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Supplemental Information: First-principles and thermodynamics comparison of compositionally-tuned delafossites: Cation release from the (001) surface of complex metal oxides

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S1: Thermodynamic Comparisons

Figure 1 shows the ΔG of dissolution, ΔG_{tot}, of FMA across the pH range of 1-9. All of the metals are predicted to have favorable release, with the dissolution of Fe and Al stopping at pH=6 and pH=5, respectively. At these pH values these metals form stable oxide solids, as is discussed in the manuscript.

To calculate the theoretical enthalpies of formation (E_f) per formula unit, we used the 72 atom bulk cell described in the manuscript. Briefly, this bulk cell includes a total of 72 atoms; 18 metals (Fe, Co, Al, Ni, etc.), 36 oxygen, and 18 Li. We divide each of these by three to use as the reactants in our calculation, as this yields a total chemical formula of $\mathrm{Li}_6(A_2B_2C_2)\mathrm{O}_{12}$ that can account for AFM coupling within the same and multiple metal sites. We subtract the DFT calculated total energies for these reactants in their standard states (bulk metals and O_2 gas) and then subtract this from the energy of the bulk structure. The chemical equation for the formation of a $2\sqrt{3}\times\sqrt{3}$ FMA surface is shown in Equation 1, and the energetic expression is shown in Equation 2 where the stoichiometry is preserved.

$$2Fe(s) + 2Mn(s) + 2Al(s) + 6Li(s) + 12O_2(g) \rightarrow Li(Fe_{1/3}Mn_{1/3}Al_{1/3}O_2) \tag{1}$$

$$E_{\mathrm{f}} = E_{\mathrm{bulk-FMA}} - (2 \times E_{\mathrm{bulk-Fe}} + 2 \times E_{\mathrm{bulk-Mn}} + 2 \times E_{\mathrm{bulk-Al}} + 12 \times E_{O_2} + 6 \times E_{\mathrm{bulk-Li}}) \tag{2}$$

S2: Spin Comparison

Spin ordering tests were run for a representative set of formulations (NMC, NVF, FMA, and FTV) to investigate favorable spin orderings for the complete set of structures. The spin tests run for these CMOs are shown in Table 1 where the most favorable spin ordering is shown in **bold**. Various spin arrangements were tested: ferromagnetic (FM) ordering with all spins

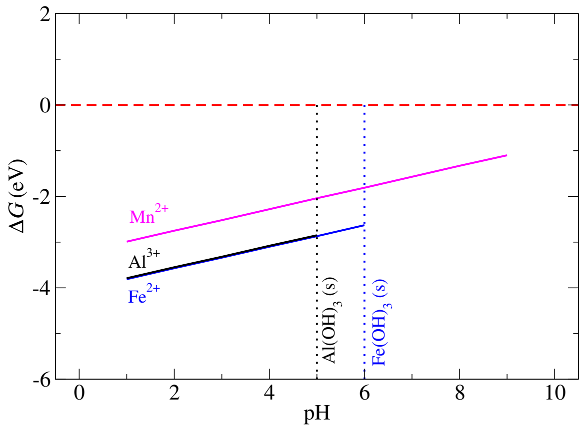


Figure 1: ΔG_{tot} of cation surface release for FMA.

aligned, antiferromagnetic (AFM) ordering where metal spins couple to opposing spins on different metals, and an antiferrimagnetic (AFiM) ordering where the metal spins self-couple (denoted as an up and down arrow). Our first representative formulation is NMC. In NMC Ni^{2+} ($3d^8$) has 2 unpaired electrons, Mn^{4+} ($3d^3$) has 3 unpaired electrons, and Co^{3+} ($3d^6$) has 0 unpaired electrons; the unpaired spins of Ni and Mn can couple either FM or AFM while Co should have no net spin. We find that the AFM ordering of NMC is energetically favorable, in agreement with our previously published work described in the manuscript. It should be clearly stated that even though Co^{3+} is predicted to have no net spin, we initialize spin as a non-zero value. This is because our prior work, discussed in the manuscript, has shown that surface transformations such as metal release or non-stoichiometric surface terminations will result in a change in oxidation state of the remaining surface metals; Ni and Co release from LCO and NMC prompts Co^{3+} to oxidize to Co^{4+}, and varying H-terminations will affect Ni oxidation state.

