



Cresyl diphenyl phosphate effect on the thermal stabilities and electrochemical performances of electrodes in lithium ion battery

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ABSTRACT

To improve the safety of lithium ion battery, cresyl diphenyl phosphate (CDP) is used as a flame-retardant additive in a LiPF₆ based electrolyte. The electrochemical performances of LiCoO₂/CDP-electrolyte/Li and Li/CDP-electrolyte/C half cells are evaluated. The thermal behaviors of Li_{0.5}CoO₂ and Li_{0.5}CoO₂-CDP-electrolyte, and Li_xC₆ and Li_xC₆-CDP-electrolyte are examined using a C80 micro-calorimeter. For the LiCoO₂/CDP-electrolyte/Li cells, the onset temperature of single Li_{0.5}CoO₂ is put off and the heat generation is decreased greatly except the one corresponding to 5% CDP-containing electrolyte. When Li_{0.5}CoO₂ coexists with CDP-electrolyte, the thermal stability is enhanced. CDP improves the thermal stability of lithiated graphite anode effectively and the addition of 5% CDP inhibits the decomposition of solid electrolyte interphase (SEI) films significantly. The electrochemical tests on LiCoO₂/CDP-electrolyte/Li and Li/CDP-electrolyte/C cells show that when less than 15% CDP is added to the electrolyte, the electrochemical performances are not worsen too much. Therefore, the addition of 5–15% CDP to the electrolyte almost does not worsen the electrochemical performance of LiCoO₂ cathode and graphite anode, and improves their thermal stability significantly; thus, it is a possible choice for electrolyte additive.

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1. Introduction

Lithium ion battery is ideal for portable devices because of its lightness and high energy density, such as laptops. In addition, lithium ion batteries have no memory effect and do not use poisonous metals, such as lead, mercury or cadmium. However, safety has always been an issue for lithium ion battery, random fires and explosions from overheating were not a widespread problem, but nevertheless, lithium ion battery manufacturer Sony, which came out with the first commercialized lithium ion battery in 1991, had to recall more than 6 million computers because of it. Fire and explosion of lithium ion battery is thought to be caused by the thermal runaway reactions occurred in the lithium ion battery [1–3].

In recent years, an intensive efforts to develop additives that improve safety by overcharge protection (via shuttle mechanisms) [4], co-solvents that may act as fire retardants [5] and non-flammable components to standard electrolyte solutions [6–10]. We have investigated cresyl diphenyl phosphate (CDP) as possible flame-retarding additive for lithium-ion battery electrolyte (1.0 M LiPF₆/ethylene carbonate (EC)+diethyl carbonate (DEC) (1:1 wt.)) in our previous study [11]. The effects of CDP

in improving both the thermal stability of the electrolyte and the cell performance of the lithium ion cell were examined. It is found that 10% CDP-containing electrolyte improves the safety of LiCoO₂/CDP-1.0 M LiPF₆/EC+DEC (1:1 wt.)/C battery and almost keeps its electrochemical performance in general. However, how the CDP would behave on the surface of electrodes is need further research and to evaluate its possibility as the flame retardant for commercial lithium ion battery.

In the present work, the effect of CDP on the thermal stability of LiCoO₂ and graphite were mainly investigated separately further, and the electrochemical performances of the half lithium ion cells also were examined.

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/EC+DEC (1:1 wt.) was prepared in an argon glove box (MBraun Labmaster 130) and used as a standard electrolyte. The CDP containing electrolytes are 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. It should be noted that the LiPF₆ concentration changes with CDP content changing, as the LiPF₆ is diluted by the addition of CDP when they were mixed together. LiCoO₂ (Tianjin B&M Science and Technology

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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 half coin cells. The cathode of LiCoO₂/Li cell was made of LiCoO₂ (84 wt.%), acetylene black (8 wt.%), and polyvinylidene fluoride (PVDF) (8 wt.%) binder. The graphite laminate of Li/C cell 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 ten hours 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/Li and Li/C cells were assembled with these disks, which provided samples for a C80 experiment.

LiCoO₂/Li cells were galvanostatically cycled on a multichannel battery cyler (Neware BTS-6V10mA, Shenzhen) at room temperature, between 4.2 V and 2.8 V at 0.2 mA cm⁻² current density for LiCoO₂/Li cells. Li/C cells were cycled between 3.0 V and 0 V at 0.2 mA cm⁻² current density. 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.

