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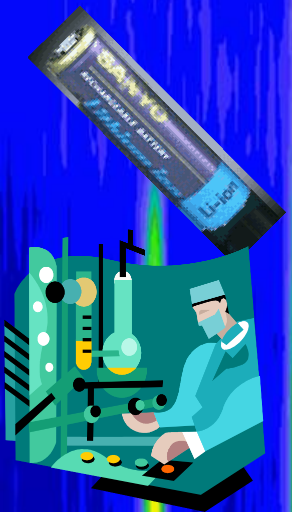
1st International Conference of Young Scientists
"TOPICAL PROBLEMS OF MODERN ELECTROCHEMISTRY AND ELECTROCHEMICAL MATERIALS SCIENCE"
September 17th, 2017



The anionic redox activity: From fundamental understanding to practical challenges

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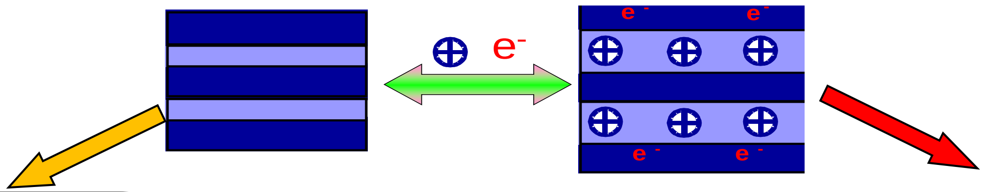
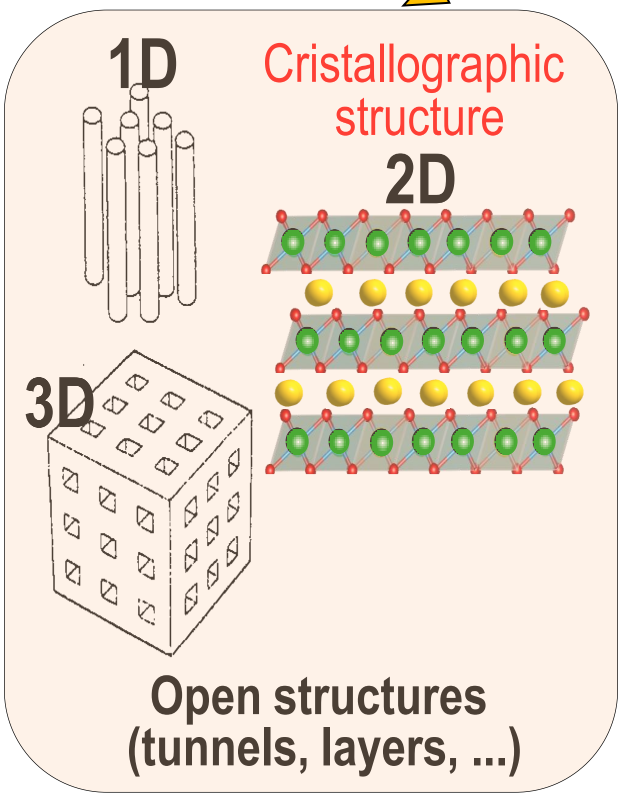
http://www.college-de-france.fr/site/en-college/index.htm

Contents

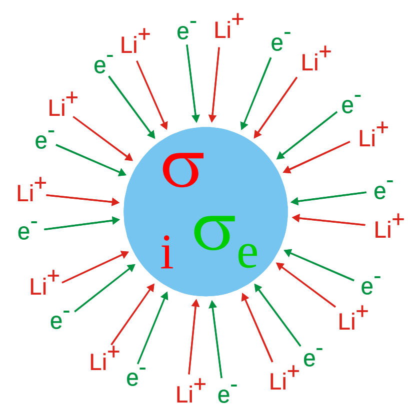
The Chemistry and Physics of Insertion Reactions

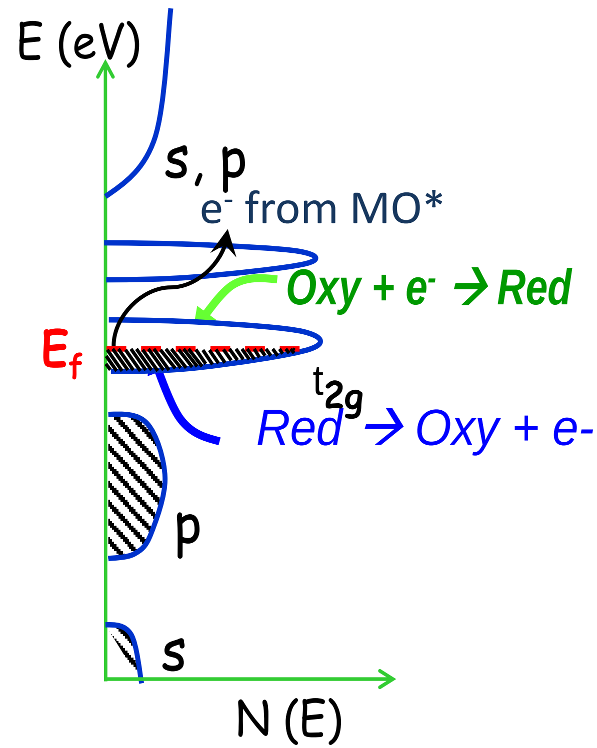
$$[Ti^{+4}S_2] + Li^{+} + e^{-} \rightarrow [LiTi^{+3}S_2]$$





Duality ions/electrons





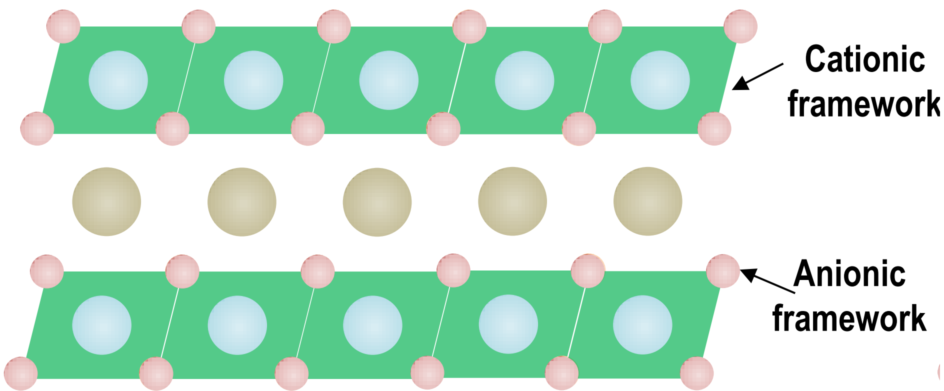
The crystallographic structure

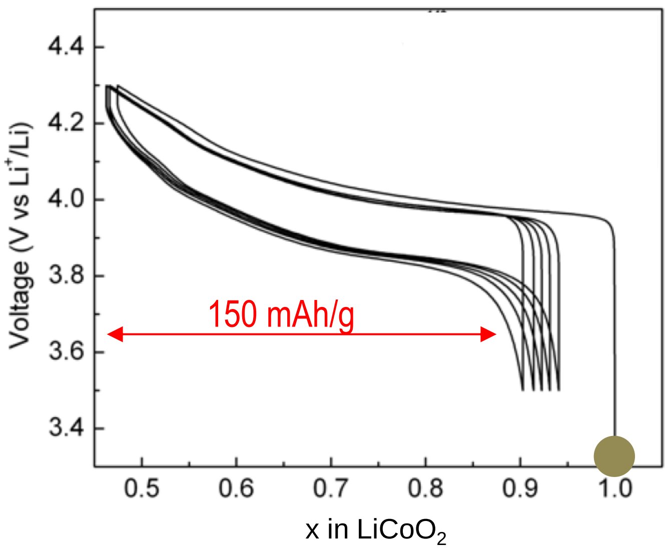
The electronic band structure

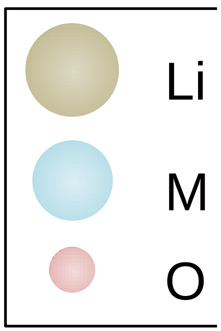
The anionic redox activity: a transformational change

LIB has relied on cationic redox reactions

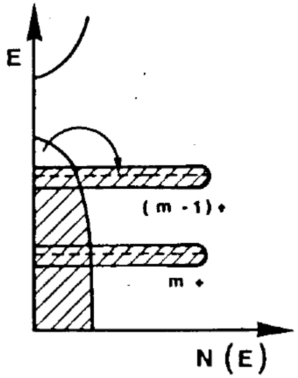
(2D Layered oxide)





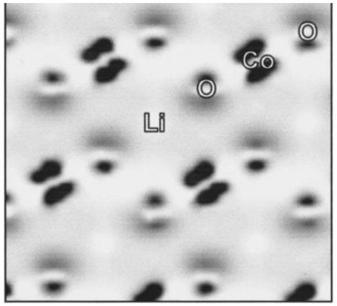


Anionic redox : It's emergence

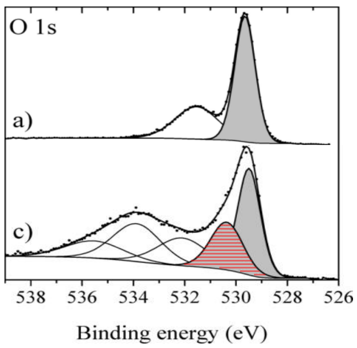


Ligand-hole chemistry in chalcogenides
Rouxel (1991)

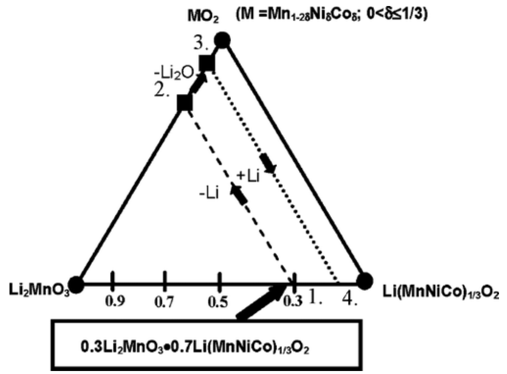
$$Li_xCo_{1-y}O_2 \rightarrow Co_{1-y}O^{2-}_{2-4y}(O_2)^{2-}_{2y}$$



Oxygen activity in $LiCoO_2$ proposed / theory confirmed it
Tarascon / Ceder (1999)



Oxygen activity in $LiCoO_2$ - Experiments
Yoon / Dedryvère (2002-2008)



Synthesis of Li-rich Li_2MnO_3-based cathodes
Dahn / Thackrey (2002-2007)

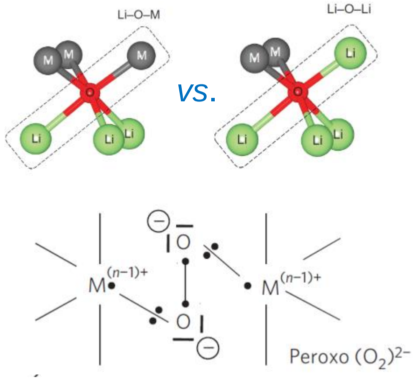
The Emergence of Anionic Redox

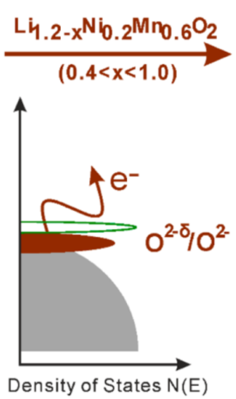
Oxygen redox in Li-rich cathodes – Theory
Ceder / Doublet (2016)

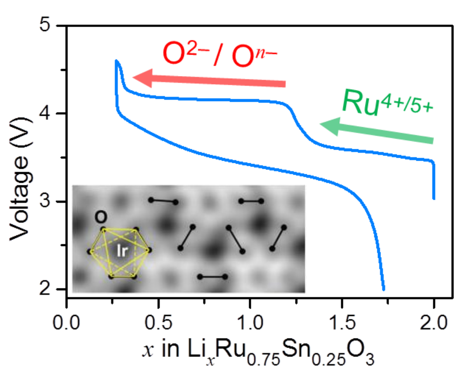
Oxygen redox in Li-rich NMC – Direct proofs
Bruce (2016)

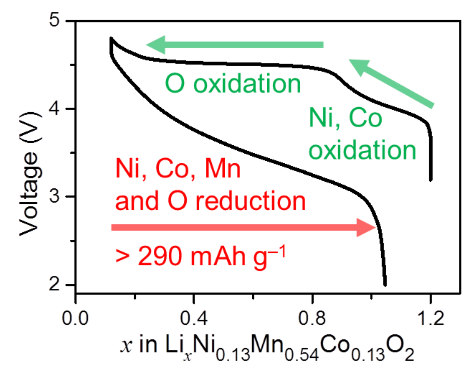
Oxygen redox in Li_2RuO_3 and Li_2IrO_3 – Direct proofs
Tarascon (2013-2016)

Suspecting oxygen redox in Li-rich NMC
Delmas (2012)



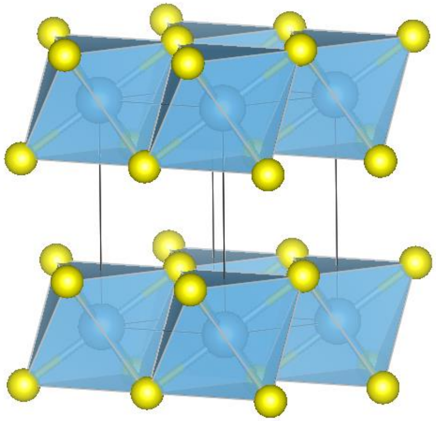


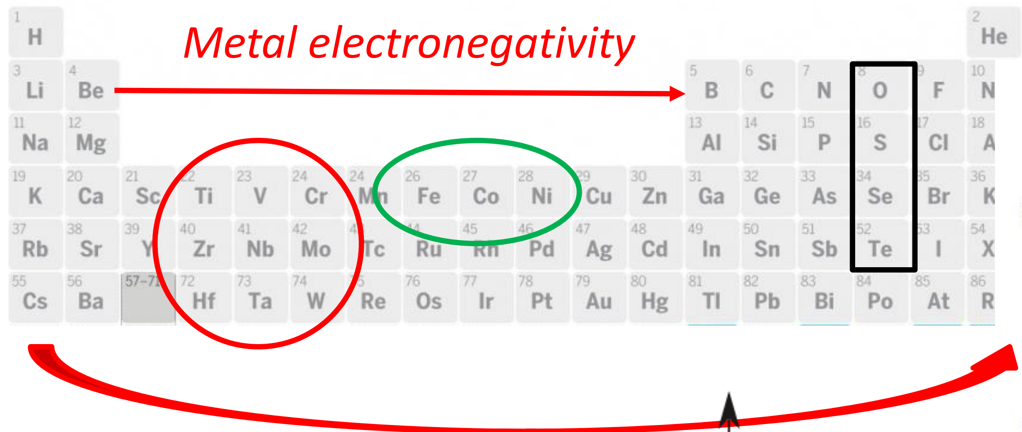




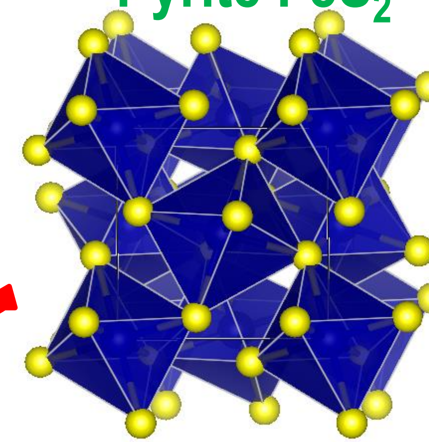
Anionic redox in chalcogenides: Rouxel's pioneering work in the 1990's

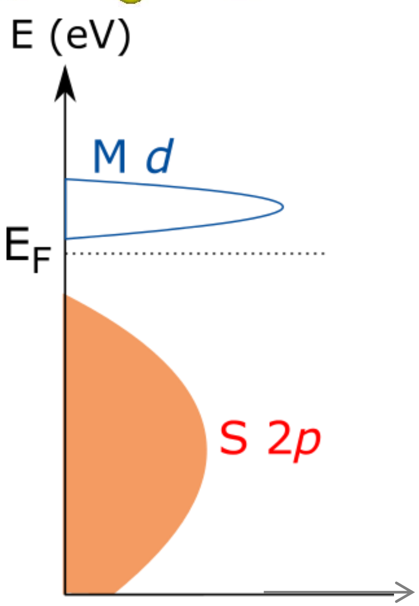
Layered TiS_2

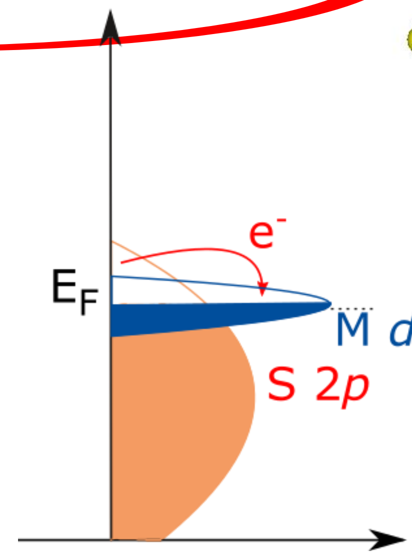




Pyrite FeS_2







- Creation of ligand holes and S_2^{2-} pairs

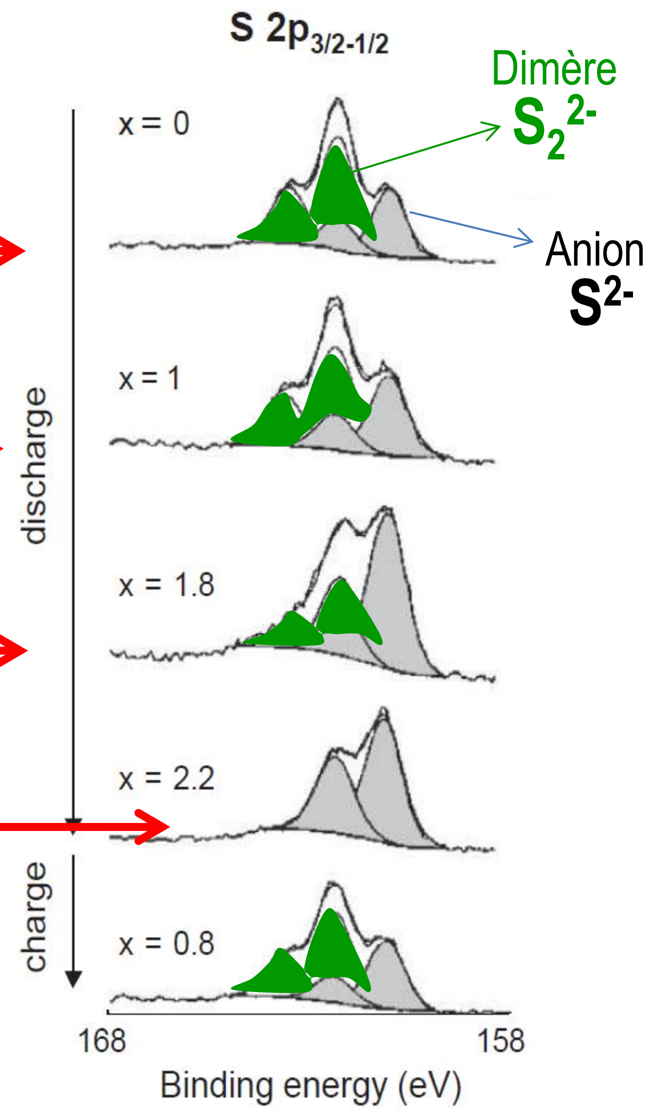
$$2\,S^{--} \rightarrow (S_2)^{2-} + 2e^-$$
$$M^{m+} \rightarrow M^{(m-1)+} - e^-$$

