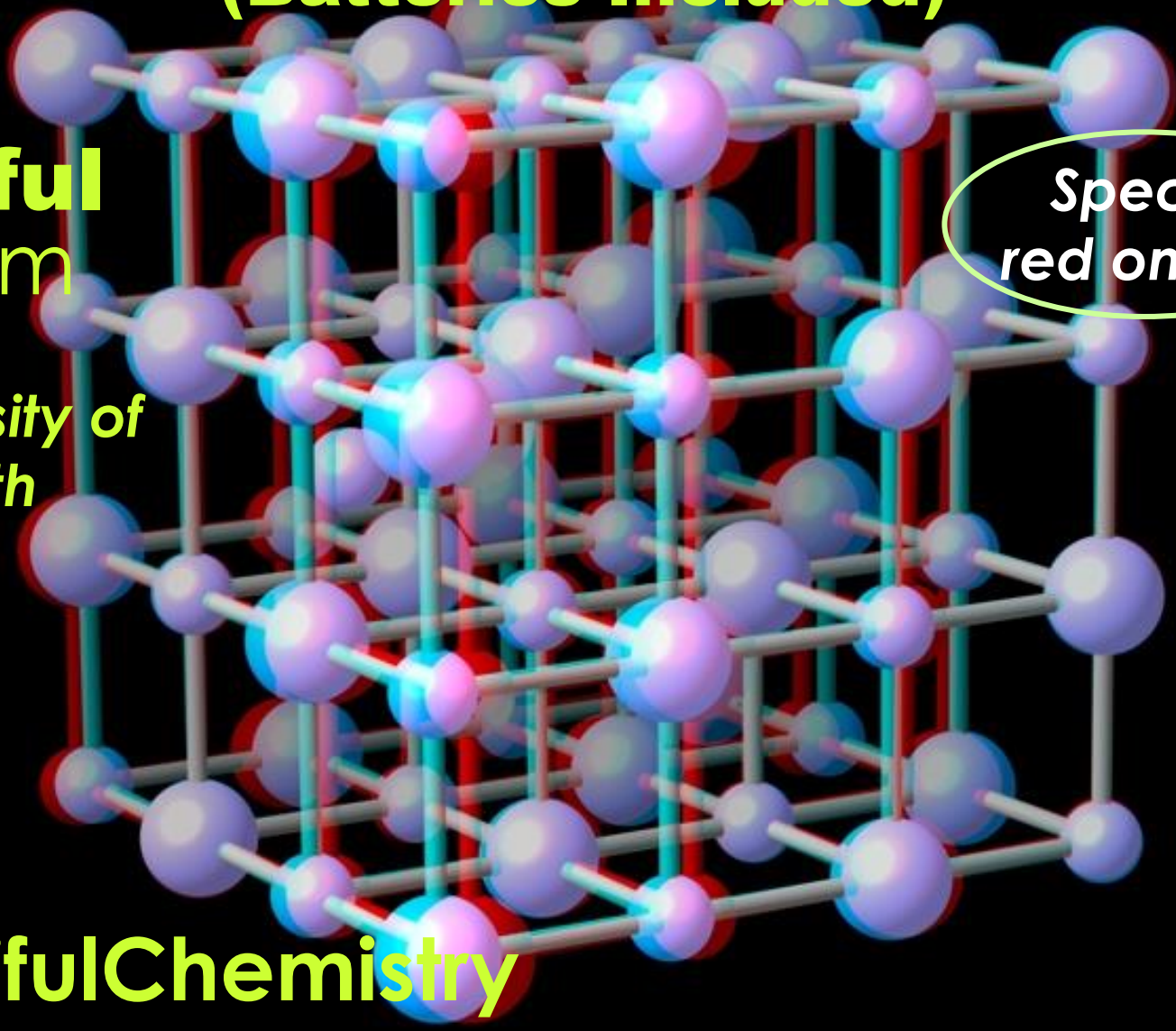
Atomic-Scale Insights into Energy Materials (Batteries Included)

Saiful Islam

University of Bath



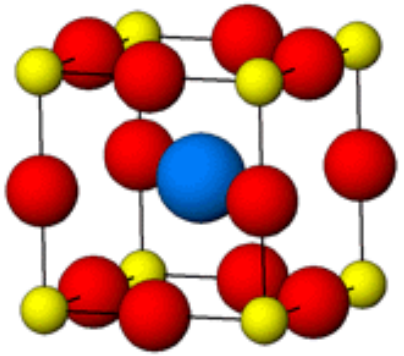
Specs: red on left

@SaifulChemistry

TALK MENU

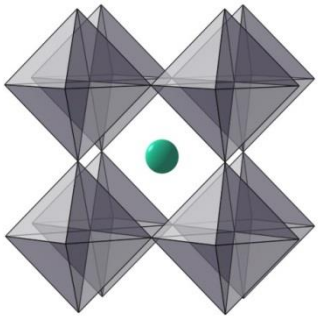
Green Energy

Solid Materials



Lithium Batteries

Solar Cells



Background: Green Energy

ENERGY CHALLENGE:
HOT TOPIC
GREENER MIX?

Energy Materials Research

Materials performance : at heart of green energy technology

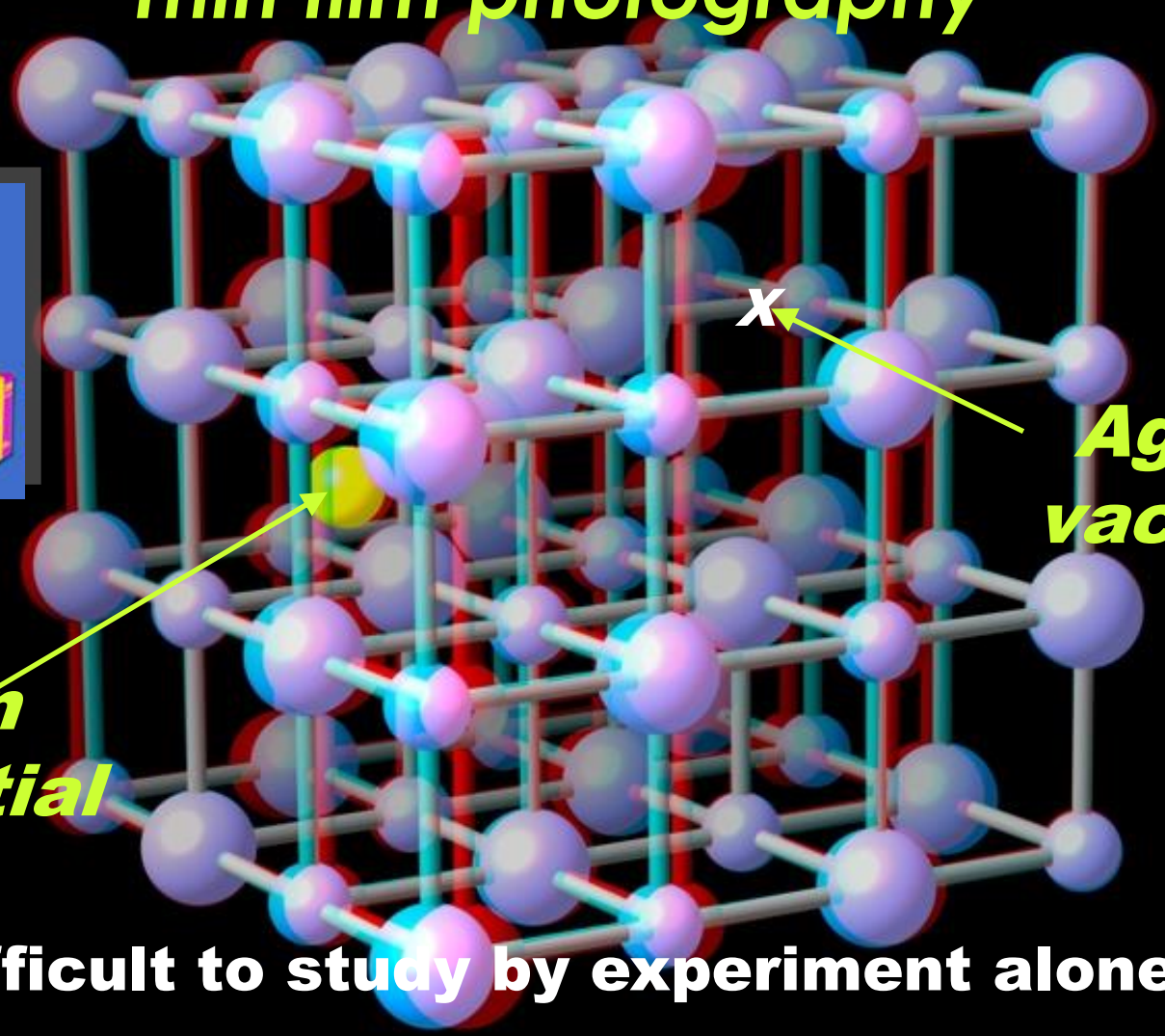
Advances? New materials & fundamental understanding

