Electronic Supplementary Information

Tin-Based Ionic Chaperone Phases to Improve Low Temperature Molten Sodium-NaSICON Interfaces

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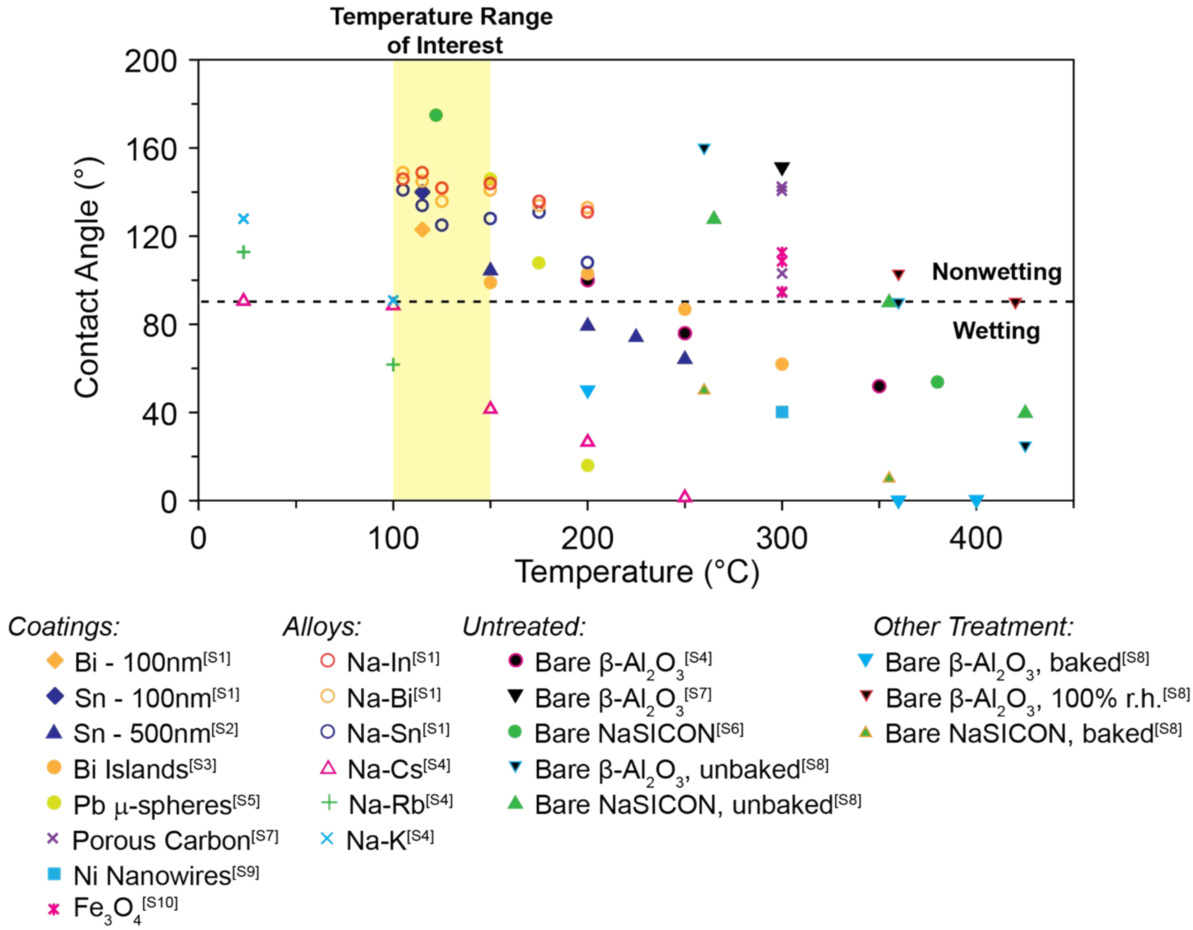

Fig. S1 Prior work of different methods to improve molten Na wetting by contact angle measurement in the temperature range of 25 – 425 °C. All work performed on β”-Al_2O_3 unless otherwise stated.

