Functional Oxides: Materials and
Devices 2023

Exploration of NaSICON frameworks as calcium-ion battery cathodes

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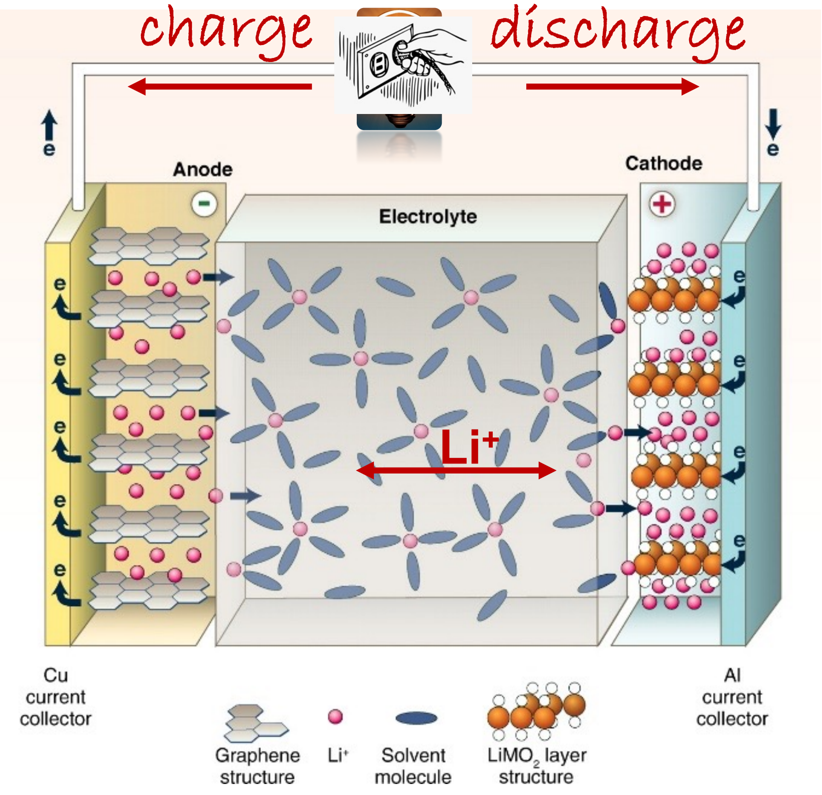
Modern Li-ion Battery (LIB)

LIBs: the state-of-the-art battery technology

- Widely utilized in electric vehicle, portable electronics, smart grids
- Plays a major role in the transition towards clean energy



Dunn et al., Science, 2011

Important battery metrics

- **Energy density**(Wh/Kg) = Voltage(V) x Capacity(mAh/g)
- **Rate(C)**: how fast is the charge/ discharge process (ion mobility)

Challenges

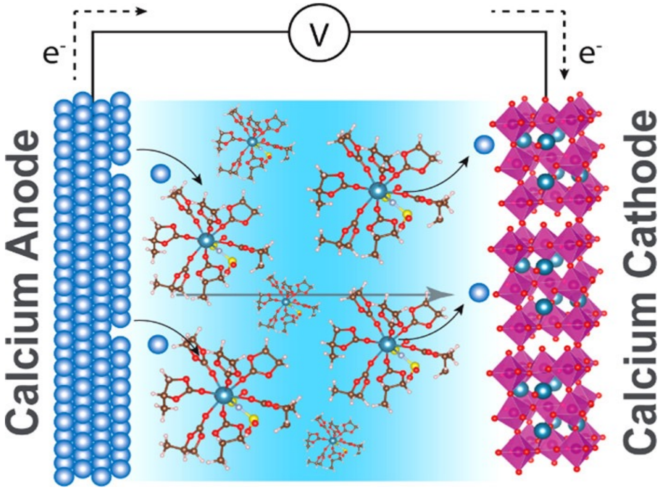
- High cost: Li is not abundant
- Safety: catches fire
- Approaching fundamental limits

Multivalent Ca-ion battery (CIB): as alternative to LIBs

Li^+ → Ca^{2+}

Why Ca?

- **Ca^{2+}**: exchanges $2e^-$ at a time instead of $1e^-$ for Li^+ case
    - Hence offers high energy density
- **Ca** is most abundant (~ 4.1%) than Li (~ 0.0017%)
- Comparable standard reduction potential (–2.87V vs SHE) with that of Li (-3.04V)
- Use of **Ca** metal anodes: higher volumetric energy density



