

Short communication

Thermal runaway inhibitors for lithium battery electrolytes

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Abstract

Flame retardancy in lithium-ion battery electrolytes has been significantly improved by the use of several new aromatic phosphorus-containing esters, which markedly suppress thermal runaway. The identification, preparation, and properties of these thermal runaway inhibitors (TRIs) are described. When used as an additive (2–5%) to the standard battery electrolyte system, these materials improve safety by preventing potential fire and explosion. The effects of these esters on electrochemical and thermal stabilities, ionic conductivity, and electrochemical cycling are presented. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Flame retardancy in lithium-ion batteries is a major challenge for battery manufacturers. Especially under abusive conditions, full size batteries may undergo thermal runaway that generates a sharp rise in temperature, with potential for explosion and/or fire [1–3]. Approaches to address this problem are a high priority. In our laboratories, we have investigated ways to substantially reduce the risk of fire by developing new materials, which could serve to suppress thermal runaway in lithium-ion batteries.

Our studies have focused on the identification of additives which, in small quantities, e.g., 2 wt.%, could minimize exothermic reactions that occur at high temperatures in the electrolyte mixture of an electrochemical cell. This approach is intended specifically to sharply reduce the likelihood that a flame will be generated as a result of thermal runaway. In marked contrast, the addition of up to 20 wt.% of certain other compounds, e.g., phospholanes, to a variety of carbonates to generate CO₂, seeks to achieve flame retardancy by providing a blanket to extinguish a flame [4].

In a recent patent [5], we introduced the term ‘thermal runaway inhibitor’ (TRI) for a number of new aromatic phosphorus-

containing esters, which significantly mitigate the potential of thermal runaway. We outlined one-step preparations of 12 such compounds. After detailed testing, three materials (Fig. 1) emerged as the most promising candidates for extended evaluation. While TRI-001 and TRI-013 are new compounds, TRI-311 has been reported previously [6,7]. These compounds possess two structural features, each of which can contribute favorably to flame retardancy. The phosphate moiety is a well-recognized flame-retarding group, while the aromatic moiety is a known precursor of free radicals, which serve as antioxidants capable of effectively scavenging the oxygen required to sustain propagation of a flame.

2. Synthesis of TRIs

The following procedures for TRI-001 and TRI-013 are illustrative of the preparations of the other TRI compounds described in the patent [5].

2.1. Diethyl(2,6-di-*tert*-butyl-4-methylphenyl)phosphate (TRI-001)

A solution of 2,6-di-*tert*-butyl-4-methylphenol (38.32 g, 0.17 mol) (Aldrich) in 100 mL of dry THF was added dropwise to a stirred suspension of sodium hydride (5.52 g, 0.23 mol) in 250 mL of dry THF at 0 °C under argon. After the addi-

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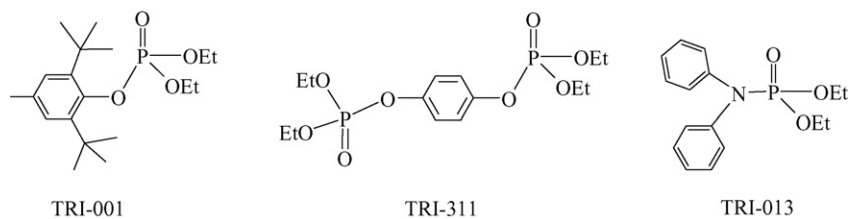


Fig. 1. Structures of most promising TRIs.

tion was complete, the reaction mixture was heated at 50 °C for 6 h. The reaction mixture was cooled to 0 °C, and a solution of diethylchlorophosphate (23.77 g, 0.13 mol) in dry THF was added dropwise. The reaction mixture was heated at 50 °C for 18 h. The solvent was removed on a rotary evaporator, 300 mL diethyl ether was added, the mixture stirred for 30 min, filtered, and washed again with ether. The ether was removed on a rotary evaporator. The product, a viscous colorless liquid, was distilled and redistilled under reduced pressure, bp 120–125 °C/0.02 Torr. Anal. Calcd. for C₁₉H₃₃O₄P: 64.04; H, 9.27; Found: C, 63.90; H, 8.94.

