

# Computational Screening of Positive Electrode Materials for Ca-Ion Batteries

Sai Gautam Gopalakrishnan, Ankit Kumar, Dereje Tekliye, Xie Weihang, Wang Lu,  
Juefan Wang, Pieremanuele Canepa

Materials Engineering, Indian Institute of Science

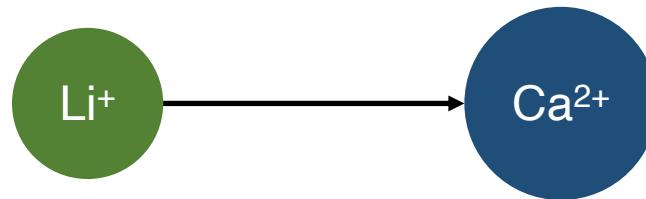
[saigautamg@iisc.ac.in](mailto:sagautamg@iisc.ac.in); <https://sai-mat-group.github.io>

DS04: Recent advances in data-driven discovery of materials for energy conversion and storage  
Materials Research Society Spring 2022 Meeting  
May 9, 2022

# 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

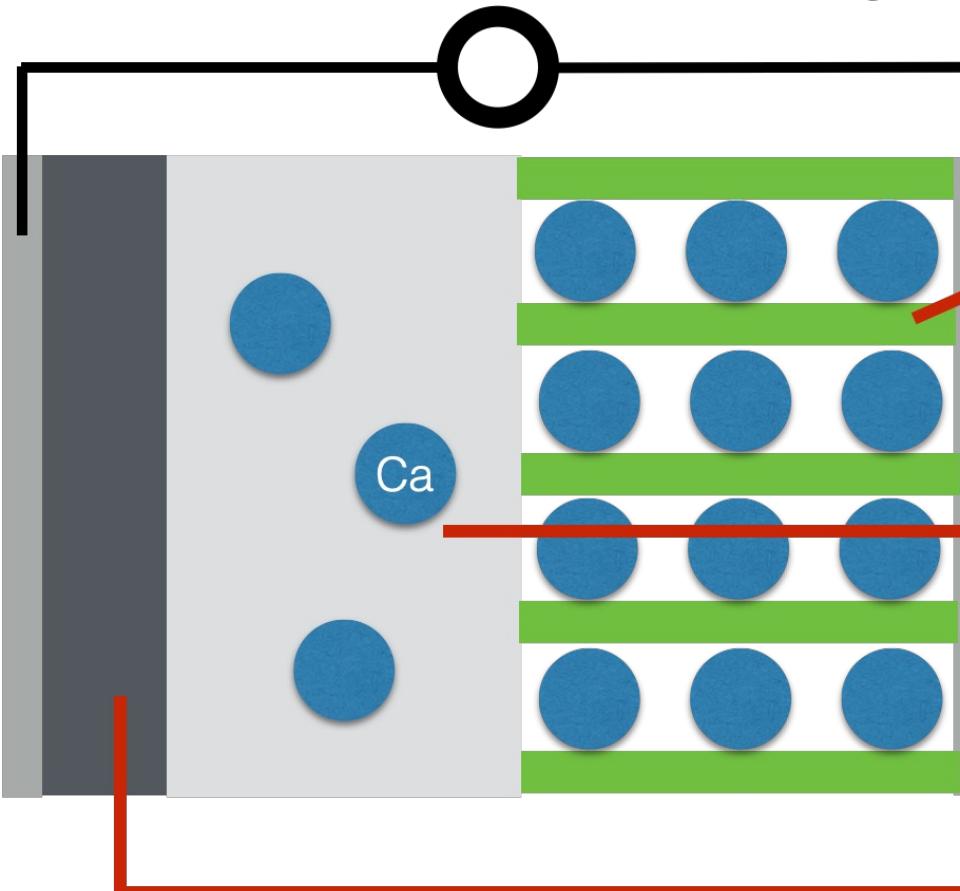


Why Ca?

- 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:

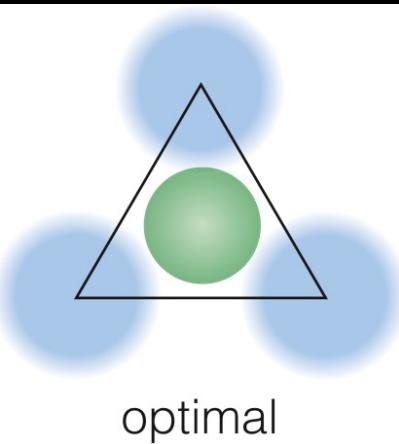
Stable electrolyte (at both electrodes) with good conductivity

## Metal Anode:

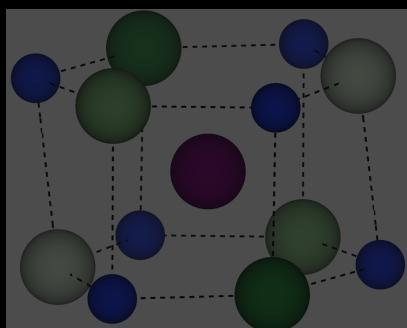
Understand plating and stripping in organic electrolytes

Ca: Find cathodes with reasonable voltage, capacity, and mobility, and be thermodynamically stable

