

Comparative study of trimethyl phosphite and trimethyl phosphate as electrolyte additives in lithium ion batteries

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Abstract

Safety concerns of lithium ion batteries have been the key problems in their practical applications. Trimethyl phosphite (TMP(i)) and trimethyl phosphate (TMP(a)) were used as the electrolyte additives to improve the safety and electrochemical performance of lithium cells. Galvanostatic cell cycling, flammability test and thermal stability measurements by means of accelerated rate calorimeter (ARC) and micro calorimeter were performed. It is found that both TMP(i) and TMP(a) reduce the flammability of the electrolyte. The TMP(i) additive not only enhances the thermal stability of the electrolyte, but also improves its electrochemical performance. The TMP(a) additive can improve the thermal stability of the electrolyte at the expense of some degree of degradation of its electrochemical performance. Therefore, TMP(i) is a better flame retardant additive in the electrolyte compared with TMP(a).

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1. Introduction

Lithium rechargeable cells possess high energy density compared to other secondary batteries. Small lithium ion batteries are commercially available to power portable electronic devices such as camcorders, computers, cellular phones, etc. The demand for high power and energy storage sources has resulted in substantial research and development of rechargeable lithium batteries. For instance, lithium ion batteries are being developed as power sources for electrical vehicles to provide longer driving ranges, higher accelerations, and longer lifetimes. However, safety concerns have limited the full utilization of Li-ion batteries in EV applications [1]. Under abusive conditions and even under normal operating conditions, Li-ion cells always undergo thermal runaway, which may result in high temperature, smoke, and even explosions of cells. Because of these safety limitations and tendencies

toward thermal runaway, the use of lithium ion batteries in the marketplace has largely been limited to small cells [2].

One of the effective strategies to address this safety issue is to reduce the electrolyte flammability and in the ideal situation to use a nonflammable electrolyte. Up to now, attempts to formulate an electrolyte that is nonflammable and also works well in lithium ion cells have not been very successful [3–10]. There always exists a trade-off between the electrolyte flammability and its performance in cell. Therefore, studies to reduce the flammability of the electrolytes have been made by incorporating a flame-retardant as the additive or cosolvent [3–7]. The flame retardants that have been explored so far include trimethyl phosphate [3–6], triethyl phosphate [4,6], tris(2,2,2-trifluoroethyl) phosphate [4,7], hexamethylcyclo-phosphazene [4,6], triphenylphosphate and tributylphosphate [8], ethylene ethyl phosphate [9], methyl nonafluorobutyl ether [10]. Among them, the flame retardants based on phosphate or P(V) compounds have been found to be able to suppress the flame propagations at the expense of battery performance [4,5]. Namely, the reduction of electrolyte

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flammability by the known phosphorus-based flame retardants is always realized at the expense of cell performance, i.e., either electrochemical instability causing severe capacity fading or high viscosity of these cosolvents affecting both capacity utilization and power. Trimethyl phosphate, referred as TMP(a) hereafter, is the only flame retardant (FR) that has been fully investigated with respect to its electrochemical stability on the carbonaceous anode and metal oxide cathode [3–6]. There has been no report published on the electrochemical performance and thermal stability of trimethyl phosphite, referred as TMP(i) hereafter. In the study described in this paper, we have found that TMP(i) in which the oxidation state of phosphorus is three instead of five, is very effective in improving both the thermal stability and electrochemical behavior of LiPF₆-based electrolytes.

2. Experimental

2.1. Flammability of electrolyte

To examine the effect of additives TMP(a) and TMP(i) on the liquid electrolytes of Li-ion batteries, we selected 1 M LiPF₆ in a mixture of 1:1 (w/w) ethylene carbonate (EC) and diethyl carbonate (DEC) as a baseline electrolyte. About 5, 10, and 20 wt.% of TMP(a) and TMP(i) were added directly to the electrolyte. The preparation of electrolyte was performed in an argon-filled glove box (MBrun Labmaster 130).

Fiberglass wicks (4 cm in length, 8 mm in diameter) were first immersed in the electrolyte, 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 electrolyte. Each test was repeated four times and the burning times recorded were averaged for the electrolyte samples containing different amount of TMP(a) and TMP(i).

