Supporting Information

Lithium-Sulfur Full Cell with Ultralong Cycle Life: Influence of Cathode Structure and Polysulfide Additive

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Structural Characterization of DUT-107 and DUT-107/S composite:

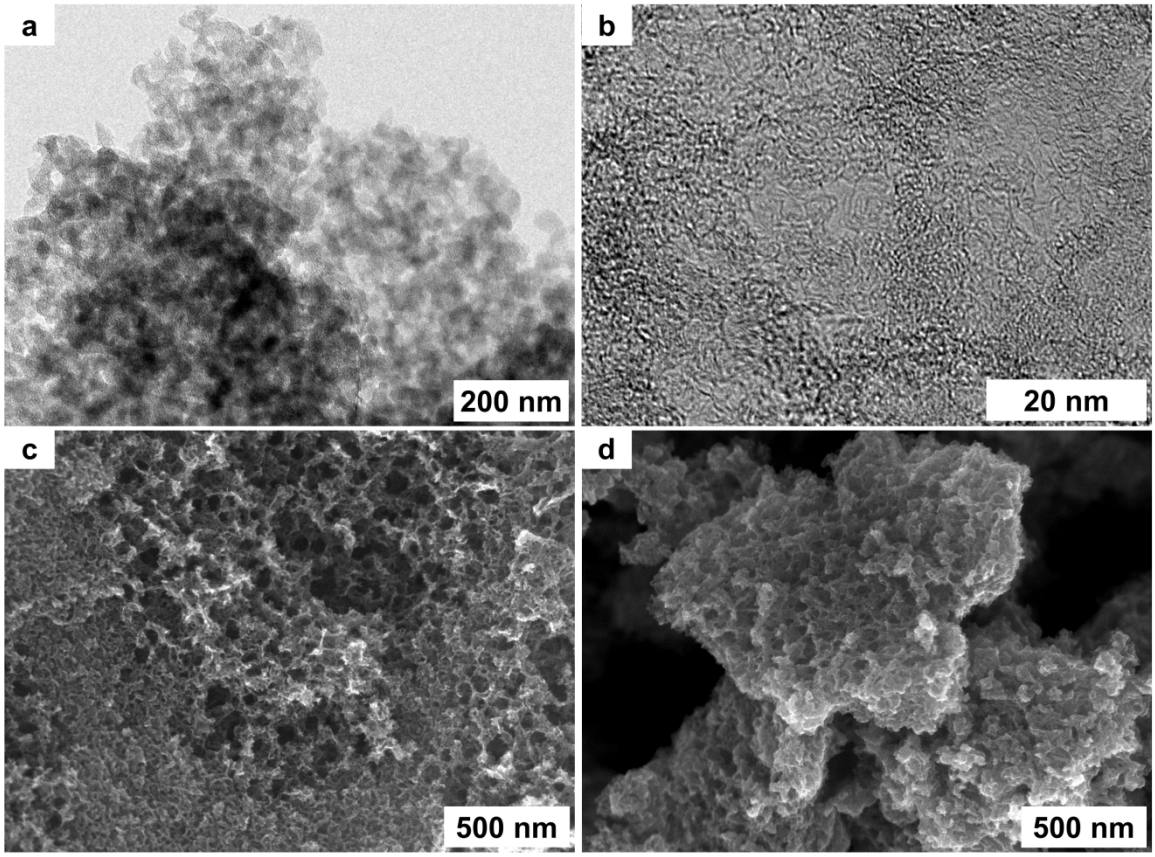

Figure S1. (a) Representative TEM image of silica-template. (b) HR-TEM image of DUT-107. (c,d) Representative SEM image of DUT-107 and DUT-107/S composite.

