In situ electron diffraction tomography using a liquid-electrochemical TEM cell for crystal structure determination of cathode materials for Li-ion batteries

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MATERIAL SYNTHESIS AND CHARACTERIZATION

$LiFePO_4$ was synthesized by hydrothermal method, using $FeSO_4 \times 7H_2O$, H_3PO_4 (85%) and LiOH as precursors[1]. The reaction was performed in a Berghof autoclave containing inner Teflon vessel. The obtained sample was characterized by powder X-ray diffraction (Figure S1, PXRD, Huber Guinier camera G670, an ImagePlate detector, $CuK\alpha_1$ radiation). Jana 2006 software was used for the structure refinement (**Table S2**, **Table S3**)[2]. The pattern corresponded to $LiFePO_4$ olivine-type structure (**Table S1**, Figure S1, **Table S2**, **Table S3**). Fe:P ratio was 49.4±0.5/50.6±0.5 determined by energy-dispersive X-ray spectroscopy (EDX) using a transmission electron microscope (TEM) FEI Tecnai Osiris (200kV) equipped with Super-X EDX detector (Figure S2**Error! Reference source not found.**). To prepare the TEM specimen for the *ex situ* EDX analysis, a few drops of $LiFePO_4$ suspension in ethanol were deposited on a Cu grid coated with holey carbon layer.

The resulting $LiFePO_4$ powder was carbon coated by decomposition of glucose in Ar/H_2 environment. The annealing process was carried out in a quartz combustion tube which was placed in a furnace and was rapidly warmed up to 700 °C (50 °C/min) under forming gas (95% Ar, 5% H_2). Then, the sample was kept at constant temperature (500 °C) in 50 sccm of forming gas (95% Ar, 5% H_2) for 2 hours.

Table S1. Crystallographic data and refinement parameters for the $LiFePO_4$, $LiFePO_4$/C and $FePO_4$ structures.

Sample	$LiFePO_4$	$LiFePO_4$/C	$FePO_4$ (4.2V)
Method	PXRD	*In situ* EDT in liquid	*In situ* EDT in liquid
Formula	$LiFePO_4$	$LiFePO_4$	$FePO_4$
Space group	*Pnma*	*Pnma*	*Pnma*
a, Å	10.3298(3)	10.198(6)	9.840(3)
b, Å	6.0049(2)	6.016(2)	5.742(4)
c, Å	4.6936(2)	4.752(2)	4.779(2)
V, $Å^3$	291.14(2)	291.5(2)	270.0(2)
Z	4	4	4
ρ, g/cm^3	3.601	3.783	3.881
Radiation	X-ray, $CuK\alpha_1$	Electron	Electron
Wavelength, Å	1.54056	0.0251	0.0251
2θ range, deg.	10 - 95	-	-
Scanned angular range, deg.	-	35	62
Number of reflections, $I>\sigma(I)$	-	359	582
Unique reflections:	-		
$I>\sigma(I)$	-	171	151
$I>3\sigma(I)$	-	166	147
Used in refinement	-	157	124
Parameters refined	12	14	12
R_F (R_P, R_{wP})	0.072, 0.007, 0.009	0.310	0.280