2.2. Electrochemical evaluation of the electrolytes with additives

A positive electrode laminate was prepared by casting a slurry containing LiCo_{0.8}Co_{0.2}O₂ (84 wt.%), acetylene black (8 wt.%) and poly(vinylidene fluoride) (PVDF) (8 wt.%) onto aluminum foil. It was dried at 70 °C in a vacuum oven and then punched into small discs. Coin cells (CR2032 size) were assembled in an argon-filled glove box with the LiCo_{0.8}Co_{0.2}O₂ as positive electrode, lithium as counter electrode and the above-mentioned electrolytes.

The cells were galvanostatically cycled on a multi-channel battery cycler (Neware BTS 2300, Shenzhen) at a current density of 0.1 mA cm⁻² in the first three formation cycles, and then at 0.2 mA cm⁻² for the rest of cycles in the 4.2–2.7 V voltage range. The ac impedance measurement was also carried out on these cells with a CHI 604 A Electrochemical Workstation. The frequency range and voltage amplitude were set as 10 kHz to 0.01 Hz and 5 mV, respectively.

2.3. Thermal stability measurements

The thermal stability of different electrolytes was evaluated by using a Calvet-type calorimeter (Setaram C80). About 0.2 g electrolyte was placed in a high-pressure stainless steel vessel with dry argon atmosphere. The measurement was performed in the temperature range from 30 to 300 °C at a heating rate of 0.5 °C min⁻¹. The thermal effects of the sample with temperate were recorded automatically by the apparatus.

An accelerated rate calorimeter (ARC) (ARC 2000 model, Arthur D. Little) was also used to evaluate the thermal stability of the electrolyte. The ARC samples (typically consisted of 0.2 g of electrolyte) were placed in the titanium bomb. Each of the samples was initially heated to 50 °C and then equilibrated for 10 min, followed by a 10 min search for an exotherm (self-heating rate >0.02 °C min⁻¹). If no exotherm was detected, the temperature was increased by 5 °C at a rate of 5 °C min⁻¹ with the subsequent repetition of the wait-and-search periods. This heat-wait-search mode continued until the temperature reached 300 °C.

3. Results and discussion

3.1. Flammability test

The results of the electrolyte flammability test are shown in Fig. 1. It should be noted that the burning time recorded in these experiments is longer than the flame-propagation time. The latter parameter is not used in this study because (i) flame does not always propagate from one end to the other end of the wick, and (ii) the measurement error of the propagation time is large considering the fact of short wick length (4 cm) and small amount of electrolyte (1 g). Therefore, the burning time here can be regarded as the self-distinguishing time of the wick samples with specified geometry. It can be seen from Fig. 1 that the control electrolyte, i.e. 1 M LiPF₆ in EC:DEC (1:1), is very flammable. As a flame retardant (FR), either TMP(a) or TMP(i), is added in the electrolyte, the burn-

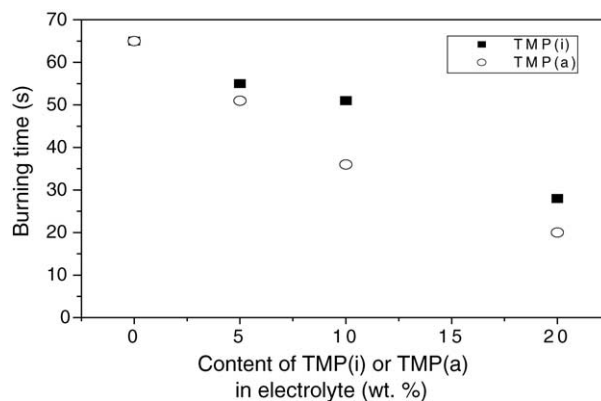


Fig. 1. Graph of burning test of electrolytes containing TMP(a) and TMP(i).

