

Supporting information

EXPERIMENTAL METHODS

LiFePO₄ starting material

The experiments were performed with battery grade LiFePO₄ supplied by Tantung. According to the technical data sheet, this material has a specific surface area of 11.66 m²/g and an average particle size of 2.35 μm (D₅₀=2.35 μm, D₉₀=4.63 μm, D₁₀=1.30 μm). The material is carbon coated, but the final carbon content is < 3%. According to the specifications, this material provides a capacity of 152 mAh/g at C/5 and of 140 mAh/g at 1C. In our measurements, we obtain values of capacity around 5-10% lower, which we attribute to the fact that our method of electrode preparation and cell design is not optimal. However, this difference in capacity is reasonably small. In addition, in this work, we use the electrochemical test in order to characterize the Li content in Li_xFePO₄ samples and in order to compare the performance of LiFePO₄ samples prepared following different procedures. LiFePO₄ acts here as an internal standard and therefore the results are corrected from the experimental inaccuracies associated to cell design and electrode preparation.

Electrode preparation and electrochemical tests

LiFePO₄ composite electrodes were prepared as follows. 75%wt of powder sample (LiFePO₄), 20%wt of acetylene carbon (Chevron), and 5%wt polytetrafluoroethylene (PTFE, DuPont) were mixed, grinded, and pressed to ~100 μm thick sheets. The electrodes were cut in discs of 1 cm diameter, which were dried under vacuum at 120°C for approximately 18 hours. The electrochemical tests were performed in Swagelok® type cells, which were dried at 80°C overnight. The cells were assembled in an argon glovebox (< 1 ppm water content, < 10 ppm oxygen content). The cells were assembled with a sample pellet, followed by a 1.4 cm-diameter separator (glass microfiber filters; Whatman®) soaked with 8 drops of LP30 (1 M LiPF₆ in EC:DMC, BASF) and a 1 cm-diameter lithium disc. Galvanostatic cycling with potential limitation (GCPL) measurements were done at 25°C with a BMP3 multichannel potentiostat.

Digestion of samples for inductive coupled plasma (ICP) analysis

0.1 g of each powder sample was digested in 2 ml of a solution of 20%wt of HCl (Analar Normapur, BDH) and 20% wt HNO₃ (Aristar, BDH) in deionized water. The mixture was stirred at ~60°C for approximately 2 hours. In order to verify that the entire sample has been digested, the mixture was filtered with a Gooch funnel. The filtered solid was dried and weighted. The solid accounted for less than 5% of the sample weight, and it was tentatively ascribed to the carbon content in the sample.

Chemical delithiation of LiFePO₄

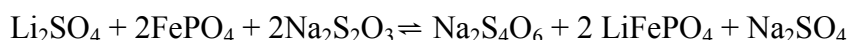
The procedure for delithiation of LiFePO₄ followed the work by Raman et al. (C. V. Ramana, A. Mauger, F. Gendron, C. M. Julien, and K. Zaghib, *J. Power Sources*, 2009, 187, 555–564). Lithium iron phosphate (LiFePO₄, TATUNG) and potassium persulfate (K₂S₂O₈, Sigma-Aldrich ≥99.0 %) were mixed in a molar ratio of K₂S₂O₈ : LiFePO₄ equal to 1:2. 11.7 g of LiFePO₄ and 10 g of K₂S₂O₈ were mixed in 370 ml of deionized water and the reaction was held for 24 hours at room temperature under stirring. The precipitate was washed, filtered, and dried at 80°C for 24 hours. Under these conditions, full delithiation of LiFePO₄, forming

FePO₄, was confirmed by X-ray diffraction (XRD), electrochemical tests and ICP analysis.

Chemical lithiation of FePO₄

1. Characterization of the kinetics of lithiation of FePO₄

The experimental procedure followed in the study of the kinetics of chemical lithiation of FePO₄ is as follows. Delithiated FePO₄ (prepared as above explained) was mixed with lithium sulphate (Li₂SO₄, Sigma-Aldrich, ≥98.5 %) and sodium thiosulphate (Na₂S₂O₃, Sigma-Aldrich, ≥99.5 %). The stoichiometry of the lithiation reaction is as follows:



Our experiments were done with a ratio of Li₂SO₄: Na₂S₂O₃: FePO₄ equal to 2:4:1. Therefore, these experiments are performed in the presence of an excess of reducing agent and lithium salt. This was done in order to guarantee that the lithiation of FePO₄ will not be coupled to major changes in the concentration thiosulphate or lithium cations in solution. The mixture of Li₂SO₄ and Na₂S₂O₃ were first dissolved in deionized water. FePO₄ was then added into the solution and stirred at room temperature as time was started. Precipitated samples were taken at 5, 20, 60, 120, 240, and 600 minutes, respectively. The samples were washed, filtered, and dried at 80°C for 24 hours. The powder samples were examined by XRD, electrochemical measurements and ICP analysis.

