Atomistic modelling studies of electrode materials for rechargeable lithium and sodium batteries

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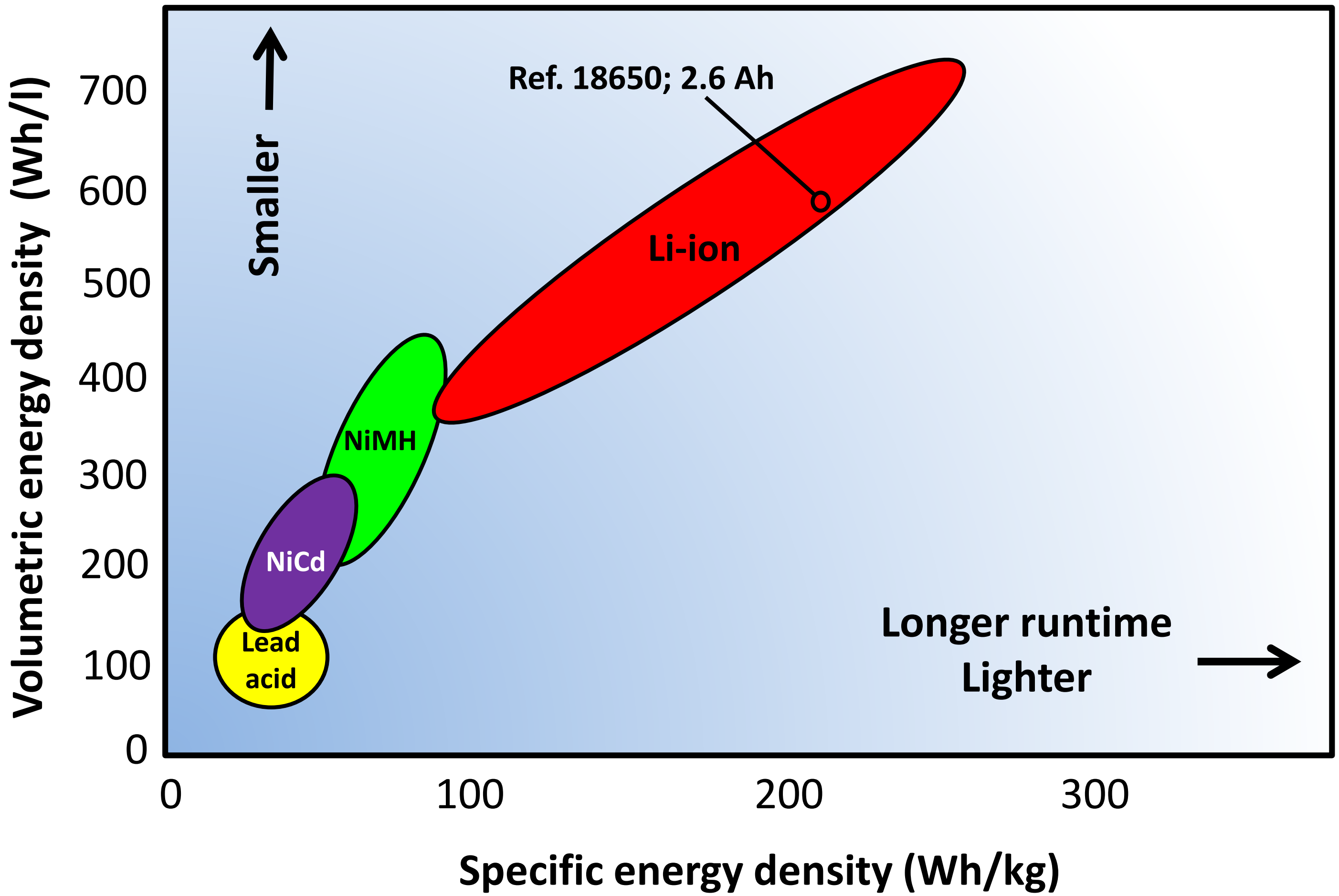
Advances in battery technology

