INSTITUT DE CIÈNCIA DE MATERIALS DE BARCELONA

EXCELENCIA SEVERO OCHOA

XI AUSE Conference and VI ALBA Users Meeting

Synchrotron Radiation to Solve the Puzzles of Capacity Limitation in Aqueous Zn-MnO_2 Batteries

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2nd September 2024, Oviedo, Spain

ALBA

AUSE Asociación Usuarios Sincrotrón España

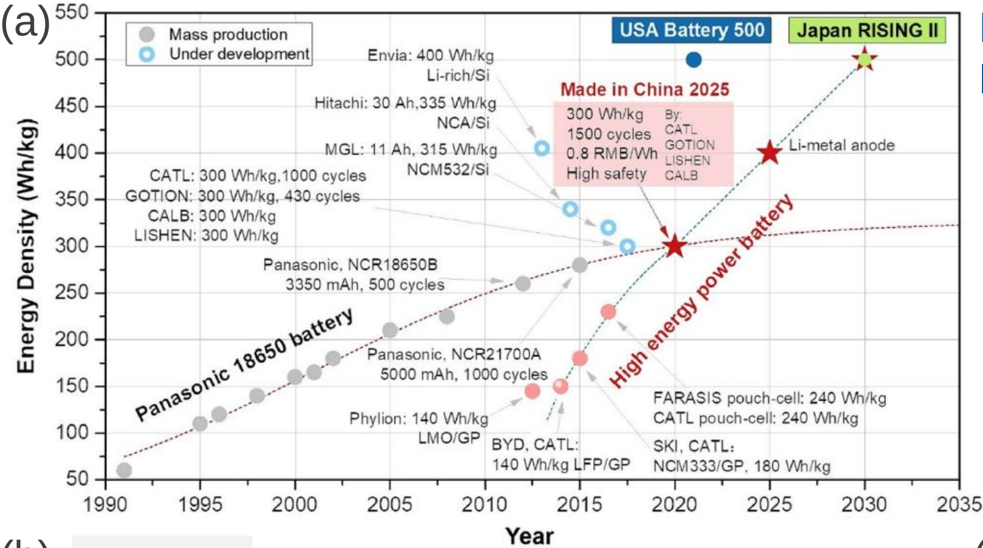
Universidad de Oviedo

Spain XFEL HUB

XI AUSE Conference
VI ALBA Users Meeting
Oviedo
2 – 6 September 2024

Background: Aqueous Zn Batteries

(a)

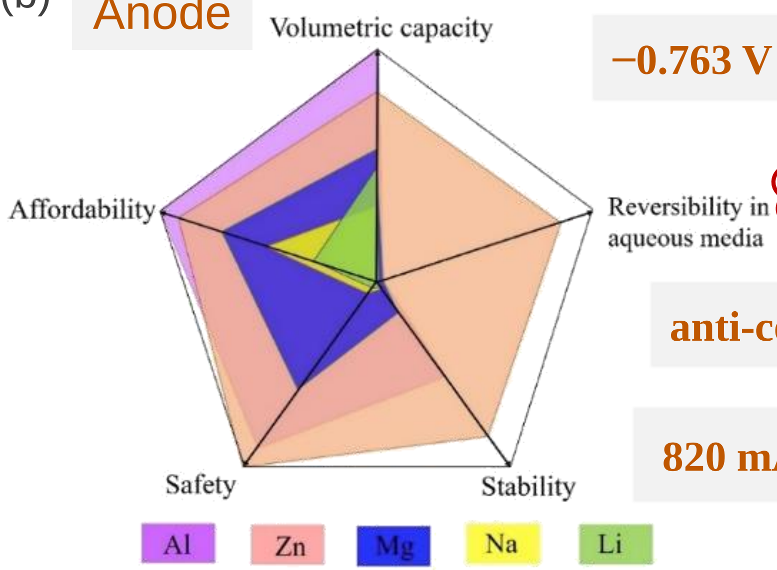


Battery 2030+[1] and Battery 500 consortium[2]
In EV, and HEV Manufactory:

- High Safety[1-2]
- Sustainable System[2]
- Instantaneous Power Density[1-2]
- Long Term Cyclability[1-2] (Over 1000 cycles)
- High Energy Density >500 Wh kg^{-1}[2]

Aqueous Rechargeable Zn Batteries!

