Crystal Structure Prediction for Low-Cost Battery Materials

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ESDG Presentation

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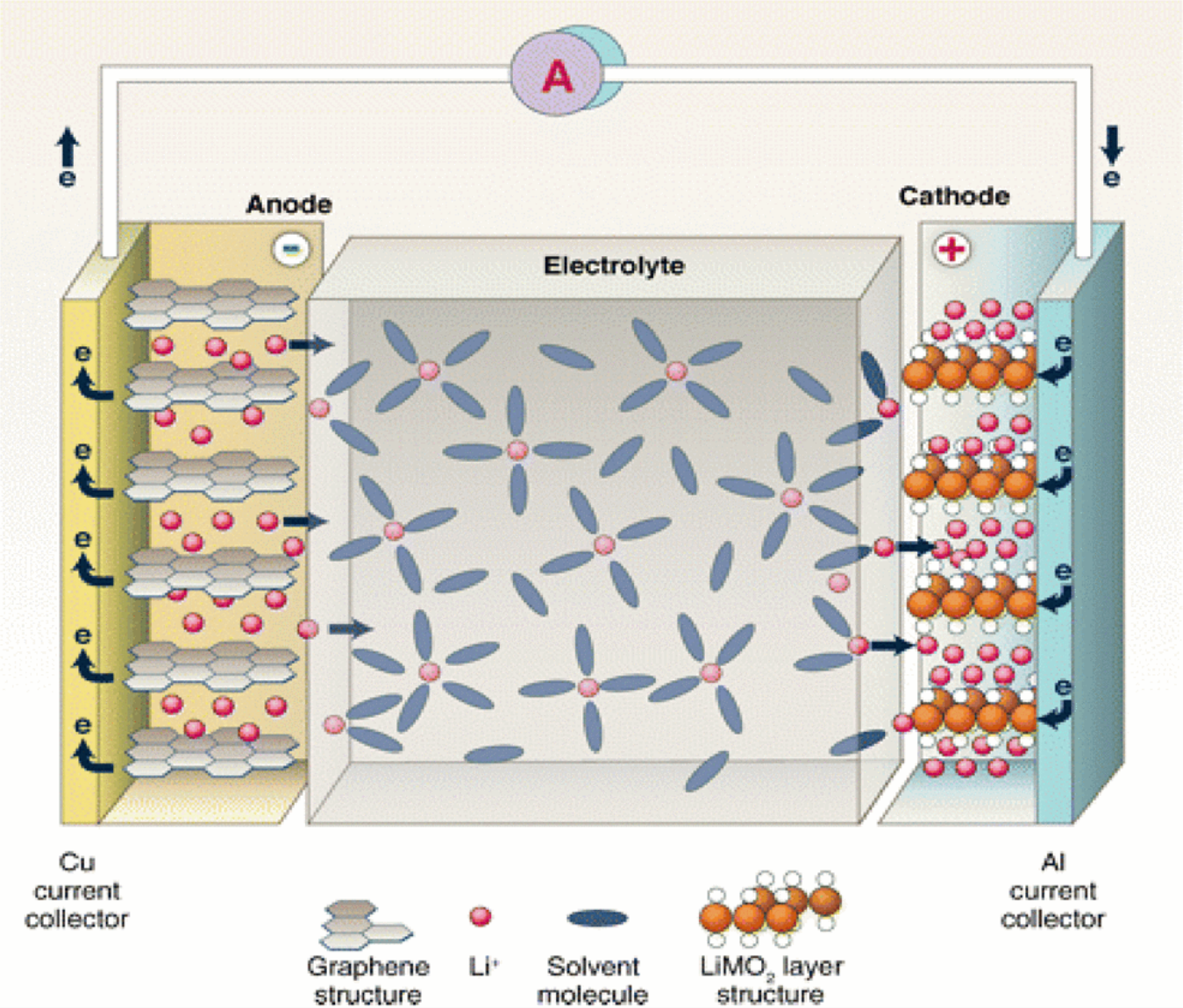
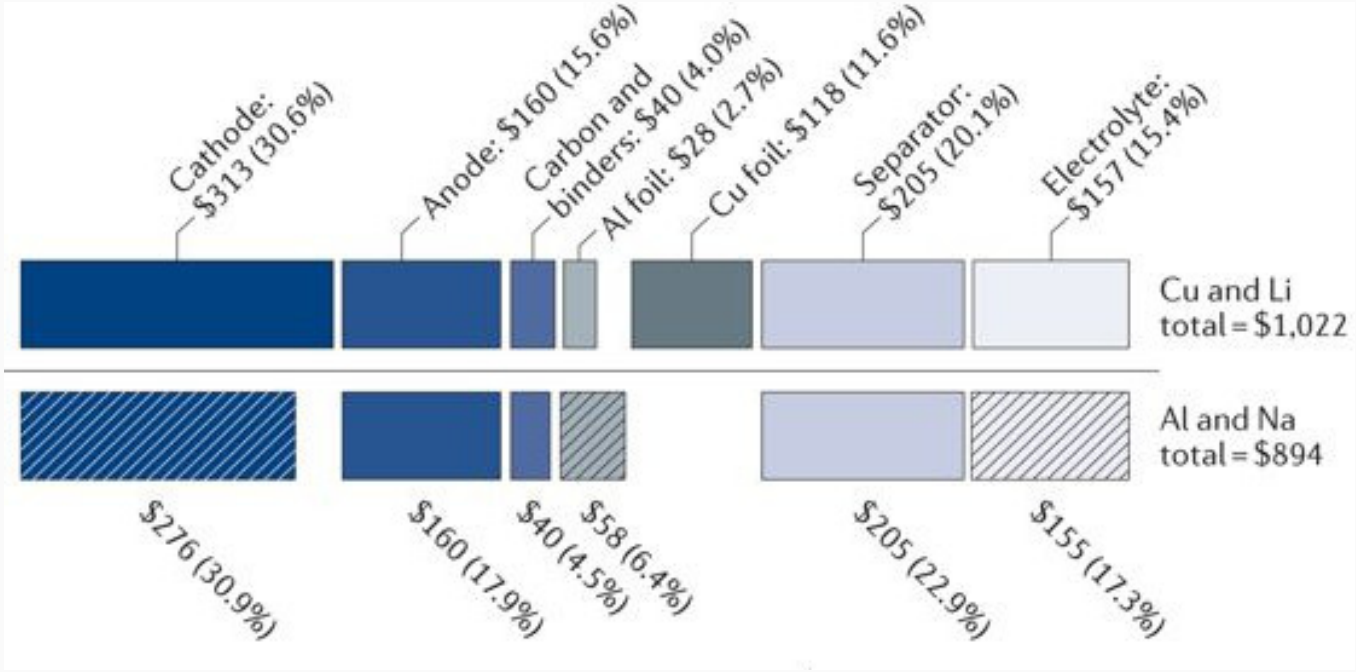
Li-ion battery



