UNIVERSITÀ DI PAVIA

Exploring diffusion mechanisms and energetics in battery materials

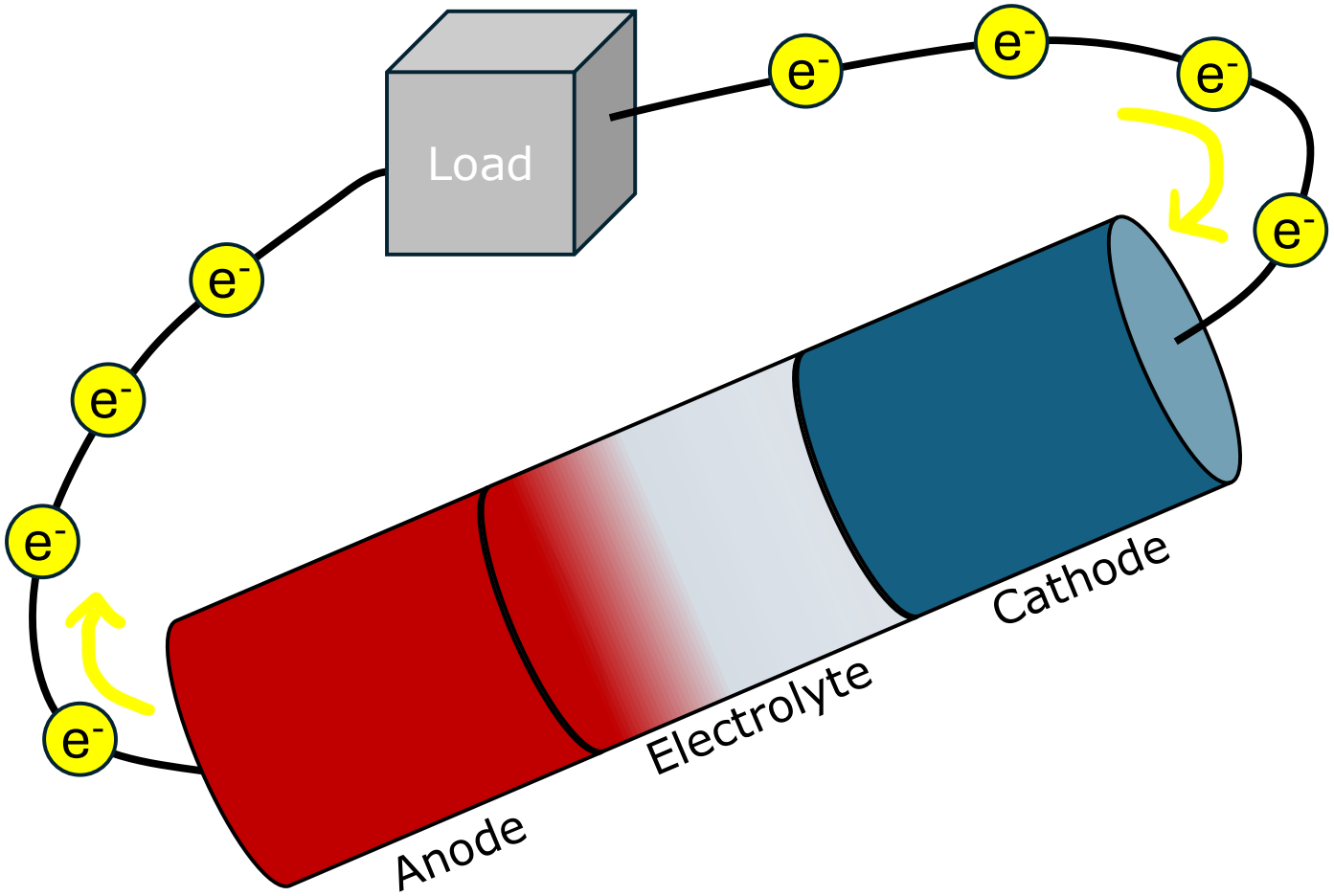
Lorenzo Marti

XXXIX PhD cycle

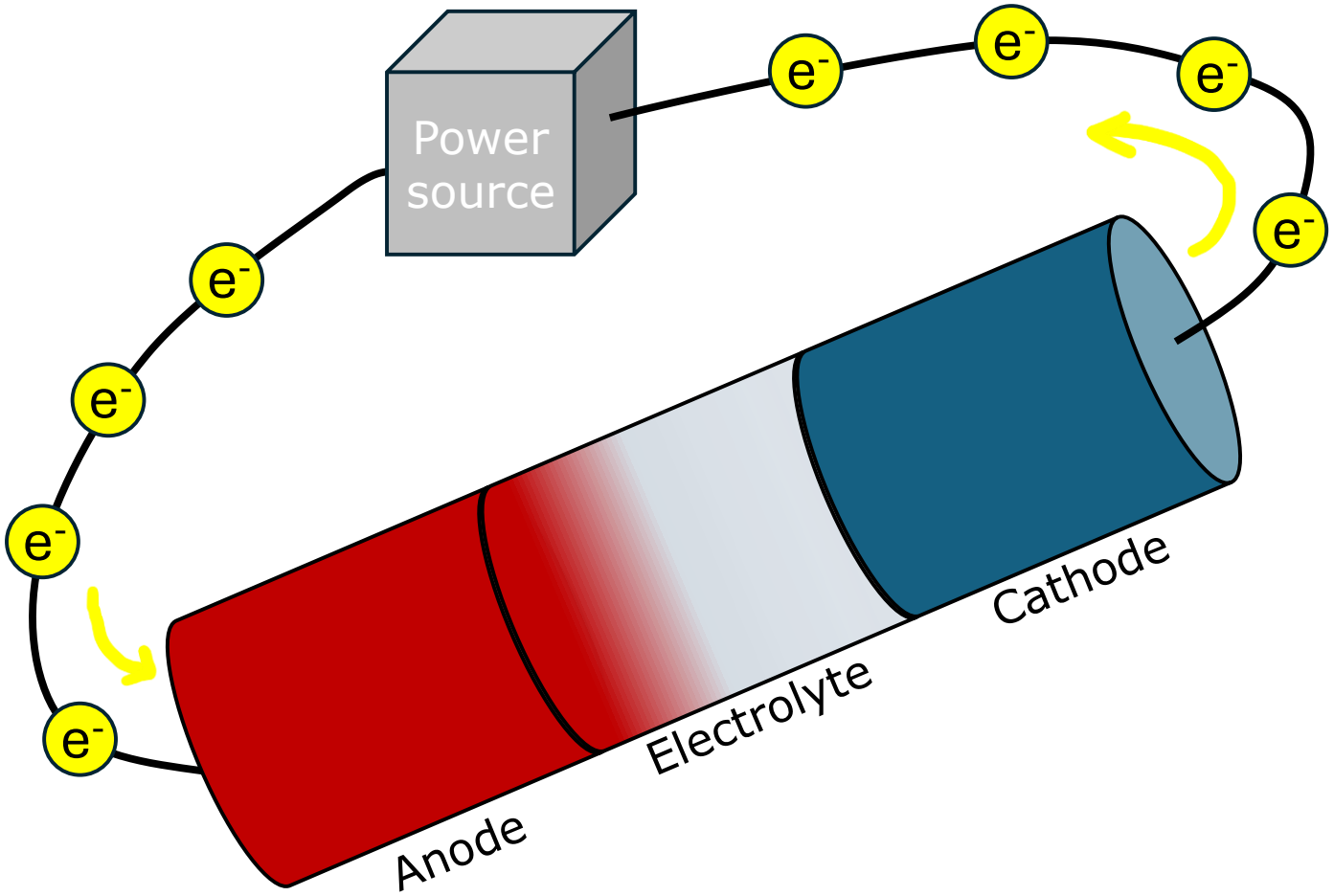
End-of-year seminar a.y. 2024/2025

Supervisors: Prof. M. Cococcioni, Prof. P. Galinetto

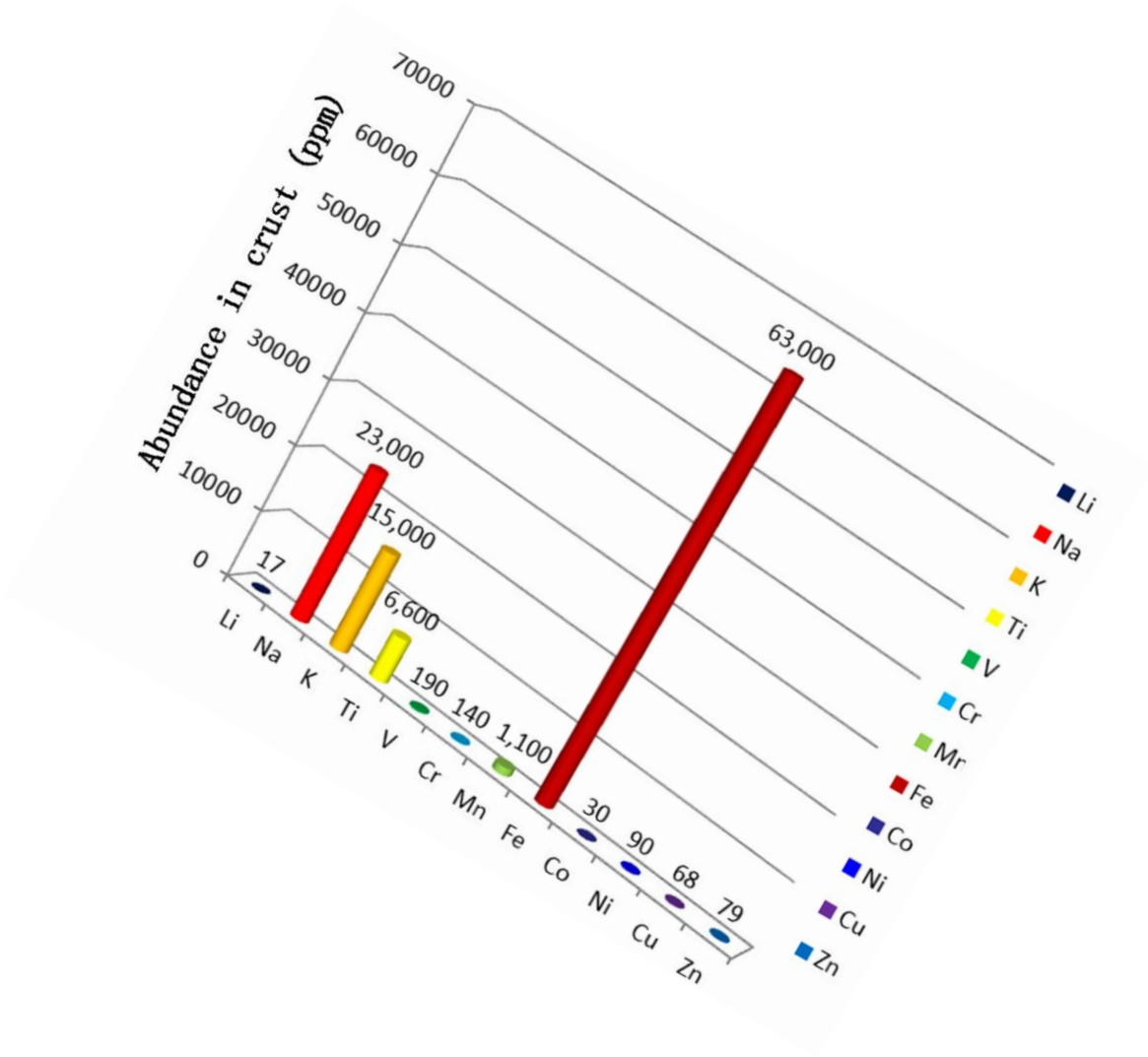
How a rechargeable battery works



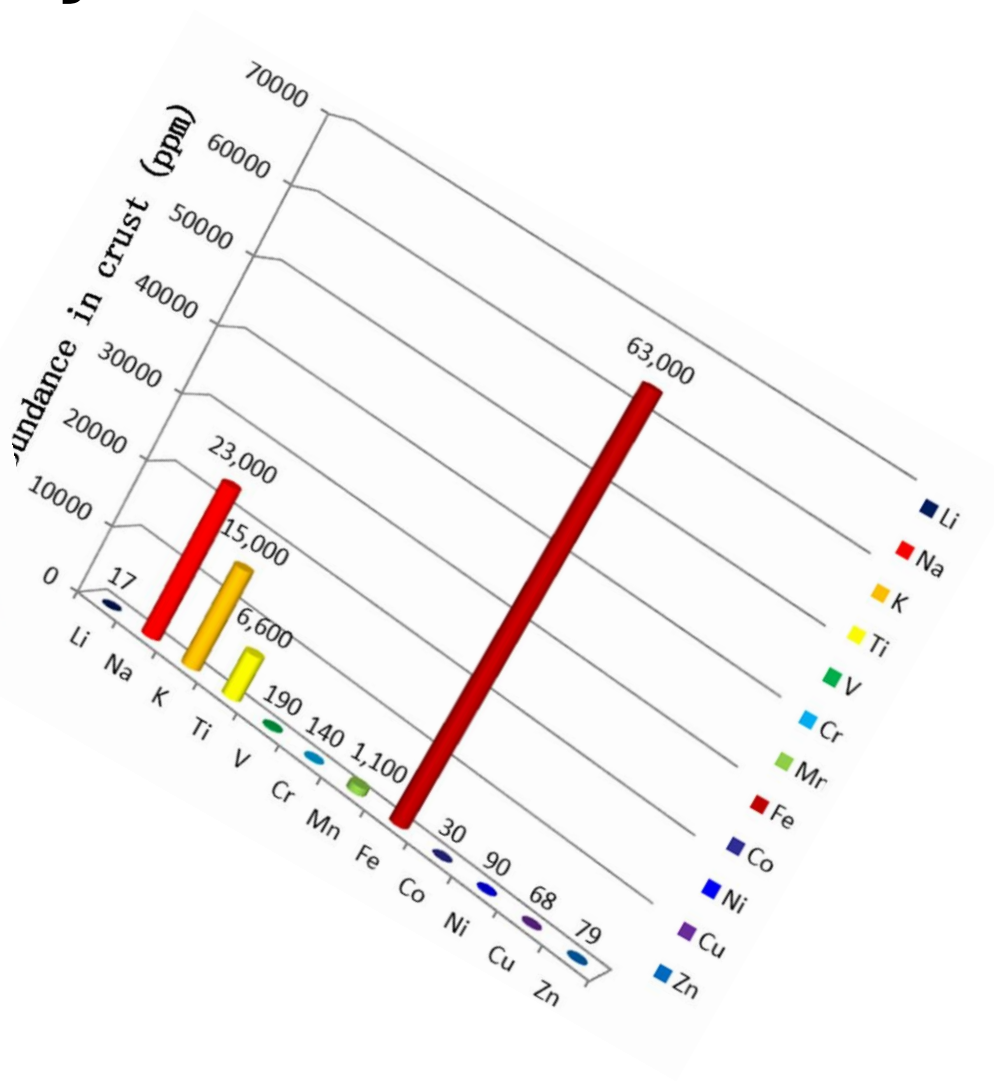
How a rechargeable battery works



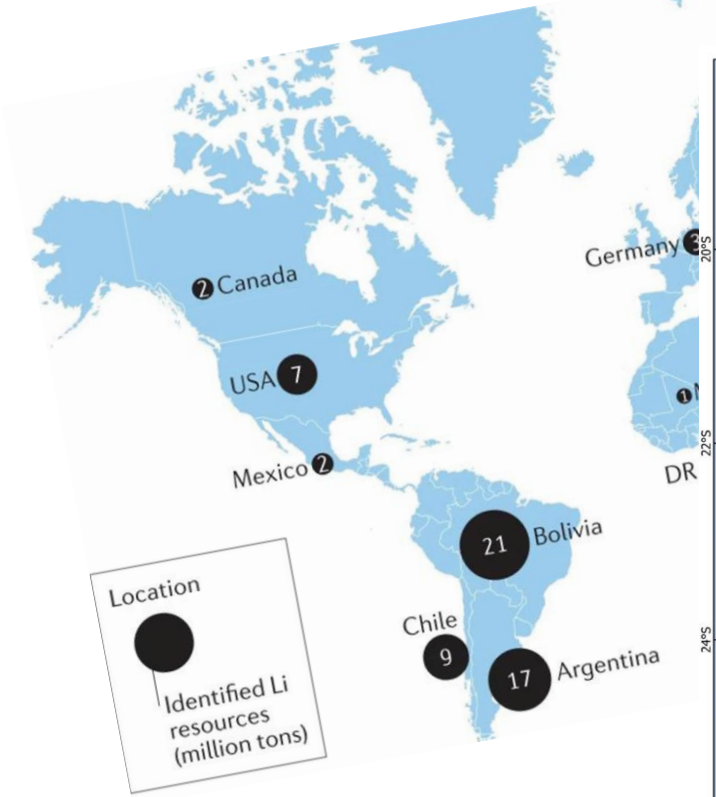
Issues of lithium global supply chain

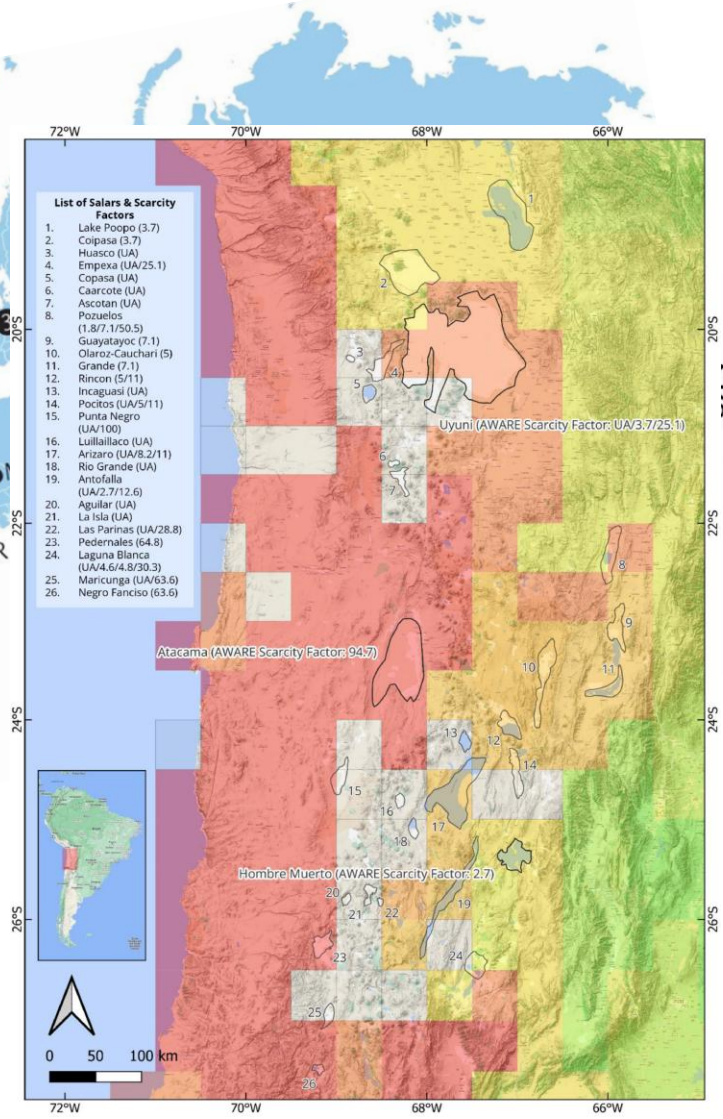


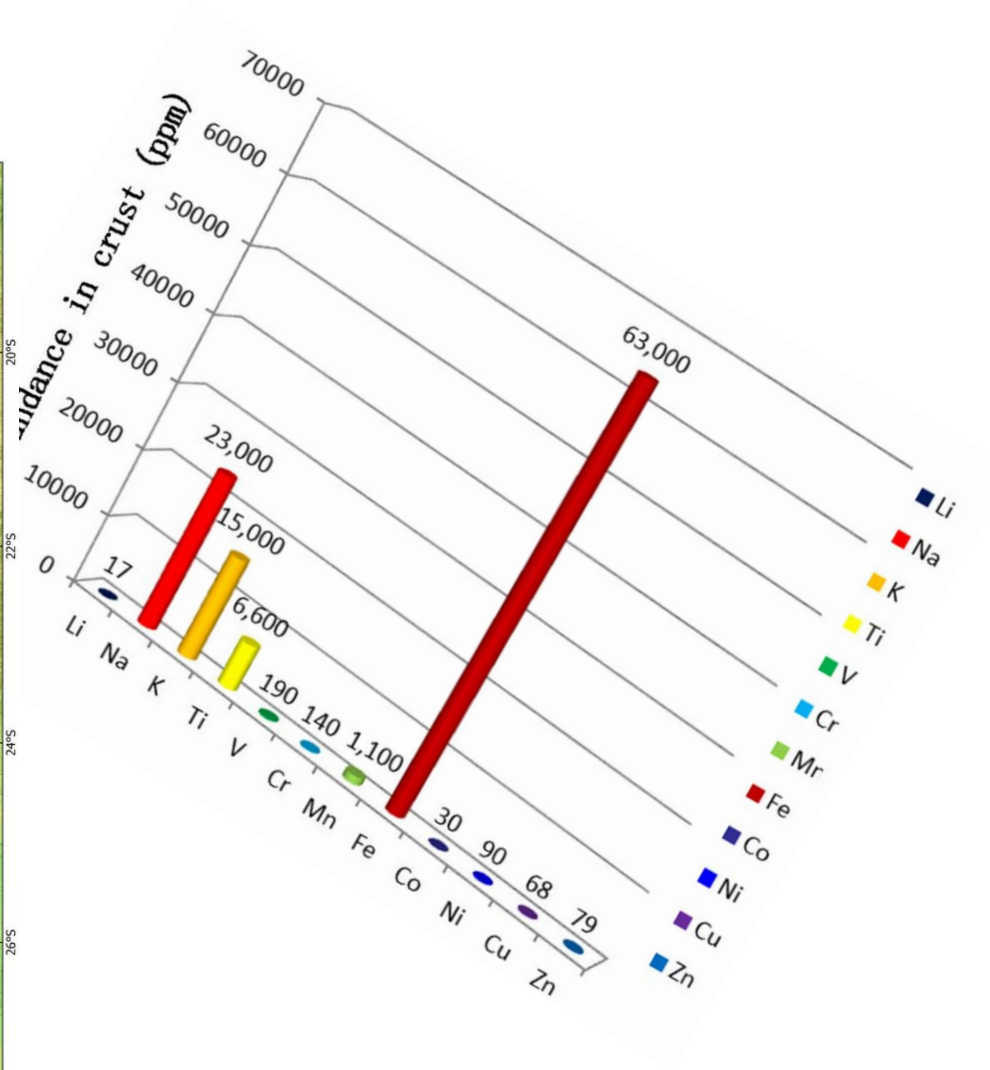
Issues of lithium global supply chain



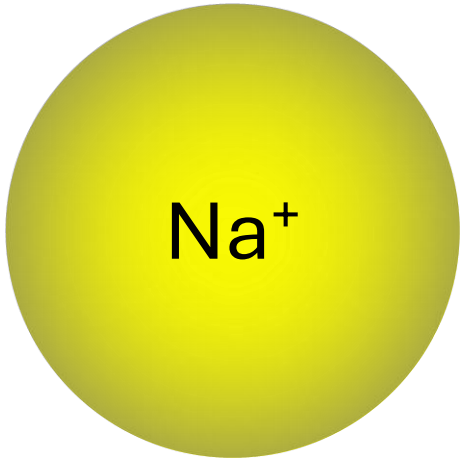
Issues of lithium global supply chain

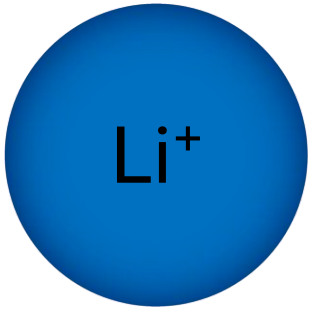


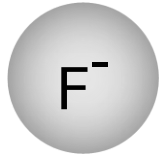




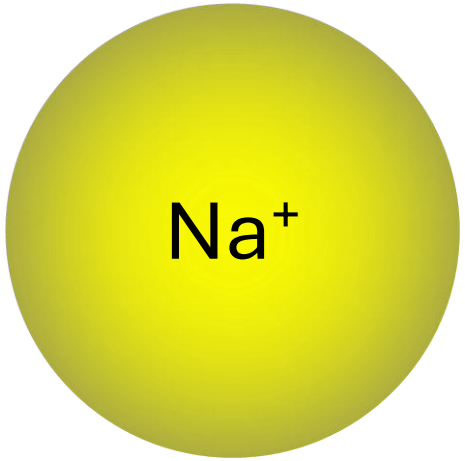
Alternative chemistries for future batteries

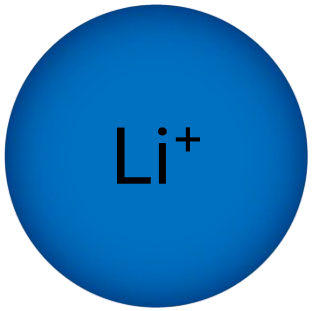


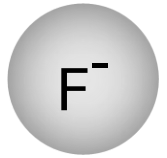


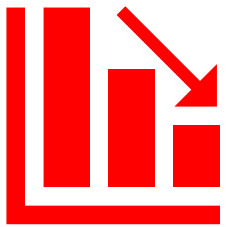


Alternative chemistries for future batteries

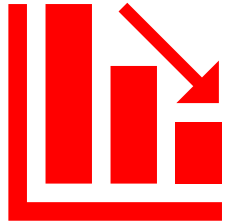






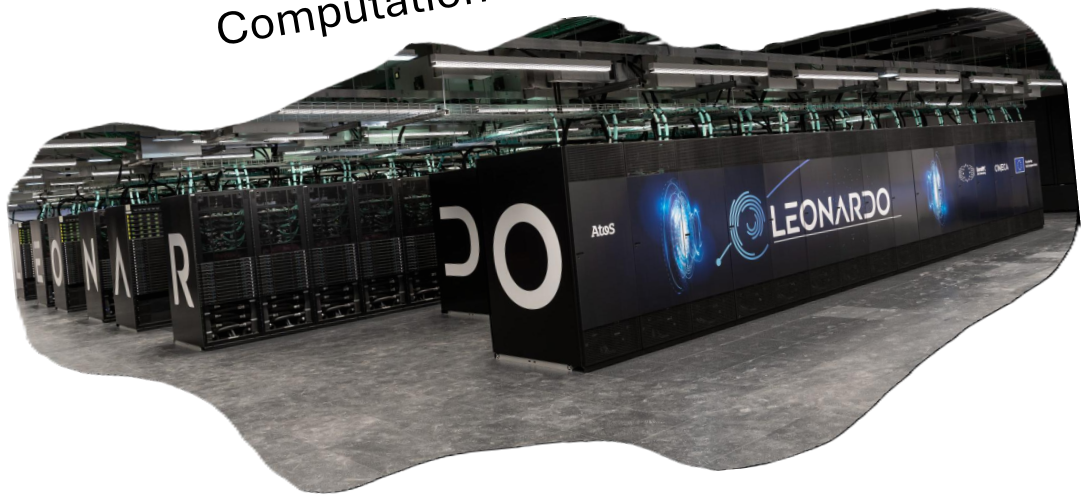


LIMITED
PERFORMANCE



MODERATELY
TOXIC

Computational modeling



Synthesis