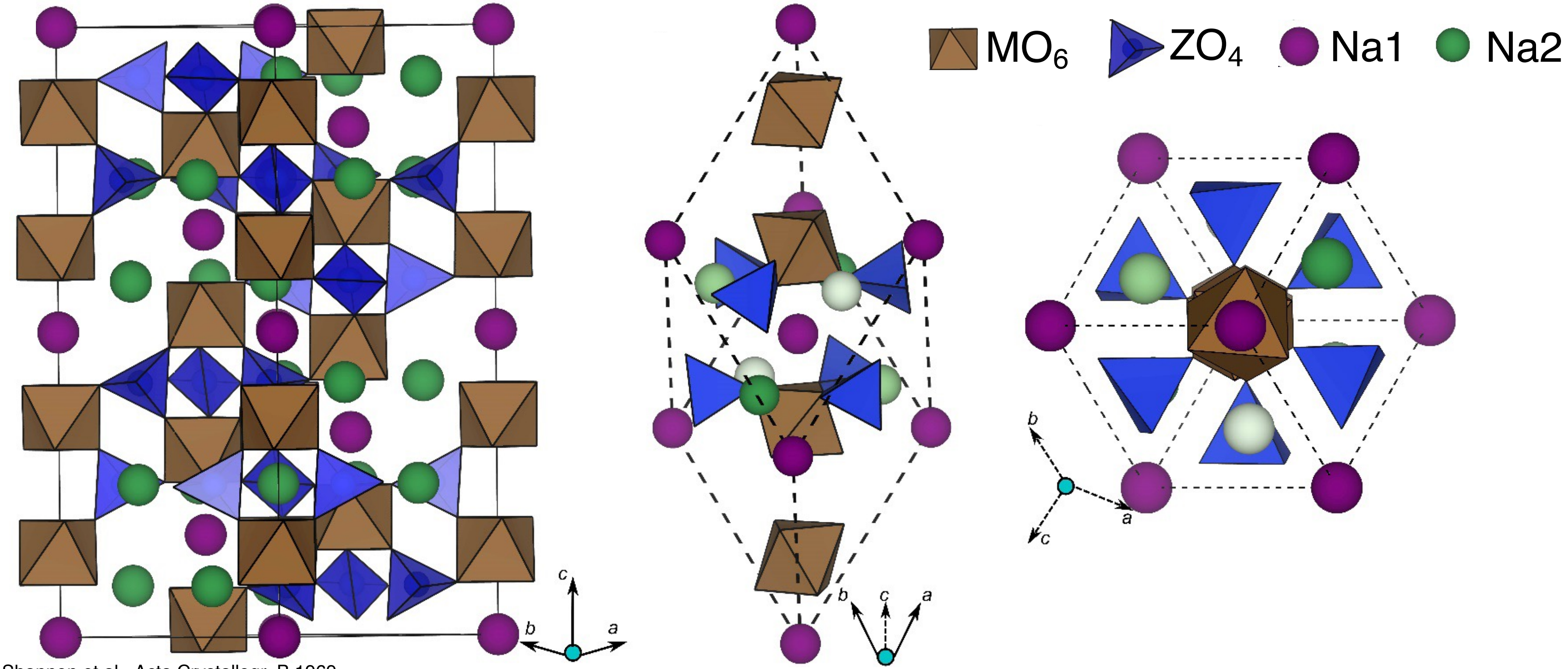
Hosein, ACS Energy Lett. 2021

Ca-cathode design challenges:

- Thermodynamically stable
- High energy density
- High ionic mobility
- Good cycle life

NaSICON: polyanionic framework with robust structural stability

- Known for their excellent ionic conductivity
- Widely explored as Na-electrode and solid electrolyte
- Usually crystallize in rhombohedral structure
  - $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$, $(0 \le x \le 3)$ NaSICON = sodium superionic conductor
  - $A_xM_2(ZO_4)_3$: A = Na, Li etc., M = transition metals, Z= Si, P, S etc.
- MO_6 polyhedra is coordinated via corner sharing with ZO_4 tetrahedral



1. Shannon et al., Acta Crystallogr. B 1969

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Given the similar ionic radius of Na^+ (~1.02 Å)[1] and Ca^{2+} (~1.00 Å), **NaSICON** could be a potential **Ca-cathode**

- Motivated by experimental evidence that $NaV_2(PO_4)_3$ intercalates Ca ion (Kim et al., ACS Energy Lett. 2020)

$Ca_xM_2(ZO_4)_3$: where M = Ti, V, Cr, Mn, Fe, Co or Ni and Z = Si, P, or S

- **Charge-neutrality constraint** is maintained for **Ca** contents of:
  - $2 \leq x \leq 4$ in $Ca_xM_2(SiO_4)_3$, $0.5 \leq x \leq 2.5$ in $Ca_xM_2(PO_4)_3$, $0 \leq x \leq 1$ in $Ca_xM_2(SO_4)_3$
- For example, **Ca** composition in $\mathbf{Ca_xMn_2(SiO_4)_3}$ is calculated as follows:
  - Charged: $Ca_{\mathbf{x}}^{2+}Mn_2^{4+}(SiO_4)_3^{4-} \rightarrow 2\cdot\mathbf{x} + 4\cdot2 + - 4\cdot3 = 0$, $\rightarrow \mathbf{x = 2}$
  - Discharged: $Ca_{\mathbf{x}}^{2+}Mn_2^{2+}(SiO_4)_3^{4-} \rightarrow 2\cdot\mathbf{x} + 2\cdot2 - 4\cdot3 = 0$, $\rightarrow \mathbf{x = 4}$

