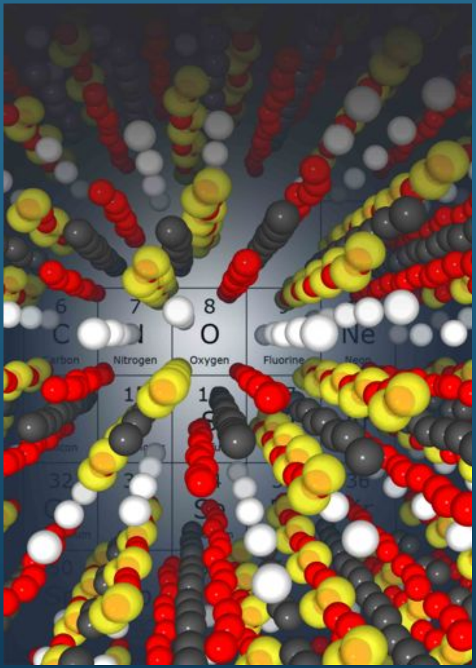
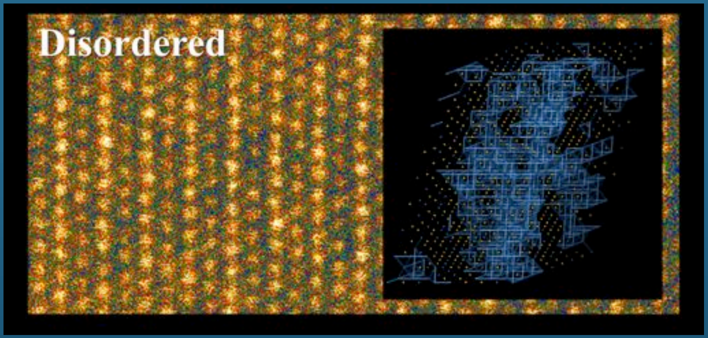
Combining Reversible Oxygen Charge Transfer and Li-excess to achieve High Capacity Cathodes





Gerbrand Ceder
UC Berkeley
Lawrence Berkeley National Laboratory

IMLB Meeting, June 22 2016, Chicago

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This presentation is available at http://ceder.berkeley.edu/

Oxygen redox activity

D.-H. Seo,† J. Lee,† A. Urban, R. Malik, S. Kang, G. Ceder, Nature Chem., Advance Online Publication (2016)

Percolation in cation-disordered structures

J. Lee, et al., Science, 343 (6170), 519-522 (2014)

A. Urban, et al. *Adv. Energy Mater.* **4** (2014) 1400478.

Covalency and hybridization of the TM-3d and O-2p in layered cathodes

MK. Aydinol, AF. Kohan, G. Ceder, K. Cho, J. Joannopoulos, Phys. Rev. B, **56**, 1354-1365 (1997).

Ceder et al. Nature, **392**, 694-696 (1998).

D.-H. Seo et al. Physical Review B, 92, 115118 (2015)

Electronic Structure effects on Transition Metal Migration

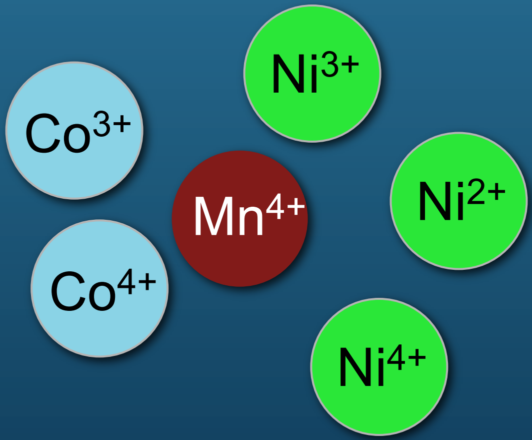
J. Reed, A. Van der Ven and G. Ceder, Electrochem. and Sol. St. Lett., **4**, A78-A81 (2001)

J. Reed and G. Ceder, Chemical Reviews, **104** (10), 4513-4533 (2004).

Layered Cathodes: Why only Co, Ni and Mn ?

$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$

$LiCoO_2$



LRNMC

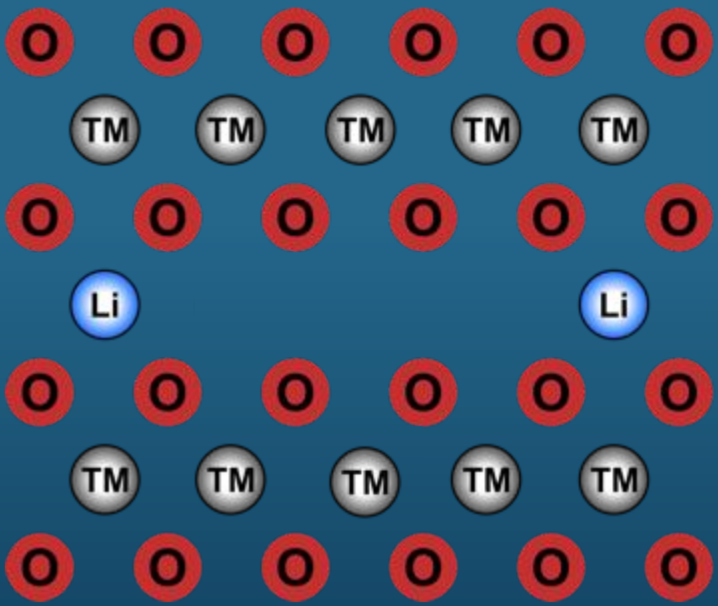
$Li(Ni_{0.8}Co_{0.15}Al_{0.5})O_2$

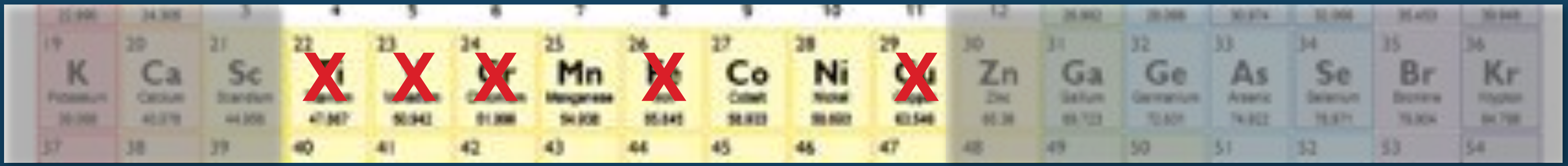
Our best materials all contain the same elements

Most transitions metals migrate into the Li sites upon charge

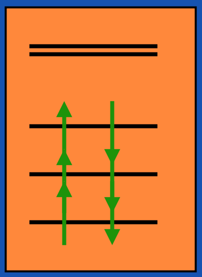
$LiMO_2$

- Many transition metals migrate into the Li-sites when Li is extracted, in effect creating disorder in-situ
- Mobility of TM is set by the amount of t_{2g} (good) and e_g (bad) electrons

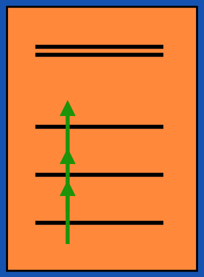




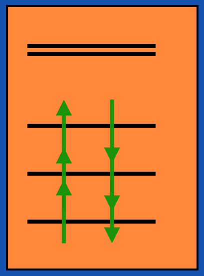
Co^{3+}



Mn^{4+}



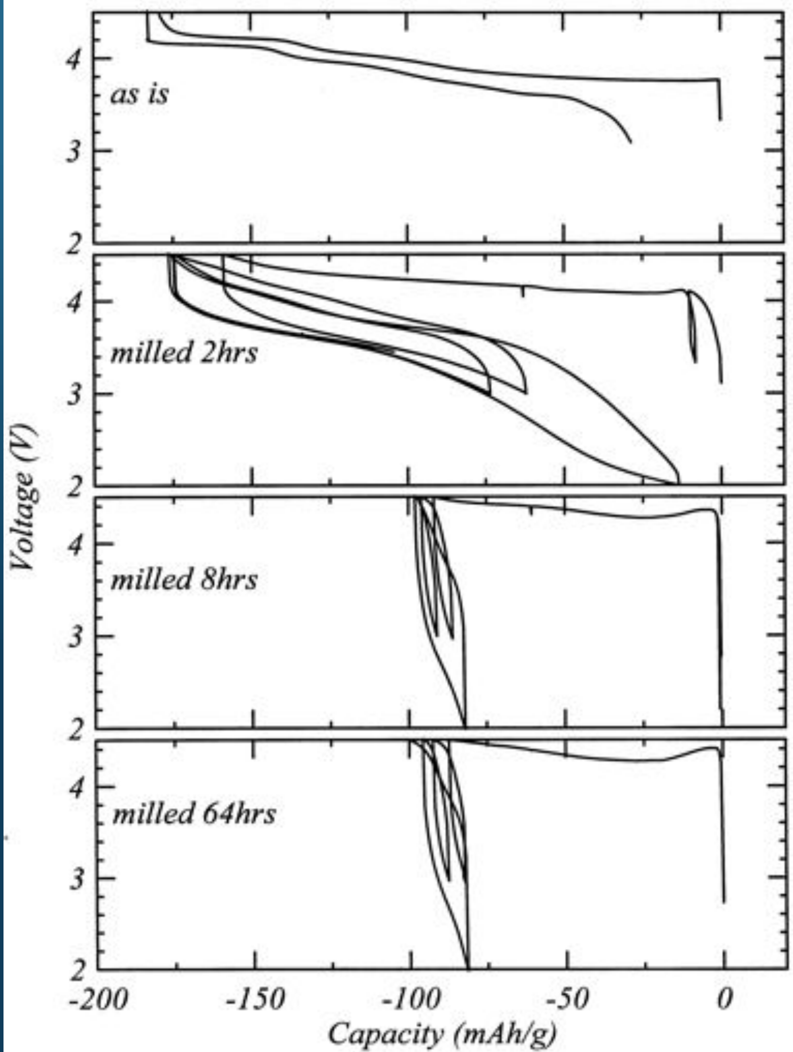
Ni^{4+}



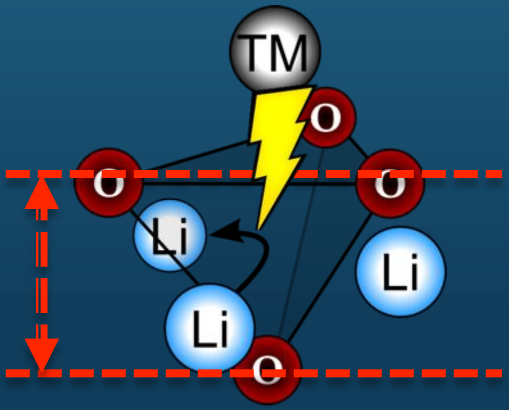
Reed and GC Chemical Reviews, **104** (10), 4513-4533 (2004).
Reed et al. Electrochem. Solid State Lett. (2001)

