Electronic structure of battery materials

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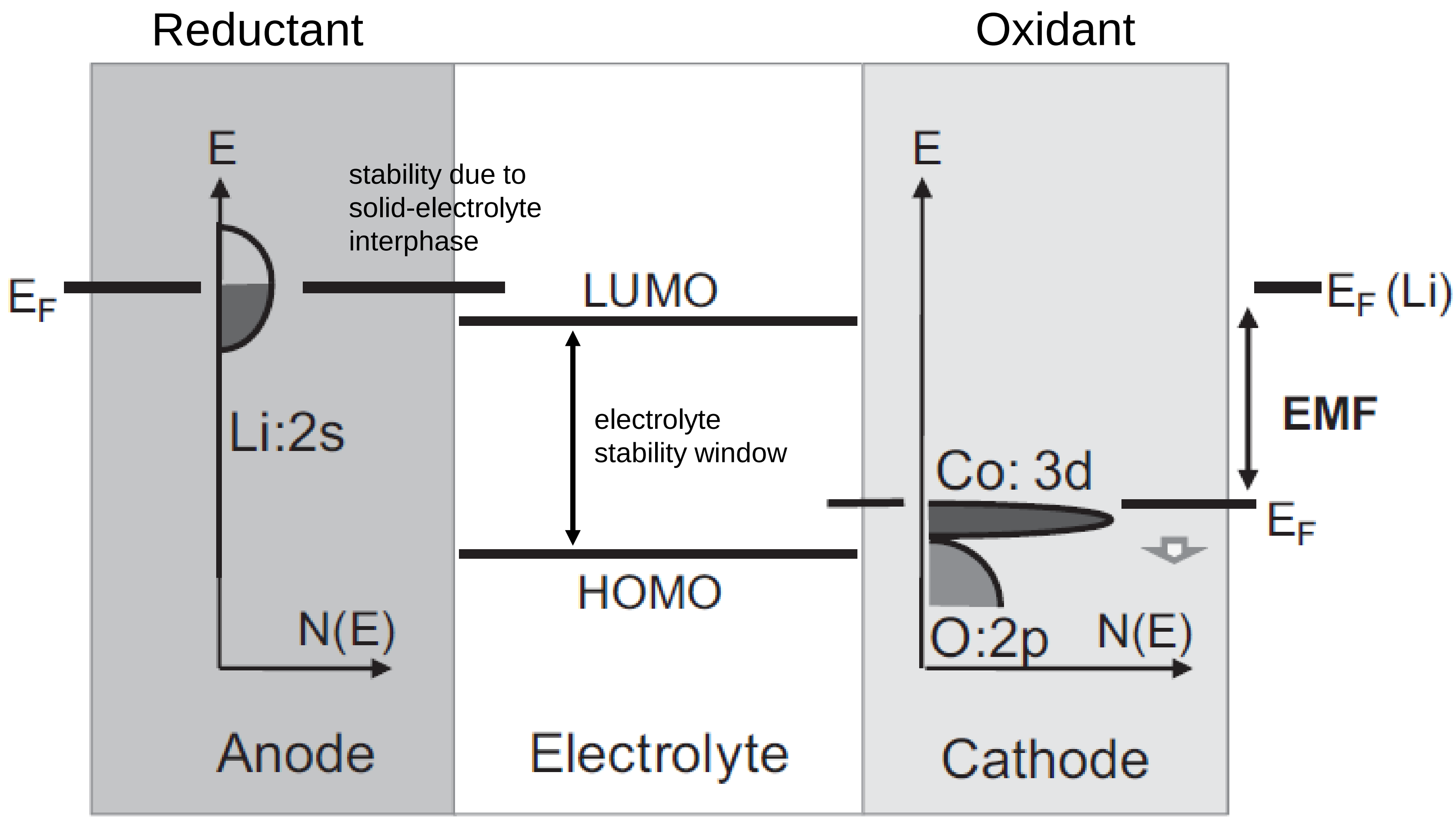
Li-ion battery energy diagram



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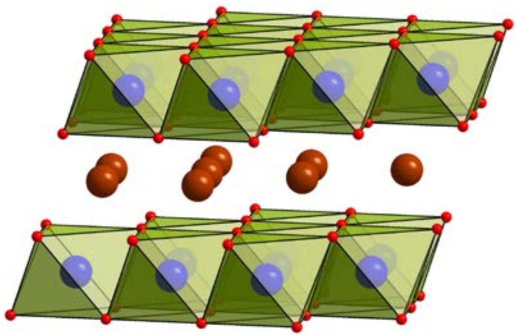
Cathode materials

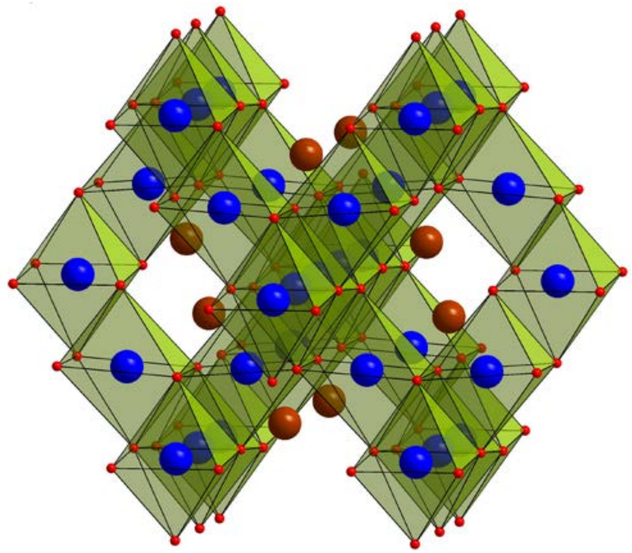
Complex oxides

Polyanion compounds



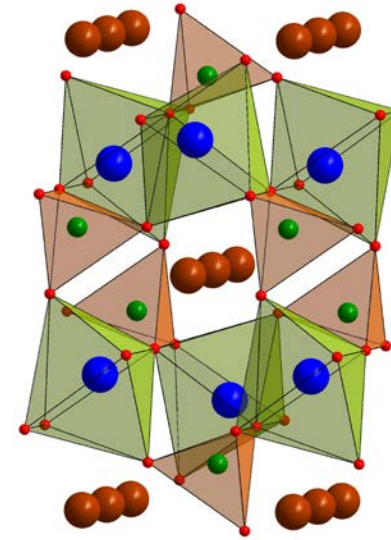
$LiCoO_2$
$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

2D Li transport



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

3D Li transport



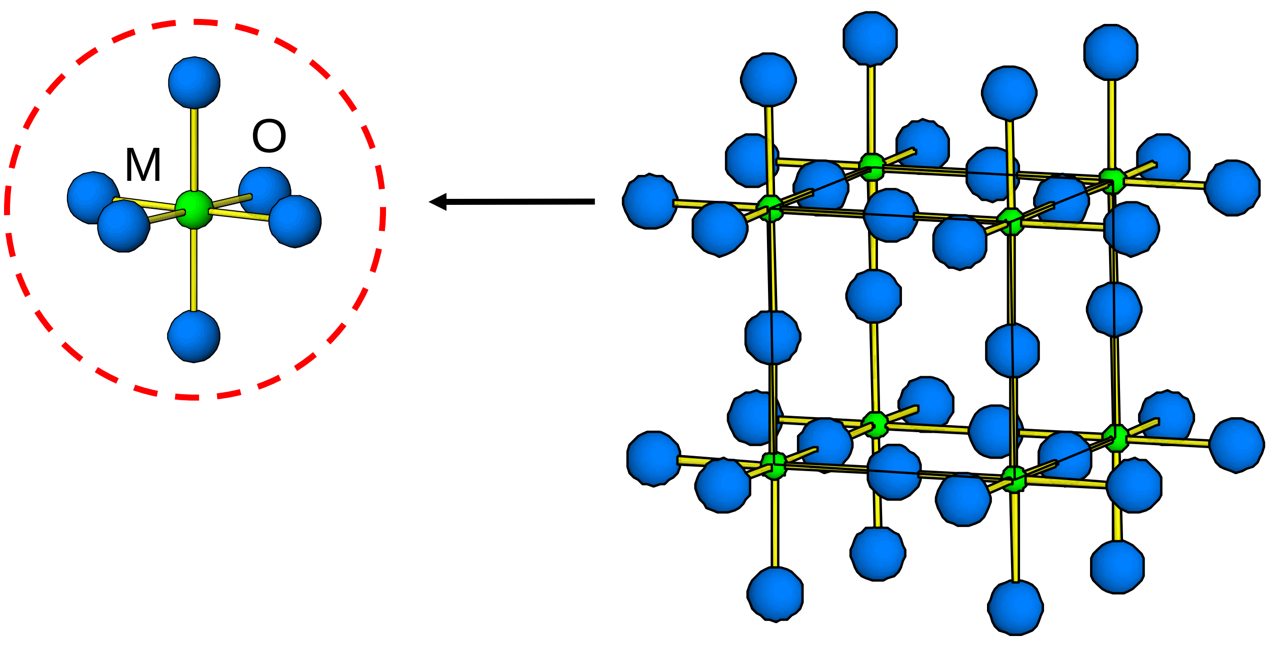
$LiFePO_4$

1D Li transport

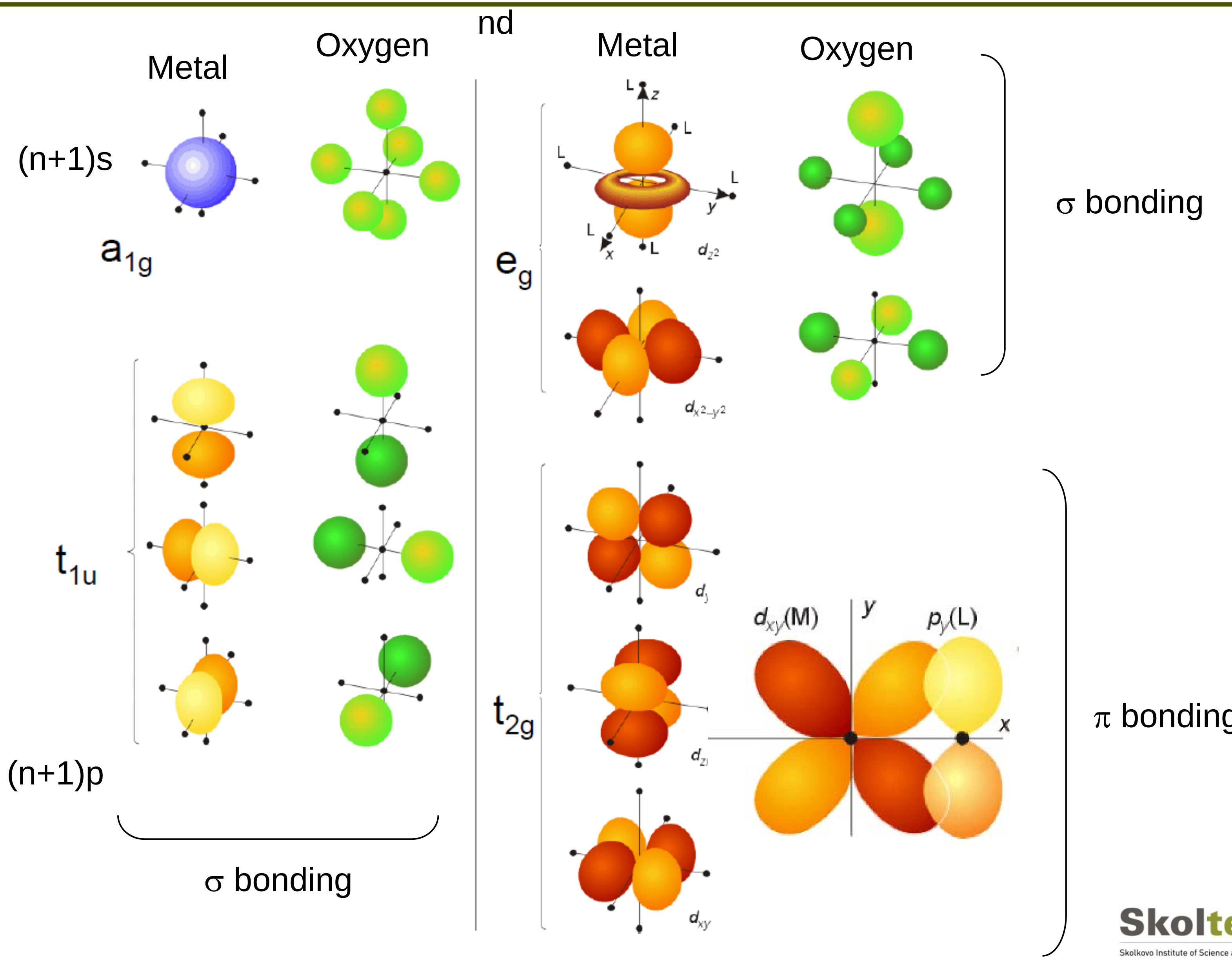
Bonding in oxides

MO diagram for the MO_6^{n-} octahedral complex – a building unit of many oxide structures

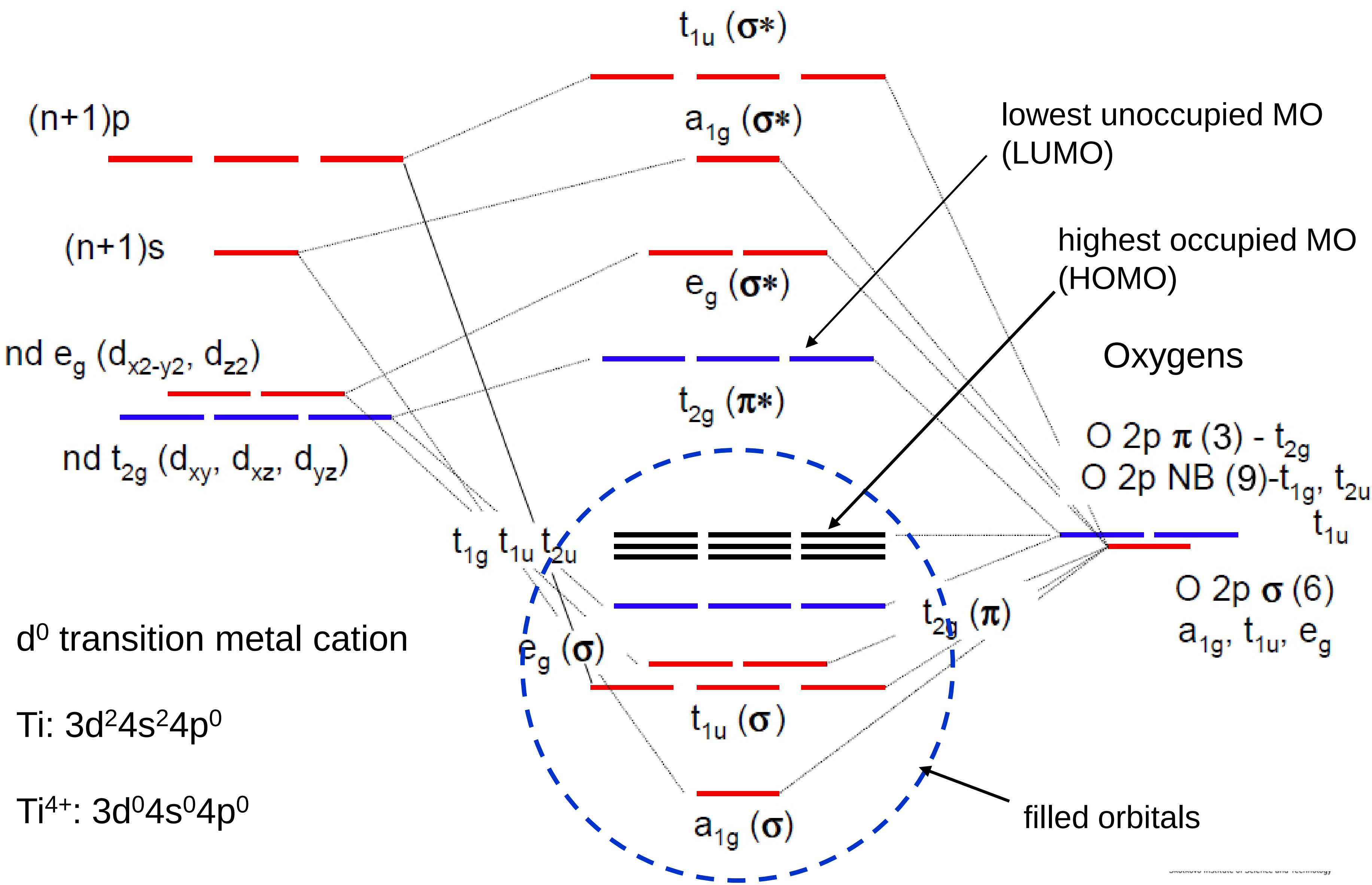
M – transition metal with the electronic configuration nd^m $(n+1)s^2$ $(n+1)p^0$