2.2. Diethylphosphorodiphenylamide (TRI-013)

A solution of *n*-butyl lithium (Aldrich) in hexane (2.5 M, 23.6 mL) was added dropwise to a solution of diphenylamine (10.00 g, 0.06 mol) in 150 mL of dry THF at –70 °C under argon. After the addition was complete, the reaction was allowed to come to room temperature and the mixture was heated at 50 °C for 6 h. The reaction mixture was cooled to –70 °C and a solution of diethyl chlorophosphate (10.20 g, 0.06 mol) in 100 mL of dry THF was added dropwise. The mixture was allowed to come to room temperature and heated further to 50 °C for 18 h. The solvent was removed on a rotary evaporator, 300 mL diethyl ether was added, the mixture stirred for 30 min, filtered, and washed again with ether. The ether was removed on a rotary evaporator. The product was purified by column chromatography (silica gel, Aldrich) using chloroform as the eluent.

3. Electrochemical stability of TRI-containing electrolytes

The electrochemical stability window for the electrolyte formulations with TRI additives was investigated by cyclic voltammetry. The formulations are 1 M solutions of LiPF₆ in an EC (ethylene carbonate) and DMC (dimethyl carbonate) mixture (1:1, v/v) each containing TRI-311, TRI-001, and TRI-013. The experiments were carried out in an O-ring sealed glass cell under a flow of argon, with a glassy carbon as working electrode against lithium as counter electrode, as well as reference electrode. The cell was cycled between 0.0 and 5.2 V at different scan rates ranging from 1.0 to 20 mV s⁻¹ to establish the oxidation and reduction potentials of the electrolyte formulations. It was observed that lithium metal was electroplated on the surface of the electrode as the potential approached 0 V. The quantitative values of the reduction and oxidation limits shown in Table 1 indicate that these additives, especially TRI-

Table 1
Electrochemical stability of the TRI additives (temperature: 25 °C)

Compound	Oxidation limit (V)	Reduction limit (V)
TRI-311	4.1	0
TRI-013	4.9	0
TRI-001	4.3	0

013, are stable in the working voltage window of the lithium-ion cells.

4. Ionic conductivity of TRI-containing electrolytes

Ionic conductivities were determined using the alternating current impedance (ACI) technique, which involves application of sinusoidal signals of known amplitude in a selected frequency range and measuring the resulting ‘in phase’ and ‘out of phase’ components. The data are typically handled as Nyquist plots. For this measurement, lithium metal was used as the working electrode as well as counter and reference electrode within the frequency range of 0.01 Hz to 100 kHz. The calculation of the real and imaginary components of impedance allowed the creation of a Nyquist plot detailing the resistive and capacitive responses of the material under test. The high-frequency intercept of the plot on the real-axis gave the bulk resistance of the electrolyte from which conductivity of the electrolyte was calculated. Table 2 shows the conductivities of solutions containing TRI-311, TRI-013 and TRI-001 on the ac impedance behavior of the baseline electrolyte.

5. Thermal studies of TRI-containing electrolytes

Thermal studies of TRI-containing electrolytes were performed by both accelerated rate calorimetry (ARC) and differential scanning calorimetry (DSC).

Accelerated rate calorimetry: We have measured the effect of addition of TRI-001 on the thermal stability of Li-ion battery electrolytes with and without the presence of lithium metal.

Table 2
The conductivity of the electrolyte solution with and without TRI additives measured by the ac impedance technique

Composition	σ (S cm ⁻¹)
1 M LiPF ₆ in EC-DMC (1:1)	1.04×10^{-2}
With 2 wt.% TRI-311	7.82×10^{-3}
With 2 wt.% TRI-013	7.53×10^{-3}
With 2 wt.% TRI-001	7.45×10^{-3}

The thermal stability was measured using an accelerating rate calorimeter over the temperature range of 70–275 °C. The ARC measures the self-generated heating rate of the sample material under adiabatic conditions while monitoring the pressure of the generated gases. The sample solutions were prepared in a 1 in. diameter titanium reaction vessel, which allows good thermal contact with the sample thermocouple while maintaining pressure integrity up to several hundred psi. The ARC measures the heating rate during a heat/wait/search mode of operation. The sample is heated in 5 °C increments. After a wait period of 20 min, the ARC monitors the temperature of the sample bomb for another 20 min to determine the average heating rate. If the heating rate is below the threshold limit of 0.02 °C min⁻¹, the ARC steps up another 5 °C and repeats the process. Once the heating rate exceeds the threshold limit, the ARC switches to an exotherm mode of operation where it closely matches the temperature of the sample bomb during its self-generated heating period, thus maintaining adiabatic conditions. The heating rate is then determined by the heat generation of the sample and the heat capacity of the sample and holder assembly.

