



Short communication

A new phosphoramidate as flame retardant additive in electrolytes for lithium ion batteries

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ABSTRACT

A new phosphoramidate, bis(N,N-diethyl)(2-methoxyethoxy)methylphosphoramidate (DEMEMPMA) has been synthesized as N-P collaborative flame retardant additive in electrolytes for lithium ion batteries (LIBs). It is found that adding 10 vol.% of DEMEMPMA to 0.9 M LiPF₆/EC/DMC can significantly inhibit the burning of electrolytes and provide a wide electrochemical window. Further studies indicate that the electrolytes with and without DEMEMPMA have similar electrochemical behavior with natural graphite and LiFePO₄ electrodes. These support the feasibility of using DEMEMPMA as a flame retardant additive for LIBs.

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1. Introduction

The replacement of lithium by carbonaceous materials led to the successful commercialization of lithium ion technology in the 1990s. Although the highly reactive anode surface as a possible trigger for thermal runaway has been eliminated, safety remains an issue since the state-of-the-art electrolytes systems are of potential fire hazards. The organic solvents such as EC and DMC can serve as fuel for various combustion processes, whether in open air or under hermetic conditions [1–4].

Currently most of the research efforts are concentrated on the reformulation of electrolytes by using flame retardant additives or co-solvents with the goal that their presence, kept at a minimum, could result in nonflammability. Up to the present, varieties of flame retardant compounds have been investigated, focusing on phosphates, phospholanes, phosphazenes, borates, siloxanes, silanes, fluorinated carbonates, fluorinated ethers and ionic liquids [5–10]. Some of these additives are of excellent self-extinguishing properties but suffer from severe reductive decomposition on the graphitic carbon anodes. Worse still, most of them are so expensive that they are difficult to meet the practical application of LIBs. Therefore most of the additives can only be applied in LIBs with non-graphitic carbon anodes [11] or with the presence of some film-forming additives in the case of graphitic anode materials [12].

The polyethylene oxide (PEO) has been widely used to form complexes with a wide variety of lithium salts [13]. Some organic nitrogen compounds can be served as flame retardant additives in many fields of industry [14,15]. Lewis base such as dimethylacetamide (DMAc) was first reported to be used as a stabilizing additive by Lucht's research group [16,17]. It is acknowledged that Lewis base can capture Lewis acidic PF₅ generated during the thermal dissociation of LiPF₆ [18]. As far as we know, little has been published about the use of phosphoramidates as flame retardant additives. The present work reported a new EO-containing phosphoramidate – DEMEMPMA as N-P collaborative flame retardant additive for lithium ion batteries. The performance of flame retarding and the electrochemical behavior of this additive were investigated. In addition, we analyzed the similar role of DEMEMPMA and DMAc that can enhance the stability and compatibility of electrolytes.

2. Experimental

2.1. Apparatus and procedures

2-Methoxyethanol and trimethyl phosphite (Sancaitang Chemical Industry and Technology Co. Ltd., China) were directly distilled prior to use. N,N-Dimethylformamide and diethylamine (Sinopharm Chemical Reagent Co. Ltd.) were dried and distilled prior to use. LiFePO₄ (ALEES), mesocarbon microbeads (MCMB) (SHENZHEN BAK), ethylene carbonate (EC), dimethyl carbonate (DMC) and other chemicals were used as received.

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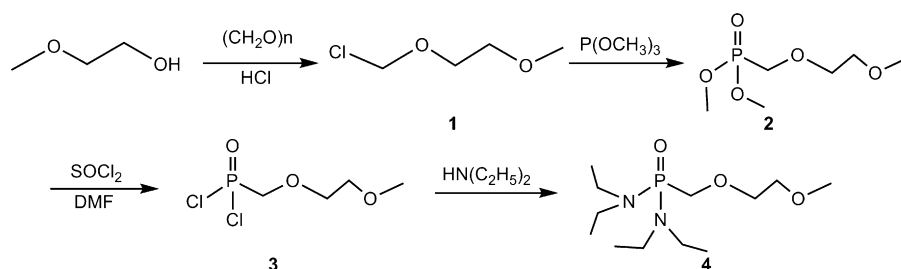


Fig. 1. The synthetic route of DEMEMPA (4).

