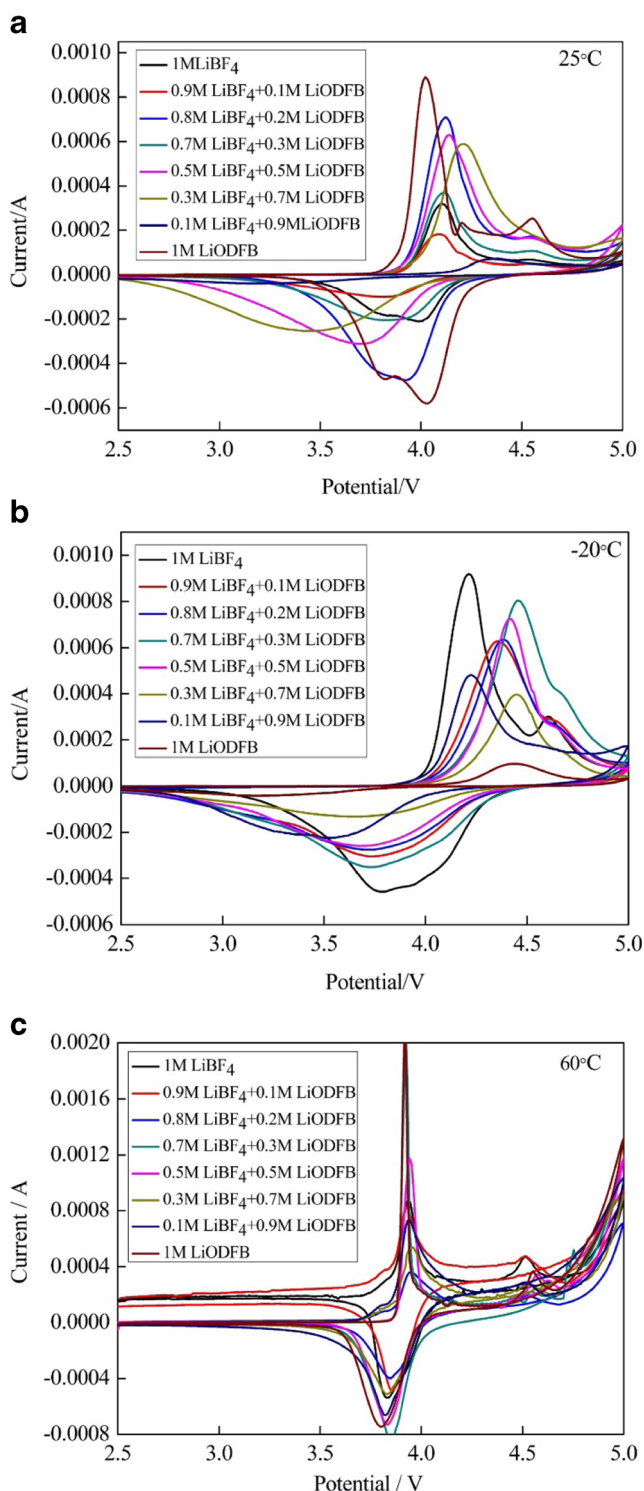


**Fig. 1** Conductivity of different electrolyte systems at different temperatures

the highest conductivity. This phenomenon may be ascribed to the fact that LiODFB has a greater anionic radius and less ionic association than LiBF<sub>4</sub> in the PC/EC/EMC (1:1:3, v/v) + FEC (5%) solution system. However, this trend is not apparent at low temperatures. This is because the viscosity of the electrolyte is directly proportional to the size of the anion. The larger radius of ODFB<sup>-</sup> in comparison to BF<sub>4</sub><sup>-</sup> causes LiODFB to have a higher viscosity than BF<sub>4</sub><sup>-</sup>, which causes the reduced conductivity of the electrolyte [25]. In other words, LiBF<sub>4</sub>-containing electrolyte systems exhibit a preferable conductivity property at low temperature. This result is consistent with that reported by Zhang [26]. In conclusion, LiODFB can enhance both the conductivity and the viscosity of LiBF<sub>4</sub>-based electrolytes. We should optimize ratio of the two lithium salts, so that the cells have the best electrochemical performance.

### The CV of LiCoO<sub>2</sub>/Li half cell

Figure 2a–c presents CV curves of LiCoO<sub>2</sub>/Li half cells, assembled using the electrolytes prepared in this paper, at 25, -20, and 60 °C, respectively. All CV curves displayed an apparent pair of redox peaks. At 25 °C (Fig. 2a), the pure LiBF<sub>4</sub>-based electrolyte had the smallest. Considering the results at this temperature, the rise in concentration of LiODFB led to an increase of the potential difference. Moreover, the results indicate that as the concentration of LiODFB increases, the reversible performance of the cell declines. The reason behind this phenomenon can be related to the decomposition of LiODFB into the film on the electrode surface. Due to the fact that LiODFB has good film-forming properties, it can form a dense and effective interfacial protection film on the surface of the electrode with a small amount of decomposition. This film could enhance the cycling stability of the cell, but it could also induce an increase in the interfacial resistance of the cell [27].



