

## Supporting Information

### **MOFs-derived fluorine and nitrogen co-doped porous carbon for integrated membrane in lithium–sulfur batteries**

Xinzuo Fang,<sup>a</sup> Yu Jiang,<sup>b</sup> Kailong Zhang,<sup>\*c</sup> Guang Hu,<sup>c</sup> and Weiwei Hu<sup>c</sup>

<sup>a</sup> School of Materials Engineering, Jiangsu University of Technology, Changzhou, 213001, P. R. China.

<sup>b</sup> School of Chemistry and Environment Engineering, Jiangsu University of Technology, Changzhou, Jiangsu, 213001, P. R. China.

<sup>c</sup> Key Laboratory for Palygorskite Science and Applied Technology of Jiangsu, National & Local Joint Engineering Research Center for Mineral Salt Deep Utilization, School of Chemical Engineering, Huaiyin Institute of Technology, Huaian, Jiangsu, 223003, P. R. China.

## Section 1. Materials and Instrumentation.

All chemicals were purchased and used without further purification: zinc nitrate hexahydrate (99 %), 2-methylimidazole (99 %), ammonium fluoride (99 %), Sulfur powder, N-methyl-2-pyrrolidone (NMP) and methanol (AR) were obtained from Energy Chemical (Shanghai, China). Super P and PVDF (HSV900) were bought from Lizhiyuan Store (Taiyuan city, Shanxi Province, China). Power X-ray diffraction (PXRD) were performed on Japan Rigaku DMax- $\gamma$ A rotation anode X-ray diffractometer equipped with Cu K $\alpha$  radiation. Field-emission scanning electron microscopy (FE-SEM) were obtained on the Zeiss Supra 40 scanning electron microscope with an accelerating voltage of 5 kV. The transmission electron microscopy (TEM) and elemental mapping were carried out on JEOL ARM-200F. Nitrogen sorption measurement was obtained from Micromeritics ASAP 2020 system at 77 K and analyzed by the conventional Brunauer–Emmett–Teller (BET) method. X-ray photoelectron spectroscopy (XPS) measurements were performed by using an ESCALAB 250 XPS spectrometer equipped with monochromatized Al K $\alpha$  ( $h\nu = 1486.7$  eV) as excitation source.

## Section 2. Material Synthesis

### Preparation of ZIF-8 precursor

The ZIF-8 precursor was synthesized according to previous procedure with some modifications. Typically, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.68 g) was dissolved in 80 mL of methanol. Then 80 mL methanol dissolved with 3.70 g 2-methylimidazole was added to the above solution with vigorous stirring for 24 h. After centrifugation, washed thoroughly with methanol, and finally dried overnight at 50 °C, the ZIF-8 powder was obtained. Prior to use, the powder was further activated at 200 °C under vacuum for 24 h.

### Preparation of F-N-C-1000

Typically, ZIF-8 powder (500 mg) was heated to 1000 °C with a heating rate of 5 °C min<sup>-1</sup> and pyrolyzed at 1000 °C for 2 h under N<sub>2</sub> atmosphere, and then cooled to room temperature naturally to obtain porous carbon materials N-C-1000. Then the N-

C-1000 was fluorided with  $\text{NH}_4\text{F}$  solution at  $80\text{ }^\circ\text{C}$  for 12 h. After washed thoroughly and dried at  $120\text{ }^\circ\text{C}$ , the products were obtained.

#### Modification of separator

The obtained F-N-C-1000 (80 mg), Super P (10 mg), and PVDF (10 mg) binder were dispersed in NMP to form homogeneous slurry. Then the slurry was coated on one side of a Celgard separator. The modified membrane was vacuum dried at  $40\text{ }^\circ\text{C}$  for 12 h. Finally, the modified membrane was punched into a disk with a diameter of 19 mm. The areal loading mass of F-N-C-1000 on the modified Celgard is about  $0.5\text{ mg cm}^{-2}$ . Digital photo of F-N-C-1000 on the modified Celgard separators (top) and origin Celgard separators (bottom) are shown in Figure S7.

