

A Long-life Lithium-ion Sulfur Battery exploiting High Performance Electrodes

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Supplementary Information

Experimental Section

Synthesis of activated ordered mesoporous carbon-sulfur (AOMC-S) composite

Activated ordered mesoporous carbon (AOMC) was synthesized as follows: 0.0056 g of Na₂CO₃ (Sigma Aldrich) was completely dissolved in 1.04 mL of formaldehyde (Aldrich, 37% wt) in a water bath at about 18 °C, following added by 1.10 g of resorcinol (Sigma Aldrich) and stirred for 1 h. The resulting solution was mixed with other solution formed by dissolving 0.8 g of Pluronic F-127 (Sigma Aldrich) in ethanol/water (6:4 ratio), and following by 1 mL of HCl solution (2M). After vigorous stirring for 1 min, the mixture turned white turbid which is an indication of phase separation. The mixture was stirred for 1h and then left to stand for 10 h for gel polymerization. The obtained gel polymer was dried at room temperature overnight and then cured at 80 °C for 24 h in an air oven. The orange transparent solid gel was annealed in a tubular furnace at 800 °C for 3h under N₂ atmosphere using a flow of 50 mL min⁻¹ and a rate of 1 °C min⁻¹, to obtain the ordered

mesoporous carbon. The powder was ball-milled at 300 rpm for 1 h using a planetary milling system (Retsch PM 100). Finally, the OMC sample was activated in a tubular furnace at 900 °C for 3 h under a CO₂ atmosphere using a 50 mL min⁻¹ flow and a ramp of 1 °C min⁻¹ to obtain the activated ordered mesoporous carbon (named by the acronym AOMC).¹ The Sulfur-Carbon composites were prepared by in-situ sulfur deposition from an aqueous solution of sodium thiosulfate acidified with hydrochloric as following: 4.22 g of Na₂S₂O₃·5H₂O was dissolved in 200 mL of H₂O containing 1% Triton X-100. The obtained solution was mixed with a suspension of 0.3 g of AOMC in 200 mL of H₂O under magnetic stirring. The mixture was heated to 70 °C in an oil bath and 20 mL of HCl (12M) was slowly added. The system was kept at 70 °C for 15 min under vigorous magnetic stirring, cooled down to room temperature and stirred for 24 h. The composite was filtered and washed several times with water, ethanol and acetone and finally dried in an air-oven at 80 °C overnight. The sulfur content of the activated ordered mesoporous carbon-sulfur composite (named by the acronym AOMC-S) determined by thermo-gravimetric analysis was of 60% w:w. The sulfur mass loading of the AOMC-S electrode (13 mm-diameter) was of about 3 mg cm⁻².

Sn-C composite anode

The nanostructured Sn-C electrode (35% Sn:C w:w) was prepared according to a procedure described in previous papers.^{2,3} Prior to use in a lithium-ion cell, the nanostructured Sn-C composite was chemically lithiated by direct contact with a lithium foil wet by a 1M LiPF₆ solution in EC:DMC, for 8 h under 1 kg cm⁻² of pressure to reach a composition approaching Li₄Sn-C corresponding to an overall capacity of about 400 mAh g⁻¹.²⁻⁴ The Sn-C electrode (16 mm-diameter) mass loading was of about 4 mg cm⁻².

Electrolyte preparation

The electrolyte was prepared in argon-filled glove box by dissolving 1 mole of LiTFSI (Aldrich) in 1 L of DME (Dimethoxyethane, Aldrich)/DOL (Dioxolane, Aldrich) with a 1:1 volume ratio. LiNO₃ was added to the DME-DOL-LiTFSI solution above described to reach the final electrolyte configuration, *i.e.* 1M LiTFSI, 0.4M LiNO₃ in DME/DOL (1:1 = v/v).

Materials characterization.

The structural properties of carbons and composite cathode were examined by XRD, STEM, TEM, EDX and HRTEM. The XRD (WAXS mode) patterns were recorded with a Siemens D5000 X-ray diffractometer and Bruker D8 Advance X-ray diffractometer (SAXS mode). The STEM, TEM and EDX images were obtained with a Jeol Jem 1400 electron microscope and HRTEM images with a Jeol Jem 2100 electron microscope. The sulfur content was determined by thermogravimetric analysis using a Mettler Toledo-TGA/DSC at heating rate of 5 °C min⁻¹ from 25 to 600 °C under nitrogen atmosphere. The textural properties were determined with a Micromeritics ASAP 2020, using nitrogen as adsorbent.

Electrode preparation and electrochemical tests.

