



# Materials discovery for energy storage using computations and machine learning

Sai Gautam Gopalakrishnan

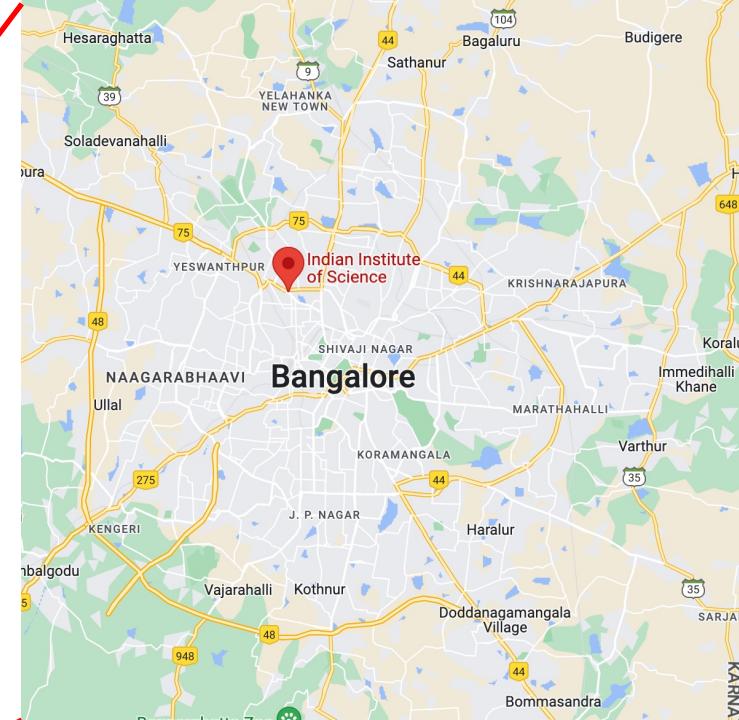
Simulations And Informatics of MATerials (SAI-MAT) group

Materials Engineering, Indian Institute of Science

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Various locations in Germany  
May, 2023

# Where are we?



# Where are we?

- IISc is 114 years old (as of 27 May)
- Six divisions
  - Biological sciences
  - Chemical sciences
  - Electrical, electronics, and computer sciences
  - Physical and mathematical sciences
  - **Mechanical sciences**
  - Interdisciplinary sciences
  - ~500 faculty, ~4000 graduate students
- Department of **Materials Engineering** (formerly Metallurgy): established 1945
  - 26 faculty (including permanent scientists)
  - 4 Honorary faculty
  - 4 Visiting/Adjunct faculty
  - 3 Inspire faculty fellow
  - ~140 graduate students



# Acknowledgments



Group picture in Dec 2022



Dr. Piero Canepa



**IGSTC**  
INDO-GERMAN SCIENCE AND TECHNOLOGY CENTRE

NSCC (Singapore)

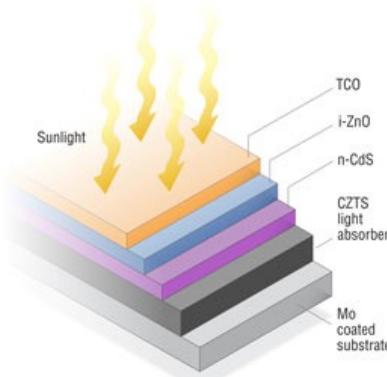


Dereje Vijay  
SERC (IISc)

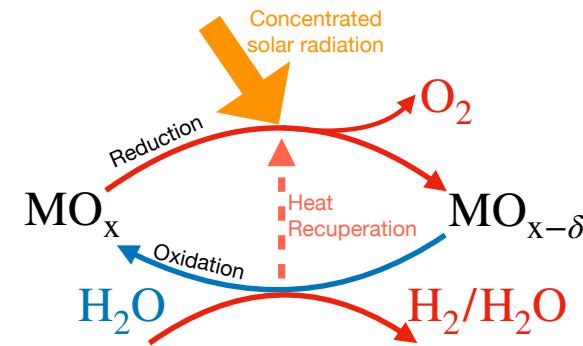
# We work broadly on energy materials



Design better electrodes and solid electrolytes



Develop better light-absorbing semiconductors



Identify better thermochemical  $\text{H}_2\text{O}$ -splitters

## Identify novel materials for applications

- Use high-throughput screening +/- machine learning (**ML**) to generate key performance-determining descriptors
- Collaborate with experimental groups for validation of theoretical predictions

## Understand underlying materials phenomena better

- In-depth studies focused on thermodynamic, kinetic or electronic behavior of a given (candidate) material
- Predict "stable" configurations, mobility bottlenecks, suppress/enhance defect formation, etc.

## Make theory better

- Benchmark existing theoretical models against experimental data to identify best ones
- Develop better models for simulating complex phenomena

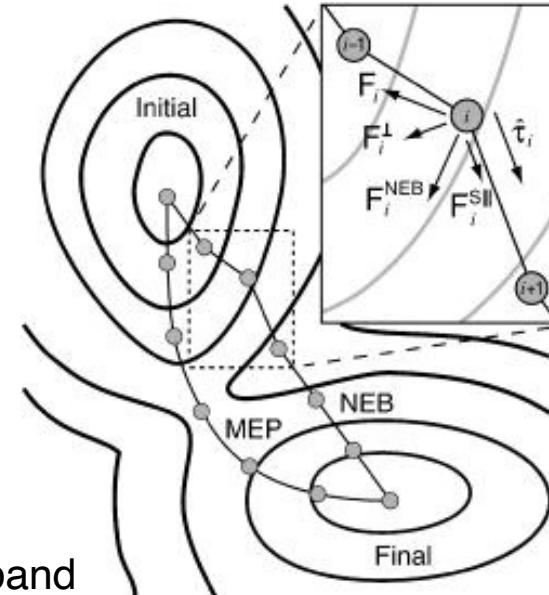
# We do theory, computations, & ML



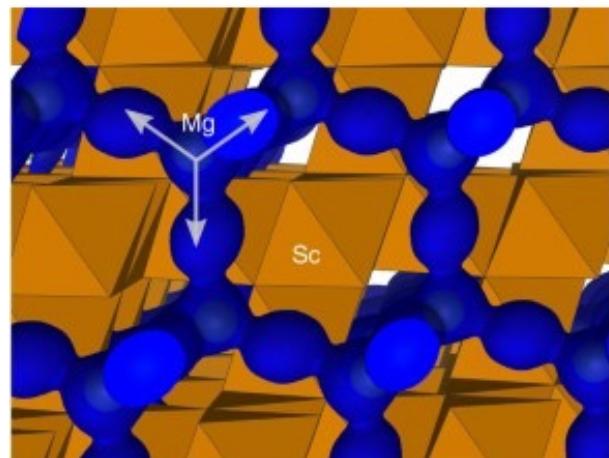
Density functional theory  
**(DFT)**: (Approximately) predict material properties

- Structural (lattice parameters)
- Thermodynamic (voltages, stabilities, phase diagrams)
- Electronic (band gaps)
- Magnetic (oxidation states, magnetic moments)
- High-throughput “screening”

Nudged elastic band  
**(NEB)**: migration barriers



ML: regressions and interatomic potentials



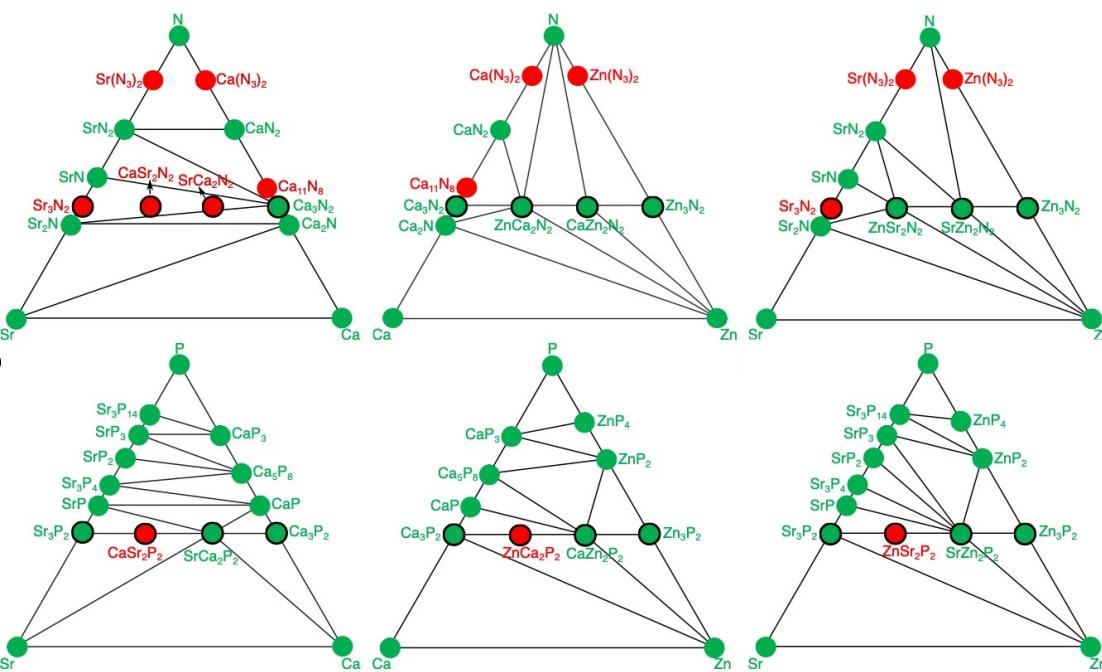
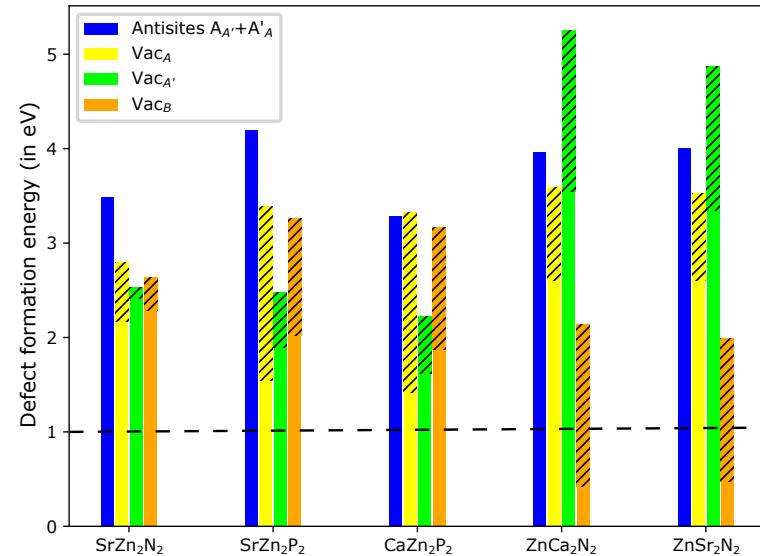
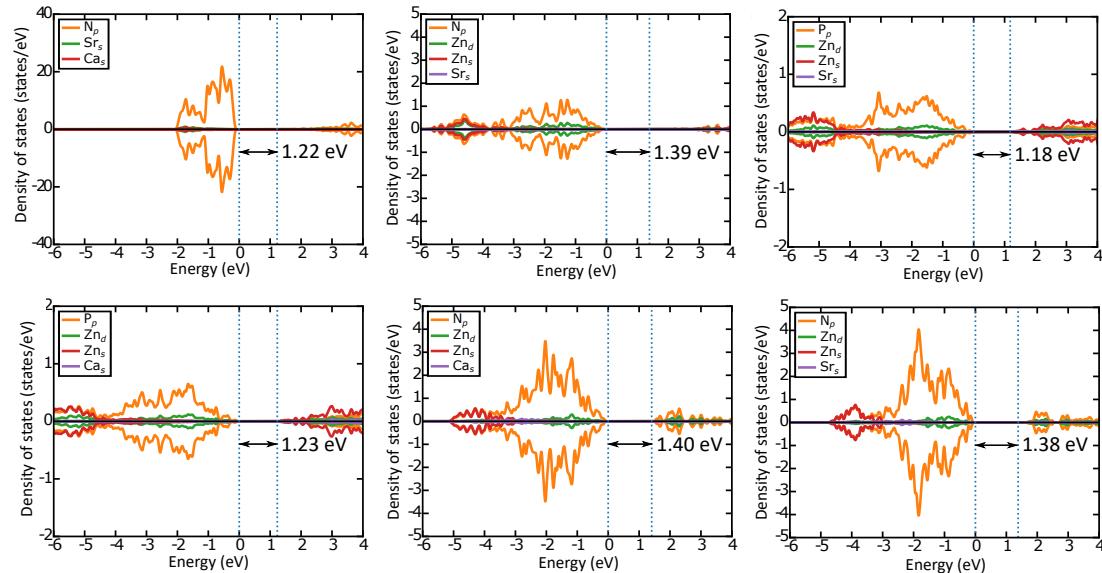
Ab initio and classical (ML) molecular dynamics: kinetic properties