Characterization

Engineering

Computational modeling

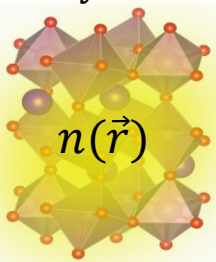
Synthesis

Characterization

Engineering

The tools of the trade

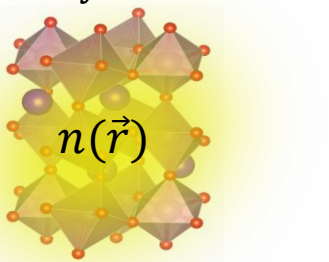
$$E_{gs} = \min_{n} \left(F_{HK}[n(\boldsymbol{r})] + \int d^3r \, V_{ext}(\boldsymbol{r}) n(\boldsymbol{r}) + E_{nuclei} \right)$$



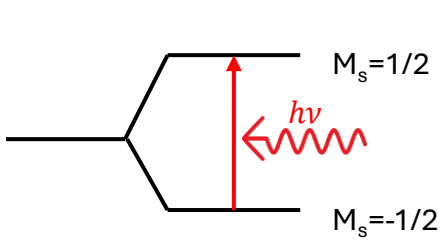
Density Functional Theory (DFT)

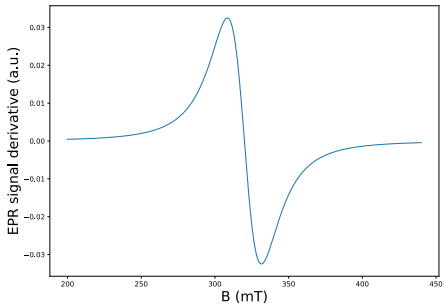
The tools of the trade

$$E_{gs} = \min_{n} \left(F_{HK}[n(\boldsymbol{r})] + \int d^3r\, V_{ext}(\boldsymbol{r}) n(\boldsymbol{r}) + E_{nuclei} \right)$$



Density Functional Theory (DFT)

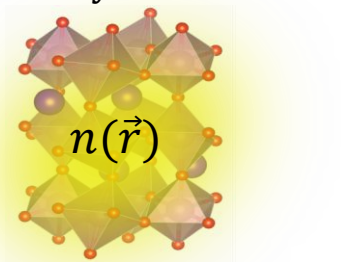




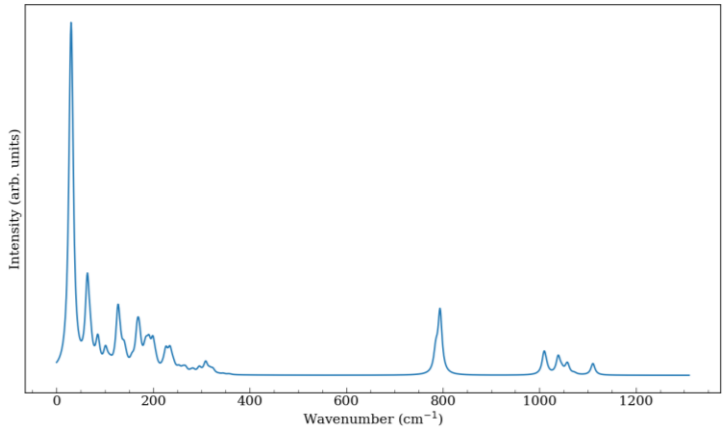
Electron Paramagnetic Resonance (EPR) spectroscopy

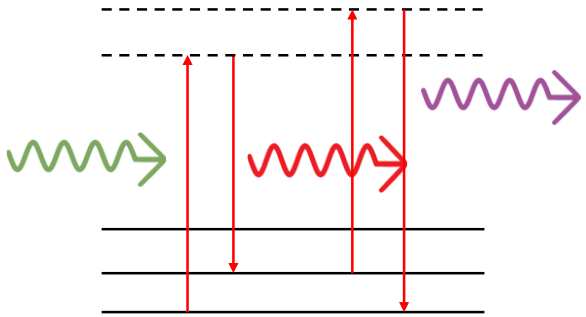
The tools of the trade

$$E_{gs} = \min_{n}\left(F_{HK}[n(\boldsymbol{r})] + \int d^3r\, V_{ext}(\boldsymbol{r})n(\boldsymbol{r}) + E_{nuclei} \right)$$

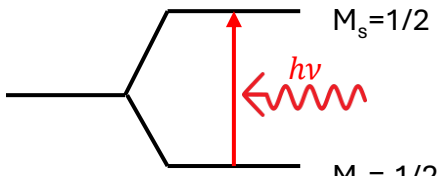


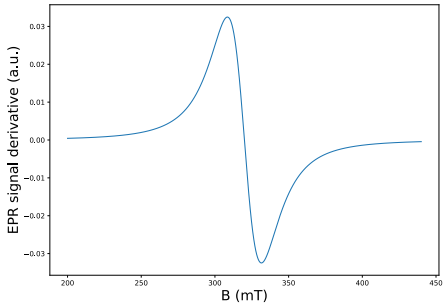
Density Functional Theory (DFT)





Raman spectroscopy

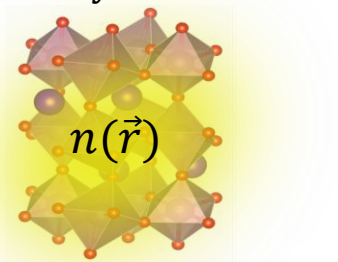




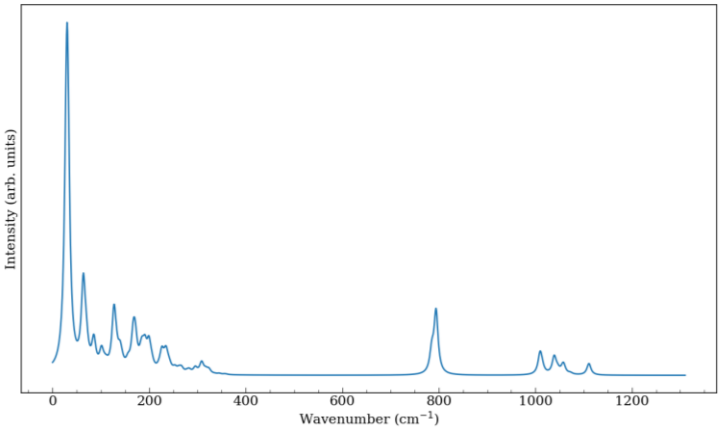
Electron Paramagnetic Resonance (EPR) spectroscopy

