Novel high phosphorus content phosphaphenanthrene-based efficient flame retardant additives for lithium-ion battery

Jinyun Zheng · Xiao Li · Yujian Yu · Xiangming Feng · Yufen Zhao

Abstract The novel phosphate derivatives of phosphaphenanthrene with high-density phosphorus were synthesized and used as flame retardant additives for Li-ion batteries. The structures of compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, FT-IR, and HR-MS. The excellent thermal stability of compounds was ascertained by thermogravimetric analysis and differential scanning calorimetry. The compounds were added to conventional electrolytes as flame retardant additives and evaluated their ionic conductivity, electrochemical stability, self-extinguishing properties, and combustion performance. The results showed that the compound containing higher phosphorus content has efficient flame retardant properties.

Keywords Phosphaphenanthrene · High-density phosphorus · Thermal stability · Flame retardant · Lithium-ion battery

Introduction

Lithium-ion batteries have high-voltage and high-energy density characteristics, they have found widespread use in small power portable electronic devices, such as camcorders, cell phones, and computers since their commercialization in 1990s [1, 2]. However, the high-energy density of lithium batteries is accompanied by the high potential hazard, and the safety concern has been a key obstacle for further development and applications of Li-ion batteries, especially for high-power battery packs designed for electric vehicle (EV) or hybrid electric vehicle (HEV) applications. The electrolytes of Li-ion batteries contain organic small-molecule solvents, such as dimethyl carbonate, diethyl carbonate, and ethylene carbonate. This makes them susceptible to combustion or even explosions under abusive conditions, short circuits, and even under normal operating conditions [3, 4]. A number of strategies have been implemented to improve the fire safety of secondary lithium batteries [5]. Adding the flame retardant additives to the electrolyte is an effective method [6, 7], but a major challenge is development of new flame retardant additives with excellent performance. The flame retardants that have been explored so far include organophosphorus compounds, such as phosphates: trialkyl phosphates, triphenyl phosphates, tri(fluorinated alkyl) phosphates and cyclotriphosphazenes, fluorinated ethers and ionic liquids [8–12]. Among them, the flame retardants based on phosphate or P(V) compounds have been found to be able to suppress the flame propagations at the expense of battery performance [13], such as ionic conductivity of the electrolyte. Therefore, most of the organophosphorus compounds have to be used in low concentrations, usually no more than 20 % either by mass or by volume. It is important to find the efficient flame retardant with little side effects or without. The previous studies have demonstrated that effective flame retardant properties can be imparted with low concentrations (i.e., <20 %) with minimal impact on performance [13]. In general, the high

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Scheme 1 Synthesis of
compound A
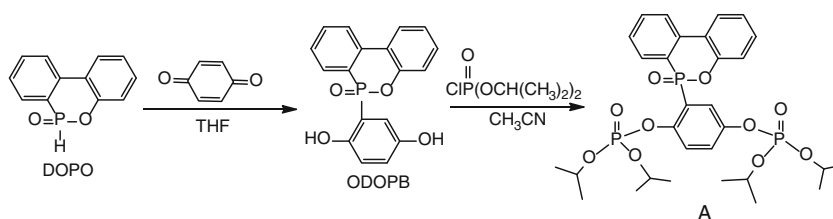
Scheme 2 Synthesis of
compound B
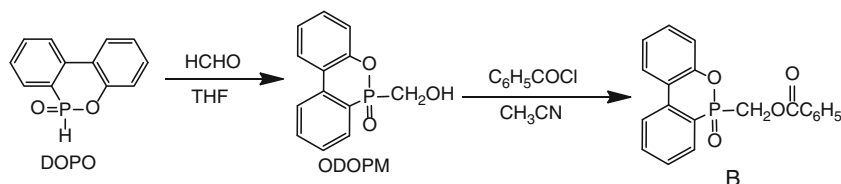
phosphorus content of the flame retardant additive means
high flame retardant effect. So it is important to design the
high-density "Phosphorus" compounds.