Materials: Crystal Gazing

A SALT ON YOUR SENSES

DEFECTS IN SOLIDS, AgCl

Thin film photography



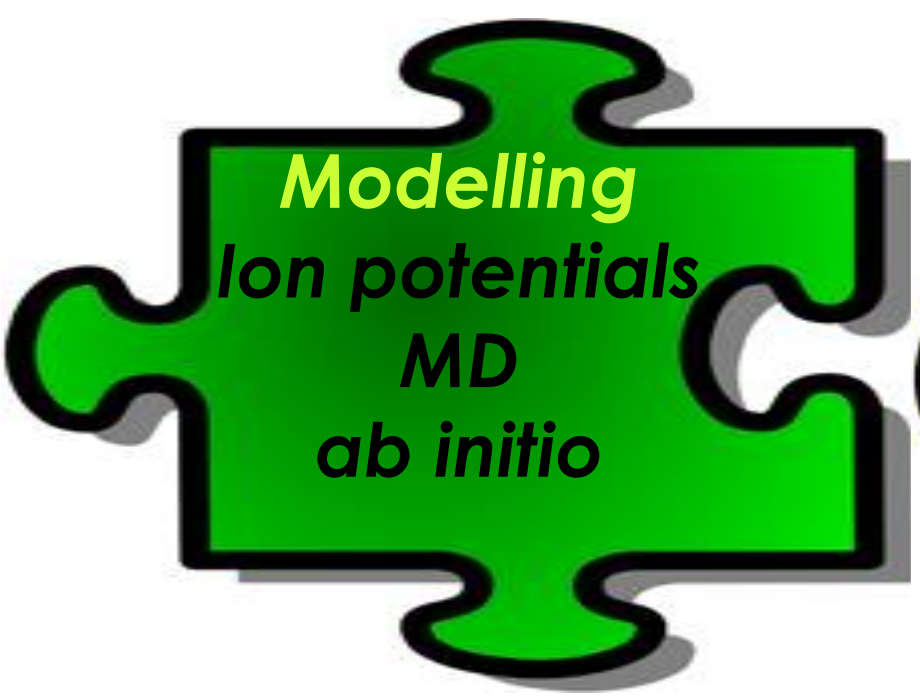
Ag ion vacancy

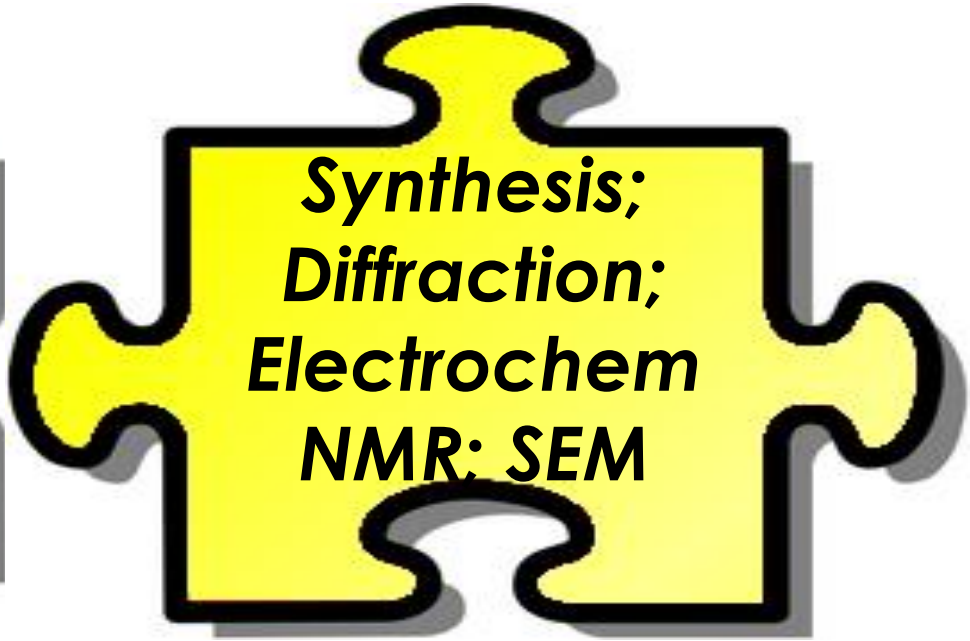
Ag ion interstitial

Difficult to study by experiment alone

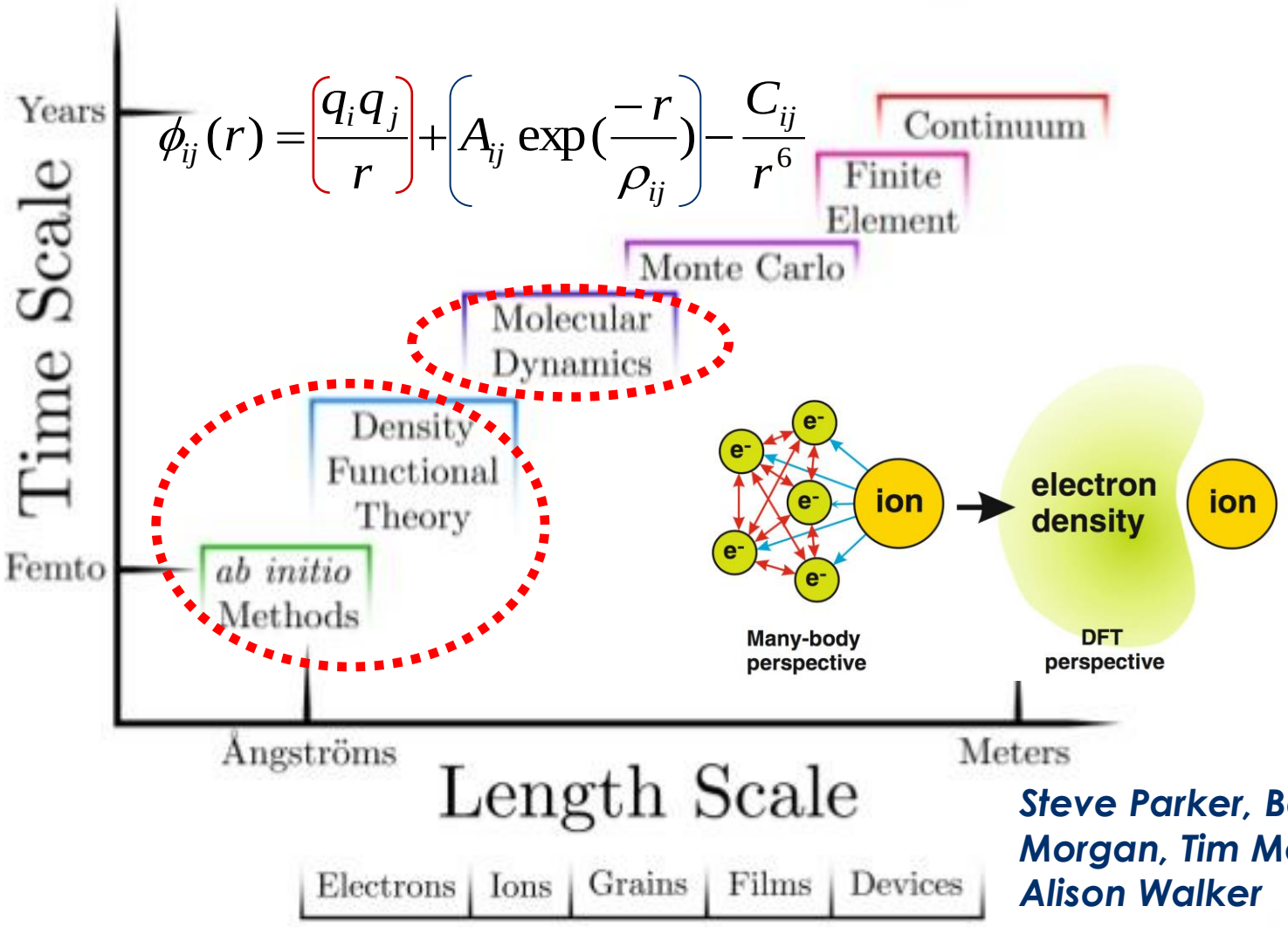
Computer Modelling

Modelling-Experimental Synergy





Methods: Materials Modelling



Steve Parker, Ben Morgan, Tim Mays, Alison Walker

Lithium-ion Battery
Applications

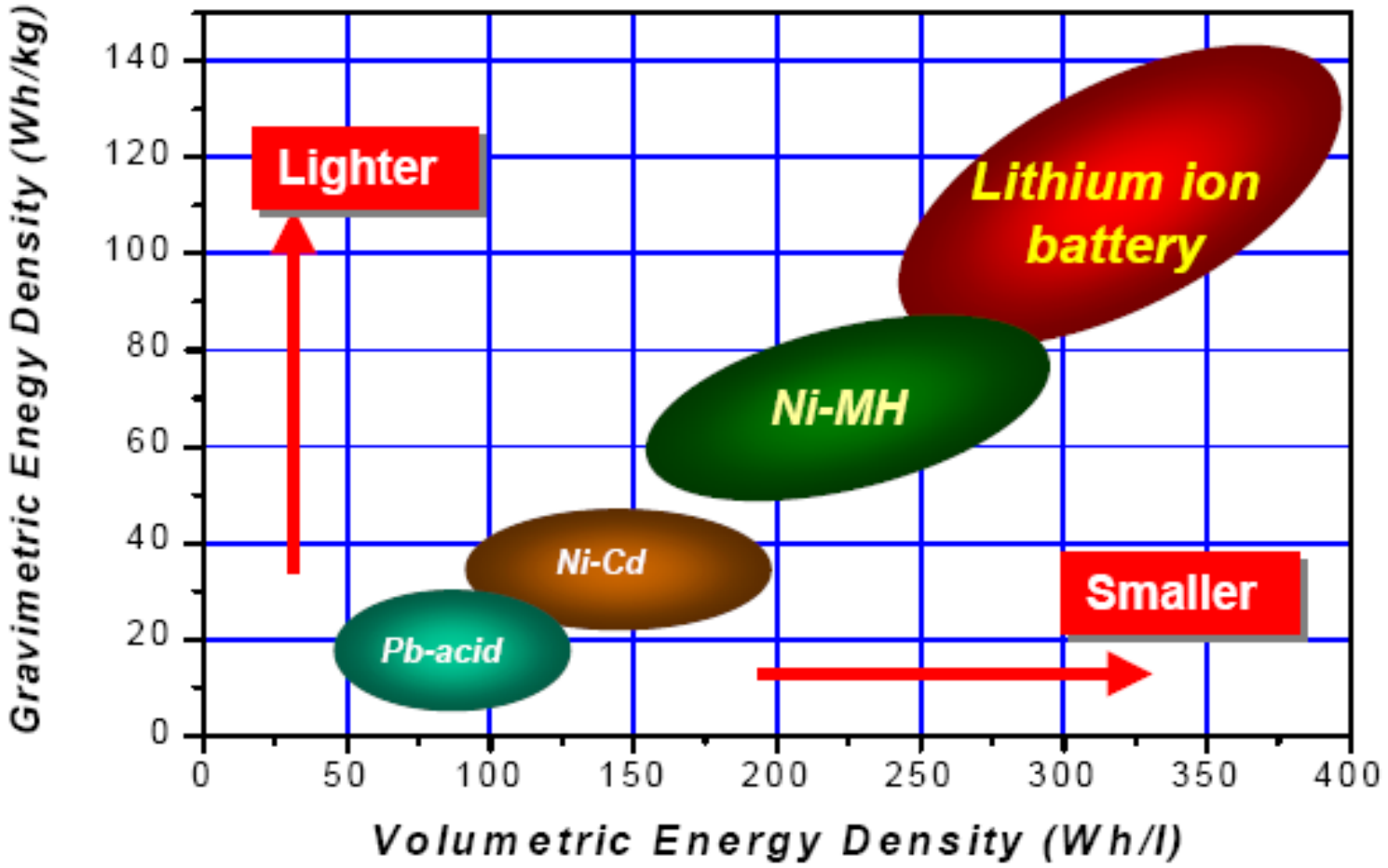
Portable Revolution

Energy density of Li-ion battery: small & light

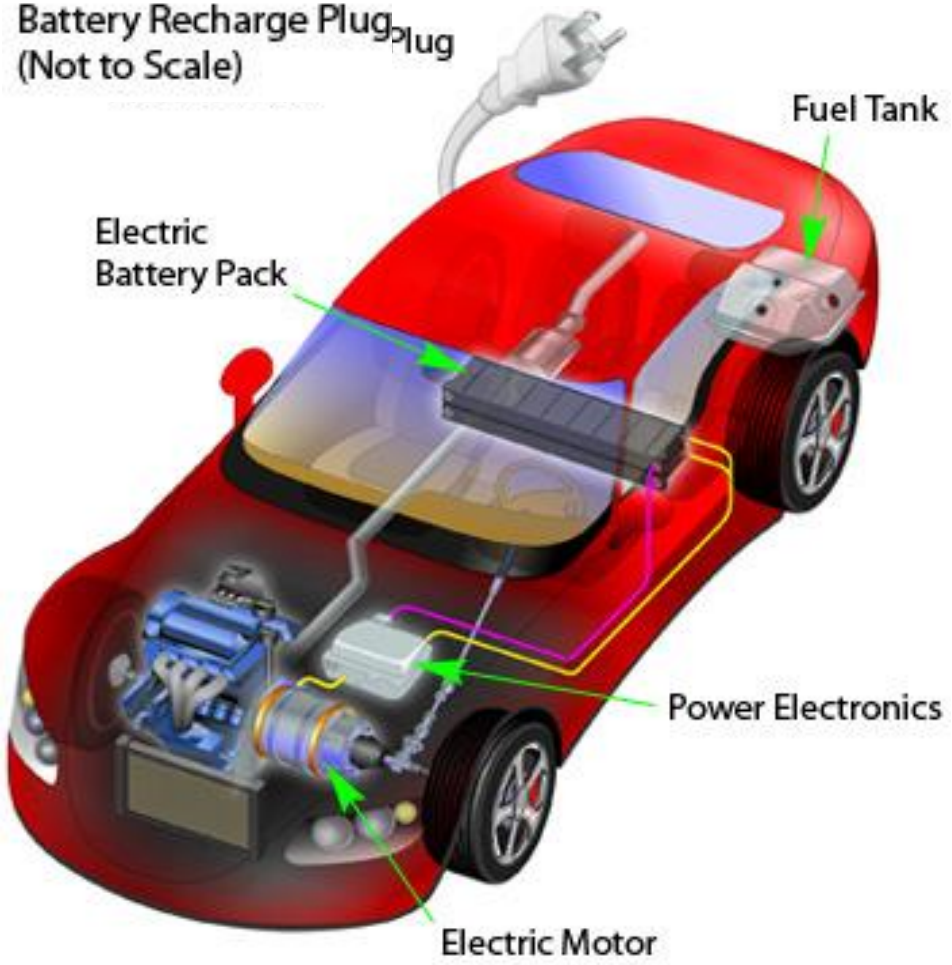
3 billion cells per year. Fundamental chemistry