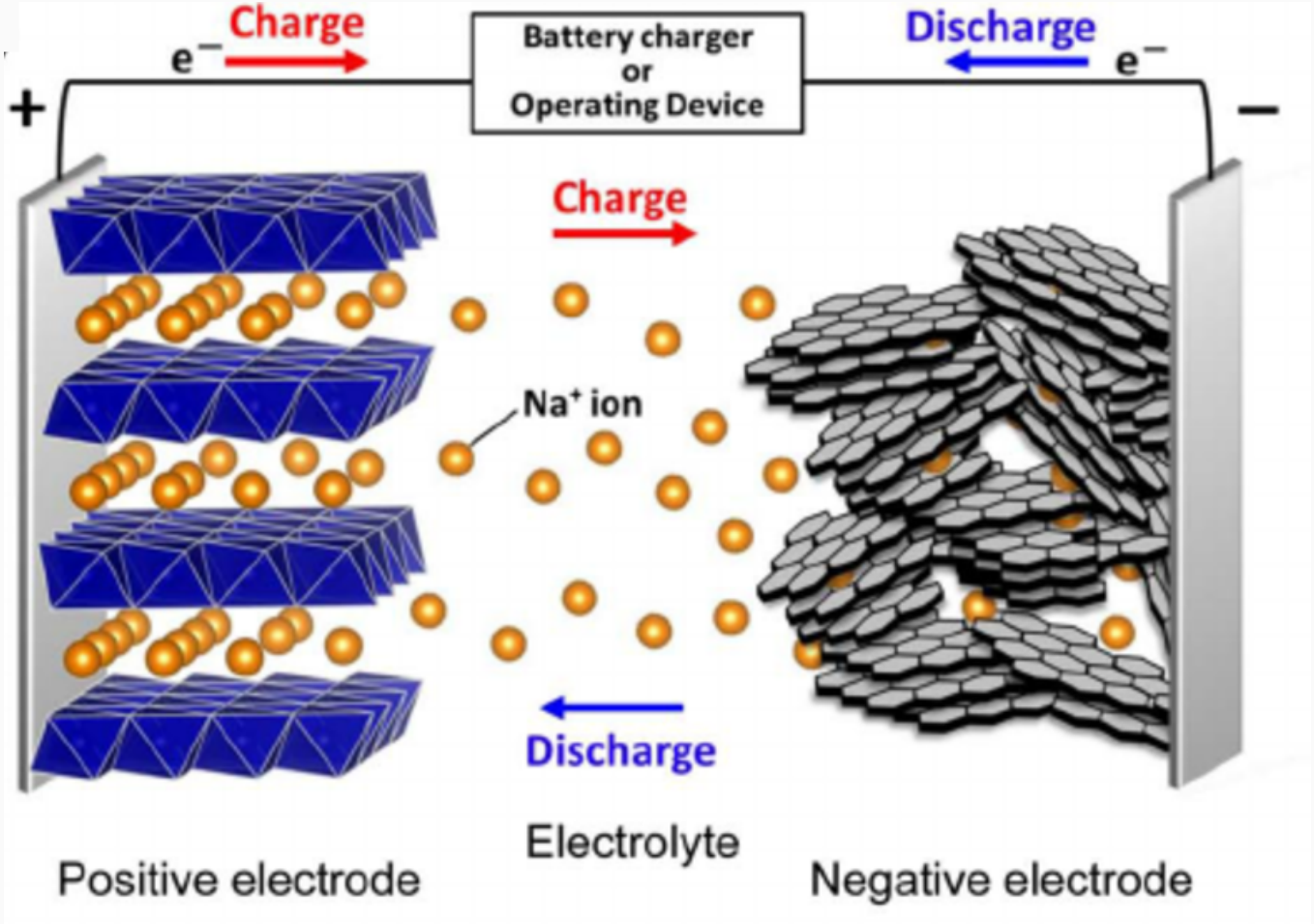
The cost of Li-ion



The Cu current collector and rare earth metal cathode contribute most to the overall battery cost

Nature Reviews Materials, **3**, 18013 (2018)

