Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


# Considerations in applying neutron depth profiling (NDP) to Li-ion battery research

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## Supplementary Information

**Table S1**. Unit cell parameters, density, concentration and observed potential of known $Li_xSn$ intermetallic phases

| Phases | Li:Sn | a/A | b/A | c/A | density ($g/cm^3$) | [Li] ($atoms/cm^3$) | [Li] ($moles/cm^3$) | Observed E (V vs. $Li/Li^+$)* |
|---|---|---|---|---|---|---|---|---|
| b-Sn | 0 | 5.83 | 5.83 | 3.18 | 7.29 | 0 | | |
| $Li_2Sn_5$ | 0.5 | 10.27 | 10.27 | 3.125 | 6.11 | $6.07 \times 10^{21}$ | 0.010 | 0.71 → 0.61 |
| LiSn | 1 | 5.17 | 7.74 | 3.18 | 5.08 | $7.86 \times 10^{21}$ | 0.013 | 0.55 → 0.45 |
| $Li_7Sn_3$ | 2.3 | 9.45 | 8.56 | 4.72 | 3.66 | $1.83 \times 10^{22}$ | 0.030 | 0.45 → 0.30 |
| $Li_5Sn_2$ | 2.5 | 4.74 | 4.74 | 19.83 | 3.51 | $1.12 \times 10^{22}$ | 0.019 | |
| $Li_{13}Sn_5$ | 2.6 | 4.7 | 4.7 | 17.12 | 3.47 | $3.44 \times 10^{22}$ | 0.057 | |
| $Li_7Sn_2$ | 3.5 | 9.8 | 13.8 | 4.75 | 2.96 | $1.09 \times 10^{22}$ | 0.018 | 0.30 → 0.20 |

- Observed potential obtained from ref [1]

## Depth – Energy Calibrations

### Depth-Energy Calibration Equation

$$Depth\ (\mu m\ Sn) = -\left(1.4945\ x10^{-6} \pm 0.0578\ x10^{-6}\right)E^2 - 0.0066E + (19.34\ \pm\ 0.52)$$

