Supporting Information

Multi-functional nanowall arrays with unrestricted Li⁺ transport channels and integrated conductive network for high-areal-capacity Li-S batteries

Xiaofei Yang^{‡a,b,c}, Ying Yu^{‡b,c}, Xiaoting Lin^a, Jianneng Liang^a, Keegan Adair^a, Yang Zhao^a, Changhong Wang^a, Xia Li^a, Qian Sun^a, Hongzhang Zhang^{*b,d}, Xianfeng Li^{b,d}, Ruying Li^a, Huamin Zhang^{*b,d}, Xueliang Sun^{*a}

^{*a*} Department of Mechanical and Materials Engineering, University of Western Ontario, London, Ontario, N6A 5B9, Canada

^b Division of Energy Storage, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China

^cUniversity of Chinese Academy of Sciences, Beijing 100049, China

^{*d*} Collaborative innovation Center of Chemistry for Energy Materials (iChEM), Dalian 116023, China

⁺ The authors contributed equally to this work

Experimental Section

Fabrication of S/MWNA and S/D-MWNA: The MWNA was fabricated by a one-pot carbonization of the Ni foam@MOF arrays as well as growing carbon nanotubes via chemical vapor deposition (CVD) method, where Ni foam@MOF arrays were synthesized according a previous report. ¹Typically, Ni foam was first treated with 3 M HCl solution for 30 min to remove the pollutions and Nickle oxide on the surface and then washed with deionized water for several times. After that, 3 pieces of Ni foam ($2*4 \text{ cm}^2$) were immersed into a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.075 M) and hexamethylenetetramine (0.25 M) dissolved in 30 mL methanol and 3 mL of 2 M solution HNO₃ aqueous solution. The HNO₃ aqueous solution is to control the PH value as well as preventing the oxidization of Ni-foam during hydrothermal reaction. For $Zn(NO_3)_2 \cdot 6H_2O$ and hexamethylenetetramine, they are the raw materials for the fabrication of Zn-nanowall array (Zn-

NWA) with nanowall arrays structure, which acts as self-sacrificing template for fabricating Co-MOF with nanowall arrays structure. Soon after, the mixed solution was sealed and heated at a 60 °C oven for 48 h. After cooling to room temperature, the obtained white products were washed with water for several times and then simply immersed into 250 mL of 0.01 M 2-methylimidazole aqueous solution and 40 mL of 0.5 M Co (NO₃)₂·6H₂O methanol solution for 6 h and 24 h stepby-step. The products obtained from this step were labeled as Ni foam@MOF arrays after washed with methanol for several times. The Ni foam@MOF arrays were subsequently transfer into a tube furnace, whose temperature was quickly heated to 550 °C with a heating rate of 20 °C min⁻¹ under a mixed flow of Ar (100 mL min⁻¹) and H₂ (10 mL min⁻¹). The temperature was kept at 550 °C for 10 min and then another C₂H₄ flow with a flow rate of 15 mL min⁻¹ as carbon precursor was pumped in to grow carbon nanotube for another 2 h. In order to remove the residua Zn species and improve the samples' electrical conductivity, the temperature was further increased to 950 $^\circ\,$ C with a heating rate of 20 °C min⁻¹ under the Ar flow and kept for 1 h. The MNWA was obtained after naturally cooling to the room temperature. The density of materials coated on MNWA except Ni foam is around ~ 4 mg cm⁻². For comparison, The D-MNWA was synthesized by removing the Ni foam with 3M HCl and broken the arrays structure via grinding. The S/MNWA and S/D-MNWA were obtained via directly absorb 20 mg mL⁻¹ sulfur dissolved CS₂ and then naturally remove the solvent at room temperature. The sulfur contents are around 50 wt.% and 70 wt.% (determined by TGA results), respectively, for S/MNWA cathodes with sulfur loadings of 4 mg cm⁻² and 10 mg cm⁻². The sulfur content of S/D-MNWA composite is around 50 wt.%.

