Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Microstructurally Engineered Nanocrystalline Fe-Sn-Sb Anode: Towards Stable High Energy Density Sodium-ion Batteries

Eldho Edison,[a] Sivaramapanicker Sreejith,*[b] Hao Ren,[a] Chwee Teck Lim *[b,c] and Srinivasan Madhavi *[a]

[a.] *School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore. Email: madhavi@ntu.edu.sg*

[b.] *Biomedical Institute for Global Health Research and Technology, National University of Singapore, 117599, Singapore. Email: bigsiv@nus.edu.sg ; sreejith.siva@gmail.com*

[c.] *Department of Biomedical Engineering, National University of Singapore, 2 Engineering Drive 3, 117581, Singapore. Email: ctlim@nus.edu.sg*

Table of Contents

Item	Page no.
Figure S1	S-3
Figure S2	S-3
Figure S3	S-4
Figure S4	S-4
Figure S5	S-5
Figure S6	S-5
Figure S7	S-6
Figure S8	S-6
Figure S9	S-7
Figure S10	S-8
Figure S11	S-9
Figure S12	S-9
Table S1	S-10
Table S2	S-10
References	S-11

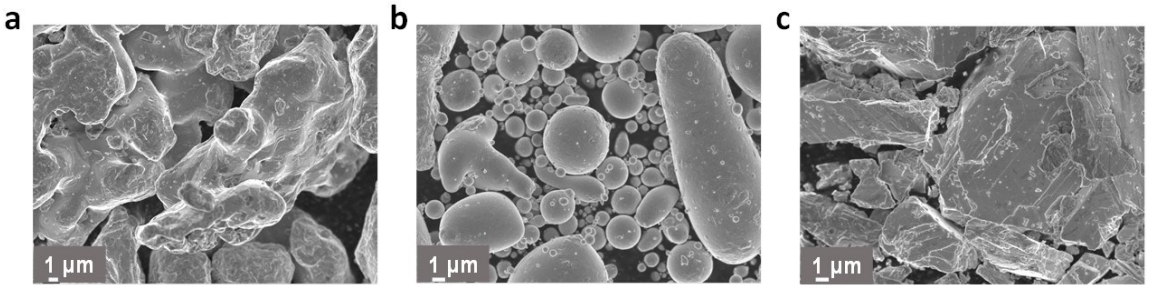


Figure S1. Metal powders used as precursor for the rapid solidification process. a) Fe powder. b) Sn powder. c) Sb powder.

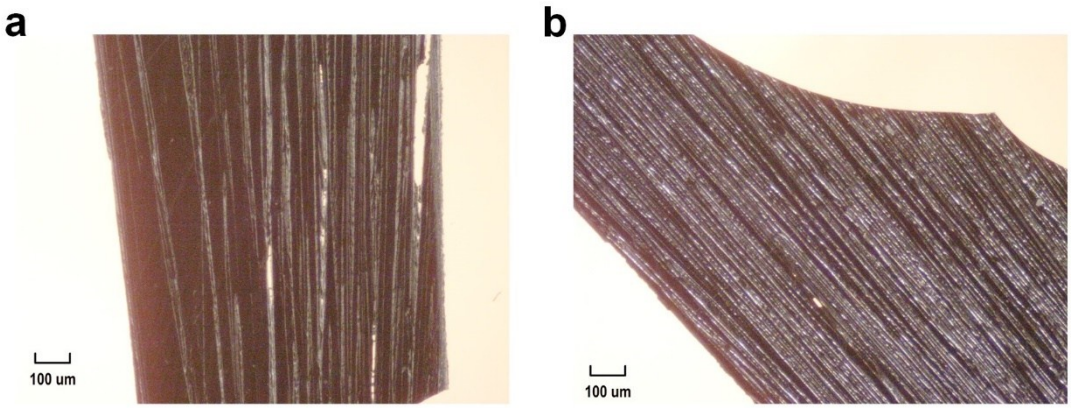


Figure S2. Optical microscopy images of the rapidly solidified ribbons of a) SnSb and b) $Fe_{1.0}$-SnSb.