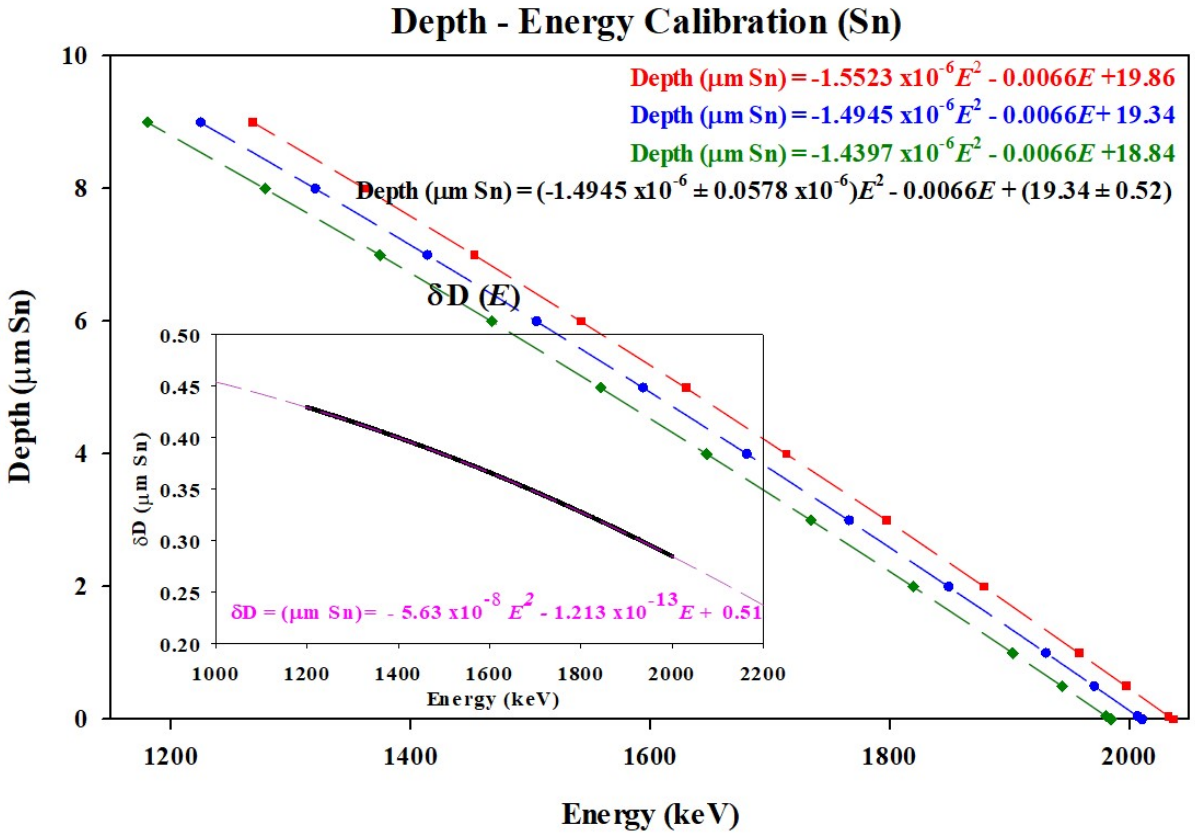


**Figure S1.** Depth – Energy calibration for pure Sn phase. The blue, red, and green lines/equations represent the actual, upper, and lower bound fits for the TRIM histograms. The black equation is the depth calibration equation with term-specific uncertainties derived from the upper and lower bound fits. **Inset:** Function showing the energy-dependent depth uncertainty δD (*E*). A polynomial (pink dashed lined/equation) is fitted.