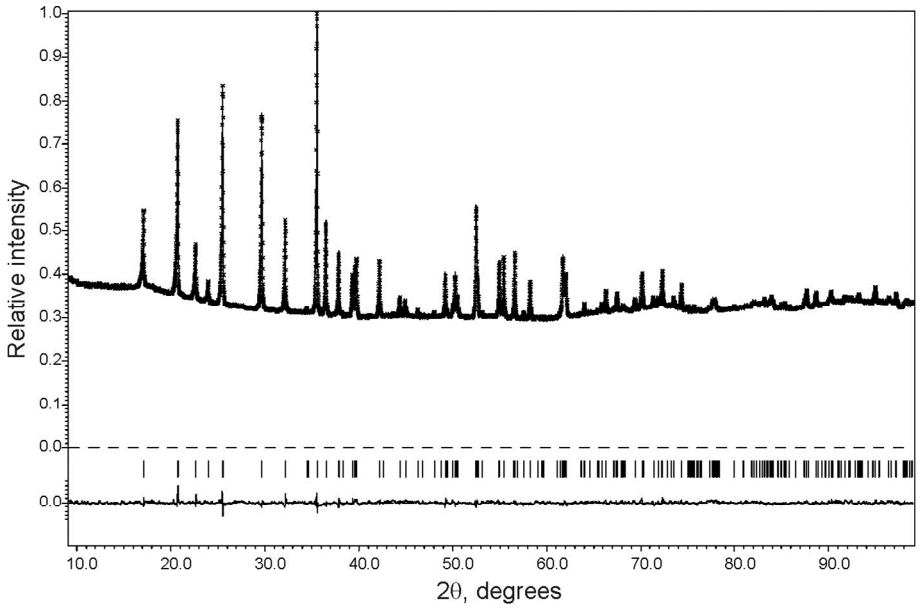

Figure S1. Experimental, calculated and difference PXRD profiles after Rietveld refinement of the $LiFePO_4$ structure. The bars mark the reflection positions for $LiFePO_4$.

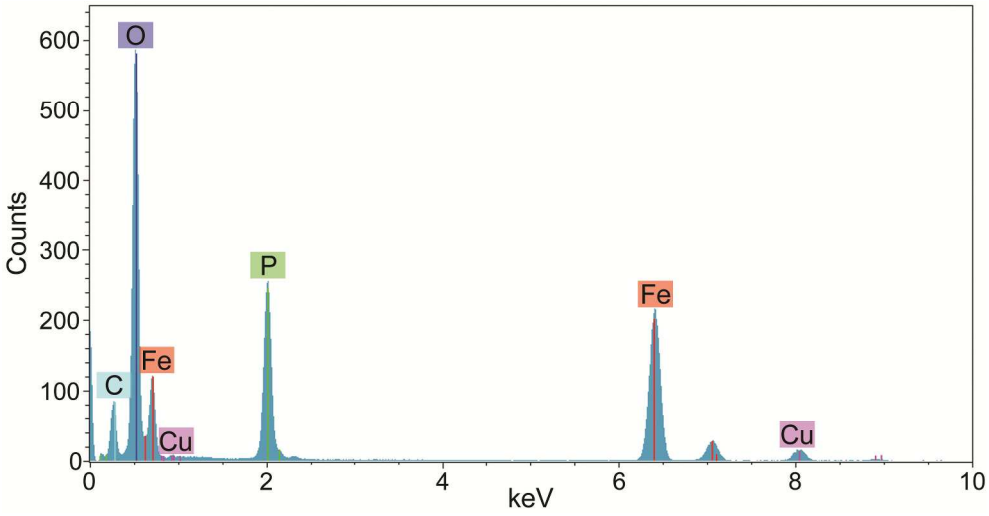

Figure S2. EDX spectrum of $LiFePO_4$. The compound contains Fe, P and O. Cu and C signals originate from a TEM grid.

Table S2. Fractional atomic coordinates, atomic displacement parameters for $LiFePO_4$ refined from PXRD.

Atom	Position	Occupancy	*x/a*	*y/b*	*z/c*	U_{iso}, Å^2
Li1	4*a*	1	0	0	0	0.0026(3)
Fe1	4*c*	1	0.28265(6)	1/4	0.9749(2)	0.0026(3)
P1	4*c*	1	0.0958(1)	1/4	0.4215(3)	0.0026(3)
O1	4*c*	1	0.0969(3)	1/4	0.7476(5)	0.0026(3)
O2	4*c*	1	0.4536(3)	1/4	0.2017(4)	0.0026(3)
O3	8*d*	1	0.1658(2)	0.0494(3)	0.2857(3)	0.0026(3)

Table S3. Selected interatomic distances for $LiFePO_4$ refined from PXRD.

