Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

First-principles study of structural stability and electro-chemical properties of Na_2MSiO$_4$ (M = Mn, Fe, Co and Ni) polymorphs

Electronic Supplementary Information (ESI)

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1 Structural Minima

We report here in Table 1 the lattice parameters and atomic coordinates for two relaxed geometries. These structures are obtained from full relaxation (as specified in the main text) of structures presenting Pmn2_1-modi and Pmn2_1-ncycled symmetry. Geometries corresponding to these space group are not stable, as specified in the main text (cf. Table 1) and relax to other geometries corresponding to the Pc space group.

Table 1: Lattice parameters and atomic coordinates for the Na_2FeSiO_4 minima with space group Pc (7). Wyckoff positions account for multiplicity

	Pc (Pmn2_1-modi)				Pc (Pmn2_1-ncycled)			
	a (Å)	b (Å)	c (Å)	γ	b (Å)	c (Å)	γ	
	6.84159	5.75163	5.35012	90.667	6.80725	5.75627	5.3713	90.870
atom	x	y	z	Wyckoff pos.	x	y	z	Wyckoff pos.
Fe1	0.48209	0.68082	0.74266	$2a$	-0.05526	0.68190	0.24277	$2a$
Na1	-0.00274	0.32088	0.75548	$2a$	-0.06210	0.15562	0.49961	$2a$
Na2	0.74733	0.15802	0.00013	$2a$	-0.05672	0.67828	0.75620	$2a$
O1	-0.09907	0.79878	-0.02551	$2a$	0.31680	0.69755	0.30033	$2a$
O2	0.34324	0.08751	0.02648	$2a$	0.37390	0.65905	0.69940	$2a$
O3	0.16832	0.69928	0.80165	$2a$	0.36585	0.08512	0.52660	$2a$
O4	0.50908	0.33922	0.69885	$2a$	0.25546	0.20229	-0.02556	$2a$
Si1	0.23333	0.81095	0.00015	$2a$	-0.04989	0.19070	0.00020	$2a$

These structures are are isoenergetic to the Pc structure obtained starting from within the same space group, and produce the same fitting parameters of the Murnaghan equation within DFT accuracy. However, the b/a and c/a ratios show small deviation between these structures, indicating that equivalent structural minima presenting the same space group symmetry are likely to exist.

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2 Energy-volume curves

In this Section we report the parameters for the Murnaghan equation of state for Na_2MSIO$_4$ compounds for M = Mn, Co and Ni. The energy volume curves are displayed in Figure 1, and the fitting parameters are reported in Table 2. The curves exhibit similar characteristics for varying M. The Pc structure is found to be the ionic ground state, and Pna2_1 and C222$_1$ are always within 0.1 eV from this structural minimum. Notably , in the case of M = Ni, a phase transition from Pc to C222$_1$ is predicted under moderate pressure. The C2 phase exhibits different properties for varying M, being more favourable in the case of Co and Mn (between 0.1 eV and 0.15 eV from Pc) and least favourable in the case of Fe and Ni ($\sim$ 0.2 in both cases). This phase is expected to be relevant at high pressure regimes, due to the small value for the derivative of the bulk modulus with respect to pressure (cf. Table I main text).

