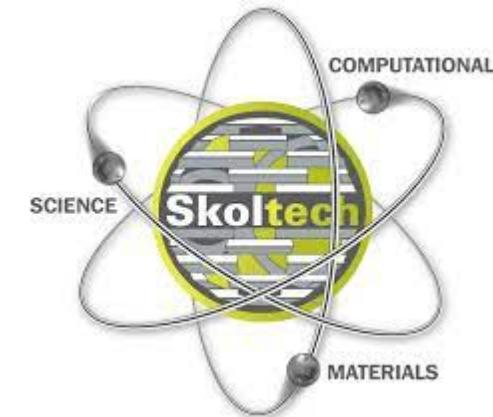


Study of Na-ion cathode

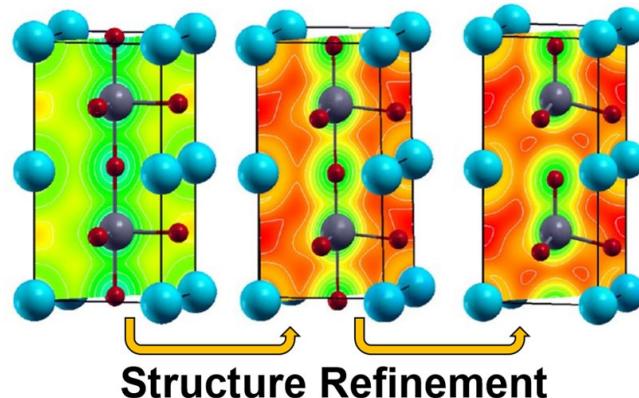
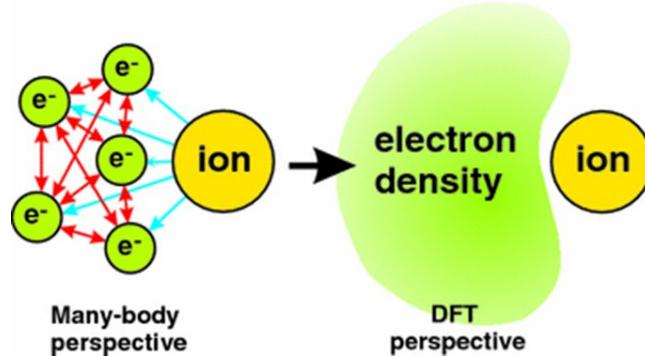
S

yuk S., Sirotin M., Goryacheva T.

ov, Dr. A. Boev, A. Burov



DFT concept



$$\hat{H}\Psi_0 = E_0\Psi_0$$



Fictitious non-interacting electrons (+ Slater determinant)

$$\left[-\frac{1}{2} \nabla_{\mathbf{r}}^2 + v(\mathbf{r}) \times \right] \varphi_i(\mathbf{x}) = \varepsilon_i \varphi_i(\mathbf{x}), \quad i = 1, 2, \dots, N.$$



Kohn-Sham DFT

$$\hat{W}_{ee} \rightarrow 0$$

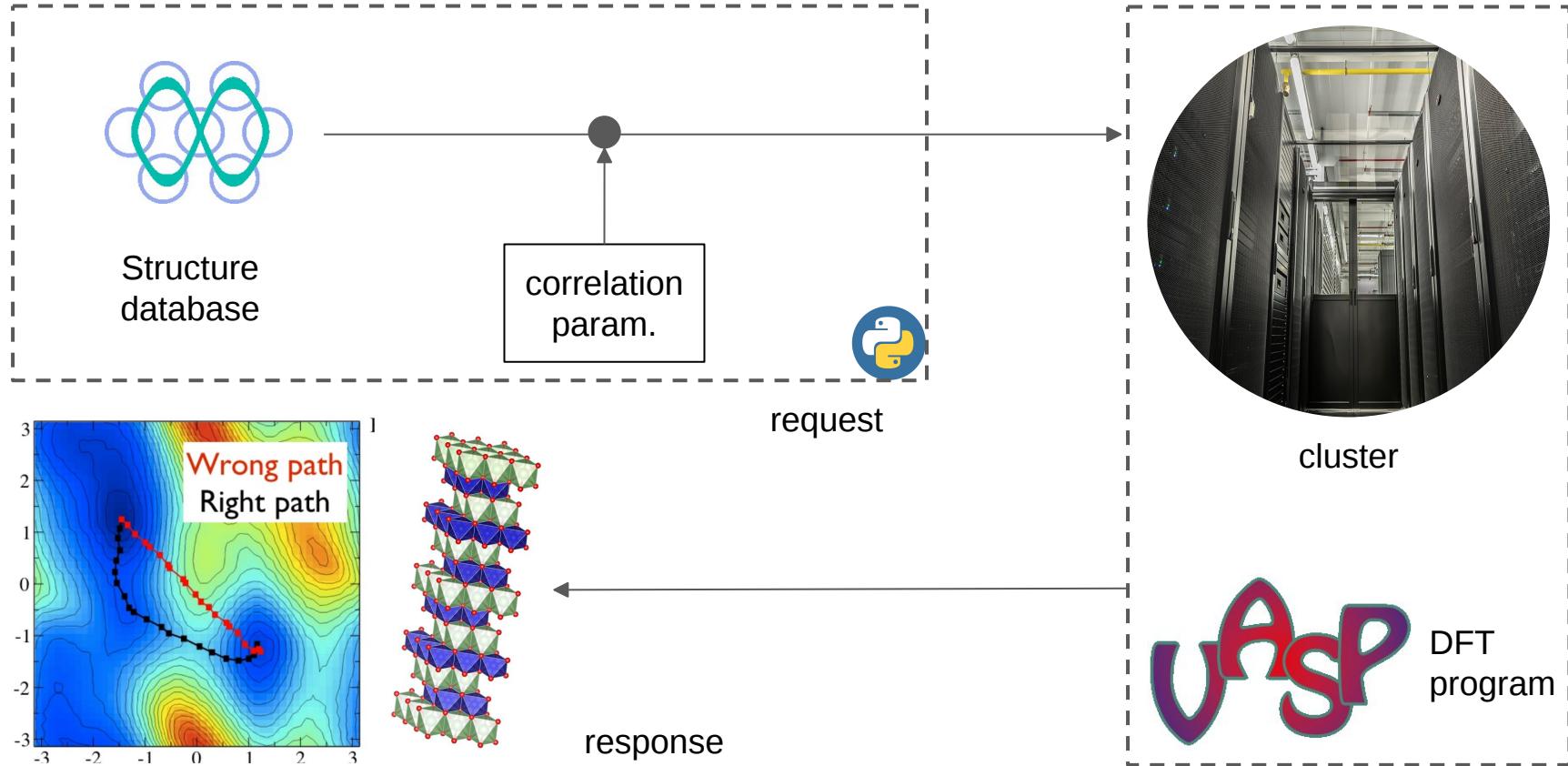
$$v[n](\mathbf{r}) \rightarrow v^{KS}[n](\mathbf{r})$$

