



Supporting Information

for *Small*, DOI: 10.1002/sml.201804609

Dual-Function, Tunable, Nitrogen-Doped Carbon for High-Performance Li Metal–Sulfur Full Cell

*Hongyan Li, Zheng Cheng, Avi Natan, Ahmed M. Hafez, Daxian Cao, Yang Yang, and Hongli Zhu**

Supporting Information

Dual functions, Tunable, Nitrogen-doped Carbon for High Performance Li Metal-Sulfur Full Cell

Hongyan Li¹, Zheng Cheng¹, Avi Natan¹, Ahmed M. Hafez¹, Daxian Cao¹, Yang Yang¹,
Hongli Zhu^{*,1}

¹Department of Mechanical and Industrial Engineering, Northeastern University, Boston, Massachusetts 02115, United States.

*Corresponding author: Dr. Hongli Zhu **E-mail:** h.zhu@neu.edu

Contents list

I. Experimental Procedure

II. Supplementary Results and Discussion

Experimental Procedure:

1. Chemicals

LUDOX® TM-40 colloidal silica (40 wt% suspension in H₂O), Aniline, ammonium sulfate ((NH₄)₂SO₄), Hydrochloric acid, Ammonium persulfate, PEO-PPO-PEO (P123), Sodium hydroxide, 2-amino-2-hydroxymethylpropane-1, 3-diol (Tris), Dopamine hydrochloride and Sulfur were purchased from Sigma-Aldrich and were used without further purification.

2. Preparation of nitrogen-doped mesoporous carbon spheres (MCS)

The MCS was prepared via controlled self-assembly of hard template method in the presence of polyaniline (PANI) using SiO₂ nanoparticles as the sacrifice template. Initially, 6 mL of SiO₂ (40%, 22nm) were dispersed in distilled water followed by addition of 10 ml of 1M HCl. After stirring for 10 min, 0.8 g aniline monomer was added to the solution. Then 4 ml of 1M HCl solution with 2 g ammonium persulfate was added dropwise while vigorously stirred. The polymerization occurred in an ice bath for 24 hours. After the reaction, the product PANI-SiO₂ was collected by centrifugation and washed 3 times with water. The carbonization process was performed in a temperature programmable tube furnace

at 900 °C and 1100 °C under N₂ flow. The SiO₂ template was removed by the etching treatment in 2M NaOH solution for 24 hours. The resultant products are MCS900 and MCS1100.

3. Preparation of carbon covered mesoporous carbon spheres (CMCS)

The above PANI-SiO₂ (100 mg) was re-dispersed in 100 mL of distilled water containing 60 mg of PEO-PPO-PEO (P123) and 120 mg of 2-amino-2-hydroxymethylpropane-1, 3-diol (Tris). After that, 50 mL of distilled water containing 100 mg of dopamine was added with continuous stirring in air for 5 hours. The precipitates were collected by filtration, washed several times with absolute ethanol and dried at 60 °C. Finally, the resulting product was annealed in N₂ gas at 1100 °C for 2 hours to prepare the carbon covered PANI-SiO₂. The SiO₂ template was removed by etching treatment in 2M NaOH solution for 24 h. The resultant products are CMCS1100.

4. Preparation of S@CMCS and other control composites

A mixture of CMCS and sulfur powder (1:5, weight ratio) was sealed in a glass vessel with argon gas. It was heated at 300 °C for 12 hours in a quartz tube furnace to synthesize S@CMCS. Then, the composite was placed in an open porcelain boat and heated at 200 °C for 1 hour in a quartz tube furnace under flowing argon gas. This evaporates the extra sulfur molecules outside the CMCS. After cooling down, S@CMCS was obtained.

