

Supporting Information

Highly dispersed Zn nanoparticles confined in nanoporous carbon network: promising anode materials for sodium and potassium ion batteries

Chunliu Yan,^{ab} Xin Gu,^{*a} Li Zhang,^a Ying Wang,^a Liting Yan,^a Dandan Liu,^a
Liangjun Li,^a Pengcheng Dai,^a and Xuebo Zhao^{*ab}

a. Research Center of New Energy Science and Technology, Research Institute of Unconventional Oil & Gas and Renewable Energy, China University of Petroleum (East China), Qingdao, 266580, P. R. China. E-mail: guxin@upc.edu.cn

b. State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering, China University of Petroleum (East China), Qingdao, 266580, P. R. China. E-mail: zhaoxuebo@upc.edu.cn

Experimental section

Synthesis of zeolitic imidazolate framework-8 (ZIF-8)

Firstly, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.95 g) and 2-methylimidazole (6.57 g) were each dissolved in anhydrous methanol (200 ml). Secondly, the two solutions were mixed, stirred for 0.5 h, and aged at 25 °C for 24 h. Finally, ZIF-8 precursor was collected by centrifuging, washing with anhydrous methanol, and drying under vacuum at 80 °C for 12 h.

Synthesis of highly dispersed Zn nanoparticles confined in nanoporous carbon network (ZNP/C)

ZNP/C was achieved by calcining ZIF-8 precursor at a specific temperature for 3 h in N_2 flow at a heating rate of 1 °C min^{-1} . The ZNP/C composites obtained at 550 °C, 600 °C, 650 °C and 700 °C were denoted as ZNP/C-550, ZNP/C-600, ZNP/C-650 and ZNP/C-700, respectively. For comparison, nanoporous carbon material was also synthesized by treating ZNP/C-600 with hydrochloric acid for several hours at 60 °C and denoted as NPC-600.

Material characterization

X-ray diffraction (XRD) was conducted on an X-ray diffractometer (Bruker D8 Adv., Germany). Raman spectrum was measured by a Raman spectrometer (NEXUS 670, USA). SEM images were collected by a scanning electron microscope (JSM 6700F, Japan). TEM images and energy-dispersive X-ray spectroscopy (EDX) were performed on a transmission electron microscope (JEM 2100, Japan). X-ray photoelectron spectroscopy (XPS) was performed on an X-ray photoelectron spectrometer (ESCALAB 250, USA). N_2 sorption measurements were measured at 77 K by Quadrasorb SI. Nonlocal Density Functional Theory (NLDFT) and Brunauer-Emmett-Teller (BET) methods were utilized to study the pore structure and surface area of ZNP/C composites and NPC-600.

Electrochemical measurements

Working electrodes were made by active materials, super P and sodium carboxy methyl cellulose (mass ratio, 8:1:1). The average loading density of active materials was $\sim 1.0 \text{ mg cm}^{-2}$. Na half cells were assembled by using sodium foil as counter electrode, 1 M NaClO_4 in EC/DMC (volume ratio, 1:1) with 2 wt% FEC as electrolyte, and glass fiber (Whatman GF/D) as separator. For the assembling of K half cells, potassium foil was employed as counter electrode, and 0.8 M KPF_6 in EC/DEC (volume ratio, 1:1) was utilized as electrolyte. Cyclic voltammetry was carried out on an electrochemical workstation (CHI760E, China) in the potential range of 0.01-3.0 V (vs. Na/Na^+ or K/K^+). Galvanostatic cyclings were realized at current densities of 0.1-2 A g^{-1} in the potential range of 0.01-3.0 V (vs. Na/Na^+ or K/K^+) on a battery cycler (LAND CT-2001A).

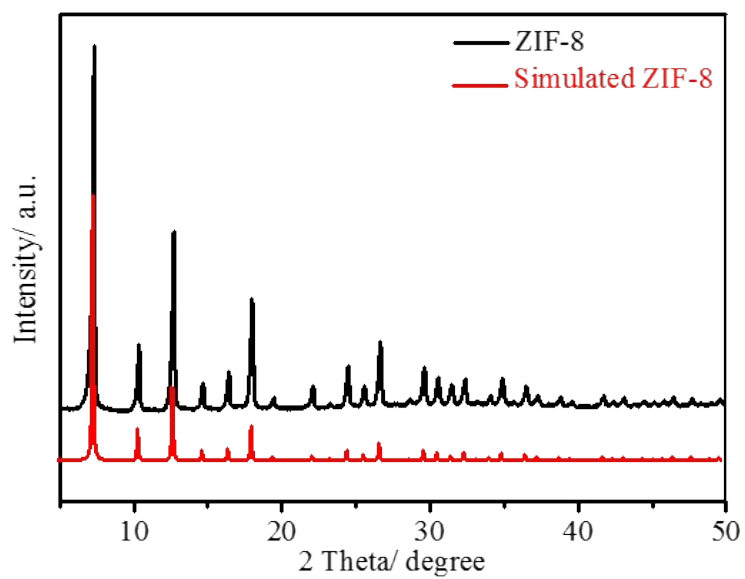


Figure S1 XRD patterns of as-prepared ZIF-8 and simulated ZIF-8.

