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Short communication

Cresyl diphenyl phosphate as flame retardant additive for lithium-ion batteries

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ABSTRACT

To improve the safety of lithium-ion batteries, cresyl diphenyl phosphate (CDP) was used as a flame retardant additive in a $LiPF_6$ electrolyte solution. The flammability of the electrolytes containing CDP and the electrochemical performances of the cells, $LiCoO_2$/Li, graphite/Li and the battery $LiCoO_2$/graphite with these electrolytes, were studied by measuring the self-extinguishing time of the electrolytes, the variation of surface temperature of the battery and the charge/discharge curve of the cells or battery. It is found that the addition of CDP to the electrolyte provides a significant suppression in the flammability of the electrolyte and an improvement in the thermal stability of battery. On the other hand, the electrochemical performances of the cells become slightly worse due to the application of CDP in the electrolyte. This alleviated trade-off between the flammability and thermal stability and cell performances provides a possibility to formulate a nonflammable electrolyte by using CDP.

1. Introduction

Lithium-ion batteries have been widely used, but their safety needs to be improved. The composition of electrolyte is essential for the performance improvement of lithium-ion batteries [1–5]. However, the safety of the batteries is related to flammability of the electrolyte. Thus, flame retardancy is a major challenge for the safety improvement of lithium-ion batteries [6]. Although much effort has been devoted to formulating an electrolyte that is nonflammable and also works well in lithium-ion batteries, the results have not been very satisfactory.

The attempt to improve the electrolyte flammability is always accompanied by the capacity loss of the batteries. The flame retardants that have been explored so far include trimethyl phosphate (TMP) [7], hexamethoxycyclotriphosphazene (HMPN) [8], tri(β-chloromethyl) phosphate (TCEP) [9], tris(2,2,2-trifluotohyl) phosphate (TFP), bis(2,2,2-trifluoroethyl) methylphosphate (BMP), (2,2,2-trifluotoethyl) diethyl phosphate (TDP) [10], and so on. Most of them are phosphate-containing compounds. With the application of these flame retardants, the electrolyte flammability is suppressed but the batteries suffer from severe capacity fading.

To reach good flame retardancy of an electrolyte, the flame retardant used should be have a high boiling point. On the other hand, the flame retardant should have a low melted point and a low viscosity for an electrolyte to reach good conductivity. Cresyl diphenyl phosphate (CDP) is a new flame retardant reagent, which has not been reported for the application in lithium-ion batteries. Compared with other phosphates [10], CDP has a higher boiling point, appropriate viscosity and melted point, as shown in Table 1. Thus it should be a good flame retardant for lithium-ion battery use. The application of CDP as the flame retardant in 1 M $LiPF_6$ in a mixture of 1:1:1 (in mass) ethylene carbonate (EC) and dimethyl carbonate (DMC) and ethylene methyl carbonate (EMC) was considered in this paper.

2. Experimental

As-purchased CDP was purified with a distillation step under vacuum and dried over molecular sieves (4 A) before use. An electrolyte of 1 M $LiPF_6$/EC + DMC + EMC (1:1:1 in mass) was selected as a base electrolyte.

5, 10, 15, 20, 30, and 40% (in mass) of CDP were added directly to the 1 M $LiPF_6$/EC + DMC + EMC electrolyte to prepare the CDP-containing electrolytes for the determination of self-extinguishing time. Fiberglass wicks (4 cm in length, 8 mm in diameter) were first immersed in the electrolytes for absorbing about 1 g electrolyte and then set horizontally on the stand. A lighter was used to burn one end of the fiber, and a timer was used to record the burning time of the electrolytes. Each test was repeated seven times and the burning times recorded were averaged for the electrolyte samples containing different amount of CDP. The electrolytes containing TMP and TEP were used for comparison.

2016-Type cells, $LiCoO_2$/Li and graphite/Li, and prismatic battery of 980 mAh (063448) $LiCoO_2$/graphite were assembled in the argon-filled glove box for the determination of anode, cathode and battery performances. The preparation of the cells and the bat-

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Table 1
Physical properties of some phosphates used as flame retardants

	Phosphate					
	CDP	TCEP	HMNP	TMP	TFP	BMP
Boiling point (°C)	360	194	>250	197	178	203
Melted point (°C)	<−30	−64	50	−46	−19.6	−22.5
Viscosity, $\varepsilon_{20\,^\circ\mathrm{C}}$ (mPa s)	33	40		2.47	1.25	12

tery is shown in Fig. 1. A positive electrode consisting of LiCoO$_2$ (84 wt.%), acetylene black (8 wt.%) and poly(vinylidene fluoride) (PVDF) (8 wt.%) and a negative electrode consisting of a surface-modified graphite (SMG, 92 wt.%) and PVDF (8 wt.%) were made on aluminum and copper foils, respectively.

