

Flame-retardant additives for lithium-ion batteries

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Abstract

To enhance the resistance of lithium-ion battery components to ignition and to reduce the flammability of the electrolyte with minimal effect on performance, we added flame-retardant additives to the electrolyte. The flame retardants were selected from a group of organic phosphate compounds, triphenylphosphate (TPP) and tributylphosphate (TBP), to provide superior thermal safety in lithium-ion cells at the fully charged state. The cycling characteristics of the lithium-ion cells containing flame-retardant additives were found to be similar or superior to the cells that contained no additives. Horizontal burning tests of electrolytes were carried out in a flame test chamber referenced by Underwriters Laboratories (UL) test standard 94 (UL 94) and ASTM D4986-98 to evaluate the electrolytes' flammability characteristics. The thermal stability characteristics of the electrodes and electrolytes with and without flame-retardant additives were investigated by accelerating rate calorimetry (ARC). Negative electrode samples with electrolytes containing flame-retardant additives revealed less heat generation and higher-onset decomposition temperatures. The results disclose that the thermal safety of lithium-ion cells can be improved by incorporating small amounts of suitable additives such as triphenylphosphate and tributylphosphate to the electrolyte.

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1. Introduction

The demand for high power and energy storage sources has resulted in substantial research and development of rechargeable lithium batteries. For example, lithium-ion batteries with carbon anodes have succeeded in the marketplace because of their long cycle lives and high power and energy densities [1]. However, safety concerns remain because lithium-carbon is a highly reactive material. Electrolyte flammability is also an important safety issue, not only in liquid electrolyte systems, but in most gel polymer systems. Because of these safety limitations and tendencies toward thermal runaway, the use of lithium-ion batteries in the marketplace has been limited to small cells, 2–5 Ah. Applications where larger cells are required such as in electric or hybrid vehicles have simply not materialized. While the exact process leading to thermal runaway of lithium-ion batteries is not well understood, it probably involves several steps. The first step likely is an endothermic pyrolysis to form flammable gases, which then mix with air or oxygen and ignite. This leads to an exothermic process of flame propagation and heat release. Thermal feedback rein-

forces pyrolysis, fueling the flame at an increasing level. Flame retardants can act chemically and/or physically in the condensed or vapor phase, and can thus interfere with the combustion process during heating, pyrolysis, ignition, or flame propagation. The most significant chemical process that interferes with combustion can take place in either the vapor or condensed phase [2]. It was the purpose of this study to determine whether the tendency of lithium-ion batteries to experience thermal runaway problems might be addressed by the use of organic phosphate electrolyte additives. It was also hoped that the additives would limit gas generation during near-normal cell operation.

2. Experimental

The stability of the electrolyte containing flame-retardant additives was investigated by cyclic voltammetry. The cell for these studies utilized a glassy carbon electrode as the working electrode, and a lithium electrode that served as both the counter and the reference electrode. The potential initially at open circuit was scanned between 0 and 5.5 V at 1 mV/s in an argon-filled globe box.

Two types of cell configuration were used for our electrochemical studies. The 2032 type lithium-ion coin cells were used for electrochemical testing, while larger fixture

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cells were prepared to evaluate the safety-abuse characteristics of the cell chemistry. The cells contained $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ as the positive electrode and graphite as the negative electrode. The electrolyte for the cells was 1 M LiPF_6 in 1:1 ethylene carbonate:diethylene carbonate. The flame-retardants triphenylphosphate (TPP) and tributylphosphate (TBP), were added directly to the electrolyte. Aluminum and copper foils were used as the positive and negative electrode current collectors, respectively. PVDF binder was used in the fabrication of both electrodes. The cells used Celgard 2500 separators.

