

Supplementary information

for

Insights on the chemical and electronic interface evolution of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in cycled $\text{Li}_2\text{S-P}_2\text{S}_5$ enabled by *operando X-ray photoelectron spectroscopy*

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Operando XPS experiment performed on LTO/LPS/VGCF (25/70/5) WE-composite

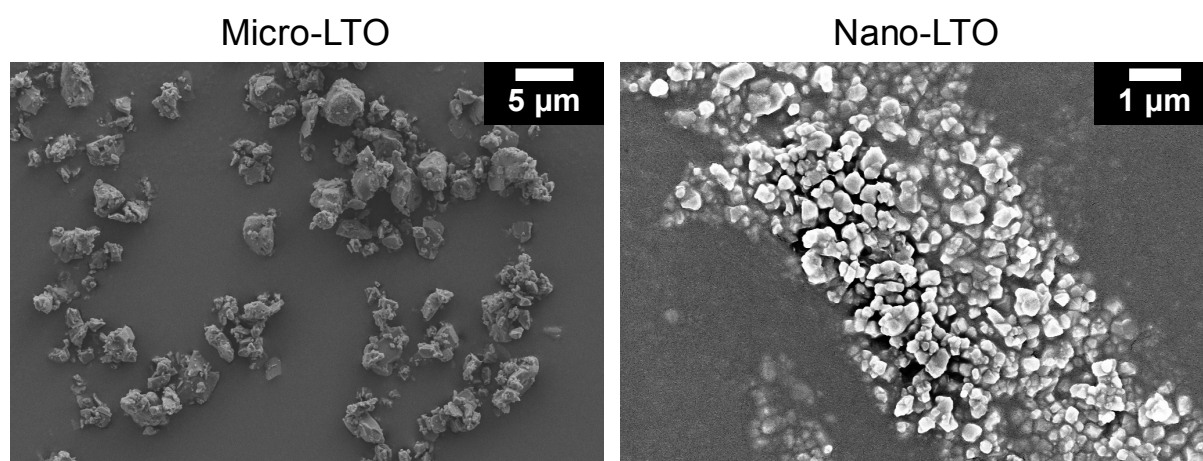


Figure S1 SEM images of micron- and nano-sized LTO particles.

