Favorable Interfacial Chemomechanics Enables Stable Cycling of High Li-Content Li-In/Sn Anodes in Sulfide Electrolyte Based Solid-State Batteries

Christian Hänsel\textsuperscript{a}, Baltej Singh\textsuperscript{b}, David Kiwic\textsuperscript{a}, Pieremanuele Canepa\textsuperscript{b,c,*}, and Dipan Kundu\textsuperscript{d,*}

\textsuperscript{a} Multifunctional Materials, Department of Materials, ETH Zurich, Switzerland
\textsuperscript{b} Department of Materials Science and Engineering, National University of Singapore, Singapore 117575, Singapore.
\textsuperscript{c} Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585
\textsuperscript{d} School of Chemical Engineering and School of Mechanical and Manufacturing Engineering, UNSW Sydney, Kensington, NSW 2052, Australia

* Corresponding author. Email: pcanepa@nus.edu.sg

* Corresponding author. Email: d.kundu@unsw.edu.au

Additional Experimental Details

Materials. \(\text{Li}_2\text{S}\) (99.9 % Alfa Aesar), \(\text{P}_2\text{S}_5\) (98+ % Acros Organics), lithium ribbon (99.9 % Sigma-Aldrich), indium powder (99.99 % abcr GmbH) and tin foil (99.9 % Alfa Aesar) were used without any further purification and stored in an argon filled glovebox at room temperature. \(\text{LiCl}\) anhydrous (\(\geq\) 99.9 % Aldrich-Fine Chemicals) was dried overnight at 200 °C under vacuum and stored in an argon filled glovebox at room temperature.

Synthesis of \(\text{Li}_6\text{PS}_5\text{Cl}\). \(\text{Li}_6\text{PS}_5\text{Cl}\) was prepared by ball milling using a planetary ball mill (Pulverisette 7PL, Fritsch) and \(\text{ZrO}_2\) jars (20 mL) followed by a heat-treatment. 2 g batches of stoichiometric amounts of \(\text{Li}_2\text{S}\), \(\text{P}_2\text{S}_5\) and \(\text{LiCl}\) were mechanically milled at 500 rpm for 192 min (5 min of milling, 3 min pause – 2h total milling time) using 10 \(\text{ZrO}_2\) balls (10 mm in diameter). The obtained powder was pelletized and sealed in a carbon coated quartz ampoule under \(10^{-5}\) bar pressure. The sealed powder was heated at 550 °C for 10 hours (heating rate 183 °C h\(^{-1}\)). The annealed SE was hand-ground in a mortar, and the powder was stored in an argon-filled glovebox until it was used.
Table S1. The amount of precursors used for alloy synthesis

|       | Li$_{0.5}$In | LiIn | Li$_{13}$In$_3$ | Li$_2$Sn$_5$ | LiSn | Li$_{17}$Sn$_4$ |
|-------|--------------|------|-----------------|-------------|------|----------------|
| Li [mg]| 14.7         | 28.5 | 104             | 11.4        | 27.6 | 99.5           |
| In or Sn [mg] | 485 | 471 | 396 | 489 | 472 | 400 |

**Materials Characterization.** Powder X-ray diffraction was conducted on a PANalytical Empyrean diffractometer in Bragg-Brentano geometry using Cu-Kα radiation ($\lambda = 1.5405$ Å) and a PIXcel detector with a Ni Kβ filter. The diffraction data were collected from 10° to 80° (2θ) with a collection time of 1 h. During the measurement, the air and moisture sensitive samples were covered with a 25 µm thick Kapton foil. The morphology of the SE pellets was analyzed by scanning electron microscopy (SEM) on a DSM 982 Gemini instrument (Zeiss). A thin Pt layer (3 nm) was sputtered onto the samples before transferring them quickly into the SEM.