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
(DOPO) and its derivatives, as a kind of phosphorus-con-
taining common flame retardants, have been used to epoxy,
polyurethanes, polyesters, and novolac resins [14–17]. This
rigid and bulky group contains a cyclic phosphate with a
diphenyl structure, which has high thermal stability, good
oxidation, and water resistance. Because higher phosphorus
content means higher performance of flame retardant and
lower additive concentrations. It is based on the good flame
retardant properties of DOPO, we designed a novel higher
phosphorus content DOPO derivative—compound A
(Scheme 1) and used as efficient flame retardant additive
for Li-ion batteries. In order to compare the different flame
retardant properties due to the different phosphorus con-
tents, we also designed compound B (Scheme 2), which
had lower phosphorus content. In this work, the compounds
A and B were applied to Li-ion batteries flame retardant
additives, which have not been reported. On the other hand,
the effect of "P" density on the flame retardant properties
was discussed in detail.

Experimental

Materials and intermediates

DOPO was synthesized according to Ref. [18]. Diisopropyl
phosphoryl chloride was prepared by the reaction of
diisopropyl phosphite with sulfonyl chloride. Benzoyl
chloride was prepared by the reaction of benzoic acid with
thionyl chloride. 2-(6-Oxido-6H-dibenz<c,e><1,2>oxa-
phosphorin-6-yl)-1,4-benzenediol (ODOPB) was prepared
by the reaction of DOPO and benzoquinone in THF, and

was purified by recrystallization from methanol to give
pure product, m.p.: 255–256 °C, HR-MS m/z: calcd for
$C_{18}H_{13}NaO_4P$: 347.0449 $[M+Na]^+$, found 347.0445. 2-(6-
Oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-metha-
nol (ODOPM) was prepared by the reaction of DOPO and
formaldehyde in THF, and was purified by recrystalliza-
tion from methanol/petroleum to give pure product, m.p.:
155–156 °C, HR-MS m/z: calcd. for $C_{13}H_{11}NaO_3P$:
269.0344 $[M + Na]^+$, found 269.0348. Benzoquinone, o-
phenylphenol, formaldehyde, tetrahydrofuran, acetoni-
trile, and other reagents were used as supplied. The elec-
trolytes (JN908) were purchased from China Tianjin
Jinniu Power Supply Material Co., Ltd.

Synthesis of compounds A

ODOPB (10.00 g, 0.03 mol), K_2CO_3 (4.80 g, 0.035 mol),
and anhydrous CH_3CN (500 mL) were placed in a
1,000-mL three-necked flask, after the suspension became
clear at raised temperature, diisopropyl phosphoryl chlo-
ride (14.00 g, 0.07 mol) in 50 mL CH_3CN was added in a
dropwise manner over 2 h. The reaction solution was
refluxed for 6 h. The insoluble solid was isolated from the
hot solution by filtration. The filtrate was cooled and as the
white solid occurred, then it was filtered and washed with
dichloromethane, dried and recrystallized from dichlor-
omethane/petroleum. The pure compound A was obtained
as white solid, yield 18.71 g (93 %), m.p.: 94–95 °C. ^{1}H
NMR (400 MHz, CDCl$_3$): δ = 7.99–8.06 (m, 2H), 7.89–
7.93 (d, 1H), 7.60–7.70 (m, 3H), 7.50 (d, $J_{H–H}$ = 9.0 Hz,
1H), 7.36–7.45 (m, 2H), 7.23–7.28 (m, 2H), 4.71–4.80
(m, 2H), 4.40–4.48 (m, 1H), 4.22–4.30 (m, 1H), 1.11
(d, $J_{H–H}$ = 6.2 Hz, 3H), 1.05 (d, $J_{H–H}$ = 6.2 Hz, 3H), 0.98
(d, $J_{H–H}$ = 6.1 Hz, 6H), 0.87 (d, $J_{H–H}$ = 6.8 Hz, 12H)
ppm; ^{31}P NMR (162 MHz, CDCl$_3$): δ = 18.5, −8.2, −
9.7 ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 149.5, 149.2,

146.9, 146.7, 135.6, 133.0, 130.4, 128.1, 126.5, 124.9, 123.4, 121.7, 120.4, 73.9, 73.7, 23.5, 23.3, 23.1 ppm; FT-IR (KBr): v = 3101, 2985, 1598, 1475, 1277, 1209, 1145, 1017, 939, 759 cm^{-1}. HR-MS (ESI): m/z: calcd for $C_{30}H_{39}NaO_{10}P_3$+Na$^+$: 675.1654 [M+Na]$^+$, found 675.1645.