Disorder systematically decreases performance

$LiNiO_2$



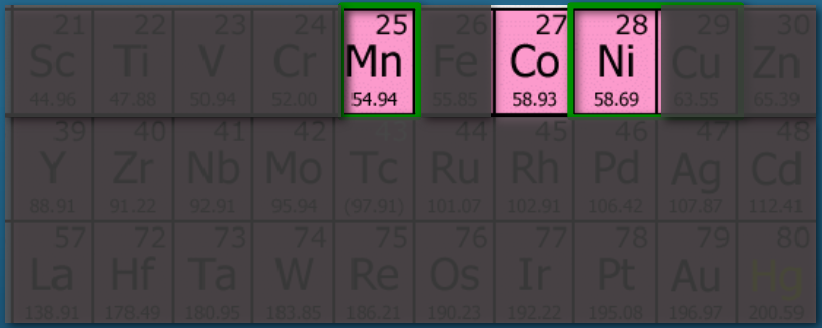
Disorder materials by ball milling



Disorder reduces the tetrahedron size, shutting of the migration channel

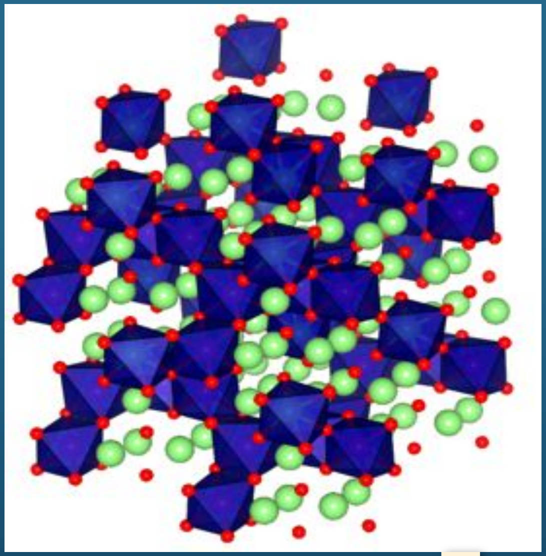
Obrovac, Mao and Dahn, SSI, 112, p9 (1998)

How do we enable oxide cathodes with a larger chemistry range ?

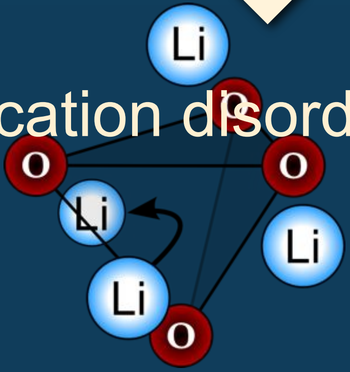


21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39
39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (97.91)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41
57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59

Structures will disorder upon synthesis or upon delithiation



0-TM channels are only active Li pathways

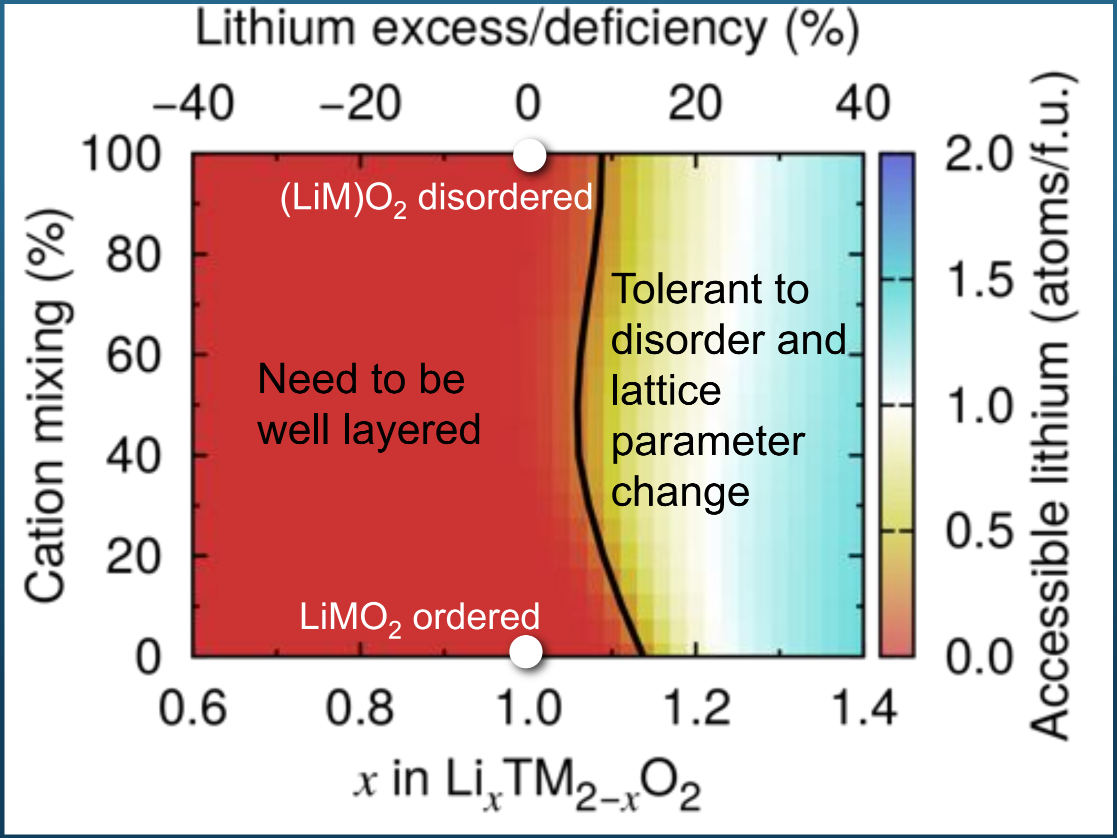


We need to make materials tolerant to cation disorder

PERCOLATION of 0-TM

A. Urban, et al. *Adv. Energy Mater.* **4** (2014) 1400478.

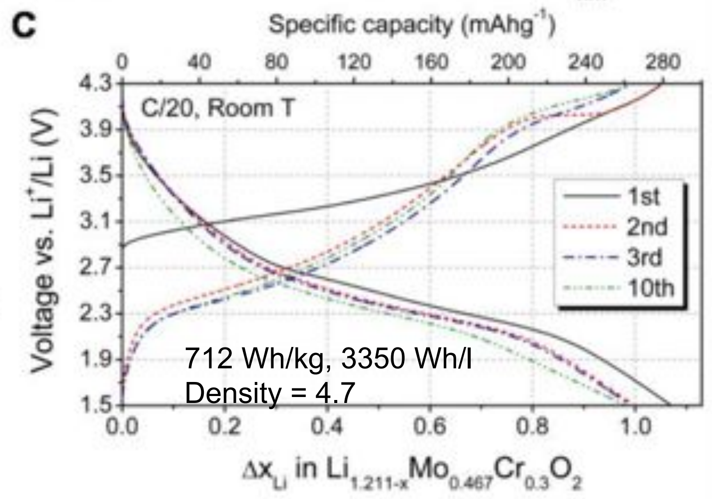
Li-excess is key to making materials tolerant to cation disorder



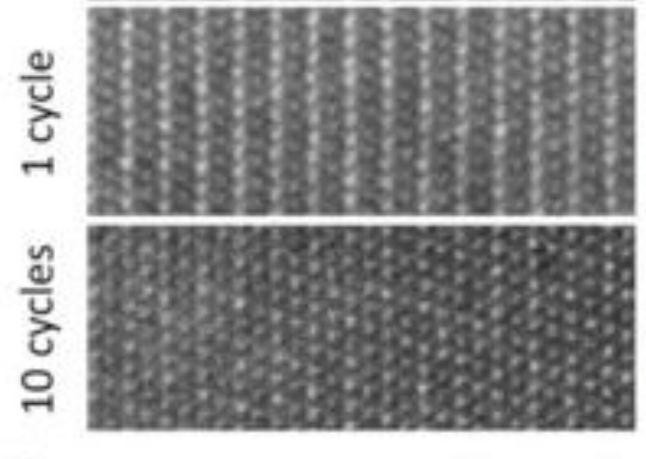
By adding Li excess > 10% the material achieves an additional Li diffusion mechanism which is insensitive to lattice parameter

