Simulations And Informatics of
MATerials Group

28th Jan 2023
36th Student Symposium

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

- Debolina Deb

P.I. Dr. Sai Gautam Gopalakrishnan

Materials Engineering Department,
Indian Institute of Science

The Nobel Prize in Chemistry 2019

John B. Goodenough

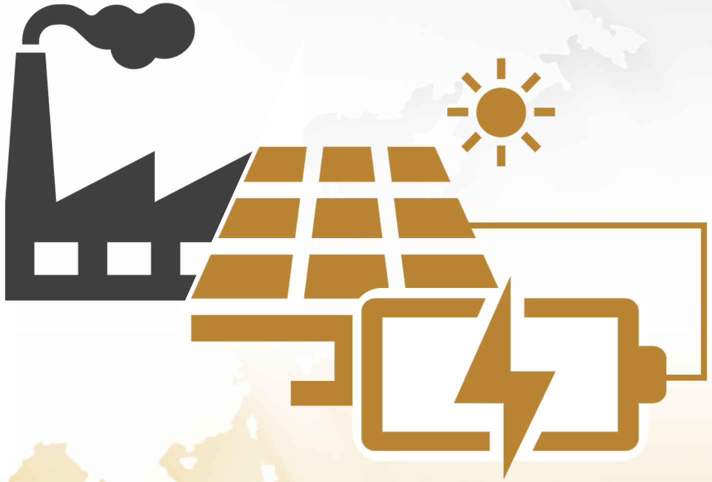
M. Stanley Whittingham

Akira Yoshino

“for the development of lithium-ion batteries”

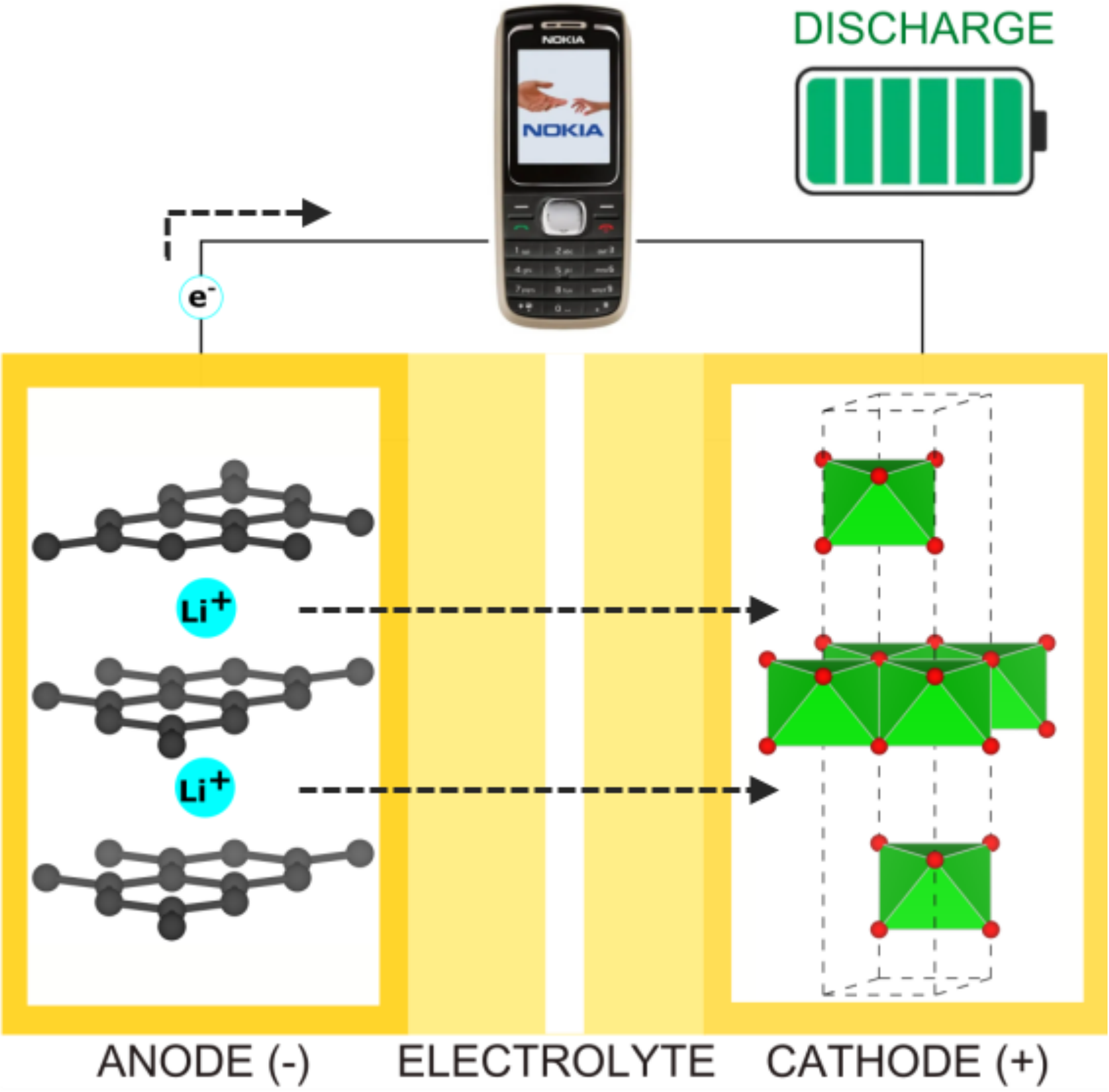
TRANSPORTATION

CONSUMER ELECTRONICS

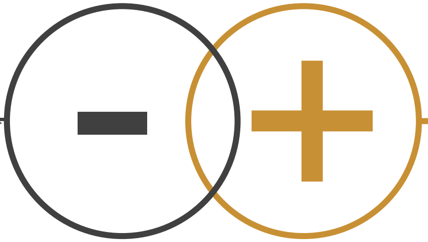


ENERGY INDUSTRY

"World transitioning to fossil fuel-free and wireless society"



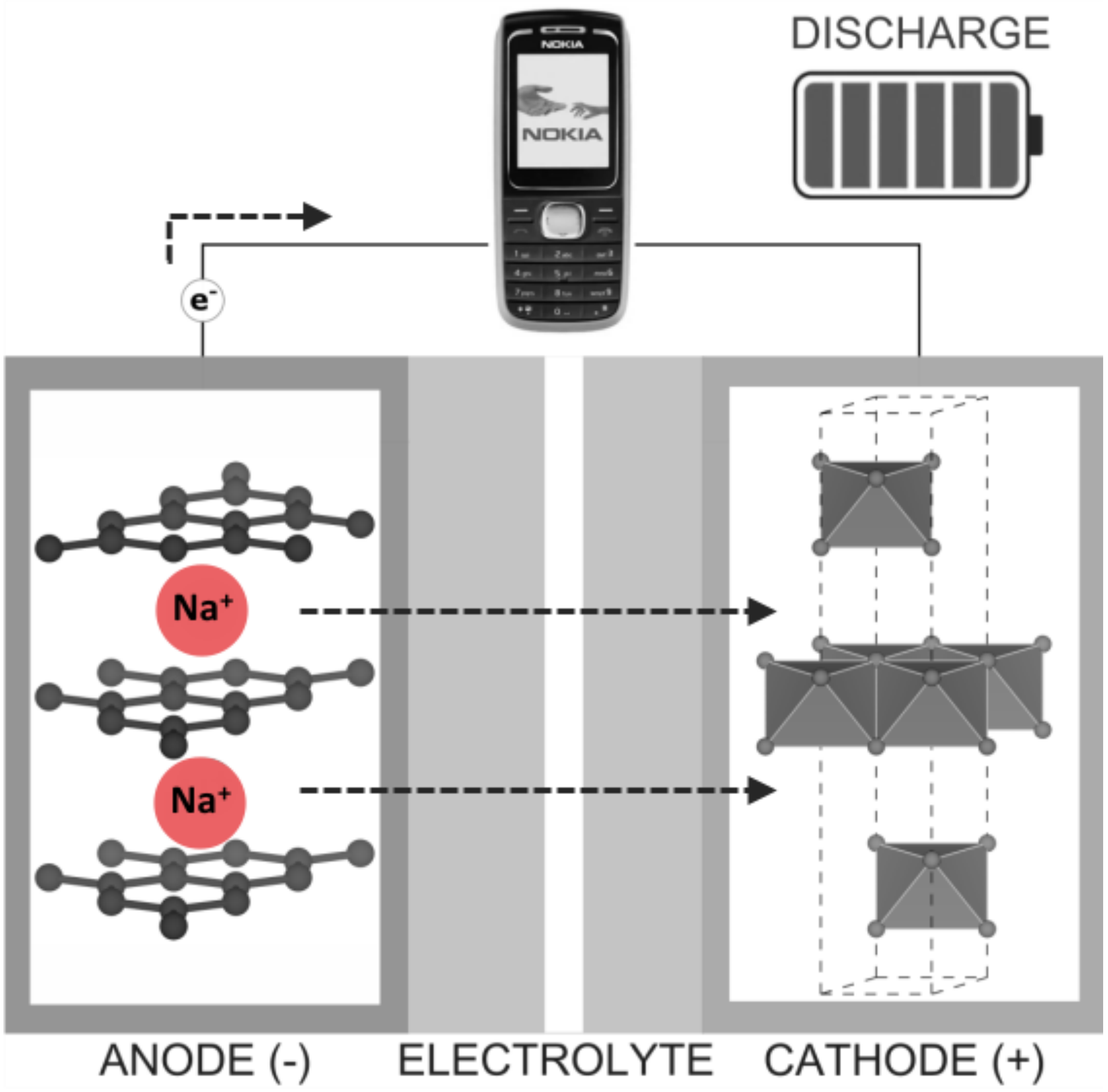
Li-ion battery has **outperformed** ***other storage systems*** *in terms of* ***energy density*** *&* ***battery life***



Supply chain concerns *with Li & Co*

Increasing cost *of Li & Co*

These concerns encourage us to look for beyond Li-ion battery



Na-ion battery **utilize similar engineering & production methods** *as the well-established protocols in Li-ion battery*

Abundant & affordable *Na reserves makes Na-ion battery a viable alternative to Li-ion battery*

INNOVATIONS IN
POSITIVE ELECTRODES (Cathodes)
CAN OVERCOME INTRINSIC DRAWBACKS

Because cathodes influence energy
& power performance significantly

Lower voltage & larger size *of Na results in poor performance of Na-ion battery*

Abundant & affordable *Na reserves makes Na-ion battery a viable alternative to Li-ion battery*