Synthesis of compound B

In a 250-mL three-necked flask fitted with electro-magnetic stirrer, condenser, thermometer, nitrogen inlet and outlet, ODOPM (10.00 g, 0.04 mol) and CH$_3$CN (150 mL) were placed, and four drops of pyridine were added in sequence. The solution was stirred at raised temperature and became clear under nitrogen, next benzoyl chloride (8.40 g, 0.06 mol) was added in a dropwise manner. The solution was refluxed and was monitored by thin layer chromatography until the reaction finished. The solvent was removed by distillation in vacuum, and the residue was washed with the mixture of dichloromethane and petroleum, then the solid was purified by recrystallization from methanol to give pure product 13.80 g (yield 95 %). m.p.: 139–140 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.25–8.05 (m, 13H), 4.86 (d, 2H) ppm; ^{31}P NMR (162 MHz, CDCl$_3$): δ = 28.8 ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 60.8, 120.2, 121.7, 121.69, 122.3, 123.5, 124.6, 125.0, 128.8, 129.6, 130.8, 131.0, 131.1, 133.6, 134.2, 136.7, 149.9, 165.1 ppm; FT-IR (KBr): v = 3416, 2962, 1719, 1237, 1148, 925, 746 cm^{-1}. HR-MS (ESI): m/z: calcd for $C_{20}H_{15}NaO_4P$+Na$^+$: 373.0606 [M+Na]$^+$, found 373.0603.

Apparatus and procedures

The NMR (400 MHz) spectra were obtained using a Bruker AV 400 spectrometer with CDCl$_3$ as solvents. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. The ^{31}P NMR (162 MHz) spectra were referenced relative to 85 % H$_3$PO$_4$ (δ = 0 ppm) with broadband ^{1}H decoupling model. HR-MS was recorded on Water Q-Tof Micro mass spectrometer. FT-IR spectra were recorded on a Bruker-Alpha spectrometer with KBr pellets. TG and DSC were performed on Germany STA 409PC thermal analyzer at a heating rate of 10 °C per minute in nitrogen. The cyclic voltammetry (CV) tests were carried out on CH instruments electrochemical workstation (CHI 660C) in 1M LiPF$_6$ EC-DMC (1:1 by mass) solution at a scan rate of 2 mVs^{-1} with a Pt powder microelectrode as working electrode and a larger lithium sheet as both counter electrode and reference electrode. The data of ionic conductivity were obtained on HANNA EC215 conductivity tester. The melting points were obtained using a XT4A micro melting point determination instrument.

Flammability test procedures

Electrolyte preparation

The electrolyte solutions of 1 M LiPF$_6$/EC:DMC (1:1 by mass) containing different concentrations of flame retardant additive were prepared by mixing with compound A in 2.5, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0 mass% ratio, and B in 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 50.0 mass% ratio, respectively.

The self-extinguishing time measurements

A 2-mL electrolyte sample was contained in a small glass cup, and a 2-cm cotton fiber wick was soaked in the electrolyte for 1 min. The wick was then supported by the side of the glass cup container, and was ignited by a match held in contact with the edge of the wick until either a free-standing flame was observed for 3 s, then the ignition source was removed, the flame was timed until it self-extinguished. Repeat the tests three times and take the average value.

