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Electronic Supplementary Information

Graphene wrapped chromium-MOF(MIL-101)/sulfur composite for performance improvement of high-rate rechargeable Li-Sbatteries

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1. Experiment

1.1 Preparation of MIL-101(Cr)crystals

The MIL-101(Cr) were synthesized by following procedures reported previously.[1] $Cr(NO_3)_3 \cdot 9H_2O$ (99% +, from Aldrich), 1,4-benzene dicarboxylic acid (H_2BDC, 99.0% +, from Acros), HF (48%, from Merck) were used as received without further purification. The MIL-101 crystals were synthesized in the equal molar ratio of $Cr(NO_3)_3 \cdot 9H_2O$, H_2BDC, and HF but with 280 times of H_2O at 220°C for 60 min in a microwave oven (Mar-5, CEM). After the reaction, the autoclave was cooled naturally to room temperature. Then, the solution was filtered and the green colored precipitate was washed with DMF and ethanol (10 mL × 3 times) successively. Finally, the fine green colored crystals were obtained and dried in a vacuum oven at 150 ºC overnight.

1.2 Preparation of MIL-101(Cr)/S composite

The preparation of the MIL-101(Cr)/S composite was performed by following a melt-diffusion method.[1] The MIL-101(Cr) crystals were first dried under vacuum (≤

133 Pa) at 423 K overnight. Considering the volume expansion of sulfur during discharge, the mass ratio of sulfur/MIL-101(Cr) was adjusted to about 1.7. The mixture of sulfur and MIL-101(Cr) was ball milled at 300 rpm for 120 min, and then heated to 160 ºC for sulfur to infiltrate into the pores of the MIL-101(Cr).

1.3 Preparation of GNS-MIL-101(Cr)/S composite

Graphite oxide was synthesized by oxidation of natural graphite flakes using improved hummers' method. The graphene sheets used in this work were prepared via chemical reduction of grapheme oxide. The GNS-MIL-101(Cr)/S composite was prepared by taking the advantage of strong electrostatic attraction using a liquid process.[2] Briefly, an appropriate amount of graphene and theMIL-101(Cr)/S were dispersed together in deionized water. The wrapping of graphene to the MIL-101(Cr)/S was realized by slowly decreasing the pH of the solution until pH ~ 3-4 under mild stirring. Hence, the graphene can be wrapped on the surface of the MIL-101(Cr)/S composite particles by charge attraction. After that, the obtained GNS-MIL-101(Cr)/S composite were collected by repeated centrifugation and dried at 100 ºC for 6h.

2. Material Characterization

The surface morphology of the samples was obtained by scanning electron microscopy (SEM, FEIXL-30) operated by using a 25 kV accelerating voltage after gold deposition. The precipitates on the copper meshes were examined under TEM (Philips CM20, Philips Analytic).Powder X-ray pattern was obtained in a D/max-IIIA diffractometer using CuKα radiation. Langmuir and Brunauer-Emmett-Teller (BET) surface areas and pore volume of the samples were measured with a Micromeritics ASAP 2010 sorptometer using N_2 adsorption at 77 K. Thermogravimetric analysis was carried out with TGA- STA449C.

3. Electrochemical Measurements

The cathodes of the MIL-101(Cr)/S and GNS-MIL-101(Cr)/S were prepared by mixing with acetylene blackand PVDF binder in NMP solvent in a mass ratio of 7:2:1. After stirring, the slurry was coated onto aluminum foil disks (Cyprus Foote Mineral, 99.98%, USA) with a diameter of 11 mm. After drying at 70 °C under vacuum oven overnight, the electrodes were assembled into coin-type cells (CR2032) in an argon-filled glovebox (O_2 and H_2O less than 0.3 ppm) using lithium metal as the counter electrode, Celgard 2400 (Hoechst Celanese) membrane as separator and 1 Mbis-(trifluoromethane) sulfonamide lithium (LiTFSI, Alfa) in a mixture solution of dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1 vol.%) as the electrolyte. The charge/discharge tests were conducted at a range of current densities between 0.1 and 3.0 C (calculated on the basis of sulfur mass) in a voltage interval of 1.0 to 3.0 V, using a LAND electrochemical station.