Bond	Length, Å	Bond	Length, Å
Li1-O1	2.158(2) x2	Fe1-O3	2.074(2) x2
Li1-O2	2.108(2) x2	Fe1-O3	2.244(2) x2
Li1-O3	2.195(2) x2	P1-O1	1.530(3)
Fe1-O1	2.195(3)	P1-O2	1.578(4)
Fe1-O2	2.061(3)	P1-O3	1.543(2) x2

IN SITU ELECTROCHEMISTRY TEM

In situ electrochemical experiments in liquid were performed in a Protochips Poseidon TEM holder. A Tecnai G2 TEM operated at 200 kV was used. It was equipped with electron energy loss spectrometer (EELS) (Tridiem Gatan). The electron diffraction tomography (EDT) patterns were recorded using a Gatan OneView CMOS camera.

The electrochemical chip has silicon nitride windows, and an amorphous carbon glass working electrode, which is transparent under the electron beam in TEM. A drop of $LiFePO_4$/C suspension in ethanol was put on the electrochemical chip and dried in air. The cell was sealed and the holder was inserted in the microscope column. 1.0 M $LiPF_6$ EC/DMC (1:1) electrolyte was injected in the cell using a motorized pump. The liquid flow was stopped during TEM investigations.

In a completely filled 500 nm cell (bottom chip without spacer) the central beam in diffraction was not observed due to significant scattering of electrons by liquid media. EELS showed the absence of elastically scattered electrons. Therefore, the thickness of liquid was reduced by irradiation by the beam ("beam shower"). According to EELS, the liquid layer was still present, but became thinner, since elastically scattered electrons were observed (zero loss peak, 0 eV appeared (Figure S3)).

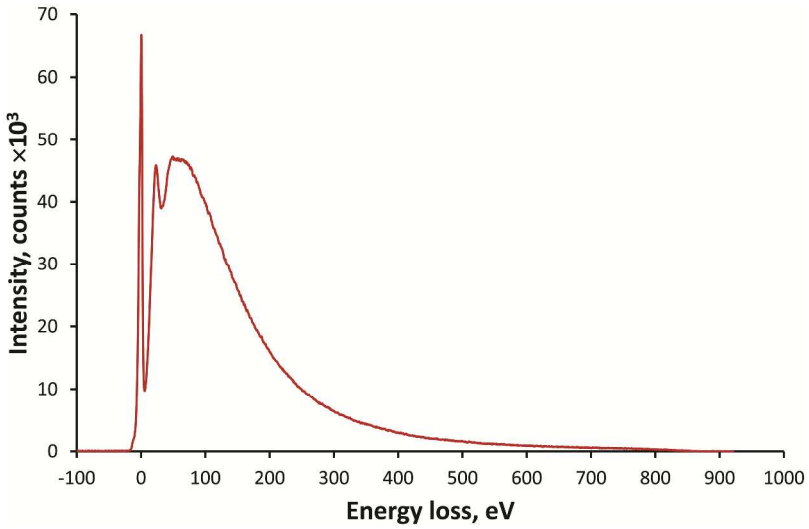

Figure S3. EELS spectrum of electrochemical cell filled with 1.0 M $LiPF_6$ EC/DMC (1:1) electrolyte after applying "beam shower".

EDT was performed by collecting electron diffraction patterns with an angular step of 1 degree within $\pm 30^{o}$ angular range. In case of the $LiFePO_4$ experiment only 35° of the series were suitable for the reconstruction of the reciprocal space, since the crystal orientation had been affected by the liquid movement during the experiment.

Another cell was charged galvanostatically in potential range from 2.5 to 4.2 V using SP200 Bio logic ultra low current potentiostat as shown in the Figure S4. Immediately after charging the electron diffraction tomography was performed in the same manner as for $LiFePO_4$. For this charged sample, the whole 60° series was suitable for the three-dimensional reconstruction of the reciprocal lattice.

