Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

Mesoporous carbon host material for stable lithium metal anode

Jooyoung Jeong, Jinyoung Chun, Won-Gwang Lim, Won Bae Kim, Changshin Jo* and Jinwoo Lee*

Experimental section

Preparation of mesoporous carbon & material characterization

CMK-3 was synthesized using a hard template method with SBA-15 mesoporous silica as template.[1] The SBA-15 silica was synthesized as described previously.[2] For synthesis of CMK-3, 0.008 g of oxalic acid (anhydrous, 99%, Fluka) was dissolved in 2 mL of furfuryl alcohol (98%, Aldrich) and stirred for 5 min. The resulting solution was poured on 2 g of SBA-15 and mixed. The mixture of silica and carbon precursor was moved to a round-ball-flask (r.b.f) and dried under vacuum for 30 min. The r.b.f with mixture was moved to an oven and held at 85 °C for 8 h to polymerize the furfuryl alcohol. Then the mixture was heated in a furnace at 850 °C in Ar atmosphere; the result was a black silica-carbon composite. The composite was etched using 1.5 M HF solution to remove the silica, then washed, dried overnight at 85 °C in an oven to yield mesoporous carbon.

To characterize materials, N_2 sorption isotherm analysis (Micromeritics, Tristar II 3020), scanning electron microscope (SEM) (Hitachi, S-4800), and transmission electron microscope (TEM) (FEI, Tecnai F20) were used.

Electrochemical test

For the fabrication of anode, slurry was prepared by mixing a carbon (CMK-3 or MSP-20 (Kansai Coke and Chemicals, Japan)) with poly(vinylidene fluoride) (PVdF) binder in 9:1 weight ratio with N-methyl-2-pyrrolidone (NMP) as solvent. Each slurry was coated on Cu foil, then dried overnight at 110 °C under vacuum. Loading mass of both MSP-20 and CMK-3 was targeted to 0.66 mg cm^{-2}.

For the electrochemical half-cell test of Cu foil, MSP-20, and CMK-3, CR 2032-type coin cells were assembled in the glove box using prepared electrodes as working electrode, and Li metal foil as the counter-electrode. All electrolytes were purchased from Panax Etec.

Electrolyte composition for the half-cell test was 1 M lithium hexafluorophosphate ($LiPF_6$) dissolved in ethyl methyl carbonate (EMC) and fluoroethylene carbonate (FEC) (volume ratio 7:3). As a separator, Celgard 2325 was used. Electrochemical test condition was current density = 1 mA cm^{-2}, capacity cut = 1 ~ 2.5 mA h cm^{-2}, and voltage cut = −0.2 ~ 0.2 V. To run a Cu foil half-cell, the voltage cut of the first Li plating was changed to −0.4 V to obtain stable Li nucleation.

For the full-cell test, a Li-S battery system was applied. To fabricate the cathode, sulfur and reduced graphene oxide (rGO) composite were mixed in 7:3 weight ratio, followed by heat treatment at 155 ^{o}C for 1 h. After then, S-rGO was mixed with PVdF binder (9:1 weight ratio) with NMP solvent. The slurry was spread on carbon-coated Al foil. As an electrolyte, 20 μL of 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in dimethoxy ethane (DME)-1,3-dioxolane (DOL) (volume ratio 1:1) with 2% $LiNO_3$ additive was applied. For the full-cell test, Li metal was electrochemically plated on electrodes by using a half-cell, then used as the anode in the full cell. Test condition was rate = 0.5 C (1 C = 1672 mA h g^{-1}) with voltage cut = 1.7 ~ 2.8 V. Loading mass of sulfur and rGO composite was targeted to 1 mg cm^{-2}. Voltage cut = 1.7 ~ 2.8 V. Loading mass of sulfur and rGO composite was targeted to 1 mg cm^{-2}. For more detail, we targeted to fix E/S ratio ~30 and N/P ratio ~4 in each full-cells.

