Cathodes for Li-Ion Batteries: Challenges and Prospects

Artem Abakumov

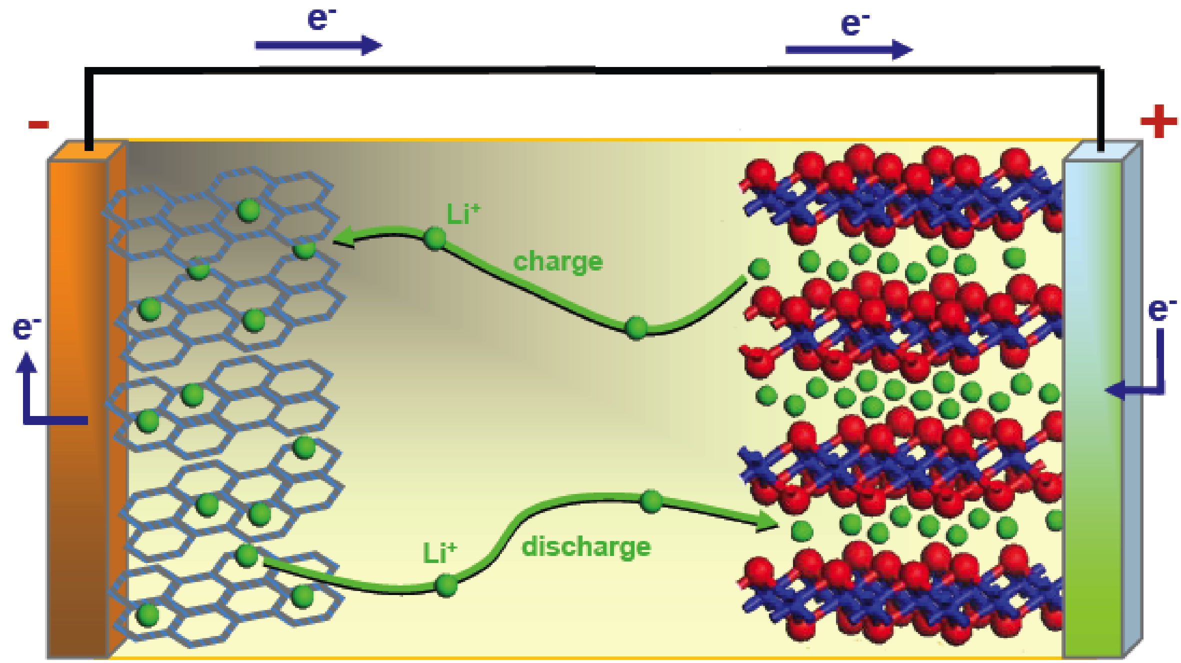
Center for Electrochemical Energy Storage, Skoltech

Skoltech
Skolkovo Institute of Science and Technology

Outline

1. Li-ion batteries
2. Cathode materials: key parameters and structures
3. Layered Li-rich cathodes: lattice oxygen redox
4. Layered Li-rich cathodes: cation migration and voltage fade
5. Polyanion cathodes: adjusting the redox potential
6. Conclusions

Li-ion batteries



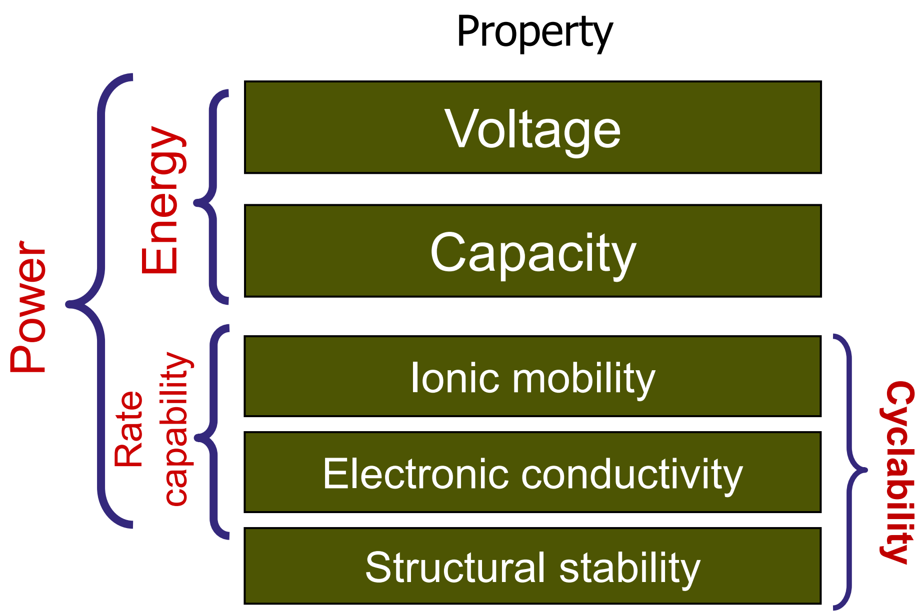
Li_xC_6 graphite | Li^+-conducting electrolyte | $LiMO_2$

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

Voltage 3.6 V, $x \approx 0.5\text{-}0.6\ e^-$

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

Cathode materials: key properties



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

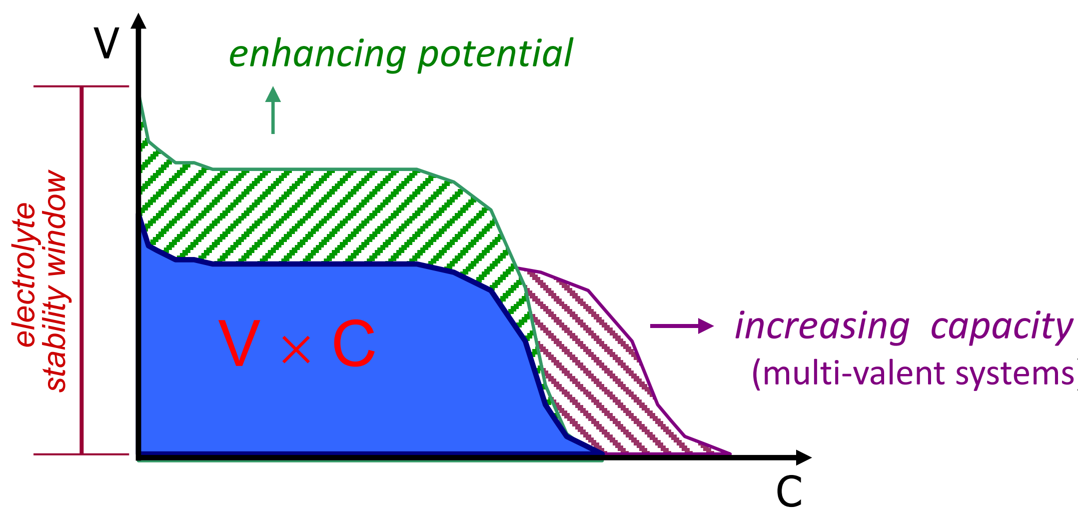
$$C_T\,(\mathrm{A\ h\ g^{-1}}) = \frac{26.8 \times \Delta n}{M}$$

number of e^- or Li^+

Molecular weight (g)

Energy = Voltage x Capacity

≤ 4.8 V (vs. Li/Li^+)

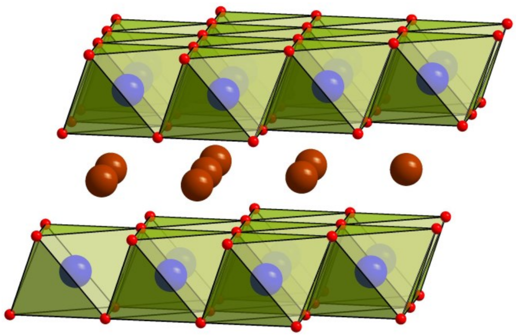


Skoltech
Skolkovo Institute of Science and Technology

Cathode materials

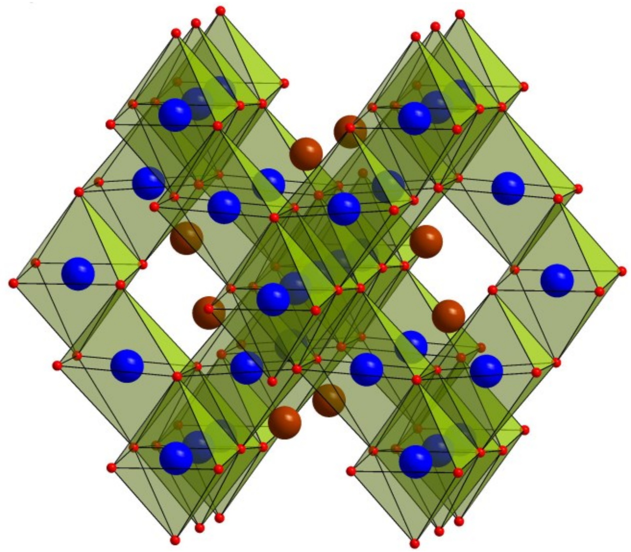
Complex oxides

Polyanion compounds



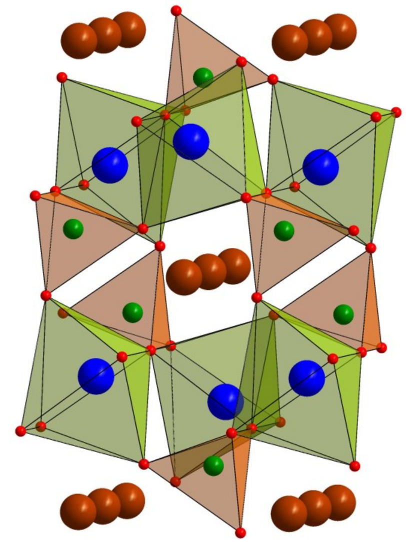
$LiCoO_2$
$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

