Using computations and machine learning in designing materials for energy storage

Sai Gautam Gopalakrishnan

Materials Engineering, Indian Institute of Science

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

Computational modelling and simulations of materials for energy and environment
Theoretical Sciences Unit, JNCASR
December 14, 2022

Acknowledgments

Sai Gautam Gopalakrishnan
Principal Investigator

Reshma Devi Parthasarathy
Ph. D. student

Debolina Deb
Ph. D. student

Dereje Bekele Tekliye
Ph. D. student

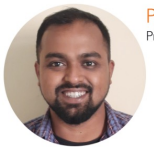
Ankur Srivastava
Ph. D. student (co-advised)

Vijay Choyal
Institute of Eminence Fellow

Adilakshmi Chirumamilla
Masters student

Sachin Kumar
Masters student

Javeed Ahmad Dar
Ph.D. student

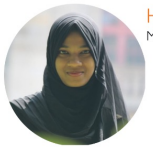


Pritam Ghosh
Project Associate

Sougat Purohit
Ph.D. student

Ankit Kumar Gupta
Masters student

Arnab Pyne
Masters student



Hasna Sabreen
Masters student

Piero Canepa
NUS
+CaRe group

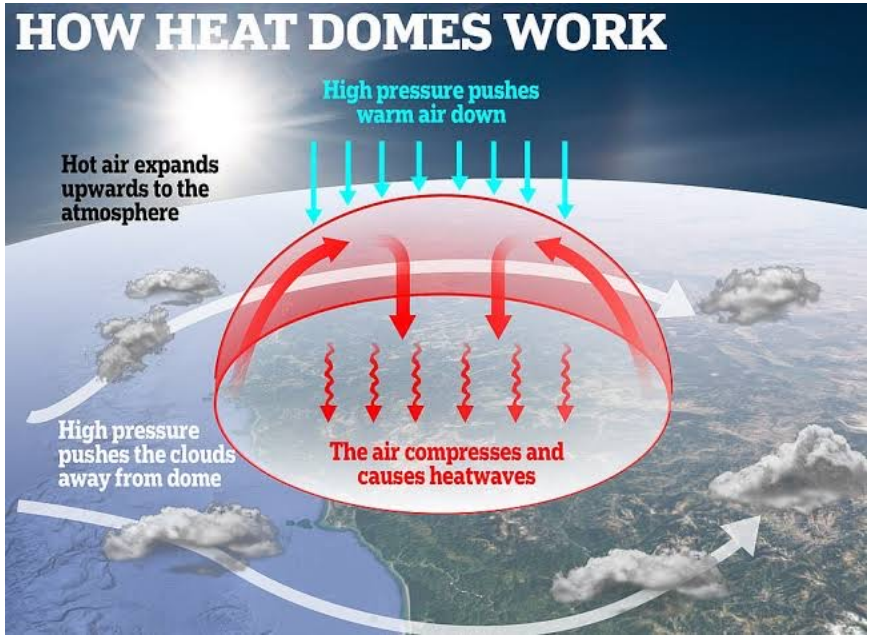
Prabeer Barpanda
MRC
IISc

Premkumar Senguttuvan
New Chemistry Unit
JNCASR

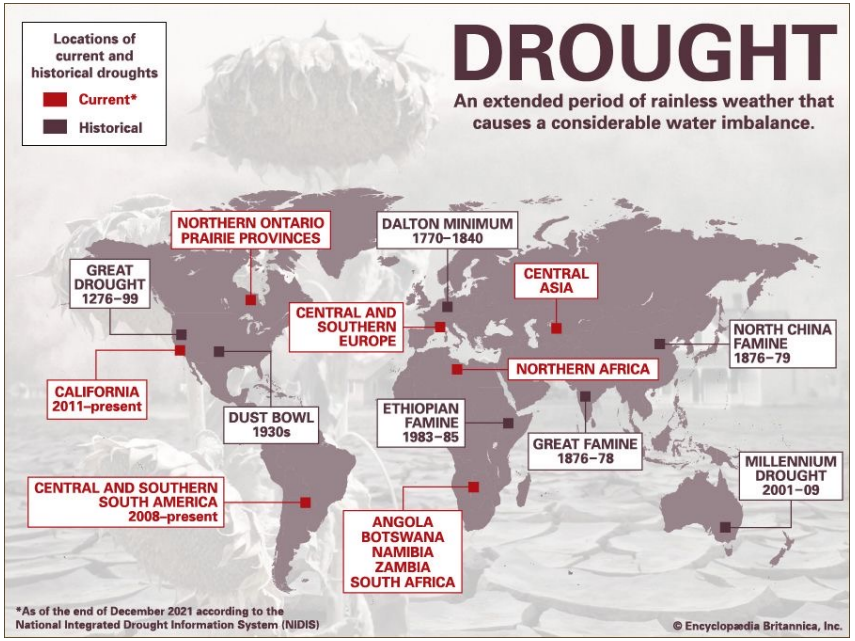
May 2022

+other collaborators, computing resources, …

Climate change is here

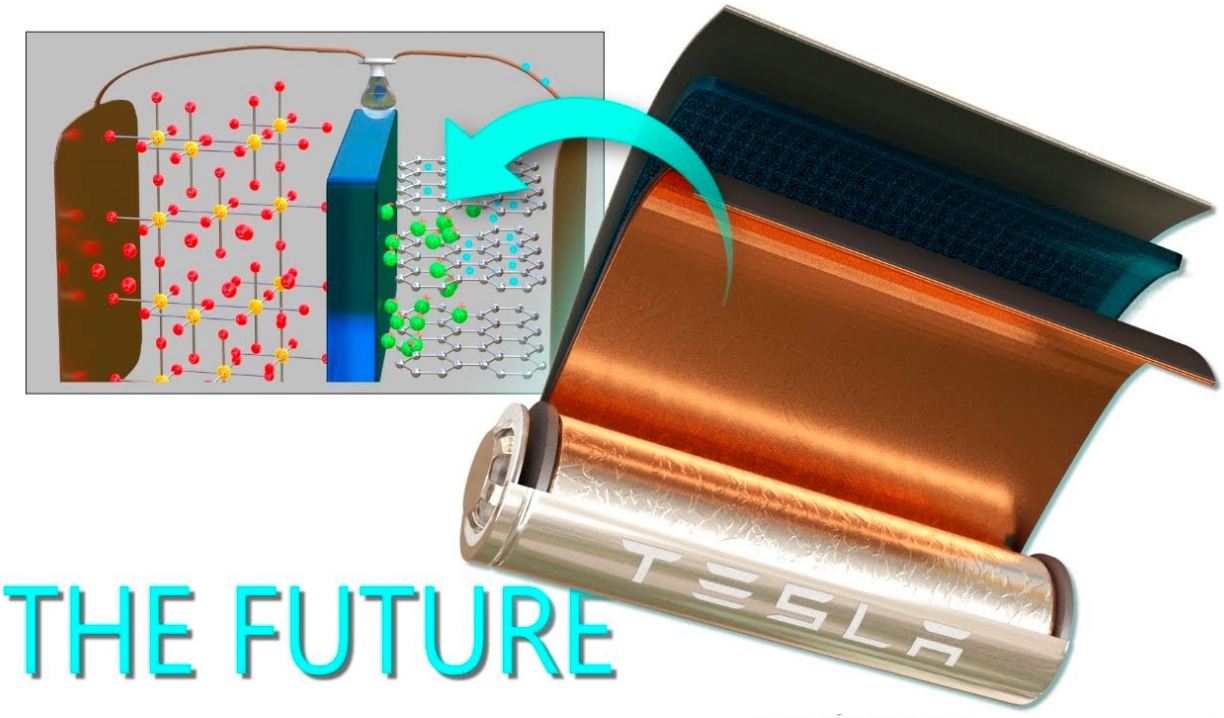


Heat waves and wildfires



Droughts and floods

Non-fossil-fuel options for mitigating climate change



When the sun doesn't shine or the wind doesn't blow

Materials form the performance-bottlenecks of most renewable energy devices: **how do we understand and improve the material bottlenecks?**

- Look at what material properties govern energy devices first
- How can we improve the amount of energy stored (i.e., energy density) and rate performance (i.e., power density) in a battery?
- Novel materials have to be synthesized first: thermodynamic stability!

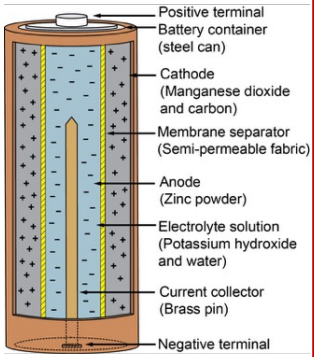
How batteries work?

Batteries: what type do you need?

Primary:
"Use once"

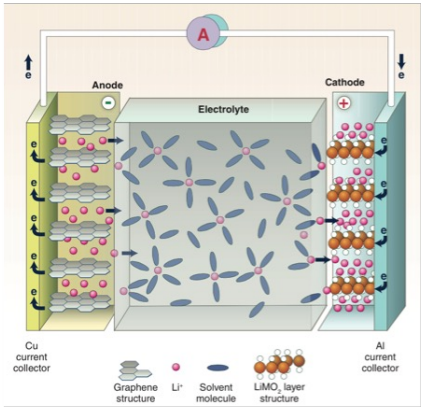
Secondary:
"Rechargeable"

Solid-liquid-solid



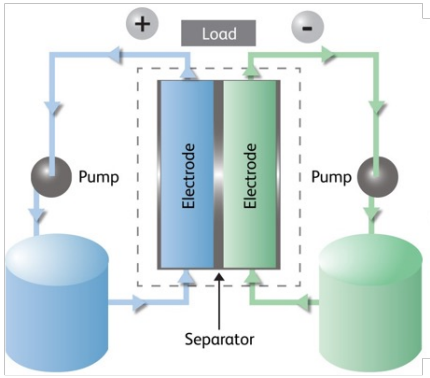
Alkaline

Intercalation-liquid-Intercalation



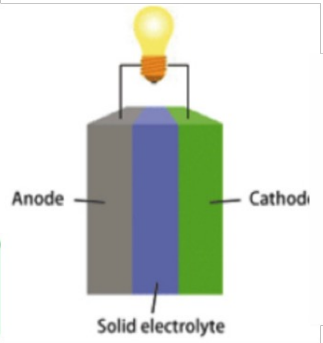
Li-ion

Liquid-Solid-Liquid



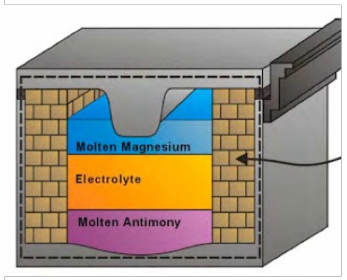
Flow

Solid-solid-solid



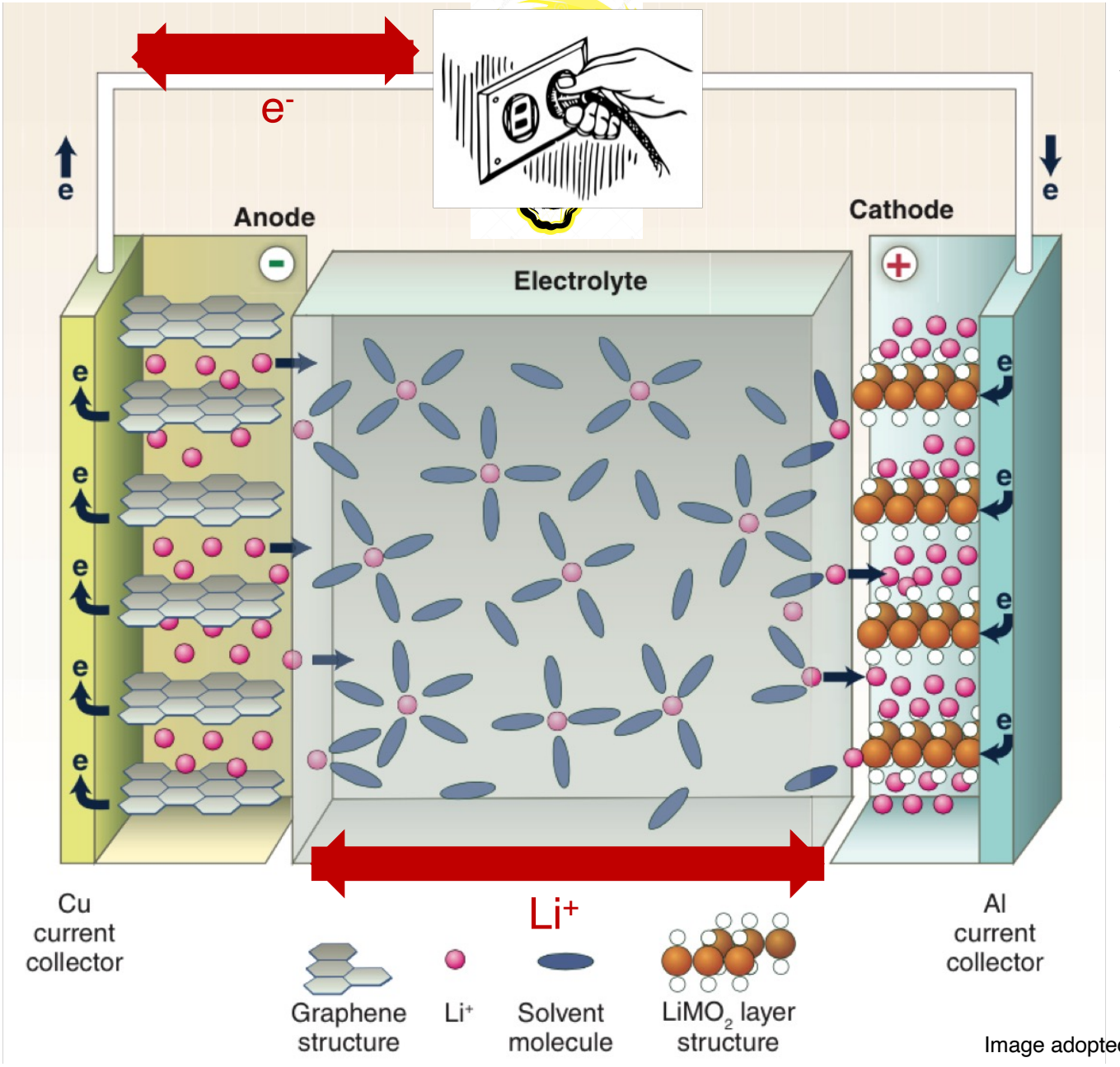
All-solid-state

Liquid-liquid-liquid



Liquid metal

How does the modern Li-ion battery work?