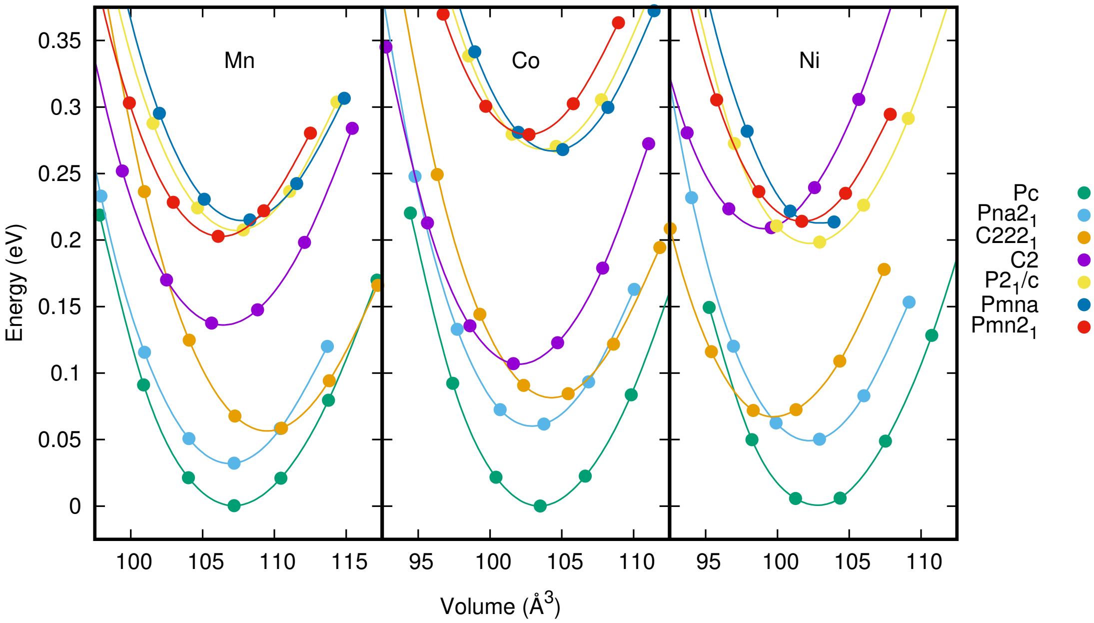

Figure 1: Energy-volume curves per formula unit for the seven more favourable stable configurations for Na_2MSiO$_4$ (M = Mn, Co, Ni) compounds. The zero of the energy axis is fixed to the minimum energy of the Pc structure.

Table 2: Space group for the initial and the optimised structures and parameters of the equation of state. Volume and energies are given per formula unit. The zero value for the latter is set to the value of the most stable structure

Symmetry	E(eV)			V(Å^3/f.u.)			B(GPa)			B'		
	Mn	Co	Ni	Mn	Co	Ni	Mn	Co	Ni	Mn	Co	Ni
Pc (7)	0.00	0.00	0.00	107.12	103.39	102.71	70.64	75.67	75.82	5.79	5.10	4.85
Pna2_1 (33)	0.03	0.06	0.05	106.85	102.98	102.15	72.12	77.61	77.73	5.06	5.03	4.41
C222$_1$ (20)	0.06	0.08	0.07	109.51	104.30	99.83	73.42	75.43	71.50	4.47	4.56	5.48
C2 (5)	0.14	0.11	0.21	109.51	102.02	98.94	71.80	76.76	75.29	4.66	4.21	4.21
P2_1/c (14)	0.20	0.27	0.20	107.46	103.71	102.67	74.91	79.43	78.01	4.76	4.80	5.12
Pnma (62)	0.21	0.27	0.22	107.84	104.32	103.02	73.09	78.23	79.59	5.00	4.34	4.02
Pmn2_1 (31)	0.20	0.28	0.21	106.28	102.58	101.64	75.46	77.13	76.03	4.22	5.35	5.03
P$3_1$2 (159)	0.84	0.92	0.77	104.87	101.49	99.96	77.12	86.63	89.96	5.71	4.55	4.59

3 Density of states

In this section we show the density of states of systems analysed in the main text. In Figure 2 the DOS for $Na_2 M SiO_4$ orthosilicates in Pc symmetry are compared for varying M = Mn, Co, Ni. The plot for iron is presented in the main text (Figure 3), and here at the bottom panel of Figure 3. The Na and Co systems present similar shapes to the Fe case. The DOS peaks observed in the spin down channel, for instance, are not as neat as in the M = Fe case, due to the presence of a larger number of d electrons. For the same reason, the gap observed between the valence band and the other filled states becomes smaller in the case of Co and vanishes in the case of Ni. The smallest band gap is observed for the spin down channel, larger with respect to the M = Fe case, as reported in the main text (Table IV). A different behaviour can be observed for M = Mn. The spin down channel present very similar DOS peaks as the Fe case, but the peak below the Fermi level is no longer present, consistently with the lack of 1 d electron, and a double peak is observed for the conduction band.

