Solid State Ionics 2024
24TH INTERNATIONAL CONFERENCE

Simulations And Informatics of MATerials Group


# Exploration of oxyfluoride frameworks as Na-ion cathodes

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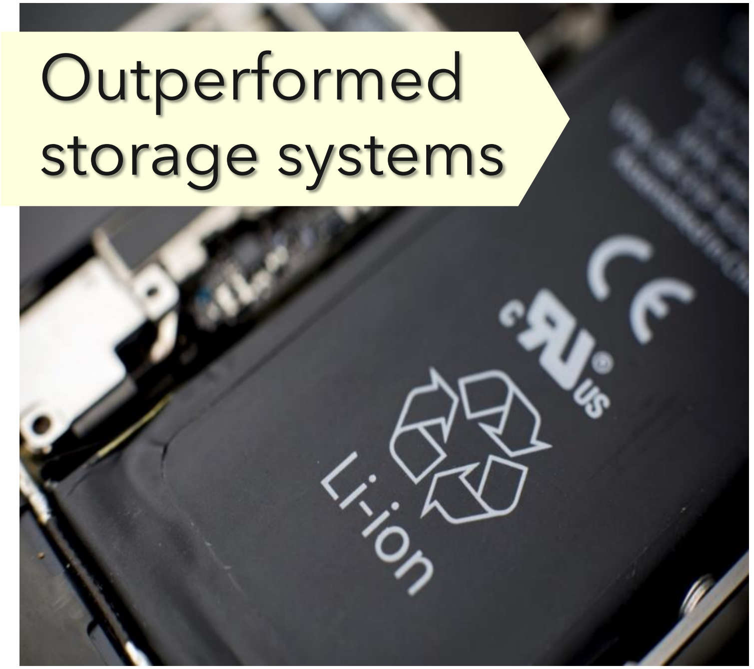
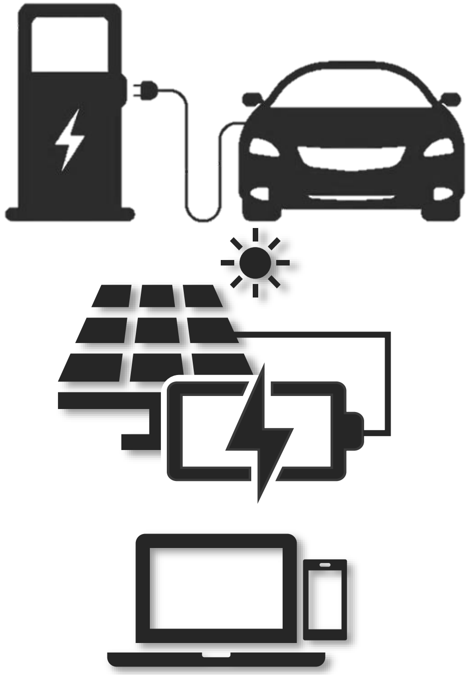
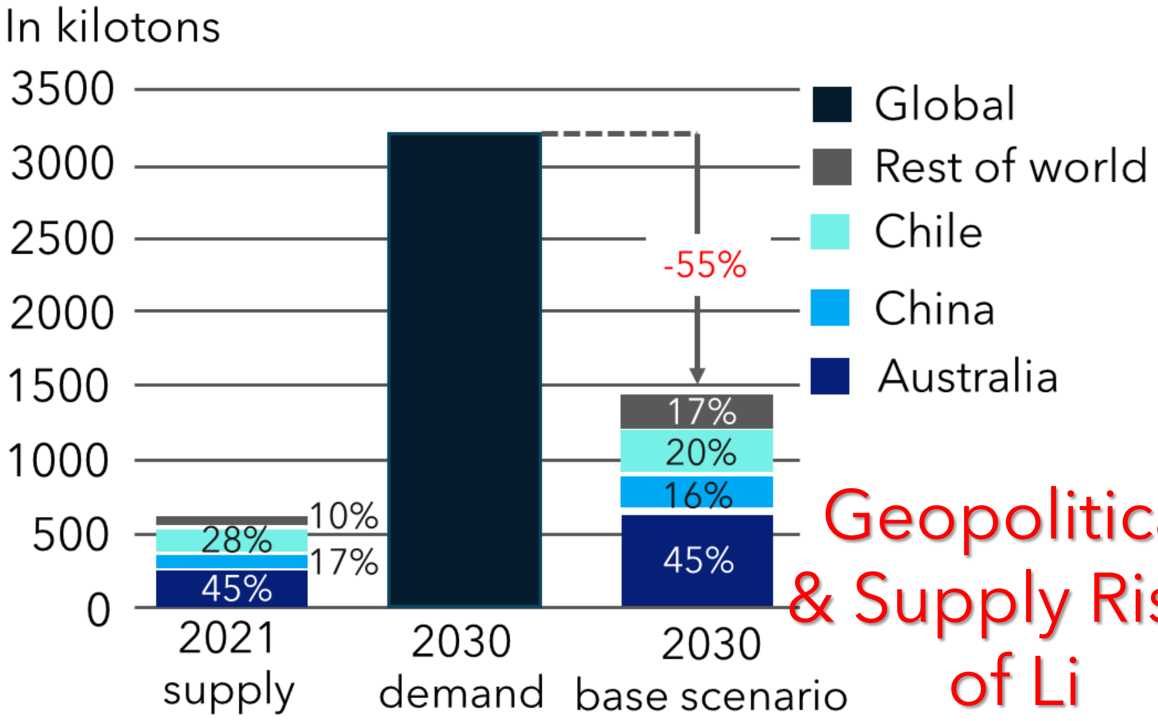
# A paradigm shift to Na-ion battery