The electrolytes were prepared by adding predetermined amounts of DEMEMPA to the mixed organic solvents (EC:DMC = 1:1, v/v), then LiPF_6 was dissolved into the mixture of the solvents to form a 0.9 M solution. All the operations were carried out in a glove box under argon atmosphere.

The method of Wang et al. [19] was adapted for the test of self-extinguishing time (SET). Thus a ball of glass wick was first immersed in the electrolytes for a sufficient interval, and then the ball-wick was ignited. The burning time was recorded with a stop watch. For each sample, the test was repeated 10 times to obtain the SET time.

Electrochemical performances were evaluated with 2016 coin cells by Land battery tester (Land Co. Ltd., China). The cathode was prepared by LiFePO_4 , acetylene black and PTFE at a ratio of 75:20:5 (wt.%). The coin cells were fabricated with the as-prepared cathode, metallic lithium anode, 0.9 M LiPF_6 in 1:1 (v/v) ethylene carbonate (EC)/dimethyl carbonate (DMC) electrolyte and Celgard 2300 separator. Cells were assembled in the argon filled glove box (MECAFLEX, MECABOX80-1“s”, Switzerland). These cells were typically cycled between 2.0 and 4.0 V, at 30 °C and 75 mA g^{-1} . However, a few measurements with anode material were performed to observe influences on the MCMB electrode, which was prepared by MCMB, acetylene black and PVdF at a ratio of 80:10:10 (wt.%). These cells were typically cycled between 0.005 and 2.0 V, at 30 °C and 50 mA g^{-1} .

The electrochemical stability of the tested electrolytes was investigated by linear sweep voltammograms (LSVs) on a three-electrode cell, where stainless steel acts as the working electrode (1.0 cm in diameter) and lithium foil as the counter and reference ones. LSVs measurements were carried out by CHI600B Electrochemical Workstation with a scan rate of 1 mV s^{-1} . The synthetic route of the new target compound, DEMEMPA (4) was shown in Fig. 1.

2.2. Synthesis of DEMEMPA (4)

2.2.1. Synthesis of compounds 1 and 2

1-(Chloromethoxy)-2-methoxyethane (1) and dimethyl-(2-methoxyethoxy)-methyl phosphonate (DMMEMP, 2) were prepared according to the literature procedure [20].

2.2.2. Synthesis of compound 3

(2-Methoxyethoxy)-methylphosphonic dichloride (MEMPCI, 3) was synthesized through the Maier's method [21]. To a solution of 59.50 g (0.5 mol) thionyl chloride was added dropwise the mixture of 39.63 g (0.2 mol) DMMEMP (2) and 0.15 g (0.002 mol) DMF under reflux over 2 h. After refluxing for 12 h the excessive thionyl chloride was evaporated at 30 °C in a rotary evaporator. The crude product was immediately thrown to the next reaction to avoid hydrolysis in the air.

2.2.3. Synthesis of compound 4

Bis(N,N-diethyl)methoxyethoxymethylphosphonamidate (DEMEMPA, 4) was synthesized through the modified method of Corey and Kwiatkowski [22]. To a stirred solution of 65.83 g (0.9 mol) of diethylamine in 250 mL of ethyl ether was added MEMPCI (3) obtained from the former response at 0 °C and under nitrogen. The resulting solution was stirred at 0 °C for 1 h and 25 °C for 5 h. The precipitate of diethylamine hydrochloride was removed by filtration and the filtrate was evaporated under vacuum. Distillation of the residue afforded 44.29 g of DEMEMPA (total yield 79%). b.p.: 184–185 °C (11 mmHg); ^1H NMR (300 MHz, CDCl_3): δ /ppm 1.11 (t, 12H, $-\text{CH}_3$), 3.04–3.14 (m, 8H, $-\text{NCH}_2\text{CH}_3$), 3.38 (s, 3H, $-\text{OCH}_3$), 3.54 (t, 2H, $-\text{OCH}_2\text{CH}_2\text{OCH}_3$), 3.68 (t, 2H, $-\text{OCH}_2\text{CH}_2\text{OCH}_3$), 3.82 (d, 2H, $-\text{P}-\text{CH}_2-$); ^{13}C NMR (75 MHz, CDCl_3): δ /ppm 12.93–13.11, 37.01–37.03, 57.68–57.70, 65.77, 67.57, 70.69–71.30; ^{31}P NMR (CDCl_3): δ /ppm 29.64.