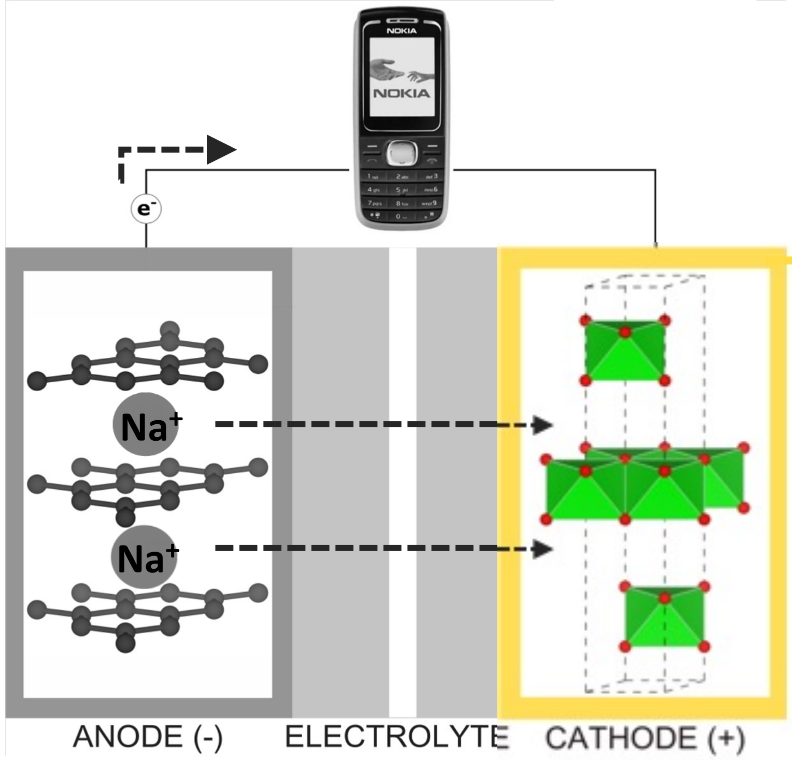
State-of-the-art Na-ion battery cathode

Layered Oxide Framework

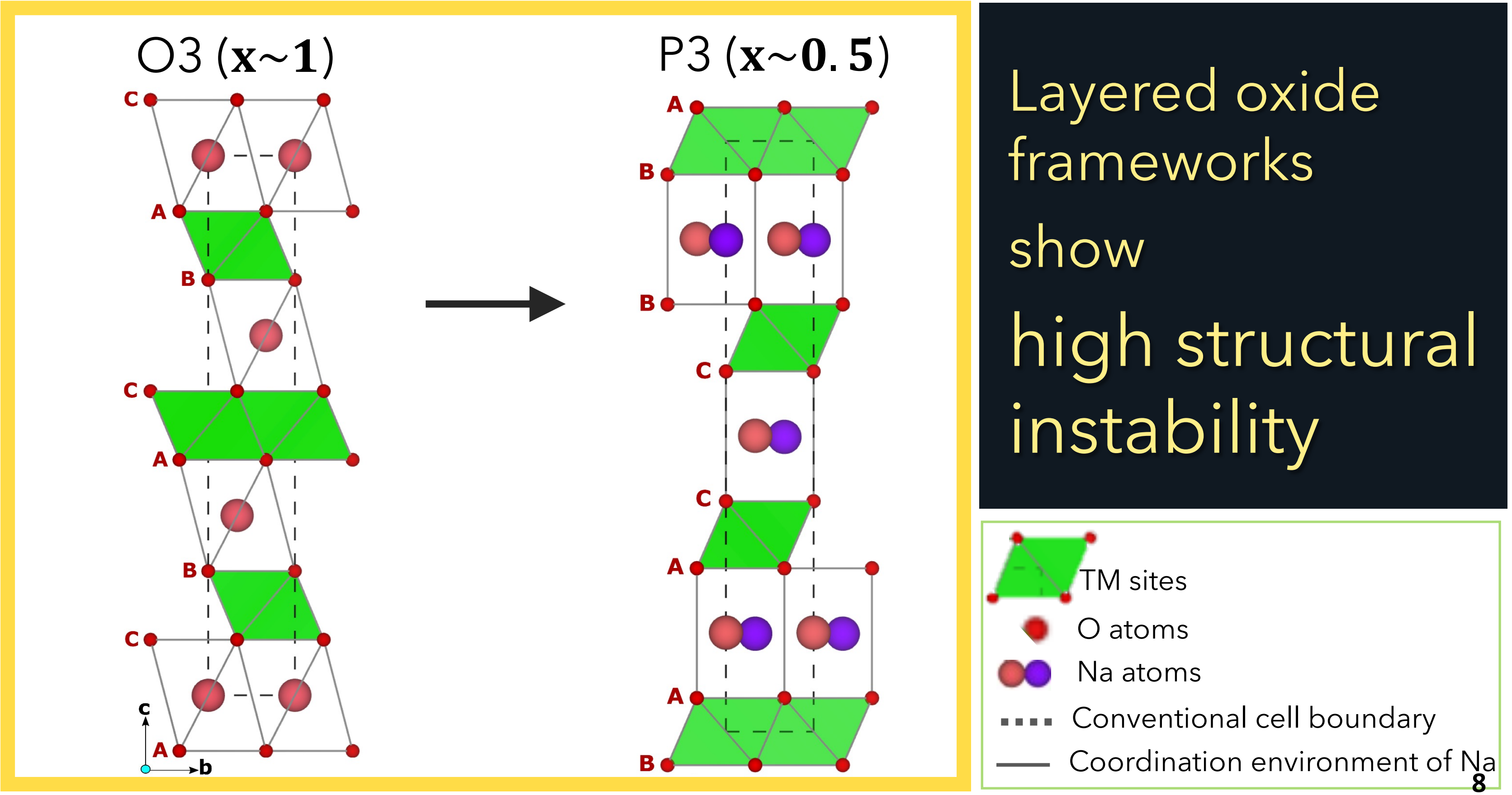
They show appreciable energy density

General formula: Na_xMO_2

Where, M = Transition metal
x = Na content



During charge-discharge cycle



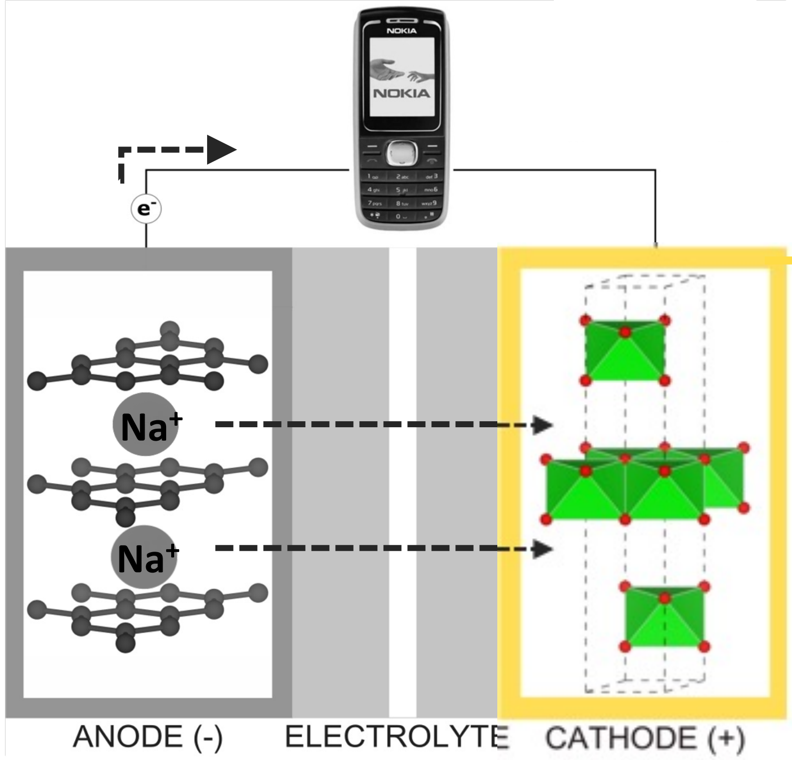
Layered oxide frameworks show high structural instability

State-of-the-art Na-ion battery cathode — Layered Oxide Framework

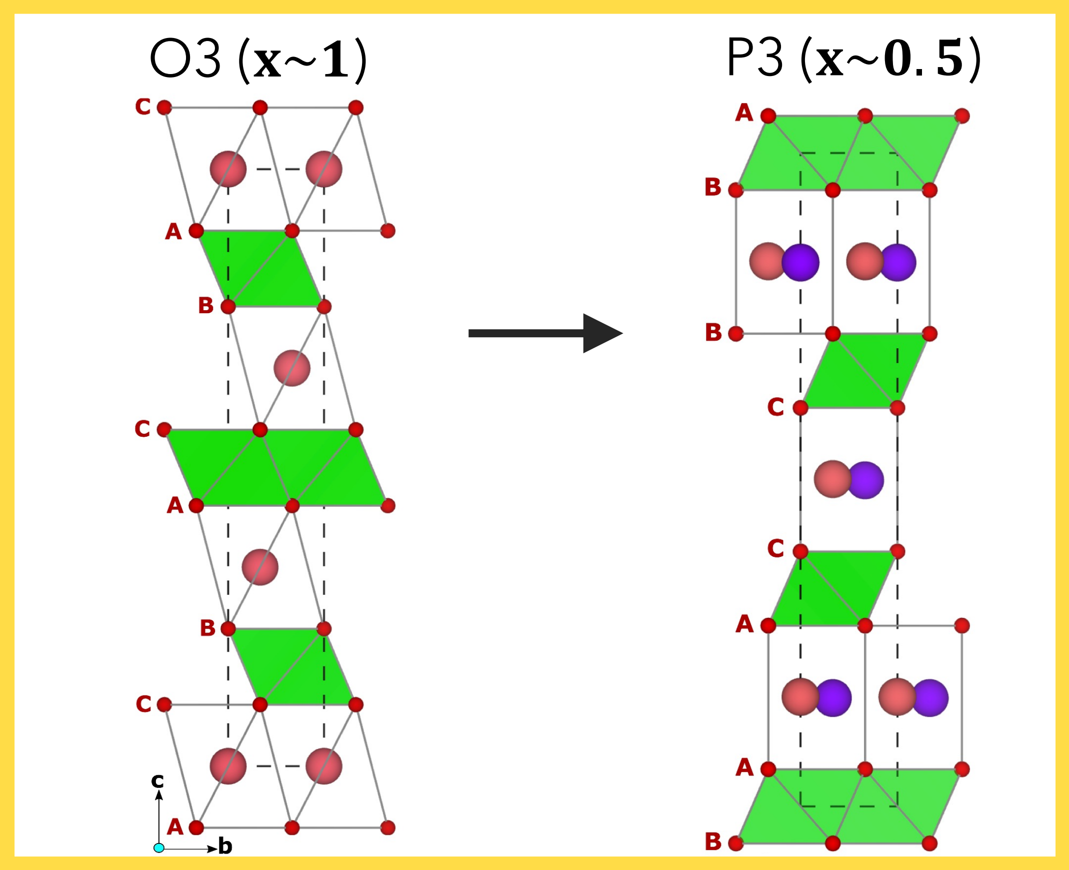
They show appreciable energy density

General formula: Na_xMO_2

Where, M = Transition metal
x = Na content



During charge-discharge cycle



Layered oxide frameworks show high structural instability

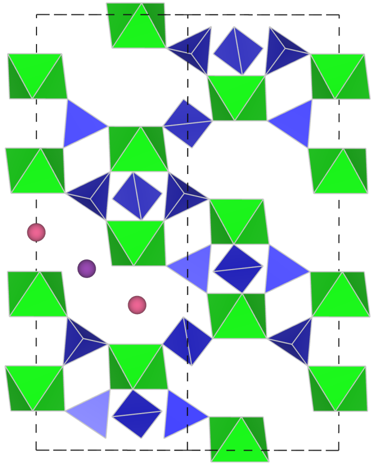
NEED TO EXPLORE STRUCTURALLY RIGID FRAMEWORKS

Polyanionic Frameworks

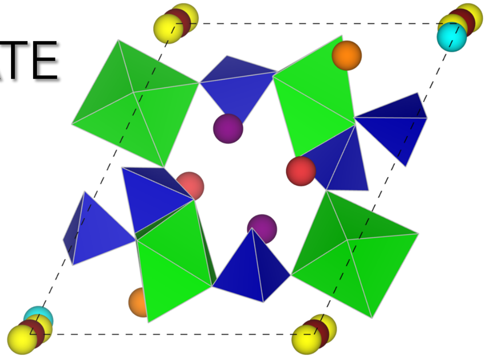
as
Na-ion battery cathode

Show structural integrity
upon Na-ion exchange during cycle

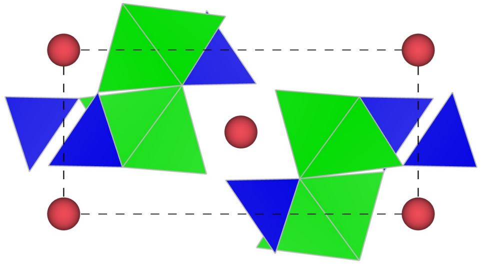
NaSICON



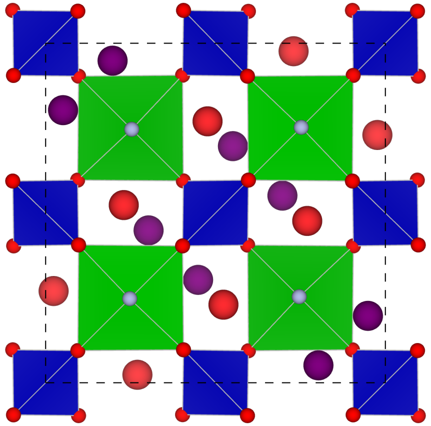
PYRO-
PHOSPHATE



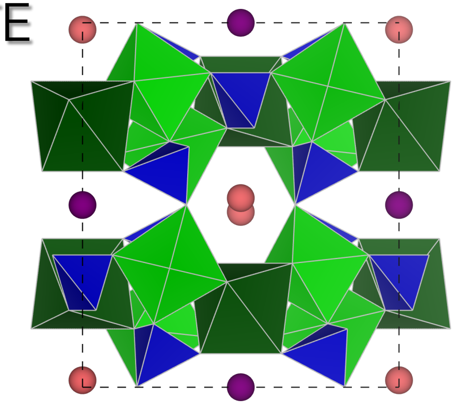
OLIVINE



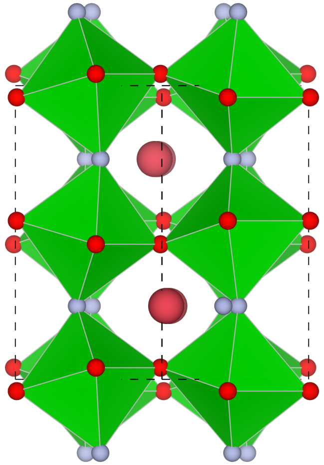
FLUORO-
POLYANION



ALLUAUDITE



PEROVSKITE



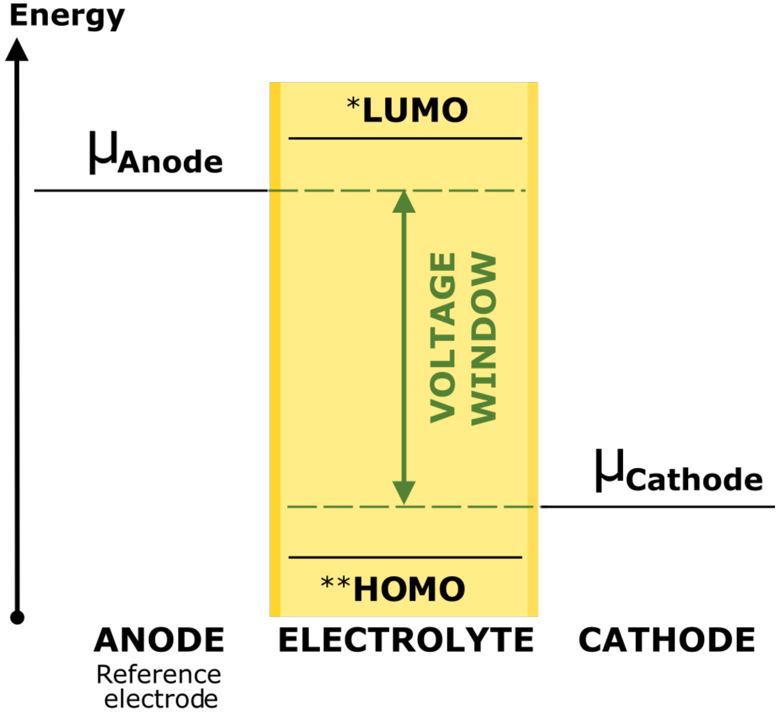
What factors determine the choice of cathodes?

1. Energy density of cathode:

Voltage, V × Capacity, mAh g^{-1}

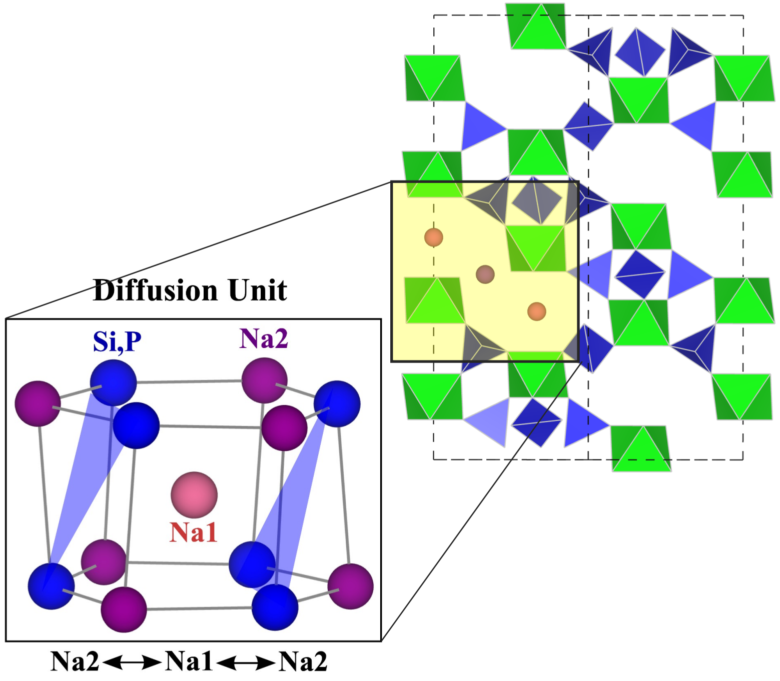
(driving force for Na-ion to flow to cathode)