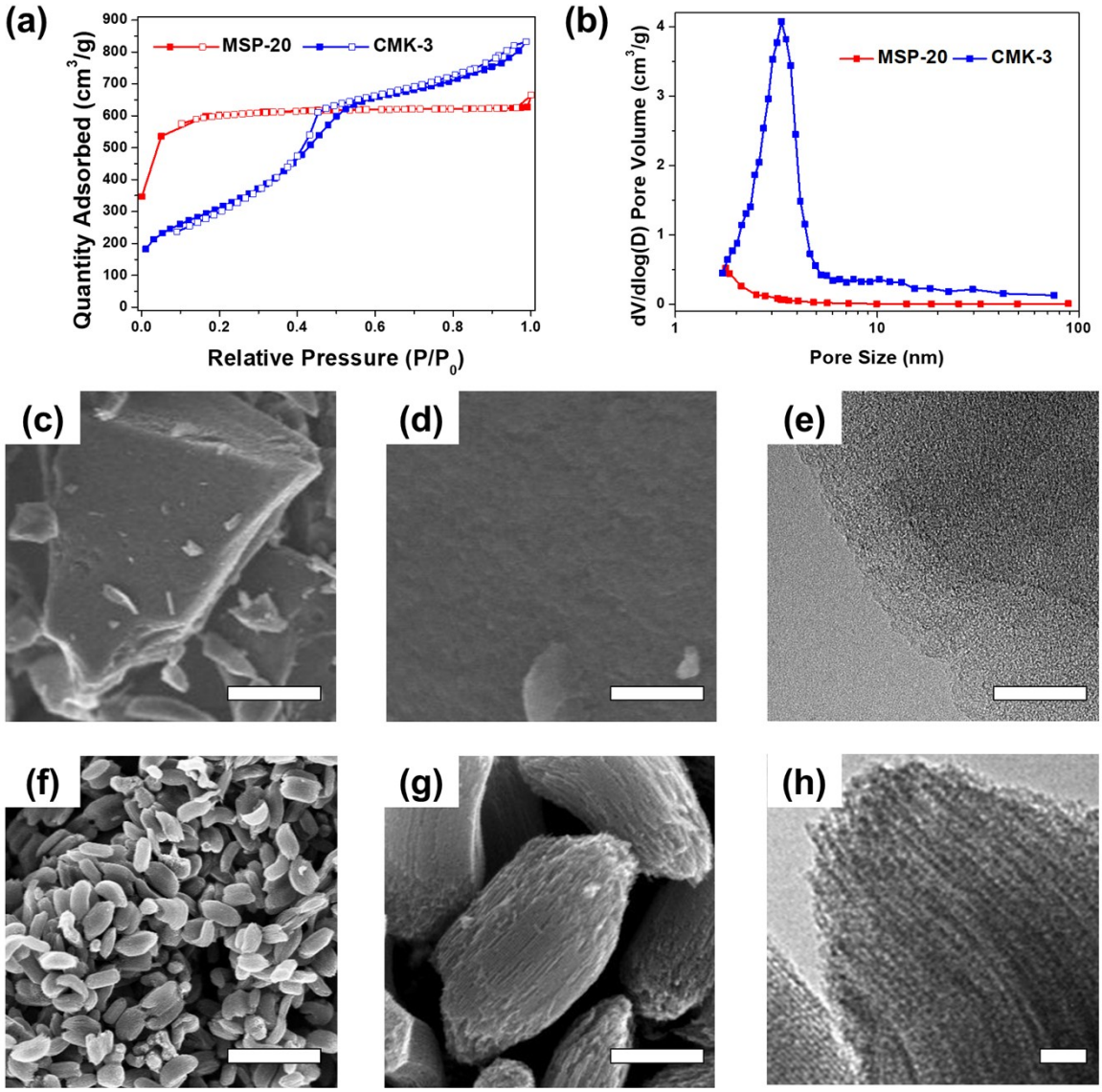

Fig. S1 N_2 physisorption isotherm result of MSP-20 and CMK-3:(a) quantity adsorbed and (b) pore size distribution. SEM images of (c), (d) MSP-20, and (f), (g) CMK-3 at (c), (h) low magnification (scale bar: 2 μm) and (e) high magnification (scale bar: 300 nm). TEM images of (e) MSP-20 and (h) CMK-3 (scale bar: 40 nm).

