

# Ti / Ni doping effects on formation energy and electronic structure of NaMnO<sub>2</sub> cathodes

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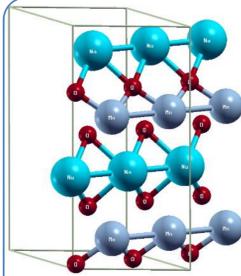
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In the last years, the research of efficient substitution of Lithium Ion Batteries (LIB) with Sodium Ion Batteries (NIB) has rapidly attracted the attention of the researchers. The Na is cheap and widely distributed worldwide making the Na a promising alternative with respect to the Li which, instead, is more expensive, presents very limited resources availability and difficulties to satisfy the growing market demand. Our research is mainly focused on the study by "ab-initio" computational simulations of structural/geometrical and electronic properties of sodium-based cathodes (like Na<sub>x</sub>Ni<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>). More specifically, using Density Functional Theory (DFT) we have mainly focused on the calculation of Hubbard (U) parameter (within linear response theory) which takes into account the correlation effects which are extremely important in the transition metal oxides.

We have investigated the geometric and electronic structure for different magnetic phases, and for each one we have obtained information about stability calculating formation energy calculations and also about redox potential. We have evaluated the modification of the electronic structure of the original NaMnO<sub>2</sub> crystal after doping/substitution with Nickel and Titanium (Na<sub>x</sub>Ni<sub>1/3</sub>Mn<sub>1/2</sub>Ti<sub>1/6</sub>O<sub>2</sub>). We found that small quantities of doping by heteroatoms increase the structure stability even if the Na concentration does not change. Moreover, doping generates new conduction bands helping to lower the electric resistance without affecting the redox potential that remains almost the same.

In the next step, we plan to recalculate the main observables using Hybrid Exchange-Correlations Functionals in order to compare the results with the previous DFT+U calculations and increase the theoretical level of the study.



Our research is mainly focused on transition metals based cathodes with the form: **NaXMnO<sub>2</sub>** where **X** is a transition metal, more specifically **Ni** or **Ti**. We first considered **Ni** in a 1/3 from 2/3 ratio with respect to **Mn** which is the cathode that shows the highest stability after several charge/discharge cycles. Furthermore we considered also **Ti** as **Mn** substitutional element in Na<sub>x</sub>Ni<sub>1/3</sub>Mn<sub>1/2</sub>Ti<sub>1/6</sub>O<sub>2</sub> cathode for which we studied the electronic properties for different Na concentrations. [1]  
For the study of cathodes of Na based batteries we start, as a preliminary model, from the **P2** phase of NaMnO<sub>2</sub>, an **8 hexagonal layers** structure [2] in which, to facilitate the symmetry breaking, we have considered the **24 atoms cell** instead of the simple 8 atoms one (see Fig. on the left).  
All simulations are performed within the **Density Functional Theory (DFT)** framework. [3,4]. For all systems under study we have investigated: 1) ground state geometry, 2) magnetic phase of the system (ferromagnetic (FM) or antiferromagnetic (AFM)), 3) formation energies, 4) electronic structure and bands, 5) redox potential.

[1] P. Prohini et al. Materials, 12(7), 1074, (2019)  
[3] P. Hohenberg and W. Kohn; Phys. Rev. B, 136, 864, (1964)

[2] J. M. Paulsen et al. Chem. Chem. Mater., 12, 2257, (2000)  
[4] W. Kohn, L. J. Sham; Phys. Rev. 140, A1133, (1965)

**DFT + U** In order to go beyond the limit of local and semilocal Exchange-Correlation (XC) functionals we adopt the **DFT+U** approach with **U Hubbard parameter** which takes into account the effects of electronic correlation. We have calculated the **U** parameter "ab-initio" within the **linear response theory** [5,6], starting from the response function  $\chi$  for the interacting system defined as

$$\chi = \frac{\partial n}{\partial \alpha}$$

In fact, once we know the response function  $\chi_{KS}$  for the Kohn-Sham system, we can obtain the **U** parameter by the expression [5,6]:

$$U = \frac{1}{\chi_{KS}} - \frac{1}{\chi}$$

We have also taken into account the magnetic phase of the material (FM or AFM) in order to choose the most stable phase.

**RedOx Potentials:** Intercalation potentials (RedOx potentials) are obtained using the following expression:

$$V(x_1, x_2) = \frac{E(\text{Na}_{x_2}\text{MO}_2) - E(\text{Na}_{x_1}\text{MO}_2) - (x_1 - x_2)E(\text{Na})}{F(x_1 - x_2)}$$

where **E(NaXMnO<sub>2</sub>)** is the total energy (for unit formula) of the host material, **X<sub>i</sub>** the intercalation value, **E(Na)** is the total energy of the cubic bulk Na and **F** is the Faraday constant.