High Energy Density in Li Battery

- Stores 2 to 3 times more energy

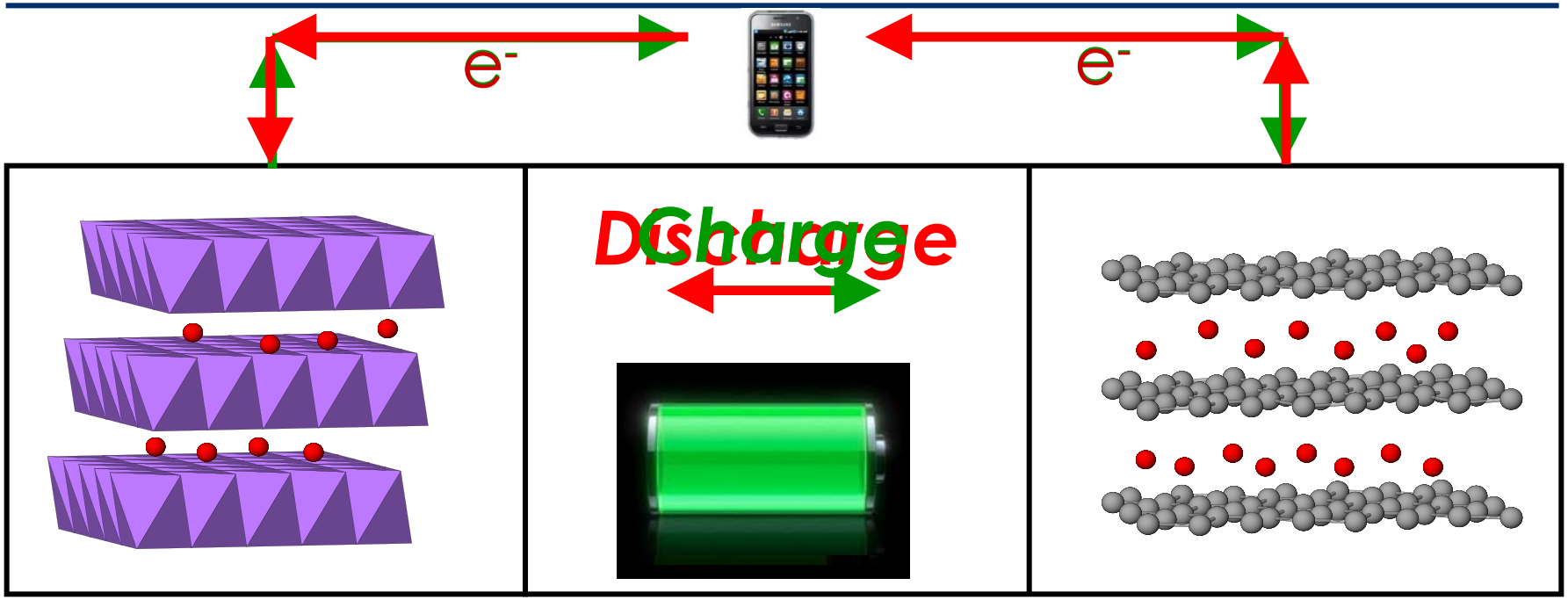


ELECTRIC CARS



Lithium-ion Battery
Materials

Inside Lithium-ion Battery



$LiCoO_2$ electrode

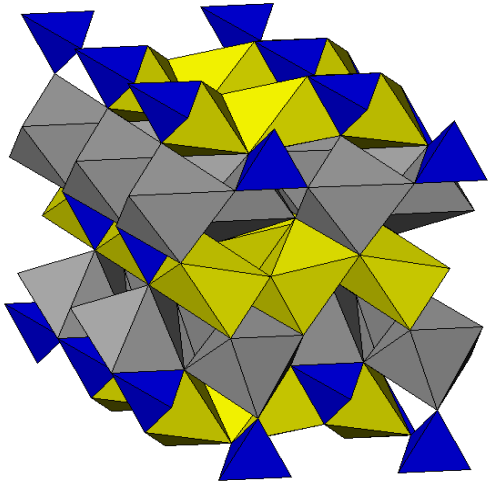
Electrolyte

Graphite electrode

Cathode Materials for Li-Ion

Challenge: energy (and power) density, materials cost, safety, toxicity

Layered oxide | **Spinel oxide** | **Polyanion type**



$Li(Ni,Mn,Co)O_2$

Li-rich $Li[Li,Mn,Ni]O_2$

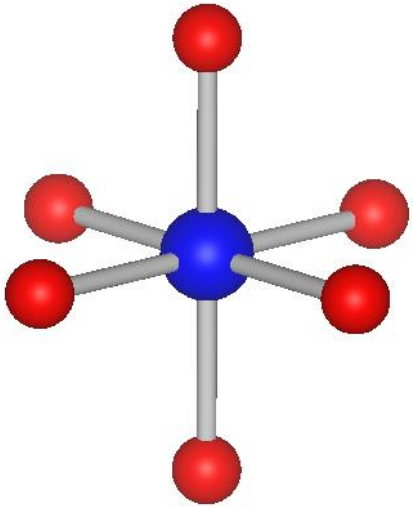
$LiMn_2O_4$

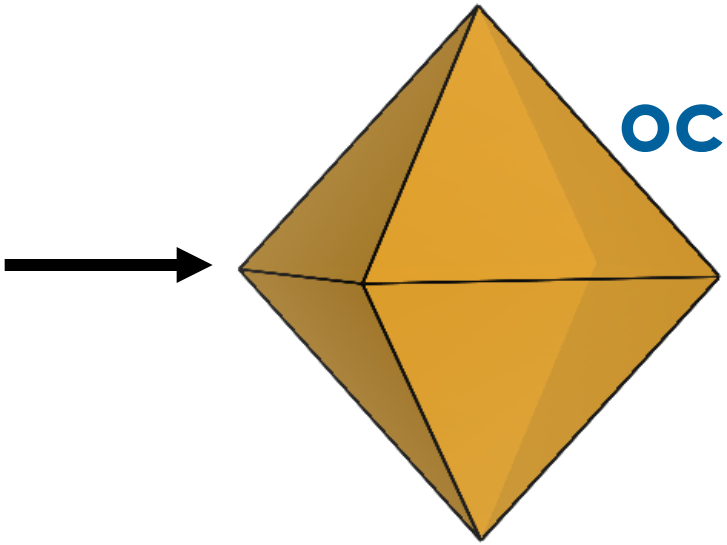