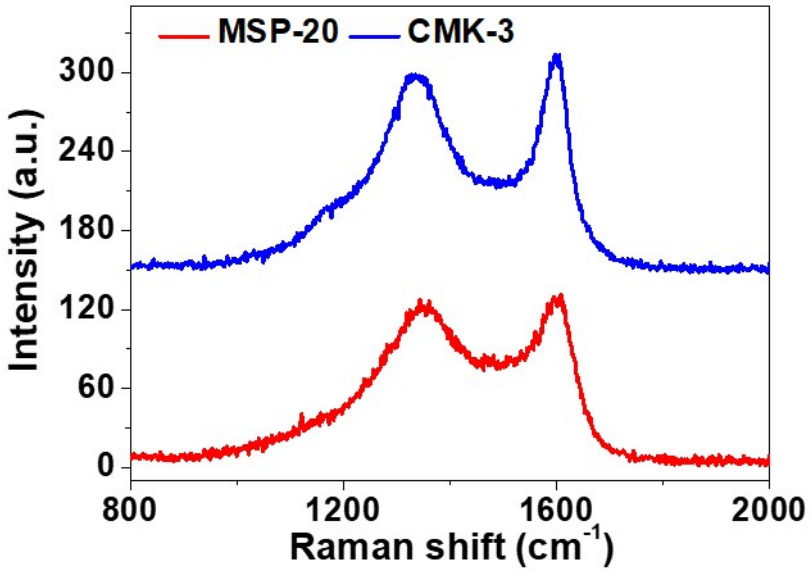

Fig. S2 Raman spectra of MSP-20 and CMK-3.

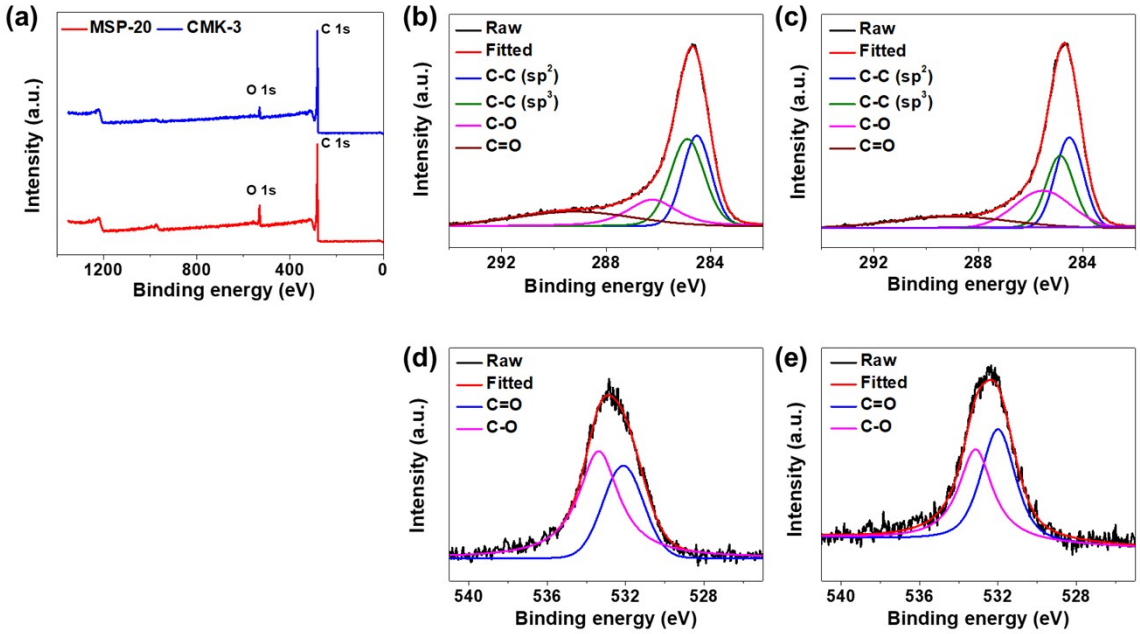

Fig. S3 XPS spectra of two carbon host materials. (a) Survey, (b),(c) C 1s spectra, and (d),(e) O 1s spectra of (b),(d) MSP-20, and (c),(e) CMK-3.