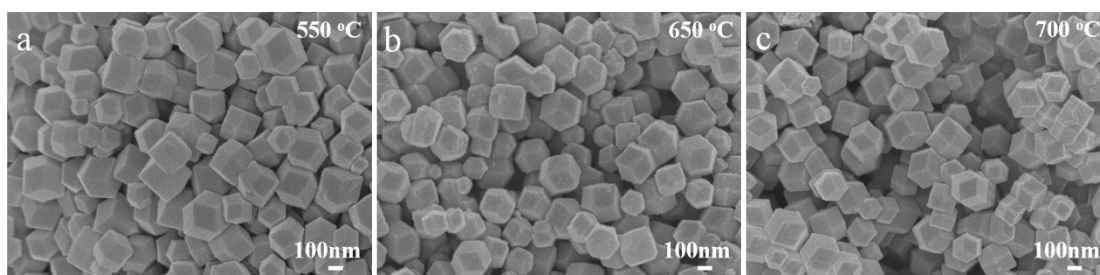


Figure S2 SEM images of (a) ZNP/C-550, (b) ZNP/C-650 and (c) ZNP/C-700.

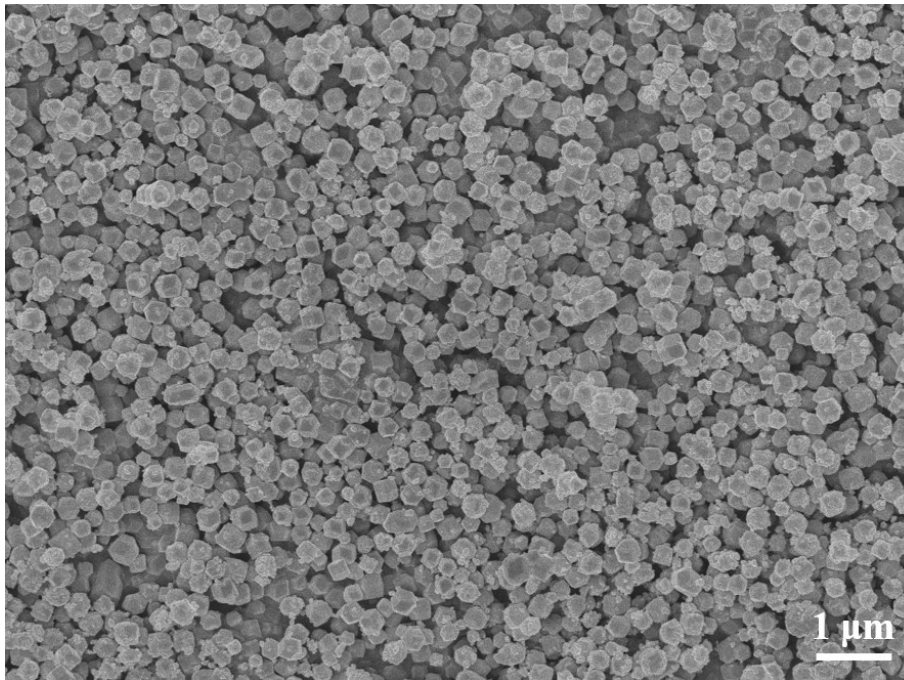


Figure S3 SEM image of ZIF-8 precursor.