5. Electrochemical Measurements

Preparation the S@CMCS1100 half cell (Cathode side): The electrochemical performances were conducted using the CR2032 coin type half cells. The electrode film was prepared by mixing 70 wt% of active material, 20 wt% of conductive carbon and 10 wt% of polyvinylidene fluoride in an appropriate amount of N-methyl-2-pyrrolidinone as solvent. After stirring, the resulting paste was spread on aluminum foil by automatic film coater with a vacuum pump and micrometer doctor blade (MTI). After evaporation of N-methyl-2-pyrrolidinone solvent in a vacuum oven at 60 °C for 12 h, the electrodes were pressed and cut into disks. The 2032-type coin cells were assembled using Celgard 2400

membrane as separator and Li metal as anode. The electrolyte was prepared by dissolving 1.0 mol L⁻¹ lithium bis(trifluoromethanesulfonyl) imide in a mixture of 1,3-dioxolane and dimethoxymethane (1:1, v/v) with addition of 0.2 mol L⁻¹ of LiNO₃. The volume of electrolyte injected in coin cells is controlled to about 20 ul per 1 mg of electrode. The cells were assembled in an Ar-filled glove box with moisture and oxygen content of less than 0.1 ppm. Galvanostatic charge and discharge tests were carried out using a LAND-CT2011A battery-testing instrument at room temperature under different current densities in a voltage range of 1.7-2.8 V. The capacities were calculated based on the mass of sulfur. Cyclic voltammetry measurements were conducted at a scan rate of 0.1 mV s⁻¹ and electrochemical impedance measurements (EIS) were performed in the frequency range from 100 kHz to 0.01 Hz on Biological SP150 electrochemical workstation at room temperature.

Preparation the Li@MCS900 half cell (Anode side): The electrochemical performances were conducted using the CR2032 coin type half-cells. The electrode film was prepared by mixing 90 wt% of MCS900 and 10 wt% of polyvinylidene fluoride in an appropriate amount of N-methyl-2-pyrrolidinone as solvent. After stirring, the resulting paste was spread on Cu foil by automatic film coater with vacuum pump and micrometer doctor blade (MTI). After evaporation of N-methyl-2-pyrrolidinone solvent in a vacuum oven at 60 °C for 12 h, the electrodes were pressed and cut into disks. The 2032-type coin cells were assembled using Celgard 2400 membrane as separator and Li metal as anode. The electrolyte was prepared by dissolving 1.0 mol L⁻¹ lithium bis(trifluoromethanesulfonyl) imide in a mixture of 1,3-dioxolane and dimethoxymethane (1:1, v/v) with addition of 2 wt.% of LiNO₃. The cells were assembled in an Ar-filled glove box with moisture and oxygen content of less than 0.1 ppm. Galvanostatic charge and discharge tests were carried out using a LAND-CT2011A battery-testing instrument at room temperature. In the Coulombic efficiency measurement, MCS900/Cu and bare Cu acted as the working electrode, and Li foil as the counter electrode in batteries. Prior to test, batteries were cycled between 0.01-1V for 5 cycles at a current of 10 μA, in order to form stable SEI on the electrode and remove the surface contamination. Then in each cycle, Li plated on the cathode side and followed with stripped to 1V (vs. Li⁺/Li), at a constant current density of 1 mA cm⁻² and 3 mA cm⁻². The Coulombic efficiency was calculated by the ratio of stripping/plating time in each cycle. In the long term

plating/stripping cycle test, in separately, Li with areal charge of 1 mA h cm^{-2} were pre-deposited in the MCS900/Cu and bare Cu to form Li@MCS900/Cu and Li@Cu anodes, respectively. Following, the cells were measured in repeated stripping/plating processes with areal charge of 1 mA h cm^{-2} at the current density of 1 and 3 mA cm^{-2} . The cycling stability of anodes was evaluated according to the stability of the voltage hysteresis.

Preparation the full Li-S cell: Full Li-S cells were assembled with Li@MCS900 as the anode and S@CMCS1100 as the cathode. Li@MCS900 anodes were prepared by pre-plating 3 mA h cm^{-2} of Li metal onto MCS900 coated Cu foil electrode at 1 mA cm^{-2} . S@CMCS1100 cathodes and electrolyte were the same as that in the half cells. The galvanostatic charge/discharge tests were performed by using a LAND CT2001A battery tester at different current densities within a cutoff voltage window of 1.7-2.8 V.

