

# **Supporting Information for**

## **A joint computational and experimental evaluation of $\text{CaMn}_2\text{O}_4$**

### **polymorphs as cathode materials for Ca ion batteries**

M. Elena Arroyo-de Dompablo<sup>1,\*</sup>, Christopher Krich<sup>2</sup>, Jessica Nava-Avendaño<sup>3</sup>, Neven Biškup<sup>4</sup>,

M. Rosa Palacín<sup>3</sup> and Fanny Bardé<sup>2</sup>

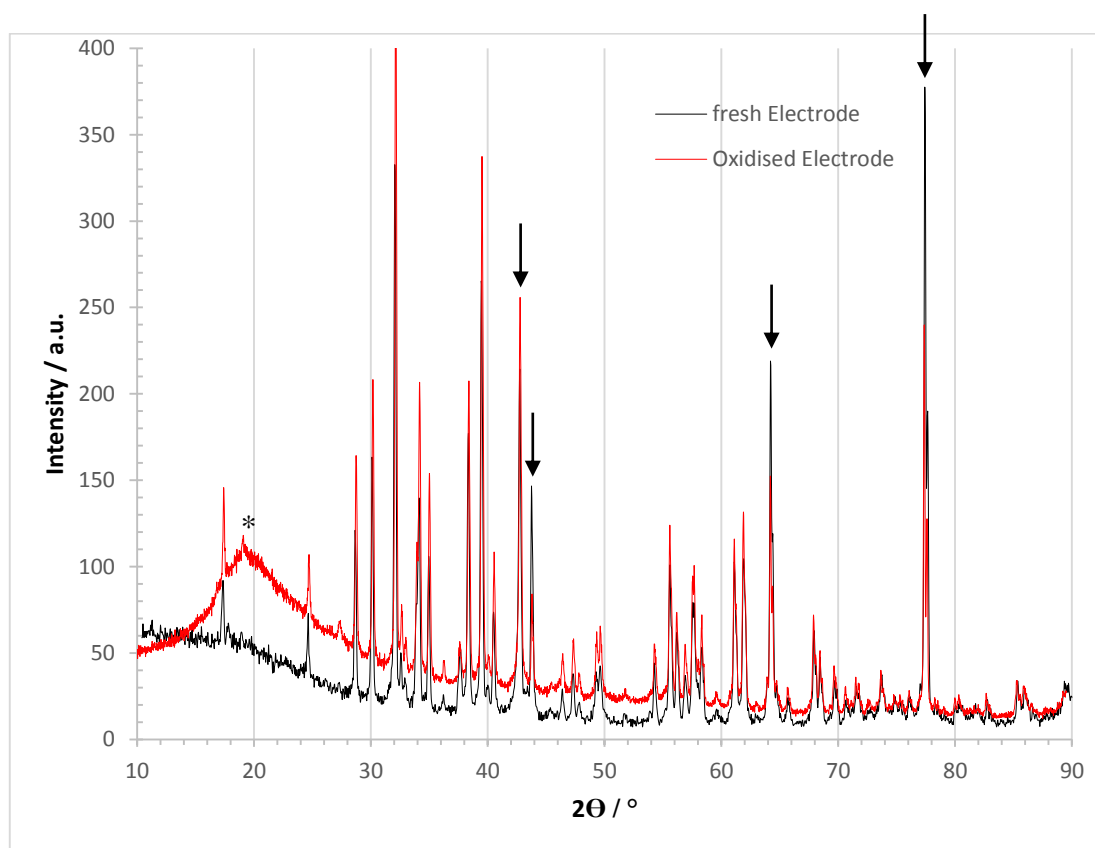
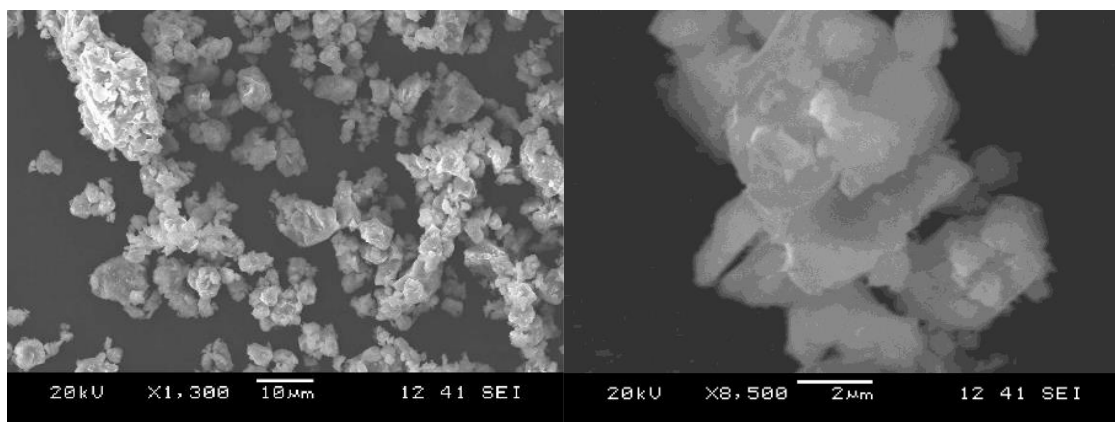
<sup>1</sup>Malta Consolider Team, Departamento de Química Inorgánica, Universidad Complutense de Madrid, 28040 Madrid, (Spain)