2. Study of the effect of the effect of the lithium to sodium concentration ratio.

The chemical lithiation of FePO₄ in solutions with different ratio of concentrations of lithium and sodium cations was studied as follows. Delithiated FePO₄ (prepared as above explained) was mixed with Li₂SO₄ (Sigma-Aldrich, ≥98.5 %) or LiCl (Sigma-Aldrich, ≥99.0 %), NaCl (Sigma-Aldrich, ≥99.0 %) and Na₂S₂O₃ (Sigma-Aldrich, ≥99.5 %). In all these experiments, [Na₂S₂O₃]=0.3M. The molar ratio of Li⁺: Na⁺: S₂O₃²⁻: FePO₄ is given in the table below. Therefore, all these experiments were performed in the presence of an excess of reducing agent and lithium salt. All concentrations are given in the table below.

[Li ⁺] : [Na ⁺] : [S ₂ O ₃ ²⁻] : [FePO ₄]	Chemicals	Amount/ g	Deionized water / L
1 : 10 : 5 : 0.5	LiCl	0.51	0.201
	Na ₂ S ₂ O ₃	15.0	
	FePO ₄	0.91	
1 : 50 : 5 : 0.5	LiCl	0.51	0.201
	Na ₂ S ₂ O ₃	15.0	
	FePO ₄	0.91	
	NaCl	28.6	

1 : 100 : 5 : 0.5	LiCl	0.51	0.201
	Na ₂ S ₂ O ₃	15.0	
	FePO ₄	0.91	
	NaCl	63.6	

3. Study of the lithiation of FePO₄ in artificial brines

The chemical lithiation of FePO₄ was also studied in artificial brines. The composition of the natural brines is very varied. In this work, we have prepared two types of artificial brines whose composition is the same as two typical brines found in the lithium reserve in Central Altiplano, Bolivia (F. Risacher and B. Fritz, *Chem. Geol.*, 1991, 90, 211–231). We performed these experiments in the presence of [Na₂S₂O₃]=0.3M. The molar ratio of Li⁺: Na⁺: S₂O₃²⁻: FePO₄ is given in the table below. Therefore, all these experiments were performed in the presence of an excess of reducing agent and lithium salt. All concentrations are given in the table below.

[Li ⁺] : [Na ⁺] : [S ₂ O ₃ ²⁻] : [FePO ₄]	Chemicals	Amount/g	Deionized water / L
1 : 76.6 : 5 : 0.5	LiCl	0.34	0.134
	Na ₂ S ₂ O ₃	10.0	
	FePO ₄	0.61	
	NaCl	31.4	
	KCl	2.00	
	MgCl ₂	8.19	
1 : 15 : 1.5 : 0.5	LiCl	0.57	0.067
	Na ₂ S ₂ O ₃	5.00	
	FePO ₄	1.01	
	NaCl	9.42	
	K ₂ SO ₄	3.51	
	MgCl ₂	17.8	

