Supplemental Information

A Multi-Functional Interface Derived from Thiol-Modified Mesoporous Carbon in Lithium-Sulfur Batteries

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Experimental procedures

NMR: ⁷Li, ¹⁹F, and ¹³C MAS NMR were performed on a Varian Inova spectrometer with a 600 MHz (14.1 T) magnet, using 1.6 mm rotors operating at a spinning speed of 36 kHz. The 90° pulse width was 3 µs for ⁷Li, 1.5 µs for ¹³C, and 5 µs for ¹⁹F. The ⁷Li spectra were obtained with 640 scans, using a flip angle of 9° (a pulse width of 0.3 µs) with a recycling delay of 5 s for quantitative comparison. The ¹⁹F spectra were obtained using a spin-echo pulse sequence with 48 scans and a recycling delay of 5 s. Due to the low sensitivity of ¹³C in the naturally abundant materials, 10240 scans were used with a 30° pulse and a recycling delay of 5 s. Temperature was maintained at 25 °C for all NMR measurements. For the preparation of the first set of samples, 0.6 ml of 0.1M Li₂S₈ in DME was added to 20 mg MJ430/20% SH-MJ430 carbon material to form a homogenous slurry. Both slurries with MJ430/20% SH-MJ430 carbon material were dried for 12 h in a glove box to form concentrated samples and then packed into the NMR rotors. For the second series of samples, the cycled coin cells were disassembled at different voltage stages in a glovebox, and the composites were scratched off from the cathodes immediately and filled into the NMR router.

XPS: All XPS spectra were taken on a Surface Science Instruments S-Probe photoelectron spectrometer. This instrument has a monochromatized Al K α X-ray source which was operated at 20 mA and 10 kV, and a low energy electron flood gun for charge neutralization. The samples were mounted on double-sided tapes that run as insulators. X-ray analysis area for these acquisitions was approximately 800 μ m across. Pressure in the analytical chamber during spectral acquisition was less than 5 x 10⁻⁹ torr. The take-off angle (the angle between the sample normal and the input axis of the energy analyzer) was 0°, (0° take-off angle \cong 100 Å sampling

depth). Service Physics Hawk version 7 data analysis software was used to calculate the elemental compositions from peak areas measured above an inelastic scattering (Shirley) background. Powder samples were transported to instrument in air. Cycled cathode samples were disassembled in an Ar atmosphere glovebox, transferred to instrument in sealed vials, then mounted in ambient conditions.



Fig. S1 Schematic of *in-situ* functionalization of modifiers ("R"=SH) onto the surface of MJ430 carbon *via* diazotization. The diazonium ions dissociate into N_2 gas and a phenylthiol radical, which can react with sp²-hydridized carbon frameworks to form sp³ C-C bonds. This approach is advantageous for many applications because of the ability to tune the functionality of grafted small molecules, as well as controlling the degree of functionalization.



Fig. S2 TGA of resultant modified MJ430 carbons from mixing purified MJ430 with 20 and 50 mol% diazonium precursors, respectively. The former displays a 25 wt% of overall mass loss (20 wt% among which comes from the modifiers), while the latter only shows a 3% increase of overall mass loss with overwhelming increase of diazonium precursors.



Fig. S3 The N₂ isotherms at 77 K for the (a) MJ430, (b) 5% SH-MJ430, (c) 10% SH-MJ430, (d) 15% SH-MJ430, (e) 20% SH-MJ430 carbon and (f) their related pore size distribution. The distribution plot of MJ430 reveals that mesoporous carbon MJ430 has three pore types. These pore types originated from capillary condensation in micropores (from the carbon walls), primary mesopores, and secondary mesopores (from interparticle capillary condensation), ¹ with pore diameters of approximately 3.8, 7.4, and 14 nm, respectively. After surface modification, the primary mesopores decrease from 7.4 to 5.4 nm, as shown with the arrow.



Fig. S4 (a) XPS wide spectra of MJ430 and 20% SH-MJ430 (O_{1s} 529-535 eV, C_{1s} 284-289 eV, $S_{2s} \sim 220$ eV, S_{2p} 161-169 eV). High-resolution C_{1s} and S_{2p} spectra of (b,c) MJ430 and (d,e) 20%SH-MJ430 carbon.



Fig. S5 Additional TEM images of (a) MJ430 and (b) 20% SH-MJ430.