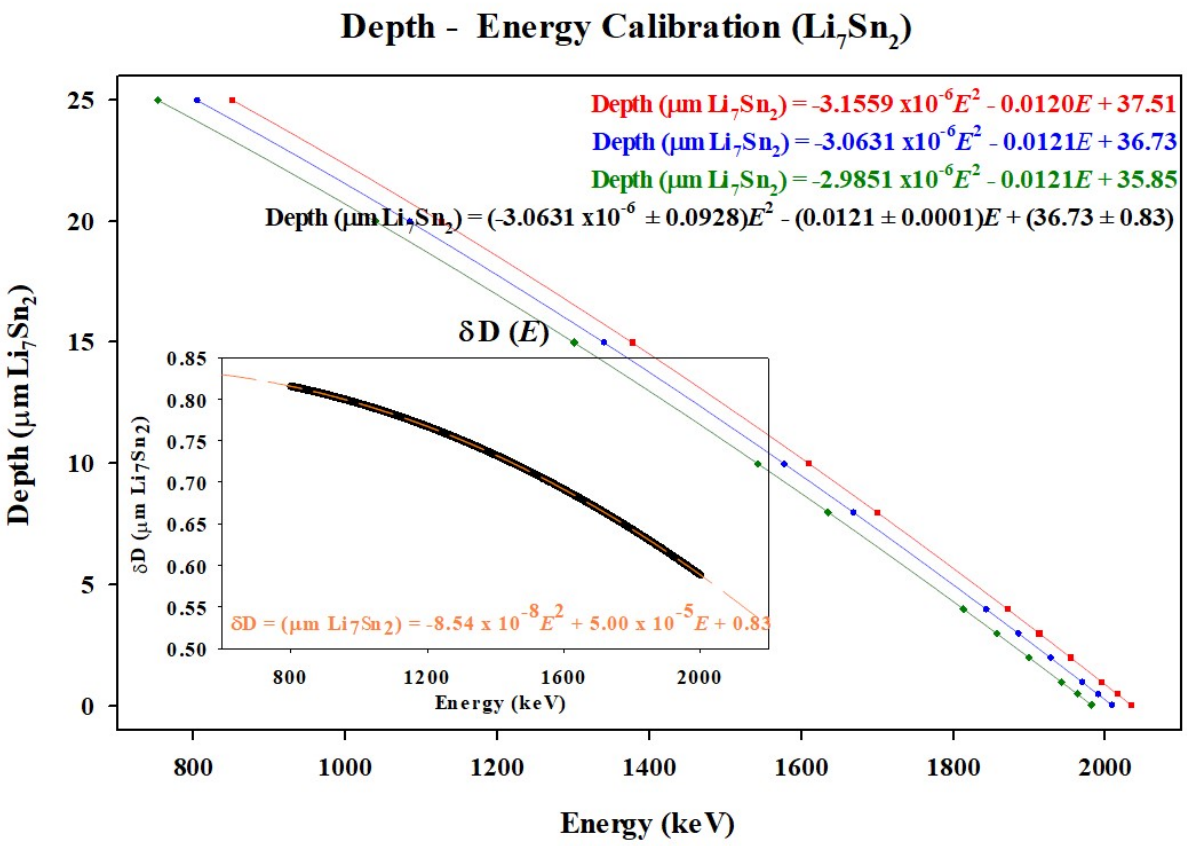


**Figure S2.** Depth – Energy calibration for pure $Li_7Sn_2$ phase. The blue, red, and green lines/equations represent the actual, upper, and lower bound fits for the TRIM histograms. The black equation is the depth calibration equation with term-specific uncertainties derived from the upper and lower bound fits. **Inset:** Function showing the energy-dependent depth uncertainty δD (E). A polynomial (orange dashed lined/equation) is fitted.

## $dC_{Li}\,dx^{-1}$ Deming Fits for the 600 mV potential hold

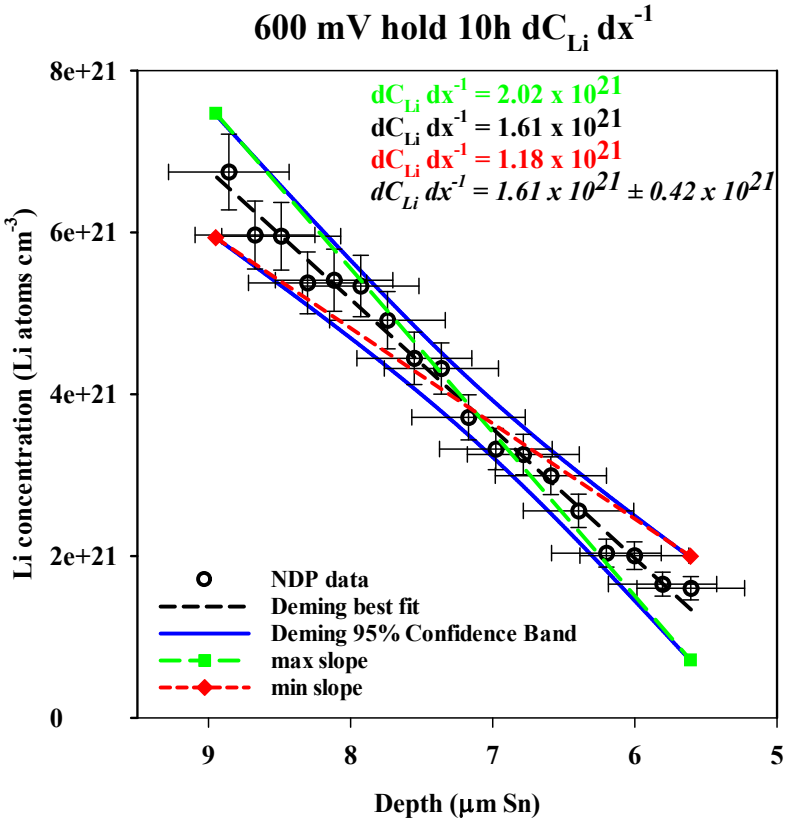


**Figure S3.** Deming analysis of the fitted $dC_{Li}\,dx^{-1}$ for the 10 hours spectrum of the 600 mV hold. Uncertainty is reported to 1σ based on experimental counting statistics and density uncertainty.