Na-ion batteries

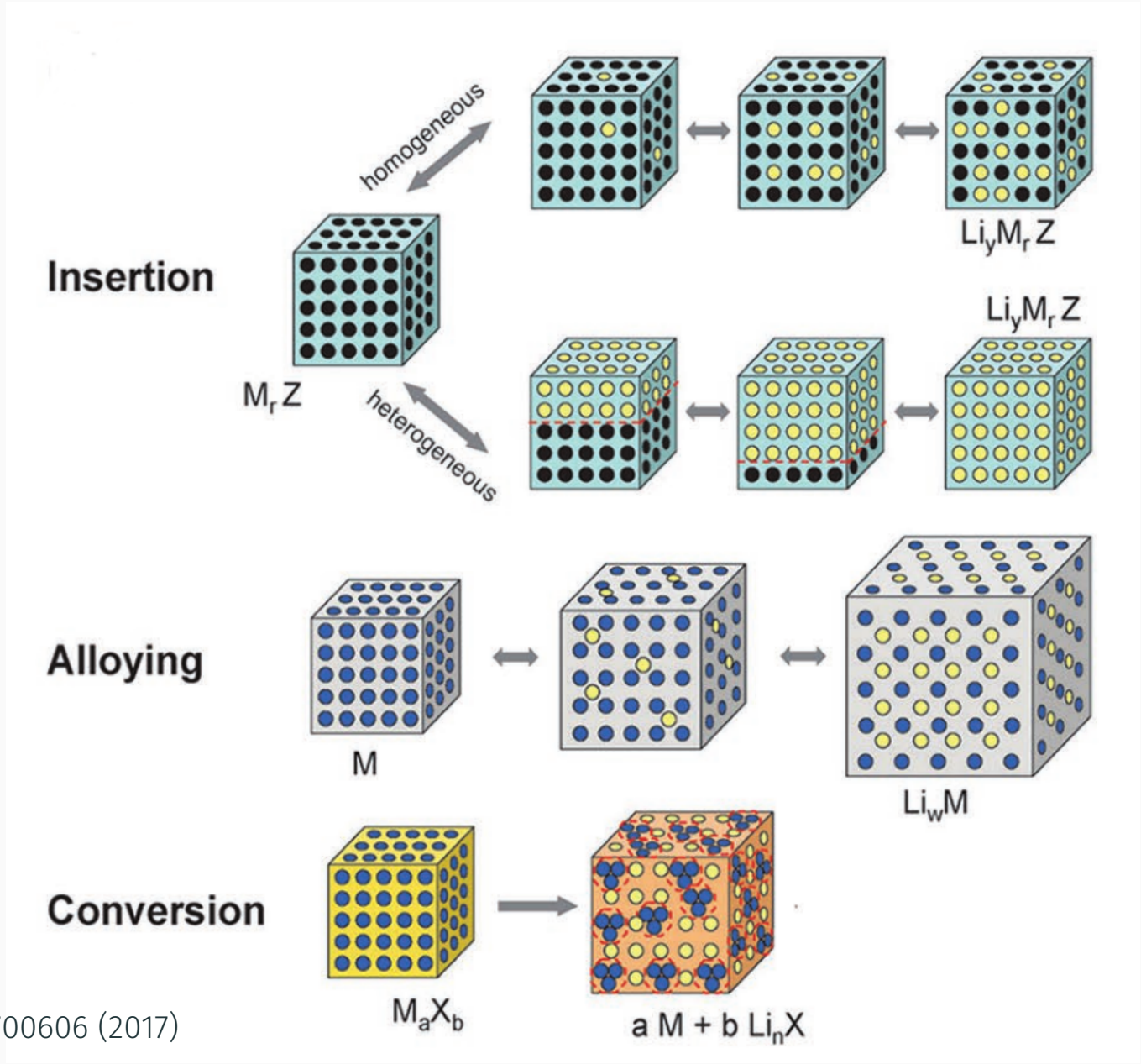


J. Electrochem. Soc. , **162**, 14 (2015)

Na-ion challenges

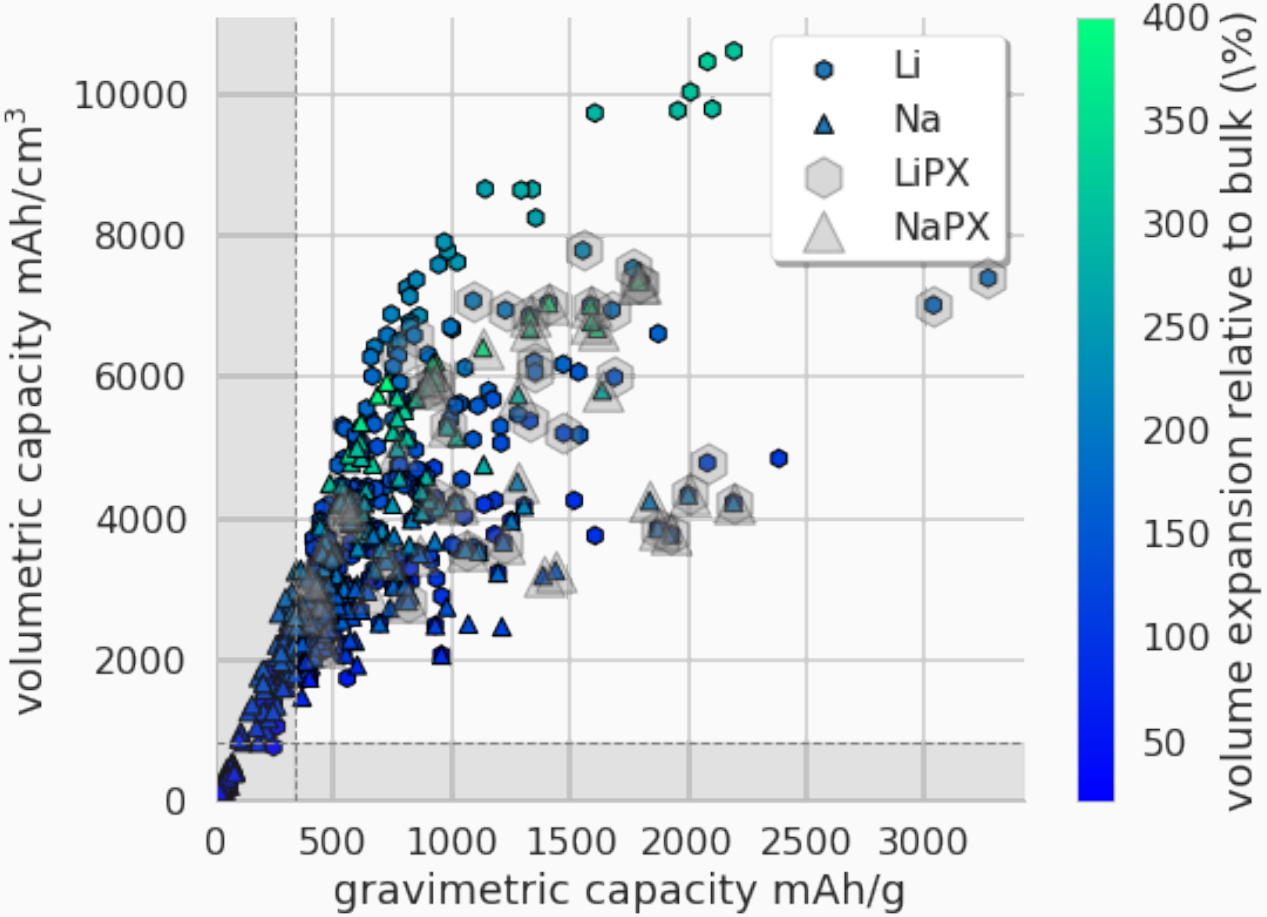
- Na^+ does not intercalate into graphite
- Large Na^+ ions decrease cycling capability
- Na-ion batteries have lower energy densities than Li-ion