Fixture cells having an electrode area of 15.5 cm^2 were prepared to evaluate safety-abuse characteristics of the cell chemistry. The cells were charged to 4.2 V and discharged to 3.0 V at $C/20$ rate for two formation cycles. After formation, the cells were charged to 4.2 V followed by a 2 h constant voltage charge to ensure a 100% cell state of charge (SOC) for the accelerating rate calorimetry (ARC) test while the 2032 cells were cycled galvanostatically using a $C/2$ rate in the voltage window 3.0–4.1 V at room temperature to investigate the effect of the additives on cells cycle life performance.

The techniques used to investigate the thermal stability of the cells included the flammability test (based on Underwriters Laboratories (UL) test standard 94), and the ARC [3–5]. UL 94 is a standard test for plastic materials; some test conditions of UL 94 were modified to make it suitable for testing the electrolyte by incorporating a fiberglass wick. The fiberglass wicks were used for measuring flammability of the liquid electrolyte. The dimensions of the fiberglass wicks were 140 mm long and 6.35 mm in diameter. For the test, 5 g of sample electrolytes were soaked into fiberglass wicks. The soaked fiberglass wicks were then allowed to equilibrate for 24 h in a sealed test tube prior to the flammability test. The soaked fiberglass wicks were set horizontally on the thin Ni wire bed. Each sample was marked with two lines perpendicular to the longitudinal axis of the fiberglass wick, 25 ± 1 and 100 ± 1 mm from the end that was to be ignited. A gas burner was used to ignite the soaked wick samples. Test burns were carried out in ambient air. The flame propagation rate was calculated from the following equation:

$$\text{propagation rate (mm/min)} = 60 \times \left[\frac{\text{damaged length (mm)}}{\text{time (sec)}} \right],$$

where the damaged length was typically 100 mm from the initiation mark.

ARC samples were prepared from the fixture cells that had been charged to 100% SOC. The sample was initially heated to 80°C and then equilibrated for 17 min followed by a 10 min search for an exotherm (self-heating rate $>0.02^\circ\text{C/min}$). If no exotherm was detected, the temperature was increased by 5°C at a rate of 5°C/min with the subsequent repetition of the wait-and-search periods. This heat-wait-search mode continued until an exotherm was detected or until the temperature reached 400°C . When an

exotherm was detected, the self-heating of the sample was tracked by matching any increase in the sample temperature with an identical increase in the temperature of the calorimeter walls, thus ensuring that adiabatic conditions were met. This temperature matching of the calorimeter and sample was maintained until the self-heating rate decreased below the detection limit or reached the end temperature [4]. The ARC samples placed in the titanium bomb typically consisted of 0.2 g of the charged electrode material and/or 0.35 g of electrolyte.

3. Results and discussion

Cyclic voltammograms of electrolytes with various flame-retardant additives in the 1 M LiPF_6 EC:DEC (1:1) electrolyte are shown in Fig. 1. These studies clearly show that there were no significant reactions or decomposition of the flame-retardant additive up to 5.0 V. Above 5 V, an oxidation peak was observed that could have resulted from the decomposition of the TPP flame retardant, since no peak was observed at this voltage in the electrolyte without additive. The electrolytes containing flame-retardant additives were stable up to 5.0 V and can be safely used in the operating voltage range of 2.5–4.3 V, which is used for nearly all lithium-ion battery applications.

The differential chronopotentiometry study on the full coin cells has confirmed the stability of the flame retardant in the full cell system after the formation cycles. Fig. 2 shows dQ/dV plots of coin cells that were made with and without flame-retardant additives in the electrolyte. All tested coin cells showed similar electrochemical behavior regardless of flame-retardant additive. These results indicate that the electrolyte with flame retardant was electrochemically stable in the presence of cell electrodes at the operating voltage range of 3.0–4.2 V. Five peaks in dQ/dV corresponding to phase transitions of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode active

