

## Supporting information

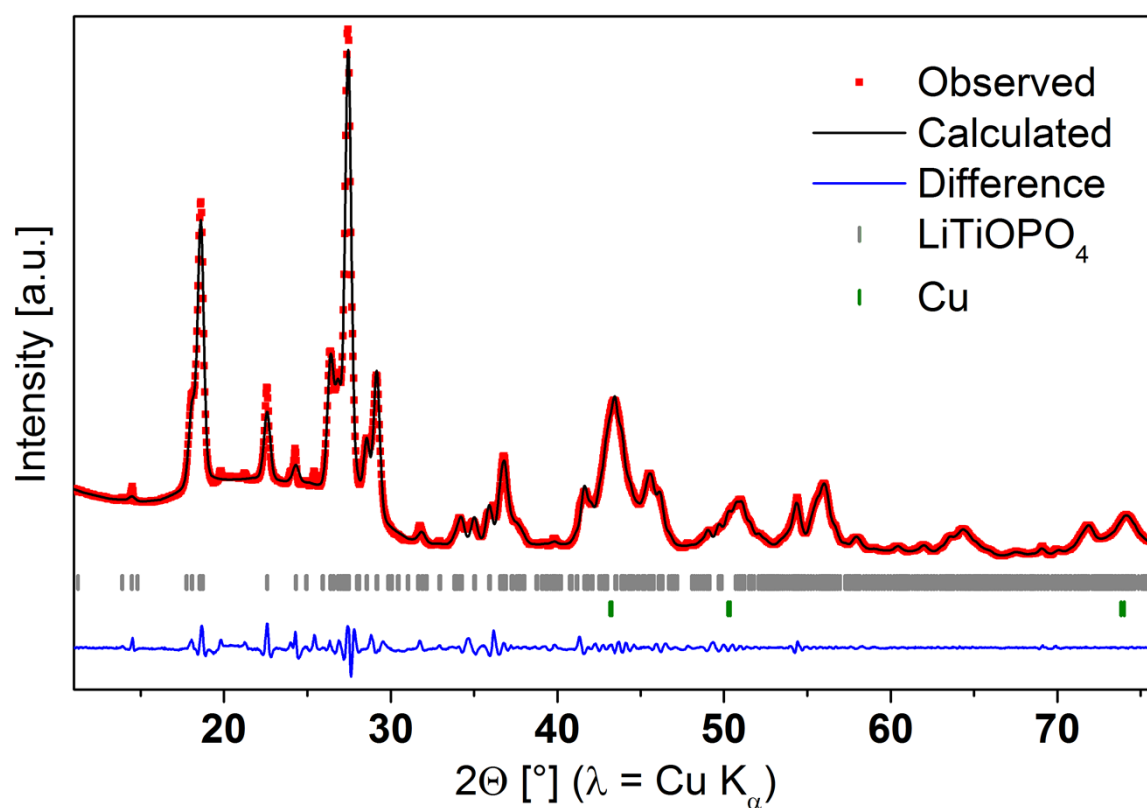


Figure S1: Refinement of the XRD of  $\text{Cu}_{0.5}\text{TiOPO}_4$  lithiated to 1.71 V (sample c).

