

Core–Shell Microcapsules Containing Flame Retardant Tris(2-chloroethyl phosphate) for Lithium-Ion Battery Applications

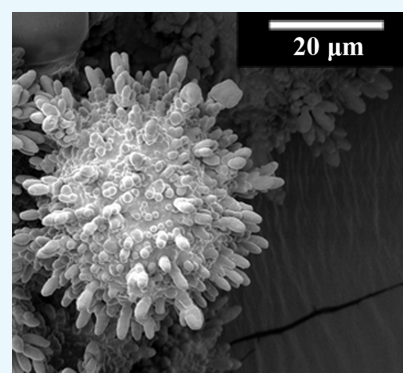
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ABSTRACT: Flame retardant tris(2-chloroethyl phosphate) (TCP) is successfully encapsulated in core–shell poly(urea-formaldehyde) microcapsules by in situ polymerization. The microcapsules are electrochemically stable in lithium-ion (Li-ion) battery electrolytes and thermally stable to ca. 200 °C. Thermal triggering of these microcapsules at higher temperatures ruptures the shell wall, releasing the liquid core (flame retardant), and NMR spectroscopy confirms the presence of the flame retardant in the electrolyte solution. Li-ion pouch cell experiments demonstrate that microencapsulation of TCP and its incorporation into the battery electrolyte provide latent fire retardants that improve battery safety while maintaining inherent battery performance and cycling capability.



INTRODUCTION

Lithium-ion batteries are widely used in consumer electronics, such as cell phones and laptops. However, safety concerns have been an obstacle for the large-scale development of Li-ion batteries and high-power battery modules, such as those required for electric vehicle applications.^{1–3} Many of the safety hazards arise from chemical reactions between electrode materials and electrolyte constituents at elevated temperatures. These reactions are highly exothermic, and the generated heat can accelerate reactions, causing catastrophic thermal runaway.^{2,4–7} Cells undergoing thermal runaway vent violently, and flammable electrolyte solvents coupled with O₂ exposure can trigger combustion of the battery.

Recent research on battery safety has focused on the development of nonflammable electrolytes by incorporating additives that inhibit the chemical reactions that occur during combustion.^{1,8–12} Many flame-retardant species contain phosphorus compounds,^{13,14} which are efficient radical scavengers. The combustion process is exothermic, powered by free-radical reactions, and the existence of radical stabilizers impedes combustion.¹⁵ Other types of flame retardants include nitrogen-containing compounds that release inert gaseous byproducts (such as CO₂, SO₂, or N₂) to form a highly porous char that provides thermal insulation and impedes the combustion front from propagating and spreading.^{16,17} Most flame-retardant additives for Li-ion batteries are directly added to the electrolyte; however, it has been found that this approach significantly compromises battery performance (i.e., cycling

capacity^{4,8,12,13,18} and ionic conductivity^{1,19}) at the concentrations required to reduce flammability.

To avoid sacrificing battery performance while retaining improved safety, we propose the use of core–shell microcapsules for sequestering flame retardants within the battery electrolyte. Encapsulation isolates the flame retardant from the electrolyte so that the normal operation of the battery is unaffected. The shell wall of the capsules provides a barrier for the (often highly toxic) flame-retardant chemicals from outgassing over time. The incorporation of microcapsules also provides a uniquely tailorable delivery platform for their chemical payload. In this case, the capsules are designed to rupture upon exposure to a critical temperature, thus enabling on-demand release when thermal runaway is imminent. Given the variety of capsule shell wall compositions and thicknesses available, the triggering temperature can be tailored to particular applications and cell designs. The venting temperature of a battery is highly dependent on the chemistry of the active materials, battery packaging design, and the individual cell geometry. Finally, isolating the flame retardant within polymeric microcapsules allows for the use of a broader spectrum of flame retardants in Li-ion batteries because the compound is sequestered (and chemically isolated) from the battery electrolyte.