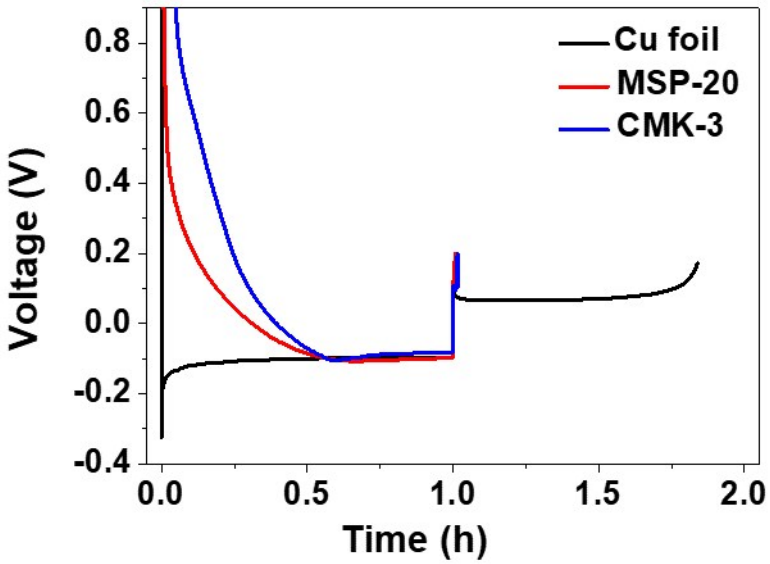

Fig. S4 First half cell cycle (voltage profile vs time) of Cu foil, MSP-20, and CMK-3 at rate = 1 mA cm^{-2}, capacity cut = 1 mA h cm^{-2} with 1 M $LiPF_6$ in EMC-FEC electrolyte.

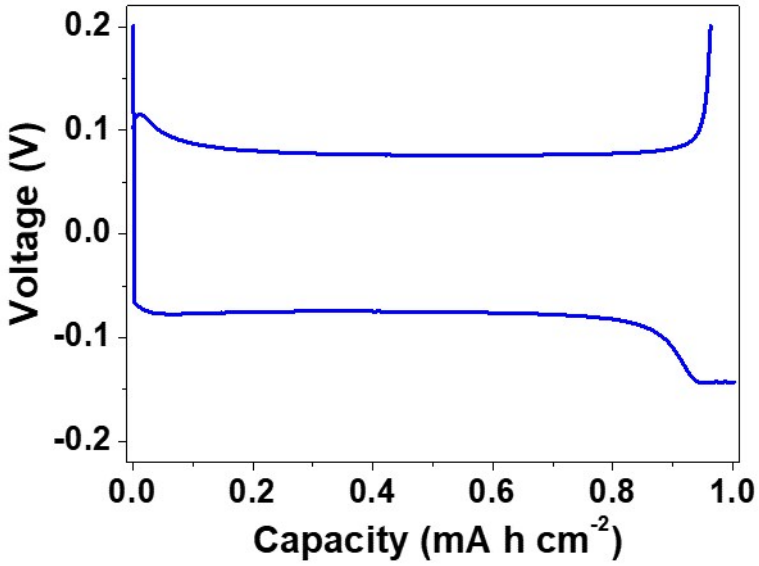

Fig. S5 Voltage profile of CMK-3 at rate = 1 mA cm^{-2}, capacity cut = 1 mA h cm^{-2} with 1 M $LiPF_6$ in EMC-FEC electrolyte at 200th cycle.

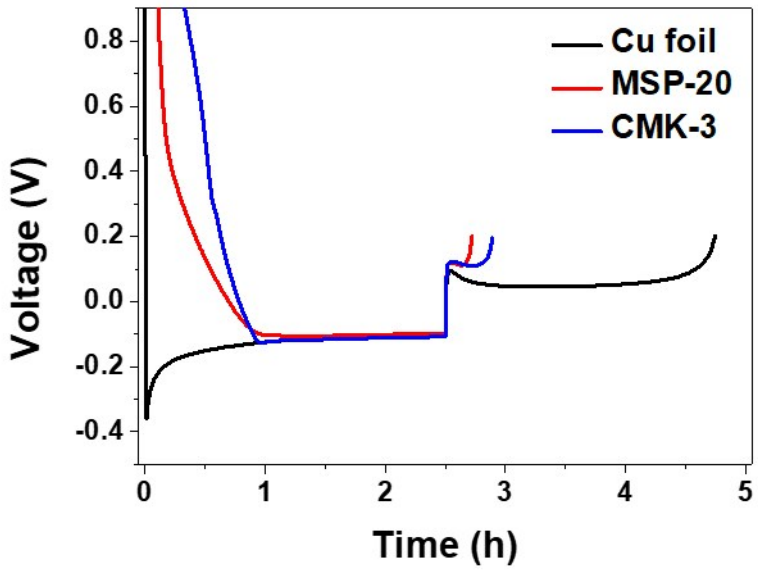

Fig. S6 First half cell cycle (voltage profile vs time) of Cu foil, MSP-20, and CMK-3 at rate = 1 mA cm^{-2}, capacity cut = 2.5 mA h cm^{-2} with 1 M $LiPF_6$ in EMC-FEC electrolyte.

