

Supporting Information

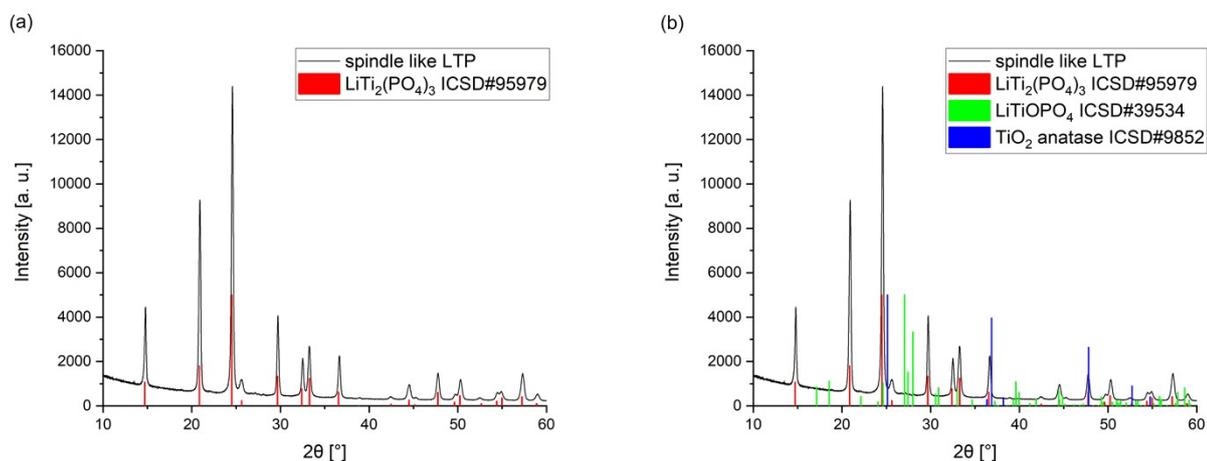


Figure S1: XRD-pattern of spindle like $\text{LiTi}_2(\text{PO}_4)_3$ [17] calcined at 800 °C.

Figure S1 shows the XRD-pattern of the investigated sample charge. When only a single phase is considered ($\text{LiTi}_2(\text{PO}_4)_3$ (ICSD#95979), Figure S1 (a) phase purity can be assumed. Some minor humps are visible around 27° and 28° but these cannot be identified as clear secondary phase reflections for phase matching. With the knowledge based on secondary phase identification by (S)TEM in Figure S1 (b) these weak humps can be attributed to the two strongest reflections of LiTiOPO_4 (ICSD#39534, green bars). The three reflections of anatase (ICSD#9852, blue bars) overlap with the reflections of $\text{LiTi}_2(\text{PO}_4)_3$, thus, small amounts of anatase are difficult to detect as secondary phase in LTP by XRD.

Figure S2 one particle with the 2 μm wide central part marked by a box indicating the lift-out for TEM-lamella preparation. STEM images of this lamella are shown in Figure 2 and 3.

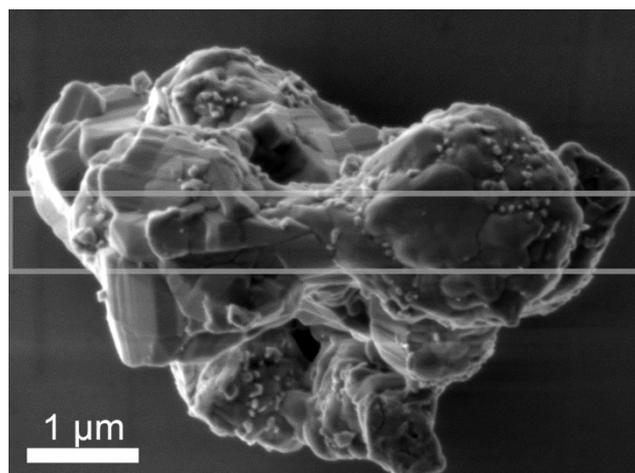


Figure S2: (a) SEM top view image of a spindle-like particle containing the secondary phase with different morphology in the left part, from which a TEM-lamella was lifted out as indicated by the framed box.

Table S1 list the theoretical compositions, excluding lithium, which cannot be detected by EDS, for $\text{LiTi}_2(\text{PO}_4)_3$, and LiTiOPO_4 and TiO_2 , which were attributed to the secondary phase and the nanoparticles respectively. Also listed are the results of quantification from the ED-spectra from the three areas marked in Figure 2. Table S2 summarizes the results obtained from Quantification of EDS from the three areas marked in Figure 3(b) and EELS core loss spectra from the three boxes marked in Figure 3(a).

Table S1: EDS quantification of the three areas marked in Figure 2.

	O [at%] (excl. Li)	P [at%] (excl. Li)	Ti [at%] (excl. Li)	Atomic ratio Ti/O
$\text{LiTi}_2(\text{PO}_4)_3$	70.6	17.7	11.8	0.167
LiTiOPO_4	71.4	14.3	14.3	0.2
TiO_2	66.7	0.0	33.3	0.5
Area 1	75.5±5.8	14.3±2.9	10.1±1.5	0.134±0.030
Area 2	75.8±5.6	10.2±2.1	14±2.1	0.185±0.041
Area 3	71.7±7.6	3.7±0.9	24.6±4.1	0.343±0.094

Table S2: EDS- and EELS quantification of the three areas marked in Figure 3b.