Anode options



Adv.Mater. **29**, 1700606 (2017)

High capacity anodes



Iron phosphide anodes in Li and Na batteries

- Li-ion batteries show conversion reactions between FeP + Li and FeP_2 + Li
- The conversion mechanism for FeP_4 is not yet known for Li or Na-ion batteries
- FeP_4 shows good reactivity vs. Li with a capacity of 1137 mAh/g

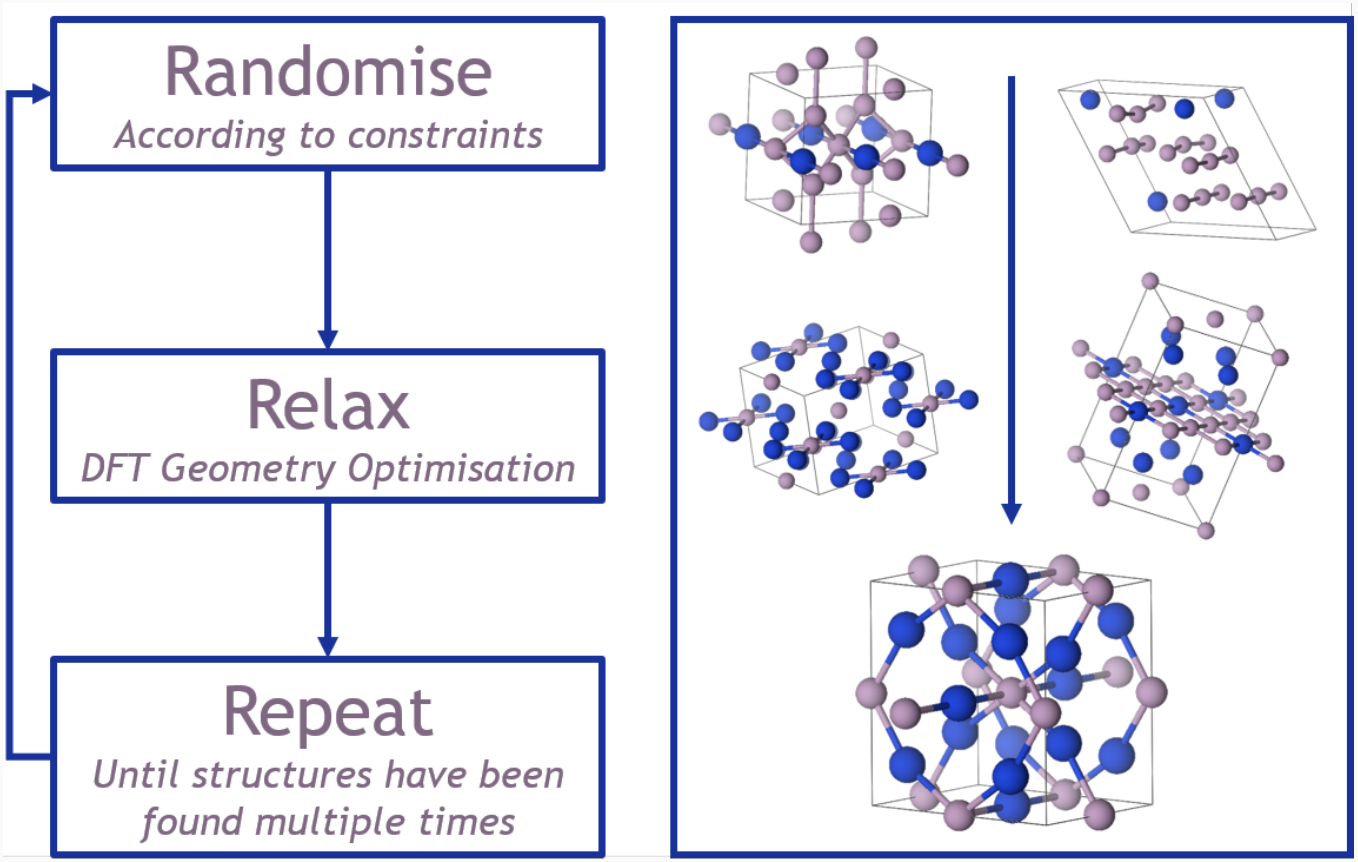
Electrochem. Comm., **69** 11–14 (2016)