2D Li transport



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

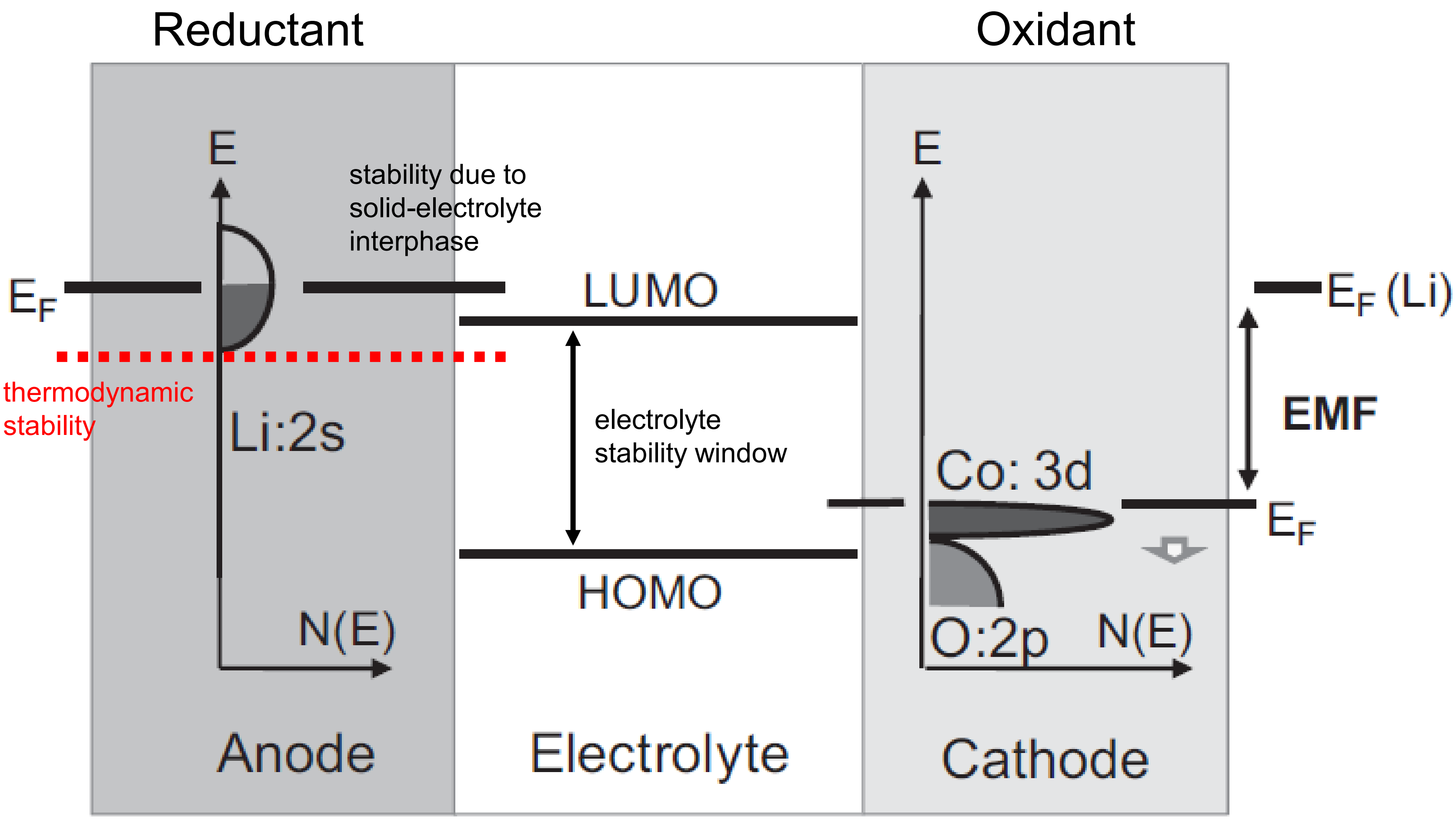
3D Li transport



$LiFePO_4$

1D Li transport

Li-ion battery energy diagram

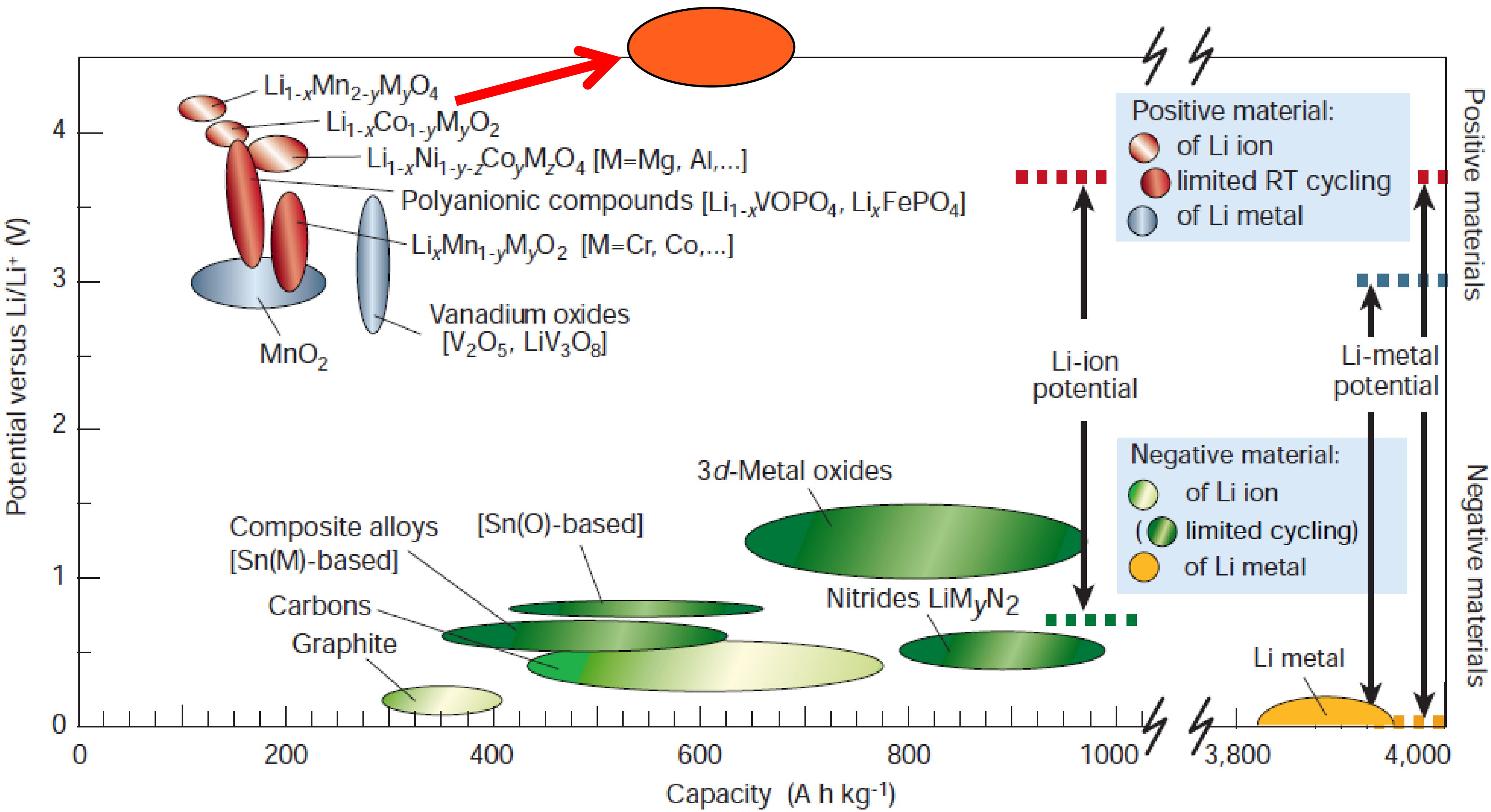


Cathode materials

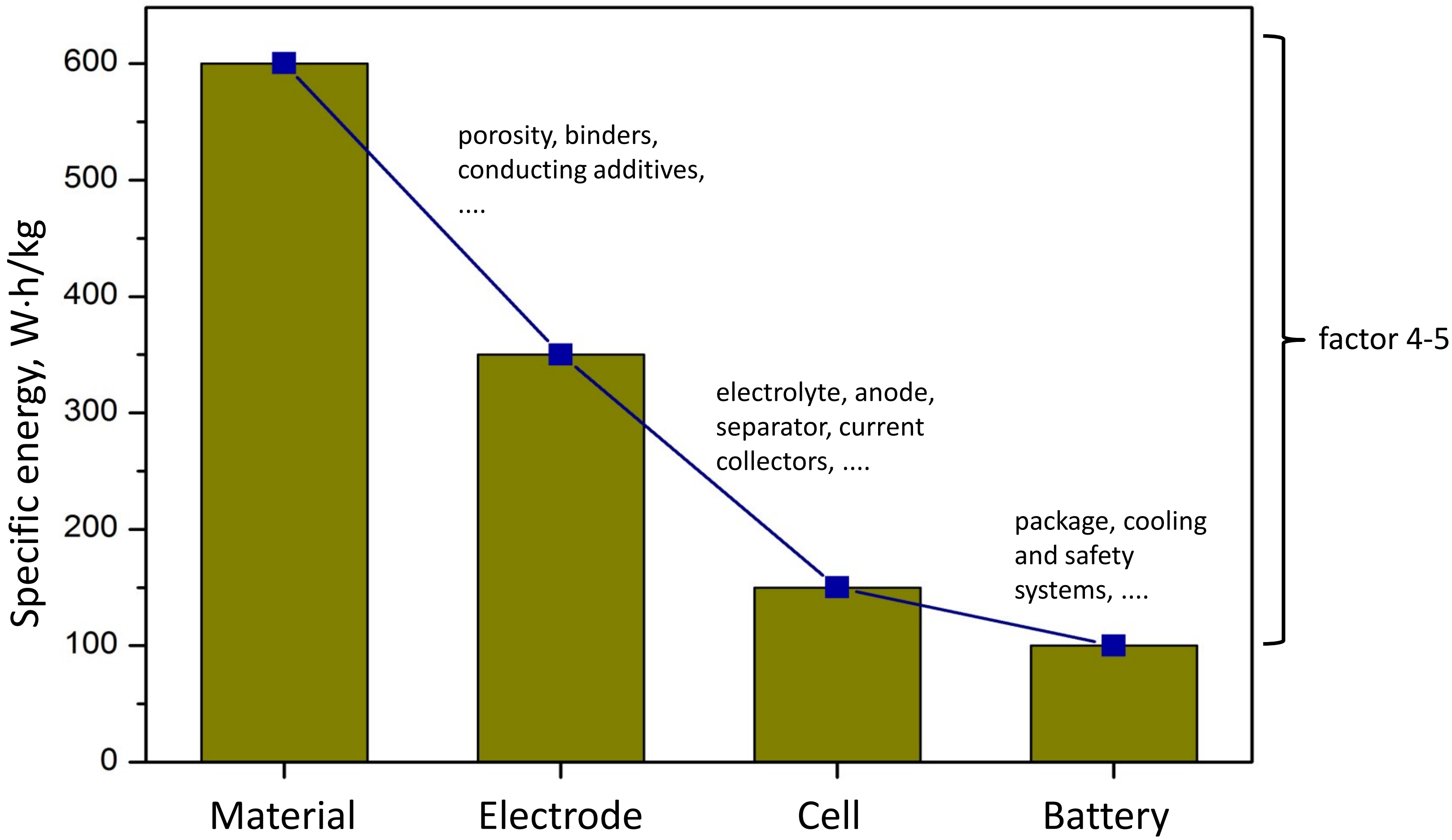
Cathode	LCO	LNO	NCA	NMC	LMO	LFP
Formula	$LiCoO_2$	$LiNiO_2$	$LiNi_{0.85}Co_{0.1}Al_{0.05}O_2$	$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$	$LiMn_2O_4$	$LiFePO_4$
Average potential vs Li^+/Li, V	3.7	3.6	3.65	3.9	4.0	3.5
Capacity, mA h/g	~150	~180	~130	~170	~110	~150
Specific energy, W·h/kg	~550	~650	~480	~660	~440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

Skoltech
Skolkovo Institute of Science and Technology

Cathode and anode materials

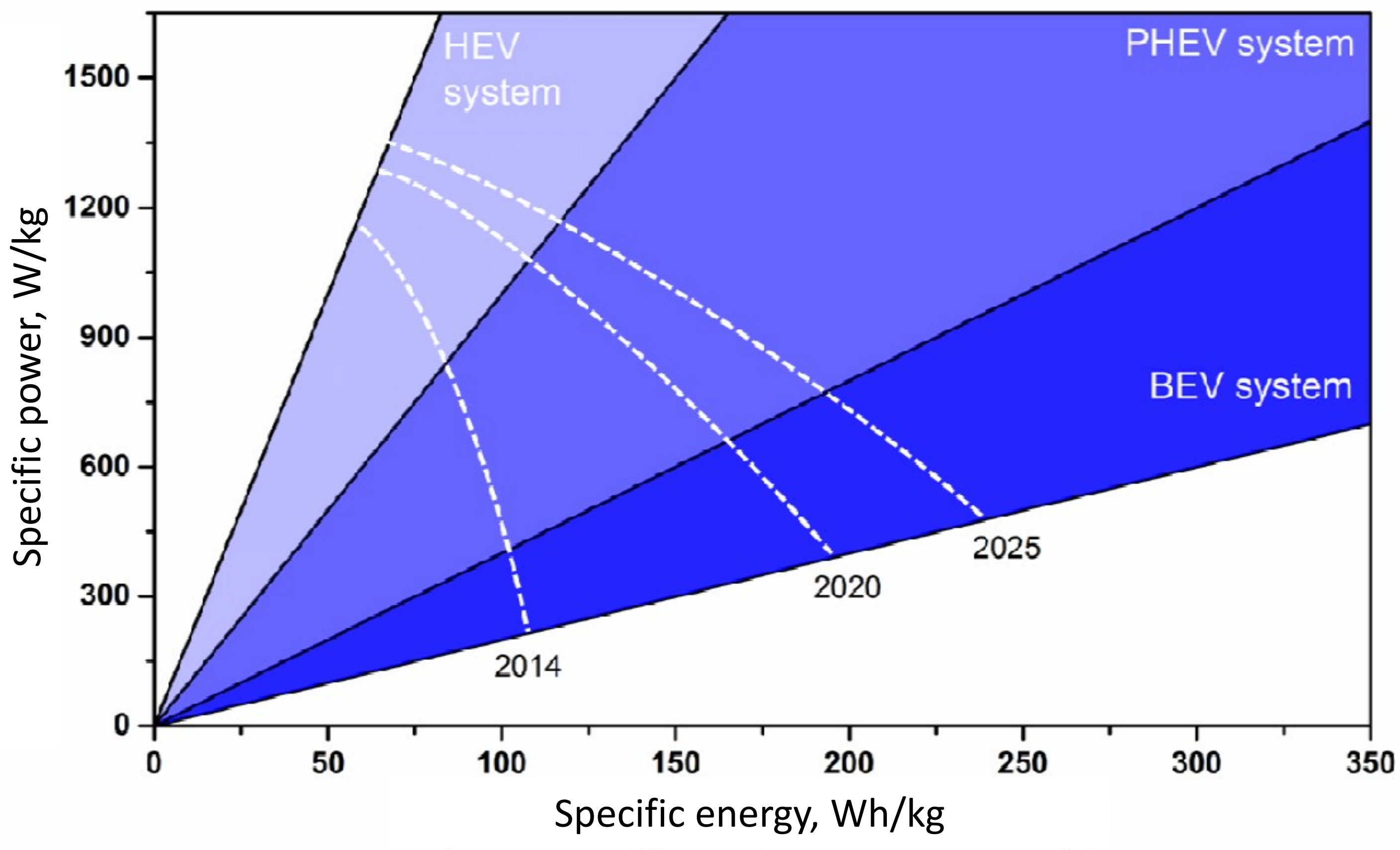


From cathode material to battery



Battery with specific energy of **200 W·h/kg** → cathode with specific energy of **800 – 1000 W·h/kg**

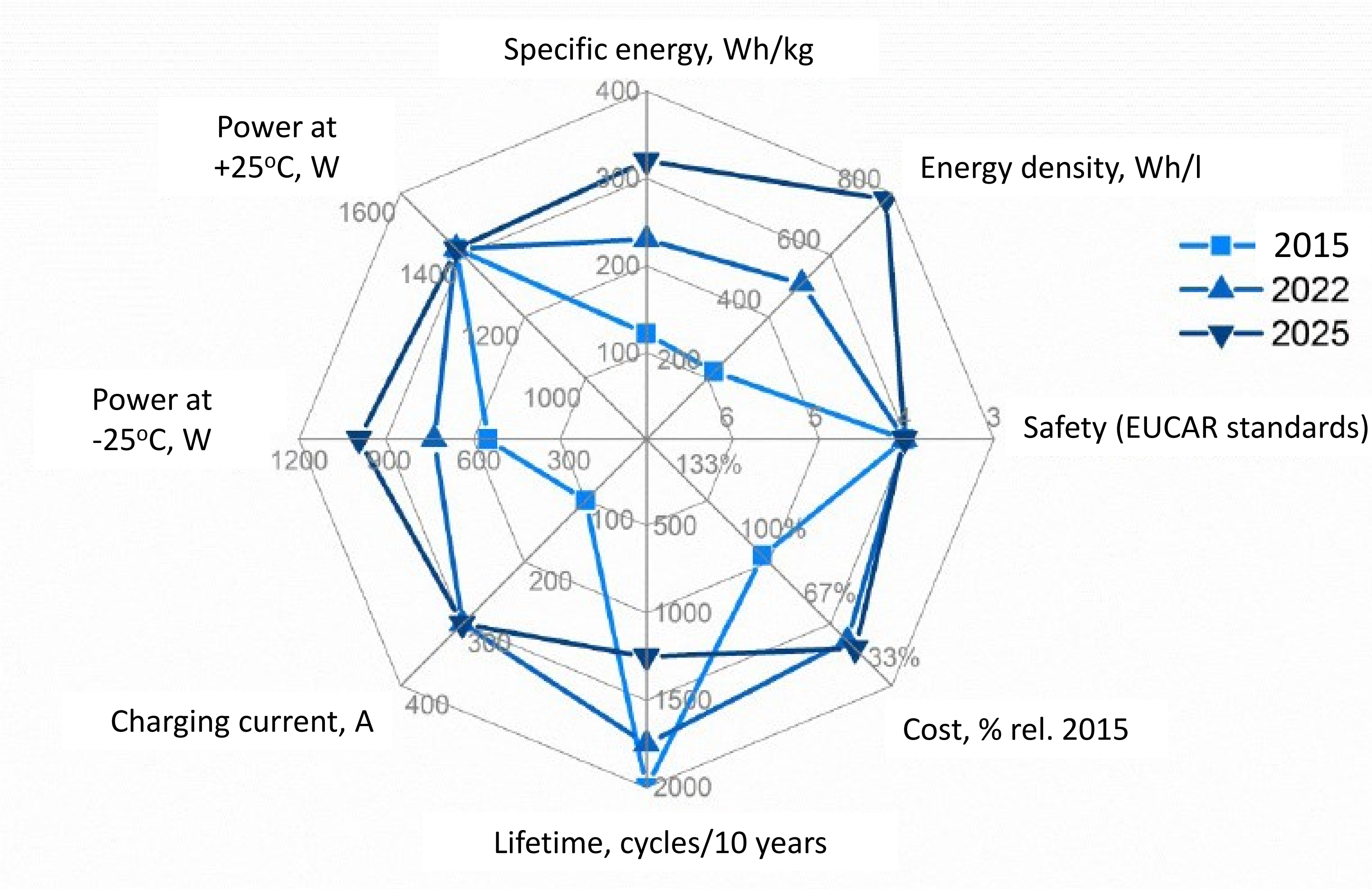
Batteries for automotive applications



Energy-power diagram for different types of electric vehicles and prospects for 2020 – 2025

D Andre et al, J. Materials Chem., 2015

Эволюция основных параметров

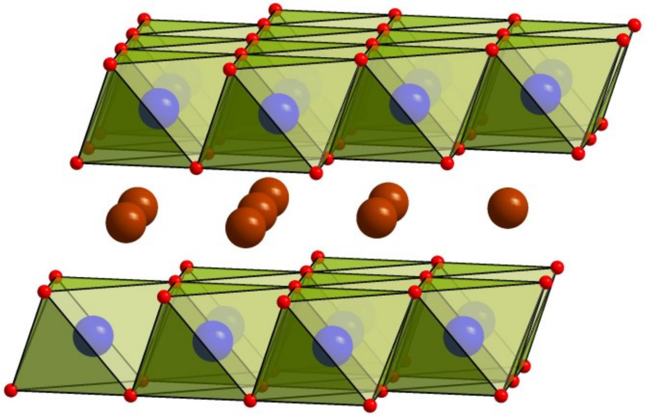


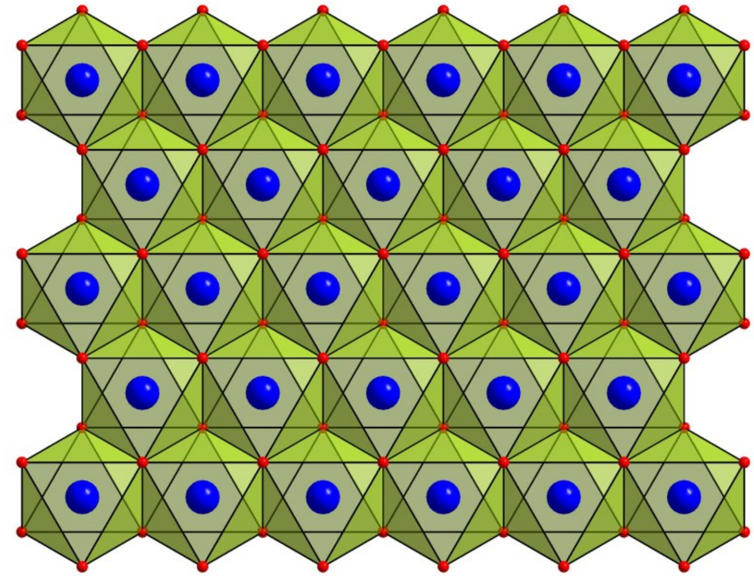
Key performance parameters road map on cell level for fully electrified vehicles from today to 2025.

D Andre et al, J. Materials Chem., 2015

Skoltech
Skolkovo Institute of Science and Technology

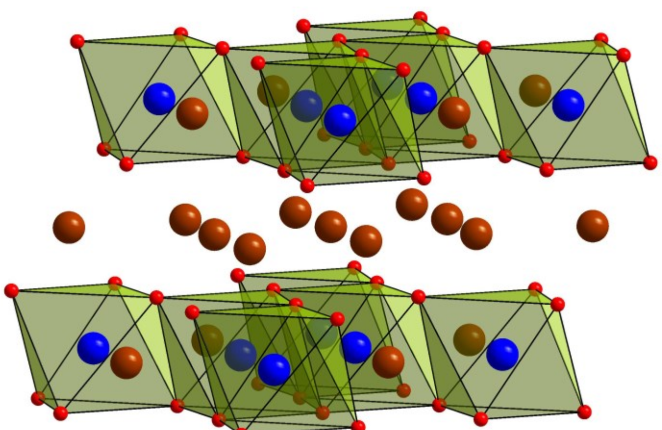
High capacity layered cathodes

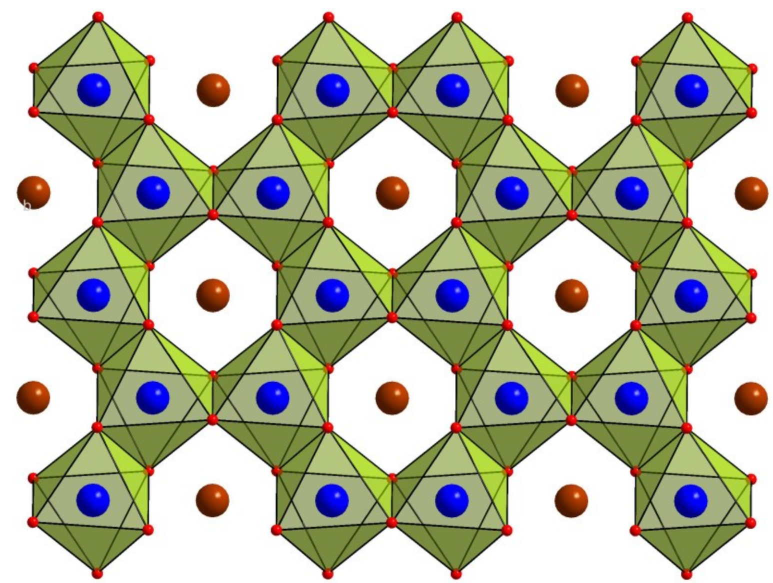




$LiCoO_2$

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





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

High capacity layered cathodes

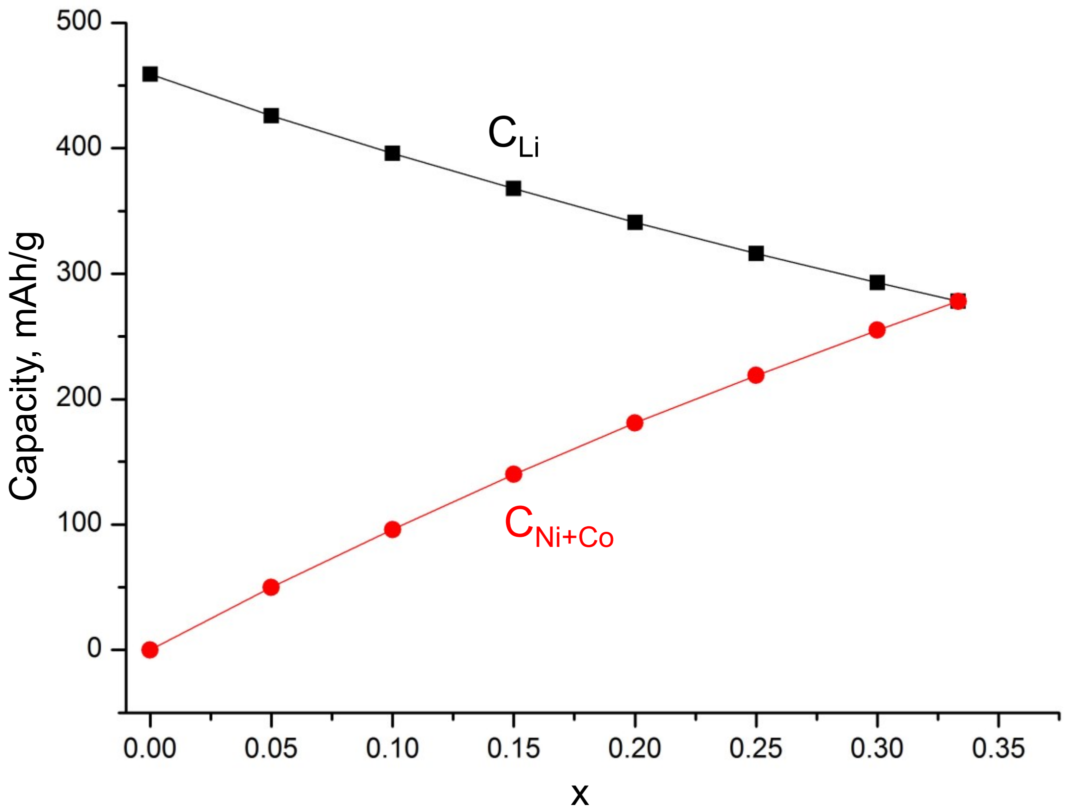
$Li_{4/3-x}Ni^{2+}_xMn^{4+}_{2/3-x}Co^{3+}_xO_2$

