



## Safer lithium ion batteries based on nonflammable electrolyte



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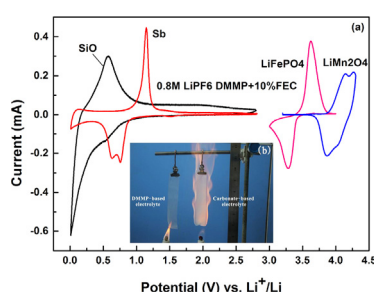
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### HIGHLIGHTS

- The safe lithium ion battery is studied based on DMMP nonflammable electrolyte.
- The alloy anode and LiFePO<sub>4</sub> cathode show excellent compatibility in DMMP with FEC.
- The SiO/LiFePO<sub>4</sub> full cell exhibits good electrochemical performance in DMMP with FEC.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The safety of lithium ion batteries has long been a critical obstacle for their high-power and large-scale applications because of the flammable nature of their carbon anode and organic carbonate electrolytes. To eliminate the potential safety hazards, lithium ion batteries should be built up with thermal-stable electrodes and nonflammable electrolytes. Here we report safer lithium ion batteries using nonflammable phosphonate electrolyte, thermal-stable LiFePO<sub>4</sub> cathode and alloy anodes. Benefiting from the electrochemical compatibility and strong fire-retardancy of the phosphonate electrolyte, the cathode and anode materials in the nonflammable phosphonate electrolyte demonstrate similar charge–discharge performances with those in the conventional carbonate electrolyte, showing a great prospect for large-scale applications in electric vehicles and grid-scale electric energy storage.

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## 1. Introduction

Lithium ion batteries are actively explored as an alternative power source for high-rate and high-capacity applications from electric vehicles to large-scale renewable power stations. [1–3] However, safety issue remains a serious concern for such applications. At present technologies, lithium ion batteries are composed

of a highly oxidative cathode, a carbonaceous anode and an ignitable organic carbonate electrolyte, which can be accidentally triggered to cause thermal runaway, firing, or explosion. To solve this problem, various strategies including external and internal designs have been applied to prevent the safety hazards of lithium ion batteries. However, the external protective designs such as positive temperature coefficient (PTC) device, [4] pressure valve, [5] and current breaker, [6] can only improve the safety to some extent, but are slow to response on the internal temperature changes of the batteries. The internal protective designs such as overcharge protection additives, [7] temperature-sensitive separators [8,9] and

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thermally stable electrode materials, [10] can respond rapidly the changes in the internal temperature and potential of the batteries, but can not prevent the electrolyte from firing at overheated conditions due to the high flammability of the carbonate electrolyte. Therefore, development of fire-retardant electrolytes is a most convenient and effective way to eliminate the safety hazards of lithium ion batteries.

Among various nonflammable solvents including ionic liquids, [11] organosilicon compounds, [12] hydrofluoroethers (HFEs) [13–15] and phosphates, [16–21] phosphate molecules seem to be a good choice for fire-retardant electrolyte because of their low viscosity and high solubility. [16,17,22,23] In the past years, quite a number of small molecule phosphates such as trimethyl phosphate (TMP), [17,19,24,25] triethyl phosphate (TEP), [18,19] diethyl ethylphosphonate (DEEP) [26,27], bis(diphenyl phosphate) [21] and so on have been studied as fire-retardant additives or electrolyte cosolvents for lithium ion batteries. However, most of these phosphates as primary solvent are difficult to form a stable solid electrolyte interphase (SEI) film on graphite surface, thus leading to a very low anodic efficiency during charge–discharge cycles. [28] To develop safer lithium ion batteries, the critical issue is to find an appropriate nonflammable electrolyte that can establish a stable electrochemical interface on the anode of interest. Here, we develop a safer lithium ion battery using nonflammable dimethyl methyl phosphonate (DMMP) as electrolyte solvent, thermal-stable  $\text{LiFePO}_4$  (or  $\text{LiMn}_2\text{O}_4$ ) and SiO (or SiFe and Sb alloys) as cathode and anode, respectively. The DMMP electrolyte with the addition of a SEI-forming additive shows an excellent electrochemical compatibility with the alloy anode and  $\text{LiFePO}_4$  (or  $\text{LiMn}_2\text{O}_4$ ) cathode, thus rendering the batteries with similar capacity and cyclability to conventional Li-ion batteries. To our best knowledge, such high electrochemical compatibility of alloy anode in inherently non-flammable DMMP electrolyte has not been reported so far.

## 2. Experimental

### 2.1. Sample preparation and characterization

The DMMP reagent used in this work was purchased commercially from San Caitang Ltd., Hubei, China. DMMP was purified with a re-distillation step under vacuum after its dehydration with  $\text{CaH}_2$  under the atmosphere of inert gas for 12 h.