Linear flame propagation rate test method

This test was a modified procedure based on ASTM D-5306 [19]: a 12-cm length of cotton fiber wick was weighed and soaked in the electrolyte solution for 1 min. The yarn was weighed to calculate the average amount of electrolyte absorbed per unit length, then suspended horizontally and ignited from one end. The flame was allowed to burn over 1 cm before the timing was started, and the timing ended either when the flame self-extinguished or when the flame had traveled 10 cm, whichever came first. The flame propagation was calculated by dividing the actual distance the flame traveled by the time taken for the flame to travel. The average fuel consumption rate was calculated by multiplying the electrolyte mass per length by the flame propagation rate.

Results and discussion

Compound A was prepared by the phosphorylation reaction of ODOPB and phosphoryl chloride. Compound B was prepared by the acylation reaction of ODOPM and benzoyl chloride. The products were purified by recrystallization and the pure target compounds were obtained with high yields. The structures of compounds A and B to be char-
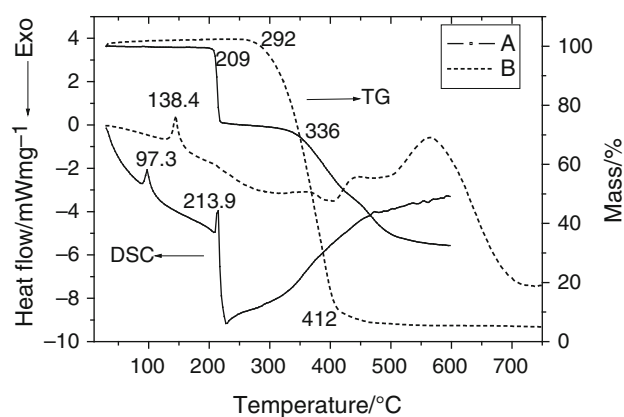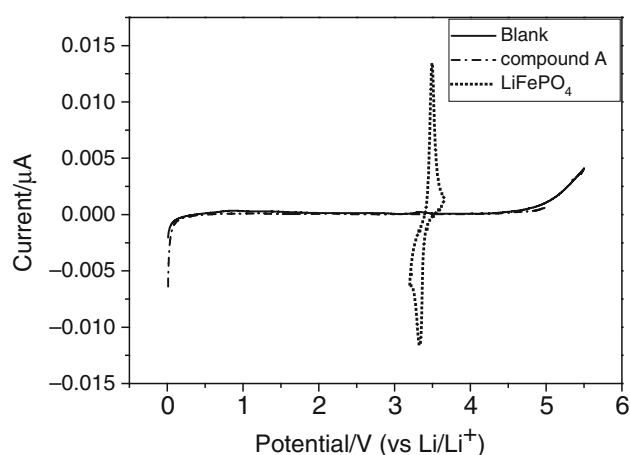
Fig. 1 TG and DSC curves of compounds A and B

Fig. 2 The cyclic voltammetry curves of compound A

acterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, FT-IR, and HR-MS.

Because of containing rigid benzene rings and high-density P, the good thermal stability of compounds was ascertained by TG and DSC. The TG and DSC curves are shown in Fig. 1. The compound A has two decomposition stages, and the mass loss of compound A started at 209 °C, and reached at 26 % till 230 °C. By calculating the relative molecular mass of compound A, this decomposition stage belonged to the four isopropyl chains. Then the main aryl structure started decomposition at 336 °C, and mass loss reached at 41 % till 600 °C. The residual amount remained more than 30 % till 600 °C. Compound B started its decomposition temperature at 292 °C, and mass loss reached at 96 % directly till 412 °C. The DSC curves displayed the melting points of compounds A and B were 97 and 138 °C, which were consistent with the data of the melting point determination instrument. Figure 1 shows

compound B has higher onset decomposition temperature due to its rigid structure, and compound A has higher char yield due to its higher "P" content.

The cyclic voltammetry curves of compounds A and B were very similar, which indicated that they have similar electrochemical stability. Figure 2 displays the cyclic voltammetry of compound A, blank electrolyte and LiFePO$_4$. As it can be seen, the CV curve of compound A is very similar to the blank's. There is no obvious oxidation and reduction current in the potential range of 0–5.0 V (vs. Li$^+$/Li), indicating a sufficiently wide electrochemical window, which means they can be safely used in the operating voltage window of lithium-ion battery. The flame retardant additives and cathode material LiFePO$_4$ have good compatibility too.

