



Materials discovery for energy storage using computations and machine learning

Sai Gautam Gopalakrishnan

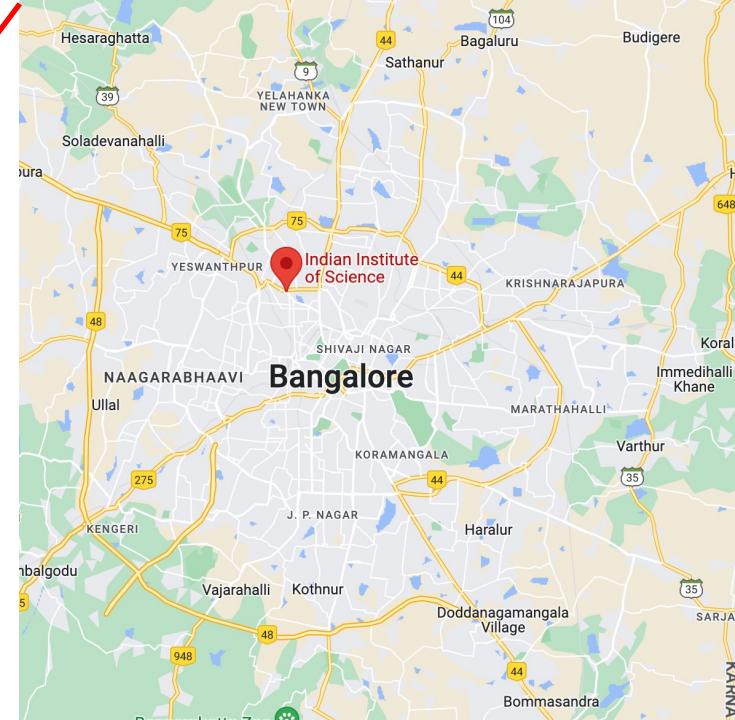
Simulations And Informatics of MATerials (SAI-MAT) group

Materials Engineering, Indian Institute of Science

saigautamg@iisc.ac.in; <https://sai-mat-group.github.io>

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)



ASPIRE 1
Advanced Supercomputer for Petascale Innovation Research & Enterprise

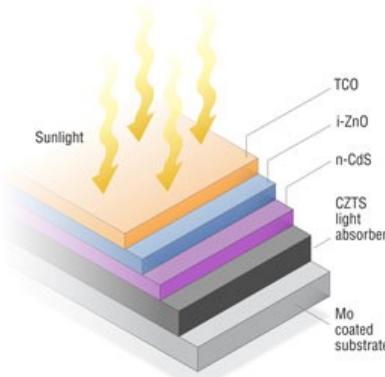


Dereje Vijay
SERC (IISc)

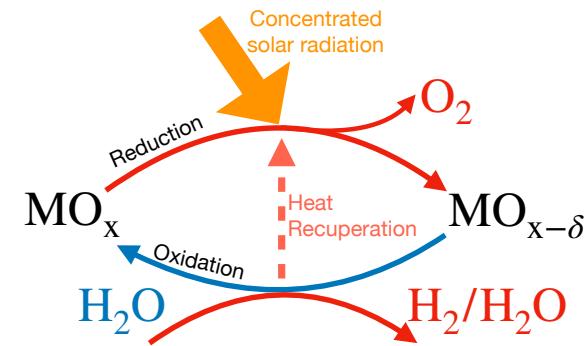
We work broadly on energy materials



Design better electrodes and solid electrolytes



Develop better light-absorbing semiconductors



Identify better thermochemical H_2O -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

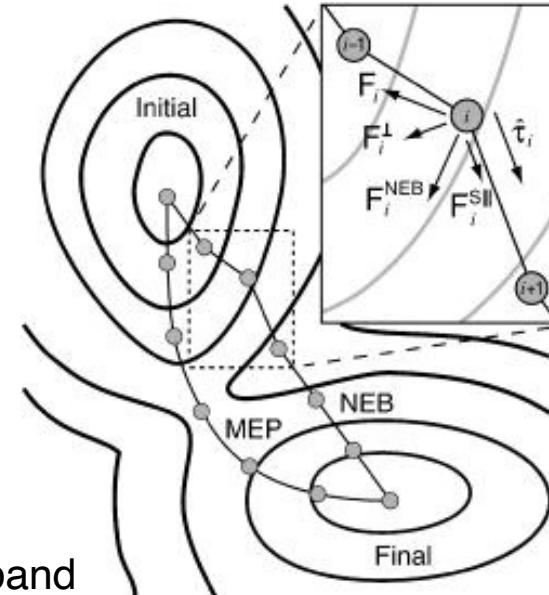
We do theory, computations, & ML



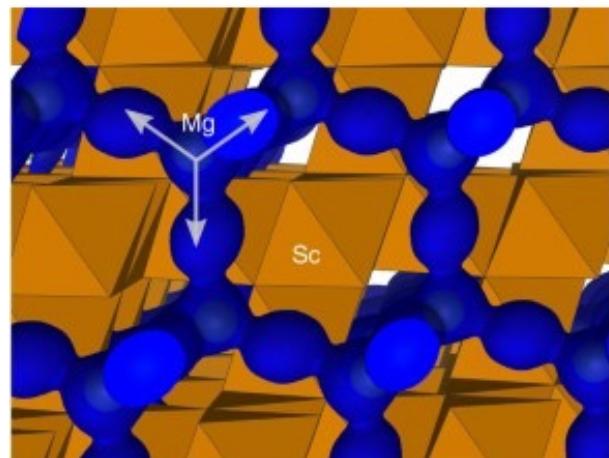
Density functional theory
(DFT): (Approximately) predict material properties

- 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



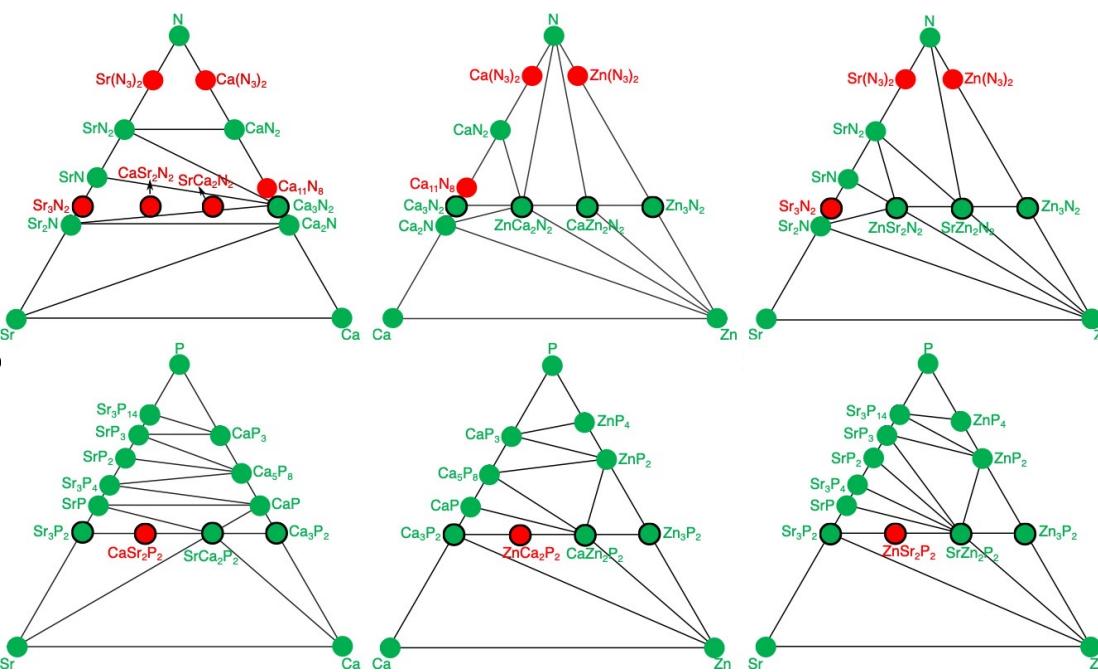
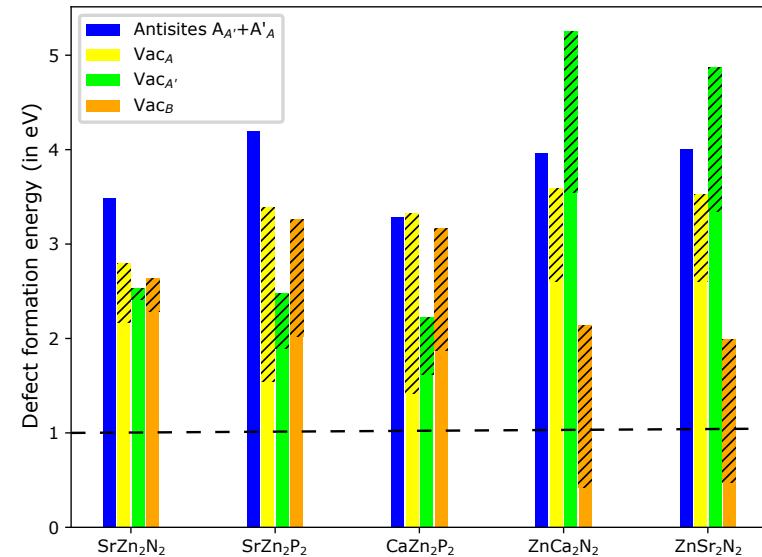
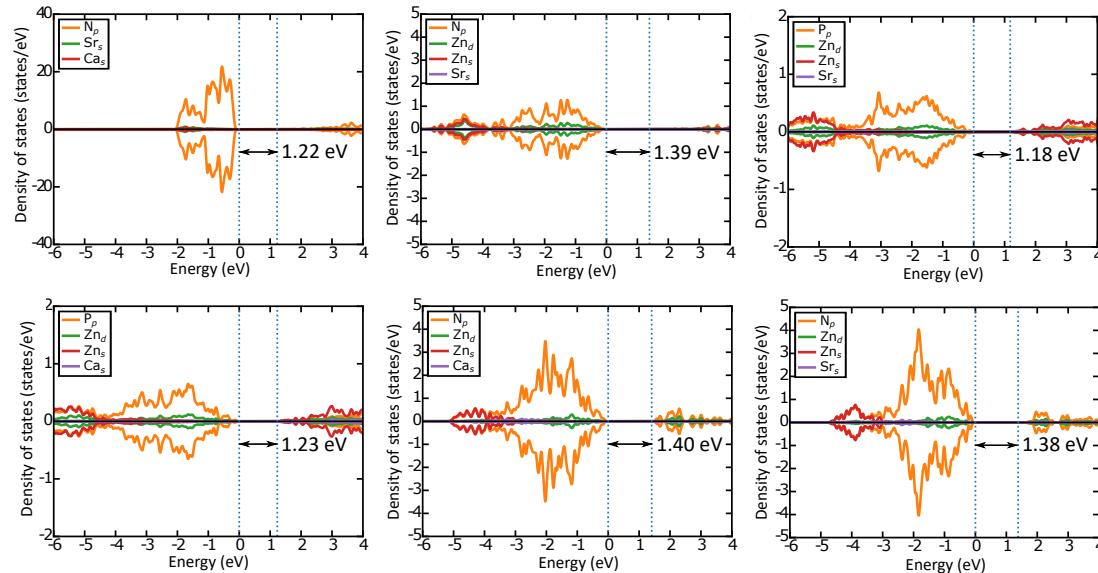
Ab initio and classical (ML) molecular dynamics: kinetic properties





