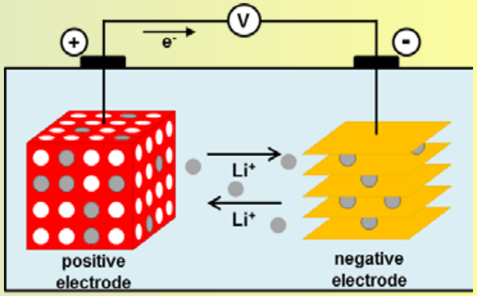
Joint French-Swedish school on X-rays and Neutrons techniques for the study of functional materials for energy

13-17 May 2019 Lund (Sweden)

Materials for Batteries



Gwenaëlle ROUSSE

Chimie du Solide et de l'Energie, Collège de France-Sorbonne Université, Paris

Outline of the course

Introduction to Li-ion batteries: fondamentals

I. Trends in positive electrode materials for Li-ion

a) Polyanionic compounds: classical redox

b) Rocksalt-based derivatives: anionic redox

II. Beyond Li-ion batteries

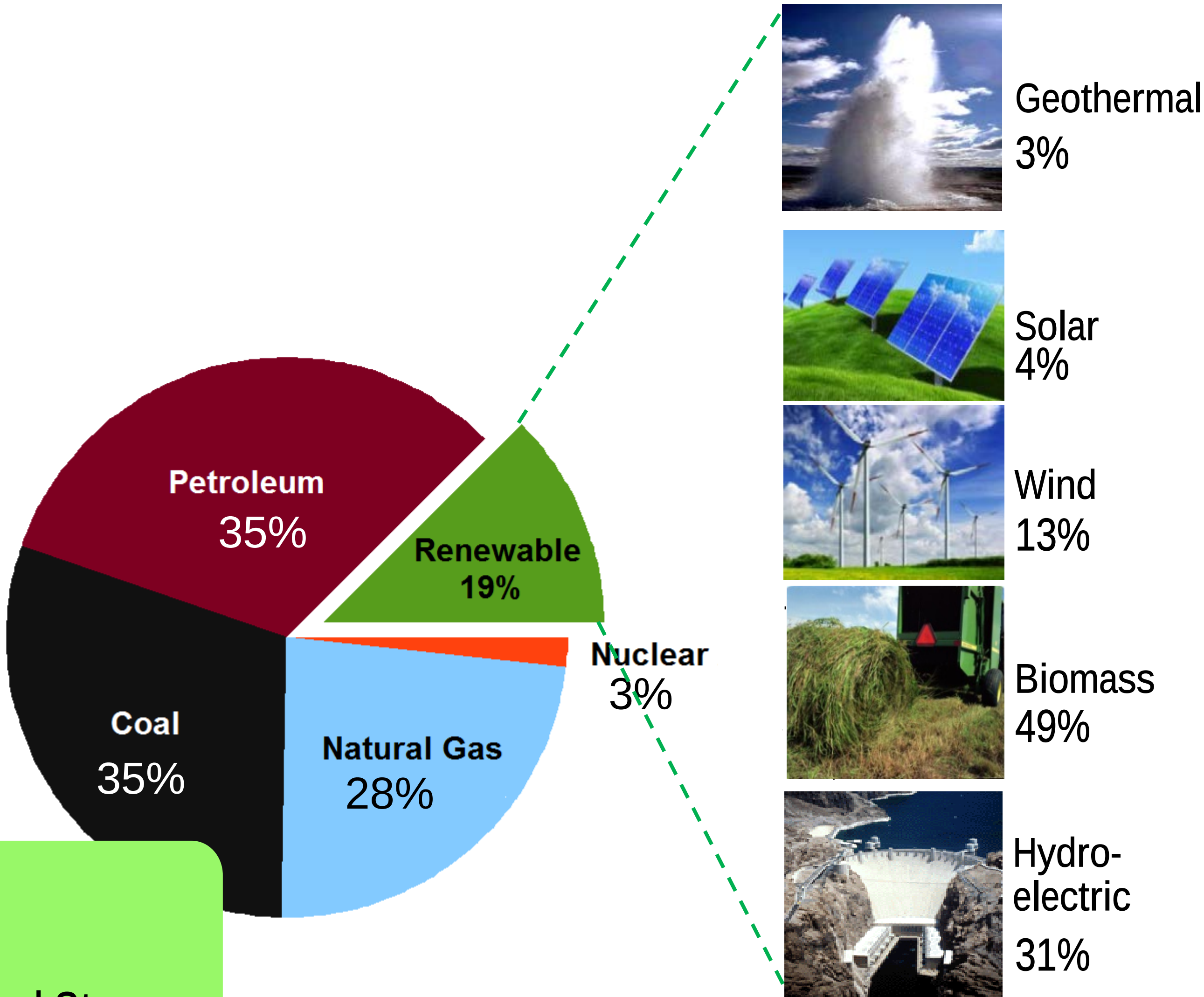
a) Solid state batteries

b) Na-ion batteries

Today's energy overview

(14 TW) → (28 TW)

http://americanenergyindependence.com/energychallenge.aspx



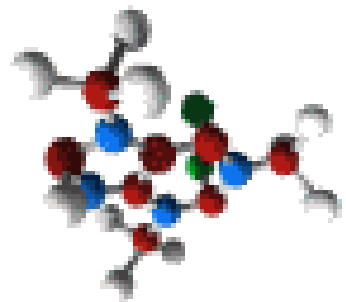
Renewable energies

↓

Production, Transport, Conversion and Storage

Electrochemical energy storage

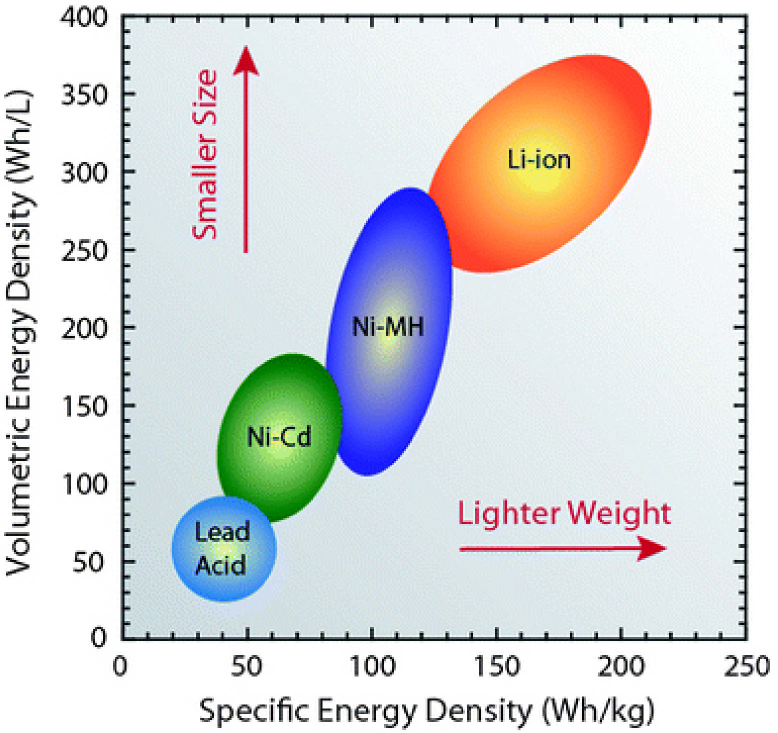
1801 Alessandro Volta
(Cu/Zn)



