



Short communication

A novel flame retardant and film-forming electrolyte additive for lithium ion batteries

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ABSTRACT

Allyl tris(2,2,2-trifluoroethyl) carbonate (ATFEC) was synthesized as a bi-functional additive of flame retardant and film former in electrolytes for lithium ion batteries (LIBs). The flame retardancy of the additive was characterized with differential scanning calorimetry (DSC) and self-extinguishing time (SET). It is shown that adding 1 vol.% ATFEC in 1 M LiPF₆/propylene carbonate (PC) can effectively enhance the thermal stability of the electrolyte and suppress the co-intercalation of PC into the graphitic anode. Further evaluation indicates that the additive hardly affect the conductivity of electrolyte. These support the feasibility of using ATFEC as an additive on formulating an electrolyte with multiple functions such as film-forming enhancement, high thermal stability and high ionic conductivity.

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1. Introduction

Safety issue has been harassing the application of lithium ion batteries (LIBs) with high energy density (energy storage batteries) and high power density (e.g. batteries for hybrid electric vehicles). Overcharge and over-discharge of a lithium ion battery will result in electrolyte decomposition, producing various flammable gaseous species, increasing the inner pressure and temperature of the battery. Any of these issues will increase the explosion hazard of the battery [1]. Clearly an internal-built safety mechanism is more reliable and effective than the external-built safety mechanism such as the positive temperature coefficient (PTC) devices and current intermitted devices (CID) when the temperature, internal pressure, voltage and/or the current of the battery increase(s) very quickly.

Currently most studies intended to enhance the electrolyte safety are focused on the (fluorinated) phosphates [2–9] as the flame retardant either in the form of an additive or a co-solvent of the electrolyte. However, some additives such as the commonly studied trimethyl phosphate (TMP) [10–12] and dimethyl methylphosphonate (DMMP) [3–5] characteristic of excellent

self-extinguishing properties suffer from severe reductive decomposition on the graphitic anodes. Therefore they can only be applied in LIBs with non-graphitic carbon anode [11] or with the presence of some film-forming additives in the case of graphitic anode materials [4,5,12].

Propylene carbonate (PC) based electrolytes are attractive due to the low cost of the solvent and the wide temperature window of the resultant electrolyte. However, significant co-intercalation will occur when PC-based electrolytes are combined with graphitic anode, resulting in severe exfoliation of the latter. Molecules containing vinyl groups are commonly used as the additive for the formation of the solid electrolyte interphase (SEI) layer on the graphite-based anode because they can reductively decompose prior to the co-intercalation of the electrolyte. In addition, electron-drawing groups such as –F make the vinyl group more electrophilic and thus facilitate the reduction, helpful for the formation of the SEI layers on the graphitic anodes [13]. Moreover, introduction of fluorine into organic molecules usually reduces their boiling temperature and viscosity and suppresses the flammability of the molecule [9]. Therefore, allyl tris(2,2,2-trifluoroethyl) carbonate (ATFEC) was synthesized in this work as a flame retardant and film-forming additive in electrolyte for LIBs. It will be seen that ATFEC is a promising bi-functional additive in enhancing the thermal stability of the electrolyte and in preventing the co-intercalation of PC into graphitic anode materials during discharge.

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2. Experimental

The ATFEC solvent (purity <99%) was similarly synthesized as 4-methoxymethyl ethylene carbonate (MEC) by esterification of 2,2,2-trifluoroethanol and allyl chloroformate [14]. Ethylene carbonate (EC), PC, dimethyl carbonate (DMC) (battery grade, H₂O < 5 ppm; Shanghai Topsol) solvents were further dried with 4 Å molecular sieves. LiPF₆ (battery grade, Shanghai Topsol) was used as received. The electrolyte preparation was performed in an argon-filled glove box.

The measurements of the conductivity of the electrolytes were performed on Hewlett-Packard 4192A impedance analyzer with Pt wires as the electrodes. The cell constant was determined with 0.01 M KCl standard aqueous solution for each sample. The cyclic voltammetry (CV) of a three-electrode cell was carried out on a CHI660 electrochemical workstation with natural graphite (NG) as the working electrode and lithium foils (99.9%) as both the counter and reference electrodes.

Differential scanning calorimetry (DSC) analysis was carried out on NETSCH STA 449C. About 20 mg liquid sample was sealed in an aluminum pan in the glove box. A pinhole was punched on the pan prior to the DSC testing. The pan was heated from 25 to 300 °C at a rate of 10 °C min⁻¹ in oxygen.