**Fig. 2** The CV curves of LiCoO<sub>2</sub>/Li cells in different electrolyte systems at different temperatures **a** 25 °C, **b** -20 °C, and **c** 60 °C

When the temperature was reduced to -20 °C, as illustrated in Fig. 2b, the oxidation and reduction peaks of the cells exhibited a significant shift in potential. More specifically, the oxidation peak shifted to a higher voltage and the reduction peak to a lower voltage. Also, the difference in the voltage

levels increased significantly. The fact that this change was more pronounced in the pure LiODFB electrolyte indicates that the reversible performance of the cell may be affected to a greater extent by the decomposition products of LiODFB at lower temperature. Furthermore, the lower temperature caused a decrease in the peak intensities and increase in peak widths. This indicated that the reversible intercalation and deintercalation of the Li<sup>+</sup> into or out of the LiCoO<sub>2</sub> cathode are hindered due to weakening dynamic factors [28].

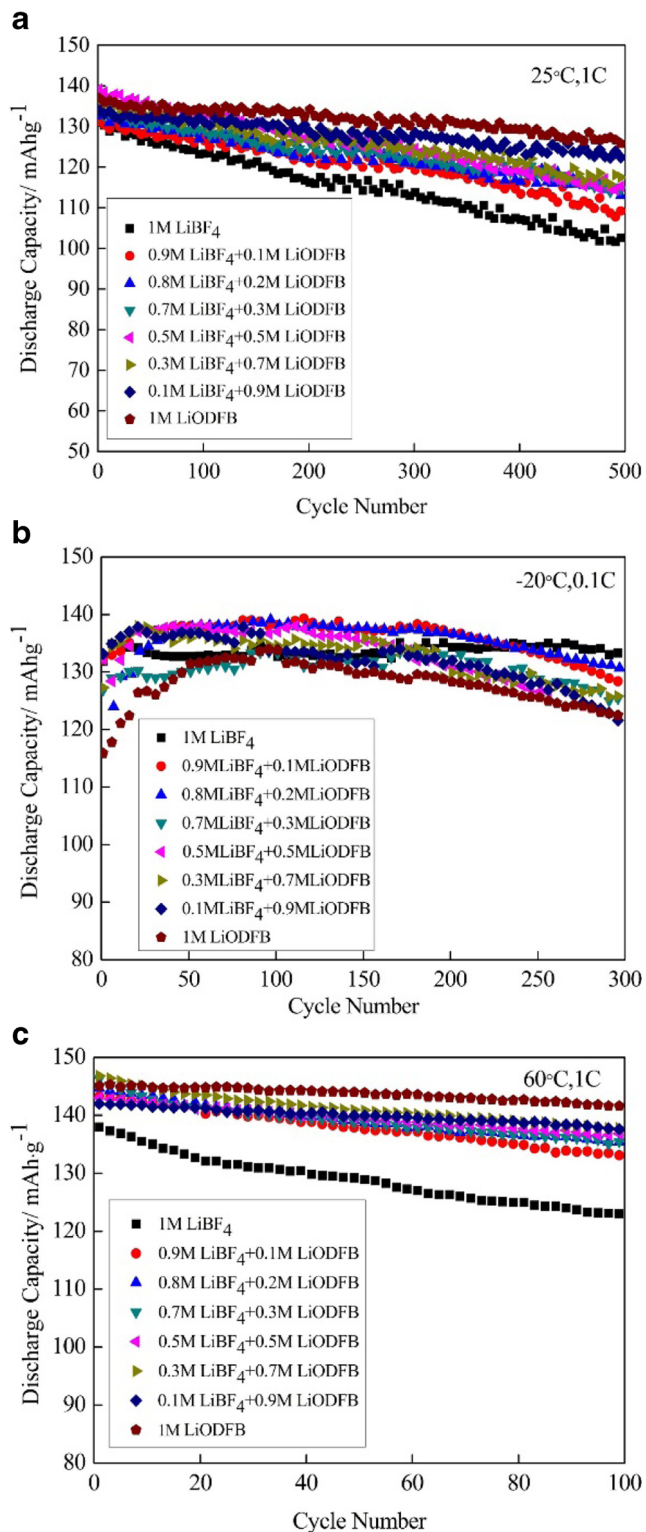
At 60 °C (Fig. 2c), the potential difference in the oxidation and reduction peaks in each electrolyte system was relatively small. This indicated that the LiCoO<sub>2</sub>/Li cells exhibit good dynamic properties at high temperature. The pure LiBF<sub>4</sub> electrolyte system at this temperature showed relatively small peak intensity and rather wide peak width. The addition of a small amount of LiODFB to the system led to a further decrease in the potential difference in the oxidation and reduction peaks. This can be contributed to the fact that at the higher temperature, LiODFB enhances the conductivity of the electrolyte, which improves the cycling performance of the cell.

The results from the CV measurements in different temperatures indicated that LiBF<sub>4</sub>/LiODFB lithium salt mixture combines the good low-temperature performance of LiBF<sub>4</sub> and good high-temperature performance of LiODFB. This demonstrates the good synergistic effect created from the combination of different lithium salts.

### The cycling performance of the LiCoO<sub>2</sub>/Li cell

The loss in capacity of LIBs in the cycling process is due to the loss of Li<sup>+</sup>, caused by the formation and growth of the SEI film. Additionally, capacity loss was caused by the gradual increase in interfacial resistance between the electrode and electrolyte during the charge-discharge process of the cells [29]. Figure 3 shows the cycling performances of the LiCoO<sub>2</sub>/Li half cells in different electrolytes at different rates (1, 0.1, and 1 C) and temperatures (25, -20, and 60 °C).