The tools of the trade

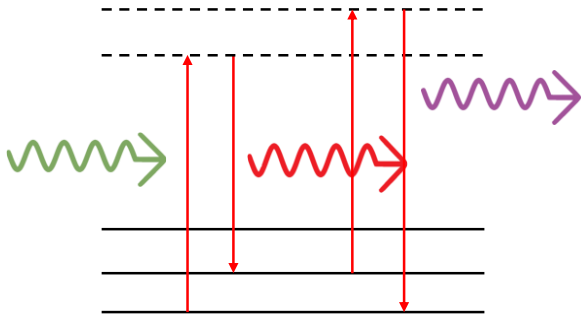
$$E_{gs} = \min_{n} \left(F_{HK}[n(\boldsymbol{r})] + \int d^3r\, V_{ext}(\boldsymbol{r}) n(\boldsymbol{r}) + E_{nuclei} \right)$$

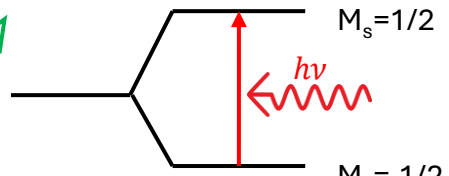


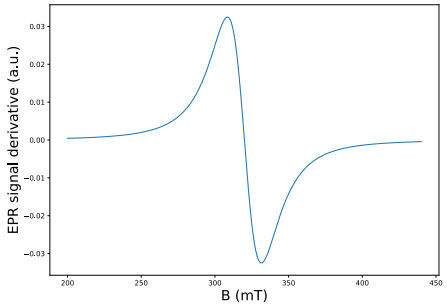
Density Functional Theory (DFT)



Raman spectroscopy

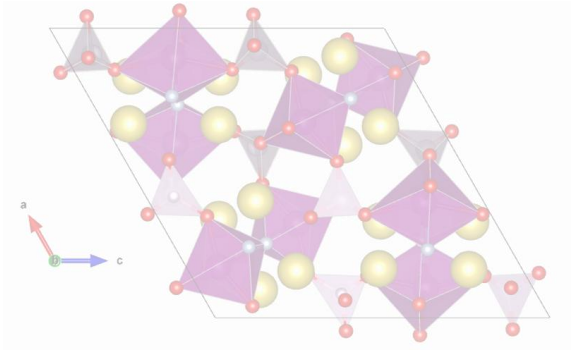


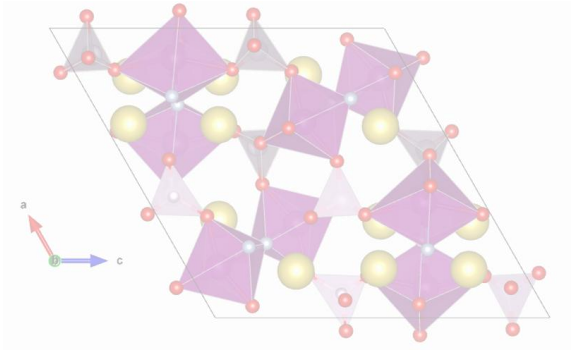


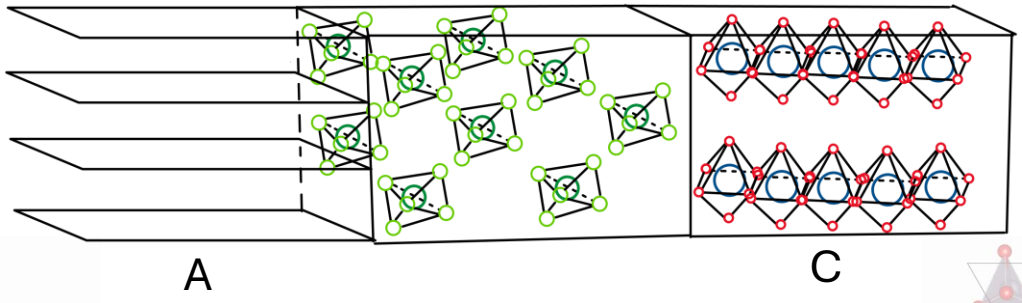


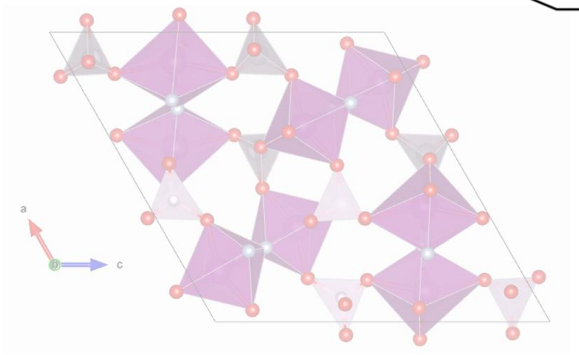
Electron Paramagnetic Resonance (EPR) spectroscopy

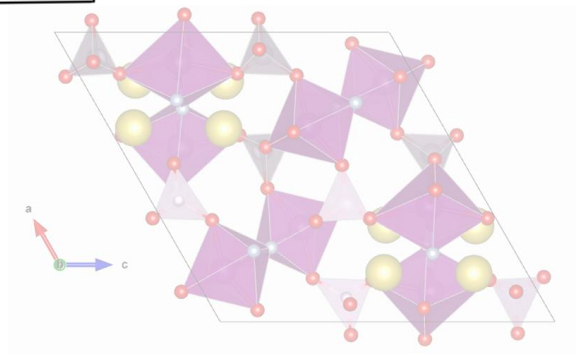
The case of Na_xMnPO_4F cathode material



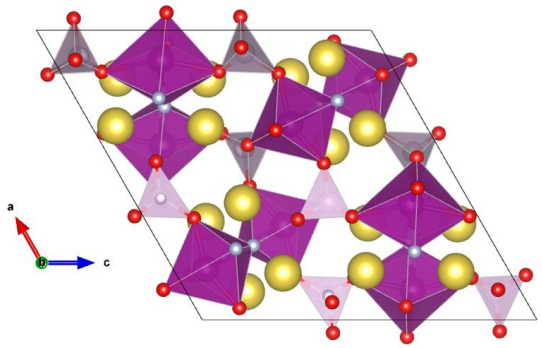




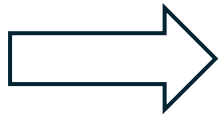




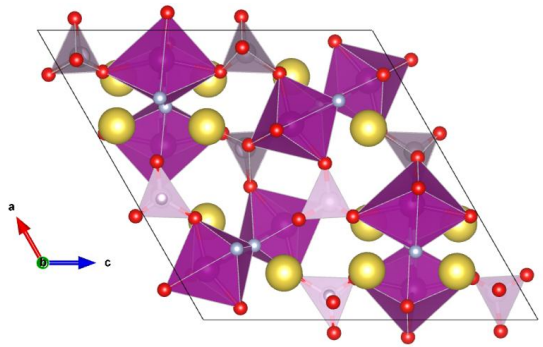
The case of Na_xMnPO_4F cathode material



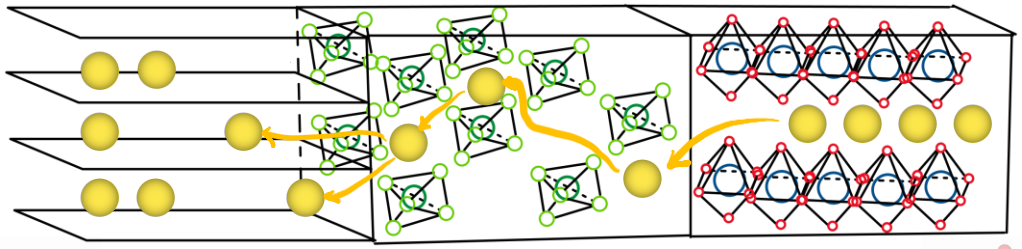
X = 2



- 0.5 Na^+

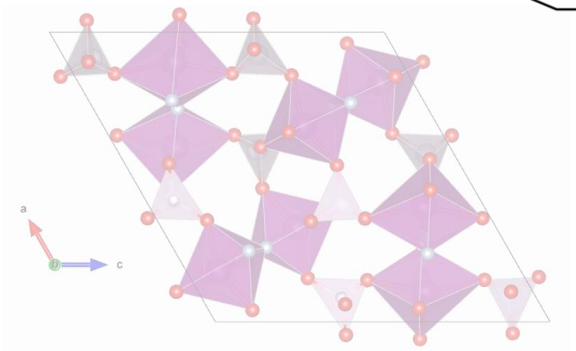


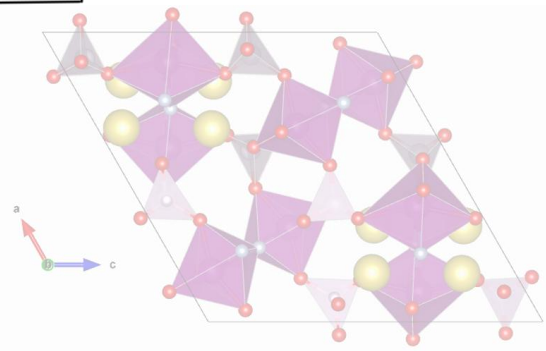
X = 1.5



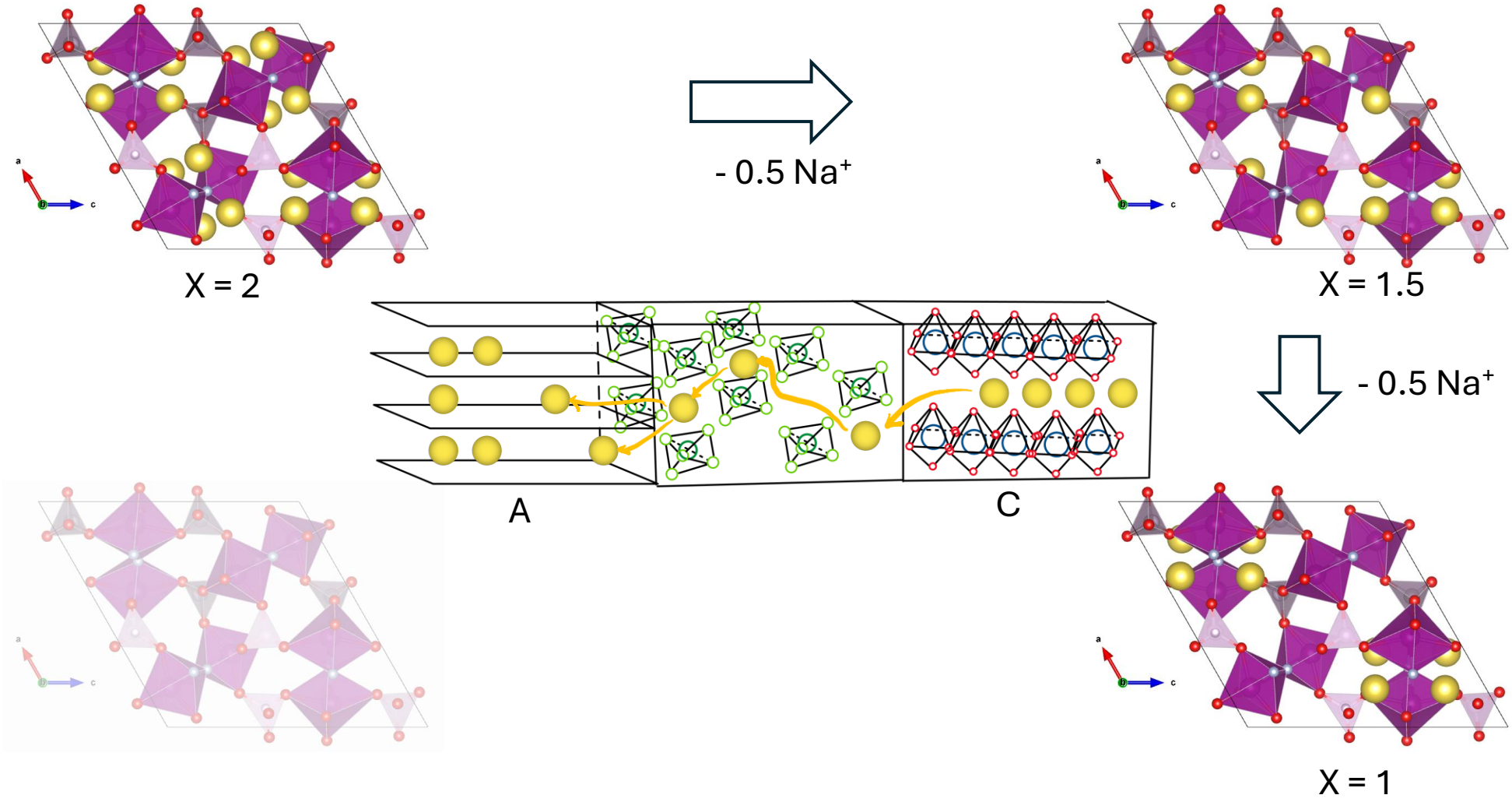
A

C

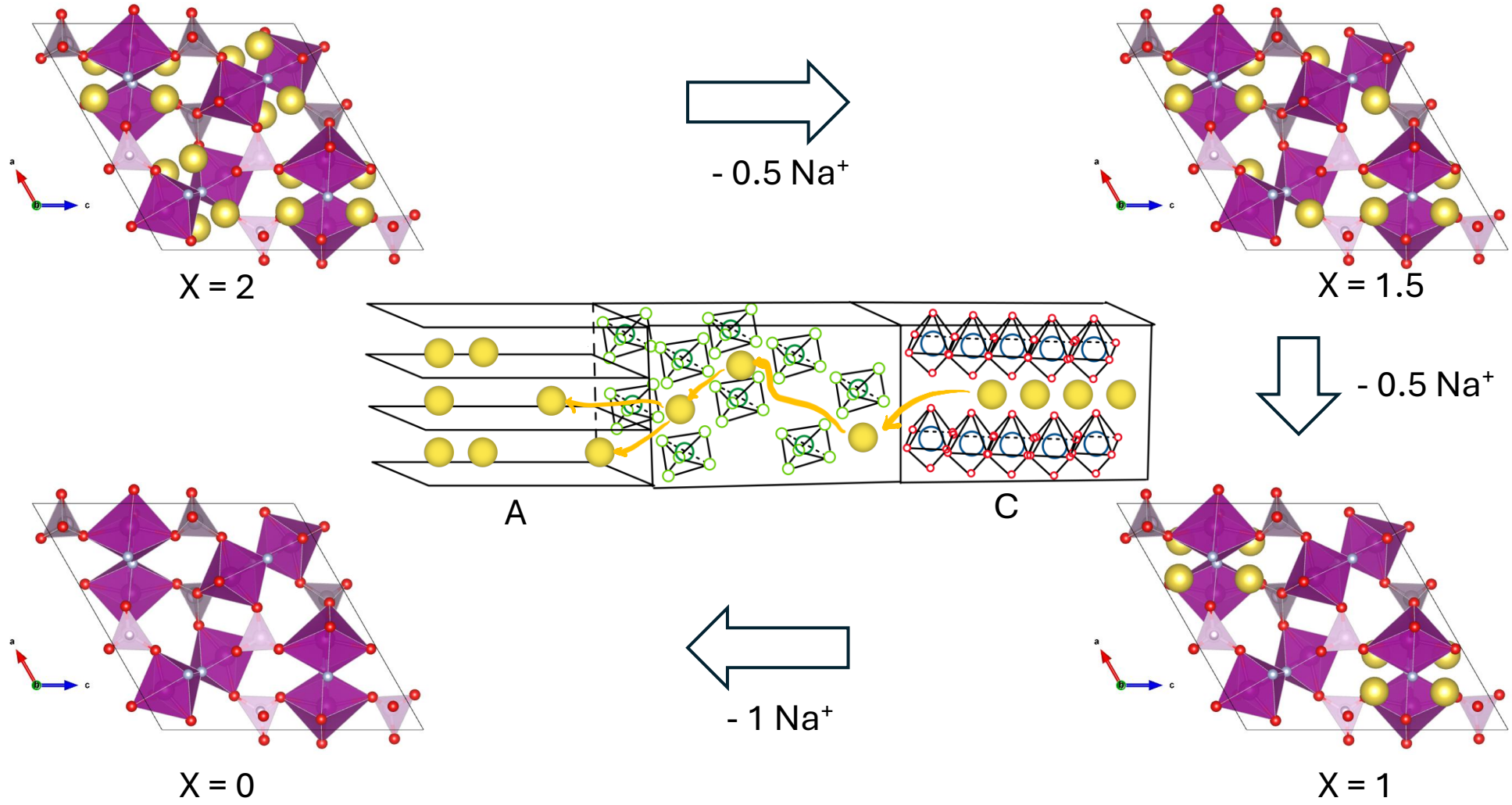




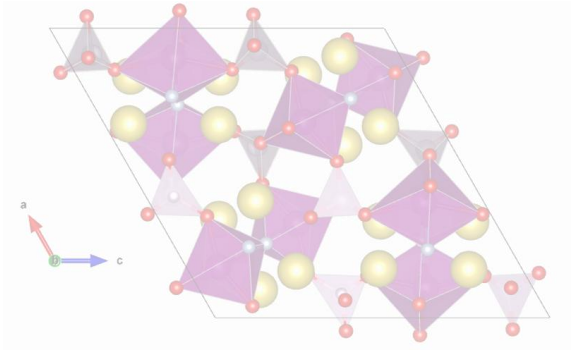
The case of Na_xMnPO_4F cathode material