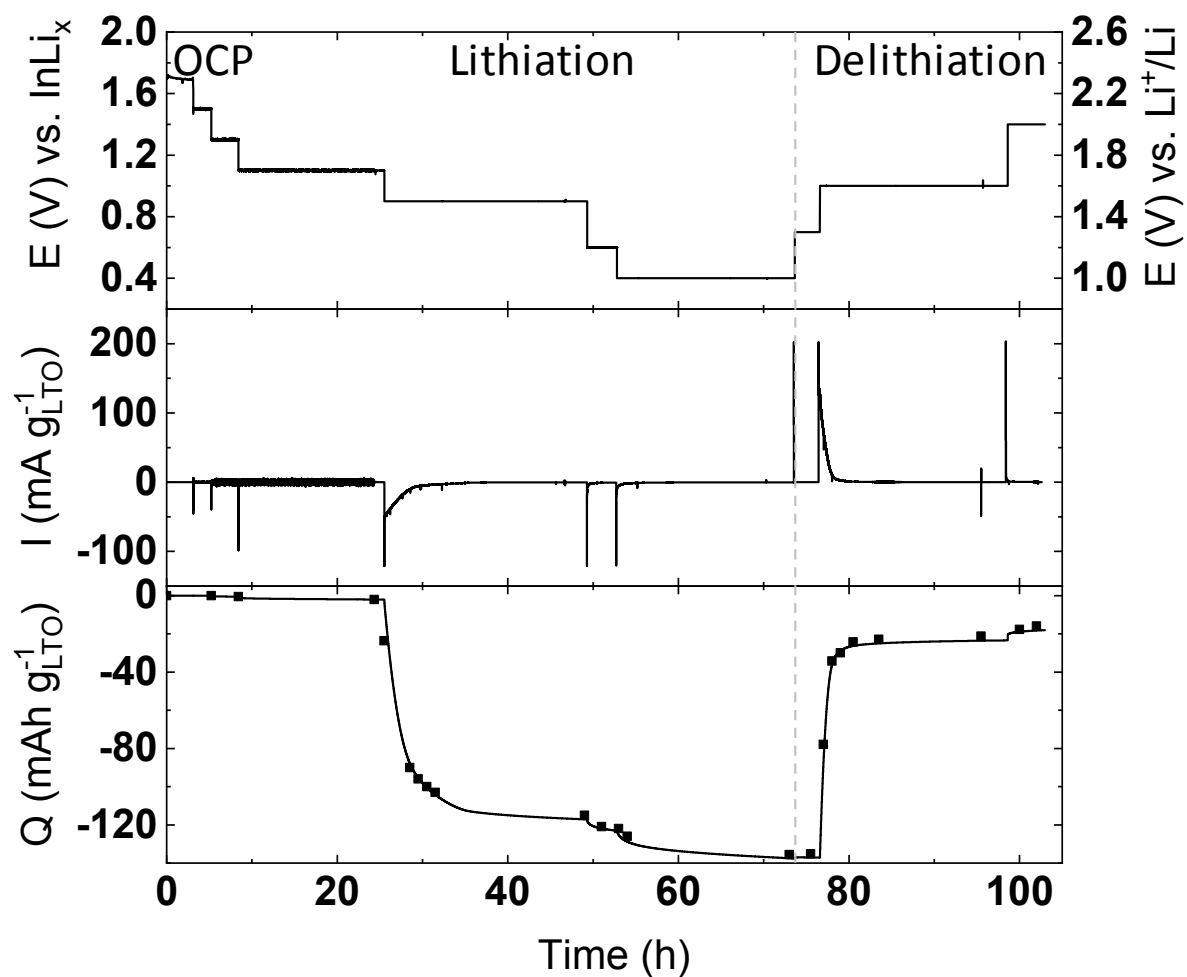


Figure S2 Potential (E), specific current (I) and specific charge (Q) profile collected during the operando XPS experiment performed on the nano-LTO/LPS/VGCF (25/70/5) WE-composite cycled vs. InLi_x in UHV chamber.

