## Supplementary Information for

## Mechanochemical synthesis of fast sodium ion conductor Na<sub>11</sub>Sn<sub>2</sub>PSe<sub>12</sub> enables first sodium-selenium all-solid-state battery

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Figure S1. XRD data of ball milled samples for various number of hours followed by annealing at 550C for 6 h (for 2h and 5h ball milled samples) and 12h for samples ball milled for 10h and 15h.



Figure S2. SEM image of Na11Sn2PSe12 (i) ball milled for 15 h (ii) ball milled for 15h followed by annealing at 550 °C for 6h.



Figure S3. EDX elemental mapping of C-Se-S.E. composite electrode after ball milling for 30 minutes. The figures are SEM image (top left), elements C (top right), Sn (middle left), Na (middle right), Se (bottom left), and P (bottom right). The uniform distribution in the maps confirms a homogeneous distribution of the elements in the composite cathode.



Figure S4. Correlation between the room temperature conductivity and the lattice parameter c for the mechanochemically synthesized samples in this work (open squares) as well as for single crystal data from Duchardt et al.<sup>1</sup> and Yu et al.<sup>2</sup> (filled symbols). The solid line represents a polynomial fit as a guide to the eye.



Figure S5. XPS data of samples ball milled for 10h followed by annealing at 600  $^{\rm o}$ C.



Figure S6. XPS data of Sn element for samples (a) 2h ball milled for 2h (b) 10h ball milled followed by annealing at 500 ° for 6h (c) 2 h ball milled followed by annealing 550 °C for 18h.



Figure S7. Charge discharge studies of  $Na/Na_{11}Sn_2PSe_{12}/C$ -Se battery.

## References

- 1 M. Duchardt, S. Neuberger, U. Ruschewitz, T. Krauskopf, W.G. Zeier, J. Schmedt auf der Günne, S. Adams, B. Roling and S. Dehnen, *Chem. Mater.* 2018, 30, 4134-4139.
- Z. Yu, S.L. Shang, D. Wang, Y.C. Li, H.P. Yennawar, G. Li, H.T. Huang, Y. Gao, T.E. Mallouk, Z.K. Liu and D. Wang, Energy Storage Materials 2019, 217, 70–77.