Soft X-ray XAS and RIXS:

- An ALS tutorial on technical principles
- Examples of Battery Material Characterizations

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Batteries: Problems/Questions are EVERYWHERE!

Battery Electrode: a mechanically and electrically integrated unit!

Charging Anode: \[ x\text{Li}^+ + \text{C}_6 + e^- \rightarrow \text{Li}_x\text{C}_6 \]

Charging Cathode: \[ \text{Li}_{1-x}\text{CoO}_2 \rightarrow x\text{Li}^+ + \text{CoO}_2 + e^- \]

- Transportation of Li$^+$
- Reduction/Oxidation (Redox)

Oxygen? Co? Surface?

Discharged

Charged

Surface/Bulk

280 mAh/g

140 mAh/g

Battery Electrode: a mechanically and electrically integrated unit!

& Many others, interphase, solvation......
Spectroscopy for batteries?: for WHAT?

• Direct probes of the relevant valence states
  • *2p states of Oxygen (O-K)*
  • *3d states of 3d transition metals (TM-L)*

• Elemental and Chemical Sensitivity

• Data could be quantified, to some extend
  • Absolute *quantification of TM redox*
  • The *reversibility of oxygen activities*

→ *Soft X-ray Spectroscopy*

• Both surface and *bulk (100 nm above) sensitivity*

→ *Soft X-ray Spectroscopy*
(General) Synchrotron Radiation: how it works and how it looks

Principle, reality, and limitations of soft X-ray absorption spectroscopy (sXAS)
  • Transition metal $L$-edges: valence $3d$ states
  • Low-Z (O, C, N...) $K$-edges: chemical bonds, surfaces and interfaces

Limitations of sXAS $\rightarrow$ Resonante Inelastic X-ray Scattering (RIXS)
  • The missing information and distortions in Photon-in-photon-out sXAS
    • Why sXAS is often NOT a “elemental sensitive” probe?
  • What is RIXS and its association to sXAS
    • How RIXS is collected
    • Channels of sXAS: TEY, TFY, PFY, iPFY, (ccPFY, bRIXS)

Information from full energy range mapping of RIXS (mRIXS)
  • Transition metal $L$-edge mRIXS: $3d$ electron excitations & chemical sensitivity
  • Oxygen $K$-edge mRIXS: Intrinsic Oxygen states in TM oxides
When Photons hit Atoms/Molecules... ...

**BOOK**: Attwood, Soft X-rays and Extreme Ultraviolet Radiation, 2000

**Diffraction/Scattering**

**Absorbed (Spectroscopy)**

Wikipedia  

Lin et al., Chem. Rev. (2017)
Dipole selection rule & Soft X-ray energy coverage of elemental excitations

Electrons excited by photons: two types of spectroscopy

**X-ray Photoelectron Spectroscopy**
- **Incidence:** Fixed photon
- **Excitation:** Core-electrons $\rightarrow$ unoccupied states
- **Detection:** Core-electrons

**X-ray Absorption + Inelastic Scattering Spectroscopy**
- **Incidence:** Tunable photon
- **Excitation:** Core-electrons $\rightarrow$ unoccupied states

- Energy absorbed by electrons, which conquer the binding and **emit** from the samples.
  - **Photoelectron** Spectroscopy: XPS, UPS, ARPES

- Energy absorbed by electrons, which get **excited** to unoccupied states of the samples, i.e., **stay** within the material.
  - **Absorption** spectroscopy
  - Released electrons (EY)
  - Released photons (FY)
  - **Emission** spectroscopy
  - Elastic scattering
  - Inelastic scattering

Animation: Denlinger & Yang @ALS  (https://youtu.be/nCeoYN9exL0)
Principles & Realities of sXAS

- Excitations & decays
- Detection channels of “conventional” sXAS: TEY & TFY
XAS: how/what we measure **in reality**?

**Transmission mode**

```
Incident photons -> Sample -> Photon Detector

Channeltron
MCP
Photodiode
SDD
Photon Spectrometer
```

```
Sample (compensation) Current
```

```
(e^-) Sample (partial) Photoelectron Detector
```

```
Transmission
Absorption
```

```
Photon Energy → Absorption Edge
```

**“INDIRECT” XAS experiments detect the DECAYS after photon excites electrons!**

Limited to “thin” samples for soft X-rays

-XAS Image: Courtesy of Jonathan Denlinger @ALS
A side topic: What if we have a DL-ring (fully coherent)?