Amount of Na-ion stored in cathode

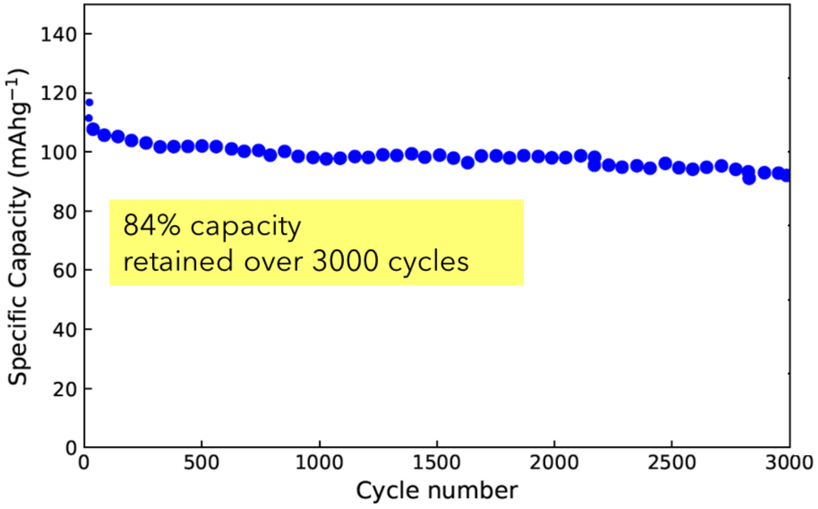


*Lowest Unoccupied Molecular Orbital
**Highest Occupied Molecular Orbital

2. Na-ion migration within framework

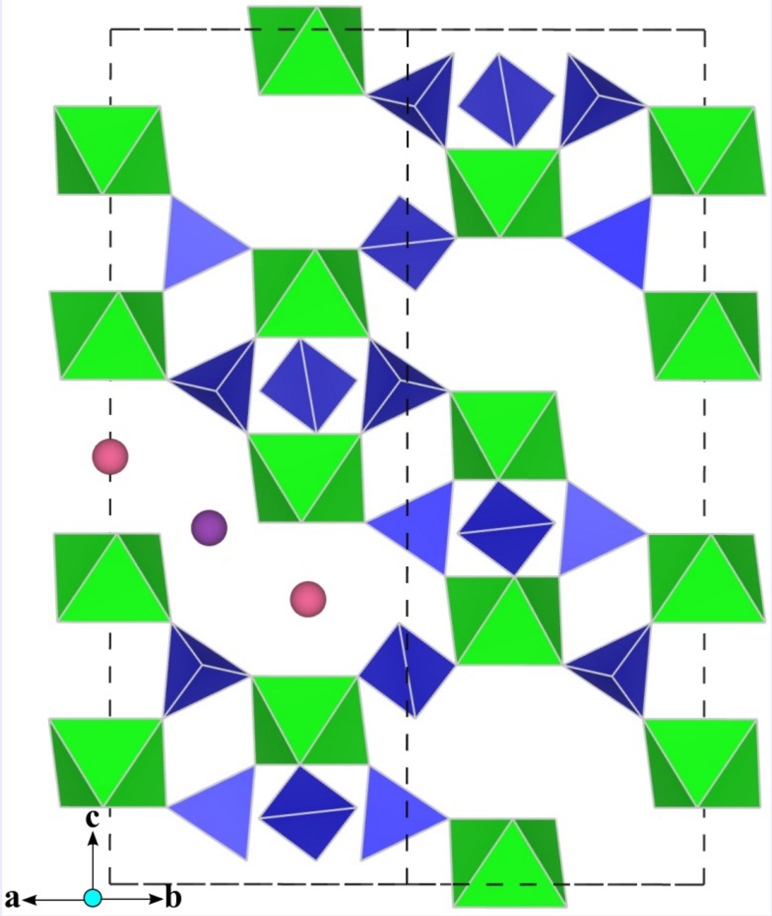


3. Cycle number (battery life)



X. Yao, et al. ACS Appl. Mater. Interfaces 10(12), 10022 (2018)

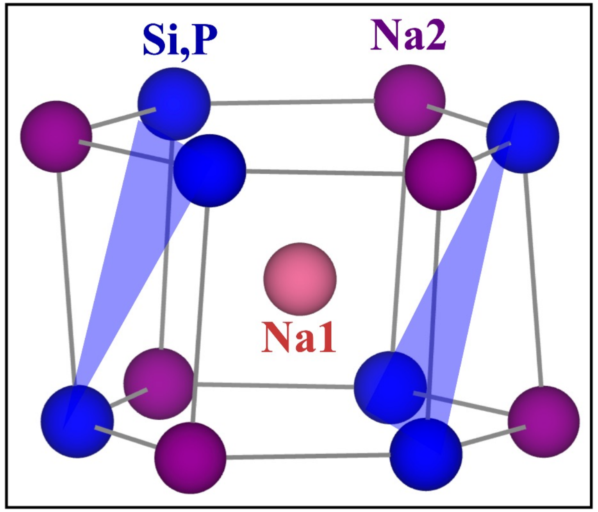
1 NaSICONs



"NaSICONs were first characterized by Goodenough & Hong in the 1970s as frameworks that exhibited swift Na mobility"

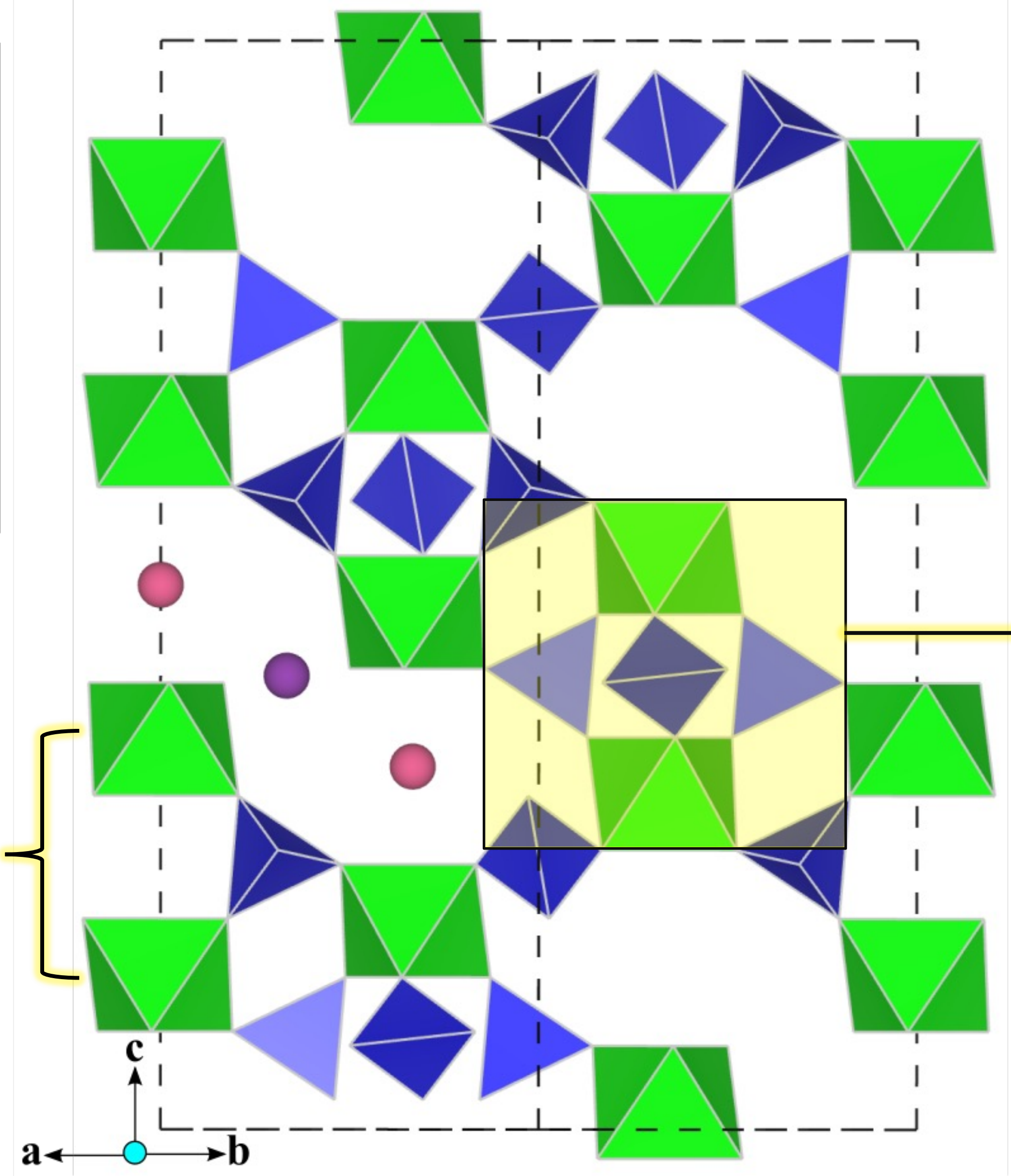
STRUCTURE & MIGRATION

Diffusion Unit



Na2⟷Na1⟷Na2

Isolated MO_6 octahedra contribute to poor electronic conductivity



General formula: $Na_xM_2(XO_4)_3$

Where, M = Transition metal

X = P^{5+}, S^{6+}, Si^{4+}, Nb^{5+} etc.

(High-valent non-redox active cation)

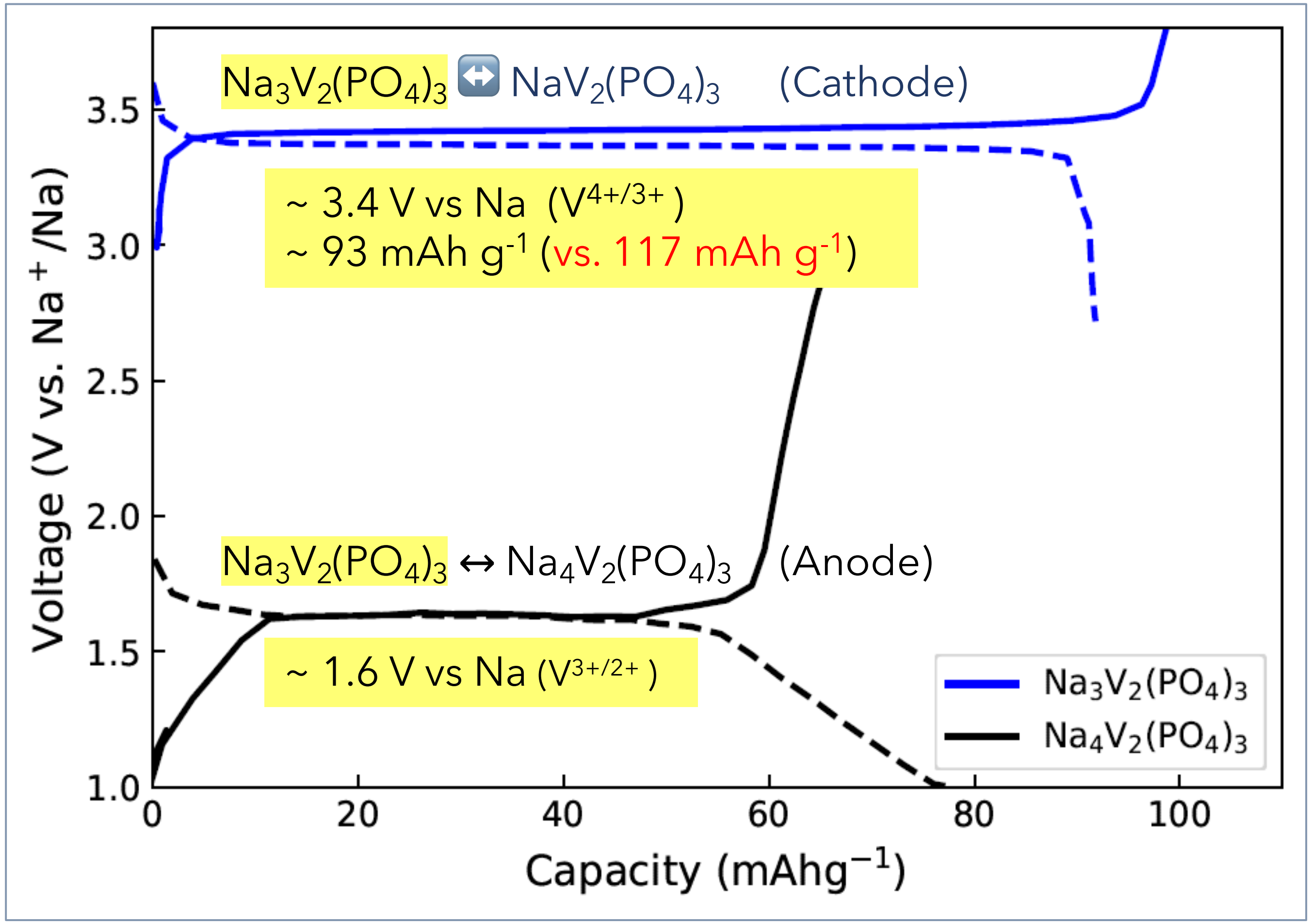
Symmetry: $R\bar{3}m$

Na1 (Wyckoff position: 6b)

Na2 (Wyckoff position: 18e)

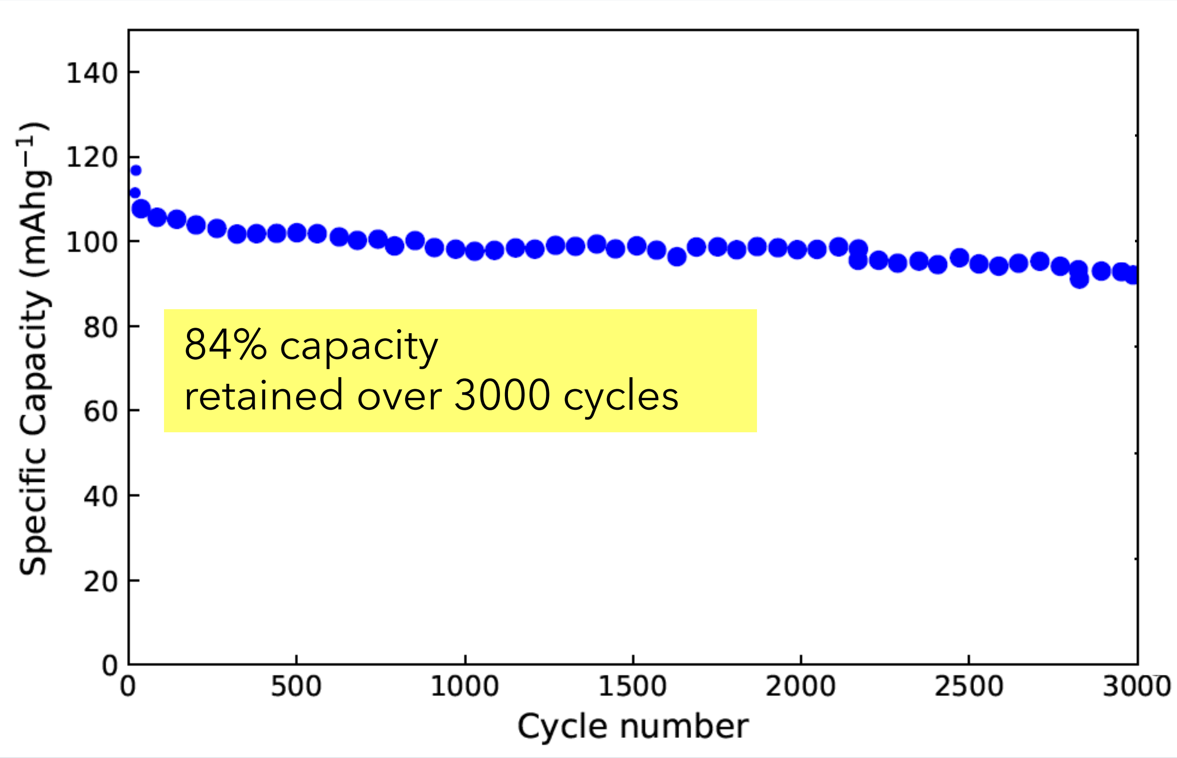
ELECTROCHEMICAL PERFORMANCE

$Na_3V_2(PO_4)_3$ or NVP (theoretical capacity of 117 mAh g^{-1})