Primarily driven factor: Improvement in energy density



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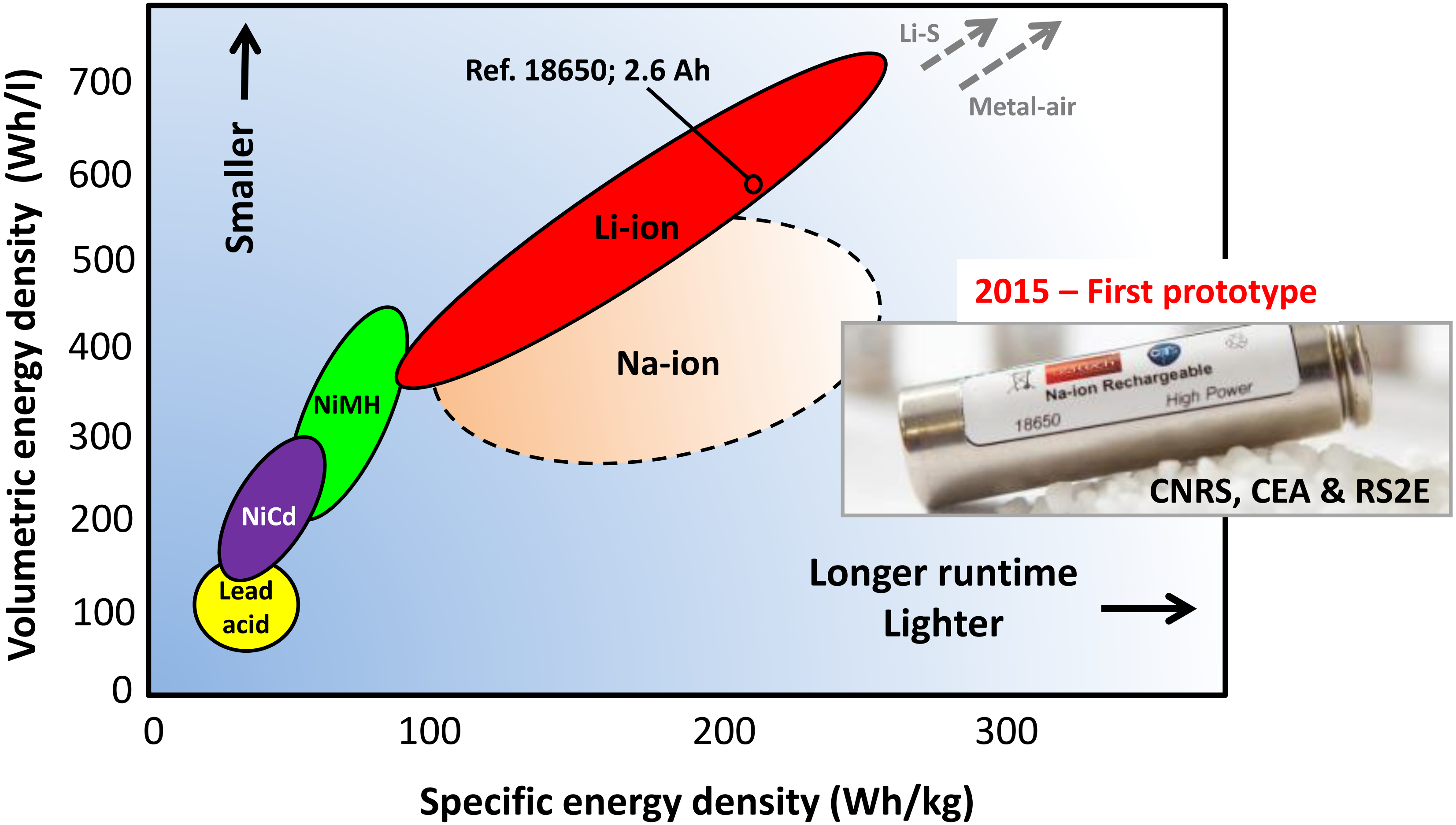
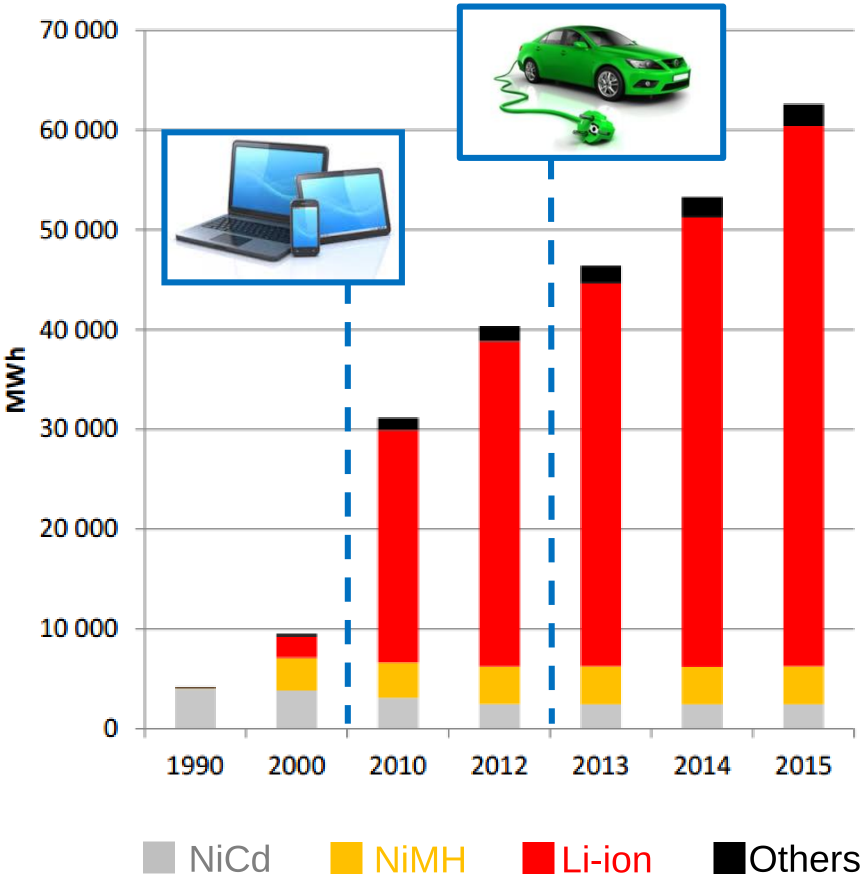


The “perfect battery” **doesn’t exist**, however the potential global impact that even **relatively moderate improvements** can have is astonishing

Electric Powered Vehicles: The rising trend

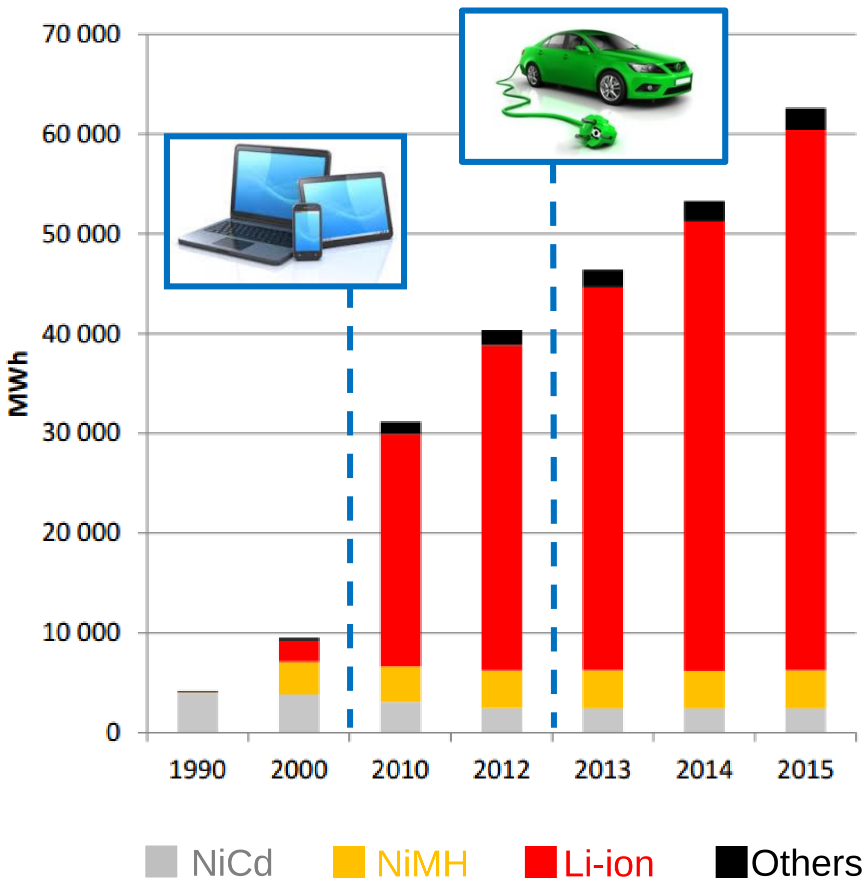


Source: AVICENNE ENERGY, 2015

Worldwide battery market

Historical evolution, future trends and new requirements

Electric Powered Vehicles: The rising trend



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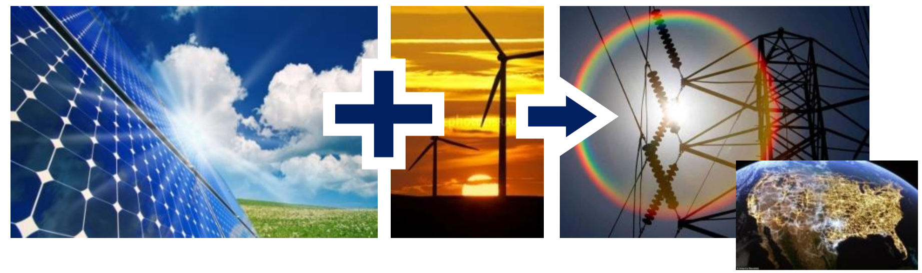
New applications: Stationary energy storage