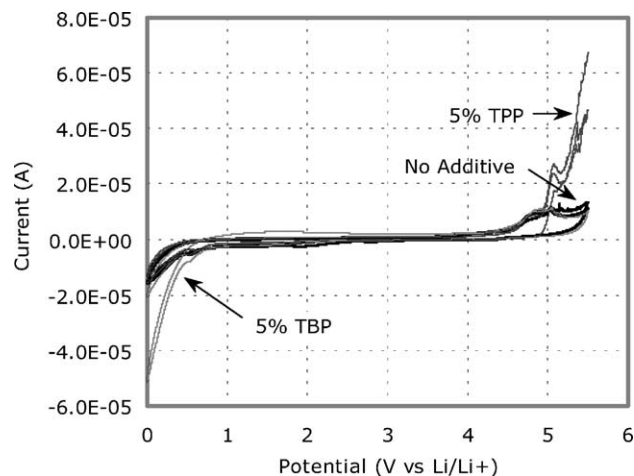


Fig. 1. Cyclic voltammograms of samples with various contents of TPP as a flame-retardant additive in the 1 M LiPF_6 EC:DEC (1:1) electrolyte.

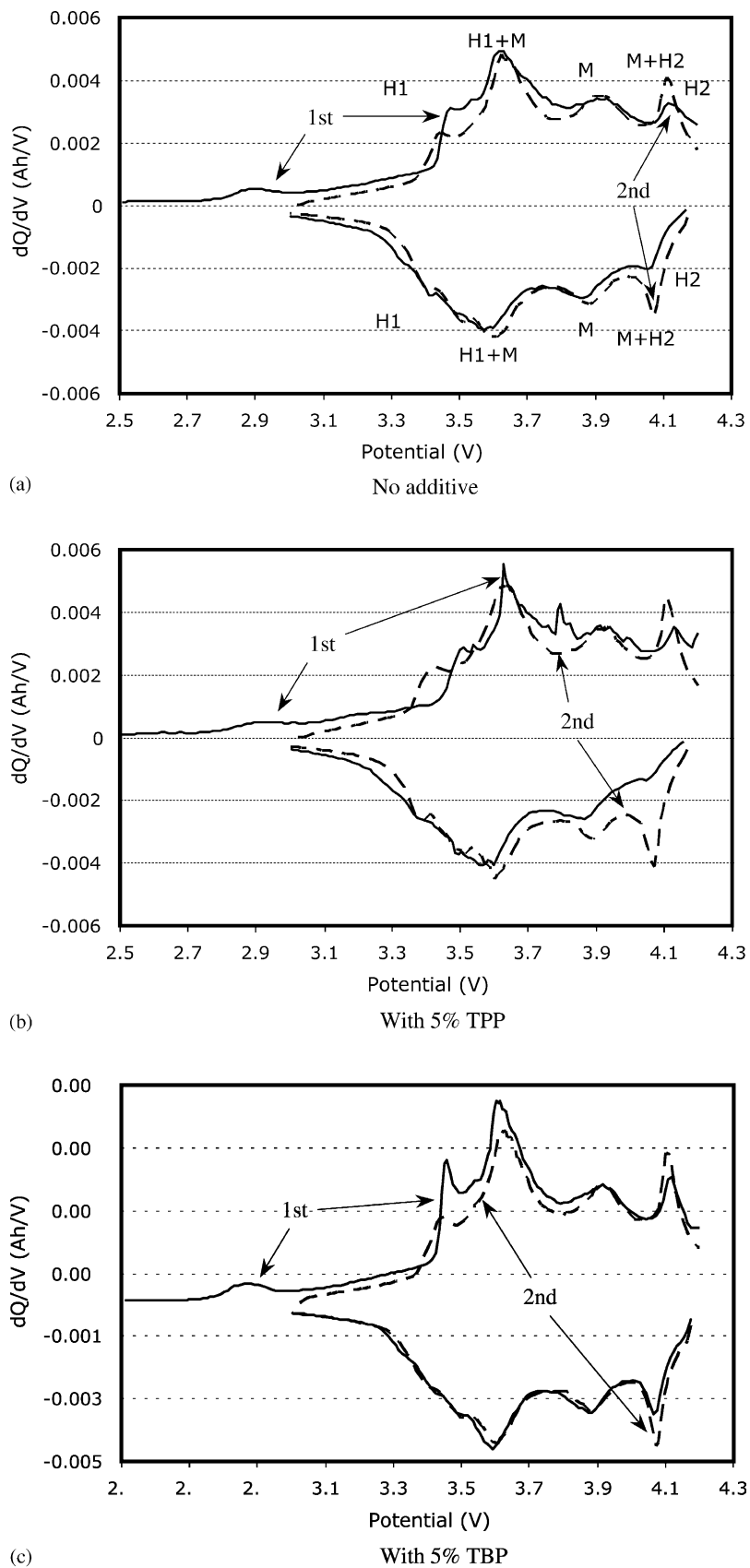


Fig. 2. Differential chronopotentiograms of the coin cells with and without flame-retardant additives in the 1 M LiPF₆ EC:DEC (1:1) electrolyte.

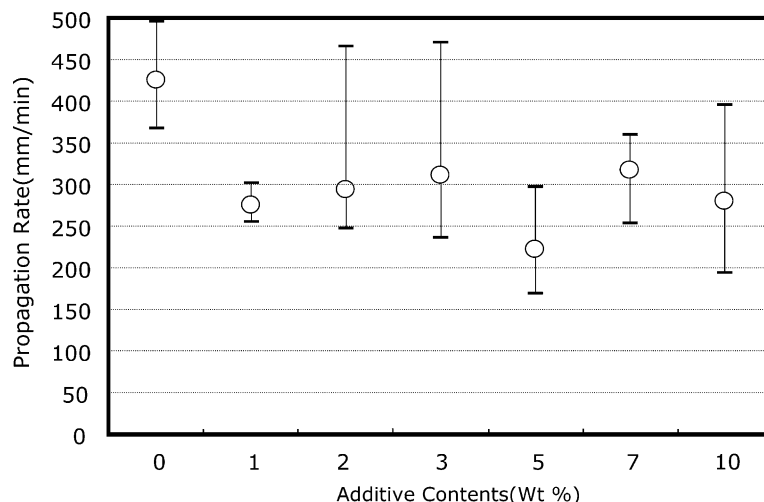


Fig. 3. The flame propagation rate measured by UL 94 with various contents of TPP as a flame-retardant additive in the 1 M LiPF₆ EC:DEC (1:1) electrolyte.

materials were observed between 3.4 and 4.1 V. Similar results have been observed from an in situ X-ray diffraction study of Li_{1-x}NiO₂ by monitoring peaks of hexagonal structure such as (0 0 3), (1 0 1), (1 1 0), and (1 1 3) planes [6]. The structure of the cathode