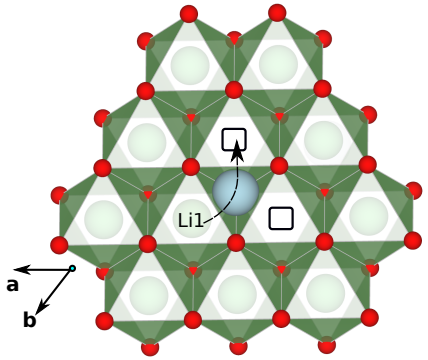

Role of exchange-correlation functionals in migration barrier predictions

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Photo-rechargeable and high-capacity batteries session, Energy storage and batteries track
6th IEEE-ICEE Meeting, Bengaluru
December 12, 2022

Acknowledgments

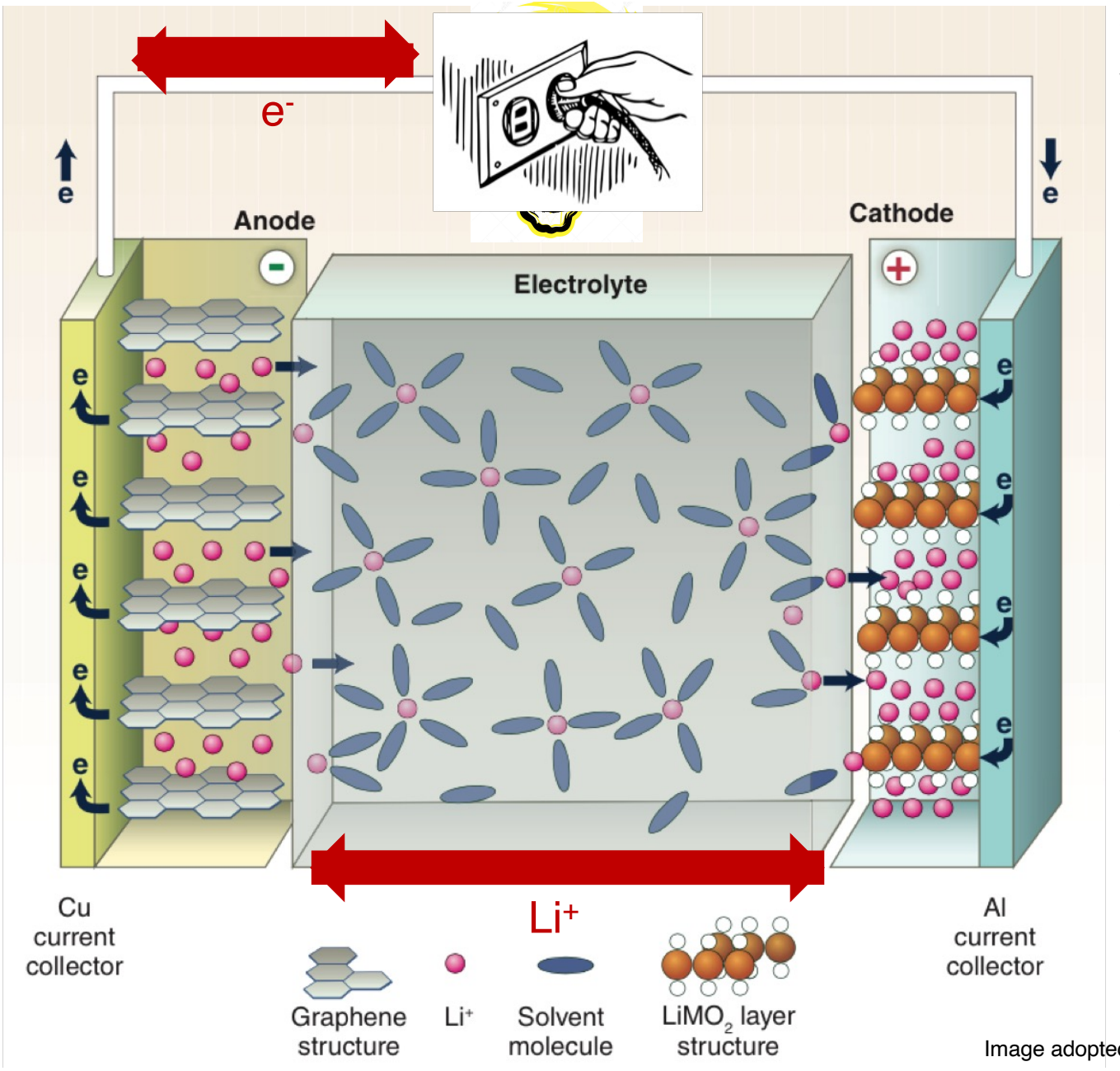
Reshma

+CaRe group

NSCC (Singapore)

SERC (IISc)

How does the modern Li-ion battery work?



Voltage (V): Potential to do work

Capacity (mAh): Amount of charge stored

Voltage*capacity: Energy stored

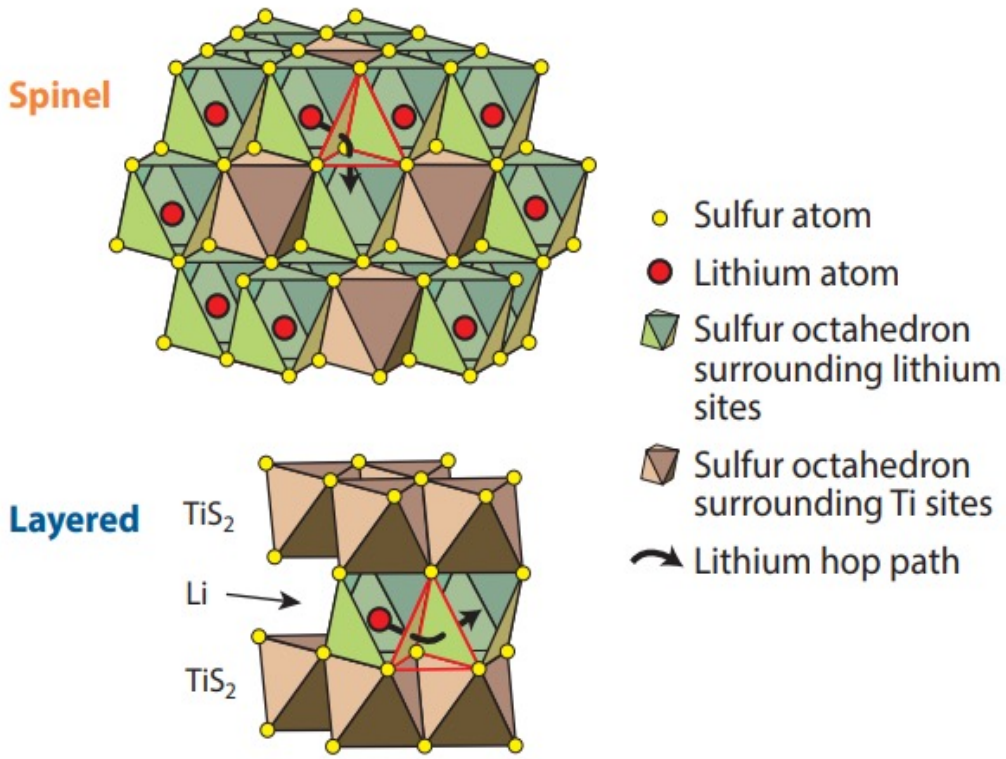
Rate (C): How fast can a battery be charged and discharged?