Worldwide battery market

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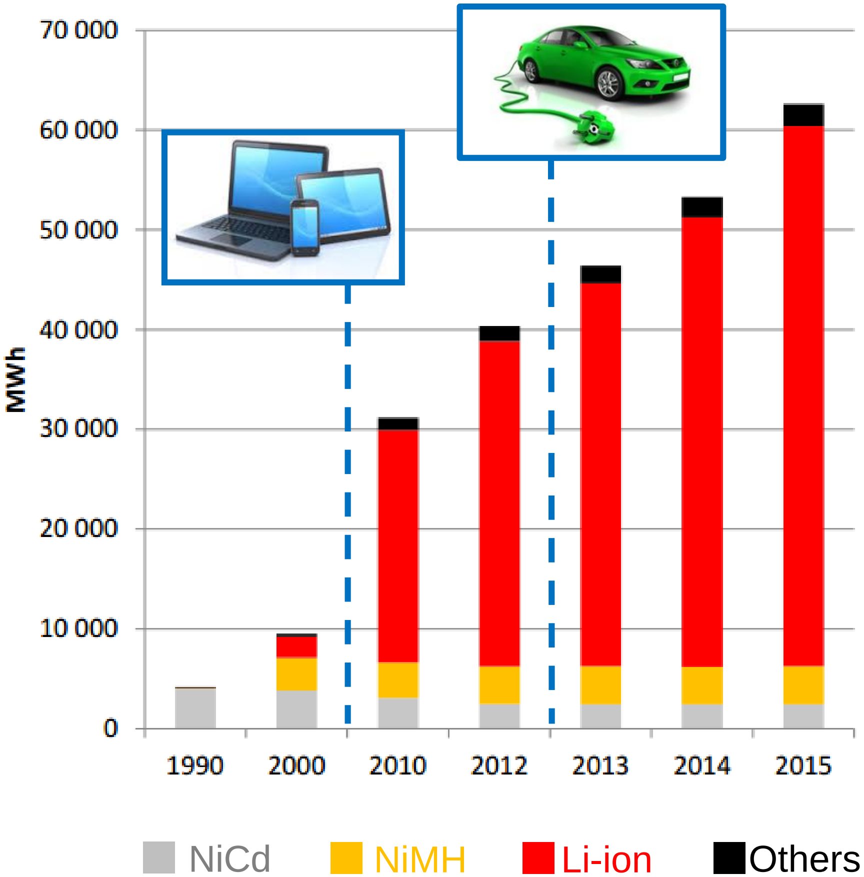
Electric Powered Vehicles: The rising trend



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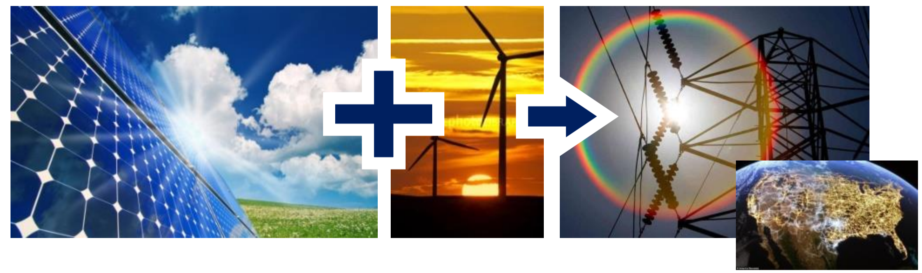
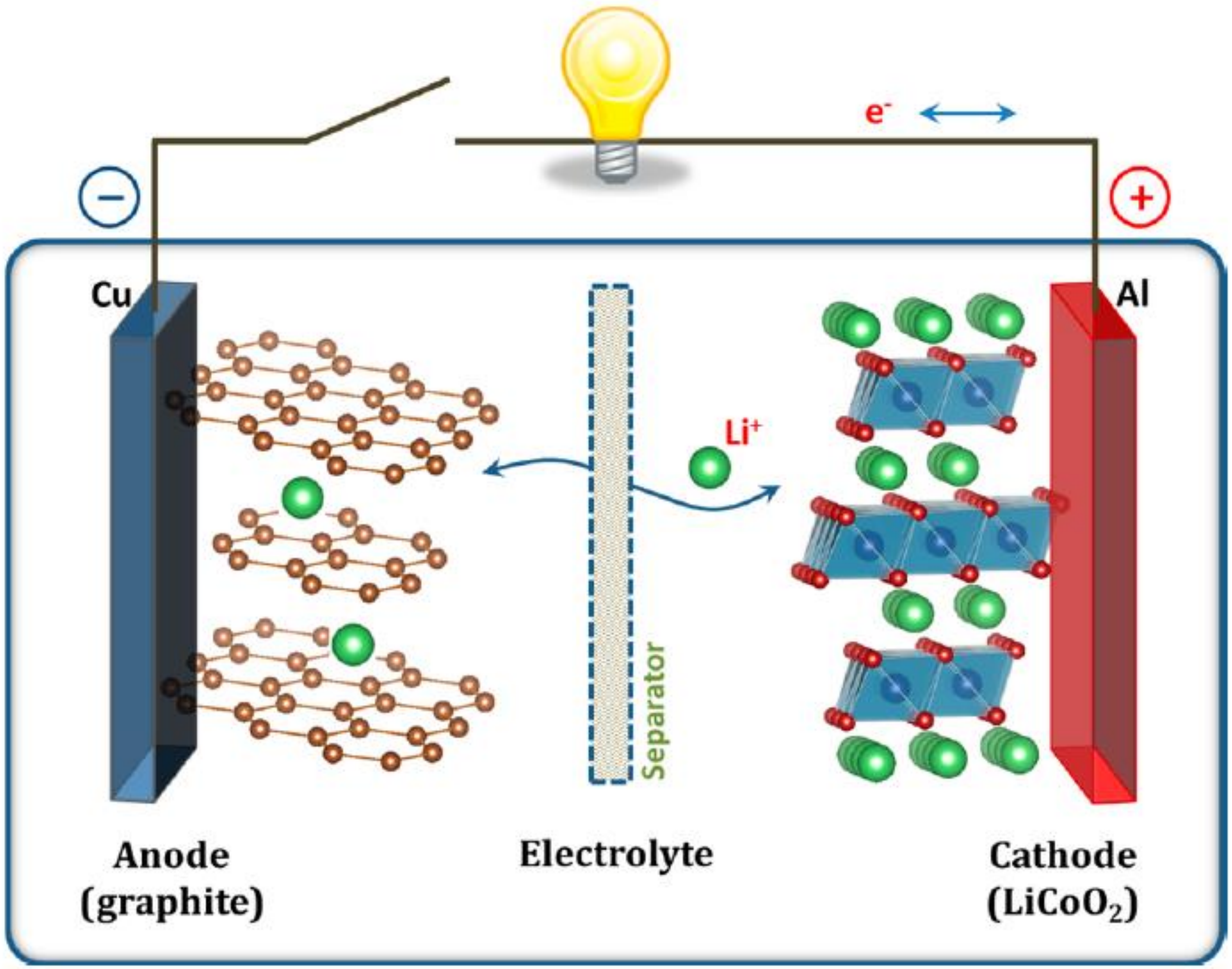
New applications: Stationary energy storage



