Supporting Information

Accelerated Removal of Fe-antisite defects while Nanosizing Hydrothermal $LiFePO_4$ with Ca^{2+}

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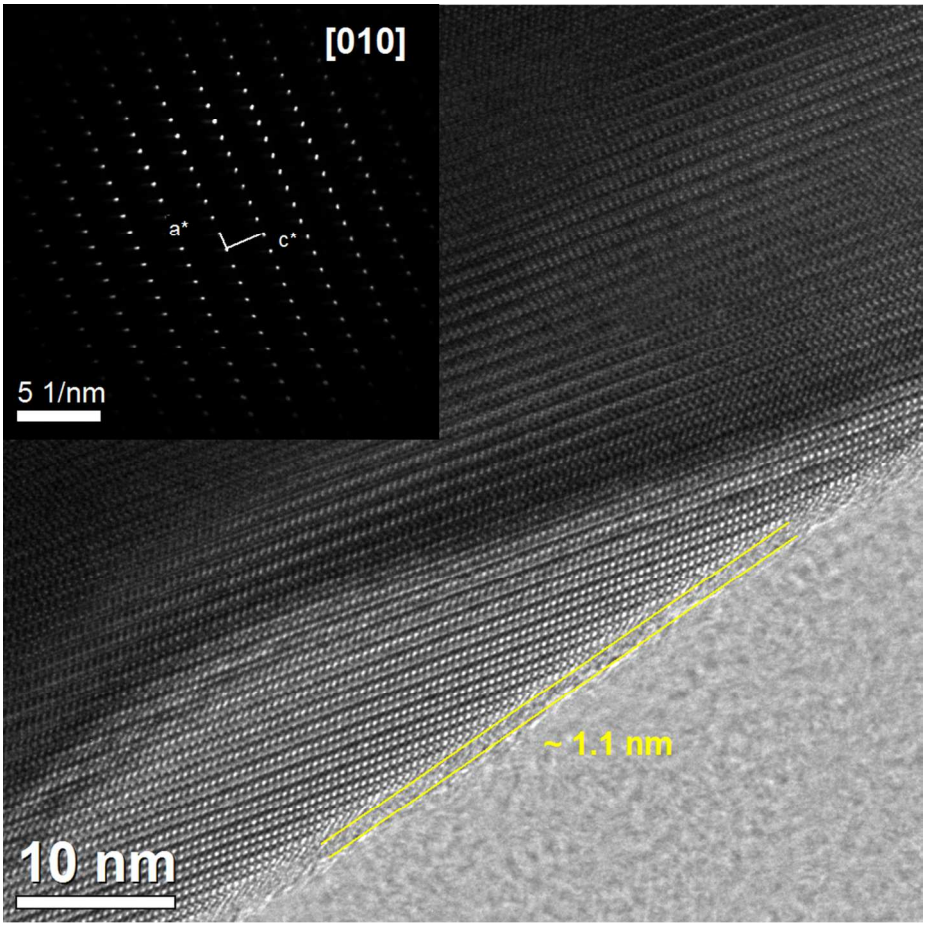