$$\Psi[n] \rightarrow \Phi^{KS}[n]$$

$$F[n] \rightarrow T_s[n] = \langle \Phi^{KS}[n] | \hat{T} | \Phi^{KS}[n] \rangle$$

$$F[n] = T_s[n] + E_{Hxc}[n]$$

Architecture of calculations



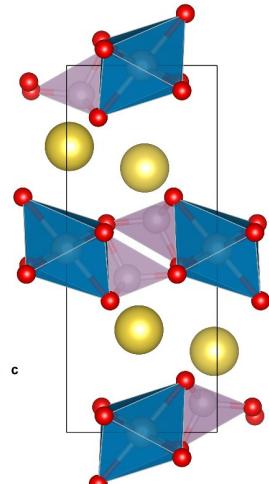
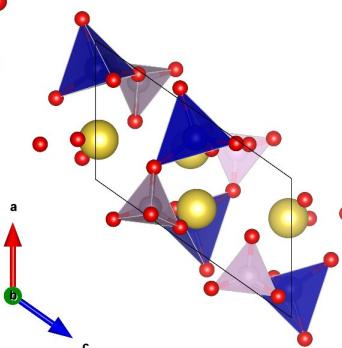
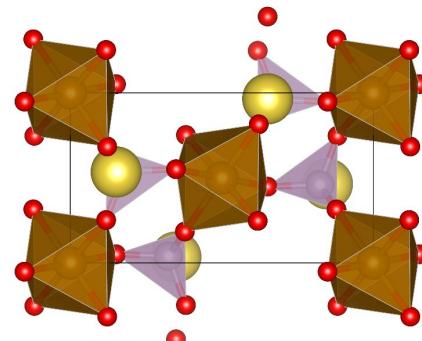
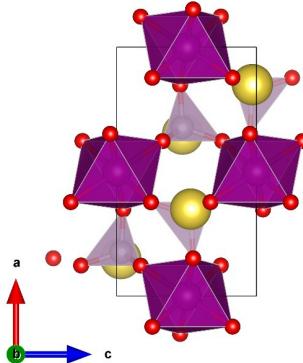
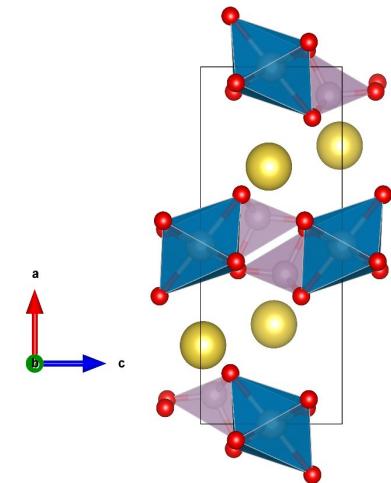
Goals

Apply the DFT model to cathode material and determine following dependencies:

1. Effect of transition metal on NaMPO₄ redox potential
1. Effect of ligand on Na_xFe-L redox potential
1. Migration barrier of Na for different SEI structures

