SUPPLEMENTARY INFORMATION

Unravelling the electrochemical activation and the reaction mechanism of *maricite*-$NaFePO_4$ using multimodal operando techniques

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Tables and Figures

Table SI1. Summary of the unit cell parameters and average crystallite size obtained from the Le Bail refinement of the XRD patterns of the 5 samples depending on the ball-milling time

S.G. *Pnma*	***a* (Å)**	***b* (Å)**	***c* (Å)**	***V* (Å)**	**Crystallite size (nm)**
NFP_0h	8.9959(9)	6.8617(8)	5.0459(6)	310.90(3)	170 ± 3
NFP_3h	8.9903(3)	6.8573(5)	5.0437(4)	310.90(4)	30 ± 0.5
NFP_6h	8.9902(8)	6.8582(6)	5.0437(5)	310.98(5)	24 ± 0.3
NFP_9h	8.990(2)	6.858(1)	5.034(1)	310.9(1)	20 ± 0.3
NFP_12h	8.987(1)	6.856(1)	5.0408(8)	310.98(5)	15 ± 0.1

Table SI2. Summary of first charge and discharge capacity of the $NaFePO_4$/C after different ball milling times 0h (NFP_0h) 3h (NFP_3h), 6h (NFP_6h), 9h (NFP_9h) and 12h (NFP_12h) and valence of the iron contained in the samples as determined from Mössbauer spectroscopy

Sample	**Galvanostatic cycle**		**Mössbauer spectroscopy**	
	1st charge (mAh g^{-1})	**1st discharge (mAh g^{-1})**	**Fe^{2+}**	**Fe^{3+}**
NFP_0h	21	13	100%	0
NFP_3h	50	65	83 %	17 %
NFP_6h	62	85	72 %	28 %
NFP_9h	64	92	66 %	34 %
NFP_12h	72	100	63 %	37 %

Table SI3. Mössbauer spectroscopy parameters of NFP_12h ball milled under different atmospheres (air and neutral atmosphere of Argon)

		ISO (mm s^{-1})	QUA (mm s^{-1})	WID (0.3 mm s^{-1})	Fe%
NFP_12h_Air	**Fe^{2+}**	1.21	2.20	0.35	63%
	Fe^{3+}	0.36	0.99	0.55	37%
NFP_12h_Argon	**Fe^{2+}**	1.20	2.20	0.37	64%
	Fe^{3+}	0.39	0.93	0.60	36%

Table SI4. Crystallographic data (unit cell parameters, atomic positions, isotropic agitation factors B_{iso}, site occupancies) of NFP_12h obtained from the Rietveld refinement of its SXRD pattern (R_p = 7.42; R_{wp} = 7.16; R_e = 2.40; Chi_2 = 8.90)

S.G. *Pnma*		*a* = 8.9927(5) Å	*b* = 6.8604(3) Å	*c* = 5.0446(3) Å	
Atom	**Wickoff site**	***x/a***	***y/b***	***z/c***	**Occ**
O1	8d	0.121(1)	0.066(1)	0.328(2)	1.0000
O2	4c	0.350(1)	0.250	0.463(3)	0.5000
O3	4c	0.123(2)	0.250	0.747(3)	0.5000
Fe1	4a	0	0	0	0.5000
P1	4c	0.176(1)	0.250	0.456(2)	0.5000
Na1	4c	0.345(1)	0.250	0.969(3)	0.480(8)

Table SI5. Summary of the in situ Mössbauer spectroscopy data. Evolution of the voltage capacity, time and valence of the iron extracted from figure 9

Voltage (V)	Capacity (mAh g^{-1})	Time (h)	Fe^{2+}	Fe^{2+}	Fe^{2+}(A)	Fe^{2+}(B)	Fe^{3+}(A)	Fe^{3+}(B)
OCV	0	0	58.5	41.5	50.5	10.3	28.7	10.5
4.5	50	16	50.2	49.8	45.2	7.8	34.4	12.6
1.5	80	40	90.5	9.5	71	20.1	6.5	2.4
4.5	82	64	53.5	46.5	47.3	8.8	32.1	11.6