For the battery thermal test, the LiCoO₂/Li cell was cycled three times between 2.8 V and 4.2 V at 0.2 mA cm⁻² current density, and then was charged to 4.2 V and continues 1 h to ensure its voltage keeps at 4.2 V before it was disassembled. The Li/C cell was cycled three times between 3.0 V and 0 V at 0.2 mA cm⁻² current density, and then was discharged to 0 V and continues 1 h to ensure its voltage keeps at 0 V before it was disassembled. Great cares were taken to disassemble the cell in the argon filled glove box to avoid short circuit. To remove the electrolyte from the electrode, the wet charged electrode powder was placed into a bottle. To this bottle a portion of dimethyl carbonate (DMC), a volatile organic solvent, was added and the bottle was then 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. As DMC can lead to partial dissolution of the polymeric components of the solid electrolyte interphase (SEI), which in turn may decrease the integrity and real thermal stability of the SEI, the DMC rinsing procedure was repeated not more than twice. After drying, the electrode material was scraped from the current collectors carefully for thermal testing.

To characterize the thermal stability of the electrodes in the presence of electrolyte, approximately equal amounts of electrode material (including PVDF) and 1.0 M LiPF₆/EC+DEC electrolyte (corresponding CDP containing electrolyte) were transferred into a high-pressure stainless steel vessel (8.5 ml in volume) of a micro-calorimeter (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 °C min⁻¹ in the temperature range 30–300 °C in an argon filled vessel. The thermal effects of 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

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

Fig. 1 shows the first cycle voltage profiles of the LiCoO₂/Li cells with CDP containing electrolytes. For the 0%-CDP contain-

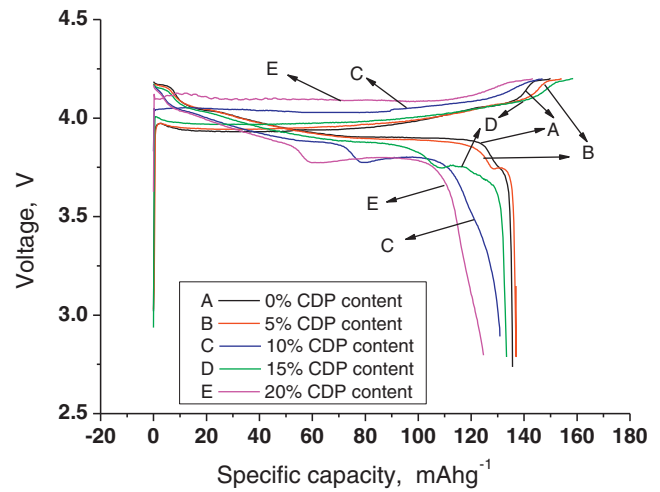


Fig. 1. First charge/discharge plots of LiCoO₂/Li batteries with different CDP content in 1.0 M LiPF₆/EC + DEC (1:1 wt.) electrolyte. The batteries were cycled between 2.8 and 4.2 V at a 0.2 mA cm⁻² charge/discharge current density.

ing electrolyte, a high discharge plateau is observed in the first cycle, with the addition of CDP, the voltage of the discharge plateau decreases gradually. The cell with 20%-CDP electrolyte shows the lowest discharge voltage plateau, and the lowest specific capacity is 124 mAh g⁻¹. In contrast, the addition of 5–15% CDP to electrolyte decreases the electrochemical performance at a small degree. The capacity losses, that is the capacity difference between first charge and discharge, of the cells are 15, 17, 15, 25 and 19 mAh g⁻¹ corresponding to the 0%, 5%, 10%, 15% and 20% CDP content in the electrolyte, respectively. The capacity loss percents are 10%, 11%, 10.3%, 15.8% and 13% corresponding to the 0%, 5%, 10%, 15% and 20% CDP content in the electrolyte. Based on the charge and discharge plateaus shown in Fig. 1, the CDP addition increases the ohmic drop of the cells. The possible reason is that the CDP addition results in the decrease of the electrical conductivity of the electrolyte.

