

Enhancing electrochemical performance of micron size Ge anode through in-situ surface composite flowerlike Zn_2GeO_4 for Li ion batteries

Jian Hao^{a*}, Jun Bai^a, Jing Wang^a, Lu Xu^a, Junli Guo^b, Caixia Chi^c, Haihong Li^d

^a State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, College of Chemistry & Chemical Engineering, Ningxia University, Yinchuan 750021, China, E-mail: haojian2017@126.com.

^b College of Mechanical Engineering, Ningxia University, Yinchuan 750021, China.

^c Food and Pharmaceutical Engineering College, Suihua University, Suihua 152061, China.

^d The Chemical Engineering Department, Hulunbuir Vocational Technical College, Hulunbuir, Inner Mongolia 021000, China.

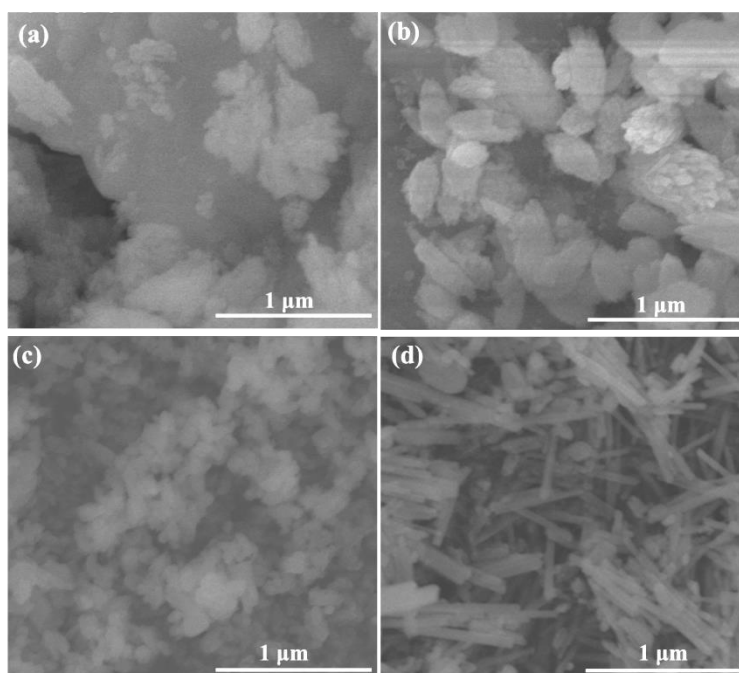


Fig S1 Detailed morphology of samples, in EDTA:water=1:1 solvent system without NaOH(a), in EDTA:water=1:2 solvent system the without NaOH(b), in

EDTA:water=1:1 solvent system the with 1ml NaOH(c), and in EDTA:water=1:1 solvent system the with 2ml NaOH(d).

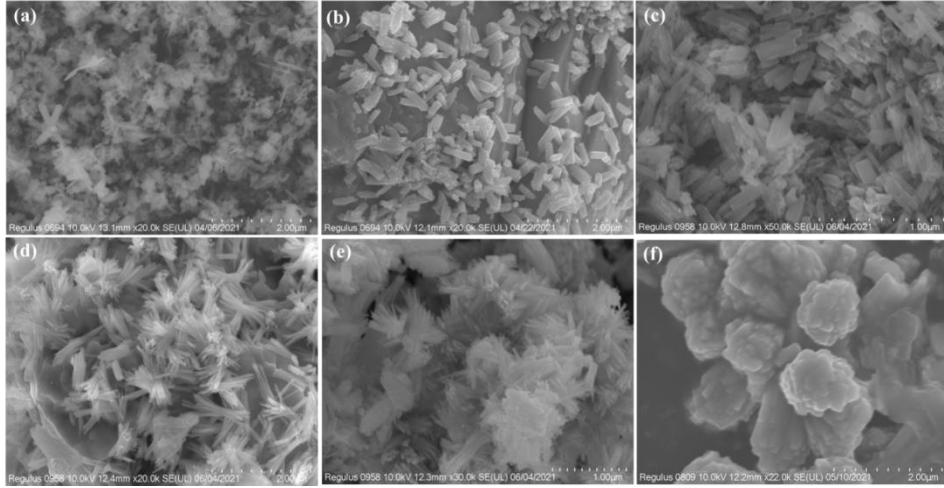


Fig.S2 SEM images of Ge/Zn₂GeO₄ products obtained at different reaction temperatures: (a) 120 °C, (b) 140 °C, (c) 160 °C, (d) 180 °C, (e) 200 °C, and (f) 220 °C.