Voltage (V): Potential to do work

Capacity (mAh): Amount of charge stored

Voltage*capacity: Energy stored

Rate (C): How fast can a battery be charged and discharged?

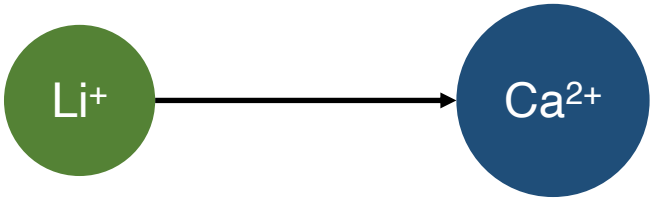
All performance metrics of a battery system are **material dependent**: anode, cathode, and electrolyte

Image adopted from B. Dunn et al., Science 2011

Why beyond-Li-ion batteries?

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

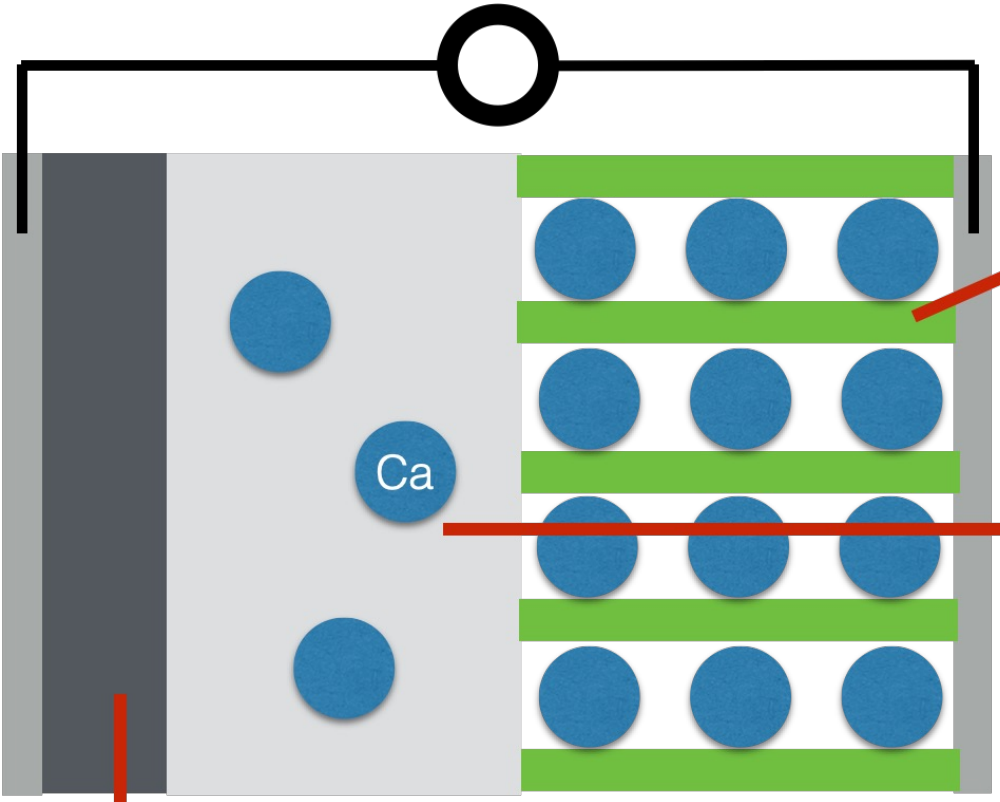
- Multi-valent == More electrons (Ca^{2+}, Mg^{2+}, Al^{3+}, etc.)
- Large volumetric energy density == Smaller batteries
- Li-ion technology approaching fundamental limits
  - Safety, supply-chain constraints; limits on achievable energy densities



Why Ca?

- Superior volumetric capacity for Ca metal (~2077 Ah/l) than Li in graphite (~800 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



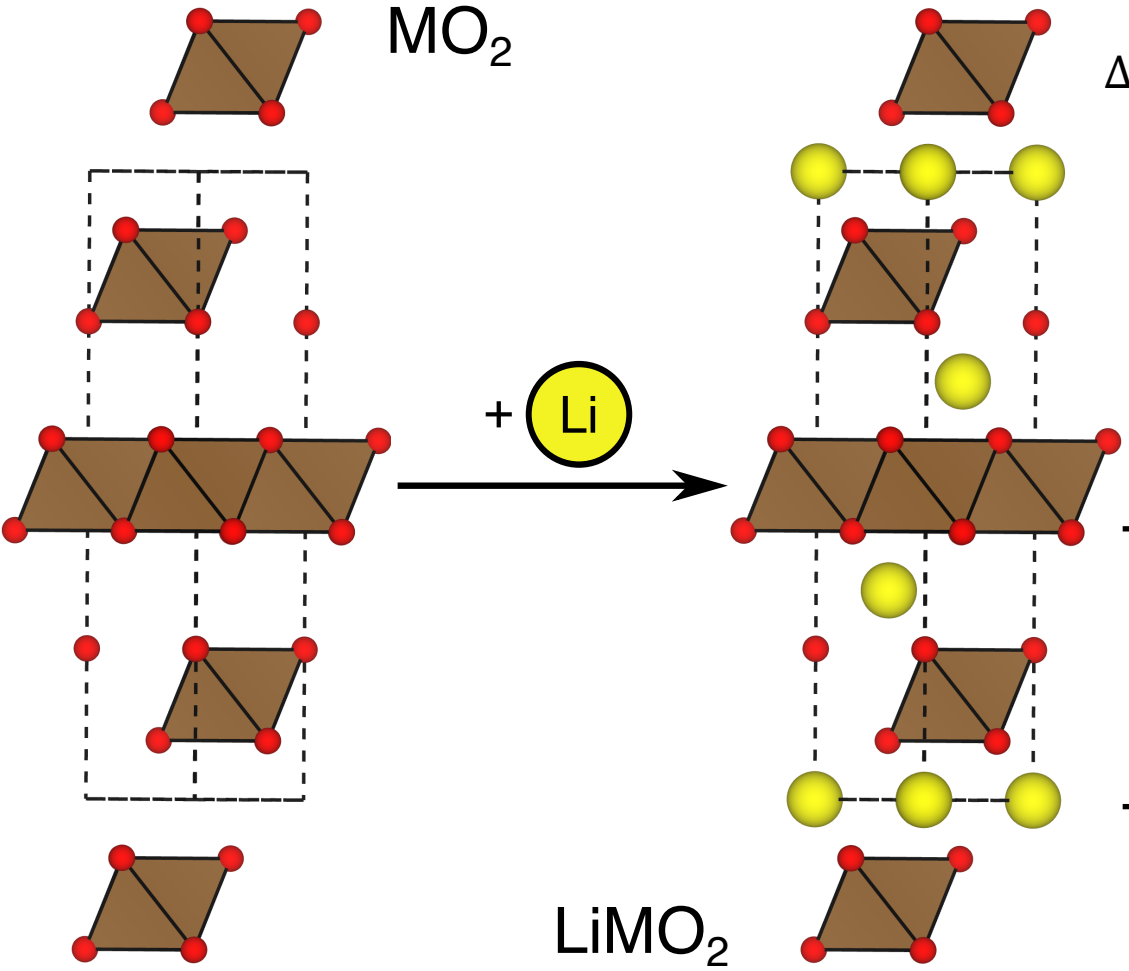
Intercalation Cathode:
High Voltage
High Capacity
High Mobility
Good cycle life

Electrolyte:
Stable electrolyte (at both electrodes) with good conductivity

Metal Anode:
Understand plating and stripping in organic electrolytes

Ca: Find cathodes with reasonable voltage, capacity, and mobility, and be stable
If possible: find solid electrolytes with good stability and ionic mobility!

Voltage, capacity, and rate in Li-ion batteries



Charged cathode Discharged cathode

$$\Delta G_{intercalation} = G_{LiMO_2} - G_{MO_2} - G_{Li}$$

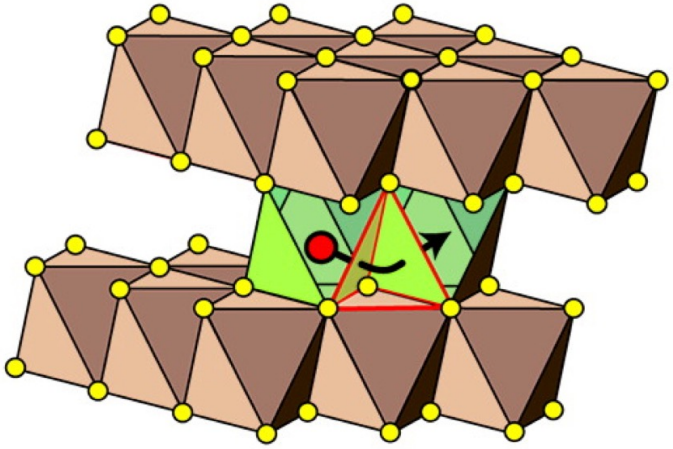
Nernst Equation

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

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

1 Li moved = 1 electron stored

$$\text{Capacity} \propto \frac{\#\ Li\ moved}{\#\ 'Framework'\ atoms}$$

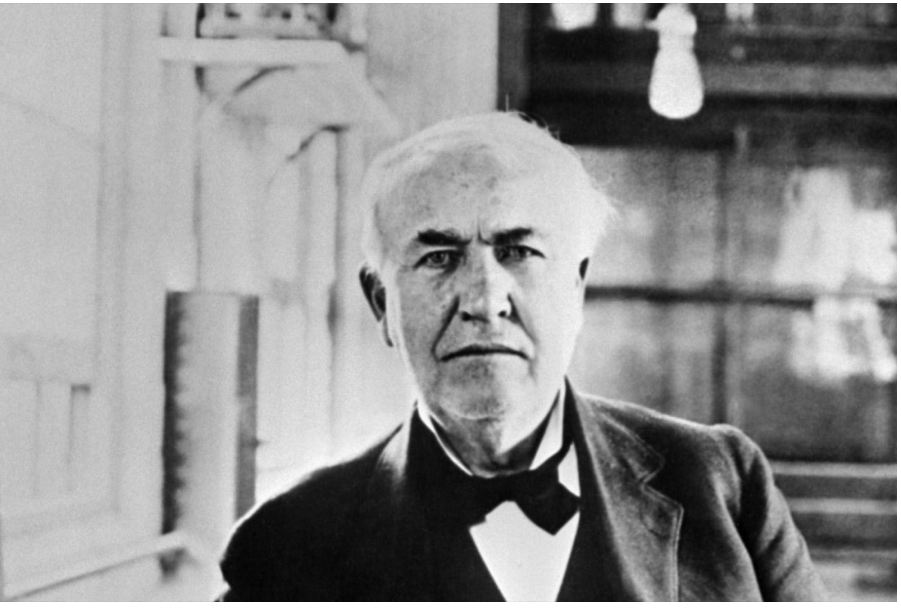


Rate: how fast can Li move (or diffuse) within electrode?

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

How do computations contribute?

Edison vs. Iron Man



Trial and error of candidates in a lab

Simulate and identify candidates
(on a transparent touch screen preferably)

Reality: Do an accelerated Edison on a (big) computer

- Key: **predict/calculate** material properties
- Can be smarter than simple trial-and-error (human intuition +/- machine learning)

Density functional theory (DFT): Predict material properties

$$H\psi = E\psi$$

Total energy at 0 K ≈ Gibbs energy → Voltage + Stability

Density of states → Band gap → Electronic conductivity

Barriers for atomic migration → Kinetics → Rate

Defects → Electronic conductivity → Solid electrolytes

Large data using DFT → Use machine learning (ML)

Schrödinger equation: can't be solved analytically for multi-electron systems (and not solvable numerically for most solids)

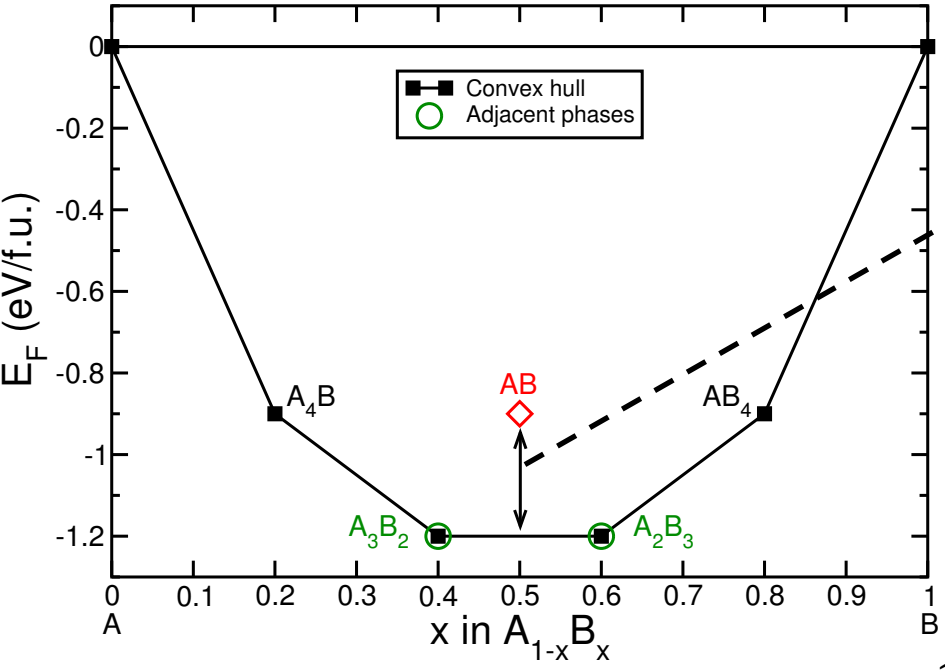
DFT: Approximate the many-body electronic wavefunction Hamiltonian (of Schrödinger) into a simpler, non-interacting mean-field model

- Replace ψ with electron density (ρ)
- Key approximation: how quantum mechanical interactions are treated (exchange and correlation)