Bonding in oxides



BO_6^{n-} octahedron: MO diagram

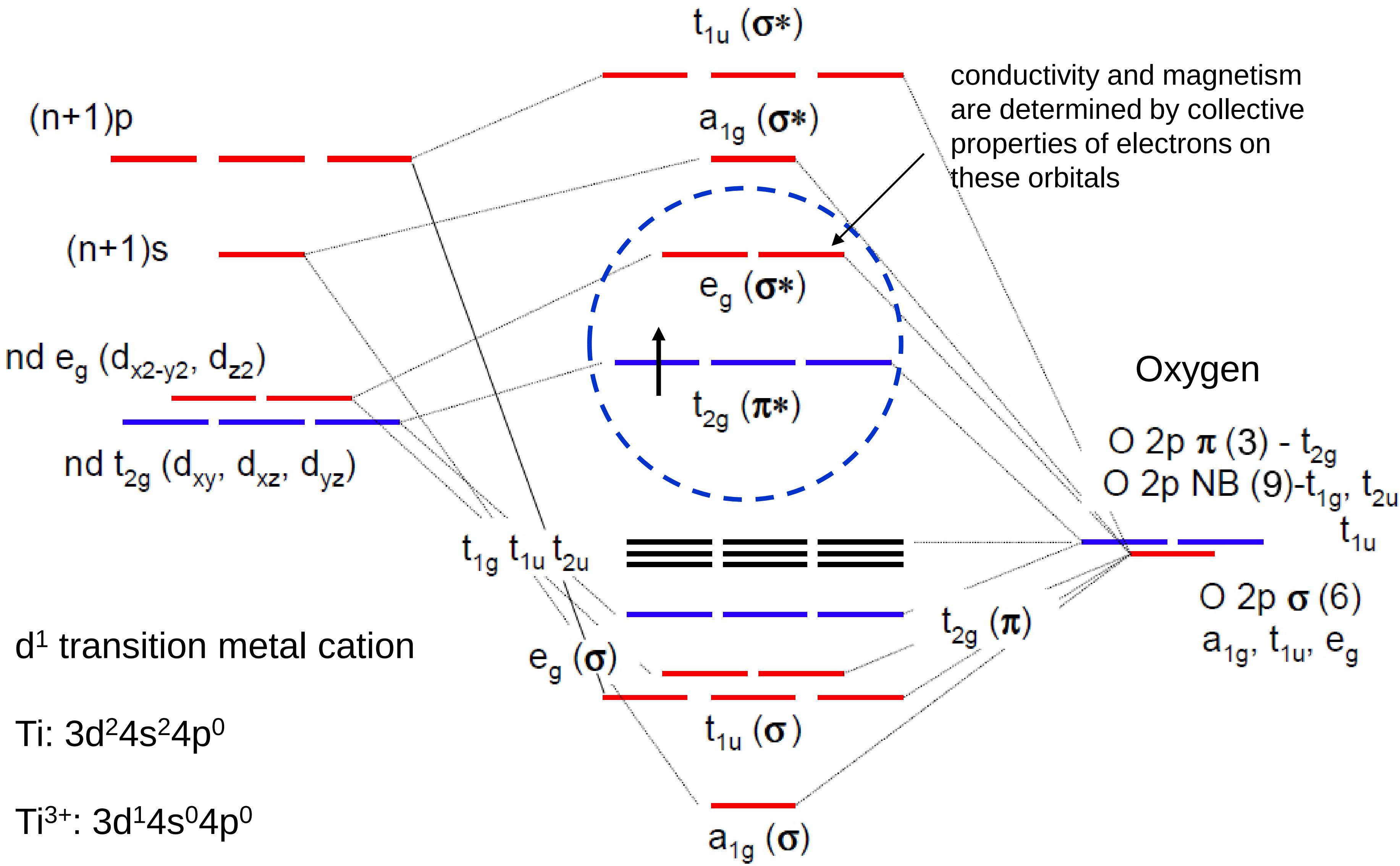


d^0 transition metal cation

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

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

BO_6^{n-} octahedron: MO diagram

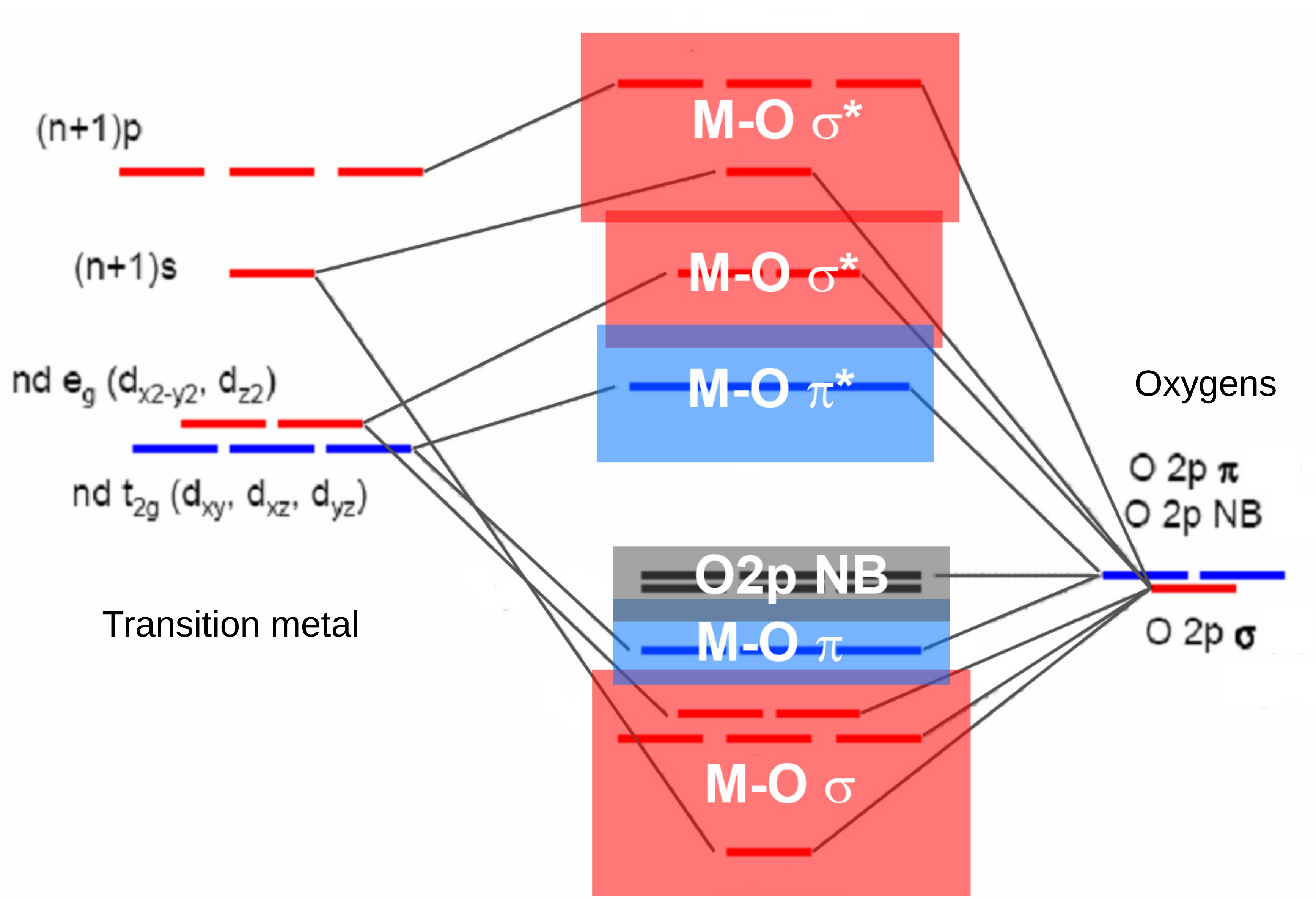


d^1 transition metal cation

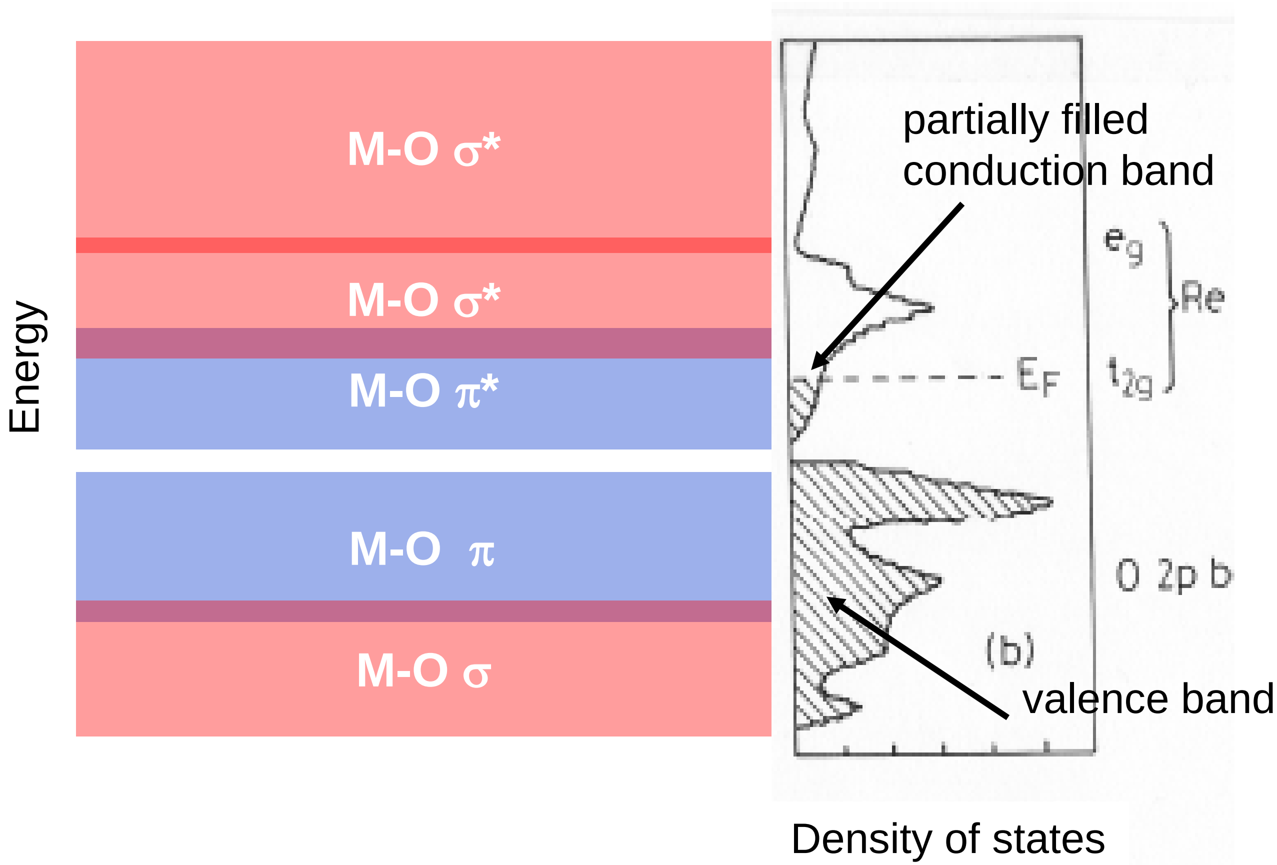
Ti: $3d^2 4s^2 4p^0$

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

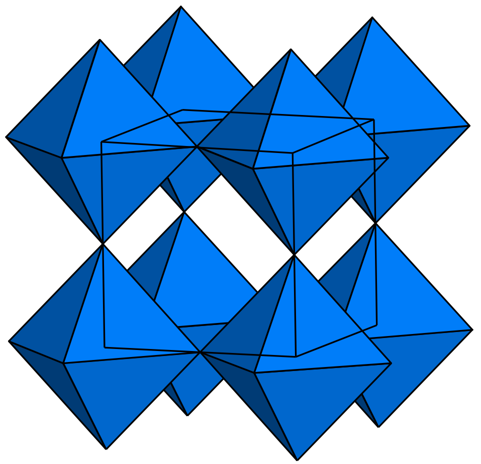
Simplified band structure



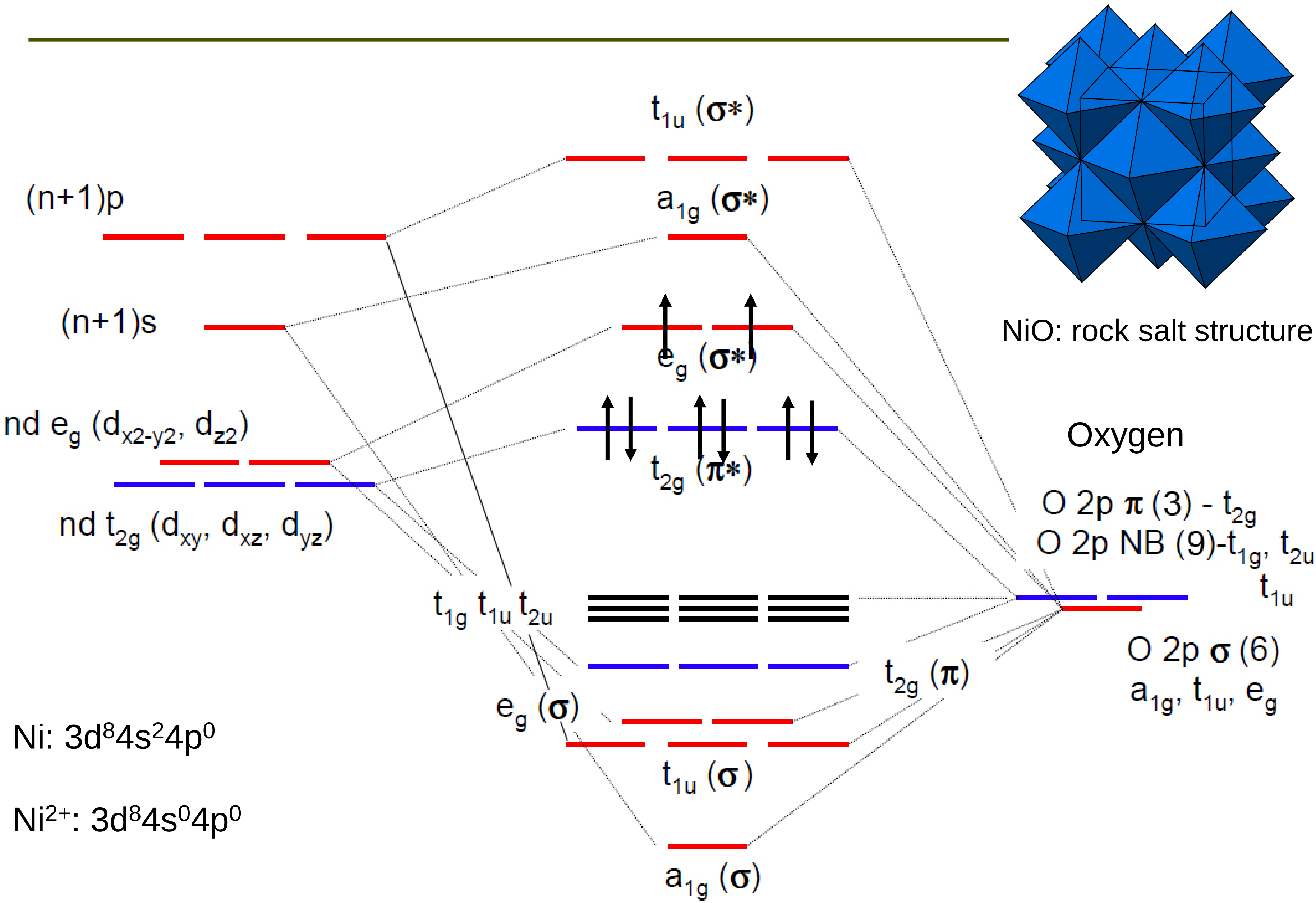
ReO_3: band structure



$ReO_3 : Re^{+6}\ d^1,\ t_{2g}^{\ 1}e_g^{\ 0}$



NiO: metal or insulator?

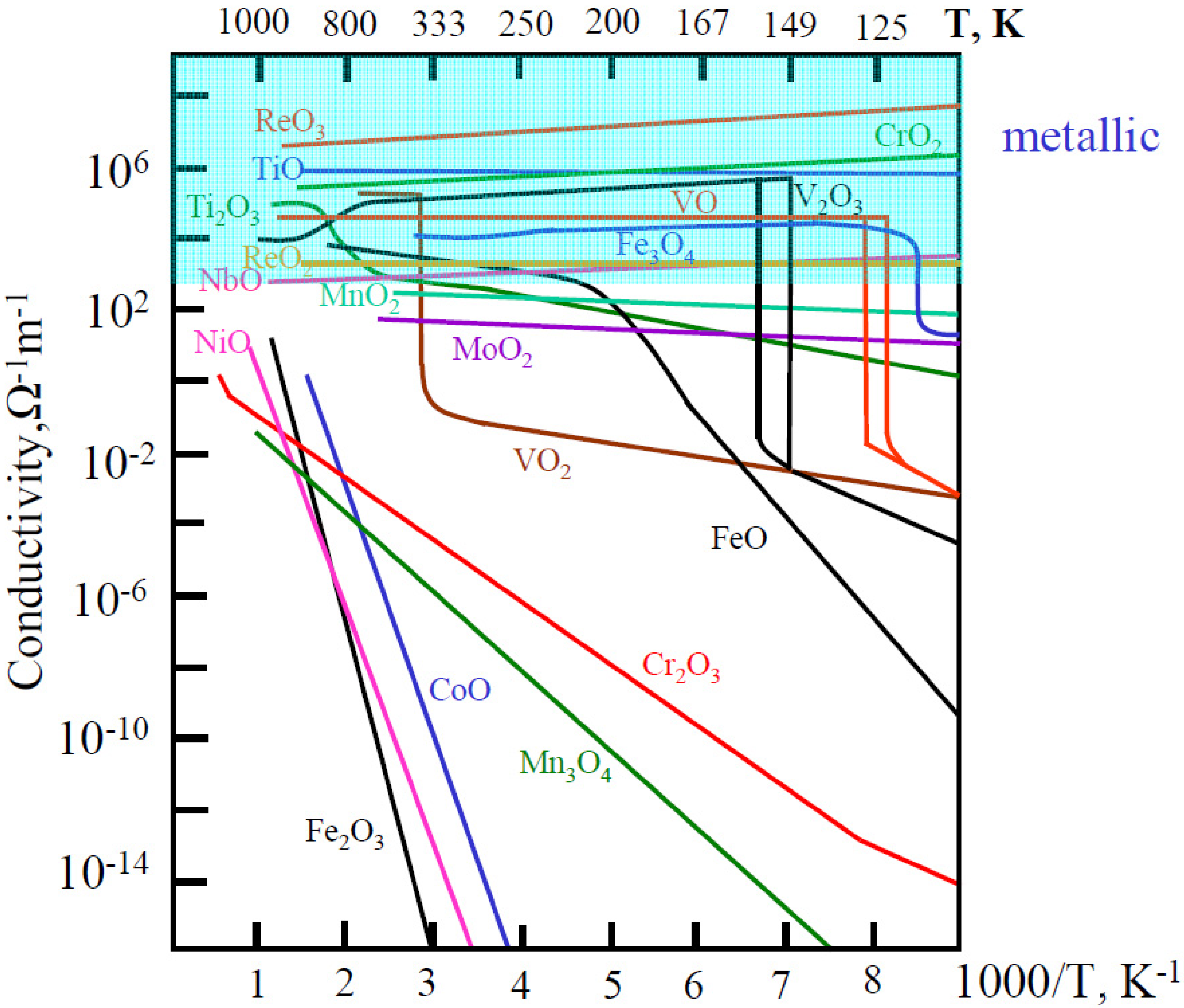


NiO: rock salt structure

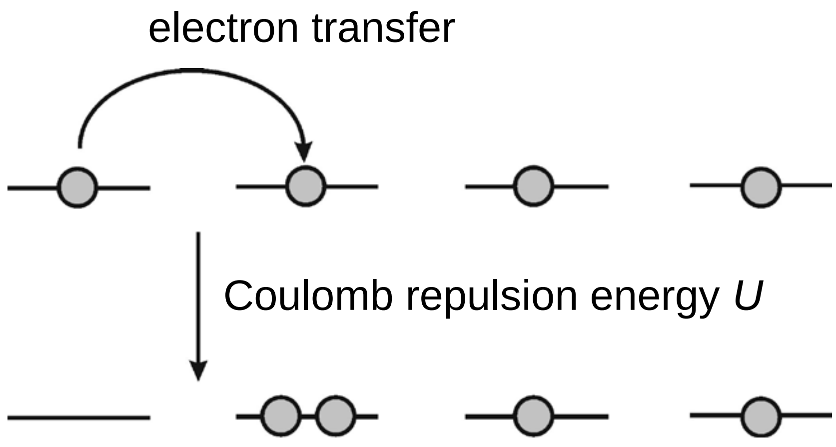
Ni: $3d^8 4s^2 4p^0$

Ni^{2+}: $3d^8 4s^0 4p^0$

NiO: metal or insulator?



