Discovery and Evaluation of Cathode Materials for Calcium-ion Batteries through First-Principles and Machine Learning

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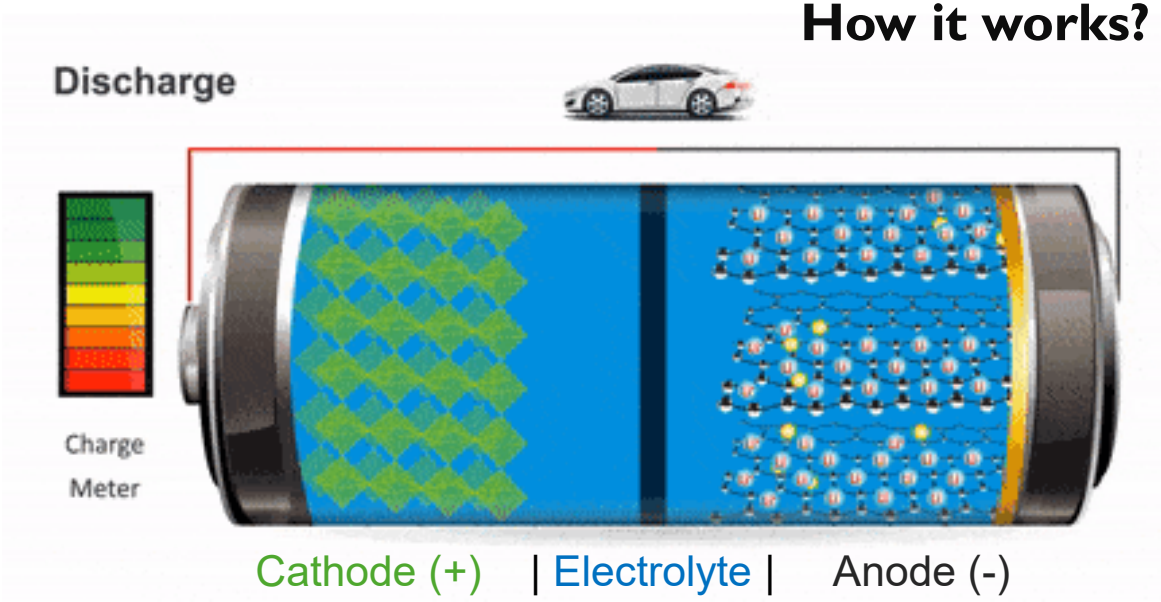
PhD Thesis Defense • July 31, 2026

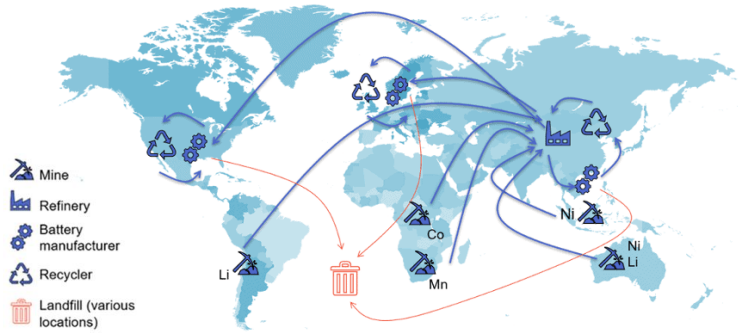
Modern lithium-ion batteries (LIBs)

How it works?



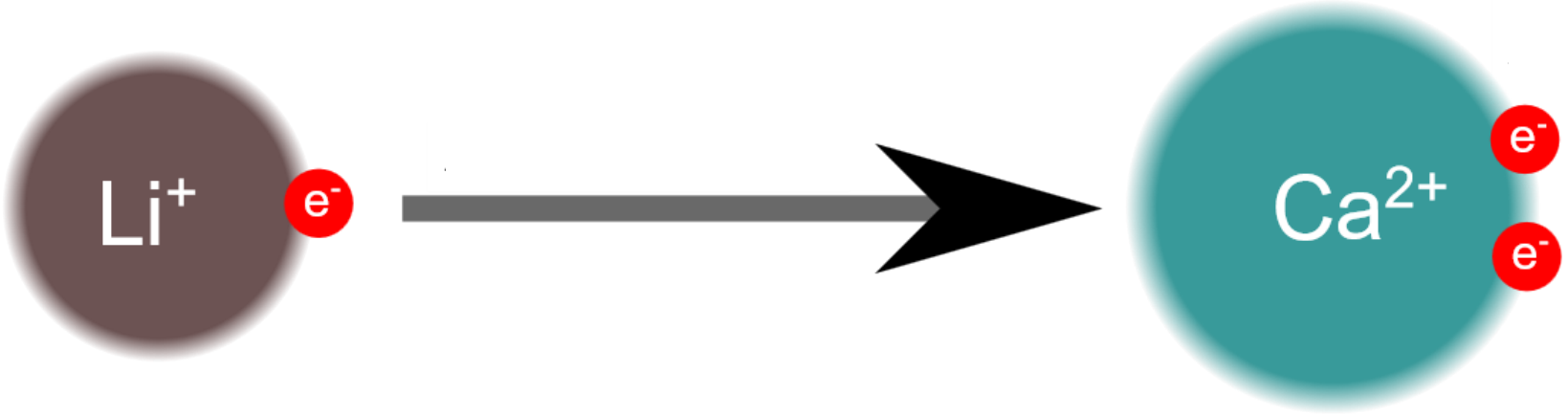
Safety concerns

Limited supply chain



https://www.intechopen.com/chapters/84482 https://www.mangrovelithium.com/decentralizing-the-lithium-supply-chain https://www.indiatimes.com

Calcium-ion batteries (CIBs): alternative to LIBs

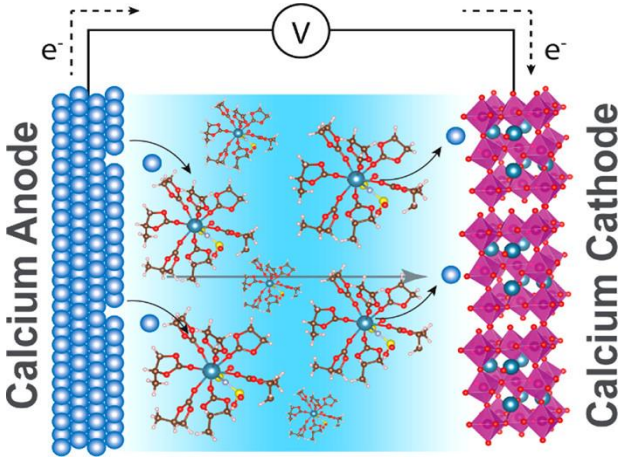


Monovalent, Lower Charge Capacity

Calcium: multivalent advantage & sustainability

Divalent, Higher Charge Capacity, Abundance & Use of Ca Metal Anode

- Comparable standard reduction potential (-2.87 V vs SHE) with that of Li (-3.04 V)
- Leverages similar electrochemical mechanism as that of LIBs



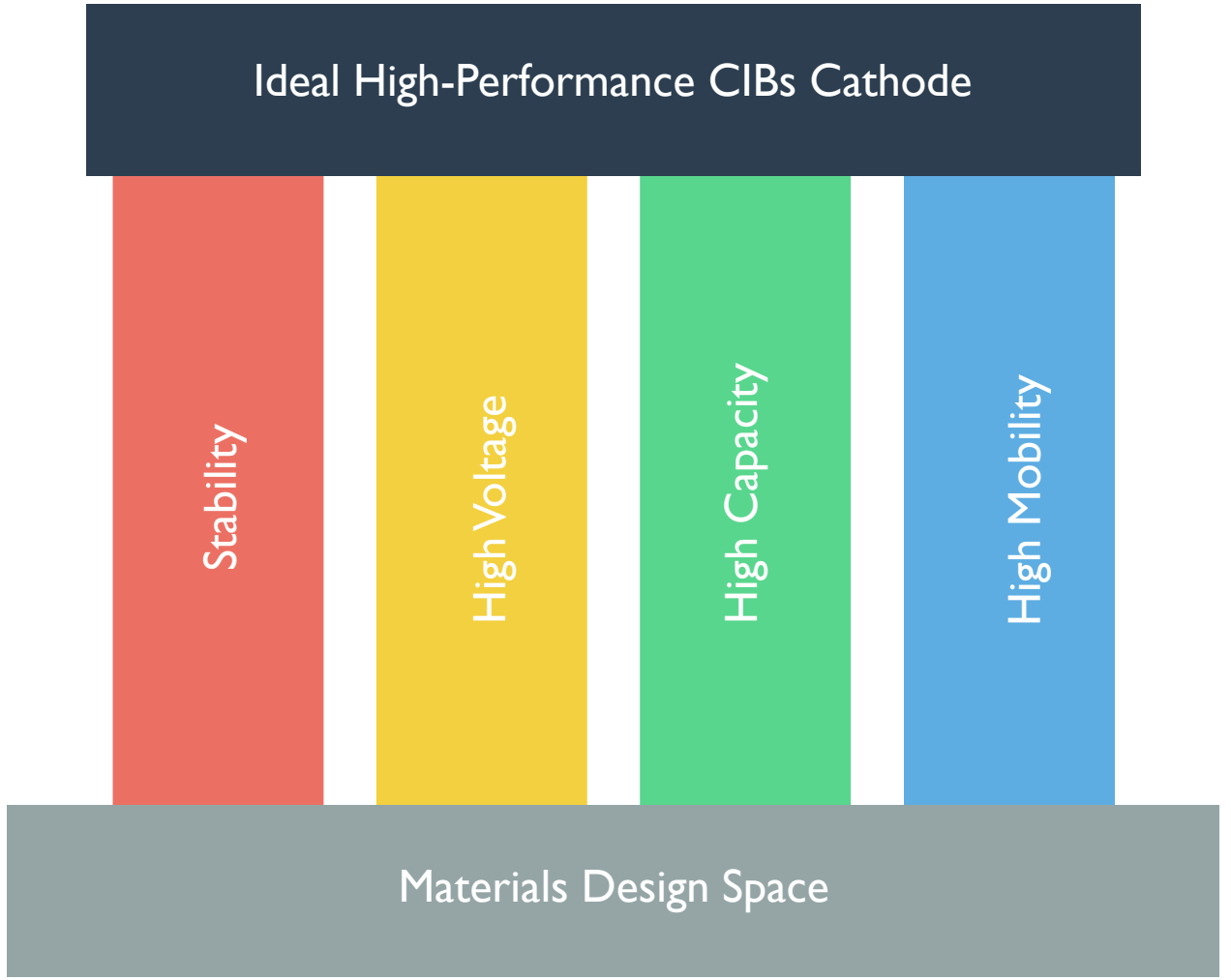
Battery performance metrics:

- Energy density (Wh/g): Voltage x Capacity
  - Voltage (V): Potential to do work
  - Capacity (mAh/g): Amount of charge stored (per electrode)
- Rate: How fast can you charge or discharge?
  - Depends on ionic "mobility"

Hosein et al. **ACS Energy Lett.** 6, 1560–1565 (2021)

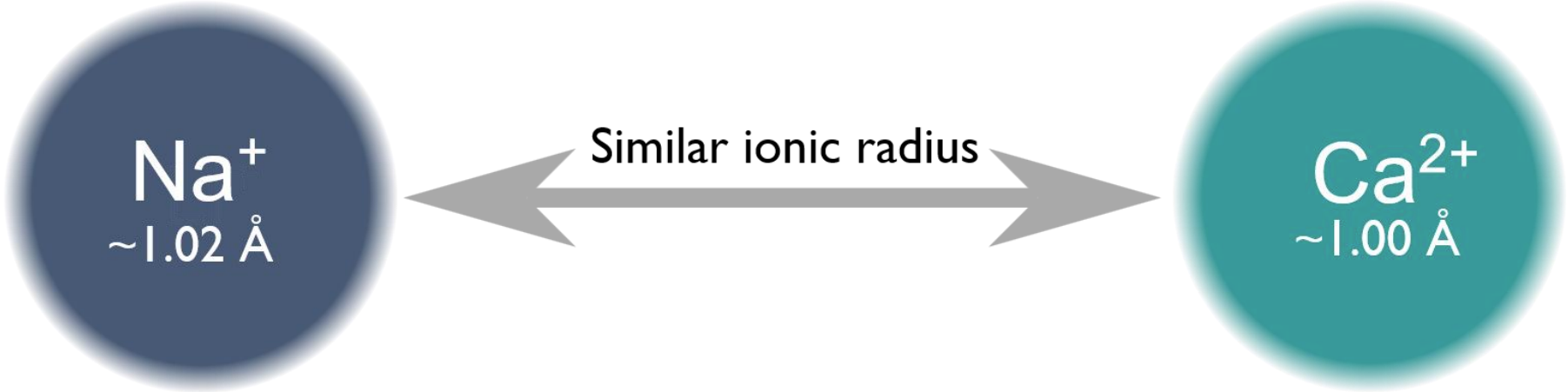
State-of-the-art Ca-cathodes and their challenges

- **Oxides:** CaV_2O_4, $CaMn_2O_4$, CaV_2O_5
  - High voltage (~2.8–3.1 V) and capacity (~240–310 $mAhg^{-1}$)
  - Large volume expansion and/or sluggish Ca^{2+} kinetics limit
- **Polyanions:** $NaV_2(PO_4)_3$, $Na_{0.5}VPO_{4.8}F_{0.7}$, $NaV_2(PO_4)_2F_3$
  - Robust 3D open frameworks with structural stability
  - Limited reversible Ca content and phase separation effects
- **Sulfides:** TiS_2, Mo_6S_8
  - Favorable thermodynamics with multi electron redox capability
  - High Ca migration barriers and low operating voltage



Lu et al. **Chem. Mater.** 33, 5809–5821 (2021)
Black et al. **Energy Storage Mater.** 47, 354–364 (2022)
Hosein et al. **ACS Energy Lett.** 6, 1560–1565 (2021)
Kim et al. **ACS Energy Lett.** 5, 3203–3211 (2020)
Sai Gautam et al. **Chem. Commun.** 51, 13619–13622 (2015)
Xu et al. **Nat. Commun.** 12, 3369 (2021)

The Na-Ca connection: ionic size similarity as a design principle



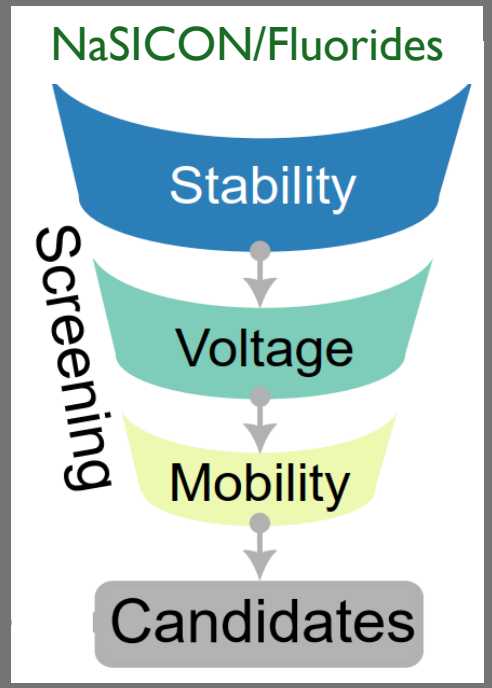
Given the comparable ionic radii of Na^+ and Ca^{2+}, established Na-based cathode frameworks may serve as hosts for reversible Ca^{2+} intercalation

Shannon et al. **Acta Crystallogr. B** 25, 925–946 (1969)

Ca-cathode design space

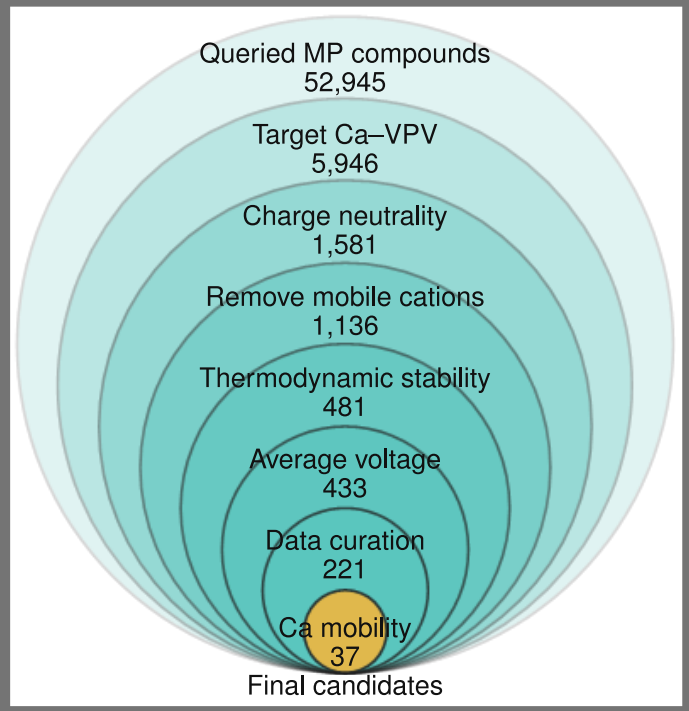
DFT-based high-throughput exploration

NaSICON and Fluoride frameworks



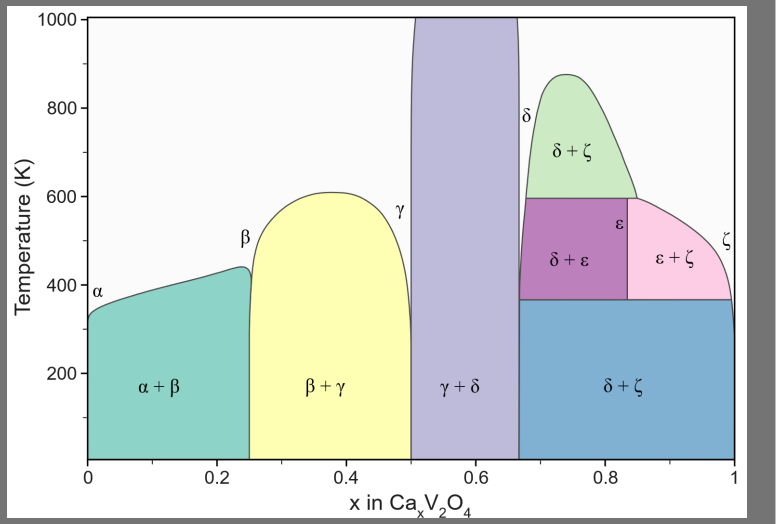
MLIP-accelerated high-throughput screening

Explore entire Materials Project structures



Deep dive into understanding Ca-cathode

Post-spinel CaV_2O_4

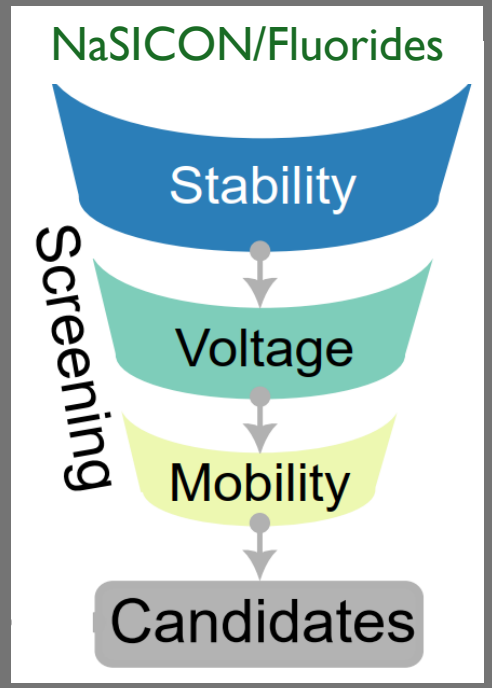


DFT == density functional theory ML==machine learning MLIP == machine learned interatomic potential

Ca-cathode design space

DFT-based high-throughput exploration

NaSICON and Fluoride frameworks



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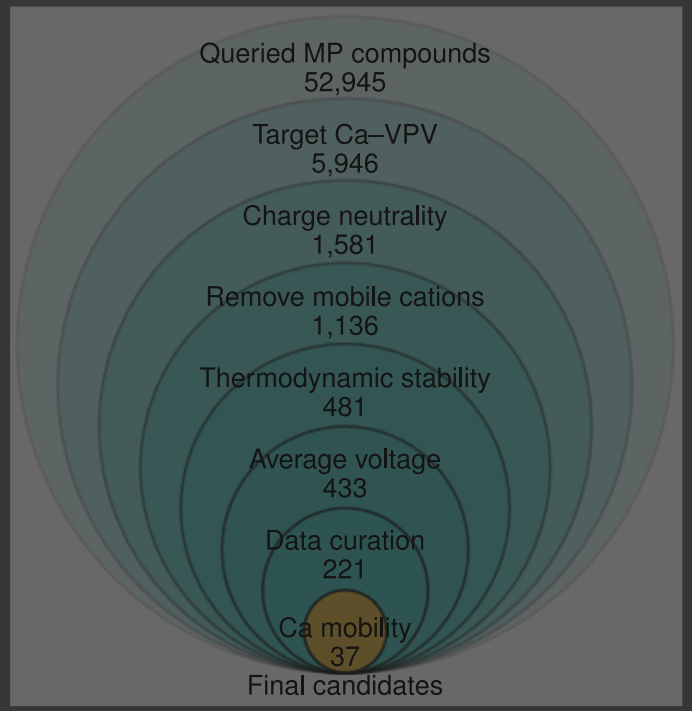

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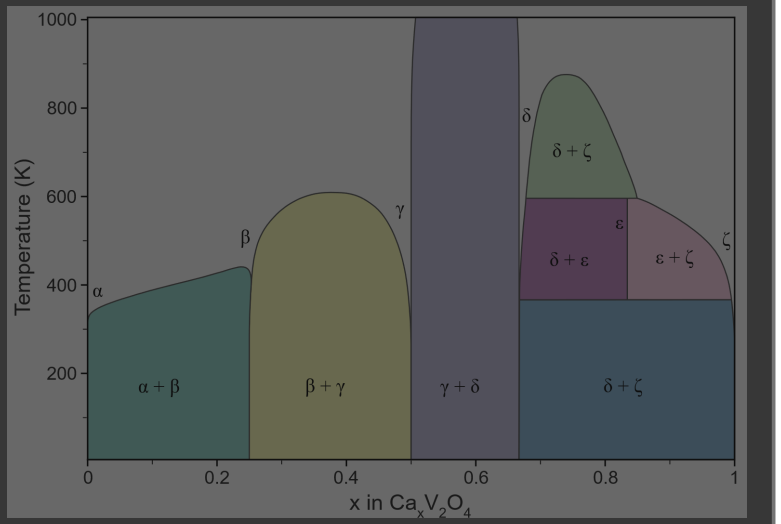

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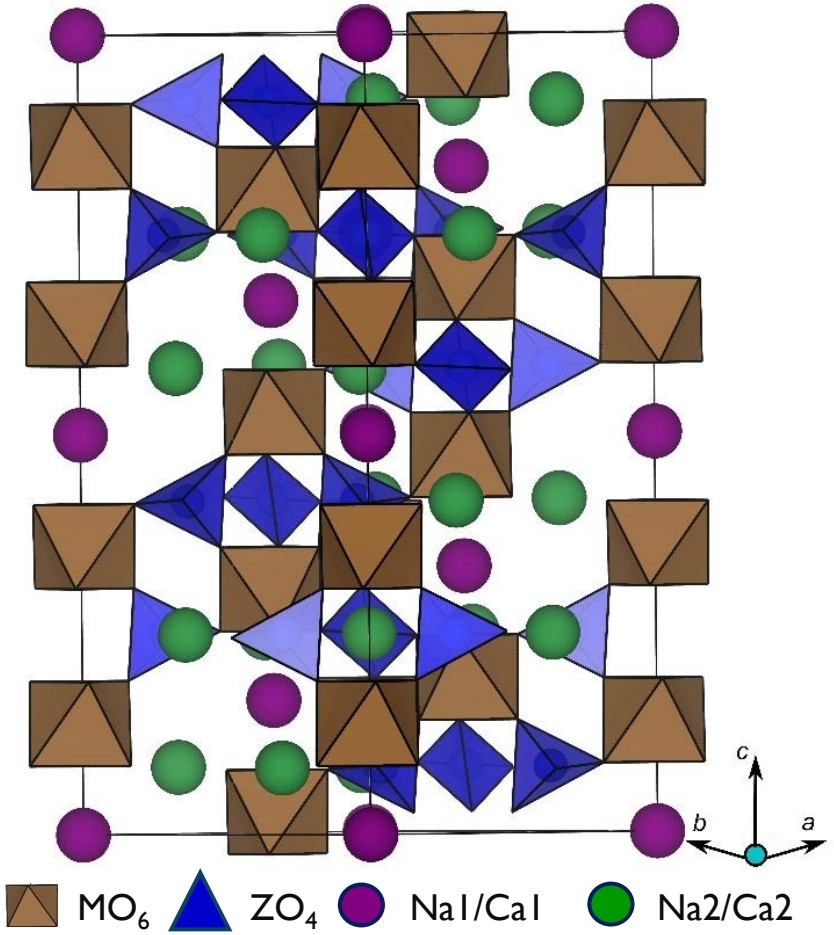
NaSICON: polyanionic framework with robust structural stability and excellent ionic conductivity



NaSICON==sodium superionic conductor
SCAN==strongly constrained and appropriately normed
ICSD==inorganic crystal structure database

- Widely explored as Na-electrode and solid electrolyte
  - $A_xM_2(ZO_4)_3$: A = Na, Li etc., M = transition metals (TMs), Z= Si, P, S etc.