The results of our spin test could be used to initialize AFM coupling in similar compositions, where only 2 of the 3 metals (i.e. A and B of A, B, and C) are spin active, such as FMA, NMA, VMA, and FTV. To test this hypothesis we investigate the formulations FTV and FMA, where we perform two different sets of calculations. For FTV we allow FM, AFM, and AFiM spin ordering, allowing for the spins of Fe and V to start off as half up and half down to test whether or not each metal will be AFM coupled by itself in an overall AFM

Table 1: Tabulated here are the spin orderings tested for NMC, NVF, FMA, and FTV. Here we examine which spin orderings are most favorable for a representative set of delafossite formulations. The arrows represent the initial direction of the spin and metals with a double arrow are antiferromagnetically coupled with itself. A - in the final spin column indicates that the site relaxed to a spin moment of 0, or had no unpaired spins. All differences in total energy (ΔE) are reported in units of eV per total bulk cell.

CMO	Ordering	Initial Spins (A, B, C)	Final Spins (A, B, C)	ΔE (eV, bulk cell)
NMC	FM	↑, ↑, ↑	↑, ↑, -	0
	AFM	↓, ↑, ↑	↓, ↑, -	**-0.095**
FTV	FM	↓, ↓, ↓	↓, -, ↓	0
	AFM	↑, ↓, ↓	↑, -, ↓	-0.419
	AFiM	↑↓, ↓, ↑↓	↑↓, -, ↑↓	**-0.422**
FMA	AFM	↑, ↓, ↓	↓, ↓, -	0
	AFiM-1	↑↓, ↑, ↓	↑, ↑, -	0
	AFiM-2	↑↓, ↑↓, ↓	↑↓, ↑↓, -	0
	AFiM-3	↑, ↑↓, ↓	↓, ↓, -	0
NVF	AFM	↑, ↑, ↓	↑,↑,↓	0
	AFiM	↑↓, ↑↓, ↑↓	↑↓,↑↓,↑↓	**-0.041**

coupled surface. For FMA we test 4 different AFM-type orderings, which include multiple antiferrimagnetic couplings.

For FTV we find a substantial decrease in total energy of 0.4 eV for the AFM and AFiM states when compared to the FM state. This is $4\times$ the ΔE between FM and AFM ordering observed in NMC. This comparison shows that either the AFiM or AFM coupling is favored across varied compositions, and that ΔE also varies by composition. We are also able to infer that the difference in AFM and AFiM initialization results in very similar total energies for the 72 atom bulk cells. If we were to compute this energy difference per unit cell the difference is less than 1 meV, which is almost negligible compared to $\approx$ 1-10 eV differences computed for ΔG_1 of the surface transformations.

We can investigate this further with the FMA composition. FMA shows no preference for AFM or AFiM initialization, as over the course of the calculation the spins reorder and result in the same total energies per bulk structure. Knowing that the AFM ordering should be favorable across multiple compositions, and that energy differences are small between the

AFM and AFiM setups, we can be sure that initializing formulations where 2 of the 3 metals have non-zero spin moments as AFM will result in structures where major metal-metal spin interactions are accounted.

With this information we go on to investigate how AFM coupling would affect a composition where all three metals (A, B and C) could support spin-coupling using the formulation NVF as our test case. As shown in Table 1, it is necessary to include AFiM spin order initialization; ΔE for the AFiM bulk cell is 0.041 eV lower in energy than for an AFM bulk cell. This difference between AFM and AFiM is an order of magnitude larger than for our FTV test described in the paragraph above, so the AFiM initialization needs to be applied to compositions where all 3 metals may contain nonzero spin: the NVF and NMF compositions.

We did not perform these FM, AFM, AFiM comparative tests for formulations where only one metal site, i.e. only A of A, B, and C, contained a non-zero spin moment, such as CFA, FTA and VTA.