Materials Characterization: The morphologies and structures of the samples except Li anodes were characterized by Hitachi S-4800 field emission scanning electron microscope (FE-SEM), and Tecnai G2 F20 S-TWIN and FEI Quanta FRG 200 F transmission electron microscopy (TEM)

equipped with energy dispersive spectroscopy (EDS). The morphologies of Li anodes were taken using a Hitachi 3400N environmental scanning electron microscopy. The Bruker D8 Advance Xray diffraction (XRD) with Cu-Ka radiation was used for crystal structure analysis and the XRD dates were collected from 10 ° to 70 ° in 2θ at a scanning rate of 1° min⁻¹. The sulfur contents in the composites/electrodes were determined by SDT Q600 thermogravimetric analyzer (TGA) under a nitrogen atmosphere from room temperature to 600 °C with a heating rate of 10 °C min⁻¹. The Folio Micromeritics Tristar II Brunauer-Emmett-Teller (BET) surface area analyzer was employed for detail pore structure investigation. Except the SEM images and related EDS results, such materials characterizations as XRD, TGA, BET of MNWA and S/MNWA composites/electrodes were obtained from the samples with Ni foam removal.

Electrochemical measurements: The electrochemical performance of the S/MNWA (sulfur loading: ~4 mg cm⁻² and ~10 mg cm⁻²) and S/D-MNWA electrodes (sulfur loading: 3.0~3.5 mg cm⁻²) were tested with CR2032 coin cells, constructed in an Ar-filled glove box. The S/MNWA composite was used as cathode directly, while S/D-MNWA cathode were fabricated by casting the slurry (solvent: 1-methyl-2-pyrrolidinone (NMP)) containing 80 wt.% S/D-MNWA, 10 wt.% acetylene black, and 10 wt.% Polyvinylidene fluoride (PVDF) onto aluminum (Al) foils and dried at 70 °C for 12 h under vacuum. The cathode and Li anode were separated by a celgard 2325 membrane. The electrolyte used in this study is 1 M bis(trifluoromethylsulfonyl) imide (LiTFSI) in 1, 2-dimethoxymethane (DME) /1, 3-dioxolane (DOL) (1:1 v/v) with 2 wt.% LiNO₃ additive. The ratio of electrolyte to sulfur (E/S) are 15 µL mg⁻¹ and 6 µL mg⁻¹ for the electrodes with sulfur loadings of 4 mg cm⁻² and 10 mg cm⁻², respectively.

Electrochemical impedance spectroscopy (EIS) was tested at an open-circuit condition with a frequency range from 5.0×10^5 Hz to 1.0×10^{-2} Hz on a versatile multichannel potentiostation

3/Z (VMP3). Cyclic voltammograms (CV) were tested on same instrument and the data were collected under a scanning rate of 0.1 mV s⁻¹ between 1.7 V and 2.8 V. The charge-discharge tests were carried out using a LAND CT-2001A system and Arbin BT-2000 battery testing equipment with voltages arrange from 1.7 V to 2.8 V at room temperature. Unless mentioned otherwise, the specific capacities mentioned in this work were calculated based on sulfur and the voltages were respected to Li⁺/Li (vs. Li⁺/Li).

Electrolyte uptake and porosity: The electrolyte uptake of the S/MNWA and S/D-MNWA electrodes was determined by the following method: firstly, using S/MNWA and S/D-MNWA electrodes to assemble two coin cells with excess electrolyte and let them stand for 12 h. After that, the cells were disassembled and the electrodes were subsequently taken out, wiped out the surface electrolyte with a tissue paper, and quickly measure the thickness and weight.

The electrolyte uptake of the samples can be obtained based on the weight difference between the dry and wet electrodes by the equation as follow:

$$Electrolyte uptake = \frac{W_{wet} - W_{dry}}{W_{dry} - W_{current collector}}$$
(1)

Where W_{wet} , W_{dry} are the weight of wet electrodes and dry electrodes, respectively. $W_{current}$ _{collector} are the Ni foam and Al foil in S/MNWA and S/D-MNWA electrodes, respectively.

The porosity of S/MNWA electrode was calculated by the equation as follow:

$$Porosity = \frac{W_{wet} - W_{dry}}{\rho \, S \, T_{wet}} \times 100\% \tag{2}$$

The porosity of S/D-MNWA electrode was calculated by the equation as follow:

$$Porosity = \frac{W_{wet} - W_{dry}}{\rho S (T_{wet} - T_{current \ collector})} \times 100\%$$
(3)

Where ρ is the density of the electrolyte, S is the geometric area of the electrode, T_{wet} is the thickness of wet electrode and T_{current collector} is the thickness of Al foil.

Electrical conductivity: The electrical conductivity of the MNWA, S/MNWA and S/D-MNWA electrodes were measured via pressing the materials/electrodes between two steel pieces with a pressure of 0.1 MPa and testing the resistance (R) by a digital multi-meter (Fluke 15 B). The electrical conductivity was calculated by the following equation:

 $\kappa = L / RA \tag{4}$

where L and A are the thickness and sectional area of the pressed samples.