Snapshots of our research

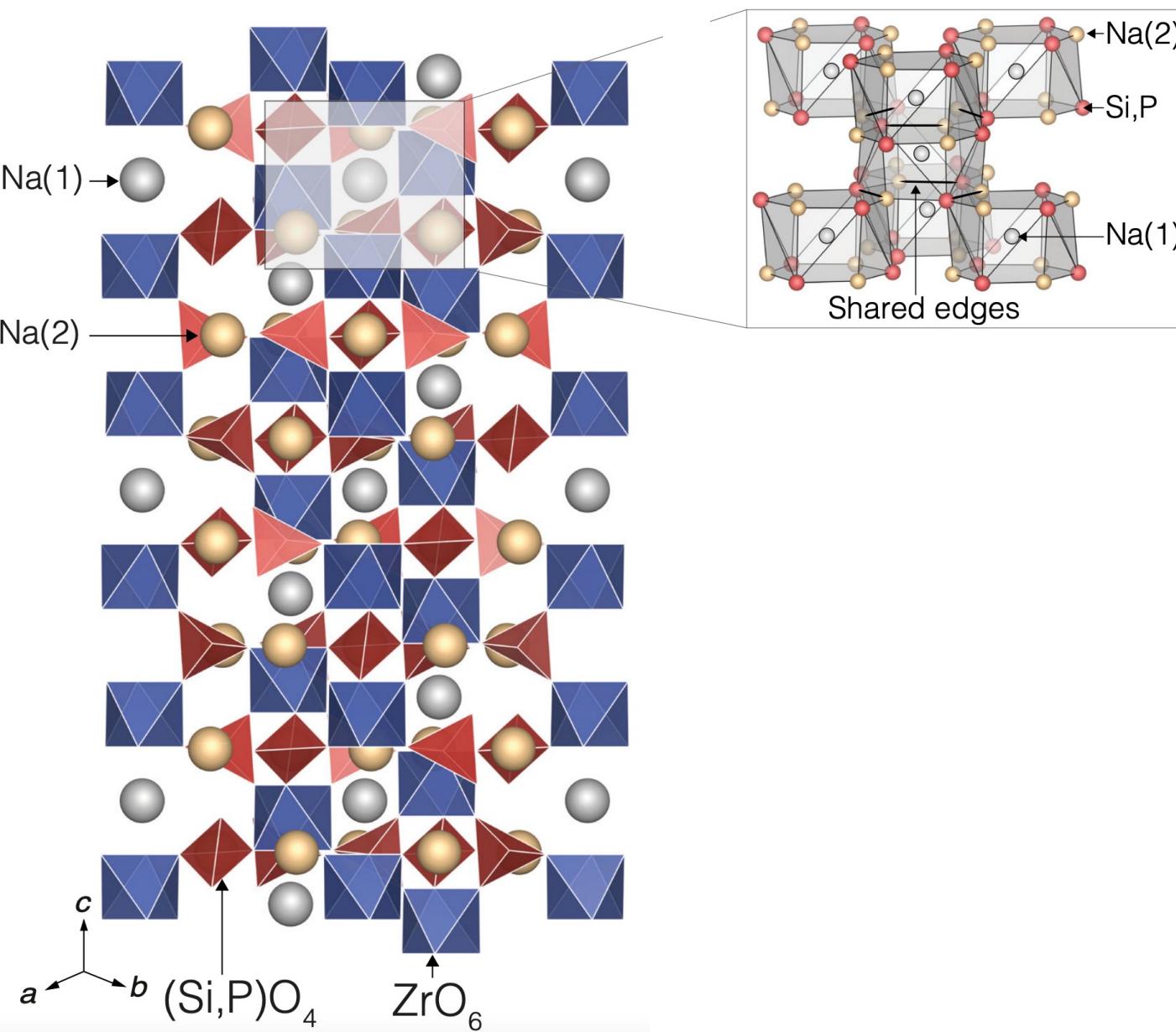
Phictides as possible photovoltaics



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

$SrZn_2N_2$, $SrZn_2P_2$, and $CaZn_2P_2$: predicted candidates

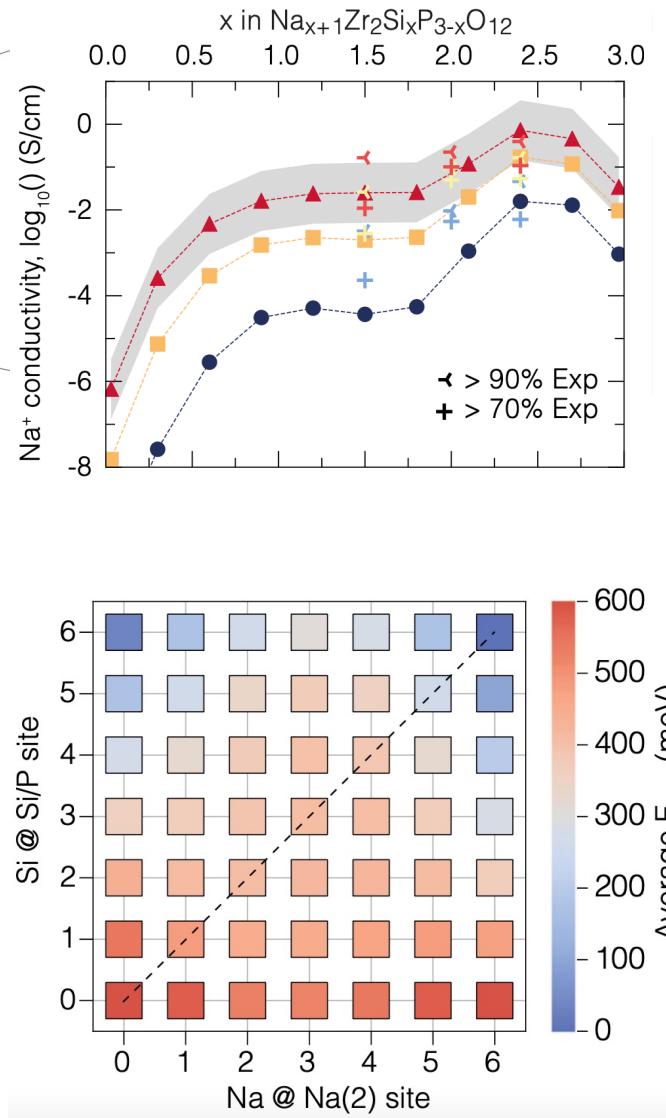
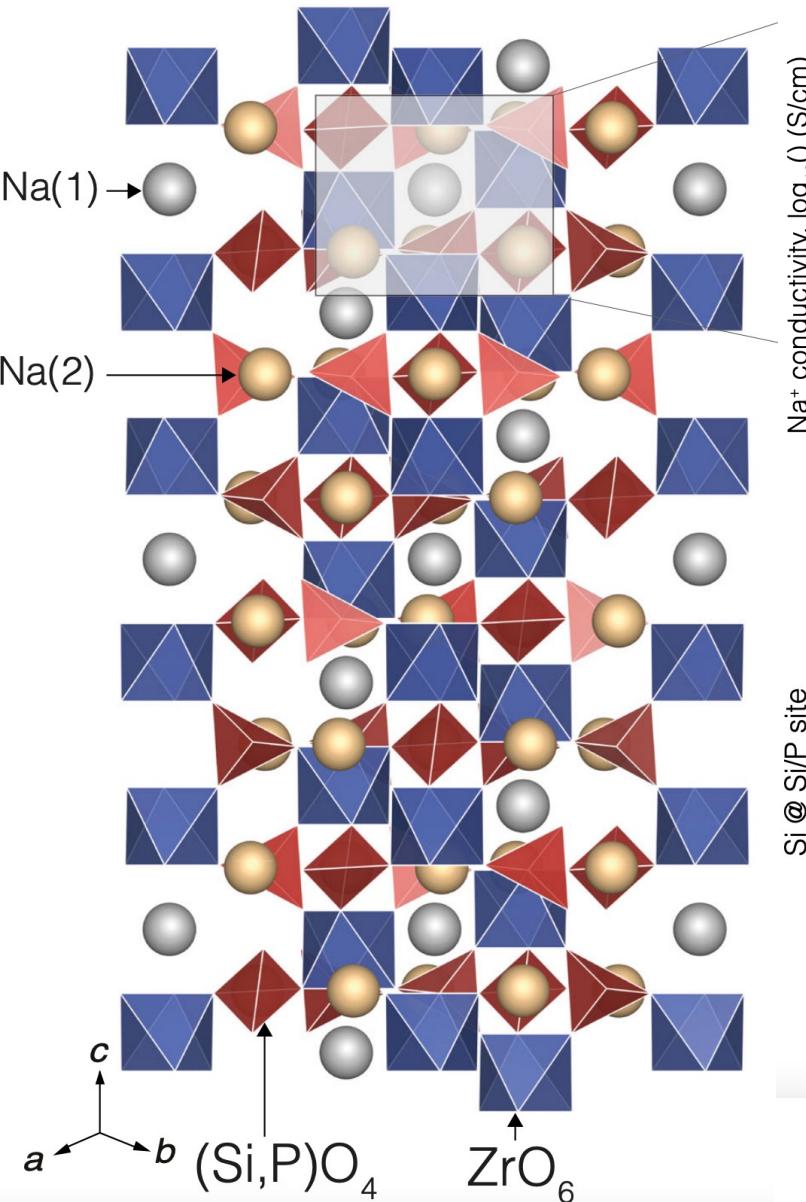
Quantify ionic mobility in solid electrolytes



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

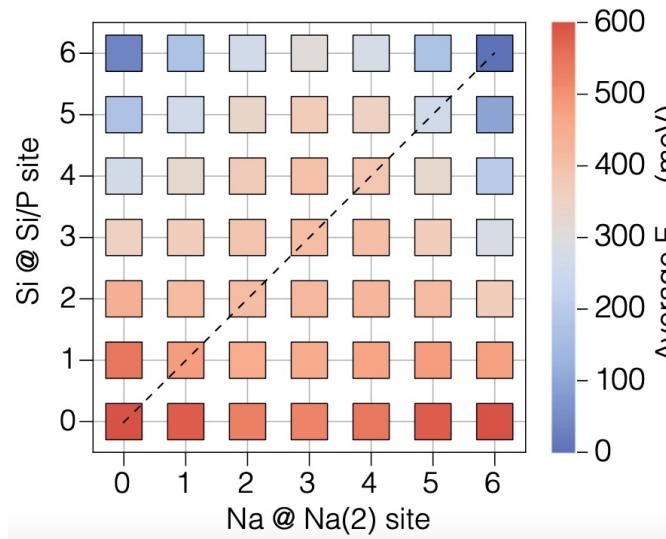
Conductivity not known as a function of composition

Quantify ionic mobility in solid electrolytes



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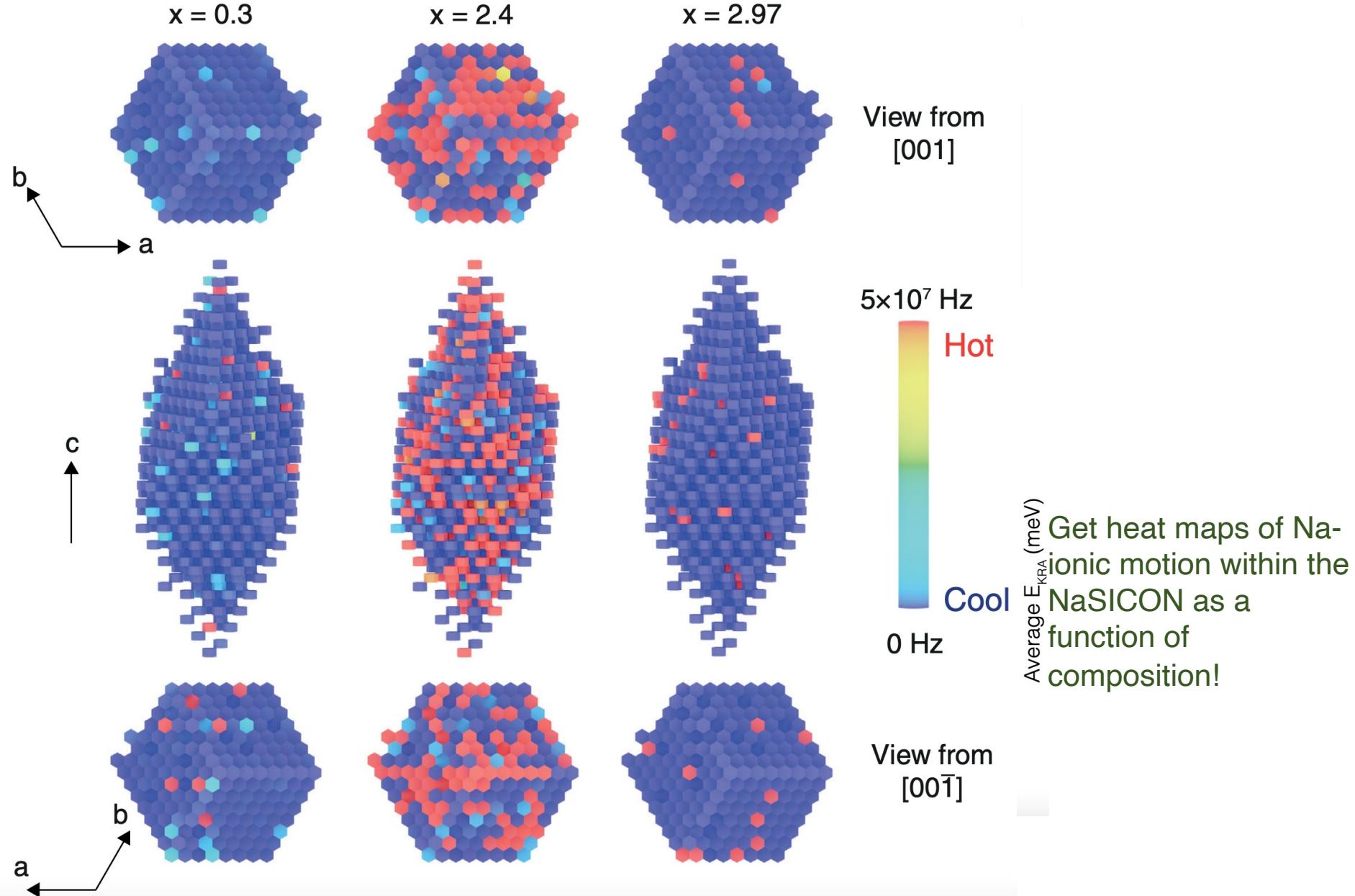
Conductivity not known as a function of composition