The self-extinguishing time (SET) measurements using a cotton fiber wick method were performed with a container of electrolyte containing different concentrations of flame retardant additive ignited from a piece of cotton fiber supported by the side of the glass cup container, and the extinguish time of the resulting flame was timed. The data of SET are listed in Tables 1 and 2, and the relationships between SET and flame retardant content are shown in Fig. 3. It can be seen from Fig. 3 that the blank electrolyte is very flammable with SET of 28 s. However, when the flame retardant materials, compounds A and B were applied, the SET of the electrolytes were significantly reduced, and the SET was decreased rapidly with the increased additive content. Compound A has obvious retarding effect with the content of 2.5 %, and has efficient retarding effect with the content of 15 %. By comparing the reducing tendency of the SET of the electrolytes with the contents of the retardants, as shown in Fig. 3, it can be found that compound A shows better flame retardancy for the electrolyte than compound B with a significantly shorter self-extinguish time. With the content of 15 %, the SET is 4 and 8.5 s for A and B, respectively. The results showed that the compound with higher content of flame retardant element "P" has better flame retardant effect. Combined with the thermal data of TG and DSC, it was also observed that samples with a high content of phosphorus tend to produce large amounts of char after combustion, which is consistent with the radical stabilization effect of organic phosphorus fragments. Those are expected to hinder exothermic chain reactions and thus, lowering the temperature of the flame and promoting char formation on the surface, which caused the samples to self-extinguish after a short period of time.
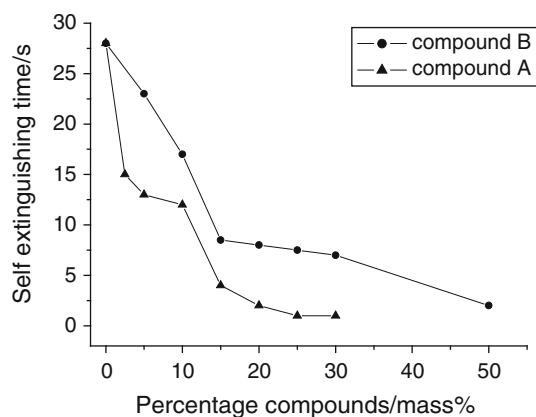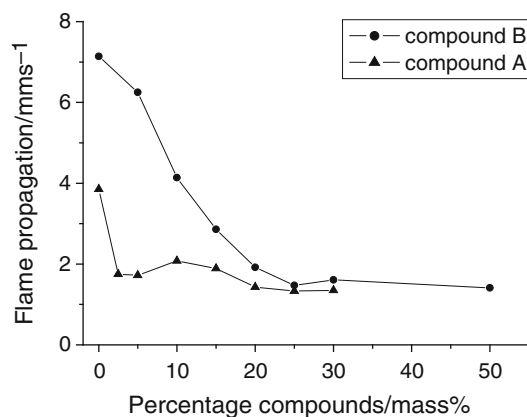
The ionic conductivity of the electrolytes was decreased in different degrees by adding DOPO-based flame retardants. The ionic conductivity data are shown in Tables 1 and 2, and the relationships between electrolyte's conductivity and flame retardants' content are shown in Fig. 4.

