Critical overview of polyanionic frameworks as positive electrodes for Na-ion batteries

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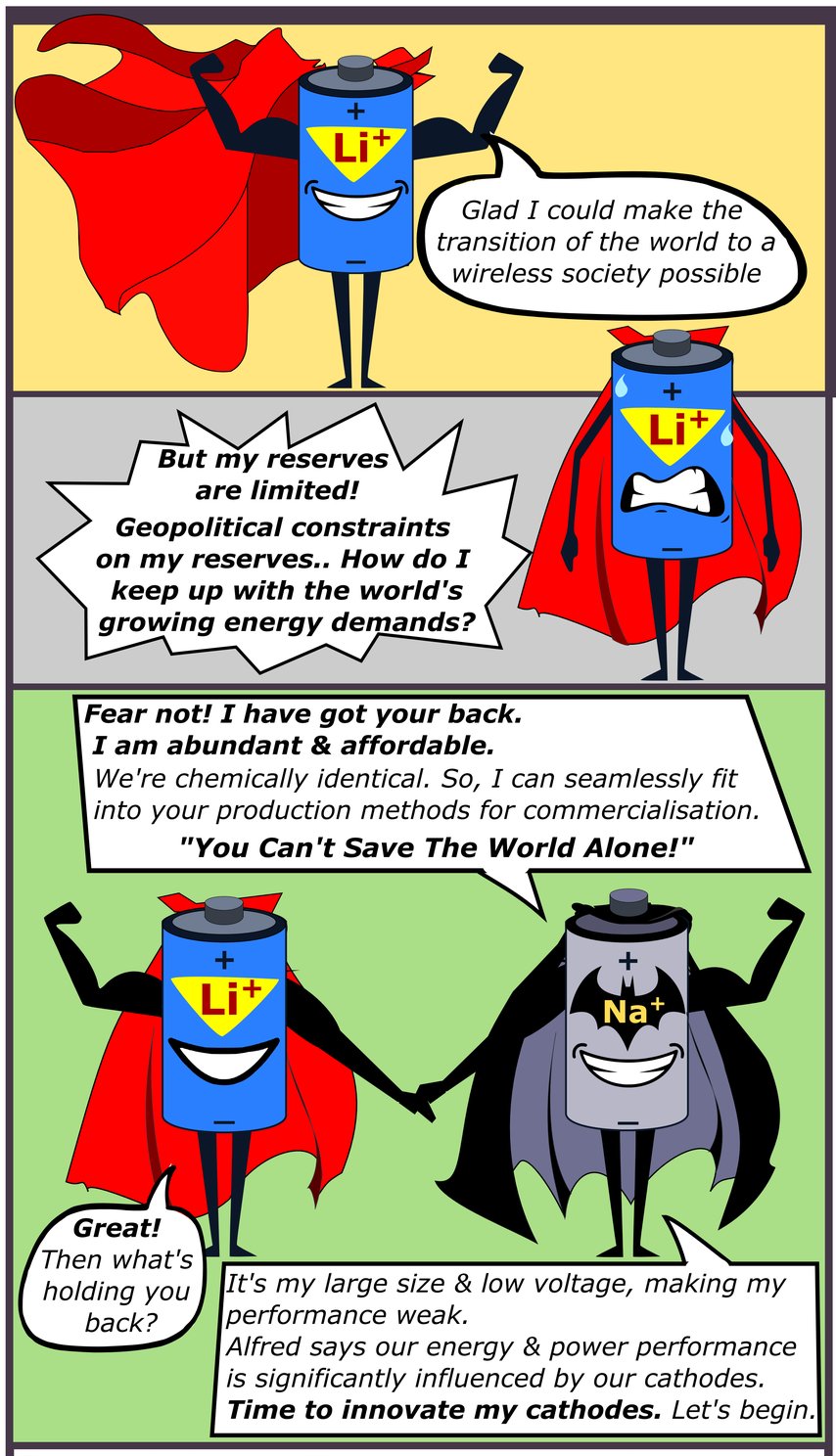
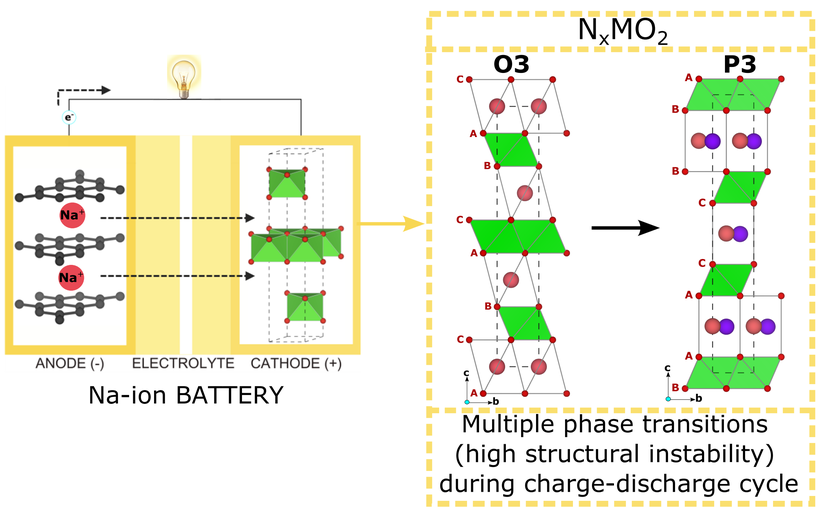


