Bimetallic Bi-Sn Microspheres as High Initial Coulombic

Efficiency and Long Lifespan Anodes for Sodium-Ion Batteries

Yansong Zhu,^a Chunting Wang,^a Zhenjie Cheng,^a Qian Yao,^a Jie Su,^a Bo Chen^{*b}, Jian Yang^{*a}, and Yitai Qian^{ac}

^aKey Laboratory of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China. E-mail: yangjian@sdu.edu.cn

^bDepartment of Chemistry, City University of Hong Kong, Hong Kong, China. E-mail: bchen005@e.ntu.edu.sg

^cHefei National Laboratory for Physical Science at Microscale, Department of Chemistry, University of Science and Technology of China, Hefei, 230026, P. R. China.

Experimental section

Materials

Bismuth (Figure S1a, Bi, beads of 2-3 mm, 99.99 %) and Tin (Figure S1b, Sn, beads of 3-5 mm, 99.99 %) were purchased from Aladdin and Macklin, respectively. Glycerol ($C_3H_8O_3$, analytical grade) and ethanol (C_2H_5OH , analytical grade) were obtained from Sinopharm.

µ-BiSn bimetallic microspheres synthesis

µ-BiSn: The BiSn eutectic alloy was prepared by melting together a mix of Bi and Sn beads at the eutectic ratio of 57 wt% Bi and 43 wt% Sn. The respective mixtures were then melted in a muffle furnace (VBF-1200X) at 300 °C for 3 h in air atmosphere. The µ-BiSn bimetallic microspheres were prepared by sonication of a melted drop of alloys in a glycerol solution (1:1, alloy:glycerol, wt:wt%) in a glass beaker. The thermal-assisted sonication process was performed by using a probe sonicator (Ymnl-1500Y) at 30% power for 30 min. The temperature was kept constant at 150 °C using a hot plate. After sonication, the dispersions were washed five times with ethanol via centrifugation (8000 rpm). Bi35Sn65 and Bi70Sn30 were prepared by the same method (the numbers are the mass ratio). Because of the flash point of glycerol is 170 °C, and the melting points of the two are close to 200 °C, the ultrasonic temperature needs to be increased to 200 °C. Thus, methyl silicone oil with a higher flash point (300 °C) was used as the solvent for safety consideration.

Na₃V₂(PO₄)₃/rGO synthesis

 $Na_3V_2(PO_4)_3/rGO$ was prepared by the previously reported method.^{S1} A stoichiometric ratio (1.5:2:3) of Na_2CO_3 , $V(C_5H_7O_2)_3$, and $NH_4H_2PO_4$ were added in a beaker containing 40 mL deionized water. After ultrasonic treatment for 1 h, the solution was stirred 12 h at room temperature in order to obtain a homogenous solution and then was transferred into a 50 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 6 h, then naturally cooled to room temperature. Subsequently, a green jelly-like NVP gel precursor was obtained. Then, 1 mL GO solution (3 mg mL⁻¹) was added into the gel precursor under vigorous stirring until get a stable dispersion, followed by a freezedrying process. The product was annealed at 750 °C for 8 h with a heating rate of 2 °C min^{-1} in Ar/H₂ (95:5 in vol.) to finally obtain the NVP/rGO composite.

Materials characterizations

X-ray diffractometer (XRD) patterns were recorded on an XRD diffractometer (Bruker D8 Advanced, Germany), with mono-chromatic Cu k α as the radiation source ($\lambda = 1.5418$ Å).

Scanning electron microscope (SEM) images and X-ray energy dispersive spectra (EDS) were obtained from a field-emission scanning electron microscope (ZEISS Gemini SEM 300, Germany).

X-ray photoelectron spectra (XPS) were achieved from an X-ray photoelectron spectrometer (Thermo Sci. ESCA LAB 250, USA). All the high-resolution spectra were calibrated by referencing the binding energy of C 1s (C sp2) as 284.5 eV.

The masses of Bi and Sn in the sample were determined using a NexION 350X inductively-coupled plasma mass spectrometer (ICP-MS)

Electrochemical measurements

Electrochemical properties of μ -BiSn were evaluated in CR2025-type coin cells. The working electrode was fabricated by mixing μ -BiSn, carbon black and sodium carboxymethyl cellulose (CMC) in a weight ratio of 7:2:1 homogeneously with a trace of deionized water. The slurry was then spread on a clean copper foil by a doctor blade. After staying overnight in a vacuum oven at 60 °C, the foil was punched into discs with a diameter of 10 mm. The mass loading of the active material was found to be ~1.2-1.4 mg cm⁻². As a comparison, Sn and Bi mixture electrodes with the same Sn/Bi ratio as in μ -SnBi alloys were prepared by the same method (μ -Sn/Bi). The thick electrodes were fabricated using multi-walled carbon nanotubes as the conductive agent with high mass loading of 3.4-9.8 mg cm⁻². Finally, this working electrode was transferred to an Argon-filled glove box (Mikrouna, Super 1220/750/900, H₂O < 1 ppm, O₂ < 1 ppm) and assembled with a hand-made sodium foil as the counter and reference electrode, a

Glassfiber (Whatman GF/F) as the separator, and 1.0 M NaPF₆ in diethylene glycol dimethyl ether (DGM) as the electrolyte together for half-cells. Commercial Bi and Sn particles with similar particle size distribution were used as the comparison samples (Figure S2).

