Supplementary Information

Dual-role electrolyte additive for simultaneous polysulfide shuttle inhibition and redox mediation in sulfur batteries

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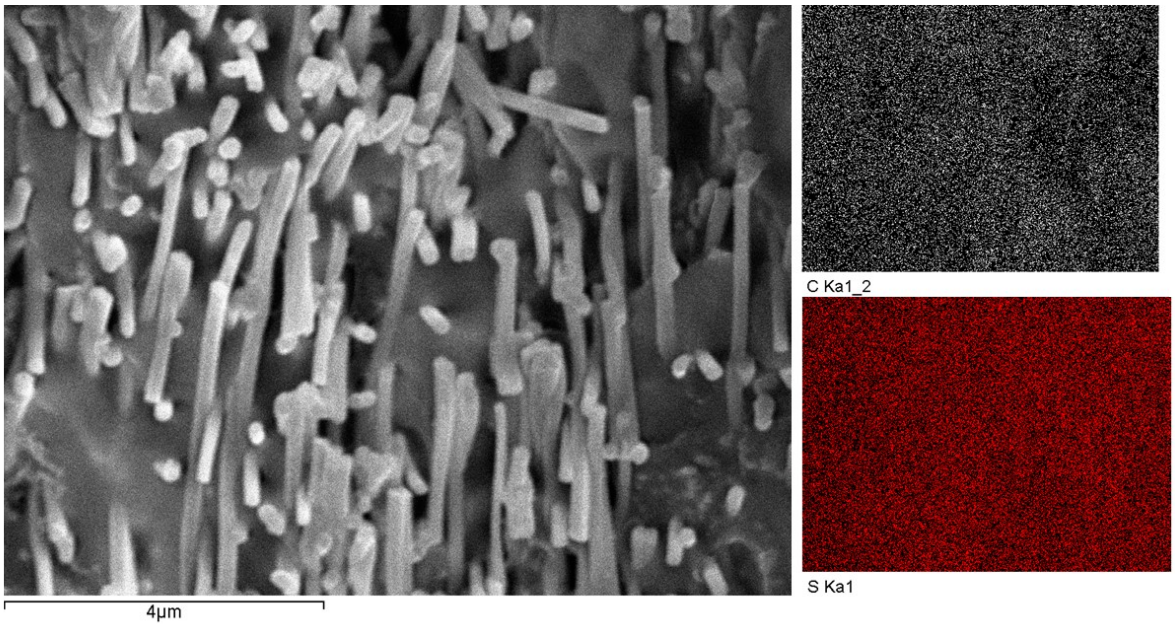

Figure S1. Cross section SEM and elemental mapping for SCNF cathode, showing sulfur distribution throughout the CNFs