<sup>2</sup>Toyota Motor Europe, Research & Development 3, Advanced Technology 1, Battery team, Technical Centre, Hoge Wei 33 B, B-1930 Zaventem, (Belgium).

<sup>3</sup> Institut de Ciència de Materials de Barcelona (ICMAB-CSIC) Campus UAB, E-08193 Bellaterra, Catalonia (Spain)

<sup>4</sup> Instituto Pluridisciplinar, Universidad Complutense de Madrid, 28040 Madrid, (Spain)

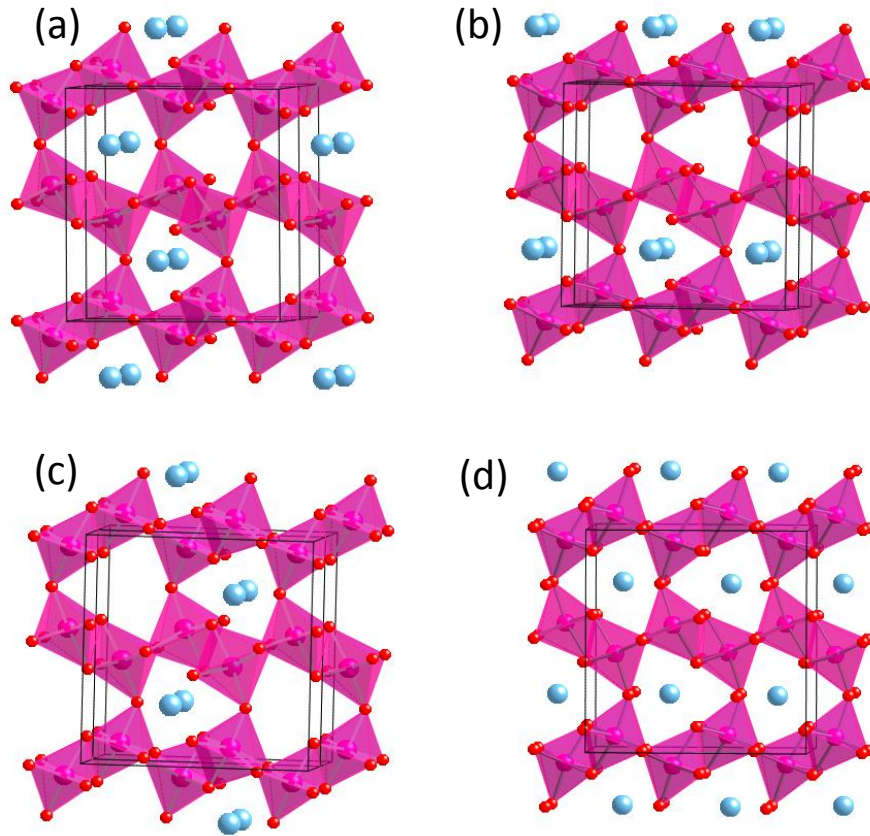
\*Corresponding author: e.arroyo@quim.ucm.es



**Figure S.1.-** (a) SEM images of synthesized  $\text{CaMn}_2\text{O}_4$  powder. (b) Comparison of XRD patterns of the electrodes before and after oxidation. The arrows indicate the diffraction peaks of the aluminium current collector. The broad feature indicated with \* originates likely from solvent residues and carbon black present in the electrode as additive to enhance electronic conductivity.

