Supporting Information – (Electro)chemical Expansion during Cycling: Monitoring the Pressure Changes in Operating Solid-State Lithium Batteries

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Index

1. Electrochemical impedance spectroscopy (EIS) and long cycle stability
2. \textit{In situ} XRD
3. Estimating volume expansion in the electrodes
4. Additional information extracted from X-ray tomography
5. Dilatometer test
6. Baseline of the \textit{in situ} measured pressure change
Electrochemical impedance spectroscopy (EIS) and long cycle stability

Supplementary Figure S1: Electrochemical impedance spectroscopy (EIS) measurements of a SSB (In / LGPS / LNTO-LCO). The decrease in the resistance during the charge process indicates the consolidation of the SE.

The measurements of EIS for the SSBs were carried out in our standard SSB setup, as described in a previous paper. The red data is the EIS measured directly after the assembly of the cell. Only a spike starting from 21 Ohm is observed. The yellow data represent the EIS result measured after a short galvanostatic charging step (0.1 C) of the cell for 6 min (1 % charge). A shift of Re(Z) to 19 Ohm is observed. The blue data were measured after the full charge of the cell to 3.6 V vs. In/InLi. Two semicircles corresponding to LNTO-LCO/LGPS and In/LGPS interfaces are observed, corresponding well with previous results. A further shift of Re(Z) at the zero-crossing to 16 Ohm is shown. Based on previous results, we attribute the resistance in the high frequency region to the contribution of bulk solid electrolyte (SE). The decrease in the resistance with the charge process indicates the microstructural consolidation (densification) of the SE.
Supplementary Figure S2: EIS evolution of a model SSB during 1st charge, using coated LiCoO$_2$ as active material and Indium as anode, with LGPS as solid electrolyte. The galvanostatic charge was carried out at 0.1C and EIS was carried out after one-hour charge followed by a rest of 30 min rest. The two semicircles were observed only when the cell potential reached the plateau of LiCoO$_2$, i.e. 3.3 V vs. In/InLi. Even though, the impedance evolves with the increasing potential, the total value was maintained below 100 Ohm in the whole charge process. The small interfacial resistance ensures good electrochemical performance of the SSB.

The small interfacial resistance ensures a stable electrochemical performance of the SSB using coated LiCoO$_2$ as active material, as shown in Figure S2. After 100 cycles at 0.1 C, the SSB could maintain 80% of its original capacity, as shown in Figure S3. More details concerning the electrochemical characterization of the SSB are shown in another paper of our group$^1$. 

Supplementary Figure S3: Long cycle performance of a model SSB used in the study. 80% of its initial capacity could be maintained after 100 cycles at 0.1 C and the Coulombic efficiency was maintained above 99% from the 2nd cycle on.

In situ X-ray diffraction

In situ X-ray diffraction was carried out in a home-made sample holder. The SSB was fabricated and charged in the same manner as for the tomography analysis. The XRD data were recorded every 1 h and repeated during the continuous galvanostatic charge using an Empyrean diffractometer (0/0 geometry, with a PIXcel3D area detector (PANalytical)).
Supplementary Figure S4: In situ XRD measurements of the In/LGPS/LNTO-LCO SSB. The SSB was charged with a current density of 19.1 µA/cm², corresponding to a C-rate of C/33. The charging curve is shown in the insertion. Upper: the complete diffraction patterns recorded at different state of charge. Lower left: evolution of the (003) reflections with decreasing x in LiₓCoO₂. Lower right: evolution of the
(104) reflections with decreasing \( x \) in \( \text{Li}_x\text{CoO}_2 \) showing the increasing unit cell parameter.

The in situ XRD results clearly demonstrate the first-order phase transition of \( \text{LiCoO}_2 \) during the de-intercalation. The gradual splitting of the (003) reflection and the steady decrease of the (003) Bragg angle indicate an increase in \( c \)-axis length, as already reported by Dahn. et al.\(^3\) Complementary is the change observed for the (104) reflections around 45°. The appearance of a new reflection at lower Bragg angle is a clear indication of the first-order transition with a new phase with longer \( c \)-axis. Clearly, the volume expansion of \( \text{LiCoO}_2 \) upon delithiation contributes to the pressure changes observed.