Question

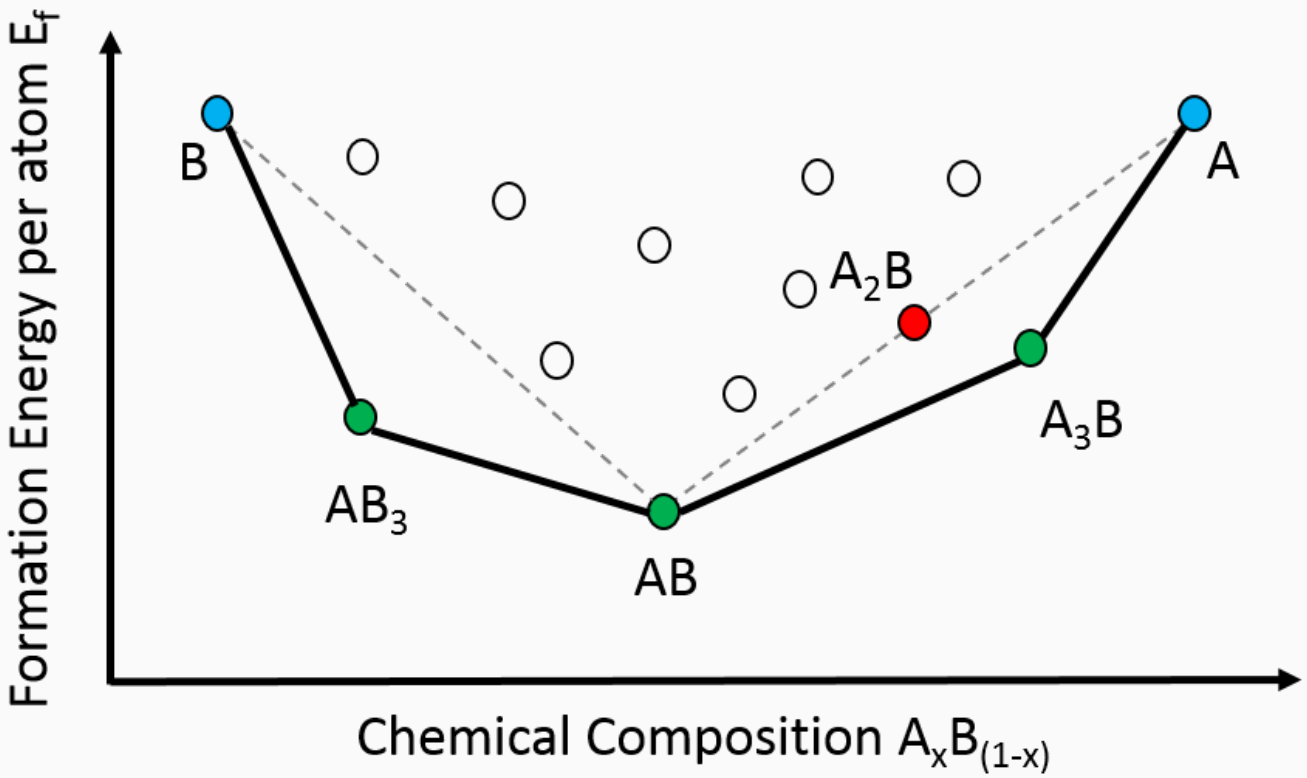
What are the steps of sodiation from iron phosphide, specifically FeP_4, to Na?
Are there any other high capacity anodes in this system?

Crystal structure prediction

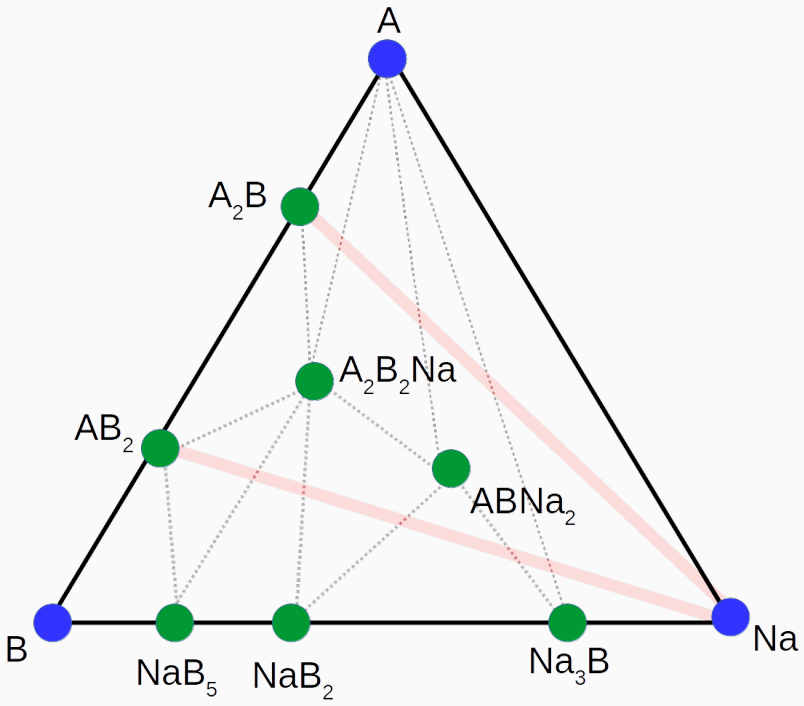
AIRSS


Randomise
According to constraints
Relax
DFT Geometry Optimisation
Repeat
Until structures have been found multiple times