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

Good agreement with experimental measurements

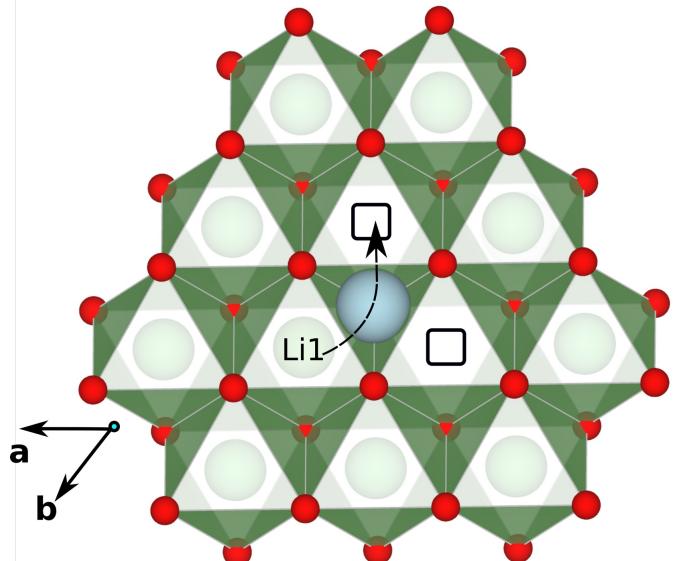
Quantify ionic mobility in solid electrolytes



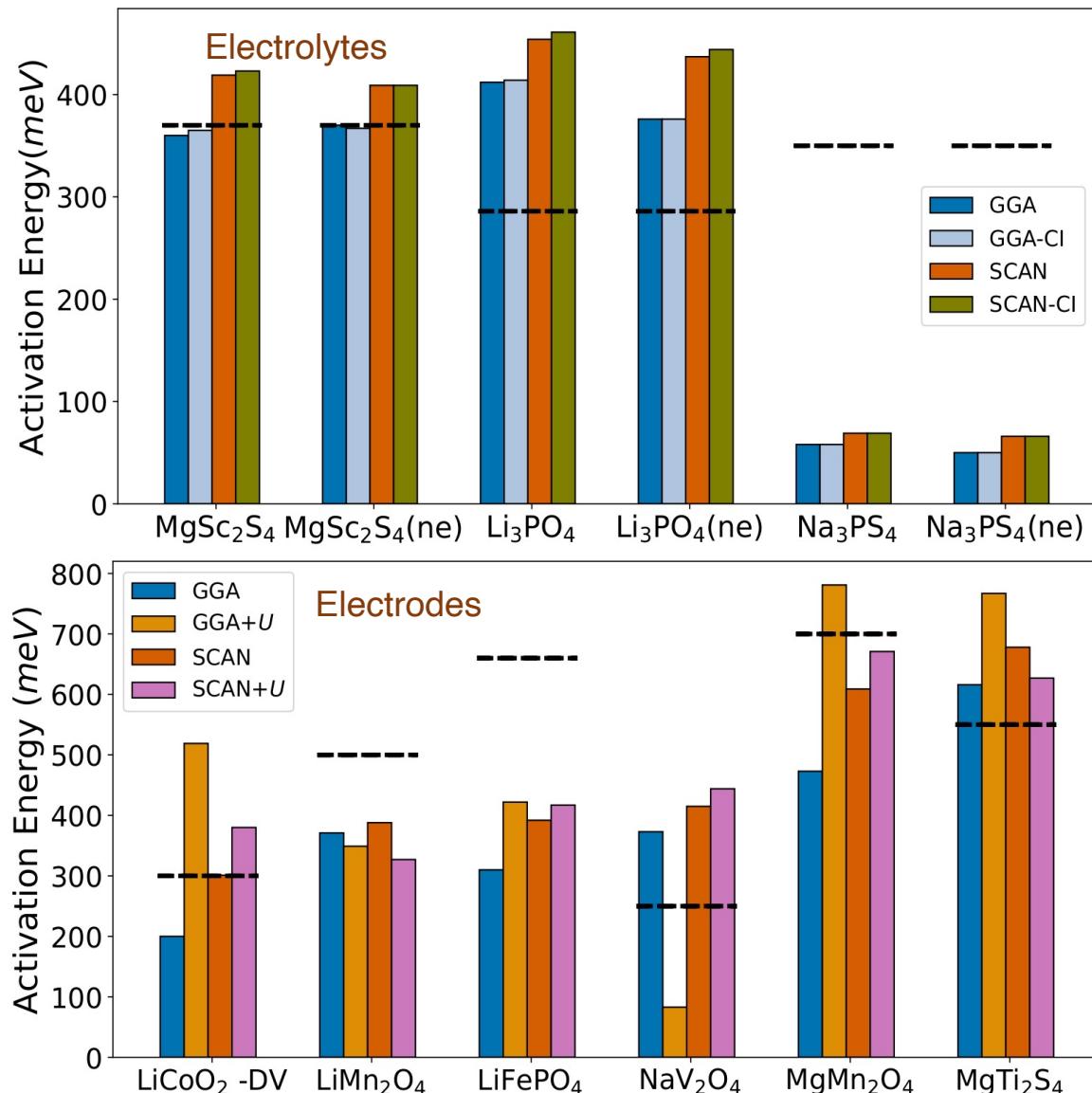
Which "functional" predicts migration barriers well?

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

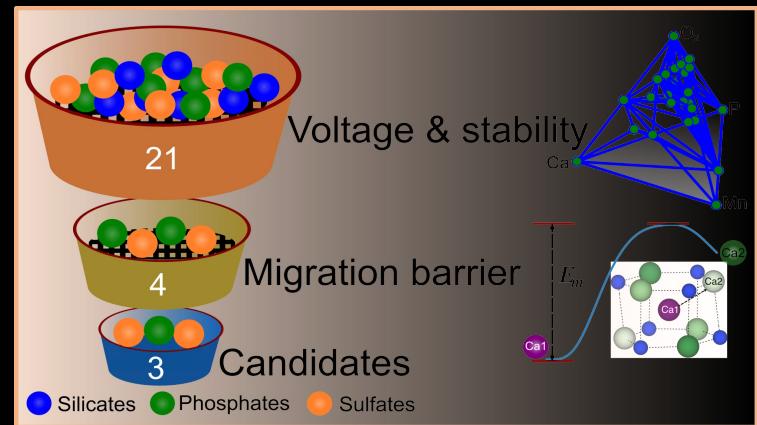
Which exchange-correlation functional is best suited for migration barrier predictions in battery materials?

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



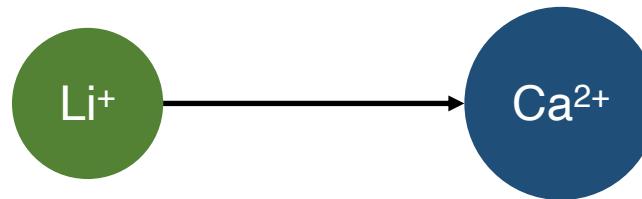
Deep dives Ca-cathode screening



Why beyond-Li-ion batteries?

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

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

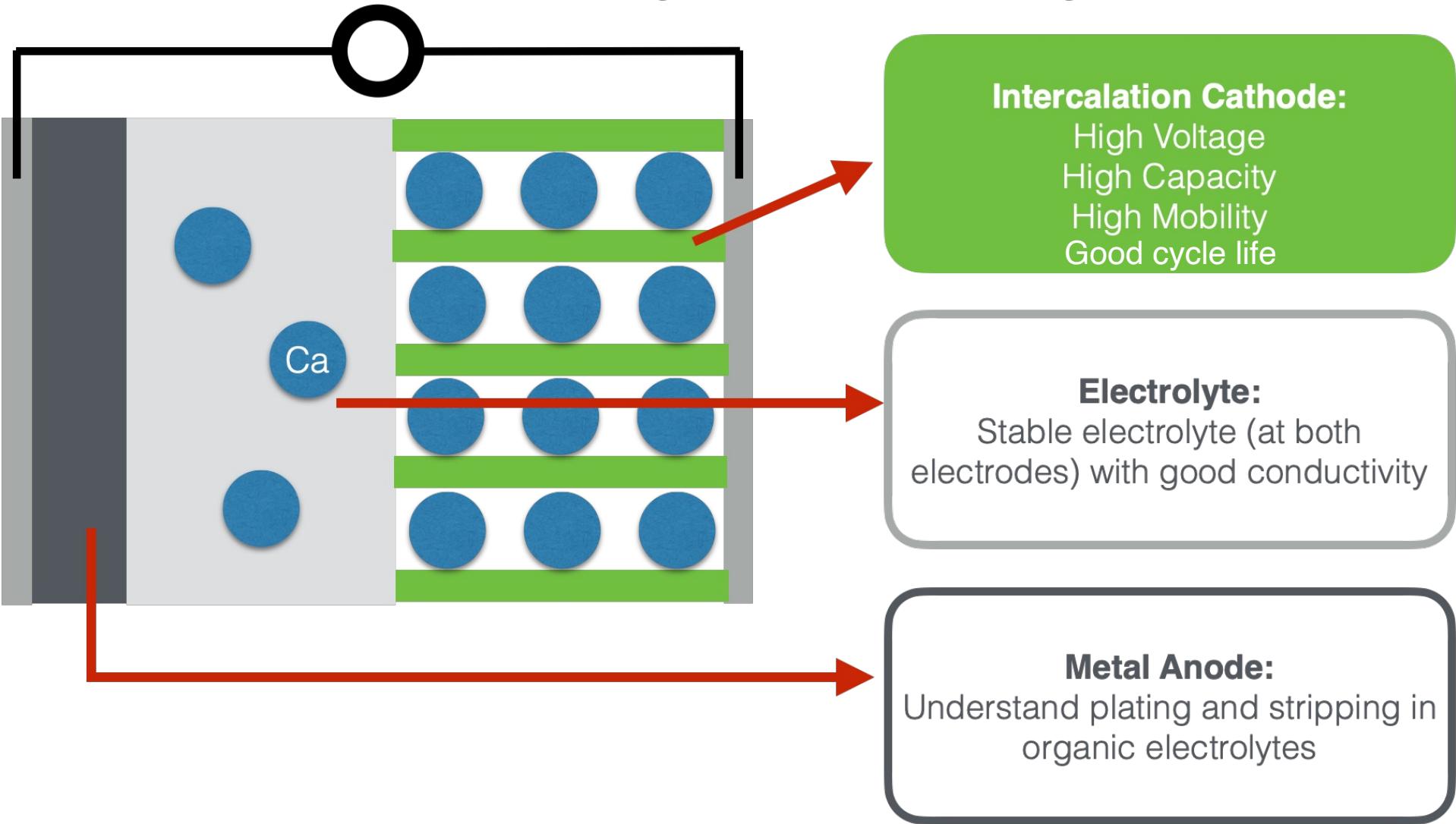


Why Ca?

- 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)

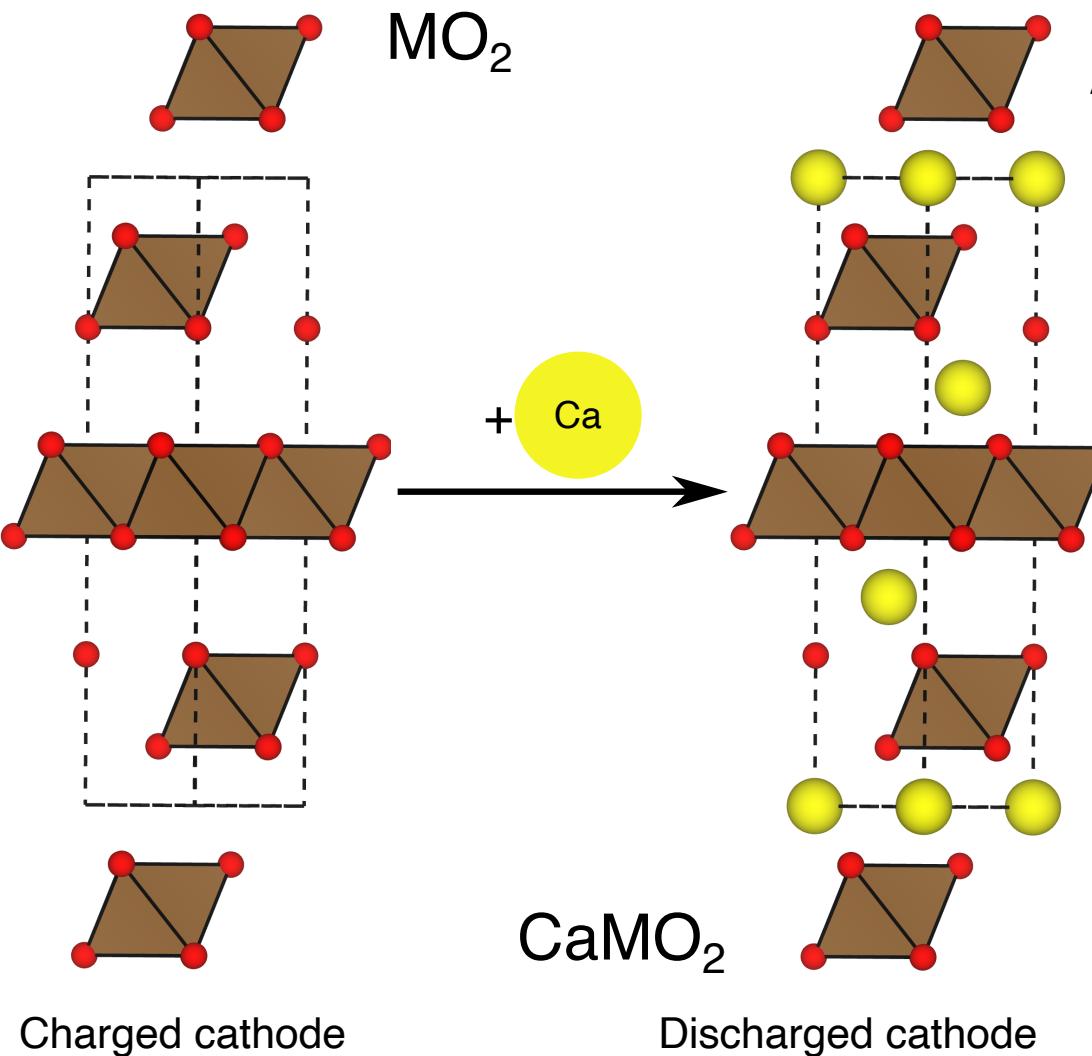


Cathode design challenge



Ca: Find thermodynamically *stable* cathodes with reasonable *voltage, capacity, mobility & stability*¹⁶

