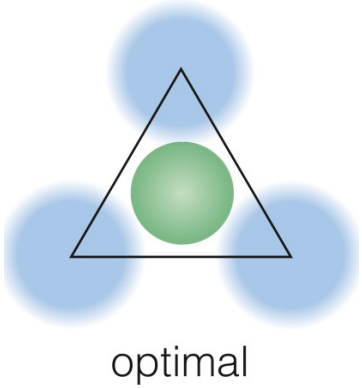

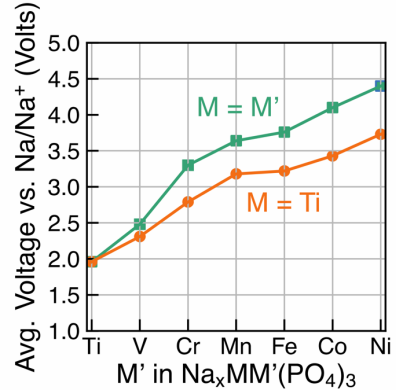

Screening chemical spaces for positive electrodes in beyond-Li-ion batteries using computational techniques

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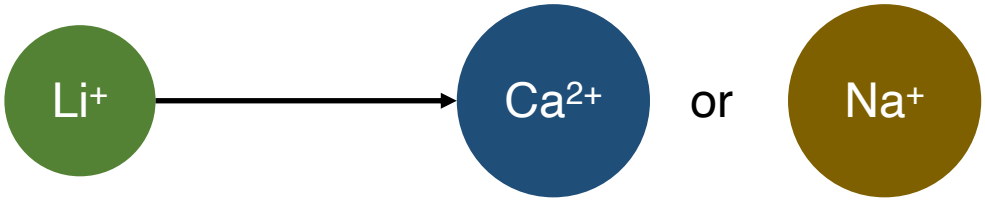
Annual General Meeting, Materials Research Society of India, IIT Madras
Dec 23, 2021

Why beyond-Li-ion batteries?

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

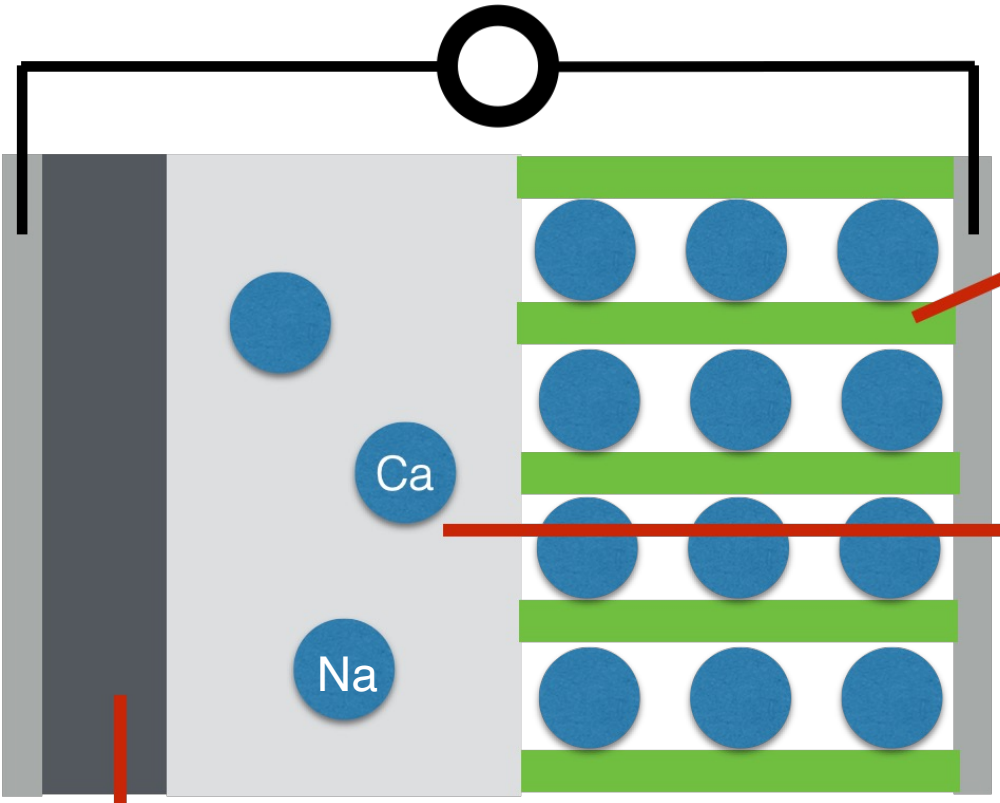
- Multi-valent == More electrons (Ca^{2+}, Mg^{2+}, Al^{3+}, etc.)
- Na-ion == earth abundance, cost-effective
- Li-ion technology approaching fundamental limits
  - Safety, supply-chain constraints; limits on achievable energy densities



Why Ca/Na?

- Superior volumetric capacity for Ca metal (~2077 Ah/l) than Li in graphite (~800 Ah/l)
- Ca/Na is safer than Li, less constrained geopolitically
- Na compatible with stainless-steel current collectors vs. Cu for Li

Cathode design challenge



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

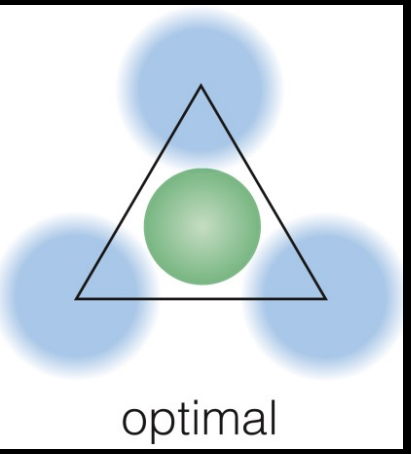
Electrolyte:
Stable electrolyte (at both electrodes) with good conductivity

Metal Anode:
Understand plating and stripping in organic electrolytes

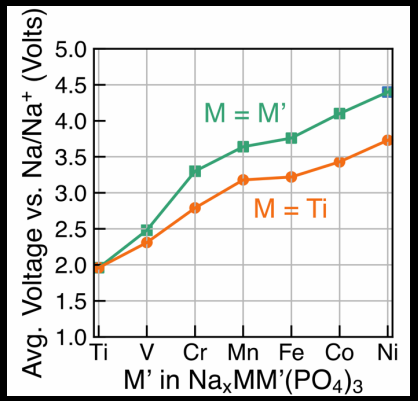
(For Ca batteries)

Ca: Find cathodes with reasonable voltage and capacity, and be thermodynamically stable
Na: Find cathodes with robust structural stability (for cycle life) with reasonable energy density