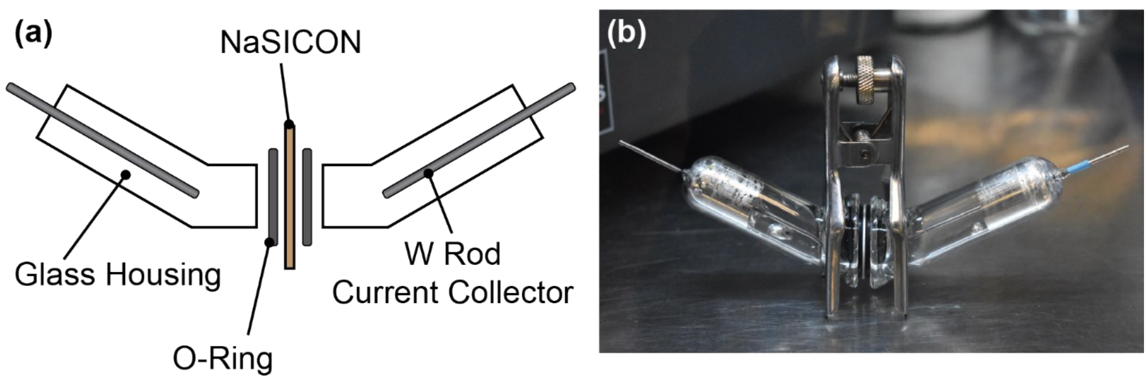

Fig. S2 a) Schematic and b) image of assembled symmetric cell with custom glass parts.

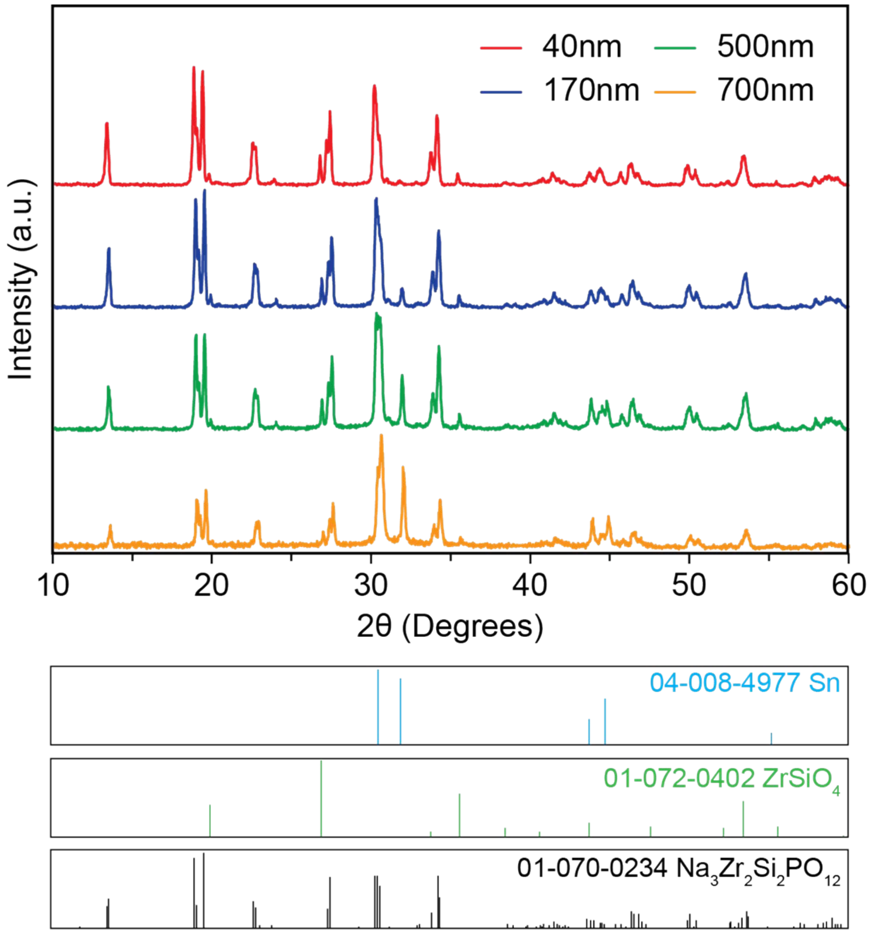

Fig. S3 XRD of Sn coatings on NaSICON after deposition.

