HZB Helmholtz
Zentrum Berlin

WHAT X-RAY ABSORPTION SPECTROSCOPY CAN TELL US ABOUT THE ACTIVE STATE OF EARTH-ABUNDANT ELECTROCATALYSTS?

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Understanding
Water splitting

Acknowledgements

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Recently graduated: **Max**

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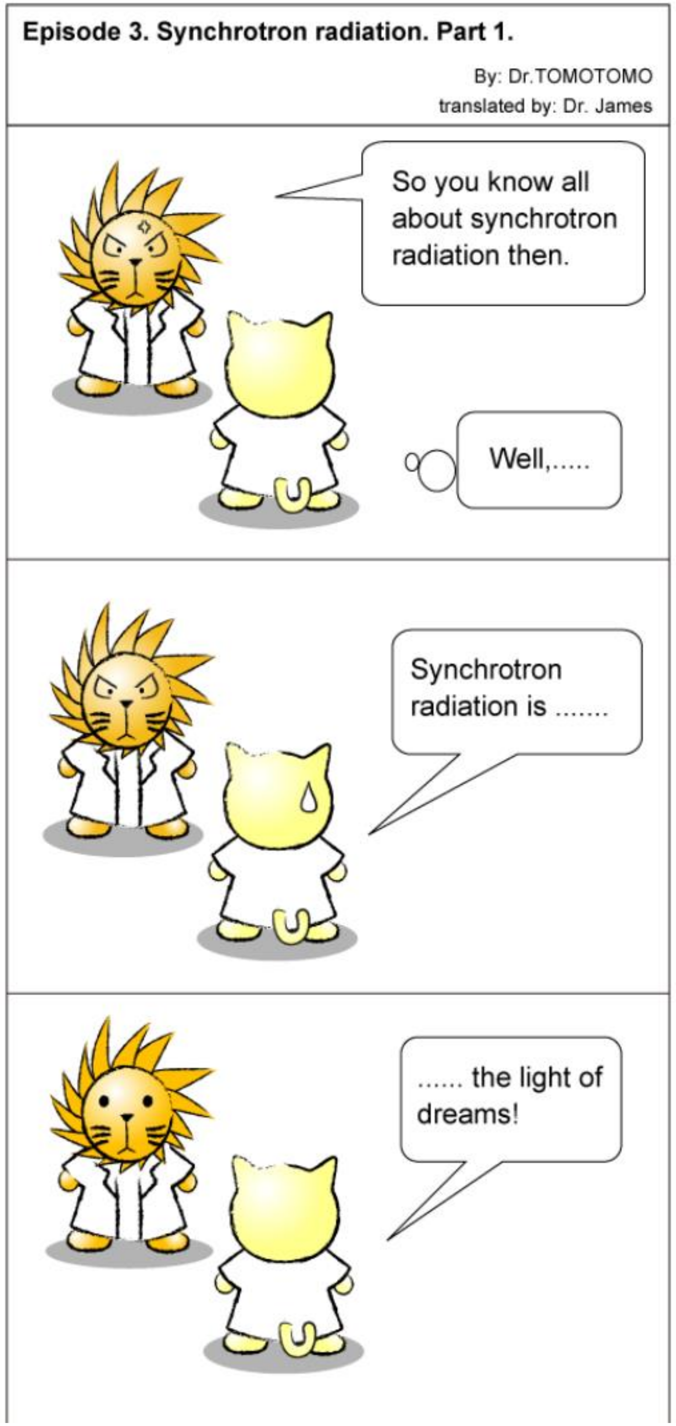
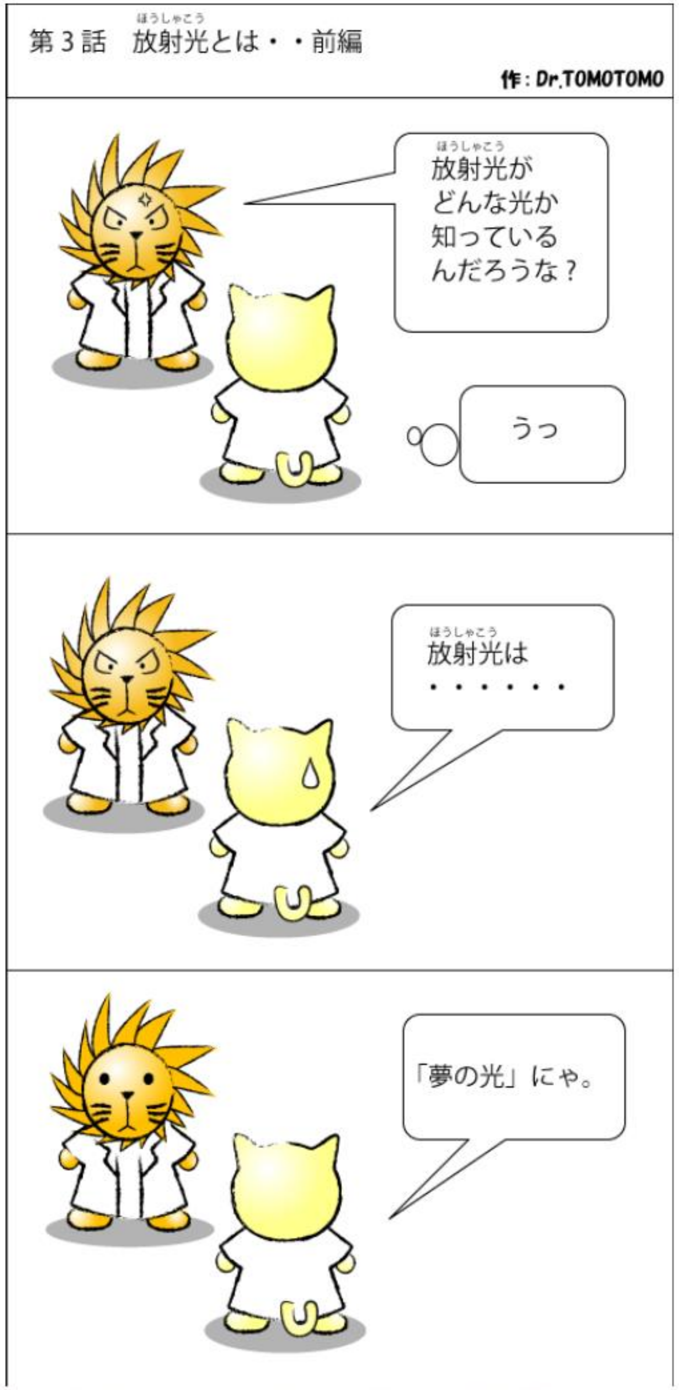
Canadian Light Source
Centre canadien de rayonnement synchrotron

Agenda

- Introduction
- Changes prior to electrocatalysis
- Changes during electrocatalysis
- Summary and Conclusion