Chemical

Batteries

Electric



Lithium = highly reductive metal (-3.04 V vs SHE) + small weight

Li-ion Batteries

versatility + high energy density

Li-ion batteries:
versatility and high energy density

Portable electronics

Transport
Electric Vehicles

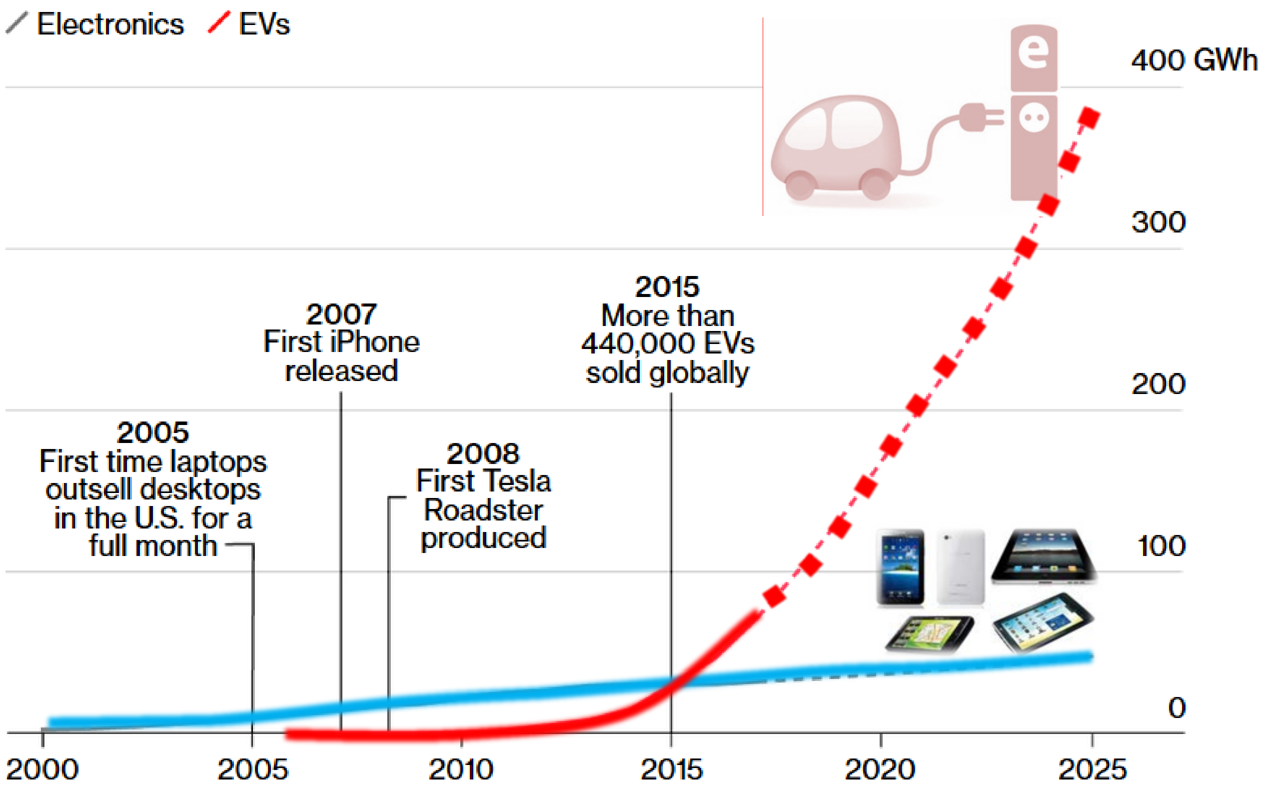
Storage
Renewable energies

Bright future of Li-ion batteries

Research boosted by business

EVs Dominate Demand for Lithium-Ion Batteries

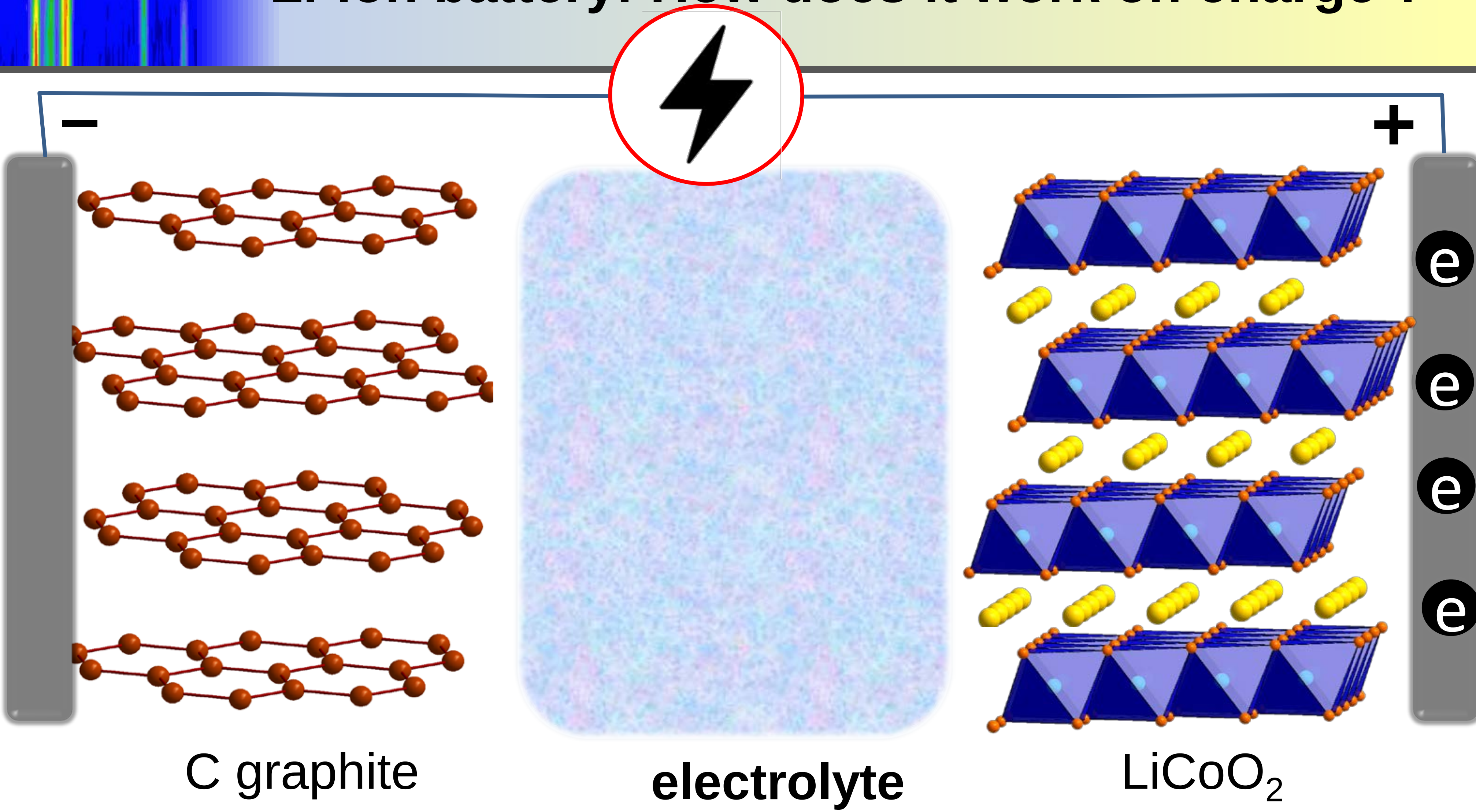
Estimated global demand by product, in gigawatt-hours



Sources: Avicenne; BNEF; Current Analysis; Bloomberg reporting

2025: 9% EV's (Bloomberg) 100 $/kWh, 700 Wh/L, 350 Wh/kg

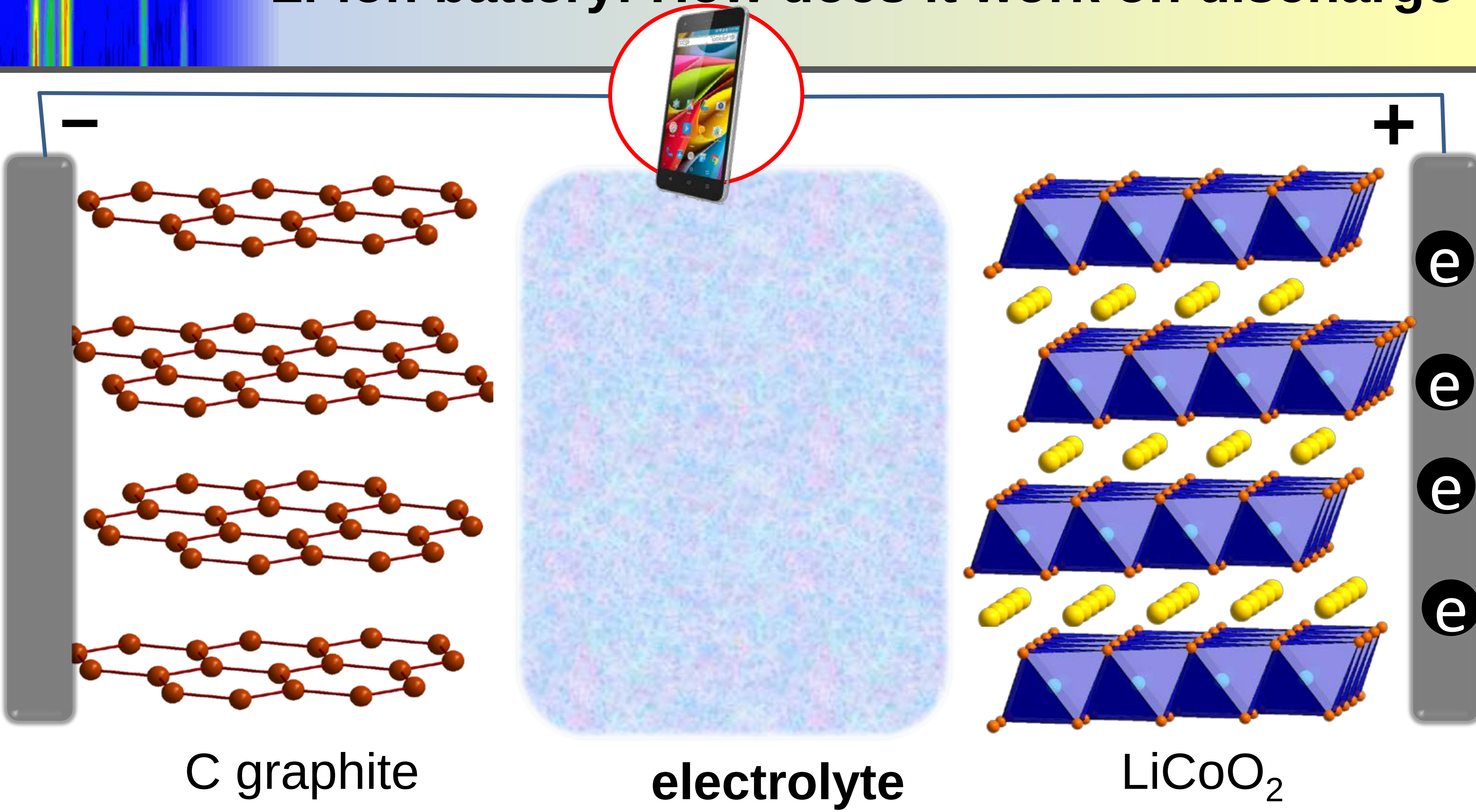
Li-ion battery: How does it work on charge ?



$C_6 + x\,Li^+ + x\,e^- \longrightarrow Li_xC_6$

$LiCoO_2 \longrightarrow Li_{1-x}CoO_2 + x\,Li^+ + x\,e^-$

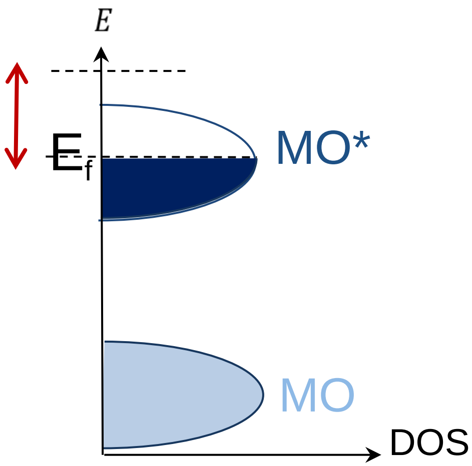
Li-ion battery: How does it work on discharge ?



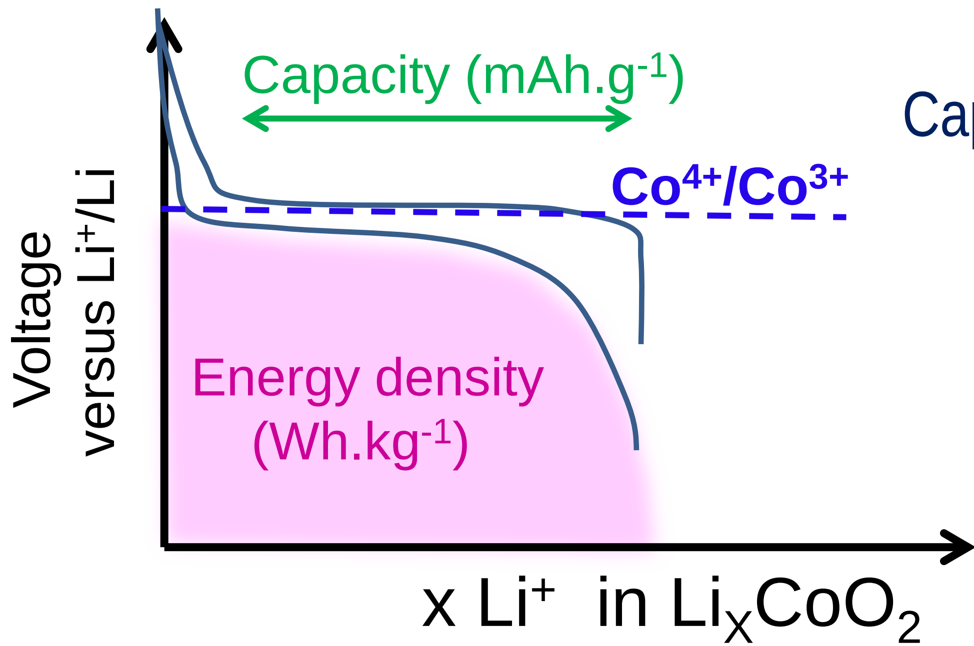
$C_6 + x\,Li^+ + x\,e^- \longrightarrow Li_xC_6$

$LiCoO_2 \longrightarrow Li_{1-x}CoO_2 + x\,Li^+ + x\,e^-$

Li-ion battery: How does it work ?

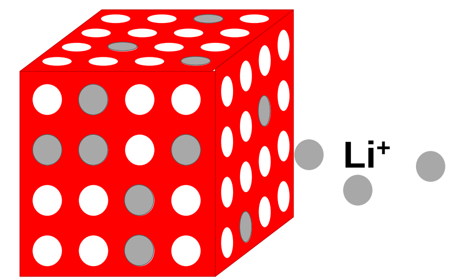


Electronic structure



Nb of e^-/Li^+

Capacity (Ah/kg) $= 26.8 \times \frac{x}{M}$



Crystallographic structure

Energy density (Wh.kg-1) = Voltage V (volts) x Capacity (Ah/kg)

strategy 1:
Polyanionic compounds

strategy 2:
Anionic redox

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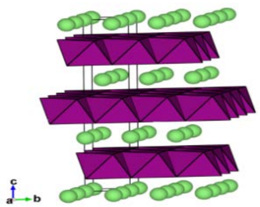
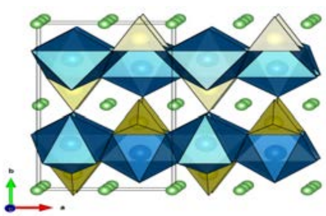
Electrode materials for Li-ion batteries

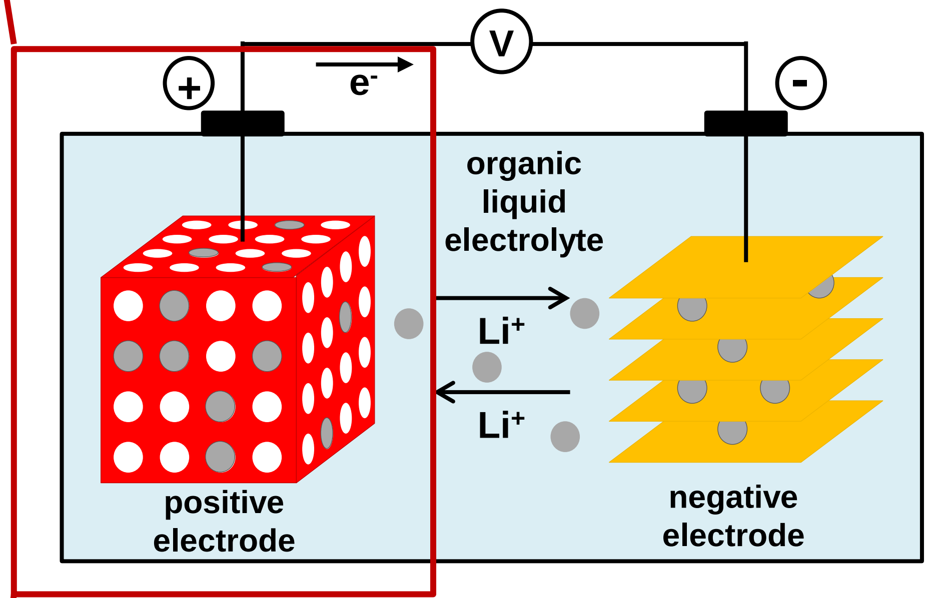
Spinel $LiMn_2O_4$
4.2 V *vs.* Li^+/Li^0