Requirements for next-generation batteries	
Usual	Additional
High energy density	Sustainability
Durability	Temperature tolerance
Safety	Cost
…	Toxicity

The pathway to improved batteries

Need for new battery materials

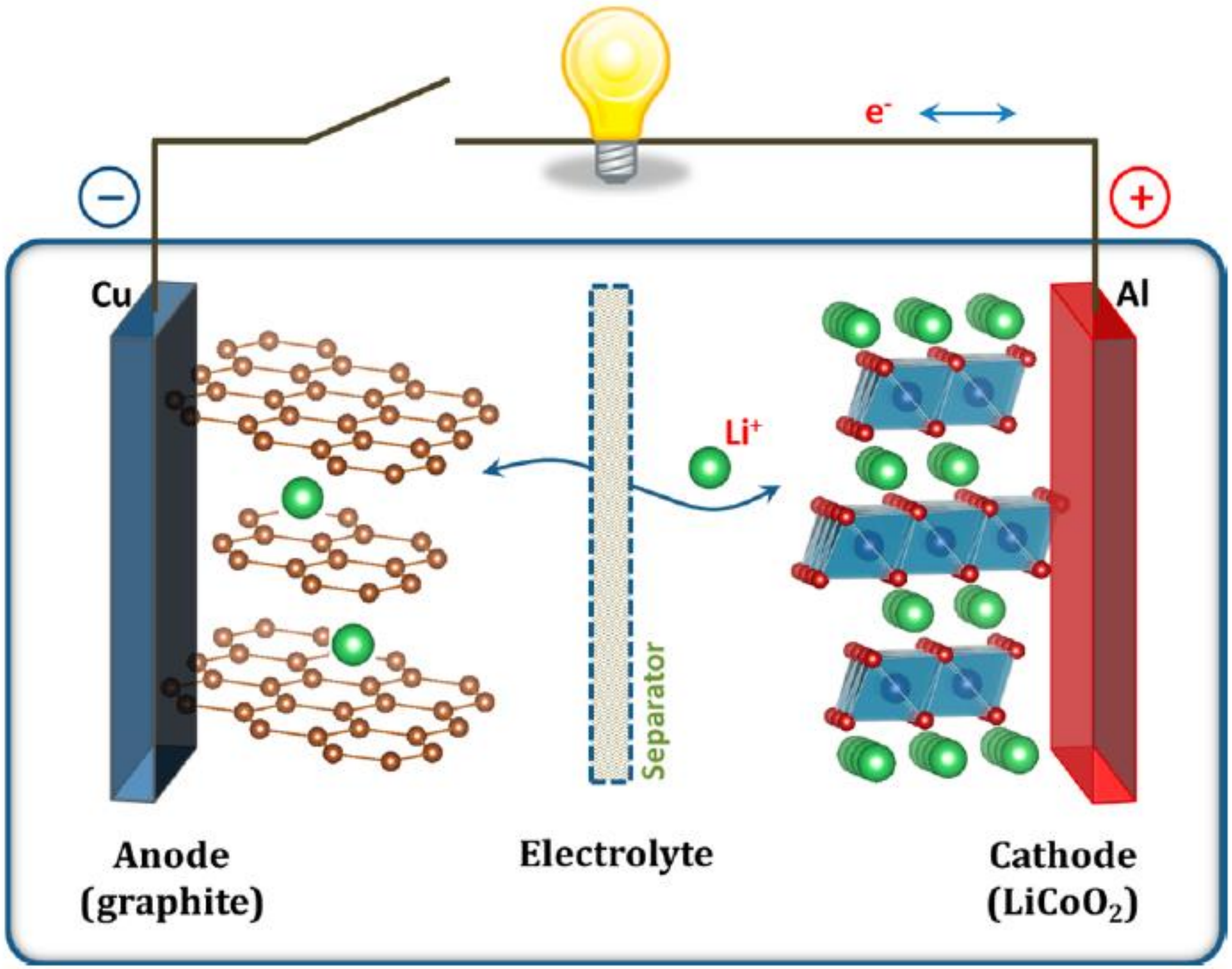


Source: J. B. Goodenough, K.-S. Park J. Am. Chem. Soc. **2013**, 135, 1167

The pathway to improved batteries

Need for new battery materials

- Cathode
- Anode
- Electrolyte
- Separator
- Binder
- Current collector



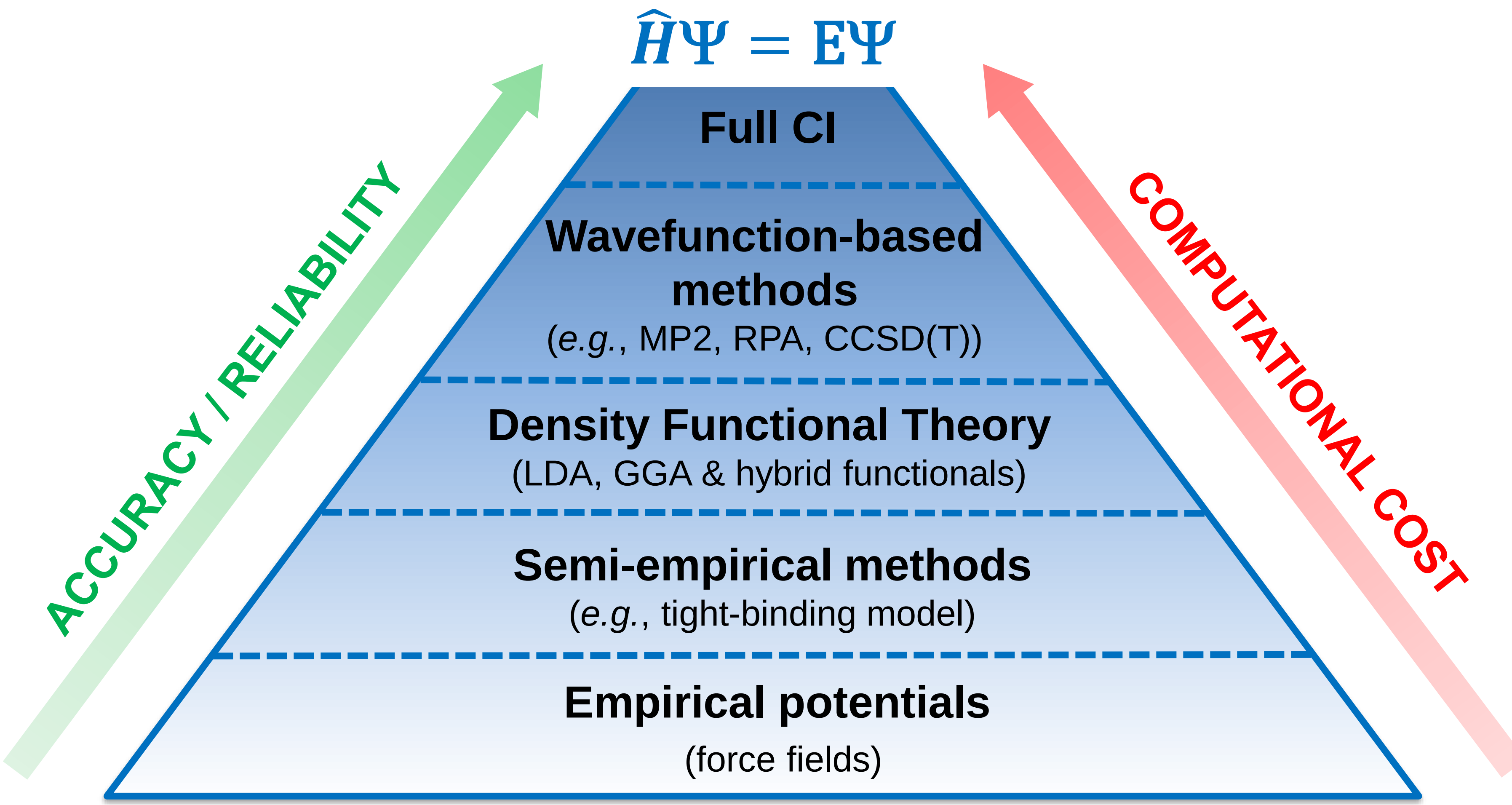
Source: J. B. Goodenough, K.-S. Park J. Am. Chem. Soc. **2013**, 135, 1167