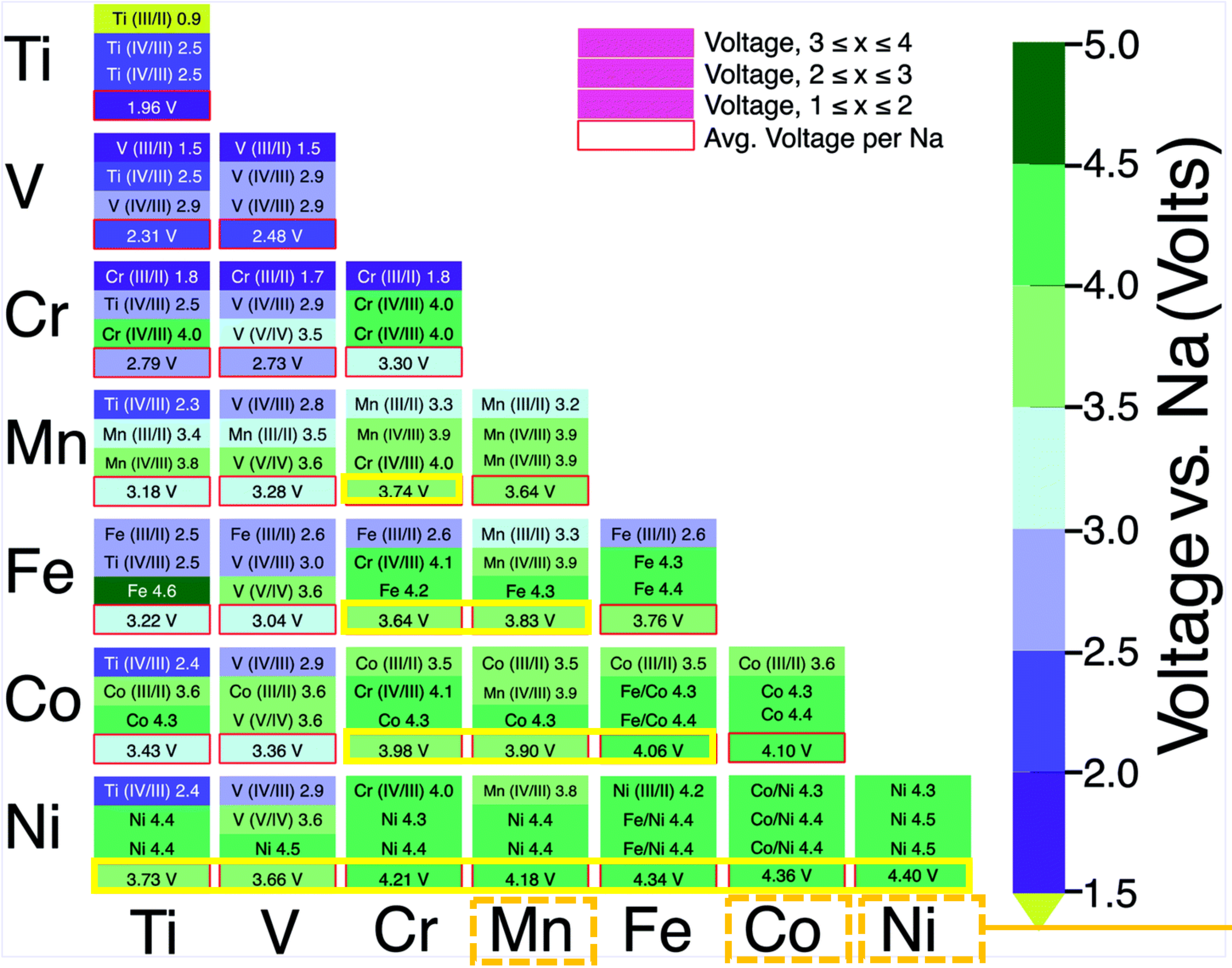
Z. Jian, et al. Electrochem. Commun. 14(1), 86 (2012)

NVP symmetric cell



X. Yao, et al. ACS Appl. Mater. Interfaces 10(12), 10022 (2018)

ELECTROCHEMICAL PERFORMANCE



B. Singh, et al. J. Mater. Chem. A 9(1), 281 (2021)

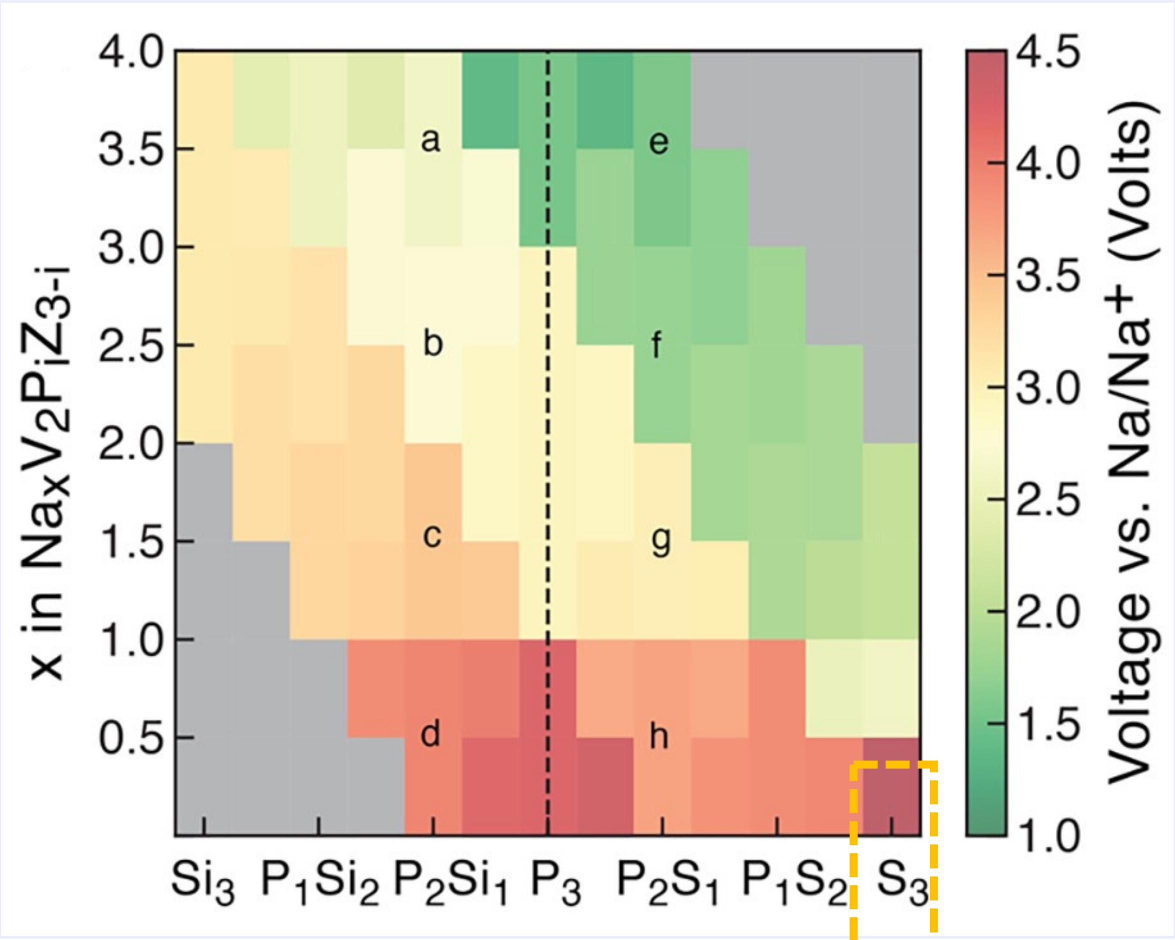
Predicted intercalation voltage for 28 different $Na_xMM'(PO_4)_3$ compositions

Where, M & M' = Ti, V, Cr, Mn, Fe, Co, or Ni.

Mixed Transition metal NaSICONs show better performance

Mn, Co, & Ni-based NaSICONs may be experimentally synthesizable

SULPHATE NaSICON



V. Kapoor, et al. Chem. Mater. 34(7), 3373 (2022)

Increase in average voltage due to strong inductive effect of $\mathbf{SO_4^{2-}}$ moiety

BUT

Sulphate NaSICONs have lower capacity:

4 Na^+ in phosphate NaSICON ($Na_4V_2(PO_4)_3$)

2 Na^+ in sulphate NaSICON ($Na_2Fe_2(SO_4)_3$)

Sulphate NaSICONs have higher migration barrier energy:

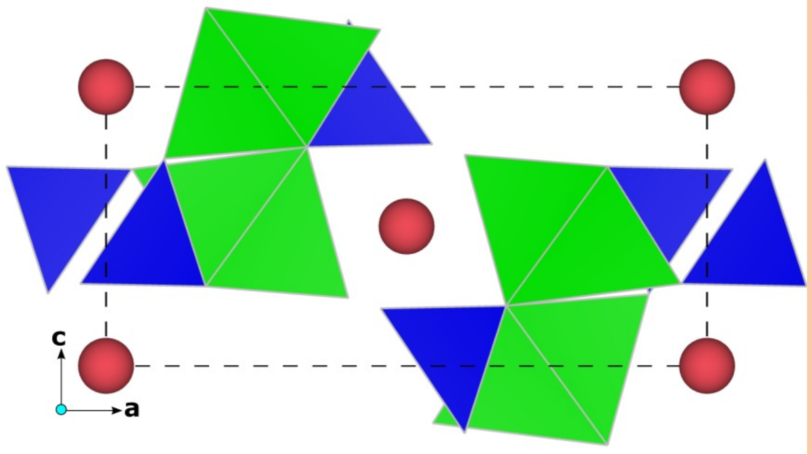
~0.31 eV in phosphate NaSICON

~0.89 eV in sulphate NaSICON

S.C. Chung, et al. J. Mater. Chem. A 6(9), 3919 (2018)

So complete substitution of phosphates with sulphates may not be entirely beneficial

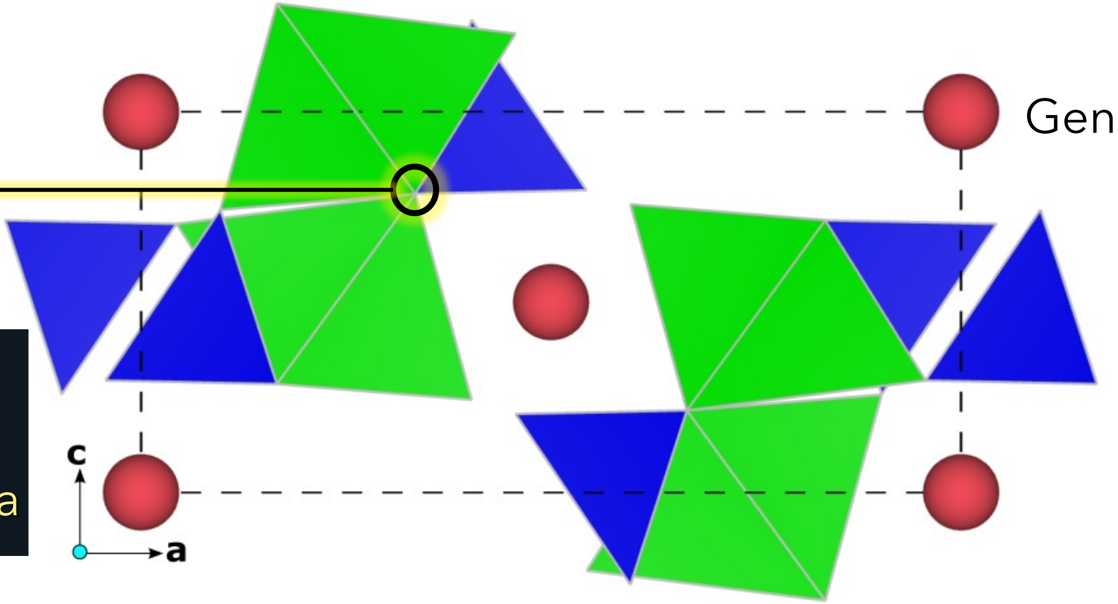
2 Olivines



"Olivines are inspired by their commercially successful Li analog, $LiFePO_4$"

STRUCTURE & MIGRATION

Poor electronic conductivity prevails due to only corner-shared MO_6 octahedra



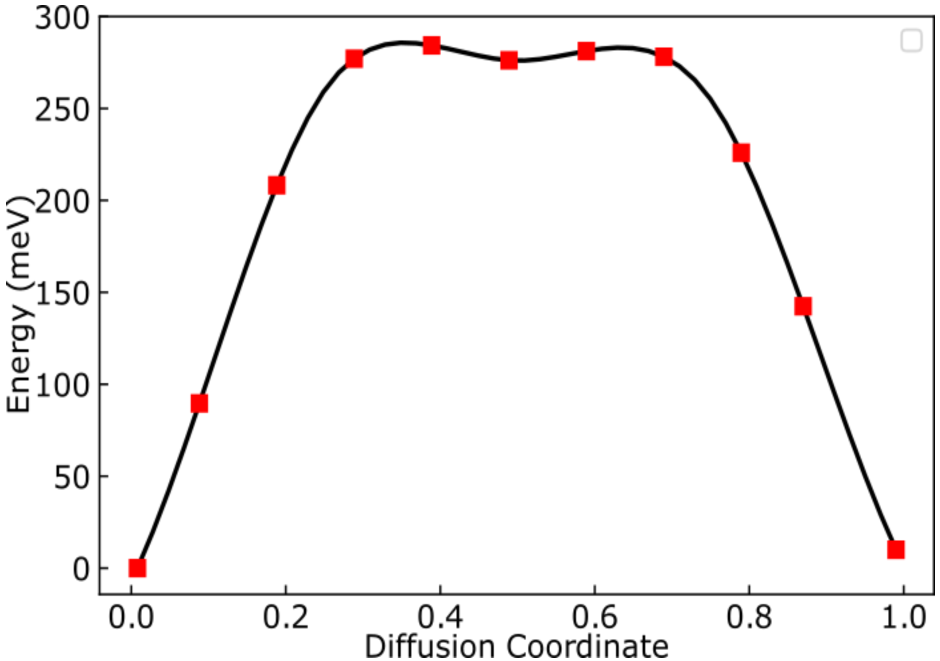
General formula: Na_xMXO_4

Where, M = Transition metal (Usually Fe, Mn, Ni)