The dependence of the self-extinguishing time (SET) of the electrolyte on the content of the flame-retarding additive was determined as Xu et al. [15] previously described. A glass fiber ball (~1 cm in diameter) was soaked in the electrolyte and adsorbed ~0.5 g liquid. The ball-wick was then ignited. The burning time was recorded with a stop watch. The SET shown in the paper was obtained by averaging the flame burning time against the mass of the adsorbed electrolyte. For each sample, the test was repeated 10 times to obtain the SET time. The weight instead of the volume of the electrolyte adsorbed into the glass fiber balls was measured here because it is difficult to determine the volume of the electrolyte absorbed in the glass fiber balls.

3. Results and discussion

The DSC traces of pure ATFEC, 1 M LiPF₆ /EC+DMC and 1 M LiPF₆/EC+DMC+10% ATFEC are shown in Fig. 1. The exothermic reaction of pure ATFEC starts at about 110 °C and the exothermic peak appears at 143 °C. From the thermal-gravimetric (TG) profile of pure ATFEC, it is seen that the reaction is complete because there is almost no mass left. The DSC traces indicate that the

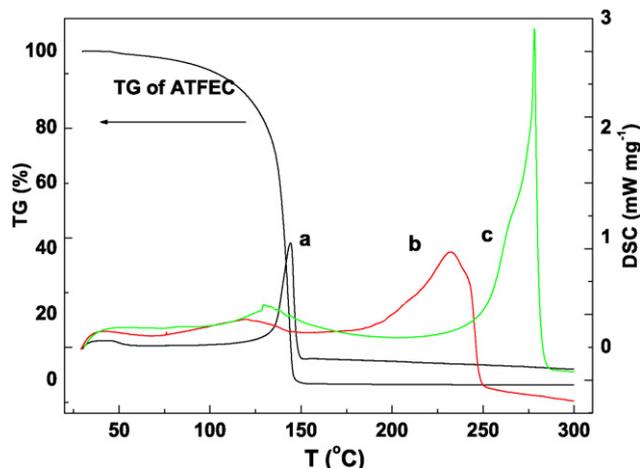


Fig. 1. The TG of ATFEC and the DSC traces of pure ATFEC (a), 1 M LiPF₆ /EC+DMC (b) and 1 M LiPF₆ /EC+DMC+10%ATFEC (c).

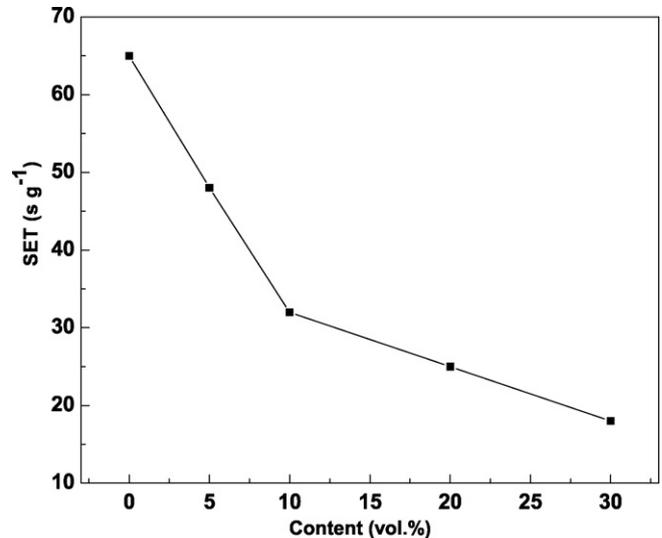


Fig. 2. Self-extinguishing time (SET) with various contents of ATFEC in 1 M LiPF₆/EC+DMC.

onset temperature of the exothermic reaction of the original (1 M LiPF₆/EC+DMC) electrolyte is 180 °C. However, this temperature is elevated to around 220 °C when 10% ATFEC is added. These results strongly suggest that the addition of ATFEC improves the thermal stability of the electrolyte.

The flame-retarding effect of the ATFEC additive in the electrolytes is also obvious (Fig. 2). It is seen that the SET of the electrolyte decreases from 65 s g⁻¹ for the original electrolyte to 48 s g⁻¹ when 5 vol.% ATFEC is added. When the content of the flame retardant increases to 30 vol.%, the SET of the electrolyte decreases to 18 s g⁻¹; the electrolyte becomes almost nonflammable. These suggest that addition of ATFEC results in a significant reduction of the flammability of the electrolyte. ATFEC is an efficient flame-retarding reagent.

The flame-retarding mechanism of ATFEC is not quite clear yet but we try to describe it as follows. Upon overheating, the molecules of the gaseous carbonate solvent break down and produce hydrogen radicals (H[•]) [10], the main active agent of combustion chain branching reactions. Meanwhile, the gaseous ATFEC is decomposed to small fluorinon radicals to scavenge the H[•] radicals. As a result, the combustion chain branching reactions of the electrolyte are hindered due to deficiency of the H[•] radicals.