6. Sample characterization instruments

The morphology of the MCS and CMCS was characterized by the scanning electron microscopy (SEM) (Hitachi S4800) and transmission electron microscopy (TEM) (JEOL 1010). High-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDX) measurements were performed on a JEOL 2010F (Tokyo, Japan) HRTEM at an acceleration voltage of 200 kV. The samples for TEM images were prepared by dropping the dilute colloidal suspension ($\sim 0.05 \text{ mg mL}^{-1}$) onto a lacey carbon copper grid and dried in ambient air at room temperature. The SEM images were obtained using a field-emission gun SEM (Quanta 400 FEG FEI) at an accelerating voltage of 10.0 kV. X-Ray photoelectron spectroscopy (XPS) analysis was measured on an ESCALAB MKII X-ray photoelectron spectrometer (VG Co.) with Al $K\alpha$ X-rays radiation as the X-ray source for excitation. X-ray diffraction (PANalytical/Philips X'Pert Pro) patterns were recorded for 2θ -values ranging from 10° to 60° with Cu $K\alpha$ radiation. Raman spectroscopy was carried out on a LabRam HR800 UV NIR with a 532 nm laser excitation. The nitrogen adsorption-desorption measurements were performed on a Quantachrome ASiQwin-Autosorb Iq Station 2 and the bath temperature was 77.35K (The outgas Temp. is 453.15K). Thermogravimetric analysis (TGA) was measured under a N_2 atmosphere with a Perkin Elmer Thermal Analyzer at a heatingrate of 5°C min^{-1} .