NaSICON as Ca-ion battery cathodes

- Motivated by experimental evidence that $NaV_2(PO_4)_3$ intercalates Ca-ion
  - **$Ca_xM_2(ZO_4)_3$:** M = Ti, V, Cr, Mn, Fe, Co or Ni and Z = Si, P, or S

- Ca composition under **charge neutrality constraint**
  - Charged: $Ca_x^{2+}Mn_2^{4+}(SiO_4)_3^{4-} \rightarrow 2\cdot x + 4\cdot 2 - 4\cdot 3 = 0, \rightarrow x = 2$
  - Discharged: $Ca_x^{2+}Mn_2^{2+}(SiO_4)_3^{4-} \rightarrow 2\cdot x + 2\cdot 2 - 4\cdot 3 = 0, \rightarrow x = 4$
  - Similarly
    - $2 \le x \le 4$ in $Ca_xM_2(SiO_4)_3$
    - $0.5 \le x \le 2.5$ in $Ca_xM_2(PO_4)_3$
    - $0 \le x \le 1$ in $Ca_xM_2(SO_4)_3$

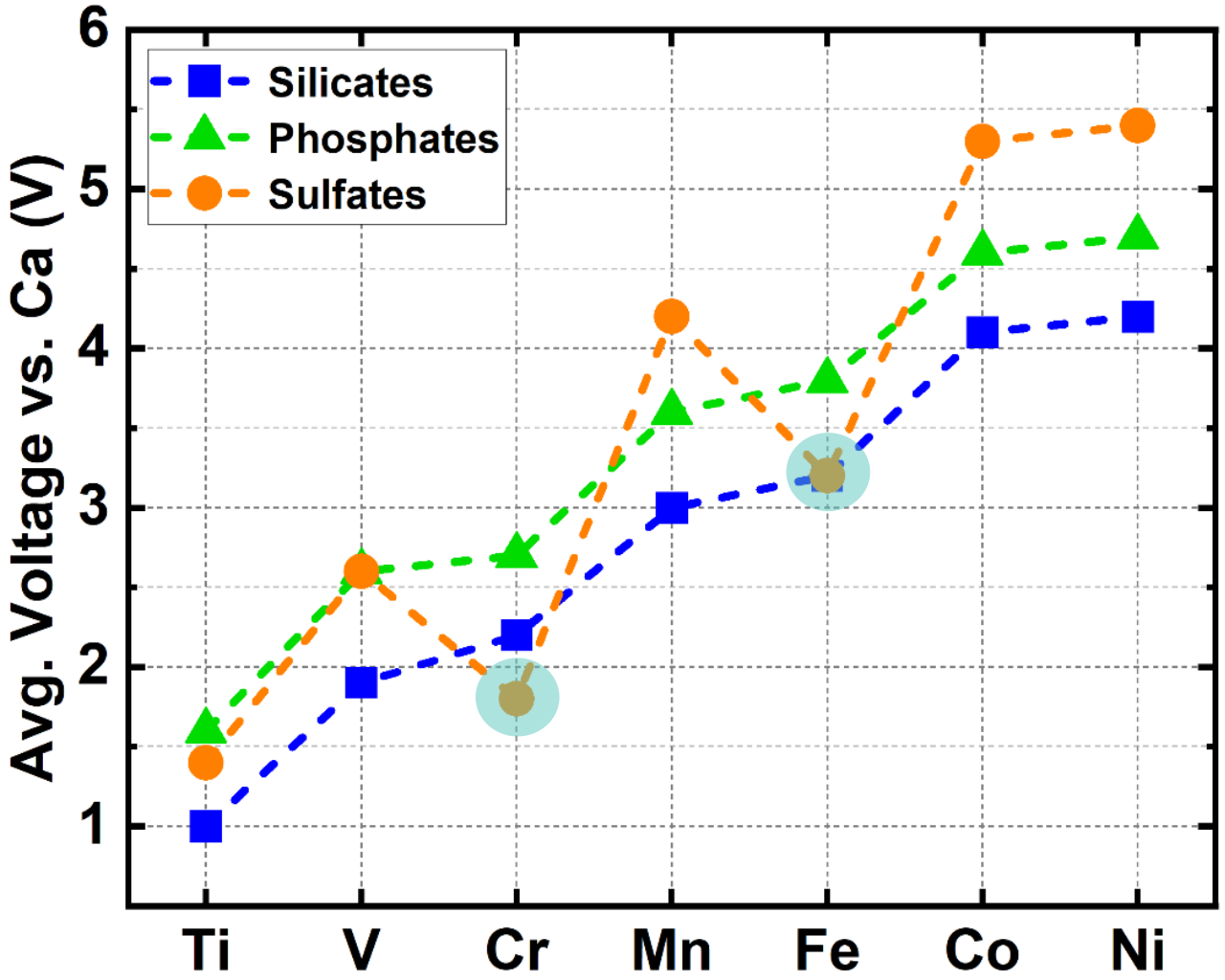
    $M^{4+} \leftrightarrow M^{2+}$ (first two); $\rightarrow M^{3+} \leftrightarrow M^{2+}$ (third)

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

- DFT SCAN+U relaxation of 200 Pymatgen-enumerated structures
  - $Na_4Zr_2(SiO_4)_3$ structure is used as a starting template from ICSD
  - **42 (7x3x2)** lowest-energy configurations for further investigation

Kim et al. **ACS Energy Lett.** 5, 3203–3211 (2020)
Ong et al. **Comput. Mater. Sci.** 68, 314–319 (2013)
Sun et al. **Phys. Rev. Lett.** 115, 036402 (2015)

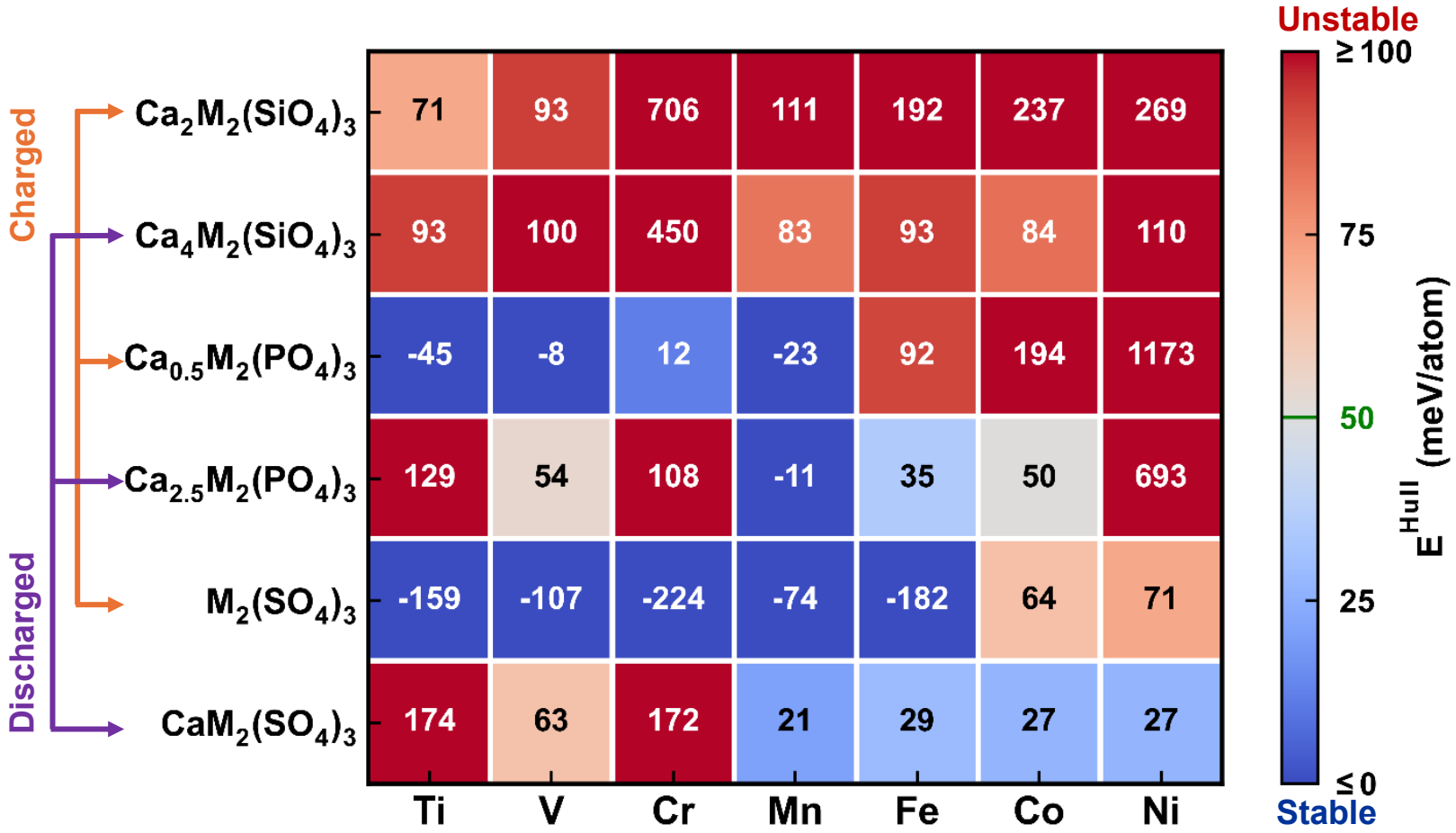
Average voltage: increases monotonically from Ti to Ni except for SO_4



- Voltage is *monotonically* increasing from Ti-Ni for PO_4 and SiO_4
  - Consistent with standard reduction potentials
- PO_4 voltage is consistently higher than SiO_4
  - Due to stronger inductive effect exerted by P^{5+} compared to Si^{4+} on the TM octahedra
- SO_4 voltage increment is *non-monotonic*
  - "Local" minima at Cr and Fe, attributed to the stability of Cr^{3+} (t_{2g}^3) and Fe^{3+} ($t_{2g}^3 e_g^2$)
- Ti-based Ca-NaSICONs are suitable for anode instead of cathode due to their low voltage

Manthiram and Goodenough **J. Power Sources** 26, 403–408 (1989)

Thermodynamic stability: discovered several stable/metastable phosphates and sulfates



- E^{hull} is based on DFT calculations of all available structures (~250) in ICSD
- $E^{Hull} > 0$: largest energy release upon decomposition

Threshold for synthesizability

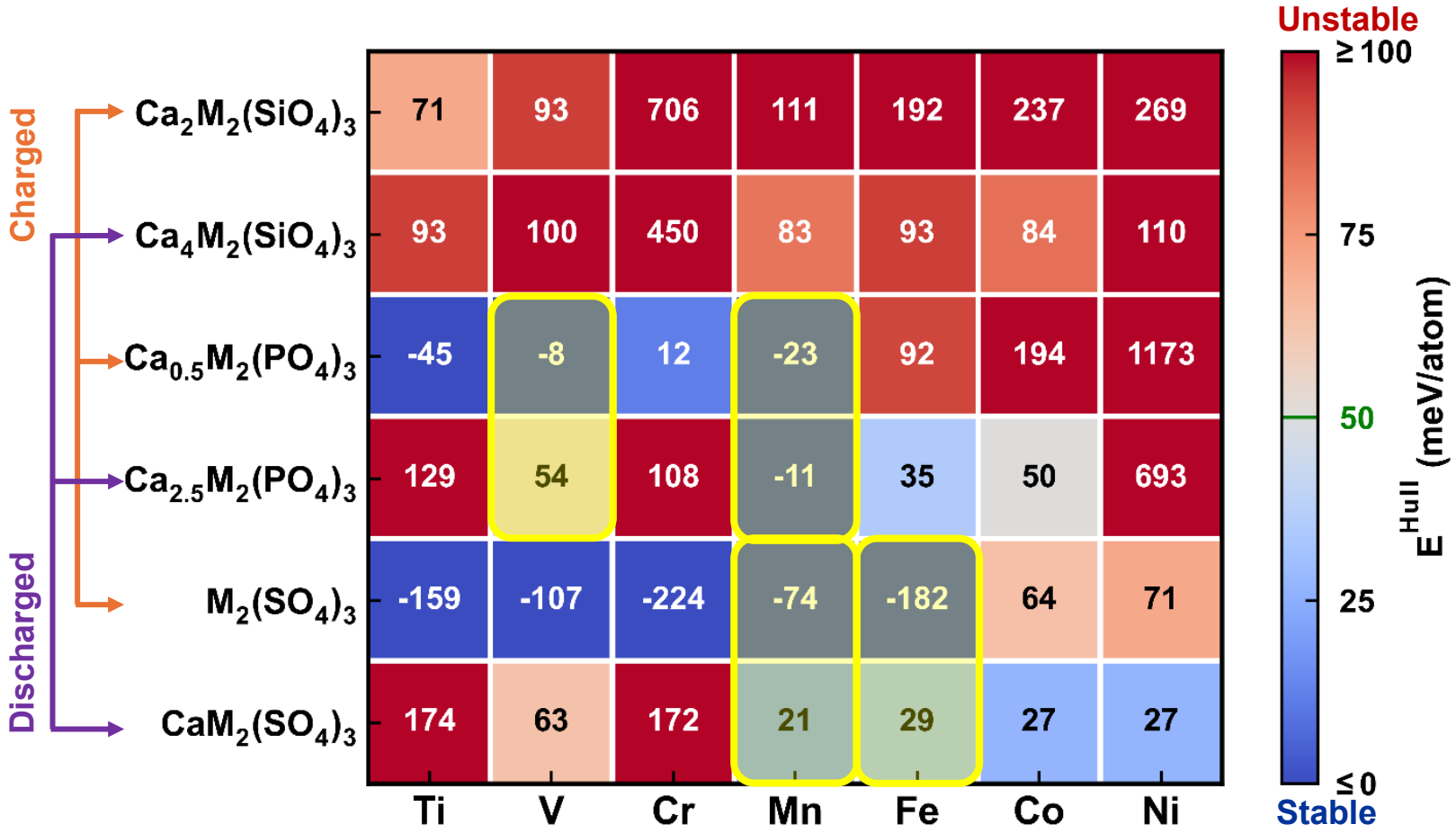
- $E^{Hull} \leq 0$: lowest energy release upon formation

$Ca_xV_2(PO_4)_3$, $Ca_xMn_2(PO_4)_3$, $Ca_xMn_2(SO_4)_3$ and $Ca_xFe_2(SO_4)_3$: stable/metastable

ICSD==inorganic crystal structure database

Sun et al. **Sci. Adv.** 2, e1600225 (2016) Senguttuvan et al. **Chem. Mater.** 25, 2391–2393 (2013) Hellenbrandt **Crystallogr. Rev.** 10, 17–22 (2004)

Thermodynamic stability: discovered several stable/metastable phosphates and sulfates



- E^{hull} is based on DFT calculations of all available structures (~250) in ICSD
- Both charged and discharged phases should preferably be thermodynamically stable/metastable
- $Ca_{0.5}V_2(PO_4)_3$ (~-8 meV/atom); $NaV_2(PO_4)_3$: experimentally synthesised
- Experimentally synthesised phases (Ti, Cr and Fe-SO_4) exhibit high stability as predicted
- All SiO_4 are unstable: not a candidate for Ca-cathode

$Ca_xV_2(PO_4)_3$, $Ca_xMn_2(PO_4)_3$, $Ca_xMn_2(SO_4)_3$ and $Ca_xFe_2(SO_4)_3$: stable/metastable

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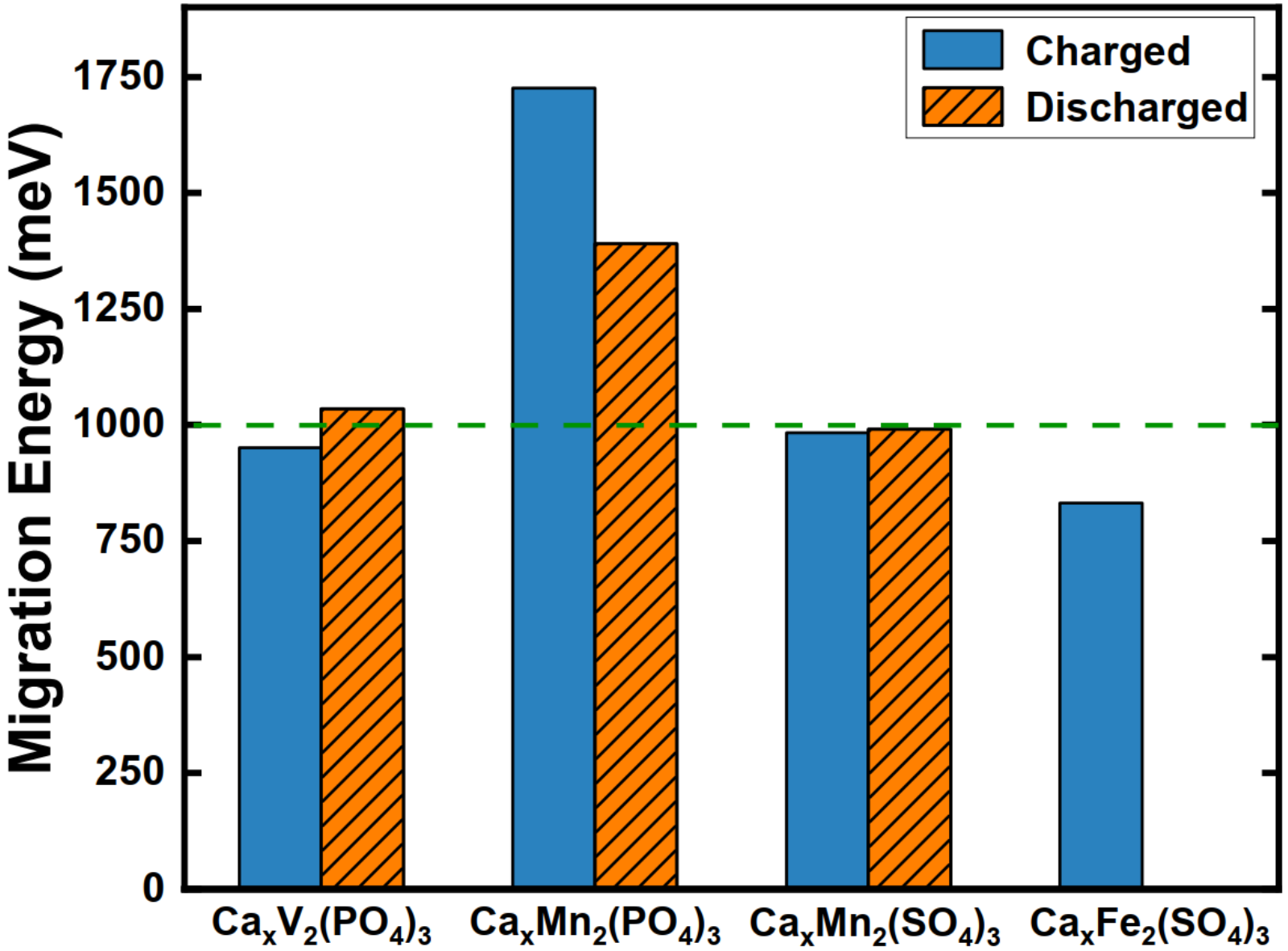
Migration barrier: 3 candidate Ca-NaSICONs



not feasible

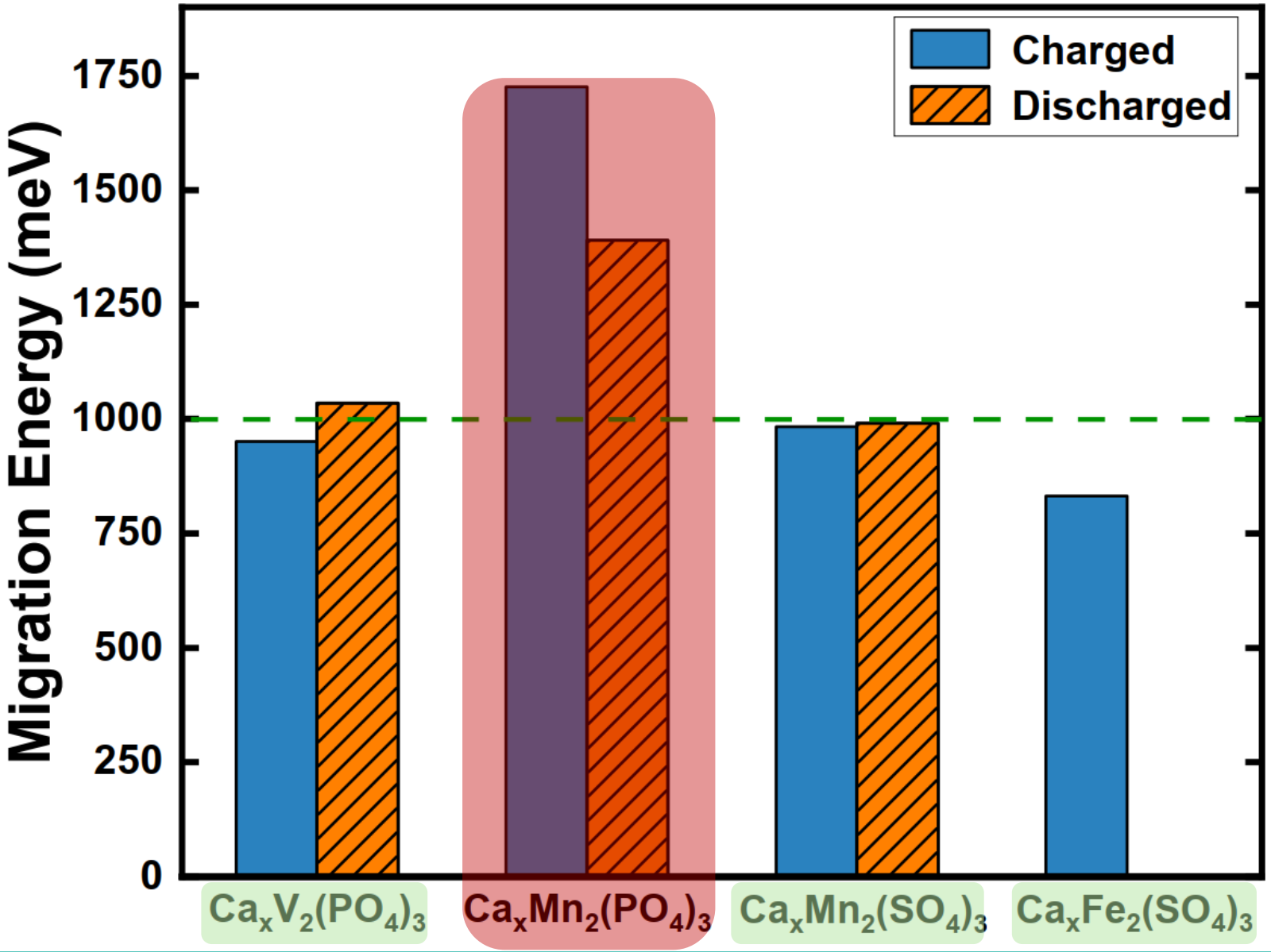
*Threshold tolerance limit

feasible

E_m is calculated using generalized gradient approximation (GGA) based NEB

NEB==nudged elastic band

Migration barrier: 3 candidate Ca-NaSICONs



not feasible

*Threshold tolerance limit

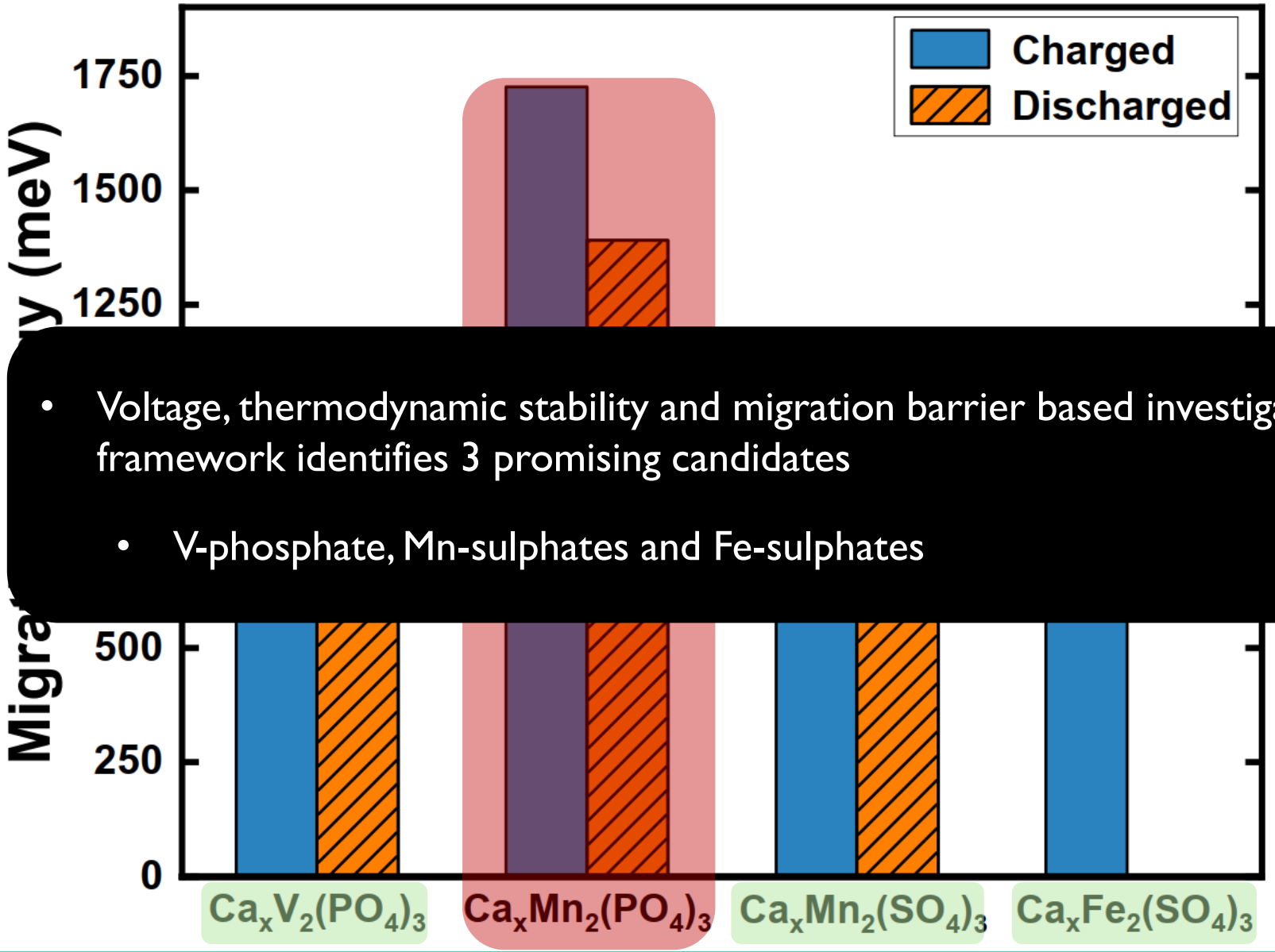
feasible

$Ca_xV_2(PO_4)_3$, $Ca_xMn_2(PO_4)_3$, ~~$Ca_xMn_2(SO_4)_3$~~ and $Ca_xFe_2(SO_4)_3$: stable/metastable and exhibit reasonable migration barrier (E_m)

