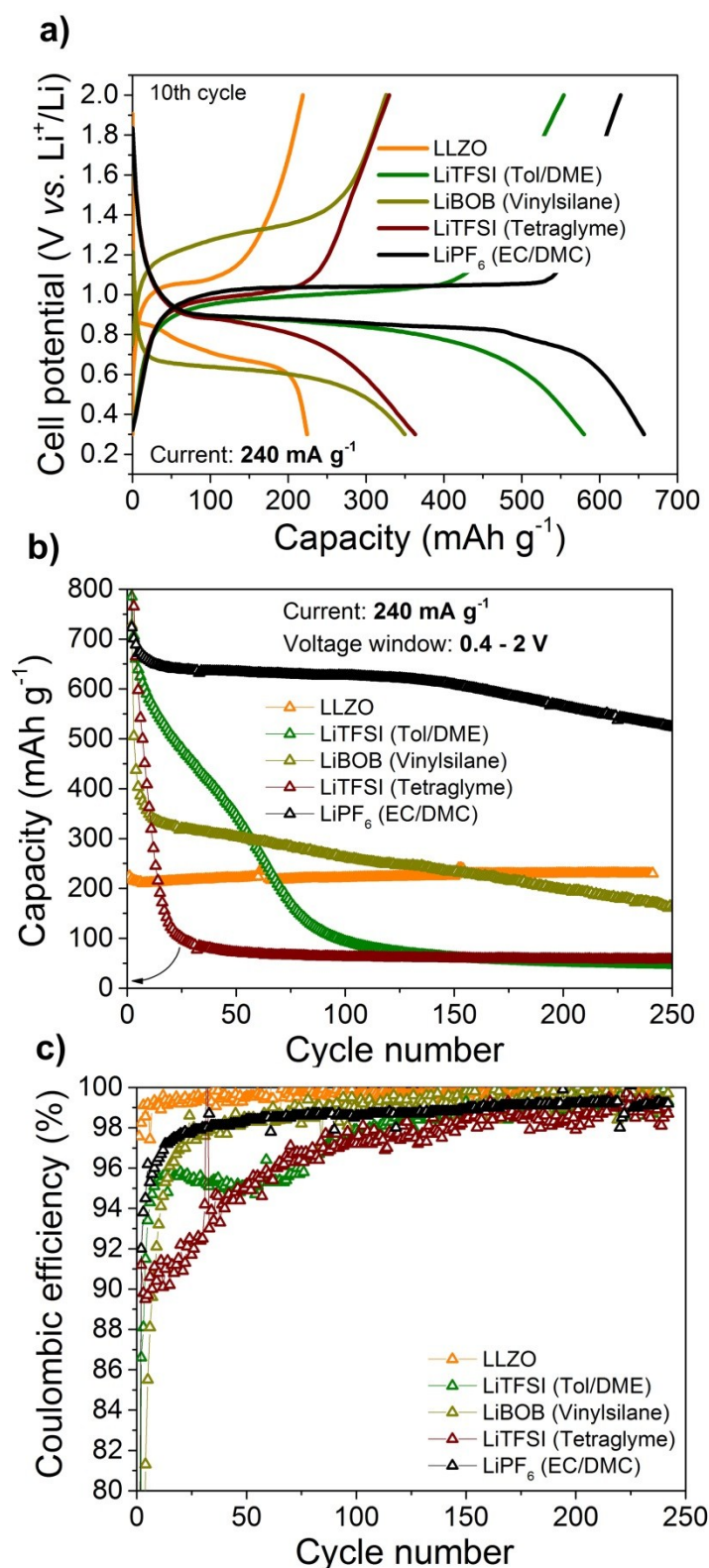