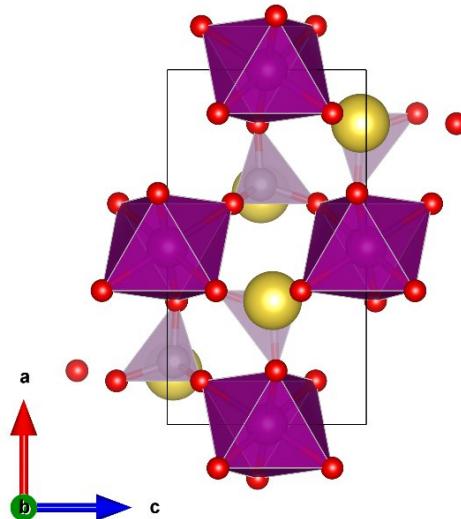
Effect of TM on redox potential

Materials

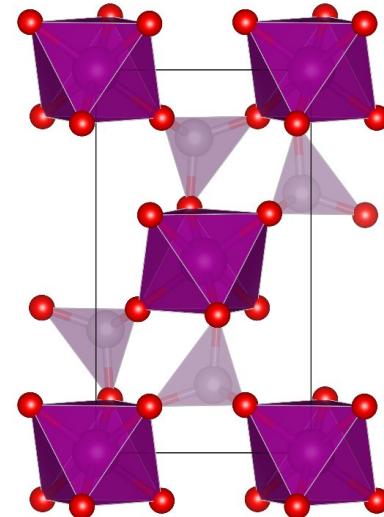
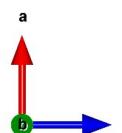
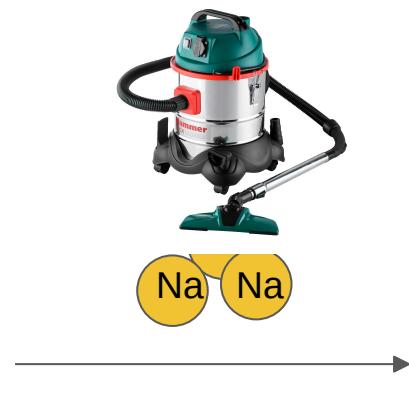


Effect of TM on redox potential

Na deintercalation



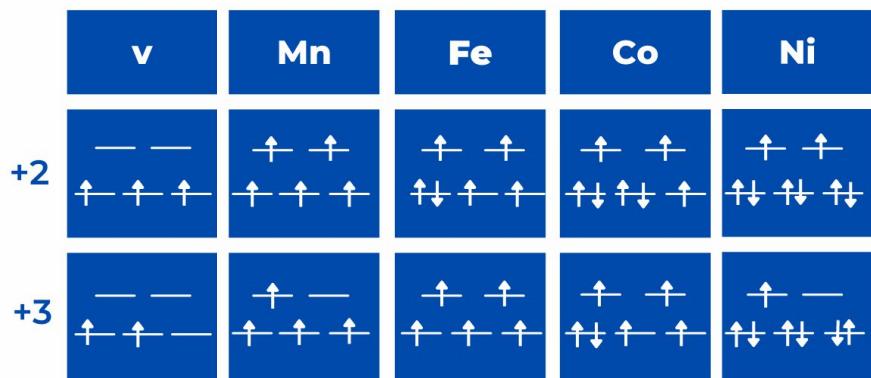
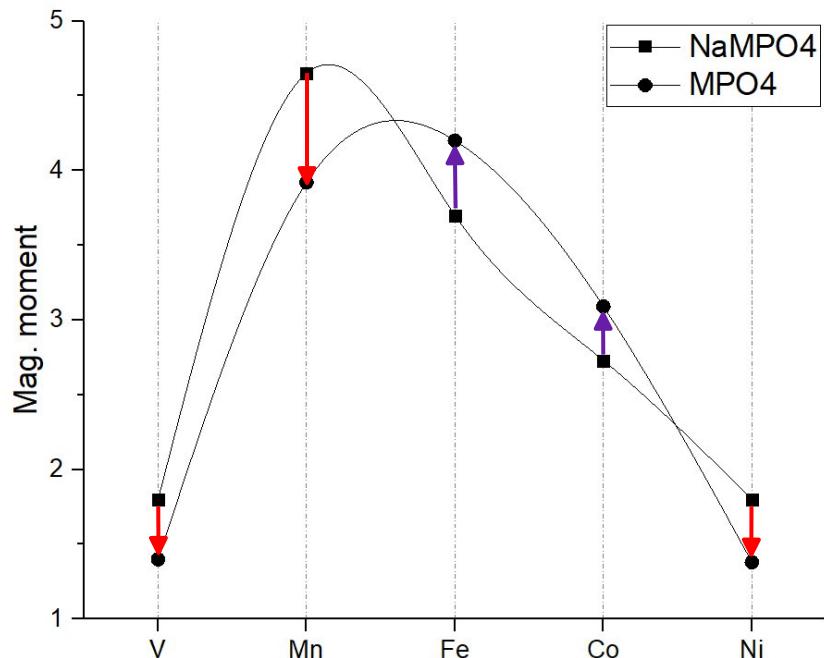
NaMnPO_4