The cells were discharged and charged on a LAND electrochemical station (Wuhan) at different current densities-sulfur to test the cycle life, rate capability and coulombic efficiency. Cyclic voltammograms (CVs) were recorded on an Autolab electrochemical workstation (ZAHNER) between 1.0-3.0 V vs. Li/Li^+ at a scan rate of 0.1 mV s^{-1} to characterize the redox behavior and the kinetic reversibility of the cells. AC impedance was measured using cells before and after cycling (fully discharged and charged for 10 and 150 cycles at a rate of 0.8 C) at the open circuit potential (OCP) using an Autolab electrochemical workstation. The AC amplitude was 5 mV.

4. Some Useful Figures

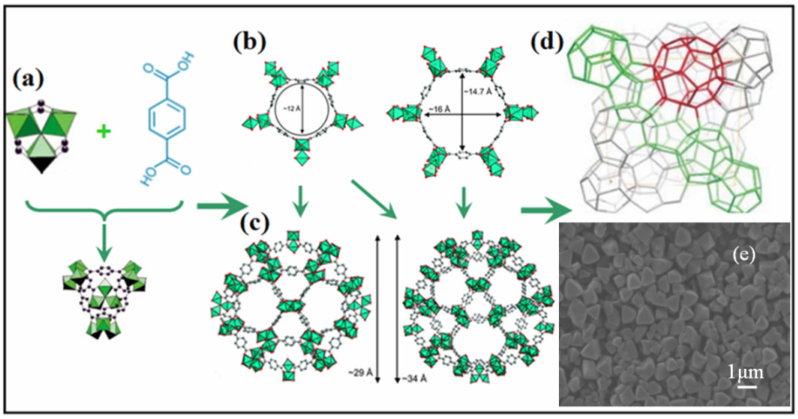

Fig. S1. Structure of MIL-101(Cr)[3] (a) cluster building unit (trimer of chromium octahedra) and the 1,4-benzendicarboxylate ligand, forming the hybrid supertetrahedron; (b) pentagonal (left) and larger hexagonal (right) windows and (c) the two types of mesoporous cages; (d) Schematic 3D representation of the MTN zeotype architecture (small cage is highlighted in green and large one is highlight in red); (e) a clear octahedral morphology with an average crystal size of ~1.0 μm.

In the present experiment, about 1.26×10^4 sulfur molecules are adsorbed in one-cell of the MIL-101 crystal.

$$Q_{sulfur} = \left. \frac{W_{sulfur}}{M_{sulfur}} N_A \middle/ \frac{W_{MIL-101}}{D_{MIL-101} V_{cell}} \right.$$

where W_{sulfur} (58.8%) and $W_{MIL-101}$ (38.1%) are the massratio of the sulfur and MIL-101; N_A is the Avogadro's constant, 6.022×10^{23}; M_{sulfur} is the molar massof sulfur, 32 g/mol; $D_{MIL-101}$ is the calculated density of the MIL-101, 0.62 g/cm^3; V_{cell} is the cell volume of the MIL-101, 701860.3 $Å^3$, and Q_{sulfur} is the total number of sulfur molecules in one-cell of the MIL-101(Cr).

The energy-dispersive X-ray (EDX) analysis revealed a rich abundance of sulfur in the composite (Fig. S2). The elemental mapping further confirms the uniform distribution of sulfur in the MIL-101(Cr) crystals, with sulfur (yellow) matching well with carbon (red) and Cr (yellow).