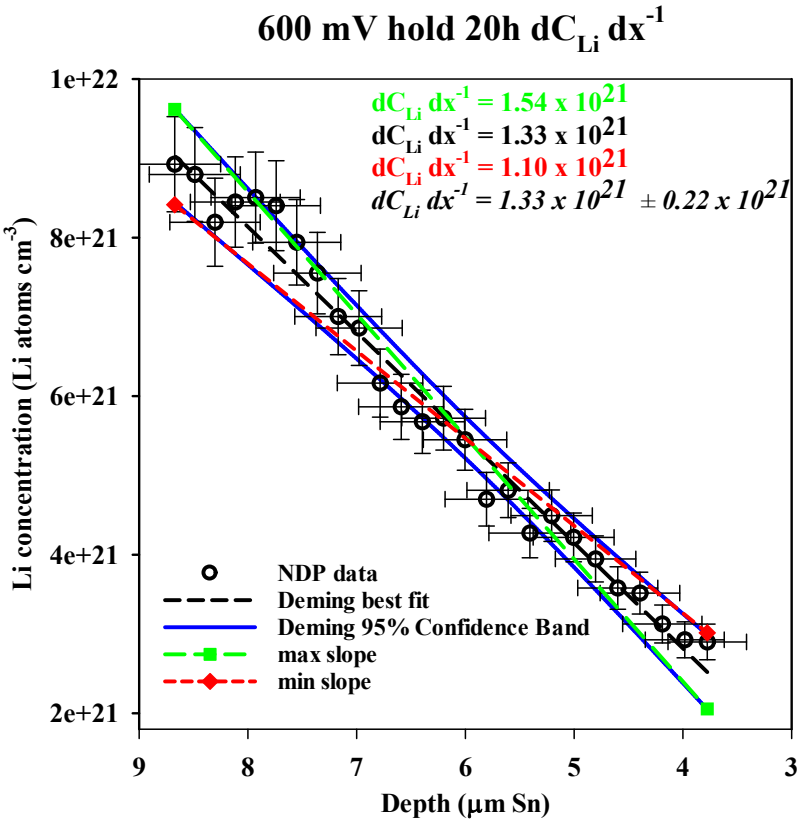


**Figure S4.** Deming analysis of the fitted $dC_{Li}\ dx^{-1}$ for the 20 hours spectrum of the 600 mV hold. Uncertainty is reported to 1σ based on experimental counting statistics and density uncertainty.

## $dC_{Li}\ dx^{-1}$ Deming Fits for the 200 mV potential hold

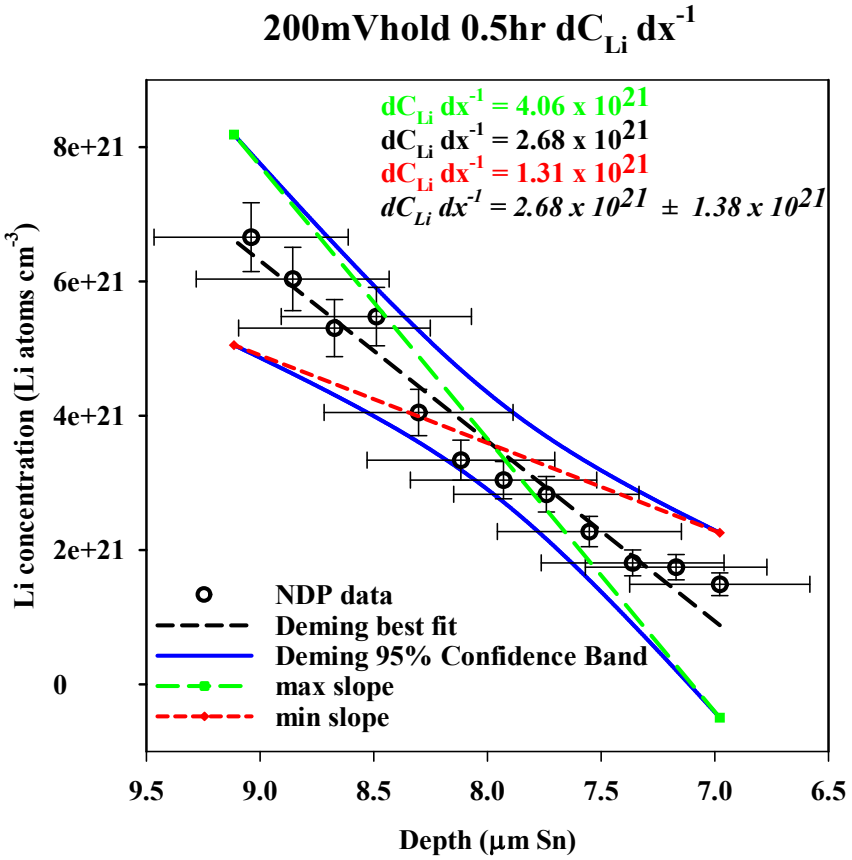


**Figure S5.** Deming analysis of the fitted $dC_{Li}\ dx^{-1}$ for the 0.5 hours spectrum of the 200 mV hold. Uncertainty is reported to 1σ based on experimental counting statistics and density uncertainty.