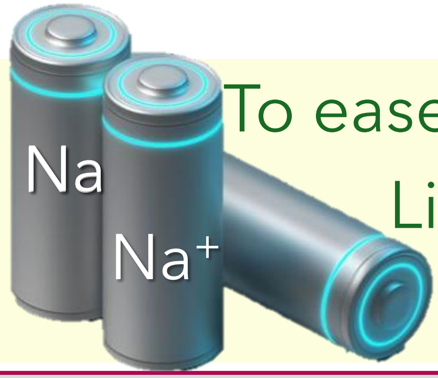

Geopolitical & Supply Risks of Li

~200-600 Wh $kg^{-1}$

>490 Wh $l^{-1}$

>1000 cycles

>40 Ah >3.5V

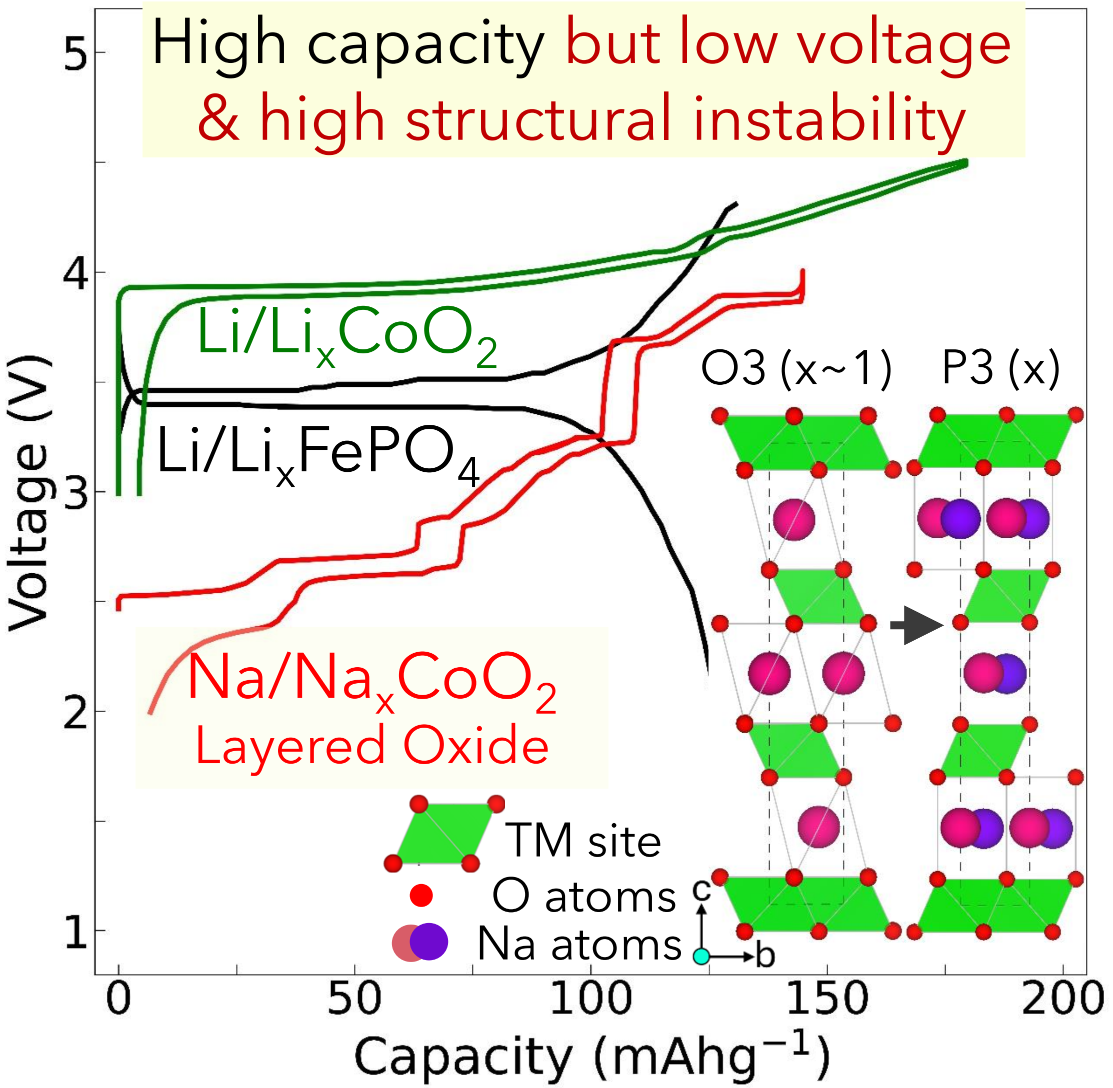


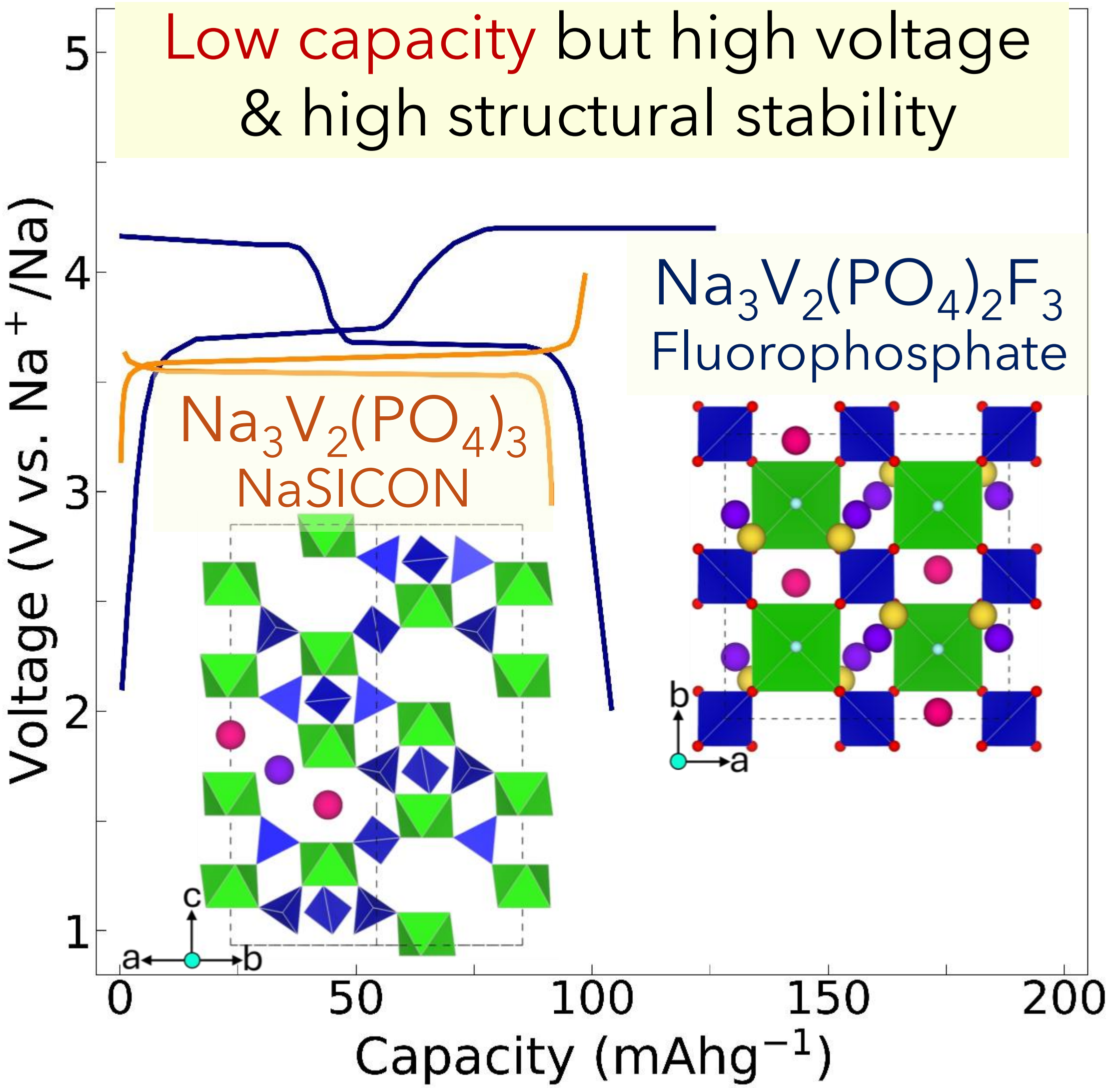

To ease our sole dependence on Li-ion battery for increasing energy demands


1. Choi, J. W., & Aurbach, D. (2016). *Nat. Rev. Mater.*, 1(4), 1-16.
2. Whittingham, M. S. (2012). *Proc. IEEE*, 100(Special Centennial Issue), 1518-1534.
3. Gifford, S. (2022). Faraday Institution. *Changes*, 2050(6), 500.
4. Fleischmann, J. et al. (2023). *McKinsey & Company*, 2-18.
5. IEA (2024), *Global Critical Minerals Outlook 2024*. IEA Paris. Licence: CC BY 4.0

# Na-ion battery cathodes compared







1. Yabuuchi, N. et al. (2014). *Chem. Rev.*, 114(23), 11636-11682.
2. Padhi, A. K. et al. (1997) *J. Electrochem. Soc.*, 144(4), 1188.
3. Shakoor, R. A. et al. (2012). *J. Mater. Chem.*, 22(38), 20535-20541.
4. Jian, Z. et al. (2012). *Electrochem. Commun.*, 14(1), 86-89.

# Explore the UNEXPLORED



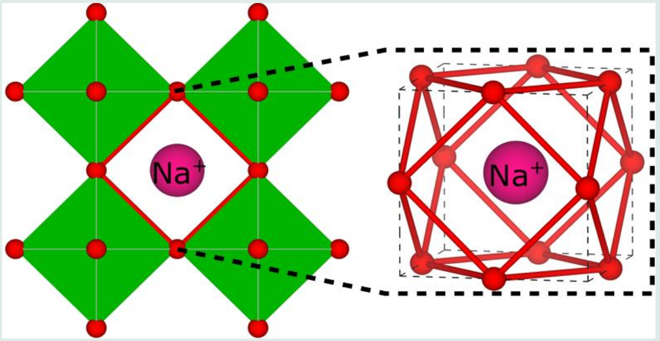
Structural Framework

Composition ($Na_xMO_yF_{3-y}$): >260 $mAhg^{-1}$ theoretical capacity

## PEROVSKITE

## Na-TRANSITION METAL OXYFLUORIDE

E.g., $ReO_3$ ($Pm\bar{3}m$)



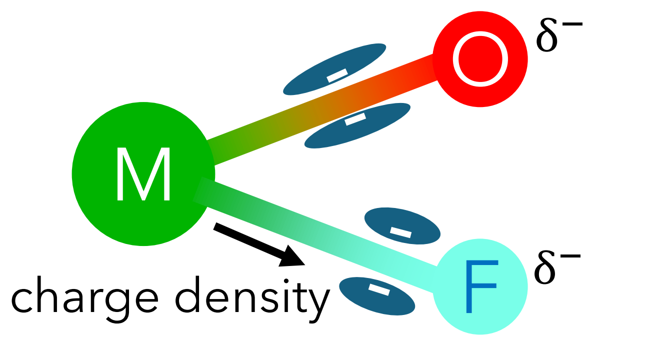

Stable framework to intercalate large $Na^+$

3d transition metals

| | | | | | | |
|---|---|---|---|---|---|---|
| 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni |

Redox-active transition metal facilitate $Na^+$ (de)intercalation

Electronegative $F^-$




Enhances voltage via inductive effect

1. Evans, H. A. et al. (2020). *Nat. Rev. Mater.*, 5(3), 196-213.
2. Goodenough, J. B. (2014). *Chem. Mater.*, 26(1), 820-829.
3. Wang, Y. et al. (2024). *Nat. Rev. Mater.*, 9(2), 119-133.

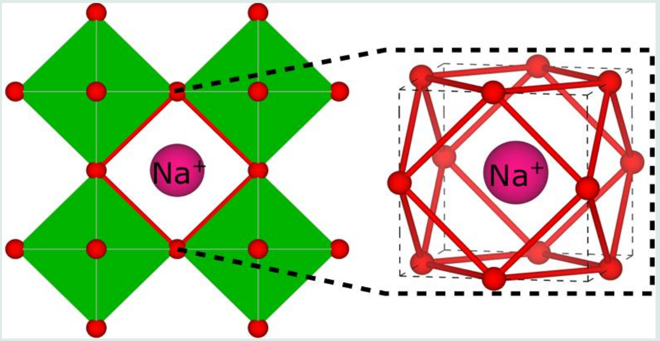
# $Na_xMO_yF_{3-y}$: Why yet UNEXPLORED?