ing time decreases and hence the flammability drops. It was observed that the burning of electrolyte added with FRs produced plenty of white smoke. This is probably due to the presence of P_2O_5 (solid) resulted from the oxidation of TMP(a) and TMP(i). According to the oxidation state of phosphorus in the compound, TMP(a) is rather nonflammable because of P(V) while TMP(i) can be burned into P_2O_5 because of P(III). When the combustion products of an electrolyte contain the solid flame retardant P_2O_5 , the risk of battery explosion is largely reduced. Therefore, TMP(i) can be used as a flame-retarding additive in an electrolyte solution. On the other hand, the flame-retarding action of TMP(a) may be explained according to the radical trap/gas phase mechanism [3]. Furthermore, it can be seen that the flame-retarding impact of TMP(a) is better than that of TMP(i) when an electrolyte contains same weight percentage of TMP(a) or TMP(i). Since the molecular weight is 140 for TMP(a) and 124 for TMP(i), the phosphorus content is 1.1, 2.2, and 4.4 wt.%, respectively, in the TMP(a)-containing electrolyte; while it is 1.25, 2.5, and 5.0 wt.%, respectively, in the TMP(i)-containing electrolyte. Therefore, the difference in the flame-retarding effect should be slightly more pronounced when comparing the electrolyte with same amount of phosphorus content.

3.2. Charge and discharge test

The effect of addition of TMP(a) and TMP(i) in the electrolyte on the cathode performance is evaluated by cycling galvanostatically a series of Li/cathode half cells with different FR content. The cycling performance of Li/LiNi_{0.8}Co_{0.2}O₂ half-cell is evaluated with 1 mol dm⁻³ EC + DEC + *x* wt.% FRs electrolyte. It was observed that TMP(a) and TMP(i) are liquids that are miscible at any ratio with the control electrolyte.

Fig. 2 shows the electrochemical cycling performance of cells made of LiNi_{0.8}Co_{0.2}O₂ with the electrolyte containing different concentration of TMP(a). Discharge capacity was calculated based on the mass of LiNi_{0.8}Co_{0.2}O₂. For comparison, also shown is the performance of the control electrolyte LiPF₆ in 1:1 EC/DEC. With the increase of FRs con-

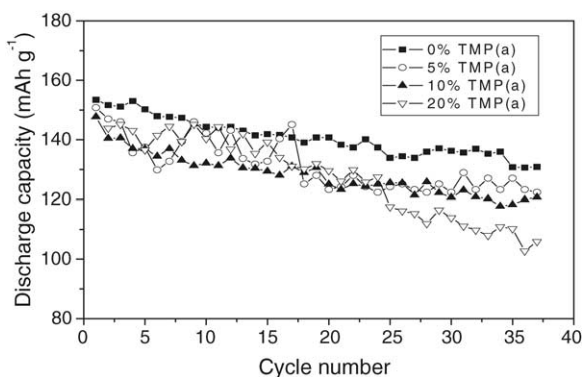


Fig. 2. Graph of discharge capacity vs. cycle number of LiNi_{0.8}Co_{0.2}O₂. Test was conducted using 5–20 wt.% TMP(a) at 0.2 mA cm⁻².

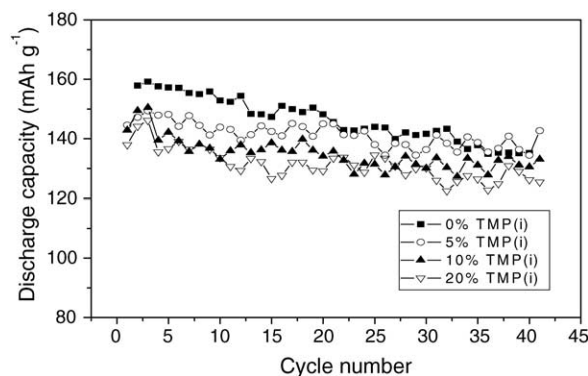


Fig. 3. Graph of discharge capacity vs. cycle number of LiNi_{0.8}Co_{0.2}O₂. Test was conducted using 5–20 wt.% TMP(i) at 0.2 mA cm⁻².

centration, the initial specific discharge capacity decreases due to the decrease of LiPF₆ concentration. The TMP(a)-containing cells show more capacity loss on cycling relative to the cell with no additives due probably to the increase of cell impedance, which is caused by the addition of viscous TMP(a).

