Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2020

Supplementary Information

Appraisal of calcium ferrites as cathode for calcium rechargeable batteries: DFT, synthesis, characterization and electrochemistry of $Ca_4Fe_9O_{17}$

A. P. Black,[1,2] A. Torres[3], C. Frontera[1], M.R. Palacín[1,2], and M. E. Arroyo-de Dompablo[3*]

[1]Institut de Ciència de Materials de Barcelona (ICMAB-CSIC) Campus UAB, E-08193 Bellaterra, Catalonia, (Spain)

[2]ALISTORE-ERI European Research Institute

[3]Departamento de Química Inorgánica, Universidad Complutense de Madrid, 28040 Madrid, (Spain)

Table 1. Experimental vs. Calculated (GGA+U, U_{eff} = 5 eV) lattice parameters for $CaFe_{2+n}O_{4+n}$

Composition	Experimental lattice parameters (Å)	Calculate lattice parameters (Å)
$CaFe_2O_4$ [1]	9.230(12), 3.024(4), 10.705(1)	9.342, 3.055, 10.852
$Ca_4Fe_9O_{17}$ [2]	10.441(2) 6.025(2) 11.384(2) ß= 98.8(2)	10.586, 6.101, 11.552 ß = 98.663
$CaFe_3O_5$ [3]	3.021(1), 10.009(1), 12.643(1	3.052, 10.292, 12.728
$CaFe_4O_6$ [4]	3.050(1), 9.986(1), 15.321(2)	3.122, 10.391, 16.396

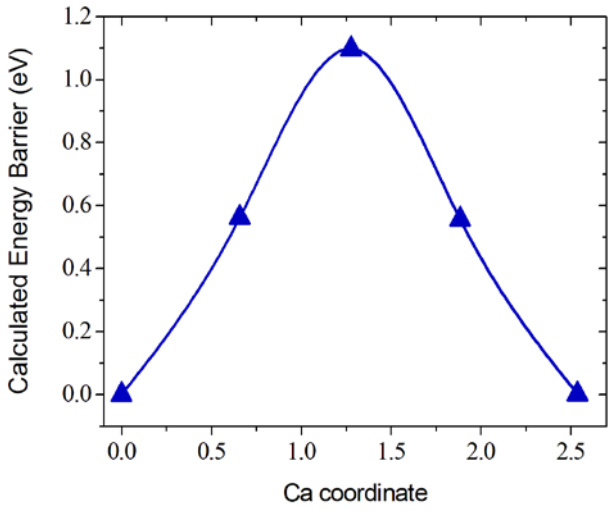

Figure S1. Calculated energy barrier for Ca migration in $CaFe_2O_4$

Table 2. Summary of literature reports on $Ca_4Fe_9O_{17}$ synthesis methods.

Reactants	Conditions	Products	[ref]
$FeO + CaFe_2O_4$	1120°C for 15 days under vacuum	$Ca_4Fe_9O_{17}$ single crystal	[2]
$CaFe_2O_4 + Ca_2Fe_2O_5 + Fe_3O_4$	1000°C for 1 to 10 days, quenched in water	undetermined	[5]
$Fe(NO_3)_3 \cdot 9H_2O$ + $Ca(NO_3)_2 \cdot 4H_2O$ ratio (1:0,5)	670-830°C for 6h in Air	$Ca_2Fe_2O_5 + Ca_4Fe_{14}O_{25} + CaFe_2O_4 + Ca_4Fe_9O_{17}$	[6]
$CaFe_2O_4 + Ca_2Fe_2O_5 + FeO$	1200°C for 8h in Air	$Ca_2Fe_2O_5 + CaFe_2O_4 + Ca_4Fe_9O_{17}$	[7]
$Fe_3O_4 + Fe_2O_3 + CaO$	2x1300°C for 1h + 1100°C for 2 days + 1000°C for 7 days in Ar and quenched in water	$Ca_2Fe_2O_5 + CaFe_2O_4 + Ca_4Fe_9O_{17}$	[8]