Rouxel, Chem. Eur. J., 2, 1996

Experimental evidence of the S participation to the redox process by XPS

Li_xTiS_3

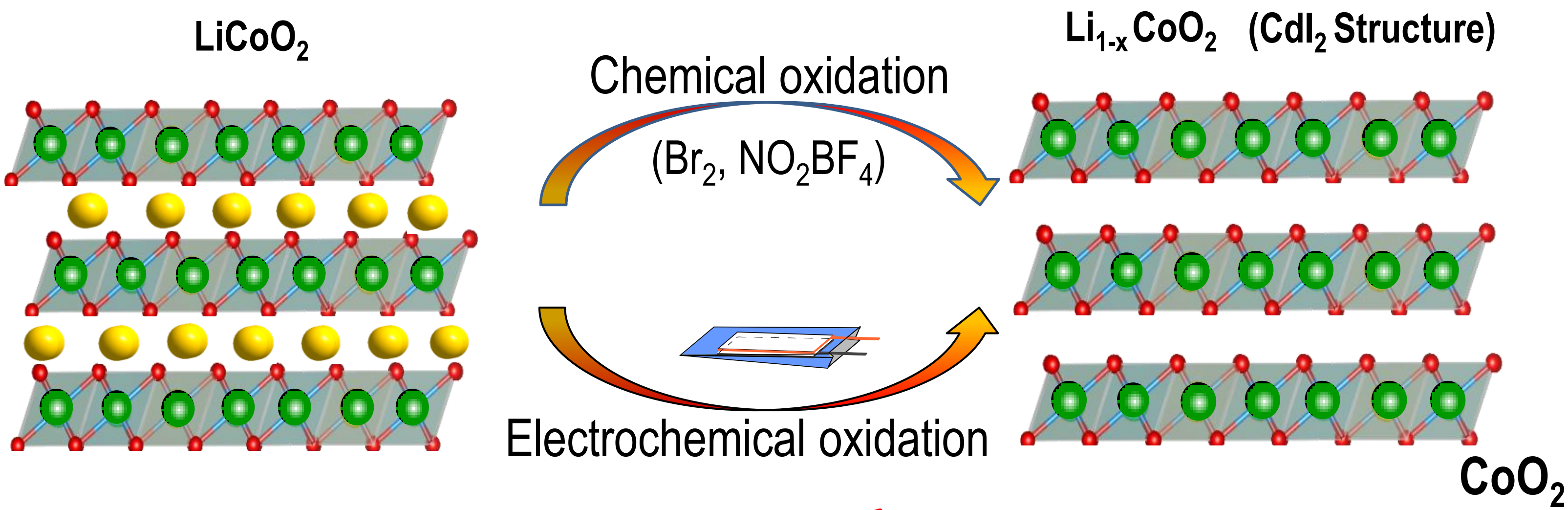
x= 0	$Ti^{4+}(S^{2-})(S_2)^{2-}$
x= 1	$Li_1Ti^{4+}(S^{2-})_2(S_2)^{2-}_{0.5}$
x= 1.8	$Li_{1.8}Ti^{4+}(S^{2-})_{2.8}(S_2)^{2-}_{0.1}$
x= 2.2	$Li_{2.2}Ti^{4+}_{0.8}Ti^{+3}_{0.2}S_3$

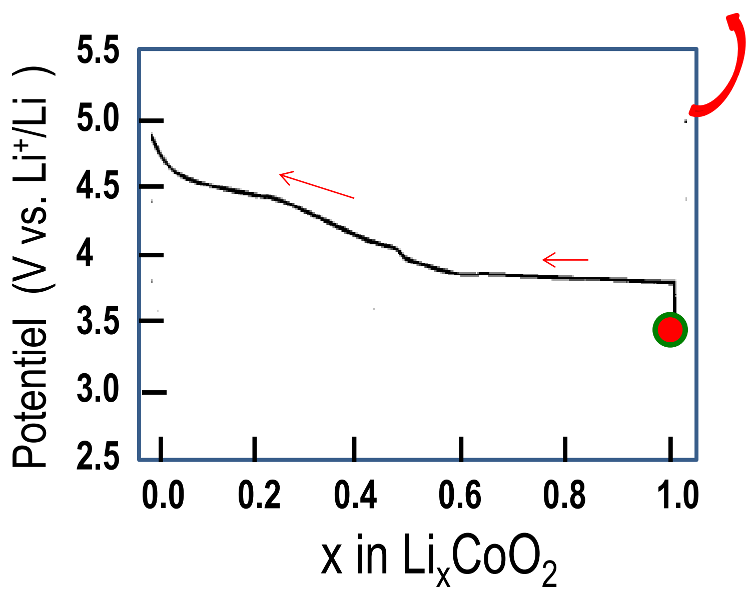


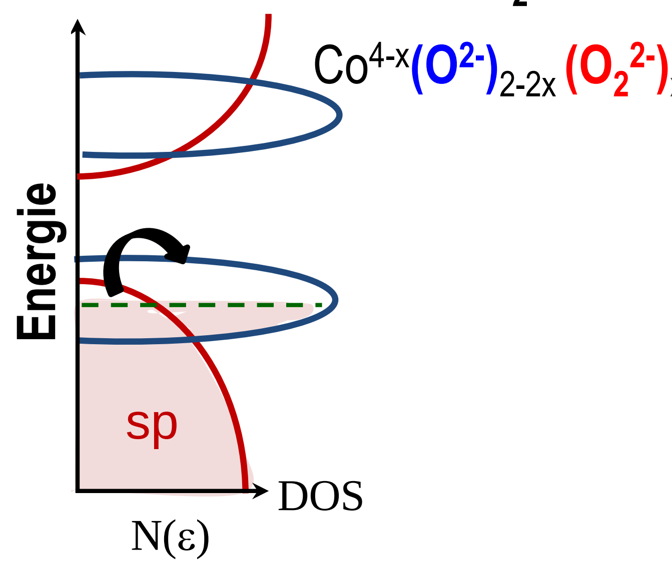
M.H. Lindic et al Solid State Ionics, 176 (2005) 1529 – 1537

Existence of CoO_2 ? No longer a mystery

Chemical/electrochemical approaches



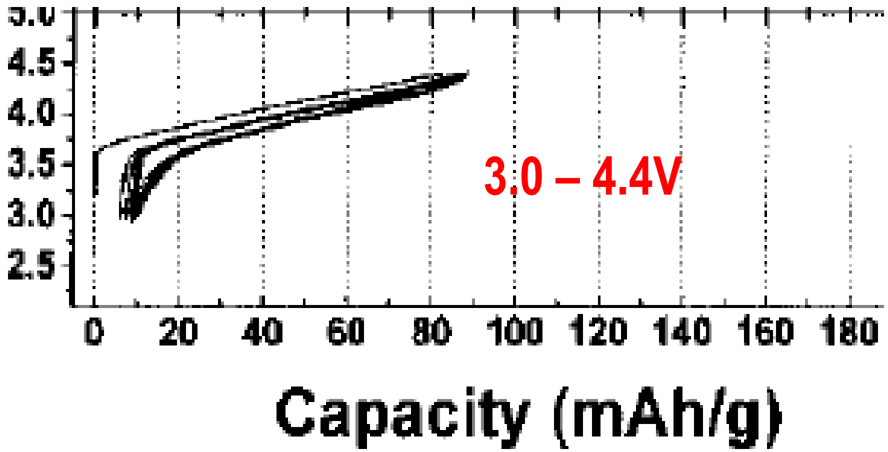


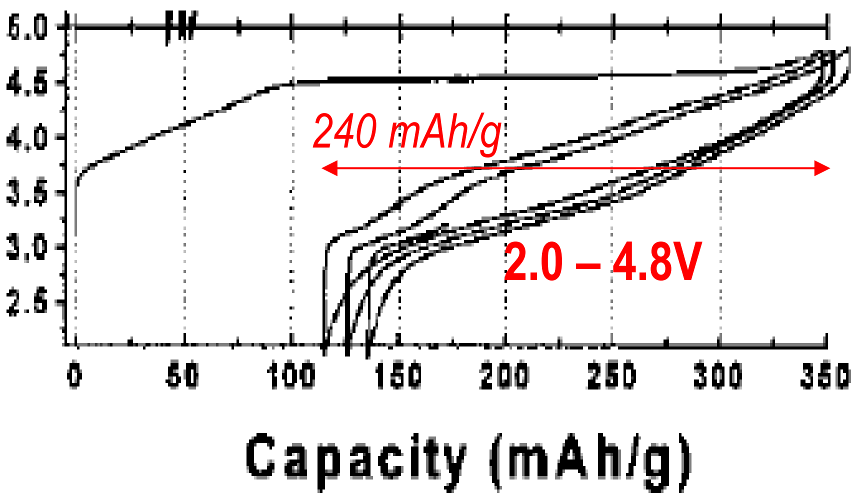


G.G. Amatucci, J.M. Tarascon, et al. , J. Electrochem. Soc., Vol. 143, N°3, March 1996 J.M. Tarascon et al. Jr. of Solid State Chemistry 1999

A few intriguing results which were overlooked

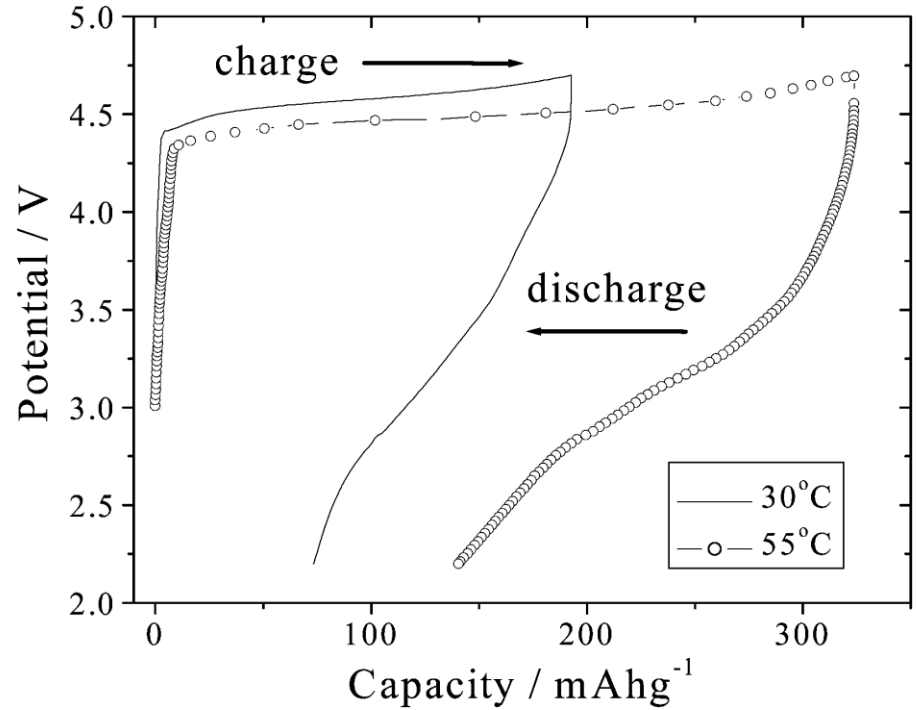
$Li(Li_{0.16}Ni_{0.25}Mn_{0.58})O_2$





► Extra-capacity triggers by oxygen deficiency

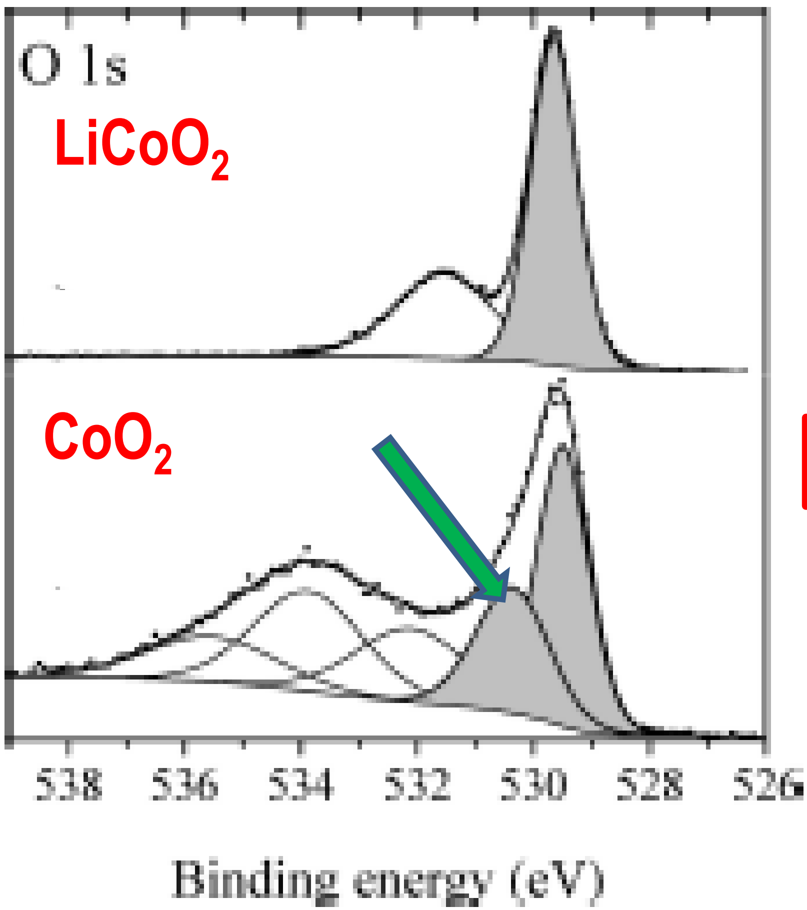
Li_2MnO_3



► Removal of O^{2-} plus exchange of Li^+ by H^+

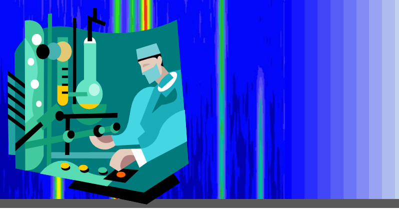
Deintercalation from $LiCoO_2$ to CoO_2 investigated by XPS

- O 1s core peaks in delithiated Li_xCoO_2 compounds



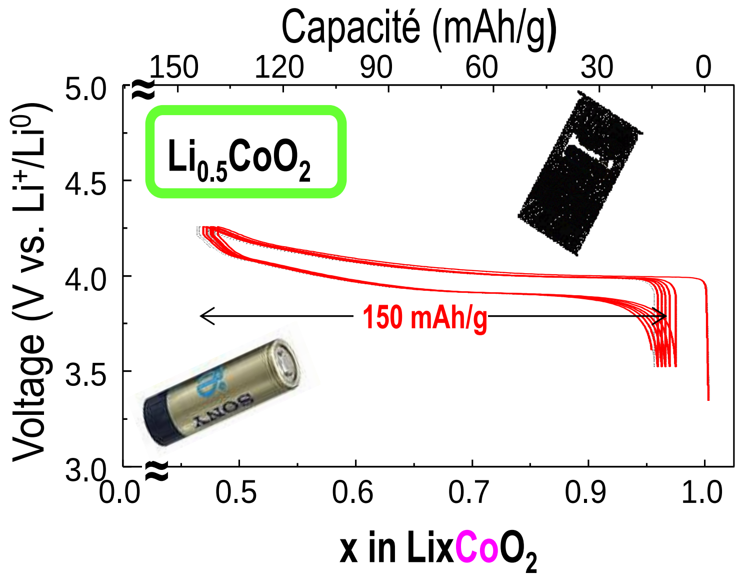
CoO_2 lattice O 1s signal. This peak broadening toward the higher binding energies with respect to $LiCoO_2$, represented here by a second peak at 530.3 eV, can be interpreted by a partial oxidation process of O^{2-} ions from $LiCoO_2$ to CoO_2. This study confirms the hypothesis that both cobalt and oxygen undergo oxidation-type changes in their electronic structure when lithium ions are deintercalated from $LiCoO_2$.

R. Debryvére, et al. Chem. Mater. 2008



The Li_xCO_2 system and its evolution

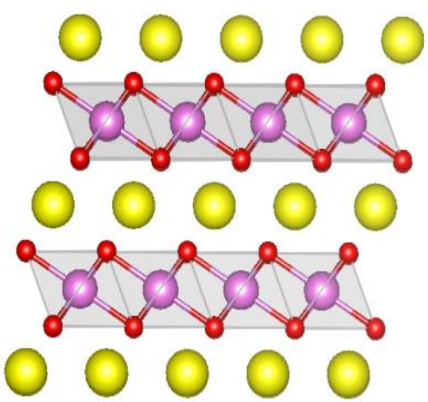
LiCoO$_2$ has been the “stellar” material for numerous years



Improvements via chemical substitutions:

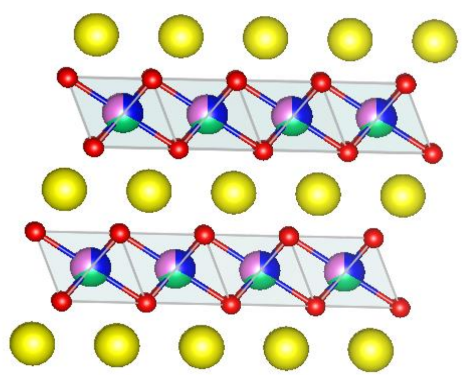
Li[Co]O$_2$

[150 mAh/g



Replace partially Co by

Mn et Ni



Li[NiMnCo]O$_2$

[180 mAh/g]

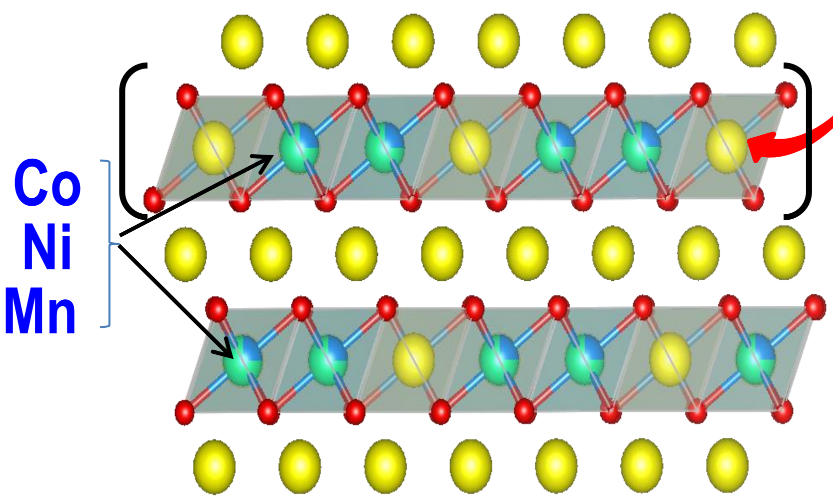
NMC phases

T.Ohzuku, Y. Makimura; Chem Lett. 642 (2001)