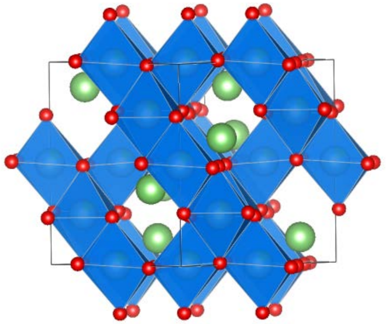


Lamellar oxides
$LiCo_xM_{1-x}O_2$
4.0-4.4 V *vs.* Li^+/Li^0

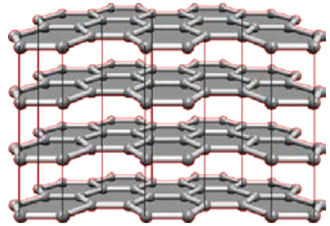


***Olivine* $LiFePO_4$**
3.45 V *vs.* Li^+/Li^0

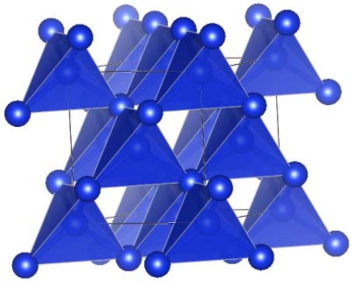




$Li_4Ti_5O_{12}$
1.5 V *vs.* Li^+/Li^0



Graphite
0.2 V *vs.* Li^+/Li^0



Silicon
0.4 V *vs.* Li^+/Li^0

Li-ion batteries : strategy for new compounds

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Improved performances

↑

New electrode materials ← Chemical Composition + Functional Properties

↑

Structural features

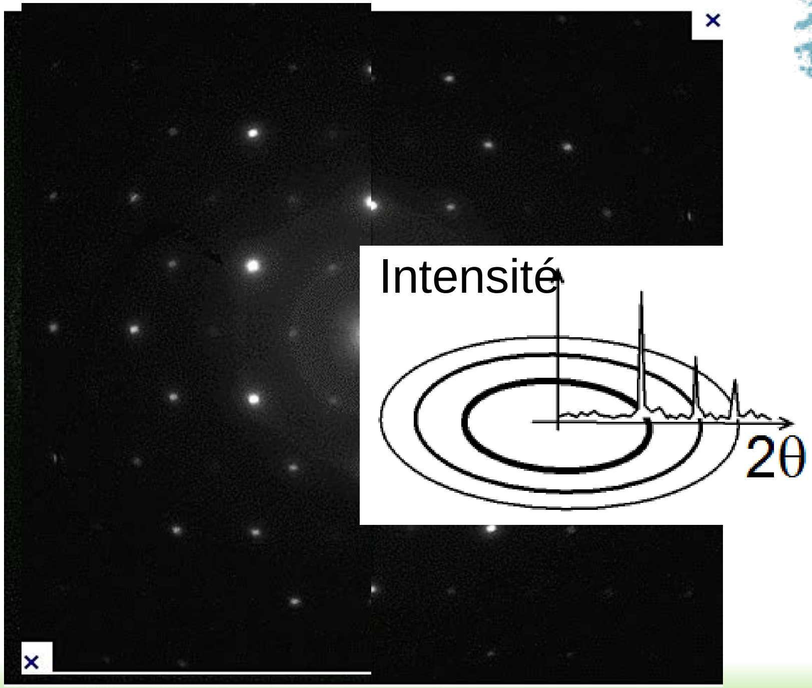
New compounds = new structures to determine

Single crystals XRD: method of choice….

Powders are sometimes the only option

Powder:
(hkl) reflections overlap

Difficult structural determination



New compounds = new structures to determine

Unknown structure

Initial structural model

Refined structure

Solving the structure

Sometimes a difficult step

Unit cell
Space group
Approached atomic positions

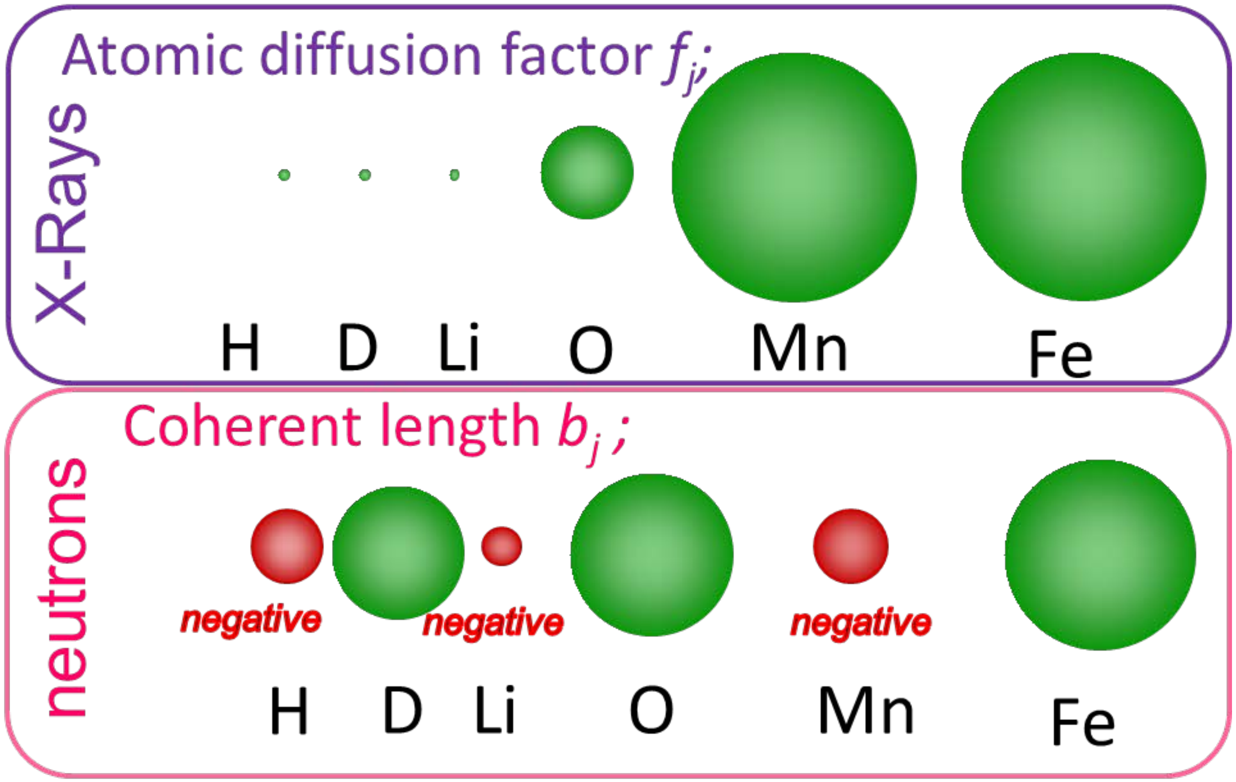
Rietveld

Structural refinement

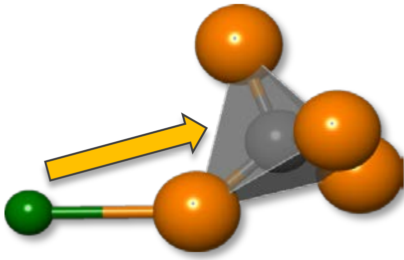
Unit cell
Space group
Precise atomic positions

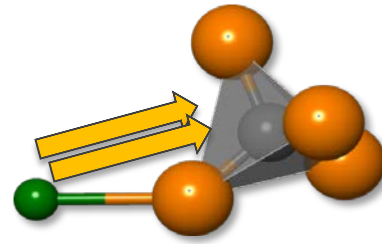
New compounds = new structures to determine

- *Ab initio* structural determination, simulated annealing, & direct methods, Fourier maps, charge flipping …
- X-Ray and neutron scattering techniques



from $LiFePO_4$ to the sulfate wealth

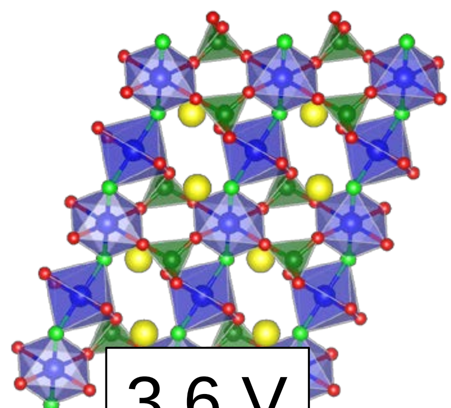
M  PO_4

M  SO_4

χ

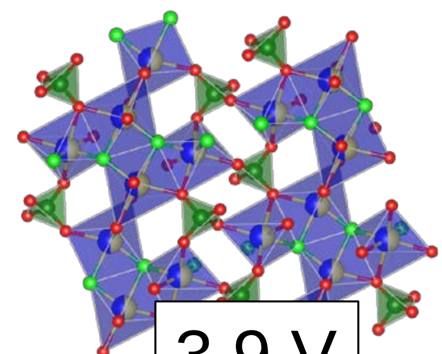
phosphates → *« inductive effect »* **Ionicity ⇈** → sulfates + Fluorine

tavorite



3.6 V

triplite



3.9 V

3.45 V

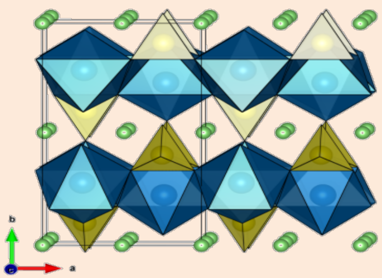
⇨ **$LiFePO_4 \rightarrow LiFeSO_4F$**

⇨ **$AFeSO_4F$**
A=Na, K

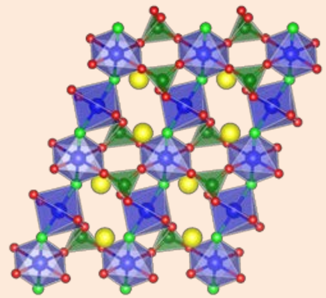
Nature Materials **2010**, 9, 68–74.
Nature Materials **2011,** 10, (10), 772-779.

From polyanionic compounds to high energy density layered oxides

Polyanionic based compounds

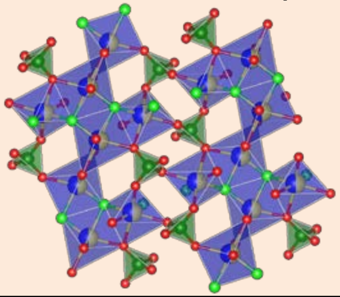


Olivine **$LiFePO_4$**
3.45 V *vs.* Li^+/Li^0



Tavorite $LiVPO_4F$, $LiFeSO_4F$

Triplite $LiFeSO_4F$

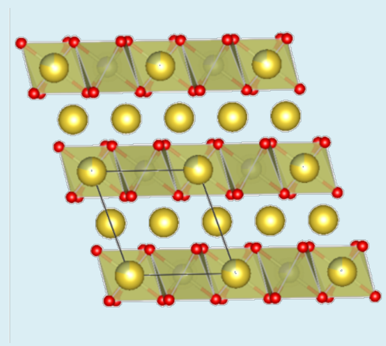


& Borates, Silicates…

Masquelier, Croguennec, *Chemical Reviews* **2013**, *113*, 6552.

Moderate voltage & capacity
Stable structural framework on cycling

Layered-type compounds

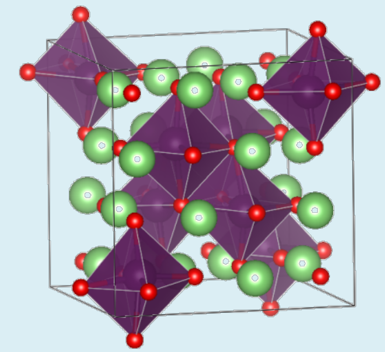


NMC, $LiCo_xM_{1-x}O_2$

Li-rich NMC, Li_2MO_3 M=3d, 4d… metals

4.0-4.5 V *vs.* Li^+/Li^0

Derivatives from the rocksalt structure



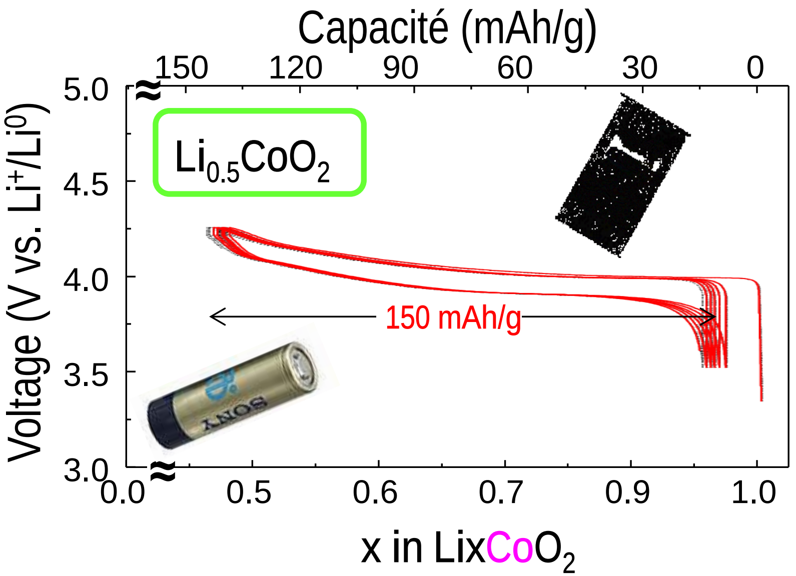
Li_3NbO_4
Yabuuchi, N. et al.
PNAS **2015**, *112* (25), 7650.
and *Chem of Mater* **2016**.