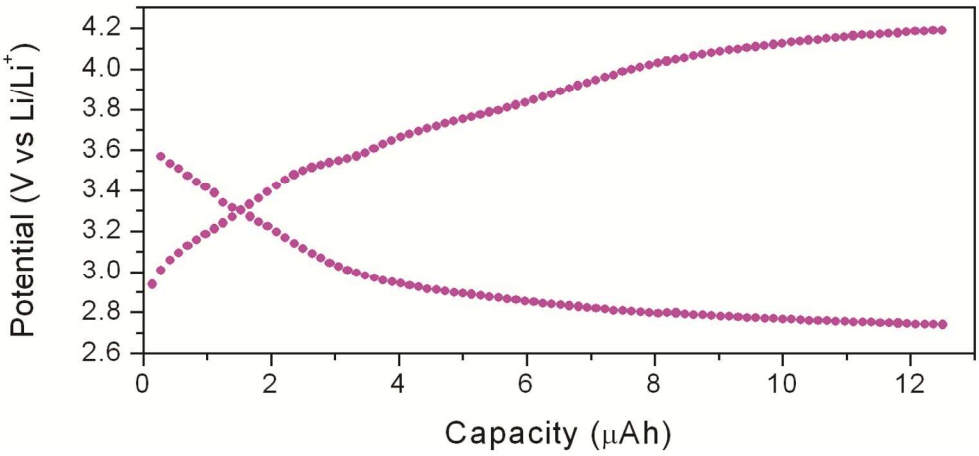

Figure S4. Galvanostatic curve for $LiFePO_4$ crystals in contact of glassy carbon electrode acquired using electrochemical cell.

The data was handled using PETS and JANA2006 software to reconstruct reciprocal space, index and extract the intensities of reflections[3,2]. The structure solution was performed by charge flipping algorithm implemented in SUPERFLIP[4]. The structure was refined in JANA2006.

The experimental details of EDT experiments are shown in **Table S1**. Only reflections with intensity I higher than $3\sigma(I)$ were used. All atomic positions were refined with common isotropic atomic displacement parameter. In case of $FePO_4$, the parameter was fixed to 0.001 $Å^2$. Liquid media significantly decreased the signal-to-noise ratio causing difficulty in precise location of some oxygens. Thus, the O1 position could not be precisely determined, resulting in quite long 1.68 Å P-O1 bond. Therefore, the P-O bond length was restricted using soft constrains. Since the dynamical effects are intrinsic in electron diffraction, significant disagreement between experimental (F_{obs}) and calculated (F_{calc}) structure factors may occur for some reflections. For $LiFePO_4$ 9 reflections which exceed $||F_{obs}|-|F_{calc}||> 60\sigma(F_{obs})$ were skipped from the refinement. In case of $FePO_4$ 23 reflections were not used ($||F_{obs}|-|F_{calc}||> 50\sigma(F_{obs})$). Atomic parameters (

Table S4, **Table S 6**), bond lengths (**Table S 5**,
Table S 7) and $|F_{obs}|-|F_{calc}|$ plots (Figure S5) are shown below.

Table S4. Fractional atomic coordinates, atomic displacement parameters for $LiFePO_4$ refined from *in situ* EDT data.

Atom	Position	Occupancy	*x/a*	*y/b*	*z/c*	U_{iso}, Å^2
Li1	4*a*	1.1(2)	0	0	0	0.005(4)
Fe1	4*c*	1	0.282(2)	1/4	0.975(3)	0.005(4)
P1	4*c*	1	0.089(3)	1/4	0.421(4)	0.005(4)
O1	4*c*	1	0.072(5)	1/4	0.749(5)	0.005(4)
O2	4*c*	1	-0.047(3)	1/4	0.279(7)	0.005(4)
O3	8*d*	1	0.153(3)	0.042(4)	0.283(5)	0.005(4)

Table S 5. Selected interatomic distances for $LiFePO_4$ refined from *in situ* EDT data.

Bond	Length, Å	Bond	Length, Å
Li1-O1	2.02(2) x2	Fe1-O3	2.04(2) x2
Li1-O2	2.02(2) x2	Fe1-O3	2.29(3) x2
Li1-O3	2.05(3) x2	P1-O1	1.53(4)
Fe1-O1	2.36(5)	P1-O2	1.55(3)
Fe1-O2	2.07(4)	P1-O3	1.52(3) x2

Table S 6. Fractional atomic coordinates, atomic displacement parameters for $FePO_4$ refined from *in situ* EDT data.

