A soft X-ray spectroscopic (RIXS) journey into the critical electron states in batteries

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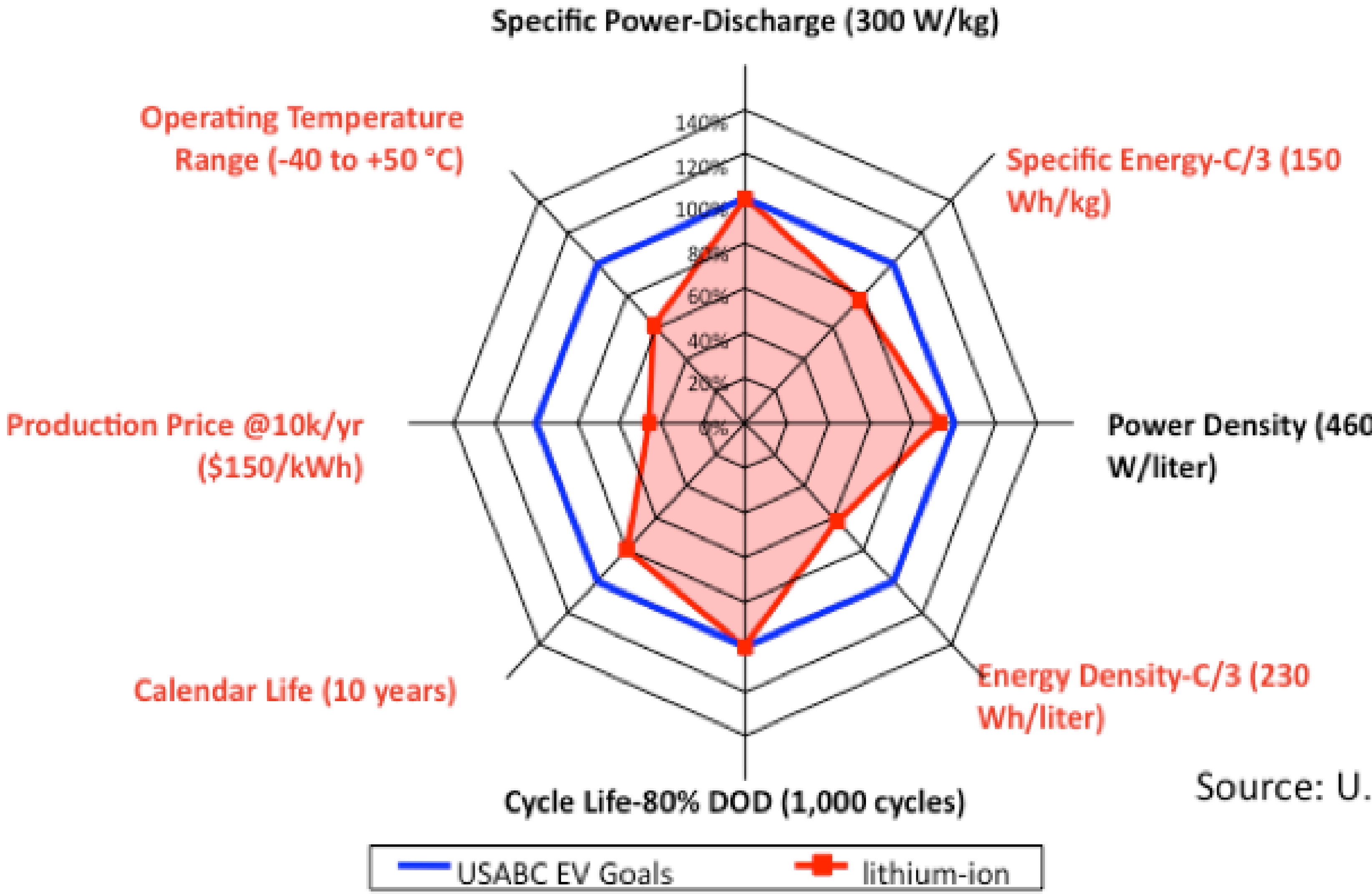
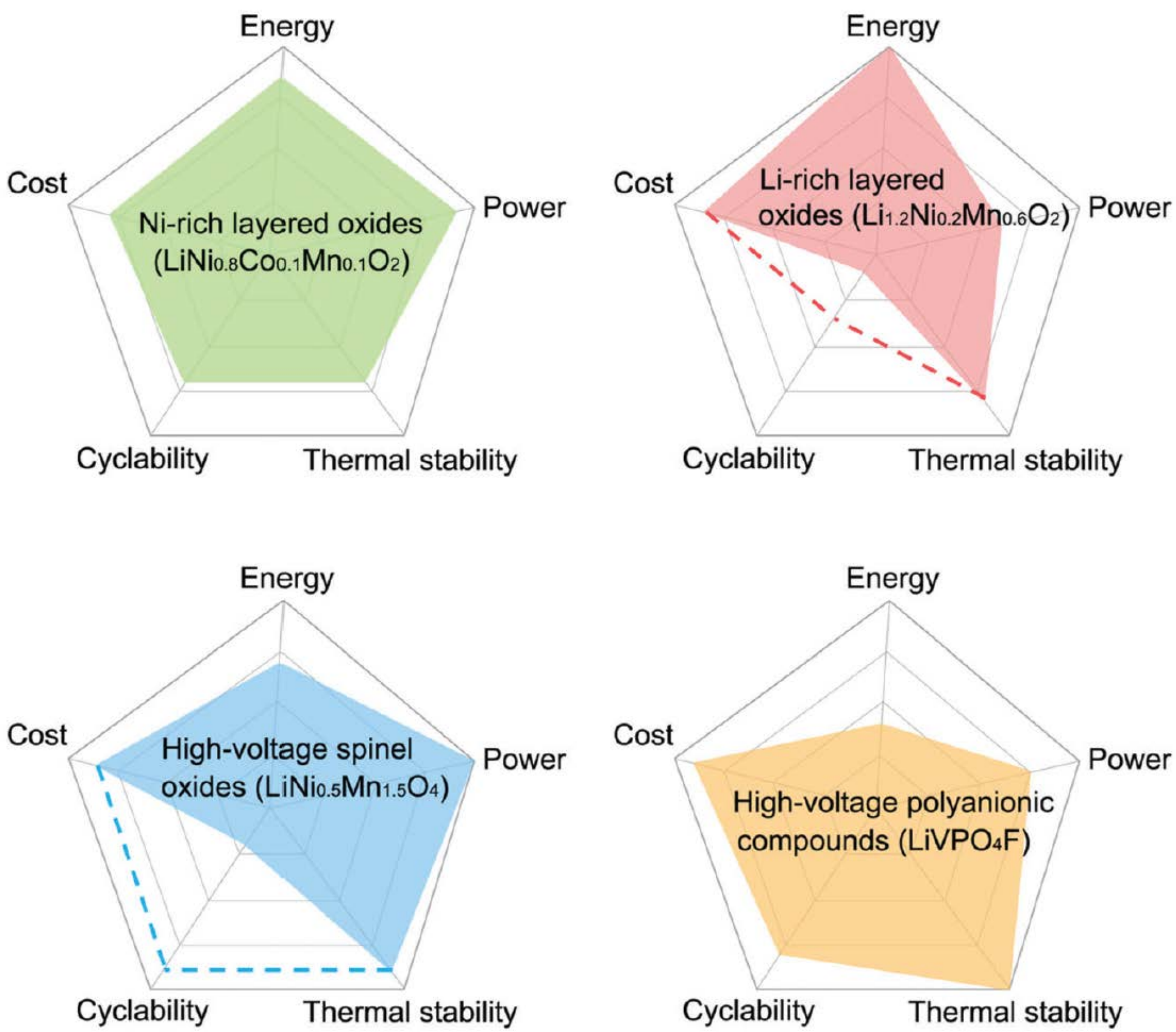
Tinkering with Batteries: a multidimensional Problem!