MnPO_4

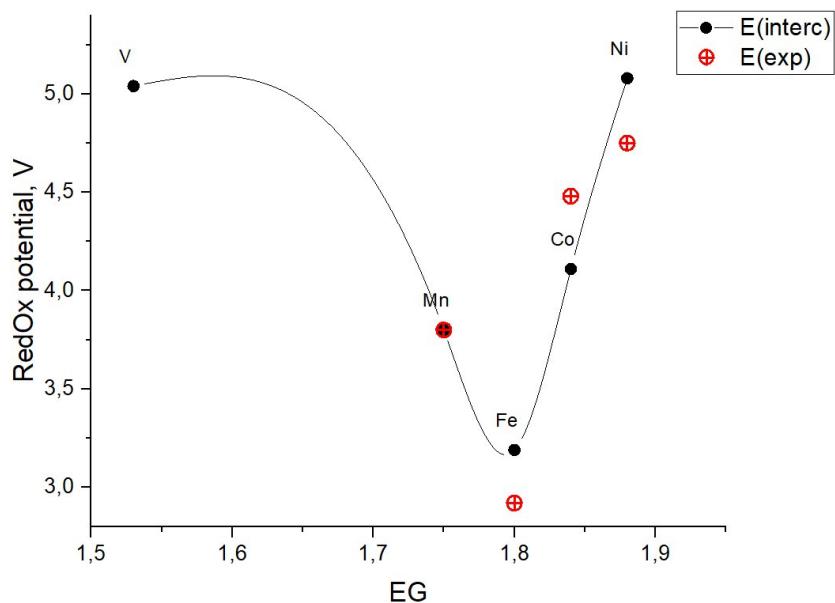
Effect of TM on redox potential

Na deintercalation

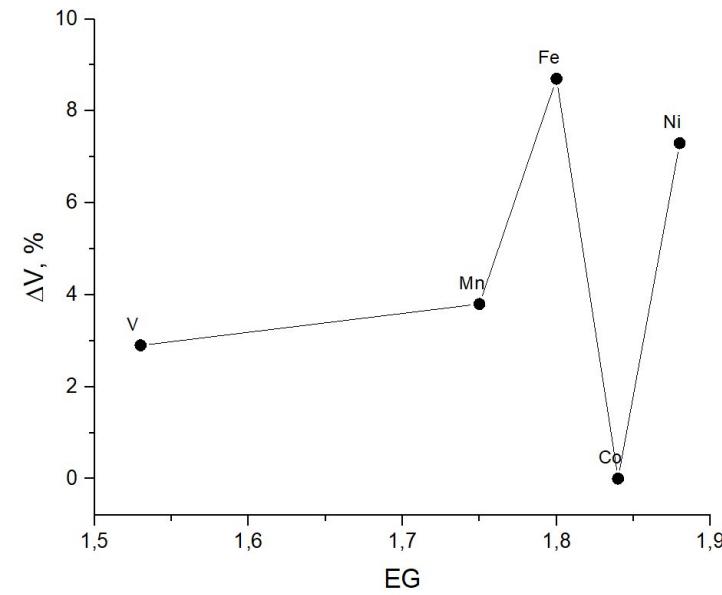


Effect of TM on redox potential

Volume changes and intercalation potentials

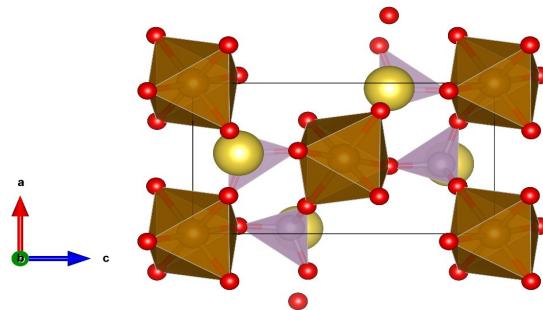


Mn: [10.1016/j.jpcs.2019.109192](https://doi.org/10.1016/j.jpcs.2019.109192)
 Fe: [10.1021/cm101377h](https://doi.org/10.1021/cm101377h)
 Co: [10.1016/j.jpcs.2019.109192](https://doi.org/10.1016/j.jpcs.2019.109192)
 Ni: [10.1039/c4ra06050d](https://doi.org/10.1039/c4ra06050d)



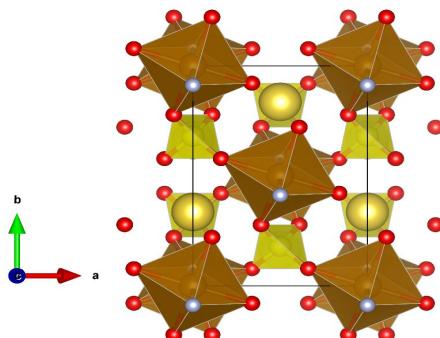
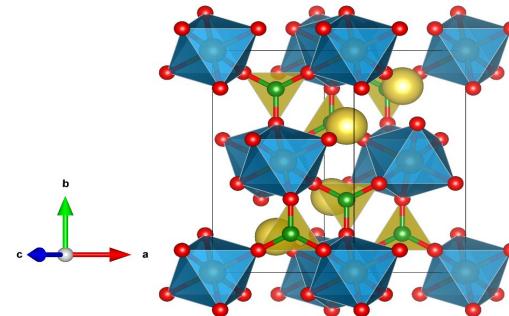
Effect of Ligand on redox potential