New Li-rich high-capacity layered oxides

- Li[**Li**CoNiMn]O_2

Li-excess



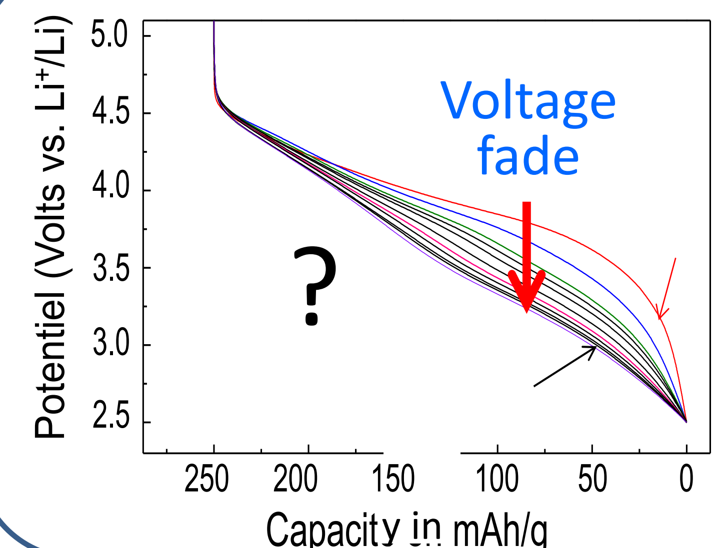
Solid Solution

$Li_1[Li_{0.2}Ni_{0.15}Mn_{0.48}Co_{0.17}]O_2$

(Dahn:3M)

Composites

$(1-z)\ [Li_{1/3}Mn_{1/3}]O_2$ –
$(z)Li[Mn_{0.5-y}Ni_{0.5-y}Co_{2y}]O_2$

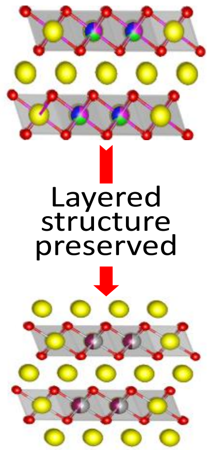


Double fundamental problem

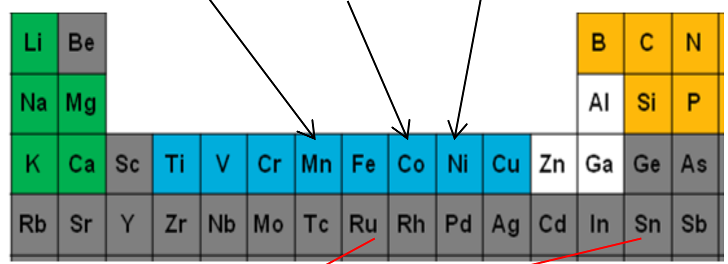
→ **Origin of capacity**

→ **Origin of drop in voltage**

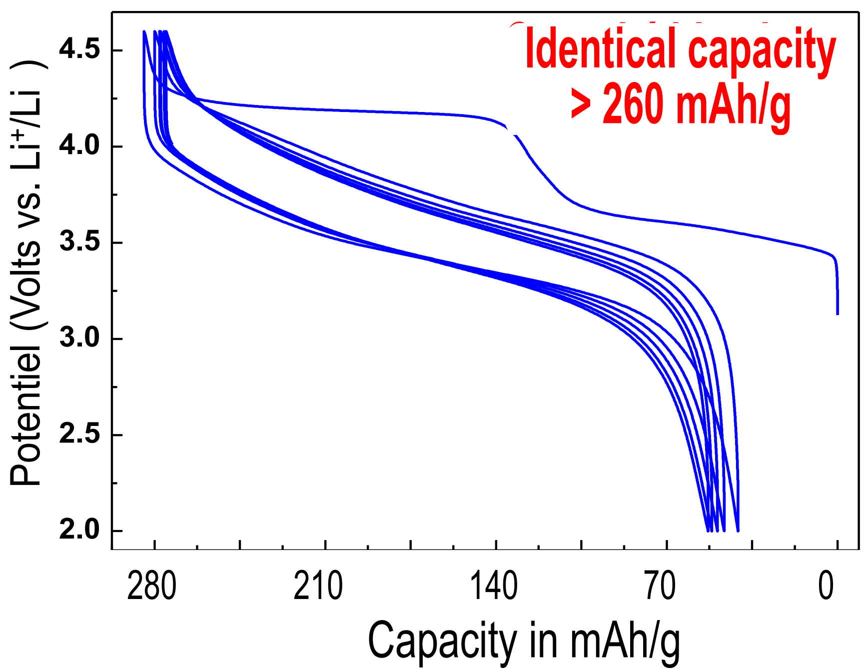
How to simplify this problem ???
a new chemical approach ..

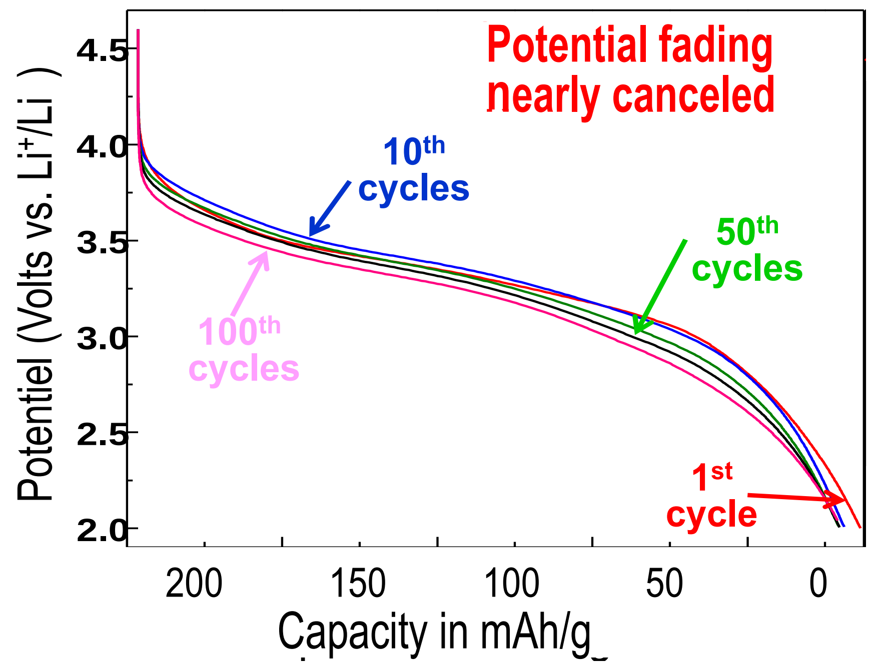


$Li[Li_{0.2}Mn_{0.53}Co_{0.14}Ni_{0.13}]O_2$ [3 redox centers]



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

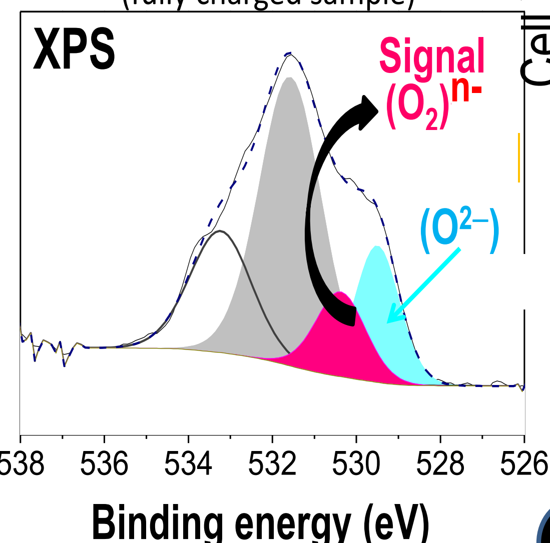


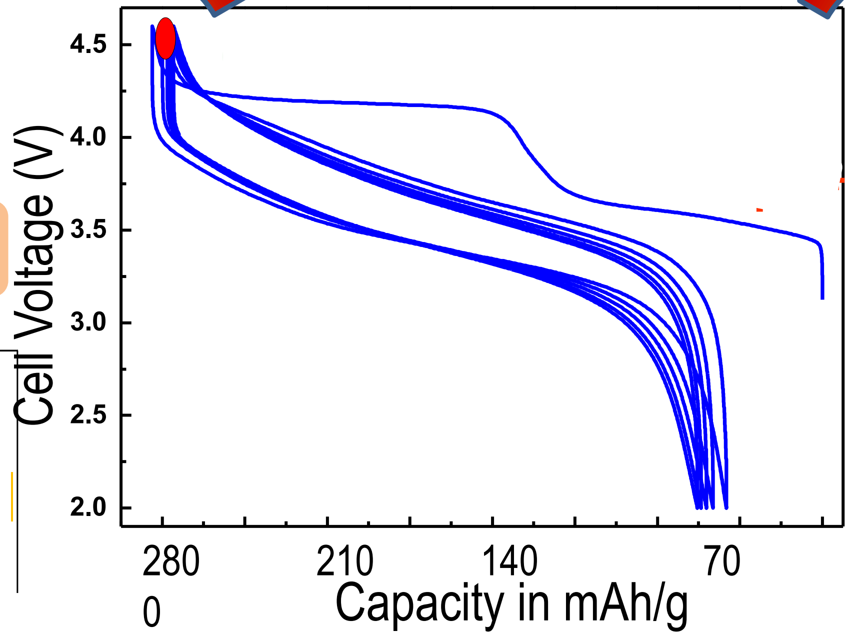


Origin of the redox activity in $Li_2Ru_{0.75}Sn_{0.25}O_3$

☞ X-ray photoemission spectroscopy (XPS)

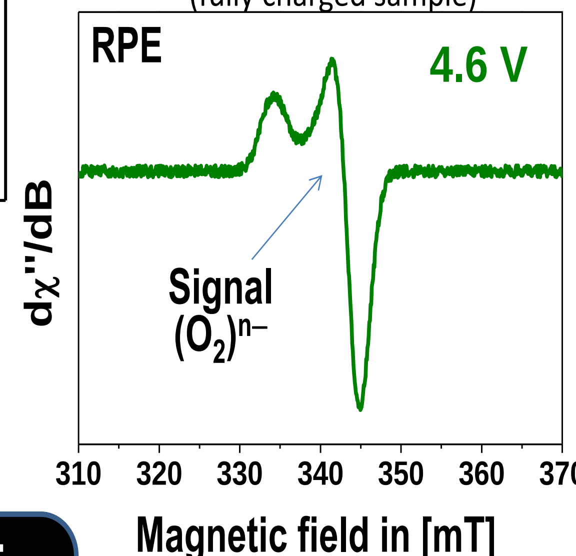
(fully charged sample)





☞ Electron paramagnetic Resonance (EPR)

(fully charged sample)

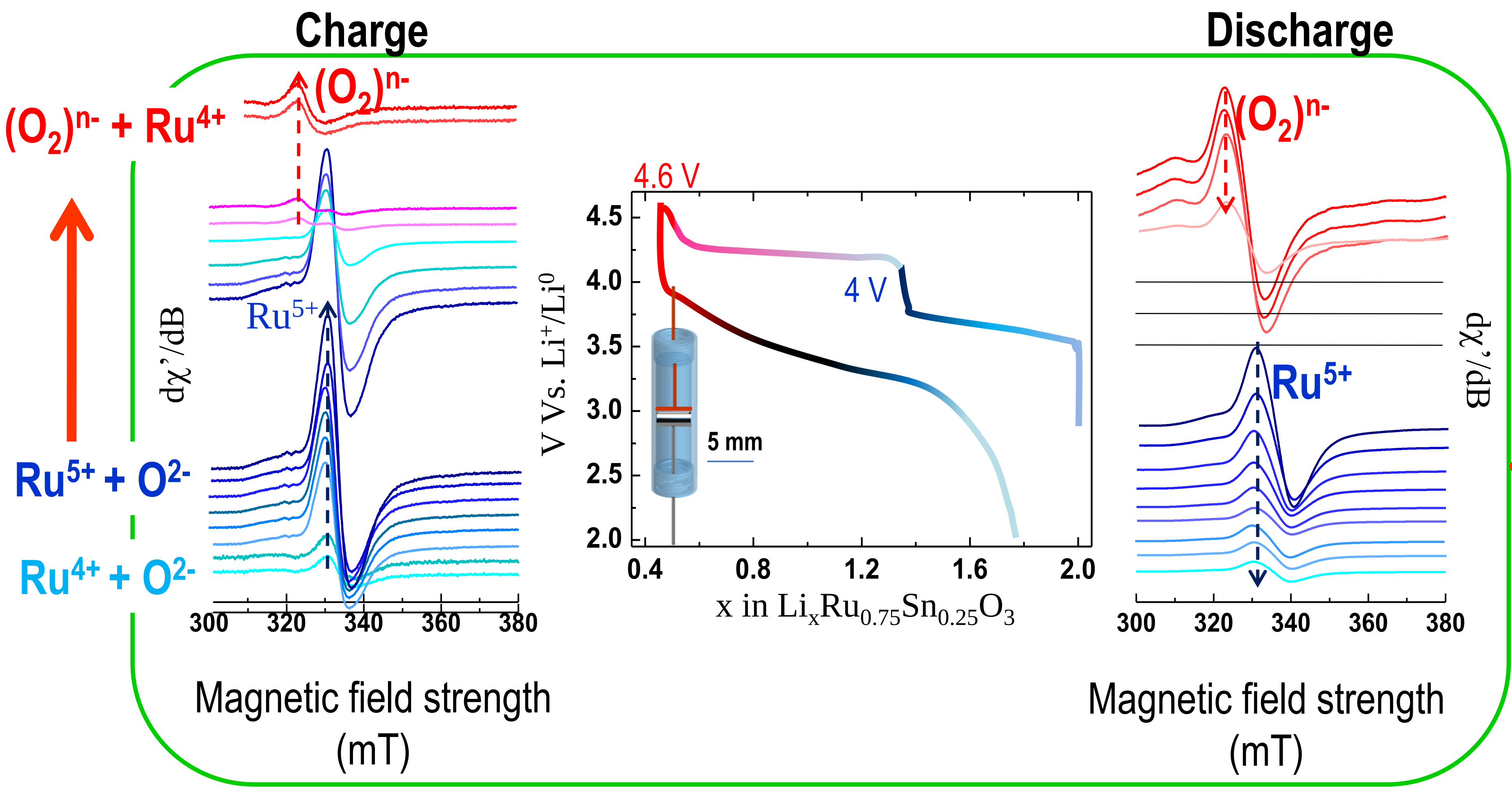


First direct evidence for an anionic redox process $(2O^{--} \leftrightarrow (O_2)^{n-})$ in Li-rich lamellar compounds

M. Sathiya et al., Nature Materials, 12, 827 (2013)

M. Sathiya et al., World patent -12197509.8-13

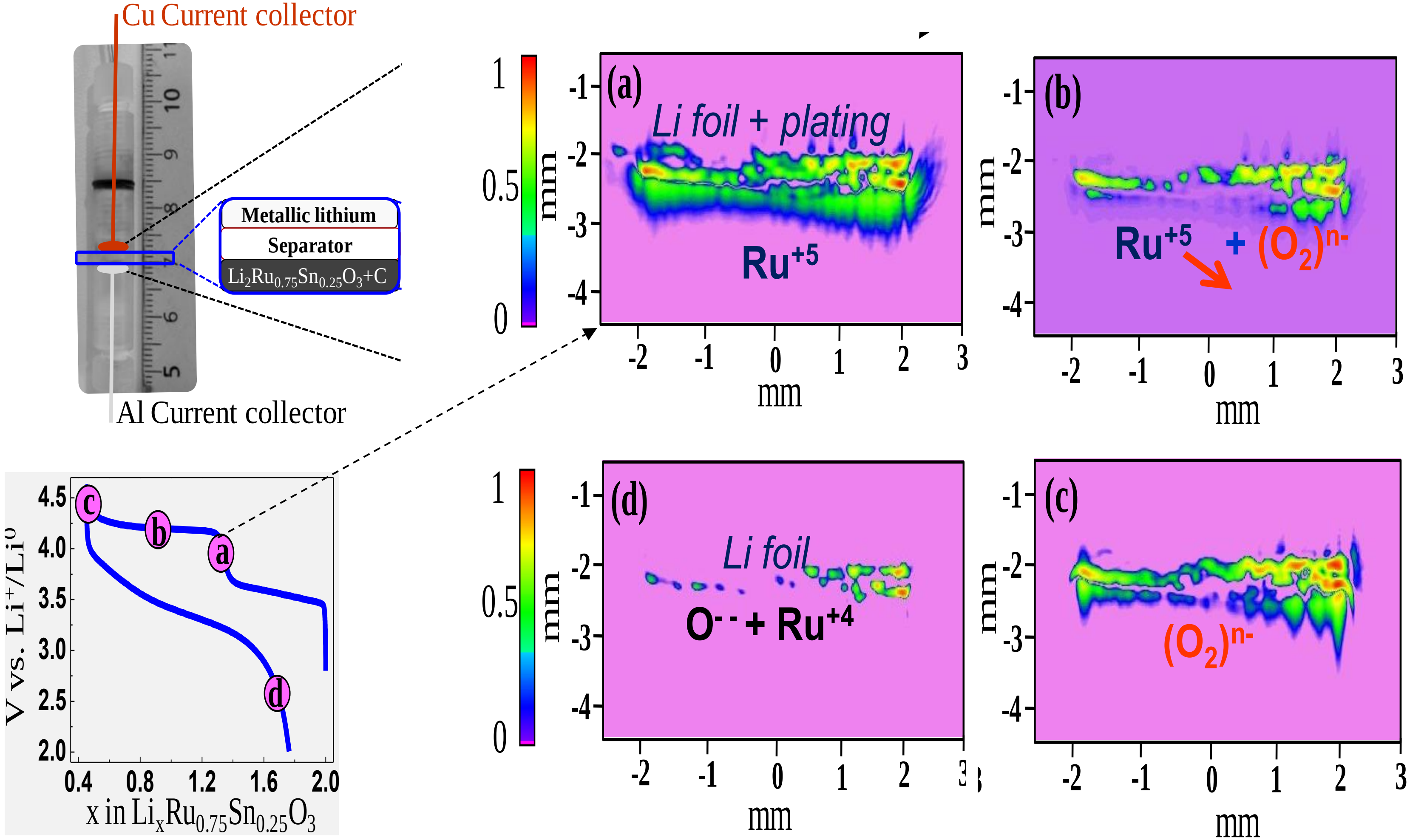
Monitoring redox processes in $Li_2Ru_{0.75}Sn_{0.25}O_2$ by operando Electron Paramagnetic Resonance (EPR)



The exacerbated capacity of Li-rich layered materials is nested in the cumulative cationic $Ru^{4+/5+}$ and anioinic ($2O^{--} \leftrightarrow (O_2)^{n-}$) redox species.

M. Sathya, et al. (Nature communications , Février 2015)

Localisation of the cationic/anionic redox species by insitu EPR Imaging: A first



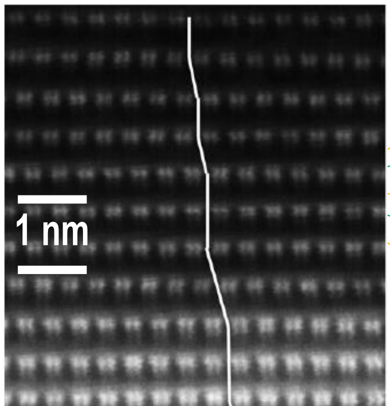
EPR imaging: Key tool for monitoring electrode homogenity and kinetics

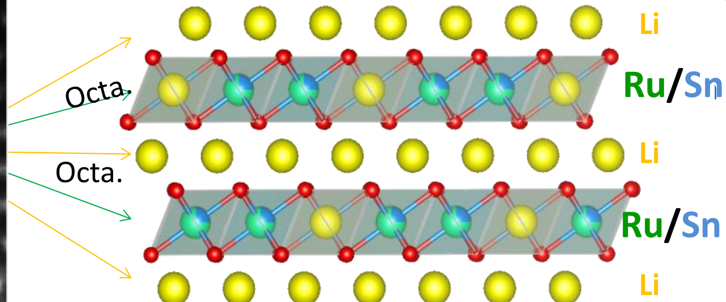
M. Sathya, J.B. Leriche, E. Salader, D. Gourrier, H. Vezin and J.M. Tarascon (Nature communications, Fevrier 2015)

What's going at the atomic scale ? . Can we visualize the O-O dimers ..