Figure S1 : *amorphous layer thickness around Ca :LFP crystal*

X-ray diffraction

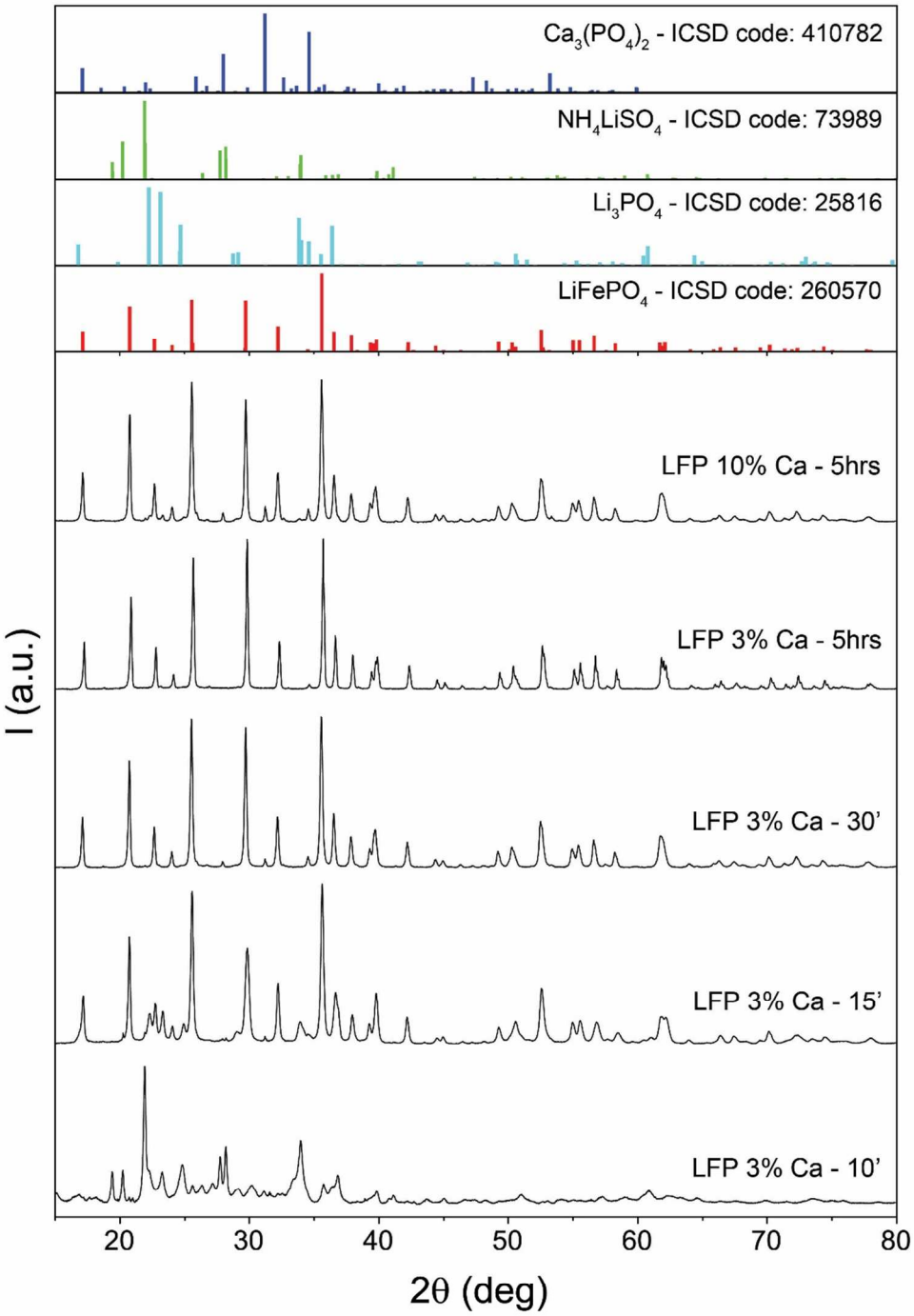

Figure S2: *XRD patterns of different calcium intermdiates*

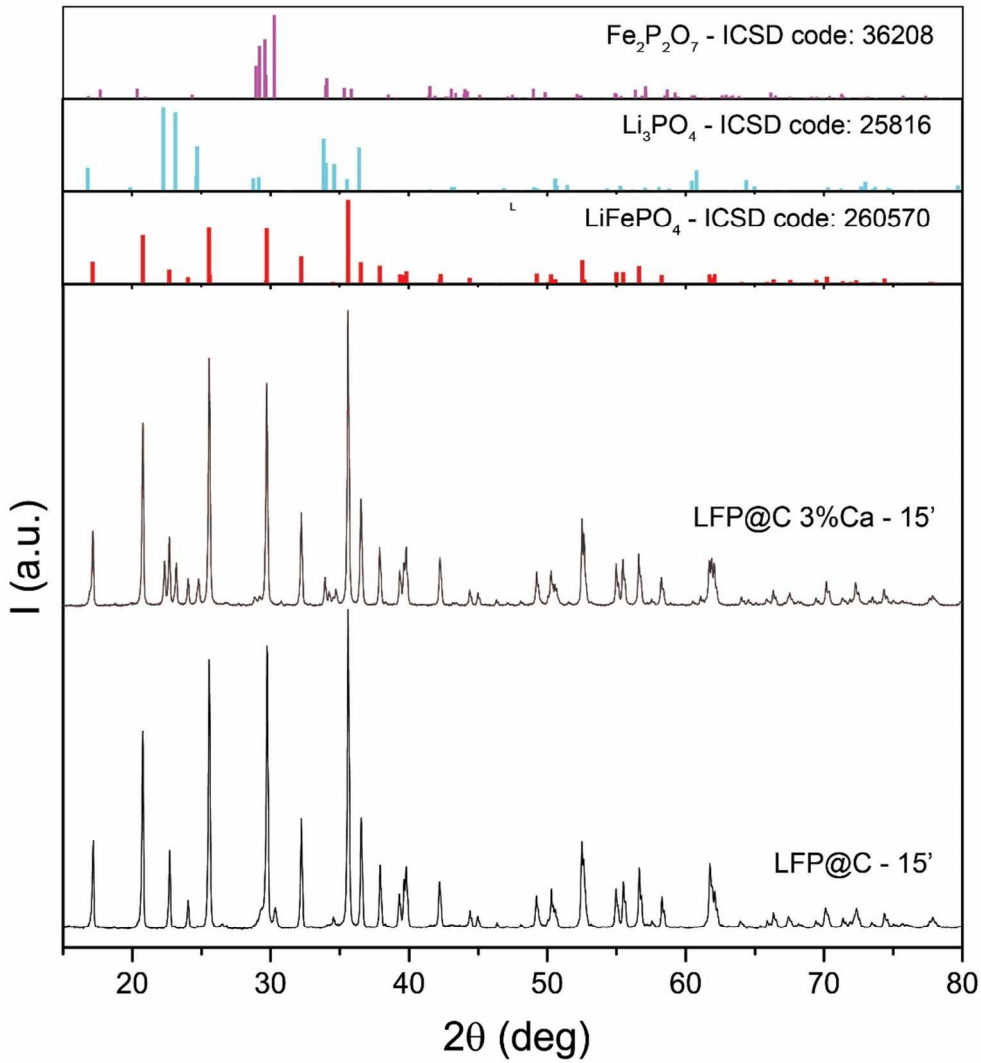

Figure S3: *XRD patterns of LFP@C and Ca:LFP@C after 15 minutes of synthesis*

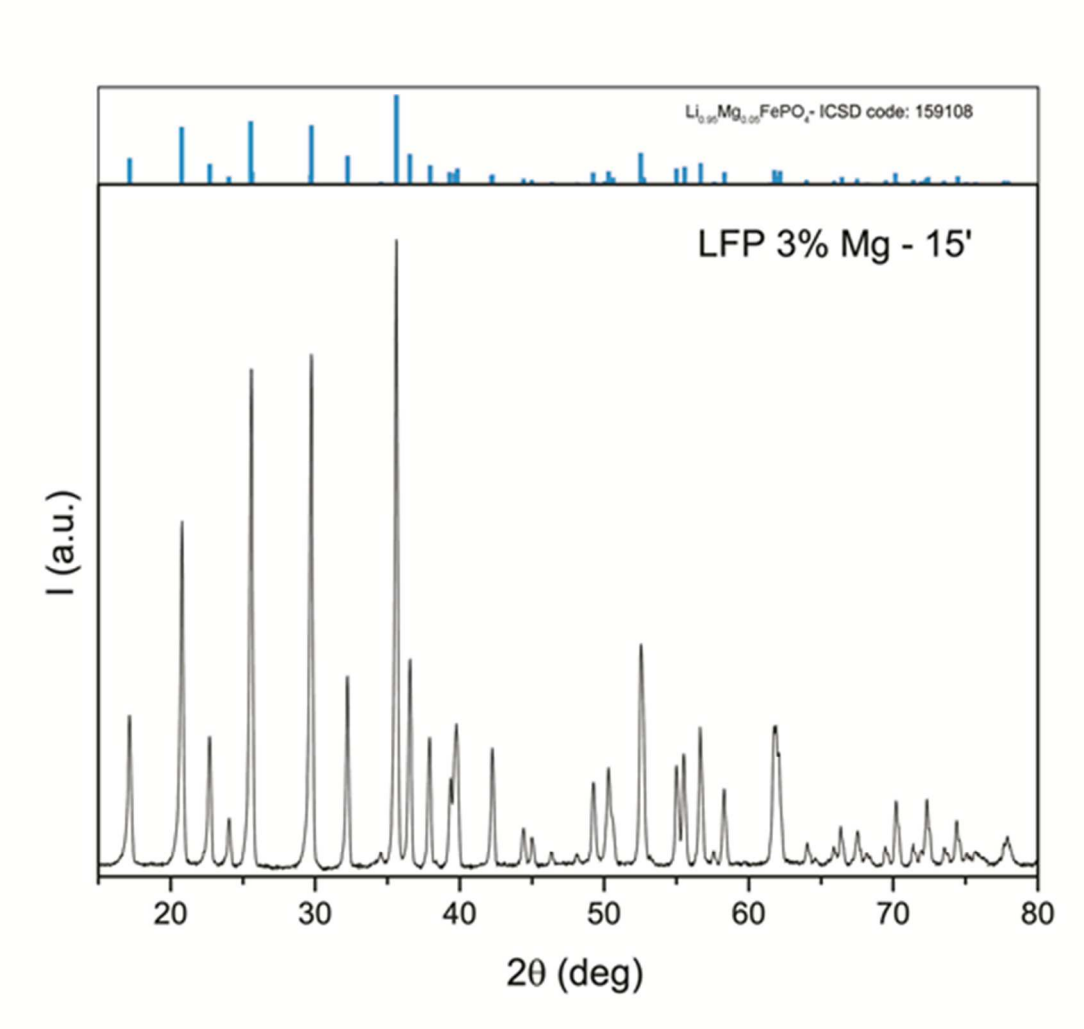

Figure S4: *XRD patterns of Mg:LFP after 15 minutes of synthesis*

EDS mapping Mg:LFP 15 minutes synthesis

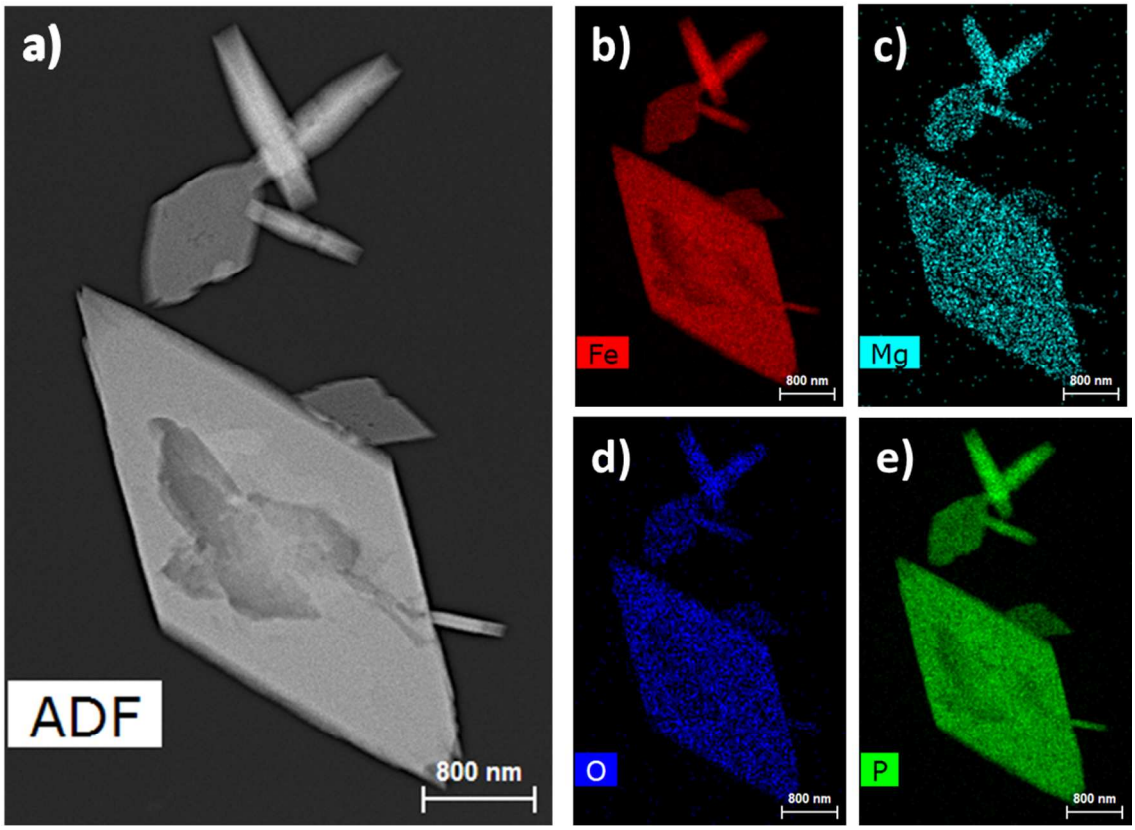

Figure S5: *EDS image mapping on hydrothermal Mg:LFP 15 minutes synthesis sample showing the homogenous distribution of b)iron, c)magnesium, d)oxygen, e)phosphorus ions inside LiFePO4 crystals (~3% vs Fe)*

Focused Ion Beam Time of Flight secondary Ion Mass Spectroscopy (TOF-SIMS)