- Crucial for power performance

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

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

Migration barriers govern rate performance in batteries



Intercalation electrodes/solid electrolytes: ionic diffusivity (D) within the bulk a major factor in rate performance

$$D = D_o \exp(-\frac{E_m}{k_B T})$$

D_o : Diffusivity pre-factor (carrier concentration, correlations, etc.)
k_B: Boltzmann constant
T: Temperature
E_m: Migration barrier

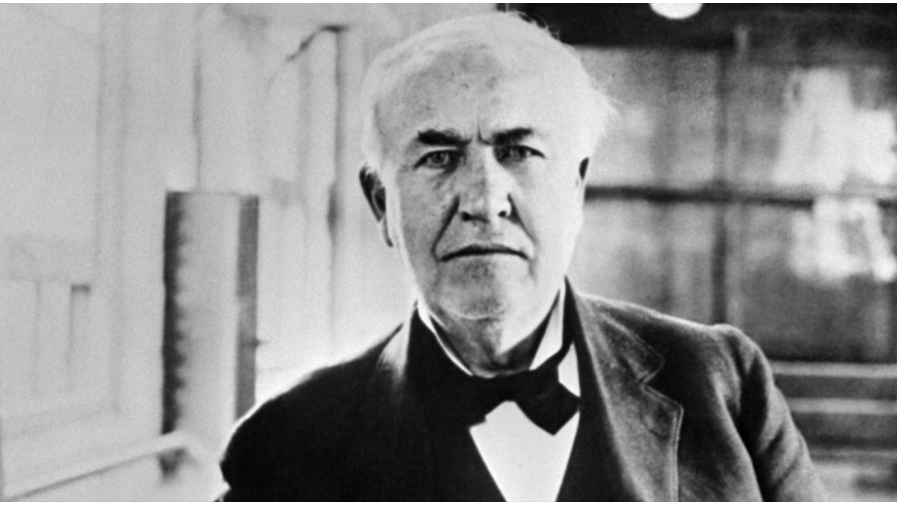
Migration barrier: dominant factor determining diffusivity

Experimental measurements of E_m: variable-temperature impedance spectroscopy, variable temperature nuclear magnetic resonance, etc.
Computational predictions of E_m: ab initio molecular dynamics, nudged elastic band (NEB)

How accurate are computational predictions?

van der Ven et al. **Ann. Rev. Mater. Res. 2018**, *48*, 27-55.

Methods: Edison vs. Iron Man



Trial and error of candidates in a lab

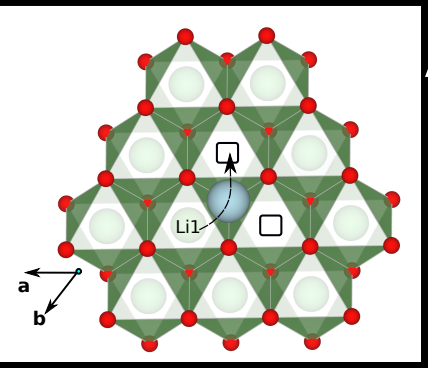
Simulate and identify candidates
(on a transparent touch screen preferably)

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

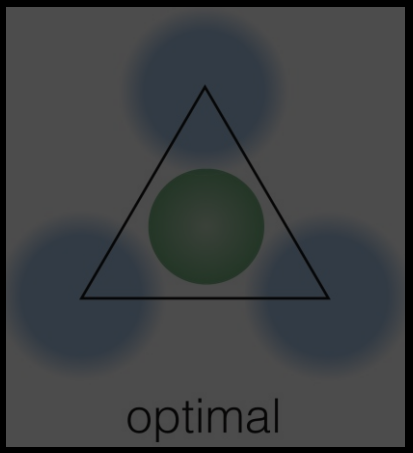
- Thermodynamic, kinetic, and electronic properties

Machine learning: learn from predictions to make better predictions

Objectives

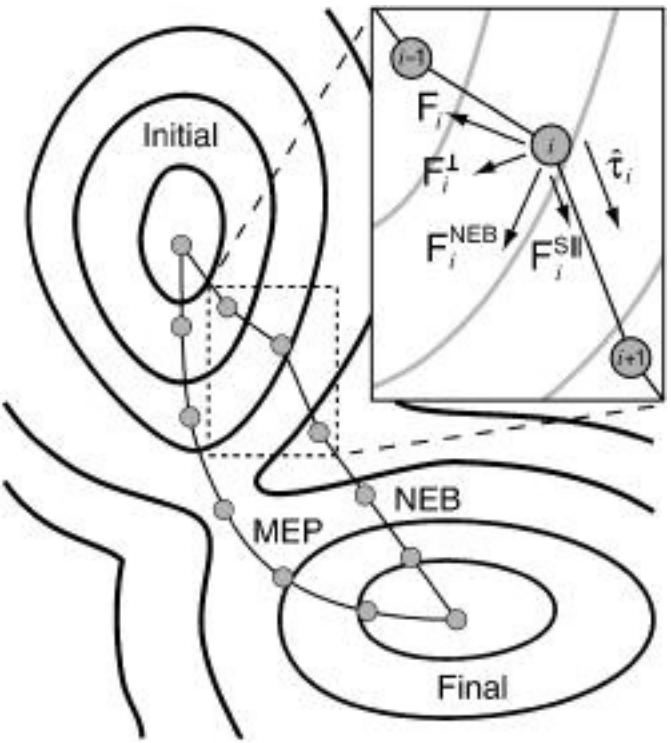


Assessing accuracy of computational predictions of ionic mobility



Examples of cathode discovery in Ca-batteries, including ionic mobility as a criterion