II. Supplementary Results and Discussion

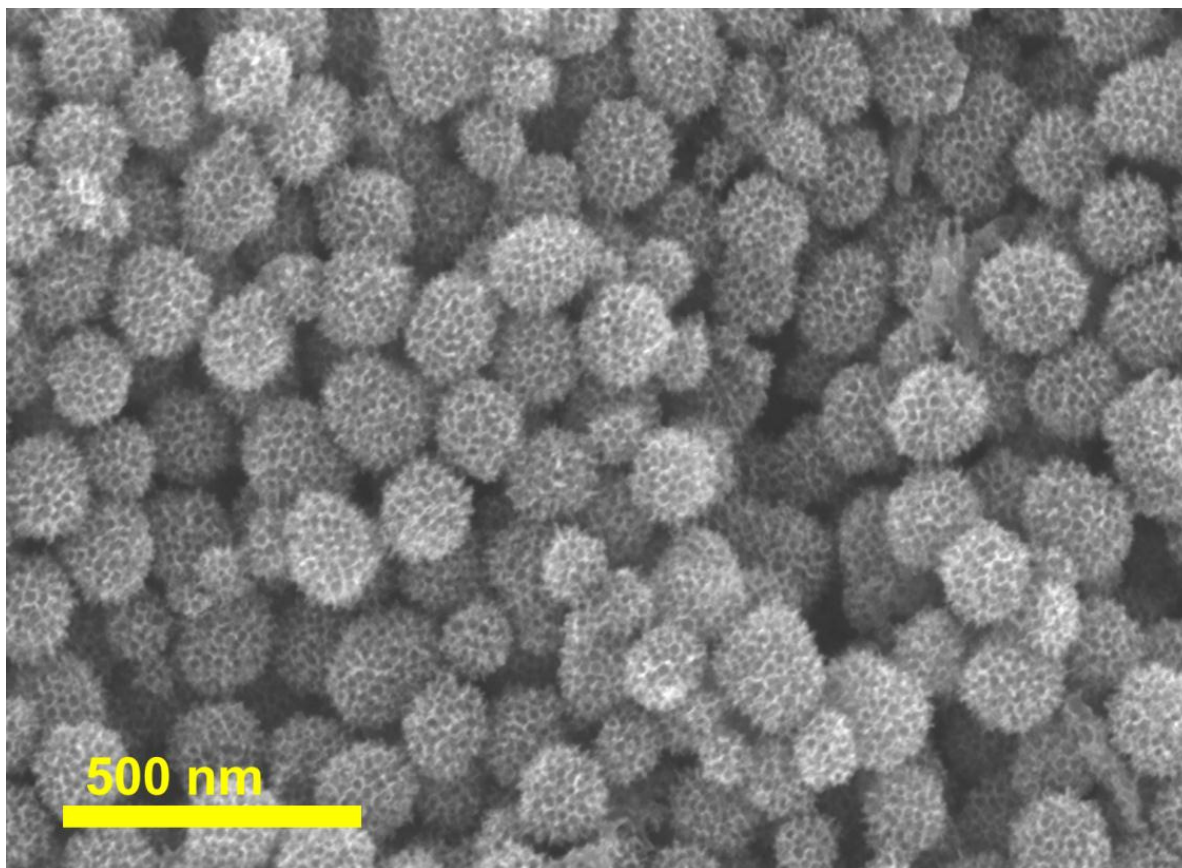


Figure S1 SEM images of the prepared MCS900.

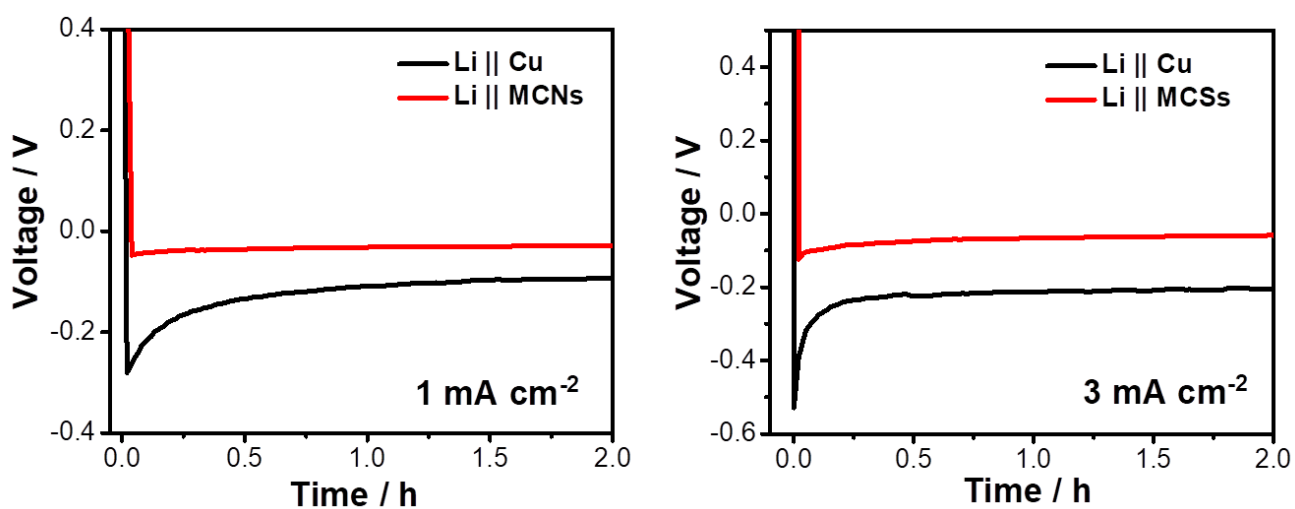


Figure S2 The first plating cycle of Li@MCS900 and Li@Cu electrode under a) 1 mA cm^{-2} and b) 3 mA cm^{-2} , respectively.

In addition, even under the high current of 3 mA cm^{-2} , the Li@MCS900 cell exhibited a stable voltage profile with overpotential of 57 mV. However, the Li@Cu counterpart showed fluctuant voltage profile with much larger overpotential of 206 mV (**Figure S2b**).