Mott-Hubbard insulators

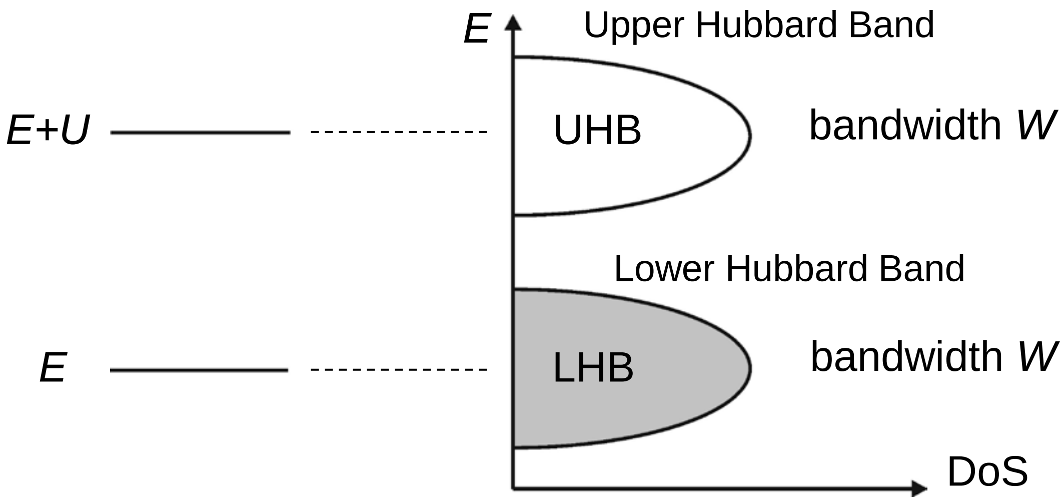


$Ni^{2+} + Ni^{2+} \rightarrow Ni^{3+} + Ni^{+}$

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

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.



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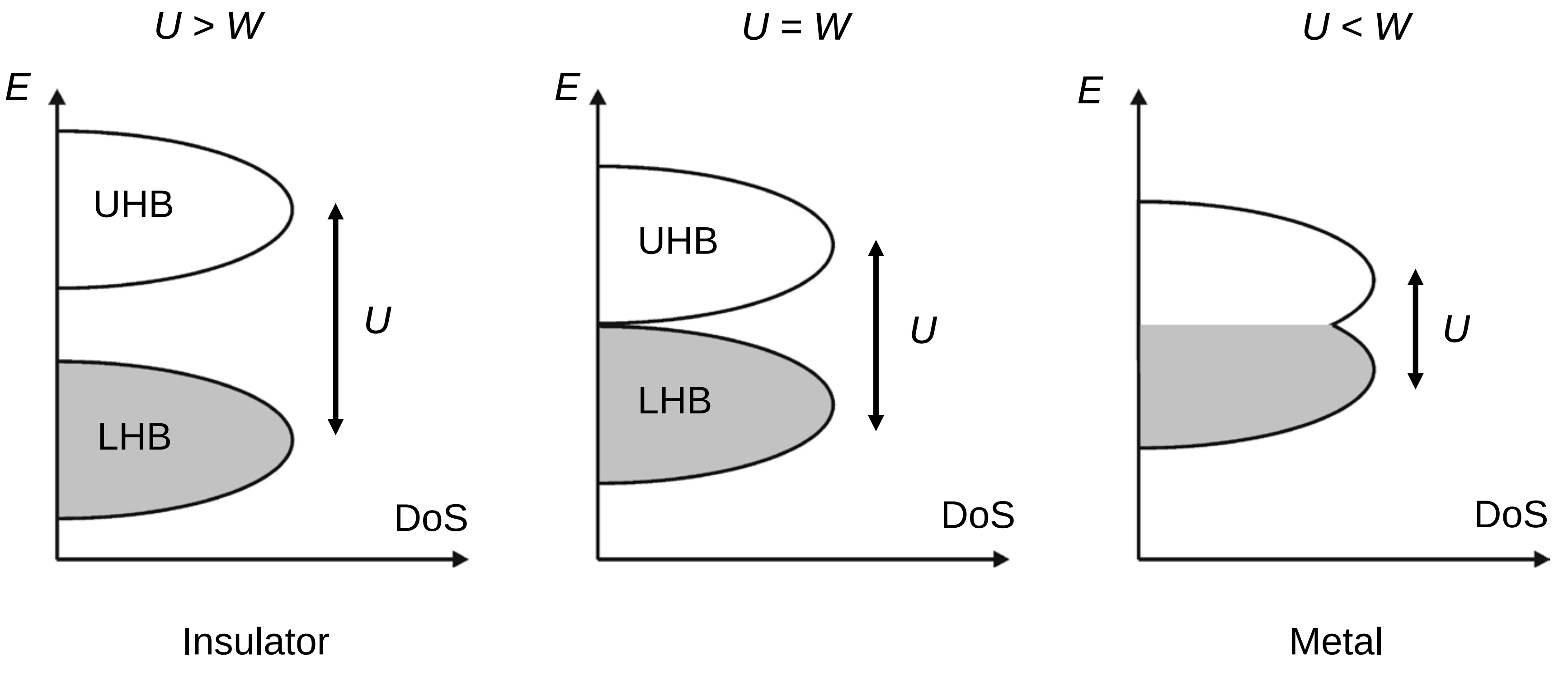
Mott-Hubbard insulators

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

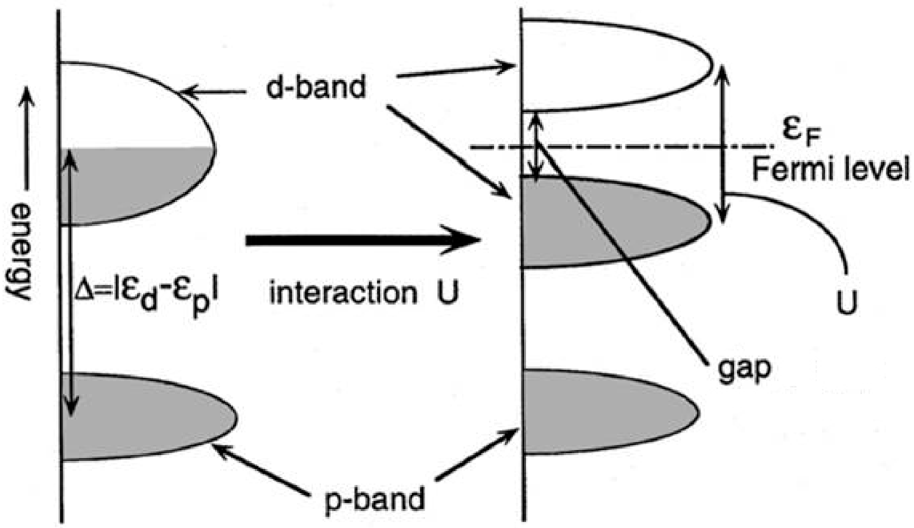


Mott-Hubbard vs charge transfer regimes

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

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

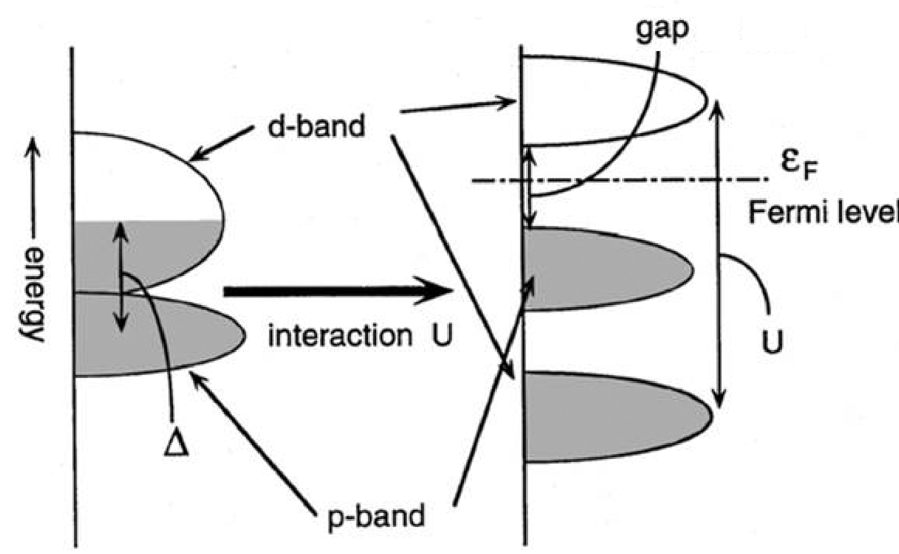
Mott-Hubbard regime



U < Δ, gap *U* – *W*

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

Charge transfer regime



U > Δ, gap Δ – *W*

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

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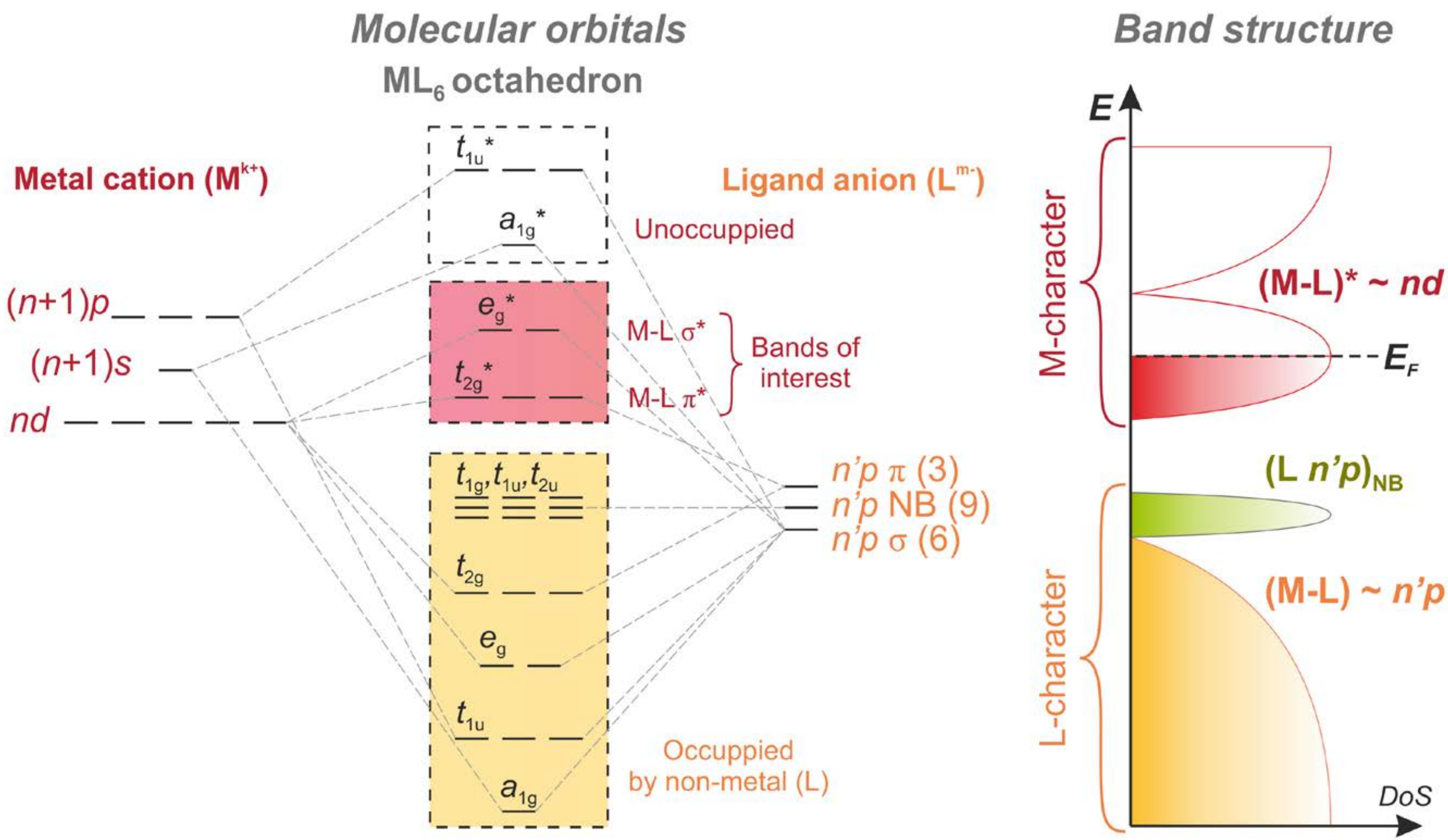
Cathode materials



Abakumov, Fedotov, Antipov, Tarascon, *Nature Comm.*, 11, 4976 (2020)

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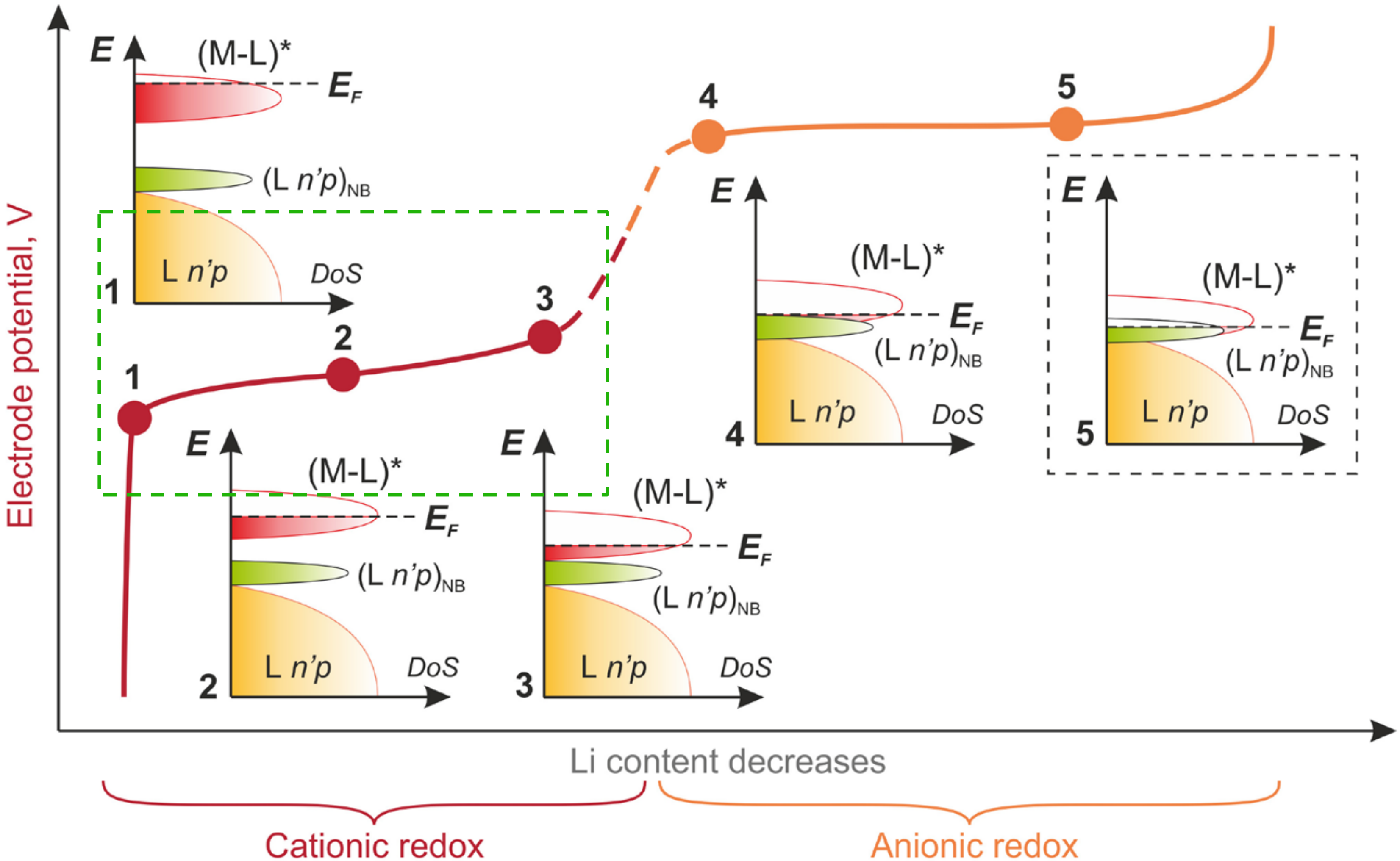
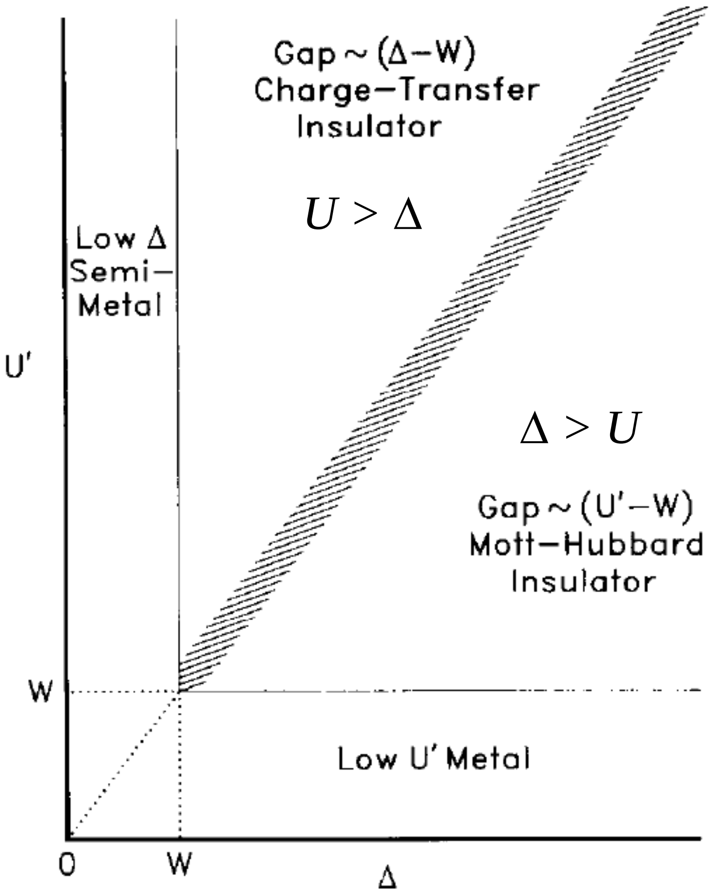
Cathionic redox