PV == Photovoltaic

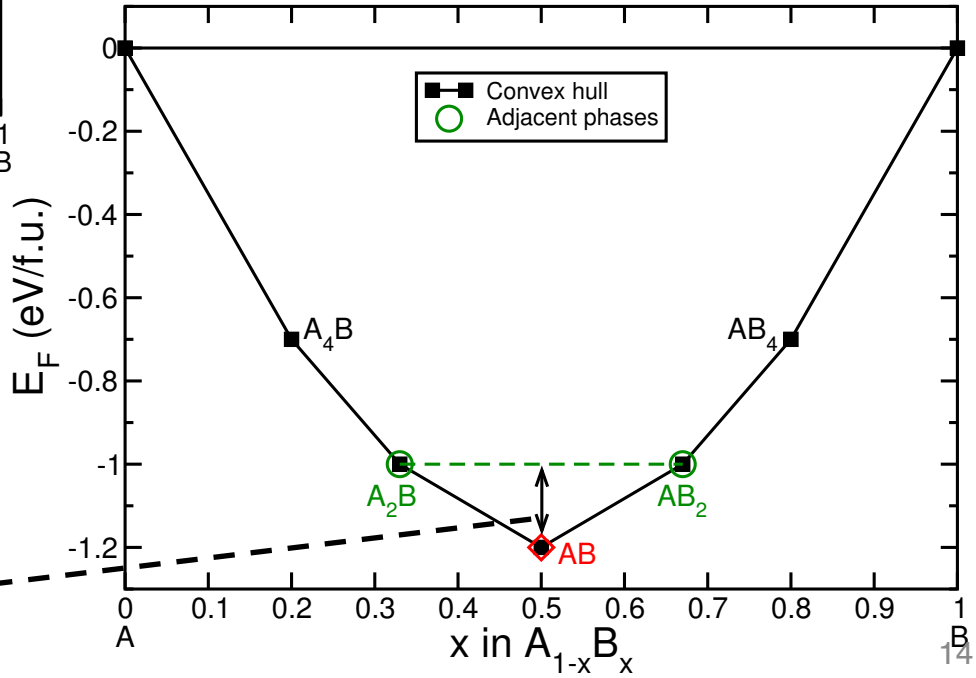
0 K thermodynamics: convex hull

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)

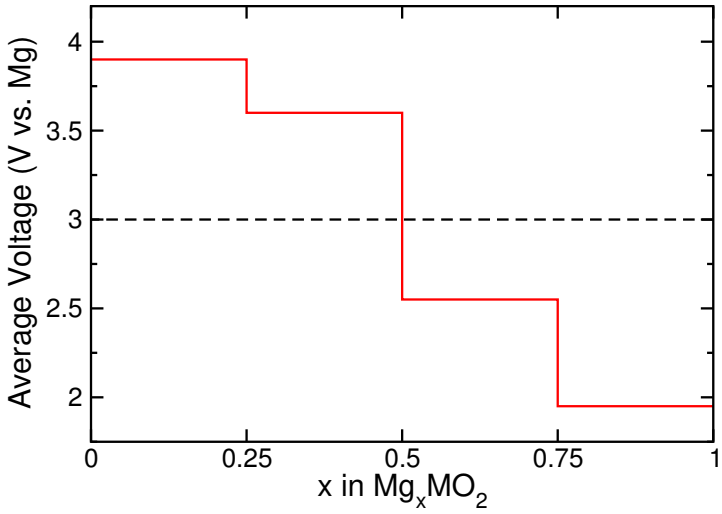
- Largest energy release via decomposition of AB



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

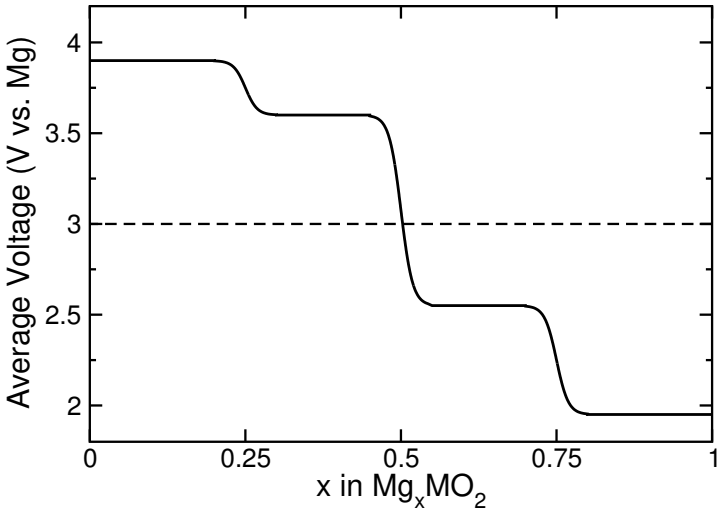
- Lowest energy release via formation of AB

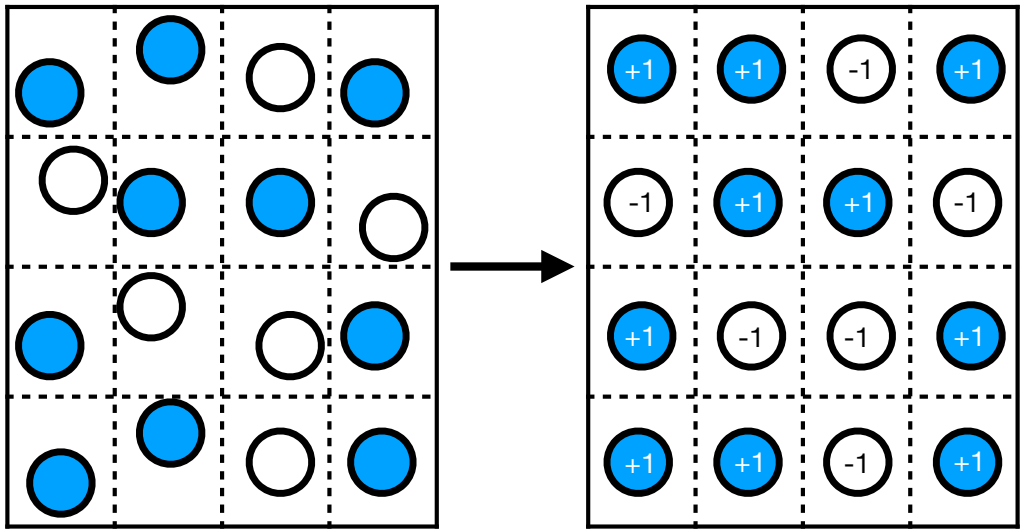
Lattice models and Monte Carlo



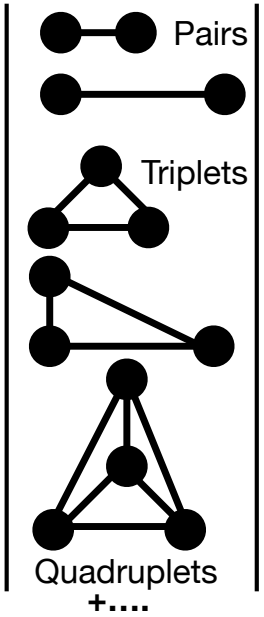
As temperature rises

Entropic contributions
Mainly configurational





=



Generalized Ising model (cluster expansion)

+

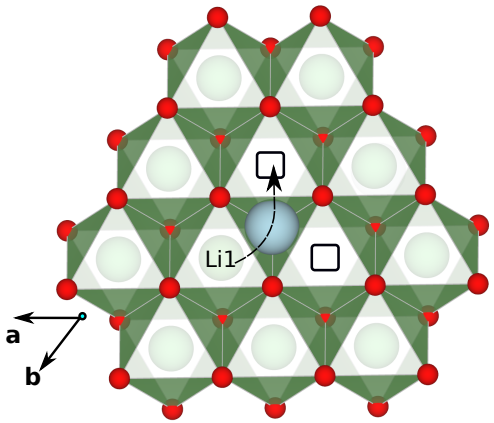
Grand-canonical Monte-Carlo (Metropolis)

=

Configurational entropy contributions

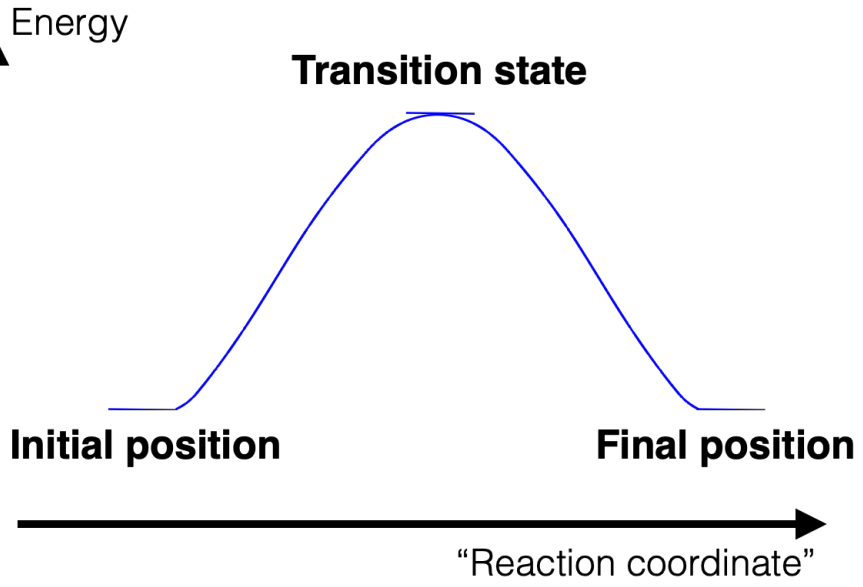
$$E(\sigma) = \sum_{\alpha} m_{\alpha} V_{\alpha} \left\langle \prod_{i \epsilon \beta} \sigma_i \right\rangle$$

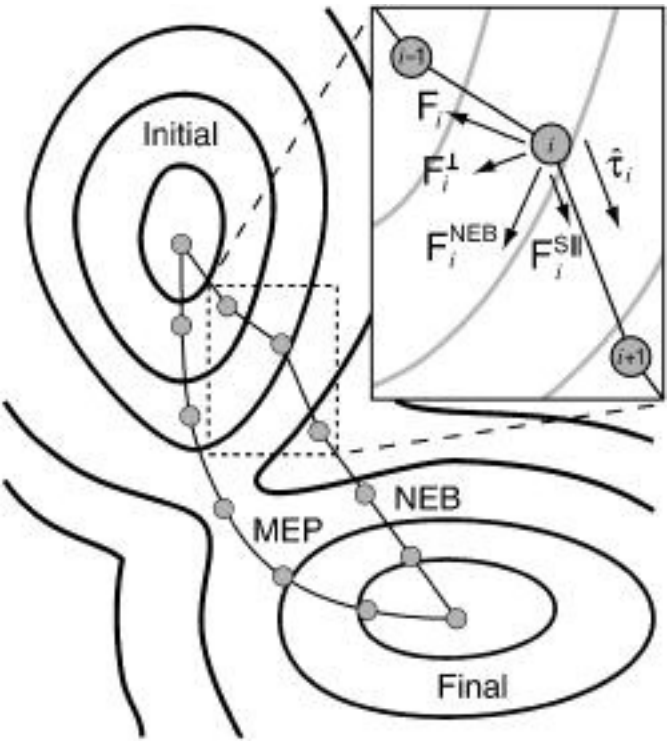
Nudged elastic band (NEB)



Diffusion in solids = series of ionic migrations or hops

Each migration event can be modelled via transition-state-theory





NEB: can estimate E_m for an ionic hop from one "stable" site to another

Saddle-point finder by optimizing forces "perpendicular" to the potential energy surface

NEB often used with DFT: approximations within DFT affect NEB estimates

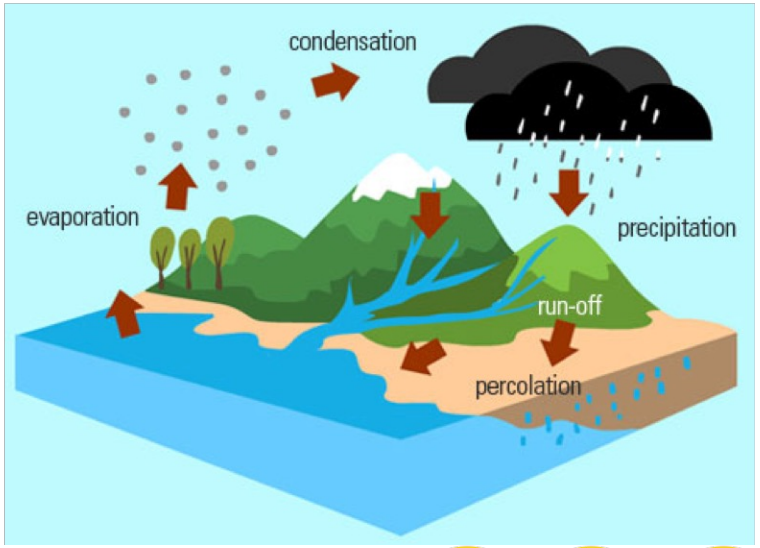
Molecular dynamics (MD): can also be used to estimate diffusivity and/or migration barriers

Sheppard et al., **J. Chem. Phys. 2008**, *128*, 134106

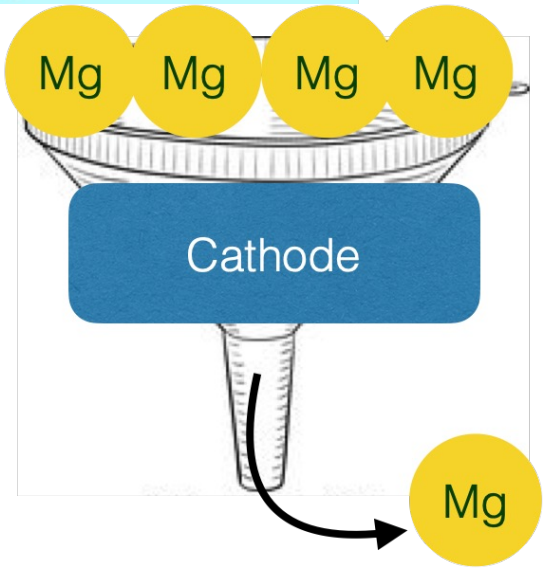
How do random ionic hops translate to macroscopic ionic transport?