[Left] Chemical map: LiFePO4 (red) / FePO4 (blue)

[Right] Segmentation: LFP-rich (red) / Mixed (green) / FP-rich (blue)

A typical XAS system: inside ALS BL8.0 iRIXS

- Sample Current
  - Total Electron Yield / TEY

- Channeltron /MCP /photodiode:
  - Total Fluorescence Yield / TFY
  - Partial Electron Yield / AEY

- Photon Spectrometer (later...)
  - Partial fluorescence yield /PFY
  - Inverse PFY / iPFY
  - Core-core PFY / ccPFY

http://bl8.lbl.gov/iRIXS/Operation/iRIXSMANual.html
Conventional XAS: counts the **number** of decays & ignores the **types** of decays

**Incidence:**
*Tunable photon*

**TEY** corresponds to absorption coefficient:
Gudat & Kunz PRL 29, 169 (1972)

**TFY:** NO 😞
(Spectral Distortions)

**Auger+2\textsuperscript{ndary} Emission**

**XAS-TEY**, 99%
Photon-In-Electron-Out

**Detection:**
Emitted *electrons*

**Soft x-ray Fluorescence**

**XAS-TFY**, <1%
Photon-in-Photon-out

**Detection:**
Emitted *photons*

- **Total number** of emitted particles (electrons / photons) are counted in XAS experiments upon incident X-ray photon energy.
- Properties of emitted particles, e.g., emitted photon energies, are ignored.
- **Dipole selection rules** of the transitions: orbital sensitivity

**Denlinger & Yang:** https://youtu.be/nCeoYN9exL0  Yang et al., J Elec Spec Rel Phenom 190 64 (2013)
sXAS (I) - 3d Transition metal L-edges

- **Excitations**: TM $2p \rightarrow 3d$

![Graph showing excitations and energy levels for transition metals](image-url)
2p/3d coupling leads to characteristic TM-L edge sXAs features that could be used to analyze the TM 3d states directly!

These multiplet features are sharp and well defined in both lineshape and positions.

These multiplet features could be utilized for sensitive determinations of TM oxidation states, local TM configurations, spin states, and ligand hybridizations, etc.
Dipole Selection Rule: **Hard** XAS / **Soft** sXAS / Hard X-ray **Raman**

**Fe-K**  
Fe-K XAS Intensity (Arb. Unit)  
Li$_x$FePO$_4$  
$x=1$  
$x=0.75$  
$x=0$

**Fe-L**  
Fe-L$_3$ sXAS Intensity (Arb. Unit)  
Li$_x$FePO$_4$  
$x=1$  
$x=0.75$  
$x=0$

**XRS_Fe-L**  
Fe-L$_3$ hard-XRS Intensity (Arb. Unit)  
Li$_x$FePO$_4$  
$x=1$  
$x=0.75$  
$x=0$

Every technique has its own advantages and disadvantages – always!

Fe-L sXAS of Li$_x$FePO$_4$: Valence, Spin, structural, hybridization...

Fe-L edge
Spectral lineshape evolution

Fe-3d states
Energy Diagram

- A simple linear combination fitting could quantify precisely the Fe oxidation states!

Liu et al., JACS 134 13708 (2012)
**TM-L sXAS**: a direct & quantitative Probe of the TM-3d States!

![Graphs and intensity plots showing the potential vs. specific capacity and state of charge for different materials such as Na$_x$MnO$_2$, Li$_x$FePO$_4$, and Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$.](image)

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Qiao, et al., Nano Energy 16, 186 (2015); Liu et al., JACS 134, 13708 (2012); Qiao et al., JPCC 119, 27228 (2015)

TM-L sXAS is also sensitive to the spin states!

The spin state configuration, a **fundamental** parameter, defines the **practical** electrochemical profile!

*(Sharp) Wang et al., JACS 137, 2548 (2015)*
Interstitial water effect on an electrochemical system with competing factors:
- Ionization energies
- Spin states
- Crystal fields

- more complex but approachable through TM-L sXAS

*Wu et al., JACS 139 18358 (2017)*
sXAS-II: Low-Z element K-edges

- **Low-Z element (C, N, O, F) K-edges**
- Excitations: $1s \rightarrow 2p$

*NOTE:* More samples in different aspects here, but only **TWO** examples will be discussed during the tutorial.
**Li-K & O-K: Lineshapes & Chemical Sensitivity (general)**

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**Li-K**

- $\text{Li}_2\text{O}_2$
- $\text{Li}_2\text{CO}_3$
- $\text{Li}_2\text{O}$

**O-K**

- $\sigma^*_{(O-O)}$
- $\pi^*_{(C=O)}$

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*Unfortunately, does NOT work for TM oxides... will come to this point later...*
**C-K: Chemical evolution of solid-electrolyte interphase upon cycling**

- **C-K sXAS** lineshape changes dramatically upon electrochemical cycling!
- A breathing and oscillating growth of carbonates in SEI

*Zhuo et al., Chem Comm 54, 814 (2017)*
Distinct SEI formation on Sn (100) & (001) surfaces

O-K sXAS: a highly ordered surface hydroxyl layer

- **Supercapacitor**: novel surface layer stabilizes the interface with water and facilitate ion migration!