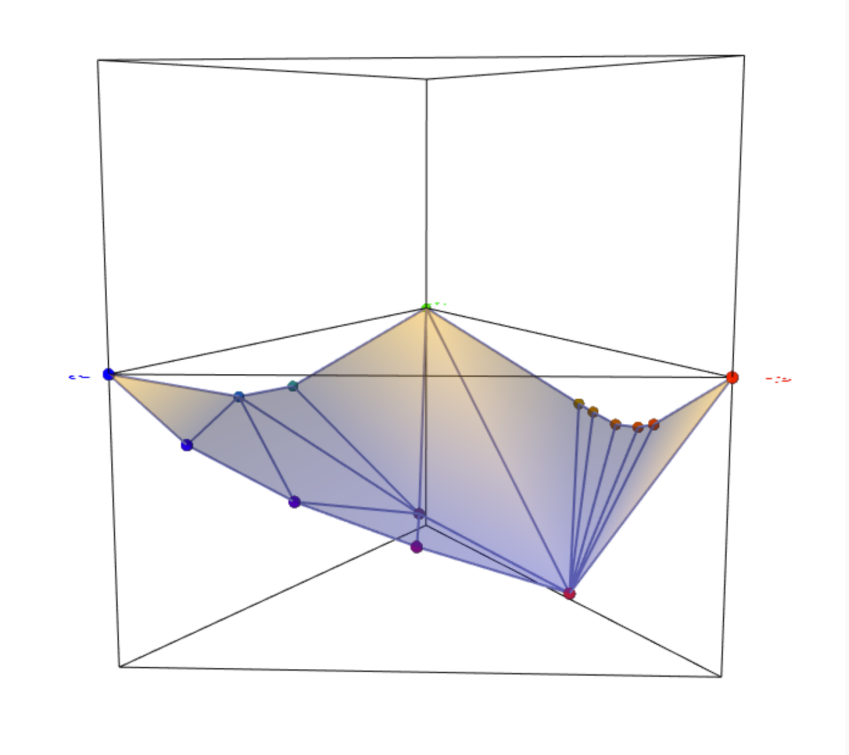
Binary phase diagram



Ternary phase diagram



2D ternary phase diagram



3D ternary phase diagram

Ternary voltage profile

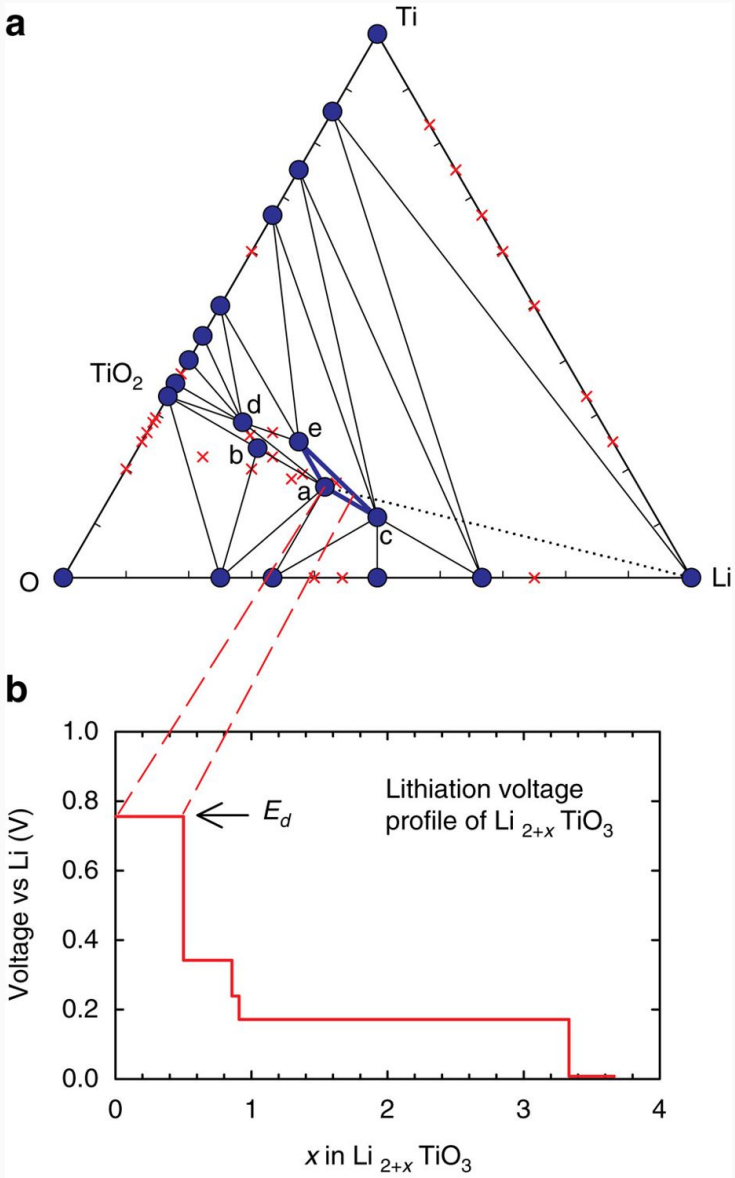
The electrical energy upon charging from $Na_{x_1}AB$ to $Na_{x_2}AB$:

$$\begin{aligned} E &= -\int_{x_1}^{x_2} [\mu_{Na}(x) - \mu_{Na}^0] dx_{Na} \\ &= -[G_{Na_{x_2}AB} - G_{Na_{x_1}AB} - (x_2 - x_1)G_{Na}] \\ &\equiv -\Delta G_{rxn} \end{aligned} \tag{1}$$