$LiFePO_4$

Li_2FeSiO_4

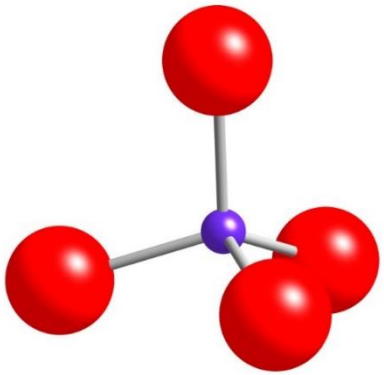
Battery Materials: 3D Structures

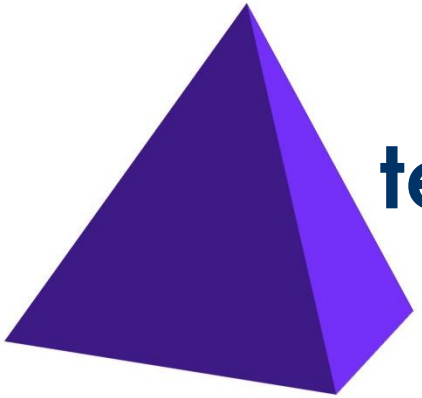
Structure Units in Oxides





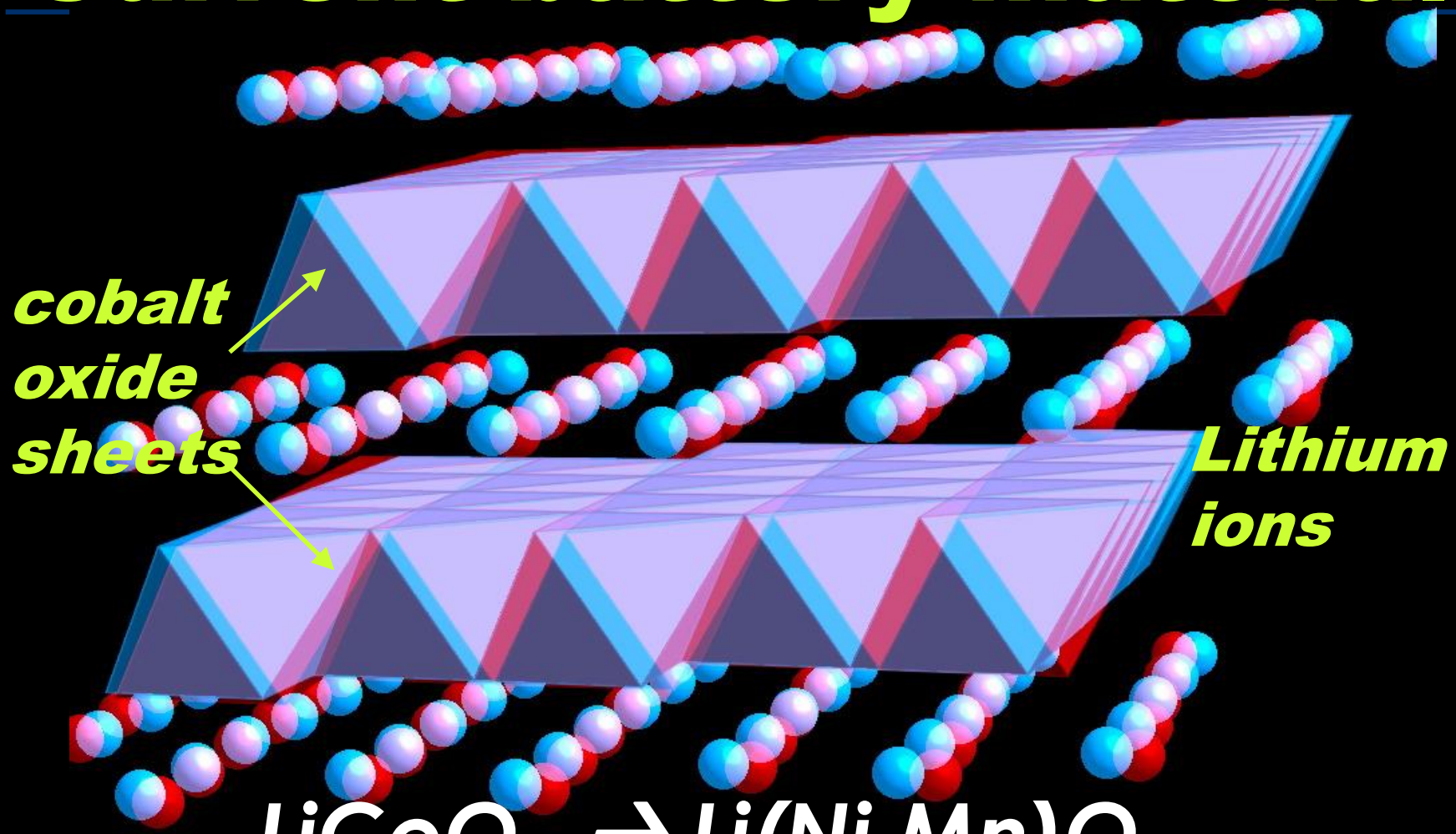
octahedron





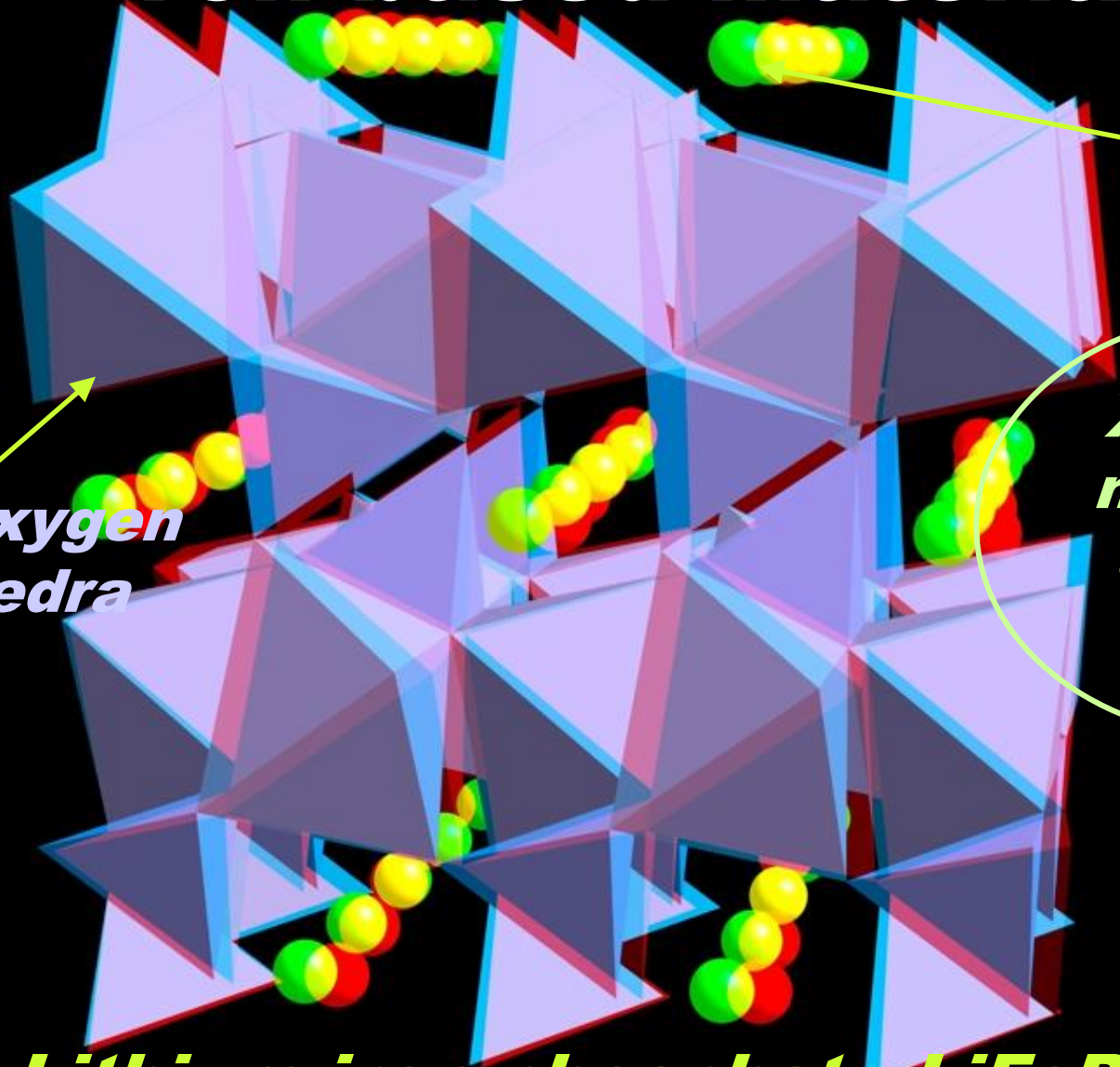
tetrahedron

Current battery material



$LiCoO_2 \rightarrow Li(Ni,Mn)O_2$

Iron-based material



Lithium ions

Iron-oxygen octahedra

X-Factor: non-toxic, cheaper, safer

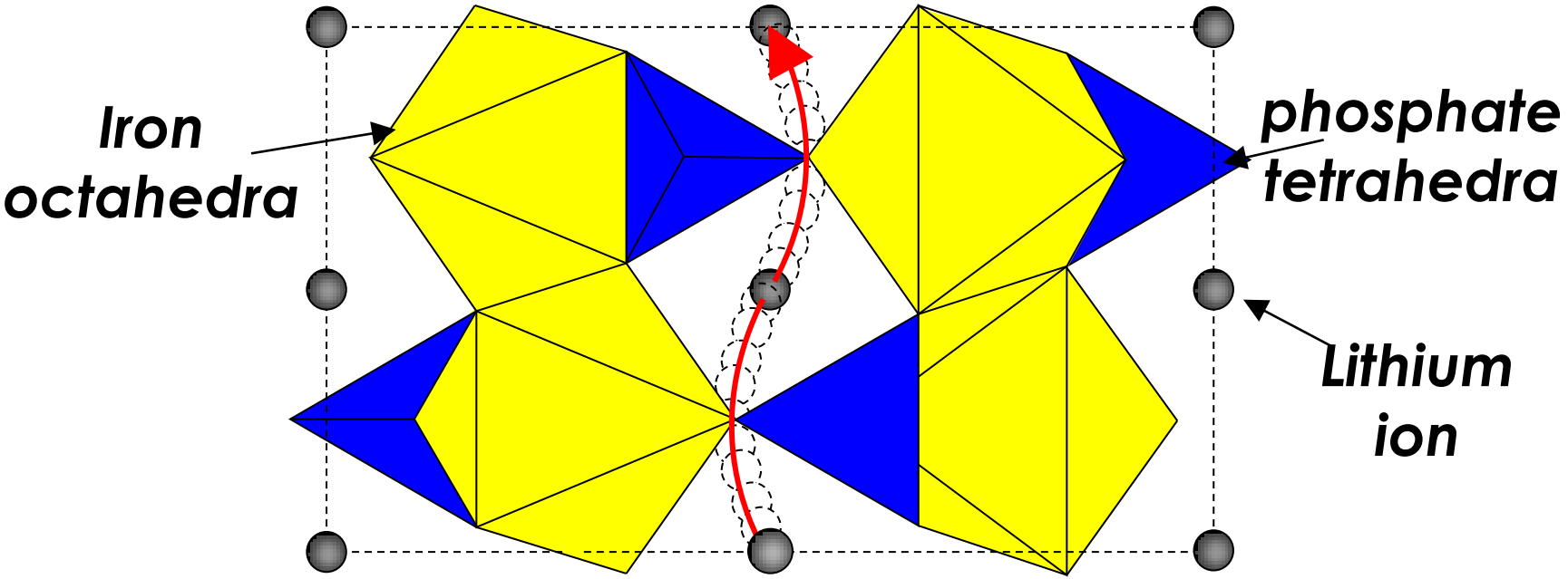
Lithium iron phosphate $LiFePO_4$

HYBRID TEST CAR IN GLASGOW

AC Cobra

Pathway for Lithium Ions?