Voltage, capacity, and rate: intercalation batteries



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

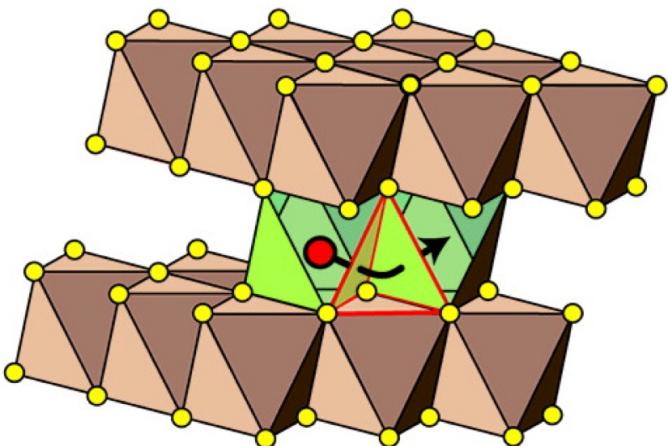
Nernst Equation

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

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

1 Ca moved = 2 electrons stored

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

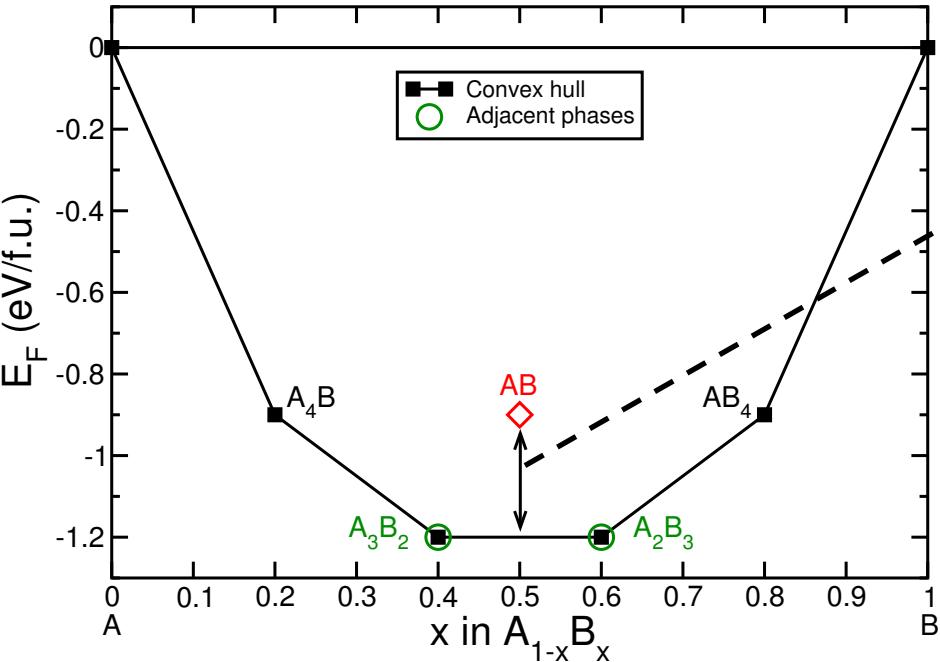


Rate: how fast can Ca move (or diffuse) within electrode?

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

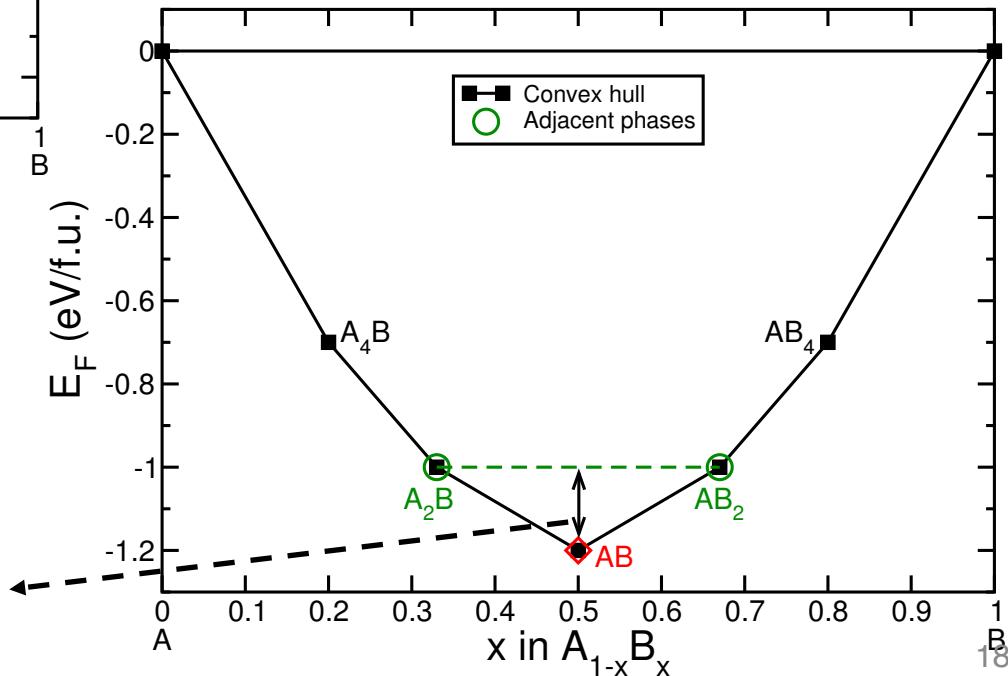
0 K thermodynamics: convex hull

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

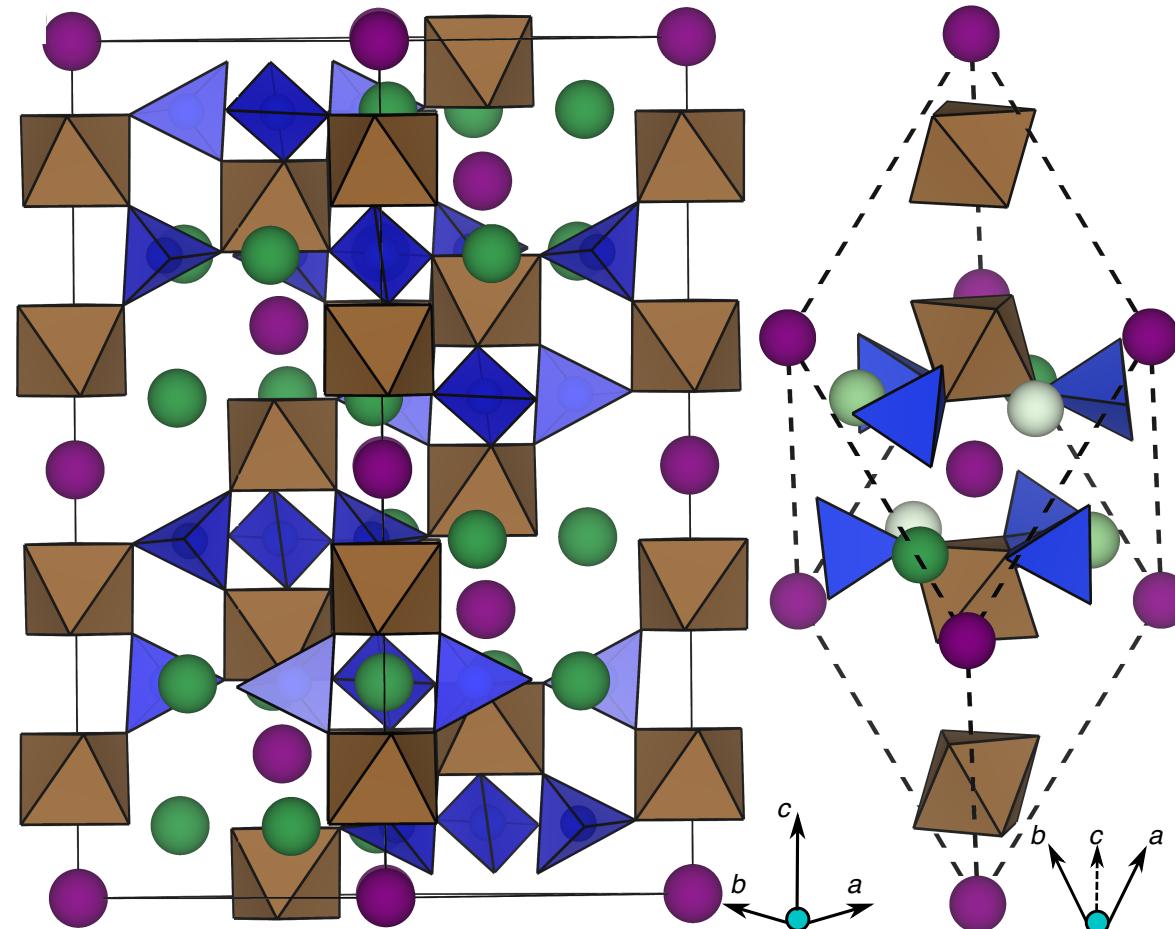


Negative (or zero) E^{hull} : stable

- 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 PO_4 , SiO_4 , or 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

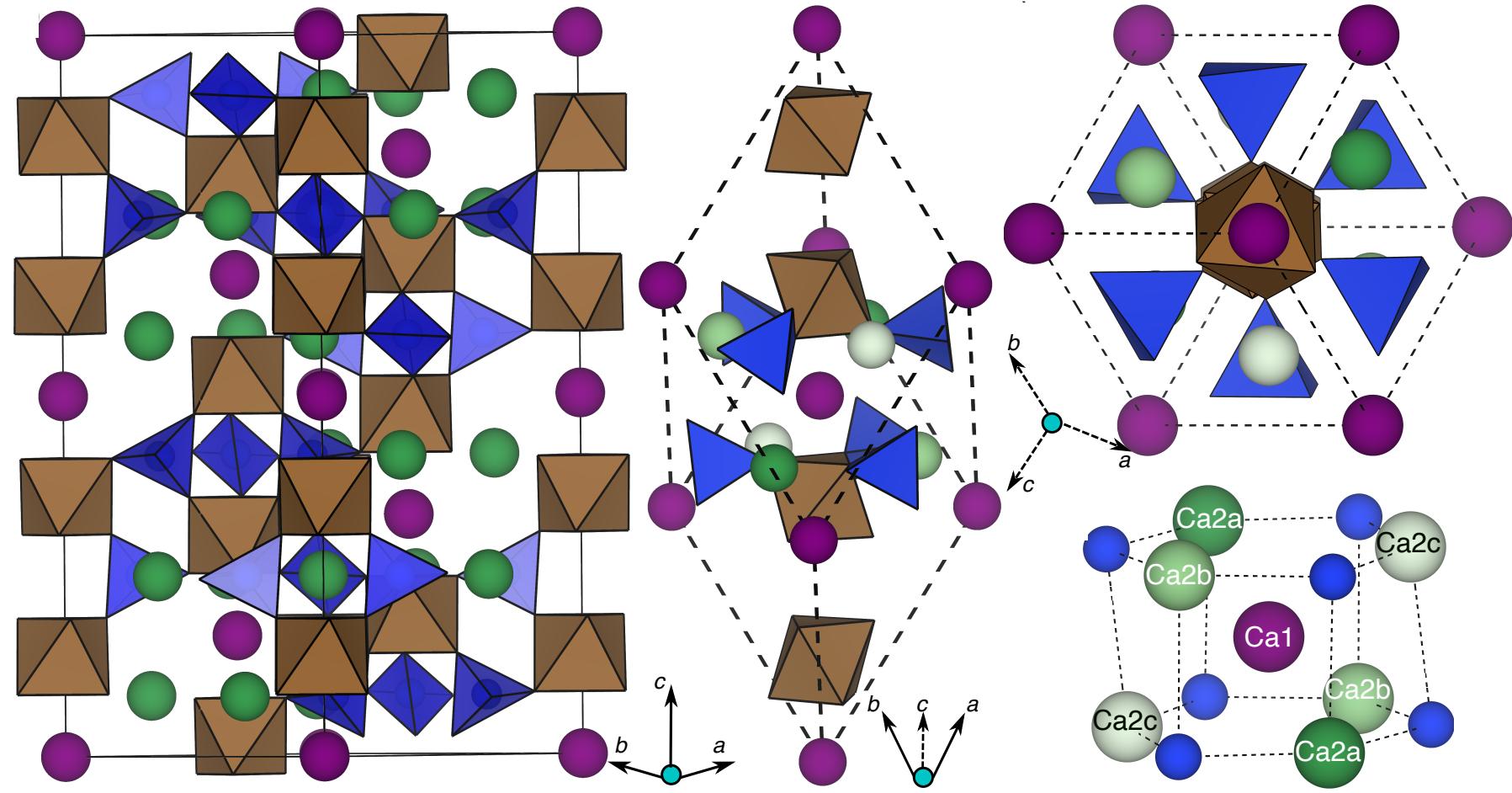
Conventional cell: 6 $\text{M}_2(\text{ZO}_4)_3$ formula units