Fig. 3 shows the electrochemical cycling performance of cells made of LiNi_{0.8}Co_{0.2}O₂ with the electrolyte containing different concentration of TMP(i). At the first few cycles, the difference of specific discharge capacity between the control electrolyte and electrolyte containing TMP(i) is obvious due to the decrease of LiPF₆ concentration. Nevertheless, during cycling the cells containing TMP(i) show less capacity loss than the cell with the control electrolyte. Hence, we can deduce that TMP(i) has a stabilization effect on the surface of cathode and thus the electrolyte containing TMP(i) can work in a lithium-ion cell. The core of lithium ion cell technology lies in the formation of an interfacial film between electrode surfaces and liquid electrolyte. The electrolyte components including its solvent and salt may decompose oxidatively on a cathode surface upon initial charging of the cell, and deposit insoluble products on the electrode surfaces. Such a thin surface layer may be an electronically insulating film known as SEI [11]. In the most ideal situation, this film prevents sustained decomposition of the electrolyte but is permeable to ion transport, so that reversible lithium intercalation/deintercalation could proceed repetitively with quantitative coulombic efficiency. Obviously, the addition of TMP(i) leads to a long term stabilization effect for the cycling of lithium cells.

3.3. Cell impedance

The ac impedance spectra of LiNi_{0.8}Co_{0.2}O₂/Li half cells containing 0, 5, 10, and 20% TMP(i) and TMP(a) that are charged approximately to 4.05 V after different cycles are shown in Figs. 4 and 5. It can be seen that all spectra are consisted of two semicircles in the high-to-medium frequency range and a straight line in the low frequency range. According to our previous study and Jow et al.'s work [12,13], the