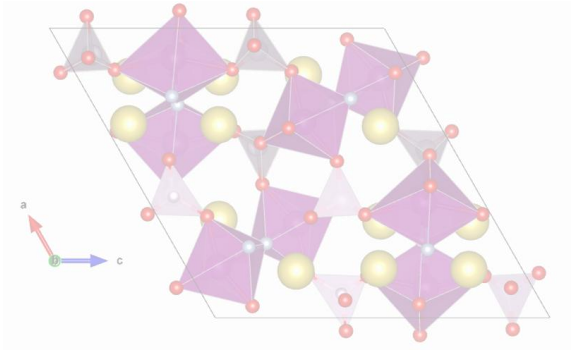


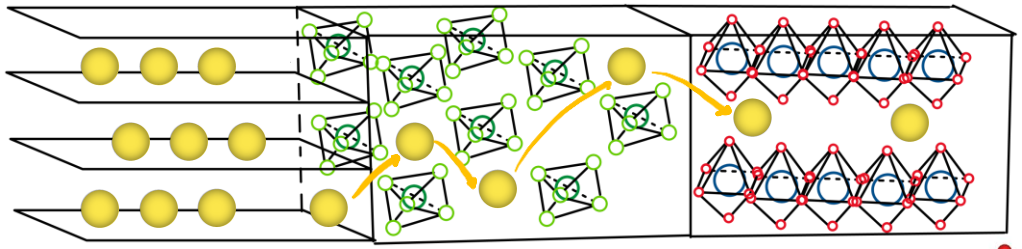
The case of Na_xMnPO_4F cathode material



The case of Na_xMnPO_4F cathode material

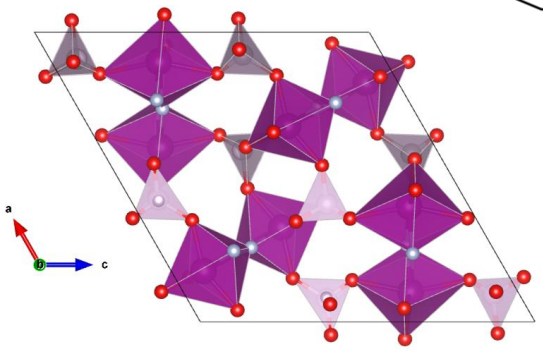






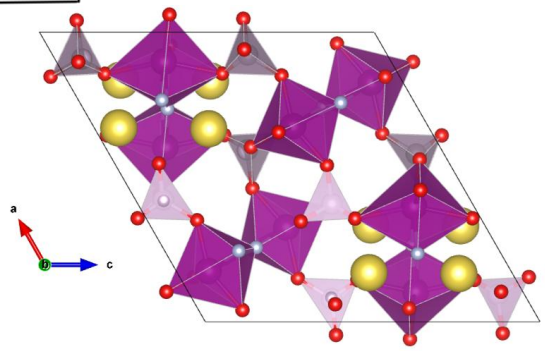
A

C



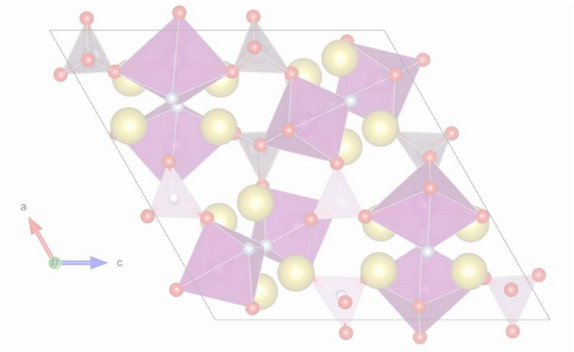
X = 0

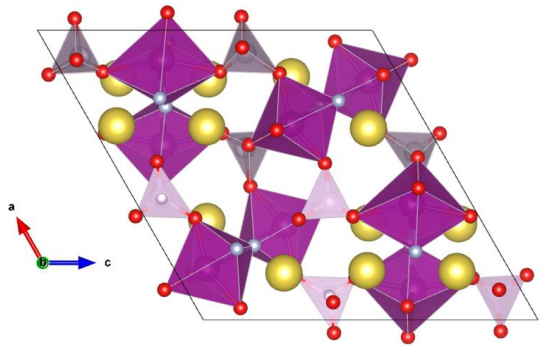
+ 1 Na^+



X = 1

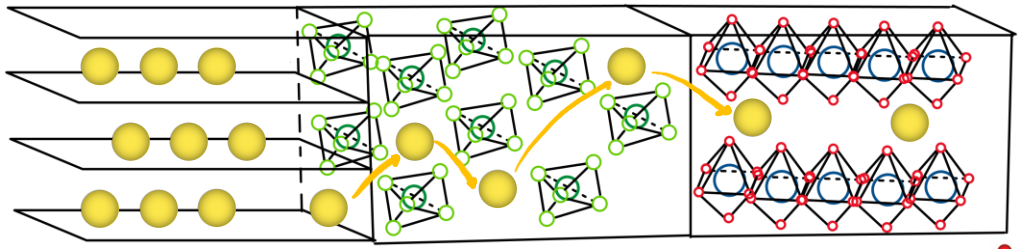
The case of Na_xMnPO_4F cathode material





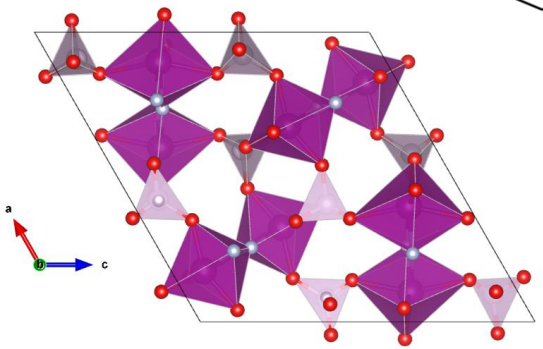
X = 1.5

+ 0.5 Na^+



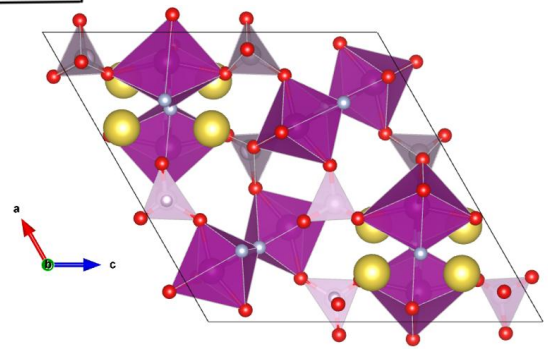
A

C



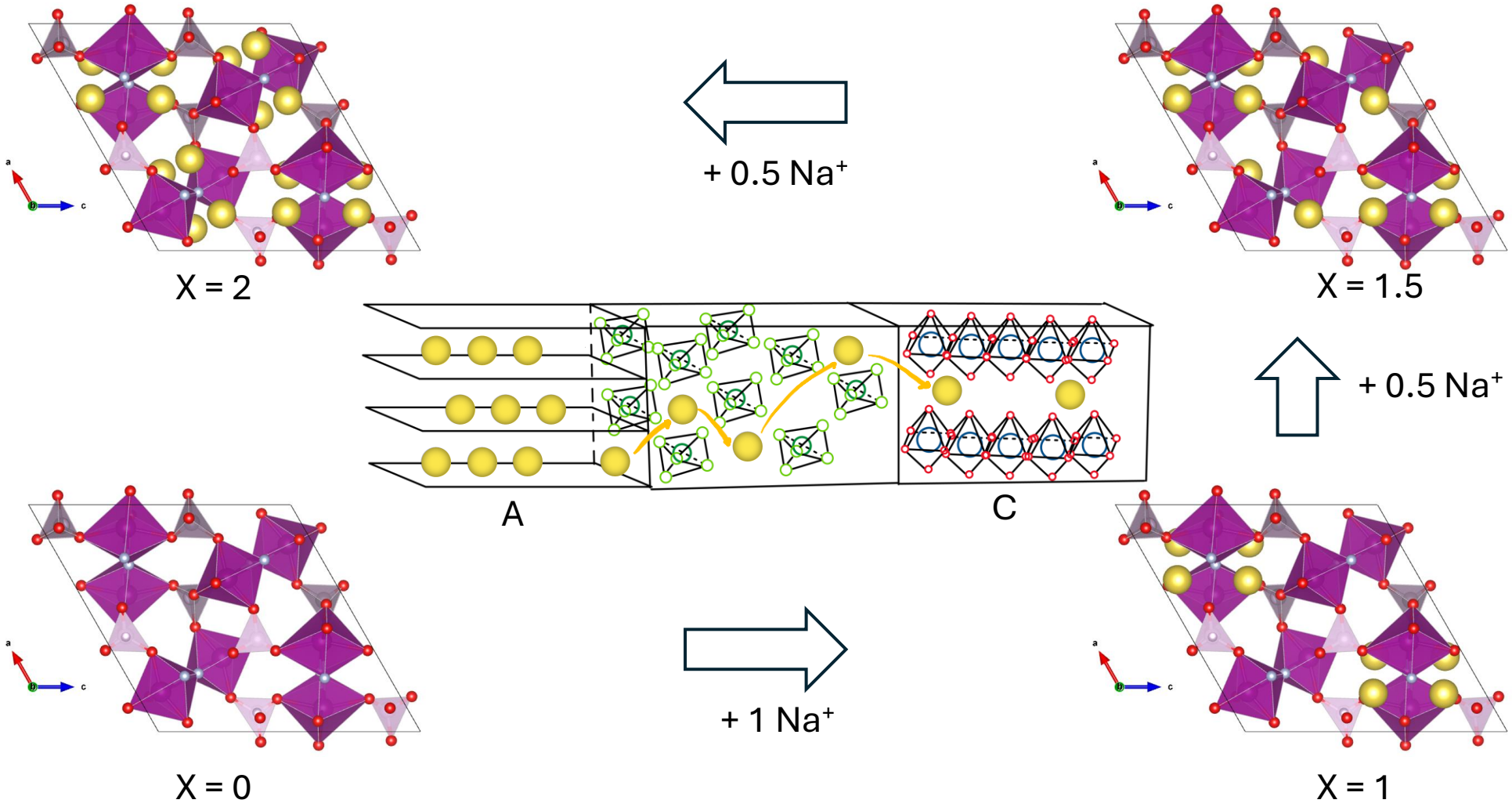
X = 0

+ 1 Na^+



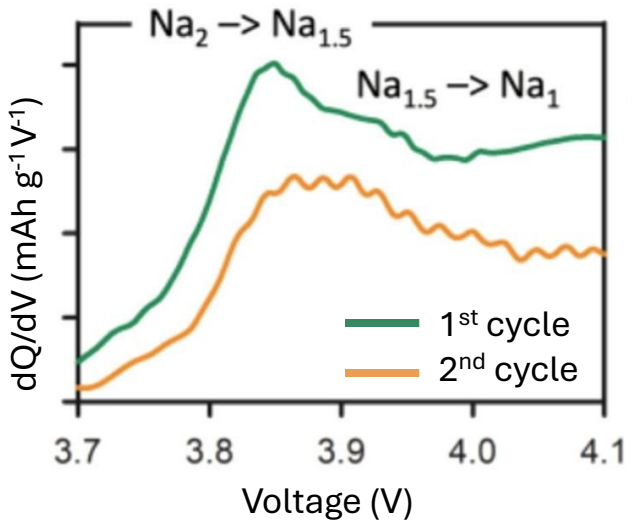
X = 1

The case of Na_xMnPO_4F cathode material

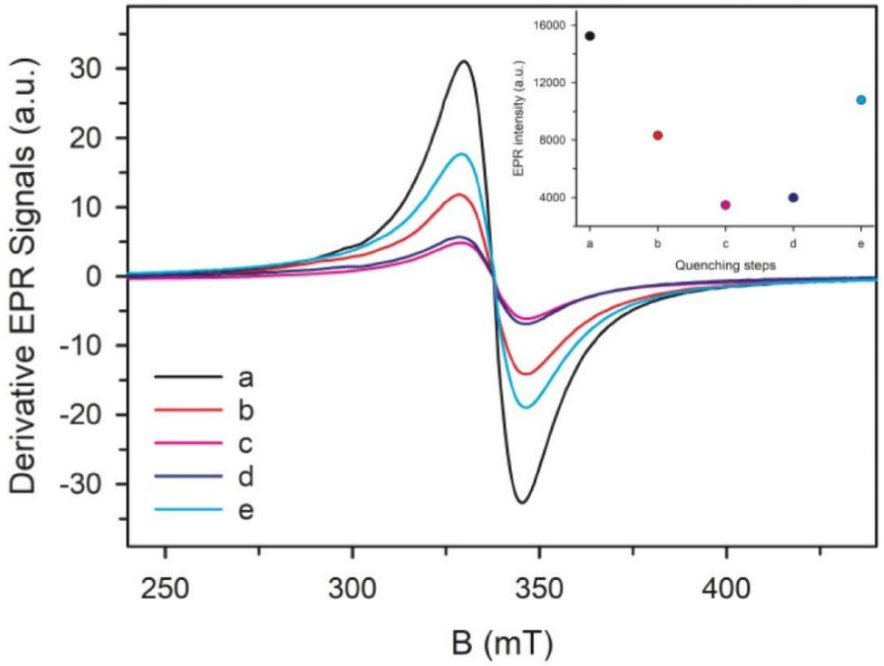


The case of Na_xMnPO_4F cathode material

Redox process	Computed voltage (V)
$Na_2MnPO_4F \rightarrow Na_{1.5}MnPO_4F + 0.5\ Na$	3.64
$Na_{1.5}MnPO_4F \rightarrow NaMnPO_4F + 0.5\ Na$	3.71