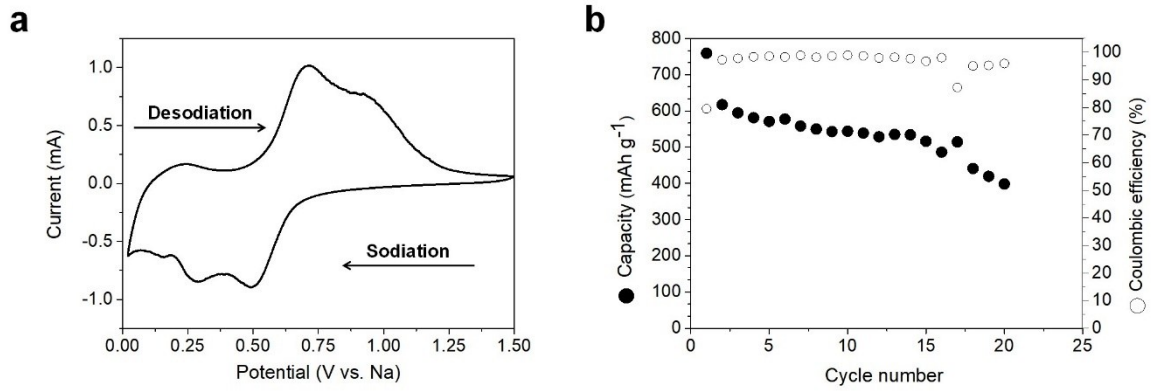


Figure S3. Electrochemical performance of SnSb anode. a) Cyclic voltammogram at 0.1 mV s^{-1} and b) Galvanostatic charge-discharge test at 50 mA g^{-1} in the potential window 0.005 – 2 V vs. Na.

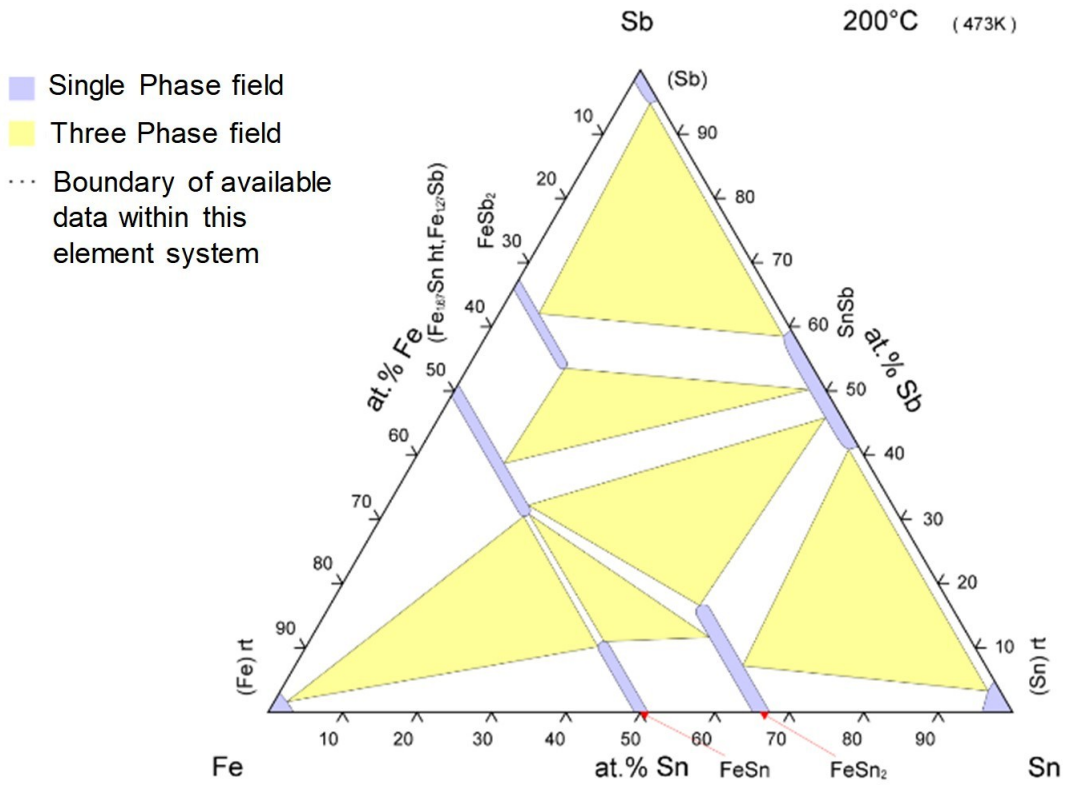


Figure S4. Fe-Sb-Sn isothermal section of ternary phase diagram.[1] ©Springer & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan, 2016.