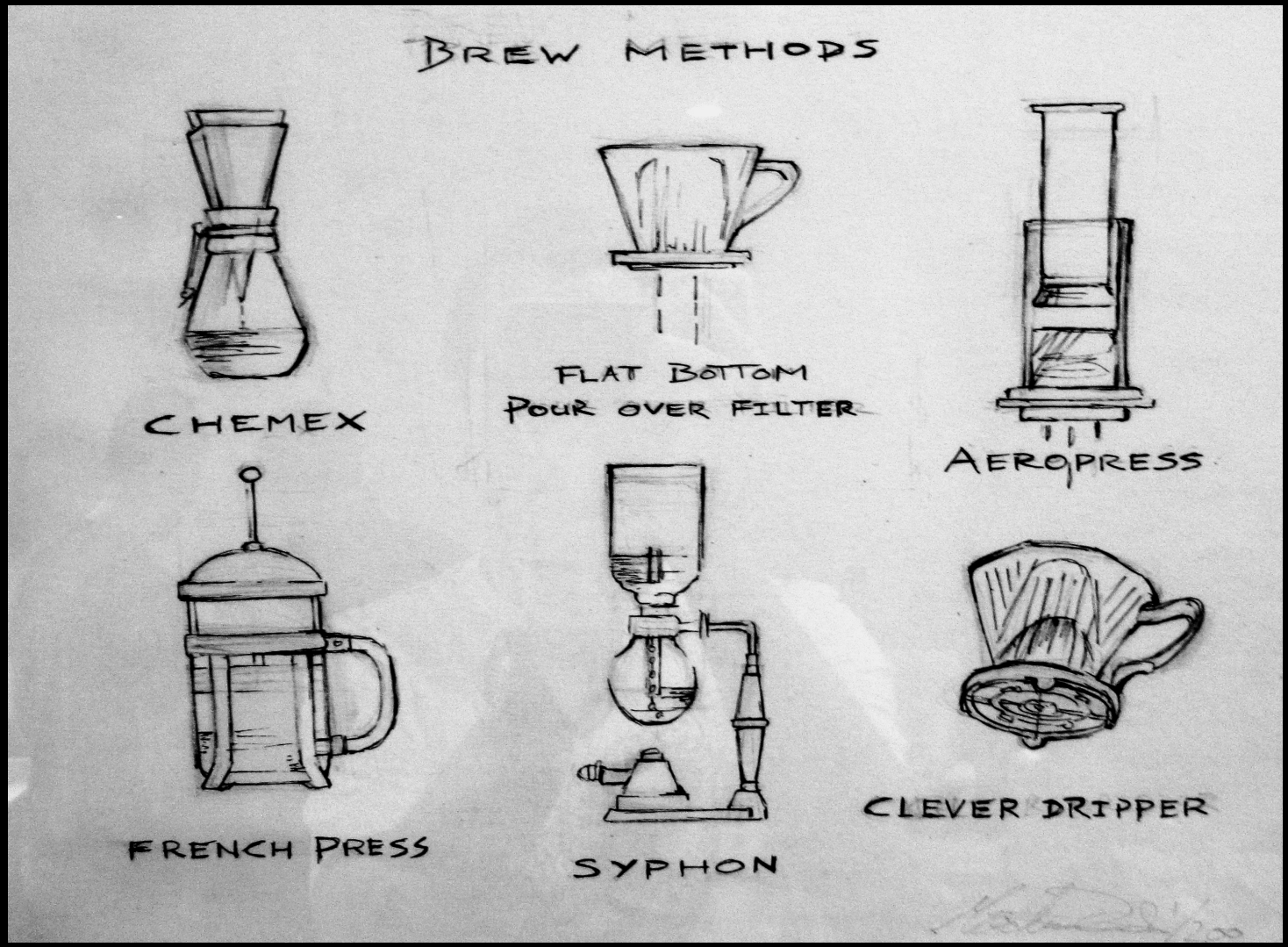
Objectives



Discover new cathodes for Ca batteries

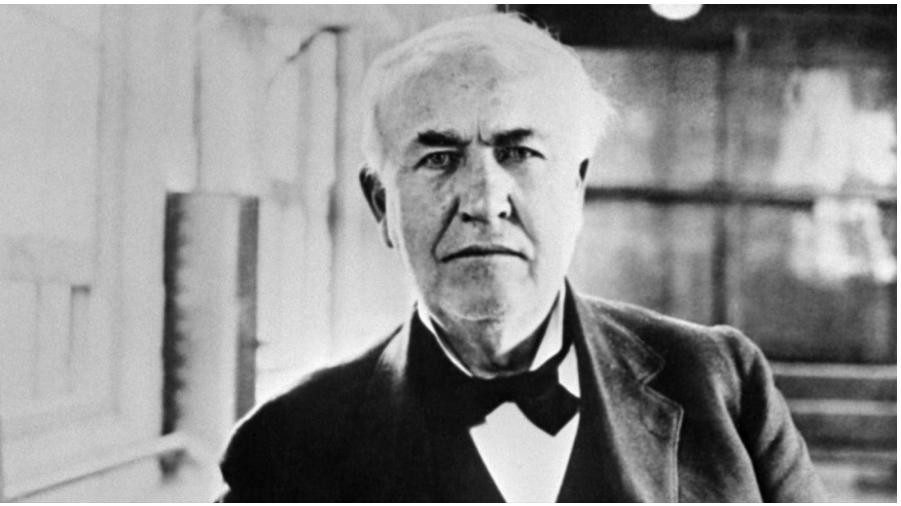


Screen for cathodes with robust structural stability for Na-ion batteries



Methods detour (and stability)

Methods: Edison vs. Iron Man



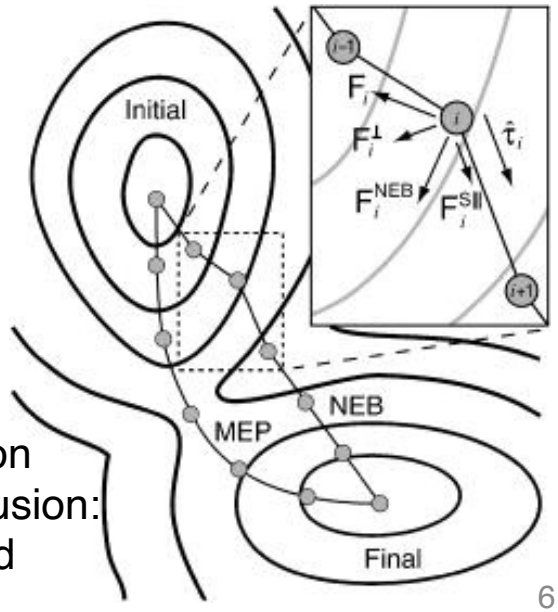
Trial and error of candidates in a lab

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

Density functional theory: (Approximately) predict material properties

- Exchange-correlation functional: Hubbard *U* corrected generalized gradient approximation (GGA+*U*)[1]

1. Perdew et al., **Phys. Rev. Lett. 1996**, *77*, 3865

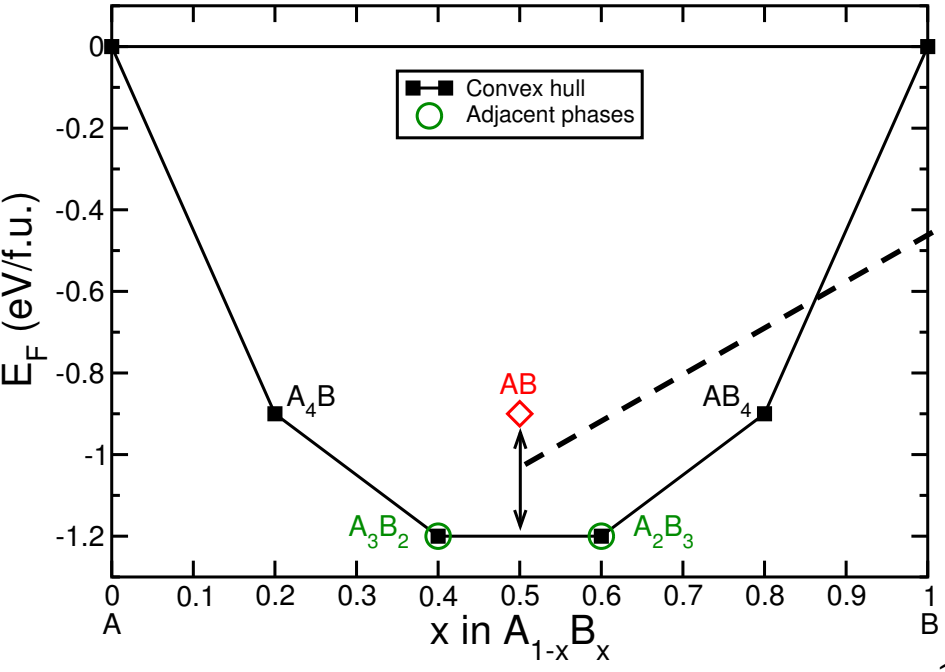


Calculating migration barrier for ionic diffusion: nudged elastic band (NEB)[2]