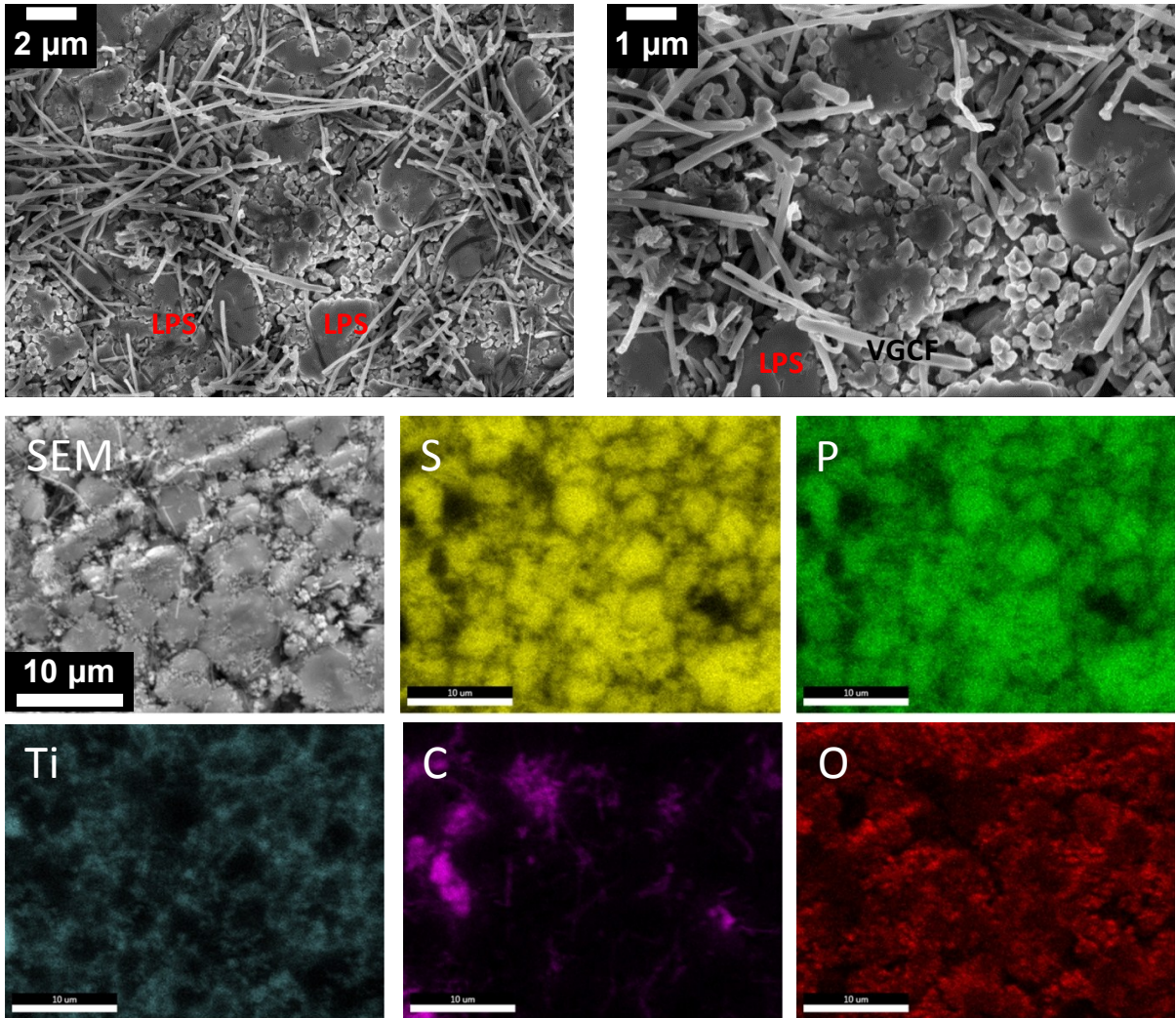


Figure S3 Morphology of the composite WE containing nano-LTO/LPS/VGCF (25/70/5) as used for the operando XPS experiment. The SEM images (top row) and EDX mapping confirm the homogeneous distribution of elements.

Note S1: Post-mortem XPS on lithiated LTO/LPS/VGCF electrodes

The cycling profiles of the nano-LTO/LPS/VGCF (45/50/5) WE-composite vs. InLi_x under various conditions are presented in Figure S4. The abbreviation CC and CC-CV describes the cycling protocol using constant current ($C/10$ rate) only and constant current followed by a constant voltage (potentiostatic step) at the cut-off voltage until the current drops below $1 \mu\text{A}$. There is a general trend, that more carbonates are formed when the cells are cycled outside of the glove box (GB) which also scales with the time during which the cells are cycled (Figure S5). However, even by the cut-off lithiation at $0.85 \text{ V vs. InLi}_x$ ($1.45 \text{ V vs. Li}^+/\text{Li}$) and cycling inside the GB, the surface layer formation is still visible with strongly attenuated C1s signals from the conductive carbon and additional BE shift for the surface species. In all lithiated electrodes, due to the parasitic surface reactivity, the determination of Li_2S is ambiguous.

