Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

Dual-spatially-confined Reservoir by Packing Micropores within Dense Graphene for Long-life Lithium/Sulfur Battery

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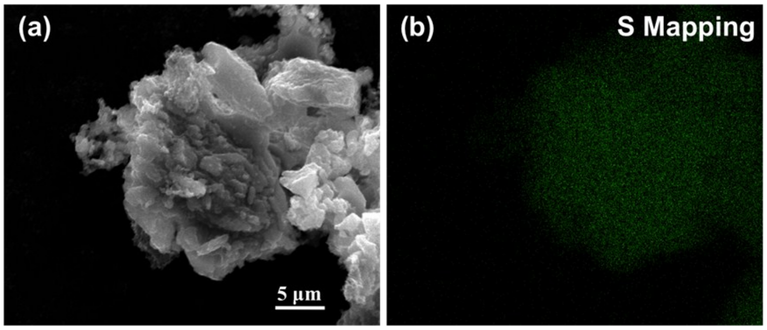

Fig. S1 (a) a selected area of S-micro@meso-porous DSC for Energy dispersive X-ray spectroscopy mapping analysis and (b) EDS elemental mapping result for S.

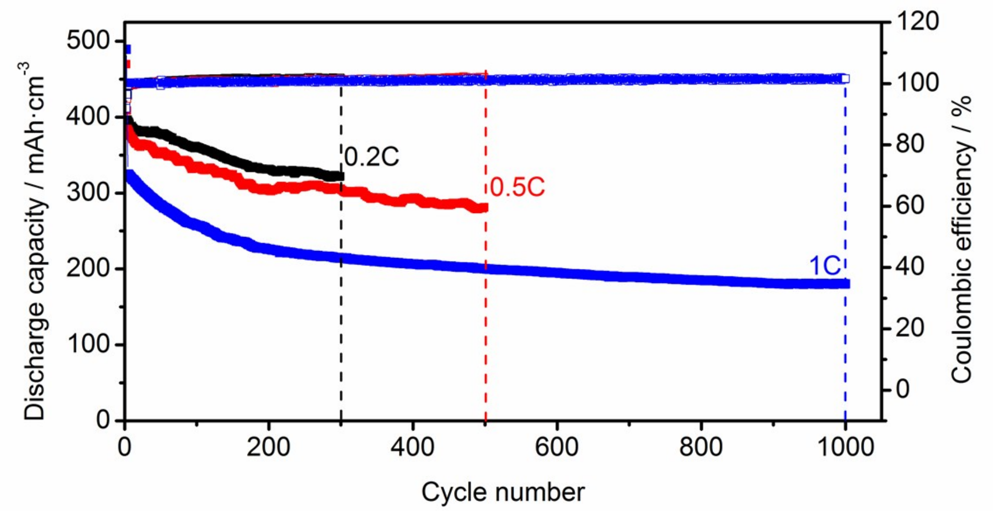

Fig. S2 Volumetric capacity profiles of S-micro@meso-porous DSC cells at 0.2C, 0.5C and 1C.

Comparison of dual-spatial porous carbon (DSC) with single-spatial carbon (SSC)

The micro@meso-porous DSC in main text was based on wrapping microporous carbon into dense graphene, developing a dual-spatial porous carbon. Herein, another SSC was carried out based on our previous work [1] to further demonstrate the advantage of DSC.

In brief, a 10 mL sample bottle filled with homogeneous GO colloidal suspension (5 mL, 5 mg·mL^{-1}), was placed into a 50 mL Teflon-lined autoclave, and treated by a hydrothermal process in an oven (180 ^{o}C) for 3 h, resulting in a black cylindrical graphene hydrogel. The graphene hydrogel was immersed in sodium thiosulfate solution ($Na_2S_2O_3$, 5 M, 5 mL) at the ambient temperature of 50 ^{o}C for 3 hr. After lightly wiped the redundant solution on the surface, the hydrogel was then reacted with precooled hydrochloric acid (HCl, 1 M, 3 mL) for another 3 hr at ambient temperature of 3 ^{o}C. As obtained sulfur-graphene hydrogels were washed several times, and then subjected to oven drying at 60 ^{o}C for 12 hr, to produce S-SSC. The S-SSC was subjected to EIS, CV and galvanostatic cycling measurements.