# Objectives

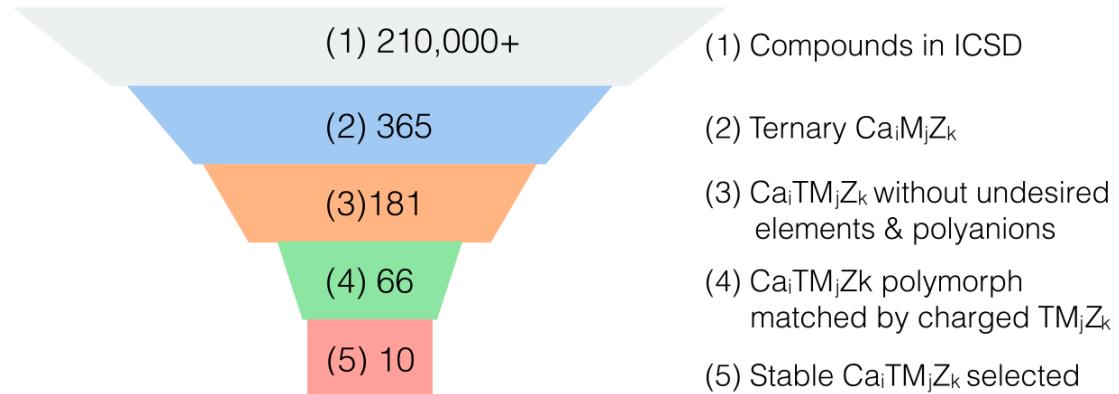
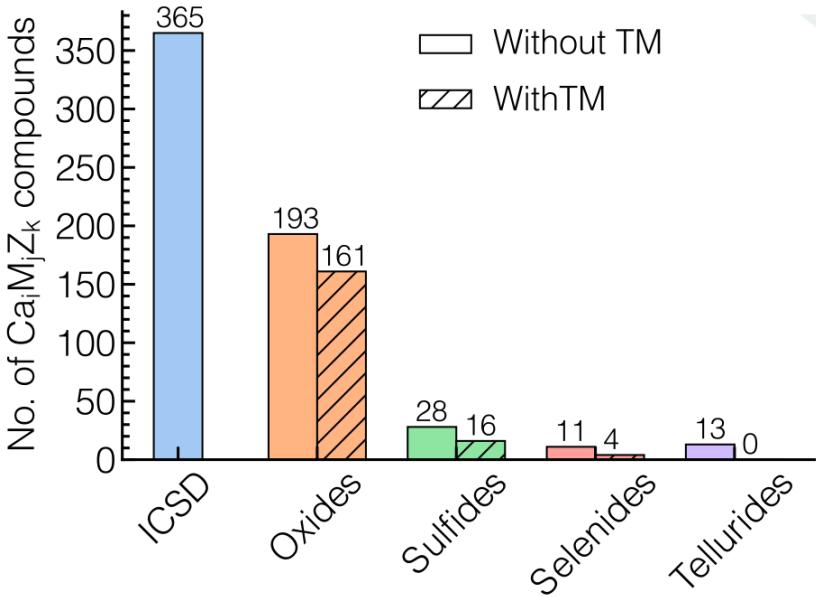


Screening ternary chemical space  
(Exchange-correlation functional: Hubbard  $U$  corrected  
Perdew-Burke-Ernzerhof or PBE+ $U$ )



Searching through the “NaSICON” chemical space

# Let's look at ternary Ca-compounds



Inorganic crystal structure database (ICSD<sup>1</sup>): has **> 210,000** compounds

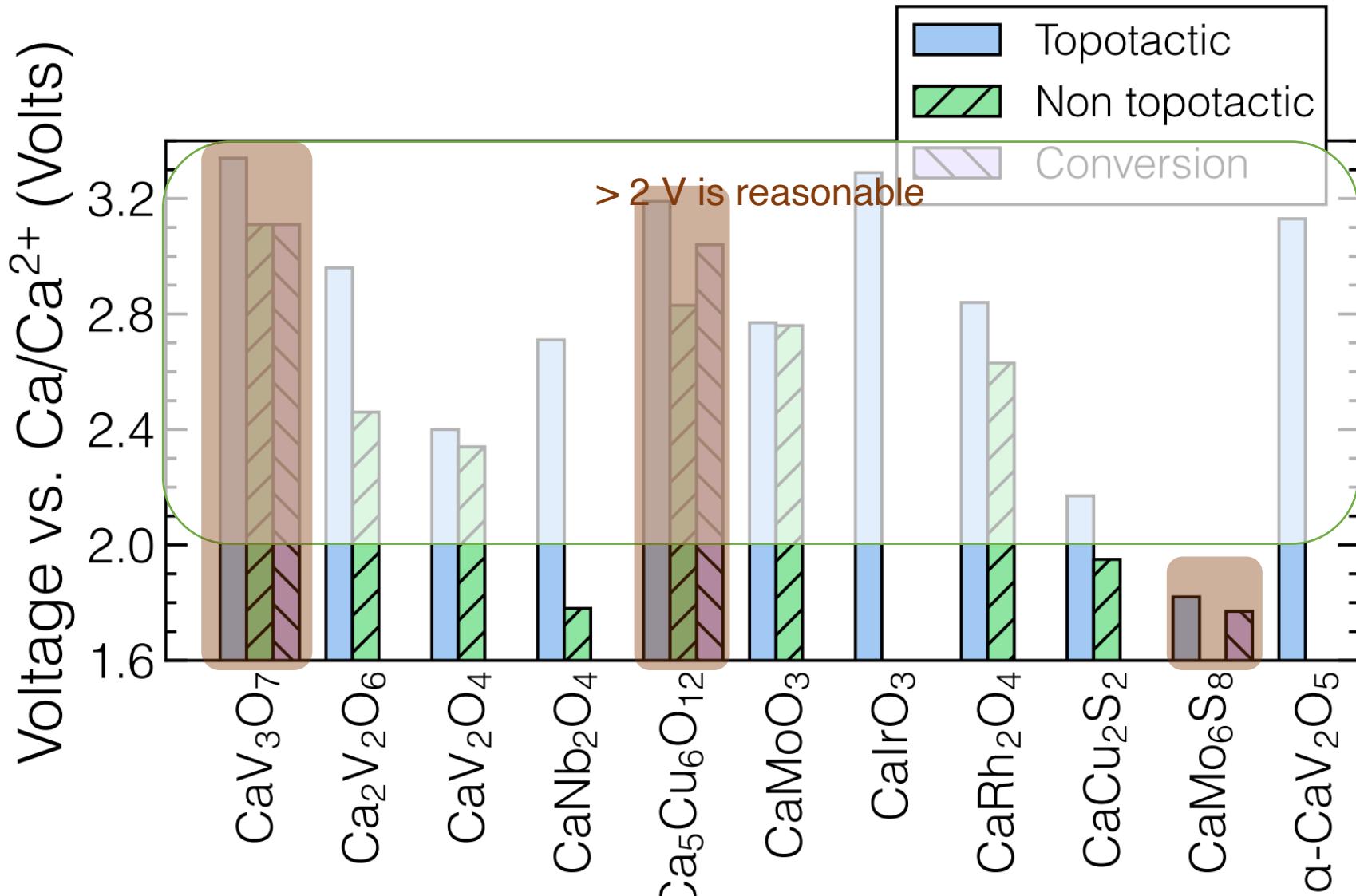
- Only **365** are ternary compounds containing Ca
  - Compounds of composition  $\text{Ca}_i\text{M}_j\text{Z}_k$ ; M, Z = elements other than Ca
- Let M = TM (i.e., transition metal) and Z = O, S, Se, or Te
  - Results in **181** unique compounds
- Charge-neutral charged compound ( $\text{TM}_j\text{Z}_k$ ) available for  $\text{Ca}_i\text{TM}_j\text{Z}_k$ ?
  - $\text{CaMn}_2\text{O}_4$ - $\text{Mn}_2\text{O}_4$  is ok,  $\text{CaVO}_3$ - $\text{VO}_3$  not ok
  - 66** unique structures
- Either of  $\text{Ca}_i\text{TM}_j\text{Z}_k$  or  $\text{TM}_j\text{Z}_k$  thermodynamically (meta)stable?
  - $E^{hull} \leq 30$  meV/atom (based on Materials Project<sup>2</sup>)
  - 10** unique compounds → evaluate voltage, mobility

Final candidates!