# Snapshots of our research

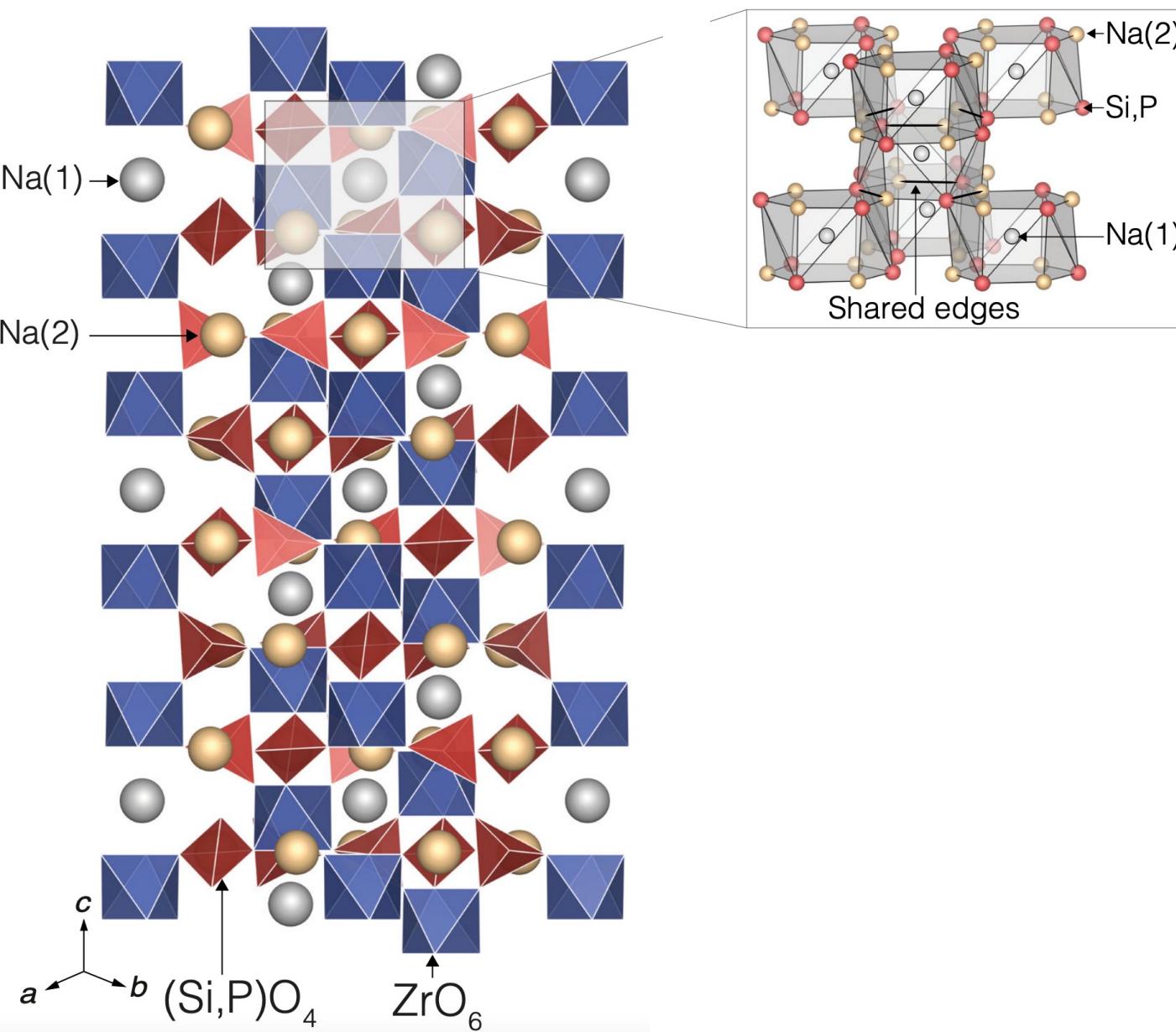
# Phictides as possible photovoltaics



Band gap estimates  
 + 0 K thermodynamic stability screening  
 + resistance to point defects  
 = candidate beyond-Si photovoltaics

SrZn<sub>2</sub>N<sub>2</sub>, SrZn<sub>2</sub>P<sub>2</sub>, and CaZn<sub>2</sub>P<sub>2</sub>: predicted candidates

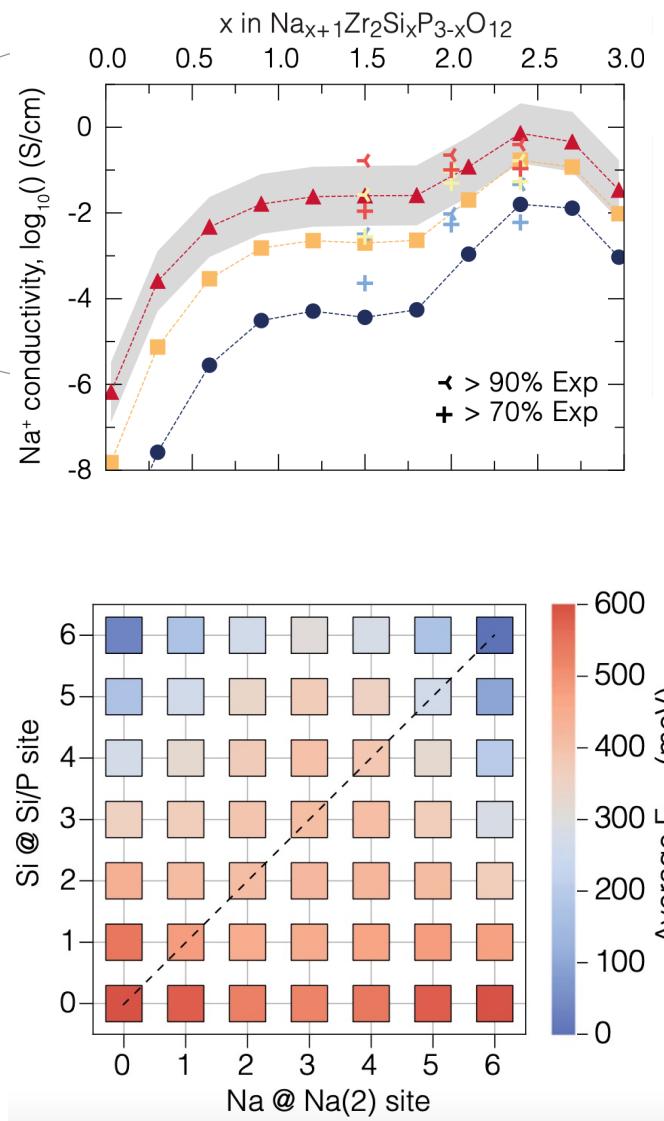
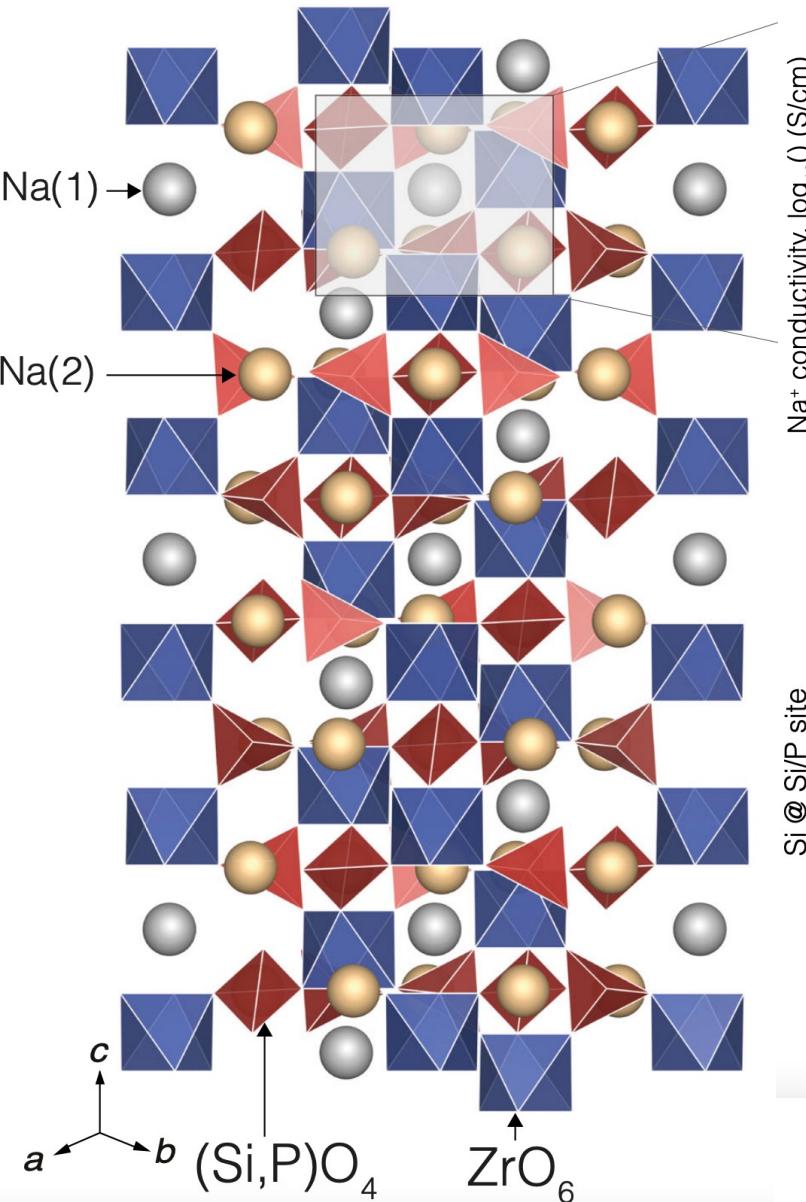
# Quantify ionic mobility in solid electrolytes



Sodium superionic conductor (NaSICON): known Na solid ionic conductor

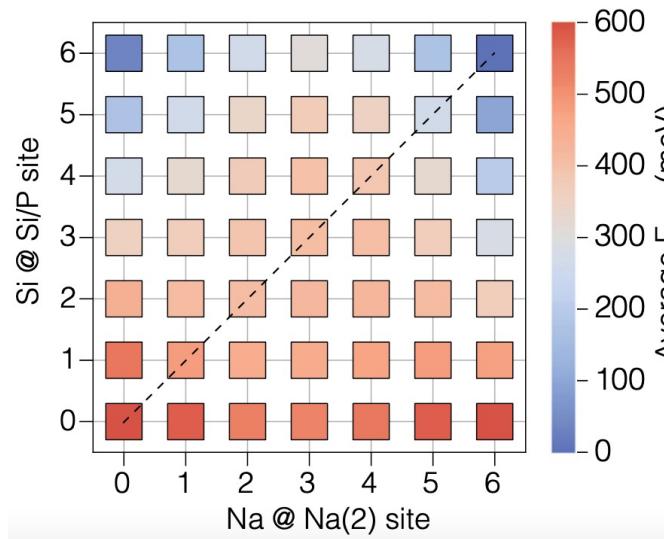
Conductivity not known as a function of composition

# Quantify ionic mobility in solid electrolytes



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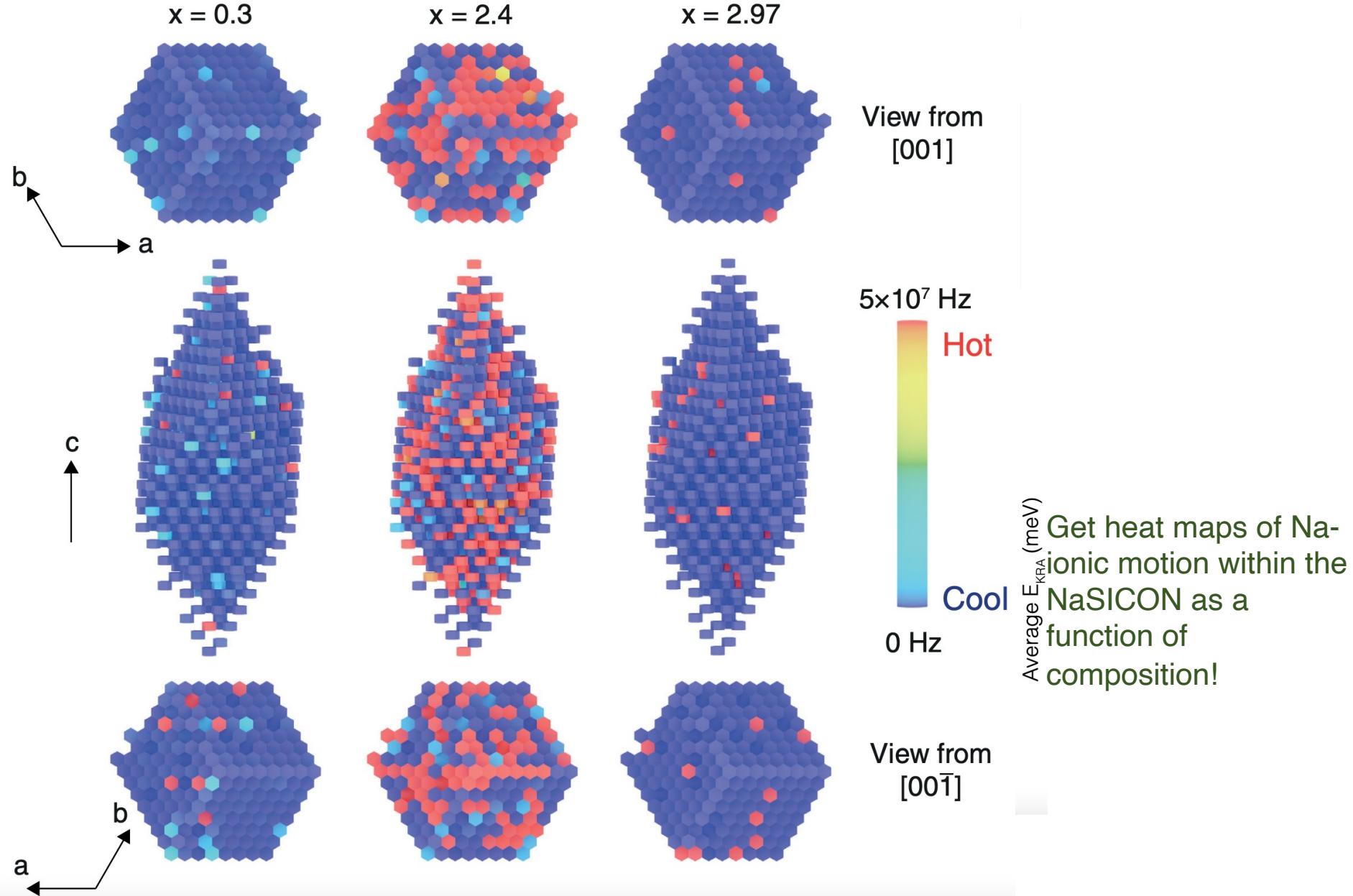
Conductivity not known as a function of composition



Perform DFT+NEB at different compositions and subsequently use kinetic Monte Carlo simulations

Good agreement with experimental measurements

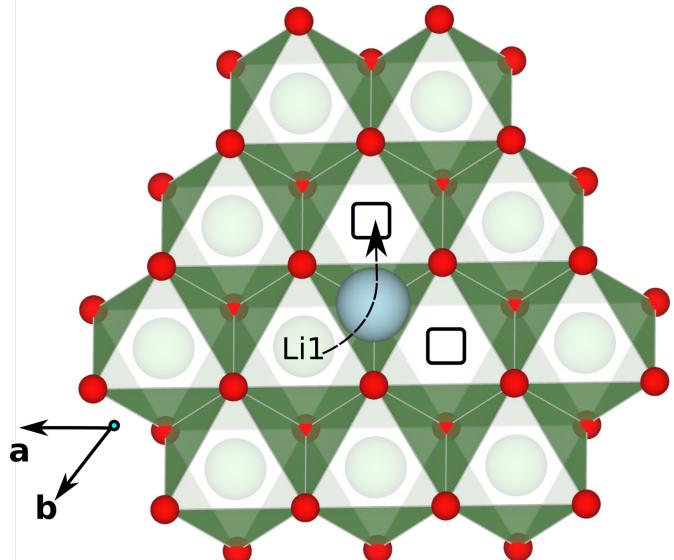
# Quantify ionic mobility in solid electrolytes



