

Short communication

# Enhancing the thermal stability of LiCoO<sub>2</sub> electrode by 4-isopropyl phenyl diphenyl phosphate in lithium ion batteries

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## Abstract

To enhance the thermal stability of LiCoO<sub>2</sub> in lithium ion batteries, 4-isopropyl phenyl diphenyl phosphate (IPPP) was investigated as an additive in 1.0 M LiPF<sub>6</sub>/EC + DEC (1:1 wt.%) electrolyte. The thermodynamics and kinetics parameters of the single LiCoO<sub>2</sub> and Li<sub>x</sub>CoO<sub>2</sub>-IPPP-electrolyte are detected and calculated based on the C80 microcalorimeter data. The results indicated that IPPP can enhance the thermal stability of LiCoO<sub>2</sub> electrode in lithium ion battery more or less corresponding to the IPPP content in electrolyte. Furthermore, the electrochemical performances of LiCoO<sub>2</sub>/IPPP-electrolyte/Li cells become slightly worse after using IPPP additive in the electrolyte. This alleviated trade-off between thermal stability and cell performance provides a possibility to formulate an electrolyte containing 5–10% of IPPP and enhance the LiCoO<sub>2</sub> electrode thermal stability with minimum sacrifice in performance.

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**Keywords:** Lithium ion battery; LiCoO<sub>2</sub>; Thermal stability; C80 microcalorimeter

## 1. Introduction

The development of lithium ion batteries with good performance, safety, and reliability has been an active area of research for the past three decades [1–5]. Lithium ion batteries contain flammable organic electrolytes and, under certain abuse conditions (uncontrolled charging above 4.6 V), flame and smoke may result, and then the safety of lithium ion batteries is an essential requirement for its further development, especially for larger sizes lithium ion batteries [6–8]. To improve the safety of lithium ion batteries, many efforts have been focused on the development of nonflammable electrolytes [2,9–24]. These additives can improve the electrolyte flammability and decrease the batteries electrochemical performance more or less. In previous studies, we have reported on the use of 4-isopropyl phenyl diphenyl phosphate (IPPP) as a flame-retardant additive for lithium ion battery electrolyte [25]. The addition of IPPP in electrolyte can reduce its flammability and delay the onset temperature of the major exothermal reaction. Recently, we extended our study on

the enhanced the thermal stability of LiCoO<sub>2</sub> cathode by IPPP in lithium ion batteries.

## 2. Experimental

IPPP (Lianrui Chemical Co.), carbonate solvents (Guotai-Huarong New Chemical Materials Co.), and LiPF<sub>6</sub> (Tianjin Jinniu Power Sources Material Co.) were used as received. The solution of 1.0 M LiPF<sub>6</sub>/EC + DEC (1:1 wt.%) was prepared in an argon glove box (MBraun Labmaster 130) and used as a standard electrolyte. LiCoO<sub>2</sub> (Tianjin B&M Science and Technology Joint-stock Co.) was used to prepare a laminate of positive electrode mixed with acetylene black and polyvinylidene fluoride (PVDF) binder.

The effect of flame-retardant additive on the cell performance was tested in CR2032 coin cells of LiCoO<sub>2</sub>/Li. The composition of the cathode was 84% LiCoO<sub>2</sub>, 8% acetylene black, and 8% PVDF binder. Celgard 2400 polyethylene separator (20 μm thick) was used in the cell. The electrodes were obtained ready for use, dried over night in vacuum at 70 °C, and handled in an argon filled glove box (MBraun Labmaster 130, <1 ppm O<sub>2</sub> and H<sub>2</sub>O). The electrodes were cut as a 14 mm diameter disk of about 400 μm thickness for get more mass of sample for C80

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experiment. The cells were galvanostatically cycled on a multi-channel battery cycler (Neware BTS 2300, Shenzhen) at room temperature, between 4.2 V and 2.8 V at  $0.2 \text{ mA cm}^{-2}$  current density for  $\text{LiCoO}_2/\text{Li}$  cells.