Source: U.S. DOE

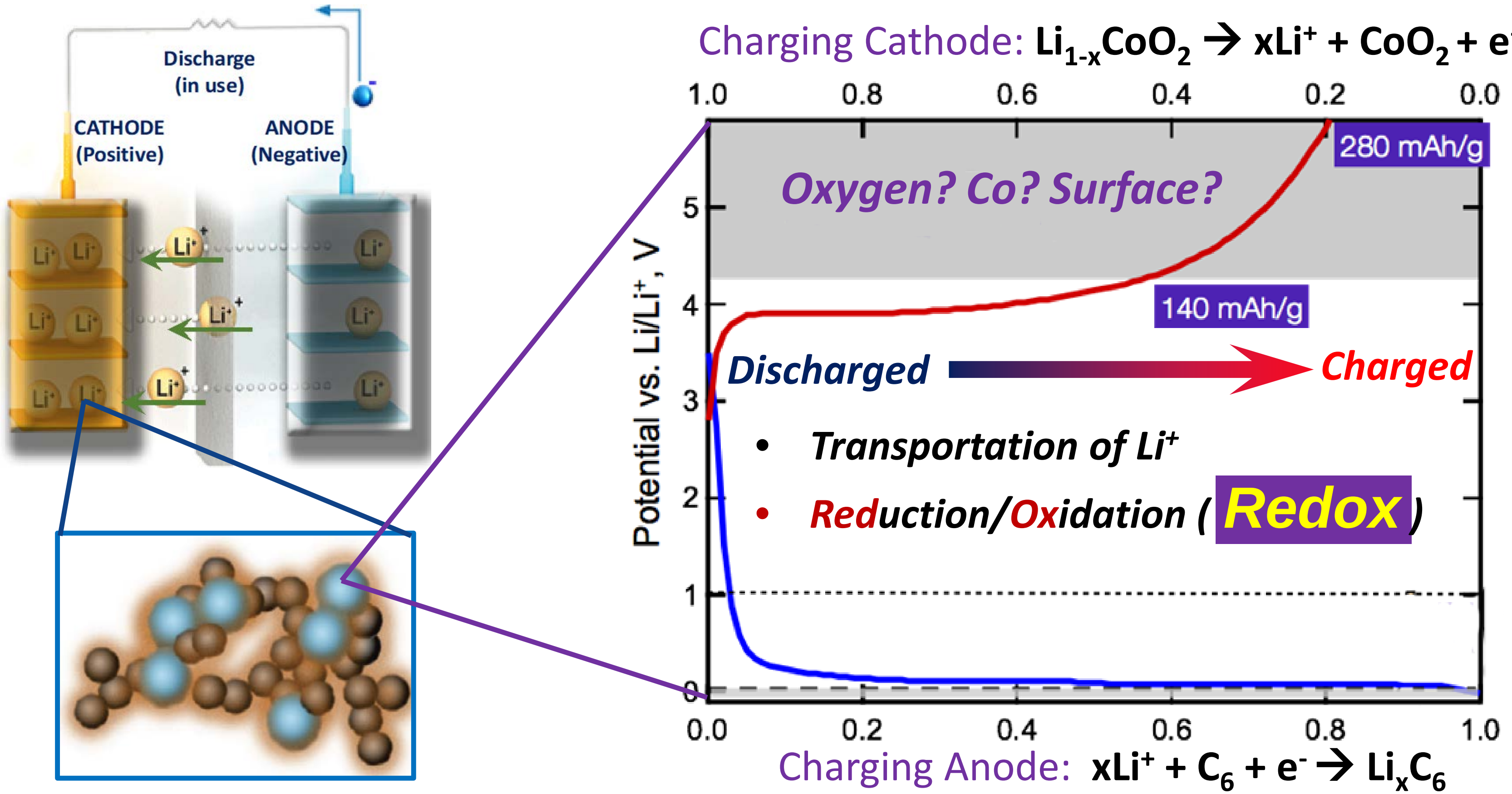
Image Source: US DOE

e.g., "Co-free" electrode? – Sorry, NO good solution ☹



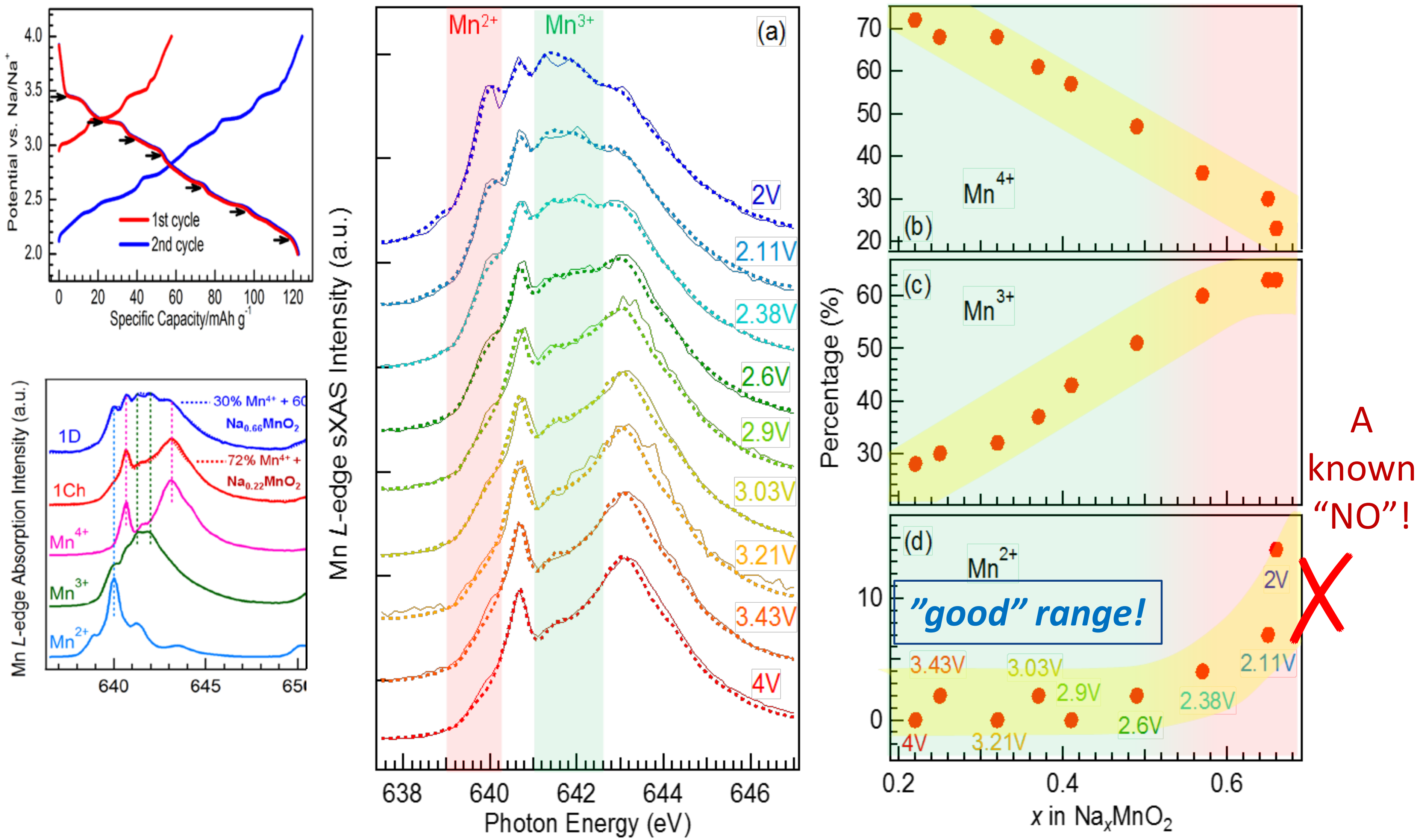
(Only cathodes shown here)   Li et al., Chem. Soc. Rev. 46, 3006 (2017)

What kind of information matters for (practical) battery materials?



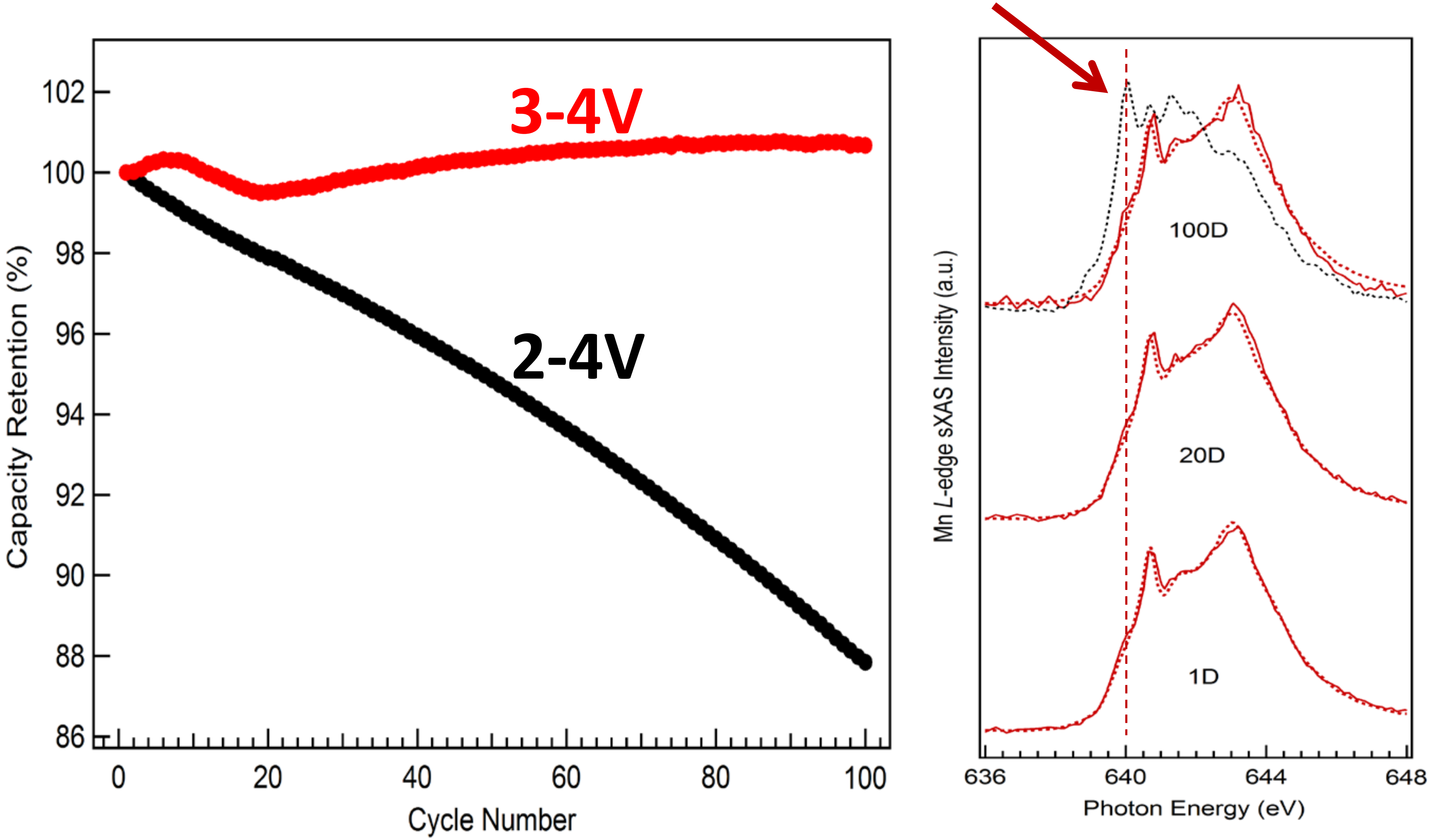
- *Redox reactions **in BULK** electrodes*
- *Chemical activities **on SURFACE** / interface*
- *Solvation shells **in LIDUID** (electrolyte)*

$Na_{0.44+x}MnO_2$: Mn states upon cycling and surface Mn^{2+} evolution



Qiao et al., Nano Energy 16, 186 (2015)

A rational approach to improve $Na_{0.44+x}MnO_2$ cyclability!

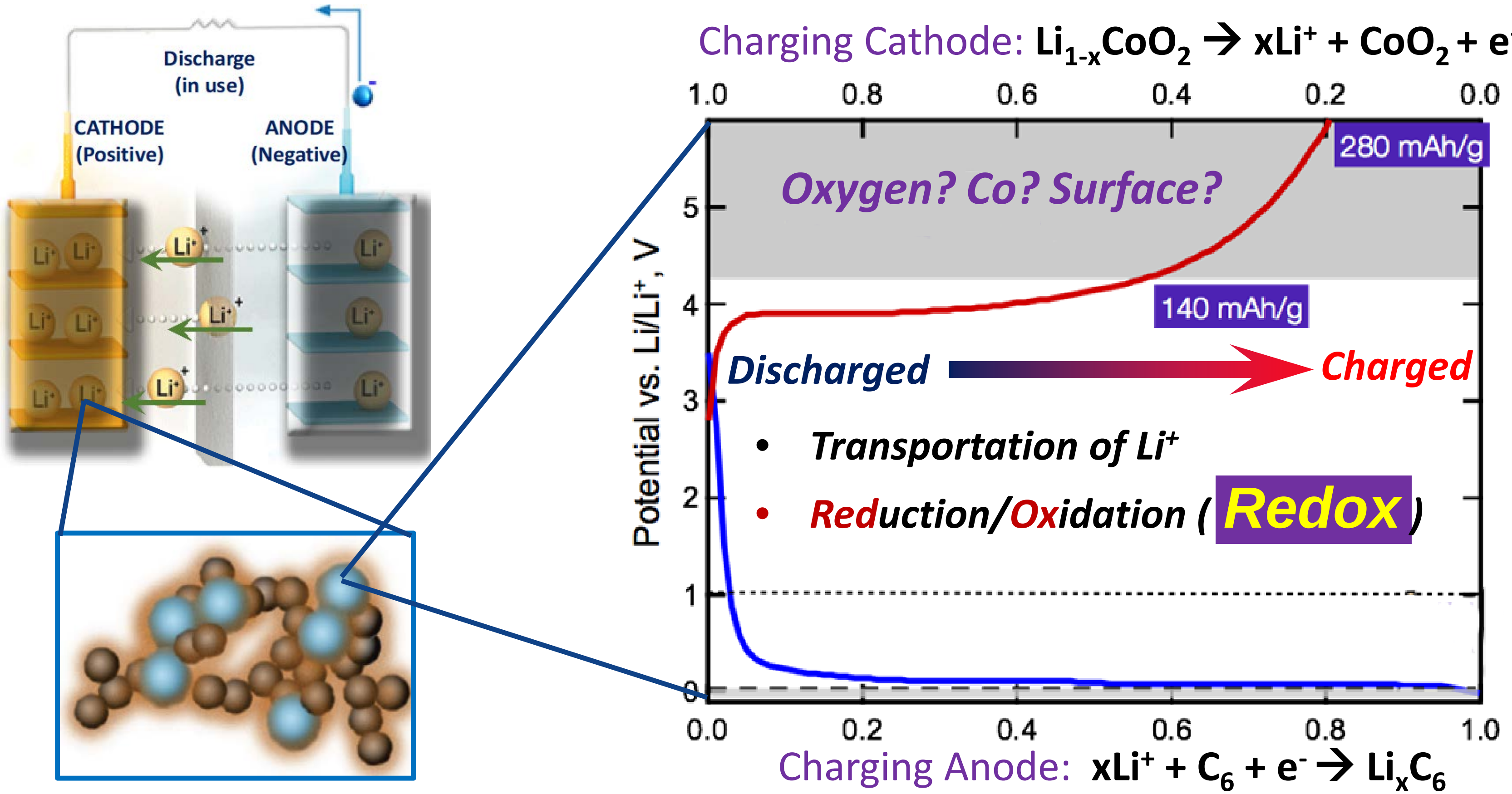


Improved Cycling Stability from Multiple effects (shallow cycling)!