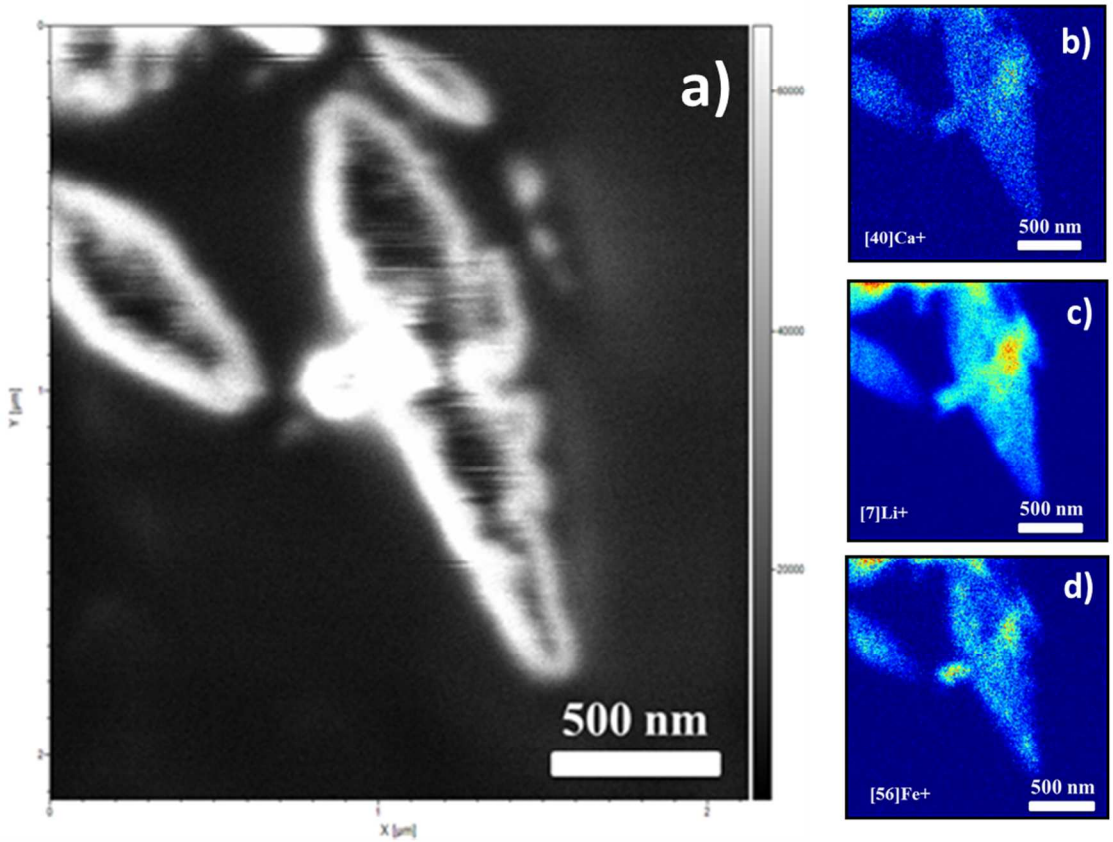

Figure S6: *Focused Ion Beam Time of Flight secondary Ion Mass Spectroscopy (TOF-SIMS) analysis of Ca 3% 15 minutes sample showing (a) induced Secondary electron images, (b) Ca+ , (c), Li+ and (d) Fe+ chemical maps. We can still clearly see the homogeneous distribution of Ca inside the LiFePO4 crystals with TOF-SIMS which has a much lower detection limits than EDS analysis*

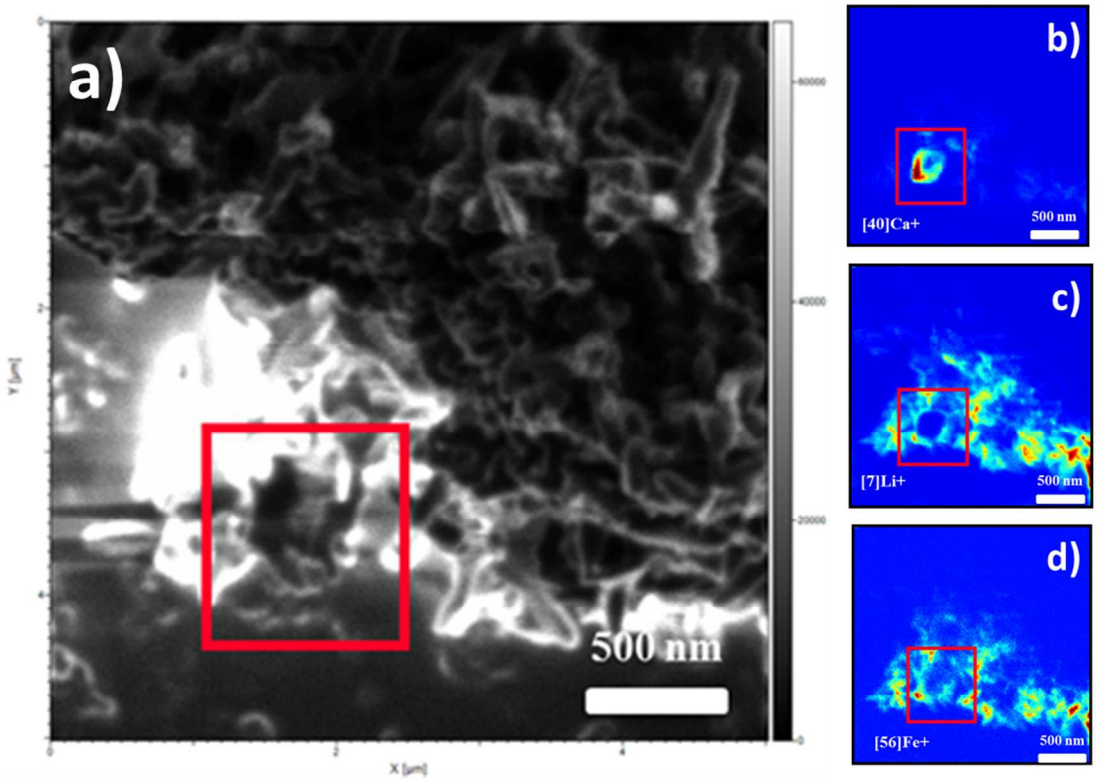

Figure S7: *TOF-SIMS analysis of Ca 3% 15 minutes sample showing another area (a) induced Secondary electron images, (b) Ca+ , (c), Li+ and (d) Fe+ chemical maps. We can clearly notice in this area that this Ca rich particles did not contains any Li confirming the presence of Ca rich phase.*