(b) Anode



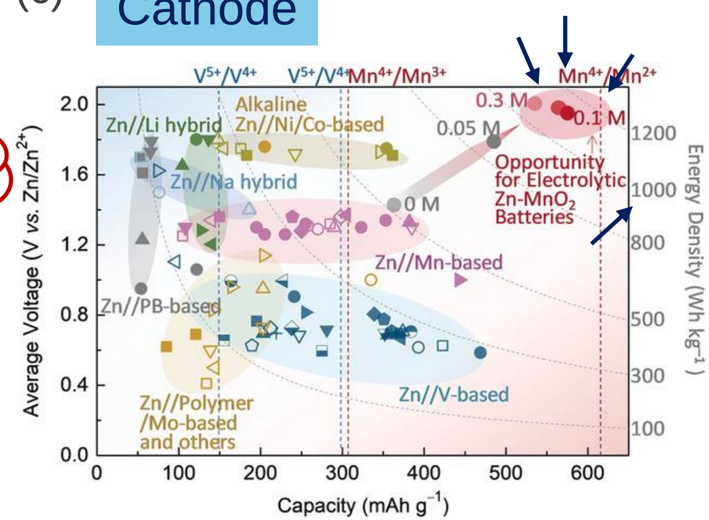
Zn[3]

−0.763 V vs. SHE

anti-corrosion

820 mAh g^{-1}_{Zn}

(c) Cathode



Low-cost

Mn[4]

616 mAh g^{-1} theoretically

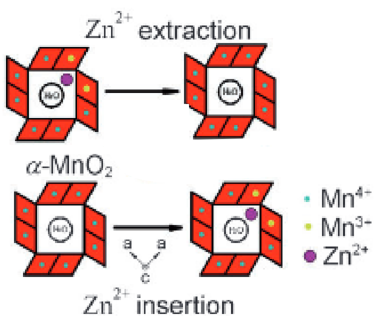
natural abundance

[1] https://battery2030.eu/research/roadmap. [2] https://www.pnnl.gov /projects/battery500-consortium.
[3] Chem. Rev. **2020**, 120, 7795-7866. [4] Angew Chem Int Ed **2019**, 58 (23), 7823–7828. (a) Energy Storage Materials 23 (**2019**) 144–153

Background: Mechanisms and Capacities

Path I: Zn intercalation

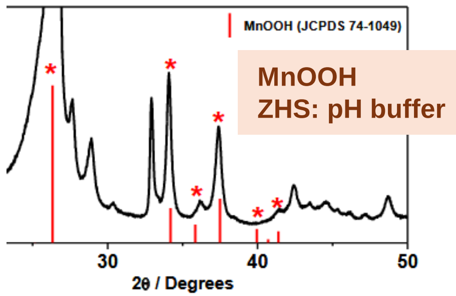
$Zn + 2MnO_2 \leftrightharpoons ZnMn_2O_4$



Angew. Chem. - Int. Ed. **2012**, 51 (4), 933–935.

Path II: H conversion

1. $H_2O + MnO_2 \leftrightharpoons MnOOH + [OH^-]$
2. $4Zn^{2+} + 6[OH^-] + SO_4^{2-} + xH_2O \leftrightharpoons Zn_4SO_4(OH)_6 \cdot xH_2O$ (ZHS)

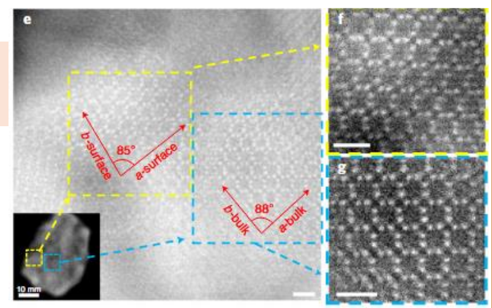


Nat. Energy **2016**, 1 (5), 16039.

Mn(III) reaction with H^+ or/and Zn^{2+}

Path III: H intercalation

1. $H_2O + MnO_2 \leftrightharpoons HMnO_2 + [OH^-]$
2. $4Zn^{2+} + 6[OH^-] + SO_4^{2-} + xH_2O \leftrightharpoons Zn_4SO_4(OH)_6 \cdot xH_2O$ (ZHS)

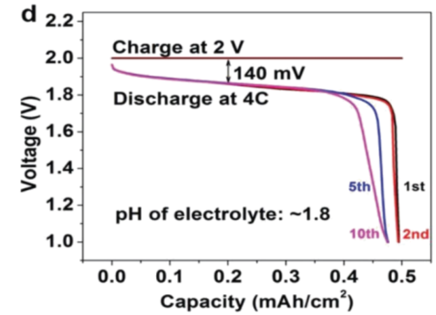


Nat. Sustain. **2022**, 5 (10), 890–898.

