# Crystal structure, electronic structure, chemical bonding and defects in metal-ion battery materials

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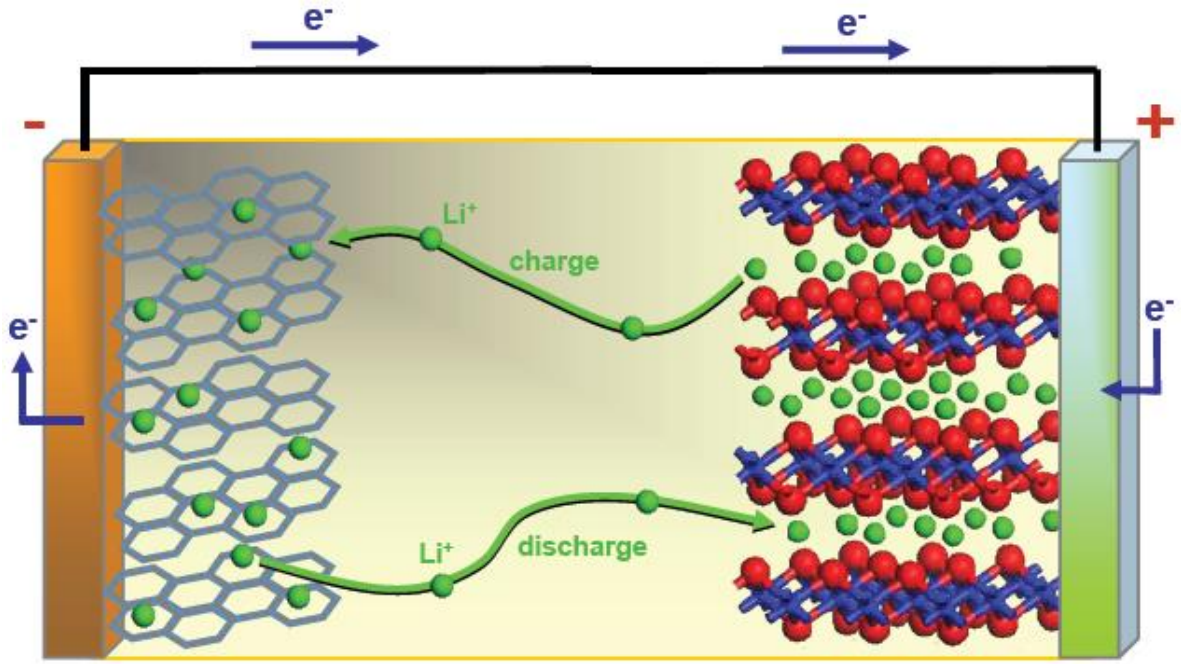
# Li-ion batteries




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

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

Voltage 3.6 V, x ≈ 0.5-0.6 $e^-$

Electrolyte:
Li-salt - $LiPF_6$, $LiBF_4$ ($LiClO_4$, $LiAsF_6$), $LiCF_3SO_3$
Solvent – ethylene carbonate $(CH_2O)_2C$, dimethyl carbonate $(CH_3O)_2CO$ ….

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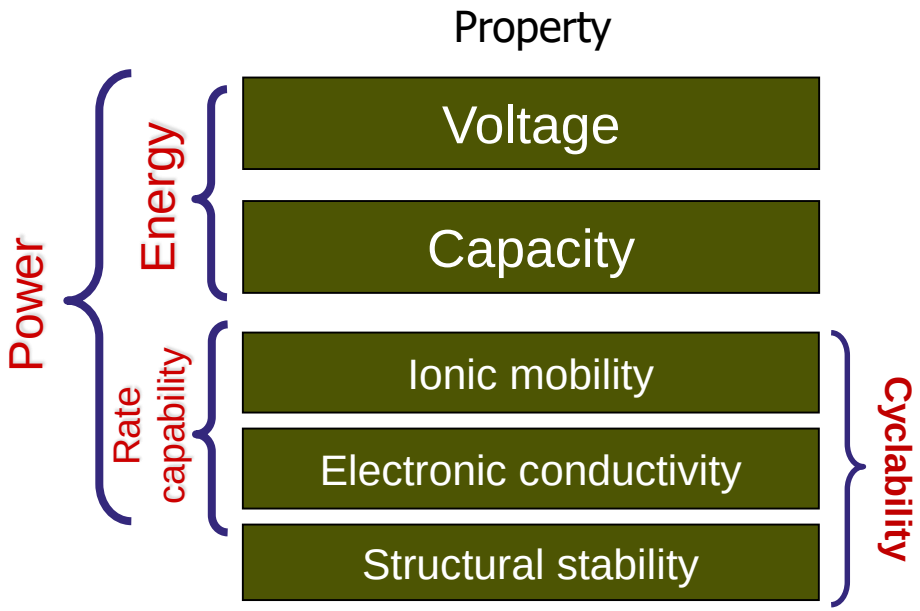
# Cathode materials: key properties




$M^{n+}/M^{(n+1)+}$ redox potential

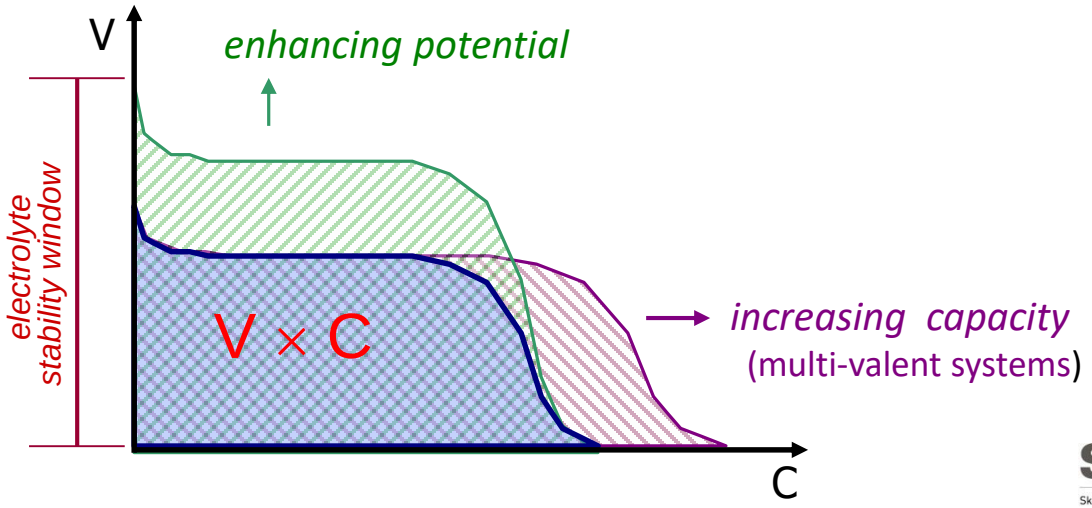
$$C_T\,(A\ h\ g^{-1}) = \frac{26.8 \times \Delta n}{M}$$

$\Delta n$: number of $e^-$ or $Li^+$

$M$: Molecular weight (g)

Energy = Voltage x Capacity

≤ 4.8 V (vs. $Li/Li^+$)

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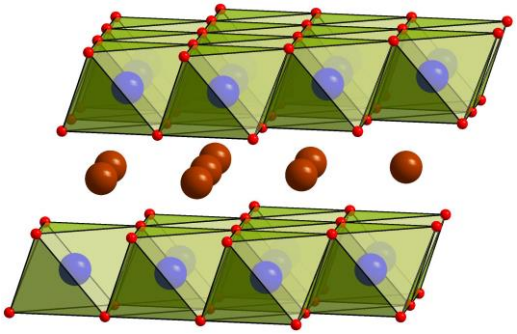
# Cathode materials

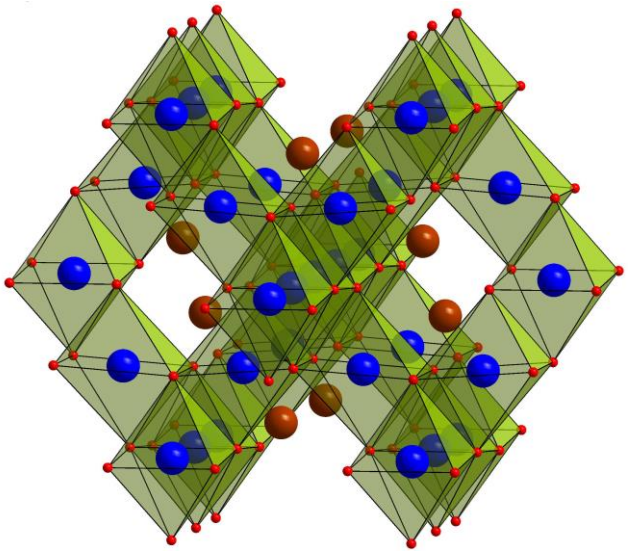
| Cathode | LCO | LNO | NCA | NMC | LMO | LFP |
|---|---|---|---|---|---|---|
| Formula | $LiCoO_2$ | $LiNiO_2$ | $LiNi_{0.85}Co_{0.1}Al_{0.05}O_2$ | $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ | $LiMn_2O_4$ | $LiFePO_4$ |
| Average potential vs $Li^+/Li$, V | 3.7 | 3.6 | 3.65 | 3.9 | 4.0 | 3.5 |
| Capacity, mA h/g | ~150 | ~180 | ~130 | ~170 | ~110 | ~150 |
| Specific energy, W·h/kg | ~550 | ~650 | ~480 | ~660 | ~440 | ~500 |
| Power | + | 0 | + | 0 | + | + |
| Safety | - | 0 | 0 | 0 | + | ++ |
| Life time | - | 0 | + | 0 | 0 | + |
| Cost | -- | + | 0 | 0 | + | + |

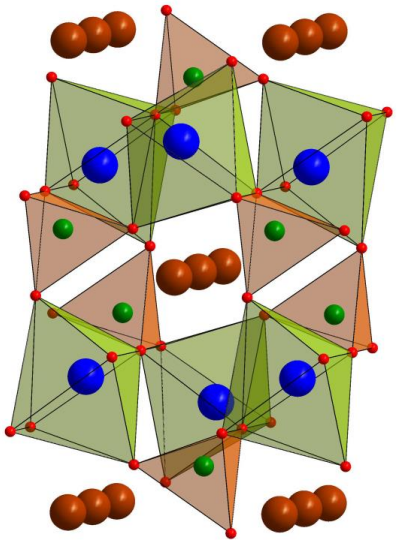
# Cathode materials

Complex oxides

Polyanion compounds







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

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

$LiFePO_4$

2D Li transport

3D Li transport

1D Li transport

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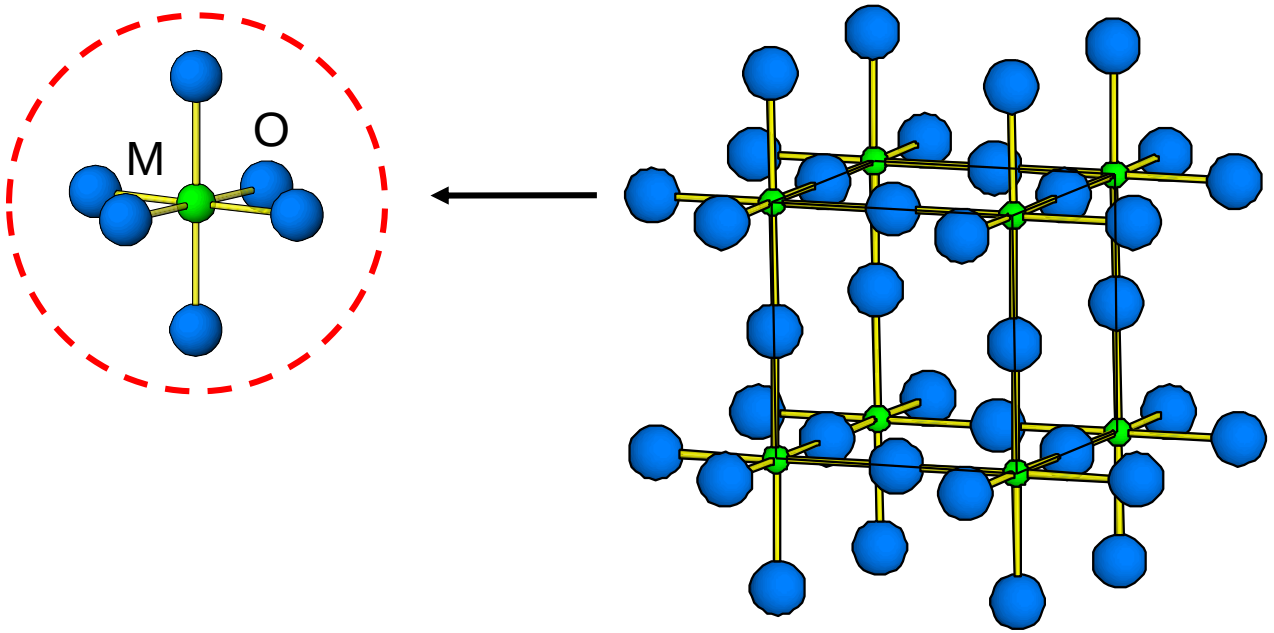
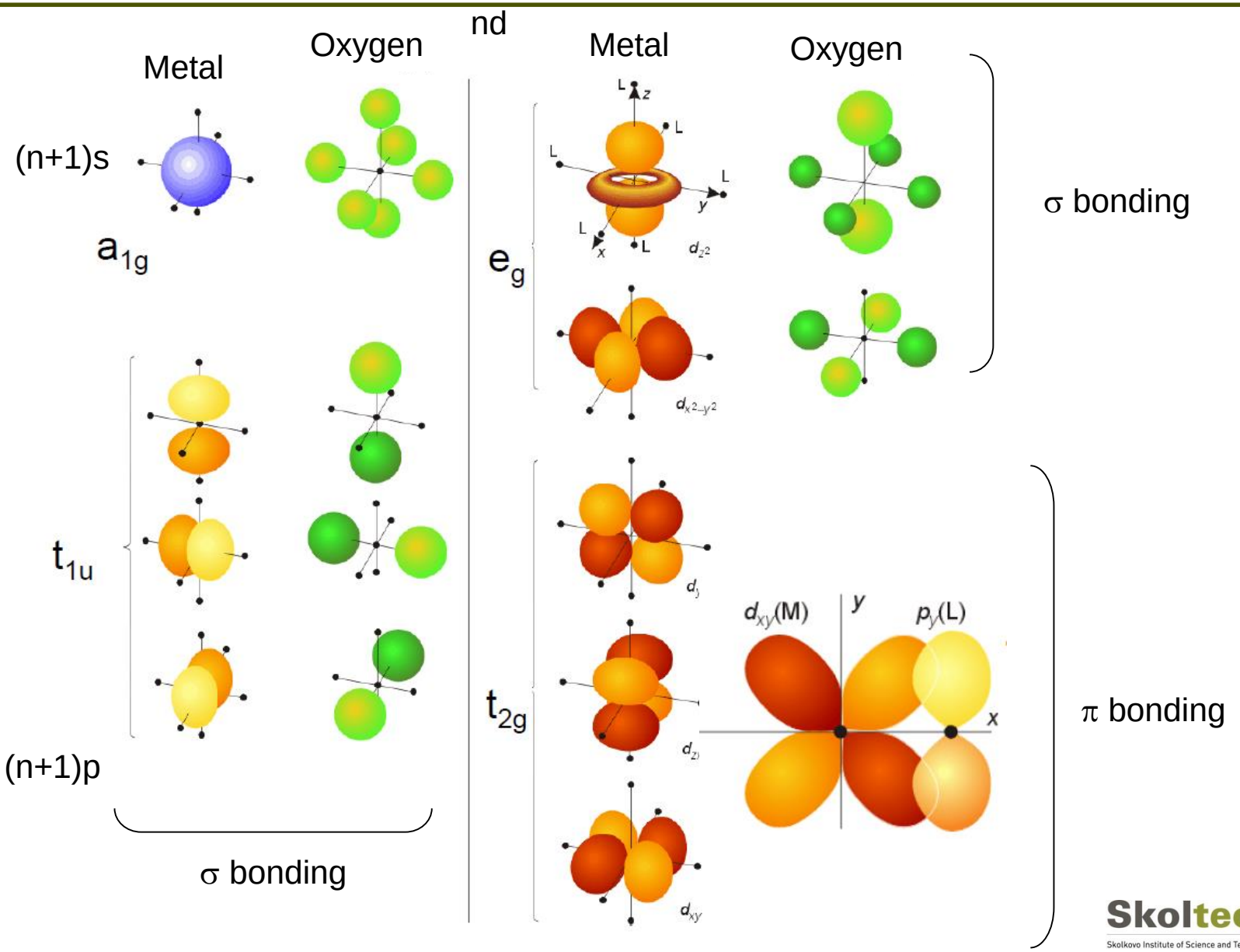
# Bonding in oxides