The LiCoO<sub>2</sub>/Li cells in pure LiBF<sub>4</sub>-based electrolyte exhibited a significant fade and relatively low capacity after cycling at 25 and 60 °C (Fig. 3a, c). However, as the concentration of LiODFB increased, the capacity and cycling performance of the cell significantly improved. Following this trend, the best performance was measured in the pure LiODFB-based electrolyte. The capacity retention efficiencies of the cells with pure LiBF<sub>4</sub>-based and LiBF<sub>4</sub>/LiODFB (8:2)-based electrolyte were 77.86 and 87.5%, respectively, after 500 cycles at 25 °C and 89.13 and 93.50%, respectively, after 100 cycles at 60 °C. The increase in efficiency could be contributed to the fact that LiODFB significantly increased the conductivity of the electrolyte and enhanced the stability of the interface film. This, in turn, improved the discharge capacity and cycling stability of the electrolyte.



**Fig. 3** Cycling curves of the LiCoO<sub>2</sub>/Li cells with different electrolyte systems at different temperature **a** 25 °C, **b** –20 °C, **c** 60 °C

The cycling performances of LiCoO<sub>2</sub>/Li half cells in different electrolytes at –20 °C are displayed in Fig. 3b. The results indicate that the pure LiBF<sub>4</sub> and mixed-lithium salts system exhibit better cycling performance than the LiODFB-

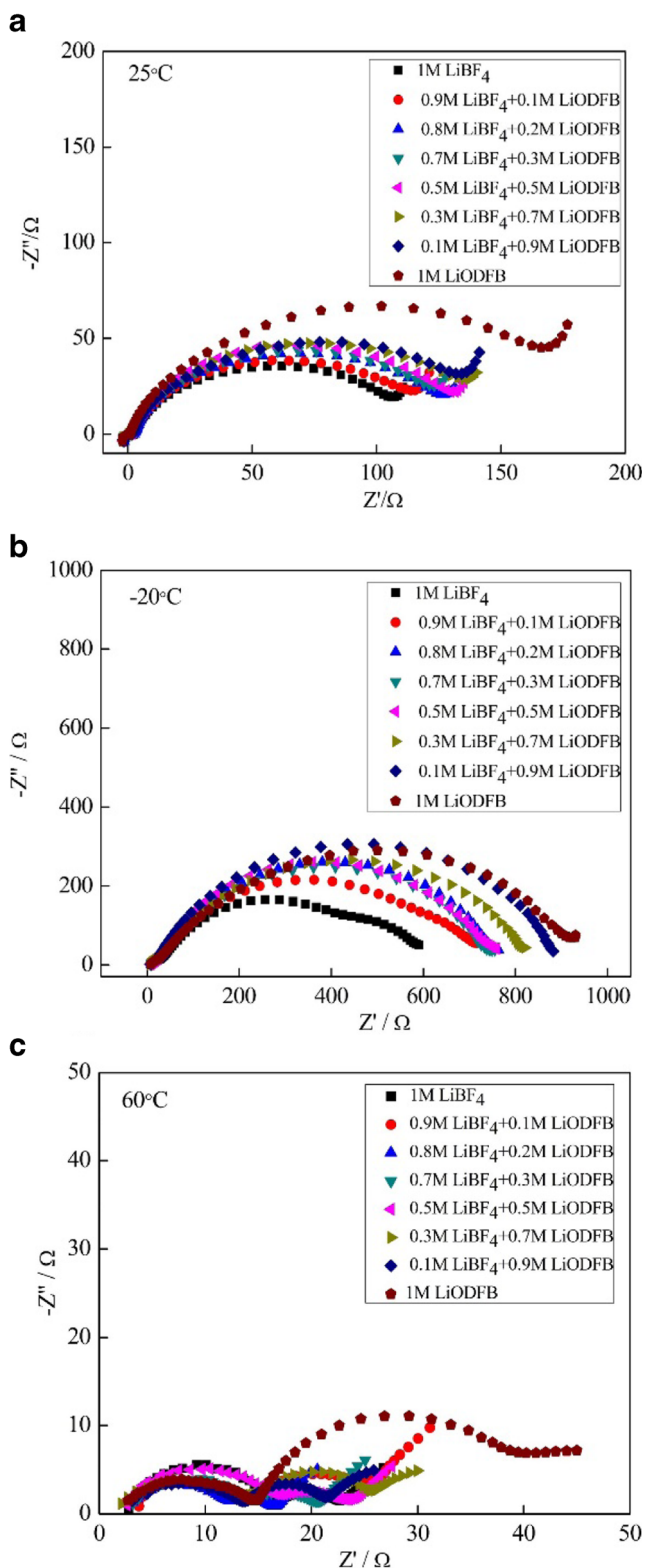
based electrolyte. After 300 cycles, the LiBF<sub>4</sub>-based and LiBF<sub>4</sub>/LiODFB (8:2)-based electrolytes showed an excellent cycling stability and capacity efficiencies of 94.64 and 98.67%, respectively. Conversely, the capacity of the LiODFB-based electrolyte decreased severely and the efficiency was merely 89.47%. This change was due to the thick electrode interfacial film that was formed by LiODFB, which caused a severe electrode polarization and destroyed the cycling stability of the cell. This effect is consistent with the phenomenon observed in the CV measurements at the low temperature. The results from the cycling performance showed that the LiBF<sub>4</sub>/LiODFB(8:2)-based electrolyte displays a good cycling performance at wide temperature range. This implies that a small amount of LiODFB increases the conductivity of the electrolyte, which makes it easy to form a dense and stable interface film.