Materials



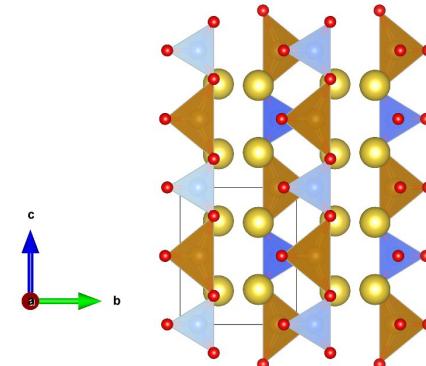
NaFePO_4

NaFeBO_3



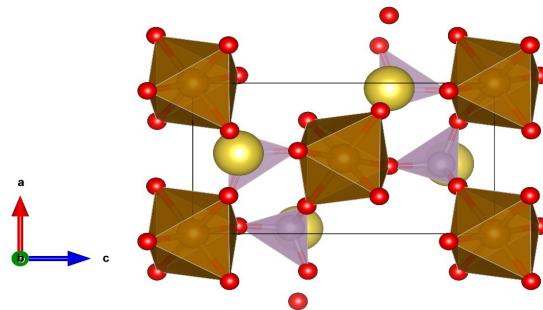
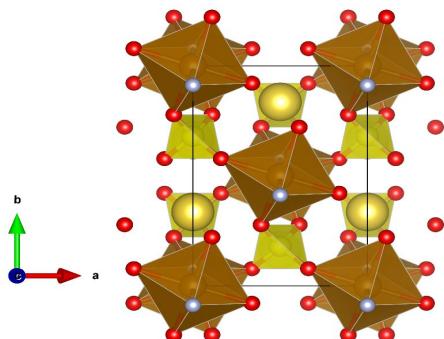
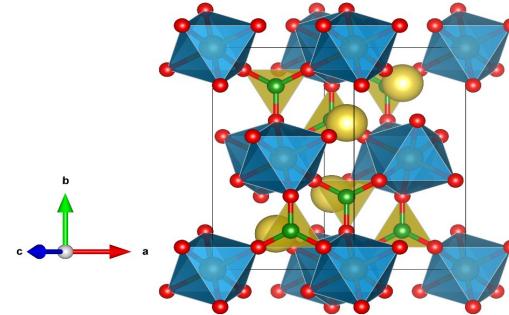
NaFeSO_4F