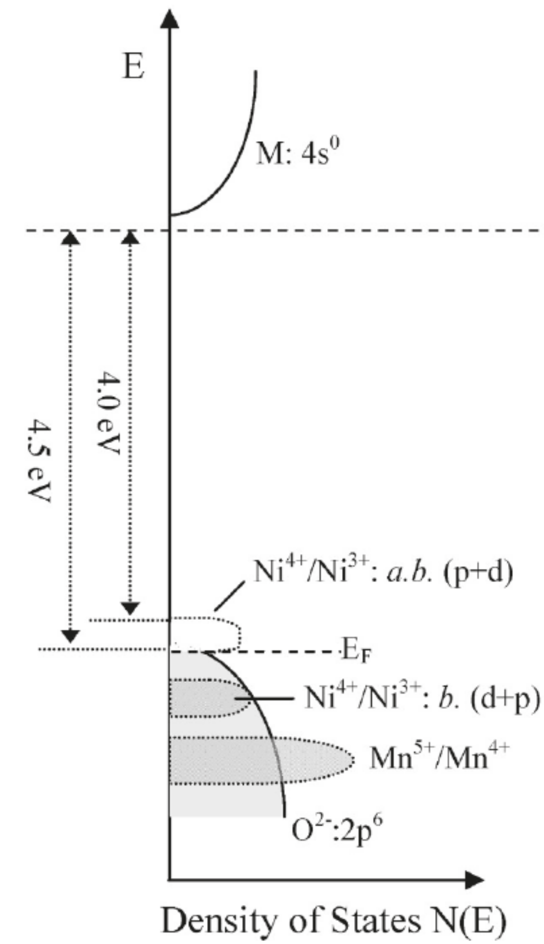
$Ni^{2+} \rightarrow Ni^{3+}, Ni^{4+}$

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

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

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

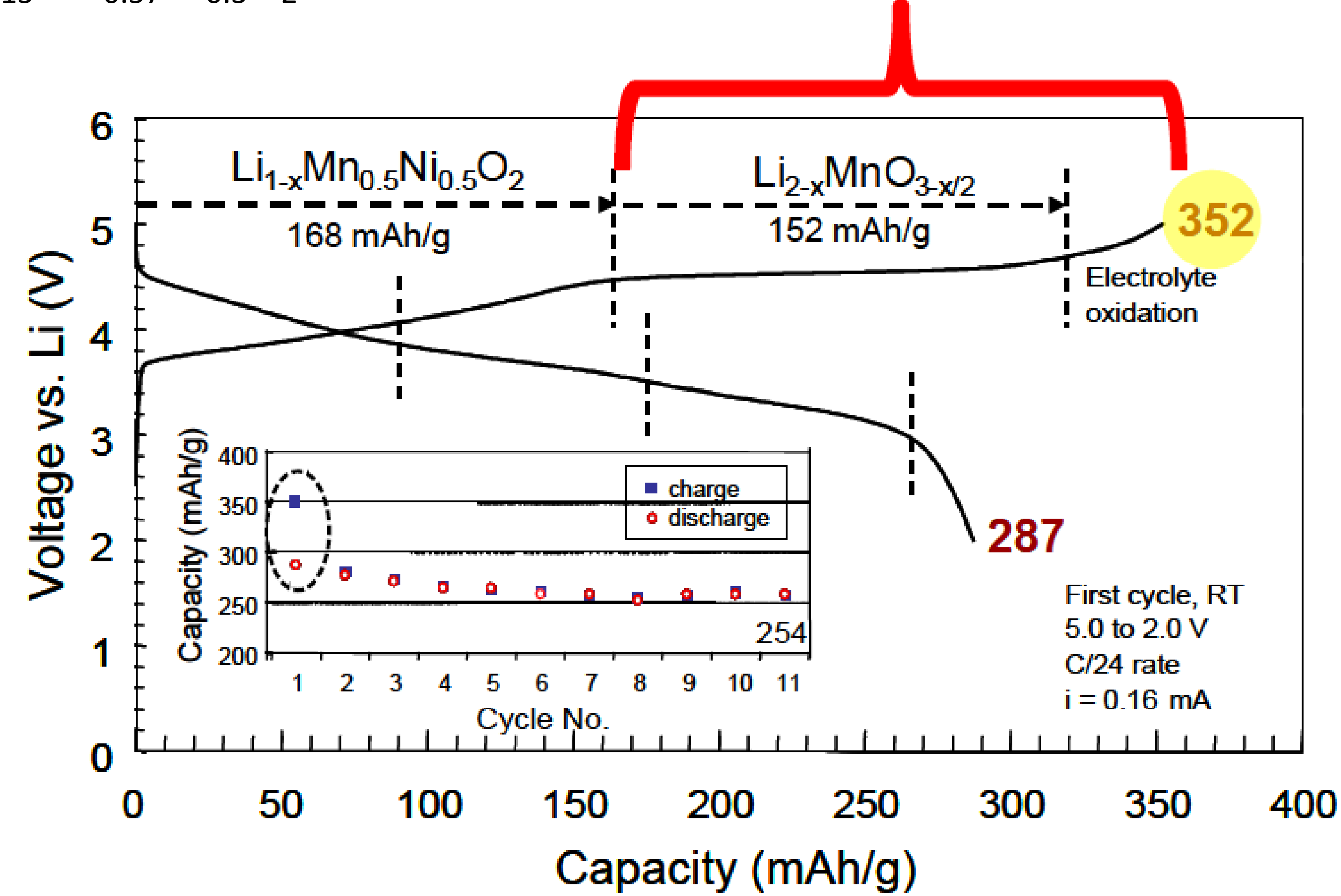




High capacity layered cathodes: excess capacity

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

What is the cause of the excess capacity?



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

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

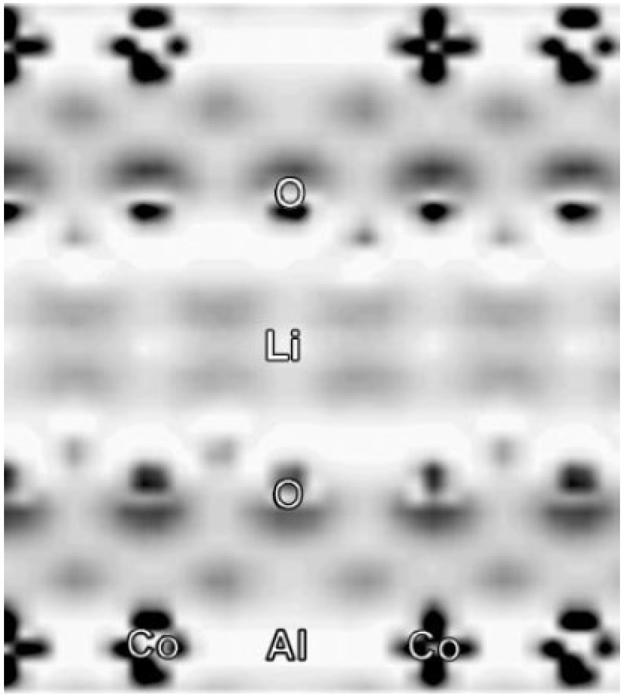
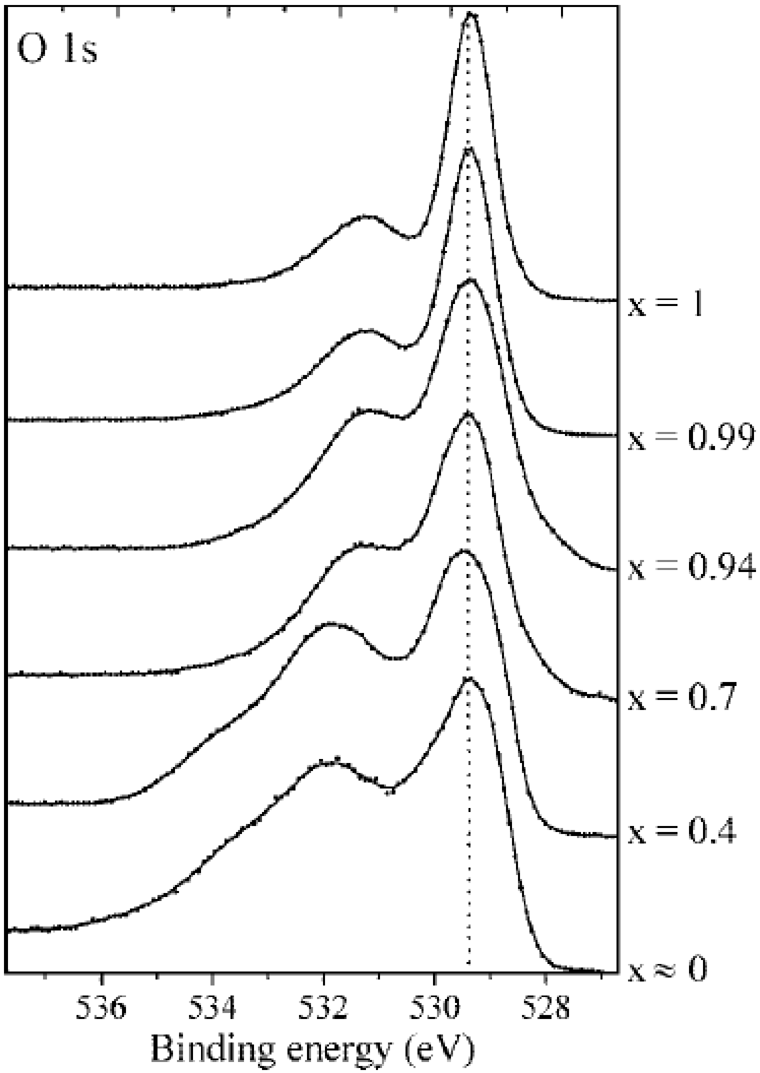
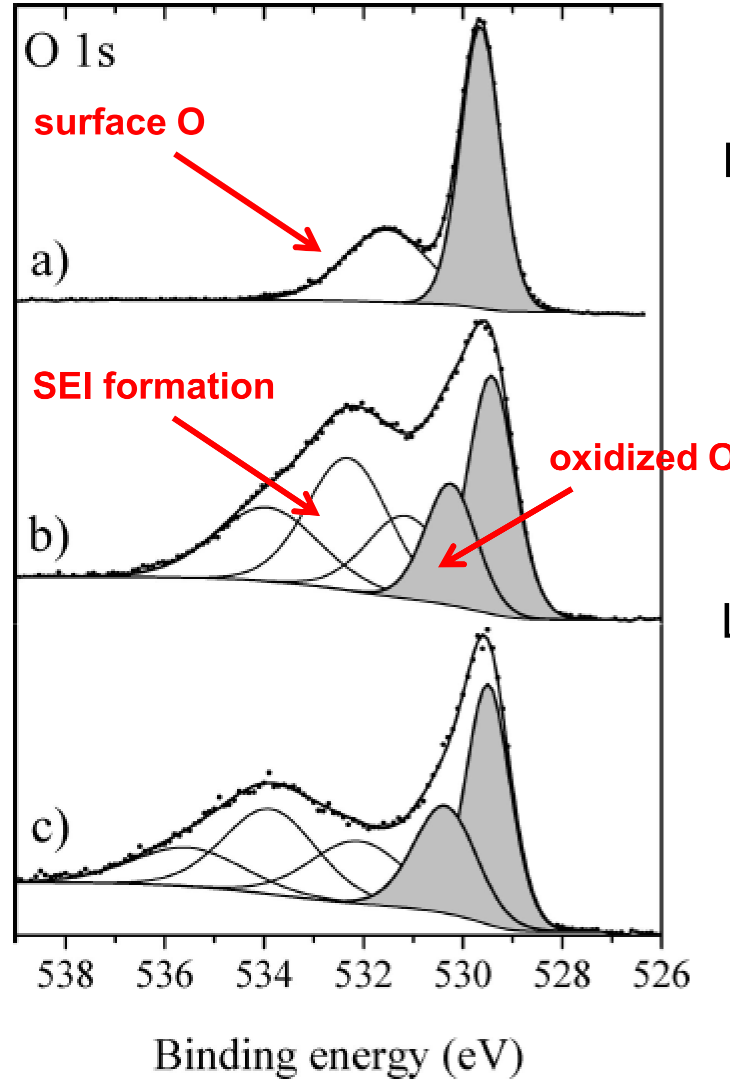


Figure 1 Positive part of the electron density difference between $Li(Al_{0.33}Co_{0.67})O_2$ and $(Al_{0.33}Co_{0.67})O_2$ in a plane perpendicular to the direction of layering in the structure. Darker indicates larger electron density.