**Pressure monitoring.** Detailed information on the pressure monitoring of the cells can be found in a previous publication.¹

**Figures and Tables**

**XRD Analysis**

**Figure 1a** shows the reference spectra for the 25 µm thick Kapton foil, which was used to cover the air and moister sensitive samples during the measurement. The XRD pattern shows broad peaks around 14, 21 and 26 °. **Figure S1b** shows the XRD powder pattern of Li$_{0.5}$In and highlights that the Li$_{0.5}$In alloy is actually a solid-solution of LiIn and metallic as demonstrated in the Li-In phase diagram in Figure 1b. **Figure S1c** shows the XRD powder pattern of the synthesized LiIn phase before and after ball-milling and shows that the LiIn phase could be synthesized phase pure after ball-milling as the pattern matches well with the reference spectra taken from the Inorganic Chemical Structure Database (ICSD).

**Figure S2a** shows the XRD powder patterns of the targeted Li-Sn alloy Li$_2$Sn$_5$ before and after ball-milling. The phase could not be synthesized phase pure. Before the ball-milling step, the mixture is composed of Li$_2$Sn$_5$, LiSn and Sn. After ball-milling, the sample consists only of Li$_2$Sn$_5$ and Sn with a much stronger Sn peak intensity. **Figure S2b** shows the XRD powder
patterns of the targeted Li-Sn alloy LiSn before and after ball-milling. The LiSn could be obtained almost phase pure after ball milling with minor impurities of Sn and Li₂Sn₅.

**Figure S1. Diffraction patterns of Li-In alloys.** (a) XRD pattern of the Kapton foil used to protect the air-sensitive samples. XRD patterns of (b) the LiIn + In (1:1 atomic ratio - Li₀.₅In) alloy and the reference peaks for the LiIn (ICDS-no. 639882)² and In (ICSD-no. 64794)³ phase and (c) the LiIn alloy before and after ball milling and the reference peaks for the LiIn (ICDS-no. 639882)³ and In (ICSD-no. 64794)³ phase.

**Figure S2. Diffraction patterns of Li-Sn alloys.** XRD pattern of (a) the Li₂Sn₅ alloy before and after ball milling and the reference peaks for the Li₂Sn₅ (ICDS-no. 26200)⁵, LiSn (ICSD-no.104782)⁶ and Sn (ICSD-no. 242009)⁷ phases and (b) the LiSn alloy shown before and after ball milling and the reference peaks for Li₂Sn₅ (ICDS-no. 26200)⁵, LiSn (ICSD-no.104782)⁶ and Sn (ICSD-no. 242009)⁷ phases. The phases Li₂Sn₅ and LiSn could not be synthesized completely phase pure. The XRD pattern for Li₂Sn₅ shows a mixture of Li₂Sn₅, LiSn and Sn and XRD pattern for LiSn shows a mixture of LiSn, Li₂Sn₅ and Sn. While for LiSn, ball milling results in almost phase pure LiSn, in the case of Li₂Sn₅ ball milling results in an increase of the Sn peaks. We therefore tried to increase the solid-state reaction temperature for the two samples above their melting point and homogenized the Li₂Sn₅ sample at 450 °C and the LiSn sample at 500 °C for one day, followed by an annealing step at 350 °C for 1 week, according to [5]. However, we were still not able to obtain phase pure samples for Li₂Sn₅ and LiSn.
Figure S3. Diffraction pattern of a Li$_{13}$In$_3$ alloy. XRD pattern of Li$_{13}$In$_3$ prepared by repeated folding and pressing of Li and In foil together at 150 MPa and the reference peaks for the LiIn (ICDS-no. 639882)$^2$, In (ICSD-no. 64794)$^3$, Li (ICSD-no. 44367)$^8$ and Li$_{13}$In$_3$ (ICDS-no.51963)$^9$ phases.

Alloy processing and electrode preparation

Figure S4. SEM micrographs of the LiIn powder (a) before and (b) after ball milling and the LiIn foil pressed from the (c) non-ball-milled and (d) ball-milled powder.