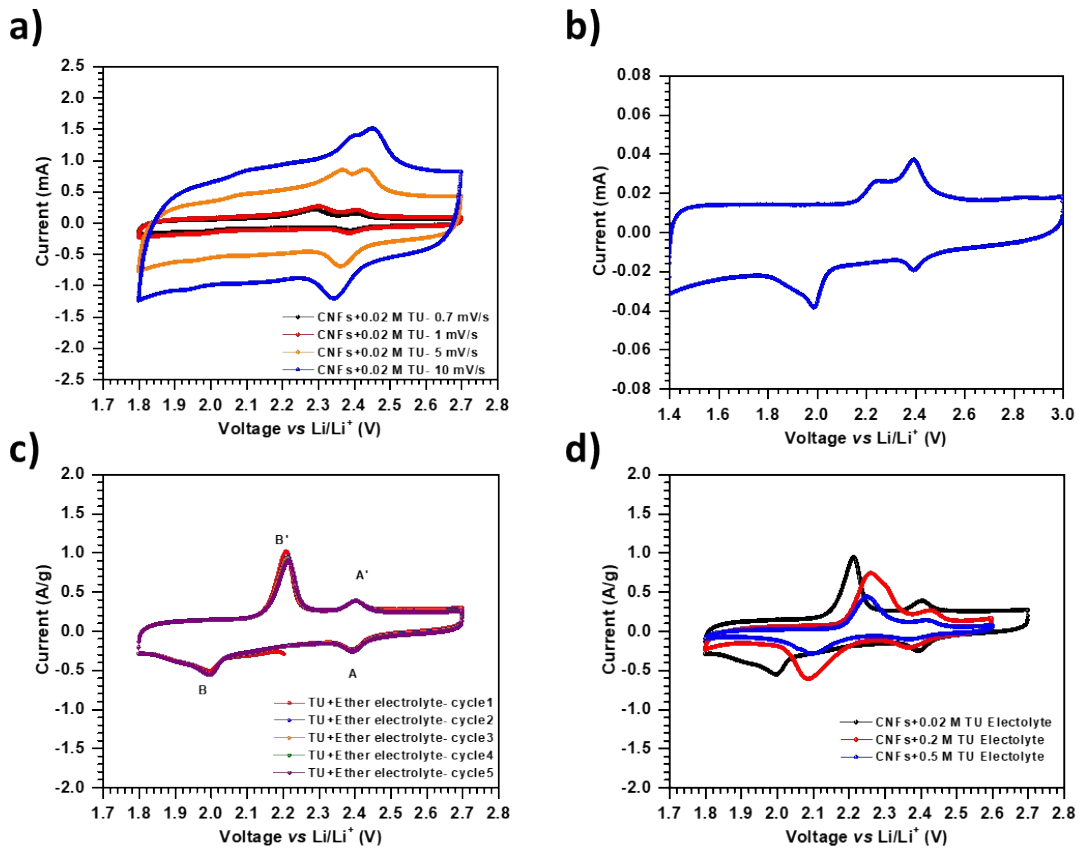

Figure S2. Cyclic voltammetry results of Li-S batteries when using SCNFs as cathode where a) 0.02 M TU additive added to electrolyte at different scan rates up to 10 mV/s, and b) same coin cell from part was used over an extended voltage range between 1.4 to 3.0 V at a scan rate of 0.1 mV/s, c) 0.02 M TU was added to electrolyte and cycled for 5 cycles and current is adjusted based on the weight of TU, and d) 0.02 M, 0.2 M and 0.5 M TU were added to ether electrolyte, and current is adjusted based on the weight of TU

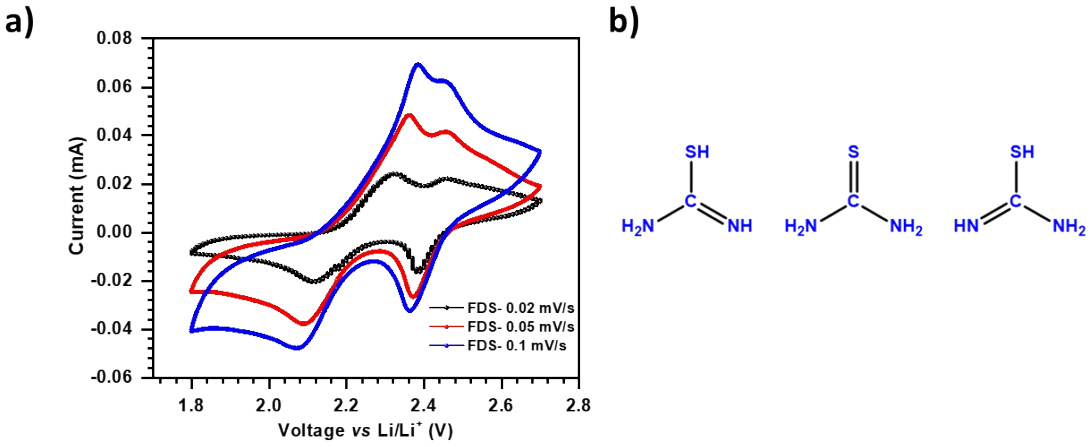

Figure S3. a) Cyclic voltammetry results of Li-S batteries with FDS-based cathodes and ether-based electrolyte (without TU additive), and b) Different TU mesomers

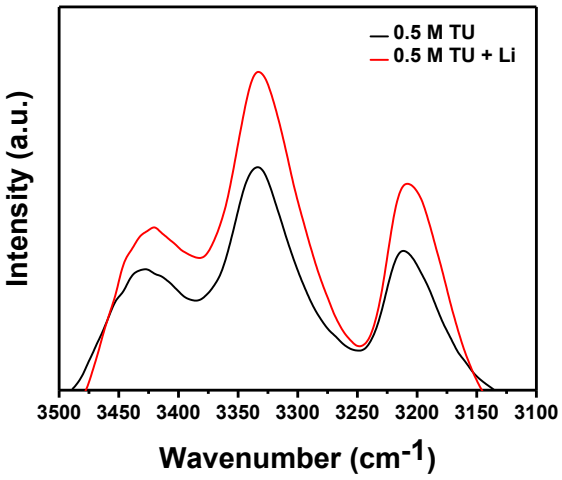

Figure S4. FTR spectra of the TU added electrolyte before and after exposure to Li metal, this figure confirms that the N-H peaks of the TU additive remains unchanged after exposure to Li metal, therefore TU is not lithiated.