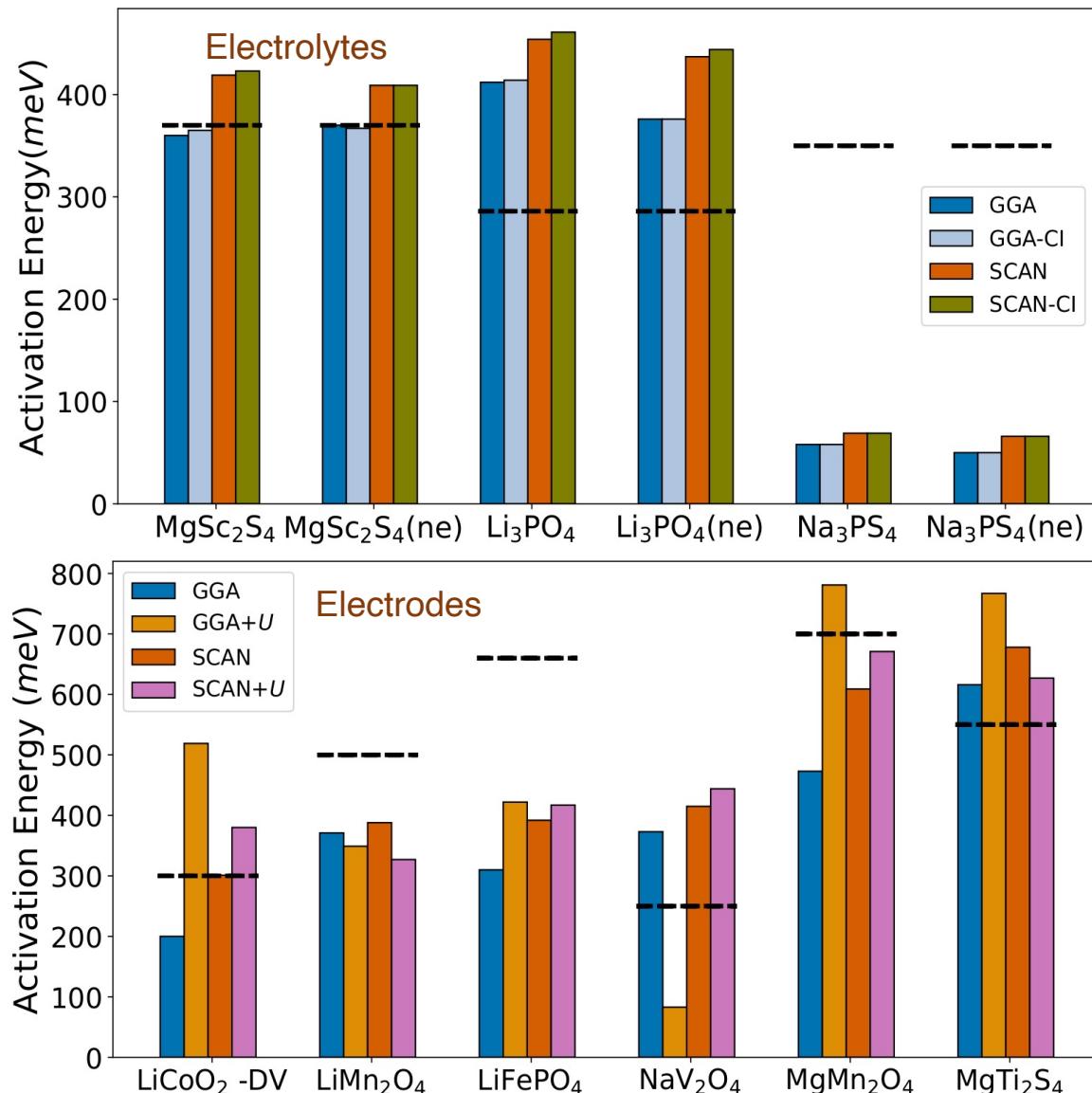
# Which "functional" predicts migration barriers well?

Migration barriers: crucial for power performance

Which exchange-correlation functional is best suited for migration barrier predictions in battery materials?



# Which "functional" predicts migration barriers well?



Migration barriers: crucial for power performance

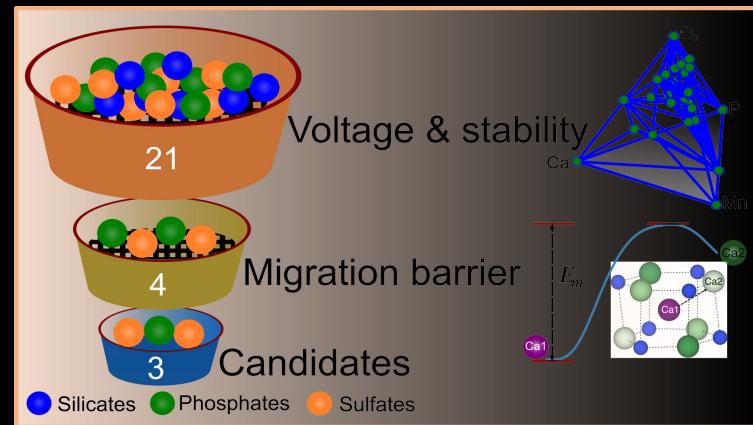
Which exchange-correlation functional is best suited for migration barrier predictions in battery materials?

Strongly constrained and appropriately normed (SCAN) more accurate on average

- Describes right electronic structure
- Computationally expensive and difficult to converge
- Generalized gradient approximation (GGA): not bad either



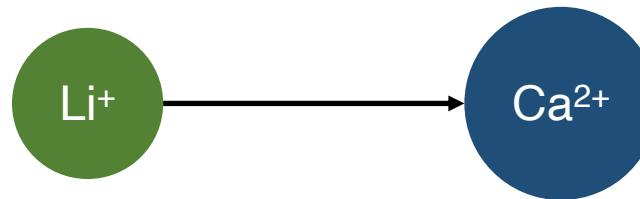
## Deep dives Ca-cathode screening



# Why beyond-Li-ion batteries?

Next generation of electric devices will benefit from higher energy density storage systems

- Multi-valent == More electrons ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ , etc.)
- Large volumetric energy density == Smaller batteries
- Li-ion technology approaching fundamental limits
  - Safety, supply-chain constraints; limits on achievable energy densities

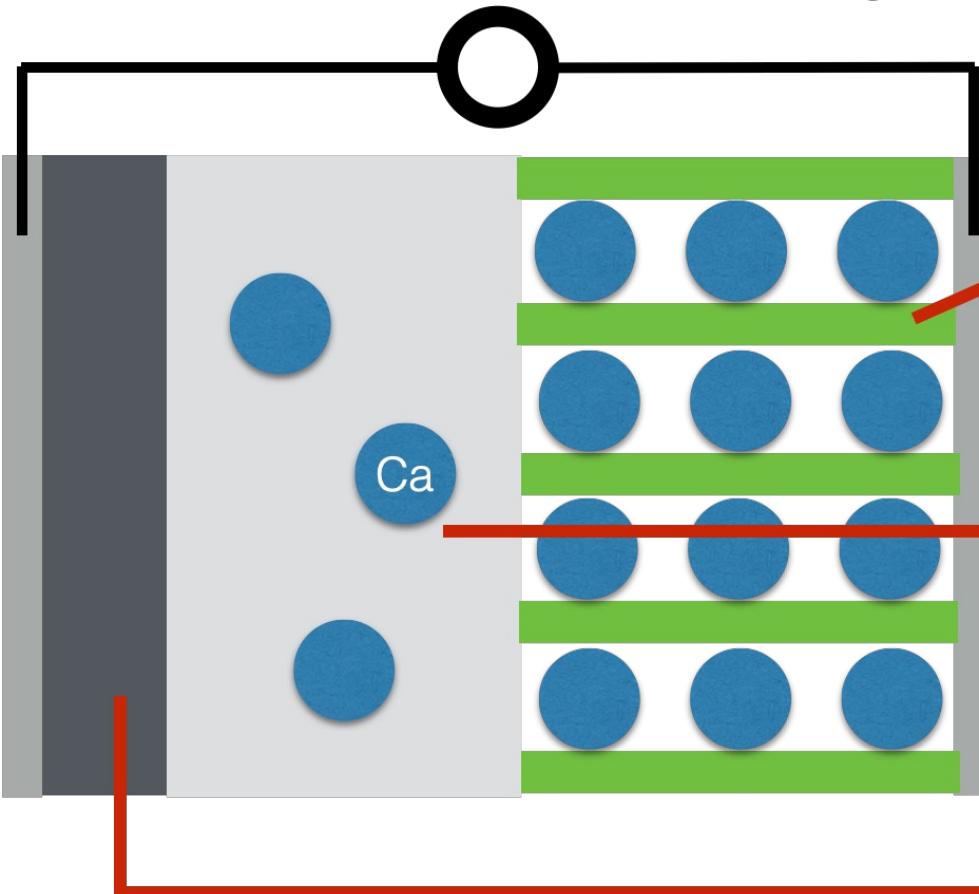


Why Ca?

- Superior volumetric capacity for Ca metal ( $\sim 2077 \text{ Ah/l}$ ) than Li in graphite ( $\sim 800 \text{ Ah/l}$ )
- Ca is safer than Li, less constrained geopolitically
- Similar standard reduction potential for Ca (-2.87 V vs. SHE) vs. Li (-3.04 V)



# Cathode design challenge



## Intercalation Cathode:

High Voltage  
High Capacity  
High Mobility  
Good cycle life

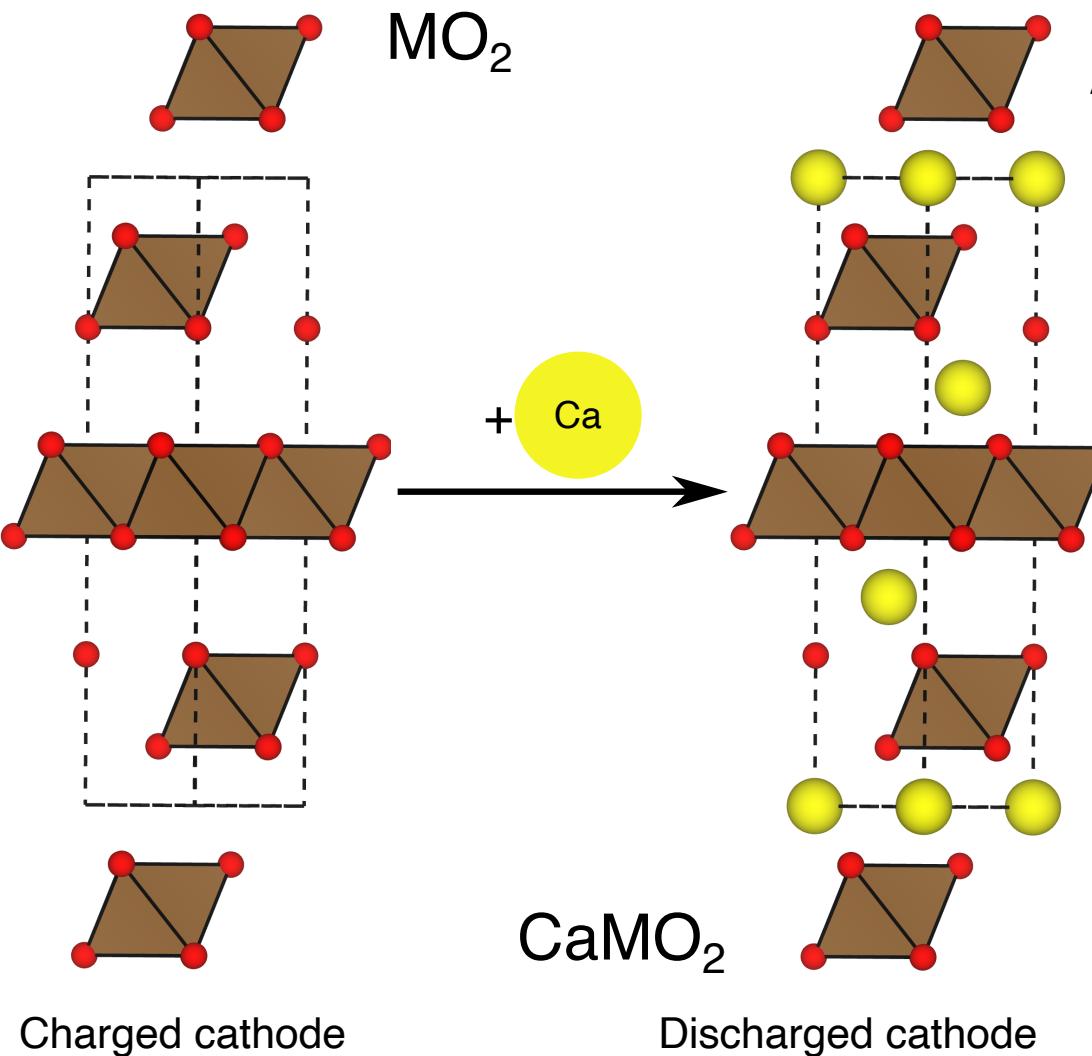
## Electrolyte:

Stable electrolyte (at both electrodes) with good conductivity

## Metal Anode:

Understand plating and stripping in organic electrolytes

# Voltage, capacity, and rate: intercalation batteries



$$\Delta G_{\text{intercalation}} = G_{\text{CaMO}_2} - G_{\text{MO}_2} - G_{\text{Ca}}$$

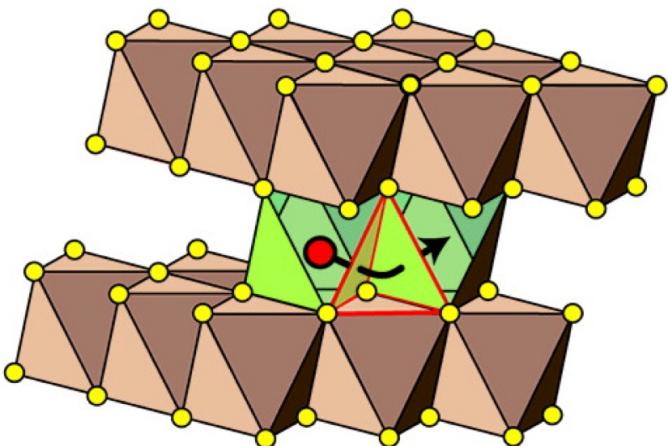
Nernst Equation

$$V = - \frac{\Delta G_{\text{intercalation}}}{nF}$$

(Do similar process for anode, take V difference!)