X = P^{5+} (But Si^{4+} is known too)

Symmetry: **Pmna**

Na1 (Wyckoff position: 4c)



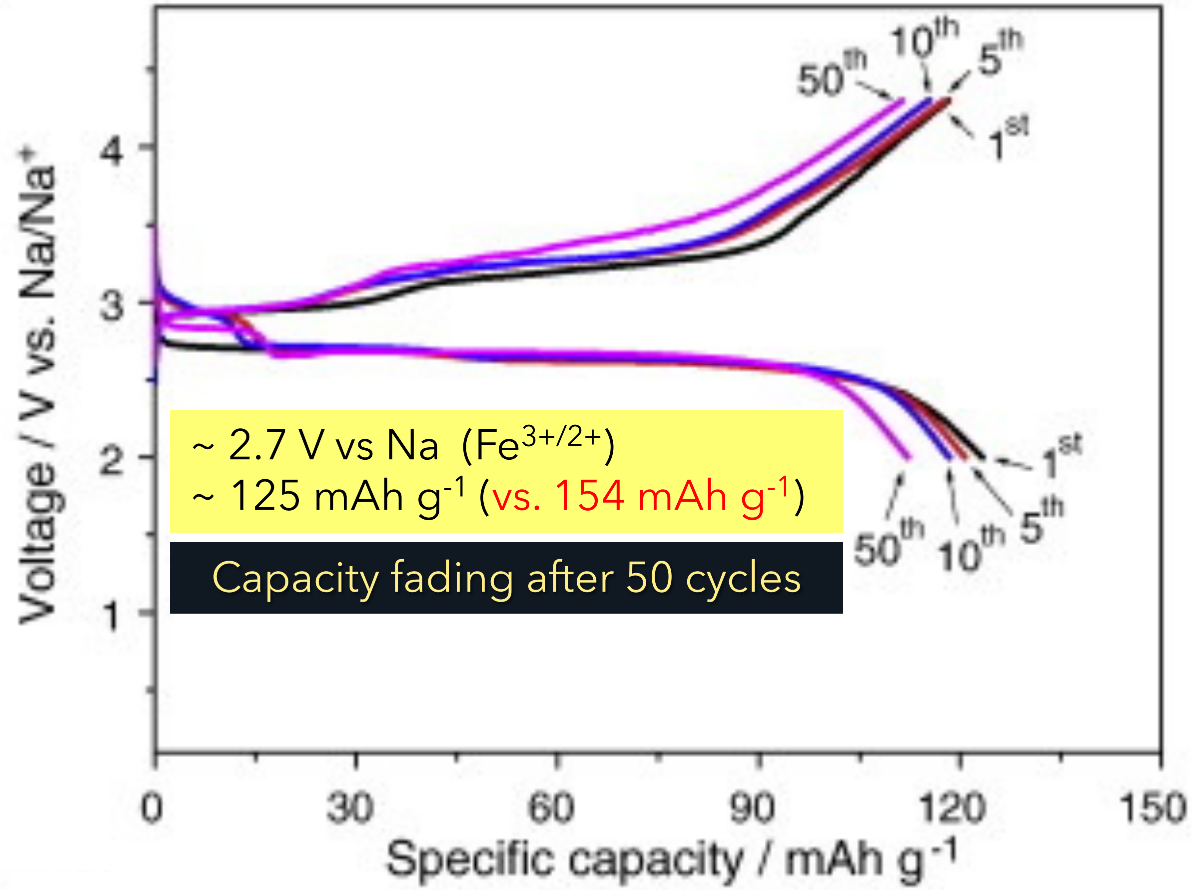
1D "tunnel" along b-axis

~0.28 eV migration barrier energy estimated theoretically

S.P. Ong, et al. Energy Environ. Sci. 4(9), 3680 (2011)

ELECTROCHEMICAL PERFORMANCE

$NaFePO_4$ (theoretical capacity of 154 mAh g^{-1})

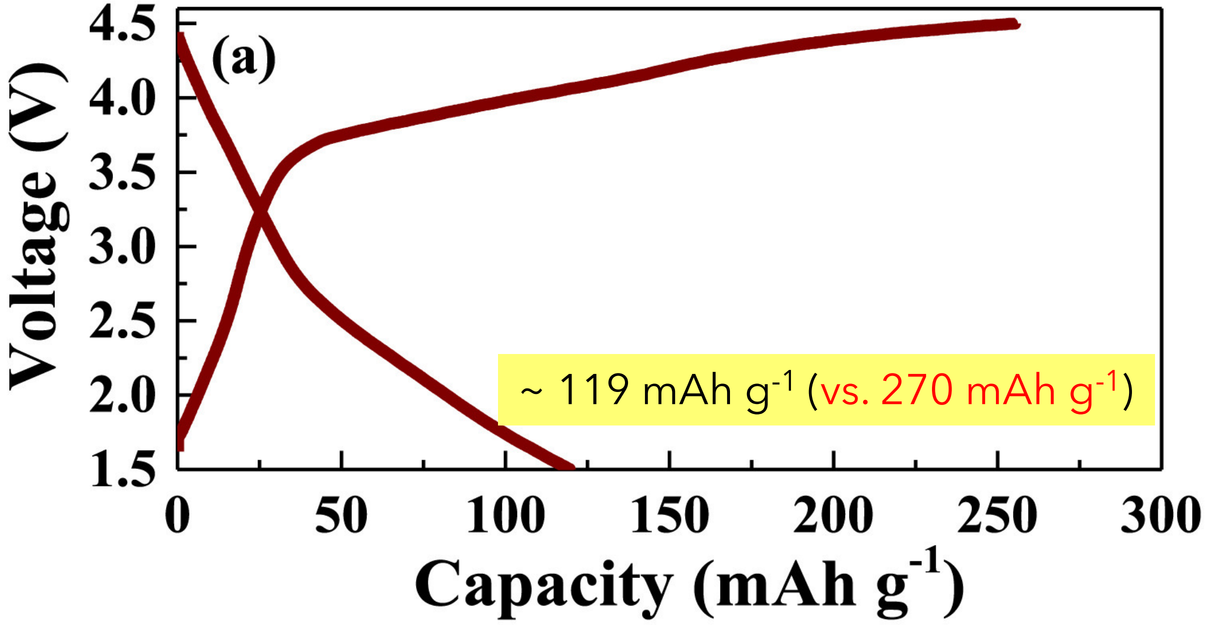


~ 2.7 V vs Na ($Fe^{3+/2+}$)
~ 125 mAh g^{-1} (vs. 154 mAh g^{-1})

Capacity fading after 50 cycles

S.M. Oh, et al. Electrochem. Commun. 22(1), 149 (2012)

Na_2FeSiO_4 (theoretical capacity of 270 mAh g^{-1})



~ 119 mAh g^{-1} (vs. 270 mAh g^{-1})

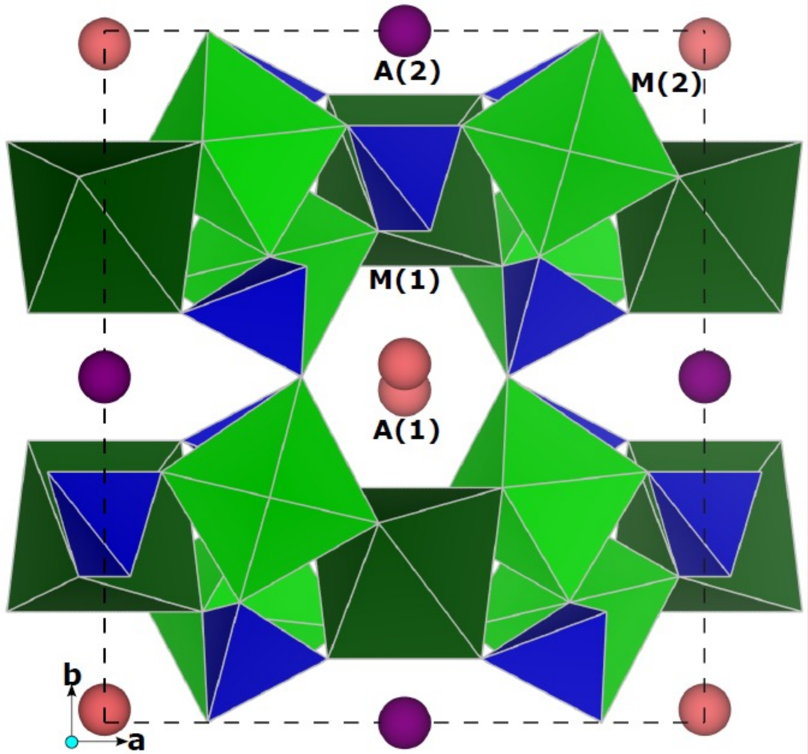
After the first cycle only 50% of Na-ion could be stored back;
Reducing the capacity to less than half

K. Kaliyappan, et al. Electrochim. Acta 283, 1384 (2018)

Much improvement needed for olivines

3

Alluaudites



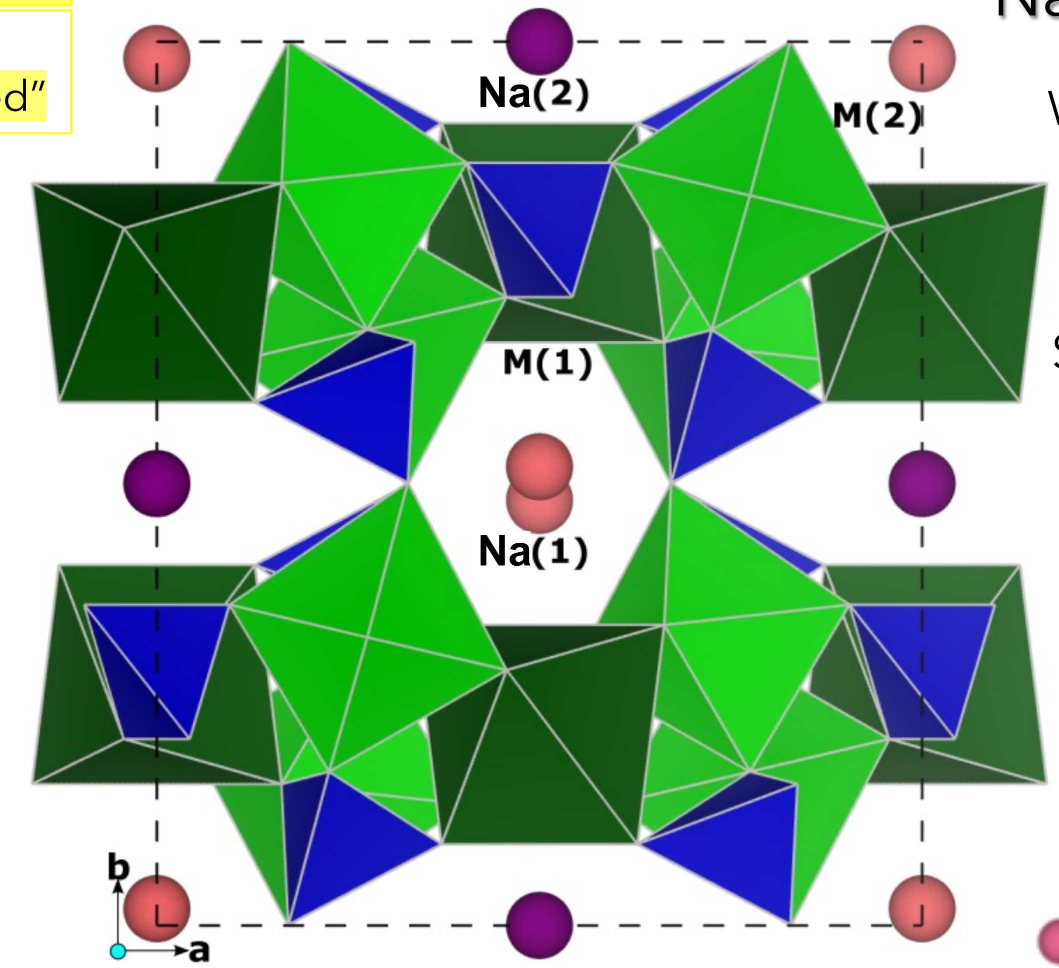
"Alluaudites are primarily phosphate-based minerals with a rigid "open" framework, suitable for Na (large ion) intercalation"

STRUCTURE & MIGRATION

1D "tunnel" along c-axis

~1.28 eV along tunnel_1 "Corners"
~0.31 eV along tunnel_2 "Edge-centred"

D. Dwibedi, et al. Electrochem. Acta 283, 850 (2018)



General formula:

$Na(2)Na(1)M(1)M(2)_2(PO_4)_3$

Where, M = Transition metal

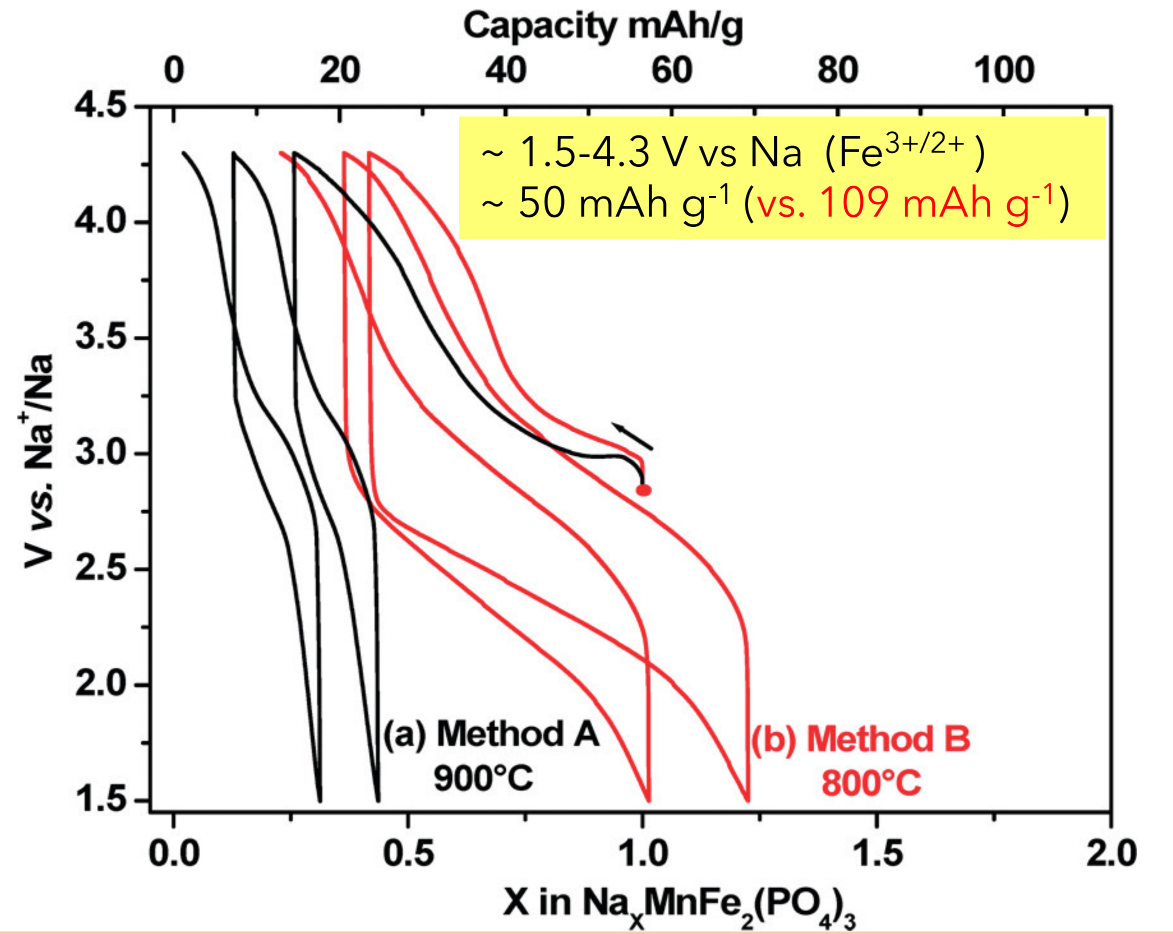
Symmetry: C2/c

Na1 (Wyckoff position: 4e)