Oven tests were conducted in a specially designed explosion-box for the determination of thermal stability of lithium-ion battery. The battery was fully charged to 4.2 V after three cycles and the oven temperature was raised from environment temperature to 150 °C, and then the temperature was kept stable. A type K thermal couple was attached to the center of the largest face of the battery to record the temperature change of the battery. The thermocouple outputs from the test batteries were connected to monitoring equipment outside the box.

Charge and discharge tests were conducted on BK-7128L/2 lithium-ion battery testing device (Guangzhou Blue-Key Electronic Industry Co., Ltd.). LiCoO$_2$/Li 2016-type cells were charged with 0.1 mA to 4.2 V and discharged with 0.1 mA to 3.0 V. Graphite/Li 2016-type cells were charged with 0.1 mA to 3.0 V and discharged with 0.1 mA to 0.0 V. LiCoO$_2$/graphite batteries were charged with 980 mA (1*C*) to 4.2 V and discharged with 980 mA to 3.0 V.

3. Results and discussion

Fig. 2 presents the results of the self-extinguishing time (SET) of electrolyte using CDP as flame retardant, with comparison of the electrolytes using TMP and TEP as flame retardants, which were believed to be good for the application in lithium-ion battery [6].

It can be seen from Fig. 2 that the base electrolyte, i.e. 1 M LiPF$_6$/EC + DMC + EMC (1:1:1 in mass), is very flammable with self-extinguishing time of 60 s. However, when the retardants, TMP, TEP and CDP, are applied, the SET of the electrolytes are significantly reduced. The mechanism for organophosphorus compounds as flame retardants has been well known [11]. P$_2$O$_5$ is formed from the oxidation of the flames retardants as soon as the electrolyte is burnt. It captures the radicals, $H^\bullet$ and $HO^\bullet$, in the flame zone, so that the chain reactions for combustion are weakened or terminated.

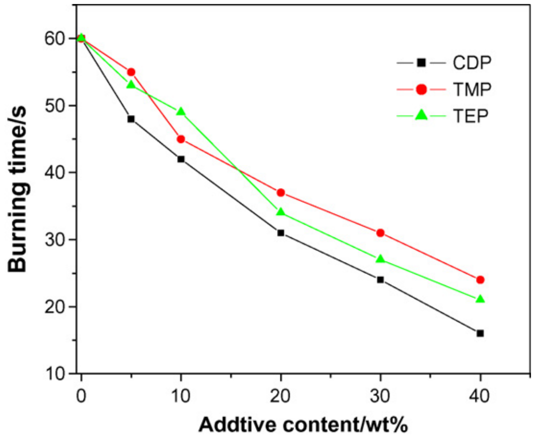

Fig. 2. Variation of self-extinguishing time with the content of flame retardants in 1 M LiPF$_6$/EC + DMC + EMC (1:1:1 in mass).

By comparing the reducing tendency of the SET of the electrolytes with the content of the retardants, as shown in Fig. 2, it can be found that CDP shows its better flame retardancy for the electrolyte than TMP and TEP. With the content of 40%, the SET is 24 s, 22 s and 16 s for TMP, TEP and CDP, respectively.

The application of a flame retardant in lithium-ion batteries is always accompanied by the capacity decay of the battery. In practice, the content of less than 5% of a flame retardant in electrolyte is used. To understand the effect of the CDP on battery performances, the electrolyte with 5% CDP was used in this paper. With this content, the SET of the electrolyte using CDP as flame retardant is 47 s, far shorter than that of the electrolytes using TMP and TEP as the retardants, which is 56 s and 54 s, respectively.