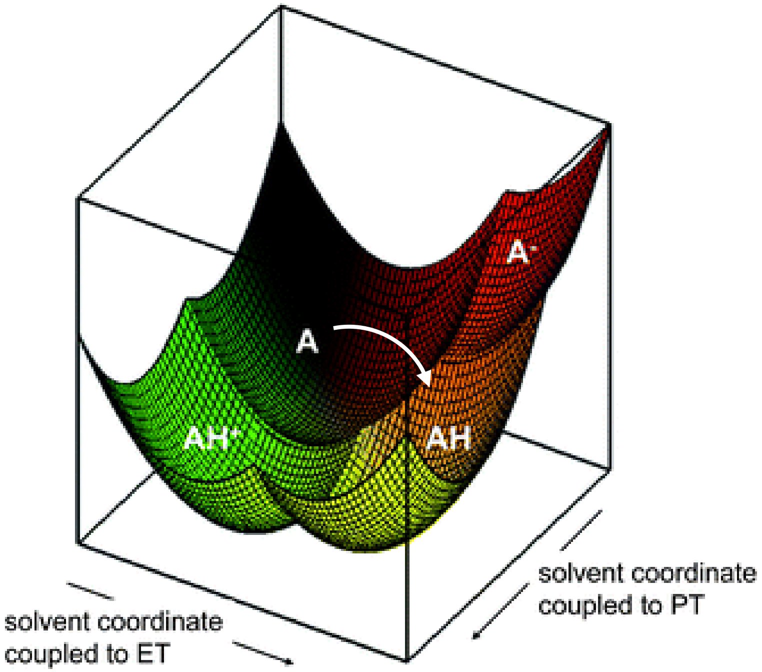
Synchrotron radiation - light of dreams





Dream: Identification of catalytic states and tracking their evolution

"Hiking map" of electrocatalysis



The need to measure faster

Sampling at 5 s

Current X-ray absorption studies

Sampling at 5 ms

Desired time resolution

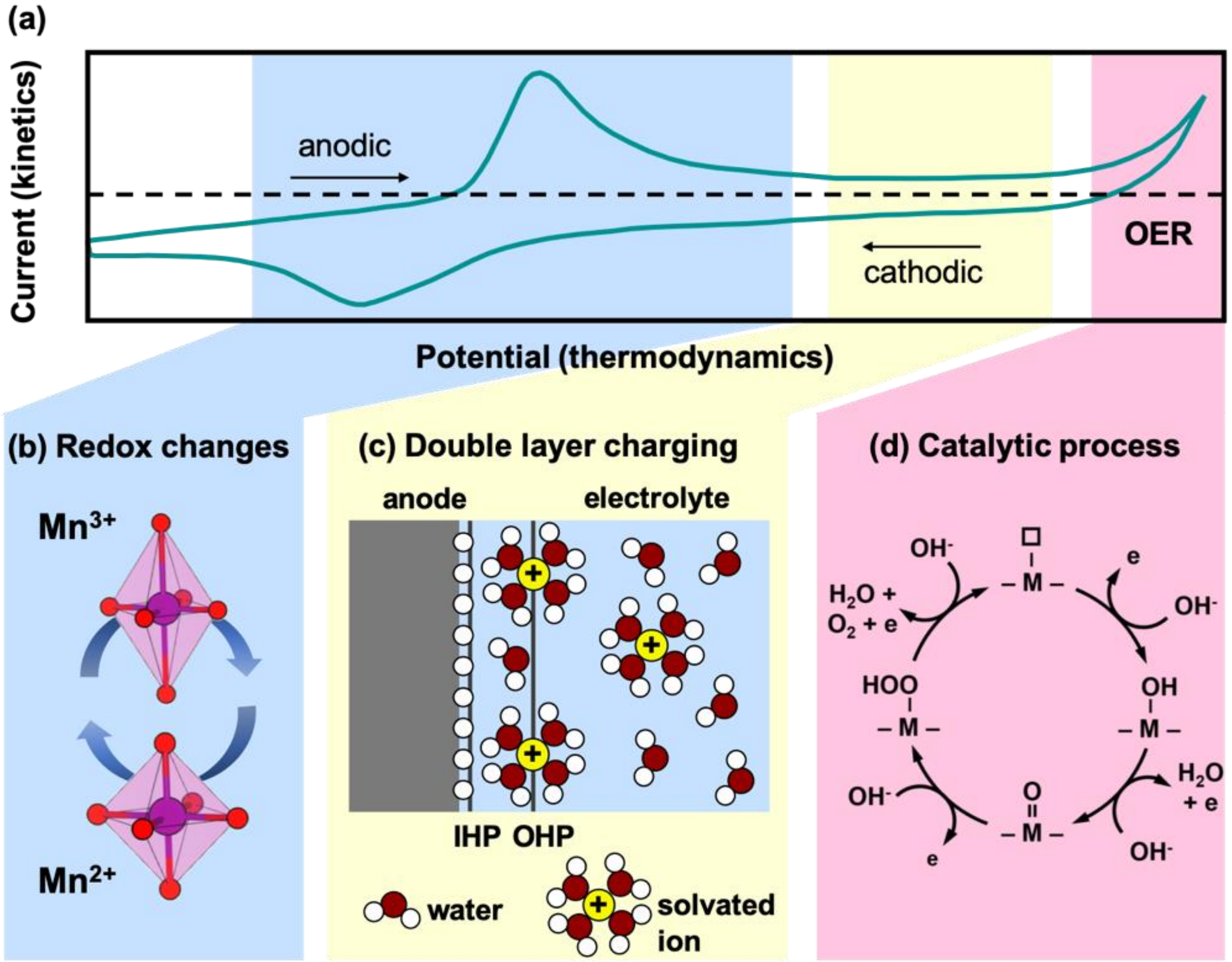
Sampling time needs to be matched to kinetics for a "hiking map" of electrocatalysis

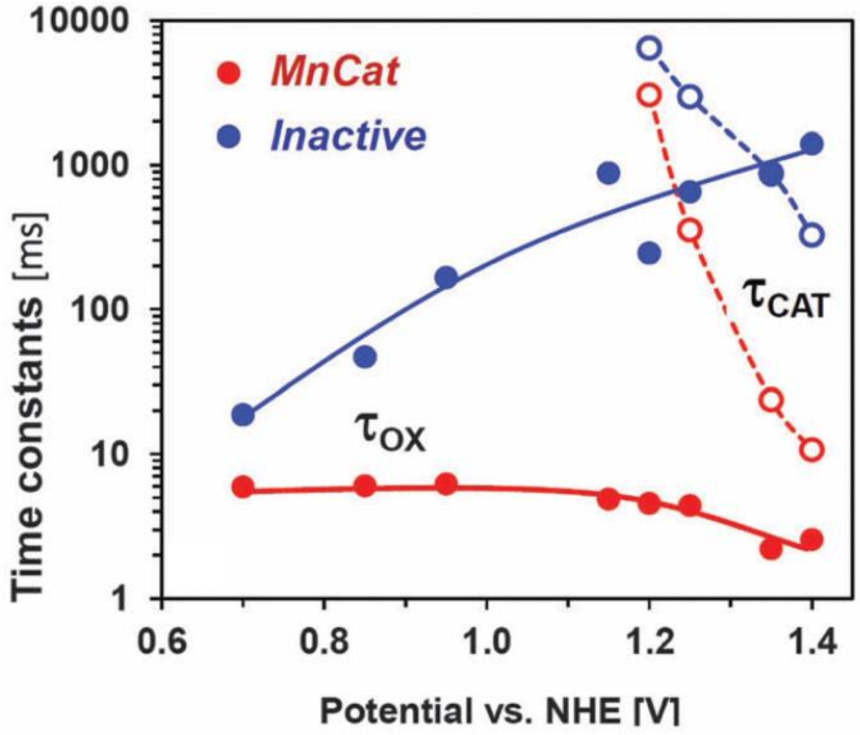
Graphics: Koper, Chem. Sci. 2013, 4, 2710-2723, David Bergman, https://www.picturecorrect.com/tips/how-to-make-a-crowd-disappear-from-a-photo-without-photoshop/