Structural Characterization of DUT-107/S cathodes:

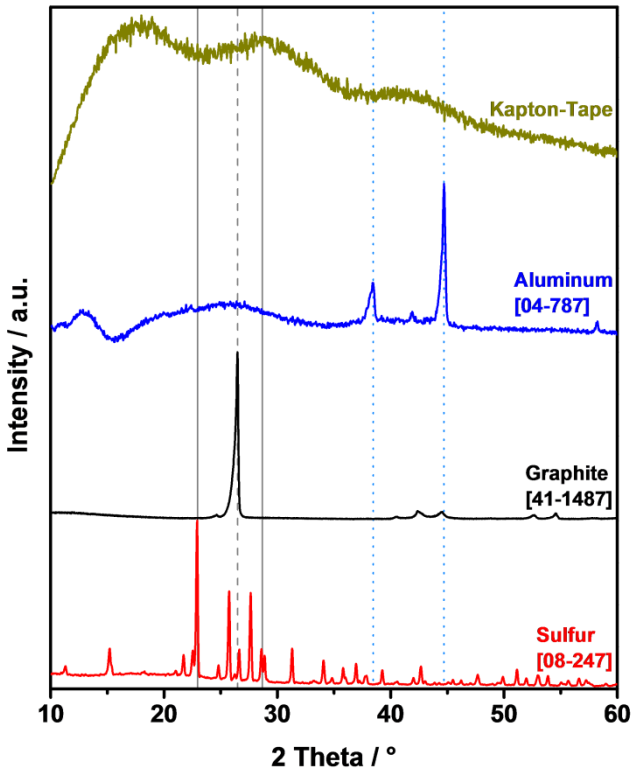

Figure S2. Reference XRD pattern of sulfur, graphite, one-sided primer-coated aluminum current collector and Kapton-Tape. The vertical lines correspond to sulfur (solid), graphite (dashed) and aluminum (dotted), respectively.

