Химия твердого тела в электрохимической энергетике: катодные материалы литий-ионных аккумуляторов

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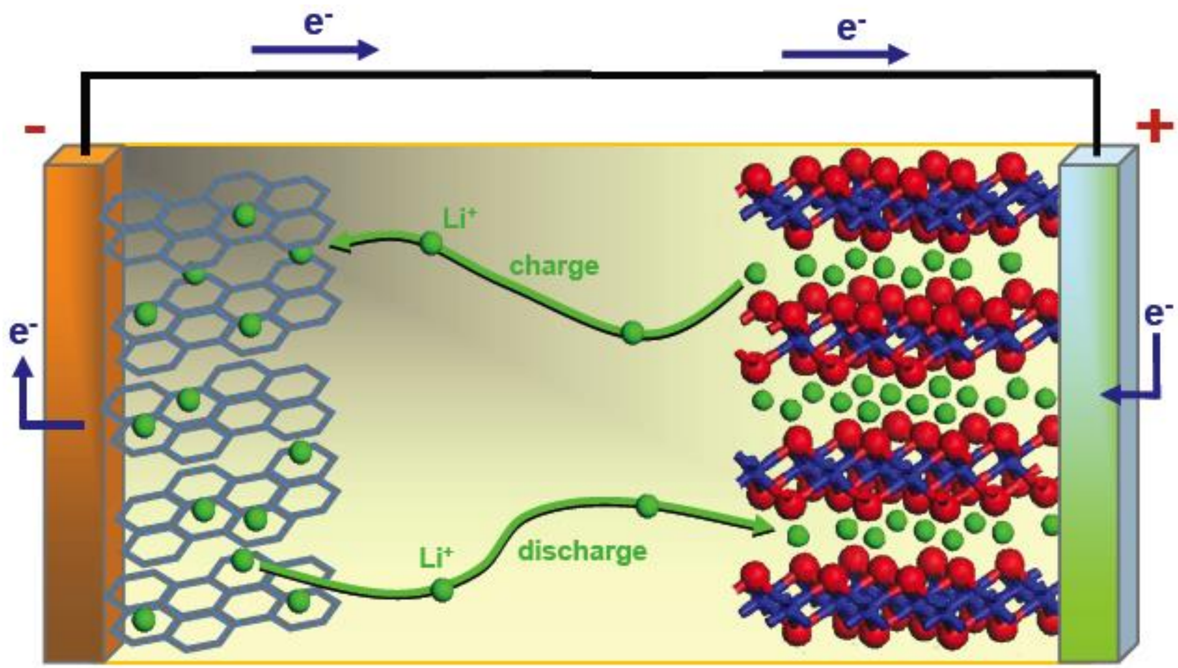
Li-ion batteries



Li_xC_6 graphite | Li^+-conducting electrolyte | $LiMO_2$

$$C_6 + LiCoO_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_xC_6 + Li_{1-x}CoO_2$$

0.5-0.6 e^-

Voltage 3.6 V, x ≈ 0.5-0.6

Where these electrons come from?

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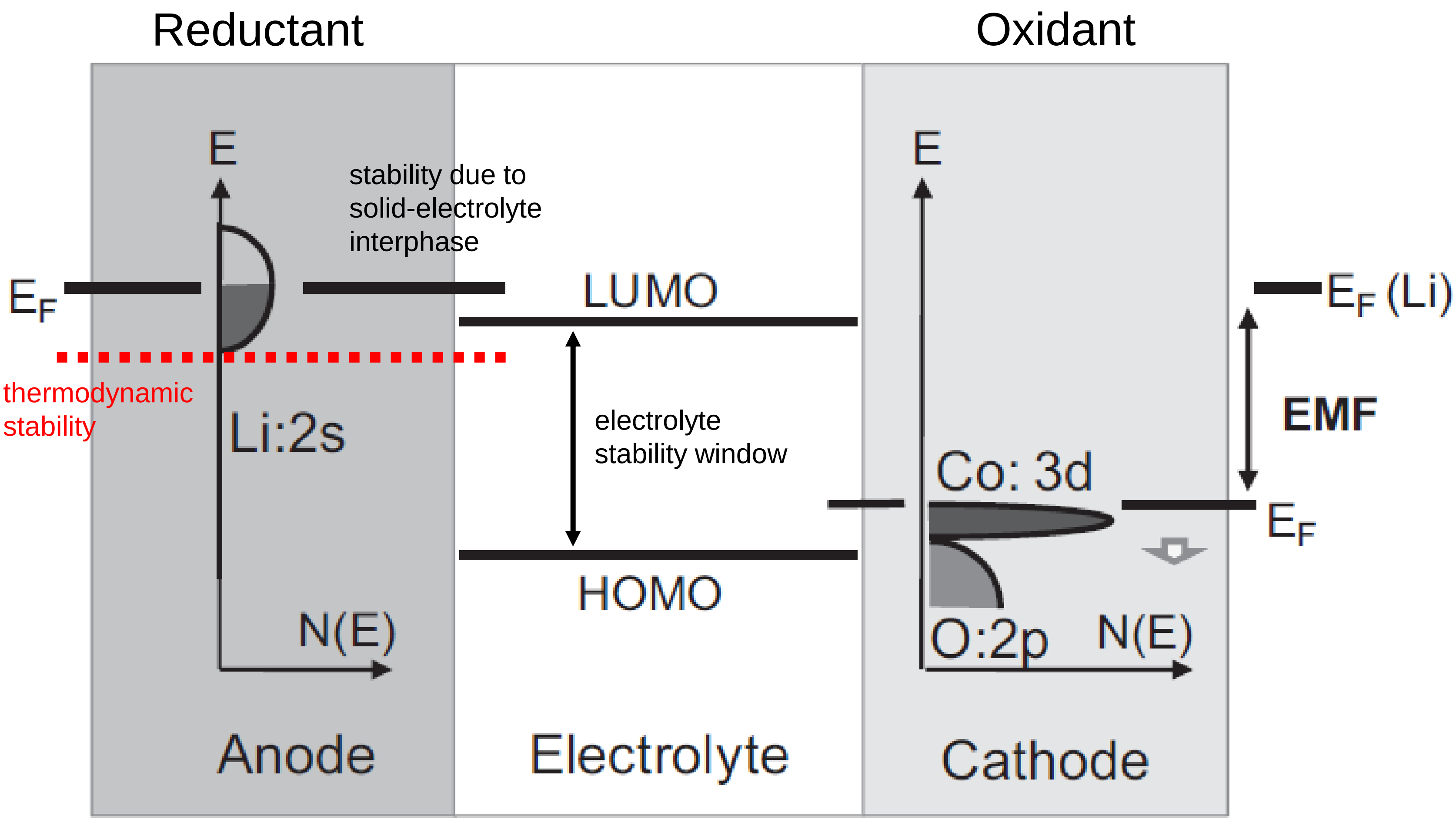
Li-ion battery energy diagram



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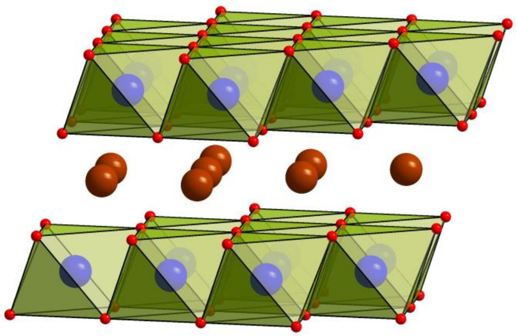
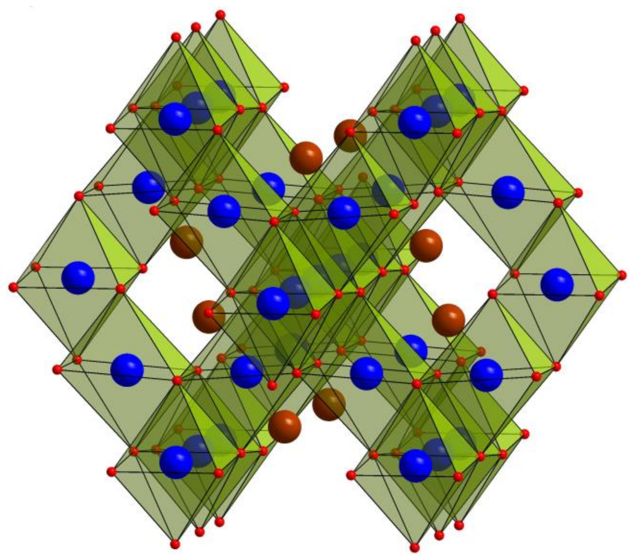
Cathode materials: crystal structures