Abakumov, Fedotov, Antipov, Tarascon, *Nature Comm.*, 11, 4976 (2020)

Cationic redox in ZSA diagram

Zaanen – Sawatsky – Allen diagram



Pure ionic model neglecting the orbital overlap:

$$U_0 = I_{\nu+1}(\mathrm{M}) - I_\nu(\mathrm{M}) - e^2/d_{\mathrm{M\text{-}M}}$$

I – ionization potential

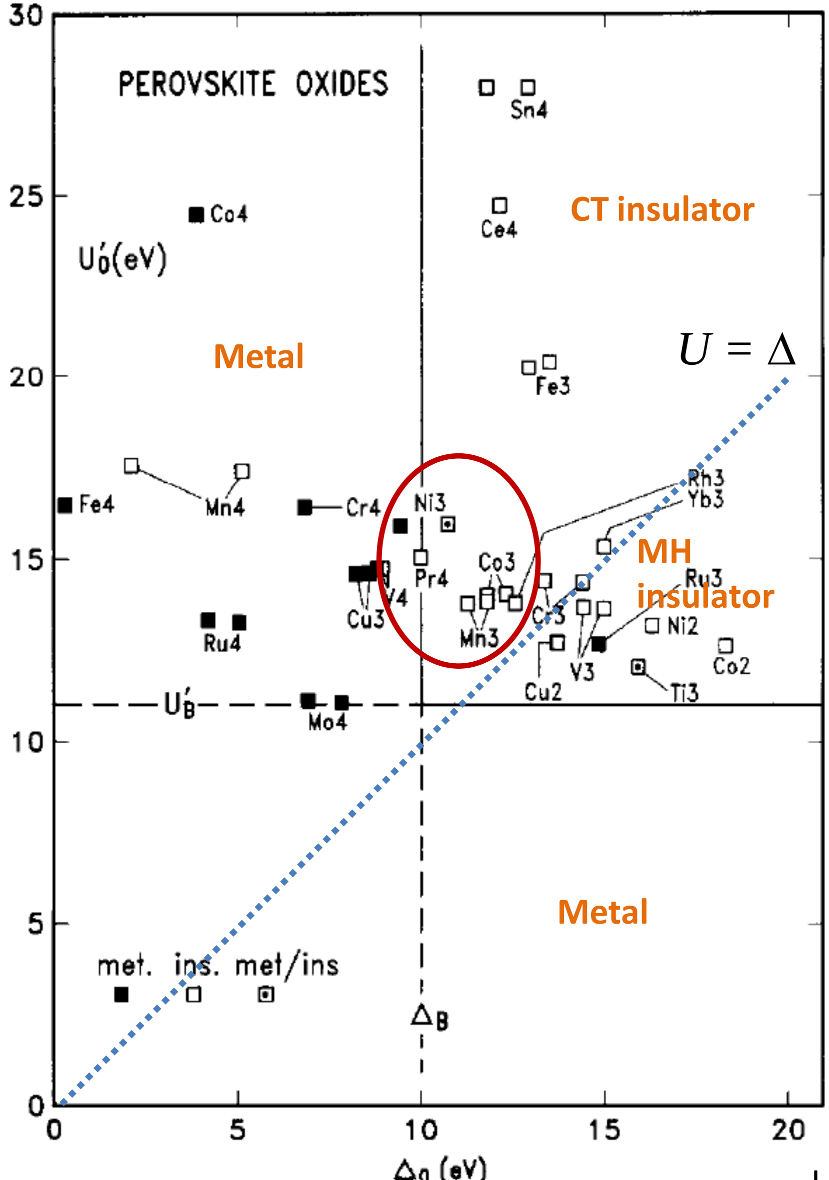
$$\Delta_0 = e\Delta V_\mathrm{M} + A(\mathrm{O}^-) - I_\nu(\mathrm{M}) - e^2/d_{\mathrm{M\text{-}O}}$$

ΔV_M – change in Madelung potential

A – electron affinity

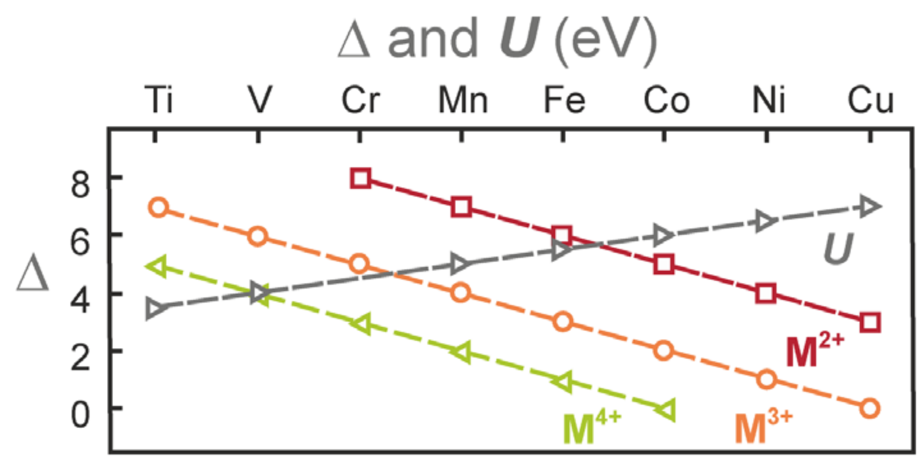
J.B. Torrance et al., Physica C, 182, 251, 1991

Cationic redox in ZSA diagram



$Z\uparrow, \nu\uparrow : U\uparrow$

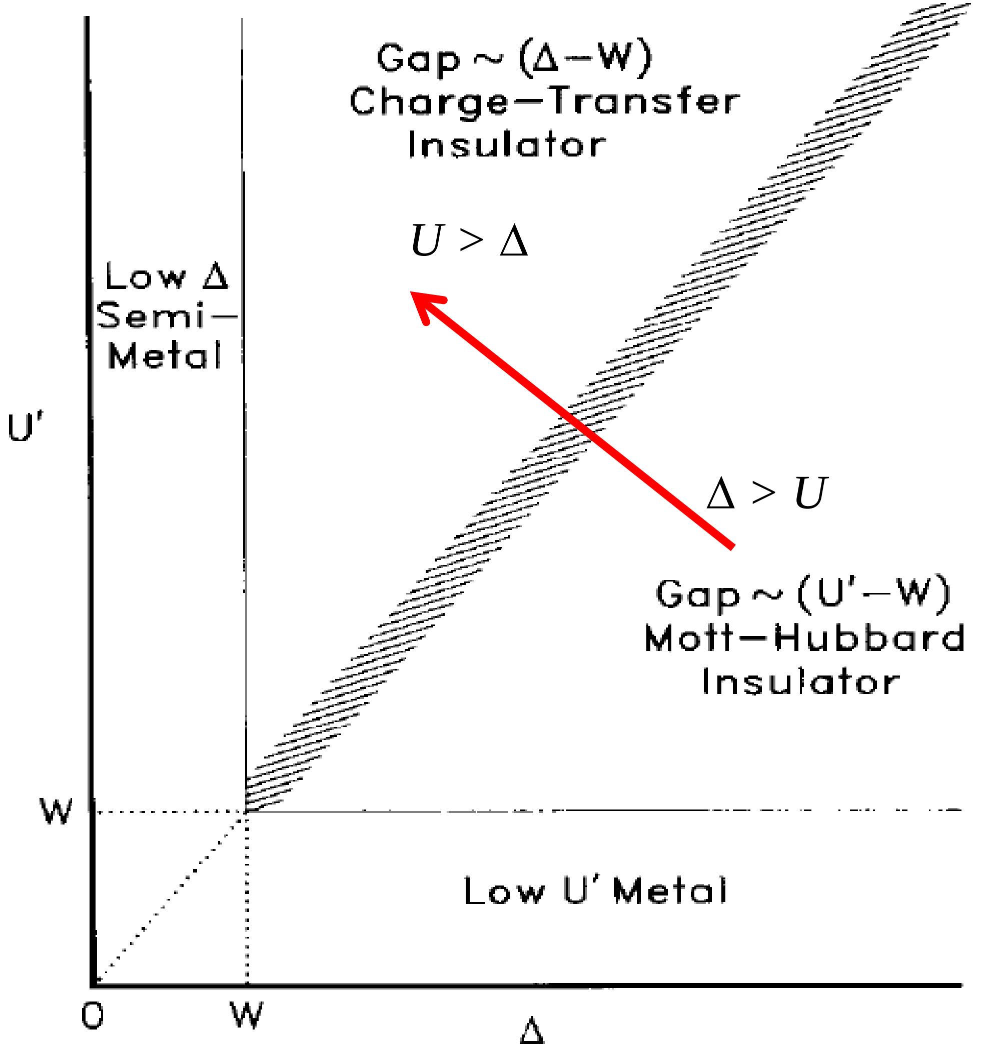
$Z\uparrow, \nu\uparrow : \Delta\downarrow$



J.B. Torrance et al., Physica C, 182, 251, 1991

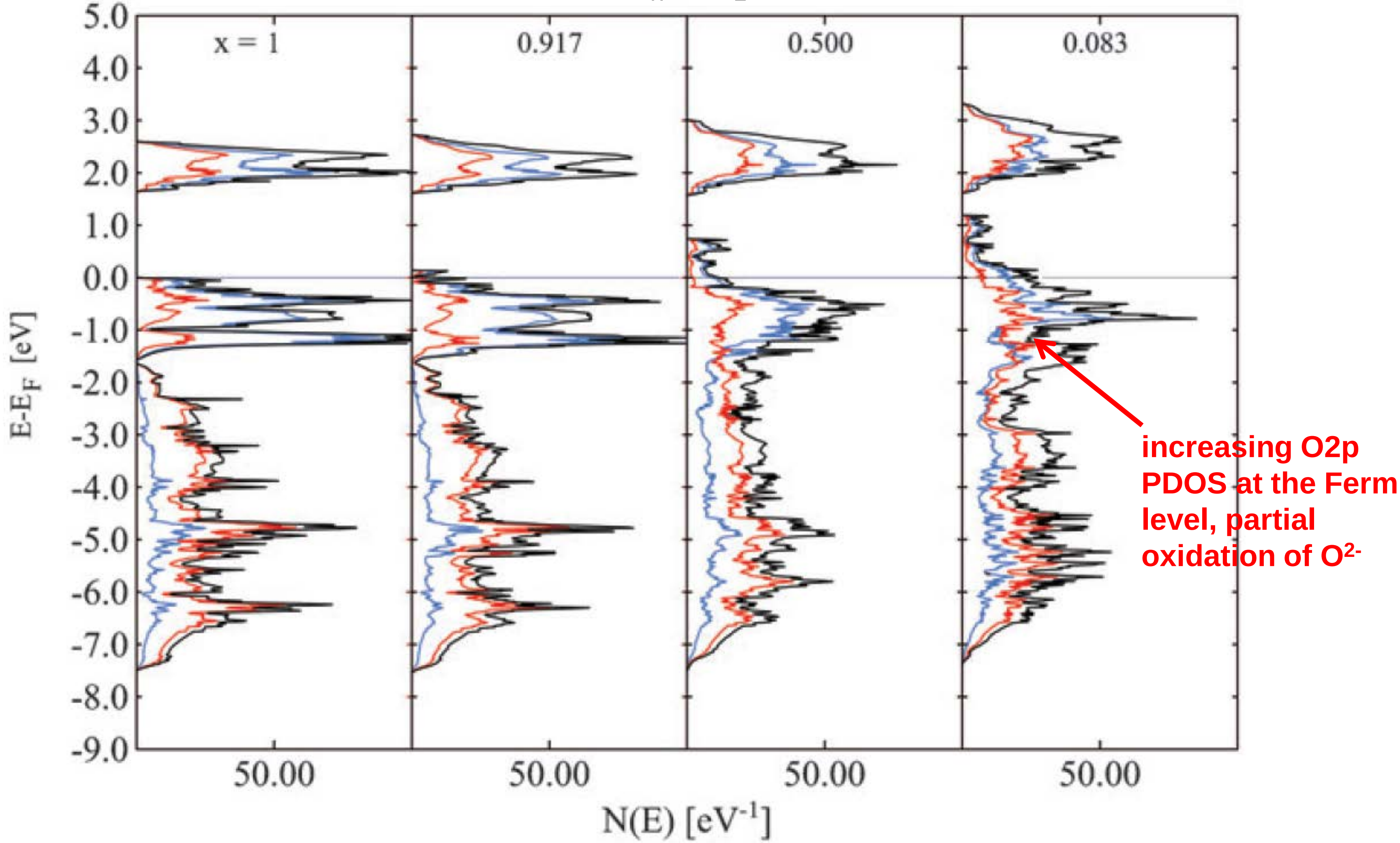
Cationic redox in ZSA diagram

Zaanen – Sawatsky – Allen diagram



Band structure upon charge/discharge

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



increasing Co3d-O2p hybridization

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

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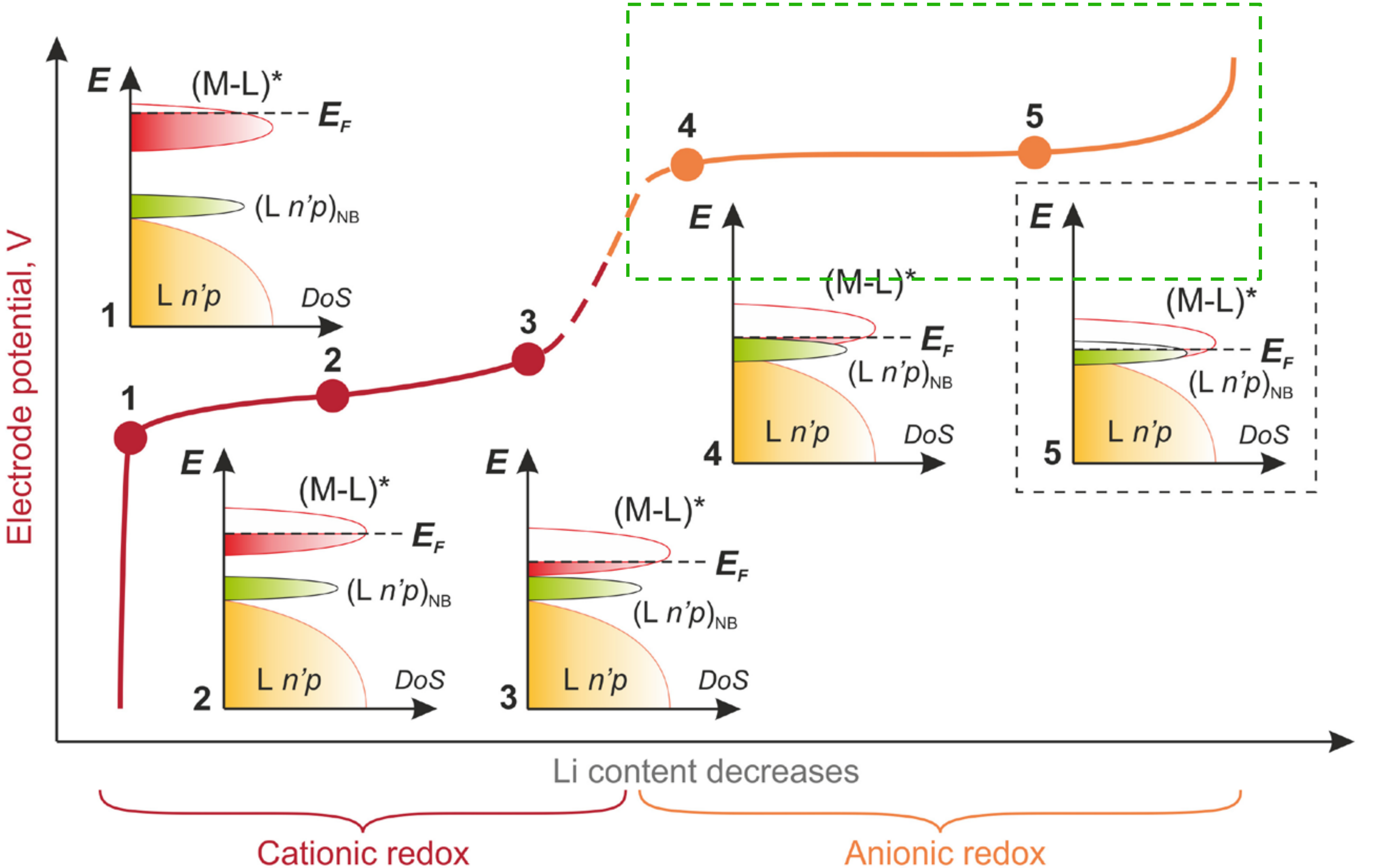
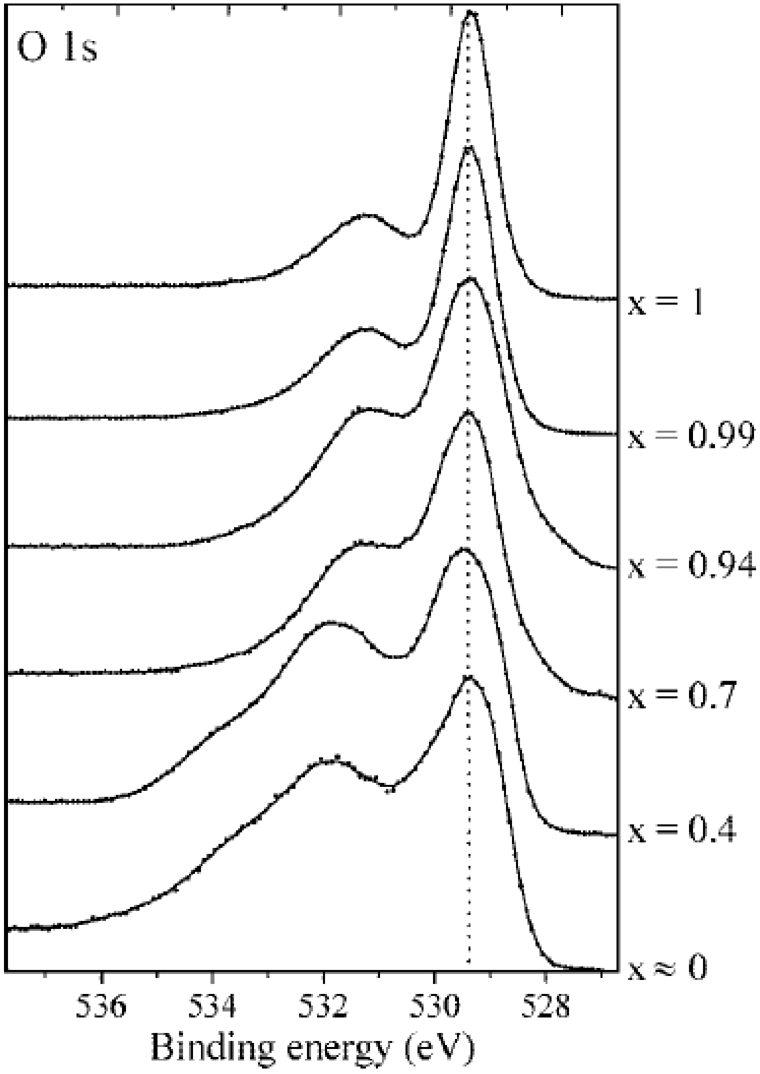
Anionic redox