- Xiaowei Teng Group @U. NH

Shan et al., Nat. Comm. 7, 13370 (2016)
**C-K sXAS**: Key electron states that define physical properties!

<table>
<thead>
<tr>
<th>Key Function Group</th>
<th>Key Electron State</th>
<th>Energy (eV) ( k (2\pi/c) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron transfer &amp; distribution</td>
<td>X-ray Photon Energy (eV)</td>
<td>SOFT x-ray C-K absorption Intensity (Arb. Units)</td>
</tr>
</tbody>
</table>


(Gao Liu)

(PFFO + Li)

(Lin-wang Wang)
Is everything perfect with XAS?

Conventional XAS could have two modes (collected simultaneously)

- TEY: probe depth, \(\sim 10\) nm
- TFY: probe depth, 100-200 nm, photon energy dependent

*However, with lineshape distortion!*

Information from sXAS:

- TM: direct 3d state probe of Oxidation states, spin states etc.
- O, N, C- K-edges: chemical bonds and chemical states.

*However, not “clean” especially for oxides!*
3 “dark clouds” of modern sXAS

**Distortions in FY sXAS**
- Material dependent
- Element dependent
- “self-absorption correct”?

**Lack of Chemical sensivity**
- Interface signals buried in bulk contributions
- Unconventional chemical states
- Entangled signals from different spectroscopic channels 😞

- The core-hole lifetime broadening sets a principle limit on the XAS energy resolution ever since monochromator resolution reached ~0.2 eV (for most soft XAS excitations)

- Wanli Yang (2019 APS March Meeting)

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

Frank de Groot et al. PRB (1990)

Jeyachandrani, et al., JPCL, 5 4143 (2014)
What do we really want from batteries? – EVERYTHING!

Charging Cathode: $\text{Li}_{1-x}\text{CoO}_2 \rightarrow x\text{Li}^+ + \text{CoO}_2 + e^-$

Charging Anode: $x\text{Li}^+ + \text{C}_6 + e^- \rightarrow \text{Li}_x\text{C}_6$

**Oxygen?**

Safety/stability issue!!

**Transportation of Li$^+$**

**Reduction/Oxidation (Redox)**
Spectroscopy for batteries: *for WHAT?*

- Direct probes of the relevant valence states
  - *2p states of Oxygen (O-K)*
  - *3d states of 3d transition metals (TM-L)*
- Elemental and Chemical Sensitivity
- Data could be quantified, to some extend
  - Absolute quantification of TM redox
  - The *reversibility of oxygen redox*

→ *Soft X-ray Spectroscopy*

- Both surface and *bulk (100 nm above) sensitivity*

→ *Soft X-ray Spectroscopy?*

*The success of XAS for studying batteries in the *conventional* range provides the *illusion* that it will also work in the *unconventional* (high-voltage) range!*
mRIXS (I): Transition-metal L-edge (non-metal)

• What does “RIXS” mean technically?

• Why XAS-TFY of TM-L is not necessarily an elemental sensitive probe!

✓ Extract non-distorted XAS-FY signals from mRIXS

✓ Much improved chemical sensitivity from L-edge RIXS
From XAS to Map of Resonant Inelastic X-ray Scattering

review: Yang & Devereaux, JPS 389, 188 (2018)
What we get from a full-range map of RIXS (mRIXS)?

- **Non-resonant Mn-L XES**
- **Inverse PFY**
- **Core-core PFY**

review: Yang & Devereaux, JPS 389, 188 (2018)
O-K sXAS: "pre-edges" & long "tail" ...

Long "tail" of O-K intensity ...

Mn-L energy range
O-K sXAS: "pre-edges" & long "tail" ... ...  

→ The looooooooooooong “tail” of O-K XAS ...  

- O-K signals in Mn-L mRIXS are excitations to O-2p continuum states, i.e., should be a constant “background” WITHOUT excitation energy dependence!