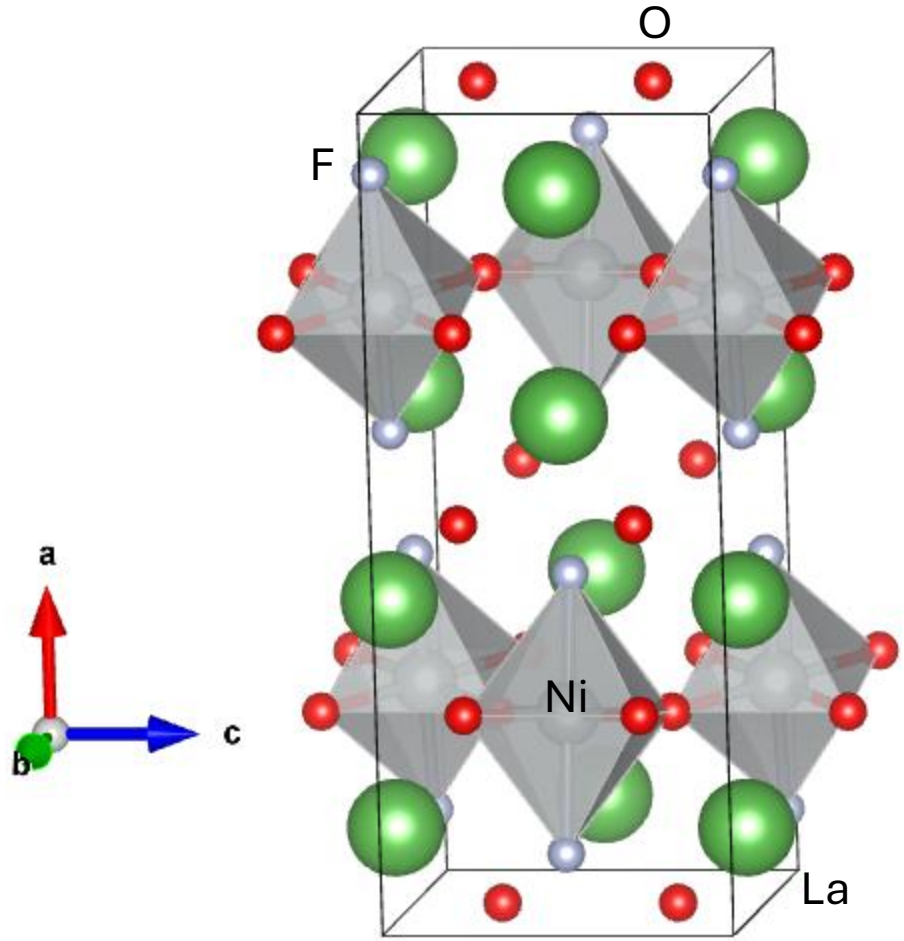


Mn^{2+} EPR line intensity at different voltages

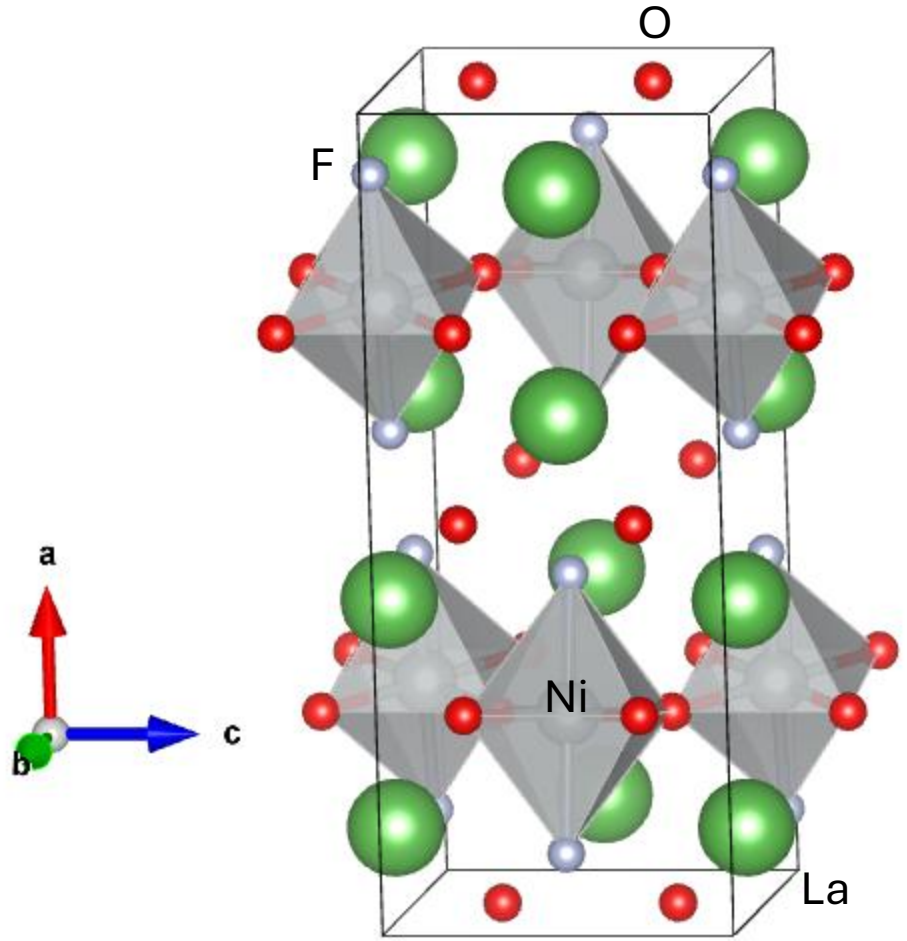


Journal of Energy Storage **127**, 117143 (2025)

A possible electrode material for FIBs: $La_2NiO_3F_2$



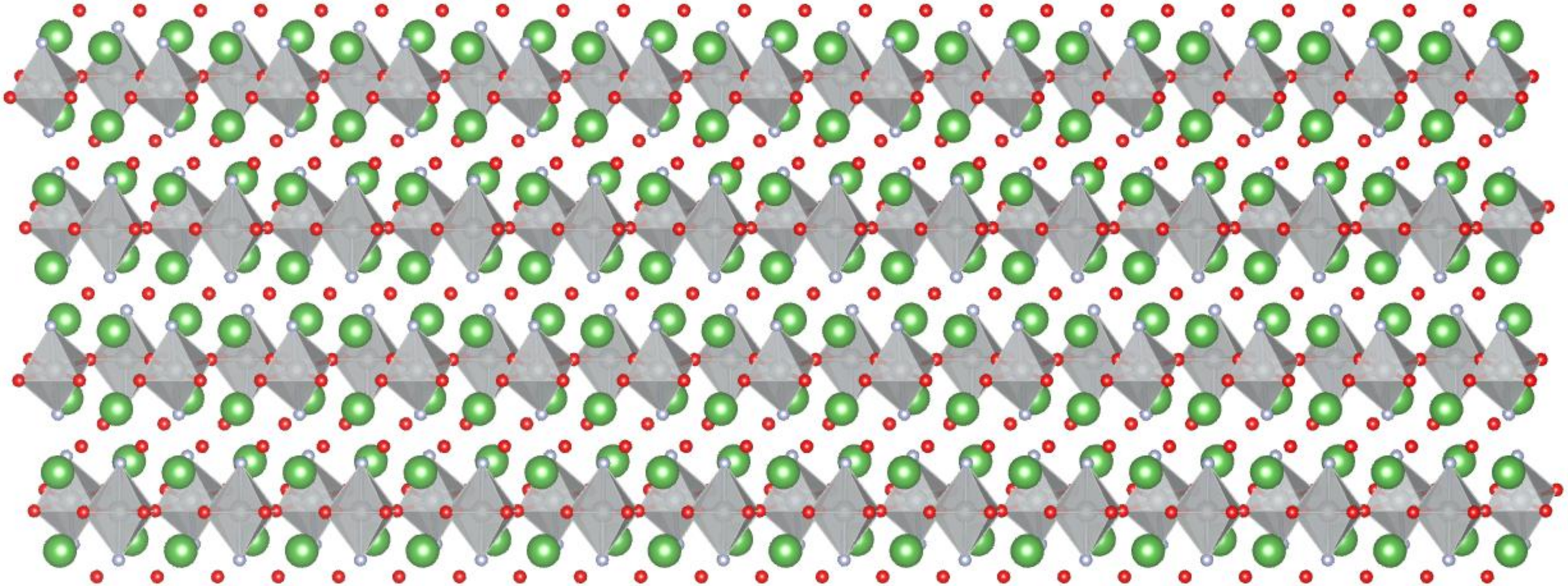
A possible electrode material for FIBs: $La_2NiO_3F_2$



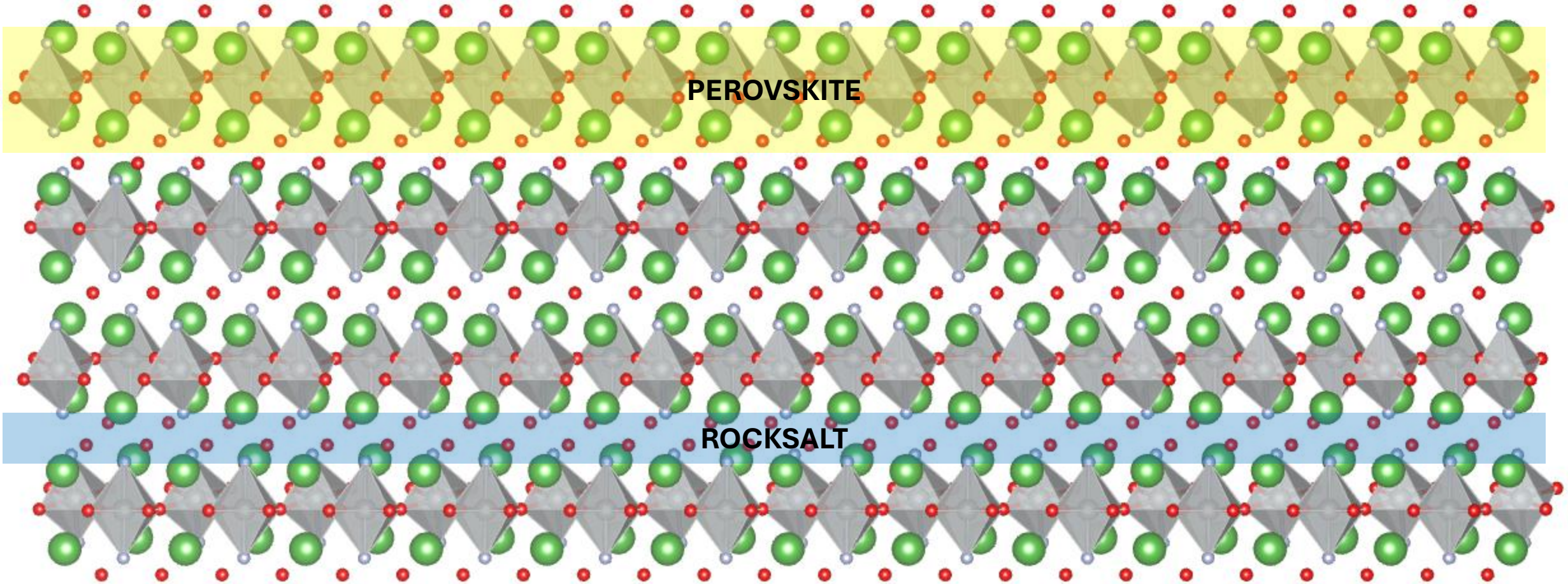
$La_2NiO_3F_{2+\delta}$ → cathode
$(Ni^{2+\delta})$

$La_2NiO_3F_{2-\delta}$ → anode
$(Ni^{2-\delta})$

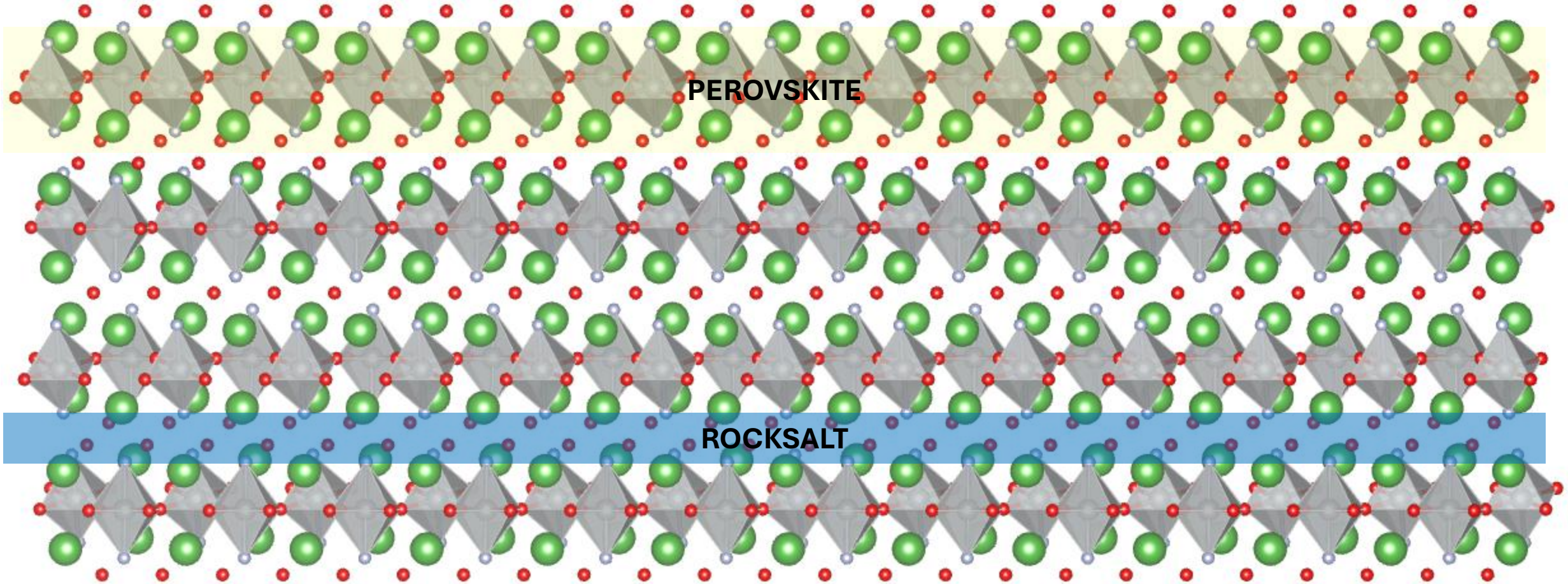
A possible electrode material for FIBs: $La_2NiO_3F_2$



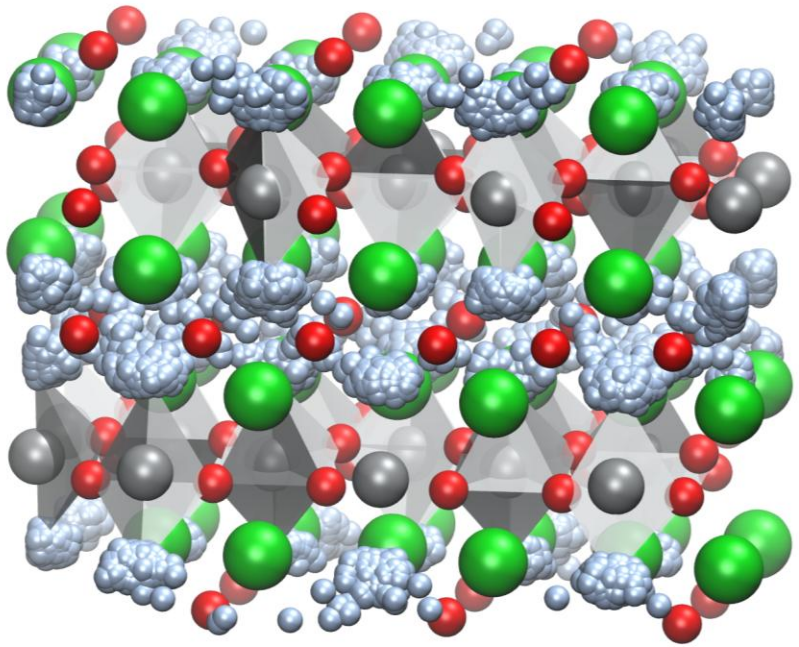
A possible electrode material for FIBs: $La_2NiO_3F_2$

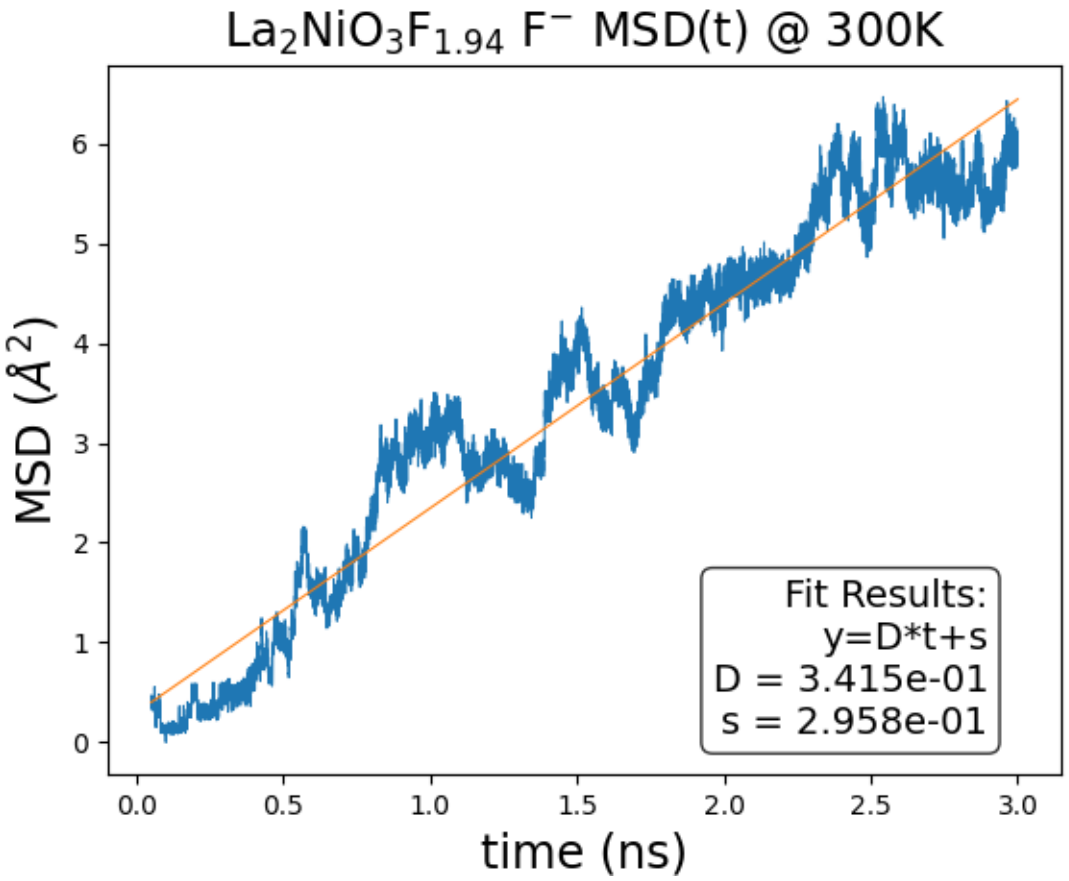


A possible electrode material for FIBs: $La_2NiO_3F_2$



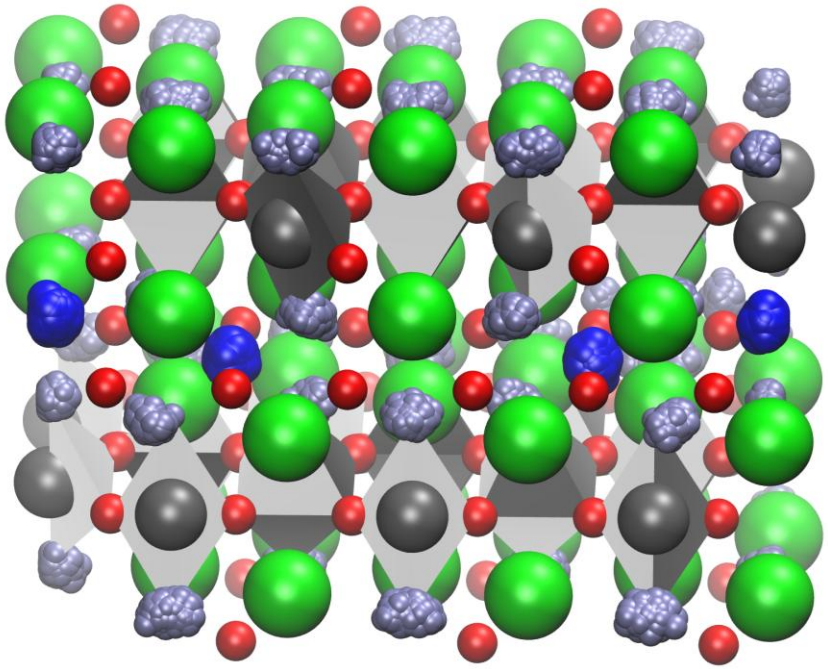
Diffusion coefficient of $La_2NiO_3F_2$ from MD

