

Supporting Information

Safer Lithium-Sulfur Battery Based on Nonflammable Electrolyte with Sulfur-Based Composite Cathode

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Experiment Selection

Electrode Preparation

Poly(acrylonitrile) (PAN, weight-averaged molecular mass, M_w 150000, Aldrich) element sulfur (Aladdin, AR 99.5%) were mixed homogeneously by ball milling at weight ratio 1:8 for 6h with isopropyl alcohol (Aladdin, ACS, 99.5%) as a dispersant. The mixed powder was dried to remove the solvent and then heated at 300°C for 450 minutes in nitrogen (N_2) atmosphere. The collected black powder S@pPAN composite with sulfur content 44.5 wt% was ball milling before electrode preparation. The cathode was fabricated by mixing 80 wt% S@pPAN composite, 10 wt% conductive carbon (Super P), and 10 wt% carbonyl-beta-cyclodextrin as a binder¹, then coating the slurry onto a piece of aluminium (Al) foil (with a carbon coating) and cutting the foil into small disks with a diameter of 12 mm after drying; the weight loads of the foil disks were ca. 1.0 mg cm⁻².

Electrolyte Preparation

The TEP solvent was purchased commercially from Aladdin Shanghai China. TEP used in this paper was purified with a re-distillation step under vacuum after its dehydration with calcium hydride (CaH_2 , Aladdin, AR 95%) under the atmosphere of N_2 for 6h at 100°C. After collected the distilled TEP, it should quickly transferred to argon-filled glove box. The contents ratio of TEP and FEC is calculated by volume. Four salts were used in this paper and all of them were purchased from Capchem. Co. Ltd. (battery grade). Lithium bis(oxalate)borate (LiBOB), Lithium Difluoro(oxalato)borate (LiODFB), Lithium nitrate ($LiNO_3$), Lithium bis (fluorosulfonyl)imide (LiFSI), their concentration in mixture solvent was 1 mol/L.

Electrochemical measurements

The CR2016-type Li-S coin cells were assembled in an argon (Ar)-filled glove box, pure lithium foil as anode, Celagrd2300 as separator, the S@pPAN electrode as cathode. To evaluate the electrochemical performance of electrolyte, different electrolyte was added into the coin cell. The galvanostatic discharge/charge tests were carried out at 1C on a LAND-CT 2001A Cell Test System (Wuhan, China) in the voltage range of 1.0~3.0 V (vs. Li/Li^+). The rate performance of cells was evaluated using the same equipment at the discharged current density of 0.2C, 0.5C, 1C, 2C, 3C, 4C respectively.

Physical characterizations

Ionic conductivity tests of the electrolyte were carried out with a DDS-307A conductivity meter at ambient temperature. The morphological changes of the sulfur cathode and Li anode were observed using SEM (FEI Nova Nano-scanning electron microscope). Before examination, the Li-S coin cells in the full-charged state after 100 cycles were disassembled in an argon-filled glove box and then obtained electrodes were rinsed with dimethylcarbonate (DMC) thoroughly. It is noted that the dried Li anode must be sealed in a Ar-filled container and transferred quickly into the SEM equipment to avoid oxidation. Surface composition of the electrode after 100 cycles in TEP-based electrolyte and standard electrolyte was analyzed by the X-ray photoelectron spectroscopy (XPS), using a Kratos Axis UltraDL spectrometer (Kratos Analytical-A Shimadzu Group Company) with monochromatic Al K α source (1486.6 eV) under ultra-high vacuum. Also, the samples should be pretreated in the similar method to remove any electrolyte salt residuals.