NEB and computational handles for ionic mobility



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

Uniform background charge (NE or ne) [solid electrolytes]

Climbing image (CI) approximation [solid electrolytes]

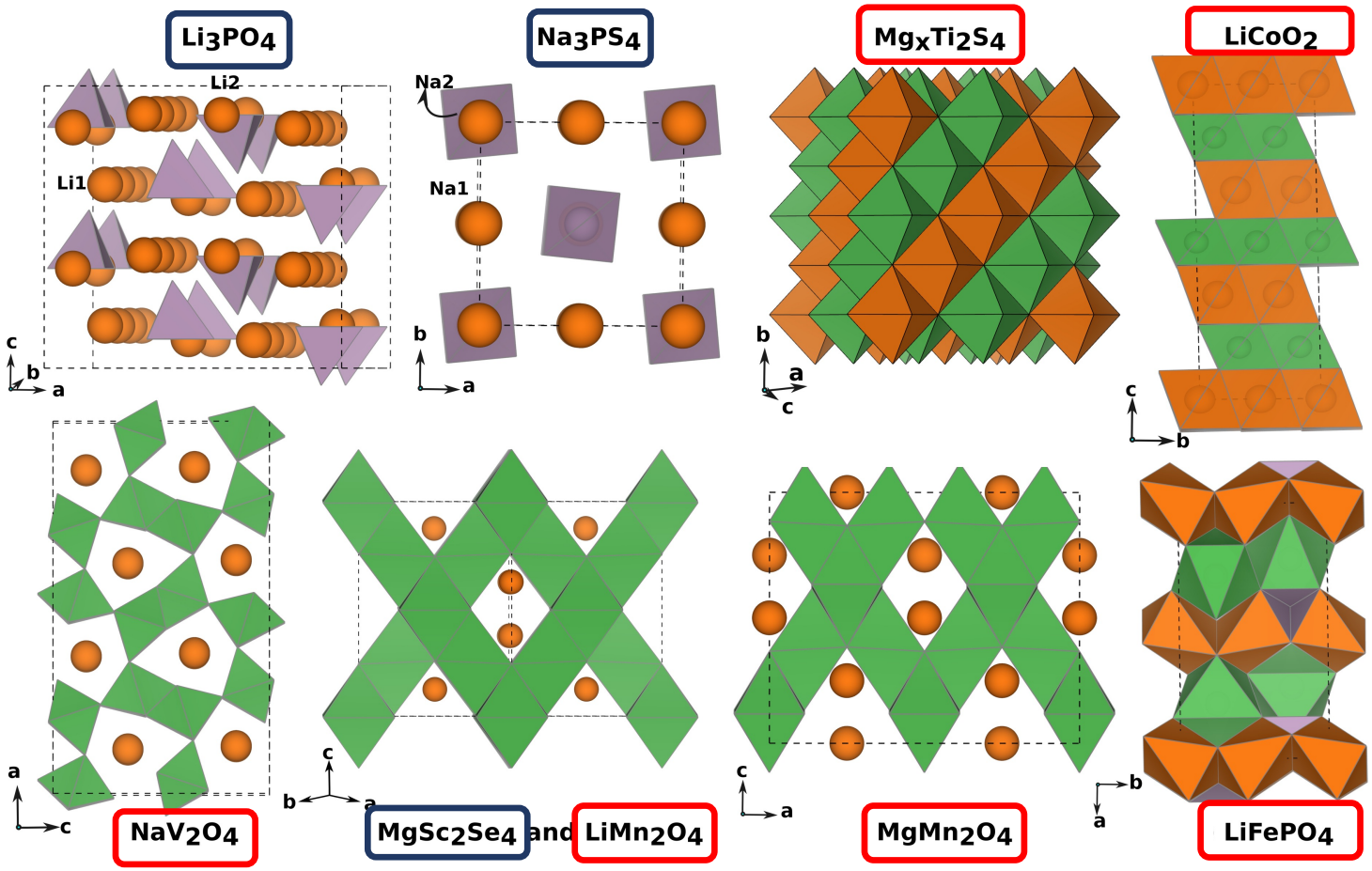
Exchange-correlation (XC) choice

- Generalized gradient approximation (GGA)
  - Perdew-Burke-Ernzerhof[2]
- Strongly constrained and appropriately normed (SCAN)[2]
- Hubbard *U* corrected frameworks[3]: GGA+*U*, SCAN+*U*
  - For electrodes only

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

1. J.P. Perdew et al., Phys. Rev. Lett. 77, 3865 (1996)
2. J. Sun et al., Phys. Rev. Lett. 115, 036402 (2015)
3. V. Anisimov et al., Phys. Rev. B 44, 943 (1991)

