Supplementary material

Synthesis of Ordered Mesoporous Silica: KIT-6. The ordered mesoporous silica with a cubic *Ia3d* mesostructure, KIT-6, was synthesized as described in a previous report.[1,2] Pluronic triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$, MW = 5,800) was utilized as the structure-directing agent for the synthesis of KIT-6. Typically, 90.0 g of P123 was dissolved in a mixture of 3255 g of distilled water, 90 g of 1-BuOH (99.7 wt%, Aldrich), and 177 g of c-HCl (35 wt%, Aldrich). After stirring at 35 °C for 10 min, 193.5 g of tetraethylorthosilicate (98 wt%, TEOS, Aldrich) was added to this solution under vigorous stirring. The resulting mixture was stirred for 24 h at 35 °C and subsequently kept immobile at 100 °C for 24 h in an oven. The solid product was filtered, washed with doubly distilled water, and dried at 100 °C overnight. The white powder thus obtained was washed with EtOH, dried at 80 °C for 12 h, and finally calcined under static air conditions at 550 °C for 3 h to remove the structure-directing agent.

Synthesis of Ordered Mesoporous Carbon (OMC). The procedure for the synthesis of OMC materials is the same as the nano-replication method published elsewhere.[3–5] A precursor solution containing 3.0 g of distilled water, 3.75 g of sucrose (reagent grade, Aldrich), and 0.423 g of sulfuric acid (95%, Samchun) was infiltrated into the mesopores of 3.0 g of KIT-6. The composite material was dried at 100 °C for 6 h and subsequently at 160 °C for 6 h. The infiltration and drying process was repeated once more with an additional 66 wt% precursor solution of the first infiltration. Then, the composite was carbonized at 900 °C for 5 h under N_2 flow. Finally, the OMC was obtained by removing the inorganic framework using an HF solution, followed by several filtrations and washing with distilled water.

Infiltration of Sulfur into OMC. Infiltration of sulfur within the mesopores of OMC (*i.e.*, S/OMC composite) was performed by a melt-assisted diffusion procedure. 0.5 g of the OMC material was mixed with specific quantities of sulfur (99.5 %, Samchun), and the mixture was ground for 10 min, leading to sulfur loadings of 10, 20, 30, 35, 40, 50, 60, 70, 80, and 90 wt%. Afterward, the mixture was heated at 160 °C for 24 h in closed vessels, thereby improving the sulfur distribution within the mesopores of the OMC material *via* capillary diffusion.

Material Characterization. Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku X-ray diffractometer (D/MAX Ultima IV) with Cu Kα radiation at 30 kV and 40 mA. N_2 adsorption–desorption isotherms were collected on a Micromeritics Tristar ASAP 3020 system at liquid N_2 temperature, after degassing the samples at room temperature for 24 h to avoid sublimation of the sulfur in nanopores. The specific Brunauer–Emmett–Teller (BET) surface areas were calculated from the adsorption branches in the range of relative pressure (p/p_0) = 0.05–0.20, and the pore size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method using the adsorption branch. The total pore volumes were measured at p/p_0 = 0.99. The morphology of the samples was observed by SEM using a JSM-7100F FE-SEM (JEOL) operating at 15 kV.

Electrochemical Measurement. The electrodes were prepared by coating the slurries composed of 35 wt% S/OMC (70 wt %), a conductive agent (Super-P, MMM, 10 wt %), and polyvinylidene fluoride (PVDF, Kureha, 20 wt %) dissolved in N-methyl pyrrolidone (NMP, Aldrich, 99.5 %) on the Al foil substrate. After coating, the electrodes were dried at 50 ℃ for 24 h under vacuum. Each electrode was assembled using a coin-type half cell (CR2032) with Li metal as the counter and reference electrode in a dry room, and a polyethylene (PE) membrane was used as a separator. 1 M LITFSI dissolved in a mixed solvent of dimethyl ether (DME) and dioxolane (DOL) (1:1, v/v; Panax Etec Co. Ltd.) with 0.3 M $LiNO_3$ was used as an additive for the electrolyte. The galvanostatic charge–discharge experiments were carried out with a WBCS-3000 battery cycler (WonATech, Korea) at a constant current of 0.1 C (theoretical capacity of 1675 $mAh \cdot g^{-1}$ for sulfur).