J. Lee, et al., Science, 343 (6170), 519-522 (2014)

$Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$

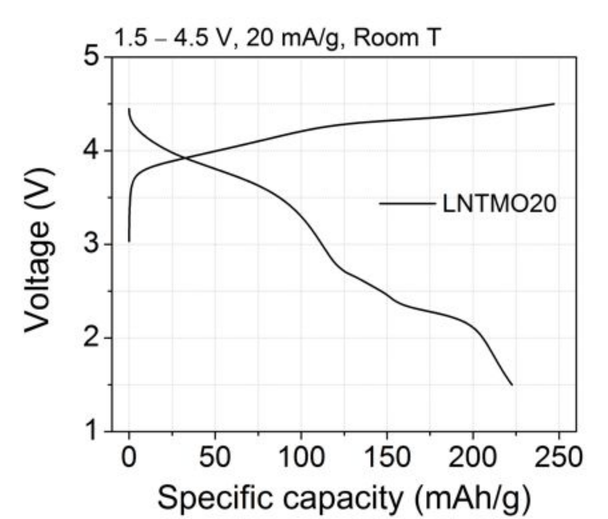


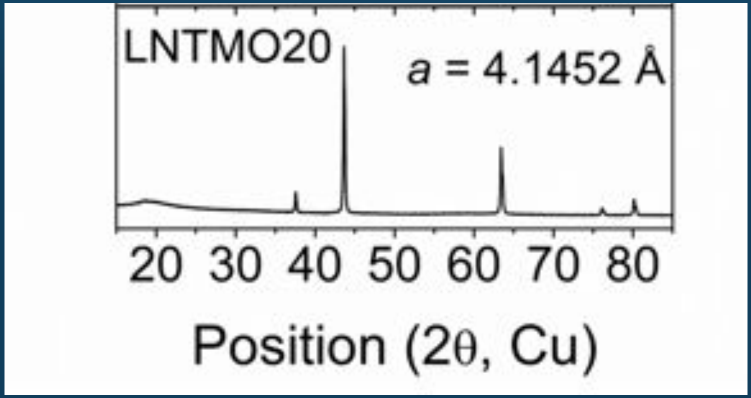
712 Wh/kg, 3350 Wh/l
Density = 4.7



J. Lee, et al. Science, 343 (6170), 519-522 (2014)

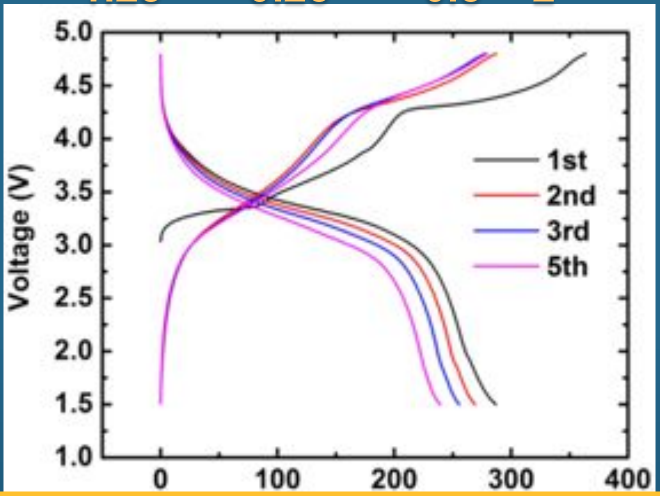
$Li_{1.2}Ni_{0.32}Ti_{0.35}Mo_{0.135}O_2$



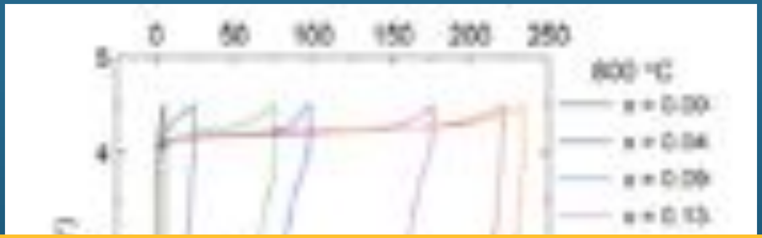


J. Lee and G. Ceder, Energy Environ. Sci., 8 (11), 3255-3265 (2015).

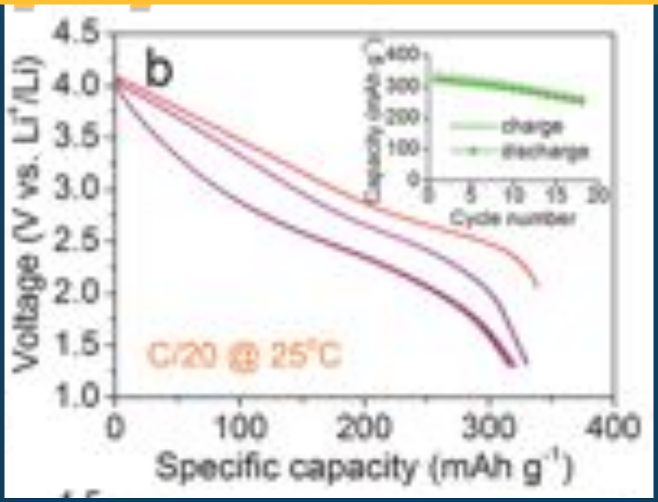
$Li_{1.25}Nb_{0.25}Mn_{0.5}O_2$



$Li_{(1+x)}Ti_{2x}Fe_{(1-3x)}O_2$



In less than 3 years multiple materials, based on the disordered rocksalt concept, have demonstrated capacity at > 200 mAh/g

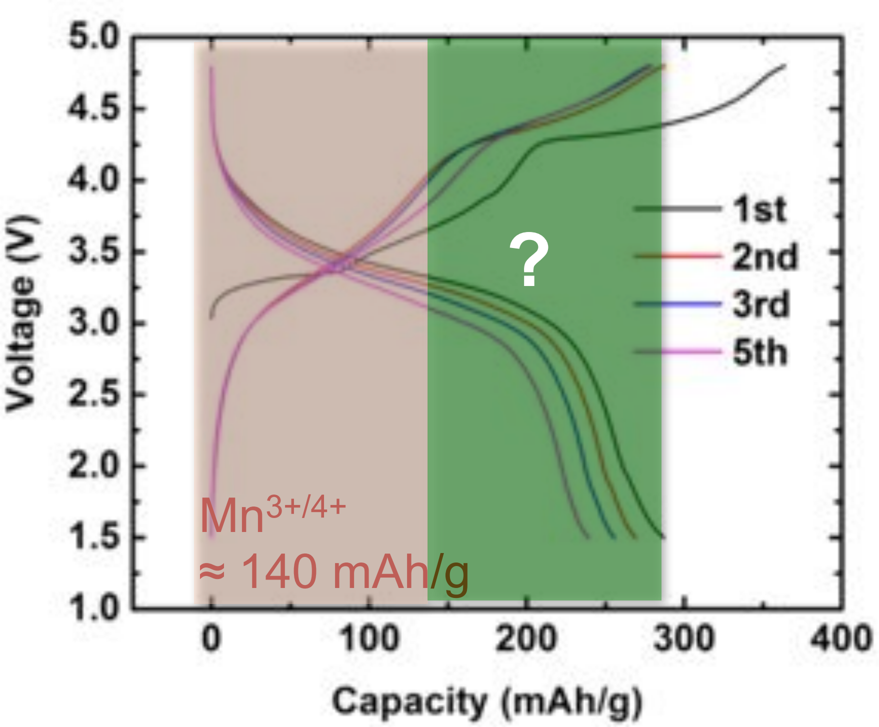


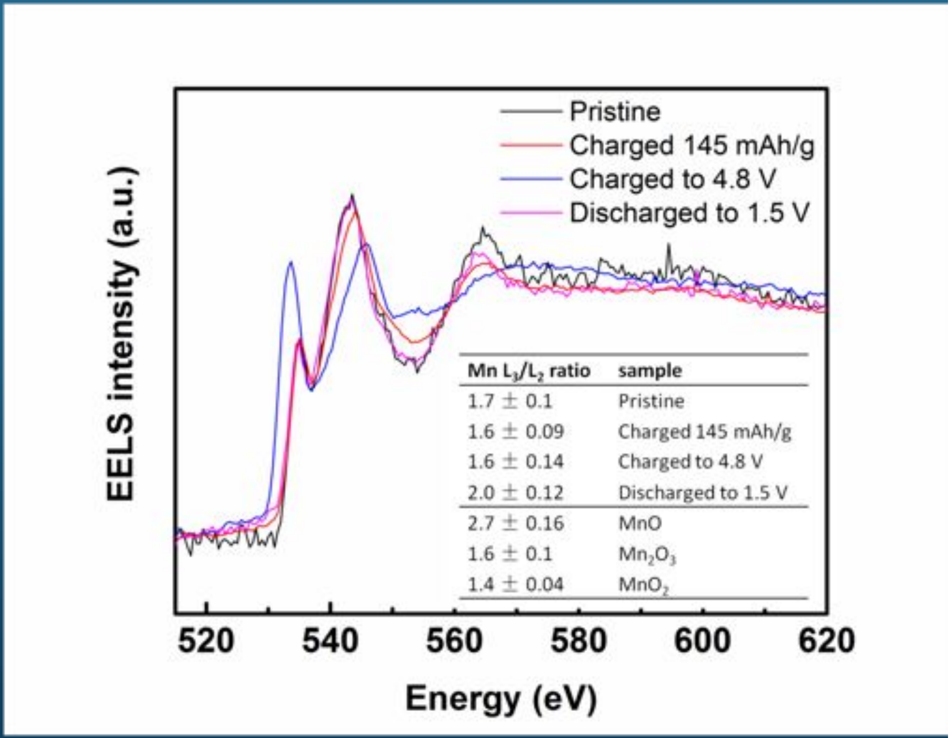
Chen R.,Fichtner Adv. Energy Mater., 5: 1401814. 2014

Glazier, SL et al. Chem Mat DOI: 10.1021/ 2015, 27, 7751−7756

Novel redox mechanisms in the disordered rocksalts $Li_{1.25}Nb_{0.25}Mn_{0.5}O_2$

Oxygen edge starts to move after 140 mAh/g





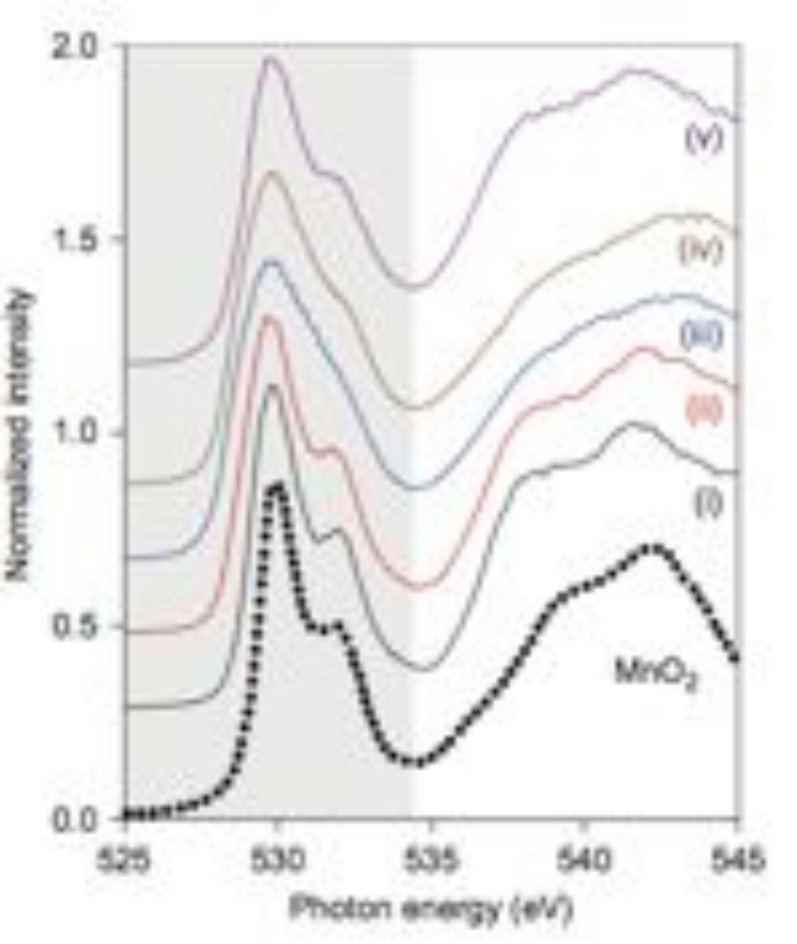
Mn L_3/L_2 ratio	sample
1.7 ± 0.1	Pristine
1.6 ± 0.09	Charged 145 mAh/g
1.6 ± 0.14	Charged to 4.8 V
2.0 ± 0.12	Discharged to 1.5 V
2.7 ± 0.16	MnO
1.6 ± 0.1	Mn_2O_3
1.4 ± 0.04	MnO_2