Fig. 2 shows the electrochemical capacity of the LiCoO₂/Li cells with CDP containing electrolytes. Discharge capacity is calculated based on the mass of LiCoO₂. It can be seen that the cell with 5% CDP contenting electrolyte shows good performance and the other ones with 10% and 15% CDP contenting electrolytes decrease slightly than the normal one, and the 20% CDP content electrolyte lowers the capacity too much to be accepted. In general, with the increas-

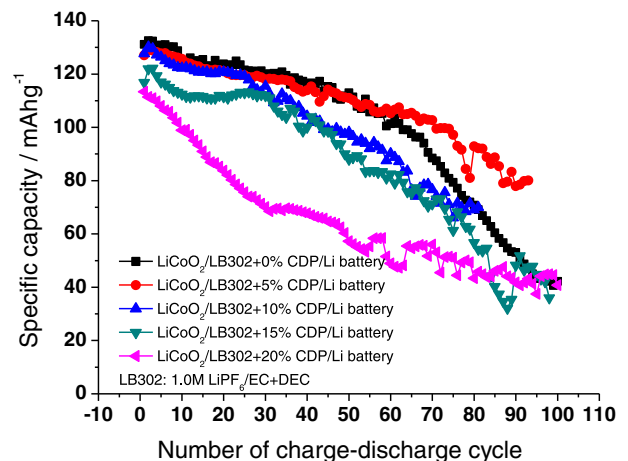


Fig. 2. Cycle performance of LiCoO₂/Li batteries with different CDP content in 1.0 M LiPF₆/EC + DEC (1:1 wt.) electrolyte. The batteries were cycled between 2.8 and 4.2 V at a 0.2 mA cm⁻² charge/discharge current density.

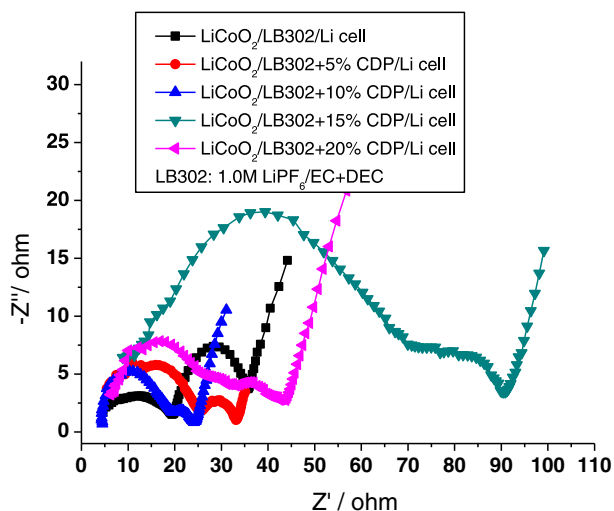


Fig. 3. AC impedances of LiCoO₂/Li batteries with different CDP content in 1.0 M LiPF₆/EC + DEC (1:1 wt.) electrolyte. The batteries were cycled three cycles between 2.8 and 4.2 V and then were charged approximately to 4.05 V.

ing of CDP content, the initial discharge specific capacity of the cell is decreasing, which may be due to the oxidation of CDP on the cathode surface.

The AC impedance spectra of LiCoO₂/Li half cells, which contain 0%, 5%, 10%, 15%, and 20% CDP were charged approximately to 4.05 V after three cycles, the results are shown in Fig. 3. All spectra consist 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, that is SEI layer mainly formed on the Li anode, while the high-to-medium frequency semicircle to the charge-transfer process between the interfaces and the electrodes LiCoO₂ cathode [12]. As the battery is in 4.05 V state, the lithium ion concentration in the cathode is small, and the resistance from the charge transfer is small, and then the AC impedance is controlled by the electrochemical process. In lithium anode, there are plentiful lithium ion and have high potential rush through the film and shows less resistance. When the CDP content is below 10% in the electrolyte, the resistance is smaller than that of without CDP in the electrolyte, and when more CDP is evolved in the electrolyte, the resistance increases greatly, while the charge-transfer resistance is stable. Again, the AC impedance rise might be explained by the oxidation of CDP into a lithium-ion conducting Li₃PO₄ layer on the cathode surface at charged states.

3.2. Thermal stability of Li_{0.5}CoO₂

Fig. 4 is the heat flow curves of Li_{0.5}CoO₂ alone at a 0.2 °C min⁻¹ heating rate in argon filled atmosphere. The Li_{0.5}CoO₂ is obtained from the LiCoO₂/CDP-electrolyte/Li cells charged at 4.2 V with different CDP content in 1.0 M LiPF₆/EC + DEC electrolyte. Without the effect of CDP, Li_{0.5}CoO₂ starts to release heat at 160 °C and reaches to peak temperature at 258.6 °C with heat reaction of -426.6 J g⁻¹. For the Li_{0.5}CoO₂ cycled in 5% and 10% CDP-containing electrolyte, another small exothermic process was detected before the main exothermic peak. The onset temperature and two exothermic peaks of (5% CDP) locate at 140 °C, 173 °C and 255 °C, with the total reaction heat of -540.7 J g⁻¹. For the Li_{0.5}CoO₂ cycled in 10% CDP containing electrolyte, the temperatures locate at 158 °C, 186 °C and 239 °C, respectively, with total heat generation of -287.6 J g⁻¹. When the CDP content is 15%, the onset temperature of Li_{0.5}CoO₂ is 188 °C, and reaches to exothermic peak at 242 °C, with heat generation of -359.7 J g⁻¹. When the CDP content is 20%, the onset