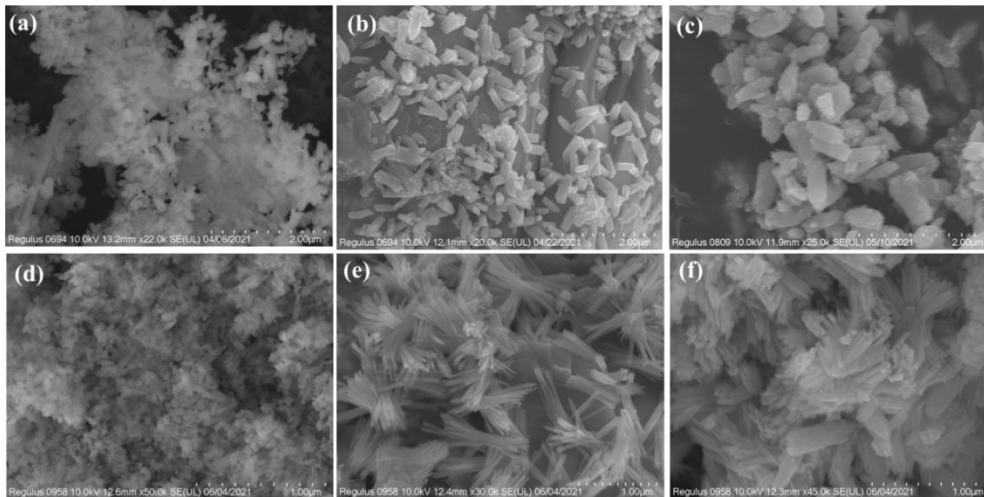


Fig.S3 SEM images of Ge/Zn₂GeO₄-140 °C with different reaction times, (a) 12h, (b) 24h, (c) 48h, and Ge/Zn₂GeO₄-180 °C with different reaction times, (d) 12h, (e) 24h, (f) 48h.

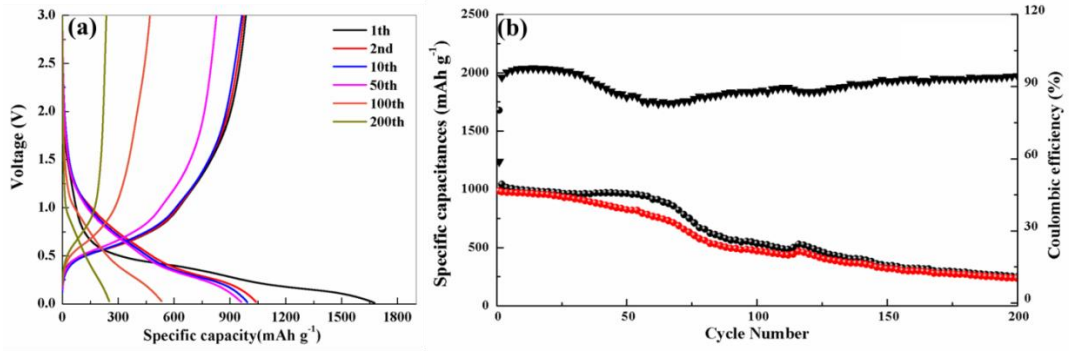


Fig.S4 Galvanostatic charge-discharge profiles for different cycles (a), and cycling performance and Coulombic efficiency (b) of micron Ge electrode.