Table 2: Tabulated here are the average and standard deviation of spins for each cation, given in units of μB, taken from all DFT calculations, for each type of system; bulk, (001) surface (before release), and (001) surface vacancies (after release). The most likely average oxidation states are presented in parentheses.

element	bulk	surface	vacancy
Al	0.00 ± 0.00 (Al^{3+})	0.00 ± 0.00 (Al^{3+})	0.00 ± 0.00 (Al^{3+})
Ti	0.21 ± 0.13 (Ti^{4+})	0.07 ± 0.07 (Ti^{4+})	0.08 ± 0.07 (Ti^{4+})
V	1.27 ± 0.53 (V^{3+})	1.22 ± 0.49 (V^{3+})	0.64 ± 0.54 (V^{4+})
Mn	2.27 ± 0.34 (Mn^{4+})	2.27 ± 0.36 (Mn^{4+})	2.44 ± 0.36 (Mn^{4+})
Fe	2.59 ± 1.47 (Fe^{2+})	1.33 ± 1.42 (Fe^{3+})	2.04 ± 0.82 (Fe^{2+})
Co	0.01 ± 0.01 (Co^{3+})	0.01 ± 0.01 (Co^{3+})	0.23 ± 0.30 (Co^{3+})
Ni	1.54 ± 0.05 (Ni^{2+})	1.45 ± 0.06 (Ni^{2+})	0.85 ± 0.51 (Ni^{3+})

We tabulate the average values of spin for each cation in the bulk structures and (001) surfaces both before and after metal release to better understand how each cation responds to changes in chemical environment via compositional tuning, surfacing effects, and metal release. Table 2 shows that a few elements in the set are resistant to oxidation and reduction as a function of compositional tuning in the bulk; Al, Ti, Co, Ni, nominally found in the solid as Al^{3+}, Ti^{4+}, Co^{3+}, and Ni^{2+}. Of the remainder Fe has the largest range in oxidation states, followed by V and then Mn. These mid-row $3d$ elements also exhibit the greatest range in oxidation states of the set in nature.

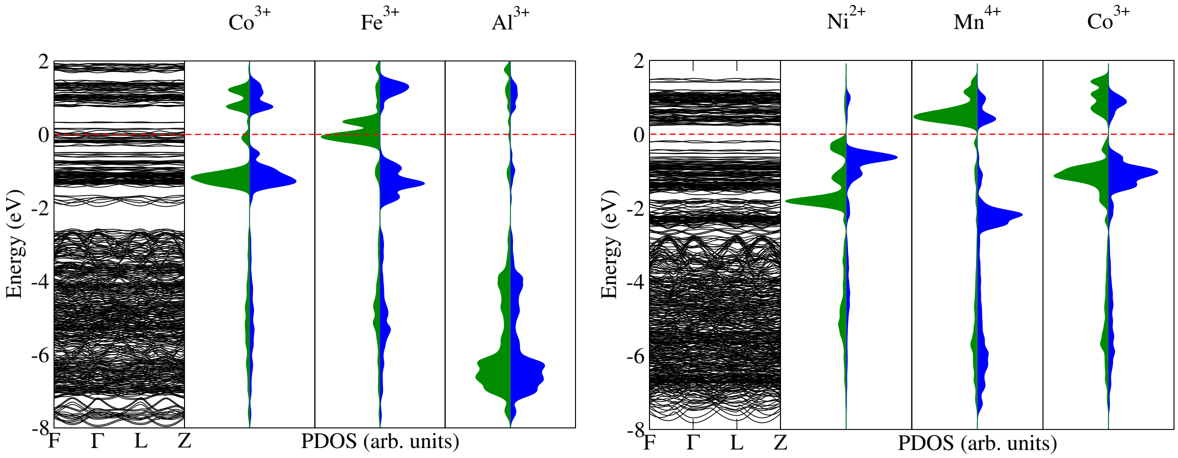
Going from the bulk to the cleaved (001) surface, the average spins of the set remain relatively constant except Fe, where the average spin decreases from 2.59 to 1.22. This implies that Fe will accommodate other cations by changing its own spin and oxidation state. Of the seven cations in the set, Fe is the most sensitive to its chemical environment. We also compare the surface to vacancy structures to better understand the trends in electronic reorganization. Al, Ti, Mn, Co are relatively insensitive whereas V, Fe, and Ni are more prone to redox changes when comparing the surface and vacancy structures. For example, V^{3+} oxidizes to V^{4+} and Ni^{2+} oxidizes to Ni^{3+}, while Fe most likely reduces and oxidizes, depending upon the chemical environment.