The sulfur electrode was prepared by dispersing active material (AOMC-S), Super P carbon (Timcal) and polyvinylidene difluoride (PVdF, 6020, Solvay) binder in an 80:10:10 mass ratio, in N-Methyl-2-pyrrolidone (NMP). The slurry was coated on an aluminum foil current collector, the electrodes cut as 14-mm diameter disks and dried in a vacuum oven at 50 °C for 24 h. The nanostructured Sn-C electrode was prepared according to previous work,^{2,3} by mixing active material, Super P carbon and PVdF in the weight ratio of 80:10:10. The slurry was coated on a Cu-foil current collector, cut as 15-mm diameter disks and dried in a vacuum oven at 110 °C for 24 h.

The cycling tests were performed using a Maccor Series 4000 Battery Test System within the potential window of 1.9-2.8V for the Li/AOMC-S half-cell, and 1-3.0V for the Sn-C/AOMC-S Li-ion battery. All the electrochemical measures were performed using a coin-type cell (CR2032) assembled in an Ar-filled glove box, with H₂O and O₂ content less than 1 ppm.

Sample	S _{BET} (m ² g ⁻¹)	V _T (cm ³ g ⁻¹)	V _{MICRO} (cm ³ g ⁻¹)	S _{MICRO} (m ² g ⁻¹)
AOMC	1049	0,88	0,32	631
AOMC/S 60	6	0,031	-	-
Values obtained from t-plot method				

Table1 Textural properties of the AOMC precursor and the AOMC-S composite cathode

Determination of the theoretical specific energy for various Li-ion batteries.

We report here the specific energy calculated considering the capacity and the average voltage of both the anode and cathode, following the equation reported in the reference 26 in the manuscript text:

$$E = (C_c \times C_a / C_c + C_a) (V_c - V_a)$$

where E= energy, C_a= anode specific capacity, C_c=cathode specific capacity , V_c-V_a =cell voltage.

Table 1 reports the specific energy calculated for our cell and for lithium ion cell combining LiCoO₂,⁵ LiFePO₄,⁶ LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂,⁷ Li[Li_{0.2}Ni_{0.4/3}Co_{0.4/3}Mn_{1.6/3}]O₂ (lithium rich NMC),⁸ and sulfur⁹ cathodes with graphite,¹⁰ Sn¹¹ anodes. Accordingly, the specific energy of our Li₄Sn-C/AOMC-S system takes into account the specific capacity for cathode (800 mAh/g), the anode (400 mAh/g) and the average working voltage of the cell (1.7V) is calculated to be of about 450 Wh kg⁻¹. This value, reflected by a practical energy of about 280 Wh Kg⁻¹ considering the overall cell weight and a proper balance, may be further improved by selecting an anode material comparing the cathode capacity, such as silicon.¹²

Cathode/Anode	Cathode Capacity (mAh/g)	Anode Capacity (mAh/g)	Voltage Difference (V)	Specific Energy (Wh/kg)
C ₆ /LiCoO ₂	140	372	3.75	380
C ₆ /LiFePO ₄	170	372	3.3	385
C ₆ /LiNi _{1/3} Mn _{1/3} Co _{1/3} O ₂	175	372	3.75	445
C ₆ /Li[Li _{0.2} Ni _{0.4/3} Co _{0.4/3} Mn _{1.6/3}]O ₂	200	372	3.75	485
Sn(limited)/LiNi _{1/3} Mn _{1/3} Co _{1/3} O ₂	175	500	3.3	400
Sn-C/Li[Li _{0.2} Ni _{0.4/3} Co _{0.4/3} Mn _{1.6/3}]O ₂	200	400	3.3	440
Li ₄ Sn-C/AOMC-S (this work)	800	400	1.7	450

Table 2 Specific energy determination for various full, Li-ion systems.

Sn-C anode performance in Lithium-half cell.

The performance of the Sn-C anode has been evaluated in a Li-half cell configuration by using the DME:DOL (1:1) LiTFSI 1M, LiNO₃ 0.4M electrolyte solution.