	O [at%] (excl. Li)	P [at%] (excl. Li)	Ti [at%] (excl. Li)	Atomic ratio Ti/O
EDS				
Area 1	71.8±6.1	16.2±3.4	12±2	0.17±0.04
Area 2	70.1±6.2	12.1±2.5	17.7±2.8	0.25±0.06
Area 3	70.2±6.8	5.7±1.2	24.1±4	0.34±0.09
EELS				
Area 1	86.95		13.05	0.15±0.021
Area 2	79.86		20.14	0.25±0.036
Area 3	67.15		32.85	0.49±0.069

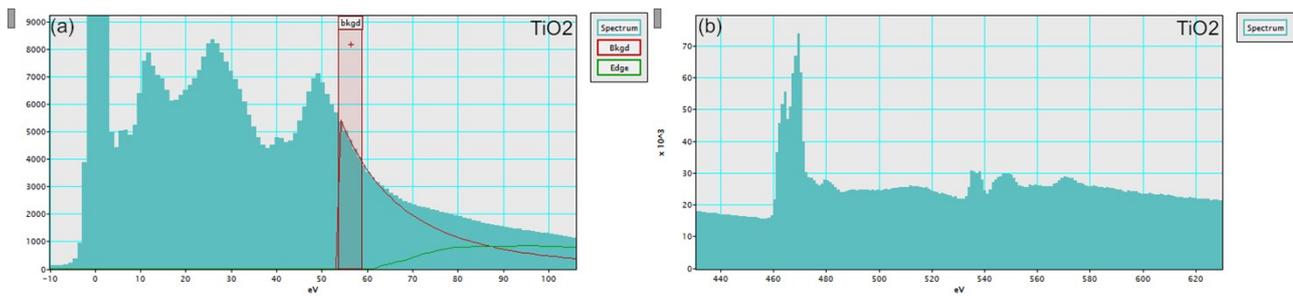


Figure S3: (a) low loss spectrum of TiO_2 from the EELS-atlas. (b) Core loss spectra of TiO_2 taken from the EELS atlas.

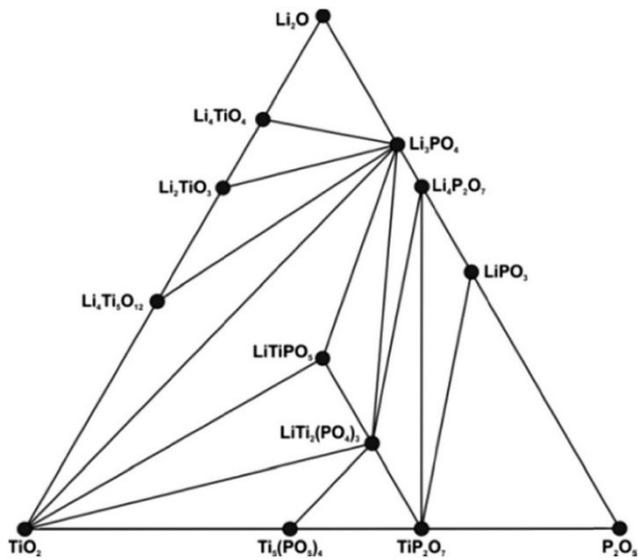


Figure S4: Quasi-ternary phase diagram $\text{Li}_2\text{O-TiO}_2\text{-P}_2\text{O}_5$ calculated with materials project reused from reference 32.

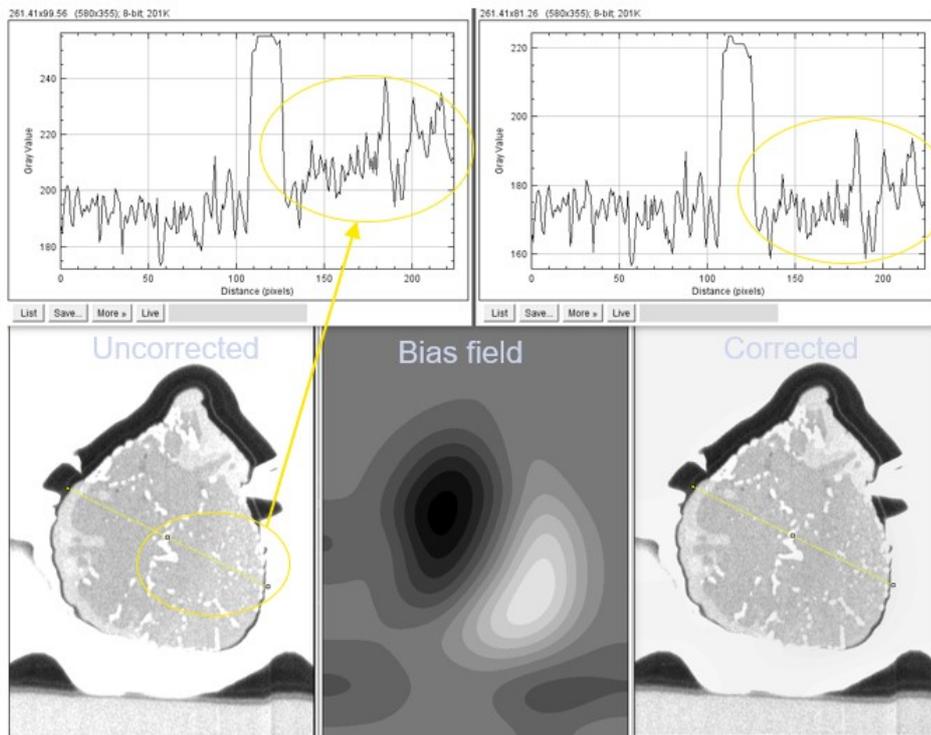


Figure S5: (top) Histograms equalization and (bottom) removal of lateral bias.