3. Results and discussion

Fig. 2 shows the flame retarding effect of the electrolytes containing various contents of DEMEMPA. As can be seen, the SET decreases from 174 s g^{-1} for bare electrolytes to 133 s g^{-1} when 5 vol.% DEMEMPA is added; when the content of the flame retardant increases to 10 vol.%, the SET of the electrolytes is significantly reduced. These suggest that the addition of DEMEMPA results in an efficient flame resistance of the electrolytes.

Fig. 3 shows the LSV curves with DEMEMPA added to the electrolytes. As is shown in this figure, electrolytes with and without DEMEMPA have similar electrochemical behavior before 5.2 V, the obvious onset of the anodic current can be observed until the voltage is heightened to above 5.2 V compared with bare electrolytes.

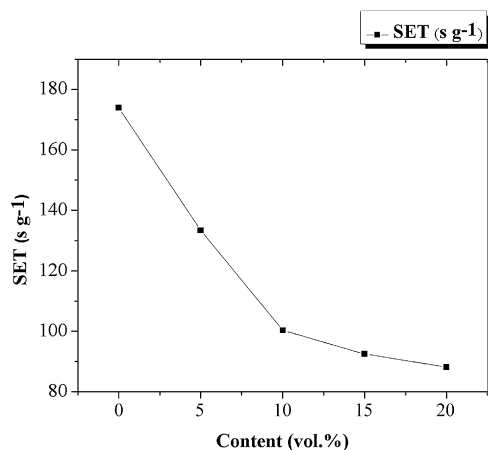


Fig. 2. Self-extinguishing time (SET) with various contents of DEMEMPA in 0.9 M LiPF_6 /EC + DMC (1:1, v/v).

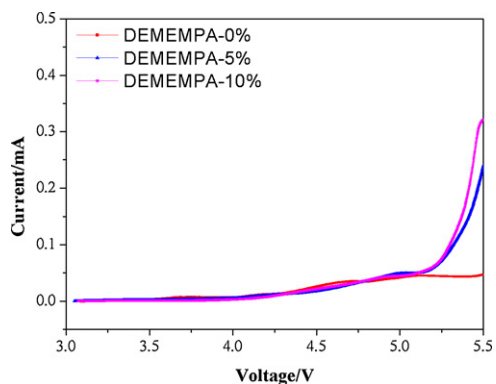


Fig. 3. LSV curves with DEMEMPA added to the electrolyte. The potential was scanned at a 1 mV s^{-1} rate.

The intensity of oxidative current increases with the concentration of DEMEMPA after 5.2 V vs. Li^+/Li . These results indicate that DEMEMPA cannot be oxidized before 5.2 V that supports the feasibility of using DEMEMPA as flame-retarding additive for lithium ion batteries.

The influence of DEMEMPA on the electrochemical performances of $\text{LiFePO}_4/\text{Li}$ cells is shown in Fig. 4. The cycling behavior of the LiFePO_4 cathode in bare electrolytes and electrolytes containing various contents of DEMEMPA at a current density of 75 mA g^{-1} is shown in Fig. 4a. In the case of bare electrolytes there is little capacity fading even after 50 cycles. The electrolytes containing 5% and 10% DEMEMPA exhibit almost the same cycling performance compared with bare electrolytes. It suggests that adding DEMEMPA to electrolytes has no harm to the cycling behavior. The voltage profiles of the 5th charge/discharge cycle of the electrode are shown in Fig. 4b, the voltage platforms corresponding to these electrodes are 0.0988 V, 0.1158 V and 0.1227 V, respectively. These results show that the 5th voltage platform of LiFePO_4 cathode increases slightly with the adding of DEMEMPA, and the kinetics of lithium extraction/insertion reaction becomes a little poor.