Materials' discovery

Impact of computer simulation

Atomistic modelling

DFT: A good trade-off



Overview

Li-ion

- **Electrochemical delithiation of $Li_2Fe(SO_4)_2$**

  L. Lander, M. Reynaud, J. Carrasco, N. A. Katcho, C. Bellin, A. Polian, B. Baptiste, G. Rousse, J.-M. Tarascon, Phys. Chem. Chem. Phys. **2016**, 18, 14509.

Na-ion

- **Phase stability of Na_xFePO_4 ($0 \leq x \leq 1$)**

  A. Saracibar, J. Carrasco, D. Saurel, M. Galceran, B. Acebedo, H. Anne, M. Lepoitevin, T. Rojo, M. Casas Cabanas, Phys. Chem. Chem. Phys. **2016**, 18, 13045.

- **Phase transformations in layered $Na_{2/3}Fe_{2/3}Mn_{1/3}O_2$ polymorphs**

  N. A. Katcho, J. Carrasco, D. Saurel, E. Gonzalo, M. Han, F. Aguesse, T. Rojo, Adv. Energy Mater. **2016**, 6, 1601477.

Polymorphs of $Li_2Fe(SO_4)_2$

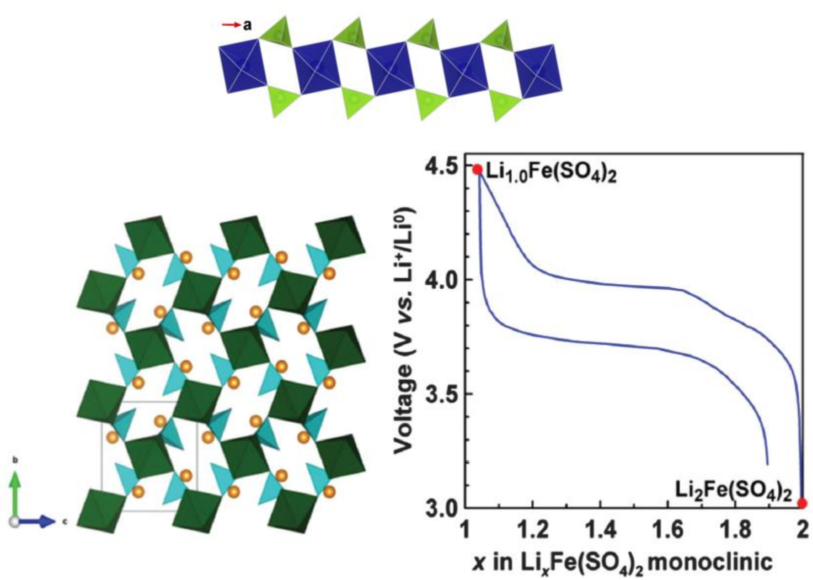
Monoclinic versus orthorombic structures

$Li_2M(SO_4)_2$
(Fe, Mn, Co, Ni, Zn)
High voltage materials
(> 3.6 V)

$Li_2SO_4 + Fe^{II}SO_4 \rightarrow Li_2Fe^{II}(SO_4)_2$

Ceramic route | *Ball-milling*

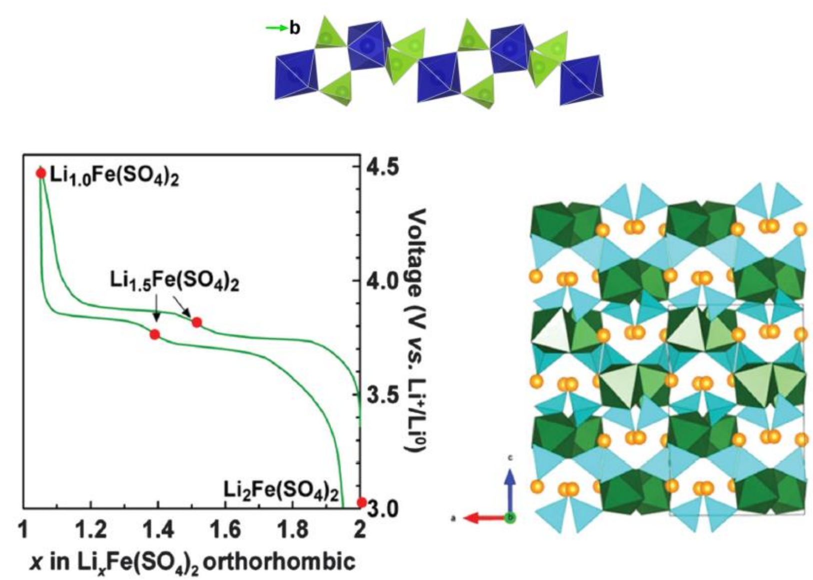
Monoclinic $P2_1/c$



High polarization

1 biphasic mechanism

Orthorhombic *Pbca*



Low polarization

2 successive biphasic mechanisms

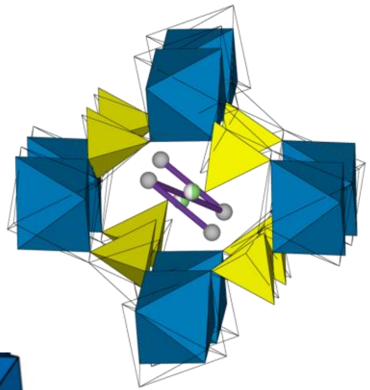
Electrochem. Commun. 2012, 21, 77; Chem. Mater. 2014, 26, 4178