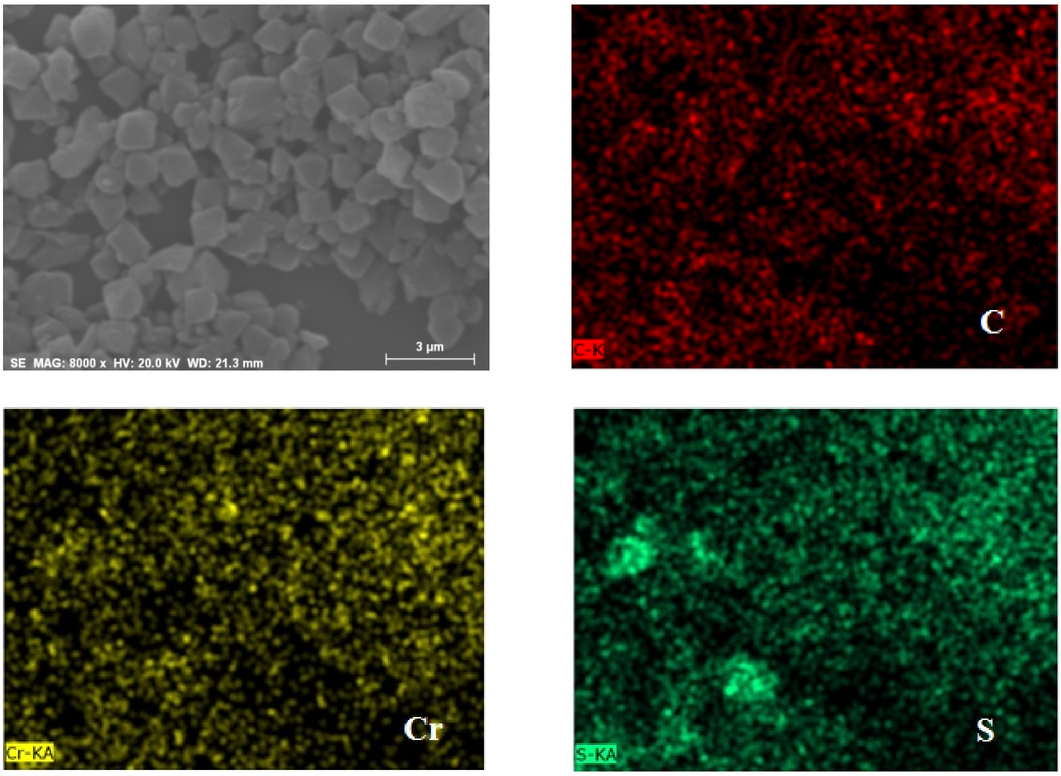

Fig. S2 SEM image and the corresponding elemental mapping of the MIL-101(Cr)/S composite particles.

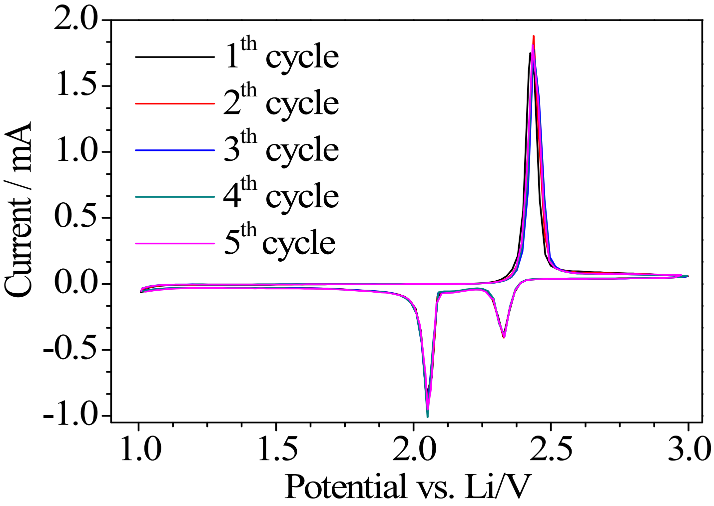

Fig. S3 Representative cycles from the continuous cyclic voltammetry scan of the GNS-MIL-101(Cr)/S between 1.0 and 3.0 V at scan rate of 0.1 mV s^{-1}.