**Formation Energy:** Formation Energies (**E<sub>Form</sub>**) are obtained as difference between the total energy of the cell and the total energy of the single atomic species in their stable form and at room temperature. More specifically the formation energy is calculated by the expression:

$$E_{\text{Form}} = \frac{E_{\text{Tot}} - \sum_{\text{For each X element}} n_X E_{\text{X-Bulk}}}{n_{\text{Tot}}}$$

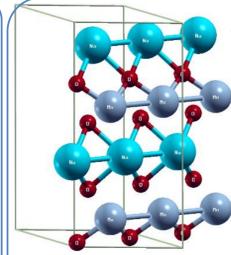
where **E<sub>Tot</sub>** is the total energy of the final compound, **E<sub>X-Bulk</sub>** are the total energy of each atomic species, **n<sub>Tot</sub>** is the total number of atoms and **n<sub>X</sub>** is the number of atoms of the **X** element.

**Doping Energy:** Doping Energies (**E<sub>Dop</sub>**) are obtained using the expression:  $E_{\text{Dop}} = E_{\text{DS}} - E_{\text{US}} + E_{\text{Mn}} - E_{\text{X}}$

where **E<sub>DS</sub>** and **E<sub>US</sub>** are the total energies for the doped and undoped system and **E<sub>X</sub>** are the total energy of the dopant element that substitute the **Mn** in the studied system

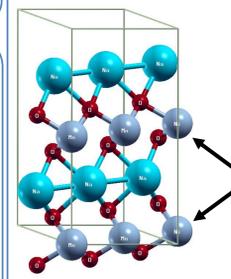
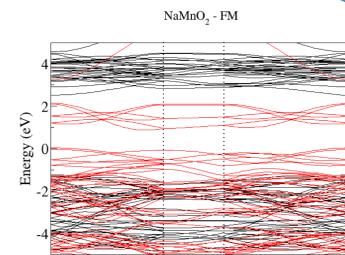
[5] F. Zhou et al. Phys. Rev. B 70, 235121 (2004)

[6] M. Cococcioni, S. De Gironcoli, Phys. Rev. B, 71, 035105 (2005)



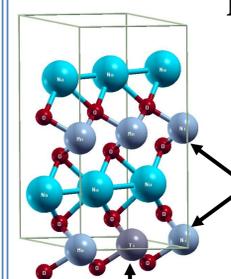
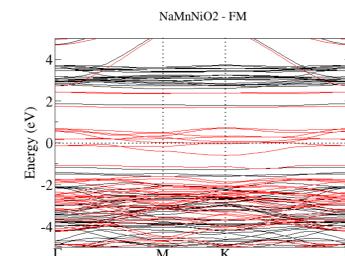
NaMnO<sub>2</sub>

**E<sub>Gap</sub> = 1.2 eV**



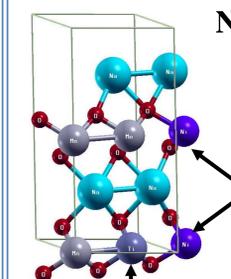
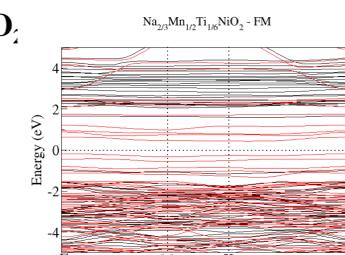
NaNiMnO<sub>2</sub>

**Metallic**



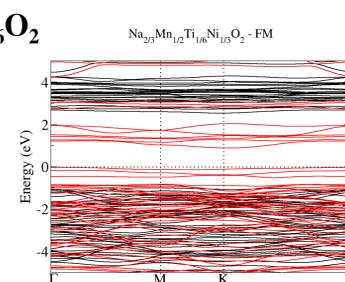
NaNi<sub>1/3</sub>Mn<sub>1/2</sub>Ti<sub>1/6</sub>O<sub>2</sub>

**E<sub>Gap</sub> = 0.4 eV**



Na<sub>2/3</sub>Ni<sub>1/3</sub>Mn<sub>1/2</sub>Ti<sub>1/6</sub>O<sub>2</sub>

**E<sub>Gap</sub> = 0.9 eV**



## Formation Energies, RedOx Potentials and Doping Energies

System	Na	E <sub>form</sub> /atom [eV]
NaNaO <sub>2</sub>	0% Na	-1.13
NaMnO <sub>2</sub>	66.7% Na	-1.65
NaMnO <sub>2</sub>	100% Na	-1.72
NaNiMnO <sub>2</sub>	0% Na	-0.92
NaNiMnO <sub>2</sub>	66.7% Na	-1.38
NaNiMnO <sub>2</sub>	100% Na	-1.52
Na <sub>0</sub> Ni <sub>1/3</sub> Mn <sub>1/2</sub> Ti <sub>1/6</sub> O <sub>2</sub>	0% Na	-1.23
Na <sub>2/3</sub> Ni <sub>1/3</sub> Mn <sub>1/2</sub> Ti <sub>1/6</sub> O <sub>2</sub>	66.7% Na	-1.67
NaNi <sub>1/3</sub> Mn <sub>1/2</sub> Ti <sub>1/6</sub> O <sub>2</sub>	100% Na	-1.76

It is known that **lower values of formation energy correspond to more stable systems**. From the values reported in Tab. 1 we can observe that the **increase of Na** concentration in the compounds leads to a corresponding **rise of the stability**. The substitution of two **Mn** atoms with **Ni** atoms increases the values of formation energies and this means that this substitution produces a decrease of the systems stability.