The cell cycling performance of the electrolytes with and without DEMEMPA in the MCMB/Li cells which charge/discharge

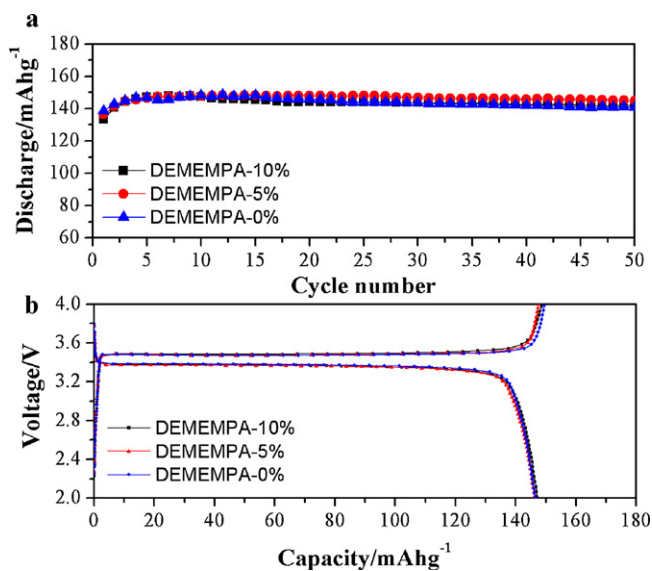


Fig. 4. (a) Discharge capacity vs. cycle number of LiFePO_4 electrode in 0.9M $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1, v/v) electrolyte containing 0%, 5% and 10 vol.% DEMEMPA between 2.0 and 4.0 V at a current density of 75 mA g^{-1} ; (b) the 5th charge/discharge profiles of LiFePO_4 electrode in 0.9M $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1, v/v) electrolyte with various contents of DEMEMPA.

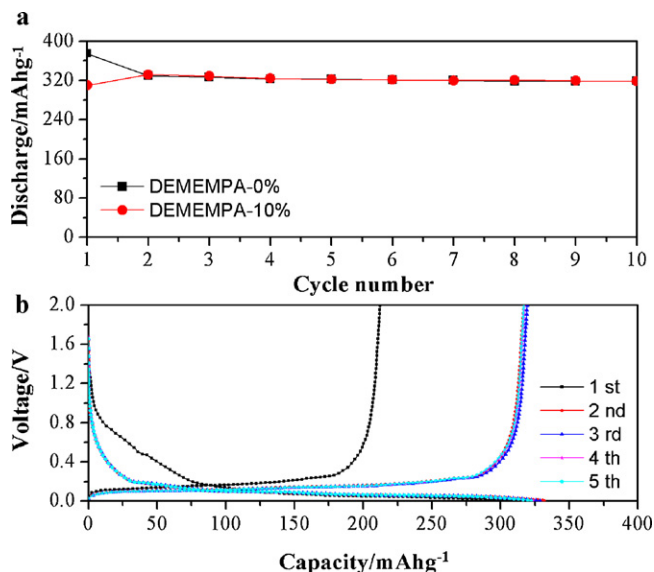


Fig. 5. (a) Discharge capacity vs. cycle number of MCMB in 0.9M $\text{LiPF}_6/\text{EC} + \text{DMC} + \text{PC}$ (1:3:1, v/v) electrolyte containing 0% and 10 vol.% DEMEMPA between 0.005 and 2.0V at a current density of 50 mA g^{-1} ; (b) the 1st–5th charge/discharge profiles of MCMB electrode in 0.9M $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1 v/v) electrolyte with 10 vol.% DEMEMPA.