The conductivities of 1 M LiPF₆/EC+DMC (1:1 in volume) electrolyte with various contents of ATFEC were investigated between -20 and 60 °C (Fig. 3). It seems that addition of ATFEC only slightly decreases the conductivity of the electrolyte. For example, the conductivity of the electrolyte decreases from 9.79 × 10⁻² S cm⁻¹ at 0% ATFEC to 8.34 × 10⁻² S cm⁻¹ at 15 vol.% ATFEC at 20 °C. The negligible decrease of the electrolyte conductivity is attributed to the low viscosity and low melting temperature of the linear ATFEC molecules. The high conductivity of the additive-containing electrolyte means that such an additive is expected to find an application in electrolyte for power-type lithium ion batteries. This feature encourages us to evaluate the electrochemical performance of ATFEC in a lithium battery.

Fig. 4 shows the film-forming effect of 1% ATFEC on natural graphite in 1 M LiPF₆/PC electrolyte. The potential plateau at around

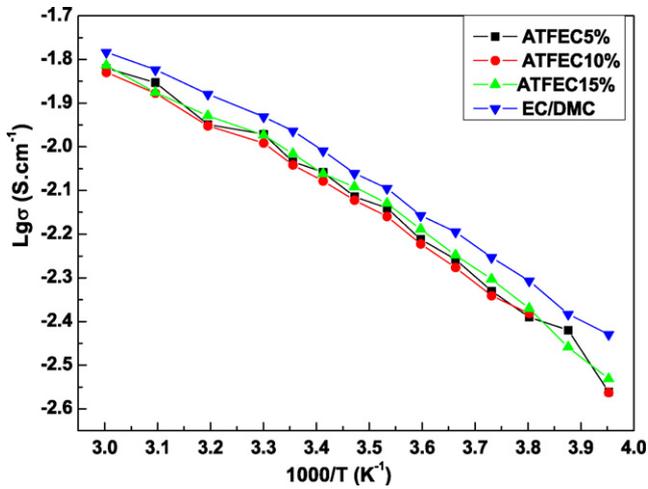


Fig. 3. Dependence of the electrolyte conductivity on the ATFEC content (in volume) in 1 M LiPF₆ / EC + DMC electrolyte.

1.2 V vs. Li. in the first discharge is ascribed to the decomposition of ATFEC (corresponding to the cathodic peak between 1.2 and 1.9 V in the inset cyclic voltammograms). The potential plateau between 0.7 and 0.3 V is attributed to the decomposition and co-intercalation of PC solvent into the natural graphite. The lithium intercalation mainly occurs below 0.3 V. Because of the decomposition of the ATFEC additive and the PC solvent, the coulombic efficiency of the cell is only 29% in the first cycle. In the subsequent cycles, however, the efficiency continuously increases with, probably, the increasing thickness and compactness of the SEI layer as a decomposition product of the additive. The coulombic efficiency of the cell increases to 92% after four cycles. This means that the formed SEI layer is stable and effective in preventing the co-intercalation of PC. The slight decrease of the reversible capacity is attributed to the slight conductivity reduction when ATFEC is added in the electrolyte.

The cycling behaviors of commercial LiCoO₂ in Li/LiCoO₂ half-cells using electrolyte with and without ATFEC additive were also evaluated. Fig. 5 compares the discharge capacity and coulombic efficiency of two cells using the original electrolyte and that containing 10 vol.% ATFEC additive in the first eight cycles. Obviously, both cells show good cycling stability. Without additive the discharge capacity and coulombic efficiency in the first cycle are 135 mAh g⁻¹ and 95%, respectively. When 10% ATFEC is added, they decrease to 121 mAh g⁻¹ and 87%, respectively. In the second cycle, the coulombic efficiency increases to 93% though the discharge capacity remains 121 mAh g⁻¹. The extra irreversible capacity loss for the additive using cell (15 mAh g⁻¹) is attributed to the decomposition of the additive at low discharge voltages but is still acceptable in comparison with other flame retardant additives [3,10,11].

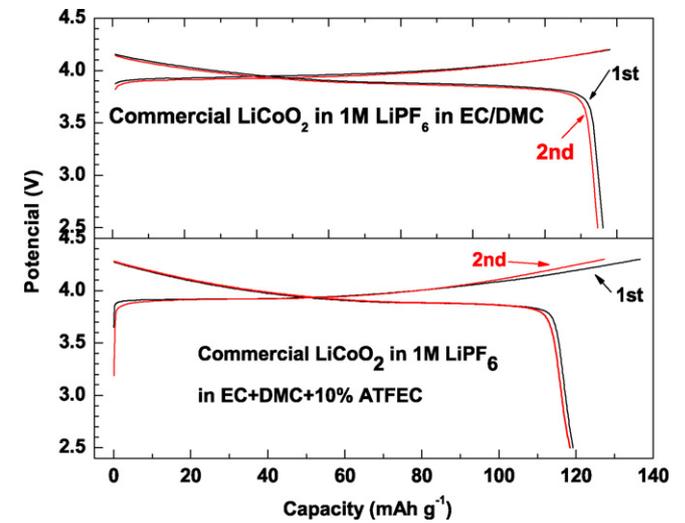


Fig. 5. The charge/discharge curve at the first two cycles of the Li/LiCoO₂ half-cells with different electrolytes. Current density: 0.1 mA cm⁻².

