Amorphous ZnO and Oxygen Vacancies Modified Nitrogen-Doped Carbon Skeleton with Lithiophilicity and Ionic Conductivity for Stable Lithium Metal Anode

Fei Wang^a, Jingxia Gao^b, Yong Liu^{a,c,*}, Fengzhang Ren^{a,*},

^a School of Materials Science and Engineering, Henan University of Science and Technology, Provincial and Ministerial Co-construction of Collaborative Innovation Center for Non-ferrous Metal new Materials and Advanced Processing Technology, Luoyang 471023, China

^b Faculty of engineering, Huanghe Science and Technology College, Zhengzhou, Henan 450006, China

^c Henan Key Laboratory of Non-Ferrous Materials Science & Processing Technology,

Luoyang 471023, China

* Corresponding author and E-mail address:

Prof. Yong Liu, liuyong209@haust.edu.cn;

Prof. Fengzhang Ren, renfz@haust.edu.cn;



Figure S1. XRD patterns of (a) ZIF-8 and MA/ZIF-8, and (b) ZIF-8-C and MA-Zn-C.



Figure S2. SEM images of MA-Zn-C, and the corresponding elemental mapping.



Figure S3. SEM image of MA-C.



Figure S4. (a) C 1s and (b) Zn 2p XPS spectra of MA-Zn-C.



Figure S5. ESR spectra of prepared MA-Zn-C-Ar and MA-Zn-C.



Figure S6. The pore size distribution curve of MA-Zn-C.



Figure S7. Electric field intensity distribution diagrams of (a) Cu foil, (b) MA-C, and (c) MA-Zn-C.



Figure S8. Cyclic voltammetry curves of MA-Zn-C at the scan rate of 0.1 mV s⁻¹.



Figure S9. CE of Cu, MA-C and MA-Zn-C electrode with lithium deposition amount of 1 mAh cm⁻² at 1 mA cm⁻².



Figure S10. SEM image of MA-Zn-C-Li after Li stripping.



Figure S11. SEM images of (a,b) MA-C and (c,d) MA-Zn-C electrode after cycles at 1 mA cm⁻²-1 mAh cm⁻².



Figure S12. Nyquist plots of the MA-Zn-C-Li//MA-Zn-C-Li cells after cycles at 1 mA cm^{-2} and 5 mA cm^{-2} .



Figure S13. Consecutive cyclic performance of MA-Zn-C-Li//MA-Zn-C-Li symmetrical cell at 5 mA cm⁻²-5 mAh cm⁻².



Figure S14. Cyclic performance of MA-Zn-C-Li//MA-Zn-C-Li symmetrical cell at 15 mA cm⁻²-15 mAh cm⁻².



Figure S15. The SEM image of MA-Zn-C-Li after Li stripping.



Figure S16. Electrochemical performances of cycled Cu-Li/Li and cycled MA-Zn-C-Li/Li at 5 mA cm⁻² and 5 mAh cm⁻² after long cycles.



Figure S17. Cyclic performance of MA-Zn-C-Ar-Li//MA-Zn-C-Ar-Li symmetrical cell at 5 mA cm⁻²-5 mAh cm⁻².



Figure S18. Cyclic performance of MA-C-J-Zn-Li// MA-C-J-Zn-Li symmetrical cell at 1 mA cm⁻²-1 mAh cm⁻².



Figure S19. The sectional view of MA-Zn-C-Li composite used as the composite anode in full cells.



Figure S20. Charge/discharge curves of Cu-Li//LFP and MA-C-Li//LFP at various current densities.



Figure S21. SEM images of Cu-Li//LFP (a,b) and MA-Zn-C-Li//LFP (c,d) at 0.44C after 200 cycles.



Figure S22. Charge/discharge curves of Cu-Li//LFP and MA-C-Li//LFP at 0.44C.



Figure S23. SEM images of Cu-Li//LFP (a,b), MA-C-Li//LFP (c,d) and MA-Zn-C-Li//LFP (e,f) at 1.77C after 500 cycles.