State-of-the-art Na-ion battery cathode:
LAYERED TRANSITION METAL OXIDE FRAMEWORK



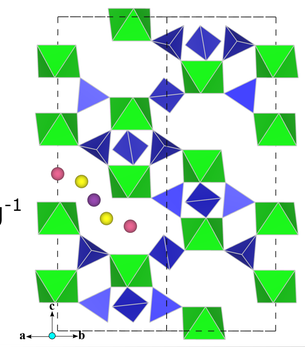
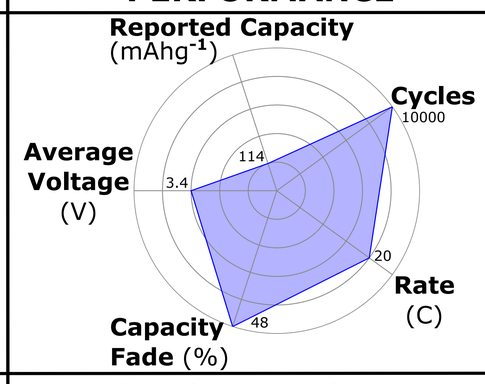
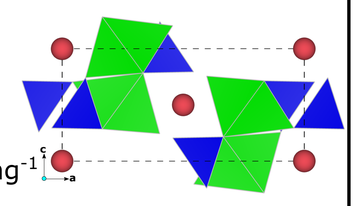
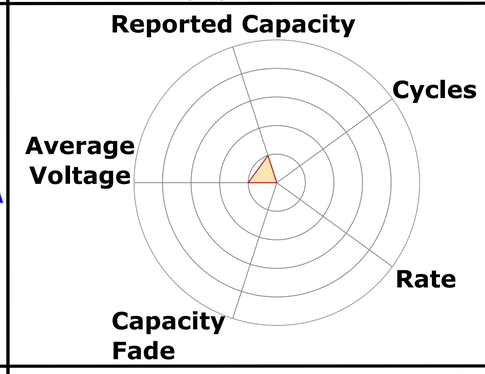
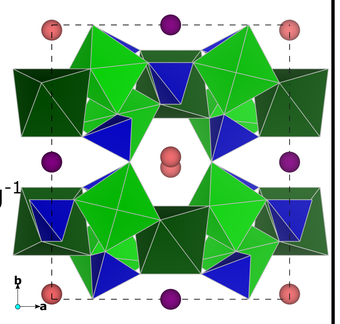
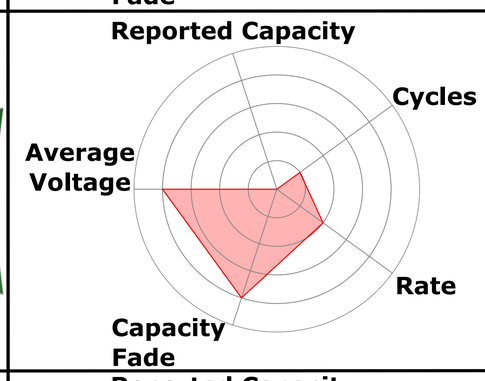
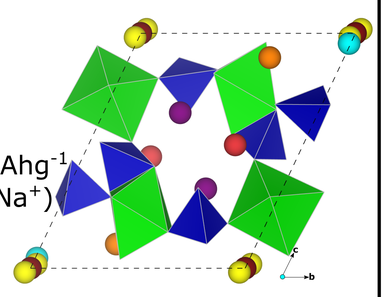
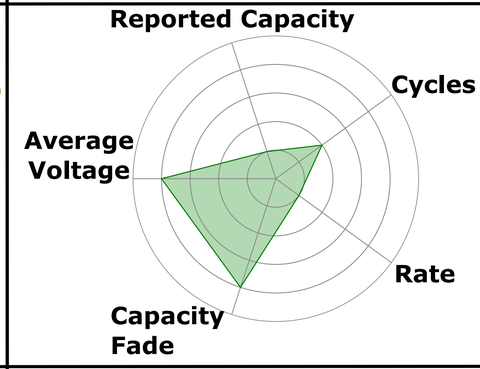
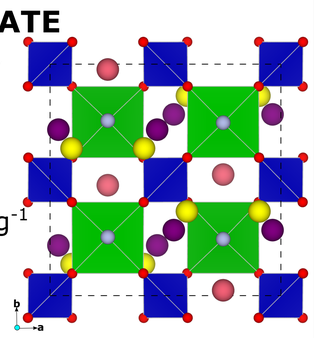
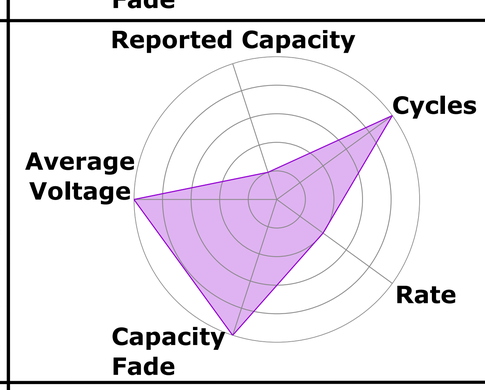
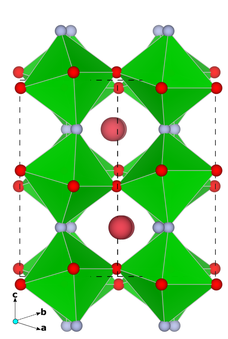
Hence, we need to explore polyanionic frameworks as Na-ion battery cathode because they show high structural integrity upon Na-ion exchange during cycle & elevated voltage