Percolation in nature

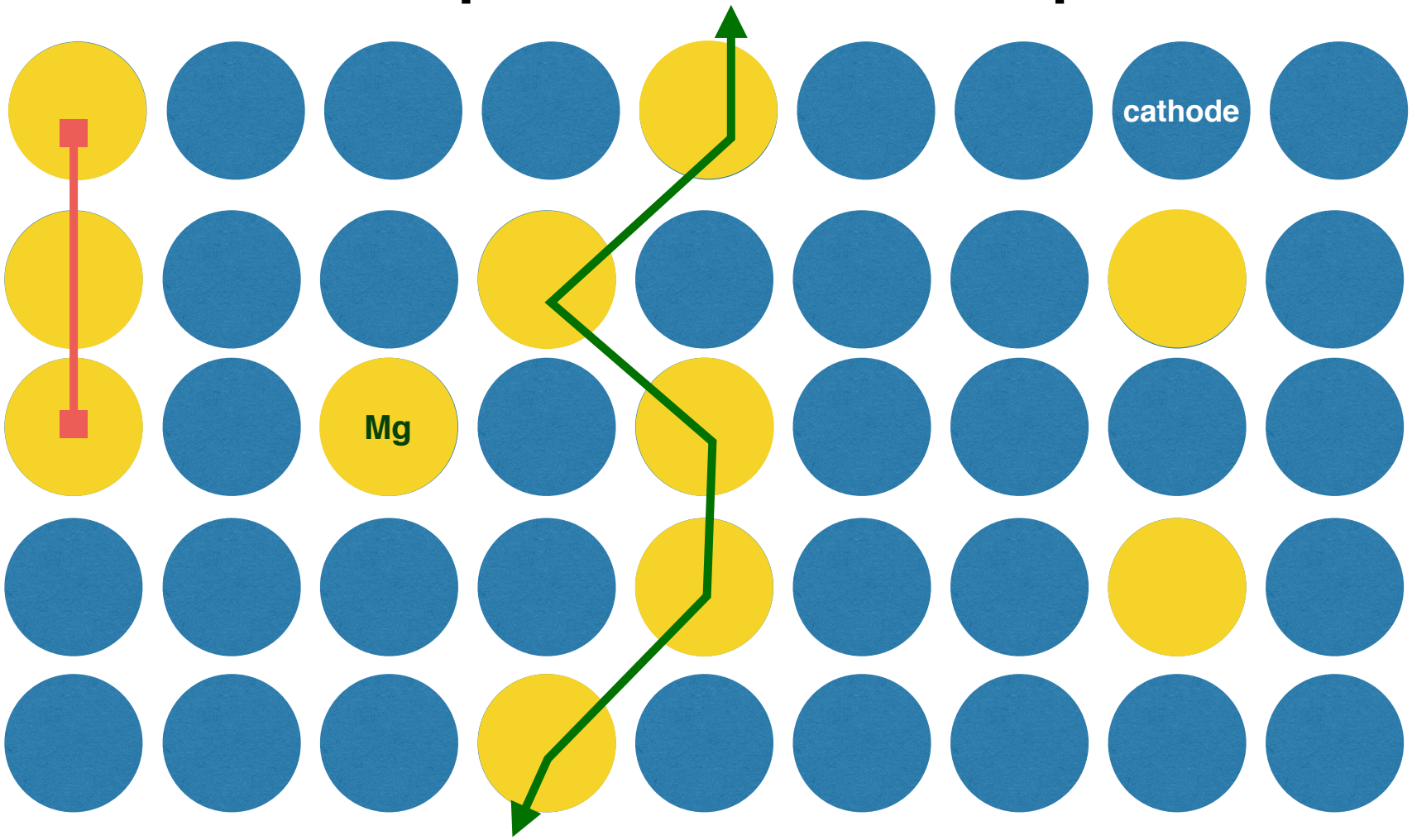
Ground water



Coffee

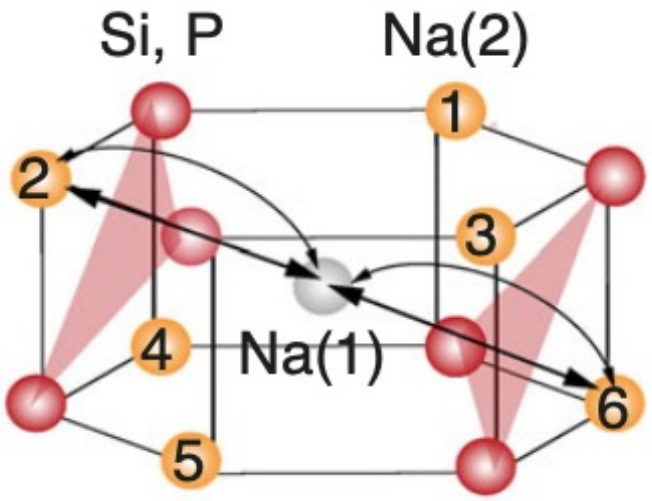


How do random ionic hops translate to macroscopic ionic transport?



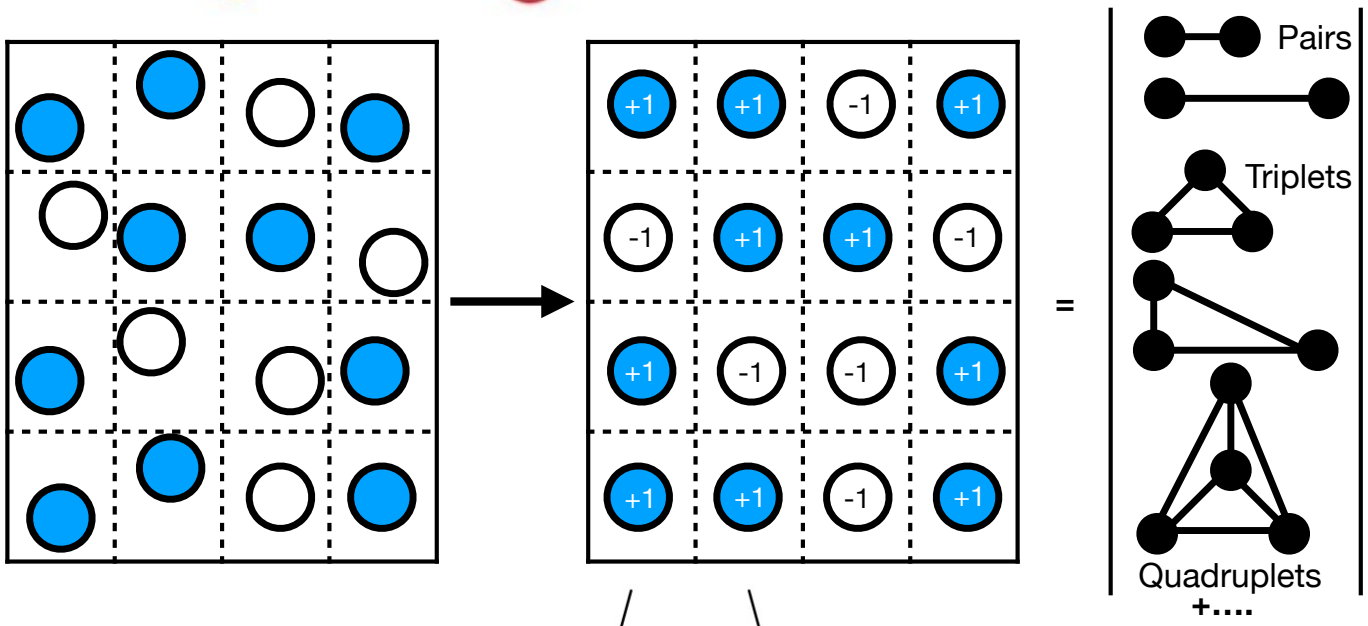
Need “enough” number of “active” channels to percolate: “**threshold**” value
Fraction of sites present in a percolating network: “**extractable**” content

Lattice models and kinetic Monte Carlo



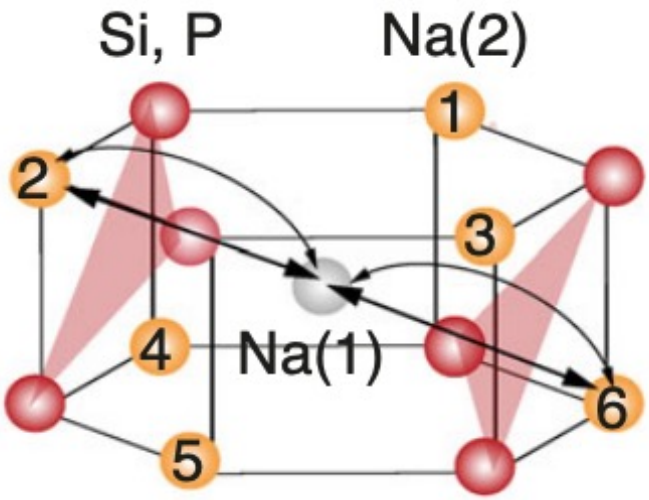
Migration barriers in a "local" environment can be modelled using a local version of a cluster expansion

Such local cluster expansion can be used with kinetic Monte Carlo to estimate diffusivity, conductivity, etc.

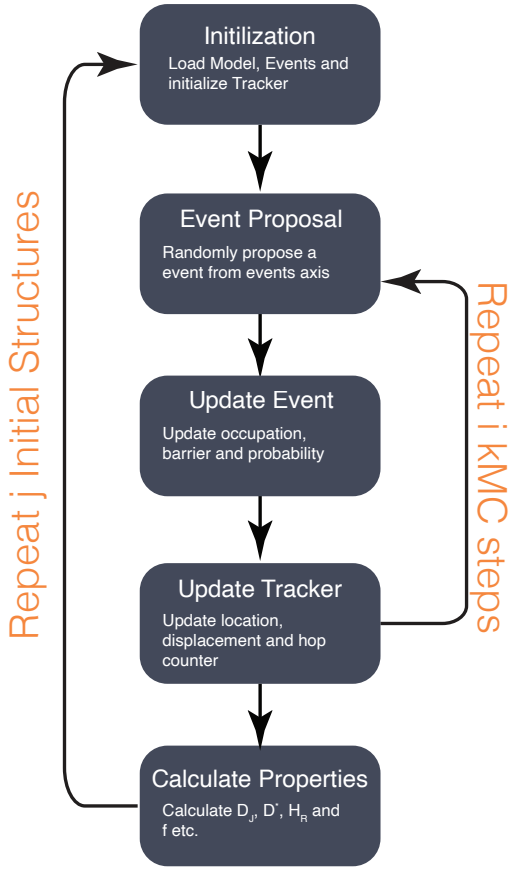


$$E(\sigma) = \sum_{\alpha} m_{\alpha} V_{\alpha} \left\langle \prod_{i \epsilon \beta} \sigma_i \right\rangle$$

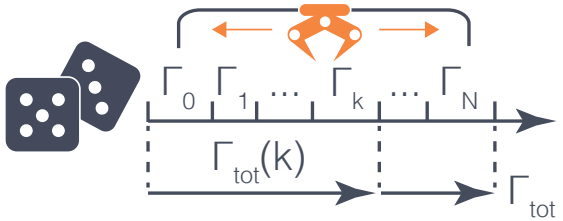
Lattice models and kinetic Monte Carlo



Rejection-free Kinetic Monte Carlo



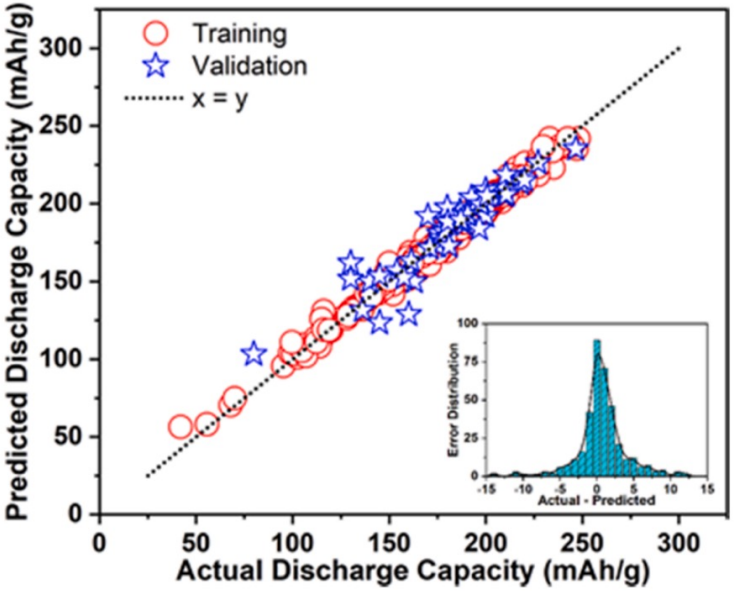
Event Proposal



Machine learning

Machine learning: learn from predictions to make better predictions

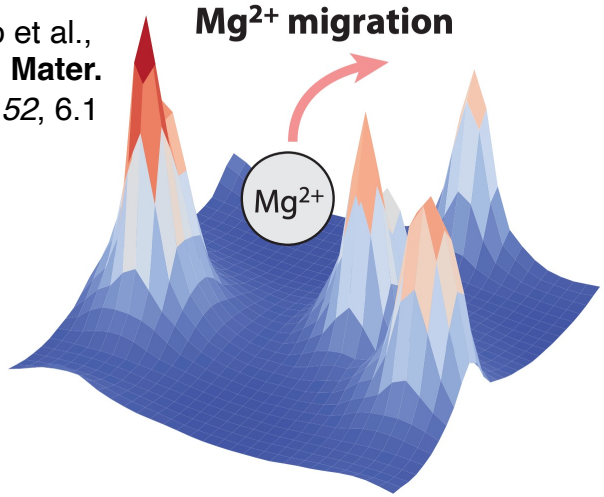
Regressions: quickly predict a property via training on existing dataset of large sets of materials



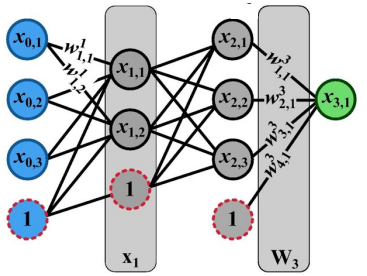
LASSO, Ridge, Decision trees, etc.