between 0.005 and 2.0V at a current density of 50 mA g^{-1} is shown in Fig. 5. The cycling behavior of two MCMB/Li cells (Fig. 5a) are almost identical except the first cycle, the first discharge capacity of the MCMB/Li cell with DEMEMPA is lower than that without DEMEMPA, and the capacity of other cycles exhibit the same result. The 1st–5th voltage profiles of the cells at room temperature (Fig. 5b) show that an irreversible capacity loss of about 97 mAh g^{-1} occurs in the first charging. The coulombic efficiency of the first five cycles are 83.1%, 96.8%, 98.2%, 98.8%, 99.1% for bare electrolytes and 68.5%, 95.5%, 97.2%, 98.0%, 98.4% when 10 vol.% DEMEMPA is added. From the third cycle, the coulombic efficiency of bare electrolytes and the electrolytes containing DEMEMPA are almost the same. This irreversible capacity loss also appears in the experiments conducted with bare electrolytes and this result is reproducible, but the difference is that the value of capacity loss is smaller with bare electrolytes. We believe that this result is due to the incomplete immersion of the electrolytes on the electrode during the first cycle. The additive is supposed to be involved in the SEI formation on MCMB, so the irreversible capacity loss may relevant to the formation of a solid electrolyte interface SEI layer on the negative electrode.

It is generally accepted that PF_5 will be generated during the thermal decomposition of LiPF_6 based electrolytes, and then HF and POF_3 is formed rapidly owing to the presence of trace protic impurities, such as ROH or H_2O [23]. The strong Lewis acid PF_5 tends to initiate a series of reactions in the presence of solvents [24,25]. Lewis base such as dimethylacetamide (DMAC) was first reported to be used as a stabilizing additive by Lucht's research group [16,17]. Further research has been carried out by Xu and coworkers [18]. Just as DMAC, DEMEMPA plays a similar role that acts as Lewis base capturing Lewis acid PF_5 . Fig. 6 shows this progress that enhances the stability of electrolytes and improves the electrochemical compatibility with natural graphite and LiFePO_4 electrodes.

Finally, it must be pointed out that further extensive investigations are still in progress, including the testing of its conductivity at lower and higher temperatures, the stability on the much longer cycle life of the LIBs and the performances of its serving as single electrolyte with the commercial carbonate-based anode and LiFePO_4 cathode.

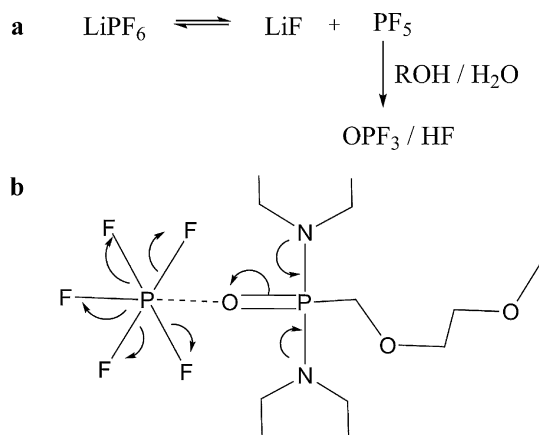


Fig. 6. (a) Thermal dissociation mechanism of LiPF₆; (b) the interaction between DEMEMPA and the gaseous product generated from LiPF₆.

4. Conclusions

A new phosphonamidate, DEMEMPA has been synthesized as flame retardant additive for lithium ion batteries. It is indicated that when the amount of the new phosphonamidate in the electrolyte is above 10%, the flammability of the electrolyte is significantly reduced. It is also found that, the electrolyte has good electrochemical stability windows. However, the electrochemical compatibility between electrolytes and natural graphite electrode becomes a little poor when DEMEMPA is added, so further considerations are necessary in order to construct nonflammable lithium ion batteries with the new EO-containing phosphonamidate.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2011.09.012.

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