So the voltage drop between these two compounds is:

$$V = \frac{-\Delta G_{rxn}}{(x_2 - x_1)F} \tag{2}$$

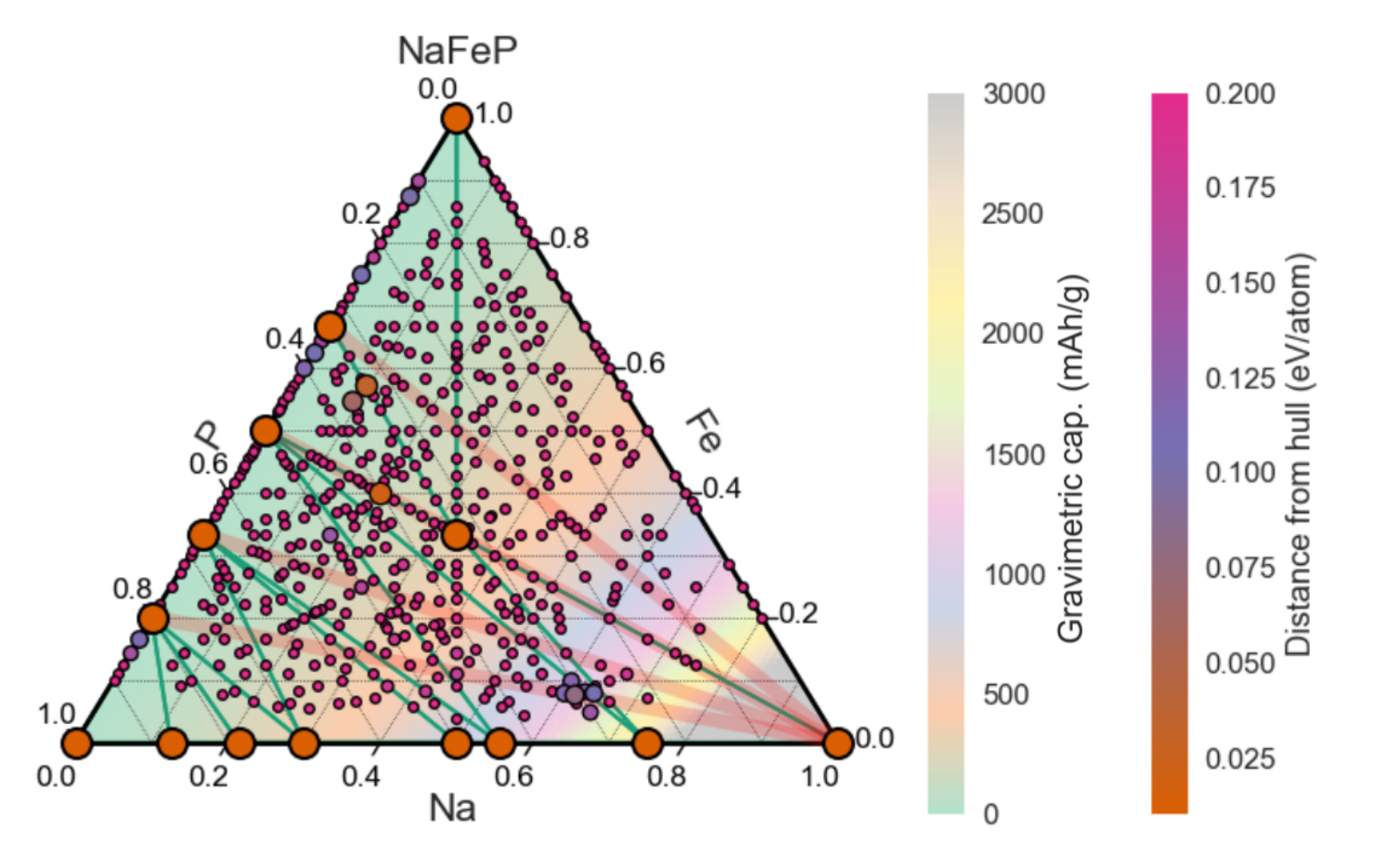
Ternary voltage profile



Nature Communications, **7**,13779 (2016)

