Electronic Supplementary Material (ESI) for Industrial Chemistry & Materials.

Supporting Information

Strategies to enable microsized alloy anodes for high-energy and long-life alkali-ion batteries

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Table 1: Summary of different alloy anodes for LIBs

Anodes Materials	1st Discharge Capacity (mAh/g) [Current density]	ICE	Retention rate @ cycle no.	Fast Charging (mAh.g^{-1} @ A. g^{-1})	Synthesis method	Ref.
Nano-porous-Si	2600 [0.06 A/g]	86%	62% @ 60 cycles.	-	HCl etching	1
Microparticle-Si	3100 [0.1 A/g]	85.1%	40% @ 360 cycles.	1183 @ 1	Magnesiothermic reduction	2
Micro-sized bulk Porous Si	2222 [50 mA/g]	88.1%	63% @ 100 cycles.	558 @ 5	Ball milling and acid etching	3
Prickle-like Si@C	2300 [0.4 A/g]	87.5%	65% @ 100 cycles.	1400 @ 4	metal-assisted chemical etching and chemical vapor deposition (CVD)	4
Micro-size Si-C composite	2004 [0.4 A/g]	77.2%	97.8% @ 50 cycles.	700 @ 12.8	Etching and Carbon filling	5
Hierarchical micro/nanostructures Black Phosphorus Carbon composite (BPC)	2775.2 [0.52 A/g]	91%	87% @ 100 cycles	1637 @ 6.24	High Energy Ball Milling (HEBM)	6
Cross-linked BP-CNT	2000 [0.52 A/g]	70%	87.5% @ 400 cycles	1098 @ 11.7	HEBM	7
Red P/CNT	2870 [0.11 A/g]	74.3%	46% @ 50 cycles	816.6 @ 1.1	Planetary ball milling	8
Red P-Graphene	2517 [130 mA/g]	84%	74% @ 200 cycles	1100 @ 7.8	HEBM	9
Fibrous Red P	2500 [0.2 A/g]	81%	80% @ 80 cycles	1316 @ 2	chemical vapor Transport (CVT)	10
Nano-Sn/C composite	1029 [0.2 A/g]	69%	98% @ 130 cycles	600 @ 15.12	Aerosol spray pyrolysis	11
Sn@C yolk-shell	1414 [0.2 A/g]	69%	44% @ 800 cycles	-	CVD	12

Micro-size porous Sn	818 [0.2 A/g]	65%	37% @ 10 cycles	-	Dealloying	13
Double-shelled hollow Carbon spheres-Sn	2267 [0.1 A/g]	62%	77.8% @ 130 cycles	430 @ 5	Chemical etching	14
Graphene networks anchored with Sn@graphene	1803 [0.2 A/g]	69%	87.5% @ 100 cycles	459 @ 5	CVD	15
Hierarchical micro/nanostructures Silicon Black Phosphorus Carbon composite (SPC)	2140 [0.68 A/g]	84%	95% @ 120 cycles	1000 @ 15.3	HEBM	16
2D SiP Flake	1650 [0.2 A/g]	87%	53% @ 10 cycles	400 @ 2	Exfoliation method	17
3D micro-Sn-Sb-Co alloy	816 [0.13 A/g]	83%	90% @ 100 cycles	500 @ 16	Electrodeposition	18
SiP_2/C0/0/00 0:00:00 AM	1999 [0.1 A/g]	83%	45% @ 100 cycles	800 @ 3.3	HEBM	19
Micro-Sn-Ge flake like ribbons	1242 [0.14 A/g]	85%	94% @ 60 cycles	500 @ 7.15	Melt spinning	20

Table 2: Summary of different alloy anodes for SIBs

Anodes Materials	**1st Discharge Capacity (mAh/g) [Current density]**	**ICE**	**Retention rate @ cycle no.**	**Fast Charging ($mAh.g^{-1}$ @ $A.g^{-1}$)**	**Synthesis method**	**Ref.**
Si nanoparticles	1027 [20 mA/g]	26%	91% @ 100 cycles	90 @ 0.5	CVD	21
Micro-Si-graphite	650 [0.1 A/g]	54.4%	79% @ 100 cycles	170 @ 1	Grinding	22
Amorphous Si	420 [36 mA/g]	60%	56% @ 100 cycles	143 @ 0.725	Mechanical fusion	23