Path IV: Mn stripping

$2H_2O + MnO_2 \leftrightharpoons Mn^{2+} + 2[OH^-]$

Lower pH, ZHS not formed

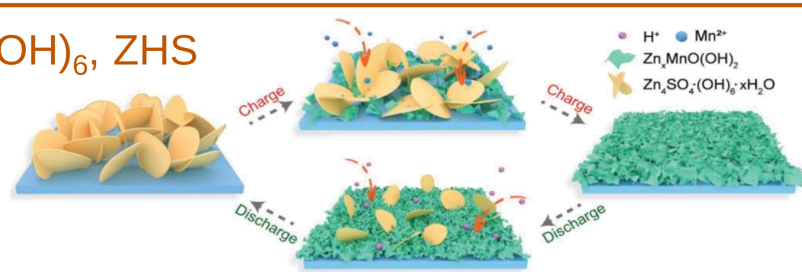


Adv. Energy Mater. **2020**, 10 (9), 1902085.

Mn(II/IV) reaction with H^+

Path V: $Zn_4SO_4(OH)_6$, ZHS

$ZHS + Mn^{2+} \leftrightharpoons ZnMn_2O_4$
$\leftrightharpoons ZnMn_xO_y \leftrightharpoons ZnMn_3O_7$



J. Mater. Chem.A **2018**, 6 (14), 5733–5739.
Adv. Mater. **2022**, *34* (15), 2109092.

Mn(II) reaction with ZHS and Zn-Mn(III) phase

Path VI: Combinations

- Zn/H co-intercalation
- Zn intercalation/Mn stripping
- Zn/H intercalation-conversion

J. Am. Chem. Soc. **2017**, *139* (29), 9775–9778.

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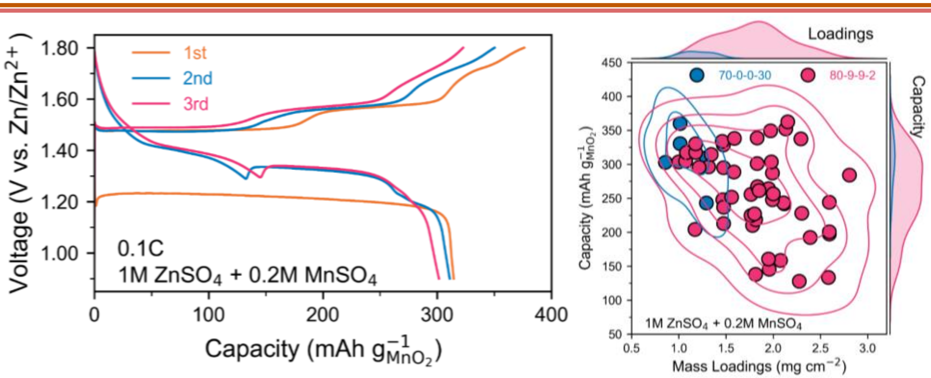
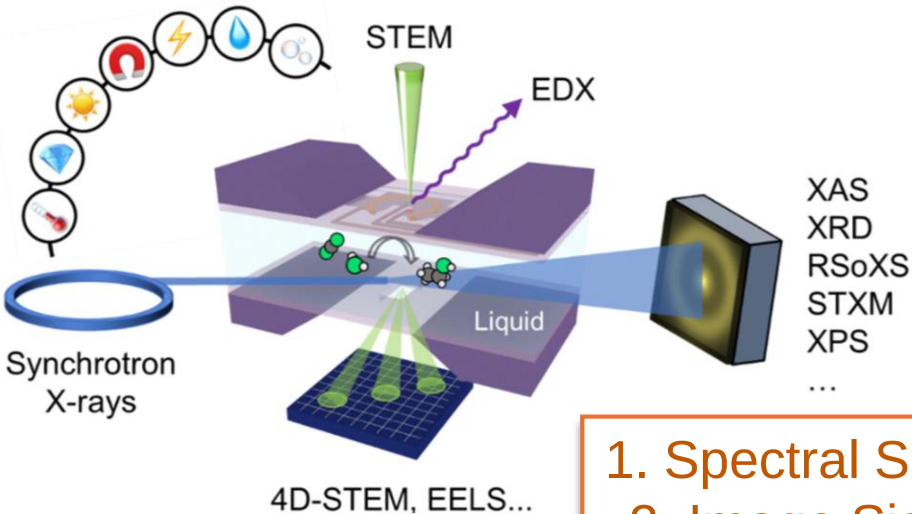
Mixtures of Mn(II/III/IV) with Zn^{2+}, and H^+



Mechanism Puzzles?
Capacity Limitation?