S3: Electronic Structure

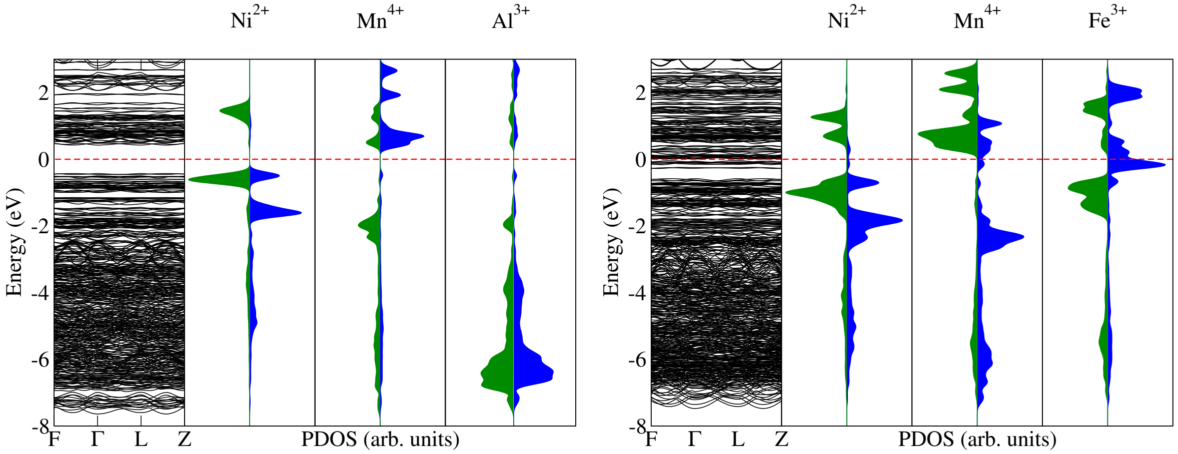
Figures 2 and 3 show the calculated band structure and projected density of states (PDOS) for the d-electrons for each of the metals on the surface.

S4: Surface Termination Effects

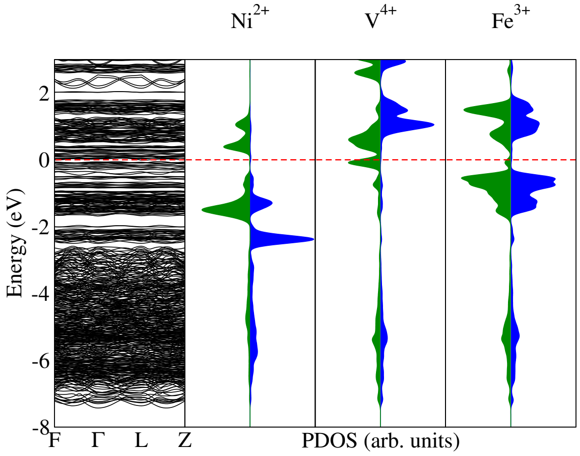
Another aspect of the environment that will affect the oxidation states of surface metals are the functional groups present. Each surface metal is bonded to three surface O, therefore, there are 4 configurations surface metal sites can have, depending on the amount of protonation. Figure 4 shows theses four distinct sites from a top view of NMC.