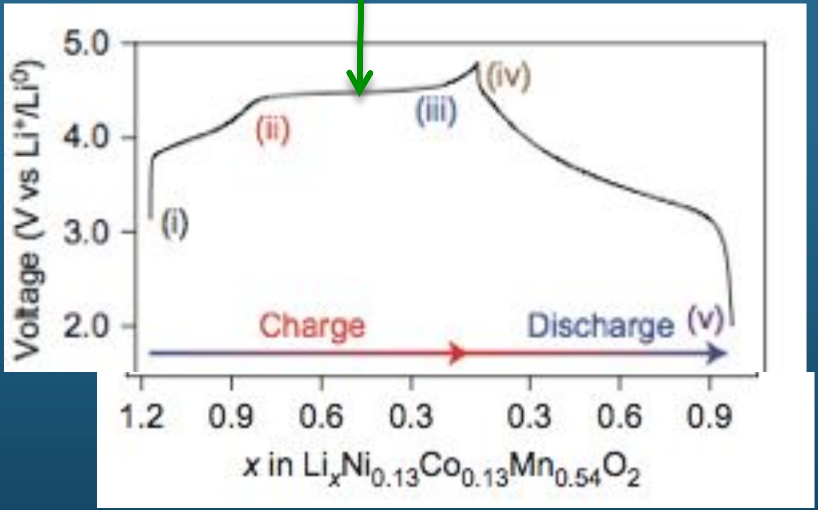
Wang *and Ceder.*, *Electrochem*. *Commun.* (2015)

Reversible solid state oxygen oxidation ?

Novel redox mechanisms in the disordered rocksalts

$Li_{1.2}[Ni_{0.13}^{2+}Co_{0.13}^{3+}Mn_{0.54}^{4+}]O_2$





Oxygen redox in this area ?

K. Luo and PG Bruce, Nat. Chem 2016

Important questions

- What really is oxygen redox. Is it due to covalency ?
- Can one actually get more capacity out of oxygen redox ?
- What are the structural and chemical features that cause oxygen redox ?
- Can oxygen redox be predicted ?

Covalency ?

*"O-O pairing in the oxygen lattice resulting from the formation of O2 (n-) species predominantly occurs in compounds that have highly **covalent M-O bonding** – that is systems showing a high degree of M(d) – O(sp) band overlap. "*

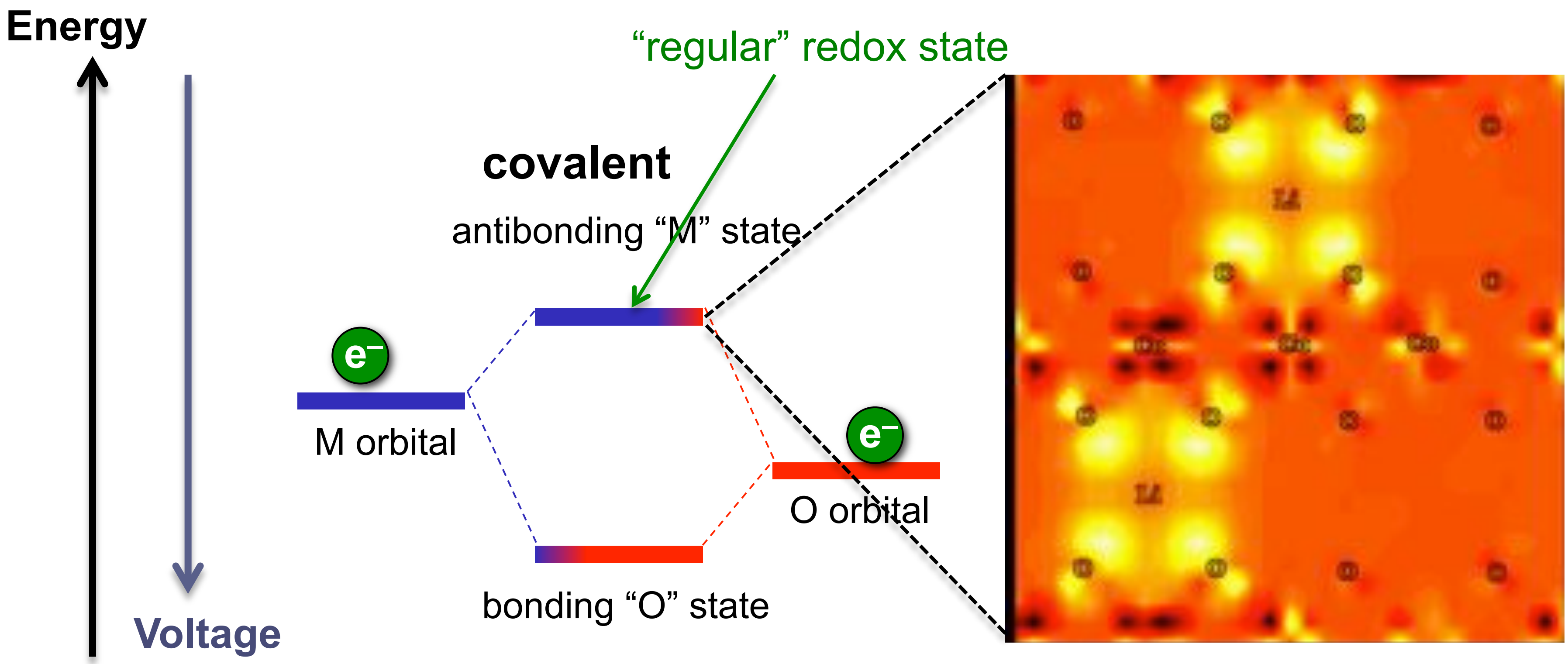
Science 2016

*… a redox active anion network … This can occur in a highly **covalent network** where the transition metal d band penetrates the ligand p band, so that electrons from the O p band are poured into the d-band*

Nat Mat. 2016

Note that all recent claims of oxygen redox have been shown for highly Li-excess materials

A simple look at Metal-Oxygen bonding



Energy

Voltage

“regular” redox state

covalent

antibonding “M” state

e⁻

M orbital

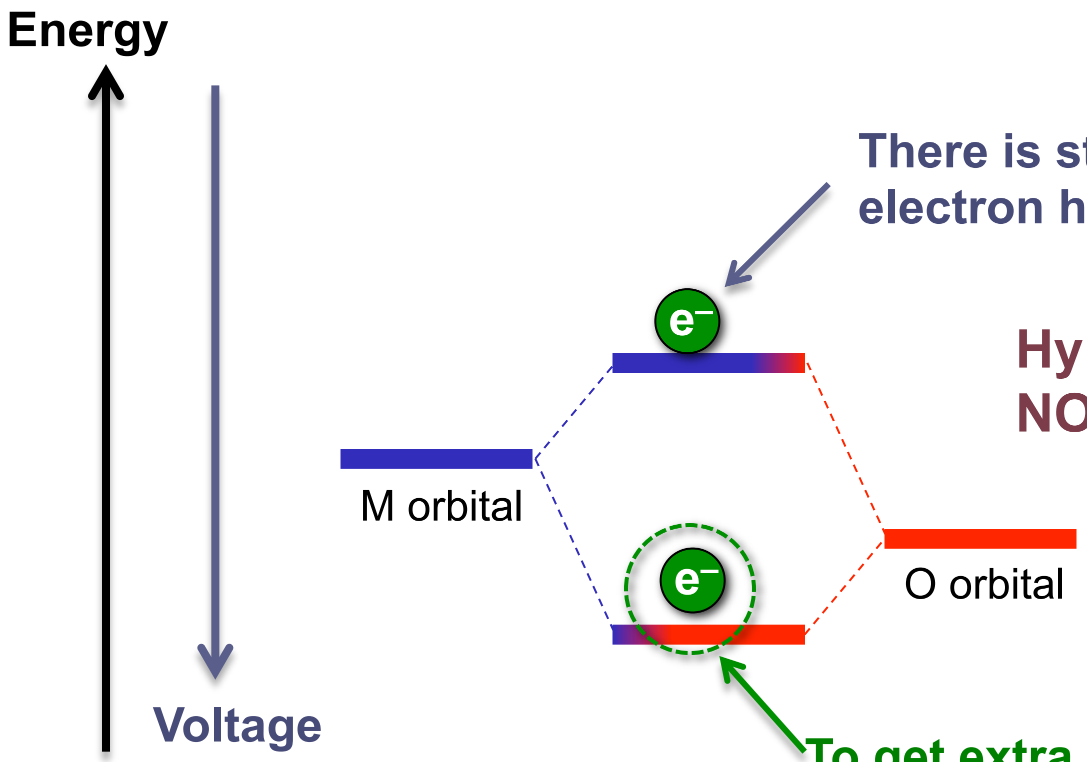
e⁻

O orbital

bonding “O” state

Ceder et al. Nature, **392**, 694-696 (1998).