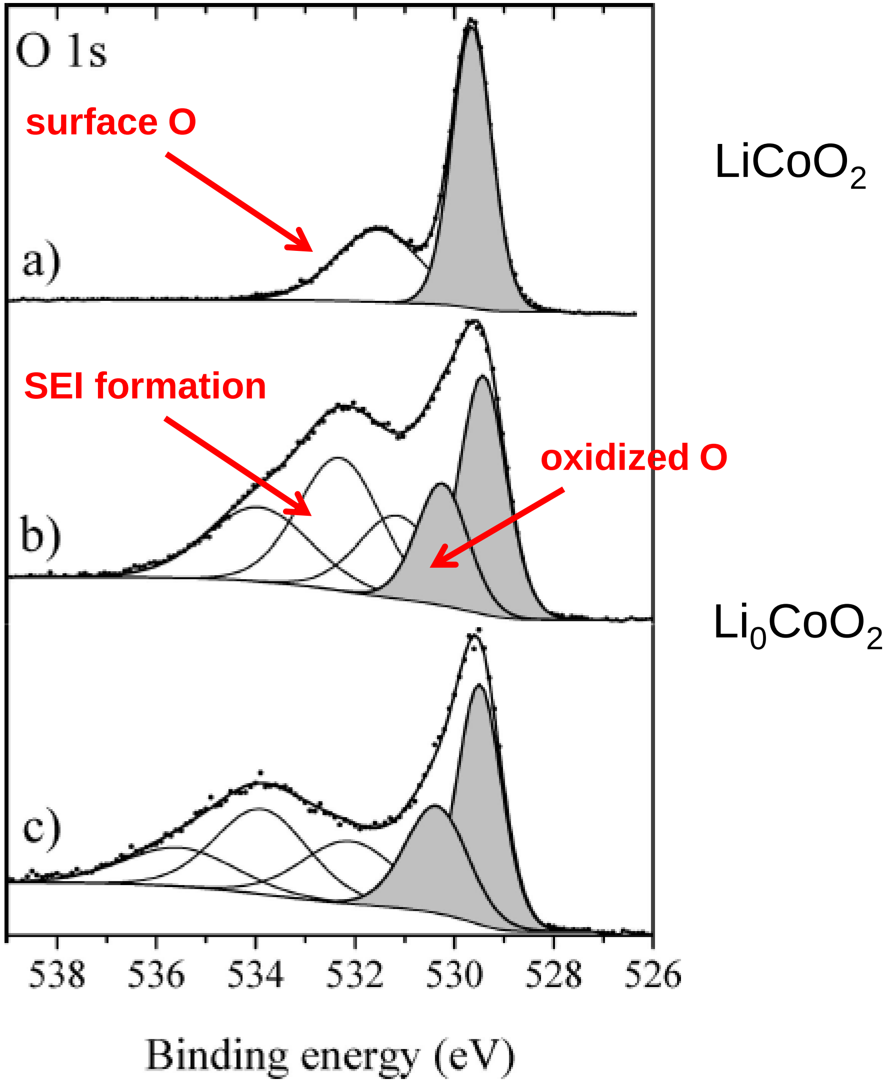


Abakumov, Fedotov, Antipov, Tarascon, *Nature Comm.*, 11, 4976 (2020)

Lattice oxygen oxidation



Li_xCoO_2 XPS O1s



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

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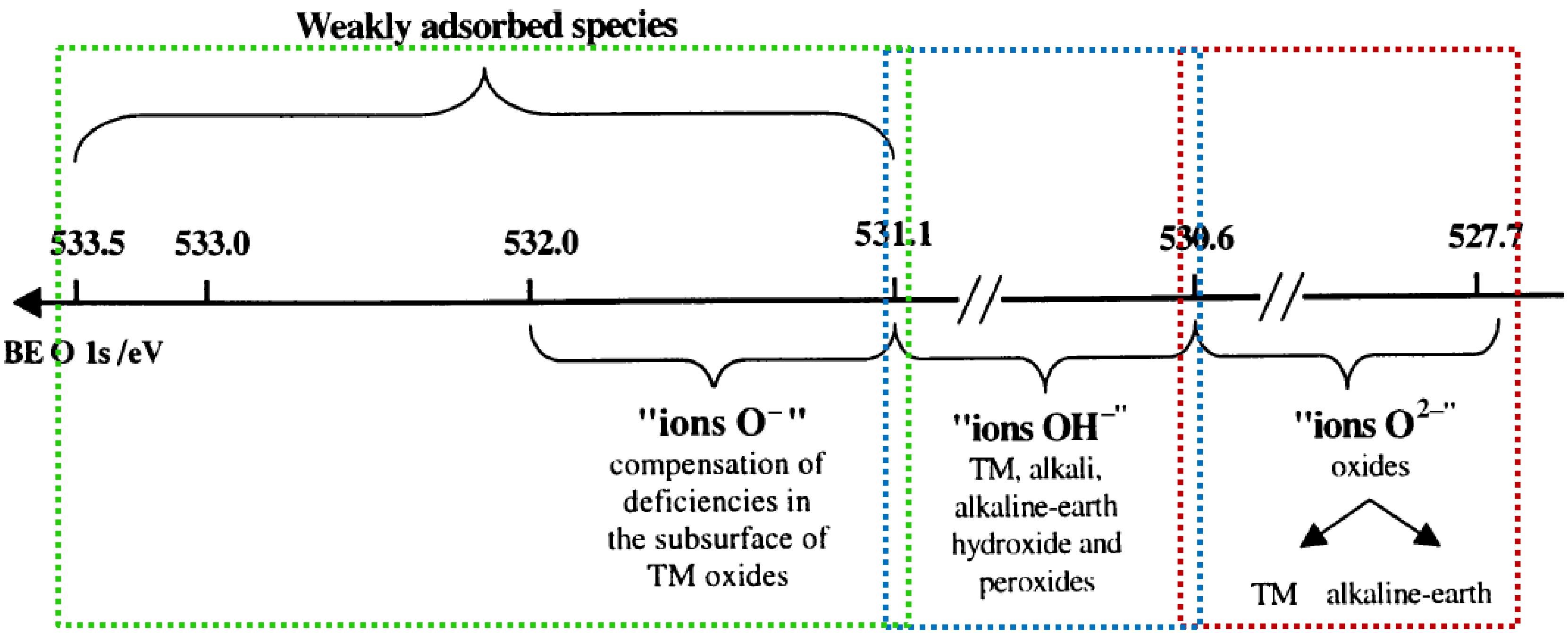
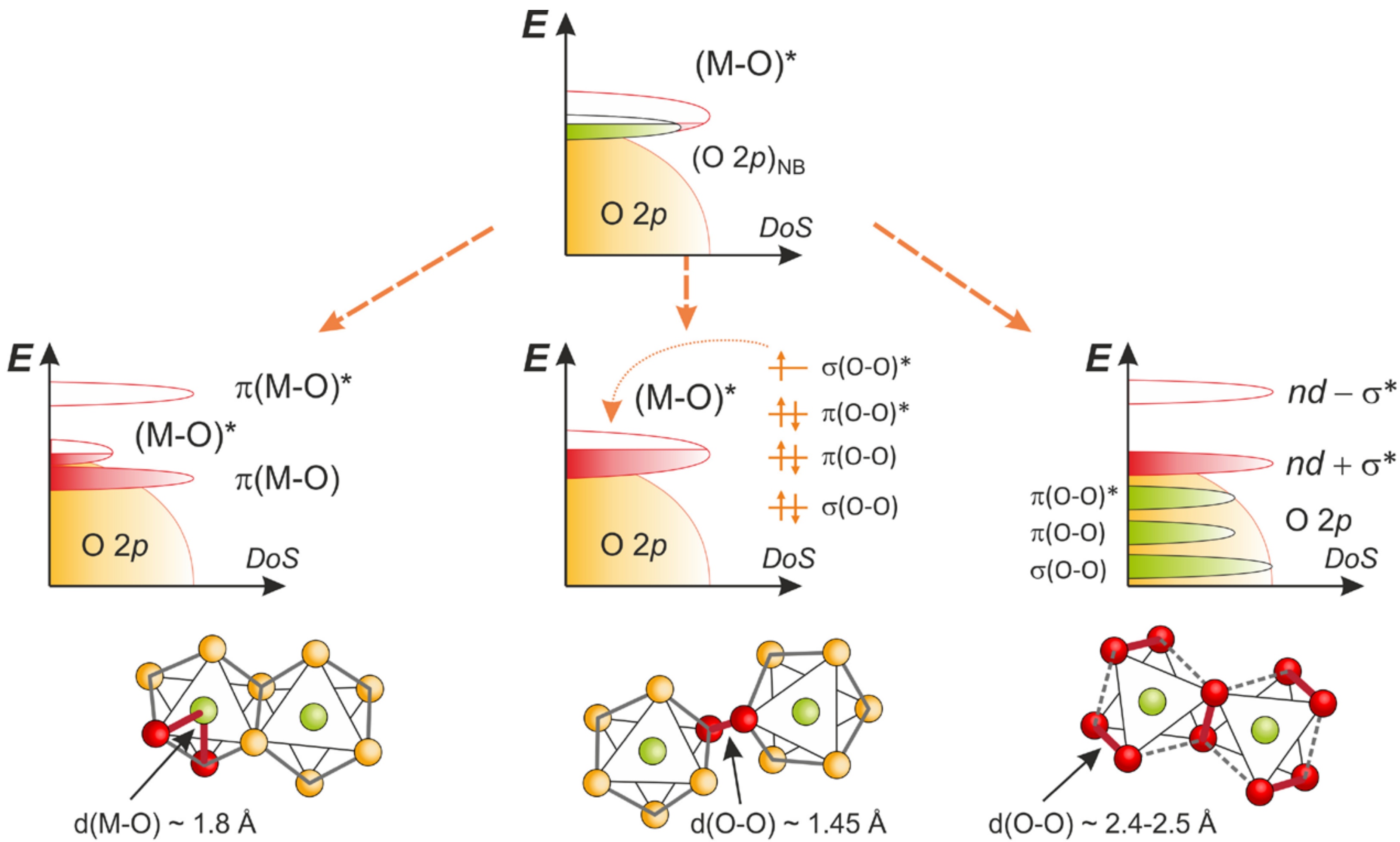
Lattice oxygen oxidation



surface O species | peroxogroup O_2^{2-} | lattice O^{2-}

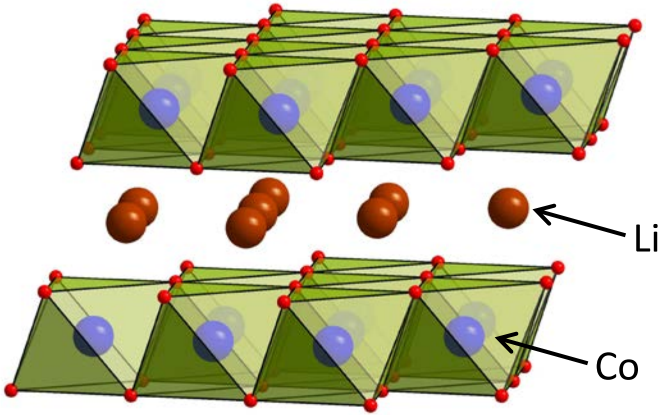
J.-C. Dupin et al., Phys.Chem.Chem.Phys.,2000,2,1319

Anionic redox



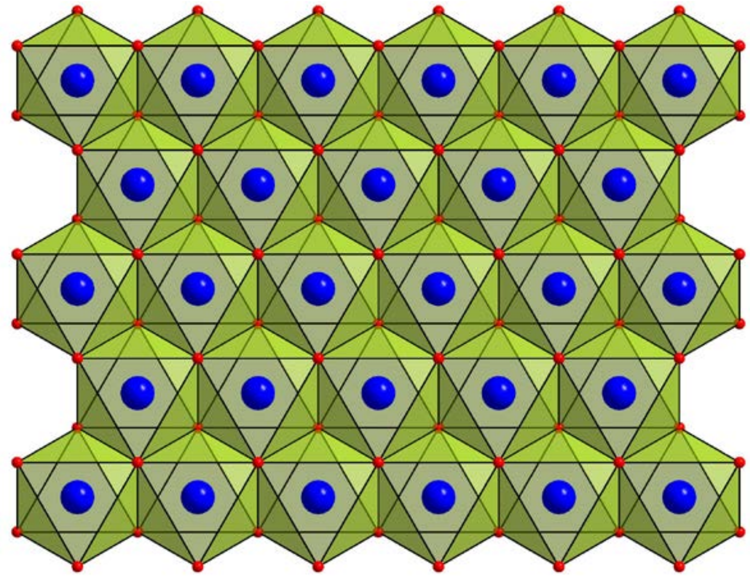
Abakumov, Fedotov, Antipov, Tarascon, *Nature Comm.*, 11, 4976 (2020)

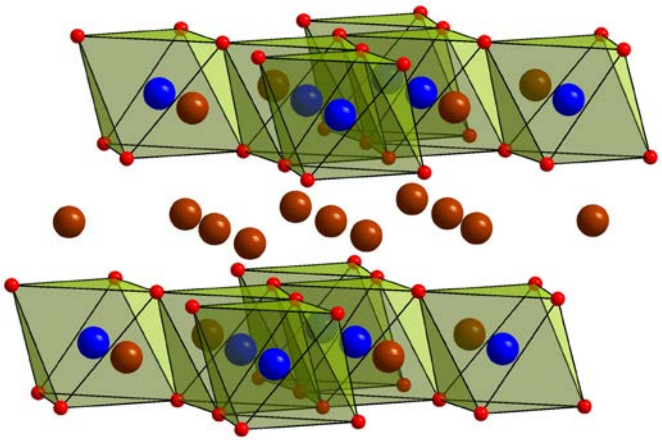
Li-rich layered oxides



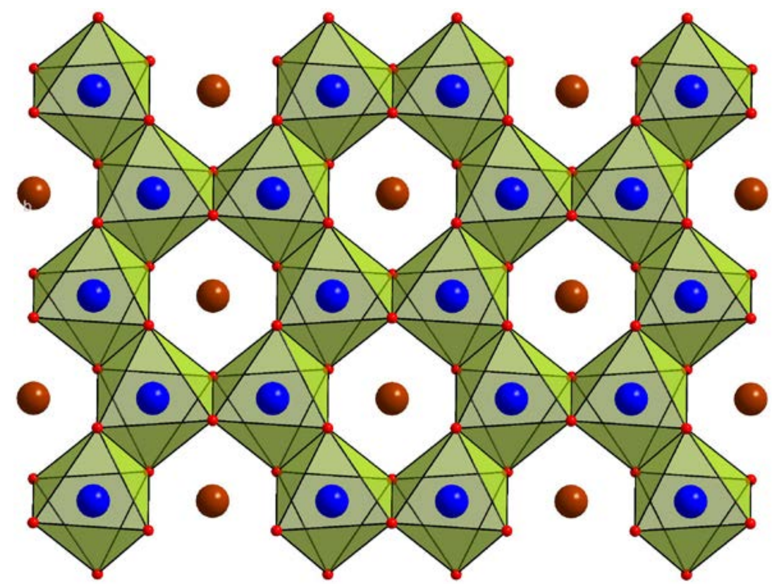
$LiCoO_2$

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





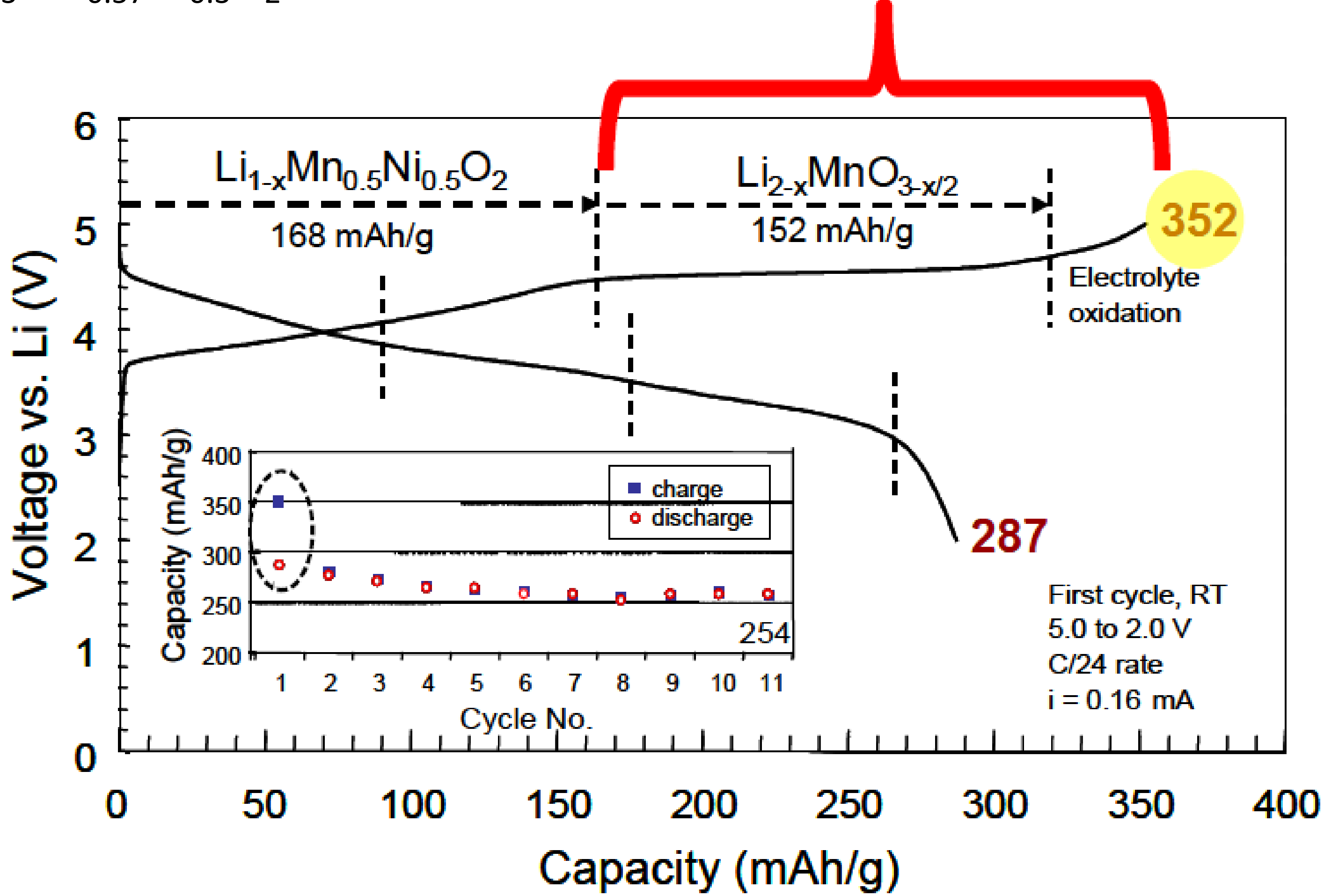
$Li_{1+y}(Ni,Mn,Co)_{1-y}O_2$



High capacity layered cathodes: 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