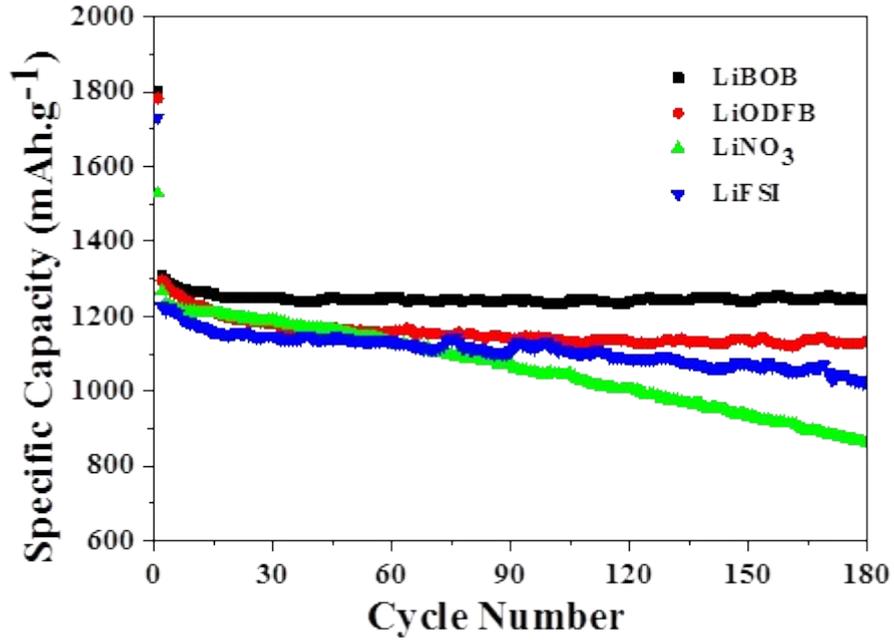


Fig. S1 Cyclic performance of Li-S batteries at 1C in TEP:FEC (9:1, v/v) blending solvents with different salts.

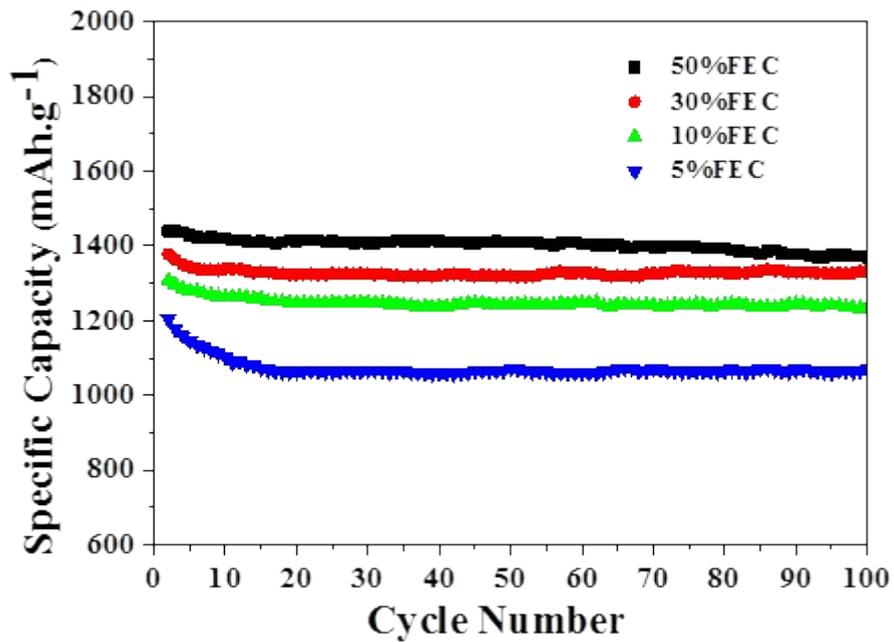


Fig. S2 Cyclic performance of Li-S batteries at 1C in TEP/FEC with different FEC contents.