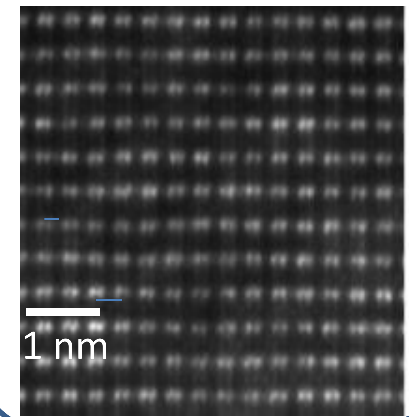
Visualize the material at the microscopic scale (HAADF-STEM)

Pristine $Li_2Ru_{0.75}Sn_{0.25}O_3$



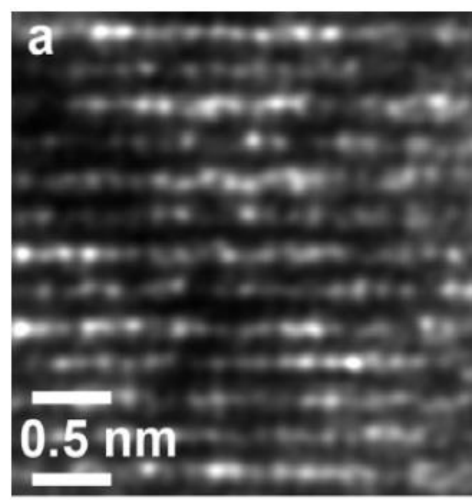


1st Discharge



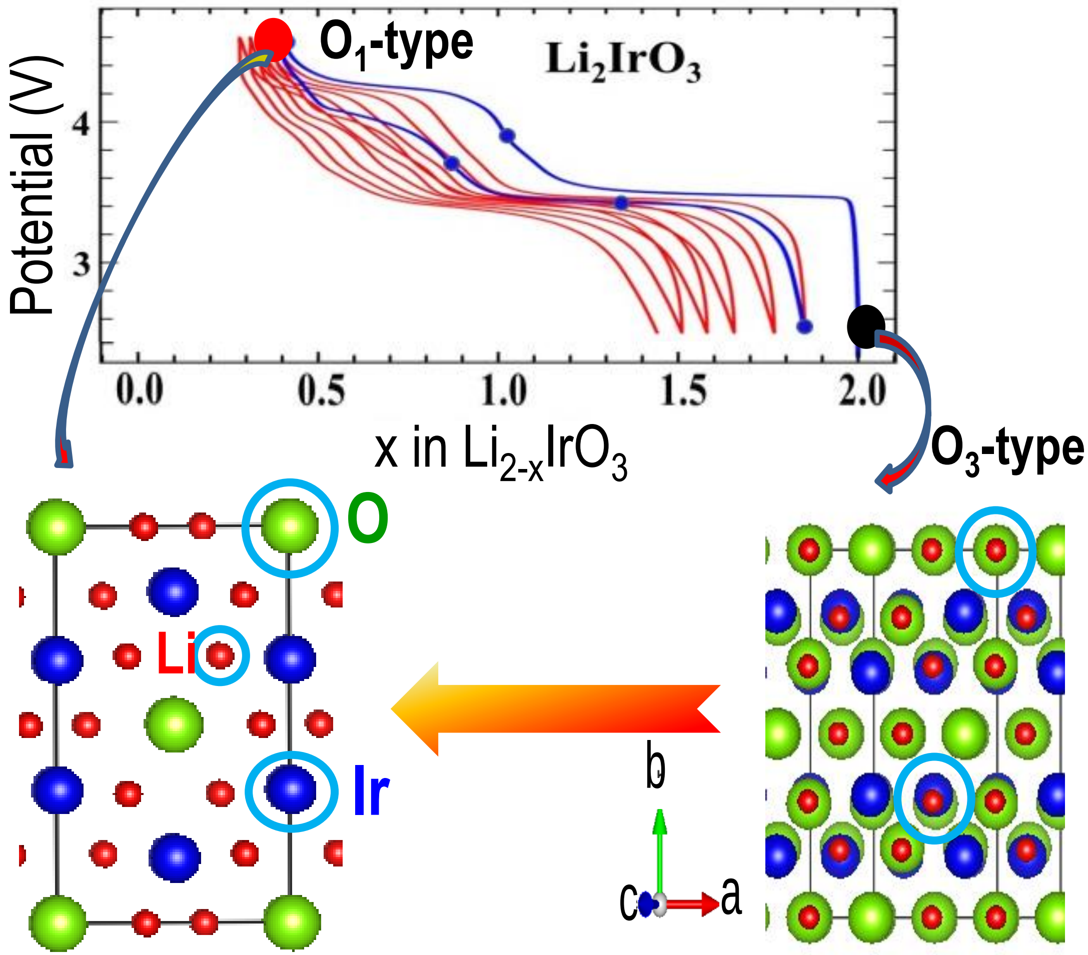
A massive cationic migration which is reversible

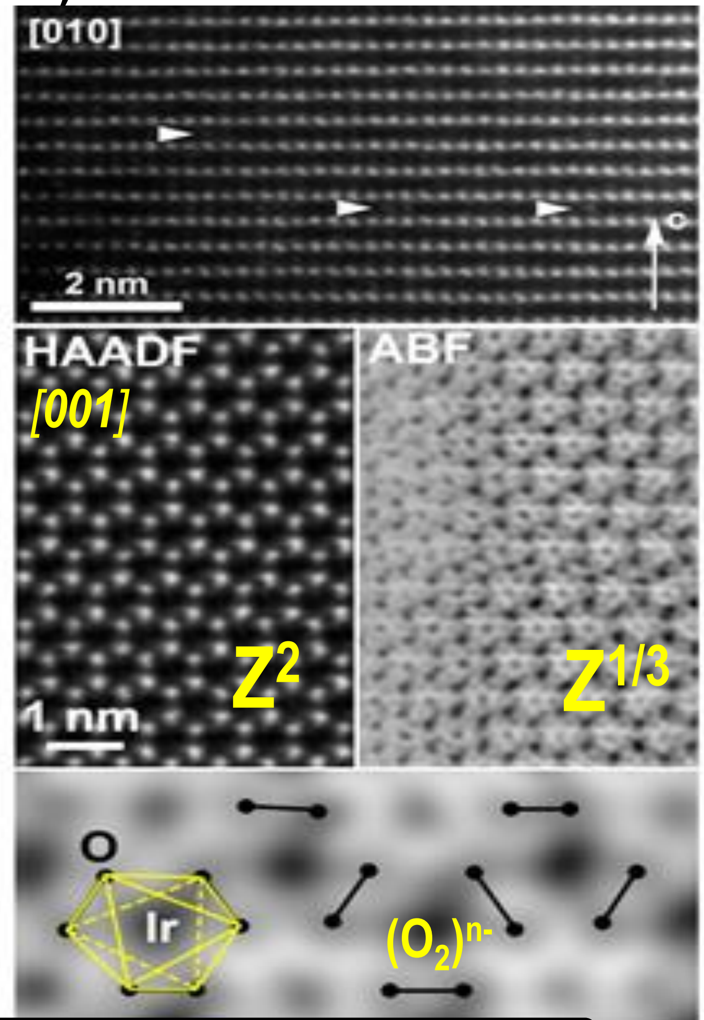
Charged till 4.6V



How to prevent this cationic migration ?
Play with chemistry

Explore ≠ members of the Li_2MnO_3 family (M=Ir)



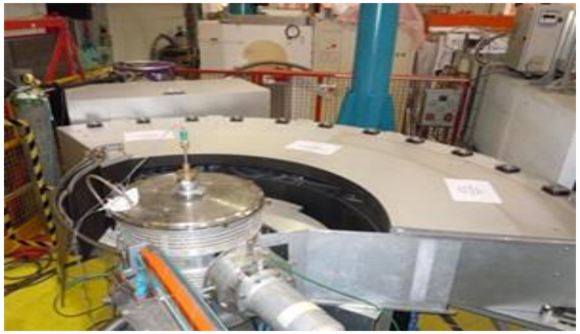


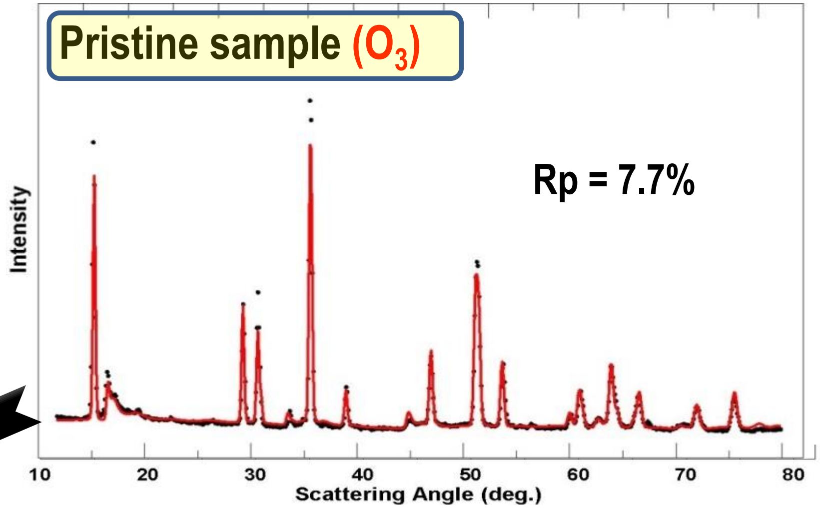
First visualization of (O-O) dimers in Li-rich layered oxide electrodes

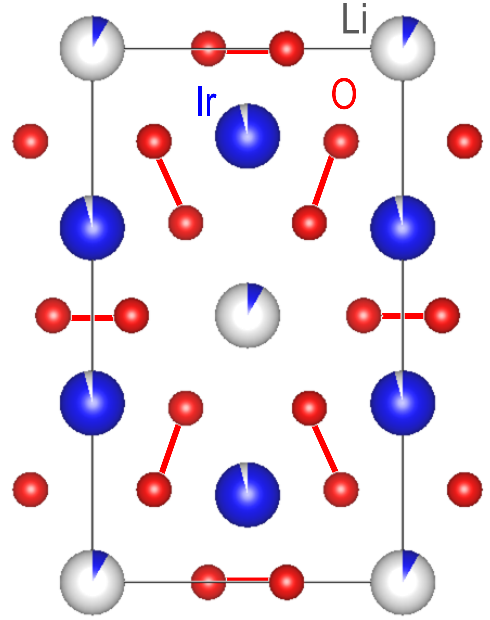
E. McCalla, A. Abrakusov, .. and J.M. Tarascon Science , Décembre 2015

Can we directly measure the (O-O) dimer lengths ?

- Use of the D1B Neutron line at ILL

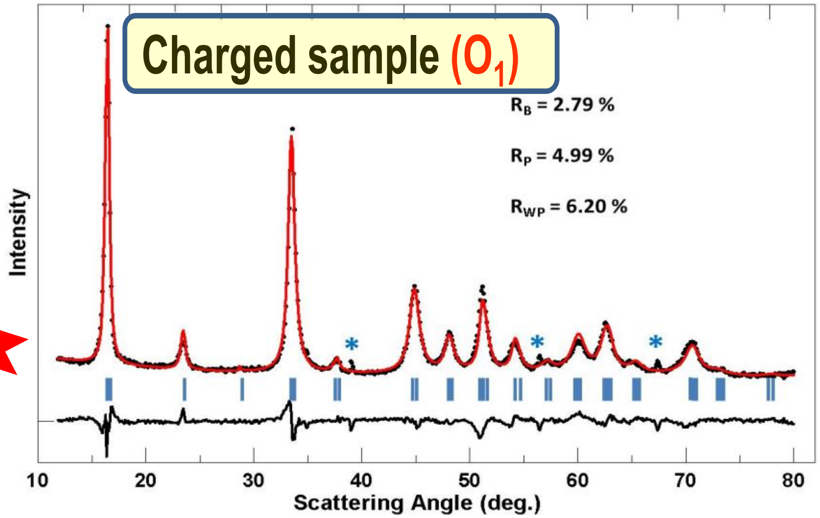






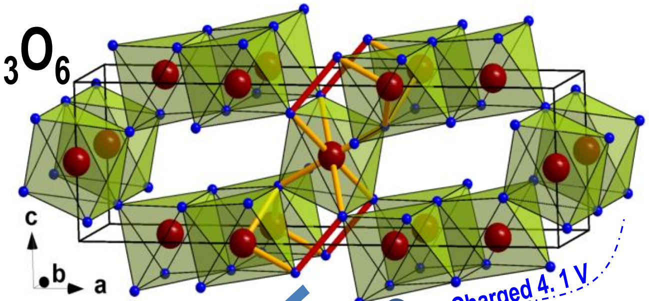
(O-O) 2.84 Å

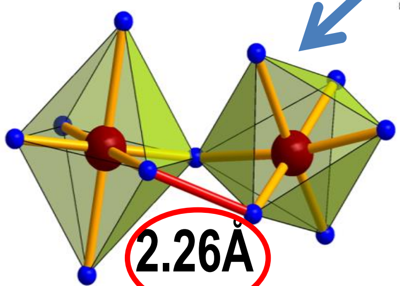
(O-O) 2.45 Å

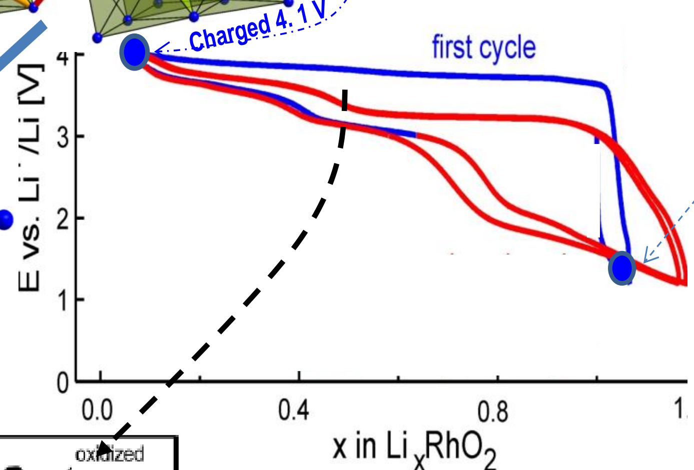


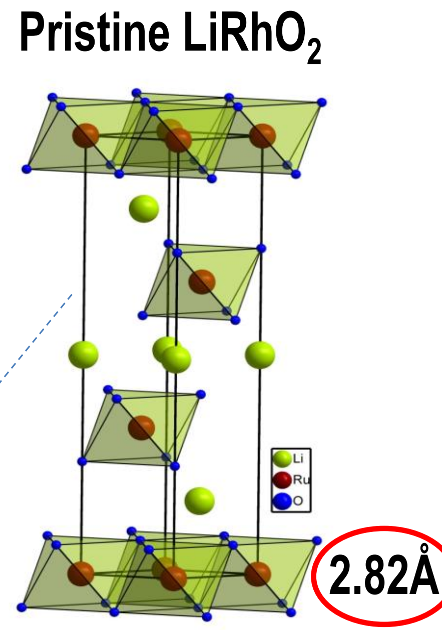
Direct evidence for shorter (O-O) bonds in Li-rich layered oxides electrodes

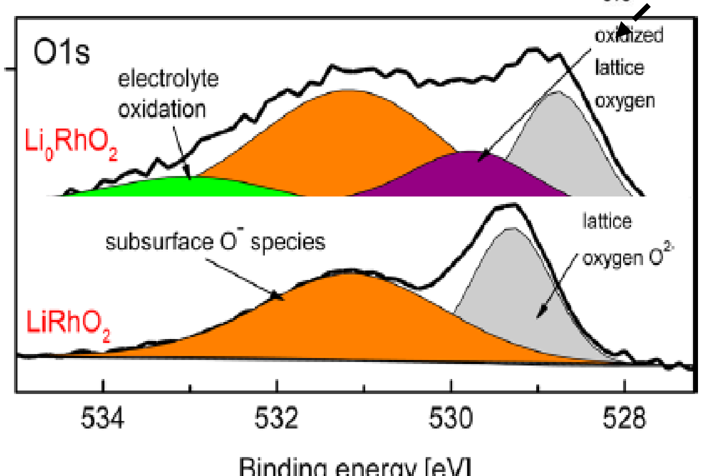
Recent evidence of (O-O) dimers in Li-rich layered oxides: $LiRhO_2$











Shortening of the bonds between O belonging to two ≠ octahedras

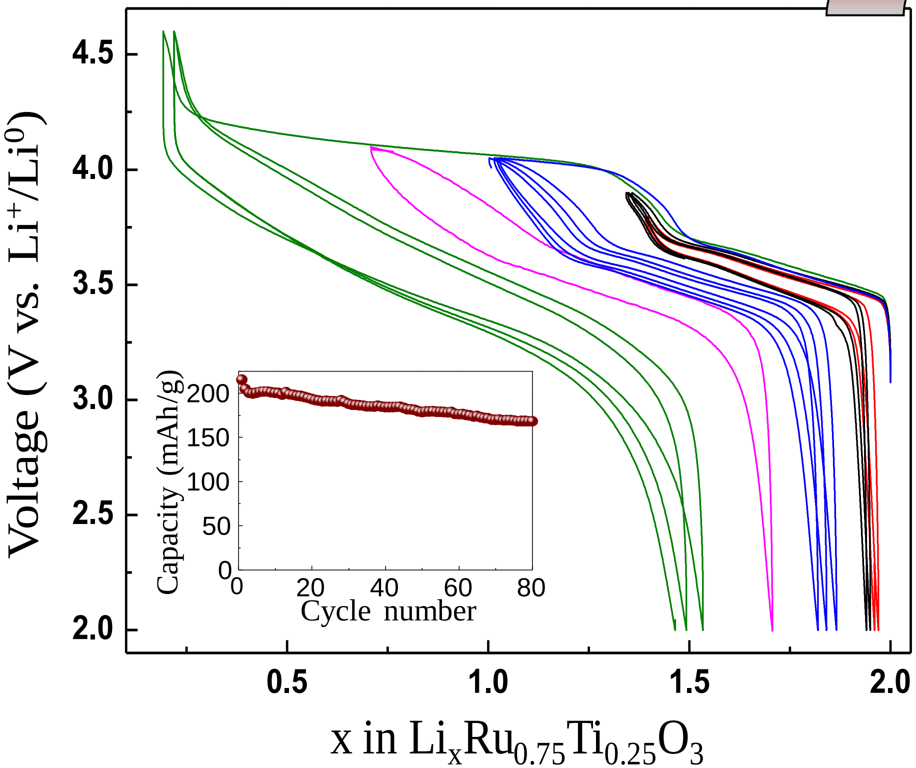
What abput the origin of the voltage fade ?