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

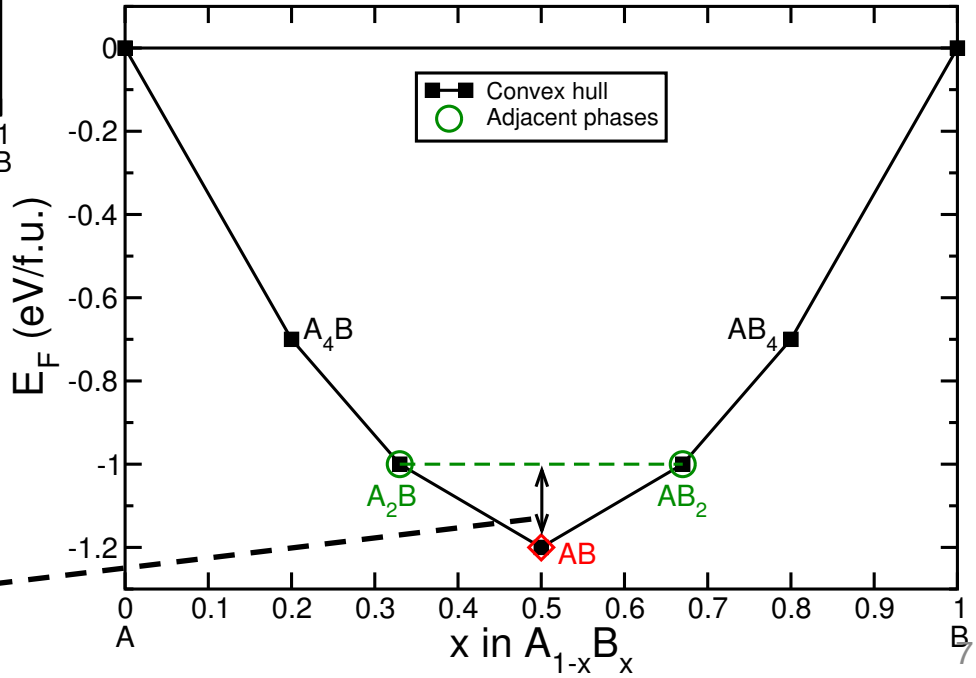
0 K thermodynamics: convex hull

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



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

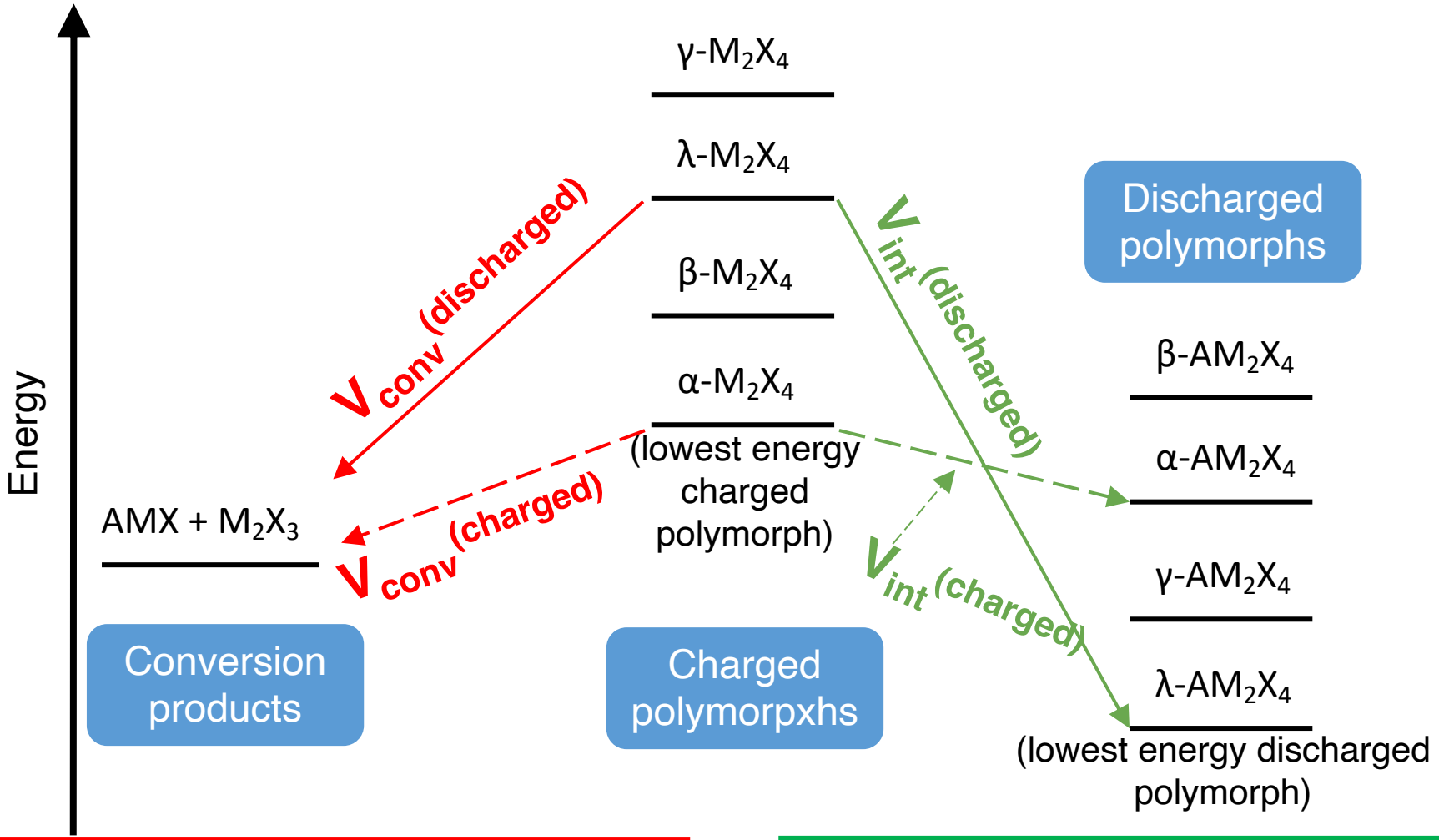
- Largest energy release via decomposition of AB



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

- Lowest energy release via formation of AB

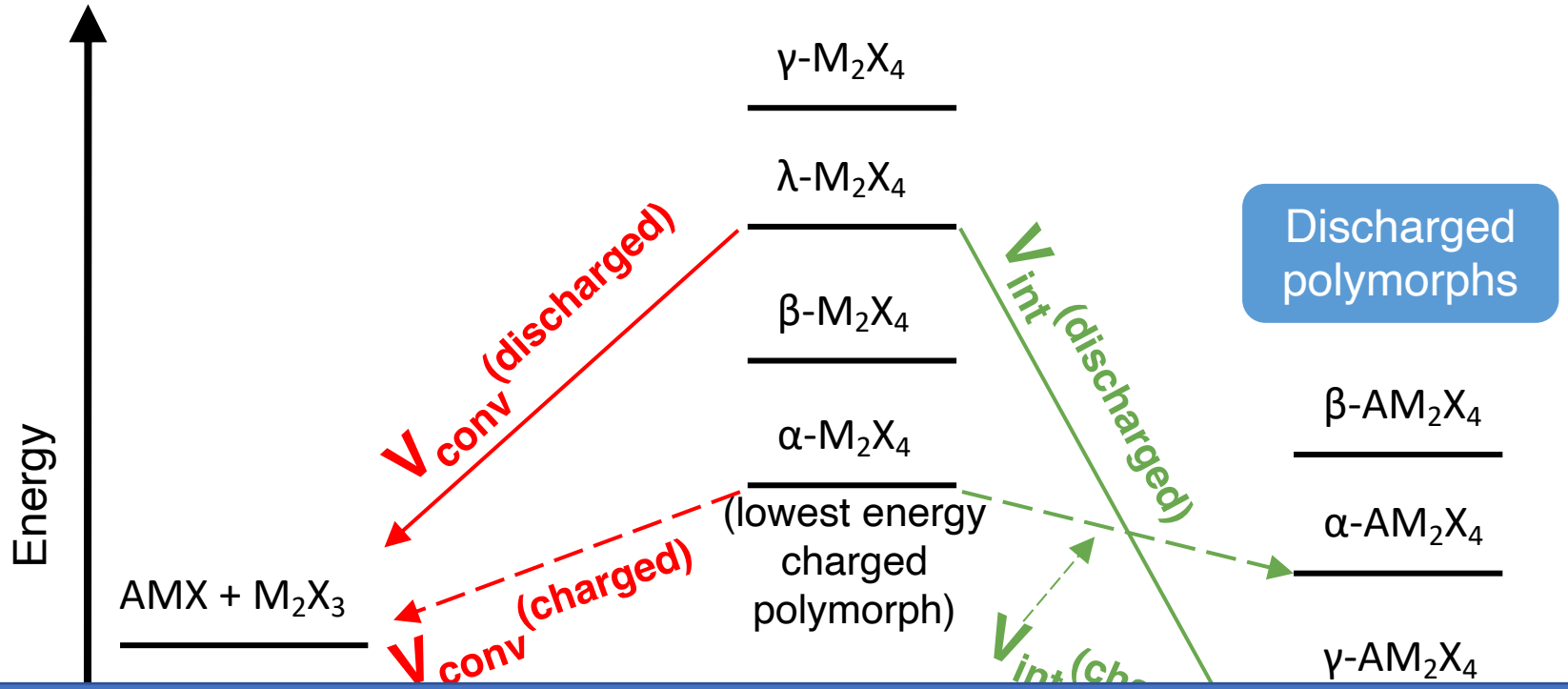
Intercalation vs. Conversion voltage



Conversion	
Discharged	A + λ-M_2X_4 → AMX + M_2X_3
Charged	A + α-M_2X_4 → AMX + M_2X_3

Intercalation	
Discharged	A + λ-M_2X_4 → λ-AM_2X_4
Charged	A + α-M_2X_4 → α-AM_2X_4

Intercalation vs. Conversion voltage

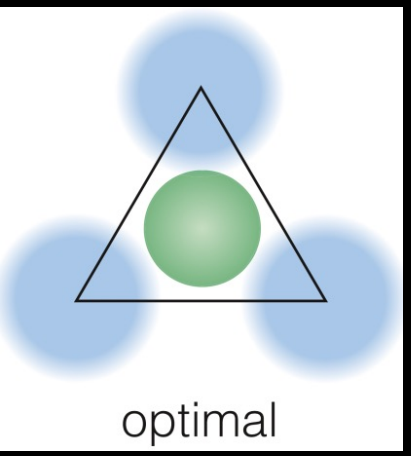


- A discharge (reduction) process will always favor the reaction that yields higher voltage
- Whether intercalation or conversion wins is polymorph (structure) dependent: particularly important in multivalent systems, such as Ca
- Ideally, we want intercalation ≫ conversion voltages

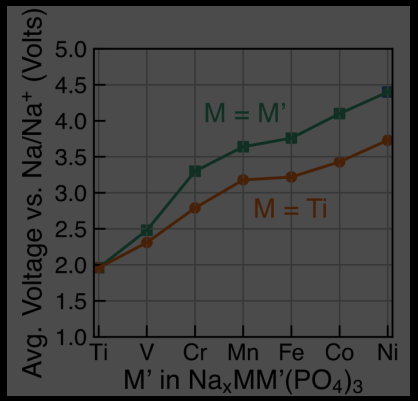
Conversion	
Discharged	A + λ-M_2X_4 → AMX + M_2X_3
Charged	A + α-M_2X_4 → AMX + M_2X_3

Intercalation	
Discharged	A + λ-M_2X_4 → λ-AM_2X_4
Charged	A + α-M_2X_4 → α-AM_2X_4