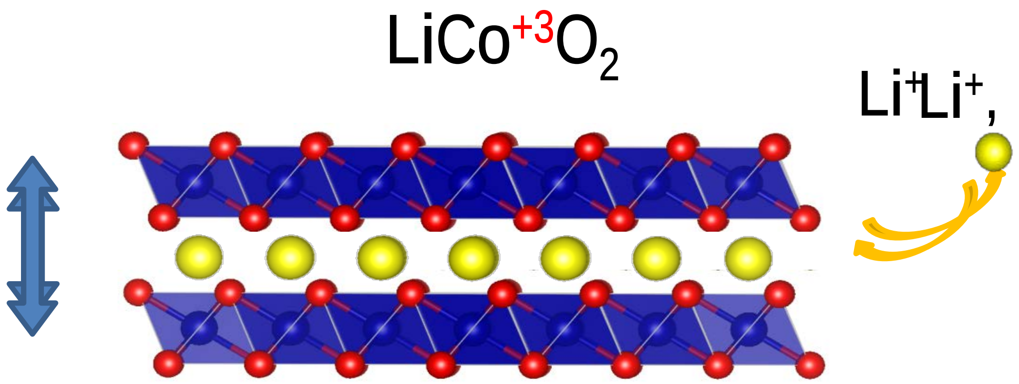
$Li_4Mn_2O_5$
Freire, M.; … Pralong, V. A
Nature Materials **2015**, *15* (2), 173

Large capacity & high voltage
but stability on cycling not yet fully mastered

From polyanionic compounds to high energy density layered oxides

$LiCoO_2$ has been the "stellar" material for numerous years





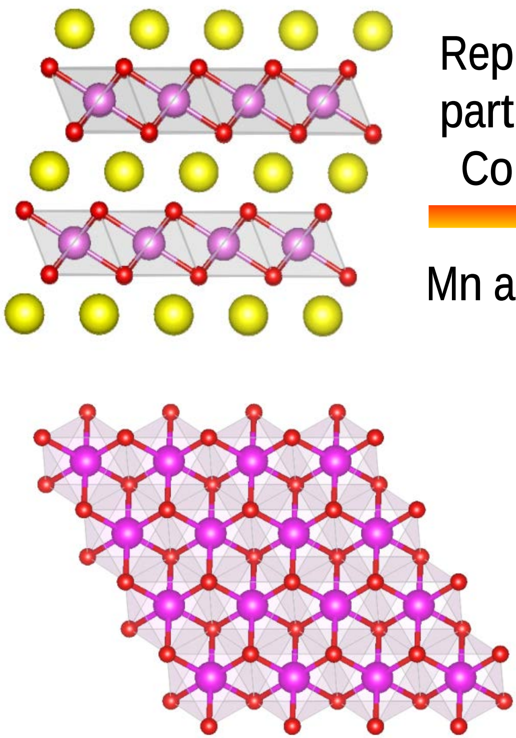
Redox process solely involves cations

The Li_xCoO_2 electrode: evolution in the last 25 years

1991 — **2001-2008** — **2006 …. 2019**

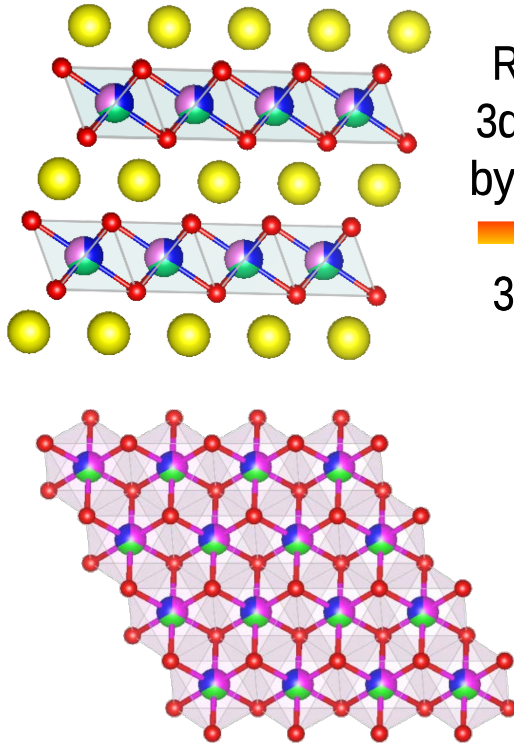
NMC — Li-rich NMC

$Li[Co]O_2$



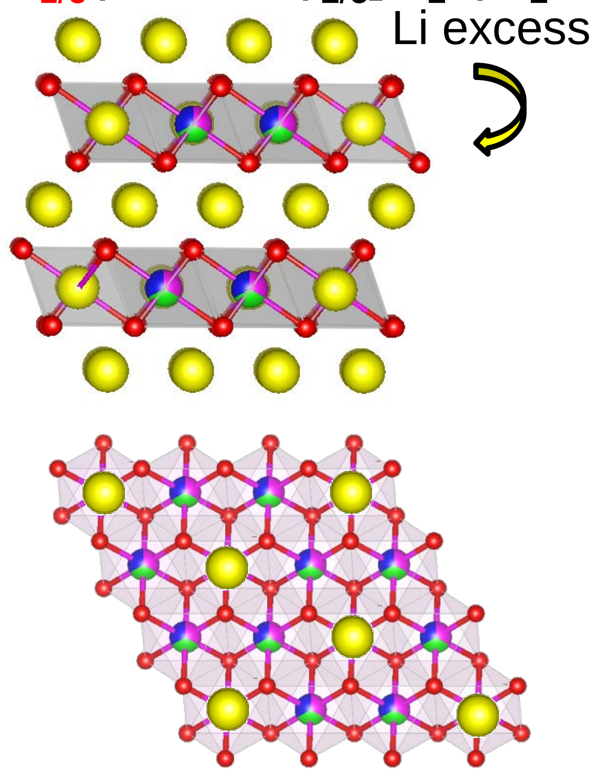
Replace partially Co by Mn and Ni

$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$



Replace 3d-metals by Li in the 3d-metal layer

$Li[Li_{1/3}(NiMnCo)_{2/3}]O_2$ (Li_2MO_3)



150 mAh/g

180 mAh/g

270 mAh/g

Origin of extra-capacity ?

Origin of exacerbated capacity

$Li[Li_{0.2}Mn_{0.53}Co_{0.14}Ni_{0.13}]O_2$

[3 redox centers]

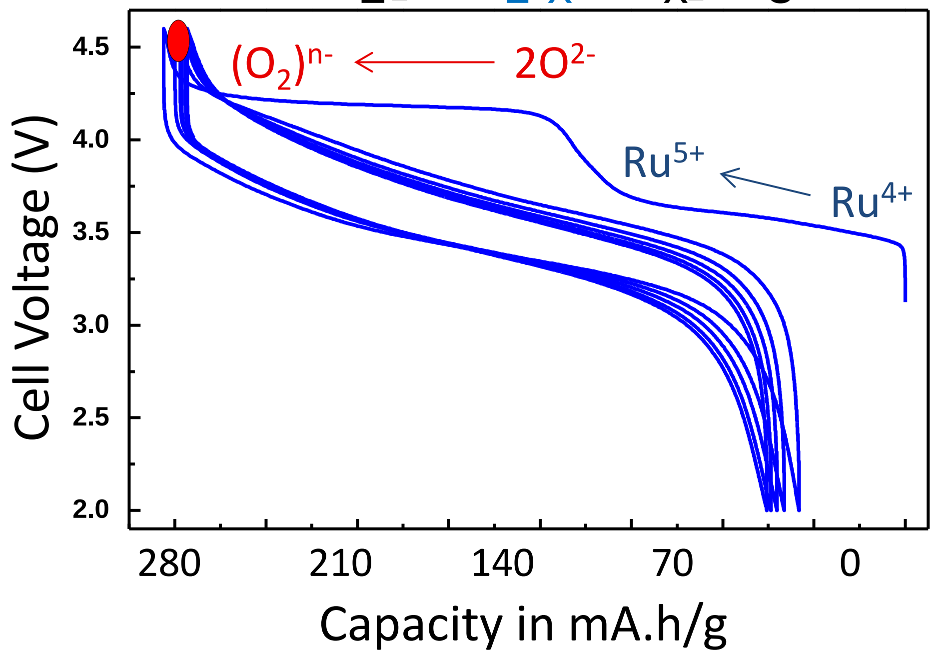
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

[1 redox center]

$Li_2[Ru_{1-x}Sn_x]O_3$

Li_2IrO_3

$Li_2[Ru_{1-x}Sn_x]O_3$



Electron Paramagnetic Resonance

Hard X-Ray Photoelectron Spectroscopy

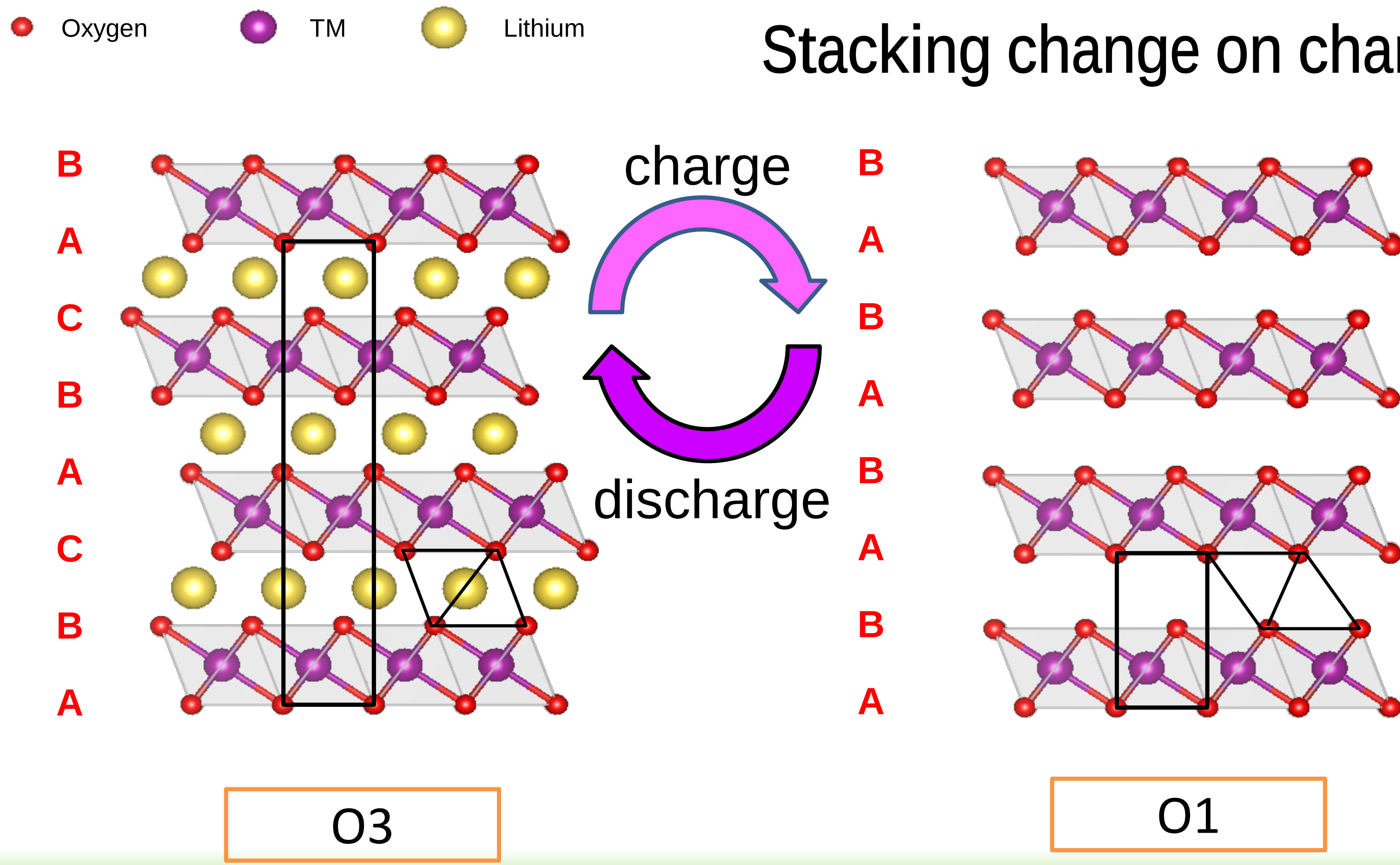
Anionic redox : $2\ O^{2-} \leftrightarrow O_2^{2-} + 2\ e^-$

Structural signature of oxygen redox?