**Estimating volume expansion in the electrodes**

1) Expansion of the Indium metal anode when lithiated: In the first charge, a capacity of 1.53 mAh was achieved. Thus the corresponding molar amount \( n(\text{Li}^+) \) of transferred lithium is:

\[
 n(\text{Li}^+) = \frac{Q}{x F} = \frac{(1.53 \times 10^{-3} \text{Ah} \cdot 3600 \text{s/h})/96485 \text{C/mol}}{5.7 \times 10^{-5} \text{mol}}
\]

\( x \): charge number of transferred ion; For \( \text{Li}^+ \), \( x \) is 1

\( Q \): total transferred charge

\( F \): Faraday constant: 96485 As/mol

In the case studied here, the anode was always kept within the In-rich region (89 mg In foil used as anode, which equals to 774.5 \( \mu \)mol, corresponding to a nominal composition of the lithiated In anode of InLi\(_{0.0736}\)).

The constant potential of the two-phase anode is maintained throughout the entire battery cycling, as In is in equilibrium with indium-rich InLi\(_{0.87}\), i.e. 1 mol indium requires 0.87 mol lithium to form cubic InLi\(_{0.87}\). Thus, with \( 5.7 \times 10^{-5} \) mol \( \text{Li}^+ \) transferred, the formed InLi\(_{0.87}\) is calculated:

\[
 n_{\text{InLi}_{0.87}} = (5.7 \times 10^{-5} \text{mol}) \div 0.87 = 65.5 \mu \text{mol}
\]

Thus, in the charged state about 8\% of the In metal is lithiated.

As depicted in Figure 2, the reaction from indium to InLi\(_{0.87}\) is accompanied by the expansion of the indium tetragonal unit cell in all directions. The resulting volume
expansion driven by the solid-state reaction is partly responsible for the pressure change. As depicted in Figure 2, the transformation from In \((V_m = 15.71 \text{ cm}^3/\text{mol})\) to InLi\(_{0.87}\) \((V_m = 23.597 \text{ cm}^3/\text{mol for the stoichiometric phase})\) is accompanied by a volume expansion of 105.6 %. If we assume polycrystalline character of the formed InLi\(_{0.87}\) with fully randomly oriented crystallites, we can assume that one third of the total volume expansion contributes to the volume expansion in the vertical direction, which is 35.2 %.

Based on this data, a theoretical estimation of the change in thickness during the first charge process is carried out as follow: the volume change corresponding to the formation of 65.5 \(\mu\text{mol}\) InLi\(_{0.87}\) is:

\[
\Delta V_{\text{InLi}_{0.87}} = (23.597 - 15.71) \text{ cm}^3/\text{mol} \times 65.5 \times 10^{-6} \text{mol} = 516.6 \times 10^{-6} \text{ cm}^3
\]

We assume only one third of the total volume expansion contributes to the vertical direction, i.e. 172 \(\times 10^{-6}\) cm\(^3\). Considering the cell area of 1.103 cm\(^2\), the vertical displacement due to the formation of InLi is estimated as 1.56 \(\mu\)m.

2) Expansion of other anodes when lithiated: If Li metal were used instead of In, we estimate the change in thickness of a Li metal anode as 2.2 \(\mu\)m (based on the molar volume of 12.97 cm\(^3\)/mol Li). In the present paper, we use In/InLi as anode, as its half-cell potential is high enough to keep LGPS stable, i.e. to avoid reduction and SEI formation. Anode materials such as \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) and graphite show quite different volume expansion. A near zero-cell volume change is estimated for lithiation of \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) forming \(\text{Li}_7\text{Ti}_5\text{O}_{12}\) (only \(\sim 0.2\%\). When Li intercalates into graphite, a comparably large expansion by 10 % is generally observed upon formation of \(C_6\text{Li}\). And of course, the deposition of Li on a Li metal anode increases the anode thickness linearly with the charge flow. Consequently, external confinement is required to compensate the volume expansion from electrode materials in SSBs.
3) Expansion of LiCoO$_2$ when lithiated: On the cathode side, 14 mg LiCoO$_2$ as active materials were cycled in the SSB, which corresponds to a volume of $2.76 \times 10^{-3}$ cm$^3$ (based on the density of LiCoO$_2$ of 5.07 g/cm$^3$). Considering 2 % volume expansion after charge, the expansion in all direction is calculated to be $5.52 \times 10^{-5}$ cm$^3$ and one third of which is estimated to be the volume expansion in vertical direction, namely $1.84 \times 10^{-5}$ cm$^3$, which equals to an increase in thickness of 0.163 µm.