c-Si/C hybrid	813.7 [50 mA/g]	53.8%	100.3% @ 200 cycles	269 @ 5	Electrospinning / etching	24
Multilevel Gradient-Ordered Si	950 [50 mA/g]	-	40 % @ 20 cycles	108 @ 1	Electrochemical reconstruction	25
Hierarchical micro/nanostructures Black Phosphorus Carbon composite (BPC)	2206 [0.416 A/g]	91.1%	90% @ 50 cycles	982 @ 3	HEBM	26
Hierarchical micro/nanostructures Red Phosphorus Carbon composite (RPC)	2300 [0.416 A/g]	87.8%	77% @ 50 cycles	-	HEBM	26
Red P / SWCNT	985 [50mA/g]	68%	80% @ 2000 cycles	300 @ 2	Vaporization-Condensation method	27
BP/AB Composite	2125 [125 mA/g]	76%	91% @ 23 cycles	500 @ 25	HEBM	28
Sandwiched BP/Graphene	3050 [50 mA/g]	80%	85% @ 100 cycles	645 @ 26	Liquid-phase exfoliation	29
Porous nano-Sn	550 [40 mA/g]	90.9%	55% @ 95 cycles	300 @ 0.2	Dealloying	30
3D Porous Sn	850 [0.2 A/g]	96%	85% @ 400 cycles	700 @ 6.5	Replacement reaction	31
Microsized Sn (Glyme)	920 [0.25 A/g]	92%	90 % @ 100 cycles	622 @ 1.69	HEBM	32
Microsized Sn (Diglyme)	900 [0.085 A/g]	84%	80% @ 300 cycles	300 @ 1.6	HEBM	33
Sn@Graphene	730 [0.1 A/g]	60%	95% @ 100	106 @ 3.2	hydrogen assisted thermal reduction method	34
Yolk-shell Sn_4P_3@C	1804 [0.1 A/g]	43%	65 % @ 50 cycles	421 @ 3	Solvothermal	35
Micro/nano SB-RP@MWCNT-KB	2801 [0.86 A/g]	88%	96% @ 70 cycles	1779 @ 5.2	HEBM	36
Sb porous Microspheres	981.7	64.6%	97.2% @ 100	312.9 @ 3.2	Templates method	37

	[0.1 A/g]		cycles			

References:

1. T. Jiang, R. Zhang, Q. Yin, W. Zhou, Z. Dong, N. A. Chernova, Q. Wang, F. Omenya and M. S. Whittingham, Morphology, composition and electrochemistry of a nano-porous silicon versus bulk silicon anode for lithium-ion batteries, *J. Mater. Sci.*, 2017, **52**, 3670–3677.
2. T. Mu, B. Shen, S. Lou, Z. Zhang, Y. Ren, X. Zhou, P. Zuo, C. Du, Y. Ma, H. Huo and G. Yin, Scalable mesoporous silicon microparticles composed of interconnected nanoplates for superior lithium storage, *Chem. Eng. J.*, 2019, **375**, 121923.
3. W. He, H. Tian, F. Xin and W. Han, Scalable fabrication of micro-sized bulk porous Si from Fe–Si alloy as a high performance anode for lithium-ion batteries, *J. Mater. Chem. A*, 2015, **3**, 17956–17962.
4. J. S. Kim, M. Halim, D. Byun and J. K. Lee, Amorphous carbon-coated prickle-like silicon of micro and nano hybrid anode materials for lithium-ion batteries, *Solid State Ionics*, 2014, **260**, 36–42.
5. R. Yi, J. Zai, F. Dai, M. L. Gordin and D. Wang, Dual conductive network-enabled graphene/Si–C composite anode with high areal capacity for lithium-ion batteries, *Nano Energy*, 2014, **6**, 211–218.
6. R. Amine, A. Daali, X. Zhou, X. Liu, Y. Liu, Y. Ren, X. Zhang, L. Zhu, S. Al-Hallaj, Z. Chen, G.-L. Xu and K. Amine, A practical phosphorus-based anode material for high-energy lithium-ion batteries, *Nano Energy*, 2020, **74**, 104849.
7. S. Haghighat-Shishavan, M. Nazarian-Samani, M. Nazarian-Samani, H.-K. Roh, K.-Y. Chung, B.-W. Cho, S. F. Kashani-Bozorg and K.-B. Kim, Strong, persistent superficial oxidation-assisted chemical bonding of black phosphorus with multiwall carbon nanotubes for high-capacity ultradurable storage of lithium and sodium, *J. Mater. Chem. A*, 2018, **6**, 10121–10134.
8. D. Yuan, J. Cheng, G. Qu, X. Li, W. Ni, B. Wang and H. Liu, Amorphous red phosphorous embedded in carbon nanotubes scaffold as promising anode materials for lithium-ion batteries, *J. Power Sources*, 2016, **301**, 131–137.
9. Z. Yu, J. Song, M. L. Gordin, R. Yi, D. Tang and D. Wang, Phosphorus-Graphene Nanosheet Hybrids as Lithium-Ion Anode with Exceptional High-Temperature Cycling Stability, *Adv. Sci.*, 2015, **2**, 1400020.
10. L. Liu, X. Gao, X. Cui, B. Wang, F. Hu, T. Yuan, J. Li, L. Zu, H. Lian and X. Cui, Chemical Vapor Transport Synthesis of Fibrous Red Phosphorus Crystal as Anodes for Lithium-Ion Batteries, *Nanomater.*, 2023, **13**, 1060.
11. Y. Xu, Q. Liu, Y. Zhu, Y. Liu, A. Langrock, M. R. Zachariah and C. Wang, Uniform Nano-Sn/C Composite Anodes for Lithium Ion Batteries, *Nano Lett.,* 2013, **13**, 470–474.
12. W. Ni, Y. Wang and R. Xu, Formation of Sn@C Yolk–Shell Nanospheres and Core–Sheath Nanowires for Highly Reversible Lithium Storage, *Part. Part. Syst. Charact.*, 2013, **30**, 873–880.
13. T. Song, M. Yan and M. Qian, A dealloying approach to synthesizing micro-sized porous tin (Sn) from immiscible alloy systems for potential lithium-ion battery anode applications, *J. Porous Mater.*, 2015, **22**, 713–719.
14. L. Sun, T. Ma, J. Zhang, X. Guo, C. Yan and X. Liu, Double-shelled hollow carbon spheres confining tin as high-performance electrodes for lithium ion batteries, *Electrochim. Acta*, 2019, **321**, 134672.