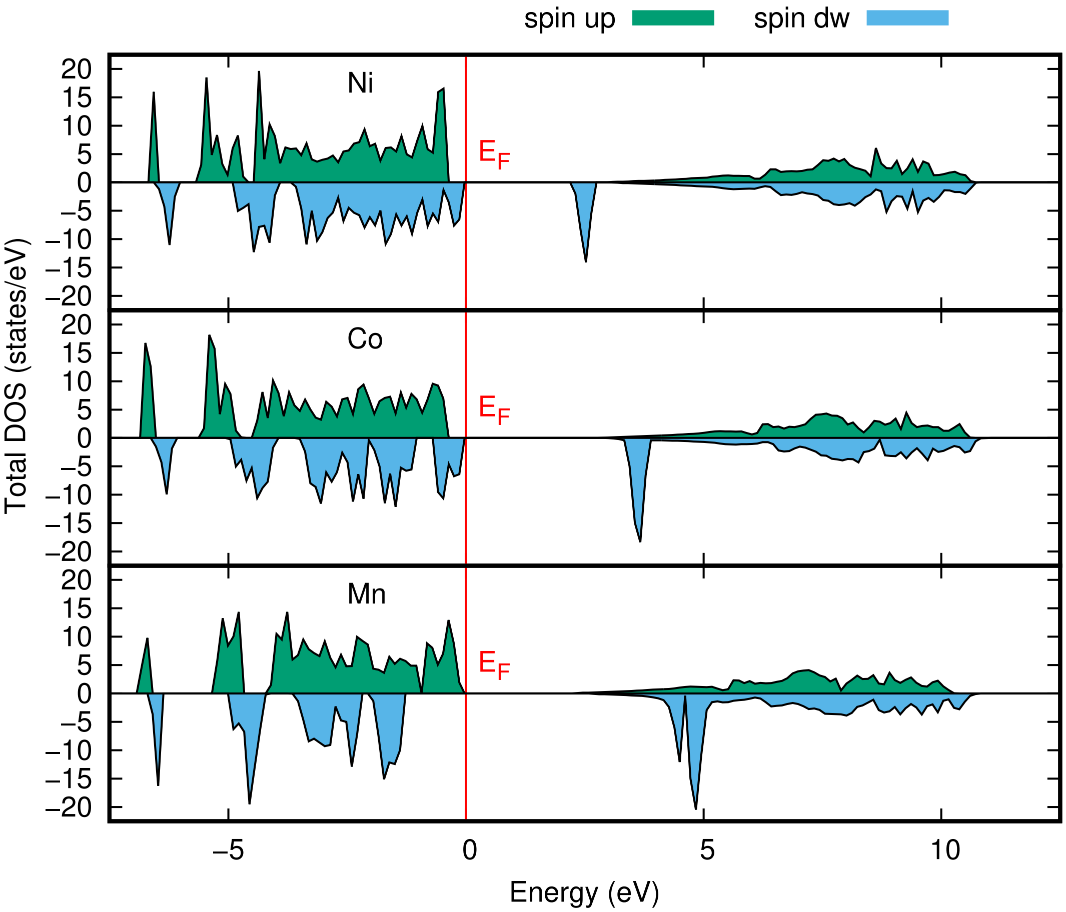

Figure 2: Total DOS for Pc-symmetric structural minima of $Na_2 M SiO_4$ (M = Mn, Co, Ni) compounds. The DOS for the spin down channel is conventially displayed for negative y values. The Fermi level E_F is indicated with a red line.

Finally, we report in Figure 3 the DOS plots for the desodiated stable phases $NaFeSiO_4$ and $FeSiO_4$. In the first case, the DOS peak corresponding to the valence band for the perfect structure vanishes, similarly to the case of $Na2MnSiO_4$ (notably, these two systems have the same number of valence electrons). The band gap, still characteristic of the spin down channel due to a lack of unoccupied state or the spin up one in the 0–4 eV interval, is 2.64 eV, larger by a factor of two with respect to the perfect structure. Notably, an inverse trend is observed upon complete desodiation: in the case of $FeSiO_4$ the DOS of the spin up channel exhibits crossing of the Fermi level. This structure has therefore a semi-metallic nature. In the desodiated structures $NaFeSiO_4$ and $FeSiO_4$ the magnetic shift due to Fe d orbitals has a larger influence on states below -4 eV, compatible with the more pronounced Ni–O interaction (charger transfer) expected for these systems.

