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Supplementary Information

A novel class of functional additives on cyclability enhancement of sulfur cathode in lithium sulfur batteries

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Method and procedures

The synthesized samples were identified *via* X-ray diffraction (XRD) (RigakuD/MAX-2550-PC) with Cu K radiation (λ=1.54059 Å). Their morphological observation was conducted with field emission scanning electron microscopy (FESEM, Zeiss Ultra55) at 5 kV.

The hierarchical macroporous carbon (MPC) was synthesized as previously reported.[1, 2] Sulfur-loaded MPC (S/MPC, S:MPC=7:3) was prepared *via* calcination of the ball-milled mixture of sulfur and MPC at 155 °C for 4 h in N_2 atmosphere.[3]

The Li_2S_4 solution was prepared by adding sublimed S and Li_2S in a molar ration of 3:1 by stoichiometrically into anhydrous tetrahydrofuran (THF) at the same time. Then aging for 10 h and homogeneous solution was obtained.

Coin cells (CR2025) were assembled in an Ar-filled glove box by using a lithium foil as the counter electrode and Celgard 2400 membrane as the separator. The working electrode was prepared by casting the electrode slurry on an Al foil before drying at 60 °C for 12 h in vacuum. The S/MPC, S/MPC-741 and S/MPC+LCO electrodes were prepared by mixing S/MPC, SP, PVDF and LCO at the mass ratio of 7:2:1:0, 7:4:1:0 and 7:2:1:2, respectively. The sulfur content in cathode was measured by the thermogravimetric analyzer. A total of 80 μL electrolyte and 2 mg electrode materials including sulfur, additive, and PVDF were employed in the test cell. The electrolyte consisted of lithium bis (trifluoromethane sulfonimide) (LiTFSI: 1 mol L^{-1}) and $LiNO_3$ (1 wt.%) in a DOL-DME solution (1:1 ratio in volume, DOL: 1, 3-dioxolane, DME:1, 2-dimethoxyethane).

Cyclic voltammograms (CV) were recorded at a scan rate of 0.1 mV s^{-1}. The galvanostatic charge and discharge tests were conducted within 1.8-2.6 V (*vs.* Li^+/Li). Electrochemical impedance spectroscopy (EIS, CHI604E) measurements were carried out from 0.1 Hz to 100 kHz with the amplitude of 5 mV. All electrochemical measurements were performed at 25 °C.

2. **Supporting Figures**

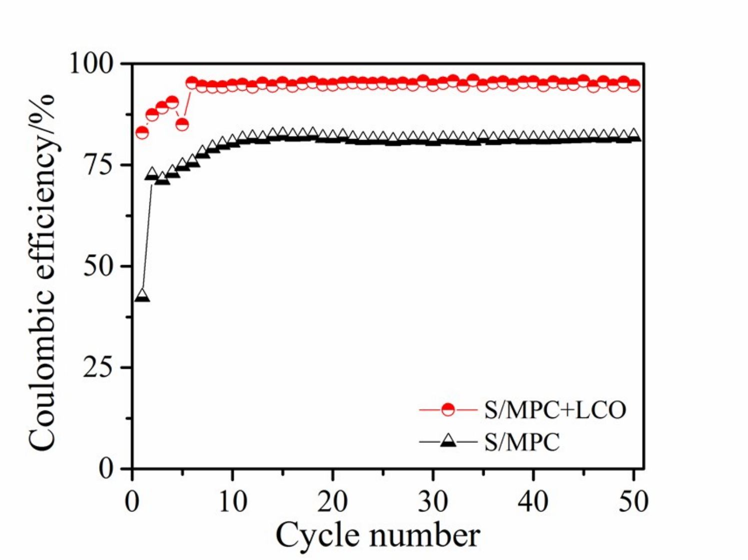

Figure S1. The comparison of the coulombic efficiency for S/MPC and S/MPC+LCO electrodes.

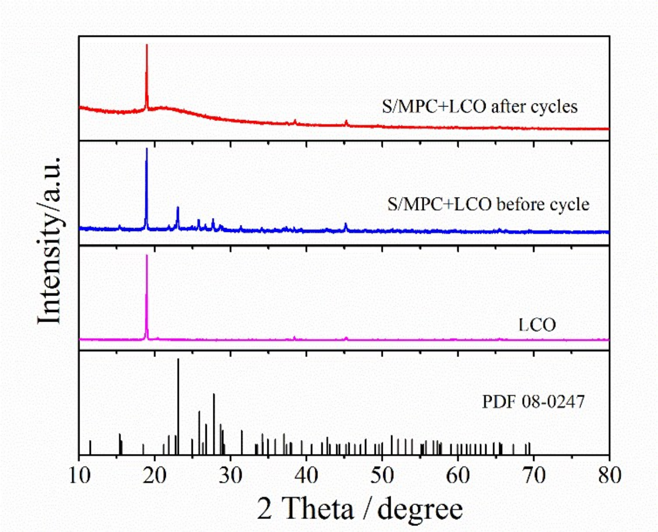

Figure S2 XRD patterns of the S/MPC+LCO electrode before and after cycling.

