



Short communication

Improved thermal stability of lithium ion battery by using cresyl diphenyl phosphate as an electrolyte additive

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ABSTRACT

To enhance the safety of lithium ion battery, cresyl diphenyl phosphate (CDP) is explored as an additive in 1.0 M LiPF₆/ethylene carbonate (EC)+diethyl carbonate (DEC) (1:1 wt.). The electrochemical performances of LiCoO₂/CDP-electrolyte/C cells are tested. At the thermal aspect, the thermal stability of the electrolyte with CDP is detected firstly by using a C80 micro-calorimeter, and then the charged LiCoO₂/CDP-electrolyte/C cells are disassembled and wrapped to detect the thermal behaviors. The results indicate that CDP-containing electrolyte enhances the thermal stabilities of electrolyte and lithium ion battery, and the electrochemical performances of LiCoO₂/CDP-electrolyte/C cell become slightly worse by using CDP in the electrolyte. Furthermore, the cell with 10% (wt.) CDP-containing electrolyte shows better cycle efficiency than that of other CDP-containing electrolyte, such as containing 5% (wt.) CDP and 15% (wt.) CDP. This maybe because that the mass ratio between CDP and electrolyte is close to the reaction stoichiometric ratio in the 10% (wt.) CDP-containing electrolyte, where stable solid electrolyte interphase (SEI) is formed. Therefore, 10% CDP-containing electrolyte improves the safety of lithium ion battery and keeps its electrochemical performance.

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1. Introduction

In spite of the widespread use and deserved promise of lithium batteries, safety issues are still a substantial issue of concern [1–4]. Some battery makers and users recorded fire and explosion accidents concerning lithium ion batteries. The fire and explosion accidents are caused by the thermal runaway reactions in the battery. When a cell is heated above a certain temperature, exothermic chemical reactions between the electrodes and the electrolyte can take place and lead to an increase of the cell internal temperature. If the generated heat is greater than the energy that can be dissipated, exothermic processes will occur and the cell temperature will increase rapidly. The rise in temperature will further accelerate the chemical reactions, rather than the desired galvanic reactions, causing even more heat to be produced, eventually resulting in thermal runaway [5].

Much effort has been devoted to improve the safety concern of lithium ion batteries. Use of electrolyte additive is one of the most economic and effective methods for the improvement of lithium ion battery performance. Zhang [6] reviewed the electrolyte additives and drawn that the reduction in flammability with the addition of

the fire-retardant (FR) is at an expense of the other performances, such as ionic conductivity of the electrolyte and reversibility of the cell. For example, trimethyl phosphate (TMP) has better effectiveness but shows inferior reductive stability on the graphite anode surface. Some other kinds of additives were explored later, such as, lithium tetrafluoro oxalato phosphate (LTFOP) [7], diphenyloctyl phosphate (DPOF) [8–10], allyl tris(2,2,2-trifluoroethyl) carbonate (ATFEC) [11], tri-(4-methoxythphenyl) phosphate [12], dimethyl methylphosphonate (DMMP) [13], and so on. These additives also worsen the electrochemical performance of the battery, and new kind of flame-retardant still need to be explored to improve the safety of battery and without the sacrifice at electrochemical performance.

Therefore, to find the effective approach becomes significant for retarding the fire and explosion tendencies of lithium-ion batteries. Cresyl diphenyl phosphate (CDP) is a new flame-retardant agent with good compatibility, anti-flammability and thermal stability. Its molecular formula is C₁₉H₁₇O₄P and the chemical structure is shown in Fig. 1. CDP is a clear colorless liquid, the phosphorus content is 9.1%, viscosity is 0.033 Pa s, melting point is –38 °C, boiling point is 360 °C and flash point is 232 °C. Since CDP has widespread industrial uses as fire-retardant in plastics production, it may be expected that CDP based electrolyte has a nonflammable performance. Zhou et al. [15] and Shim et al. [14] both reported that the addition of 5% (wt.) CDP to the electrolyte provides a significant suppression in the flammability of the

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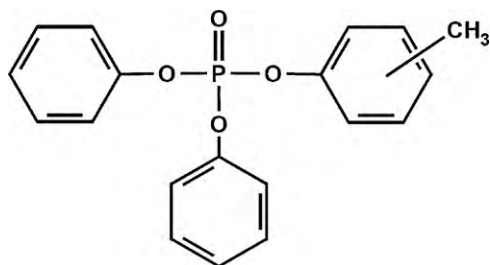


Fig. 1. Chemical structure of CDP.

electrolyte and an improvement in the thermal stability of battery, but the electrochemical performances of the cells become slightly worse. In this work, we mainly characterize the fundamental electrochemical and thermal properties of LiCoO₂/CDP-containing electrolyte/C coin cells. Also, the difference with the previous studies were compared and addressed.