Hybridization does not increase capacity

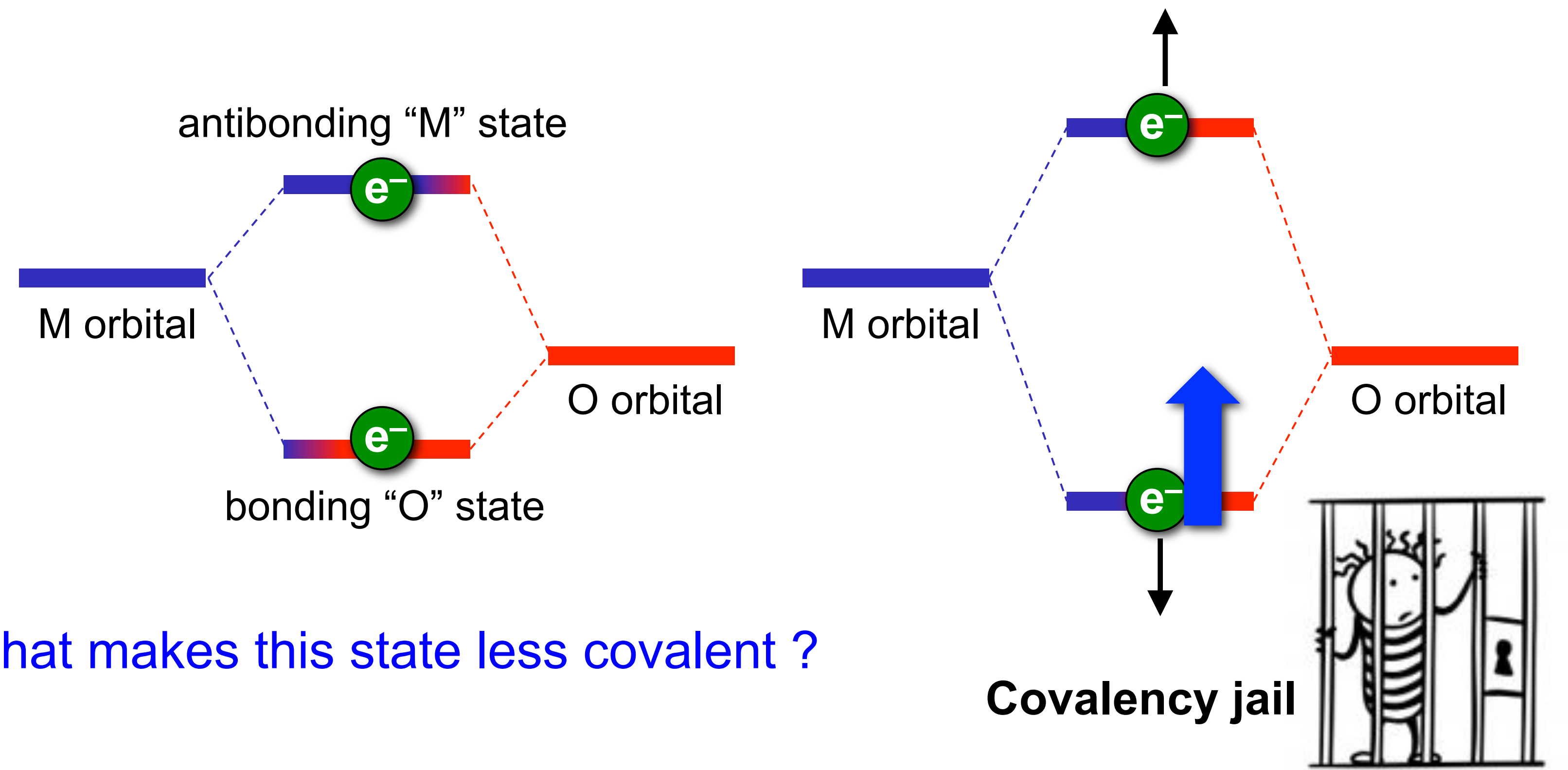


There is still only one electron here.

Hybridization (covalency) does NOT increase the capacity

To get extra capacity one needs to extract this electron. This is the true oxygen redox

COVALENCY actually makes oxygen redox MORE DIFFICULT



less covalent

antibonding “M” state

e^-

M orbital

O orbital

e^-

bonding “O” state

more covalent

e^-

M orbital

O orbital

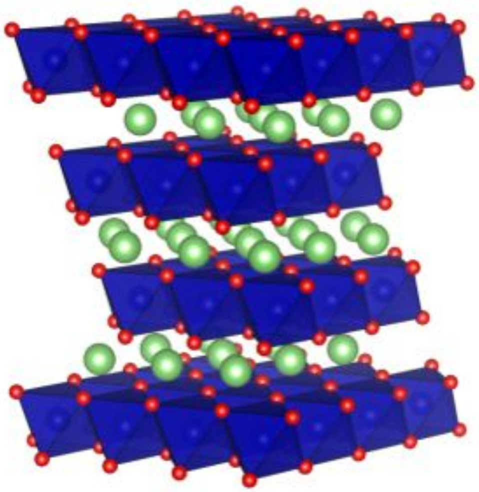
e^-

What makes this state less covalent ?

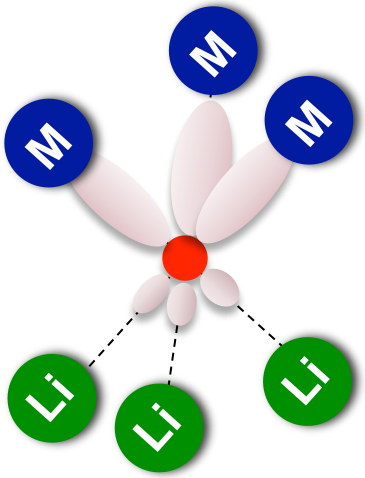
Covalency jail

COVALENCY is not the source of extra capacity through anion redox

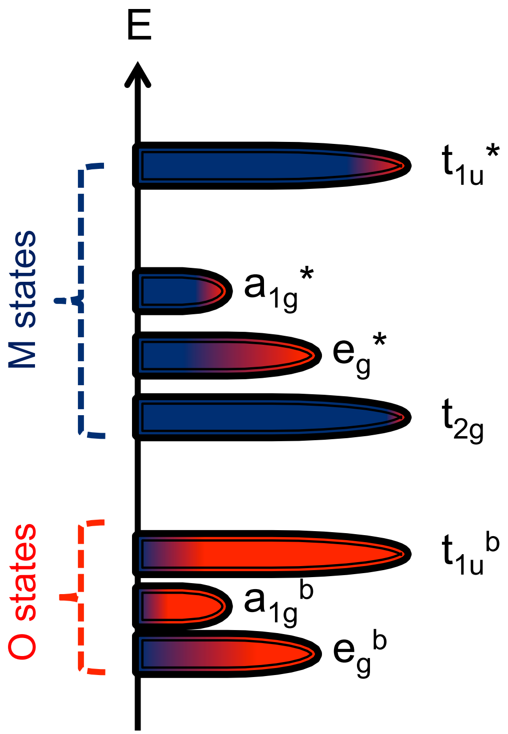
Layered structure: Each oxygen-p orbital is strongly hybridized with a transition metal



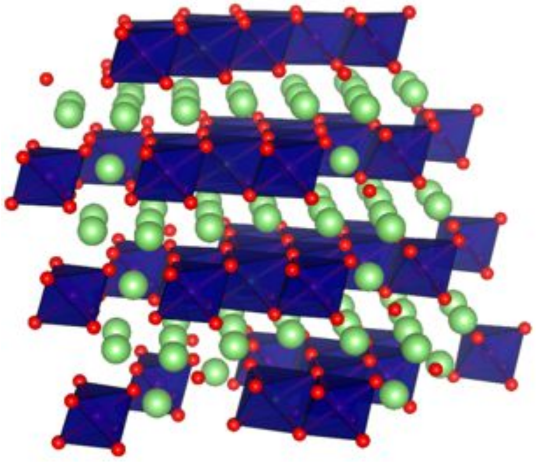
Stoichiometric layered Li-M oxides



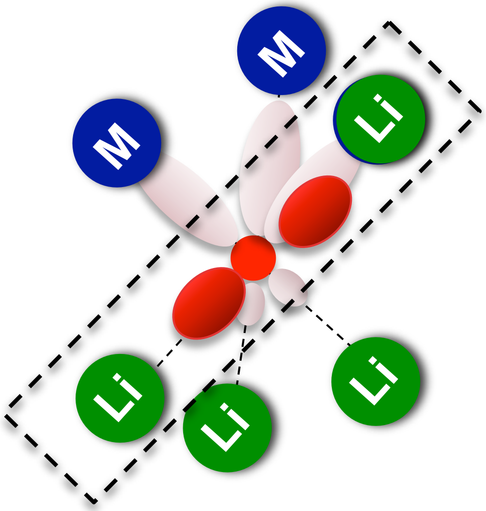
three Li–O–M



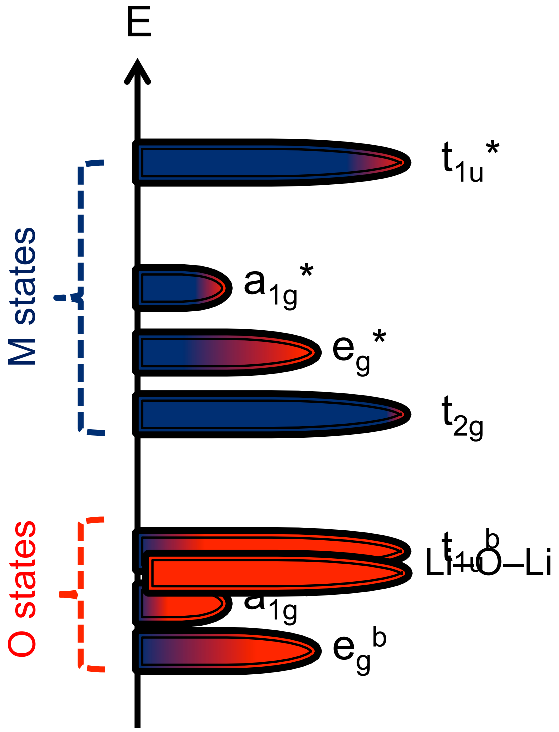
Li-excess layered compounds: Some oxygen-p orbitals are only coordinated with Li-ions