In full-cells, $Na_3V_2(PO_4)_3/rGO$ was used as the cathode material. It was blended with carbon black and poly(vinylidenefluoride) (PVDF) in a weight ratio of 8:1:1, which was then used for the cathode by a procedure similar to that for μ -BiSn except on an aluminum foil. The capacity ratio of the N/P was controlled to be 1:1.2. The electrolyte was 1.0 M NaPF₆ in DGM. Based on these cells, cyclic voltammetry (CV) curves were measured by an electrochemical workstation (Lanlike LK2005A, China) at room temperature. Galvanostatic discharge/charge voltage profiles were achieved by programmable battery cyclers (LAND CT2001A, China).



Figure S1. Digital photos of Bi (a) and Sn (b) beads.



Figure S2. SEM images of μ -BiSn (a), μ -Bi (b), and μ -Sn (c).



Figure S3. SEM images at different magnifications and corresponding elemental mappings of Bi35Sn65 (a-d) and Bi70Sn30 (e-h) particles. Insets in a and e are particle size distributions of Bi35Sn65 and Bi70Sn30 particles, respectively.



Figure S4. Surface components of μ -BiSn. High-resolution spectra of Sn 3d (a-c), and Bi 4f (d-f).



Figure S5. (a-c) Electrochemical performances of Bi35Sn65, μ -BiSn, and Bi70Sn30 in SIBs. (a) The first cycle galvanostatic charge/discharge curves at 0.1 A g⁻¹. (b, c) Cycling and rate performances of Bi35Sn47, μ -BiSn, and Bi70Sn30.

The charge/discharge voltage profiles of Bi35Sn65, μ -BiSn, and Bi70Sn30 at a current density of 0.1 A g⁻¹ are shown in Figure S5a. Due to the different Bi/Sn ratios, the corresponding plateau capacities of Bi and Sn also vary. The intial Coulombic efficiencies (iCE) of Bi35Sn65, μ -BiSn and Bi70Sn30 anodes are 86.5%, 90.6% and 83.3%, respectively. This is related to the different particle sizes of the three materials. The larger particle size has a smaller specific surface area, resulting in a higher iCE. Although Bi35Sn65 has the highest specific capacity (Figure S5b), its rate performance

is the worst (Figure S5c). Because of the higher Bi content, Bi70Sn30 exhibits the lowest specific capacity.



Figure S6. CV curves of μ -BiSn (a), μ -Bi (b), and μ -Sn (c) with a scan rate of 0.1 mV s⁻¹ during the initial three cycles.

Typical cyclic voltammetry (CV) curves of μ -BiSn electrode of the first three cycles were displayed in Figure S6a. In the first cathodic scan, the distinct reduction peak located at about 0.43 V can be attributed to activation of the Bi^{S2} while the reduction peak of Sn is not obvious, except for a wide peak at 0.15 V.^{S3} Moreover, the broad peak centered at 0.64 V can be identified in the formation of SEI layer^{S2}. Notably, the two obvious peaks (0.63 and 0.76 V) which illustrate the multistep dealloying of Na₃Bi and the peaks at 0.24, 0.28 and 0.55 V corresponding to multistep dealloying of Na₁₅Sn₄ can easily be detected in the subsequent anodic scan. After the first activation cycle, the cathodic peaks of Bi are transferred into two peaks of 0.68 and 0.47 V which correspond to the formation of NaBi and Na₃Bi. After the comparison, the peaks of μ -BiSn are consistent with the combination of the peaks for pure μ -Sn and μ -Bi (Figure S6b and c).



Figure S7. Voltage vs. capacity profiles (the first three cycles) of μ -BiSn (a), μ -Bi (b), and μ -Sn (c) at a current density of 0.1 A g⁻¹.



Figure S8. (a) EIS spectra and (b) CV curves of the μ -BiSn electrode after different numbers of cycles.



Figure S9. SEM images of μ -BiSn electrodes with different mass loading. (a) 3.2 mg cm⁻², (b) 7.6 mg cm⁻², (c) 10.4 mg cm⁻², (d) 14.8 mg cm⁻², (e) 20.1 mg cm⁻².



Figure S10. SEM images of μ -BiSn after 200 cycles at different magnifications and the corresponding elemental mappings.



Figure S11. The structural details and electrochemical properties of $Na_3V_2(PO_4)_3/rGO$. (a) XRD pattern. (b) SEM image. (c) Charge/discharge profiles. (d) Cycling performance at a current density of 0.5 A g⁻¹.