Monoclinic $Li_2Fe(SO_4)_2$

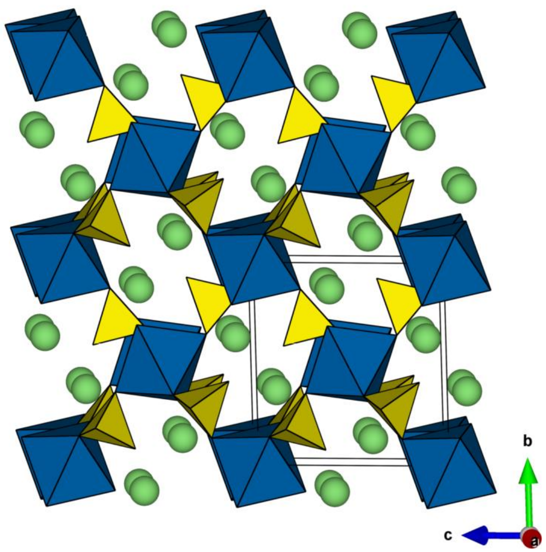
Li removal/insertion mechanism

CASM → Electrostatics (Ewald summaion) → DFT

A. Van der Ven et al.
PRB 2008, 78, 104306



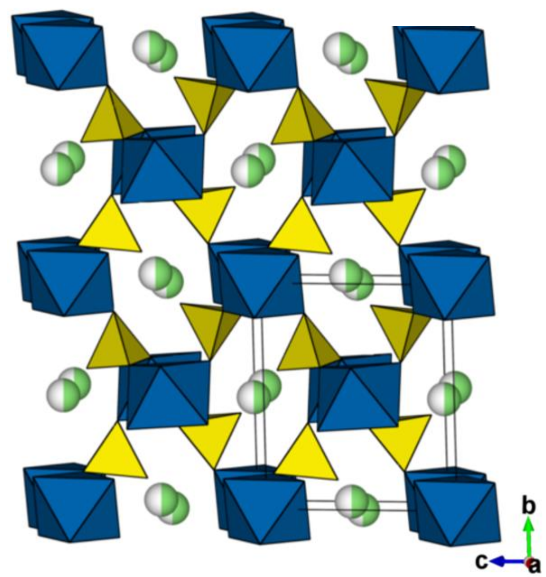
$Li_2Fe(SO_4)_2$



$\pm Li^+$

$\rightleftarrows$

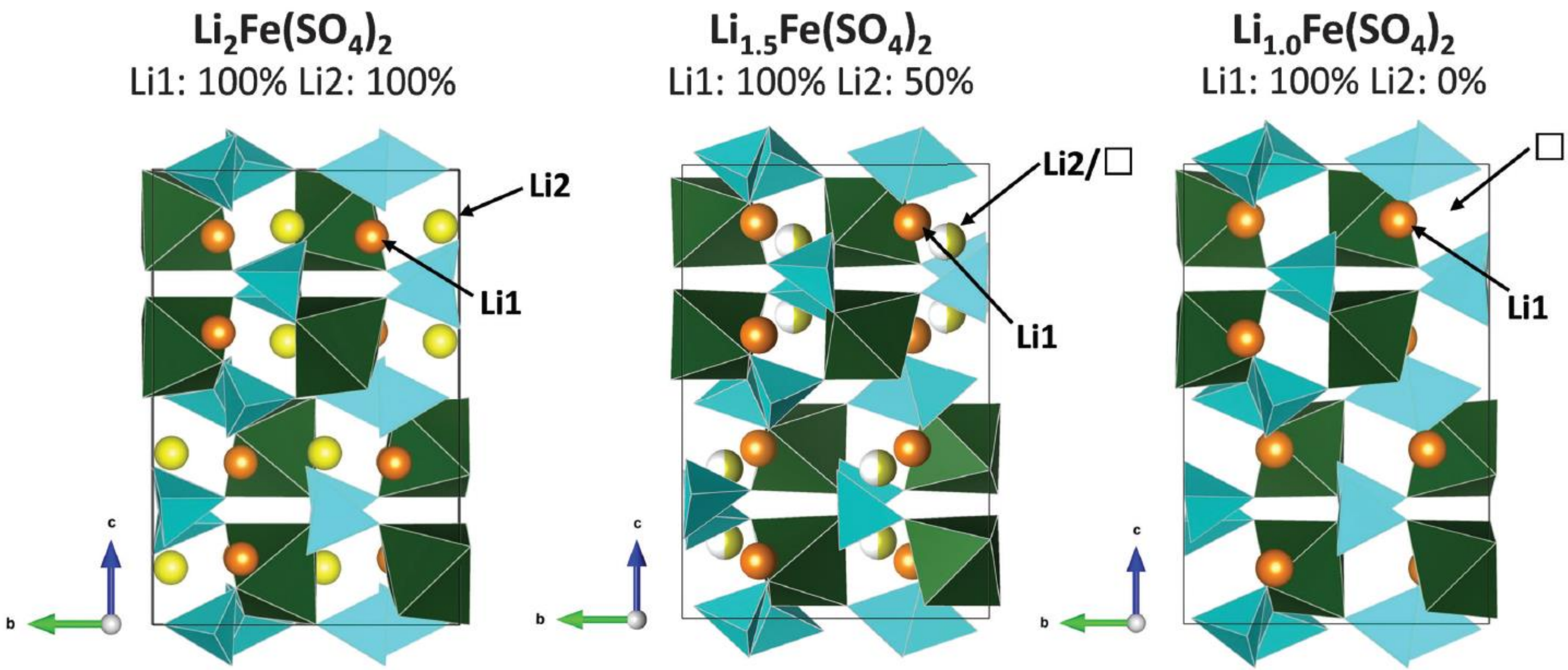
$Li_1Fe(SO_4)_2$



All Li atoms are involved in the electrochemical process

Orthorhombic $Li_2Fe(SO_4)_2$

Li removal/insertion mechanism

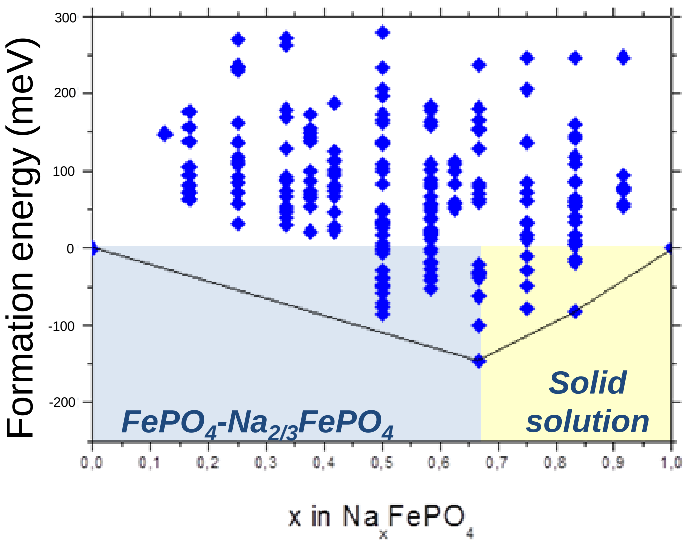


Only Li2 atoms are involved in electrochemical processes

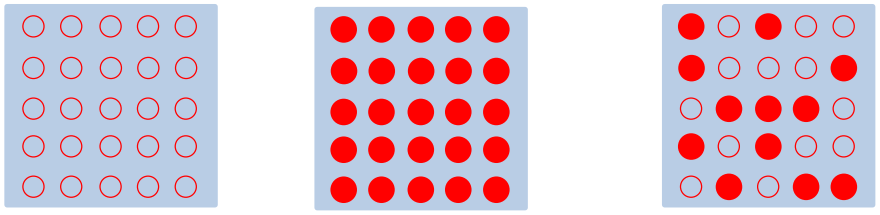
The Li1 sublattice does not participate in the electrochemistry