Objectives

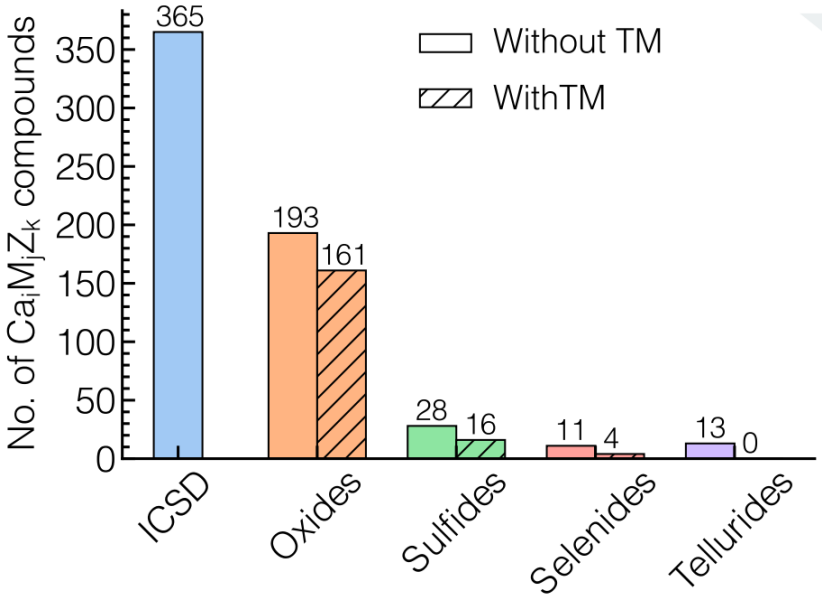


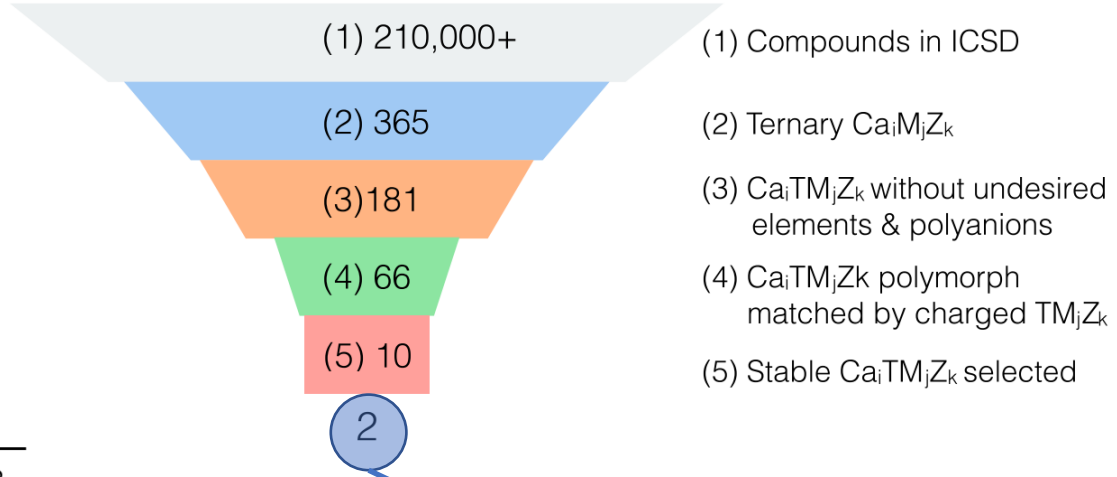
Discover new cathodes for Ca batteries



Screen for cathodes with robust structural stability for Na-ion batteries

Let's look at ternary Ca-compounds





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

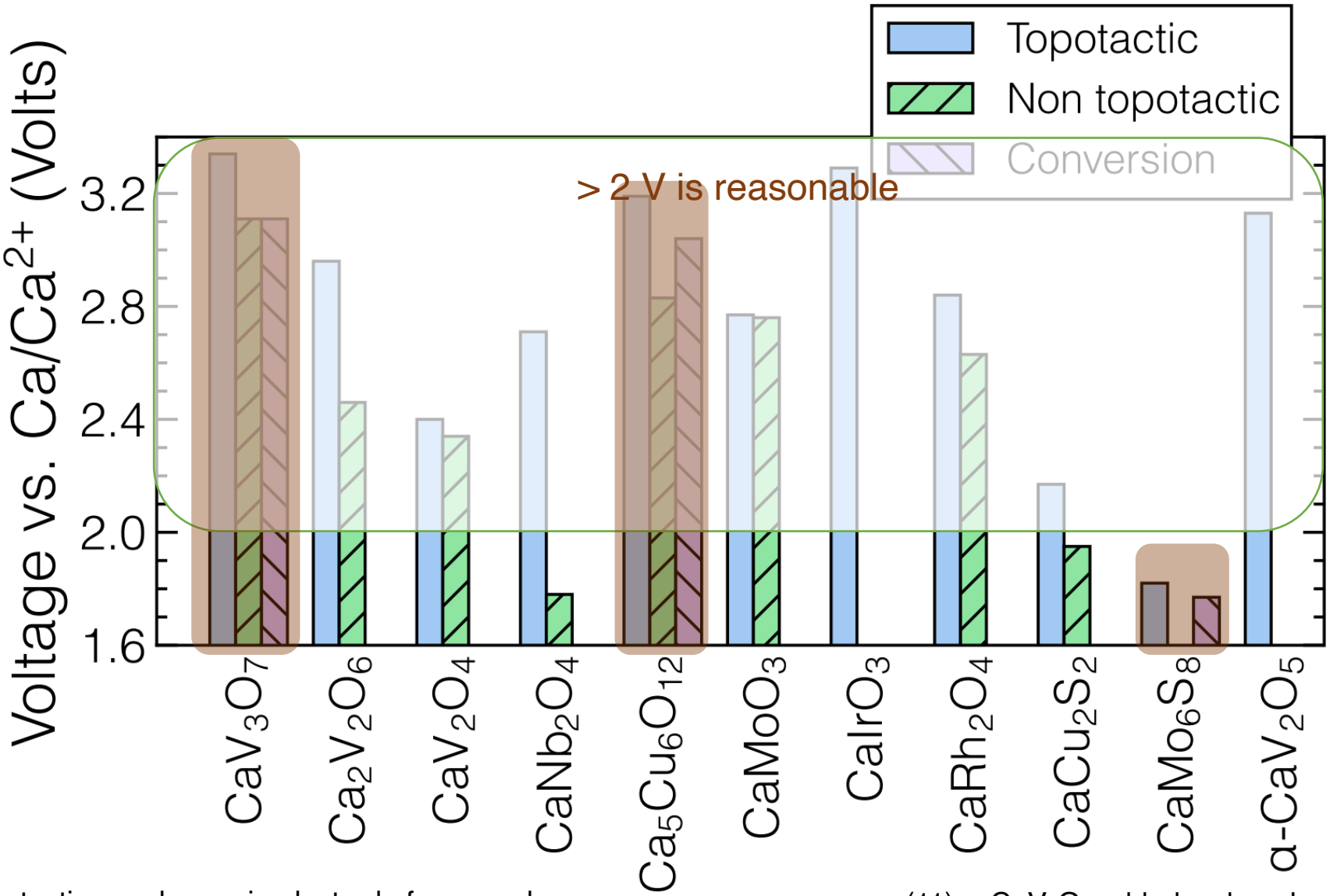
- Only **365** are ternary compounds containing Ca
  - Compounds of composition $Ca_iM_jZ_k$; M, Z = elements other than Ca
- Let M = TM (i.e., transition metal) and Z = O, S, Se, or Te
  - Results in **181** unique compounds
- Charge-neutral charged compound (TM_jZ_k) available for $Ca_iTM_jZ_k$?
  - $CaMn_2O_4$-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, mobility

Final candidates!