The SiO–C (SiC/SiO/C) composite was prepared by a two-step ball-milling process. First, a 8:2 mass ratio of the commercial SiO (Aldrich, 325 mesh) and nano SiC (99.5% purity, ~40 nm) were mixed and ball-milled in an SPEX-8000 high-energy mechanical mill for 8 h. Then, the reactant product was further ball milled with graphite powder (99% purity, <5  $\mu\text{m}$ ) in a planetary mill (QM-1SP04, Nanjing, China) with the rotation speed of 200 rpm for 10 h. The weight ratio of graphite to the total amount of SiC/SiO was designed as 2:8, so that the final composite contains 16 wt % of SiC, 64 wt % of SiO, and 20 wt% of graphite. The weight ratio of milling balls to the powder materials in the planetary milling process was 20:1. All the milling processes were performed under Ar atmosphere.

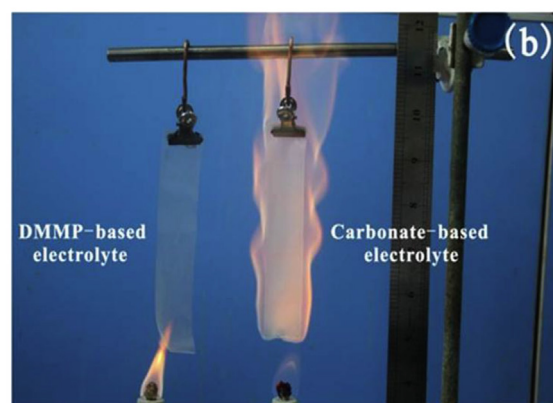
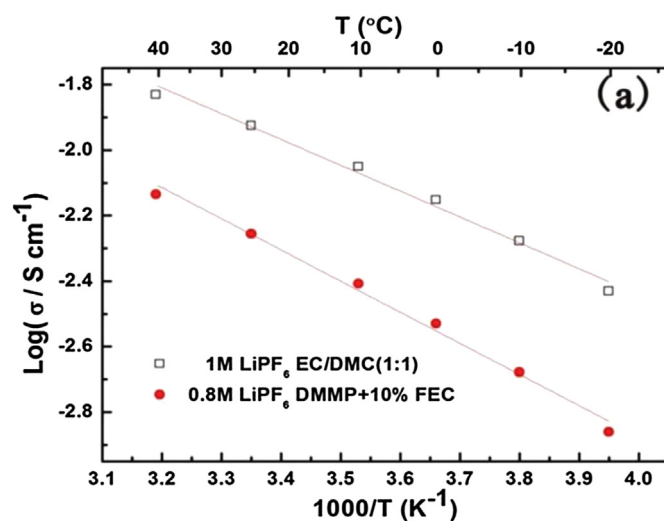
The SiFe–C composite was prepared by a two-step ball-milling process according to the previous works [33]. The typical experiment is below. First, a 3:1 weight ratio of commercial Si (Alfa Aesar, 325 mesh) and Fe powder (Alfa Aesar, 325 mesh) was mixed and ball-milled in an SPEX-8000 high-energy mechanical mill for 10 h. Then, the reactant product was further ball milled with graphite powder (99% purity, <5  $\mu\text{m}$ ) in a planetary mill (QM-1SP04, Nanjing, China) with the rotation speed of 200 rpm for 6 h. The weight ratio of graphite to the total amount of Si + Fe was designed as 1:9, so that the final composite contains 67.5 wt % Si, 22.5 wt % Fe, and

10 wt % graphite. The weight ratio of milling balls to the powder materials in the planetary milling process was 20:1. All the milling processes were performed under Ar atmosphere.

The Sb–C composite (SiC–Sb–C) was prepared according to the previous works [31,35]. Sb (99.0% purity, 74  $\mu\text{m}$ , National Medicine Co., Ltd., Shanghai, China), SiC (99.5% purity, 40–60 nm), and super P (TIMCAL, Graphite & Carbon Inc.) were used as received. The SiC–Sb–C nanocomposites with a mass ratio of SiC/Sb/C = 20:70:10 wt% were prepared by high-energy ball milling (8000 M mixer/mill, SPEX, USA) of Sb and SiC powders under an argon atmosphere for 8 h, and then modified with carbon by ball-milling the SiC–Sb particles with super P carbon using a planetary mill (QM-1SP04, Nanjing, China) under an argon atmosphere with the rotation speed of 200 rpm for 6 h. The weight ratio of milling balls to the powder materials was maintained as 20 to 1.

### 2.2. Electrochemical measurements

The cyclic voltammetry (CV) were performed on CHI600C Electrochemical Analytical Instrument (Chenhua, Shanghai, China) in 0.8 M  $\text{LiPF}_6$  in DMMP electrolyte with 10 vol. % fluoroethylene carbonate (FEC) by using microelectrode with a Pt disk of 0.5 mm diameter as working electrode, Li foil as both reference electrode and counter electrode. The voltage range and scan rate is  $-0.2$ – $5$  V and  $50$   $\text{mV s}^{-1}$  respectively. Cyclic voltammetry of electrodes



**Fig. 1.** (a) Ionic conductivity of 0.8 M  $\text{LiPF}_6$ /DMMP + 10 vol% FEC electrolyte. Temperature dependences of the ionic conductivities of the DMMP electrolyte. The ionic conductivity of 1 mol  $\text{L}^{-1}$   $\text{LiPF}_6$ /EC/DMC(1:1) electrolyte is also shown as a comparison. (b) Combustion behaviours of DMMP electrolyte and carbonate electrolyte.

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