Supplementary Information for

Synthesis, Phase Evolution Pathways and Electrochemistry of Phosphate-Based Cathode Materials Obtained Using Hydro/Solvothermal Treatment from Simple Oxides Precursors

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Table S1. Cell parameters of the hydro/solvothermally synthesized samples.

Sample	Phase Composition	**$LiFePO_4(OH)$**						
		a, Å	b, Å	c, Å	α, °	β, °	γ, °	V, Å^3
150°C Cit	$LiFePO_4(OH)$	5.3510(5)	7.2997(6)	5.1226(4)	109.271(5)	97.844(6)	106.382(6)	175.29(4)
170°C Cit	$LiFePO_4(OH)$	5.3554(5)	7.2985(5)	5.1246(4)	109.266(4)	97.869(6)	106.383(6)	175.46(3)
190°C Cit	$LiFePO_4(OH)$, ($LiFePO_4$)	5.3541(4)	7.2922(4)	5.1210(3)	109.257(4)	97.875(5)	106.383(4)	175.15(2)
210°C Cit	$LiFePO_4(OH)$, $LiFePO_4$	5.3553(3)	7.2925(3)	5.1220(3)	109.262(3)	97.881(4)	106.384(4)	175.22(2)
230°C Cit	$LiFePO_4(OH)$, $LiFePO_4$	5.3547(3)	7.2915(3)	5.1217(3)	109.251(3)	97.887(4)	106.384(4)	175.18(2)
250 °C Cit	$LiFePO_4(OH)$, $LiFePO_4$	5.3558(3)	7.2920(3)	5.1223(3)	109.253(3)	97.887(4)	106.388(4)	175.23(2)
Ox	$LiFePO_4(OH)$, $LiFePO_4$	5.3568(2)	7.2919(3)	5.1228(2)	109.247(3)	97.906(3)	106.381(3)	175.28(1)

Sample	Phase Composition	**$LiFePO_4$**			
		a, Å	b, Å	c, Å	V, Å^3
210°C Cit	$LiFePO_4(OH)$, $LiFePO_4$	10.345(1)	6.016(1)	4.6929(7)	292.12(3)
230°C Cit	$LiFePO_4(OH)$, $LiFePO_4$	10.3445(9)	6.0137(8)	4.6932(5)	291.96(3)
250 °C Cit	$LiFePO_4(OH)$, $LiFePO_4$	10.3463(8)	6.0139(6)	4.6943(4)	292.09(3)
Ox	$LiFePO_4(OH)$, $LiFePO_4$	10.3473(9)	6.0146(8)	4.6939(5)	292.12(2)
Asc	$LiFePO_4$	10.3425(5)	6.0078(2)	4.6966(3)	291.83(3)
EDTA	$LiFePO_4$	10.3416(4)	6.0116(3)	4.6965(3)	291.99(4)
EG	$LiFePO_4$	10.3375(6)	6.0083(3)	4.6940(2)	291.55(3)
EG Cit	$LiFePO_4$	10.3390(7)	6.0058(4)	4.6948(3)	291.52(5)
EG EDTA	$LiFePO_4$	10.3417(6)	6.0087(3)	4.6967(3)	291.86(4)