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

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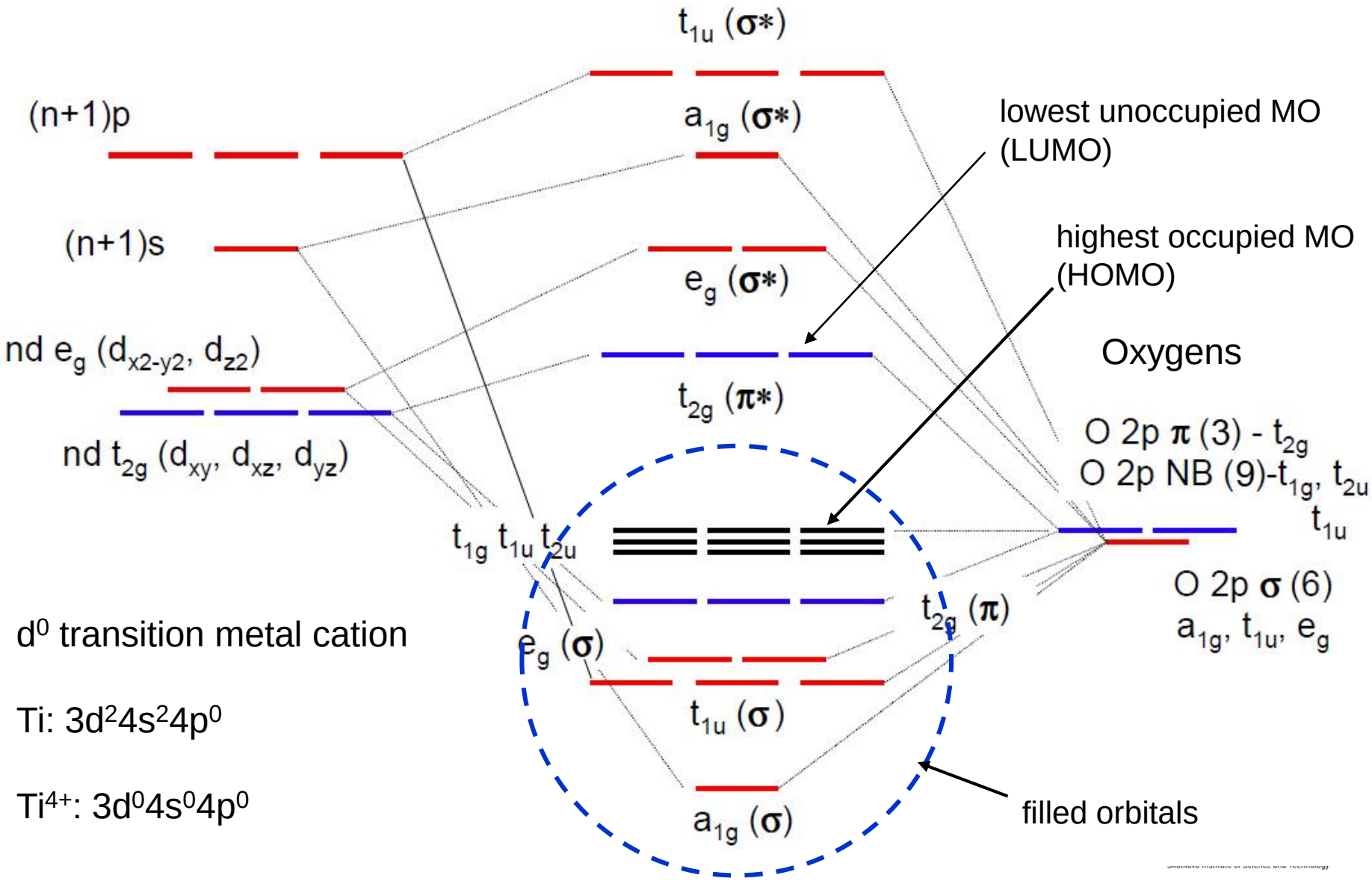
# $BO_6^{n-}$ octahedron: MO diagram

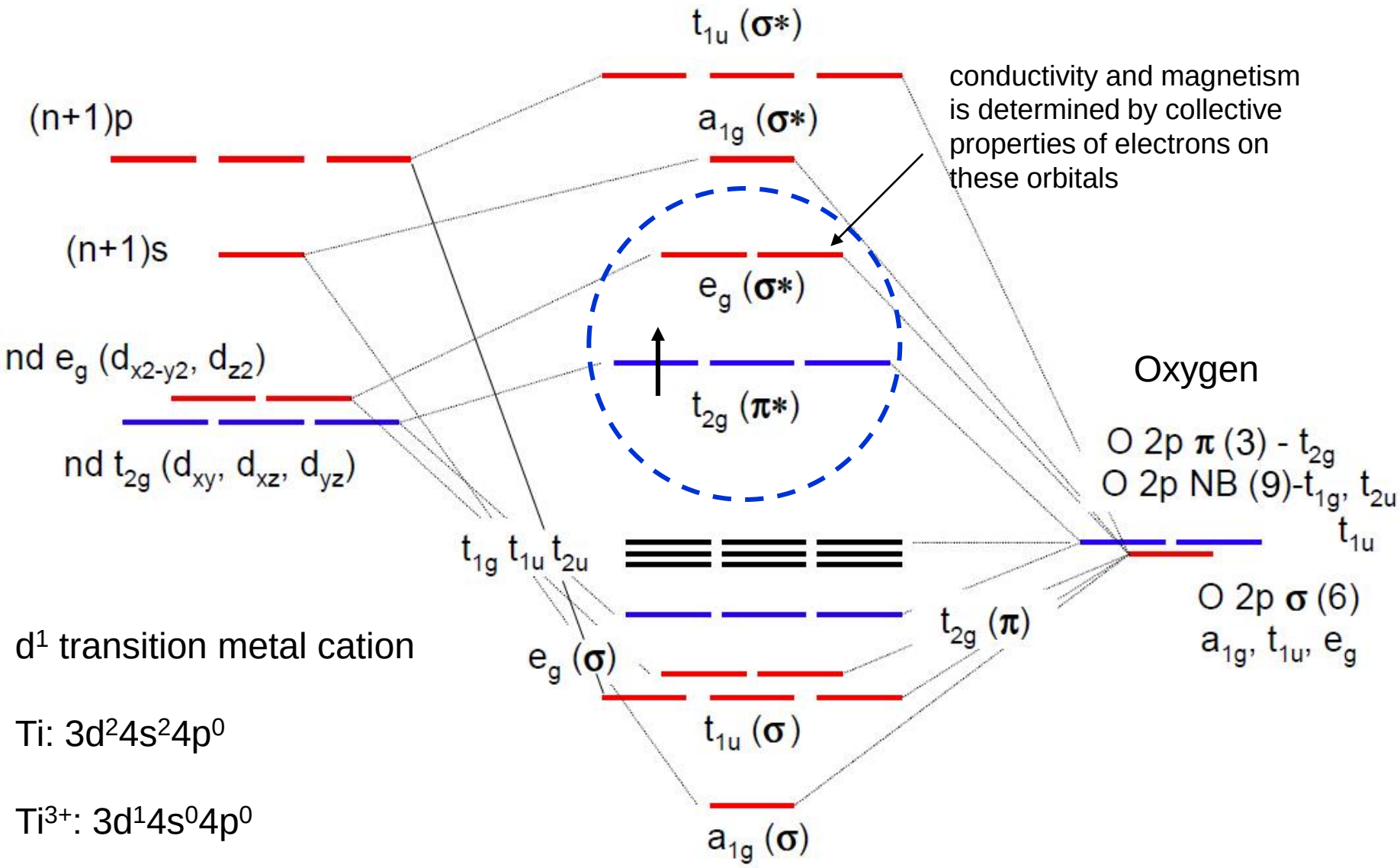



$d^0$ transition metal cation

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

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

# $BO_6^{n-}$ octahedron: MO diagram

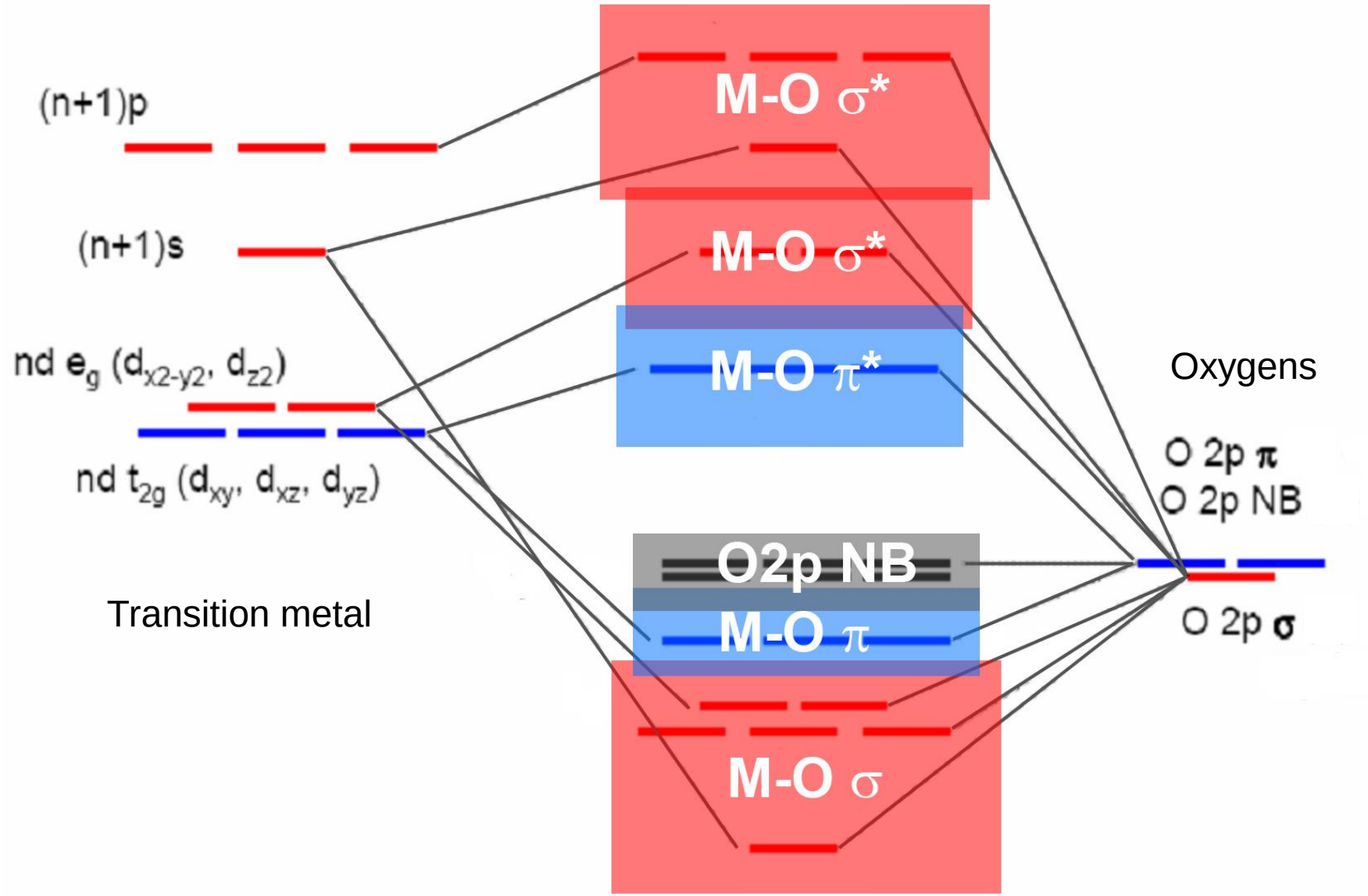



$d^1$ transition metal cation

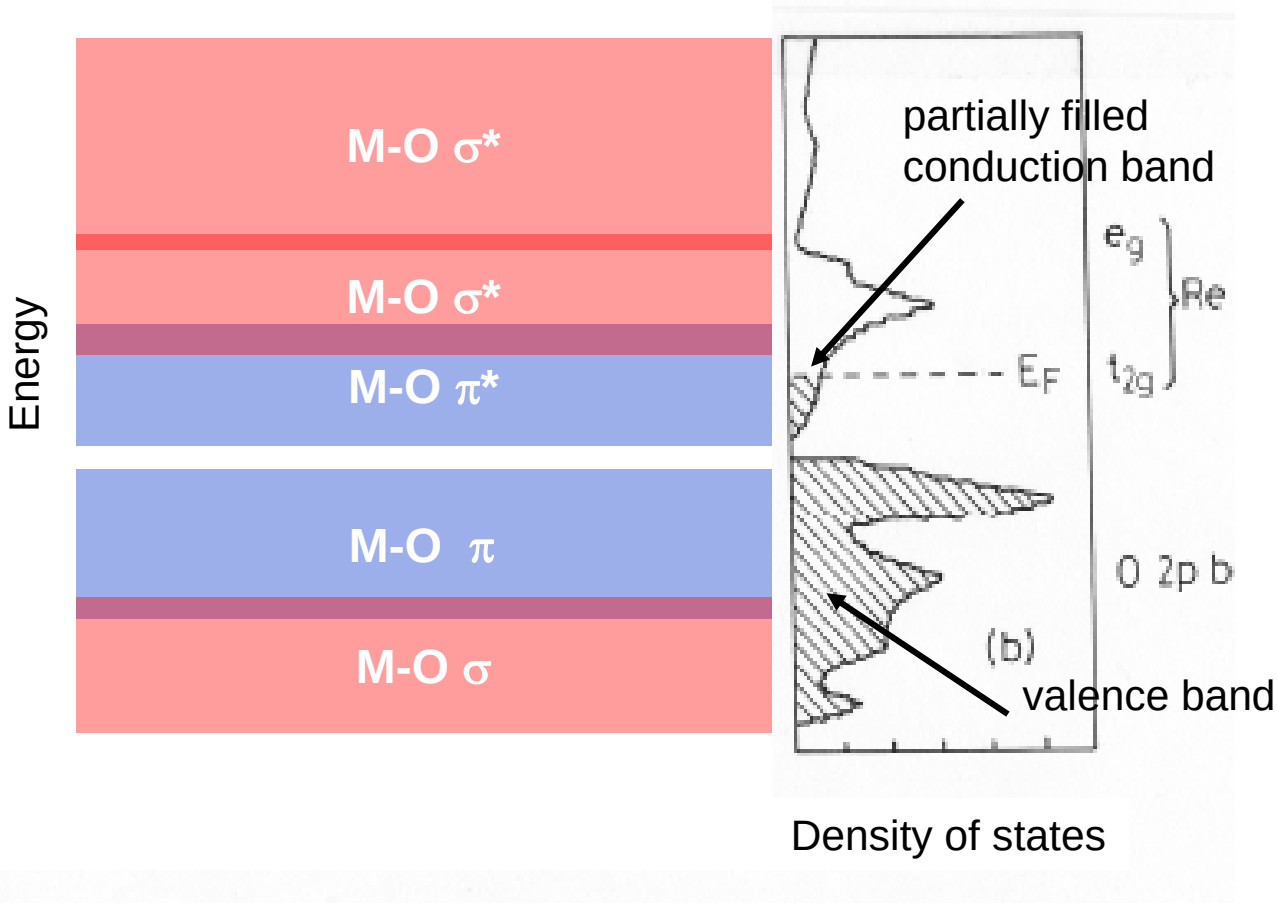
Ti: $3d^2 4s^2 4p^0$

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

# Simplified band structure

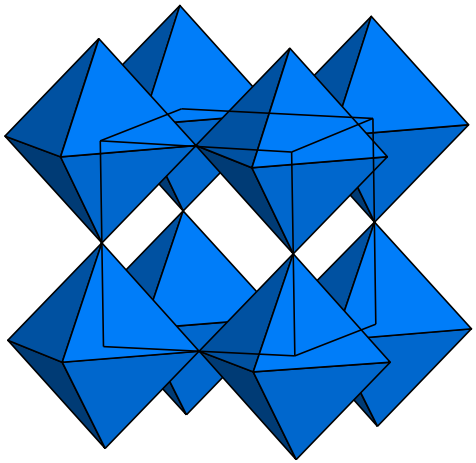


# $ReO_3$: band structure

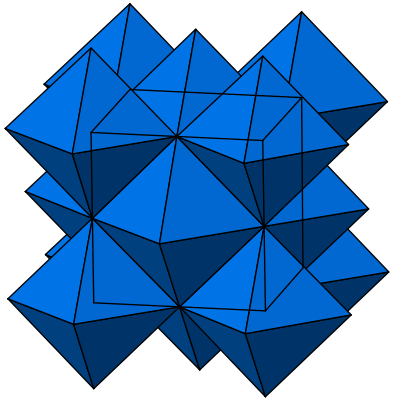



Density of states

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



# NiO: metal or insulator?



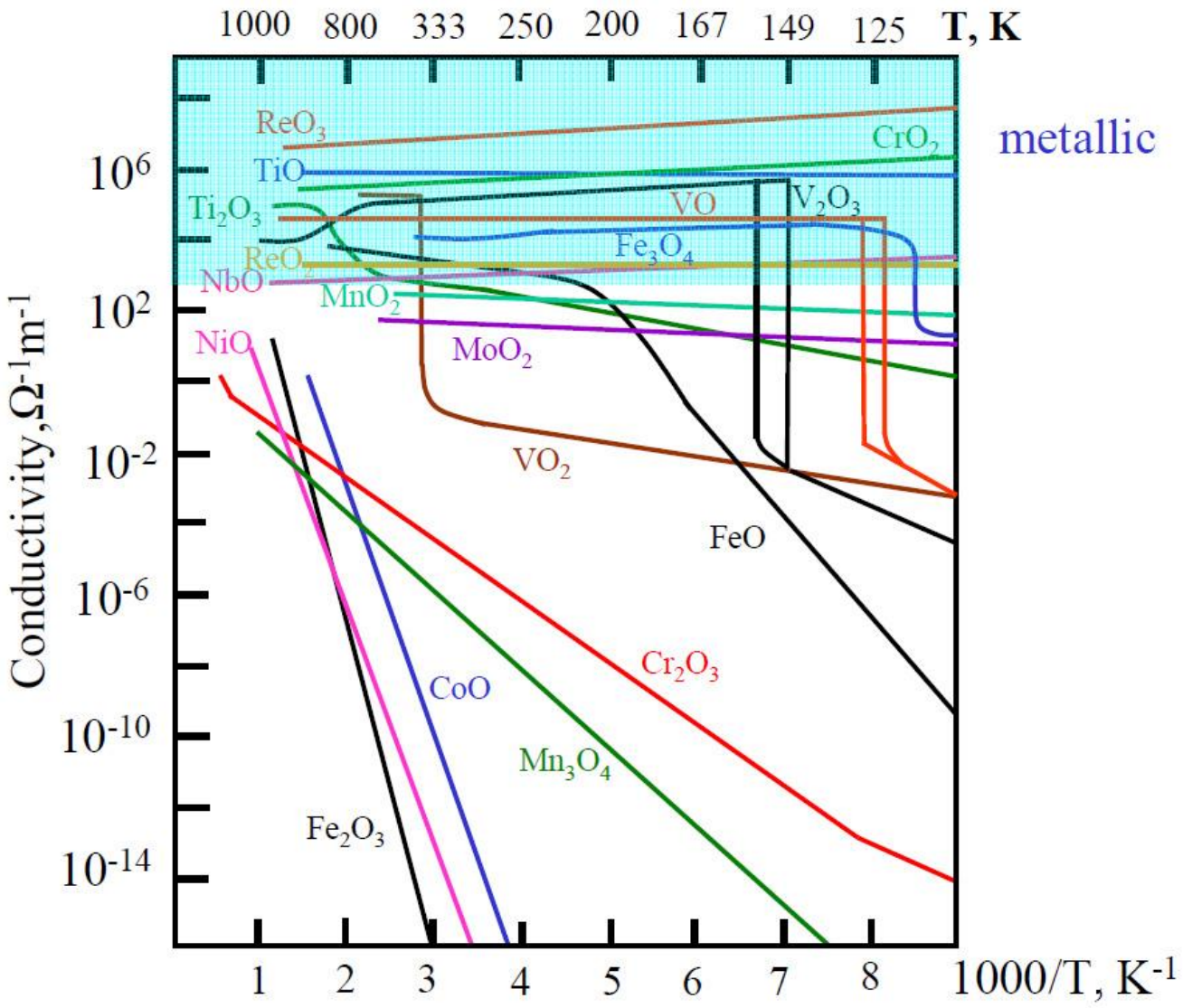
NiO: rock salt structure




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

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

# NiO: metal or insulator?

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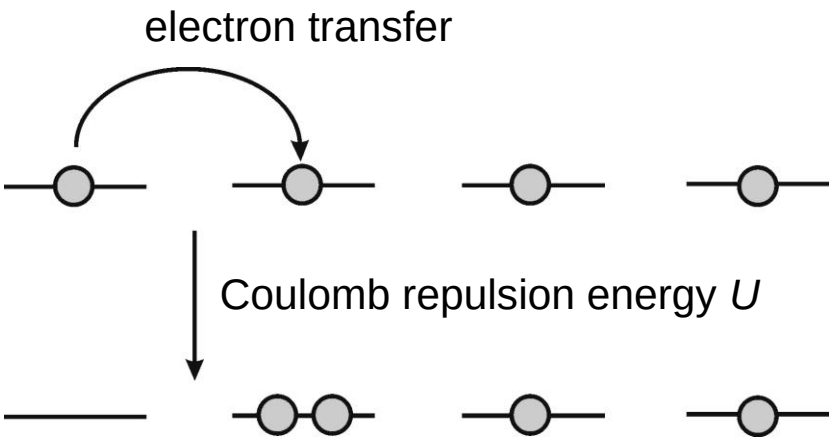
# Mott-Hubbard insulators