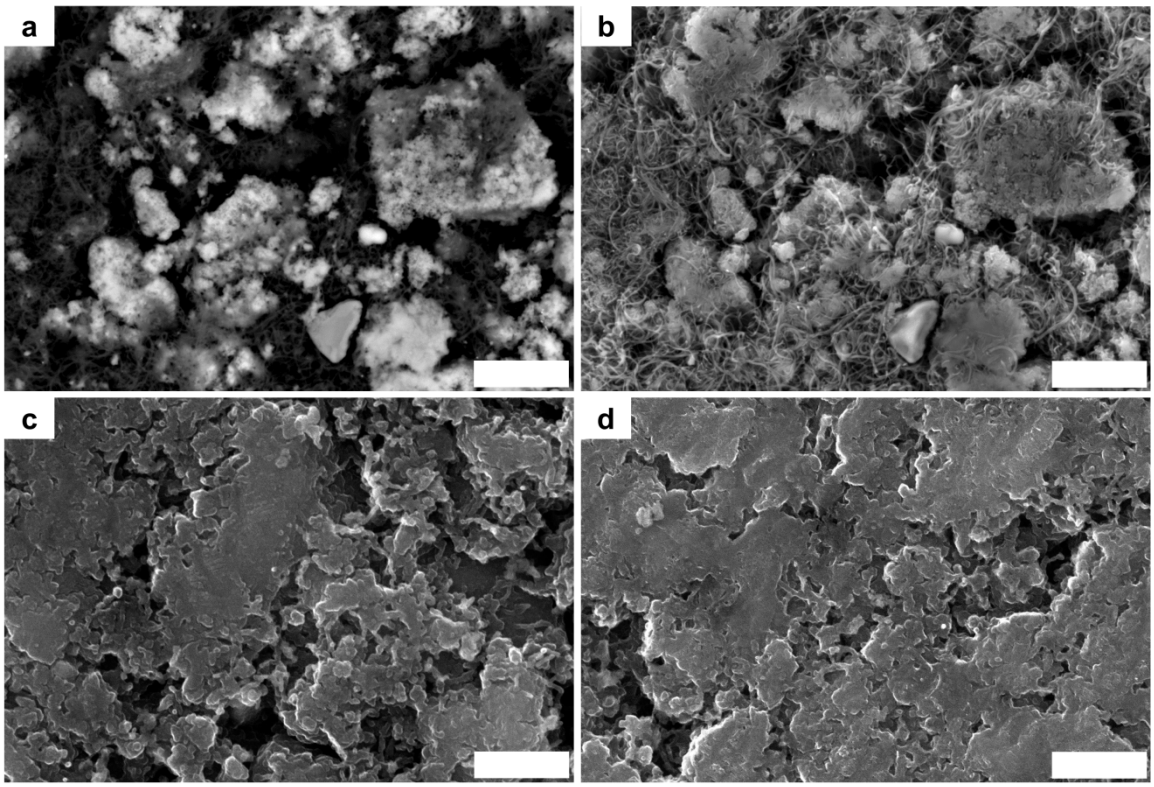

Figure S3. (a,b) SEM images of the as-prepared DUT-107/S cathode recorded using BSE and SE detector, respectively. (c,d) SEM images of discharged DUT-107/S cathodes cycled with reference electrolyte (R-E) and polysulfide electrolyte (PS-E), respectively. Scale bars: 2 μm.

Physicochemical Properties of Electrolytes and Electrochemical Characterization of DUT-107/S cathodes:

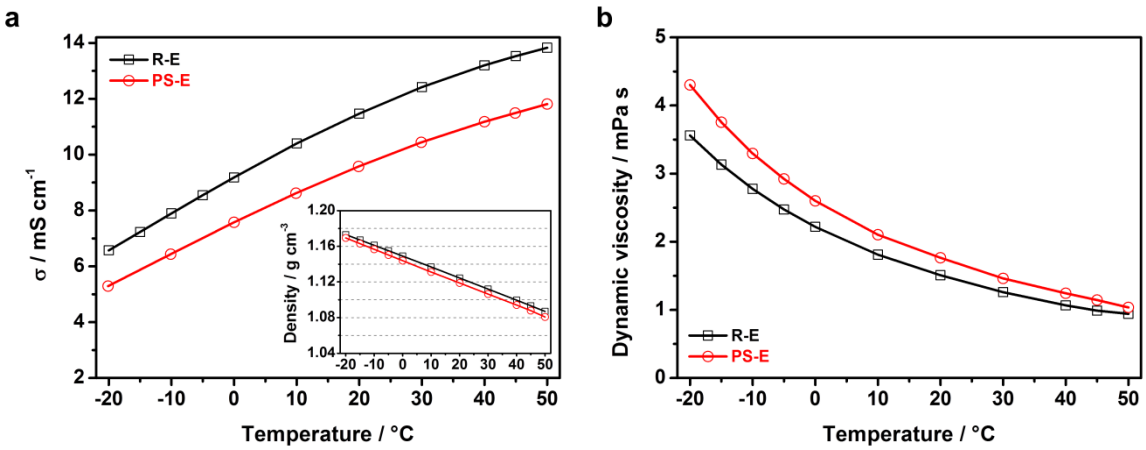

Figure S4. (a,b) Ionic conductivities as well as dynamic viscosities of both reference electrolyte (R-E; 1 M LiTFSI + 0.25 M $LiNO_3$ in DME/DOL) and polysulfide electrolyte (PS-E; 0.8 M LiTFSI + 0.25 M $LiNO_3$ + 0.15 M Li_2S_6 in DME/DOL). The inset shows the density of R-E and PS-E.

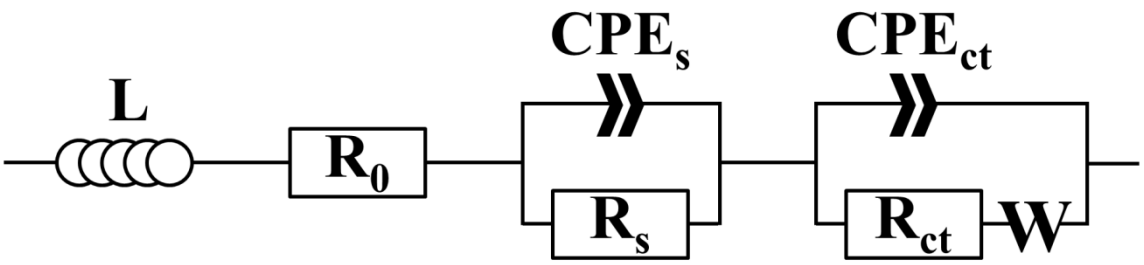

Figure S5. Equivalent circuit used for fitting of both Li-S half cells and LiHC@GDL-S full cells in charged and discharged state, respectively.