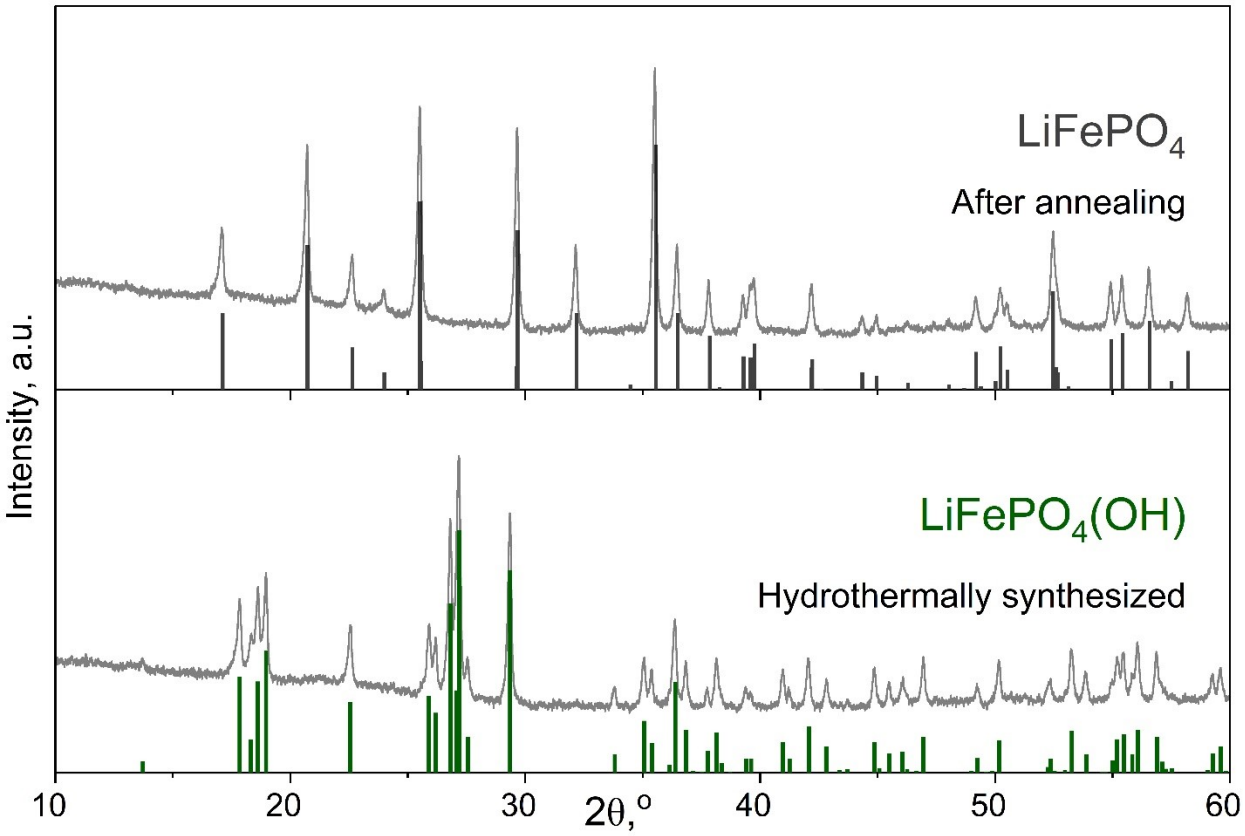
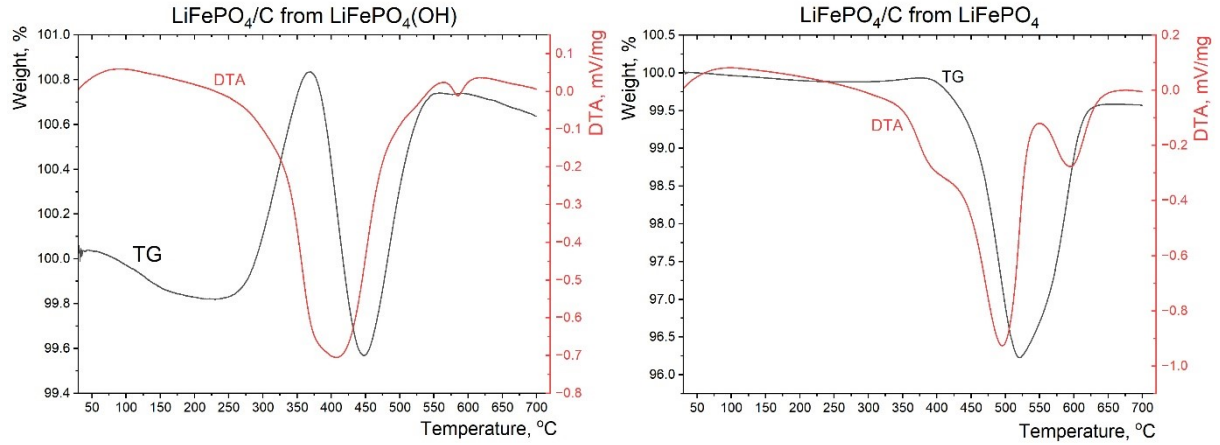


Fig. S1. The comparison of PXRD patterns of hydrothermally synthesized sample with citric acid and of its after the annealing procedure proves the successful conversion of $LiFePO_4(OH)$ into $LiFePO_4$.