Fig. 2 shows the self-heat rate profile of a strip of lithium metal in commercial electrolyte: 1 M solution of LiPF₆ in a mixture of EC and DMC (1:1, v/v) and electrolyte formulations containing 5 wt.% of TRI additives, respectively. In the case of electrolyte without any TRI additive, the maximum self-heat rate is 0.68 °C min⁻¹, which occurs at $T=177.6$ °C. This behavior can be attributed to the reaction of lithium metal with the electrolyte. As the reaction proceeds, the lithium metal is consumed, and thus, the exothermic peaks decrease as the temperature increases beyond 177.6 °C. By contrast, the onset of the exothermic peak with additive TRI-311 is shifted to higher temperature (203 °C) with a self-heat rate of 0.84 °C min⁻¹. Notably, with addition of TRI-013, the exothermic reaction is effectively suppressed up to a temperature beyond 300 °C. Moreover, the maximum self-heat rate of the electrolyte with TRI-013 is also dramatically reduced. We attribute the suppression or inhibition of thermal runaway reactions for the electrolyte formulations with these additives to a passivation layer that is formed on the surface of the lithium metal by the additive.

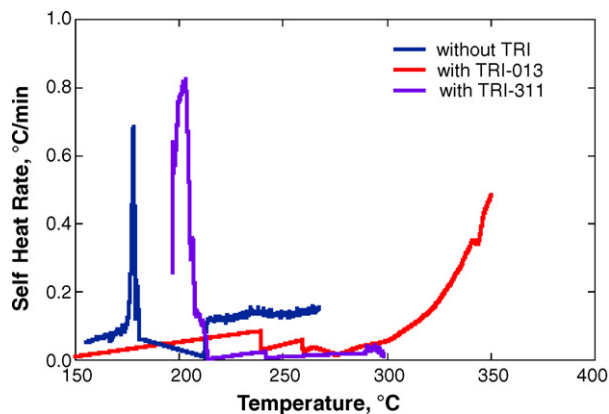


Fig. 2. Thermal behavior of electrolytes containing a strip of lithium in 1 M LiPF₆, EC-DMC (1:1), 5 wt.% TRI-013 or 5 wt.% TRI-311. Note. For TRI-311, self-heat data do not appear, since, using heat and search, no activity was observed below 195 °C.

Table 3

ARC data for the major exothermic reaction of a strip of lithium metal in electrolyte containing 5 wt.% additive

Composition	Exothermic temperature (°C)
1 M LiPF ₆ in EC-DMC (1:1)	177
With 5 wt.% TRI-311	203
With 5 wt.% TRI-013	>300
With 5 wt.% TRI-001	240

Table 4

DSC data for the major exothermic reaction of a fully charged cathode and anode containing 5.0 wt.% TRI additive

Formulation	Maximum heat flow (W g ⁻¹)		Onset temperature (°C)	
	Cathode	Anode	Cathode	Anode
1 M LiPF ₆ in EC-DMC (1:1)	15.3	5.1	213	248
With 5 wt.% TRI-311	4.9	4.2	220	280
With 5 wt.% TRI-013	7.2	1.2	210	203
With 5 wt.% TRI-001	5.7	2.5	200	263

Results of these thermal investigations strongly suggest that the additive in the electrolyte significantly reduces the self-heat rate and improving the non-flammability of the electrolyte. The ARC studies on the electrolytes with and without the additives are summarized in Table 3.