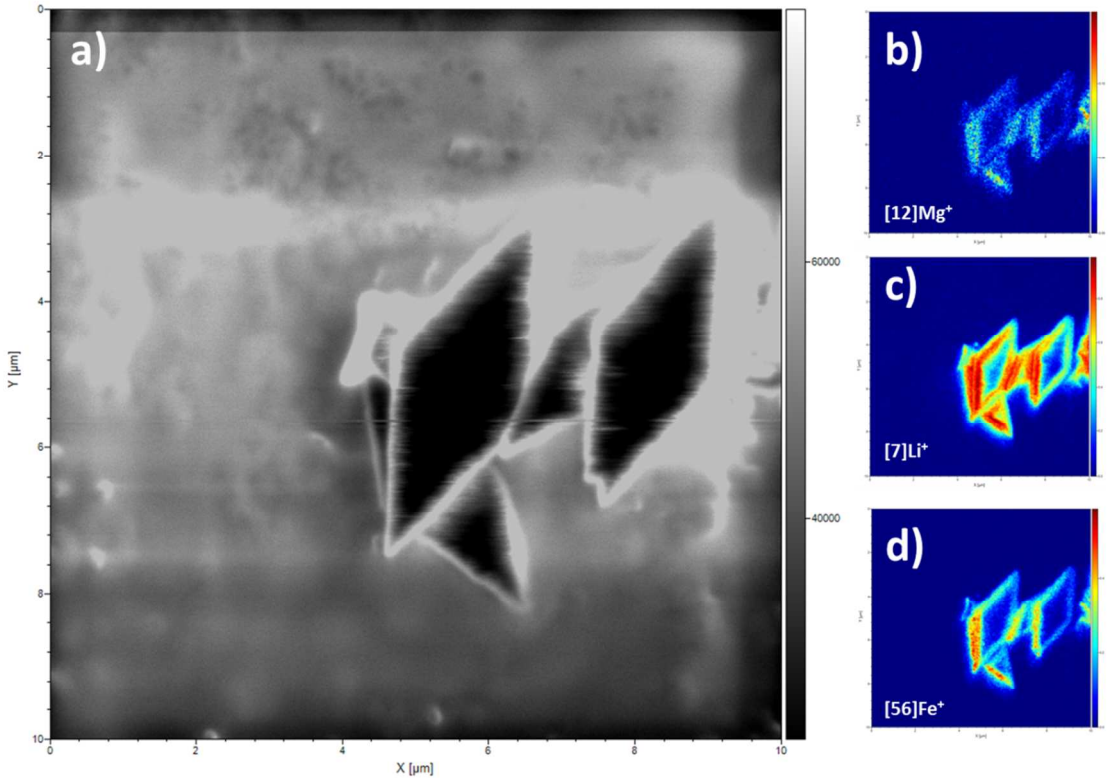

Figure S8: *TOF-SIMS analysis of Mg 3% 15 minutes sample showing another area (a) induced Secondary electron images, (b) Mg+ , (c), Li+ and (d) Fe+ chemical maps. We can still clearly see the homogeneous distribution of Mg inside the* $LiFePO_4$ *crystals with TOF-SIMS which has a much lower detection limits than EDS analysis*

Theoretical calculations

A quick density functional theory calculation (details in method section) shows that, assuming a total number of atoms equivalent to 30 formula units of $LiCaPO_4$, the total electronic energy of Li_3PO_4 plus $Ca_3(PO4)_2$ is 6.28eV higher than that of Li_3PO_4 plus $LiCa_{10}(PO_4)_7$, which is in turn 1.63eV higher than that of $LiCaPO_4$, as shown in **Figure S6**. When $LiCaPO_4$ is formed, it transforms into $LiFePO_4$ by Ca^{2+}/Fe^{2+} ion exchange; this process has an energy gain of 1.45eV (assuming one atom being exchanged) in aqueous solution.

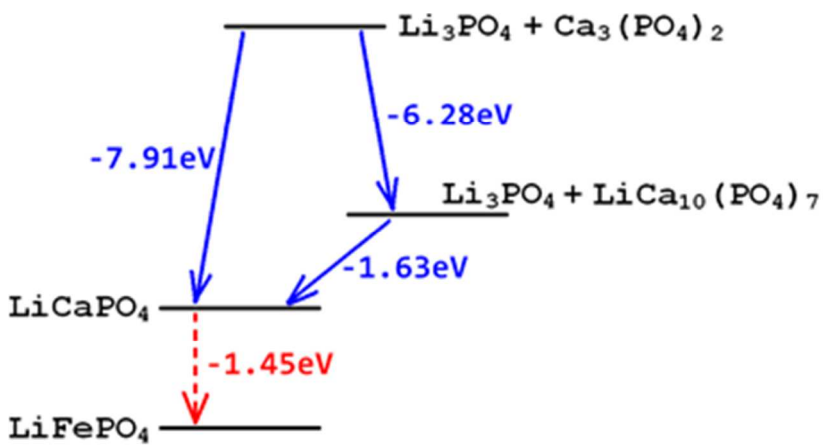

***Figure S9**: Energy scales of the compounds relevant to the reaction pathway. Blue arrows indicate crystalline energy changes per 30 formula unit of $LiCaPO_4$; the red arrow indicate the energy gain of one Ca^{2+} cation replaced by one Fe^{2+} cation in an aqueous solution.*

Neutron scattering

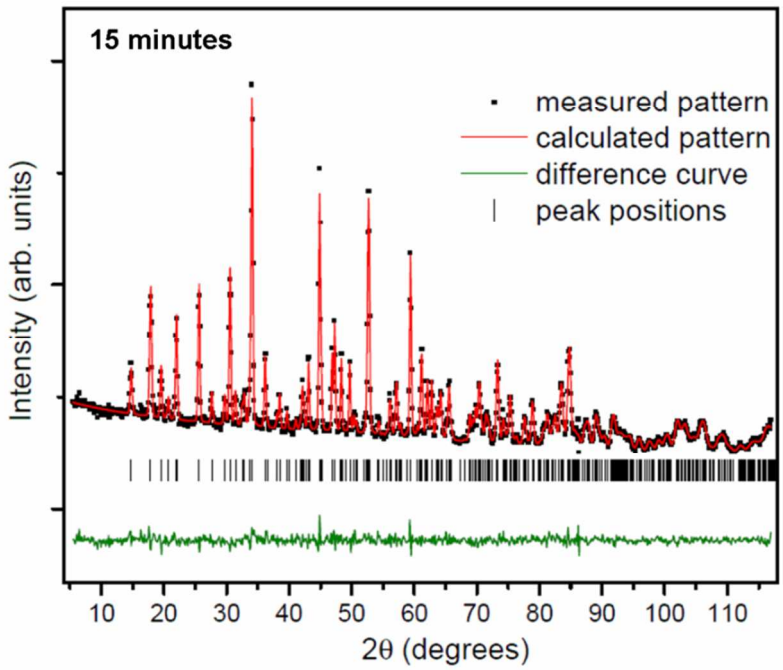

Figure S10. *Rietveld analysis of NPD pattern collected on the LFP 15 min sample (without any calcium). The bottom curve represents the difference between the measured and calculated pattern. The goodness-of-fit factors for the Rietveld fit are* R_{wp} *= 2.83%,* R_p *= 2.12% and* χ^2 *= 1.63.*