E_m is calculated using generalized gradient approximation (GGA) based NEB

NEB==nudged elastic band

Migration barrier: 3 candidate Ca-NaSICONs



not feasible

feasi

- Voltage, thermodynamic stability and migration barrier based investigation of NaSICON framework identifies 3 promising candidates
  - V-phosphate, Mn-sulphates and Fe-sulphates

$Ca_xV_2(PO_4)_3$, $Ca_xMn_2(PO_4)_3$, ~~$Ca_xMn_2(SO_4)_3$~~ and $Ca_xFe_2(SO_4)_3$: stable/metastable and exhibit reasonable migration barrier (E_m)

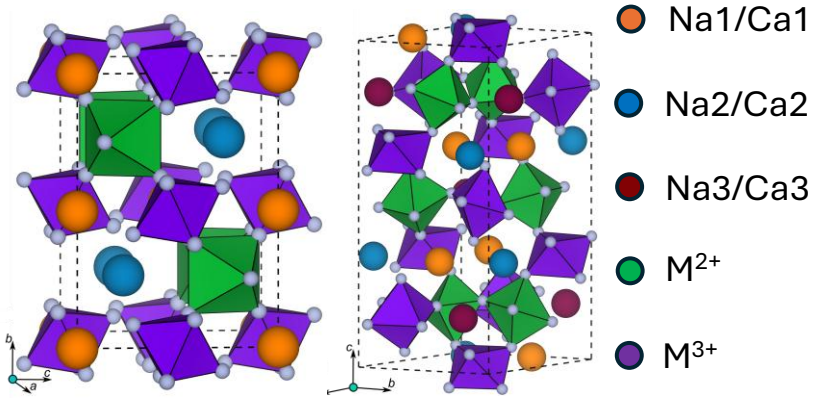
E_m is calculated using generalized gradient approximation (GGA) based NEB

NEB==nudged elastic band

Weberite and perovskite fluorides as Ca-cathode?

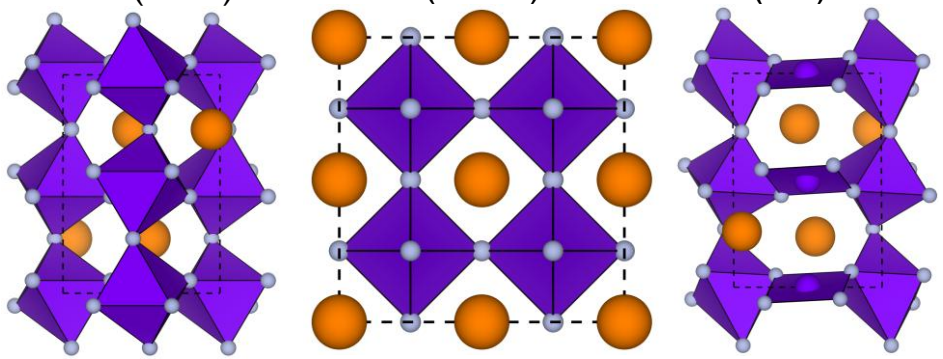
Weberites–$Na_2M_2F_7$

Orthorhombic ($Imma$) Trigonal ($P3_121$)



Perovskites-$NaMF_3$

Orthorhombic ($Pnma$) Cubic ($Pm\bar{3}m$) Triclinic ($P\bar{1}$)



TMFs==transition metal fluorides

- **$Ca_xM_2F_7$ & Ca_xMF_3**: M = Ti, V, Cr, Mn, Fe, Co, or Ni
  - $0 \le x \le 1.5$ in $Ca_xM_2F_7$ $M^{2+} \leftrightarrow M^{3.5+}$
  - $0 \le x \le 0.5$ in Ca_xMF_3 $M^{2+} \leftrightarrow M^{3+}$
- Evaluated accuracy of SCAN and r^{2}SCAN functionals in describing TMFs
  - Suffers from residual self interaction error in TMFs
  - Optimized a Hubbard *U* for all the 3*d*-redox active TMs

"Accuracy of metaGGA Functionals in Describing Transition Metal Fluorides", D. B. Tekliye and G. Sai Gautam, **Phys. Rev. Materials**, 8, 093801, **2024**

- DFT SCAN+U relaxation of 140 Pymatgen-enumerated configurations
  - 28 (weberite + perovskite) ground state structures
- Several weberites & perovskites are stable/metastable exhibit reasonable average voltage
  - **Ti**, **V**, **Cr**, **Mn**, **Ni-weberites** and **V**, **Mn**, **Co**, **Ni-perovskites** are identified as candidate
- **$Ca_xCr_2F_7$** and **$Ca_xMn_2F_7$**-weberites: promising Ca-cathodes due to their reasonable Ca^{2+} migration barrier
  - None of the perovskites are feasible as Ca-cathode: high E_m

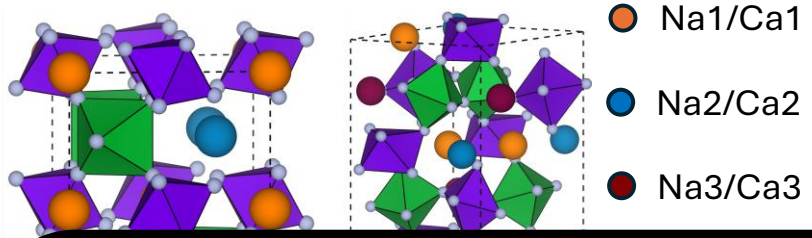
Tekliye and Sai Gautam **Phys. Rev. Mater.** 8, 093801 (2024)

Tekliye and Sai Gautam **J. Mater. Chem. A** 12, 18993–19007 (2024)

Weberite and perovskite fluorides as Ca-cathode?

Weberites–$Na_2M_2F_7$

Orthorhombic ($Imma$) Trigonal ($P3_121$)



- **$Ca_xM_2F_7$ & Ca_xMF_3**: M = Ti, V, Cr, Mn, Fe, Co, or Ni
  - $0 \leq x \leq 1.5$ in $Ca_xM_2F_7$ $M^{2+} \leftrightarrow M^{3.5+}$
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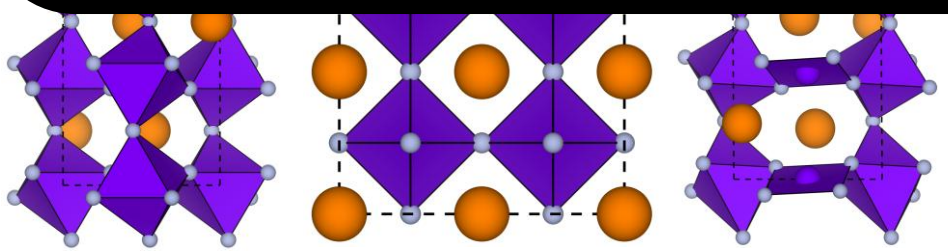
- Evaluated accuracy of SCAN and r^{2}SCAN functionals in describing TMFs
  - Suffers from residual self interaction error in TMFs

Comprehensive DFT-based screening of NaSICON and fluoride frameworks successfully identified five promising Ca-cathodes

- **5 promising candidates**: V-phosphate, Mn-sulphates, Fe-sulphates, Cr-weberites, and Mn-weberites

1. D. B. Tekliye et al., Exploration of NaSICON Frameworks as Calcium-ion Battery Electrodes, **Chem. Mater.**, 34, 10133–10143, **2022**
2. D. B. Tekliye and G. Sai Gautam, Accuracy of metaGGA Functionals in Describing Transition Metal Fluorides, **Phys. Rev. Mater.**, 8, 093801, **2024**
3. D. B. Tekliye and G. Sai Gautam, Fluoride Frameworks as Potential Calcium Battery Cathodes, **J. Mater. Chem. A**, 12, 18993–19007, **2024**



identified as candidate

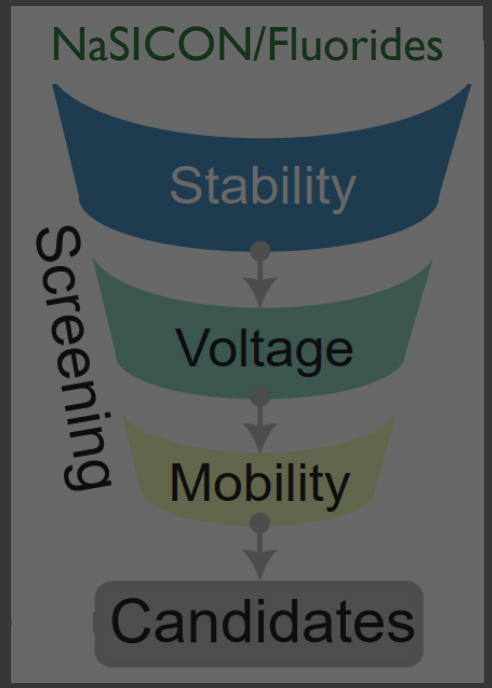
- **$Ca_xCr_2F_7$** and **$Ca_xMn_2F_7$-weberites**: promising Ca-cathodes due to their reasonable Ca^{2+} migration barrier
  - None of the perovskites are feasible as Ca-cathode: high E_m

TMFs==transition metal fluorides

Ca-cathode design space: from DFT to ML

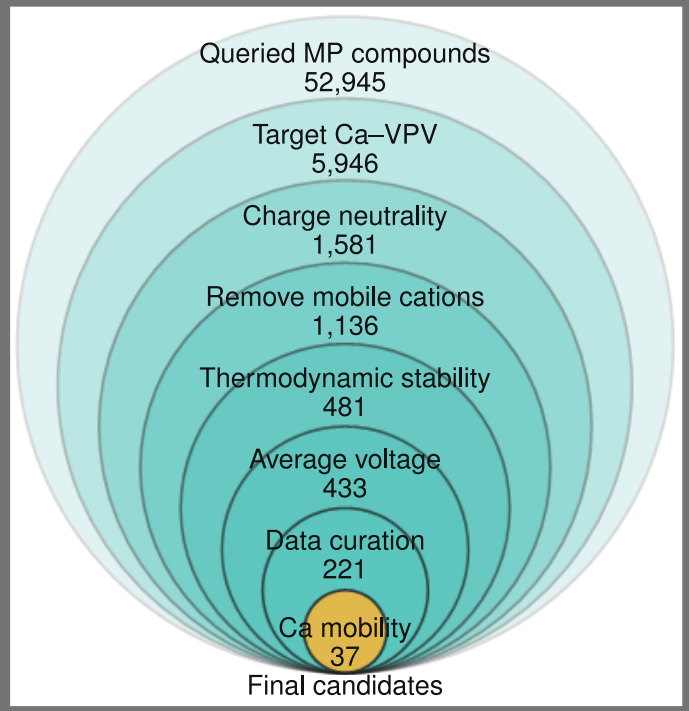
DFT-based high-throughput exploration

NaSICON and Fluoride frameworks



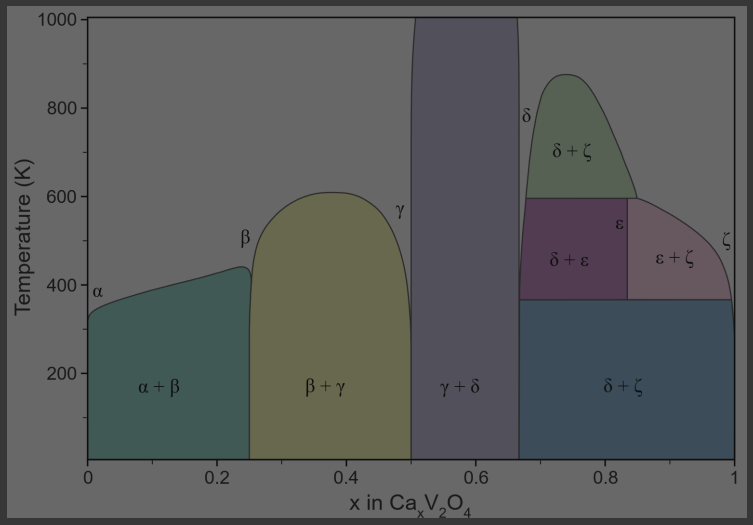
MLIP-accelerated high-throughput screening

Explore entire Materials Project structures



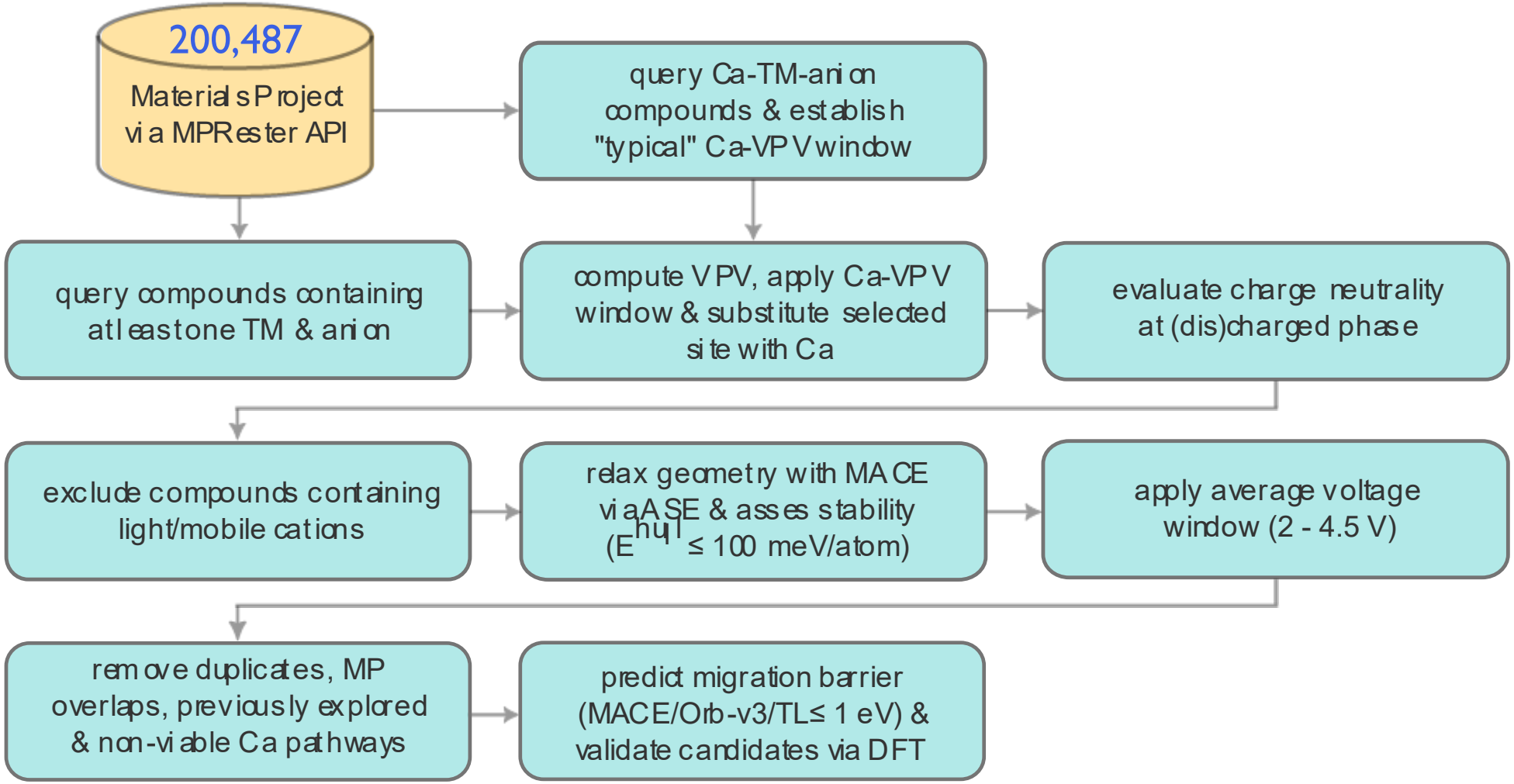
Deep dive into understanding Ca-cathode

Post-spinel CaV_2O_4



DFT == density functional theory ML==machine learning MLIP == machine learned interatomic potential

Find cathode frameworks that don't contain Ca *a priori*



- Query MP structure
- Apply geometric and chemical heuristics

- Thermodynamic stability and practical voltage

- Deduplication and data curation

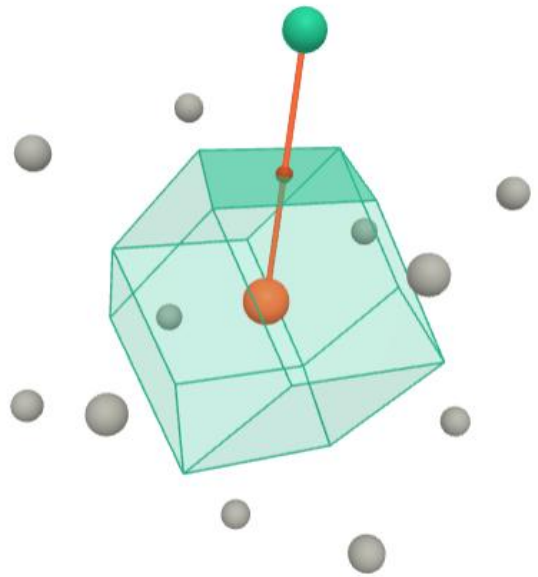
- Evaluate Ca-mobility
- DFT-NEB validation of final candidates

VPV==Voronoi polyhedral volume MP==Materials Project

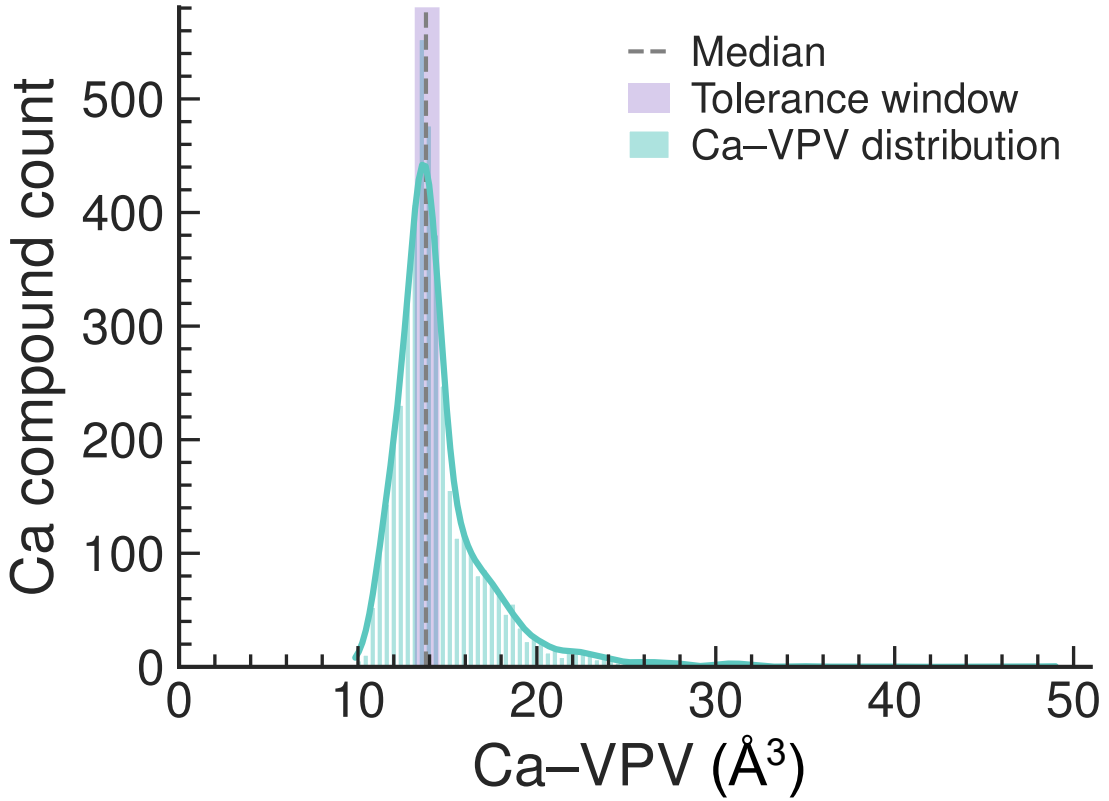
Geometry-based Ca-cathode design: VPV as a metric for Ca-site compatibility

- **Ionic radii:** not transferable across large chemical/structural space
- **VPV:** local free volume surrounding an atom in a crystal
  - Captures the true local coordination environment and robust than ionic radii