Lattice oxygen oxidation



Li_xCoO_2 XPS O1s

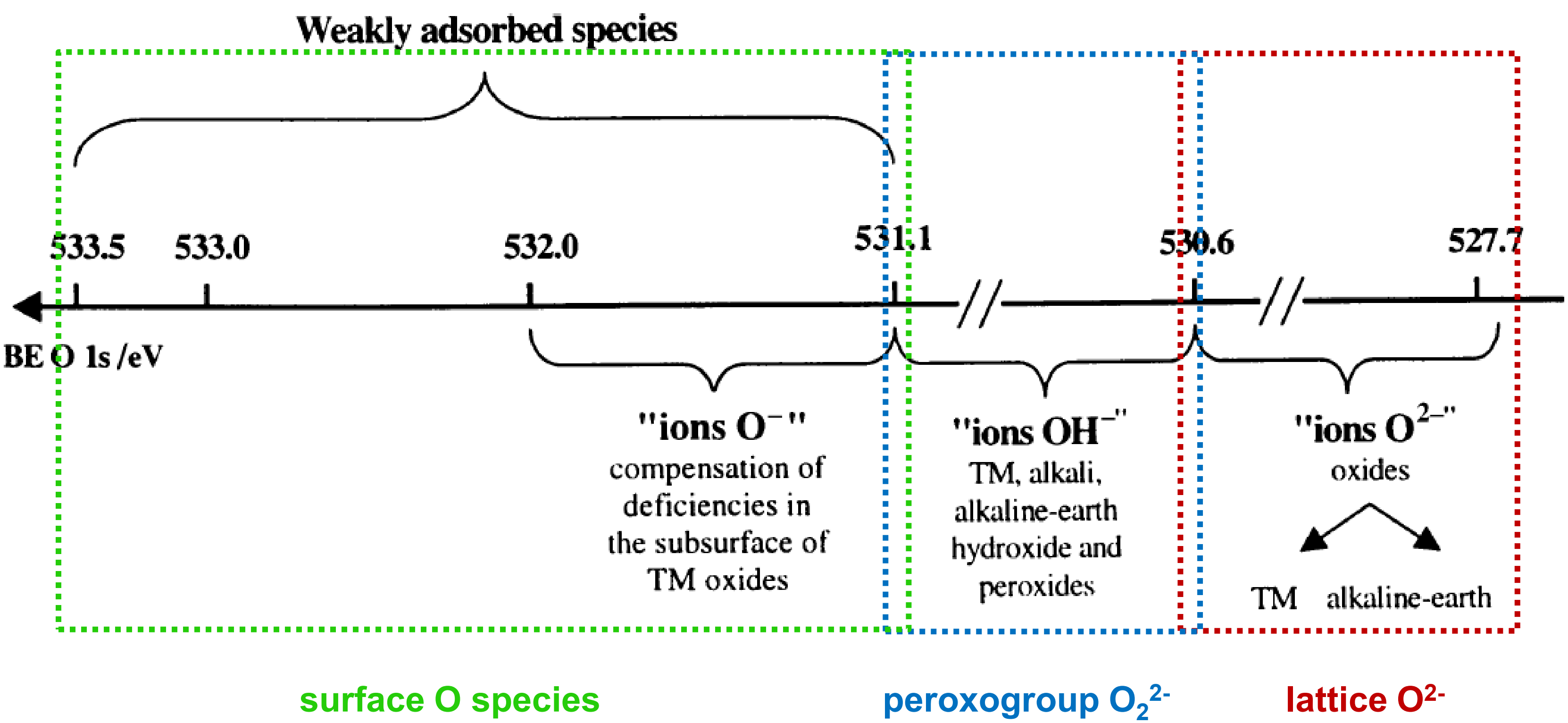


$LiCoO_2$

Li_0CoO_2

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

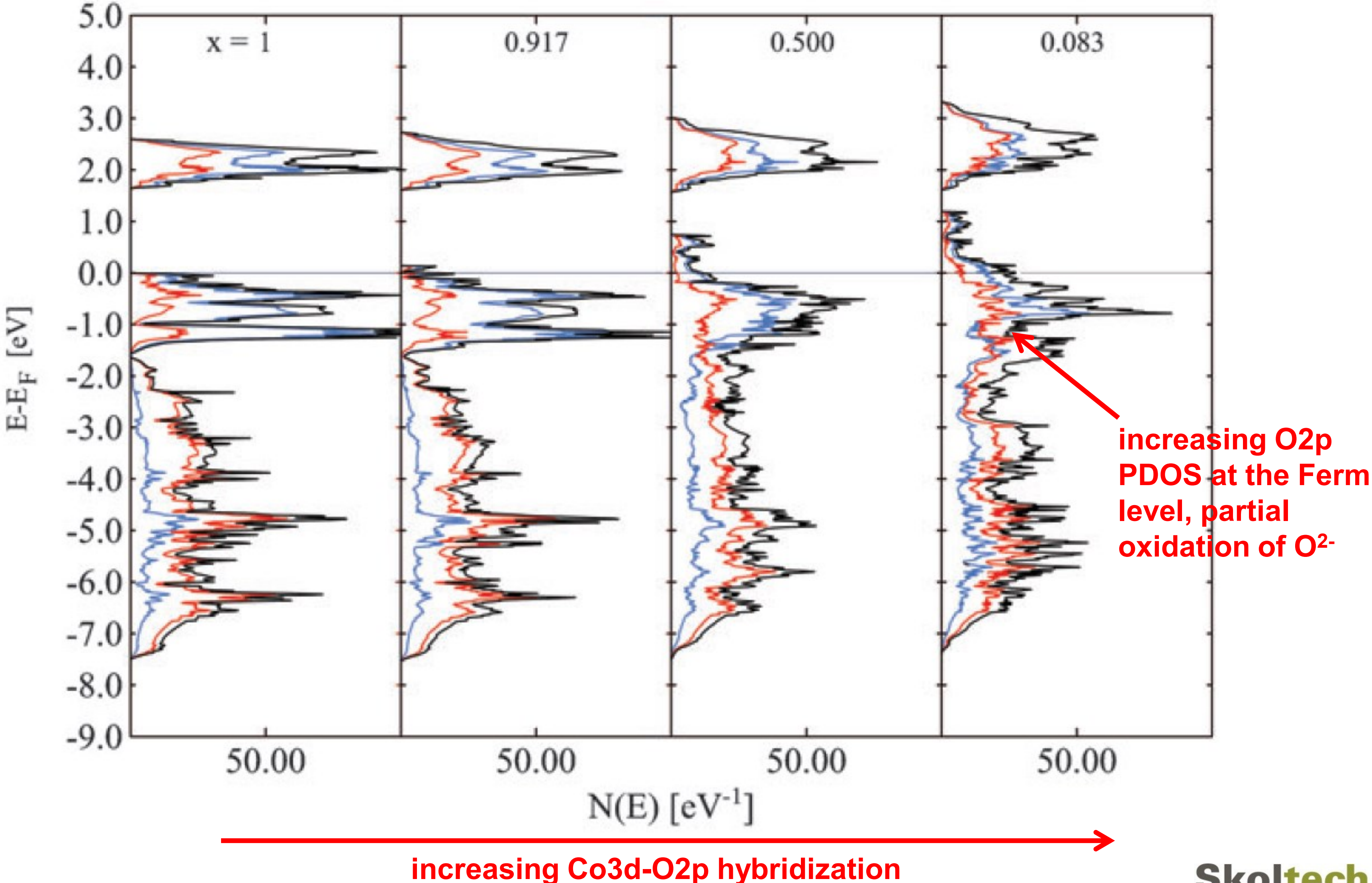
Lattice oxygen oxidation



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

Lattice oxygen oxidation

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

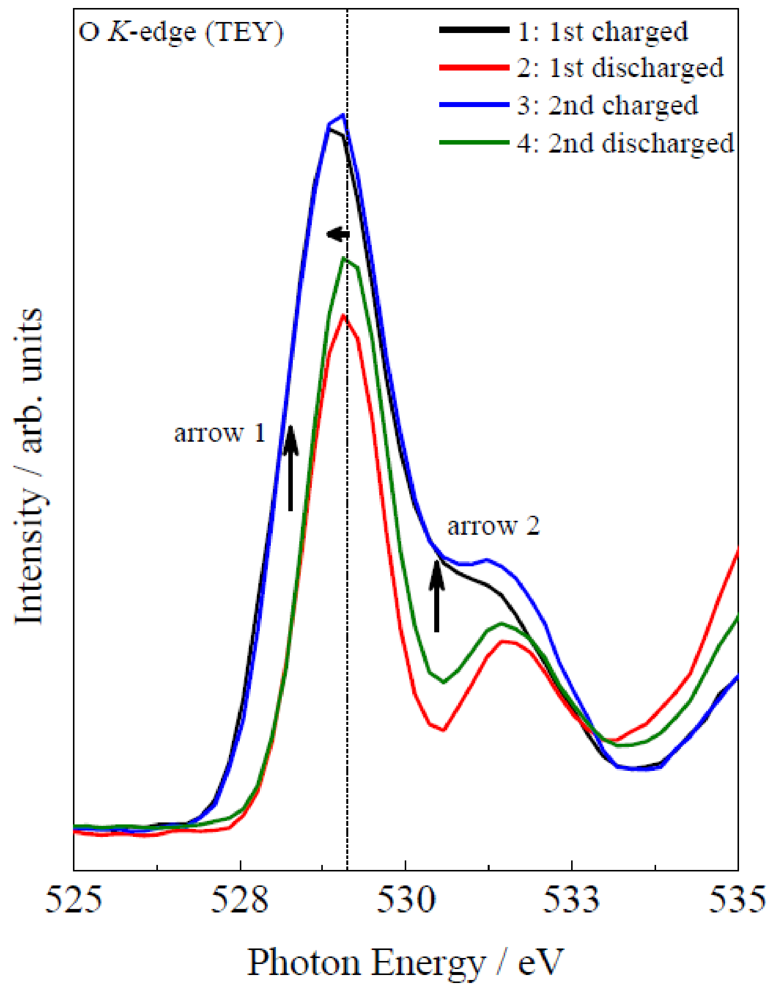


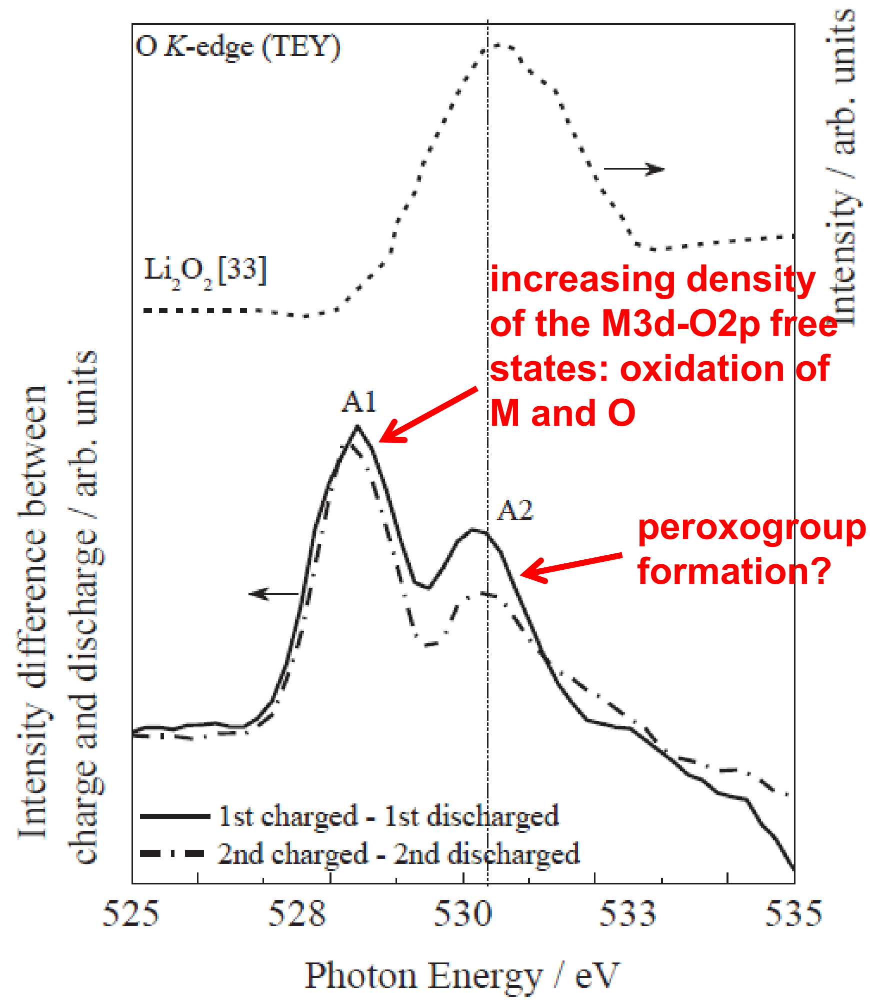
S.Laubach et al., Phys.Chem.Chem.Phys.,2009, 11, 3278

Skoltech
Skolkovo Institute of Science and Technology

Lattice oxygen oxidation

Li-rich NMC: O-K edge XAFS

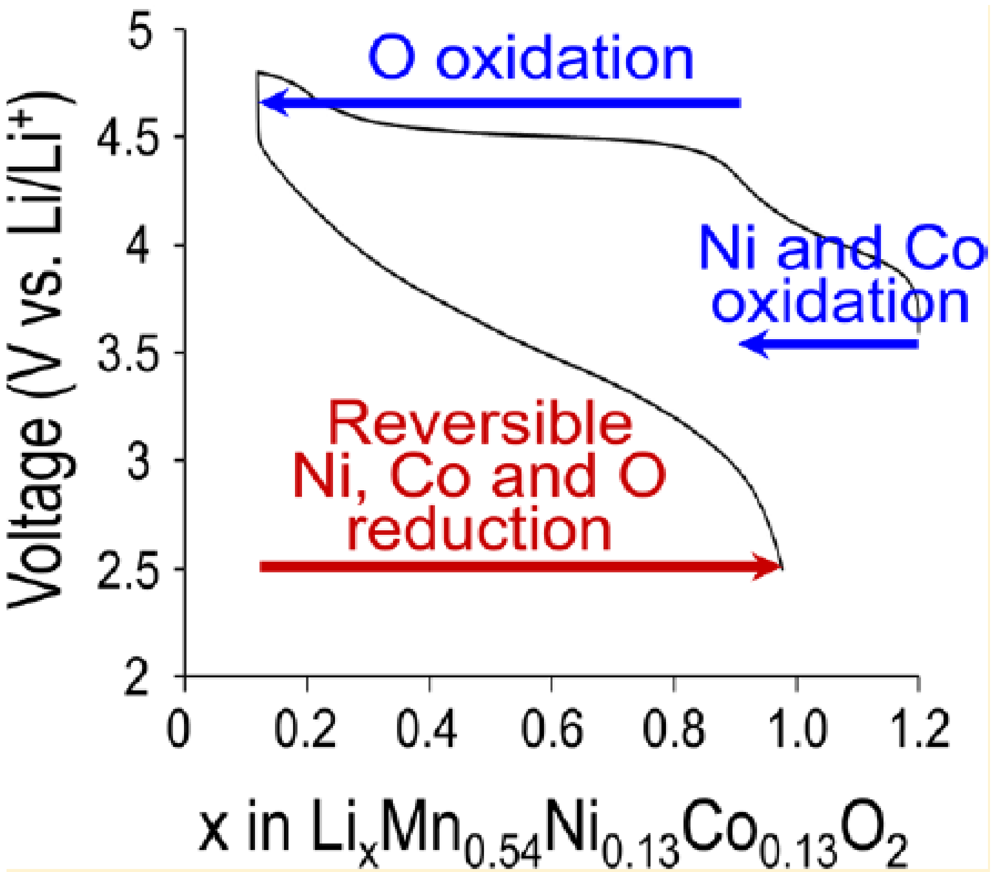




M.Oishi et al., J. Power Sources, 276, 89 (2015)

Skoltech
Skolkovo Institute of Science and Technology

Lattice oxygen oxidation



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

Two redox processes:

Ni^{2+}, Co^{3+} ↔ Ni^{4+}, Co^{4+}

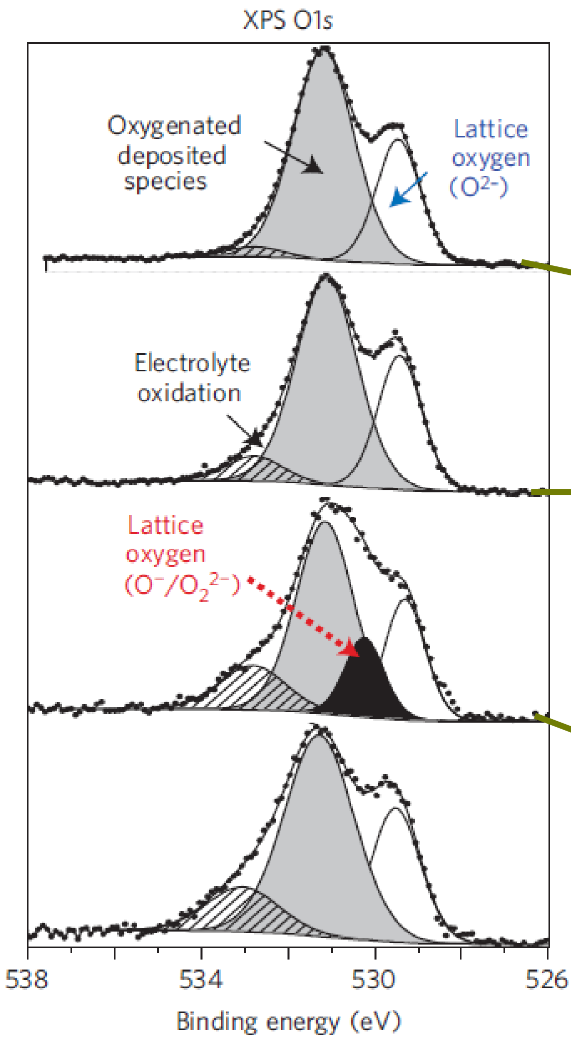
(Mn^{4+} is neither oxidized nor reduced)

Reversible oxygen oxidation

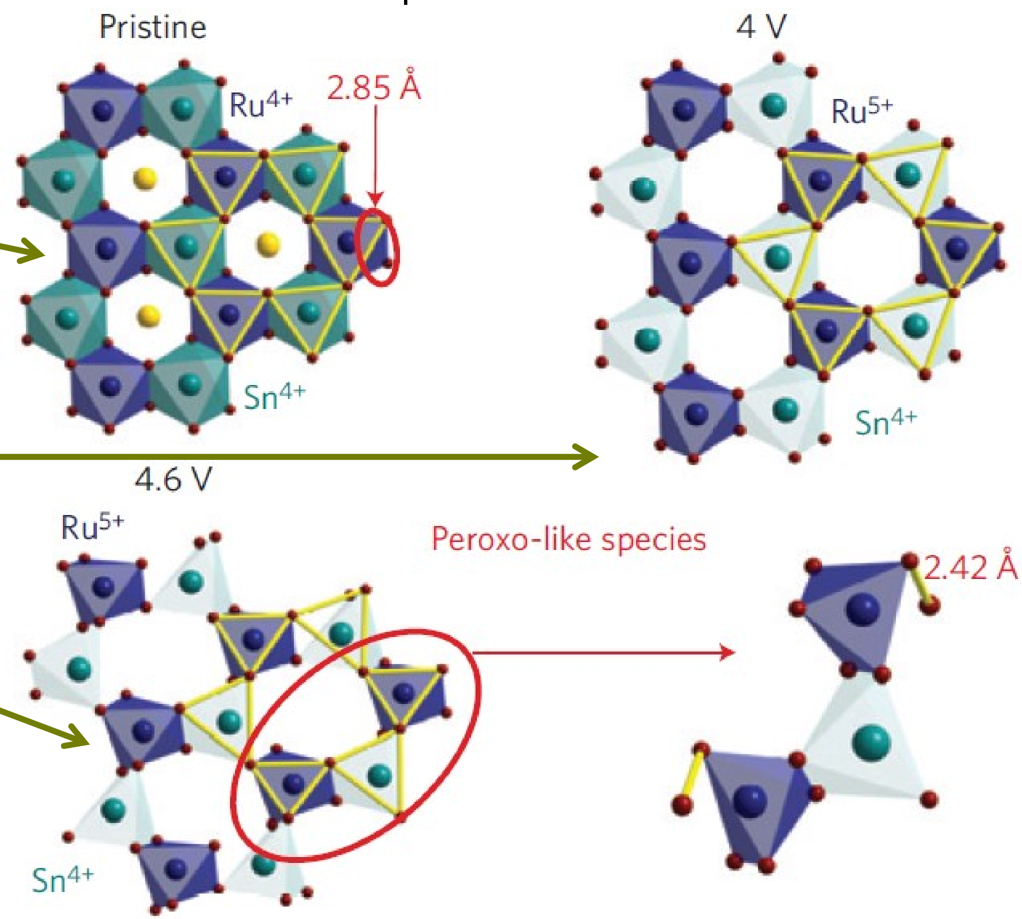
H.Koga et al., J. Phys. Chem. C, 118, 5700 (2014)

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)