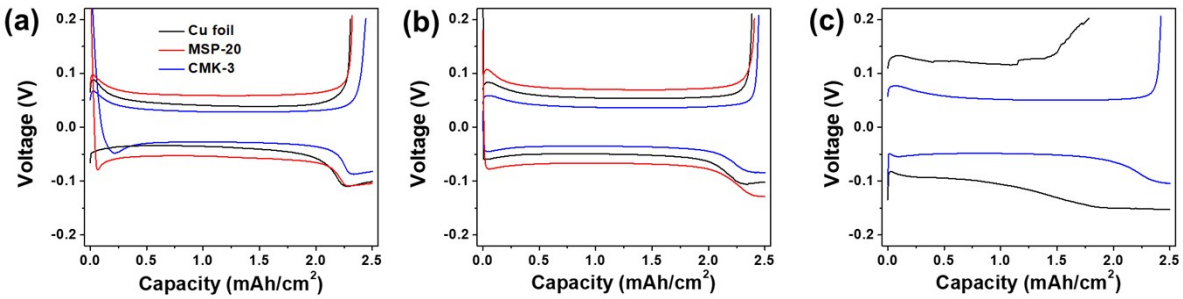

Fig. S7 Voltage profile of Cu foil, MSP-20, and CMK-3 at rate = 1 mA cm^{-2}, capacity cut = 2.5 mA h cm^{-2} with 1 M $LiPF_6$ in EMC-FEC electrolyte at (a) 10^{th}, (b) 25^{th}, and (c) 50^{th} cycle.

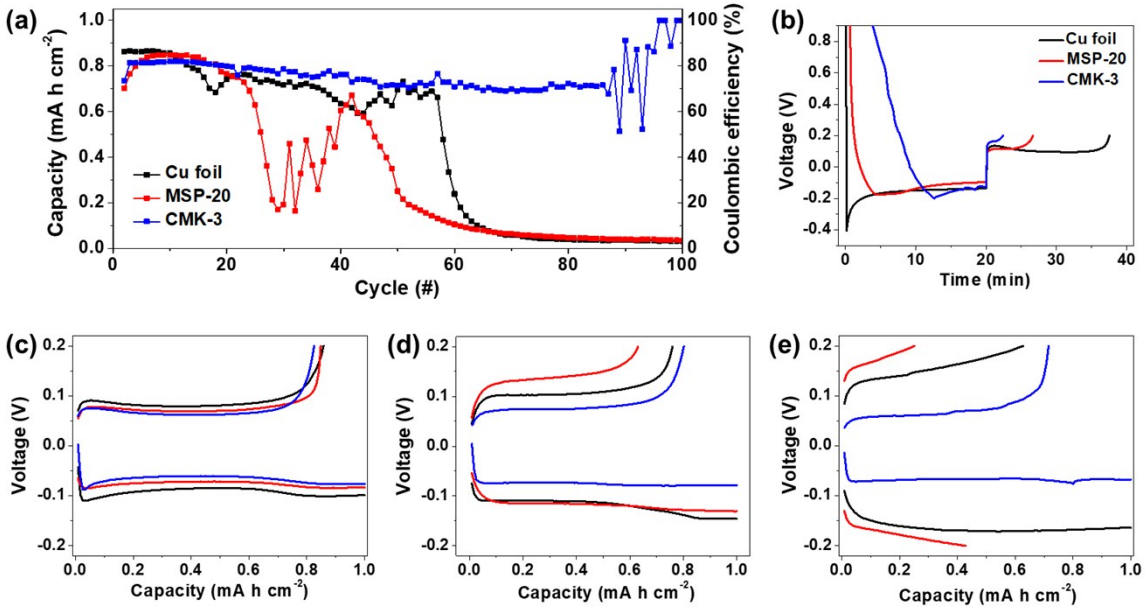

Fig. S8 Electrochemical test result of Cu foil, MSP-20, and CMK-3 at rate = 3 mA cm^{-2}, capacity cut = 1 mA h cm^{-2} with 1 M $LiPF_6$ in EMC:FEC=7:3 electrolyte. (a) Cycle stability from second cycle, voltage profile of (b) initial cycle versus time, and voltage profiles versus capacity at (c)10^{th}, (d) 25^{th}, and (e) 50^{th} cycle.