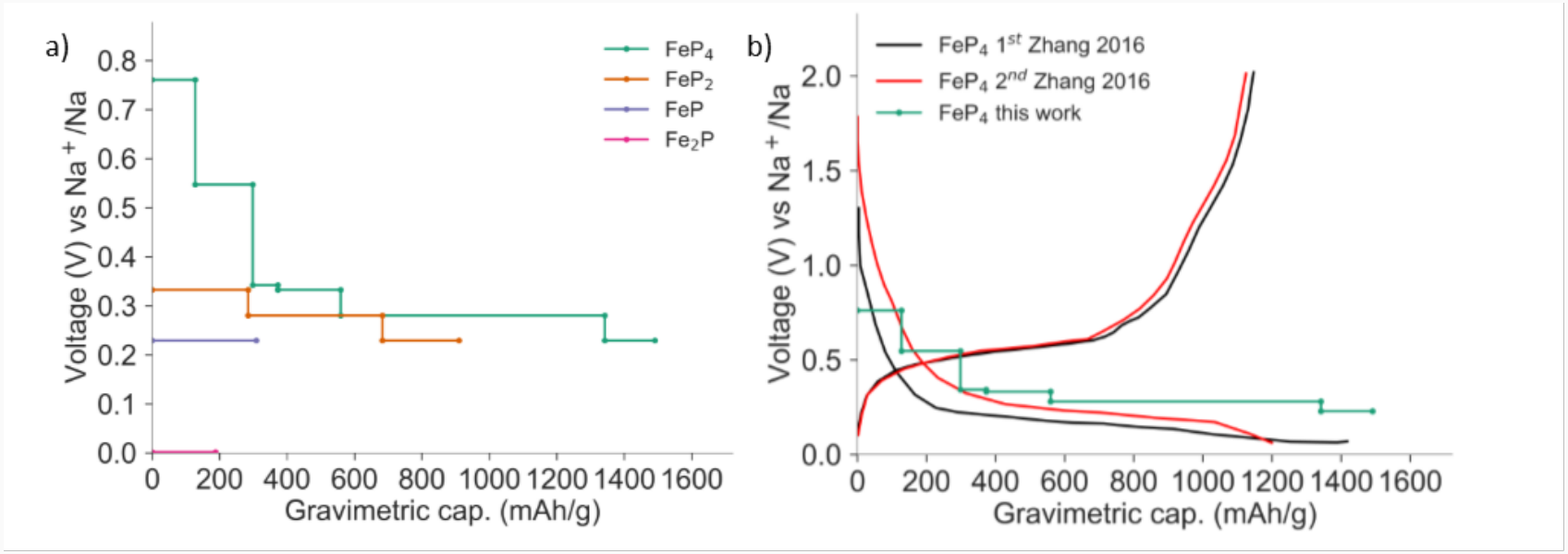
Iron phosphide anodes

Na+Fe+P ternary phase diagram



Phase diagram for 3,000 AIRSS-identified structures, including those found in the ICSD, OQMD, and Materials Project

FeP_4 comparison to experimental voltage profile

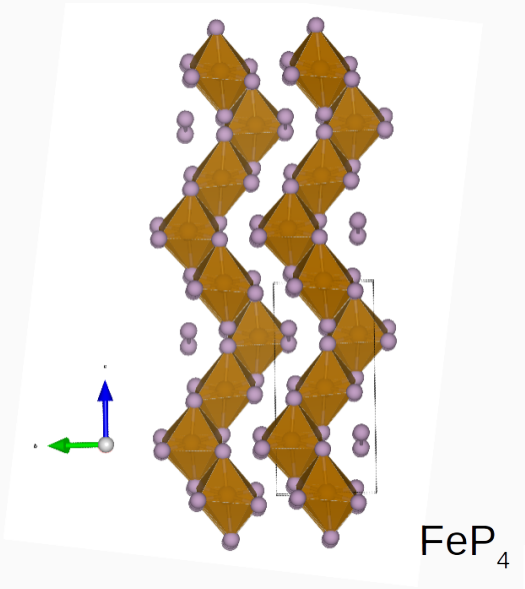


The green curve, FeP_4 shows good comparison with experiment, especially for the 1^{st} cycle of the Na-ion battery

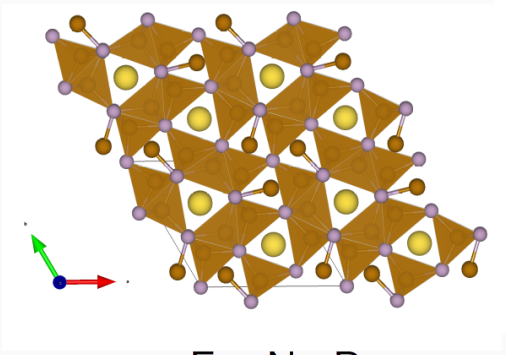
Reaction mechanism for FeP_4

$FeP_4 + 10Na \rightarrow Na_3P + NaFeP$		
Gravimetric Capacity (mAh/g)	Voltage (V)	Reaction
128	0.76	$FeP_4 + xNa \rightarrow Na_3P_7 + FeP_2$
298	0.54	$FeP_2 + Na_3P_7 + xNa \rightarrow NaP + FeP_2$
373	0.34	$FeP_2 + NaP + xNa \rightarrow Na_5P_4 + FeP_2$
559	0.33	$FeP_2 + Na_5P_4 + xNa \rightarrow Na_5P_4 + FeP$
1342	0.28	$FeP + Na_5P_4 + xNa \rightarrow FeP + Na_3P$
1491	0.23	$FeP + Na_3P + xNa \rightarrow Na_3P + NaFeP$

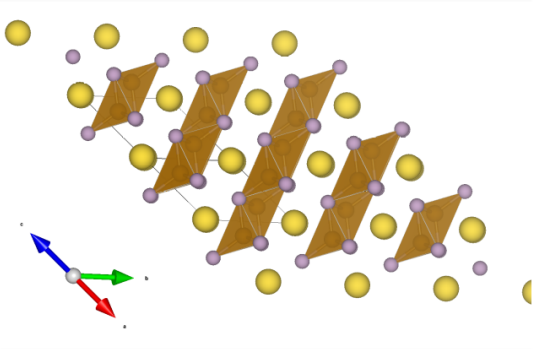
Layered FeP structures



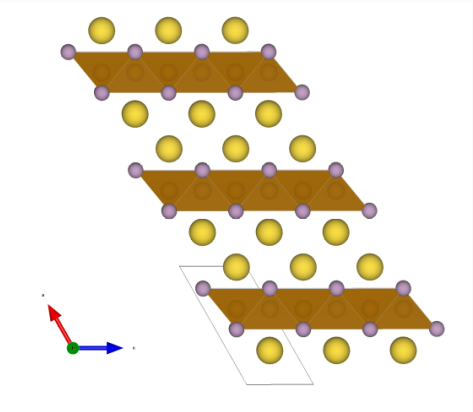
FeP_4



$Fe_{12}Na_2P_7$



Fe_2NaP_2



FeNaP

Upon sodiation it is possible a layered structure is formed suggesting an insertion mechanism for FeP_4

Future work

Future work

- Fully characterise the ternary system and complete AIRSS searches
- Understand the different ground state magnetic orderings
- Compare with more experimental data, and potentially translate to Li-ion batteries
- Make a temperature dependent voltage profile, or one that considers phases not on the convex hull