Supporting Information

Reaction heterogeneity in practical high-energy lithium–sulfur pouch cells

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Pouch cell energy estimation

The parameters used for the pouch cell energy estimation at both coin cell and pouch cell conditions: cell capacity = 2 Ah, cell average voltage = 2.1 V, cell dimensions = 54 mm x 36 mm (cathode dimension), 55.5 mm x 37.5 mm (anode dimension), specific discharge capacity based of S = 1000 mAh g^{-1}, S content in the whole electrode = 64 wt.%, electrolyte = 1 M LiTFSI/DOL+DME (1:1, v/v) + 0.3 M LiNO$_3$, electrolyte density = 1.1 g mL^{-1}, 12 µm Al foil as cathode current collector, and Cu mesh (9 µm with 50% porosity) as anode current collector.

Table S1 Cell parameters for the pouch cell energy estimation with coin and pouch cell conditions.

Cell parameter		Unit	Coin cell condition	Pouch cell condition
S loading		mg cm^{-2}	2	6
Layer			27	9
E/S ratio		mL g^{-1}	38	2.3
E/C ratio		g (Ah)$^{-1}$	42	2.5
N/P ratio			25.0	1.7
$M_{cathode}$		g	3.3	3.3
M_{Li}		g	14.0	0.9
$M_{electrolyte}$		g	87.8	5.3
$M_{inert\ materials}$	M_{Al}	g	1.9	0.7
	M_{Cu}	g	2.2	0.7
	$M_{separator}$	g	1.2	0.4
	$M_{package,\ tabs}$	g	1.2	1.2
Specific energy		Wh kg^{-1}	40	351

Table S2 Cell parameters for the 313 Wh kg^{-1} pouch cell

Cell parameter	Unit	313 Wh kg^{-1} pouch cell
S loading	mg cm^{-2}	6
Layer		9
E/S ratio	mL g^{-1}	2.5
E/C ratio	g (Ah)$^{-1}$	2.4
N/P ratio		1.4
$M_{cathode}$	g	3.4
M_{Li}	g	0.9
$M_{electrolyte}$	g	6.1
M_{Al}	g	0.8
M_{Cu}	g	0.9

$M_{separator}$	g		0.4
$M_{package, tabs}$	g		1.2

The pore-filling E/S ratio and active E/S ratio are estimated by:

$$\frac{E}{S^p} = \frac{l_c\varepsilon_c + 1.17 l_{sep}\varepsilon_{sep}\left(1 + \frac{1}{N}\right)}{L_s}$$

$$\frac{E}{S^{act}} = \frac{E}{S^{app}} - \frac{E}{S^p}$$

where E/S_p is the pore-filling E/S ratio; E/S_{act} is the active E/S ratio; E/S_{app} is the applied E/S ratio; l_c is the thickness of the cathode (cm); ε_c is the porosity of the cathode; l_{sep} is the thickness of the separator (cm); ε_{sep} is the porosity of the separator; N is the layer of the anode in a pouch cell; L_s is the sulfur loading (g cm^{-2}). 1.17 is the separator area (60 mm x 38 mm) to the cathode area (54 mm x 36 mm) in the pouch cell.
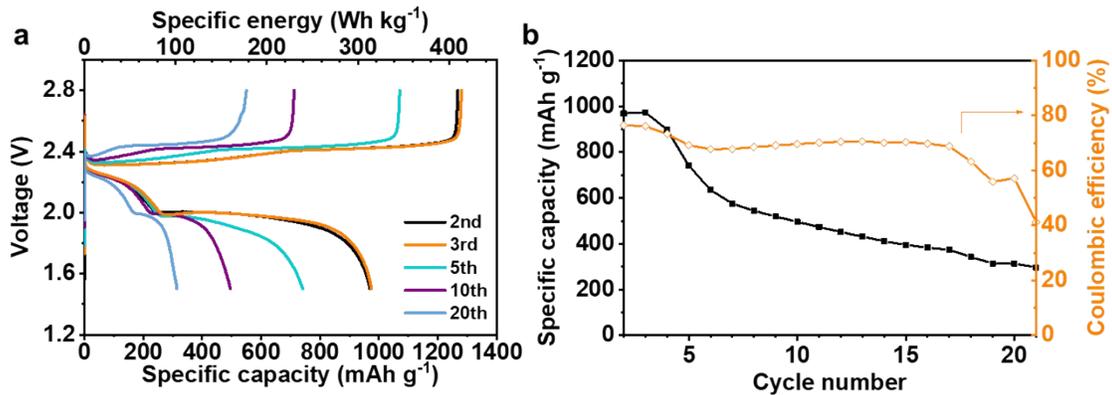