2. Experimental

CDP (Lianrui Chemical Co.), carbonate solvents (Guotai-Huarong New Chemical Materials Co.) and LiPF₆ (Tianjin Jinniu Power Sources Material Co.) were used as received. The solution of 1.0 M LiPF₆/ethylene carbonate (EC)+diethyl carbonate (DEC) (1:1 wt.) was prepared in an argon glove box (MBraun Labmaster 130) and used as a standard electrolyte. The CDP-containing electrolytes were the mixture of CDP and referenced electrolyte (1.0 M LiPF₆/EC+DEC) at the given mass/weight ratios (wt.%), which were operated in an argon glove box. LiCoO₂ (Tianjin B&M Science and Technology Joint-stock Co.) and graphite (Hongyuan Carbon Industry Co., Ltd) were used to prepare a laminate of positive and negative electrodes, respectively.

The effect of CDP additive on the cell performance was tested in CR2032 coin cells. The composition of the cathode was made of LiCoO₂ (84 wt.%), acetylene black (8 wt.%) and polyvinylidene fluoride (PVDF) (8 wt.%) binder. The graphite laminate was made of graphite (92 wt.%) and PVDF (8 wt.%) binder. A Celgard 2400 polyethylene separator (20 μm thick) was used. The electrodes were dried 10 h in vacuum at 70 °C and handled in the argon filled glove box (MBraun Labmaster 130, <1 ppm O₂ and H₂O). Then electrodes were punched in disk-shaped pieces of 14 mm diameter and 400 μm thickness. The LiCoO₂/C cells were assembled with these disks, which provided samples for a C80 experiment.

The cells were cycled on a multi-channel battery cyler (Neware BTS-6V 10 mA, Shenzhen) at room temperature, between 4.2 V and 2.8 V at 0.2 mA cm⁻² current density for LiCoO₂/C cells. Between the charge and discharge, 1 min standing time was set for the cell. Alternating current (AC) impedance measurement was also carried out on the cells with a CHI 604A electrochemical workstation. The frequency range and voltage amplitude were set as 10 kHz to 0.01 Hz and 5 mV, respectively.

The electrolyte solutions were prepared in the glove box, and the CDP-containing electrolytes alone were sealed in the high-pressure stainless vessels (8.5 ml in volume) for C80 experiment. The electrolyte mass in each sample was about 0.5 g and it was heated from ambient temperature to 300 °C at a 0.2 °C min⁻¹ heating rate. For the battery thermal test, the LiCoO₂/C cell was cycled three times between 2.8 V and 4.2 V, and then was charged to 4.2 V and continues 1 h to ensure its voltage keeps at 4.2 V when it was disassembled. Great cares were taken to disassemble the cell in the argon filled glove box to avoid short circuit. The electrodes were taken out as original form and about two to three drops electrolyte were added, and then were wrapped with separator to avoid it contact with the stainless steel vessel. The electrodes and separator were

weighed before the cell was made, and then the weights of the reactants are known. The wrapped cell was transferred into a high-pressure stainless steel vessel of C80 micro-calorimeter and 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 °C min⁻¹ in the temperature range 30–300 °C in argon filled vessel. The thermal effects of sample with temperature were thus recorded automatically.