Atom	Position	Occupancy	*x/a*	*y/b*	*z/c*	Uiso, $Å^2$
Fe1	4c	1	0.282(1)	1/4	0.962(3)	0.001
P1	4c	1	0.105(2)	1/4	0.403(3)	0.001
O1	4c	1	0.115(2)	1/4	0.732(6)	0.001
O2	4c	1	-0.049(3)	1/4	0.314(5)	0.001
O3	8d	1	0.176(2)	0.028(5)	0.285(4)	0.001

Table S 7. Selected interatomic distances for $FePO_4$ refined from *in situ* EDT data.

Bond	Length, Å	Bond	Length, Å
Fe1-O1	1.98(3)	P1-O1	1.58(3)
Fe1-O2	1.97(3)	P1-O2	1.58(3)
Fe1-O3	1.86(2) x2	P1-O3	1.56(2) x2
Fe1-O3	2.26(2) x2		

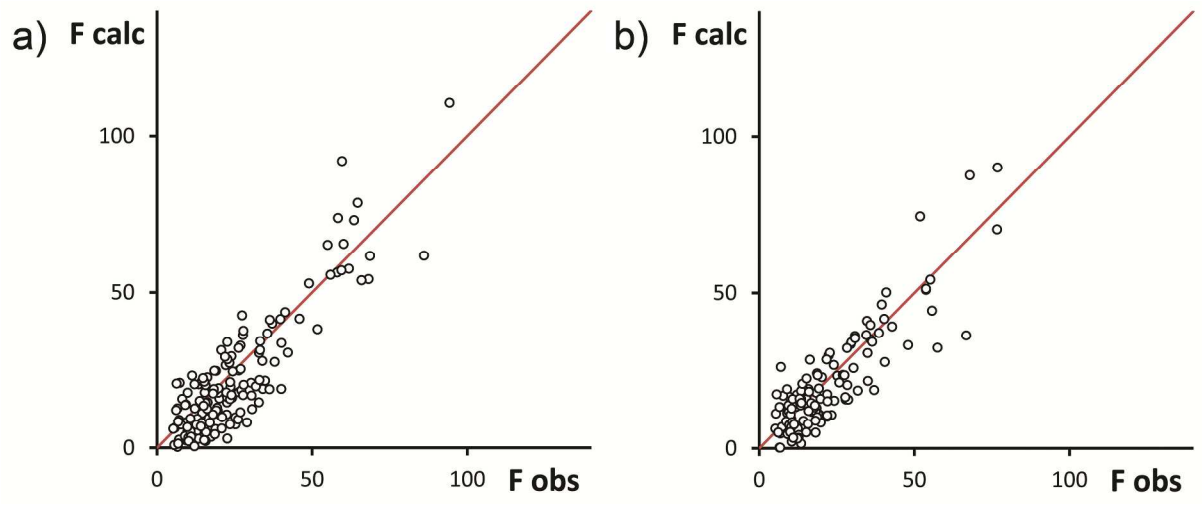

Figure S5. $|F_{obs}|$-$|F_{calc}|$ plots for the $LiFePO_4$ (a) and $FePO_4$ (b) for *in situ* EDT experiments.

(1) Drozhzhin, O. A.; Sumanov, V. D.; Karakulina, O. M.; Abakumov, A. M.; Hadermann, J.; Baranov, A. N.; Stevenson, K. J.; Antipov, E. V. *Electrochim. Acta* **2016**, *191*, 149–157.

(2) Petrícek, V.; Dušek, M.; Palatinus, L. *Zeitschrift fur Krist.* **2014**, *229* (5), 345–352.

(3) Palatinus, L. *PETS–program for analysis of electron diffraction data*; Institute of Physics: Prague, Czech Republic, 2011.

(4) Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* **2007**, *40* (4), 786–790.