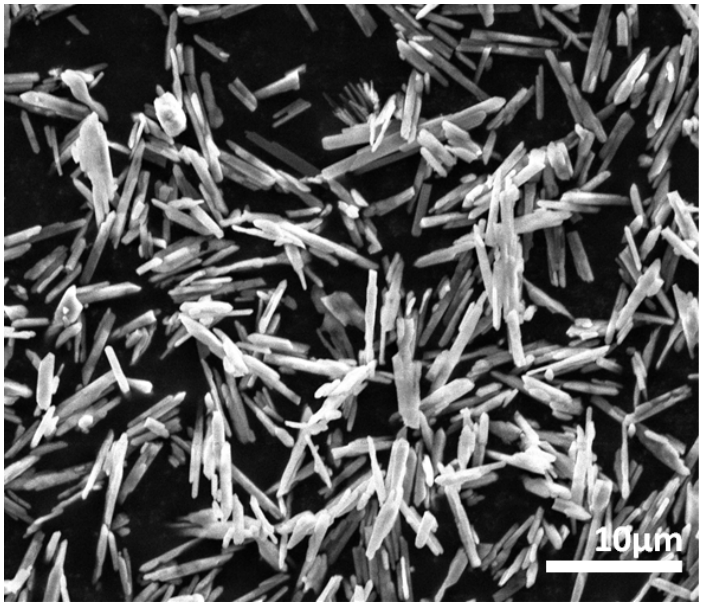

Figure SI1. SEM image of the pure maricite $NaFePO_4$ obtained by hydrothermal synthesis (NFP_0h)

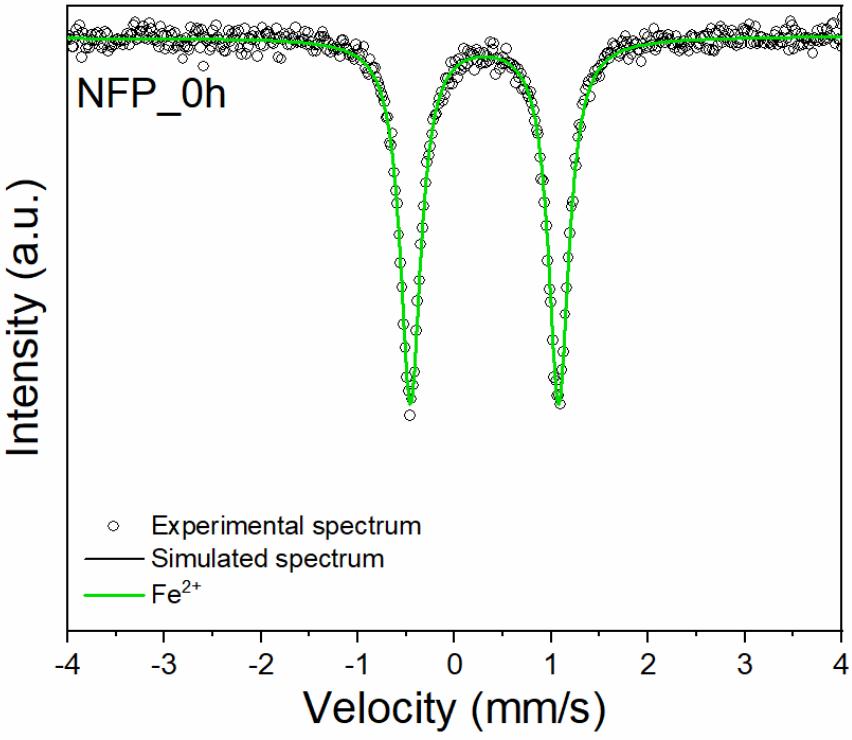

Figure SI2. Mössbauer spectrum of pristine maricite $NaFePO_4$ (NFP_0h) prepared by hydrothermal synthesis