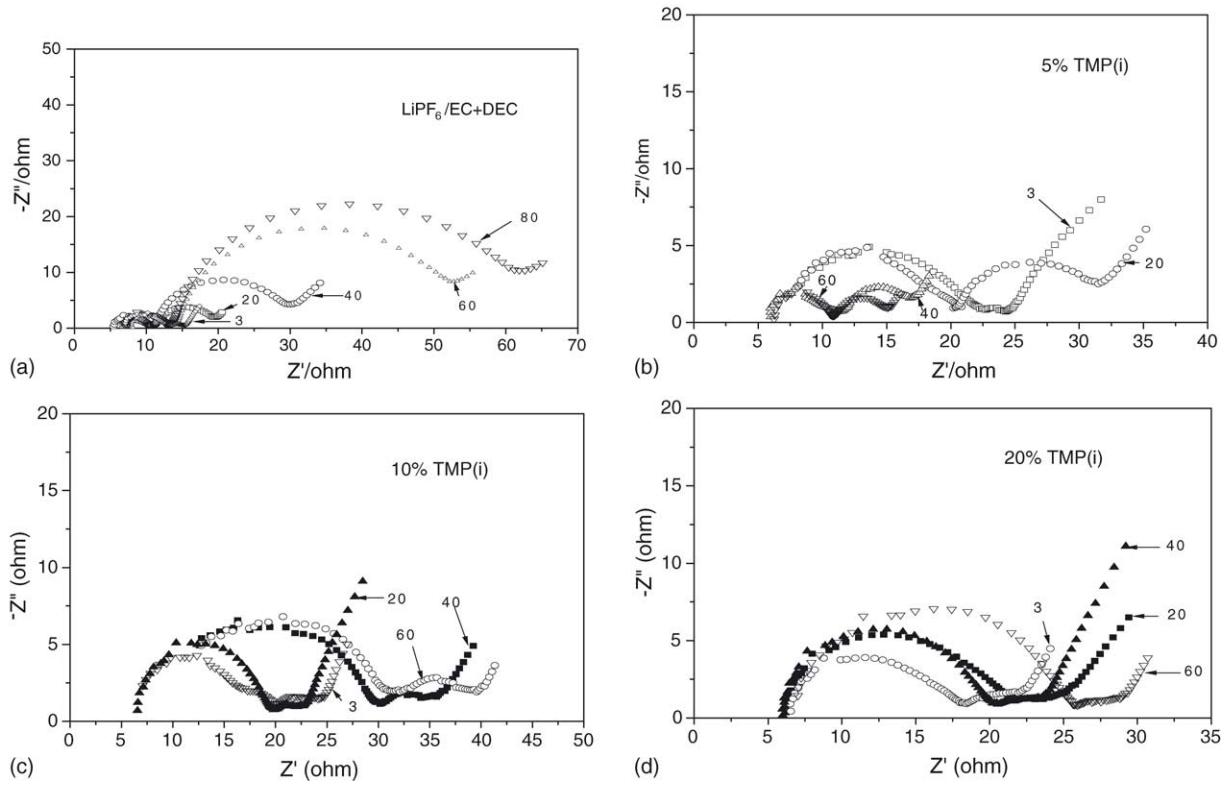


Fig. 4. Impedance spectra of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ in 1 M $\text{LiPF}_6/\text{EC} + \text{DEC} + x\%$ TMP(i) electrolyte amplitude: 5 mV (a) $x=0$ (b) $x=5$ (c) $x=10$ (d) $x=20$.

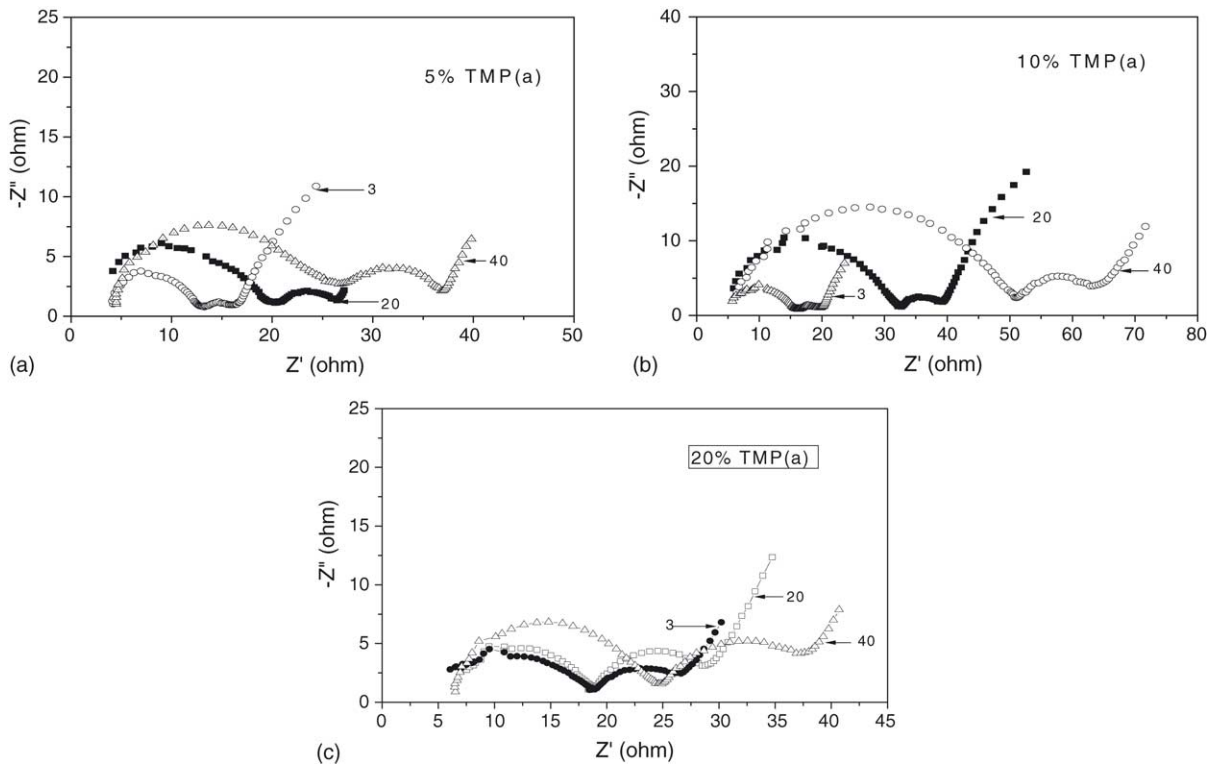


Fig. 5. Impedance spectra of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ in 1 M $\text{LiPF}_6/\text{EC} + \text{DEC} + x\%$ TMP(a) electrolyte amplitude: 5 mV (a) $x=5$ (b) $x=10$ (c) $x=20$.