Key electrochemical processes and their time constants

Electrochemical processes

Time constants



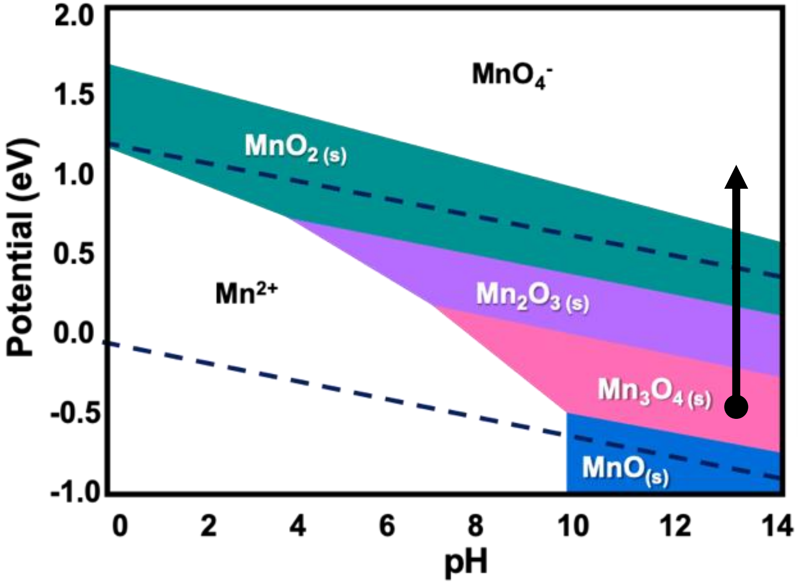


Redox: about 1 – 1000 ms
Electrocatalysis: about 1000 ms near onset

Risch et al., chemRxiv, doi 10.26434/chemrxiv-2022-lhwmb: Zaharieva et al. Energy Environ. Sci 9 2433 (2016)

Synergy between electrochemistry and X-ray absorption spectroscopy (XAS)

E-pH diagram



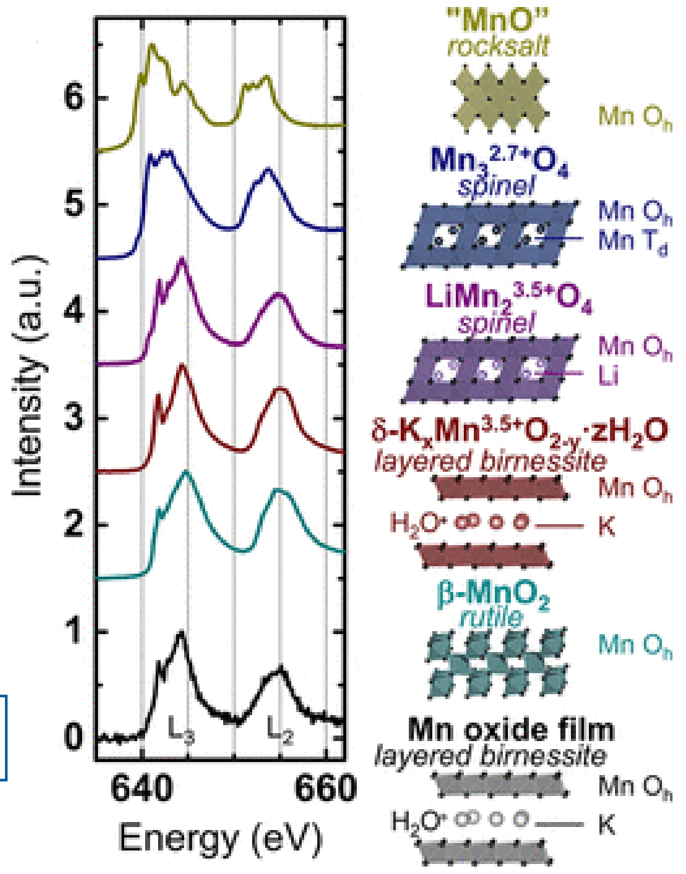
Electrocatalysis

- ➢ Macroscopic insight
- ✓ Electrons flow through material and across surface
- ✓ Electrode potential

X-ray absorption spectroscopy

- ➢ Atomistic insight
- ✓ Electrons in outer shell (oxidation state)
- ✓ Local coordination environment

