



Short communication

A novel bifunctional additive for safer lithium ion batteries

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H I G H L I G H T S

- A phosphate ester with aromatic group as a bifunctional additive is synthesized.
- RDP addition could lower the self-extinguishing time (SET) of the electrolyte.
- RDP could be electro-polymerized and postpone the voltage runaway.

A R T I C L E I N F O

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A novel flame retardant, Resorcinol bis(diphenyl phosphate) (RDP), is successfully synthesized and investigated as electrolyte additive for lithium ion batteries. It is found that RDP can be electro-polymerized at 4.4 V (vs. Li/Li⁺), which will protect the batteries from voltage runaway by consuming the overcharge current. Moreover, RDP addition could lower the self-extinguishing time (SET) of the electrolyte. The influence of proper RDP addition on the cycling performance and capacity is negligible. Thus, RDP could be used as a novel electrolyte additive for lithium ion batteries functioned as both overcharge protection and flame retardant. The results may also be helpful for the further design of advanced lithium ion battery electrolytes.

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1. Introduction

Lithium ion batteries are now widely used in various portable electronics and also considered as promising candidates for energy storage and electric vehicles. However, one key hindrance for further applications of Lithium ion batteries is its safety concern. Since the state-of-the-art electrolytes of lithium ion batteries use highly flammable and voltage sensitive carbonate based electrolytes, which might causes serious hazards of firing and explosion under abused conditions such as overcharge, heat, crash etc [1–3].

To solve these problems, much effort has been focused on developing safety additives such as flammable retardants [4–9] and overcharge inhibitors [10–18]. Among them, phosphates esters have been proved to be effective as flame-retardant additives for lithium ion batteries [4–7]. In the other way, many benzene derivatives were verified as applicable safety additives, which act

by forming conducting [10,11,13] or isolating polymers [15] inside the batteries to bypass or interrupt the internal current flow. If one additive can have the functions of both flame-retardant and overcharge protection, it would provide more reliable protection for Li-ion batteries in more burdensome conditions [16–19].

Based on the previous researches, by combining phosphate group and a benzene derivative, Resorcinol bis(diphenyl phosphate) (RDP) was synthesized and test as a safety additive for Li-ion batteries. It is found that this electrolyte additive can not only reduce the flammability of the electrolyte but also provide overcharge protection for 4 V class batteries. The overcharge protection mechanism is also discussed.

2. Experimental

RDP was synthesized by a one pot phosphorylation reaction (shown in Fig. 1), similarly to the etherification of phosphates reported in Ref. [17]. All the chemicals were of analytical grade and used without further purification except otherwise noted. In a typical experimental procedure, 0.1 mol of resorcinol, 0.24 mol of

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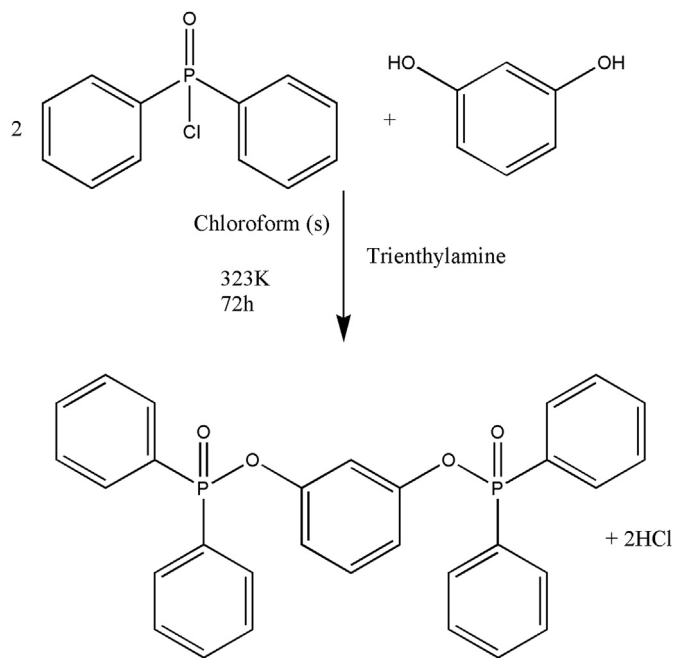


Fig. 1. Synthetic route of RDP.

triethylamine (Et_3N) in 100 ml of dehydrated chloroform in a three-necked 500 ml flask, and then add 0.2 mol of diphenyl chlorophosphate in the flask. The reaction mixture was stirred at 323 K for 72 h; the resultant was filtered off and then dried to give a colorless liquid, and then the product was washed with 5% HCl solution and 5% NaOH solution successively, finally purified by distillation under vacuum over molecular sieve 4 A. Yield: 85% based on resorcinol.

The FT-IR spectra of RDP were recorded on a NICOLET AVATAR360 FT-IR spectrometer with KBr pellets. Elemental analysis of RDP was performed on VarioEL III instrument. ^1H NMR spectra of RDP were recorded on a Mercury VX-300 (300 Hz) apparatus with tetramethylsilane (TMS) as internal standard and CDCl_3 as solvent.