#### Preparation of S cathode

Melt-diffusion strategy was used to prepare S cathode. A mixture of Super P and S with a weight ratio of 4:6 was grounded in a mortar for 30 min and then heated in a quartz tube at  $155\text{ }^\circ\text{C}$  for 24 h to obtain S cathode. Then, Super P/S composite and PVDF (Arkema, HSV900) were mixed with a weight ratio of 9:1 to form homogeneous slurry with some N-Methyl pyrrolidone. The slurry was coated onto aluminum foil, and the coating aluminum foil were dried in a vacuum oven at  $60\text{ }^\circ\text{C}$  for 12 h and punched into discs of diameter 12 mm. The sulfur loading is about  $1.2\text{ mg cm}^{-2}$ .

### **Section 3. Electrochemical Measurements.**

Electrochemical measurements were carried out with coin-type 2016 half cells in an Ar filled glove box. The Li-S cell was assembled with S cathode, one piece of F-N-C-1000 modified membrane and lithium metal with  $1\text{ mol L}^{-1}$  LiTFSI dissolved in a mixture of DME and DOL ( $v/v = 1/1$ ) containing  $\text{LiNO}_3$  (2 wt.%). The cells were cycled in the voltage range of 1.7 to 2.8 V. E/S (electrolyte/sulfur) ratio is about  $0.02\text{ mL mg}^{-1}$  for normal test. The cyclic voltammograms (CV) of the batteries were measured on a CHI600e potentiostat from 1.7 to 2.8 V at a scan rate of  $0.1\text{ mV s}^{-1}$ . The electrochemistry impedance spectroscopy (EIS) were tested on CHI660e electrochemical workstation ( $100\text{ kHz} \sim 0.01\text{ Hz}$ ) using an open circuit voltage.

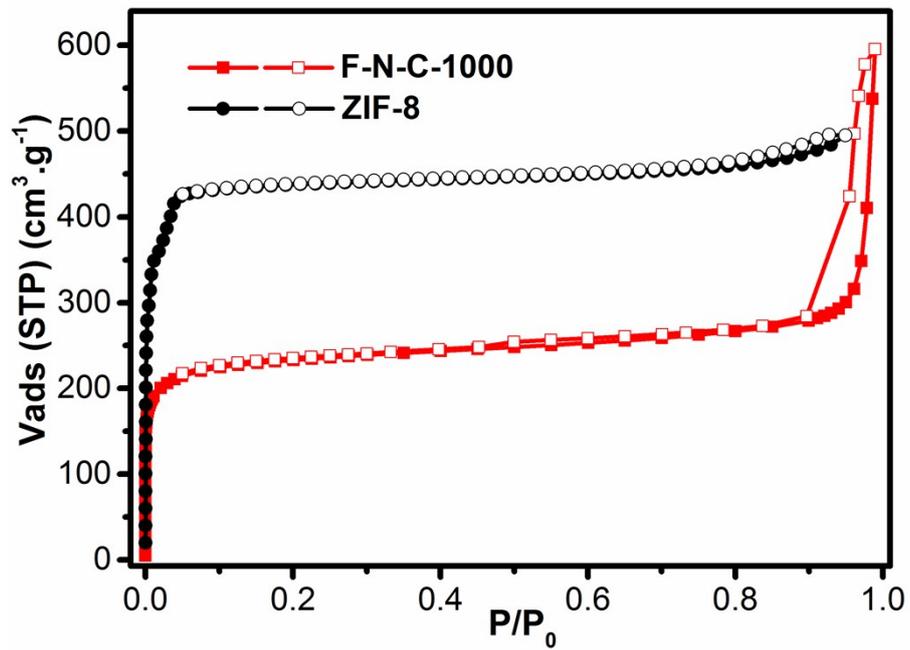


Figure S1. N<sub>2</sub> sorption isotherms for ZIF-8 and F-N-C-1000 at 77 K.