Visualized adsorption test: Li_2S_4 solution was prepared according to previous report by mixing sulfur and Li_2S with a molar ratio of 3:1 in DME followed by vigorous magnetic stirring. ² 1 mL Li_2S_4 solution with a concentration of 10 mM and 10 mg absorbed materials were used for adsorption test.



Figure S1. SEM images of (a)~(b) Ni foam, (c)~(d) Ni foam@ Zn-NWA (e)~(f) Ni foam@MOF arrays at different magnifications. The insets are the corresponding optical images.



Figure S2. (a)~(d) SEM images of S/MNWA electrode at different magnifications and (e) corresponding EDS elemental mapping of C, S, Co and Ni elements collected from the area in (d). (f) EDS spectrum of S/MNWA.



Figure S3. SEM images of MNWA-NR at different magnifications.



Figure S4. (a) Nitrogen adsorption-desorption isotherms, (b) Pore size distribution curves of MNWA-NR. (c)TGA curvers of MNWA-NR with 4 mg cm⁻² and 10 mg cm⁻² sulfur loadings. (d) XRD patterns of MNWA-NR before and after 4 mg cm⁻² and 10mg cm⁻² sulfur impregnated.



Figure S5. CV profiles of the S/MNWA electrode for 5 cycles.



Figure S6. (a) Electrolyte uptake and porosity and (b) electrical conductivity of S/MNWA and S/D-MNWA electrodes.

Table S1. Comparison of this work with recent publications from the Li-S literature with high sulfur loadings around 4 mg cm⁻². A: Material. B: Sulfur content based on whole cathode (not including current collector). C: Areal sulfur loading (mg cm⁻²). D: Current density (C, 1C=1672 mA g⁻¹). E: Initial specific discharge capacities (mAh g⁻¹, the data were recorded from the cycle number in the bracket for some batteries with obvious activate process). F: Cycle number G: Specific discharge capacity after cycling. H: Capacity retention. I: Capacity attenuation rate per cycle. (ACC: Activated carbon cloth; CF: Carbon fiber; ACF: Activated carbon fiber; CP: Carbon paper; CNT: Carbon nanotube; G: graphene; NS-GS: N,S co-doped graphene sponge; GA: Graphene aerogel; GO: Graphene oxide; Amy-GO: Amylopectin wrapped graphene oxide; PC:

Porous carbon; N-PC: N-doped porous carbon; SP: Super P; KB: Ketjen black: A-KB: Activated ketjen black; LDH: NiFe layered double hydroxide; PPy: Polypyrrole; PAN: polyacrylonitrile; PP: polypropylene;)

Α	В	C	D	Ε	F	G	Η	Ι
This work	50%	4	0.5	854	100	822	96%	0.04%
This work	50%	4	0.5	854	200	739	87%	0.07%
This work	50%	4	0.5	854	300	667	78%	0.07%
This work	50%	4	0.5	854	400	617	72%	0.07%
S/Amy-GO ³	52%	4	0.13	870	100	580	67%	0.33%
S/KS-6 ⁴	63%	4.5	0.01	612	15	580	95%	0.35%
S/GA ⁵	49%	5	0.06	1662	50	539	32%	1.35%
S/GA ⁵	73%	5	0.06	1310	50	481	37%	1.27%
S/GA ⁵	74%	5	0.06	1190	50	716	60%	0.80%
S/PPy (8.4mmol	46%	45	0.06	1043	30	510	400/	1 700/
FeCl ₃ additive) ⁶	40%	ч.Ј	0.00	1045	50	510	49%	1.70%
S/ACC (Al ₂ O ₃		5	0.04	080(4)	100	640	- - • /	
protected Li) ⁷		- 5 0.	0.04	0.04 980(4)	100	640	65%	0.35%
S/KB ⁸	64%	4.7	0.2	900(4)	90	710	79%	0.23%
S/N-PC ⁹	58%	4	0.2	750	200	600	80%	0.10%
S/N-PC ⁹	58%	4	0.2	800	200	650	81%	0.09%
Li ₂ S ₆ /NS-GS ¹⁰	67%	4.6	0.2	1200	100	822	69%	0.32%
S/SP (CNT								
interlayer, PC	600/	4.2		1242	200	940		
interlayer on	60%	4.2		1242	200	840	68%	0.16%
separator) ¹¹								
Pure S (g-C ₃ N ₄								
interlayer on	60%	5		1135(3)	40	902	79%	0.51%
separator) ¹²								
S/Carbon felt ¹³		4.6	0.33	1120	100	550	49%	0.51%
S/GA 14	67%	4	0.1	1050	75	810	77%	0.30%
S/Co ₉ S ₈ ¹⁵	60%	4.5	0.05	956	60	778	81%	0.31%