Fig. S1 Electrochemical performances of the 313 Wh kg^{-1} pouch cell at 0.05 C (0.3 mA cm^{-2}, 1 C=1000 mA g^{-1}). (a) Discharge and charge curves at the 2nd, 3rd, 5th, 10th, and 20th cycle. (b) Cycle performance and Coulombic efficiency.
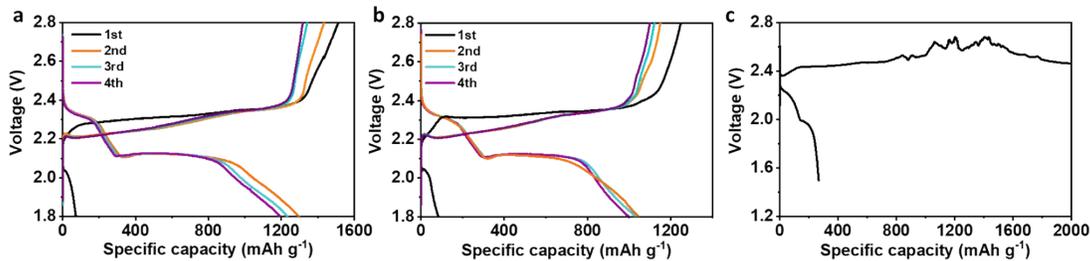

Fig. S2 Discharge and charge curves of the cycled sulfur cathode, harvested from the 313 Wh kg^{-1} Li–S pouch cell, with fresh lithium and electrolyte. (a) E/S = 10 mL g^{-1}, N/P = 17. (b) E/S = 6 mL g^{-1}, N/P = 1.4. Current density is 0.05 C for the 1st discharge and 0.02 C for the following cycles. (c) Last cycle (22nd) discharge and charge curves of the 313 Wh kg^{-1} pouch cell.
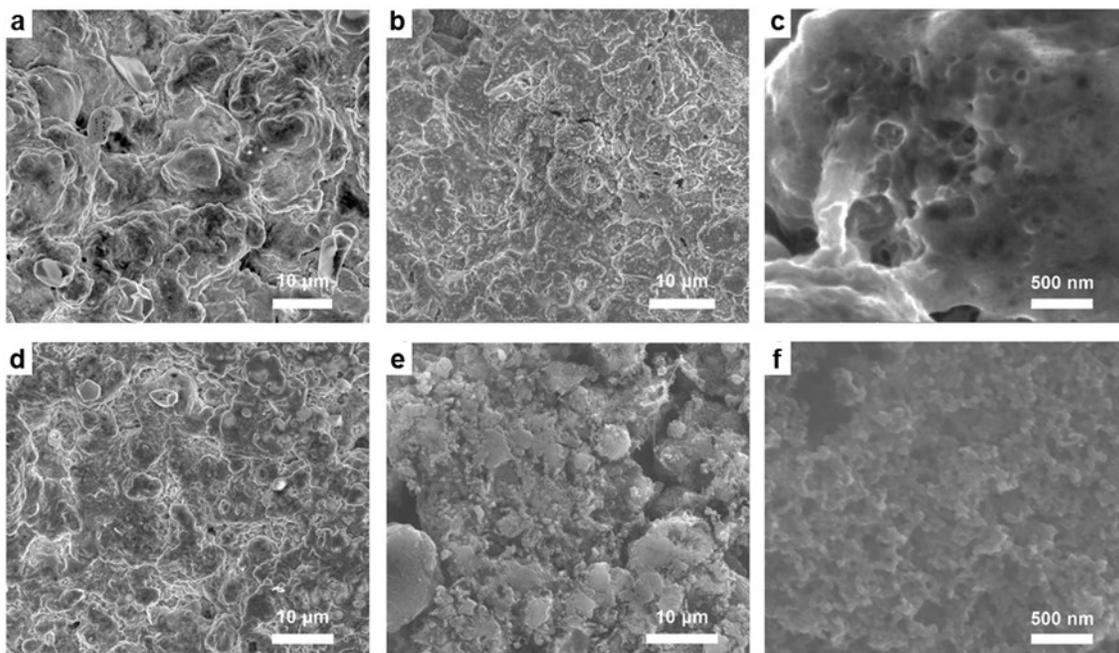
Fig. S3 SEM images of different regions of the sulfur cathode. (a, b, d) R1, R2, and R3 on cycled cathode from the 313 Wh kg^{-1} Li–S pouch cell, respectively. (e) Pristine cathode. (c and f) High-resolution images of b and e, respectively.
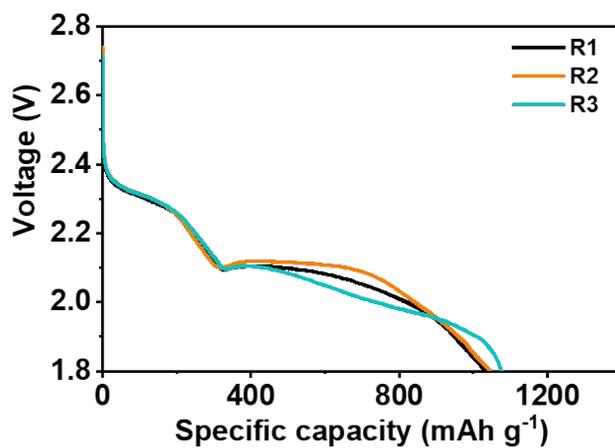