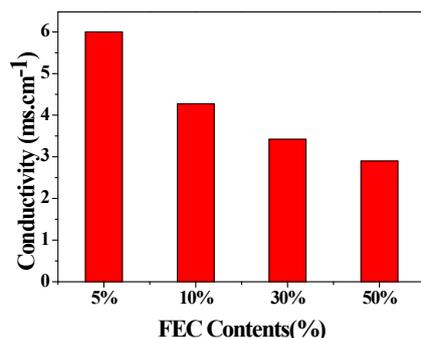


Fig. S3 Ionic conductivity tests of the TEP-based electrolytes with different FEC contents

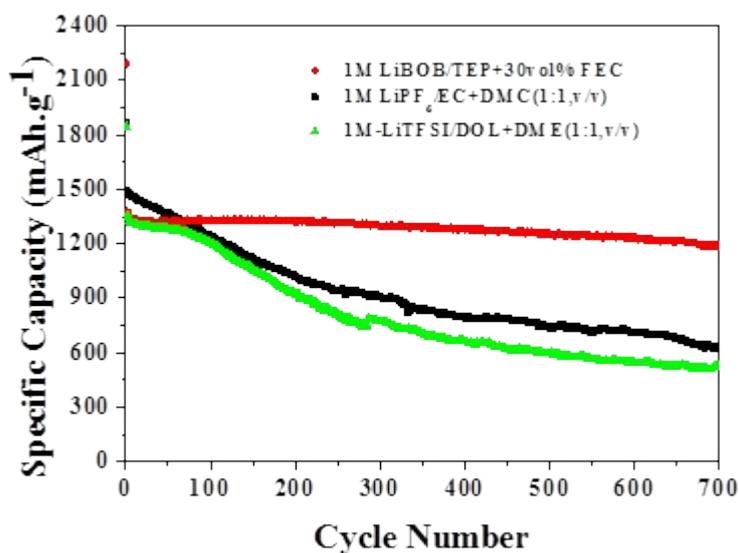


Fig. S4: Cycling performances of sulfur composite cathodes in the common electrolytes using in lithium sulfur batteries.

Notes: The common carbonated electrolyte is 1mol/L LiPF₆/EC-DMC (1:1, v/v), ether electrolyte with LiNO₃ stands for 1mol/L LiTFSI/DOL-DME (1:1, v/v)+1 wt% LiNO₃. The comparison test were conducted in Li-S batteries with S@pPAN cathode. The rapid decline of capacity in ester electrolyte could attributed to the discharge product polysulfide dissolution, which reduces active material in current collector and causes “shuttle phenomenon”.

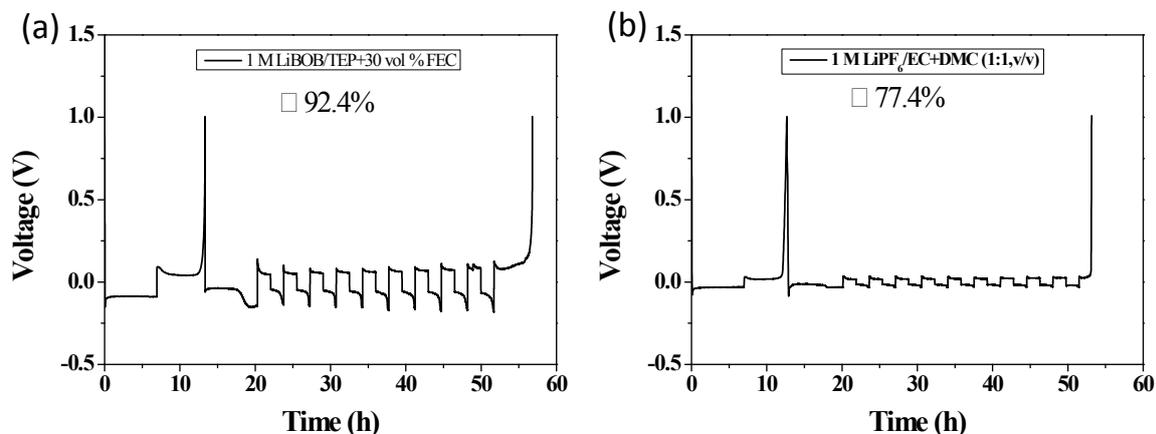


Fig. S5 Coulombic efficiency test of (a) LiBOB/TEP electrolyte; (b) standard carbonate electrolyte.