Complex oxides



$LiCoO_2$
$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

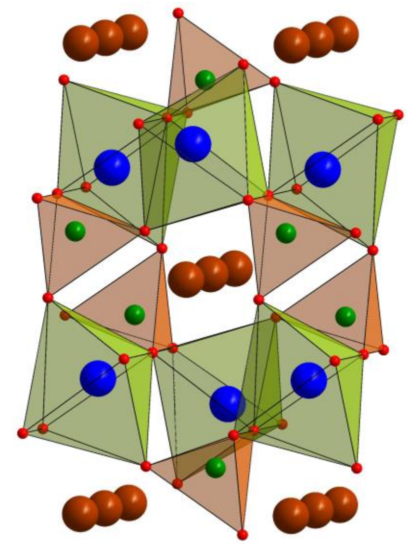
2D Li transport



$LiMn_2O_4$, $LiNi_{0.5}Mn_{1.5}O_4$

3D Li transport

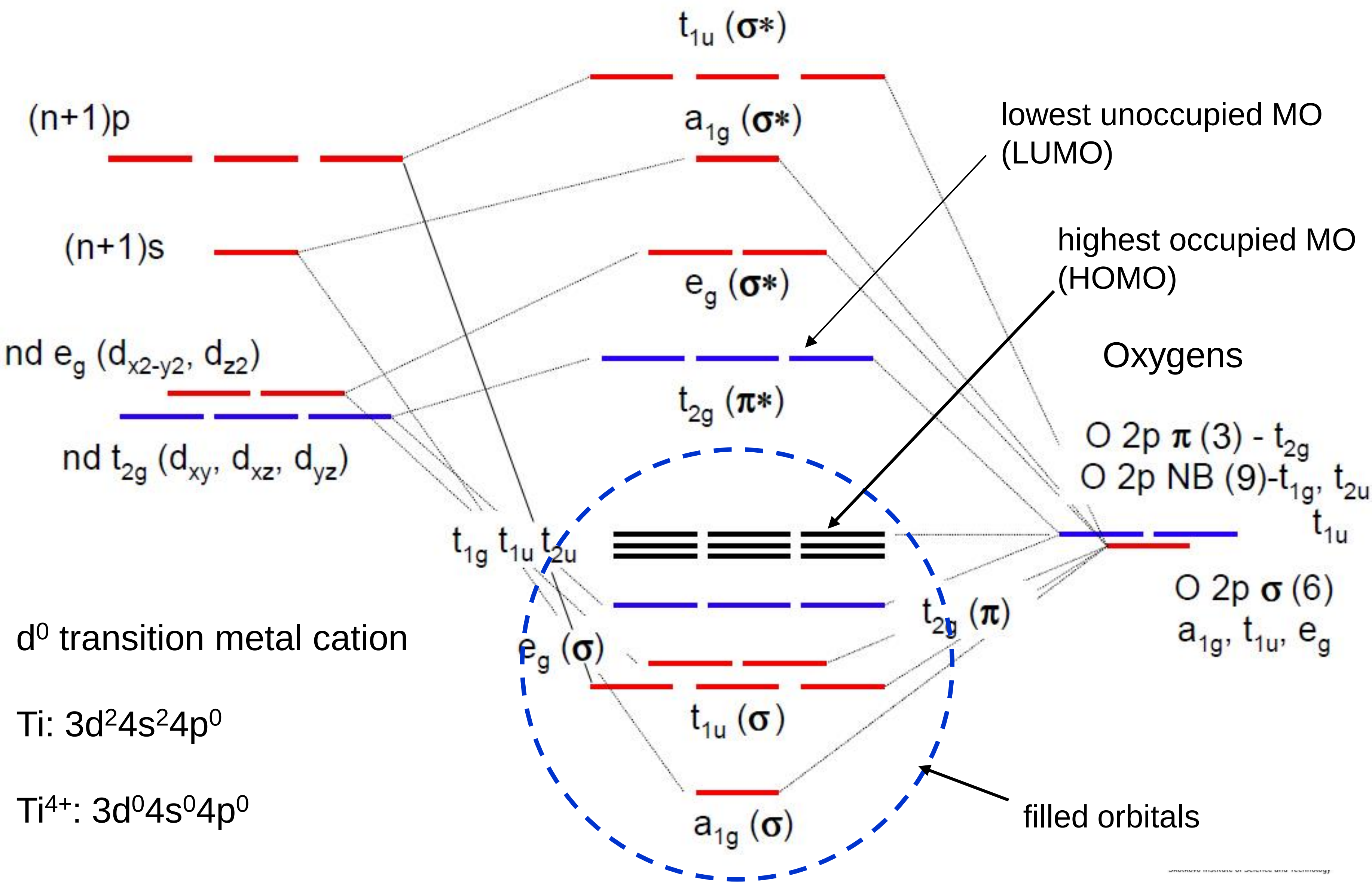
Polyanion compounds



$LiFePO_4$

1D Li transport

BO_6^{n-} octahedron: MO diagram

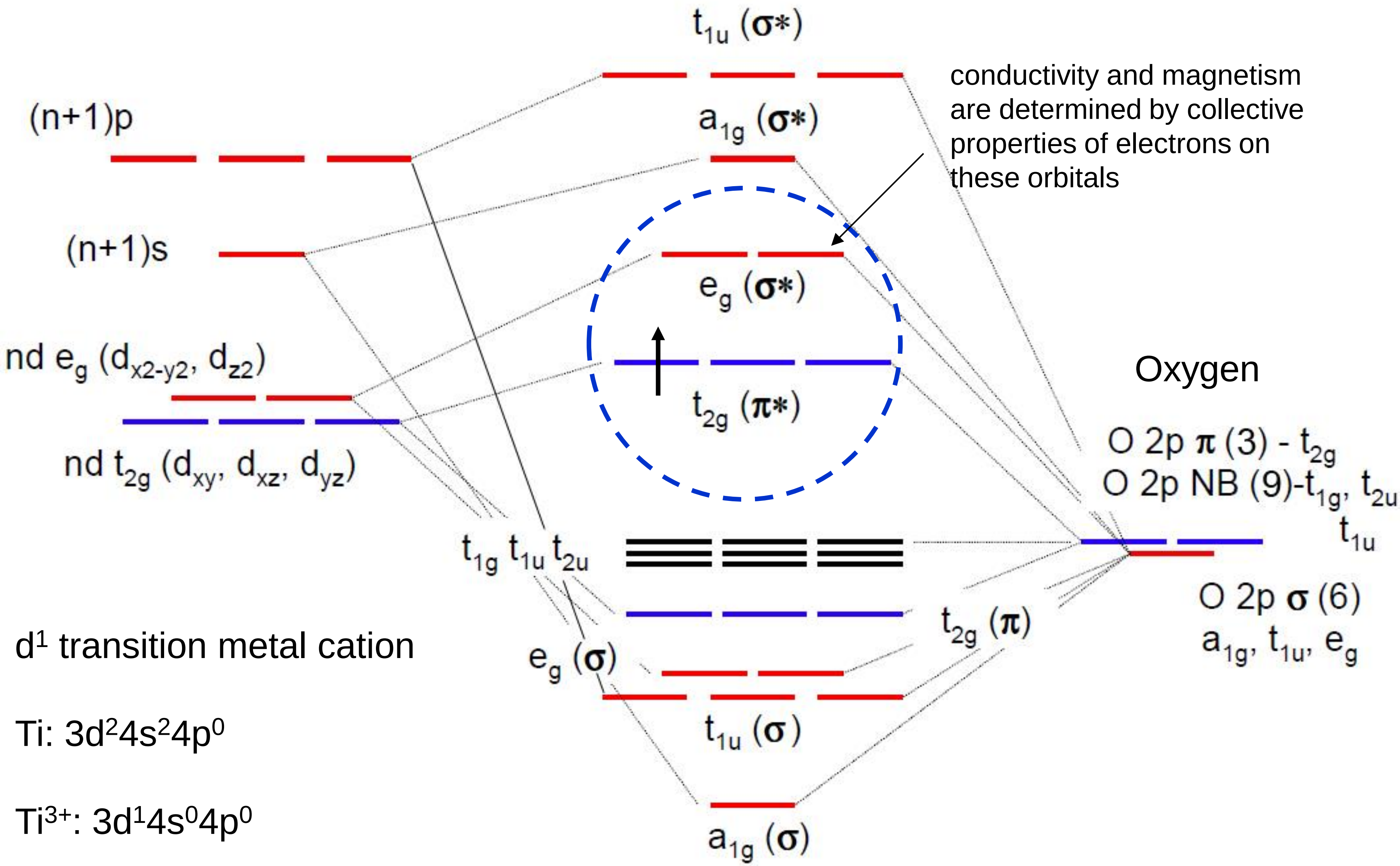


d^0 transition metal cation

Ti: $3d^2 4s^2 4p^0$

Ti^{4+}: $3d^0 4s^0 4p^0$

BO_6^{n-} octahedron: MO diagram

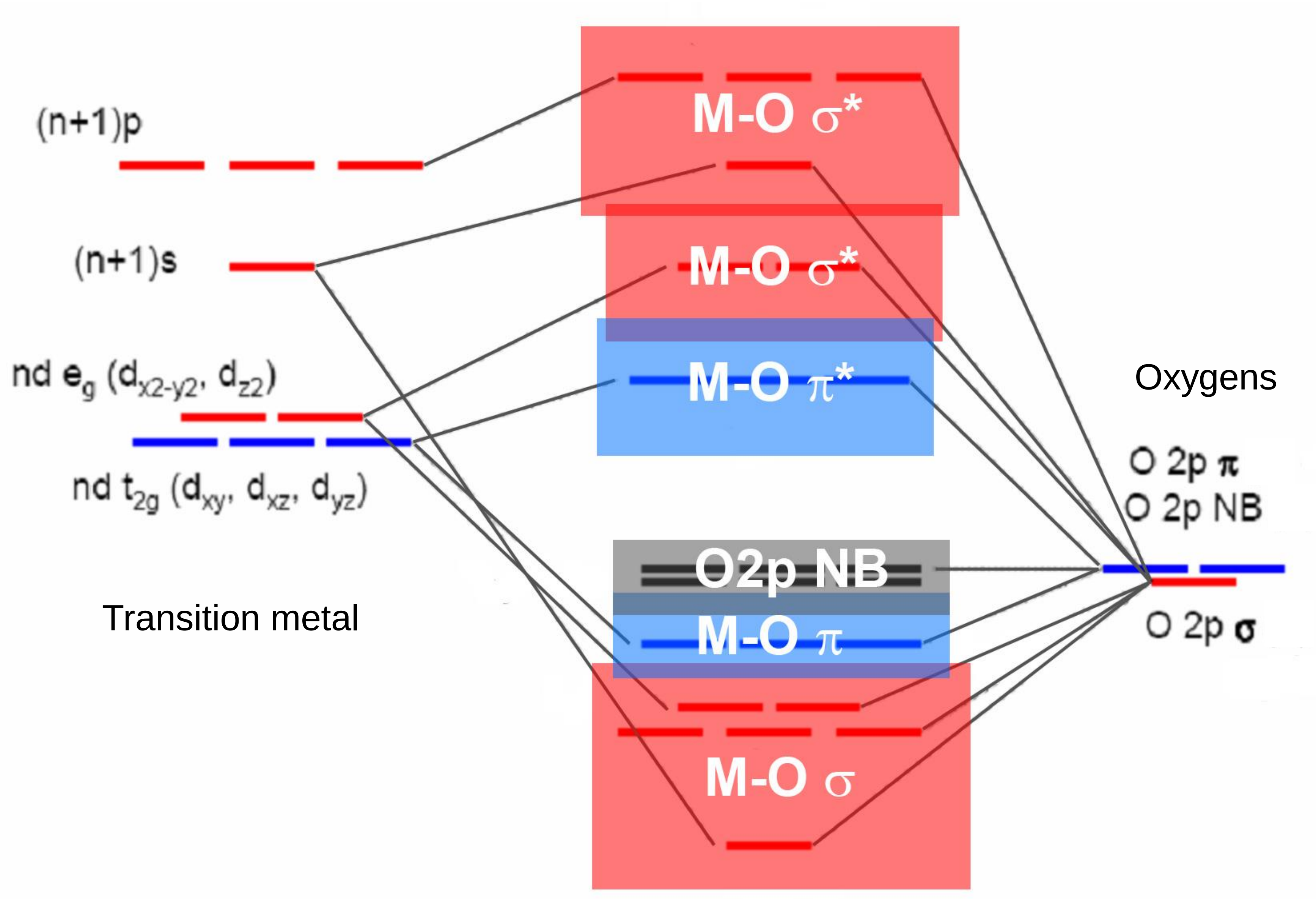


d^1 transition metal cation

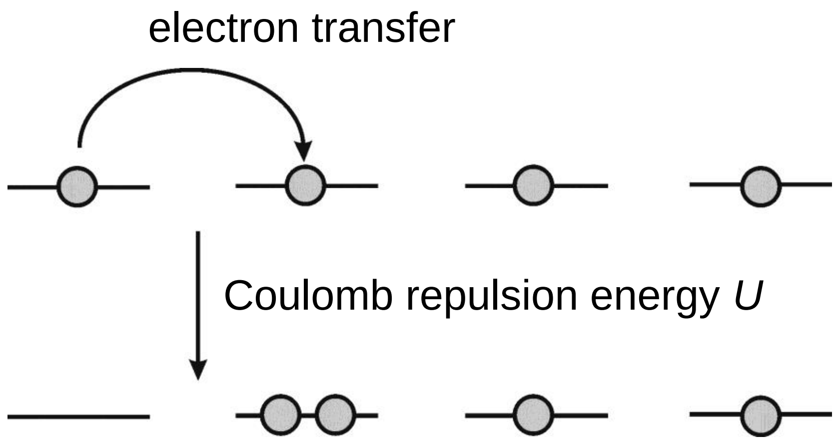
Ti: $3d^2 4s^2 4p^0$

Ti^{3+}: $3d^1 4s^0 4p^0$

Simplified band structure



Mott-Hubbard insulators

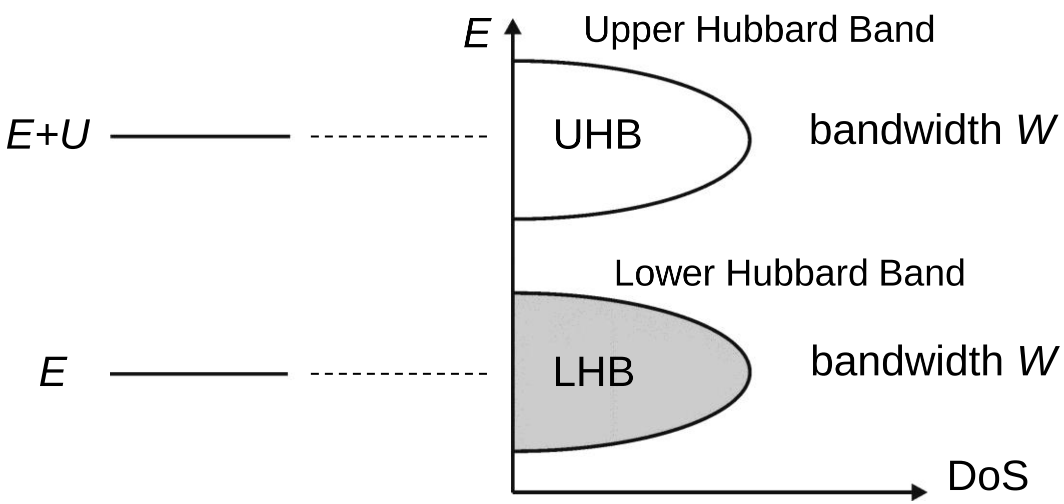


$Ni^{2+} + Ni^{2+} \rightarrow Ni^{3+} + Ni^{+}$

$d^8 + d^8 \rightarrow d^7 + d^9$

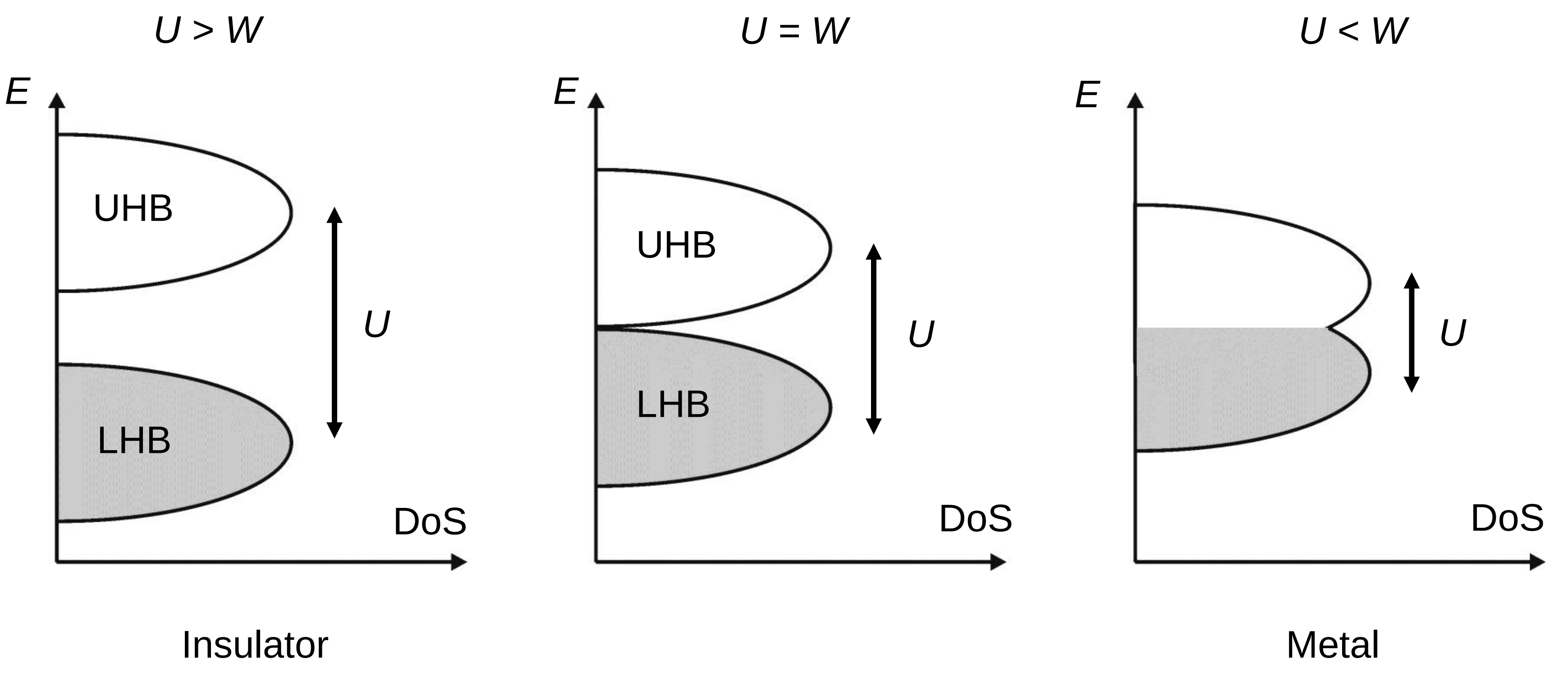
Two competing trends:

- the kinetic energy acts to delocalize the electrons, leading to metallic behaviour.
- the electron-electron Coulomb repulsion energy *U* wants to localize the electrons on sites.