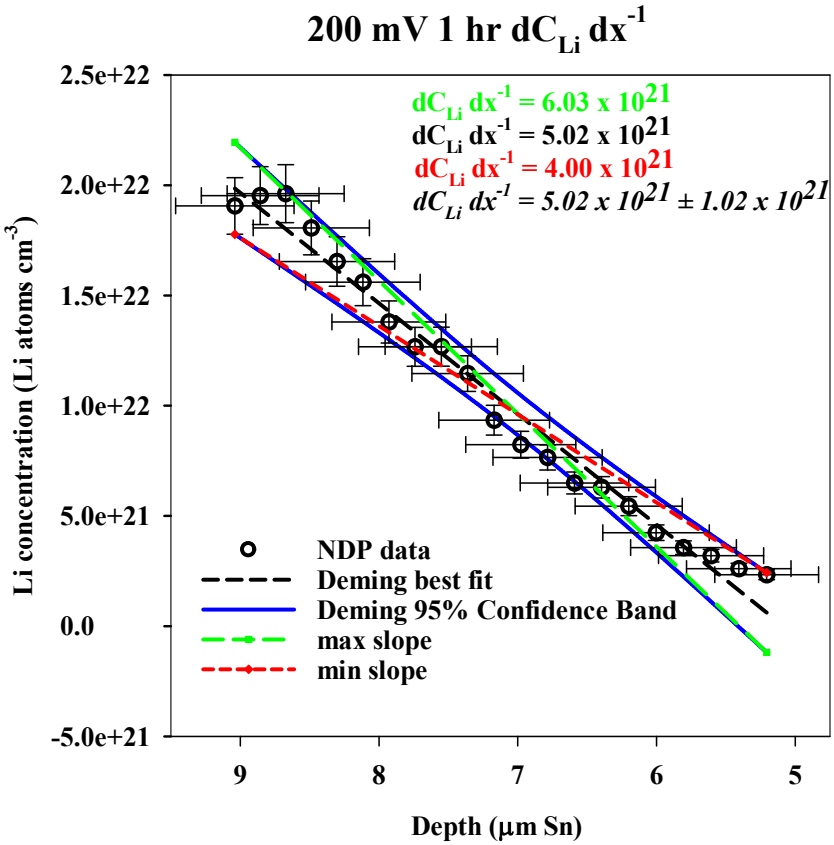


**Figure S6.** Deming analysis of the fitted $dC_{Li}\ dx^{-1}$ for the 1 hour spectrum of the 200 mV hold. Uncertainty is reported to 1σ based on experimental counting statistics and density uncertainty.