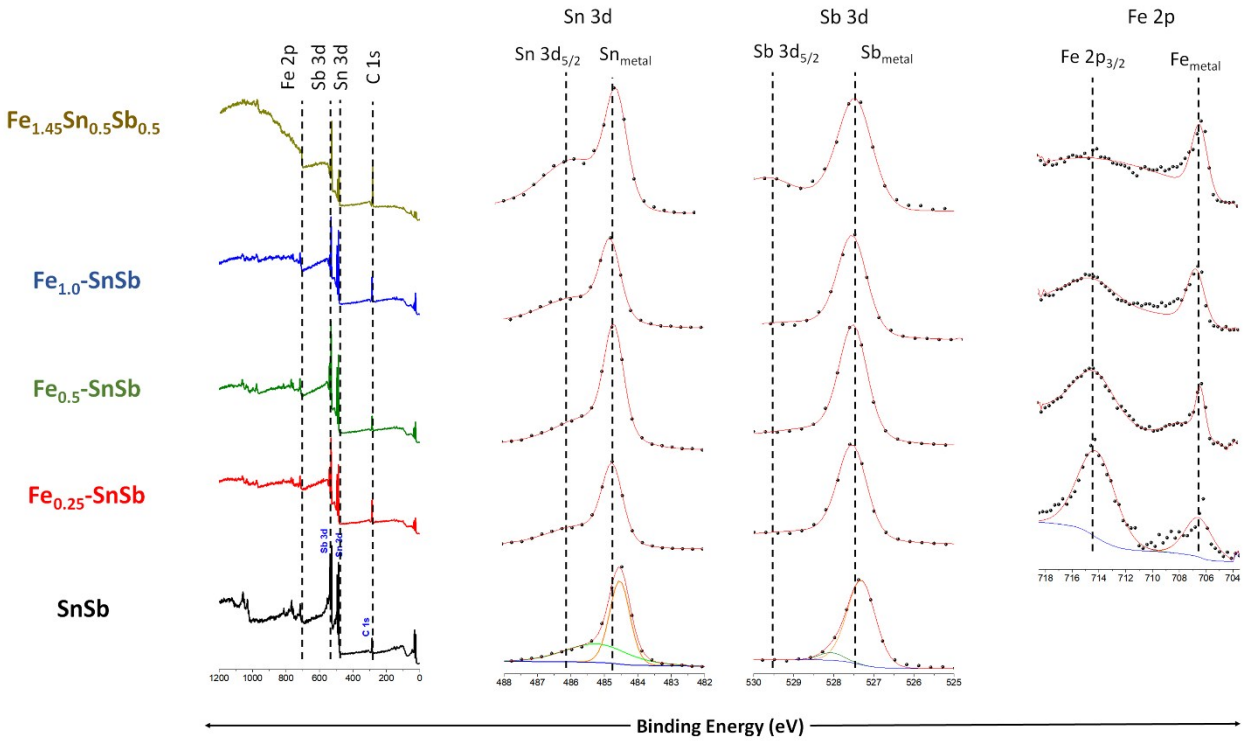


Figure S5. XPS analysis of the Fe-Sn-Sb alloys.