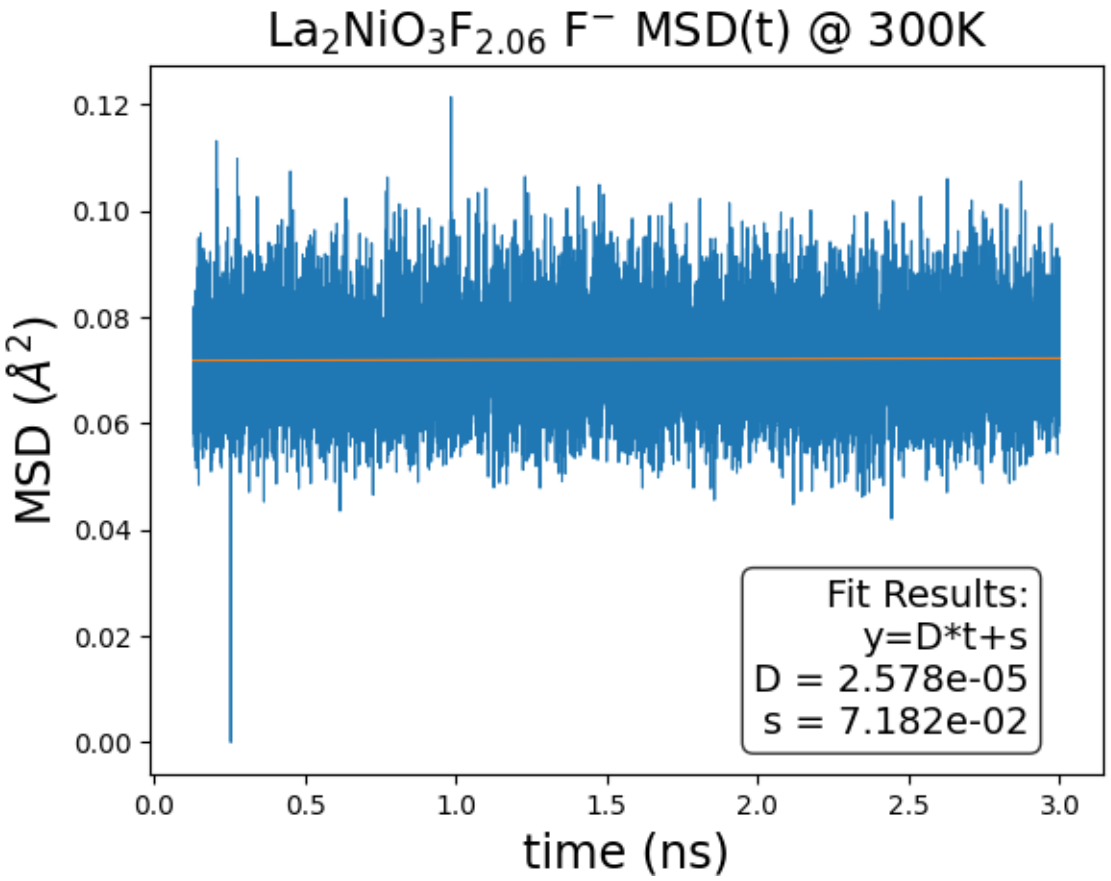




$$MSD = \langle (\boldsymbol{x}(t) - \boldsymbol{x_0})^2 \rangle = 2nDt$$

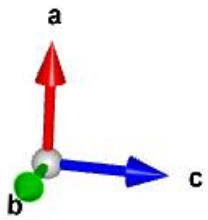
Diffusion coefficient of $La_2NiO_3F_2$ from MD