- However, ***one of the keys*** is the suppression of ***surface Mn^{2+}*** evolution

Qiao et al., Nano Energy 16, 186 (2015)

What kind of information matters for (practical) battery materials?



- *Redox reactions **in BULK** electrodes*
- *Chemical activities **on SURFACE** / interface*
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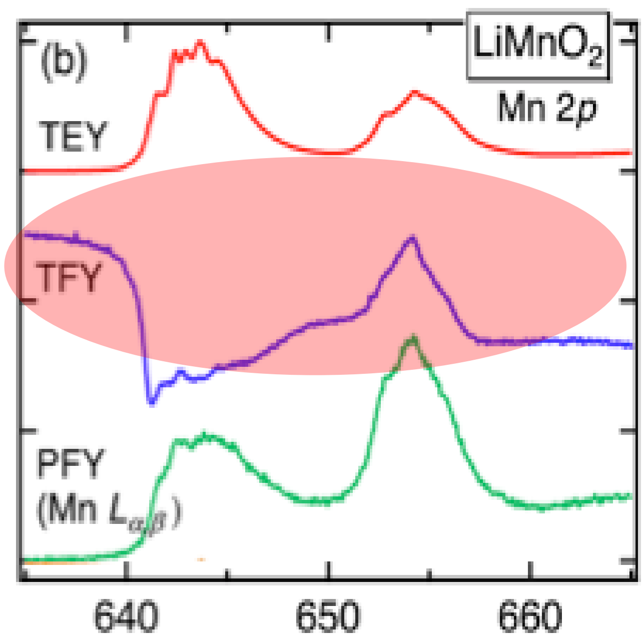
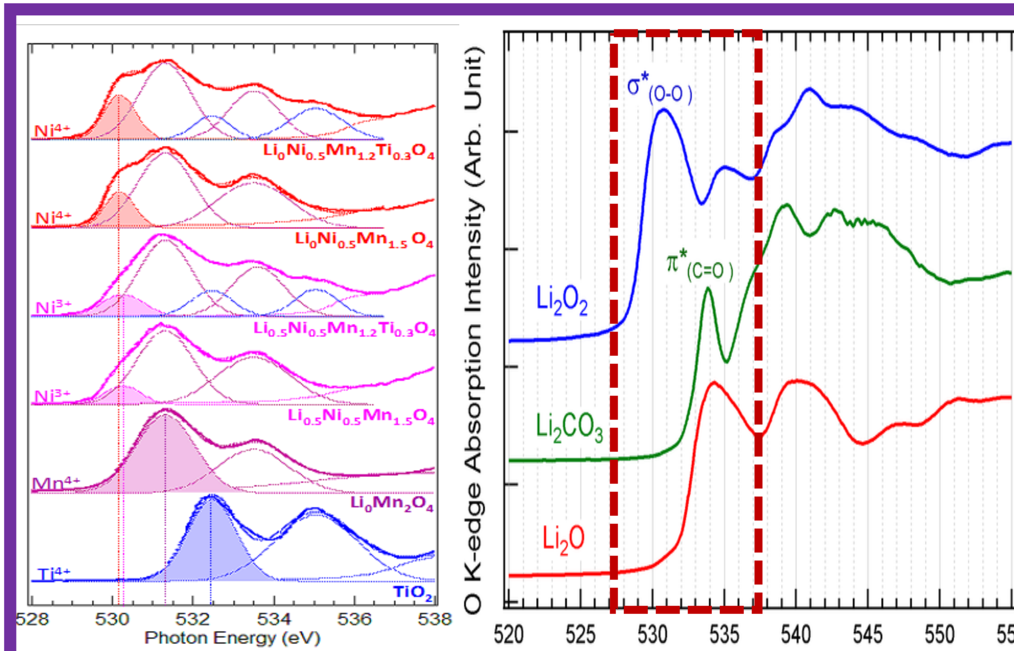
Two problems of "bulk-sensitive" XAS of oxide electrodes

- Distortions of TM-L in photon-in-photon-out modes !
- Lack of chemical sensitivity for O-K !!



Wadati et al., APL 100, 193906 (2012)

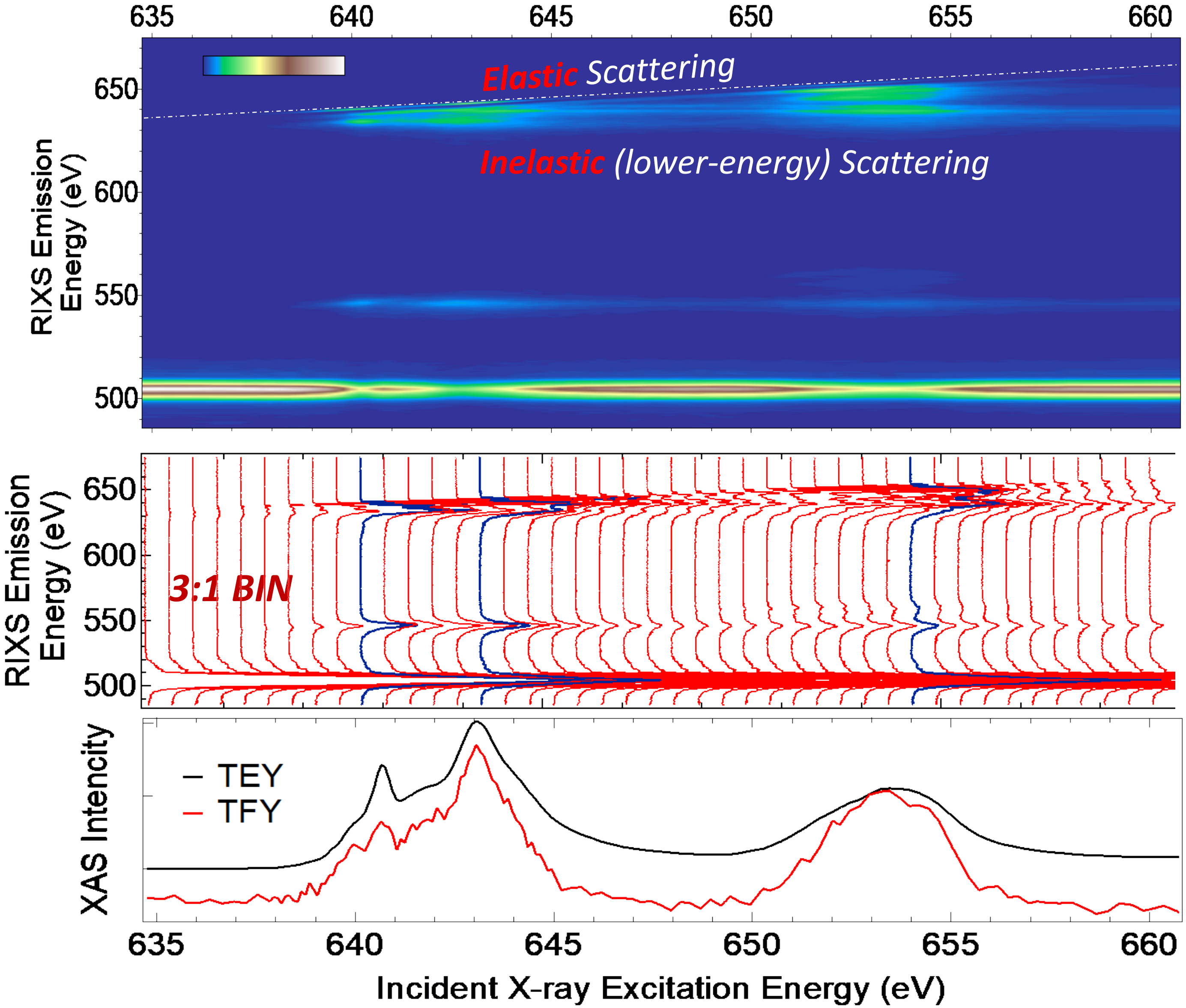
- Material dependent
- Element dependent
- "self-absorption correct" -N/A



Ruimin Qiao et al., unpublished

- Strong 3d character in O-K "pre-edge"
- Chemical sensitivity lost due to the overlapping energy range ☹

Seemingly problem solved: full energy-range mapping of RIXS (mRIXS)

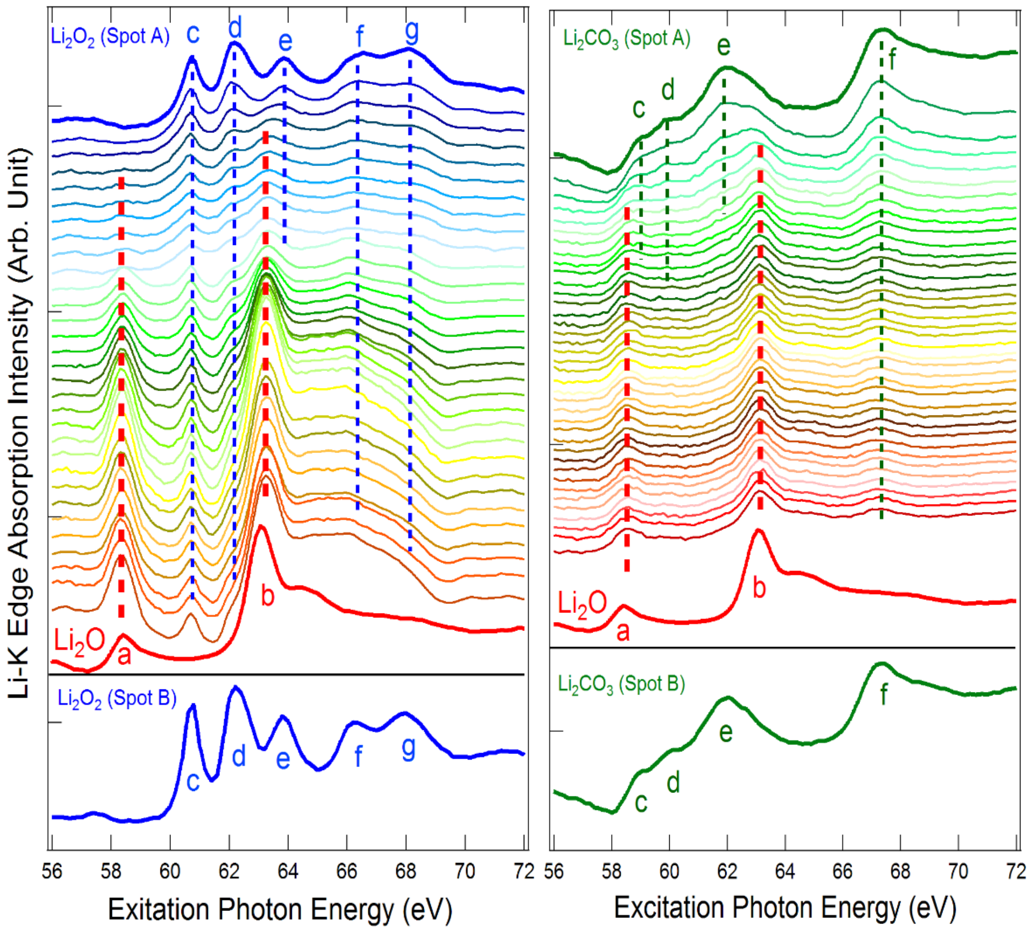


O-K (XES)
→ iPFY

O-K (XES)

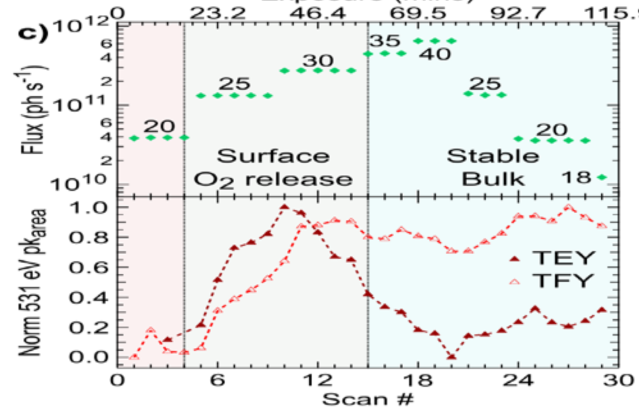
Yang & Devereaux, J. Power Sources 389, 188 (2018)

The real challenge !