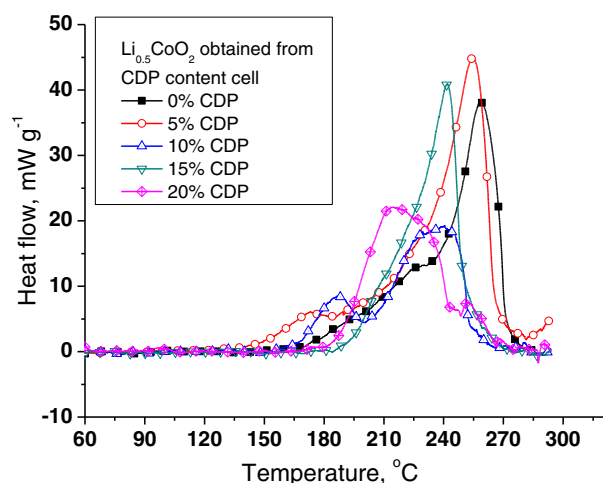


Fig. 4. Heat flows of Li_{0.5}CoO₂ alone at a 0.2 °C min⁻¹ heating rate.

temperature of Li_{0.5}CoO₂ is 180 °C and reaches to exothermic peak at 214 °C with heat generation of -311.7 J g⁻¹. The above results indicate that the CDP improves the thermal stability of Li_{0.5}CoO₂ except that cycled in 5% CDP-containing electrolyte. The Li_{0.5}CoO₂ obtained from the cell with 5% CDP-containing electrolyte shows lower onset temperature maybe caused by the unstable SEI film decomposition. As in the real battery system, the cathode is coexisting with the electrolyte, and then, the thermal stability of charged cathode with electrolyte can reveal the real effect of CDP on the improvement of cathode.

The thermal behaviors of Li_{0.5}CoO₂ with the presence of CDP containing electrolyte are shown in Fig. 5. In the Li_{0.5}CoO₂-CDP containing electrolyte system, the CDP concentration in electrolyte is corresponding to that used in LiCoO₂/CDP-electrolyte/Li cells. In Fig. 5, the Li_{0.5}CoO₂-1.0 M LiPF₆/EC + DEC coexisting system shows two main exothermic peaks at 196 °C and 230 °C, respectively, with the total heat generation of -920.1 J g⁻¹. Before the main exothermic process, one mild exothermic was detected starts at 74 °C, and reaches to peak at 78 °C. This process is thought as the decomposition of SEI formed on the cathode surface. For the CDP content electrolyte and Li_{0.5}CoO₂ system, its thermal behaviors changes greatly. When the CDP content is 5% in the Li_{0.5}CoO₂-electrolyte coexisting system, the decomposition of SEI starts at 97 °C, and the following main exothermic process reaches

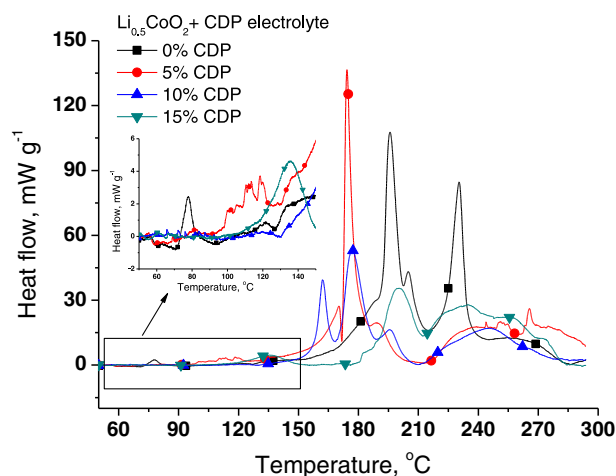


Fig. 5. Heat flows of Li_xCoO₂-CDP electrolyte at a 0.2 °C min⁻¹ heating rate, the Li_xCoO₂ were obtained from LiCoO₂/CDP-electrolyte/Li cells at about 4.2 V, and the CDP content in electrolyte are corresponding to that of Li/CDP-electrolyte/C cells.