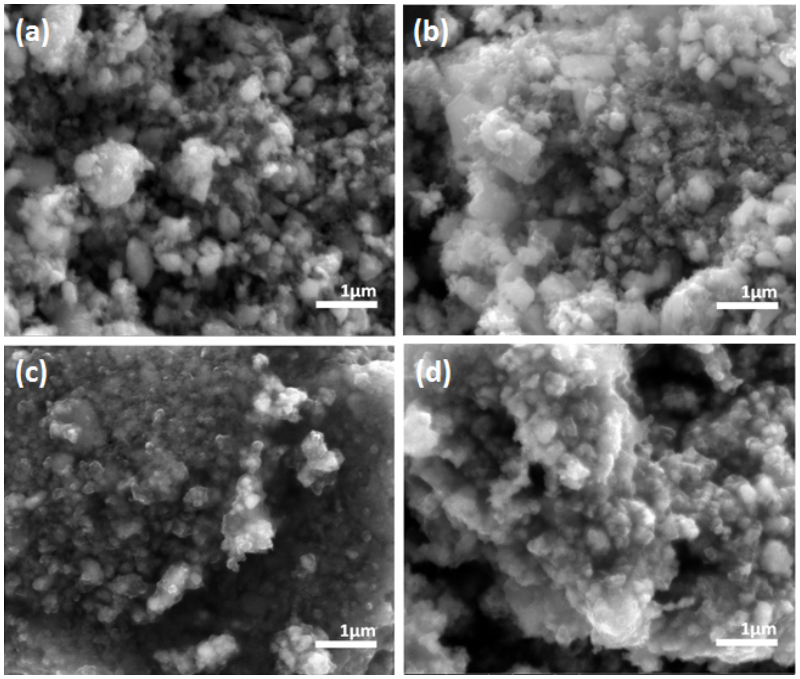

Figure SI3. SEM images of the $NaFePO_4$/C after different ball milling times (a) 3h (NFP_3h), (b) 6h (NFP_6h), (c) 9h (NFP_9h)and (d) 12h (NFP_12h).