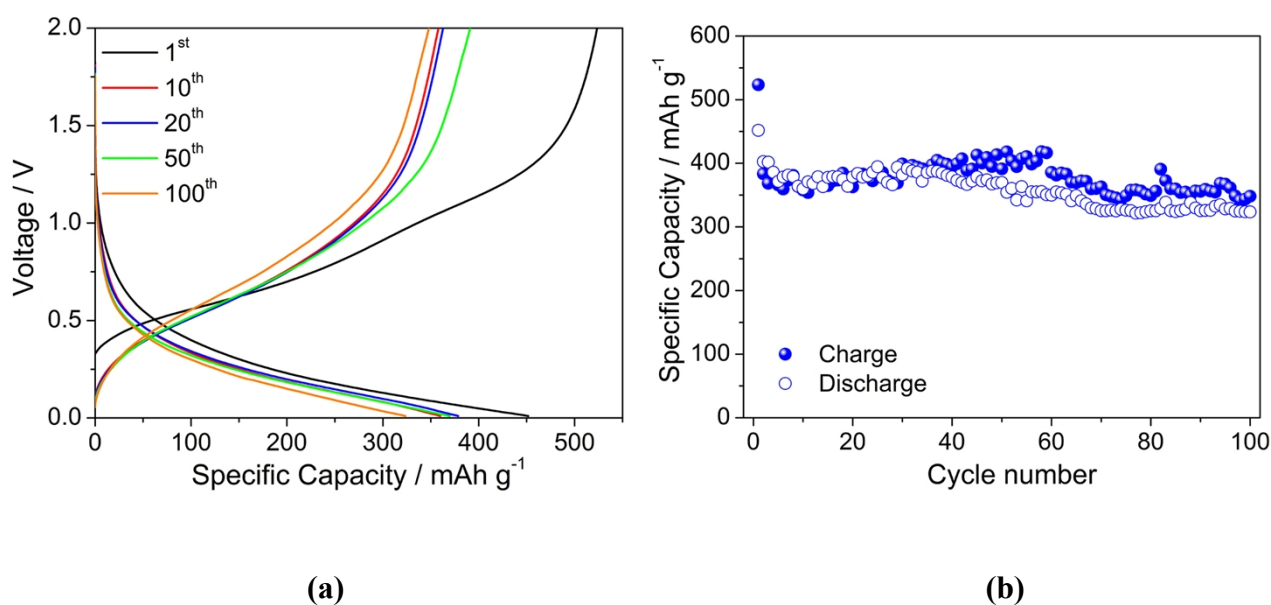


Figure S1: a) Voltage profiles at the 1st, 10th, 20th, 50th, 100th cycle and b) cycling response of a Li/DME:DOL (1:1) LiTFSI 1M, LiNO₃ 0.4M/Sn-C cell cycled using a current-rate of 100 mA g⁻¹ and a voltage ranging between 0.01V and 2V; temperature 25 °C.

Figure S1 reports the voltage profiles (a) and the cycling behavior (b) of the Li/ DME:DOL (1:1) LiTFSI 1M, LiNO₃ 0.4M/Sn-C cell cycled using a current-rate of 100 mA g⁻¹ and a voltage range between 0.01V - 2V. The cell delivers a stable capacity of about 400 mAh g⁻¹, i.e., the approaching the theoretical value for the Sn-C composite anode here studied, with an average working voltage of about 0.5V.

Lithium-ion cell: voltage profile during the 1st cycle.

The voltage profile during the 1st cycle of the Li₄Sn-C/AOMC-S Li-ion cell described in Figure 3 of the manuscript is reported in Figure S2.

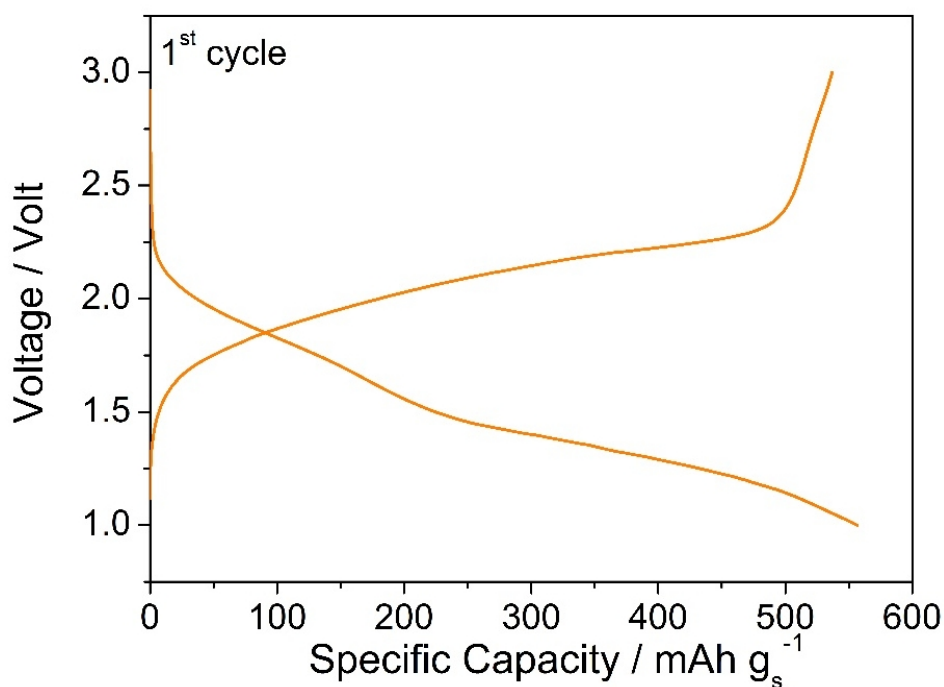


Figure S2: Voltage profile during the 1st cycle of the Li₄Sn-C/DME:DOL (1:1) LiTFSI 1M, LiNO₃ 0.4M/AOMC-S lithium ion cell. Voltage limits: 1–3V. Current-rate 300mA g_s⁻¹. Temperature 25°C.

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