Figure S5. SEM micrographs of the Li$_2$Sn$_5$ powder (a) before and (b) after ball milling and the Li$_2$Sn$_5$ foil pressed from the (c) non-ball-milled and (d) ball-milled powder. SEM micrographs of the LiSn powder (e) before and (f) after ball milling and LiIn foil pressed from the (g) non-ball-milled and (h) ball-milled powder.
Figure S6. SEM micrographs of the surfaces of (a) a metallic Li-foil and (b) a non-ball-milled Li$_{0.5}$In foil.

**Constant stripping experiments**

For the constant stripping experiment 150 mg of Li$_6$PS$_5$Cl were pressed at 510 MPa and an indium disk (100 mg, thickness 125 µm) was pressed onto one side of the SE pellet at pressure of 150 MPa. Subsequently, the respective alloy equivalent to a capacity of 10 mAh (see Table S2) was spread over the opposite side of the SE pellet and the entire stack was pressed at an assembly pressure of 45 MPa for 2 min to ensure a good interfacial contact between the SE and the alloy electrode.

**Table S2.** Used mass for the working electrode for the assembly of non-symmetrical (Figure 3) and symmetrical (Figure 5) solid-state cells and corresponding capacity and the theoretical thickness of.

| WE        | Li   | Li$_{0.5}$In | LiIn  | Li$_{13}$In$_3$ | Li$_2$Sn$_5$ | LiSn  | Li$_{17}$Sn$_4$ |
|-----------|------|--------------|-------|-----------------|--------------|-------|----------------|
| Mass [g]  | 0.0026 | 0.088        | 0.046 | 0.0125          | 0.113        | 0.047 | 0.013          |
| Capacity [mAh] | 10.04 | 10.13        | 10.12 | 10.02           | 9.97         | 10.03 | 9.99           |
| Specific Capacity (mAh g$^{-1}$) | 3861 | 115          | 220   | 801             | 88           | 213   | 768            |
| Crystal density [g cm$^{-3}$] | 0.53$^{10}$ | 6.23$^{[a]}$ | 5.16$^{3}$ | 2.23$^{9}$ | 6.11$^{4}$ | 5.08$^{5}$ | 2.58$^{11}$ |
| Theor. Electrode Thickness [µm]$^{[a]}$ | 43 | 125 | 79 | 50 | 164 | 82 | 45 |
| Volumetric capacity (Ah L$^{-1}$) | 2046 | 717 | 1135 | 1787 | 539 | 1084 | 1982 |

$^{[a]}$ The crystal density was calculated according to: ($\rho_{(In)} + \rho_{(LiIn)})/2$ with $\rho_{(In)} = 7.30$ g cm$^{-3}$. $^{[b]}$ Theoretical Thickness of the electrode based on the theoretical crystal density and an electrode area of 1.13 cm$^2$. 

S-5
Figure S7. Schematic illustration of the solid-state cell preparation.

Figure S8. Bulk resistance of the 750 µm thick Li<sub>6</sub>PS<sub>5</sub>Cl SE pellet. (a) Dependence of the Steel|Li<sub>6</sub>PS<sub>5</sub>Cl|Steel cell resistance on the applied stack pressure. A perfect interfacial contact is reached at a stack pressure of 120 MPa and the measured resistance is equal to the bulk resistance of the SE pellet. (b) Stack impedance of a In|Li<sub>6</sub>PS<sub>5</sub>Cl|In cell assembled at an assembly pressure of 150 MPa which results in a perfect interfacial contact. (c) Stack impedance of a Li<sub>0.5</sub>In|Li<sub>6</sub>PS<sub>5</sub>Cl|Li<sub>0.5</sub>In cell assembled at with an assembly pressure of 150 MPa which results in a perfect interfacial contact.
Figure S9. Equivalent circuit used to fit the measured impedance data (Figure 3; main manuscript) of the In|Li$_6$PS$_5$Cl|M cells (M = Li, Li$_{17}$Sn$_4$) stripped at a constant stack pressure of 0 MPa and 45 MPa. Q1/R1 corresponds to the bulk impedance of the solid electrolyte membrane, Q2/R2 represents the impedance corresponding the Li/alloy-SE interface, and Q3/R3 represents the impedance of the In-SE interface. Q4 was included to represent all the diffusion processes. EC Lab (Biologic) Zfit software was used to fit the impedance data.