Note: Li anode CE was measured using a reported protocol to remove the influence of current collector.^{2, 3} After common Li-Cu cell assembled and rest, a Li film (5C cm^{-2}) was first deposited onto the Cu foil and then fully stripped. Another Li film (5C cm^{-2}) was deposited again, but only 25% of the Li film (1.25C cm^{-2}) was stripped and deposited for 10 cycles. Finally, the Li film was fully stripped off at a cutoff voltage of 1V. The current density during test was 0.2 mA cm^{-2} . Experimental electrolyte and control electrolyte was test by this method. The average CE was calculated as the equation below.

$$\text{Coulombic efficiency} = (n \times Q_r + Q_{s,\text{final}}) / (Q_{d,2^{\text{nd}}} + n \times Q_r) \times 100\%$$

Where the n is the cycle number, $Q_r = 1.25\text{ C cm}^{-2}$, $Q_{d,2^{\text{nd}}} = 5\text{ C cm}^{-2}$, $Q_{s,\text{final}}$ is the charge during the final stripping. The CE of LiBOB/TEP electrolyte is 92.4%, much higher than the 77.4% in standard electrolyte.

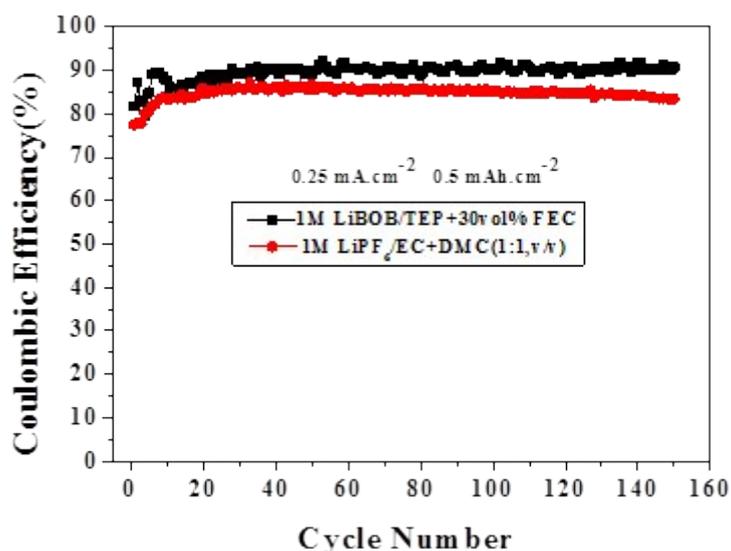


Fig. S6 Li anode stability using Li-Cu cell plating/stripping method in (a) LiBOB/TEP electrolyte; (b) standard carbonate electrolyte.