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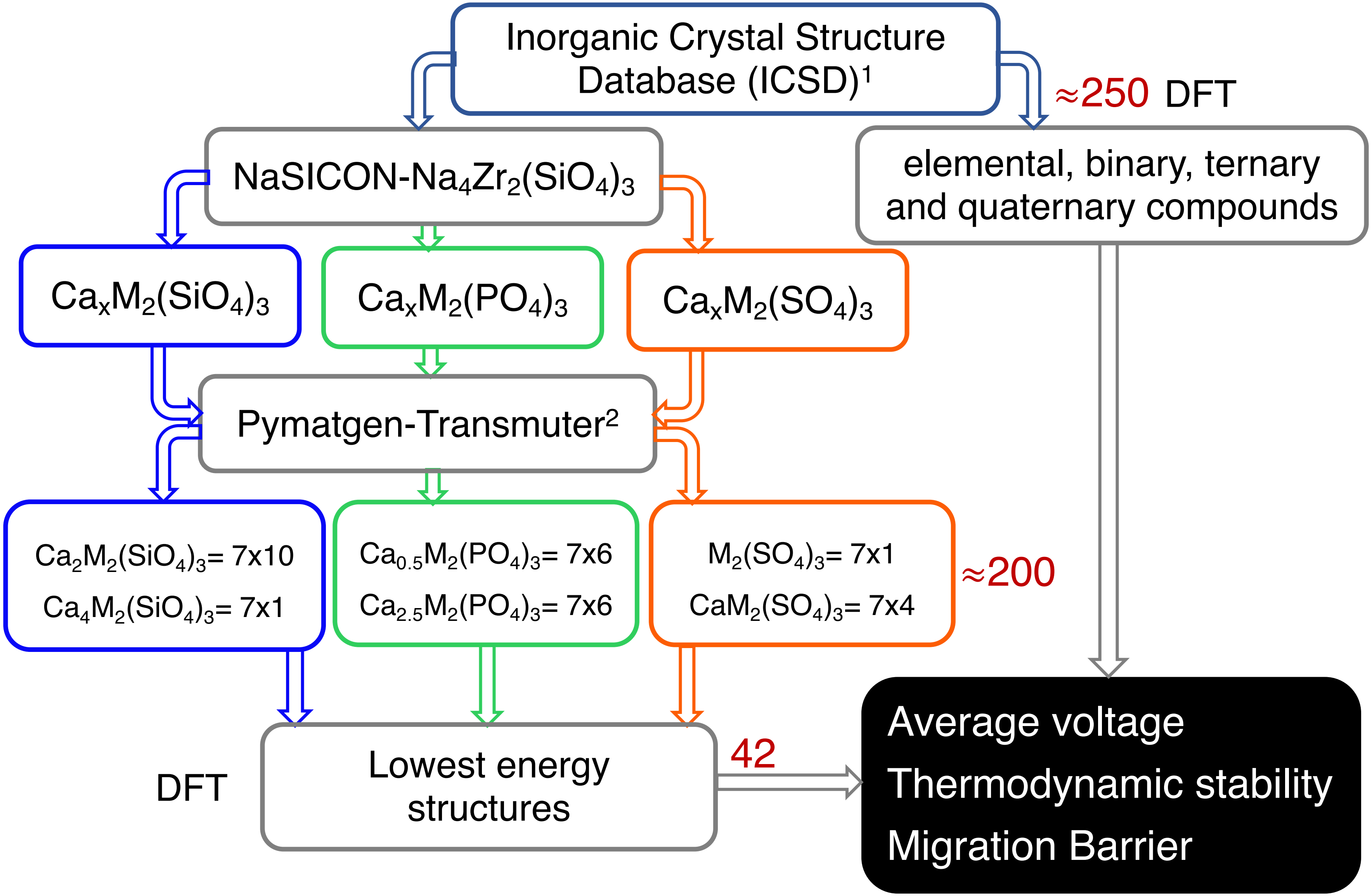
[1] Shannon et al., Acta Crystallogr. B 1969

Generating Ca-NaSICON compositions



Inorganic Crystal Structure Database (ICSD)[1]

≈250 DFT

elemental, binary, ternary and quaternary compounds

NaSICON-$Na_4Zr_2(SiO_4)_3$

$Ca_xM_2(SiO_4)_3$

$Ca_xM_2(PO_4)_3$

$Ca_xM_2(SO_4)_3$

Pymatgen-Transmuter[2]

$Ca_2M_2(SiO_4)_3$= 7x10
$Ca_4M_2(SiO_4)_3$= 7x1

$Ca_{0.5}M_2(PO_4)_3$= 7x6
$Ca_{2.5}M_2(PO_4)_3$= 7x6

$M_2(SO_4)_3$= 7x1
$CaM_2(SO_4)_3$= 7x4

≈200

DFT

Lowest energy structures

42

Average voltage
Thermodynamic stability
Migration Barrier

≈450 + 18 NEB

DFT = Density Functional Theory
NEB = Nudged Elastic Band

[1] M. Hellenbrandt, Crystallogr. Rev. 2004

[2] Ping Ong et al., Comput. Mater. Sci. 2013

Computational methods

- All spin-polarized total ground state energy is calculated using DFT
    - The Vienna *ab initio* simulation package (VASP[1]) and projector-augmented-wave (PAW[2]) potential is used
    - Hubbard *U* corrected strongly constrained and appropriately normed[3,5] (SCAN+*U*)
    - *U* value is obtained from previous work[4]
    - 520 eV plane wave kinetic energy cutoff and minimum 32/Å *k*-point density is used
    - 10^{-5} eV (total energy) and |0.03| eV/Å (forces) convergence criteria were used
- Average voltage is calculated using Nernst equation:

$$\langle V \rangle = -\frac{\Delta G}{2(x-y)F} \approx -\frac{E(Ca_xM_2(ZO_4)_3) - [E(Ca_xM_2(ZO_4)_3) + (x-y)\mu_{\mathrm{Ca}}]}{2(x-y)F}$$

- Pymatgen package is used to construct 0 K convex hull of Ca-M-Z-O systems
- DFT-based NEB[6] is used to calculate the migration barrier (E_m)