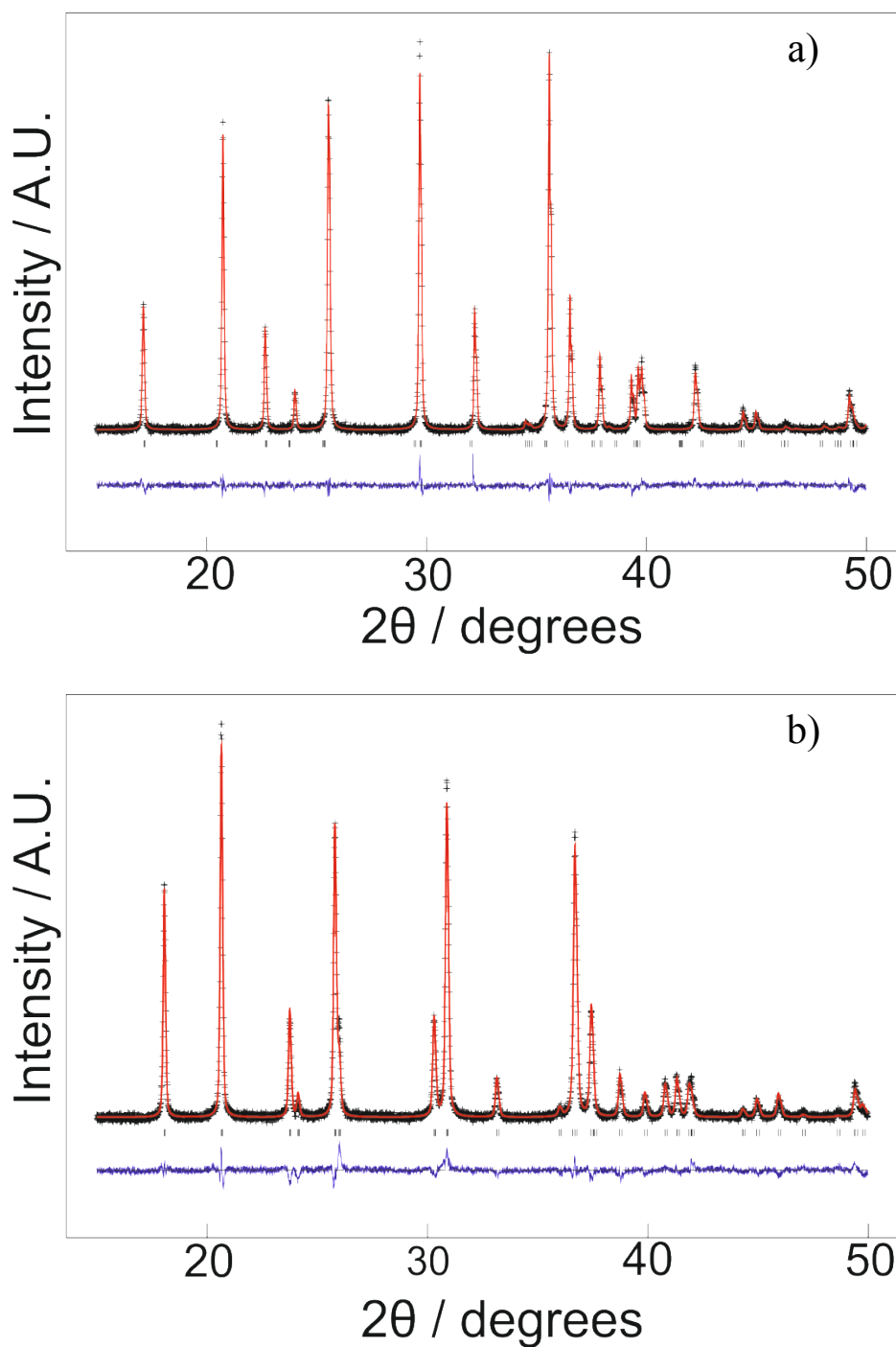


Fig S1. Fit to XRD data of a) LiFePO_4 (Tatung) and b) FePO_4 , where the latter was prepared by chemical delithiation of LiFePO_4 using a 6-fold molar excess of $0.1\text{M K}_2\text{S}_2\text{O}_8$ for 24 hours. Crosses mark the data points, red line is the fit and blue line is the difference. Tick marks show the allowed reflection positions for

a) LiFePO_4 : R_{wp} 1.3%, R_{p} 1.0% and lattice parameter $a = 10.3154(2)$, $b = 5.99938(12)$, $c = 4.6889(1)$ Å

b) FePO_4 : R_{wp} 1.5%, R_{p} 1.1% and lattice parameter $a = 9.8173(3)$, $b = 5.7879(1)$, $c = 4.7815(2)$ Å

R_{p} and R_{wp} are the profile and weighted profile reliability factors as defined in the GSAS manual, reference A. C. Larson and R. B. von Dreele, General Structure Analysis System, Los Alamos National Laboratory report LAUR 86-748 (2004).