S/Co ₉ S ₈ ¹⁵	60%	4.5	0.2	933	150	600	64%	0.24%
$S/g-C_3N_4$ ¹⁶	60%	4	0.2	975	50	600	62%	0.77%
S/g - C_3N_4 ¹⁶	60%	5	0.2	854	50	620	73%	0.55%
S/G ¹⁷	90%	4.3	0.1	1077	50	746	69%	0.61%
S/CNT(LDH/G	63%	4.3	0.14	1078	100	800	74%	0.26%
separator) ¹⁸							/4/0	0.2070
S/PAN-KB ¹⁹	72%	4.4	0.5	600(8)	100	513	86%	0.15%
S/PC (C interlayer	60%	4.1	0.05	810(12)	50	730	90%	0.20%
on separator) ²⁰							2070	0.2070
S/CP ²¹	29%	4.4	0.05	1116	40	750	67%	0.82%
Li2S6/CNT/ACF@	70%	48	0.5	800	100	696	070/	0.100/
MnO ₂ ²²	/0/0	т.0	0.5	000	100	070	87%	0.13%
S/A-KB ²³	42%	4	0.1	995(5)	100	891	90%	0.10%
S/G/CNT (PP/GO/	5/10/	1	0.2	1225	20	068		
Nafion separator) ²⁴	3470	4	0.2	1223	50	908	79%	0.70%
S/CNT/CF (layer	600/	1	0.1	096	100	621		
by layer) ²⁵	00%	4	0.1	980	100	021	63%	0.37%
S/ACF ²⁶	64%	4.6	0.5	991	200	753	76%	0.12%
S/PC ²⁷	49%	4	0.1	908	100	739	81%	0.19%
S/G/CNT ²⁸	76%	4.7	0.1	630(3)	200	442	70%	0.15%
S/CNT/MoP/GO 29	55%	4	0.2	950	200	708	75%	0.13%



Figure S7. Visualized absorption of Li_2S_4 on MNWA-NR (a) before and (b) after 2 h standing.



Figure S8. Charge /discharge profiles of S/D-MNWA electrode at various current densities.



Figure S9. (a) Schematic diagram of the S/D-MNWA electrode during lithiation. (b)~(d) SEM images of S/D-MNWA electrode after cycling at different magnifications. (e) Optical image, (f) cross-section and (g) surface morphology of the Li anode coupled with S/D-MNWA electrode after cycling.



Figure S10. Optical images of the separators coupled with (a) S/MNWA electrode and (b) S/D-MNWA electrode after cycling.



Figure S11. (a) EIS plots of S/MNWA and S/D-MNWA electrodes after cycling. Inset is the equivalent circuit. (b) Relationship between Z' and square root of frequency ($\omega^{-1/2}$) in the low-frequency region.

Tuble 52. Relieve parameters of Shint (11) and Shi Mit (11) electrodes after cycling.							
Kinetic parameters	$R_s(\Omega \text{ cm}^{-2})$	$R_{sf} (\Omega \text{ cm}^{-2})$	$R_{ct} (\Omega \text{ cm}^{-2})$	σ	$D(cm^{-2} s^{-1})$		
S/MNWA	7.26	2.57	2.68	2.48	5.84× 10 ⁻¹⁰		
S/D-MNWA	7.80	44.10	104.32	6.36	8.99× 10 ⁻¹¹		

Table S2. Kinetic parameters of S/MNWA and S/D-MNWA electrodes after cycling.

[1] D. Yu, B. Wu, J. Ran, L. Ge, L. Wu, H. Wang, T. Xu, J. Mater. Chem. A, 2016, 4, 16953-16960.

[2] Z. Yuan, H. J. Peng, T. Z. Hou, J. Q. Huang, C. M. Chen, D. W. Wang, X. B. Cheng, F. Wei, Q. Zhang, *Nano Lett.*, 2016, 16, 519-527.