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

Voltages calculated with GGA+*U*

GGA+*U* chosen instead of SCAN(+*U*) to lower computational cost



Topotactic: no change in electrode framework

(11) α-CaV_2O_5 added as benchmark

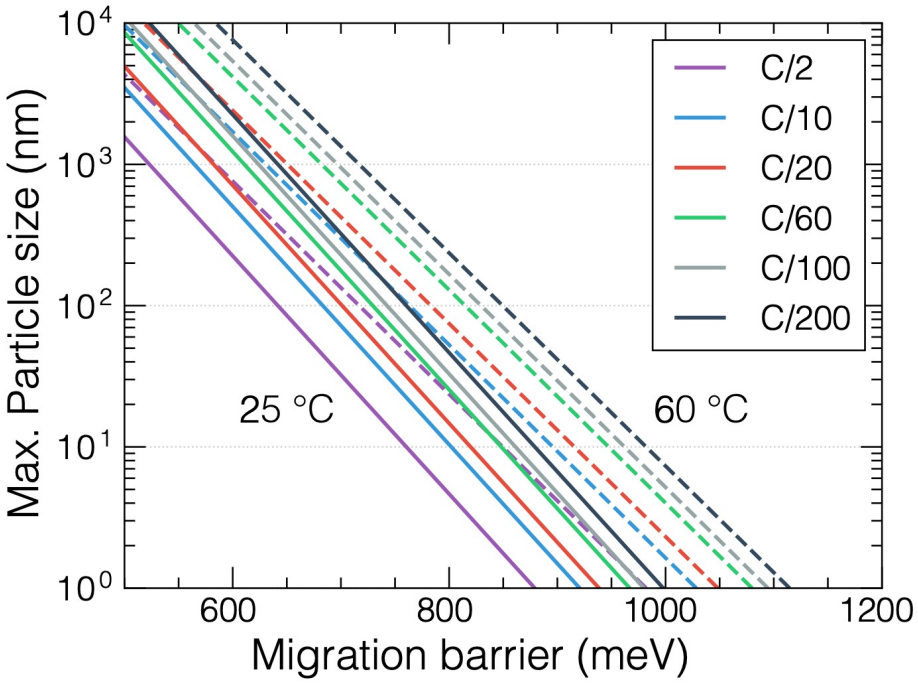
Ca diffusivity: nudged elastic band

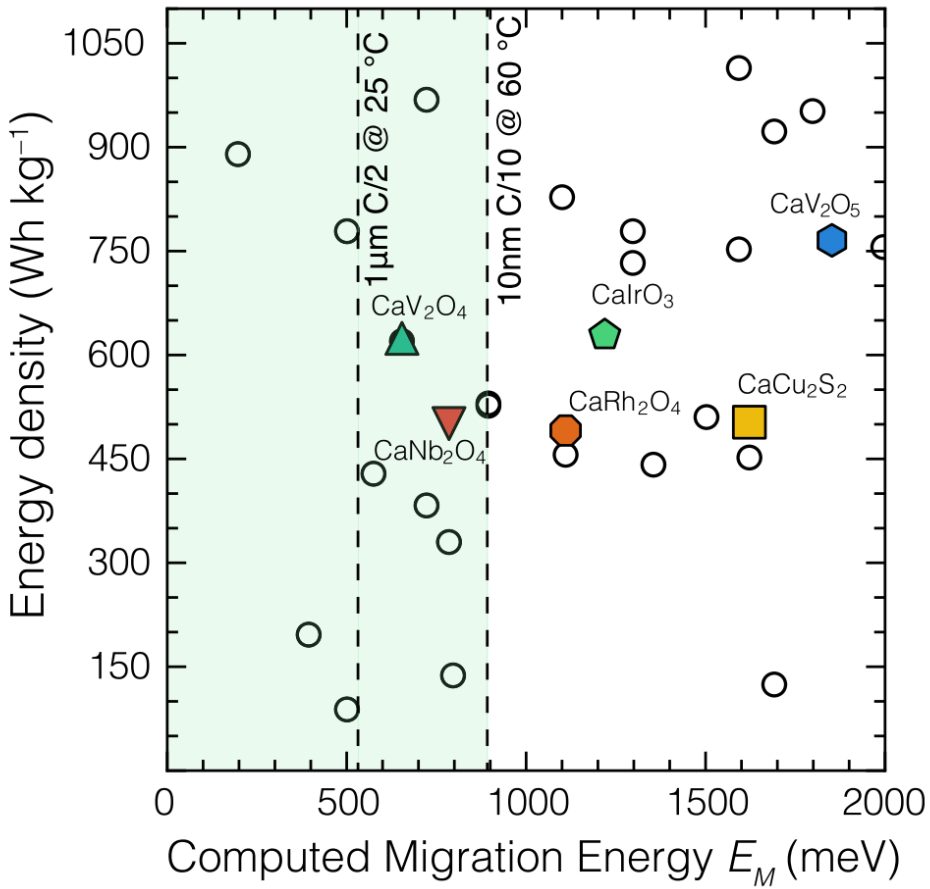
$$D \approx \frac{x^2}{t}$$ Electrode particle size

Diffusion time (rate of operation)

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

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





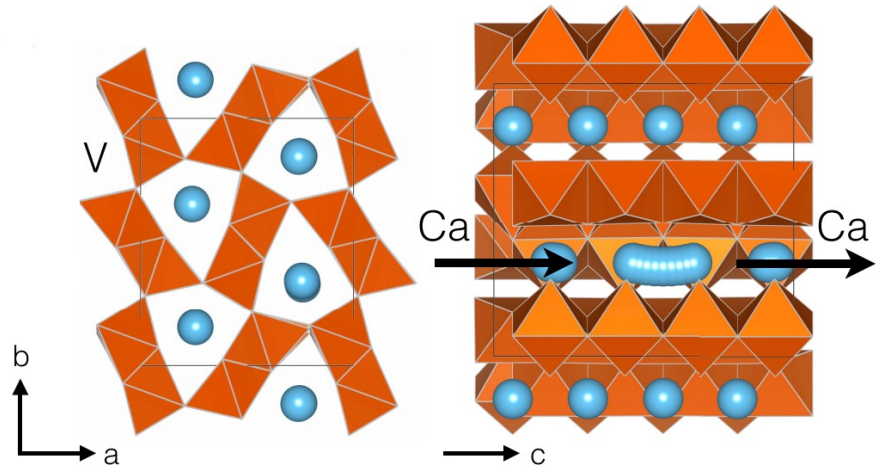
Max. tolerable barrier ~ 980 meV

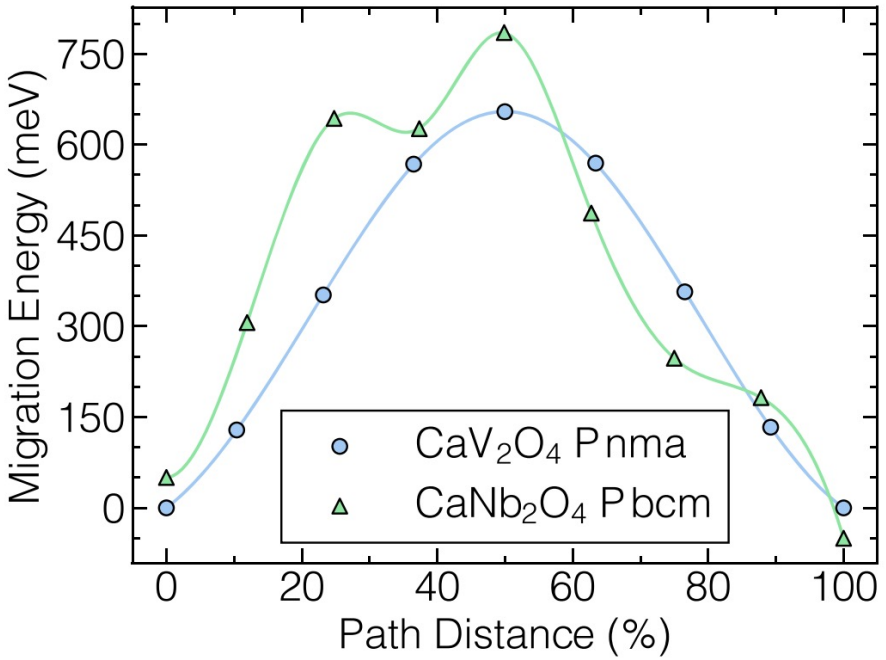
2 candidates display reasonable E_m

- CaV_2O_4: 654 meV
- $CaNb_2O_4$: 785 meV

Nudged Elastic band: Sheppard et al., **J. Chem. Phys. 2008**, *128*, 134106

Migration pathways of candidates





CaV_2O_4: 8→3→8 $CaNb_2O_4$: 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[1] doesn't work for Ca:

- Avoid structures with Ca's "preferred" coordination of 8
  - CaV_2O_4 (E_m = 654 meV) and $CaMoO_3$ (2072 meV) have Ca in 8-coordination
- Reduce changes in coordination number during migration
  - CaV_2O_4 (coordination change of 5) and $CaNb_2O_4$ (change of 2) have low barriers
- Increase volume per anion (i.e., prefer S^{2-} instead of O^{2-}) to reduce E_m
  - $CaCu_2S_2$ (E_m = 1622 meV) has higher barriers than several oxides

Summary:

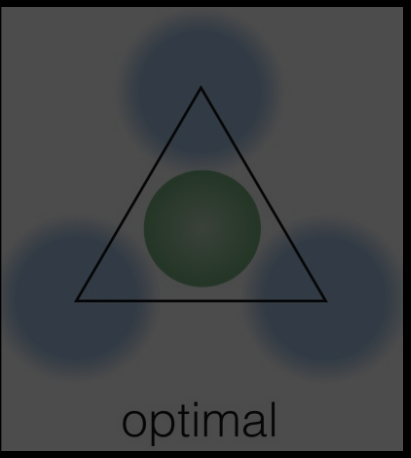
- Identified two Ca-cathode candidates: CaV_2O_4 (post-spinel) and $CaNb_2O_4$ (layered)
- Updated design rules to identify other facile Ca conductors

Updated design rules for identifying facile Ca conductors:

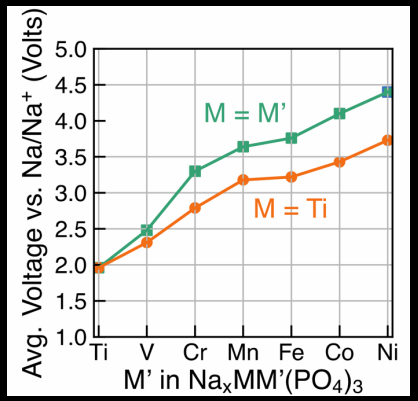
- Structures should exhibit optimal area/diagonal/volume fraction of Ca at transition state
- Avoid face-sharing cations at transition state
- Minimize volume fraction change during migration