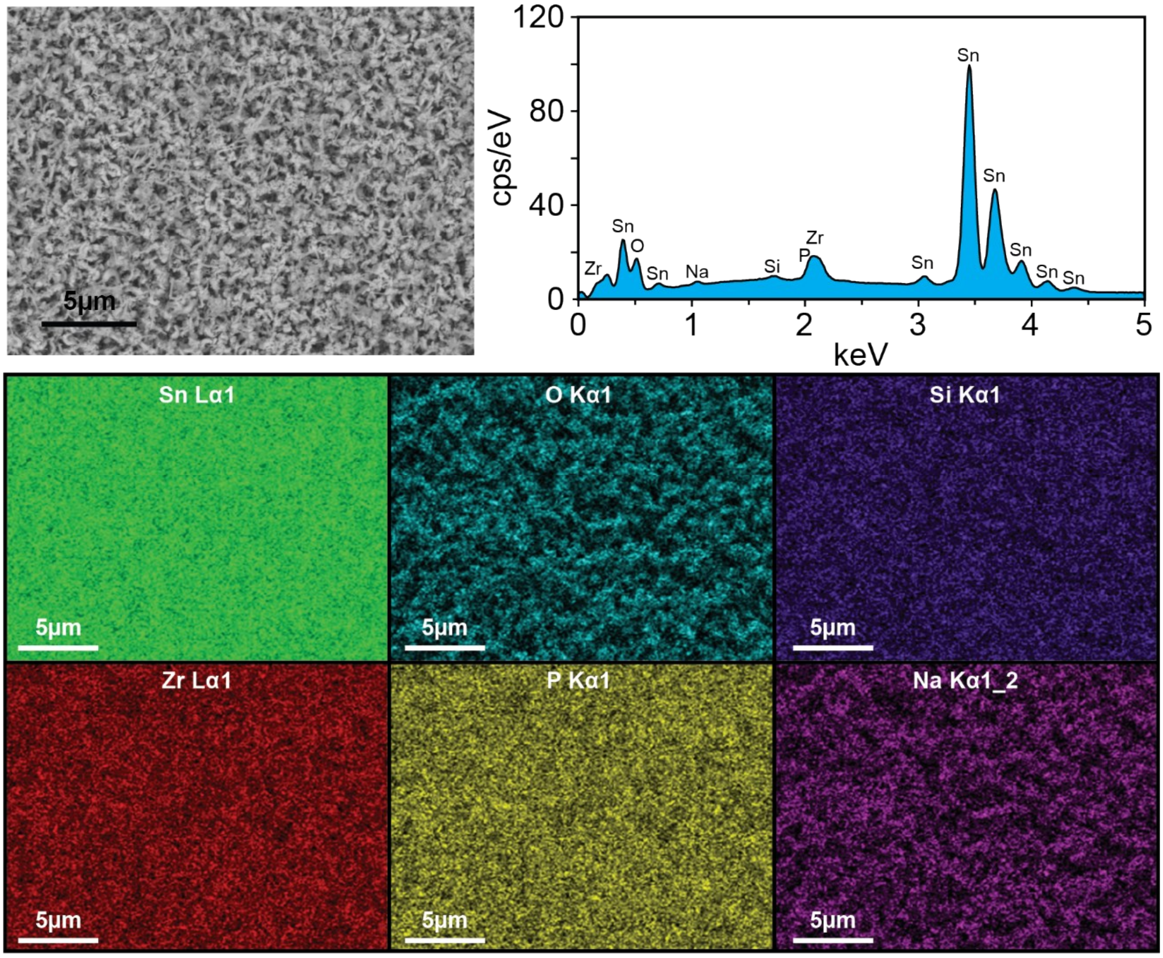

Fig. S4 Energy-dispersive x-ray (EDX) spectra and maps of 700 nm Sn coating on NaSICON at low magnification. Zr, O, Si, P, and Na are all from the underlying NaSICON substrate. Textured morphology in maps of lighter elements (e.g., O, and Na) is a measurement artifact resulting from the rough morphology of the sample surface.