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

# Voltages calculated with GGA+U

Conversion voltage: tendency of Ca-discharged composition to decompose (CaO+MO)



Topotactic: no change in electrode framework

(11)  $\alpha\text{-CaV}_2\text{O}_5$  added as benchmark

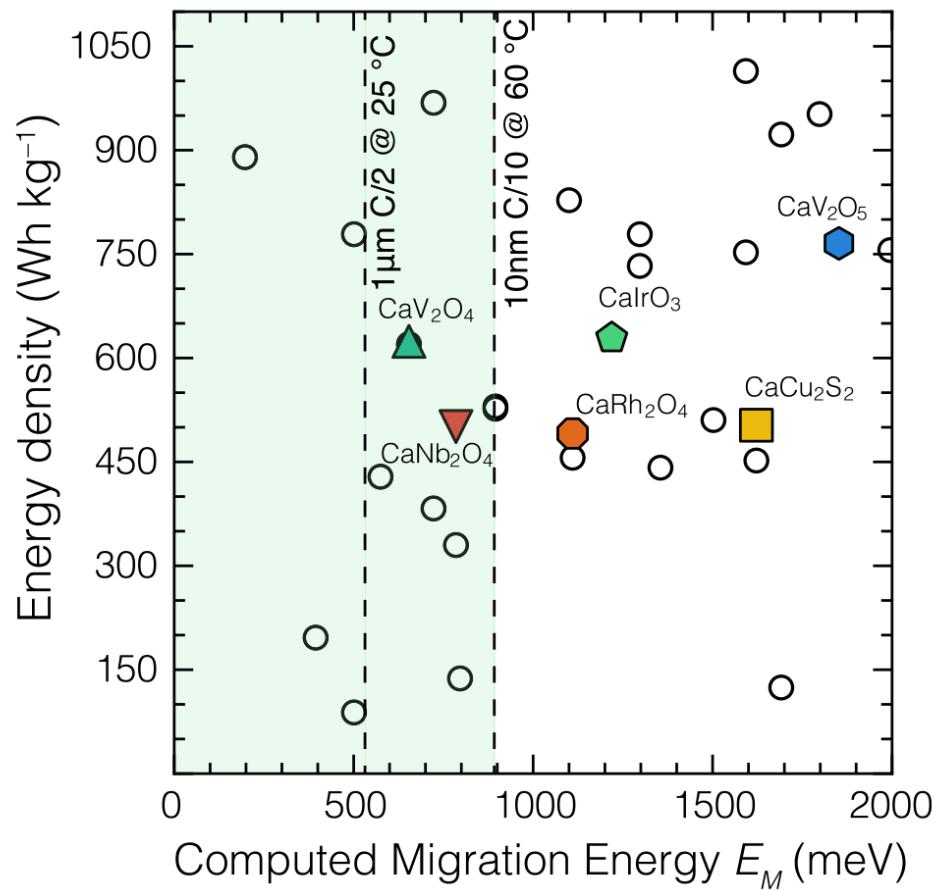
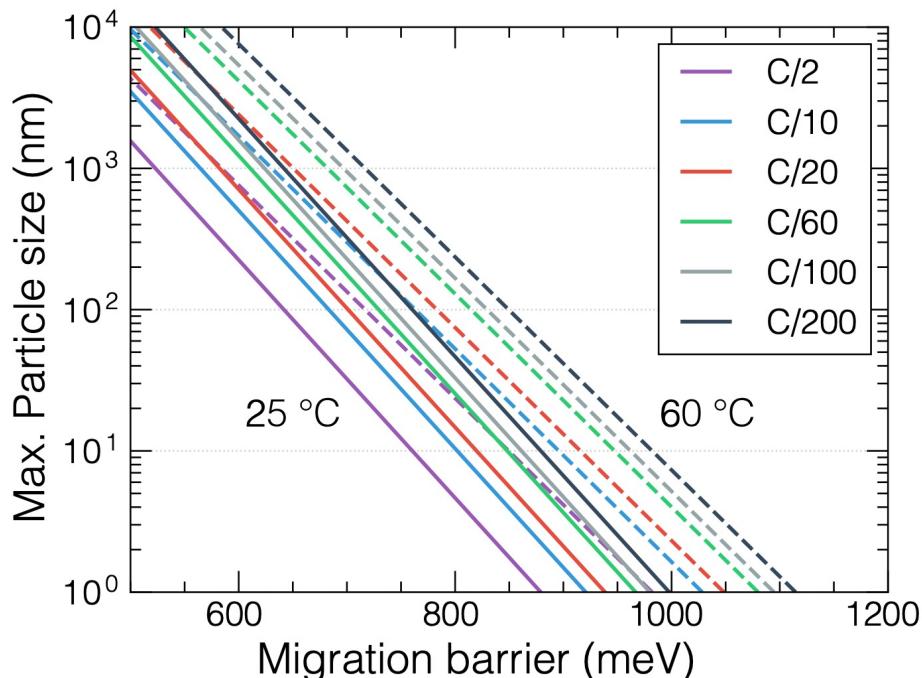
# Ca diffusivity: nudged elastic band

$$D \approx \frac{x^2}{t}$$

Electrode particle size  
Diffusion time (rate of operation)