Table S3. Fitted stack impedance data. Parameters obtained from fitting the stack impedance data shown in Figure 3 using the equivalent circuit presented in Figure S9. It must be noted that the fitting is rather qualitative here as we disregarded the data at low frequencies. The fitting quality (goodness of fit) was poor when the low frequency range data was included.

| Cell | In|Li$_6$PS$_5$Cl|Li - Fig. 3c | In|Li$_6$PS$_5$Cl|Li$_{17}$Sn$_4$ - Fig. 3e | In|Li$_6$PS$_5$Cl|Li$_{17}$Sn$_4$ - Fig. 3f |
|------|----------------|----------------|----------------|
| Stack pres. [MPa] | Before | After | Before | After | Before | After |
| Q1 [F] | 0 | 0 | 0.503E-9 | 0.124E-9 | 0.541E-9 | 0.402E-9 |
| a1 | 1 | 1 | 0.75 | 0.861 | 0.79 | 0.78 |
| R1 [Ohm] | 38 | 38 | 38 | 38 | 38 | 38 |
| Q2 [F] | 0.395E-9 | 8.18E-9 | 1.38E-9 | 1.52E-9 | 1.42E-15 | 17.55E-18 |
| a2 | 0.718 | 0.786 | 0.898 | 0.861 | 0.893 | 1 |
| R2 [Ohm] | 68 | 54E3 | 96 | 1708 | 0.01 | 0.63E-3 |
| Q3 [F] | 55.4E-6 | 8.54E-6 | 8.45E-3 | 22.43E-6 | 0.02 | 1.04E-3 |
| a3 | 0.744 | 0.267 | 0.185 | 0.419 | 0.232 | 0.649 |
| R3 [Ohm] | 24 | 29 | 27 | 30 | 1.58E-6 | 0.942E-3 |
| Q4 [F] | 0.18E-9 | 78.11E-9 | 0.106E-6 | 0.468E-6 | 0.124E-3 | 0.405E-3 |
| a4 | 0.912 | 1 | 0.889 | 0.708 | 0.665 | 0.589 |
Figure S10. Stack impedance before and after the long-term stripping of In|Li₆PS₅Cl|A (A = Li₂Sn₅, Li₀.₅In, and Li₁₃In₃) cells. Stack impedance of an In|Li₆PS₅Cl|Li₂Sn₅ cell stripped at a constant stack pressure of (a) 0 MPa and (b) 45 MPa. Stack impedance of an In|Li₆PS₅Cl|Li₀.₅In cell stripped at a constant stack pressure of (c) 0 MPa and (d) 45 MPa. Stack impedance of an In|Li₆PS₅Cl|Li₁₃In₃ cell stripped at a constant stack pressure of (e) 0 MPa and (f) 45 MPa.

Table S4. Stack Resistance (R_{SE} + R_{int}) of In|Li₆PS₅Cl|WE (WE =Li, Li₀.₅In, Li₁₃In₃, Li₂Sn₅ Li₁₇Sn₄) before and after the long-term stripping at a stack pressure of 0 or 45 MPa.

|        | 0 MPa       | 45 MPa       | 0 MPa       | 45 MPa       |
|--------|-------------|-------------|-------------|-------------|
|        | Before [Ohm]| After [Ohm] | Before [Ohm]| After [Ohm] |
| Li     | 70          | 54501       | -           | -           |
| Li₀.₅In| 105         | 121         | 51          | 40          |
| Li₁₃In₃| 100         | 1842        | 40          | 43          |
| Li₂Sn₅ | 98          | 99          | 39          | 39          |
| Li₁₇Sn₄| 103         | 1864        | 39          | 40          |
**Figure S11.** Potential profile for a In||Li$_6$PS$_5$Cl||Li cell at $I = 200$ µA and a constant stack pressure of 45 MPa with a maximum Li capacity of 10 mA h.

