Exploration of NaSICON Frameworks as Calcium-ion Battery Cathodes

Dereje Bekele Tekliye[1], Ankit Kumar[1], Xie Weihang[2], Thelakkattu Devassy Mercy[3], Pieremanuele Canepa[2,4], Sai Gautam Gopalakrishnan[1]

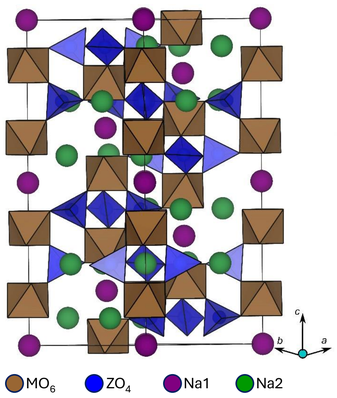
[1]Department of Materials Engineering, Indian Institute of Science, Bengaluru, 560012, Karnataka, India
[2]Department of Materials Science and Engineering, National University of Singapore, Singapore 117575, Singapore
[3]Vikram Sarabhai Space Centre, Thiruvananthapuram, 695022, Kerala, India
[4]Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117575, Singapore

INDIAN INSTITUTE OF SCIENCE
भारतीय विज्ञान संस्थान

INTRODUCTION

- Calcium-ion batteries (CIBs) show promise as alternative to the state-of-the-art lithium-ion batteries
- Why Ca-based electrochemical system?
  - Comparable standard reduction potential (−2.87 V vs SHE) with that of Li (-3.04 V)
  - Use of Ca metal anodes—delivering high volumetric energy density
  - Ca^{2+}: exchange $2e^-$ instead of $1e^-$ for Li^+
  - Ca is abundant (~ 4.15%) than Li (~ 0.002%) on Earth's crust—cost-effective
- However, the development of CIBs is challenged by the lack of suitable cathodes

NaSICON: Na Super-Ionic CONductor



- Polyanionic framework with robust structural stability and excellent ionic conductivity
- Widely explored as Na-electrode and solid electrolyte
- Usually crystallize in rhombohedral crystal structure
  - $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$, (0 ≤ x ≤ 3)
  - General formula: $A_xM_2(ZO_4)_3$, A = Na, Li etc., M = transition metals, Z= Si, P, S etc.

NaSICON as Ca-ion battery cathodes?

- Given the similar ionic radius of Na^+ (~1.02 Å) and Ca^{2+} (~1.00 Å), NaSICON could be a potential Ca-cathode
  - Motivated by experimental evidence that $NaV_2(PO_4)_3$ (de)intercalates Ca[1]

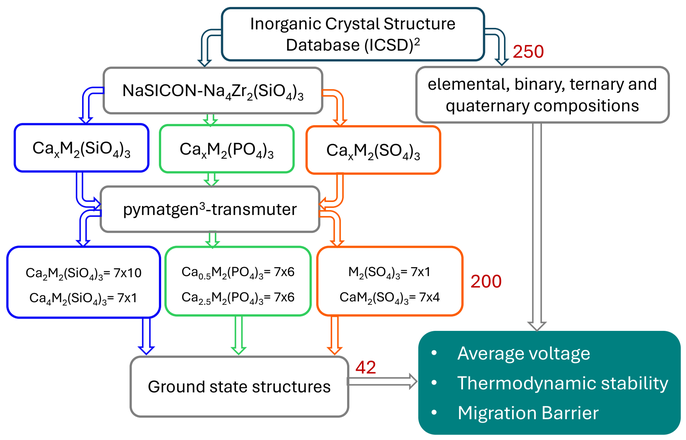
$Ca_xM_2(ZO_4)_3$: where M = Ti, V, Cr, Mn, Fe, Co or Ni, and Z = Si, P, or S

Charge neutrality constraint

- Ca composition in NaSICON is constrained by the overall **charge neutrality**
- Ca composition in $Ca_xMn_2(SiO_4)_3$:
  - Charged: $Ca_x^{2+}Mn_2^{4+}(SiO_4)_3^{4-}$ → 2·**x** + 4·2 - 4·3 = 0, → **x = 2**
  - Discharged: $Ca_x^{2+}Mn_2^{2+}(SiO_4)_3^{4-}$ → 2·**x** + 2·2 - 4·3 = 0, → **x = 4**
- Similarly
  - 2≤x≤4 in $Ca_xM_2(SiO_4)_3$
  - 0.5≤x≤2.5 in $Ca_xM_2(PO_4)_3$ } $M^{4+} \leftrightarrow M^{2+}$
  - 0≤x≤1 in $Ca_xM_2(SO_4)_3$ ⟶ $M^{3+} \leftrightarrow M^{2+}$