From Sn ($4d^{10}$) to Ti($3d^{0}$) substitute

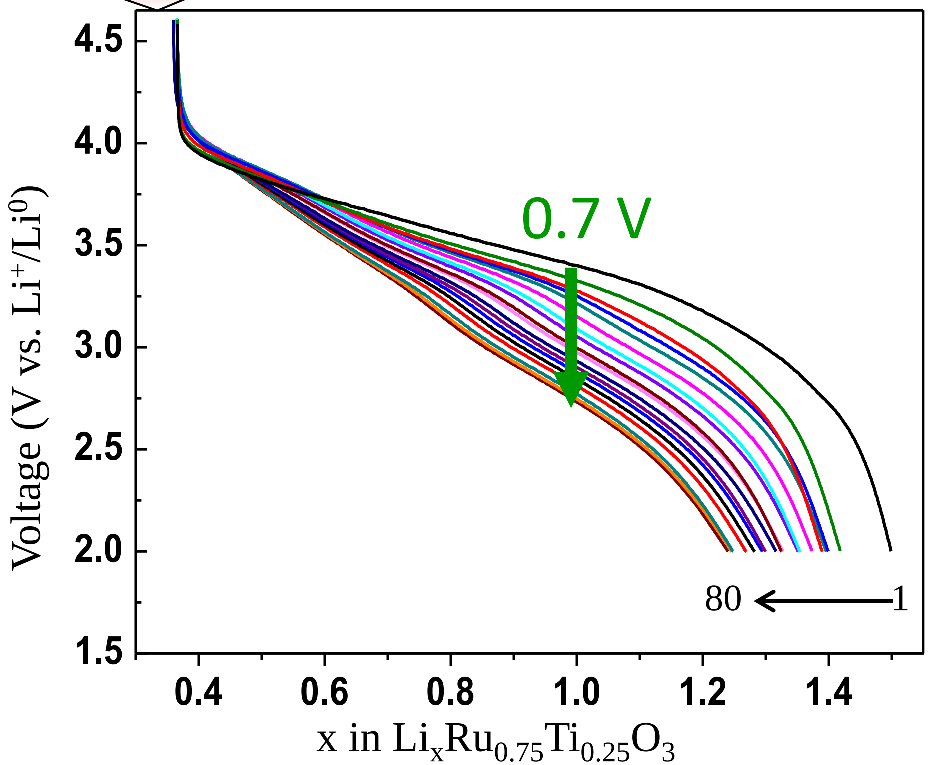
Studying the $Li_2Ru_{0.75}Ti_{0.25}O_3$ system

$Li_2CO_3 + 0.75RuO_2 + 0.25TiO_2 \xrightarrow[\text{Ball mill + 24 hours at 800°C}]{\text{800° C}} Li_2Ru_{0.75}Ti_{0.25}O_3$

☞ Capacity/cycling



☞ Voltage fade



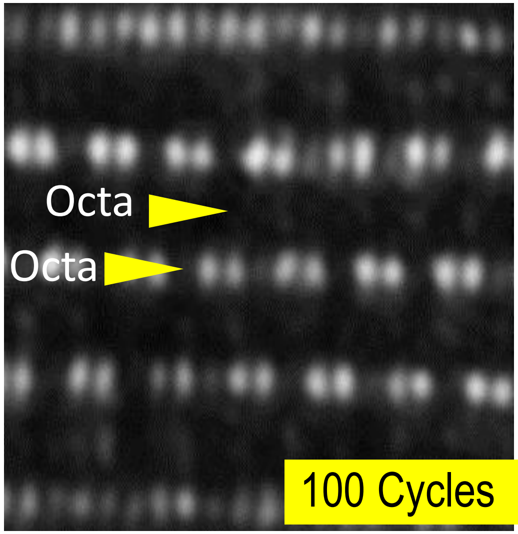
☞ Ti^{+4}, seems to be the worst substitute ..

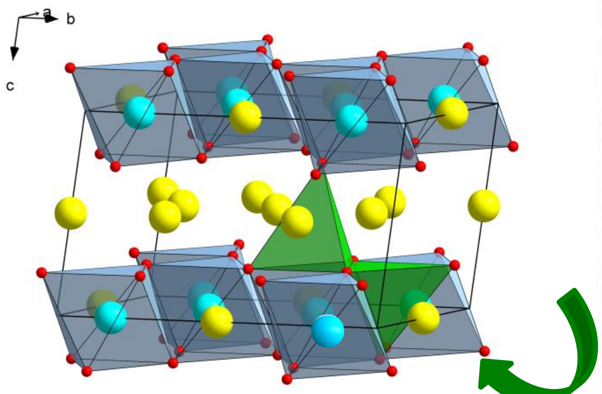
M. Sathya, A.M. Abakumov, K. Ramesha, D. Foix, G. Rousse and J.M. Tarascon, Nature Materials (2015)

Suppression of the potential fade upon cycling by Tin: Why ?

2

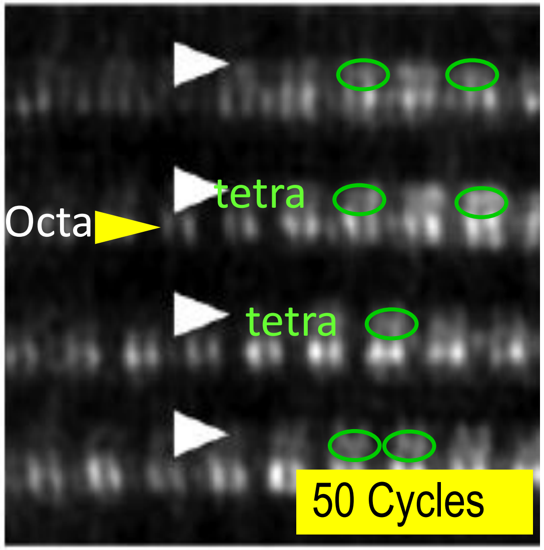
$Li_2Ru_{0.75}Sn_{0.25}O_3$

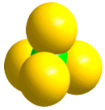




Cations trapped in tetrahedral sites

$Li_2Ru_{0.75}Ti_{0.25}O_3$



Voltage fade upon cycling is linked to the capturing of small cations Ti^{4+} < Sn^{4+} ions in tetrahedral sites 

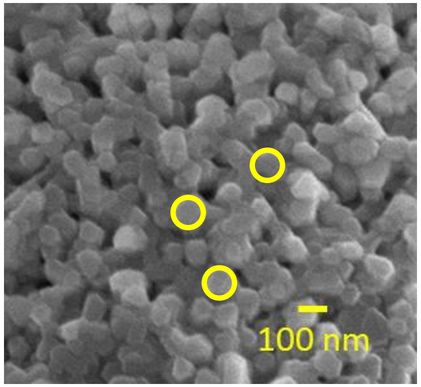
0.6 Å   0.69 Å

Provide chemical clues to enable the development of Li-rich NMC for the next generation of Li-ion batteries

From modem materials to Li-rich NMC

From model compounds to Li-Rich $Li_{1.2}Ni_{0.14}Mn_{0.54}Co_{0.13}O_2$: What's the story?

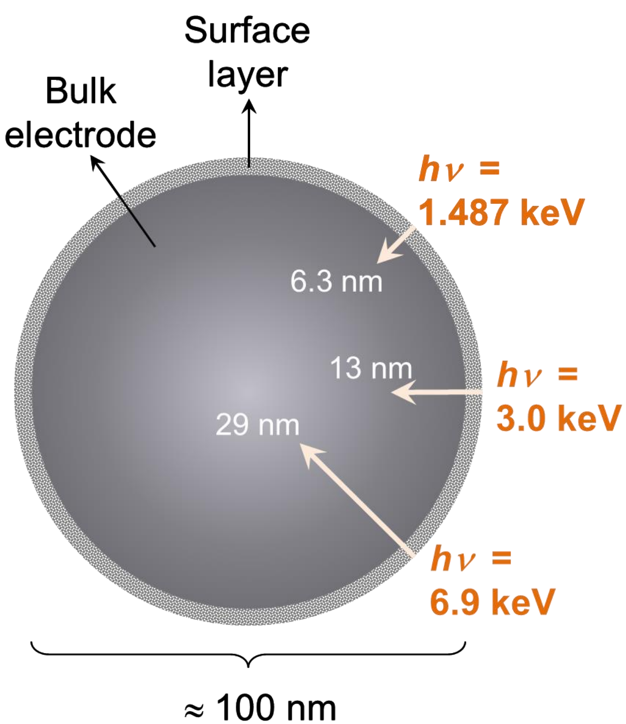
Anionic redox in Li-rich NMC –via bulk-sensitive hard-XPS

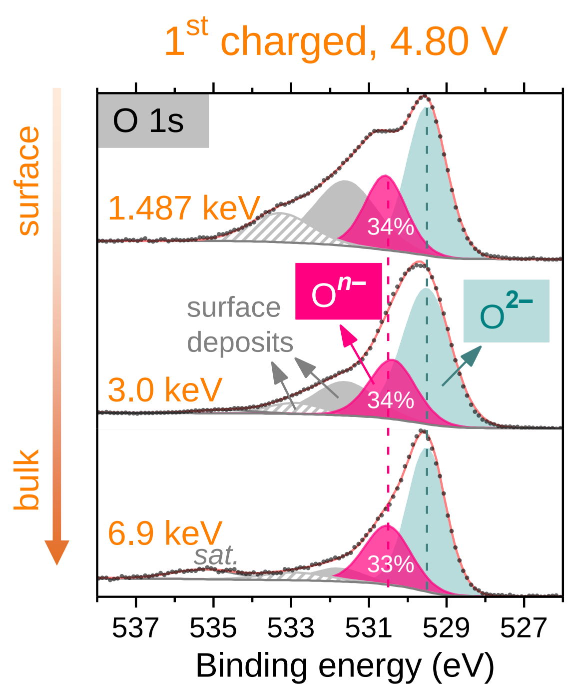


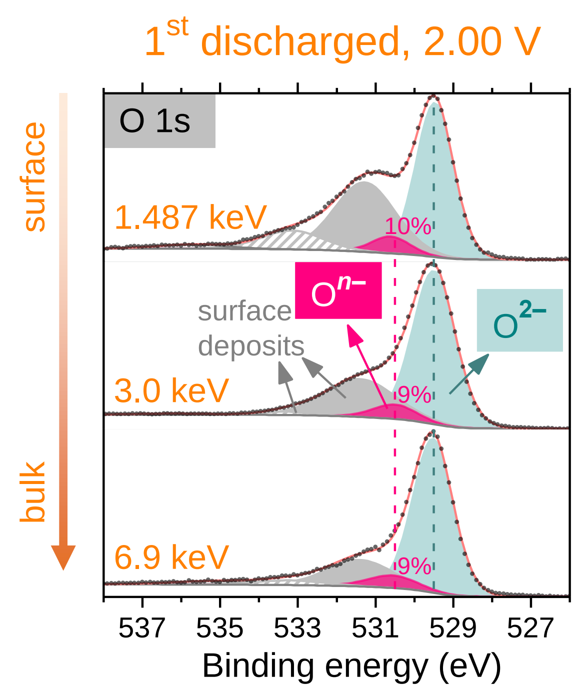
Li-rich NMC

What are the cationic / anionic redox potentials ?

Direct evidence of bulk anionic redox







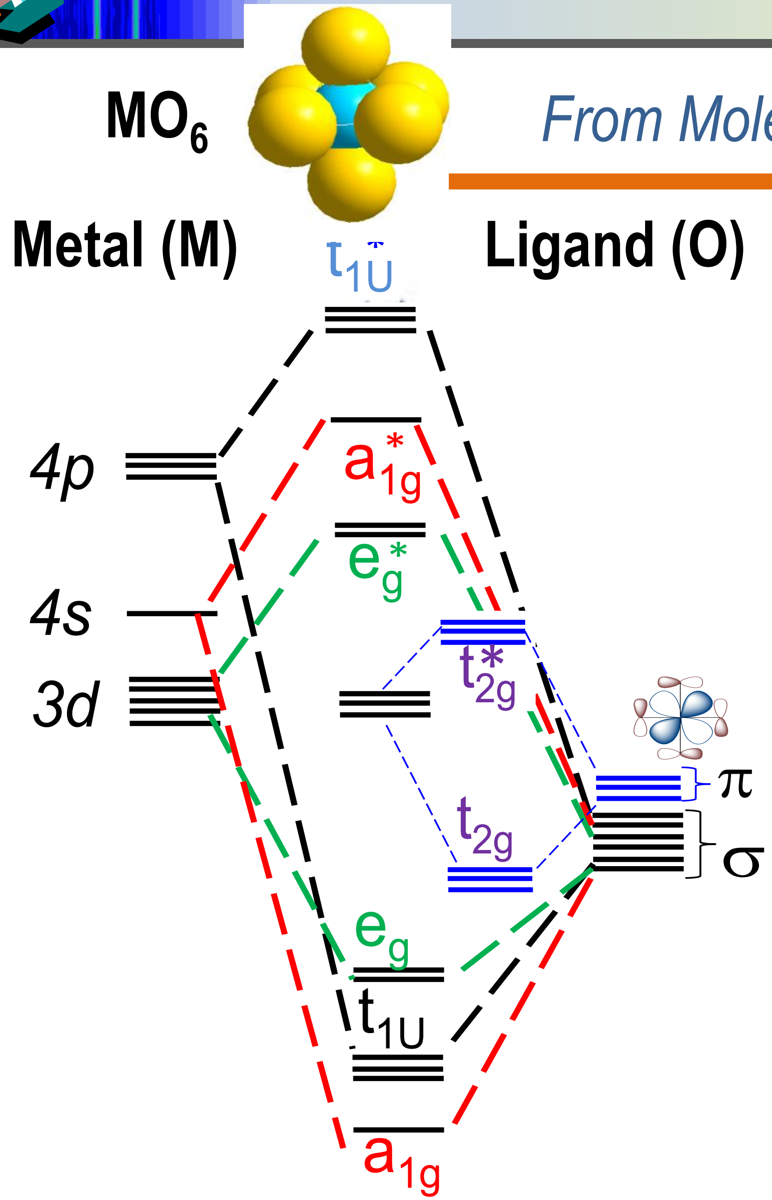
The science underlying the anionic redox process

→ The source of controversial debates

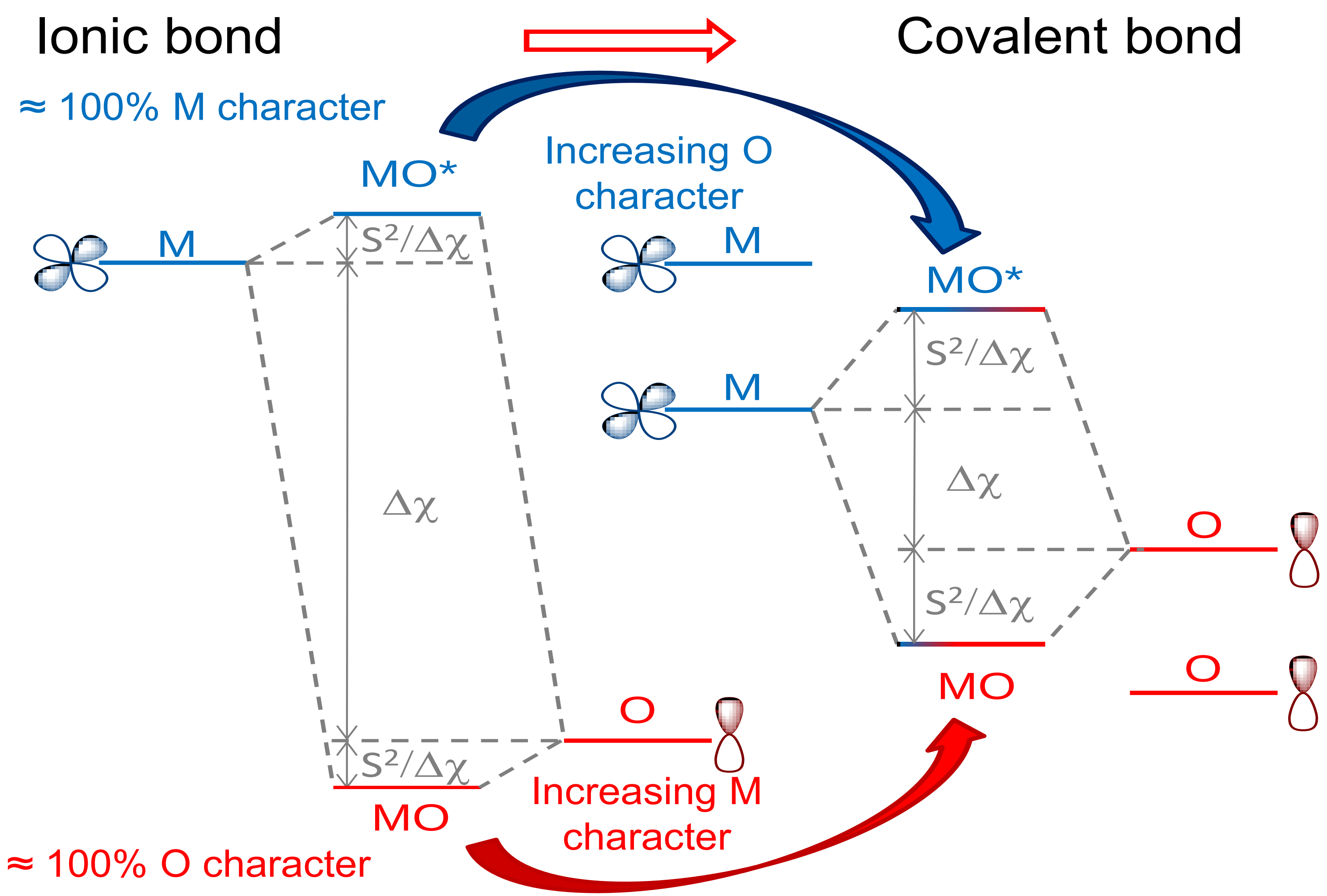
(need to go back to basics)

Some basic recalls ….