Fig. S6 (a) TGA of a series of [SH]-MJ430-S composites with an increasing weight percentage of the thiol modifier from 0% to 20%, controlled via reaction conditions. Their corresponding (b) discharge/charge voltage profiles and (c) cycling performance.



(a) 20% SH-MJ430 + S₈ physical mixing at room temperature

Fig. S7 EDS elemental mapping images and the corresponding selected SEM images of (a) the physically mixed 20% SH-MJ430 and S_8 powders at room temperature and (b) 20% SH-MJ430-S powders after S_8 infiltration at 155 °C.



Fig. S8 N₂ isotherms for the MJ430, 20% SH-MJ430, MJ430-S, 20% SH-MJ430-S. Surface area and pore volume of the composites are 170 m² g⁻¹ and 0.876 cm³ g⁻¹ for the MJ430-S and 52.0 m² g⁻¹ and 0.271 cm³ g⁻¹ for the 20% SH-MJ430-S, respectively.



Fig. S9 CV of the Li-S cells using MJ430-S and 20% SH-MJ430-S cathodes at the seep rate of 0.02 mV s⁻¹.



Fig. S10 SEM images of (a) MJ430-S and (b) 20% SH-MJ430-S cathode discharged to 1.9 V after long-term cycling.



Fig. S11 SEM images of the Li metal surface (a) before and (b) after the cycling process with the MJ430-S cathode and (c) with the 20% SH-MJ430-S cathode.



Fig. S12 ¹⁹F (left) and ¹³C (right) MAS NMR spectra of cathode materials with the MJ430-S (top two) and 20% SH-MJ430-S (bottom two) from Li-S batteries that are discharged to different voltages.

Cathode	Active	Areal S	Electrolytes	Cycling performance (based on S loading mass				g mass)
components	materials	Loading		С	Initial	Cycle	Residual	Capacity
		(mg cm ⁻²)		Rate	Discharge	Numb	Reversible	Decay/
					Capacity	-er	Capacity	Cycle
					(mAh g ⁻¹)		(mAh g ⁻¹)	(%)
20%SH-	Melt-	4.0	1M LiTFSI-	0.25C	956	180	865	0.05
MJ430-S (this	infiltrated S8		DOL/DME(1:1)+1wt%LiNO ₃					
work)								
Mo ₂ C/Carbon	Melt-	1	1M LITFSI-DOL/DME	0.2C	1177	300	789	0.11
Cloth-S ²	infiltrated S_8	4.68	(1:1)+1.5wt%LiNO ₃	0.1C	692	50	500	0.55
NiCo ₂ S ₄ @Carbo	Li ₂ S ₆	1.5	1M LITFSI-DOL/DME (1:1) +	0.1C	1600	100	1100	0.31
n textile ³	catholyte		0.2M Li ₂ S ₆	0.5C	923	500	836	0.02
HCNCs ^a /S ⁴	Melt-	1.4	1M LITFSI-	1C	852	300	630	0.09
	infiltrated S_8	4	DOL/DME(1:1)+0.1M LiNO ₃	0.2C	883	100	622	0.30
Ketjen black-S	Melt-	-	1M LiTFSI-	0.2C	988.9	100	798.5	0.19
with plasma-	infiltrated S_8		DOL/DME(1:1)+0.1M LiNO ₃					
modified								
separators⁵								
amCMK-S ⁶	Li ₂ S	-	1M LiTFSI-	0.2C	1211	100	920	0.24
			DOL/DME(1:1)+0.25M LiNO ₃					
N-Doped	Melt-	0.5-0.7	1M LiTFSI-	0.2C	1113	100	980	0.12
$HCS^{b}-S^{7}$	infiltrated S ₈		DOL/DME(1:1)+0.4M LiNO ₃					
HCv ^{c,8}	Melt-	1	1M LiTFSI-	0.2C	1380	150	730	0.31
	infiltrated S ₈		DOL/DME(1:1)+0.1M LiNO ₃					
TiO@C-HSd/S9	Melt-	4	1M LiTFSI-	0.05C	886	50	821	0.14
	infiltrated S ₈		DOL/DME(1:1)+0.2M LiNO ₃					
Graphene-S ¹⁰	Graphene-	1.2	1M LiTFSI-	0.2C	705	50	500	0.58

work.