15. J. Qin, C. He, N. Zhao, Z. Wang, C. Shi, E.-Z. Liu and J. Li, Graphene Networks Anchored with Sn@Graphene as Lithium Ion Battery Anode, *ACS Nano*, 2014, **8**, 1728–1738.
16. A. Daali, X. Zhou, C. Zhao, I. Hwang, Z. Yang, Y. Liu, R. Amine, C.-J. Sun, W. Otieno, G.-L. Xu and K. Amine, In situ microscopy and spectroscopy characterization of microsized Sn anode for sodium-ion batteries, *Nano Energy*, 2023, **115**, 108753.
17. H. Shen, Y. Huang, R. Hao, Y. Chang, Z. Ma, B. Guo, P. Wang, H. Yang, J. Cheng, Q. Li, H. Wang, Z. Liu and A. Nie, Mechanical robustness two-dimensional silicon phosphide flake anodes for lithium ion batteries, *ACS Sustain. Chem. Eng.*, 2020, **8**,.
18. L.-J. Xue, Y.-F. Xu, L. Huang, F.-S. Ke, Y. He, Y.-X. Wang, G.-Z. Wei, J.-T. Li and S.-G. Sun, Lithium storage performance and interfacial processes of three dimensional porous Sn–Co alloy electrodes for lithium-ion batteries, *Electrochim. Acta*, 2011, **56**, 5979–5987.
19. H.-. T. Kwon, C. K. Lee, K.-. J. Jeon and C.-. M. Park, Silicon diphosphide: a Si-based three-dimensional crystalline framework as a high-performance Li-ion battery anode, *ACS Nano*, 2016, **10**,.
20. S. Fan, L. Y. Lim, Y. Y. Tay, S. S. Pramana, X. Rui, M. K. Samani, Q. Yan, B. K. Tay, M. F. Toney and H. H. Hng, Rapid fabrication of a novel Sn–Ge alloy: structure–property relationship and its enhanced lithium storage properties, *J. Mater. Chem. A*, 2013, **1**, 14577–14585.
21. Y. Xu, E. Swaans, S. Basak, H. Zandbergen, D. Borsa and F. Mulder, Reversible Na-Ion Uptake in Si Nanoparticles, *Adv. Energy Mater.*, 2015, **6**, 1501436.
22. Q. Zhao, Y. Huang and X. Hu, A Si/C nanocomposite anode by ball milling for highly reversible sodium storage, *Electrochem. Commun.*, 2016, **70**, 8–12.
23. C.-H. Lim, T.-Y. Huang, P.-S. Shao, J.-H. Chien, Y.-T. Weng, H.-F. Huang, B. J. Hwang and N.-L. Wu, Experimental Study on Sodiation of Amorphous Silicon for Use as Sodium-Ion Battery Anode, *Electrochim. Acta*, 2016, **211**, 265–272.
24. L. Zhang, X. Hu, C. Chen, H. Guo, X. Liu, G. Xu, H. Zhong, S. Cheng, P. Wu, J. Meng, Y. Huang, S. Dou and H. Liu, In Operando Mechanism Analysis on Nanocrystalline Silicon Anode Material for Reversible and Ultrafast Sodium Storage, *Adv. Mater.*, 2017, **29**, 1604708.
25. Y. Li, F. Wu, Y. Li, X. Feng, L. Zheng, M. Liu, S. Li, J. Qian, Z. Wang, H. Ren, Y. Gong, C. Wu and Y. Bai, Multilevel Gradient-Ordered Silicon Anode with Unprecedented Sodium Storage, *Adv. Mater.*, **2024**, 2310270.
26. G.-L. Xu, Z. Chen, G.-M. Zhong, Y. Liu, Y. Yang, T. Ma, Y. Ren, X. Zuo, X.-H. Wu, X. Zhang and K. Amine, Nanostructured Black Phosphorus/Ketjenblack–Multiwalled Carbon Nanotubes Composite as High Performance Anode Material for Sodium-Ion Batteries, *Nano Lett.,* 2016, **16**, 3955–3965.
27. Y. Zhu, Y. Wen, X. Fan, T. Gao, F. Han, C. Luo, S.-C. Liou and C. Wang, Red Phosphorus–Single-Walled Carbon Nanotube Composite as a Superior Anode for Sodium Ion Batteries, *ACS Nano*, 2015, **9**, 3254–3264.
28. M. Dahbi, N. Yabuuchi, M. Fukunishi, K. Kubota, K. Chihara, K. Tokiwa, X. Yu, H. Ushiyama, K. Yamashita, J.-Y. Son, Y.-T. Cui, H. Oji and S. Komaba, Black Phosphorus as a High-Capacity, High-Capability Negative Electrode for Sodium-Ion Batteries: Investigation of the Electrode/Electrolyte Interface, *Chem. Mater,* 2016, **28**, 1625–1635.
29. J. Sun, H.-W. Lee, M. Pasta, H. Yuan, G. Zheng, Y. Sun, Y. Li and Y. Cui, A phosphorene-graphene hybrid material as a high-capacity anode for sodium-ion batteries, *Nat. Nanotechnol.*, 2015, **10**, 980–985.