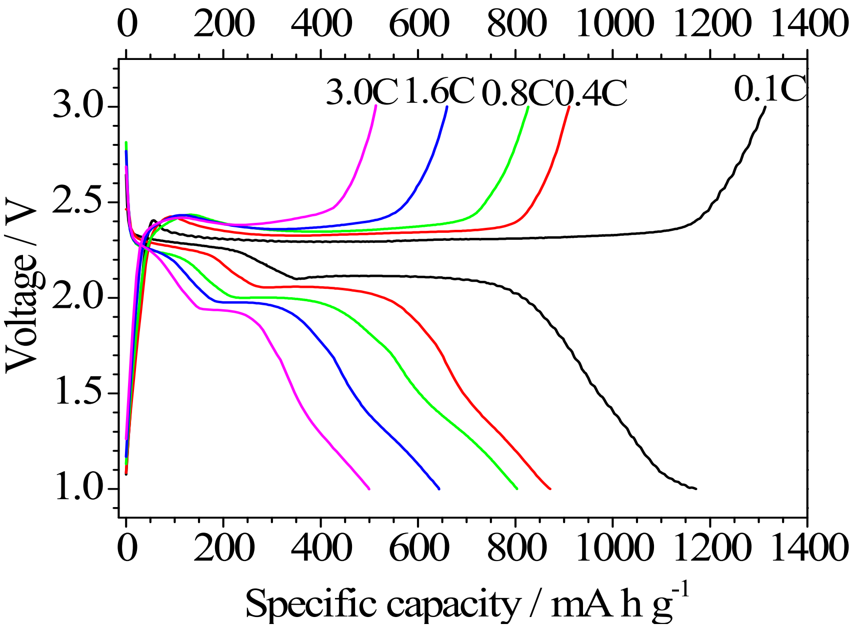

Fig. S4 Typical voltage capacity profiles of the MIL-101(Cr)@S+GNS/AB composite at various rates for the voltage range between 1.0 and 3.0 V vs Li.

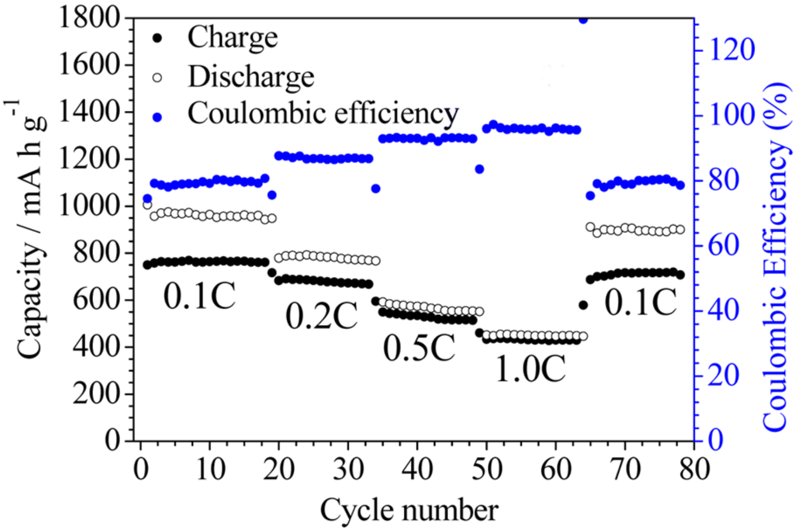

Fig. S5 Rate capability of MIL-101(Cr)/S composite for the voltage range between 1.0 and 3.0 V vs Li.