active material seemed to change from the original hexagonal phase (H1) to monoclinic (M), and then to a new hexagonal phase (H2) according to intercalation of lithium, as shown in Fig. 2a. H1 and H2 denote a hexagonal structure having a slightly different lattice constant.

The flame propagation rate was measured using 1 M LiPF₆ in EC:DEC (1:1) electrolyte with and without flame-retardant additives, as shown in Fig. 3.

The effect of flame-retardant additives was significant even with 1% TPP additive. All TPP-containing electrolytes showed reduced flame propagation rates. The optimum content of the TPP additive that reduced the flame propaga-

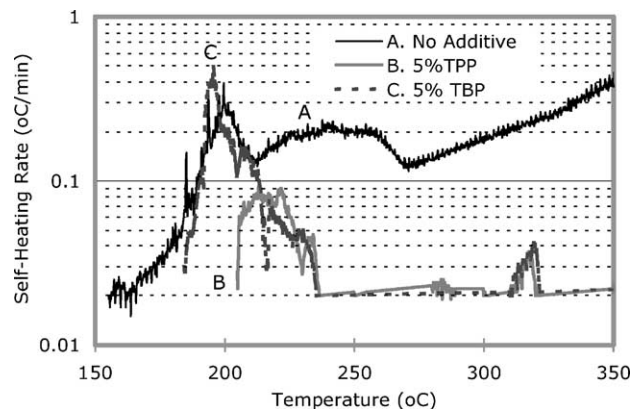


Fig. 4. Self-heating rate profiles for 100% SOC graphite electrodes in the 1 M LiPF₆ EC:DEC (1:1) electrolyte with and without flame-retardant additives.