C %wt = 4.21 %

C %wt = 5.23 %

Carbon content calculated according to the following reaction:

$$LiFePO_4/C + \frac{5}{2}O_2 \rightarrow \frac{1}{3}Li_3Fe_2(PO_4)_3 + \frac{1}{6}Fe_2O_3 + CO_2\uparrow$$

Fig. S2. TGA analysis for $LiFePO_4$/C obtained by annealing of tavorite $LiFePO_4(OH)$ and triphylite ($LiFePO_4$) with 20 wt% glucose.

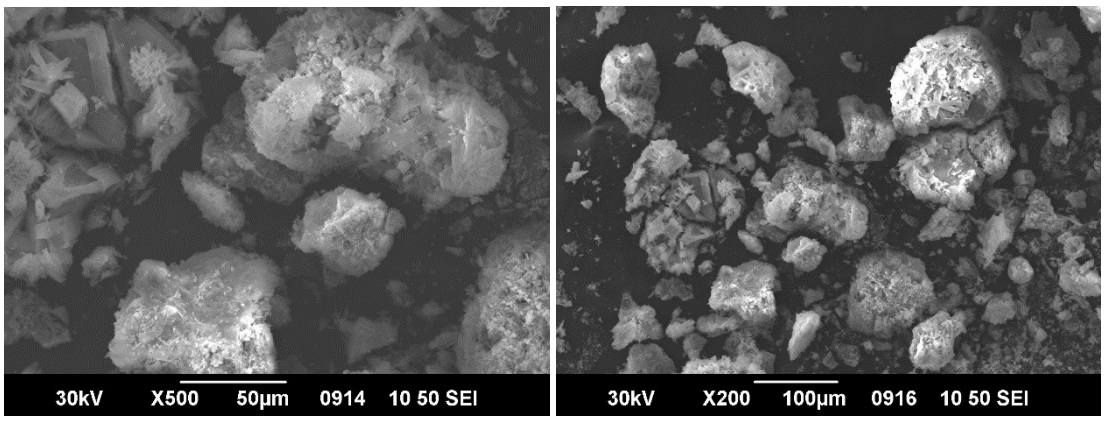


Fig. S3. The SEM images of commercial (pristine) α-Fe_2O_3.

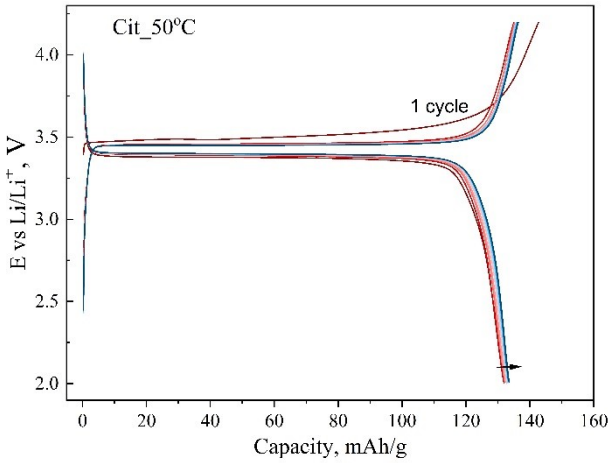


Fig. S4. Charge-discharge curves under 50°C for the $LiFePO_4$/C, hydrothermally synthesized with citric acid (Cit).