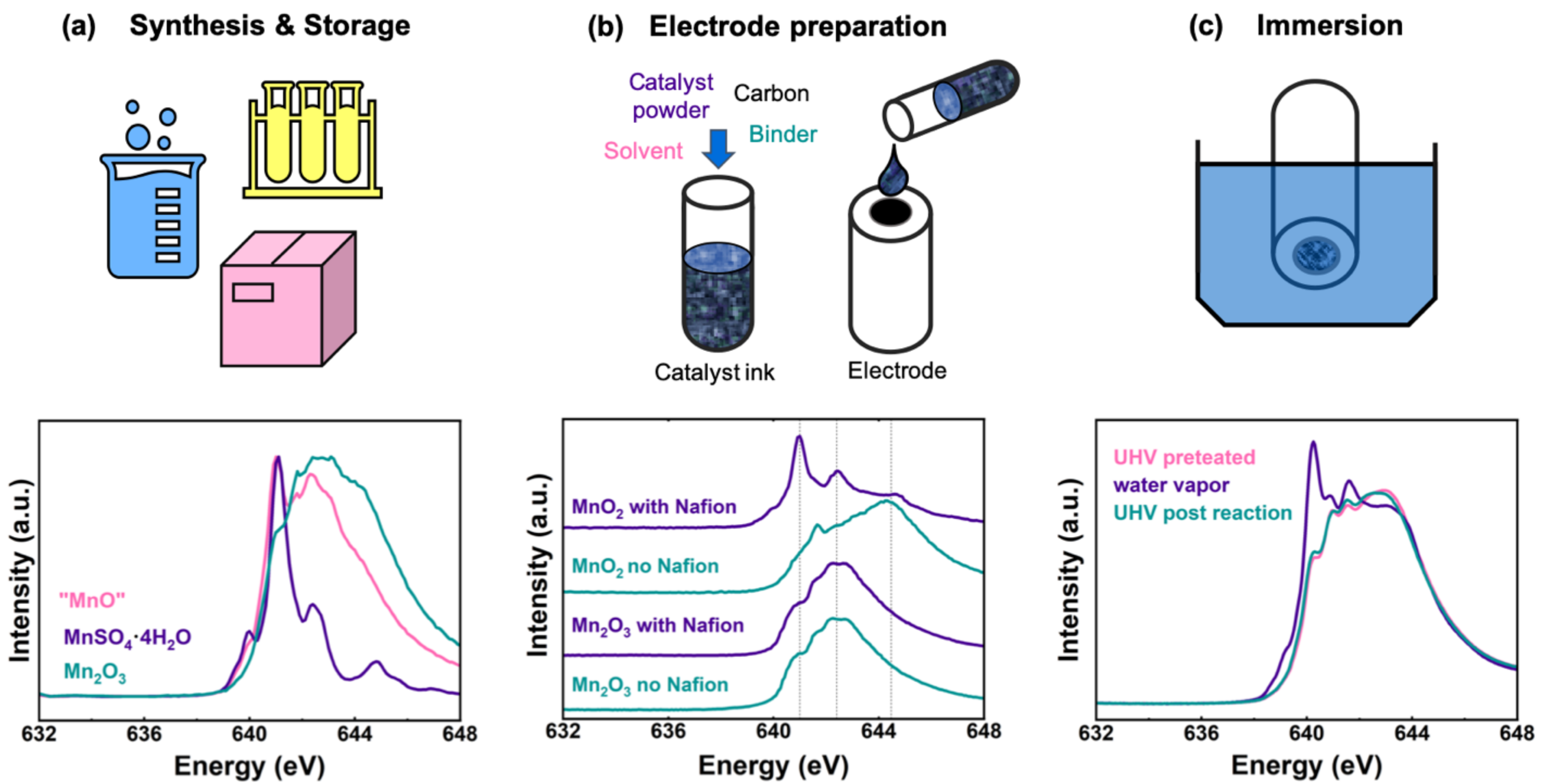
Mn-L edge XAS



Electrochemistry and XAS complement each other perfectly!

Risch et al., chemRxiv, doi 10.26434/chemrxiv-2022-lhwmb; Risch et al., JPCC 121, 17682 (2017)

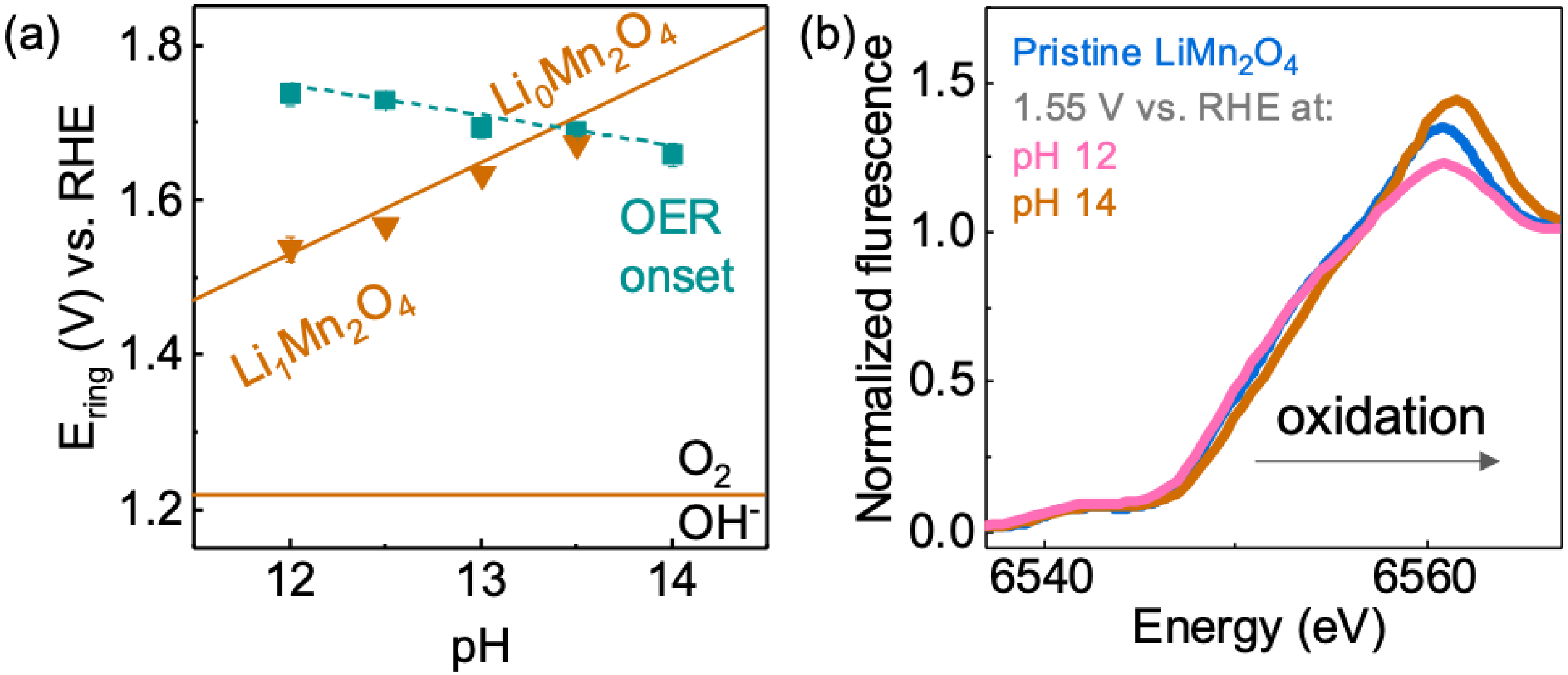
Possible modification of electrocatalysts before any electrocatalysis



Electrocatalysts usually have reactive surfaces. Unwanted side reactions are likely

Risch et al., chemRxiv, doi 10.26434/chemrxiv-2022-lhwmb; Morales et al., ChemElectroChem 8, 2979 (2021): Mierwaldt et al. Catalysts 4, 129 (2014)