From Molecular Orbitals to the Band Structure

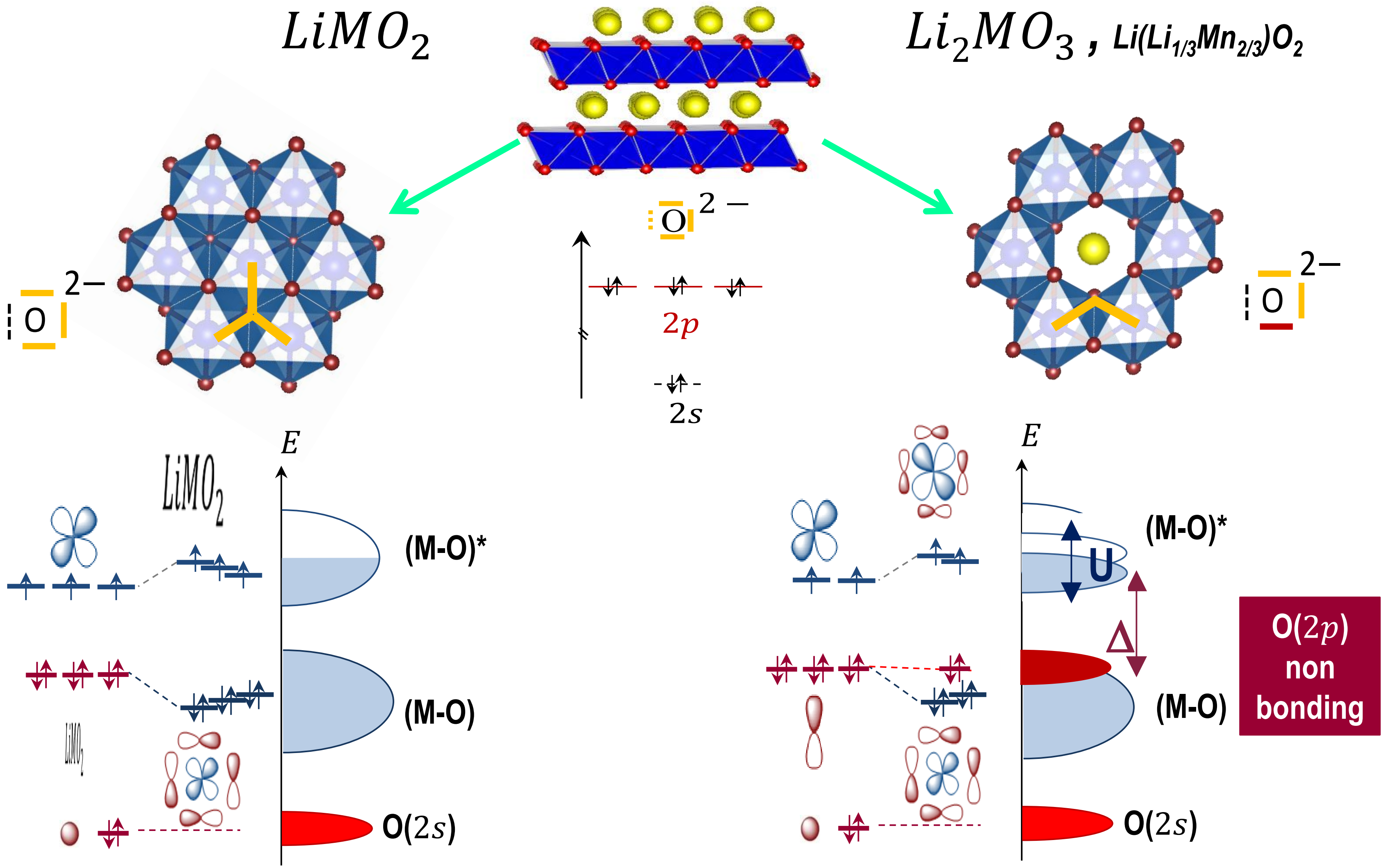


The iono-covalence: Its influence on band positions



Energy difference MO/MO* given by $\Delta\chi + 2S^2/\Delta\chi$

How this can happen ?
What is the underpinning science …



Classical situation: 1 Redox band

An illicit situation: 2 Redox bands

Anionic redox depends upon the competition between U and Δ

U << Δ

Cationic redox

(One band)

Δ ~ U/2

Anionic redox

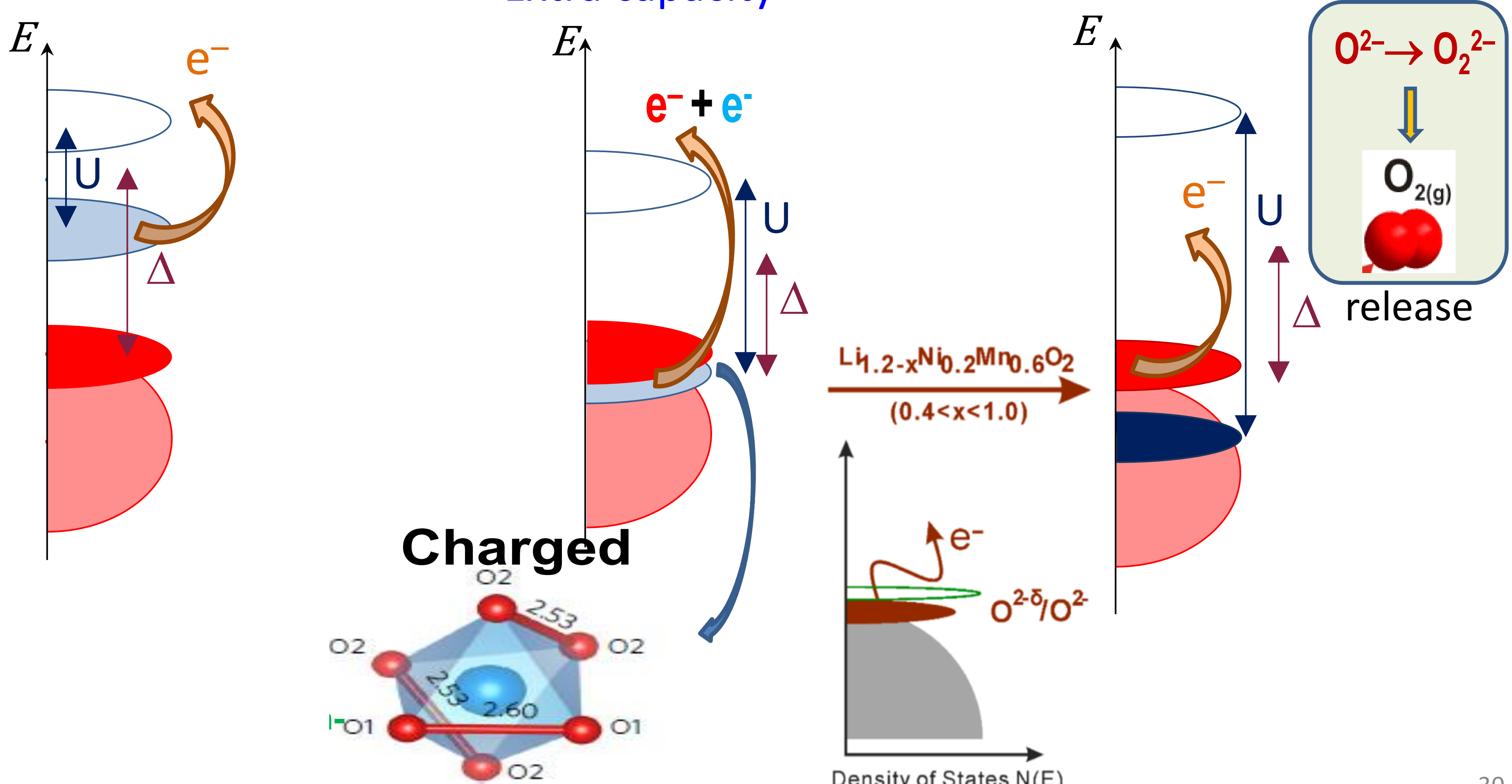
(two bands)

Extra capacity

Δ << U

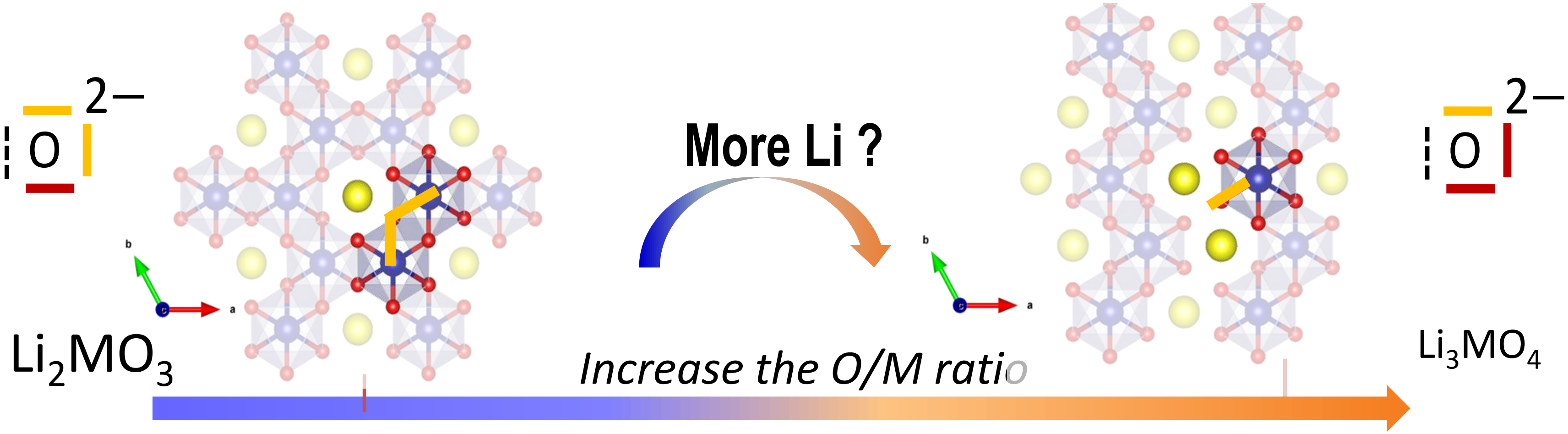
Anionic redox

(One band but irreversible)

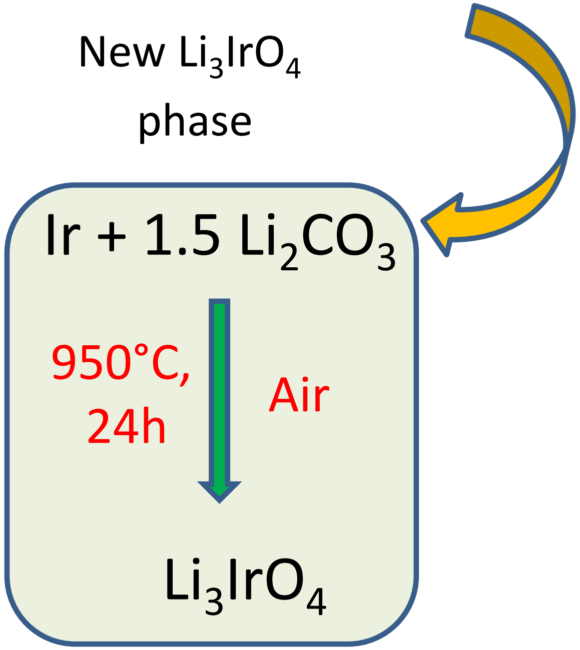


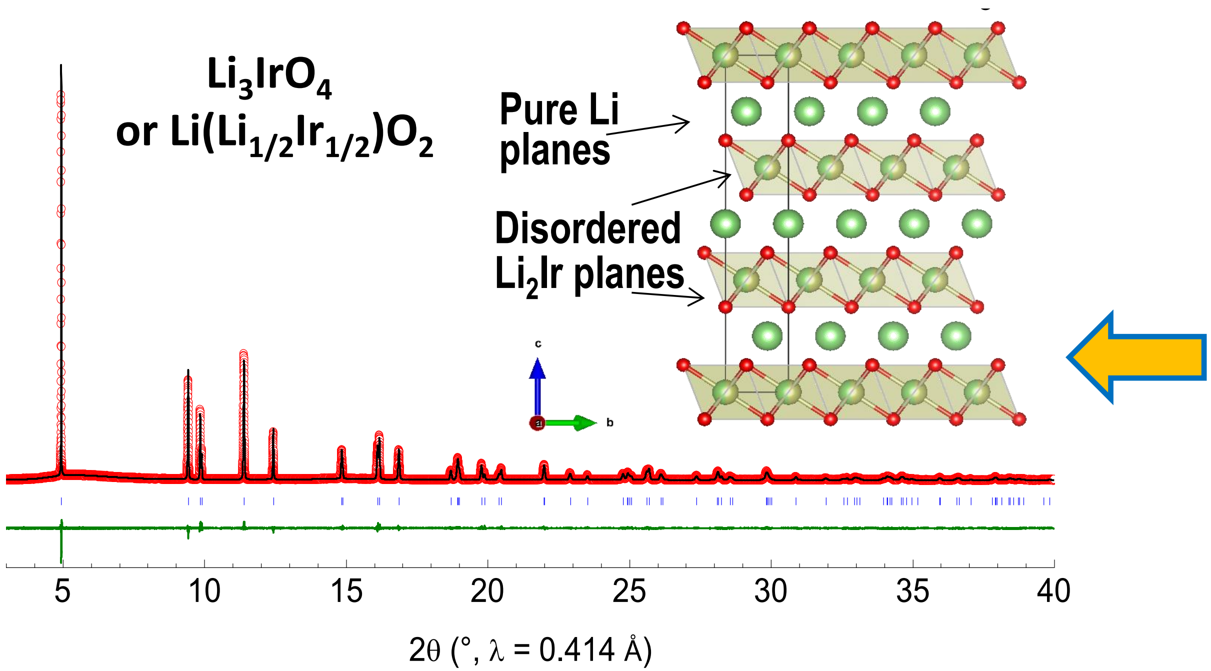
Pearce, Tarascon et al, Nature Mater. (2017) P. Bruce, Nature chemistry (2016) Saubanère, Tarascon et al, EES 9 (20

To which extreme can we push the capacity using the anionic redox concept?



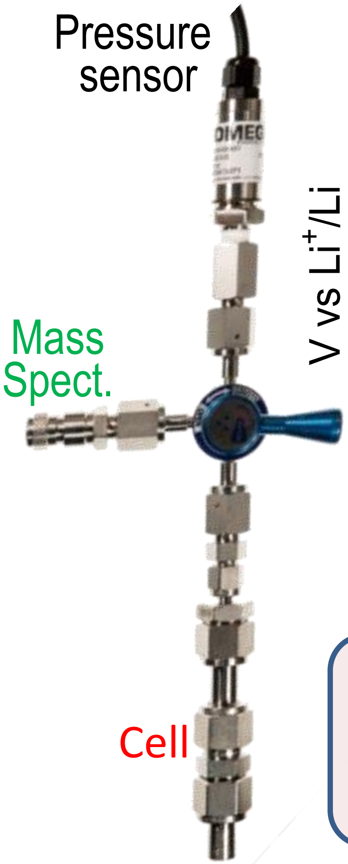
New Li$_3$IrO$_4$ phase

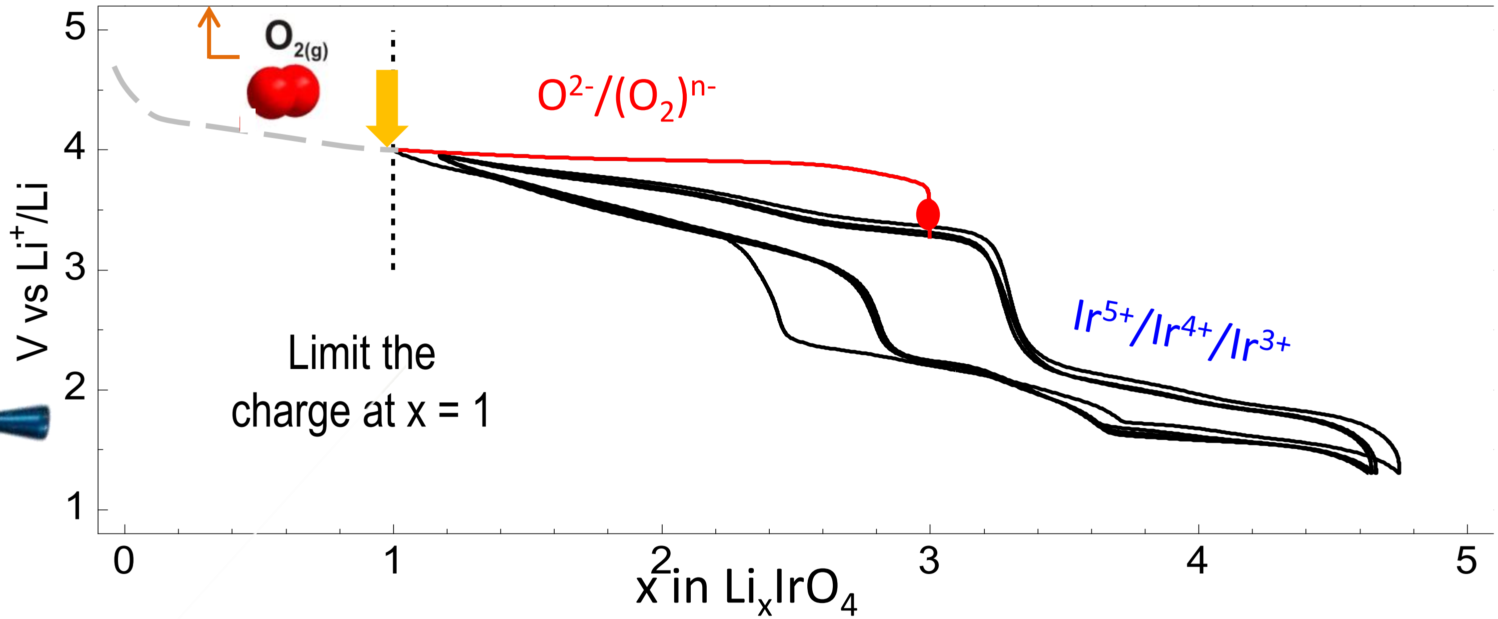




A. Perez et al. Submitted

Electrochemical performance of Li_3IrO_4 vs. Li^+/Li while monitoring pressure





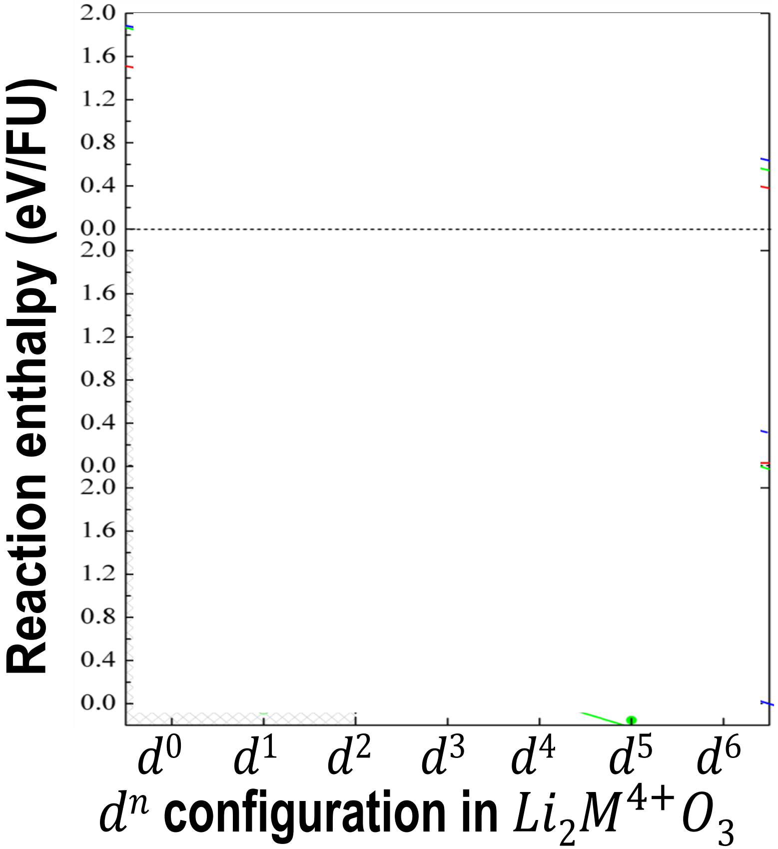
Li_1IrO_4 ← **3.5 e^- are exchanged by transition metal ….** (340 mAh/g) → $Li_{4.5}IrO_4$

Highest value ever reported for insertion cathode materials in Li-ion batteries

Increasing the O/M ratio: a trade-off would have to be found between extra-capacity and structural stability

$(O_2)^{n-}$ stability against recombination into O_2 : a DFT approach

3d	Ti	V	Cr	Mn	Fe	Co	Ni
4d	Zr	Nb	Mo	Tc	Ru	Rh	Pd
5d	Hf	Ta	W	Re	Os	Ir	Pt



Network stability w.r.t O_2 release

$$Li_xMO_3 \rightarrow Li_xMO_{3-\delta} + {}^{\delta}/_{2}\ O_2$$

Positive enthalpy => formation of O_2 vacancies is not favorable

- ✓ nd-shell : M-O covalence is to stabilize the network

- ✓ Li-content : all $M(3d)$-based materials are unstable w.r.t. O_2 release once the first Li is removed