high frequency semicircle can be attributed to the lithium transport through the surface layers of electrodes while the high-to-medium frequency semicircle to the charge-transfer process at the interfaces between the electrolyte and the electrodes. Thus, for the cell with control electrolyte (Fig. 4a), the charge-transfer resistance increases with the number of cycles while the resistance associated to the surface layers remains almost unchanged. This trend is consistent with the results obtained with symmetric cell study [13]. The reason of the impedance rise is mainly linked to the increase of the charge-transfer resistance on the cathode side namely the electrolyte/ $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ interface. When TMP(i) or TMP(a) is added into the electrolyte (Figs. 4b–d, 5a–c), the surface layer resistance and the charge-transfer resistance undergo different changes during cell cycling. Although we cannot separate here the contributions from the cathode $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ side and from the anode Li side without using reference electrode or symmetric cells, the general effect of TMP(i) and TMP(a) can be recognized from these spectra. Compared with the spectra of the cell using the control electrolyte, the use of TMP(i) and TMP(a) additives results in the increase in the surface layer resistance, but stabilize the charge-transfer resistance. This stabilization effect is more pronounced when using TMP(i) additive than TMP(a) additive. This might be explained by the oxidation of TMP(i) into a lithium-ion conducting Li_3PO_4 layer on the cathode surface at charged states. The stabilization mechanism of TMP(a) is not clear at this moment. A careful surface

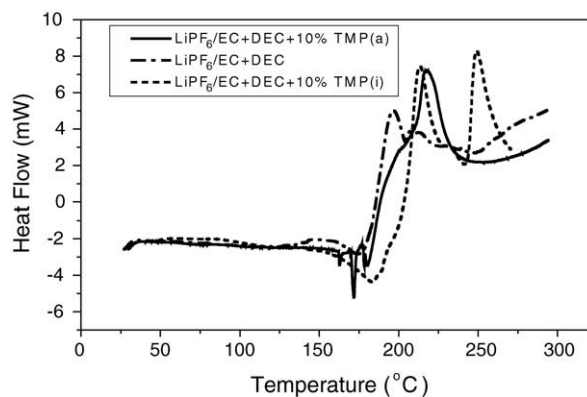


Fig. 6. Thermal behavior of 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}$ containing 0 and 10 wt.% of the flame-retardant using C80 calorimeter.

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.

3.4. Thermal stability

Fig. 6 shows thermal behavior of 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}$ containing 10.0 wt.% of TMP(a) and TMP(i) compared with that of the control 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}$ measured with the C80 calorimeter. It is observed for the control electrolyte