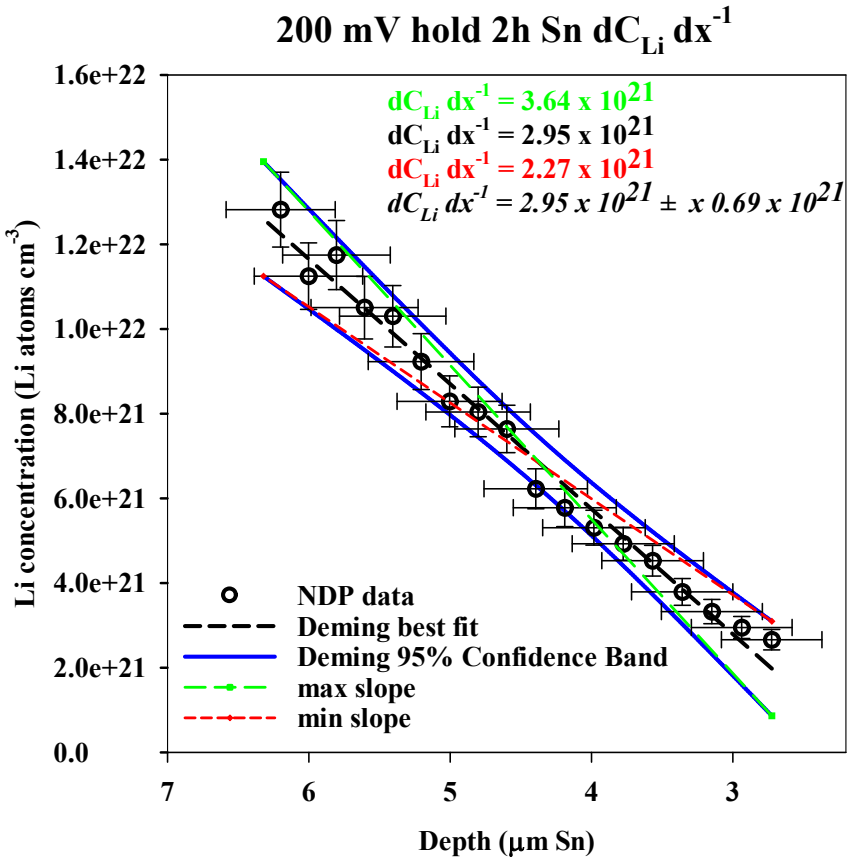


**Figure S7.** Deming analysis of the fitted $dC_{Li}\ dx^{-1}$ for the 2 hours spectrum of the 200 mV hold. Uncertainty is reported to 1σ based on experimental counting statistics and density uncertainty.

**Table S2.** Vertices used to determine the area change within the red polygon between spectra in Figure 4A. Total area of the polygon is 14.39 unit areas.

| Vertex # (n) | x coordinate (µm) | y coordinate (x $10^{21}$ Li atoms $cm^{-3}$) | $x_i y_{(i+1)}$ | $x_{(i+1)} y_i$ | $x_i y_{(i+1)} - x_{(i+1)} y_i$ |
|---|---|---|---|---|---|
| **1** | 8.90 | 6.75 | 60.08 | 47.3 | 12.78 |
| **2** | 7.00 | 6.75 | 20.30 | 27.0 | -6.7 |
| **3** | 4.00 | 2.90 | 8.00 | 5.22 | 2.78 |
| **4** | 1.80 | 2 | 2.25 | 3.60 | -1.35 |
| **5** | 1.80 | 1.25 | 2.43 | 7.00 | -4.57 |
| **6** | 5.60 | 1.35 | 37.80 | 11.95 | 25.85 |
| **1** | 8.85 | 6.75 | **Area=** | | 14.39 |

**Table S3.** Polynomial fits used for the curvature calculation of the for 0 hours, 0.5 hours, 1 hour and 2 hours spectra in Figure 9A.

| Spectrum Time (hours) | Polynomial Fit (y = Li atoms $cm^{-3}$, x = µm Sn) |
|---|---|
| ***Figure 4A*** | |
| **10** | $1.61 \times 10^{21}x - 7.68 \times 10^{21}$ |
| ***Figure 4B*** | |
| **20** | $1.33 \times 10^{21}x - 2.53 \times 10^{21}$ |
| ***Figure 4C*** | |
| **10** | $2.14 \times 10^{20}x^2 - 1.50 \times 10^{21}x + 3.44 \times 10^{21}$ |
| **20** | $9.80 \times 10^{19}x^2 + 2.54 \times 10^{19}x + 1.57 \times 10^{21}$ |
| ***Figure 9A*** | |
| 0 | $2.18 \times 10^{19}x^2 - 2.50 \times 10^{20}x + 1.67 \times 10^{21}$ |
| 0.5 | $5.16 \times 10^{18}x^4 - 6.84 \times 10^{19}x^3 + 2.99 \times 10^{20}x^2 - 7.15 \times 10^{20}x + 1.93 \times 10^{21}$ |
| 1 | $5.48 \times 10^{19}x^3 - 1.64 \times 10^{20}x^2 - 6.96 \times 10^{20}x + 2.67 \times 10^{21}$ |
| 2 | $-3.92 \times 10^{19}x^3 + 8.67 \times 10^{20}x^2 - 2.44 \times 10^{21}x + 3.90 \times 10^{21}$ |