**The EIS of the LiCoO<sub>2</sub>/Li cell**

The internal resistance of a cell is a key parameter of performance of LIBs. The internal resistance affects the power and discharge rate of a cell. Moreover, it evaluates the internal structure of a cell and the characteristics of the interface between an electrode and electrolyte. By testing the fully charged LiCoO<sub>2</sub>/Li half cells assembled with different electrolytes, via the AC impedance method, the influence of the working temperature on the electrochemical process of the cell can be further analyzed, and the results are shown in Fig. 4.

The semi-cycles in the high-frequency zone represent the resistance of the surface films on the cathode and anode (R<sub>f</sub>), which reflects the migration of Li<sup>+</sup> on the film surface. The middle-frequency zone was assigned to R<sub>ct</sub>, which reflects the migration of Li<sup>+</sup> on the surface of the active material. The inclined line in the low-frequency represents the Warburg resistance (Z<sub>w</sub>), which represents the diffusion of Li<sup>+</sup> inside the active material, and its slope is the diffusion rate of Li<sup>+</sup> in the electrode material [30]. The cell resistance of pure LiBF<sub>4</sub>-based electrolyte was the lowest (Fig. 4). However, as the concentration of LiODFB increased, the resistance of the cells became higher. Following this trend, the cell with pure LiODFB-based electrolyte exhibited the highest resistance. This effect was due to the fact that LiODFB was preferentially oxidized on the electrode surface and formed a thick interfacial film, which increased the cell resistance.

At 25 °C (Fig. 4a), the rise in LiODFB concentration did not cause a significant increase in the resistance. This is mainly due to fact that the cell resistance does not have a large impact on the discharge capacity and cycling stability at room temperature. These results were consistent with the ones obtained in the cycling performance tests. Therefore, it is evident that pure LiODFB-based electrolyte has good performances. In other words, a high conductivity electrolyte shows



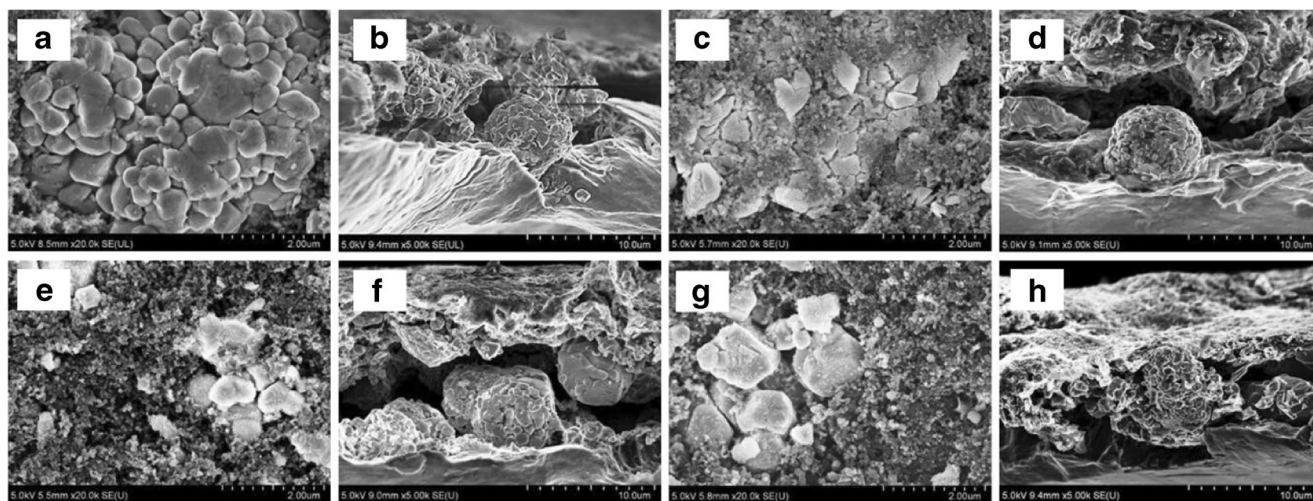
**Fig. 4** AC impedance spectra of the  $\text{LiCoO}_2$  cathode with different electrolyte systems at different temperature **a** 25 °C, **b** -20 °C, **c** 60 °C

relatively good discharge capacity and cycling stability at room temperature. At lower temperature ( $-20\text{ }^\circ\text{C}$ ), in contrast, the resistance increased significantly as the amount of

$\text{LiODFB}$  increased (Fig. 4b). In this case, the electrochemical performance of the cell was mainly determined by the resistance. This result was consistent with the results from the CV and cycling performance measurements. Consequently, the increase in the concentration of  $\text{LiODFB}$  improved the conductivity of the electrolyte. However, it also increased the electrochemical resistance, which affected the discharge capacity of the cell at low temperatures. At higher temperature ( $60\text{ }^\circ\text{C}$ ), the resistance of the cell decreased significantly, which indicated that the resistance of  $\text{Li}^+$  migration is relatively low (Fig. 4c). In this case, the electrochemical performance may be affected by both the conductivity of the electrolyte and the interfacial resistance.