Operando SAXS Measurement. The *operando* SAXS experiments were performed at the BL 9A U-SAXS beamline (PLS-II) using a 2D CCD Detector (Rayonix SX165, USA), which was positioned 2 m away from the sample and measured scattering in the 2θ range of 0.3–2.5 (λ = 1.54 Å). The focused beam was 300 μm in diameter, and the energy of the beam was 11 keV. Electrochemical measurement patterns of the mesoporous samples during electrochemical cycling were recorded with a 1 s exposure time and 8 s detector readout time. The 2D patterns were scanned with the FIT2D software package to obtain the one-dimensional (1D) patterns in the form of intensity vs. 2θ. The storage ring was operated at 3.0 GeV with a ring current of 300 mA.

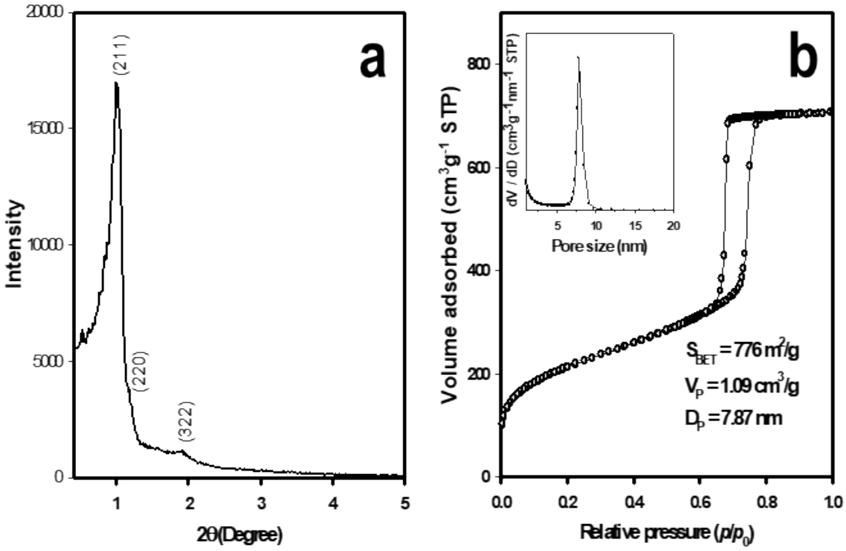


Fig. S1 (a) Small-angle X-ray scattering patterns; (b) N_2-adsorption–desorption isotherms; the pore size distribution was calculated by the BJH method (inset) for the KIT-6 template material.