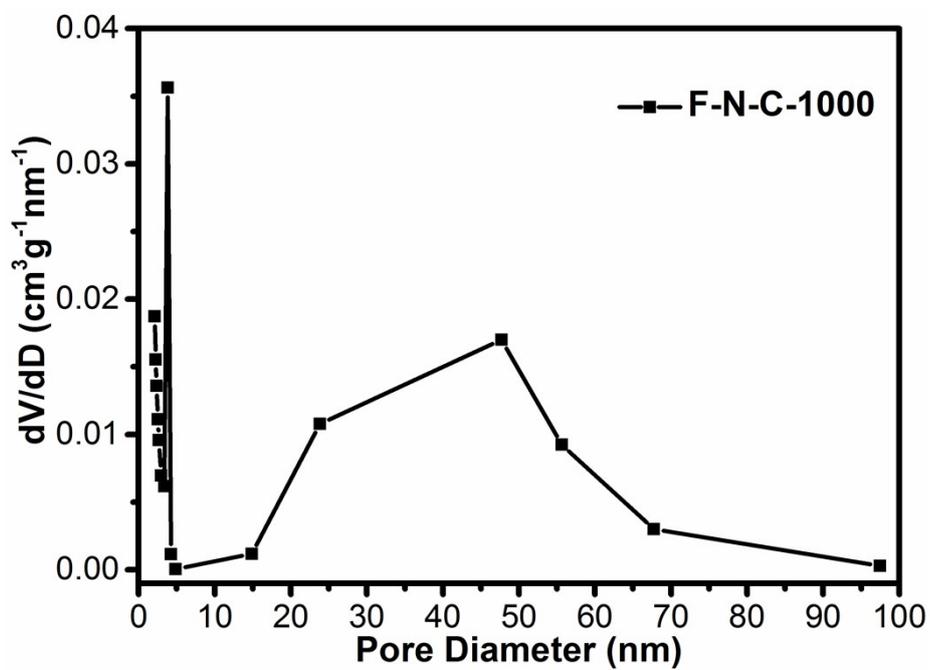


Figure S2. The distributions of pore size for F-N-C-1000.

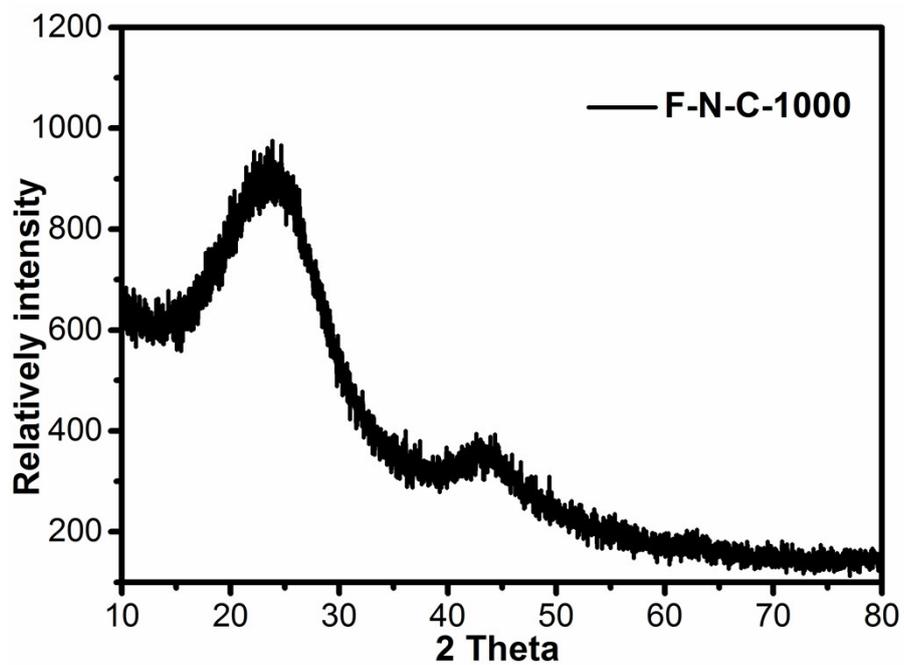


Figure S3. The powder X-ray diffraction of F-N-C-1000.