9 distinct systems considered



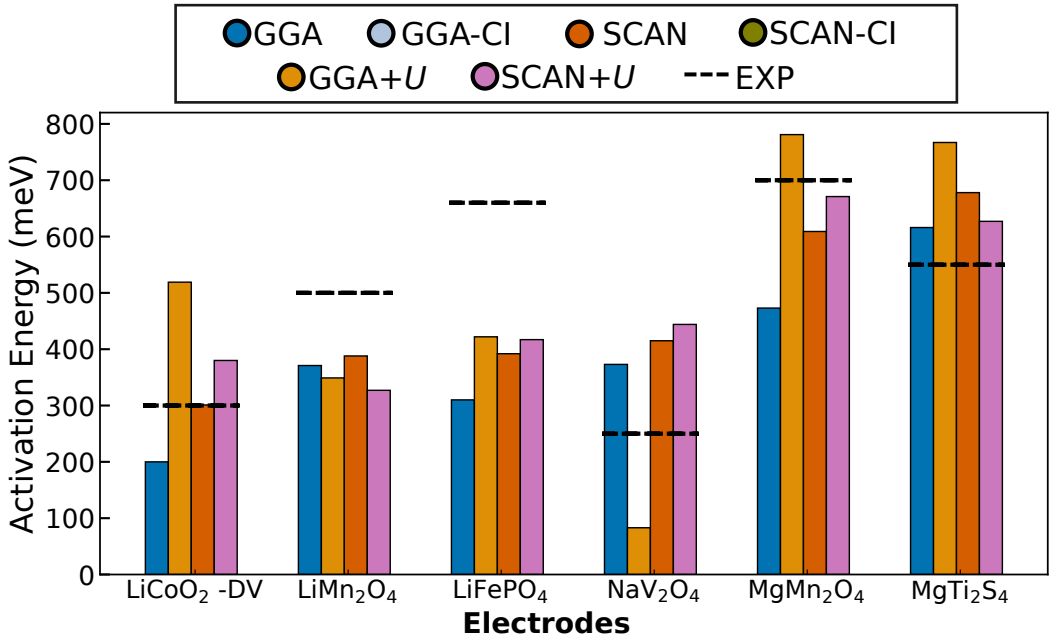
6 Electrodes

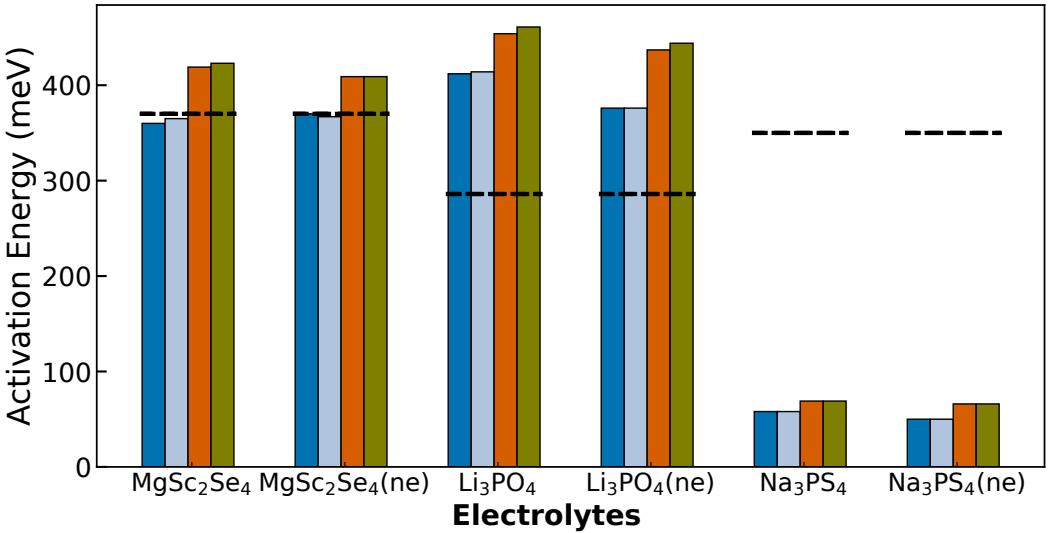
3 Solid electrolytes

Why these systems?

- Availability of experimental data
- Heterogeneity of intercalation ion
- Diversity of structural frameworks

SCAN exhibits better numerical accuracy, *on average*





MAE of SCAN (140 meV) lower than other XC frameworks (>145 meV)

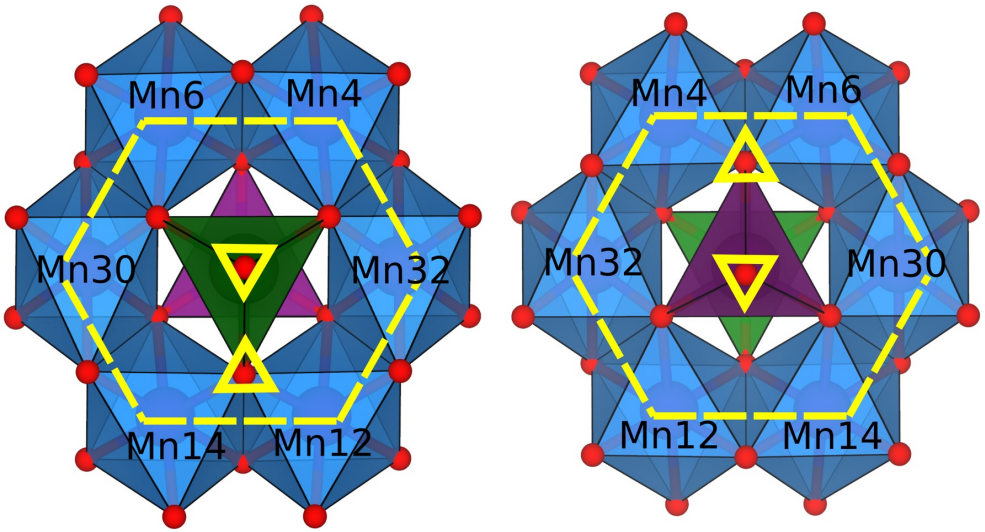
SCAN E_m > GGA E_m

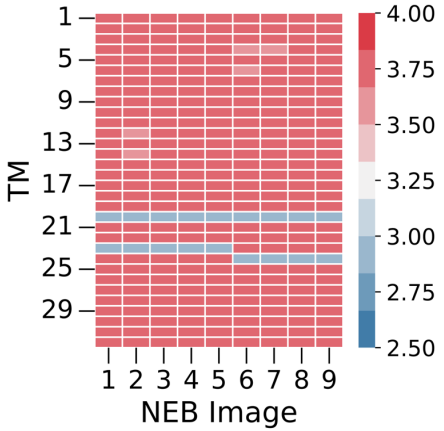
SCAN+U E_m < GGA+U E_m

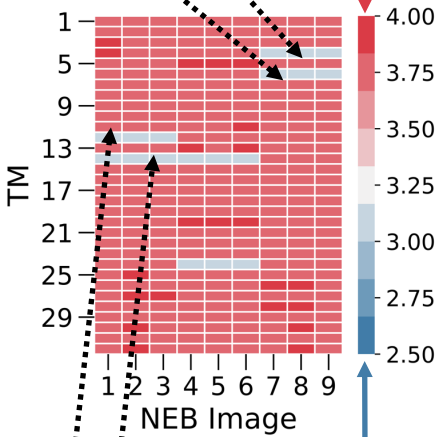
Addition of ne or CI doesn't seem to matter for solid electrolytes