1 Ca moved = 2 electrons stored

$$\text{Capacity} \propto \frac{2 \times \# \text{ Ca moved}}{\# \text{ 'Framework' atoms}}$$

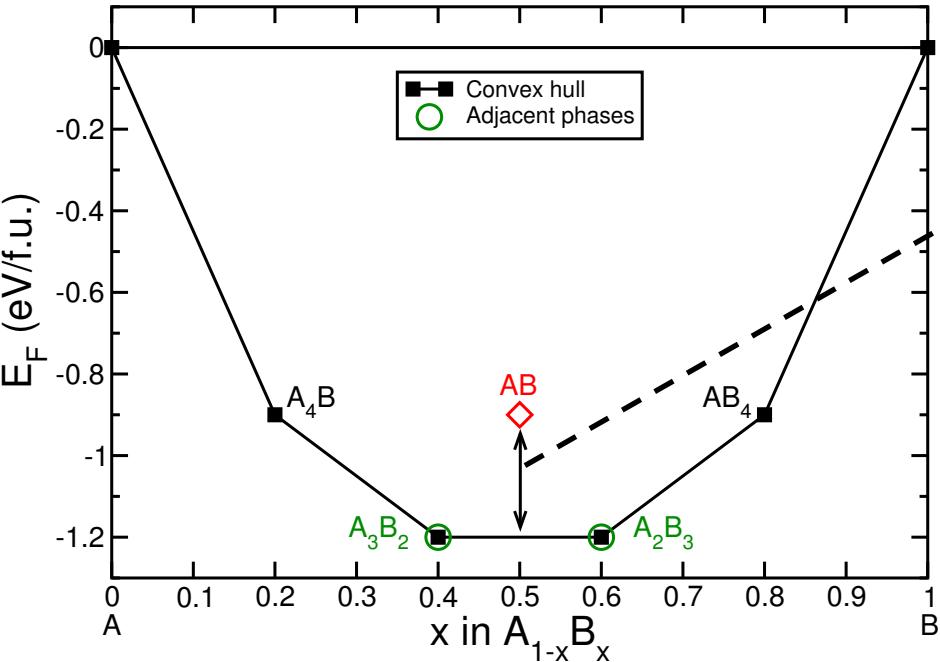


Rate: how fast can Ca move (or diffuse) within electrode?

$$\text{Rate} \propto D = D_o \exp\left(-\frac{E_m}{k_B T}\right)$$

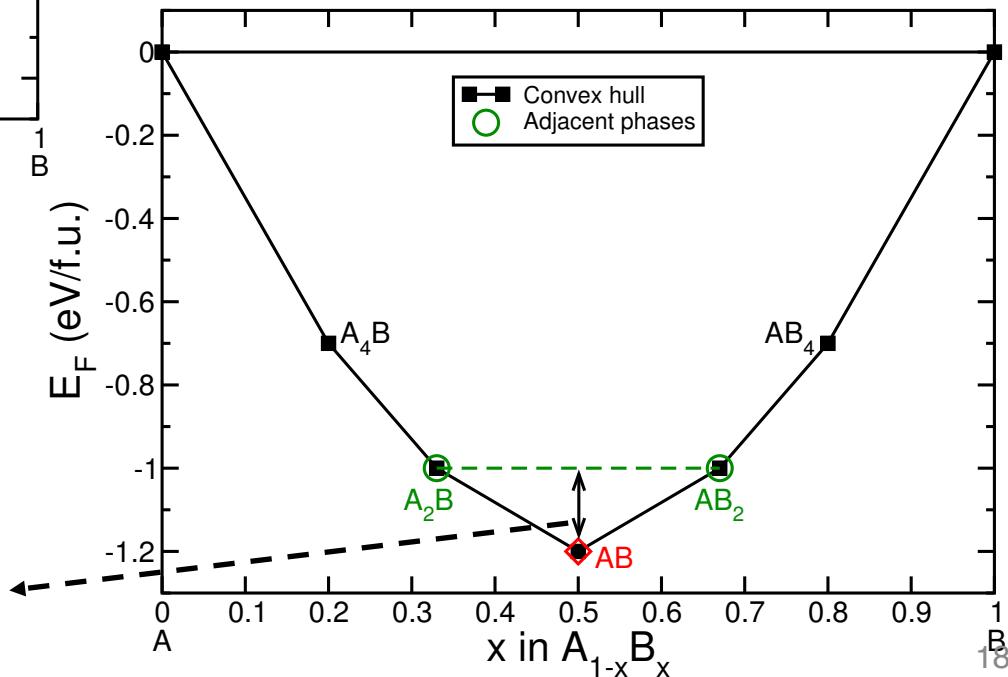
# 0 K thermodynamics: convex hull

$E^{hull}$ : measure of **stability** of a given structure+composition combination (at 0 K)



Positive  $E^{hull}$ : metastable (< 25-50 meV/atom) or unstable (>50 meV/atom)

- Largest energy release via decomposition of AB

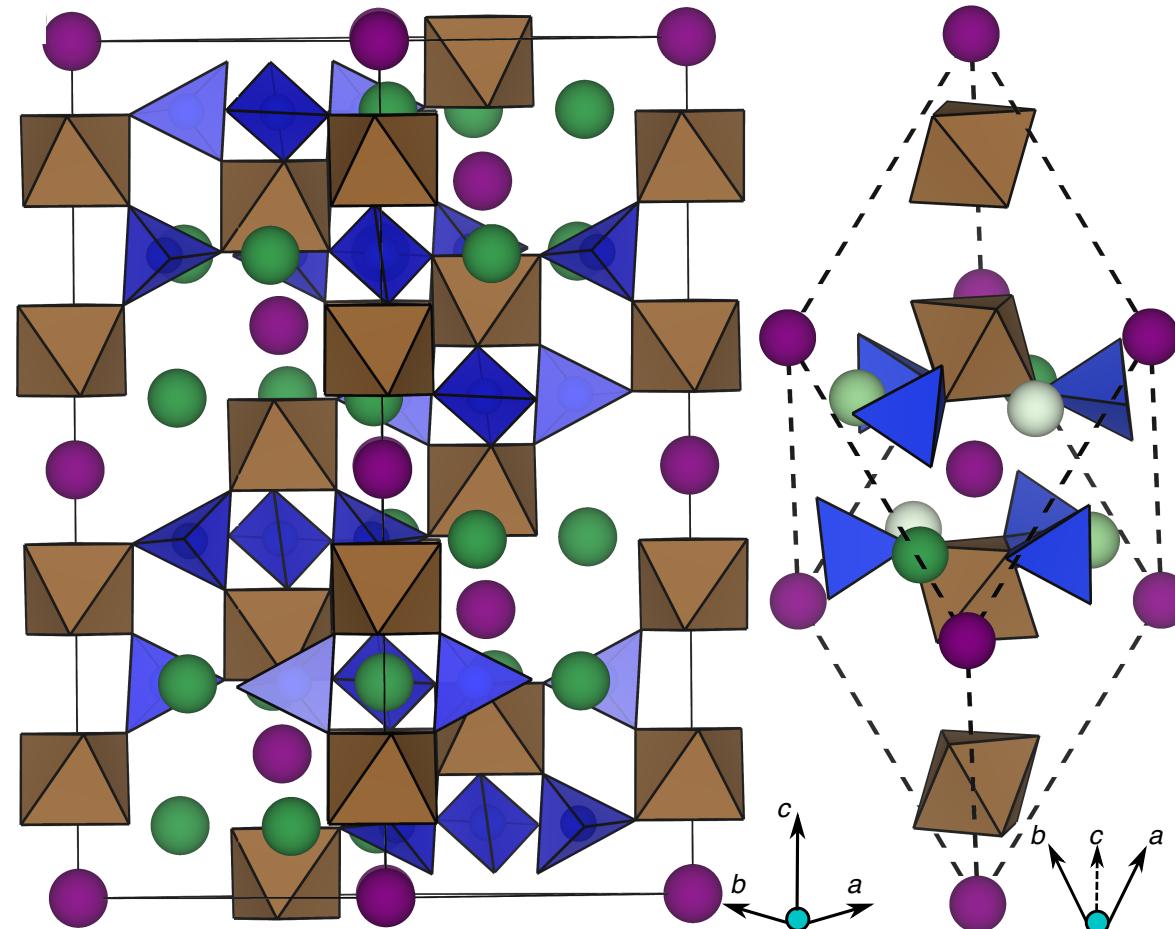


Negative (or zero)  $E^{hull}$ : stable

- Lowest energy release via formation of AB

# NaSICONs: Polyanionic hosts with robust structural stability

- Na superionic conductors: NaSICONs, polyanionic hosts
  - Original composition:  $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ ; General composition:  $\text{Na}_x\text{M}_2(\text{ZO}_4)_3$
- Polyanionic hosts: better structural stability with Na removal
  - Transition metal polyhedra usually connected via  $\text{PO}_4$ ,  $\text{SiO}_4$ , or  $\text{SO}_4$  groups



Theoretically, 4 moles of Na exchange possible in  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$

- $x = 0$  to 4
- 2 Na sites (Na1 and Na2)

Structure is rhombohedral or monoclinic depending on Na concentration

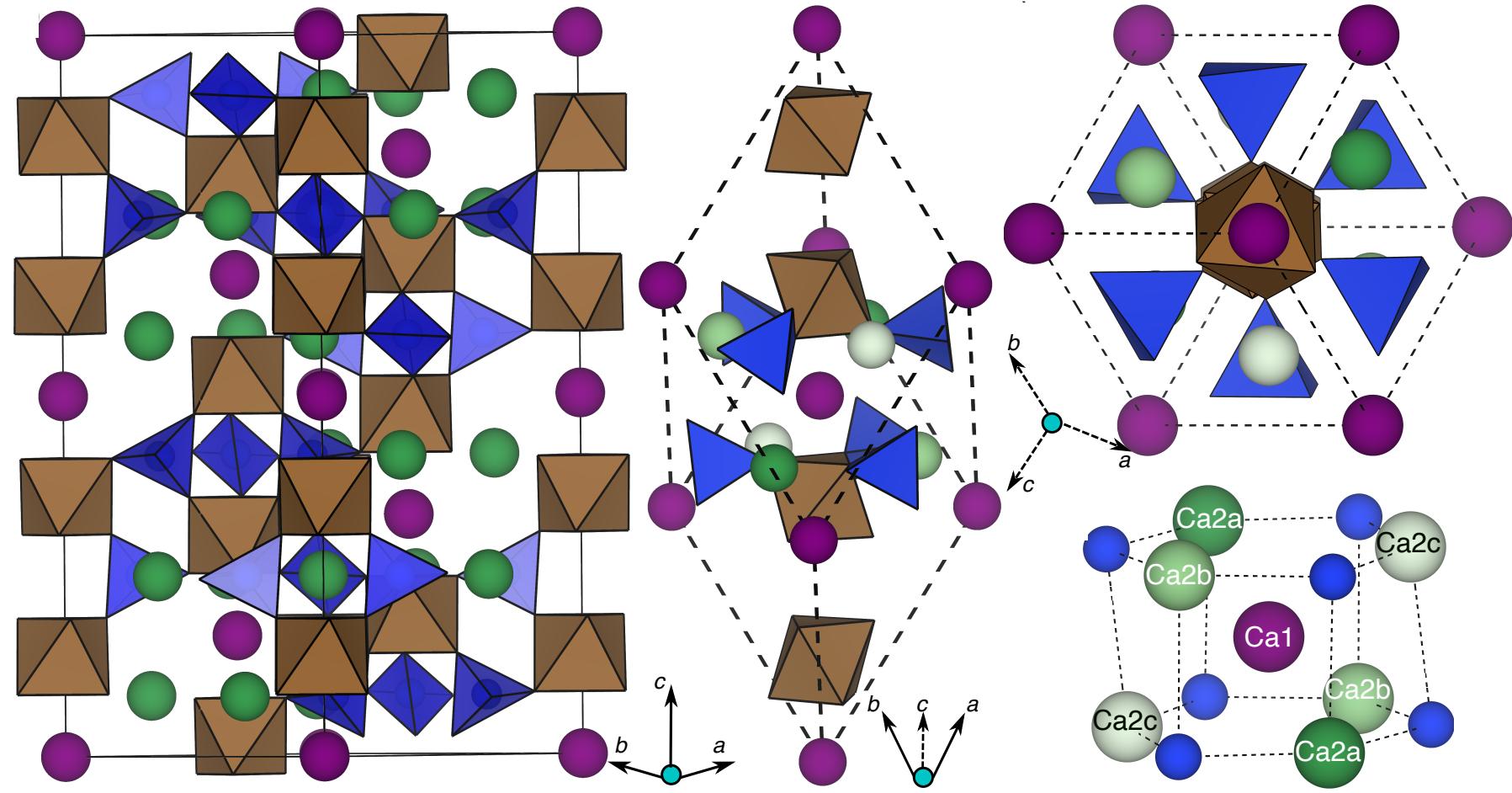
Conventional cell: 6  $\text{M}_2(\text{ZO}_4)_3$  formula units

Primitive cell: 2 formula units

# NaSICONs: Polyanionic hosts with robust structural stability

$\text{Na}^+$  (1.02 Å) and  $\text{Ca}^{2+}$  (1.0 Å) have similar ionic radii: can NaSICONs act as Ca-intercalation hosts?