Voronoi polyhedral

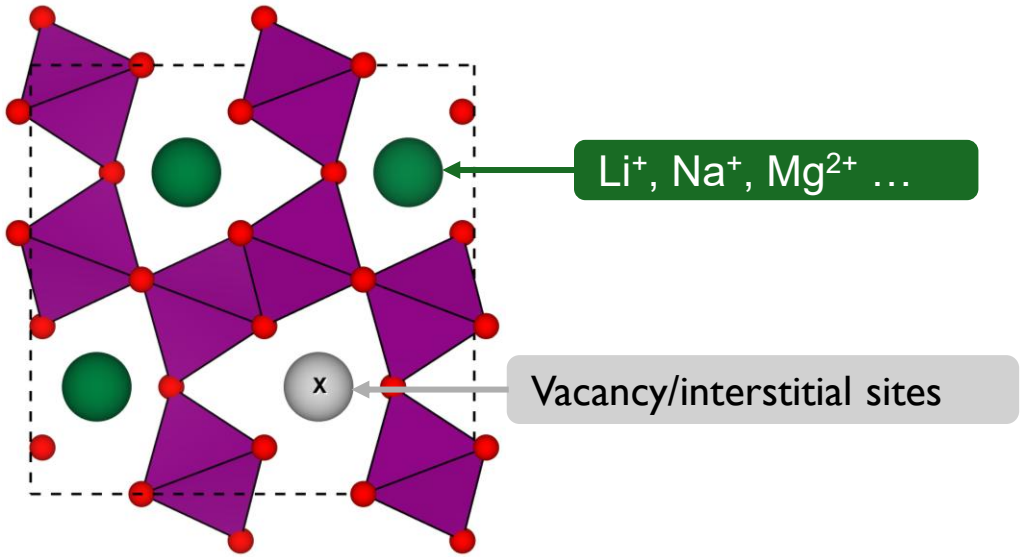


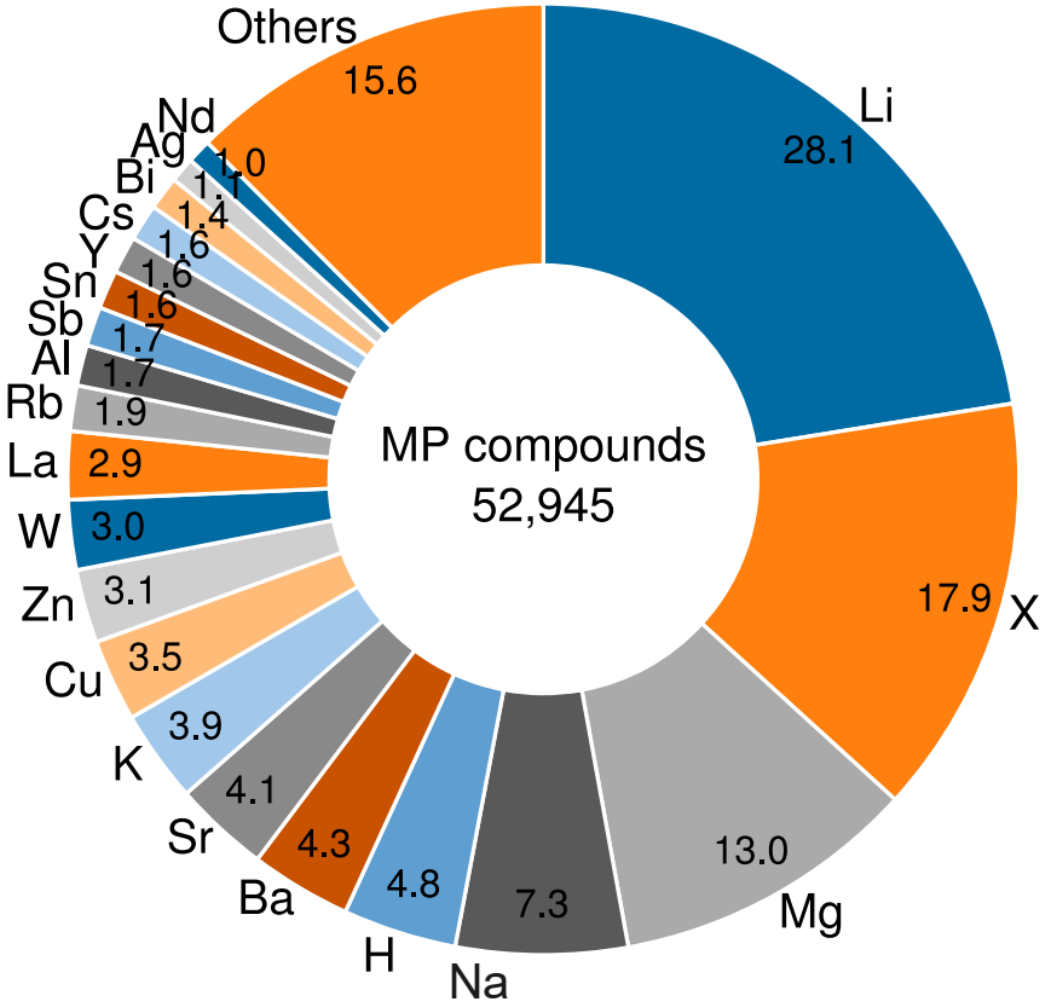
- Set an 'ideal' Ca-VPV by calculating VPV of Ca in Ca-compounds
  - Query MP for **Ca–TM–anion(s)** compounds: 4,350
  - Ca-VPV median: **13.86 Å^3**; window: **[13.17 - 14.56 Å^3]** (±5% around the median)



Query MP structures don't contain Ca *a priori*

- Query compounds containing at least one transition metals and one anion from MP (no Ca)
  - TMs: Ti, V, Cr, Mn, Fe, Co, Ni, Nb, or/and Mo
  - p-block: O, F, Cl, I, S, P, B, C, N, etc.
- Example compounds: LiV_2O_4, $LiMnV(P_2O_7)_2$, $Na_3Mn_4(TeO_6)_2$, $Na_3Ti_2Mn_3Si_4(O_8F)_2$, $MgVP_2O_7$, V_9O_{12} etc.
- Using pymatgen's locate interstitial/vacancy sites ("X")
  - Compute VPV of a potential Ca substitution species (non-TMs & non-anions) and interstitial/vacancy sites ("X")

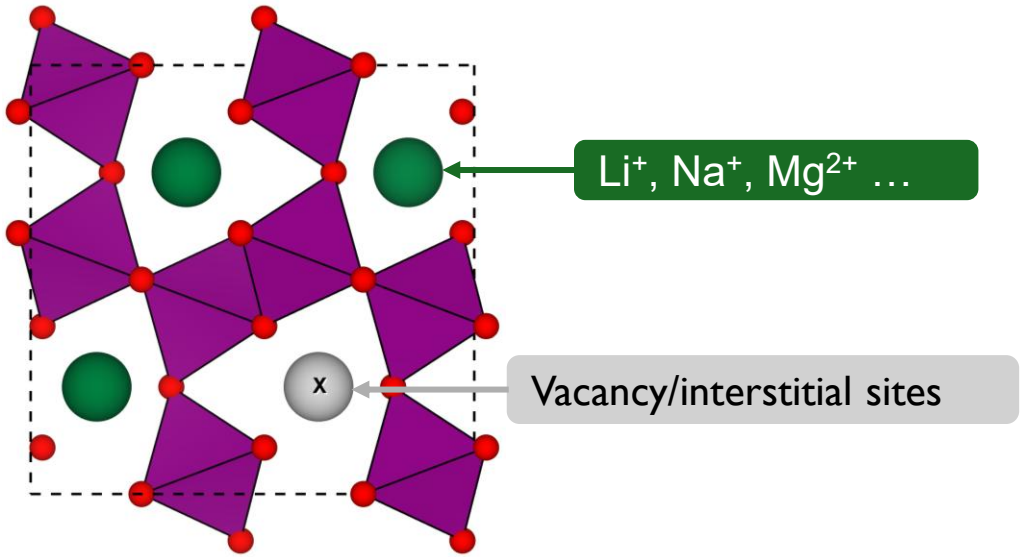


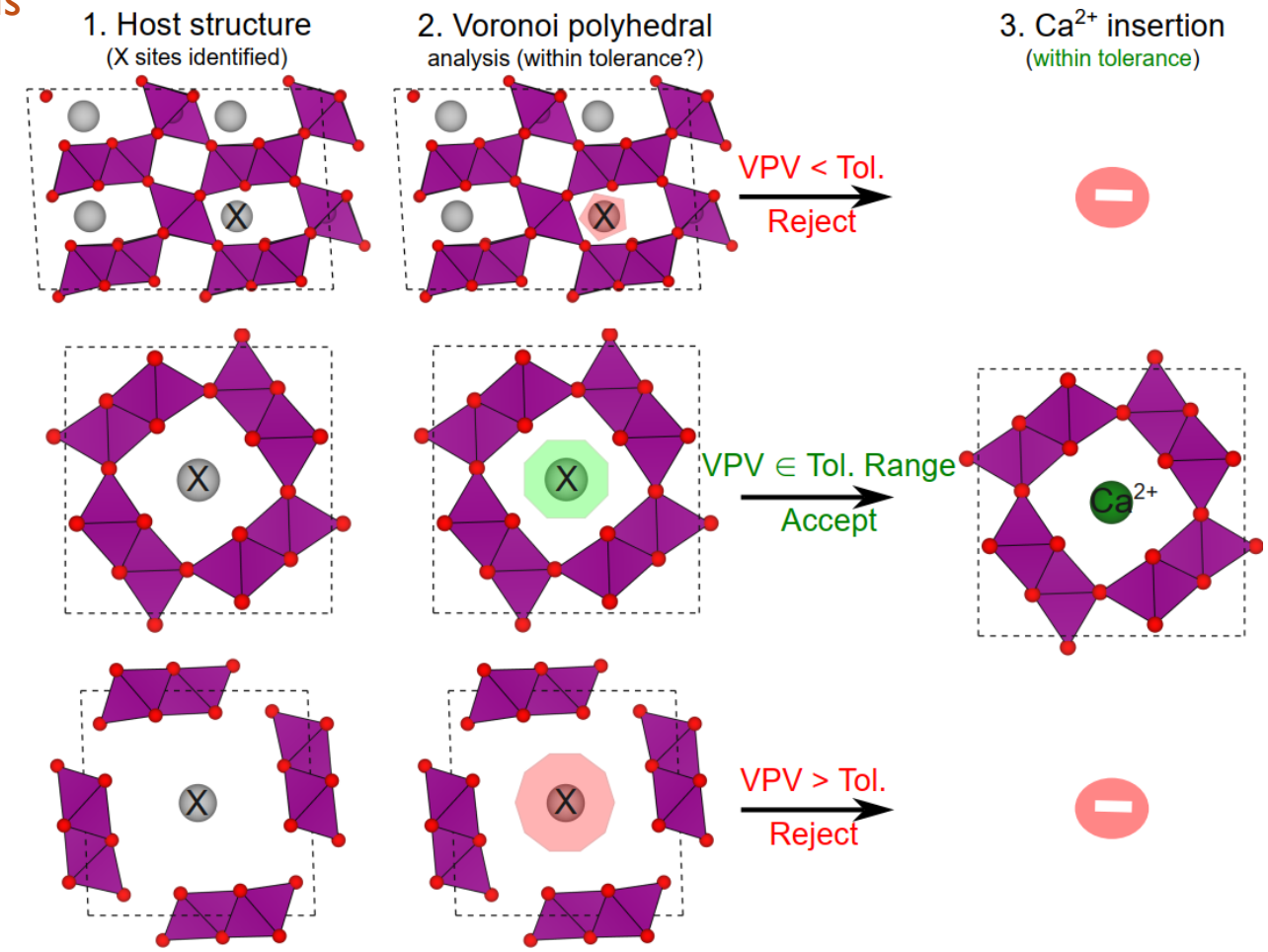


Mathew et al., **Nat. Mater.** 24, 1522–1532 (2025)

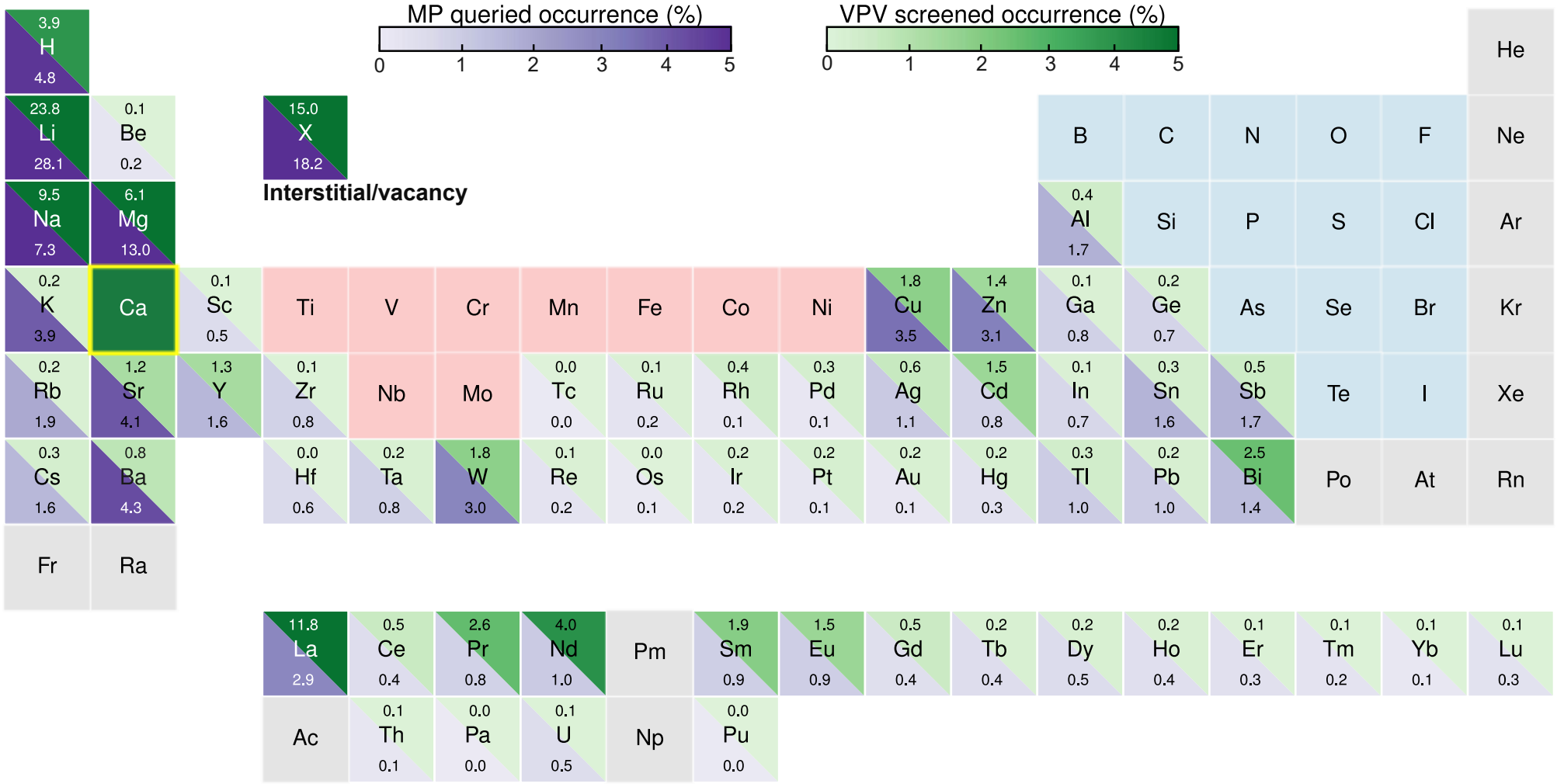
Query MP structures don't contain Ca *a priori*

- Query compounds containing at least one transition metals and one anion from MP (no Ca)
  - TMs: Ti, V, Cr, Mn, Fe, Co, Ni, Nb, or/and Mo
  - p-block: O, F, Cl, I, S, P, B, C, N, etc.
- Example compounds: LiV_2O_4, $LiMnV(P_2O_7)_2$, $Na_3Mn_4(TeO_6)_2$, $Na_3Ti_2Mn_3Si_4(O_8F)_2$, $MgVP_2O_7$, V_9O_{12} etc.
- Using pymatgen's locate interstitial/vacancy sites ("X")
  - Compute VPV of a potential Ca substitution species (non-TMs & non-anions) and interstitial/vacancy sites ("X")





Apply Ca-VPV tolerance window: 52,945 → 5,946



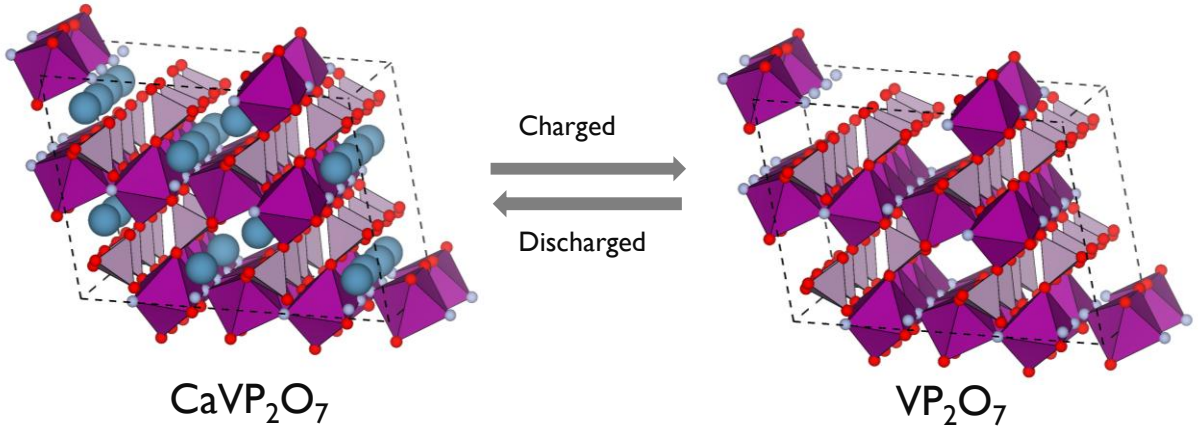
Li, **X**, **Na**, and **Mg** dominate both VPV-filtered and full dataset

Substitute **Ca** at potential substitution sites (Li, X, Na, Mg, etc.)

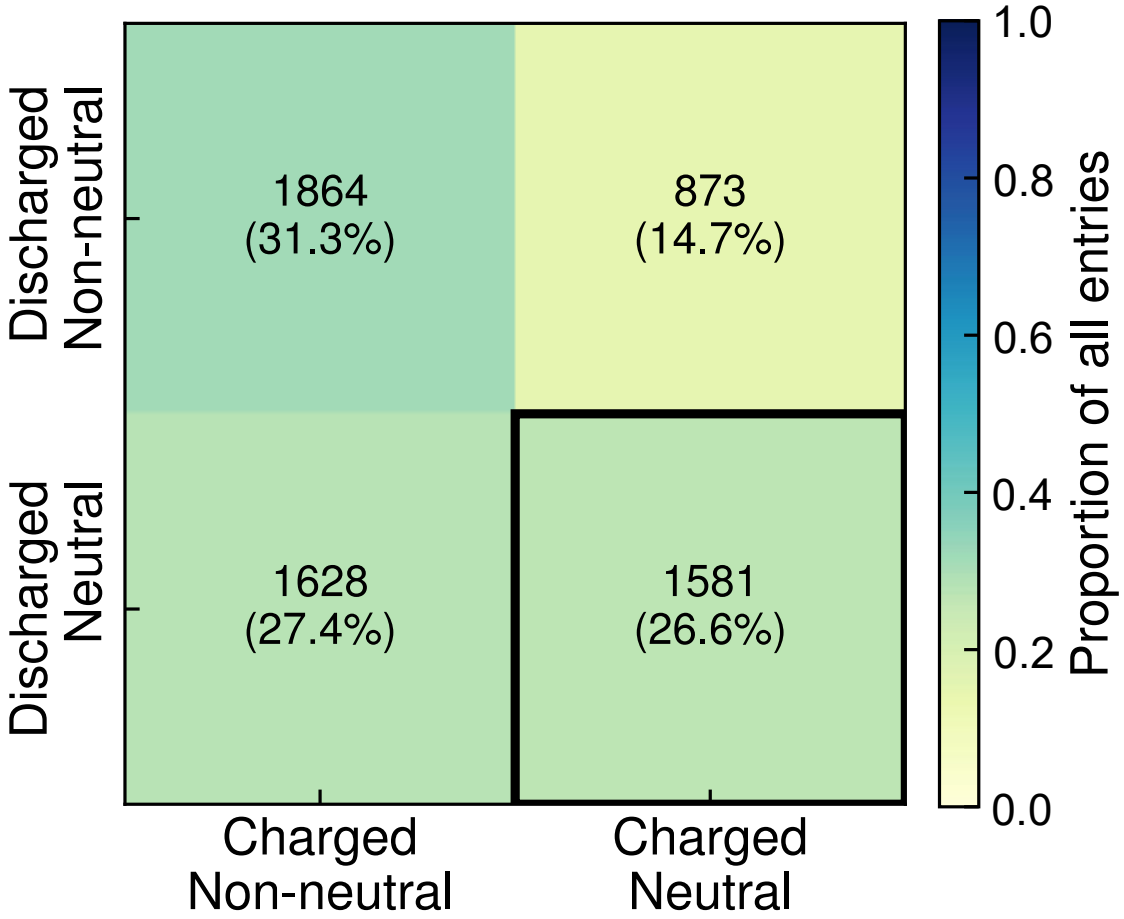
- Yielded a set of 5,946 Ca-substituted structures with Ca-based formulas for subsequent evaluation

Filtering on charge neutrality: 5,946 → 1,581

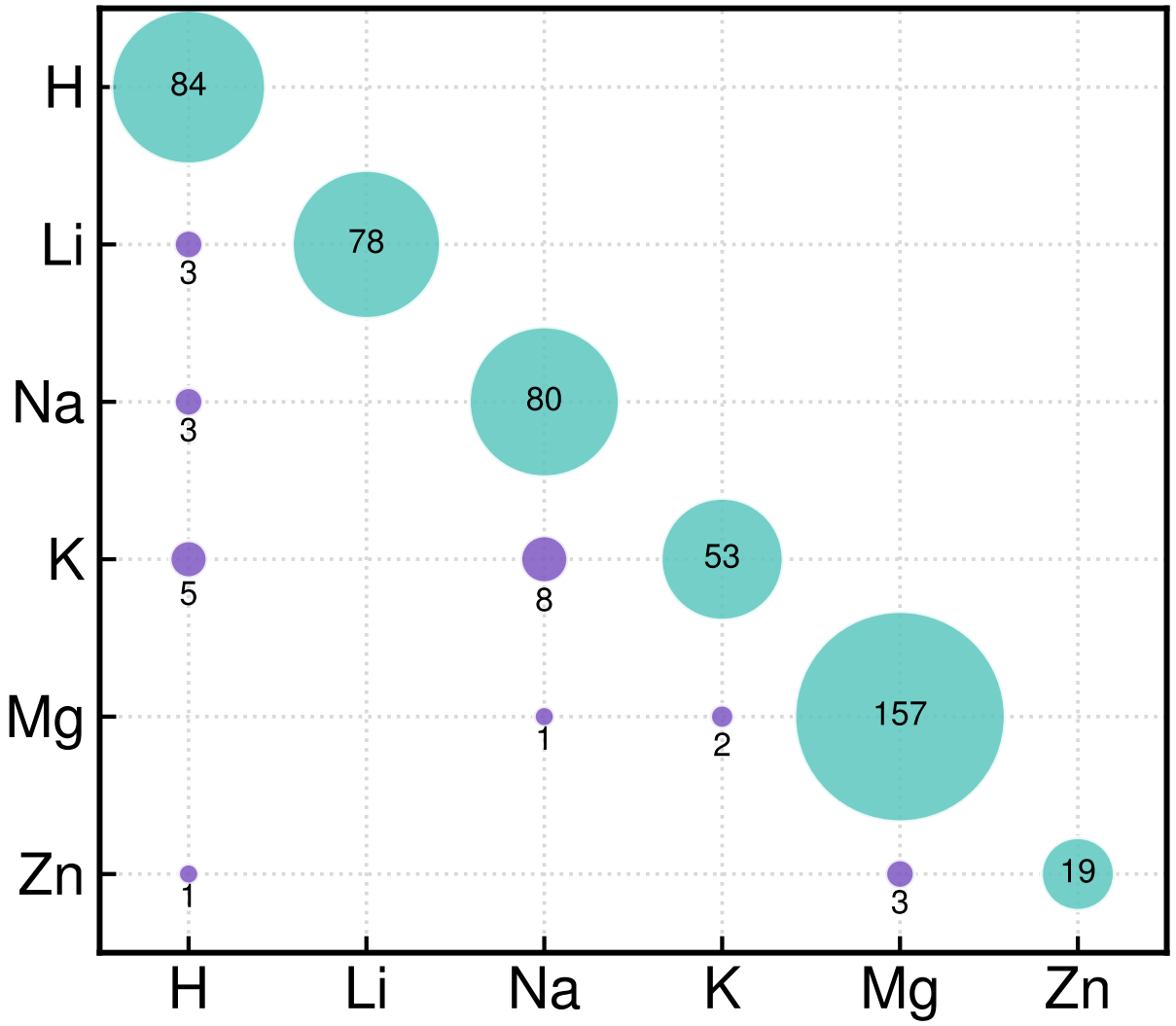
- Fully charged and discharged cathode states are considered
  - The charged state is obtained by removing all Ca from the discharged structure



- For TMs: allowed oxidation-state ranges of +2 to +4 except for V (+2 to +5)
  - Fractional oxidation state is allowed for redox-active TMs
- s- and p-block elements are restricted to integer values