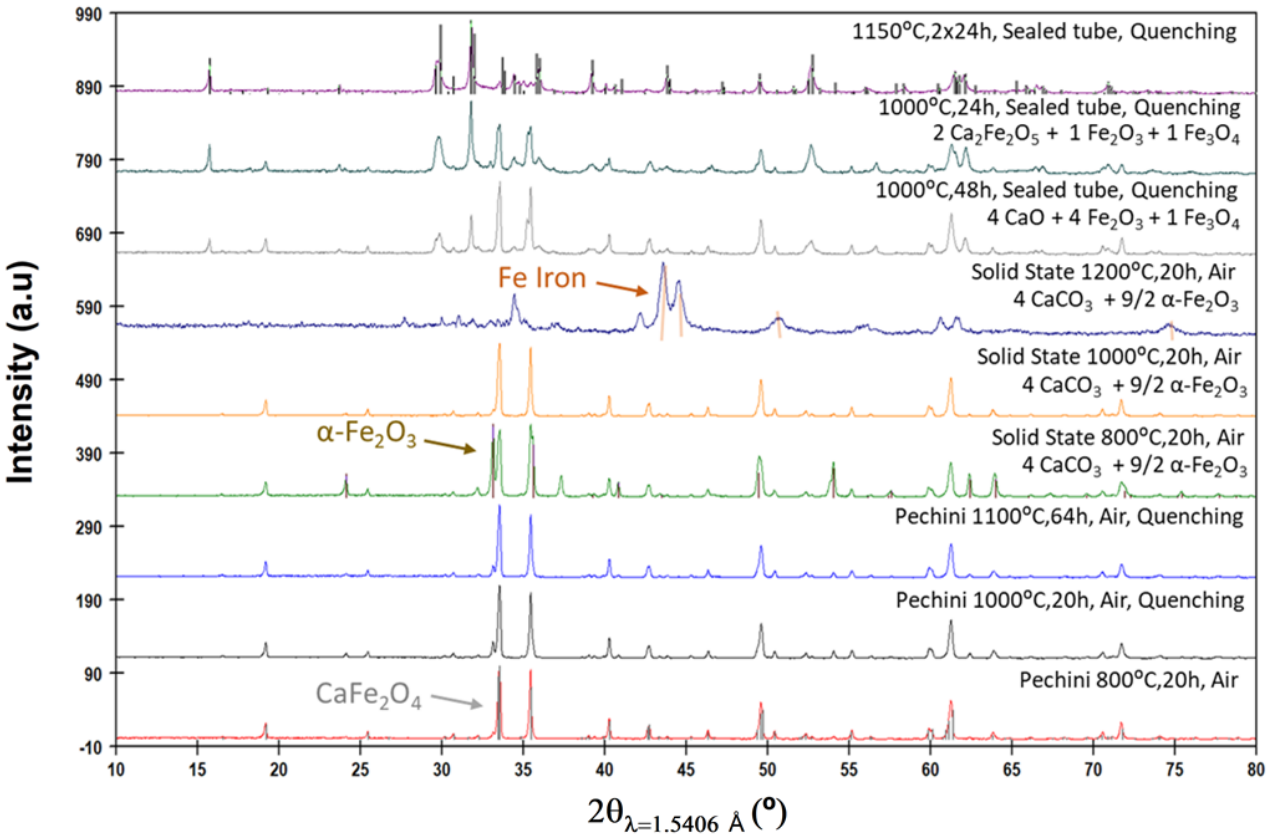

Figure S2. Selected x-ray diffraction patterns of $Ca_4Fe_9O_{17}$ synthesis attempts during synthesis route optimization.