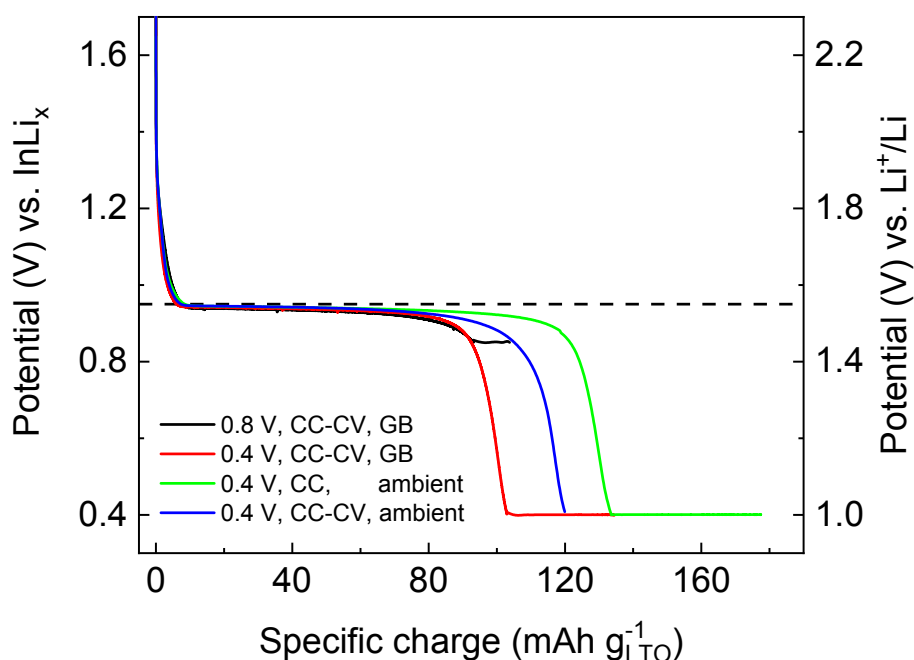


Figure S4 1st Lithiation profile of the composite WE (nano-LTO/LPS/VGCF, 45/50/5) using various cycling conditions to prepare samples for post-mortem XPS analysis. The information in the legend are: cut-off voltage, cycling protocol, atmosphere conditions. CC: constant current at $C/10$ rate; CC-CV: constant current with subsequent constant voltage at the cut-off voltage until the current drops below $1 \mu\text{A}$; GB: cycling in glovebox; ambient: cells are sealed using rubber rings and cycled in temperature-controlled chamber outside of the glovebox.