Theoretical capacity (mAh/g):
PO_4 (254-267) > SiO_4 (227-237) >> SO_4 (132-140)

Workflow for designing Ca-NaSICONs



METHODS

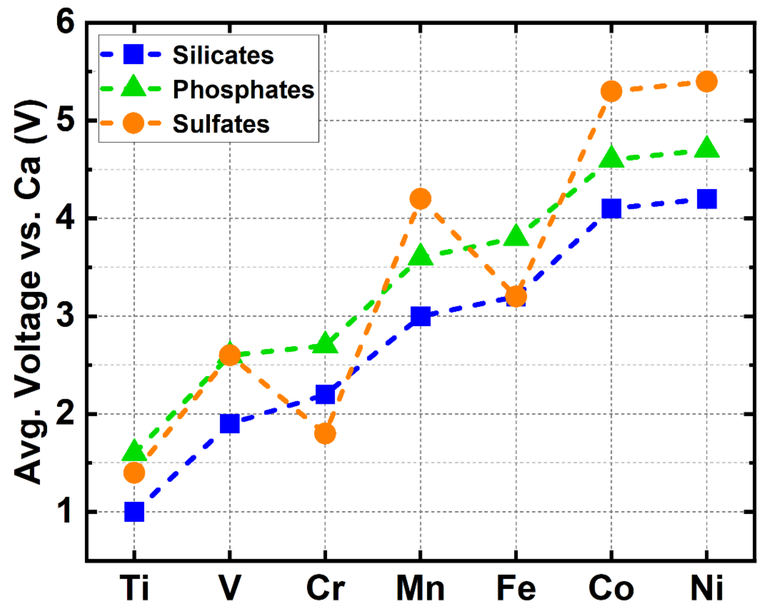
- All density functional theory (DFT) calculations done with Vienna *ab initio* simulation package (VASP[4])
  - Hubbard *U* corrected strongly constrained and appropriately normed (SCAN+*U*)[5-7]
  - 520 eV energy cutoff, 32/Å *k*-point density, 10^{-5} eV (energy) and |0.03| eV/Å (forces) convergence criteria were used
- Average voltage is calculated using Nernst equation:

$$\langle V \rangle = -\frac{\Delta G}{2(x-y)F} \approx -\frac{E(Ca_xM_2(ZO_4)_3) - [E(Ca_yM_2(ZO_4)_3) + (x-y)\mu_{Ca}]}{2(x-y)F}$$

- Pymatgen package is used to construct 0 K convex hull of Ca-M-Z-O systems
- DFT-based nudged elastic band (NEB)[8] for migration barrier (E_m) calculations
  - NEB settings: 32/Å *k*-point, 7 images, spring force of 5 eV/ Å, converged within |0.05| eV/Å