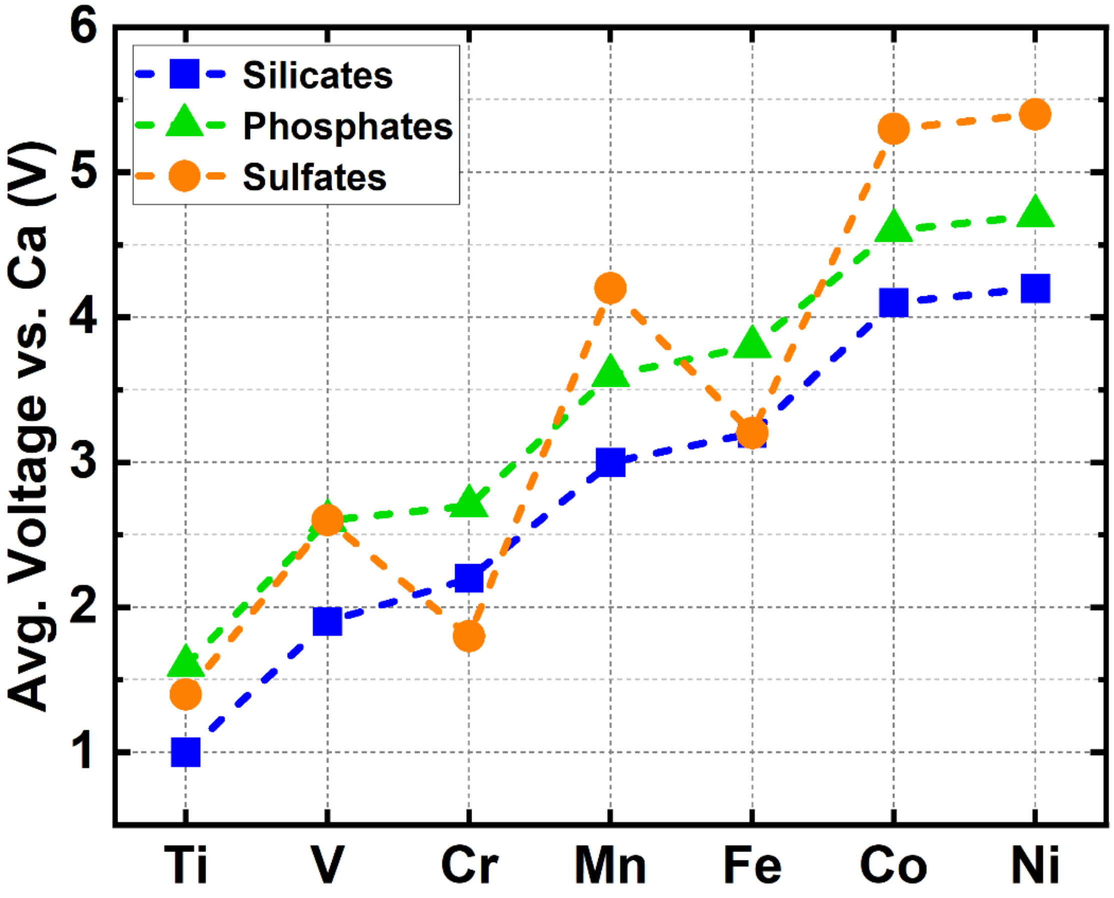
$$D \propto \exp\left(\frac{-E_m}{RT}\right)$$

D = diffusivity
E_m = activation energy for migration

- At least 48/Å (for endpoint) and 32/Å (for NEB) *k*-point density is used
- Between endpoints seven images are considered, with spring force constant of 5 eV/Å between images
- NEB converges if elastic band force of each image is less than |0.05| eV/Å

1. Kresse et al., Phys. Rev. B 1996
2. Blöchl et al., Phys. Rev. B 1994
3. Sun et al., Phys. Rev. Lett. 2015
4. Sai Gautam et al., Phys. Rev. Mater. 2018
5. Dudarev et al., Phys. Rev. B 1998
6. Henkelmann et al., J. Chem. Phys. 2000

Average voltage: increases monotonically from Ti to Ni except for SO_4



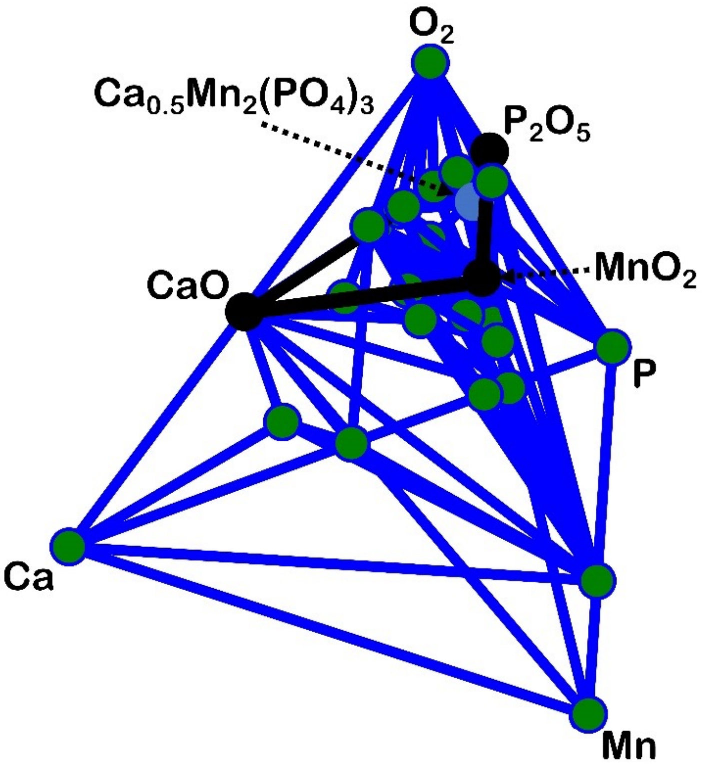
- Voltage is *monotonically* increasing from Ti-Ni for PO_4 and SiO_4
  - Consistent with the standard reduction potentials
- PO_4 voltage is consistently higher than SiO_4
  - Due to inductive effect
- SO_4 voltage increment is *non-monotonic*
  - "Local" minima at Cr and Fe, attributed to the stability of Cr^{3+} and Fe^{3+}

