

Short communication

Dimethyl methylphosphonate (DMMP) as an efficient flame retardant additive for the lithium-ion battery electrolytes

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Abstract

Dimethyl methylphosphonate (DMMP) was used as a flame retardant additive to 1 M LiPF₆/EC + DEC system. The flammability, electrochemical stability and cycling performance of electrolyte containing DMMP were studied. The addition of DMMP to electrolytes provides a significant suppression in the flammability of the electrolyte concluded from the measurements of self-extinguish time and limited oxygen index. The totally non-flammable electrolytes can be achieved with only 10 wt.% DMMP addition—the highly efficient retardant additive. The addition of DMMP causes little damage on the cell electrochemical performance. DMMP is a promising flame retardant additive to improve the safety of lithium-ion batteries. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Non-aqueous electrolytes are widely used in energy storage devices, such as super-capacitors and lithium-ion batteries, because of their wider electrochemical window than aqueous solution. However, non-aqueous electrolyte can be ignited in the situations of various types of accidents and abuses, which has imparted the state-of-the-art electrolyte systems with potential fire hazards. The efforts aiming to improve the thermal safety of electrolytes have intensified in recent years, especially driven by the more stringent safety requirements for large industry lithium-ion batteries intended for electric vehicles. The most efficient and economical way are using flame retardants (FRs) as electrolyte additives or cosolvents [1,2].

Alkyl phosphates and aryl phosphates have been earlier introduced in Li-ion batteries electrolyte as FRs [3–8]. Unfortunately, the content of FRs usually must be as much as 20% to obtain a marked effect, which will bring some adverse impacts on the cell performance, i.e. the improvement in the safety of electrolytes based on these FRs is almost always accompanied by deteriora-

tion in cell performance. Fluorinated alkyl phosphates [9,10] and hexamethoxycyclotriphosphazene [4,11] are very promising FRs because an electrolyte containing some of them becomes nonflammable while having no adverse impacts on the cell performance. However, the introduction of these additives has greatly increased the cost of the Li-ion batteries.

In order to find an ideal FR taking both the performance and the cost into account, we attempt to use an alkyl phosphonate (Scheme 1 in Fig. 1), which is better than an alkyl phosphate (Scheme 2 in Fig. 1) and an alkyl phosphite (Scheme 3 in Fig. 1) in flame retarding capability [3–5]. Among commercially available phosphonates, dimethyl methylphosphonate (DMMP) seems a suitable choice with the advantages of low viscosity (1.75 mPa s), moderate dielectric constant (22.3), low melting point (–50 °C) and high boiling point (180 °C). This study also indicates that DMMP is compatible with LiCoO₂/Li half-cells and LiCoO₂/graphite full cells if the graphite has been treated by a surface modification.

2. Experimental

As-purchased DMMP was purified with a distillation step under vacuum and dried before use over molecular sieves (4A). An electrolyte of 1 M LiPF₆ in a mixture of 1:1 (w/w) ethylene

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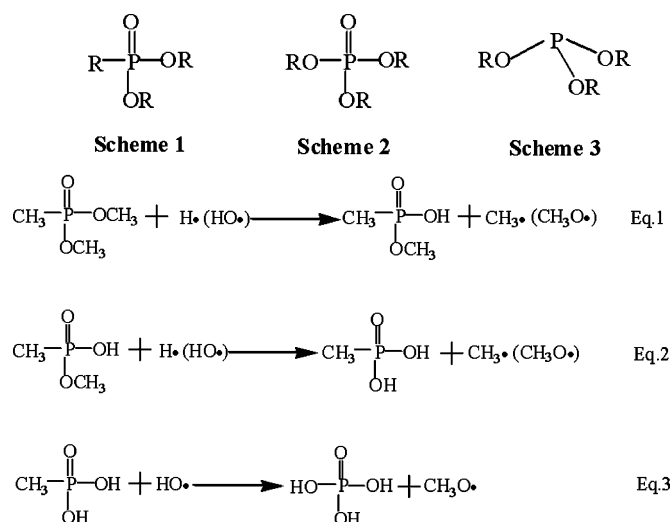


Fig. 1. The schemes of three kinds of phosphorus-containing flame-retardants and possible flame-retarding mechanism of DMMP.