$$D = v a^2 f g x_D \exp\left(-\frac{E_m}{k_B T}\right)$$

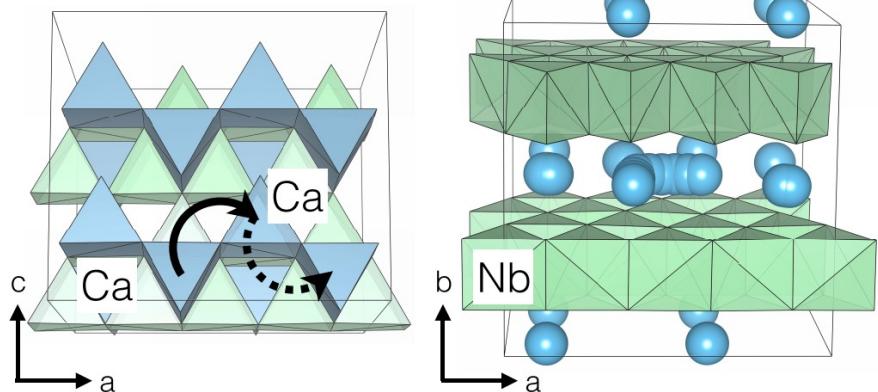
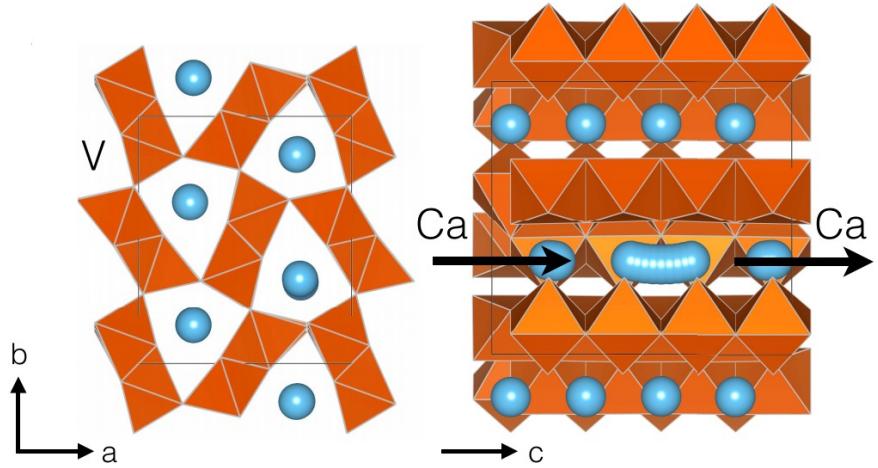
Diffusivity mainly governed by barrier  
Required diffusivity  $\rightarrow$  maximum of  $E_m$   
Variables: size, time, and temperature



Max. tolerable barrier  $\sim 980$  meV

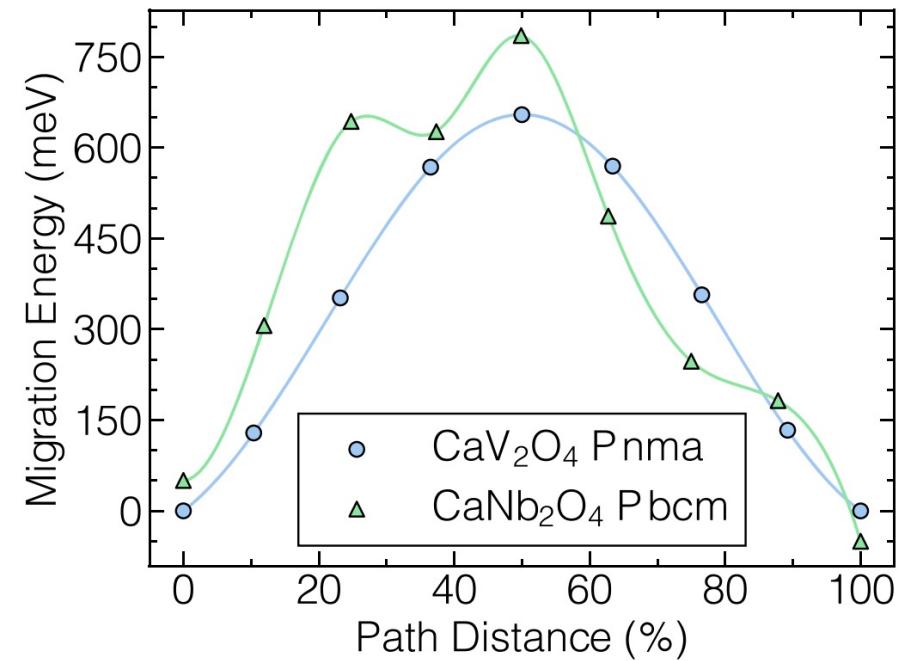
- 2 candidates display reasonable  $E_m$
- CaV<sub>2</sub>O<sub>4</sub>: 654 meV
  - CaNb<sub>2</sub>O<sub>4</sub>: 785 meV

# Migration pathways of candidates



$\text{CaV}_2\text{O}_4$ : 8 → 3 → 8

$\text{CaNb}_2\text{O}_4$ : 6 → 4 → 6 → 4 → 6

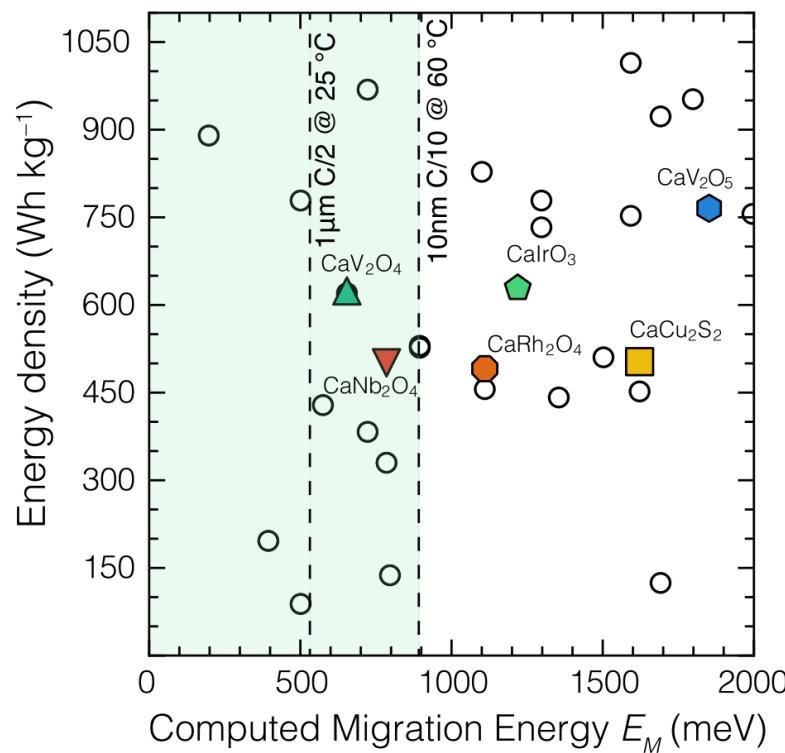


Can we frame some design rules to discover more facile Ca diffusers?