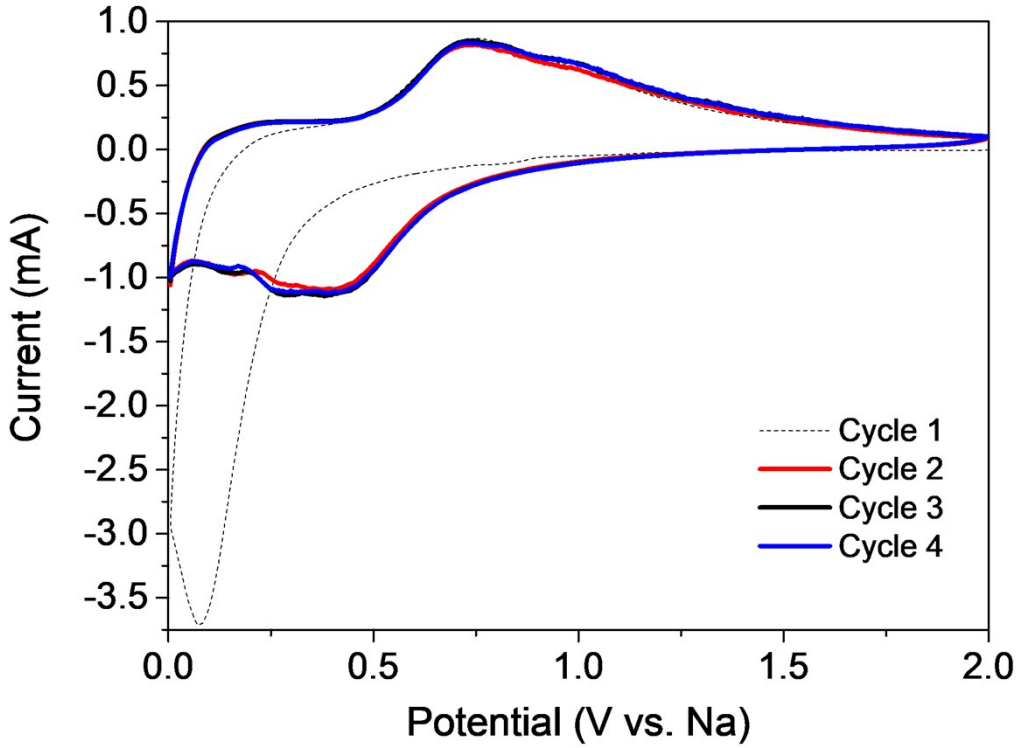
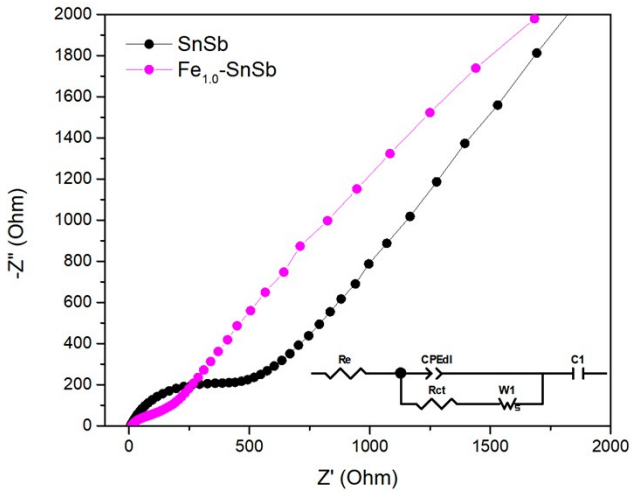


Figure S6. Cyclic voltammogram of $Fe_{1.0}$-SnSb alloy anode.



Alloy	R_{ct} (ohm)
SnSb	499
$Fe_{1.0}$-SnSb	115.2

Figure S7. Impedance spectra of SnSb and $Fe_{1.0}$-SnSb anodes.