3. Results and discussion

3.1. Electrochemical performance of LiCoO₂/CDP-electrolyte/C cells

Fig. 2 is the first charge/discharge plots of LiCoO₂/CDP-electrolyte/C cells. Without the effect of CDP in electrolyte, the discharge flat is high and the discharge specific capacity is 133 mAh g⁻¹. After the addition of CDP in electrolyte, the cells discharge flat lower a little, and the discharge specific capacity are 134 mAh g⁻¹, 124.5 mAh g⁻¹, 112 mAh g⁻¹ and 127 mAh g⁻¹ corresponding to 5%, 10%, 15% and 20% CDP content in electrolyte, respectively. The discharge specific capacity decrease may be contributed by the reaction of lithium with CDP. As the lithium is possible reacts with CDP to form C₁₉H₁₇O₄PLi₂, which consume part of the lithium. The discharge specific capacity of the cell with 5% CDP-electrolyte without any decrease, for the 10%, 15% and 20% CDP content cells they decrease 6.4% and 15.8% and 4.5%, respectively. Zhou et al. [15] report the cathode capacity loss is 4.2% after using 5% CDP in the 1 M LiPF₆/EC+dimethyl carbonate (DMC)+ethylenemethyl carbonate (EMC) (1:1:1 wt.) at 0.1 mA cm⁻² charge/discharge current density. The related data for more CDP in the electrolyte was not found. Comparing the 5% CDP in different electrolytes, the cell with CDP in 1 M LiPF₆/EC+DEC electrolyte shows less cathode capacity loss.

Fig. 3 is the cycle efficiency of LiCoO₂/CDP-electrolyte/C cells between 2.8 V and 4.2 V at a 0.2 mA cm⁻² charge/discharge current density. Without the effect of CDP in electrolyte, the cycle efficiency of LiCoO₂/C cell keeps at 94.1% with the standard deviation of 2.4. Here the standard deviation is a statistic that means how tightly all the various efficiency are clustered around the mean in a set of data. The pretty tightly bunched together the standard deviation

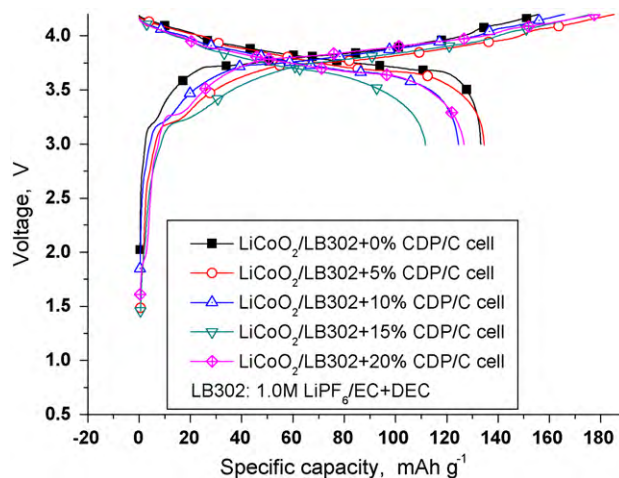


Fig. 2. First charge/discharge plots of LiCoO₂/C cells with different CDP content in 1.0 M LiPF₆/EC+DEC (1:1 wt.) electrolyte. The cells were cycled between 2.8 V and 4.2 V at a 0.2 mA cm⁻² charge/discharge current density.

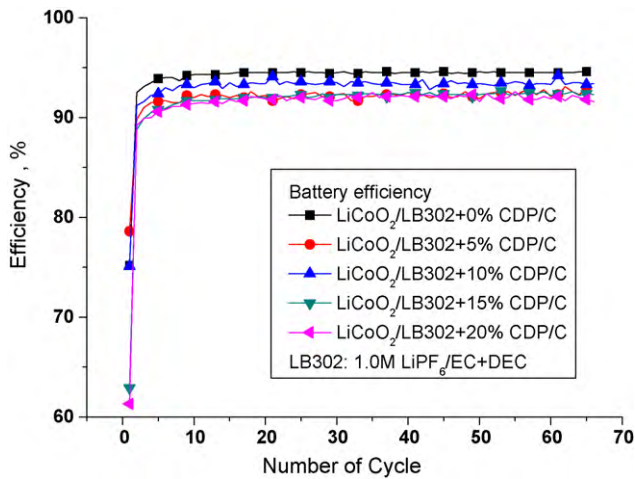


Fig. 3. Cycle efficiency of LiCoO_2/C cells with different CDP content in 1.0M $\text{LiPF}_6/\text{EC} + \text{DEC}$ (1:1 wt.) electrolyte. The cells were cycled between 2.8 V and 4.2 V at a 0.2 mA cm^{-2} charge/discharge current density.