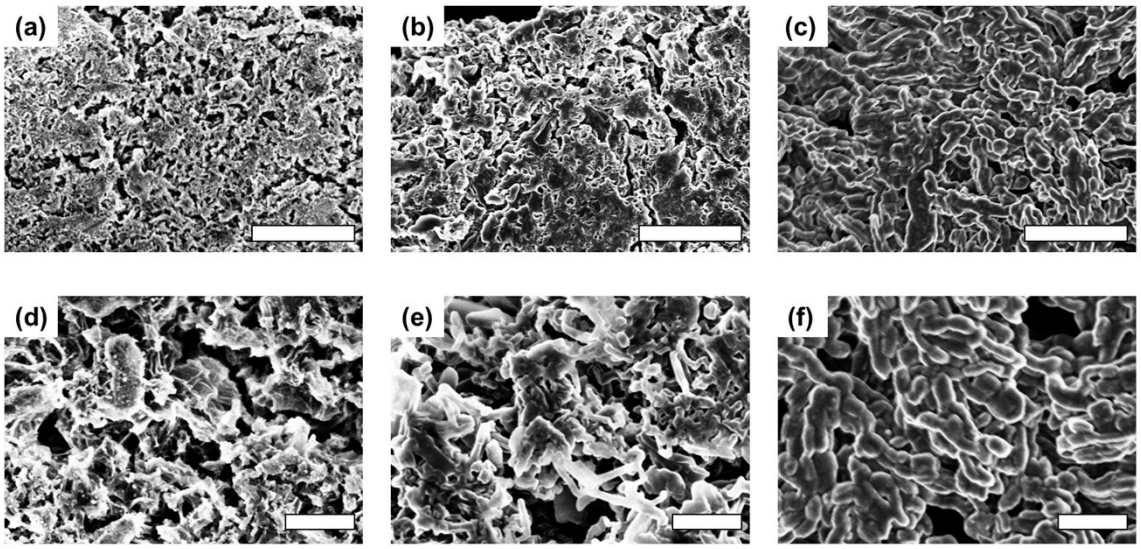

Fig. S9 SEM images of (a), (d) Cu foil, (b), (e) MSP-20, and (c), (f) CMK-3 at rate = 3 mA cm^{-2}, capacity cut = 1 mA h cm^{-2} with 1 M $LiPF_6$ in EMC:FEC=7:3 electrolyte for 50 cycles. (a)-(c) At low magnification (scale bar: 5 μm), and (d)-(f) at high magnification (scale bar: 1 μm)

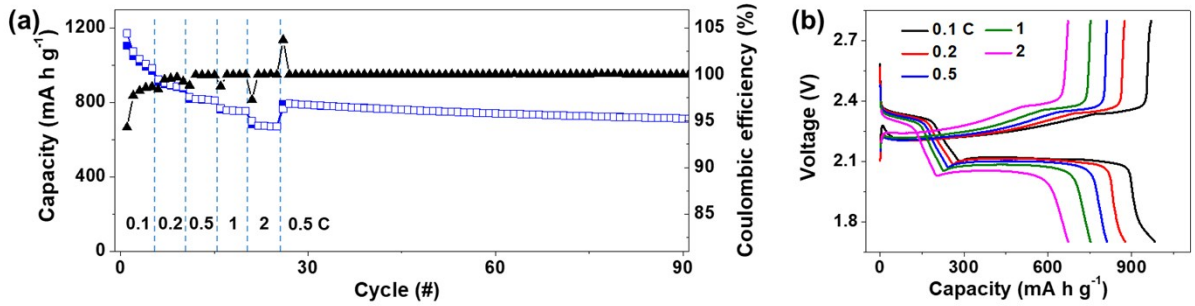

Fig. S10 (a) Li-S battery rate test using S-rGO cathode and Li-plated (2.5 mA h cm^{-2}) CMK-3 with 1 M LiTFSI in DME-DOL + 2% $LiNO_3$ electrolyte and (b) voltage profile at 0.1, 0.2, 0.5, 1, and 2 C rate.