Effect of change in composition on OER electrocatalysis



E^{RHE}-pH diagram

Mn-K edge XAS

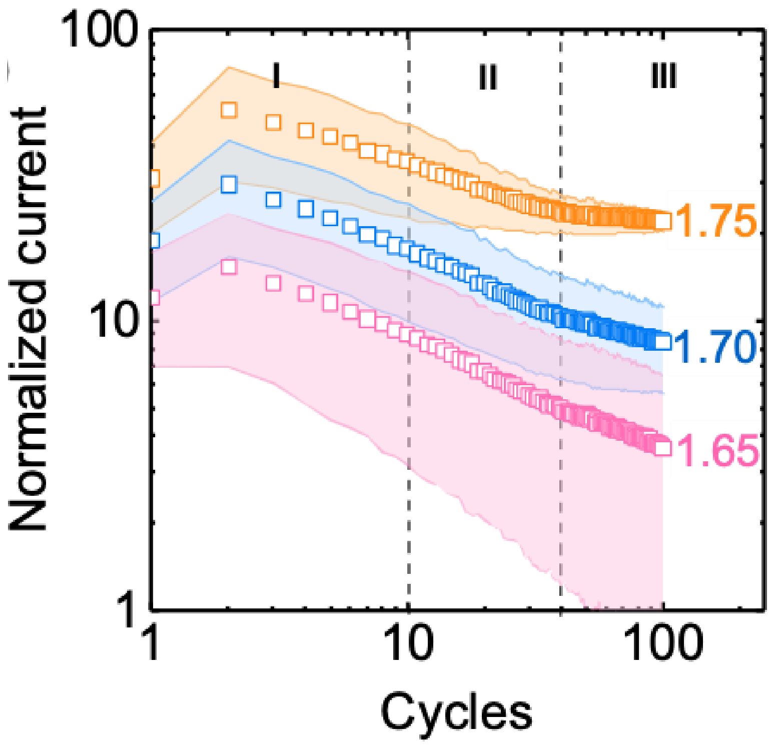
- OER = Oxygen evolution reaction
- Delithiation at pH < 13.5 → Mn oxidation
- Mn oxidation verified by XAS

More Mn^{4+} in $Li_xMn_2O_4$ results in less O_2 evolution (as expected)

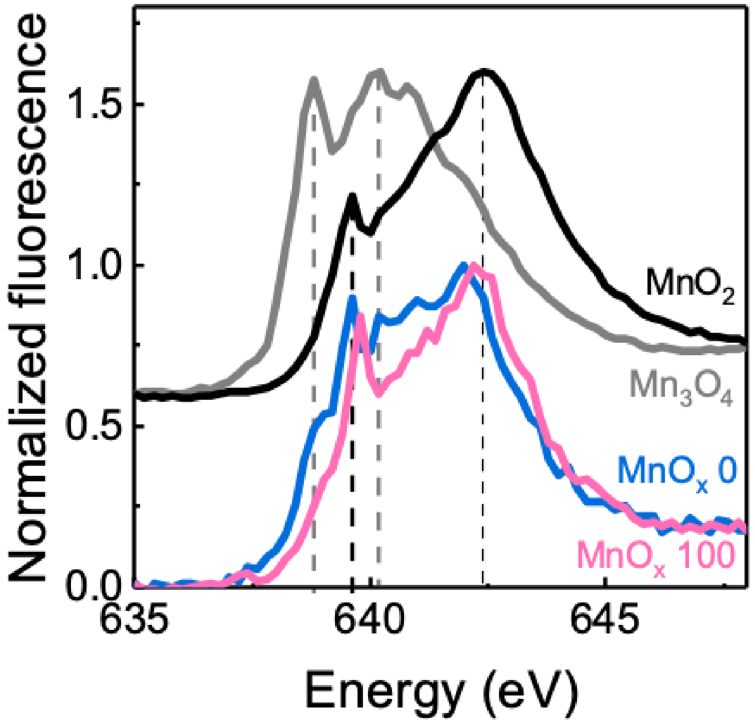
Risch et al., chemRxiv, doi 10.26434/chemrxiv-2022-lhwmb; Baumung, et al. (2019) ChemPhysChem 20, 1-9.

Post-mortem soft XAS study of a manganese oxide

Catalytic trend



Mn-L edge XAS



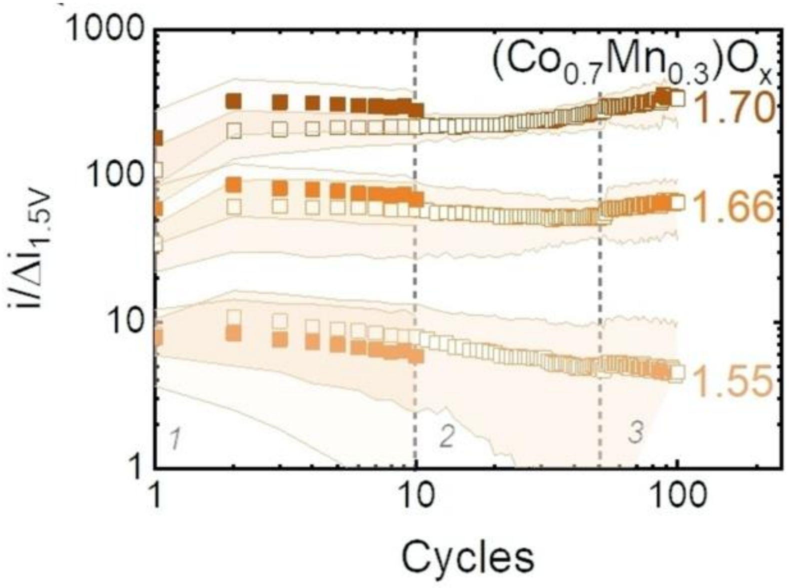
- Oxygen evolution reaction is studied in an accelerated test
- Decay of current (=product/activity) each cycle
- Mn oxidizes with cycling

Mn oxidation is detrimental to electrocatalytic activity of (undoped) Mn oxides

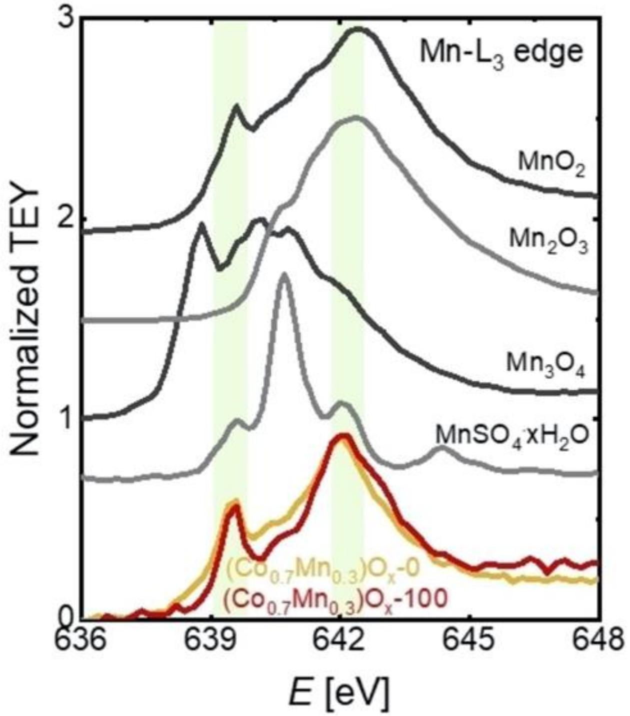
Risch et al., chemRxiv, doi 10.26434/chemrxiv-2022-lhwmb