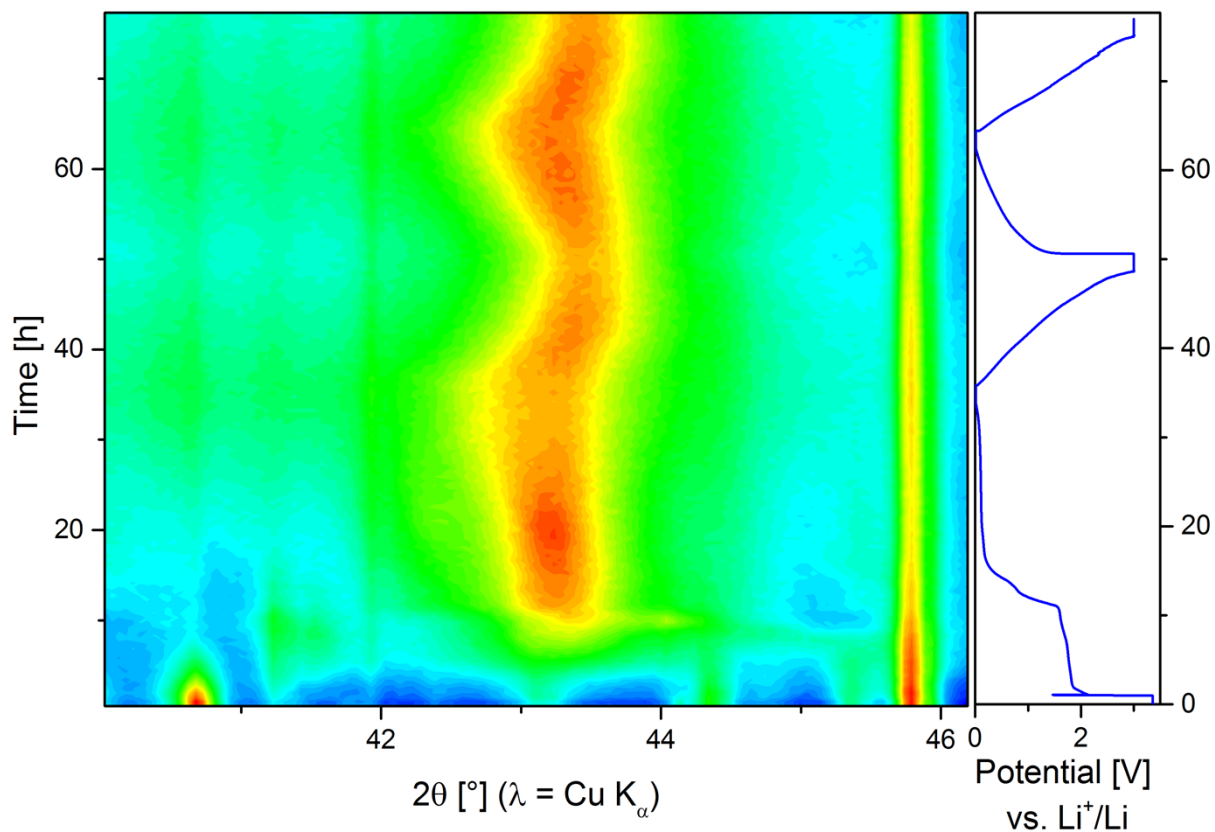


Figure S2: Contour plot of an in situ XRD measurement of an electrode containing  $\text{Cu}_{0.5}\text{TiOPO}_4$  around the copper 111 reflection ( $43.3^\circ$ ) for two cycles at a specific current of  $21.1 \text{ A/kg}$  (blue: low intensity; red: high intensity). On the right hand side, the corresponding galvanostatic curve is shown.