is small, the spread apart the standard deviation is large. The cells cycle efficiencies with 5% CDP, 10% CDP, 15% CDP and 20% CDP in the electrolyte change to 92.0%, 93.0%, 91.8% and 91.5% with standard deviation of 1.45, 2.22, 2.98 and 2.8, respectively. Here, the cell with 10% CDP-electrolyte shows the higher cycle efficiency than other cells with CDP-containing electrolyte, which maybe because that the 10% CDP in electrolyte is close to the reaction stoichiometric ratio and the stable solid electrolyte interphase (SEI) film is formed on the graphite surface. CDP maybe reacts with electrolyte, lithium, graphite and LiCoO_2 , and then the stoichiometric ratio is the ratio that CDP reacts with them in a reasonable way. Some of the reactions maybe are reversible with the charging and discharging. The detail reaction mechanism should be complex and interesting, and more experimental and theoretic works are needed to discover it. Comparing with our previous studies on 4-isopropyl phenyl diphenyl phosphate (IPPP) as electrolyte additive [16], they both show better efficiency at 10% content than that of 5% content, which indicates this kind of phosphate works well with 1.0M $\text{LiPF}_6/\text{EC} + \text{DEC}$ electrolyte at 10% content. Furthermore, the mean cycle efficiency of the cell with CDP-containing electrolyte is higher than that of IPPP (92.0%, 92.7%, 91.5% and 91.1% for 5%, 10%, 15% and 20% IPPP, respectively), and its standard deviation is smaller than that of IPPP (2.6, 3.1, 3.6 and 2.9 for 5%, 10%, 15% and 20% IPPP, respectively) [16]. Therefore, it can be speculated that CDP is better than IPPP as an electrolyte additive to enhance the thermal stability of the lithium ion battery.

Fig. 4 is the discharge specific capacity of $\text{LiCoO}_2/\text{CDP}$ -electrolyte/C cells. At the first cycles, the specific capacities are close to each other for the cells with 0%, 5% and 10% CDP-containing electrolyte. With the increasing of cycle numbers, the cell capacity of with 0% CDP-electrolyte decreases gradually, and reaches 105 mAh g^{-1} after 65th cycles. With the effect of CDP in electrolyte, the cells capacities attenuate more quickly, for the cell with 5% CDP-containing electrolyte, its capacity decreases from 121 mAh g^{-1} (2nd cycle) to 70 mAh g^{-1} (96th cycle). For the cell with 10% CDP-containing electrolyte, its specific capacity shows decreasing trend and its specific capacity is 94 mAh g^{-1} at the 74th cycle, which is larger than that of with 5% CDP-containing at the 74th cycles (82 mAh g^{-1}). When the CDP content increases to 15% and 20%, the cells specific capacities are lower at the first cycles, they are 114 mAh g^{-1} and 98 mAh g^{-1} , respectively. The capacity of $\text{LiCoO}_2/20\%$ CDP-electrolyte/C cell decreases too quickly to meet the requirement of practical usage, it decreases to 64 mAh g^{-1} at the 100th cycle. The cell with 20% CDP in electrolyte may be safer, but

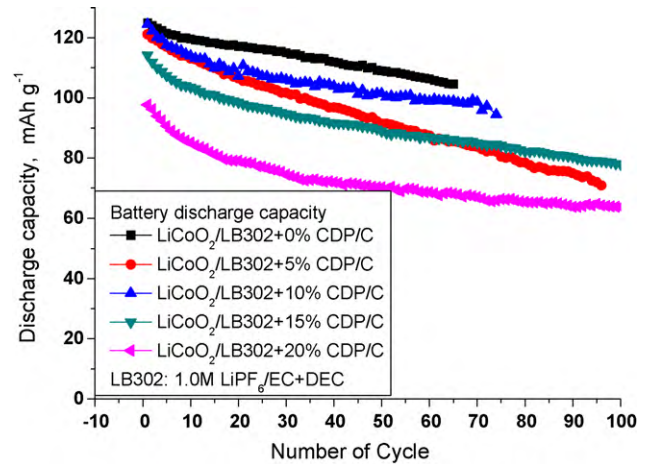


Fig. 4. Discharge specific capacity of LiCoO_2/C cells with different CDP content in 1.0M $\text{LiPF}_6/\text{EC} + \text{DEC}$ (1:1 wt.) electrolyte. The cells were cycled between 2.8 V and 4.2 V at a 0.2 mA cm^{-2} charge/discharge current density.

it sacrifices more specific capacity. The cells with 5%, 10% and 15% CDP-containing electrolyte have the less specific capacity loss with enhanced safety, which is acceptable CDP content in electrolyte.