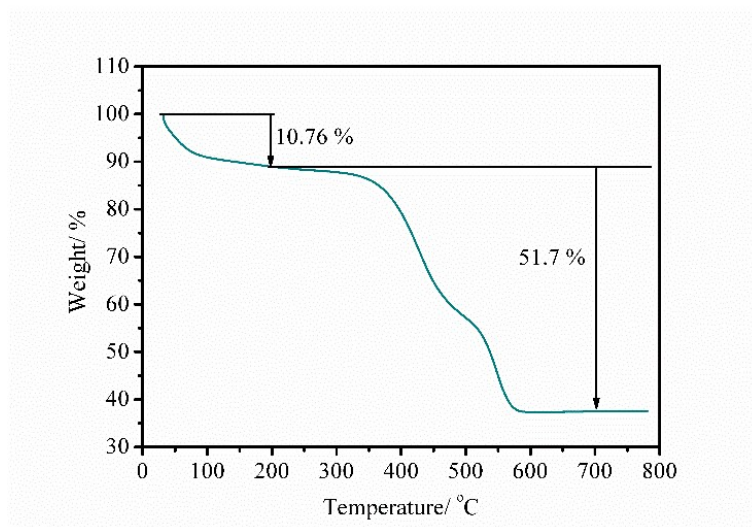


Figure S4 TG curve of ZNP/C-600 at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in air.

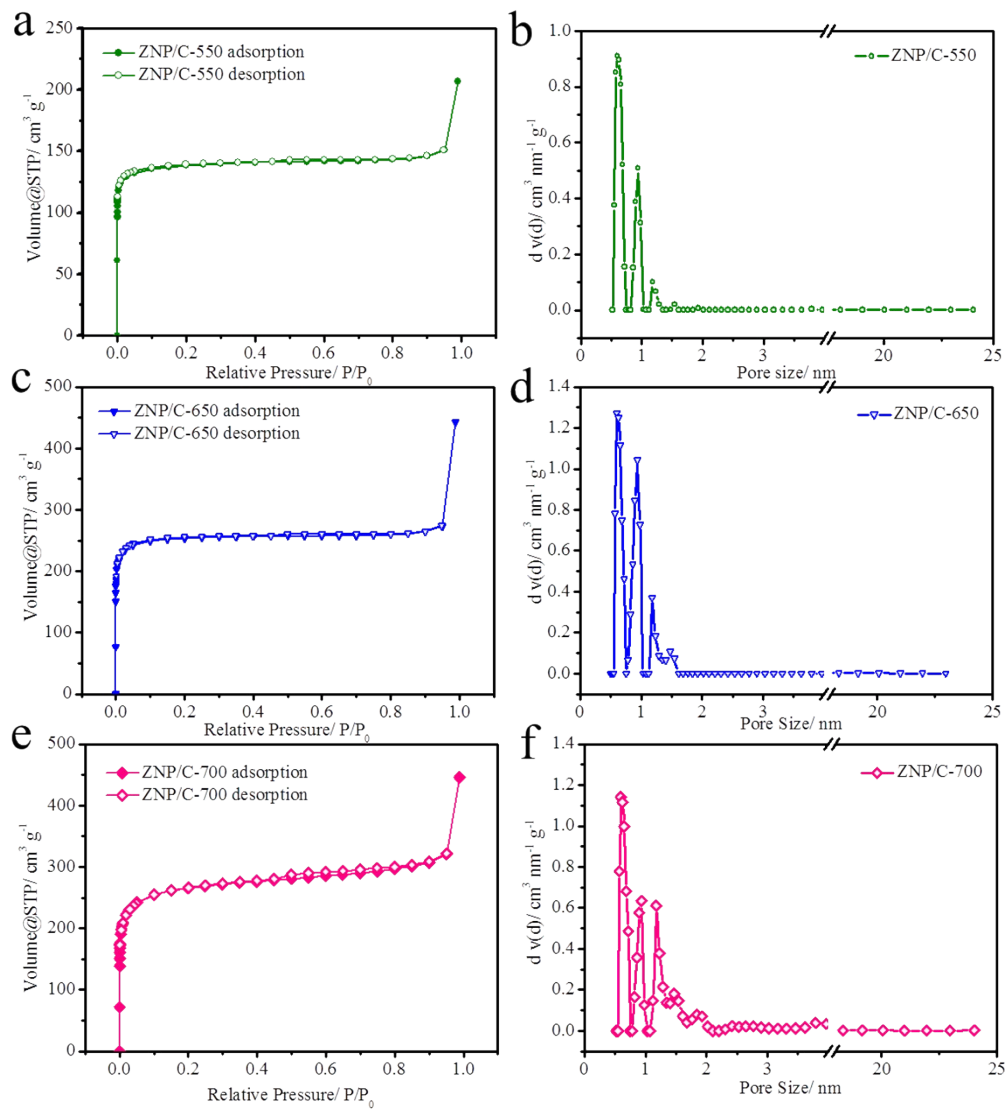


Figure S5 (a, c, e) N₂ sorption isotherms and (b, d, f) NLDFT pore-size distribution curves of ZNP/C-550, ZNP/C-650 and ZNP/C-700.