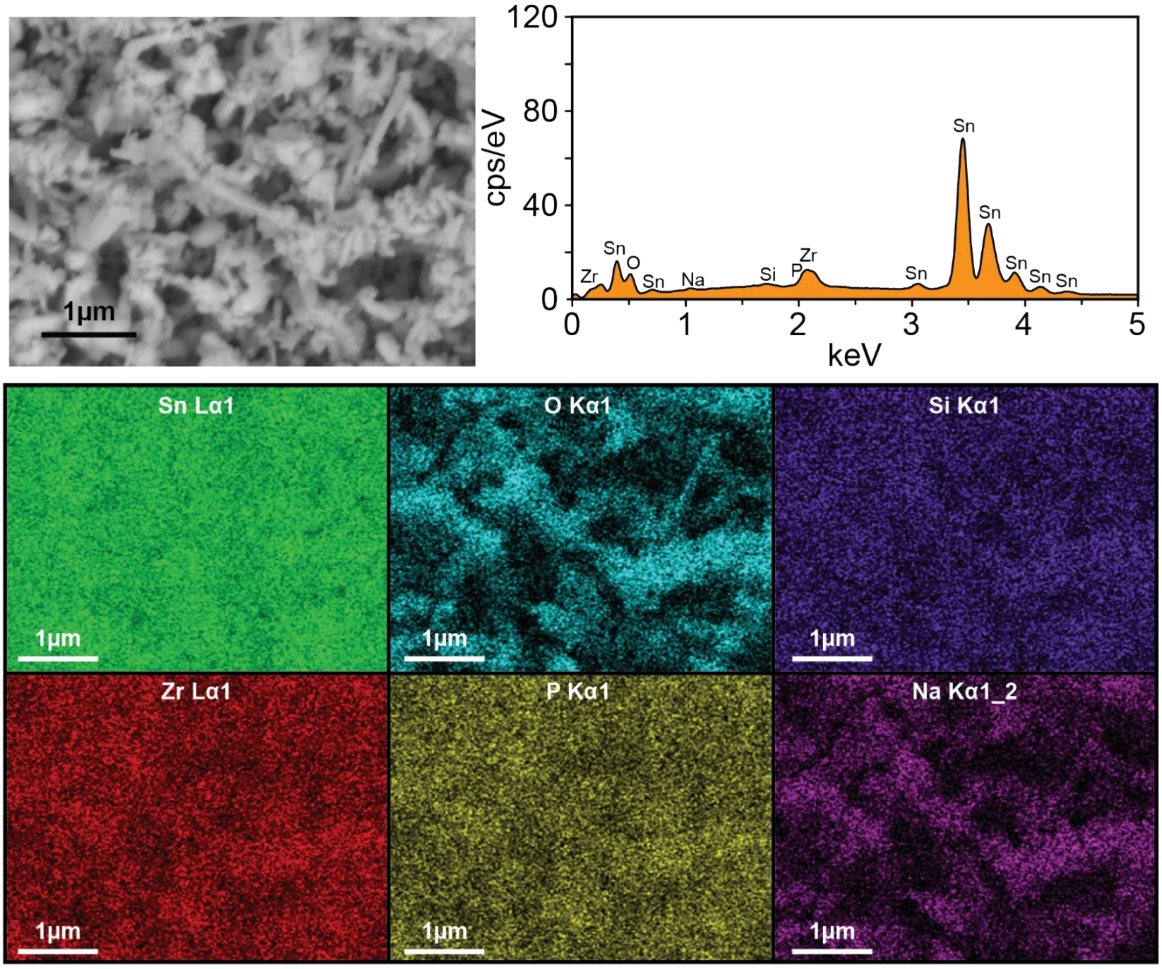

Fig. S5 Energy-dispersive x-ray (EDX) spectra and maps of 700 nm Sn coating on NaSICON at high magnification. Zr, O, Si, P, and Na are all from the underlying NaSICON substrate. Textured morphology in maps of lighter elements (e.g., O, and Na) is a measurement artifact resulting from the rough morphology of the sample surface.