Comparing with the cycle efficiency (Fig. 3) and discharge specific capacity (Fig. 4), the battery with 10% CDP-containing electrolyte shows better performance than that of 5% CDP-containing electrolyte, and they show worse performances than the battery without CDP-containing. It's hard to draw an exact cause that why the 5% CDP-containing battery performances are worse than 10% CDP-containing battery. It can be speculated that the possible cause is that the mass ration between CDP and electrolyte is close to the stoichiometric ratio of CDP react with lithium, anode, cathode and even electrolyte during charging and discharging, the new formed SEI film has better stability and better penetrability for the lithium. The structure morphology of the SEI can give more information and will be investigated further.

Fig. 5 is the AC impedances of $\text{LiCoO}_2/\text{CDP}$ -electrolyte/C cells at 4.05 V. It can be seen that all spectra are consisted of two semicircles in the high frequency range and a straight line in the low frequency range. The high frequency semicircle can be attributed to the lithium transport through the surface layers of electrodes

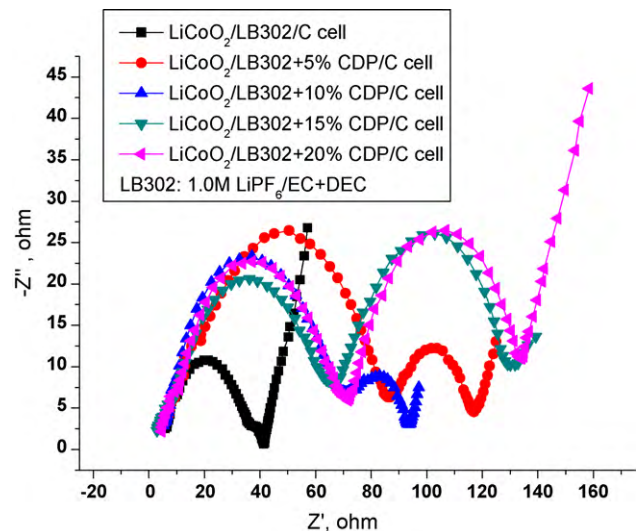


Fig. 5. AC impedances of LiCoO_2/C cells with different CDP content in 1.0M $\text{LiPF}_6/\text{EC} + \text{DEC}$ (1:1 wt.) electrolyte. The cells were cycled three times between 2.8 V and 4.2 V and then were charged approximately to 4.05 V.

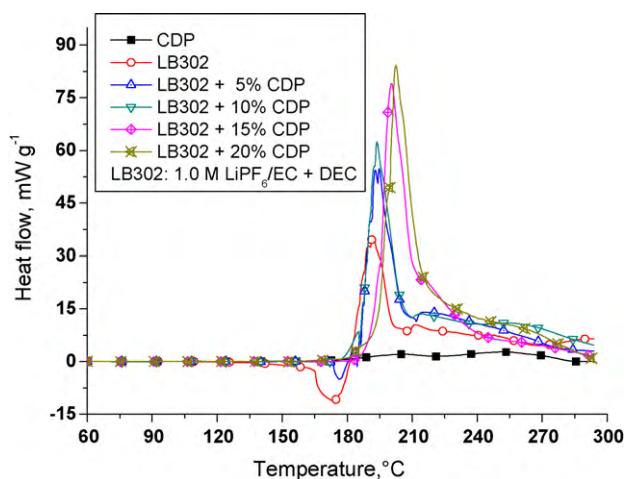


Fig. 6. C80 Heat flow profiles of electrolytes alone in argon filled vessel. The electrolyte are 1.0 M LiPF₆/EC:DEC (1:1 wt.) mixed with different CDP content, and the heating rate is 0.2 °C min⁻¹.