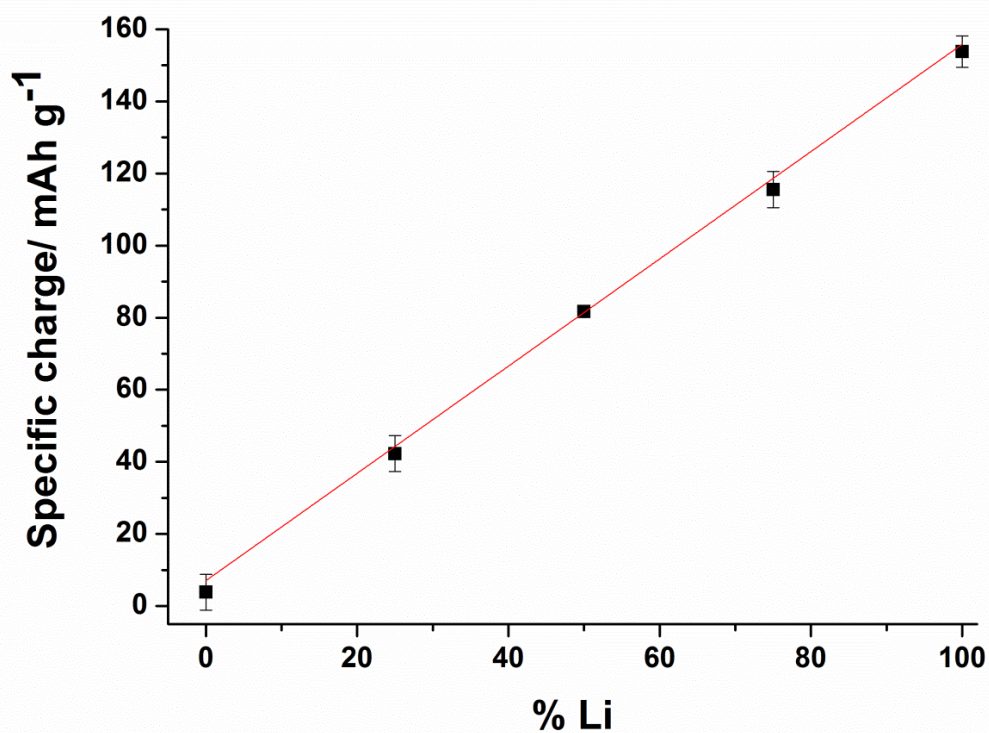


Fig S2. Validation curve for the estimation of the lithium molar content of Li_xFePO_4 samples by potentiometric titration. The results presented in this graph were obtained by mixing weighted amounts of FePO_4 and LiFePO_4 . The powder was then grounded with PTFE and acetylene black in order to prepare electrodes that were then cycled vs. lithium counter electrodes in a cell containing LP30 electrolyte.