$\text{Na}_2\text{FeSiO}_4$

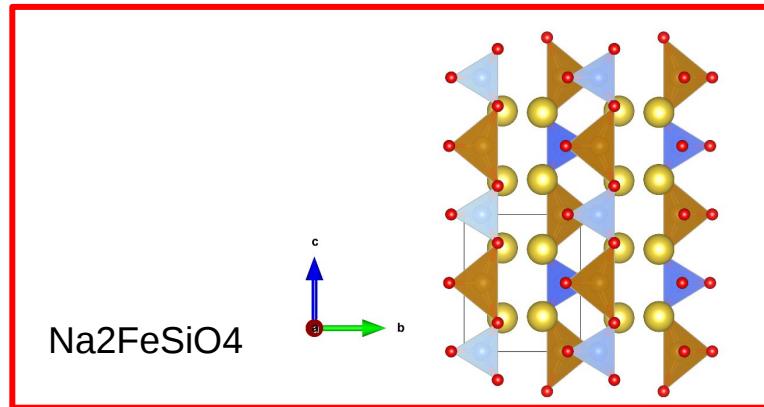


Effect of Ligand on redox potential

Materials

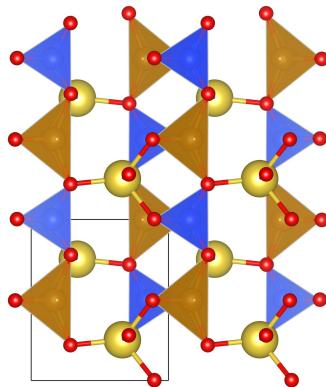
NaFeBO₃

it possessed two unequal Na-positions

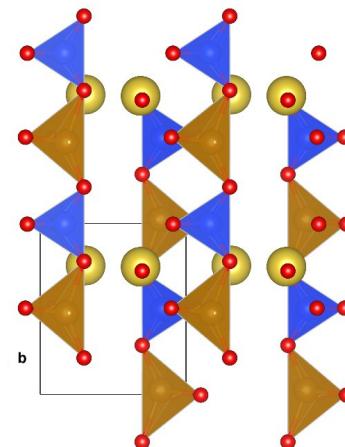
Na₂FeSiO₄

Effect of Ligand on redox potential

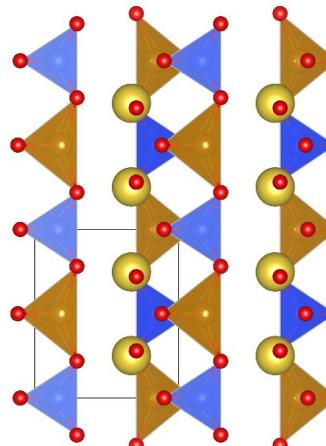
Na deintercalation



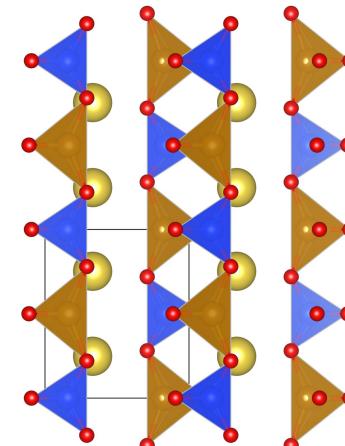
(12,14)
2,54 V



(12,13)
2,67 V



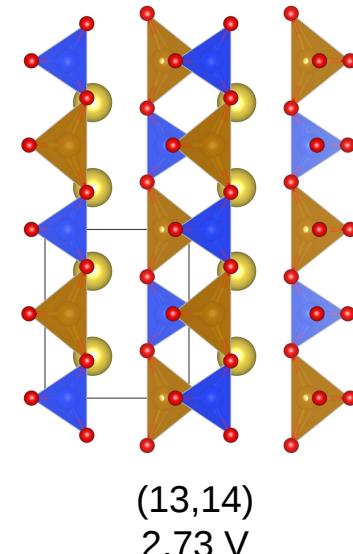
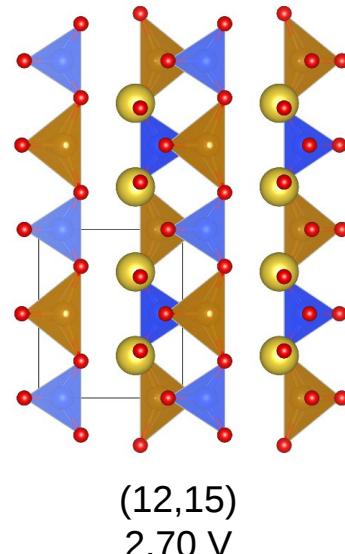
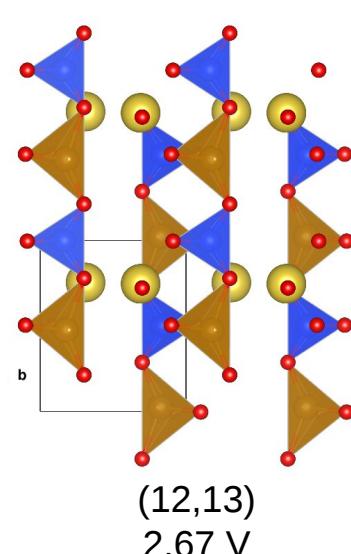
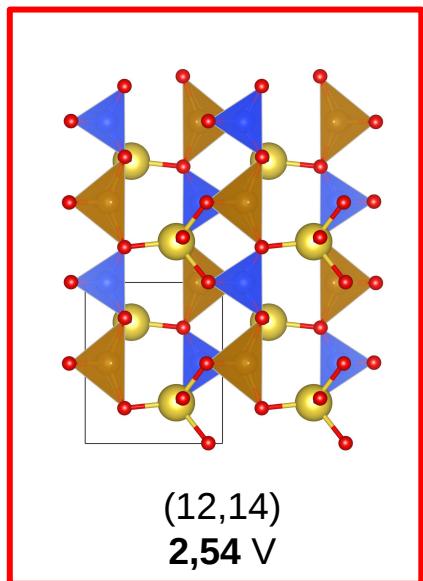
(12,15)
2,7 V