Structural Framework — PEROVSKITE

Composition ($Na_xMO_yF_{3-y}$): >260 $mAhg^{-1}$ theoretical capacity — Na-TRANSITION METAL OXYFLUORIDE

E.g., $ReO_3$ ($Pm\bar{3}m$)




Stable framework to intercalate large $Na^+$

3d transition metals

| 22 | 23 | 24 | 25 | 26 | 27 | 28 |
|---|---|---|---|---|---|---|
| Ti | V | Cr | Mn | Fe | Co | Ni |

Redox-active transition metal facilitate $Na^+$ (de)intercalation

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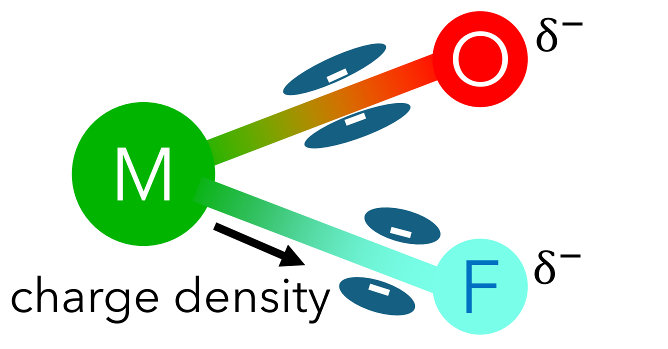



Enhances voltage via inductive effect

Difficulty in synthesis from stable fluoride precursors

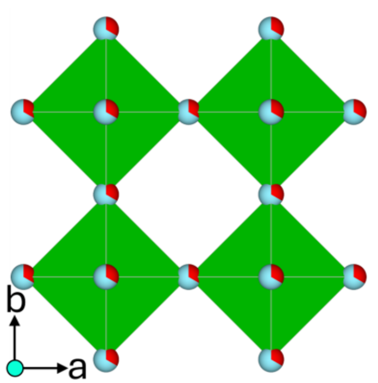

1. Evans, H. A. et al. (2020). *Nat. Rev. Mater.*, 5(3), 196-213.
2. Goodenough, J. B. (2014). *Chem. Mater.*, 26(1), 820-829.
3. Wang, Y. et al. (2024). *Nat. Rev. Mater.*, 9(2), 119-133.
4. Deng, D. (2017). *ChemNanoMat*, 3(3), 146-159.

# Oxyfluorides as Na cathode: Limited Studies

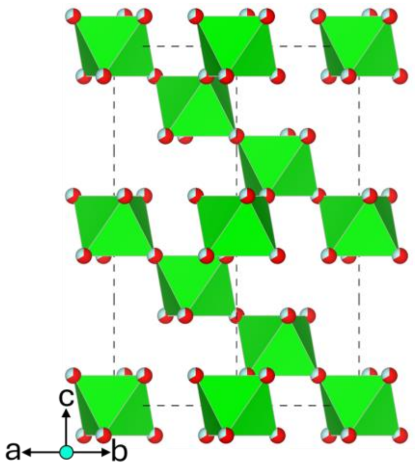


## Perovskite oxyfluoride as Li cathode

TiOF$_2$ & NbO$_2$F (Cubic)

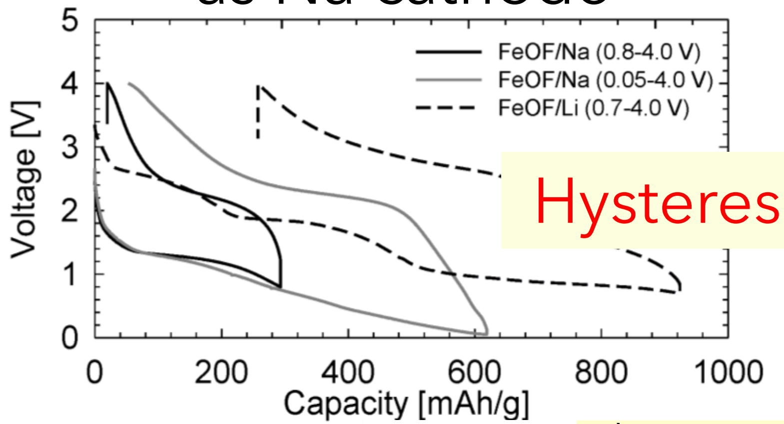


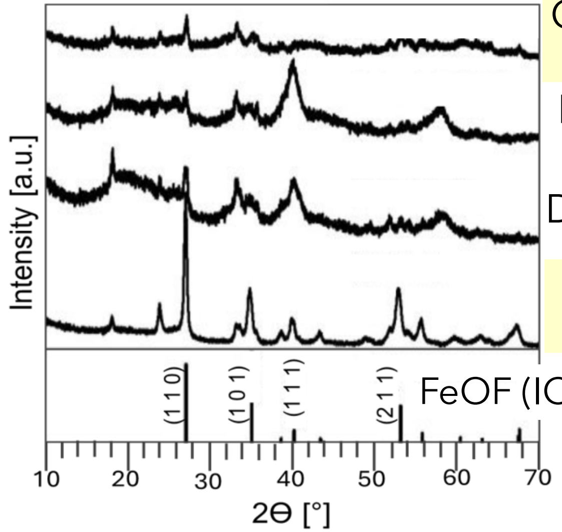

VO$_2$F (Rhombohedral)




Perovskite ⇄ Disordered Rocksalt

## Rutile oxyfluoride (FeOF) as Na cathode




## Disordered rocksalt oxyfluoride as cathode

$Li_2MO_2F$ as Li cathode

$Na_2MnO_2F$ as Na cathode

NOTE:

$Li^+$ mobility unaffected

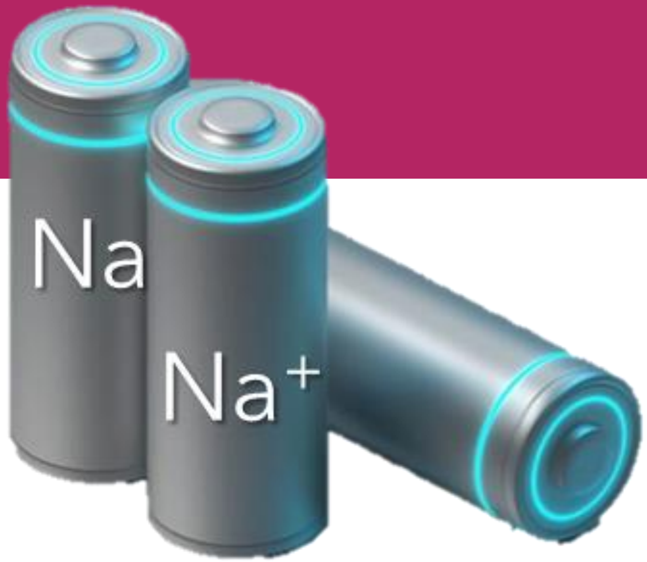
$Na^+$ mobility in disordered rocksalt or amorphized framework not reported yet

1. Reddy, M. V. et al. (2006). *J. Power Sources*, 162(2), 1312-1321.
2. Kuhn, A. et al. (2020). *Inorg. Chem.*, 59(14), 10048-10058.
3. Kitajou, A. et al. (2018). *Batteries*, 4(4), 68.
4. Xu, X. et al. (2021). *J. Electrochem. Soc.*, 168(8), 080521.
5. Shirazi Moghadam, Y. et al. (2022). *ACS Mater. Lett.*, 5(1), 125-132.
6. Clément, R. J. et al. (2020). *Energy Environ. Sci.*, 13(2), 345-373.

# Objective of the work



**To assess feasibility of Perovskite-based Transition Metal Oxyfluoride as practical Na cathode**




Considered Stoichiometries ($M^{4+/3+}$ redox-couple):

I. $Na_xMOF_2$ (F-rich oxyfluoride ; $0 \leq x \leq 1$)

II. $Na_{1+x}MO_2F$ (O-rich oxyfluoride; $0 \leq x \leq 1$)

# Workflow



## STRUCTURE IDENTIFICATION

- Groundstate polymorph identification:
  $MOF_2$ (F-rich )
  $NaMO_2F$ (O-rich )

## THERMODYNAMIC ANALYSIS

- Average voltage (V) prediction:
  $MOF_2 \leftrightarrow NaMOF_2$
  $NaMO_2F \leftrightarrow Na_2MO_2F$
- Convex hull construction & energy above hull ($E^{hull}$) for stability determination

