On the applicability of molybdite as an electrode material in calcium batteries: a structural study of layer-type Ca_xMoO_3

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Supplementary information

XRD and Rietveld refinement

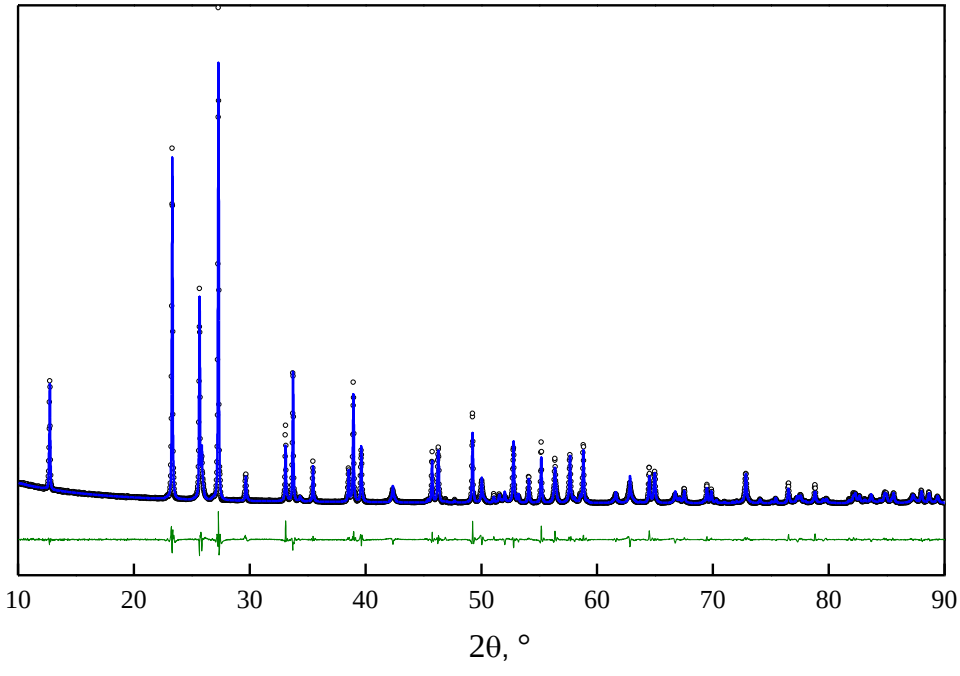

Figure S1. XRD pattern and Rietveld refinement for pristine MoO_3.

Table S1. Structural parameters of MoO_3 refined by Rietveld method, and after geometry optimization (GGA-LBE+Grimme+U=3) (s.g. Pbnm, 62)

		Rietveld refinement	**Geometry optimization**
Unit cell parameters	a / Å	3.96156(8)	3.903
	b / Å	13.8550(3)	14.018
	c / Å	3.69642(8)	3.675
Crystallographic sites 4c (x, y, ¼)			
Oxygen 1	x	0.480(3)	0.500
	y	0.4222(7)	0.434
Oxygen 2	x	0.577(3)	0.520
	y	0.0922(8)	0.088
Oxygen 3	x	0.048(3)	0.033
	y	0.2297(8)	0.222
Molybdenum	x	0.0727(3)	0.076
	y	0.1013(1)	0.104
Reliability Factor	R_{wp}	5.6	
	R_B	3.0	

Geometry Optimization of $CaMoO_3$

The different positions studied are illustrated in Fig. S2. Departing from these positions, the geometrical optimization allowed inferring several structures with minimized energy (Fig. S2). The most favored $CaMoO_3$ structure is that represented by point "d". It results in the lower free energy, and thus in the higher voltage of the reaction (1) with x=1 as reflected in the voltage values included in Table S2.

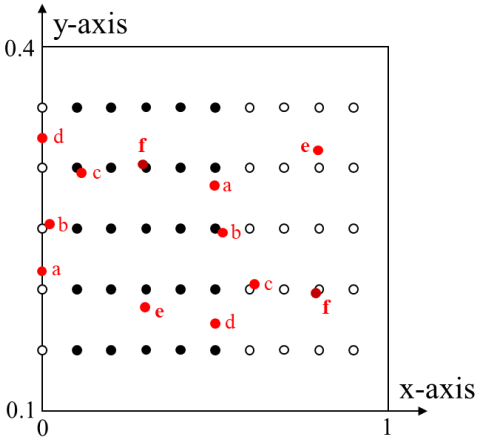

Figure S2. Projection on the ab plane of the different starting coordinates of Ca atoms used for the geometrical optimization of the $CaMoO_3$ phase. In solid black circle, the position used, in open circle, position generated by symmetry operations; in red color the different minima obtained during the optimization.

Table S2. Calculated voltage of the reaction $MoO_3 + Ca \rightarrow CaMoO_3$ for the different minima obtained during the geometry optimization process.

Minimum	a	b	c	d	e	f
Voltage, V	1.80	1.70	1.60	2.23	1.16	0.88