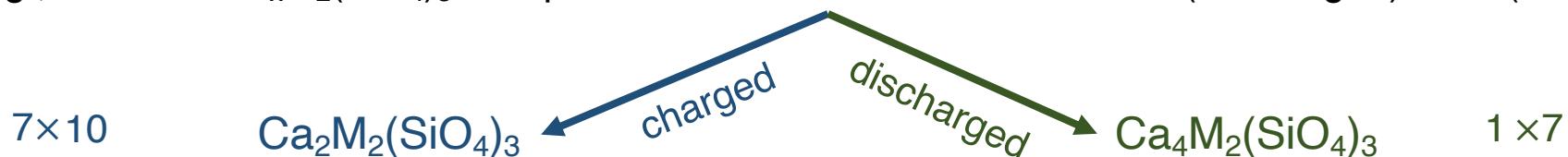
Preliminary experimental evidence is positive [Kim et al., *ACS Energy Lett.* **2020**, 5, 3203–3211]



# Charge neutrality constraints

Depending on polyanionic species: Ca concentration is constrained by possible oxidation states of the 3d transition metal (M), i.e., charge neutrality of the structure

E.g., consider  $\text{Ca}_x\text{M}_2(\text{SiO}_4)_3$  with possible M oxidation states to be +2 (discharged)  $\leftrightarrow$  +4 (charged)



Similarly, for  $\text{Ca}_x\text{M}_2(\text{PO}_4)_3$  and  $\text{Ca}_x\text{M}_2(\text{SO}_4)_3$ ,

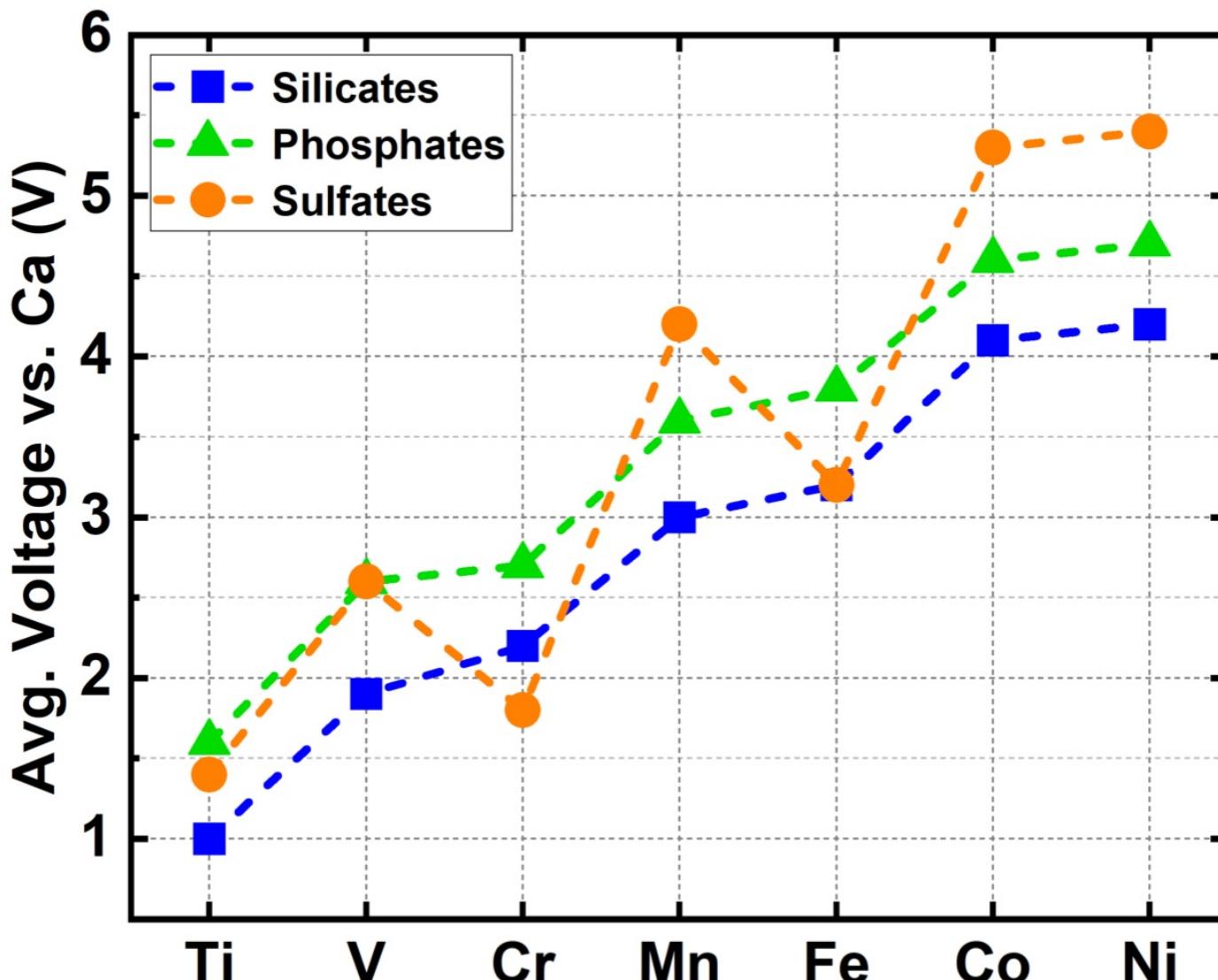


Enumerate Ca-vacancy configurations in primitive NaSiCON with pymatgen<sup>1</sup> for a given M

## Repeat process for M = Ti, V, Cr, Mn, Fe, Co, and Ni (168 structures)

Perform SCAN+ $U$  calculations to estimate ground state configurations, average voltage and stability

# Average voltages: Co and Ni are highest across polyanionic groups



Monotonic increase in average voltage across  $\text{Ti} \rightarrow \text{Ni}$  for  $\text{PO}_4$  and  $\text{SiO}_4$

- Consistent with standard reduction potentials

$\text{PO}_4$  voltages >  $\text{SiO}_4$

- Inductive effect
- Also responsible for  $\text{SO}_4 > \text{PO}_4$  in Mn, Co and Ni

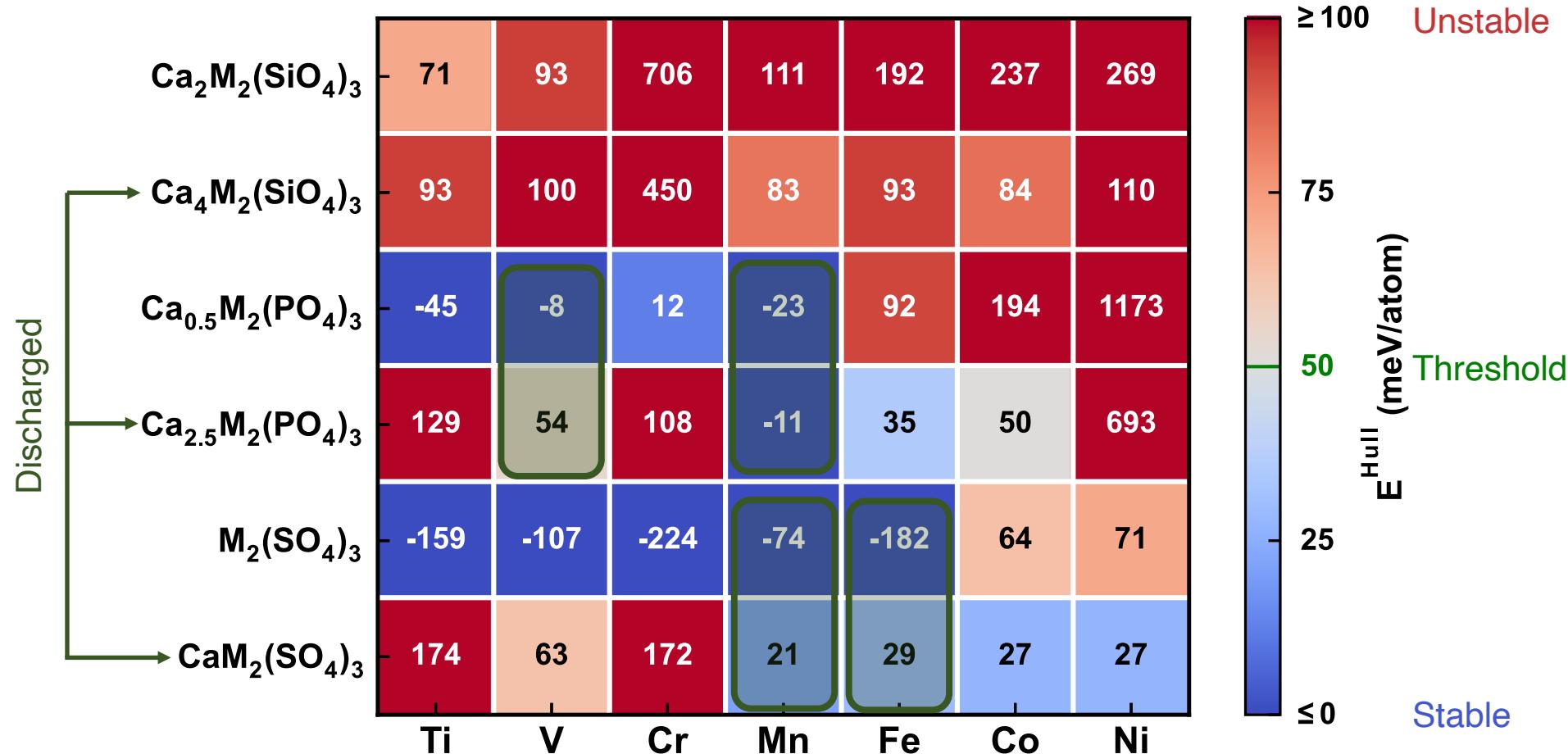
“Local” minima in voltage trends for Cr and Fe  $\text{SO}_4$

- Stability of  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  states

Voltage $\times$ capacity:  $\text{PO}_4$  may be optimal

# Phosphates and sulfate Ca-NaSiCONs: likely to be stable

$E^{\text{hull}}$  based on 0 K DFT calculations of all available "ordered" structures (~250) in ICSD



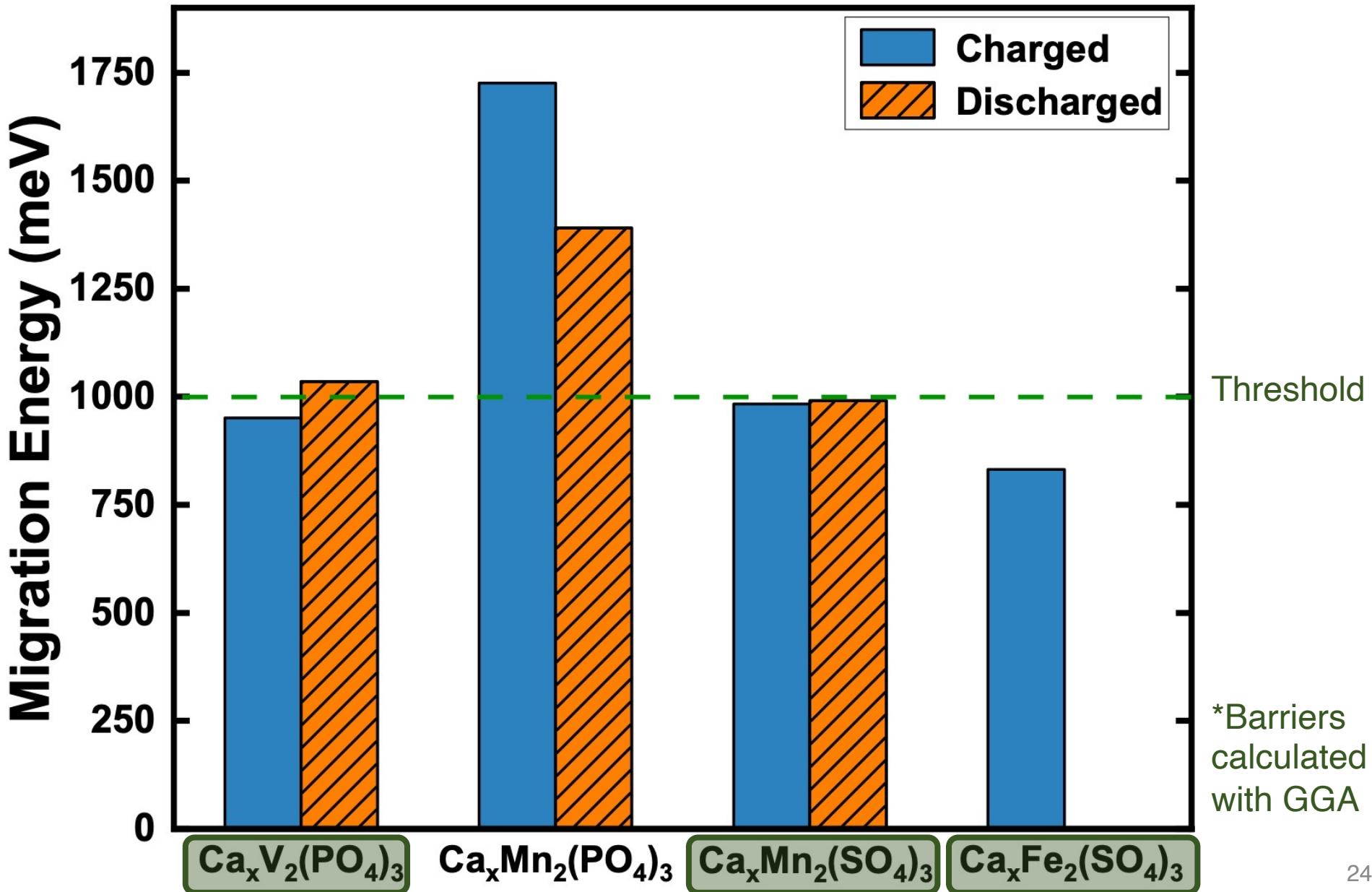
All charged and discharged silicates unstable: unsuitable for Ca-cathodes

Several  $\text{M}_2(\text{SO}_4)_3$  ( $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}$ , and  $\text{Fe}$ ) are stable: consistent with experimental synthesis

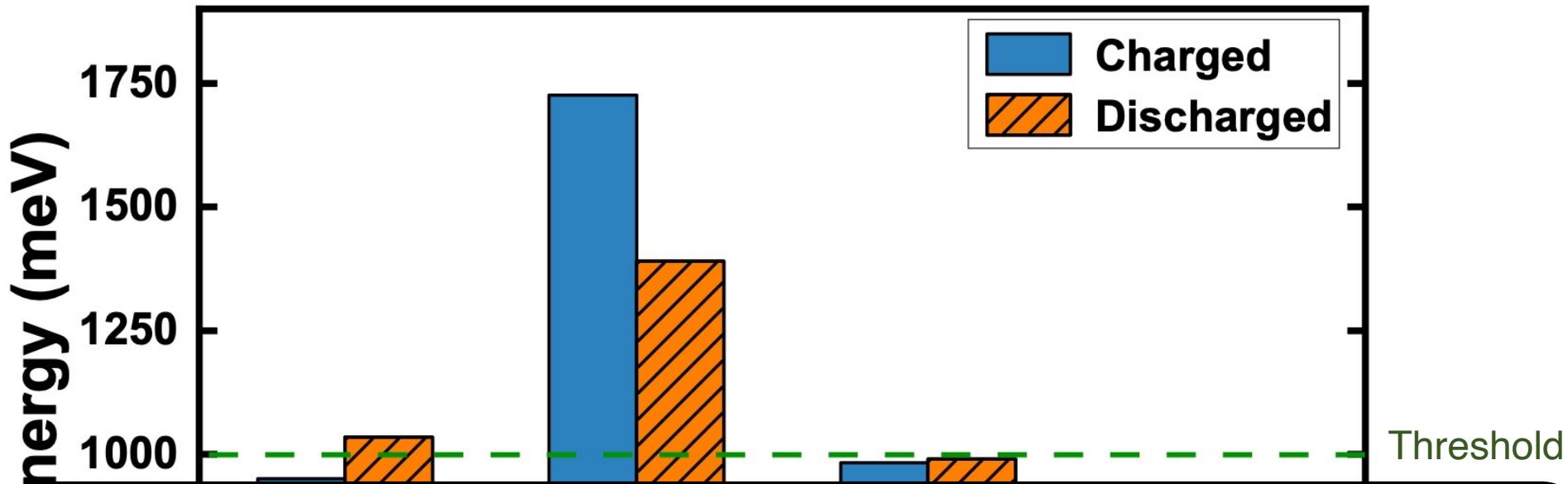
$\text{Ca}_{0.5}\text{Mn}_2(\text{PO}_4)_3$  and  $\text{Ca}_{2.5}\text{Mn}_2(\text{PO}_4)_3$  stable: promising candidate!