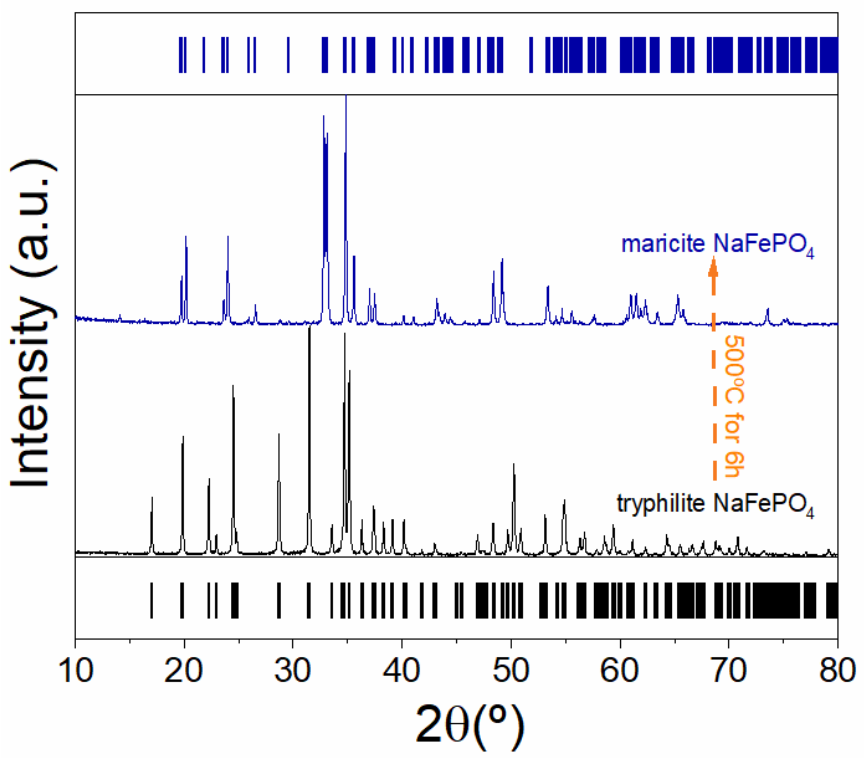

Figure SI4. XRD patterns of triphylite carbon coated NFP (cc-*t*-NFP) obtained after chemical delithiation and posterior chemical sodiation of commercial carbon coated $LiFePO_4$, and maricite NFP (cc-*m*-NFP) obtained from carbon coated NFP after heat treatment. The short vertical lines indicate the Bragg peak positions of the maricite NFP (blue vertical lines) and triphylite NFP (black vertical lines)

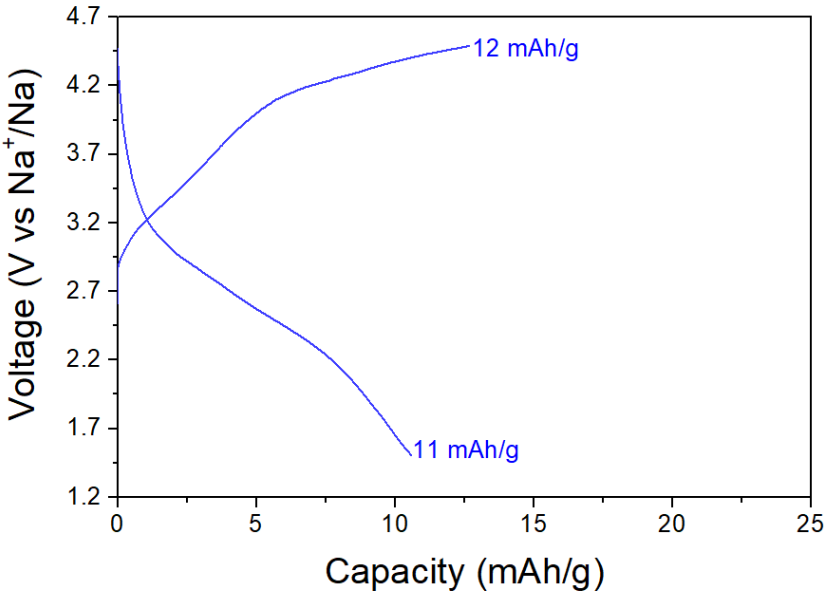

Figure SI5. First charge and discharge curve of pristine maricite carbon coated $NaFePO_4$ (*cc*-m-NFP) obtained by heat treat of triphylite carbon coated NFP (cc-t-NFP)