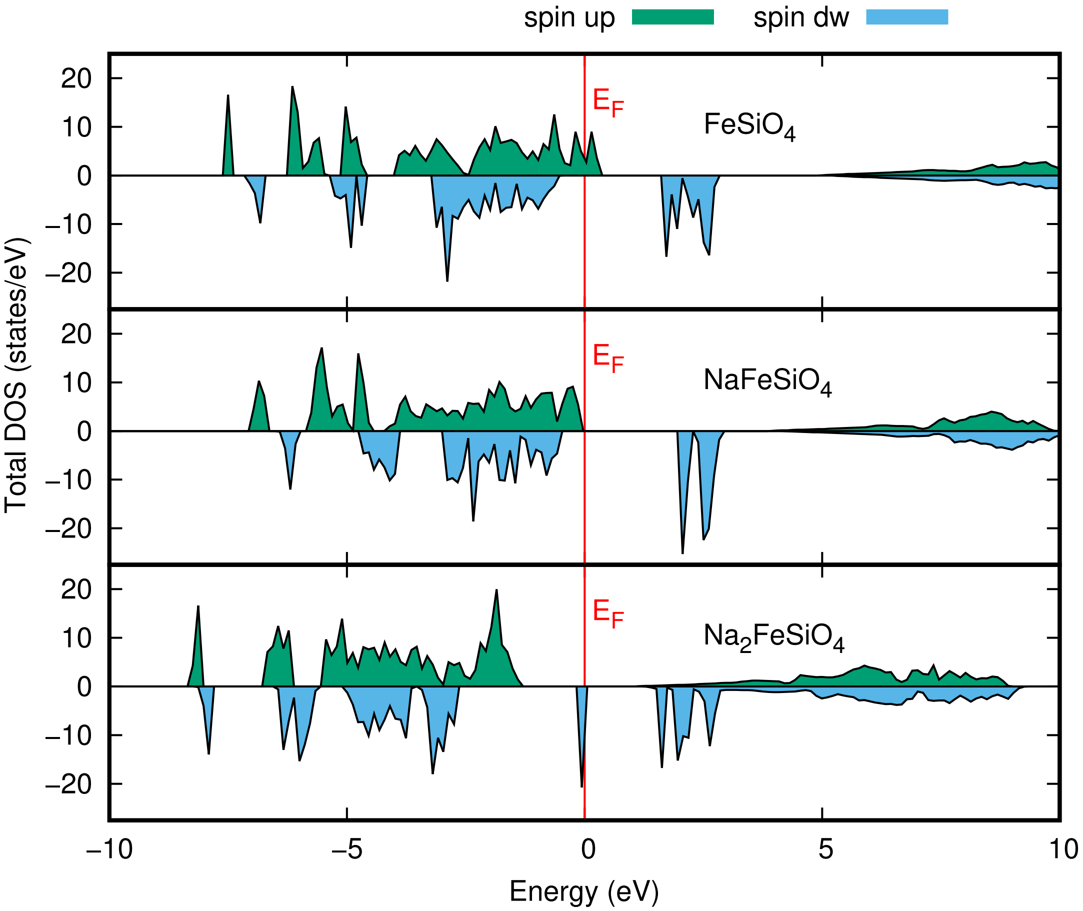

Figure 3: Total DOS for partially and fully desodiated Na_2FeSiO_4. The spin down channel is conventially displayed for negative y values. The Fermi level E_F is indicated with a red line.

4 Structure of NaMSiO$_4$

The polymorphism of Na$_2M$SiO$_4$ orthosilicates is explicitly discussed in the main text. However, as it is known from the case of Li-based orthosilicates, the electrochemical cycling can easily lead to the transformation between different polymorphs. In order to investigate this point, we have performed structural optimisation for the four most stable structures (space groups number 5, 7, 20, 33) for the NaFeSiO$_4$ system. We have removed equivalent Na atoms for each of the optimised Na$_2M$SiO$_4$, obtaining two different structures for each starting symmetry. Upon relaxation, these structures conserved the original symmetry. However, they are found to be non-degenerate, the total energy per formula unit showing a deviation between 0.1–0.2 eV. We have considered for data analysis only the most stable structure for each space group. These results indicate that upon partial desodiation these structures get closer in energy. The same energy per formula unit is found for the Pna2_1 and the Pc-symmetric systems, while geometries consistent with space group 5 (C2) and 20 (C222$_1$) are unfavourable by 20 meV. Altogether, these results indicate that it is more likely to have a phase transition at this stoichiometry. However, the Pc-symmetric structure is still the most energetically favourable, so that a phase transition may not necessarily occur, as opposed to the Li case and in agreement with experimental data, according to which the cathode is stable upon cycling.