Figure: Liow et al., **Nano Energy 2022**, *98*, 107214

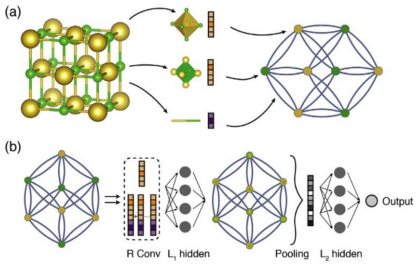
Figure: Gao et al., **Annu. Rev. Mater. Res. 2022**, *52*, 6.1



Interatomic potentials: learn potential energy surface of a given material



Feed forward neural networks



Crystal graph convolutional neural networks

In what ways do computations contribute?

Design better electrodes and solid electrolytes

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, etc.

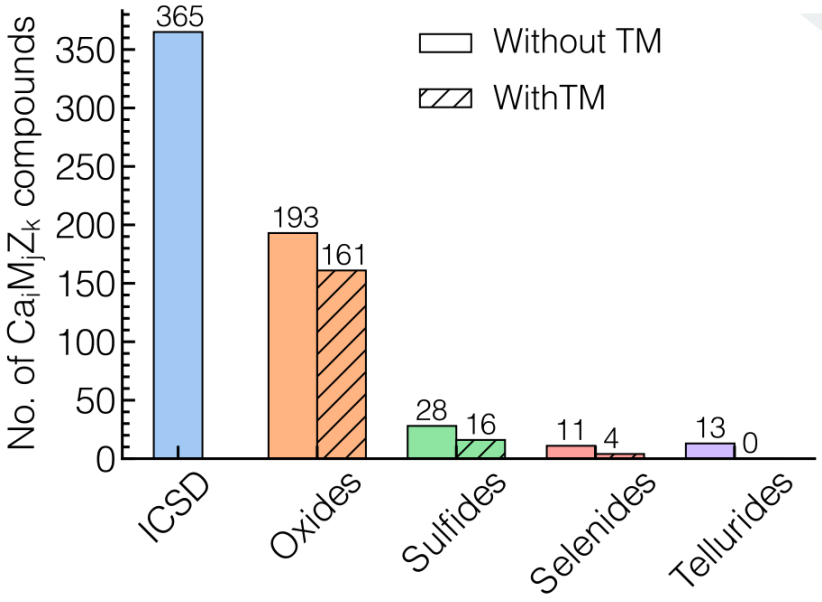
Make theory better

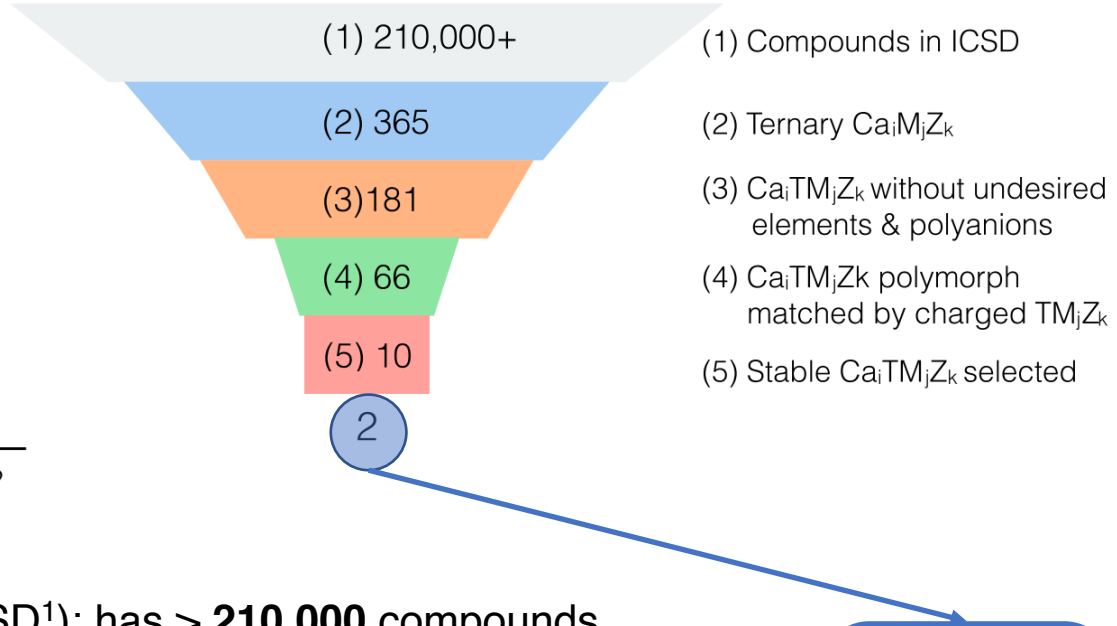
- Benchmark existing theoretical models against experimental data to identify best ones
- Develop better models for simulating complex phenomena

Examples of computations in action

Identify novel materials

Ternary Ca-compounds as Ca-cathodes





Inorganic crystal structure database (ICSD[1]): has > **210,000** compounds

- Only **365** are ternary compounds containing Ca
  - Compounds of composition $Ca_iM_jZ_k$; M, Z = elements other than Ca
- Let M = TM (i.e., transition metal) and Z = O, S, Se, or Te: **181** compounds
- Charge-neutral charged compound (TM_jZ_k) available for $Ca_iTM_jZ_k$?
  - $CaMn_2O_4$-Mn_2O_4 is ok, $CaVO_3$-VO_3 not ok
  - **66** unique structures
- Either of $Ca_iTM_jZ_k$ or TM_jZ_k thermodynamically (meta)stable?
  - $E^{hull} \leq 30$ meV/atom (based on Materials Project[2])
  - **10** unique compounds → evaluate (voltage and) mobility

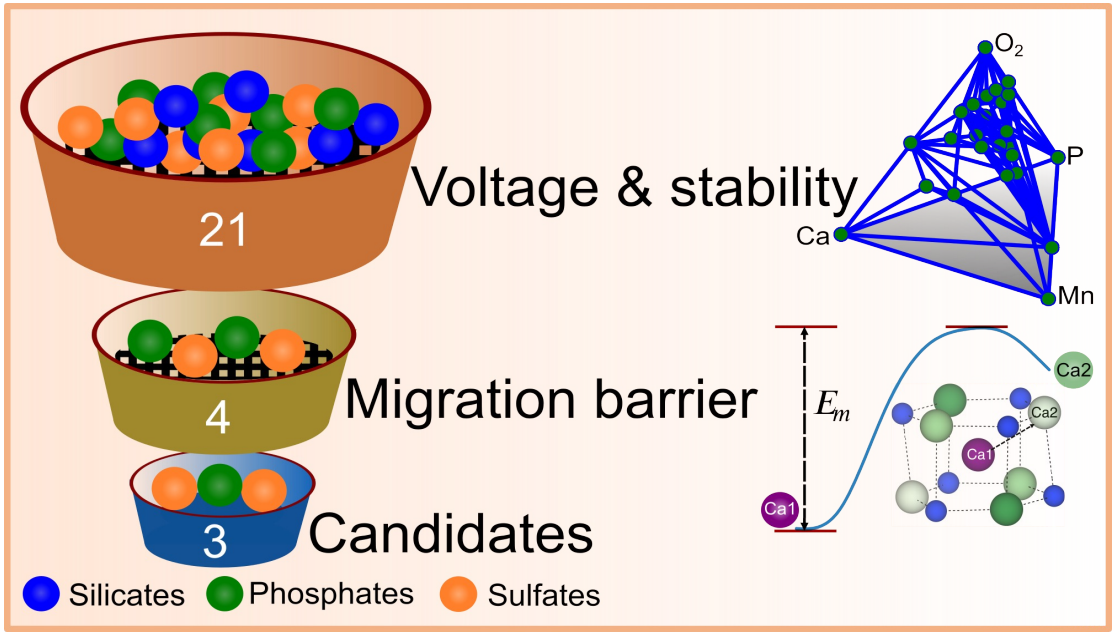
Final candidates!

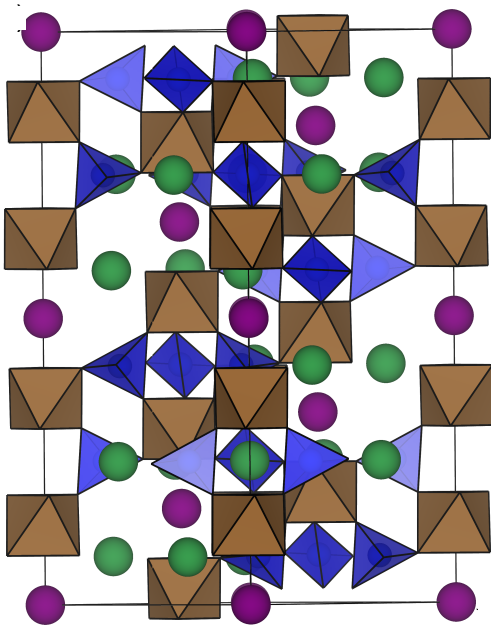
CaV_2O_4 and $CaNb_2O_4$

Lu et al., **Chem. Mater. 2021**, *33*, 5809

1. https://icsd.products.fiz-karlsruhe.de/
2. https://materialsproject.org/

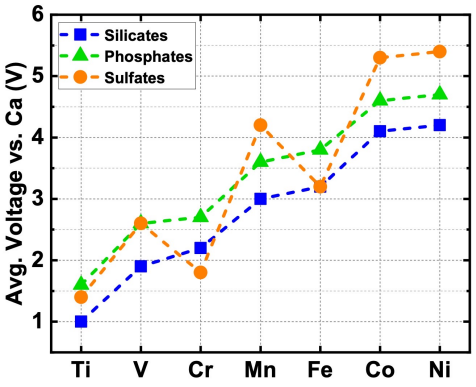
Sodium superionic conductors (NaSICONs) as Ca-cathodes