Skoltech
Skolkovo Institute of Science and Technology

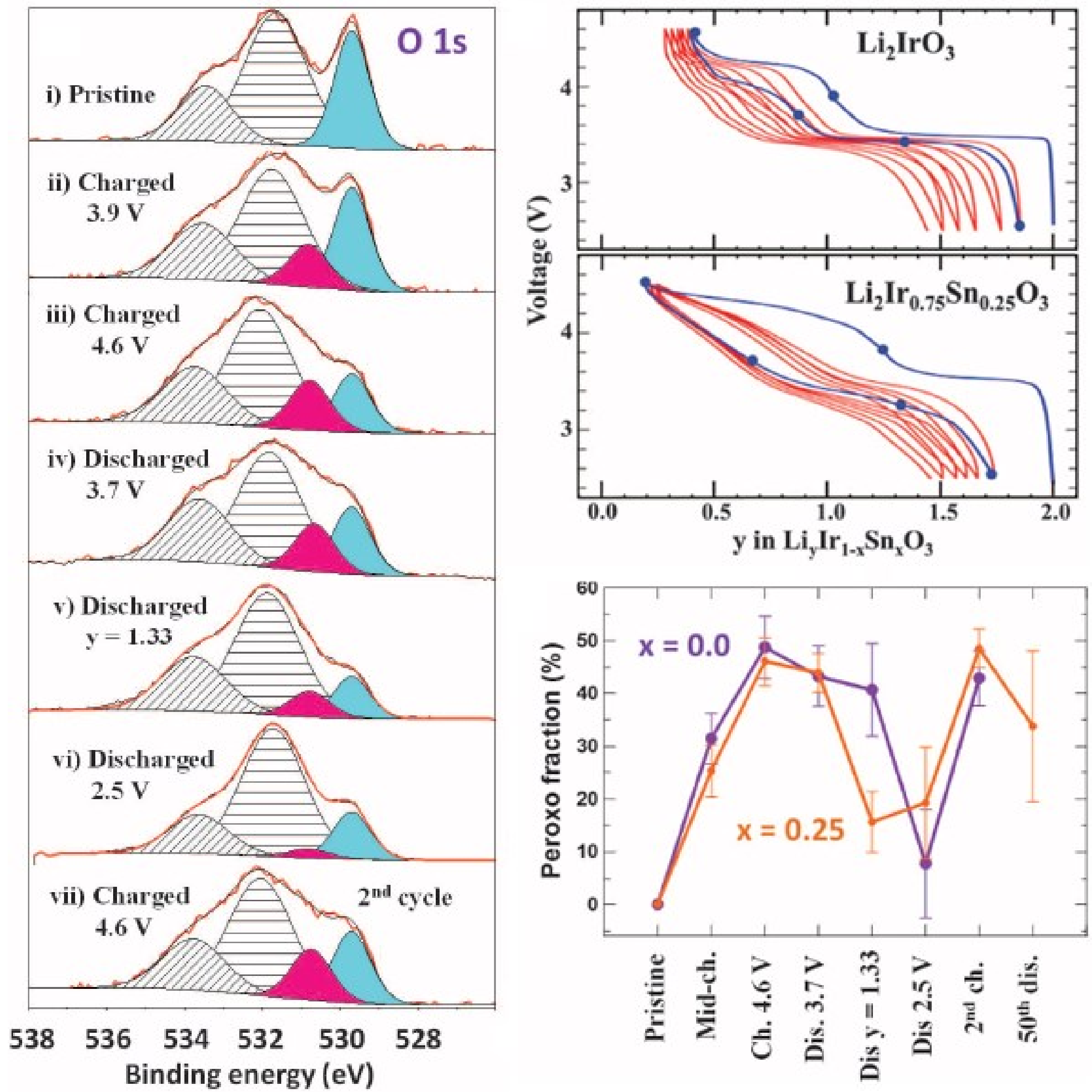
Formation of O_2^{n-}

Li_2IrO_3

Two redox processes:

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

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



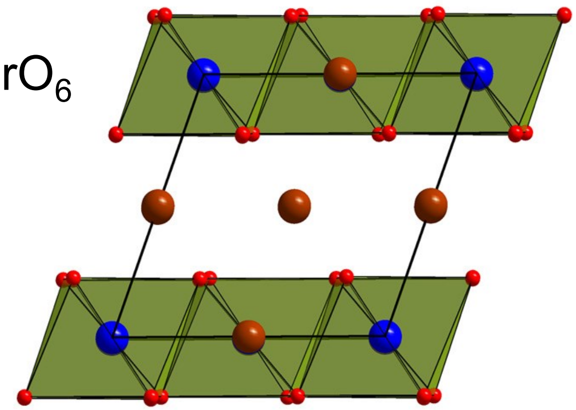
E.McCalla et al., Science, 350, 1516 (2015)

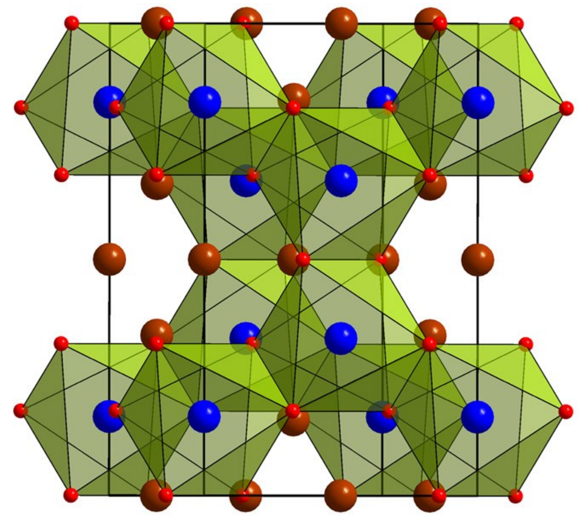
Formation of O_2^{n-}

Li_2IrO_3

LiO_6, IrO_6

Li



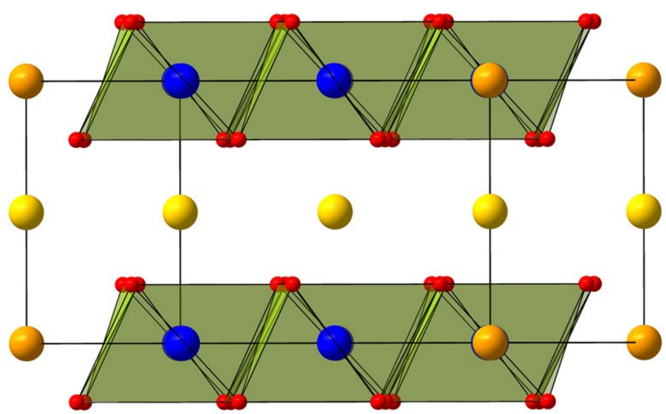


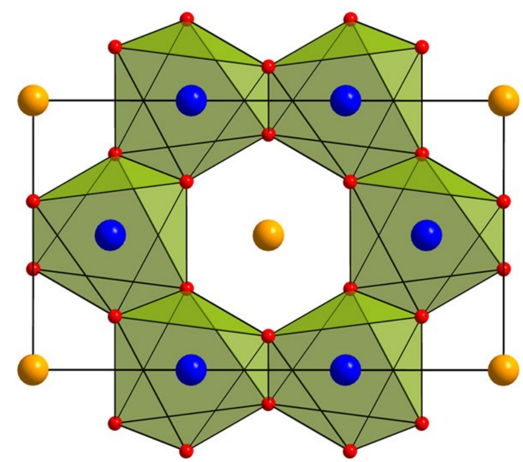
O3

$Li_{0.5}IrO_3$

IrO_6

Li_x

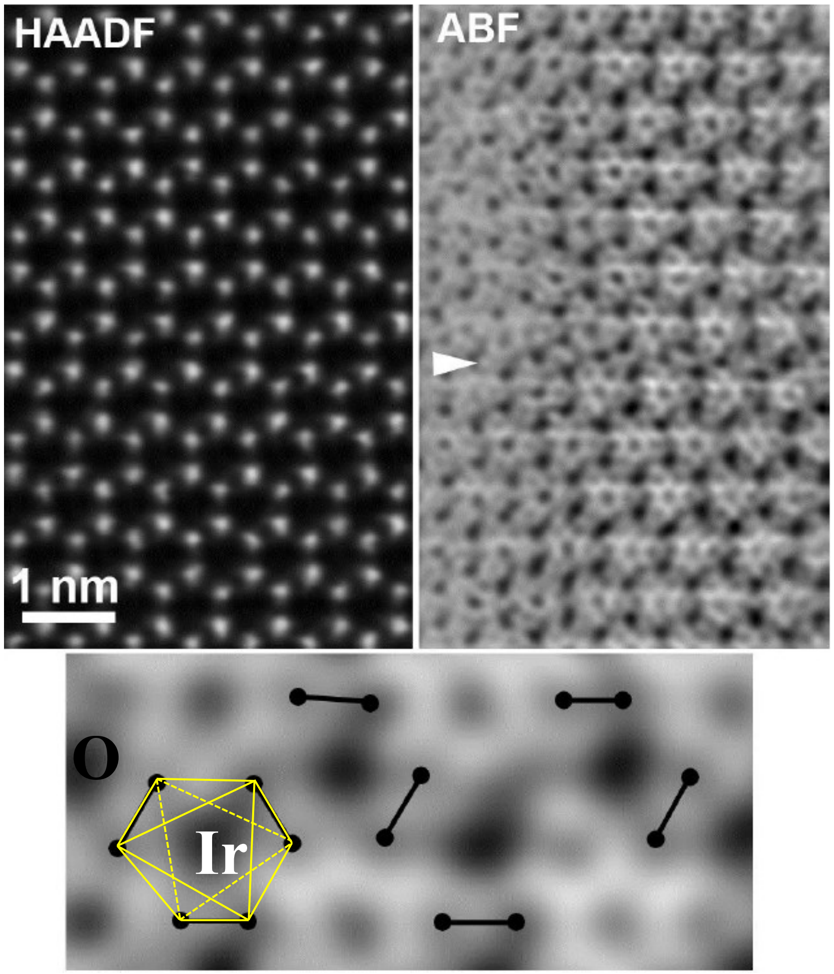




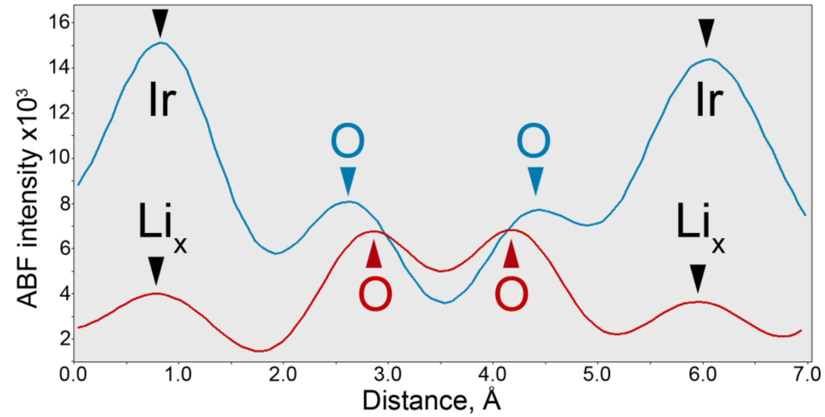
O1

E.McCalla et al., Science, 350, 1516 (2015)

Formation of O_2^{n-}



$Li_2IrO_3 \rightarrow Li_{0.5}IrO_3$: 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

E.McCalla et al., Science, 350, 1516 (2015)

Skoltech
Skolkovo Institute of Science and Technology

Formation of O_2^{n-}

Table 1. Average O-O distances obtained by DFT, NPD, and TEM. "Short" refers to two oxygen atoms between two nearest-neighbor Ir atoms, as viewed in the [001] projection in Fig. 3, E and F. "Long" refers to distances at which the oxygen atoms lie between an Ir atom and a vacancy. In all cases, the distances are averages for the structure. Projected distances are shown for the O1 structure only. N/A, not applicable; ND, not determined.

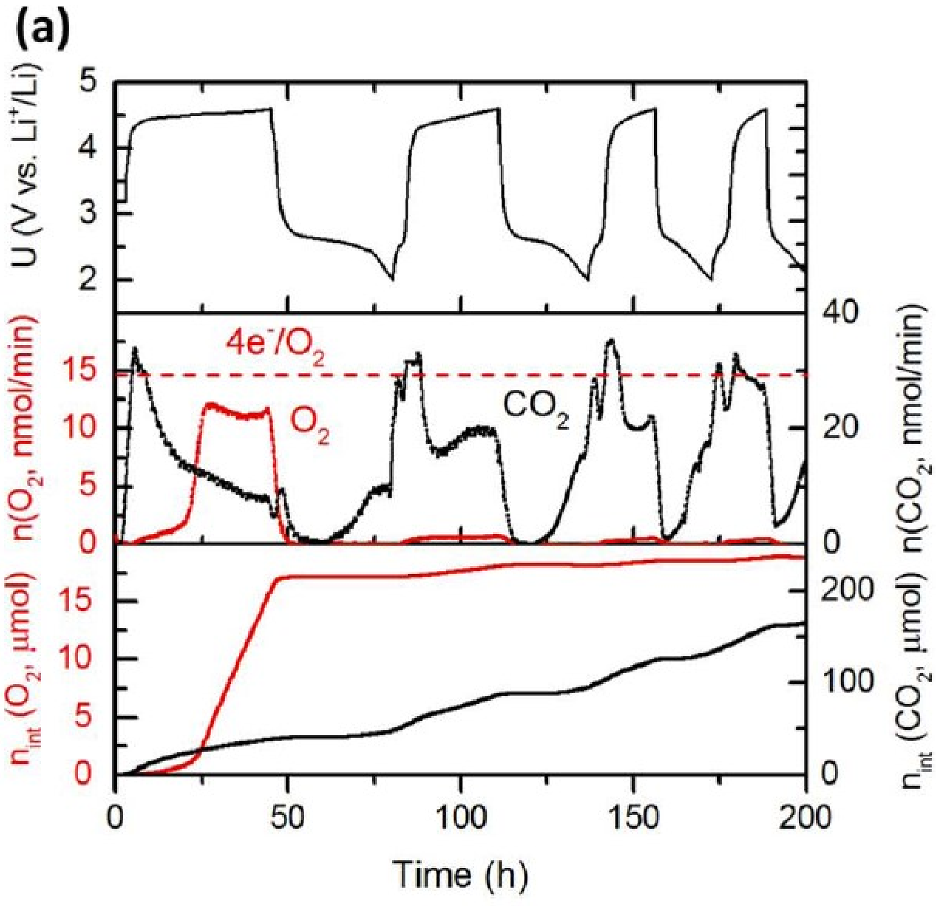
Sample	O-O distance (Å)		O-O distance in [001] projection (Å)	
	Short	Long	Short	Long
Li_2IrO_3				
Neutron	2.77(2)	2.84(2)	N/A	N/A
DFT	2.74	2.89	N/A	N/A
$Li_{0.5}IrO_3$				
Neutron	2.45(2)	2.73(4)	1.42(1)	1.86(3)
DFT	2.54	2.77	1.51	1.88
TEM	ND	ND	1.56	1.83
$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$*	2.686	2.686	N/A	N/A
$Li_{0.04}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$*	2.553	2.553	N/A	N/A

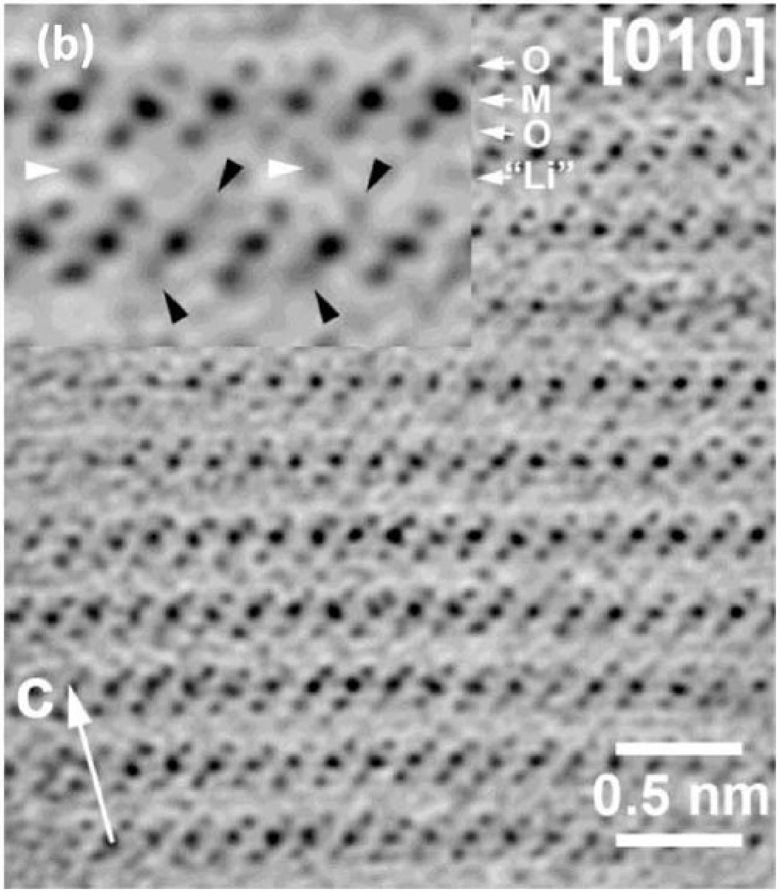
E.McCalla et al., Science, 350, 1516 (2015)

Skoltech
Skolkovo Institute of Science and Technology

Oxygen evolution and thermal runaway

partially charged $Li_{3.27}Fe_{0.56}TeO_{5.5}$

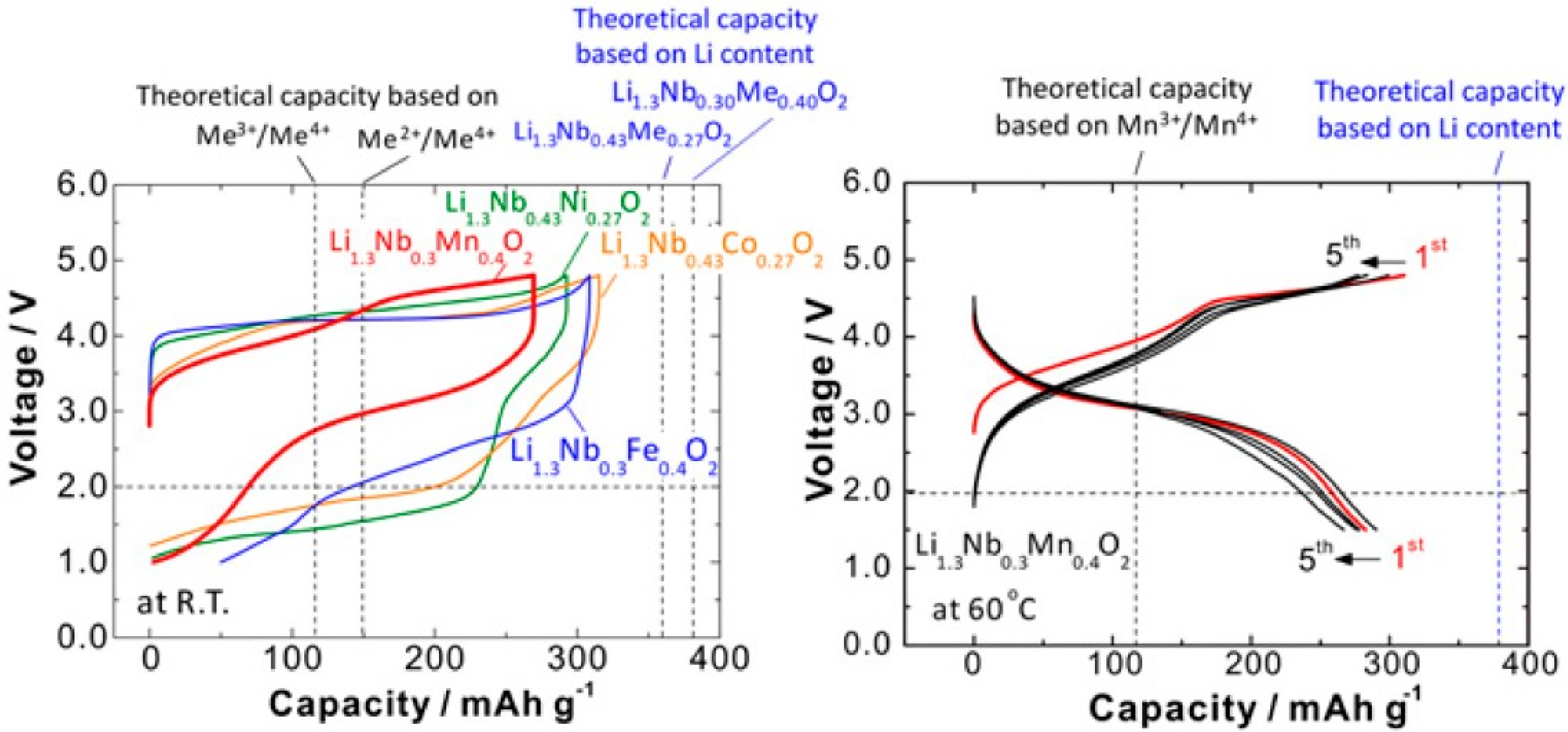




Irreversible capacity solely due to the oxygen evolution

McCalla et al., JES, 162, A1341 (2015)