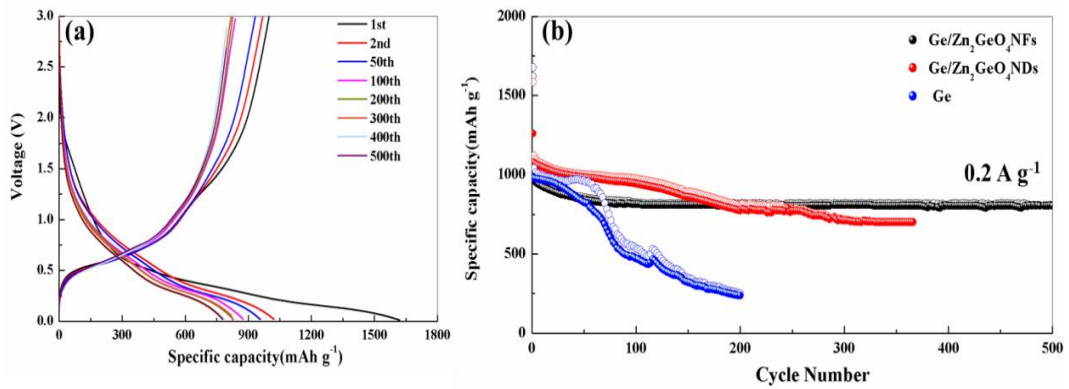


Fig.S5 (a) Galvanostatic charge-discharge profiles for different cycles of Ge/Zn₂GeO₄NFs at 0.2 A g⁻¹, (b) cycling performance of Ge/Zn₂GeO₄NFs, Ge/Zn₂GeO₄NDs, and Ge at 0.2 A g⁻¹.

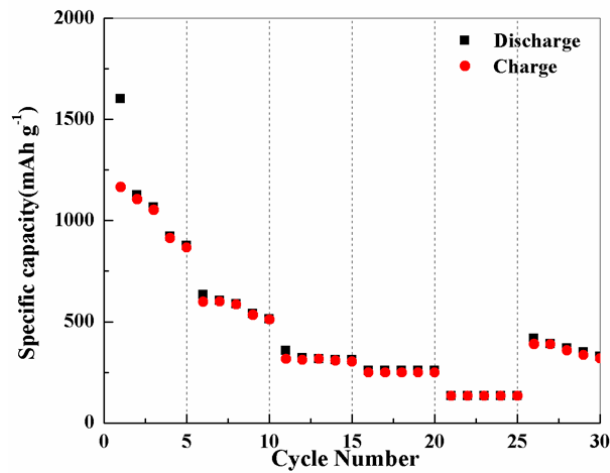


Fig.S6 Rate performance of micron Ge electrode, at current density of 0.2, 0.5, 1.0, 2.0, 5.0 A g⁻¹

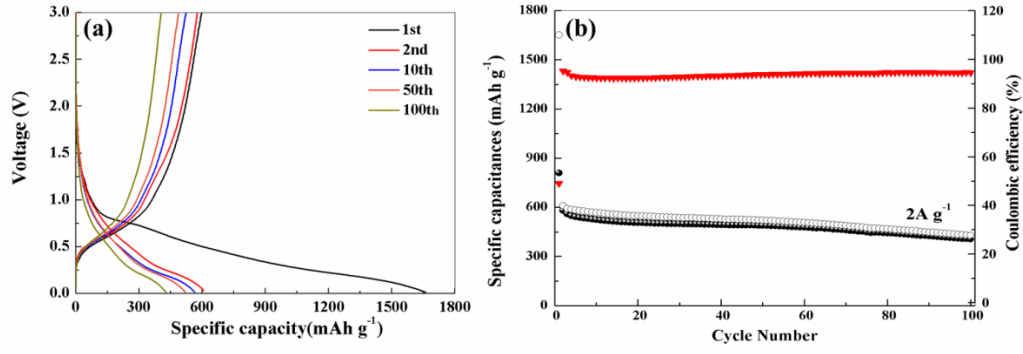


Fig.S7 (a) Galvanostatic charge-discharge profiles for different cycles of Ge/Zn₂GeO₄NFs at 2 A g⁻¹, (b) cycling performance and Coulombic efficiency of Ge/Zn₂GeO₄NFs, at 2 A g⁻¹.