## KINETIC ANALYSIS

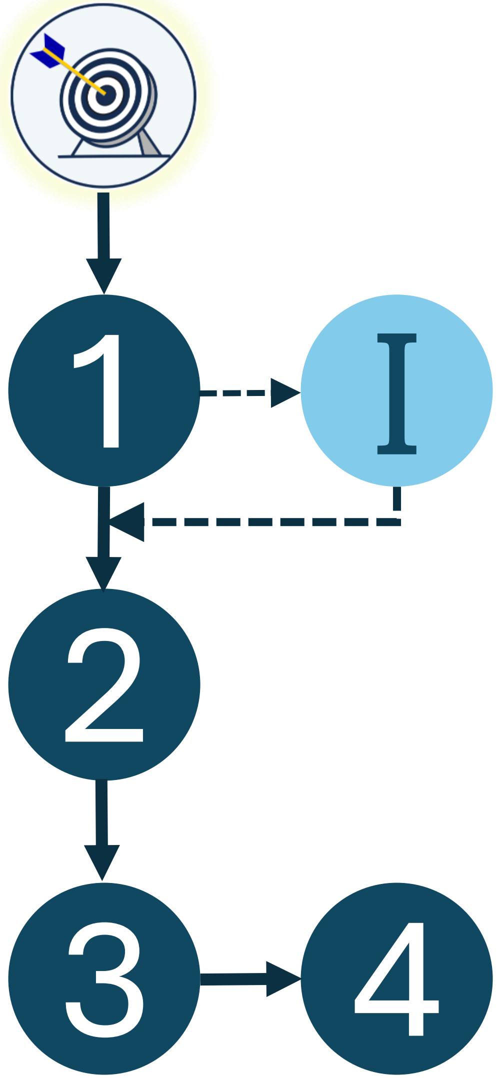
- Na-ion migration energy determination

# Groundstate Polymorph: Methodology



Identify groundstate polymorph for perovskite $MOF_2$ & $NaMO_2F$

*M : Ti, V, Cr, Mn, Fe, Co, Ni

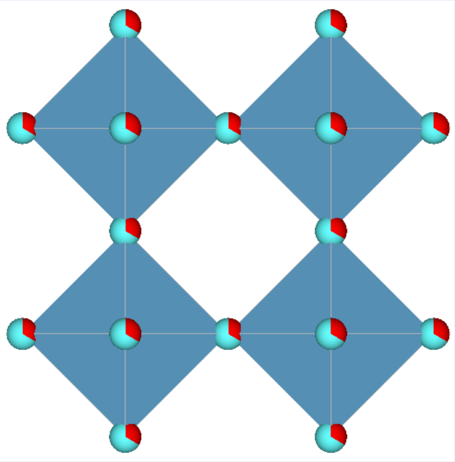


# Groundstate Polymorph: Methodology

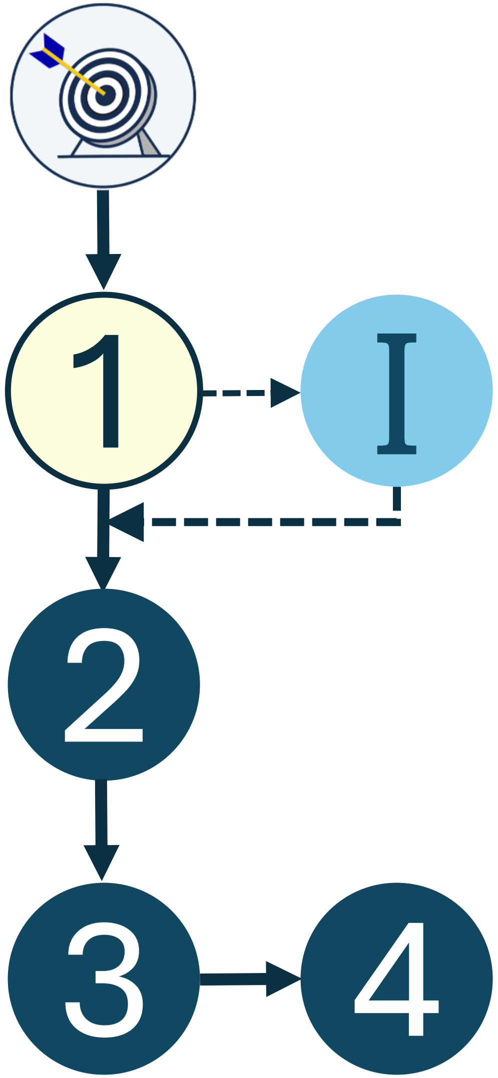


Search perovskites $MOF_2$ & $NaMO_2F$ in ICSD

E.g., $TiOF_2$ available on ICSD



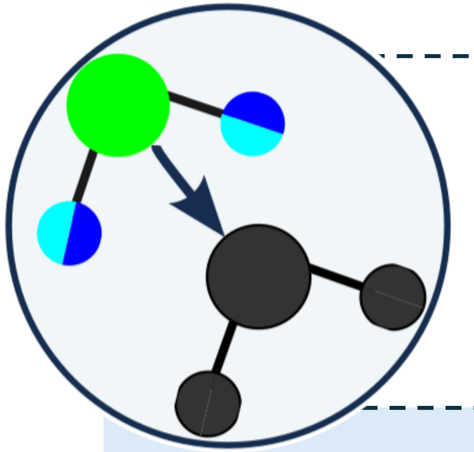
$TiOF_2$ ($Pm\bar{3}m$)




1. Hellenbrandt, M. (2004). *Crystallogr. Rev.*, 10(1), 17-22.

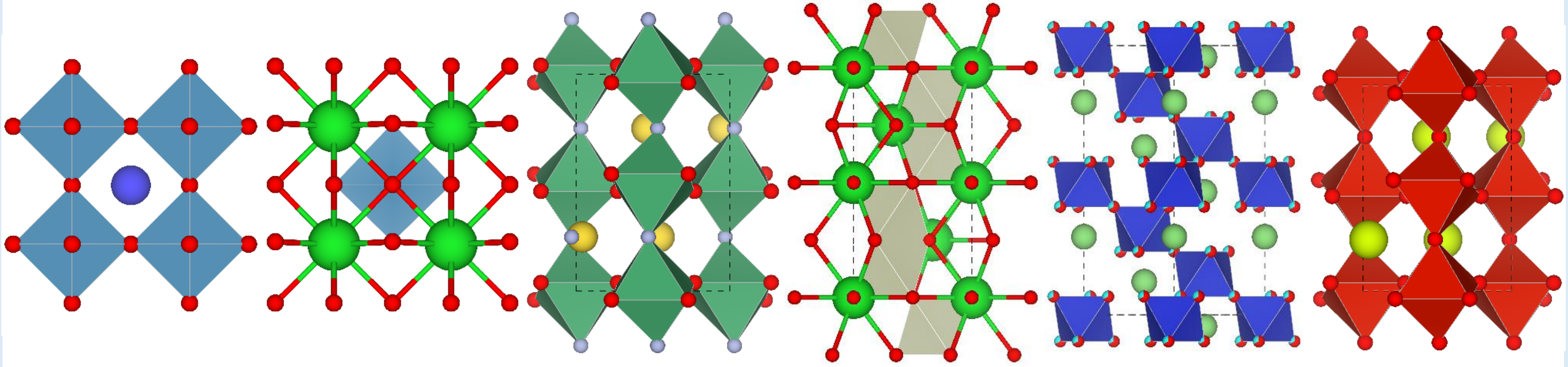
# Groundstate Polymorph: Methodology



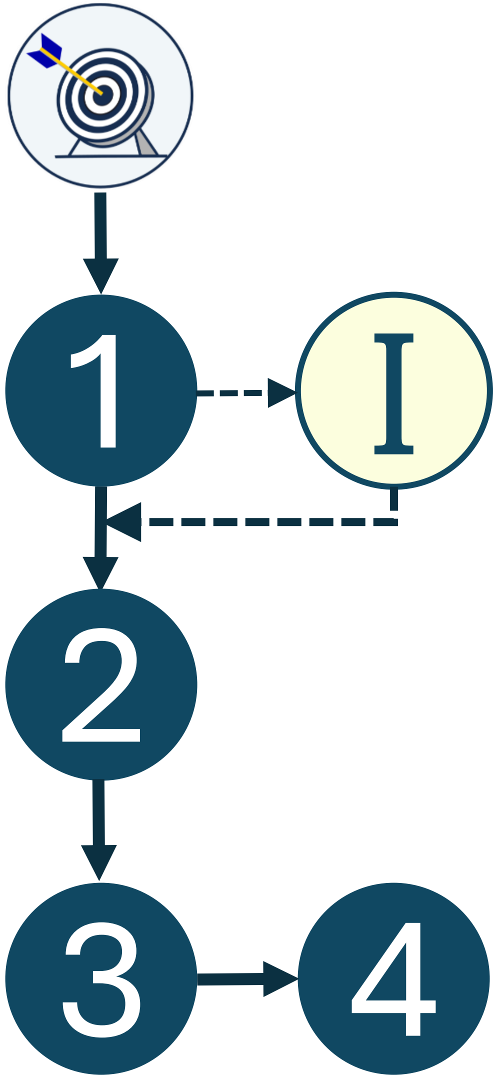


In absence of ICSD structures

Use ideal perovskite structures from ICSD as templates for $MOF_2$ & $NaMO_2F$



| $CaTiO_3$ | $BaTiO_3$ | $NaNbO_2F$ | $BaRhO_3$ | $LiVO_2F$ | $CeVO_3$ |
|---|---|---|---|---|---|
| ($Pm\bar{3}m$) | ($P4mm$) | ($Pbnm$) | ($P63/mmc$) | ($R\bar{3}c$) | ($P2/b$) |

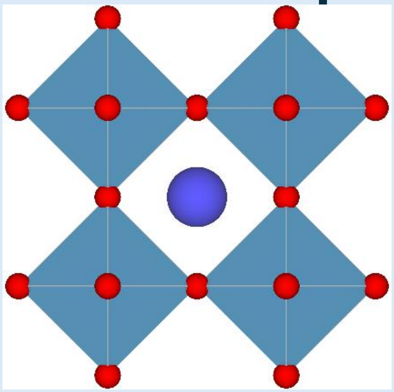



1. Hellenbrandt, M. (2004). *Crystallogr. Rev.*, 10(1), 17-22.

# Groundstate Polymorph: Methodology



Predict $MOF_2$ & $NaMO_2F$ volume by scaling the lattice of template

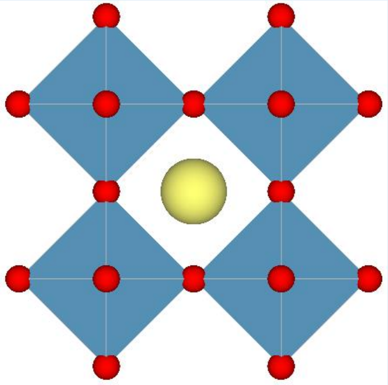


$CaTiO_3$
($Pm\bar{3}m$)