Table S1. *Atom parameters and their e.s.d's as determined from the Rietveld analysis of the 15 min neutron diffraction pattern. The unit cell parameters of the* $LiFePO_4$ *(Pnma) refined structure are a= 10.3368(3) Å, b= 5.9905(2) Å and c= 4.6975(1) Å.*

Atom	x	y	z	Occupancy	$U_{eq/iso}$
Li (*4a*)	0	0	0	0.837(7)	0.2(8)
Fe (*4c*)	0.2808(3)	0.25	0.9769(9)	1	0.47(6)
Fe (*4a*)	0	0	0	0.08(1)	0.5(5)
P (*4c*)	0.0951(6)	0.25	0.414(1)	1	0.7(1)
O (*4c*)	0.0961(6)	0.25	0.738(1)	1	0.6(1)
O (*4c*)	0.4553(5)	0.25	0.207(1)	1	0.7(1)
O (*8d*)	0.1667(5)	0.0462(6)	0.2825(8)	1	0.2(8)

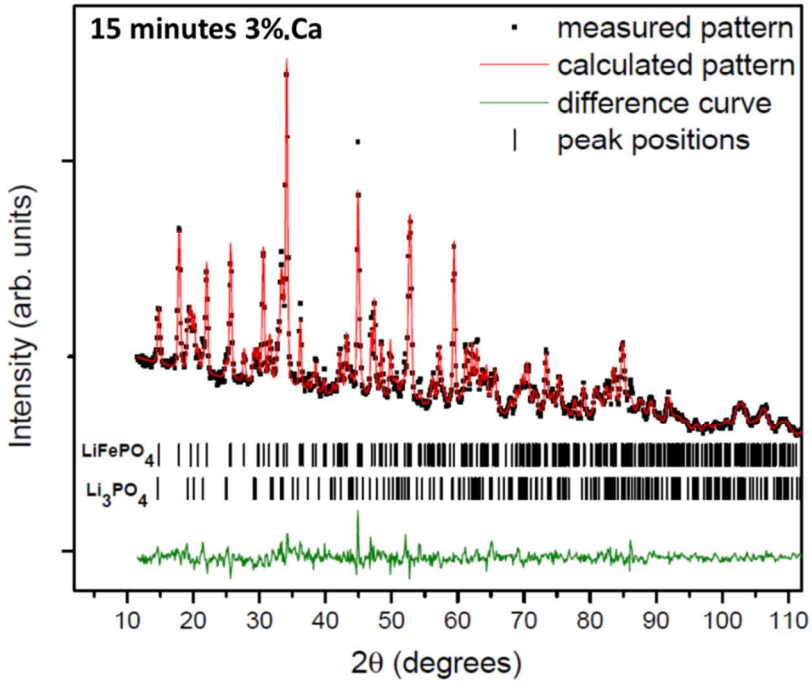

Figure S11. *Rietveld analysis of NPD pattern collected on the Ca 3% 15 min sample. The bottom curve represents the difference between the measured and calculated pattern. The top row of ticks mark the calculated positions for $LiFePO_4$ (Pnma) phase and the bottom one the calculated positions for Li_3PO4 ($Pmn2_1$) phase. Goodness-of-fit factors: R_{wp} = 2.69% and R_p = 2.03%.*

Table S2. *Atom parameters and their e.s.d's for $LiFePO_4$ (Pnma) phase as determined from the Rietved analysis of the 3% Ca 15 min neutron diffraction pattern. The unit cell parameters are: a= 10.3154(6) Å, b= 5.9812(3) Å and c= 4.6992(2) Å. The analysis indicated that the sample is a mixture of 80(2)% $LiFePO_4$ and 20(1)% Li_3PO_4.*

Atom	x	y	z	Occupancy	$U_{eq/iso}$
Li (*4a*)	0	0	0	0.86(2)	4(1)
Fe (*4c*)	0.2820(4)	0.25	0.971(1)	1	1.1(1)
Fe (*4a*)	0	0	0	0.07(1)	4(1)
P (*4c*)	0.0987(9)	0.25	0.417(1)	1	0.6(1)
O (*4c*)	0.0944(9)	0.25	0.742(2)	1	1.2(2)
O (*4c*)	0.4535(7)	0.25	0.206(2)	1	0.8(2)
O (*8d*)	0.1666(6)	0.0453(9)	0.280(1)	1	0.71(8)

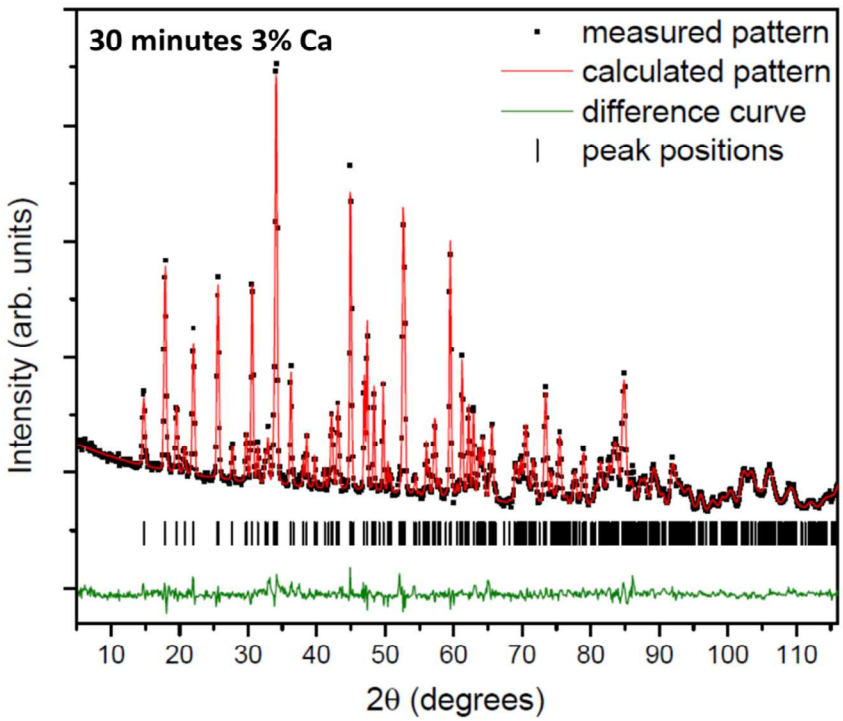

Figure S12. *Rietveld analysis of NPD pattern collected on the Ca 3% 30 min sample. The bottom curve represents the difference between the measured and calculated pattern. Goodness-of-fit factors:* R_{wp} *= 3.07 % and* R_p *= 2.28%* .