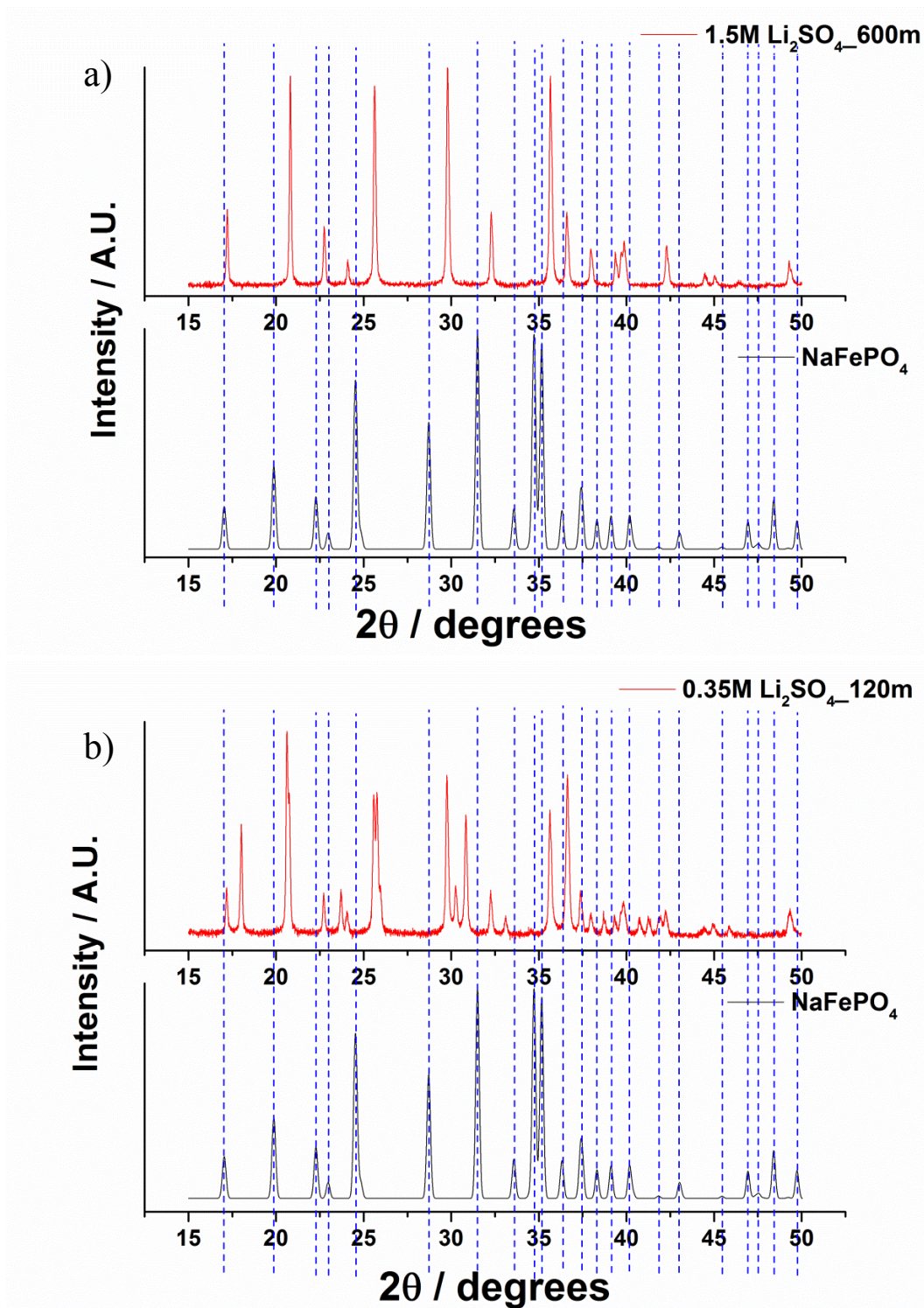


Fig. S3. Comparison of the XRD spectrum of Li_xFePO_4 samples (red curves) with literature database for olivine NaFePO_4 (black curves, from: P. Moreau, D. Guyomard, J. Gaubicher and F. Boucher, *Chemistry of Materials*, 2010, 22, 4126-4128). To help with the comparison, blue vertical lines have been drawn in the reflection positions of olivine NaFePO_4 . a) totally lithiated LiFePO_4 sample obtained by lithiation of FePO_4 with $3\text{M Na}_2\text{S}_2\text{O}_3 + 1.5\text{M Li}_2\text{SO}_4$ for 10 hours, b) partially lithiated Li_xFePO_4 sample obtained by lithiation of FePO_4 with $0.7\text{M Na}_2\text{S}_2\text{O}_3 + 0.35\text{M Li}_2\text{SO}_4$ for 120 minutes.