carbonate (EC) and diethyl carbonate (DEC) was selected as a baseline electrolyte. Different contents of DMMP were added in the baseline electrolyte in an argon-filled glove box (MBrun Labmaster 130). A positive electrode consisting of LiCoO₂ (84 wt.%), acetylene black (8 wt.%) and poly(vinylidene fluoride) (PVDF) (8 wt.%) and a negative electrode consisting of a surface-modified graphite (SMG, 92 wt.%) and PVDF (8 wt.%) were made on aluminum and copper foils, respectively. The SMG powder was prepared by a thermal vapor decomposition treatment [12]. It can also be prepared by a pyrolytic polymer encapsulation [13] or a hydrothermal treatment [14]. CR2032 coin cells of LiCoO₂/Li and LiCoO₂/graphite were assembled in the glove-box. In the LiCoO₂/graphite cells, the mass ratio of LiCoO₂ and SMG was controlled at about 2:1, so that the cell capacity was determined by the positive electrode. These cells were cycled between 2.8 and 4.2 V at a current density of 0.20 mA cm⁻² initially and 0.65 mA cm⁻² after the third cycle.

Following a similar procedure used by Xu et al. [4,15], we measured the self-extinguishing time (SET) for pre-weighed samples of the electrolyte solutions. Igniting a cotton ball-wick of 0.3–0.5 cm diameter absorbing 0.05–0.10 g electrolyte, we recorded the time it took for the flame to extinguish. The SET was obtained by normalizing the flame burning time against the electrolyte mass. We also measured limited oxygen index (LOI) to evaluate the flammability of the electrolytes. Here we introduced the similar test method (GB/T 16581-1996) to that for polymer (ASTM D2863) for the determination of LOI of the electrolytes. By igniting about 1.2 mL electrolyte sample injected into the burning cup, we recorded the time it took for the flame to extinguish under an O₂/N₂ atmosphere with a certain oxygen concentration. If the time was shorter than 60 s, the percentage of oxygen in the O₂/N₂ mixture must be increased in order for at least three of five liquid samples to burn longer than 60 s. Then, that point of the oxygen percentage that just met above criterion was the LOI of the tested sample.

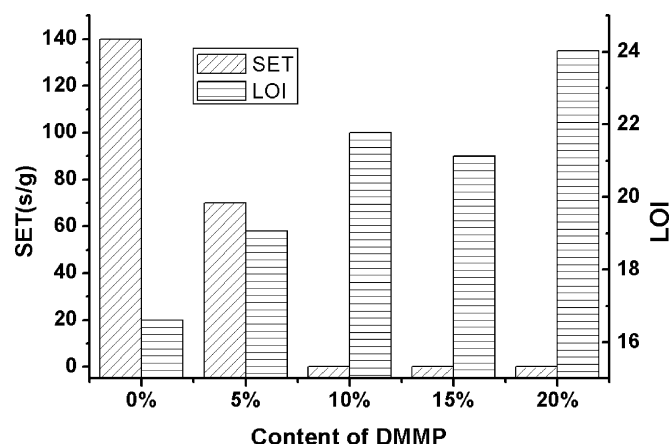


Fig. 2. The results of flammability test of SET and LOI for electrolyte solutions containing different percentages of DMMP.

3. Results and discussion

The results of the electrolyte flammability test are shown in Fig. 2. Obviously, the baseline electrolyte, i.e. 1 M LiPF₆ in EC:DEC (1:1), is very flammable with SET of 140 s g⁻¹ and LOI of 17. As DMMP is added in the electrolyte, the SET greatly decreases to 70 s g⁻¹ even with only 5 wt.% DMMP and the electrolytes cannot be ignited (i.e. SET = 0 s g⁻¹) when the content of DMMP exceeds 10 wt.%. This result is consistent with the LOI test since the DMMP addition increases its LOI from 17 at 0% to 19 at 5 wt.%, 22 at 10 wt.%, 21 at 15 wt.% and 24 at 20 wt.%, respectively. Therefore, DMMP can efficiently suppress the flammability of the nonaqueous electrolyte.

In general, organophosphorus compounds are known as flame retardants that can function in the vapor phase by a radical mechanism [16]. Usually the phosphorus content of this kind of flame-retardants can reflect the efficiency of flame retarding. DMMP has higher phosphorus content than the previous investigated FRs additives such as trimethyl phosphate (TMP) [3], triethyl phosphate (TEP) [4], tributyl phosphate (TBP) and triphenyl phosphate (TPP) [7] so that it is more feasible to make the electrolyte become flame retardant or even totally nonflammable. The possible reactions involved in the flame-retarding process of DMMP in a fire situation can be proposed as Eqs. (1)–(3) in Fig. 1 [17,18]. DMMP gas is a good radical inhibitor by capturing the radicals H[•] and HO[•] in the flame zone so that it can weaken or terminate combustion chain branching reactions. Also, H₃PO₄ can be decomposed further to produce the radicals PO[•] and PO₂[•], which can also capture H[•] and HO[•] [16].