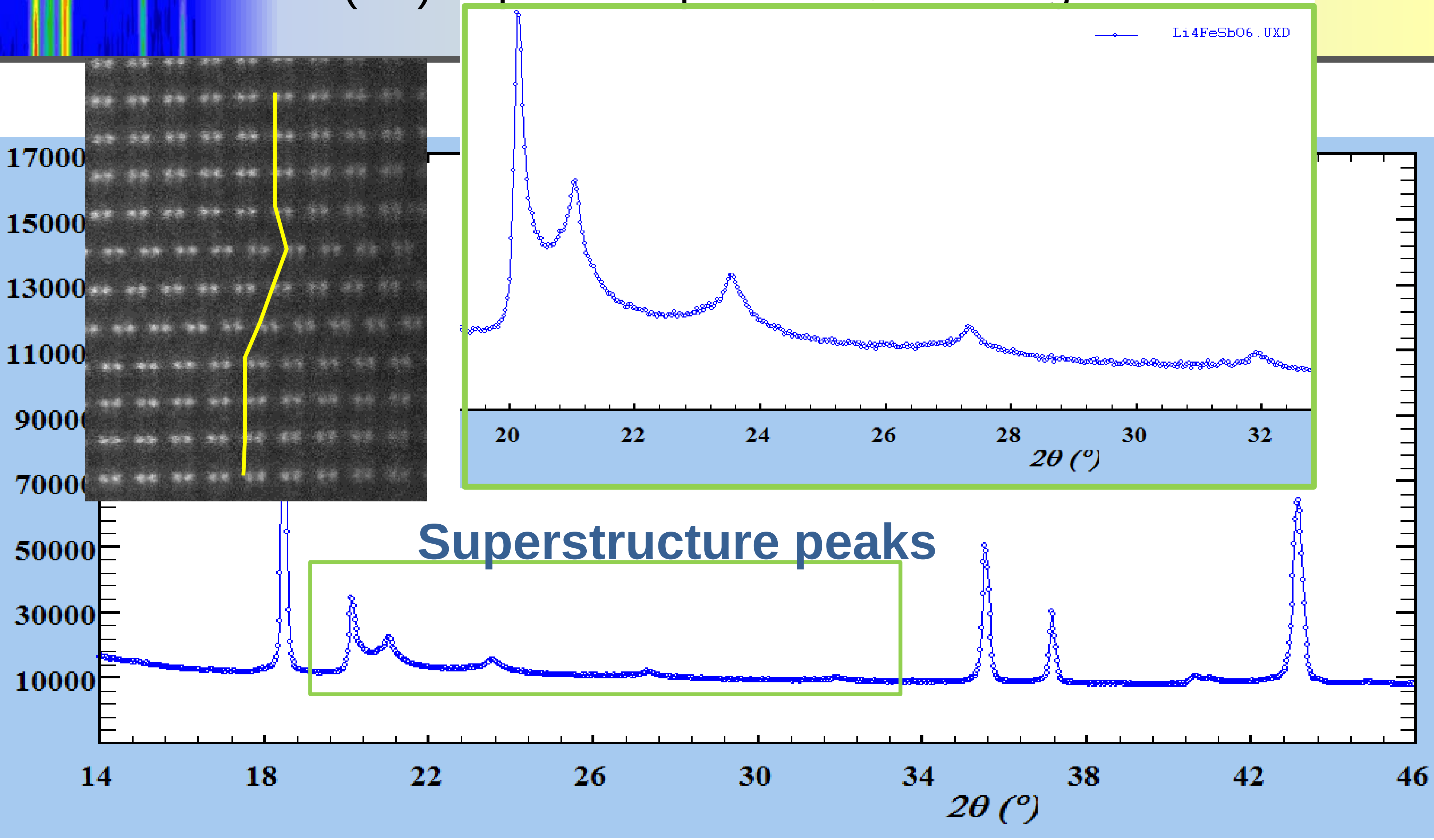
Sathiya, M. *et al.* Reversible anionic redox chemistry in high-capacity layered-oxide electrodes. *Nature Materials* **12,** 827–835 (2013).

Structural changes on cycling ?

Stacking change on charge



(hkl) dependent profiles → stacking faults

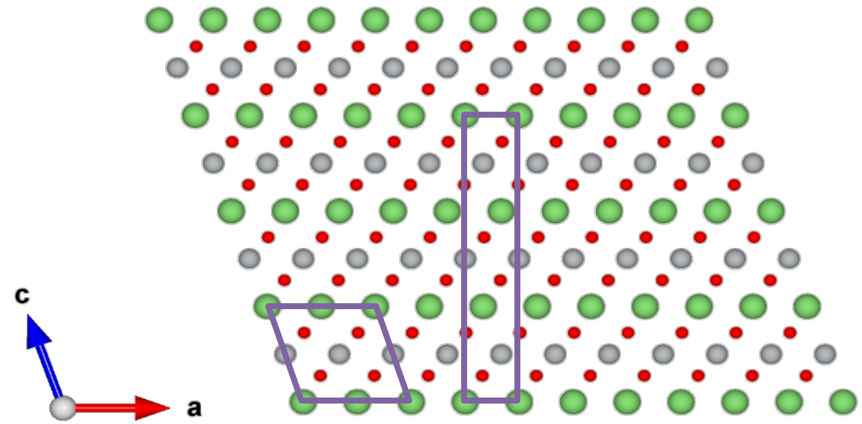


How to handle such patterns ?

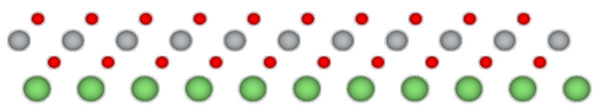
Structural description

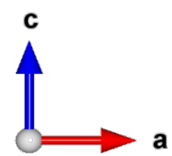
No cell

No space group



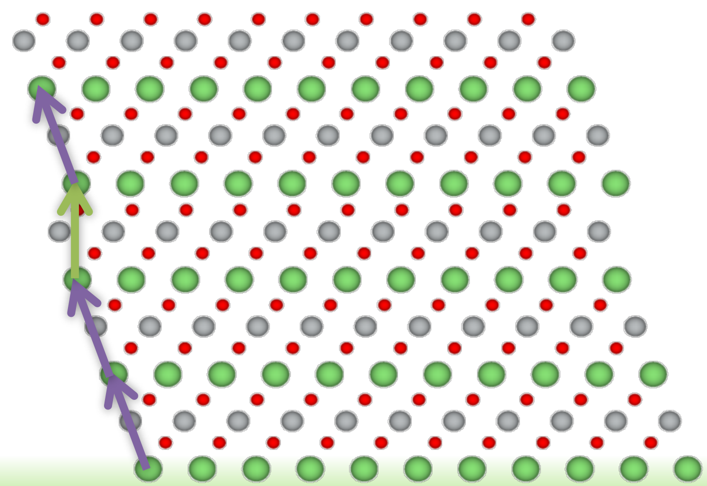
Superposition of layers stacked with a certain probability

layer1 

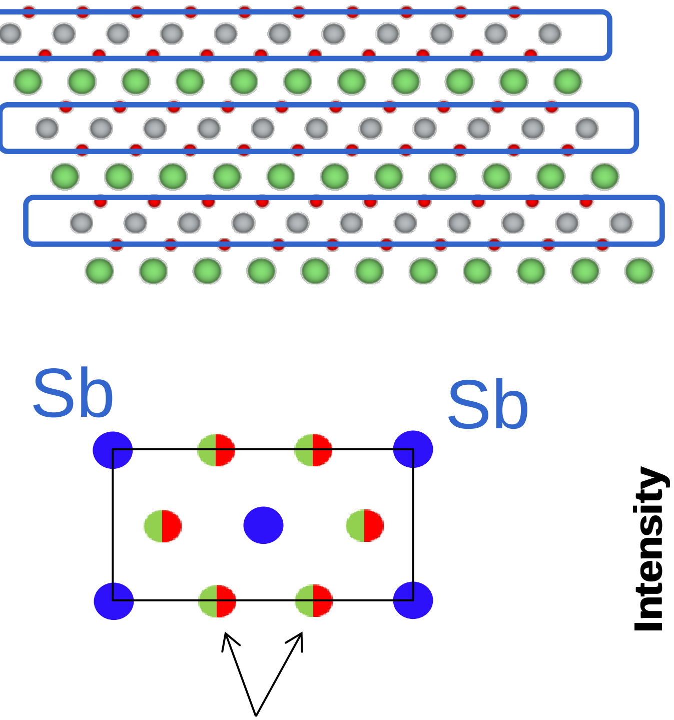


Stacking vector 1  Probability α_1

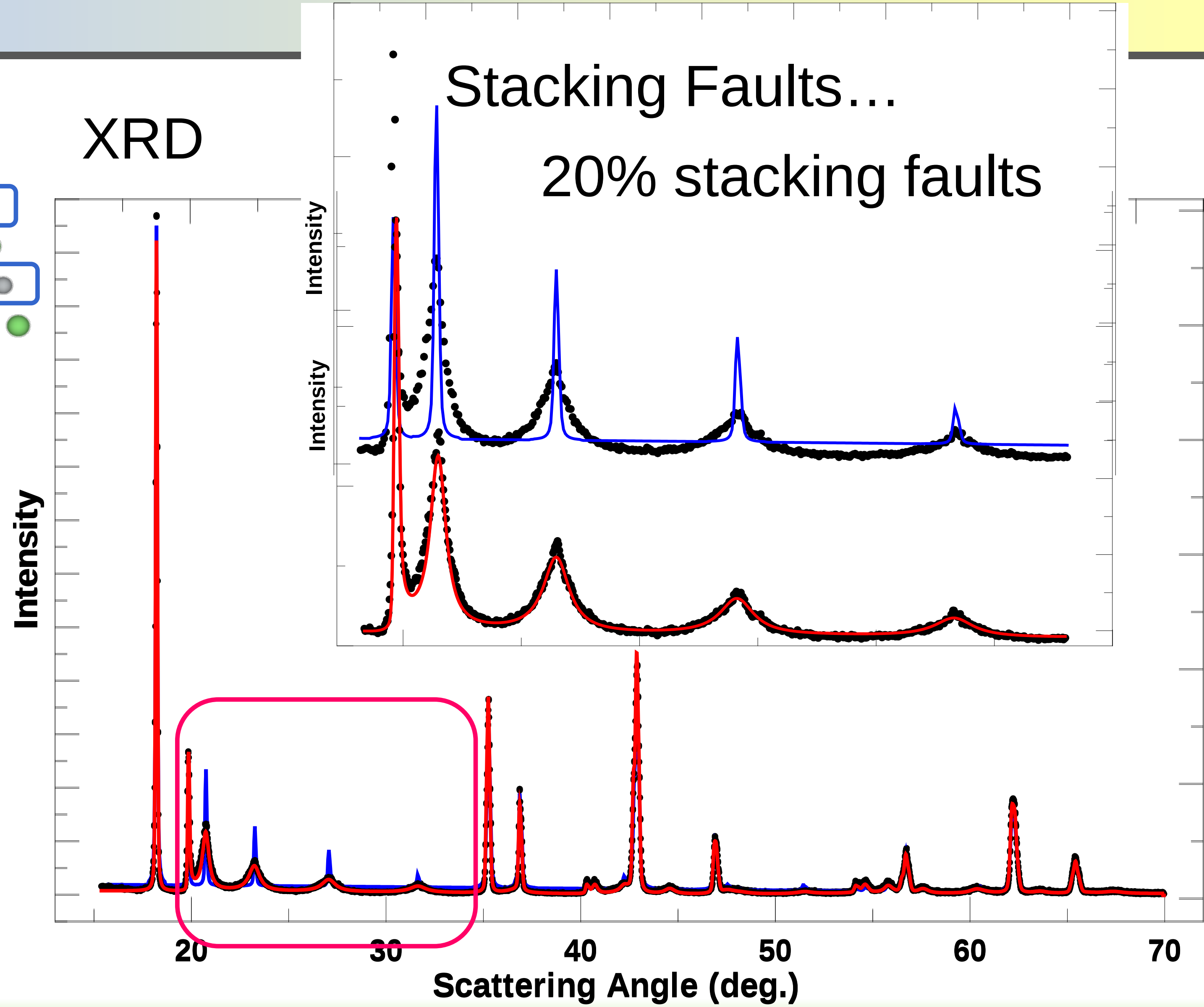
Stacking vector 2  Probability α_2



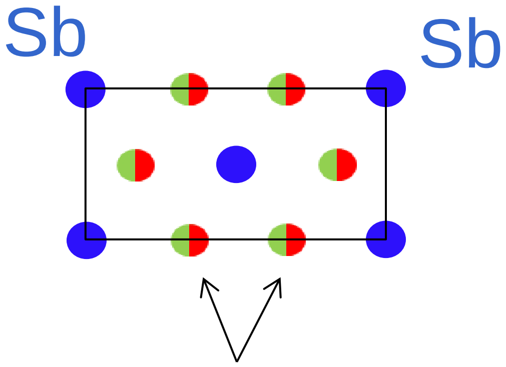
Example 1: the layered compound $Li_2Fe_{0.5}Sb_{0.5}O_3$



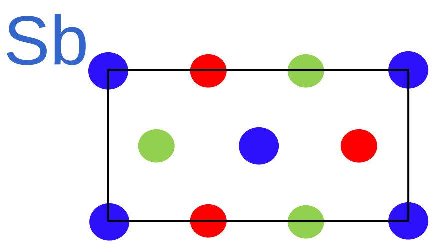
Li/Fe
statistical
distribution



Is this model reflecting reality ???

