Supporting Information –

Chemo-mechanical expansion
of lithium electrode materials - On the route to mechanically optimized solid-state batteries

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OCV vs. pressure curves of InLi \| SE \| LTO and LCO \| SE \| InLi

**Supplementary Figure S1:** a) The open cell voltage of an InLi \| LGPS \| LTO/LGPS after 6 and 8 hours charge at 0.1 C (90 µA) as a function of the ramped up stress and corresponding linear regression. As expected, no change in the slope is observed. b) The open cell voltages of an InLi \| LGPS \| LCO/LGPS cell upon pressure for different states of charge x(Li). For a material like LCO, the reaction volume is related to the lithiation state.

**Table S1:** Slope and reaction volume of InLi obtained from linear regression of Figure S1a.

<table>
<thead>
<tr>
<th>InLi</th>
<th>m / V (\times 10^5) Pa</th>
<th>m / mV MPa</th>
<th>(-\frac{\partial E}{\partial p}) (\text{cm}^3) \text{mol}^{-1}</th>
<th>(-\frac{V_m(\text{Li}<em>{\text{InLi}})}{V</em>{\text{InLi}}}) (\text{cm}^3) \text{mol}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.22 E-5</td>
<td>0.122</td>
<td>11.81</td>
<td>11.81</td>
</tr>
</tbody>
</table>
Table S2: Slopes and partial molar volume of Li in Li_xCoO_2 at different SOCs. x(Li) calculated using the crystallographic reaction volume of Indium and the value obtained from the above OCV experiment in Figure S1a.

<table>
<thead>
<tr>
<th>x in Li_xCoO_2</th>
<th>m / 10^5 Pa</th>
<th>Δm / 10^5 Pa</th>
<th>-F(∂E/∂p) / cm^3 mol^-1</th>
<th>ΔV_p (Li_xCoO_2) from OCV</th>
<th>V_B (Li_xCoO_2) from OCV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>2.27 E-6</td>
<td>0.58 E-6</td>
<td>2.19</td>
<td>+9.62</td>
<td>+5.70</td>
</tr>
<tr>
<td>0.75</td>
<td>3.40 E-6</td>
<td>0.58 E-6</td>
<td>3.28</td>
<td>+8.53</td>
<td>+4.61</td>
</tr>
<tr>
<td>0.80</td>
<td>10.17 E-6</td>
<td>1.40 E-6</td>
<td>9.84</td>
<td>+1.97</td>
<td>-1.95</td>
</tr>
<tr>
<td>0.86</td>
<td>8.56 E-6</td>
<td>0.71 E-6</td>
<td>8.26</td>
<td>+3.55</td>
<td>-0.37</td>
</tr>
<tr>
<td>0.94</td>
<td>8.43E-6</td>
<td>1.11 E-6</td>
<td>8.13</td>
<td>+3.68</td>
<td>-0.24</td>
</tr>
</tbody>
</table>

Supplementary Figure S2: Experimental setup of the operando stress measurement of battery cells. The previously described cell casing is implemented in an outer frame which holds a force sensor. By allowing one of the steel pistons to move, the uniaxial strain of the cell can be monitored during electrochemical experiments.

Pressure estimation for SSBs
Supplementary Figure S3: a) Cross section through a simplified (cylindrical) 3D model of a single electrode cell for estimation of the hydrostatic pressure. The cell has the dimensions 1000 µm (diameter) x 500 µm (height) and the cathode layer has a thickness of 50 µm. In the cathode layer, the volume fraction of the CAM is similar to the SE fraction. The cell is fully confined, except for the top side on which the stress component $\sigma_{11}$ is measured. After homogenization of the cathode (b), the final homogenized model assumes that the cell is composed of a single material (c) with effective elastic moduli and experiences an effective eigenstrain.

I. Approximation via linear strain

In a very simple first order approach, we assume that the SSB is composed of a single material, which in this case has the mechanical properties of the herein employed $\beta$-Li$_3$PS$_4$ glass ceramic. We further assume that due to the sufficient elasticity of the solid electrolyte it behaves like a fluid in a system, which is constrained on all sides. We can now derive the pressure change inside the SSB by using the isothermal compressibility $\kappa_T$ which is composed of Poisson’s ratio $\nu$ and Young’s modulus $E$. For simplicity reasons, we handle the ASSB as a single component system, which is constrained on all sides.

$$\kappa_T = \frac{1}{K} = \frac{3(1-2\nu)}{E} \quad (S1)$$

By integration of the isothermal compressibility, we obtain Hencky’s logarithmic strain, with $V_0$ being the initial and $V$ the current volume which is increased or reduced by $\Delta V$. The volumetric strain $\varepsilon_{vol} = \Delta V/V_0$ expresses the relative change in volume.