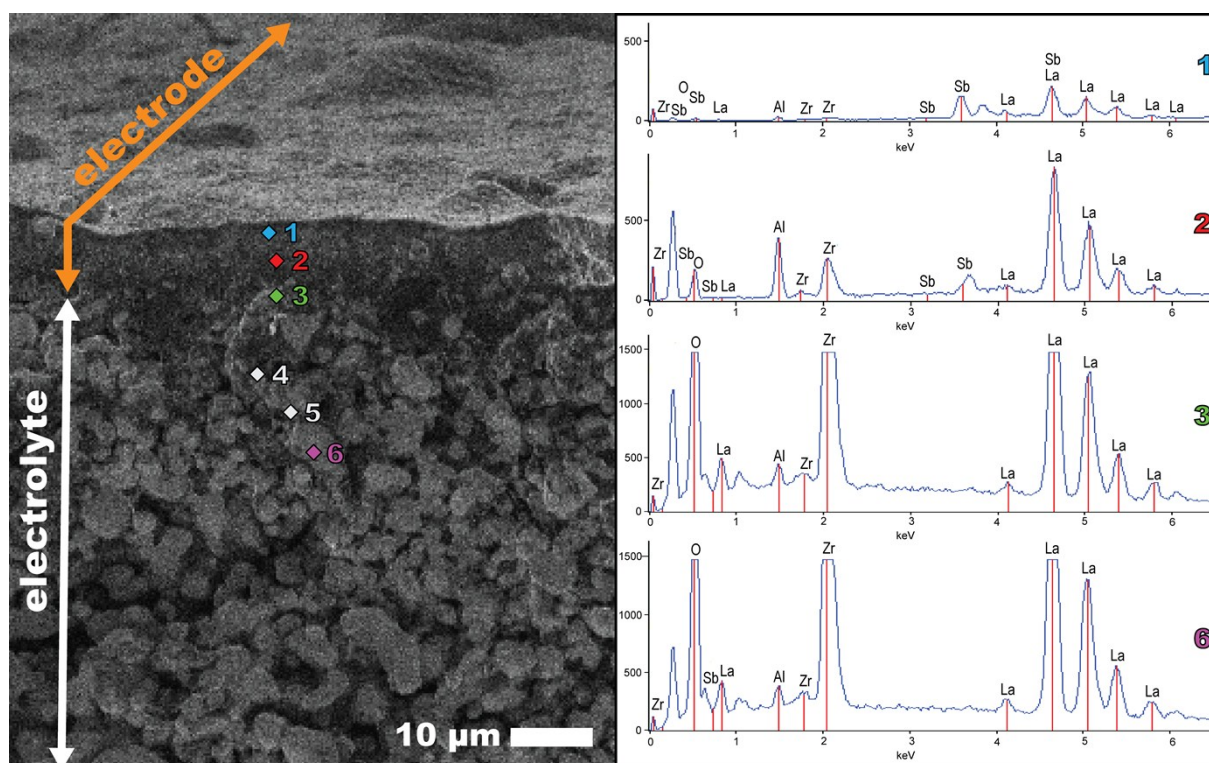