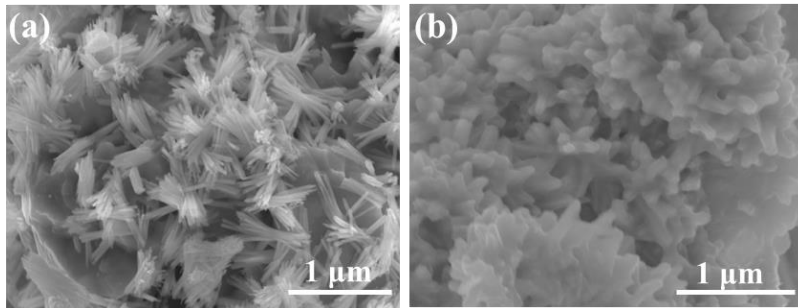


Fig.S8 SEM images of the Ge/Zn₂GeO₄NFs anode before cycle (a) and after the 200th cycle (b) at 0.2 A g⁻¹.

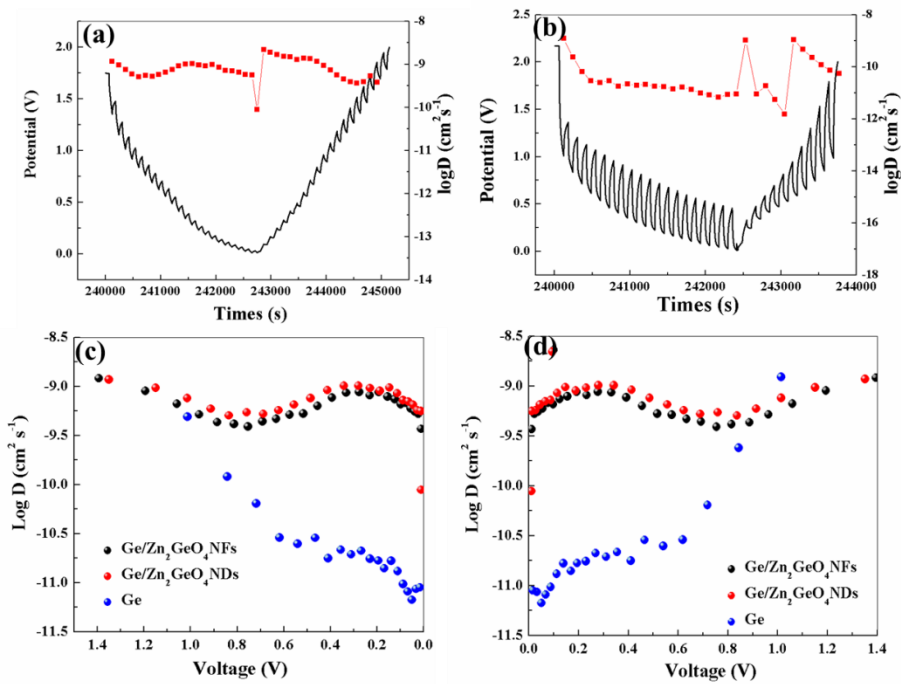


Fig.S9 The GITT curves (voltage vs. time) and (LogD vs. time) for the

Ge/Zn₂GeO₄NDs (a), and Ge (b) anode at room temperature 4th cycle, Li⁺ ion diffusion coefficients calculated from the GITT potential profiles as a function of depth of discharge (c), and Li⁺ ion diffusion coefficients as a function of state of charge (d).

Table S1. The comparison of electrochemical performance of Ge and Zn₂GeO₄ anodes for LIBs.