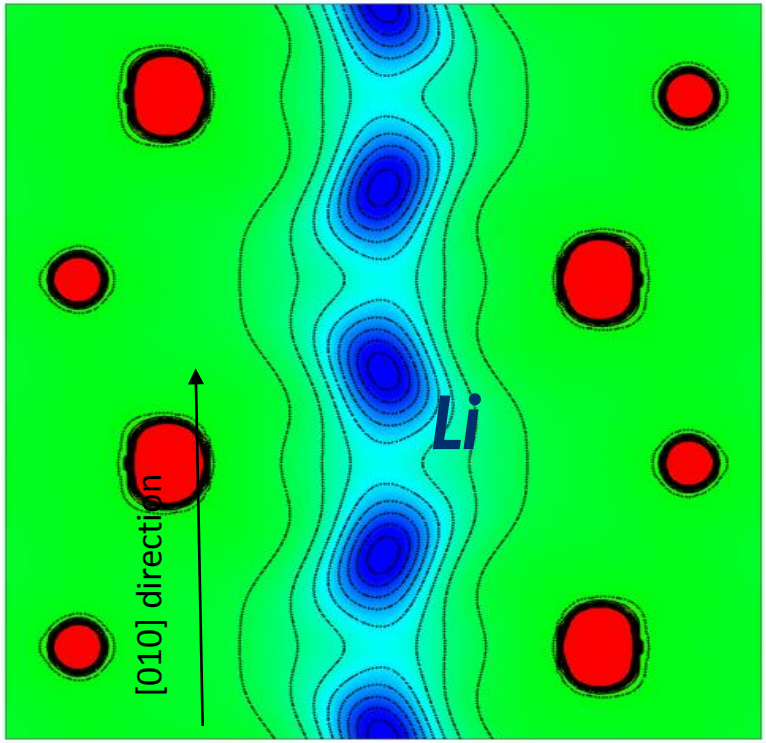
- PREDICTION: 1D channel – but curved

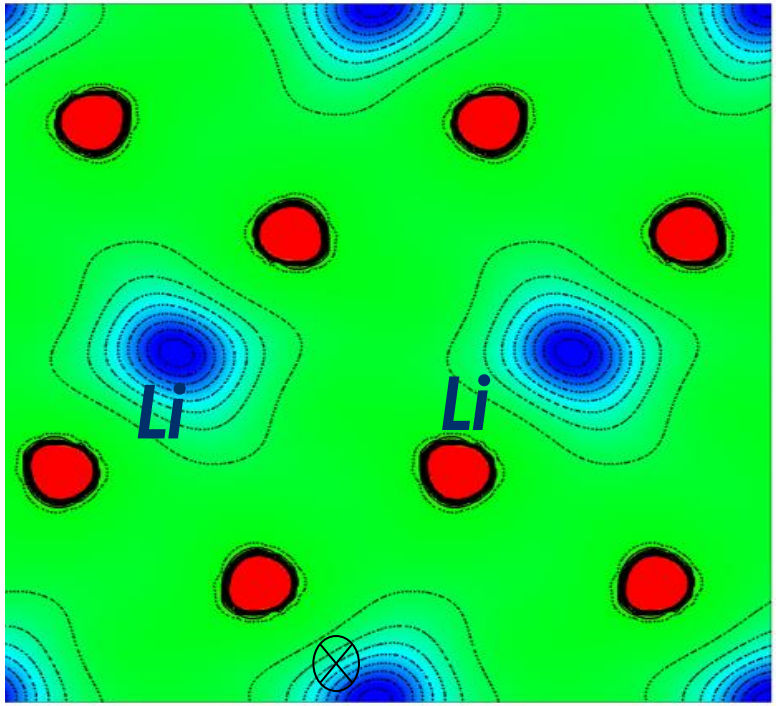


$LiFePO_4$

Ion Path From Experiment

Confirms prediction





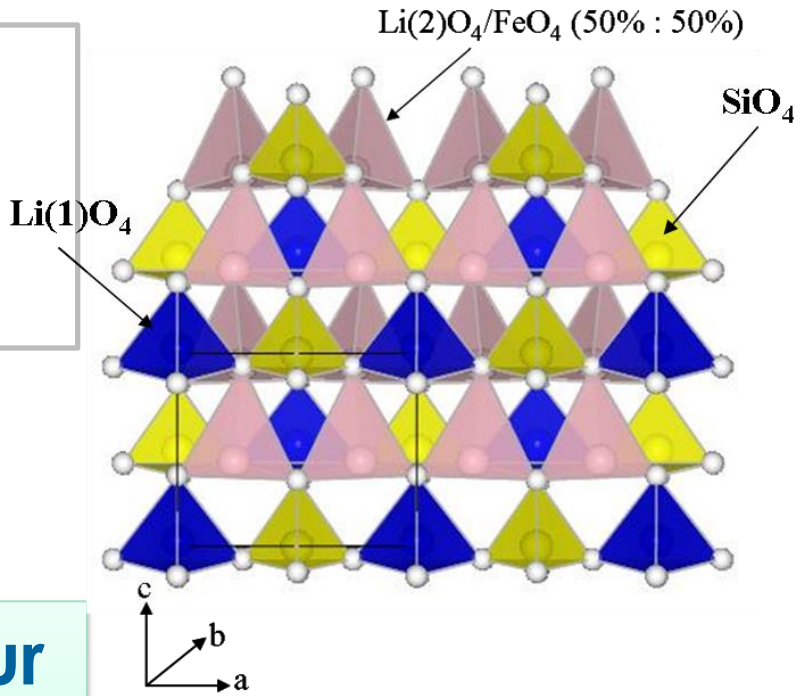
[010] direction

Yamada, *Nature Materials* (2008)

Lithium Battery
Silicate Materials

Li_2FeSiO_4 Cathode

- Fe and Si: abundant, low cost (> 1e- redox?)
- Stable: strong Si-O bonds



- Issues: poor rate behaviour (slow diffusivity) & structural change

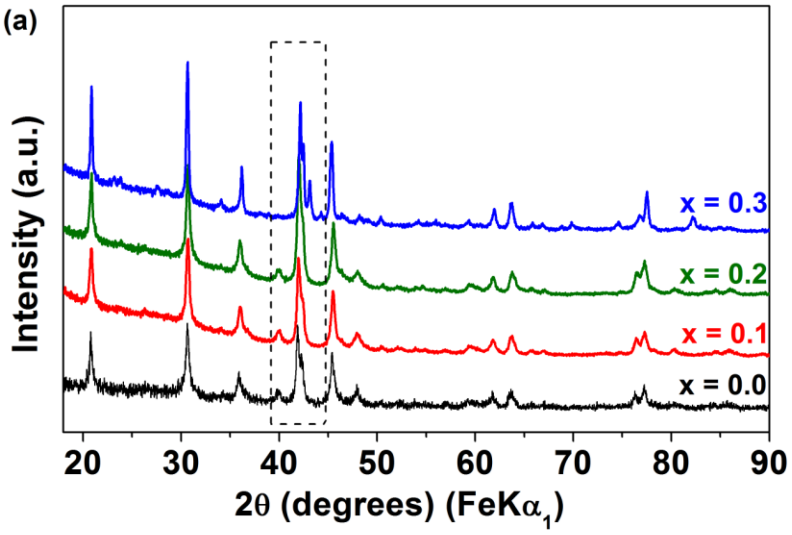
Tune Performance of Li_2FeSiO_4 ?

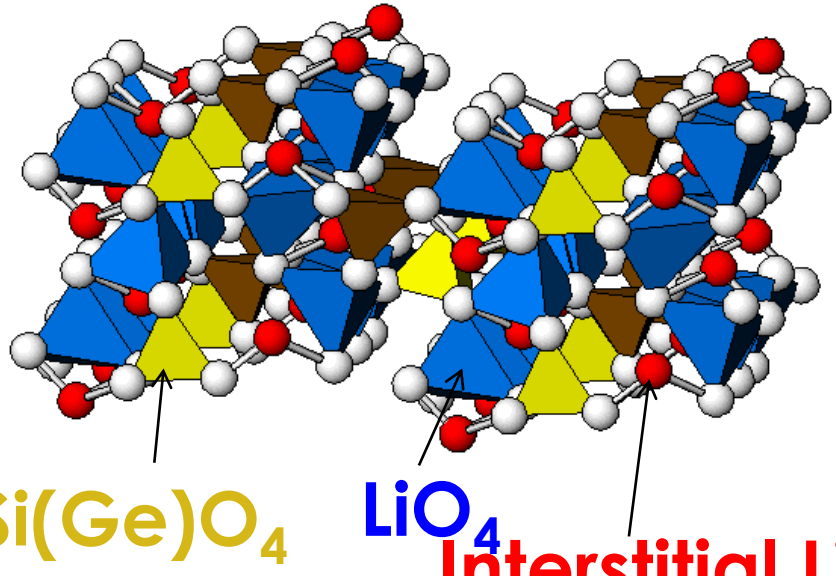
- Inspired by 'superionic' LISICON
- $Li_{2+2x}Zn_{1-x}GeO_4$