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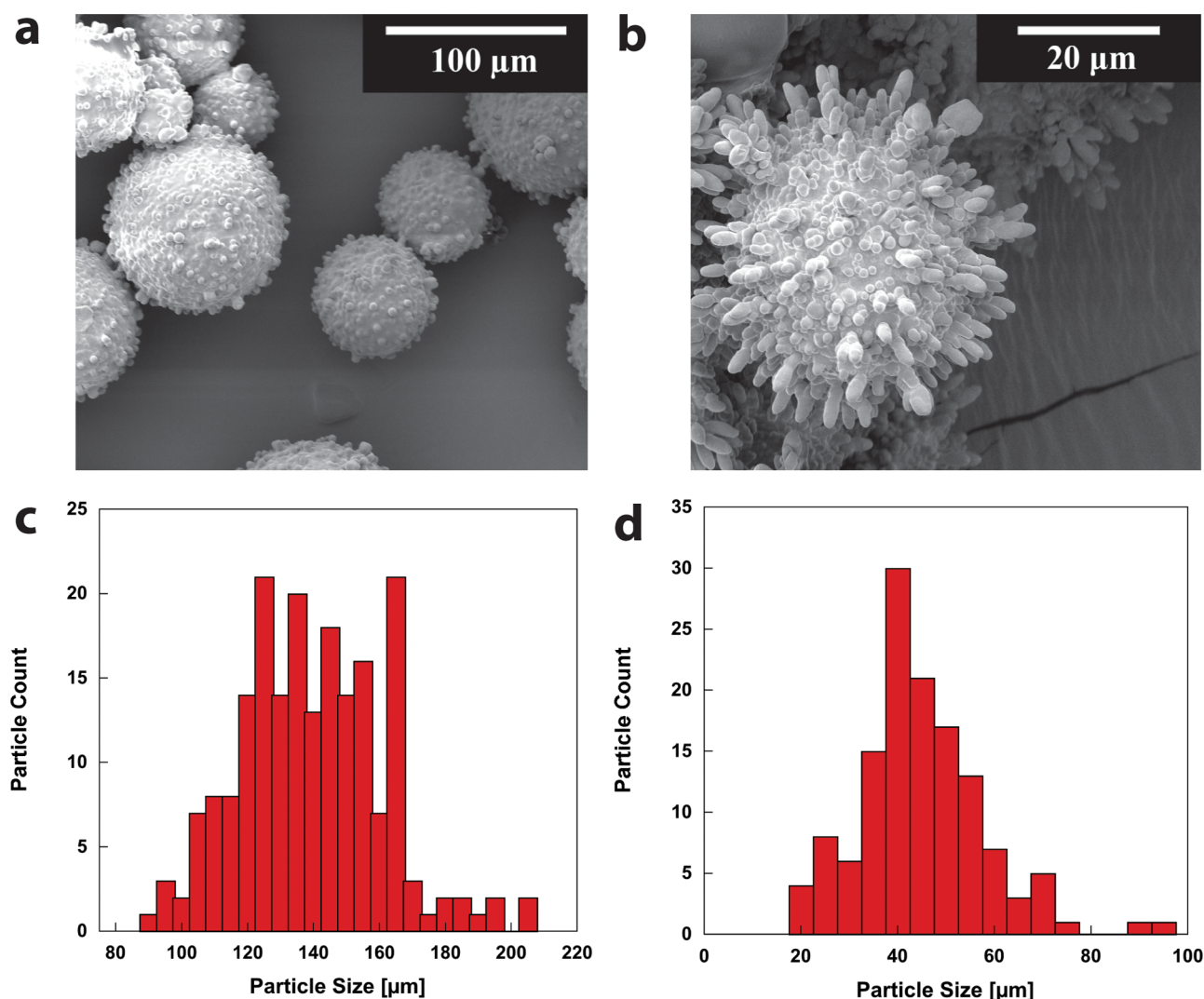


Figure 1. Characterization of microcapsules containing TCP. (a) Scanning electron microscopy (SEM) image of microcapsules prepared at 1500 rpm. (b) SEM image of microcapsules prepared at 3000 rpm. (c) Histogram of microcapsules prepared at 1500 rpm. (d) Histogram of microcapsules prepared at 3000 rpm.

Although encapsulation of flame retardants to improve battery safety has been attempted in the past,^{20–22} electrochemically stable microcapsules with a core–shell morphology containing flame retardants have not been achieved to date. In this work, we describe the encapsulation of tris(2-chloroethyl phosphate) (TCP), a commercial flame retardant that is used in commodity plastics, foams, textiles, and, most recently, in Li-ion batteries,²³ in a poly(urea-formaldehyde) (pUF) core–shell microcapsule. The microcapsules are electrochemically stable in two commercial Li-ion electrolytes and are thermally stable until triggering rupture at ca. 200 °C.