- The strong energy dependence of O-K signal at Mn-L edge excitations corresponds to the Abrupt change of X-ray attenuation rate at Mn-L absorption edges, i.e., an intrinsic probe of Mn-L XAS in a “reversed” manifestation – iPFY!

**Details**

PHYSICAL REVIEW B 83, 081106(R) (2011)

Bulk sensitive x-ray absorption spectroscopy free of self-absorption effects

A. J. Achkar,¹ T. Z. Regier,² H. Wadati,³ Y.-J. Kim,⁴ H. Zhang,⁴ and D. G. Hawthorn¹
One Map Rules Them All! – XAS-iPFY, -PFY, -ccPFY, XES, RIXS

Full-energy-range mapping of RIXS (mRIXS)

review: Yang & Devereaux, JPS 389, 188 (2018)
mRIXS-iPFY & TEY Mn-L: bulk and surface Mn redox quantification

Bulk (~150nm) Mn states

Surface Mn states

Direct (TM-3d/O-2p) probe to quantify the chemical reactions in battery electrodes with elemental sensivity

Dai et al., Joule 3, 518 (2019)
Obviously, we are not collecting mRIXS only for XAS (iPFY): **3 components** of “true” RIXS signals

_Firouzi, Qiao et al., Nat Comm 9, 861 (2018); Yang & Devereaux, JPS 389, 188 (2018)_
Sharp Mn-L mRIXS Contrasts of Mn-redox electrodes

- Mn-L sXAS does NOT provide much contrast

- mRIXS: Greatly improved chemical sensitivity
- mRIXS: A new dimension of information (emission energy)!

Firouzi, Qiao et al., Nat Comm 9, 861 (2018)
Mn-L mRIXS reveals Mn\(^{1+}\): a 90-year speculation!

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) (available online)
Information from Mn-L
Full-range mapping of RIXS (mRIXS)

Excitations

XES “RIXS”

\[ T_{\text{Total}} \] FY

\[ \text{iPFY} \]

\[ \text{ccPFY} \]

\[ \text{PFY} \]

Yang & Devereaux, JPS 389, 188 (2018); Firouzi et al., Nat Comm 9, 861 (2018)
mRIXS (II): Oxygen K-edge

• Greatly improved chemical sensitivity of O-K mRIXS vs XAS
  • Solvation shell of water molecules
  • Inductive effect on Oxygen states

• Misuse of O-K XAS for Detecting “oxidized oxygen” in TM oxides
  • A “perfectly wrong” logic of using O-K XAS to discussed oxidized oxygen
  • “pre-edge” of O-K XAS of oxides is dominated by TM-3d character
  • O-K XAS pre-edge is NOT a reliable probe of oxidized oxygen

• O-K mRIXS: a reliable probe of “oxidized oxygen” in TM oxides
  • Distinguish oxidized oxygen states from hybridized TM-3d characters
    • Different emission energies of O-K mRIXS features
    • Oxidized oxygen displays distinct mRIXS feature at a different emission energy
O-K RIXS (I): Solvation shell through improved chemical sensitivity

**Challenge:**

"Interface" molecules are the same as the bulk in vicinity 😊

Jeyachandran, et al., JPCL, 5 4143 (2014)
**O-K RIXS (II)**: Oxygen state weakly affected by inductive H⁺

- Acid treated Li-rich compound
- H⁺ affects oxygen activities

**HOWEVER**
- mRIXS reveals Oxygen is not in the form of (OH)⁻
  - A weakly bonded H⁺ to oxygen provides the inductive optimization of oxygen activity!

Jue Wu, Yong Yang et al. @ Xiamen University

*Wu et al., ACS Appl. Mater. Interf. 12, 7277 (2020)*
O-K XAS “pre-edge” for detecting non-divalent oxygen states?

Incident X-ray Excitation Energy (eV) - “pre-edge” (528-536 eV) + a very long tail...

A “perfectly” WRONG (but very popular) logic:

- XAS detects the unoccupied electron states (holes)
- O-K XAS detects the oxygen holes
- The pre-edge intensity enhancement means more oxygen holes (oxidation)
- “O-K XAS pre-edge enhancement is the evidence of oxidized oxygen!”

Neither the intensity nor the lineshape of O-K pre-edge indicates oxygen redox states!

Roychoudhury et al., Energy & Environmental Materials 4 246 (2021)
O-K XAS “pre-edge” is of TM-3d character! NOT a probe of OR states

de Groot et al., “Oxygen 1s x-ray-absorption edges of transition-metal oxides”

- O-K pre-edge features are of TM-3d characters through TM-O hybridization!
- NEITHER the intensity NOR the lineshape is a reliable probe of oxidized oxygen states!