Table S1. Resistance data obtained by fitting EIS spectra of Li-S half cells as well as LiHC@GDL-S full cells in a frequency range of 100 kHz to 1 Hz.

Sample	Cycle	Voltage / V	R_0 / Ω	R_s / Ω	R_{ct} / Ω	Fit quality / χ^2
Li-S R-E	2	1.80	0.13	9.94	9.11	0.0053
Li-S R-E	2	2.60	0.96	1.73	8.66	0.0088
Li-S R-E	50	1.80	3.17	6.37	19.74	0.0100
Li-S R-E	50	2.60	3.29	3.67	9.96	0.0099
Li-S PS-E	2	1.80	0.93	20.07	5.39	0.0063
Li-S PS-E	2	2.60	3.24	1.22	6.04	0.0081
Li-S PS-E	50	1.80	2.77	4.94	30.61	0.0092
Li-S PS-E	50	2.60	3.23	3.58	11.05	0.0093
LiHC@GDL-S R-E	2	0.80	2.42	4.14	12.52	0.0046
LiHC@GDL-S R-E	2	2.60	2.91	5.58	16.03	0.0270
LiHC@GDL-S R-E	4101	0.80	5.97	18.57	15.16	0.0160
LiHC@GDL-S R-E	4101	2.60	7.05	17.85	7.32	0.0340
LiHC@GDL-S PS-E	2	0.80	1.00	4.51	16.15	0.0073
LiHC@GDL-S PS-E	2	2.60	1.02	11.22	21.01	0.0240
LiHC@GDL-S PS-E	4101	0.80	8.95	29.56	49.63	0.0230
LiHC@GDL-S PS-E	4101	2.60	9.26	23.18	6.03	0.0450

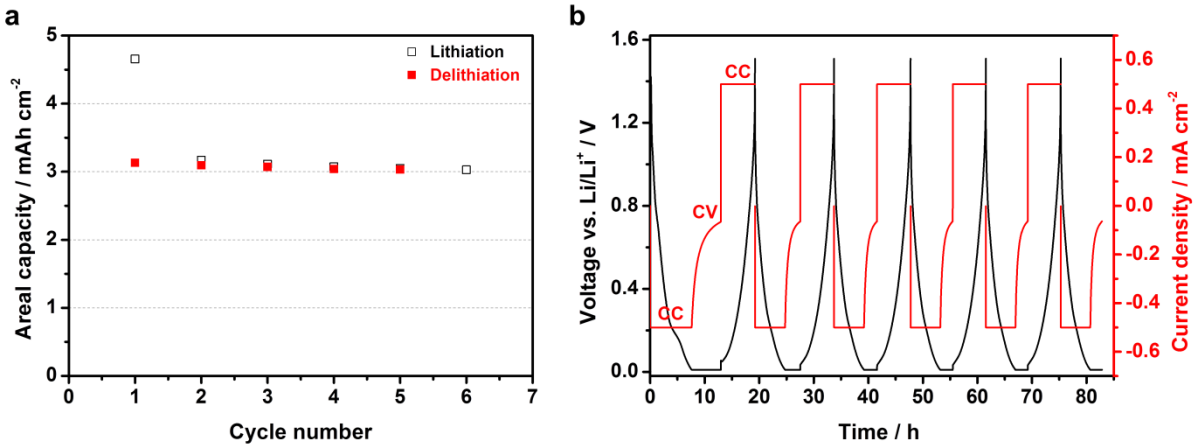

Figure S6. (a) Areal capacity of HC@GDL measured in prelithiation process. (b) Corresponding voltage profile as well as current density profile applied for electrochemical prelithiation.