**TABLE I.** Calculated lattice parameters (in Å) for the spinel (SP) and the two post-spinel CM (S.G. *Pbcm*) and CF (S.G. *Pnma*)  $\text{Ca}_x\text{Mn}_2\text{O}_4$  ( $x = 0,1$ ) structures. Experimental values from this work are also listed.

x	method	<i>a</i>	<i>b</i>	<i>c</i>	$V(\text{\AA}^3)$
CF-1	GGA	10.681	9.256	3.089	305.39
	GGA+U	10.730	9.233	3.149	311.95
CF-0	GGA	10.309	8.586	2.837	254.16
	GGA+U	10.393	8.632	2.922	262.20
CM-1	GGA	3.207	10.132	9.754	317.02
	GGA+U	3.199	10.193	9.825	320.36
CM-0	GGA	2.838	9.489	9.299	250.50
	GGA+U	2.901	9.614	9.414	262.61
SP-1	GGA + U	5.949	5.949	10.219	361.73
SP-0	GGA + U	5.819	5.819	8.291	280.76
CM-1	Exp.	3.159	9.994	9.675	304.55



**Figure S.2.-** (a-c) Optimized crystal structures of the possible  $\text{Ca}_{0.5}\text{Mn}_2\text{O}_4$  configurations within the unit cell. The three configurations have positive formation energies. (d) Optimized crystal structure of the most stable  $\text{Ca}_{0.5}\text{Mn}_2\text{O}_4$  configuration found in this study ( $2a \times b \times c$  supercell)

## Thermodynamics of $\text{CaMn}_2\text{O}_4$ polymorphs

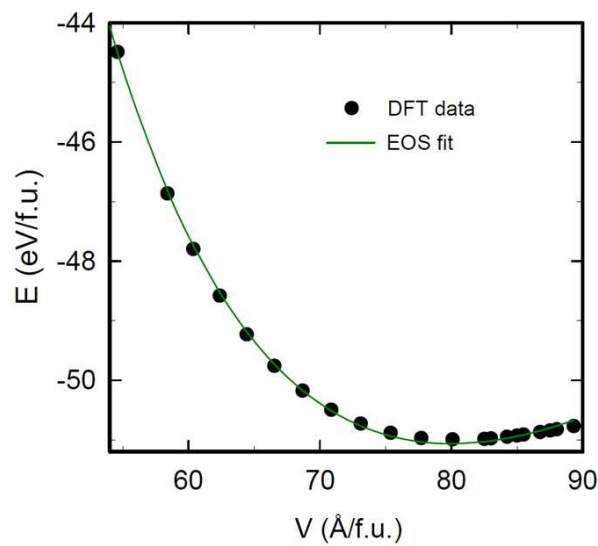
As indicated in **figure 3** of the main text, the CF and SP phases are both 0.3 eV/ f.u. less stable than the CM phase. The CF has a greater density, this is to say, CF is the high-pressure polymorph. It is well documented <sup>1 2</sup> that the CM polymorph transforms to the high pressure CF-polymorph at 30 GPa (room temperature). With the present computational results, we can make a fast evaluation of the pressure required for the CF $\rightarrow$  CM transformation ( $P = \Delta E/\Delta V$ ). This yields a calculated pressure of 24 GPa (0 K), which is of the same order than the experimentally observed. The SP phase has lower density than the CM phase, thus, it is a potential high temperature polymorph, a possibility to examine by means of calculated equations of state of the CM and SP polymorphs. **Figure 6** in the main text shows the calculated total energy vs. volume curves of the  $\text{CaMn}_2\text{O}_4$  polymorphs; spinel (SP in red circles) and marokite (CM in black diamonds). Symbols correspond to the DFT calculated data, and lines show the fitting to the Birch-Murnaghan equation of state.