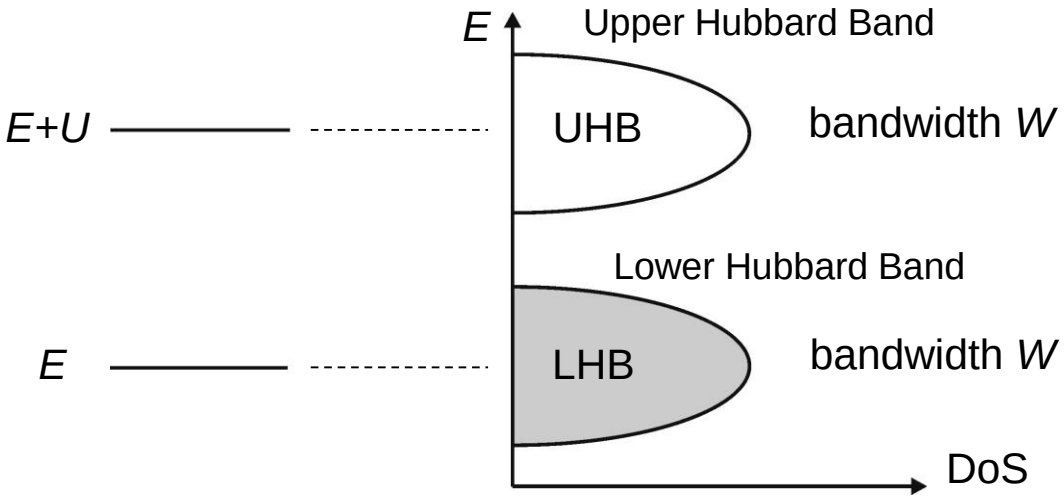



$Ni^{2+} + Ni^{2+} \rightarrow Ni^{3+} + Ni^{+}$

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

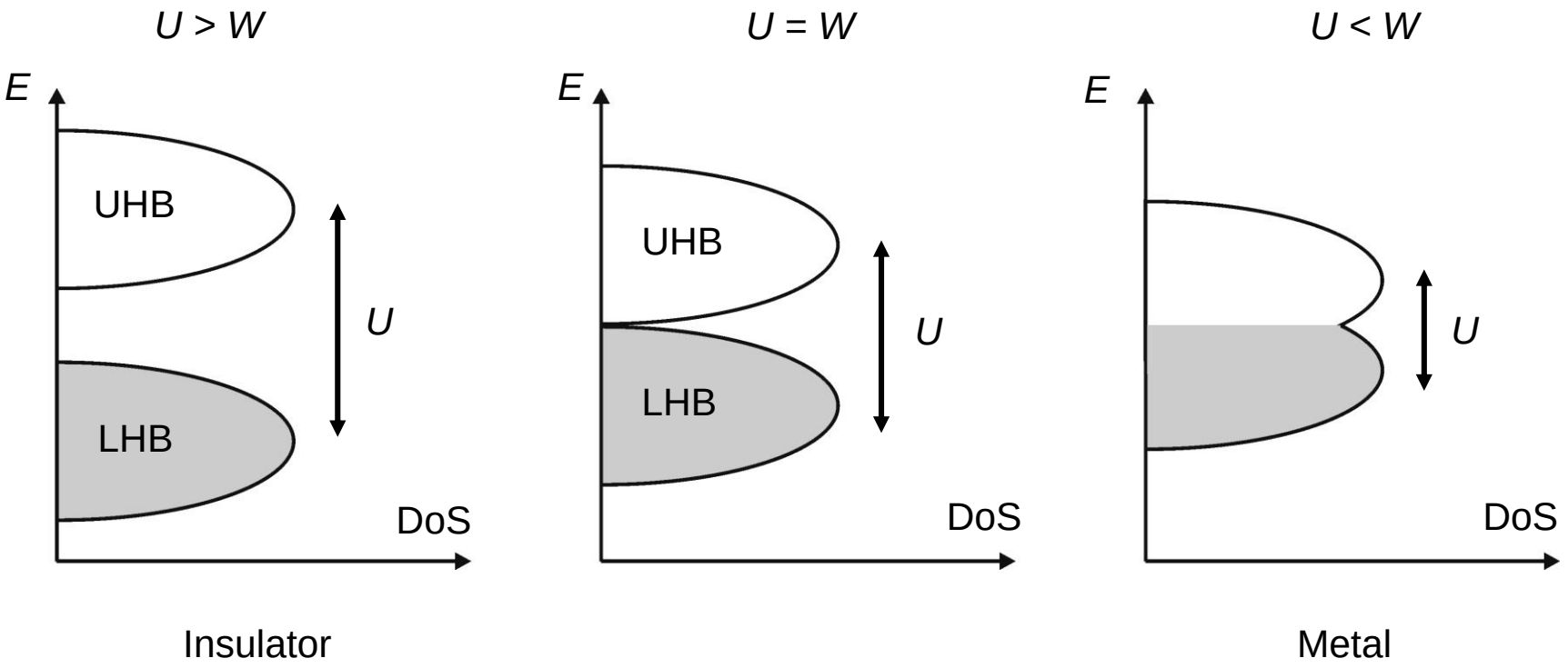
Two competing trends:

- 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




Insulator

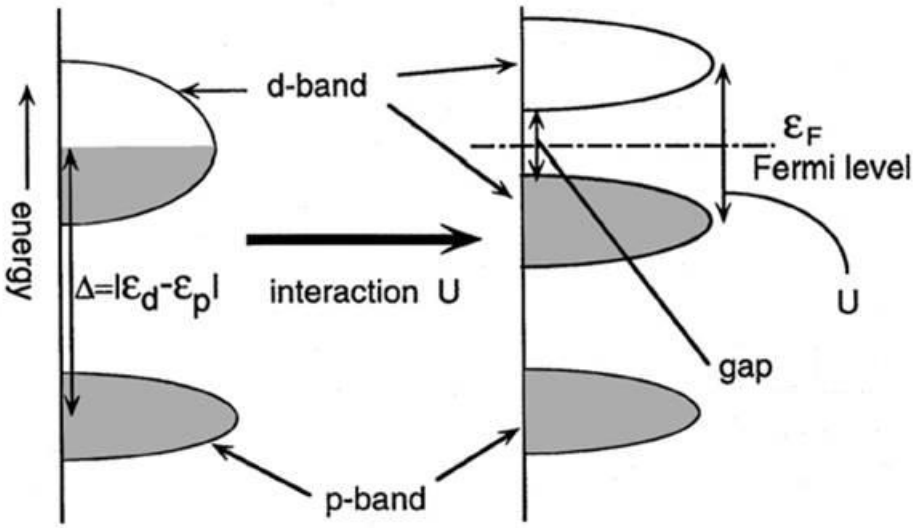
Metal

# 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) $\Delta$

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

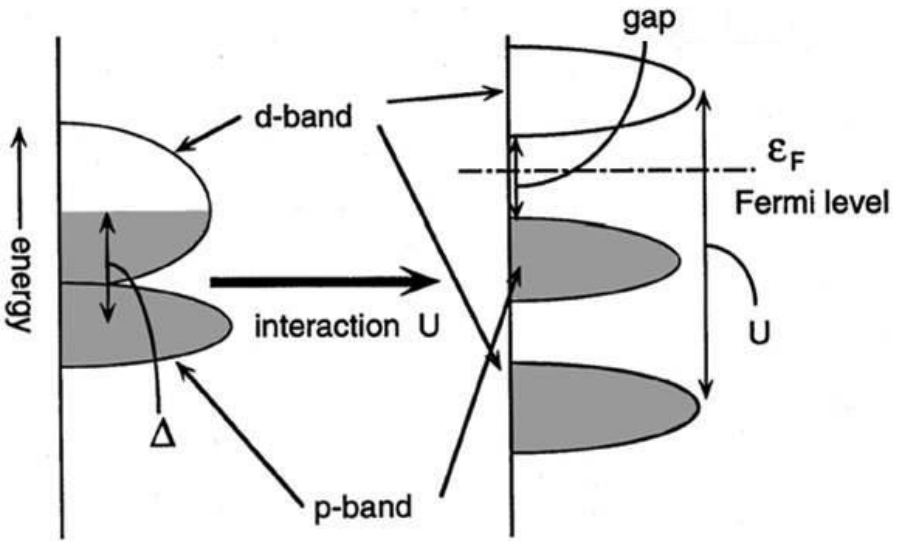
Mott-Hubbard regime




$U < \Delta$, 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

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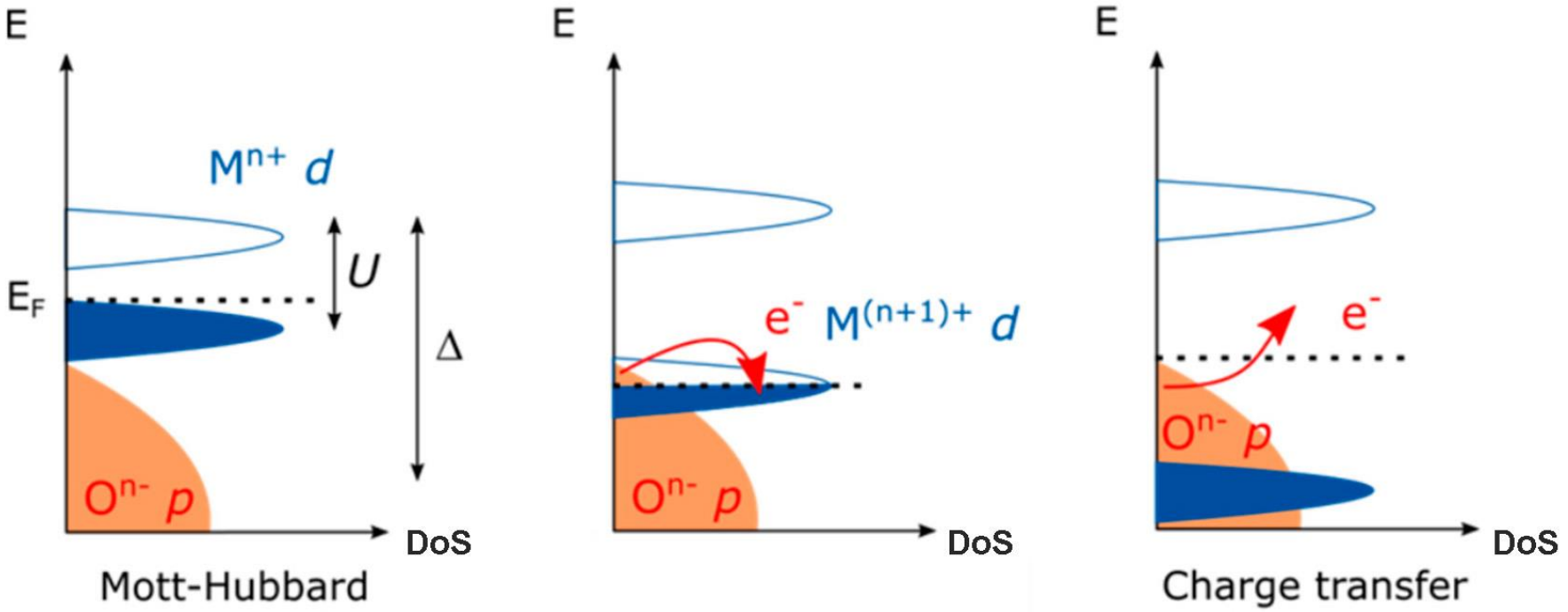
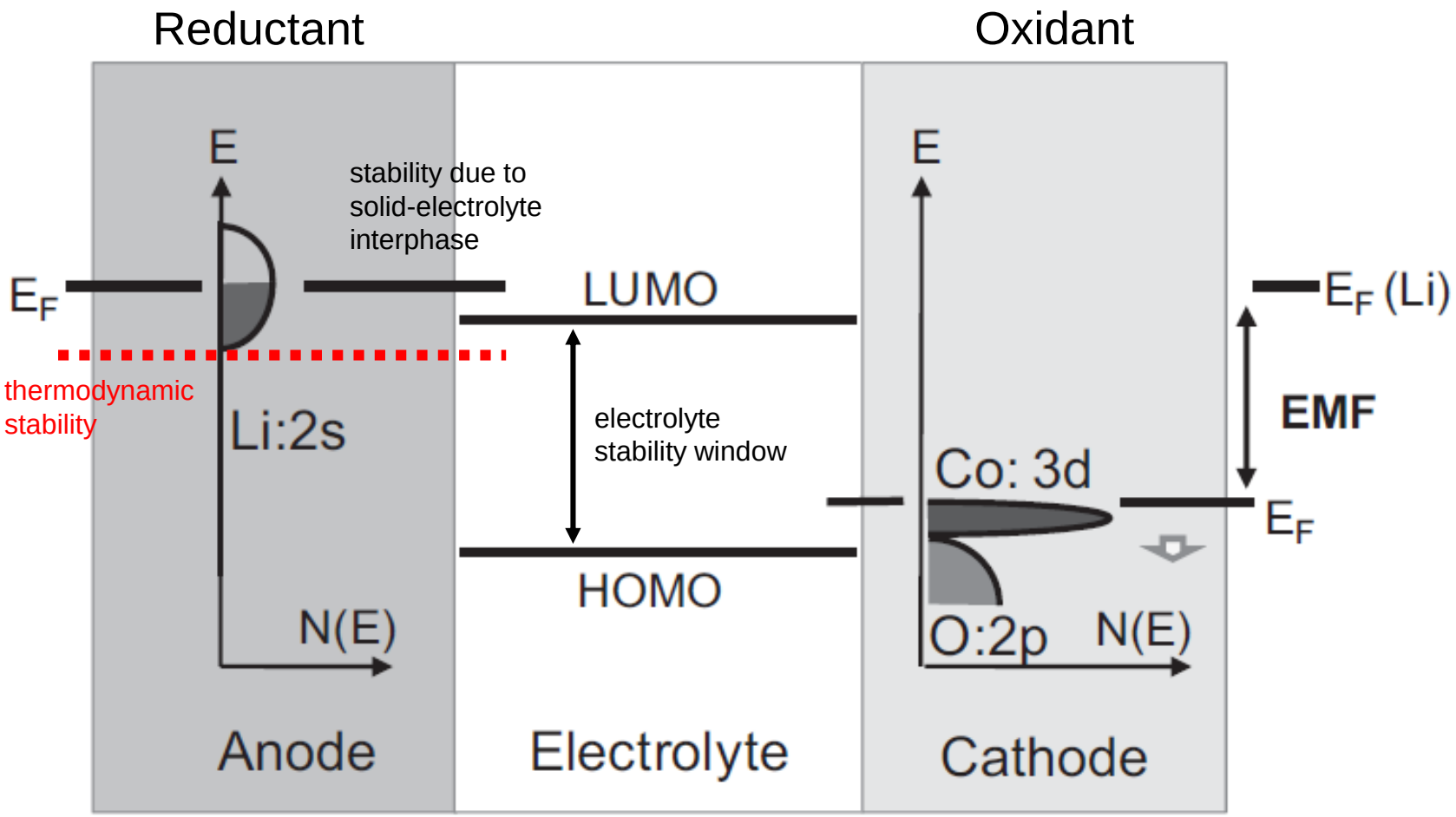
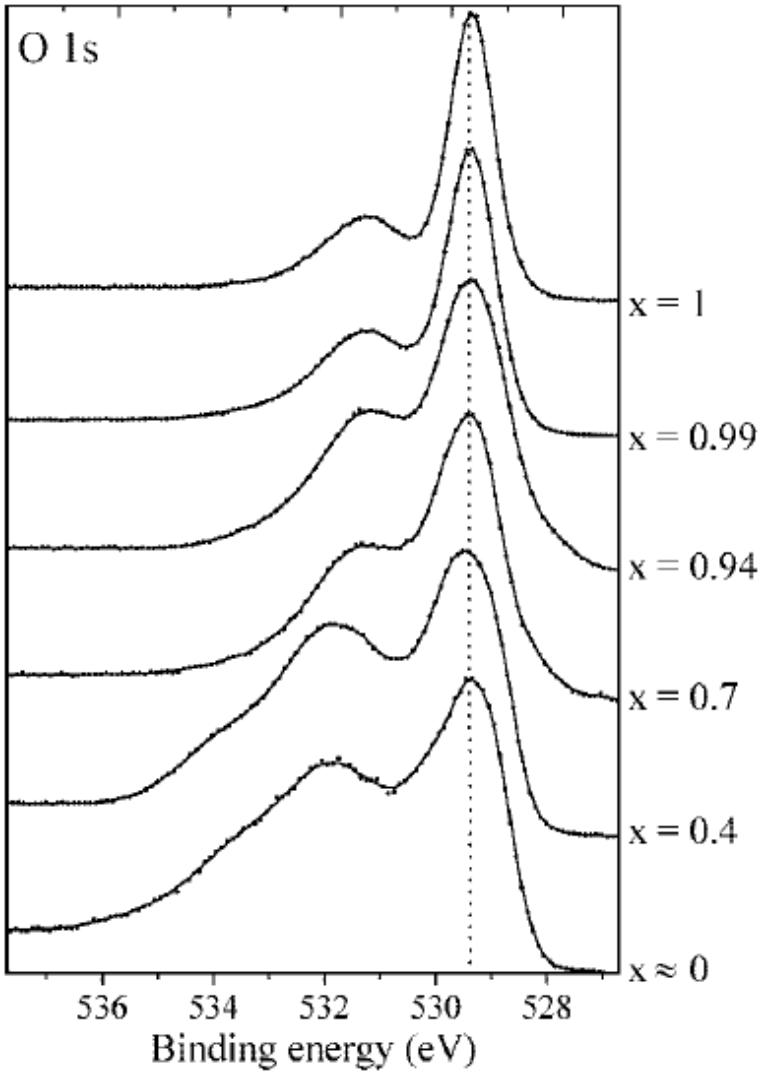
# Mott-Hubbard vs charge transfer regimes