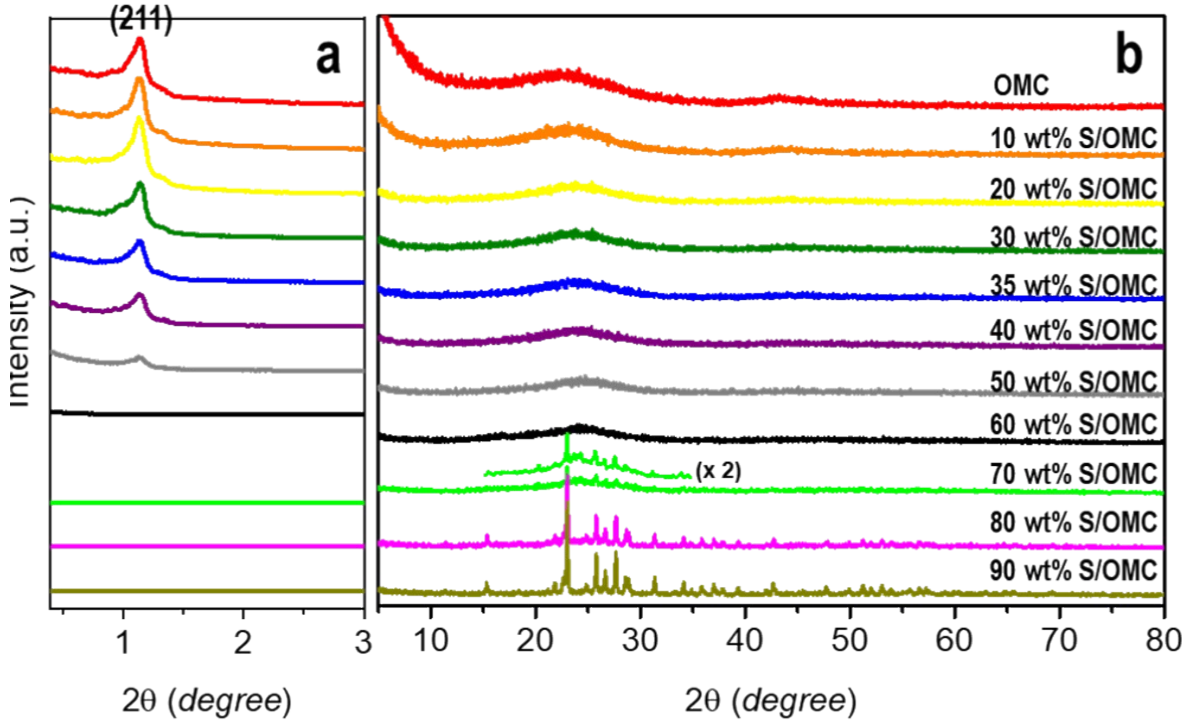


Fig. S2 (a) Small-angle X-ray scattering patterns; (b) wide-angle XRD patterns of OMC (red), 10 wt% S/OMC (orange), 20 wt% S/OMC (yellow), 30 wt% S/OMC (green), 35 wt% S/OMC (blue), 40 wt% S/OMC (purple), 50 wt% S/OMC (gray), 60 wt% S/OMC (black), 70 wt% S/OMC (light green), 80 wt% S/OMC (pink), and 90 wt% S/OMC (dark yellow).

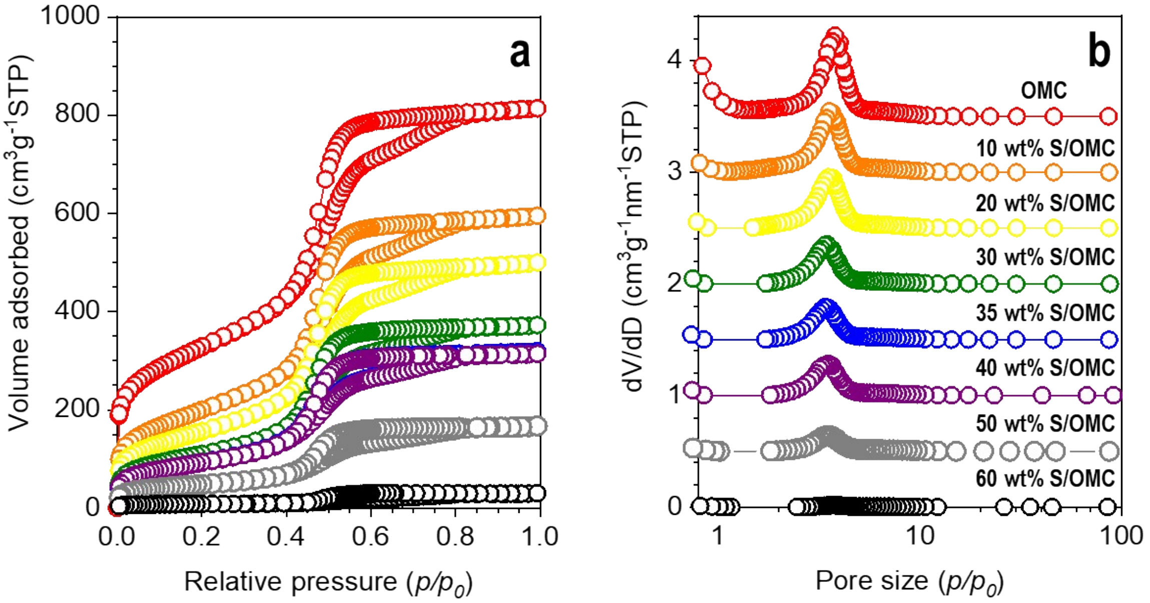
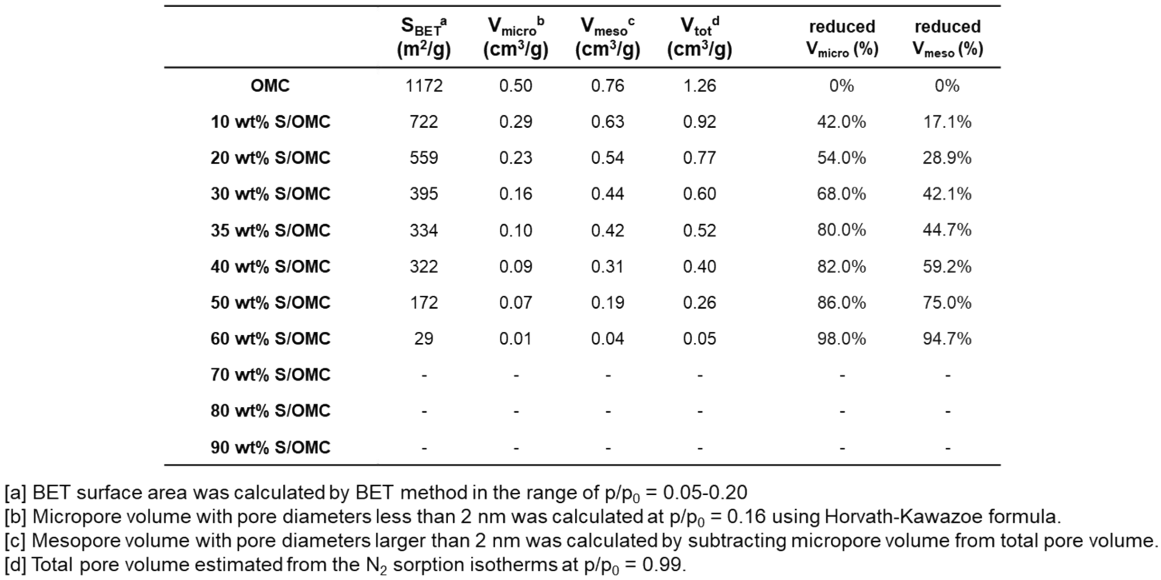