The influence of the ATFEC content in the electrolyte on the coulombic efficiency of the cell was also studied in Fig. 6. It is found that the efficiency reaches about 96% after four, five and six cycles for the electrolytes containing 10%. This means that further increasing the ATFEC content does not help in improving the electrochemical performance of the SEI layer. Rather it increases the irreversible capacity due to the decomposition of the additive. A plausible explanation is that the compactness of the formed SEI layer increases with cycling rather than with its thickness alone.

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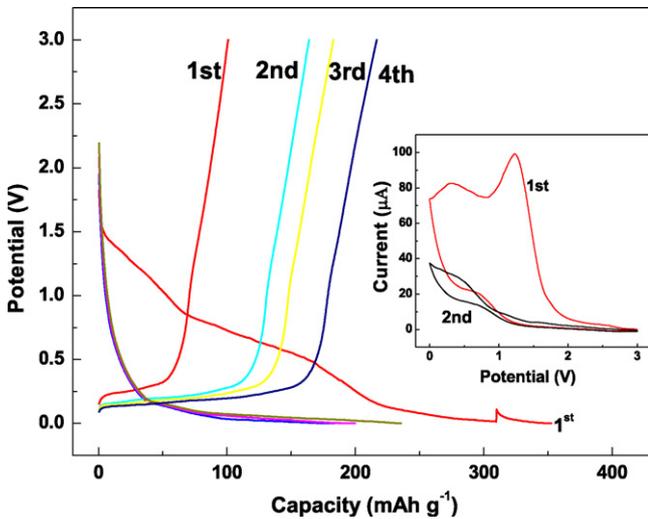


Fig. 4. The voltage profiles of a Li/NG cell in the first four cycles using 1 M LiPF₆ / PC + 1 vol.% ATFEC electrolyte and cycled at a current density of 0.1 mA cm⁻² between 0 and 3.0 V vs Li. The inset is for the cyclic voltammograms of a three-electrode Li/NG cell using the same electrolyte in the first two cycles at a scan rate of 0.1 mV s⁻¹.

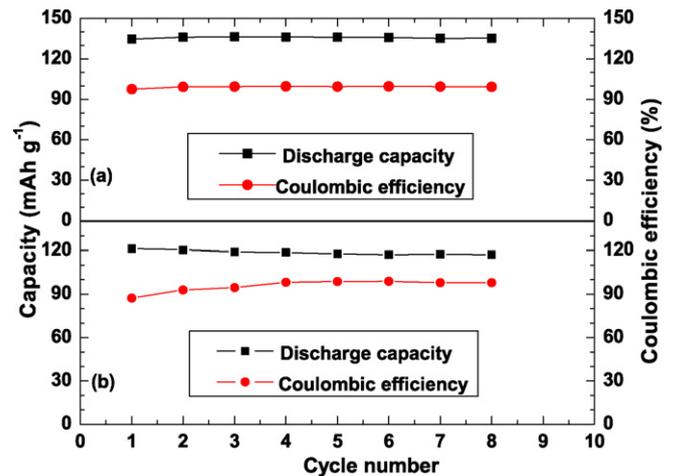


Fig. 6. The electrochemical performances of commercial LiCoO₂ in 1 M LiPF₆ / EC + DMC electrolyte containing no (a) and 10 vol.% (b) ATFEC between 2.5 and 4.2 V at a current density of 0.1 mA cm⁻².

The reason for the abnormal dependence of the efficiency variation on the ATFEC content needs to be further studied. After the first few cycles, all the cells using ATFEC-added electrolyte can cycle steadily with high (over 99%) coulombic efficiency.

4. Conclusions

Fluorinated carbonate ATFEC is synthesized as a bi-functional additive in carbonate-based electrolyte for lithium ion batteries. It is indicated that addition of ATFEC can enhance the thermal stability and significantly shorten the flame extinguishing time of the electrolyte. Addition of up to 15 vol.% ATFEC in the electrolytes does not remarkably affect the conductivity of the commercial electrolyte. In addition, the ATFEC additive exhibits good electrochemical compatibility with natural graphite anode and LiCoO₂ cathode materials. These results demonstrate that ATFEC is a promising bi-functional additive in improving the thermal stability of the electrolytes and the cell performance for Li-ion batteries.

Acknowledgments

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