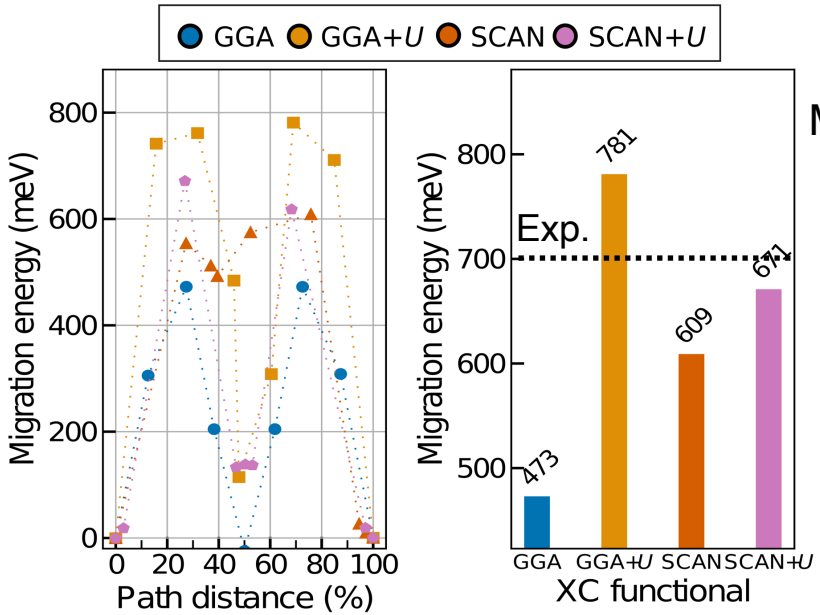
Let's look at some specific cases

$MgMn_2O_4$ (semiconductor)
GGA underestimates

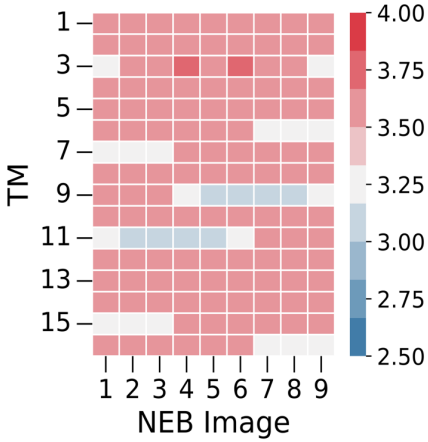




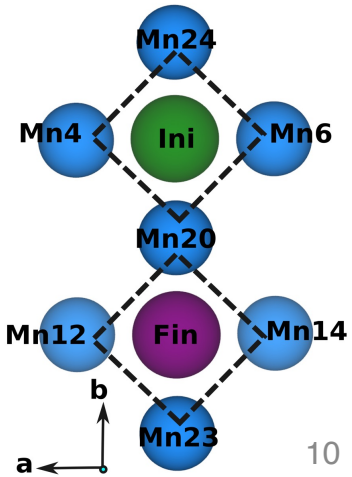




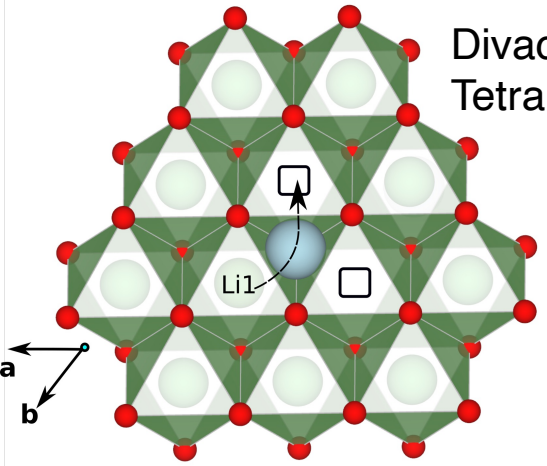
Mg^{2+} and holes should migrate in opposite directions