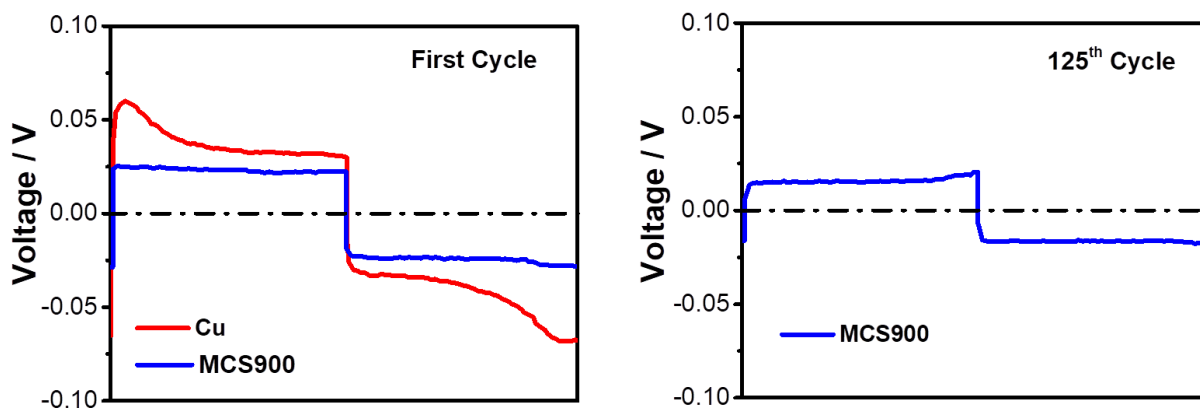


Figure S3 a) Lithium plating and stripping performance for first and 125th cycle of Li@MCS900 and Li@Cu electrode at a current density of 1mA cm^{-2} .