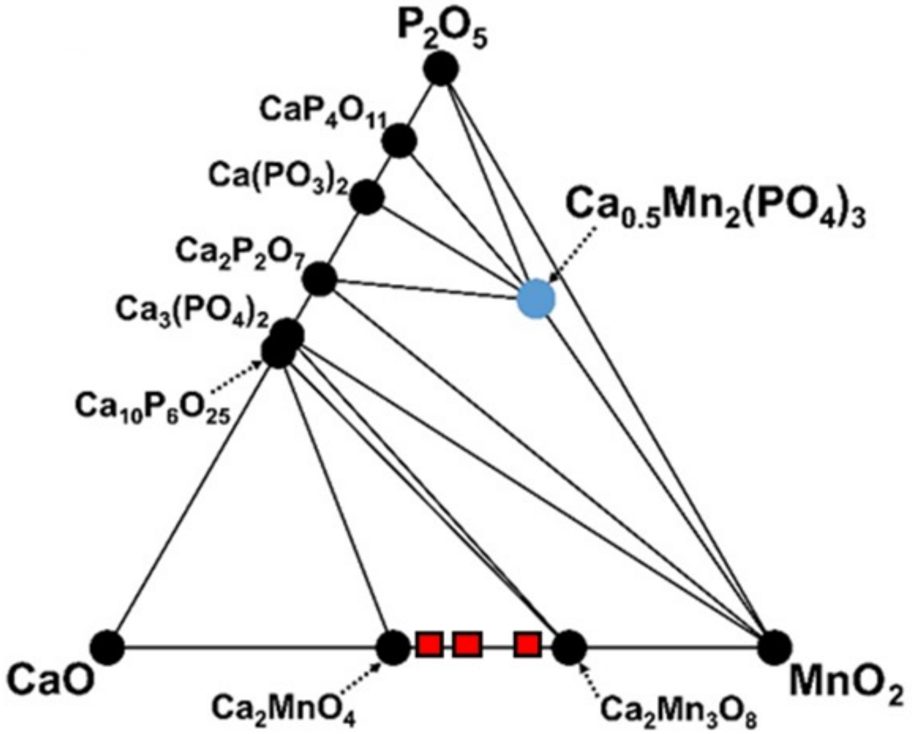
- Ti-based PO_4 (1.6V), SiO_4 (1.0V) and SO_4 (1.4V) have low voltage and hence they are suitable for anode instead of cathode
- **Theoretical capacity (Ni-Ti)**: C = nF/(3600xM) $mAhg^{-1}$
  - PO_4 (254-267) > SiO_4 (227-237) >> SO_4 (132-140)

D.B Tekliye et al., Chem. Mater., 2022

Thermodynamic stability of Ca-NaSICONs

- Convex hull (phase diagram) is constructed for all Ca-NaSICONs[1]
  - Convex hull: envelope of the lowest Gibbs energy state of the system
  - Phase diagram: for 21 charged and discharged Ca-NaSICONs





- Energy above/below convex hull ($\mathbf{E}^{\mathbf{Hull}}$):
  - $\mathbf{E}^{\mathbf{Hull}} > \mathbf{0}$: indicates metastability/instability (energy release upon decomposition)
  - $\mathbf{E}^{\mathbf{Hull}} \leq \mathbf{0}$: indicates stability (energy release upon formation)