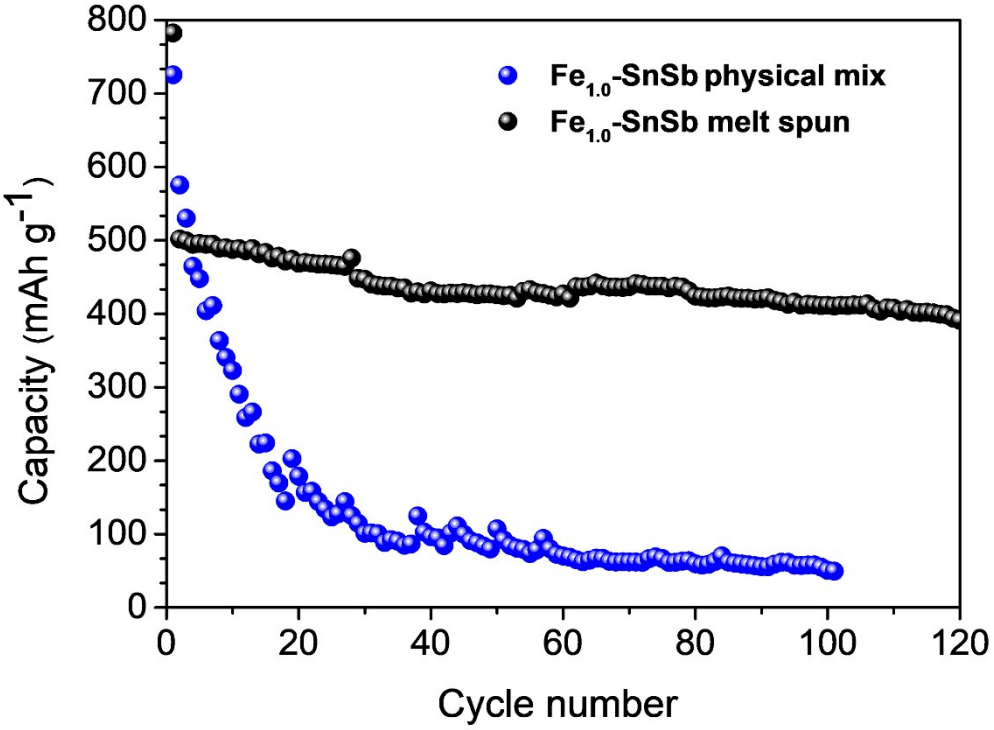


Figure S8. Enhanced cycling stability of the rapidly solidified $Fe_{1.0}$-SnSb alloy against the control sample which is a physical mix of the Fe, Sn and Sb metal powders in the same ratio.

