Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2016

Supporting Information

Gel Based Sulfur Cathodes with High Sulfur Content and Large Mass Loading for

High-Performance Lithium-Sulfur Batteries

Shiqi Li¹, Tong Mou², Guofeng Ren¹, Juliusz Warzywoda³, Zidong Wei⁴, Bin Wang², Zhaoyang Fan^{1*}

 Department of Electrical and Computer Engineering and Nano Tech Center, Texas Tech University, Lubbock, Texas 79409, USA.

2. School of Chemical, Biological and Materials Engineering and Center for Interfacial Reaction Engineering (CIRE), University of Oklahoma, Norman, OK 73019, USA

3. Materials Characterization Center, Whitacre College of Engineering, Texas Tech University,

Lubbock, Texas 79409, USA.

4. Chongqing Key Laboratory of Chemical Process for Clean Energy and Resource Utilization,

School of Chemistry and Chemical Engineering, Chongqing University, Shazhengjie 174,

Chongqing 400044, China.

(* Email: Zhaoyang.Fan@ttu.edu)

Experimental methods

Fabrication of carbon nanoribbon (CNR) aerogels. The bacterial cellulose (BC) hydrogel, kindly provided by Ms. Chunyan Zhong (Hainan Yeguo Foods Co., Ltd., Hainan, China), was freeze-dried at a sublimation temperature of -80 °C and a pressure of 0.04 mbar. Subsequently, the obtained BC aerogel was transferred into a tube furnace and pyrolyzed under the ammonia flow (50 sccm) at 800 °C for 2 hours with a heating rate of 2.5 °C/min to obtain black Am-CNR aerogel. For Ar-CNR aerogel fabrication, the process was the same, but heating was performed under the argon flow.

Fabrication of carbon microfiber (CMF) membranes. The laboratory filter paper (FP, Fisherbrand Quantitative Q8) was selected as the precursor for fabricating CMF membranes. The FP was successively rinsed in ethyl alcohol and distilled water, and then dried at 80 °C in air. Thus cleaned FP was carbonized in a tube furnace under ammonia flow (50 sccm) at 800 °C for 2 hours with a heating rate of 2.5 °C/min to obtain Am-CMF membrane. For Ar-CMF membrane fabrication, the process was the same except that the atmosphere for heating was argon.

Characterization. The morphology and structure of CNR aerogels and CMF membranes were characterized by a field emission scanning electron microscope (FE-SEM) and a transmission electron microscope (TEM, Hitachi H-9500 TEM). X-Ray powder diffraction (XRD) was conducted through a Bruker AXS D5005 X-ray diffractometer (Cu K α radiation, 40 kV, 30 mA). X-ray photoelectron spectra (XPS) were acquired using a Physical Electronics PHI 5000 VersaProbe spectrometer. The photoelectrons were excited by monochromatic Al K $_{\alpha}$ radiation (1486.6 eV) with a step of 0.1 eV and pass energy of 23.5 eV for high-resolution XPS spectra. Raman spectra were recorded using a Bruker Optics Senterra dispersive Raman microscope spectrometer with an excitation laser beam wavelength of 532 nm and a spectral resolution of ~3-5 cm⁻¹. The nitrogen sorption measurements were conducted at 77 K using a Quantachrome Autosorb iQ (ASiQ) instrument.

Preparation of lithium polysulfide catholyte. The blank electrolyte was a solution of lithium bis(tri-fluoromethanesulfonyl)imide (1 M) in 1, 2-dimethoxyethane (DME) and 1, 3-dioxolane (DOL) (1:1 by volume) containing LiNO₃ (1 wt %). The lithium polysulfide catholyte was prepared by chemically reacting sulfur (99.999%, Acros Organics) and lithium

sulfide (99.9%, Alfa Aesar) in the blank electrolyte to form Li_2S_6 (0.25 M) in the solution. Then the solution was stirred at 60 °C in an argon-filled glove box for 12 hours.