	enveloped		DOL/TEGDME(1:1)						
	micron sized								
	S								
MWCNT-S	Melt-	6.3	1M LiTFSI-	0.05C	995	150	696	0.2	
with	infiltrated S ₈		DOL/DME(1:1)+0.25M LiNO ₃						
VACNT ^{e,11}									
IKB ^f -S ¹²	Melt-	3.5	1M LiTFSI-	0.1C	1000	100	750	0.25	
	infiltrated S ₈		DOL/DME(1:1)+0.1M LiNO ₃						
Nano-	S	1.66	1M LiTFSI-DOL/DME(1:1)	0.25C	1120	50	930	0.34	
S@PEDOT ¹³	nanoparticles								
S@ZIB-8 ^{g,14}	Melt-	1	0.6M LiTFSI-	0.5C	750	250	600	0.08	
_	infiltrated S ₈		DOL/DME(1:1)+0.1M LiNO ₃						
Graphene-S63	G-S hybrids	1.26	1M LiTFSI-	0.45C	725	100	541	0.25	
hybrid ¹⁵			DOL/DME(1:1)+0.5wt%LiNO						
-			3						
N,S-codoped	Li ₂ S ₆	4.6	1M LiCF ₃ SO ₃ DOL/DME (1:1)	0.2C	1200	100	822	0.32	
graphene-S ¹⁶	catholyte	8.5	+ 0.1M LiNO ₃	0.5C	925	200	670	0.14	
polvSGN ¹⁷	S-rich	3.7	1.85M LiCF ₃ SO ₃ DOL/DME	0.2C	978	100	655	0.33	
1 5	$\begin{array}{c} \text{copolymer} \\ \hline 10.5 \\ \hline (1.1) + 0 \\ \hline \end{array}$		$(1:1) + 0.1M \text{ LiNO}_3$	0.1C	992	100	717	0.28	
CATB-coated	S-GO	0.8	1 M LiTFSI in	1C	880	160	780	0.07	
nanoS-GO ¹⁸	nanocomposi	0.0	PYR ₁₄ TFSI/DOL/DME			100	,		
	tes		mixture $(2.1.1) + 0.1M \text{ LiNO}_2$						
Porous CNTs-S	Melt-	3 51	1M LiTESI-	0.20	1262	200	984	0.11	
with	infiltrated S.	5.51	DOL/DME(1·1)+1wt%LiNO ₂	0.20	1202	200	501	0.11	
Graphene/DTT									
additional									
interlaver ¹⁹									
PEI ^h -CNT-S ²⁰	Melt-	1.2	1M LiTESI-	0.5C	949	300	750	0.07	
	infiltrated S.		DOL/DME(1:1)+0.2M LiNO ₃						
S-GSH ^{i,21}	S-rich	1	1M LiTFSI-	1C	985	450	857	0.03	
5 0511	copolymer		DOL/DME(1·1)+1wt%						
	copolymor		$LiNO_2 + 0.02 M Li_2S_8$						
S-TTCA ^{j,22}	S-rich	0.8	1M LITESI-DIOX/TEGDME	0.2C	1050	100	945	0.08	
5 11011	copolymer	$\frac{1}{11} + 0.2 \text{ M LiNO}$		0.20	1000	100	10	0.00	
S-DIB-OLC ^{k,23}	S-rich	3-5	1M LiTESI-	0.1C	1150	100	880	0.24	
	copolymer		DOL/DME(1:1)+0.25M LiNO ₃						
PVDF-S with	S.	5	1M LiTESI-	0.06C	650	100	600	0.08	
VGCF-	58		DOL/DME(1·1)+1wt%LiNO ₂	0.000		100		0.00	
PEOCMC									
interlaver ²⁴									
70S/d-Ti ₂ C ²⁵	Nano-S	1	1M LiTESI-	0.5C	1071	650	723	0.05	
2			DOL/DME(1:1)+2wt%LiNO ₃						
^a Hollow Carbon Nanosphere Clusters (HCNCs): ^b Hollow Carbon Spheres (HCS): ^c Hollow Carbon Fiber (HCF): ^d Hollow Spheres (HS): ^c									
Vertically Aligned CNTs (VACNTs) as the binders for the hierarchical free-standing paper cathode: ^f Integrated Ketien Black with conductive									
amorphous carbon as a "binder" (IKB); ^g A metal-organic framework (MOF), assembled by Zn ions and 2-methylimidazolate (ZIF-8): ^h									
Polyethylenimine (PEI); ^{<i>i</i>} Copolymerization of sulfur with Sulfydryl-functionalized rGO (GSH) to form sulfur copolymers; ^{<i>j</i>}									
Copolymerization of sulfur with porous trithiocyanuric (TTCA) frameworks; ^k the sulfur-rich copolymer cathode was synthesized via inverse									

vulcanization of sulfur and 1,3-diisopropenylbenzene (DIB) while using carbon onions (OLC) as hosts.