# Design rules: update

Existing rules to identify facile ionic conductors<sup>1</sup> doesn't work for Ca:

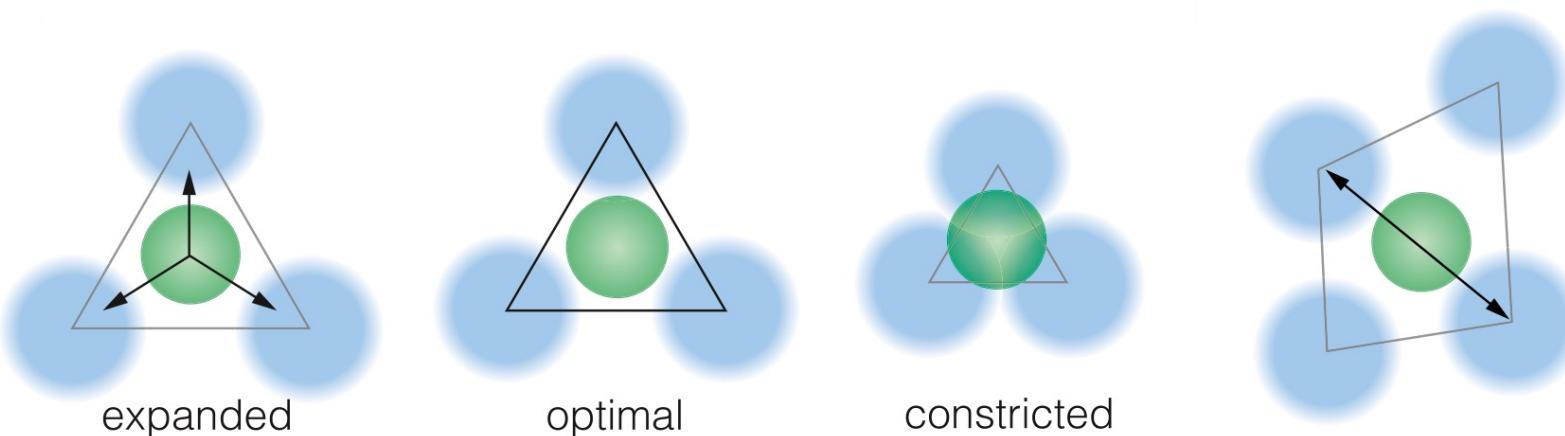
- Avoid structures with Ca's "preferred" coordination of 8
  - $\text{CaV}_2\text{O}_4$  ( $E_m = 654$  meV) and  $\text{CaMoO}_3$  (2072 meV) have Ca in 8-coordination
- Reduce changes in coordination number during migration
  - $\text{CaV}_2\text{O}_4$  (coordination change of 5) and  $\text{CaNb}_2\text{O}_4$  (change of 2) have low barriers
- Increase volume per anion (i.e., prefer  $\text{S}^{2-}$  instead of  $\text{O}^{2-}$ ) to reduce  $E_m$ 
  - $\text{CaCu}_2\text{S}_2$  ( $E_m = 1622$  meV) has higher barriers than several oxides



# Design rules: update

Existing rules to identify facile ionic conductors<sup>1</sup> doesn't work for Ca:

- Avoid structures with Ca's "preferred" coordination of 8
  - $\text{CaV}_2\text{O}_4$  ( $E_m = 654$  meV) and  $\text{CaMoO}_3$  (2072 meV) have Ca in 8-coordination
- Reduce changes in coordination number during migration
  - $\text{CaV}_2\text{O}_4$  (coordination change of 5) and  $\text{CaNb}_2\text{O}_4$  (change of 2) have low barriers
- Increase volume per anion (i.e., prefer  $\text{S}^{2-}$  instead of  $\text{O}^{2-}$ ) to reduce  $E_m$ 
  - $\text{CaCu}_2\text{S}_2$  ( $E_m = 1622$  meV) has higher barriers than several oxides



Updated design rules for identifying facile Ca conductors:

- Structures should exhibit optimal area/diagonal/volume fraction of Ca at transition state
- Avoid face-sharing cations at transition state
- Minimize volume fraction change during migration

# Design rules: update

Existing rules to identify facile ionic conductors<sup>1</sup> doesn't work for Ca:

- Avoid structures with Ca's "preferred" coordination of 8
  - $\text{CaV}_2\text{O}_4$  ( $E_m = 654$  meV) and  $\text{CaMoO}_3$  (2072 meV) have Ca in 8-coordination
- Reduce changes in coordination number during migration
  - $\text{CaV}_2\text{O}_4$  (coordination change of 5) and  $\text{CaNb}_2\text{O}_4$  (change of 2) have low barriers
- Increase volume per anion (i.e., prefer  $\text{S}^{2-}$  instead of  $\text{O}^{2-}$ ) to reduce  $E_m$ 
  - $\text{CaCu}_2\text{S}_2$  ( $E_m = 1622$  meV) has higher barriers than several oxides

## Summary:

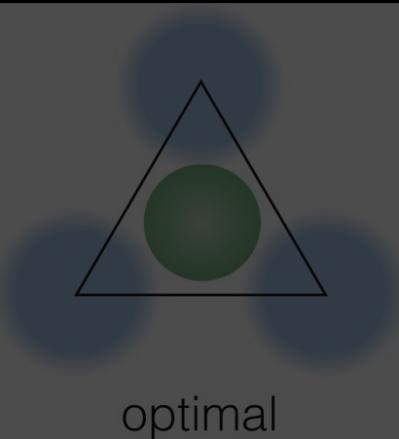
- Identified two Ca-cathode candidates:  $\text{CaV}_2\text{O}_4$  (post-spinel) and  $\text{CaNb}_2\text{O}_4$  (layered)
- Updated design rules to identify other facile Ca conductors

Updated design rules for identifying facile Ca conductors:

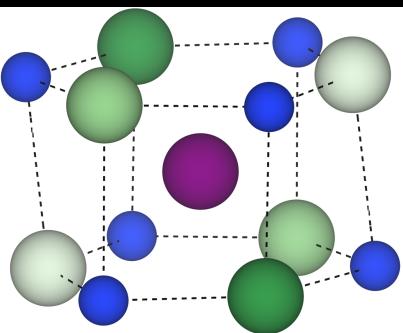
- Structures should exhibit optimal area/diagonal/volume fraction of Ca at transition state
- Avoid face-sharing cations at transition state
- Minimize volume fraction change during migration