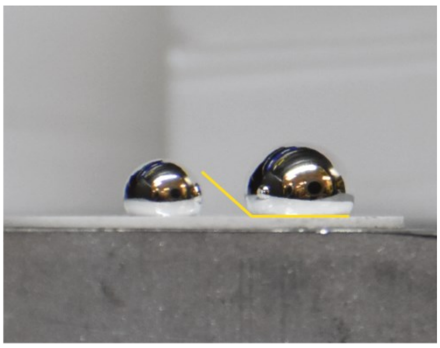

Fig. S6 Wetting test of Na alloy saturated with Sn on bare NaSICON.

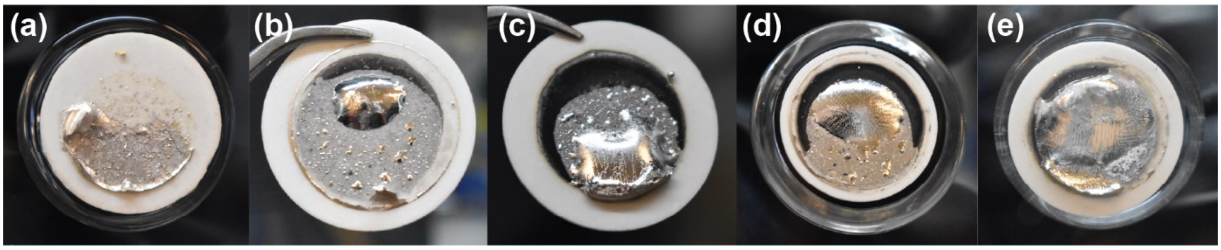

Fig. S7 Images of NaSICON after cycling in a symmetric cell. a) Bare, and with a Sn coating of b) 40 nm, c) 170 nm, d) 500, and e) 700 nm thickness.

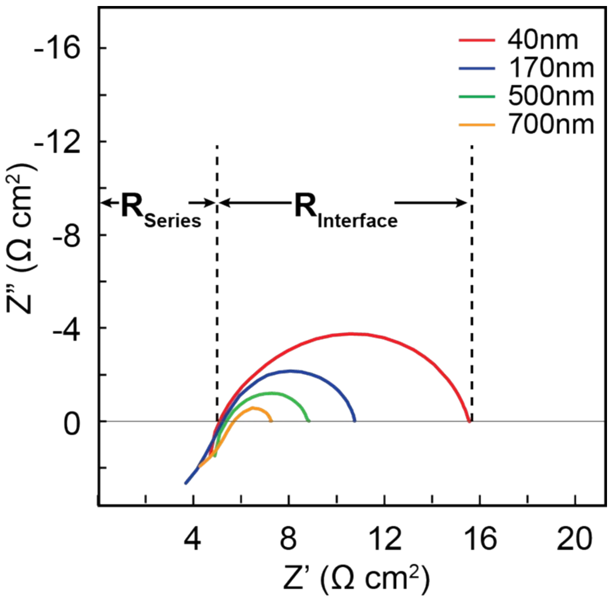

Fig. S8 Illustration of how values for series and interfacial resistances were determined.