Other candidates:  $\text{Ca}_x\text{V}_2(\text{PO}_4)_3$ ,  $\text{Ca}_x\text{Mn}_2(\text{SO}_4)_3$ , and  $\text{Ca}_x\text{Fe}_2(\text{SO}_4)_3$

# Migration barriers: 3 candidates

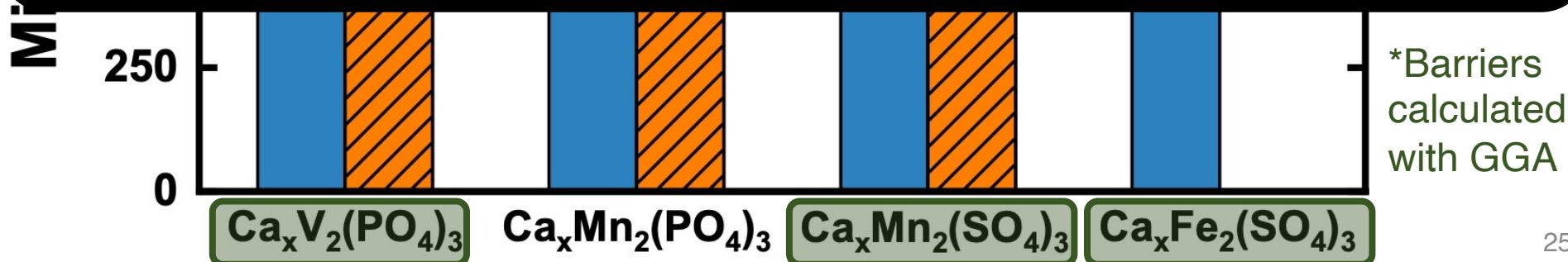


# Migration barriers: 3 candidates



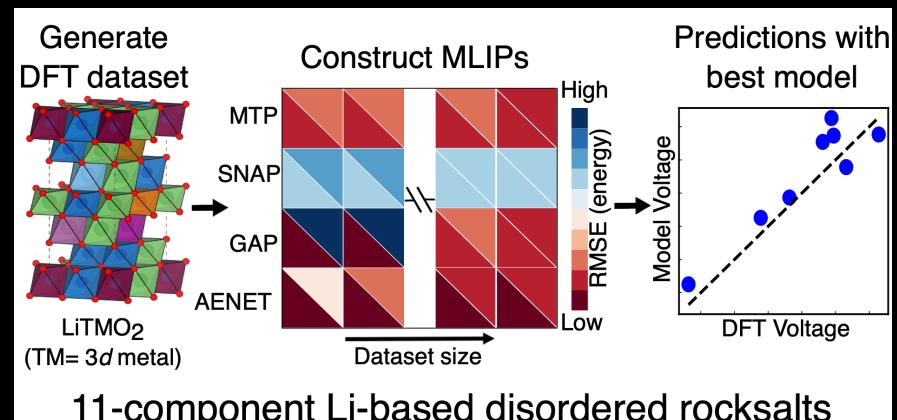
Voltage, stability and mobility screening of the NaSICON chemical space: 3 candidates

- V-phosphate, Mn-sulfate, and Fe-sulfate

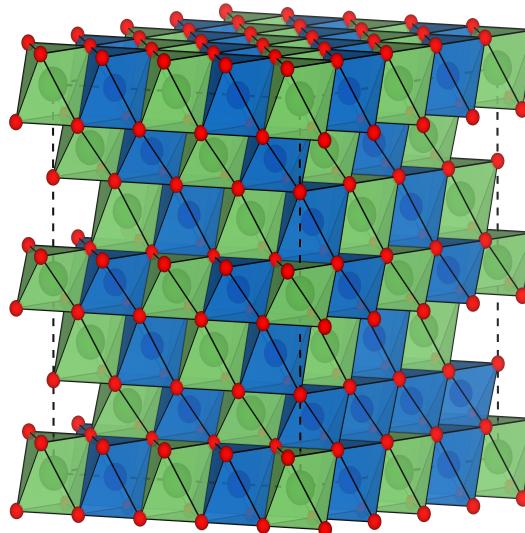
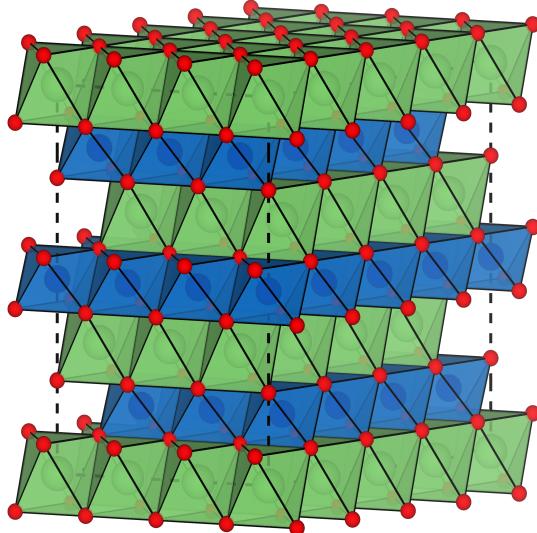




## Deep dives Constructing MLIPs



# Li-excess disordered rocksalts are an important class of Li-ion cathodes



Classical Li-ion cathodes: “layered” oxides (or “ordered” rocksalt)

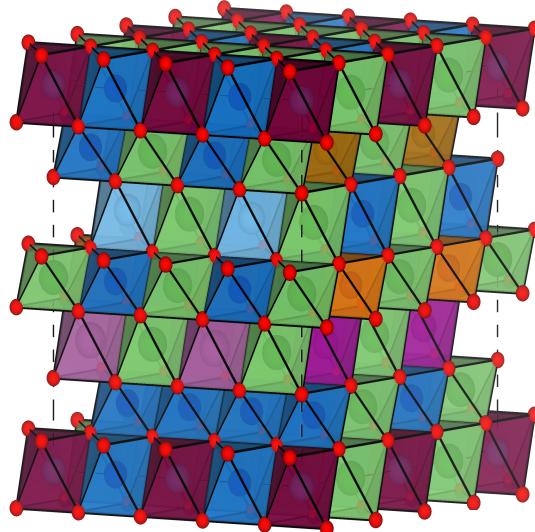
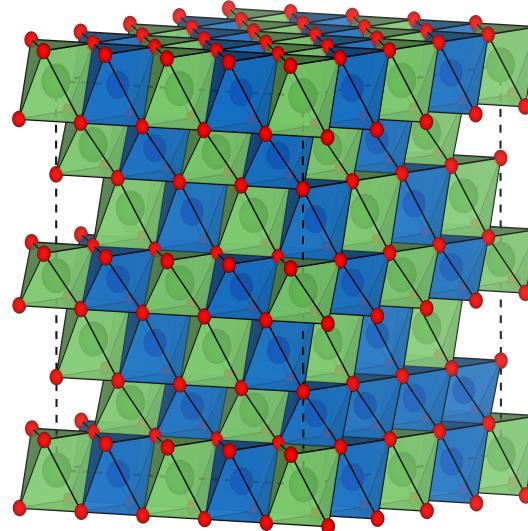
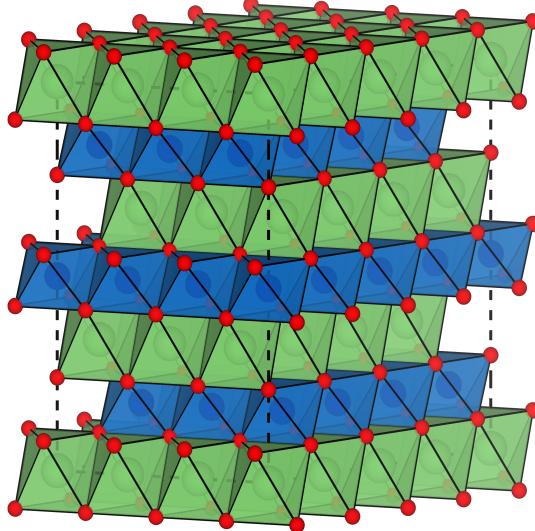
Oxygen: Face-centered-cubic lattice

Cation-lattice: “Ordered” face-centered-cubic

Cation arrangement: distinct Li and transition metal (TM) layers

Disordered rocksalts: no distinct long-range order in cation sub-lattice  
Usually not electrochemically active at  $\text{LiTMO}_2$  composition

# Li-excess disordered rocksalts are an important class of Li-ion cathodes



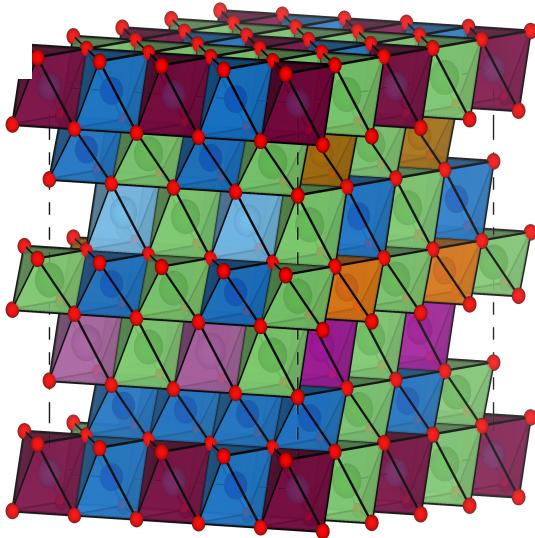
Li-excess disordered rocksalts (DRX): electrochemically active

Important class of advanced Li-ion cathodes

Distinctive features:

- Anionic redox: high voltages
- Li-transport via percolation channels
- Requires Li-excess, and often several TMs
- Usually operate at low rates and for low cycles

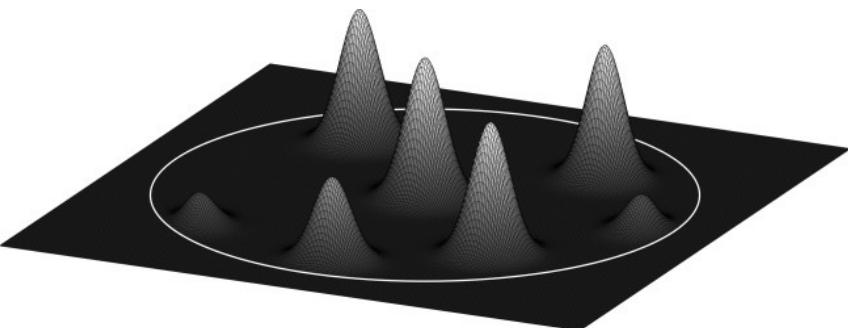
# Modelling DRX is non-trivial: use MLIPs?



Large configurational space: several different arrangements of Li and TM

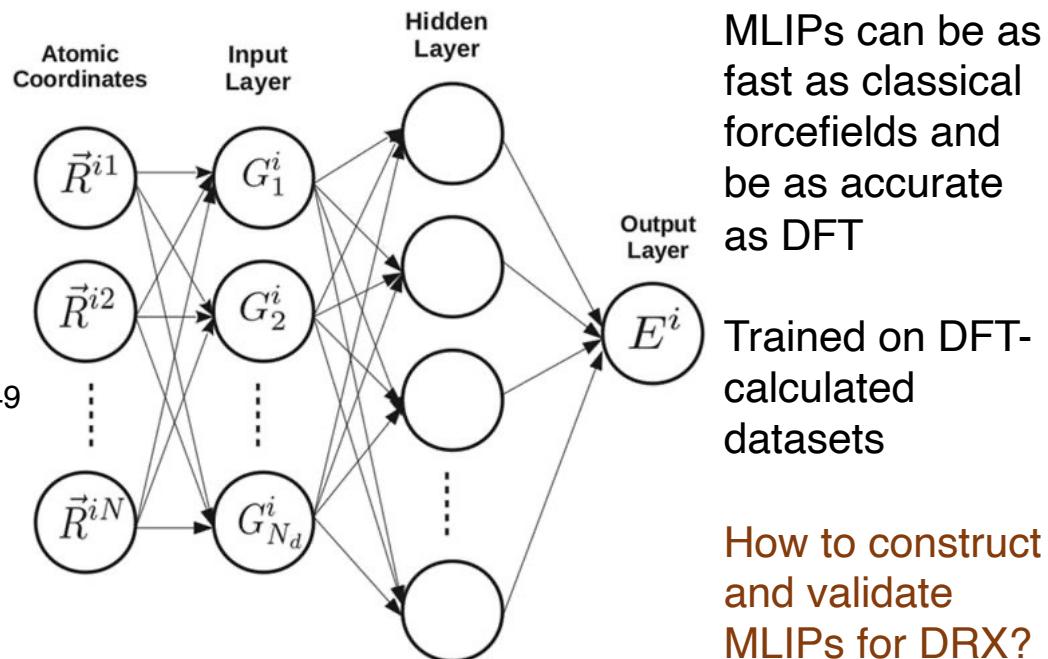
Large supercell size: for breaking long-range order

Requires computations quicker than DFT but as accurate for screening



Bartók and Csányi, Int. J. Quantum Chem. 2016, 116, 1049

Fingerprint a local environment around a reference atom  
+ machine-learning model  
= machine-learned interatomic potential (MLIP)



MLIPs can be as fast as classical forcefields and be as accurate as DFT

Trained on DFT-calculated datasets

How to construct and validate MLIPs for DRX?