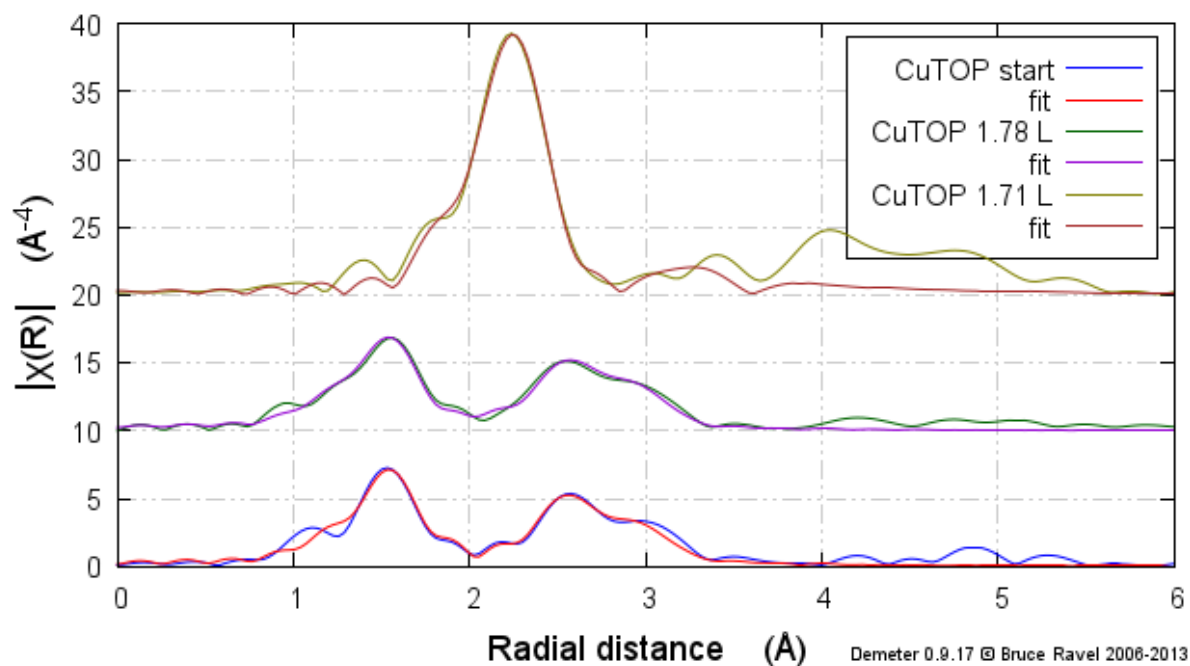
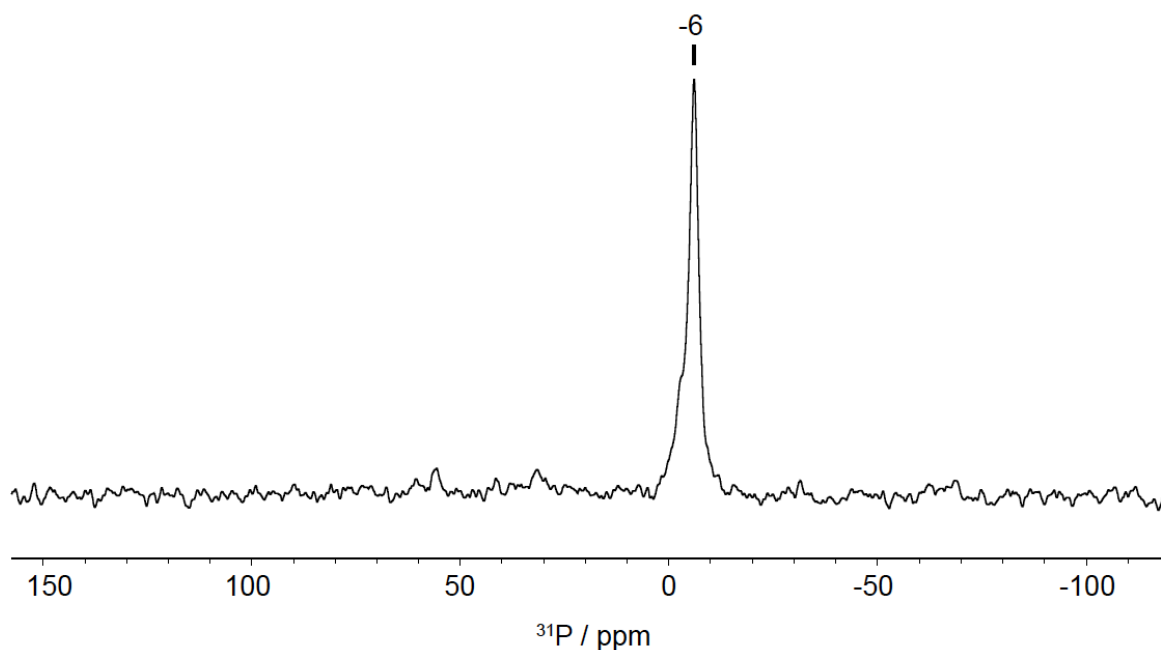


Figure S3: Fit of the Fourier transform of EXAFS-spectra of pristine  $\text{Cu}_{0.5}\text{TiOPO}_4$  and of  $\text{Cu}_{0.5}\text{TiOPO}_4$  lithiated to  $1.78 \text{ V}$  (sample b) and  $1.71 \text{ V}$  (sample c) (from bottom to top).