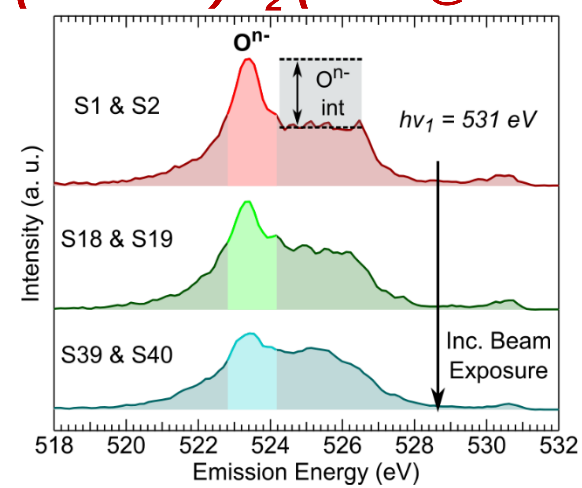


Qiao, Chuang, et al, Plos ONE 7, e49182 (2012)

$LiAlO_2$ (O-K XAS)



$Li(NiMnCo)O_2$ (RIXS@531 eV)

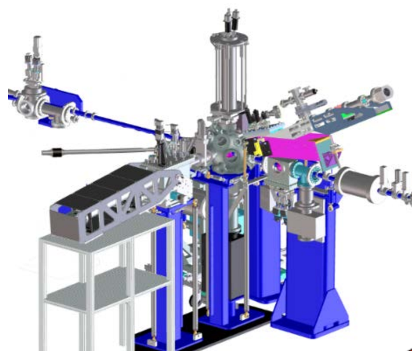


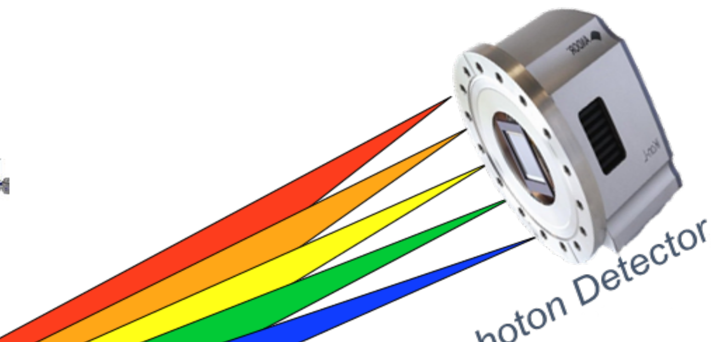
***Detection efficiency** is NOT a speed/quality issue; it is a **FEASIBILITY** issue for chemistry and material sciences!*

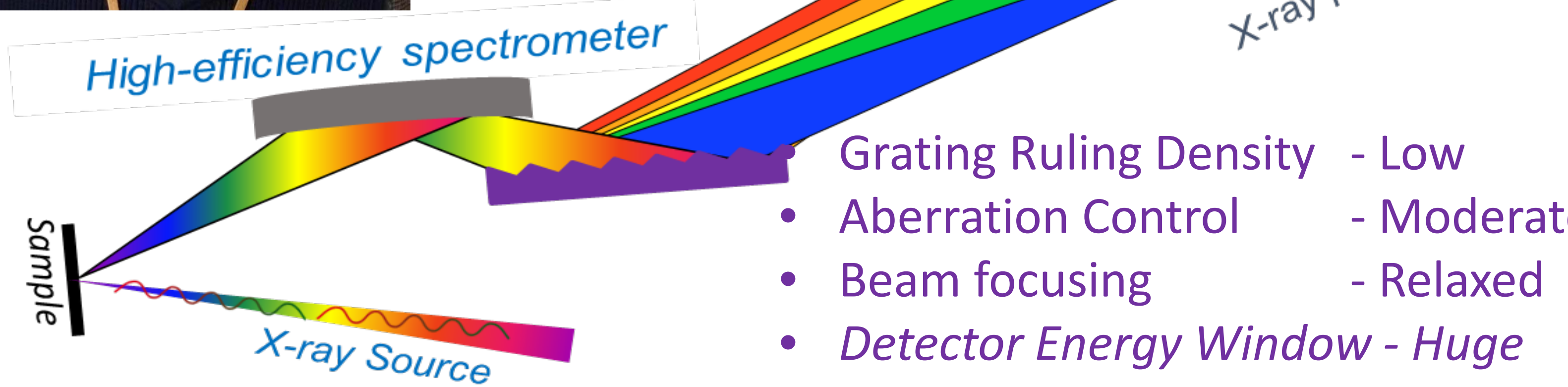
Lebens-Higgins et al., JPCC 123, 13201 (2019)

A dilemma of resolution vs **efficiency** for Energy materials

Qiao, et al., RSI 80, 063102 (2017)
Chuang, et al., RSI 88, 013110 (2017)





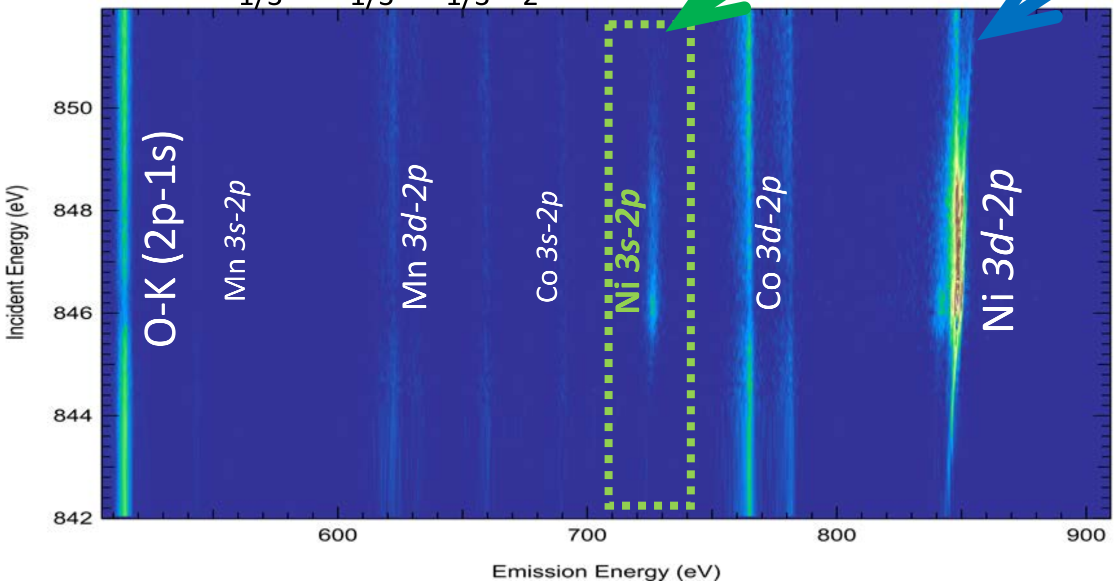


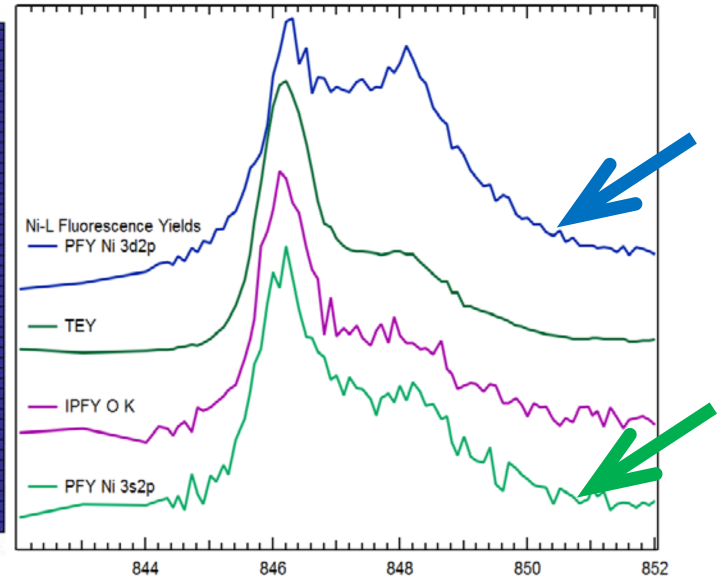
- Grating Ruling Density - Low
- Aberration Control - Moderate
- Beam focusing - Relaxed
- *Detector Energy Window - Huge*
- Angles, etc… …

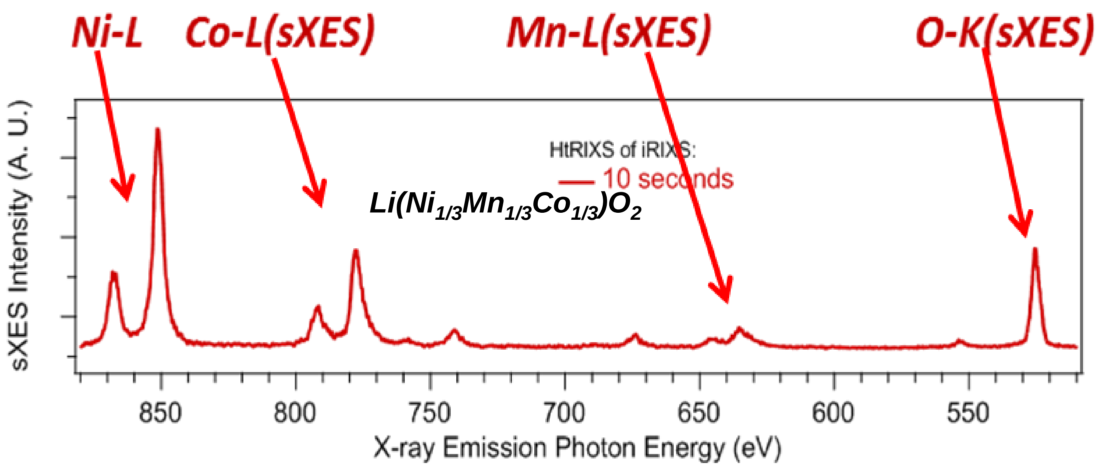
Of course, the true reason is: poor & out of real-estate!