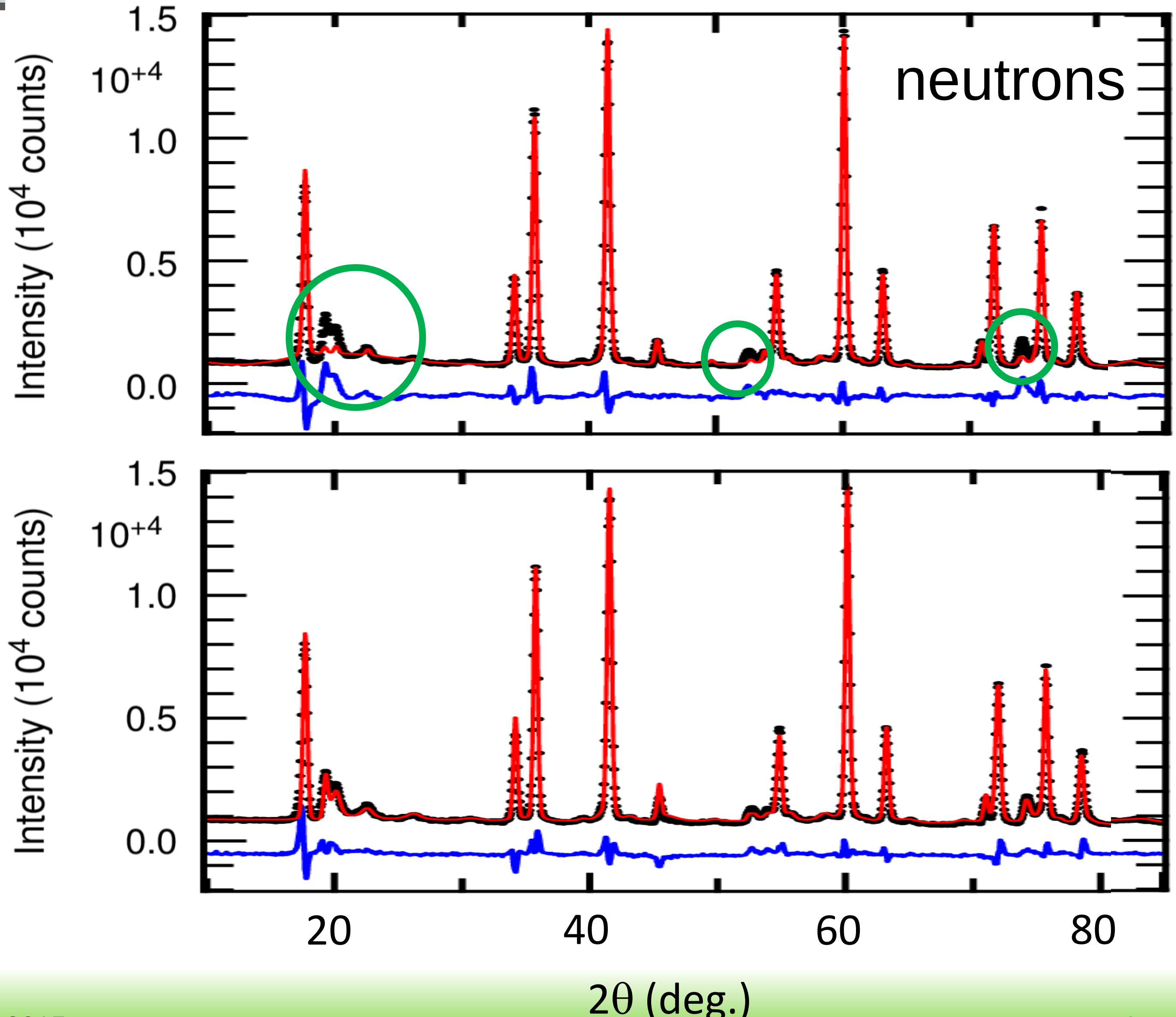


Li/Fe
statistical
distribution



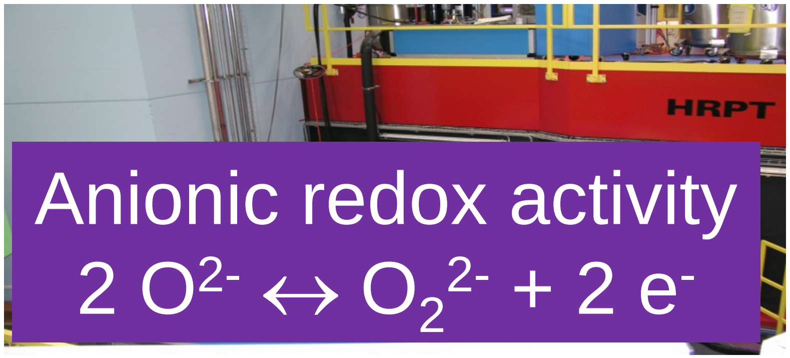
Fe Li

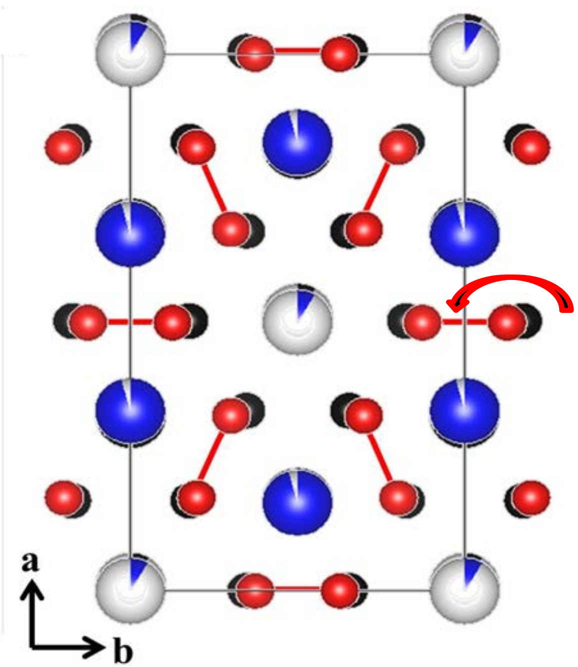
Li, Fe and Sb all ordered



Example 2: Li_2IrO_3: (O-O) dimers

Use of the HRPT neutron diffractometer at PSI-SINQ

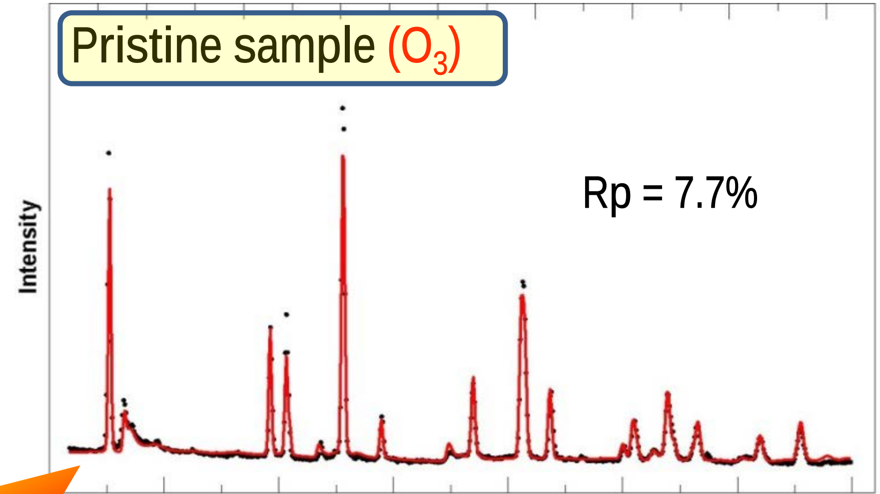


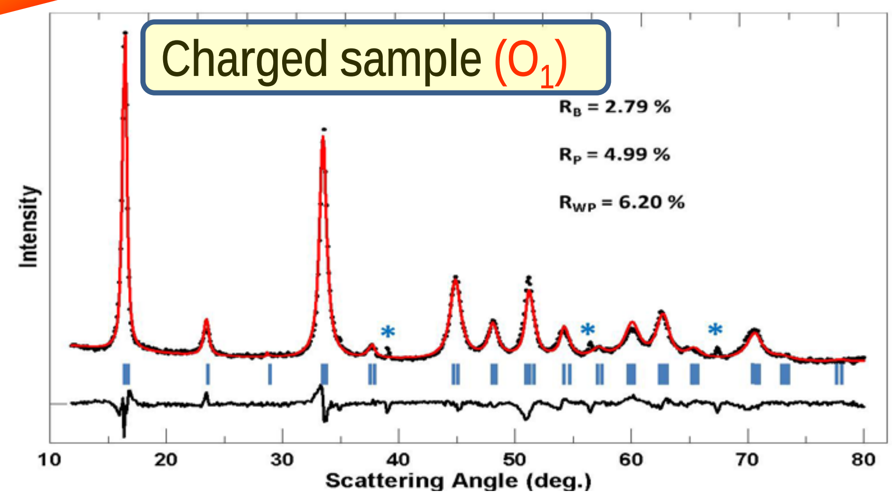


(O-O) dimers 2.45 Å

vs.

2.84 Å (O-O)

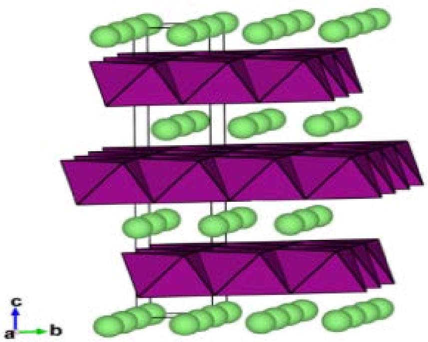




First evidence for shorter O-O bonds in Li-rich layered oxides electrodes

E. McCalla, A. Abakumov, G. Rousse, M.L. Doublet and J.M. Tarascon , Science ; 2015

Trends on electrode materials for Li-ion batteries



Anionic oxygen redox in 2D and 3D compounds

NMC compounds ?
Cobalt: costly and ethical issues: from NMC 333 to 622, 811…

How to apply in **Li-rich NMC** that in addition suffer from cationic migrations, O_2 release ?

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   a) Solid state batteries
   b) Na-ion batteries

a) All-solid-state batteries
Recent revival : industrial rush announcements

Toyota Announce

Nov 22, 2010 19:06
Kouji Kariatsumari, Nikkei Electronics

Toyota Motor Cor
battery Nov 18, 2
measuring about

electrive.com
industry service for electric mobility

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Battery & Fuel Cell >

Jun 18, 2018

Japan's industry join forces to beat China to solid-state batteries

BATTERIES | HONDA | JAPAN | NEDO | NISSAN | PANASONIC | SOLID-STATE | TOYOTA

ight Get Solid State
ears

14 SHARES | SHARE | TWEET

es the following on Samsung's

or smartphones will be mature
sung Electronics whether it will
echnology of our rival firm (LG
r smartphones first and then for
ion for automobiles may be

Toyota plans to le
fast charging soli

brian wang August 23, 2017 38 c

nsity (W/L)
Range
Lithium-ion Battery
(high storage type)
Current Status
(Research stag
200 400

electrek

Automakers | Alt. Transport | Autonomous Driving | Energy

TODAY

Volkswagen be
invest in solid-st

Fred Lambert - Jun. 22nd 2018 8:36 am ET @Fr

The Korea Herald

Samsung focuses on solid-state batteries at forum

By Song Su-hyun

Published : Jun 22, 2018 - 14:19 Updated : Jun 22, 2018 - 15:07

ne of
Daily and
day Express

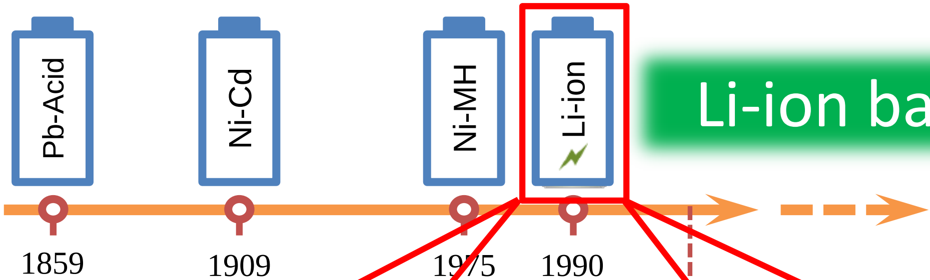
BMW's New Partn
W

By Mike Brown on December 18, 2017

BMW's electric car efforts
developer Solid Power a
working to create the next
successful, it could beat out
lithium-ion batteries.