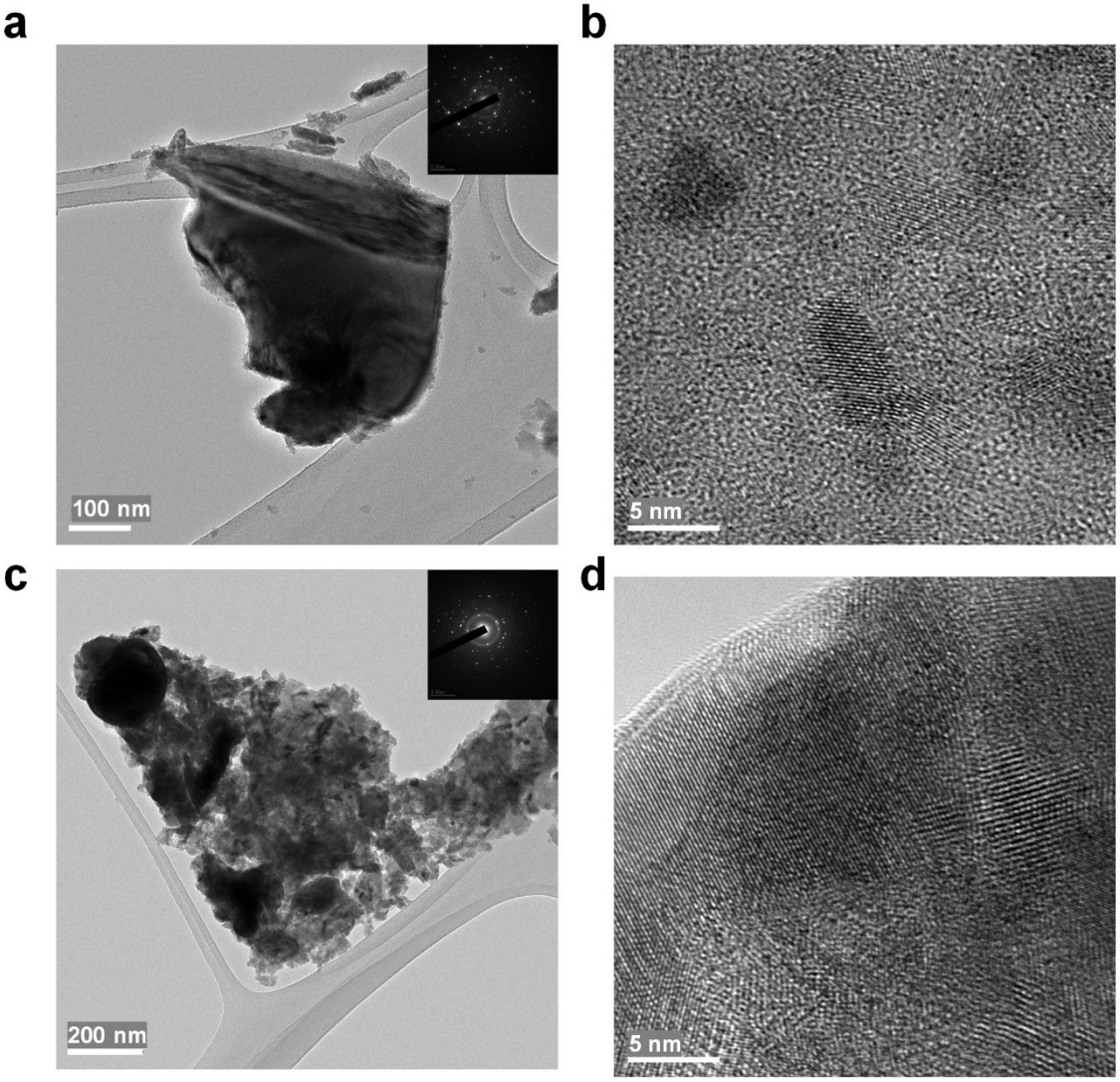
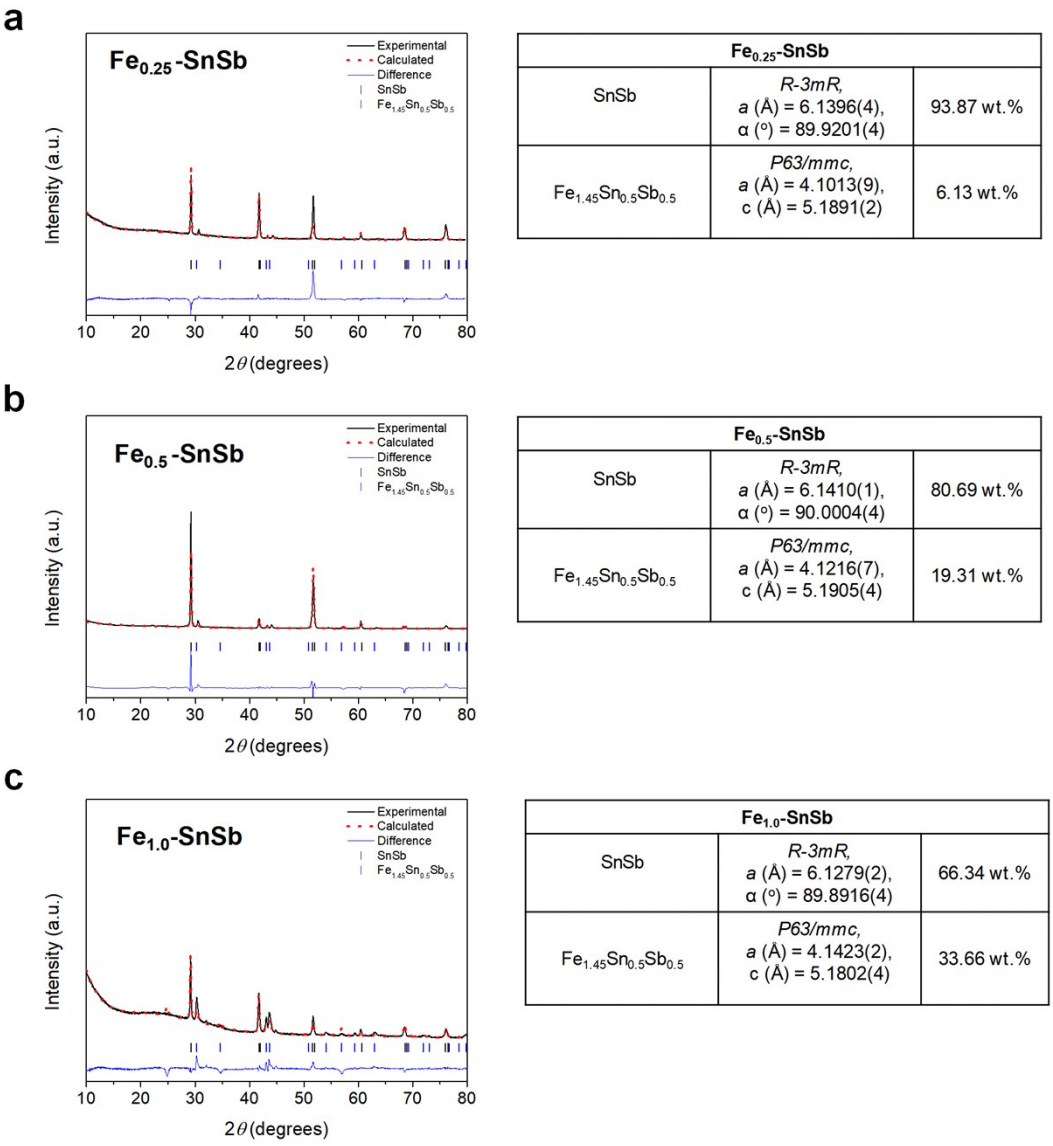


Figure S9. HRTEM images of (a, b) $Fe_{0.25}$-SnSb and (c, d) $Fe_{0.5}$-SnSb alloys