**Formation energies and intercalations voltages**

DFT provides the total energy which is an approximation to the internal energy of a system at 0 K. **Eq. S.1** shows the reaction of Li intercalation into In and Sn and the formation of Li-In and Li-Sn alloys (see main text) which were computed using DFT.

$$x\text{Li} + yZ \rightleftharpoons \text{Li}_xZ_y$$

(S.1)

where $Z$ can be either In or Sn, $x$ and $y$ are the stoichiometric coefficient and $E_f$ is the change in the Gibbs free energy at 0 K for the reaction. The thermodynamic propensity for Li to alloy with either In or Sn is evaluated by the $E_f$ of **Eq. S.2**, also known as the formation energy of the $\text{Li}_xZ_y$ alloy, and written as

$$E_f = \frac{E(\text{Li}_xZ_y) - x\mu_{\text{Li}} - yE(Z)}{(x - y)}$$

(S.2)

where $E(\text{Li}_xZ_y), \mu_{\text{Li}}$ and $E(Z)$ are the DFT total energies of the bulk alloy($\text{Li}_xZ_y$), Li, and In(or Sn), respectively. The chemical potential of Li metal $\mu_{\text{Li}}$ is equivalent to $E(\text{Li})$. Note, that we approximated the Gibbs energy of each component by the DFT total energies (i.e., $G \approx E$), thus neglecting the, zero point energy, as well as the $pV$ and entropic contributions.

The intercalation voltages for Li ions in these alloys are computed using the computed free energies of the compounds as given in **Eq. S.3 and Eq. S.4**.

$$\text{Li}_mZ_y + (n - m)\text{Li} \xrightarrow{\Delta G} \text{Li}_nZ_y$$

(S.3)
\[ V = -\frac{\Delta G}{(\text{n}-\text{m}) F} \approx -\frac{E(\text{Li}_nZ_y) - [(\text{n}-\text{m})\mu_{\text{Li}} + E(\text{Li}_mZ_y)]}{(\text{n}-\text{m}) F} \] (S.4)

where \( F \) is the Faraday’s constant. Thus, the formation energies and the voltage properties were computed on a number of alloy systems as indicated in Table S5, with provenance from the Inorganic Chemical Structure Database (ICSD)\(^{12}\) or the Materials Project\(^{13}\) unless noted differently.

Table S5 Alloys and bulk metal crystallographic structure and their provenance. The ratio between Li and Z (In or Sn) is also reported.

| Compound | Li/Z | ICSD/MP Code | Space Group |
|----------|------|--------------|-------------|
| Li       | –    | 44367        | Im\(\overline{3} m\) |
| Sn       | –    | 242009       | I4\(_1\)/amd |
| Li\(_2\)Sn\(_5\) | 0.40 | 26200        | P4/mbm  |
| LiSn     | 1.00 | 104782       | P2/m     |
| Li\(_7\)Sn\(_3\) | 2.33 | 104785       | P2\(_1\)/m |
| Li\(_5\)Sn\(_2\) | 2.50 | 104783       | R\(\overline{3} m\) |
| Li\(_3\)Sn\(_5\) | 2.60 | 51963        | P\(\overline{3} m\) |
| Li\(_8\)Sn\(_3\) | 2.66 | Mayo & Morris\(^{14}\) | R\(\overline{3} m\) |
| Li\(_7\)Sn\(_2\) | 3.50 | 104784       | Cmmm     |
| Li\(_7\)Sn\(_4\) | 4.25 | 240046       | F\(\overline{4} 3 m\) |
| In       | –    | 64794        | I4/mmm   |
| LiIn\(_3\) | 0.33 | mp-973748\(^{13}\) | I4/mmm  |
| LiIn\(_2\) (Li\(_{0.5}\)In) | 0.50 | mp-1210993\(^{13}\) | Fd\(\overline{3} m\) |
| Li\(_3\)In\(_2\) | 1.50 | 10051        | R\(\overline{3} m\) |
| LiIn     | 1.00 | 639882       | Fd\(3 m\) |
| Li\(_5\)In\(_4\) | 1.25 | mp-1079408\(^{13}\) | P\(\overline{3} m\) |
| Li\(_3\)In | 3.00 | mp-867226\(^{13}\) | Fm\(3 m\) |
| Li\(_3\)Sn | 4.34 | 51963        | Fd\(\overline{3} m\) |