Then the charged cells (4.2 V) were disassembled in glove box. To remove the electrolyte from the electrode, the wet charged electrode powder was placed into a bottle. Then, a portion of dimethyl carbonate (DMC), a volatile organic solvent, was added into the bottle and was shaken by hand. The sample was then decanted and the DMC rinsing procedure was repeated. After the second decanting, the sample was dried to remove the DMC solvent. After drying, the electrode material was scraped, trying not to abrade the film, from the current collectors carefully for thermal test. To characterize the thermal stability of the electrodes in the presence of electrolyte, about equal amount of electrode material (including PVDF) and electrolyte were transferred into a high-pressure stainless steel vessel (8.5 ml in volume) of a microcalorimeter (Setaram C80) sealed in argon atmosphere. The weight of each sample (vessel + sample) was measured before and after the experiment to verify that the system was hermetically sealed. The weight was constant in all cases, indicating that there were no leaks during the experiments. The measurements were carried out using a heating rate set at  $0.2 \text{ }^\circ\text{C min}^{-1}$  in the temperature range 30–300  $^\circ\text{C}$  in argon filled vessel. The thermal effects of each sample with temperature were thus recorded automatically and the C80 calculations were based on dry film weight of the electrode material.

### 3. Results and discussion

Fig. 1 is the heat flow curves of  $\text{Li}_x\text{CoO}_2$  alone at a  $0.2 \text{ }^\circ\text{C min}^{-1}$  heating rate in argon filled atmosphere. The  $\text{Li}_x\text{CoO}_2$  is got from the  $\text{LiCoO}_2/\text{IPPP}$ -electrolyte/ $\text{Li}$  cells charged at 4.2 V with different IPPP content in 1.0 M  $\text{LiPF}_6/\text{EC} + \text{DEC}$  electrolyte. Without the effect of IPPP,  $\text{Li}_x\text{CoO}_2$  starts to release heat at 162  $^\circ\text{C}$  and reaches to peak temperature at 259  $^\circ\text{C}$  with a heat of reaction  $-863.0 \text{ J g}^{-1}$ . The thermal stability of  $\text{Li}_x\text{CoO}_2$  got from IPPP content cells are improved more or less, and the heat generations are decreased. When the IPPP content is 5% and 10% in the electrolyte, the onset temperature and exothermic peak of  $\text{Li}_x\text{CoO}_2$  changes a little, locate at 174  $^\circ\text{C}$  and 257  $^\circ\text{C}$ , 172  $^\circ\text{C}$  and 256  $^\circ\text{C}$ , respectively, and the reaction heat are reduced to  $-361.1 \text{ J g}^{-1}$  and  $-368.9 \text{ J g}^{-1}$ , respectively. When the IPPP content is 15%, the onset temperature of  $\text{Li}_x\text{CoO}_2$  is 165  $^\circ\text{C}$ , and reaches to two exothermic peaks at 178  $^\circ\text{C}$  and 248  $^\circ\text{C}$ , with little heat generation of  $-25.6 \text{ J g}^{-1}$  and  $-171.4 \text{ J g}^{-1}$ , respectively. The first exothermic peak of  $\text{Li}_x\text{CoO}_2$ , cycled in 15% IPPP content electrolyte, may be caused by the residual electrolyte in the  $\text{Li}_x\text{CoO}_2$ . When the IPPP content is 20%, the onset temperature of  $\text{Li}_x\text{CoO}_2$  is 183  $^\circ\text{C}$  and reaches to exothermic peak at 216  $^\circ\text{C}$  with heat generation of  $-267.2 \text{ J g}^{-1}$ .

The enhanced thermal stability is characterized by delayed onset temperature, decreased heat generation and increased activation energy. The above results show that the onset temperatures of single  $\text{Li}_x\text{CoO}_2$  were not put off too much, but the heat generations are decreased obviously. The heat genera-