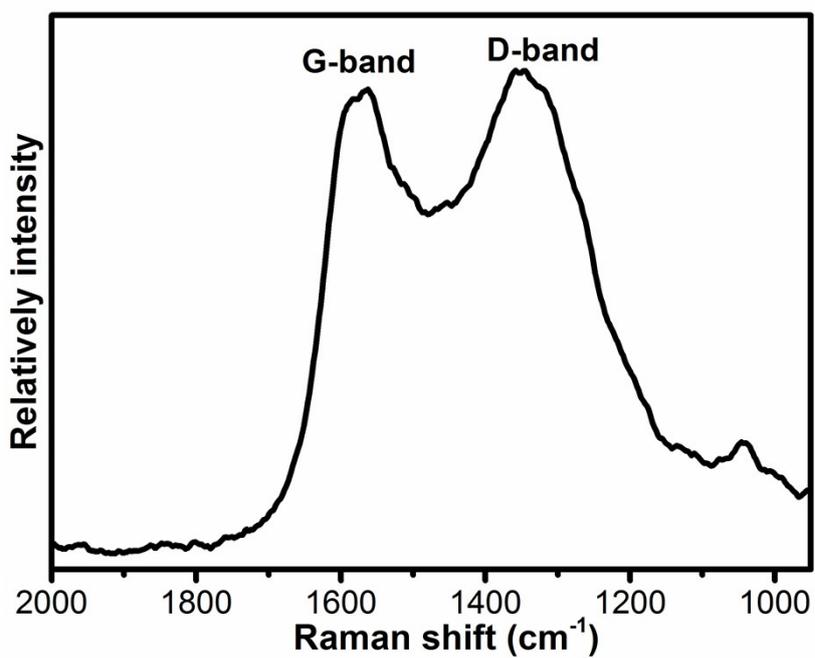


Figure S4. The Raman spectrum of F-N-C-1000.

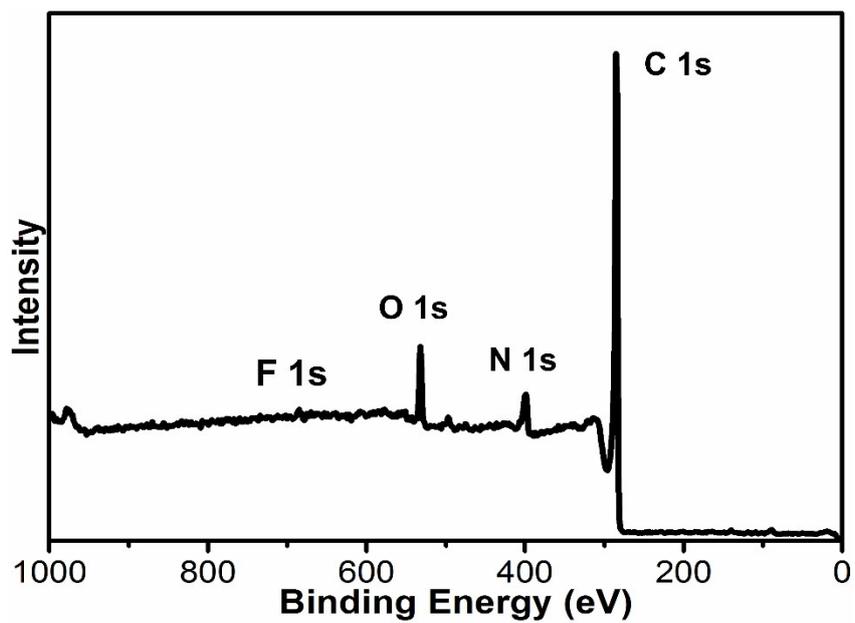


Figure S5. XPS survey spectrum of F-N-C-1000.