Computational Methodology

For the evaluation of the energies of Eq. S.2 and Eq. S.4, we employ DFT, where the unknown exchange and correlation function was approximated by the Perdew–Burke–Ernzerhof Generalized-Gradient Approximation (GGA)\(^{15}\) as implemented in the Vienna ab initio
The projector augmented wave (PAW) potentials were used for the core wave-functions. The integration of the 1st Brillouin zone was performed on extremely dense $k$-point mesh of consistent density of $2000/(\text{number of atoms per unit cell})$ across different alloys. The convergence threshold of the total energy was set to $1 \times 10^{-6} \text{ eV}$, whereas the forces during the geometry relaxations of the end-point images were converged to $1 \times 10^{-2} \text{ eV/Å}$ and stresses to 0.29 GPa.

To model the migration of Li in selected alloys, we use the nudged elastic band (NEB) method together with DFT. In the NEB calculations, seven (or when needed 11) images were linearly interpolated between the end points used to prepare the initial migration energy paths. In order to avoid spurious interactions between images during the relaxation of the NEBs, supercells of appropriate sizes were used to ensure a minimum inter-image distance of 10 Å. In the NEB calculations, the forces on the elastic band were converge to $0.05 \text{ eV Å}^{-1}$. The calculations were performed in the dilute vacancy limit, i.e. one Li atom is removed per unit cell.

**Migration energy paths in Li-In and Li-Sn alloys**

**Figure S12 a-g** shows the lowest migration energy paths (MEPs) for Li in $\text{Li}_x\text{Sn}_y$ and $\text{Li}_x\text{In}_y$ alloys, respectively. The reported paths are considered to be percolating. To this end, we have considered all the possible cases where Li can traverse the unit cell of the alloy. Green polyhedra display the In(Sn) coordination of Li. Other MEPs stemming from the search are reported in **Figure S12-15**.

![Migration energy paths in Li-In and Li-Sn alloys](image-url)
Figure S12. lowest migration energy paths that enable Li percolation in Li$_x$Sn$_y$ and Li$_x$In$_y$ alloys.
Additional migration energy paths if Li-In and Li-Sn alloys

Figure S13. An additional migration energy path of Li percolation in Li$_{13}$In$_3$ ($Fd\bar{3}m$).

Figure S14. Additional Li MEP in Li$_2$Sn$_5$ ($P4/mbm$).

Figure S15. Additional Li MEP in LiSn ($P2/m$).

Table S6. Shows the Li coordination environment in selected Li-In(Sn) alloys. Note, the determination of the Li coordination environment in Li$_{13}$In$_3$ and Li$_{17}$Sn$_4$ is not straightforward as it includes both In(Sn) as well as Li atoms. Therefore, expressing them in form of LiIn$_x$ or LiSn$_y$ polyhedra do not provide an accurate picture.
Table S6. Coordination environment of selected Li-Sn and Li-In alloys compositions and corresponding Li-Sn and Li-In bond distances (in Å).

| Composition   | Polyhedra | Li-In(Sn) distances | Li-Sn distances |
|---------------|-----------|---------------------|----------------|
| Li₂Sn₅        | LiSn₁₀    | 2.990–3.107         | 2.990–3.107    |
| LiSn          | LiSn₈     | Poly-I: 2.994–3.103  | Poly-I: 2.994–3.103 |
| LiIn₂ (or Li₉In) | LiIn₆   | Poly-II: 3.045–3.077 | Poly-II: 3.045–3.077 |
| LiIn          | LiIn₄     | 2.875               | 2.994          |