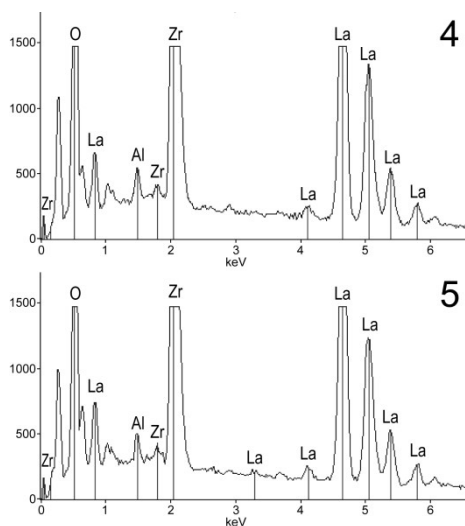
Supporting Information



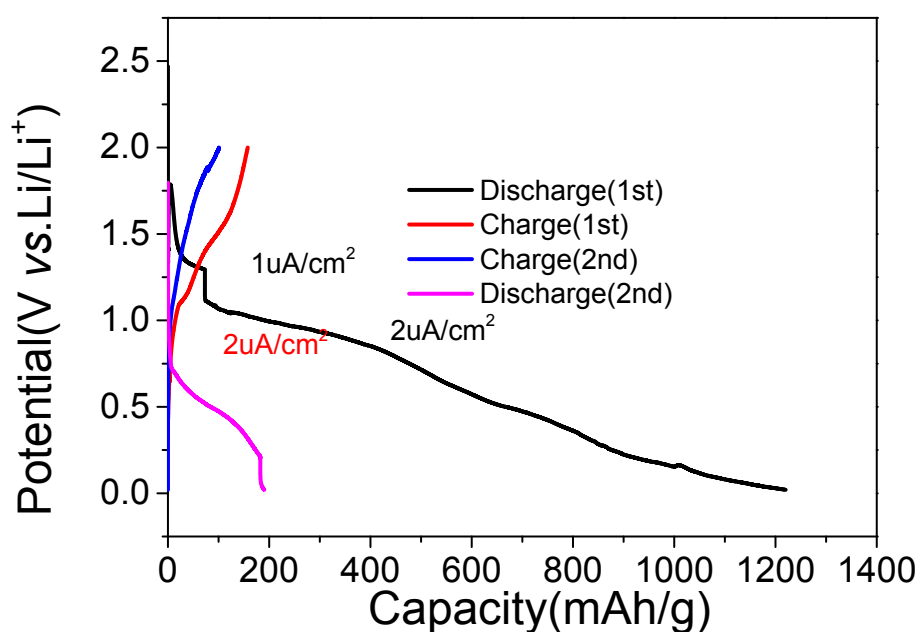
Supplementary Figure 1. Comparison of electrochemical performance of Sb NPs with LLZO solid electrolyte and various liquid Li electrolytes. **a)** galvanostatic charge/discharge curves; **b)** cyclic stability and **c)** coulombic efficiency.



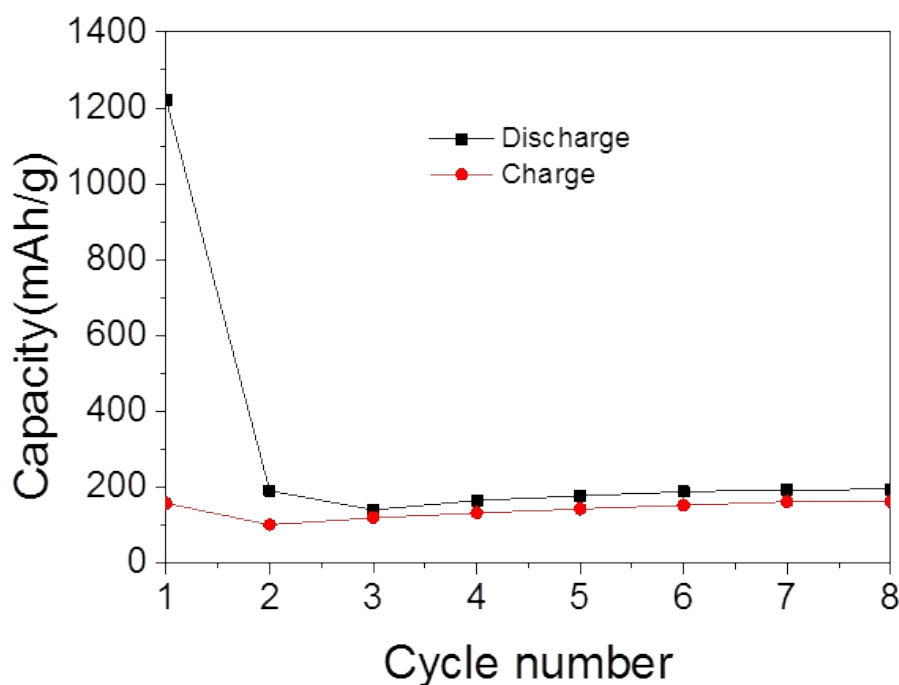
Supplementary Figure 2 a) The cross section scanning electron microscopy (SEM) micrograph from an all-solid-state battery based on $\text{c-Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ and Sb composite electrode obtained after the battery operation, displaying the solid electrolyte and the composite electrode. **b)** Energy-dispersive X-ray spectroscopy (EDXS) data from the marked regions in (a) (for spectra to measurement points 4 and 5 see below).