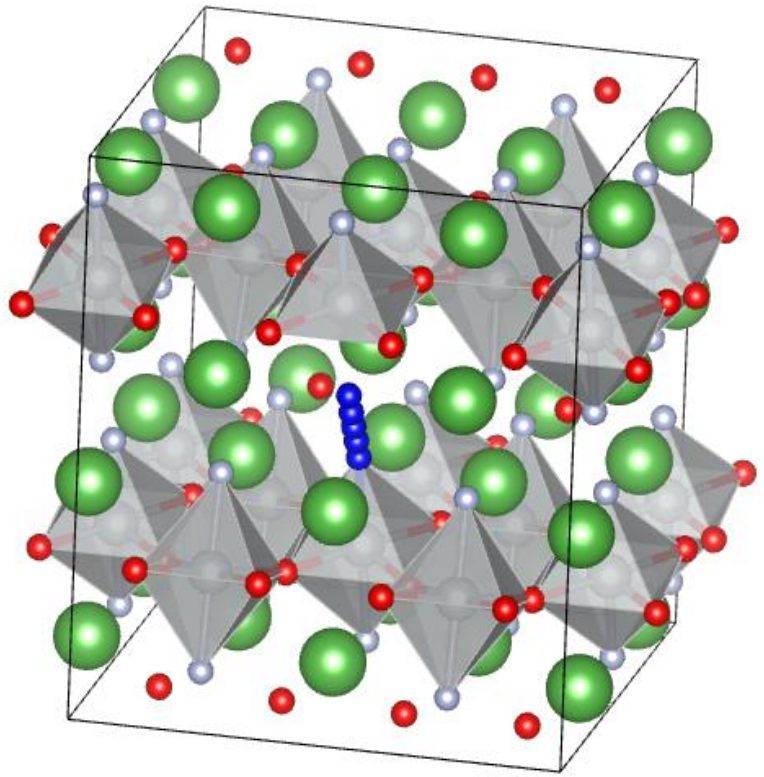


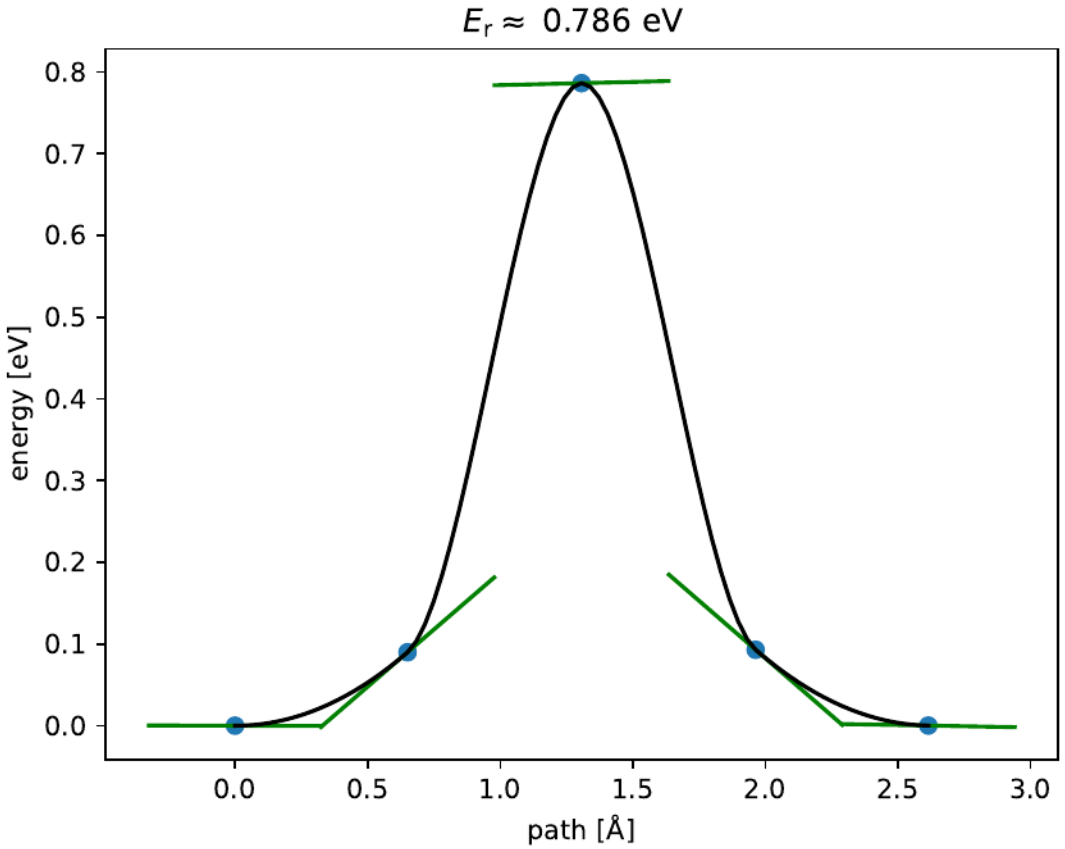


$$MSD = \langle (\boldsymbol{x}(t) - \boldsymbol{x_0})^2 \rangle = 2nDt$$

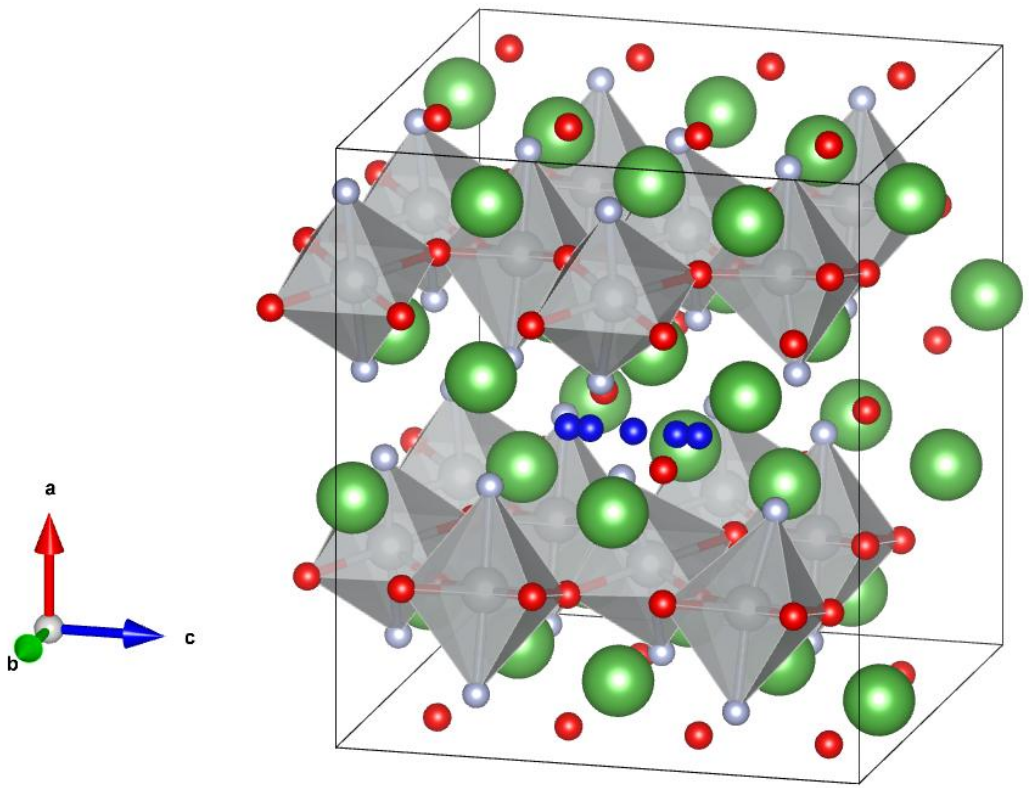
Nudged Elastic Band method

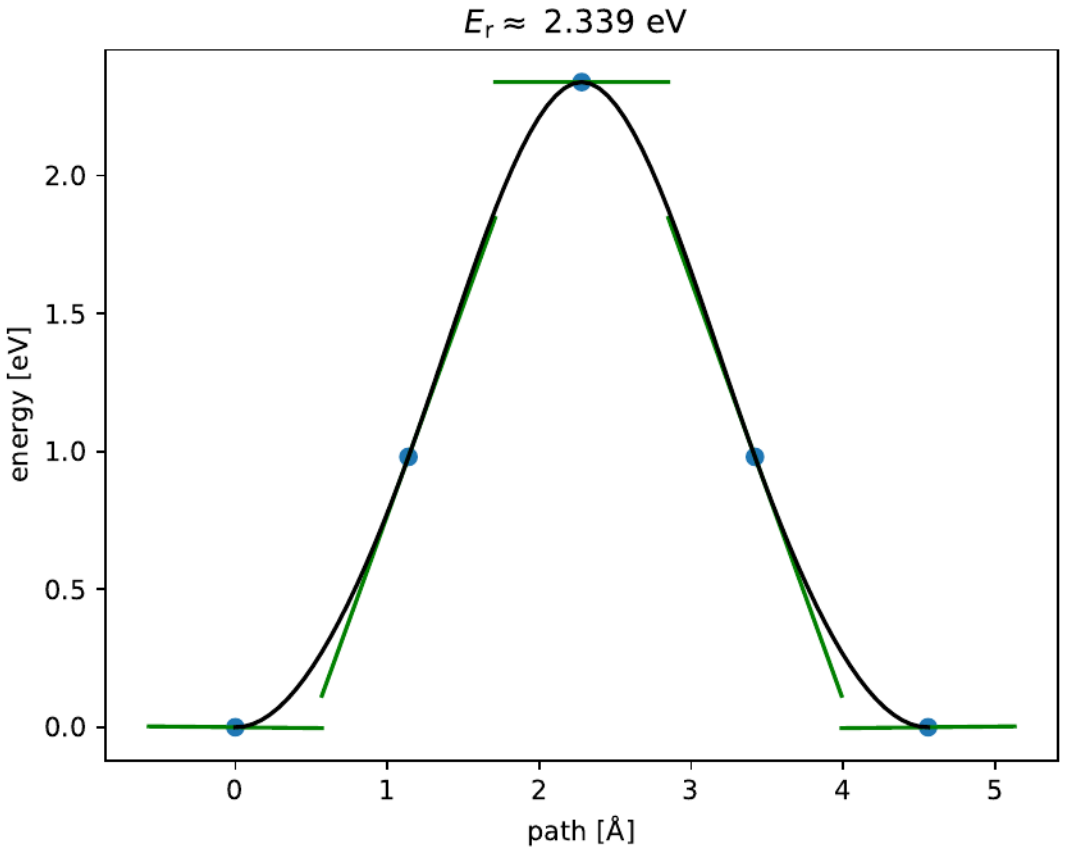




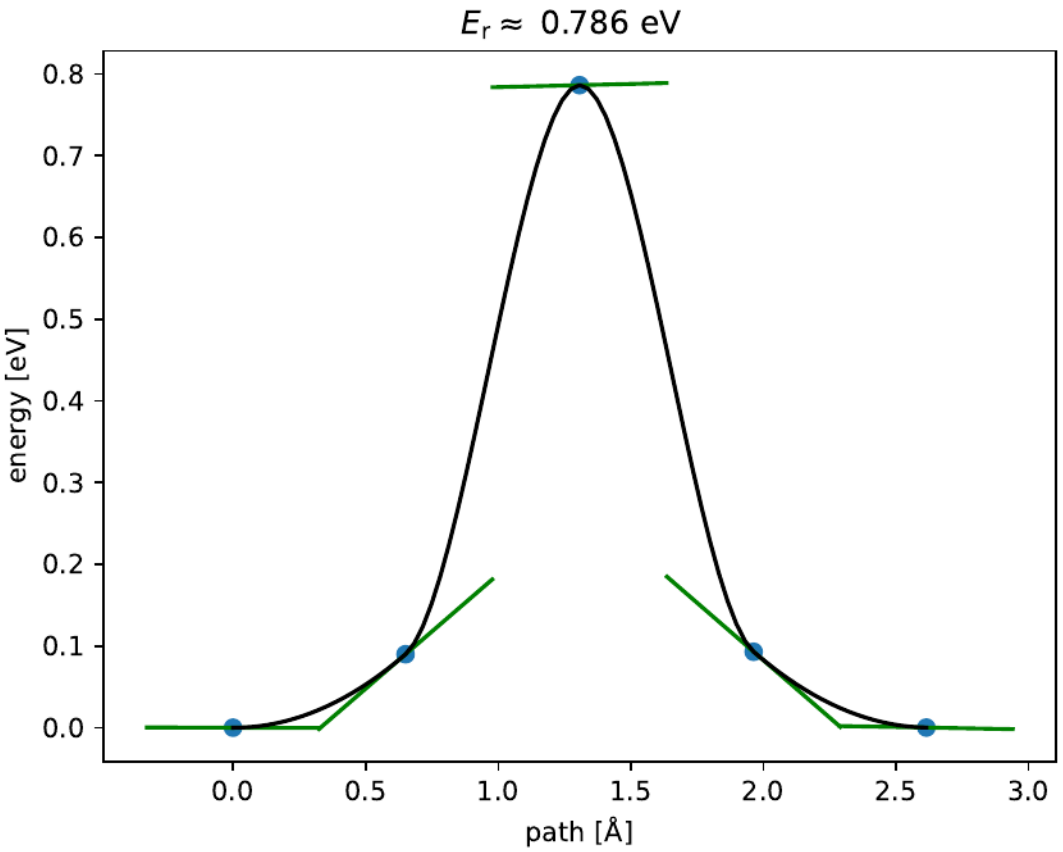


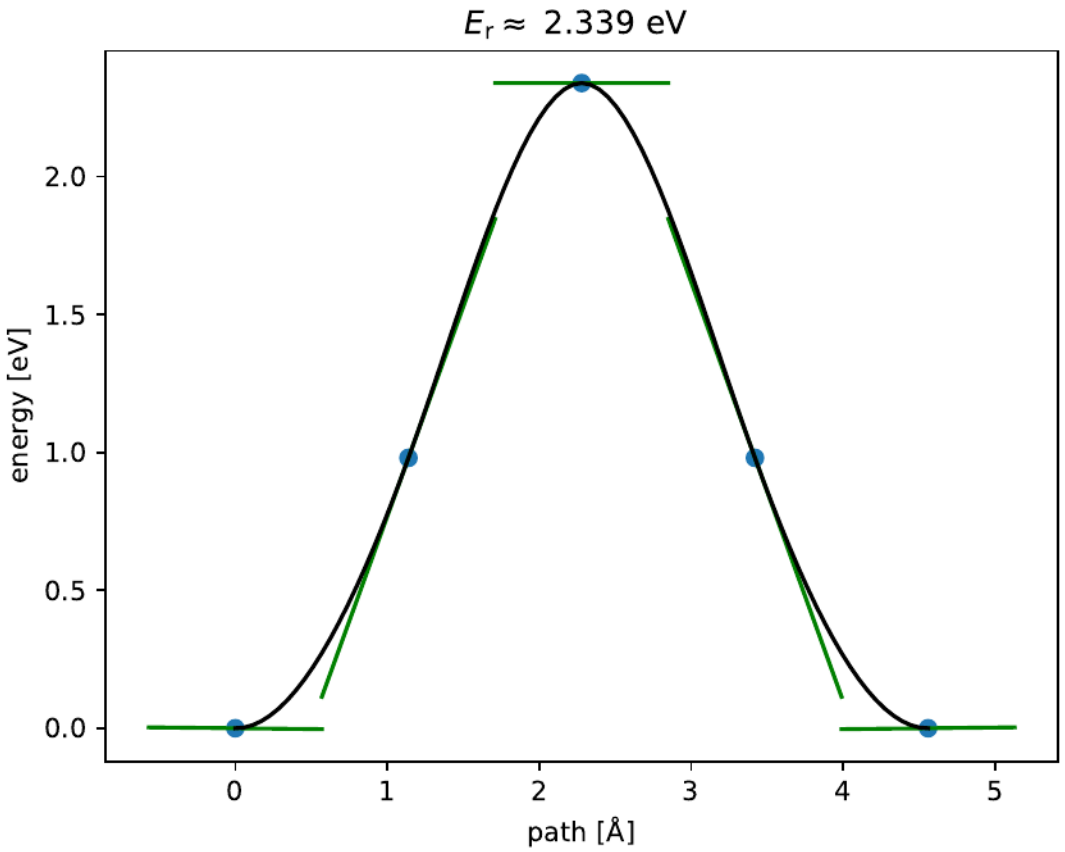
Nudged Elastic Band method



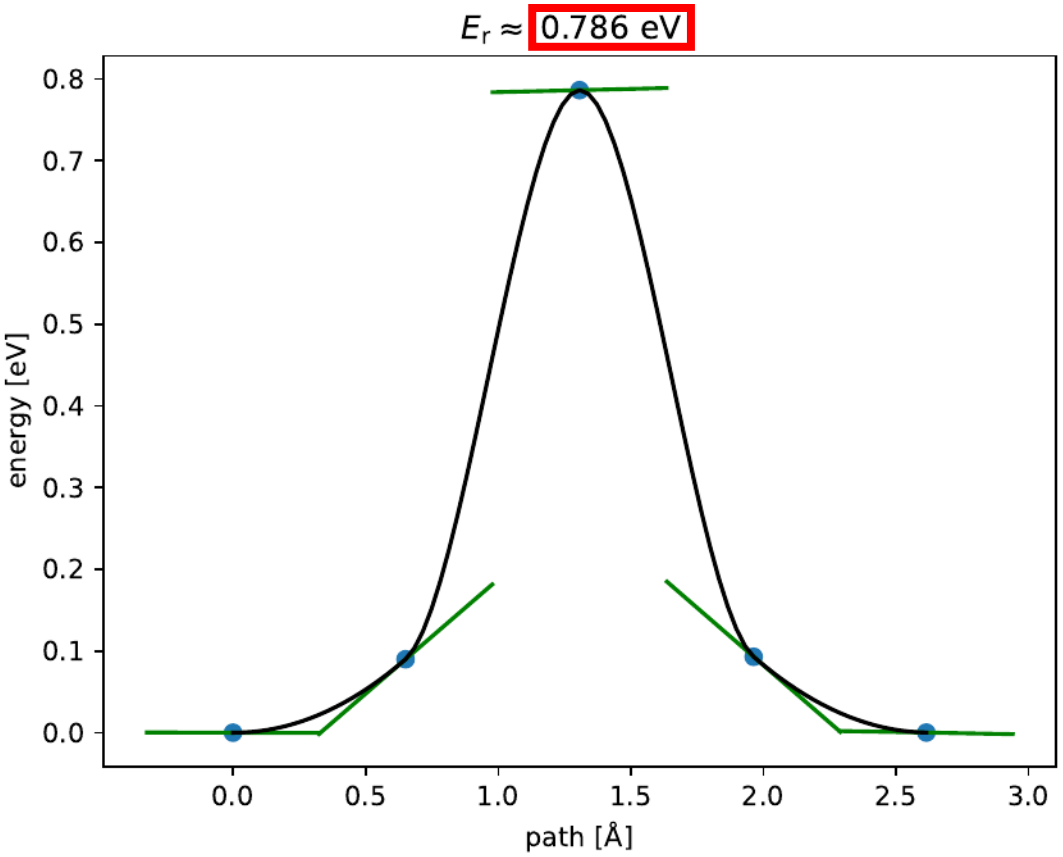


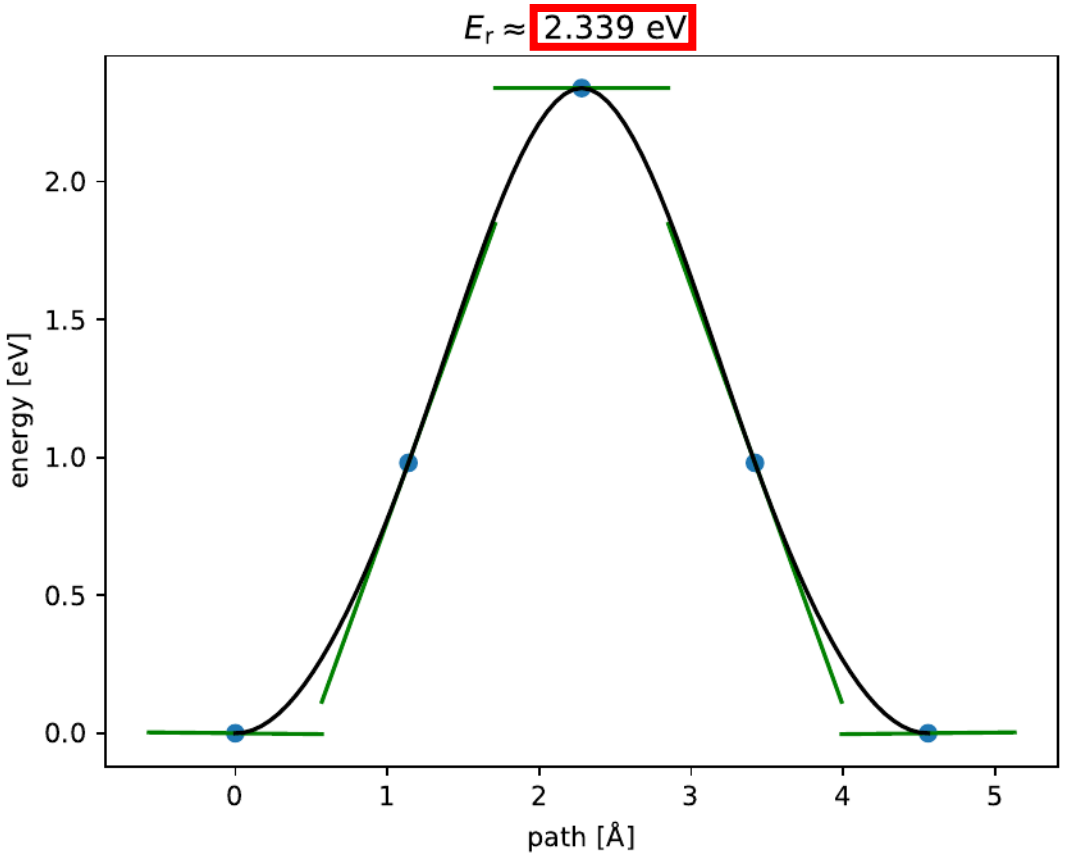
Diffusion energy barriers





Diffusion energy barriers





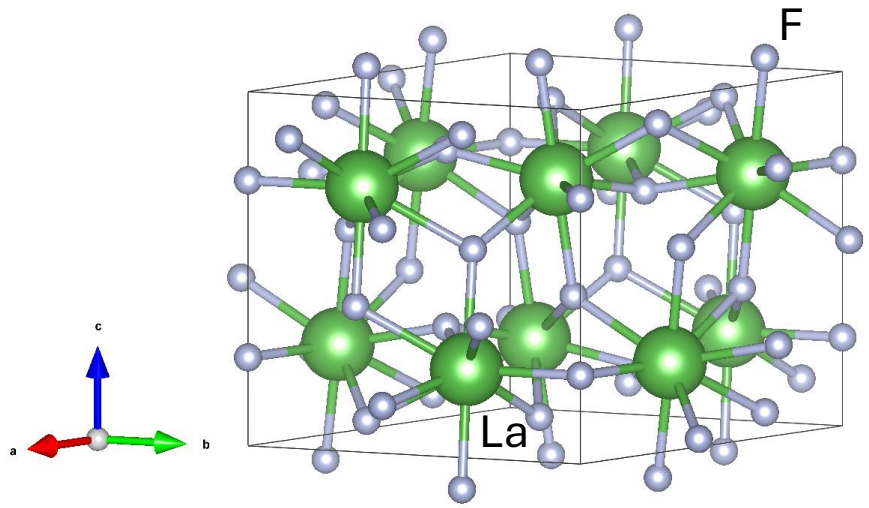
The material diffuses better in anode operation