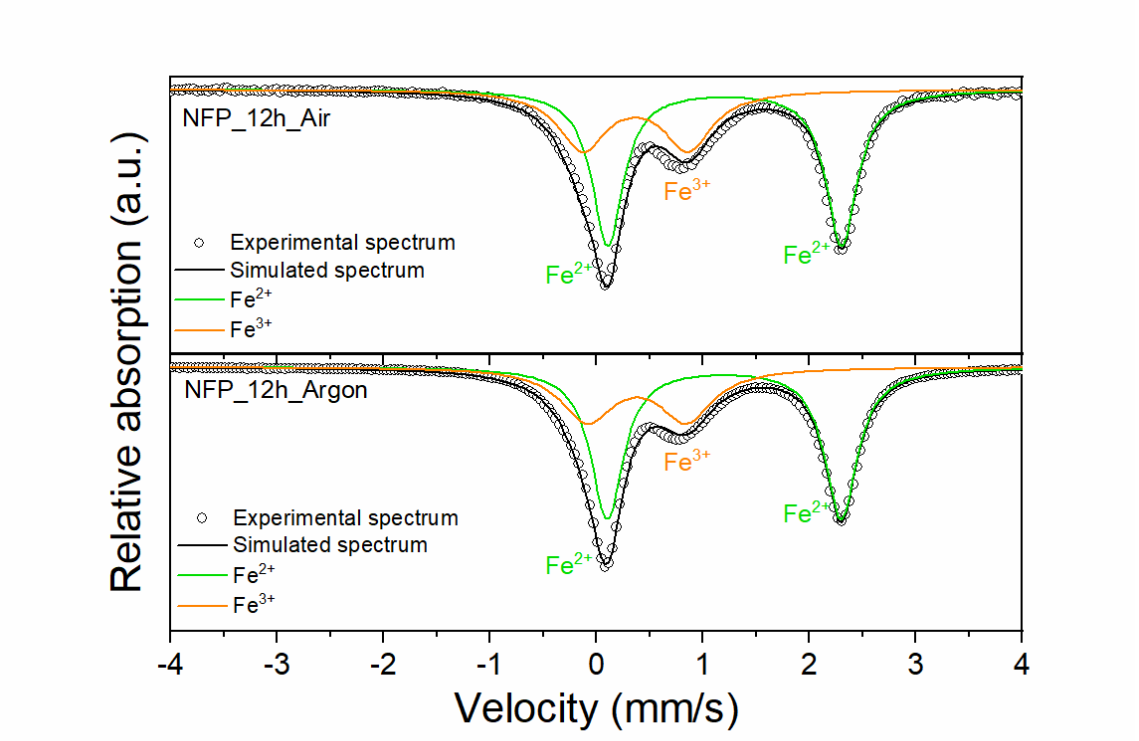

Figure SI6. Mössbauer spectra of NFP_12h in different atmospheres (air and argon). The corresponding hyperfine parameters are given in Table SI3.

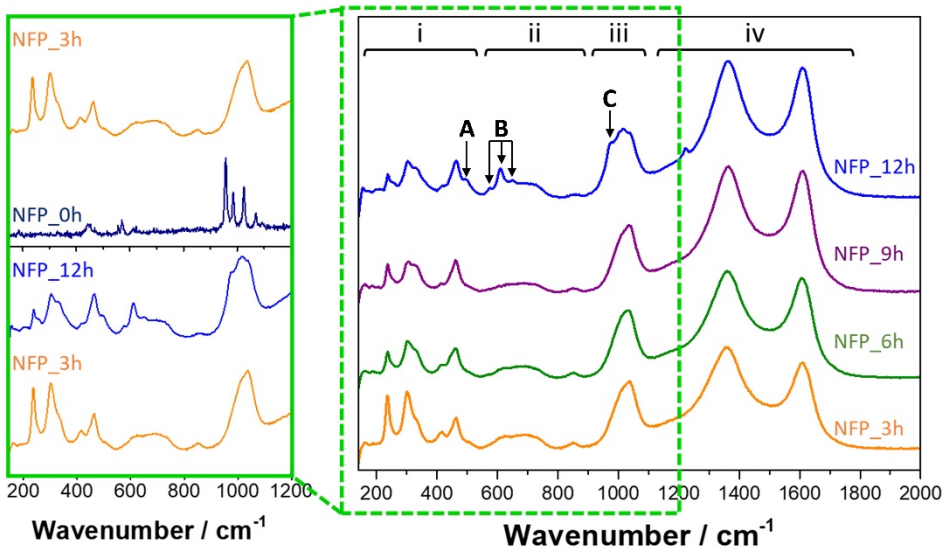

Figure SI7. Raman spectra for samples after ball milling for differing time periods