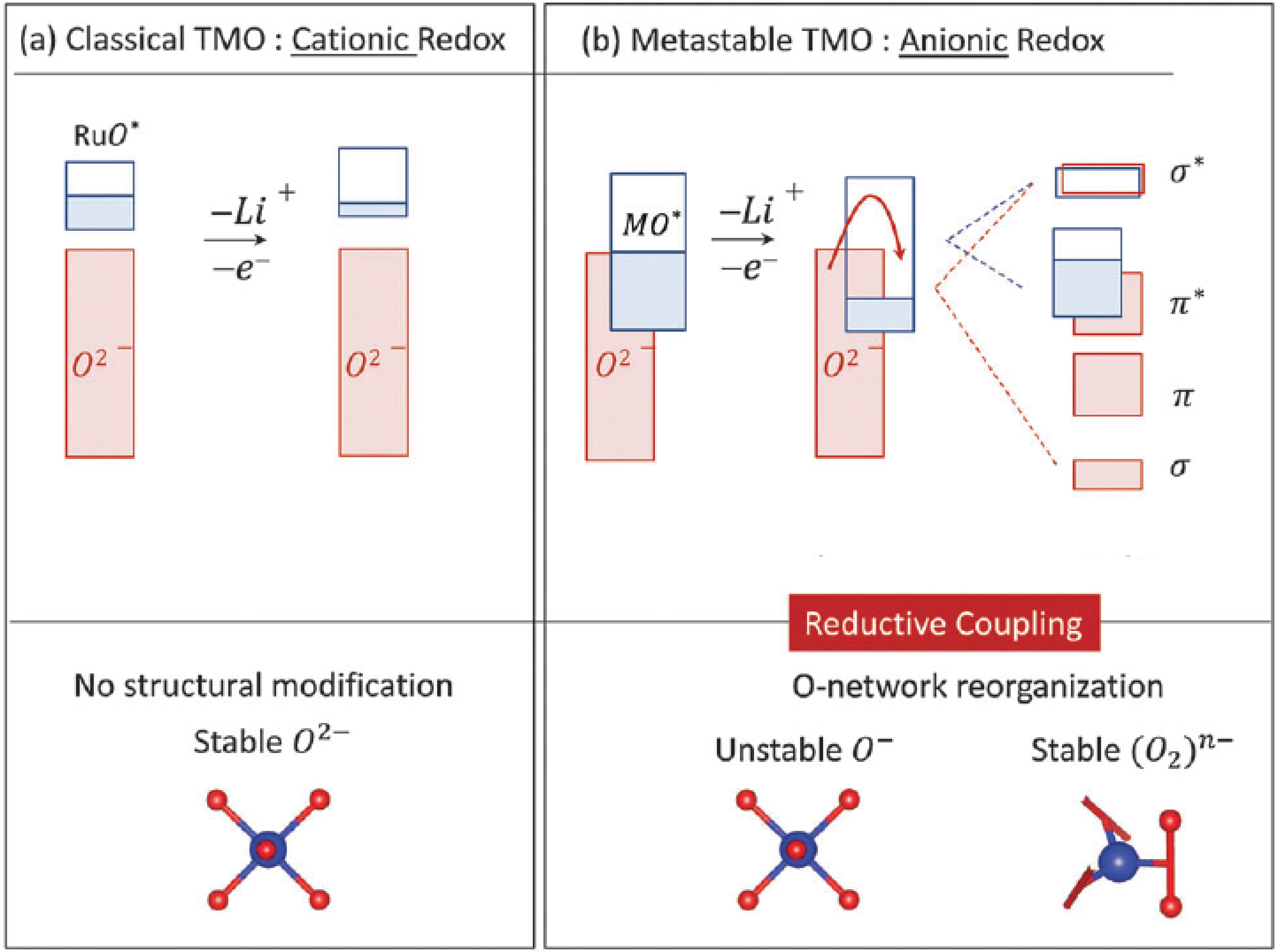
Reversible oxygen oxidation



N. Yabuuchi et al., PNAS, 2015

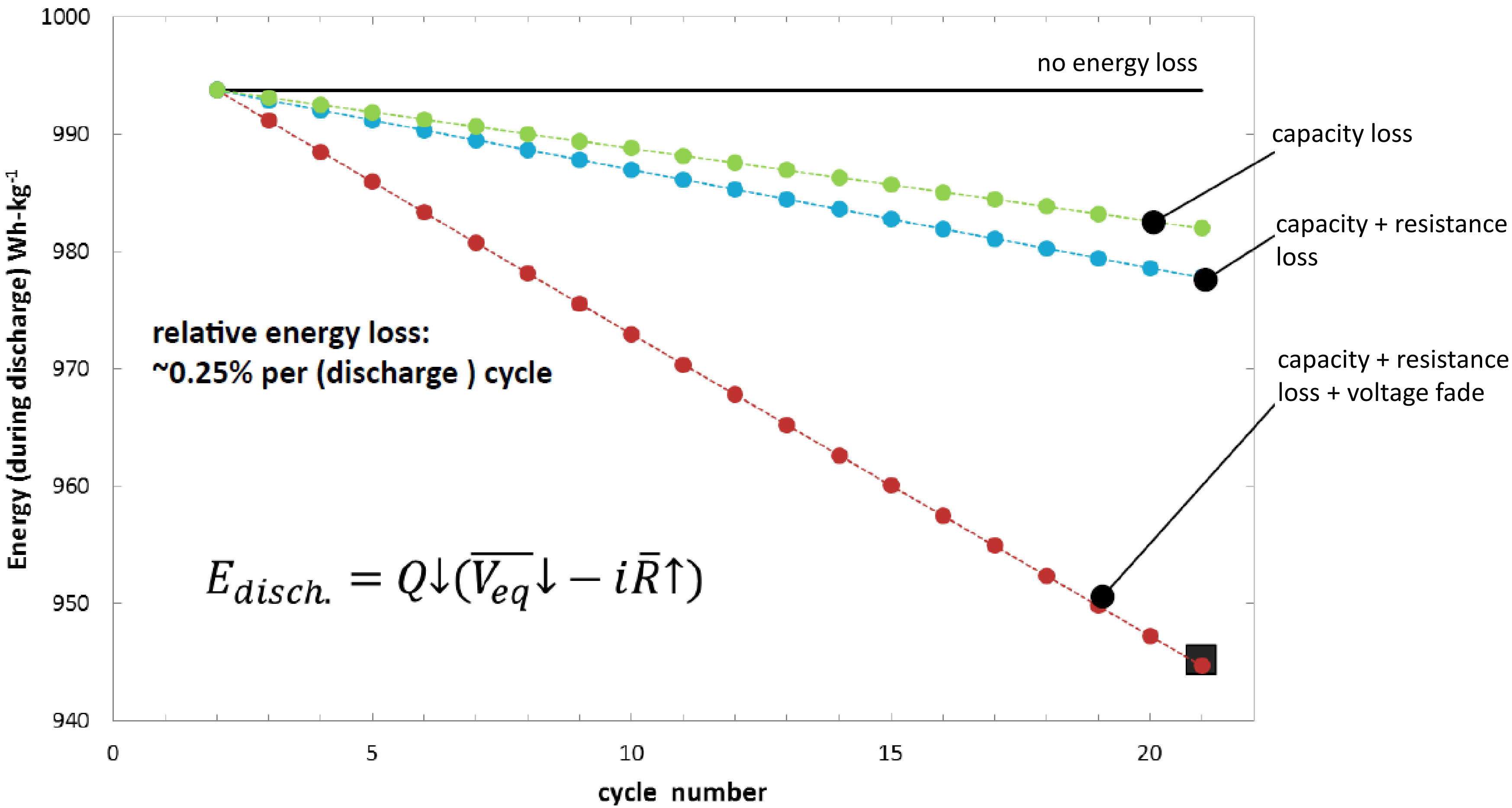
Skoltech
Skolkovo Institute of Science and Technology

Metastable anionic redox reaction



High capacity layered cathodes: energy losses

$Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$

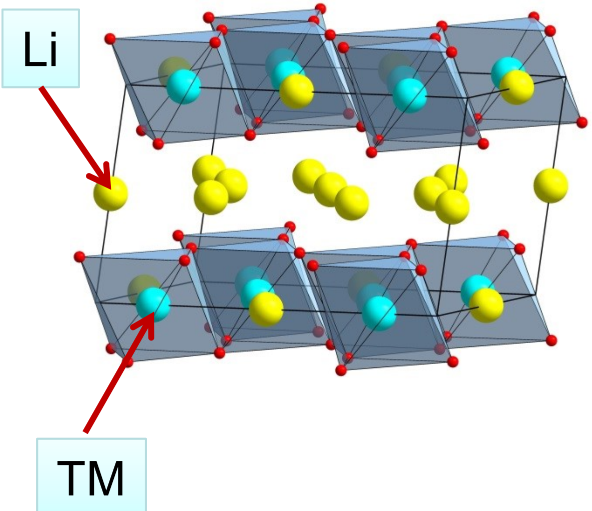


$$E_{disch.} = Q\downarrow(\overline{V_{eq}}\downarrow - i\bar{R}\uparrow)$$

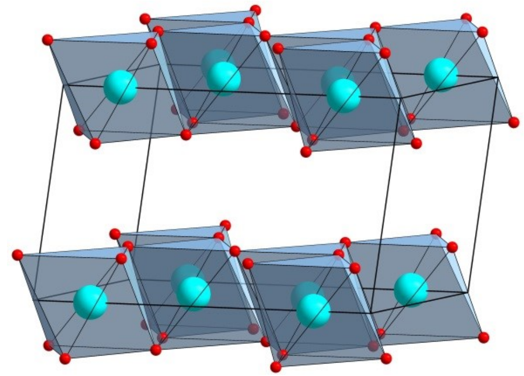
High capacity layered cathodes: energy losses

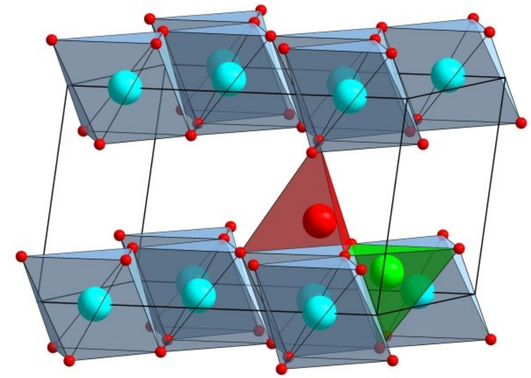
- Do the TM cations migrate?
- What are the host positions?
- Is the migration reversible?

Pristine Li_2MO_3
M – 3*d*, 4*d* transition metal

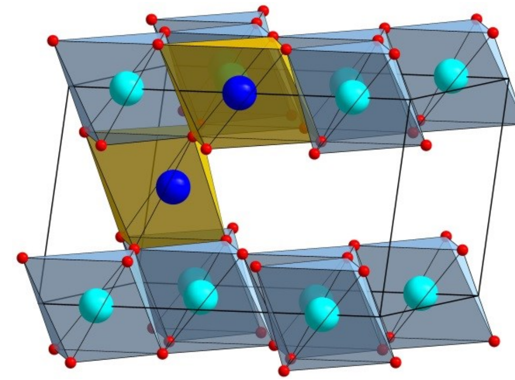


Hypothetic
fully delithiathed



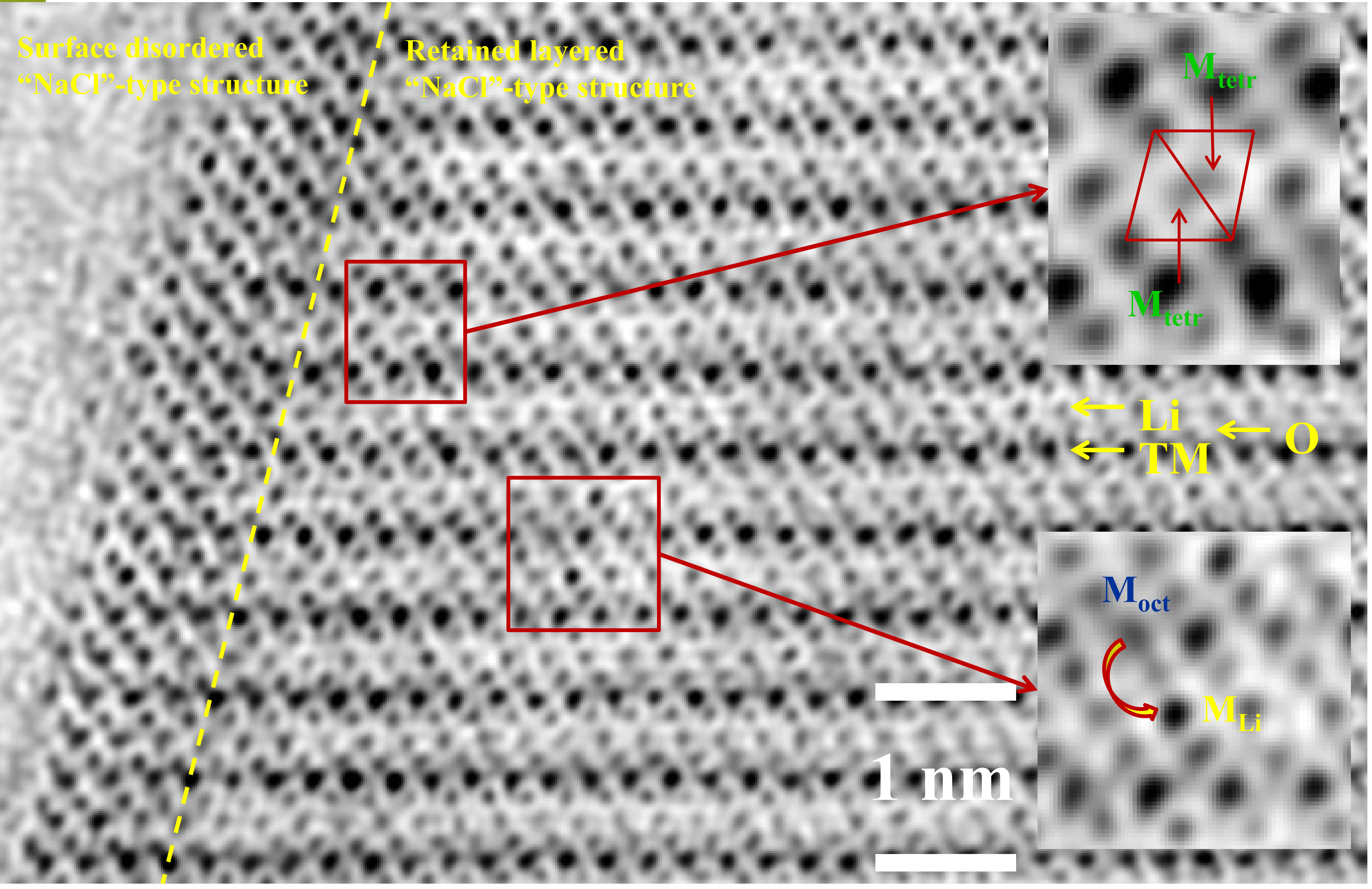


Migration of the M cations
to intra- and interlayer
tetrahedral sites



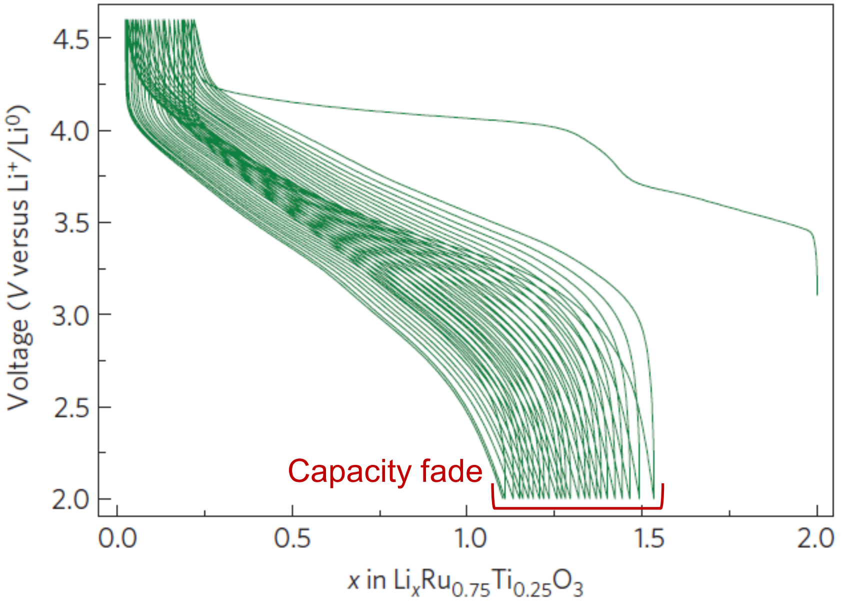
Migration of the M cations
to intra- and interlayer
octahedral sites