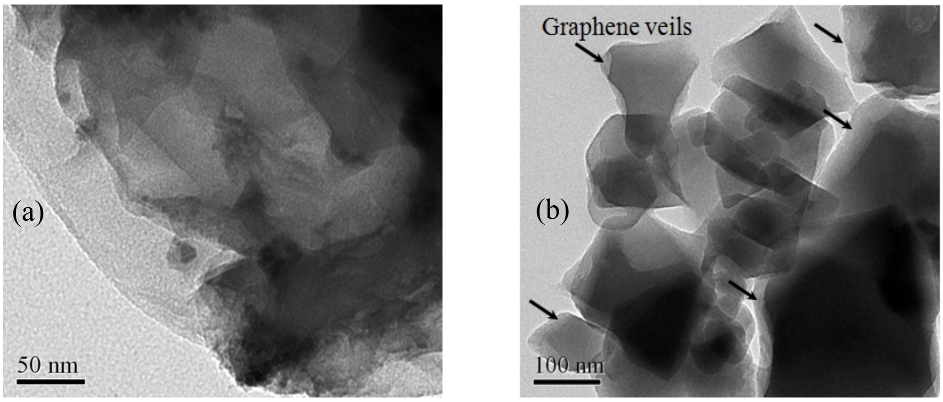

Fig. S6 TEM micrographs of (a) graphene sheets and (b) GNS-MIL-101(Cr) particles

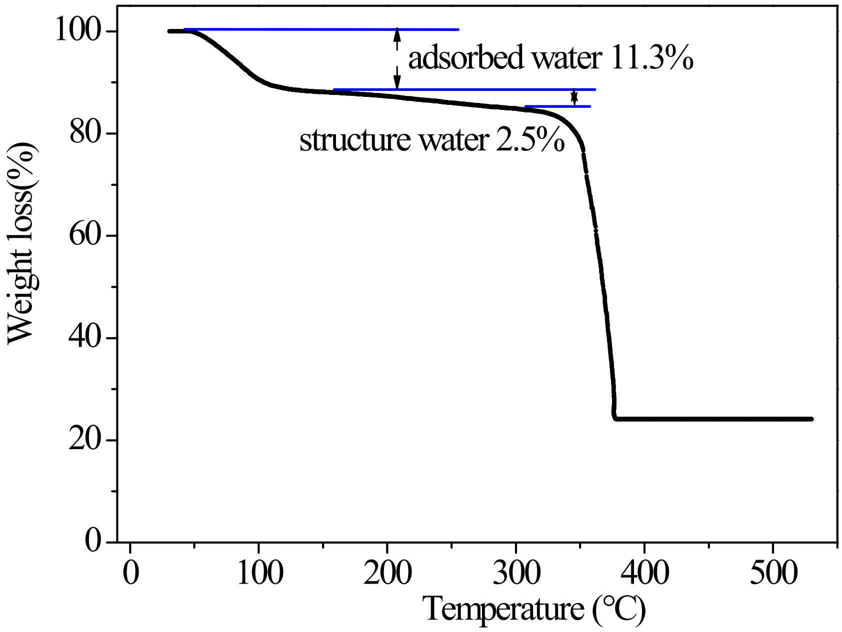

Fig. S7 TG curve of the MIL-101(Cr) crystal with drying and MIL-101 decomposition

To better understand the reasons for the good electrochemical performance of the GNS-MIL-101(Cr)/S and MIL-101(Cr)/S composites, more electrochemical impedance spectroscopy (EIS) measurements were performed on the material before and after cycling at 0.8 C (Fig. S8). For both electrodes, there is only one semicircle in the high-medium frequencyregion before cycling, which is understood to be the sumof the resistances of the surface layers (i.e., electrode/electrolyte); the linear segment in the low-frequency regioncorresponds to the diffusion limitation within the electrodes.[4] After the extended cycling, the resistance of the surface layers isreduced tremendously and another minor semicircle appeared inthe medium frequency region.