As shown in Fig. S3, the internal impedance of the S-micro@meso-porous DSC is slightly higher than that of the S-SSC, may be attributed to the outstanding electrical conductivity of graphene sheets, which indirectly demonstrate the existance of abundant micropores in S-micro@meso-porous DSC. The S-micro@meso-porous DSC shows smaller interface contact resistance than that of S-SSC, indicating the dual-spatial porous structure could supply more channel to lithium ion diffusion, thus enhance the lithium ion conductivity.

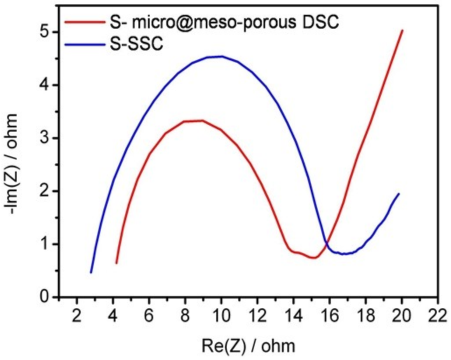

Fig. S3 EIS curves of S-micro@meso-porous DSC and S-SSC.

Compared with the S-SSC cathode (Fig. S4b), the S-micro@meso-porous DSC cathode (Fig. S4a) shows narrower oxidation and reduction peaks, indicating that the collection of current was easier in dual-spatial porous structure, ascribed to the much closer contact between sulfur and porous AC/graphene within the closed pores. During the ten cycles, CV curves of the S-micro@meso-porous DSC cathode maintain better than that of S-SSC cathode, showing that double layered porous structure as a hierarcaical reservoir can effectively prevent the dissolution of polysulfide into electrolyte, and thus keep the cathodes stable.

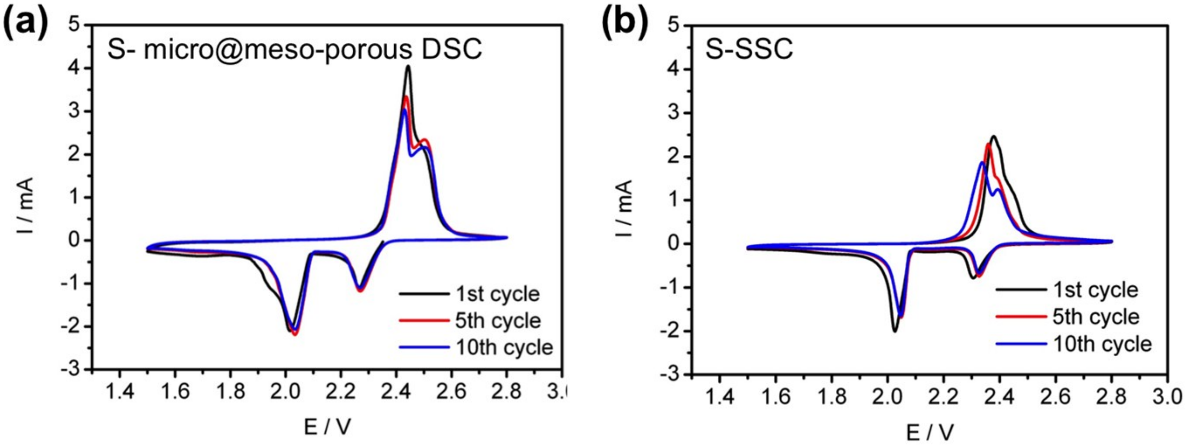

Fig. S4 CV curves of S-micro@meso-porous DSC and S-SSC.