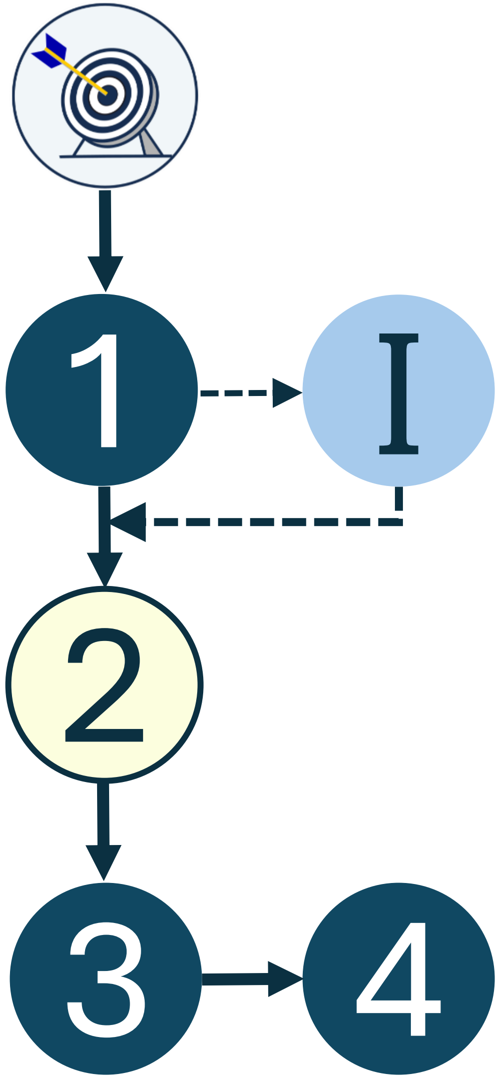
*class* RLSVolumePredictor

$$V^{NaTiO_3} = V^{CaTiO_3}\left(\frac{r^{Ca} + r^{Ti} + \sqrt[3]{3}r^{O}}{r^{Na} + r^{Ti} + \sqrt[3]{3}r^{O}}\right)^3$$

V= volume; r= atomic radius



$NaTiO_3$
($Pm\bar{3}m$)

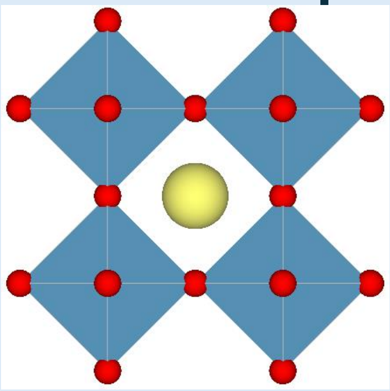



1. Chu, I. H. et al. (2018). *Comput. Mater. Sci.*, 146, 184-192.

# Groundstate Polymorph: Methodology



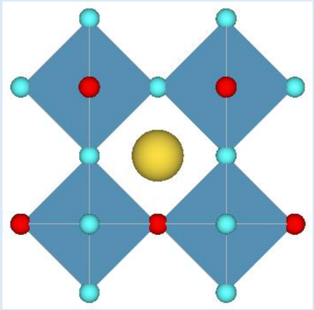
Obtain unique O:F orderings
1:2 in $MOF_2$ ; 2:1 in $NaMO_2F$

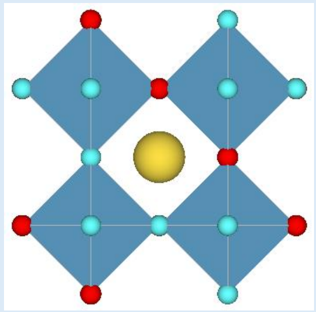


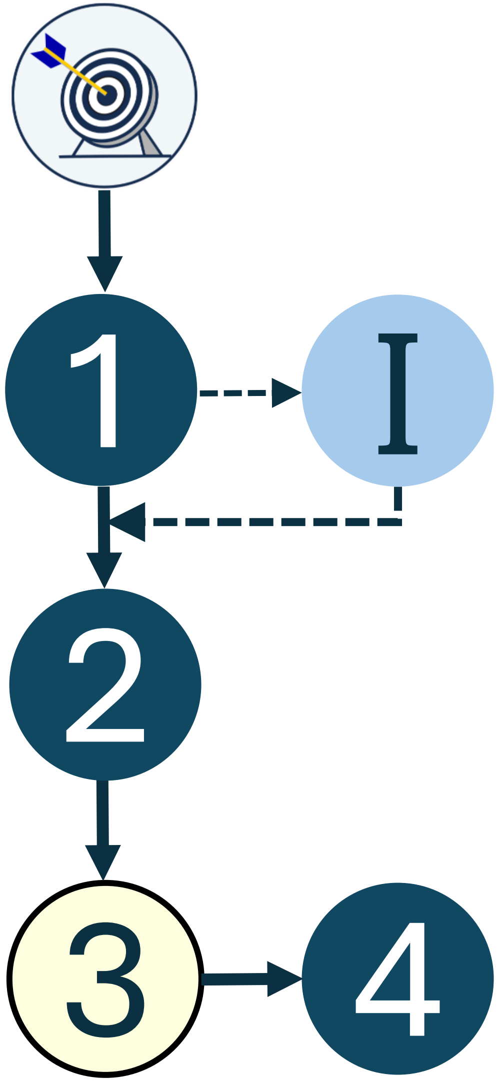
$CaTiO_3$
($Pm\bar{3}m$)

*class* SubstitutionTransformation

*class* OrderDisorderedStructure Transformation








1. Ong, S. P. et al. (2013). *Comput. Mater. Sci.*, 68, 314-319.

# Groundstate Polymorph: Methodology



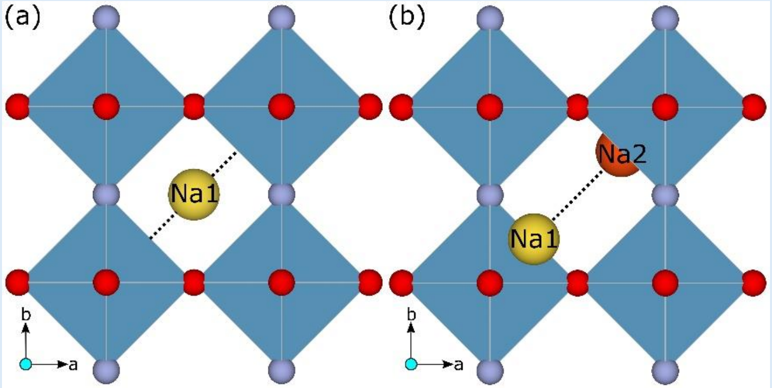
Do DFT SCAN+*U* on select orderings to identify $MOF_2$ & $NaMO_2F$ groundstate polymorph

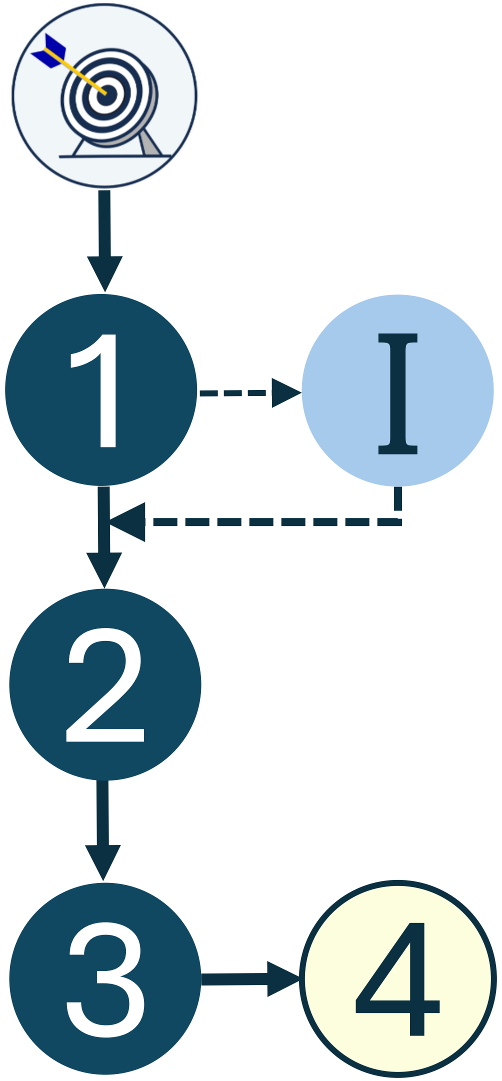
**U* values of M in their metal oxide considered;

Sodiate $MOF_2$ for $NaMOF_2$ & $NaMO_2F$ for $Na_2MO_2F$;
Do DFT SCAN+*U*

For Na-sites in:

- $NaMOF_2$ : A-sites in templates
- $Na_2MO_2F$: Manually calculated (absence of 2 Na sites)