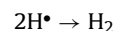
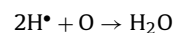
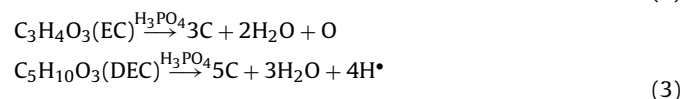
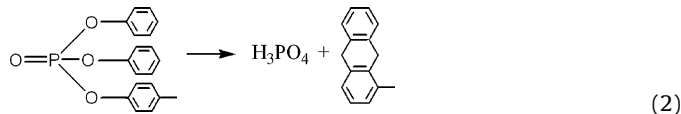
while the high-to-medium frequency semicircle to the charge-transfer process at the interfaces between the electrolyte and the electrodes [17,18]. The former semicircle is bigger than the latter semicircle. Without CDP in electrolyte, the impedance of the cell is small about 41 Ω. After the addition of CDP in electrolyte, the AC impedances of LiCoO₂/C cells increase to 116 Ω, 93 Ω, 130 Ω and 134 Ω corresponding to 5%, 10%, 15% and 20%, respectively. The AC impedance is increased with the addition of CDP in electrolyte, but the increased range shows little relationship with the content of CDP in electrolyte. The cell with 10% CDP-containing electrolyte shows smaller impedance than that of the 5%, and 15% and 20% CDP-containing electrolyte, which agrees with the results on cycle efficiency and discharge specific capacity. The AC impedance rise might be explained by the oxidation of CDP into a lithium-ion conducting Li₃PO₄ layer on the anode and cathode surface at charged states [19].

In summary, when the CDP content over 15% in electrolyte, the SEI film formed on anode is difficult for lithium ion to pass through, and the specific capacities decrease with the cycle number increasing. When the CDP content is 10% in the electrolyte, the specific capacity of LiCoO₂/CDP-electrolyte/C cell does not decrease too much, it is because the newly formed SEI film is more permeable at this CDP content range. Therefore, the addition 10% CDP into the electrolyte does not worsen the electrochemical performance of LiCoO₂/C cells too much, which is interesting and can be a perfect candidate as electrolyte additive.

3.2. Improved thermal stability

Fig. 6 shows C80 data for 1.0 M LiPF₆/EC+DEC (1:1 wt.%) electrolyte with different CDP additions. Without CDP in the electrolyte, the onset temperature is 140 °C, while with 5% CDP content, the onset temperature increases to 173 °C. The onset temperatures of electrolytes containing 10%, 15% and 20% CDP are 177 °C, 183 °C and 176 °C, respectively. Similarly, the temperature of the exothermic peaks also is put off from 191 °C (without CDP) to 193/195 °C (two peaks, 5% CDP), 194 °C (10% CDP), 200 °C (15% CDP), 202 °C (20% CDP). Without CDP in the electrolyte, an endothermic appears before the exothermic starts, as well as that with 5% CDP in electrolyte. The endothermic process disappears when the CDP content increase to 10%. This phenomenon indicates that 5% CDP is not enough to retard the reaction of electrolyte until 10% CDP is added into the electrolyte. The endothermic process of the electrolyte is thought as the PF₅ react with the DEC as Eq. (1) [20]. Phosphate

compounds are known as flame-retardants that can function in the vapor phase by a radical mechanism and can also function in the condensed phase. Here, CDP is mainly function in condensed phase as no combustion occurs. First, the CDP decomposes to H₃PO₄, as Eq. (2), and then, the charring process reacts as Eq. (3). After the addition of CDP into the electrolyte, it promotes the char formation on the surface to insulate the substrate from heat and oxygen, which can prevent the loss of decomposition products from the reaction zone. Therefore, the reaction in Eq. (1) is stopped and the endothermic process disappears either.



Although the results of these thermal investigations are inadequate to evaluate the thermal stability of electrode/CDP-containing electrolyte system, they can strongly suggest that the addition of CDP in the electrolyte significantly delays the onset decomposition temperature, and improves the thermal stability of the electrolyte. After the thermal test, the sealed vessel was opened, and it was found that with the CDP content increasing, less amount of gas products were observed. The residue is a ropy black substance that is mainly carbon. Thus, it is confirmed that char is formed in the electrolyte under the effect of CDP. Because that CDP may decomposes to phosphoric acid firstly, which can cause catalytic dehydration on organic solvent and form char as Eq. (3), the gas generation is lessened by CDP. In lithium-ion batteries, gas generation due to electrolyte decomposition involves different decomposition reactions in overcharged and overdischarged cells, which increases the battery explosion hazard. Therefore, CDP can act as a gas inhibitor to decrease the gas generation in electrolyte, and improve the batteries safety.