- *Li-rich silicate → enhanced Li transport?*
- ***BUT limited work on defects & mechanisms***

Structure: Li-rich $Li_{2+2x}Fe_{1-x}SiO_4$

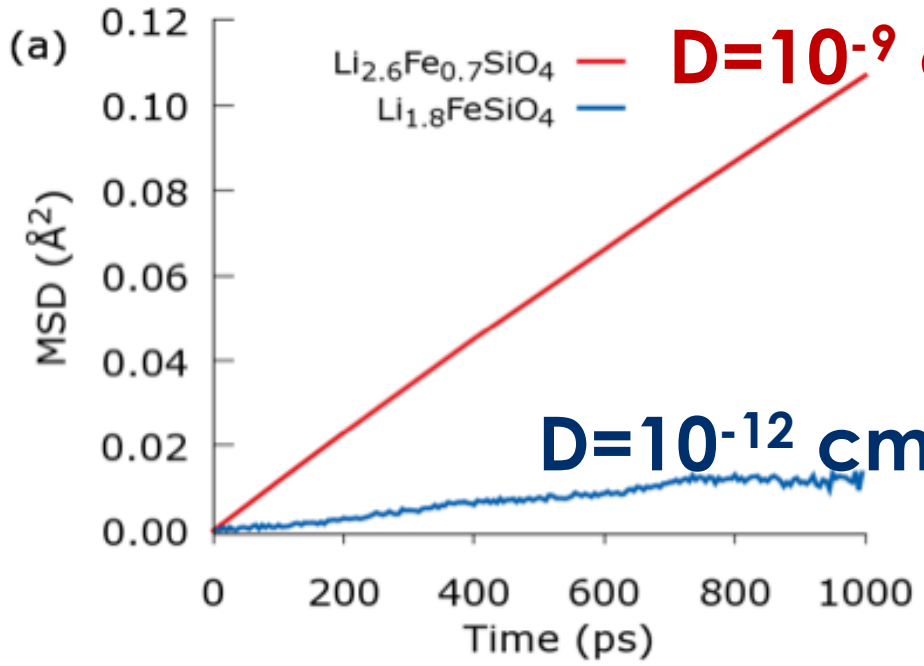
- Synthesis of Li-rich: x=0.0 to 0.3
- XRD & neutron: proportion of γ_{II} increases (Billaud,Armstrong,Bruce)





- Refinement: interstitial Li at octahedral sites
- Electrochem: higher rate observed. *WHY?*

Li-ion Diffusion: MD Results



$D=10^{-9}$ cm²/s

$D=10^{-12}$ cm²/s

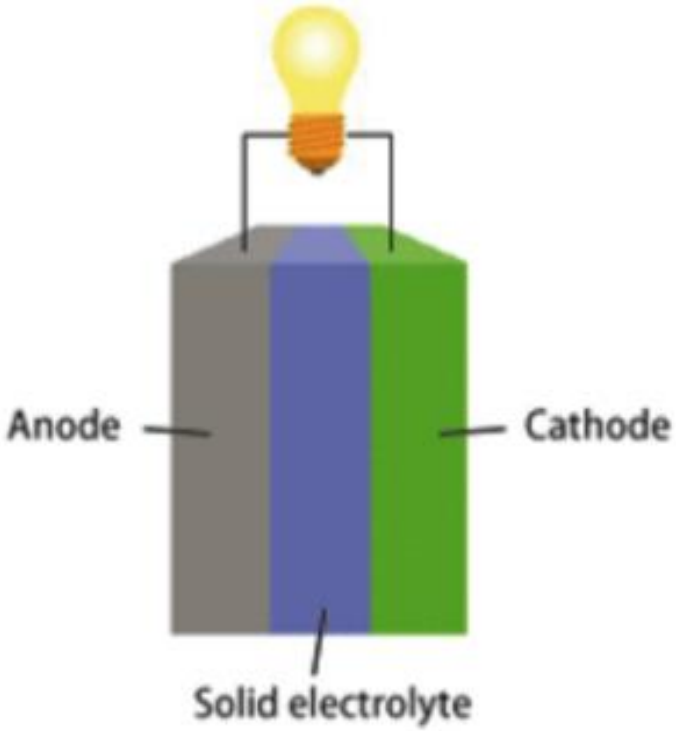
[Expt ~ 10^{-12} cm²/s Zhang, 2013]

- Faster diffusion by 3 orders of magnitude
- 3D Interstitial vs 2d vacancy mechanism

J. Billaud et al, *Adv. Energy Mater* (2017)

Beyond Current Li Batteries

All-Solid-State Batteries



- Safety
- High energy density

- Insufficient conductivities
- Grain boundaries

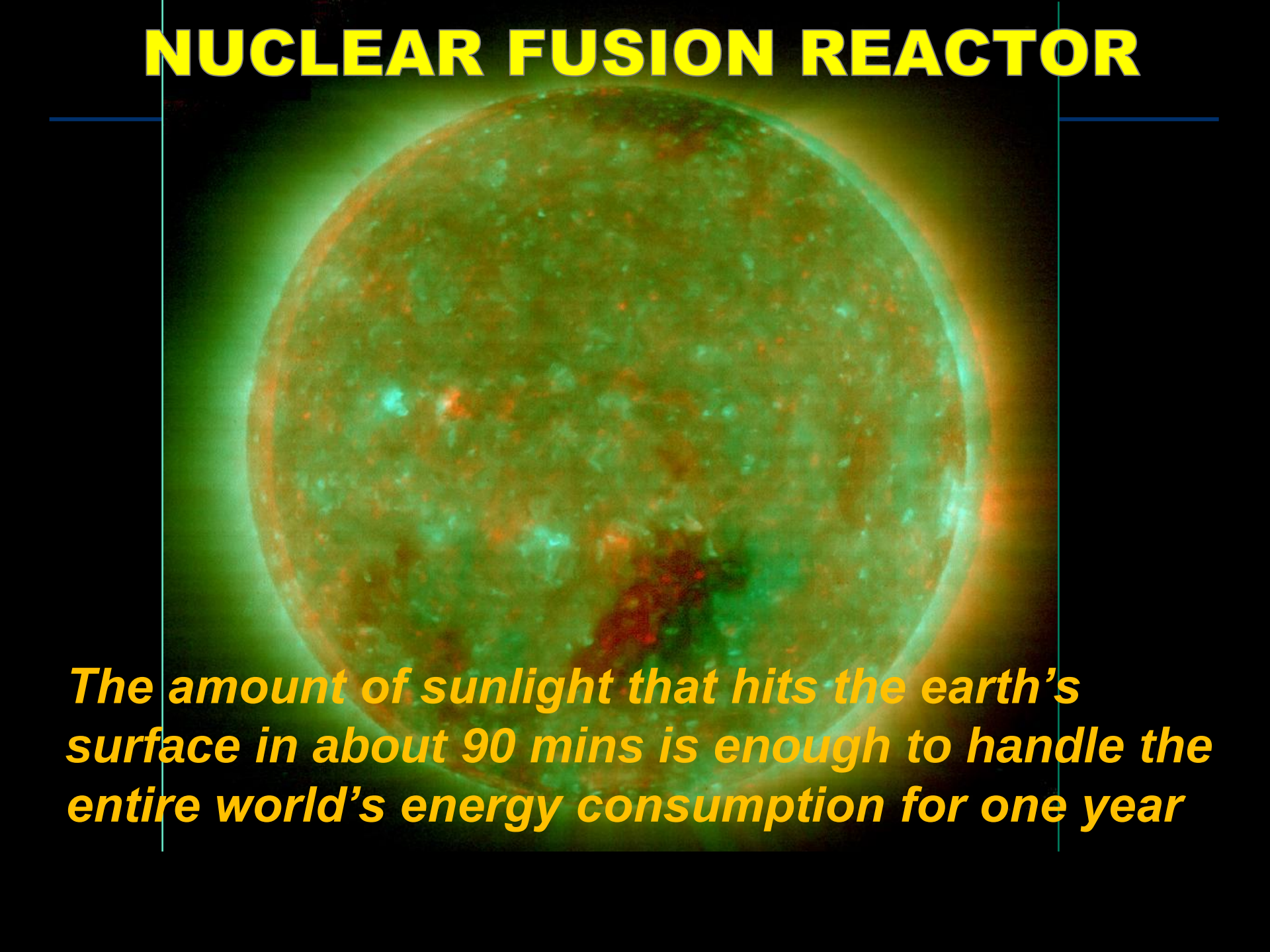



Sodium Batteries: Grid Storage?

- Similar to Li – but greater mass
- Abundant & low cost
- New materials (e.g. $NaMnO_2$)

Nuclear Reactor:
There is a light that never goes out?