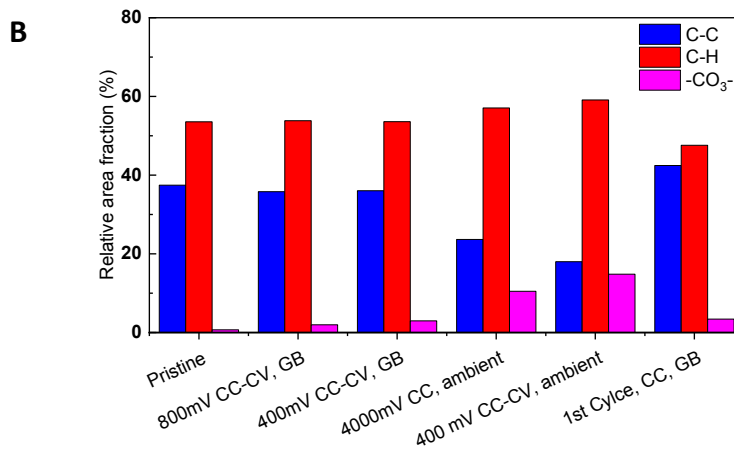
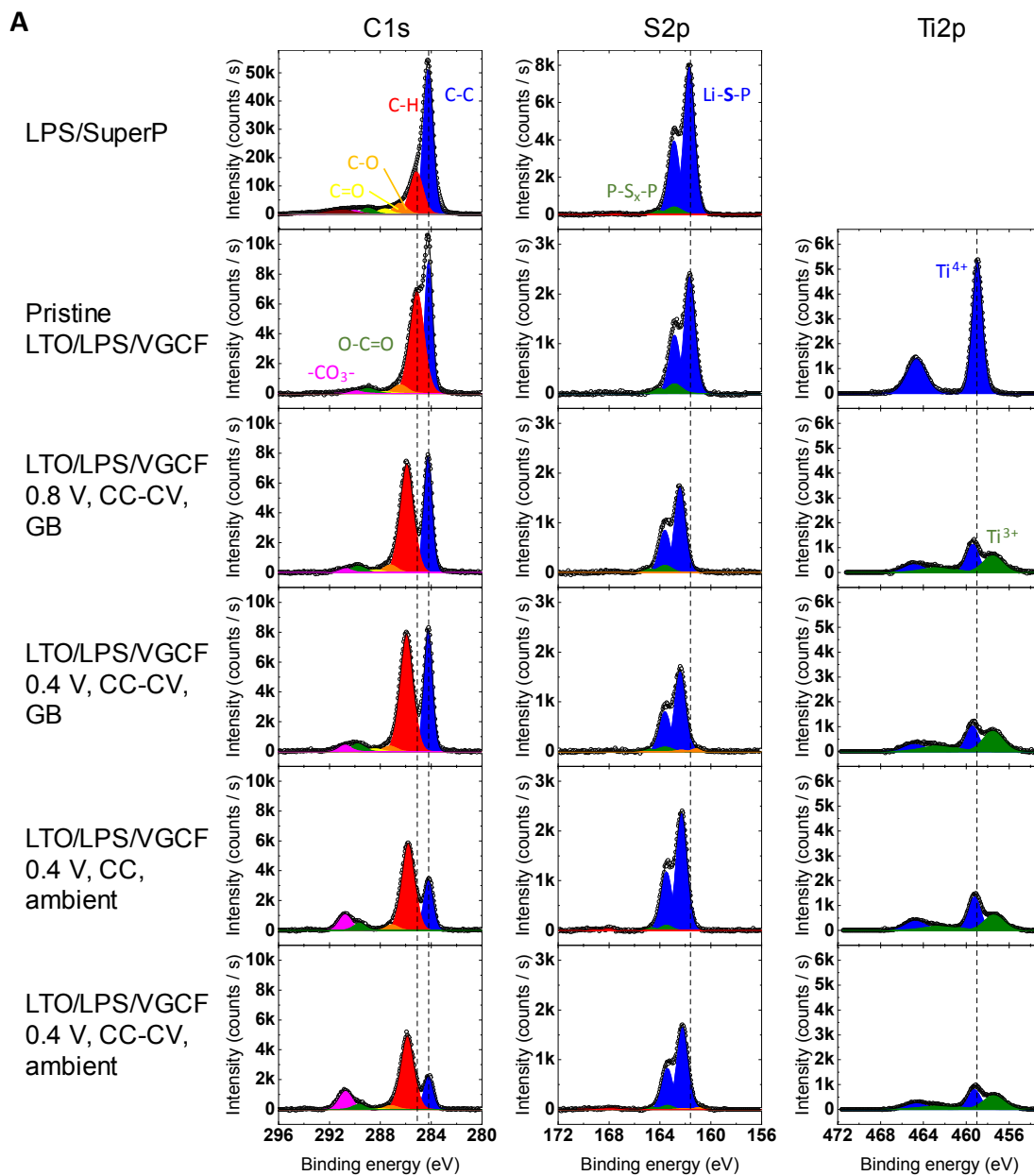


Figure S5 (a) C1s, S2p and Ti2p XPS core level spectra obtained during the post-mortem experiments performed on the composite WE containing nano-LTO/LPS/VGCF (45/50/5) after the 1st Lithiation using different cycling conditions. The formation of surface layer is observed in all samples. The same abbreviations are used for the cycling conditions as in supplementary Figure S4. (b) Relative composition of the C-C, C-H and CO₃ bonds after the deconvolution of the C1s spectra.