Stripping and plating experiments

Figure S16. Stack impedance before and after stripping and plating experiments of Li-alloys. Nyquist plots of symmetrical solid-state cells assembled with (a) Li₀.₅In, (b) LiIn, (c) Li₁₃In₃, (d) Li₂Sn₅, (e) LiSn and (f) Li₁₇Sn₄ before (blue) and after (orange) the stripping and plating experiment at various currents at a stack pressure of 45 MPa.
Table S7. Stack impedance ($R_{SE} + R_{int}$) of symmetrical A$|$Li$_6$PS$_5$Cl$|$A (A = Li$_{0.5}$In, LiIn, Li$_{13}$In$_3$, Li$_2$Sn$_5$, LiSn or Li$_{17}$Sn$_4$) solid-state cells before and after stripping and plating at various currents and a stack pressure of 45 MPa.

|                  | Before - stripping/plating [Ohm] | After - stripping/plating [Ohm] |
|------------------|----------------------------------|----------------------------------|
| Li$_{0.5}$In     | 39                               | 53                               |
| LiIn             | 43                               | 70                               |
| Li$_{13}$In$_3$  | 39                               | 41                               |
| Li$_2$Sn$_5$     | 40                               | 48                               |
| LiSn             | 39                               | 46                               |
| Li$_{17}$Sn$_4$  | 40                               | 50                               |

Figure S17. Stripping and plating performance of metallic lithium in a Li$|$Li$_6$PS$_5$Cl$|$Li stack. (a) Stack impedance before and after the stripping/plating experiment. (b) Galvanostatic cycling of the cell - assembled at 45 MPa for 2 seconds - at a constant stack pressure of 5 MPa at increasing currents of 100, 200, 400 µA for a capacity of 0.1, 0.2 and 0.4 mA h, respectively.

Figure S17 highlights the repeated stripping and plating of a symmetric Li$|$Li$_6$PS$_5$Cl$|$Li cell at various currents. Unlike the cells cycled with alloy electrodes, the cell fails at a current of 400 µA due to morphological instabilities at the interface (void formation). Due to the low yield strength of metallic lithium the symmetrical cell cannot be assembled at a fabrication pressure of 150 MPa or cycled under a constant stack pressure of 45 MPa similar to the alloy cells (Figure 5). The low stack and fabrication pressure results in a poorer interfacial contact and a higher overpotential compared to the Li$_{0.5}$In cell (Figure 5a). A more detail description on the failure mechanism of the symmetric Li$|$Li$_6$PS$_5$Cl$|$Li cell can be found in a previous publication.\textsuperscript{21}
Long-term stripping and plating experiments

Figure S18. Long-term stripping and plating performance. Repeated Li stripping and plating of symmetrical cells at a stack pressure of 45 MPa and a constant current 1 mA cm\(^{-2}\) and a capacity of 1 mA h cm\(^{-2}\). a) Recorded potential profile of the repeated stripping and plating for the symmetrical Li\(_{0.5}\)In|Li\(_6\)PS\(_5\)Cl|Li\(_{0.5}\)In cell and b) the corresponding Nyquist profiles recorded before and after the stripping experiment. c) Recorded potential profile of the repeated stripping and plating for the symmetrical LiIn|Li\(_6\)PS\(_5\)Cl|LiIn cell and d) the corresponding Nyquist profiles recorded before and after the stripping experiment.