(a) CFA (b) NMC

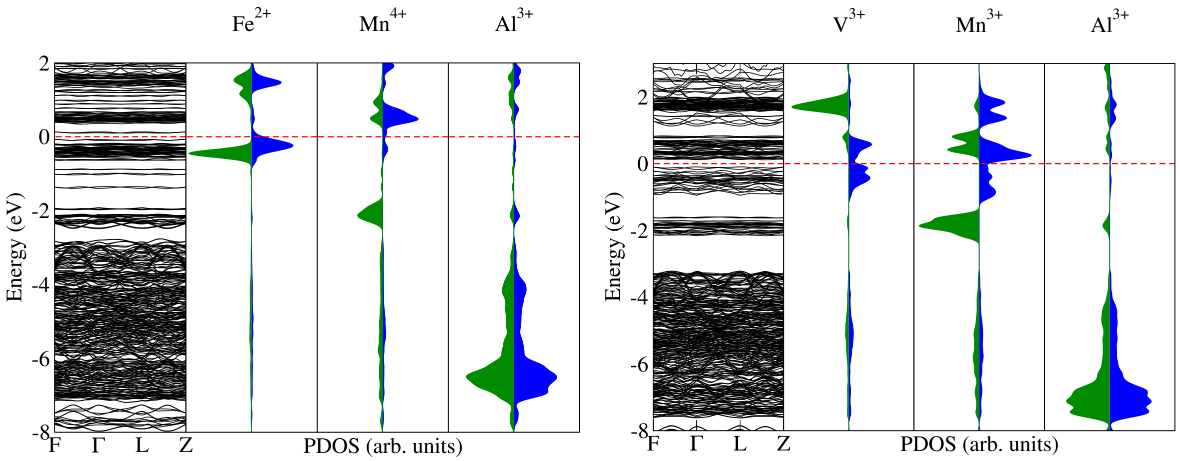


(c) NMA (d) NMF

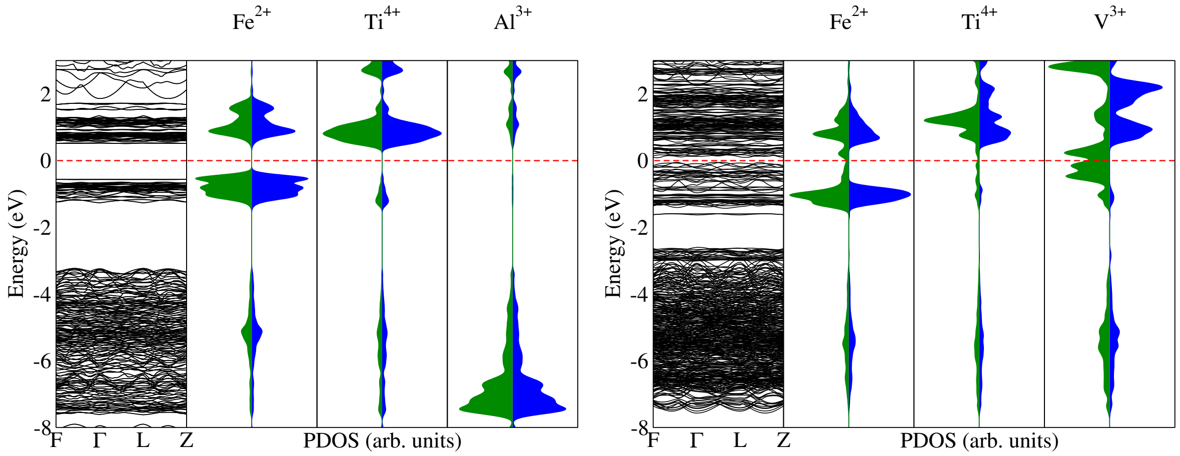


(e) NVF

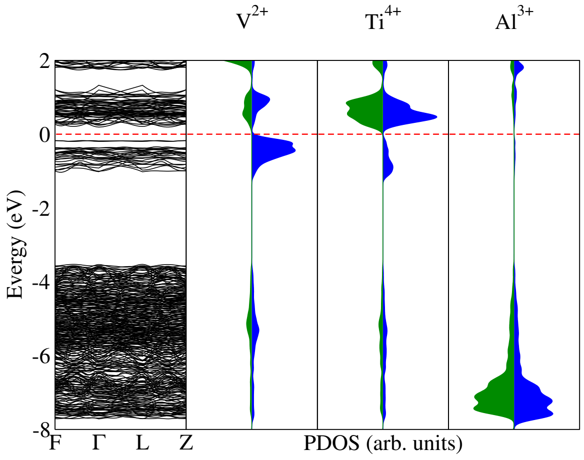
Figure 2: Bands and PDOS of the surface and surface metals of CFA, NMC, NMA, NMF, and NVF



(a) FMA (b) VMA



(c) FTA (d) FTV



(e) VTA

Figure 3: Bands and PDOS of the surface and surface metals of FMA, VMA, FTA, FTV, and VTA

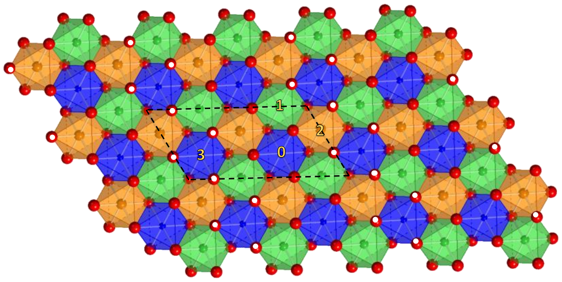


Figure 4: Shown here is the top view of NMC that is -OH terminated, to show the different metal sites that exist on the surface. The metal sites are labeled zero through three, where the numbers represent the amount of -OH groups that are directly connected to the metal. The amount of -OH on a particular site affect the oxidation state of the metal and therefore, the spin. This has the same color scheme as Figures 1 and 2 in the manuscript.