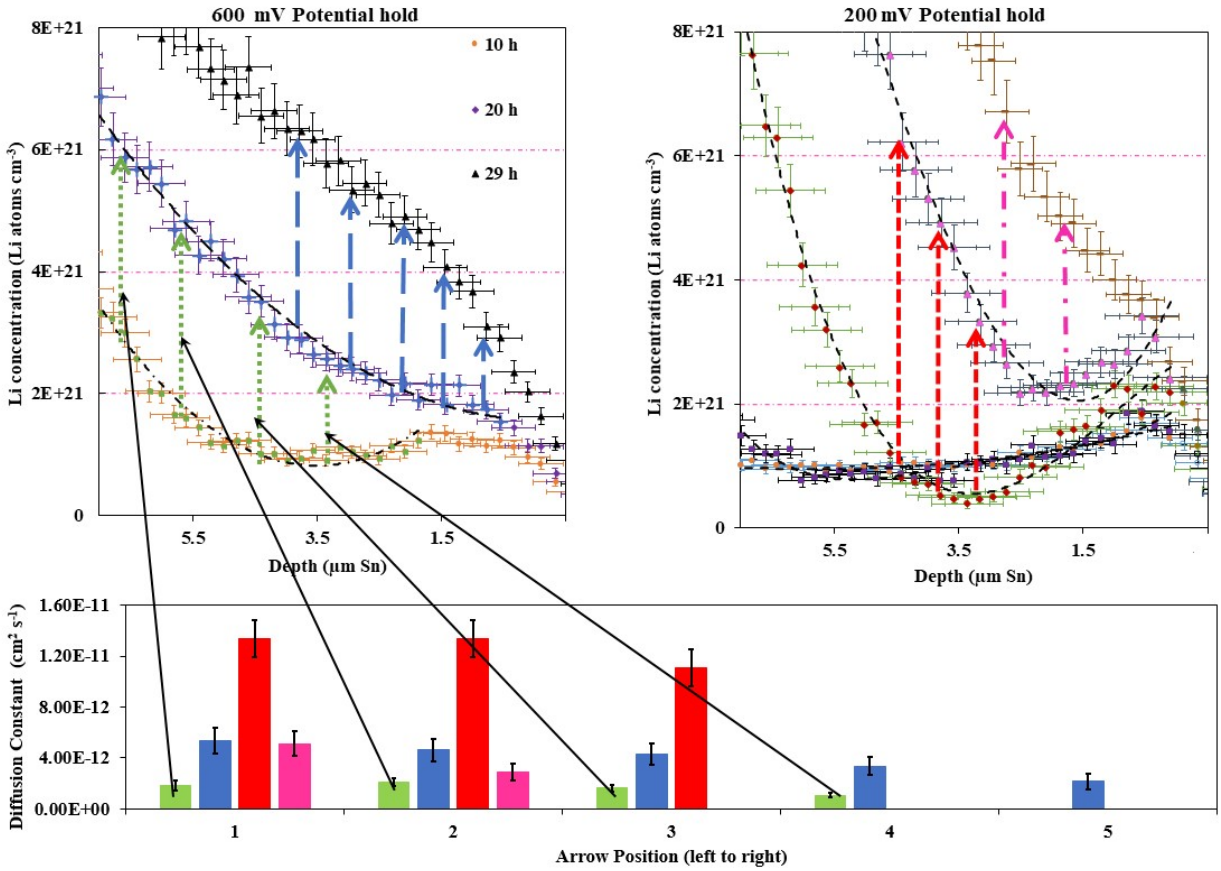


**Figure S8.** *(Left)* NDP spectra collected at 10 hours (green circles), 20 hours (blue crosses) and 29 hours (black triangles) during the 600 mV potential hold. Only the low Li concentration portion of the electrode, far from the interface is shown. Diffusion constants are calculated for multiple regions of the electrode delineated by the colored arrows (green: 10 hours to 20 hours, blue: 20 hours to 29 hours) via Fick's 2nd Law. *(Right)* NDP spectra collected at 1 hour (red diamonds), 2 hours (pink triangles) and 4 hours (brown dashes) during the 200 mV potential hold. . Only the low Li concentration portion of the electrode, far from the interface is shown. Diffusion constants are calculated for multiple regions of the electrode delineated by the colored arrows (red: 1 hour to 2 hours, pink: 2 hours to 4 hours) via Fick's 2nd Law. *(Bottom)* Diffusion constant values calculated for each arrow. Bars in the plot are color coded to their arrows and are arranged spatially for each arrow in the top two spectra starting from the leftmost arrow (shown by the black arrows for the green arrow set). Uncertainty is reported to 1σ based on experimental counting statistics and density uncertainty.