Primitive cell: 2 formula units

NaSICONs: Polyanionic hosts with robust structural stability

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

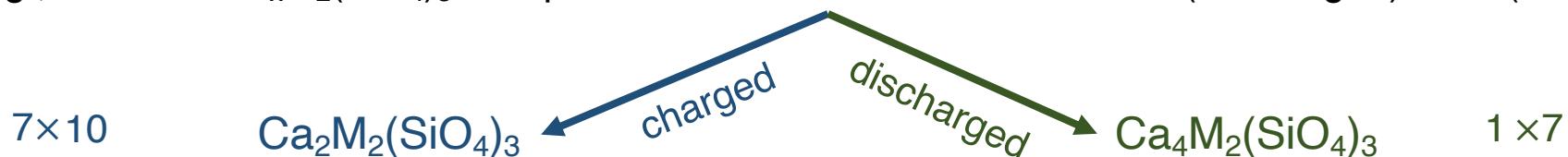
Preliminary experimental evidence is positive [Kim et al., *ACS Energy Lett.* **2020**, 5, 3203–3211]



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 $\text{Ca}_x\text{M}_2(\text{SO}_4)_3$,

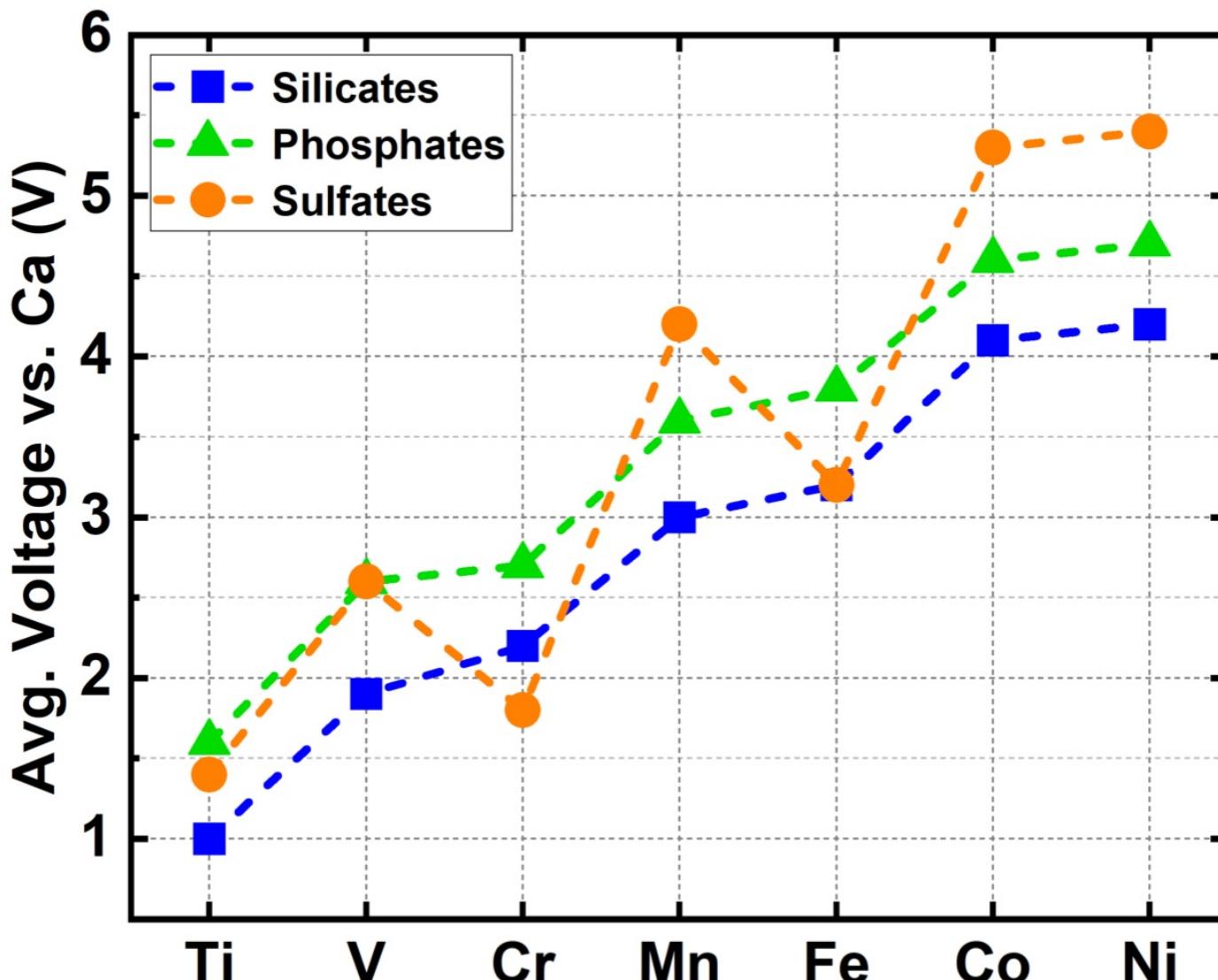


Enumerate Ca-vacancy configurations in primitive NaSiCON with pymatgen¹ for a given M

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 PO_4 and SiO_4

- Consistent with standard reduction potentials

PO_4 voltages > SiO_4

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

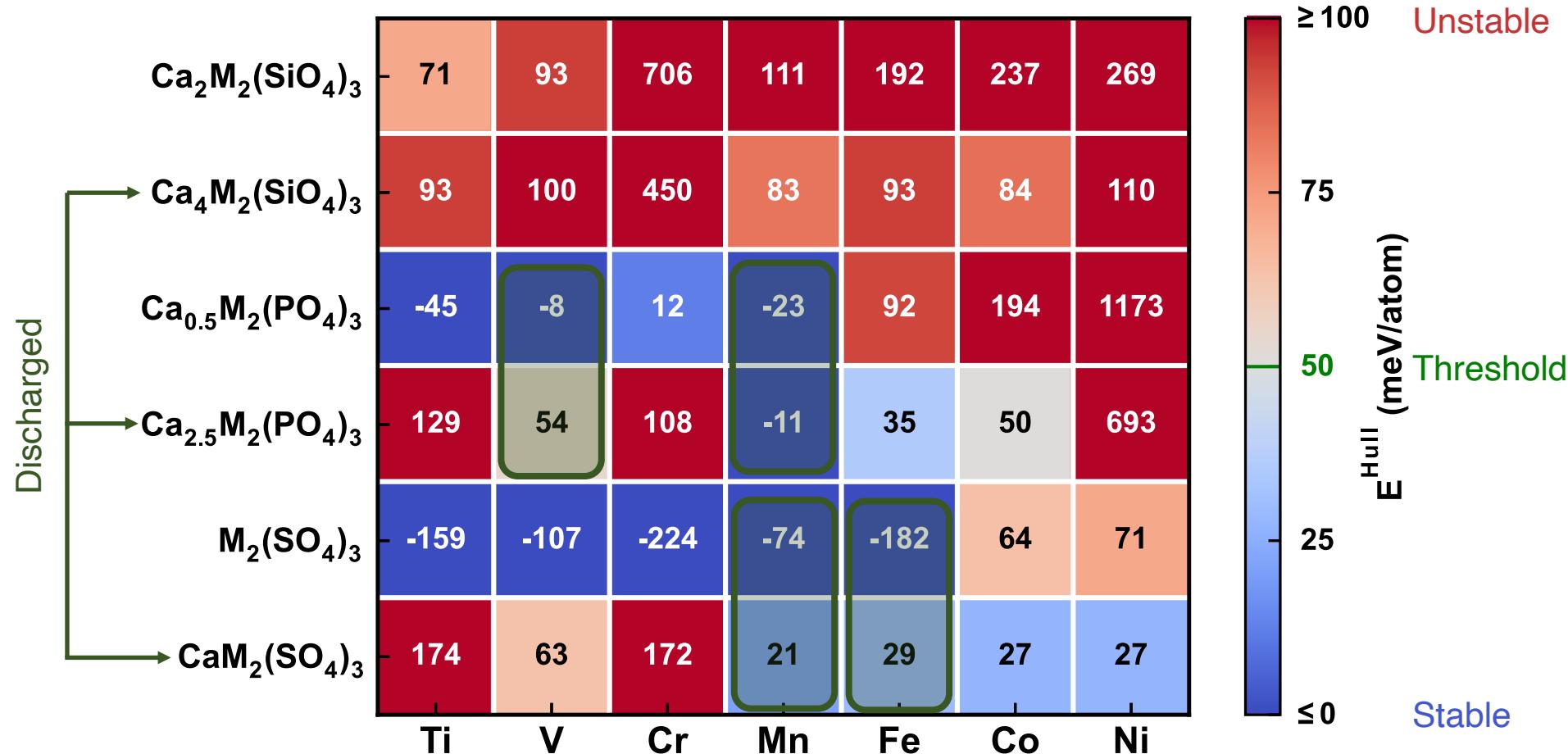
“Local” minima in voltage trends for Cr and Fe SO_4

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

Voltage \times capacity: PO_4 may be optimal

Phosphates and sulfate Ca-NaSiCONs: likely to be stable

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



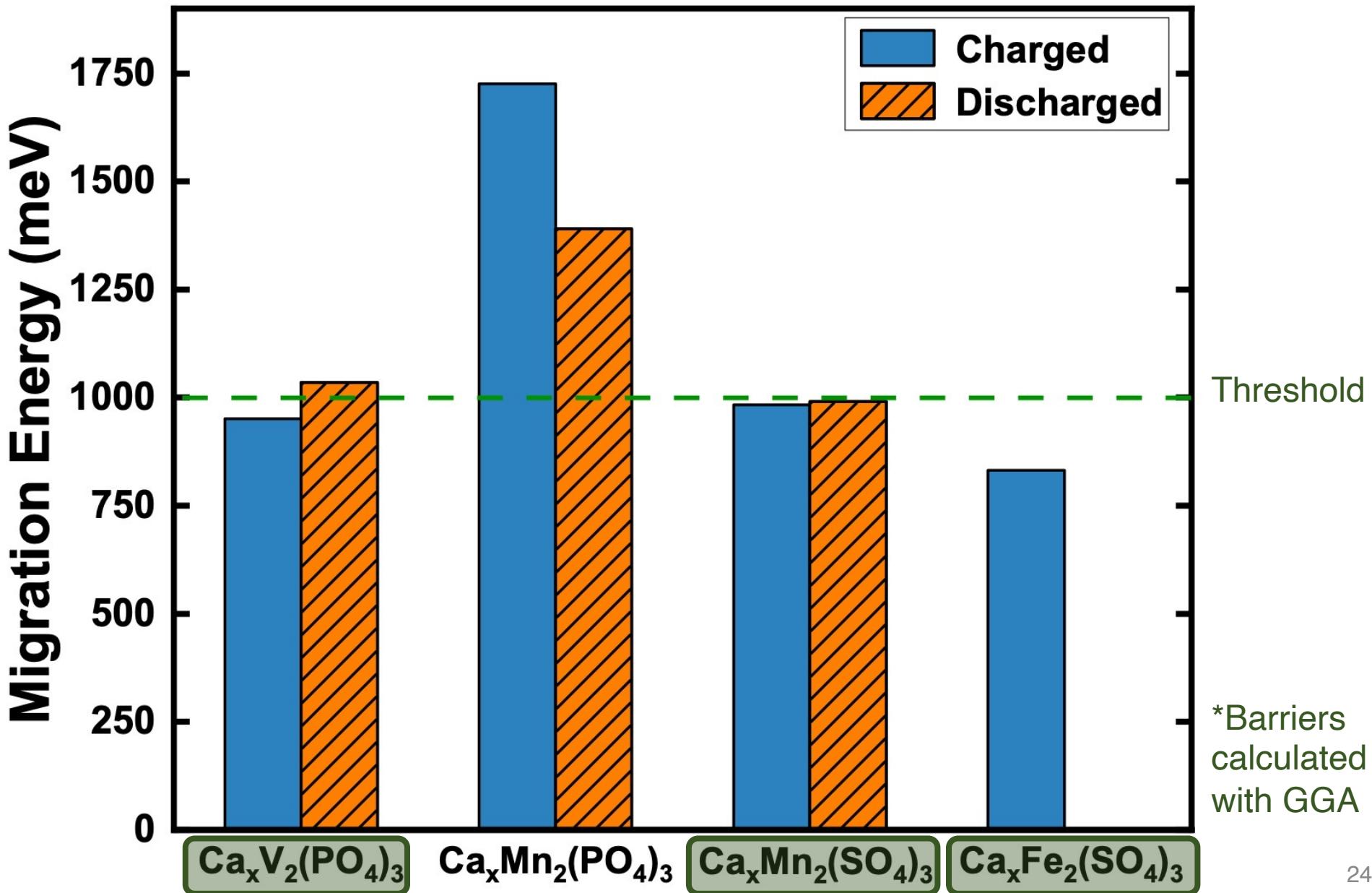
All charged and discharged silicates unstable: unsuitable for Ca-cathodes