1. Rong et al., **Chem. Mater. 2015**, *27*, 6016

Objectives



Discover new cathodes for Ca batteries



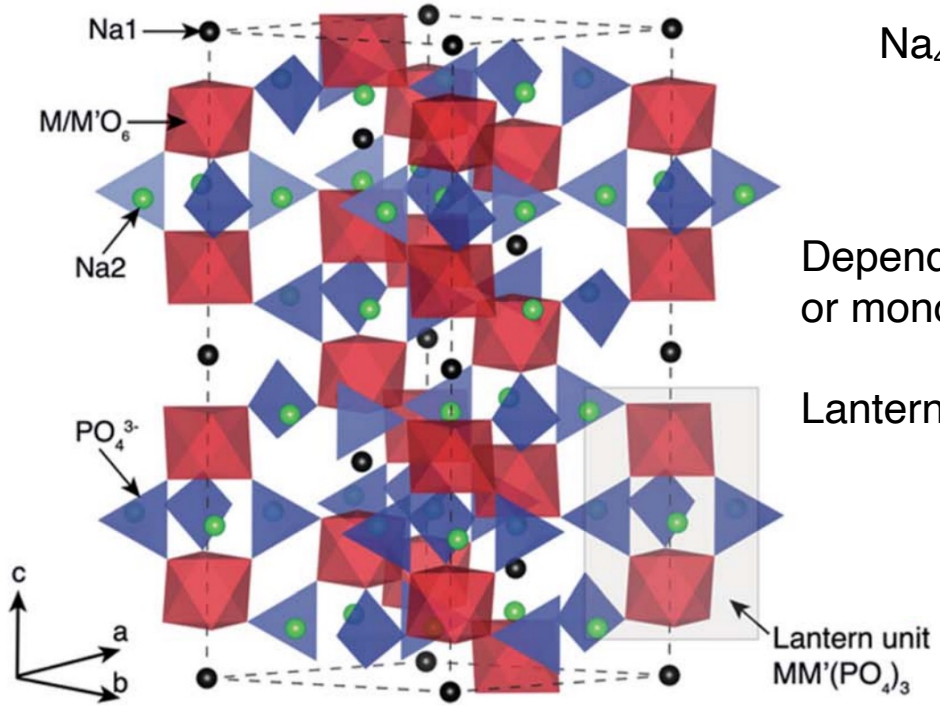
Screen for cathodes with robust structural stability for Na-ion batteries

NaSICONs: Polyanionic hosts with robust structural stability

Experimentally:
- *Single* transition-metals $Na_xM_2(PO_4)_3$; M = Ti, V, Cr, and Fe studied
- *Mixed* transition-metal $Na_xMM'(PO_4)_3$; Ti+V/Mn/Fe/Cr, V+Mn, Cr+Mn explored

Theoretically:
Systematic study missing on all 28 M, M' PO_4 combinations across Na concentrations

- Na superionic conductors: NaSICONs, polyanionic hosts
  - Original composition: $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$; General composition: $Na_xM_2(ZO_4)_3$



$Na_4M_2(PO_4)_3$ $Na_3M_2(PO_4)_3$

Depending on Na concentration is either rhombohedral or monoclinic

Lantern units are fundamental building blocks

NaSICONs: Polyanionic hosts with robust structural stability

Experimentally:
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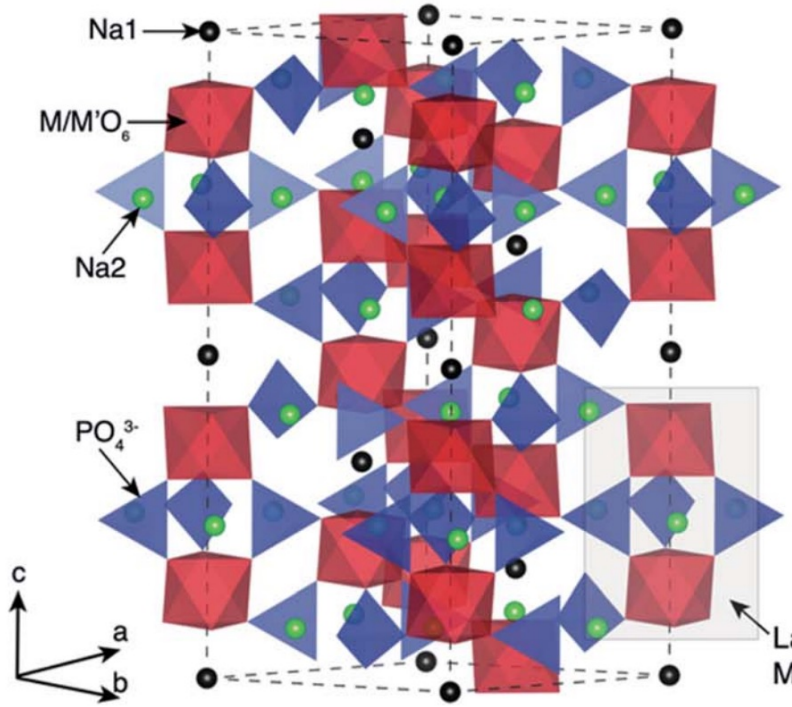
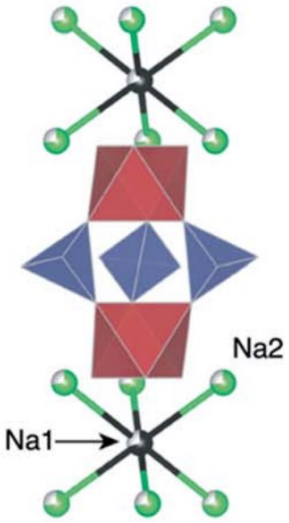
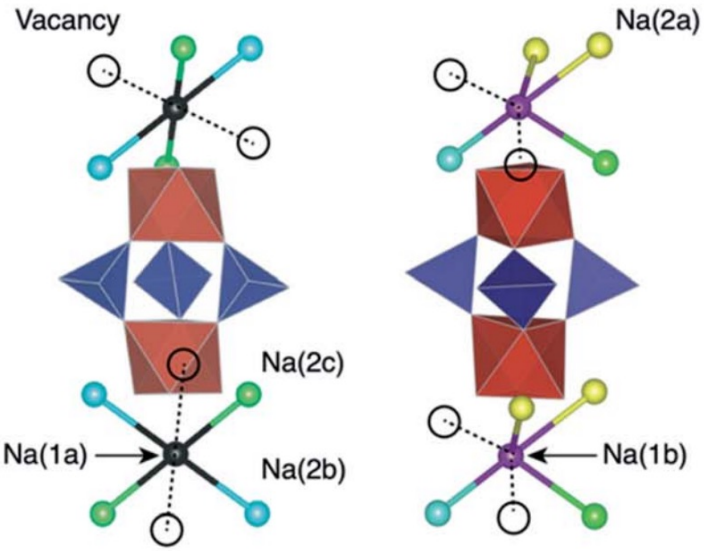