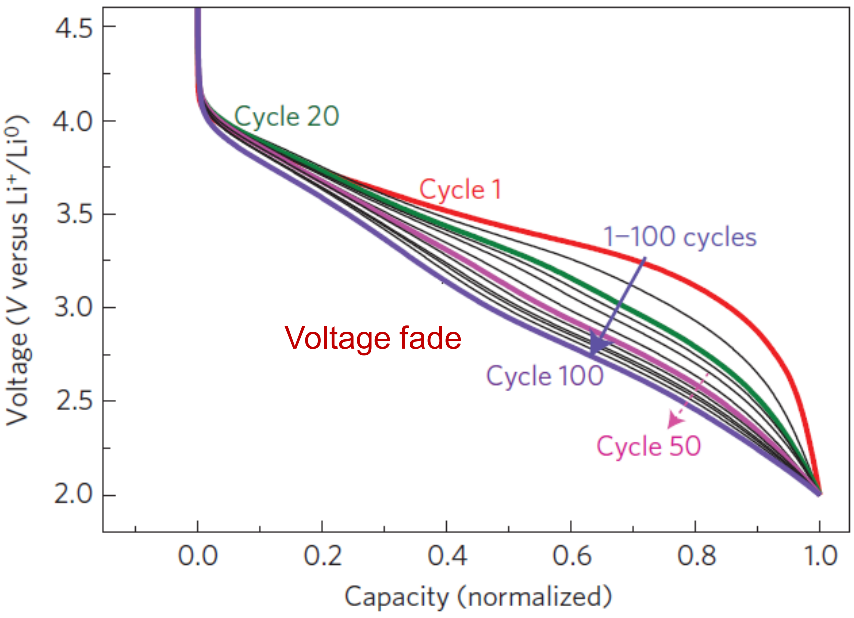
High capacity layered cathodes: energy losses



Capacity and voltage fade – $Li_2Ru_{0.75}Ti_{0.25}O_3$

100 charge/discharge cycles – discharge curves

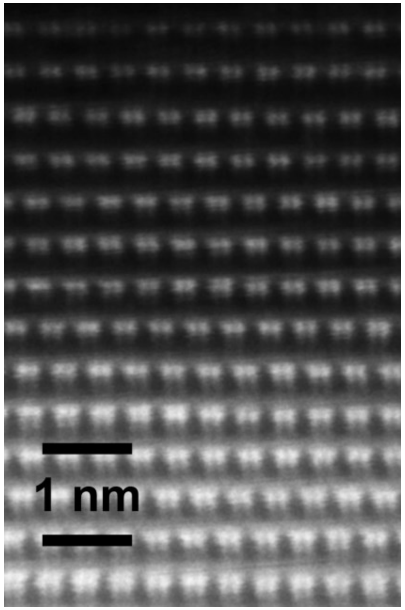




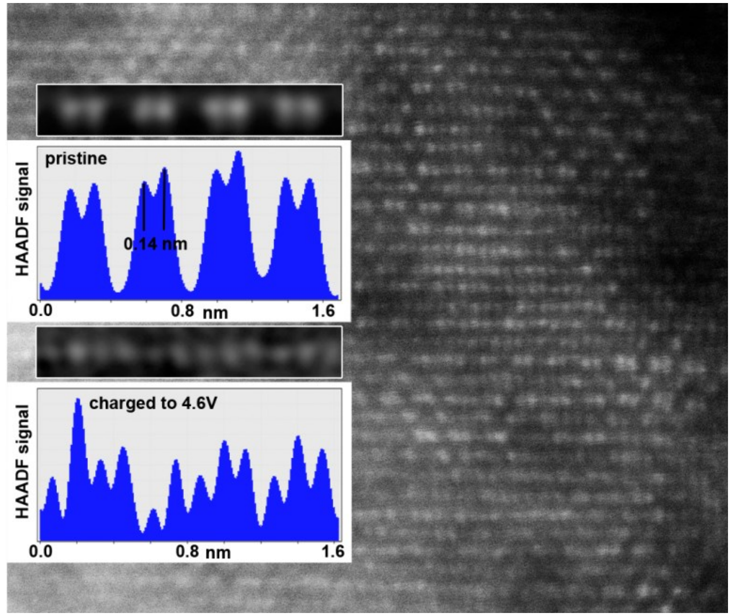
Sathiya, Abakumov, Foix, Rousse, Ramesha, Saubanère, Doublet, Vezin, Laisa, Prakash, Gonbeau, Van Tendeloo, Tarascon, *Nature Mater.*, 14, 230 2015

TM cation migration – $Li_2Ru_{0.75}Ti_{0.25}O_3$

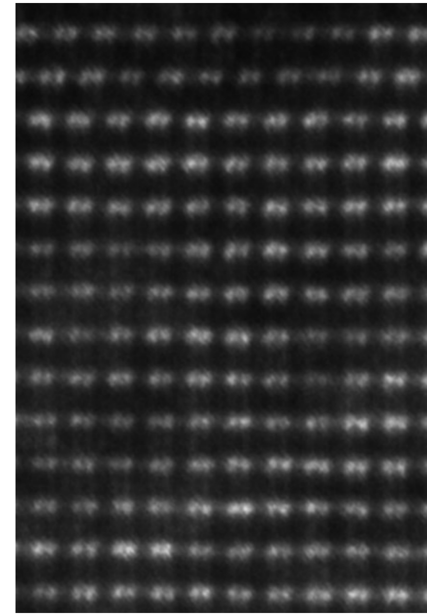
Pristine



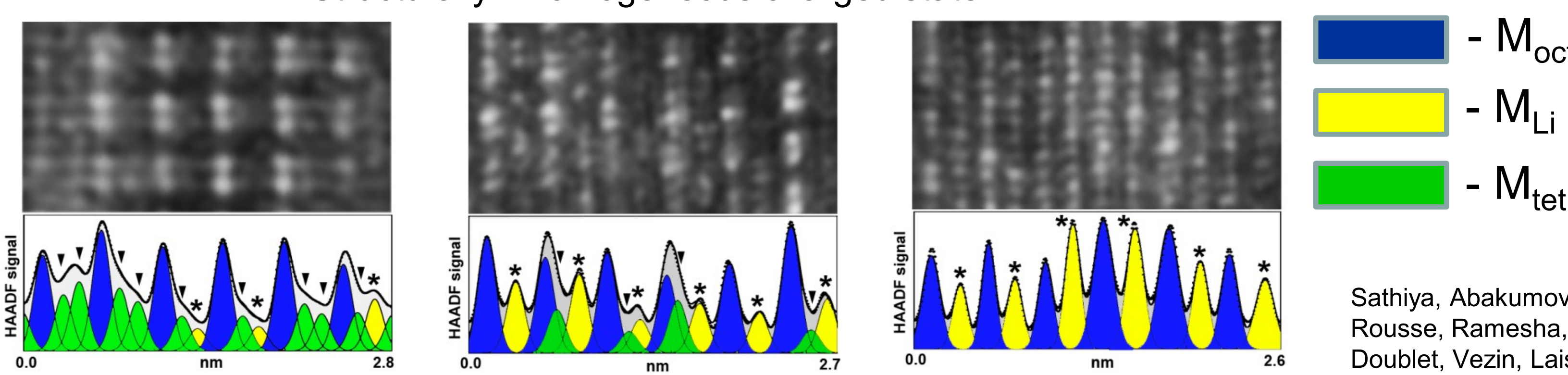
Charged to 4.6V



Discharged to 2V

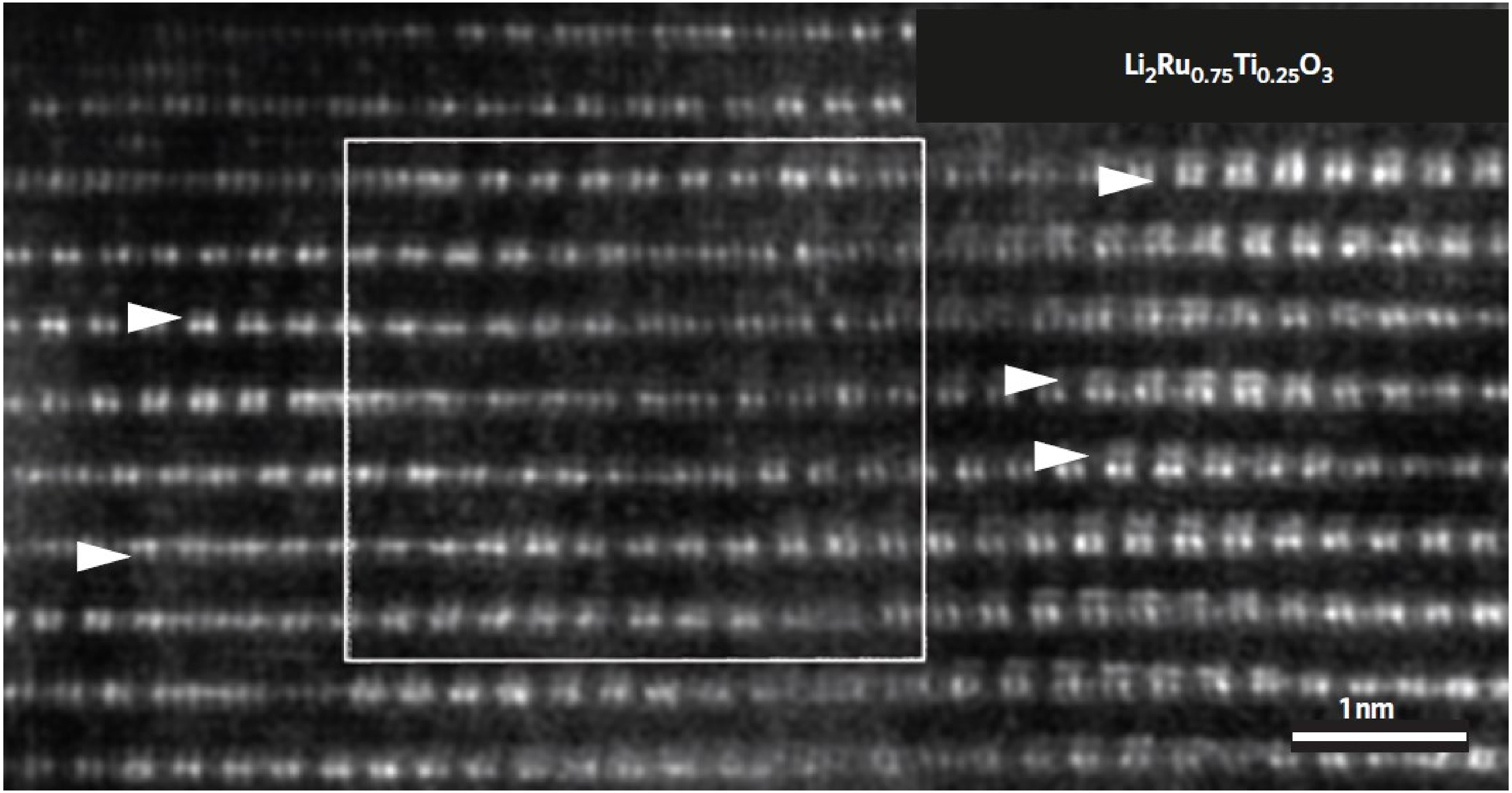


Structurally inhomogeneous charged state



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

TM cation migration – $Li_2Ru_{0.75}Ti_{0.25}O_3$

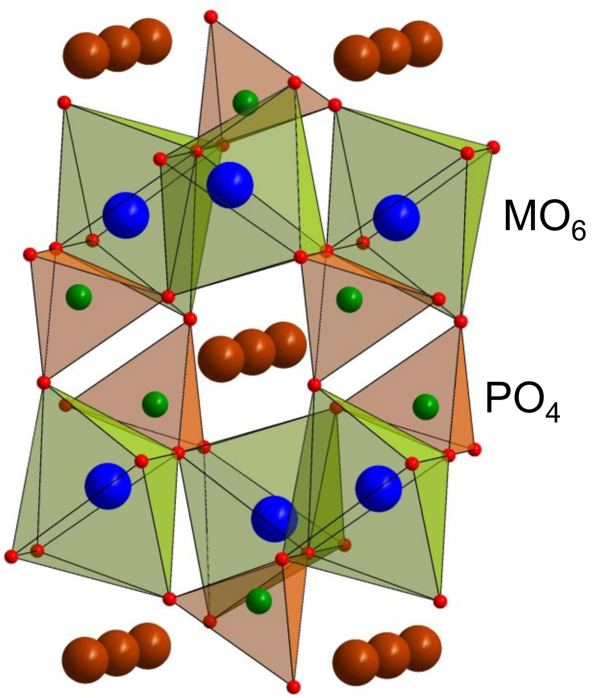


Discharged to 2V after 50 cycles: trapping of the TM cations at the tetrahedral interstices

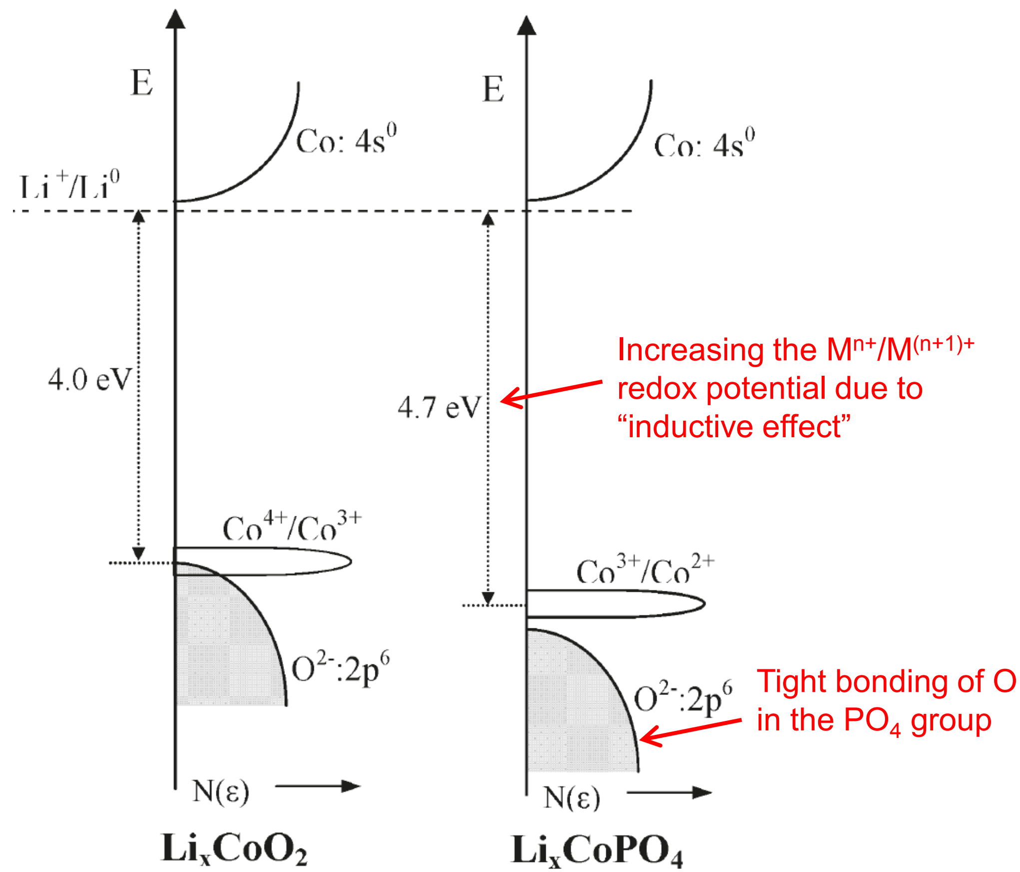
Sathiya, Abakumov, Foix, Rousse, Ramesha, Saubanère, Doublet, Vezin, Laisa, Prakash, Gonbeau, Van Tendeloo, Tarascon, *Nature Mater.*, 14, 230 2015

Skoltech
Skolkovo Institute of Science and Technology

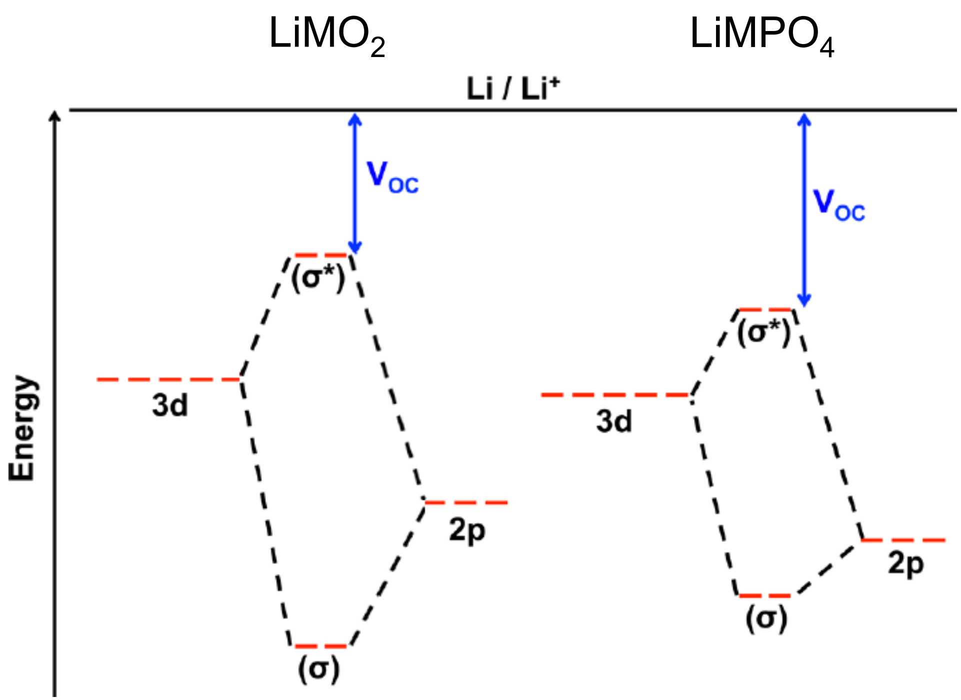
Polyanion cathode materials



LiMPO4



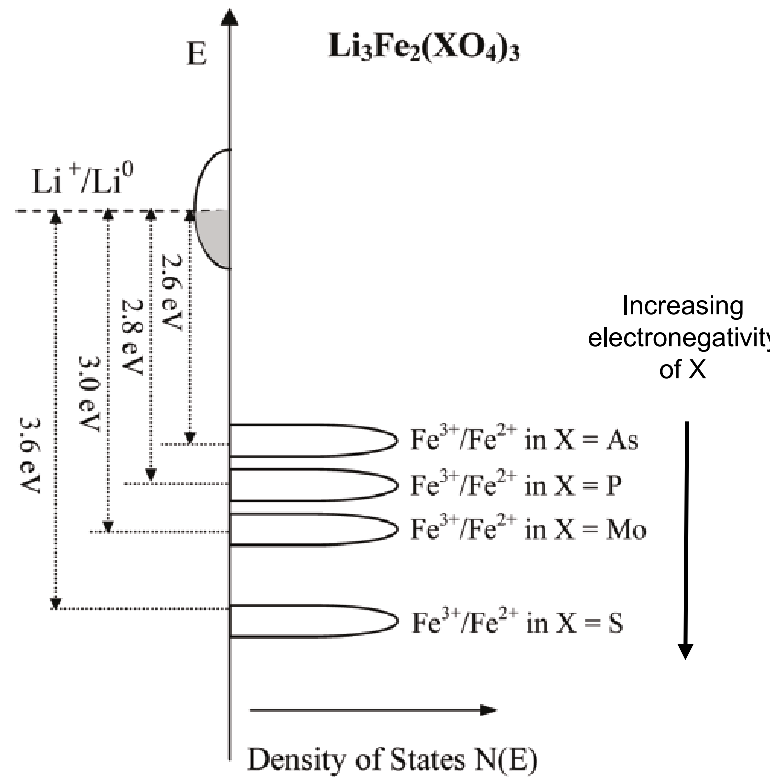
Polyanion cathode materials



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

Cathodes with the olivine structure: $LiFePO_4$

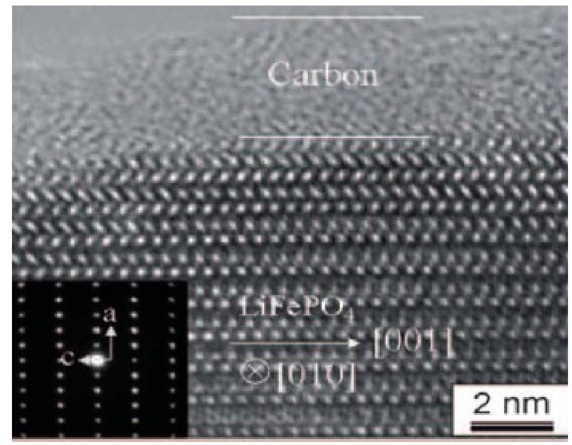
Capacity 170 mAh/g, voltage ~ 3.5 V

Pros:

- stability (3D structure + PO_4)
- $LiFePO_4 \leftrightarrow FePO_4 + Li^+ + e^-$
- environmentally benign
- low cost

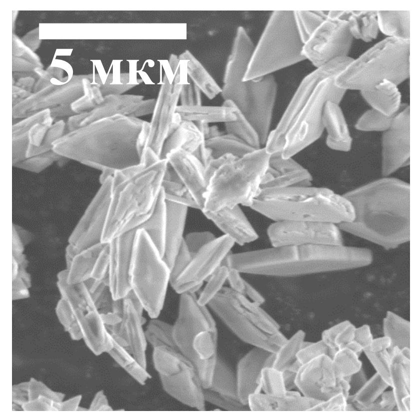
Cons:

- low conductivity ~ 10^{-9} S/cm
- low Li^+ diffusion coefficient ~10^{-15} cm^2/s
- relatively low voltage



Solution:

- conducting carbon coating
- nanosized particles
- optimized morphology



- platelets with 200 – 300 nm thickness along the fast diffusion direction
- high discharge current (50% of discharge capacity / 1 min)

Skoltech
Skolkovo Institute of Science and Technology

Cathodes with the olivine structure: $Li(Mn,Fe)PO_4$

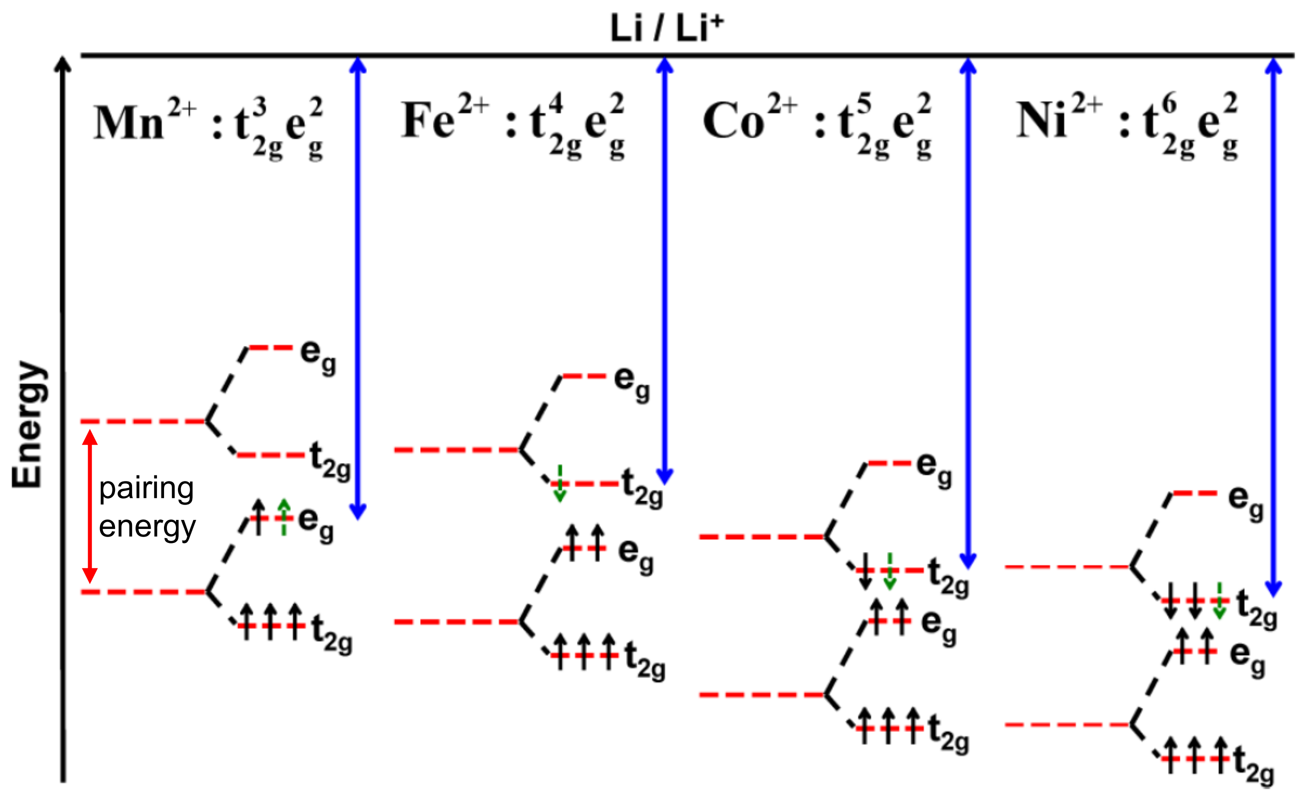
$LiFePO_4$
580 Wh/kg

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

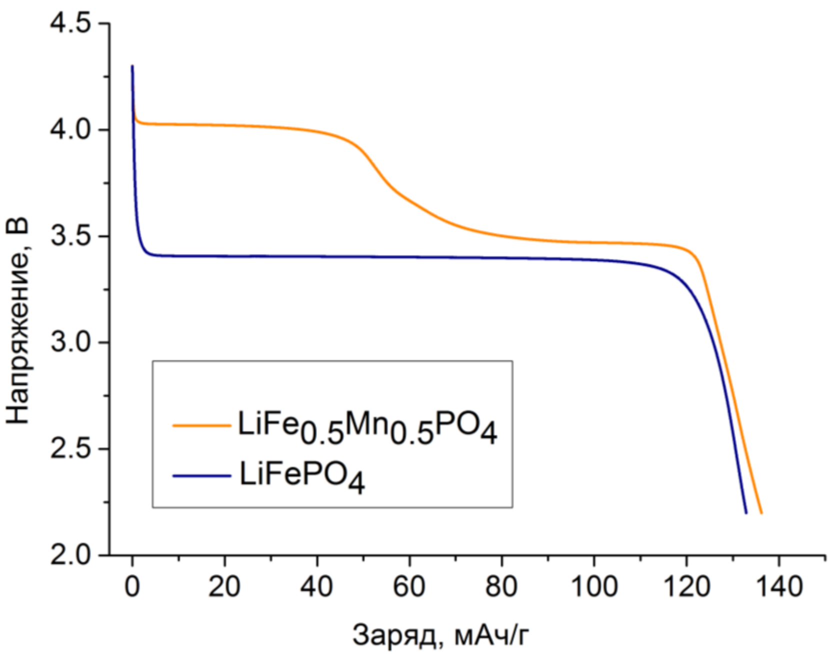
Li PO$_4$
700 Wh/kg

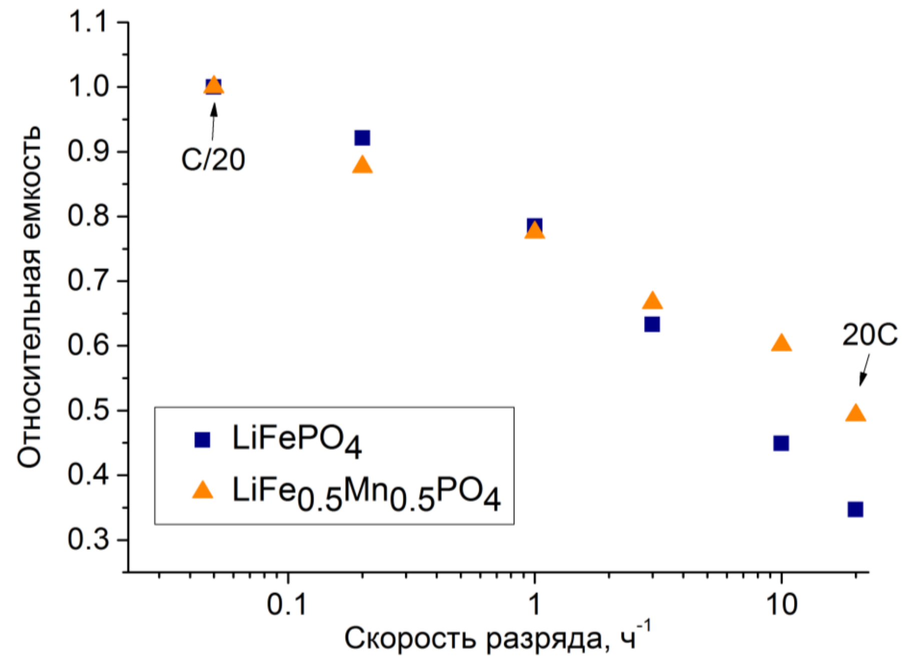
battery with ≈ 120 -140 Wh/kg

battery up to 150 - 175 Wh/kg



Cathodes with the olivine structure: $Li(Mn,Fe)PO_4$



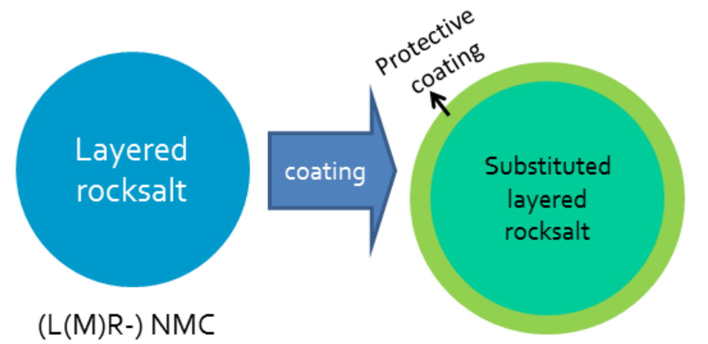


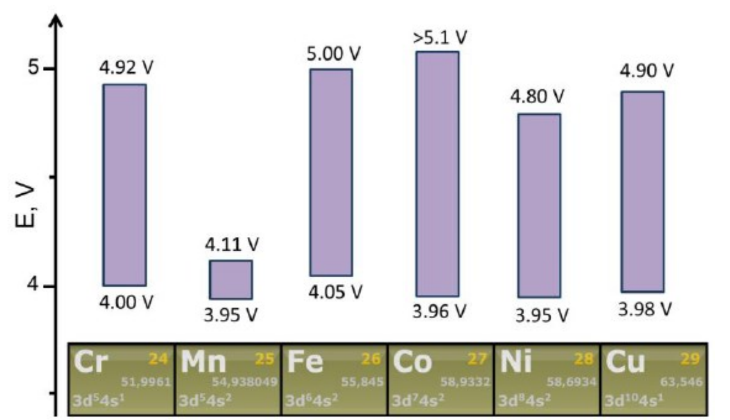
O.Drozhzhin, V.Sumanov, O.Karakulina, A.Abakumov, J.Hadermann, A.Baranov, K.Stevenson, E.Antipov, *J.Power Sources*, 2015

Conclusions

Improvement of the cathode materials

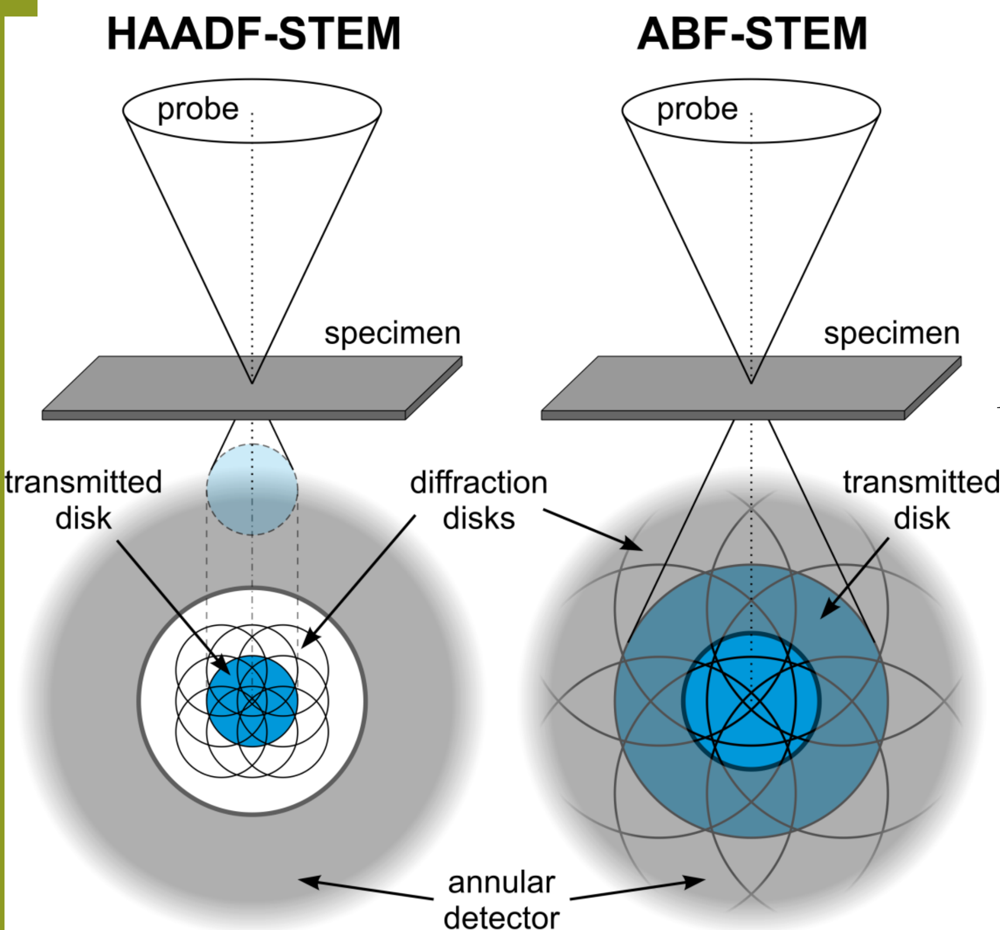
1. Chemical substitutions (metals with strong covalent bonding to O, cations blocking migration)
2. Protective coatings
3. Maximizing the energy density through tuning redox potential
4. Nanostructuring and functional coatings
5. New crystal structures and chemistries



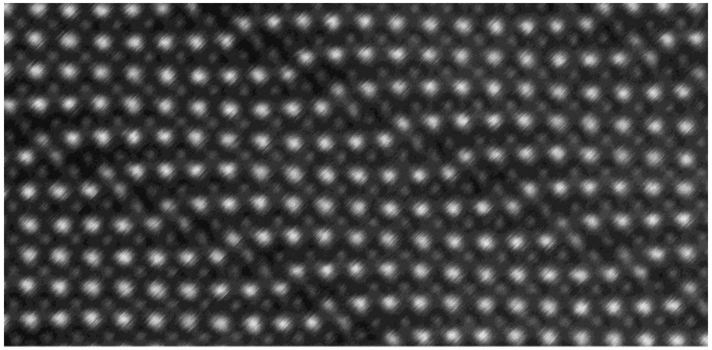


Stability windows for the $LiMn_{1.5}M_{0.5}O_4$ spinels

Thank you for your attention!

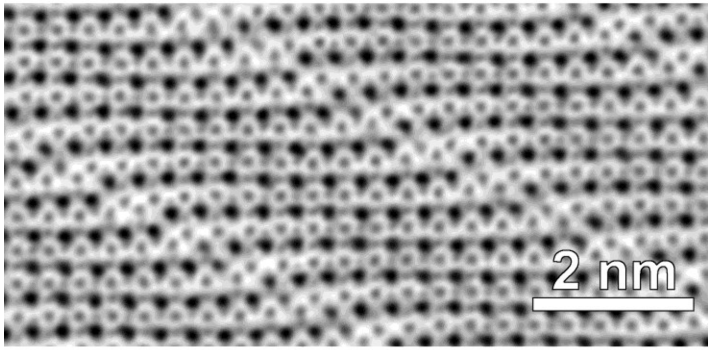


$I \sim Z^2$



HAADF-STEM

$I \sim Z^{1/3}$



ABF-STEM

HAADF-STEM – high angle annular dark field scanning transmission electron microscopy

ABF-STEM – annular bright field scanning transmission electron microscopy