Figure S24. Electrochemical performances of full cells with Cu-Li or MA-Zn-C-Li anodes and LFP cathodes (mass loading: 11.5 mg cm⁻²). (a) Rate capacity of Cu-Li//LFP and MA-Zn-C-Li//LFP. (b) Cycling stability of Cu-Li//LFP and MA-Zn-C-Li//LFP at 0.5C. (c) Cycling stability of MA-Zn-C-Li//LFP at 2C.



Figure S25. Electrochemical performances. (a) cycling performance of MA-Zn-C-Li//LFP pouch cells and (b) corresponding voltage profile.

Anode	Current Density (mA cm ⁻²)	Capacity (mAh cm ⁻ ²)	Overpotential (mV)	Cycle Life (h)	Refer.
MA-Zn-C	1	1	14	1200	This work
	5	5	16	1500	
	15	15	~82	500	
C-400	1	1	~20	200	1
CP/Sn/SnO ₂	1	1	16	800	2
	2	1	16	250	
FO-GCNs	2	1	~25	800	3
CHEMP@Ni	5	2	~25	1370	4
ACrCFs	1	1	~15	1000	5
NOCA@CF	1	0.5	~14	800	6
	10	10	~185	400	
NHCF/CN/Z nO	1	1	25	1032	7
	2	1	25	1032	
MCNFs/Ag	1	1	20	600	8
Co@NPC	10	1	31	200	9

Table S1. A survey of Li-based anodes with different carbon hosts and corresponding electrochemical properties with ether-based electrolyte.

C-400:carbon cloth derived from cotton at 400 °C

CP: carbon paper

FO-GCNs: functionalized onion-like graphitic carbon nanospheres

CHEMP@Ni: nickel particles embedded in the holes of carbonized natural porous structure (hemp)

ACrCFs:carbon nanofibers decorated with uniform $CrO_{0.78}N_{0.48}$ nanoparticles

NOCA@CF: N/O dual doped 3D porous carbon architectures are designed on commercial Cu foam current collector

NHCF/CN/ZnO: Nitrogendoped hollow carbon fiber/carbon nanosheets/ZnO

MCNFs/Ag: 3D multichannel carbon fibers (MCNFs) that are decorated with lithiophilic Ag nanoparticles

Co@NPC: 3D carbon nanotubes and a N-doped carbon polyhedron core (PC) embedded with lithiophilic Co nanoparticles

References:

(1) J. K. Meng, W. W. Wang, X. Y. Yue, H. Y. Xia, Q. C. Wang, X. X. Wang, Z. W. Fu, X. J. Wu and Y. N. Zhou, *Journal of Power Sources*, 2020, **465**.

(2) L. Tan, S. H. Feng, X. H. Li, Z. X. Wang, W. J. Peng, T. C. Liu, G. C. Yan, L. J.

Li, F. X. Wu and J. X. Wang, *Chemical Engineering Journal*, 2020, **394**.

(3) S. Ha, J. C. Hyun, J. H. Kwak, H. D. Lim and Y. S. Yun, Small, 2020, 16.

(4) P. F. Wang, Z. Gong, K. Ye, Y. Y. Gao, K. Zhu, J. Yan, G. L. Wang and D. X. Cao, *Electrochimica Acta*, 2020, **356**.

(5) J. Xiao, N. Xiao, C. Liu, H. Q. Li, X. Pan, X. Y. Zhang, J. P. Bai, Z. Guo, X. Q. Ma and J. S. Qiu, *Small*, 2020, **16**.

(6) Y. L. An, Y. Tian, Y. Li, C. L. Wei, Y. Tao, Y. P. Liu, B. J. Xi, S. L. Xiong, J. K. Feng and Y. T. Qian, *Chemical Engineering Journal*, 2020, **400**.

(7) X. L. Zhang, Z. Q. Ruan, Q. T. He, X. J. Hong, X. Song, Q. F. Zheng, J. H. Nie, Y. P. Cai and H. X. Wang, *Acs Applied Materials & Interfaces*, 2021, **13**, 3078-3088.

(8) L. Yu; Q. Su; B. Li; W. Liu; M. Zhang; S. Ding; G. Du; B. Xu. *Electrochimica Acta* **2020**, *362*.

(9) R. Jiang; W. Diao; D. Xie; F. Tao; X. Wu; H. Sun; W. Li; J. Zhang. ACS Applied Energy Materials **2021**, *4* (11), 12871-12881.