Background: Advanced Analysis Methods

Curr. Opin. Electrochem. **2023**, 42, 101403.

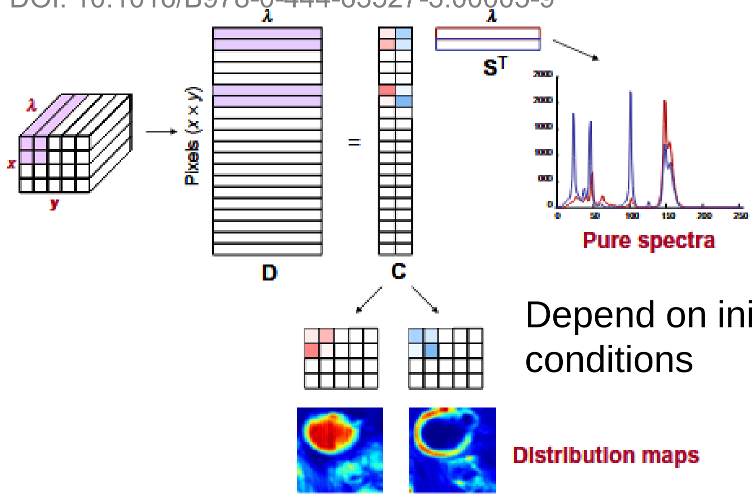


1. Spectral Signals
2. Image Signals

MCR-ALS (2D) or PARAFAC2 (Multidimensions)

Multivariate Curve Resolution-Alternating Least Squares

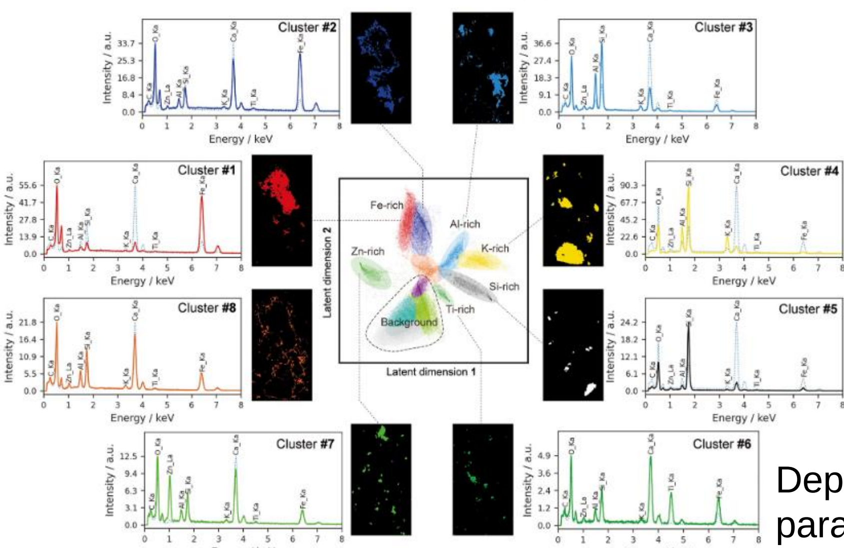
DOI: 10.1016/B978-0-444-63527-3.00005-9



Depend on initial conditions

Clusters Analysis (Machine Learning): soft-TXM, EELS, EDX

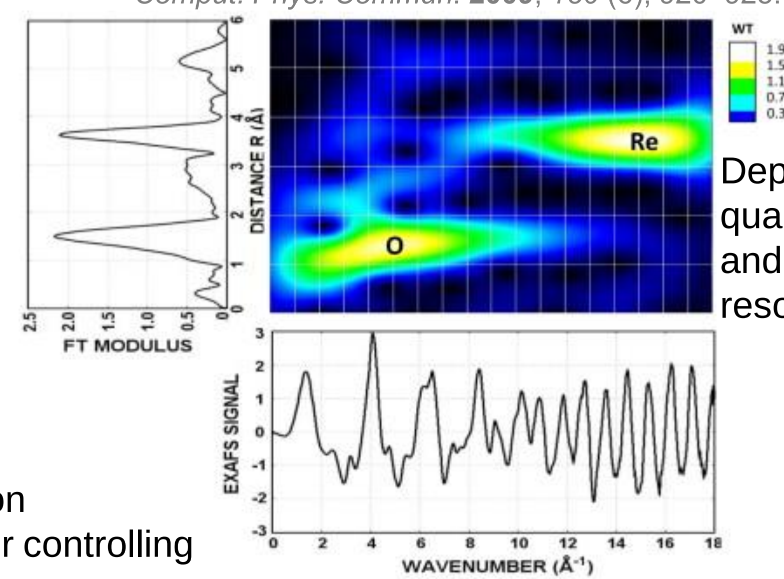
Geochem. Geophys. Geosyst. **2023**, *24* (1), e2022GC010530.