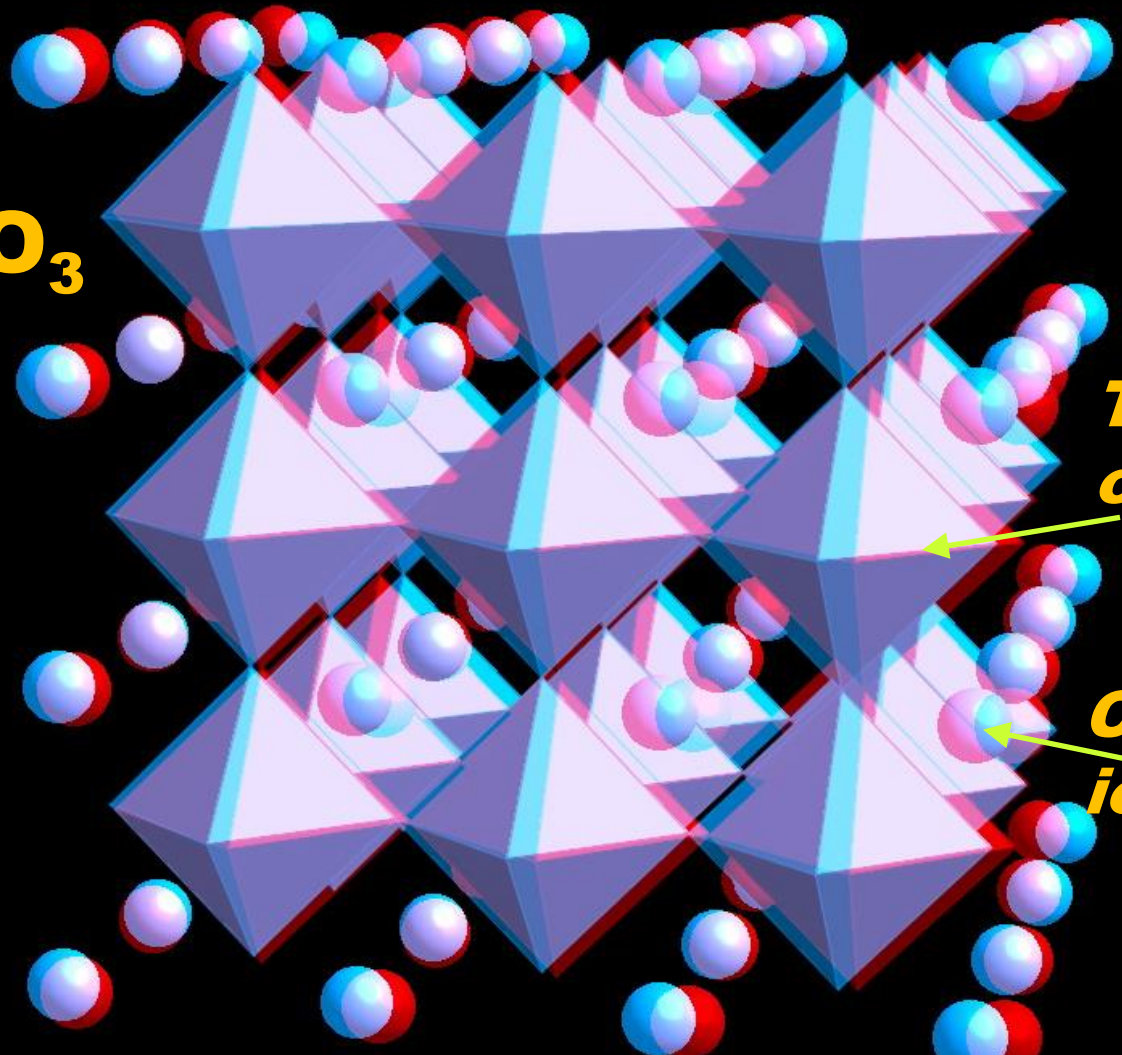
NUCLEAR FUSION REACTOR



The amount of sunlight that hits the earth's surface in about 90 mins is enough to handle the entire world's energy consumption for one year

Perovskite Structure

$CaTiO_3$



Ti-oxygen octahedra

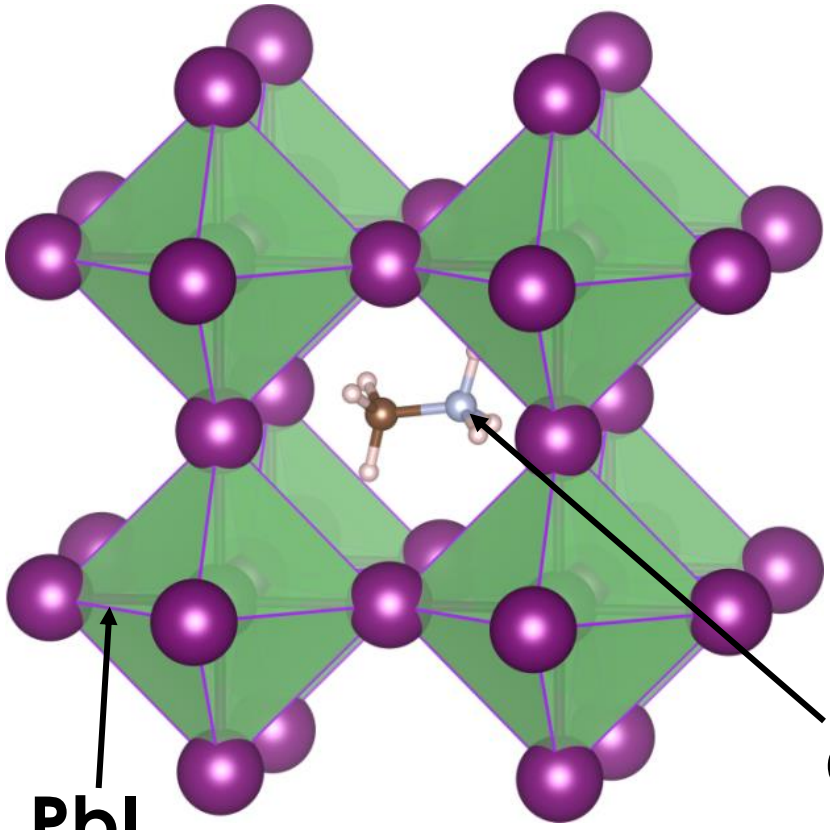
Calcium ions

'Inorganic chameleon'

SILICON SOLAR CELLS

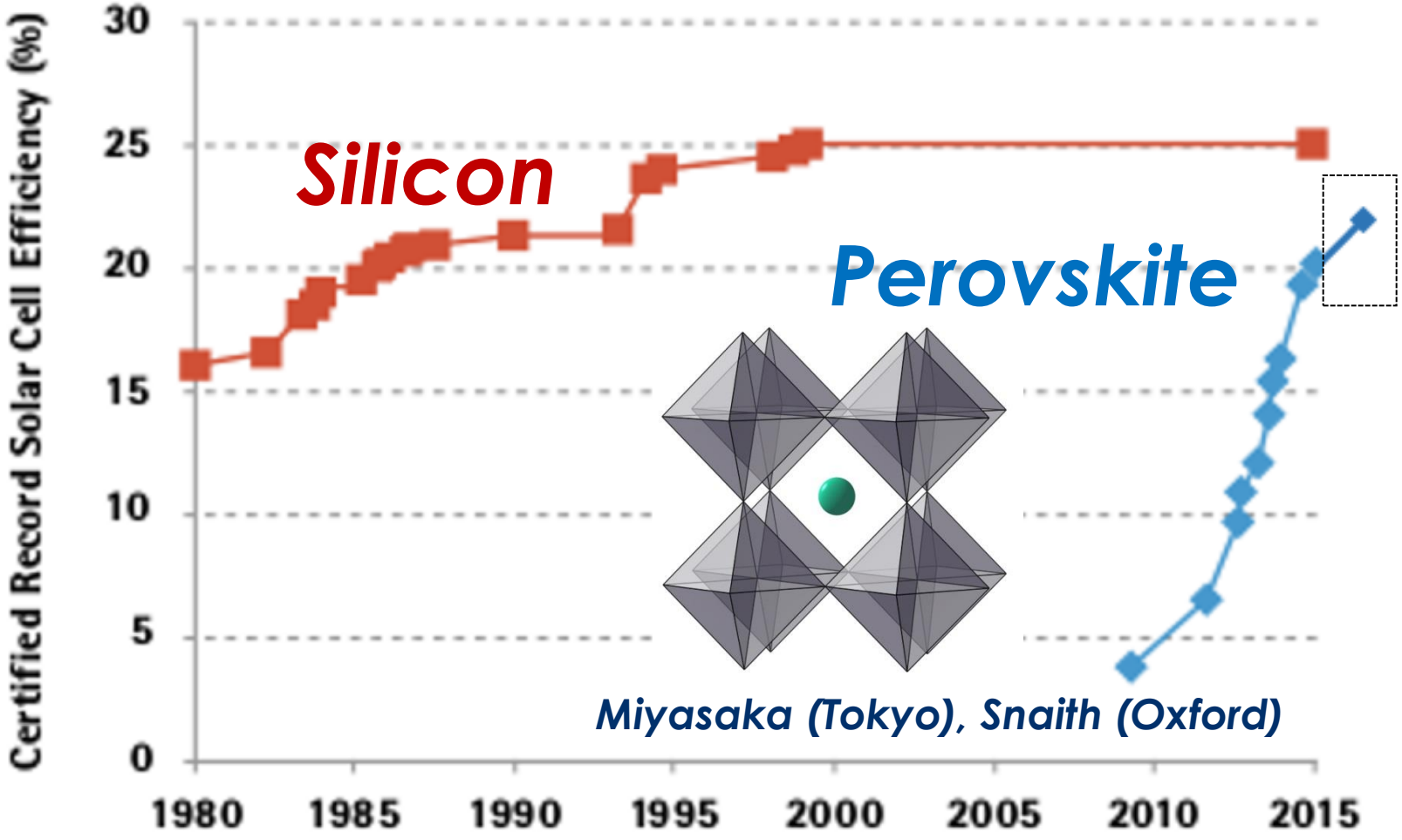
Organic-Inorganic Perovskites

Methylammonium lead iodide $CH_3NH_3PbI_3$



- HOT TOPIC
- Tune absorption
- Synthesis
- Issues: defect chemistry & stability

Why Extraordinary Attention?



$CH_3NH_3PbI_3$: Questions?

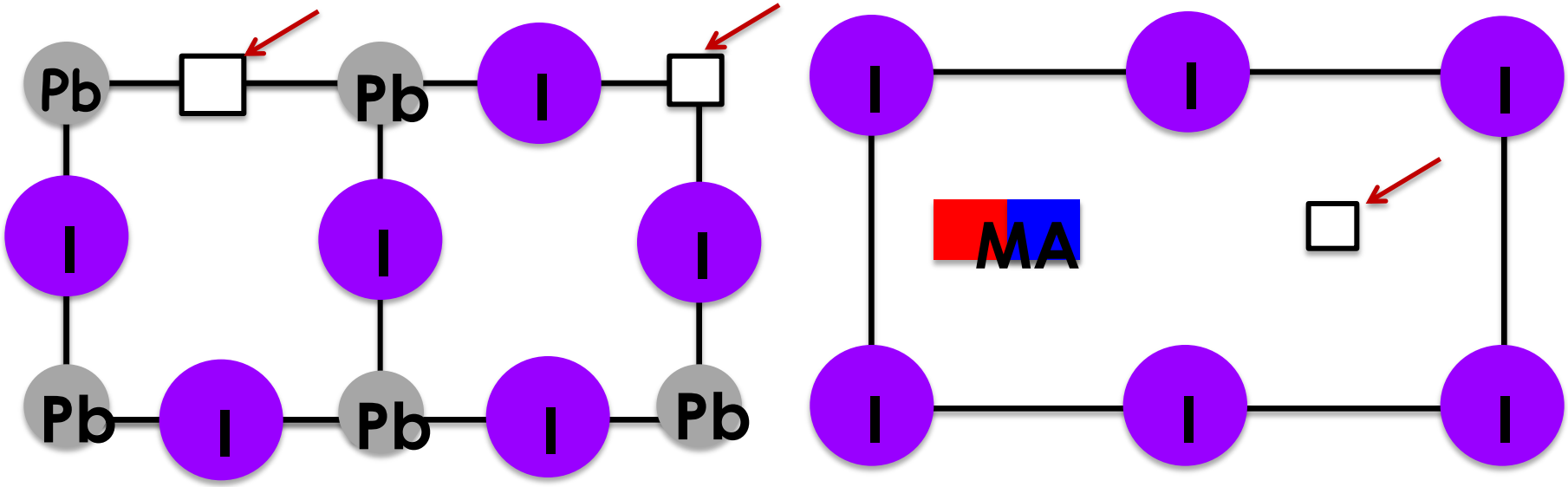
- Atomic defects & mobile ion species?
- Oxygen & light effects? Degradation & passivation?