	Binding energy (eV)				FWHM (eV)			
C1s	C-C	C-H	C-O*	C=O* O-C=O* -CO ₃ -*	C-C	Others*		
	284.4±0.03; 285.4±0.06; 286.6			287.9; 289.2; 290.3	0.77±0.02; 1.3±0.03			
O1s	LTO	C=O	C-O ⁺		LTO	C=O	C-O ⁺	
	530.4±0.04; 532±0.11; 533.2				1.35±0.01, 1.9±0.04 1.9			
S2p	Li-S-P	P-S _x -P [§]	Li ₂ S [§]		Li-S-P	P-S _x -P	Li ₂ S	
	161.8±0.04; 163		160.5		1±0.05; 1.2±0.05; 1±0.05			
P2p	Li-S-P [#]	Li _x P			Li-S-P	Li _x P		
	130.1±0.02; 132.2±0.03				1±0.02; 1.6±0.03			
Ti2p	Ti2p _{3/2} (4+)	Ti2p _{1/2} (4+) [†]	Ti2p _{3/2} (3+) [†]	Ti2p _{1/2} (3+) [†]	Ti2p _{3/2} (4+)	Ti2p _{1/2} (4+)	Ti2p _{3/2} (3+)	Ti2p _{1/2} (3+)
	459±0.07; 464.7; 457.2; 461.9				1.2±0.02; 2.2±0.03; 1.9±0.04; 3.7±0.08			

Table S1 Parameters used for the curve fittings of the core level spectra.

* C1s: The BEs of C-O, C=O, O-C=O and -CO₃- species have respectively a fixed shift of 1.2 eV, 2.5 eV, 3.8 eV and 4.9 eV with regard to the BE of C-H. All carbon species except C-C has the same FWHM.

⁺ O1s: The BE of C-O species has a fixed shift of 1.3 eV with regard to the BE of C=O species. Both C-O and C=O species have the same FWHM.

[§] S2p: The spin-orbit splitting for S2p core level spectra is 1.2 eV and the branching ratio is 0.5 eV. The BE of P-S_x-P and Li₂S species have respectively a fixed shift of 1.2 eV, -1.3 eV with regard to the BE of Li-S-P.

[#] P2p: The spin-orbit splitting for S2p core level spectra is 0.93 eV and the branching ratio is 0.5 eV.

[†] Ti2p: The spin-orbit splitting (Δ) for Ti2p (4+) and Ti2p_{3/2} (3+) are fixed to 5.7 eV and 4.7 eV, respectively. The branching ratio for all Ti2p species is 0.48. The BE difference between Ti2p_{3/2} (4+) and Ti2p_{3/2} (3+) is fixed to 1.8 eV.

Table S2 Binding energies for C1s, S2p_{3/2}, P2p_{3/2} and Ti2p_{3/2} spectra in pristine LTO, LPS, the composite LTO/LPS/VGCF electrode in its pristine state, after 1st lithiation and 1st delithiation (cycle). In order to minimize sample charging, pristine LTO and LPS was mixed with 10 wt% conductive carbon (SuperP C65). All spectra were aligned based on the C1s signal of the conductive carbon located at 284.2 eV.

Sample	C1s (C-C)	C1s (C-H)	O1s (LTO)	O1s (C=O)	S2p _{3/2} (Li-S-P)	P2p _{3/2} (Li-S-P)	Ti2p _{3/2} (4+)
LTO/SuperP (9/1)	284.2	285.4	530.4	531.9	N/A	N/A	459.0
LPS/SuperP (9/1)	284.2	285.1	N/A	531.9	161.7	132.2	N/A
LTO/LPS/VGCF, pristine	284.2	285.1	530.4	531.9	161.7	132.2	459.0
LTO/LPS/VGCF, 1st Lithiation	284.2	285.9	530.6	532.5	162.3	132.8	459.3
LTO/LPS/VGCF, 1st Cycle	284.2	285.6	530.4	532.2	162.0	N/A	459.1