Mott-Hubbard insulators

Mott-Hubbard scheme of the metal-to-insulator (MI) transition

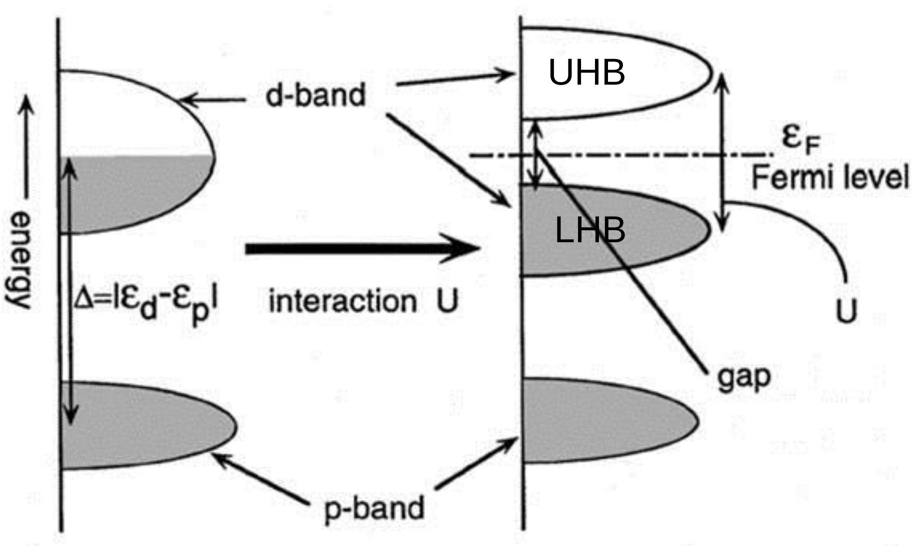


Mott-Hubbard vs charge transfer regimes

Three parameters: on-site Coulomb energy U, bandwidth W and d-band – p-band energy difference (charge transfer energy) Δ

$$U:\ d_i^n + d_j^n \rightarrow d_i^{n-1} + d_j^{n+1} \qquad \Delta:\ d_i^n \rightarrow d_i^{n+1} + L\ (L \text{ – ligand hole})$$

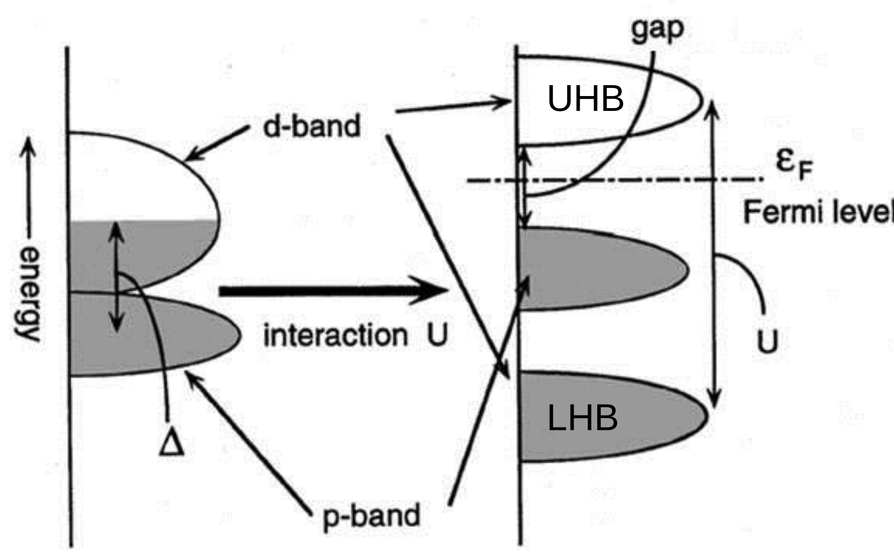
Mott-Hubbard regime



$U < \Delta$, gap $U - W$

early 3d metals: Ti-O, V-O

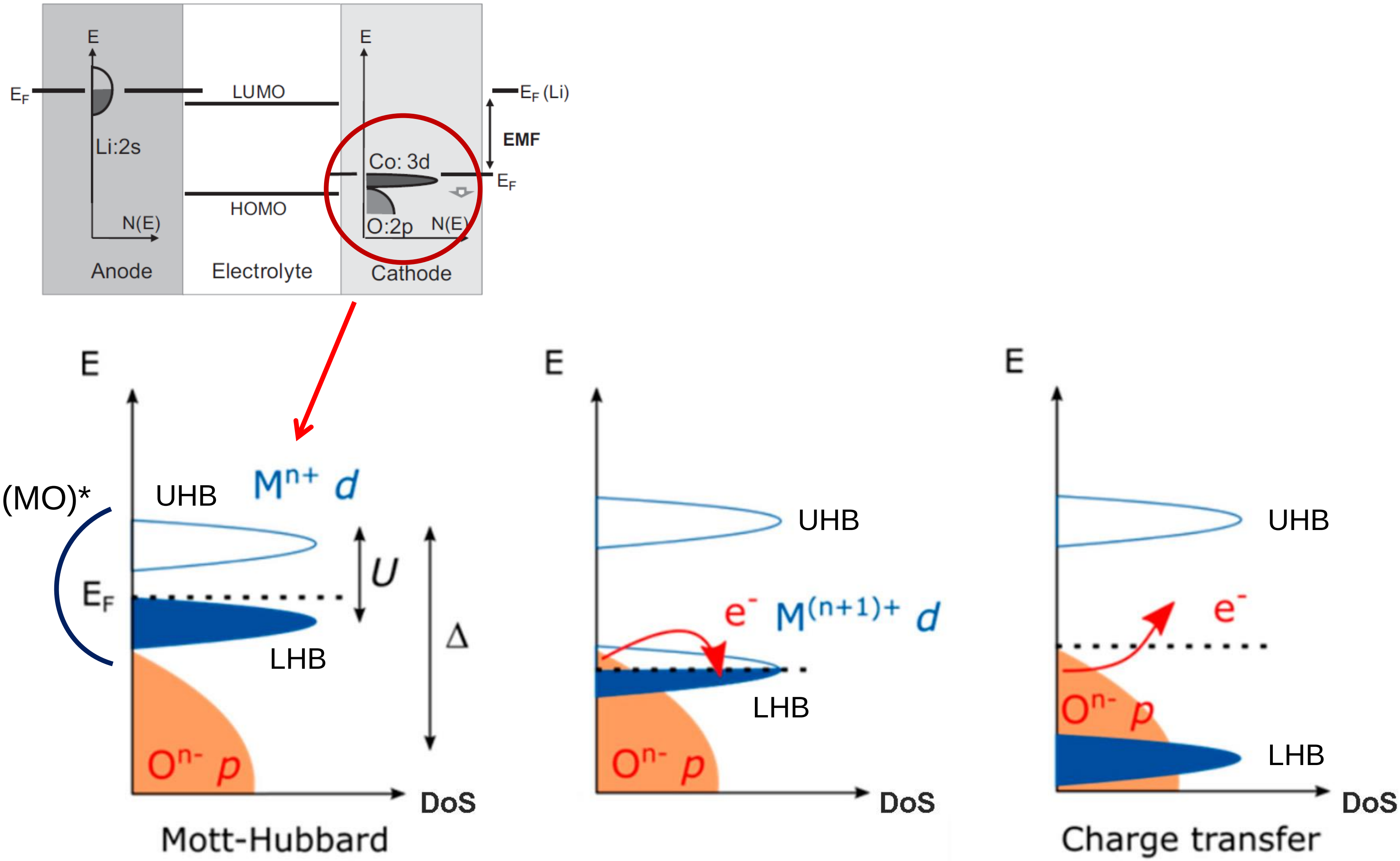
Charge transfer regime



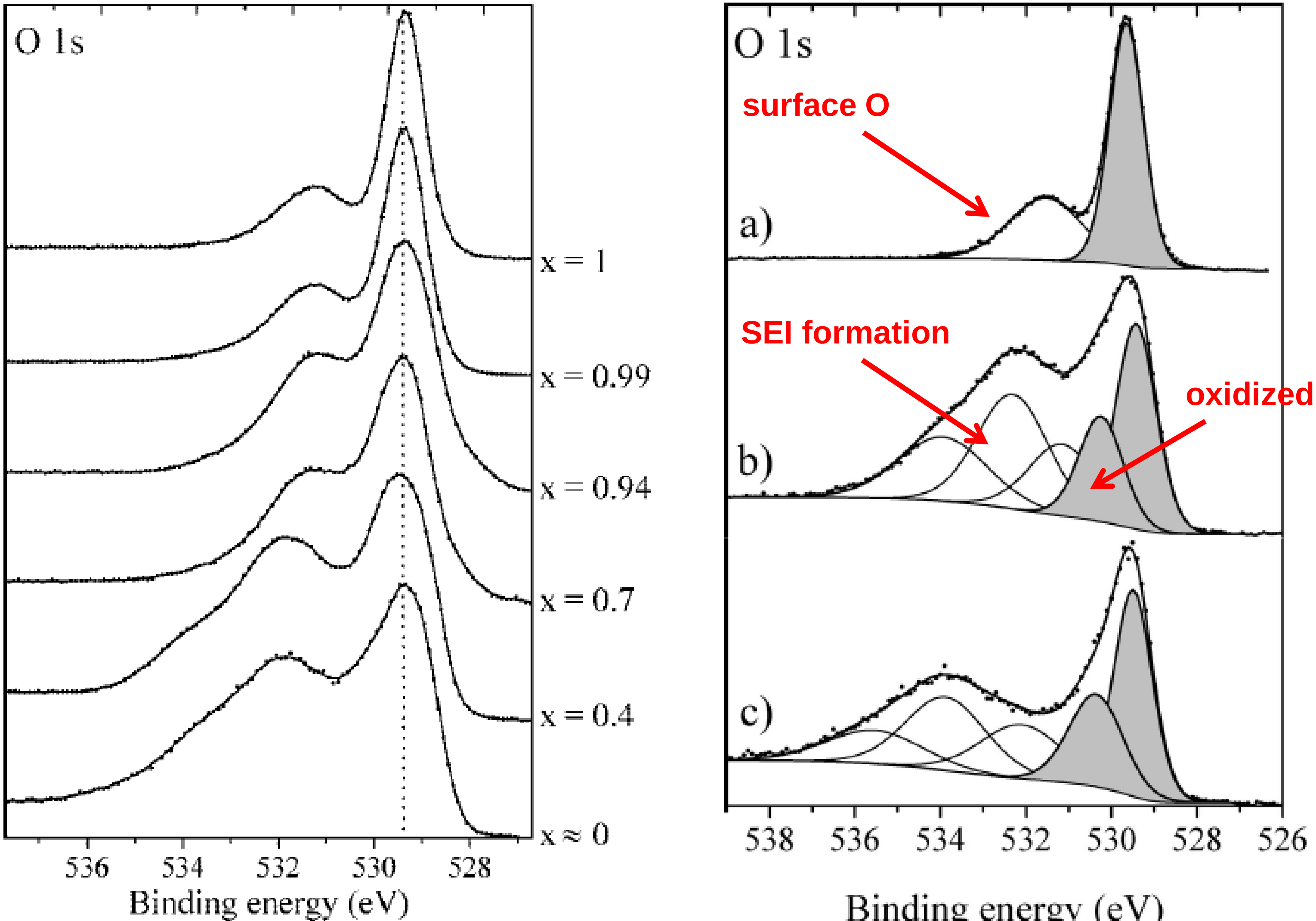
$U > \Delta$, gap $\Delta - W$

latest 3d metals: Ni-O, Cu-O

Mott-Hubbard vs charge transfer regimes



Lattice oxygen oxidation



$LiCoO_2$

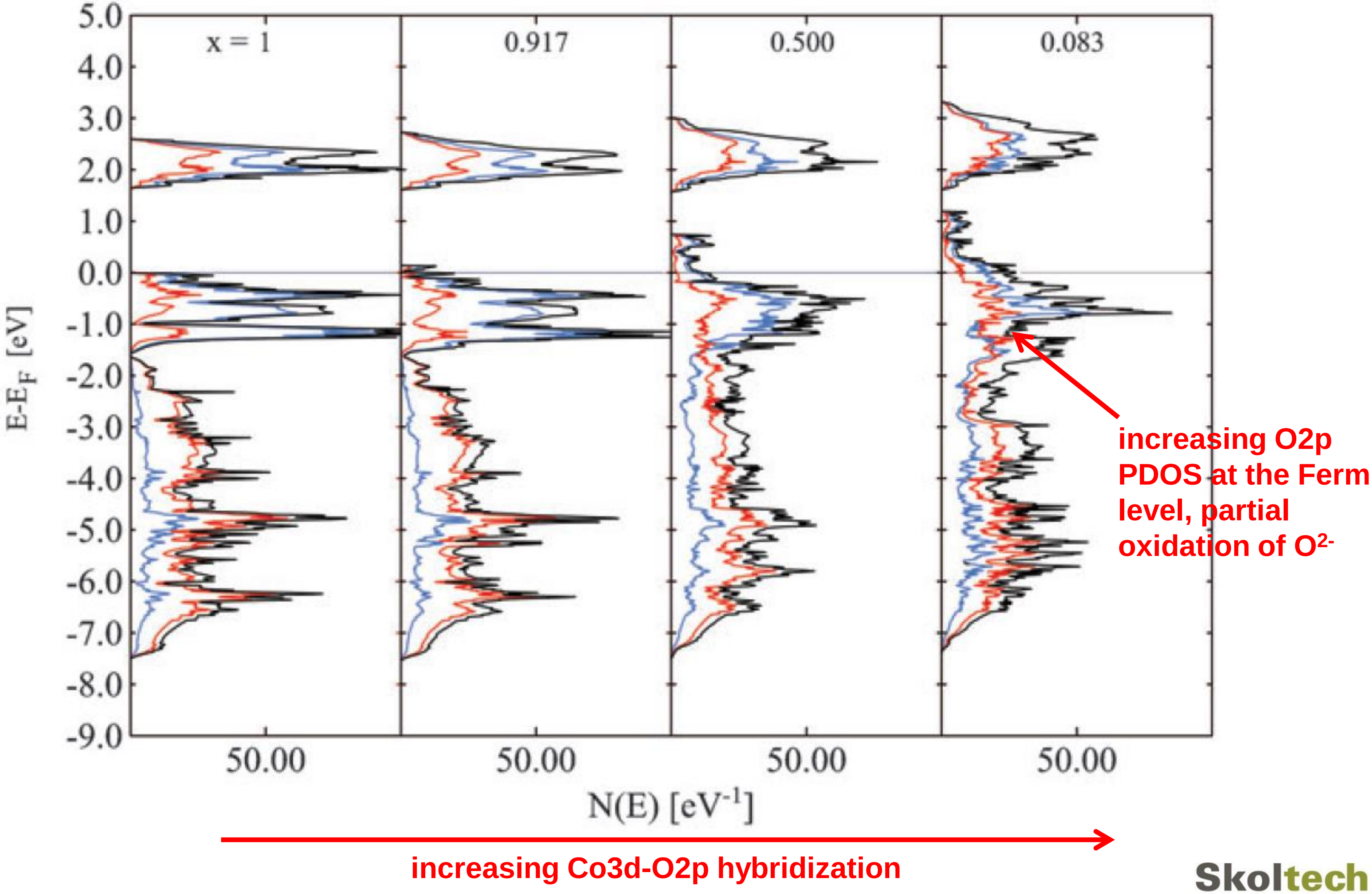
Li_0CoO_2

Li_xCoO_2 XPS O1s

L.Daheron et al., Chem.Mater., 20, 583, 2008

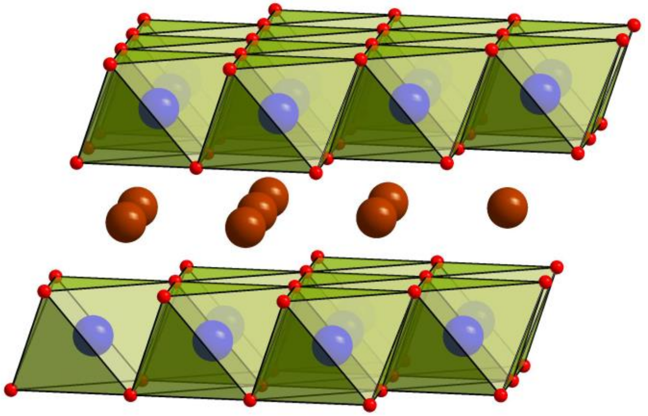
Lattice oxygen oxidation

DOS and PDOS for Li_xCoO_2: blue – Co, red - O

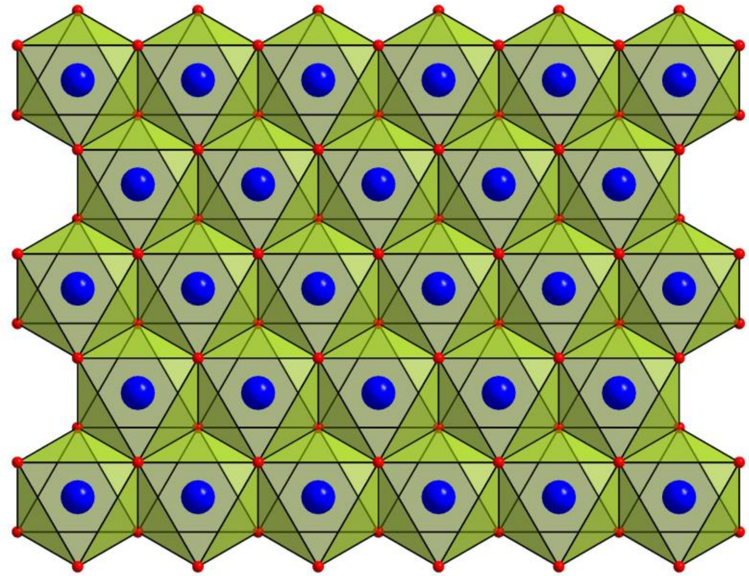


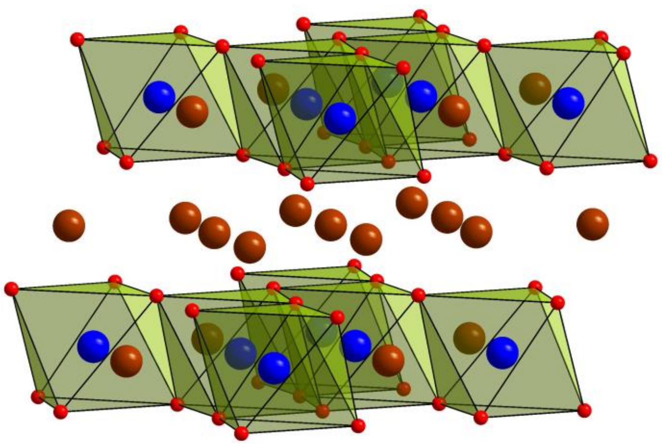
S.Laubach et al., Phys.Chem.Chem.Phys.,2009, 11, 3278