It is assigned to chargetransfer resistance.[5] The decrease of the interfacial resistanceis partially ascribed to the loss of active materials upon cycling, which leads to a high surface area of the GNS-MIL-101/S and MIL-101/S compositeelectrodes. With continued cycling, both interfacial resistance and charge transfer resistance remain unchanged, until respectively 120, 150 cycles. Clearly, the resistance of the GNS-MIL-101/S is much smaller than that of the MIL-101/S, indicating a better conductivity of the GNS-coated MIL-101/S composite.

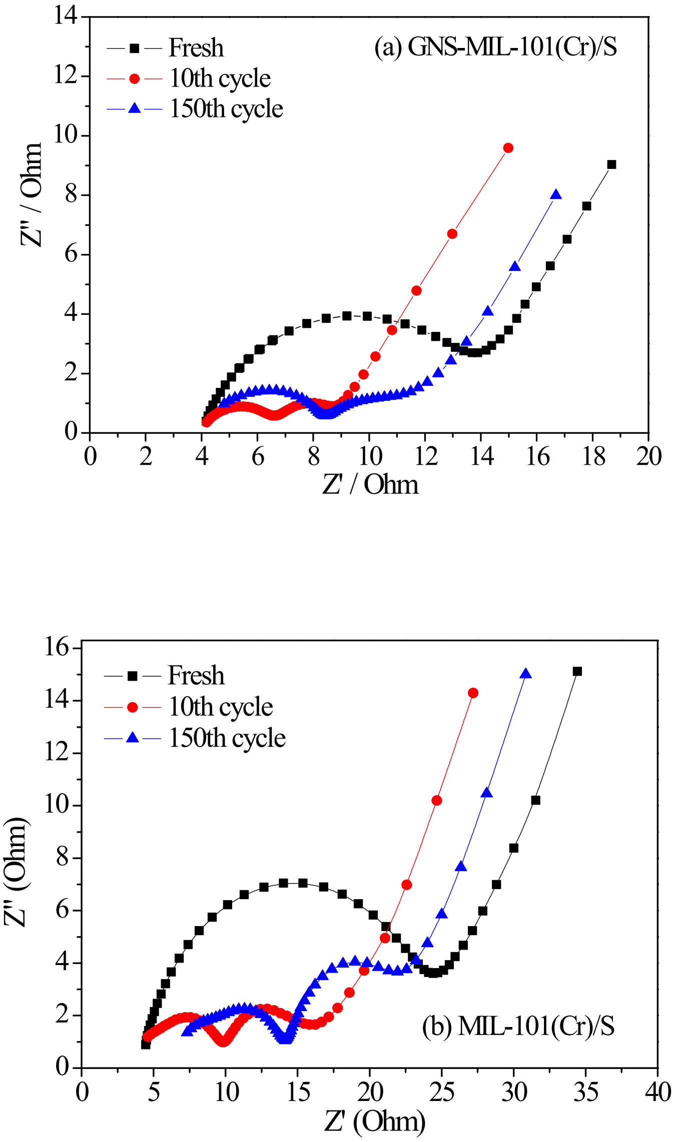

Fig. S8 EIS plots of the GNS-MIL-101(Cr)/Sand MIL-101(Cr)/S composite cathodes before and after ($10^{th}$and 150^{th}) cycles

References cited

1 R. Demir-Cakan, M. Morcrette, F. Nouar, C. Davoisne, T. Devic, D. Gonbeau, R. Dominko, C. Serre, G. Férey and J.M. Tarascon, *J. Am. Chem. Soc.*, 2011, **133**, 16154.

2 W. D. Zhou, Y. C. Yu, H. Chen, F. J. DiSalvo and H. D. Abruna, *J. Am. Chem. Soc.*, 2013, **135**, 16736.

3 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040.

4 J. Liu, B. Reeja-Jayan and A. Manthiram, *J. Phys. Chem. C*, 2010, **114**, 9528.

5 Y. Z. Fu and A. Manthiram, *Chem. Mater.*, 2012, **24**, 3081.