Phase stability of Na_xFePO_4

Formation of superstructures



$(1-x)\ FePO_4 + x\ NaFePO_4 \rightarrow Na_xFePO_4$



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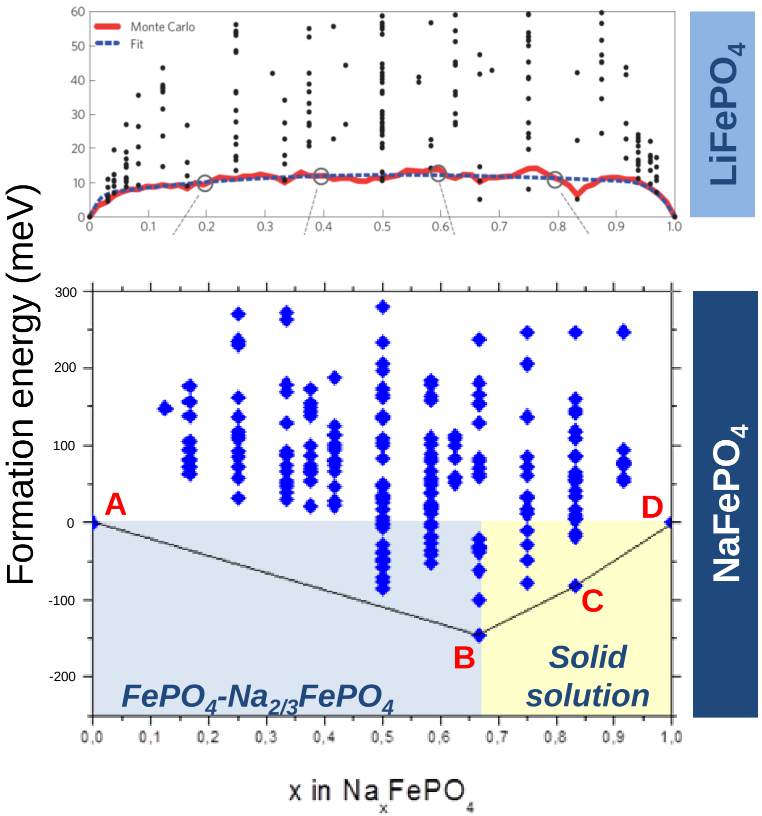
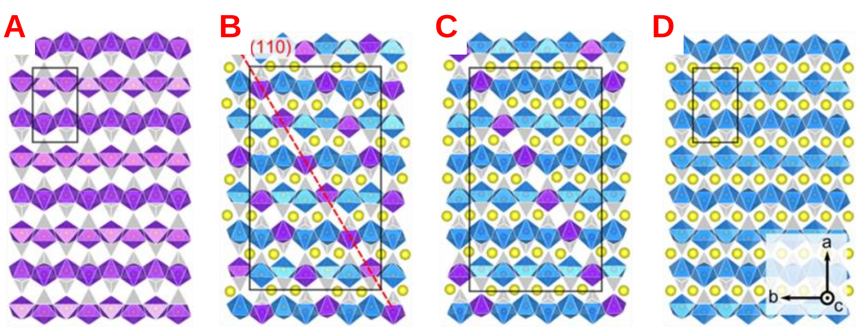


Thermodynamically disfavored but kinetically accessible Li_xFePO_4 region

G. Ceder et al., Science 2014, 344, 1252817

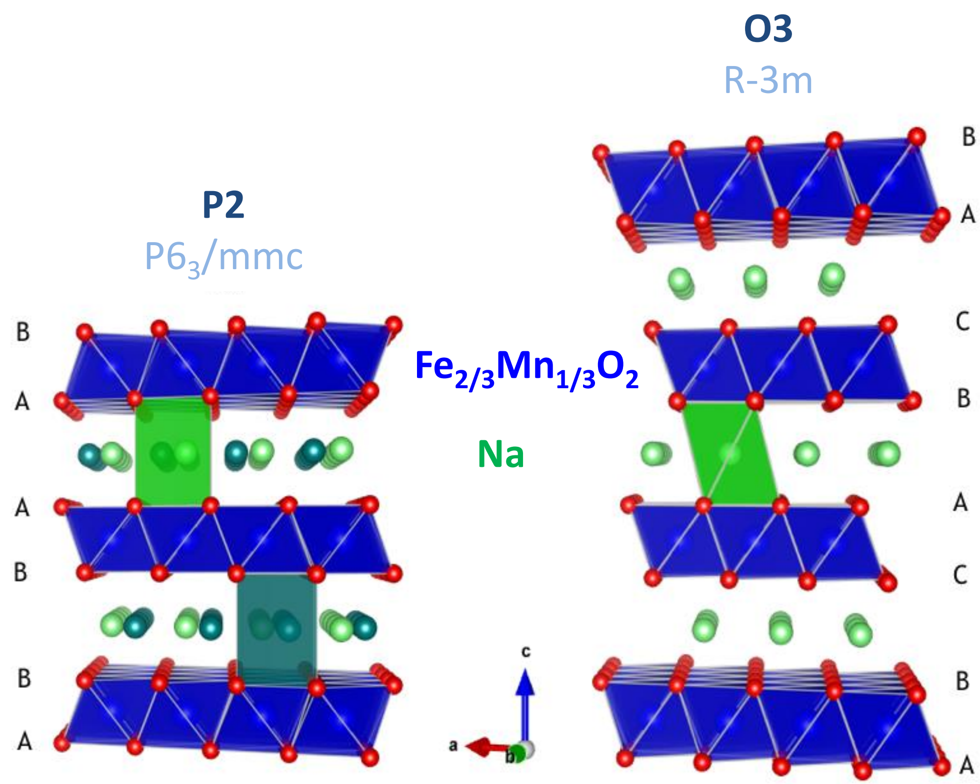
Thermodynamically favorable region at x > 0.5

- ✓ Two intermediate structures govern the phase stability: $Na_{2/3}FePO_4$ and $Na_{5/6}FePO_4$
- ✓ Both structures align vacancies diagonally within the ab plane, coupled to a Fe^{2+}/Fe^{3+} ordering
- ✓ Energetically accesible polymoprhs at a given Na composition allows for solid solution



Polymorphs of layered $Na_{2/3}Fe_{2/3}Mn_{1/3}O_2$

Phase transitions involve different stacking sequences



Two layered oxide polymorphs with exactly the same Na composition synthesized for the first time

Adv. Energy Mater. 2016, 6, 1601477.