(13,14)
2,73 V

Effect of Ligand on redox potential

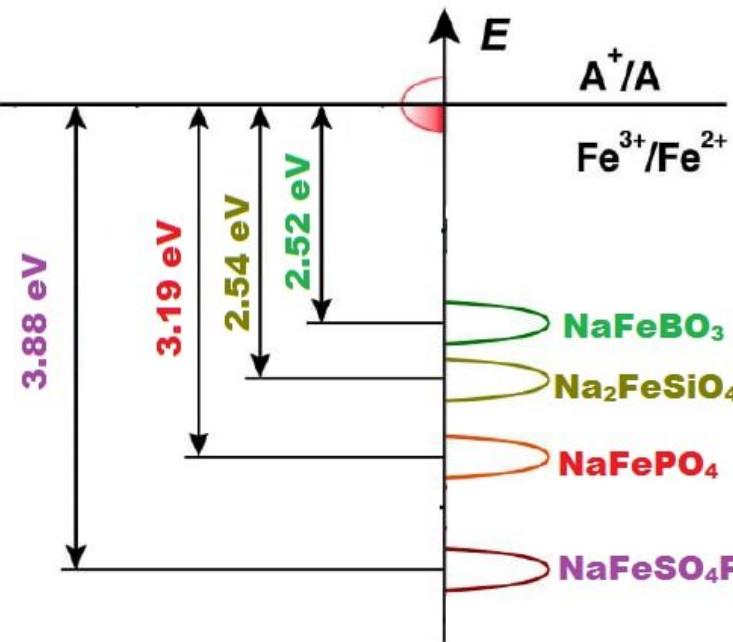
Na deintercalation



the most probable

Effect of Ligand on redox potential

Volume changes and intercalation potentials

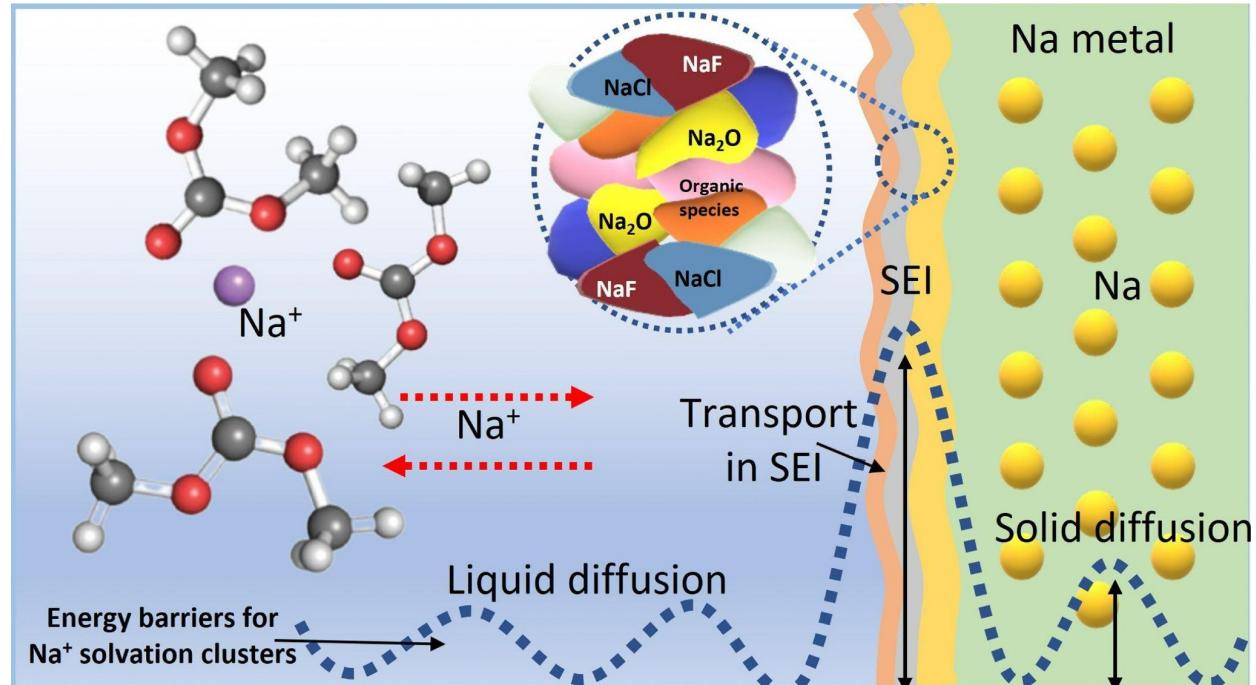


Sample	Potential of deintercalation (exp), V	Potential of deintercalation (exp), V	doi
NaFeBO ₃	2.52	2.8	10.1002/adma.20100 1039
Na ₂ FeSiO ₄	2.54	—	—
NaFePO ₄	3.19	2.92	10.1021/cm101377h
NaFeSO ₄ F	3.88	3.7	10.1021/acs.chemmater.8b02354

SEI migration barrier

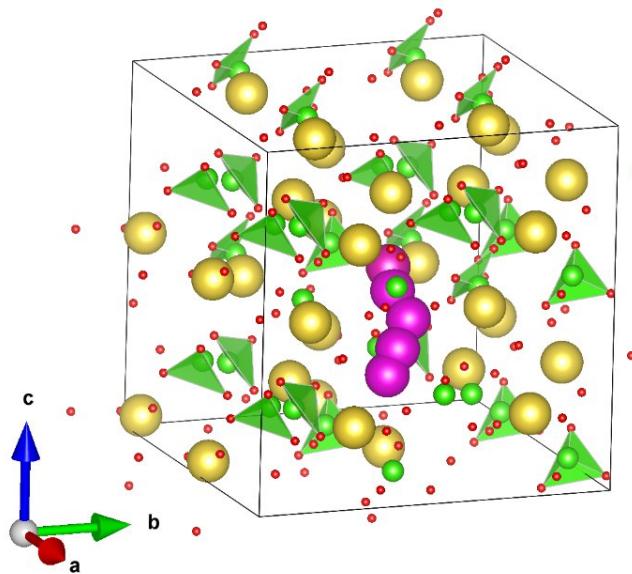
Materials

- NaF (Fm-3m)
- Na₂O (Fm-3m)
- Na₂SO₃ (P-3)
- Na₂ClO₃ (P2₁-3)
- Na₂SO₄ (Fddd)