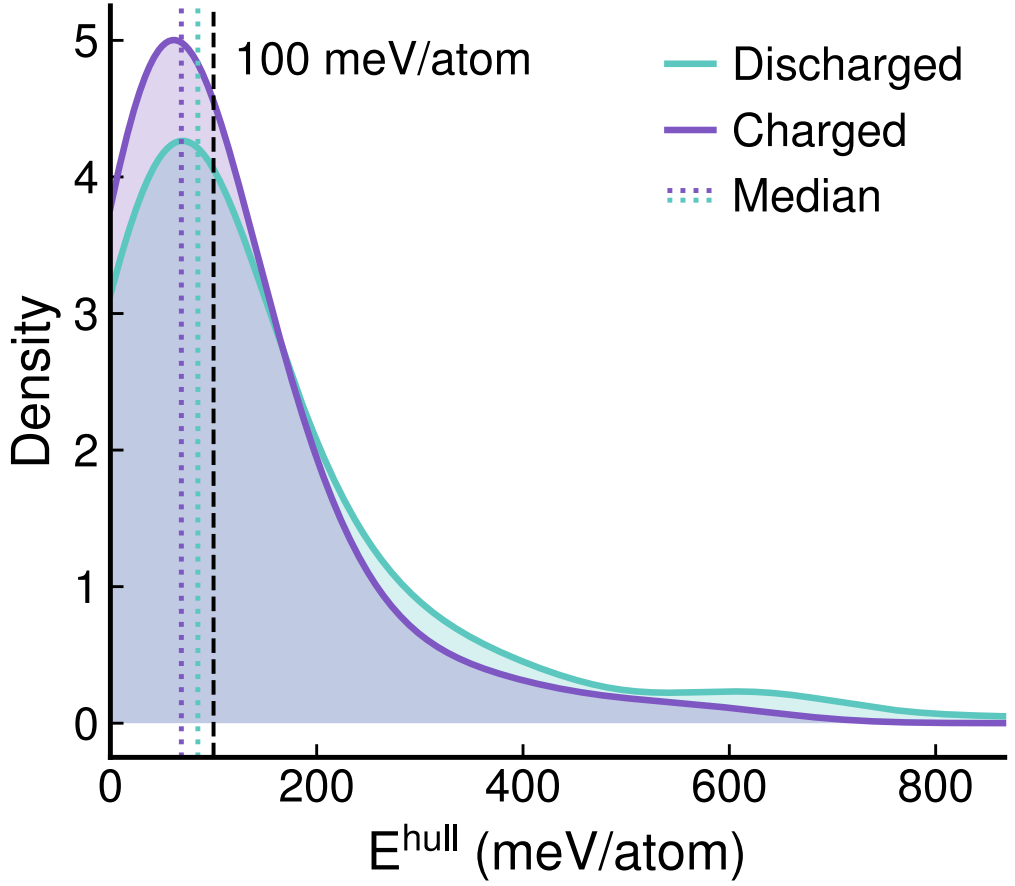
Filtering of mobile-cation compounds: 1,581→1,136

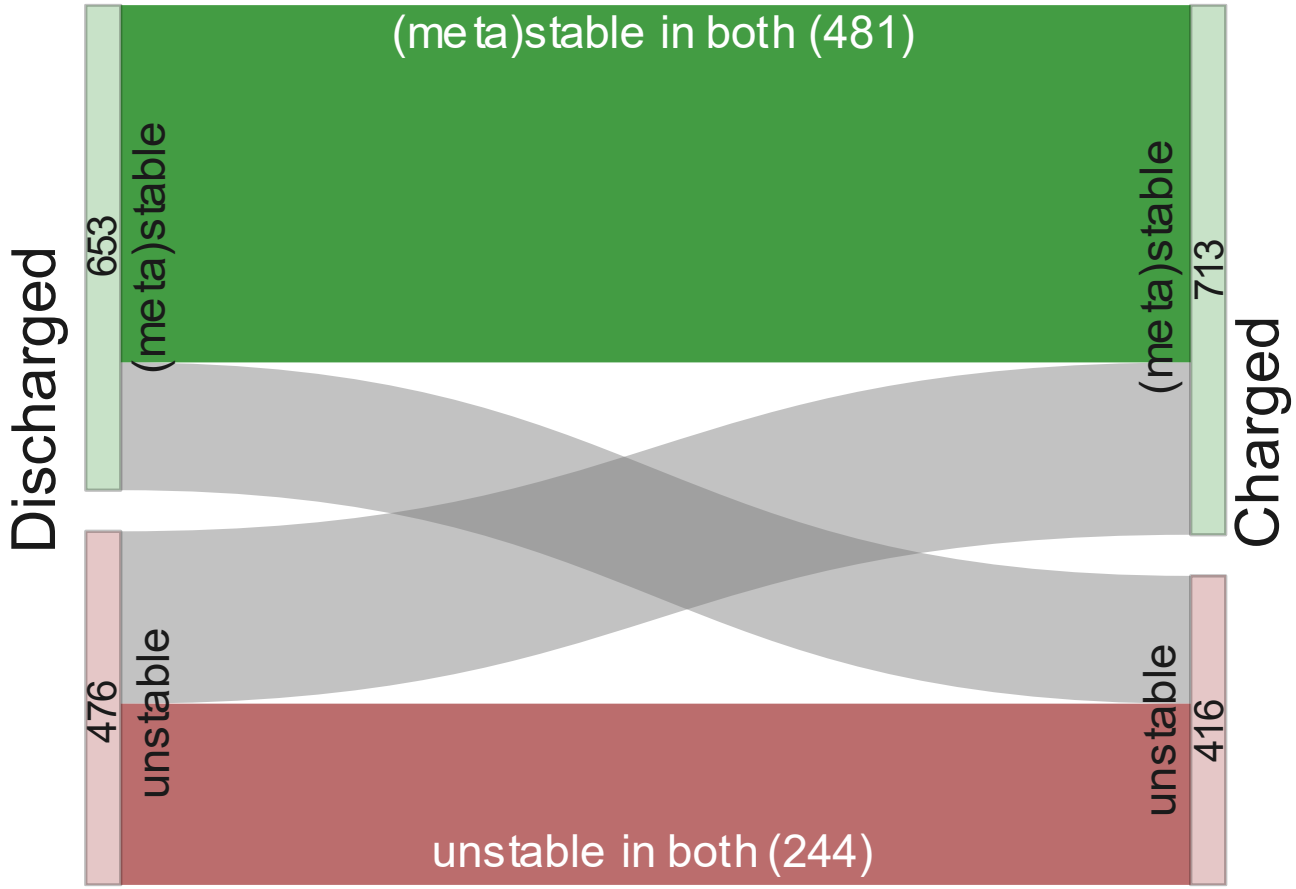


- Excluded 445/1,581 compounds containing additional mobile cations
- Filtered H^+, Li^+, Na^+, K^+, Mg^{2+}, and Zn^{2+} to ensure Ca-only electrochemistry
- Mg-containing compounds account for the largest exclusion
  - Some compounds contain multiple mobile cations (e.g., Na^+ and K^+)—off diagonal bubbles
- Final dataset: 1,136 Ca-only candidate compounds

Thermodynamic (meta)stability: 1,136 → 481

- Relax the geometry using **large-scale MACE-MP-0** (**MACE**) foundational model via ASE
  - Equivariant graph model understood as a MPNN that uses the ACE as the convolution in each layer
  - *pymatgen* is used to calculate **energy above convex hull** (E^{hull}) against competing phases from the MP





ACE==atomic cluster expansion; MACE==multi-atomic cluster expansion; MPNN==message passing neural network; ASE = Atomistic Simulation Environment

Drautz, **Phys. Rev. B**, 99, 014104 (2019)

Batatia *et al.*, **Nat. Mach. Intell.** 7, 56–67 (2025)

Sun et al. **Sci. Adv.** 2, e1600225 (2016)

Thermodynamic (meta)stability: 1,136 → 481

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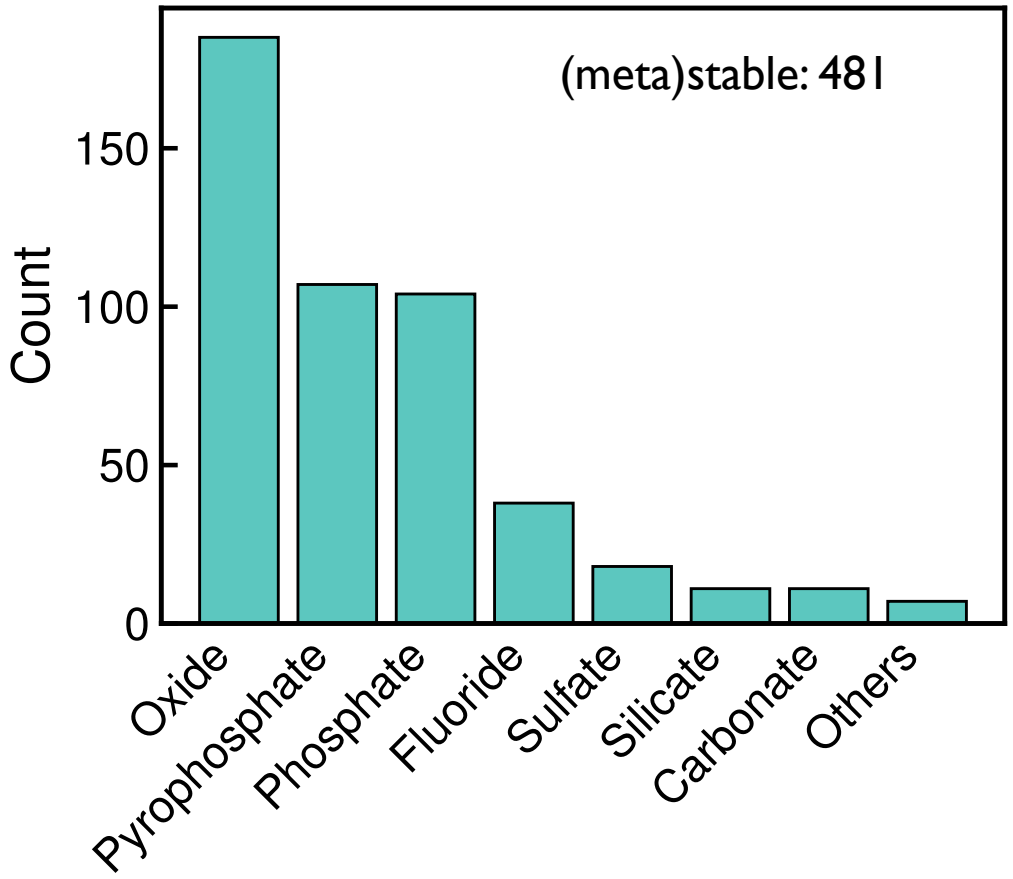
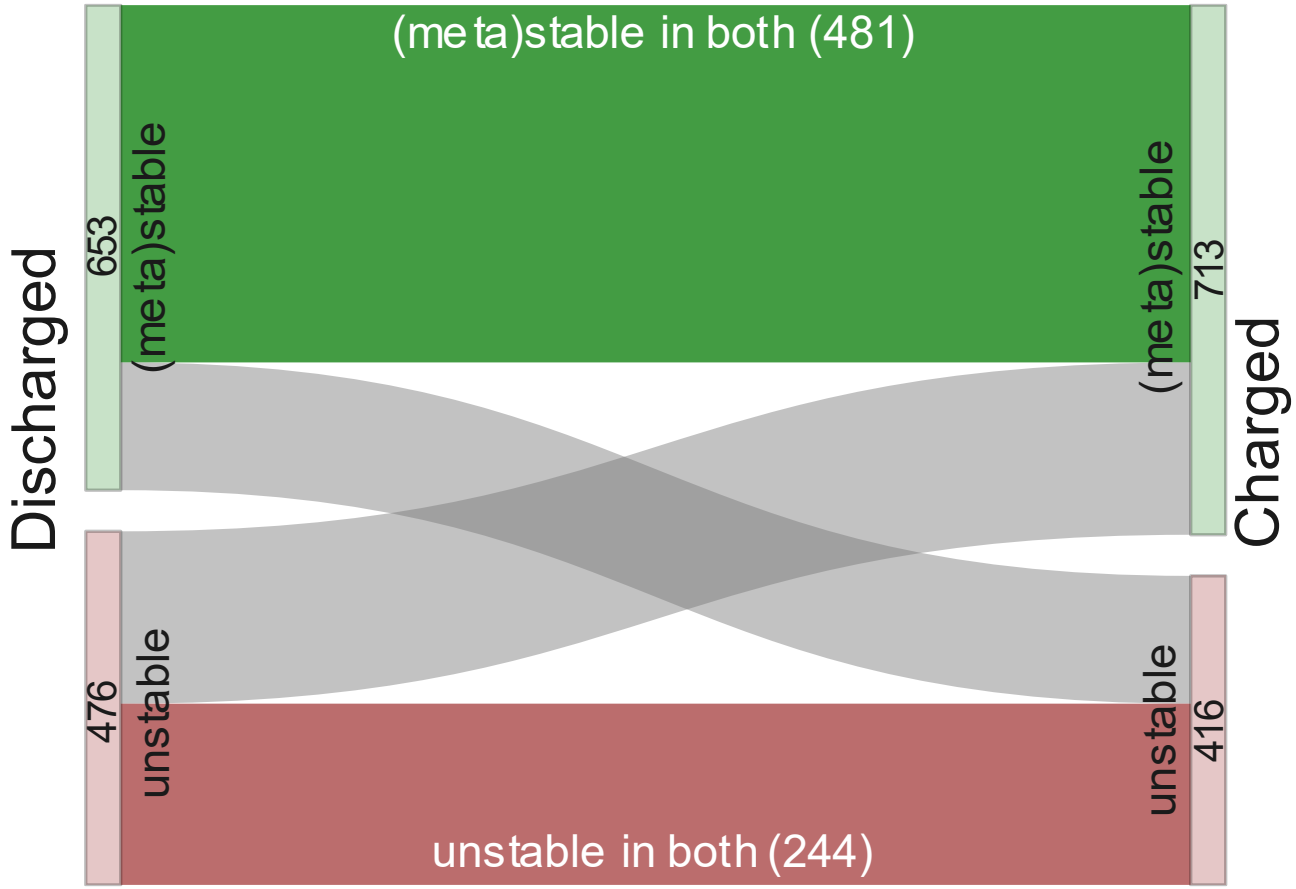
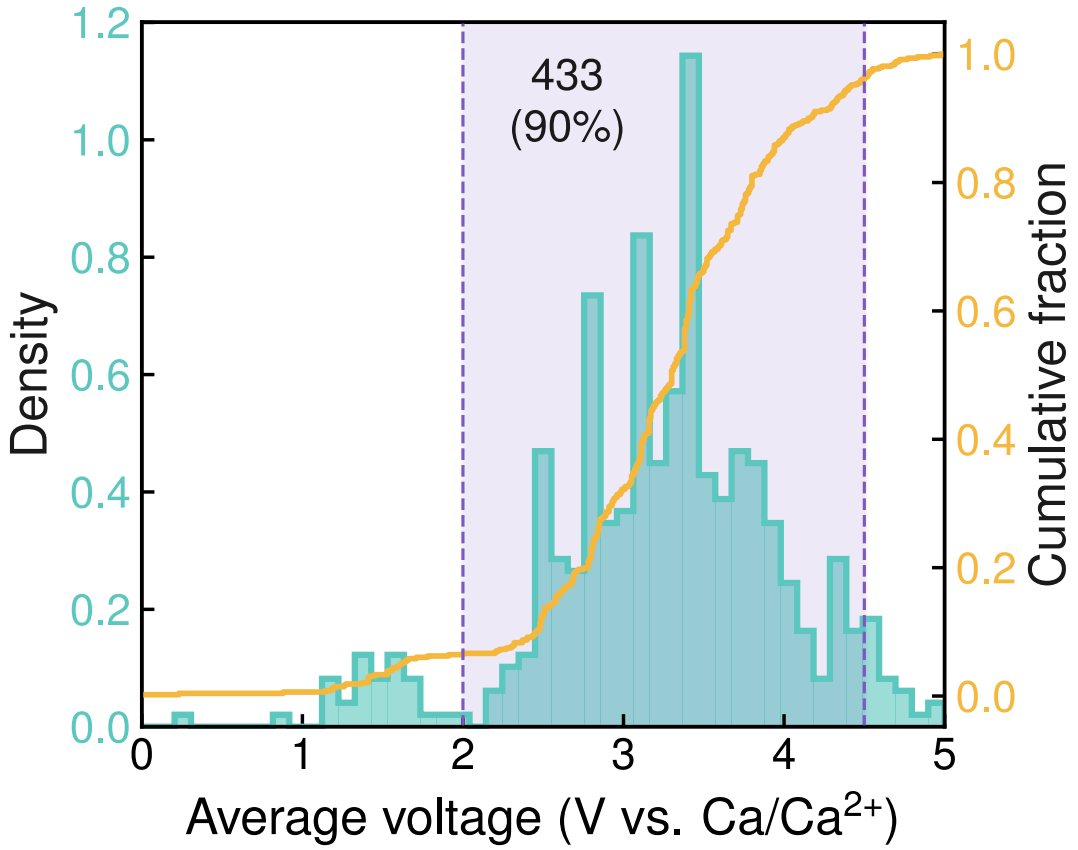




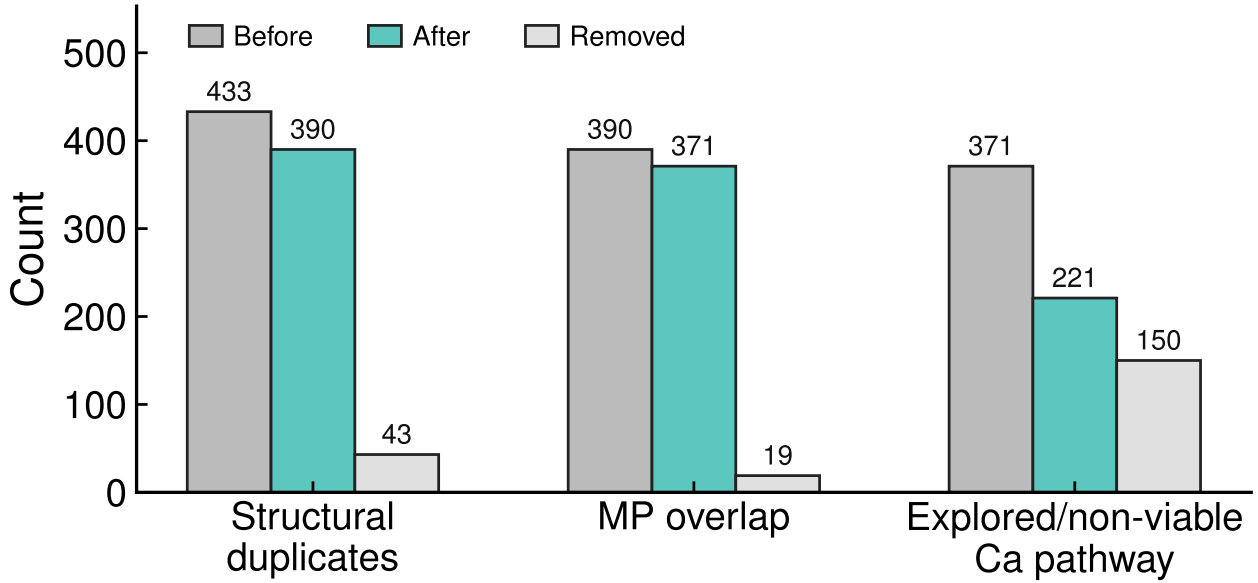
ACE==atomic cluster expansion; MACE==multi-atomic cluster expansion; MPNN==message passing neural network; ASE = Atomistic Simulation Environment

Average voltage & data curation: 481 → 433 → 221

- Average intercalation voltage calculated via Nernst equation using calculated MACE energy
  - 2.0–4.5 V a practical operating voltage window criterion



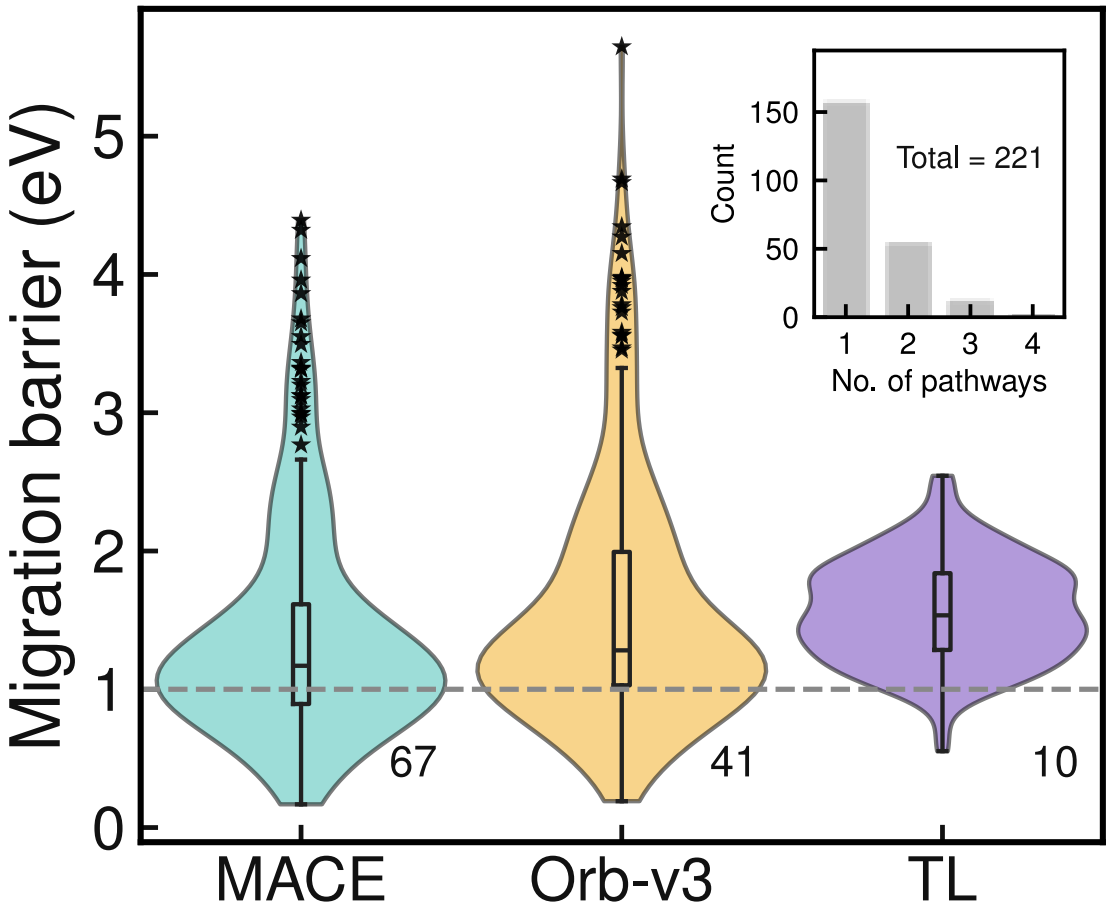
- Data curation before Ca-mobility analysis
  - Structural duplicates,
  - Previously explored compositions, and
  - Structures with non-viable Ca migration pathways