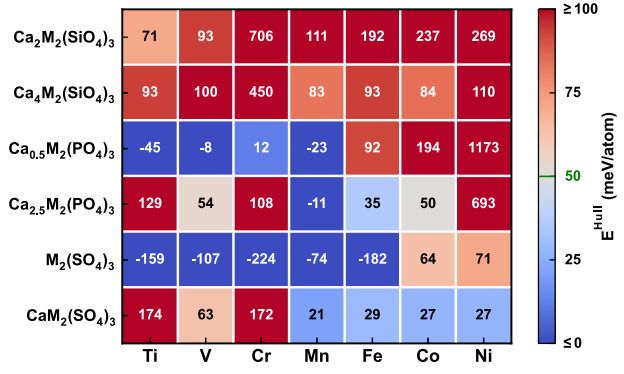


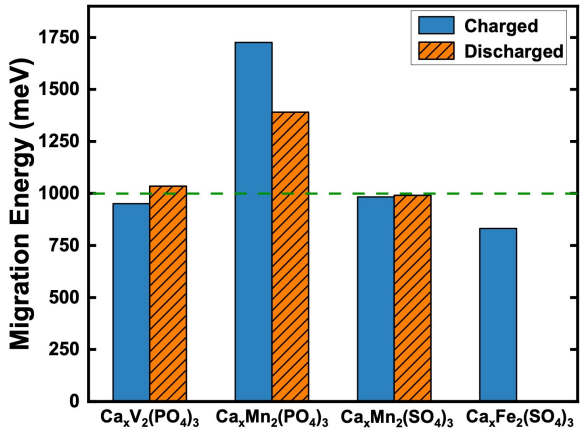


"NaSICONs"
$Ca_xM_2(ZO_4)_3$

High-throughput DFT calculations: 3 candidates



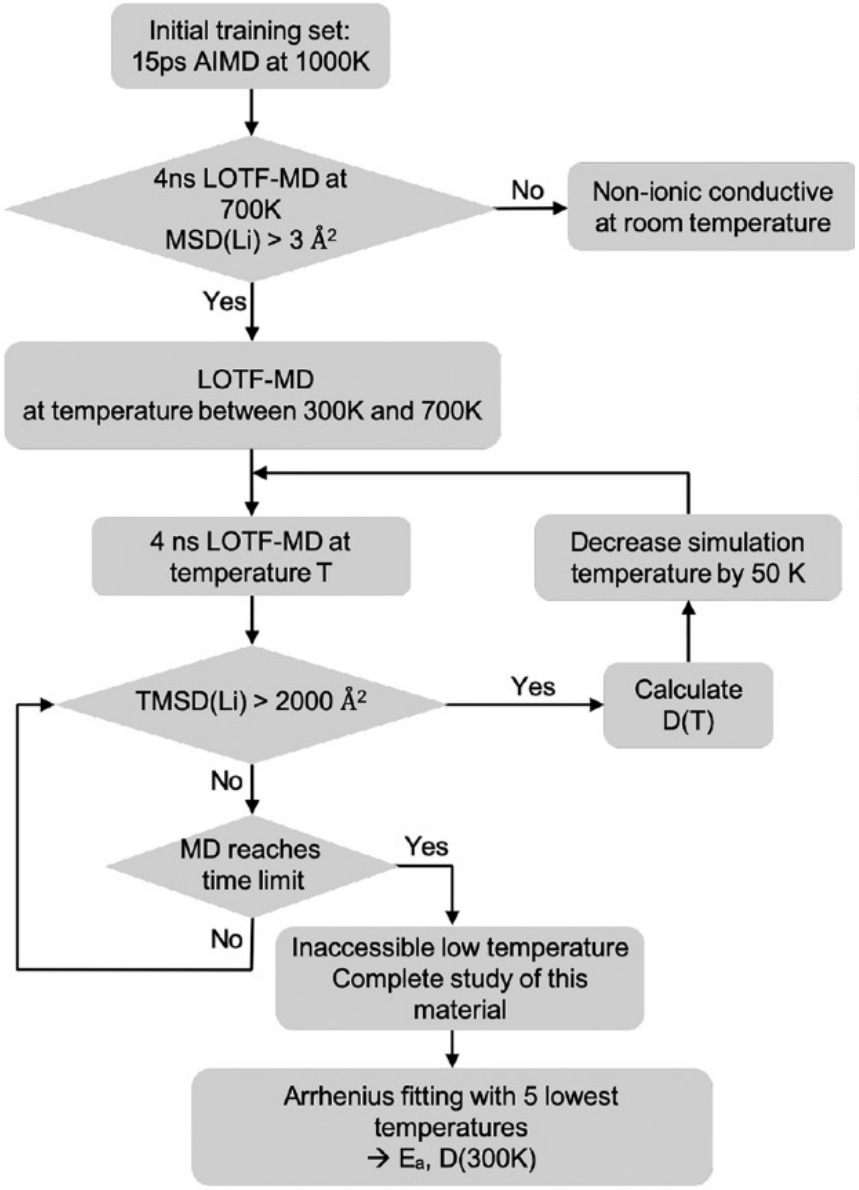


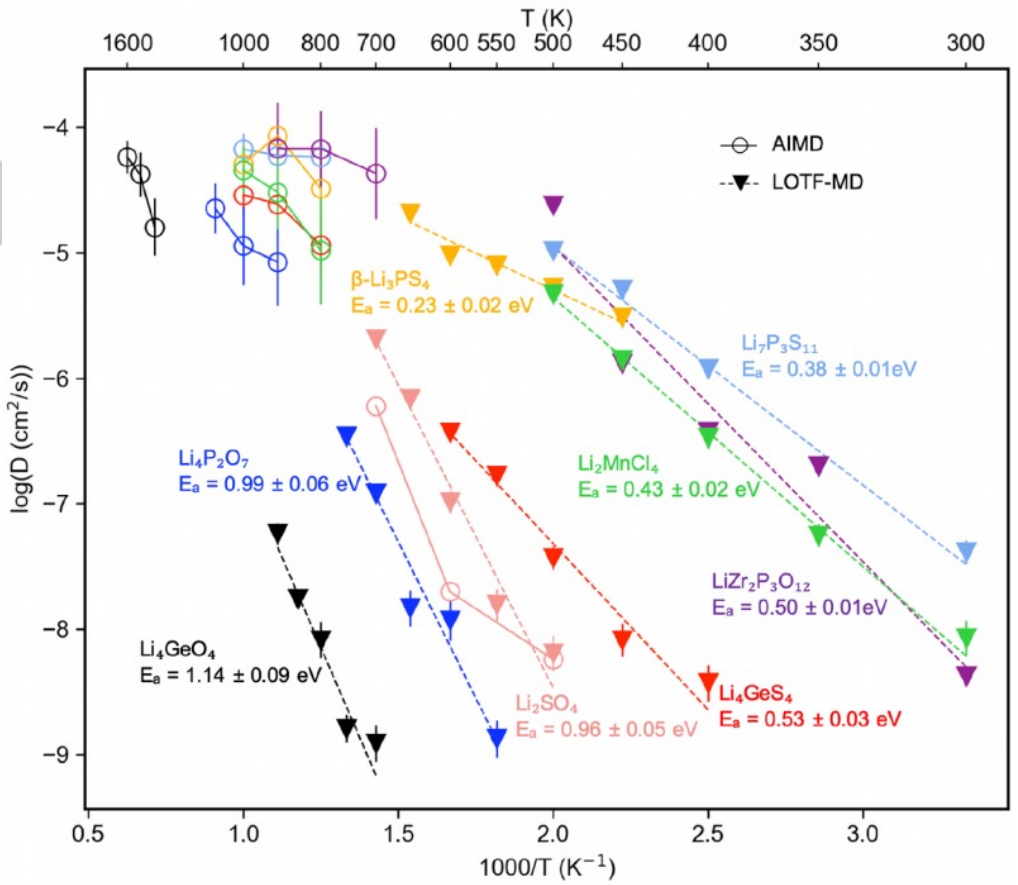


$Ca_xV_2(PO_4)_3$, $Ca_xMn_2(SO_4)_3$, and $Ca_xFe_2(SO_4)_3$

D.B. Tekliye, G.Sai Gautam, et al., **Chem. Mater. 2022**, *34*, 10133

On-the-fly ML to predict ionic conductors





Ionic conductors: important for all-solid-state batteries

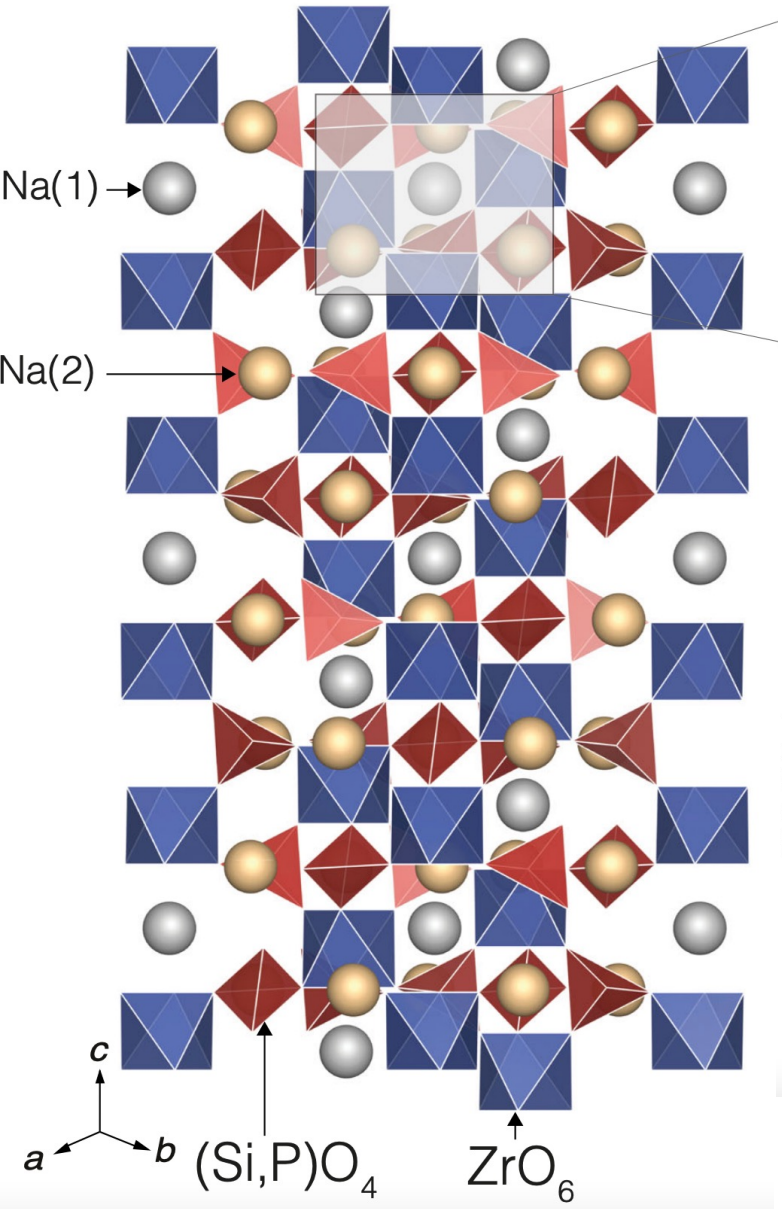
Candidates:
LiCl
$Li_2B_7O_{12}$
$Li_3Sc_2(PO_4)_3$
$Li_2B_6O_9F_2$
$Li_2B_3O_4F_3$

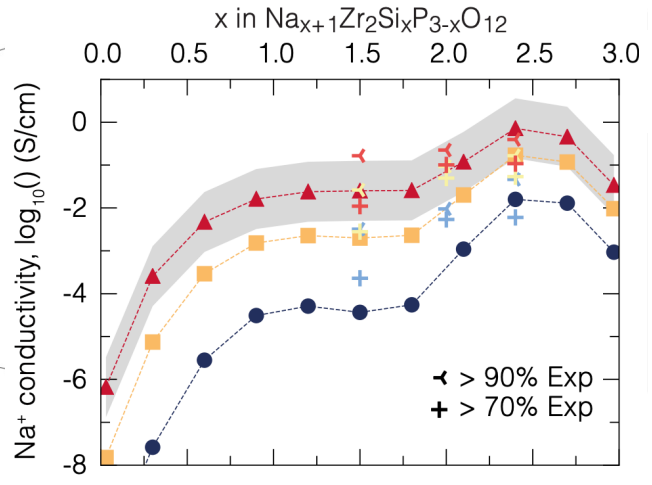
C. Wang et al., **Chem. Mater. 2020**, *32*, 3741-3752

Examples of computations in action

Understand underlying materials phenomena

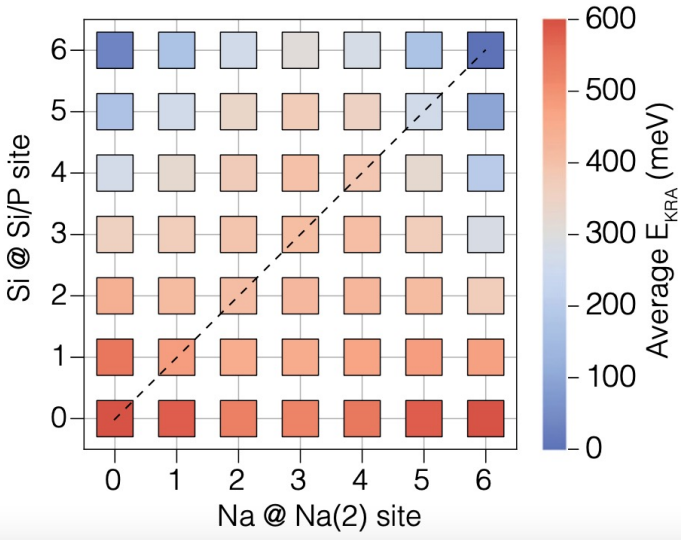
Quantify ionic mobility in solid electrolytes





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

Conductivity not known as a function of composition

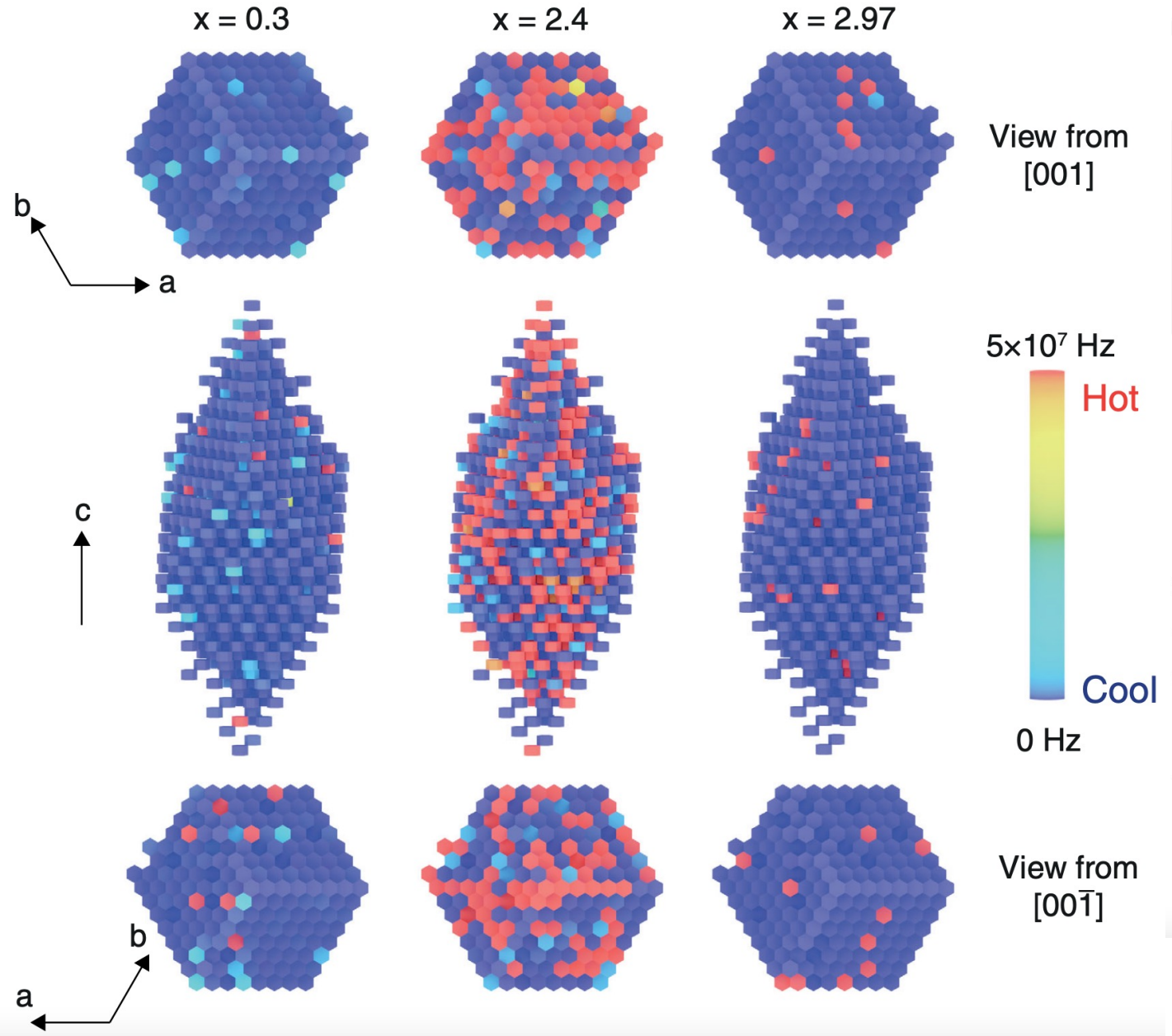


Perform DFT+NEB at different compositions and subsequently use kinetic Monte Carlo simulations