### Parameters of Energy –Volume fitting to the Birch-Murnaghan EOS

CM:  $E_0 = 50.99$  eV/f.u  $V_0 = 80.37$  Å<sup>3</sup>/f.u.  
 $B_0 = 99.50$  GPa  $B'_0 = 6.96$   
reg.coef = 0.76 E-05

SP:  $E_0 = 50.71$  eV/f.u  $V_0 = 90.88$  Å<sup>3</sup>/f.u.  
 $B_0 = 90.13$  GPa  $B'_0 = 6.09$   
reg.coef = 0.35 E-05

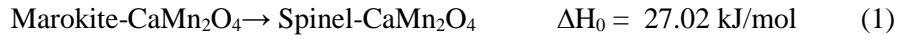
### Energy –Volume fitting to the Birch-Murnaghan EOS with $B'_0$ fixed to 4



**Figure S.3.** Calculated total energy vs. volume curves of the CM- $\text{CaMn}_2\text{O}_4$  and fitting to the Birch-Murnaghan equation of state, with  $B'_0$  fixed to 4.

Yamanaka et al.<sup>2</sup> determined, experimentally, the bulk modulus of the marokite (CM) phase. The bulk moduli were calculated by the Birch-Murnaghan equation of state using the observed volumes as a function of pressure. The calculation provided  $B_0 = 155(2)$  GPa for CM- $\text{CaMn}_2\text{O}_4$ . In the calculation  $B_0'$  was fixed to 4.0. For sake of comparison we performed a similar data analysis, fixing  $B_0'$  to 4, as shown in figure S.3. The parameters of Energy–Volume fitting to the Birch-Murnaghan EOS ( $B_0'$  fixed to 4 GPa) are  $E_0 = 51.06$  eV/f.u.  $V_0 = 79.63$  Å<sup>3</sup>/f.u. and  $B_0 = 139.75$  GPa.

At  $p = 0$ , DFT calculations yield the enthalpy of the marokite  $\rightarrow$  spinel transition at 0 K:



At constant pressure, and 300 K, the enthalpy of the transformation is expressed as:

$$\Delta H_{298} = \Delta H_0 + \int_0^{298} \Delta C_p dT \quad (2)$$

Where  $C_p$  is the heat capacity at constant pressure, and  $\Delta C_p = C_p(\text{spinel}) - C_p(\text{marokite})$ .

For solids, where expansion is relatively very small,  $C_p$  and  $C_v$  are very similar. Through the quasi-harmonic Debye model, one could calculate the thermodynamic quantities at any temperatures and pressures, from the calculated  $E-V$  data (DFT refers to  $T=0$ K). By using this method, as implemented in the GIBBS code, we estimated the heat capacities,  $C_v$ , of the  $\text{CaMn}_2\text{O}_4$  polymorphs. (157.3 and 158.9 J/mol K for marokite and spinel, respectively, at  $p=0$  and  $T=298$  K). Integration of  $\Delta C_v$  between 0 and 298K gives an enthalpy variation of 0.2 kJ/mol. Then, according to equation (2), the enthalpy of the marokite-spinel transformation at 298 K is 27.22 kJ/mol. We have also estimated the entropy variation at 298K:



(1) Wang, Z. W.; Saxena, S. K.; Neumeier, J. J. Raman scattering study on pressure-induced phase transformation of marokite ( $\text{CaMn}_2\text{O}_4$ ). *J. Solid State Chem.* **2003**, 170, 382-389.

(2) Yamanaka, T.; Uchida, A.; Nakamoto, Y. Structural transition of post-spinel phases  $\text{CaMn}_2\text{O}_4$ ,  $\text{CaFe}_2\text{O}_4$ , and  $\text{CaTi}_2\text{O}_4$  under high pressures up to 80 GPa. *Am. Mineral.* **2008**, 93, 1874-1881.