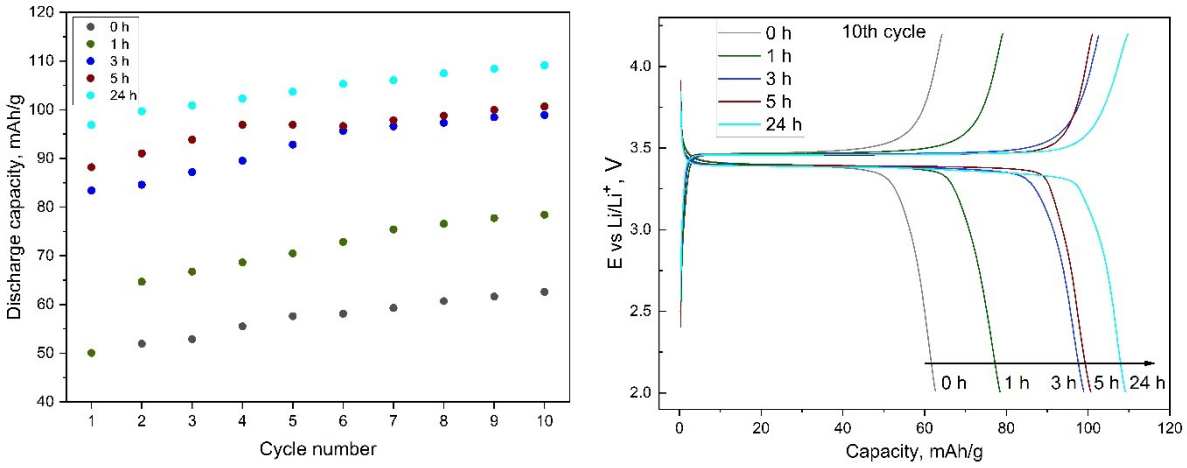


Fig. S5. Discharge capacities by cycle number and charge-discharge curves after 10 cycles for $LiFePO_4$/C, obtained under different durations of hydrothermal synthesis (0 h – after reaching 220°C, 1 h, 3 h, 5 h, 24 h – maintaining at this temperature) with citric acid.

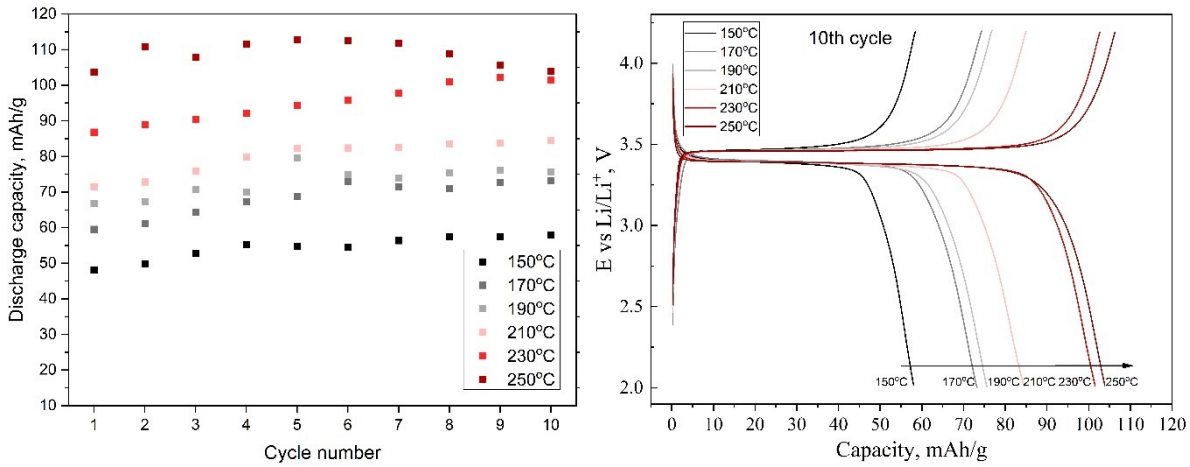


Fig. S6. Discharge capacities by cycle number and charge-discharge curves after 10 cycles for $LiFePO_4$/C, obtained under different temperatures (150-250°C) of hydrothermal synthesis with citric acid for 24 h.