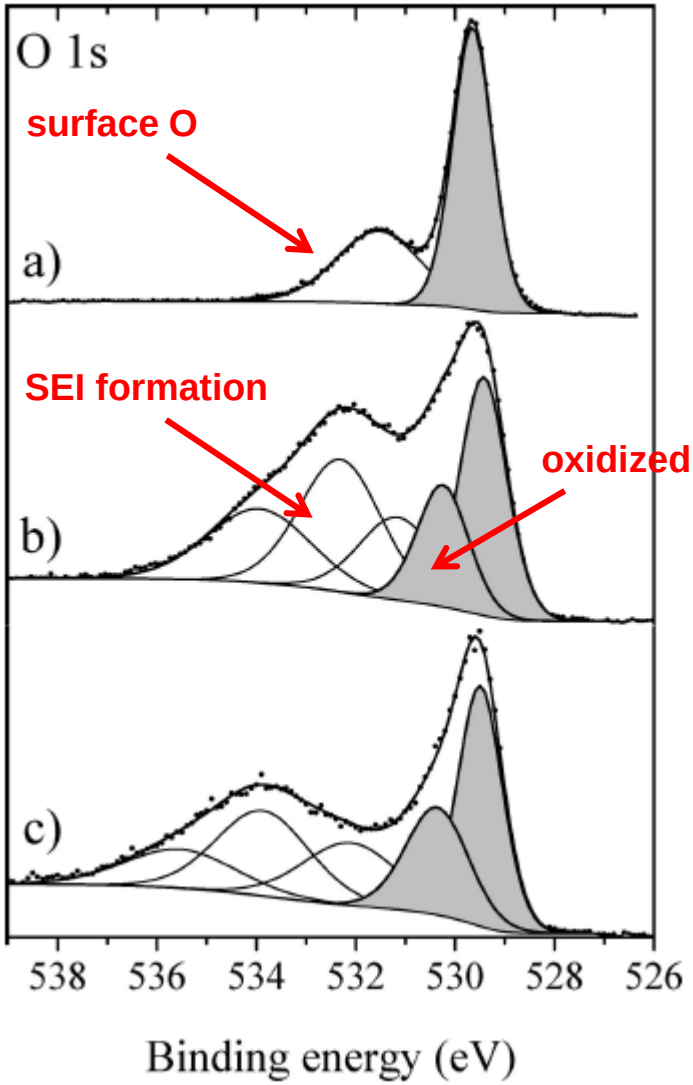
# Li-ion battery energy diagram



# Lattice oxygen oxidation




$Li_xCoO_2$ XPS O1s




$LiCoO_2$

$Li_0CoO_2$

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

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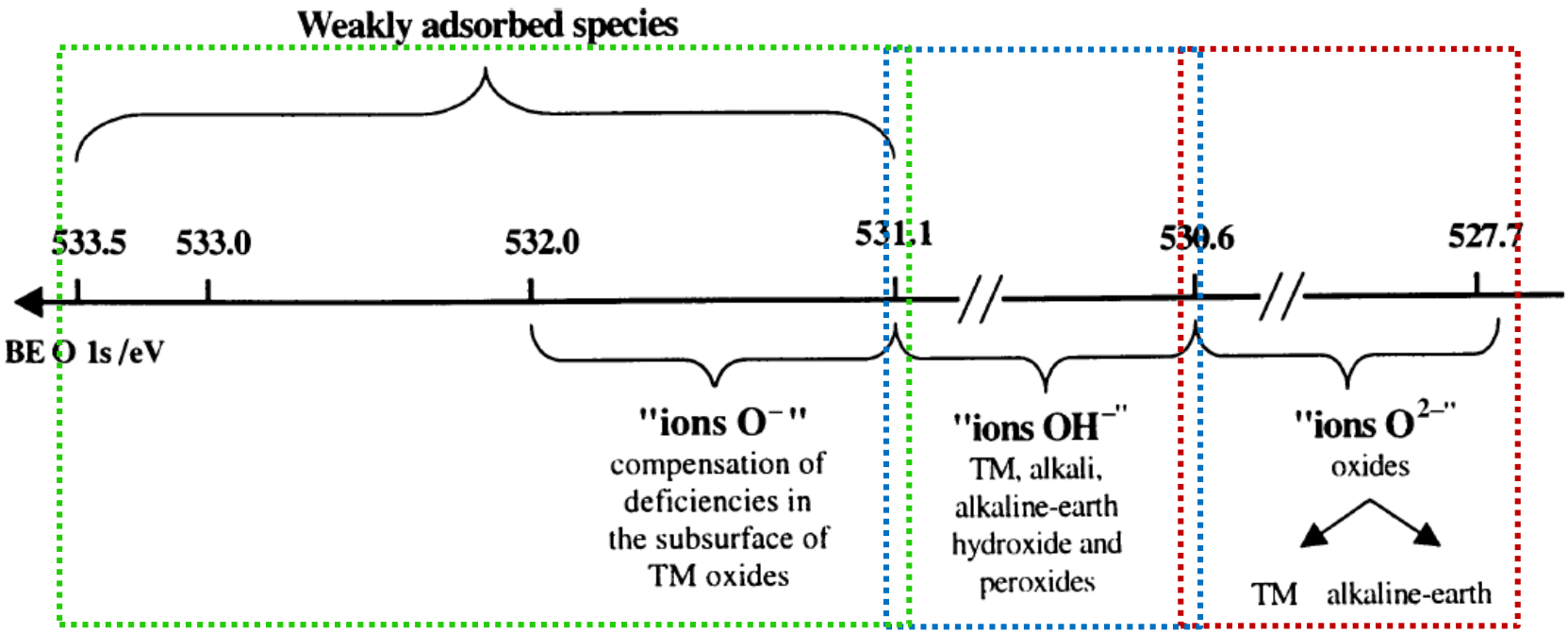
# Lattice oxygen oxidation




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

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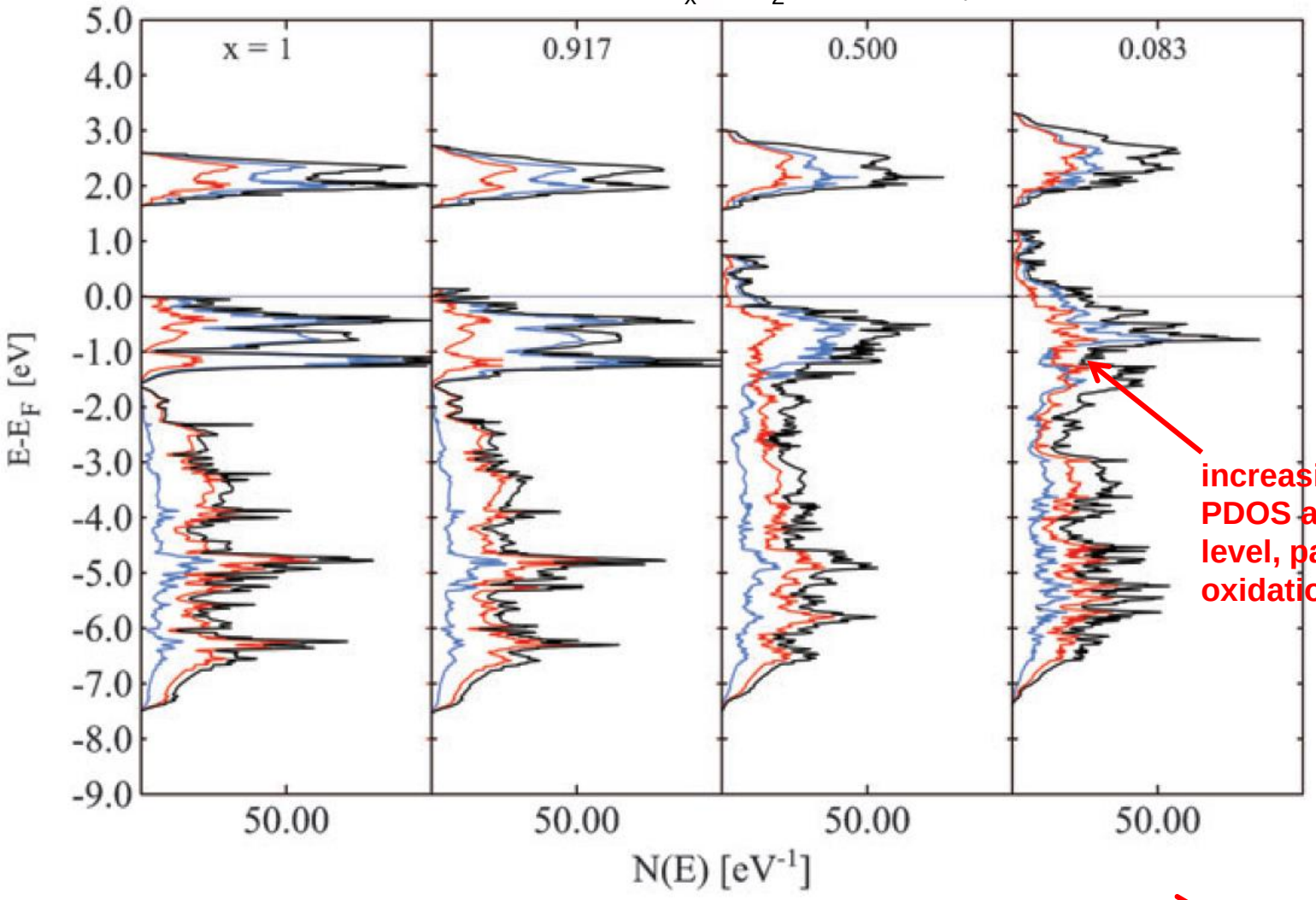
# Band structure upon charge/discharge

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




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

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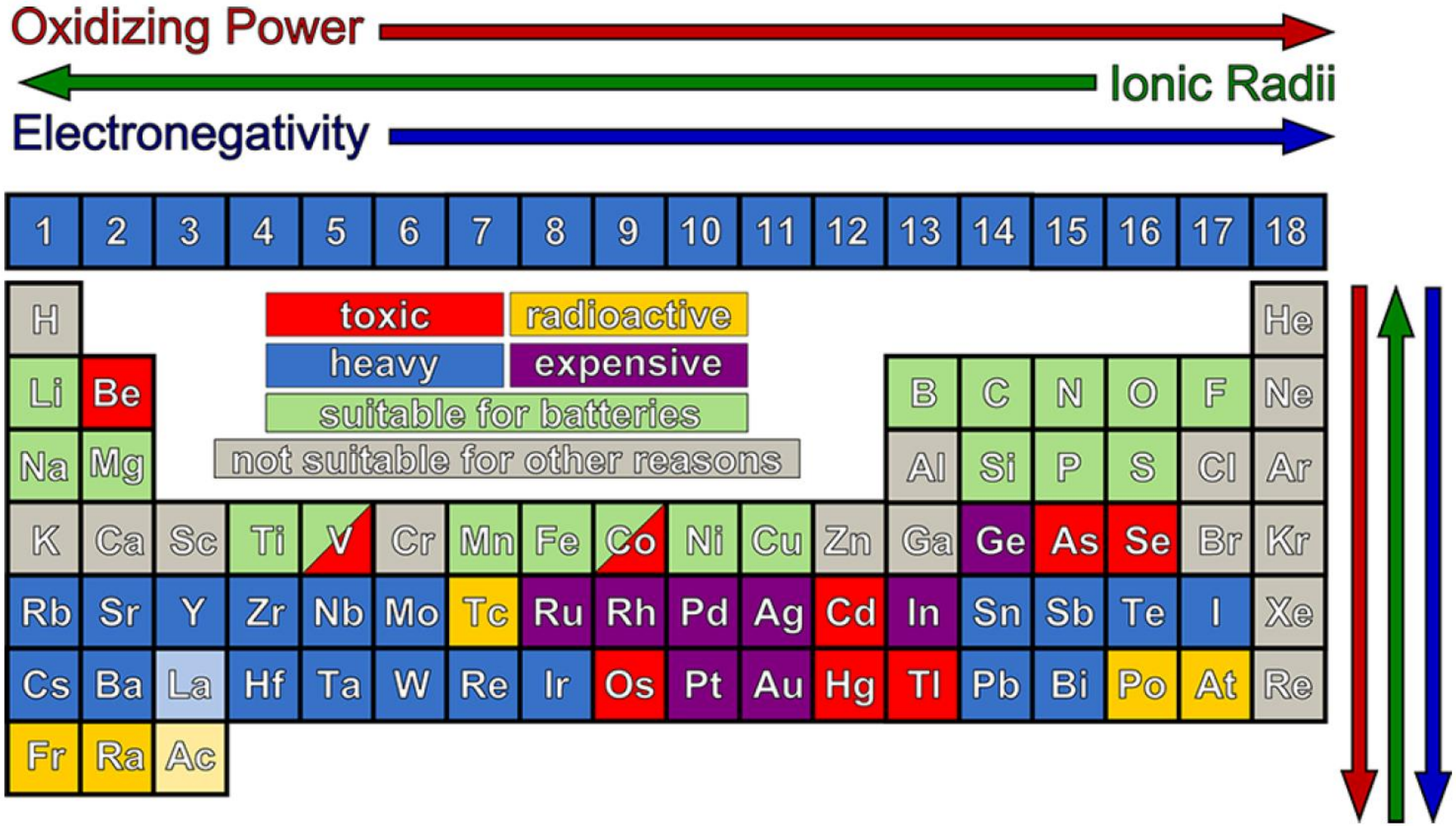
# Redox potential of the $M^{n+}/M^{(n+1)+}$ pairs