Fig. 7 is the heat flows of disassembled and wrapped LiCoO₂/CDP-electrolyte/C cells at a 0.2 °C min⁻¹ heating rate, the cells voltages are at about 4.20 V. Without the effect of CDP, the cell starts to release heat at 72 °C and appear several exother-

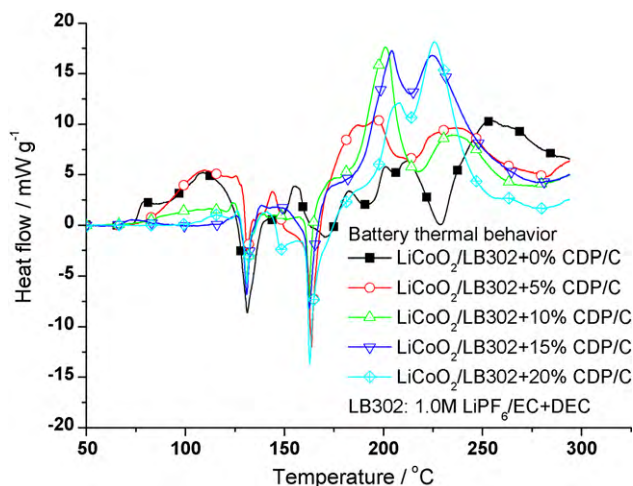


Fig. 7. Heat flows of disassembled and wrapped LiCoO₂/CDP-electrolyte/C cells at a 0.2 °C min⁻¹ heating rate, the cells voltages are at about 4.20 V.

mic peaks and an endothermic peak at 131 °C. This endothermic peak is the melting process of separator [21], before this endothermic process, the exothermic peak may be attributing to the SEI decomposition on cathode and anode [22]. The following several exothermic processes indicate that the complex reactions occurred in the cell system. After 5% CDP is added into the electrolyte, the onset temperature of LiCoO₂/C cell is put off to 80 °C with less heat generation, which is attributing to the decomposition of SEI formed on anode surface. With CDP content increasing in electrolyte, the onset temperatures of SEI are delayed to 83 °C and 109 °C corresponding to 10% CDP and 20% CDP, respectively. For the 15% CDP content in the electrolyte, a very small exothermic process from 67 °C to 88 °C with maximum heat flow of 0.53 mW g⁻¹, and later starts to release heat at 120 °C. The heat generation is integrated based on the C80 data, it was found that the addition of CDP in electrolyte also decreases the heat generation of SEI, which changes from -49.8 J g⁻¹ (no CDP in electrolyte) to -64.8 J g⁻¹, -27.6 J g⁻¹, -6.1 J g⁻¹ and -9.8 J g⁻¹ for 5% CDP, 10% CDP, 15% CDP and 20% CDP, respectively. After CDP is added into the electrolyte, two endothermic peaks near 131 °C and 162 °C are detected for the cells. The first is known as the melting of separator, and the second is unknown, but the endothermic process is a safe process for the thermal runaway of lithium ion battery, which keeps the battery in cool. Therefore, it can be concluded that when the CDP content exceeds 5% in the electrolyte, the battery shows better thermal behavior.

4. Conclusions

A novel phosphate, CDP, is characterized as a flame-retardant additive for lithium ion battery electrolyte. Its introduction into the lithium ion electrolyte can improve the battery safety while maintain a reasonably good electrochemical performance. It increases the thermal stability of electrolyte at the little expense of the electrochemical performance. In the LiCoO₂/CDP-electrolyte/C cells, the cells first discharge plates and discharge specific capacity decrease more or less, and the AC impedances increase. At the cycle efficiency, except the 10% CDP content in the electrolyte, the efficiencies decrease. At the thermal behavior aspect, not only the onset temperature of SEI is put off greatly, but also the heat generation is decreased greatly, which can put off the thermal runaway reaction and thus to enhance the safety of lithium ion battery. By comparing the electrochemical performance and the thermal

behavior of cells with different CDP content in electrolyte, a content of 5–10% CDP in the electrolyte is appropriate, and 10% CDP content shows the better performance both in electrochemical behavior and thermal stability. Therefore, 10% CDP addition should be a better choice to improve the thermal safety of lithium ion battery, and the studies on how the CDP would behave on the surface of electrodes will be carried out and the results will be reported in our future work.

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