$Fe_{0.25}$-SnSb		
SnSb	*R-3mR*, *a* (Å) = 6.1396(4), α (°) = 89.9201(4)	93.87 wt.%
$Fe_{1.45}Sn_{0.5}Sb_{0.5}$	*P63/mmc*, *a* (Å) = 4.1013(9), c (Å) = 5.1891(2)	6.13 wt.%

$Fe_{0.5}$-SnSb		
SnSb	*R-3mR*, *a* (Å) = 6.1410(1), α (°) = 90.0004(4)	80.69 wt.%
$Fe_{1.45}Sn_{0.5}Sb_{0.5}$	*P63/mmc*, *a* (Å) = 4.1216(7), c (Å) = 5.1905(4)	19.31 wt.%

$Fe_{1.0}$-SnSb		
SnSb	*R-3mR*, *a* (Å) = 6.1279(2), α (°) = 89.8916(4)	66.34 wt.%
$Fe_{1.45}Sn_{0.5}Sb_{0.5}$	*P63/mmc*, *a* (Å) = 4.1423(2), c (Å) = 5.1802(4)	33.66 wt.%

Figure S10. Rietveld refined quantitative phase analysis of Fe-Sn-Sb alloy.

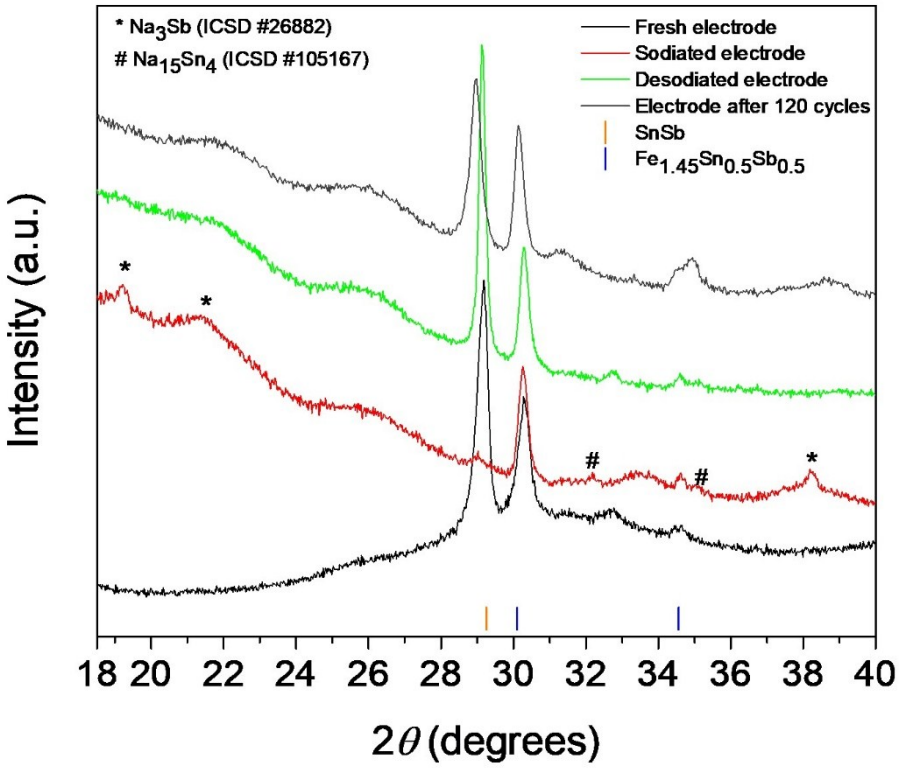


Figure S11. *Ex situ* XRD of $Fe_{1.0}$-SnSb anode at various stages of cycling.