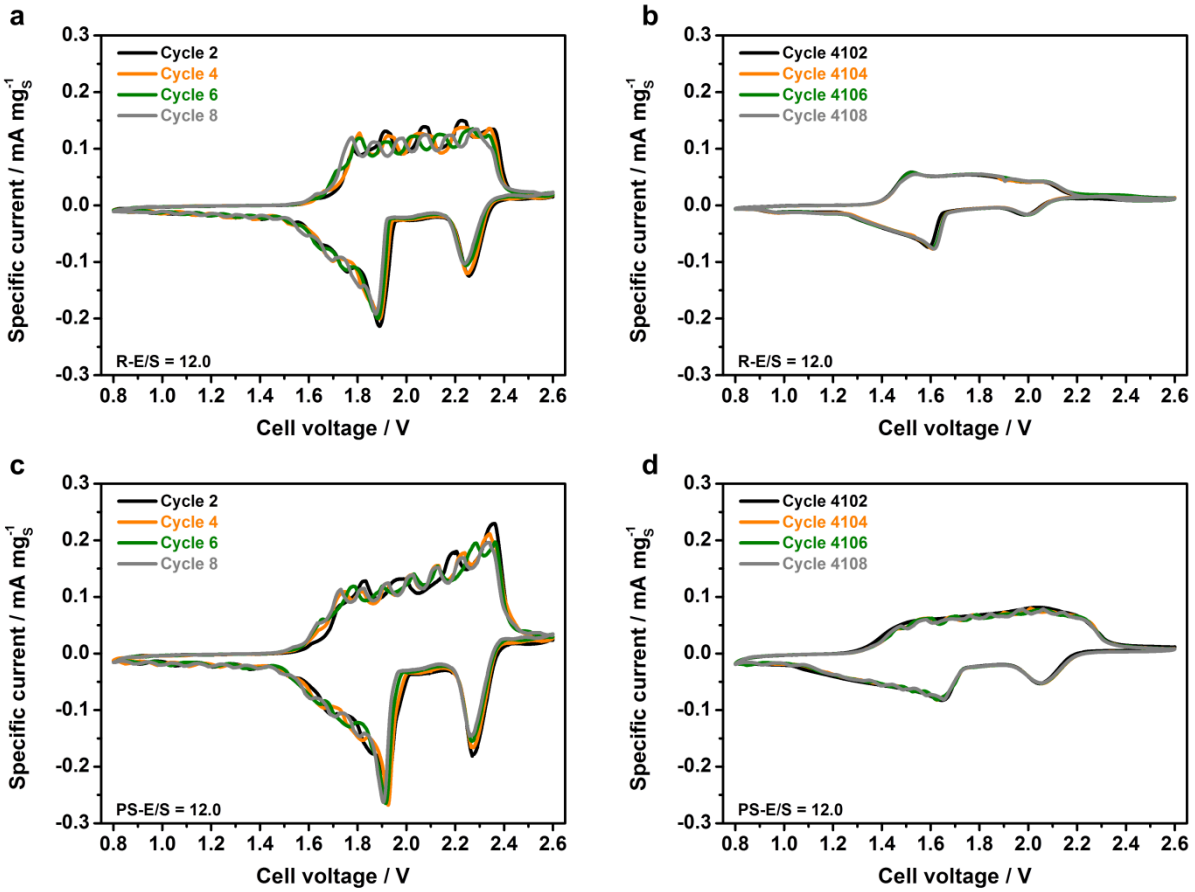

Figure S7. (a,b) CV plots of DUT-107/S cathodes cycled with reference electrolyte (R-E; E/S = 12.0 $\mu L_{R\text{-}E}$ $mg^{-1}{}_S$) for a fresh full cell (vs. LiHC@GDL) as well as after prolonged cycling of the full cell. (c,d) CV plots of DUT-107/S cathodes cycled with polysulfide electrolyte (PS-E; E/S = 12.0 $\mu L_{PS\text{-}E}$ $mg^{-1}{}_S$) for a fresh full cell as well as after prolonged cycling of the full cell.