High capacity layered cathodes

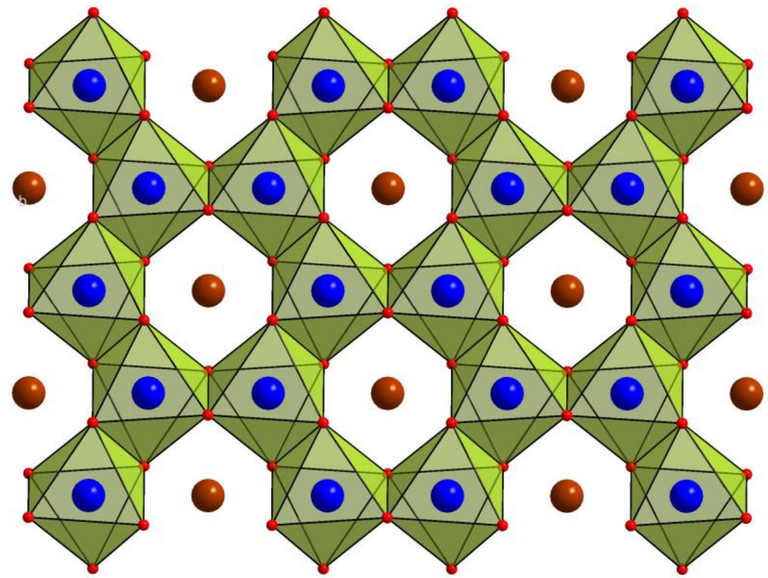


$LiCoO_2$
$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$



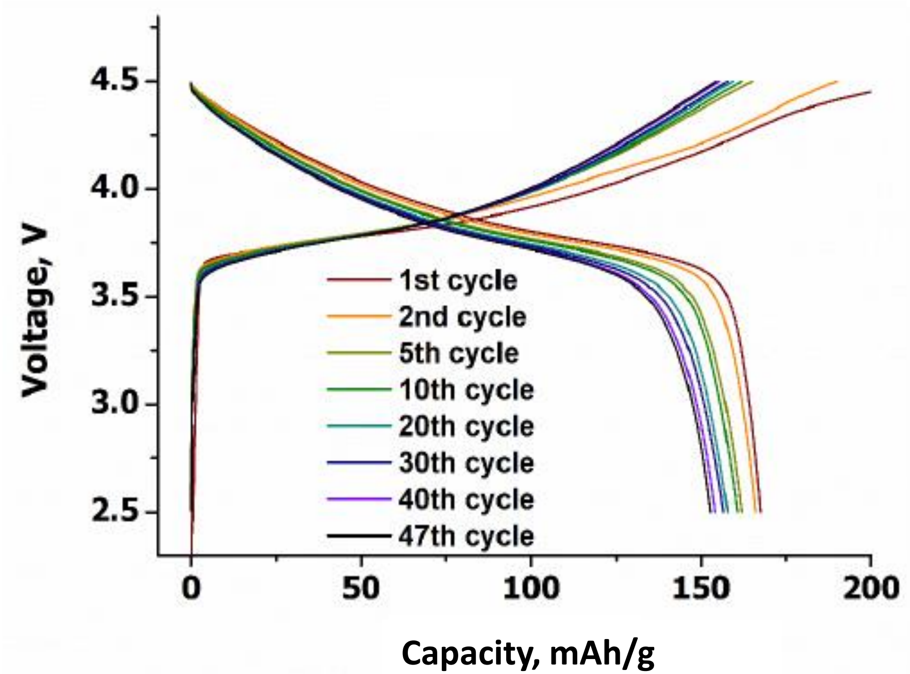


$Li_{1+y}(Ni,Mn,Co)_{1-y}O_2$

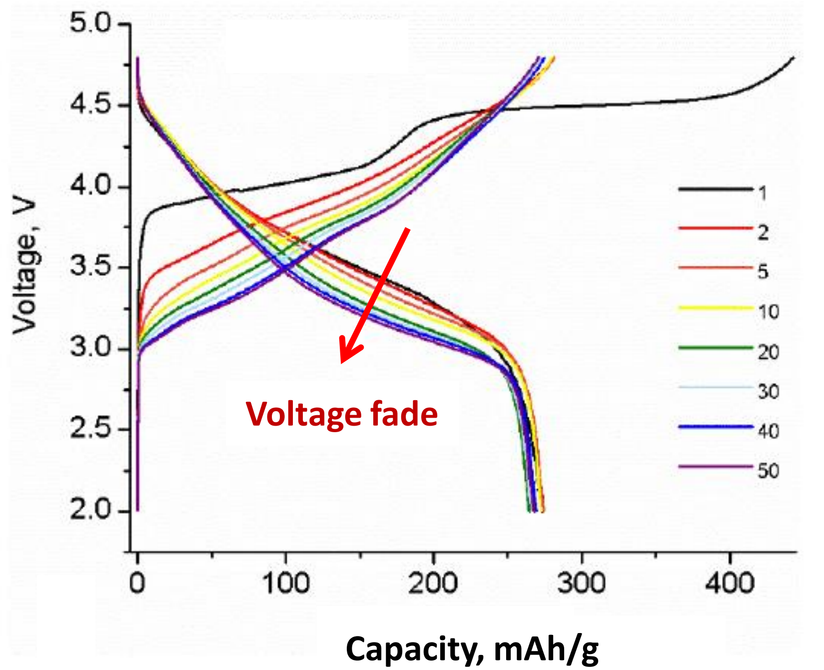


High capacity layered cathodes

$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$



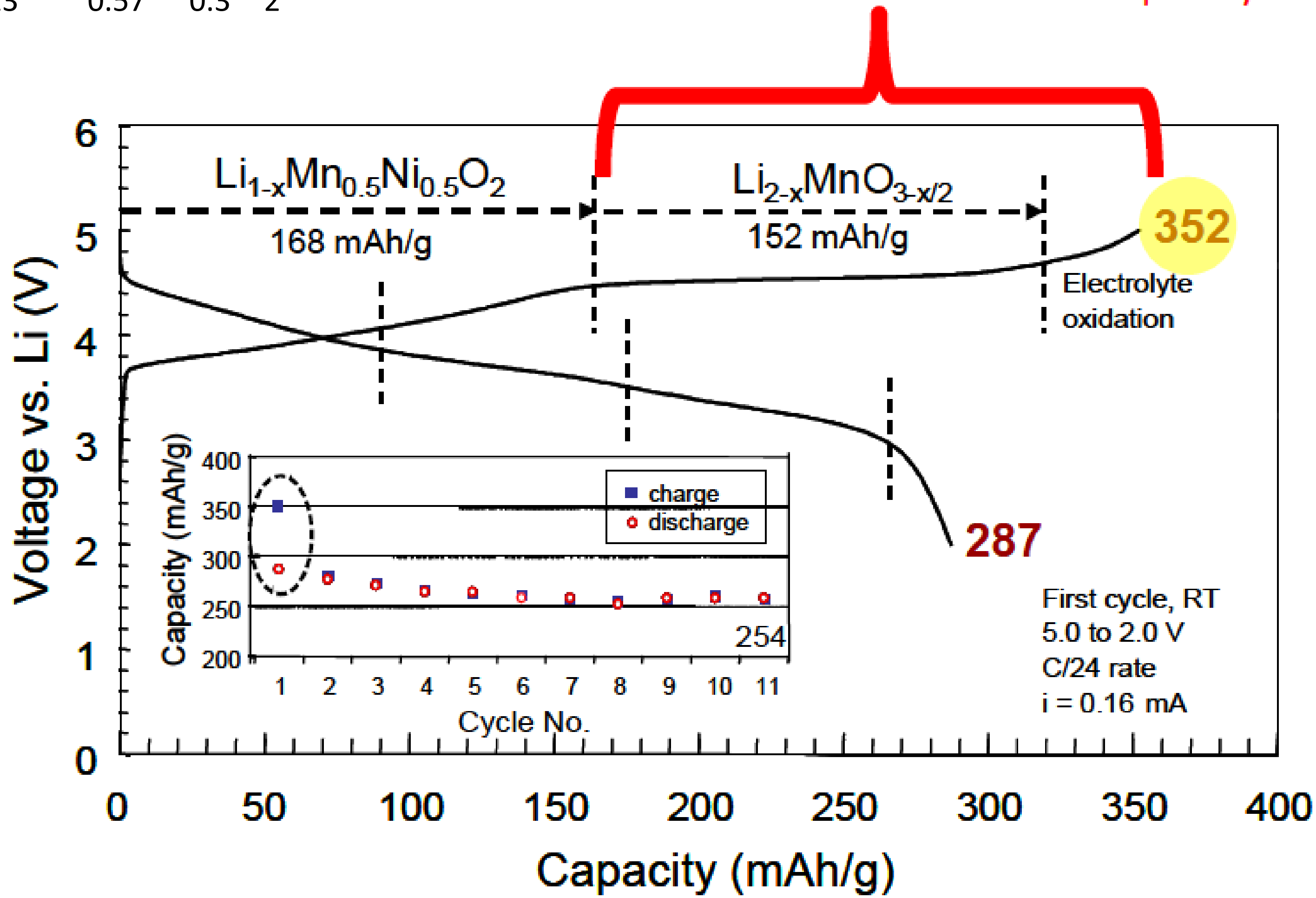
$Li_{1.2}Ni_{0.17}Mn_{0.56}Co_{0.17}O_2$



High capacity layered cathodes: excess capacity

$Li_{1.13}Mn_{0.57}Ni_{0.3}O_2$

What is the cause of the excess capacity?



A.Burrell et al., US DOE Vehicle Technologies Program, Project ES161, 2013

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High capacity layered cathodes

$Li_{4/3-x}Ni^{2+}_{x}Mn^{4+}_{2/3-x}Co^{3+}_{x}O_2$

$Ni^{2+} \rightarrow Ni^{3+}, Ni^{4+}$

$Co^{3+} \rightarrow Co^{4+}$

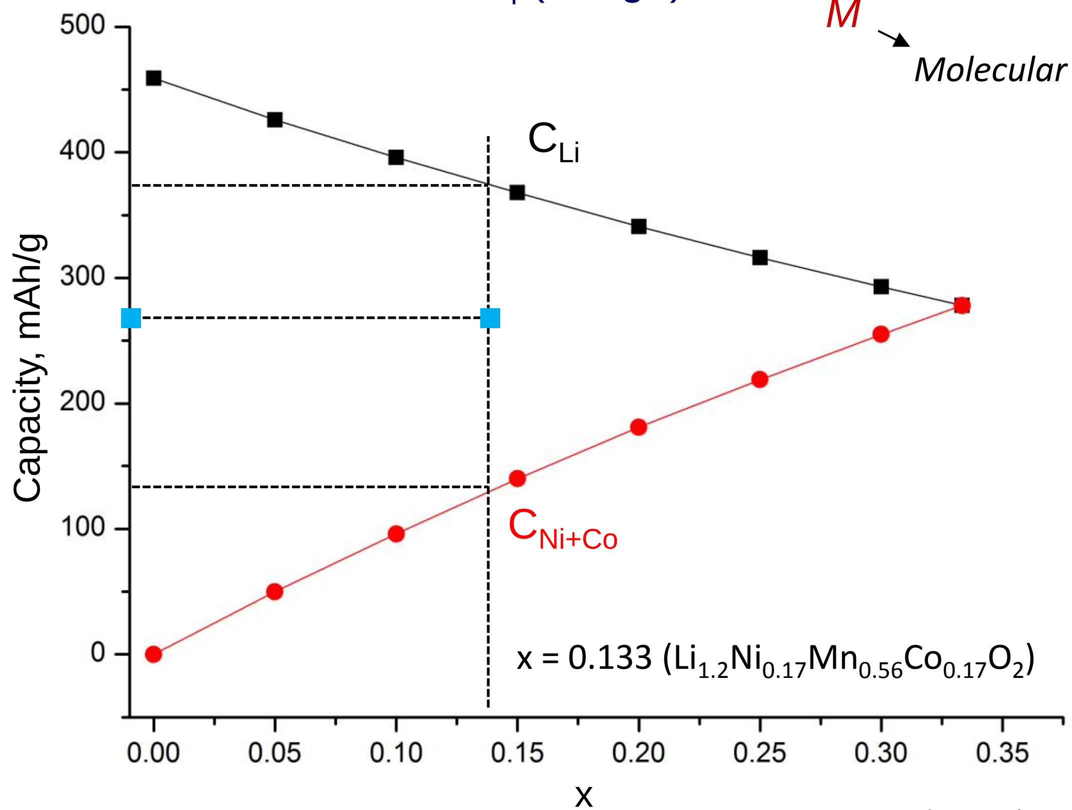
$Mn^{4+} \not\rightarrow Mn^{5+}$

Theoretical capacity:

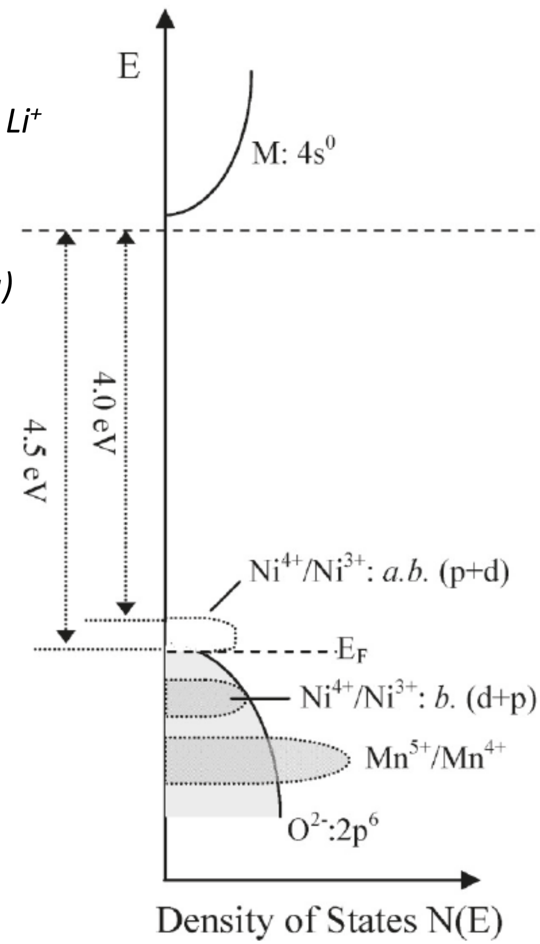
$$C_T\ (\mathrm{A\ h\ g^{-1}}) = \frac{26.8 \times \Delta n}{M}$$

number of e⁻ or Li⁺ (Δn)

Molecular weight (g) (M)



Mn^{4+}/Mn^{5+} redox couple is inaccessible



Goodenough&Kim, Chem.Mater., 22, 587, 2010

Lattice oxygen oxidation

Identification of cathode materials for lithium batteries guided by first-principles calculations

G. Ceder, Y.-M. Chiang, D. R. Sadoway, M. K. Aydinol, Y.-I. Jang & B. Huang

The replacement with non-transition metals is driven by the realization that oxygen, rather than transition-metal ions, function as the electron acceptor upon insertion of Li.