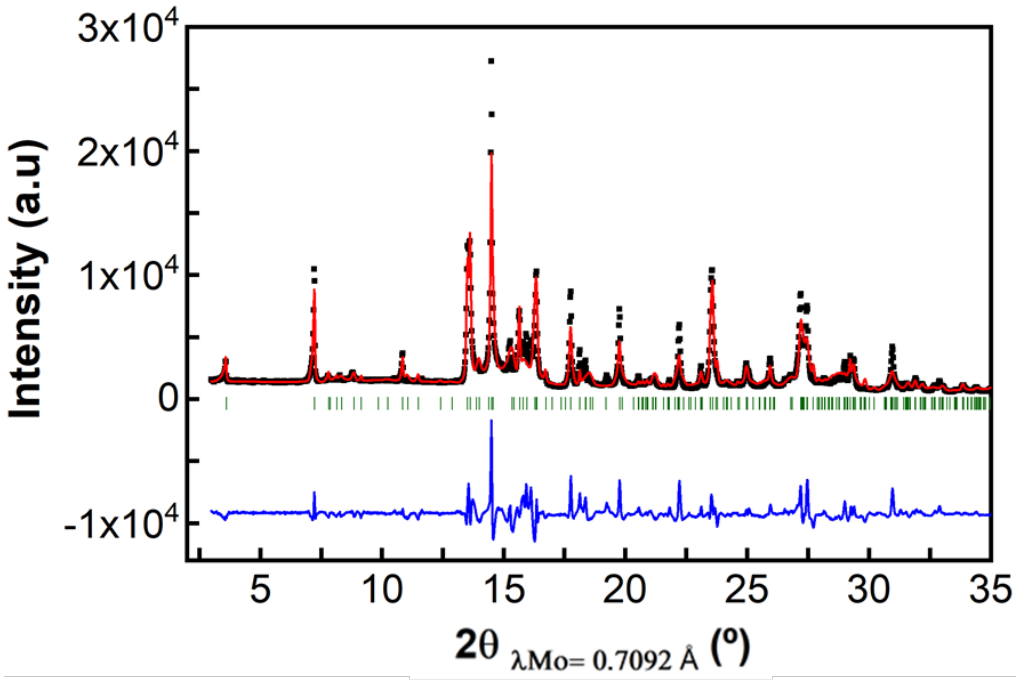

Figure S3. Rietveld refinement of the $Ca_4Fe_9O_{17}$ x-ray diffraction pattern using the structural model reported in [2].