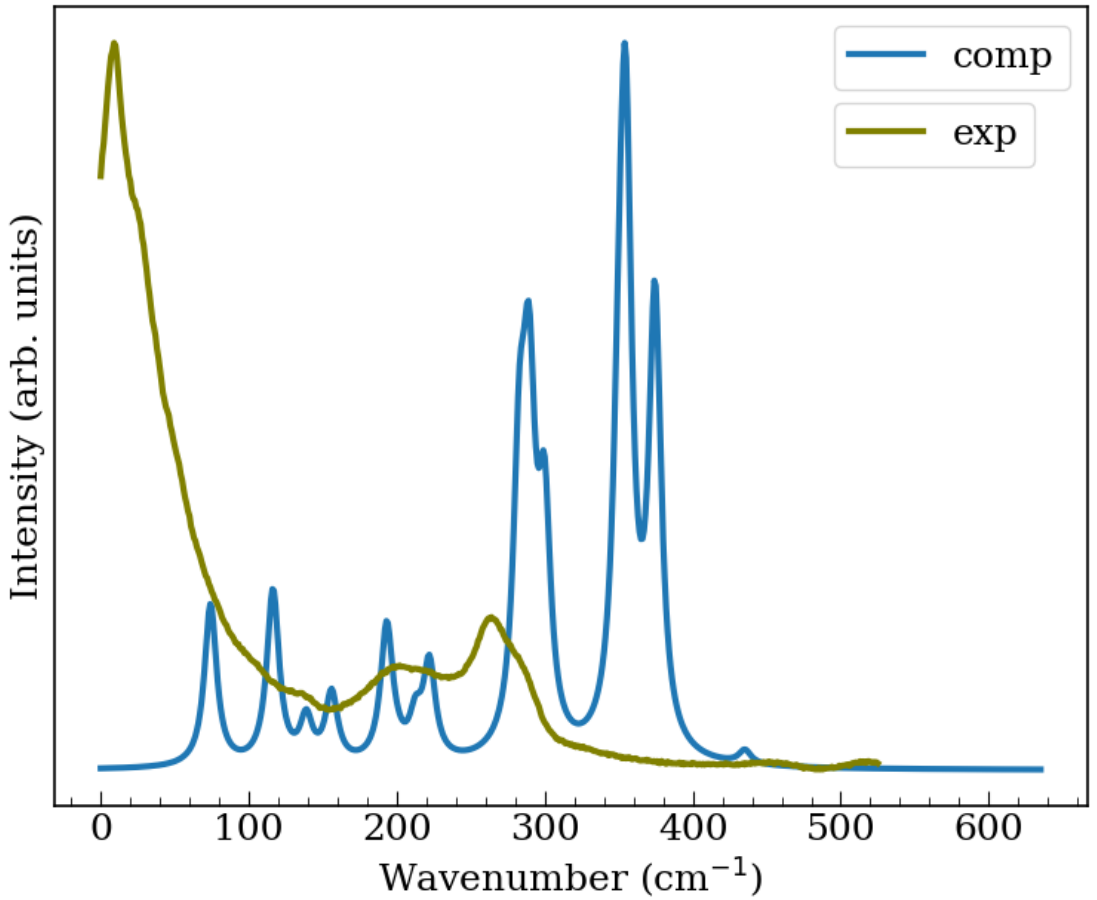
Solid state electrolytes for FIBs

Safety

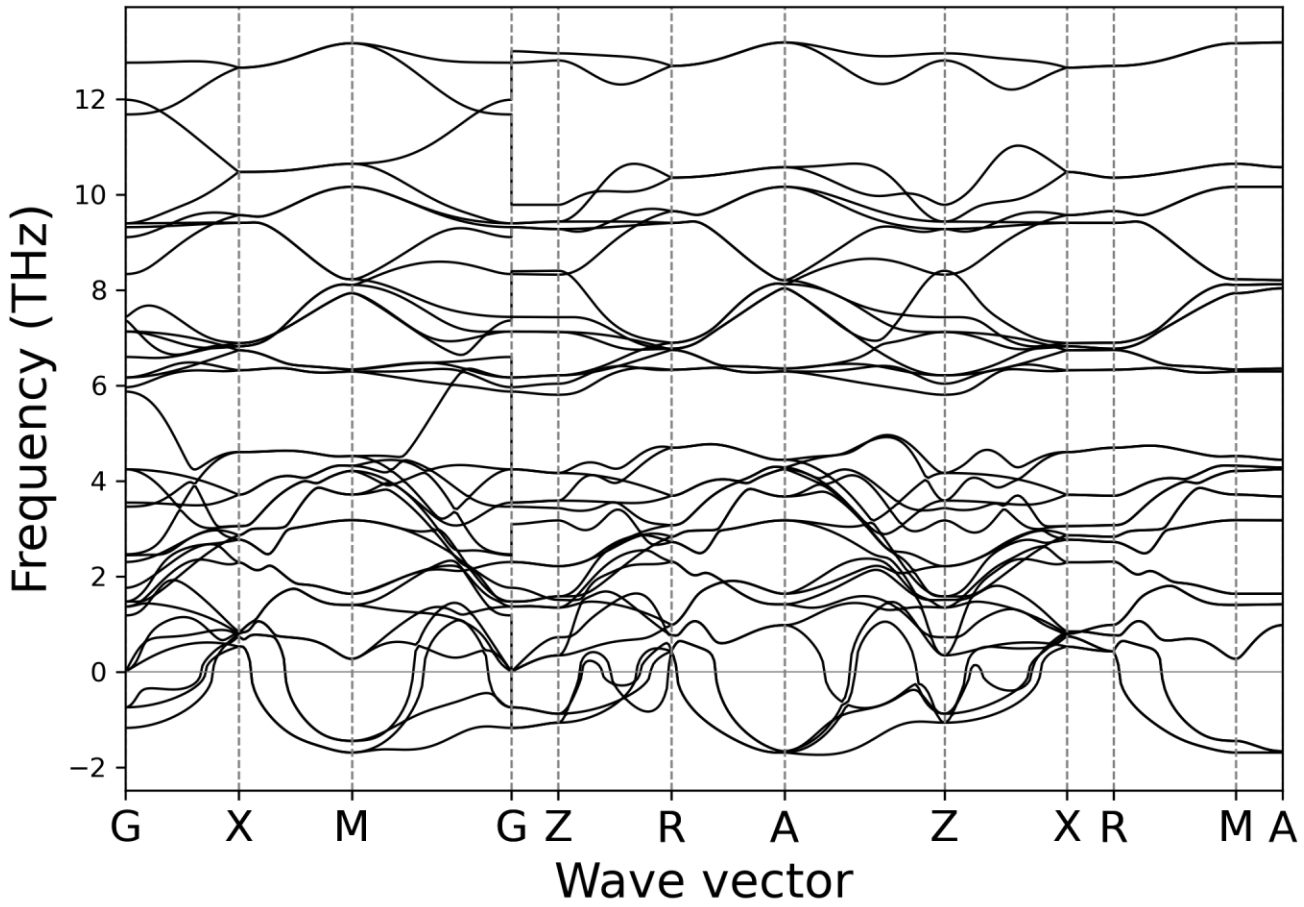
Energy density

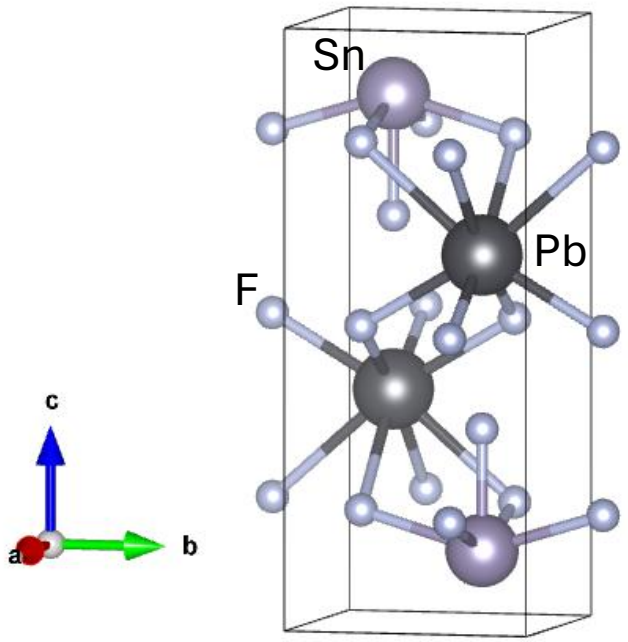
LaF_3: comparing DFT and experimental Raman spectra



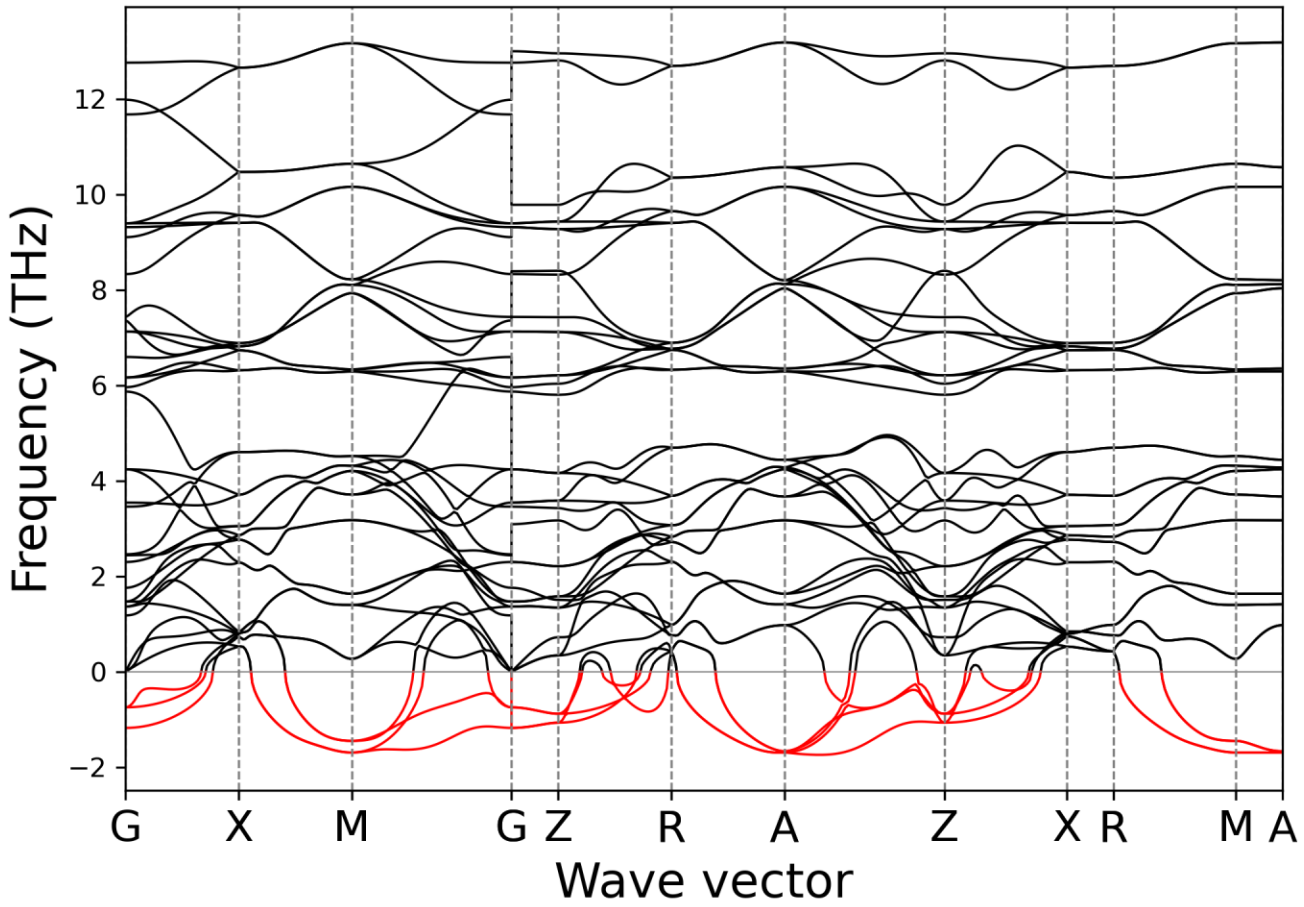


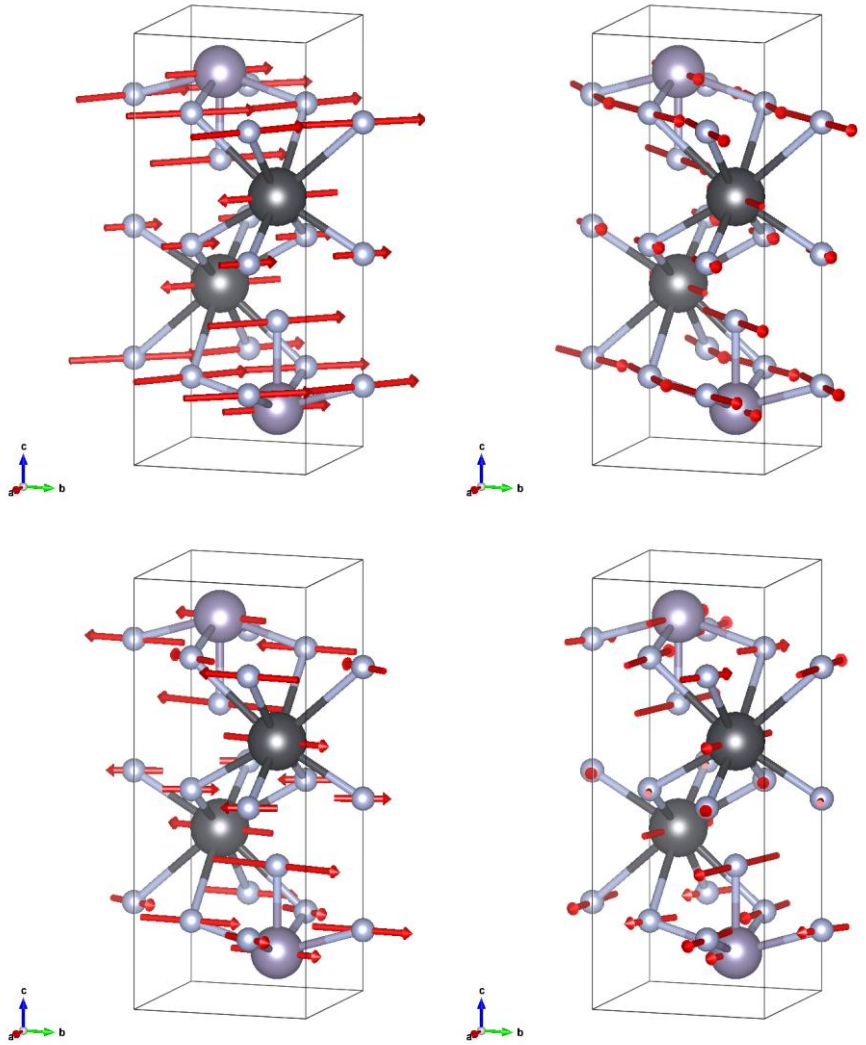
Some issues affect $PbSnF_4$



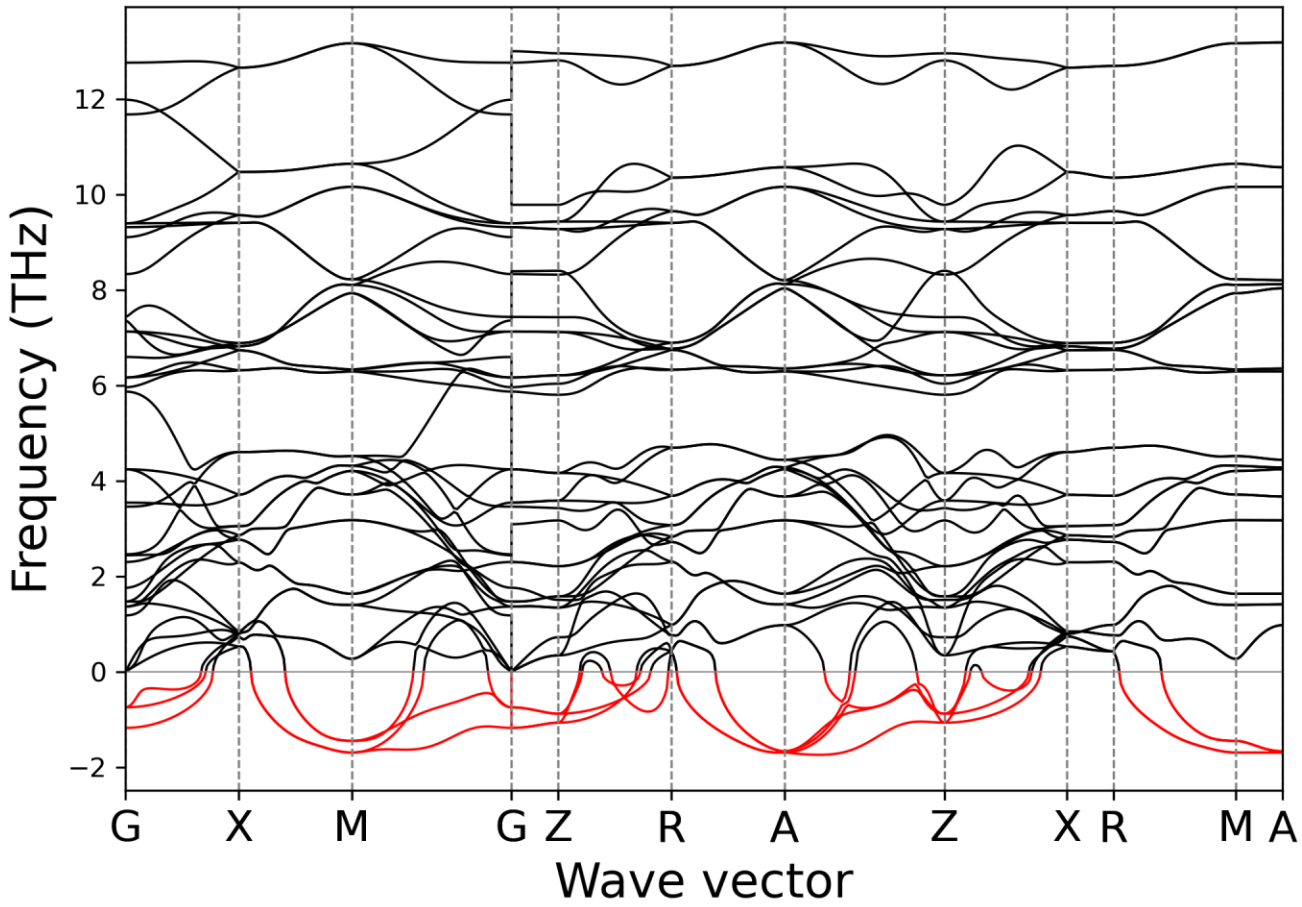


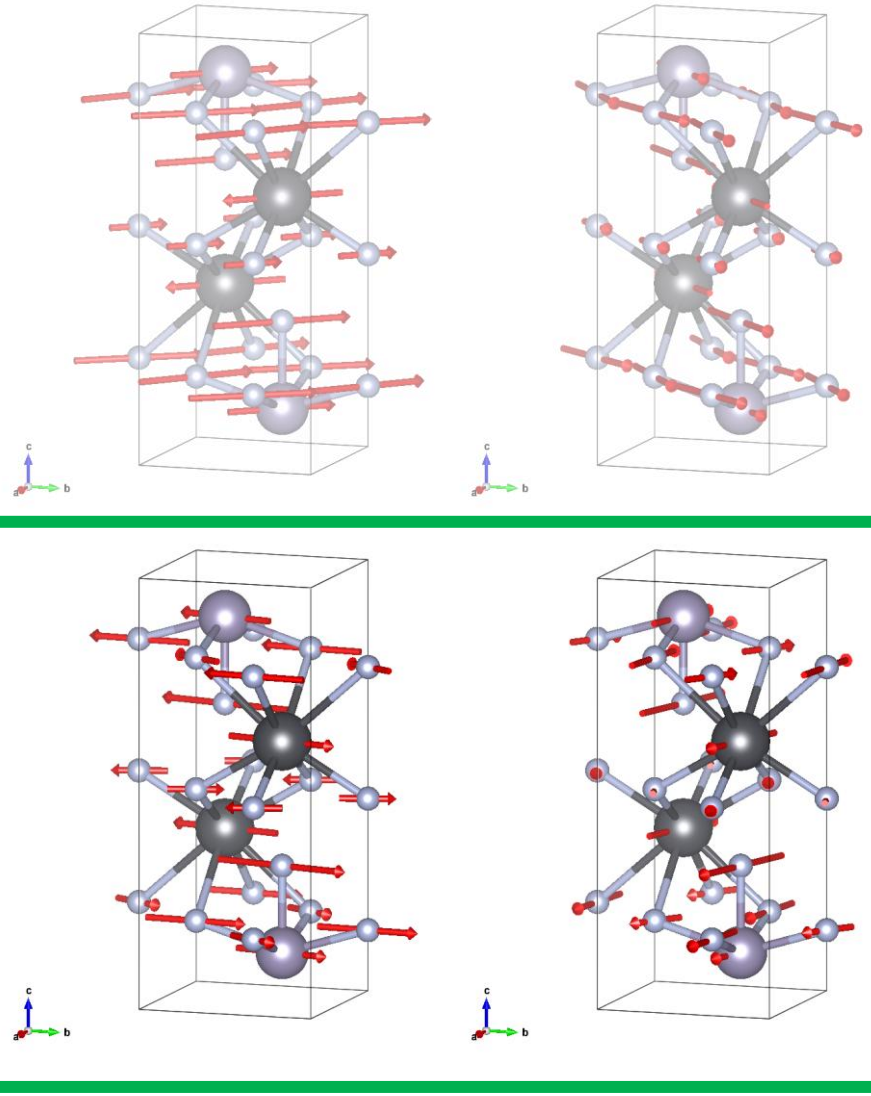
Some issues affect $PbSnF_4$





Some issues affect $PbSnF_4$





Further work needed:

Electrochemical
Stability
Window