Electrochemical measurements. 2032-type coin cells were assembled in an argon-filled glove box. For assembling coin cells based on single-layered S-electrode, 40µL of Li₂S₆ catholyte was dropped slowly on a single layer CNR aerogel with an area of 0.5 cm² to obtain S mass loading of 3.84 mg cm⁻² or 0.3 cm² to obtain S mass loading of 6.4 mg cm². After the catholyte was uniformly distributed and the solvent in the catholyte nearly evaporated, a separator was put on the S-electrode and blank electrolyte was put on the separator, followed by a Li foil as the anode. For assembling coin cells based on dual-layered S-electrode, 40 µL of Li_2S_6 catholyte was dropped slowly on one layer CNR aerogel with an area of 0.5 cm² to obtain S mass loading of 3.84 mg cm⁻². After the catholyte was uniformly distributed and the solvent in the catholyte nearly evaporated, a second layer CNR aerogel with a much smaller thickness was used to cover the first layer. A separator was put on the S-electrode and blank electrolyte was put on the separator, followed by a Li foil as the anode. In the example, the S mass percentage is 83 %. The blank electrolyte used in all the coin cells discussed herein is 20 μ L. The process for assembling cells based on CMF membranes was the same as that used for assembling cells based on CNR aerogels. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured by an electrochemical workstation (EC-Lab SP-150, BioLogic Science Instruments) for the 2032-type coin cells. CV was recorded over the potential window of 1.8 to 2.8 V versus Li⁺/Li, and the scan rate of CV was 0.05 mV s⁻¹. The EIS was taken by applying 5 mV alternative signal versus the open-circuit voltage in the frequency range of 1 MHz to 0.1 Hz. Galvanostatic cycling was carried out using a LAND CT-2001A instrument (Wuhan, China) from 1.8 to 2.8 V versus Li⁺/Li. Specific capacity values were calculated based on the mass of sulfur in the Li_2S_6 catholyte added to the CNR aerogel or CMF membrane. After cycling, the cells were disassembled and the cycled CNR aerogel and cycled lithium foil were washed with DOL and dried for further characterization. The disassembly process was carried out in an argon-filled glove box.

Computational methods. The density functional theory (DFT) calculations were performed using the VASP package.¹ The PBE-GGA exchange-correlation potential² was used, and the electron-core interactions were treated in the projector augmented wave (PAW)

method.^{3, 4} The van der Waals interaction has been taken into account through the DFT-D3 semi-empirical method.^{5, 6}

To simulate an infinite graphene monolayer, the calculations have been performed using a supercell containing 160 C atoms, with a 20 Å vacuum space between layers in adjacent supercells. When taking the adsorbate into account, the vacuum space is still larger than 14 Å. For the calculations with a graphene nanoribbon, the width of the zigzag nanoribbon is 22 Å with a vacuum layer (along the y-axis) of 21 Å between ribbons in adjacent supercells. The carbon atoms at the edges are hydrogenated. Along the other direction (x-axis) of the ribbon, which is infinite, the length of the supercell is 20 Å. The z-direction of the supercell is the same between the ribbon and monolayer calculations. The structures have been optimized using a single Γ point of the Brillouin zone with a kinetic cut off energy of 400 eV. All the atoms were fully relaxed until the atomic forces were smaller than 0.02 eV Å⁻¹. When calculating N-doped graphene, one or two carbon atoms have been replaced by the one N atom to simulate the graphitic, pyrrolic and pyridinic-N configurations. The supercell used in calculations (containing 160 C atoms for pristine graphene) is 20 and 21 Å in the x and y direction, respectively, which leads to about 2 nm separation between N (or O) impurities in adjacent supercells to reduce the interaction between them. The same supercell has been used in our previous calculations for N-related defects in graphene.⁷



Figure S1. (a) SEM image (scale bar = 1 μ m) and (b) XRD pattern of BC aerogel. Three characteristic peaks at 14.2 °2 θ , 16.7 °2 θ , and 22.7 °2 θ correspond to the (010), (001), and (011) planes of cellulose I, respectively.⁸



Figure S2. TEM image of Am-CNR aerogel (scale bar = 100 nm). The carbon nanoribbons are interwoven to form a network for the facile transport of electrons and lithium ions.^{9, 10} The 1D nanostructure of the nanoribbons with a width of tens of nanometers ensures the sufficient contact of the conductive framework with the catholyte.



Figure S3. The Am-CNR demonstrates excellent flexibility.



Figure S4. XRD pattern of Am-CNR aerogel showing a broad peak at 22.4 °20, which corresponds to diffraction from the (002) plane of graphite.¹¹ This suggests the lack of long-range order/quasi-amorphous structure.



Figure S5. Raman spectrum of Am-CNR aerogel. Two characteristic bands at approximately 1350 cm⁻¹ and 1580 cm⁻¹ correspond to the D band and G band.¹² The presence of these two bands indicates the successful conversion of BC into carbon after pyrolysis.