Na2 (Wyckoff position: 4b)

ELECTROCHEMICAL PERFORMANCE

$Na_2MnFe_2(PO_4)_3$ (theoretical capacity of 109 mAh g^{-1})



K. Trad, et al. Chem. Mater. 22(19), 5554 (2010)

Other phosphate alluaudites reported

$Na_2Co_2Fe(PO_4)_3$	(Co-Fe)
$Na_2Ni_2Fe(PO_4)_3$	(Ni-Fe)
$Na_2Co_2Cr(PO_4)_3$	(Co-Cr)
$Na_{1.47}Fe_3(PO_4)_3$ $Na_{1.86}Fe_3(PO_4)_3$	(Non-stoichiometric)

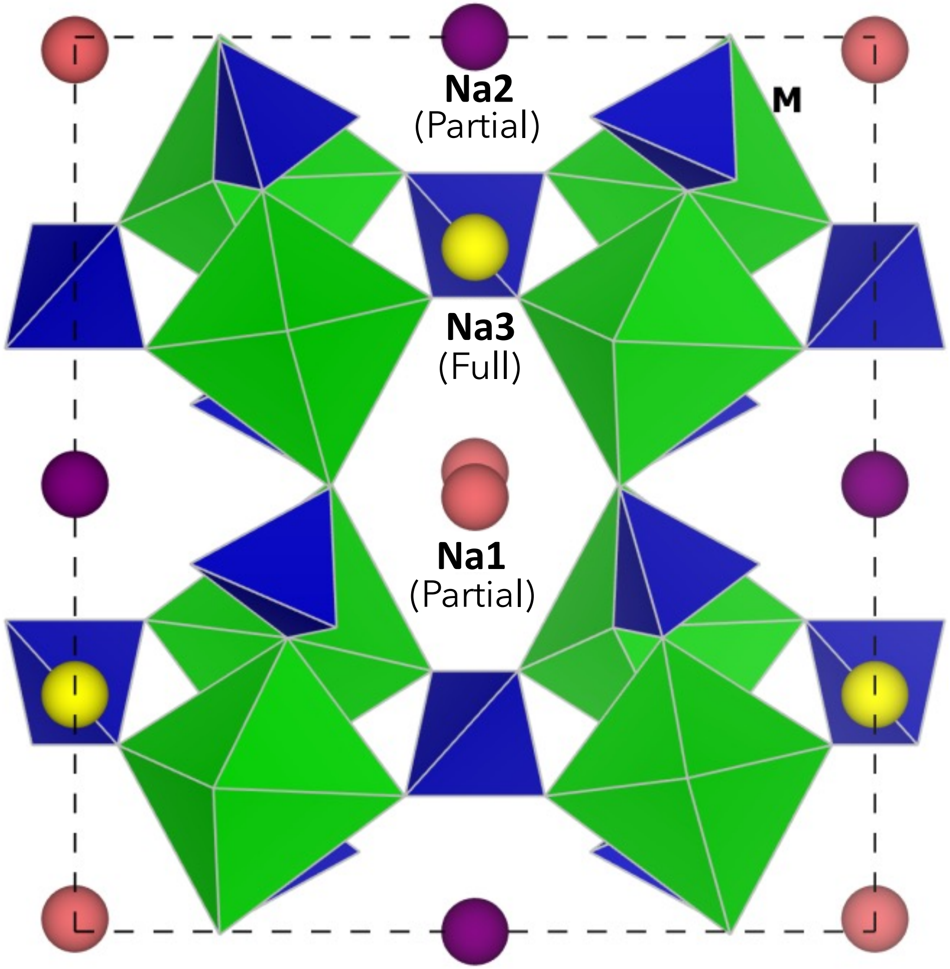
Associated with conversion reactions or electrolyte decomposition

Phosphate Alluaudites show POOR electrochemical performance.

SULPHATE ALLUAUDITES

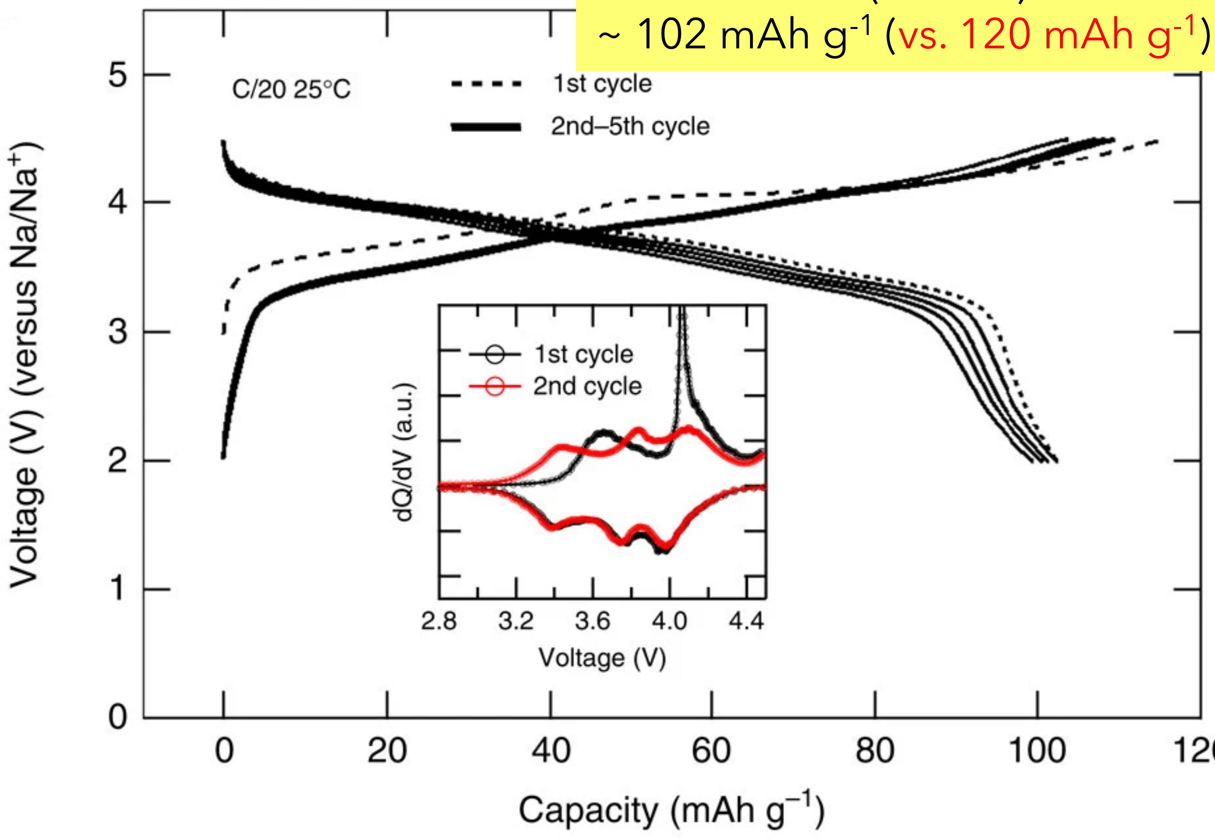
General formula:

$Na(2)Na(1)Na(3)M(2)_2(SO_4)_3$



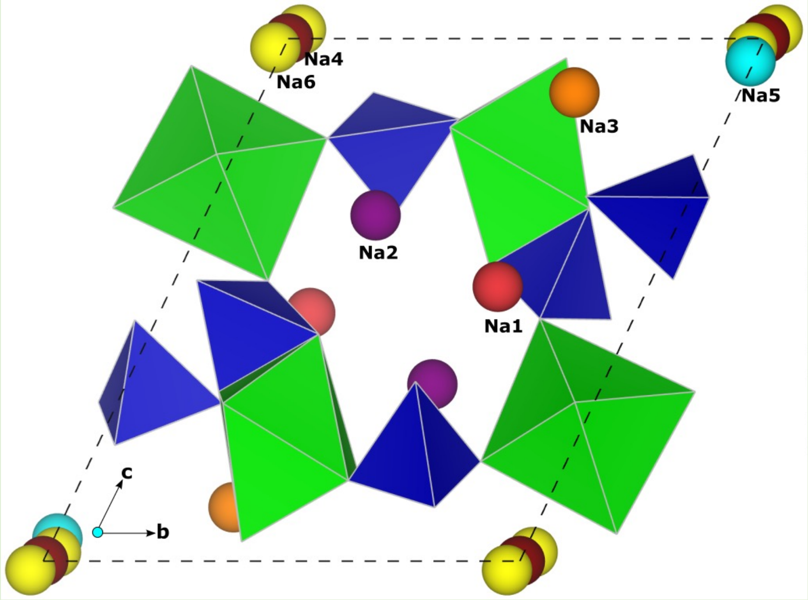
$Na_2Fe_2(SO_4)_3$ (theoretical capacity of 120 mAh g^{-1})

~ 3.8 V vs Na ($Fe^{3+/2+}$)
~ 102 mAh g^{-1} (vs. 120 mAh g^{-1})



Sulfate alluaudites are more promising than phosphate alluaudites

4 Pyro- phosphates



"Pyrophosphates exhibit better thermal stability and resistance to oxygen evolution and moisture exposure as compared to others"

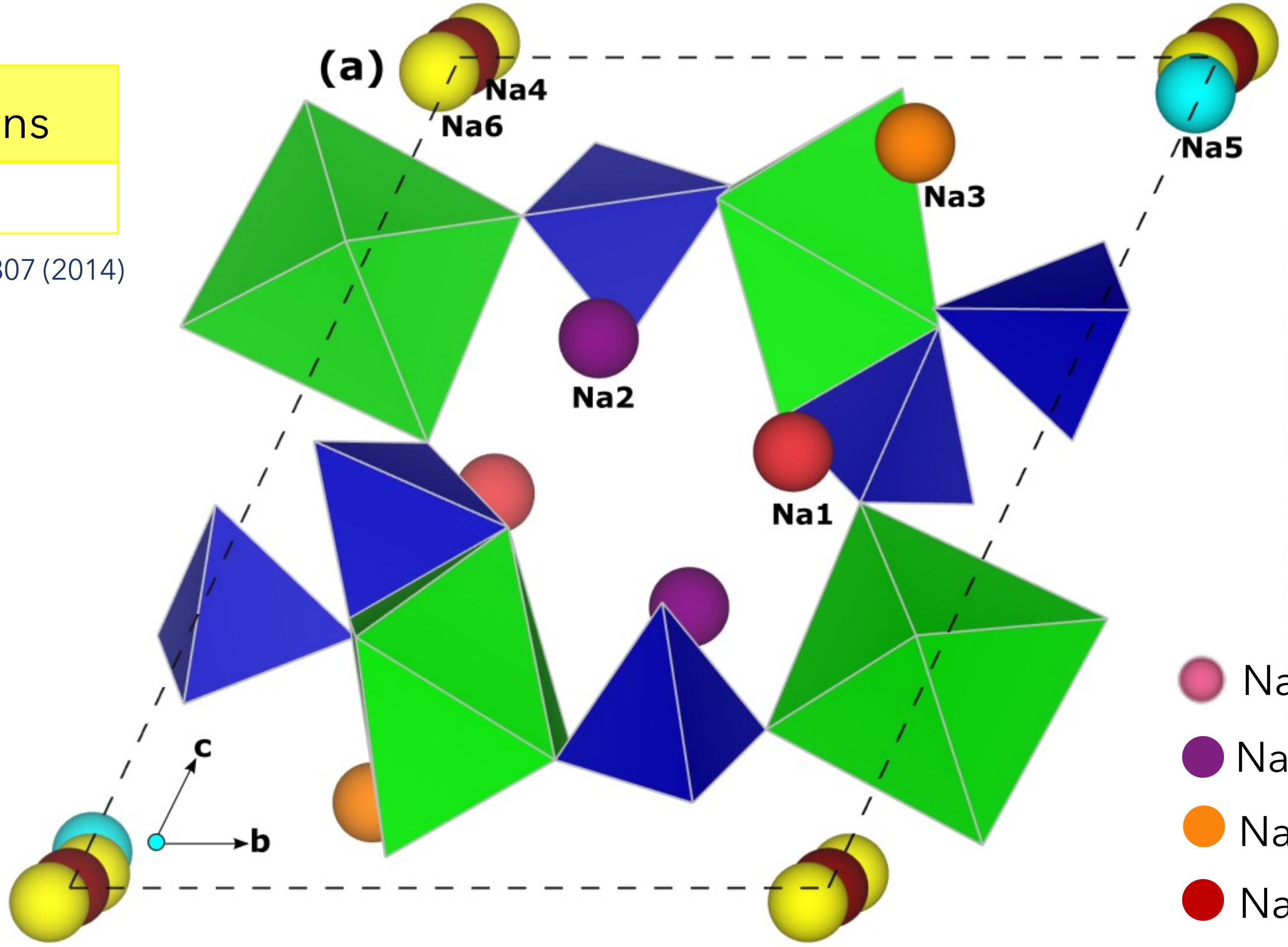
STRUCTURE & MIGRATION

Along the three directions

~0.33-0.5 eV

J.M. Clark, et al. J. Mater. Chem. A 2(30), 11807 (2014)