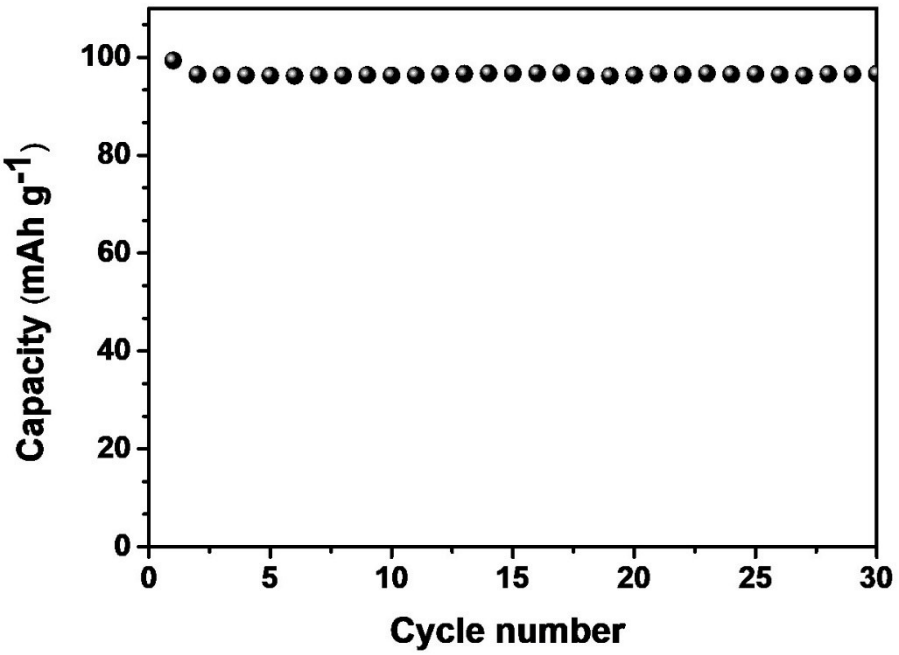


Figure S12. Galvanostatic cycling performance of $NaVPO_4F$/Na half-cell at a specific current of 50 mA g^{-1} in the potential window 2-3.8 vs. Na^+/Na.

Table S1. Rietveld-refined lattice parameters of rapidly solidified SnSb alloy

Structural formula	SnSb
Space group	*R-3mR*
Crystal system	Trigonal
Refined lattice parameters	a=b=c=6.136 Å α=β=γ=89.725°
R- values	R_{Bragg}=3.411; R_{wp}=5.62; R_p=3.52
Crystallite size Lorentzian (nm)	88.4

Table S2. Comparison of electrochemical performance of recently reported SnSb anodes

Material	Synthesis method	Capacity @ Specific current (voltage window *vs.* Na)	Cycles	Reference
SnSb nanoparticles@3D-carbon matrix	*Freeze-drying assisted solid-state method*	~350 mAh g^{-1}@0.1 A g^{-1} (0.01-2 V)	100	2
Porous SnSb	*Melt spinning and etching*	~450 mAh g^{-1} @0.05 A g^{-1} (0.005-2 V)	100	3
Reduced graphene oxide incorporated SnSb@Carbon nanofiber matrix	*Electrospinning*	~490 mAh g^{-1}@ (0.01-2.5 V)	200	4
SnSb@3D N-doped porous graphene	*Spray pyrolysis*	~450 mAh g^{-1} @0.1 A g^{-1} (0.005-3 V)	100	5
SnSb@reduced graphene oxide@carbon microfibers	*Centrifugal spinning*	~350 mAh g^{-1}@0.05 A g^{-1} (0.01-2.5)	200	6
Fe-Sn-Sb alloy	*Rapid-solidification/Melt spinning*	~500 mAh g^{-1}@0.05 A g^{-1} (0.005-2 V)	120	**This work**

References

1. Fe-Sb-Sn Isothermal Section of Ternary Phase Diagram: Datasheet from "PAULING FILE Multinaries Edition – 2012" in SpringerMaterials https://materials.springer.com/isp/phase-diagram/docs/c_0203023).
2. W. Wang, L. Shi and Q. Li, *Journal of The Electrochemical Society*, 2018, **165**, A1455-A1459.
3. J.-H. Choi, C.-W. Ha, H.-Y. Choi, J.-W. Seong, C.-M. Park and S.-M. Lee, *Journal of Power Sources*, 2018, **386**, 34-39.
4. H. Jia, M. Dirican, C. Chen, J. Zhu, P. Zhu, C. Yan, Y. Li, X. Dong, J. Guo and X. Zhang, *ACS Applied Materials & Interfaces*, 2018, **10**, 9696-9703.
5. J. Qin, T. Wang, D. Liu, E. Liu, N. Zhao, C. Shi, F. He, L. Ma and C. He, *Advanced Materials*, 2018, **30**, 1704670.
6. H. Jia, M. Dirican, J. Zhu, C. Chen, C. Yan, P. Zhu, Y. Li, J. Guo, Y. Caydamli and X. Zhang, *Journal of Alloys and Compounds*, 2018, **752**, 296-302.