RESULTS AND DISCUSSION

Microcapsules containing TCP were prepared by in situ polymerization of urea and formaldehyde following the encapsulation procedure described by Jin et al.²⁴ Formalin (27.5 g, pH adjusted to 8 with triethanolamine) and urea (10.5 g) were first prereacted at 70 °C for 1 h in a separate vessel. A surfactant solution of ethylene maleic anhydride and water was prepared and mechanically agitated. The UF prepolymer solution (6.19 g) was added to the surfactant solution under mechanical agitation, followed by emulsification of the core

material (5 mL). The reaction vessel was heated to 35 °C. When the temperature reached 30 °C, the pH was adjusted to 2.5 with formic acid. Upon reaching 34 °C, 4.16 mL of H₂O was added, followed by addition of 2.05 mL of H₂O every 15 min thereafter for 1 h. The reaction was then allowed to proceed for 4 h at 35 °C.

After completion of the reaction, microcapsules were centrifuged in water to remove excess surfactant and filter-dried in air. Microcapsules produced using this procedure have an average diameter of 137 and 43 μm when prepared at 1500 and 3000 rpm, respectively, with a rough surface morphology, as shown in Figures 1a and 2b.

The stability of microcapsules in two common battery electrolytes (1 M LiClO₄ EC/DMC and 1 M LiPF₆ EC/ethyl methyl carbonate (EMC)) was investigated. A standard concentration of 1 M was used throughout the electrolyte experiments described in this work. Microcapsules prepared at 1500 and 3000 rpm were soaked for 48 h, 1 week, and 1 month intervals in electrolytes. After the prescribed soak time had elapsed, microcapsules were filter-dried to isolate them from the electrolyte and their mass loss as a function of temperature was investigated using thermogravimetric analysis (TGA).

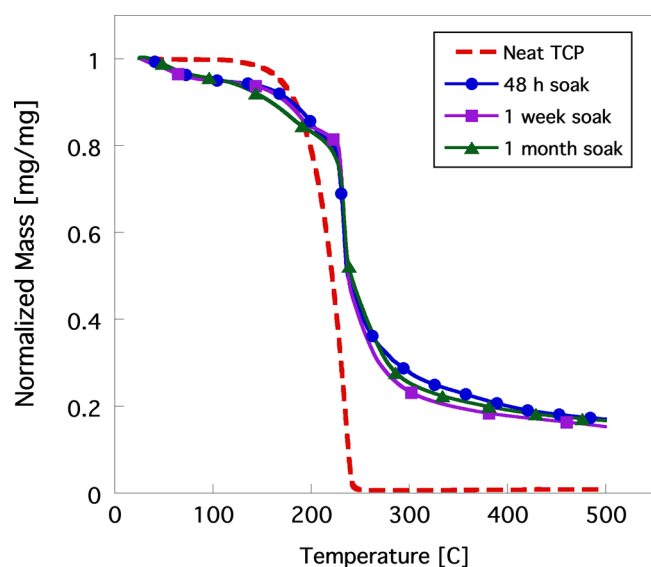


Figure 2. Thermogravimetric analysis of microcapsules. Neat capsules were prepared at 3000 rpm and were soaked in the LiClO_4 ethylene carbonate (EC)/dimethyl carbonate (DMC) electrolyte before TGA scanning at $10\text{ }^\circ\text{C/min}$.

Representative traces for 3000 rpm microcapsules soaked in LiClO_4 EC/DMC are shown in Figure 2, with mass retention data for both capsule types and both electrolytes tabulated in Table 1. Mass loss prior to $100\text{ }^\circ\text{C}$ is attributed to residual

Table 1. TCP Core Content of Microcapsules Exposed to Different Battery Electrolytes

sample type	1500 rpm (ca. $137\text{ }\mu\text{m}$) capsules		3000 rpm (ca. $43\text{ }\mu\text{m}$) capsules	
	LiClO_4 EC/DMC	LiPF_6 EC/DMC	LiClO_4 EC/DMC	LiPF_6 EC/DMC
untreated	80.4%		78.9%	
48 h	75.3%	77.2%	74.4%	77.2%
1 week	77.7%	72.2%	76.5%	75.6%
1 month	77.2%		74.4%	

moisture trapped in the rough surface morphology of the microcapsules. Microcapsules soaked in the electrolyte display nearly identical mass loss profiles consistent with stable behavior up to 1 month of electrolyte exposure. The total mass loss from 130 to $400\text{ }^\circ\text{C}$ was taken as a measure of TCP content ($\text{bp} = 192\text{ }^\circ\text{C}$) and is reported in Table 1. The TCP content is nearly identical in all cases, irrespective of the type of electrolyte, exposure time, or size of capsule.