2016: *full-energy range ultra-high efficiency* **mRIXS**

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







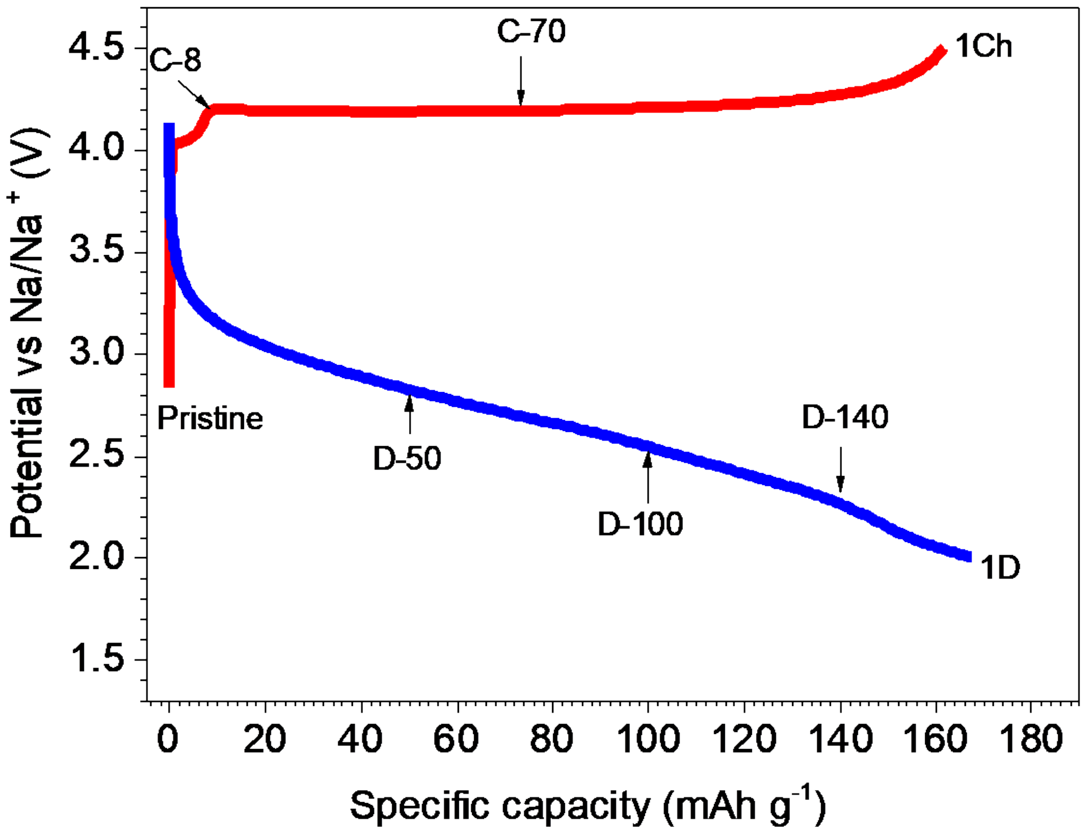
- An ultimate TM *3d* probe: mRIXS-iPFY of all TM-L edges
- An alternative: mRIXS 3s-2p decay channels

Time: ~30 minutes for mRIXS-iPFY

A ***10-second*** *spectrum of a (discharged) NMC electrode*

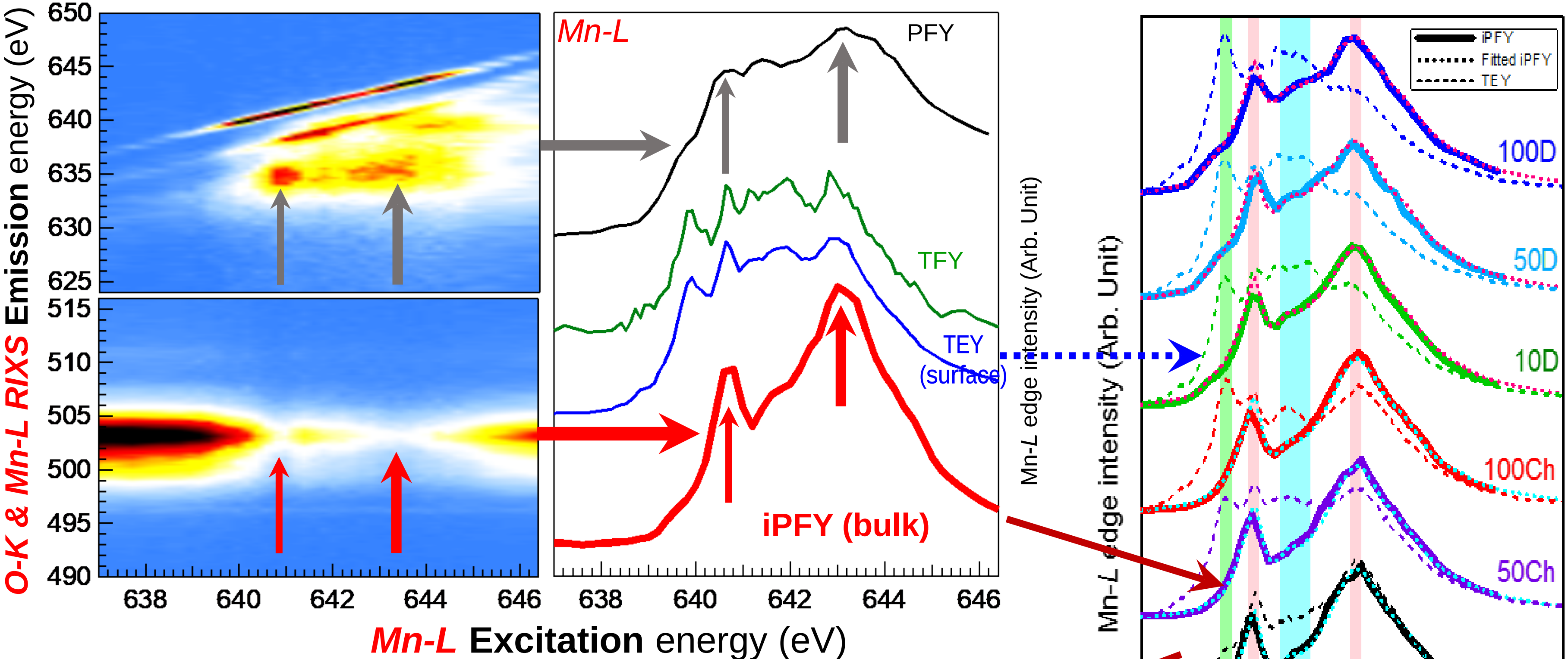
Qiao et al., RSI ***88****, 033106 (2017)*

$Na_{2/3}Mg_{1/3}Mn_{2/3}O_2$: Complex states of evolving Mn & O



- Stoichiometry adjusted to drive (pure) high-valence Mn^{4+}!
- Capacity reaches ***record high with "inactive" Mn?***!
- Change of ***Oxygen*** states is expected to be strong?

mRIXS-iPFY & *TEY* *Mn-L: bulk and surface Mn redox quantification*

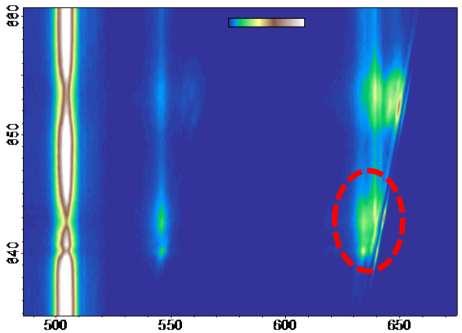


Quantify the Mn states
on surface (10nm) and in bulk (150 nm)

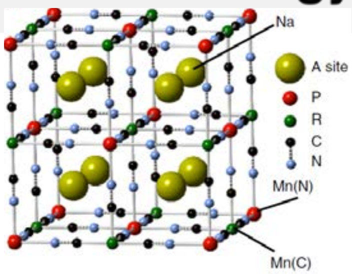
- Quantitative probes of both the surface and bulk oxidation states of TMs
- *Absolute quantification of the cycling capacity from Mn redox reactions*

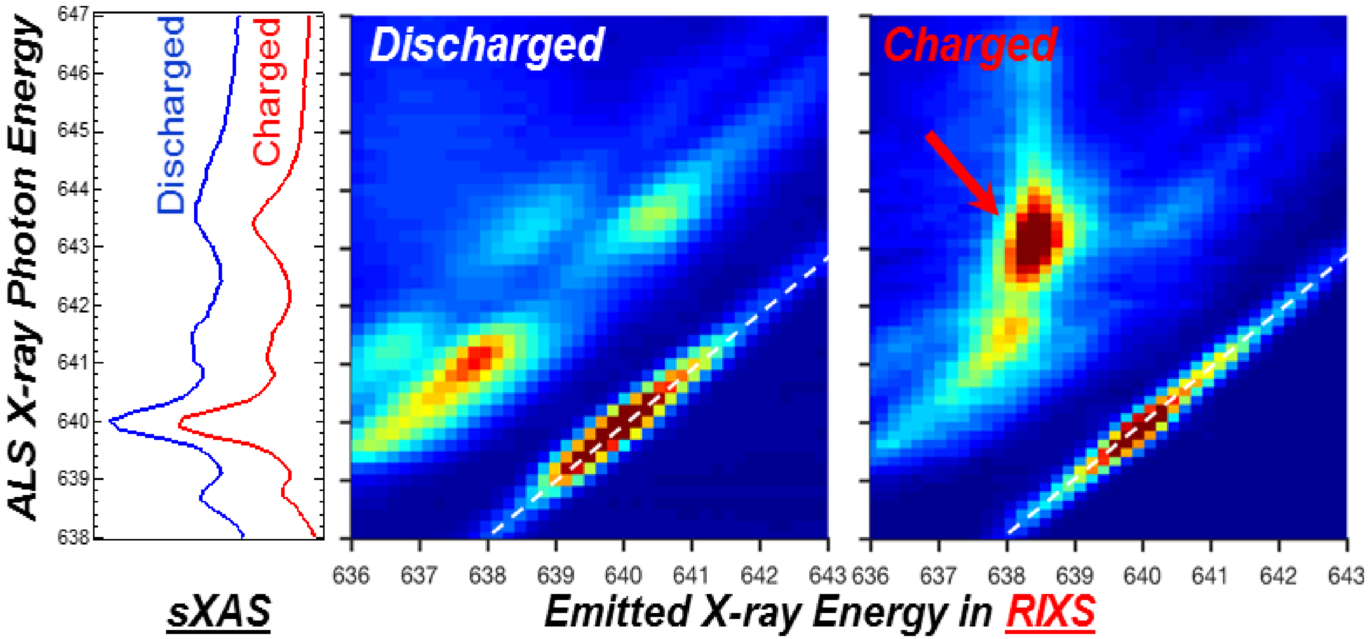
Mn-L mRIXS reveals Mn^{1+}: a 90-year speculation!