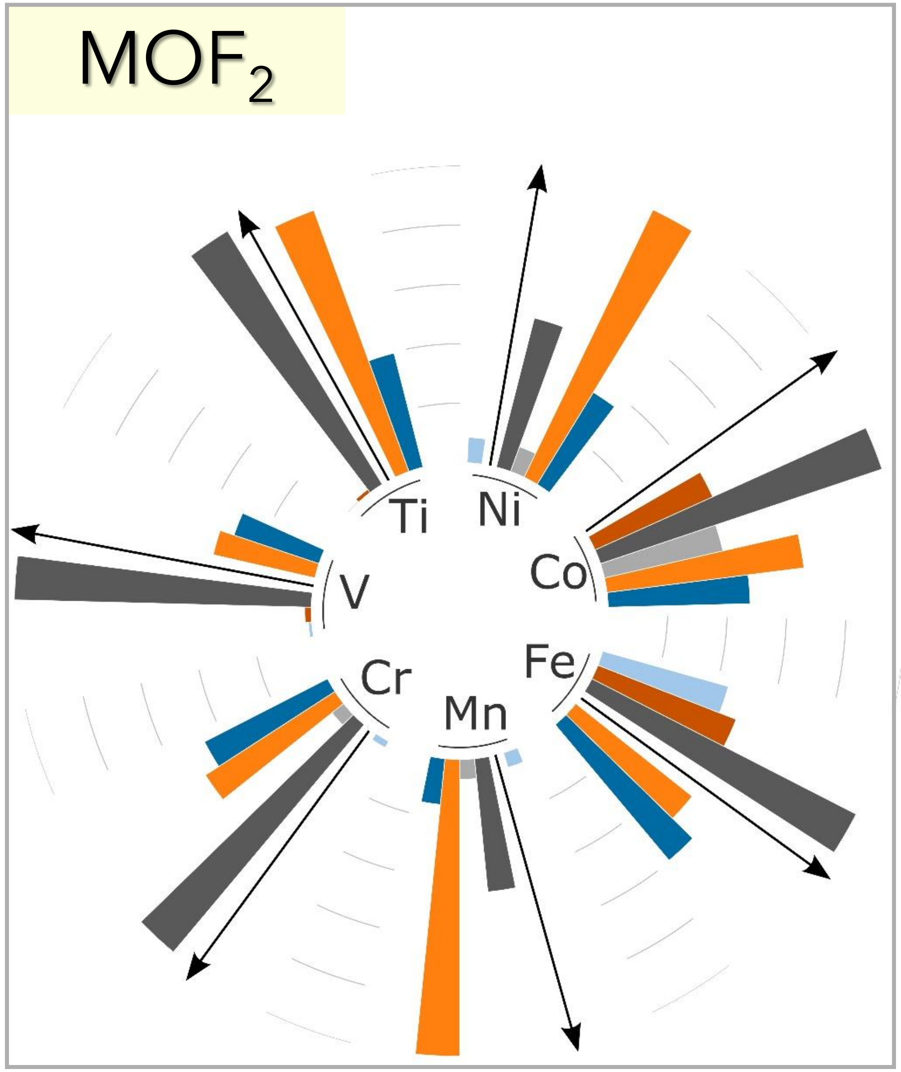


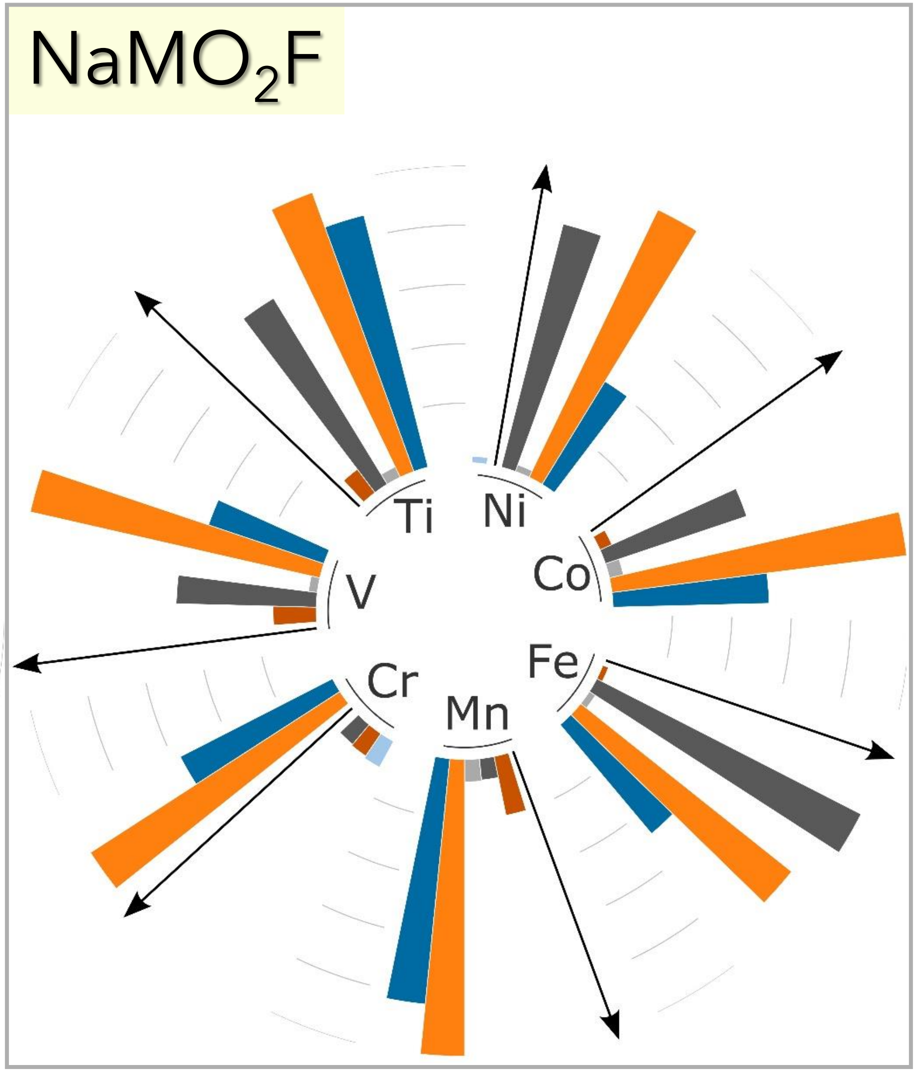




DFT SCAN+*U* calculations done for 1008 structures (i.e., 16×4 + 5 + 3= 72 structures for M in both O and F-rich)

# Groundstate Polymorph: Results






↗ GROUNDSTATE POLYMORPHS

**$MOF_2$**

Ti, V, Fe : *Pbnm*

Cr, Mn, Ni : $R\bar{3}c$

Co : *P2/b*

**$NaMO_2F$**

Ti, V, Mn, Fe, Co: *P2/b*

Cr : *Pbnm*

Ni : $R\bar{3}c$

$$\frac{E_{\text{polymorph}} - E_{\text{groundstate}}}{E_{\text{highest-energy polymorph}} - E_{\text{groundstate}}} \times 100\%$$

($Pm\bar{3}m$) (*P4mm*) (*Pbnm*) (*P63/mmc*) ($R\bar{3}c$) (*P2/b*)

# Workflow



## STRUCTURE IDENTIFICATION

- Groundstate polymorph identification:
  $MOF_2$ (F-rich )
  $NaMO_2F$ (O-rich )