The structural details and electrochemical performance of the NVP/rGO, were examined. The XRD peaks can be well indexed to NVP (JCPDS No. 24-1840) (Figure S11a) without any other impurity. The SEM image of the NVP/rGO sample shows that NVP was uniformly loaded on rGO (Figure S11b). The charge/discharge plateaus for NVP/rGO are at 3.3/3.4 V (Figure S11c). The NVP/rGO powder delivers a reversible

capacity of about 85 mAh g^{-1} after 100 cycles at a current density of 0.5 A g^{-1} in the half-cell (Figure S11d).



Figure S12. (a) Discharge/charge curves at different rates and (b) Ragone plots of μ -BiSn//NVP/rGO, where gravimetric capacity, power, and energy density are estimated based on the total masses of μ -BiSn and NVP/rGO. The inset of (b) is the average discharge voltage at different rates of μ -BiSn//NVP/rGO full batteries.

BiSn-related	iCE /%	Capacity /mAh g ⁻¹	Cycle	Capacity	Ref.
anode			life	retention /%	
Bi@N-C	36.5	235 at 10 A g ⁻¹	2000	~84	S4
Sn@C Fiber	58.54	300 at 0.5 A g ⁻¹	100	75	S5
Sn NDs@PNC	70	483 at 2 A g ⁻¹	1300	90	S6
Bi/Sn@3D-C	40.8	287.3 at 0.1 A g ⁻¹	50	98.4	S7
SnSb@rGO@CNF	61.4	490 at 0.1 A g ⁻¹	200	87.2	S8
NC@SnSb@NC	65.8	386 at 1 A g ⁻¹	120	~90	S9
SnSb/3D-NPC	43.2	266.6 at 5 A g ⁻¹	15000	48.8	S10
PCF-SnSb	80	450 at 0.1 A g ⁻¹	100	99	S11
3D SnSb@N–PG	50.4	190 at 10 A g ⁻¹	4000	100	S12
np-Bi ₂ Sb ₆	69.8	192.5 at 1 A g ⁻¹	10000	51.9	S13
BiSb ₃ /C	65.3	233.2 at 2 A g ⁻¹	2500	73.1	S14
μ-BiSn	90.6	541 at 2 A g ⁻¹	3000	88	This
					work

Table S1 The sodium storage properties of reported Bi/Sn-related anodes

References

S1. Y. Xu, Q. Wei, C. Xu, Q. Li, Q. An, P. Zhang, J. Sheng, L. Zhou and L. Mai, *Adv. Energy Mater.*, 2016, **6**, 1600389.

- S2. P. Xue, N. Wang, Z. Fang, Z. Lu, X. Xu, L. Wang, Y. Du, X. Ren, Z. Bai, S. Dou and G. Yu, *Nano Lett.*, 2019, **19**, 1998-2004.
- S3. C. Kim, I. Kim, H. Kim, M. K. Sadan, H. Yeo, G. Cho, J. Ahn, J. Ahn and H. Ahn, J. Mater. Chem. A, 2018, 6, 22809-22818.
- S4. H. Yang, R. Xu, Y. Yao, S. Ye, X. Zhou and Y. Yu, *Adv. Funct. Mater.*, 2019, 29, 1809195.
- S5. Z. Xu, J. Ye, Y. Pan, K. Liu, X. Liu and J. Shui, Energy Technol., 2022, 2101024.
- S6. Y. Liu, N. Zhang, L. Jiao and J. Chen, Adv. Mater., 2015, 27, 6702-6707.
- S7. H. Yang, L. Y. Yang, A. Abliz, S. Y. Wang, F. J. Zhao, M. Zhang, J. Li and H. B.

Li, Ionics, 2021, 27, 1429-1437.

S8. H. Jia, M. Dirican, C. Chen, J. Zhu, P. Zhu, C. Yan, Y. Li, X. Dong, J. Guo and X. Zhang, ACS Appl. Mater. Interfaces, 2018, 10, 9696-9703.

S9. X. Shi, W. Liu, D. Zhang, C. Wang, J. Zhao, X. Wang, B. Chen, L. Chang, Y. Cheng and L. Wang, *Chem. Eng. J.*, 2022, **431**, 134318.

S10. C. Li, Y. R. Pei, M. Zhao, C. C. Yang and Q. Jiang, *Chem. Eng. J.*, 2021, 420, 129617.

S11. J.-H. Choi, C.-W. Ha, H.-Y. Choi, J.-W. Seong, C.-M. Park and S.-M. Lee, *J. Power Sources*, 2018, **386**, 34-39.

S12. J. Qin, T. Wang, D. Liu, E. Liu, N. Zhao, C. Shi, F. He, L. Ma and C. He, Adv. Mater., 2018, 30, 1704670.

S13. H. Gao, J. Niu, C. Zhang, Z. Peng and Z. Zhang, ACS Nano, 2018, 12, 3568-3577.
S14. S. Guo, H. Li, Y. Lu, Z. Liu and X. Hu, Energy Storage Mater., 2020, 27, 270-278.