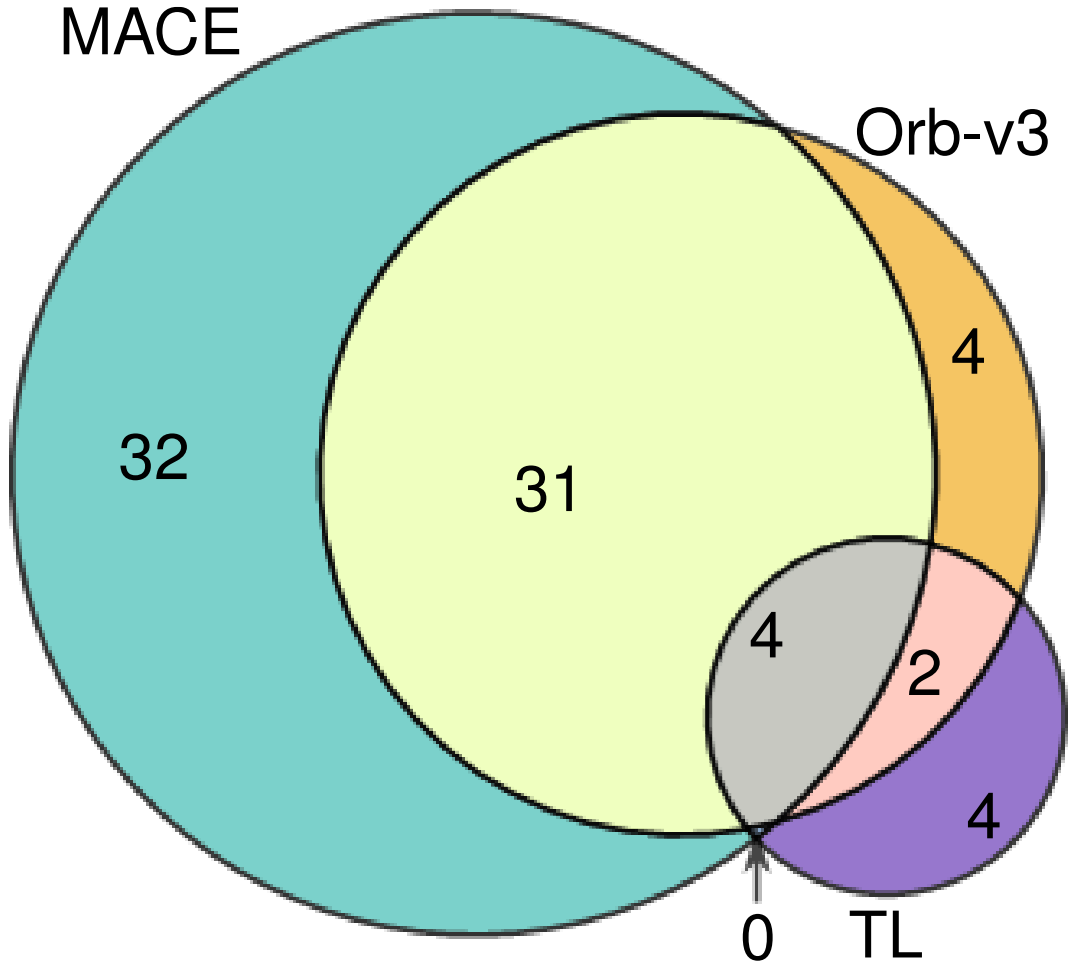


Distilled to **221** candidates for further Ca-mobility evaluation

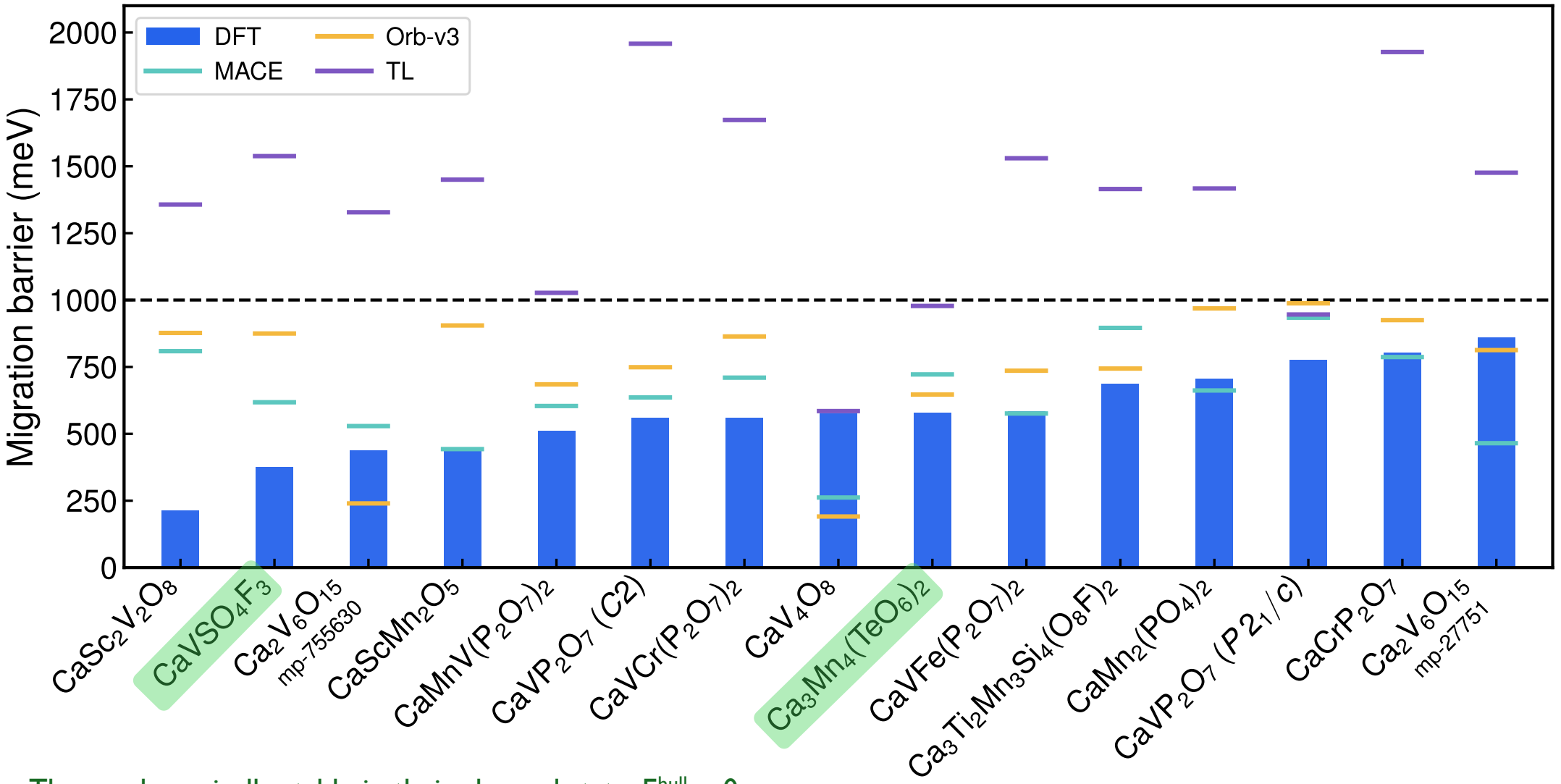
Ca mobility via 'ensemble' of ML: 221 → 37

- Ca^{2+} migration barriers were evaluated using NEB calculations with:
  - MACE, Orb-v3 and ALIGNN based transfer learning property predictor model (TL)
- Ensemble agreement used to identify robust low-barrier candidates





DFT-NEB validation: all results are within 1eV tolerance



MAE in meV:

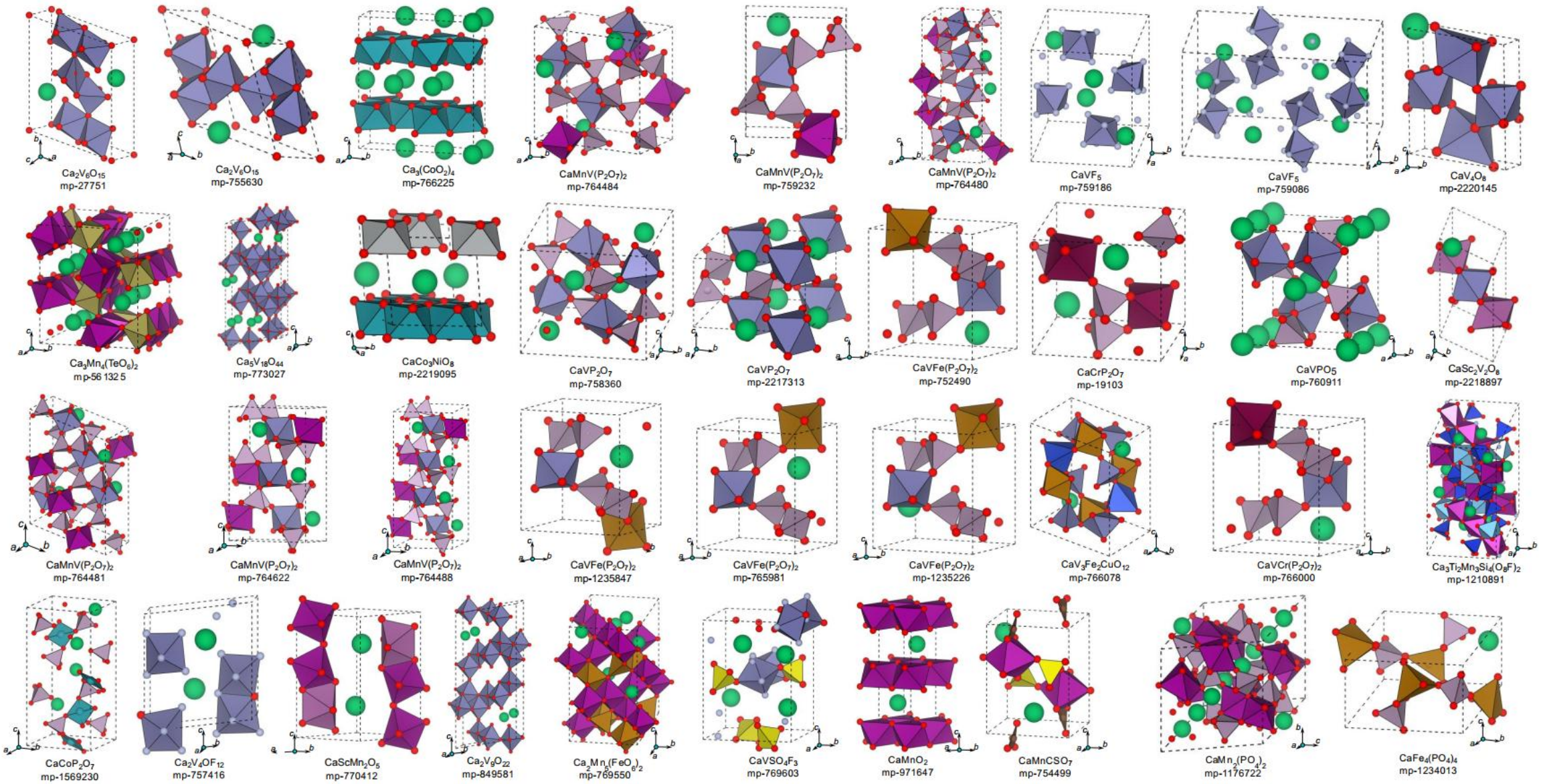
- MACE: 161
- Orb-v3: 273
- TL: 671

Thermodynamically stable in their charged state: $E^{hull} = 0$

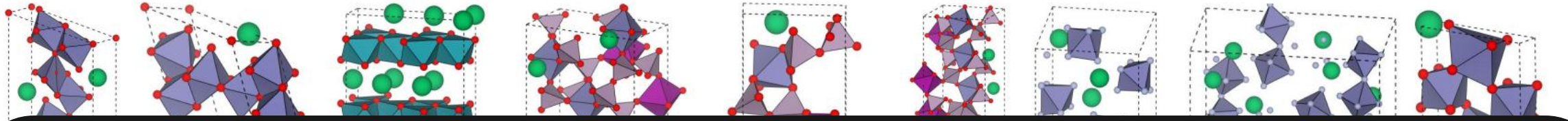
- With discharged phase being metastable

MAE==mean absolute error

Final candidate structures: 37 promising Ca-cathodes

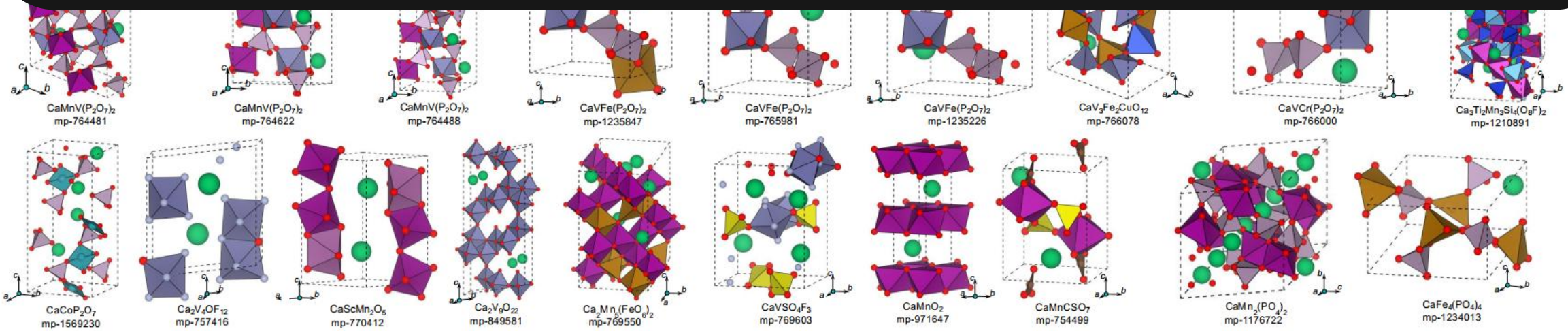


Final candidate structures: 37 promising Ca-cathodes



- Accelerated the search using a **geometry-based** design strategy and **foundational ML** models across **~52,946** MP structures
  - Found **37** new promising Ca-cathodes: validated with DFT-NEB calculation
  - **$CaSc_2V_2O_8$** and **$CaVSO_4F_3$** exhibiting lowest DFT E_m

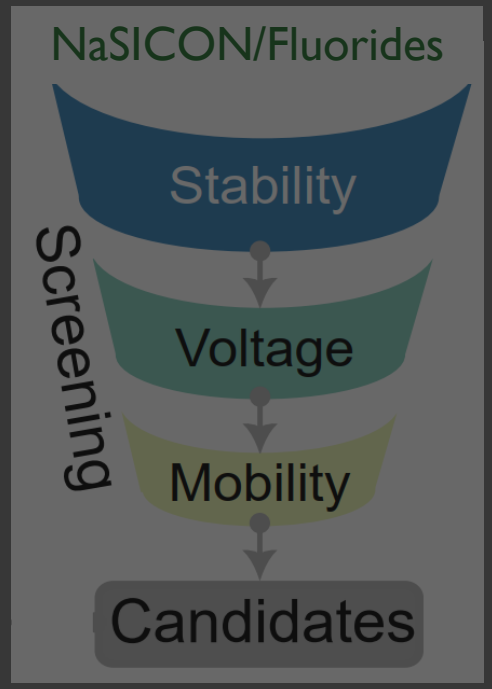
D. B. Tekliye, A. K. Bheemaguli and G. Sai Gautam, "Geometry-based Discovery of Calcium Battery Cathodes Accelerated by Foundational Machine-Learned Models," arXiv:2605.29029v1 *(under review, npj Computational Materials)*, 2026



Ca-cathode design space: from DFT to ML

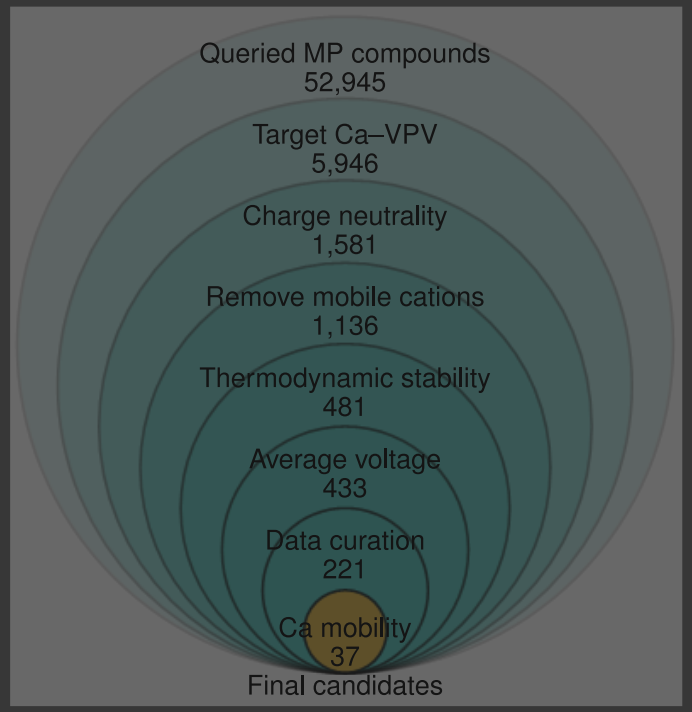
DFT-based high-throughput exploration

NaSICON and Fluoride frameworks



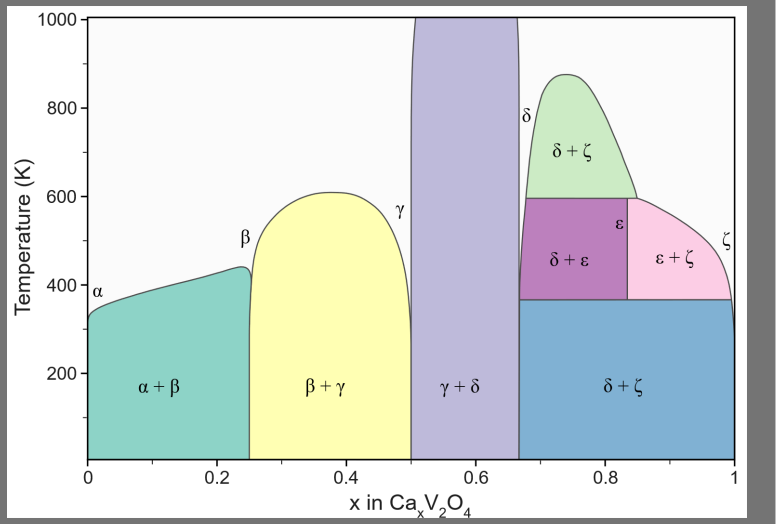
MLIP-accelerated high-throughput screening

Explore entire Materials Project structures



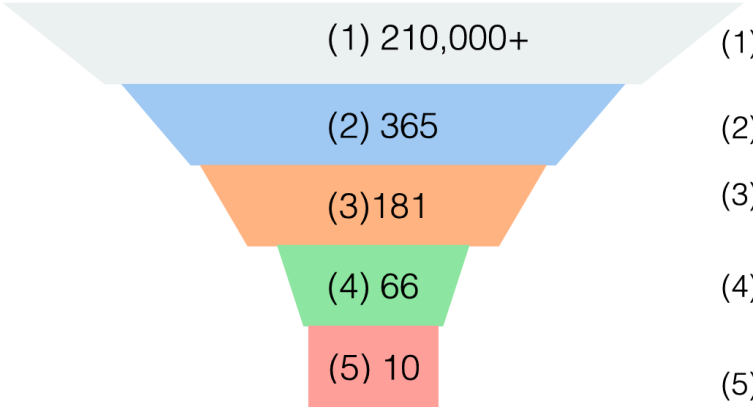
Deep dive into understanding Ca-cathode

Post-spinel CaV_2O_4



DFT == density functional theory ML==machine learning MLIP == machine learned interatomic potential

Post-spinel CaV_2O_4 as calcium battery cathodes



(1) Compounds in ICSD

(2) Ternary $Ca_iM_jZ_k$

(3) $Ca_iTM_jZ_k$ without undesired elements & polyanions

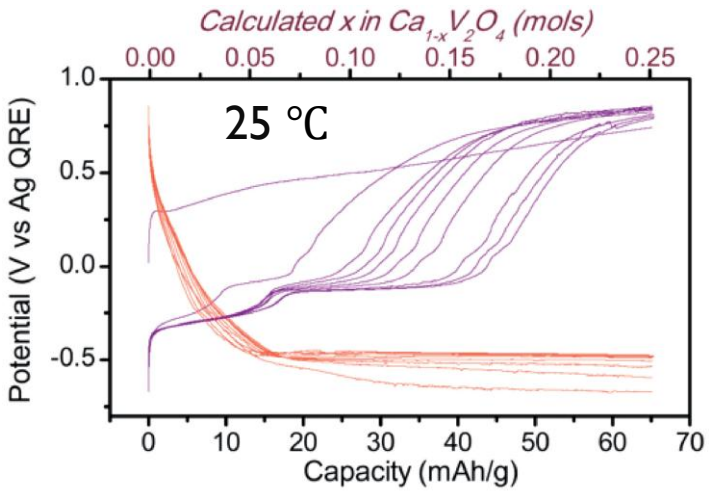
(4) Ca_iTM_jZk polymorph matched by charged TM_jZ_k

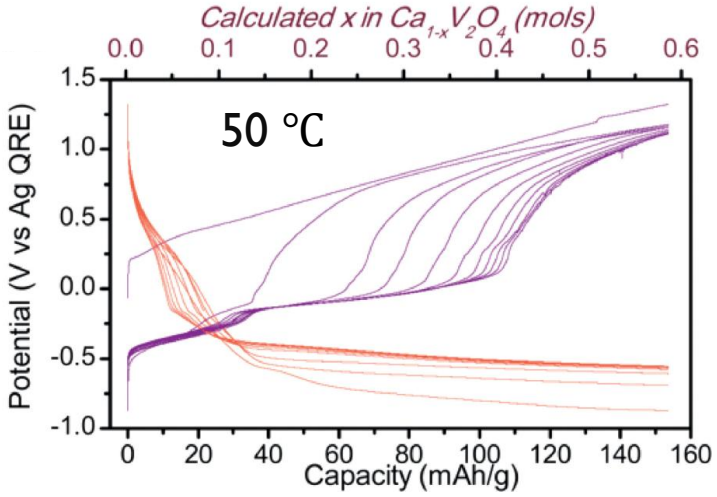
(5) Stable $Ca_iTM_jZ_k$ selected

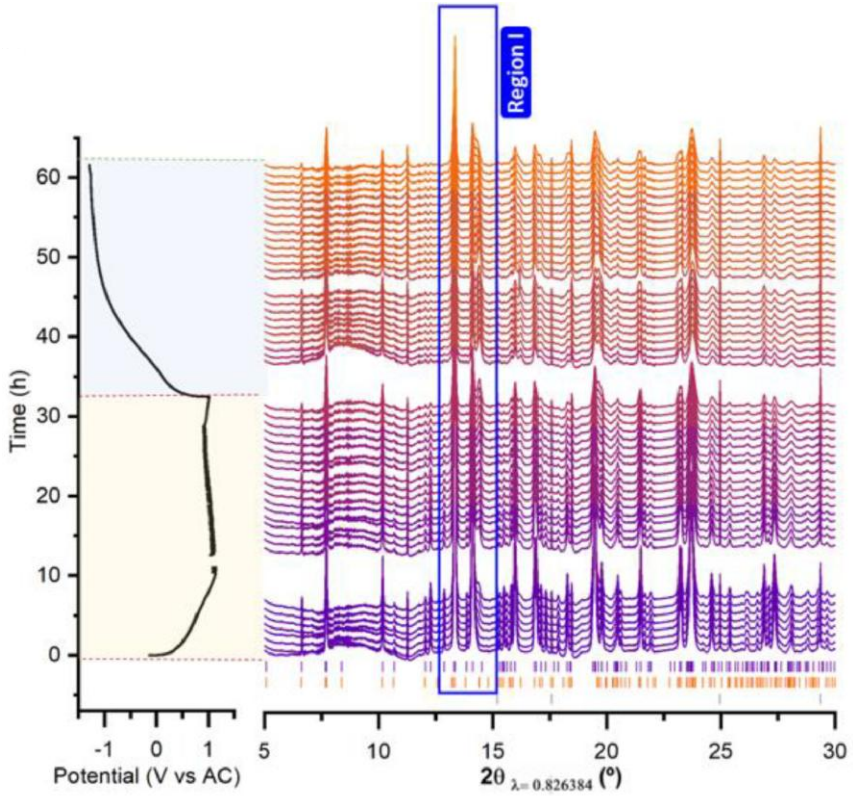
2

CaV_2O_4, $CaNb_2O_4$

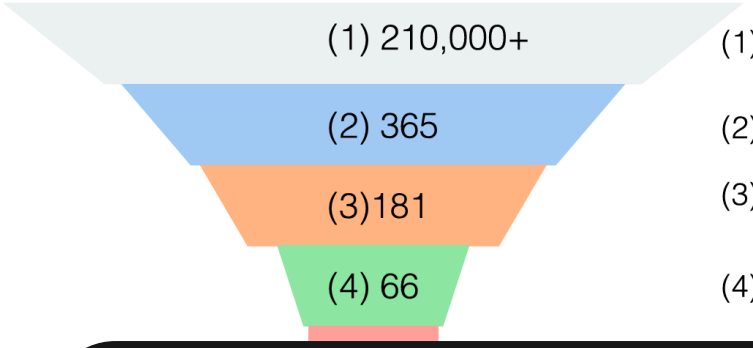
- Reversible Ca^{2+} extraction demonstrated in CaV_2O_4
- Full Ca extraction corresponds to capacity of ~288 mAh/g
- Discrepancy between operando XRD (~0.3 Ca) and electrochemical (~0.6 Ca at 50 °C) observations