High capacity layered cathodes

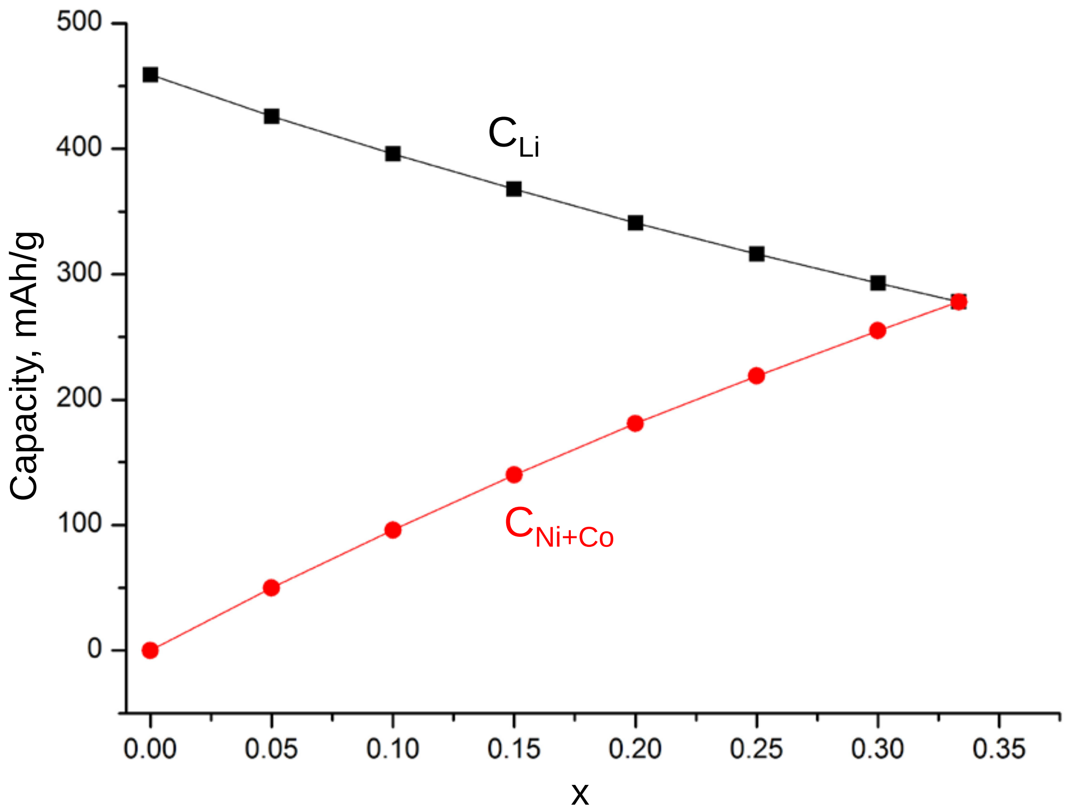
$Li_{4/3-x}Ni^{2+}_{x}Mn^{4+}_{2/3-x}Co^{3+}_{x}O_2$

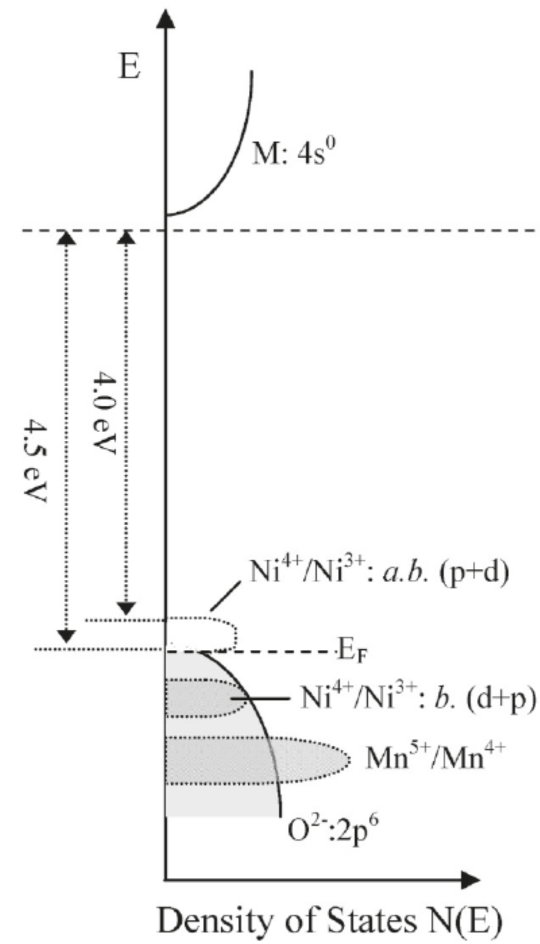
$Ni^{2+} \rightarrow Ni^{3+}, Ni^{4+}$

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

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

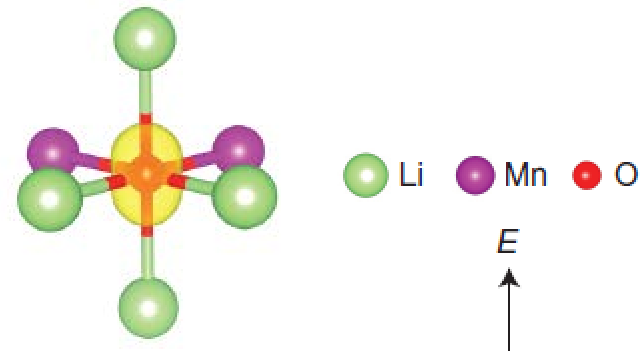
Mn^{4+}/Mn^{5+} redox couple is inaccessible

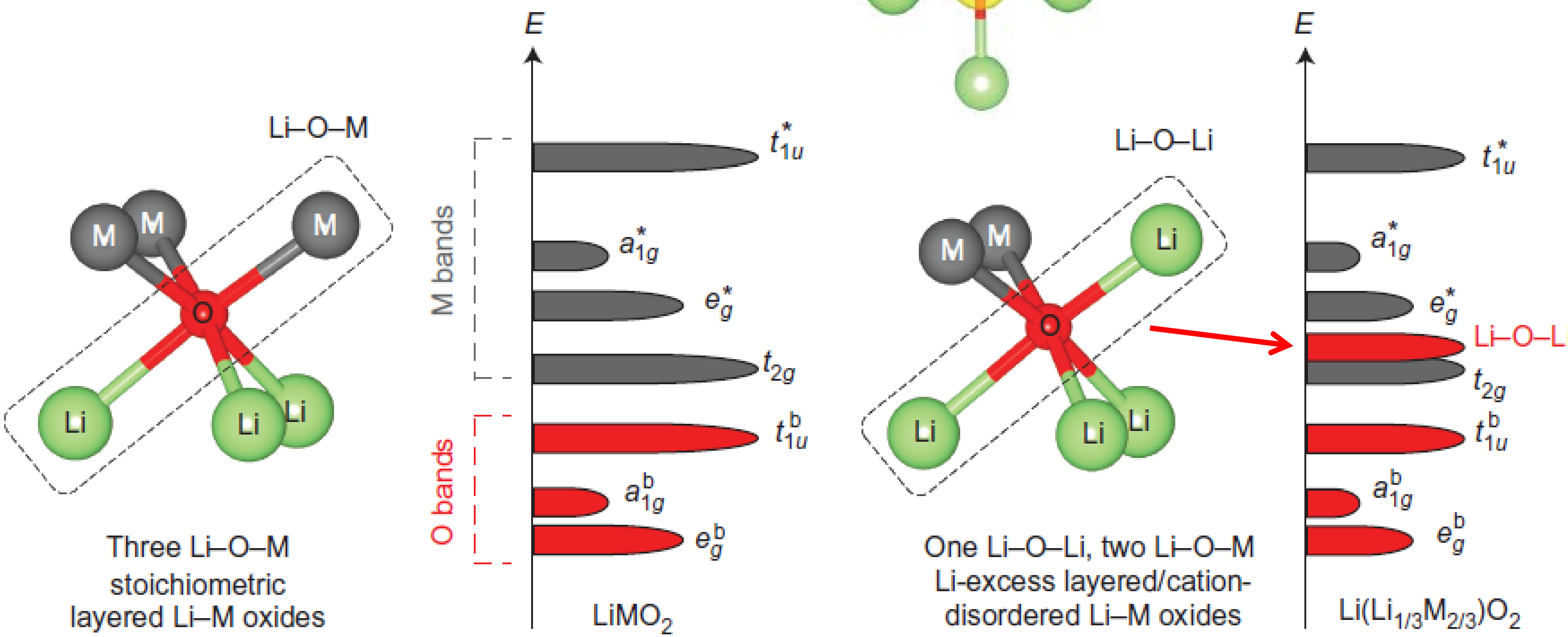




Mechanism: orphaned Li-O-Li O2p orbitals

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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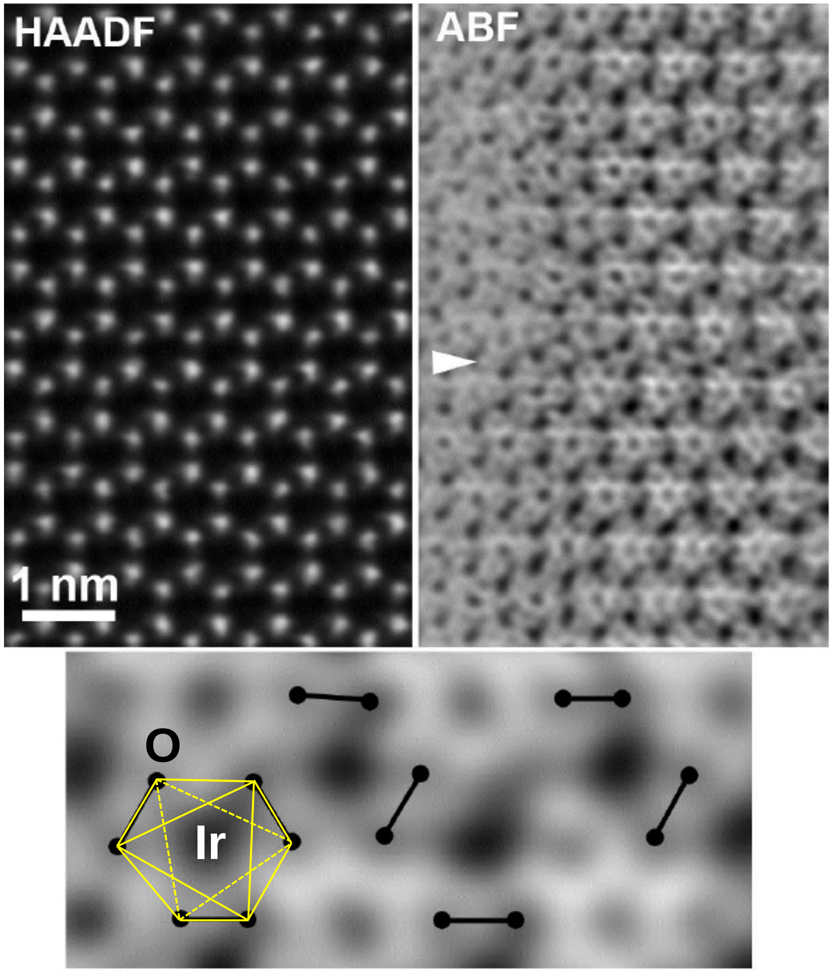
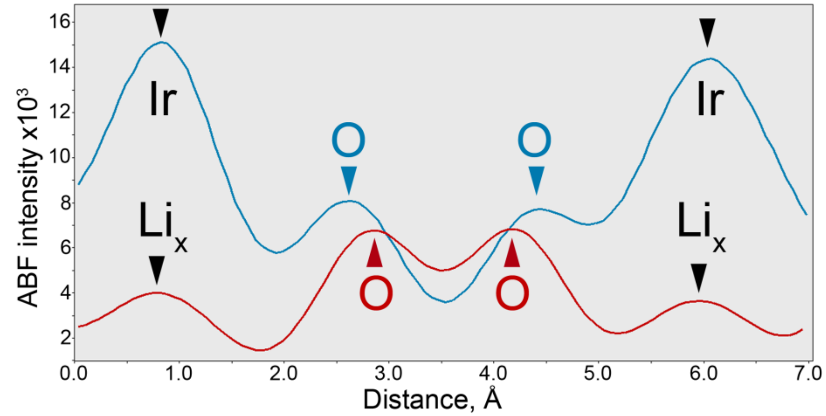
Anionic redox and oxygen evolution

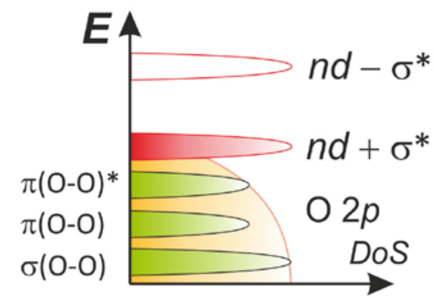


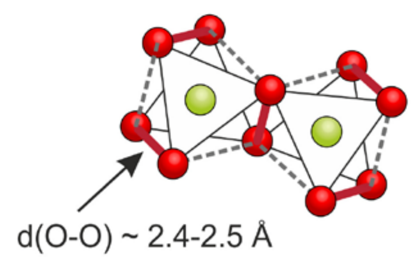
STEM on Li_2IrO_3 charged to 4.5V



Projected O-O distances from ABF-STEM:

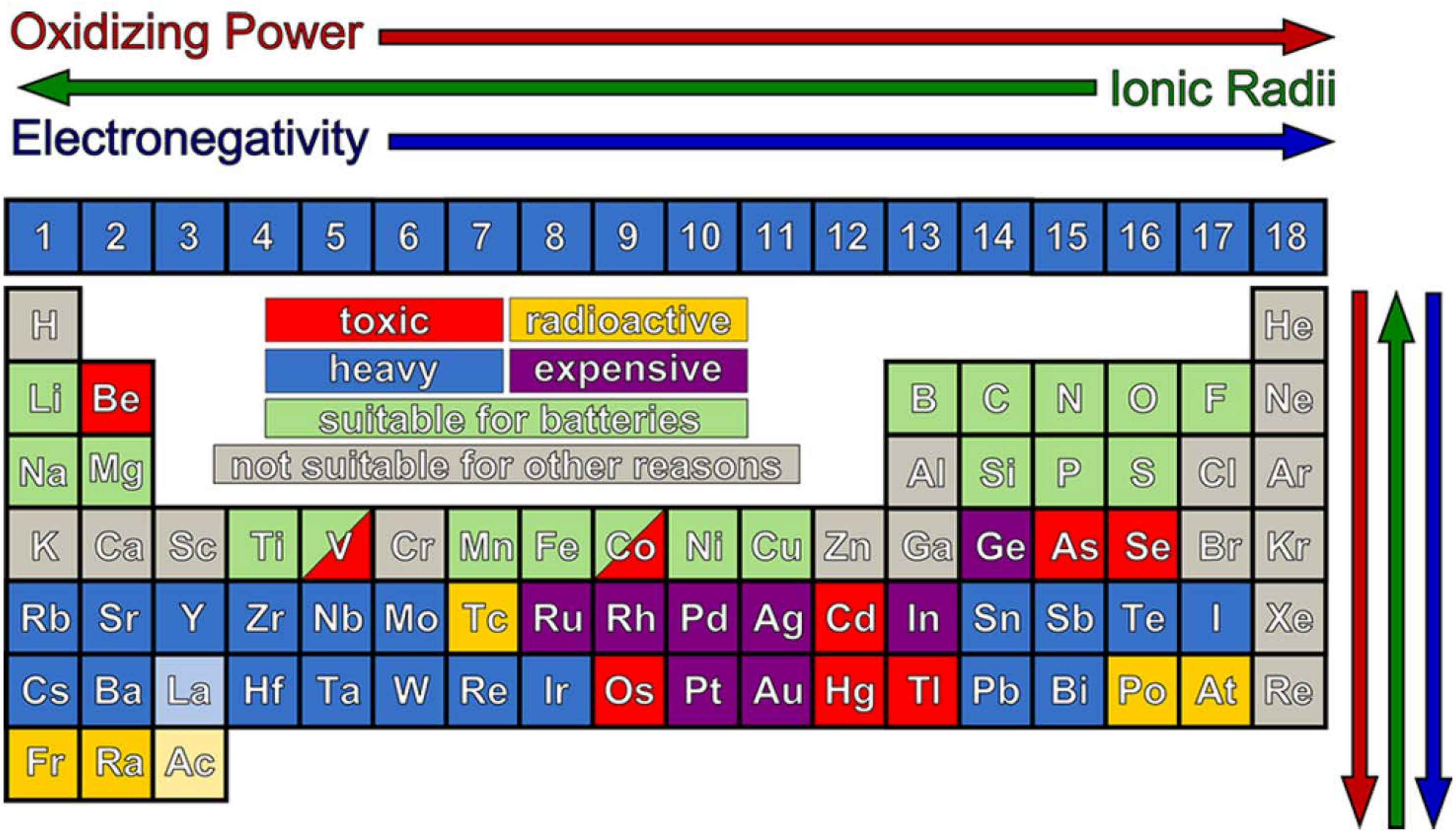
short: 1.56(1)Å long: 1.83(1) Å





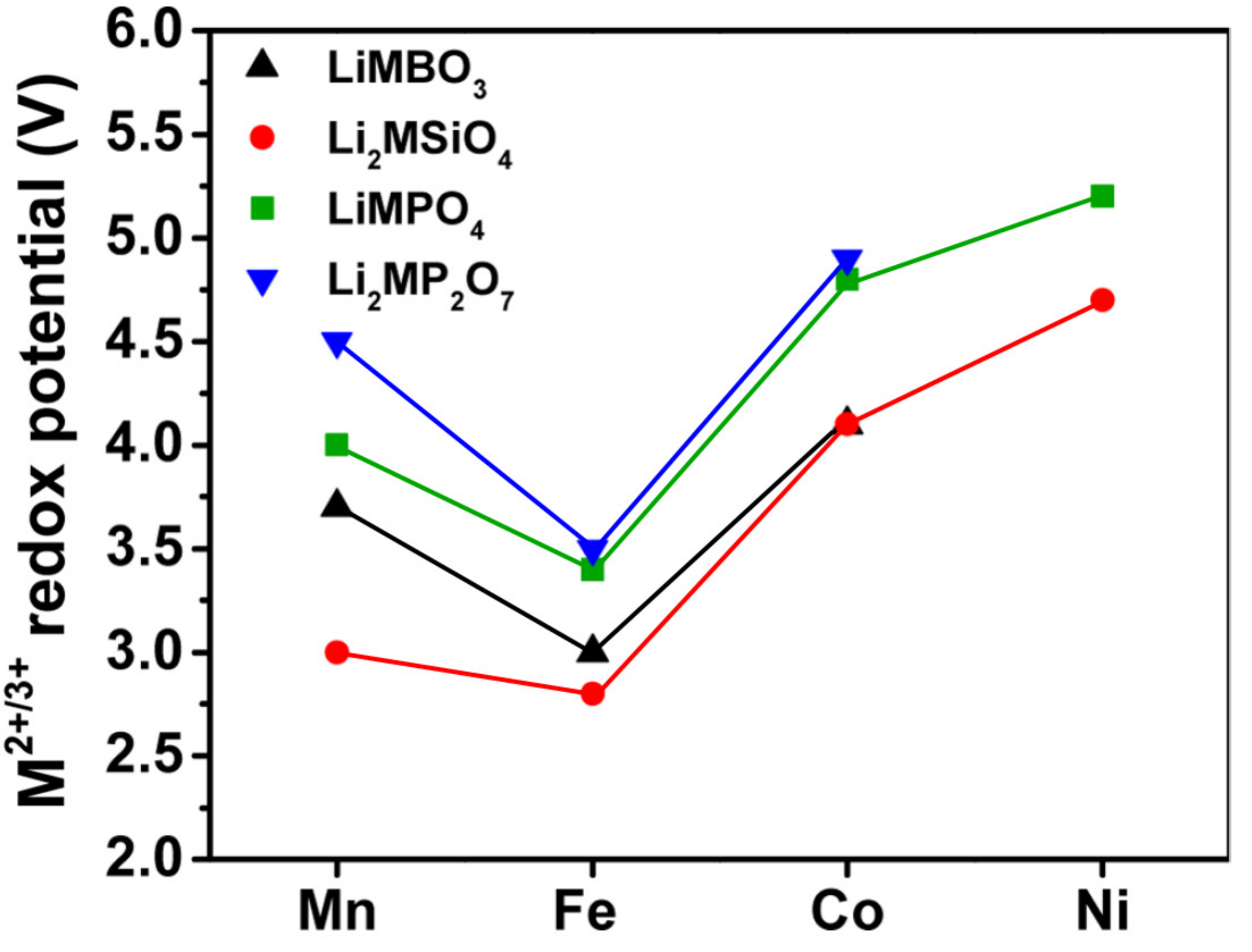
McCalla, Abakumov, Saubanère, Foix, Berg, Rousse, Doublet, Gonbeau, Novák, Van Tendeloo, Dominko, Tarascon, *Science*, 2015, 350,1516

Redox potential of the $M^{n+}/M^{(n+1)+}$ pairs



B.C.Melot, J.-M.Tarascon, Acc. Chem. Res., 2013, 46, 1226

Redox potential of the $M^{n+}/M^{(n+1)+}$ pairs



Adapted from A.Gutierrez, N.A.Benedek, A.Manthiram, Chem. Mater. 2013, 25, 4010

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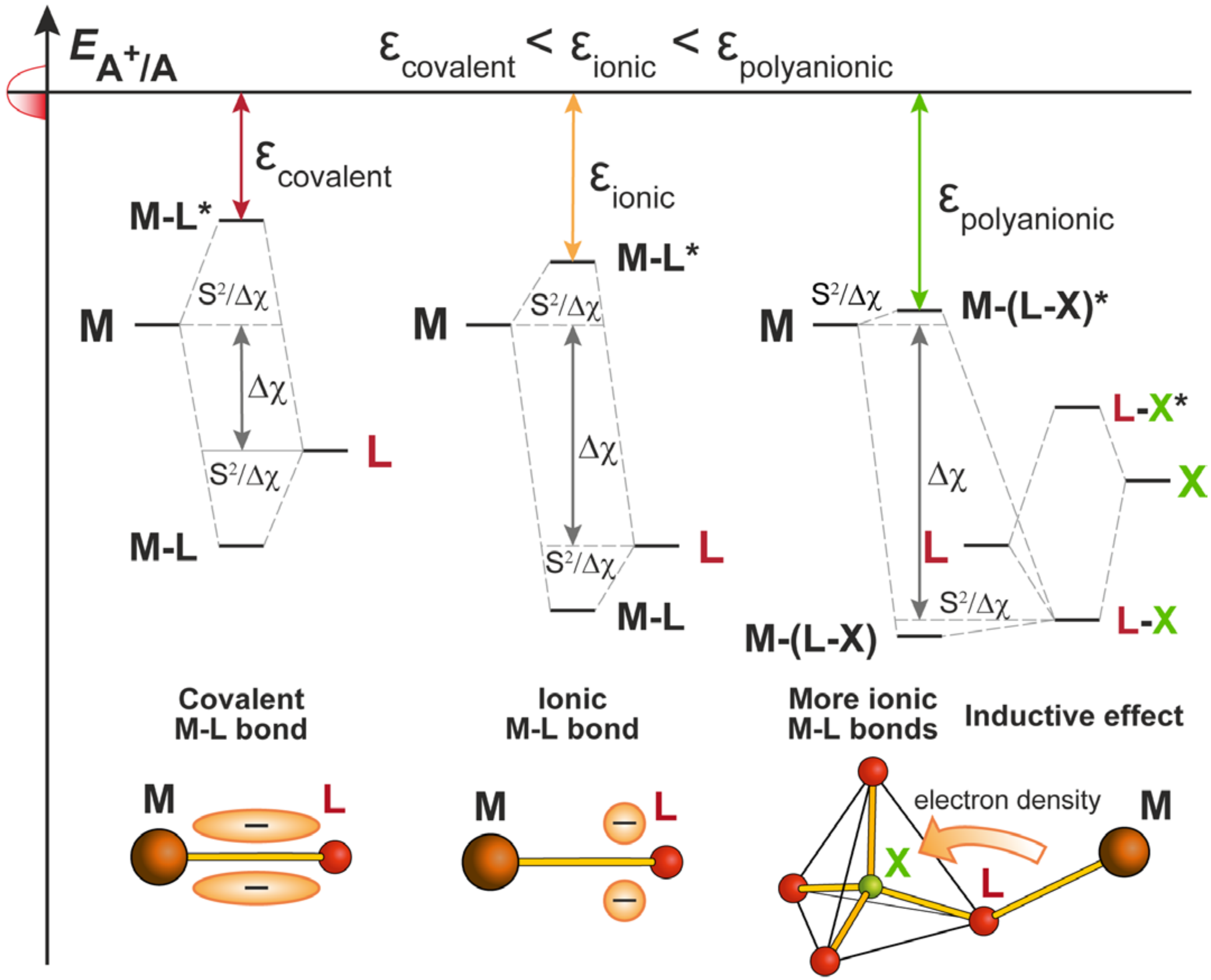
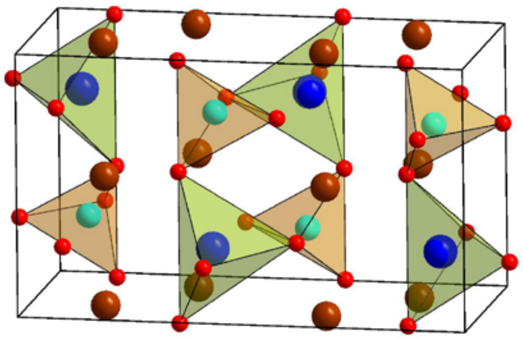
Covalency *vs* ionicity



Abakumov, Fedotov, Antipov, Tarascon, *Nature Comm.*, 11, 4976 (2020)

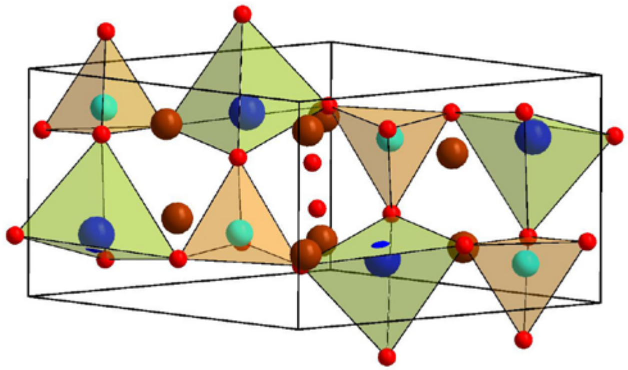
Covalency *vs* ionicity

Li_2FeSiO_4 polymorphs



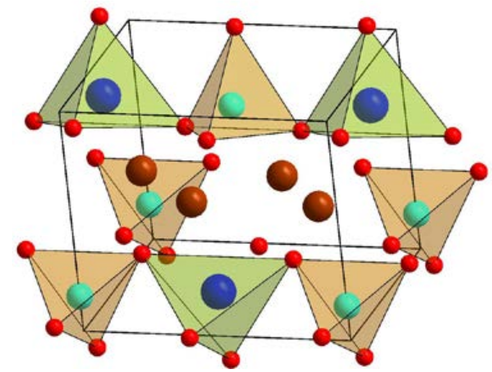
Pnmb

d_{av}(Fe-O) = 2.025Å



$P2_1/n$

d_{av}(Fe-O) = 2.035Å



$Pnm2_1$

d_{av}(Fe-O) = 2.076Å

increasing Fe-O bond covalency ←

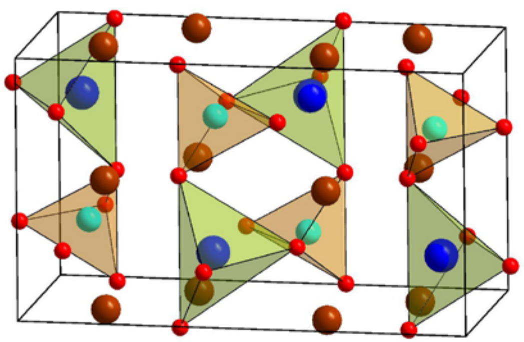
increasing Fe^{2+}/Fe^{3+} redox potential →

~ 2.9V | ~ 3.0V | ~ 3.1V

Covalency *vs* ionicity

Li_2FeSiO_4

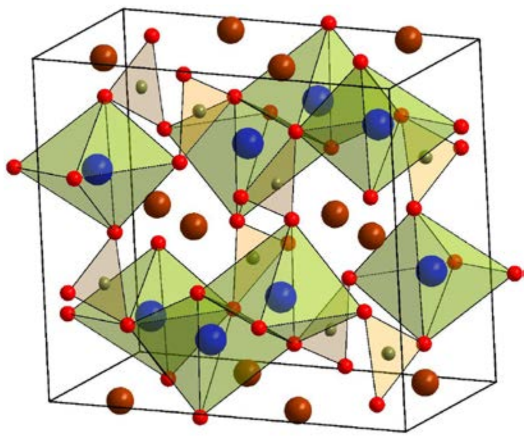
CN(Fe) = 4



d_{av}(Fe-O) = 2.025Å

$LiFeBO_3$

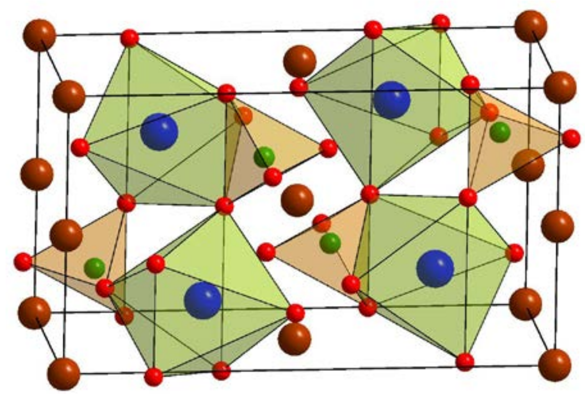
CN(Fe) = 5



d_{av}(Fe-O) = 2.092Å

$LiFePO_4$

CN(Fe) = 6



d_{av}(Fe-O) = 2.160Å

increasing Fe-O bond covalency ←

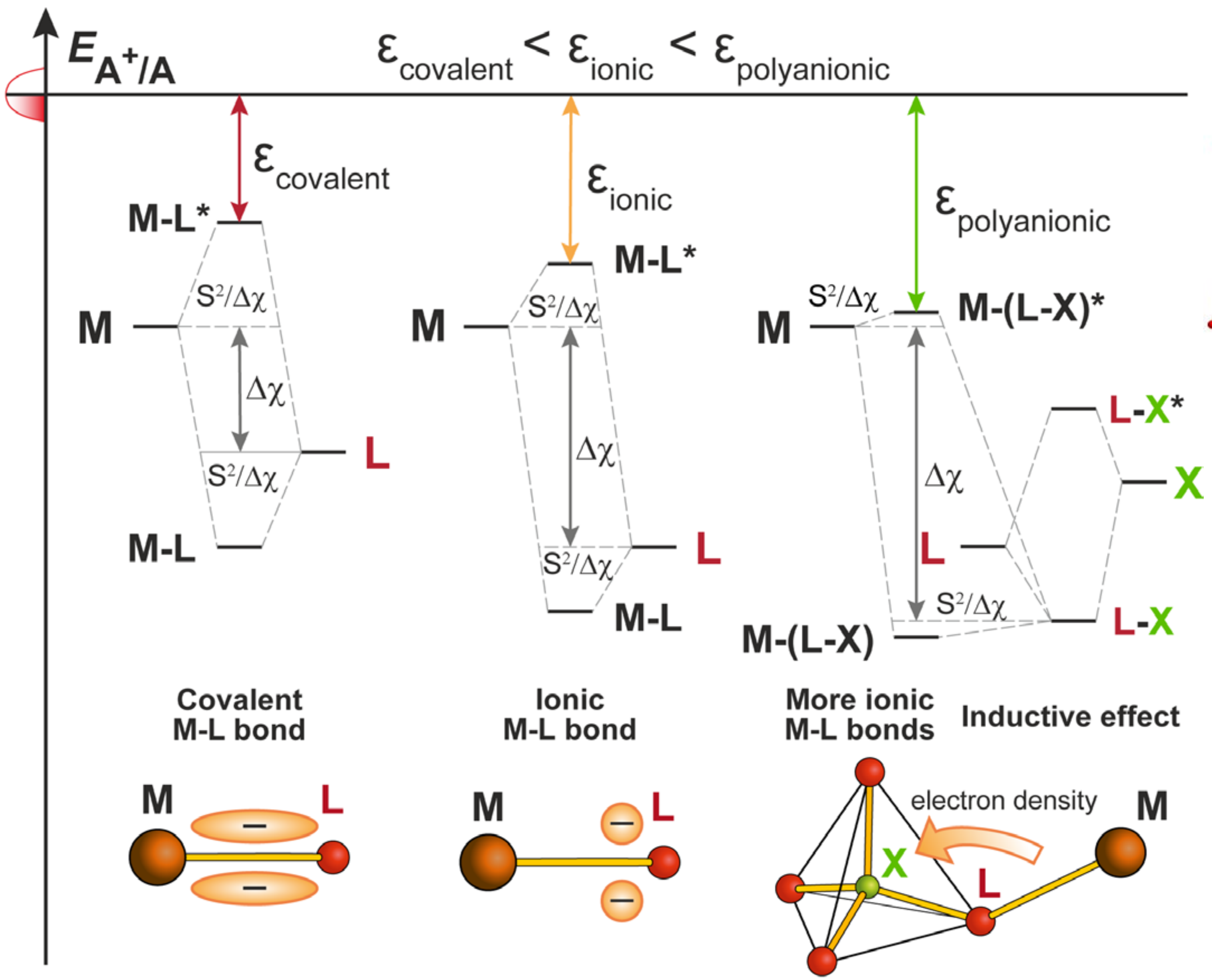
increasing Fe^{2+}/Fe^{3+} redox potential →