$$\int_{V_0}^{V} \frac{dV}{V} = - \int_{P_0}^{P} \kappa_T \, dp \quad (S2)$$

$$\Delta p = -\ln \left( \frac{V}{V_0} \right) \cdot \frac{1}{\kappa_T} \quad (S3)$$

$$\Delta p = -\ln \left( 1 + \frac{\Delta V}{V_0} \right) \cdot \frac{1}{\kappa_T} = -\ln(1 + \varepsilon_{vol}) \cdot \frac{1}{\kappa_T} \quad (S4)$$

By linearization of the logarithmic strain, we obtain an approximation for the small
strain region, \textit{i.e.} the linear elastic strain. This is used to estimate the potential maximum strain that is developed when operating the battery.

\[
\Delta p \approx -\frac{\Delta V}{V_0 \kappa_T} = -\epsilon_{vol} \frac{1}{\kappa_T} \quad \text{or} \quad \Delta p = -\epsilon_{vol} K. \quad (S5)
\]

We use Equation (S5) to estimate the maximum strain the given cell configuration would experience based on the volumetric changes of the electrode materials during delithiation. All stress tensor components are equal because the system is constrained on all sides:

\[
\sigma_{11} = \sigma_{22} = \sigma_{33} = -\frac{E}{(1-2\nu)} \epsilon_0 = -3K \epsilon_0. \quad (S6)
\]

Thus, the hydrostatic pressure is given by

\[
p = -\frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33}) = -K \epsilon_{vol} \quad \text{with} \quad \epsilon_{vol} = -3 \epsilon_0. \quad (S7)
\]

Table S3 sums up the maximum strain resulting from the volume change of the electrode materials during delithiation.

\textbf{Table S3: Theoretical estimation of the linear strain and stress (pressure) for the cell configurations shown in Figure S3, respectively, assuming a completely constrained cell casing having the dimension of a cylinder with } r = 0.5 \text{ cm and } h = 500 \mu\text{m.}

<table>
<thead>
<tr>
<th>CAM</th>
<th>m(CAM) / g</th>
<th>( \varrho / \text{g cm}^3 )</th>
<th>( \Delta V_{\text{cryst}}(\text{charge}) / % )</th>
<th>( p / \text{MPa} )</th>
<th>( p / \text{bar} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO(_2)</td>
<td>0.0084</td>
<td>4.75</td>
<td>+1.4</td>
<td>+14.39</td>
<td>+143.9</td>
</tr>
<tr>
<td>LiNi(<em>{0.8})Co(</em>{0.1})Mn(_{0.1})O(_2)</td>
<td>0.0084</td>
<td>4.64</td>
<td>-6.0</td>
<td>-65.97</td>
<td>-659.7</td>
</tr>
</tbody>
</table>

\textbf{II. Reuss approximation}

In the experimental setup, only the stress component \( \sigma_{11} \) in axial direction has been measured directly. In order to obtain the full hydrostatic pressure \( p = -\frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33}) \), the lateral components \( \sigma_{22} \) and \( \sigma_{33} \) were computed using a Reuss approximation for the effective material properties of a cell.\(^1\) The cell dimensions used for this model are shown in Figure S3. As in the tested cells, the volume ratio of CAM to SE in the cathode layer (50 \( \mu \text{m} \)) is 1:1. The Young’s modulus for the SE, \( \beta\text{-LiPS}_4 \), is \( E_\text{SE} = 28.9 \) GPa. For LCO, \( E_\text{CAM} \) is 191 GPa and for NCM 198 GPa, respectively (see Table 1). LCO undergoes a volume expansion of approximately 1.4% during delithiation, NCM-811 experiences contraction of roughly 6% when charging to 4.3 V vs. Li.\(^2\)
In the first step, we replace the two-phase CAM/SE cathode by an effective material using a 1D Reuss homogenization within a unit cell (volume $V = 1$, see Figure S3a) consisting of the volume fractions $V_{SE}$ and $V_{CAM}$. We idealize the CAM phase and the SE phase as two linear elastic springs in series with Young’s moduli $E_{SE}$ and $E_{CAM}$, see Figure S3b. The lengths of the two springs are proportional to the corresponding volume fractions $V_{SE}$ and $V_{CAM}$ so that the effective Young’s modulus can be computed directly by Reuss approximation as

$$E_{\text{eff Cathode}}^{\text{CAM}} = \left( \frac{V_{SE}}{E_{SE}} + \frac{V_{CAM}}{E_{CAM}} \right)^{-1}.$$  \hspace{1cm} (S8)