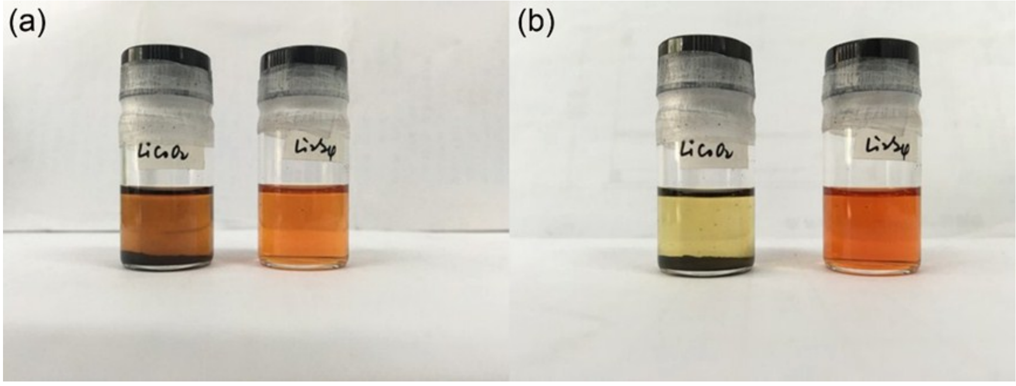

Figure S3 Visual discrimination of LCO@Li_2S_4 in THF, (a) before and (b) after 24 h.

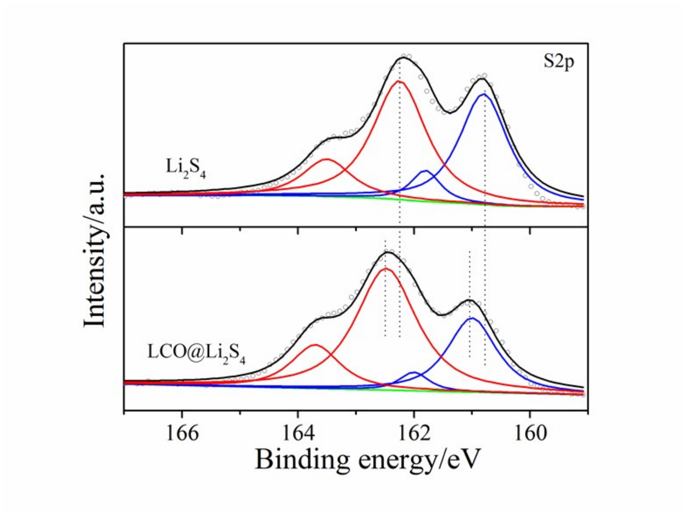

Figure S4 The S2p spectrum of polysulfide before and after adsorption.

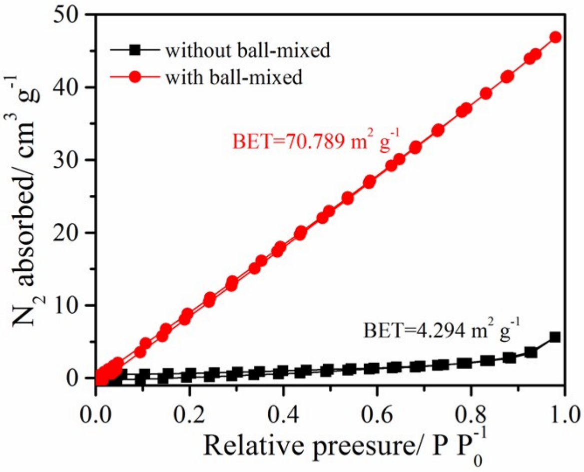

Figure S5. N_2 adsorption-desorption isotherms of LCO with ball-mixed and without ball-mixed.

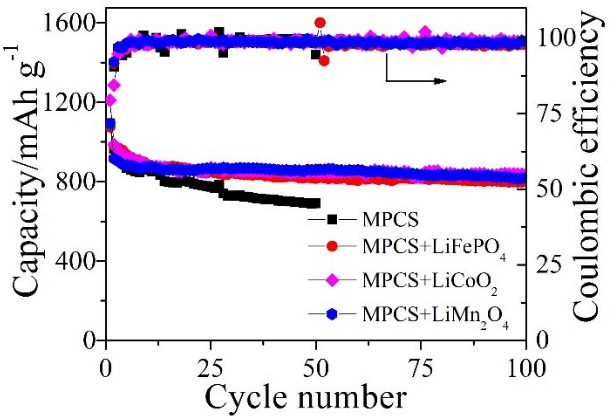

Figure S6 Cycling performance of the cell with different kind of additives.

Table S1. Performance comparison of the batteries with additives

Sulfur cathodes	Additives	Content of additives (%)	Performance (mAh g^{-1})	Decay rate (%)	Ref.
S	SBA-15	9.5	ca.370 (40th) at 1 C.	0.28	4
S	Al_2O_3	10	660 (25th)	0.23	5
S	$Mg_{0.6}Ni_{0.4}O$	16	430 (20th) at 100 mA/g	2.5	6
S/Graphene	SiO_2	3	681 (150th) at 0.1 C	0.018	7
S	Chitosan	3.5	646 (100th) at 1C	0.18	8
S/C-V_2O_5	$Mg_{0.8}Cu_{0.2}O$	10	422 (30th)	0.75	9
S	La_2O_3	10	450 (80th)	3.8	10
S	TiO_2	30	680 (100th) at 0.2 C	0.23	11
S	$LiCoO_2$	3	715 (150th) at 1 C. 375 (1200th) at 2 C.	0.13 0.034	This work

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