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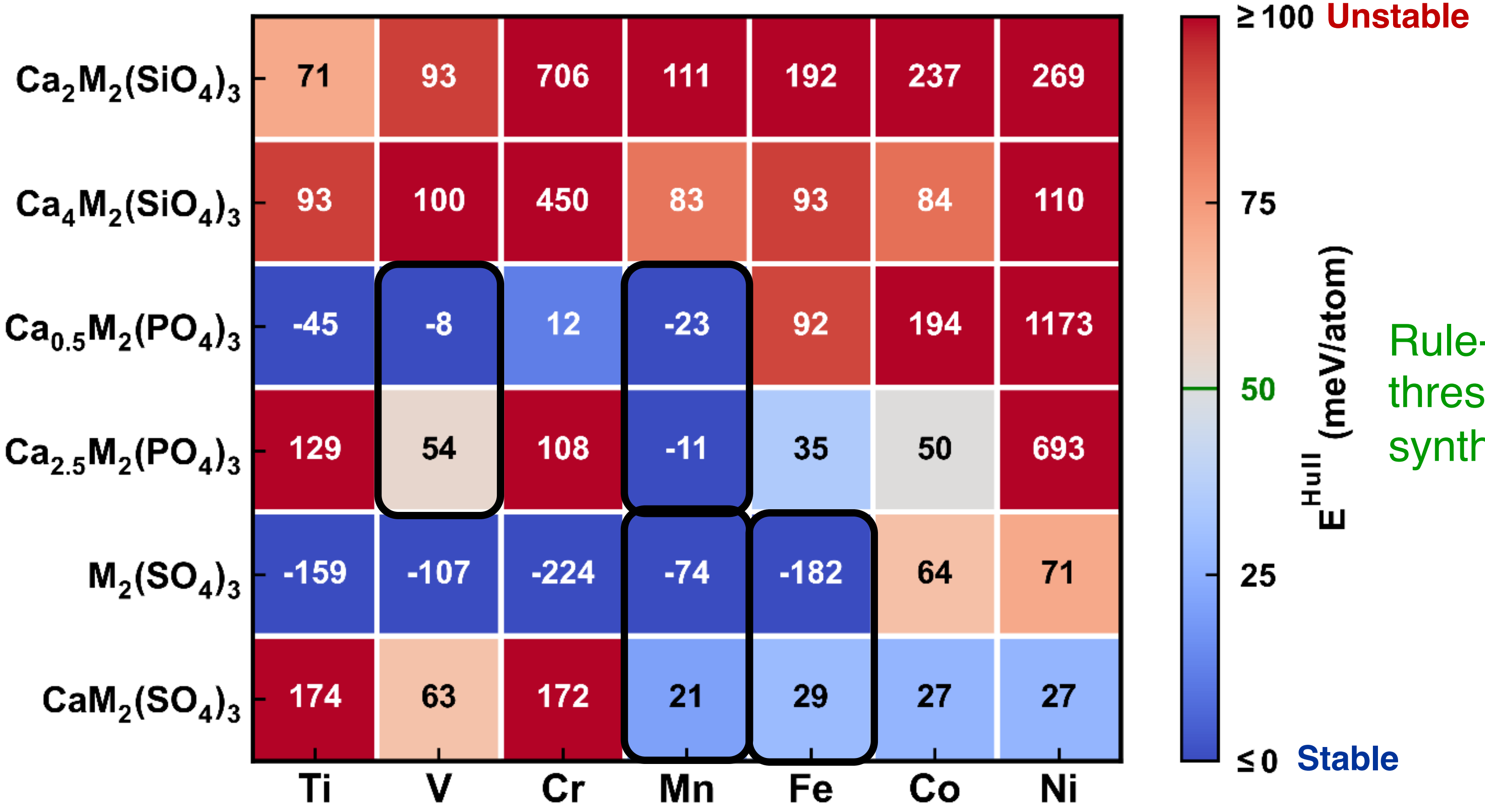
1. Ping Ong et al., Comput. Mater. Sci. 2013

Several phosphates and sulfates are found to be stable

Both charged and discharged phases should preferably be thermodynamically stable/metastable



	Ti	V	Cr	Mn	Fe	Co	Ni
$Ca_2M_2(SiO_4)_3$	71	93	706	111	192	237	269
$Ca_4M_2(SiO_4)_3$	93	100	450	83	93	84	110
$Ca_{0.5}M_2(PO_4)_3$	-45	-8	12	-23	92	194	1173
$Ca_{2.5}M_2(PO_4)_3$	129	54	108	-11	35	50	693
$M_2(SO_4)_3$	-159	-107	-224	-74	-182	64	71
$CaM_2(SO_4)_3$	174	63	172	21	29	27	27

Rule-of-thumb threshold for synthesizability [1]

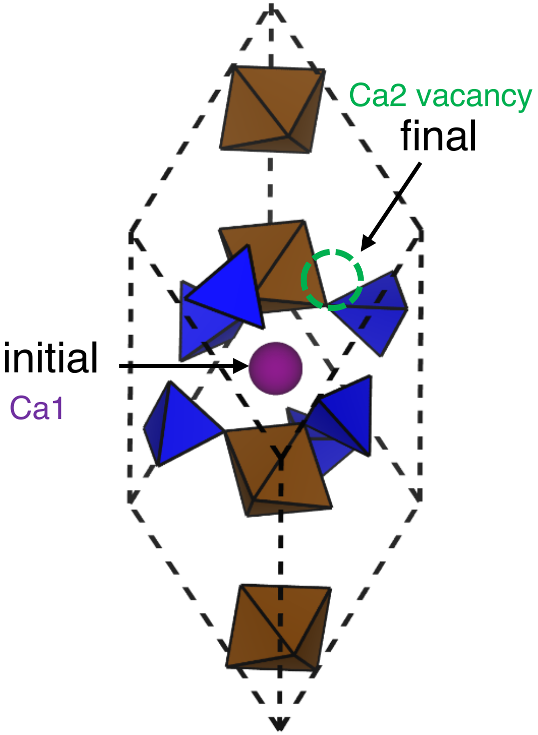
- $Ca_xV_2(PO_4)_3$, $Ca_xMn_2(PO_4)_3$, $Ca_xMn_2(SO_4)_3$ and $Ca_xFe_2(SO_4)_3$ are found to be stable/metastable
- All SiO_4 are unstable: not a candidate for Ca-cathode
- $Ca_{0.5}V_2(PO_4)_3$ (~-8 meV/atom); $NaV_2(PO_4)_3$: experimentally synthesised
- Experimentally synthesised phases (Ti, Cr and Fe-SO_4) are predicted to be highly stable