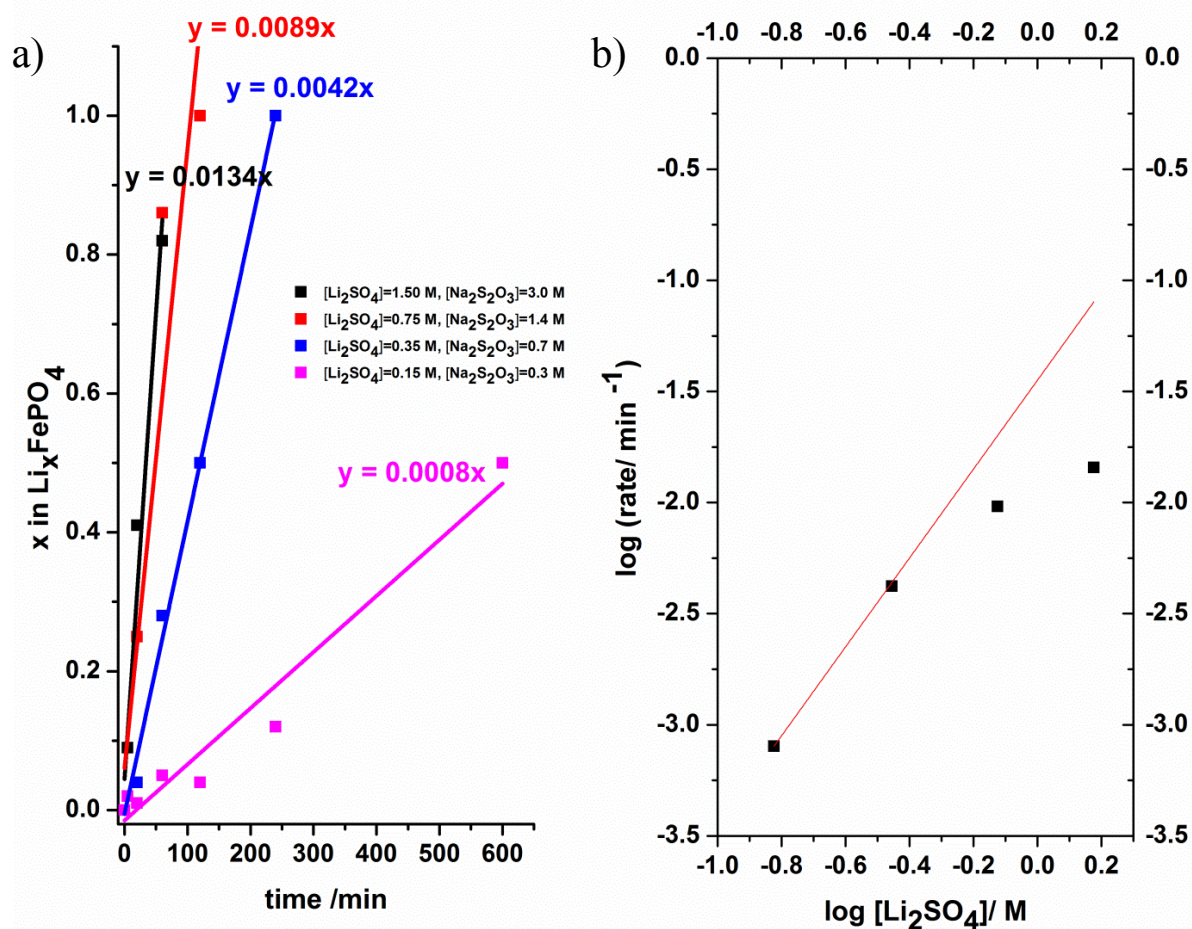


Fig S4. Analysis of the kinetics of lithiation of FePO_4 with a 4-fold excess of reagent ($\text{Li}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_3$ in molar ratio 1:2)

In Fig S4a, the initial rate is approximately constant in all cases, showing little decline until saturation of the solid phase; i.e. LiFePO_4 , is approached. The rate is less dependent on the solution concentrations between 0.75 M and 1.5 M Li_2SO_4 where rate limitations due to solid state processes may be envisaged. However, an important effect of solution dilution appears between 0.35 M and 0.15 M Li_2SO_4 , where the rate law approximates to second order in the overall concentration with a rate constant of about $0.03\text{ min}^{-1}\text{ M}^{-2}$ as shown in Fig S4b. The origin of this second order dependence may be simply a reaction that is first order in each of the reactants (thiosulfate and lithium ion).