Good agreement with experimental measurements

Z. Deng, G. Sai Gautam, P. Canepa, and coworkers, **Nat. Commun. 2022**, *13*, 4470

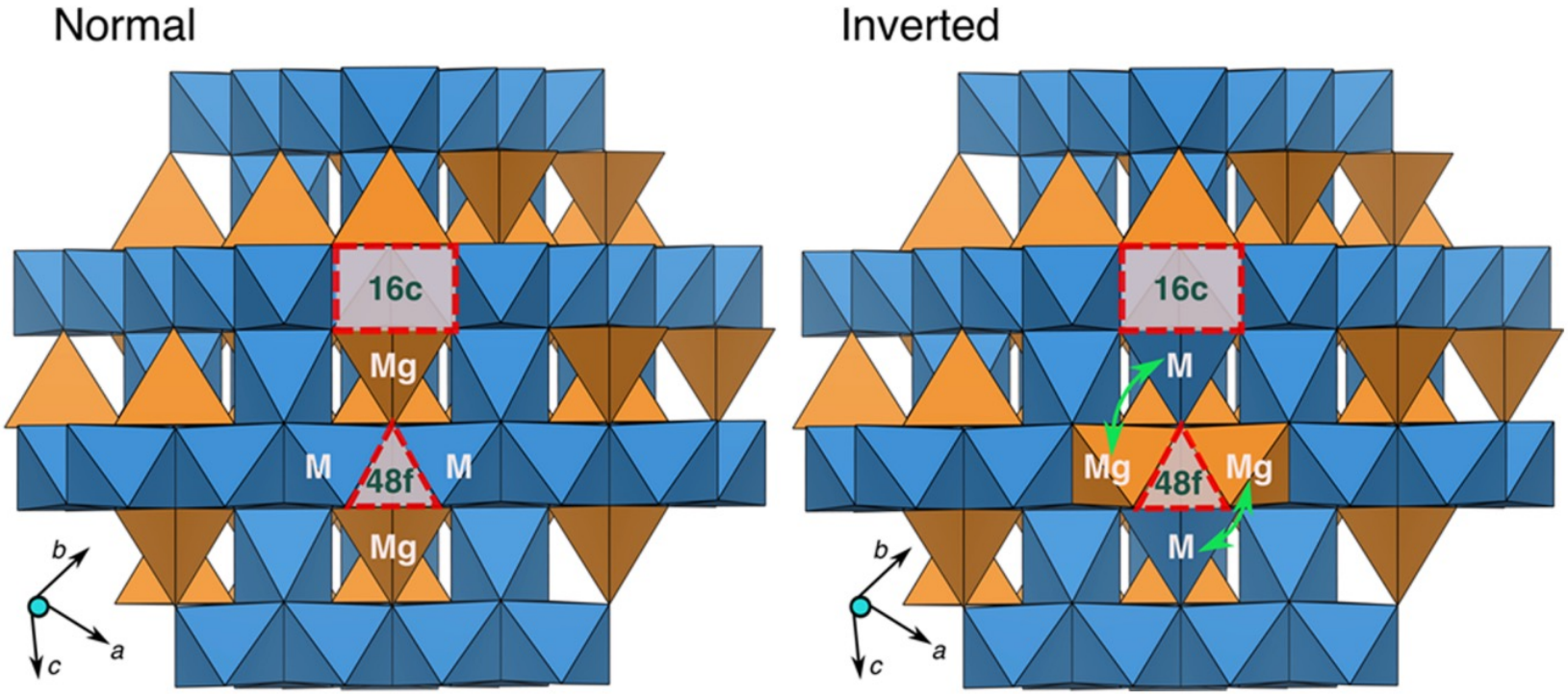
Quantify ionic mobility in solid electrolytes



Get heat maps of Na-ionic motion within the NaSICON as a function of composition!

Z. Deng, G. Sai Gautam, P. Canepa, and coworkers, **Nat. Commun. 2022**, *13*, 4470

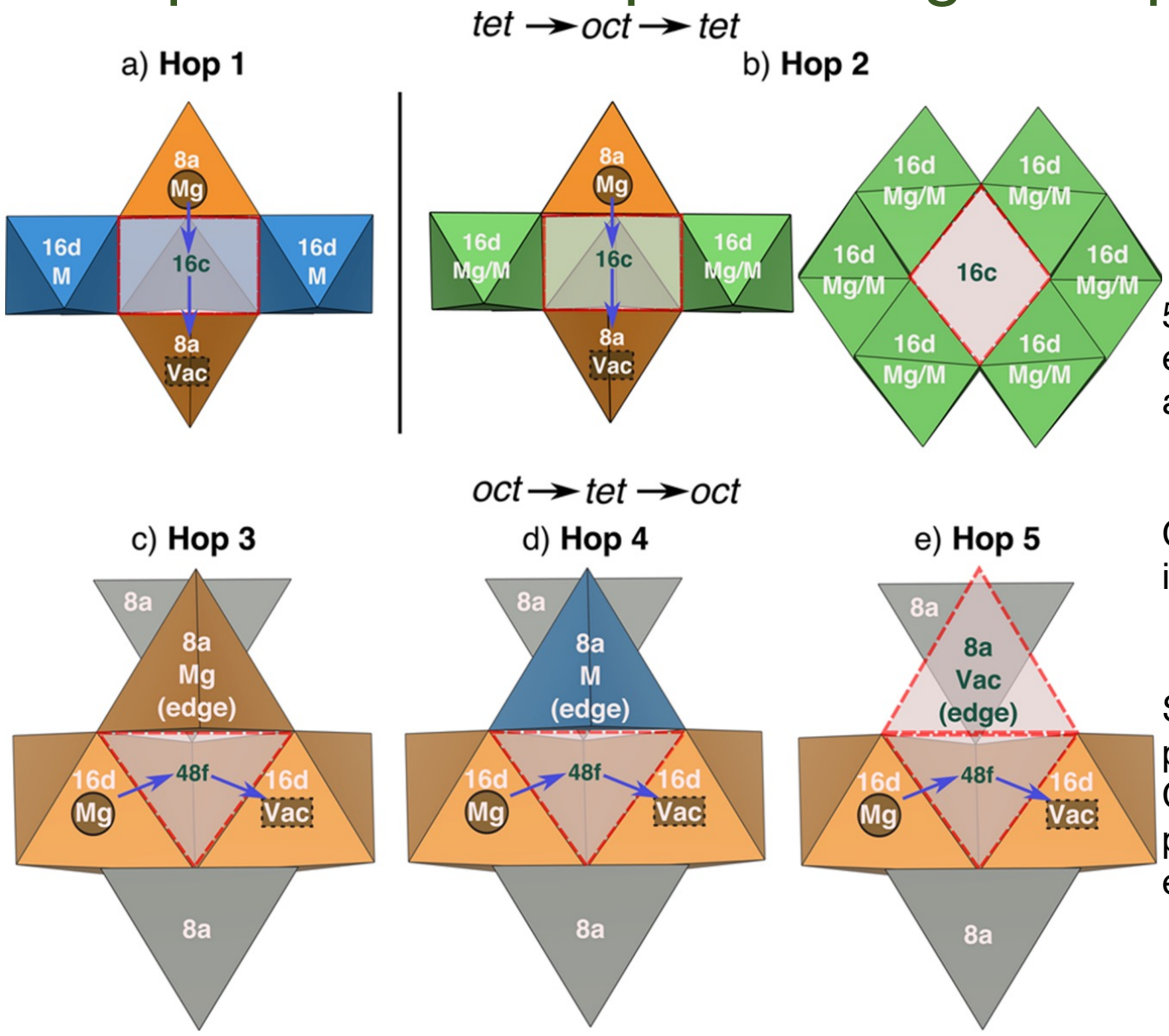
Use percolation to predict Mg transport in spinels



$MgMn_2O_4$: spinel prone to inversion

G. Sai Gautam et al., **Chem. Mater. 2017**, *29*, 7918-7930

Use percolation to predict Mg transport in spinels



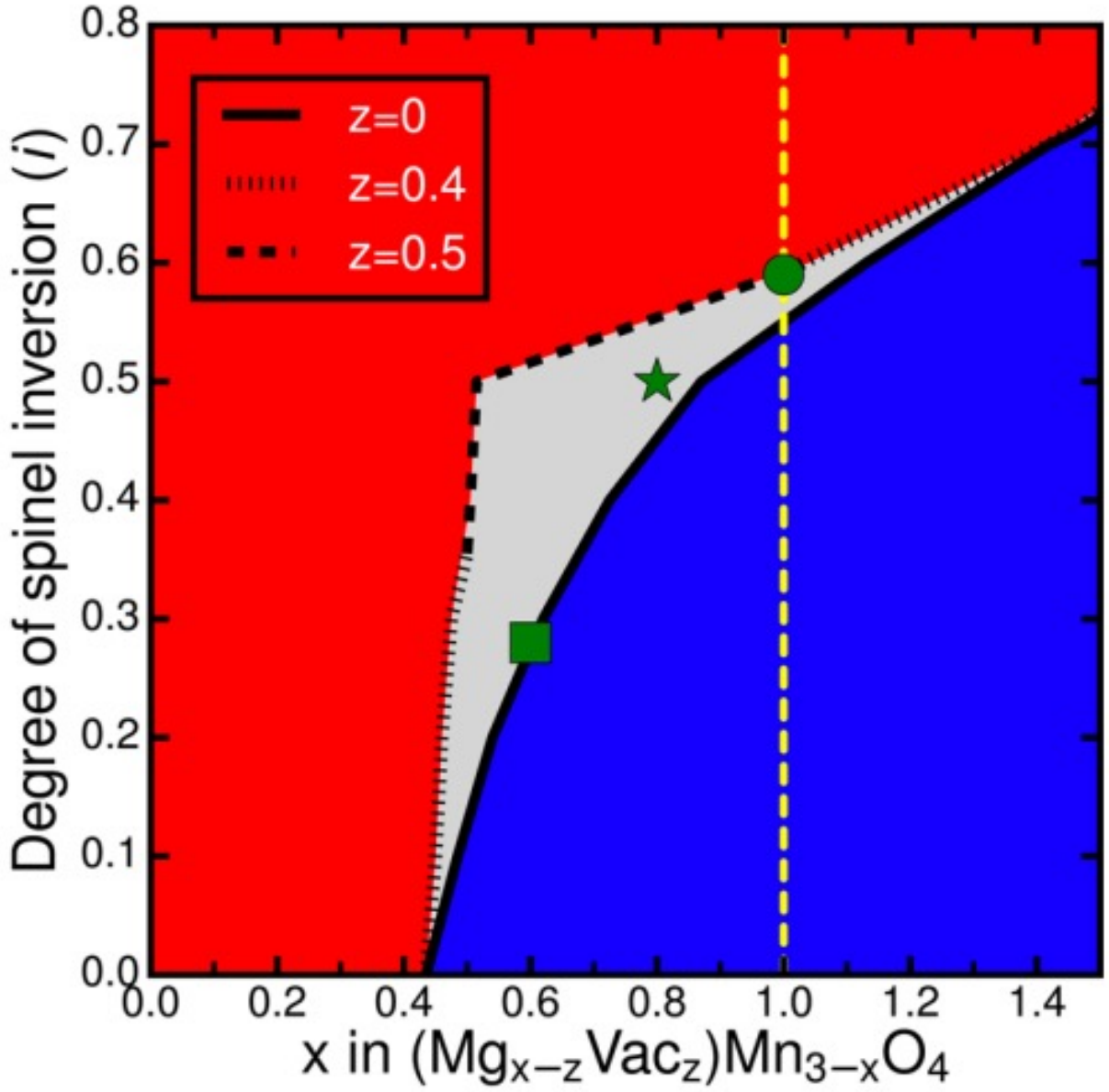
5 different local environments to consider in an inverted spinel

Calculate migration barrier in each environment

Subsequently use percolation theory (Monte Carlo) to estimate percolation threshold and extractable capacity

G. Sai Gautam et al., **Chem. Mater. 2017**, *29*, 7918-7930

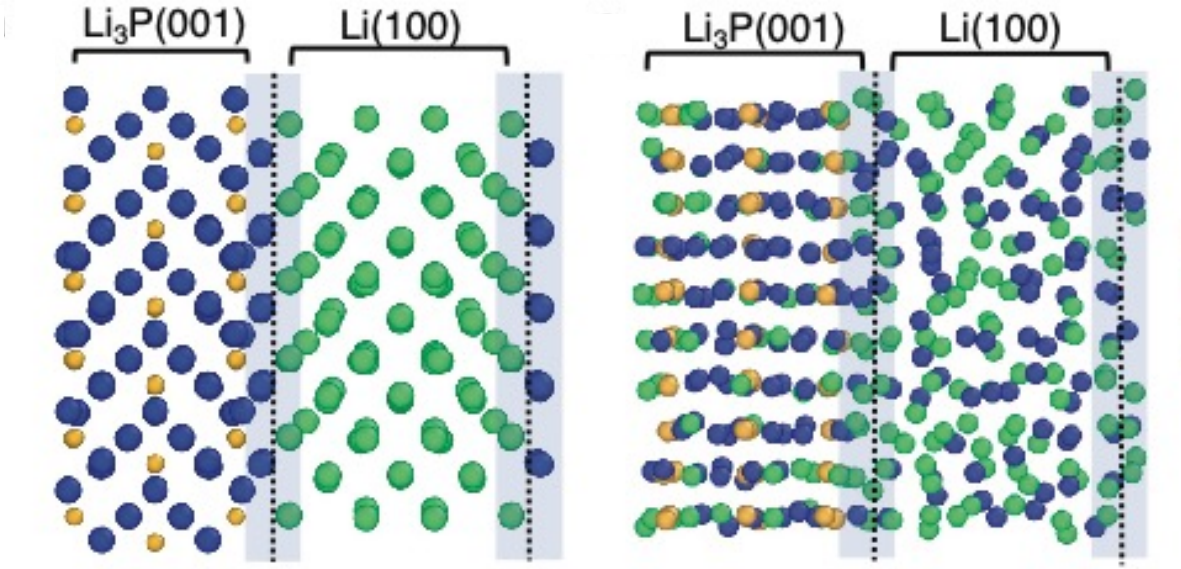
Use percolation to predict Mg transport in spinels