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

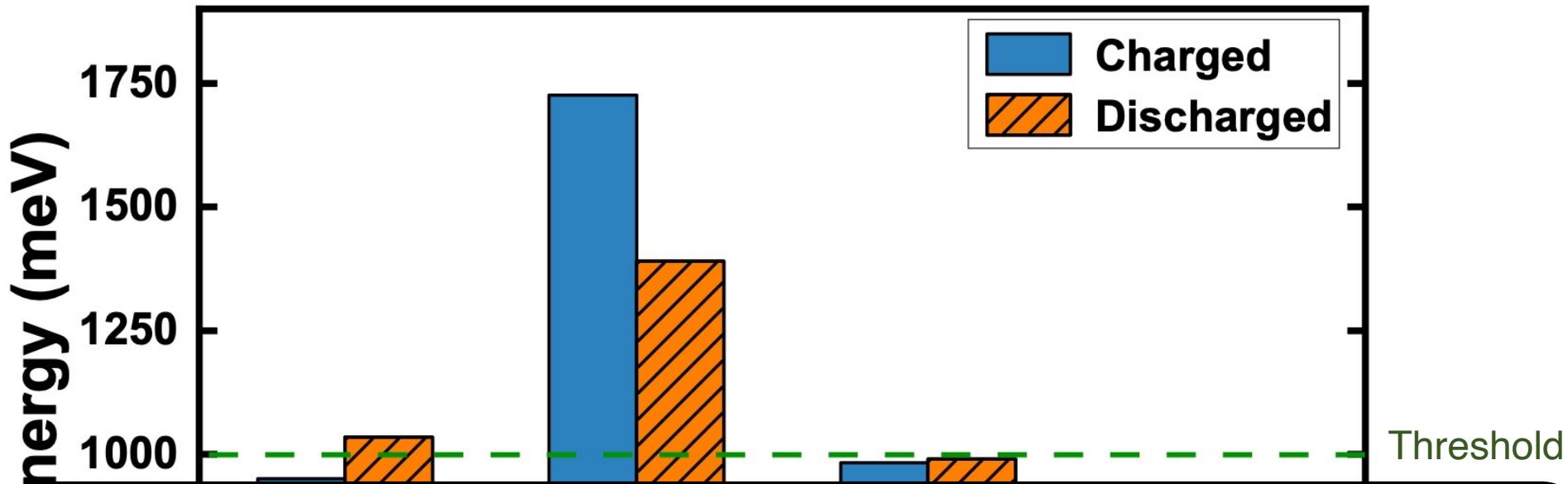
$\text{Ca}_{0.5}\text{Mn}_2(\text{PO}_4)_3$ and $\text{Ca}_{2.5}\text{Mn}_2(\text{PO}_4)_3$ stable: promising candidate!

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

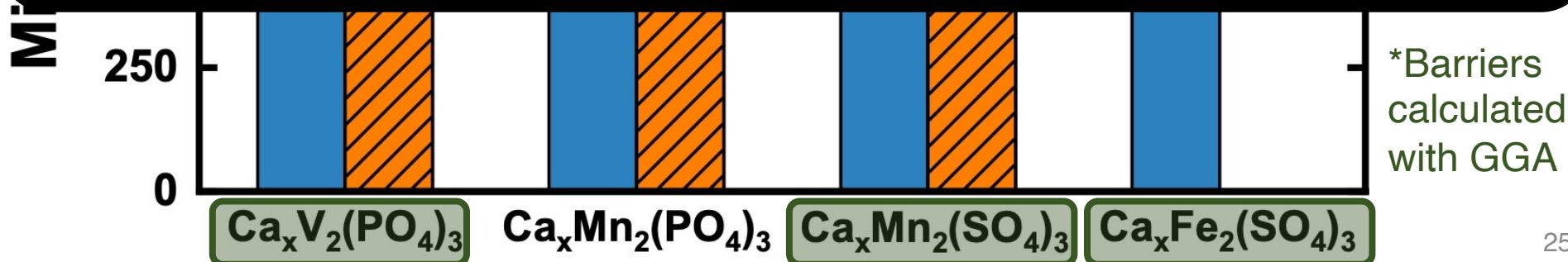


Migration barriers: 3 candidates



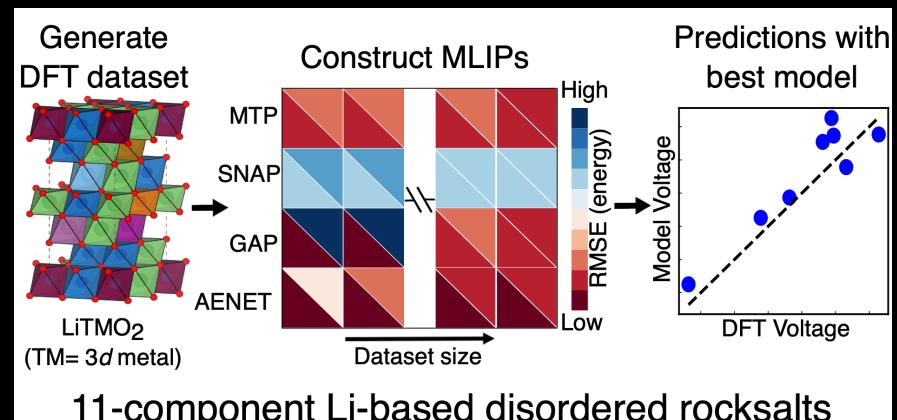
Voltage, stability and mobility screening of the NaSICON chemical space: 3 candidates

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

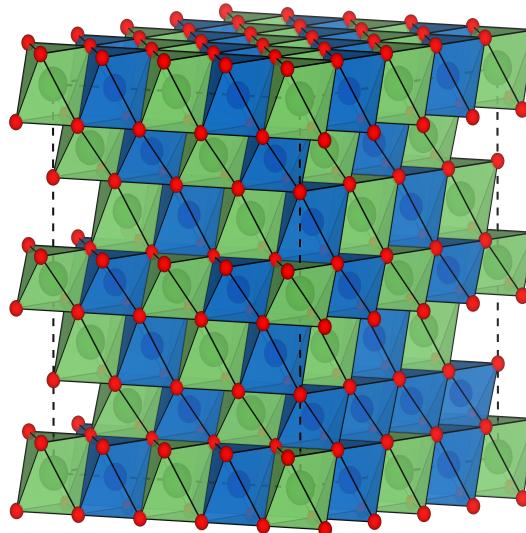
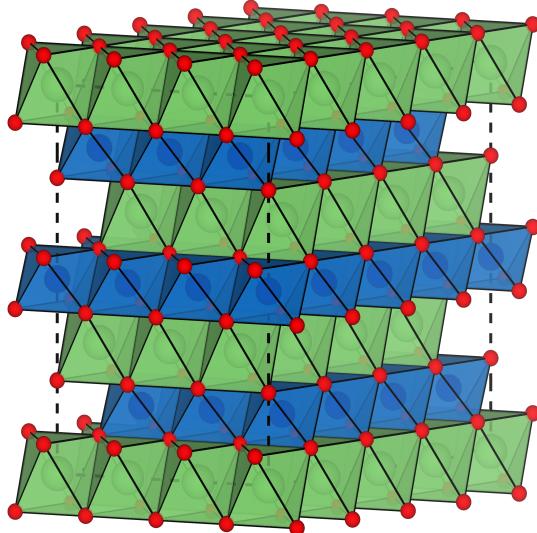




Deep dives Constructing MLIPs



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



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

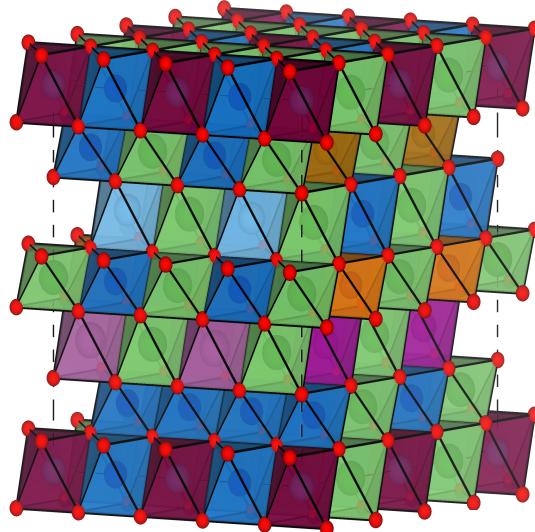
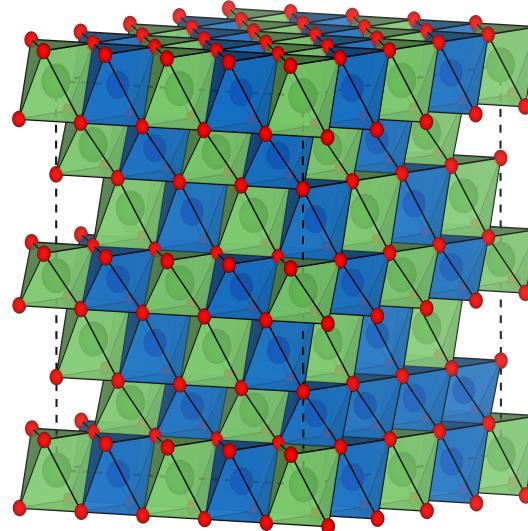
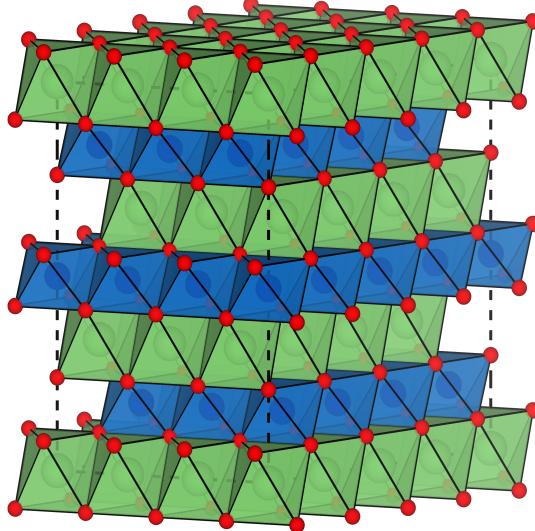
Oxygen: Face-centered-cubic lattice

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 LiTMO_2 composition

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



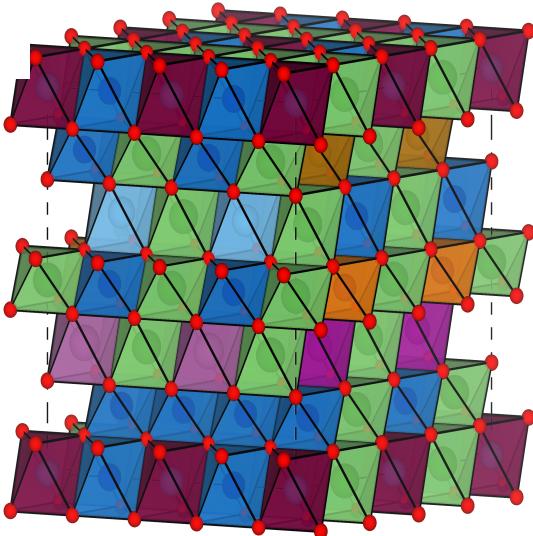
Li-excess disordered rocksalts (DRX): electrochemically active

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

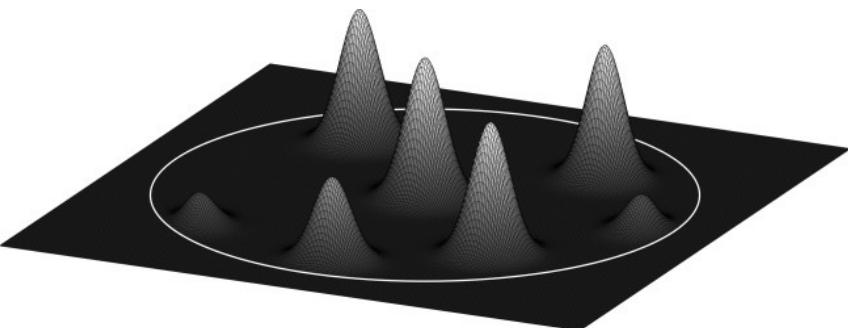
Modelling DRX is non-trivial: use MLIPs?