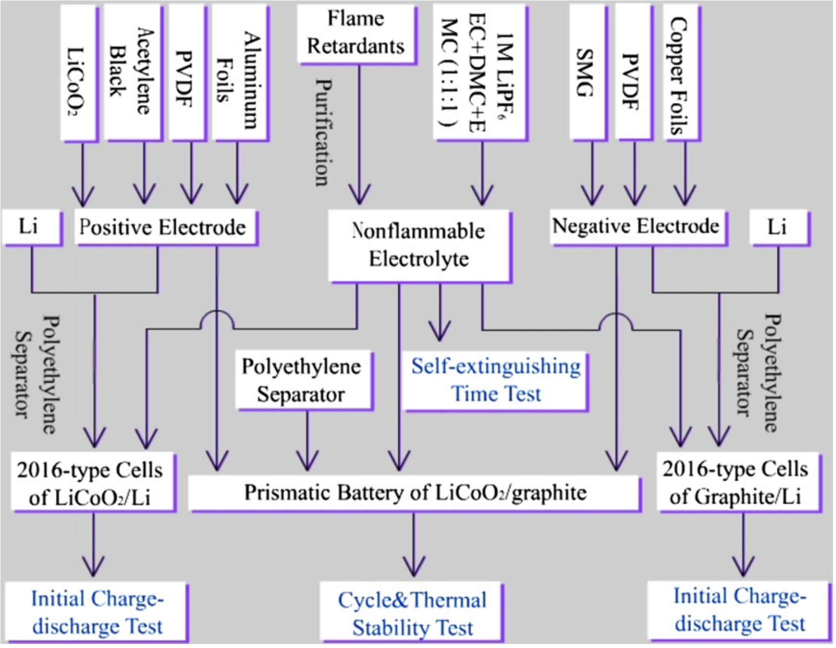

Fig. 1. Illustration for the preparation of electrolyte, cells and battery.

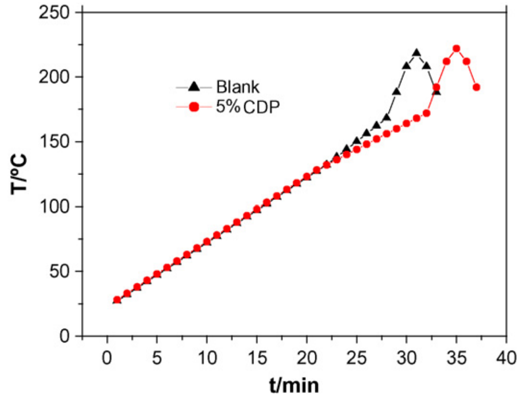

Fig. 3. Variation of surface temperature of graphite/$LiCoO_2$ batteries with time.

The safety of a lithium-ion battery is related to its thermal stability. To understand the thermal stability of the battery using CDP as flame retardant, oven test was conducted. The obtained result is shown in Fig. 3, with a comparison of the battery without use of CDP.

It can be found from Fig. 3 that the surface temperature of the batteries increases linearly with time during the oven test, but rises dramatically at a certain time. This happens because the electrolytes decompose under heating. Thus the time for the dramatic rise in the surface temperature reflects the thermal stability of the batteries. When the battery without use of CDP is heated for 28 min, the surface temperature of the battery rises dramatically to 168 °C. However, this happens for the battery containing 5% CDP when heated for 34 min. Apparently, CDP can retard the decomposition of the electrolyte.

To understand the effect of CDP on the battery performance, the charge and discharge performances of the cells, $LiCoO_2$/Li and graphite/Li, and the battery $LiCoO_2$/graphite with and without use of CDP were determined.

Fig. 4 presents the charge and discharge curves of $LiCoO_2$/Li 2016-type cells using the electrolyte (1 M $LiPF_6$/EC + DMC + EMC (1:1:1) with and without CDP. It can be seen from Fig. 4 that the application of CDP results in the capacity loss of $LiCoO_2$. The discharge capacity of the cathode is 120.3 mAh g^{-1} and 126.0 mAh g^{-1} for the cell with and without CDP, respectively. There is a cathode capacity loss of 4.2% due to the use of 5% CDP. This loss is smaller than those from other flame retardants. For example, the cathode capacity loss is 5.1% for the application of 5% TMP [7].