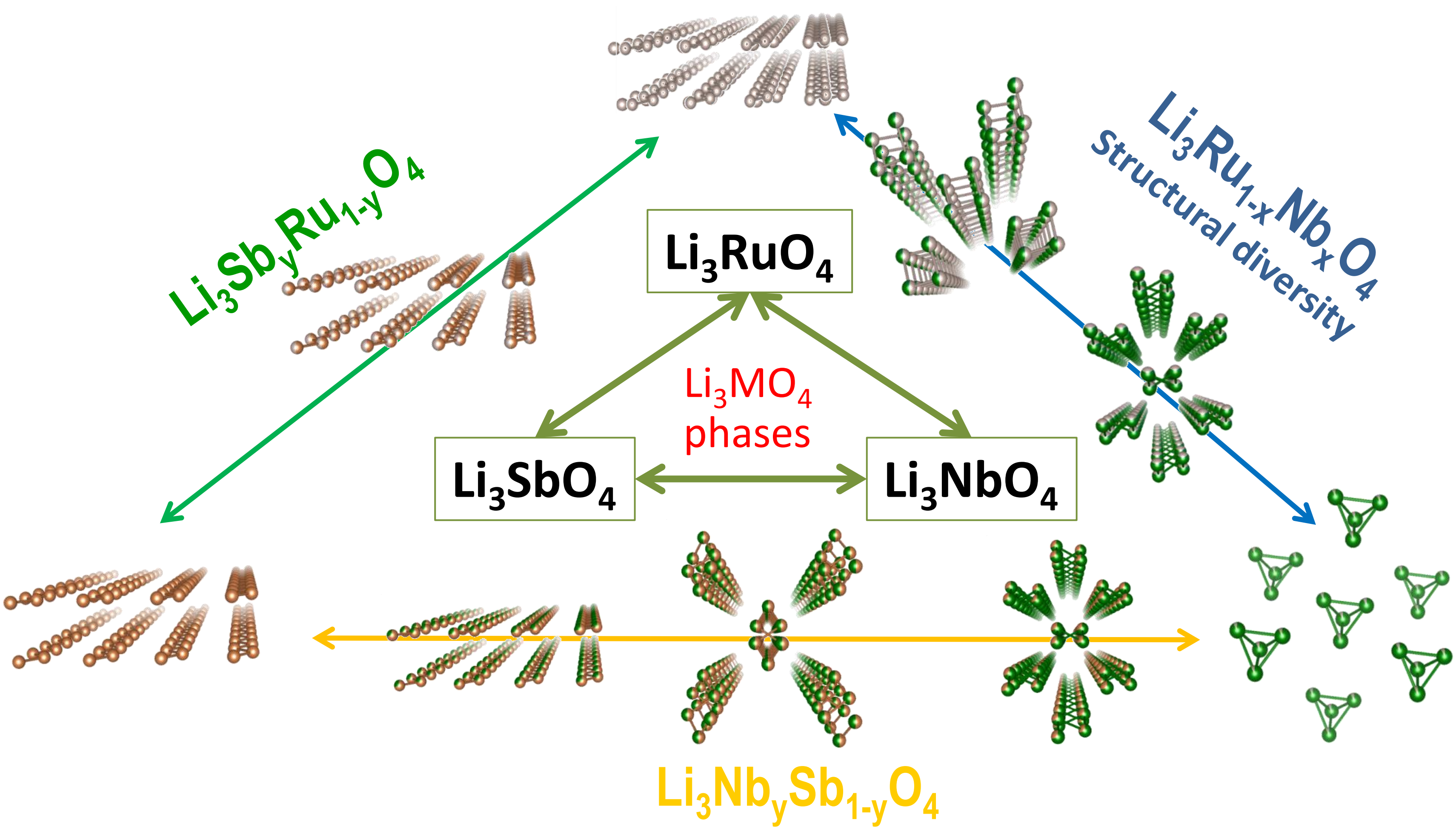
! ... Bad news for applications

Therefore 5d metals with n> 3 are stable in agreement with the use of Ir

Exploit such findings to design $Li_2MM'O_3$ phases stable against $(O_2)^{n-}$ recombination

Xie *et al*. Energy & Environ. Sci. Asap 2016

The Li_3MO_4 family: a rich crystal chemistry



Creation of a platform for identifying key indicators to manipulate anionic redox

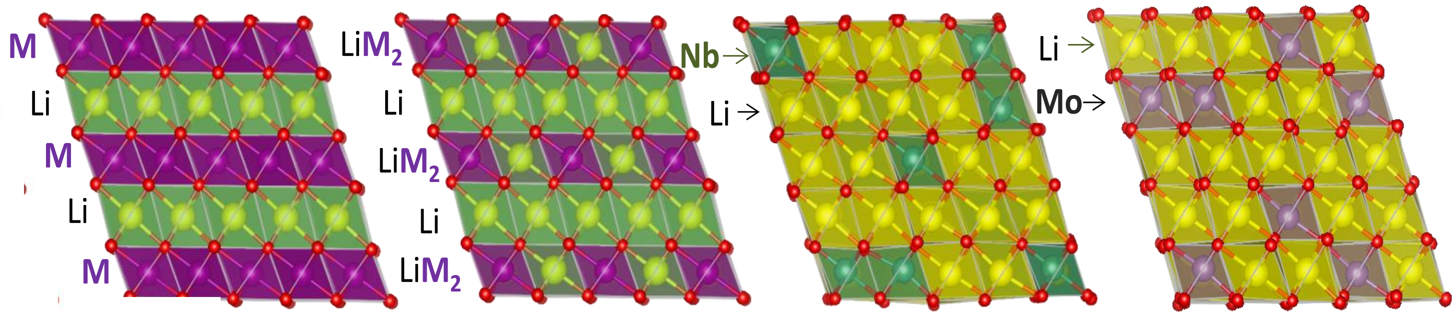
J. Quentin et al. Chemistry of materials 2017

Yabuuchi et al, PNAS 112 (2015)

Effect of dimensionality: is anionic redox limited to 2D compounds ?

Effect of modifying the crystal structure on the anionic redox reactivity

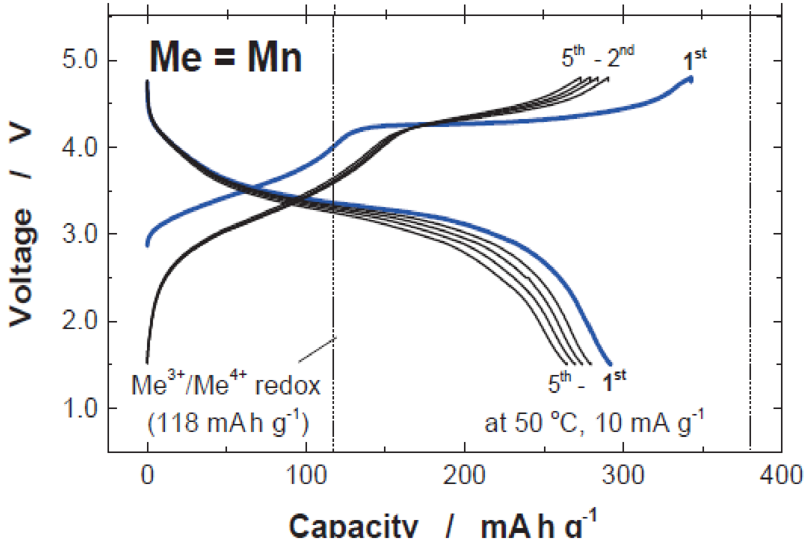
- Layered rocksalt structures as a funstion of increasing Li/M ratio.



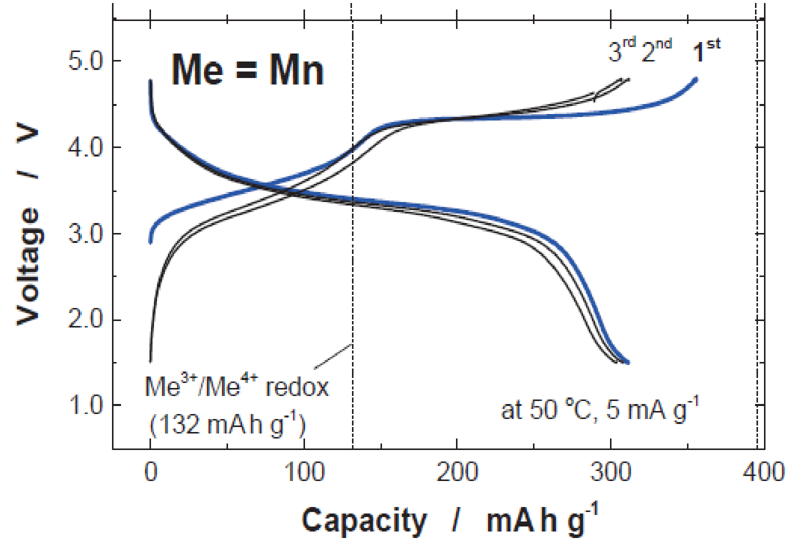
2D 3D

Increases disorder

x in $Li_{1.3-x}Nb_{0.3}Mn_{0.4}O_2$



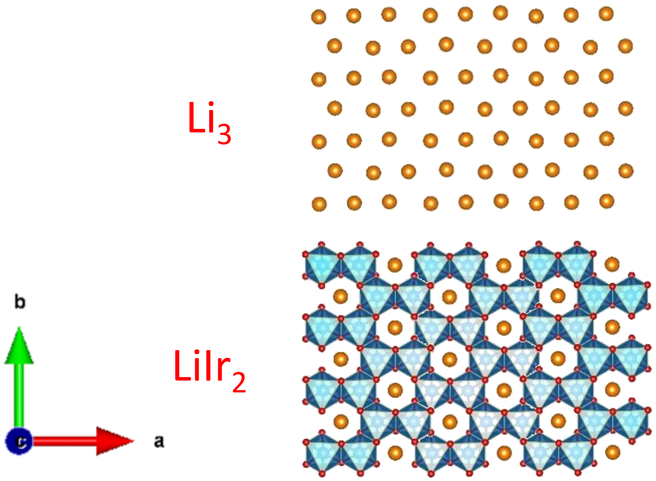
x in $Li_{1.2-x}Ti_{0.4}Mn_{0.4}O_2$

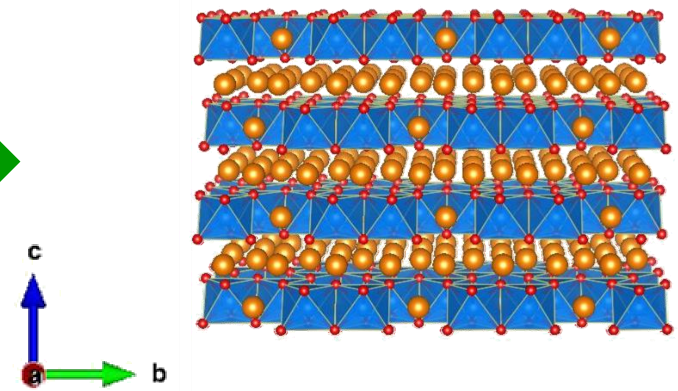


Yabuchi et al; PNAS, 2016

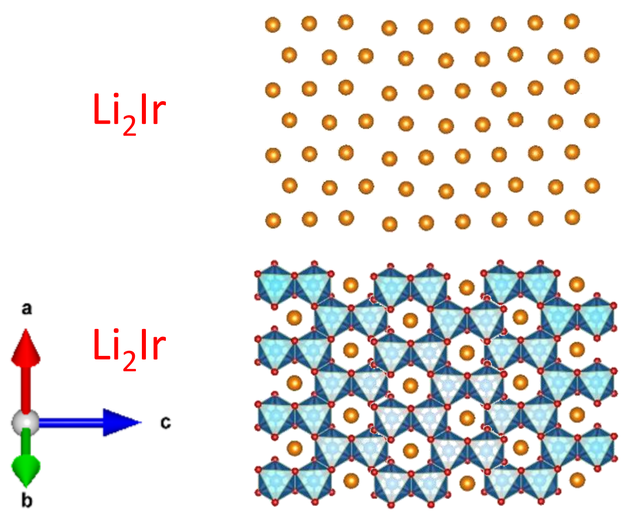
Is the anionic redox process only limited to 2D layered compounds ?:

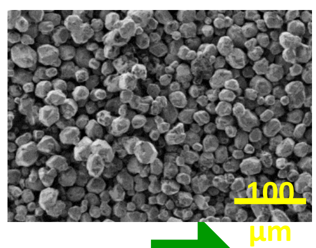
IrO_2 + Li_2CO_3 (10% excess) $\xrightarrow{< 950°C\ (24h)}$ α-Li_2IrO_3 2D structure

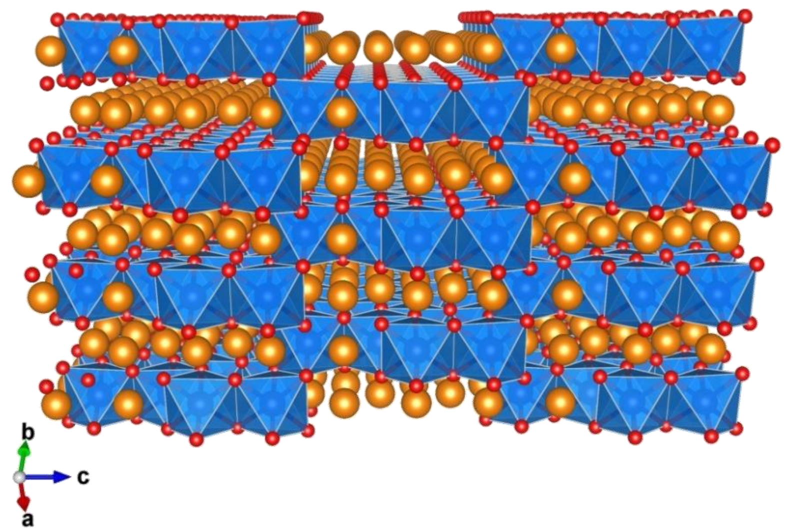


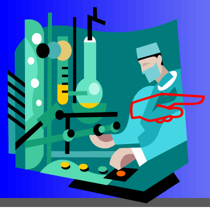


IrO_2 + Li_2CO_3 (10% excess) $\xrightarrow{> 1050°C\ (> 90h)}$ β-Li_2IrO_3 3D structure

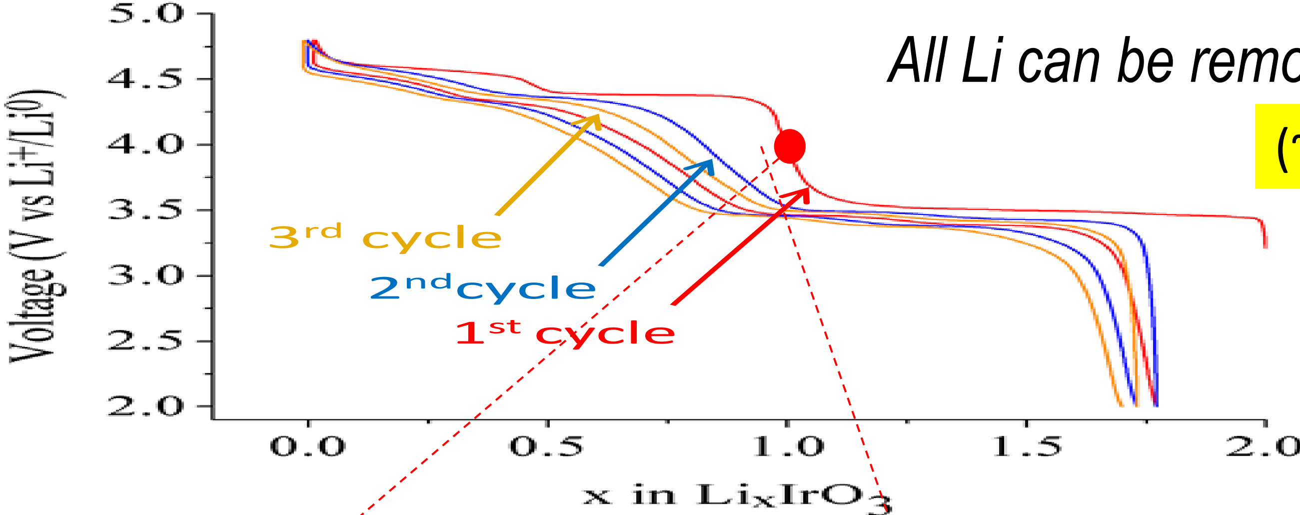








Electrochemical performance of the 3D Li-rich polymorph

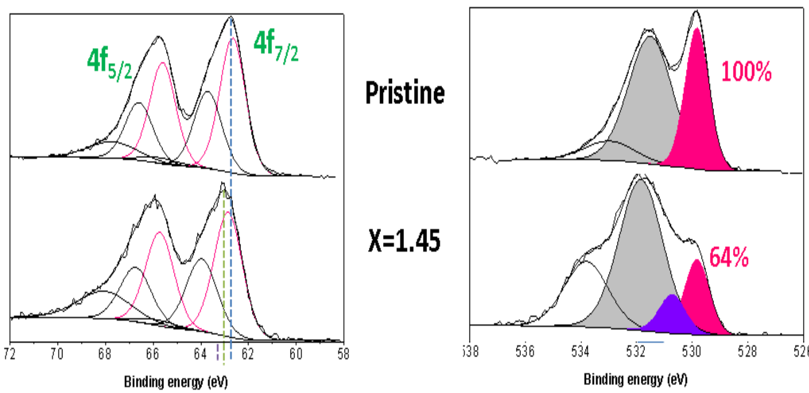


All Li can be removed "IrO_3"

(~ 2 e^- per Ir)

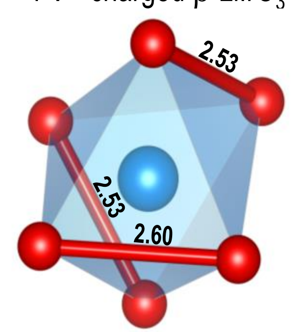
X-ray photoemission

Ir 4f *Anionic + cationic* O 1s



Neutron Powder diffraction + ABF-STEM

4 V - charged β-$LiIrO_3$



O-O distortion Δ (x10^4)= 25.2

<Ir-O> = 1.972 Å

Anionic redox activity is not solely limited to 2D systems: its implementation to 3D oxides opens wide the research field for high capacity electrodes