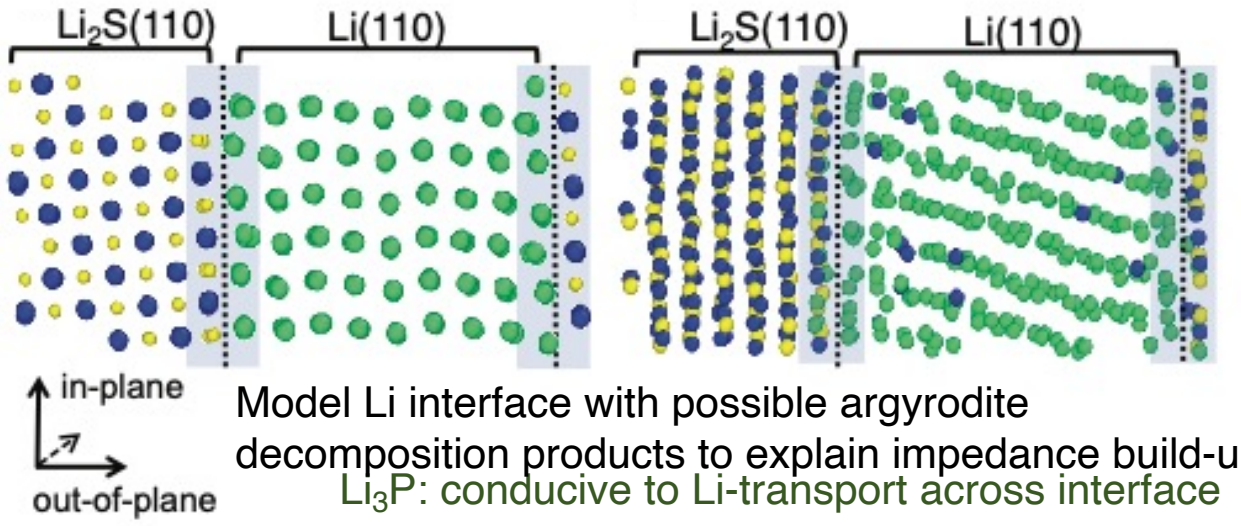
Macroscopic Mg transport possible as long as spinel is < 55% inverted

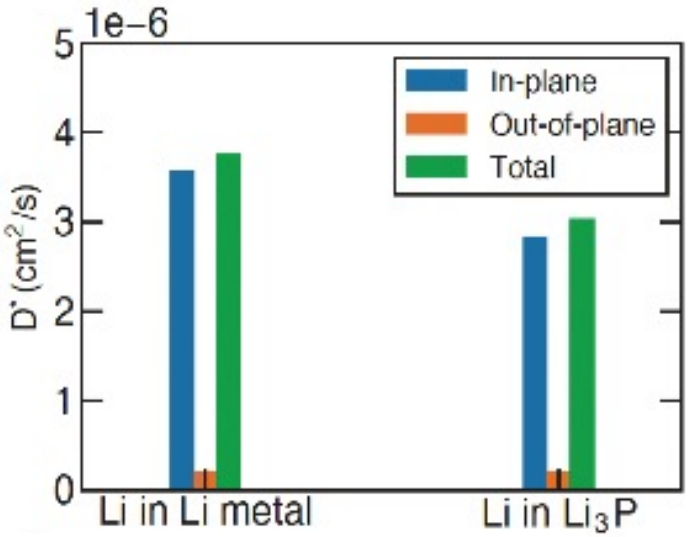
G. Sai Gautam et al., **Chem. Mater. 2017**, *29*, 7918-7930

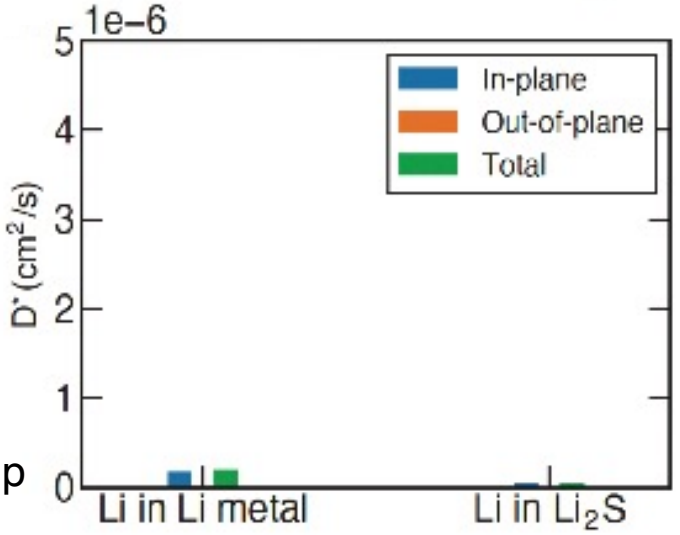
Use (ML) molecular dynamics to understand interfacial transport bottlenecks



~8000 atoms; 10 ns







Model Li interface with possible argyrodite decomposition products to explain impedance build-up

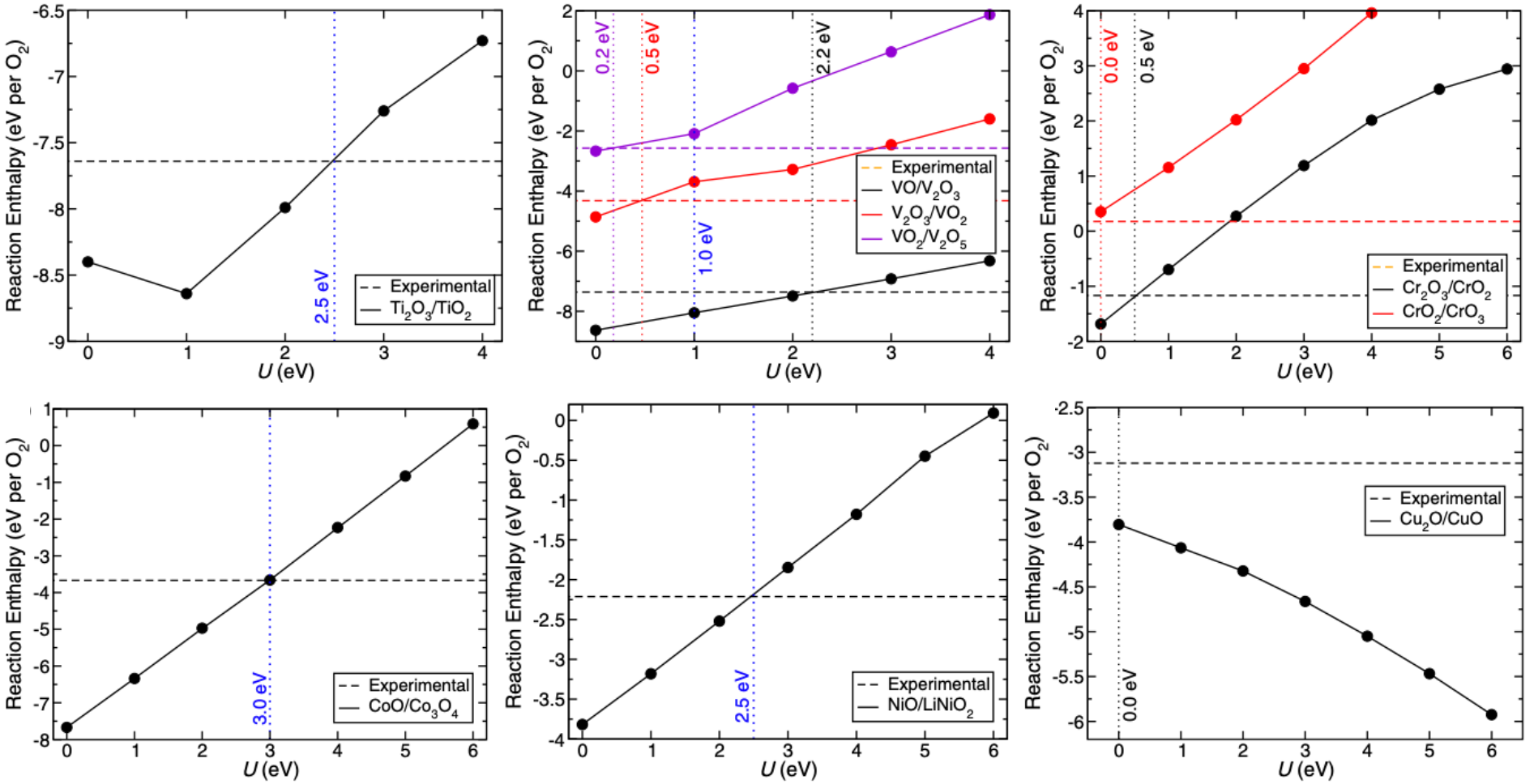
Li_3P: conducive to Li-transport across interface

J. Wang, A.A. Panchal, G.Sai Gautam, and P. Canepa, **J. Mater. Chem. A 2022**, *10*, 19732-19742

Examples of computations in action

Make theory better

Reducing errors in functionals

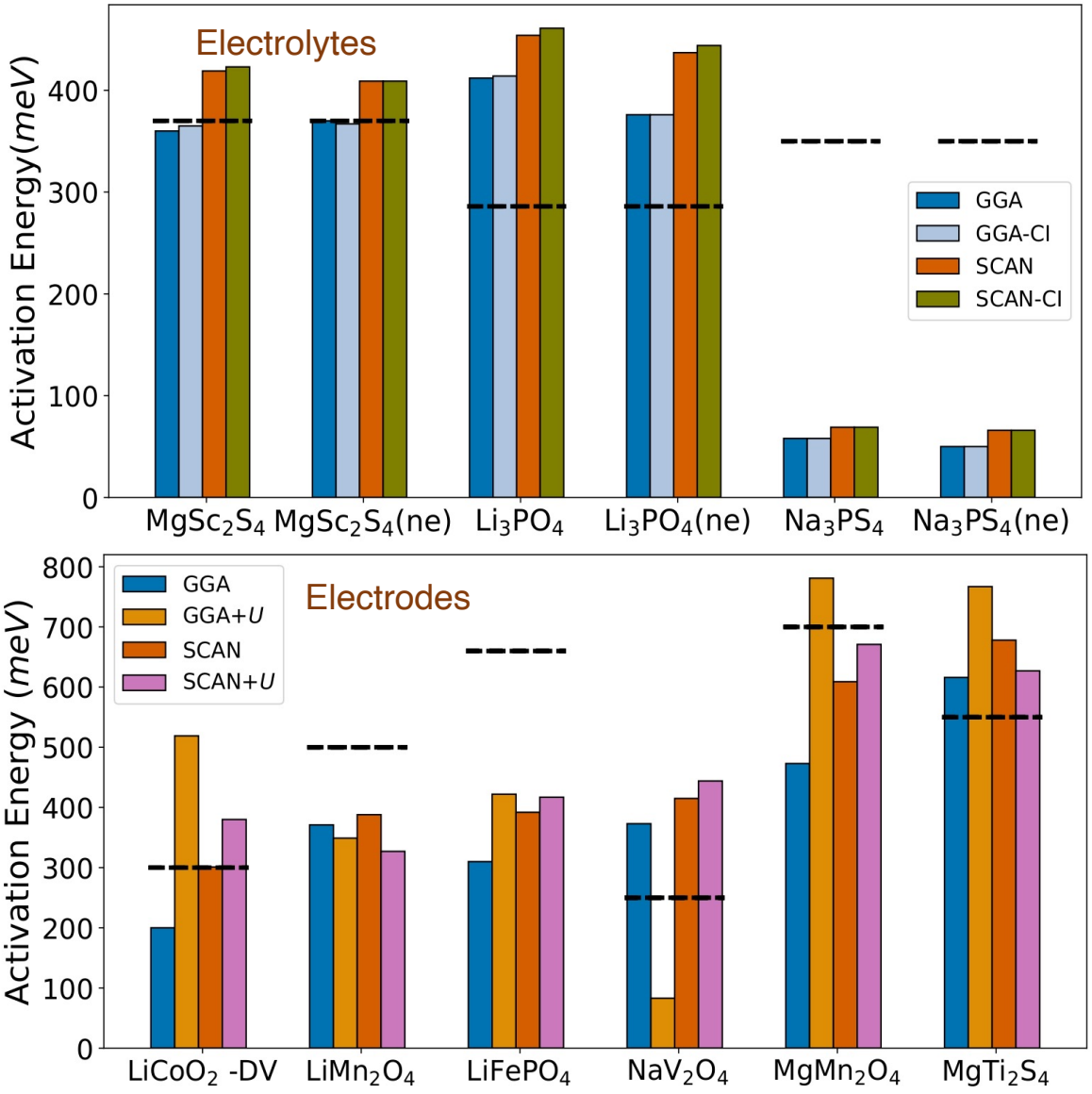


Strongly constrained and appropriately normed (SCAN) functional: suffers from self-interaction errors in correlated systems (*d* or *f* open shells)

Use experimental oxidation enthalpies to obtain "optimal" Hubbard *U* corrections

O. Long, G.Sai Gautam, and E.A. Carter, **Phys. Rev. Mater. 2020**, *4*, 045401

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?

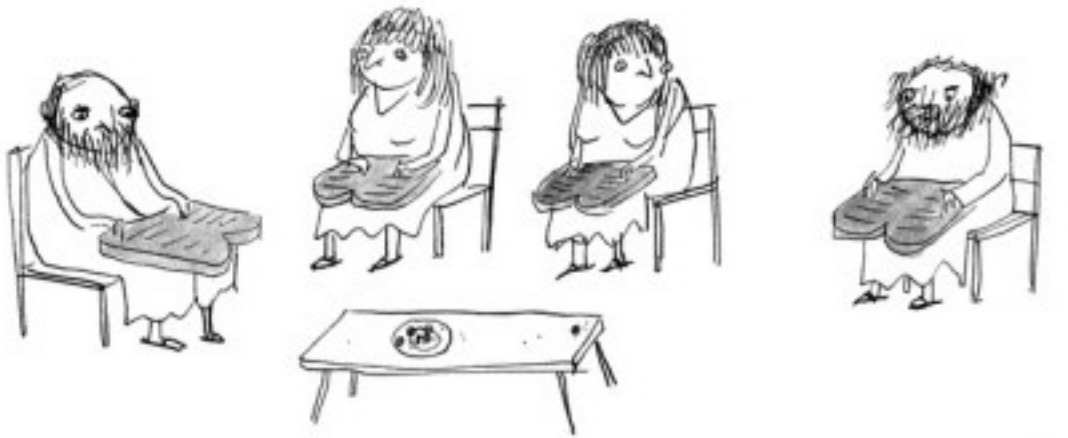
SCAN more accurate on average

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

R. Devi, B. Singh, P. Canepa, and G.Sai Gautam, **npj Comput. Mater. 2022**, *8*, 160

Summary

- Climate change requires rapid innovation and deployment of renewable technologies
  - Bottleneck of renewables: underlying materials
  - Understand materials behavior better + predict new materials for batteries and solar cells
  - Use computations +/- machine learning to accelerate materials design
- Can we discover new materials for beyond Li-ion batteries?
- Can we understand existing materials phenomena better?



"Well, I really enjoyed it, and it definitely made me want to read more by this author."

https://sai-mat-group.github.io

saigautamg@iisc.ac.in