Post-spinel CaV_2O_4 as calcium battery cathodes



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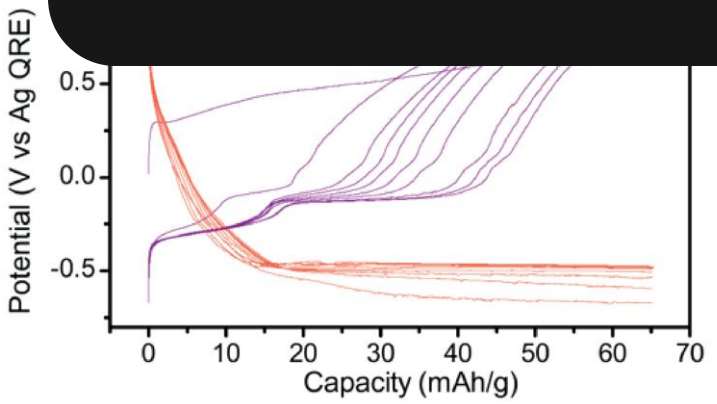
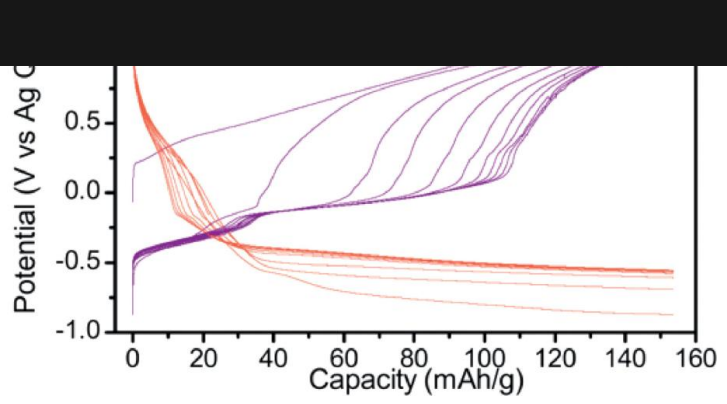
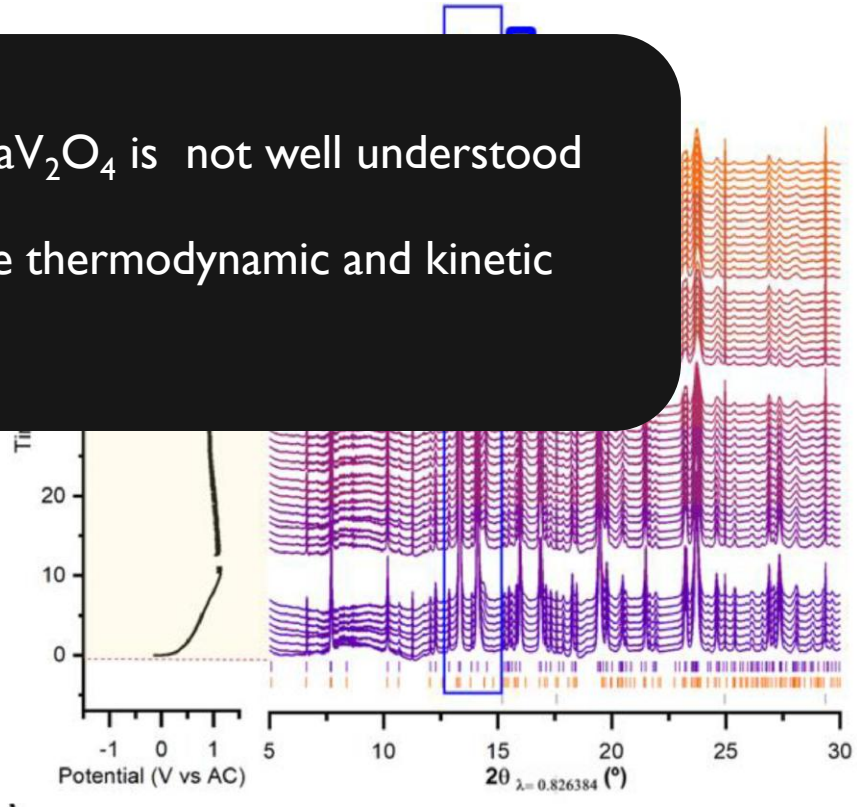
- Discrepancy between operando XRD (~0.3 Ca) and electrochemical (~0.6 Ca at 50 °C) observations

- The redox mechanism and observed electrochemical capacity limit in CaV_2O_4 is not well understood
  - Role of phase stability and Ca mobility may provide insight into the thermodynamic and kinetic constraints limiting full Ca extraction







Lu et al. **Chem. Mater.** 33, 5809–5821 (2021)

Black et al. **Energy Storage Mater.** 47, 354–364 (2022)

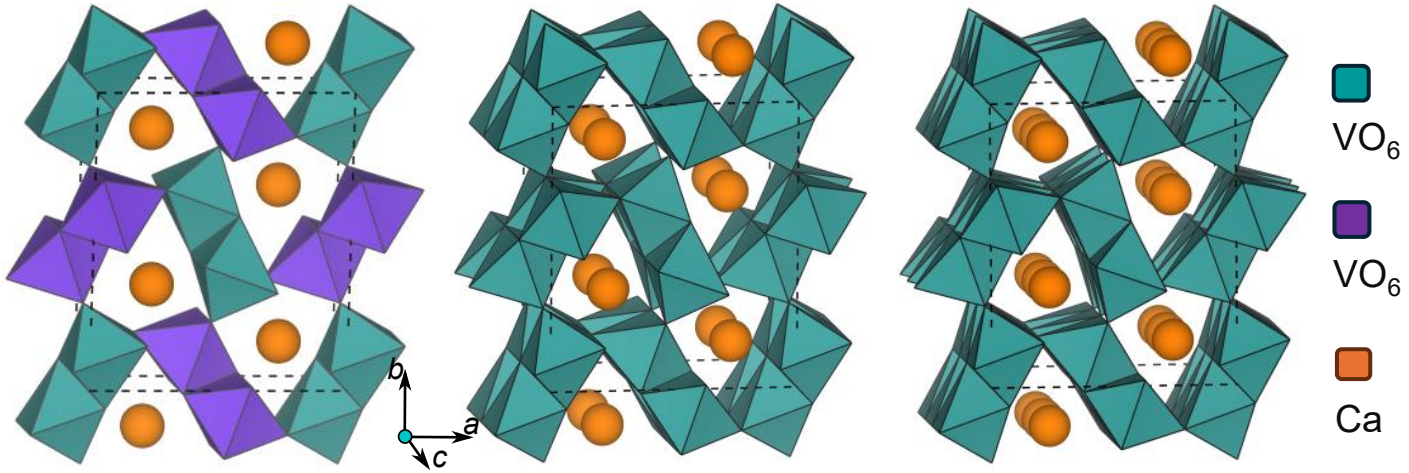
Cluster expansion + Monte Carlo: understanding the capacity limit in CaV_2O_4

- DFT alone misses high temperature entropic behaviour
- **Grand Canonical Monte Carlo (GCMC)** simulation samples configuration via statistical mechanics

$$F = -k_b T ln(Z), \qquad Z = \sum_{\vec{\sigma}} \exp(-\frac{E(\vec{\sigma}) - x\mu}{k_b T})$$

- **Cluster expansion(CE)** approximates the energetics with fast ML-fitted effective Hamiltonian

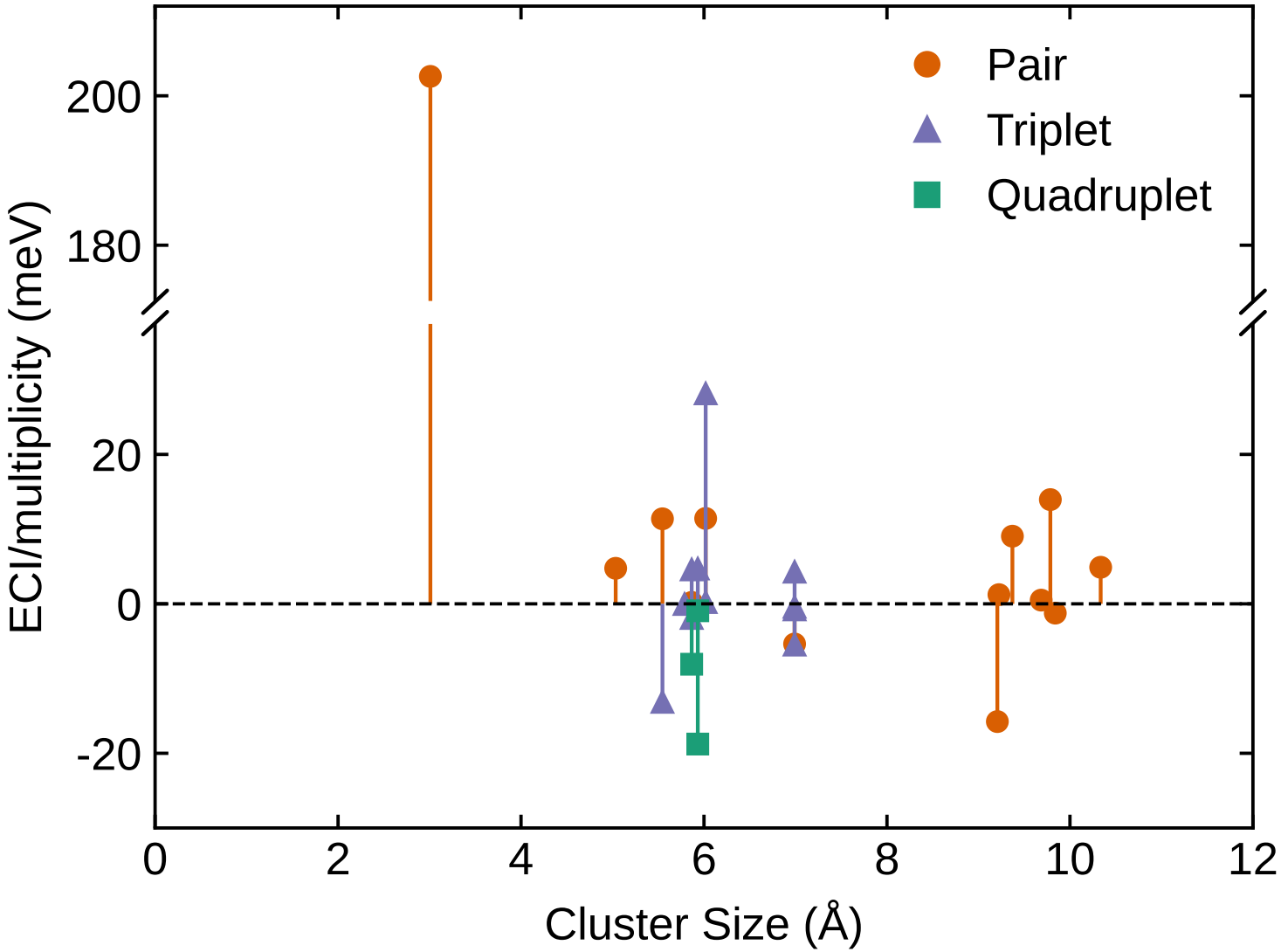
$$E(\vec{\sigma}) = V_0 + \sum_{\alpha} m_\alpha V_\alpha \langle \Phi_\alpha(\vec{\sigma}) \rangle_\alpha$$



- $1 \times 1 \times 1,\ 1 \times 1 \times 2,\ 1 \times 1 \times 3$ supercell of the conventional cell (4 f.u.) is used to generate training sets
  - **287** configurations across 17 composition were enumerated with *pymatgen*
  - Geometry is relaxed using DFT (SCAN+*U*)

Sanchez, **Phys. Rev. B,** 81, 224202 (2010)

Cluster expansion fit to 265 DFT training data



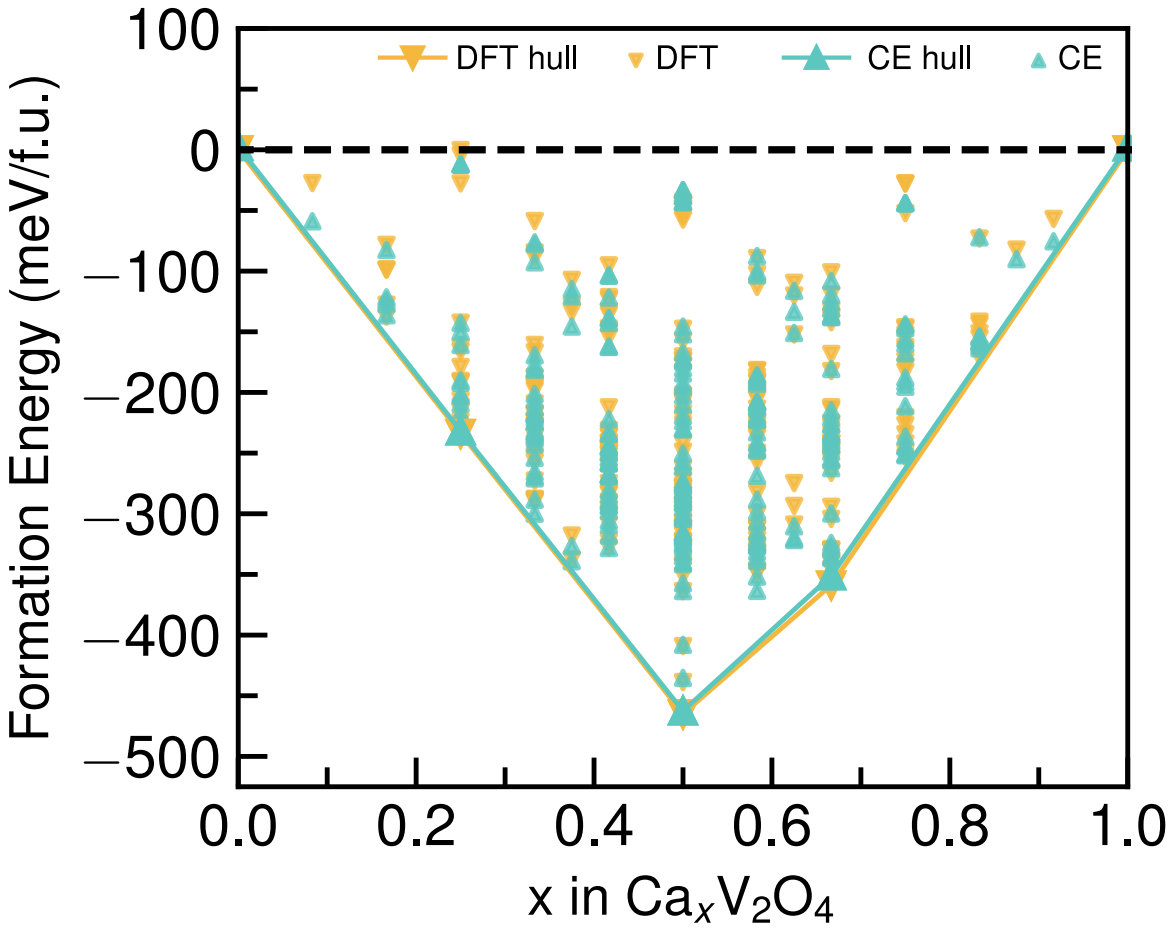
- **Training DFT data:** 265 symmetry-constrained configurations selected via CASM
- **CE fit settings:**
  - Cluster radii: Pairs (10.6 Å), Triplets (7.0 Å), Quadruplets (6.0 Å)
  - Basis functions: Chebyshev polynomials
  - Regression: LASSO ($\alpha = 10^{-4}$)
  - Validation: LOOCV score
- Fitted CE model: 29 effective cluster interactions (ECI) fitted to DFT datasets
- Pair clusters predominantly contributed to ECIs
  - The ECI strength should decrease with the order of the cluster
- Accuracy of the CE fit against DFT dataset:
  - **RMSE = 13.4 meV/f.u**
  - **CV score = 15.7 meV/f.u**

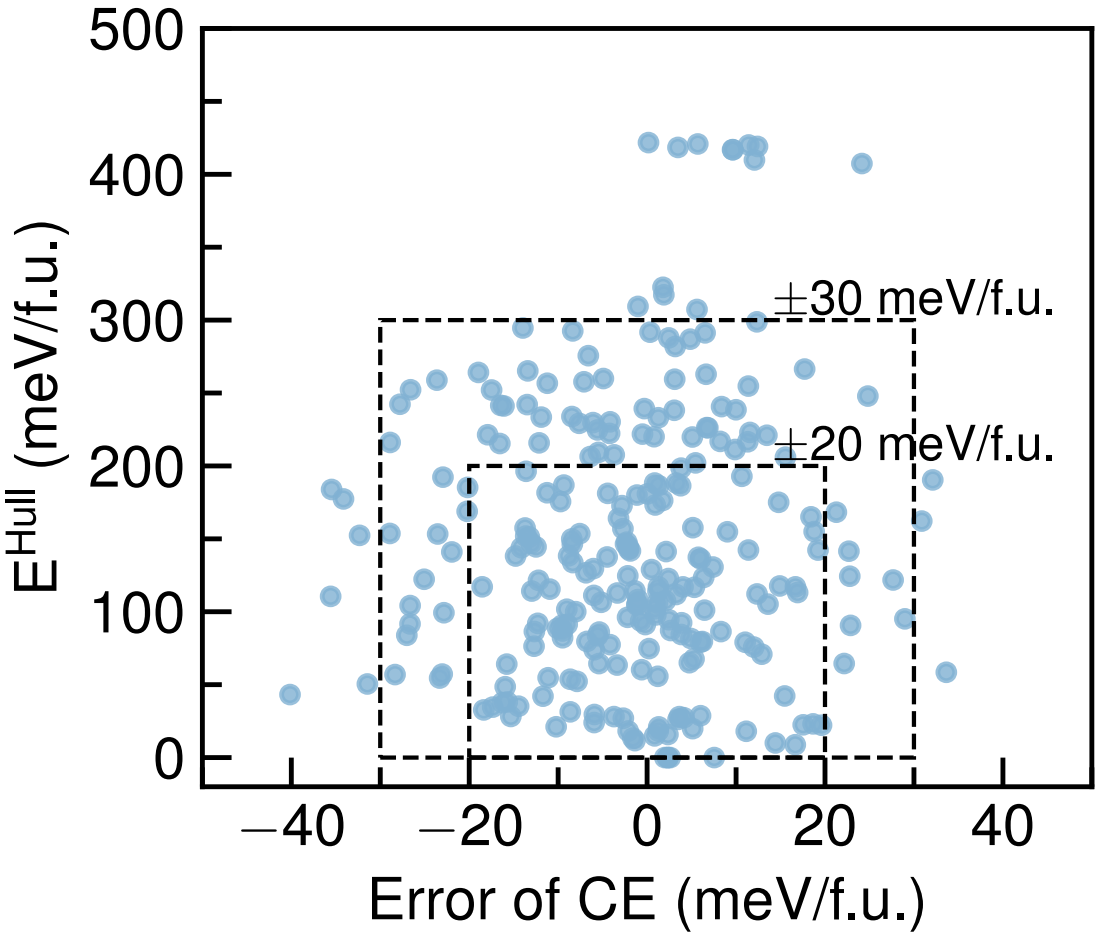
CASM==cluster approach to statistical mechanics LASSO==least absolute shrinkage and selection operator

LOOCV==leave one out cross-validation
RMSE==root mean square error

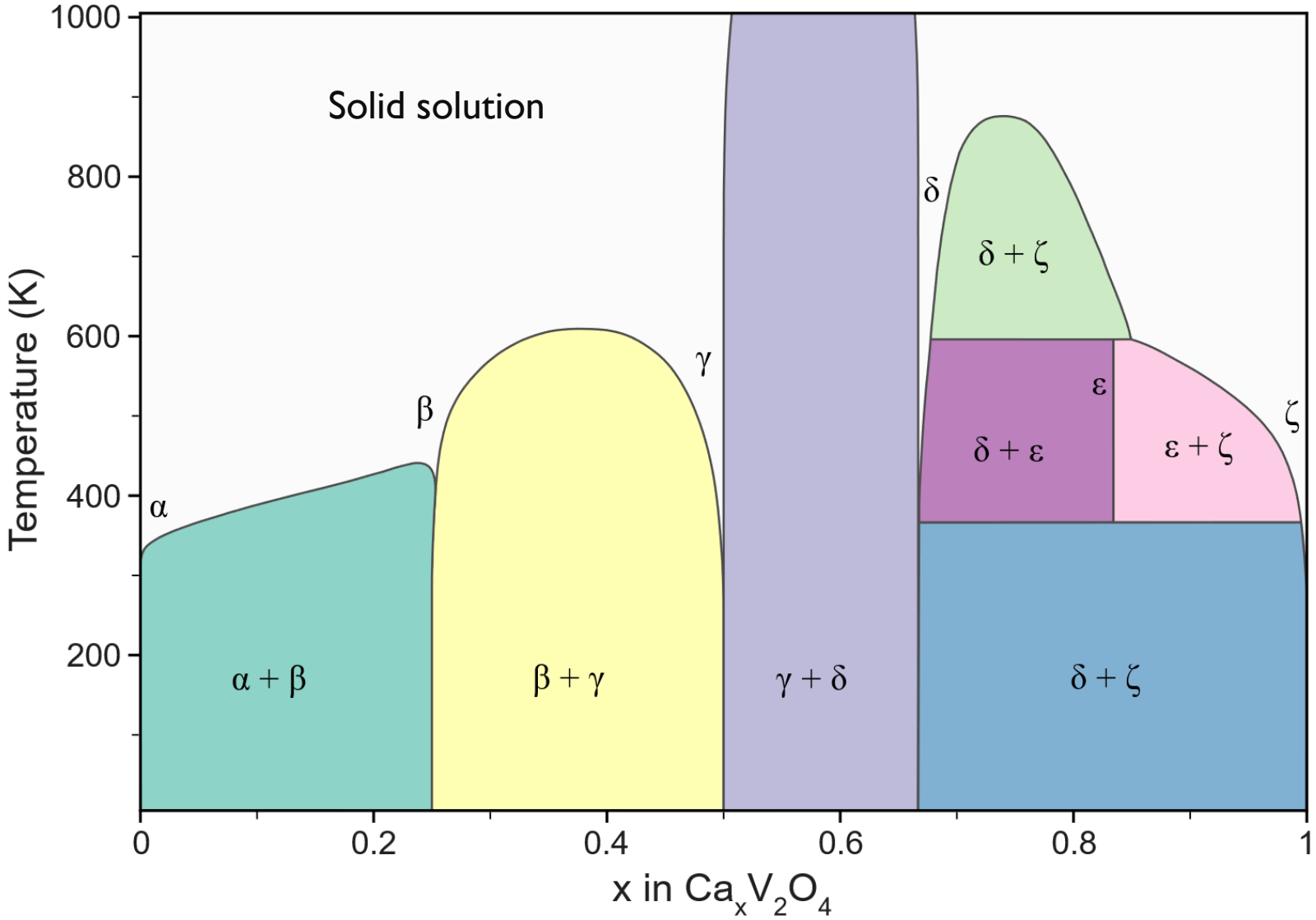
CE convex hull is in good agreement with DFT

- **Validation:** ensured accurate ground state predictions on the convex hull
  - CE accurately predicted five 0 K DFT ground state structures, at x = 0, 0.25, 0.5, 0.67, 1.0 in $Ca_xV_2O_4$





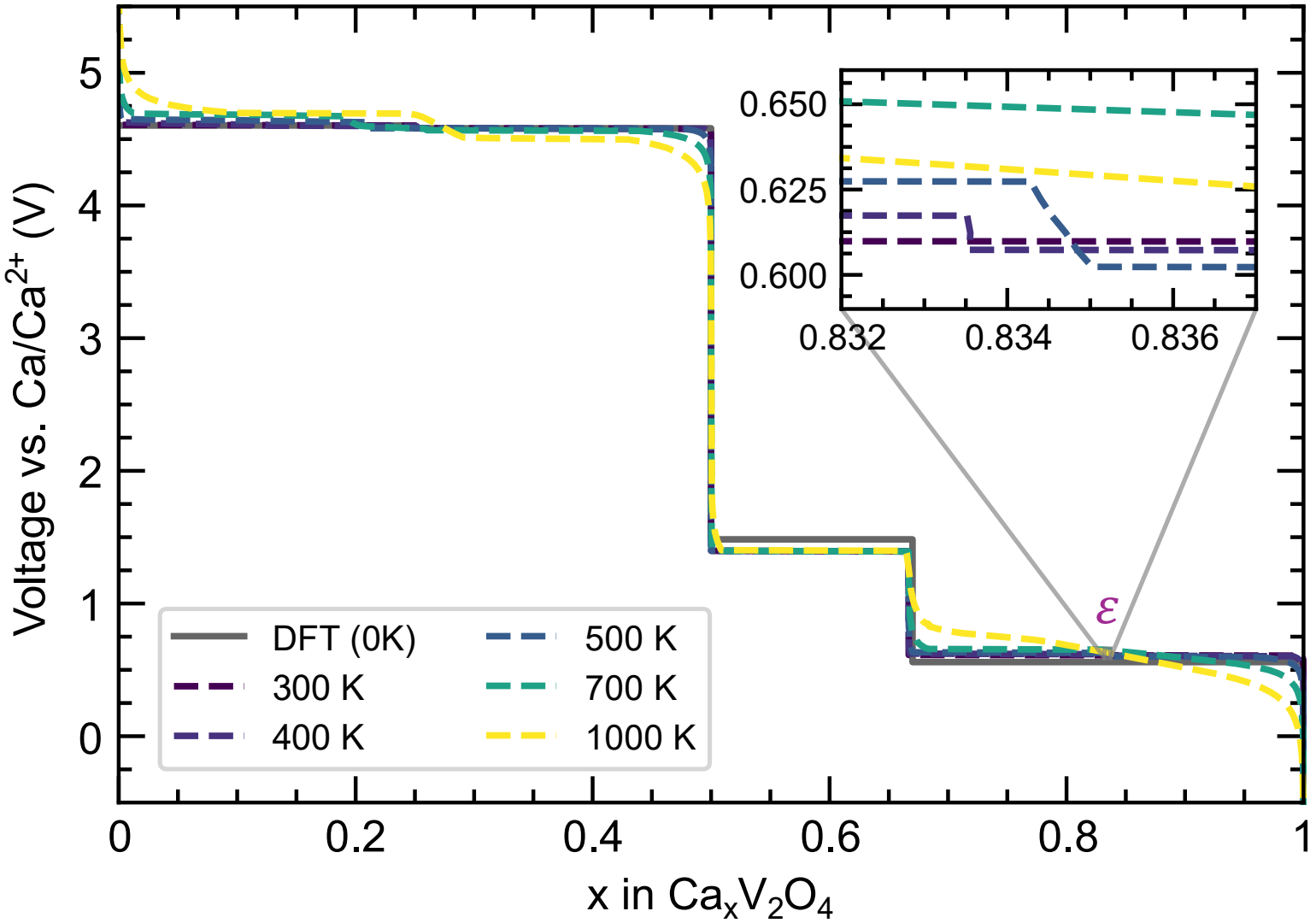
Finite-temperature phase behavior explains the electrochemical performance of CaV_2O_4