Figure S6. Survey XPS spectrum of Am-CNR aerogel. Am-CNR aerogel consisted of 92.1 at% carbon, 4.5 at% oxygen and 3.4 at% nitrogen.



Figure S7. DFT-calculated adsorption configuration of Li_2S_8 at a quaternary (a), pyridinic (b), hydrogenated pyridinic (c), pyrrolic (d) and three adjacent pyridinic (e) – N functionalized graphene. We find that to stabilize the pyrrolic-N (d), two H atoms have to be used to passivate the two nearby C atoms. Otherwise, pyrrolic-N will transform to a pyridinic configuration. The C, N, Li, S, and H atoms are colored grey, blue, green, yellow, and white, respectively. The calculated adsorption energies (in eV) are shown below the figures.



Figure S8. Cyclic voltammetry (CV) plot at a scan rate of 0.05 mV s⁻¹ within the voltage range of 1.8 V to 2.8 V vs. Li⁺/Li. The CV curve consists of two reductive peaks at approximately 2.3

and 1.9 V and two oxidative peaks at approximately 2.3 and 2.4 V.



Figure S9. Comparison of the Nyquist plots for the single-layer structure and the dual-layer sandwich structure. The high frequency intercept at the real axis corresponds to the internal impedance (R_e) of the batteries. The semicircles located in the higher and lower frequency regions correspond to the surface film resistance (R_f) and the charge-transfer resistance (R_{ct}), respectively, of the batteries.¹³ The plots show that the interlayer has effectively reduced the interfacial and charge-transfer resistances of the cells.



Figure S10. SEM image of fresh lithium foil (scale bar = $20 \mu m$). The fresh lithium foil was

smooth.



Figure S11. XRD pattern of cycled lithium foil. The peak corresponding to Li₂S was very weak, indicating that soluble polysulfides were almost completely sequestrated in the cathode and the chemical reaction between the soluble polysulfides and Li anode was alleviated.



Figure S12. Ar-CNR aerogel: (a) SEM image (scale bar=100 nm), (b) Raman spectrum.



Figure S13. Am-CMF membrane: (a) SEM image (scale bar = $10 \mu m$), (b) Raman spectrum.



Figure S14. Ar-CMF membrane: (a) SEM image (scale bar = $10 \mu m$), (b) Raman spectrum.



Figure S15. Initial discharge profiles of the fresh cells based on (a) Am-CNR aerogel, (b) Ar-CNR aerogel, (c) Am-CMF membrane and (d) Ar-CMF membrane. The high plateau was not evident herein because the starting active material was Li_2S_6 . The theoretical discharging capacity from Li_2S_6 to Li_2S was 1395 mA h g⁻¹.

References

- G. Kresse and J. Furthmuller, *Phys. Rev. B: Condens. Matter Mater.*, 1996, 54, 11169-11186.
- 2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865-3868.
- 3. P. E. Blöchl, Phys. Rev. B: Condens. Matter Mater. Phys., 1994, 50, 17953-17979.
- 4. G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758-1775.
- 5. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.
- 6. S. Grimme, S. Ehrlich and L. Goerigk, J. Comput. Chem., 2011, 32, 1456-1465.
- 7. B. Wang, L. Tsetseris and S. T. Pantelides, J. Mater. Chem. A, 2013, 1, 14927-14934.
- Y. Nishiyama, J. Sugiyama, H. Chanzy and P. Langan, J. Am. Chem. Soc., 2003, 125, 14300-14306.
- H.-W. Liang, Q.-F. Guan, Z. Zhu, L.-T. Song, H.-B. Yao, X. Lei and S.-H. Yu, NPG Asia Mater., 2012, 4, e19.
- W. Luo, J. Schardt, C. Bommier, B. Wang, J. Razink, J. Simonsen and X. Ji, *J. Mater. Chem. A*, 2013, 1, 10662-10666.
- Z.-Y. Wu, C. Li, H.-W. Liang, J.-F. Chen and S.-H. Yu, *Angew. Chem., Int. Ed.*, 2013, 52, 2925-2929.
- W. Luo, B. Wang, C. G. Heron, M. J. Allen, J. Morre, C. S. Maier, W. F. Stickle and X. Ji, *Nano Lett.*, 2014, 14, 2225-2229.
- V. S. Kolosnitsyn, E. V. Kuzmina, E. V. Karaseva and S. E. Mochalov, J. Power Sources, 2011, 196, 1478-1482.