# Five MLIPs considered over a 10842 DFT-calculated dataset

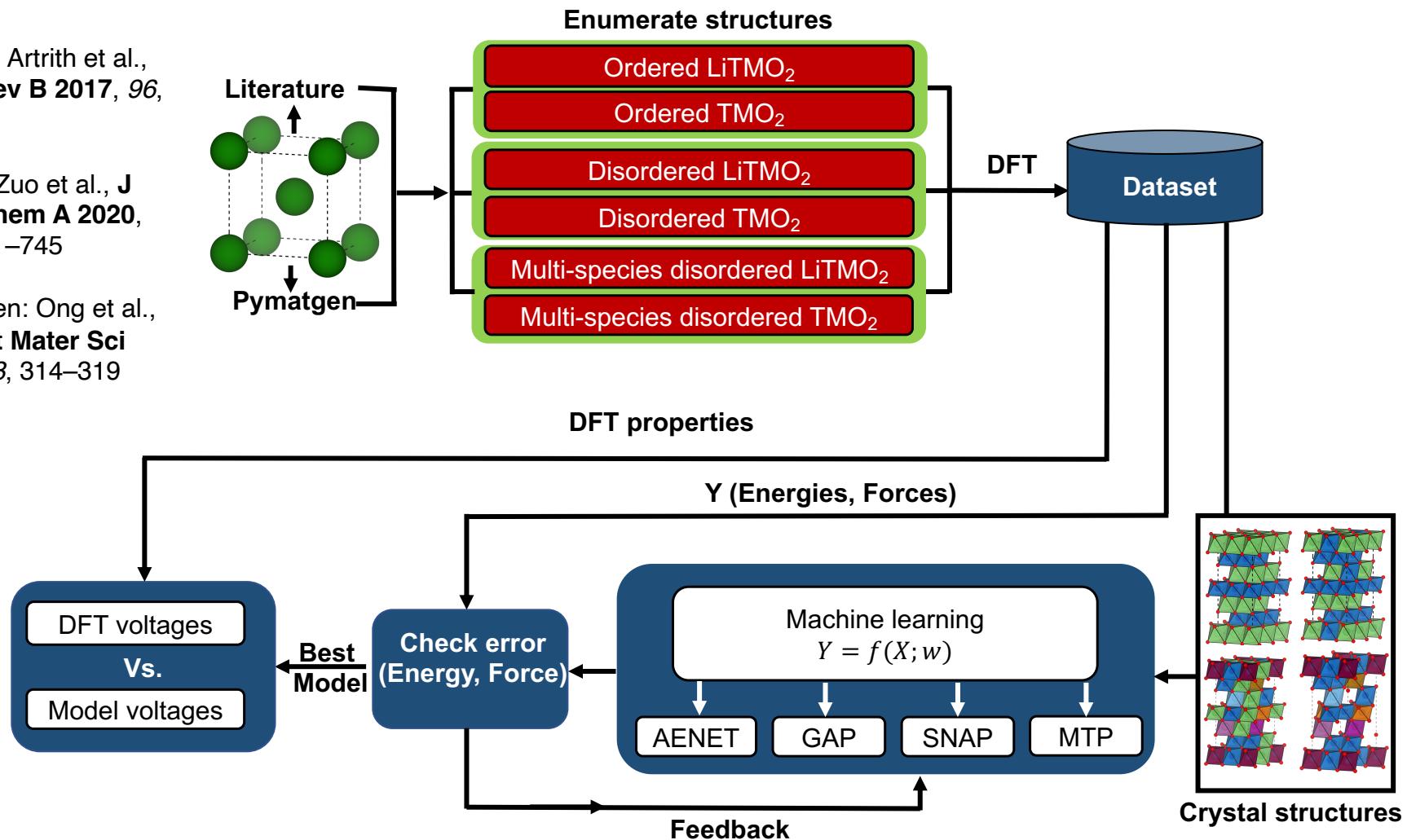
$\text{LiTMO}_2 + \text{TMO}_2$  compositions; TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and/or Cu; 11-components

“Atom-centered” MLIPs considered

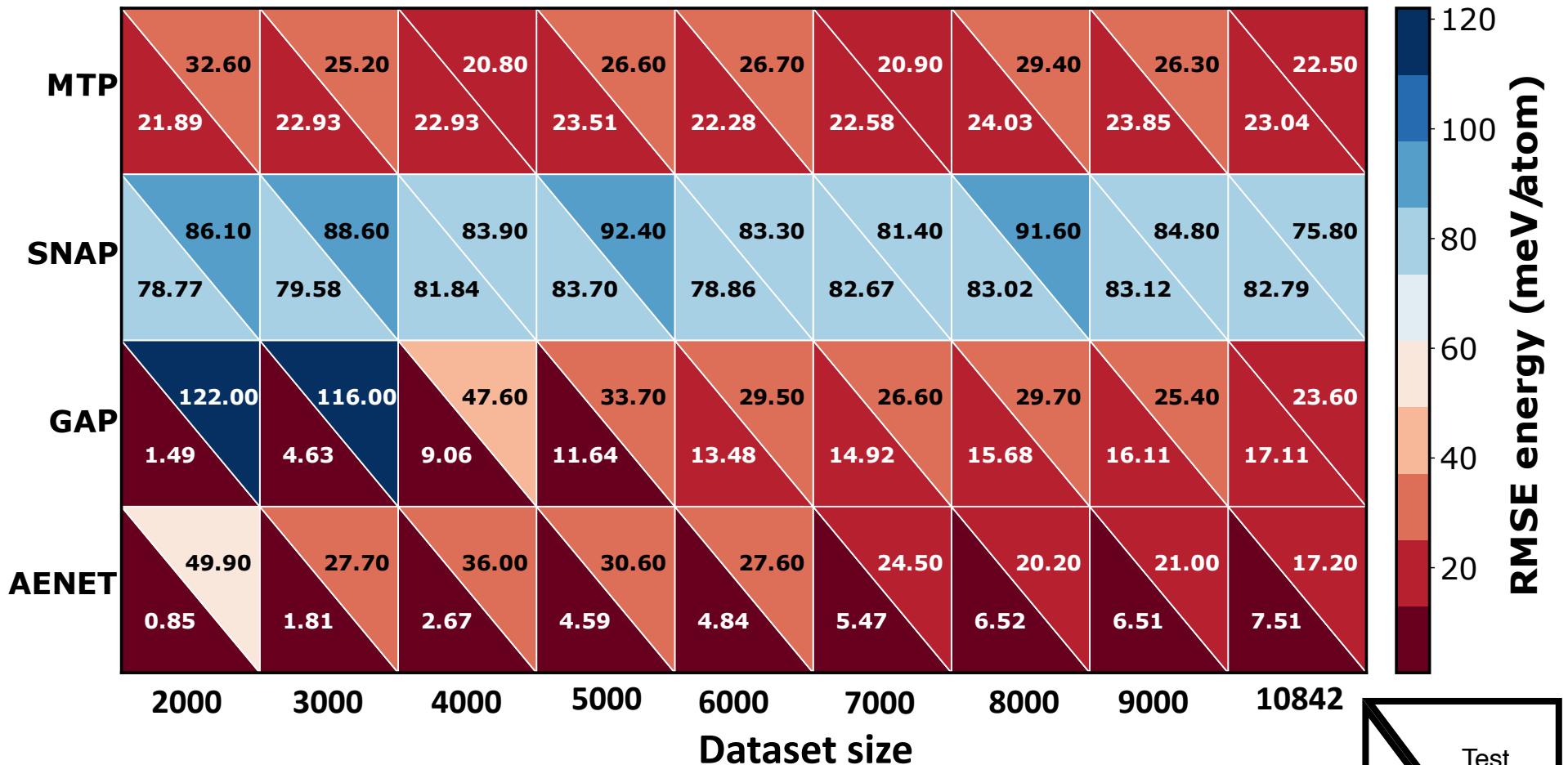
Dataset: Artrith et al.,  
**Phys Rev B** 2017, 96,  
014112

MAML: Zuo et al., **J Phys Chem A** 2020,  
124, 731–745

Pymatgen: Ong et al.,  
**Comput Mater Sci**  
2013, 68, 314–319



# AENET is best for total energy predictions



Lower training errors: Better accuracy (**AENET**)

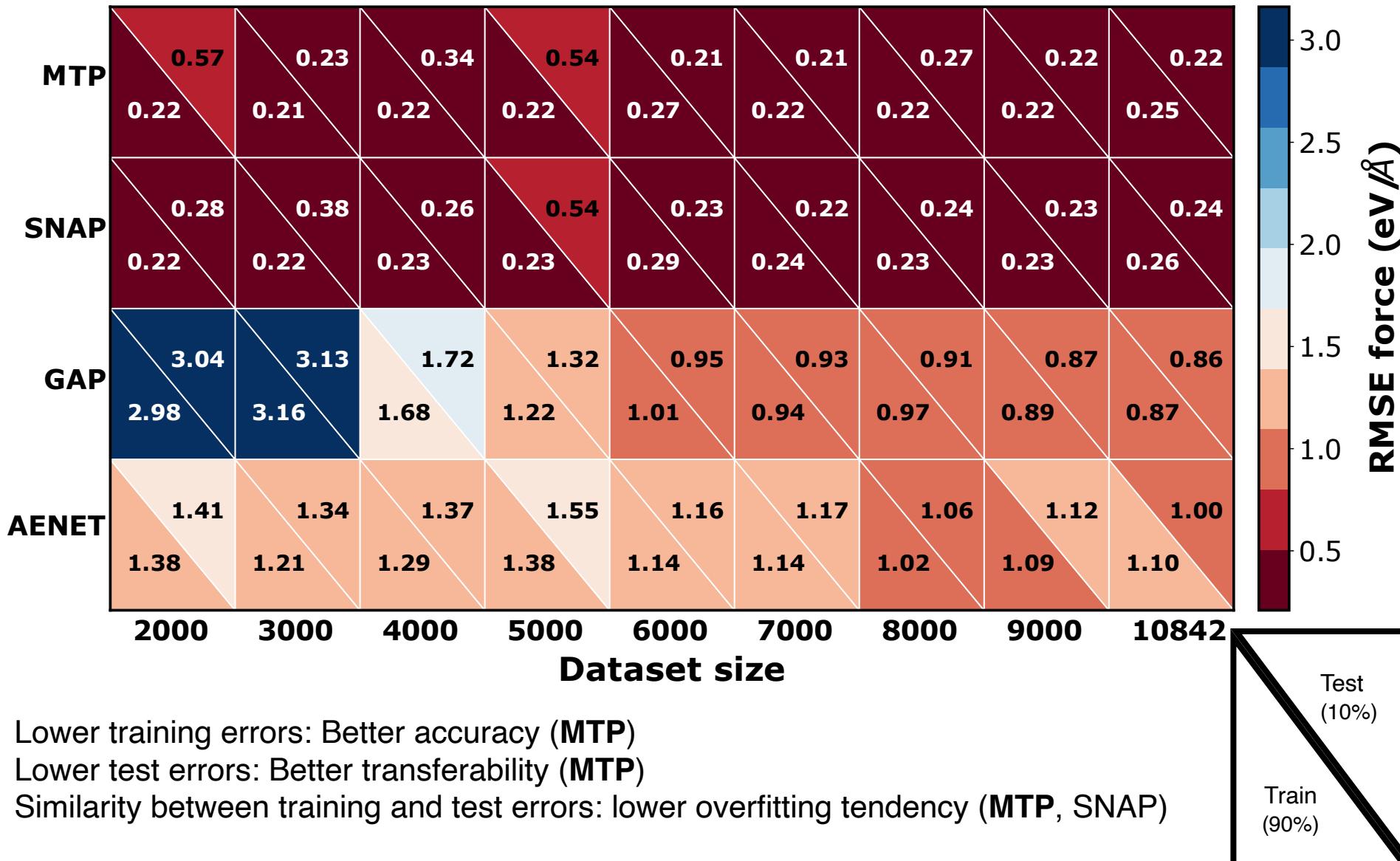
Lower test errors: Better transferability (**AENET**)

Similarity between training and test errors: lower overfitting tendency (**MTP, SNAP**)

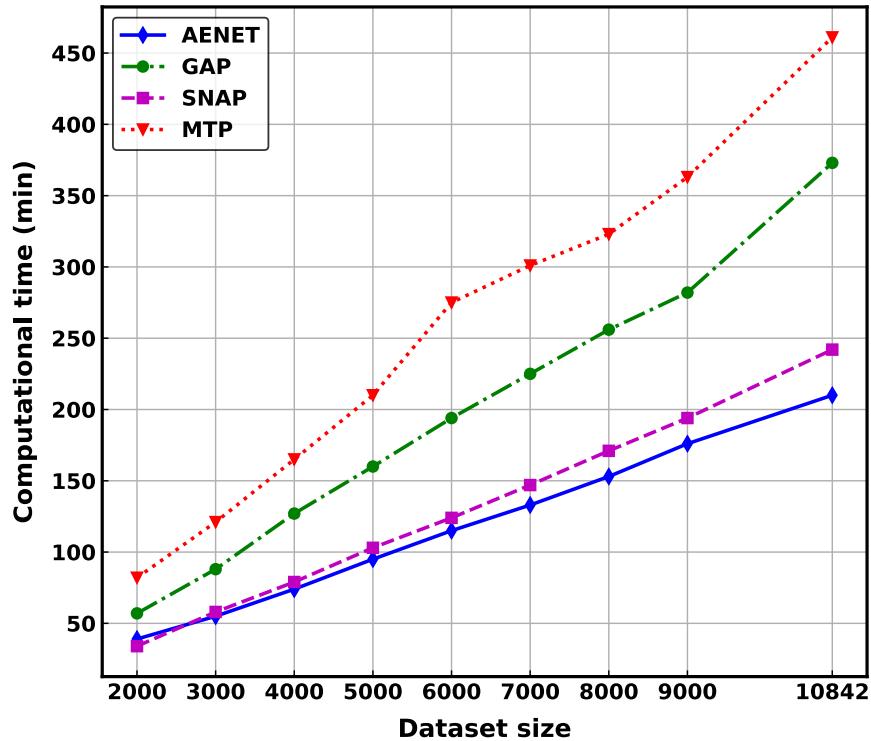
Error observations similar between **SNAP** and **qSNAP**