[1] Sun et al., Sci. Adv, 2016

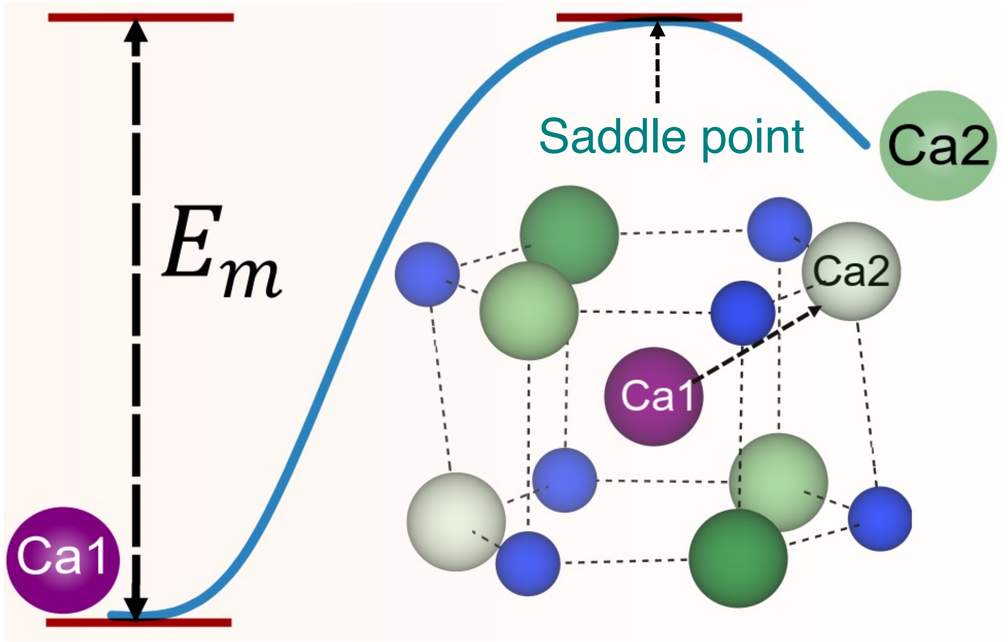
D.B Tekliye et al., Chem. Mater., 2022

Migration barrier: energy difference between saddle point and lowest energy site

- Ca-ion migration is sluggish compared to Na or Li-ion
  - Likely due to the induced stronger electrostatic interaction
- Vacancy-mediated migration mechanism is considered
  - Ca1(Na1)-Ca2(Na2): established migration path in NaSICON



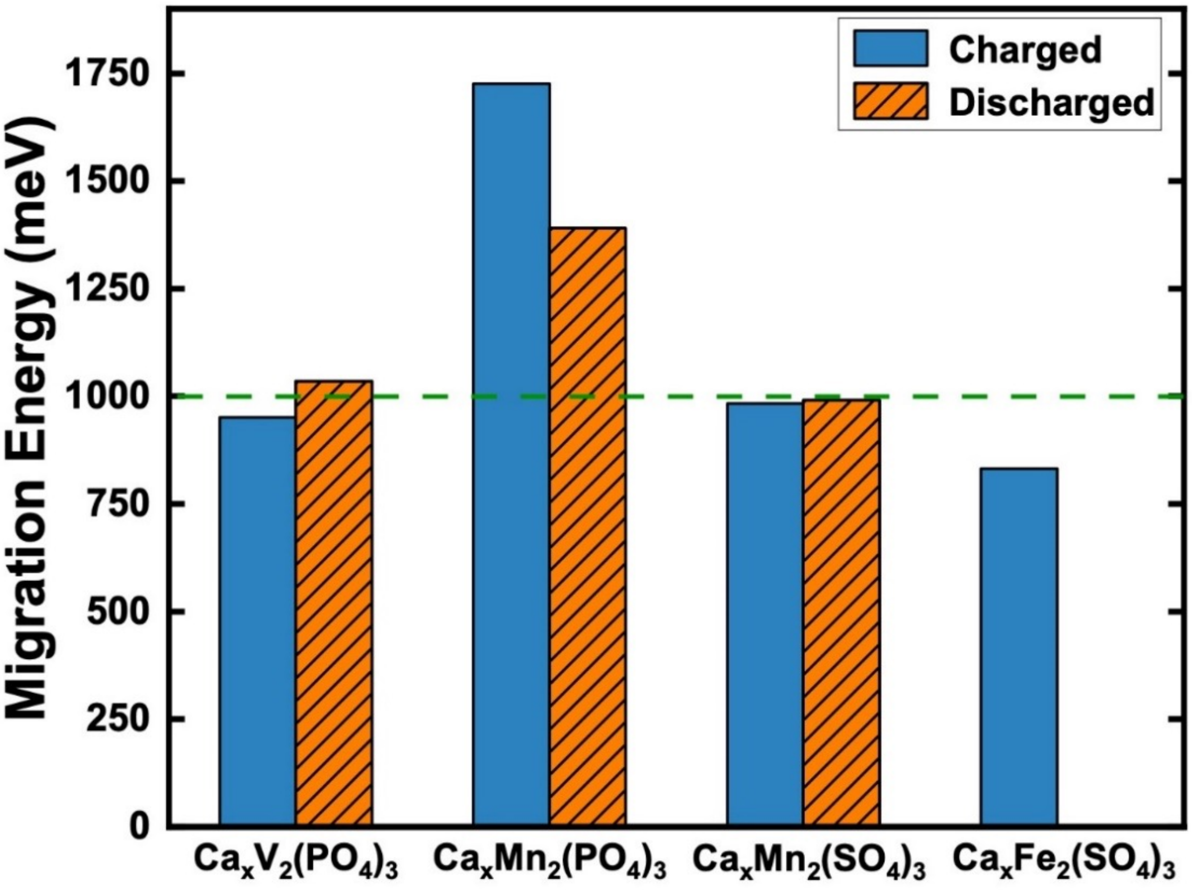
Minimum energy path



E_m is calculated using GGA[1] due to a reasonable trade-off between a computational cost and accuracy[2]