$P\bar{1}$ $Na_2Fe_2P_2O_7$



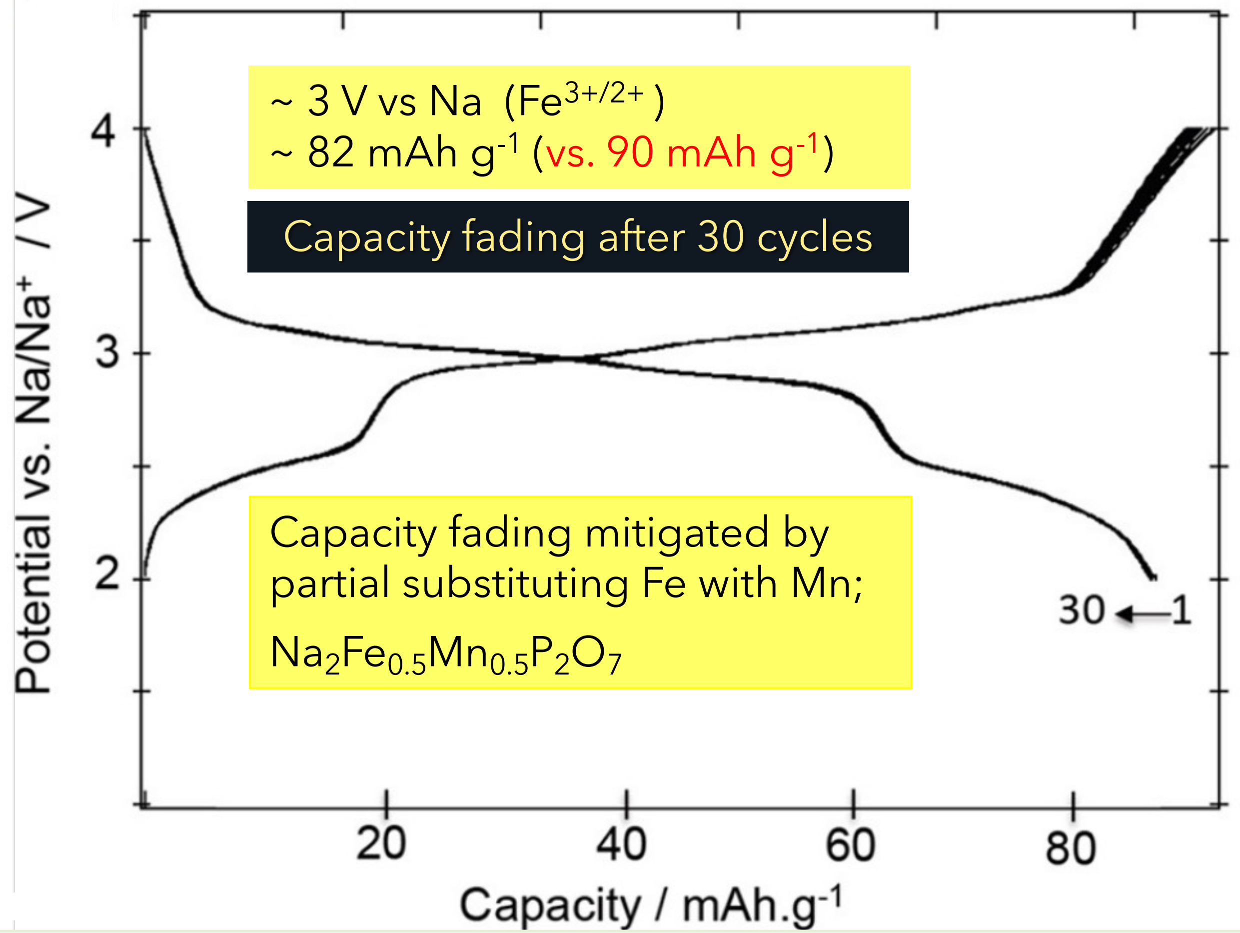
Symmetry

$Na_2Fe_2P_2O_7$	($P1$ or $P\bar{1}$)
$Na_2Mn_2P_2O_7$	($P1$ or $P\bar{1}$)
$Na_xCo_2P_2O_7$	($P1$ or $P\bar{1}$)
	($P4_2/mnm$, $Pna2_1$)

	Na Occupancy
Na1 (Wyckoff position: 2i)	Full
Na2 (Wyckoff position: 2i)	Full
Na3 (Wyckoff position: 2i)	Full
Na4 (Wyckoff position: 1d)	Partial
Na5 (Wyckoff position: 2i)	Partial
Na6 (Wyckoff position: 2i)	Partial

ELECTROCHEMICAL PERFORMANCE

P$\bar{1}$ $Na_2Fe_2P_2O_7$ (theoretical capacity of 90 mAh g^{-1})



P. Barpanda, et al. Electrochem. Commun. 24(1), 116 (2012)

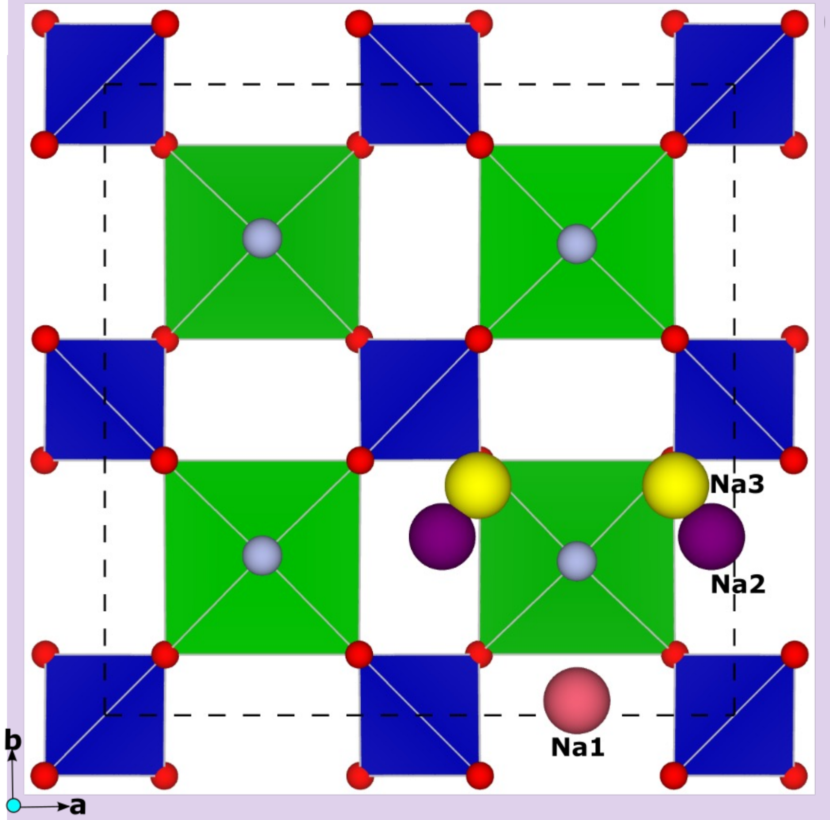
Na-excess pyrophosphate: Reasonable performance

$Na_{3.12}Mn_{2.44}(P_2O_7)_2$ displays:

- ✓ 114 mAh g^{-1} (vs 118 mAh g^{-1})
- ✓ 3.6 V vs Na ($Mn^{3+/2+}$)
- ✓ 75% capacity retention (500 cycles at 5 C)

5

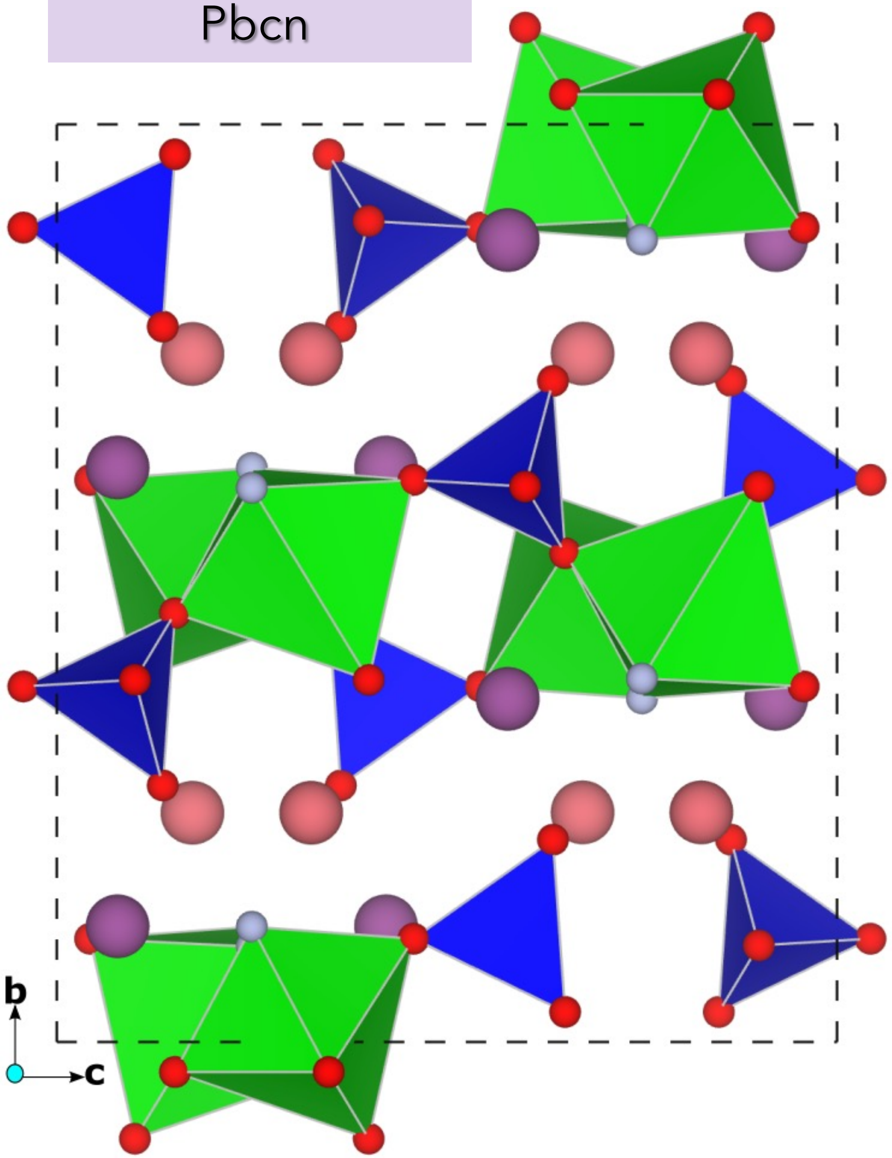
Fluoro-polyanions



"The addition of fluorine as an anion, within oxide-based polyanionic frameworks, can elevate the intercalation voltage due to the stronger inductive effect exerted by $\boldsymbol{F^-}$ than $\boldsymbol{O^{2-}}$"

STRUCTURE

Pbcn



General formula: Na_2MXO_4F

Where, M = Transition metal

X = P^{5+}or S^{6+}

Symmetry: C2/c

Pbcn

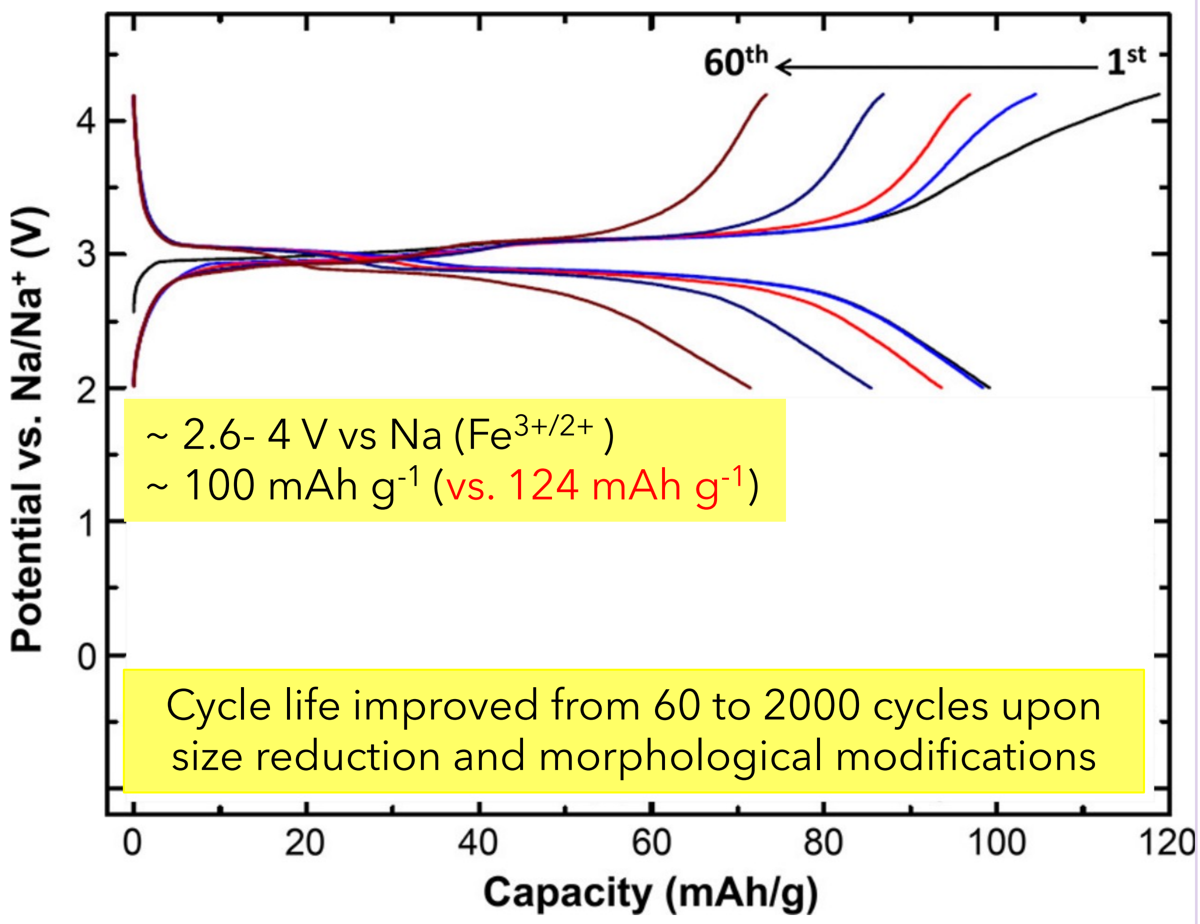
P4/mmm

Na1 (Wyckoff position: 8d)

Na2 (Wyckoff position: 8d)

ELECTROCHEMICAL PERFORMANCE

$Na_2Fe(PO_4)F$ (theoretical capacity of 124 mAh g^{-1})