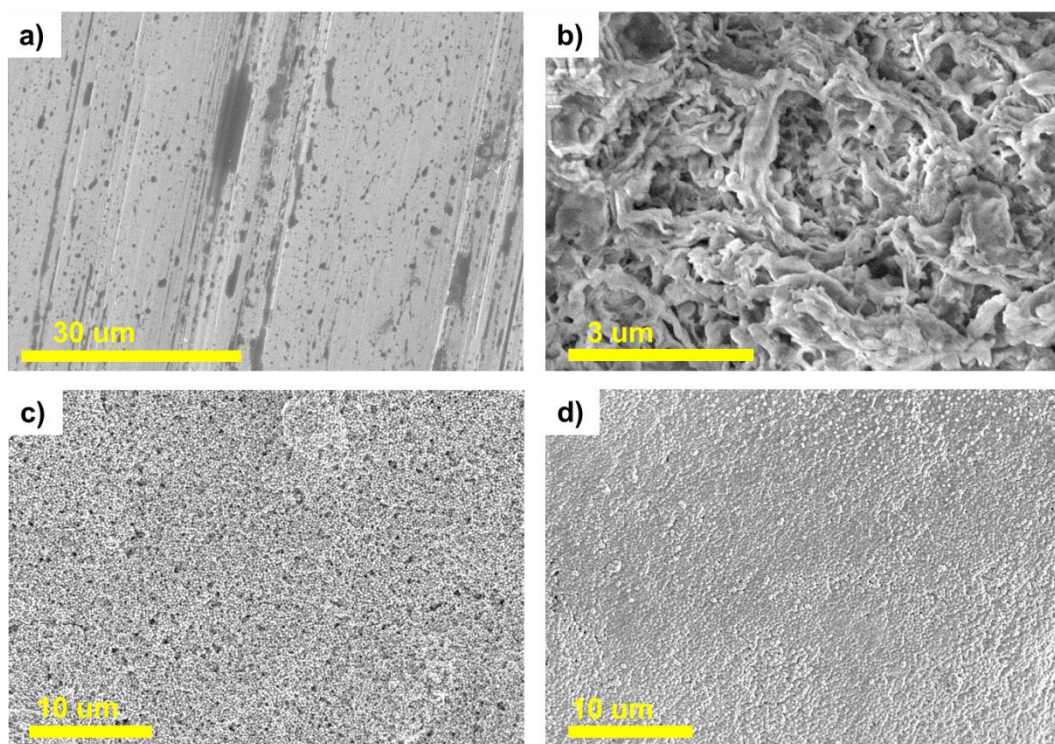


Figure S4 SEM images of Cu electrode without carbon coating and with MCS900 coating under different lithium plating and stripping procedure: a) Li@Cu electrode before cycle and b) after 100 h; and c) Li@MCS900 electrode before cycle and d) after 100 h.

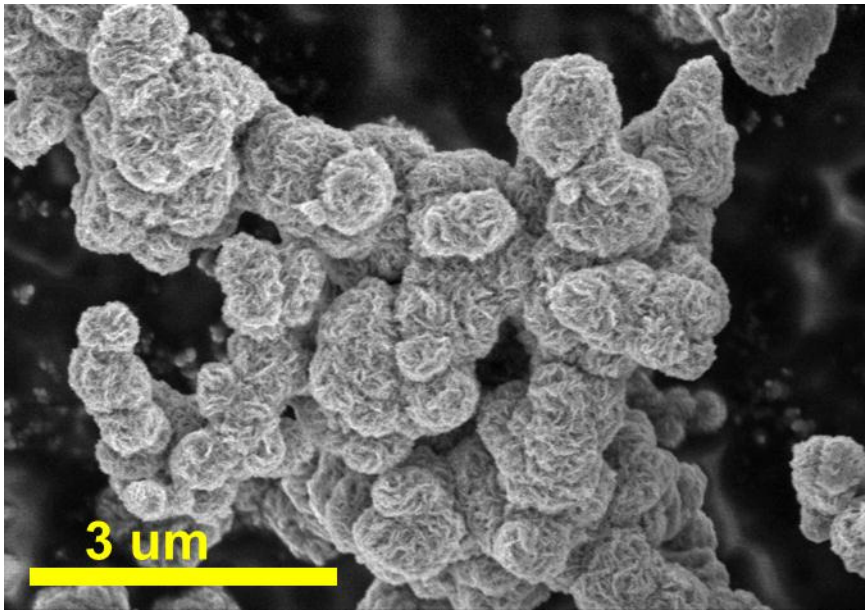


Figure S5 SEM images of the sulfur encapsulated MCS900.