peaks at 174 °C and 265 °C, respectively, with the total heat generation of -789.1 J g^{-1} . Furthermore, two shoulder peaks at 170 °C and 189 °C were detected before and after the peak at 174 °C. For the coexisting system of $\text{Li}_{0.5}\text{CoO}_2$ -10% CDP electrolyte, no obvious SEI decomposition process was detected and it starts to release heat at 134 °C, followed by three peaks at 162 °C, 177 °C, 196 °C and 245 °C with total heat generation of -547.6 J g^{-1} . With 15% CDP in the electrolyte, its coexisting system with $\text{Li}_{0.5}\text{CoO}_2$, the SEI starts to release heat at 117 °C, and reach three main peaks at 135 °C, 200 °C and 235 °C, respectively, with total heat generation of -637.7 J g^{-1} . It can be seen from the above thermal behaviors that the onset temperature of SEI is put off and the heat generation is declined after the addition of CDP into the electrolyte. More CDP is added in the electrolyte, the better thermal stability is obtained.

In the $\text{Li}_{0.5}\text{CoO}_2$ -CDP electrolyte system, the first exothermic peak maybe attributed to the SEI decomposition and then followed by $\text{Li}_{0.5}\text{CoO}_2$ /electrolyte decomposition [13]. As the SEI film component varies with the CDP content, the certain decomposition processes differ with different CDP 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 CDP, the first exothermic process is inhibited, heat generation is reduced. The above results indicated that CDP can suppress the coexisting system activity of $\text{Li}_{0.5}\text{CoO}_2$ -CDP containing electrolyte. It may be caused by the formed char from electrolyte under the effect of CDP and deposit on the cathode and then the reaction product prevents further thermal reaction of electrolyte, $\text{Li}_{0.5}\text{CoO}_2$ and theirs interactions leading safety to lithium ion batteries [11].

3.3. Electrochemical performance of Li/CDP-electrolyte/C cells

Fig. 6 shows the first discharge/charge plots of Li/CDP-electrolyte/C cells. The cells were cycled between 3.0 V and 0 V at a 0.2 mA cm^{-2} discharge/charge current density. Without the effect of CDP in the electrolyte in the Li/C cell, the specific capacity loss is 43.0 mAh g^{-1} for the first cycle. The specific capacity losses in the first cycle for the Li/C cells with 5%, 10% and 15% CDP content in the electrolyte are 53.4 mAh g^{-1} , 52.4 mAh g^{-1} and 54.3 mAh g^{-1} , respectively, which are little different among them. About 10 mAh g^{-1} capacity is increased with the addition of CDP less than 15% content in the electrolyte. The results indicate that CDP has little influence on the capacity losses for the first cycle of Li/CDP-electrolyte/C cells. When the CDP content increases to

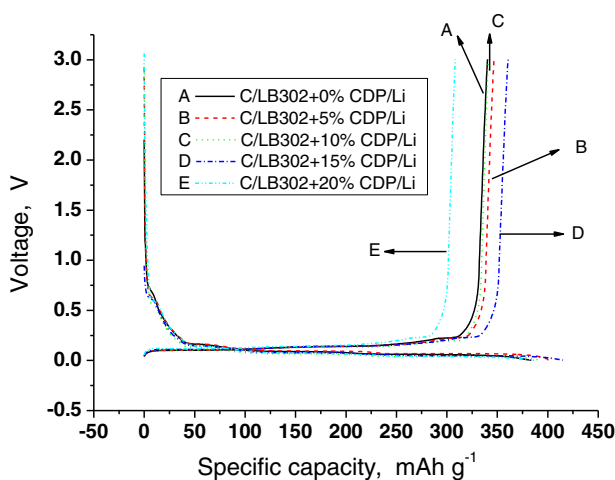


Fig. 6. First discharge/charge plots of Li/C batteries with different CDP content in 1.0 M $\text{LiPF}_6/\text{EC} + \text{DEC}$ (1:1 wt.) electrolyte. The batteries were cycled between 3.0 and 0 V at a 0.2 mA cm^{-2} discharge/charge current density.