(- Theory: Prof. Andrew Wray at NYU)



Natron Energy



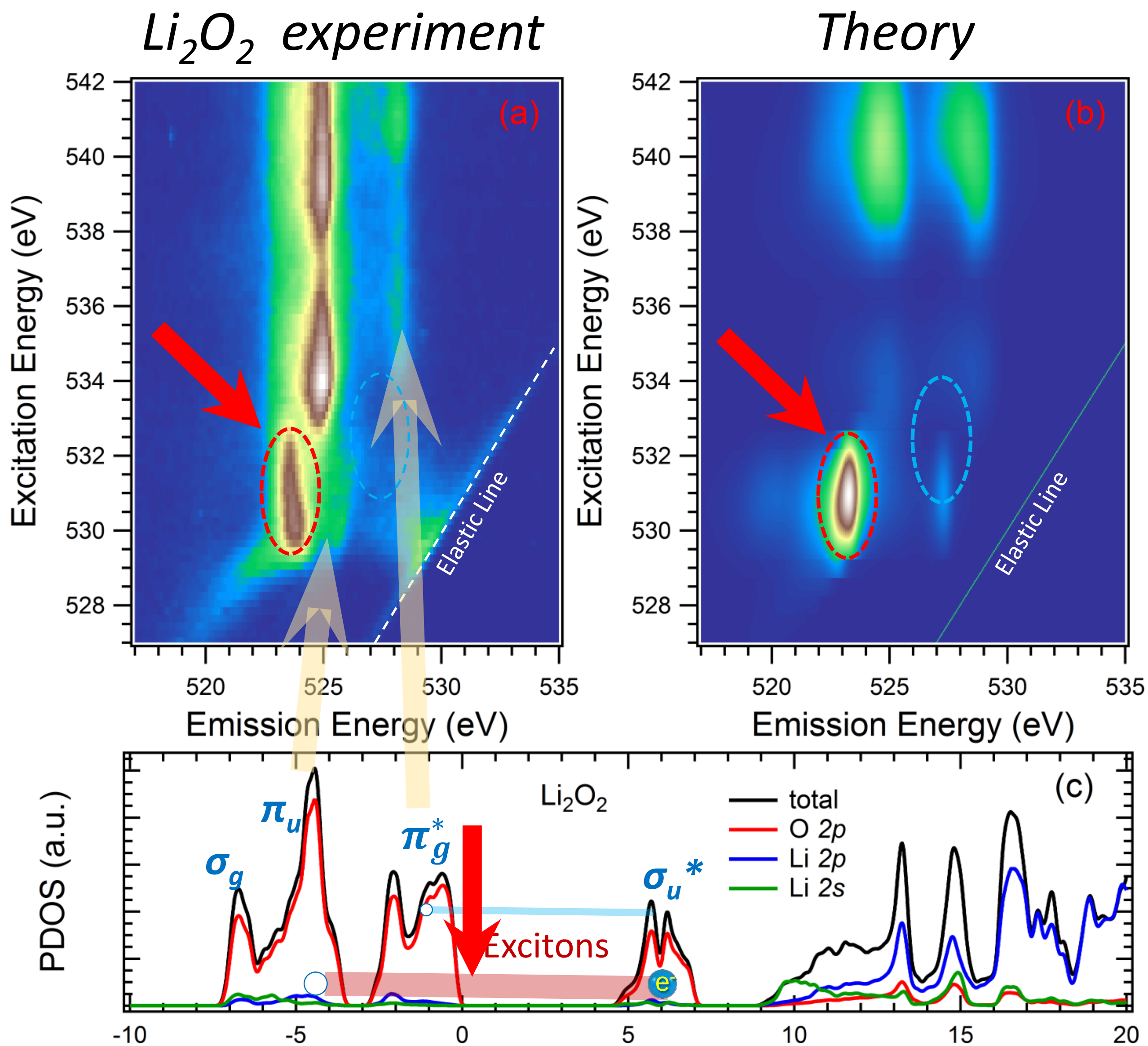


In a recent breakthrough, Berkeley Lab scientists collaborated with Natron Energy and New York University to confirm a century-old chemistry speculation, a finding with broad-reaching implications for the future of battery technology. The researchers took advantage of two Berkeley Lab user facilities, the Advanced Light Source and the Molecular Foundry, to study an unconventional, but promising, new sodium-based battery design. They discovered a key to the battery's superlative properties was a novel chemical state of the element manganese. The revelation could lead to new classes of high-performance, low-cost batteries that can quickly and efficiently store and distribute energy produced by solar panels and wind turbines across the electrical grid.

- Dr. Maxon's congressional testimony for U.S. National Labs (2018)

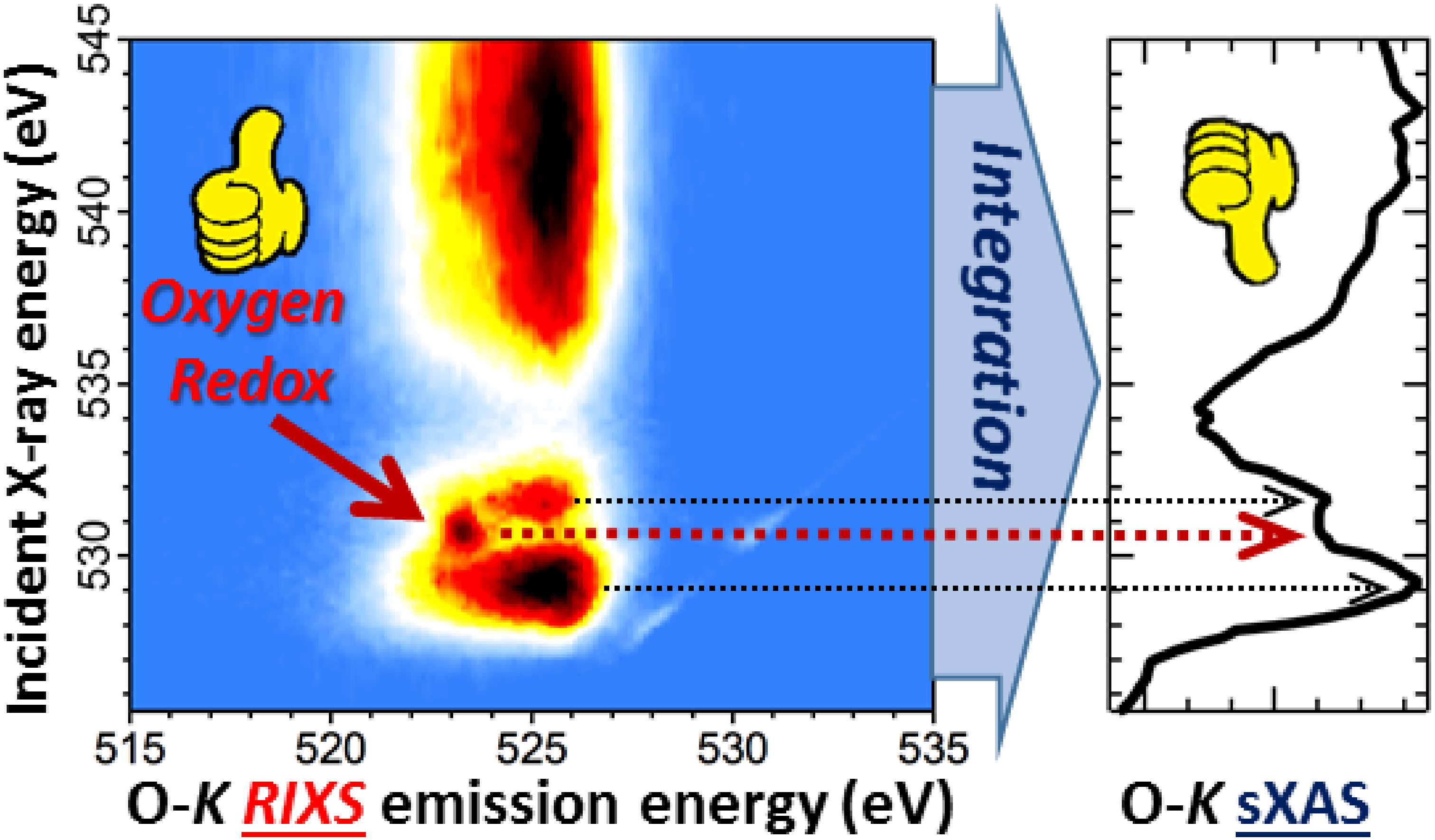
Firouzi, Qiao et al., Nat Comm 9, 861 (2018)

Fingerprint non-divalent oxygen states through mRIXS



Zhuo, Pemmaraju et al., JPCL 9, 6378 (2018)

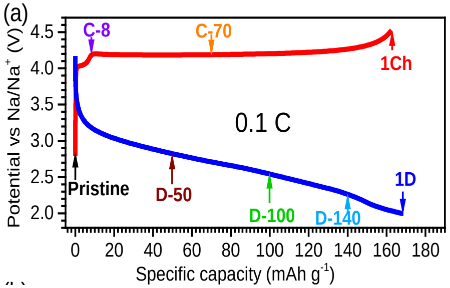
mRIXS: a reliable probe of unusual bulk Oxygen states



- TM-O hybridization is dissociated from oxygen redox reactions
- A full energy range mRIXS is necessary (signals buried in XAS)
- Theoretical calculations in process …

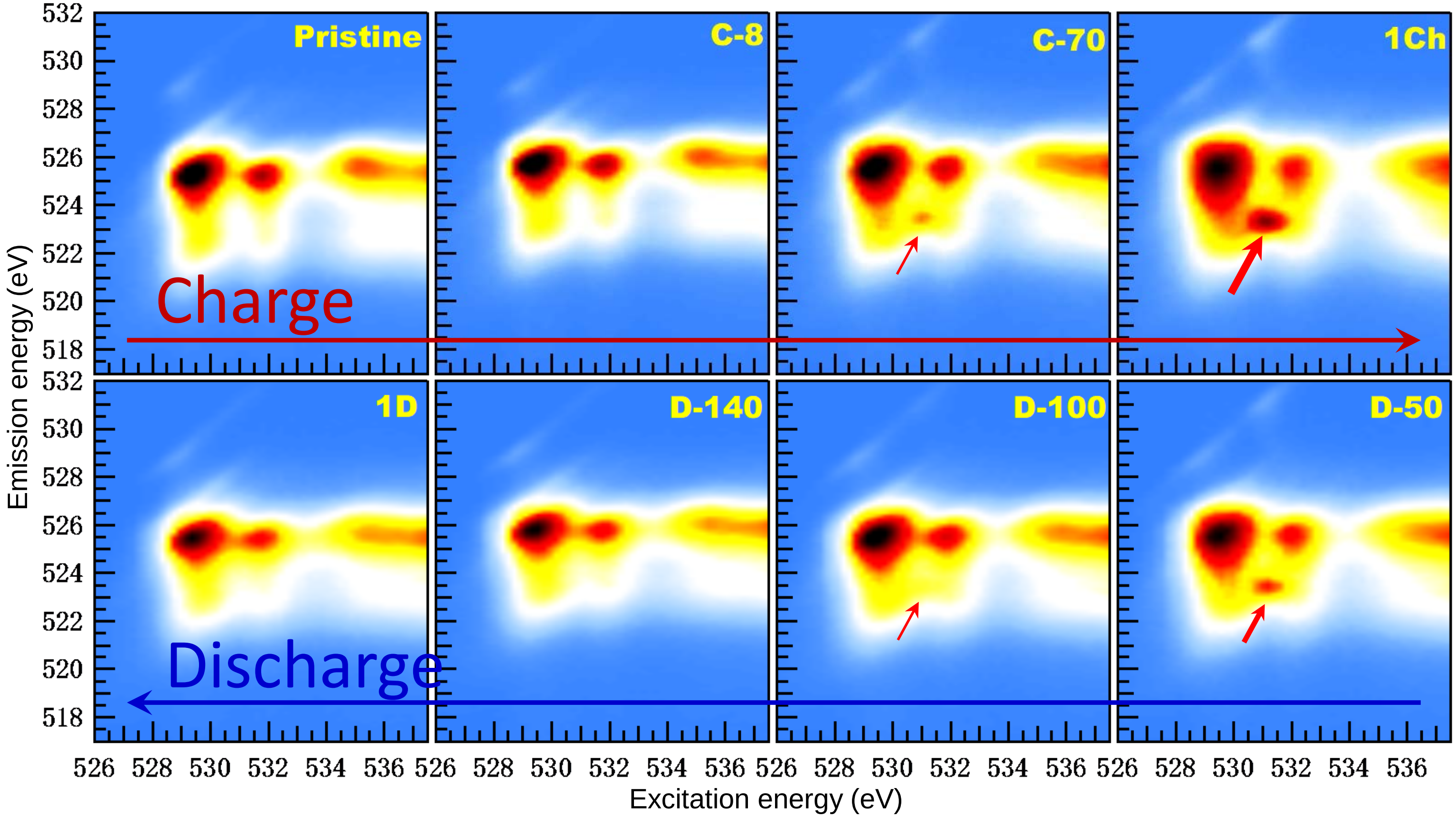
Yang & Devereaux, J Power Sources 389, 188 (2018)