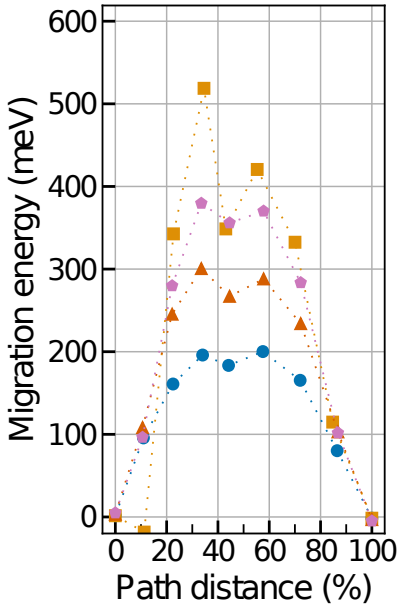
GGA

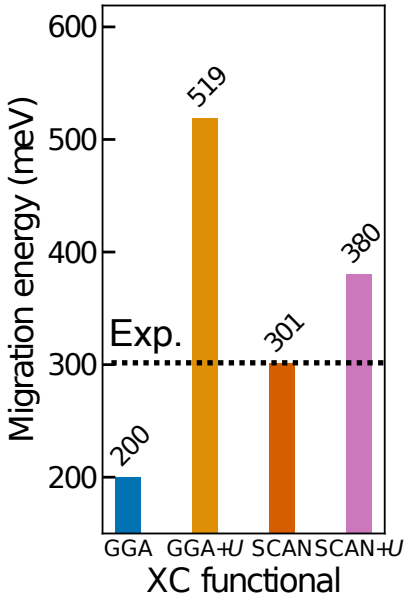


$LiCoO_2$ (metallic)
GGA+*U* overestimates

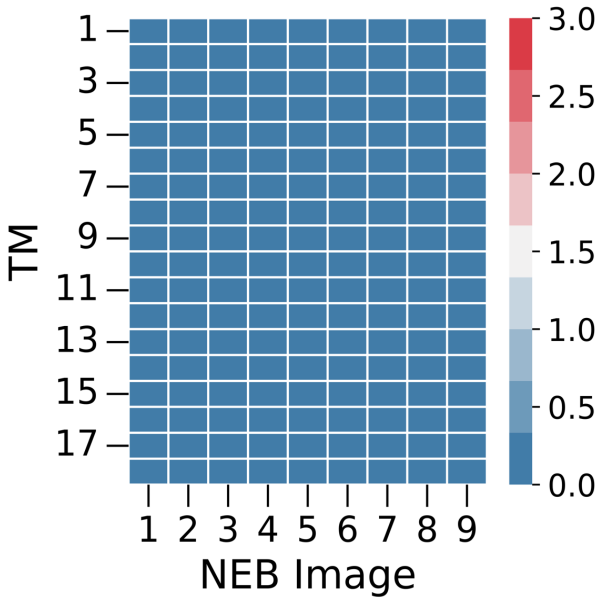


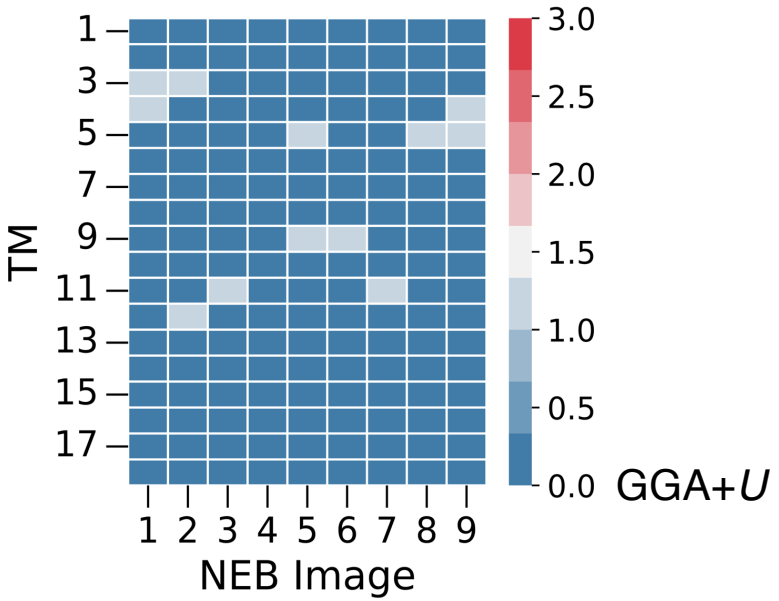
Divacancy (DV) or
Tetrahedral site hop (TSH)



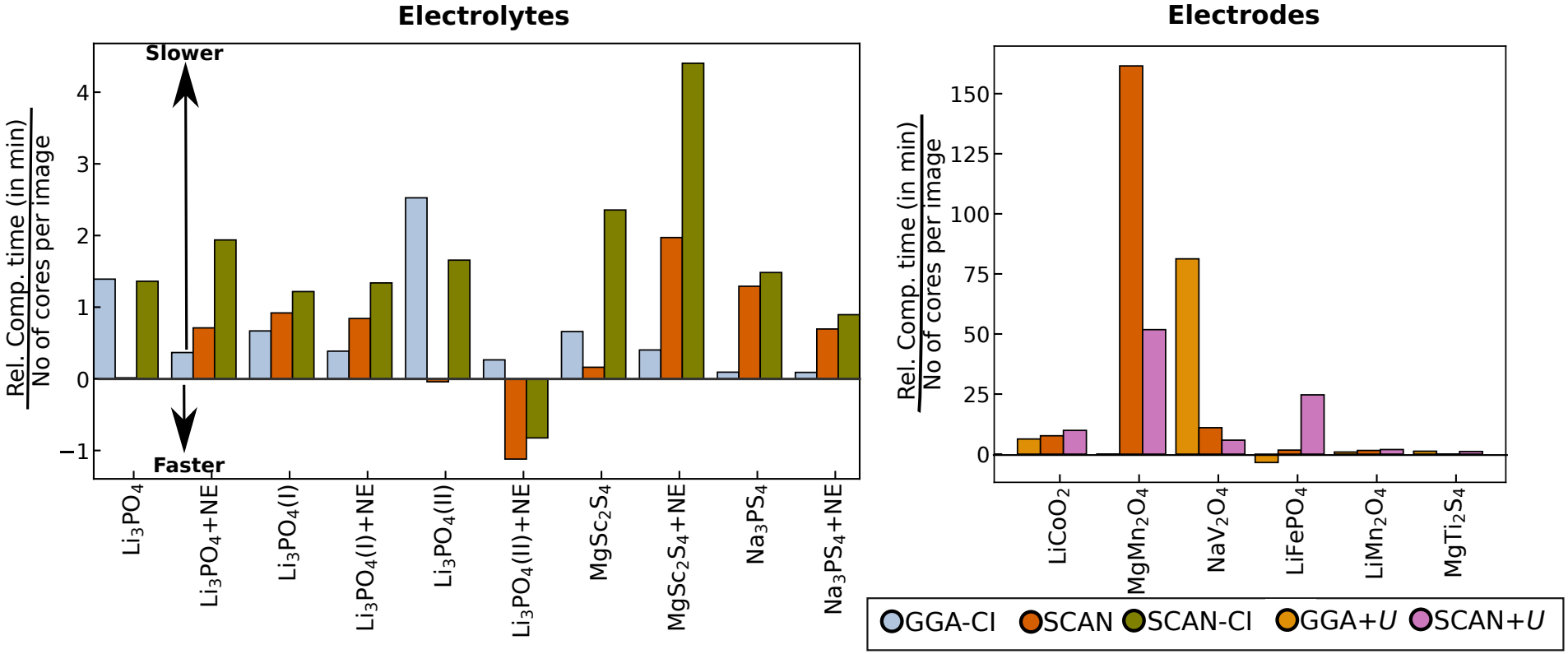


Other functionals





Computational performance
Is SCAN worth it?

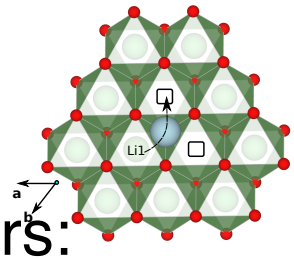


- Computational time with GGA/GGA+*U* ~75% faster than SCAN
- SCAN faster than SCAN+*U*
- Significant convergence difficulties with SCAN and SCAN+*U*

GGA for "*quicker*" estimate

SCAN for "*better*" accuracy

Summary



- Accurate computational predictions of migration barriers: important to improve rate performance of batteries

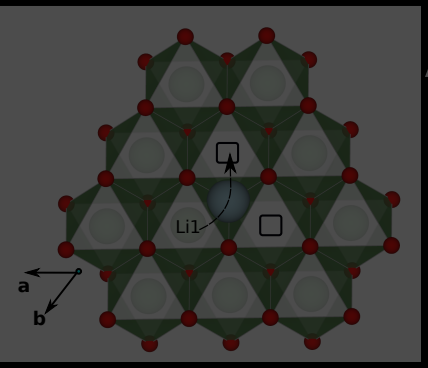
- NEB calculations – three computational handles relevant
  - XC framework
  - Uniform background charge
  - Climbing image