| Materials | Cycling performance (mAh g ⁻¹) | Rate capability (mAh g ⁻¹) | Initial Coulomb efficiency (%) | Ref. |
|---|---|--|--------------------------------|------|
| meso-porous Ge anode | 1291 after 150 cycles at 0.2 C | 673 at 10 C | ~65 | 1 |
| np-GeSn ₅ | 974 after 500 cycles at 200 mA g ⁻¹ | 778 at 1500 mA g ⁻¹ , | ~65 | 2 |
| np-Ge | 318 after 150 cycles at 200 mA g ⁻¹ | 500 at 1000 mA g ⁻¹ | | 2 |
| Ag/np-Ge | 953 after 100 cycles at 100 mA g ⁻¹ | 522 at 1000 mA g ⁻¹ | 81.8 | 3 |
| nanoporous Ge (np-Ge) | 1060 after 100 cycles at 0.2 A g ⁻¹ | 844.2 at 5 A g ⁻¹ | | 4 |
| Ge asymmetric membrane | 850 after 100 cycles at 600 mA g ⁻¹ | 840 at 800 mA g ⁻¹ | ~65 | 5 |
| porous GeO ₂ (s)/Ge(c) | 1333.5 after 30 cycles at 0.1 A g ⁻¹ | 1024.4 at 0.4 A g ⁻¹ | 60.1 | 6 |
| Zn ₂ GeO ₄ amorphous nanoparticles | 1250 after 500 cycles at 400 mA g ⁻¹ | 610 and 470 at 3.2 A g ⁻¹ and 6.4 A g ⁻¹ | 34 | 7 |
| Zn ₂ GeO ₄ nanowires | 1220 after 100 cycles, | | 52.5 | 8 |
| Mn-doped Zn ₂ GeO ₄ hierarchical nanosheet arrays | 1301 after 100 cycles at 100 mA g ⁻¹ | 500 at 2 A g ⁻¹ | 61.3 | 9 |
| Zn ₂ GeO ₄ /RGO composite | 1005 after 100 cycles at 0.5 A g ⁻¹ | 515 at 5 A g ⁻¹ | 63.2 | 10 |
| Zn ₂ GeO ₄ ultrathin nanosheets | 794 after 500 cycles at 200 mA g ⁻¹ | 537 at 2 A g ⁻¹ | ~59 | 11 |

| | | | | |
|--|---|----------------------------|----|--------------|
| Zn ₂ GeO ₄ Nanorods | 616 after 100th cycles at 400 mA g ⁻¹ | ~500 at 5C | 54 | 12 |
| Ge/Zn ₂ GeO ₄ NFs | 816 after 200th cycles at 0.2 A g ⁻¹ | 567 at 2 A g ⁻¹ | 62 | This work |

References

1. N. Lin, T. Q. Li, Y. Han, Q. L. Zhang, T. J. Xu and Y. T. Qian, *ACS applied materials & interfaces*, 2018, **10**, 8399-8404.
2. Y. H. Yan, Y. Liu, Y. G. Zhang, C. L. Qin, H. Yu, Z. Bakenov and Z. F. Wang, *J Colloid Interf Sci*, 2021, **602**, 563-572.
3. Y. H. Yan, Y. Liu, Y. G. Zhang, C. L. Qin, Z. Bakenov and Z. F. Wang, *J Colloid Interf Sci*, 2021, **592**, 103-115.
4. S. Z. Wang, W. S. Ma, W. F. Yang, Q. G. Bai, H. Gao, Z. Q. Peng and Z. H. Zhang, *J Chem Phys*, 2021, **155**, 184702.
5. I. Byrd, H. Chen, T. Webber, J. L. Li and J. Wu, *Rsc Adv*, 2015, **5**, 92878-92884.
6. S. C. Yan, H. Z. Song, S. R. Lin, H. Wu, Y. Shi and J. Yao, *Advanced Functional Materials*, 2019, **29**, 1807946.
7. R. Yi, J. K. Feng, D. P. Lv, M. L. Gordin, S. R. Chen, D. W. Choi and D. H. Wang, *Nano Energy*, 2013, **2**, 498-504.
8. Y. R. Lim, C. S. Jung, H. S. Im, K. Park, J. Park, W. I. Cho and E. H. Cha, *Journal of Materials Chemistry A*, 2016, **4**, 10691-10699.
9. Q. Li, X. G. Miao, C. X. Wang and L. W. Yin, *Journal of Materials Chemistry A*, 2015, **3**, 21328-21336.
10. Y. Chen, Z. Y. Ji, X. P. Shen, H. Y. Chen, Y. Qi, A. H. Yuan, J. X. Qiu and B. L. Li, *J Colloid Interf Sci*, 2021, **589**, 13-24.
11. G. X. Gao, Y. Xiang, S. Y. Lu, B. T. Dong, S. Chen, L. Shi, Y. K. Wang, H. Wu, Z. Y. Li, A. Abdelkader, K. Xi and S. J. Ding, *Nanoscale*, 2018, **10**, 921-929.
12. J. K. Feng, M. O. Lai and L. Lu, *Electrochem Commun*, 2011, **13**, 287-289.