After the initial two cycles of activation and stabilization, the discharge capacity in the third cycle are 1082.9 mAh·g^{-1} (1045.1 mAh·g^{-1}) and 989.7 mAh·g^{-1} (925.1 mAh·g^{-1}) for S-micro@meso-porous DSC and S-SSC respectively at the rate of 0.2C (or 0.5C) (Fig. S5). More degration of capacity occurs in the S-SSC (remaining 835.4 mAh·g^{-1} at 0.2C and 794.2 mAh·g^{-1} at 0.5C after 150 cycles) in contrast with the S-micro@meso-porous DSC (remaining 891.9 mAh·g^{-1} at 0.2C and 837.6 mAh·g^{-1} at 0.5C after 150 cycles). The S-micro@meso-porous DSC shows better cycling performance than that of S-SSC, owing to the dual-spatial hierarchical porous structure performing better in traping sulfur and resisting polysulfide dissolution, as a result of inner abundant micropores and outer mesopores to resist polysulfide dissolution at two interfaces during discharge.

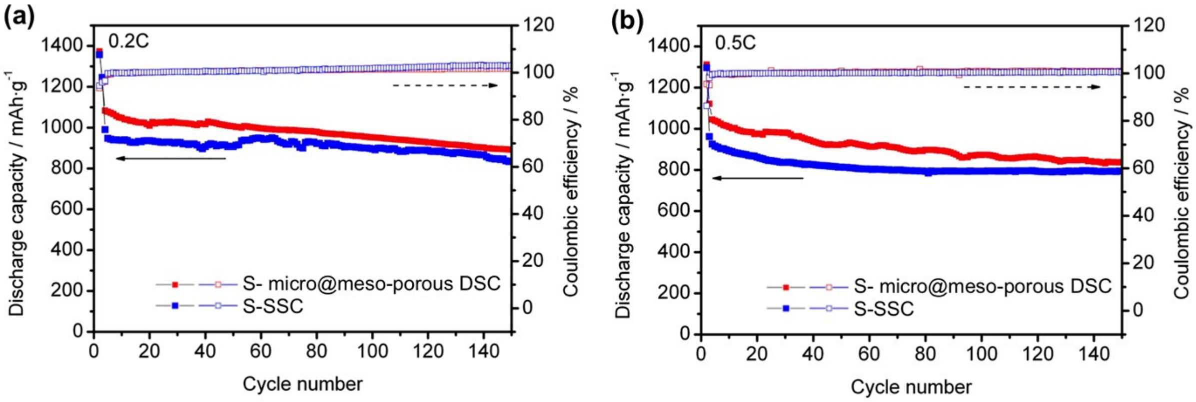

Fig. S5 Cycling specific capacity profiles of S-micro@meso-porous DSC and S-SSC continued to cycle at a rate of (a) 0.2C, and (b) 0.5C after cycled at a rate of 0.05C for two cycles between 1.6 and 2.8V.

Transparent soft-pack cells were assembled to view the polysulfide dissolution behavior in cells (Fig. S6). The electrolyte in the cell with the S-micro@meso-porous DSC and S-SSC cathodes keep colorless after 10 cycles, while the S-SSC cell turns into slight yellow color after 25 cycles caused by the dissolution of the yellow polysulfide. In contrast, the cell with the S-micro@meso-porous DSC cathode remains colorless after even 25 cycles, indicating the hierarchical pores structure could better immobilize sulfur and restrain the polysulfide within dual-spatially closed pores.

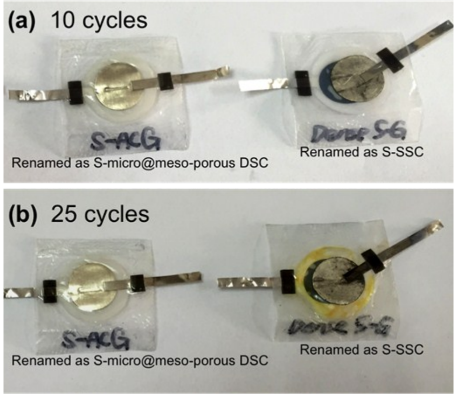

Fig. S6 Photos of the transparent soft pack cells of S-micro@meso-porous DSC and S-SSC after (a) 10 cycles, (b) 25 cycles.

Reference

(1) H. F. Li, X. W. Yang, X. M. Wang, M. N. Liu, F. M. Ye, J. Wang, Y. C. Qiu, W. F. Li and Y. G. Zhang, *Nano Energy*, 2015, **12**, 468.