- [3] W. Zhou, H. Chen, Y. Yu, D. Wang, Z. Cui, F. J. DiSalvo, H. D. Abru~na, ACS Nano, 2013, 7, 8801-8808.
- [4] N. Ding, S. W. Chien, T. S. A. Hor, Z. Liu, Y. Zong, J. Power Sources, 2014, 269, 111-116.
- [5] Y. Jiang, M. Lu, X. Ling, Z. Jiao, L. Chen, L. Chen, P. Hu, B. Zhao, J. Alloys Comp., 2015, 645, 509-516.
- [6] J. E. Hyun, P.-C. Lee, I. Tatsumi, *Electrochim. Acta*, 2015, 176, 887-892.
- [7] A. C. Kozen, C.-F. Lin, A. J. Pearse, M. A. Schroeder, X. Han, L. Hu, S.-B. Lee, G. Rublof, M. Noked, ACS Nano, 2015, 9, 5884–5892.
- [8] D. Lv, J. Zheng, Q. Li, X. Xie, S. Ferrara, Z. Nie, L. B. Mehdi, N. D. Browning, J.-G. Zhang, G. L. Graff, J. Liu, J. Xiao, Adv. Energy Mater., 2015, 5, 1402290.
- [9] A. Schneider, C. Weidmann, C. Suchomski, H. Sommer, J. Janek, T. Brezesinski, *Chem. Mater.*, 2015, 27, 1674-1683.
- [10] G. Zhou, E. Paek, G. S. Hwang, A. Manthiram, *Nat. Commun.*, 2015, 6, 7760.
- [11] S.-H. Chung, C.-H. Chang, A. Manthiram, J. Power Sources, 2016, 334, 179-190.
- [12] C. Y. Fan, H. Y. Yuan, H. H. Li, H. F. Wang, W. L. Li, H. Z. Sun, X. L. Wu, J. P. Zhang, ACS Appl. Mater. Interfaces, 2016, 8, 16108-16115.
- [13] C. Milroy, A. Manthiram, Adv. Mater., 2016, 28, 9744-9751.
- [14] F. Nitze, M. Agostini, F. Lundin, A. E. Palmqvist, A. Matic, Sci. Rep., 2016, 6, 39615.
- [15] Q. Pang, D. Kundu, L. F. Nazar, *Mater. Horiz.*, 2016, *3*, 130-136.
- [16] Q. Pang, L. F. Nazar, ACS Nano, 2016, 10, 4111-4118.
- [17] B. Papandrea, X. Xu, Y. Xu, C.-Y. Chen, Z. Lin, G. Wang, Y. Luo, M. Liu, Y. Huang, L. Mai, X. Duan, *Nano Res.*, 2016, 9, 240-248.
- [18] H. J. Peng, Z. W. Zhang, J. Q. Huang, G. Zhang, J. Xie, W. T. Xu, J. L. Shi, X. Chen, X. B. Cheng, Q. Zhang, Adv. Mater., 2016, 28, 9551-9558.
- [19] H. Sohn, M. L. Gordin, M. Regula, D. H. Kim, Y. S. Jung, J. Song, D. Wang, J. Power Sources, 2016, 302, 70-78.
- [20] K. Sun, H. Liu, H. Gan, J. Electrochem. En. Conv. Stor., 2016, 13, 021002.
- [21] S. Walus, C. Barchasz, R. Bouchet, J.-F. Martin, J.-C. Leprêtre, F. Alloin, *Electrochim. Acta*, 2016, *211*, 697-703.
- [22] H. Xu, L. Qie, A. Manthiram, *Nano Energy*, 2016, 26, 224-232.
- [23] X. Yang, Y. Chen, M. Wang, H. Zhang, X. Li, H. Zhang, Adv. Funct. Mater., 2016, 26, 8427-8434.
- [24] T. Z. Zhuang, J. Q. Huang, H. J. Peng, L. Y. He, X. B. Cheng, C. M. Chen, Q. Zhang, Small, 2016, 12, 381-389.
- [25] C.-H. Chang, S.-H. Chung, A. Manthiram, *Mater. Horiz.*, 2017, 4, 249-258.
- [26] J. S. Lee, W. Kim, J. Jang, A. Manthiram, Adv. Energy Mater., 2017, 7, 1601943.
- [27] X.-X. Peng, Y.-Q. Lu, L.-L. Zhou, T. Sheng, S.-Y. Shen, H.-G. Liao, L. Huang, J.-T. Li, S.-G. Sun, *Nano Energy*, 2017, 32, 503-510.
- [28] Z. Zhang, L.-L. Kong, S. Liu, G.-R. Li, X.-P. Gao, Adv. Energy Mater., 2017, 7, 1602543.
- [29] Y. Mi, W. Liu, X. Li, J. Zhuang, H. Zhou, H. Wang, Nano Res., 2017, 10, 3698-3705.