NATURE | VOL 392 | 16 APRIL 1998

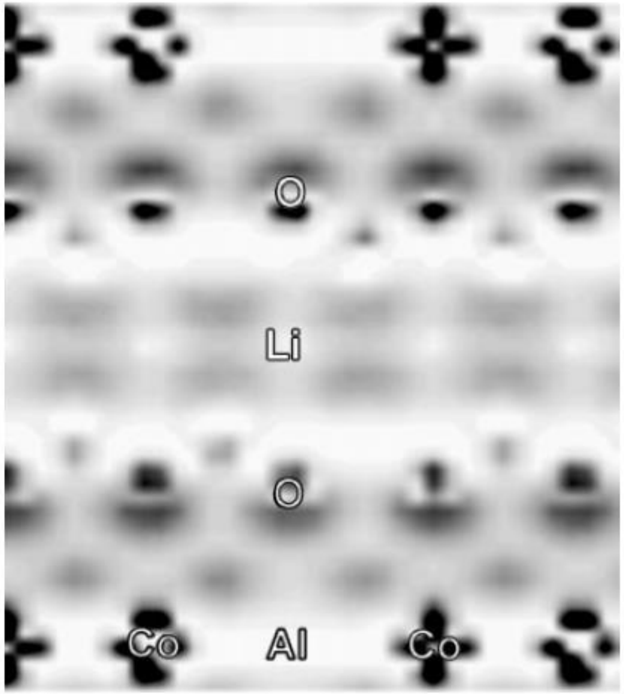


Figure 1 Positive part of the electron density difference between $Li(Al_{0.33}Co_{0.67})O_2$ and $(Al_{0.33}Co_{0.67})O_2$ in a plane perpendicular to the direction of layering in the structure. Darker indicates larger electron density.

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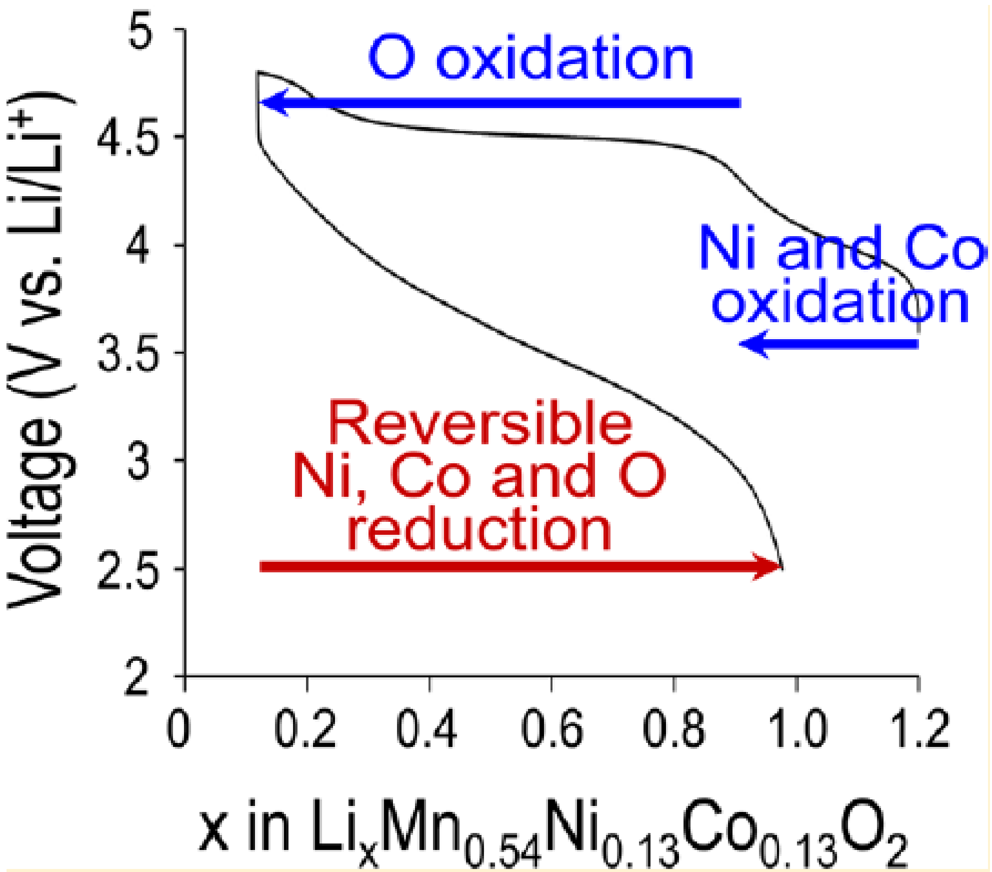
Lattice oxygen oxidation



XANES and EXAFS on Ni,Co and Mn-K edges

Two redox processes:

Ni^{2+}, Co^{3+} ↔ Ni^{4+}, Co^{4+}

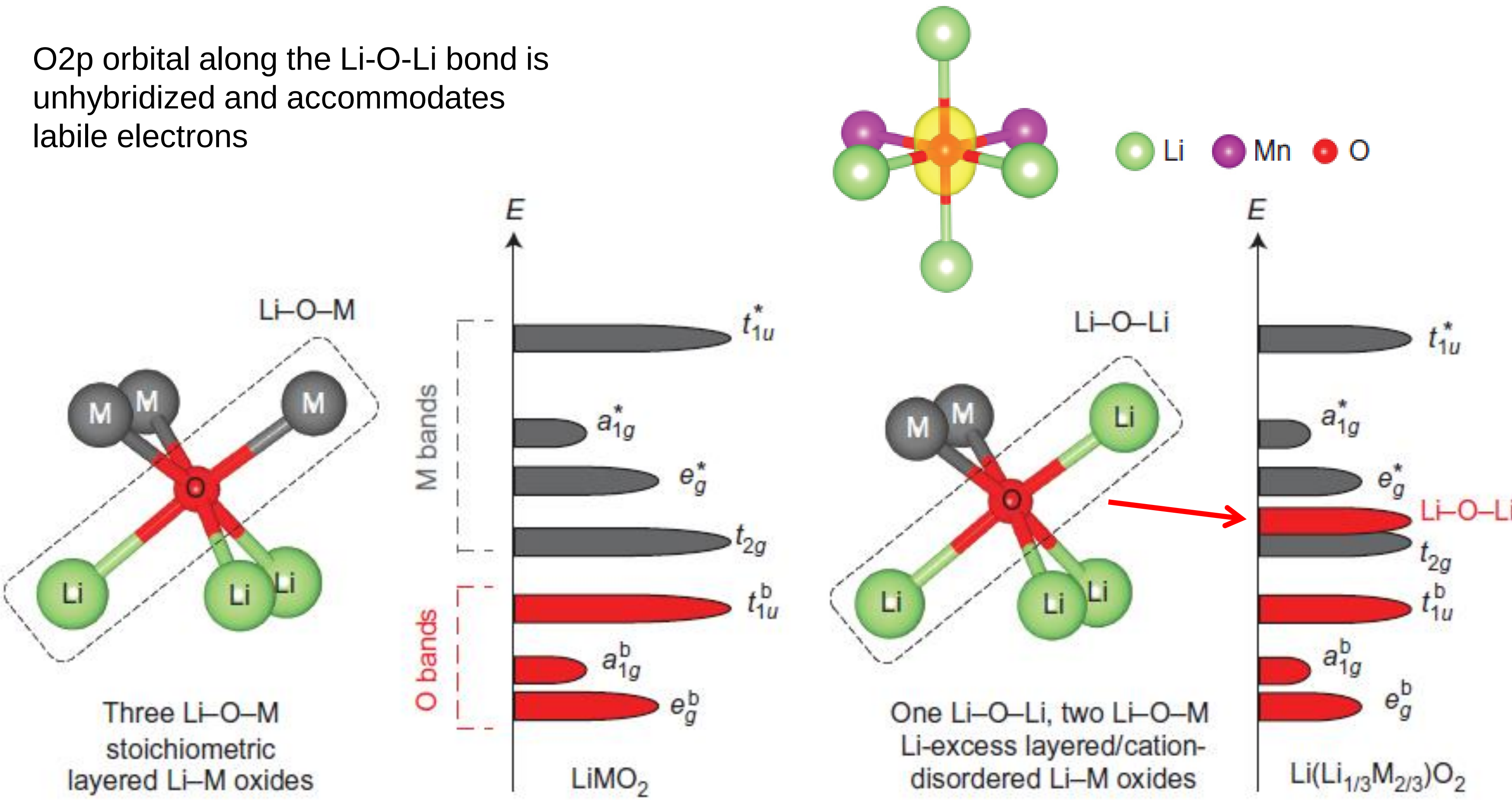
(Mn^{4+} is neither oxidized nor reduced)

Reversible oxygen oxidation

H.Koga et al., J. Phys. Chem. C, 118, 5700 (2014)

Mechanism: orphaned Li-O-Li O2p orbitals

O2p orbital along the Li-O-Li bond is unhybridized and accommodates labile electrons



D.H Seo et al., Nature Chem., 8, 692 (2016)

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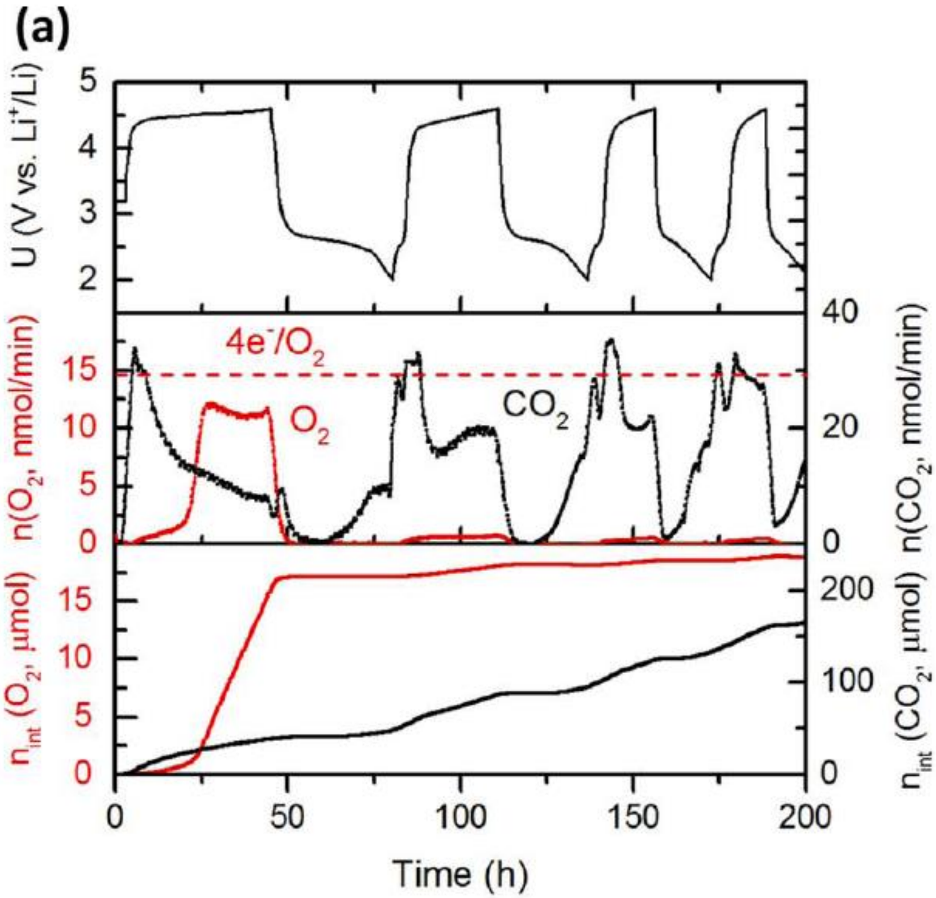
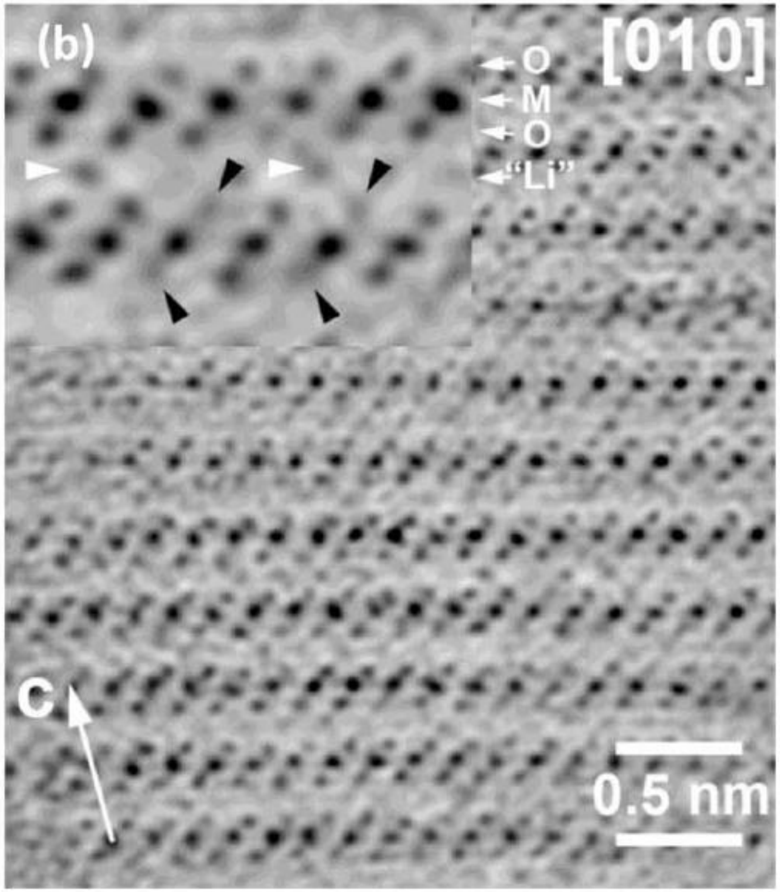
Irreversible oxygen oxidation

partially charged $Li_{3.27}Fe(III)_{0.56}TeO_{5.5}$





Irreversible capacity solely due to the oxygen evolution

McCalla , Abakumov, Rousse, Tarascon et al., JES, 162, A1341 (2015)