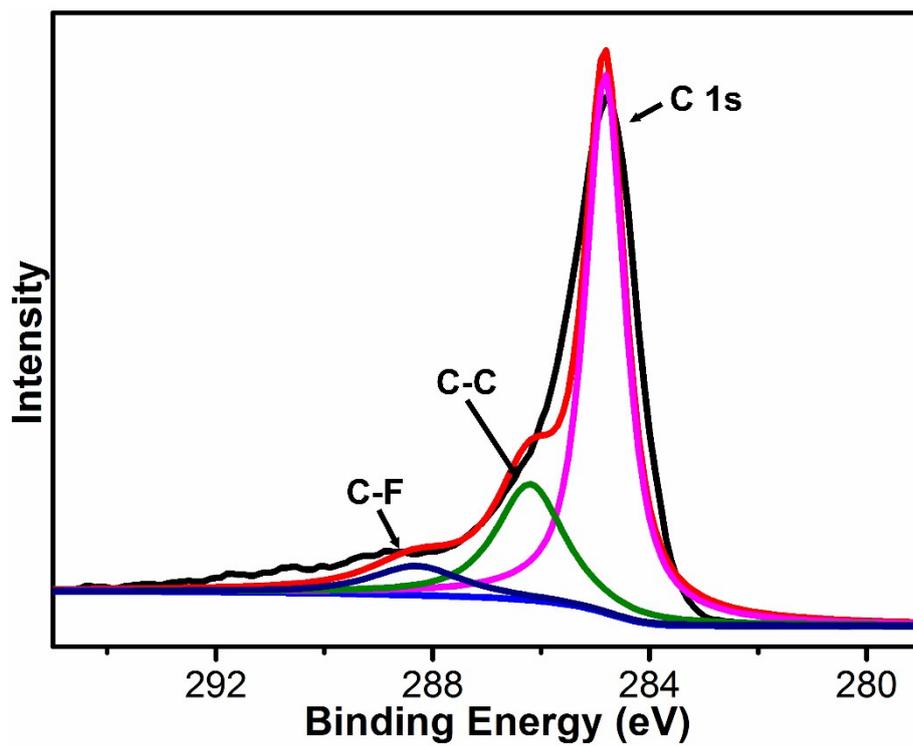


Figure S6. High-resolution XPS spectrum for C in F-N-C-1000.

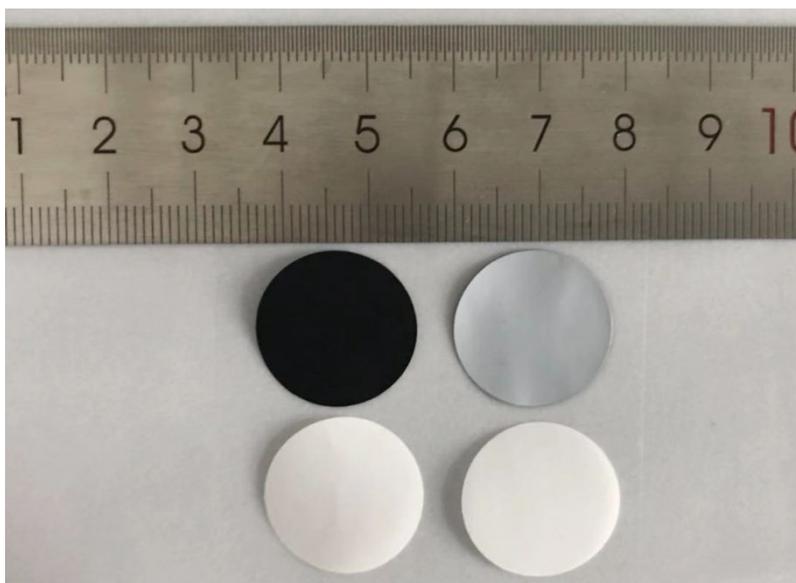


Figure S7. Digital photo of F-N-C-1000 on the modified Celgard separators (top) and origin Celgard separators (bottom).

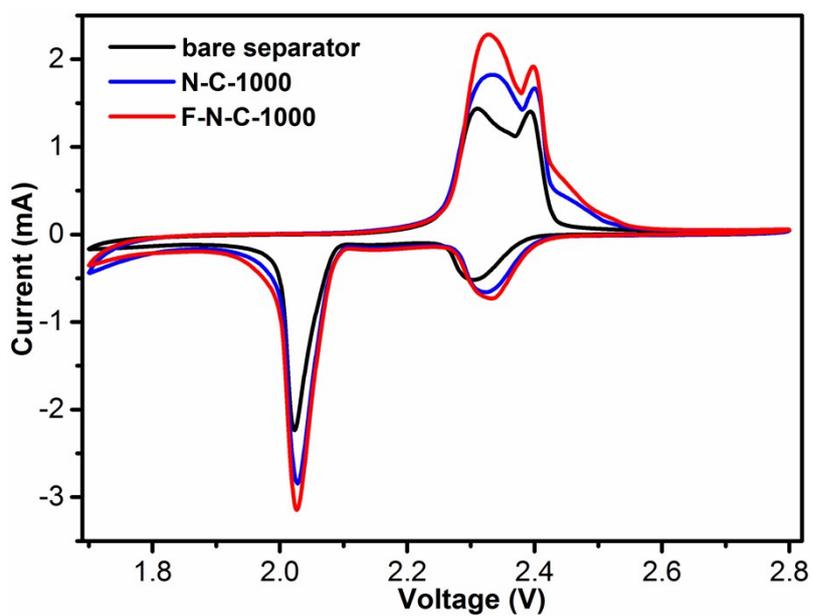


Figure S8. CV curves of Li-S cell constructed using various membranes.