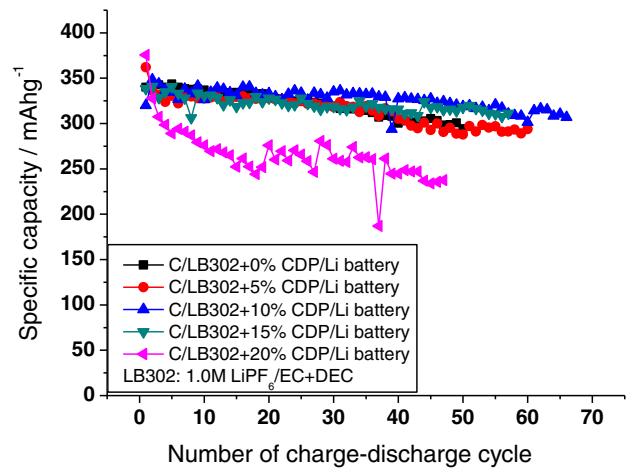


Fig. 7. Discharge capacities of Li/C batteries with different CDP content in 1.0 M $\text{LiPF}_6/\text{EC} + \text{DEC}$ (1:1 wt.) electrolyte. The batteries were cycled between 3.0 and 0 V at a 0.2 mA cm^{-2} discharge/charge current density.

20% in the electrolyte, the capacity loss reaches 78.3 mAh g^{-1} , and the increased capacity loss indicates that more lithium is consumed and the reversible capacity is decreased. Hence, CDP has little influence on the first cycle performance of cells assembled with graphite anode, and 5–15% CDP content in electrolyte is an acceptable concentration judged by this point.

Fig. 7 shows the discharge capacity plots of Li/CDP-electrolyte/C cells. The cells were cycled between 3.0 V and 0 V at a 0.2 mA cm^{-2} discharge/charge current density. Without the presence of CDP in the electrolyte, the discharge specific capacity of Li/C cell decreases with the increase of cycle number, and the average specific capacity is 322.0 mAh g^{-1} with 14.7 standard deviation for the first 50th cycles. For the Li/C cells with 5%, 10% and 15% CDP content electrolyte, the mean specific capacities are 314.5 mAh g^{-1} , 326.5 mAh g^{-1} and 321.1 mAh g^{-1} with standard deviation of 16.2, 10.8 and 8.1 for the first 60th, 66th and 57th cycles, respectively. These results indicate that the addition of CDP does not decrease the discharge capacity of Li/C cell below the content of 15% CDP in the electrolyte. However, when the CDP content in the electrolyte is 20% in the electrolyte, the mean specific capacity of Li/C cell is 265.7 mAh g^{-1} and with standard deviation of 27.8, which means the capacity fluctuates greatly with the cycle number increasing. The increased standard deviations may be caused by the formation of newly products on the anode surface by the reactions of CDP with lithium or electrolyte. In normal $\text{LiPF}_6/\text{EC} + \text{DEC}$ electrolyte, the SEI layer is mainly consist of stable (such as LiF , Li_2CO_3), and metastable components (such as polymers, ROCO_2Li , $(\text{CH}_2\text{OCO}_2\text{Li})_2$ and ROLi) [13]. After addition of CDP, may be $(\text{C}_{19}\text{H}_{16}\text{O}_4\text{P})\text{Li} \sim (\text{C}_{19}\text{H}_{14}\text{O}_4\text{P})\text{Li}_3$ is formed and involved in the SEI film according to the structure of CDP [11]. The newly formed SEI film blocks the lithium ion transfer between the electrolyte and graphite layer. Once the blocked lithium ions break out from the film, the rushed lithium ions could result in larger standard deviation of specific capacity.

Fig. 8 shows the AC impedance test results of Li/C cells with different CDP content in 1.0 M $\text{LiPF}_6/\text{EC} + \text{DEC}$ (1:1 wt.%) electrolyte. The cells were cycled three times between 3.0 V and 0 V and then discharged to approximately 0 V. The high frequency semicircle is attributed to the lithium transport through the SEI film of graphite electrode [5,14]. Only one semicircle was detected, which indicates that a stable SEI film is formed on the graphite surface. The AC impedance of the SEI film is stable and changes very little with the increases of CDP content in the electrolyte. This indicates that after the first cycle, the stable SEI is formed on the anode surface, which is no longer changing with the CDP containing in the electrolyte.

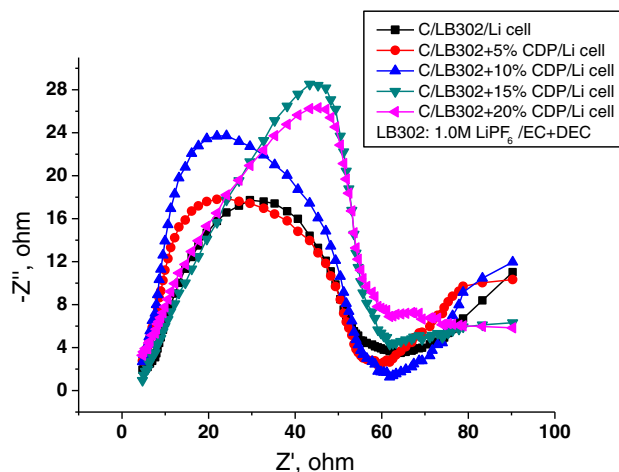


Fig. 8. AC impedances of Li/C batteries with different CDP content in 1.0M LiPF₆/EC+DEC (1:1 wt.) electrolyte. The batteries were cycled three cycles between 3.0 and 0V and then were discharged approximately to 0V.