### Morphology and composition analysis of the $\text{LiCoO}_2$ cathode surface

The complete passivation of the electrode surface and the formation an interfacial film with good  $\text{Li}^+$  transfer properties are key factors that influence wide temperature performance of LIBs [10]. The oxidation effect of solvent molecules on the surface of the cathode at room temperature is often very weak. Thus, the thickness of the film on the cathode surface is much thinner than the SEI film on the anode surface. However, the oxidation reaction rate may drastically increase during the process of storage or in the presence of high temperature, which would lead to the more oxidation products. In this case, the thickness of the cathode interfacial film would be similar to that of the SEI film. This, in turn, has a crucial effect on the cycling stability of the cathode [10]. Therefore, the impact of different electrolyte systems on the  $\text{LiCoO}_2$  cathode at high temperature was investigated. SEM was used to obtain scanning measurements of the surface and cross-sectional of the cathode after 100 cycles at  $60\text{ }^\circ\text{C}$  (Fig. 5). SEM images of the surface and cross-section of the uncycled cathode showed smooth and clean surfaces and a well-grown crystal structure (Fig. 5a, b). Additionally, measurements of the morphology of the surface and cross-section of the cathode after 100 cycles using the pure  $\text{LiBF}_4$ -based electrolyte were obtained (Fig. 5c, d). The SEM images showed that a layer of loose and uneven polymer covers the cathode surface, which led to a relatively poor thermal stability of the interfacial film. Additionally, a large amount of cracks were observed on the surface of the particles, which indicates that the cathode was eroded. This causes the electrolyte to decompose continuously and accounts for the poor high-temperature performance of cells using the  $\text{LiBF}_4$ -based electrolyte. Next, the morphology of the cathode in a cell using pure  $\text{LiODFB}$ -based electrolyte was investigated (Fig. 5g, h). The surface of the cathode was relatively smooth and did not show any signs of erosion. This was due to the fact



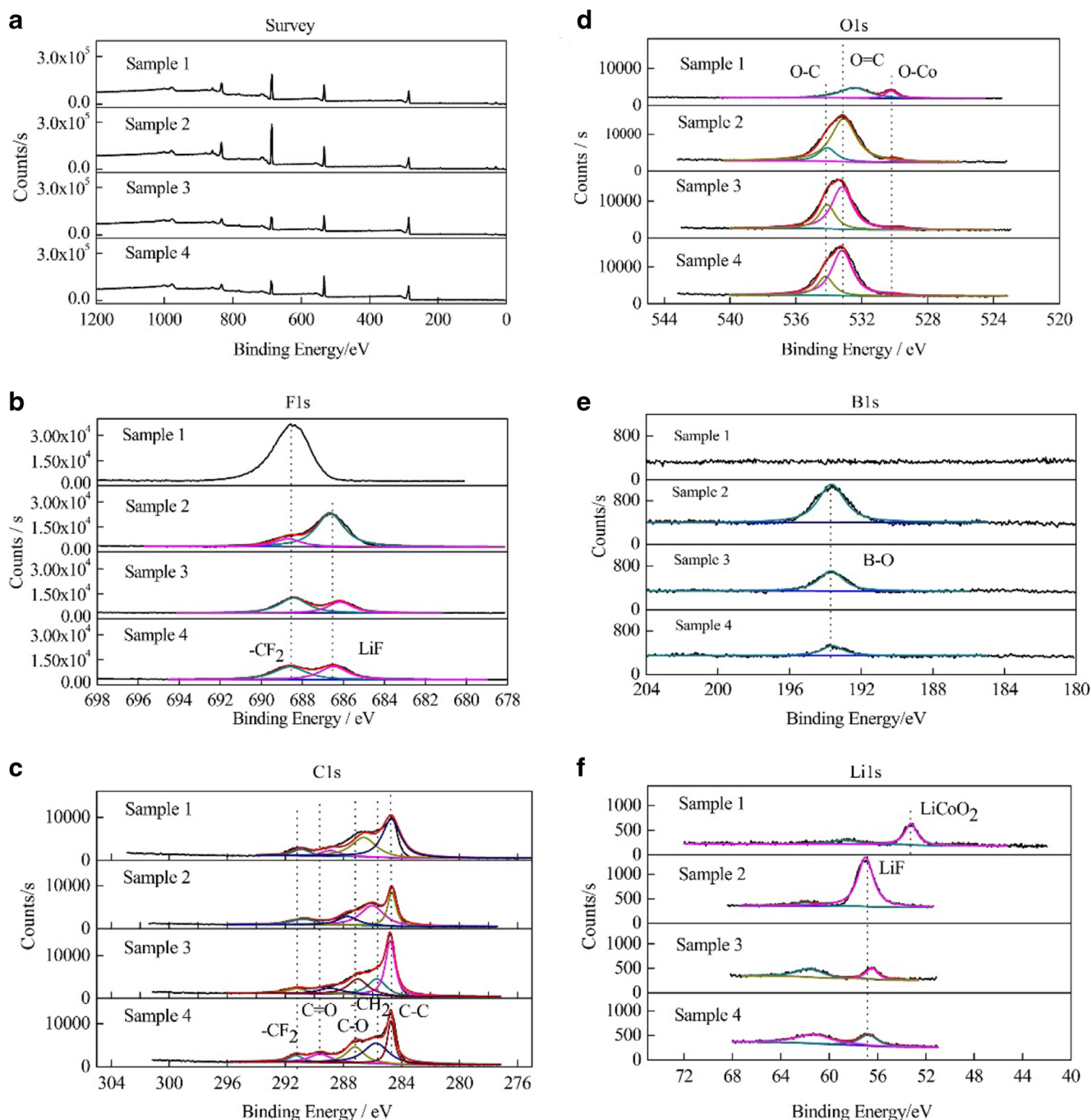
**Fig. 5** SEM images of LiCoO<sub>2</sub> electrode from LiCoO<sub>2</sub>/Li cells **a, b** uncycled at 60 °C; **c, d** LiBF<sub>4</sub>-based electrolyte system, after 100 cycles at 60 °C; **e, f** LiBF<sub>4</sub>/LiODFB blend salt with a molar ratio of 8:2

