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Supporting Information –

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

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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 μ A) 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.

InLi	<i>m /</i> V 10⁵ Pa	$m / \frac{mV}{MPa}$	$-F\left(\frac{\partial E}{\partial p}\right)_{T}/\frac{cm^{3}}{mol}$	$-\overline{V'}_{m}\left(\text{Li},\frac{\text{InLi}}{\text{In}}\right)/\frac{\text{cm}^{3}}{\text{mol}}$
	1.22 E-5	0.122	11.81	11.81

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.

<i>x</i> in Li _x CoO ₂	m /	$\Delta m / \frac{V}{10^5 \text{ Pa}}$	$-F\left(\frac{\partial E}{\partial p}\right)_{\rm T}/\frac{{\rm cm}^3}{{\rm mol}}$	$\bar{V}_{\rm m}({\rm Li}_x{\rm CoO}_2)$	$\bar{V}_{\rm m}({\rm Li}_{\rm x}{\rm CoO}_2)$
	$\frac{m}{10^5}$ Pa			from OCV	from $\overline{V'}_{m}$ (InLi) cryst.
0.65	2.27 E-6	0.58 E-6	2.19	+9.62	+5.70
0.75	3.40 E-6	0.58 E-6	3.28	+8.53	+4.61
0.80	10.17 E-6	1.40 E-6	9.84	+1.97	-1.95
0.86	8.56 E-6	0.71 E-6	8.26	+3.55	-0.37
0.94	8.43E-6	1.11 E-6	8.13	+3.68	-0.24



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 μ m (diameter) x 500 μ m (height) and the cathode layer has a thickness of 50 μ m. 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 σ_{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 β -Li₃PS₄ 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 \varkappa_{T} which is composed of Poisson's ratio v and Young's modulus E. For simplicity reasons, we handle the ASSB as a single component system, which is constrained on all sides.

$$\kappa_{\rm T} = \frac{1}{\kappa} = \frac{3(1-2\nu)}{E}$$
(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 ΔV . The volumetric strain $\varepsilon_{vol} = \Delta V/V_0$ expresses the relative change in volume.

$$\int_{V_0}^{V} \frac{dV}{V} = -\int_{p_0}^{p} \kappa_{\mathrm{T}} \, dp \tag{S2}$$

$$\Delta p = -\ln\left(\frac{v}{v_0}\right) \cdot \frac{1}{\kappa_{\rm T}} \tag{S3}$$

$$\Delta p = -ln\left(1 + \frac{\Delta V}{V_0}\right)\frac{1}{\kappa_{\rm T}} = -ln(1 + \varepsilon_{\rm vol})\frac{1}{\kappa_{\rm T}}$$
(S4)

By linearization of the logarithmic strain, we obtain an approximation for the small

strain region, *i.e.* the linear elastic strain. This is used to estimate the potential maximum strain that is developed when operating the battery.

$$\Delta p \approx -\frac{\Delta V}{V_0} \frac{1}{\kappa_{\rm T}} = -\varepsilon_{\rm vol} \frac{1}{\kappa_{\rm T}} \quad \text{or} \quad \Delta p = -\varepsilon_{\rm vol} K.$$
(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:

$$\sigma_{11} = \sigma_{22} = \sigma_{33} = -\frac{E}{(1-2v)}\varepsilon_0 = -3K\varepsilon_0.$$
 (S6)

Thus, the hydrostatic pressure is given by

 $p = -\frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33}) = -K \varepsilon_{\text{vol}} \quad \text{with} \quad \varepsilon_{\text{vol}} = -3\varepsilon_0.$ (S7)

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

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 cm and $h = 500 \,\mu$ m.

CAM	<i>m</i> (CAM) / g	<i>Q</i> / g cm ⁻³	$\Delta V_{ m cryst}(m charge)$ / %	p / MPa	<i>p</i> / bar
LiCoO ₂	0.0084	4.75	+1.4	+14.39	+143.9
LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂	0.0084	4.64	-6.0	-65.97	-659.7

II. Reuss approximation

In the experimental setup, only the stress component σ_{11} in axial direction has been measured directly. In order to obtain the full hydrostatic pressure $p = -\frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{23})$

 σ_{33}), the lateral components σ_{22} and σ_{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 μ m) is 1:1. The Young's modulus for the SE, β -Li₃PS₄, is $E_{SE} = 28.9$ GPa. For LCO, E_{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



Supplementary Figure S4: a) Unit cell of the Cathode with CAM phase and SE phase. b) 1D. Idealization by two springs in serial. c) Homogeneous material of the cathode with effective Young's modulus and effective eigenstrain.

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

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

Moreover, the CAM-phase includes a volumetric eigenstrain $\varepsilon_{0,CAM}$ 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

$$\varepsilon_{0\,\text{Cathode}}^{\text{eff}} = \varepsilon_{0\,\text{CAM}} V_{\text{CAM}} \,. \tag{S9}$$

Inserting the parameters, we get $E_{Cathode}^{eff} = 50.4$ GPa. As depicted in Figure A1, we repeat this homogenization on cell level in which $V_{Cathode}/V_{Cell} = 0.1$ and obtain $E_{Cell}^{eff} = 30.2$ GPa. The cell elastic modulus is the same for both CAMs due to their small volumetric fraction. The effective bulk modulus K_{Cell}^{eff} is 21.8 GPa whereby we assume that v^{eff} is $v(\beta-Li_3PS_4) = 0.27$, 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

$$\sigma_{11} = 3K_{\text{Cell}}^{\text{eff}} \left(\frac{1 - v^{\text{eff}}}{1 + v^{\text{eff}}} \varepsilon_{11} - \varepsilon_0 \right)$$
(S10)

and

$$\sigma_{22} = \sigma_{33} = 3K_{\text{Cell}}^{\text{eff}} \left(\frac{v^{\text{eff}}}{1 + v^{\text{eff}}} \, \varepsilon_{11} - \varepsilon_0 \right). \tag{S11}$$

Since σ_{11} is measured, we can compute the strain component ε_{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 LiCoO₂ and NCM-811 and the linear approximation (p_L) .

Cathode	σ / MPa		$p_{\rm R}$ / MPa	$p_{\rm R}$ / bar	$p_{ m L}$ / bar	
LiCoO ₂	σ_{11} =	-0.06	exp.			
	$\sigma_{22} =$	-14.94	calc.	+9.98	+99.8	+143.9
	$\sigma_{33} =$	-14.94	calc.			
NCM-811	$\sigma_{11} =$	+0.05	exp.			
	$\sigma_{22} =$	-63.96	calc.	-42.66	-426.6	-655.6
	$\sigma_{33} =$	-63.96	calc.			



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-801505/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 -Li₃PS₄ / β -Li₃PS₄55:45 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 -Li₃PS₄ | NCM-811 | β -Li₃PS₄ battery after cycling. The NCM particles contract during delithiation and lose contact with the SE. Reprinted with permission from [ref³]. Copyright 2017 American Chemical Society.

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