Table S3. *Atom parameters and their e.s.d's as determined from the Rietved analysis of the 3% Ca 30 min neutron diffraction pattern. The unit cell parameters of the* $LiFePO_4$ *(Pnma) refined structure are a=10.3197(3) Å, b= 5.9946(2) Å and c= 4.6903(1) Å.*

Atom	x	y	z	Occupancy	$U_{eq/iso}$
Li (*4a*)	0	0	0	0.974(8)	2.3(5)
Fe (*4c*)	0.2818(2)	0.25	0.9772(7)	1	0.48(5)
Fe (*4a*)	0	0	0	0.013(8)	2.3(5)
P (*4c*)	0.0950(5)	0.25	0.4160(9)	1	0.51(8)
O (*4c*)	0.0960(5)	0.25	0.738(1)	1	0.46(8)
O (*4c*)	0.4565(4)	0.25	0.204(1)	1	0.47(8)
O (*8d*)	0.1661(4)	0.0469(5)	0.2839(6)	1	0.62(5)

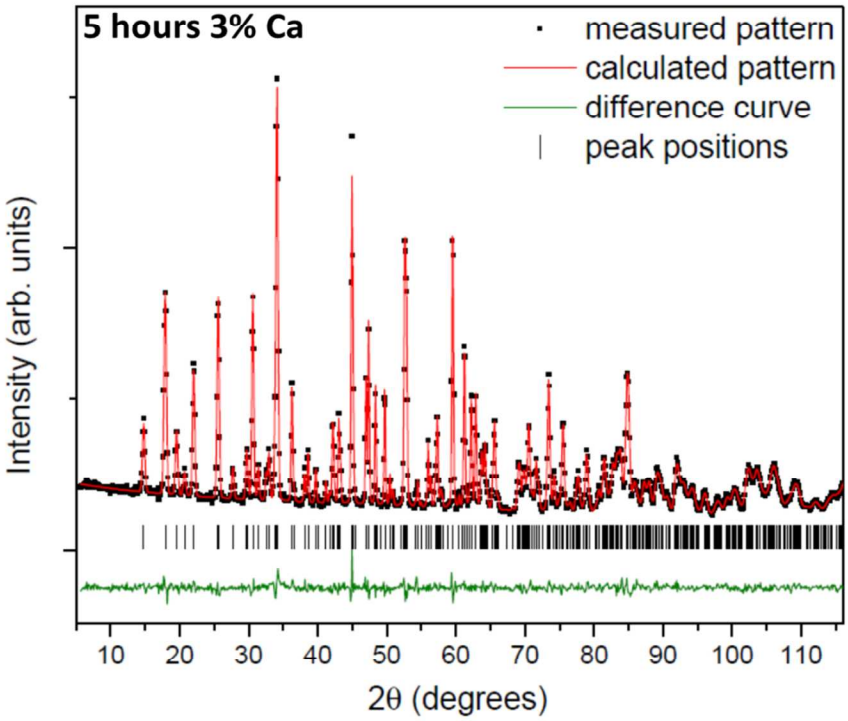

Figure S13. *Rietveld analysis of NPD pattern collected on the Ca 3% 5h sample. The bottom curve represents the difference between the measured and calculated pattern. Goodness-of-fit factors:* R_{wp} *= 4.09% and* R_p *= 3.21%.*

Table S4. *Atom parameters and their e.s.d's as determined from the Rietved analysis of the Ca 3% 5h neutron diffraction pattern. The unit cell parameters of the* $LiFePO_4$ *(Pnma) refined structure are a=10.3148(2) Å, b= 5.9965(1) Å and c= 4.6851(8) Å.*

Atom	x	y	z	Occupancy	$U_{eq/iso}$
Li (*4a*)	0	0	0	0.990(8)	1.3(3)
Fe (*4c*)	0.28200(4)	0.25	0.9752(5)	1	0.37(4)
Fe (*4a*)	0	0	0	0.005(8)	1.1(3)
P (*4c*)	0.0945(4)	0.25	0.4176(7)	1	0.31(6)
O (*4c*)	0.0964(4)	0.25	0.7404(8)	1	0.44(6)
O (*4c*)	0.4566(3)	0.25	0.2047(8)	1	0.46(6)
O (*8d*)	0.1662(3)	0.0471(4)	0.2842(5)	1	0.52(4)

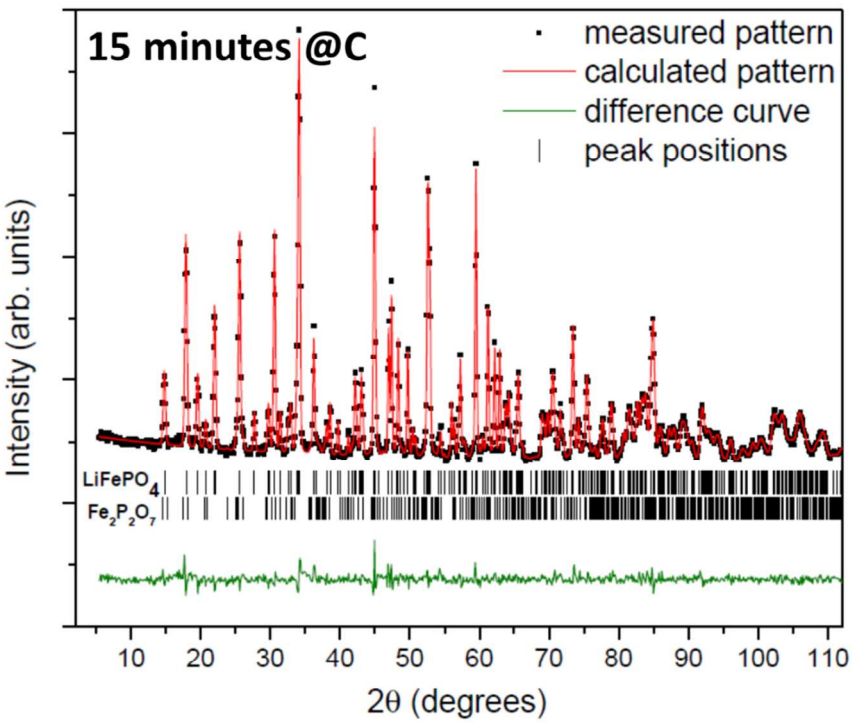

Figure S14. *Rietveld analysis of NPD pattern collected on the 15 min, Carbon coated sample. The bottom curve represents the difference between the measured and calculated pattern. The top row of ticks mark the calculated positions for $LiFePO_4$ (Pnma) phase and the bottom one the calculated positions for $Fe_2P_2O_7$ (C -1) phase. Goodness-of-fit factors: R_{wp} = 4.49% and R_p = 3.57%.*

Table S5 *Atom parameters and their e.s.d's as determined from the Rietved analysis of the 15 min Carbon neutron diffraction pattern. The unit cell parameters of the $LiFePO_4$ (Pnma) refined structure are a=10.3106(2) Å, b= 5.9960(1) Å and c= 4.6895(1) Å. The analysis indicated that the sample is a mixture of 95(1) % $LiFePO_4$ and 4.9(3) % $Fe_2P_2O_7$.*

Atom	x	y	z	Occupancy	$U_{eq/iso}$
Li (*4a*)	0	0	0	0.928(7)	1.5(4)
Fe (*4c*)	0.2817(2)	0.25	0.9742(6)	1	0.40(4)
Fe (*4a*)	0	0	0	0.036(7)	1.5(4)
P (*4c*)	0.0944(5)	0.25	0.4174(9)	1	0.26(6)
O (*4c*)	0.0966(5)	0.25	0.741(1)	1	0.83(8)
O (*4c*)	0.4567(4)	0.25	0.207(1)	1	0.56(7)
O (*8d*)	0.1662(3)	0.0469(5)	0.2839(6)	1	0.62(4)