QUESTION: where is the oxidized oxygen states in O-K XAS spectroscopy?
A lucky case! TM-O hybridization is dissociated from oxidized oxygen features in mRIXS (along emission energy)!

Still, many open questions remain...

O-K mRIXS: a challenging but interesting journey just started...

Yang & Devereaux, JPS 389, 188 (2018)
mRIXS quantifies the reversibility of oxygen redox reactions

\[ \text{Na}_{2/3}\text{Mg}_{1/3}\text{Mn}_{2/3}\text{O}_2 / \text{Li}_{1.17}\text{Ni}_{0.21}\text{Co}_{0.08}\text{Mn}_{0.54}\text{O}_2 \]

- O-K mRIXS feature follows tightly with electrochemical cycling!
- Evolution of O-K mRIXS feature intensity corresponds to oxygen redox reversibility!

Dai et al., Joule 3, 518 (2019)
Excitonic features of oxidized oxygen ($\text{Li}_2\text{O}_2$, $\text{O}_2$)

Zhuo, et al., JPCL 9, 6378 (2018); JPCL 11, 2618 (2020)
What is the lattice oxidized oxygen? – not simple!

- A cross-comparison between O₂, Li₂O₂, Li-rich NMC, and Na-Mg-Mn-O
- Oxidized oxygen state in battery electrodes is NOT a simple molecular configuration, e.g., peroxides or gas.

*Zhuo, et al., JPCL JPCL 11, 2618 (2020)*
Oxygen activity outside “conventional” operation range: Many open questions that should not be taken for granted easily!

- mRIXS detects only the Lattice (bulk) Oxygen Redox reactions.
- Where the $\text{O}_2/\text{CO}_2$ gas release comes from then?

- Is Oxygen release associated with lattice oxygen redox? How?
  
  - What is the fundamental mechanism of lattice oxygen redox?

Example: a challenge to conventional wisdom on oxygen redox effect

Contrast between NLMO and NMMO:

Lattice oxygen redox is NOT necessarily the detrimental reactions for battery electrodes!

Wu et al., Sci. Adv. 6, eaaw3871 (2020)
**Li$_2$MnO$_3$ & Li-rich layered: high voltage plateau & Oxygen redox**

Oxygen redox could be sustained for hundreds of cycles in Li-rich electrodes

NO voltage plateau after the initial cycle

Li$_2$MnO$_3$, the parent compound of “Li-rich” has been considered a model system for oxygen redox reactions – is this real?
Li$_2$MnO$_3$, “parent compound” of Li-rich, shows **NO** lattice oxidized oxygen!

- Note strong oxygen oxidation is expected, but no reversible reduction takes place.
- **Several puzzles** on understanding the Li$_2$MnO$_3$ cycling mechanism ➔➔➔

Zhuo et al., Joule 5 975 (2021)
No oxygen redox in Li$_2$MnO$_3$ $\Rightarrow$ Three critical questions?!

- The origin of the 1$^{\text{st}}$ cycle voltage plateau?
  - A characteristic feature of all Li-rich layered electrodes: **O release & surface reactions!**

- Why Li$_2$MnO$_3$ is electrochemically active with reversible capacity?
  - **Purely Mn redox** right after the 1$^{\text{st}}$ cycle charging!

$\Rightarrow$ All answered: Zhuo et al., Joule 5 975 (2021)

- Source of oxygen redox reactions in “Li-rich” (xLi$_2$MnO$_3$·(1−x)LiMO$_2$) if not Li$_2$MnO$_3$?
LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$: reversible lattice oxygen redox reactions
- conventional (non-Li-rich) electrodes

- Partially reversible oxygen redox reactions, but decays fast in conventional electrodes

Comparisons between “Li-rich”, Li(TM)O₂ (Conventional), and Li₂MnO₃

- **Commonality** of the *lattice* oxygen redox reaction in *Li-rich* and *conventional compounds*!!
- Li₂MnO₃ does **NOT** display any *lattice* oxygen redox activities.
- mRIXS interpretation promises the *universal* mechanism of oxygen redox reactions in oxide cathodes, which remains elusive by this time ... **ongoing**...

- The type of “Li-rich” oxide materials may not necessarily be the choice towards high-energy cathodes based on reversible oxygen redox reactions!
- “Conventional” materials have their own advantages that are yet to be utilized!

*Zhuo et al., Joule 5 975 (2021)*
The power of RIXS is yet TO BE fully explored ...
Welcome to a “RIXS era” of soft X-ray materials sciences...

Contents

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