

# Supporting Information

## Breaking Down a Complex System: Interpreting PES Peak Positions for Cycled Li-ion Battery Electrodes

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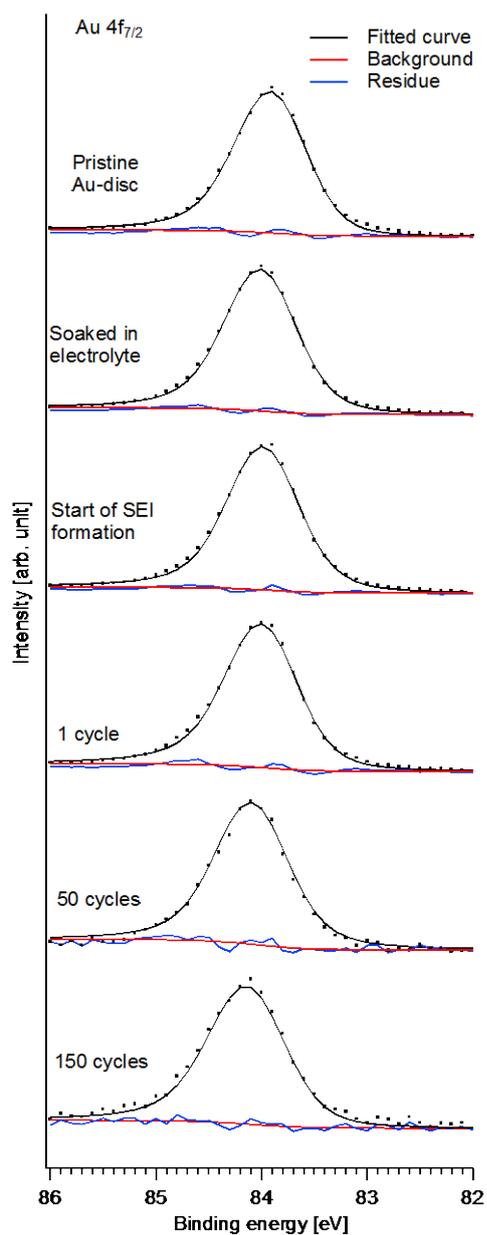


Figure S1. Au  $4f_{7/2}$  spectra as measured for gold electrodes with increasing SEI layers due to increasing electrochemical cycling.

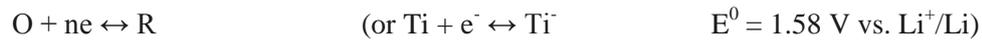
Table S1. Peak parameters for fitted peaks in Figure S1.

	Binding energy [eV]	FWHM [eV]
Pristine Au-disc	83.9	0.80
Soaked in electrolyte	84.0	0.81
Start of SEI formation	84.0	0.81
1 cycle	84.0	0.82
50 cycles	84.1	0.83
150 cycles	84.1	0.87

### Li content calculations in LTO

In sample A in figure 4, the LTO material is de-lithiated to approximately 50% and the LTO should therefore be considered a good conductor. In the subsequent samples (B to D) the degree of lithiation decreases further.

Due to the high reversibility and the flat voltage plateau of the LTO system, we consider that LTO could be described as a nernstian system. If we then express our system according to the following reactions:



Where Nernst equation is described as follows:

$$E = E^0 + \frac{RT}{nF} \ln(C_{\text{O}}/C_{\text{R}})$$

and  $n=1$ ,  $RT/F = 0.026 \text{ V}$  (assuming  $25 \text{ }^\circ\text{C}$ )

When the electrode is at a potential of 2.95 V (as it is in sample B during the LFS region) it is thereby possible to calculate the ratio between oxidized and reduced LTO according to following calculations

$$C_{\text{O}}/C_{\text{R}} = e^{(2.95-1.58)/0.026} = 4.6 \times 10^{23}$$

It is then obvious that LTO is effectively only present in its oxidized state. Since the potential in sample C and D is even higher, the relative amount of oxidized Ti should continue to increase and the LTO should in all these cases be considered a poor electron conductor.