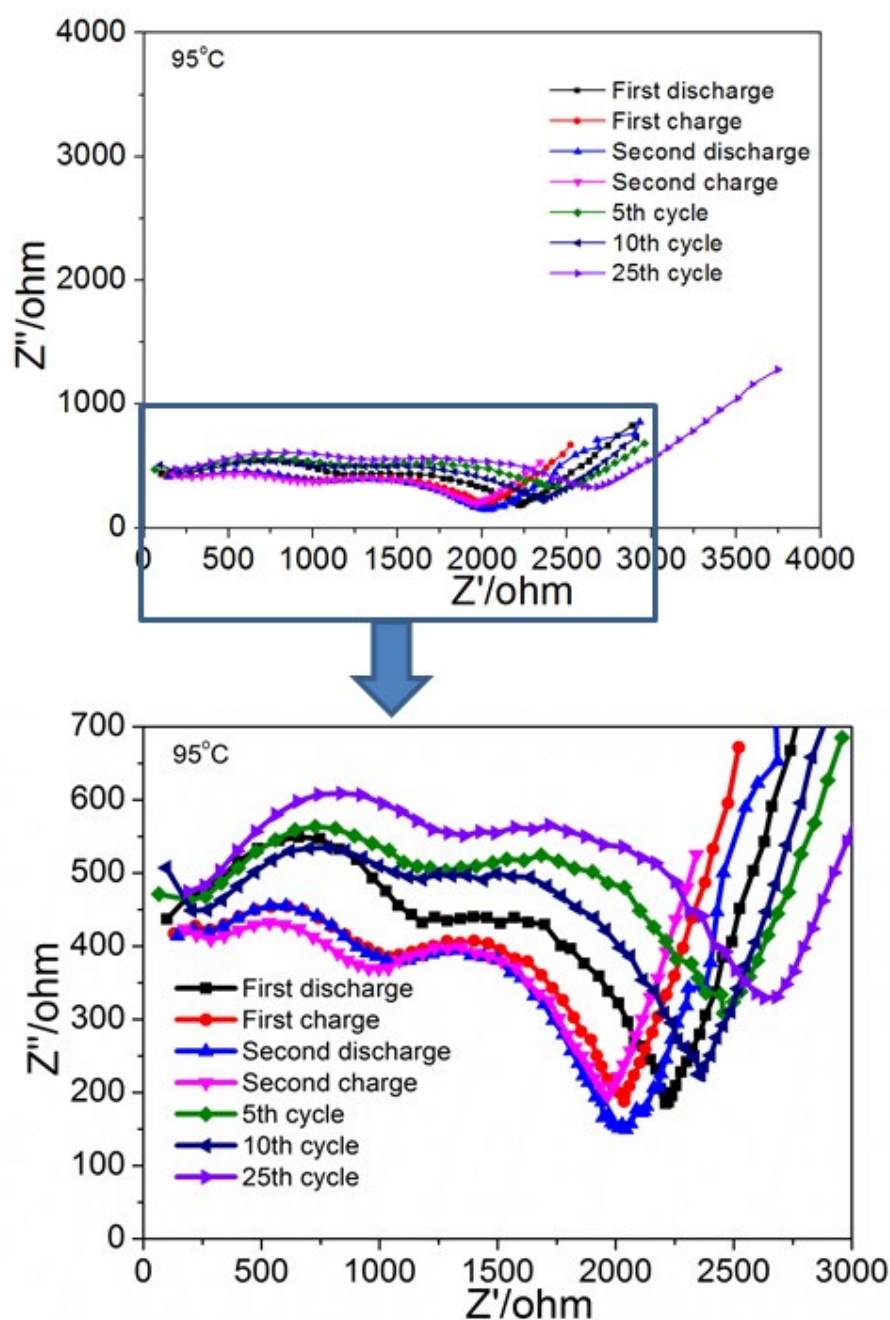
Here, EDX probing was done at different location near the interface of the battery cell, showing no new phases containing Sb in the electrolyte region next to the electrode and no mechanical deformation in the probed area.