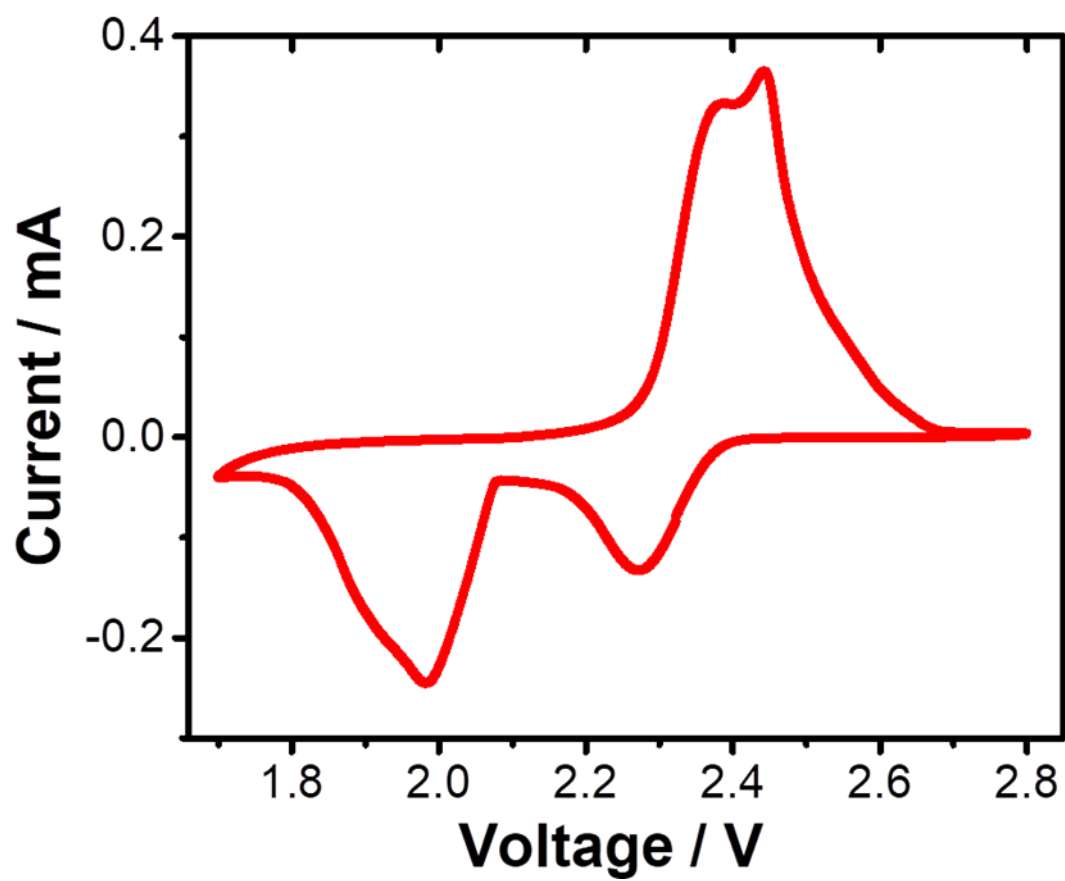


Figure S6 CV curve of the S@MCS1100 cell obtained at scan rates of 0.1 mV s^{-1} .

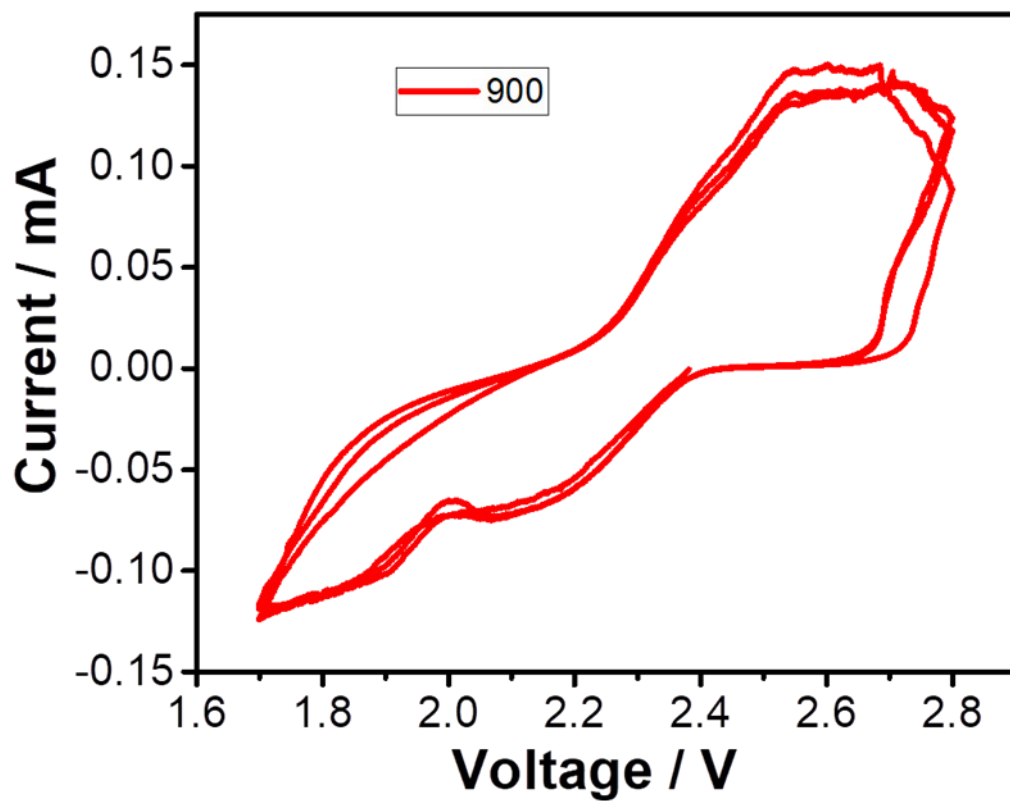


Figure S7 CV curve of the S@MCS900 cell obtained at scan rates of 0.1 mV s⁻¹.