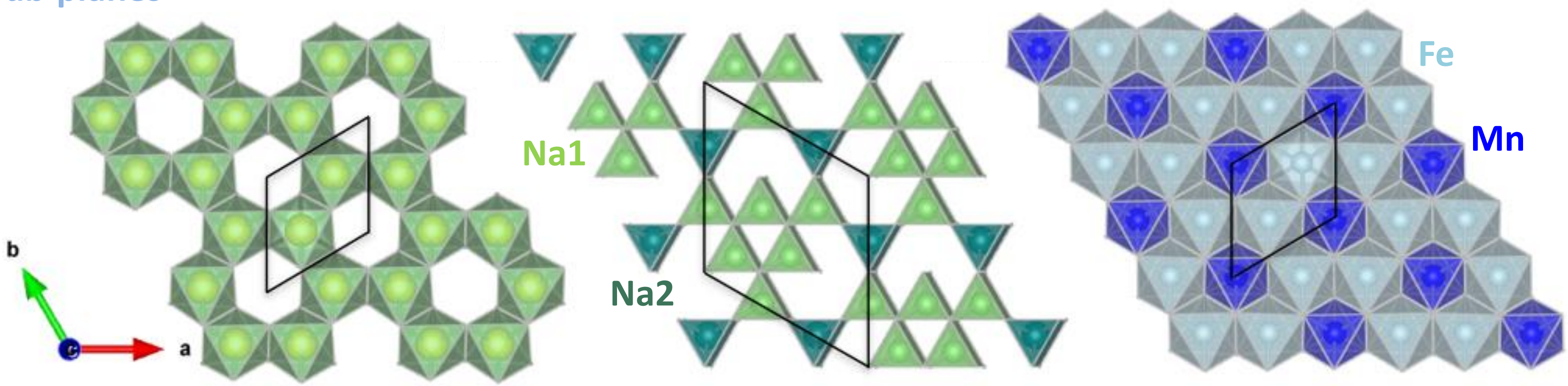
Atomic structure of $Na_{2/3}Fe_{2/3}Mn_{1/3}O_2$

Na/Fe/Mn ground-state arrangements

CASM → **Electrostatics (Ewald summaion)** → **DFT**

A. Van der Ven et al.
PRB 2008, 78, 104306

ab planes



Na
in O3

Na
in P2

Fe/Mn
in both P2 an O3

Na ion diffusion in $Na_{2/3}Fe_{2/3}Mn_{1/3}O_2$

P2 versus O3 local environments

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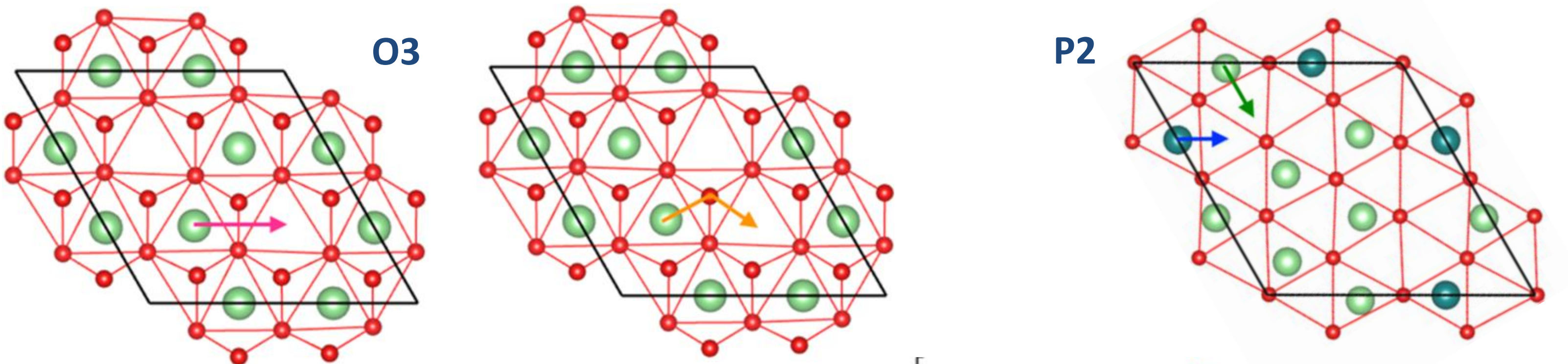
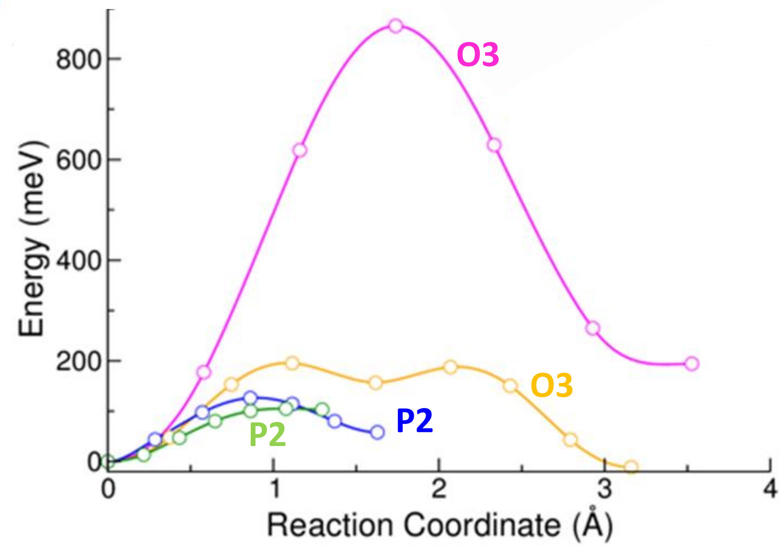


Diffusion coefficient: $D = a^2 \nu \exp\left(-\frac{E_a}{k_B T}\right)$

	E_a (meV)	D_{P2}/D_{O3} (DFT)	D_{P2}/D_{O3} (EXP)
P2	130	19	12-20
O3	200		

EXP: EIS and PITT techniques



Na diffusion is easier in P2 polymorph than in O3 phase

Conclusions

- First-principles insight into electroactive materials is an effective tool to:

  - ✓ Systematically explore compositional and structural spaces

    Relevance to clarify phase segregation/transformation and solid solution phenomena (e.g., $Li_2Fe(SO_4)_2$ and Na_xFePO_4)

  - ✓ Design materials with better electrochemical performance

    Tuning of ionic conductivity by modifying the local structure around diffusion paths (e.g., $Na_{2/3}Fe_{2/3}Mn_{2/3}O_2$)

  - ✓ Accelerate materials discovery

Acknowledgements

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❑ Team

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- ✓Univ. of New South Wales (Australia)
- ✓CEA, LITEN (France)

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