Oxygen redox activities in battery electrodes studied by mapping of resonant inelastic X-ray scattering (mRIXS)

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Define the scientific Question : BULK redox reactions

The dilemma of Oxygen in battery electrodes

- 😊 *Oxygen, if could be reversibly “cycled”, provides the hope to improve the capacity/power!*
- ☹️ Oxygen, if activated in electrochemistry, is often a disaster on safety/stability!
(a conventional wisdom)

➔ *In this new era of EVs (large-scale storage requiring high-capacity high-power), controlling Oxygen activities becomes THE key issue!!*

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 extent
 - 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!*

Conventional XAS: counts the **number** of decays & ignores the **types** of decays

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

TFY: NO 😞
(Spectral Distortions)

Incidence:
Tunable photon

Auger+2ndary 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

O-K XAS for detecting non-divalent oxygen states?

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!”**

Liu et al., PCCP 17, 26369 (2015)

Qiao et al., JPCC 119 27228 (2015)

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

O-K XAS “pre-edge” is of TM-3d character!

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

Phys. Rev. B 40, 5715 (1989)

- 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!

Velasco et al. PRB 83, 241102(R) (2011)

QUESTION: where is the oxidized oxygen states in O-K XAS spectroscopy?

O-K “pre-edge” : oxidized oxygen signal **buried** in TM characters ☹️

Qiao et al., Plos One 7, e49182 (2012)

Oxidized oxygen states in TM oxides?

Overlapping features dominated by TM characters! ❌

Go beyond XAS: Map of Resonant Inelastic X-ray Scattering

- RIXS spectra are collected by measuring the EDC curve at each XAS spot
- *Technically*, RIXS is a further resolved XAS data point along a new emission energy dimension!

The real technical challenge: *Radiation Damage Issue!*

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

Li(NiMnCo)O₂ (RIXS@531 eV)

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

2016: full-energy range ultra-high efficiency *iRIXS* system

Large (30X100um) beam size + ultra-high efficiency

15 minutes total, **15 seconds each spectrum**

Previously SXF (BL8.0@ALS)

Carlisle et al., PRL 74, 1234 (1995)

Each spectrum: **30 minutes**

***iRIXS* single-shot! 10-second XES spectrum**

mRIXS: Capture intrinsic signals from lattice oxidized Oxygen

Lee et al., *Angew. Chem.* doi:10.1002/anie.202001349; Li et al., *ACS Energy Lett.* 4 2836 (2019);
Wu et al., *ACS Appl. Mater. & Interf.* 12 7277 (2020); Zhao et al., *Angew. Chem.* 58, 4323 (2019);
Dai et al., *Joule* 3, 518 (2019); Xu et al., *Nat. Comm.* 9:947 (2018); Gent et al., *Nat. Comm.* 8:2091 (2017);

✓ **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 ...

mRIXS quantifies the reversibility of oxygen redox reactions

- O-K mRIXS feature follows tightly with electrochemical cycling!
- Evolution of O-K mRIXS feature intensity corresponds to oxygen redox reversibility!
- Strong lattice oxygen redox reaction could be highly reversible in both Na-ion and Li-ion batteries → Lattice oxygen redox not necessarily leads to detrimental effect!

1st cycle different potentials

1st to 100th cycle

Excitonic features of oxidized oxygen (Li_2O_2 , O_2)

What is the lattice oxidized oxygen?

- A cross-comparison between O_2 , Li_2O_2 , 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.

Oxygen activity: a complicated story...

- mRIXS detects only the Lattice (bulk) Oxygen Redox reactions.
- Where the O_2/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?*

What causes the destabilization of a battery?

Contrast between NLMO and NMMO:
Lattice oxygen redox is NOT necessarily the detrimental reactions for battery electrodes!

Summary

- Modern high-voltage high-capacity battery researches trigger the need of detecting unconventional oxygen states in complex transition-metal oxide systems.
- ***Conventional O-K XAS “pre-edge” features are dominated by transition metal characters and are not reliable probe of oxygen redox states in oxide electrodes!***
- ***High efficiency mapping of Resonante Inelastic X-ray Scattering (mRIXS)***
 - mRIXS is able to differentiate the lattice oxidized oxygen from the hybridization signals from transition-metal contributions
 - mRIXS is able to detect the oxygen redox activities in lattice upon electrochemical cycling
- With a reliable probe of oxygen redox states (*mRIXS*), true behaviors of lattice oxygen redox reactions could be revealed and are often contradict our conventional wisdom.
- **Open questions remain**, but mRIXS provide the powerful tool for clarifying the misunderstanding and for revealing the true nature of lattice oxygen redox states in complex transition-metal oxides (theoretical effort ongoing ...).

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