Supplementary Figure 3. Galvanostatic charge/discharge curves of the non-pressed Sb – $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ all-solid-state batteries within 0.3 – 2.0 V at two different rates, 95 °C. Please note that the cells shown here are not isostatically pressed !



Supplementary Figure 4. Capacity vs. cycle number for the non-pressed Sb/ $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ all-solid-state batteries within 0.3 - 2.0 V at 1 $\mu\text{A}/\text{cm}^2$ rate, 95 °C. Please note that the cells shown here are not isostatically pressed !



Supplementary Figure 5. Nyquist plots of Sb/Li_{6.25}Al_{0.25}La₃Zr₂O₁₂ all-solid-state batteries within 0.3–2.0 V at 40 mA/g rate of different cycles, 95 °C.

The AC impedance spectra further verified the improved contacting and reduced resistances for the pressed battery cell arrangement of all-solid nano-Sb and c-Li_{6.25}Al_{0.25}La₃Zr₂O₁₂ cells. Nyquist plots for the pressed all-solid-state batteries based on nano-Sb and c-Li_{6.25}Al_{0.25}La₃Zr₂O₁₂ cells are illustrated in **Supplementary Figure 5**. The observed impedance semi-circles could be fitted with an equivalent circuit of a resistor and a constant

phase element in parallel, and the outer intersection of the semi-circle previous to the ion-blocking electrode tail seen at high frequencies with the real axis has been estimated as the total resistance of cells; however, for the given cell and temperature range tested in, a clear separation by impedance and equivalent circuits of the many different elements contributing to the total impedance (e.g., nano-Sb and its carbon coating, c-Li_{6.25}Al_{0.25}La₃Zr₂O₁₂, PVDF, active carbon, etc.) is not possible due to the overlap of the many individual impedance arcs. It can be seen that the resistance values for the pressed cells are reduced by one order of magnitude when compared to the non-pressed battery cells of all-ceramics in literature; and even lower than the values where an additional interface modification but no isostatic pressing had been applied to the all-solid-state cells¹⁻². Thus, the isostatic pressing of cells and the use of nano-Sb anode decrease in the overall resistance values through an intimate embedding of the grains at the electrode-electrolyte interface and a better contacting. The pressed cells have a dense and well-integrated connection of the electrode into the solid-electrolyte; thereby reducing main impedances caused by the electrode – electrolyte interface and enabling the charge transfer. The overall impedance values increase through extended cycling but stays relatively stable that is line with observed capacity retention and rate capability measurements (Figure 4).

1. van den Broek, J.; Rupp, J. L. M.; Afyon, S., Boosting the electrochemical performance of Li-garnet based all-solid-state batteries with Li₄Ti₅O₁₂ electrode: Routes to cheap and large scale ceramic processing. *J. Electroceram.* **2017**, 1-7.
2. van den Broek, J.; Afyon, S.; Rupp, J. L. M., Interface-engineered all-solid-state Li-ion batteries based on garnet-type fast Li⁺ conductors. *Adv. Energy Mater.* **2016**, 6 (19), 1600736.