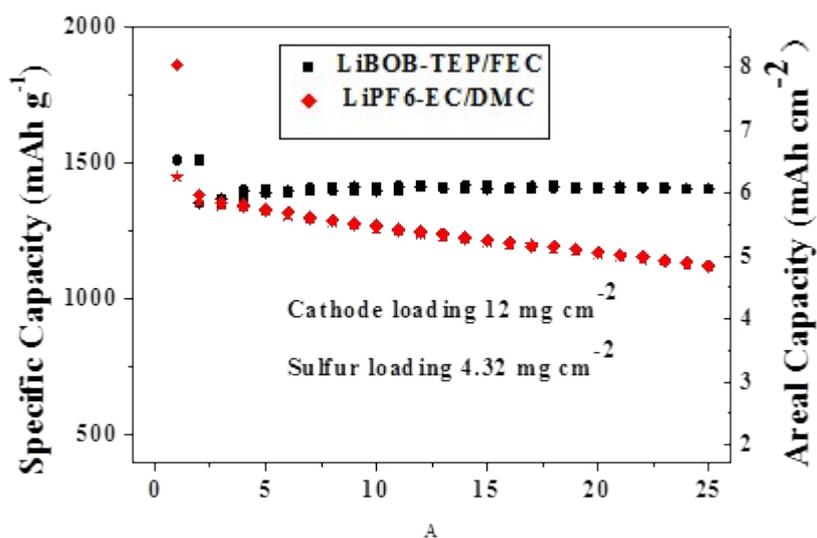


Fig. S7 High cathode loading cyclic performance comparison of LiBOB/TEP electrolyte and standard electrolyte.

Table S1: The element contents on the S@pPAN cathode after 100 cycles in different electrolyte

Elements	Units: Mass Percent (%)				
	C 1s	O 1s	F 1s	P 2p	B 1s
Standard electrolyte	49.95	48.12	1.65	0.28	--
TEP-based electrolyte	44.72	44.29	6.27	0.98	3.75

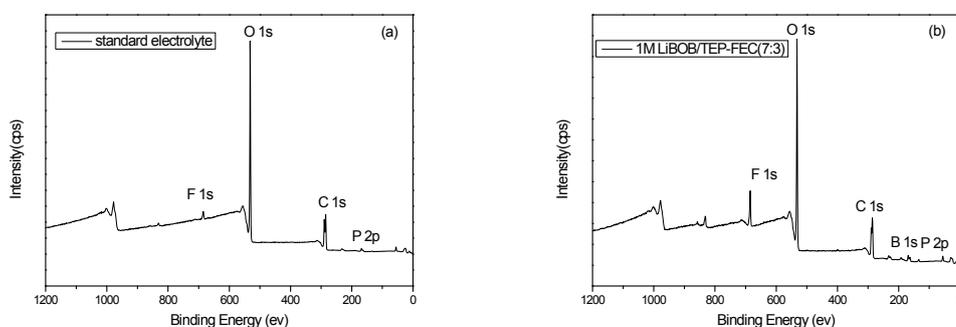


Fig. S8: Full spectra of the S@pPAN cathodes after 100 cycles at different electrolyte. (a) blank electrolyte; (b) TEP-based electrolyte.

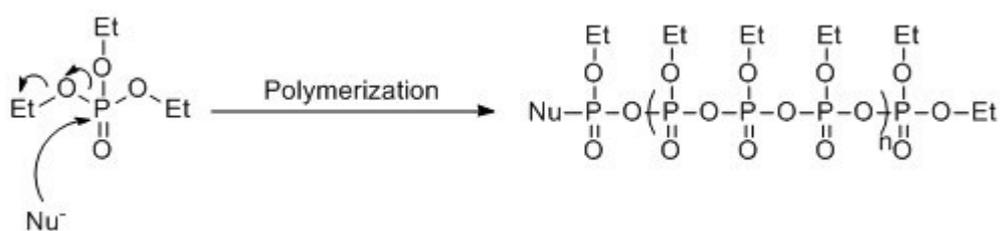


Fig. S9 Possible film formation mechanism of TEP-based electrolyte on the cathode.⁴

Note: Et means for-CH₂CH₃, Nu- stands for nucleophile.