Post-mortem soft XAS study of a manganese-cobalt oxide

Catalytic trend



Mn-L edge XAS



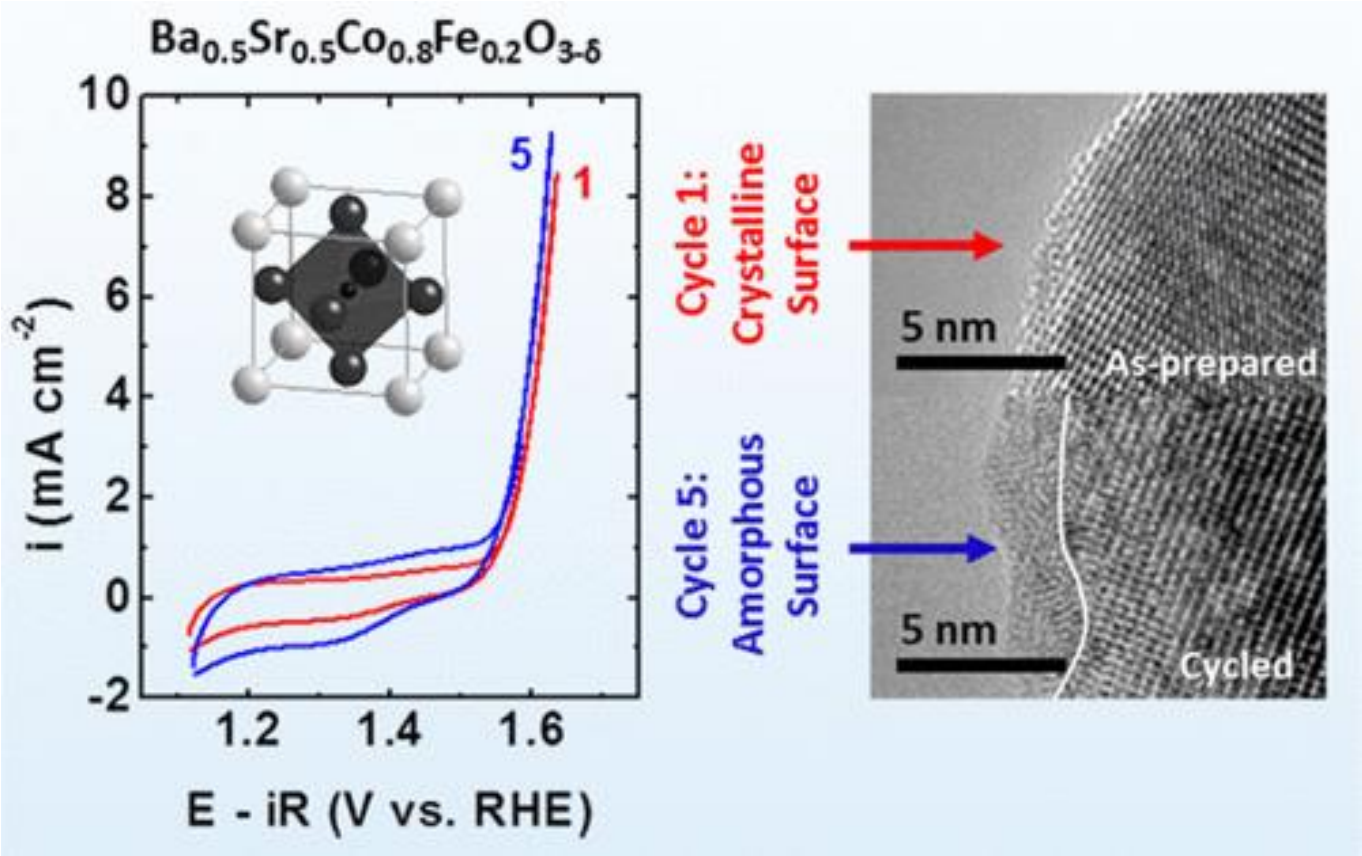
- Oxygen evolution reaction is studied in an accelerated test
- Decay of current (=product/activity) stopped by Co addition
- Little Mn oxidation with cycling

Cobalt addition stabilizes Mn oxides → relevant for application

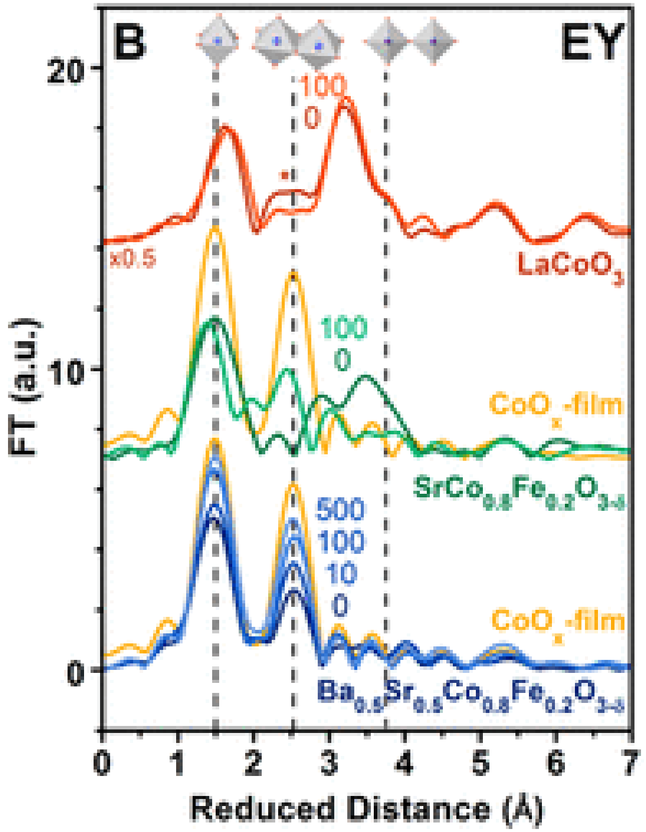
Villalobos et al., ChemElectroChem 9, e202200482 (2022)

Do all electrocatalysts degrade with operation?

