Electronic Supplementary Information for

TPPi as Flame Retardant for Rechargeable Lithium Batteries with Sulfur Composite Cathodes

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Experimental Section

1 Materials and battery preparations

Sulfur composite materials were simply prepared via mixing polyacrynonitrile (PAN) and sublimed sulfur (S₈) with ethanol served as the dispersant, then ball milling at 120 r min⁻¹ for 12h, following drying and sintering at 300°C under N₂ atmosphere. The sulfur content in the composite was 45 wt. % which was determined by elemental analysis (Vario EL III elemental analyzer, Elementar, Germany). The cathode composed of sulfur composite, Super P conductive carbon black (40 nm, Timical) and polyvinylidene fluoride (PVDF) with N-methyl-2-pyrrolidone (NMP) as solvent at a weight ratio of 80 : 10 : 10. Carbon-coated Al was adopted as current collectors. The cathode loads were ca. 2 mg cm⁻². The blank electrolytes consist of 1mol L⁻¹ LiPF₆ as solute and EC+DMC (1:1, v/v) as solvents. Different doses of TPPi were added directly into blank electrolytes, forming homogeneous functional electrolytes. The ether electrolyte composed of DOL+DME 1 mol L⁻¹ LiTFSI also adopted for comparisons. The coin cells with PE Clegard separator and lithium foil anode were assembled in a glove box filled in argon atmosphere.

2 Thermal stability and electrochemical performance measurements

The thermal stability of the electrolytes with different TPPi contents were tested by differential scanning calorimetry (DSC) via NETSCH STA 449 at a heating rate of 10 $^{\circ}$ C min⁻¹ from 30 $^{\circ}$ C to 300 $^{\circ}$ C under argon atmosphere.

The ionic conductivities were recorded via the FE30 conductivity meter and the Inlab 710 conductivity measuring cell (Mettler Toledo, Switzerland). The recharge and discharge processes were conducted on LANDBT1-10 (Wuhan, China). Electrochemical impedance spectra (EIS) were measured via CHI604D Electrochemical Workstation under the frequency varied from 10

kHz to 0.01 Hz and amplitude of 5 mV. The electrochemical windows of the electrolyte was measured via cyclic voltammetry (CV) by assembling the coin cell with stainless steel as cathode and lithium metal anode. Scan rate was 1 mV/s in the range of -0.2 to 4.5 V (vs. Li⁺/Li). All the tests were carried out at room temperature.



Fig. S1 Molecular structure of TPP(i).



Fig. S2 Effect of TPPi addition on the DSC profiles of electrolytes which were sealed in an aluminum pan in the glove box.

The electrolytes with different dose of TPPi were sealed the crucible and DSC were measured via TA Instruments Q2000. The masses of the samples were controlled at 1mg. The scan range was $30\sim300$ °C with the scan rate of 10 °C/min .

There are 3 major peaks in all these lines. The exothermic peak around 90 °C is related to the pyrolysis of LiFP₆. It is evident that the addition of TPPi did not obviously change the pyrolysis temperature of LiFP₆. The second peak is attributed to the boiling of DMC while the third, EC. The addition of TPPi postpones the boiling of solvents; more addition, bigger postponement, which indicates that TPPi stabilize the thermal properties of the electrolyte.

The black line represents the DSC curve of normal electrolyte. It should be noted that the boiling point of EC is lower than that in ambient pressure, however DMC, higher. In this sealed system, the internal pressure rises along with the temperature increase. The boiling point of EC and DMC should both move rightwards on DSC. However, EC and DMC may form negative azeotrope in that particular ratio and pressure, making the endothermic peak of EC move leftwards but DMC rightwards.



Fig. S3 CV of the electrolytes with various TPPi addition.

The addition of TPPi does not affect the electrochemical windows of the electrolyte, and benefits to the plating/stripping of Li metal on the anode.



Fig. S2 Discharge profiles for the PAN-S composite electrodes in blank electrolyte 1M LiPF₆/EC+DMC (1:1,



Fig. S4 Cycling performances of sulfur composite cathodes in the electroytes with different solvents. Black: EC+DMC 1M LiPF₆; Red: DOL+DME 1M LiTFSI; Green: DOL+DME 1M LiTFSI+0.1M LiNO₃.

It is clear that sulfur composite cathodes demonstrate the stable cycling performances in carbonate-based electrolytes.¹⁻⁴ In the ether electrolyte, there exists the discharge product polysulfides dissolution which causes "shuttle" phenomenon. The addition of TPPi benefits to restraining polysulfide shuttle, as shown in Fig. S4 (a).

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