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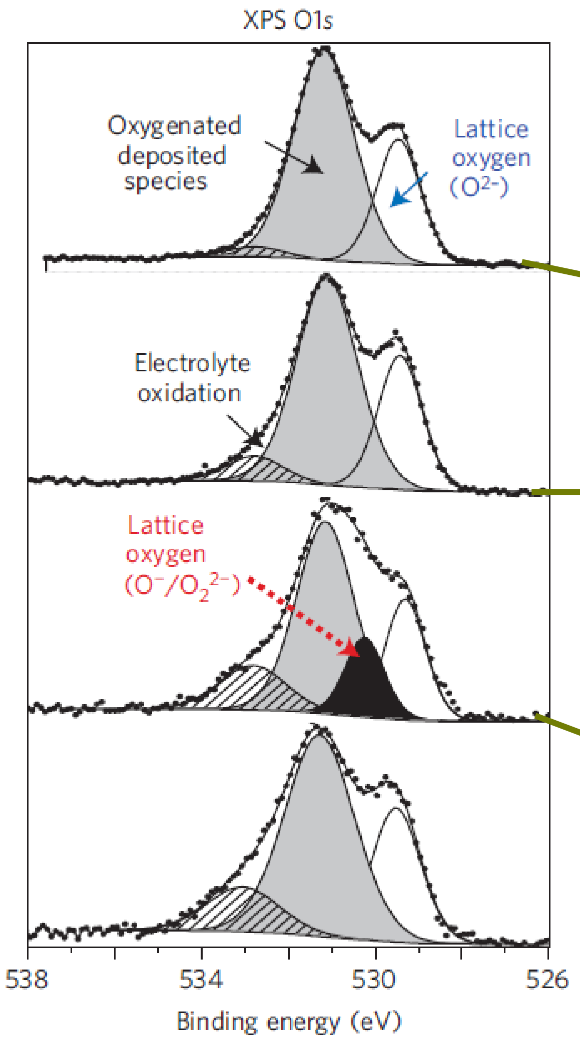
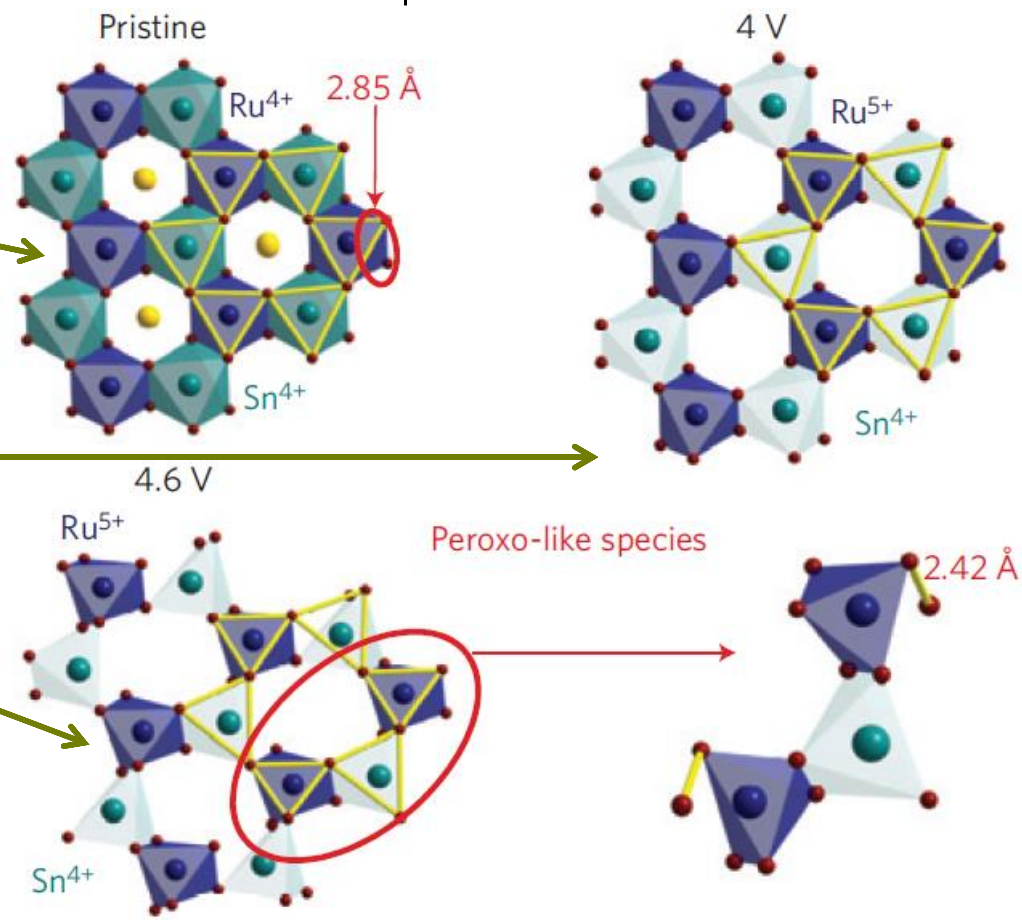
Formation of O_2^{n-}

$Li_2Ru_{0.5}Sn_{0.5}O_3$



DFT-optimized structures



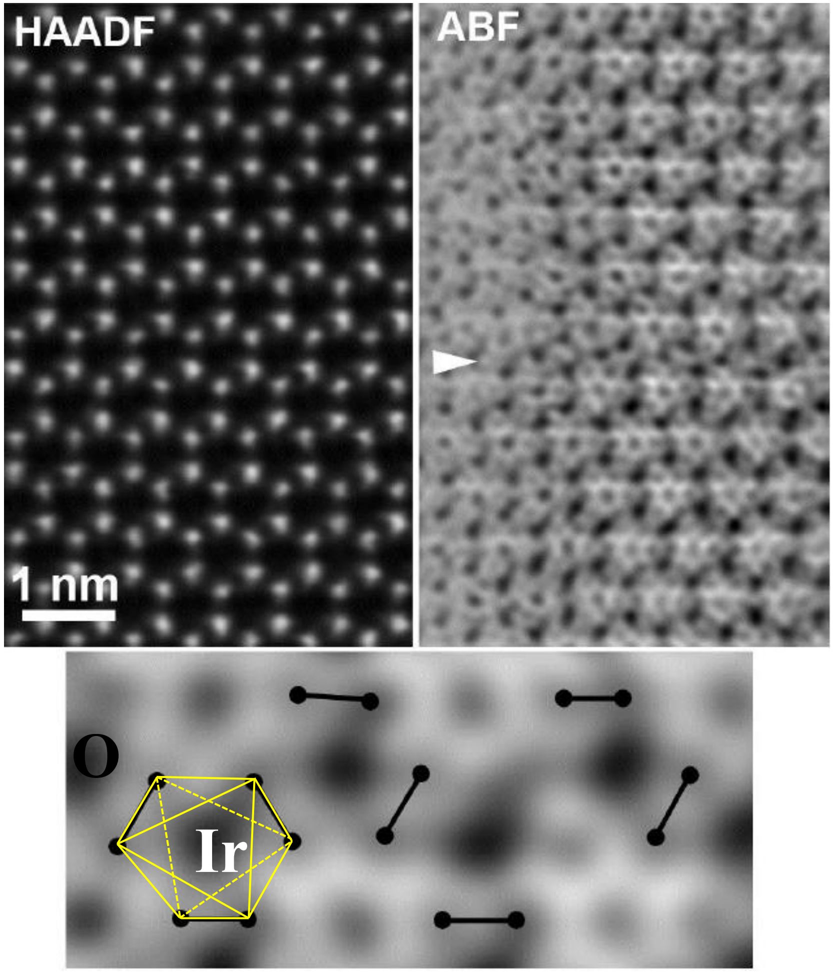
Two redox processes:

$Ru^{4+} \leftrightarrow Ru^{5+}$

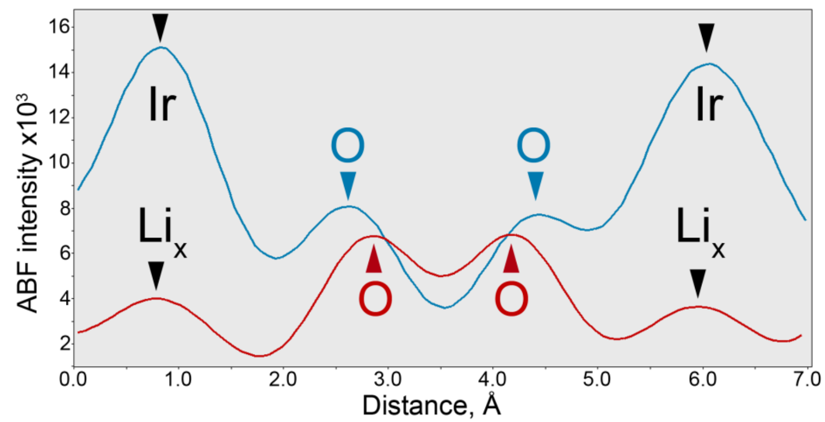
$2O^{2-} \leftrightarrow O_2^{n-}$ $(n \leq 3)$

M.Sathiya et al., Nature Mater., 118, 5700 (2014)

Formation of O_2^{n-}: layered α-Li_2IrO_3



$Li_2IrO_3 \rightarrow Li_{0.5}IrO_3$: oxidation of $Ir^{4+} \rightarrow Ir^{5+}$ and $O^{2-} \rightarrow O_2^{n-}$ (n<4), shortening the O-O distances



Projected O-O distances from ABF-STEM:

short: 1.56(1)Å long: 1.83(1) Å

Projected O-O distances from DFT ($Li_{0.5}IrO_3$):

short: 1.48Å long: 1.85Å

HAADF- and ABF-STEM for $Li_{0.5}IrO_3$ charged to 4.5V

McCalla, Abakumov, Saubanère, Rousse, Tarascon, Science, 350, 1516 (2015)

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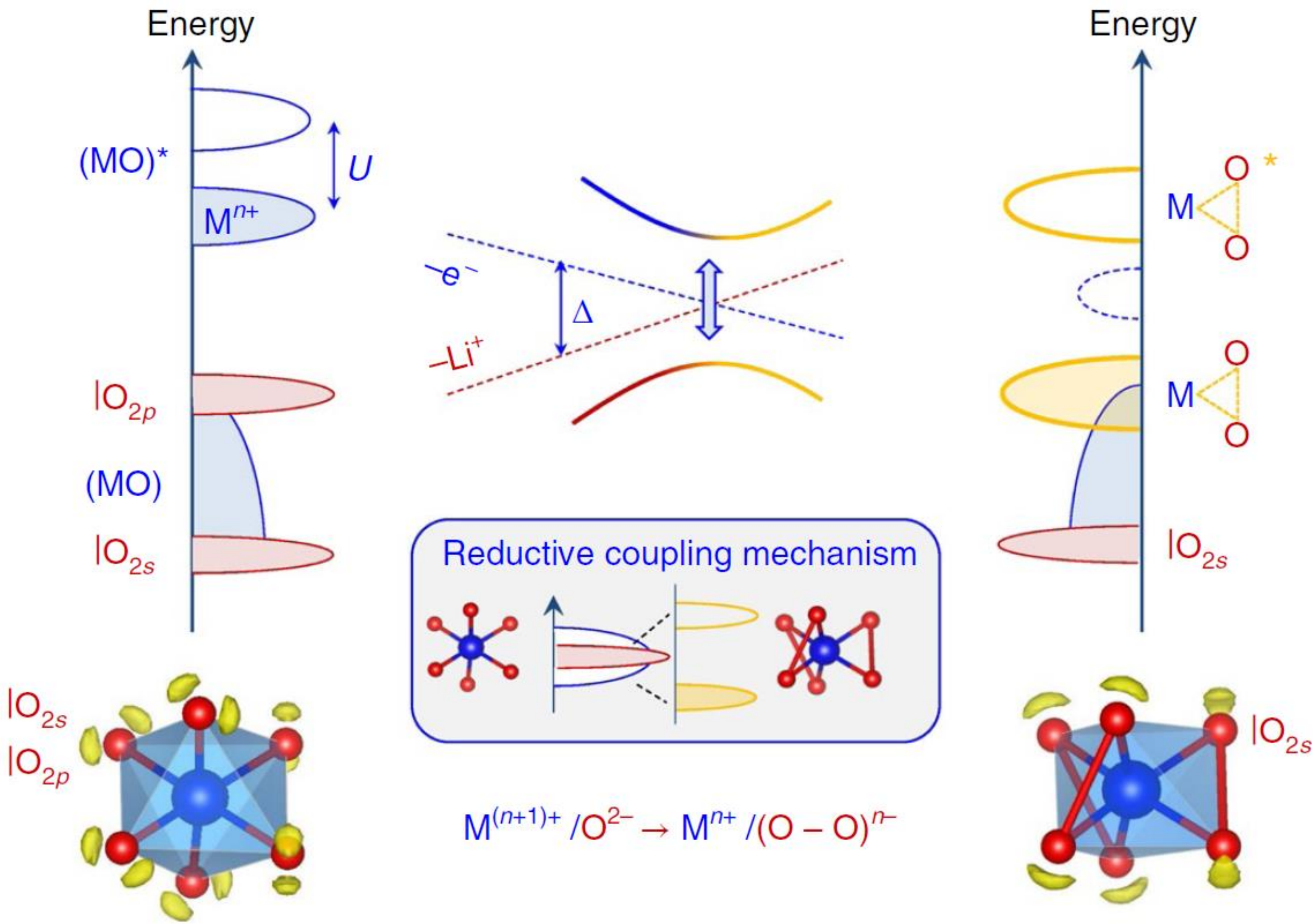
Mechanism: reductive coupling