Fig. 3 shows the electrochemical performance of Li/LiCoO₂ half-cells with the electrolytes containing different concentrations of DMMP. With the increase of DMMP concentration, the capacity slightly decreases due probably to the decrease of LiPF₆ concentration. Moreover, the electrolytes with 10% or less DMMP have resulted in acceptable capacity loss on cycling. Therefore, the adequate addition of DMMP does not bring noticeable adverse effect on the electrochemical performance of the positive electrode except for the effect of lowering concentration.

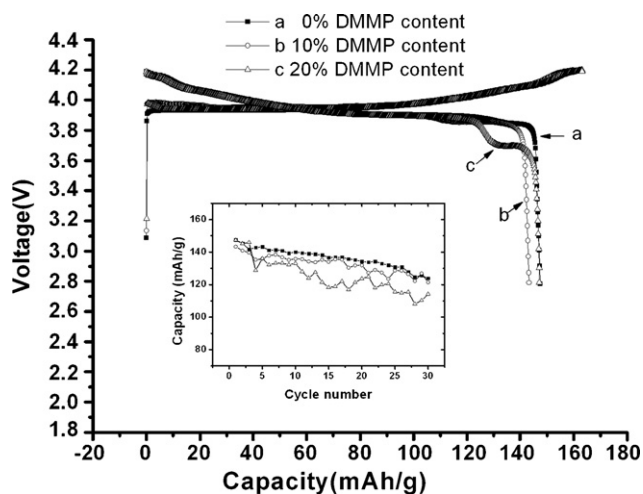


Fig. 3. The electrochemical performance of LiCoO₂/Li half-cells with the electrolytes containing different concentrations of DMMP.

To evaluate the practicability of DMMP, LiCoO₂/SMG full cells were also measured. Fig. 4 shows the capacity and its fading behavior against cycle number for electrolytes with or without DMMP. In the beginning cycles, there is no obvious difference between the two kinds of electrolytes. After six cycles, the electrolyte containing 10% DMMP leads to less capacity loss on cycling than that without DMMP so that the capacity value is even higher with the 10% DMMP electrolyte, which shows better improvement than in the case of LiCoO₂/Li half-cell (Fig. 3). This difference could be due to the film-forming characteristic of DMMP on the graphite electrode because a similar compound dibenzyl phosphonate is also used as a film-forming additive in lithium-ion batteries [19]. Nevertheless, the reason of such

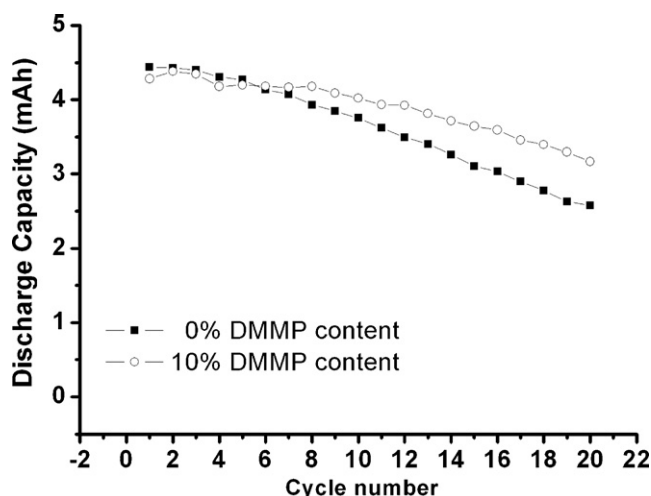


Fig. 4. Cycling performance of the full Li-ion cells using electrolytes containing 0 wt.% and 10 wt.% DMMP.

a stabilization effect should be a subject of further study. Also, it should be pointed out that the use of SMG as the negative electrode material is necessary because DMMP can lead to the exfoliation of an un-treated graphite negative electrode at a low potential versus Li/Li⁺.

4. Conclusions

DMMP is used, for the first time, as a flame retardant additive for lithium-ion battery electrolytes. Only 10 wt.% DMMP addition can result in a nonflammable electrolyte. The cell performance is hardly damaged with DMMP addition. It provides us a promising solution to settle the safety concern of lithium-ion batteries.

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