

Exploration of NaSICON frameworks as calcium-ion battery cathodes

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Ca-ion battery (CIB): as alternative to Li-ion batteries



Why Ca?

- Comparable standard reduction potential (-2.87 V vs SHE) with that of Li (-3.04 V)
- Use of Ca metal anodes: offer high volumetric energy density
- Ca²⁺: exchanges 2e⁻ at a time instead of 1e⁻ for Li⁺ case
- Ca is most abundant (~ 4.15%) than Li (~ 0.002%)¹



Challenges in Ca-cathode design:

- Thermodynamic stability
- High energy density
- Enhanced ionic mobility

NaSICON: polyanionic framework with robust structural stability and 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.
- MO₆ polyhedra is coordinated via corner sharing with ZO₄ tetrahedral



NaSICON as Ca-ion battery cathodes

Given the similar ionic radius of Na⁺ (~1.02 Å)¹ and Ca²⁺ (~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

- The transition metal choice is motivated by potential 2+, 3+, and 4+ oxidation states
- The composition is computed considering the charge neutrality constraint
 - Ca composition in Ca_xMn₂(SiO₄)₃:
 - 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 $Ca_x M_2(SiO_4)_3$ $0.5 \le x \le 2.5$ in $Ca_x M_2(PO_4)_3$ $M^{4+} \leftrightarrow M^{2+}$ $PO_4 (254-267) > SiO_4 (227-237)$

• $0 \le x \le 1$ in $Ca_x M_2(SO_4)_3 \longrightarrow M^{3+} \leftrightarrow M^{2+}$

Generating Ca-NaSICON compositions



1. M. Hellenbrandt, Crystallogr. Rev. 2004 2. Ping Ong et al., Comput. Mater. Sci. 2013 3. Sun et al., Phys. Rev. Lett. 2015 4. Dudarev et al., Phys. Rev. B 1998

Average voltage: increases monotonically from Ti to Ni except for SO₄



- Voltage is *monotonically* increasing from Ti-Ni for PO₄ and SiO₄
 - Consistent with standard reduction potentials
- PO₄ voltage is consistently higher than SiO₄
 - Due to inductive
 effect
- SO₄ voltage increment is *non-monotonic*
 - "Local" minima at Cr and Fe, attributed to the stability of Cr³⁺ and Fe³⁺
- Ti-based Ca-NaSICONs are suitable for anode instead of cathode due to their low voltage

Thermodynamic stability: several stable phosphates and sulfates are discovered



Ca_xV₂(PO₄)₃, Ca_xMn₂(PO₄)₃, Ca_xMn₂(SO₄)₃ and Ca_xFe₂(SO₄)₃: stable/metastable
 All SiO₄ are unstable: not a candidate for Ca-cathode

Thermodynamic stability: several stable phosphates and sulfates are discovered



Ca_{0.5}V₂(PO₄)₃ (~-8 meV/atom); NaV₂(PO₄)₃: experimentally synthesised

 Experimentally synthesised phases (Ti, Cr and Fe-SO₄) exhibit high stability as predicted

Migration barrier: 3 candidate Ca-NaSICONs



Conclusions and acknowledgments



- 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_xV₂(PO₄)₃, Ca_xMn₂(SO₄)₃ and Ca_xFe₂(SO₄)₃ identified as promising Ca-cathodes based on average voltage, thermodynamic stability, and migration barrier calculations



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