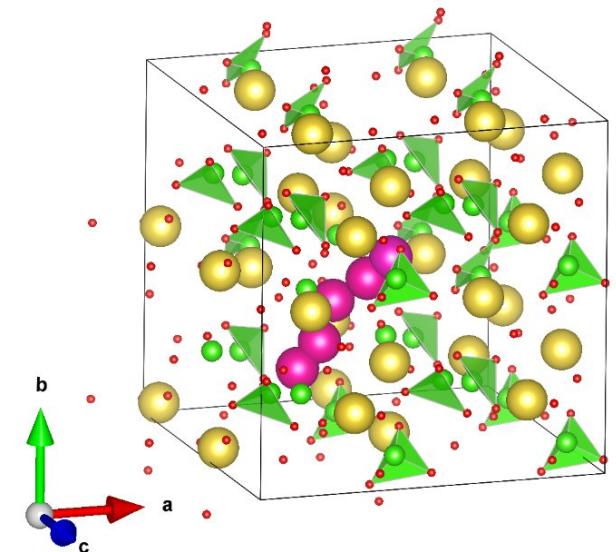


Different diffusion paths

Example NaClO_3 ($\text{P}2_1\text{-}3$ space group)



First migration path ($d = 4.26 \text{ \AA}$, $E_A = 0.37 \text{ eV}$)

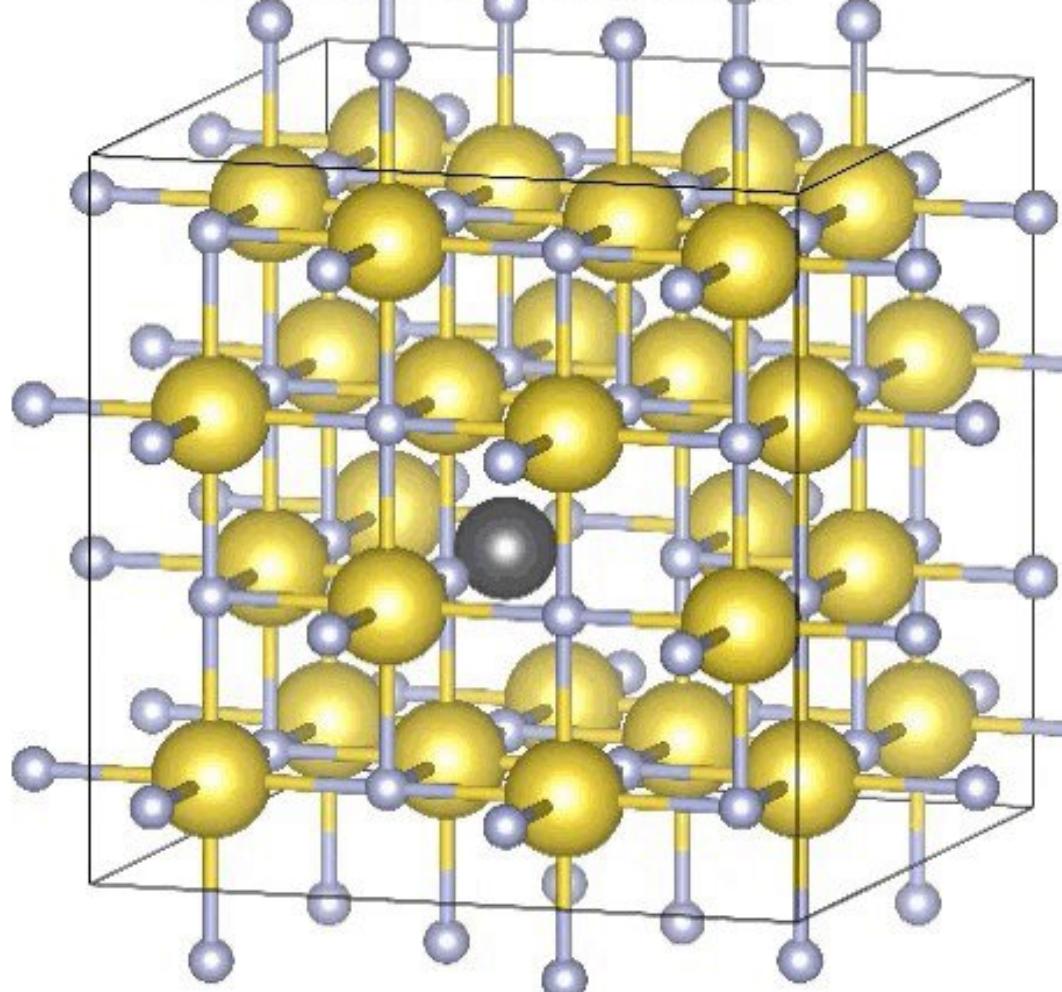


Second migration path ($d = 4.26 \text{ \AA}$, $E_A = 0.37 \text{ eV}$)

SEI migration barrier

Results

Sample	Migration energy, eV	Na Diffusion path distance, Å
NaF	0.86	3.20
Na ₂ O	0.18	2.80
	1.09	3.96
Na ₂ SO ₃	0.34	3.35
	0.62	3.79
NaClO ₃	0.37	4.26
	1.18	5.44
Na ₂ SO ₄	0.19	3.24
	0.81	3.65



Conclusions

- We have learned how to apply the DFT method to calculate the structure and energy of materials.
- We have calculated potentials of deintercalation for different cathode materials.
- SEIs were taken from those actually observed experimentally. We rated them in terms of barriers, which are worse for sodium migration. However, NaF is needed for materials since it protects against surface degradation, but it may be possible to optimize it in the future, to make it in the form of a thin film.

Th_x