# Objectives

Screening ternary chemical space



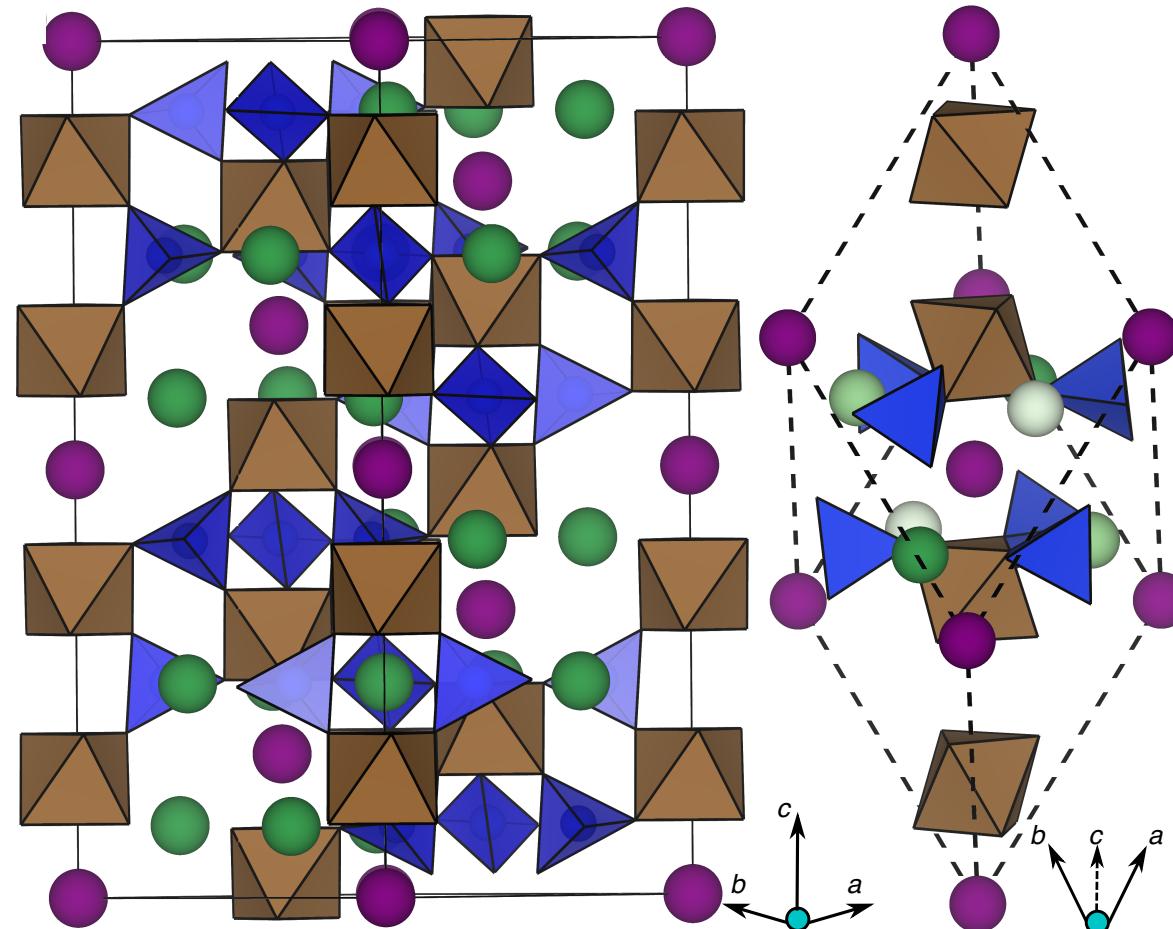
Searching through the “NaSICON” chemical space



(Exchange-correlation functional: Hubbard  $U$  corrected  
strongly constrained and appropriately normed or SCAN+ $U$ )

# 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

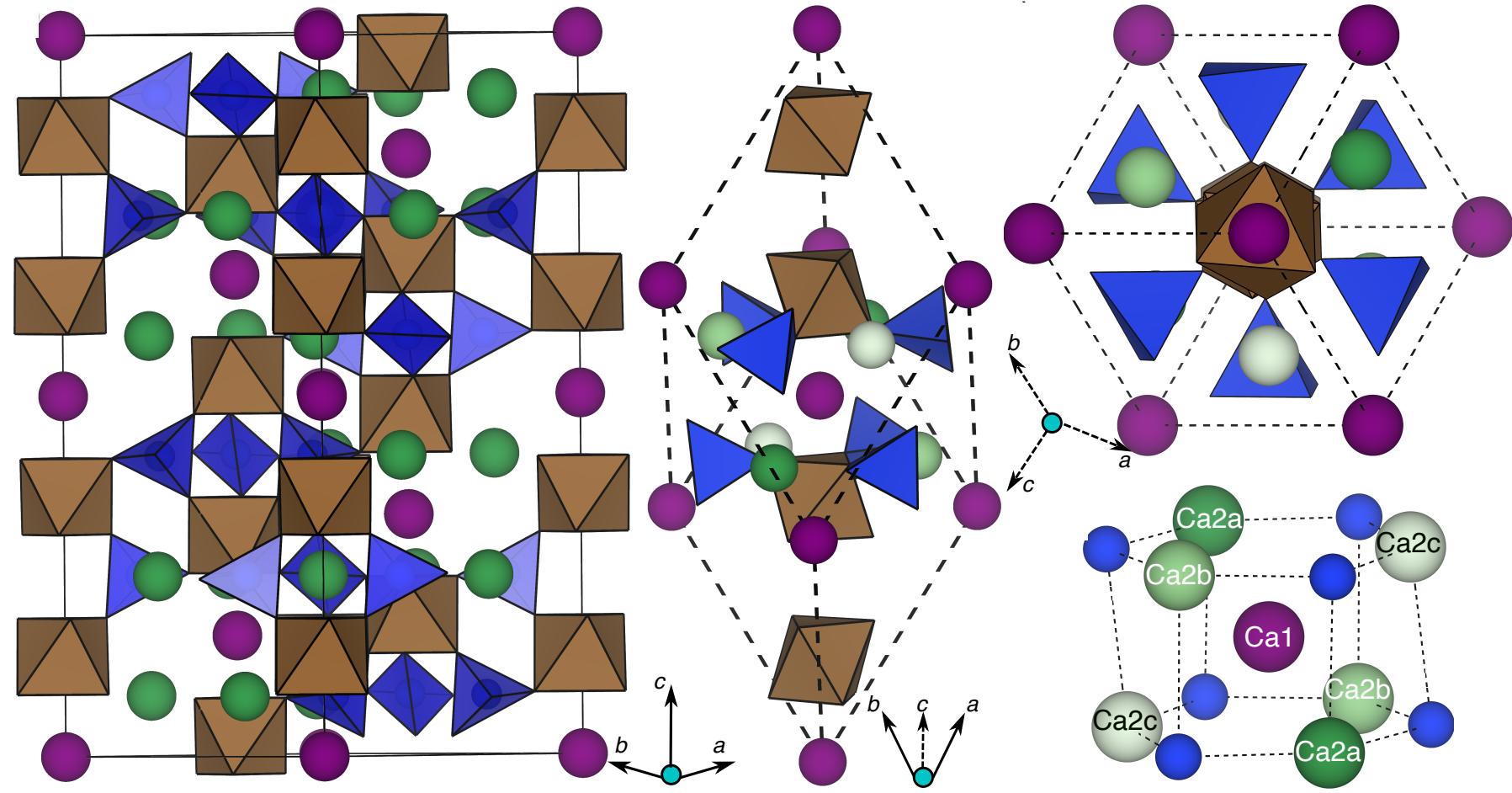
Conventional cell: 6  $\text{M}_2(\text{ZO}_4)_3$  formula units