Electrochemistry and TEM



Mn-K edge EXAFS

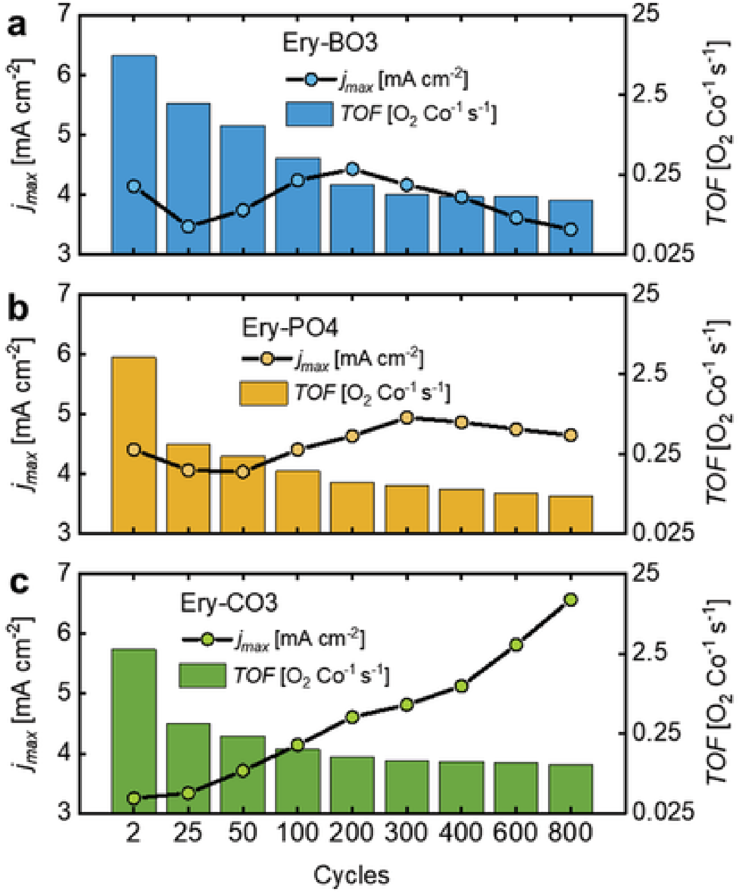


No. Some materials form a porous layer on the surface which increases the current

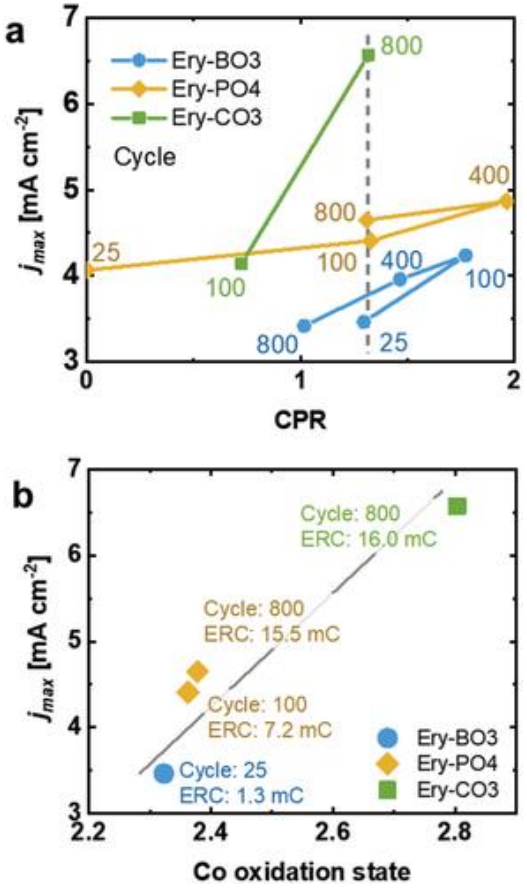
May et al., JPCL 3, 3264 (2012); Risch et al., JPCC 117, 8628 (2013)

Why do certain catalysts improve in operation?

Activity per site vs total current



Property-activity correlations



- Efficiency of active sites decreases with cycling (bars) but in the best case, the current increases

- XAS analysis shows

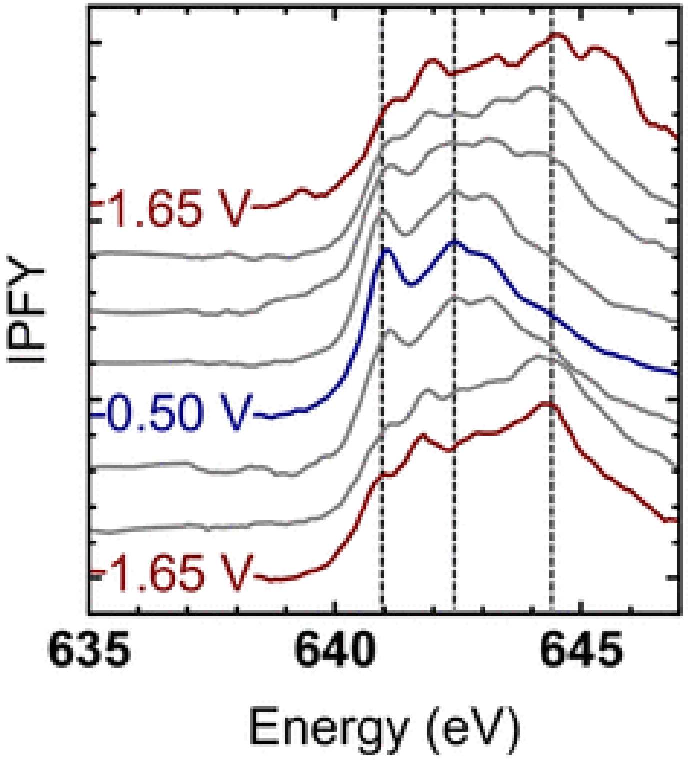
1) More order (CPR) is beneficial
2) A higher Co oxidation state is beneficial

Requirements for beneficial modifications provide new insights into the rational catalyst design

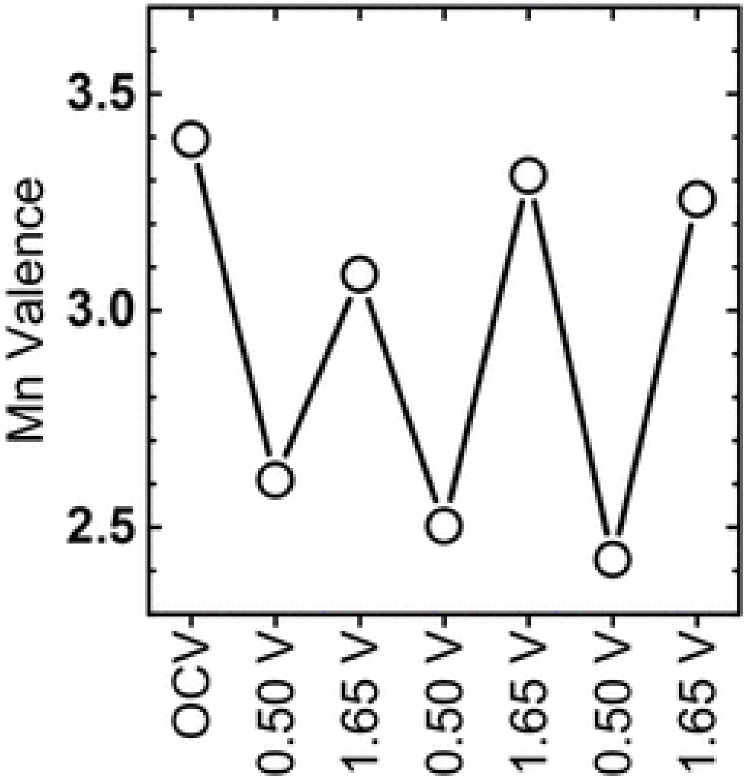
Villalobos et al., Adv. Energy Mater. 11, 2101737 (2021)