$Na_4M_2(PO_4)_3$

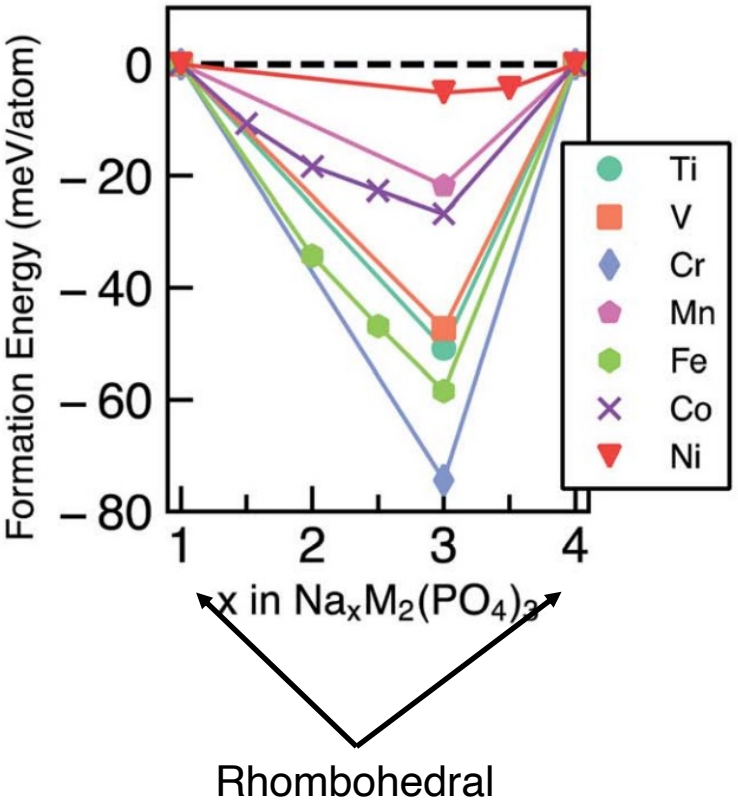


$Na_3M_2(PO_4)_3$



Single transition metal NaSICONs

$Na_xM_2(PO4)_3$; M = Ti, V, Cr, Mn, Fe, Co, Ni



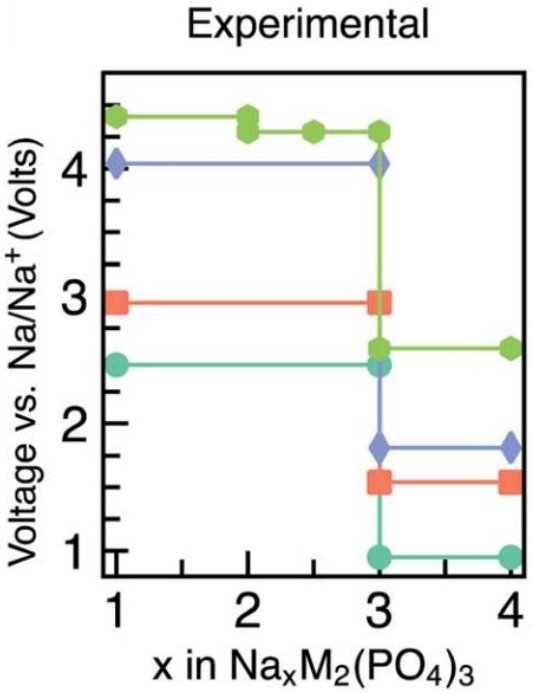
Rhombohedral

Triclinic or Monoclinic at other x

Minima at x = 3

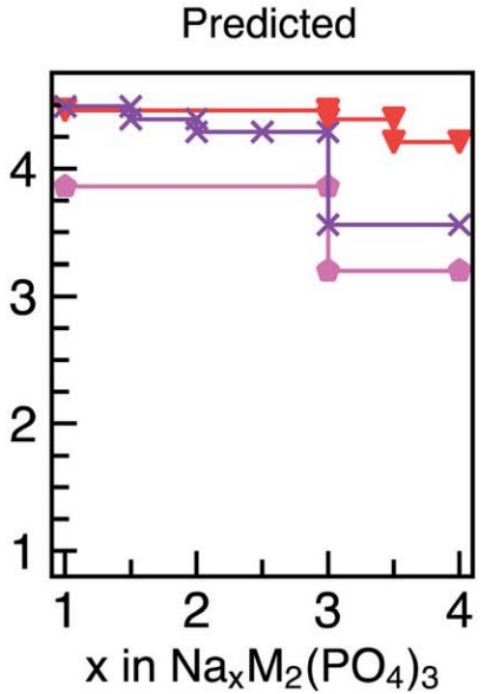
Deepest minima for Cr; shallowest for Ni

$M^{3+/4+}$ for $1 < x < 3$; $M^{2+/3+}$ for $3 < x < 4$



Predicted voltages for experimentally studied compounds

- Predictions underestimate
- E.g., for V: 3.4 and 1.63 V (experimentally) vs. 2.96 and 1.54 V (theoretically)
- Qualitative trends are ok

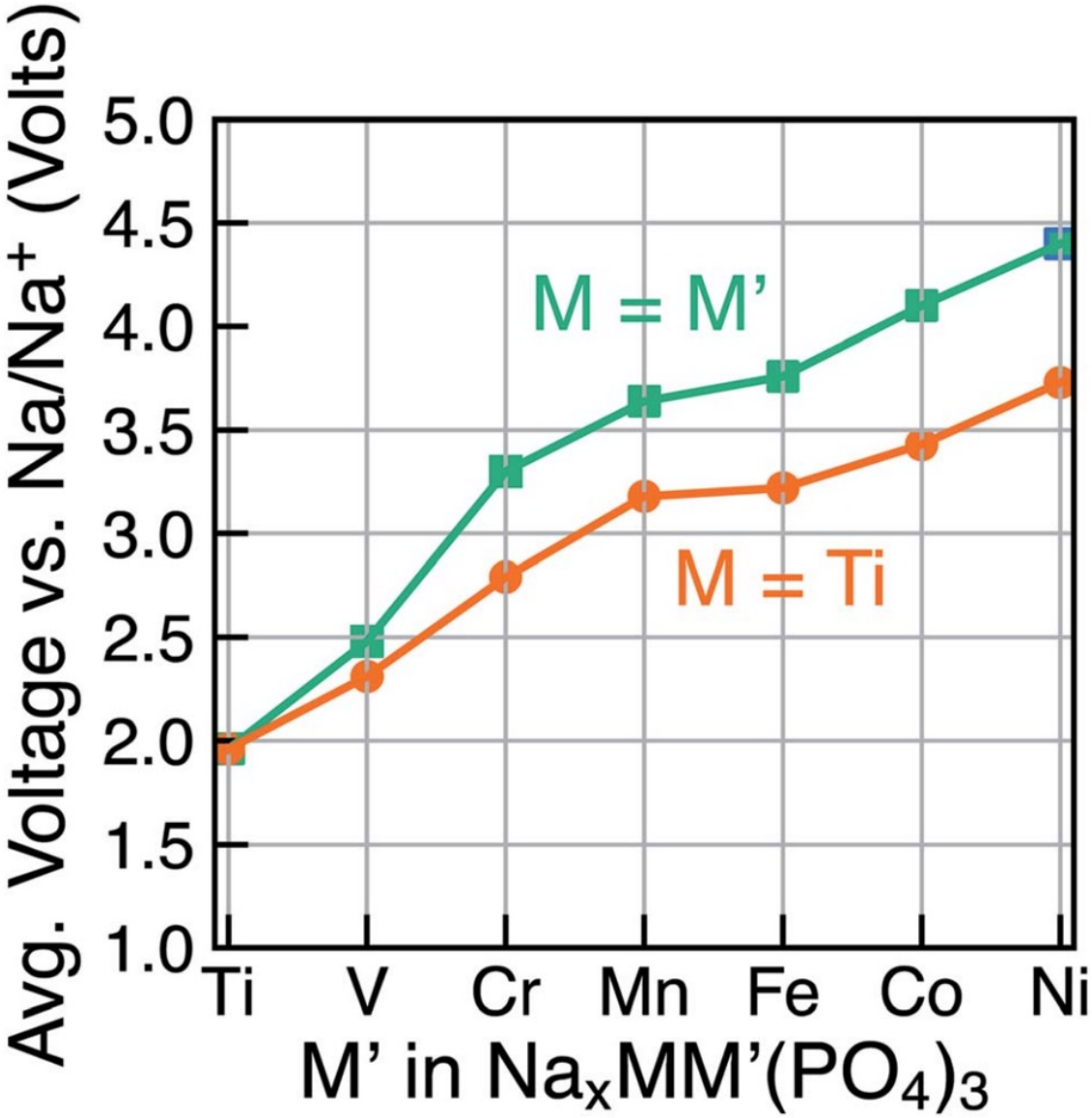


Ni and Co predicted to have the highest voltages, overall

Mn average voltage (across all Na) is higher than Cr and lower than Fe

Mixed transition metal NaSICONs

$Na_xTiM'(PO_4)_3$; M'=Ti, V, Cr, Mn, Fe, Co, Ni



Monotonic increase in average ($1 < x < 4$) voltage across Ti → Ni

- Consistent with standard reduction potentials

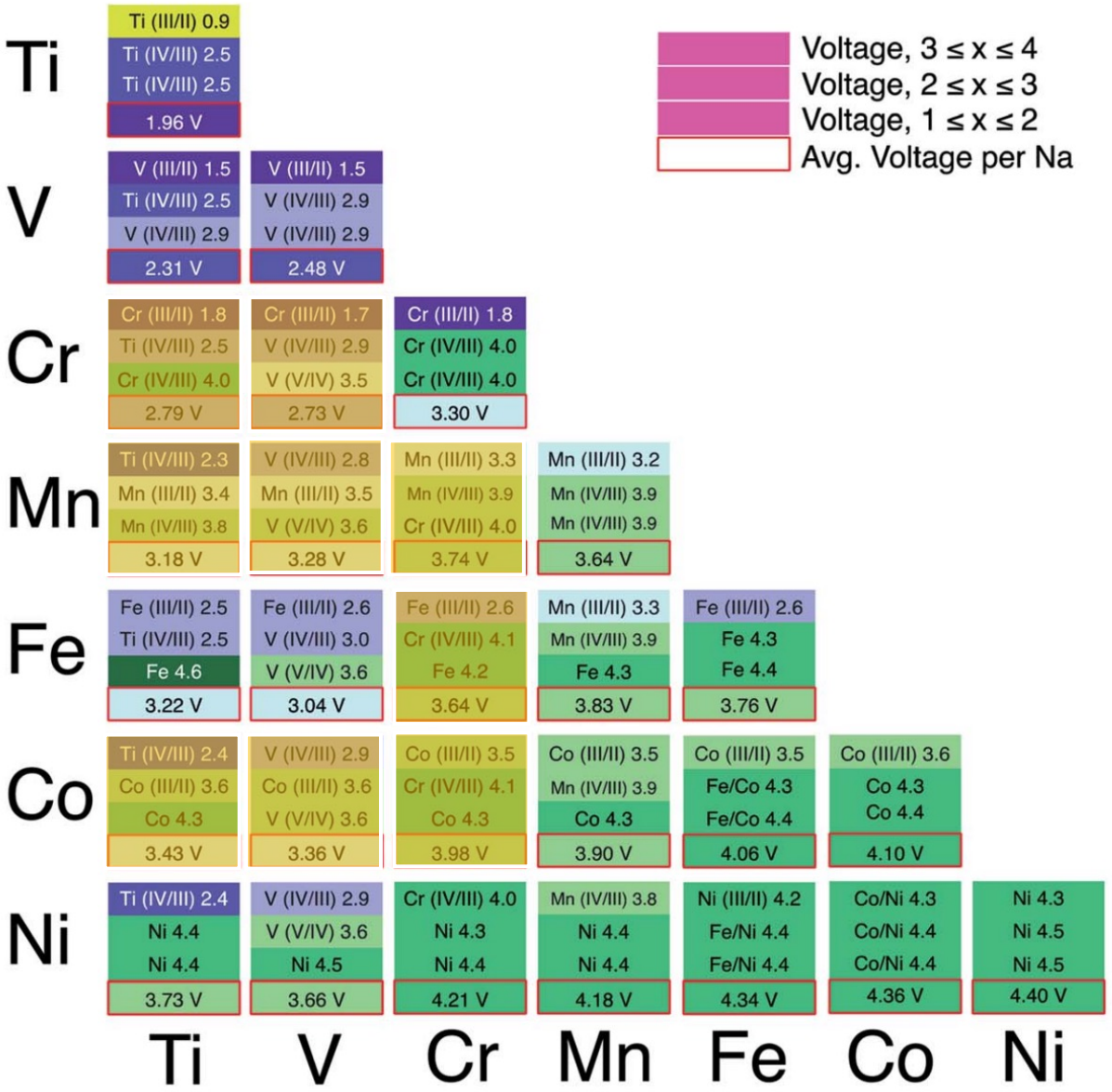
Lack of increase from Ti,Mn → Ti,Fe is due to stability of $3d^5$ configuration