## THERMODYNAMIC ANALYSIS

- Average voltage (V) prediction:
  $MOF_2 \leftrightarrow NaMOF_2$
  $NaMO_2F \leftrightarrow Na_2MO_2F$
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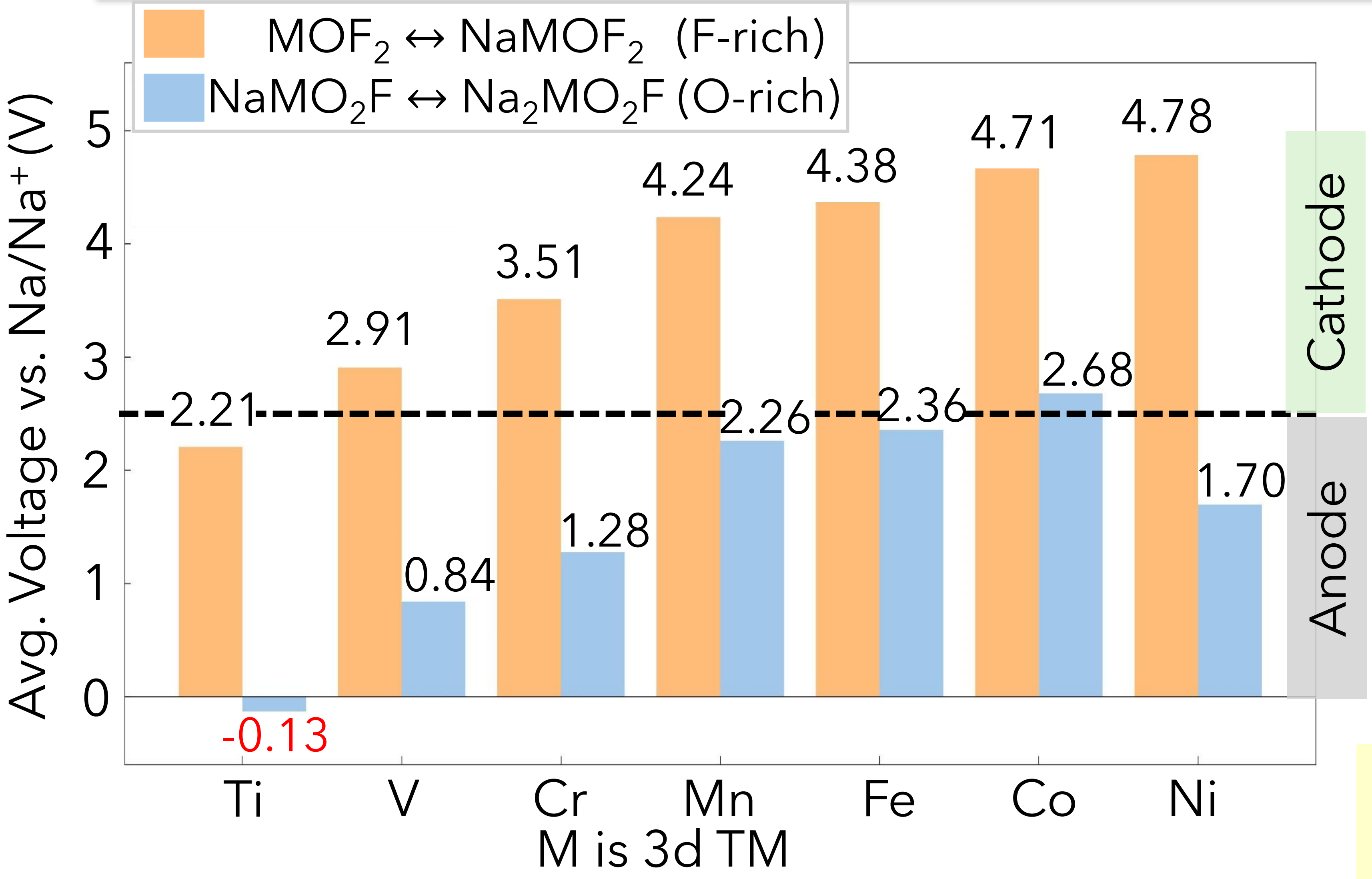
## KINETIC ANALYSIS

- Na-ion migration energy determination

# Average Voltage: Results






- $\langle V \rangle_{\text{F-rich}} > \langle V \rangle_{\text{O-rich}}$
  Inductive effect of $F^-$
- Monotonic increase in $\langle V \rangle$
  Similar Trend as $E^{M^{4+}/M^{3+}}_{reduction}$
- Deviation in $\langle V \rangle$ trend in O-rich Ni system (1.7V); Jahn-Teller distortion in Ni
- $NaTiO_2F \not\Leftrightarrow Na_2TiO_2F$
- $\langle V \rangle$ within electrolyte stability window

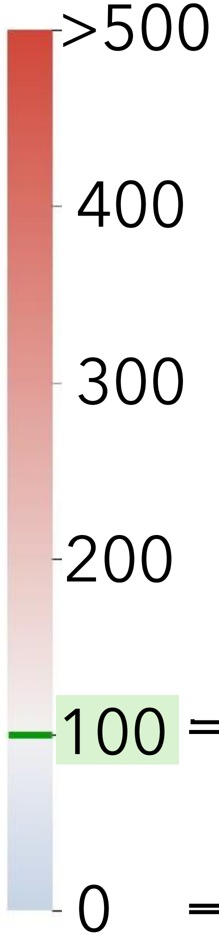
$$\langle V \rangle = \frac{\Delta G}{\Delta x\, F} \approx \frac{E(\mathrm{Na}_{x+\Delta x}\mathrm{MOF}) - [E(\mathrm{Na}_x\mathrm{MOF}) + \Delta x\, E(\mathrm{Na})]}{\Delta x\, F}$$ for $Na_xMOF + \Delta x Na \leftrightarrow Na_{x+\Delta x}MOF$

# Energy above the hull ($E^{hull}$): Results



$E^{hull}$ (meV/atom)

| | Ti | V | Cr | Mn | Fe | Co | Ni |
|---|---|---|---|---|---|---|---|
| $Na_2MO_2F$ | 187 | 247 | 333 | 237 | 289 | 336 | 638 |
| $NaMO_2F$ | 53 | 154 | 108 | 186 | 196 | 228 | 279 |
| $NaMOF_2$ | 46 | 82 | 171 | 94 | 130 | 120 | 291 |
| $MOF_2$ | 0 | 0 | 77 | 175 | 145 | 380 | 516 |




Unstable

- $\boxed{\begin{array}{c}NaTiO_2F\\ \text{Metastable}\end{array}}$ $\not\Leftrightarrow$ $Na_2TiO_2F$ (-0.13 V) → not considered

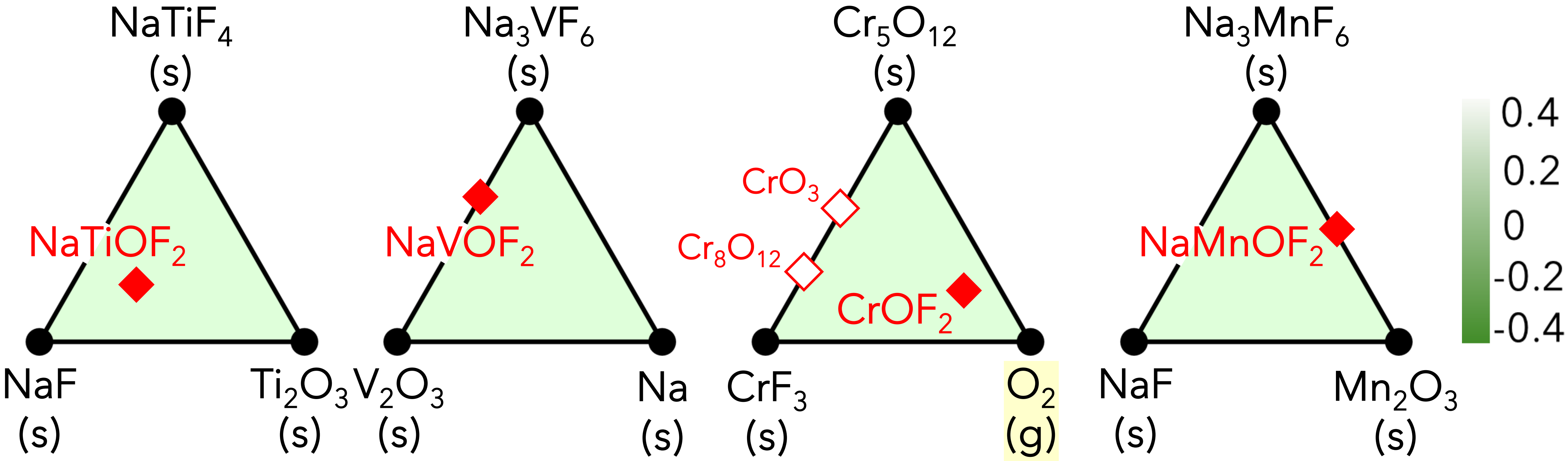
- $NaTiOF_2$, $NaVOF_2$, $CrOF_2$, $NaMnOF_2$: Metastable
- $TiOF_2$ & $VOF_2$: Stable

Metastable, Stable → Synthesizable

$E^{hull}$ ≈ Extent of Instability ∝ Difficulty in Synthesis

# Convex hull (pseudo-ternary projection)






$$\text{M-OF (s)} \xrightarrow{\text{Slow Reaction}} \text{M-O (s)} + \text{M-F (s)}$$

$NaTiOF_2$, $NaVOF_2$ & $NaMnOF_2$ unlikely to decompose during electrochemical cycle