While it is possible to estimate volume and thickness changes that occur during cycling it is not possible to fully gauge the expected pressure build up. The composite cathode and the solid electrolyte separator are polycrystalline with a certain microstructure and porosity. Therefore, the volume expansion leads to a concurrent consolidation of the solids and a lower measured pressure increase than expected if no porosity were present. Thus, all estimates of pressure build-up are theoretical upper limits.

**Additional information extracted from X-ray tomography**

The X-ray tomography results obtained for Figure 6 a) can be used to gain further information about the properties of the bulk SE using an intensity threshold filter for the reconstructed 3D-images: we estimate a porosity in the SE (ratio of void space volume filled with gas phase and total SE volume) of 5.45% for the pristine pellet and a porosity of 2.58% for the charged pellet. However, it is to be noted that due to the spatial resolution of the method applied, smallest pores below 6.25 µm size are not accounted for in those porosity values.

Moreover, volumes for cathode, SE and anode of both pellets are calculated from the voxels obtained as follows:

**Pristine pellet** → cathode: 0.94 mm$^3$; SE: 21.32 mm$^3$; anode: 1.89 mm$^3$

**Charged pellet** → cathode: 0.94 mm$^3$; SE: 24.85 mm$^3$; anode: 5.93 mm$^3$
Supplementary Figure S5: Visualization of the porosity analysis via intensity threshold analysis for the ex situ transmission X-ray tomography pristine SSB pellet and the charged SSB pellet as presented for Fig 4 a) in the main text of the manuscript: region of interest showing only the solid electrolyte (light gray color) and void space filled with gas phase (dark gray color). Porosity decreases approximately by 50% from the pristine pellet to the charged pellet, whereas pores below the spatial resolution of 6.25 μm are not accounted for.
Dilatometer test

Supplementary Figure S6: Results of the dilatometer test of a non-pressurized SSB under galvanostatic cycling with a current density of 28 µA/cm² between 2.0 – 3.6 V vs. In/LiIn. The height-change curve (red) follows well the charge-discharge curve (blue) from the third cycle on. The highly asymmetric peak and inclined baseline of the height-change curve in the first of a few cycles indicate the consolidation of SE due to the volume expansion of electrodes upon cycling. As shown at the end of the red curve, no height change could be observed once the galvanostatic cycling stops, which excludes the relaxation of setup components leading to the inclined baseline.

Supplementary Figure S6 shows the in situ dilatometer test of a non-pressurized SSB using metal (indium) anode. As the results shown in Figure 1, the height-charge curve in this case follows well with the charge-discharge curve of the SSB, even though the electrochemical performance of the non-pressurized SSB is much worse than of the pressurized one. An inclined baseline of the height-change curve indicates the consolidation of the SE caused by the pressure generated by the lattice expansion of electrode material.

Baseline of the in situ measured pressure change
Similarly, an inclined baseline is observed in the SSB In/SE/LiCoO$_2$ used for the pressure monitoring, as shown in Supplementary Figure S7. The corresponding plot after the subtraction of baseline is shown in Figure 1.

*Supplementary Figure S7: the pressure change curve of the In/SE/LiCoO$_2$ without subtracting the baseline. An inclined baseline indicates the consolidation of SE due to the pressure generated by the volume expansion of electrode materials during cycling.*
References