30. E. Detsi, X. Petrissans, Y. Yan, J. B. Cook, Z. Deng, Y.-L. Liang, B. Dunn and S. H. Tolbert, Tuning ligament shape in dealloyed nanoporous tin and the impact of nanoscale morphology on its applications in Na-ion alloy battery anodes, *Phys. Rev. Mater,* 2018, **2**, 055404.
31. L. Wang, Y. Ni, K. Lei, H. Dong, S. Tian and F. Li, 3D Porous Tin Created by Tuning the Redox Potential Acts as an Advanced Electrode for Sodium-Ion Batteries, *ChemSusChem*, 2018, **11**, 3376–3381.
32. B. Zhang, G. Rousse, D. Foix, R. Dugas, D. A. D. Corte and J.-M. Tarascon, Microsized Sn as Advanced Anodes in Glyme-Based Electrolyte for Na-Ion Batteries, *Adv. Mater.*, 2016, **28**, 9824–9830.
33. J. Huang, X. Guo, X. Du, X. Lin, J.-Q. Huang, H. Tan, Y. Zhu and B. Zhang, Nanostructures of solid electrolyte interphases and their consequences for microsized Sn anodes in sodium ion batteries, *Energy Environ. Sci.*, 2019, **12**, 1550–1557.
34. B. Luo, T. Qiu, D. Ye, L. Wang and L. Zhi, Tin nanoparticles encapsulated in graphene backboned carbonaceous foams as high-performance anodes for lithium-ion and sodium-ion storage, *Nano Energy*, 2016, **22**, 232–240.
35. J. Liu, P. Kopold, C. Wu, P. A. van Aken, J. Maier and Y. Yu, Uniform yolk–shell Sn4P3@C nanospheres as high-capacity and cycle-stable anode materials for sodium-ion batteries, *Energy Environ. Sci,* 2015, **8**, 3531–3538.
36. X. Liu, B. Xiao, A. Daali, X. Zhou, Z. Yu, X. Li, Y. Liu, L. Yin, Z. Yang, C. Zhao, L. Zhu, Y. Ren, L. Cheng, S. Ahmed, Z. Chen, X. Li, G.-L. Xu and K. Amine, Stress- and Interface-Compatible Red Phosphorus Anode for High-Energy and Durable Sodium-Ion Batteries, *ACS Energy Lett.,* 2021, **6**, 547–556.
37. H. Hou, M. Jing, Y. Yang, Y. Zhang, Y. Zhu, W. Song, X. Yang and X. Ji, Sb porous hollow microspheres as advanced anode materials for sodium-ion batteries, *J. Mater. Chem. A*, 2015, **3**, 2971–2977.