In summary, when the CDP content exceeds 15% in electrolyte, the specific capacity fluctuates greatly and with specific capacity losses. When the CDP content equal and below 15% in the electrolyte, the first discharge specific capacity, the cycle specific capacity, and AC impedance of Li/CDP electrolyte/C cells are not be worsen, because the newly formed SEI film is more permeable at this CDP content range. Therefore, the addition amount below 15% CDP into the electrolyte does not worsen the electrochemical performance of Li/C cells, which is acceptable for graphite anode.

3.4. Thermal stability of lithiated graphite

The anode plays a key role for the thermal runaway of lithium ion battery, as the SEI formed on the anode surface decomposes at low temperature. The CDP influence on the Li_xC₆ thermal stability is shown in Fig. 9. The Li_xC₆ were obtained from corresponding Li/CDP-electrolyte/C cells at approximately 0V. The single Li_{0.84}C₆ obtained from Li/C cell without CDP in the electrolyte decomposes at 50°C. As for the lithiated graphite obtained from Li/5% CDP-electrolyte/C cells, its SEI film decomposes at 76°C. The more CDP is added into the electrolyte, the higher onset temperature of the exothermic reaction between Li_xC₆ and electrolyte is detected. At

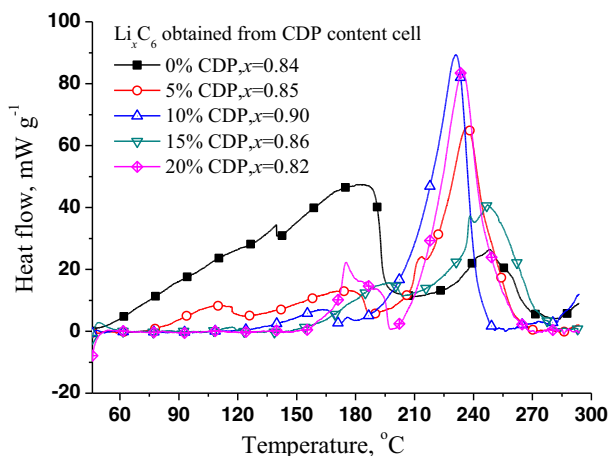


Fig. 9. Heat flows of Li_xC₆ alone at a 0.2°C min⁻¹ heating rate, the Li_xC₆ are got from corresponding Li/CDP-electrolyte/C cells at about 0V.

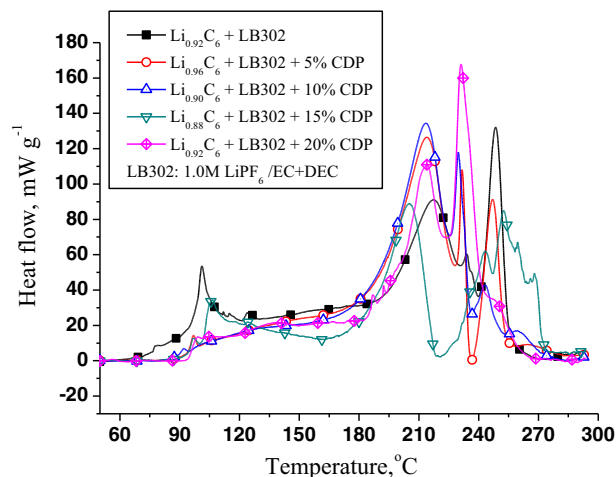


Fig. 10. Heat flows of Li_xC₆-CDP electrolyte at a 0.2°C min⁻¹ heating rate, the Li_xC₆ are got from Li/CDP-electrolyte/C cells at about 0V, and the CDP content in electrolyte are corresponding to that of Li/CDP-electrolyte/C cells.