Fig. S3 (a) N_2-adsorption–desorption isotherms; (b) pore size distribution calculated by the BJH method for OMC (red), 10 wt% S/OMC (orange), 20 wt% S/OMC (yellow), 30 wt% S/OMC (green), 35 wt% S/OMC (blue), 40 wt% S/OMC (purple), 50 wt% S/OMC (gray), and 60 wt% S/OMC (black).



	S_{BET}[a] (m^2/g)	V_{micro}[b] (cm^3/g)	V_{meso}[c] (cm^3/g)	V_{tot}[d] (cm^3/g)	reduced V_{micro} (%)	reduced V_{meso} (%)
OMC	1172	0.50	0.76	1.26	0%	0%
10 wt% S/OMC	722	0.29	0.63	0.92	42.0%	17.1%
20 wt% S/OMC	559	0.23	0.54	0.77	54.0%	28.9%
30 wt% S/OMC	395	0.16	0.44	0.60	68.0%	42.1%
35 wt% S/OMC	334	0.10	0.42	0.52	80.0%	44.7%
40 wt% S/OMC	322	0.09	0.31	0.40	82.0%	59.2%
50 wt% S/OMC	172	0.07	0.19	0.26	86.0%	75.0%
60 wt% S/OMC	29	0.01	0.04	0.05	98.0%	94.7%
70 wt% S/OMC	-	-	-	-	-	-
80 wt% S/OMC	-	-	-	-	-	-
90 wt% S/OMC	-	-	-	-	-	-

[a] BET surface area was calculated by BET method in the range of $p/p_0 = 0.05$-0.20

[b] Micropore volume with pore diameters less than 2 nm was calculated at $p/p_0 = 0.16$ using Horvath-Kawazoe formula.

[c] Mesopore volume with pore diameters larger than 2 nm was calculated by subtracting micropore volume from total pore volume.

[d] Total pore volume estimated from the N_2 sorption isotherms at $p/p_0 = 0.99$.

Table. S1 Physical properties of OMC and S/OMCs.