In situ soft Mn-K edge XAS: repeatable changes

Mn-L edge XAS



Trend

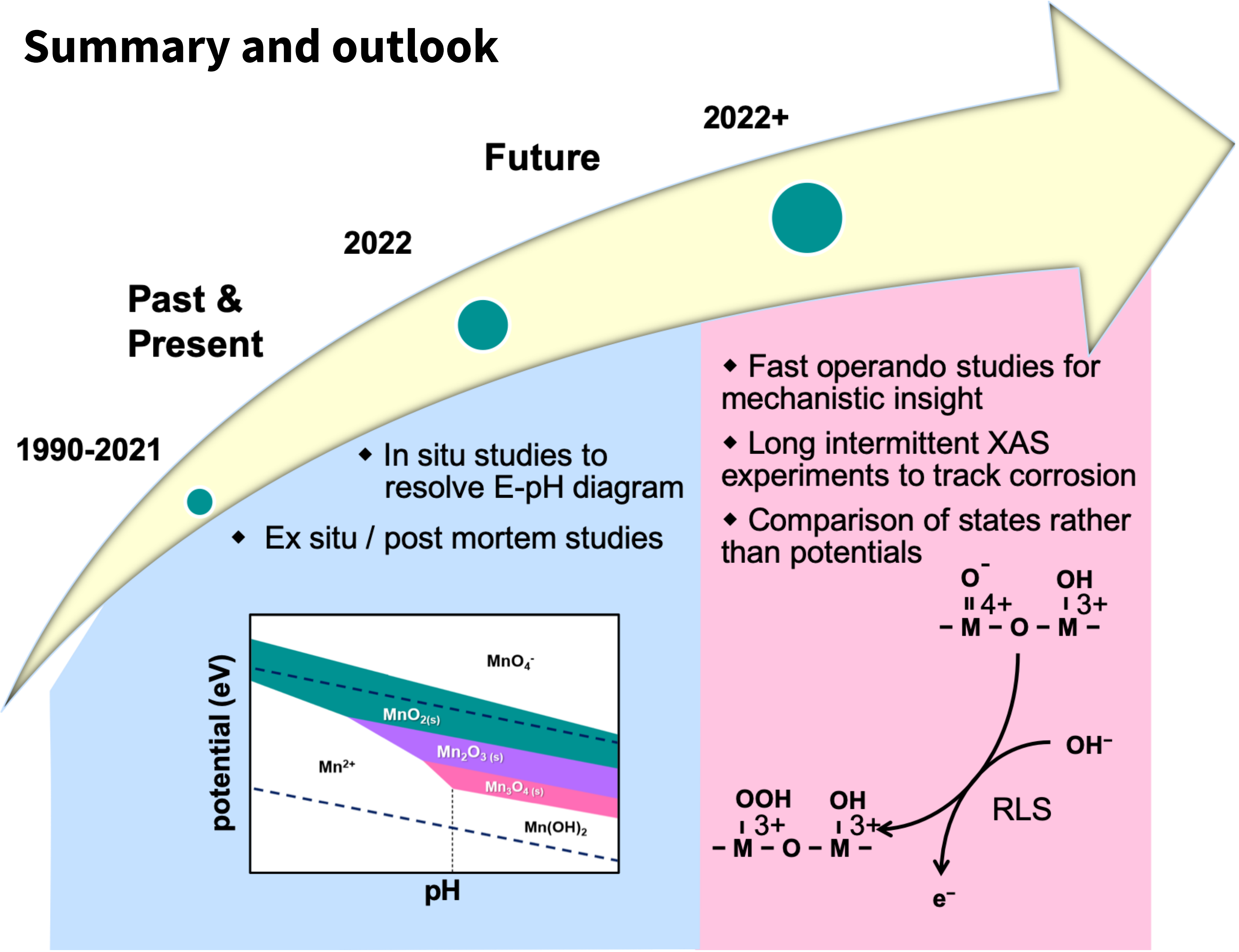


- Clear spectral changes with applied potential
- Repeatable oxidation states:
  - Mn Oxidation before oxygen evolution
  - Mn Reduction before oxygen reduction

Change in oxidation state with potential → catalysis or phase change?

Risch et al., JPCC 121, 17682 (2017

Summary and outlook



1990-2021

Past & Present

- Ex situ / post mortem studies
- In situ studies to resolve E-pH diagram

2022

Future

2022+

- Fast operando studies for mechanistic insight
- Long intermittent XAS experiments to track corrosion
- Comparison of states rather than potentials

- Electrocatalysts may change before electrocatalysis
- Oxidation state is important for electrocatalysis
  - Mn oxidation causes degradation
  - Co addition thwarts degradation and stabilizes material
  - Requirements for beneficial changes of a Co oxide
- ➢ Moving in the E-pH diagram
- Outlook
  - Better understanding of **corrosion** requires slower measurements
  - Better understanding of **catalysis** requires faster measurements

Risch et al., chemRxiv, doi 10.26434/chemrxiv-2022-lhwmb

Key publications and contact information

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What X-ray absorption spectroscopy can tell us about the active state of earth-abundant electrocatalysts for the oxygen evolution reaction
Risch et al., ChemRxiv, doi: 10.26434/chemrxiv-2022-lhwmb

Requirements for Beneficial Electrochemical Restructuring: A Model Study on a Cobalt Oxide in Selected Electrolytes
Villalobos et al., Adv Energy Mater 11, 2101737 (2021), doi: 10.1002/aenm.202101737

Stabilization of a Mn−Co Oxide During Oxygen Evolution in Alkaline Media
Villalobos et al., ChemElectroChem 9, e202200482 (2022), doi: 10.1002/celc.202200482

Reversible and irreversible processes during cyclic voltammetry of an electrodeposited manganese oxide as catalyst for the oxygen evolution reaction
Villalobos et al., J. Phys. Energy 2 034009 (2020), doi: 10.1088/2515-7655/ab9fe2

Nafion-Induced Reduction of Manganese and its Impact on the Electrocatalytic Properties of a Highly Active MnFeNi Oxide for Bifunctional Oxygen Conversion
Morales et al., ChemElectroChem 8, 2979-2983 (2021), doi: 10.1002/celc.202100744

Undesired Bulk Oxidation of LiMn2O4 Increases Overpotential of Electrocatalytic Water Oxidation in Lithium Hydroxide Electrolytes
Baumung, et al., ChemPhysChem 20, 2981-2988 (2019), doi: 10.1002/cphc.201900601

Redox Processes of Manganese Oxide in Catalyzing Oxygen Evolution and Reduction: An in Situ Soft X-ray Absorption Spectroscopy Study
Risch, et al., J. Phys. Chem. C 121, 33, 17682–17692 (2017) doi:10.1021/acs.jpcc.7b05592