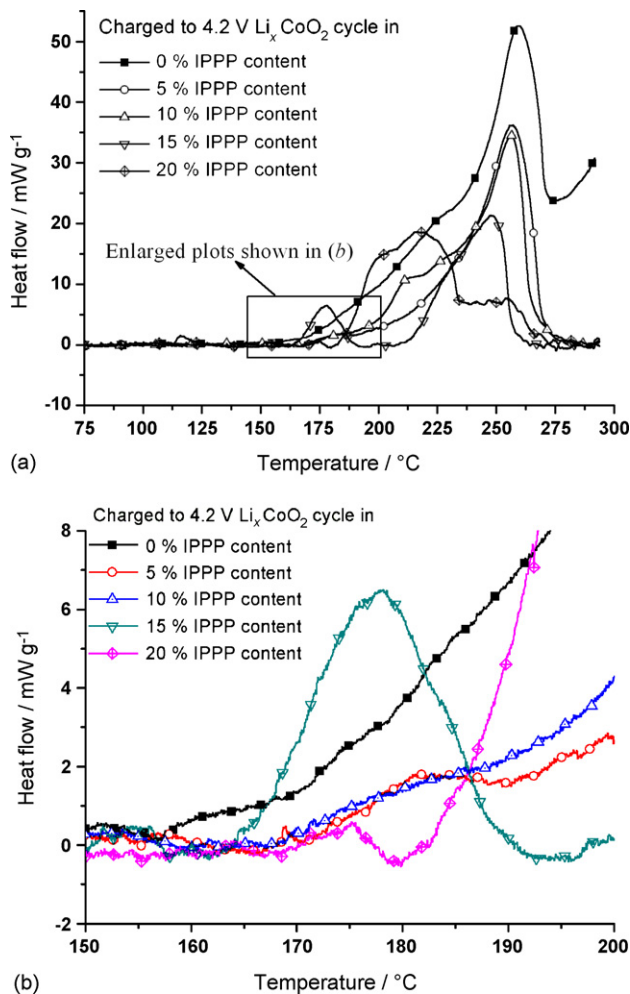


Fig. 1. Heat flows of  $\text{Li}_x\text{CoO}_2$  alone at a  $0.2 \text{ }^\circ\text{C min}^{-1}$  heating rate with different IPPP content.

tion of  $\text{Li}_x\text{CoO}_2$  got from  $\text{LiCoO}_2/15\% \text{ IPPP}$ -electrolyte/ $\text{Li}$  cell decrease most greatly, reduced  $666.0 \text{ J g}^{-1}$ . As the electrolyte adsorbed in the  $\text{LiCoO}_2$  electrode is rinsed away by DMC, therefore, the delayed onset temperature not the direct effect of IPPP, but may be delayed by the conducting surface film on the cathode. The lithium ion conducting film on the cathode surface is mainly formed by  $\text{Li}_3\text{PO}_4$ , which is the oxidation product of IPPP with  $\text{Li}^+$  at charged states [25]. A careful surface analysis on the composition of the electrodes removed from cycled cells could give more hints to clarify the detailed stabilization mechanisms. Nevertheless, it is beyond the scope of this paper. The above tests indicated that the thermal stability of  $\text{Li}_x\text{CoO}_2$  after cycled in IPPP content cell is improved, which is benefit to improve the safety of batteries.

With the addition of IPPP content electrolyte into the  $\text{Li}_x\text{CoO}_2$ , the coexist systems thermal behaviors are shown in Fig. 2. In the  $\text{Li}_x\text{CoO}_2$ -IPPP-electrolyte system, the IPPP concentration in electrolyte is corresponding to that used in  $\text{LiCoO}_2/\text{IPPP}$ -electrolyte/ $\text{Li}$  cells. In Fig. 2, the onset temperature of  $\text{Li}_x\text{CoO}_2$  with 1.0 M  $\text{LiPF}_6/\text{EC} + \text{DEC}$  electrolyte is 111  $^\circ\text{C}$  and it reaches to two exothermic peaks at 138  $^\circ\text{C}$  and 233  $^\circ\text{C}$ , respectively, with the total heat generation of