Li-excess
layered Li-M oxides

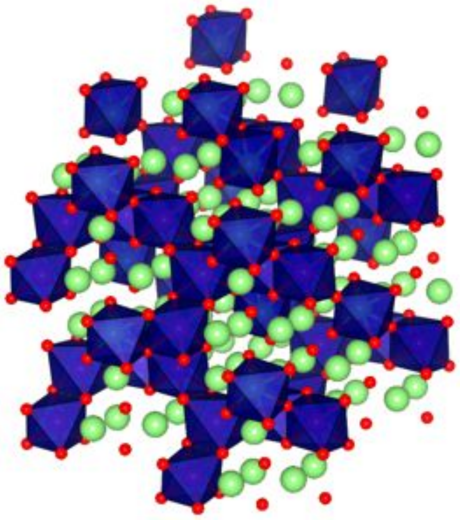


Two Li–O–M
one Li-O-Li

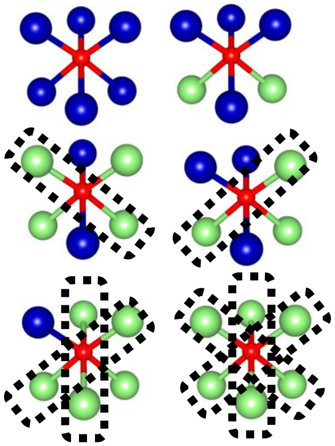


Li in the TM layer creates a Li-O-Li configuration leading to an unhybridized oxygen orbital that is higher in energy, and therefore can be oxidized

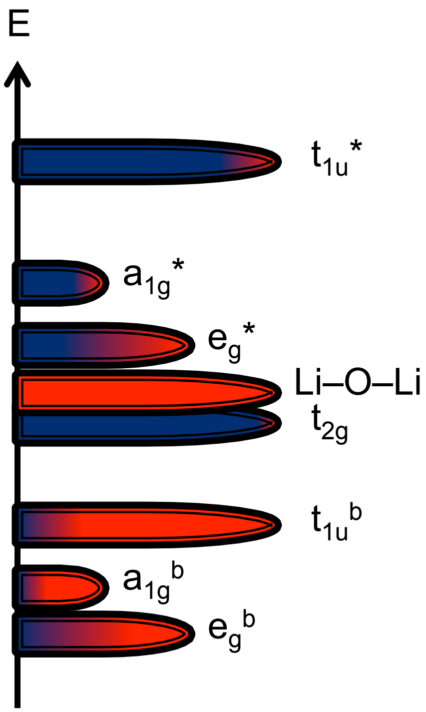
Cation disordered rocksalts: Some oxygen-p orbital are only coordinated with Li-ions



Cation disordered oxides

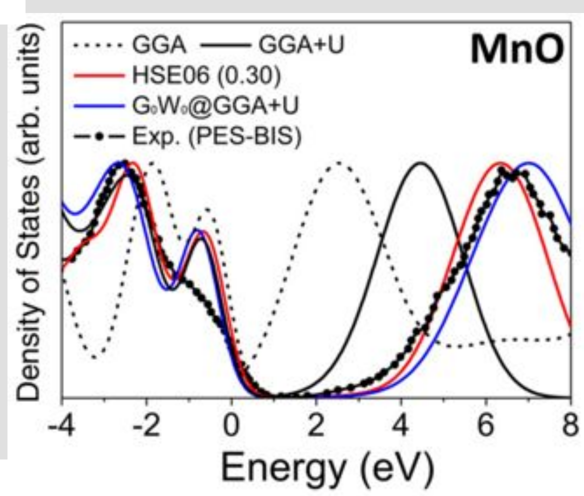


Various environments



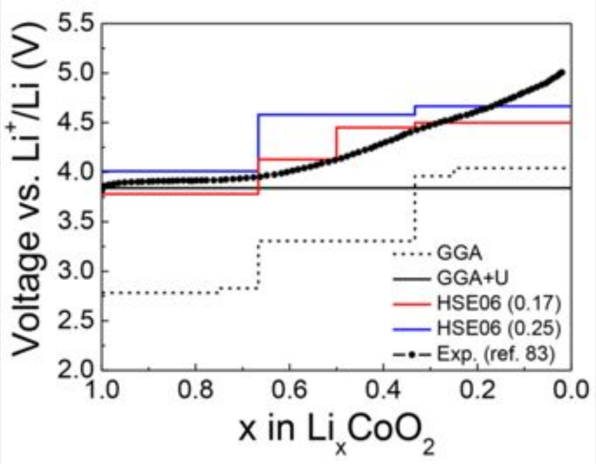
Calibrated quantum mechanics by spectroscopic data from experiments

D.-H. Seo et al.   Physical Review B, 92, 115118 (2015)