Fig. S4 Typical discharge curves of reassembled cells with cycled sulfur cathodes from different regions of the cycled 313 Wh kg^{-1} Li–S pouch cell, new lithium, and fresh electrolyte. (E/S = 6 mL g^{-1}, N/P = 1.4, and 0.02 C).
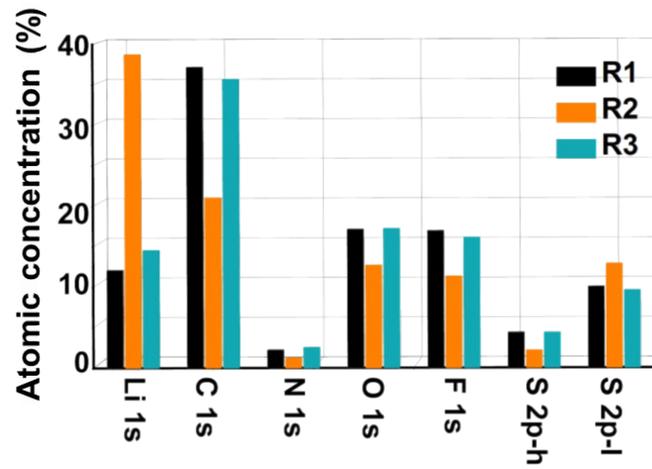
Fig. S5 XPS atomic quantification of different regions on cycled lithium.
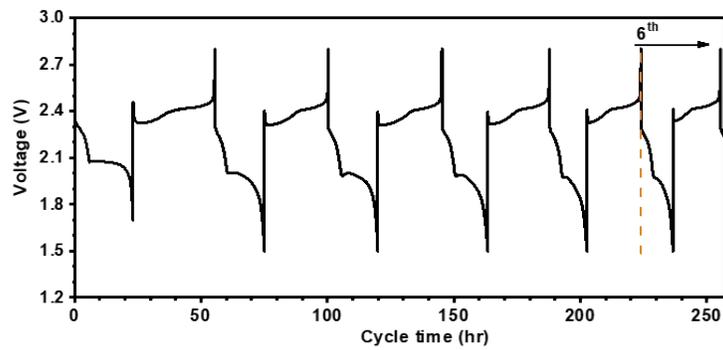