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?

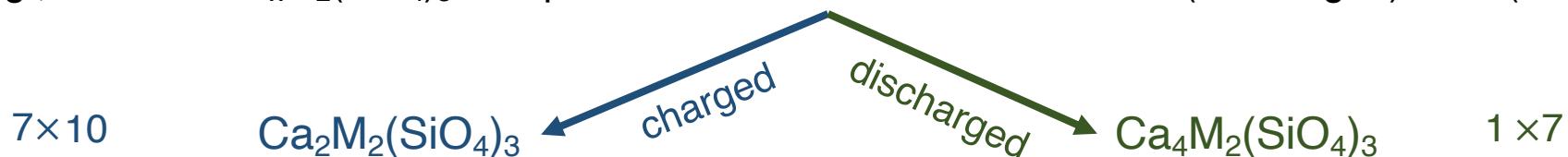
Preliminary experimental evidence is positive [Kim et al., *ACS Energy Lett.* **2020**, 5, 3203–3211]



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

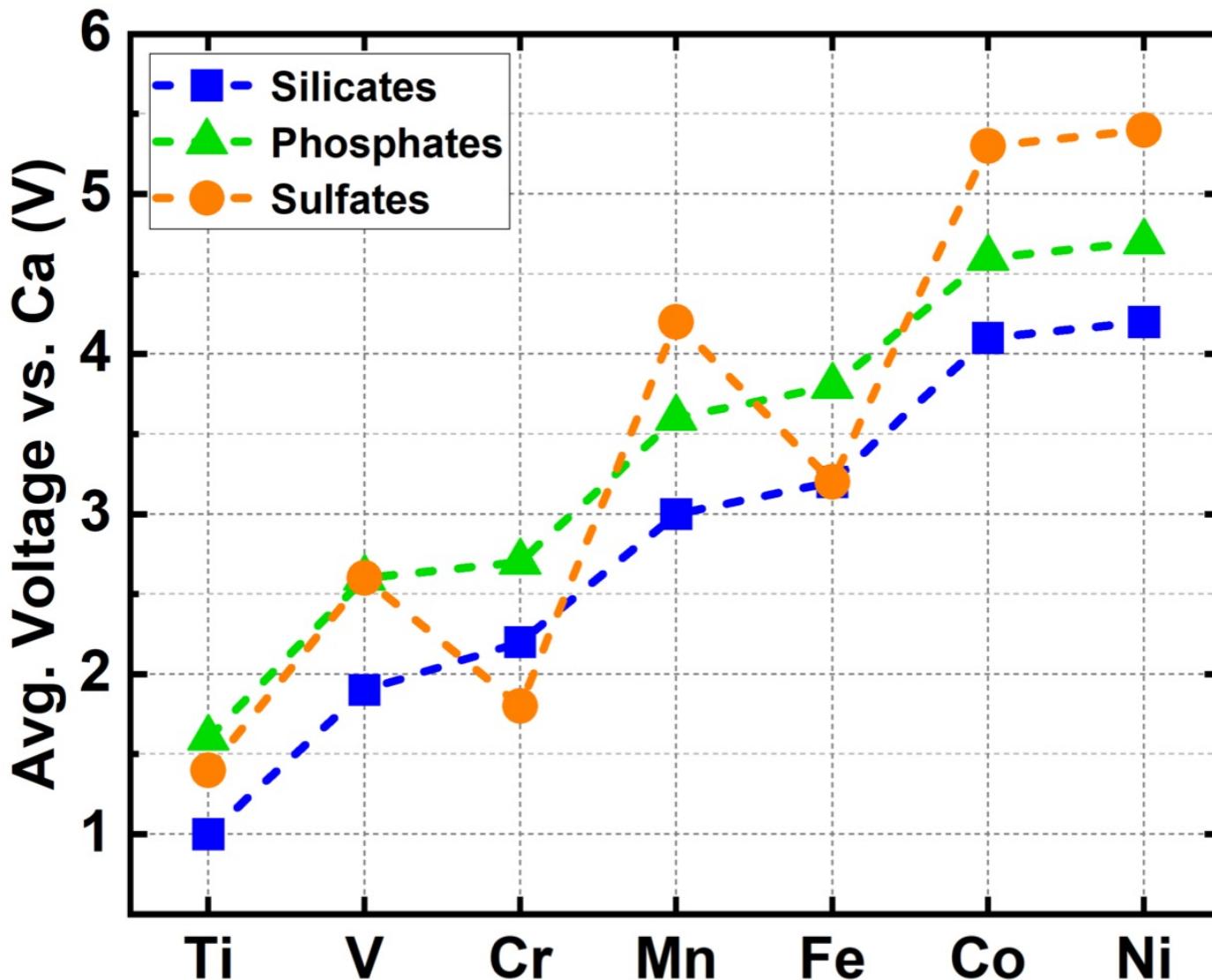


Enumerate Ca-vacancy configurations in primitive Na<sub>2</sub>SiO<sub>5</sub> with pymatgen<sup>1</sup> for a given M