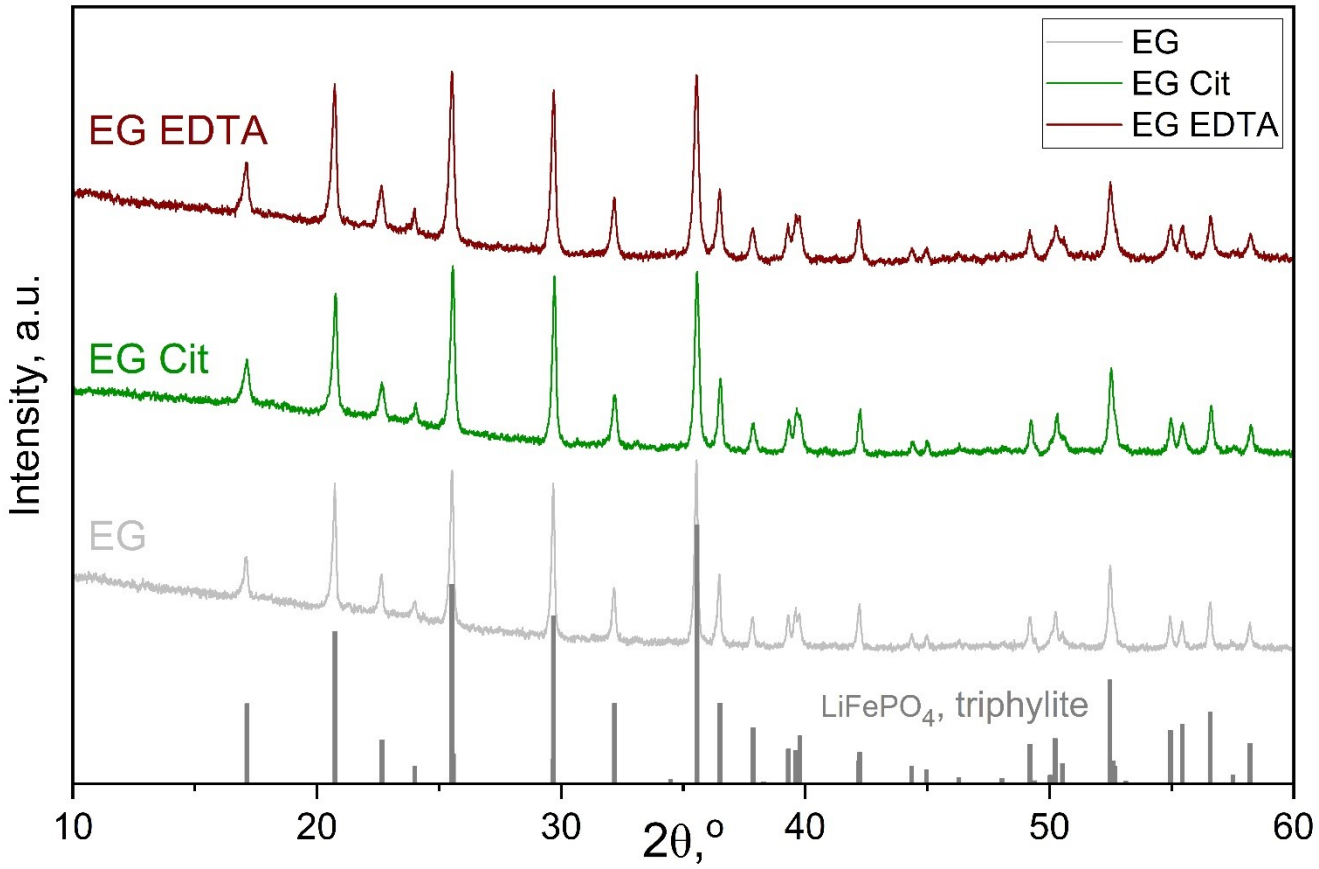


Fig. S7. PXRD patterns of solvothermally synthesized samples in EG media in the absence of organic acid, with citric acid and with EDTA, which proves the successful crystallization of $LiFePO_4$ in the reactor vessel.

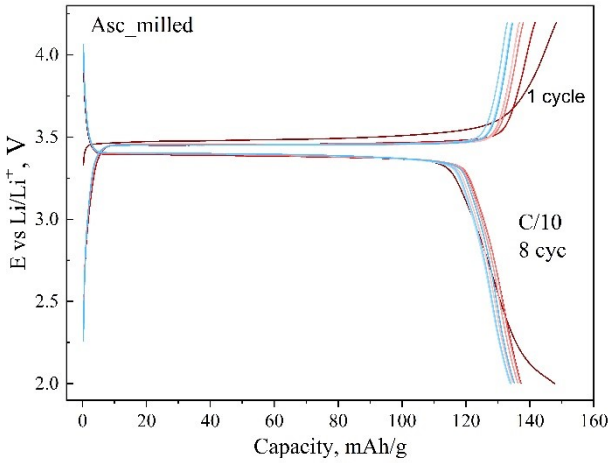


Fig. S8. Charge-discharge curves of the material, hydrothermally synthesized with ascorbic acid (Asc) and ball-milled before the annealing.