Depend on parameter controlling

Wavelet Transform: 2D EXAFS

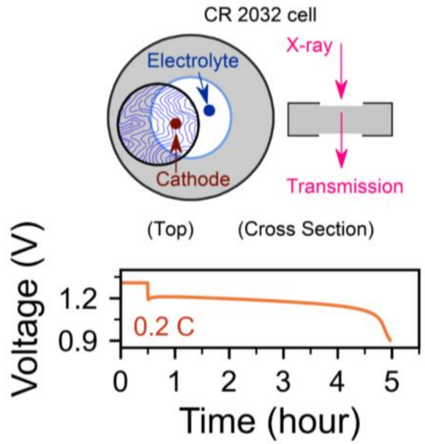
Comput. Phys. Commun. **2009**, *180* (6), 920–925.

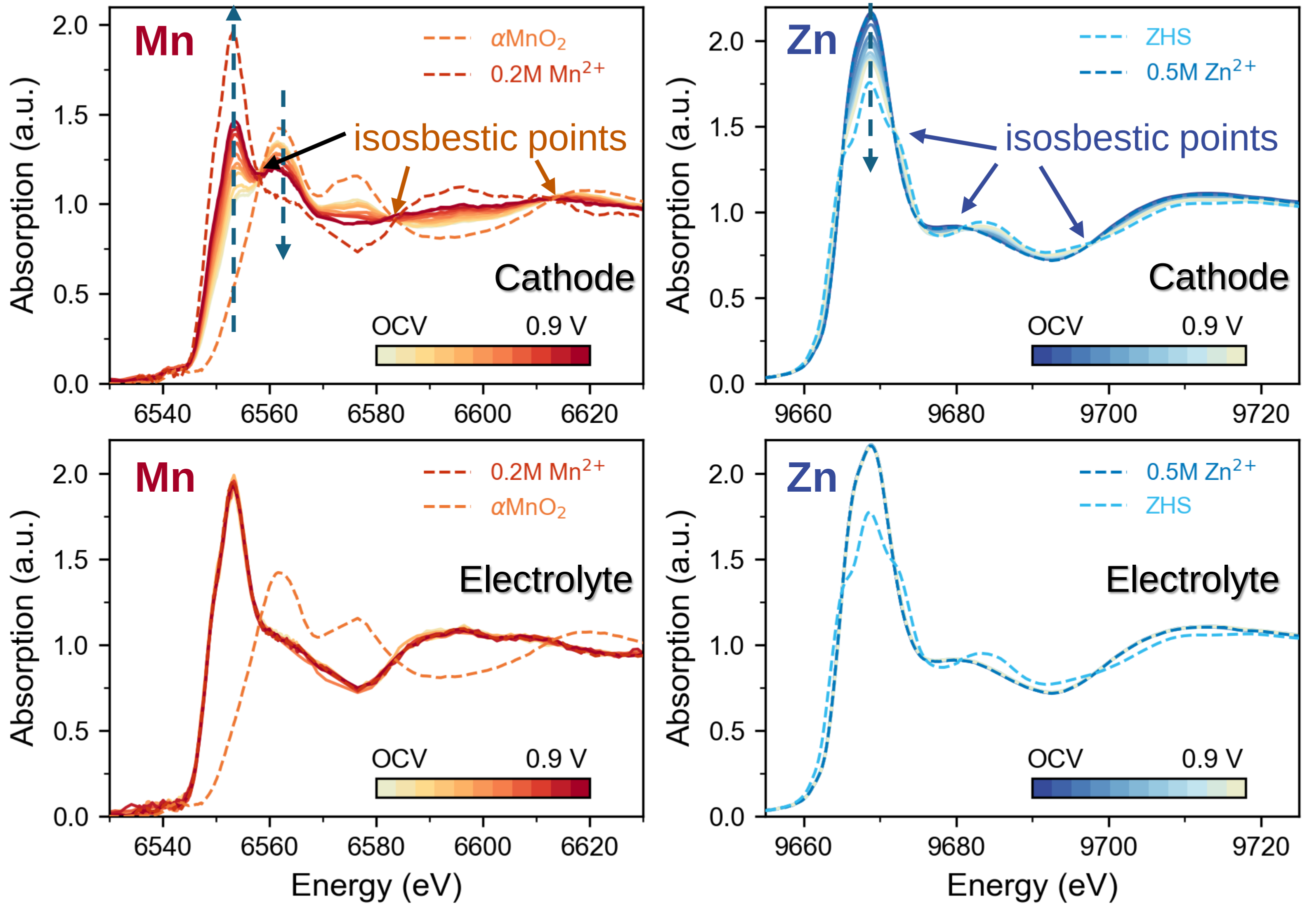


Depend on quality of Data and energy resolution

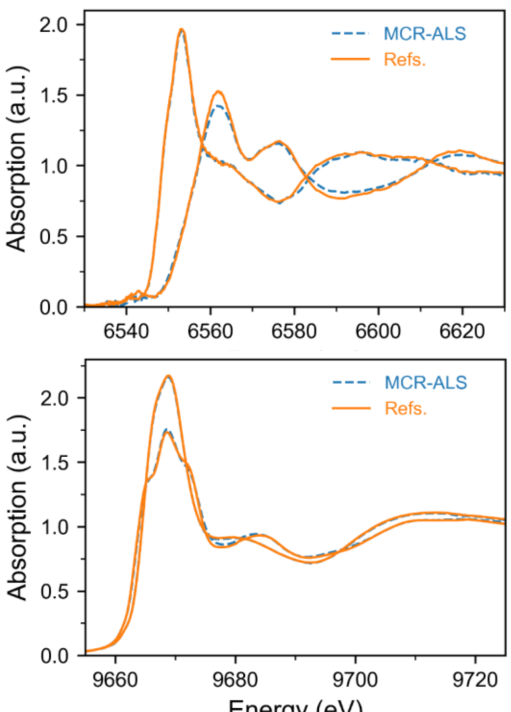
Operando XANES: Mn(IV/II) + ZHS/Zn^{2+}

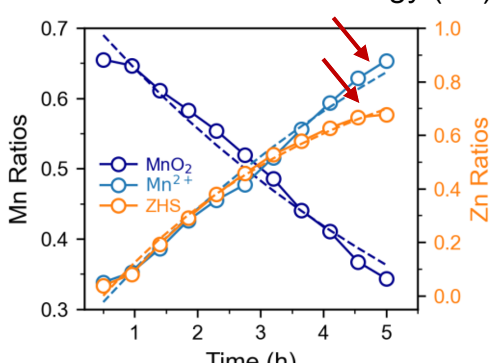
Cell Configuration





MCR-ALS





$$3MnO_2 + 8Zn^{2+} + 2SO_4^{2-} + 6H_2O \leftrightharpoons 3Mn^{2+} + 2Zn_4SO_4(OH)_6$$

Independent half reactions:

1. Prue MnO_2/Mn^{2+} reaction,
2. Pure ZHS/Zn^{2+} reaction,
3. Capacity limitations caused by Zn?
4. ZHS forms at initial.