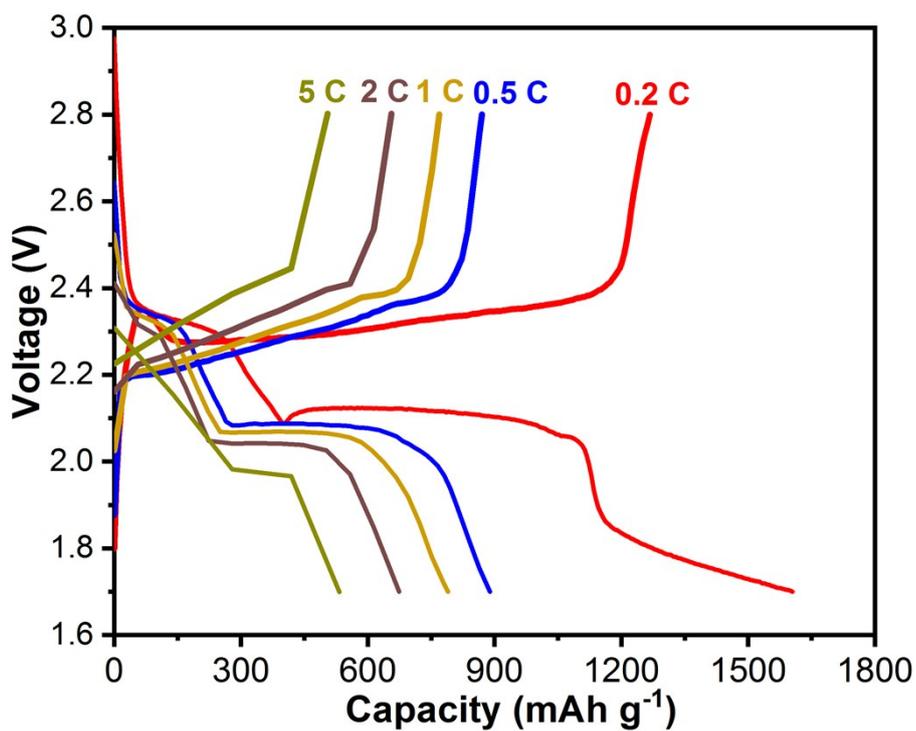


Figure S9. The C-rate properties of Li-S cell with F-N-C-1000 membrane.

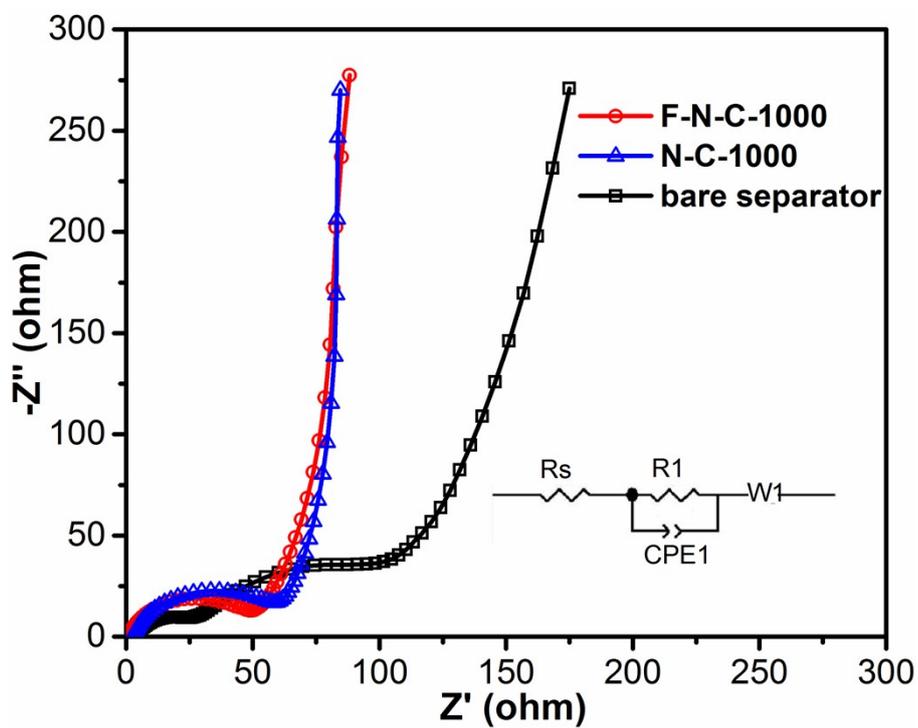


Figure S10. EIS tests of Li-S cell constructed using various membranes.