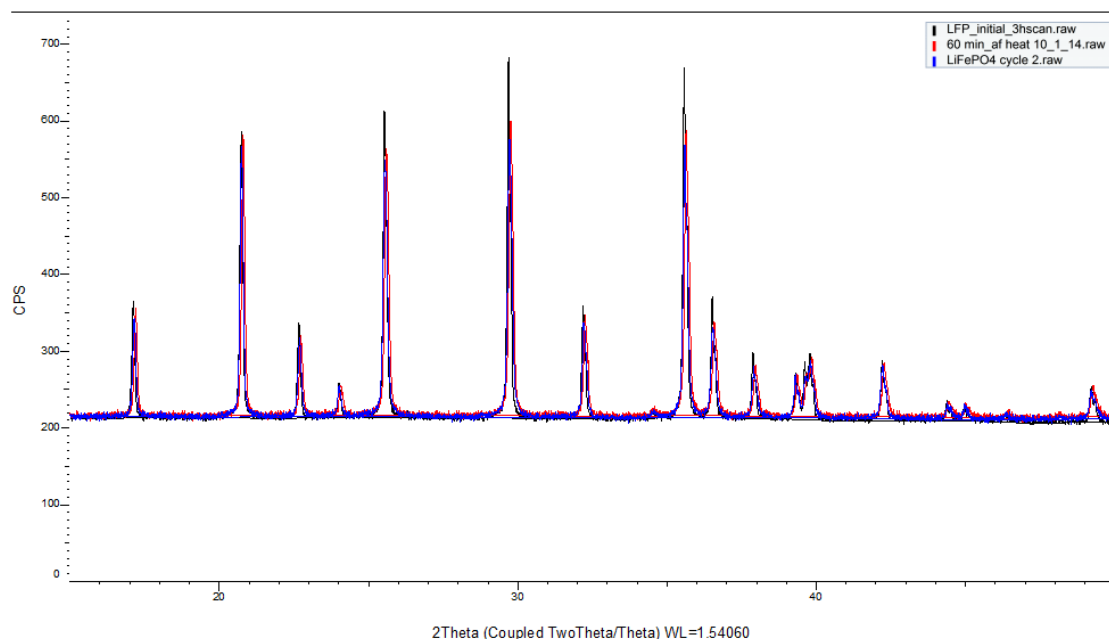


Fig. S5. Comparison of XRD pattern measured with the LiFePO_4 as received (black curve), after one cycle of delithiation + lithiation (red curve), and after 2 cycles of delithiation + lithiation (blue curve). Conditions for delithiation: 0.1M $\text{K}_2\text{S}_2\text{O}_8$ + 31mg of LiFePO_4 per ml of solution. Conditions for lithiation: 1.5M Li_2SO_4 + 3M $\text{Na}_2\text{S}_2\text{O}_3$ + 113 mg of FePO_4 per ml of solution.

The following structural parameters are obtained after Rietveld refinement of the data:

compound	a/ Å	b/ Å	c/ Å	R_{wp}	R_{p}
Initial	10.3154(2)	5.99938(12)	4.6889(1)	1.27%	0.95%
After one cycle	10.3150(2)	6.00065(13)	4.6924(1)	1.30%	1%
After 2 cycles	10.31519(23)	5.99976(13)	4.6938(1)	1.30%	1.01%