mRIXS fingerprints the evolving oxygen state upon battery cycling



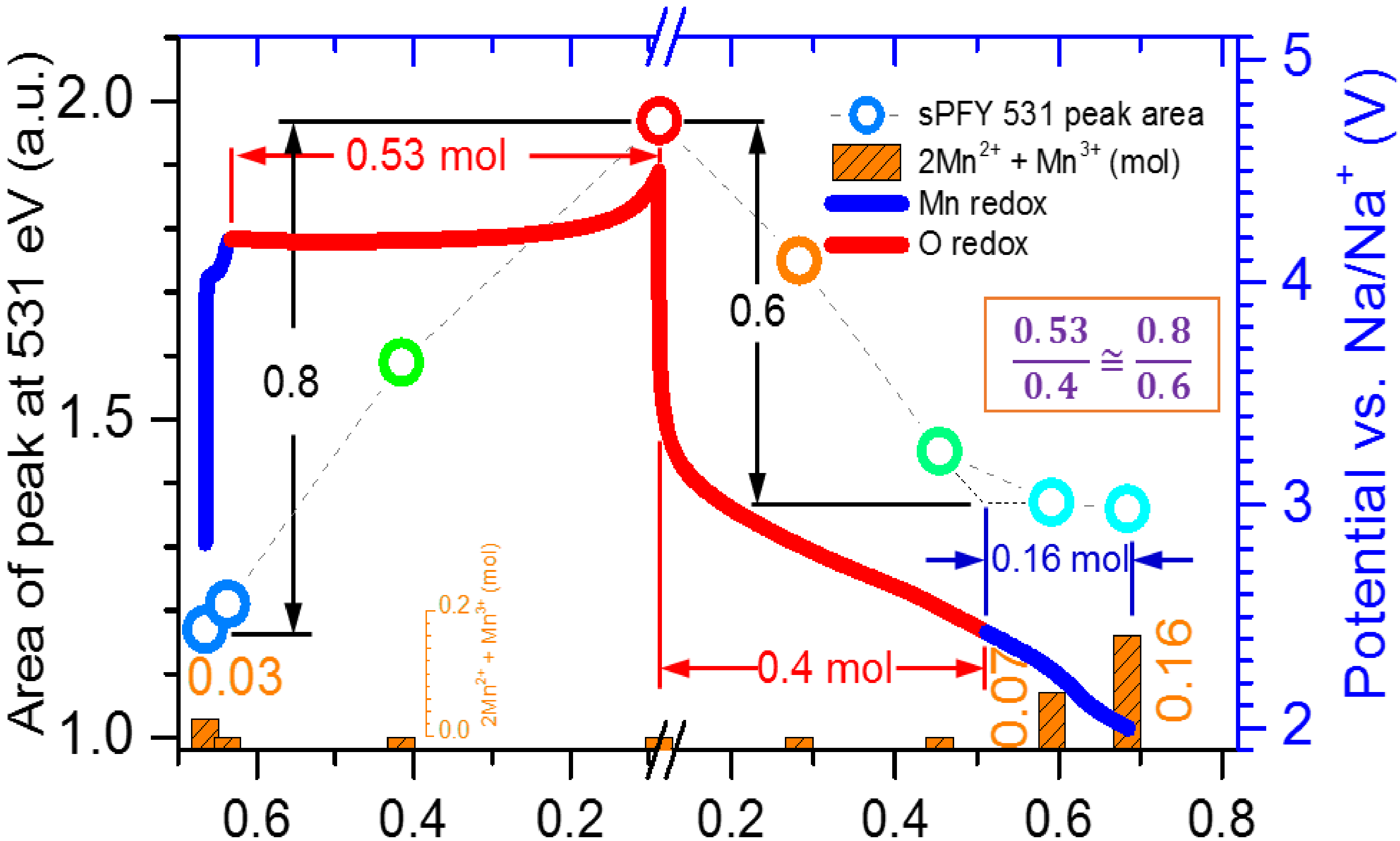
$Na_{2/3}Mg_{1/3}Mn_{2/3}O_2$

- O-K mRIXS feature follows tightly with electrochemical cycling!
- O-K mRIXS feature fingerprints the oxygen redox quantitatively!



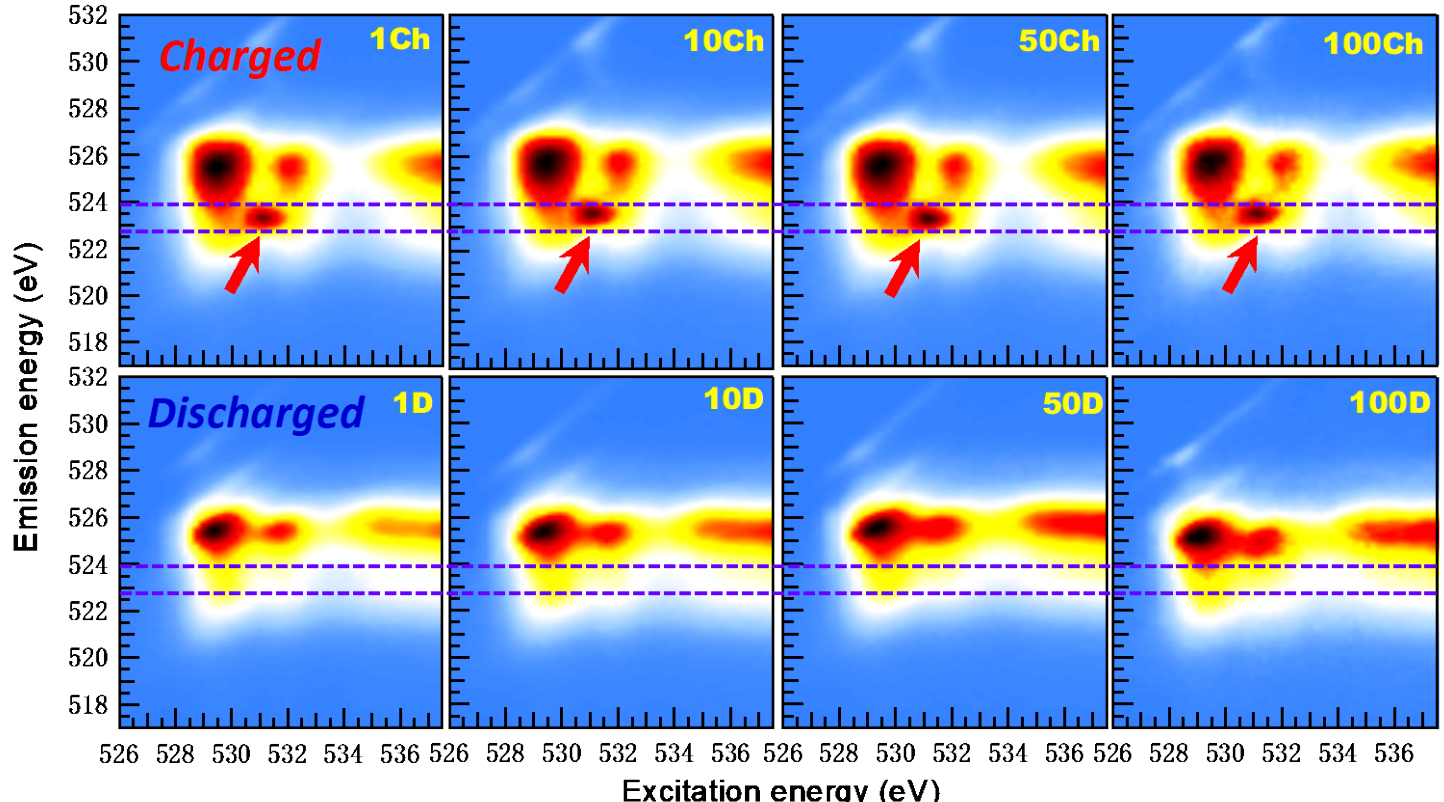
Dai et al., Joule 3, 518 (2019)

$Na_{2/3}Mg_{1/3}Mn_{2/3}O_2$: Independent probe of Mn/O states in battery



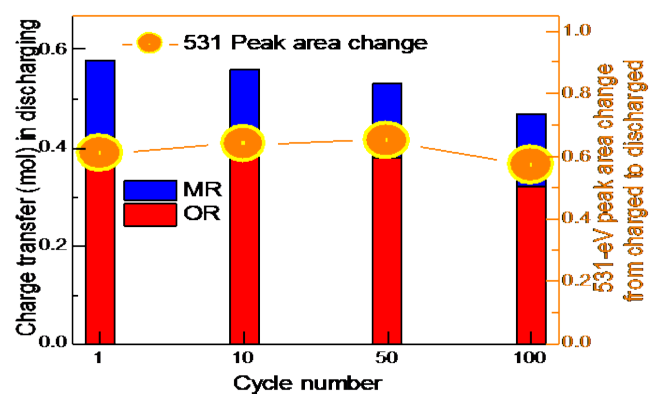
✓ *mRIXS quantifications precisely match the electrochemical capacity/profile!*

Quantify the reversibility of Oxygen redox through mRIXS

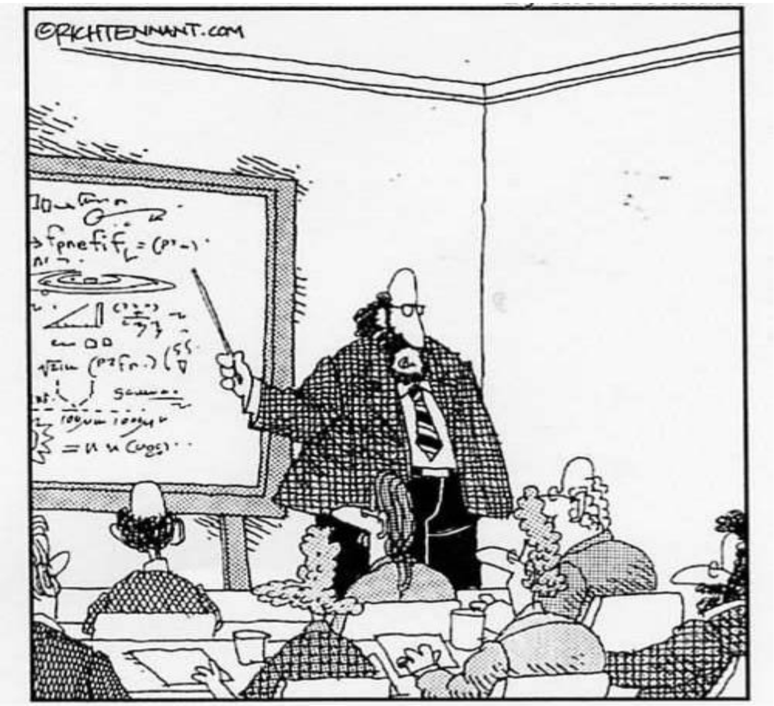


- *A strong O.R. system could also be highly reversible!*
- Assessment of the reversibility of Oxygen redox reactions upon extended cycles!