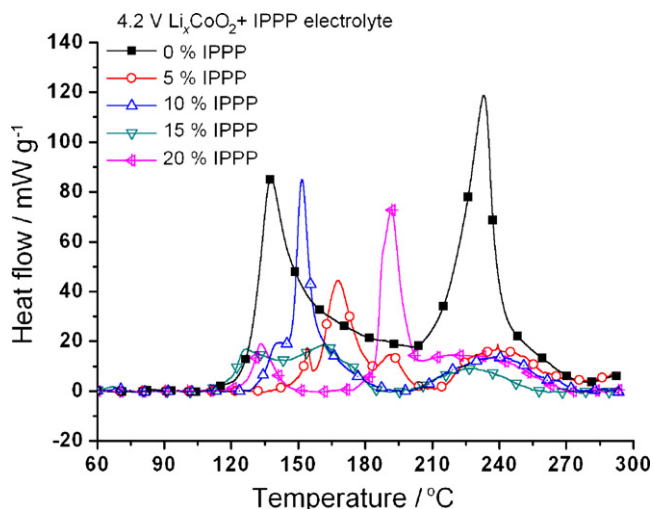


Fig. 2. Heat flows of  $\text{Li}_x\text{CoO}_2$  coexist with IPPP content electrolyte.

$-1642.3 \text{ J g}^{-1}$ . For the IPPP content electrolyte and  $\text{Li}_x\text{CoO}_2$  system, its thermal behaviors changes greatly. The onset temperatures of  $\text{Li}_x\text{CoO}_2$  coexist with 5% IPPP and 10% IPPP-electrolyte are put off to  $139^\circ\text{C}$  and  $129^\circ\text{C}$ , respectively. With the IPPP content increasing, the onset temperature of  $\text{Li}_x\text{CoO}_2$  coexist with 15% and 20% IPPP-electrolyte are decreased to  $110^\circ\text{C}$  and  $116^\circ\text{C}$ , respectively, and the exothermic peaks decreasing too. The heat releases of  $\text{Li}_x\text{CoO}_2$  coexist with IPPP content electrolytes are reduced greatly, which reduced to  $-474 \text{ J g}^{-1}$  in average level.

Assuming the reaction mechanism is dependent on the Arrhenius law, basing on the C80 data, the following Eq. (1) is got as [26,27]:

$$\ln \left( \frac{dH/dt}{\Delta H M_0} \right) = -\frac{E}{R T} + \ln A \quad (1)$$

where  $dH/dt$  is the total heat flow,  $\Delta H$  the heat of reaction,  $M_0$  the initial mass of reactant,  $E$  the activation energy,  $R$  the gas constant,  $T$  the temperature of system and  $A$  is the frequency factor. By plotting the curve of  $\ln((dH/dt)/\Delta H M_0)$  versus inverse temperature, the  $E$  and  $A$  can be easily calculated [28,29]. By this method, the thermal decomposition activation energy and frequency factor of first exothermic process in  $\text{Li}_x\text{CoO}_2$ -IPPP-electrolyte system is calculated and listed in Table 1, which exhibit the changes of thermodynamics and kinetics. From this table, it can be seen that the activation energy increase obviously, from  $85.4 \text{ kJ mol}^{-1}$  increased to  $308 \text{ kJ mol}^{-1}$  in average.

Table 1  
The thermodynamics and kinetics parameters of  $\text{Li}_x\text{CoO}_2$  coexist with IPPP-electrolyte

IPPP content in electrolyte (%)	Onset temperature ( $^\circ\text{C}$ )	Exothermic peaks ( $^\circ\text{C}$ )	Heat generation ( $\text{J g}^{-1}$ )	Activation energy, $E$ ( $\text{kJ mol}^{-1}$ )	Frequency factor, $A$ ( $\text{s}^{-1}$ )
0	111	138/233	$-1642.3$	55.8	$3.53 \times 10^4$
5	139	154/168/191/239	$-499.6$	313.0	$7.29 \times 10^{34}$
10	129	142/152/238	$-516.0$	367.1	$1.18 \times 10^{43}$
15	110	127/161/229	$-348.1$	253.7	$2.66 \times 10^{29}$
20	116	133/191	$-531.8$	297.9	$5.71 \times 10^{34}$