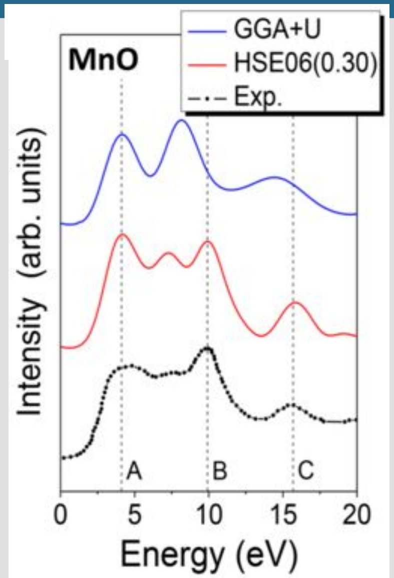


Computed DOS and Measured PES-BIS Spectra

CALIBRATION



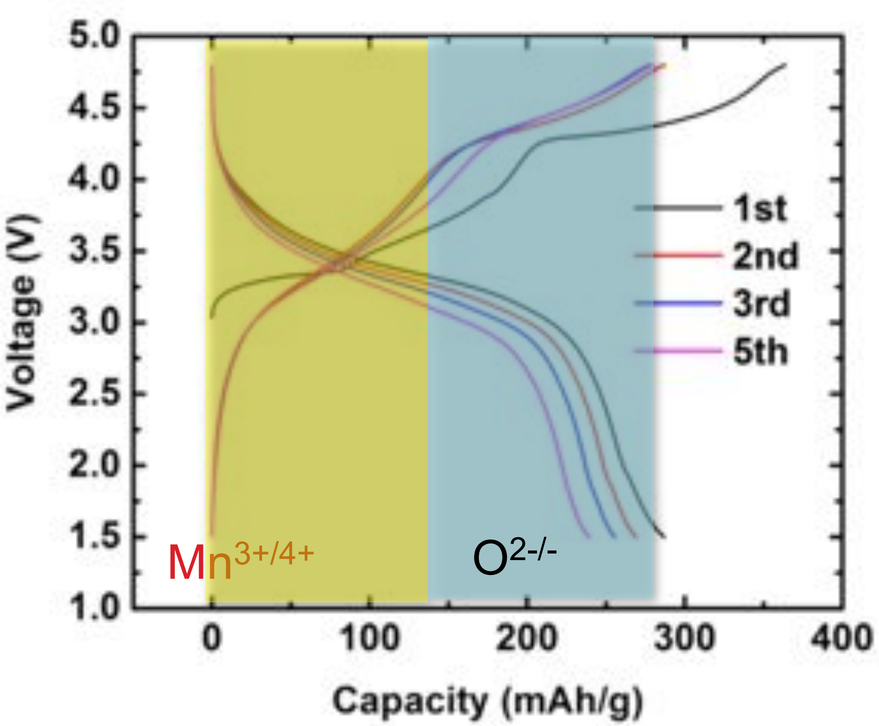
Computed and Measured Voltage Profile

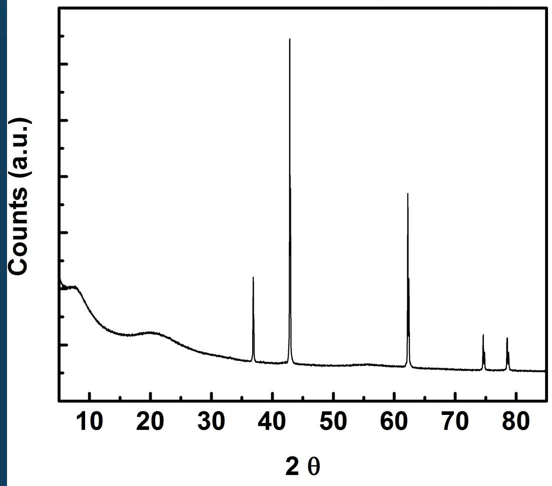


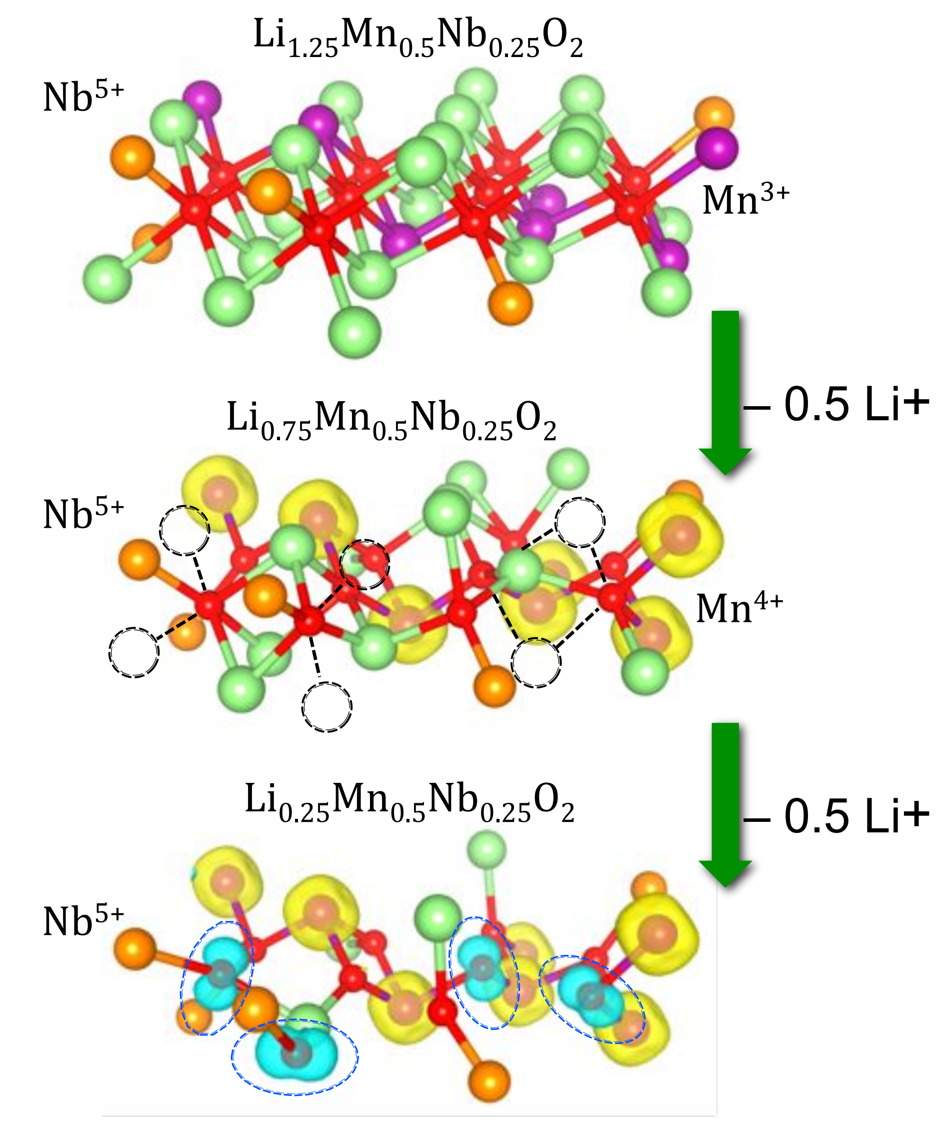
Computed and Measured O K-Edge EELS

We devised a methodology to obtain optimal HSE06 mixing parameters by calibrating with experimental photoelectron spectroscopy (PES) and Bremsstrahlung isochromate spectroscopy (BIS) or highly accurate GW calculations. Such **optimized HSE06 calculations predict EELS and voltage profiles with great accuracy** and are the basis for our investigation of oxygen redox participation.

$Li_{1.25}Nb_{0.25}Mn_{0.5}O_2$ fully cation disordered







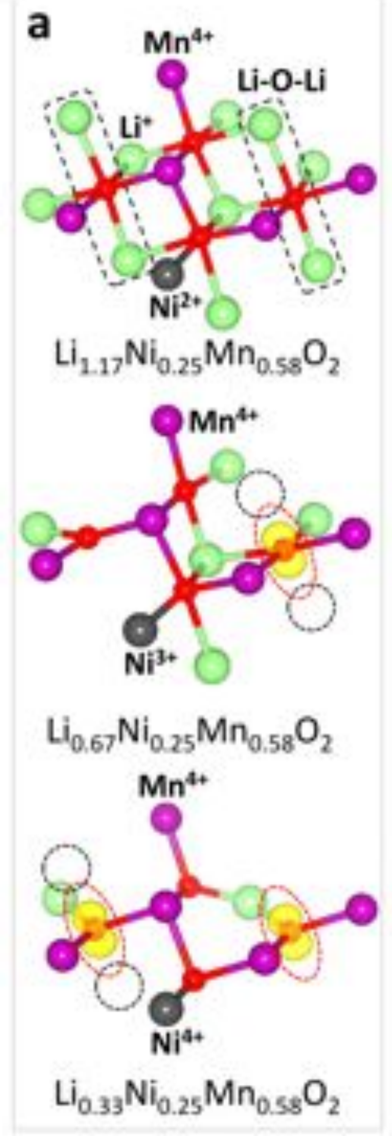
D.-H. Seo,† J. Lee,† A. Urban, R. Malik, S. Kang, G. Ceder, Nature Chem., online (2016)

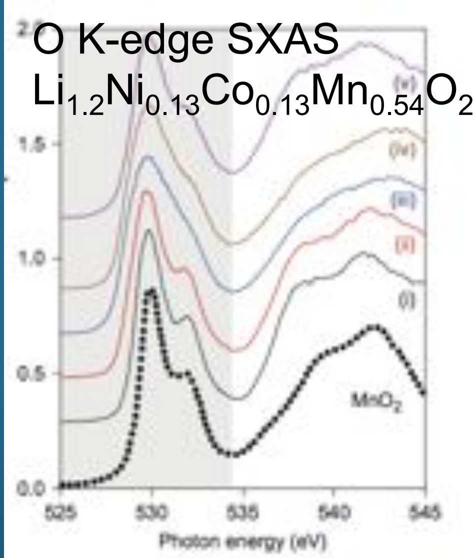
$Li_{1.17}Ni_{0.25}Mn_{0.58}O_2$ Li-excess

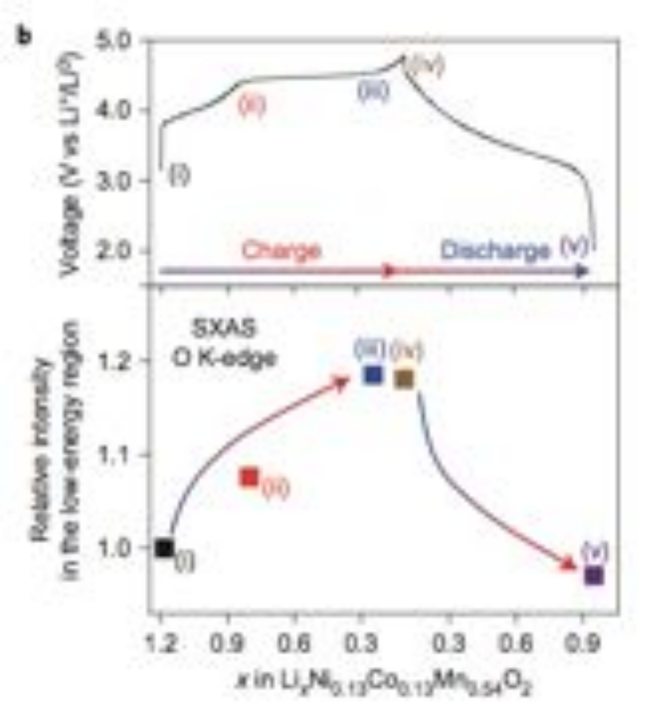
– 0.5 Li+

Some O oxidation takes place before all Ni is oxidized

– 0.5 Li+




O K-edge SXAS $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$.

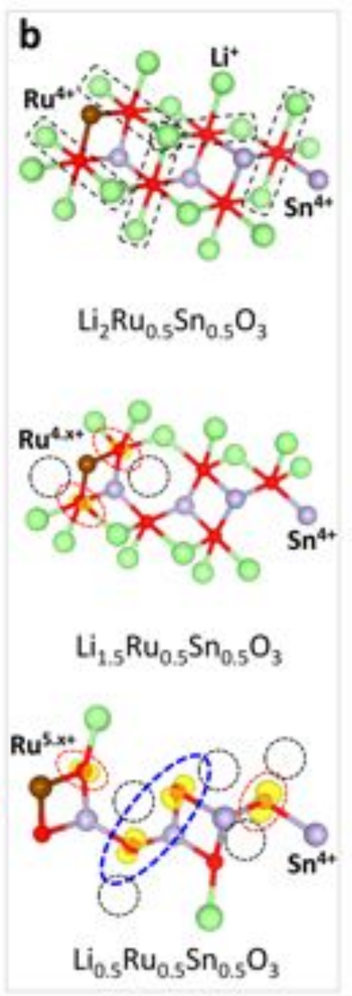


K. Luo and PG Bruce, Nat. Chem 2016

D.-H. Seo,† J. Lee,† A. Urban, R. Malik, S. Kang, G. Ceder, Nature Chem., online (2016)

In some cases oxygen oxidation occurs before complete metal oxidation

$Li_2Ru_{0.5}Sn_{0.5}O_3$



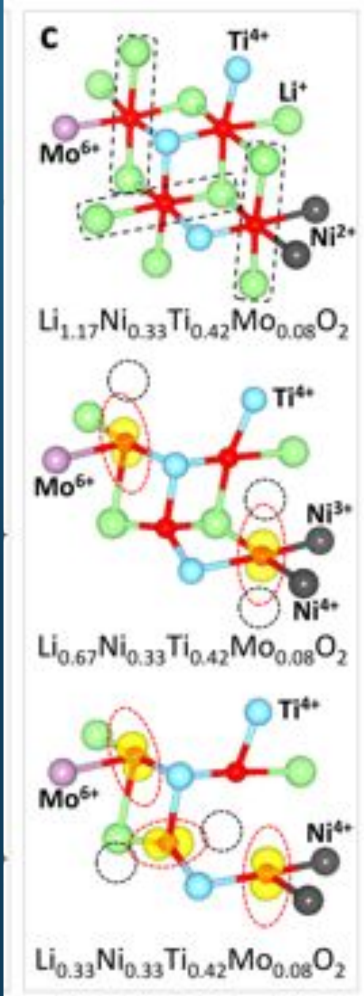
– 0.5 Li+

$Ru^{4+/5+}$ mixed with $O^{2-/-}$

– 0.5 Li+

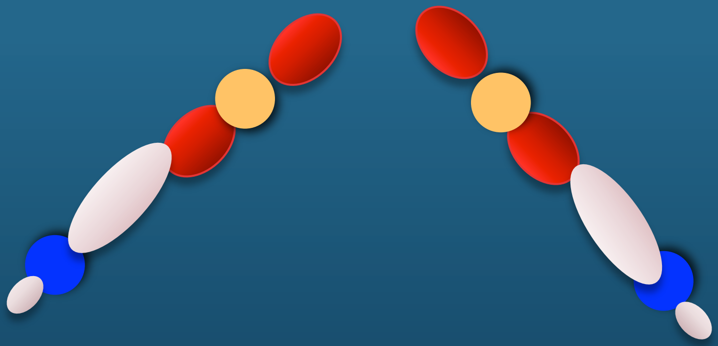
$Li_{1.2}Ni_{0.32}Ti_{0.35}Mo_{0.135}O_2$

$Ni^{2+/4+}$ mixed with $O^{2-/-}$



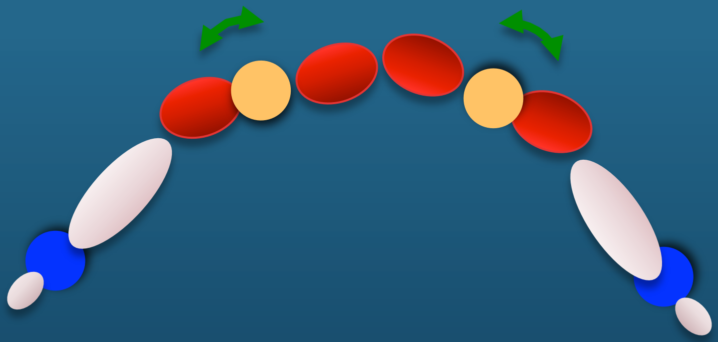
Peroxo-like O-O ?