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

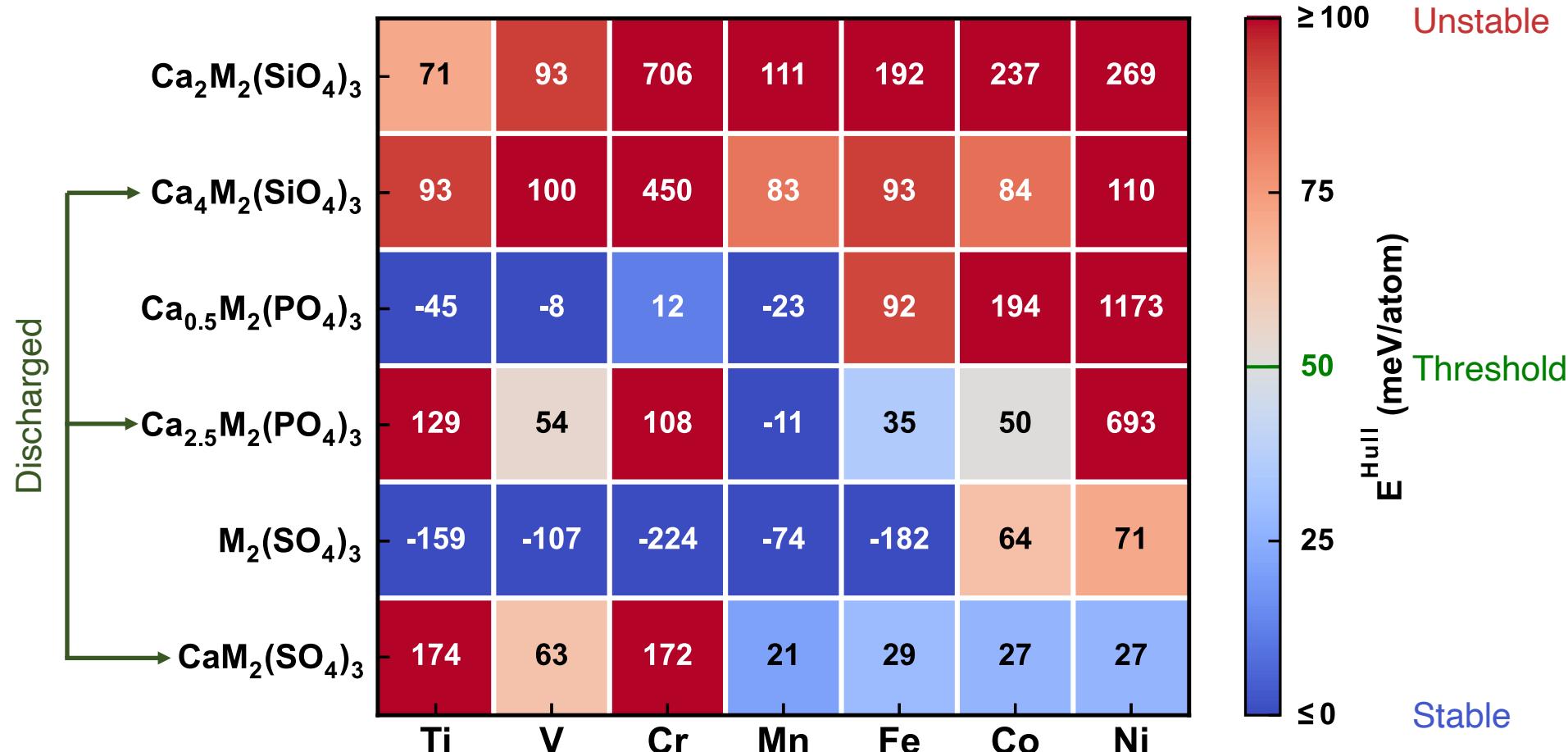
“Local” minima in voltage trends for Cr and Fe  $\text{SO}_4$

- 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



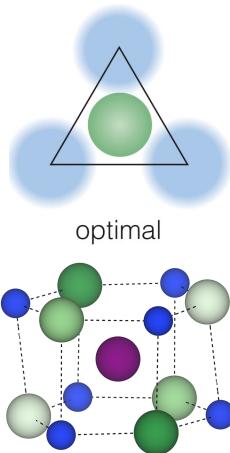
All charged and discharged silicates unstable: unsuitable for Ca-cathodes

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

# Conclusions and Acknowledgments



- Removing material bottlenecks is important for improving performance of energy devices
  - Need better, safer, and cheaper batteries (Ca vs. Li), need good Ca-cathodes
- Ca-containing ternary compounds from ICSD screened
  - Screening criteria: redox-activity, charge-neutrality, and thermodynamic stability (PBE+U)
  - 2 possible candidates:  $\text{CaV}_2\text{O}_4$  and  $\text{CaNb}_2\text{O}_4$
- Chemical space of NaSICONs explored as Ca-cathodes
  - Average voltages, theoretical capacity, and thermodynamic stability calculated (SCAN+U)
  - Mn-based phosphate and sulfate, V-sulfate, and Fe-sulfate are promising

Ca-electrodes:

“Searching ternary oxides and chalcogenides as positive electrodes for calcium batteries”, W. Lu, J. Wang, G.S. Gautam, and P. Canepa, **Chem. Mater.** **2021**, *33*, 5809-5821

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.S. Gautam, **to be submitted**



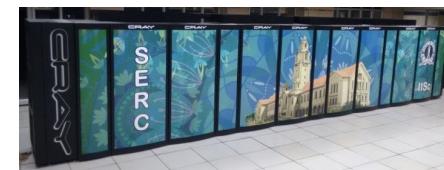
+CaRe group

[sagautamg@iisc.ac.in](mailto:sagautamg@iisc.ac.in)  
<https://sai-mat-group.github.io>

NSCC (Singapore)



SERC (IISc)



# The team



**Sai Gautam  
Gopalakrishnan**  
Principal Investigator



**Nidhish Sagar**  
Integrated Masters Student



**Reshma Devi  
Parthasarathy**  
Ph. D. student



**Rutvij Pankaj  
Kulkarni**  
Project Associate



**Debolina Deb**  
Ph. D. student



**Jayant Kumar**  
Masters student



**Sanyam Nitin  
Totade**  
Masters student



**Dereje Bekele  
Tekliye**  
Ph. D. student



**Abhirup Bhadra**  
Visiting Ph.D. Student



**Tanmay Mohan  
Bhagwat**  
Intern (Undergraduate)



**Anooj Sathyan**  
Undergraduate Student



**Swathilakshmi**  
Intern (Undergraduate)



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



**Vijay Choyal**  
Institute of Eminence Fellow



**Adilakshmi  
Chirumamilla**  
Masters student



**Sachin Kumar**  
Masters student