Theoretical capacity calculation for TU: To calculate the contribution of TU to the capacity reported in our work, we have used the following equation:

$$Q_{theoretical} = nF$$

Where, n is the number of charge carrier. Here assumed to be 1, and F is the Faraday constant. Using this equation, the theoretical capacity of TU is calculated to be 26.80 Ah/mol_{TU}. Based on the molarity of TU used, 0.02 M, 0.2M, or 0.5 M, and the amount of electrolyte used in the cells (~20 µL/mg_S), we calculated the theoretical capacity contribution from thiourea and adjusted it to the weight of active sulfur material used in the cells.

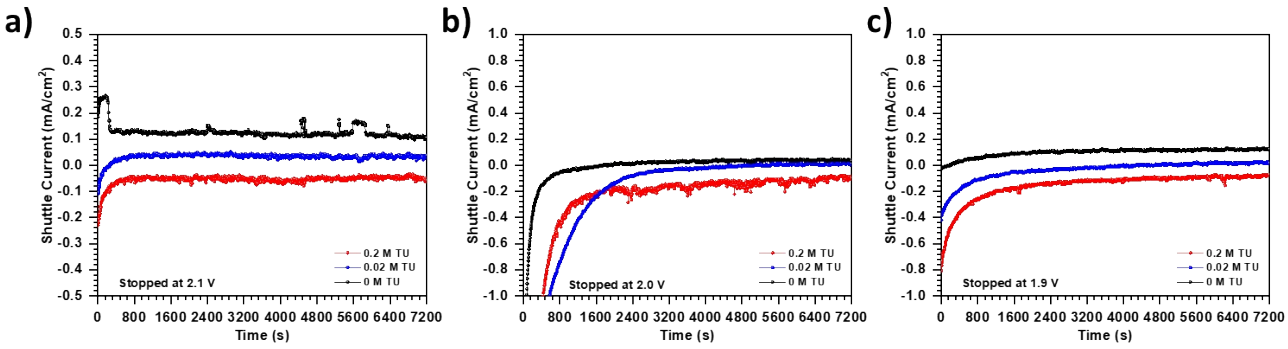

Figure S5. Steady-state shuttle current measurements of Li-S batteries in ether-based electrolyte (black line), and in presence of 0.02M (blue line) and 0.2 M TU (red line) additive when the battery is stopped at a) 2.1 V, b) 2.0 V, and c) 1.9 V

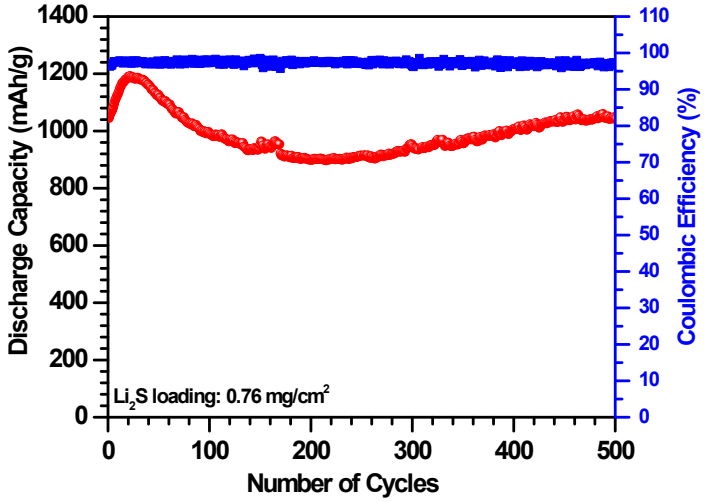

Figure S6. Cyclic result of Li metal-free coin cell with Li_2S/CNFs as cathode, and commercial graphite anode, with 0.2 M TU added to the ether electrolyte