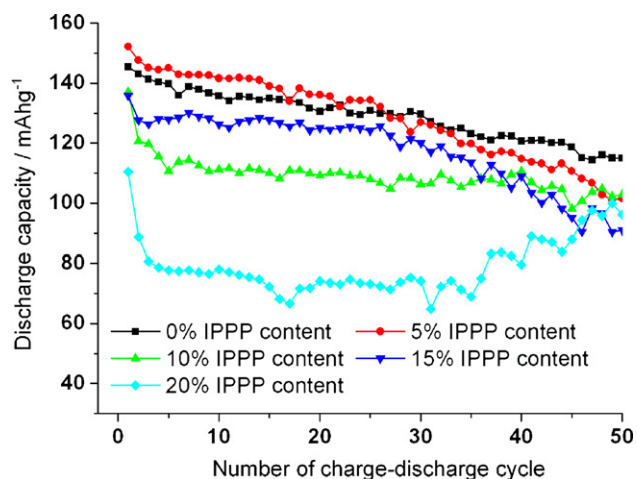


Fig. 3. Cycle performance of batteries with different IPPP content in 1.0M  $\text{LiPF}_6/\text{EC}+\text{DEC}$  (1:1 wt.%) electrolyte. The batteries were cycled between 2.8 V and 4.2 V at a  $0.2 \text{ mA cm}^{-2}$  charge/discharge current density.

The most related exothermic peak for thermal runaway is the first exothermic peak, as the first reaction heat provides the necessary energy for the following reactions. Therefore, to compare the first exothermic process and heat generation are critical to better understand the effect of IPPP for safety. In the  $\text{Li}_x\text{CoO}_2$ -IPPP-electrolyte system, the first exothermic peak may be attributed to the solid electrolyte interphase (SEI) decomposition and then followed by  $\text{Li}_x\text{CoO}_2$ /electrolyte decomposition [30]. As the SEI film component varies with the IPPP content, the certain decomposition processes differ with different IPPP content. More careful chemical experiments and analysis on the decompositions is necessary to give more hints to clarify the detailed reactions. Herein, one point is confirmed that with the effect of IPPP, the first exothermic process is inhibited, heat generation is reduced, and activation energy is increased. The above results indicated that IPPP can suppress the coexisting system activity of  $\text{Li}_x\text{CoO}_2$ -IPPP containing electrolyte. It may be caused by the formed char from electrolyte under the effect of IPPP and deposit on the cathode and then the reaction product prevents further thermal reaction of electrolyte,  $\text{Li}_x\text{CoO}_2$  and their interactions leading safety to lithium ion batteries [25].

The electrochemical performance of  $\text{LiCoO}_2/\text{IPPP}$ -electrolyte/Li cells has been reported in our previous publication [25]. The cycle efficiency, first charge and discharge performance, discharge specific capacity and ac impedance are detected. As an example, Fig. 3 shows the electrochemical capacity of the  $\text{LiCoO}_2/\text{Li}$  cells with electrolytes containing various contents

of IPPP. Discharge capacity is calculated based on the mass of  $\text{LiCoO}_2$ . It can be seen that 5% IPPP content of the electrolyte shows good performance in the first 50 cycles, and 10% and 15% IPPP content electrolytes are slightly decreased than the normal one, and the 20% IPPP content electrolyte lowers the capacity too much to be accepted. In general, with the IPPP content increasing, the initial discharge specific capacity is decreasing, which may be due to the oxidation of IPPP on the cathode surface [13,25]. The electrochemical performance experiments indicate that IPPP increases the thermal stability of electrolyte at the little expense of the electrochemical performance, and a content of 5–15% IPPP in the electrolyte is appropriate.

#### 4. Conclusions

In the  $\text{LiCoO}_2$ /IPPP-electrolyte/Li cells with different IPPP content, the onset temperature of single  $\text{Li}_x\text{CoO}_2$  is put off more or less and the heat generation is decreased greatly, which indicate the thermal stability is improved. When the  $\text{Li}_x\text{CoO}_2$  coexist with IPPP-electrolyte, the thermal stability of the coexisting system changes a little. Its thermal stability is enhanced at the 5% and 10% IPPP content in electrolyte. At the 15% and 20% IPPP content in electrolyte, the systems onset temperature is decreased a little, although the activation energy is increased, it is not benefit too much for batteries safety. The influence of IPPP on the electrochemical performance for  $\text{LiCoO}_2$ /IPPP-electrolyte/Li cells indicated that a content of 5–15% IPPP in the electrolyte is appropriate. Coupling with the result on the thermal stability of electrode, 5–10% IPPP content in electrolyte is perfect to enhance the thermal stability of  $\text{Li}_x\text{CoO}_2$  in lithium ion batteries.

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