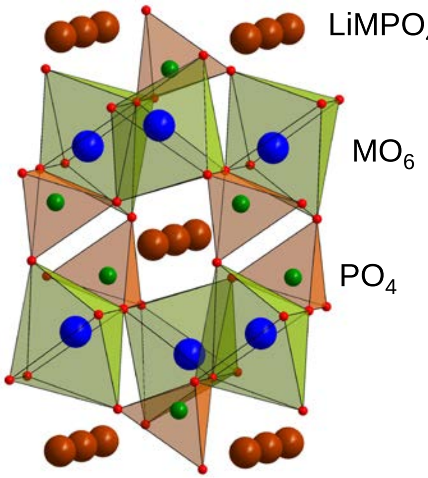
~ 2.9V

~ 3.0V

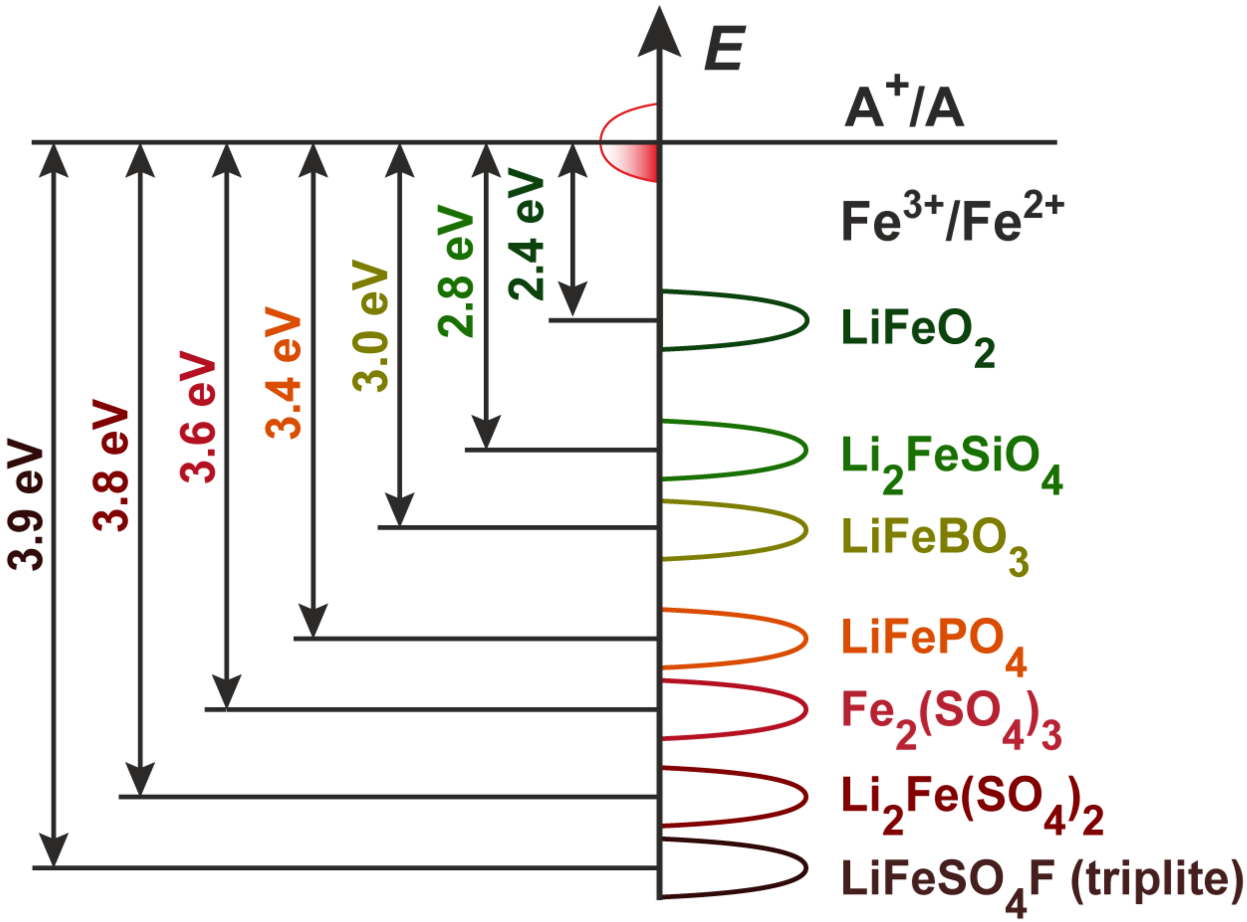
~ 3.4V

Inductive effect





Inductive effect



Abakumov, Fedotov, Antipov, Tarascon, *Nature Comm.*, 11, 4976 (2020)

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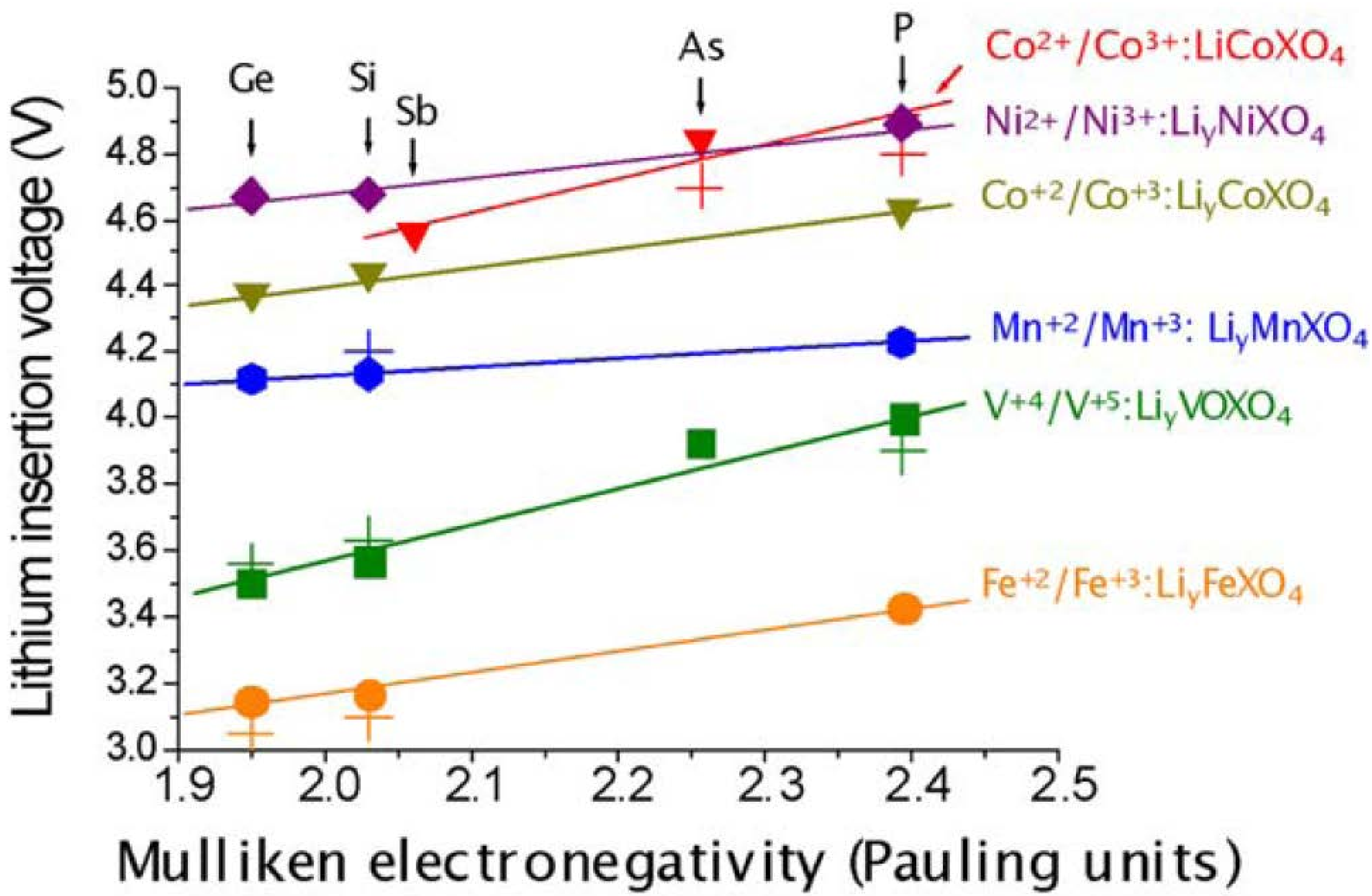
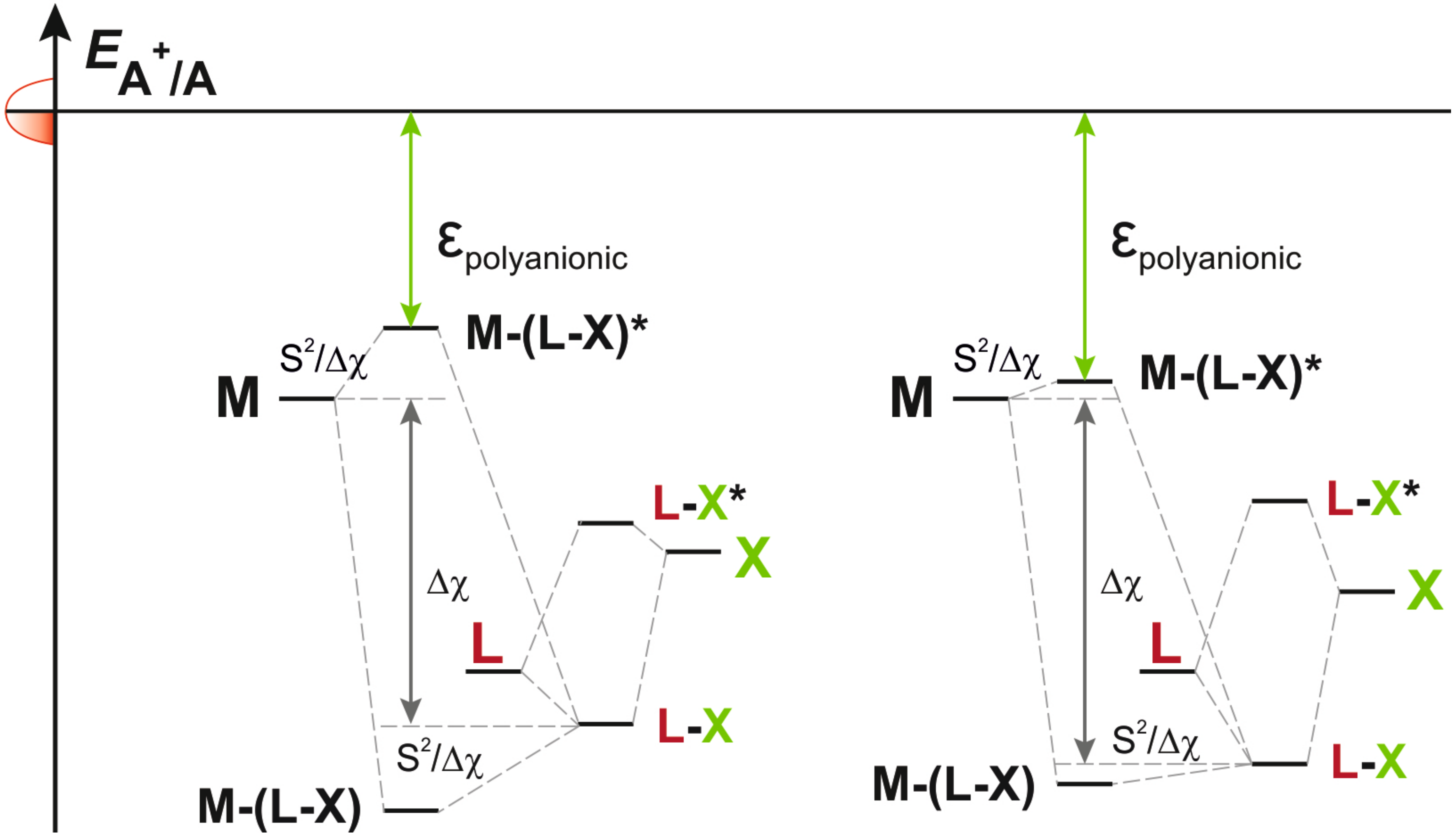
Inductive effect



M.E.Arroyo-de Dompablo, M.Armand, J.M.Tarascon , U.Amador, , Electrochem. Comm. 8 (2006) 1292–1298

Inductive effect

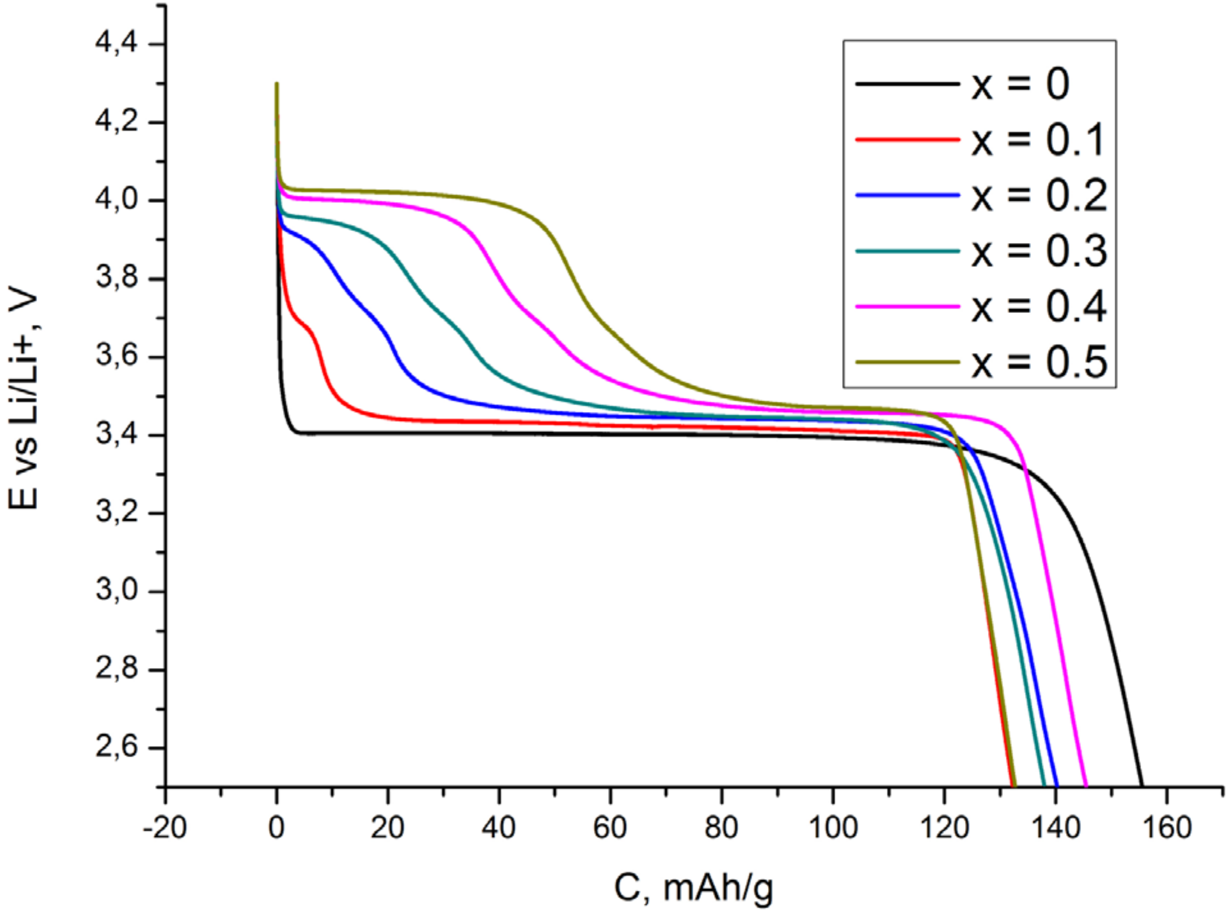


Electronic configuration

$LiFePO_4$
580 Wh/kg

$LiFe_{0.5}Mn_{0.5}PO_4$
640 Wh/kg

$LiMnPO_4$
700 Wh/kg



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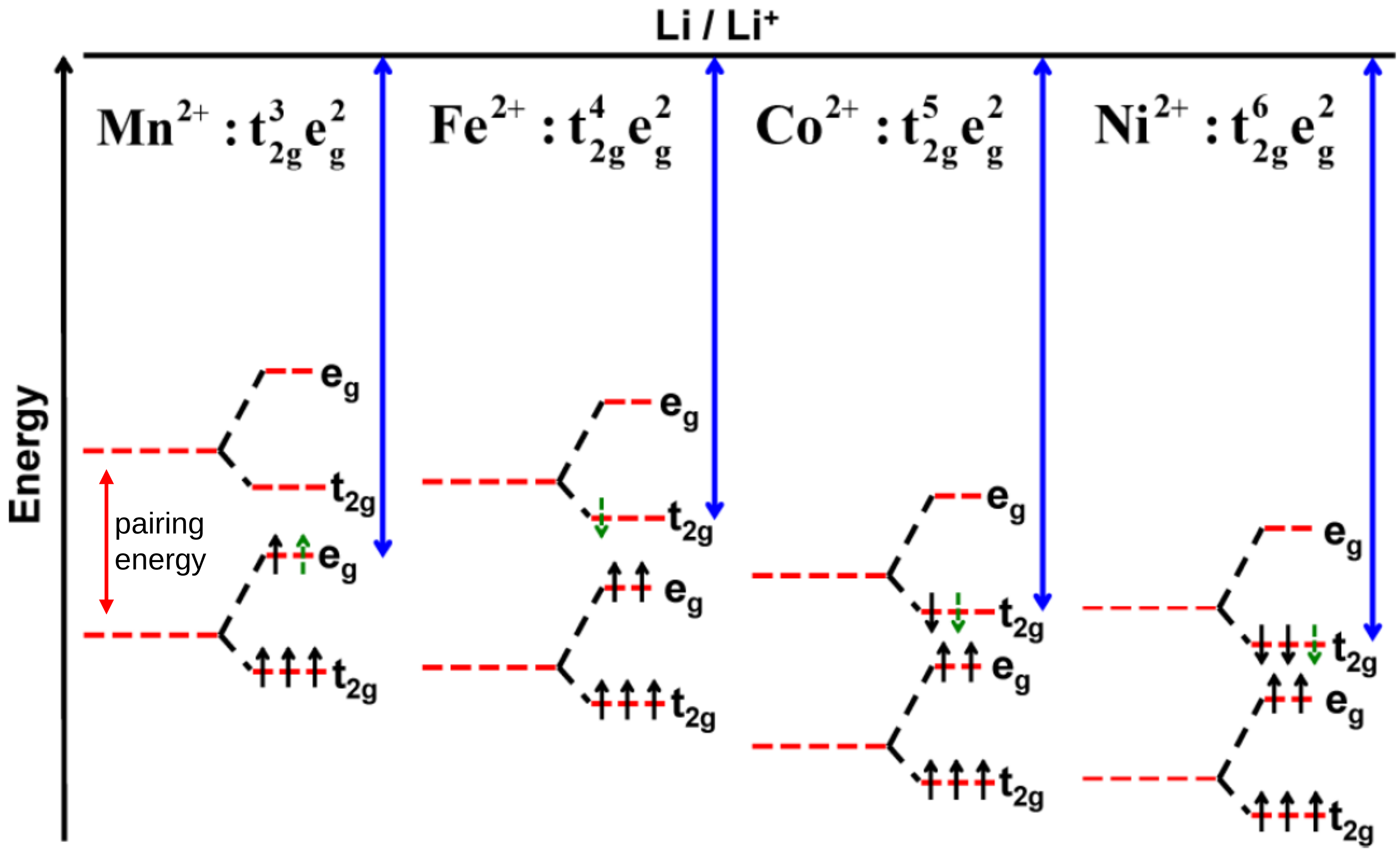
Electronic configuration



A.Gutierrez, N.A.Benedek, A.Manthiram, Chem. Mater. 2013, 25, 4010

Thank you for your attention!