However a further **substitution of Mn atom with a Ti atom**, leads, instead, to a **more stable compound** that presents the lowest formation energies between all the studied systems.

The values of **doping energy (E<sub>Dop</sub>)** are useful to provide an estimate of the better chemical environment for the **Ti** doping. Tab 2 shows that, for the systems under study, the better condition for this doping is represented by the 2/3 Na stoichiometry.

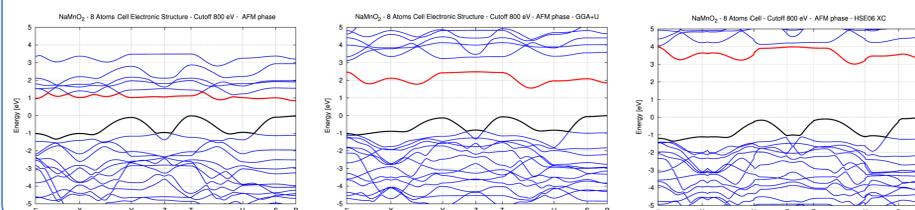
Tab 1

System	Na	E <sub>Dop</sub> (eV)
Na <sub>0</sub> Ni <sub>1/3</sub> Mn <sub>1/2</sub> Ti <sub>1/6</sub> O <sub>2</sub>	0% Na	-3.73
Na <sub>2/3</sub> Ni <sub>1/3</sub> Mn <sub>1/2</sub> Ti <sub>1/6</sub> O <sub>2</sub>	66.7% Na	-4.74
NaNi <sub>1/3</sub> Mn <sub>1/2</sub> Ti <sub>1/6</sub> O <sub>2</sub>	100% Na	-4.09

Tab 3

System	RedOx Potential V(0,1) [V]
NaMnO <sub>2</sub>	3.46
NaNi <sub>1/3</sub> Mn <sub>2/3</sub> O <sub>2</sub>	3.29
NaNi <sub>1/3</sub> Ti <sub>1/6</sub> Mn <sub>1/2</sub> O <sub>2</sub>	3.35
Na <sub>2/3</sub> Ni <sub>1/3</sub> Ti <sub>1/6</sub> Mn <sub>1/2</sub> O <sub>2</sub>	3.65

**Hybrid XC Functionals:** In order to enhance the level of theory and provide further validation about the use of DFT+U computational approach, we have also conducted a new set of simulations based on directly calculation of the band structure of the NaMnO<sub>2</sub> based materials, using **hybrid XC functionals** (more specifically **HSE-06**). We started from a smaller cell (**8 atoms** instead of 24 atoms of the previous calculations) of a different phase (**Orthorhombic** instead of the Hexagonal) in order to analyze the effect of the use of hybrid XC functional on the electronic structure. We obtained a reliable computational setup to try to attack the larger NaXMnO<sub>2</sub> systems using hybrid XC.



	Γ <sub>Gap</sub> [eV]	M/X <sub>Gap</sub> [eV]	Y <sub>Gap</sub> [eV]	Z <sub>Gap</sub> [eV]	T <sub>Gap</sub> [eV]	U <sub>Gap</sub> [eV]	S <sub>Gap</sub> [eV]	R <sub>Gap</sub> [eV]
GGA	1.98	2.00	1.10	2.10	1.20	2.06	1.10	0.87
GGA + U	3.47	2.99	2.52	3.29	2.47	2.77	2.12	1.83
HSE-06	5.16	4.76	4.07	5.00	4.02	4.32	3.55	3.33

GGA: 0.856 eV Indirect Gap T-R      GGA+U: 1.542 eV Indirect Gap      HSE-06: 3.059 eV Indirect Gap

## Conclusions:

- The (double) **Ni** substitution in the **NaMnO<sub>2</sub>** causes a transition to metallic behavior.
- Further **Ti** doping in **NaNiMnO<sub>2</sub>** restores the insulating behavior of the oxide.
- Increase of **Na** percentage in the systems produces the lowering of the formation energies of the compounds which corresponds to a rise of the stability.
- The 2/3 ratio of **Na** in the **NaXMnO<sub>2</sub>** systems presents the lowest doping energy and, therefore, the most favorable condition for **Ti** doping.
- All compounds under investigation show **RedOx potentials** in the range of **± 5%** with respect to the parent compound (**NaMnO<sub>2</sub>**)
- GGA+U** calculation appears underestimate the value of gap with respect to the corresponding hybrid functional **HSE06** one.

**Future Developments:** The future step of this research line is try to perform new calculations on the same systems in a full hybrid XC computational framework.

Our results show that GGA+U still underestimates the electronic gap. In order to get a better estimate of the exchange term, it seems that hybrid potentials are necessary. Furthermore we aim to obtain more reliable and accurate values for the RedOx potentials, which are una the most important observables in the study of next generation cathode materials.