Large configurational space: several different arrangements of Li and TM

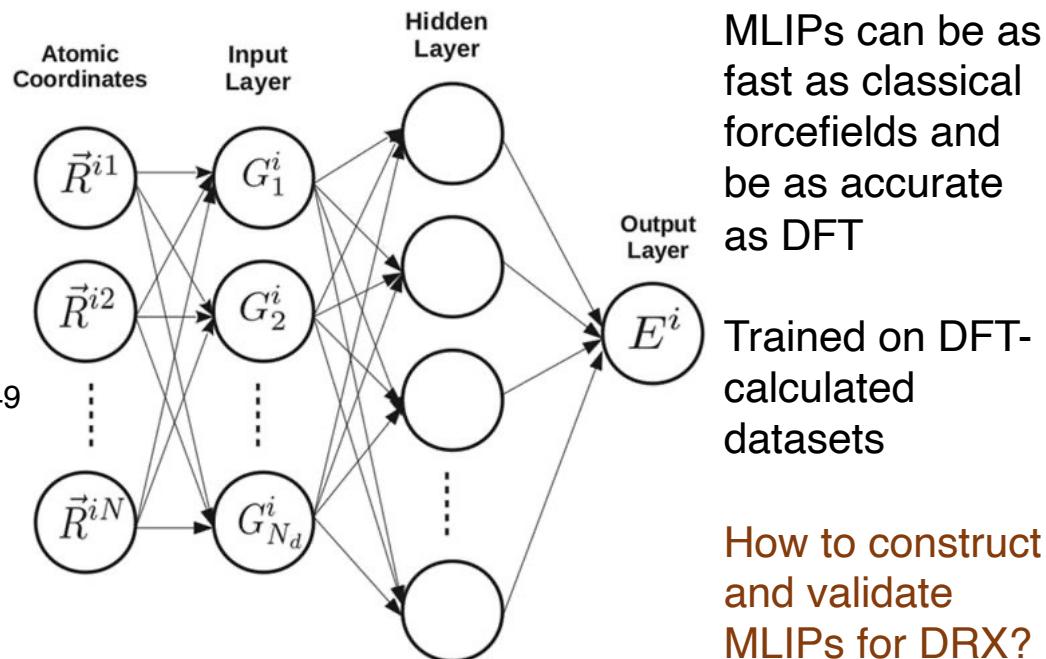
Large supercell size: for breaking long-range order

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

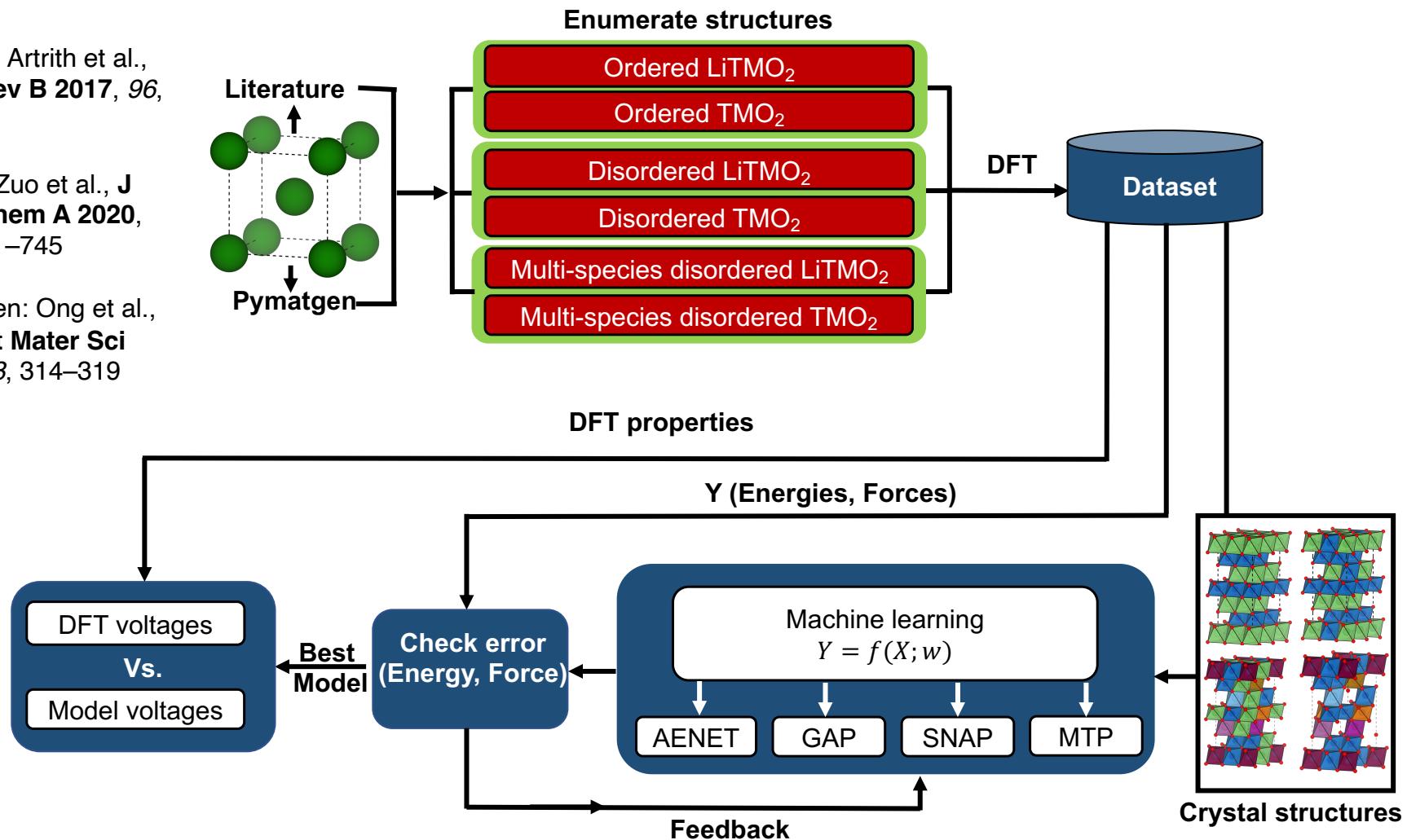
$\text{LiTMO}_2 + \text{TMO}_2$ compositions; TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and/or Cu; 11-components

“Atom-centered” MLIPs considered

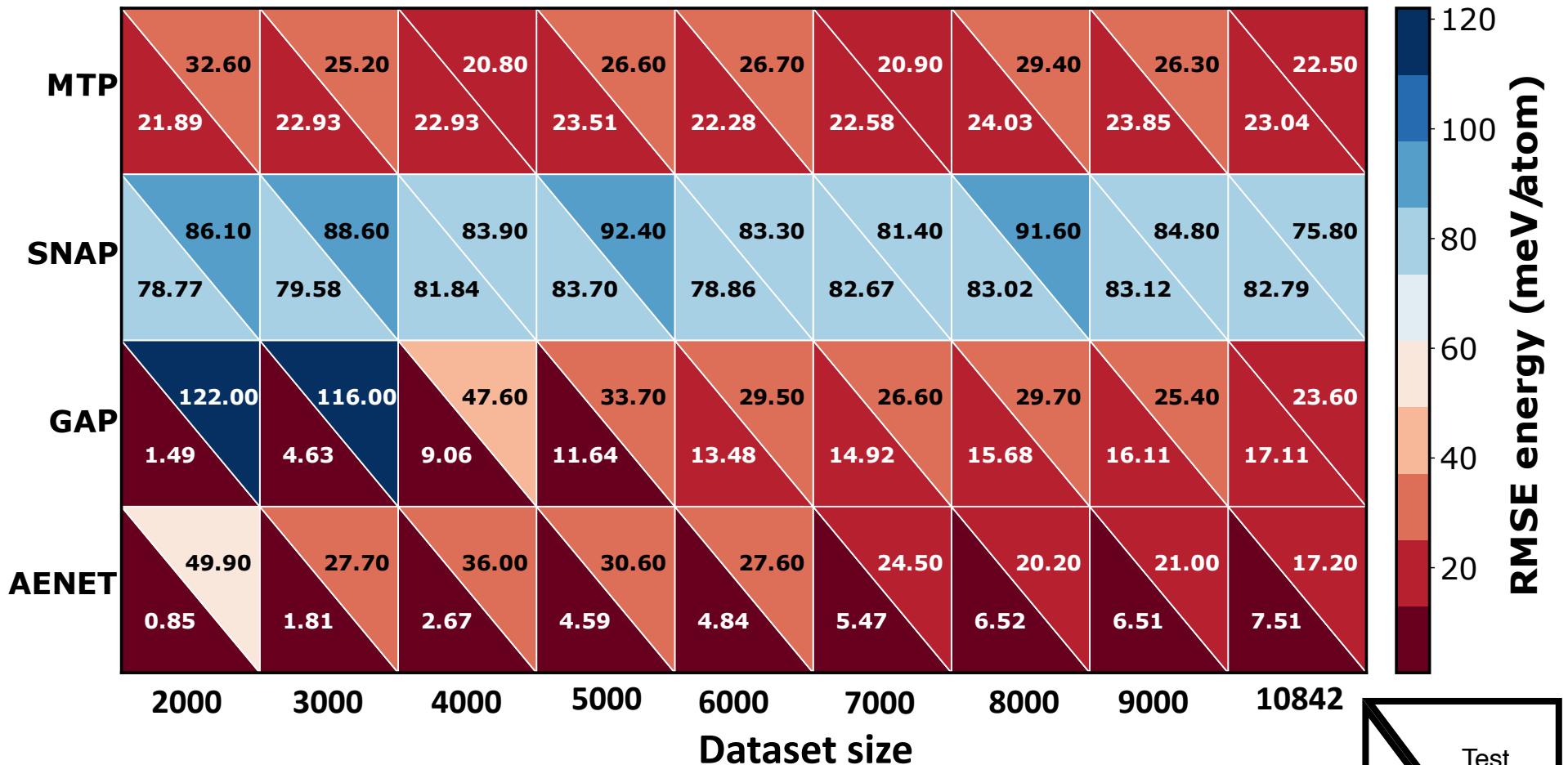
Dataset: Artrith et al.,
Phys Rev B 2017, 96,
014112

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**)

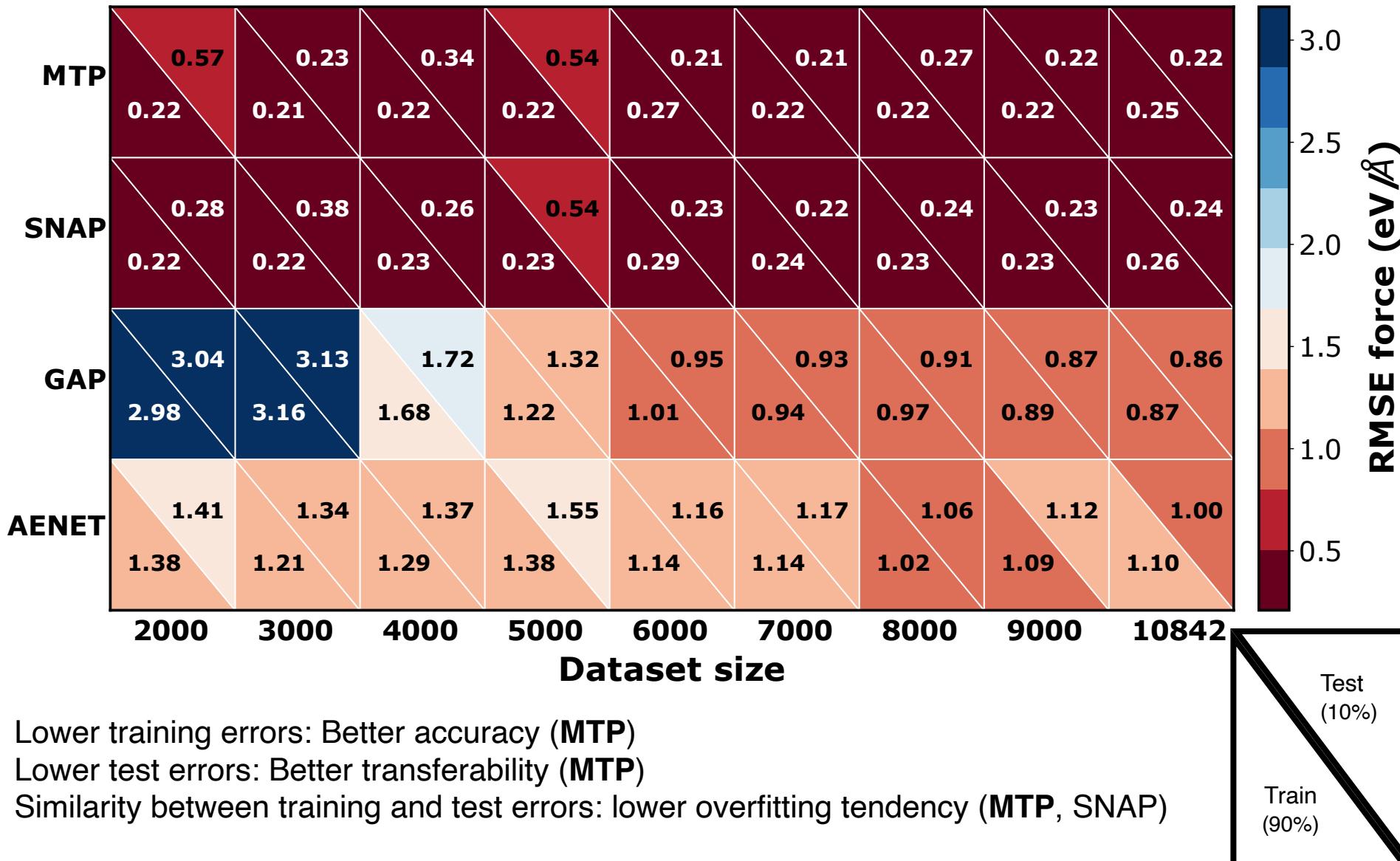
Lower test errors: Better transferability (**AENET**)