AENET performs best when dataset size is good enough, MTP reasonable at small datasets

# MTP is best for atomic force predictions



# Ease of training: AENET at low “epochs”

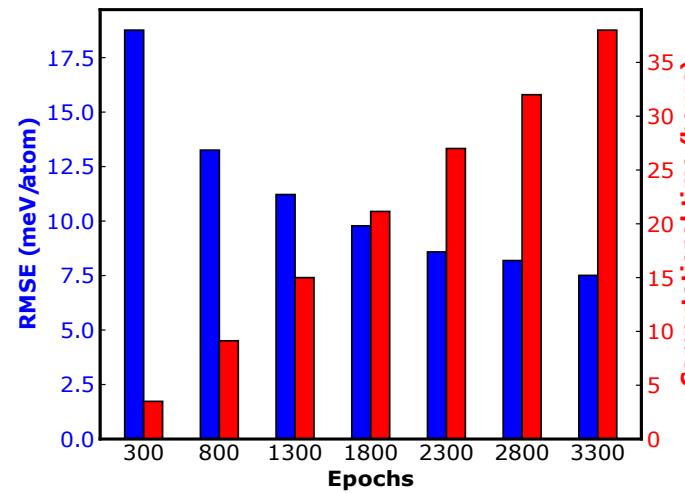
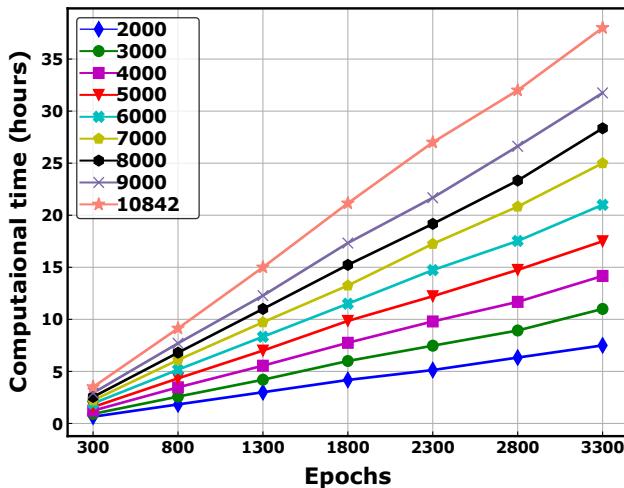


Compute training time on a single core of Intel® Xeon® Gold 6271 CPU

AENET fastest to train at 300 epochs (training iterations)

MTP slowest to train

SNAP is fastest at small datasets

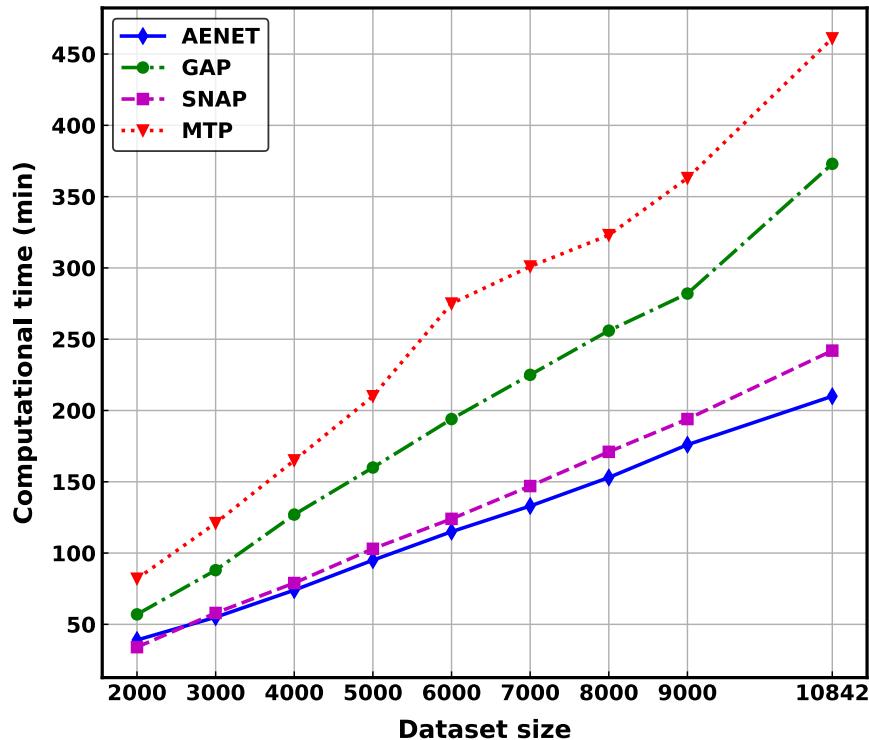


AENET training time increases significantly with higher epochs

Lowest training errors at 3300 epochs: training time increases by 6x

Training error decrease saturates after 2300 epochs

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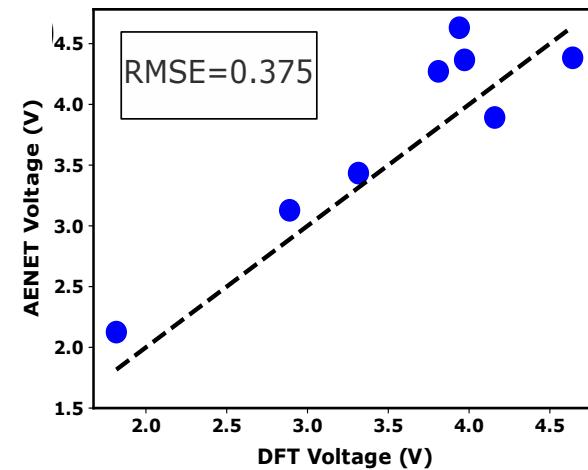
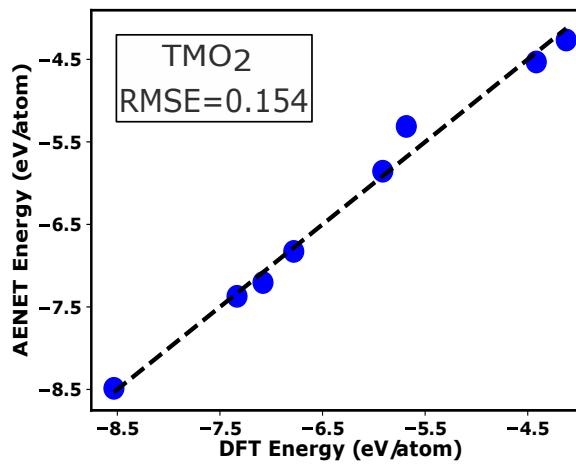
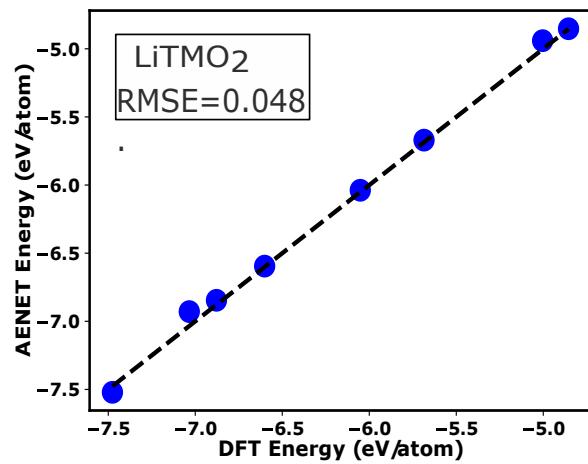
AENET training time increases significantly with higher epochs

AENET gives best total energy predictions and is not too hard to train at low epochs: how does it perform in predicting electrochemical properties?

Lowest training errors at 3300 epochs: training time increases by 6x

Training error decrease saturates after 2300 epochs

# Voltage predictions: AENET is reasonable



AENET trained at 2300 epochs versus DFT-calculated total energies in ordered, layered LiTMO<sub>2</sub> and TMO<sub>2</sub>

- Higher errors in TMO<sub>2</sub> expected: lower amount of TMO<sub>2</sub> data in training dataset
- Percentage errors are low (0.55% for LiTMO<sub>2</sub> and 2.12% for TMO<sub>2</sub>)

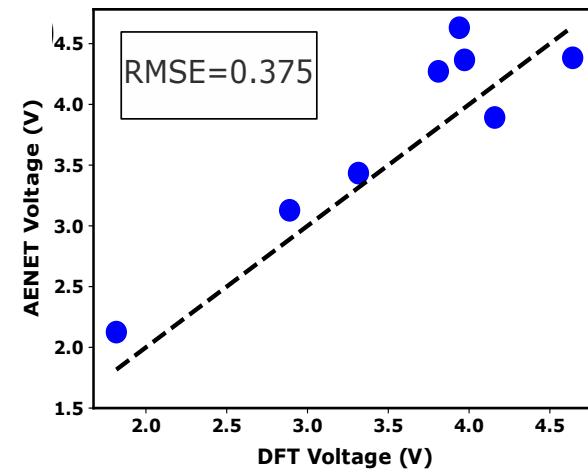
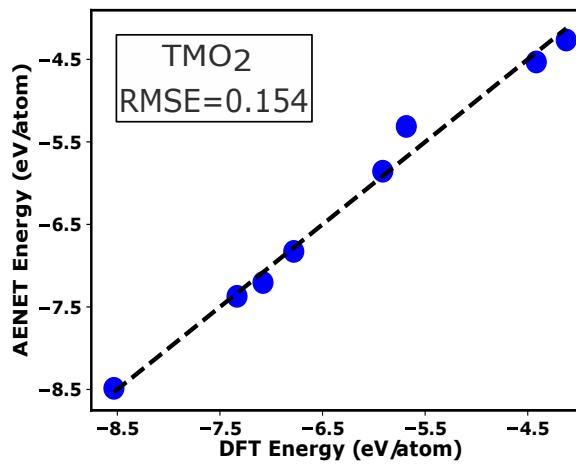
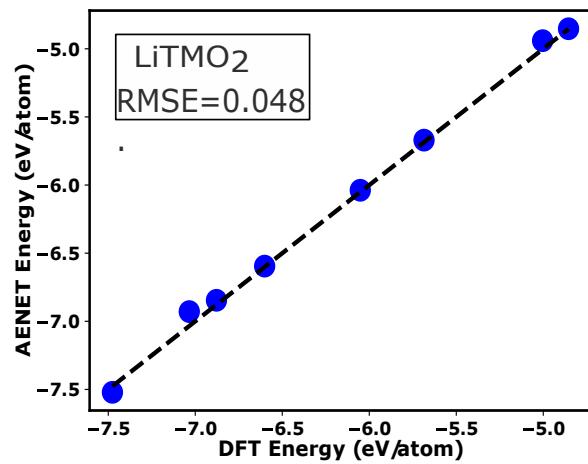
Voltage predictions: AENET has an average error of 10%

- MAE: 0.34 V; RMSE: 0.375 V
- There is compounding of error from LiTMO<sub>2</sub> and TMO<sub>2</sub>
- Largest errors in LiFeO<sub>2</sub> and LiTiO<sub>2</sub> (~17%)

Scope for improvement with more training data

- Qualitative trends may be useful for screening

# Voltage predictions: AENET is reasonable



AENET trained at 2300 epochs versus DFT-calculated total energies in ordered, layered LiTMO<sub>2</sub> and TMO<sub>2</sub>

- Higher errors in TMO<sub>2</sub> expected: lower amount of TMO<sub>2</sub> data in training dataset
- Percentage errors are low (0.55% for LiTMO<sub>2</sub> and 2.12% for TMO<sub>2</sub>)

Voltage predictions: AENET has an average error of 10%

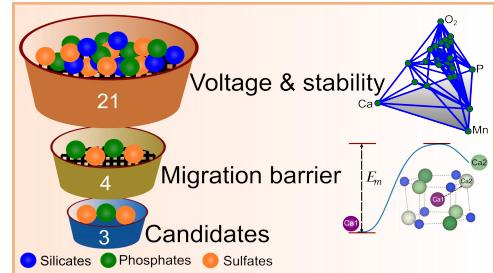
- MAE: 0.34 V; RMSE: 0.375 V

MLIPs, if carefully constructed, are useful for modelling complex configurational spaces!

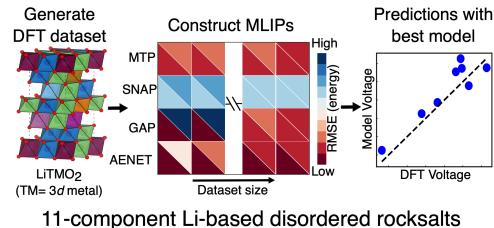
# Conclusions



- Removing material bottlenecks is important for improving performance of energy devices
  - Need better, safer, and cheaper batteries



- Ca-containing NaSICON frameworks screened
  - 3 candidates:  $\text{Ca}_x\text{V}_2(\text{PO}_4)_3$ ,  $\text{Ca}_x\text{Mn}_2(\text{SO}_4)_3$  and  $\text{Ca}_x\text{Fe}_2(\text{SO}_4)_3$



- Modelling a configurationally complex DRX space with MLIPs
  - AENET: good for total energy predictions (statics)
  - MTP: good for atomic force predictions (dynamics)

Ca-NaSICON screening:

“Exploration of NaSICON frameworks as calcium-ion battery cathodes”, D.B. Tekliye, A. Kumar, X. Weihang, T.D. Mercy, P. Canepa, and G.Sai Gautam, **Chem. Mater.** **2022**, *34*, 10133-10143

MLIP construction:

“Constructing and evaluating machine-learned interatomic potentials for Li-based disordered rocksalts”, V. Choyal, N. Sagar, and G. Sai Gautam, **arXiv 2304.01650** (2023). *Under review*