Volkswagen Invests $100
QuantumScape

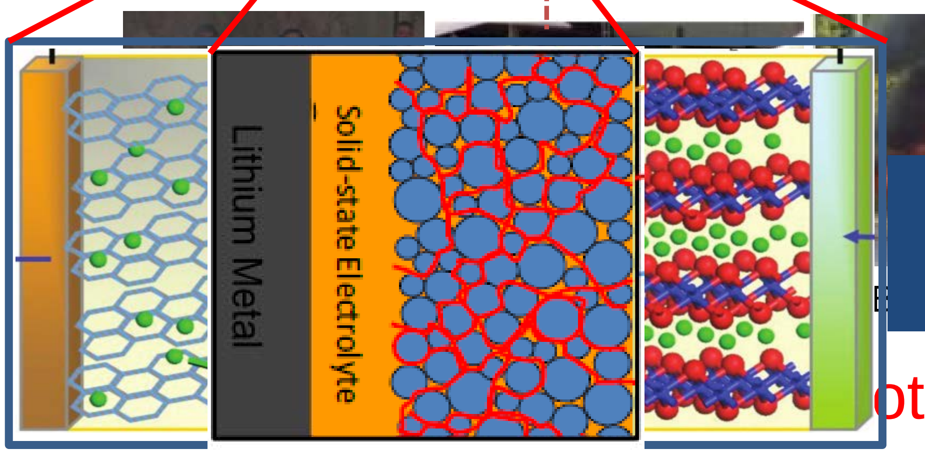
Emergence of all-solid-state batteries



Li-ion battery Era

Solid Electrolyte is SAFE!!!

✓ eliminates thermal runaway.

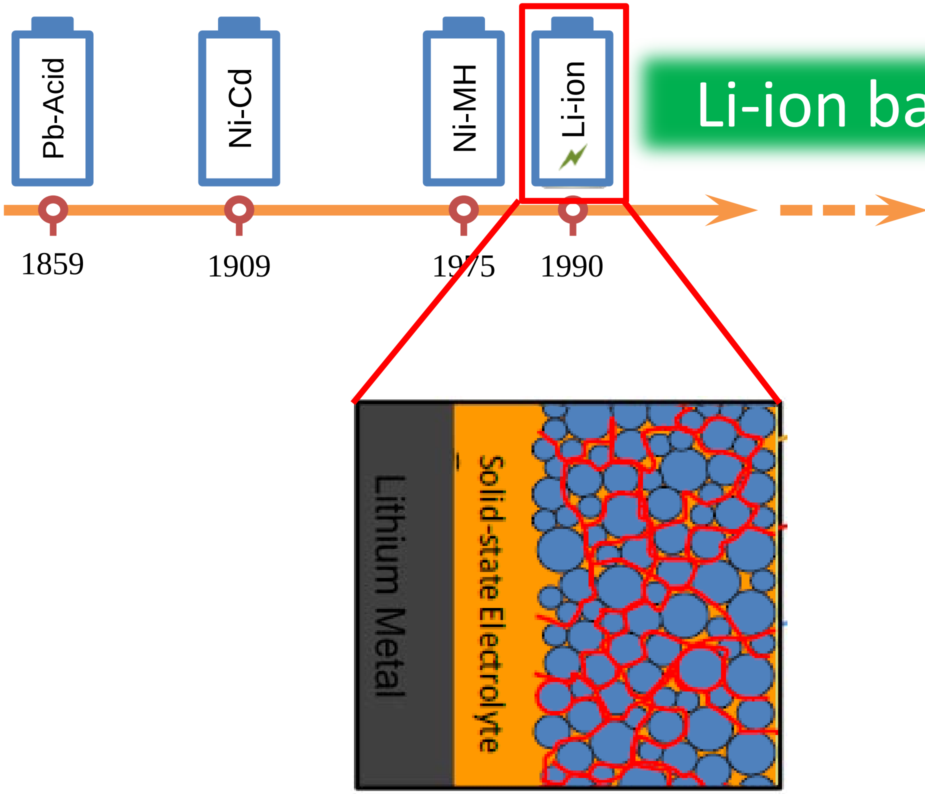


...rritz, 2016

Samsung, 2016

...ot SAFE!!!!

Emergence of all-solid-state batteries



Li-ion battery Era

Solid Electrolyte is SAFE!!!

✓ enables

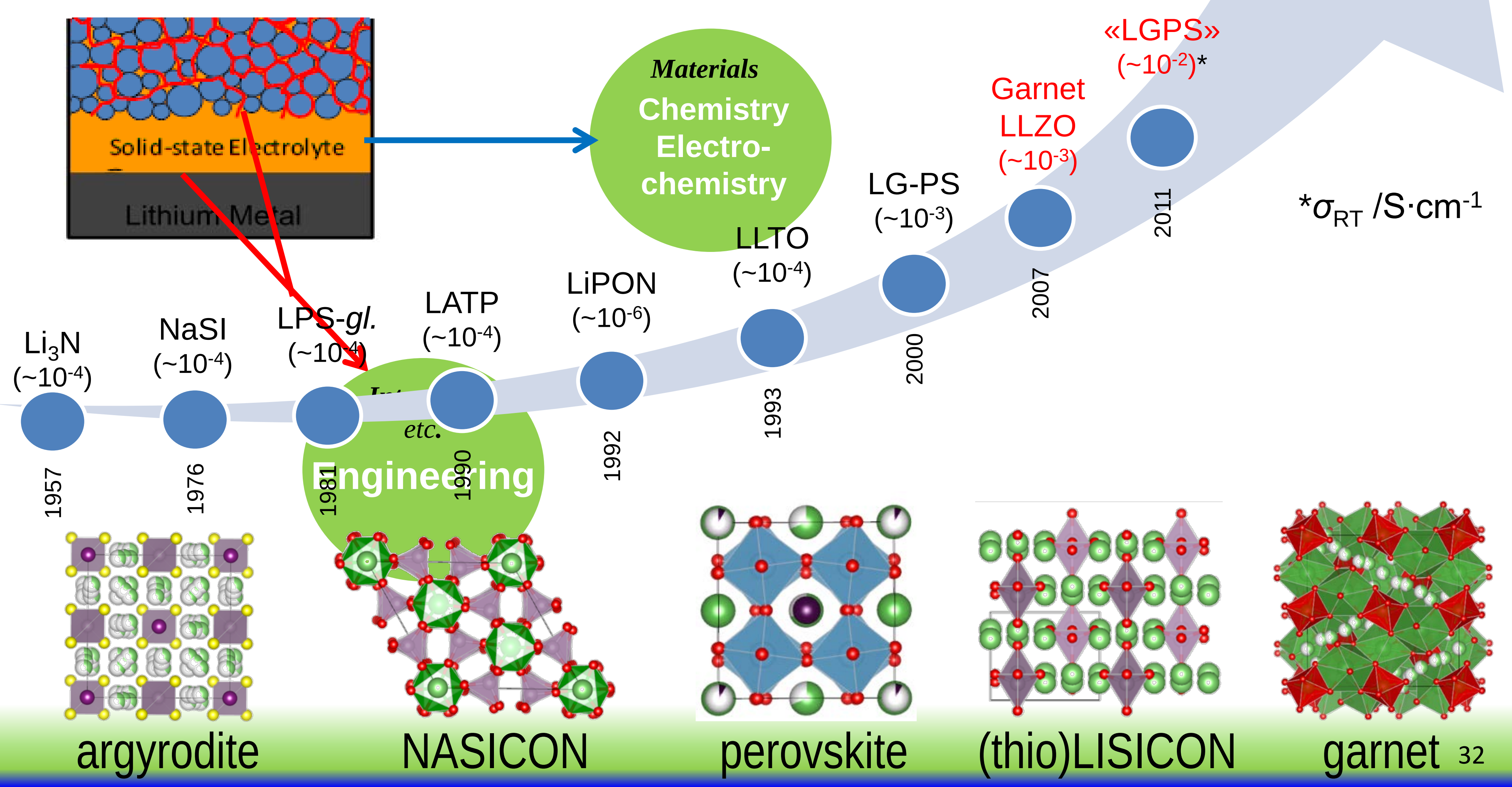
1) the use of Li at the anode

⇒ Voltage ↑ => energy density ↑

2) faster charging times

Challenges in all-solid-state batteries

Solid electrolyte as conductive as liquid ionic conductors ?



*"High conducting materials = high structural **disorder**"*

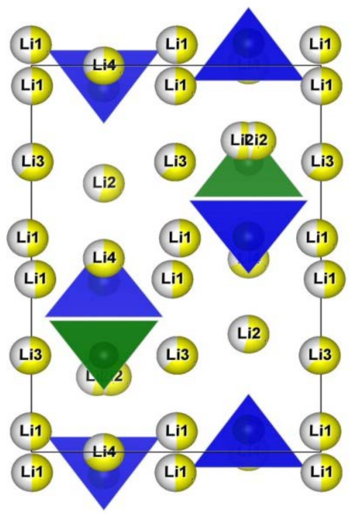
What kind of disorder ?

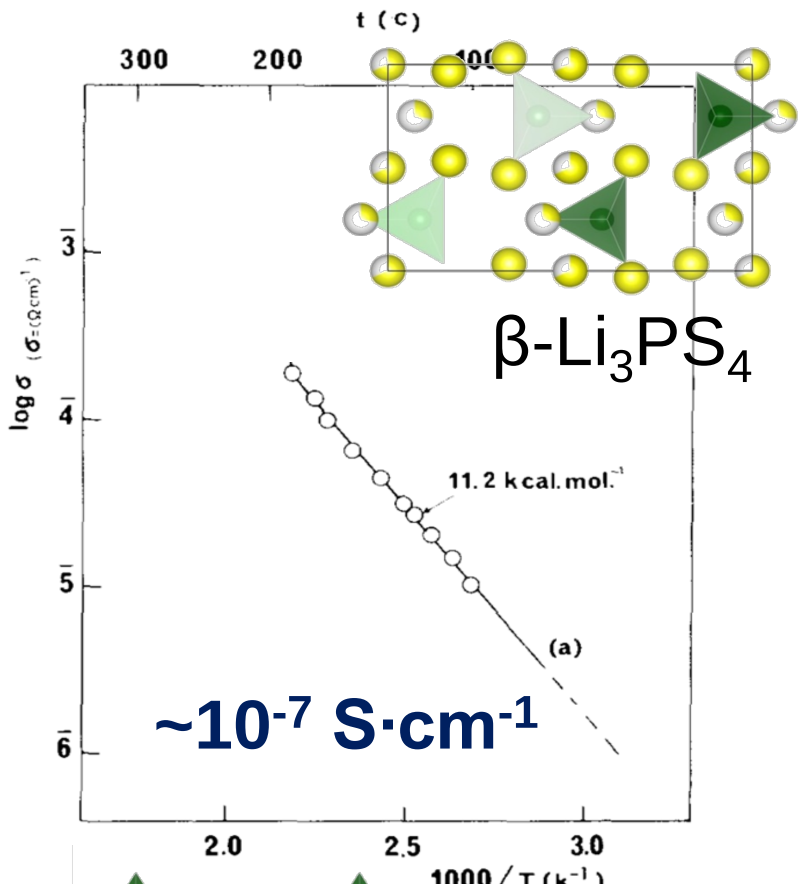
- ✓ HT phases (high symmetry, disordered)
- ✓ Heterovalent substitution

$P^{5+} \rightarrow Ge^{4+} + Li^{+}$

$Li_{10}GeP_2S_{12}$

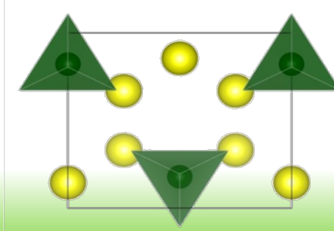
$\sigma_{RT} = 1.2\mathrm{x}10^{-2}$ S·cm^{-1}





β-Li_3PS_4

~10^{-7} S·cm^{-1}



γ-Li_3PS_4

Nat. Mater. **2011**, *10* (9), 682–686.

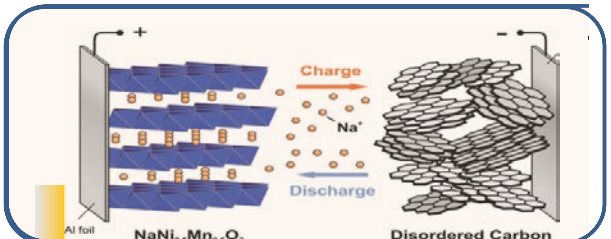
b) The Na-ion technology: an alternative for cost and sustainability reasons.