Moreover, the CAM-phase includes a volumetric eigenstrain $\varepsilon_{0,\text{CAM}}$ due to delithiation. Since the stress in the homogenized material and the stress in both springs are equal due to equilibrium condition, the effective eigenstrain yields

$$\varepsilon_{0,\text{Cathode}}^{\text{CAM}} = \varepsilon_{0,\text{CAM}} V_{\text{CAM}}.$$  \hspace{1cm} (S9)

Inserting the parameters, we get $E_{\text{eff Cathode}}^{\text{CAM}} = 50.4$ GPa. As depicted in Figure A1, we repeat this homogenization on cell level in which $V_{\text{Cathode}}/V_{\text{Cell}} = 0.1$ and obtain $E_{\text{eff Cell}} = 30.2$ GPa. The cell elastic modulus is the same for both CAMs due to their small volumetric fraction. The effective bulk modulus $K_{\text{eff Cell}}$ is 21.8 GPa whereby we assume that $\nu_{\text{eff}} = \nu(\beta-\text{Li}_{3}\text{PS}_4) = 0.27$, because the differences in Poisson’s ratios are negligible in this case. The components of the effective stress tensor for a cell with lateral confinement are given by

$$\sigma_{11} = 3K_{\text{eff Cell}} \left( \frac{1-\nu_{\text{eff}}}{1+\nu_{\text{eff}}} \varepsilon_{11} - \varepsilon_{0} \right)$$  \hspace{1cm} (S10)

and

$$\sigma_{22} = \sigma_{33} = 3K_{\text{eff Cell}} \left( \frac{\nu_{\text{eff}}}{1+\nu_{\text{eff}}} \varepsilon_{11} - \varepsilon_{0} \right).$$  \hspace{1cm} (S11)

Since $\sigma_{11}$ is measured, we can compute the strain component $\varepsilon_{11}$ from Equation (S10) and thus the stress components $\sigma_{22} = \sigma_{33}$ in Equation (S11). Finally, this allows for the calculation of the hydrostatic pressure $p = -\frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$ inside the
battery cell which is summarized in Table S4.

**Table S4:** Three-dimensional strain tensors and resulting hydrostatic pressure after Reuss ($p_R$) inside of the SSB based on the volume change of LiCoO$_2$ and NCM-811 and the linear approximation ($p_L$).

<table>
<thead>
<tr>
<th>Cathode</th>
<th>$\sigma$ / MPa</th>
<th>$p_R$ / MPa</th>
<th>$p_R$ / bar</th>
<th>$p_L$ / bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO$_2$</td>
<td>$\sigma_{11} = -0.06$ exp.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\sigma_{22} = -14.94$ calc.</td>
<td>$+9.98$</td>
<td>$+99.8$</td>
<td>$+143.9$</td>
</tr>
<tr>
<td></td>
<td>$\sigma_{33} = -14.94$ calc.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCM-811</td>
<td>$\sigma_{11} = +0.05$ exp.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\sigma_{22} = -63.96$ calc.</td>
<td>$-42.66$</td>
<td>$-426.6$</td>
<td>$-655.6$</td>
</tr>
<tr>
<td></td>
<td>$\sigma_{33} = -63.96$ calc.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Supplementary Figure S5:** Uncorrected stress profile (orange) of a cell composed of InLi $|$ SE $|$ NCM-811/SE and corresponding cycling data (blue). The grey curve represents the mechanical drift of an empty cell casing due to the plastic insulators.
Supplementary Figure S6: Galvanostatically induced change of the net stress for solid-state batteries in the configurations a) LTO/SE | SE | NCA/SE and b) InLi | SE | NCM-811/SE.

NCA shows a negative compressive nominal stress during the charging process, which is in the same order of magnitude of NCM-811 and matches the crystallographic data. The second cell undergoes a volume expansion during charge. An increase in compressive cell stress is observed of up to 10 bar. The negative partial molar volume of NCM-811 has a much smaller effect than the positive partial molar volume of indium. However, compared to lithium metal, the magnitude of the developed stress is lower, which is in good correlation with their respective different partial molar volumes.
**Supplementary Figure S7:** Scanning electron images of the LTO/β-Li$_3$PS$_4$|β-Li$_3$PS$_4$|55:45 NCM-811/LCO LTO/SE | SE | LCO/SE cell after cycling. EDX scans support the assignment of the cathode materials LCO and NCM. The magnification of the contact area between the CAMs and the SE shows an intimate connection between the materials after cycling.

**Supplementary Figure S8:** Scanning electron micrographs of the cathode of a InLi | β-Li$_3$PS$_4$| NCM-811 / β-Li$_3$PS$_4$ battery after cycling. The NCM particles contract during delithiation and lose contact with the SE. Reprinted with permission from [ref]. Copyright 2017 American Chemical Society.
References