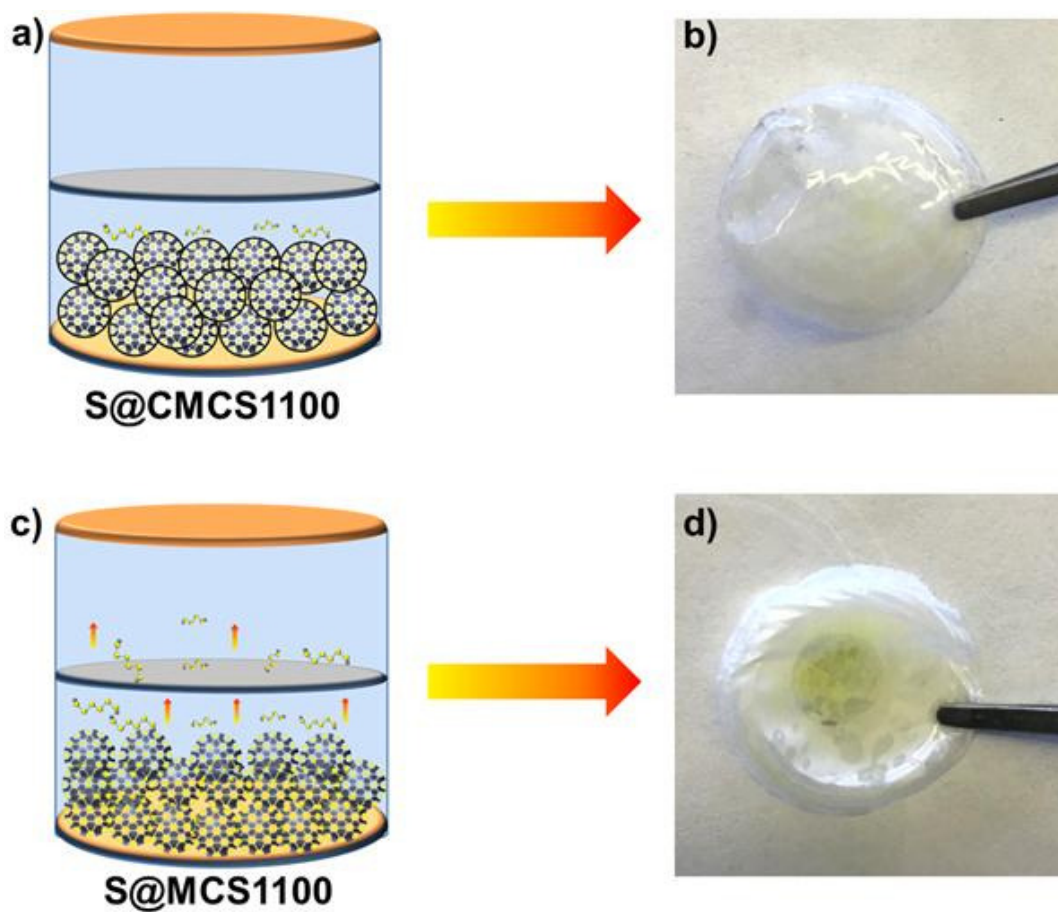


Figure S8 a) and c) Schematic illustration of the mechanisms for S@CMCS1100 and S@MCS1100 electrode in batteries. b) and d) Digital images of cycled separators of S@CMCS1100 and S@MCS1100.