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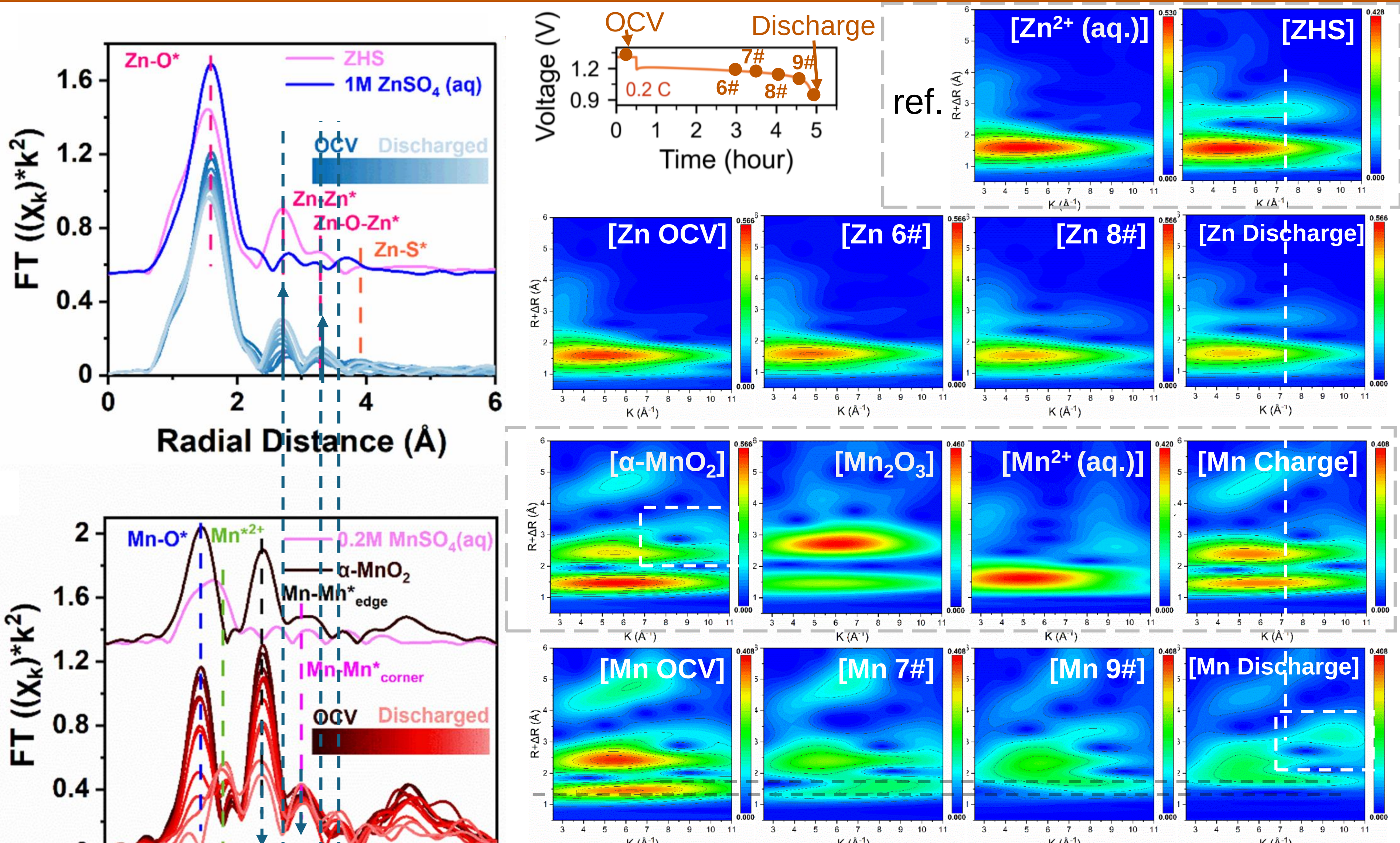
Operando 2D EXAFS: No Zn-Mn Phase