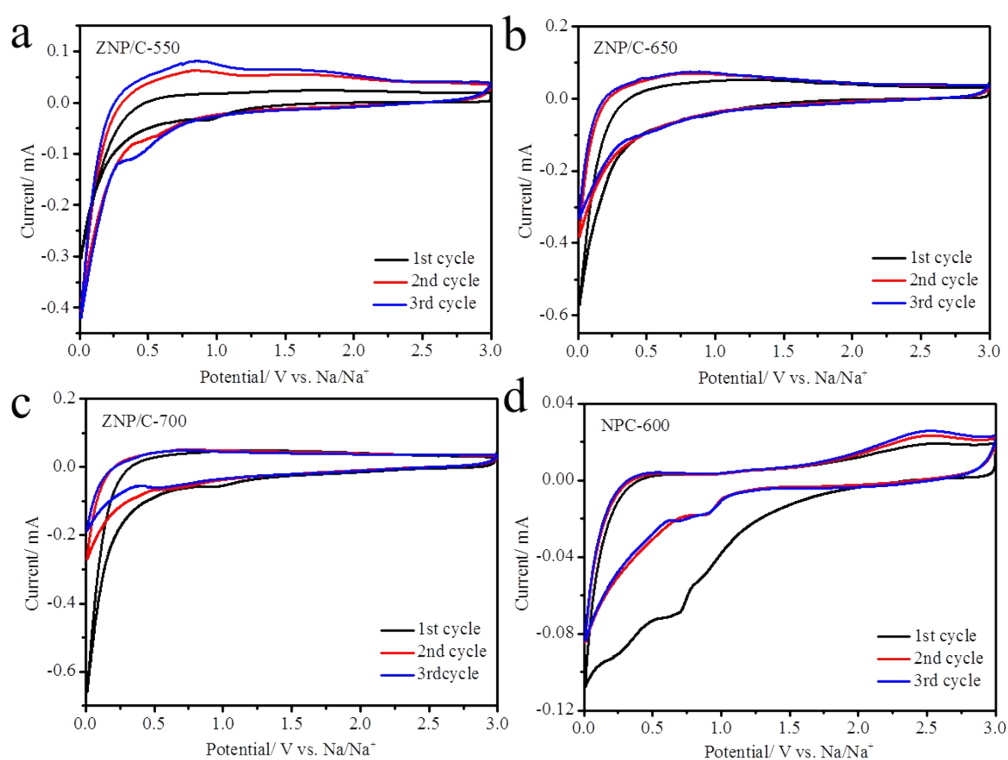


Figure S6 Cyclic voltammograms of ZNP/C-550, ZNP/C-650, ZNP/C-700 and NPC-600 between 0.01 and 3.0 V (vs. Na/Na⁺) at a scanning rate of 0.2 mV s⁻¹.

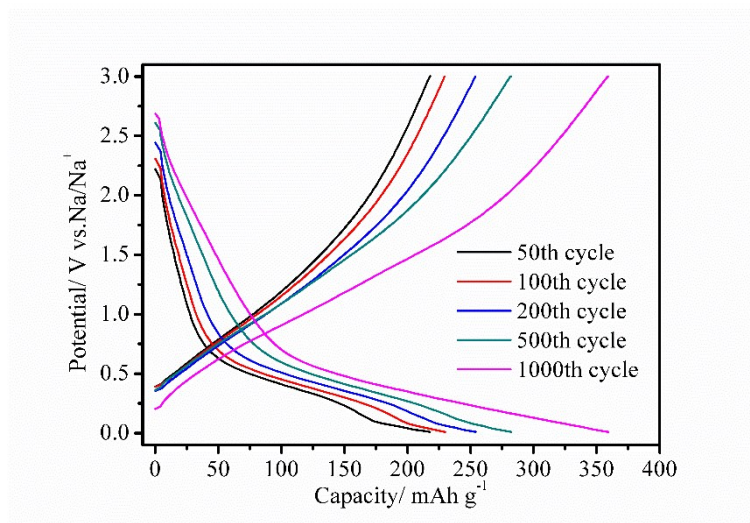


Figure S7 Discharge/charge profiles of ZNP/C-600 at 1 A g⁻¹.

Table S1 Carbonaceous and alloying materials for SIBs.