3 6.941
0.98
180.5
0.534
Li
$1s^2 2s^1$
Lithium

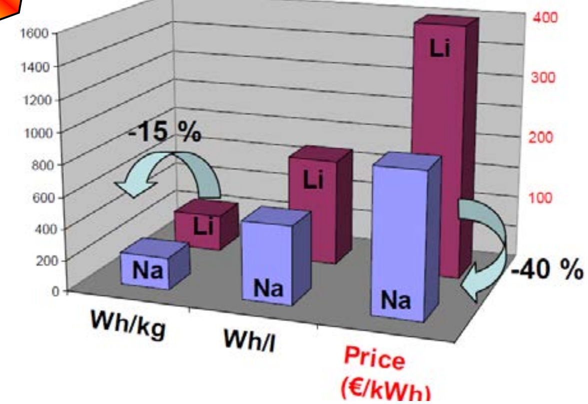
11 22.941
0.9
98
0.97
Na
$2s^2 2p^6 3s^1$
Sodium

Name	Earth abundance
Hydrogène	0.88 %
Hélium	0.00042 %
Lithium **Lithium**	0.006 % **0.006%**
Béryllium	0.00053 %
Bore	0.0016 %
Carbone	0.087 %
Azote	0.03 %
Oxygène	50 %
Fluor	0.028 %
Néon	-
Sodium **Sodium**	2.6 % **2.6%**

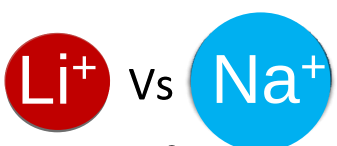
Develop
Na-ion batteries



Potentially cheaper
than Li chemistry



Challenge to find better electrode materials



Size factor

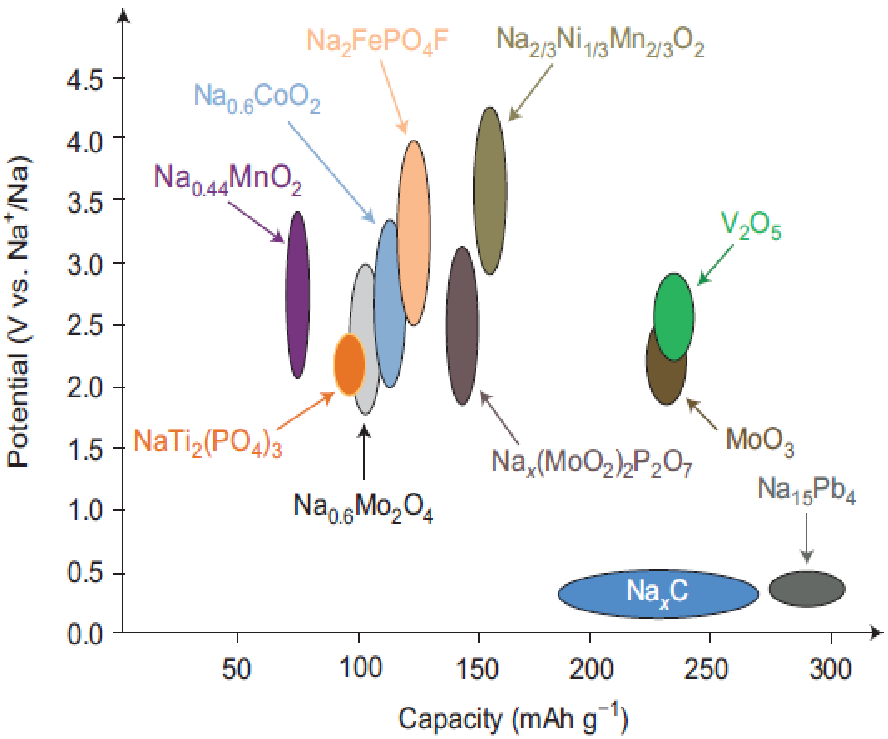
Ionic diffusion:
size vs. polarizability ?

0.3 V penalty
=> Grid applications

Blooming research on Na insertion electrodes over the last 5 years

30 years

1980 → **2012**



Polyanionic compounds

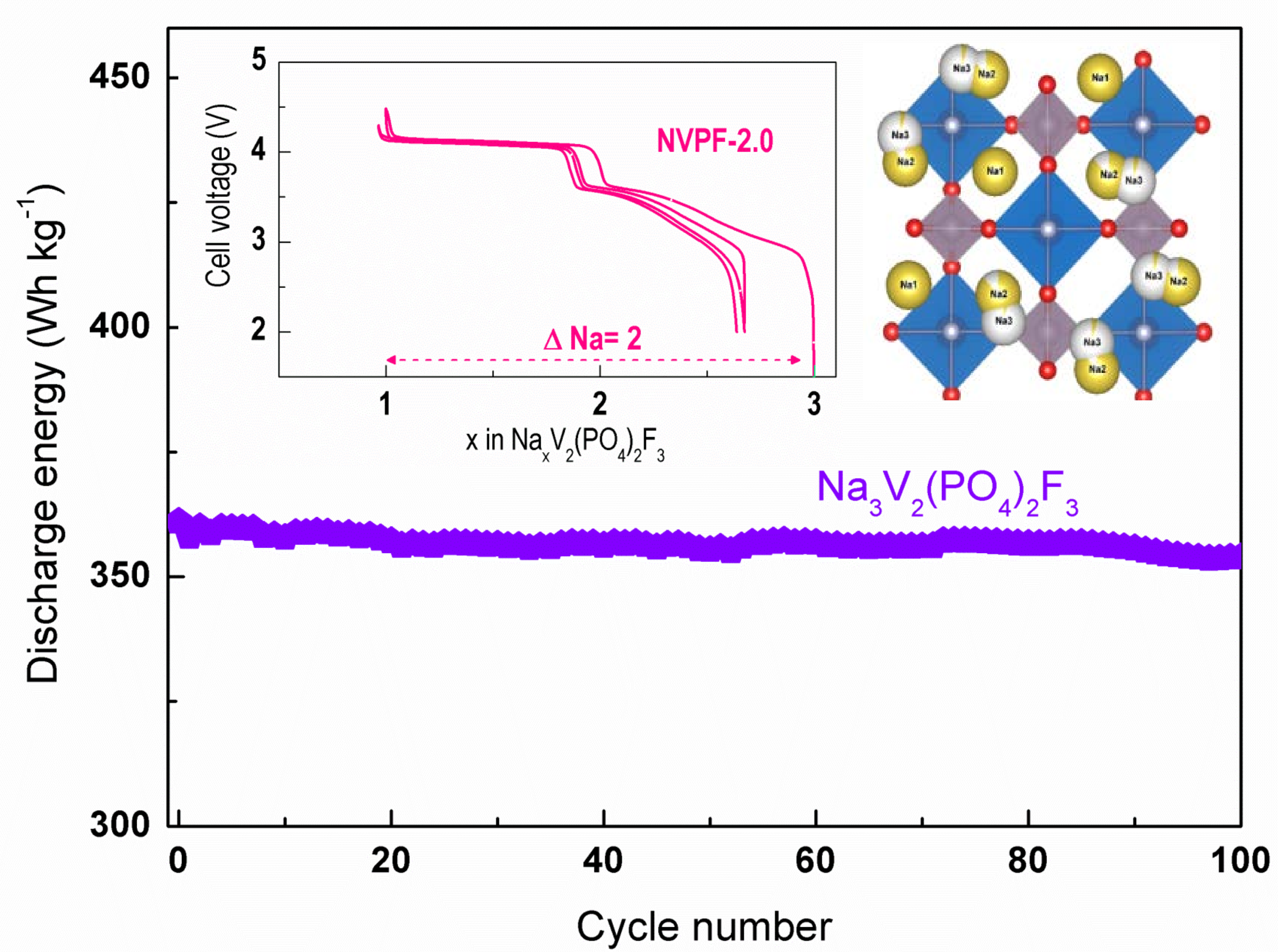
$Na_3V_2(PO_4)_2F_3$ / $NaPF_6$ / C

Layered compounds

$Na_{0.7}Fe_{0.5}Mn_{0.5}O_2$ / $NaPF_6$ / C

Demonstrated prototype :

Polyanionic $Na_3V_2(PO_4)_2F_3$ (NVPF) // 1M 1M $NaPF_6$-PC // hard carbon



$Na_3V_2(PO_4)_2F_3$ (V^{3+})

$-2\ Na^+$

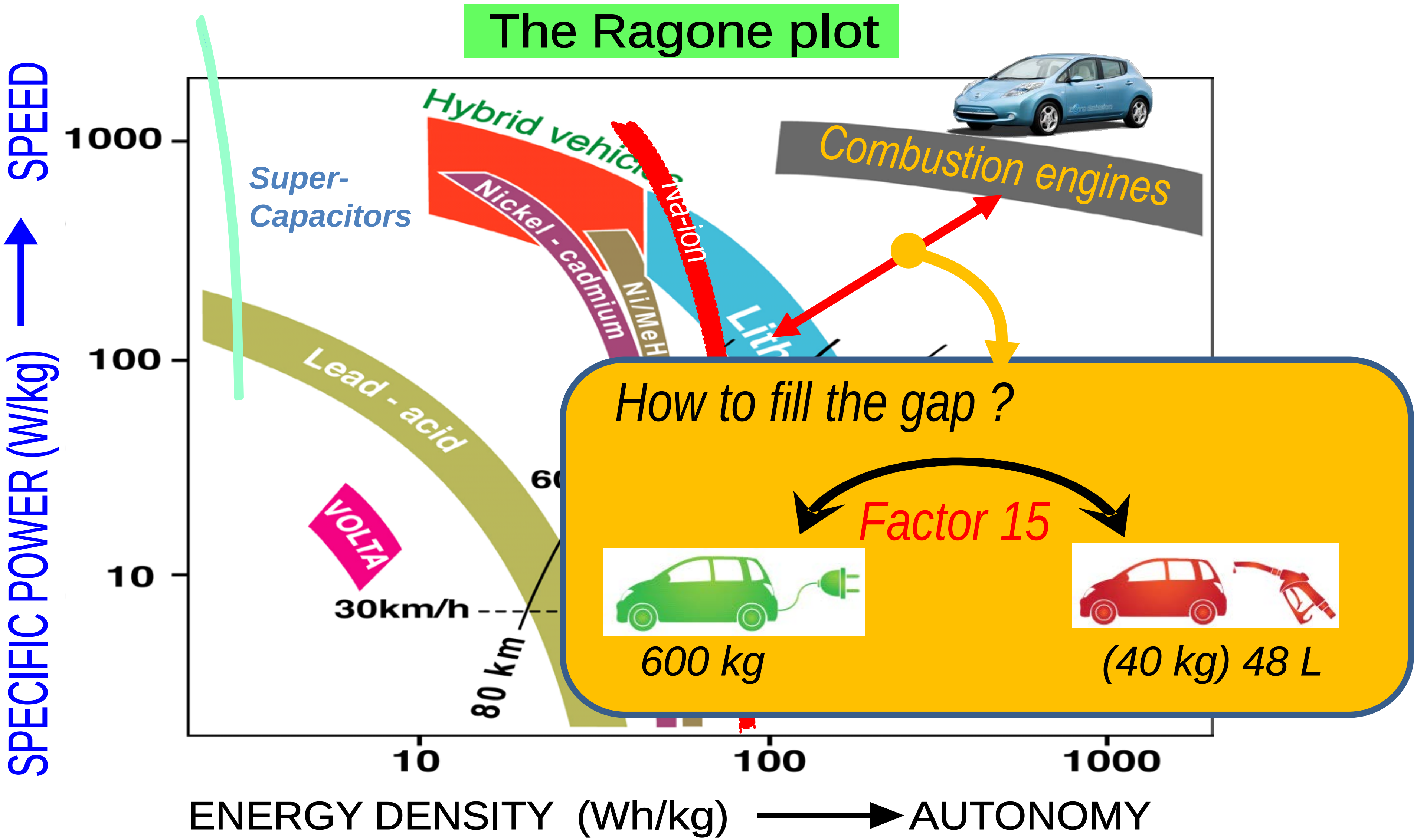
$Na_1V_2(PO_4)_2F_3$ (V^{4+})

$-1\ Na^+$

$Na_0V_2(PO_4)_2F_3$

specific energy > 370 Wh kg^{-1}

Comparison with other technologies in terms of powder and energy density



Solutions to be found via an european project that is under construction http://battery2030.eu/

BATTERY 2030+

Coordinator:
Kristina Edström,
Uppsala University.

- Tackle Interface problems
- Faster Discovery of new electrode materials with the help of artificial intelligence

THANK YOU FOR YOUR ATTENTION