To examine the non-flammability of the RDP electrolyte, we measured the self-extinguishing time (SET) for pre-weighed samples of the electrolyte solutions, in a similar method as described in Ref. [17]. The typical procedure for SET measurements is to use the fiberglass balls (~10 mm in diameter) to absorb 0.5 g electrolyte and then burn the fiberglass to record the burning time. Each test was repeated four times and the burning times were averaged. To study the change in morphology of the electrodes after overcharge, the electrode films were detached in the glove box, washed with tetrahydrofuran followed by drying in a vacuum at room temperature and then examined by field emission scanning electron microscopy (FE-SEM, SU-70, Hitachi, Japan).

The electrochemical window of RDP was examined by cyclic voltammetry (CV) using a stainless steel electrode as working electrode and lithium sheet as both counter electrode and reference electrode. The data acquisition and analysis were collected on a Princeton electrochemical workstation (PAR stat 2273, Ametek, USA). The conductivity of the electrolyte with and without RDP was measured and calibrated with reference to the conductivity of 0.1 M KCl solution, using a conductivity measuring meter (DDS-11A, Leici Co. Ltd, Shanghai, China).

The electrochemical compatibility of the RDP-containing electrolytes was examined by laboratory LiMn_2O_4 -graphite coin type cells. The positive LiMn_2O_4 electrode was consisted of 85% LiMn_2O_4 ,

7% acetylene black and 8% PVDF (wt.%) and the negative graphite electrode is consist 90% graphite, 2% carbon black and 8% PVDF. The base electrolyte was 1 M $\text{LiPF}_6/\text{EC}-\text{EMC}$ (1:3 v/v) purchased from Guotaihuarong Chemical, Co. Ltd. China. The charge–discharge measurements were carried out using a computer-controlled programmable battery charger (BTS-0518001 type, Shenzhen, China). To test the AC impedance of the cell at different charge states, the cell was charged to a given potential at 0.5 mA and rest for 1 h to reach a stable open-circuit voltage, and then the impedance was measured by applying a 5 mV of ac oscillation over the frequency range from 1000 kHz to 0.01 Hz.

3. Results and discussion

3.1. Physical properties and characterization of RDP

The molecular structures of RDP were confirmed by FT-IR bands (3070, 1580, 1495, 1297, 1162, 1120, 1034, 958 cm^{-1}), ^1H NMR (CDCl_3 , 300M) δ : 6.1–6.8 (4H, s), 6.7–7.2 (20H, s), and MS (M^+ , 574).

Fig. 2 shows the combustibility of the 1 M $\text{LiPF}_6/\text{EC}-\text{EMC}$ electrolyte at various content of RDP. It can be seen that with increasing RDP content from 0 to 72 v%, the burning time of the electrolyte decreases from 49 to 0 s g^{-1} , suggesting the RDP can lower the flammability of the electrolyte significantly [2]. Phosphate compounds are known as flame retardants that can function by the combination of radical adsorption and oxygen isolation mechanism [4]. The ionic conductivity of the electrolyte decreased slightly with the increase of the RDP content, which may due to the higher viscosity of RDP and the dilute of the LiPF_6 concentration. To get a compromise between the ionic conductivity and non-flammability of the electrolyte, we selected 10% RDP content as a balanced content to value its electrochemical characters. Further research may be on the optimization of the side effects.

3.2. Electrochemical behaviors of RDP

Fig. 3 shows the electrochemical performance of $\text{LiMn}_2\text{O}_4/\text{graphite}$ cells with the electrolytes containing different concentrations of RDP. With the increase of RDP content, the capacity and coulombic efficiency only slightly decreases due probably to the dilute of LiPF_6 concentrations and trace impurities.

Moreover, the electrolytes with 10% or less RDP have resulted in negligible capacity loss on cycling. Therefore, the adequate addition of 10% RDP does not bring noticeable harmful effect on the

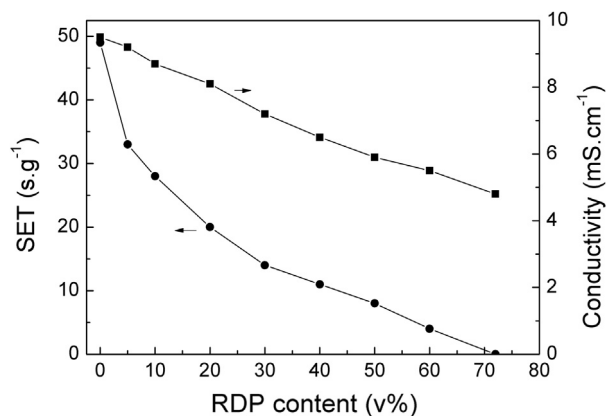


Fig. 2. Flammability and ionic conductivity of 1 M $\text{LiPF}_6/\text{EC} + \text{EMC}$ (1:3 v/v) at different contents of RDP.

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