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

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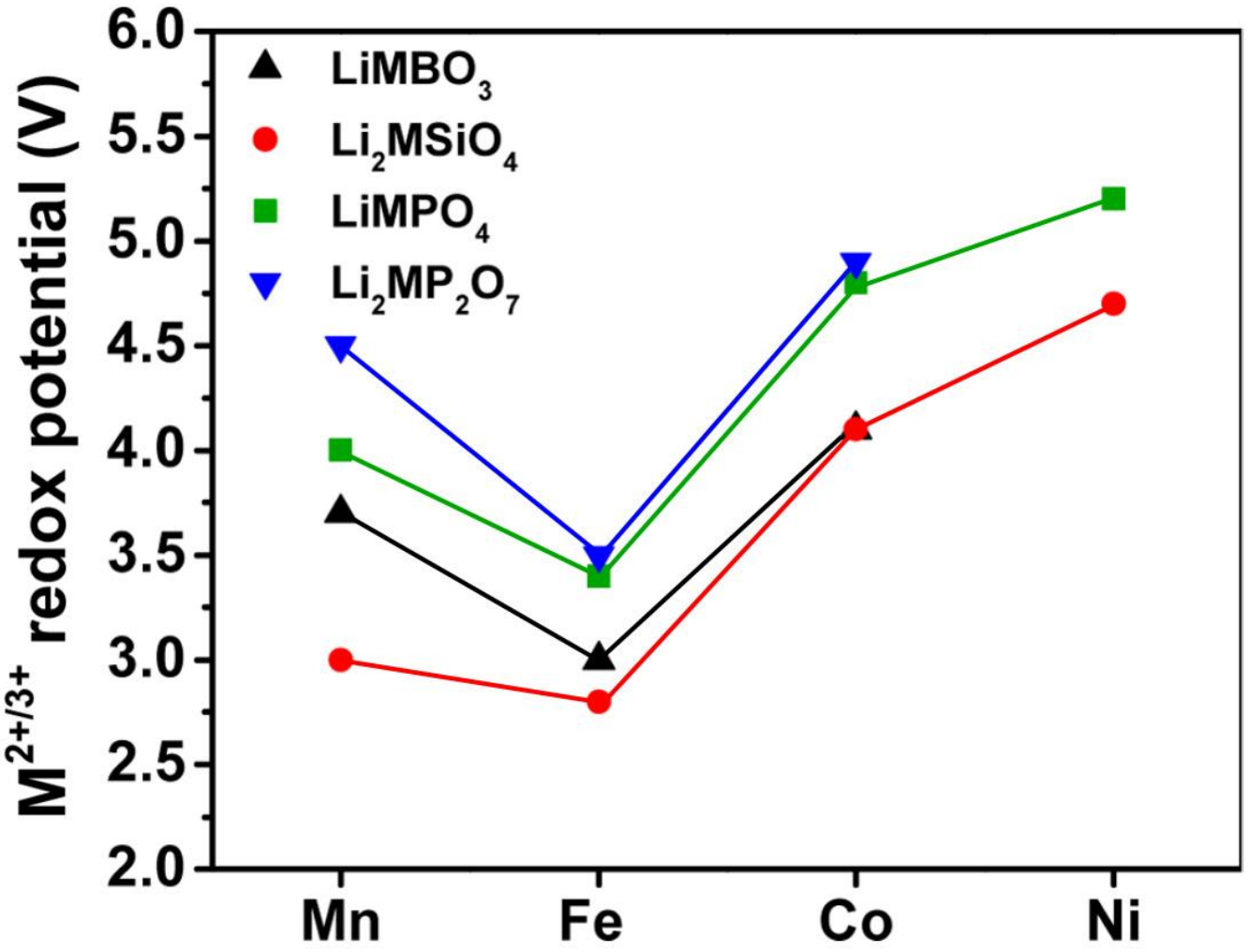
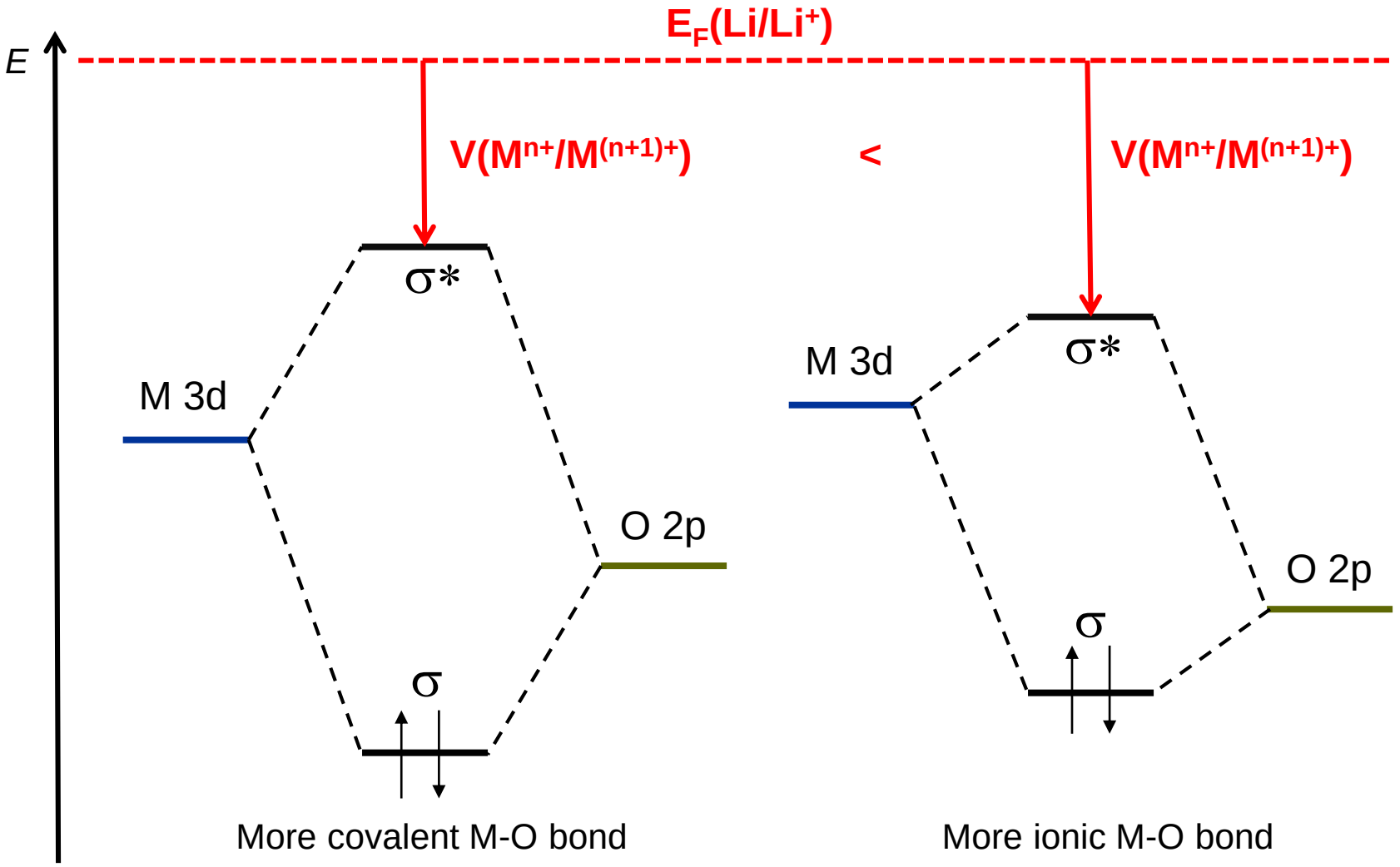
# Redox potential of the $M^{n+}/M^{(n+1)+}$ pairs



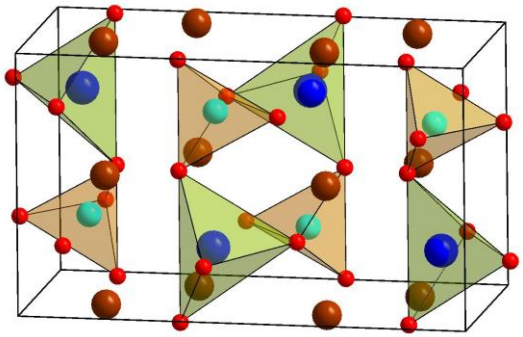

Adapted from A.Gutierrez, N.A.Benedek, A.Manthiram, Chem. Mater. 2013, 25, 4010

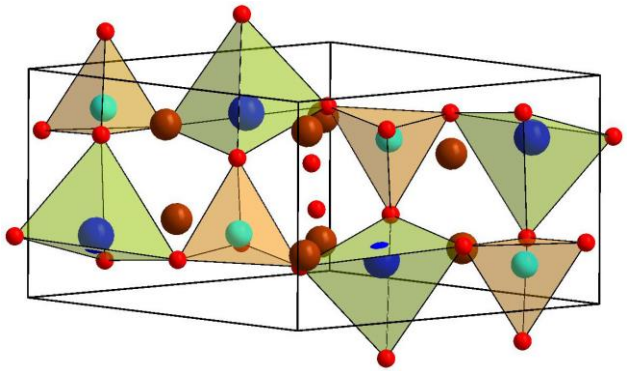
# Covalency *vs* ionicity

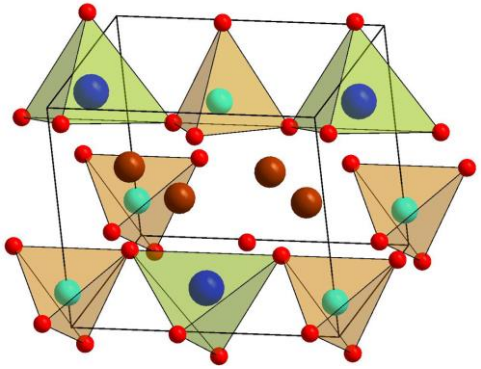


# Covalency *vs* ionicity

$Li_2FeSiO_4$ 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

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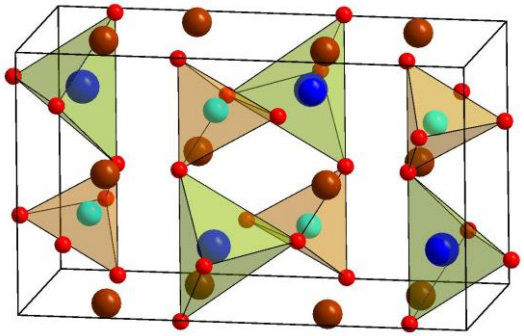
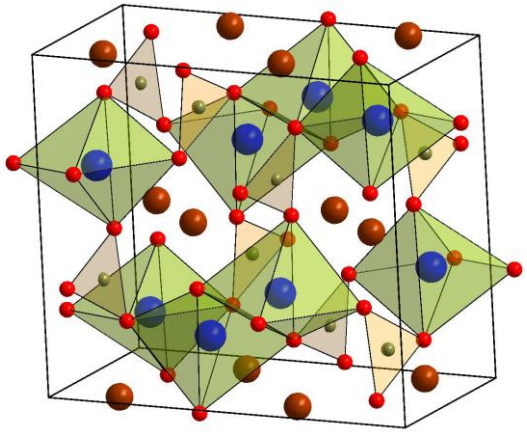
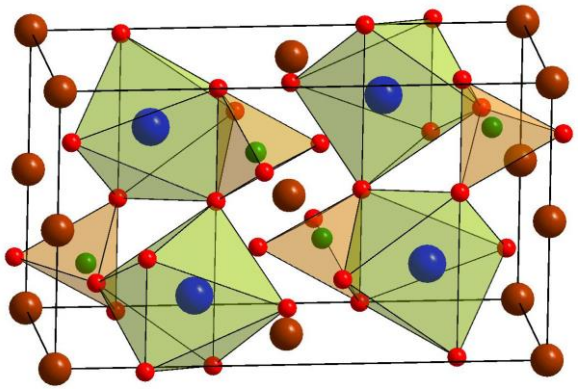
# Covalency *vs* ionicity

| $Li_2FeSiO_4$ | $LiFeBO_3$ | $LiFePO_4$ |
|---|---|---|
| CN(Fe) = 4 | CN(Fe) = 5 | CN(Fe) = 6 |
|  |  |  |
| $d_{av}$(Fe-O) = 2.025Å | $d_{av}$(Fe-O) = 2.092Å | $d_{av}$(Fe-O) = 2.160Å |

increasing Fe-O bond covalency

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

~ 2.9V ~ 3.0V ~ 3.4V

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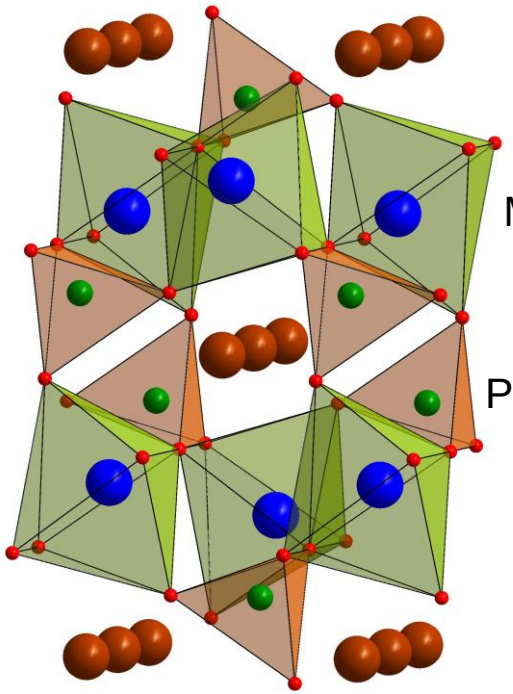
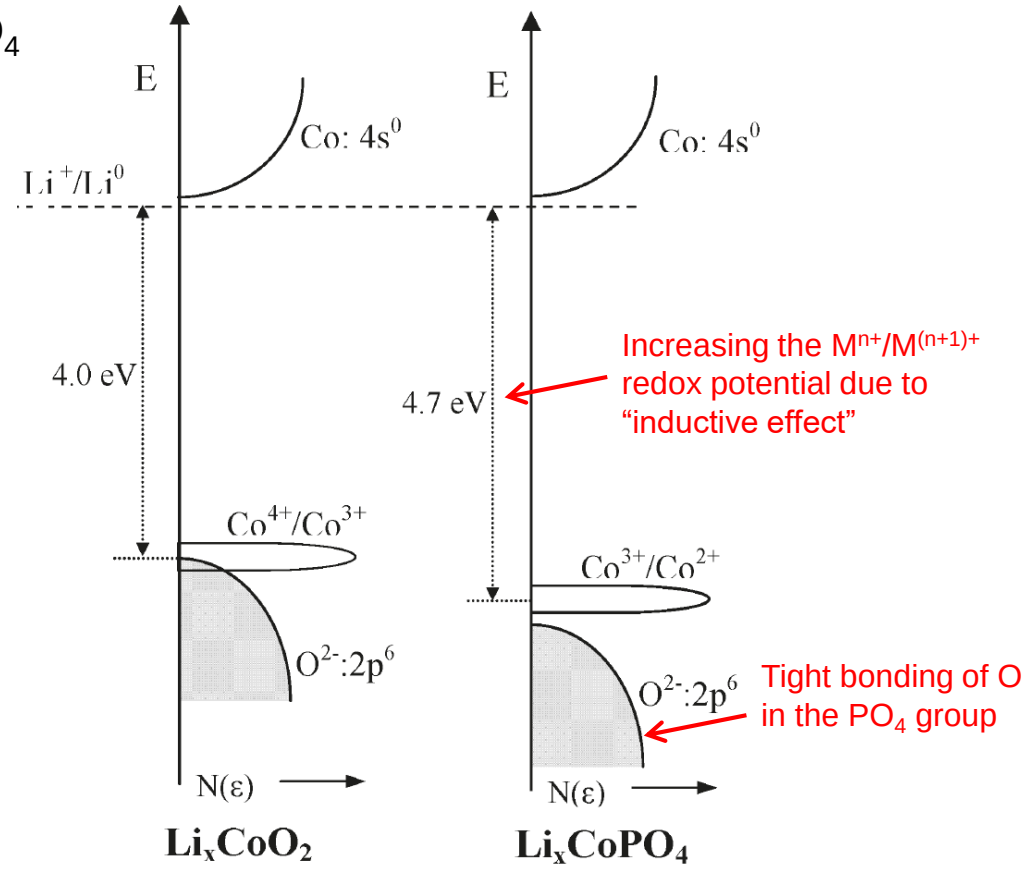
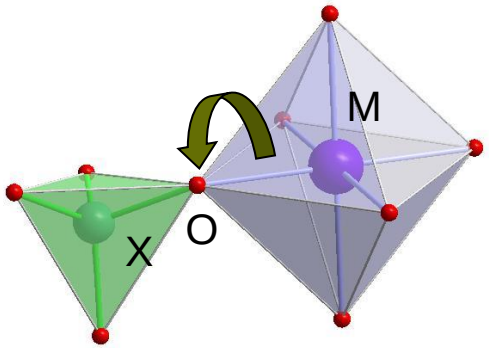
# Inductive effect




Polarization of the M-O bond by $X^{n+}$ cation

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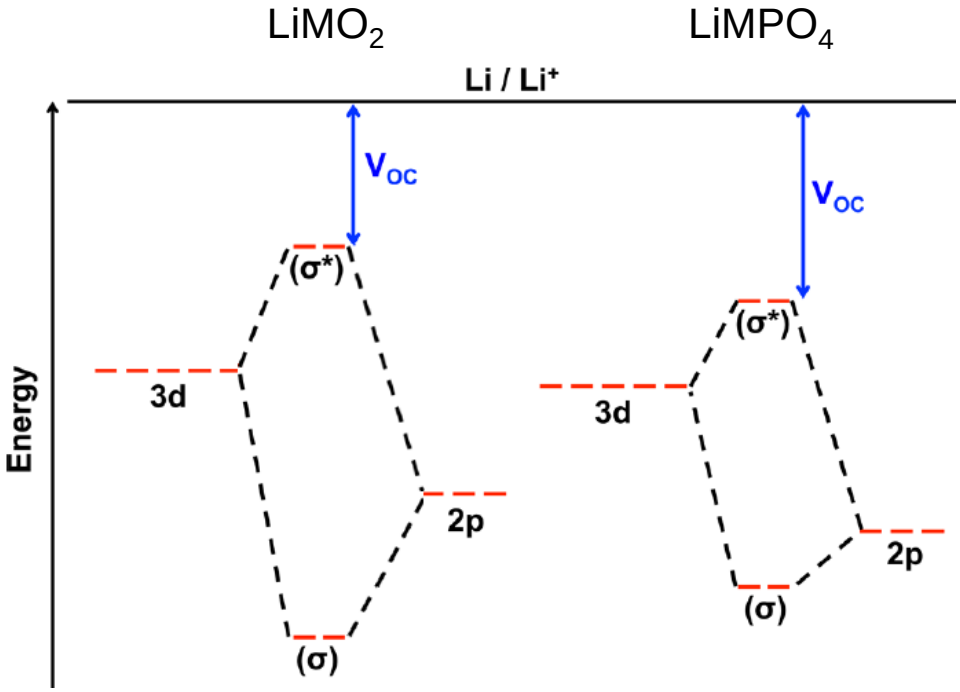
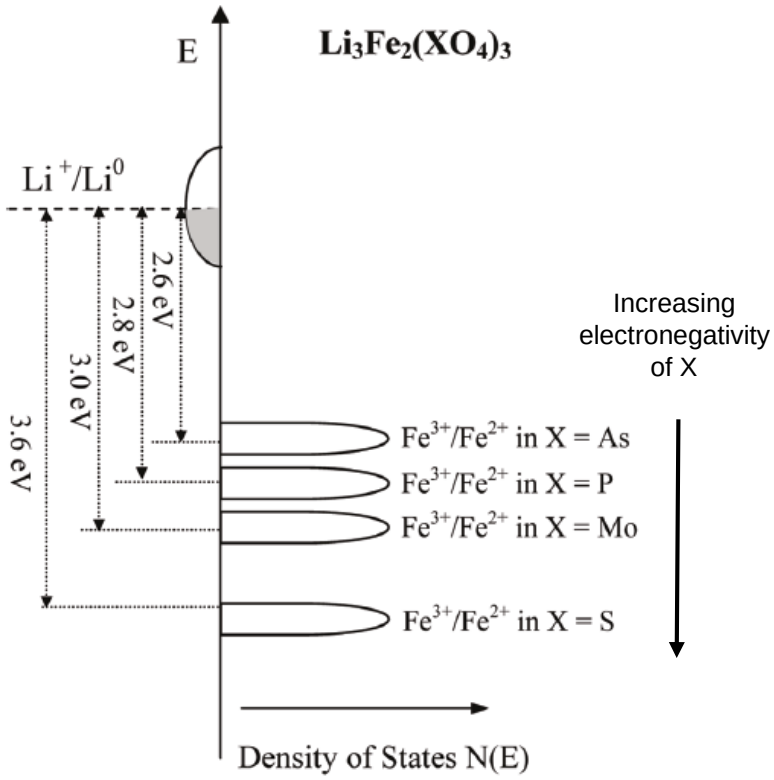
# Inductive effect