Figure S19. Recorded potential profile of the repeated stripping and plating for the symmetrical a) Li\(_{13}\)In\(_3\)|Li\(_6\)PS\(_5\)Cl|Li\(_{13}\)In\(_3\) and b) Li\(_{17}\)Sn\(_4\)|Li\(_6\)PS\(_5\)Cl|Li\(_{17}\)Sn\(_4\) cell at a stack pressure of 45 MPa, a current of 1 mA cm\(^{-2}\) and a capacity of 1 mA h cm\(^{-2}\).
References

1. Hänsel, C.; Kumar, P. V.; Kundu, D., Stack Pressure Effect in Li3PS4 and Na3PS4 Based Alkali Metal Solid-State Cells: The Dramatic Implication of Interlayer Growth. Chem. Mater. 2020, 32, 10501-10510.

2. Zintl, E. B., Ueber die Valenzelektronenregel und die Atomradien unedler Metalle in Legierungen. 10. Mitteilung ueber Metalle und Legierungen. Z. Phys. Chem. B-Chem. E 1933, 20, 245-271.

3. Zintl, E.; Brauer, G., Ueber die Valenzelektronenregel und die Atomradien unedler Metalle in Legierungen. 10. Mitteilung ueber Metalle und Legierungen. Z. Phys. Chem. B-Chem. E 1933, 20, 245-271.

4. Swanson, H. E.; Fuyat, R. K.; Ugrinic, G. M., Standard X-ray Diffraction Powder Patterns. NBS Circular 539: 1954; Vol. 3.

5. Hansen, D. A.; Chang, L. J., Crystal Structure of Li2Sn5. Acta. Cryst. 1969, B25, 2392.

6. Müller, W.; Schäfer, H., Die Kristallstruktur der Phase LiSn. Z Naturforsch. B 1973, 28, 246-248.

7. Pilloni, M.; Ennas, G.; Cabras, V.; Denotti, V.; Kumar, V. B.; Musinu, A.; Porat, Z.; Scano, A.; Gedanken, A., Thermal and structural characterization of ultrasonicated BiSn alloy in the eutectic composition. J. Therm. Anal. Calorim. 2015, 120, 1543-1551.

8. Nadler, M. R.; Kempier, C. P., Crystallographic Data 186. Lithium. Anal. Chem. 1959, 31, 2109-2109.

9. Stöhr, J.; Müller, W.; Schäfer, H., Darstellung und Kristallstruktur von Li2In und Li13In3 / Preparation and Crystal Structure of Li2In and Li13In3. Z. Naturforsch. B 1978, 33, 1434-1437.

10. Nadler, M. R.; Kempier, C. P., Crystallographic Data 186. Lithium. Anal. Chem. 1959, 31, 2109-2109.

11. Lupu, C.; Mao, J.-G.; Rabalais, J. W.; Guloy, A. M.; Richardson, J. W., X-ray and Neutron Diffraction Studies on “Li4.4Sn”. Inorg. Chem. 2003, 42, 3765-3771.

12. Zagorac, D.; Müller, H.; Ruehl, S.; Zagorac, J.; Rehmec, S., Recent developments in the Inorganic Crystal Structure Database: theoretical crystal structure data and related features. J. Applied Crystallography 2019, 52, 918-925.

13. Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A., Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. APL Mater. 2013, 1, 011002.

14. Mayo, M.; Morris, A. J., Structure Prediction of Li–Sn and Li–Sb Intermetallics for Lithium-Ion Batteries Anodes. Chem. Mater. 2017, 29, 5787-5795.

15. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865-3868.

16. Kresse, G.; Hafner, J., Ab initio molecular dynamics for liquid metals. Phys. Rev. B 1993, 47, 558-561.

17. Kresse, G.; Furthmüller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comp. Mater. Sci 1996, 6, 15-50.

18. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 1996, 54, 11169-11186.

19. Kresse, G.; Joubert, D., From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 1999, 59, 1758-1775.

20. Sheppard, D.; Terrell, R.; Henkelman, G., Optimization methods for finding minimum energy paths. J. Chem. Phys. 2008, 128, 134106.

21. Hänsel, C.; Kundu, D., The Stack Pressure Dilemma in Sulfide Electrolyte Based Li Metal Solid-State Batteries: A Case Study with Li6PS5Cl. Adv. Mater. Interfaces 2021, 2100206.