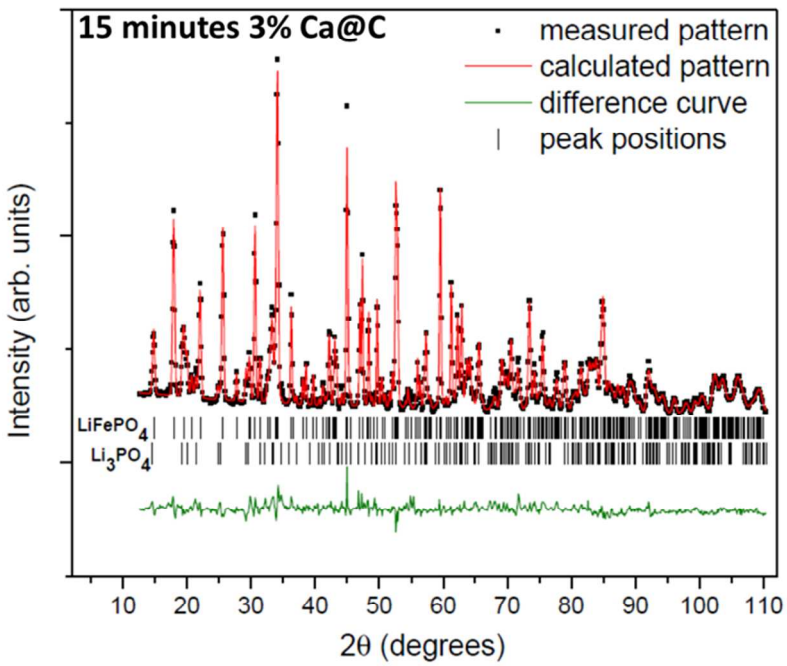

Figure S15. *Rietveld analysis of NPD pattern collected on the Ca 3% 15 min sample - Carbon. The bottom curve represents the difference between the measured and calculated pattern. The top row of ticks mark the calculated positions for $LiFePO_4$ (Pnma) phase and the bottom one the calculated positions for Li_3PO4 ($Pmn2_1$) phase. Goodness-of-fit factors: R_{wp} = 4.11% and R_p = 4.02%*

Table S6*. Atom parameters and their e.s.d's as determined from the Rietved analysis of the Ca 3% 15 min Carbon neutron diffraction pattern. The unit cell parameters of the $LiFePO_4$ (Pnma) refined structure are a=10.3097(3) Å, b= 5.9956(2) Å and c= 4.6841(1) Å. The analysis indicated that the sample is a mixture of 85(1)% $LiFePO_4$ and 25(1)% Li_3PO_4.*

Atom	x	y	z	Occupancy	$U_{eq/iso}$
Li (*4a*)	0	0	0	0.97(1)	1.4(5)
Fe (*4c*)	0.2826(3)	0.25	0.976(1)	1	0.55(9)
Fe (*4a*)	0	0	0	0.015(5)	1.4(5)
P (*4c*)	0.0963(7)	0.25	0.419(1)	1	0.2(1)
O (*4c*)	0.0925(6)	0.25	0.738(1)	1	0.7(1)
O (*4c*)	0.4576(6)	0.25	0.207(1)	1	0.1(1)
O (*8d*)	0.1655(4)	0.0469(7)	0.2839(8)	1	0.55(9)

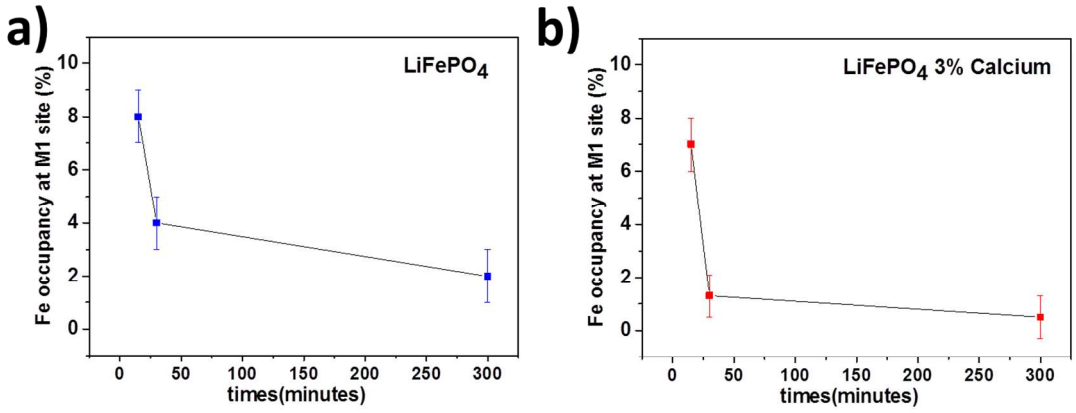

Figure S16: *Fe occupancy of M1 site as a function of time for a) $LiFePO_4$ and b) 3%Ca-$LiFePO_4$*

HAADF-STEM

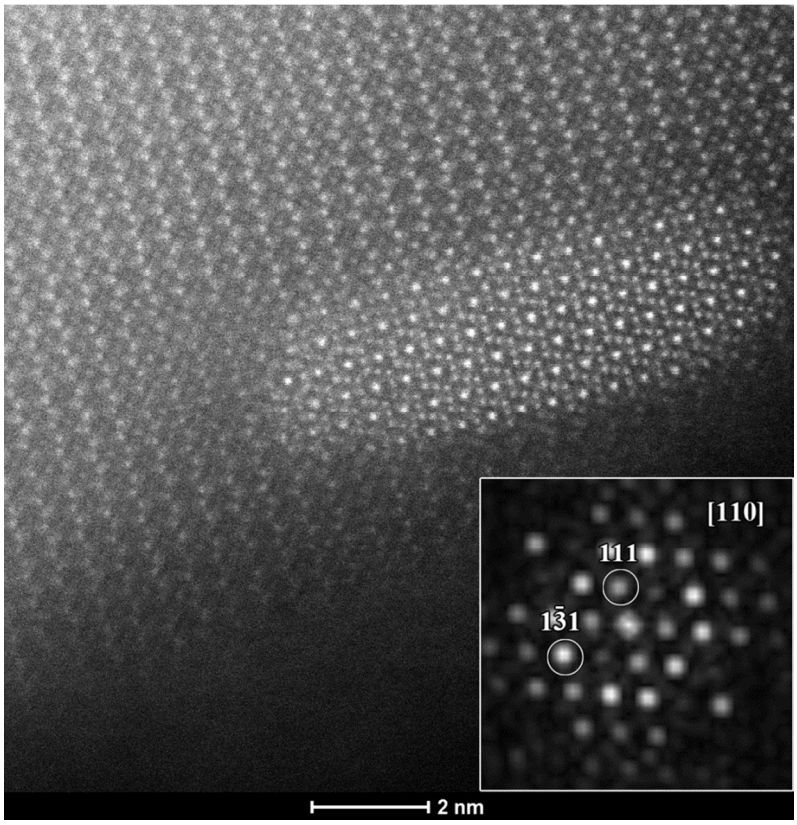

Figure S17: *HAADF-STEM image of surface LiFePO4 carbon coated crystal after 15 minutes of synthesis without calcium ions addition. Fe-antisites are still visible at the surface. Moreover it`s present iron oxide as impurity*