Table 1 The data of ionic conductivity and self-extinguishing time of compound A

Percentage compound A/mass%	0	2.5	5.0	10.0	15.0	20.0	25.0	30.0
Ionic conductivity/mScm^{-1}	7.50	6.82	6.32	5.50	4.96	3.90	3.25	2.94
Self-extinguishing time/s	28	15	13	12	4	2	1	1

Table 2 The data of ionic conductivity and self-extinguishing time of compound B

Percentage compound B/mass%	0	5.0	10.0	15.0	20.0	25.0	30.0	50.0
Ionic conductivity/mScm^{-1}	7.50	5.12	4.24	4.20	3.22	2.71	2.13	1.21
Self-extinguishing time/s	28	23	17	8.5	8	7.5	7	2

Fig. 3 Relationship between amount of flame retardants and self-extinguishing time

Fig. 5 Linear flame propagation of electrolytes containing flame retardant
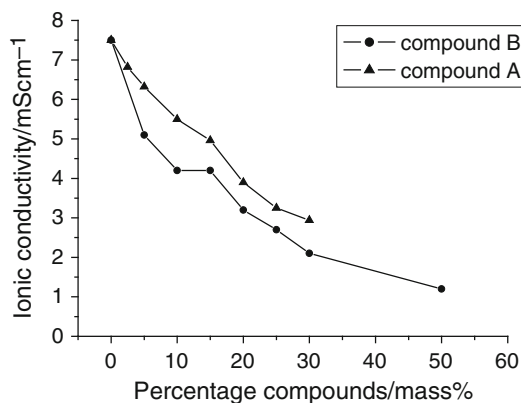
Fig. 4 Relationship between amount of flame retardants and ionic conductivity

The relationships showed that when flame retardants was added, the ionic conductivity of compound B dropped quickly than compound A. With the same additive concentration, the ionic conductivity of electrolyte containing compound A is higher than compound B. From Figs. 3 and 4, it can be seen that the curves appeared inflection point when the additive content reached to 15 %. Which showed the best additive content of flame retardant is 15 %. In this additive concentration of the electrolyte, the sample has both marked inflaming retarding effect and considerable ionic conductivity, especially for compound A (with conductivity of 4.96×10^{-3} Scm^{-1}).

The flame propagation tests using a cotton fiber wick of 12 cm were suspended horizontally and ignited from one end, where the speed of an ignited flame traveling from one end of the wick to another is used to compare flammability. Figure 5 shows that the addition of DOPO derivatives indeed reduces the average flame propagation rate in a common electrolyte, and as expected, increases the content of flame retardant additive can better reduce the flammability. For compound A, it showed a much reduced effect at start (5 %), then a slight increase (10 %), and then reduce (15 %), finally becomes flat (20 %). For compound B, it shows a much reduced effect after a certain point (25 %),
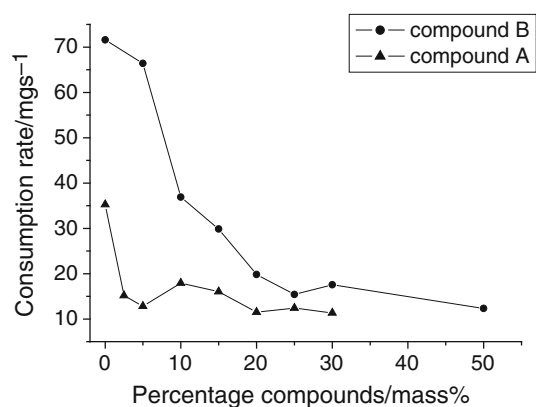
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Fig. 6 Fuel consumption rates of electrolytes containing flame retardant

then the curves become flat. The results show that the optimal concentration range of compounds A and B for electrolyte does not overlaps with the optimal ranges for ionic conductivity and SET.

Conversion of flame propagation data to fuel consumption was done by dividing mass of absorbed electrolyte over flame propagation speed, and the results are displayed in Fig. 6. The shape of the curves is very similar to Fig. 5, which means the addition of flame retardants induced a similar fuel consumption rate just as in the linear flame propagation.

Conclusions

We have developed a novel structure fire-retardant additives for Li-ion battery based on the DOPO and have estimated their flame retardant ability through the combustion experiment. The flame retardants compounds A and B both have good thermal stability and electrochemistry stability. In their flame retardant ability and ionic conductivity aspects, compound A has better performance than compound B due to containing high-density phosphorus. The results showed that compound A is an efficient flame retardant additive for Li-ion batteries, which has low concentrations, high conductivity and good flame retardant ability.

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