[1] Perdew et al., Phys. Rev. Lett. 1996 [2] Devi et al., Npj Comput. Mater. 2022

Sulfates tends to have lower migration barrier



- Maximum tolerance limit of E_m ~1000 meV[1]
- $Ca_xMn_2(PO_4)_3$: not feasible as cathode due to its higher Ca^{2+} E_m
- The E_m of **$Ca_{0.5}V_2(PO_4)_3$** (~951 meV) lies below the tolerance limit
    - In good agreement with the experimental demonstration that $NaV_2(PO_4)_3$[2] (de)intercalates Ca

- Overall, the E_m of **$Ca_xV_2(PO_4)_3$**, **$Ca_xMn_2(SO_4)_3$** and **$Ca_xFe_2(SO_4)_3$** lies below the tolerance limit, indicating facile Ca^{2+} diffusion within these frameworks

1. Lu et al., Chem. Mater. 2021 2. Kim et al., ACS Energy Lett. 2020

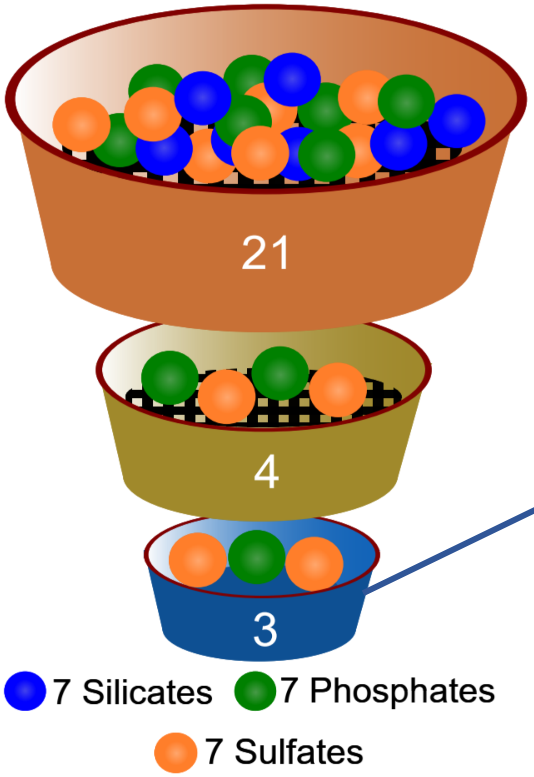
D.B Tekliye et al., Chem. Mater., 2022

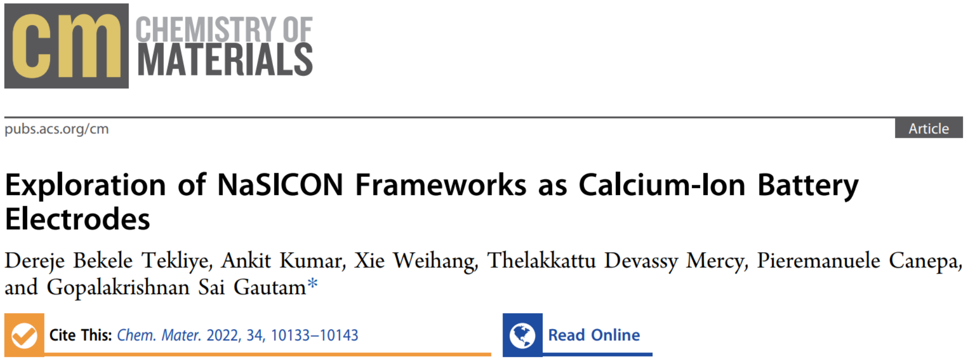
Conclusions and acknowledgments

- We explored the chemical space of Ca-NaSICON ($Ca_xM_2(ZO_4)_3$) as potential Ca cathodes
    - M = Ti, V, Cr, Mn, Fe, Co, or Ni, Z = Si, P, or S

- Based on our calculated average voltage, thermodynamic stability and migration barrier:
    - **$Ca_xV_2(PO_4)_3$**, **$Ca_xMn_2(SO_4)_3$** and **$Ca_xFe_2(SO_4)_3$** found as promising Ca-Cathodes

- All silicate-based Ca-NaSICONs are unstable
    - Unsuitable as Ca cathodes

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Exploration of NaSICON Frameworks as Calcium-Ion Battery Electrodes

Dereje Bekele Tekliye, Ankit Kumar, Xie Weihang, Thelakkattu Devassy Mercy, Pieremanuele Canepa, and Gopalakrishnan Sai Gautam*

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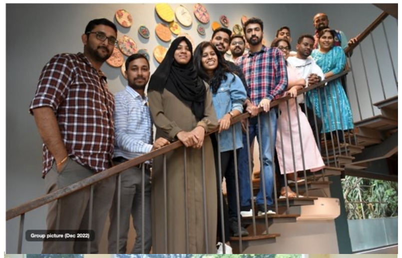

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