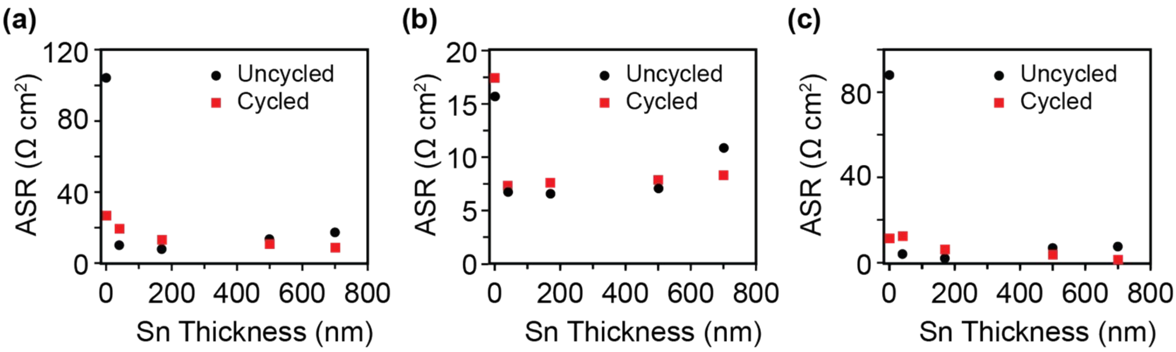

Fig. S9 Area Specific Resistance (ASR) values measured from impedance spectra. a) Total ASR, b) series ASR, and c) interfacial ASR.

ASR values were determined per the following equation: $ASR = R \cdot A$ where R is the resistance and A is the geometric area of the NaSICON.

Table S1 Values of area specific resistance obtained for Na symmetric cells with various Sn coating thicknesses on NaSICON separator.

Sn thickness (nm)	**Condition**	**ASR_{series} (Ohm cm^2)**	**ASR_{total} (Ohm cm^2)**	**$ASR_{interface}$ (Ohm cm^2)**
0	uncycled	13.9	107.5	52.9
40	uncycled	6.0	10.7	4.7
170	uncycled	5.8	8.4	2.6
500	uncycled	6.3	14.0	7.7
700	uncycled	9.6	18.0	8.4
0	cycled	15.4	28.0	12.6
40	cycled	6.5	20.2	13.7
170	cycled	6.7	13.9	7.2
500	cycled	7.0	11.4	4.4
700	cycled	7.3	9.4	2.0

Supporting References

[S1] K. Ahlbrecht, C. Bucharsky, M. Holzapfel, J. Tübke, M. J. Hoffmann, *Ionics*, 2017, **23**, 1319-1327.

[S2] D. Reed, G. Coffey, E. Mast, N. Canfield, J. Mansurov, X. Lu, V. Sprenkle, *J. Power Sources*, 2013, **227**, 94-100.

[S3] D. Jin, S. Choi, W. Jang, A. Soon, J. Kim, H. Moon, W. Lee, Y. Lee, S. Son, Y.-C. Park, H. Chang, G. Li, K. Jung, W. Shim, *ACS Appl. Mater. Interfaces*, 2019, **11**, 2917-2924.

[S4] X. Lu, G. Li, J. Y. Kim, D. Mei, J. P. Lemmon, V. L. Sprenkle, J. Liu, *Nat. Commun.*, 2014, **5**, 4578.

[S5] H.-J. Chang, X. Lu, J. F. Bonnett, N. L. Canfield, K. Han, M. H. Engelhard, K. Jung, V. L. Sprenkle, G. Li, *J. Mater. Chem. A*, 2018, **6**, 19703-19711.

[S6] W. Zhou, Y. Li, S. Xin, J. B. Goodenough, *ACS Cent. Sci.*, 2017, **3**, 52-57.

[S7] Y. Hu, Z. Wen, X. Wu, J. Jin, *J. Power Sources*, 2012, **219**, 1-8.

[S8] L. Viswanathan, A. V. Virkar, *J. Mater. Sci.*, 1982, **17**, 753-759.

[S9] Y. Hu, Z. Wen, X. Wu, Y. Lu, *J. Power Sources*, 2013, **240**, 786-795.

[S10] Y. Hu, Z. Wen, X. Wu, *Solid State Ionics*, 2014, **262**, 133-137.