10%, 15% and 20% CDP content in the electrolyte, the onset temperatures are 122°C, 152°C and 156°C, respectively. The results indicate that CDP restrains the decomposition of Li_xC₆ effectively, and the heat generation decreases greatly. The heat generation was calculated based on the C80 data. It was found that the total heat generation is reduced from -1339.0 J g⁻¹ (0% CDP) to -875.4 J g⁻¹ (5% CDP), -754.4 J g⁻¹ (10% CDP), -636.5 J g⁻¹ (15% CDP) and -780.6 J g⁻¹ (20% CDP), respectively. Therefore, CDP improves the thermal stability of Li_xC₆ anodes significantly.

In the real lithium ion battery system, the electrolyte coexists with anode, and therefore, the thermal stability of such coexisting system is closely related to the safety of lithium ion batteries. Fig. 10 shows the heat flow plots of Li_xC₆-CDP electrolyte at a 0.2°C min⁻¹ heating rate. The Li_xC₆ were obtained from Li/CDP-electrolyte/C cells at approximately 0V, and the CDP content in the electrolyte are corresponding to that of Li/CDP-electrolyte/C cells. Three to four exothermic peaks were detected, which are attributed to the SEI breakdown, lithium-electrolyte reaction, new SEI film breakdown and Li₂CO₃ formation reactions overlapped with PVDF reactions, respectively [13]. The Li_xC₆-electrolyte system starts to release heat at 60°C by the breakdown of SEI film, and reaches its exothermic peak temperature at 102°C with total heat generation of -2271.8 J g⁻¹. Once the CDP is added into the electrolyte, the onset temperatures of SEI breakdown in the coexisting systems are put off to 84°C, 82°C, 86°C and 93°C for 5% CDP, 10% CDP, 15% CDP and 20% CDP electrolyte, respectively. Furthermore, the total heat generation is reduced to -2132.8 J g⁻¹, -2137.2 J g⁻¹, -1758.9 J g⁻¹ and -2029.1 J g⁻¹ for 5% CDP, 10% CDP, 15% CDP and 20% CDP-added electrolytes, respectively. If we simply thought the SEI decomposition is completely finish at 120°C, then, the heat generation is integrated for the five curves. The heat generations of SEI are 317.0 J g⁻¹, 102.4 J g⁻¹, 100.7 J g⁻¹, 166.3 J g⁻¹, 99.0 J g⁻¹, for 0% CDP, 5% CDP, 10% CDP, 15% CDP and 20% CDP-added electrolytes, respectively. The results indicate that the CDP in the coexisting system delays the onset temperature of SEI decomposition, and the SEI decomposition heat and total heat generation are reduced.

Based on the above results and analysis, it is concluded that by the addition of CDP into the electrolyte, the onset temperature of SEI decomposition is significantly delayed and the total heat generation is significantly reduced. The using of CDP reduces the possibility of the following exothermic reactions, and thus the thermal stability of the whole lithium ion battery system is improved.

4. Conclusions

A novel phosphate, CDP, is characterized as a flame-retardant additive for lithium ion battery electrolytes. Its introduction into the lithium-ion electrolyte can improve battery safety while maintaining a reasonably good electrochemical performance as we reported before [11]. The effects of CDP on cathode and anode of lithium ion battery were investigated separately in this paper.

In the $\text{LiCoO}_2/\text{CDP-electrolyte}/\text{Li}$ cells with different CDP content, the onset temperature of single $\text{Li}_{0.5}\text{CoO}_2$ is put off somewhat and the heat generation is decreased greatly except the one corresponding to 5% CDP-containing electrolyte. When the $\text{Li}_{0.5}\text{CoO}_2$ coexists with CDP-electrolyte, the thermal stability is enhanced at the 5%, 10% CDP and 15% CDP content in electrolyte. The influence of CDP on the electrochemical performance for $\text{LiCoO}_2/\text{CDP-electrolyte}/\text{Li}$ cells indicated that a content of 5–15% CDP in the electrolyte is appropriate.

The electrochemical tests on $\text{Li}/\text{CDP-electrolyte}/\text{C}$ cells show that when less than 15% CDP is added to the electrolyte, the electrochemical performance of graphite is similar to the case when no CDP is added. When the CDP content is more than 15%, the newly formed SEI film is too robust for lithium ions to transfer between the electrodes and electrolyte, causing large fluctuations in cycle specific capacity. The thermal stability test results show that CDP improves the thermal stability of lithiated graphite anodes effectively. The addition of 5% CDP inhibits the decomposition of SEI films significantly.

Based on electrochemical performance and thermal stability studies, it is concluded that the addition of 5–15% CDP to the electrolyte has few effect on the electrochemical performance of LiCoO_2

cathode and graphite anode, and improves its thermal stability significantly, thus, it is a possible excellent choice of electrolyte additive.

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