In rocksalt-like materials O_{2p} orbitals are ≈ at 90^0 to each other



3d-TM

σ-overlap only occurs when M-O bond can rotate

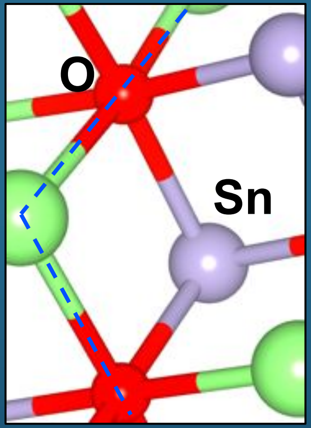


p-group element

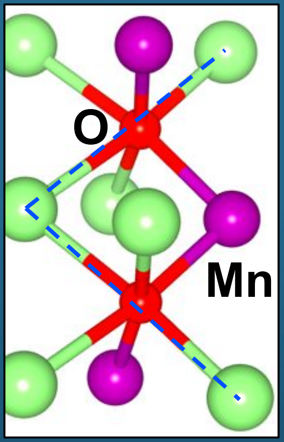
Whether these oxygen orbitals can rotate enough to form “peroxo” depends on what they bind to

Some O-O bonding in Ru-Sn compound, none in Ni-Mn

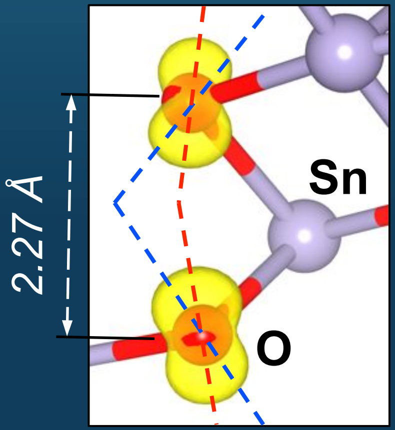
$Li_2Ru_{0.5}Sn_{0.5}O_3$



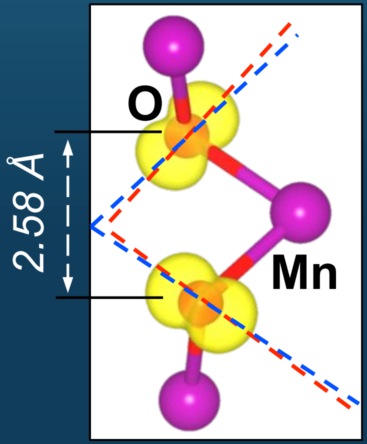
$Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$



$Ru_{0.5}Sn_{0.5}O_3$



$Ni_{0.2}Mn_{0.6}O_2$

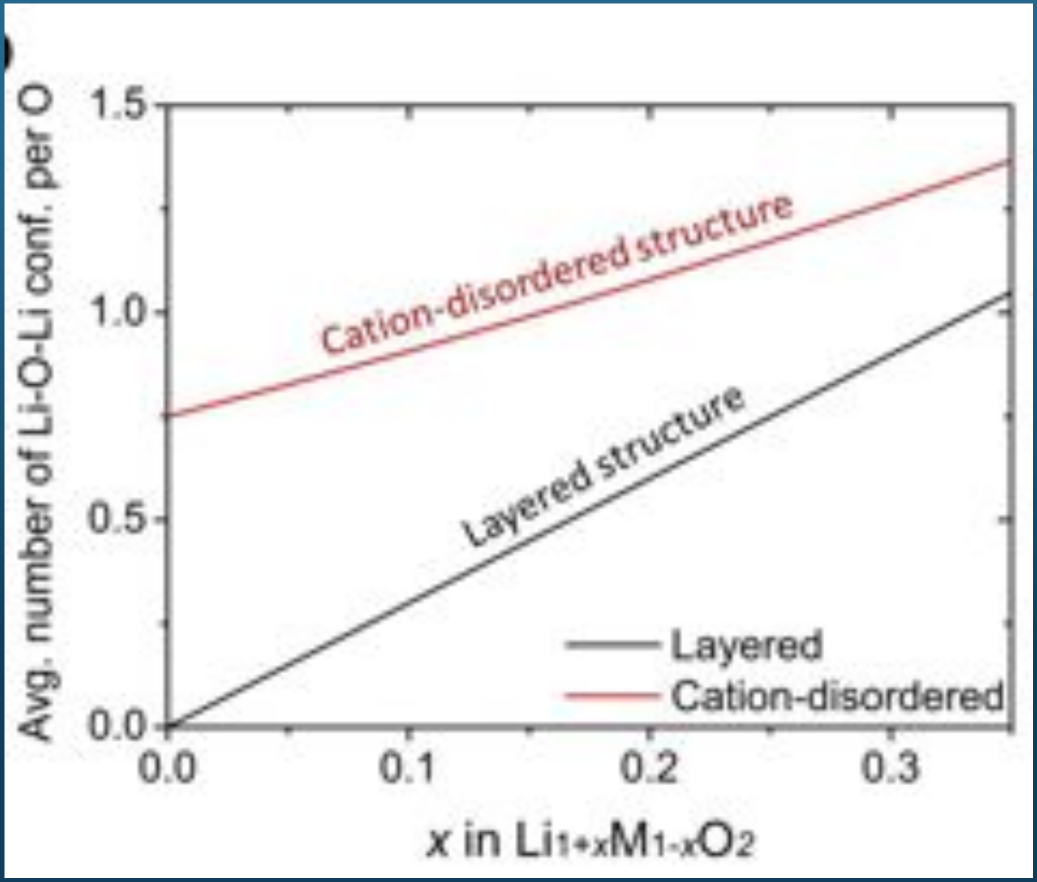


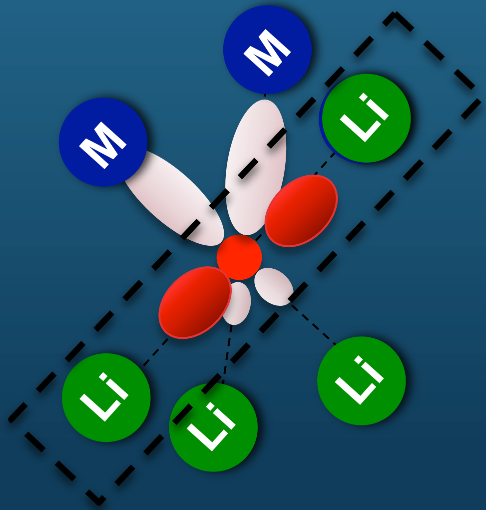
Sn allows the rotation
to form O-O bond

Mn prevents the rotation.
→ Isolated Li-O-Li oxidation

D.-H. Seo,† J. Lee,† A. Urban, R. Malik, S. Kang, G. Ceder, Nature Chem., online (2016)

Now that we understand the origin of oxygen redox, we can estimate the amount available





Just count number of
Li – O – Li configurations

Summary

- Allowing metal ions to “disorder” with Li is extending significantly our chemical options for cathodes.
- > 10% Li-excess guarantees percolation of 0-TM channels and reasonable Li transport through a cation-disordered structure
- Covalency/Hybridization between the TM and oxygen may mask as oxygen redox but it does not create extra capacity
- Stoichiometric well-ordered layered oxides (e.g. LCO, NMC) do NOT have reversible oxygen redox
- Only the Li – O – Li configurations, that occur in **Li-excess** or in **cation-disordered** compounds lead to redox active oxygen

We have a real opportunity to create novel cathode materials based on novel chemistries and true oxygen redox

This presentation is available at http://ceder.berkeley.edu/

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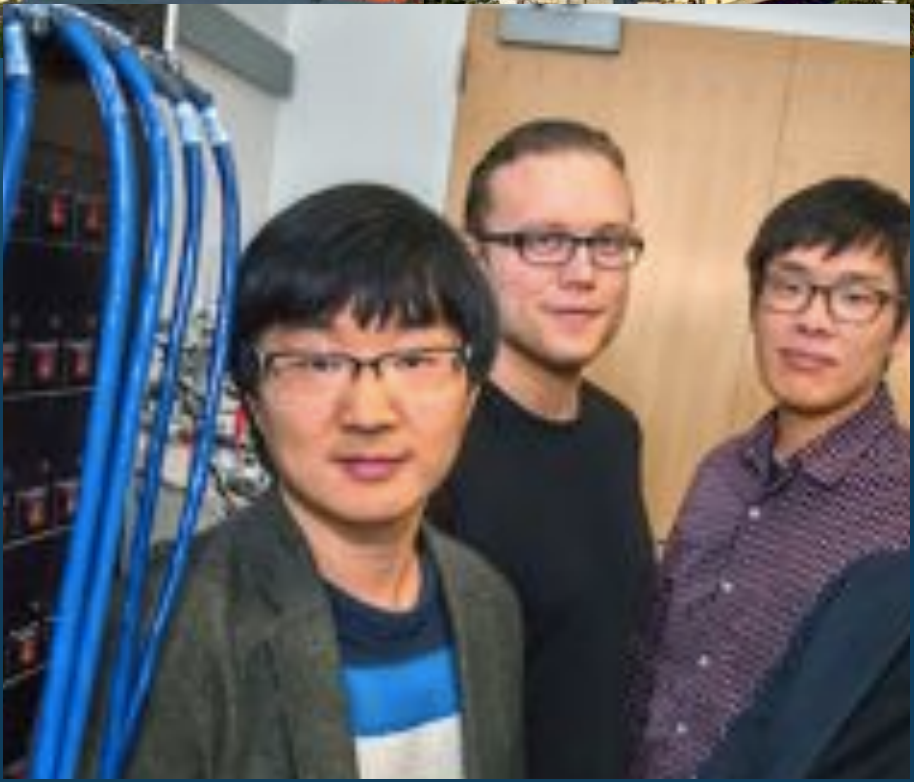

Thank You