The ability of the microcapsules to release their content in response to exposure to a critical (trigger) temperature was assessed by preparing vials of suspensions of microcapsules in the electrolyte (LiClO_4 EC/DMC) and exposing the suspensions to a hot silicone oil bath for 1 min. After the thermal exposure, the vials were allowed to cool to room temperature and phosphorus nuclear magnetic resonance (Ph-NMR) spectroscopy was used to identify and measure the amount of core (TCP) released from the microcapsules. An authentic sample with 5 wt % TCP directly added to the LiClO_4 EC/DMC electrolyte was prepared and scanned to provide a reference case for direct measurement of the TCP content. A suspension of 5 wt % microcapsules in the electrolyte was also examined by Ph-NMR to determine the

amount of residual TCP that may have remained on the exterior shell wall from the microencapsulation process. Finally, two suspensions consisting of 5 wt % microcapsules in the electrolyte were prepared and heated to 200 and $240\text{ }^\circ\text{C}$, respectively, and then examined by Ph-NMR. Using triphenyl phosphate (10 mg/mL in CDCl_3) as an internal standard for Ph-NMR, the amount of core release was calculated for each case and is reported in Table 2. For the unheated sample, only

Table 2. Ph-NMR Results for TCP Release from Microcapsules Prepared at 1500 rpm (ca. $137\text{ }\mu\text{m}$ Diameter) upon Exposure to High Temperature

sample (in LiClO_4 EC/DMC)	temperature	% TCP measured	% released
authentic 5 wt % TCP		5.1	
5 wt % capsules	unheated	0.4	9.8
5 wt % capsules	$200\text{ }^\circ\text{C}$	1.2	29.4
5 wt % capsules	$240\text{ }^\circ\text{C}$	3.3	80.9

about 9.8% core release was measured. Upon exposure to $200\text{ }^\circ\text{C}$, nearly 30% core release occurs, and at $236\text{ }^\circ\text{C}$, nearly complete (80.9%) core (TCP) release was measured.

Li-ion pouch cells were fabricated with TCP-containing microcapsules and subjected to electrochemical cycling to assess their performance. The cells consisted of a $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (Li333) cathode and mesocarbon microbead anode. The electrolyte used was 1 M LiClO_4 EC/DMC. Cells were first cycled three times at C/20 from 3.0 to 4.2 V versus Li at room temperature ($25\text{ }^\circ\text{C}$) to perform the formation cycles. Afterward, cells were cycled 50 times at 1C rate while measuring the charge capacity (Figure 3). In both the control

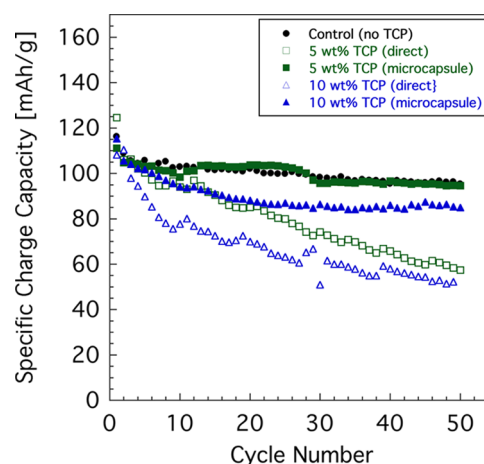


Figure 3. Effect of flame retardant (TCP) on the Li-ion pouch cell cycling performance at 1C, LiClO_4 EC/DMC electrolyte. Microcapsule fabrication at 3000 rpm (ca. $43\text{ }\mu\text{m}$ diameter). Note: three formation cycles at C/20 were performed in all cases prior to 1C cycling.

case (no TCP addition) and the 5 wt % TCP microcapsule case, the specific charge capacity stabilized quickly and was maintained throughout the experiments. For the 10 wt % TCP microcapsule case, stabilization of cycling performance took slightly longer (ca. 20 cycles) and the equilibrium-specific charge capacity was reduced by about 10%. In sharp contrast, for both 5 and 10 wt % direct addition of TCP to the