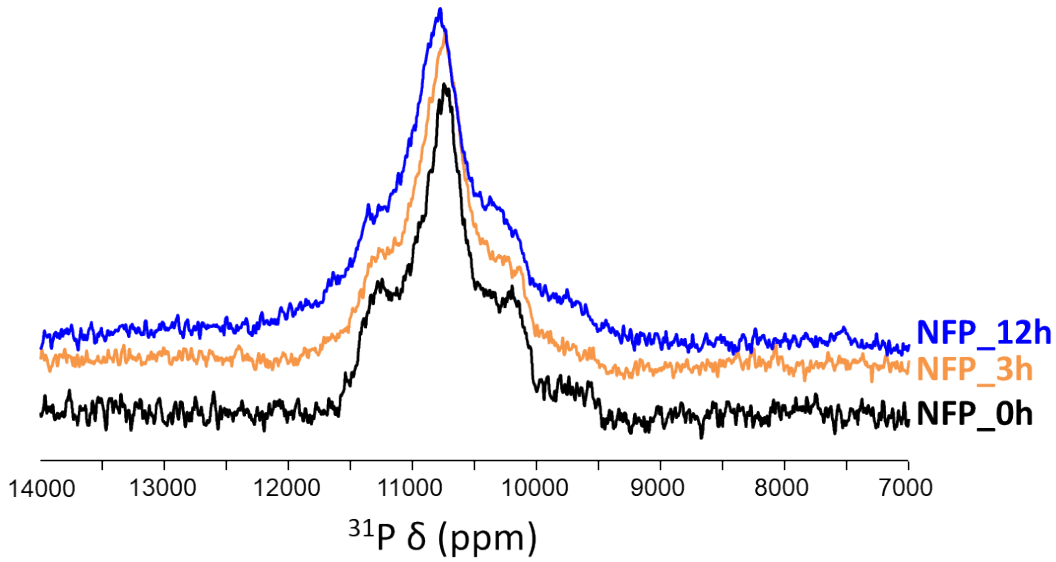

Figure SI8. ^{31}P solid state NMR spectrum of pristine NFP_0h and at 3h and 12h ball milling time.

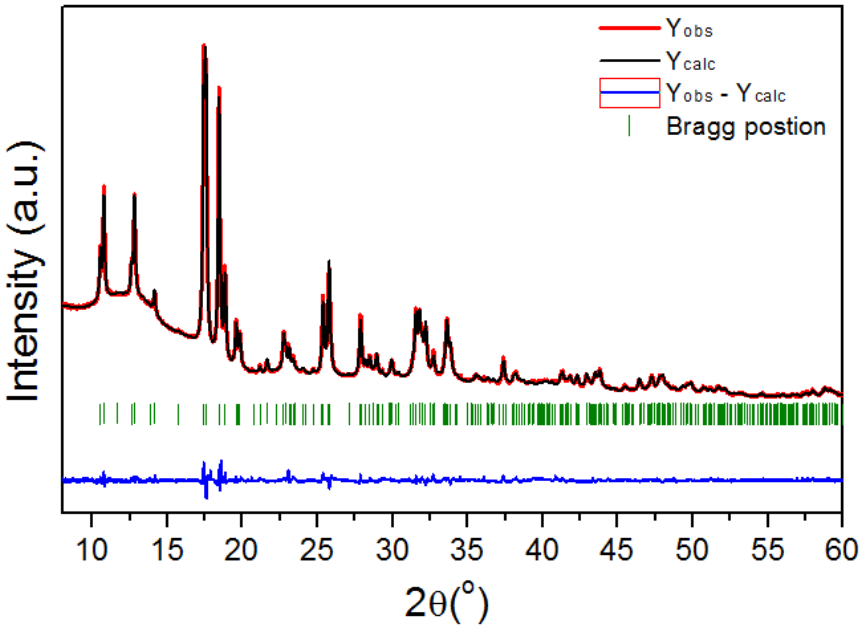

Figure SI9. Rietveld refinement of the SXRD of the NFP_12h measured on a capillary.