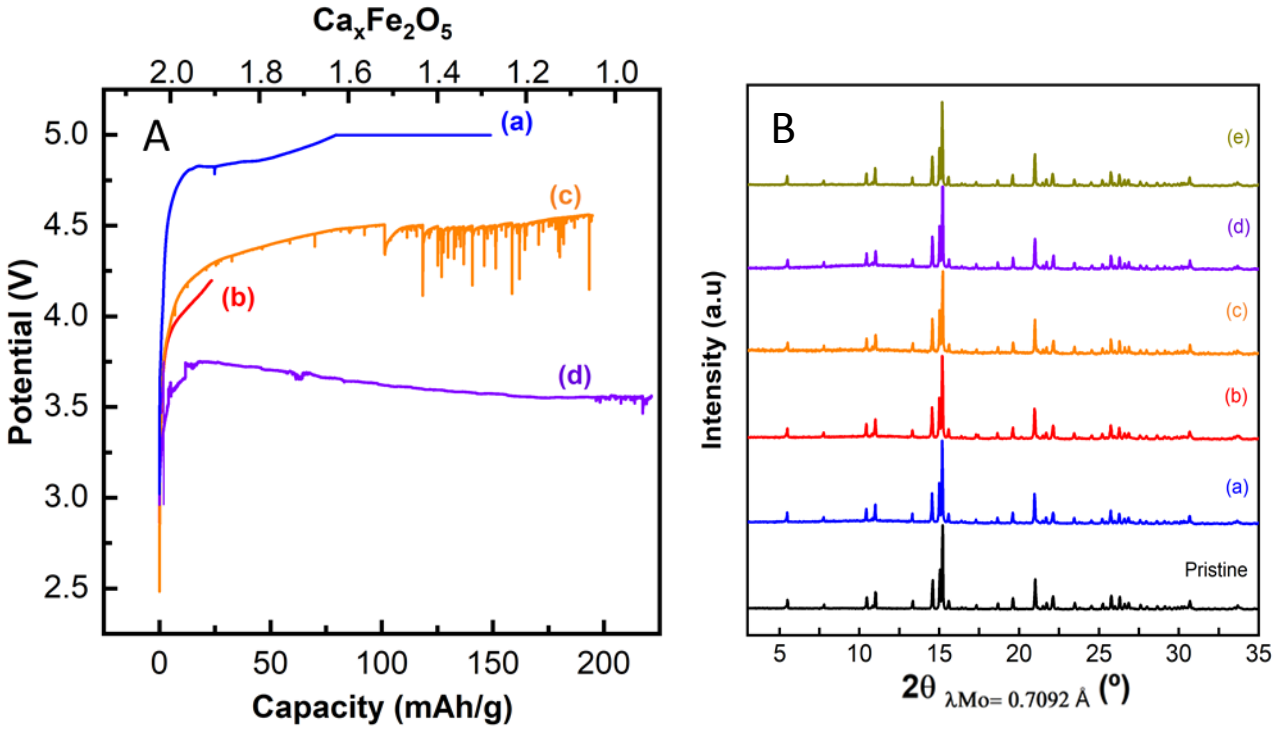

Figure S4. **(A)** Characteristic voltage profiles versus specific capacity (bottom) and versus moles of virtually de-inserted Ca^{2+} (Δx, estimated that calcium deintercalation is the only reaction taking place) (top) for $Ca_2Fe_2O_5$ in Li cells, with LP30 electrolyte at RT **(a)**, 1 m LiBOB, EC/PC (1:1 vol) electrolyte at 100°C **(b)** and in Ca cells, with 0.45 M $Ca(BF_4)_2$, EC/PC (1:1 vol) electrolyte at RT **(c)** and 100°C **(d)** and corresponding ex-situ XRD patterns in **(B)**. XRD patterns of the pristine and chemically oxidized samples are also displayed in **(B).**

References

[1] B.F. Decker, J.S. Kasper, The structure of calcium ferrite, Acta Cryst., 10 (1957) 332-337.

[2] B. Malaman, H. Alebouyeh, A. Courtois, R. Gerardin, O. Evrard, The crystalline-structure of $Ca_4Fe_9O_{17}$ - hexagonal layers of FeO_6 octahedrons and FeO_5 bipyramids linked by FeO_4 tetrahedrons, Mat. Res. Bull., 17 (1982) 795-800.

[3] B. Malaman, H. Alebouyeh, F. Jeannot, A. Courtois, R. Gerardin, O. Evrard, Preparation and characterization of calcium ferrites of the form $CaFe_{2+n}O_{4+n}$ with fractional values of n (3/2,5/2) and their incidence in the Fe-Ca-O diagram at 1120-degrees-c, Mat. Res.Bull., 16 (1981) 1139-1148.

[4] O. Evrard, B. Malaman, F. Jeannot, A. Courtois, H. Alebouyeh, R. Gerardin, The synthesis of a new calcium ferrite ($CaFe_4O_6$) and determination of calcium-ferrite crystalline-structures ($CaFe_{2+n}O_{4+n}$) - a new example of the intergrowth process, J. Solid State Chem., 35 (1980) 112-119.

[5] S. Holmquist, Two new complex calcium ferrite phases, Nature, 185 (1960) 604.

[6] H. Saleh, Synthesis and formation mechanisms of calcium ferrite compounds, J. Mater. Sci. Techol., 20 (2004) 530-534.

[7] H-Y. Li, X-M. Guo, Determination of Gibbs free energy of formation from elements for $Ca_4Fe_9O_{17}$ by Solid-State Galvanic Cell, Metall. Mat. Trans. B, 46.1 (2015), 278–85

[8] A. Markus, H. Taufiq, T. Pekka, J, Evgueni, Determination of thermodynamic properties of $Ca_4Fe_9O_{17}$ by solid state EMF method, J. Alloys Comp., 658(2016), 939-945.