- Benchmark computational predictions with experimental barriers for 6 electrodes and 3 solid electrolytes

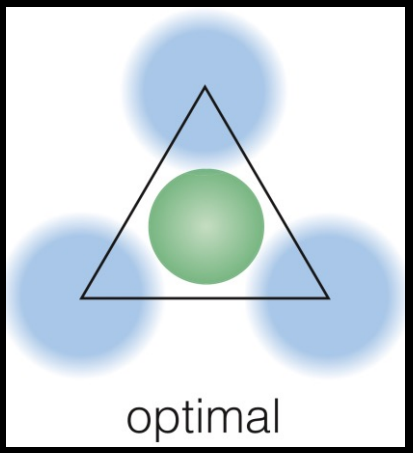
- SCAN: better accuracy on average
  - Describes better physics in both semiconducting and metallic hosts
  - CI/ne doesn't influence migration barriers significantly

- Computational hosts+ convergence difficulties: high for SCAN
  - SCAN for better accuracy, but GGA can provide good qualitative trends

Objectives

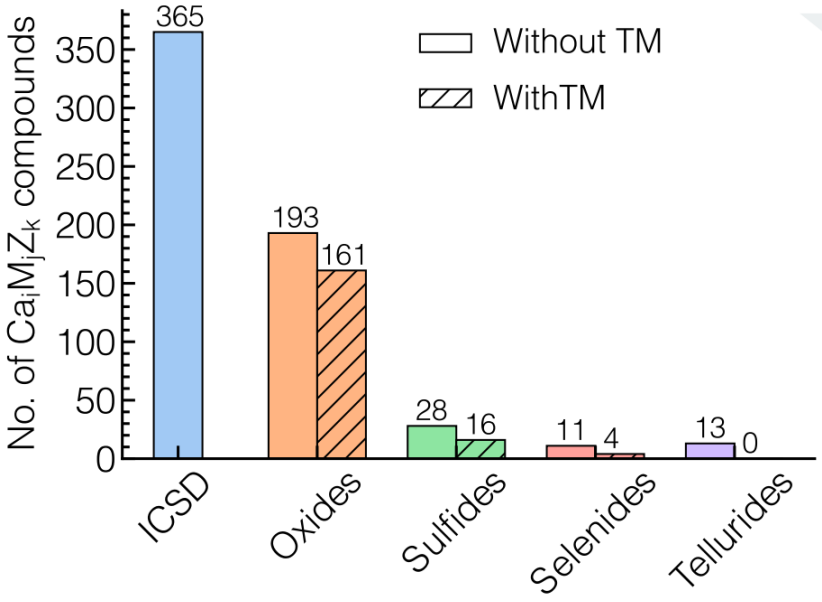


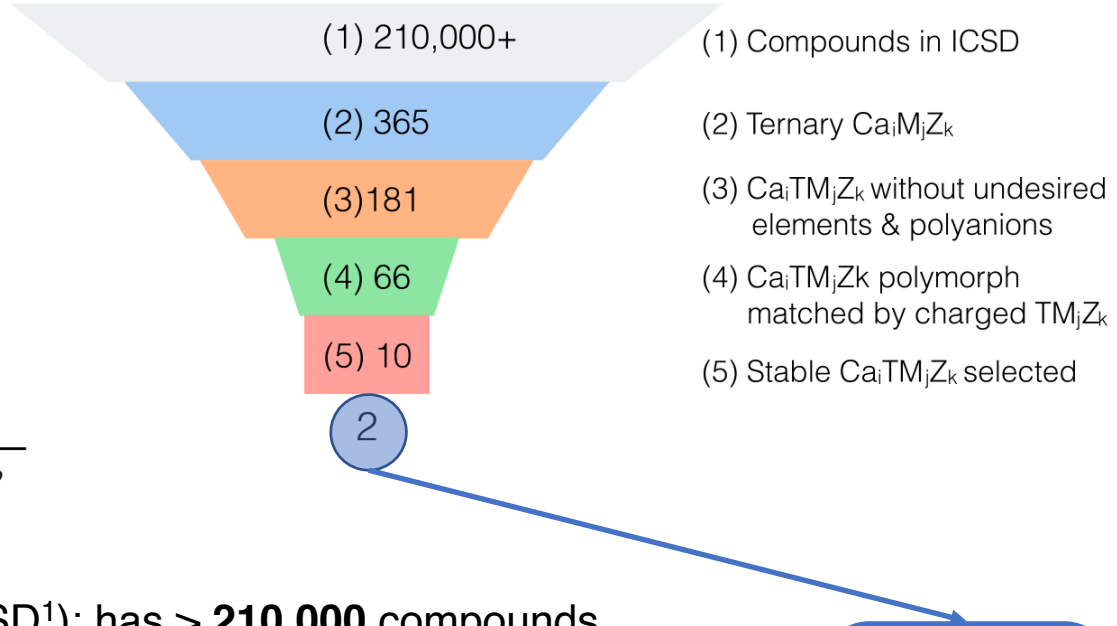
Assessing accuracy of computational predictions of ionic mobility



Examples of cathode discovery in Ca-batteries
(Ternary chemical space, NaSICONs)