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

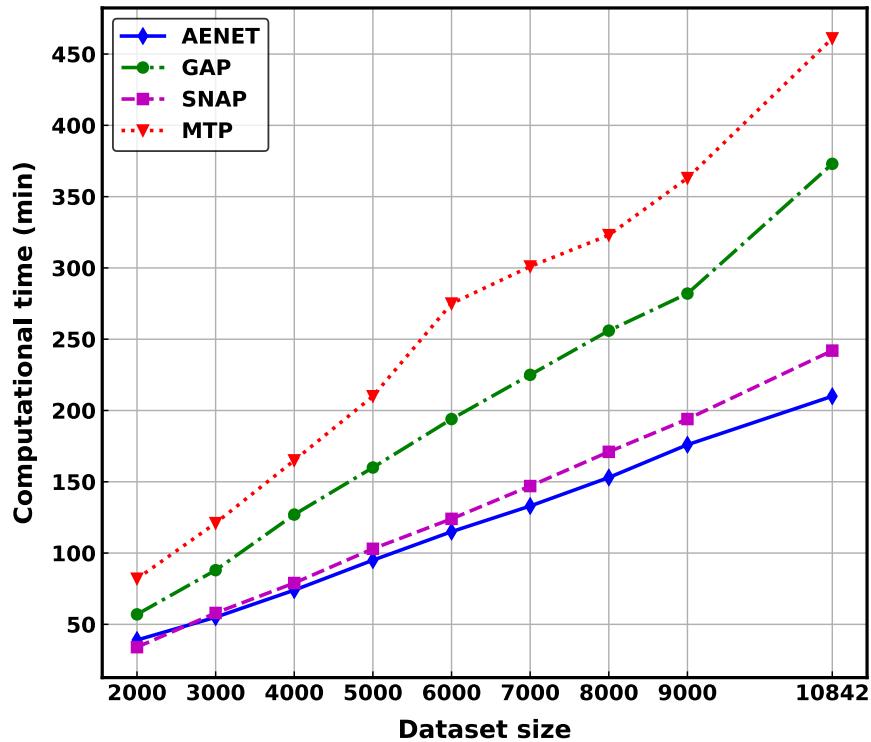
Error observations similar between **SNAP** and **qSNAP**

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”

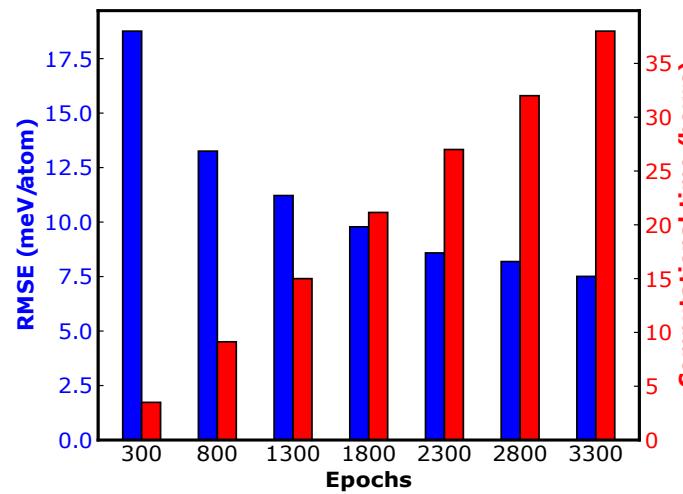
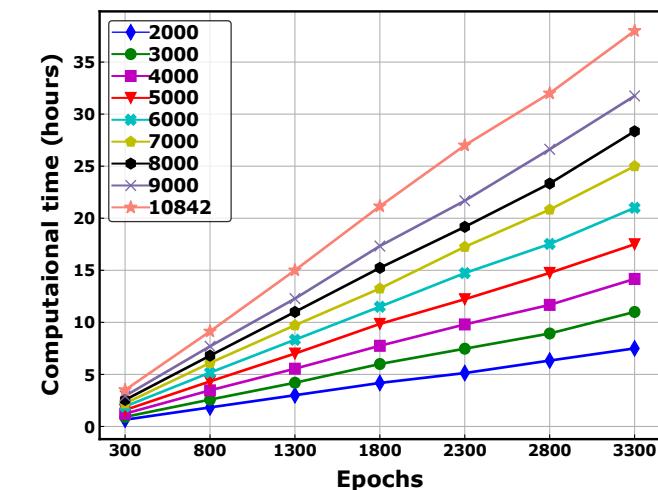


Compute training time on a single core of Intel® Xeon® Gold 6271 CPU

AENET fastest to train at 300 epochs (training iterations)

MTP slowest to train

SNAP is fastest at small datasets

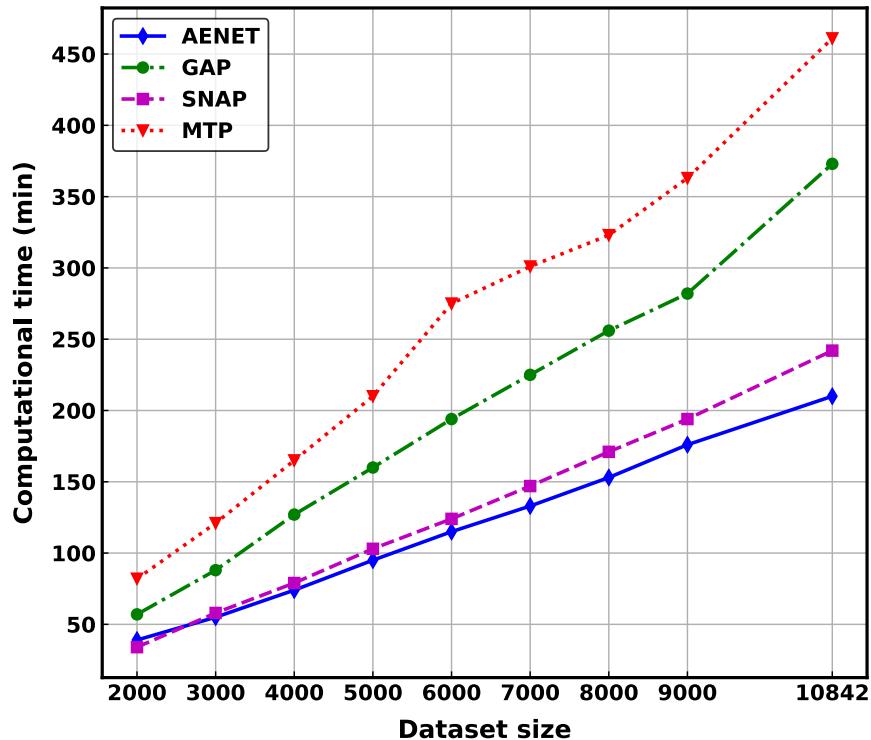


AENET training time increases significantly with higher epochs

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

Training error decrease saturates after 2300 epochs

Ease of training: AENET at low “epochs”



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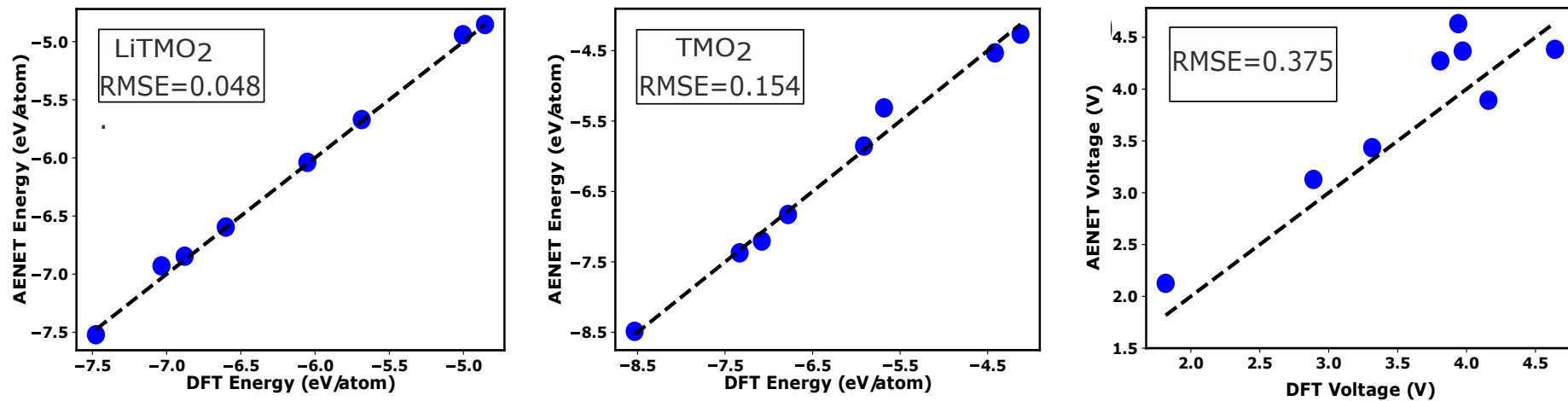
AENET training time increases significantly with higher epochs

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 LiTMO₂ and TMO₂

- Higher errors in TMO₂ expected: lower amount of TMO₂ data in training dataset
- Percentage errors are low (0.55% for LiTMO₂ and 2.12% for TMO₂)

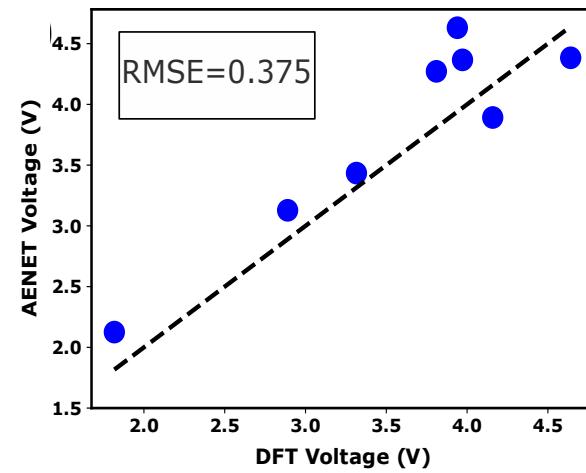
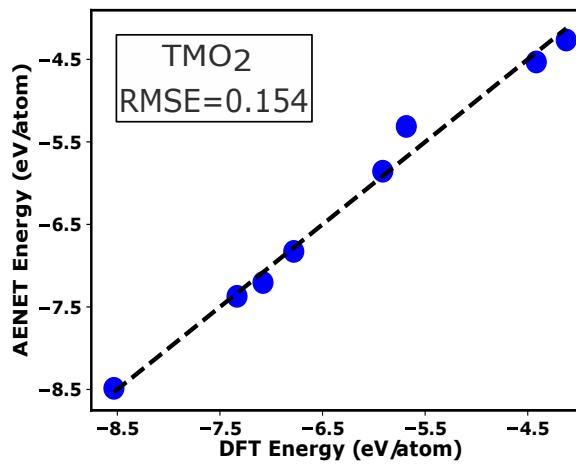
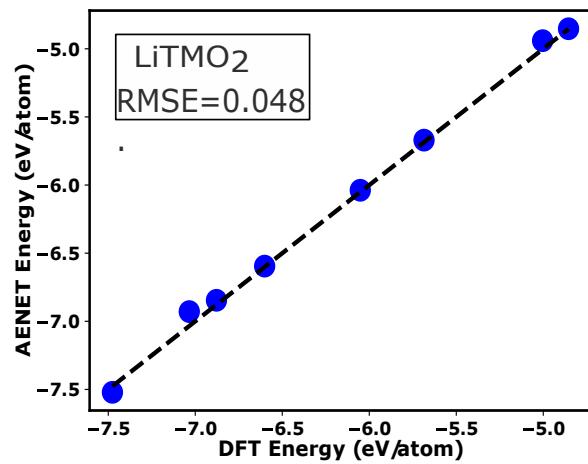
Voltage predictions: AENET has an average error of 10%

- MAE: 0.34 V; RMSE: 0.375 V
- There is compounding of error from LiTMO₂ and TMO₂
- Largest errors in LiFeO₂ and LiTiO₂ (~17%)

Scope for improvement with more training data

- Qualitative trends may be useful for screening

Voltage predictions: AENET is reasonable



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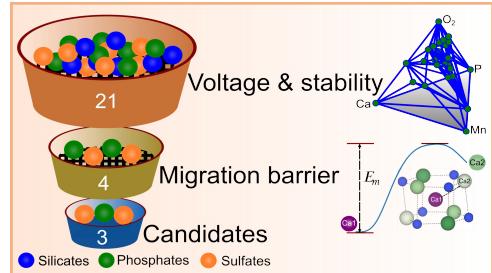
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MLIPs, if carefully constructed, are useful for modelling complex configurational spaces!

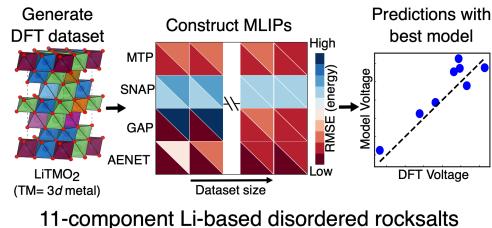
Conclusions



- 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*