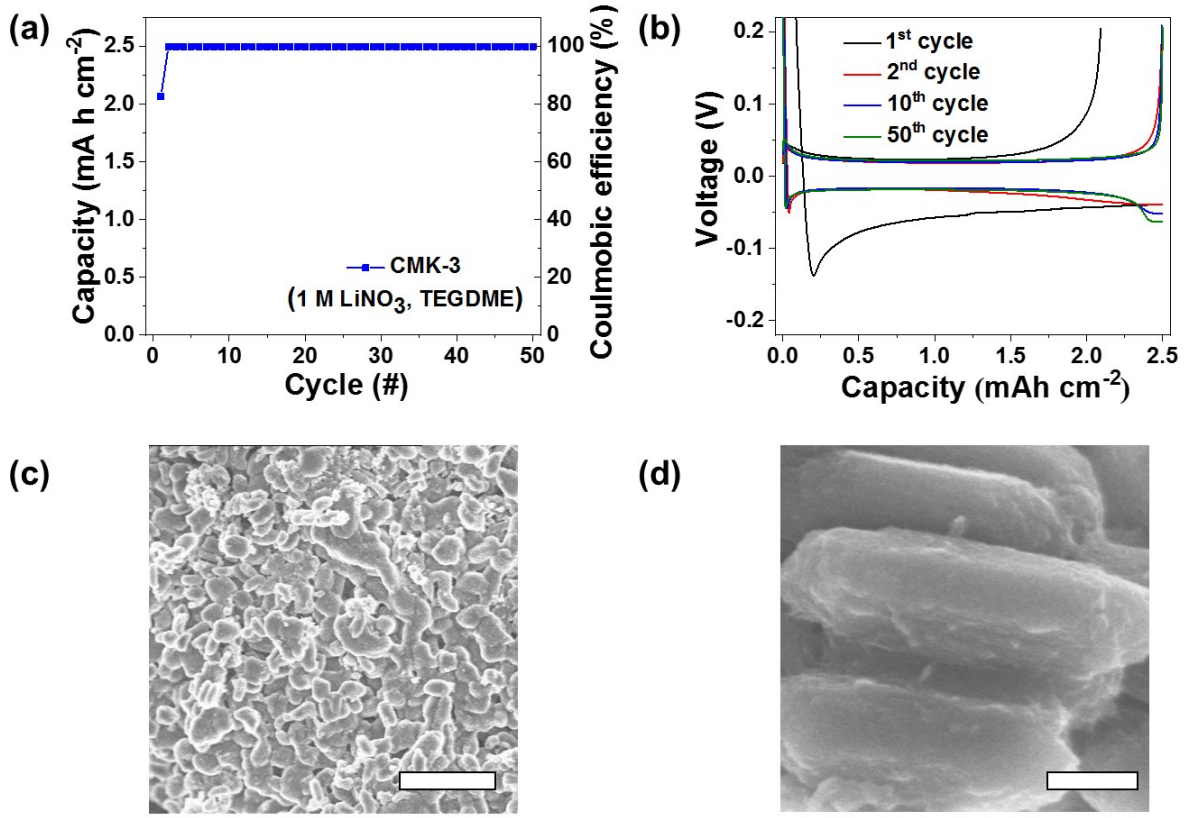

Fig. S11 (a) Cycle stability and (b) voltage profile at 1st, 2nd, 10th, and 50th cycle of CMK-3 at rate = 1 mA cm^{-2}, capacity cut = 2.5 mA h cm^{-2} with 1 M $LiNO_3$ in TEGDME electrolyte.SEM images of (c) at low magnification (scale bar: 2 μm), (d) and high magnification (scale bar: 200 nm) after 50th Li plating for 2.5 mA h cm^{-2}.

References

1. S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 2000, **122**, 10712-10713.
2. D. Margolese, J. Melero, S. Christiansen, B. Chmelka and G. Stucky, *Chem. Mater.*, 2000, **12**, 2448-2459.