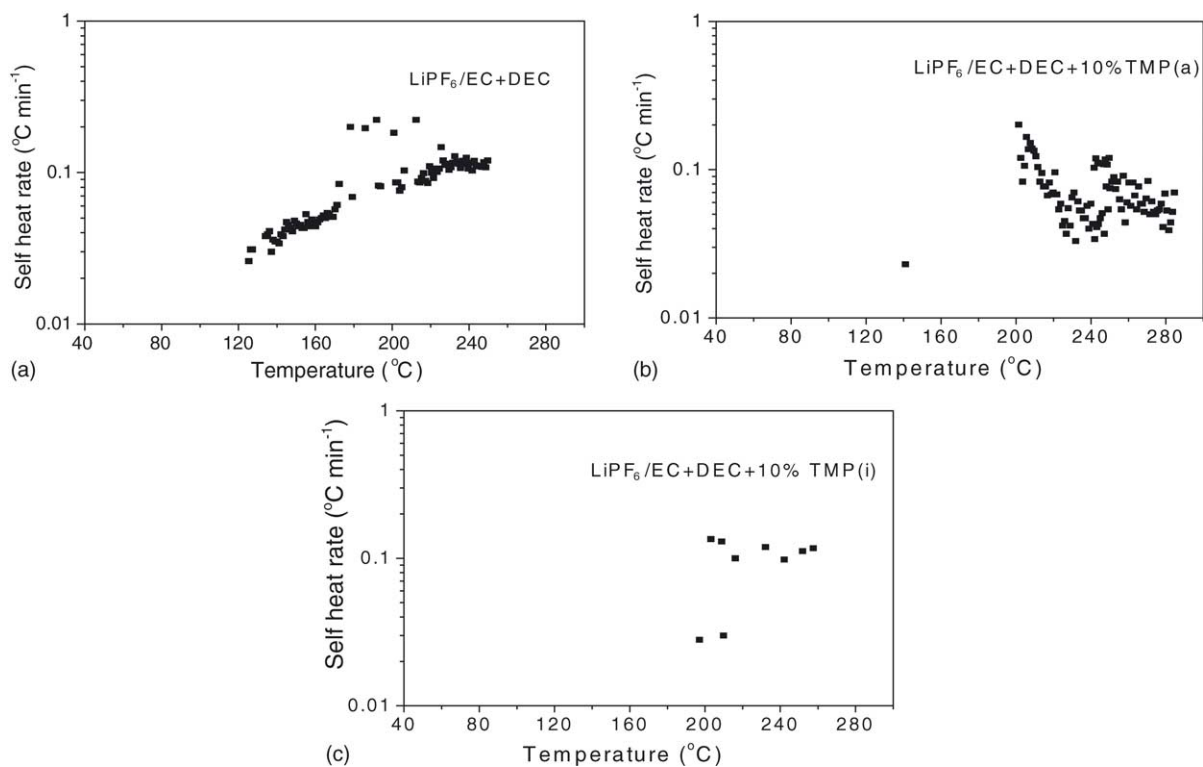


Fig. 7. Thermal behavior of 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}$ containing 0.0 and 10.0 wt.% of TMP(a) and TMP(i) using ARC.

that with increasing the temperature a small broad exothermic peak first appears at about 120 °C, which is followed by a big sharp exothermic peak with the onset temperature at 180 °C and peak temperature at about 190 °C [14]. Above this temperature, a number of big broad exothermic peaks are observed. When the electrolyte contains 10% TMP(a) or TMP(i), the first exothermic peak around 120 °C seems to be diminished and some endothermic effect appears at about 160 °C instead. The second exothermic peak shifts to higher temperature direction, i.e. at about 220 °C. After this exothermic peak, continuous exothermic processes take place at higher temperatures for all three samples. Therefore, the addition of TMP(a) and TMP(i) in the electrolyte increases the onset temperature of heat generation. Thus, the thermal stability of cells using the electrolyte with TMP(a) or TMP(i) additives is improved.

Fig. 7 shows the ARC data for the control electrolyte and the electrolytes with TMP(a) and TMP(i) as additives. It can be seen that in the temperature range from 120 to 190 °C only the control electrolyte gives evident signals with the self heat rate greater than 0.02 °C min⁻¹, while the electrolytes containing 10 wt.% TMP(a) and TMP(i) show marked signals above 190 °C. This experimental result is consistent with that of Fig. 6 obtained with C80 calorimeter. It confirms that TMP(a) and TMP(i) can enhance the thermal stability of the electrolyte.

4. Conclusions

The use of flame-retardant additives TMP(i) and TMP(a) has great impact on the safety performance and electrochemical behavior of lithium ion cells. The ARC and C80 calorimeters studies have revealed that TMP(i) and TMP(a) increase significantly the thermal stability of the control electrolyte, i.e. 1 M LiPF₆ in EC:DEC (1:1), the exothermic heat generation of the control electrolyte around 120 °C is totally suppressed by using TMP(a) and TMP(i) additives. The second exothermic peak with onset temperature around 190 °C

shifts to higher temperature direction. In addition, the use of TMP(i) additive can largely increase the impedance stability of lithium cells with LiNi_{0.8}Co_{0.2}O₂ as cathode. The TMP(a) additive is found to degrade the electrochemical behavior of a cell. Therefore, the alkyl phosphite TMP(i) is a better flame retardant additive compared with the alkyl phosphate TMP(a) that increases the safety of lithium ion batteries at the expense of the electrochemical performance.

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