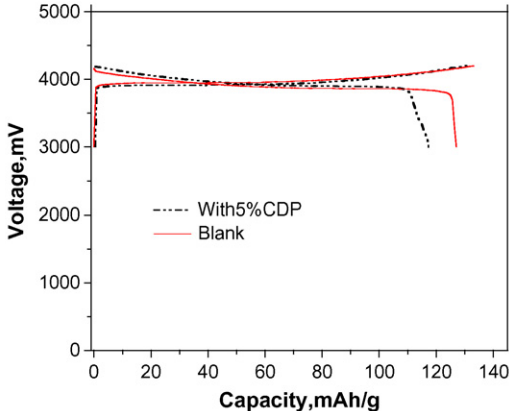

Fig. 4. Charge and discharge curves of $LiCoO_2$/Li 2016-type cells using the electrolyte (1 M $LiPF_6$/EC + DMC + EMC (1:1:1 in mass)) with and without CDP at 0.1 mA cm^{-2}.

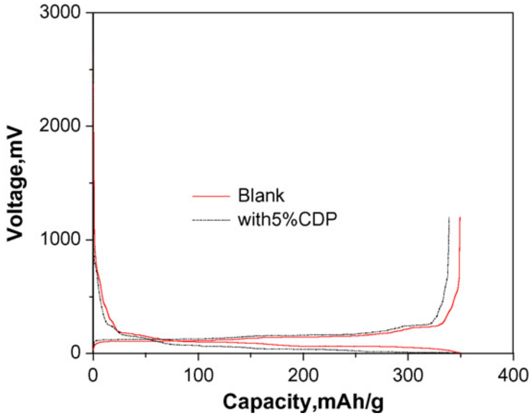

Fig. 5. Charge and discharge curves of graphite/Li 2016-type cells using the electrolyte (1 M $LiPF_6$/EC + DMC + EMC (1:1:1 in mass)) with and without CDP at 0.1 mA cm^{-2}.

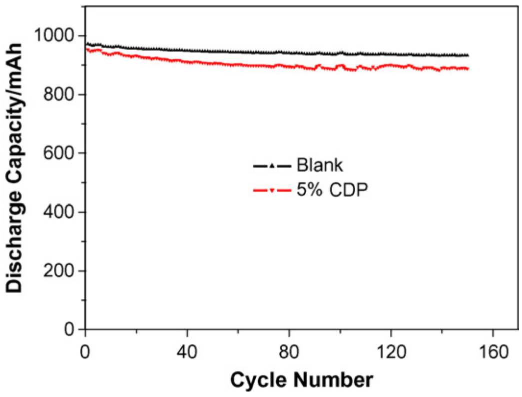

Fig. 6. Cyclic stability of graphite/$LiCoO_2$ batteries using the electrolyte (1 M $LiPF_6$/EC + DMC + EMC (1:1:1 in mass)) with and without CDP at 1*C* rate.

Fig. 5 presents the charge and discharge curves of graphite/Li 2016-type cells using the electrolyte (1 M $LiPF_6$/EC + DMC + EMC (1:1:1) with and without CDP. Different from the effect of CDP on the cathode, the charge and discharge performance of the graphite is hardly influenced by CDP. The initial capacity of the anode is 339.0 mAh g^{-1} and 349.2 mAh g^{-1} for the cell with and without CDP, respectively. There is an anode capacity loss of 2.9% due to the use of 5% CDP. It is noted that this capacity loss from CDP is far smaller than those from other flame retardants such as TMP [12], The initial capacity of the anode is 204 mAh g^{-1} and 254 mAh g^{-1} for the cell with and without TMP, respectively. The anode capacity loss is 19.7% for the use of TMP.

Fig. 6 presents the variation of discharge capacity of graphite/$LiCoO_2$ batteries cells using the electrolyte (1 M $LiPF_6$/EC + DMC + EMC (1:1:1) with and without CDP with cycles. It can be found from Fig. 6 that the initial capacity and the cyclic stability of the battery are reduced to some extent with the application of CDP. The initial capacity of the battery is 953 mAh and 972 mAh for the electrolyte with and without CDP, respectively. There is about 1.95% of capacity loss of the battery due to the use of 5% CDP. After 150 cycles, the capacity of the battery with CDP keeps 93.0% of its initial capacity, 2.9% less than the battery without CDP, whose capacity keeps 95.9% of its initial capacity. It is obvious that the reduce in initial capacity and the cyclic stability of the battery due to the application of CDP is not so significantly.

4. Conclusions

A phosphate, cresyl diphenyl phosphate (CDP) is used, for the first time, as a flame retardant additive for lithium-ion battery electrolytes. Only 5% CDP addition can result in the SET greatly decreases of electrolyte. Negative effect on the battery performances is insignificantly with the application of CDP. It provides a promising solution to the safety concern of lithium-ion battery.

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