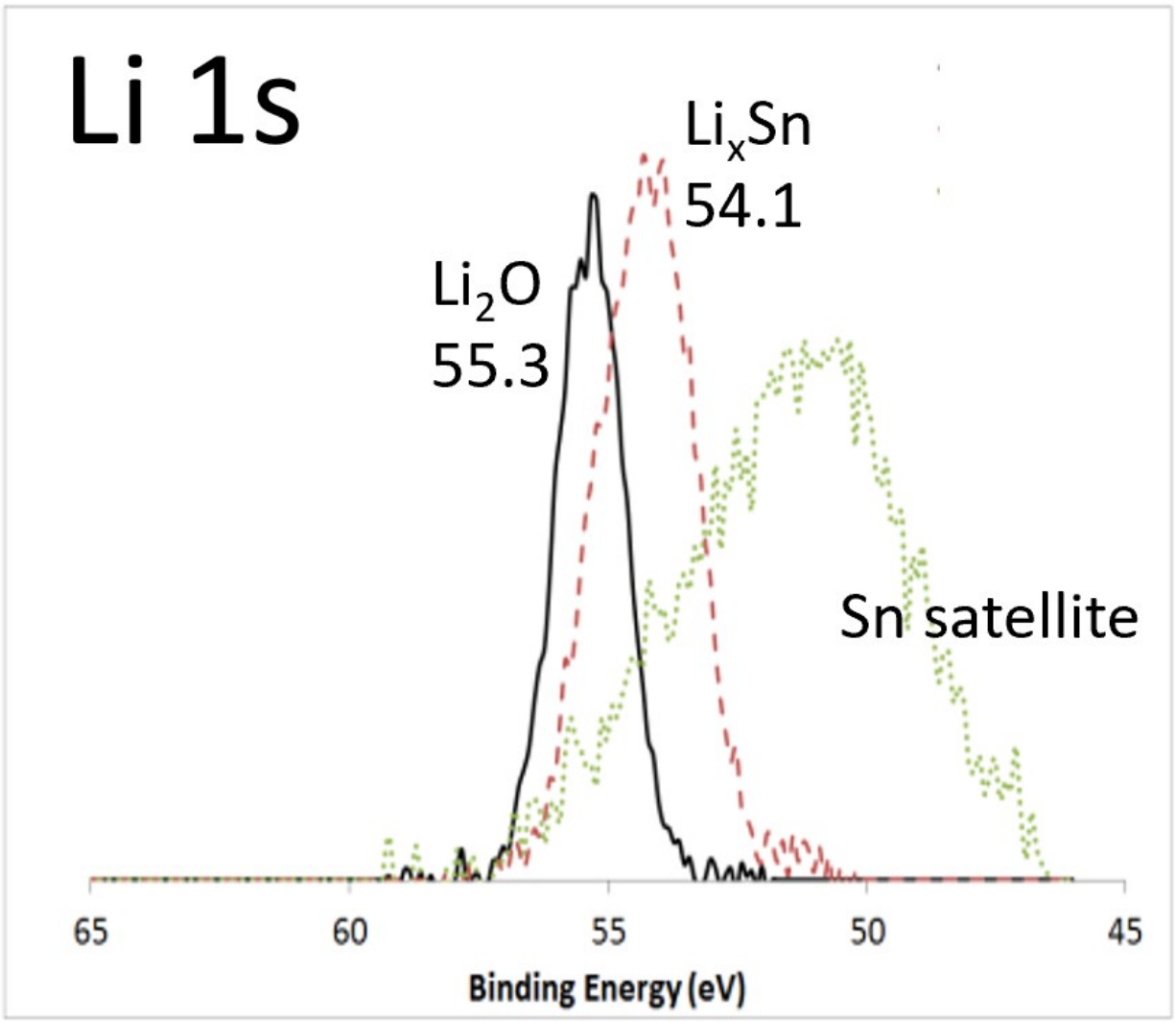


**Figure S9.** XPS spectra of $Li_2O$ and $Li_2Sn_5$ formed at 650 mV.

## References

1. Lorie Lopez, J. L.; Grandinetti, P. J.; Co, A. C., Phase transformations and capacity fade mechanism in LixSn nanoparticle electrodes revealed by operando 7Li NMR. In *Journal of Materials Chemistry A*, Royal Society of Chemistry: 2019; Vol. 7, pp 10781-10794.