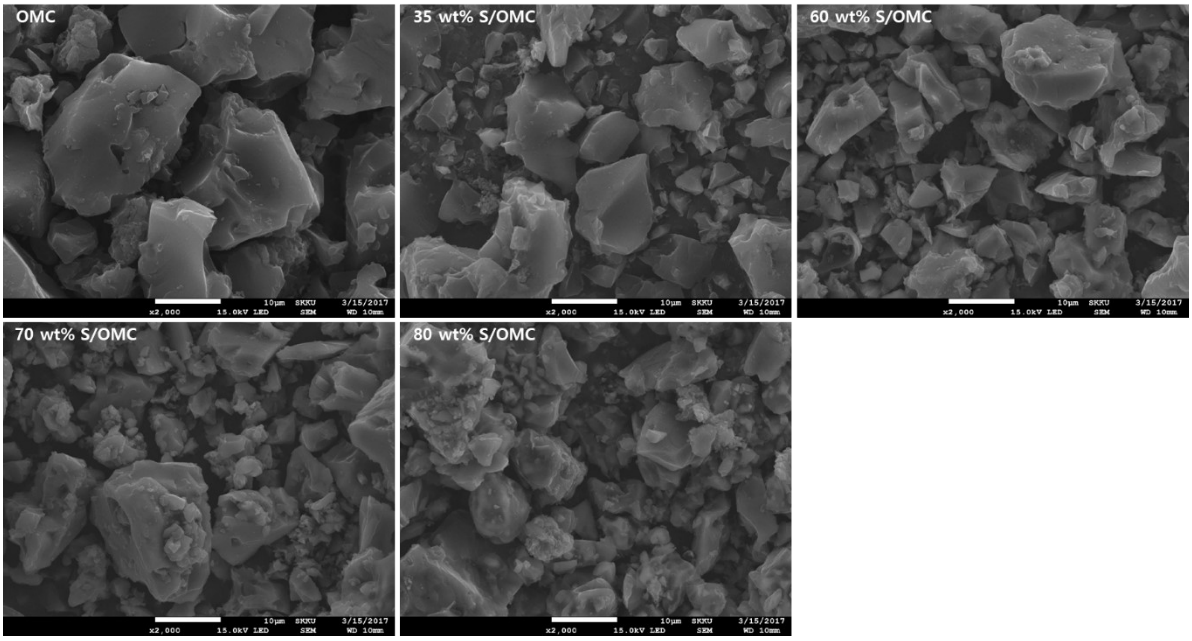


Fig. S4 SEM images of OMC, 35 wt% S/OMC, 60 wt% S/OMC, 70 wt% S/OMC, and 80 wt% S/OMC.

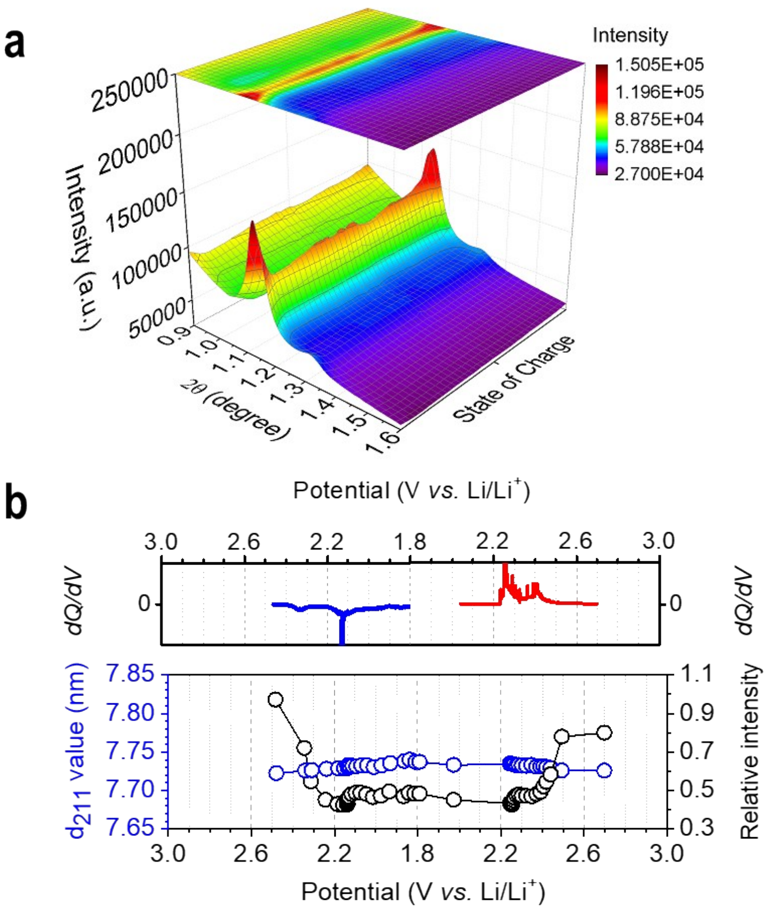


Fig. S5 (a) *Operando* SAXS spectra of 35 wt% S/OMC at 2nd cycle; (b) differential capacity *vs.* potential plot (dQ/dV) and the corresponding changes in lattice parameter and resolved peak intensity ratio calculated from the (211) reflection.

References

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