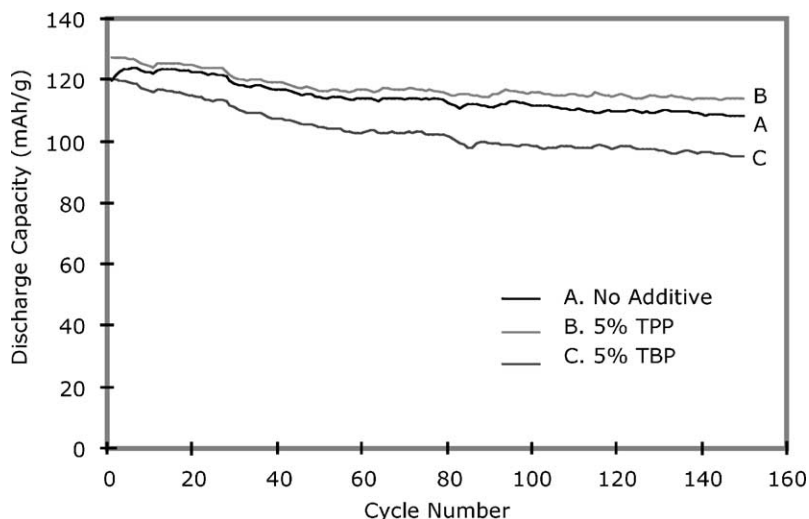


Fig. 5. Cycle performance of cells in the 1 M LiPF₆ EC:DEC (1:1) electrolyte.

tion rate significantly was 5%. Phosphate compounds are known as flame retardants that can function in the vapor phase by a radical mechanism. Phosphorus can also function in the condensed phase, promoting char formation on the surface that insulates the substrate from heat and air and interferes with the loss of decomposition products to the flame zone.

Fig. 4 shows ARC data for a fully charged graphite electrode in the presence of the electrolyte, with and without flame-retardant additives. Both TPP- and TBP-containing electrolytes showed lower exothermic heat generation compared with the electrolyte that contained no additive. The fully charged graphite with electrolyte containing TPP showed excellent thermal stability with minimal self-heating rate, higher onset temperature, and lower exothermic heat generation. One possible explanation could be due to the fact that phosphorus-based materials are known to promote char formation, leading to a protective coating of the electrode surface. As a result, the surface reaction between the lithiated graphite electrode and electrolyte will be significantly reduced.

Fig. 5 shows the electrochemical cycling performance of full cells made of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and graphite electrode. Discharge capacity was calculated based on the mass of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. The TPP-containing cell showed little decrease in capacity even after 150 cycles. The TBP-containing cell, however, showed slightly more capacity loss on cycling relative to the cell with no additives. These data clearly show that flame-retardant additives such as TPP improve the safety behavior of lithium-ion cells without significantly affecting its electrochemical performance.

4. Conclusion

The use of flame-retardant additives such as TPP and TBP significantly impact the safety performance of the lithium-ion cell. The ARC study shows that less than 5 wt.% of TPP increases significantly the onset reaction temperature from 160 to 210 °C. In addition, the exothermic heat generation due to the reaction between fully charged anode and electrolyte was significantly reduced when flame retardant was added to the electrolyte. The flame-retardant TPP was shown to be electrochemically stable up to 5 V and to have no negative effect on the cycling characteristics of the cell.

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