Factors affecting choice of cathodes:

PARAMETERS	UNITS
1. Capacity (experimentally measured/ theoretically predicated)	$mAhg^{-1}$
2. Average voltage (experimentally measured/ theoretically predicated with Density Functional Theory, DFT)	V
3. Current rate	C
4. Cycles	number
5. Capacity Fade	%
6. Migration barrier energy* for Na-ion mobility (DFT-Nudged Elastic Band, DFT-NEB, Bond Valence Site Energy, BVSE)	eV

*Only migration barrier energy estimated with DFT-NEB & BVSE are considered for this work

SUMMARY OF CATHODES STUDIED:

POLYANIONIC FRAMEWORK**	PERFORMANCE	DISCUSSION
NASICON $Na_xM_2(XO_4)_3$ Symmetry: $R\bar{3}m$ Theoretical Capacity: 117 $mAhg^{-1}$ (2 Na^+) 		Swift Na-ion diffusion but poor electronic conductivity (since isolated MO_6 octahedra) Low capacity & voltage: Improved using mixed transition metal compositions, M-M' Capacity fade is high but at high rates & high cycle life (e.g., 48% @20 C, 10000 cycles) PO_4^{3-} NaSICON show higher capacity & lower migration energy for Na than SO_4^{2-} NaSICON
OLIVINE Na_xMXO_4 Symmetry: *Pmna* Theoretical Capacity: 154 $mAhg^{-1}$ (1 Na^+) 		1D Na-ion diffusion tunnel along b-axis PO_4^{3-} olivine: ~0.28 eV SiO_4^{4-} olivine: ~0.26 eV (DFT-NEB) Poor cycle life & capacity fading at low rates (e.g., $NaFePO_4$: 125 $mAhg^{-1}$ @0.05 C, 50 cycles) Na_2FeSiO_4: 119 $mAhg^{-1}$ @0.25, ~0.9 reversible Na) Capacity fading in SiO_4^{4-} olivines improved with addition of electrolyte additives
ALLUAUDITE $Na_xMM'_2(XO_4)_3$ Symmetry: *C2/c* Theoretical Capacity: 120 $mAhg^{-1}$ (2 Na^+) 		Two 1D Na-ion diffusion tunnels along c-axis Tunnel 1: ~1.28 eV (corners) Tunnel 2: ~0.31 eV (edge-centre) (BVSE) PO_4^{3-} alluaudite show much lower capacity & voltage than SO_4^{2-} alluaudite (e.g., $Na_2MnFe_2(PO_4)_3$: 50 $mAhg^{-1}$, 1.5-4.3 V $Na_2Fe_2(SO_4)_3$: 102 $mAhg^{-1}$, 3.8 V ($Fe^{3+/2+}$) (highest reported voltage for $Fe^{3+/2+}$ redox couple)