NOTE: *NOT all systems show such a perfect match between mRIXS quantification and electrochemistry*



Always #1 question: *what matters for batteries?*



*"After the discovery of "**antimatter**" and "**dark Matter**", we have just confirmed the existence of "**doesn't matter**", which does not have any influence whatsoever!"*

- the 5th wave

Conclusions

- High-efficiency mRIXS is truly needed and provides unique information on battery material performance, especially the novel chemical states of TMs & O.
- Instrumentational and especially theoretical developments are still needed.
- ***Improvements on <u>detection efficiency</u> has opened RIXS technique as almost the only "tool-of-choice" for a wide range of topics in energy materials!***

Acknowledgements

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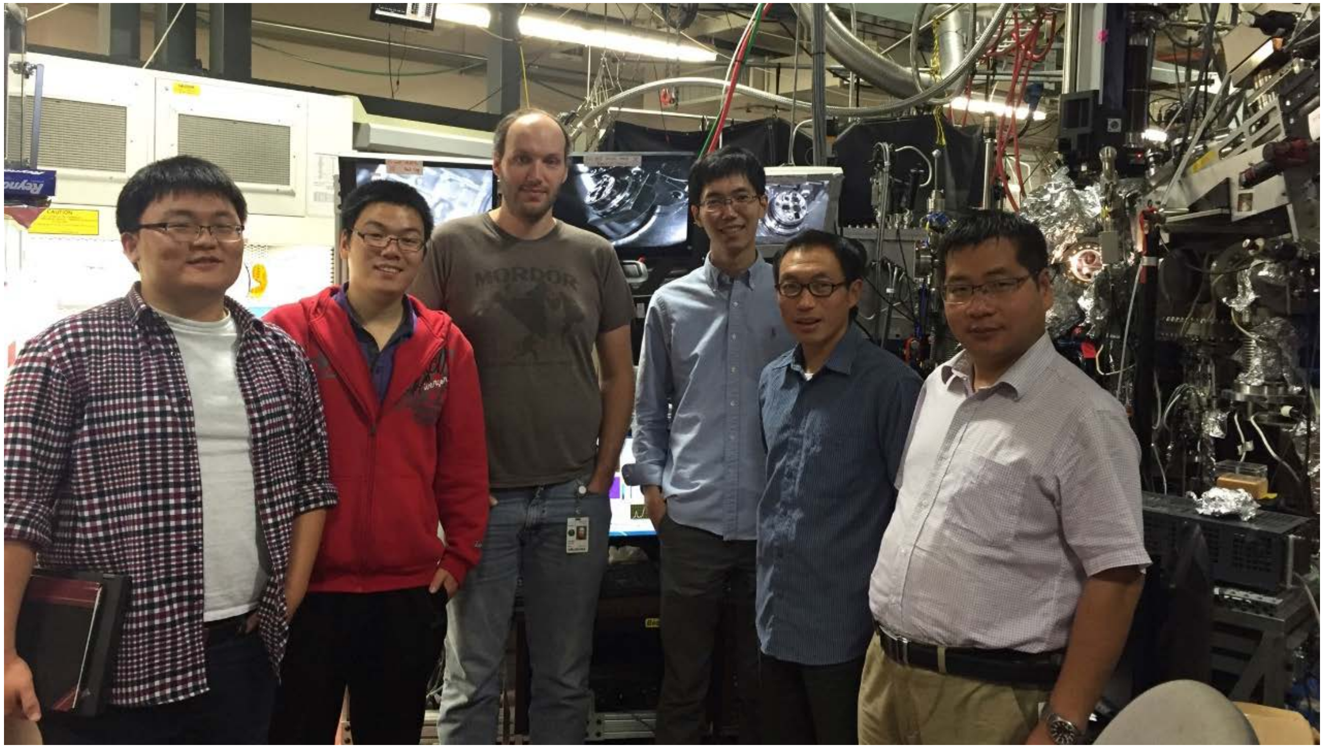

Theory :
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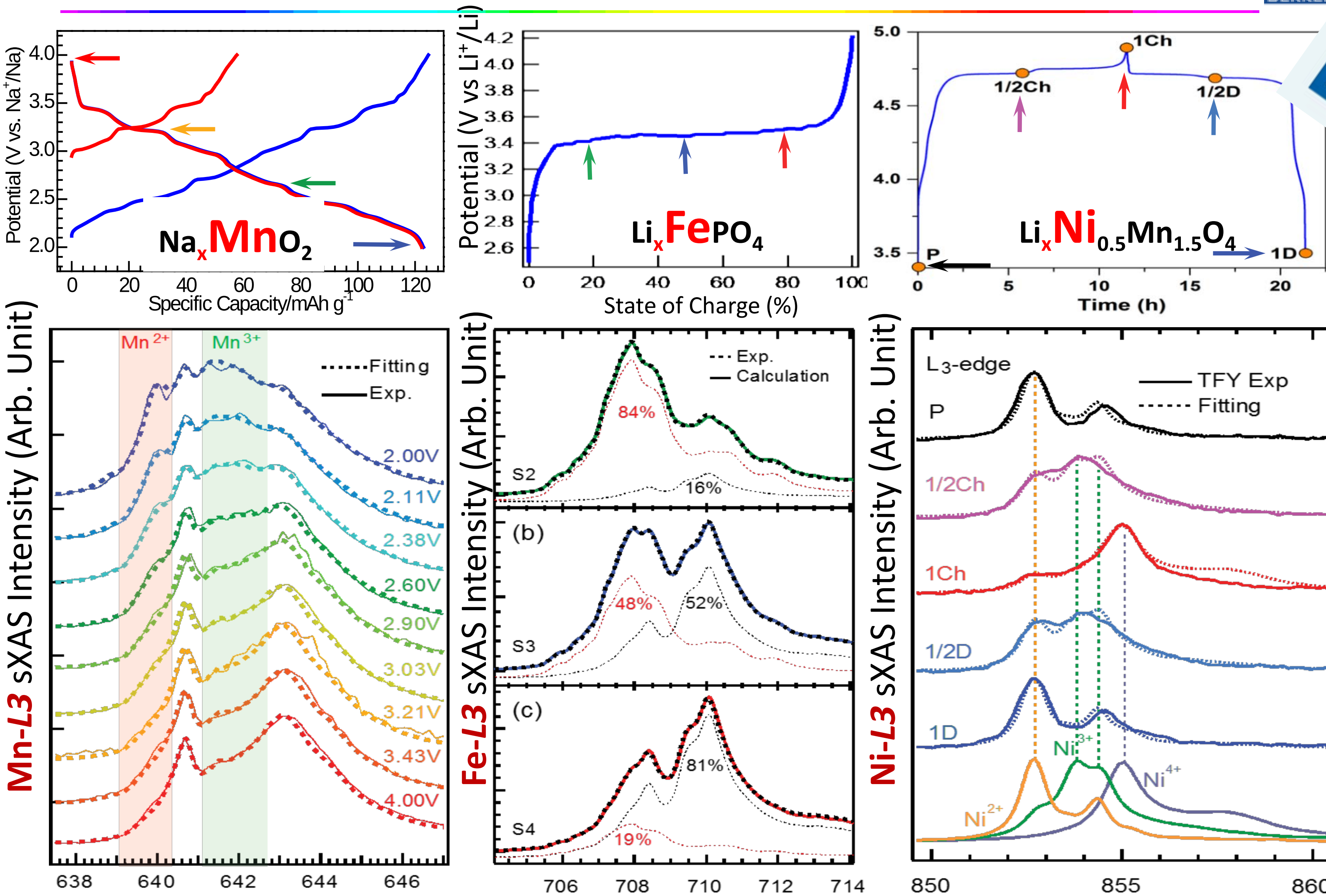
- **Tom Devereaux** (Stanford)

Industry:
- **Colin D. Wessells** (Natron Energy)

A LONG List of Materials Collaborators:
- **Gao Liu** (LBNL)
- Ning Li, **Wei Tong** (LBNL)
- **Yuhao Lu** (previously, Sharp USA)
- *& many many others …*

BACKUP SLIDES

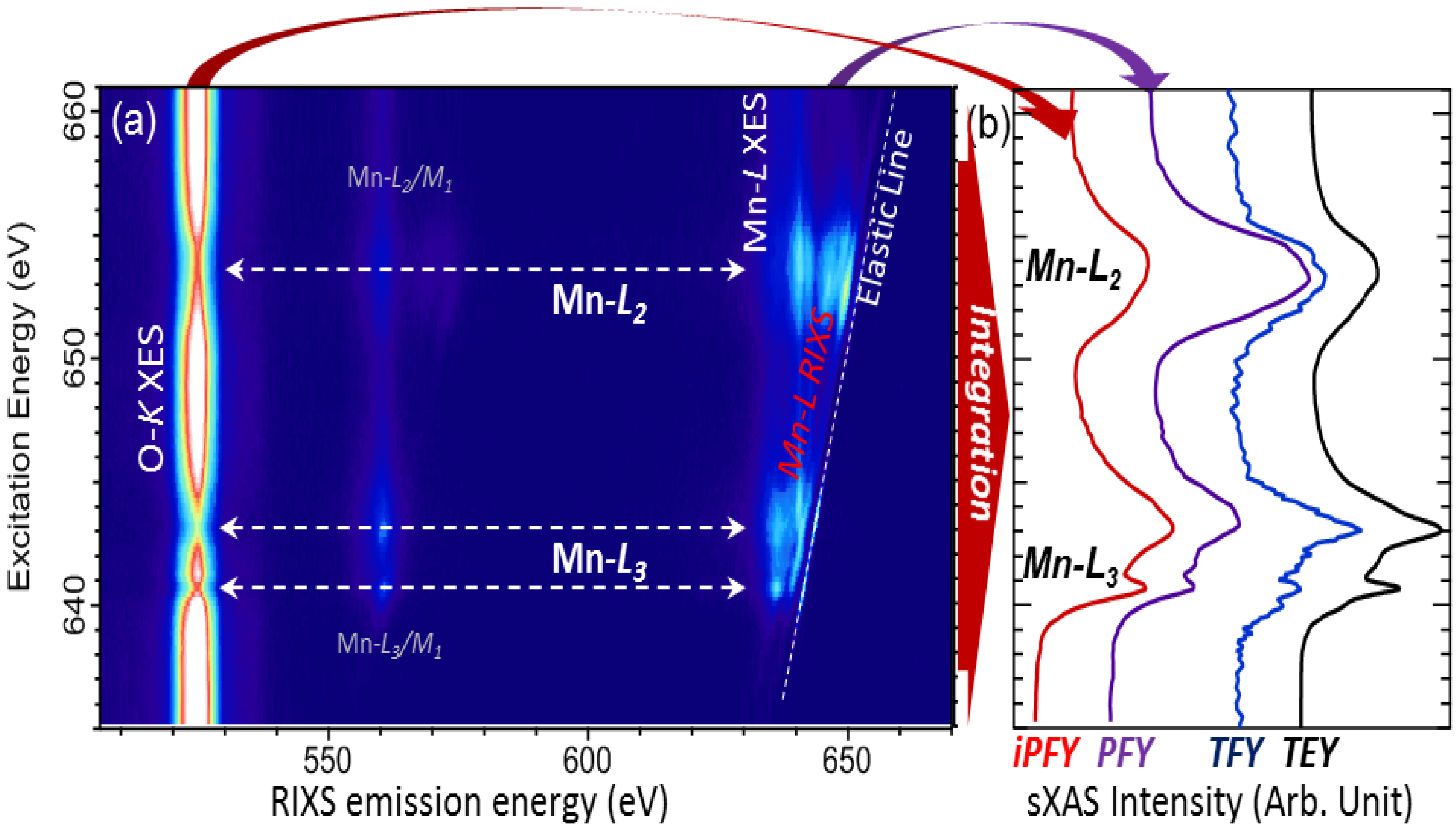
Quantitative analysis of various TM-redox in battery cathodes



Nano Energy 16, 186 (2015) *JACS 134, 13708 (2012)* *JPCC 119, 27228 (2015)*

(Review) QH Li et al., J. Phys. D 49, 413003 (2016)

5 different XAS channels through full mRIXS



Yang & Devereaux, J Power Sources 389, 188 (2018)