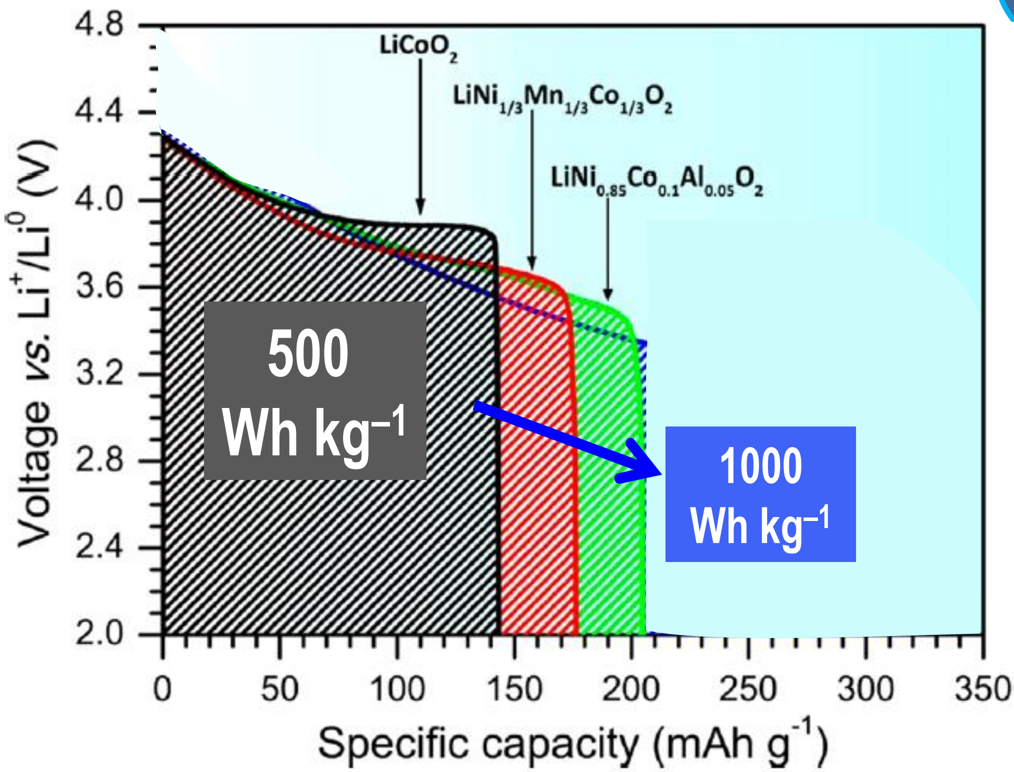
P. Pearce et al. Nature materials February 2017

Anionic redox – A transformational approach to design high energy cathodes

Classical Layered Oxides
$LiMO_2$
cationic redox only

Li-rich Layered Oxides
$Li_{1+y}M_{1-y}O_2$
combined cationic + anionic redox

Can we use Li-rich cathodes in real-world batteries…

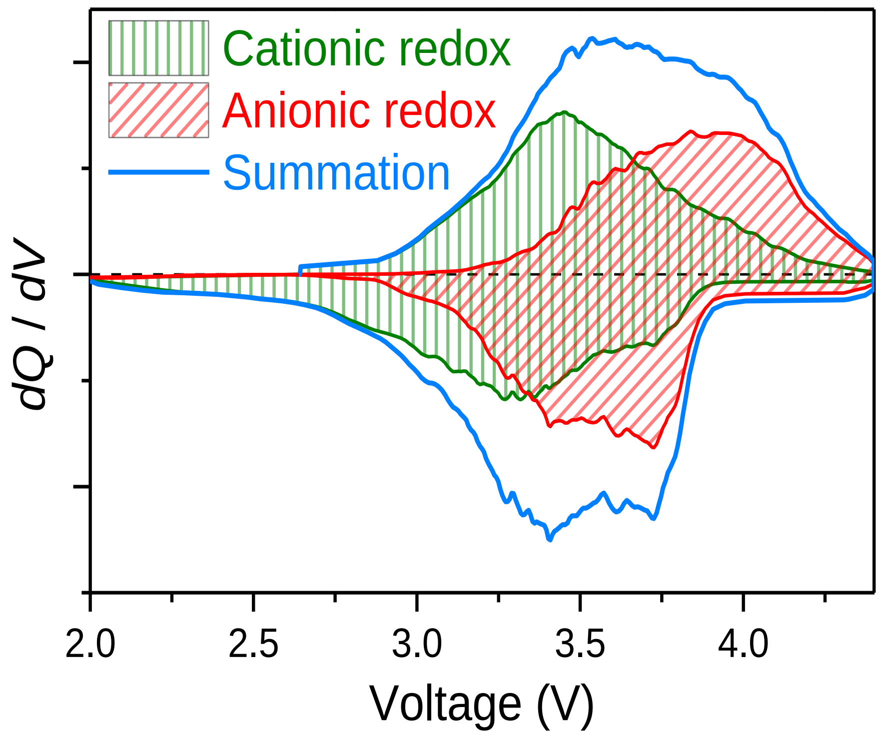


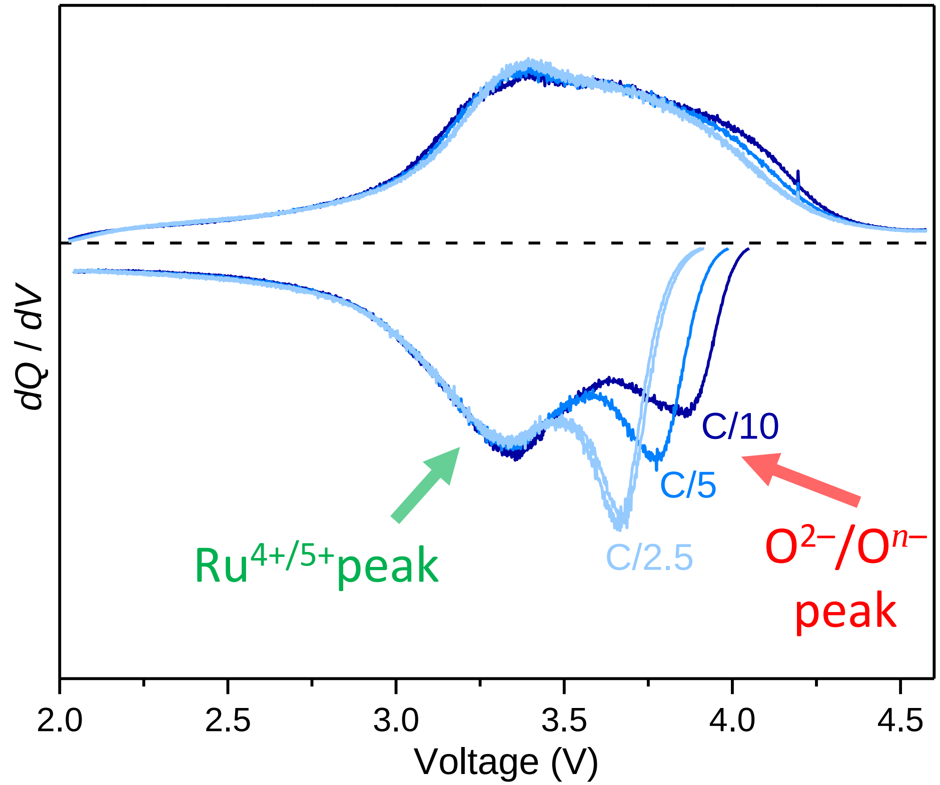
Any practical roadblocks ???

Poor kinetics
Hysteresis
Voltage decay

Poor kinetics of Li-rich NMC: ($Li_2Ru_{0.75}Sn_{0.25}O_3$)

Deconvolution via *operando* XAS



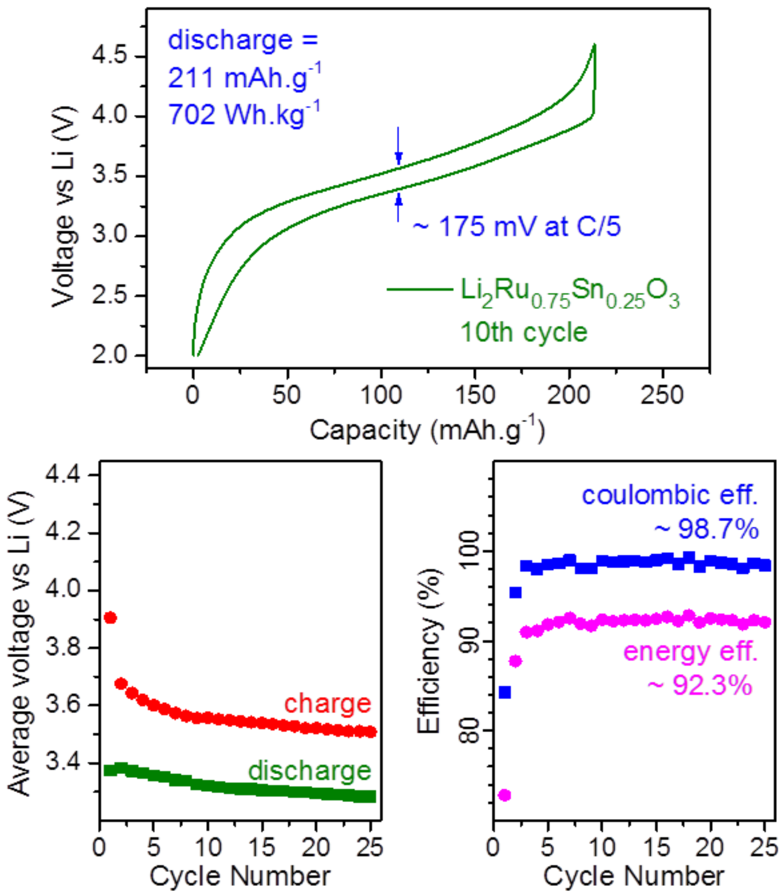


Anionic redox shows sluggish kinetics and triggers hysteresis

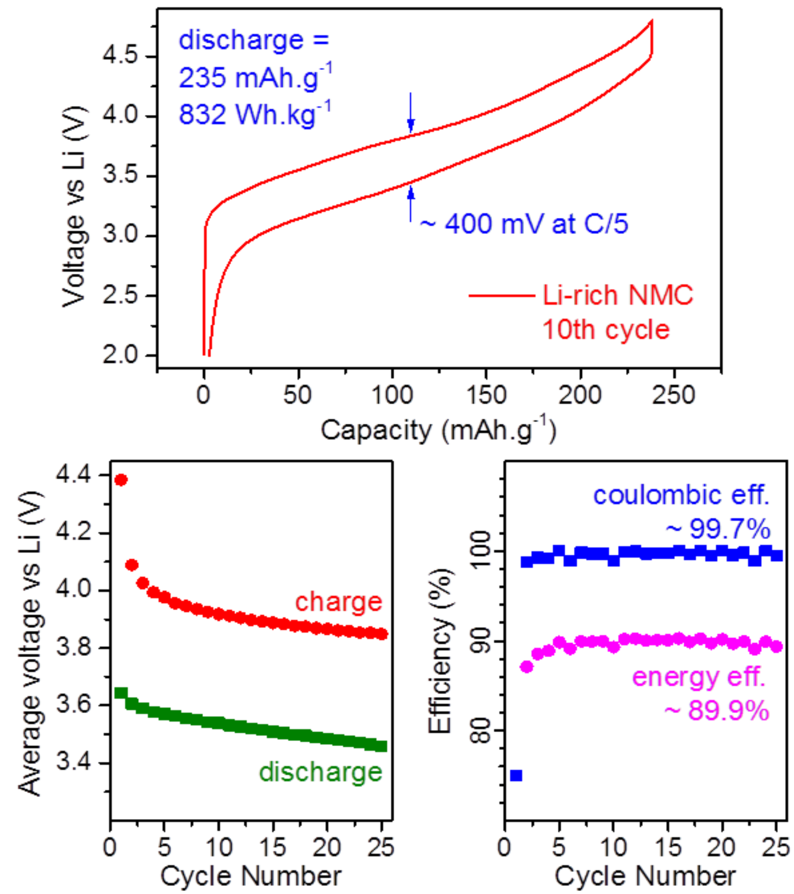
G. Assat, J-M. Tarascon et al., *J. Electrochem. Soc.*, (2016).

Consequences of poor kinetics/large polarisation: Energy efficiency ….

$Li_2Ru_{0.75}Sn_{0.25}O_3$ (*model*)



Li-rich NMC (*practical*)

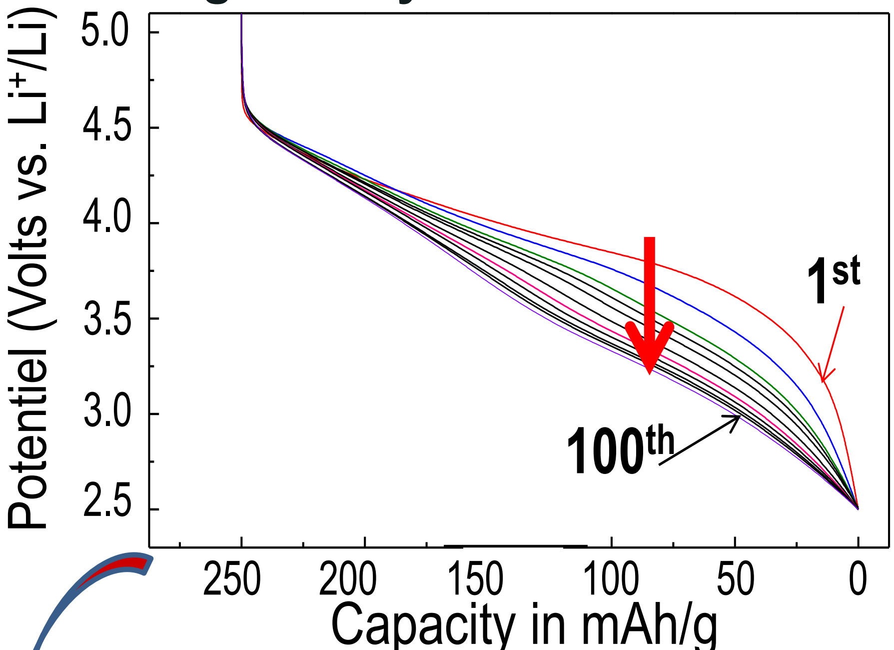


Poor round-trip energy efficiency in LR-NMC:_Role of anionic redox

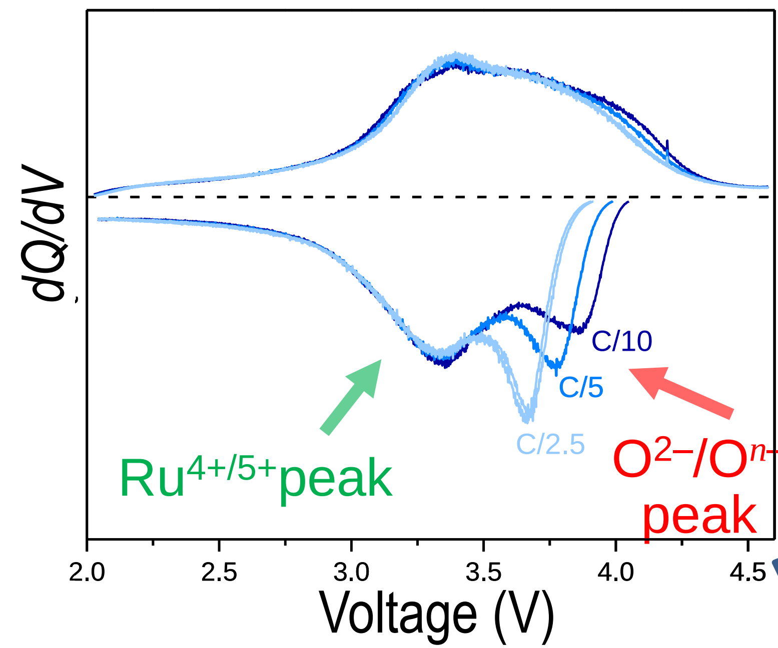
G. Assat, J-M. Tarascon et al., *J. Electrochem. Soc.*, (2016).

Practical roadblocks in Li-rich cathodes and their consequences

Voltage decay



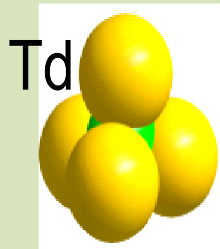
Poor kinetics



Are these practical issues surmountable ?

Importance of substituent

(chemical elements with large ionic radii)



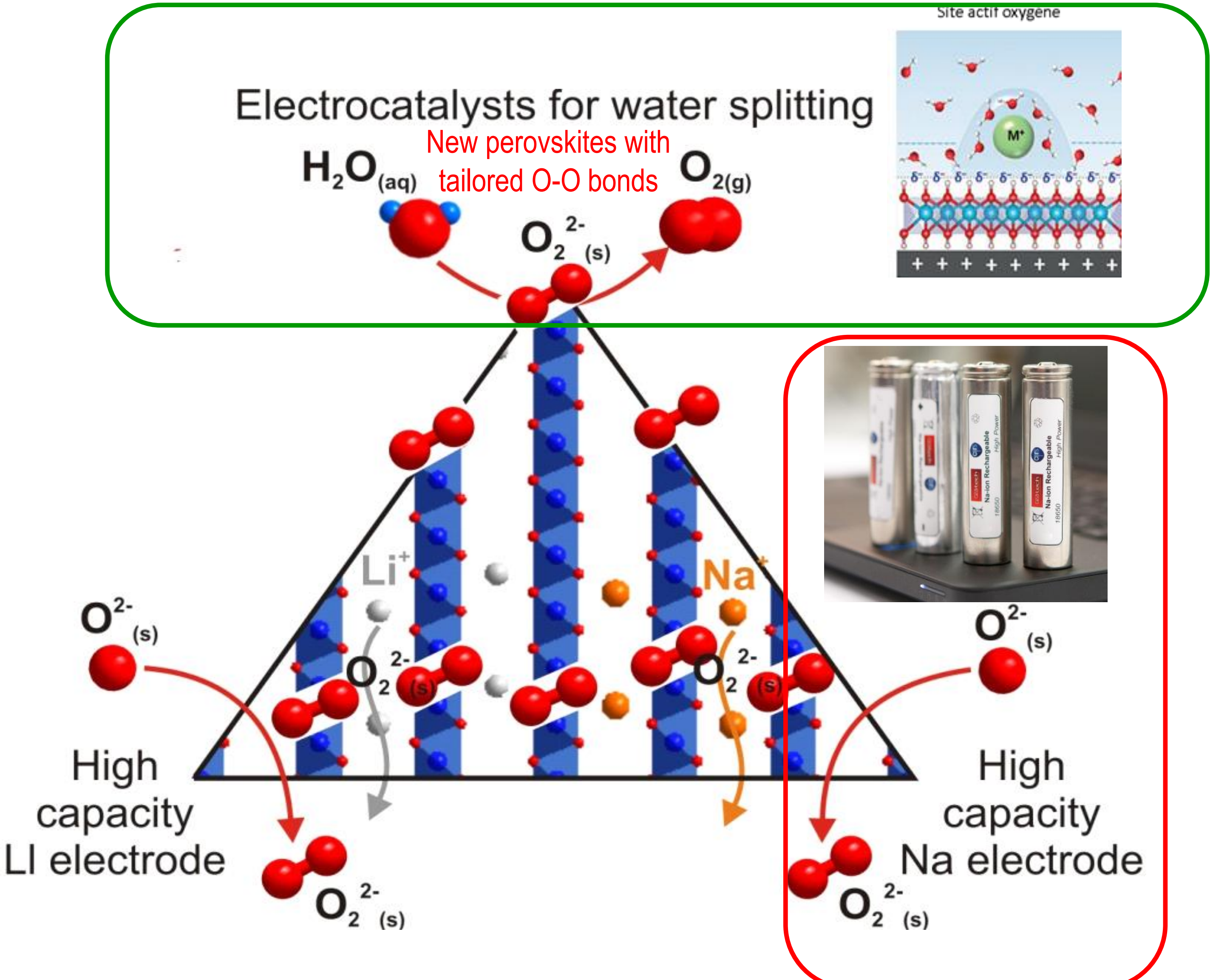
A promising direction being pursued

Design of materials within which cationic and anionic redox occur at the same potential

Sathya, Tarascon et al., Nature Materials 2015 ,vol. 14, no. 2, pp. 230–8

G. Assat, J-M. Tarascon et al., *J. Electrochem. Soc.*, (2016).

Importancy of anionic redox beyond electrode materials



N. Yabuushi et al. PNAS May 2015 M. Freire et al. Nature materials Novembre 2015 A. Grimaud, ,,, Tarascon Nature materials 15 (20

Acknowledgments

Thank you for your attention

http://www.college-de-france.fr/site/en-college/index.htm