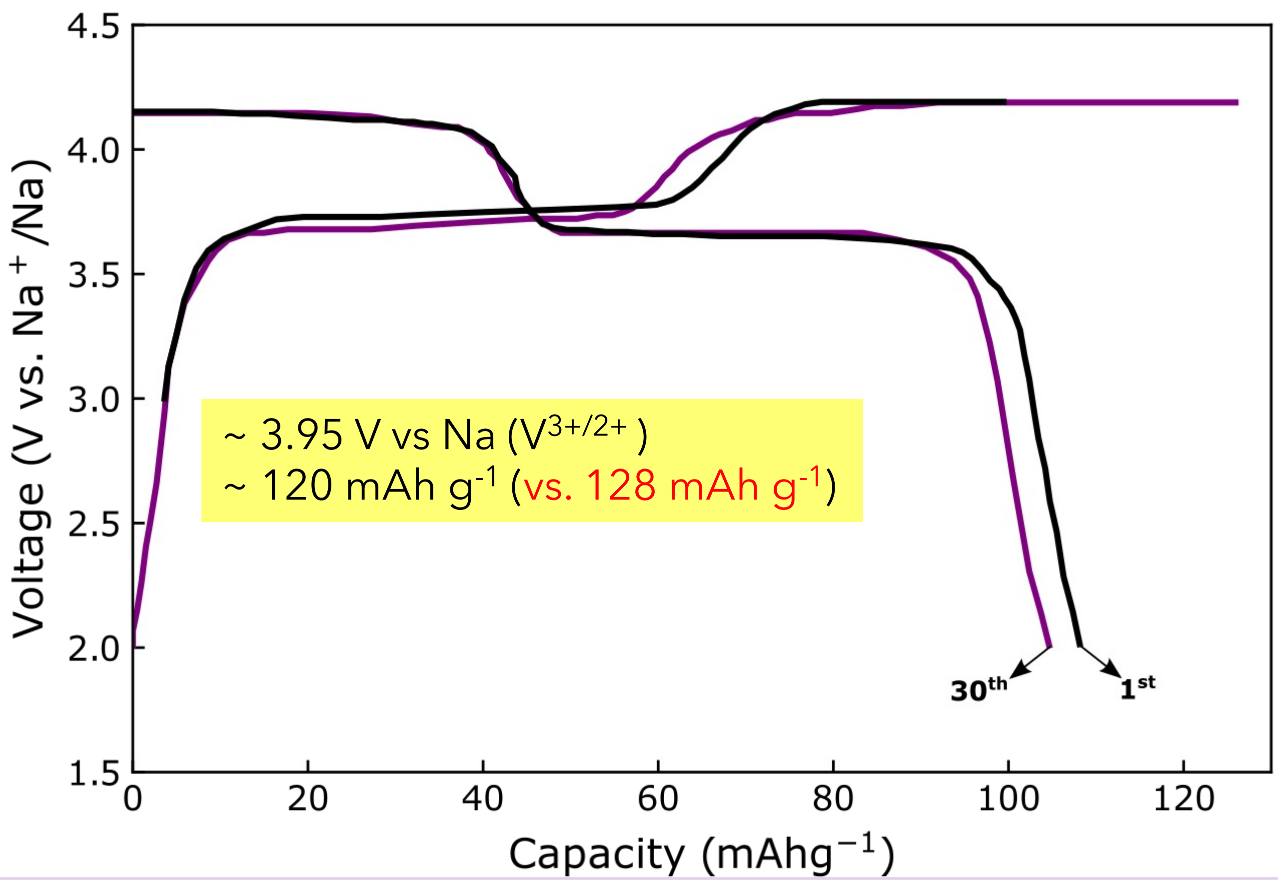


~ 2.6- 4 V vs Na ($Fe^{3+/2+}$)
~ 100 mAh g^{-1} (vs. 124 mAh g^{-1})

Cycle life improved from 60 to 2000 cycles upon size reduction and morphological modifications

L. Sharma, et al. ACS Appl. Mater. Interfaces 9(40), 34961 (2017)

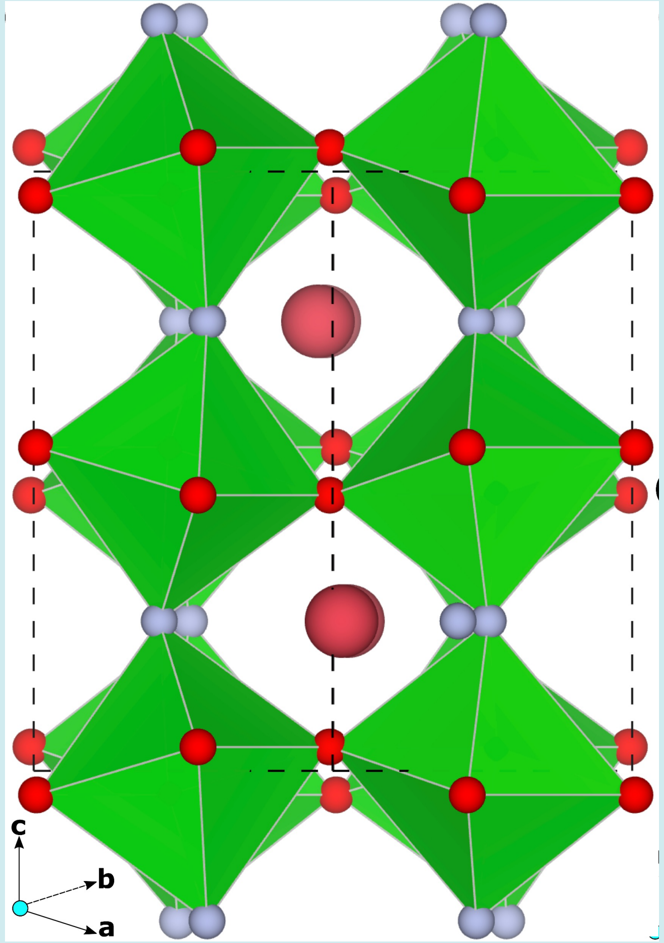
$Na_3V_2(PO_4)_2F_3$ (theoretical capacity of 128 mAh g^{-1})



~ 3.95 V vs Na ($V^{3+/2+}$)
~ 120 mAh g^{-1} (vs. 128 mAh g^{-1})

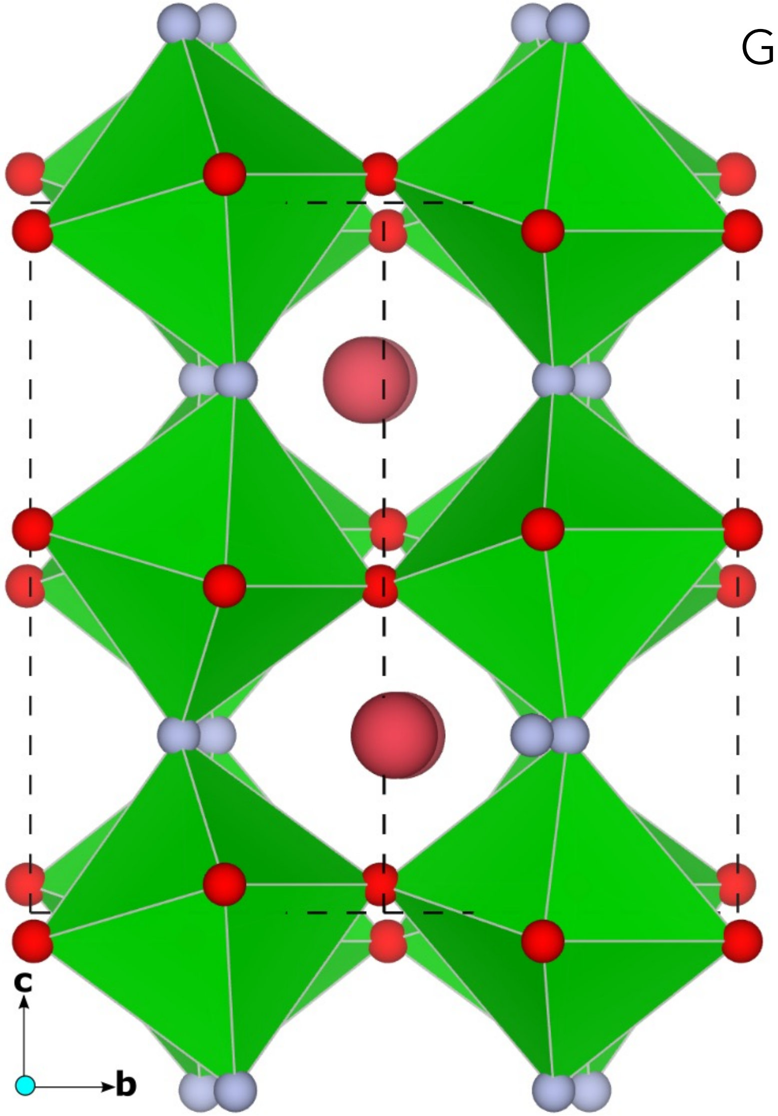
Na-excess fluorophosphate seems BETTER battery cathode than fluorophosphates

6 Perovskites



"The typical ReO_3-type perovskites are ideal frameworks to fit in large ions like Na"

STRUCTURE



General formula: $NaMO_xF_{3-x}$

Where, M = Transition metal

Symmetry: Pmna

This class of compounds needs due attention of the research community

Na1 (Wyckoff position: 4c)

CONCLUSION

STRUCTURE	AVERAGE VOLTAGE (V)	REPORTED VS. THEORETICAL CAPACITY (mAh g^{-1})	% THEORETICAL CAPACITY ACHIEVED	CYCLES @ CAPACITY FADE (%)	REFERENCES
NaSICON	3.4	114.2 (117)	97	10000 (48%)	Y. Zhao, et al. Chem. Eng. J. 339, 162 (2018)
Olivine	2.7	125 (154)	81	50 (8%)	S.M. Oh, et al. Electrochem. Commun. 22(1), 149 (2012)
Alluaudite	3.8	107.9 (120)	90	300 (10%)	M. Chen, et al. Adv. Energy Mater. 8(27), 1800944 (2018)
Pyro-phosphate	3.6	114 (118.1)	96.6	500 (25%)	H. Li, et al. ACS Appl. Mater. Interfaces 10(29), 24564 (2018)
Fluoro-polyanion	3.95	114 (128.3)	88.85	1000 (25%)	C. Zhu, et al. Chem. Mater. 29(12), 5207 (2017)

NaSICONs & Na-excess fluorophosphates appear highly promising Na-ion battery cathodes

Persistent and ongoing challenges:

Poor electronic conductivity: causing poor cycling performance

Lower theoretical capacities (compared to layered oxide framework)

- +

Possible strategies to overcome the challenges

Applying & improving electron-conducting coatings & size reduction

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

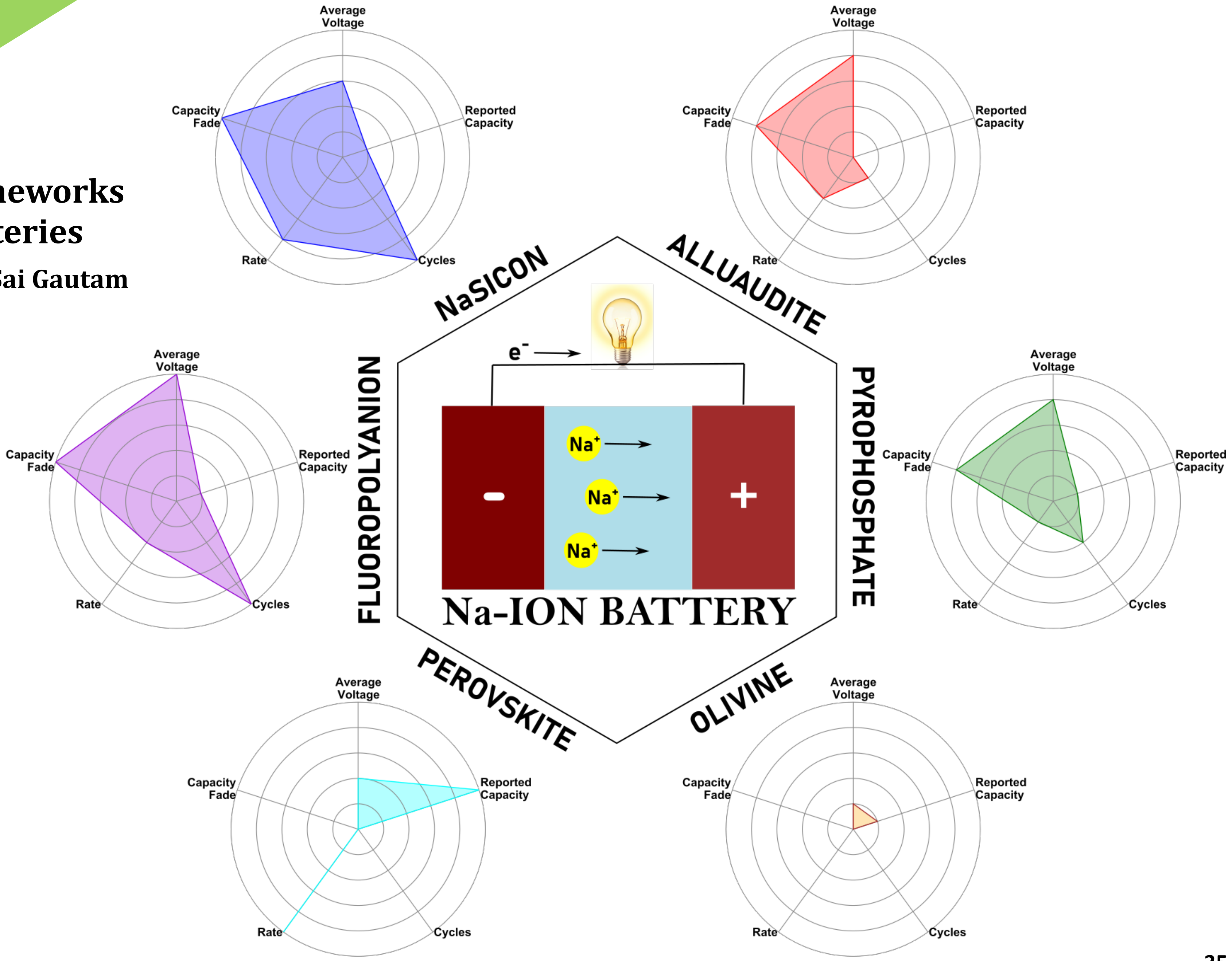
These strategies may aid the search for next generation of Na-ion battery, powered by polyanionic cathodes.

My Work

Journal of MATERIALS RESEARCH

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

-Debolina Deb, Gopalakrishnan Sai Gautam



ACKNOWLEDGEMENT

Simulations And Informatics of MATerials Group

Materials Engineering Department, IISc

Param Pravega

Supercomputer Education and Research Centre (SERC), IISc