Anode material	Reversible capacity(mAh g⁻¹)@cycle number	Current density(mA g⁻¹)	Reference
carbon nanofibers	245@280	50	1
hollow carbon nanowires	206@400	50	2
hard carbon nanoparticles	260@200	50	3
Sulfur covalently bonded graphene	150@200	1000	4
N-doped graphene sheets	187.3@50	100	5
3D hollow porous carbon microspheres	313.8@100	100	6
Nitrogen-rich hard carbon	~204@1000	1000	7
Sb/rGO	173@150	500	8
Bi@C microsphere	123.5@100	100	9
ZNP/C-600	361@100 227@1000	100 2000	This work

Table S2 Carbonaceous and alloying materials for PIBs.

Anode material	Reversible capacity(mAh g ⁻¹)@cycle number	Current density(mA g ⁻¹)	Reference
Graphite	100@50	140	10
Soft carbon	118@200	279	11
Hard carbon	144@200	279	11
Reduced graphene oxide	130@175	20	12
Few-layered graphene	150@100	100	13
Activated carbon	100@100	200	14
Few-layered N-doped graphene	165.9@200	500	15
Sn/C composite	110@30	25	16
P/C composite	195.5@20	50	17
ZNP/C-600	200@100	100	This work
	145@300	500	

1. Y. Liu, F. Fan, J. Wang, Y. Liu, H. Chen, K. L. Jungjohann, Y. Xu, Y. Zhu, D. Bigio and T. Zhu, *Nano letters*, 2014, **14**, 3445-3452.
2. Y. Cao, L. Xiao, M. L. Sushko, W. Wang, B. Schwenzer, J. Xiao, Z. Nie, L. V. Saraf, Z. Yang and J. Liu, *Nano letters*, 2012, **12**, 3783-3787.
3. L. Xiao, Y. Cao, W. A. Henderson, M. L. Sushko, Y. Shao, J. Xiao, W. Wang, M. H. Engelhard, Z. Nie and J. Liu, *Nano Energy*, 2016, **19**, 279-288.
4. X. Wang, G. Li, F. M. Hassan, J. Li, X. Fan, R. Batmaz, X. Xiao and Z. Chen, *Nano Energy*, 2015, **15**, 746-754.
5. L.-L. Tian, S.-B. Li, M.-J. Zhang, S.-K. Li, L.-P. Lin, J.-X. Zheng, Q.-C. Zhuang, K. Amine and F. Pan, *ACS applied materials & interfaces*, 2016, **8**, 26722-26729.
6. G. Zou, H. Hou, X. Cao, P. Ge, G. Zhao, D. Yin and X. Ji, *Journal of Materials Chemistry A*, 2017, **5**, 23550-23558.
7. R. R. Gaddam, A. H. F. Niaei, M. Hankel, D. J. Searles, N. A. Kumar and X. Zhao, *Journal of Materials Chemistry A*, 2017, **5**, 22186-22192.
8. F. Wan, H.-Y. Lü, X.-H. Zhang, D.-H. Liu, J.-P. Zhang, X. He and X.-L. Wu, *Journal of Alloys and Compounds*, 2016, **672**, 72-78.
9. F. Yang, F. Yu, Z. Zhang, K. Zhang, Y. Lai and J. Li, *Chemistry-A European Journal*, 2016, **22**, 2333-2338.
10. Z. Jian, W. Luo and X. Ji, *Journal of the American Chemical Society*, 2015, **137**, 11566-11569.
11. Z. Jian, S. Hwang, Z. Li, A. S. Hernandez, X. Wang, Z. Xing, D. Su and X. Ji, *Advanced*

- Functional Materials*, 2017, **27**, 1700324.
12. W. Luo, J. Wan, B. Ozdemir, W. Bao, Y. Chen, J. Dai, H. Lin, Y. Xu, F. Gu and V. Barone, *Nano letters*, 2015, **15**, 7671-7677.
 13. K. Share, A. P. Cohn, R. Carter, B. Rogers and C. L. Pint, *ACS nano*, 2016, **10**, 9738-9744.
 14. Z. Tai, Q. Zhang, Y. Liu, H. Liu and S. Dou, *Carbon*, 2017, **123**, 54-61.
 15. Z. Ju, S. Zhang, Z. Xing, Q. Zhuang, Y. Qiang and Y. Qian, *ACS applied materials & interfaces*, 2016, **8**, 20682-20690.
 16. I. Sultana, T. Ramireddy, M. M. Rahman, Y. Chen and A. M. Glushenkov, *Chemical communications*, 2016, **52**, 9279-9282.
 17. W. Zhang, J. Mao, S. Li, Z. Chen and Z. Guo, *Journal of the American Chemical Society*, 2017, **139**, 3316-3319.