- Of Mn^{2+} and Fe^{3+}

Mixed Ti,M' voltages strictly lower(except M'=Ti) than single M'-M' systems

- Ti^{4+} harder to reduce than other $3d$ metal 4+ states
- Ti-addition can be used to test systems with limited electrolyte stability

Screening all 28 NaSICON systems



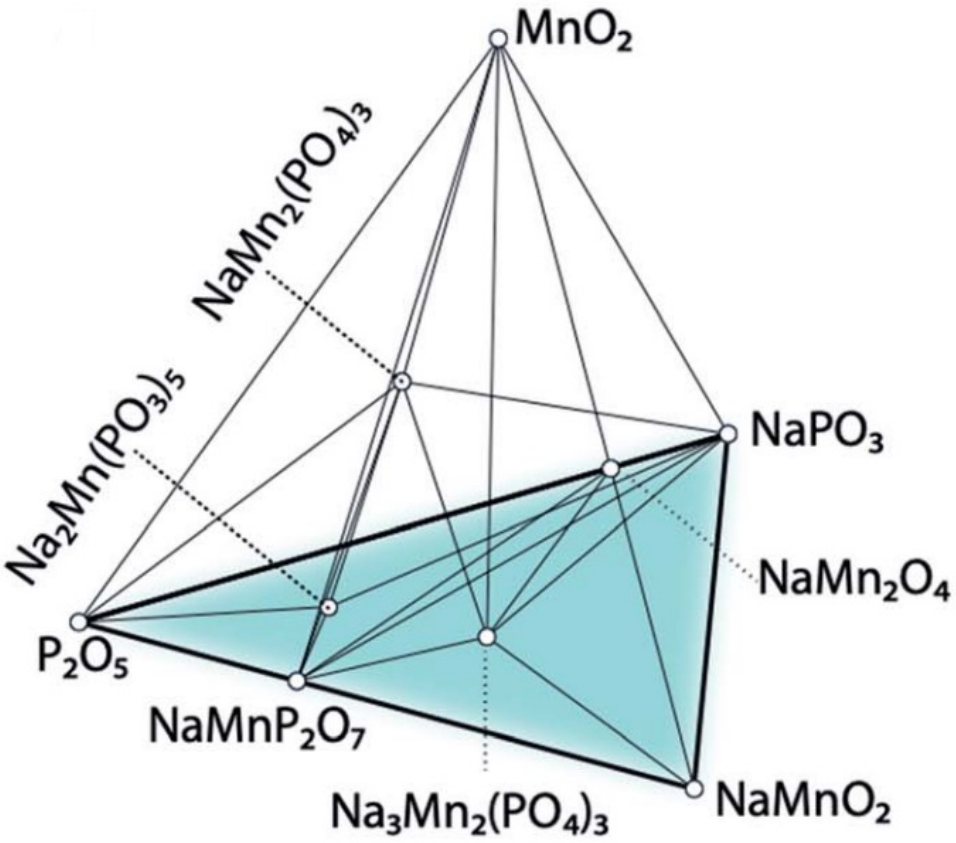
Highest voltages in Co and Ni systems

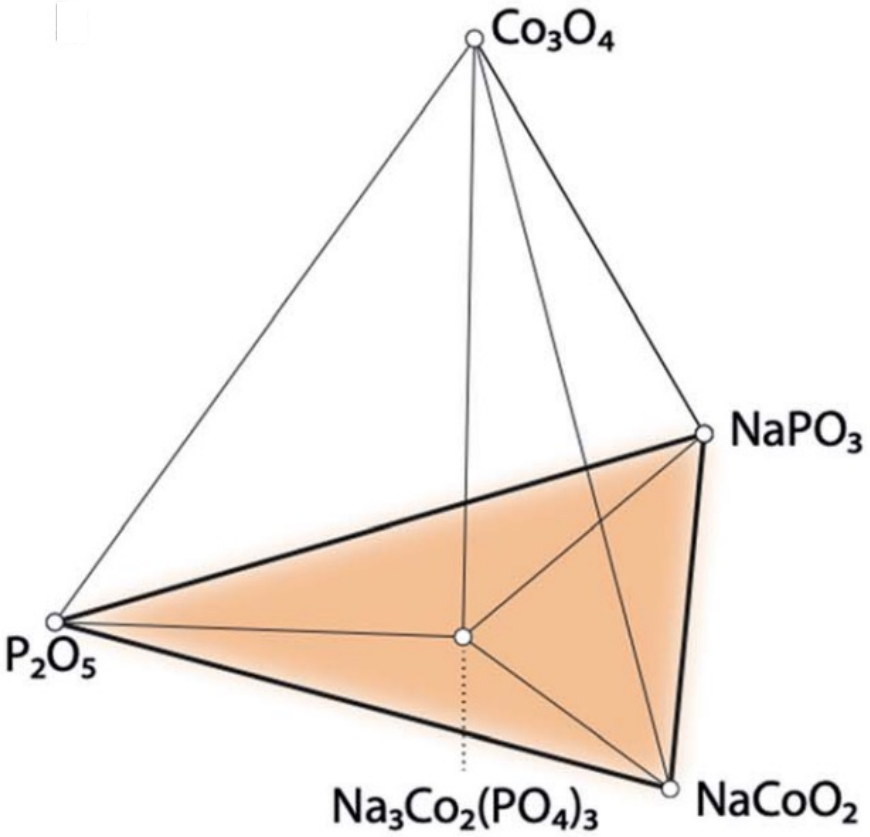
Lowest voltages in Ti or V

There are several mixed systems with unclear transition metal oxidation/metallic behavior

Thermodynamic stability of theoretical systems?

Mn and Co (single) NaSICONs are stable





$Na_3Mn_2(PO_4)_3$ and $Na_1Mn_2(PO_4)_3$ are both stable

- E^{hull} = 0 meV/atom for both compositions
- Na3 is monoclinic, Na1 is rhombohedral
- Needs more efforts to synthesise

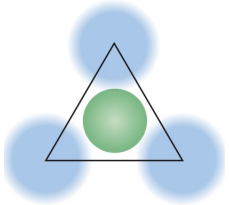
$Na_3Co_2(PO_4)_3$ is stable

- Na3 is rhombohedral
- $Na_1Co_2(PO_4)_3$ is unstable
- Co inclusion in NaSICON is ok

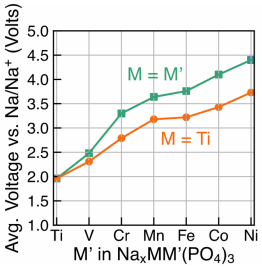
Ni compositions are unstable: not worth exploring experimentally

Phase diagrams based on 0 K DFT calculations of all available ”ordered” structures in inorganic crystal structure database

Conclusions and Acknowledgments



- Removing material bottlenecks is important for improving performance of energy devices
  - Need better, safer, and cheaper batteries (Ca/Na vs. Li)



- Ca-containing ternary compounds from ICSD screened
  - Screening criteria: redox-activity, charge-neutrality, and thermodynamic stability
  - 2 possible candidates: CaV_2O_4 and $CaNb_2O_4$

- Screening of 28 unique NaSICON compositions as Na-ion cathodes
  - Co and Mn based (theoretical) systems are promising: more efforts to synthesise them necessary
  - $Cr^{3+/4+}$ redox useful to explore; Ni not useful

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:
"A chemical map of NaSICON electrode materials for sodium-ion batteries", B. Singh, Z. Wang, S. Park, G.S. Gautam, J-N. Chotard, L. Croguennec, D. Carlier, A.K. Cheetham, C. Masquelier, and P. Canepa, **J. Mater. Chem. A 2021**, *9*, 281-292

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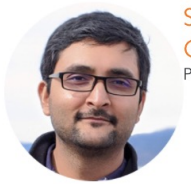

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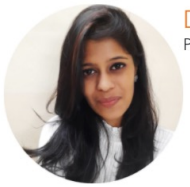

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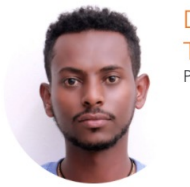

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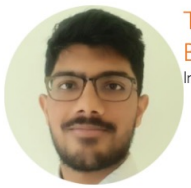

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