electrolyte system, after 100 cycles at 60 °C; **g, h** LiODFB-based electrolyte system, after 100 cycles at 60 °C

that LiODFB decomposed at a relatively high temperature and formed a dense and stable passivation film on surface of the cathode. This film prevented the electrolyte from reacting further with the cathode material. This phenomenon explains the good capacity retention of the cell using pure LiODFB-based electrolyte at high temperature. Finally, the morphology of the cathode cycled in a LiBF<sub>4</sub>/LiODFB(8:2)-based electrolyte was measured (Fig. 5e, f). The SEM images revealed no cracks on the surface of the electrode and showed a relatively dense film on the cathode surface. A comparison of these results with the ones obtained from the pure LiBF<sub>4</sub>-based electrolyte revealed that the addition of LiODFB significantly improve the thermal stability of the interface. This effect is mainly caused by the stable and dense interface film formed by LiODFB on the surface of the electrode. Thus, it can be concluded that the electrolyte system with the mixed lithium salts of LiBF<sub>4</sub>/LiODFB (8:2) has relatively good wide temperature performance.

In order to examine the effect of the electrolytes on the interfacial film of the cathode further, the composition of the film on the cathode surface after 100 cycles at 60 °C was measured by XPS (Fig. 6). Survey scans of four samples were carried out (Fig. 6a): LiCoO<sub>2</sub> cathode uncycled (sample 1); LiCoO<sub>2</sub> cathode after 100 cycles in the LiBF<sub>4</sub>-based electrolyte (sample 2); LiCoO<sub>2</sub> cathode after 100 cycles in the LiBF<sub>4</sub>/LiODFB (8:2)-based electrolyte (sample 3); and LiCoO<sub>2</sub> cathode after 100 cycles in the LiODFB-based electrolyte (sample 4). The peaks that were observed from these scans were identified as follows: carbon auger electron peak (~1220 eV), oxygen auger electron peak (~980 eV), fluoride electron peak (878, 860, and 833 eV), and photoelectron peaks: Co2p (~780 eV), F1s (~689 and 687 eV), O1s (~532 eV), C1s (~285 eV), B1s (~194 eV), and Li1s (~57 eV).

Comparison of the scans in the areas of the fluorine, carbon, oxygen, boron and lithium photoelectron peaks revealed significant differences. In the F1s spectrum (Fig. 6b), all four LiCoO<sub>2</sub> samples showed a peak at ~688.5 eV (–CF<sub>2</sub>), which is believed to result from the binder PVDF. In contrast, the uncycled LiCoO<sub>2</sub> cathode (sample 1) showed a single peak of –CF<sub>2</sub> at ~688.5 eV, another peak at ~686.5 eV present in the photoelectron spectra of samples 2, 3, and 4. That peak can be attributed to the formation of LiF. This hypothesis was supported by the occurrence of LiF (56.8 eV) in the Li1s spectrum (Fig. 6f). Moreover, the intensity of the LiF peak in sample 2 was much taller than that in sample 3 and sample 4, which implies that LiF was the major component of the film on the surface of the cycled cathode at 60 °C. The higher LiF peak intensity of sample 2 also indicates that LiBF<sub>4</sub>-based electrolyte was more likely to decompose and create a higher amount of LiF than the LiODFB-based electrolyte system. The fact that the amount of LiF decreased significantly when a small amount of LiODFB was added to the electrolyte confirmed that LiODFB inhibits the decomposition of the electrolyte. Three peaks were identified in the C1s spectrum of sample 1: 284.8, 286.5, and 291.3 eV (Fig. 6c). These peaks correspond to the C–C bond in the conductive carbon, the –CH<sub>2</sub> bond and the –CF<sub>2</sub> bond in the adhesive (PVDF), respectively. In samples 3 and 4, both the C–O peak (287 eV) and the C=O peak (289.5 eV) were visible. By contrast, in sample 2, only the C–O peak was detected. The C=O peak was not observed in the C1s spectrum of sample 2 because it overlaps with the –CF<sub>2</sub> peak. It was, however, detected in the O1s spectrum of the sample (Fig. 6d). Both the O=C peak (533.5 eV) and the O–C peak (534.3 eV) in the O1s spectrum were strengthened significantly. This implied that the



**Fig. 6** XPS patterns of the LiCoO<sub>2</sub> cathode uncycled (sample 1), after 100 cycles in the 1 mol L<sup>-1</sup> LiBF<sub>4</sub> electrolyte system (sample 2), after 100 cycles in the 1 mol L<sup>-1</sup> LiBF<sub>4</sub>-LiODFB (8:2) electrolyte system

(sample 3) and after 100 cycles in the 1 mol L<sup>-1</sup> LiODFB electrolyte system (sample 4), respectively. **a** Survey, **b** F 1s, **c** C 1s, **d** O 1s, **e** B 1s, and **f** Li 1s

electrolyte decomposition took place on the electrode and that a polymer containing C–O and C=O bond was generated in the process. The B1s spectra indicated the appearance of a B–O peak (193.6 eV) on the surface of the electrode after the cycling process (Fig. 6e). This new peak was the strongest in sample 2, which indicates that both lithium salts, LiBF<sub>4</sub> and LiODFB, participate in the interfacial reaction at high temperature. Even though both

lithium salts decomposed to generate the compound containing the detected B–O bond, the decomposition process of and LiBF<sub>4</sub> appeared stronger. Ultimately, the decomposition products deposited on the cathode surface formed a thick and loose interfacial film. Due to the relatively poor film-forming performance of the LiBF<sub>4</sub>-based electrolyte, the electrolyte decomposed continuously at high temperature. The addition of LiODFB caused the formation of a



dense interfacial film, which prevented the further oxidation and decomposition of the electrolyte. Thus, the introduction of a certain amount of LiODFB into LiBF<sub>4</sub> may improve the cycling stability of the cell at high temperature.