Ternary Ca-compounds





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

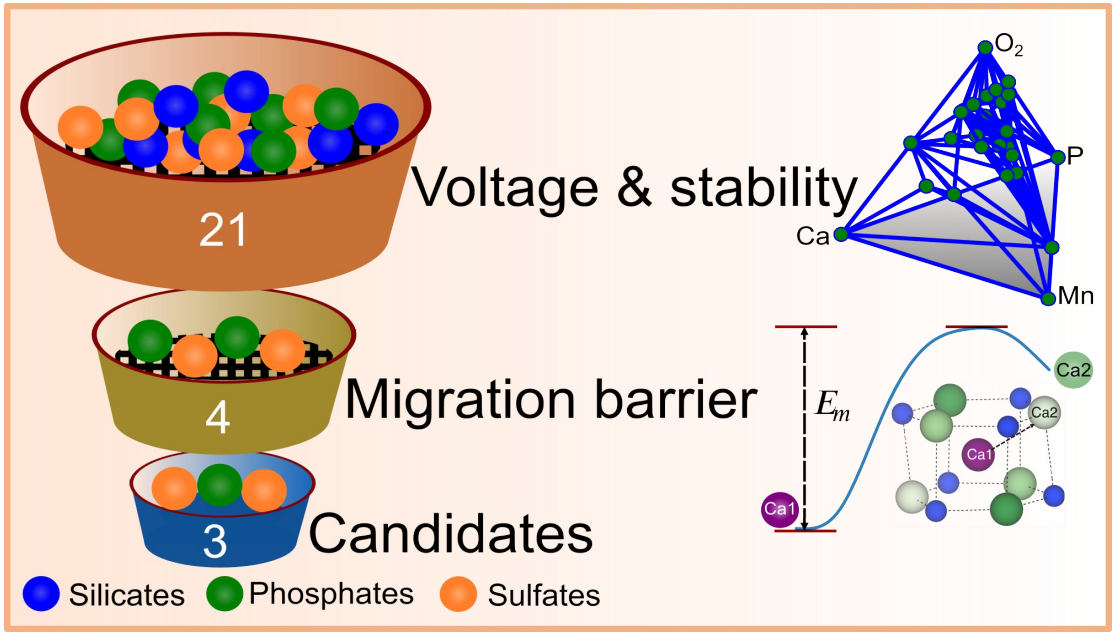
Final candidates!

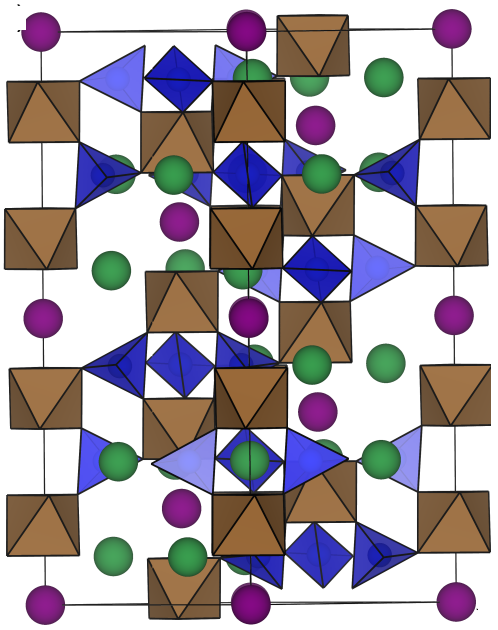
CaV_2O_4 and $CaNb_2O_4$

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

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

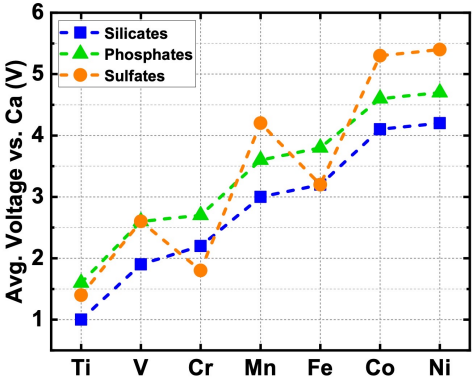
Sodium superionic conductors (NaSICONs)

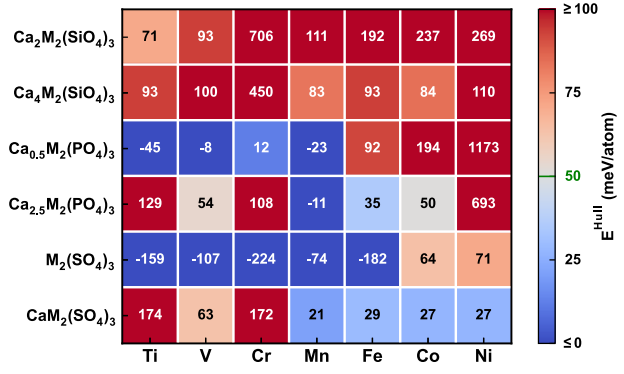


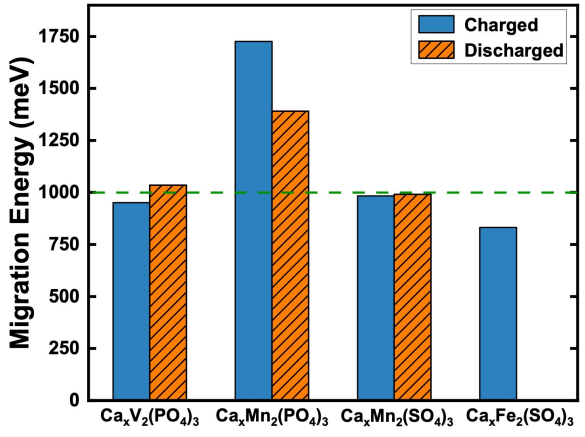


"NaSICONs"
$Ca_xM_2(ZO_4)_3$

High-throughput DFT calculations: 3 candidates







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

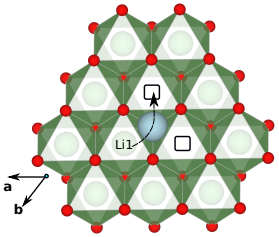
D.B. Tekliye, G.Sai Gautam, et al., **Chem. Mater. 2022**, *34*, 10133

Conclusions

- Removing material bottlenecks is important for improving performance of energy devices
  - Need cathodes and solid electrolytes with good power performance
  - Need robust computational predictions of ionic mobility

- SCAN provides better accuracy on E_m predictions, on average
  - Computational costs + convergence difficulties: high

- Ca-containing ternary compounds and NaSICONs screened
  - 2 possible candidates: CaV_2O_4 and $CaNb_2O_4$
  - $Ca_xV_2(PO_4)_3$, $Ca_xMn_2(SO_4)_3$, and $Ca_xFe_2(SO_4)_3$ are promising



NEB Benchmarking:
"Effect of exchange-correlation functionals on the estimation of migration barriers in battery materials", R. Devi, B. Singh, P. Canepa, and G. Sai Gautam, **npj Comput. Mater. 2022**, *8*, 160

Ternary Ca-cathode screening:
"Searching ternary oxides and chalcogenides as positive electrodes for calcium batteries", W. Lu, J. Wang, G.Sai Gautam, and P. Canepa, **Chem. Mater. 2021**, *33*, 5809-5821

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

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