Table S2: Physical properties of some common solvents using in this work⁵

Solvents	Molecular structure	Melting point (°C)	Boiling point (°C)	Flash point (°C)	Dielectric constant	Viscosity (mPa,25°C)	Density (g.cm ⁻³)
EC	 Ethylene carbonate	37	128	160	90.4 (at 40°C)	1.93	1.32
DMC	 dimethyl carbonate	5	90	18	3.2	0.59	1.07
FEC	 Fluoroethylene carbonate	18	249	120	96.0	4.1	1.45
TEP	 Triethyl phosphate	-56	210-220	117	13.0	1.6	1.07
DOL	 1,3-Dioxolane	-95	74-75	-6	7.1	0.6	1.06
DME	 ethylene glycol dimethyl ether	-69	83	1	7.3	0.46	0.86

Table S3: some reported safe electrolyte for Li-S batteries

Electrolyte	Electrolyte component	Sulfur cathode	Area loading (mg.cm ⁻²)	Cycling performance		Remarkable performance	Ref.
				Initial discharge capacity(mAh.g ⁻¹)	After cycling		
Ionic liquid electrolyte	1M LiTFSI-PP13TFSI-DOL-DME(2:1:1) 0.2M LiNO ₃	S:C=6:4	3.0	980	500 mAh g ⁻¹ after 100 cycles at 0.5C	zero self discharge	Ref. ⁶
	1M-LiTFSI-DOL-DME-Py14TFSI	S:C=8:2	1-1.5	700	94.3% retention after 120 cycles at 0.1C	Lithium surface modification	Ref. ⁷
	0.5 M-LiTFSI-P1A3TFSI	S/C composites	/	1457	670 mAh g ⁻¹ after 50 cycles at 0.1C	prelithiated Si/C anode	Ref. ⁸
Inorganic solid electrolyte	Li _{1.5} Al _{0.5} Ge _{1.5} (PO ₄) ₃ – PEO-LiTFSI-PEGDME	S:C=8:2	1.0	725	700 mA h g ⁻¹ after 300 cycles at 0.5C	almost no self-discharge	Ref. ⁹
	MoS ₂ -doped Li ₂ S-P ₂ S ₅ glass ceramic electrolyte	S:C=75:25	/	1020	425 mA h g ⁻¹ after 30 cycles at 0.05C	a high ionic conductivity of 4.8 mS cm ⁻¹ at room temperature	Ref. ¹⁰
Polymer electrolyte	(PMImTFSI)-based hybrid gel polymer electrolyte (ILGPE)	S:C=6:4	/	1029	885 mA h g ⁻¹ after 30 cycles at 0.1C	1.1×10 ⁻³ S cm ⁻¹ at 20 °C.	Ref. ¹¹
	starch hosted electrolyte/LiTFSI	S:C=43:57	/	1442 mA h g ⁻¹	562 ± 118 mA h g ⁻¹ at 0.5 C after 1000 cycles	ionic conductivity 3.39 × 10 ⁻⁴ S cm ⁻¹ lithium ion transference number 0.80 at 25 °C	Ref. ¹²
Inflammable additive	LiPF ₆ /EC-DMC-TTFP	S@pPAN 43wt% Sulfur	1.0	1450 reversible capacity	1000 mAh g ⁻¹ after 666cycles	Inflammability inhibiting and good rate performance	Ref. ¹³
	LiPF ₆ /EC-DMC-DMMP	S@pPAN 50 wt% Sulfur	0.5-2	1400 reversible capacity	Capacity stable in 50 cycles	/	Ref. ¹⁴
	LiPF ₆ /EC-DMC-TPPi	S@pPAN 43 wt% Sulfur	/	1380 reversible capacity	94.2% capacity retention after 45 cycles	Thermal stability	Ref. ¹⁵
This work	1M LiBOB /TEP+FEC (7:3, v/v)	S@pPAN 41.3 wt% Sulfur	1.0	1377 reversible capacity	1257 mAh g ⁻¹ after 500 cycles at 1C	High capacity retention 91.3% after 500 cycles at 1C and totally inflammable	

Table S3 collected some representative works on safe electrolyte for Li-S batteries from four groups, namely ionic liquid electrolyte, inorganic solid electrolyte, polymer electrolyte and inflammable additive into standard liquid electrolyte. The four types electrolyte are inflammable and highly-safe for Li-S batteries.

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