5.1. Differential scanning calorimetry

These studies were conducted to investigate the thermal stability of the fully charged graphite anode and LiNi_{0.8}Co_{0.2}O₂ cathode using DSC-7, Perkin-Elmer. The fully charged state was chosen as this state poses greater thermal hazards than any discharged state. The cathode and anode materials from the charged cells were recovered by opening in a dry glove box under an argon atmosphere. The recovered electrodes, including electrolyte, were sealed in a standard aluminum DSC pan. DSC scans were carried out at a heating rate of 10 °C min⁻¹, from 30 to 350 °C, under nitrogen purging. The results of the DSC investigations are shown in Table 4. The maximum heat flow for the major exotherms is lowered with addition of TRIs for both anodes and cathodes from the charged cells. In most cases, the onset temperature for the exotherms is shifted to higher temperature, indicating improved properties in the presence of TRI additives.

6. Electrochemical cycling of Li-ion cell with TRI-containing electrolytes

Electrochemical cycling studies on full large cells (30 cm²) containing 5 wt.% TRI additives were carried out at room temperature. LiNi_{0.8}Co_{0.2}O₂ and MCMB (graphite) were used as cathode and anode, respectively, with a 1 M solution of LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v). A microporous polyethylene–polypropylene membrane (Celgard 2300) was used as the separator. Electrochemical cycling of the cells was performed with a BT-2043

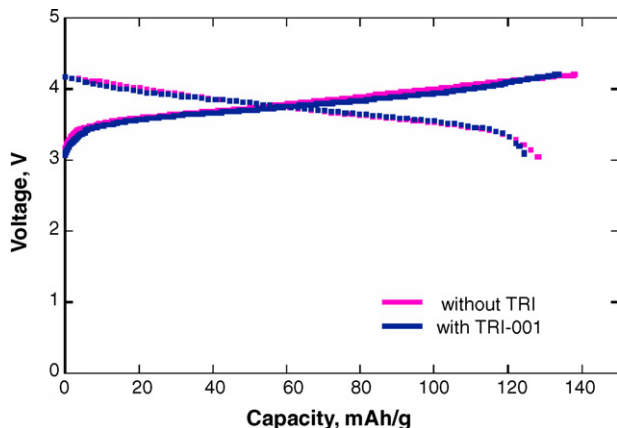


Fig. 3. Charge and discharge curves for LiNi_{0.8}Co_{0.2}O₂/graphite cell with and without TRI-001 as additive.

Arbin cyler. The voltage versus capacity curves during charge and discharge for a cell with and without TRI-001, shown in Fig. 3, reveal no effect of the TRI on the voltage profile. Similarly, the cycling behavior of the Li-ion cell at room temperature with TRI-311 exhibited excellent performance during charge–discharge cycling between 4.2 and 2.5 cut-off voltages (Fig. 4). The excellent stability of capacity over cycling indicates that TRIs do not have any detrimental effect on the cell chemistry and performance. The rate capability of a cell with TRI-013 is shown in Fig. 5, demonstrating good recovery from high C-rates to low C-rates.

The effect of TRIs on the area specific impedance (ASI), as a critical parameter related to the entire cell performance, was evaluated. The ASI is time dependent and includes ohmic, electrolyte effects, and solid-state diffusion within the electrode. Impedance corresponding to certain interruption times is more useful and practical, especially for EV and HEV applications, rather than complete relaxation equilibrium after the interruption. Projections of battery performance based on the measurement of the ASI are considered highly reliable because this calculation uses the properties that are measured under actual application conditions. A representative ASI versus capacity curve for the cell containing TRI-001 is shown in Fig. 6. It is evident that the cell ASI remains relatively flat up to 65% and then increases very sharply toward the end of discharge. The low

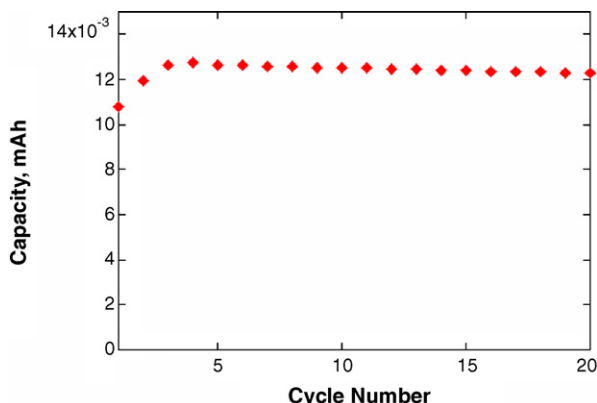


Fig. 4. Cycling behavior of a Li-ion cell containing 5 wt.% TRI-311 additive.