## Conclusion

This paper systematically investigates the temperature range of an electrolyte system based on a mixture of LiBF<sub>4</sub>/LiODFB lithium salts in a 1 M PC/EC/EMC (1:1:3) + FEC(5%) and their application in LiCoO<sub>2</sub>/Li cells.

Electrolyte cells based on pure LiBF<sub>4</sub> or LiODFB showed poor performance in a wide range of temperature. However, the addition of LiODFB as a co-salt to LiBF<sub>4</sub> improved the conductivity of the electrolyte. Also, it caused the formation of a dense and stable interfacial film on the cathode surface, which suppressed the decomposition of the LiBF<sub>4</sub>-based electrolyte. As a result, Li/LiCoO<sub>2</sub> cells using LiBF<sub>4</sub>/LiODFB(8:2)-based electrolytes exhibited high discharge capacity and excellent cycling stability.

However, the rate performance of the LiCoO<sub>2</sub>/Li cell was very poor at lower temperature (−20 °C). This study proves that mixed lithium salts used in LIB electrolytes have great potential. However, the electrolyte system presented in this paper needs to be optimized further in order to improve the rate performance. Moreover, electrochemical mechanism of the synergistic effect at high and low temperatures should be investigated.

**Acknowledgements** This work is supported by the Joint Funds of the National Natural Science Foundation of China (Nos. U1407105 and U1407106), the Applied Basic Research Program of Qinghai Province (No.2015-ZJ-740), and Qinghai Provincial Thousand Talents Program for High-level Innovative Professionals.

## References

- Goodenough JB, Kim Y (2011) Challenges for rechargeable batteries. *J Power Sources* 196(16):6688–6694. <https://doi.org/10.1016/j.jpowsour.2010.11.074>
- Scrosati B, Garche J (2010) Lithium batteries: status, prospects and future. *J Power Sources* 195(9):2419–2430. <https://doi.org/10.1016/j.jpowsour.2009.11.048>
- Liu H, Miao C, Meng Y, He Y-B, Xu Q, Zhang X, Tang Z (2014) Optimized synthesis of nano-sized LiFePO<sub>4</sub>/C particles with excellent rate capability for lithium ion batteries. *Electrochim Acta* 130:322–328. <https://doi.org/10.1016/j.electacta.2014.03.034>
- Li S, Li X, Liu J, Shang Z, Cui X (2014) A low-temperature electrolyte for lithium-ion batteries. *Ionics* 21(4):901–907
- Azeez F, Fedkiw PS (2010) Conductivity of libob-based electrolyte for lithium-ion batteries. *J Power Sources* 195(22):7627–7633. <https://doi.org/10.1016/j.jpowsour.2010.06.021>
- Li S, Zhao W, Zhou Z, Cui X, Shang Z, Liu H, Zhang D (2014) Studies on electrochemical performances of novel electrolytes for wide temperature range lithium ion batteries. *Appl Mater Interfaces* 6(7):4920–4926. <https://doi.org/10.1021/am405973x>
- Lai Y, Peng B, Zhang Z, Li J (2014) A wide operating temperature range electrolyte containing lithium salts mixture and a co-solvent for the LiFePO<sub>4</sub> cathode. *J Electrochem Soc* 161(6):A875–A879. <https://doi.org/10.1149/2.023406jes>
- Zhang Z, Chen X, Li F, Lai Y, Li J, Liu P, Wang X (2010) LiPF<sub>6</sub> and lithium oxalyldifluoroborate blend salts electrolyte for LiFePO<sub>4</sub>/artificial graphite lithium-ion cells. *J Power Sources* 195(21):7397–7402
- Zhou H, Xiao K, Li J (2016) Lithium difluoro(oxalato)borate and LiBF<sub>4</sub> blend salts electrolyte for LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode material. *J Power Sources* 302:274–282
- Wang DY, Xiao A, Wells L, Dahn JR (2015) Effect of mixtures of lithium hexafluorophosphate (LiPF<sub>6</sub>) and lithium bis(fluorosulfonyl)imide (LiFSI) as salts in li[Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>]O<sub>2</sub>/graphite pouch cells. *J Electrochem Soc* 162(1):A169–A175
- Zhang SS, Xu K, Jow TR (2002) Study of LiBF<sub>4</sub> as an electrolyte salt for a li-ion battery. *J Electrochem Soc* 149(5):A586. <https://doi.org/10.1149/1.1466857>
- Xu K, Zhang S, Jow TR, Xu W, Angell CA (2002) LiBOB as salt for lithium-ion batteries: a possible solution for high temperature operation. *Electrochem Solid-State Lett* 5(1):A26. <https://doi.org/10.1149/1.1426042>
- Agubra VA, Fergus JW (2014) The formation and stability of the solid electrolyte interface on the graphite anode. *J Power Sources* 268:153–162. <https://doi.org/10.1016/j.jpowsour.2014.06.024>
- Zhang SS (2007) Electrochemical study of the formation of a solid electrolyte interface on graphite in a LiBC<sub>2</sub>O<sub>4</sub>F<sub>2</sub>-based electrolyte. *J Power Sources* 163(2):713–718. <https://doi.org/10.1016/j.jpowsour.2006.09.040>
- Zygadlo-Monikowska E, Florjańczyk Z, Kubisa P, Biedroń T, Tomaszewska A, Ostrowska J, Langwald N (2010) Mixture of LiBF<sub>4</sub> and lithium difluoro(oxalato)borate for application as a new electrolyte for lithium-ion batteries. *J Power Sources* 195(18):6202–6206
- Lu Z, Yang L, Guo Y (2006) Thermal behavior and decomposition kinetics of six electrolyte salts by thermal analysis. *J Power Sources* 156(2):555–559. <https://doi.org/10.1016/j.jpowsour.2005.05.085>
- Aravindan V, Gnanaraj J, Madhavi S, Liu HK (2011) Lithium-ion conducting electrolyte salts for lithium batteries. *Chemistry* 17(51):14326–14346. <https://doi.org/10.1002/chem.201101486>
- Fu MH, Huang KL, Liu SQ, Liu JS, Li YK (2010) Lithium difluoro(oxalato)borate/ethylene carbonate+propylene carbonate+ethyl(methyl) carbonate electrolyte for LiMn<sub>2</sub>O<sub>4</sub> cathode. *J Power Sources* 195(3):862–866. <https://doi.org/10.1016/j.jpowsour.2009.08.042>
- Li J, Xie K, Lai Y, Za Z, Li F, Hao X, Chen X, Liu Y (2010) Lithium oxalyldifluoroborate/carbonate electrolytes for LiFePO<sub>4</sub>/artificial graphite lithium-ion cells. *J Power Sources* 195(16):5344–5350. <https://doi.org/10.1016/j.jpowsour.2010.03.038>
- Xu MQ, Zhou L, Hao LS, Xing LD, Li WS, Lucht BL (2011) Investigation and application of lithium difluoro(oxalato)borate (LiDFOB) as additive to improve the thermal stability of electrolyte for lithium-ion batteries. *J Power Sources* 196(16):6794–6801. <https://doi.org/10.1016/j.jpowsour.2010.10.050>
- Gao HQ, Zhang ZA, Lai YQ, Jie L, Liu YX (2008) Structure characterization and electrochemical properties of new lithium salt LiODFB for electrolyte of lithium ion batteries. *J Cent South Univ* 15(6):830–834. <https://doi.org/10.1007/s11771-008-0153-1>
- Liao L, Cheng X, Ma Y, Zuo P, Fang W, Yin G, Gao Y (2013) Fluoroethylene carbonate as electrolyte additive to improve low temperature performance of LiFePO<sub>4</sub> electrode. *Electrochim Acta* 87(1):466–472
- Bordes A, Eom K, Fuller TF (2014) The effect of fluoroethylene carbonate additive content on the formation of the solid-electrolyte