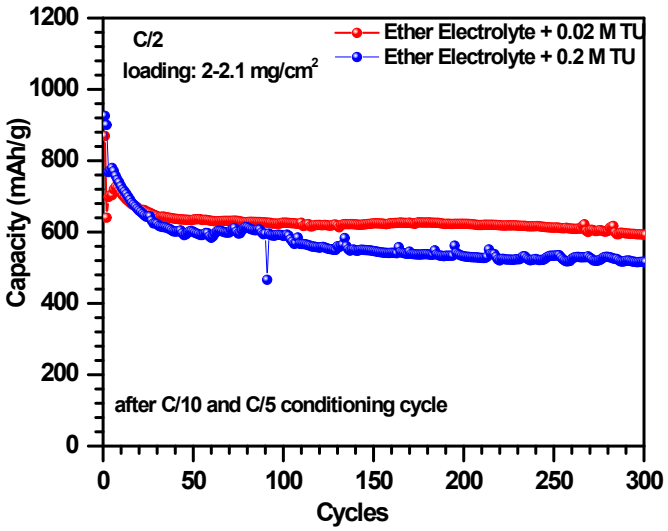

Figure S7. Long-term cycling of Li-S battery with sulfur loading of 2-2.1 mg/cm^2 and 0.01 and 0.2 M TU added to the reference electrolyte at C/2 rate

Table S1. A summary of recent studies on electrolyte additives for Li-S batteries

Additive	Role	Cycling results	Coulombic efficiency	Reference
biphenyl-4,4′-dithiol (BPD)	complex formation with polysulfides	575 mAh/g at C/10 after 300 cycles	93 ± 3%	[1]
hexafluorobenzene (HFB)	Li_2S/ Li_2S_2 activation	~ 700 mA/g after 100 cycles	-	[2]
1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE)	formation of a protective layer on sulfur-based cathode	772 mAh/g after 300 cycles	-	[3]
lithium bromide (LiBr)	formation of a protective layer on sulfur-based cathode	870 mAh/g after 200 cycles at C/5	close to 100%	[4]
pyrrole (Py)	formation of a protective layer on sulfur-based cathode	607.3 mAh/g after 300 cycles at 1C	-	[5]
Carbon disulfide (CS2)	formation of a protective layer on anode and cathode	561 mAh/g after 300 cycles at C/2	>99%	[6]
dithiothreitol (DTT)	accelerate the conversion from LiPSs to Li_2S	471 mAh/g after 500 cycles	98.5	[7]
nickel chloride dimethoxyethane adduct, NiCl2.DME, denote NiDME)	accelerates the redox reactions homogeneously	784 mAh/g after 500 cycles at 1C	-	[8]
N-aryl-substituted benzo[ghi]peryleneimide (BPI)	redox mediator	~500 mAh/g after 100 cycles at C/2	~ 90%	[9]
Thiourea (TU)	dual role as redox mediator and shuttle inhibitor	~690 mAh/g after 700 cycles at C/2 (sulfur cathode- Li metal anode) ~1007 mAh/g after 400 cycles (Li_2S cathode-graphite anode)	>97% throughout 700 cycles	This work

References:

1. Wu, H.-L., et al., *Thiol-based electrolyte additives for high-performance lithium-sulfur batteries.* Nano Energy, 2017. **32**: p. 50-58.
2. Cao, J., et al., *Tackling the Capacity Fading Issue of Li–S Battery by a Functional Additive—Hexafluorobenzene.* ACS Applied Energy Materials, 2020. **3**(4): p. 3198-3204.
3. Qian, F., et al., *Partially fluorinated ether as an electrolyte additive to modify electrode surface and suppress dissolution of polysulfides in Li-S batteries.* Electrochemical Energy Technology, 2018. **4**(1): p. 39-46.
4. Wu, F., et al., *Toward in-situ protected sulfur cathodes by using lithium bromide and pre-charge.* Nano Energy, 2017. **40**: p. 170-179.
5. Yang, W., et al., *Pyrrole as a promising electrolyte additive to trap polysulfides for lithium-sulfur batteries.* Journal of Power Sources, 2017. **348**: p. 175-182.
6. Gu, S., et al., *Carbon disulfide cosolvent electrolytes for high-performance lithium sulfur batteries.* ACS applied materials & interfaces, 2016. **8**(50): p. 34379-34386.
7. Liu, M., et al., *Dithiothreitol as a promising electrolyte additive to suppress the "shuttle effect" by slicing the disulfide bonds of polysulfides in lithium-sulfur batteries.* Journal of Power Sources, 2019. **424**: p. 254-260.
8. Luo, C., et al., *An organic nickel salt-based electrolyte additive boosts homogeneous catalysis for lithium-sulfur batteries.* Energy Storage Materials, 2020. **33**: p. 290-297.
9. Gerber, L.C., et al., *Three-dimensional growth of Li2S in lithium–sulfur batteries promoted by a redox mediator.* Nano letters, 2016. **16**(1): p. 549-554.