More covalent M-O bond

More ionic M-O bond

Tuning the $M^{n+}/M^{(n+1)+}$ redox potential through adjusting the M-O-X interactions




Tuning the $M^{n+}/M^{(n+1)+}$ redox potential through changing electronegativity of X

J.B.Goodenough, Y. Kim, Chem. Mater. 2010, 22, 587–603

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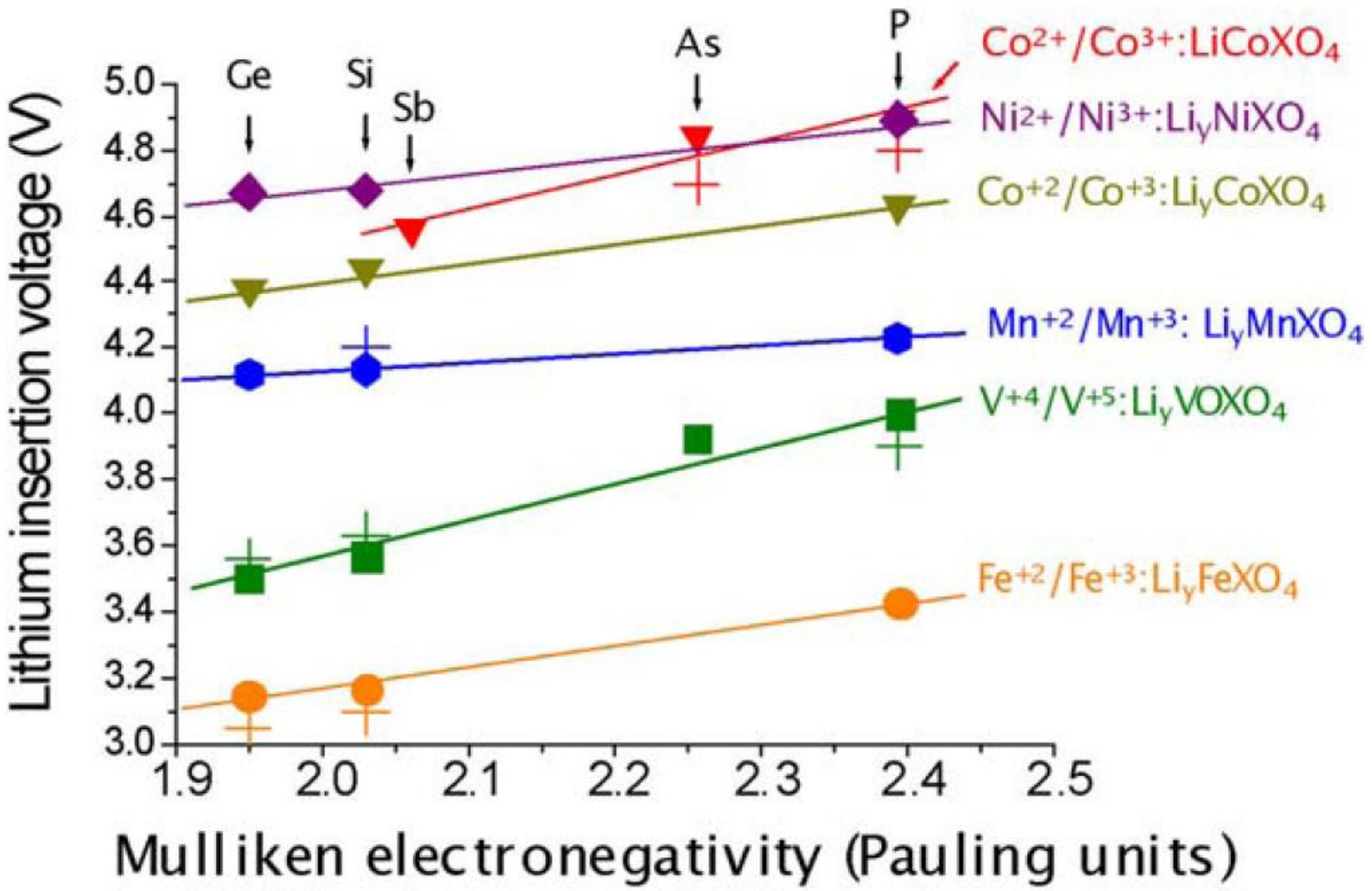
# Inductive effect




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

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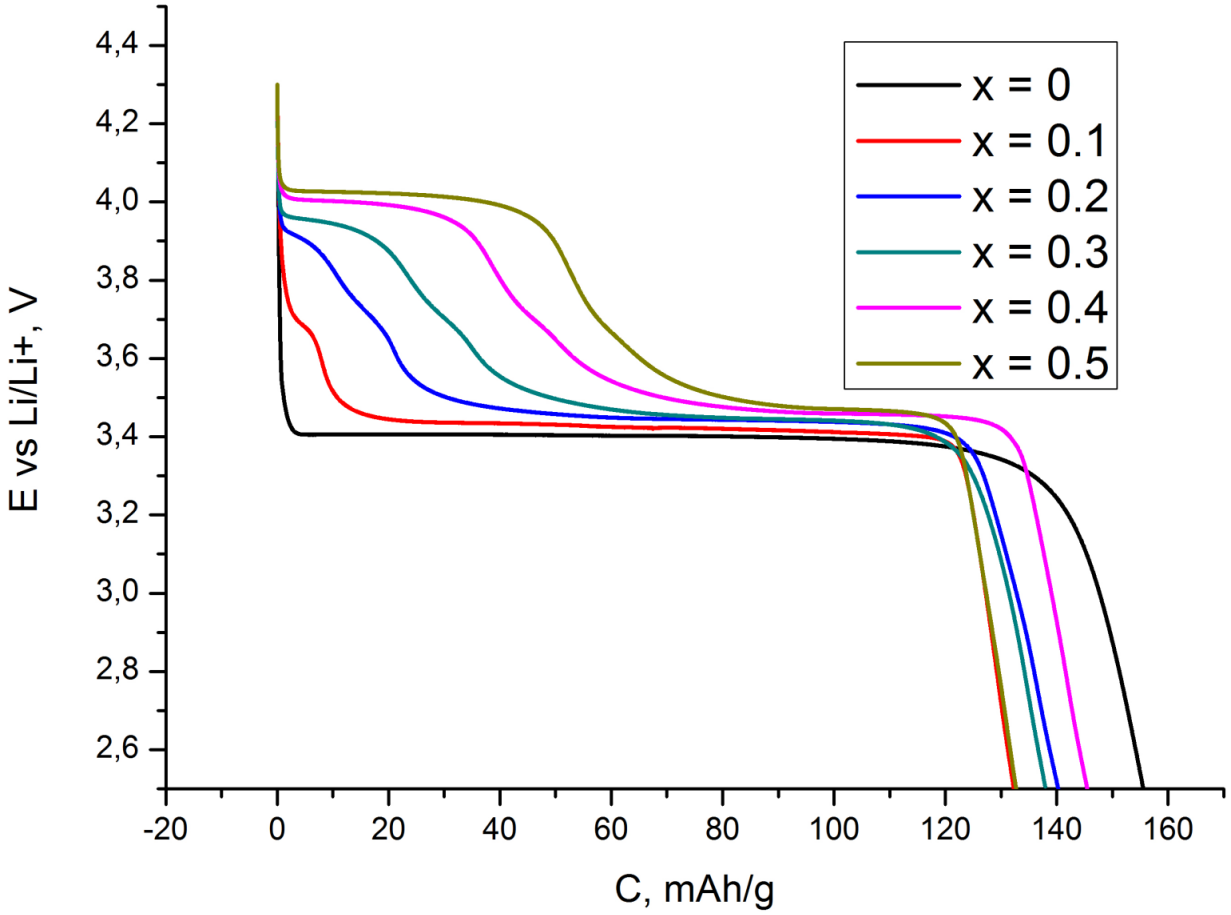
# Electronic configuration

$LiFePO_4$
580 Wh/kg

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

$LiMnPO_4$
700 Wh/kg

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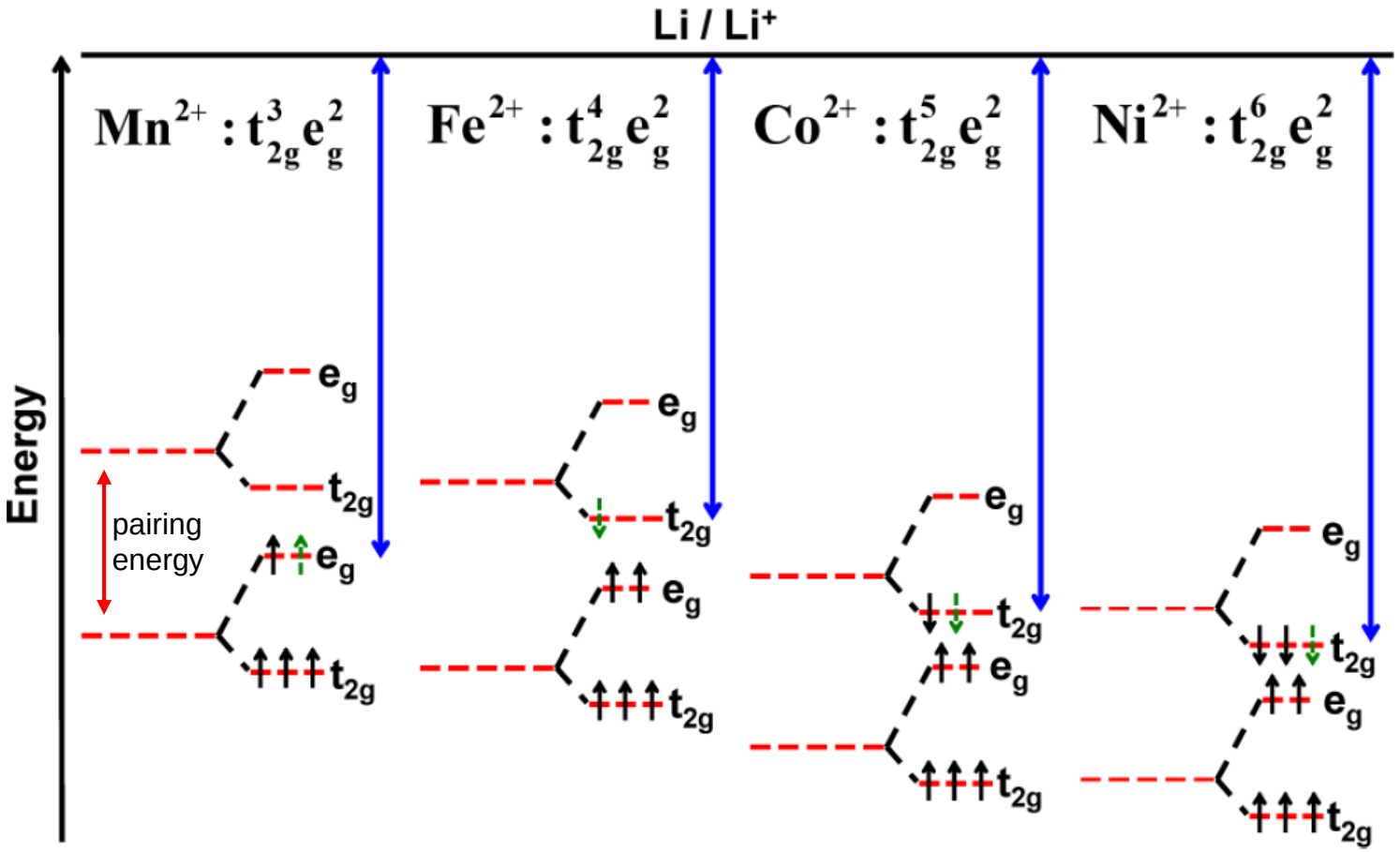
# Electronic configuration




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

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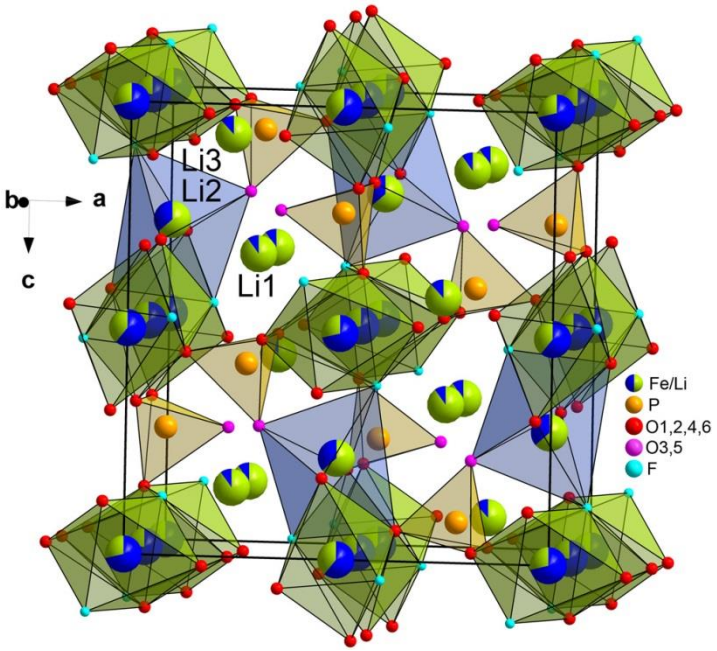
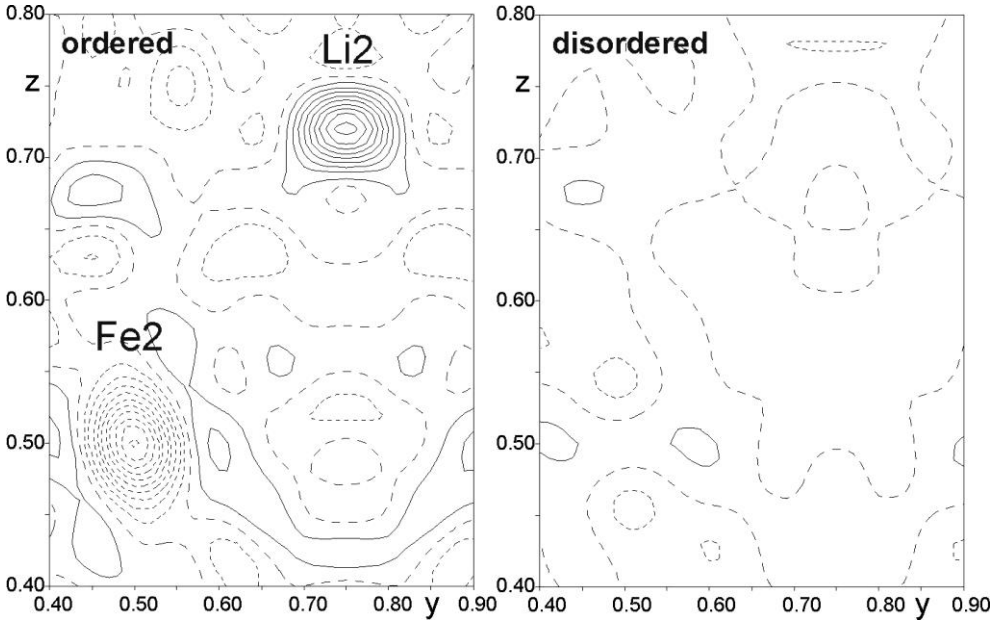
# Coordination of oxygen

$$NaLiFePO_4F \xrightarrow[75\ ^oC]{\text{10 cycles, 2.6V-4.0V}} Li_2FePO_4F$$




difference Fourier maps

Karakulina, Khasanova, Drozhzhin, Tsirlin, Hadermann, Antipov, Abakumov, *Chem. Mater.*, 2016, 28, 7578