- interphase and capacity fade of li-ion full-cell employing nano Si-graphene composite anodes. *J Power Sources* 257:163–169
24. Zugmann S, Moosbauer D, Amereller M, Schreiner C, Wudy F, Schmitz R, Schmitz R, Isken P, Dippel C, Müller R, Kunze M, Lex-Balducci A, Winter M, Gores HJ (2011) Electrochemical characterization of electrolytes for lithium-ion batteries based on lithium difluoromono(oxalato)borate. *J Power Sources* 196(3):1417–1424. <https://doi.org/10.1016/j.jpowsour.2010.08.023>
  25. Ding MS, Jow TR (2004) How conductivities and viscosities of PC-DEC and PC-EC solutions of  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiBOB}$ ,  $\text{Et}_4\text{NBF}_4$ , and  $\text{Et}_4\text{NPF}_6$  differ and why. *J Electrochem Soc* 151(12):A2007–A2015. <https://doi.org/10.1149/1.1809575>
  26. Shui Zhang S (2006) An unique lithium salt for the improved electrolyte of li-ion battery. *Electrochem Commun* 8(9):1423–1428. <https://doi.org/10.1016/j.elecom.2006.06.016>
  27. Li F, Gong Y, Jia G, Wang Q, Peng Z, Fan W, Bai B (2015) A novel dual-salts of  $\text{LiTFSI}$  and  $\text{LiODFB}$  in  $\text{LiFePO}_4$ -based batteries for suppressing aluminum corrosion and improving cycling stability. *J Power Sources* 295:47–54
  28. Schedlbauer T, Rodehorst UC, Schreiner C, Gores HJ, Winter M (2013) Blends of lithium bis(oxalato)borate and lithium tetrafluoroborate: useful substitutes for lithium difluoro(oxalato)borate in electrolytes for lithium metal based secondary batteries? *Electrochim Acta* 107(3):26–32. <https://doi.org/10.1016/j.electacta.2013.05.130>
  29. Egashira M, Sawada N, Ueda K, Yoshimoto N, Morita M (2010) Capacitance of porous carbon electrode in mixed salt non-aqueous electrolytes. *J Power Sources* 195(6):1761–1764
  30. Mun J, Kim S, Yim T, Ryu JH, Kim YG, Oh SM (2010) Comparative study on surface films from ionic liquids containing saturated and unsaturated substituent for  $\text{LiCoO}_2$ . *J Electrochem Soc* 157(2):A136–A141. <https://doi.org/10.1149/1.3265476>