P. Barnes, S. Haque (Imperial)
S. Stranks (Cambridge)

Hybrid Perovskites: Defects & Ion Transport

$CH_3NH_3PbI_3$: Defect Chemistry?

- Vacancy defects (Scanlon/Walsh, Angew. Chemie, 2015)

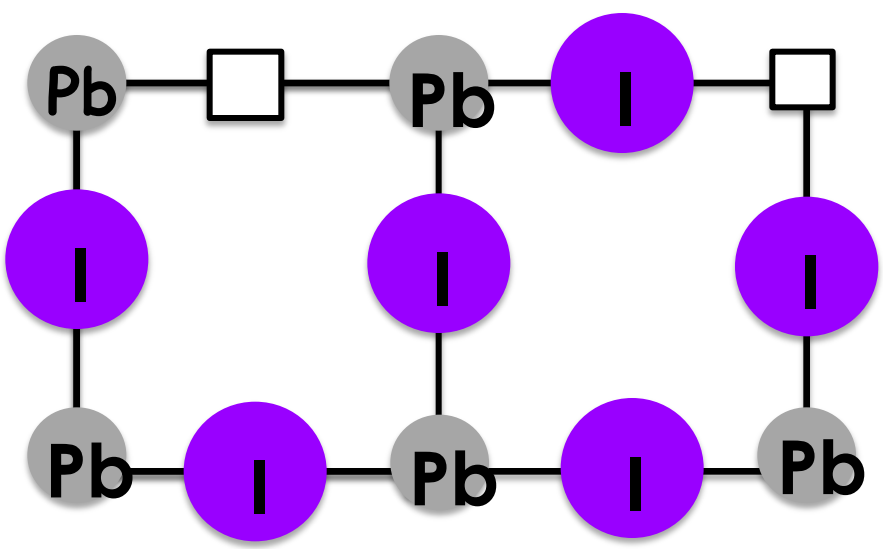


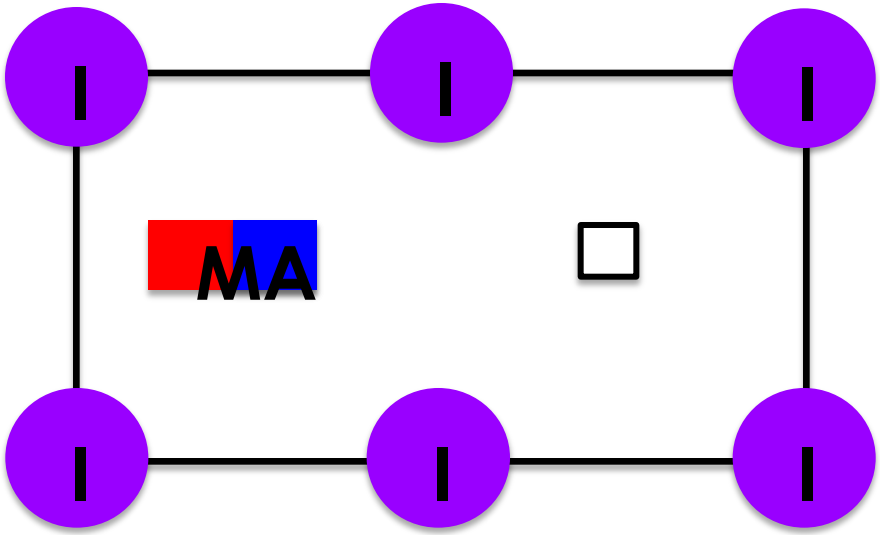
- Supports vacancy assisted diffusion

Ion Vacancy Migration

- Three paths: lowest migration energy?

→ iodide ion → mixed conductor





nature COMMUNICATIONS

Eames et al (2015)
Aristidou et al (2017)

$CH_3NH_3PbI_3$: O_2 Degradation

- Major issue: long-term stability
- Need fundamental understanding

$O_2 \rightarrow$ no degradation

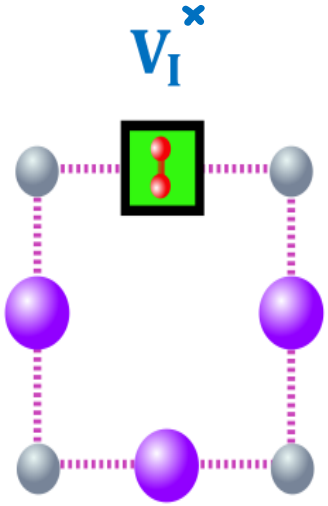
O_2 + light $\rightarrow PbI_2 + I_2 + H_2O + CH_3NH_2$

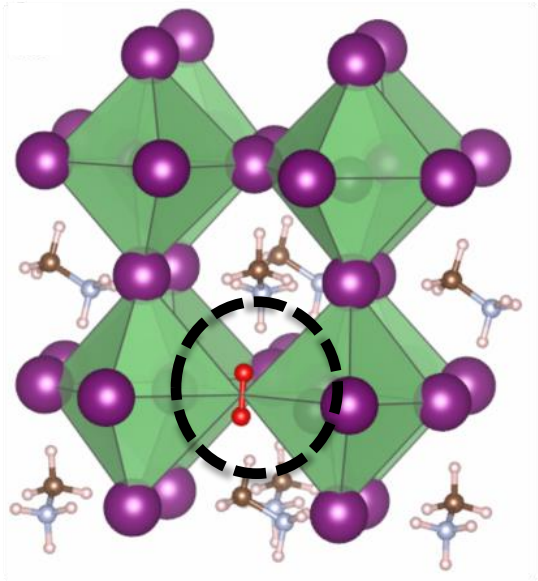
Superoxide O_2^- observed (photoluminescence expts)

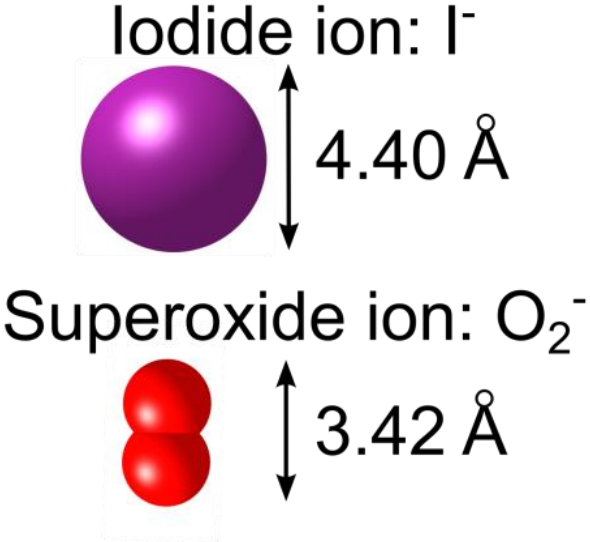
Aristidou et al, *Angew. Chem.* (2015)

Superoxide at Iodide Vacancy

- Superoxide ion restores octahedral coordn ('repairs' the vacancy)







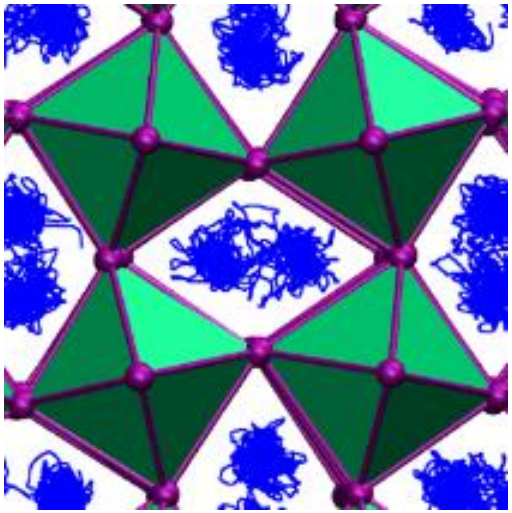
Aristidou et al, *Nature Commun.* (2017)

Other Perovskite Studies

Impact of Oxygen & Light

Joule, Issue 1 (2017)
Adv. Mater. (2018)

Dynamics of mixed cation perovskites



ACS Energy Lett (2017)

Concluding Remarks…

Take Home Messages

New complex materials & fundamental insights

Defects & transport in Li-ion battery & PV materials

Li-rich Li_2FeSiO_4: high interstitial diffusion rates

$CH_3NH_3PbI_3$ solar cell: ion migration & iodide defects

FUTURE? ENERGY MIX

Challenging & exciting time: new materials & underpinning science

Discussion Meeting

EXCELLENCE IN SCIENCE

THE ROYAL SOCIETY

EPSRC Programme Grant

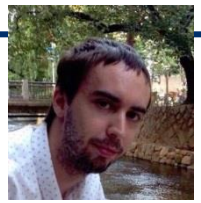
'*Energy Materials for a Low Carbon Future*'

London, Sept 17-18, 2018

Thanks & Ri Lectures

Acknowledgements


Alexandra Szemjonov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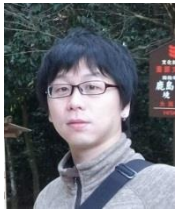
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Chris Eames


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Bethan Charles


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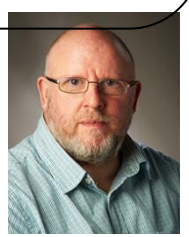
Oli Weber


Mark Weller


Alison Walker


Petra Cameron


Ben Morgan


Tim Mays

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CHRISTMAS LECTURES 2016

The Royal Institution
Science Lives Here

BBC FOUR

Supercharged: Fuelling the Future

The **End**