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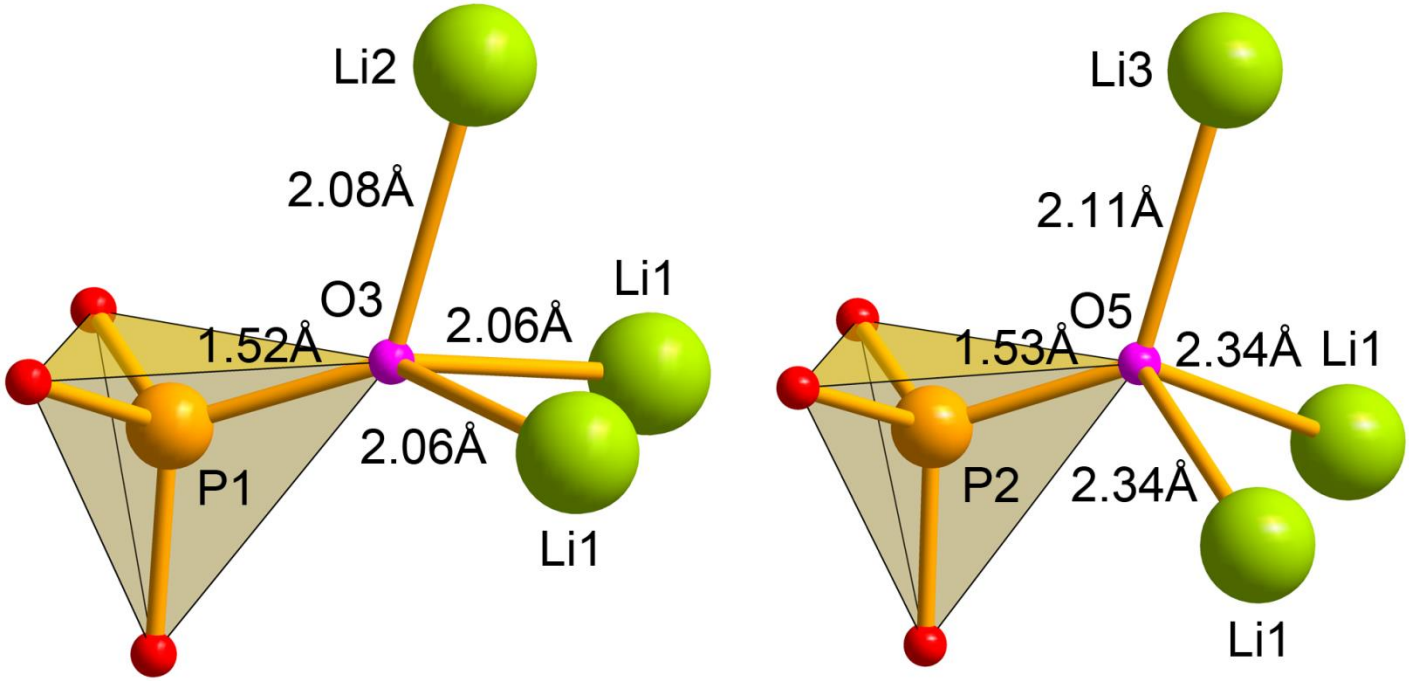
# Coordination of oxygen

$Li_2FePO_4F$




Karakulina, Khasanova, Drozhzhin, Tsirlin, Hadermann, Antipov, Abakumov, *Chem. Mater.*, 2016, 28, 7578

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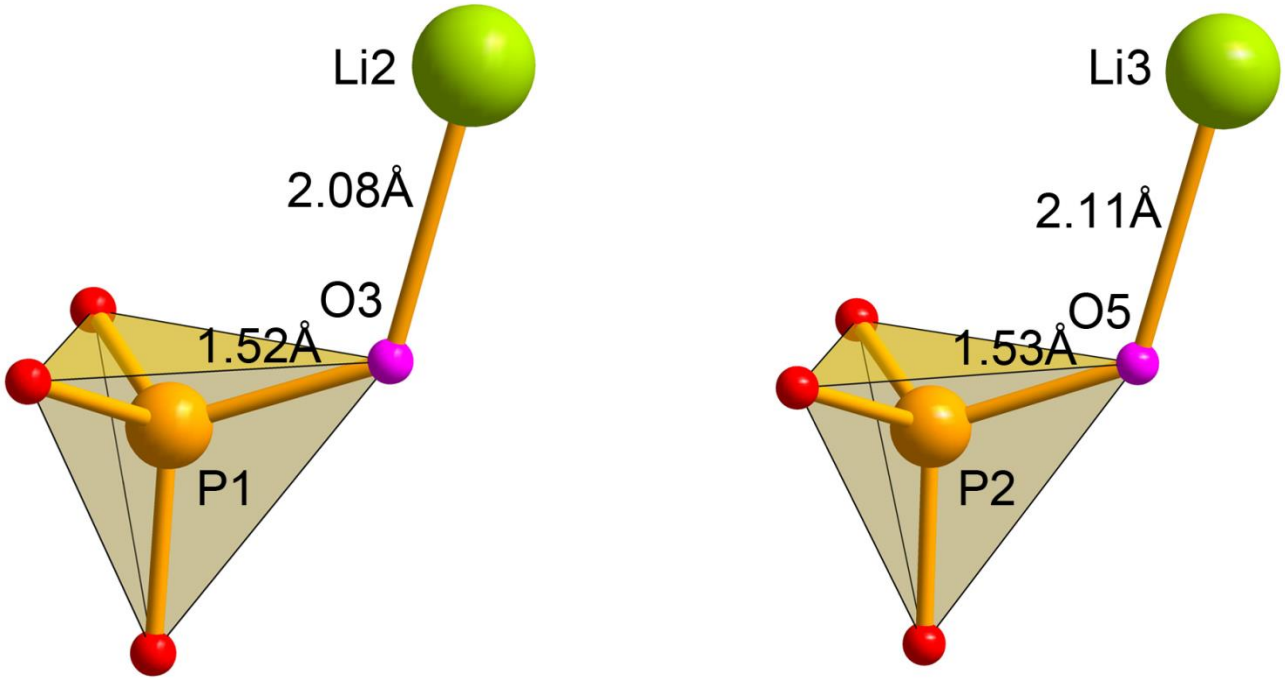
# Coordination of oxygen

$LiFePO_4F$




Karakulina, Khasanova, Drozhzhin, Tsirlin, Hadermann, Antipov, Abakumov, *Chem. Mater.*, 2016, 28, 7578

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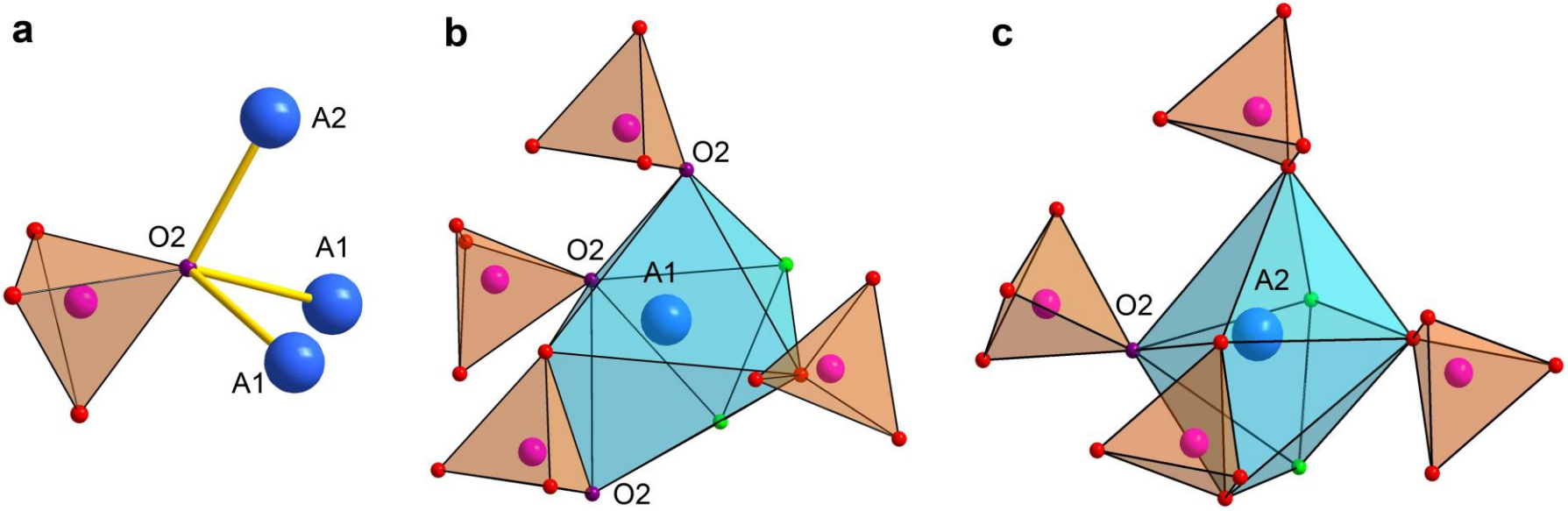
# Coordination of oxygen

Coordination of the Na atoms in layered $Na_2FePO_4F$




I.V.Tereshchenko, D.A.Aksyonov, O.A. Drozhzhin, I.A. Presniakov, A.V. Sobolev, A.Zhugayevych, K.Stevenson, E.V.Antipov, A.M.Abakumov, *JACS*, under review, 2017

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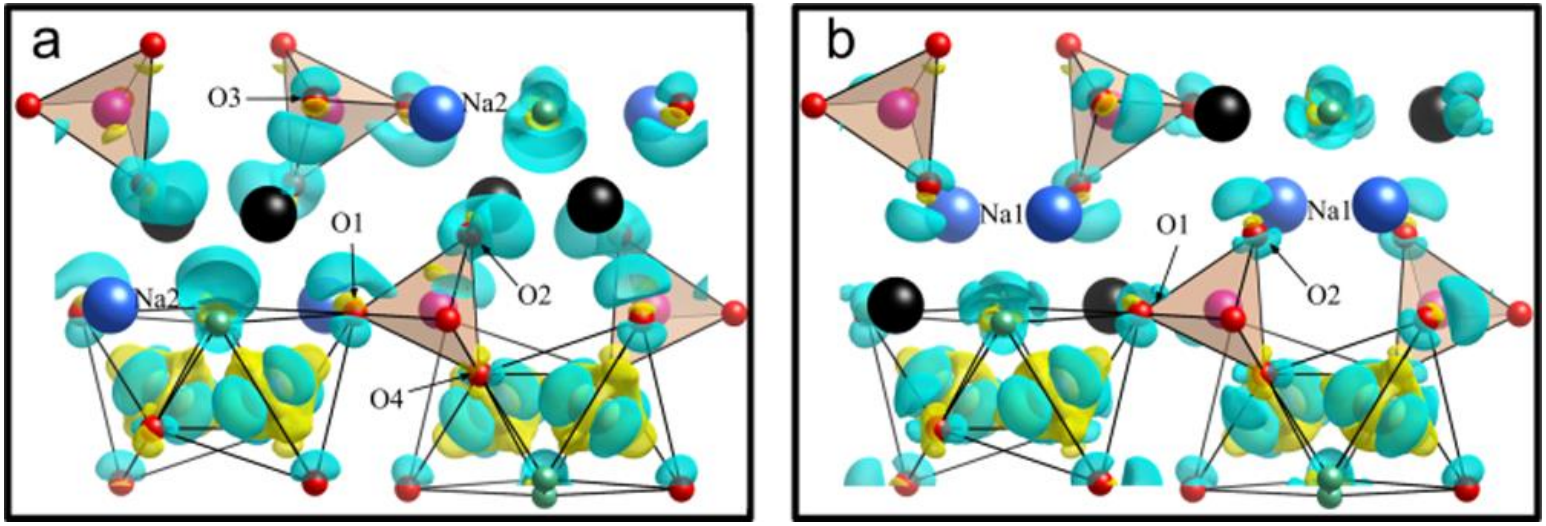
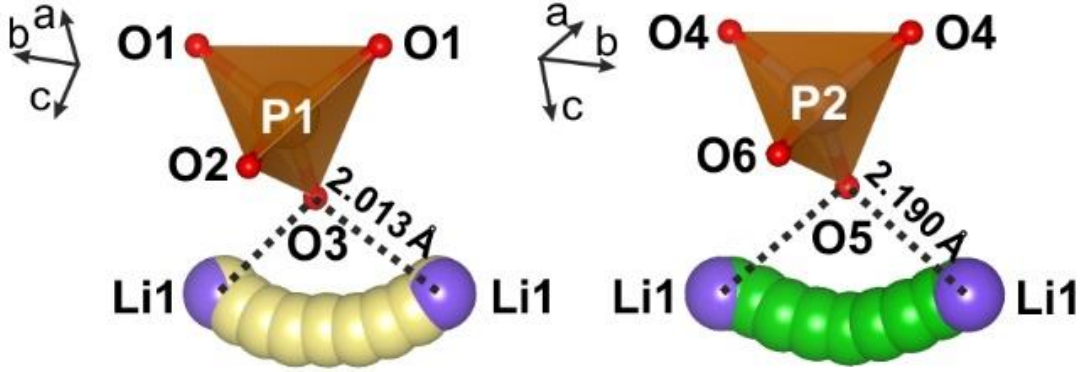
# Coordination of oxygen

Charge density difference after removing 1Na from $Na_2FePO_4F$




barrier 0.41 eV

barrier 0.12 eV

S.S. Fedotov, A.A.Kabanov, N.A.Kabanova, V.A.Blatov, A. Zhugayevych, A.M. Abakumov, N.R. Khasanova, E.V.Antipov, J. Phys. Chem. C 2017, 121, 3194−3202

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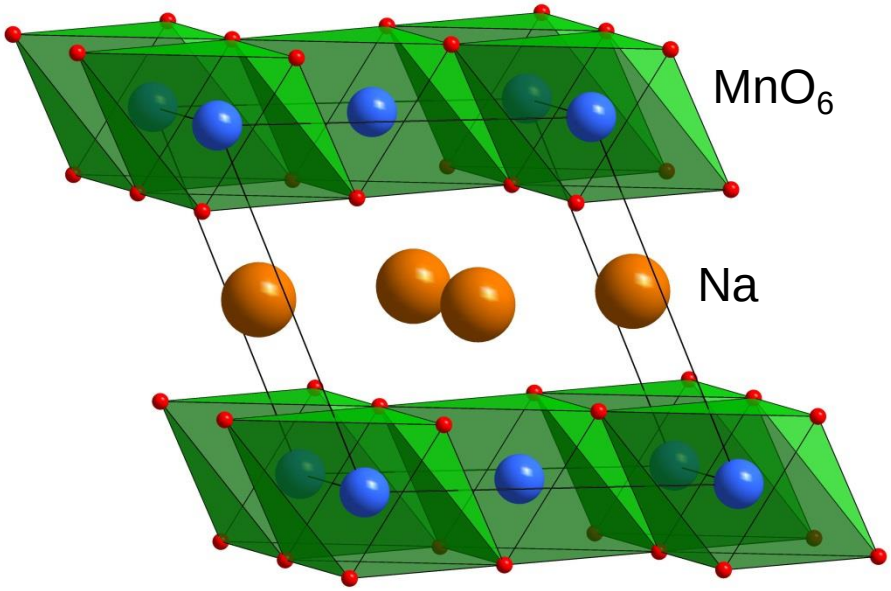
# Planar defects




Cubic close packing (O3 structure)

Layered ordering of the $Mn^{3+}O_6$ and $NaO_6$ octahedra

$d(Mn\text{-}O)_{eq}$ = 1.930Å x4
$d(Mn\text{-}O)_{ap}$ = 2.395Å x2

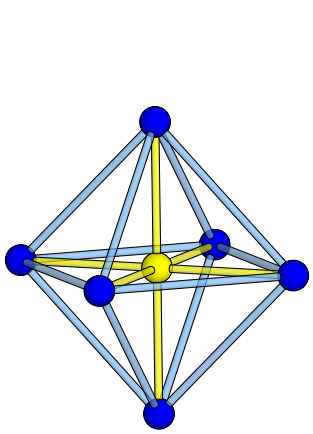
Compare with $LiCoO_2$:
$d(Co\text{-}O)$ = 1.921Å x6

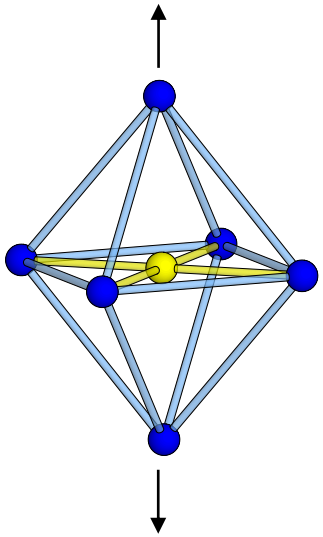
Na-ion battery cathode:

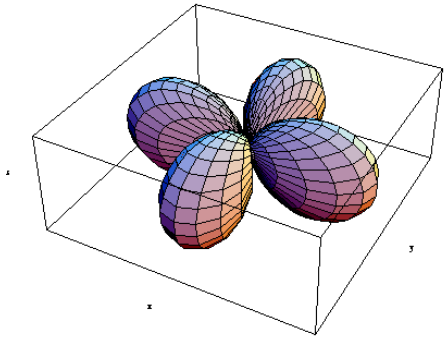
0.8 Na can be (de)intercalated reversibly with a capacity of ~132 mAh/g