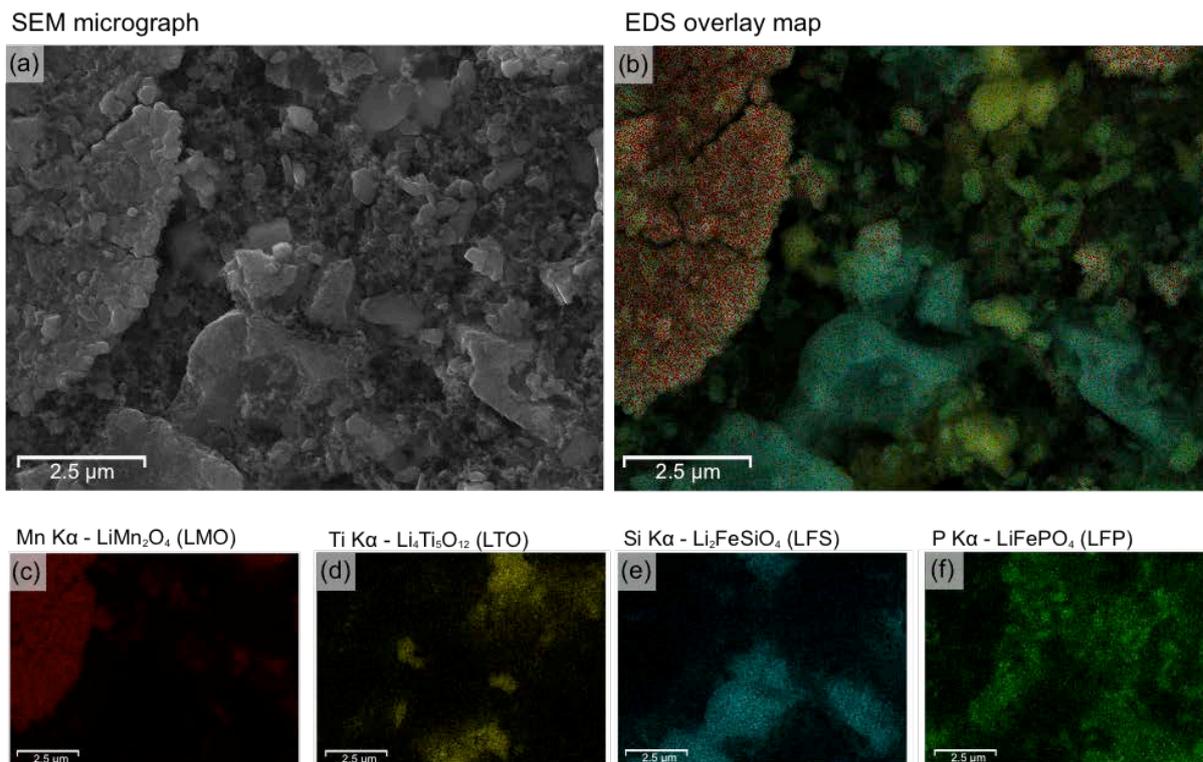


Figure S2. SEM micrograph and EDS elemental mapping of the mixed materials electrode (with four different active materials). (a) SEM micrograph of the electrode surface with (b) accompanied EDS overlay mapping of Mn, Ti, Si and P K $\alpha$  signal. Individual maps of the (c) Mn K $\alpha$  in LMO; (d) Ti K $\alpha$  in LTO; (e) Si K $\alpha$  in LFS and (f) P K $\alpha$  in LFP were analyzed and used to separate the four different electrode materials.

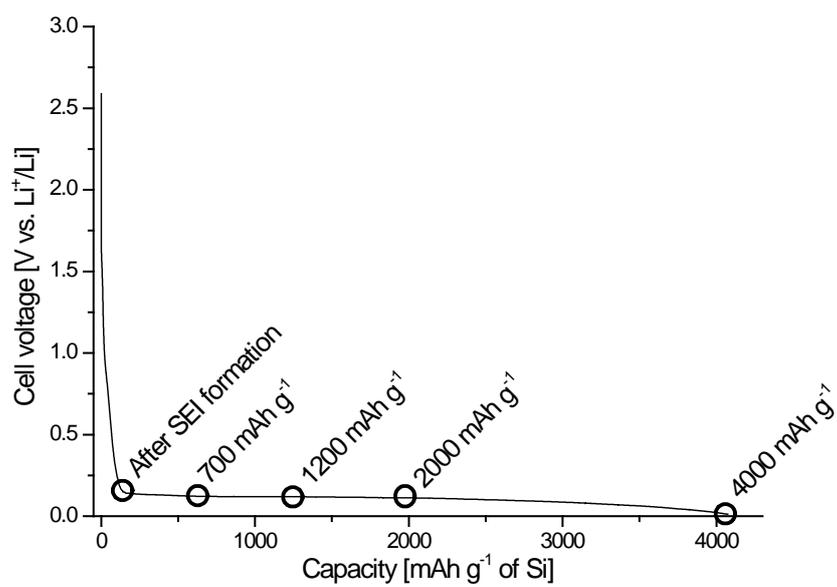


Figure S3. Voltage vs. capacity curve for the lithiation reaction of nano-Si electrodes.