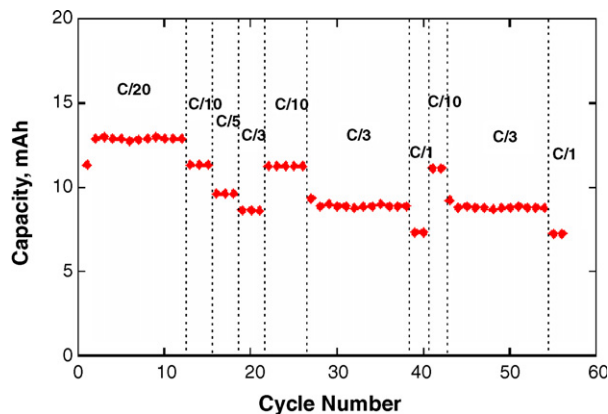


Fig. 5. Cycling behavior of a Li-ion cell containing 5 wt.% TRI-013 additive.

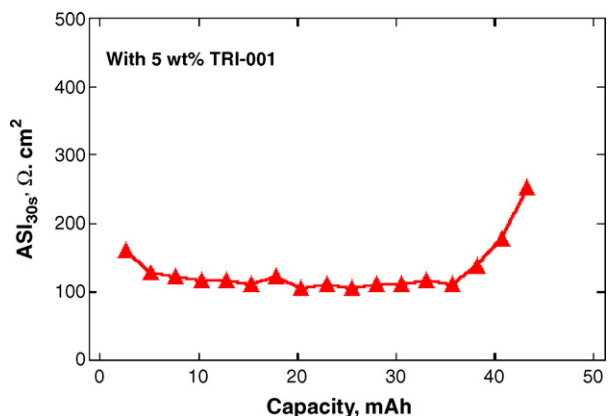


Fig. 6. Cell ASI of the graphite/LiNi_{0.8}Co_{0.2}O₂ cell with 5 wt.% TRI-001.

cell ASI at the beginning of the discharge curve is indicative of high energy and power performance of the cell, a common characteristic of lithium-ion batteries. This behavior is attributed to increased charge-transfer resistance of the cell at the discharged state. The phenomenon also exists in the fully charged state, but it is less significant [8].

7. Conclusions

We have identified and developed three compounds as novel thermal runaway inhibitors for lithium-ion battery electrolytes. These materials have been subjected to rigorous investigation. When used as an additive at 2–5 wt.%, these materials provide effective protection against thermal runaway, thus improving safety by minimizing the risk of fire and explosion.

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References

- [1] J.O. Besenhard (Ed.), Handbook of Battery Materials, Weinheim, New York, 1999.
- [2] F.M. Gray, Polymer Electrolytes RSC Monographs, The Royal Society of Chemistry, London, 1997.
- [3] D. Linden (Ed.), Handbook of Batteries, 2nd ed., McGraw-Hill, New York, 1995.
- [4] S.C. Narang, S.C. Ventura, B.J. Dougherty, M. Zhao, S. Smedley, G. Koople, U.S. Patent 5,830, 600, November 3 (1998).
- [5] B.K. Mandal, R. Filler, U.S. Patent 6746, 794B2, June 8 (2004).
- [6] E. Kobayashi, S. Kamagami, Japan Kokai 75,93,949, July 26 (1975);
E. Kobayashi, S. Kamagami, Chem. Abst. 83, P19281g (1975).
- [7] Ya.A. Mandel'baum, I.L. Vladimirova, N.N. Mel'nikov, Zhur. Obshechi. Khim. 23 (1953) 429–432;
Ya.A. Mandel'baum, I.L. Vladimirova, N.N. Mel'nikov, Chem. Abstr. 48 (1954) 3887f.
- [8] The authors thank one of the reviewers for emphasizing this point.