M. Ben Yahia et al, Nature Mater. 18, 496 (2019)

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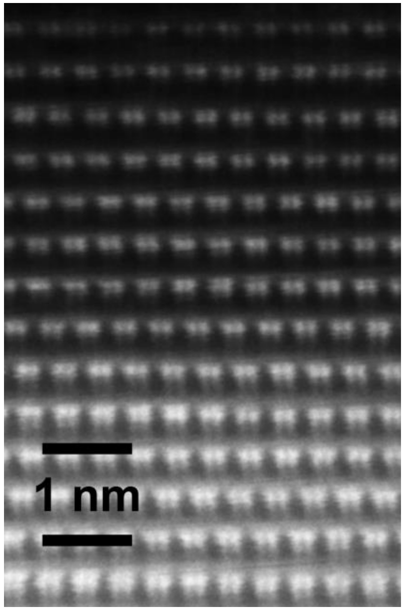
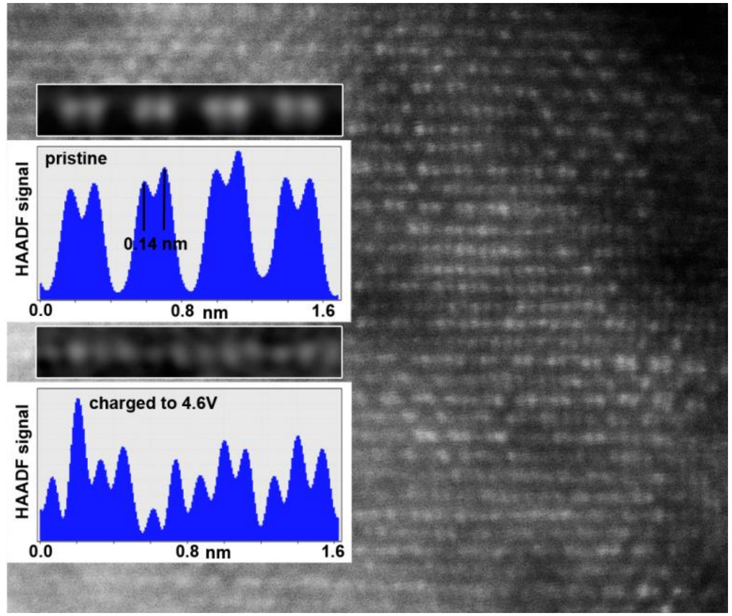
Formation of O_2^{n-} and cation migration

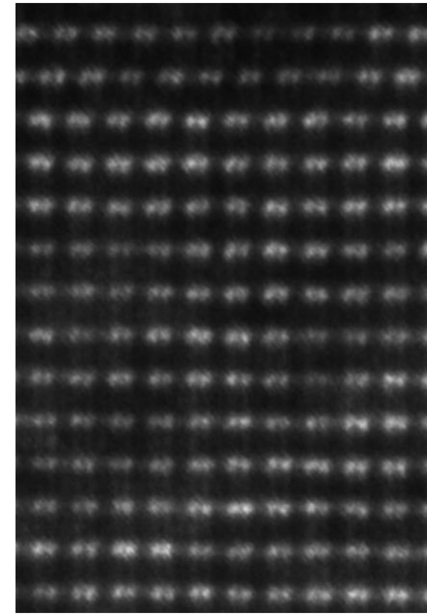
Pristine



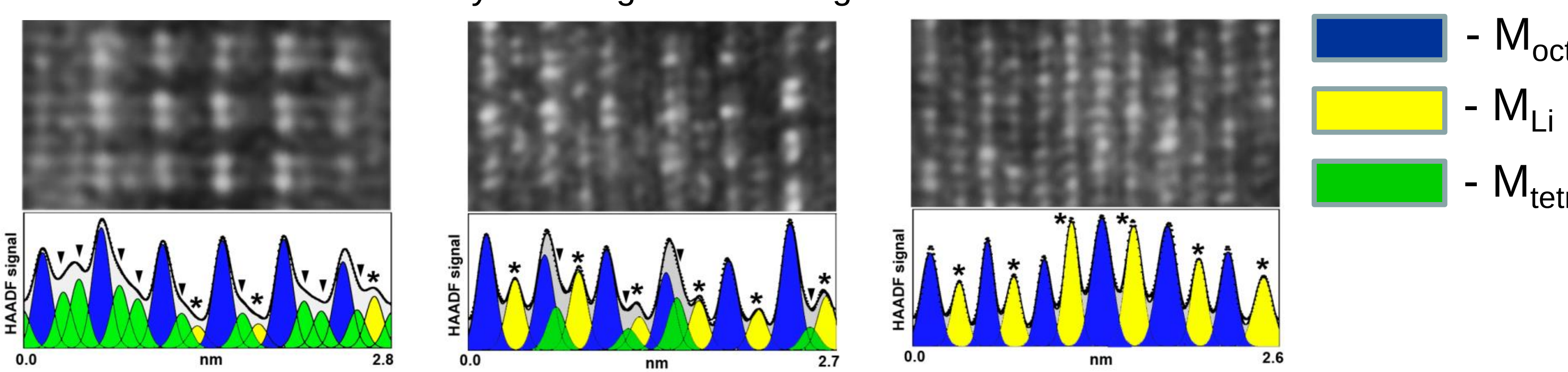
Charged to 4.6V



Discharged to 2V



Structurally inhomogeneous charged state



Mariyappan, Abakumov, Foix, Rousse, Ramesha, Saubanère, Doublet, Vezin, Laisa, Prakash, Gonbeau, Van Tendeloo, Tarascon, *Nature Mater.*, 14, 230 (2015)

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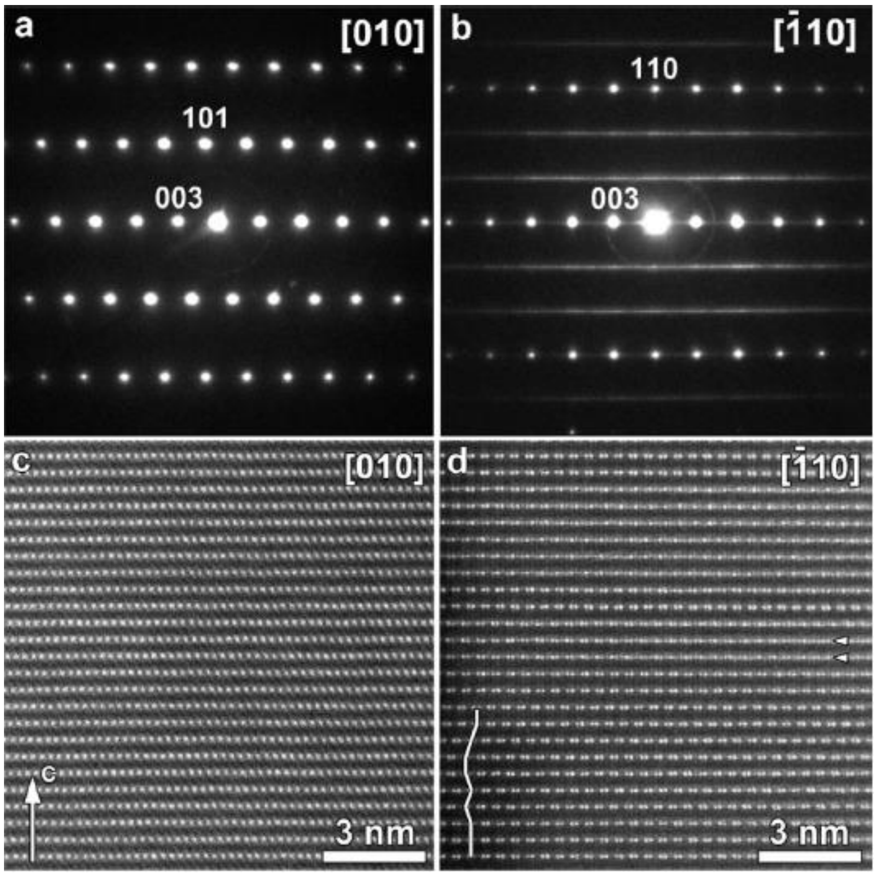
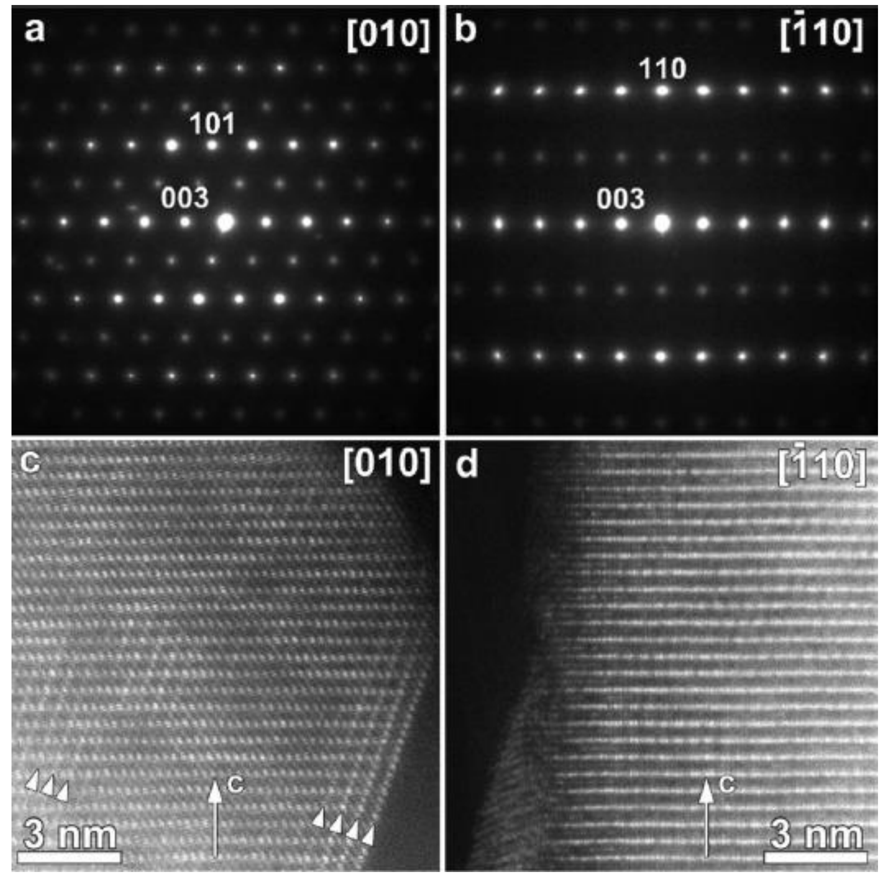
Formation of O_2^{n-} and cation migration

pristine $Li_{1+y}(Ni,Mn,Co)_{1-y}O_2$



$Li_{1+y}(Ni,Mn,Co)_{1-y}O_2$ after 50 cycles



Pimenta, Sathiya, Batuk, Abakumov, Giaume, Cassaignon, Larcher, Tarascon, *Chem. Mater.* 29, 9923 (2017).

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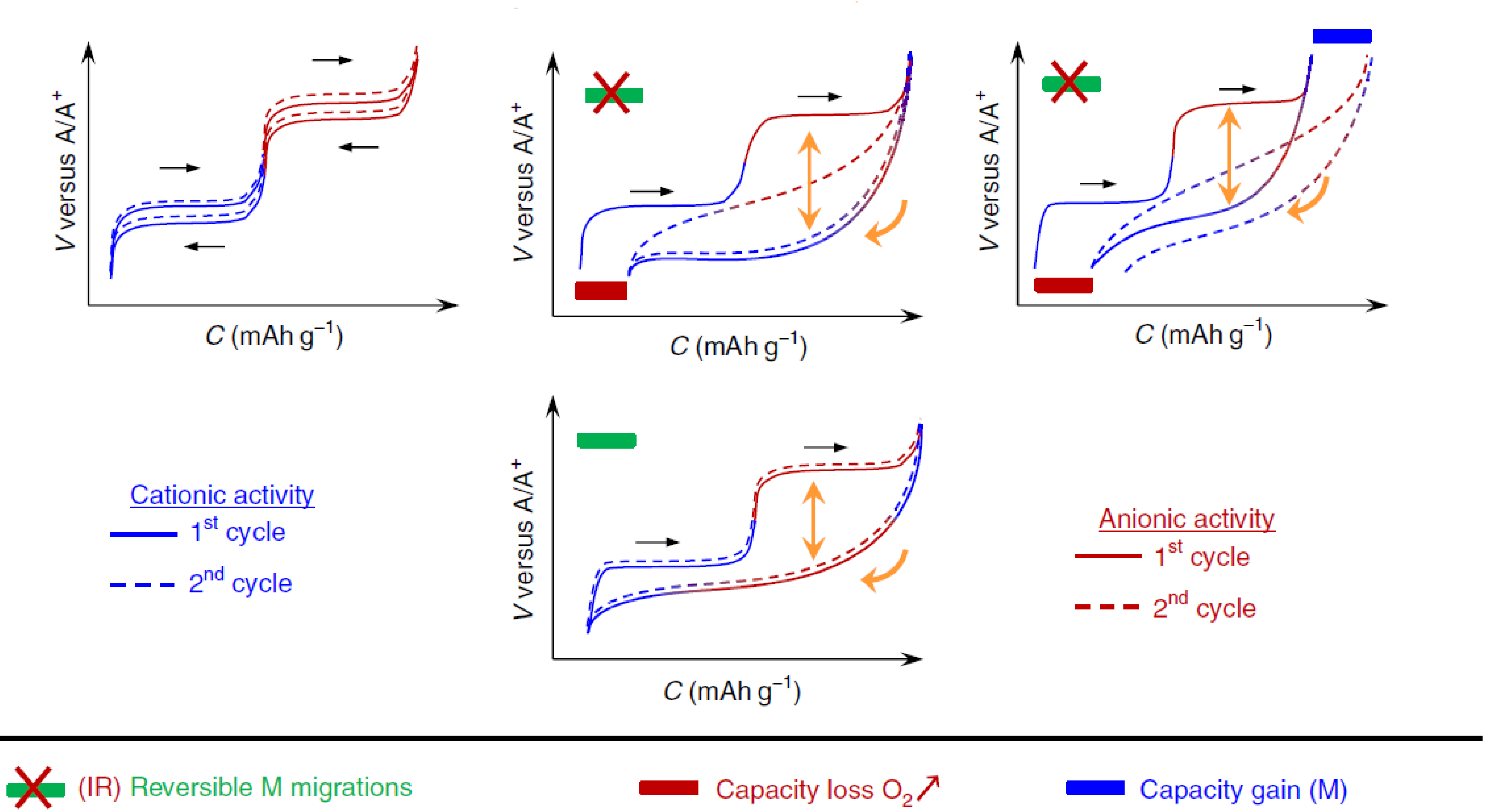
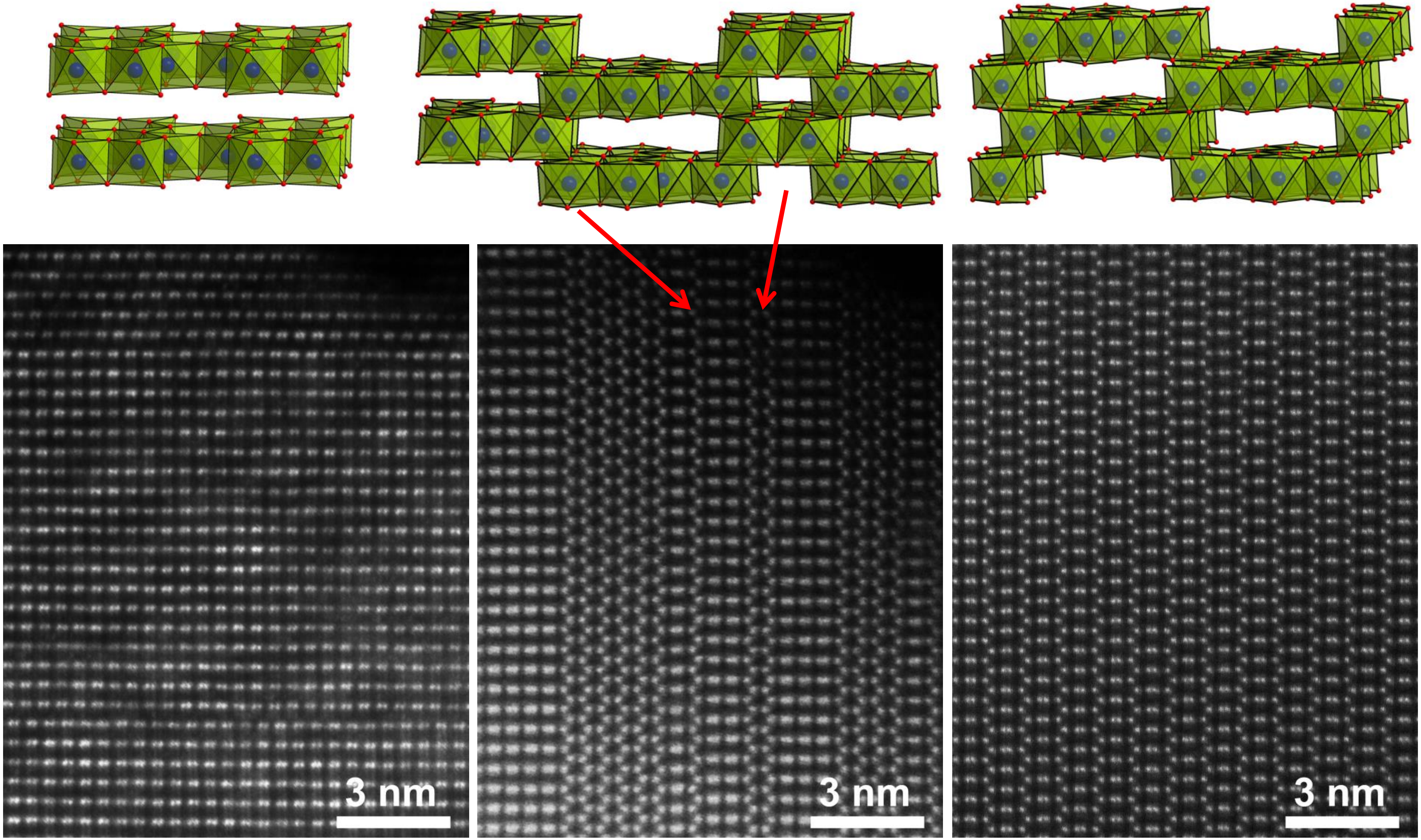
Versatility of the electrochemical behavior