*X. Ma et al, J. Electrochem. Soc. 2011, 158, A1307*

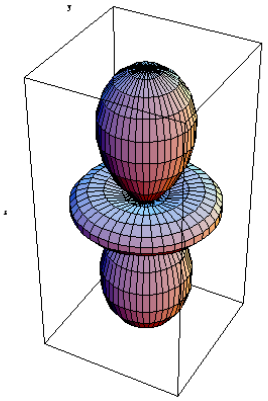
# Jahn-Teller distortion







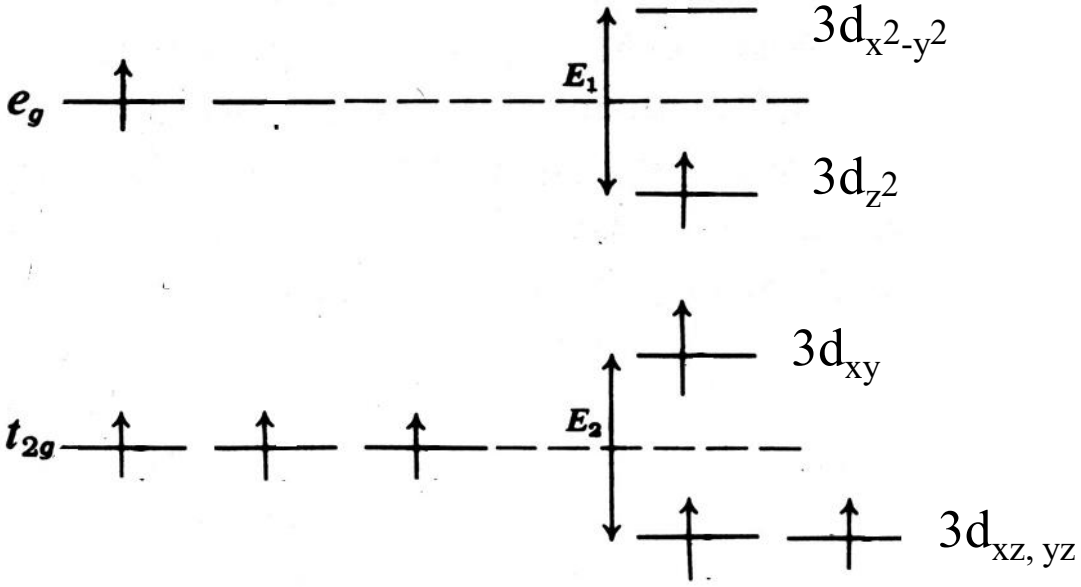
$3d_{x^2-y^2}(Mn)$



$3d_{z^2}(Mn)$

$Mn^{3+}$ $d^4$

$t_{2g}^3 e_g^1$

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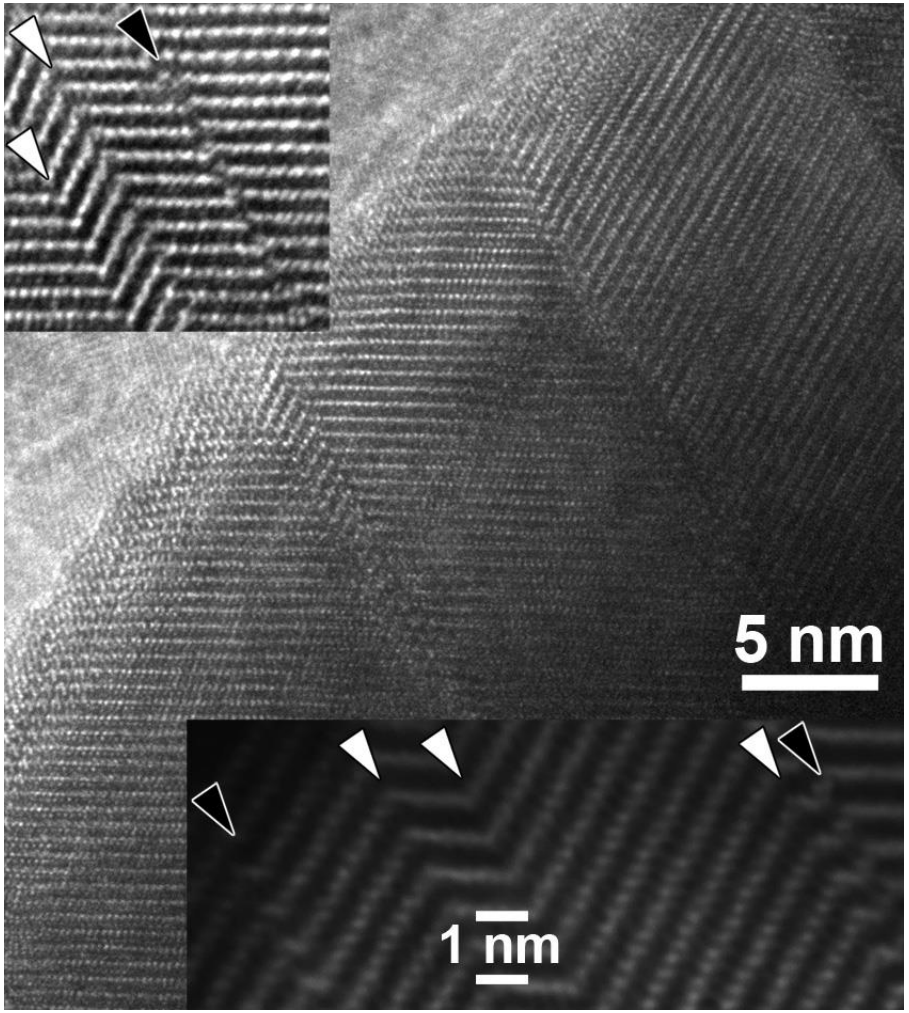
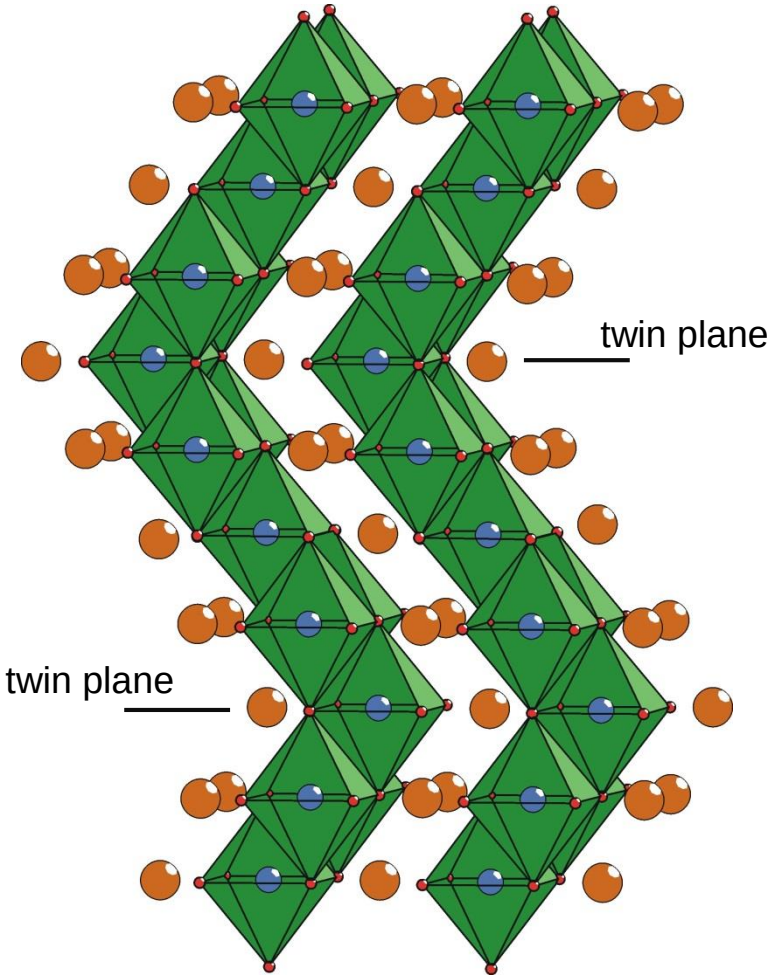
# Planar defects

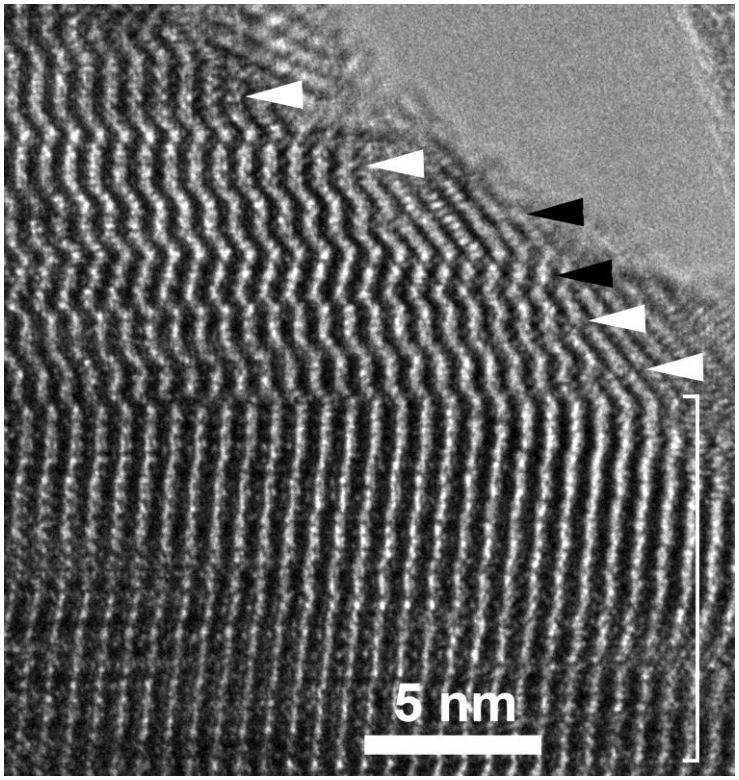


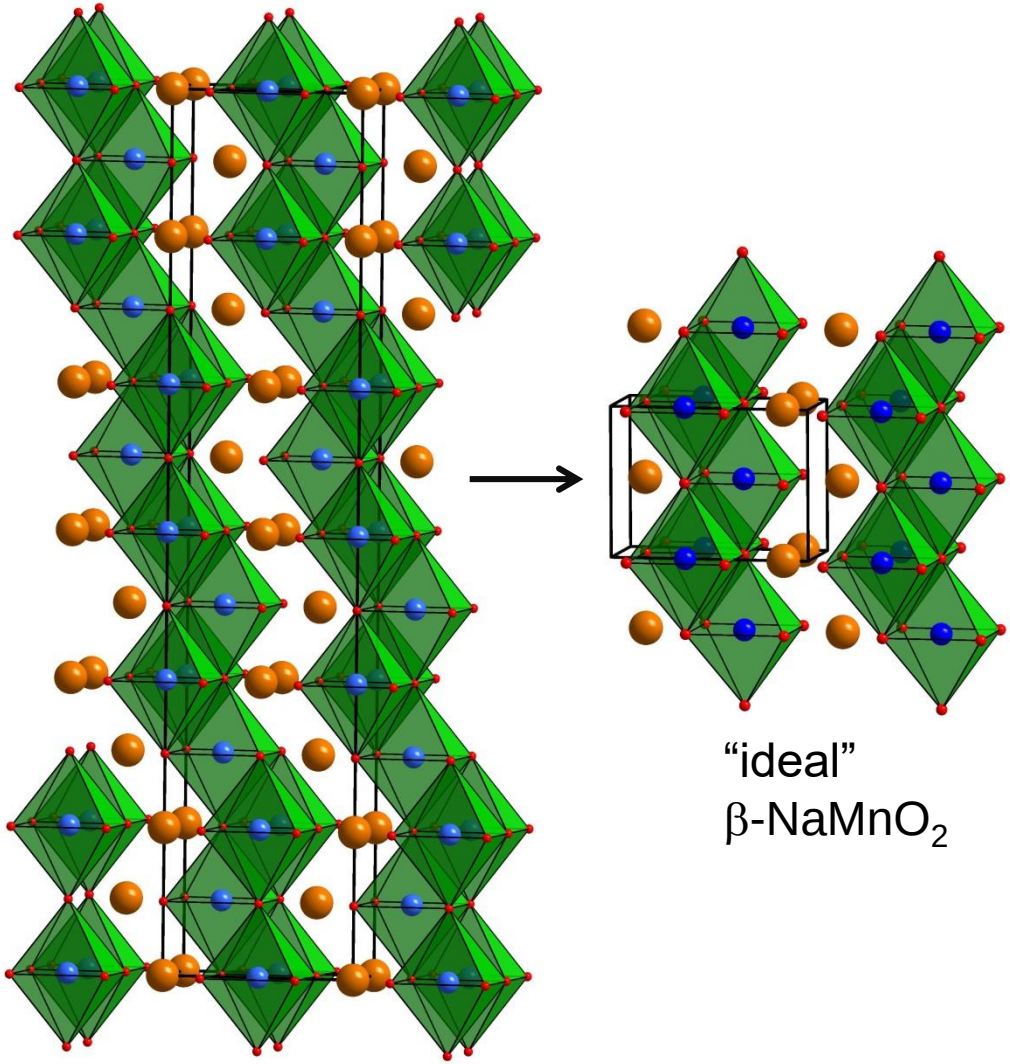

$\alpha$-$NaMnO_2$

*A.Abakumov et al., Chem. Mater. 2014, 26, 3306*

# Planar defects



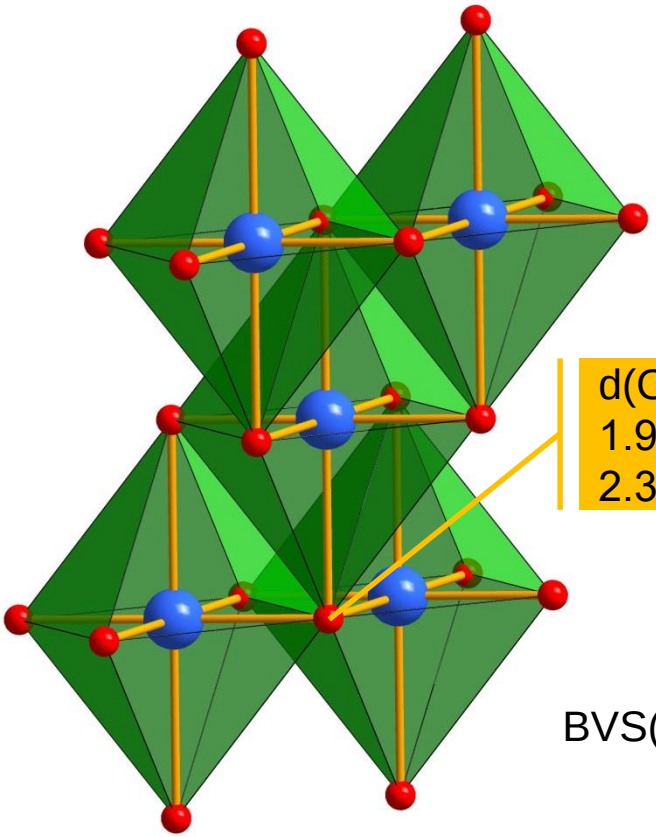

β-$NaMnO_2$



"ideal"
β-$NaMnO_2$

# Planar defects

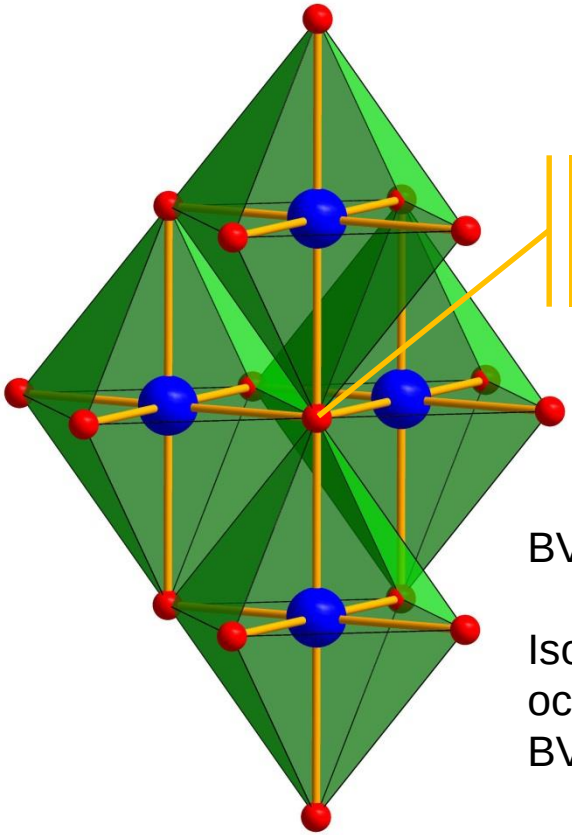
Axial Jahn-Teller distortion of the $Mn^{3+}O_6$ octahedra is necessary to relieve overbonding of oxygen atoms in the twinned structure



d(O - Mn):
1.930Å x2
2.395Å x1

BVS(O) = 2.012

$\alpha$-$NaMnO_2$



d(O - Mn):
1.947Å x2
2.409Å x2

BVS(O) = 2.013

Isotropic $MnO_6$ octahedron:
BVS(O) = 2.230

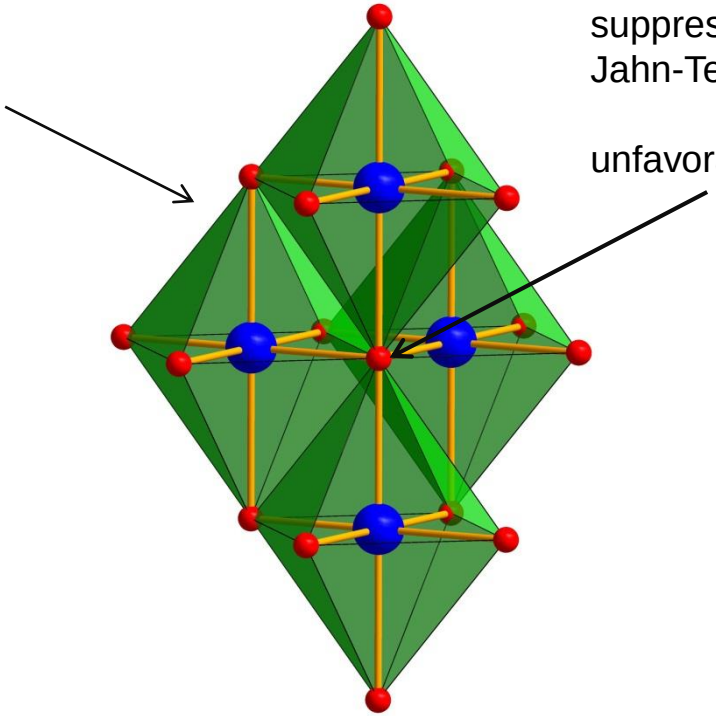
Oxygen overbonded

$\beta$-$NaMnO_2$

# Planar defects

Redox potential of Na deintercalation (DFT-based estimate):

| | |
|---|---|
| $\alpha$-$NaMnO_2$ | 2.26V (exper. ~2.5V) |
| $\beta$-$NaMnO_2$ | 2.63V (exper. 2.7V) |




Diffusion constant along and
across the twin boundary:

$D_{along}/D_{across} \sim 10^3$ (for twin plane in $LiCoO_2$)

⇓

impeding 2D Na-ion transport

*H.Moriwake et al, Adv. Mater. 2013, 25, 618*

*A.Abakumov et al., Chem. Mater. 2014, 26, 3306*

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# Thank you for your attention!