**Table S1: Fitted scattering paths of the EXAFS-spectra of pristine  $\text{Cu}_{0.5}\text{TiOPO}_4$  and  $\text{Cu}_{0.5}\text{TiOPO}_4$  lithiated to 1.78 V and 1.71 V.**

Sample	Path	N	S02	sigma <sup>2</sup>	e0	$\Delta r$	Reff	R
$\text{Cu}_{0.5}\text{TiOPO}_4$ start  R-factor: 0.0043203	O5.1	4	0.701	0.00366	-0.731	-0.03121	1.97780	1.94659
	O2.1	2	0.701	0.01308	-0.731	-0.05080	2.29030	2.23950
	Ti1.1	2	0.701	0.00431	-0.731	0.00511	2.93250	2.93762
	P1.1	2	0.701	0.01456	-0.731	-0.13074	3.17800	3.04726
	Ti1.2	2	0.701	0.00283	-0.731	0.00131	3.33290	3.33421
$\text{Cu}_{0.5}\text{TiOPO}_4$ 1.78 V  R-factor: 0.0058159	O5.1	4	0.880	0.00564	-0.358	-0.02390	1.97780	1.95390
	O2.1	2	0.880	0.01380	-0.358	-0.00977	2.29030	2.28053
	Ti1.1	2	0.880	0.00547	-0.358	0.01159	2.93250	2.94409
	P1.1	2	0.880	0.02346	-0.358	-0.11668	3.17800	3.06132
	Ti1.2	2	0.880	0.00387	-0.358	0.00808	3.33290	3.34097
$\text{Cu}_{0.5}\text{TiOPO}_4$ 1.71 V  R-factor: 0.0111593	Cu.1	12	0.625	0.00895	4.478	-0.01539	2.55270	2.53731
	Cu.2	6	0.625	0.01333	4.478	-0.02176	3.61000	3.58824
	Cu.1- Cu.1	48	0.625	0.01790	4.478	-0.02308	3.82900	3.80592
	Cu.1- Cu.1	24	0.625	0.01790	4.478	-0.02627	4.35770	4.33143
	Cu.1- Cu.2	48	0.625	0.02228	4.478	-0.02627	4.35770	4.33143
	Cu.3	24	0.625	0.02332	4.478	-0.02665	4.42130	4.39465
	Cu.1- Cu.1	48	0.625	0.01790	4.478	-0.02871	4.76330	4.73459
	Cu.1- Cu.3	96	0.625	0.03227	4.478	-0.02871	4.76330	4.73459



**Figure S4:**  $^{31}\text{P}$  NMR spectra of triphenyl phosphine. The spinning rate was set to 10 kHz. The recycling delay was set to 1 s. A 120 kHz radio frequency  $90^\circ$  pulse was used to recorded this spectra.

**Table S2:** CASTEP NMR calculations and experimental chemical shift ( $\delta_{\text{iso}}$ ) of triphenyl phosphine (external reference), triclinic  $\text{LiTiOPO}_4$ , and orthorhombic  $\text{LiTiOPO}_4$ . The coordinates were taken from COD <sup>1</sup> for  $\text{PPh}_3$  and from ICSD for  $\text{LiTiOPO}_4$ .

Compound	Calculated $\delta_{\text{iso}}$ (ppm)	Normalised $\delta_{\text{iso}}$ (ppm)	Experimental $\delta_{\text{iso}}$ (ppm)
$\text{PPh}_3$	300	6	6
$\text{LiTiOPO}_4$ triclinic	285/290*	-21/-16*	-9/-3*
$\text{LiTiOPO}_4$ orthorhombic	289	-17	-

\* The peaks have the same intensities.

1. Grazulis, S.; Daskevicius, A.; Merkys, A.; Chateigner, D.; Lutterotti, L.; Quiros, M.; Serebryanaya, N. R.; Moeck, P.; Downs, R. T.; Le Bail, A., *Nucleic Acids Res.* **2012**, *40*, D420.