- Resolved six stable phases governing finite-temperature Ca (de)intercalation in $Ca_xV_2O_4$
- Improved high-temperature electrochemical performance through enhanced Ca/vacancy solubility
- Identified strong Ca–vacancy ordering in the γ (x=0.5) phase as a key thermodynamic driving force
  - High-temperature ε phase stabilized at x ≈ 0.83

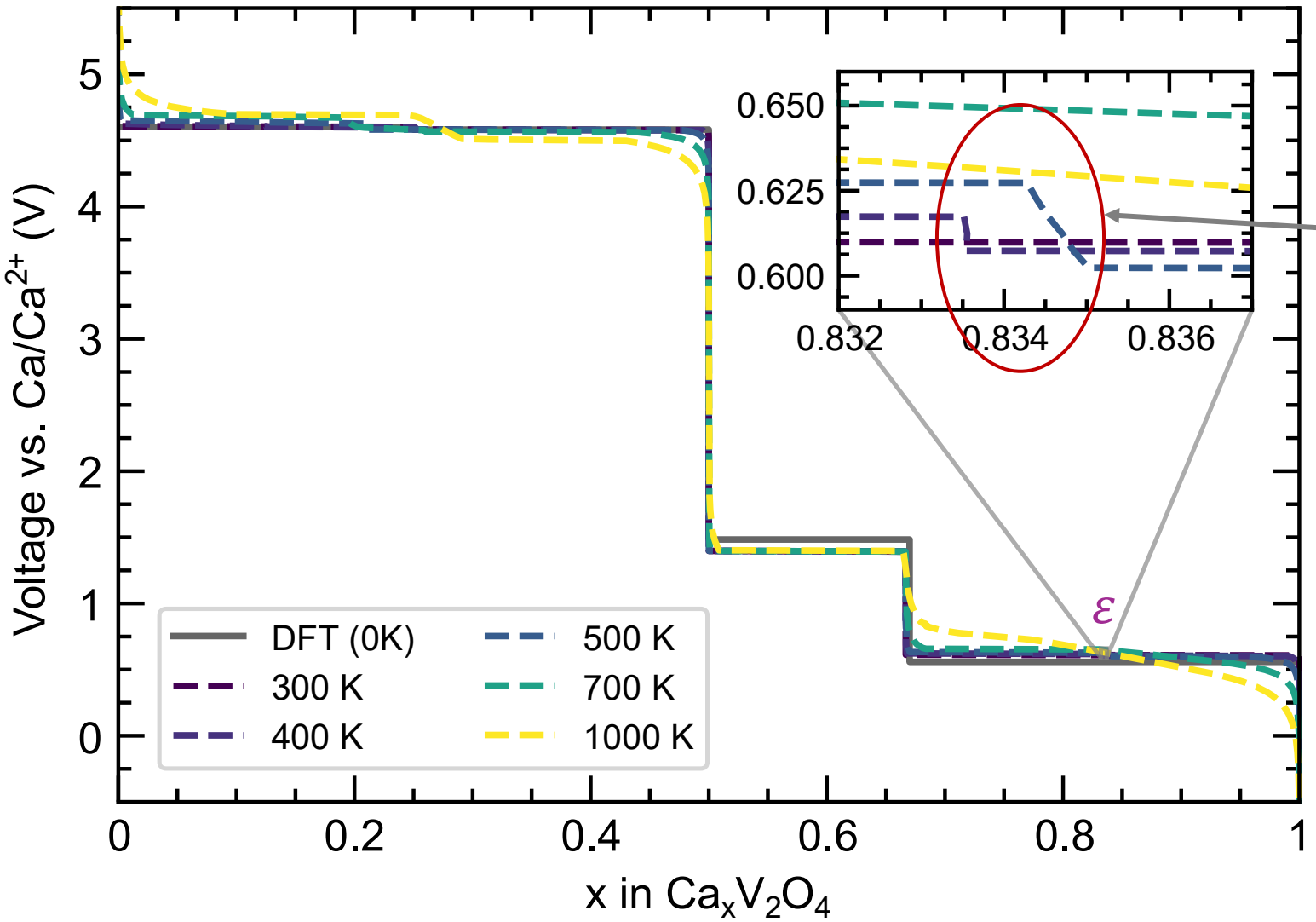
GCMC: 12 × 12 × 12 supercells(≥41,472 atoms); T: 5–1005 K(ΔT = 5 K); μ: −7–7 eV(Δμ = 0.01 eV); free-energy integration for hysteresis correction

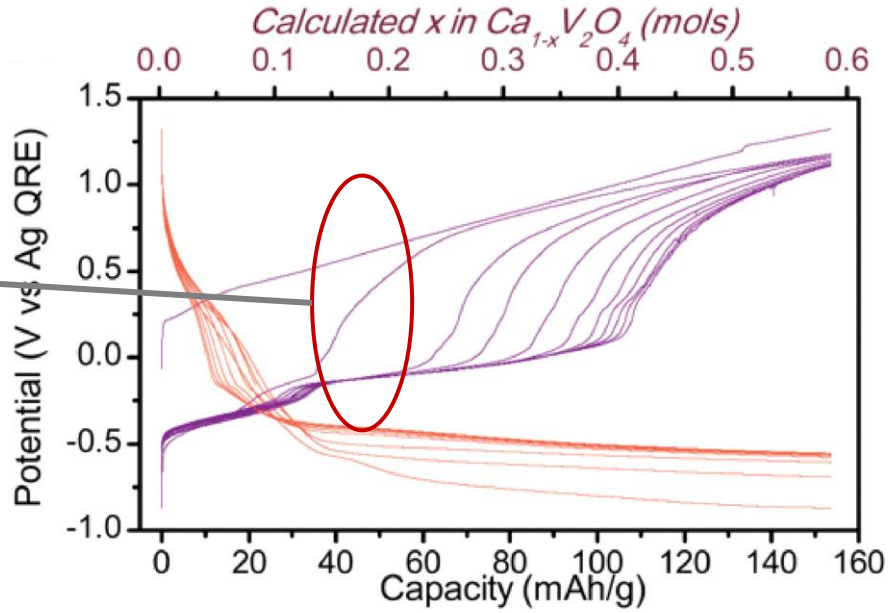
Voltage profile from GCMC compared to 0 K DFT



- 0 K DFT and 300 K GCMC profile exhibit three distinct voltage steps at x = 0.25 (β), x = 0.5(γ), and x = 0.67 (δ)
- Four well-defined voltage plateaus are observed, representing the two-phase coexistence regions
- Additional voltage step is observed at 400 K and 500 K, corresponding to the new single-phase x = 0.83 (ε)
- At 1000 K the voltage profile evolves from sharp, discrete steps into a smoother series of plateau

Voltage profile from GCMC compared to 0 K DFT





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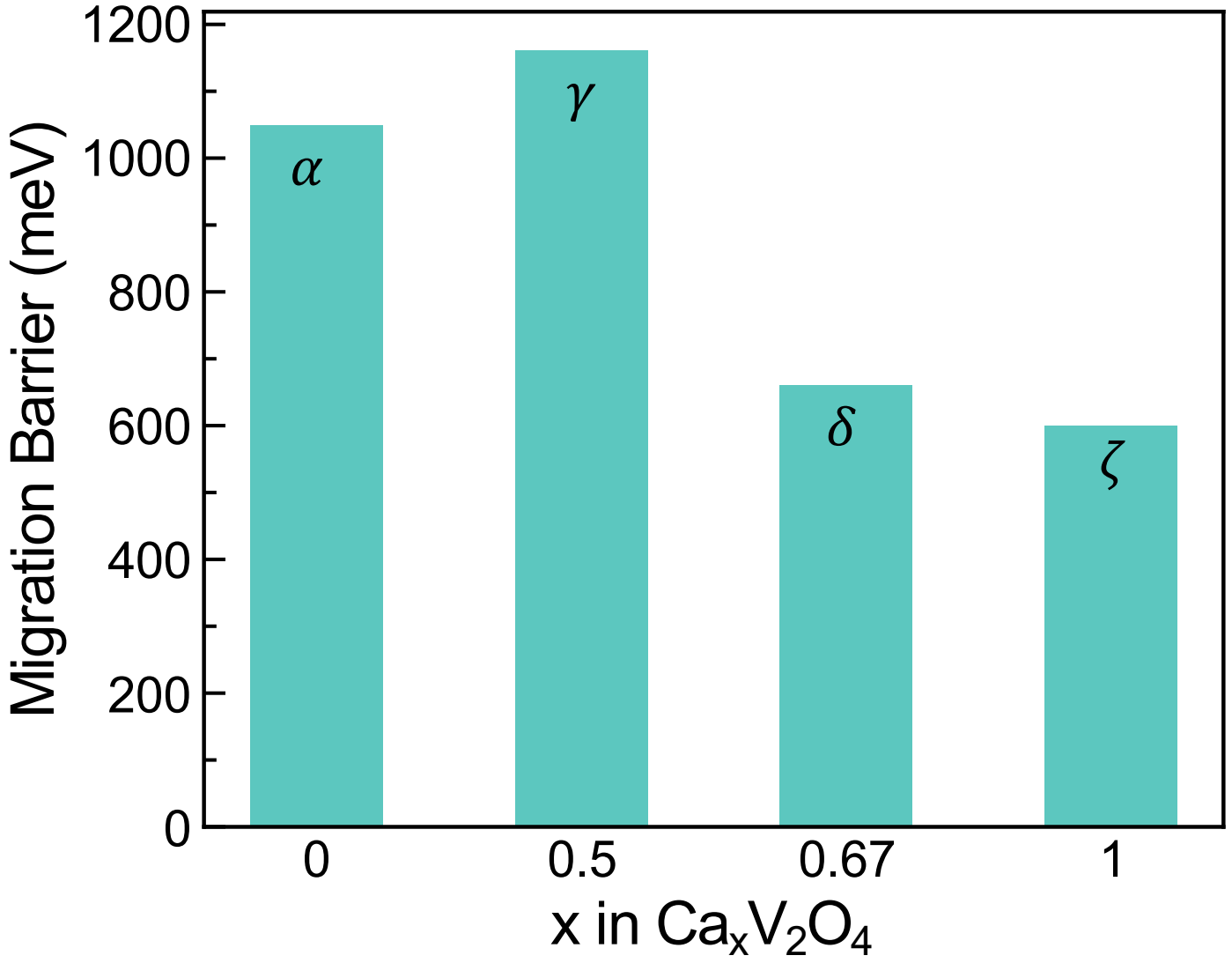
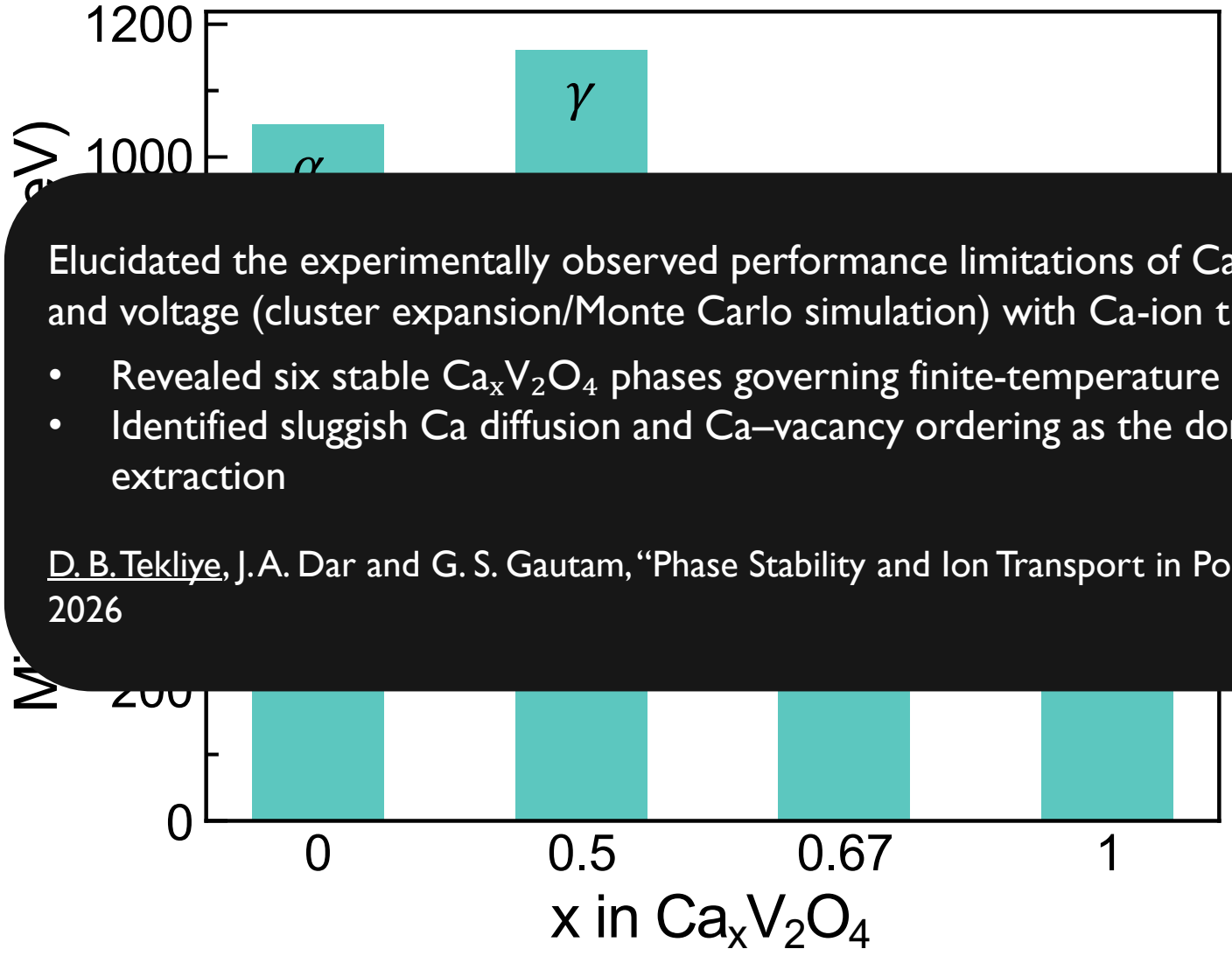
Migration barrier at single phase compositions



- Migration barrier(E_m) is calculated via DFT-based NEB using GGA
  - Ca-rich end exhibits lower E_m: x = 0.67 and 1.0
  - Ca-poor end exhibit higher E_m: x = 0 and 0.5
- High E_m at 0.5 mole of Ca, acting as bottleneck by restricting further extraction
  - Facile Ca deintercalation is limited at x= 0.5 (γ phase)
- This directly explains the limited electrochemical capacity observed in experiments

Migration barrier at single phase compositions



- Migration barrier(E_m) is calculated via DFT-based NEB using GGA

Elucidated the experimentally observed performance limitations of CaV_2O_4 by combining finite-temperature phase stability and voltage (cluster expansion/Monte Carlo simulation) with Ca-ion transport (DFT-NEB)

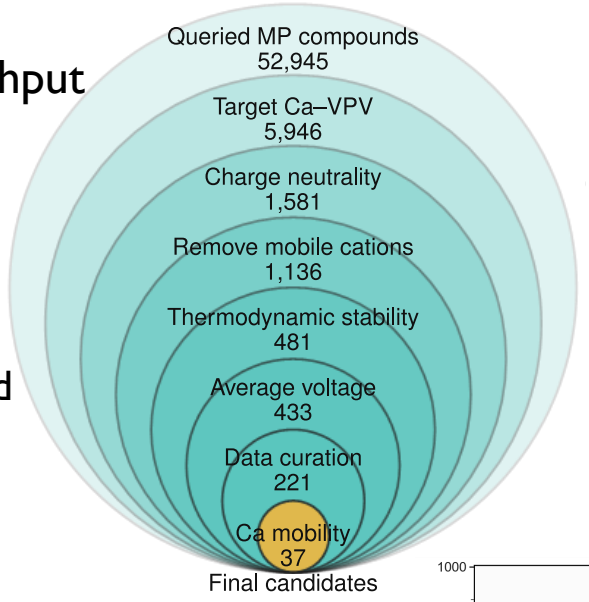
- Revealed six stable $Ca_xV_2O_4$ phases governing finite-temperature Ca (de)intercalation
- Identified sluggish Ca diffusion and Ca–vacancy ordering as the dominant kinetic bottlenecks to reversible Ca extraction

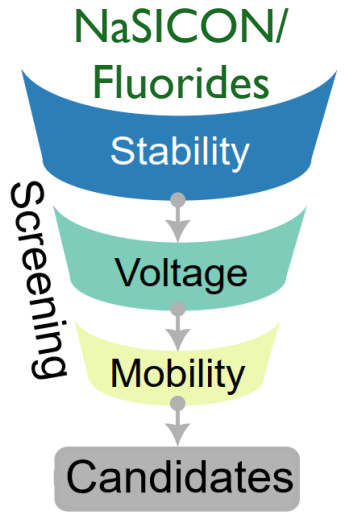
D. B. Tekliye, J. A. Dar and G. S. Gautam, "Phase Stability and Ion Transport in Post-spinel CaV_2O_4 Cathodes" arXiv:2607.08224, *(submitted)*, 2026

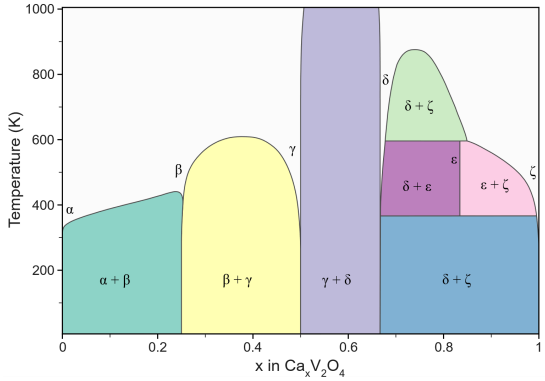
- This directly explains the limited electrochemical capacity observed in experiments

Conclusions

- Calcium-ion batteries offer high energy density using earth-abundant calcium
  - But lack thermodynamically stable cathodes with high Ca^{2+} mobility
- Explored **NaSICON** and **fluorides** (weberite, perovskite) frameworks using DFT
  - $Ca_xV_2(PO_4)_3$, $Ca_xMn_2(SO_4)_3$, $Ca_xFe_2(SO_4)_3$, $Ca_xCr_2F_7$ and $Ca_xMn_2F_7$
- Expand the search across MP structures using MLIP-accelerated high-throughput screening and identified **37** promising Ca-cathodes
  - **VPV**: a transferable geometry-based descriptor for Ca-site compatibility
  - **Ensemble ML**: robust migration-barrier screening followed by DFT validation
- Elucidated the thermodynamics and kinetics limitations in CaV_2O_4
  - Ca-extraction is limited due to phase separation during (de)intercalation and composition dependent sluggish Ca diffusion
- Current limitations and future opportunities
  - Evaluation of intermediate compositions and automated ion transport analysis
  - Generative AI-driven inverse design with closed-loop experimental validation







1. D. B. Tekliye et al., **Chem. Mater.**, 34, 10133-10143, (2022)
2. D. B. Tekliye and G. Sai. Gautam, **J. Mater. Chem. A**, 12, 18993–19007, (2024)
3. D. B. Tekliye and G. Sai Gautam, **Phys. Rev. Materials**, 8, 093801, (2024)
4. D. B. Tekliye et al., "Geometry-based Discovery of Calcium Battery Cathodes Accelerated by Foundational Machine-Learned Models," arXiv:2605.29029v1 (under review, **npj Computational Materials**), 2026
5. D. B. Tekliye, et al., "Phase Stability and Ion Transport in Post-spinel CaV_2O_4 Cathodes" arXiv:2607.08224, (submitted), 2026

"a scalable framework for accelerated Ca-cathode discovery"

Publications

1. **D. B. Tekliye**, A. Kumar, X. Weihang, T. D. Mercy, P. Canepa, and G. Sai Gautam, "Exploration of NaSICON Frameworks as Calcium-ion Battery Electrodes," ***Chemistry of Materials***, vol. 34, no. 22, pp. 10 133–10 143, 2022.
2. **D. B. Tekliye** and G. Sai Gautam, "Fluoride Frameworks as Potential Calcium Battery Cathodes," ***Journal of Materials Chemistry A***, vol. 12, no. 30, pp. 18 993–19 007, 2024.
3. **D. B. Tekliye** and G. Sai Gautam, "Accuracy of metaGGA Functionals in Describing Transition Metal Fluorides," ***Physical Review Materials***, vol. 8, no. 9, p. 093 801, 2024.
4. A. Ghosh, **D. B. Tekliye**, E. E. Foley, V. R. Reddy, R. J. Clément, G. Sai Gautam, and P. Senguttuvan, "Topochemical Modulations from 1D Iron Fluoride Precursor to 3D Frameworks," ***Inorganic Chemistry***, vol. 63, no. 31, pp. 14 335–14 344, 2024.
5. **D. B. Tekliye**, A. K. Bheemaguli and G. Sai Gautam, "Geometry-based Discovery of Calcium Battery Cathodes Accelerated by Foundational Machine-Learned Models," arXiv:2605.29029v1 *(under review, **npj Computational Materials**)*, 2026.
6. **D. B. Tekliye**, J. A. Dar and G. Sai Gautam, "Phase Stability and Ion Transport in Post-spinel CaV_2O_4 Cathodes" arXiv:2607.08224, *(submitted)*, 2026.
7. G. Das, D. Sharma **D. B. Tekliye**, A. Adukkadan, K. Subramanian, G. Sai Gautam, S. Checchia, J. Daniels and R. Ranjan, "Origin of skin effects in ferroelectric, relaxors, and related materials," (*submitted)*, 2026.
8. A. Krishna B, **D. B. Tekliye**, X. Penghao, and G. Sai Gautam, "Understanding the Polyanionic Effect on Ca Migration Barrier within V-Based NaSICON as Calcium Cathodes," *(under preparation)*, 2026.
9. J. A. Dar, **D. B. Tekliye**, D. K. J. Lee, P. Canepa and G. Sai Gautam ,"Ab initio thermodynamics of sodium-tin alloy as negative electrode for sodium-ion batteries," *(under preparation)*, 2026.

Presentations and workshop

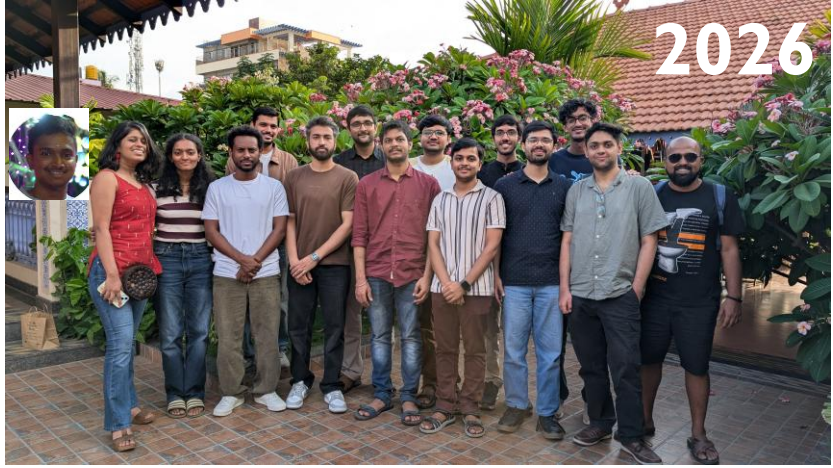
Presentation

- Fluoride Frameworks as Potential Calcium Battery Cathodes, SSI24, London (oral, Jul 15–19, 2024)
- NaSICON Frameworks as Calcium-ion Battery Cathodes, FOMAD-2023, Chikmagalur (oral, Apr 29, 2024)
- NaSICON Frameworks as Calcium-ion Battery Cathodes," ACSSI-2024, Chennai (poster, Feb 19–22, 2024)
- NaSICON Frameworks as Calcium-ion Battery Cathodes, IISc Annual Students' Symposium, Bengaluru (Oral, Apr 12–13, 2022)

Workshop conducted

- Hands-on session (2-hr), "Introduction to DFT and MD" (DFT calculations and Molecular Dynamics simulations), IMBRS, Bengaluru (Dec 6, 2025)
- Hands-on session (1.5-hr), "AI/ML for Materials Science" (ANN, CGCNN), IISc, Bengaluru (Jan 8–9, 2025)
- Hands-on session (0.5-hr), "Applications of ML to Materials Science" (cluster expansion), JNCASR/IISc, Bengaluru (Jul 24–28, 2023)

Acknowledgments



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