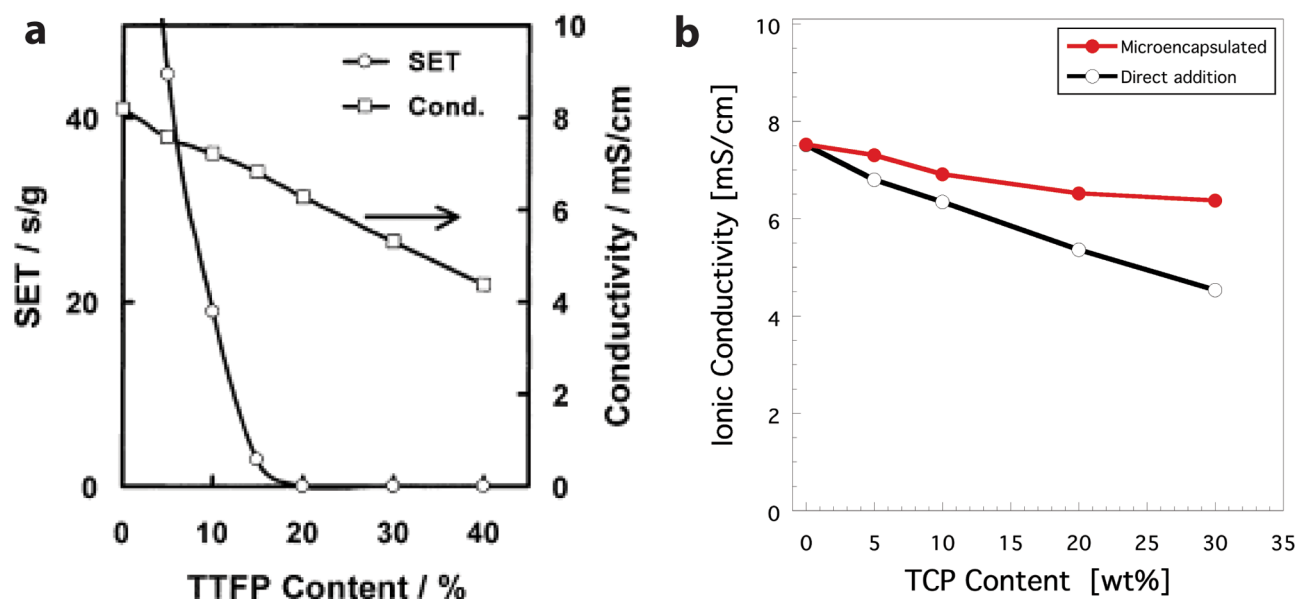


Figure 4. Effect of neat and microencapsulated flame retardants on the ionic conductivity of the LiClO_4 EC/DMC electrolyte. (a) Ionic conductivity and self-extinguishing time as a function of the tris(2,2,2-trifluoroethyl) phosphite content. Figure reprinted from ref 1. (b) Ionic conductivity as a function of the TCP content.

electrolyte, the capacity steadily decreased for 50 cycles, retaining only about 50% of the initial specific charge capacity.

We also examined the effect of flame retardant on the ionic conductivity of electrolyte. It is well known that as the flammability of the electrolyte is reduced (by the addition of flame retardants) ionic conductivity is reduced¹ (Figure 4a). However, the sequestration of the flame retardant within the polymeric microcapsule, isolated from the electrolyte, is shown to be an effective approach to maintaining ionic conductivity while simultaneously reducing electrolyte flammability by the incorporation of a flame retardant (Figure 4b).

CONCLUSIONS

A method to incorporate a flame-retardant battery additive within Li-ion battery cells in a manner that does not degrade or sacrifice the regular battery performance but allows on-demand (heat triggered) release of the additive to prevent battery combustion was developed. Polymeric (UF prepolymer) microcapsules containing the TCP flame retardant were prepared at two different capsule diameters. Microcapsules of both sizes are stable in the two commercial Li-ion battery electrolytes (LiClO_4 EC/DMC and LiPF_6 EC/EMC). Thermal triggering was investigated by dispersing the microcapsules in the battery electrolyte and simulating overheating conditions. Upon exposure to 236 °C, microcapsules released approximately 81% of the TCP core content. Finally, it was demonstrated that the presence of microcapsules neither affects the cycling performance at 1C rate nor reduces the ionic conductivity significantly. Because the microencapsulation technique produces robust and battery-stable microcapsules, it allows for a highly customizable core delivery system applicable to a wide variety of battery chemistries and their unique additive requirements.

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The authors declare no competing financial interest.

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