M. Ben Yahia et al, Nature Mater. 18, 496 (2019)

Suppressing cation migration: 3D β-Li_2IrO_3

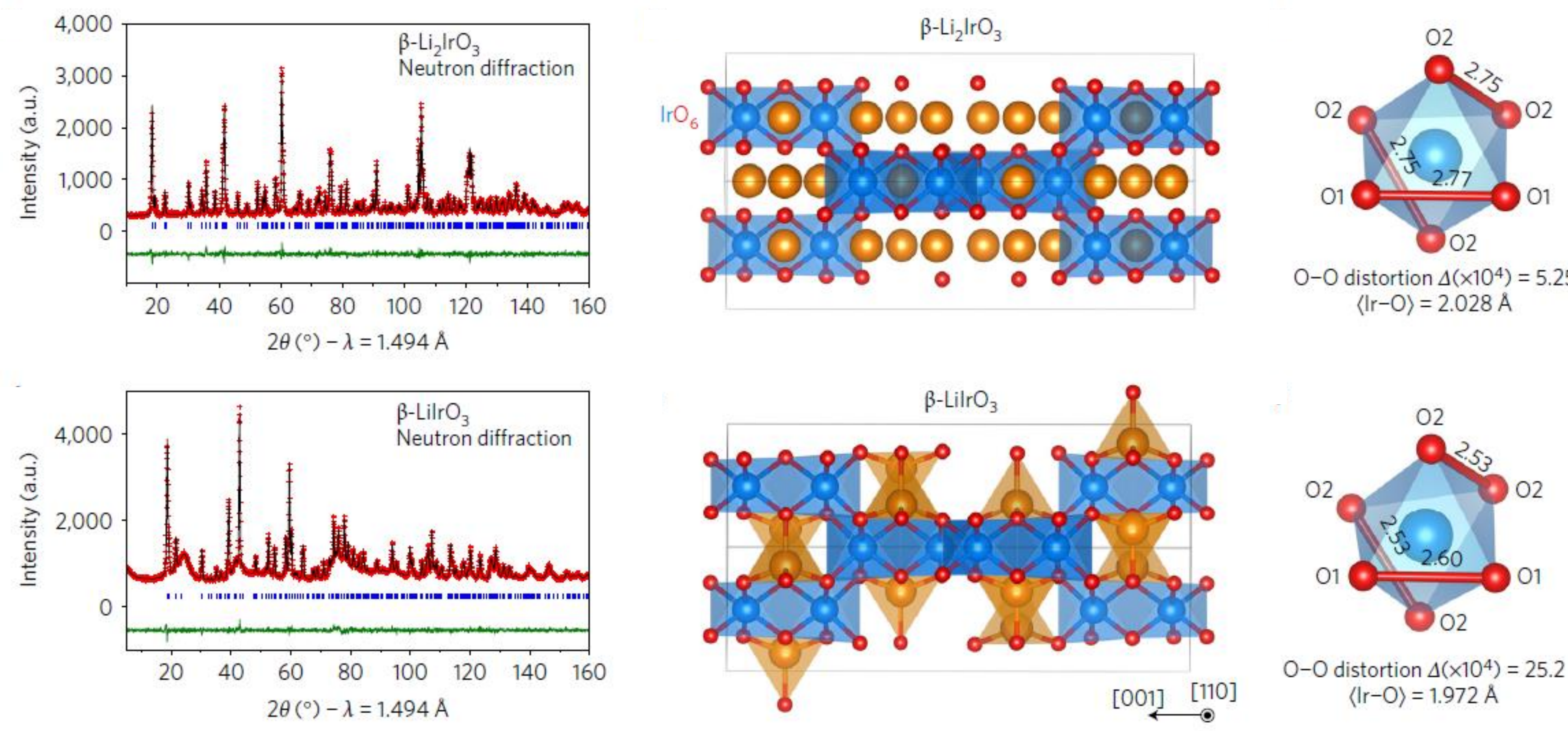


2D layered | Random stacking of APBs | 3D framework with ordered APBs

Pearce, Perez, Rousse, Saubanère, Batuk, Foix, McCalla, Abakumov, Van Tendeloo, Doublet, Tarascon, *Nature Mater*, 16, 580 (2017).

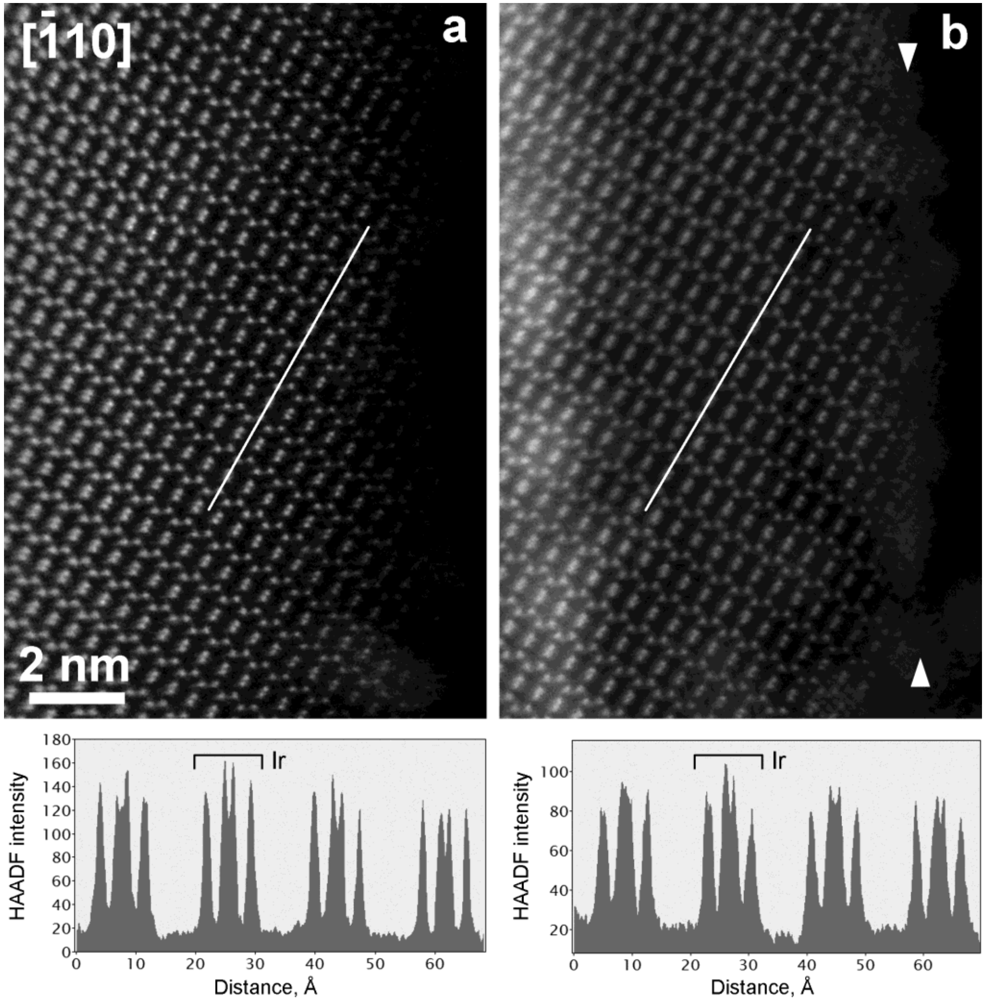
Suppressing cation migration: 3D β-Li_2IrO_3

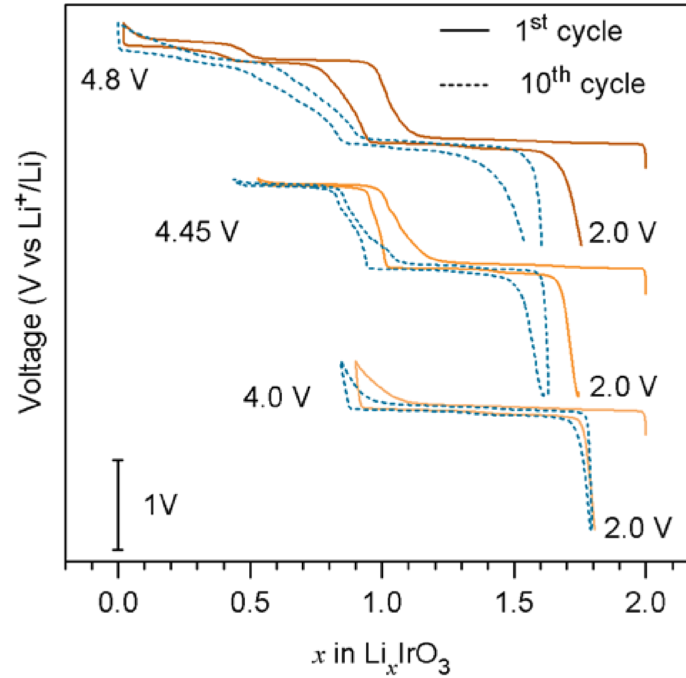
NPD refinement of β-$LiIrO_3$



Pearce, Perez, Rousse, Saubanère, Batuk, Foix, McCalla, Abakumov, Van Tendeloo, Doublet, Tarascon, *Nature Materials*, 16, 580 (2017).

Suppressing cation migration: 3D β-Li_2IrO_3





10 cycles 2.0-4.0V

10 cycles 2.0-4.8V

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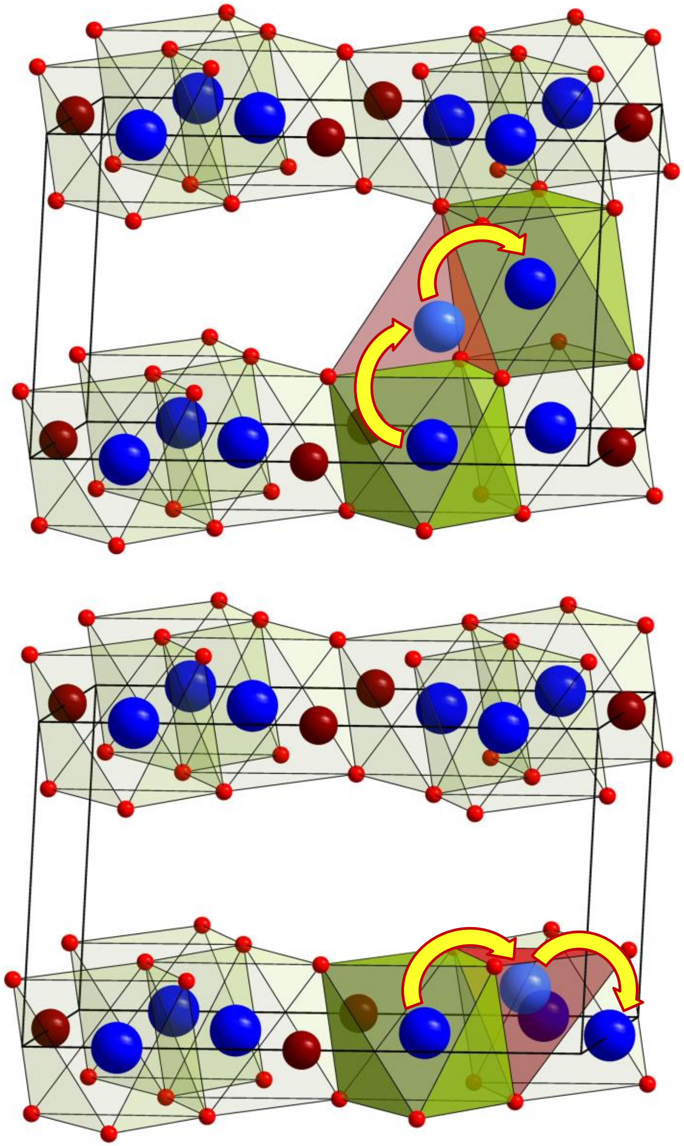
How to make these materials better?



Understanding TM cation migration and suppressing voltage fade:

1. What are the migration pathways?
2. What are the migration energy barriers?
3. What is the role of partial oxygen oxidation in the cation migration?
4. How to change chemistry to control the barriers:

- lattice contraction/expansion;
- softening of the oxygen sublattice;
- structure relaxation at the CV regime;

More complex cationic compositions and appropriate synthesis techniques have to be developed.

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Спасибо за внимание!