Fig. S13 The contact angle analysis of (a) MJ430-S and (b) 20% SH-MJ430-S cathode with LiTFSI-DOL/DME electrolyte, as well as (c) MJ430-S and (d) 20% SH-MJ430-S cathode with H₂O. The photographs were obtained by dropping the same amount of electrolyte or H₂O onto the MJ430-S/20% SH-MJ430-S electrode. The angle at the electrolyte/MJ430-S electrode interface is 24°, while that at the electrolyte/20% SH-MJ430-S electrode interface is 8°. This suggests stronger adhesion between the electrolyte and the 20% SH-MJ430-S than that at the electrolyte and the MJ430-S interface, which would significantly confine the LiTFSI-DOL/DME electrolyte with dissolved LiPSs inside the cathode. The different contact angle at the H₂O/MJ430-S and H₂O/20% SH-MJ430-S interface also verify the improved wettability of modified SH-MJ430-S cathode.

	Solid Li ₂ S		Solid Li ₂ S _n		Confined LiTFSI Solution Li ₂ S _n		Mobile Li⁺	
	PW (ppm)	Integration	PW (ppm)	Integration	PW (ppm)	Integration	PW (ppm)	Integration
MJ430- S_2.1V	0.66	0.30	1.14	0.29	1.34	0.41	-	-
MJ430- S_1.9V	0.55	0.68	1.12	0.49	1.33	0.37	-	-
20% SH- MJ430- S_2.1V	0.67	0.31	1.17	0.40	1.08	0.66	0.17	0.08
20% SH- MJ430- S_1.9V	0.58	0.93	1.09	0.56	1.2	0.37	0.16	0.14

Table S2. Peak width (PW) and integrated area of individual deconvolution peaks in Fig. 5b, the integration is normalized to MJ430-S 2.1V (the sum of its three peaks is 1.0).



Fig. S14 EIS analysis of (a-c) MJ430-S and (d-f) 20% SH-MJ430-S cells at different stages of discharge within 40 cycles. Fitted values of (g) the interface resistance R_i and (h) the charge transfer resistance R_{ct} of MJ430-S and 20% SH-MJ430-S cells at different voltage stages. The electric equivalent circuit (EEC) used to fit impedance data is an inset in (g).

The EEC has been successfully applied for Li-ion and Li-S batteries previously.^{26,27} It contains the following serial-connected elements: a bulk internal resistance (R_e), a high-frequency interphase resistance (R_i) in parallel with a constant phase element (Q_i), a mid-frequency charge transfer resistance (R_c) in parallel with a constant phase element (Q_c), and a Warburg diffusion element (Z_w). In the as prepared Li-S (MJ430-S) cell, R_i can be clearly observed even though there is no thiol modifier on the carbon surface and no surface film generated by cycling (Fig. 5e). It is known that carbon surfaces can be unintentionally functionalized by environmentally abundant elements or groups, such as -O, -H, and -OH, etc., during the synthesis and storage, especially for the type of mesoporous carbon used in this work.²⁸ These functional groups could easily transfer to sulfur surface during the infusion process and form a surface film, which impedes the Li⁺ transport.²⁹ Thereby, we speculate that R_i and Q_i associated with the high frequency semicircle should originate from this kind of surface film. The observation that R_i will decrease with extended cycling well supports this speculation, since the electrochemical cycling gradually removes the functional groups and thus improve the electrolyte wetting. In addition, the comparable $R_{et,fresh}$ after the modification

 $(R_{ct,fresh,MJ430} = 14.4 \Omega \text{ vs.} R_{ct,fresh,SH-MJ430} = 17.7 \Omega)$ suggests that electron and lithium transport across solid/liquid interface in the initial charge transfer process is not significantly affected, even though the modified cathodes have a thicker surface film. This may be due to the highly conductive carbon hosts and improved electrolyte wettability, which facilitates the charge transfer between the electrolytes and S particles. The electrical conductivity was also measured using a four-point probe technique. It showed an electrical conductivity of 48 S m⁻¹ after the modification, which should still be sufficient for electron conduction throughout the entire cathode in Li-S cells.^{23,30–32}

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