$O_2$ (g) evolution during cycle maybe difficult to prevent

◆ Metastable compositions ◇ Other unstable compositions (s) : solids

● Stable compositions (g): gas

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  $NaMO_2F \leftrightarrow Na_2MO_2F$
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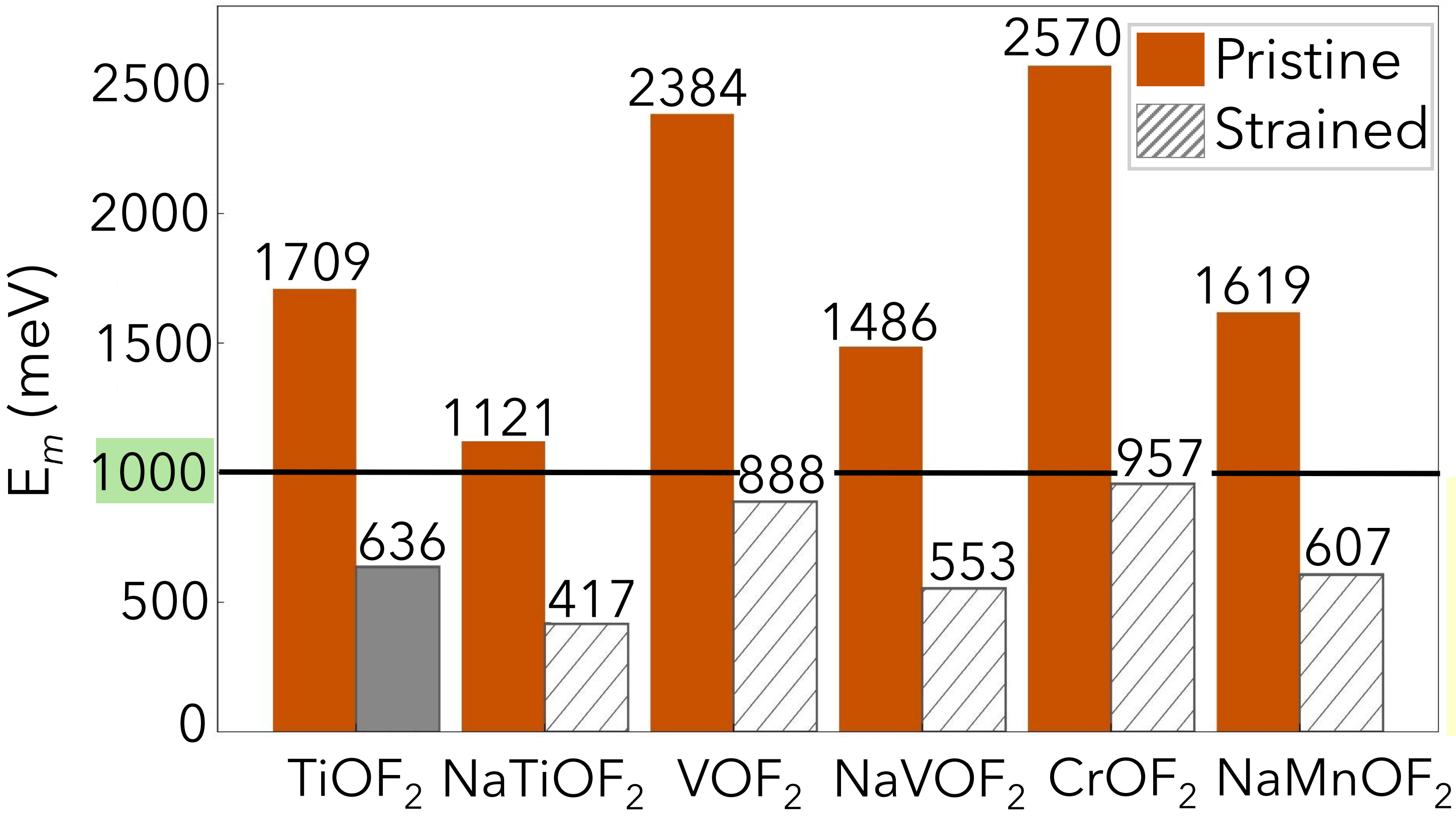
## KINETIC ANALYSIS

- Na-ion migration energy determination

# Migration barriers to $Na^+$ mobility: Results





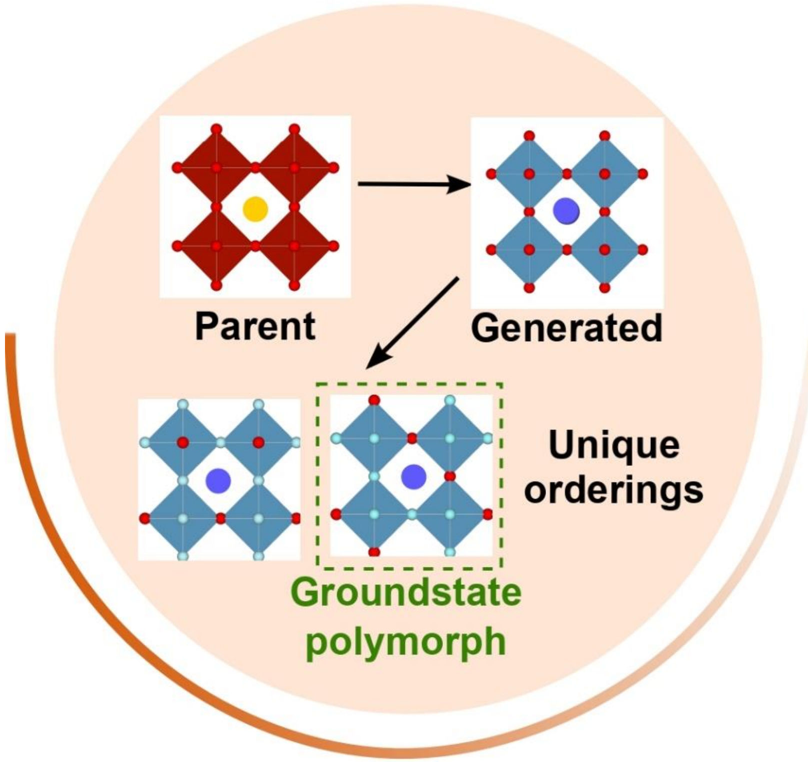

- High migration energies

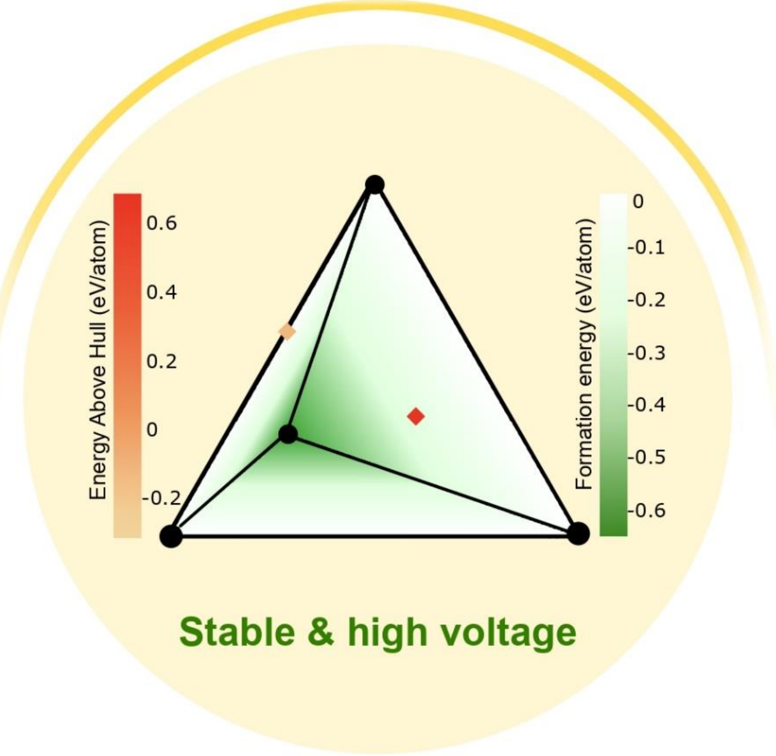
- 5% homogeneous tensile strain introduced in $TiOF_2$; 62.8% barrier reduction

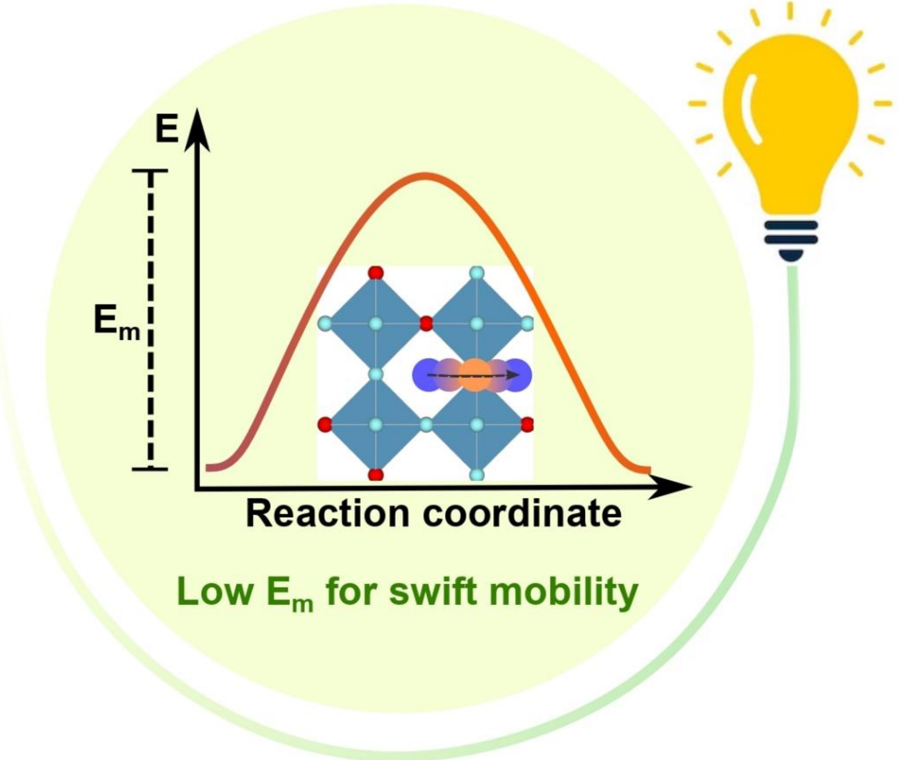
$E_m$ estimation with GGA-based DFT-Nudged Elastic Band method (1000 meV threshold)

# Conclusion






Structure Generation & Groundstate Polymoph Identification

Stable
$TiOF_2$ & $VOF_2$
Metastable:
$NaTiOF_2$, $NaVOF_2$, $CrOF_2$, $NaMnOF_2$

Potential Na cathodes:
Strained
$TiOF_2$, $VOF_2$, $CrOF_2$, $NaTiOF_2$, $NaVOF_2$, $NaMnOF_2$

Solid State Ionics 2024

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