Fig. S6 Variation of discharge capacity along with cycle time of the 313 Wh kg^{-1} Li–S pouch cell in the first 6 cycles.
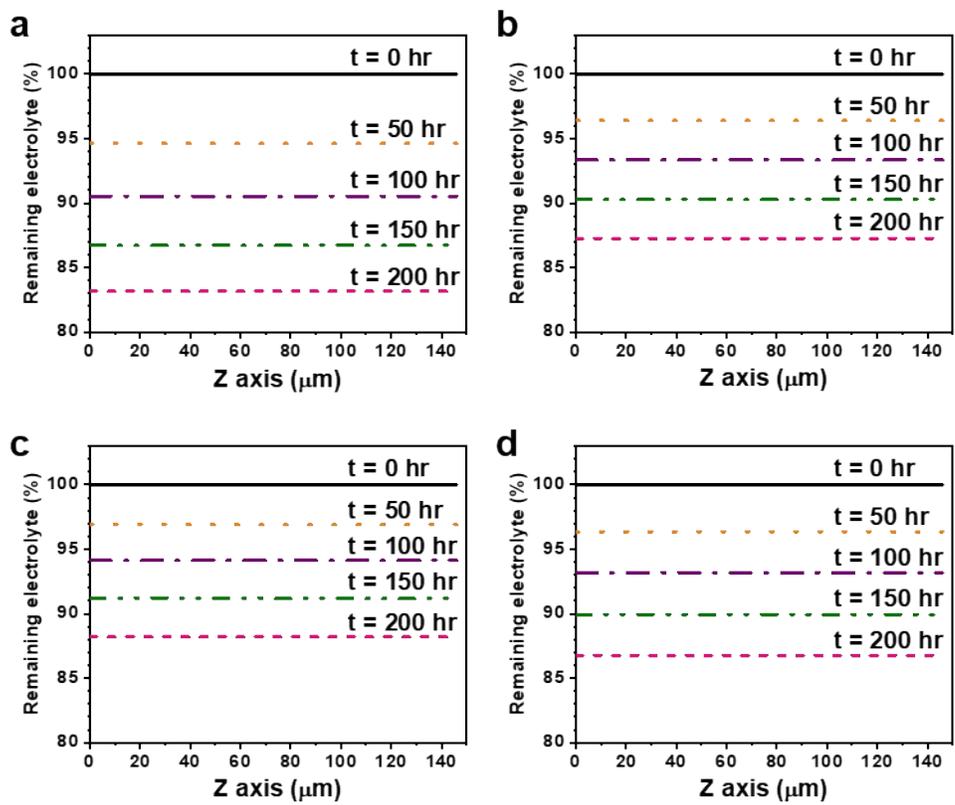
Fig. S7 Variation of electrolyte content in S cathode along with the z-axis at different times and locations. (a) The center of the electrode (0 cm, 0 cm, z). (b) Corner 1 (2.69 cm, 0 cm, z). (c) Corner 2 (2.69 cm, 1.79 cm, z). (d) Corner 3 (0 cm, 1.79 cm, z).
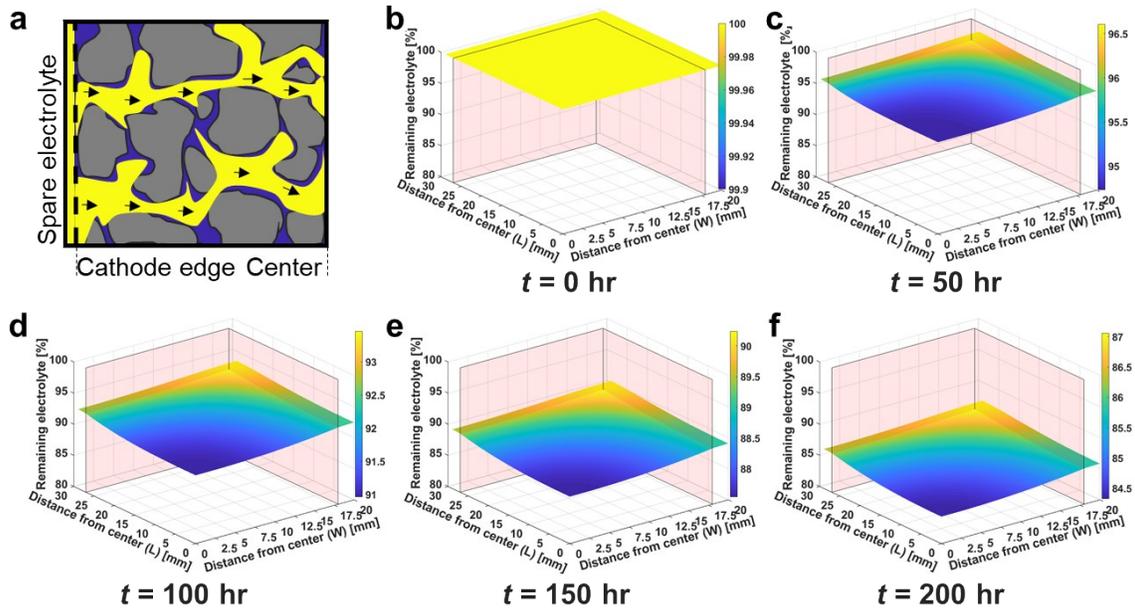
Fig. S8 Simulation of electrolyte diffusion and redistribution along the large electrode with low tortuosity cathode. (a) Schematic illustration of electrolyte diffusion through pores of the cathode. The color from yellow to dark blue corresponds to the electrolyte content (%) filling in the electrode from high to low. (b) t = 0 hr. (c) t = 50 hr. (d) t = 100 hr. (e) t = 150 hr. (f) t = 200 hr.
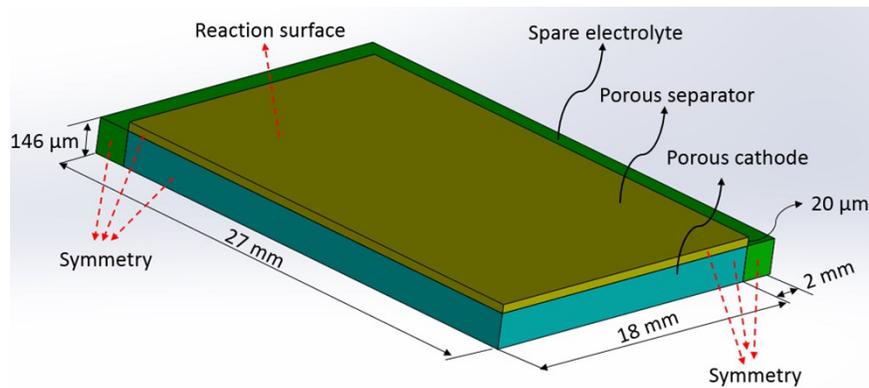

Fig. S9 Schematic illustration of the simulation model.