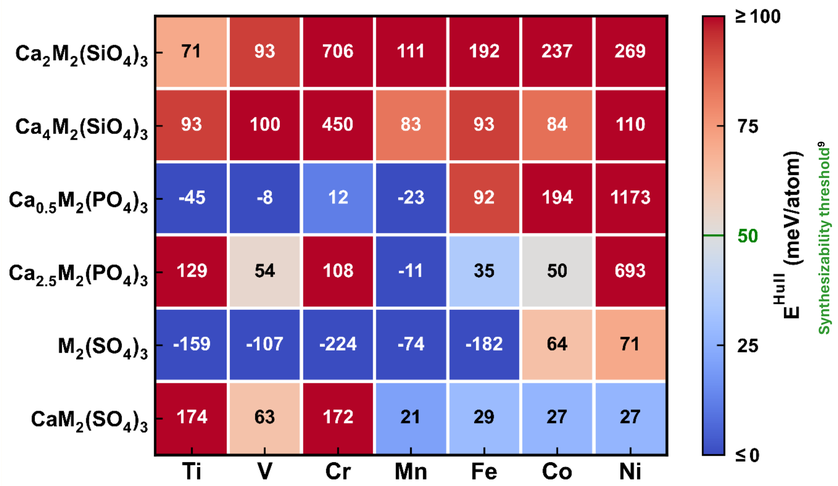
RESULTS

Average voltages



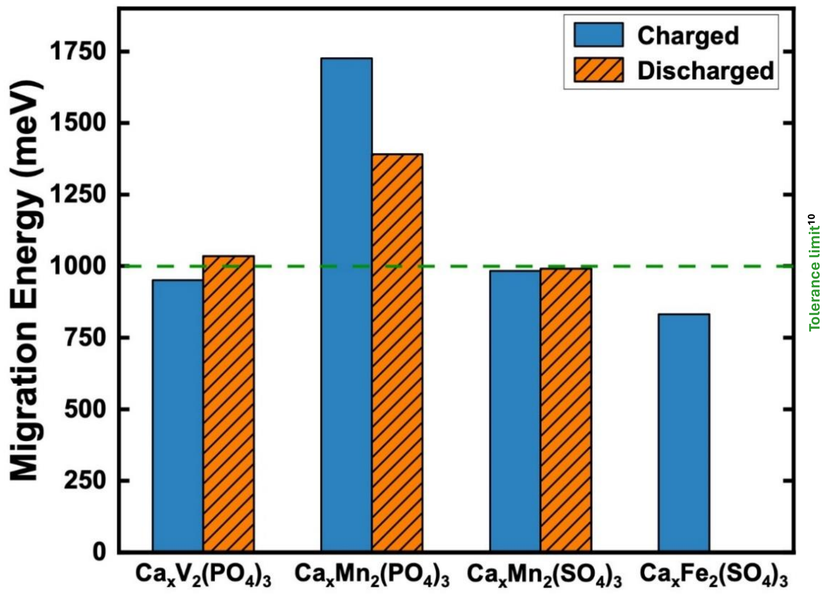
- Voltage *monotonically* increases from Ti-Ni for PO_4 and SiO_4
- PO_4 voltage is consistently higher than SiO_4–due to inductive effect
- SO_4 voltage variation is *non-monotonic*
  - "Local" minima at Cr and Fe, attributed to the stability of Cr^{3+} and Fe^{3+}

Thermodynamic stabilities



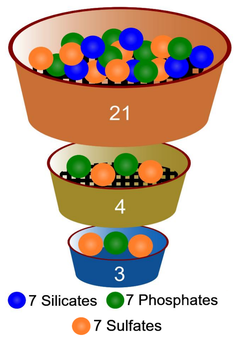
- All SiO_4 are unstable with E^{Hull} > 50 meV/atom—not candidate
- We find **V-, Mn-PO_4** and **Mn-, Fe-SO_4** as stable/metastable Ca-NaSICONs, exhibiting E^{Hull} < 50 meV/atom—possible candidates as Ca-cathodes

Migration barriers



- $Ca_xMn_2(PO_4)_3$: 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 agreement with experimental (de)intercalation of Ca in $NaV_2(PO_4)_3$[1]
- The E_m of **$Ca_xMn_2(SO_4)_3$** and **$Ca_xFe_2(SO_4)_3$** are within the tolerance limit

CONCLUSION



- CIBs offer high energy density and abundant Ca resources but lack suitable cathodes
- We explored the chemical space of Ca-NaSICON as potential Ca cathodes
- **$Ca_xV_2(PO_4)_3$**, **$Ca_xMn_2(SO_4)_3$** and **$Ca_xFe_2(SO_4)_3$** identified as promising Ca-cathodes based on average voltage, thermodynamic stability, and migration barrier calculations

ACKNOWLEDGMENTS

1. Indian Space Research Organisation (ISRO), India
2. National Research Foundation, Singapore
3. Ministry of Education, Singapore
4. Supercomputer Education and Research Centre, Indian Institute of Science
5. National Supercomputing Centre, Singapore

REFERENCES

1. Kim et al., ACS Energy Lett. 2020, 5, 3203−3211
2. M. Hellenbrandt, Crystallogr. Rev. 2004, 10, 17-22
3. S.P. Ong et al., Comput. Mater. Sci. 2013, 68, 314-319
4. G. Kresse and J. Hafner, Phys. Rev. B 1993, 48, 13115
5. J. Sun et al., Phys. Rev. Lett. 2015, 115, 036402
6. Dudarev et al., Phys. Rev. B 1998, 57, 1505
7. Sai Gautam et al., Phys. Rev. Mater. 2018, 2, 095401
8. D. Sheppard et al., J. Chem. Phys. 2008, 128, 134106
9. Wenhao Sun et al. Sci. Adv. 2016, 2, e1600225
10. Lu et al., Chem. Mater. 33, 2021, 5809-5821

Tekliye, D. B.; Kumar, A.; Weihang, X.; Mercy, T. D.; Canepa, P.; Sai Gautam, G. "Exploration of NaSICON Frameworks as Calcium-ion Battery Electrodes", **Chem. Mater. 34(22)**, 10133-10143 (2022).

18th Asian Conference on Solid State Ionics (ACSSI-2024), Chennai, India

Dereje Bekele Tekliye
PhD Student
Advisor: Prof. Sai Gautam Gopalakrishnan
Department of Materials Engineering
Indian Institute of Science
Email: derejebekele@iisc.ac.in

INDIAN INSTITUTE OF SCIENCE
भारतीय विज्ञान संस्थान
इसरो isro
NUS National University of Singapore