EC

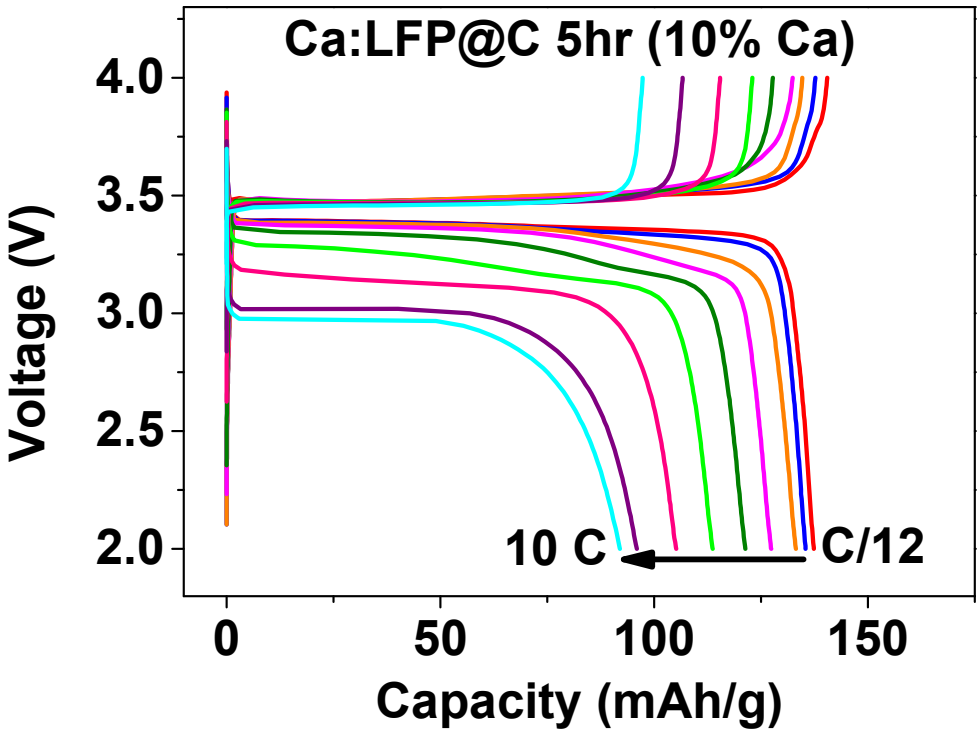

Figure S18: *Charge/discharge test of Ca:LFP with 10% calcium after 5 hours of synthesis. The discharge rate C/12 is in red, C/8 in blue, C/4 in orange, C/2 in magenta, 1C in olive green, 2C in green, 4C in pink, 8C in purple and 10C in cyan.*

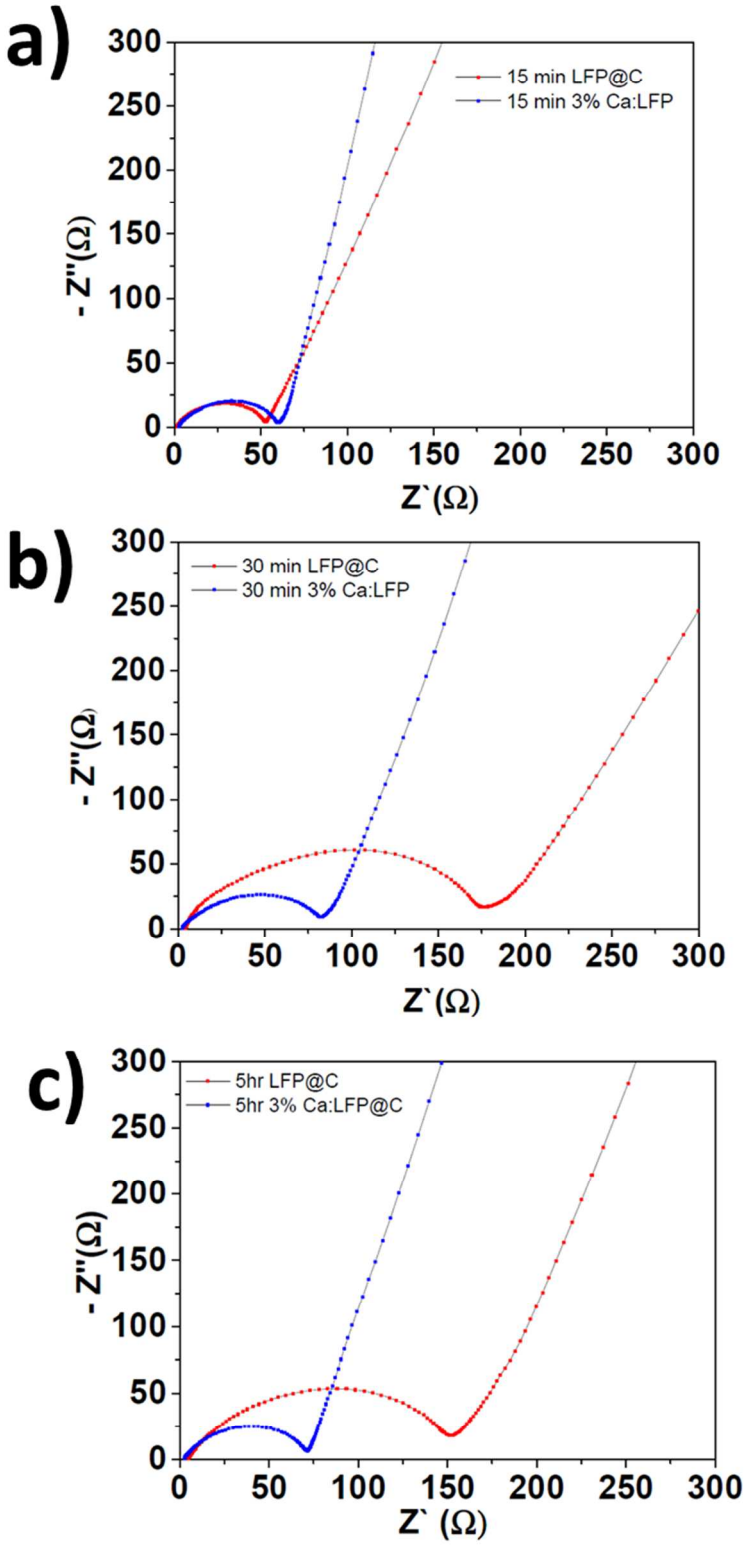

Figure S19: *Electrochemical Impedance Spectra in form of Nyquist plot for LFP@C (red curve) and Ca:LFP@C (blue curve) after15 minutes, 30 minutes and 5 hours of synthesis.*

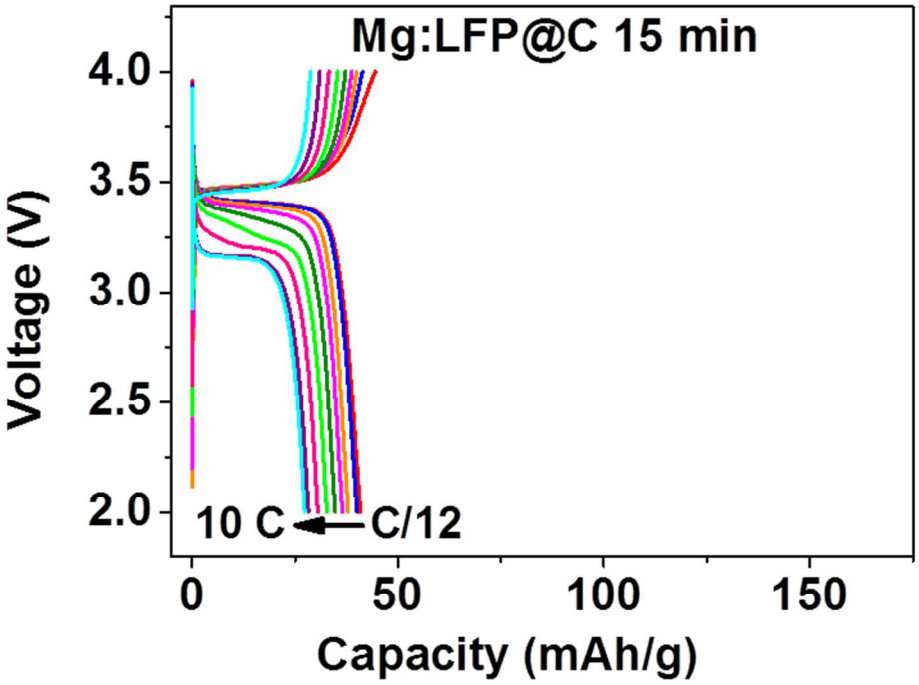

Figure S20: *Charge/discharge test of Mg:LFP with 3% magnesium after 15 minutes of synthesis. The discharge rate C/12 is in red, C/8 in blue, C/4 in orange, C/2 in magenta, 1C in olive green, 2C in green, 4C in pink, 8C in purple and 10C in cyan.*