PYROPHOSPHATE $Na_xMP_2O_7$ Symmetry: $P\bar{1}$ Theoretical Capacity: 118 $mAhg^{-1}$ (2.44 Na^+) 		3D Na-ion diffusion (0.33-0.5 eV, DFT-NEB) Low capacity at reasonable voltage, capacity fade & low cycle life at low rates: Improved in Na-excess pyrophosphate (x>2) (e.g., $Na_2FeP_2O_7$: 82 $mAhg^{-1}$, 3 V, 30 cycles @0.1 C $Na_{3.12}Mn_{2.44}(P_2O_7)_2$: 114 $mAhg^{-1}$, 3.6 V, 75% capacity retention at 500 cycles @5 C)
FLUOROPHOSPHATE $Na_xMO_{2y}(PO_4)_2F_{3-2y}$ Symmetry: *Amam* Theoretical Capacity: 128.3 $mAhg^{-1}$ (2 Na^+) 		High capacity & voltage for both stoichiometric (x upto 2) & Na-excess (x>2) Capacity fade & low cycle life: Improved with particle size reduction & morphological modification (e.g., from 60 to 2000 cycles @0.1 C) Voltage elevates significantly in Na-excess fluorophosphate (e.g., $Na_3V_2(PO_4)_2F_3$: 3.95 V ($V^{3+/2+}$)
PEROVSKITE $Na_xMO_yF_{3-y}$ Symmetry: *Pmna* Theoretical Capacity: 197 $mAhg^{-1}$ (1 Na^+) 	Not enough data available	This cathodic framework has the potential to exhibit high capacity & voltage due to presence of light weight yet highly electro-negative anionic group. However, the framework has been predominantly explored as Li-ion battery cathode. For Na-ion battery, due attention of the scientific community is needed.

**M/M'= Transition metal, x=Na content, X= High-valent non-redox active cation i.e., P^{5+}, S^{6+}, Si^{4+} etc., y= O content, MO_6/XO_4= green/blue polyhedra, Na^+= pink, purple, yellow balls, O/F= red/grey balls

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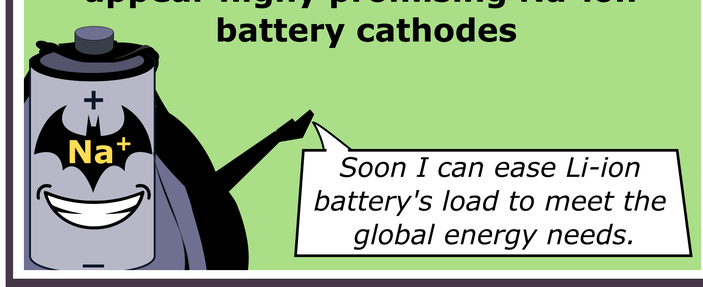
CONCLUSION:

So far NaSICONs & Fluorophosphates appear highy promising Na-ion battery cathodes



Persistent & ongoing challenges:

Poor electronic conductivity & capacity fading:
Result in poor cycle life

Low intrinsic theoretical capacity due to presence of heavy anionic groups

Possible strategies:

Apply & improve electronically conductive coating & size reduction

Explore mixed transition metal compositions

Rigorous computational study for predicting new cathode chemistries & understand Na-ion migration within the framework.

D. Deb, and G. Sai Gautam, "Critical overview of polyanionic frameworks as positive electrodes for Na-ion batteries", J. Mater. Res. 37, 3169-3196 (2022)

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