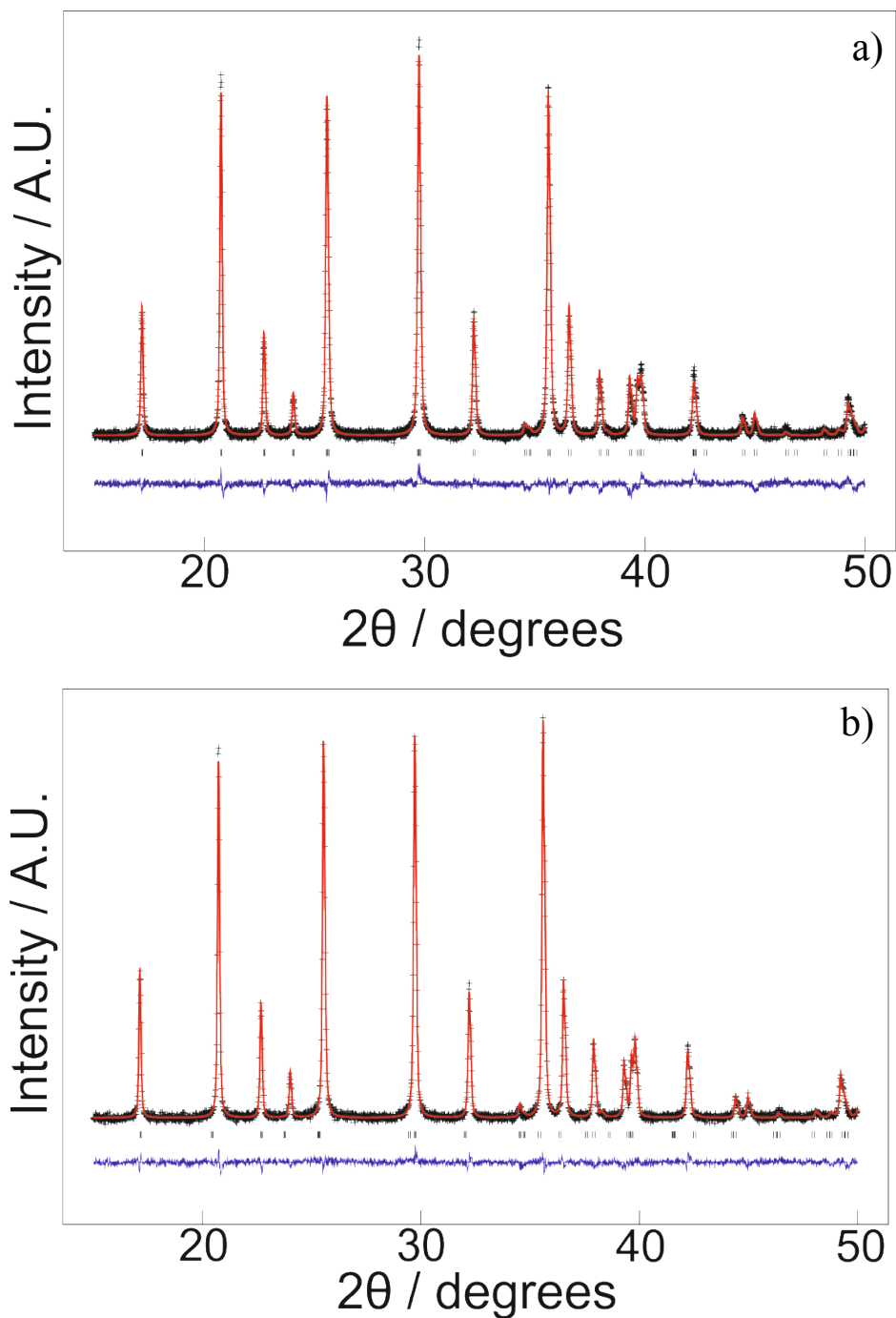


Fig S6. Fit to XRD data for LiFePO₄ prepared by chemical lithiation of FePO₄ in natural brines. Crosses mark the data points, red line is the fit and blue line is the difference. The tick marks show the allowed reflection positions for LiFePO₄.

a) 0.6g FePO₄ with [Na₂S₂O₃]=0.3M + [LiCl]=0.06M + [NaCl]=4M + [KCl]=0.2M + [MgCl₂]=0.3M for 24 hours; R_{wp} 1.3%, R_p 1.0% and lattice parameter a = 10.3080(2), b = 5.99556(13), c = 4.69349(14) Å

b) 1g FePO₄ with [Na₂S₂O₃]=0.3M + [LiCl]=0.2M + [NaCl]=2.4M + [K₂SO₄]=0.3M + [MgCl₂]=1.3M for 24 hours; R_{wp} 1.1%, R_p 0.9% and lattice parameter a = 10.31288(24), b = 5.9981(1), c = 4.6927(1) Å

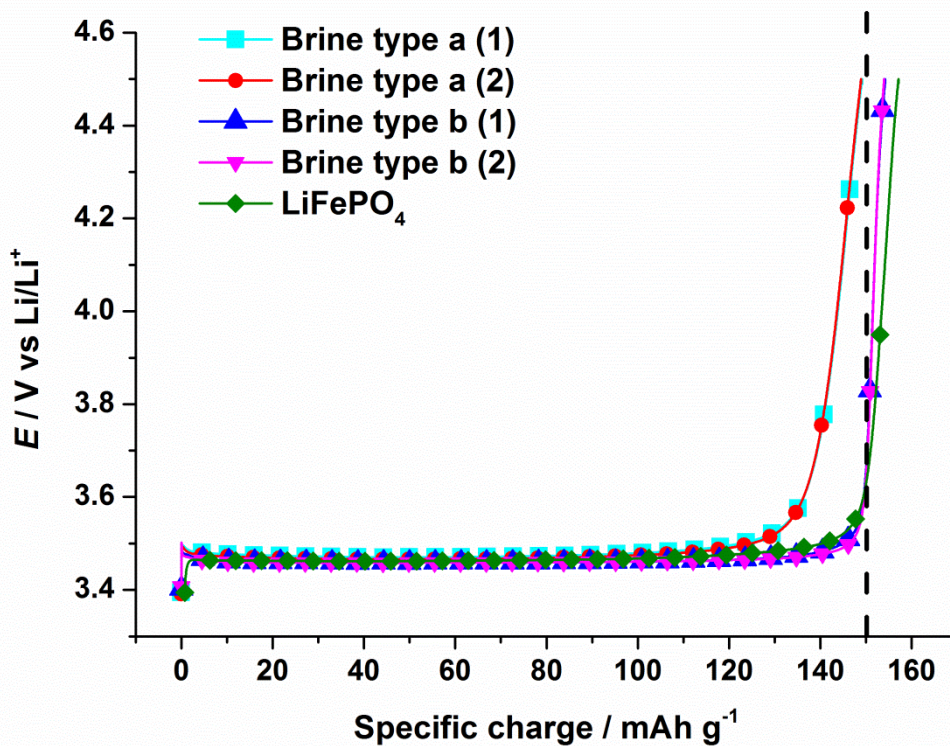


Fig S7. Electrochemical data of LiFePO₄ prepared by chemical lithiation of FePO₄ in natural brines. a) 0.6g FePO₄ with [Na₂S₂O₃]=0.3M + [LiCl]=0.06M + [NaCl]=4M + [KCl]=0.2M + [MgCl₂]=0.3M; b) 1g FePO₄ with [Na₂S₂O₃]=0.3M + [LiCl]=0.2M + [NaCl]=2.4M + [K₂SO₄]=0.3M + [MgCl₂]=1.3M. The results obtained with LiFePO₄ (Tantung) are also included in the graph for the sake of comparison.