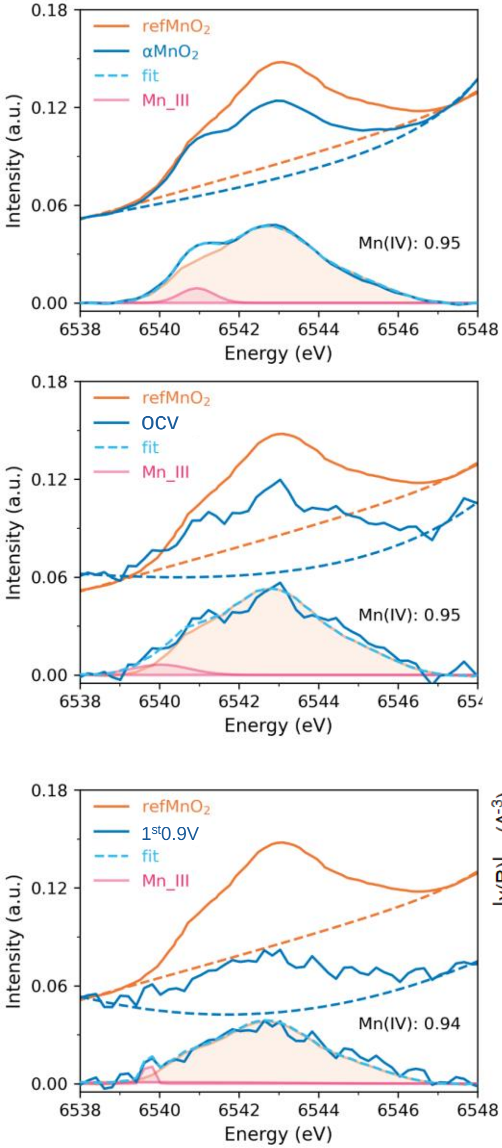


1. No Zn-Mn bonds in EXAFS in operando.
2. No Zn contribution shown in Mn Wavelet Transform.

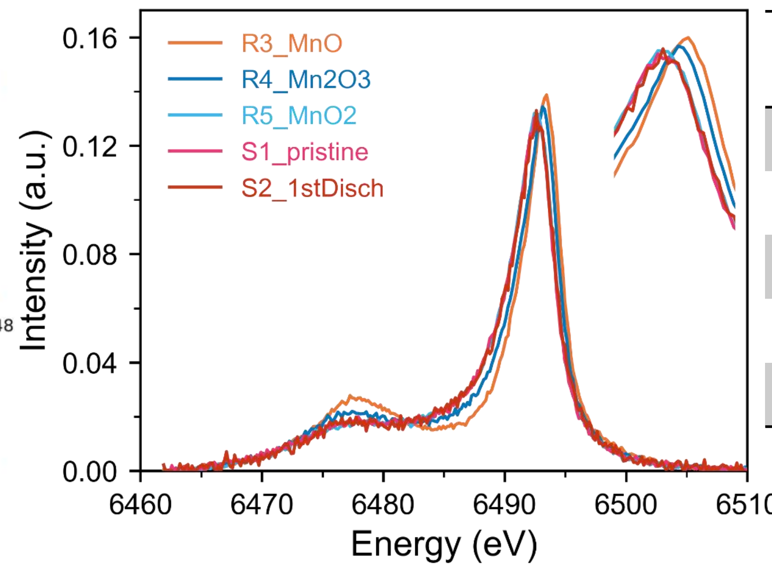
In preparation

Discoverable Mn(III) phase in Discharge?
- Pre-Edge, K-beta, EXAFS simulations: No

Pre Edge



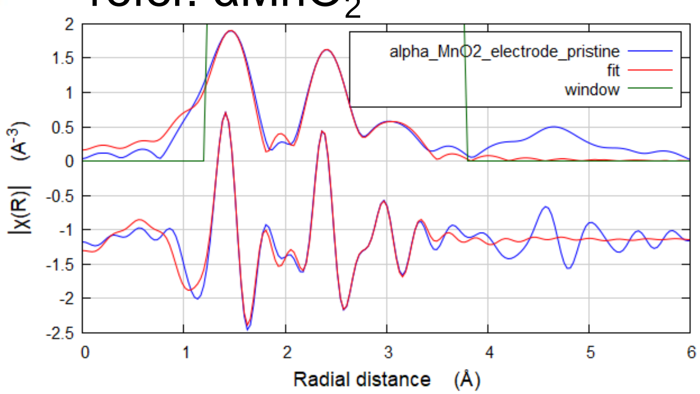
Kβ-XES



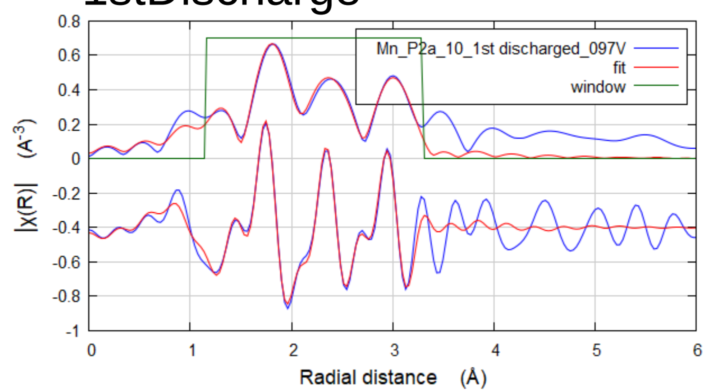
Sample	Peak	Area (IAD)
R3_MnO	6493.26	0
R4_Mn2O3	6492.97	0.135
R5_MnO2	6492.53	0.280
Pristine	6492.49	0.281
1st0.9V	6492.53	0.276

EXAFS simulations with two refers (Mn2+(aq.), and αMnO_2)

refer. αMnO_2



1stDischarge



Being consistent with XANES results!

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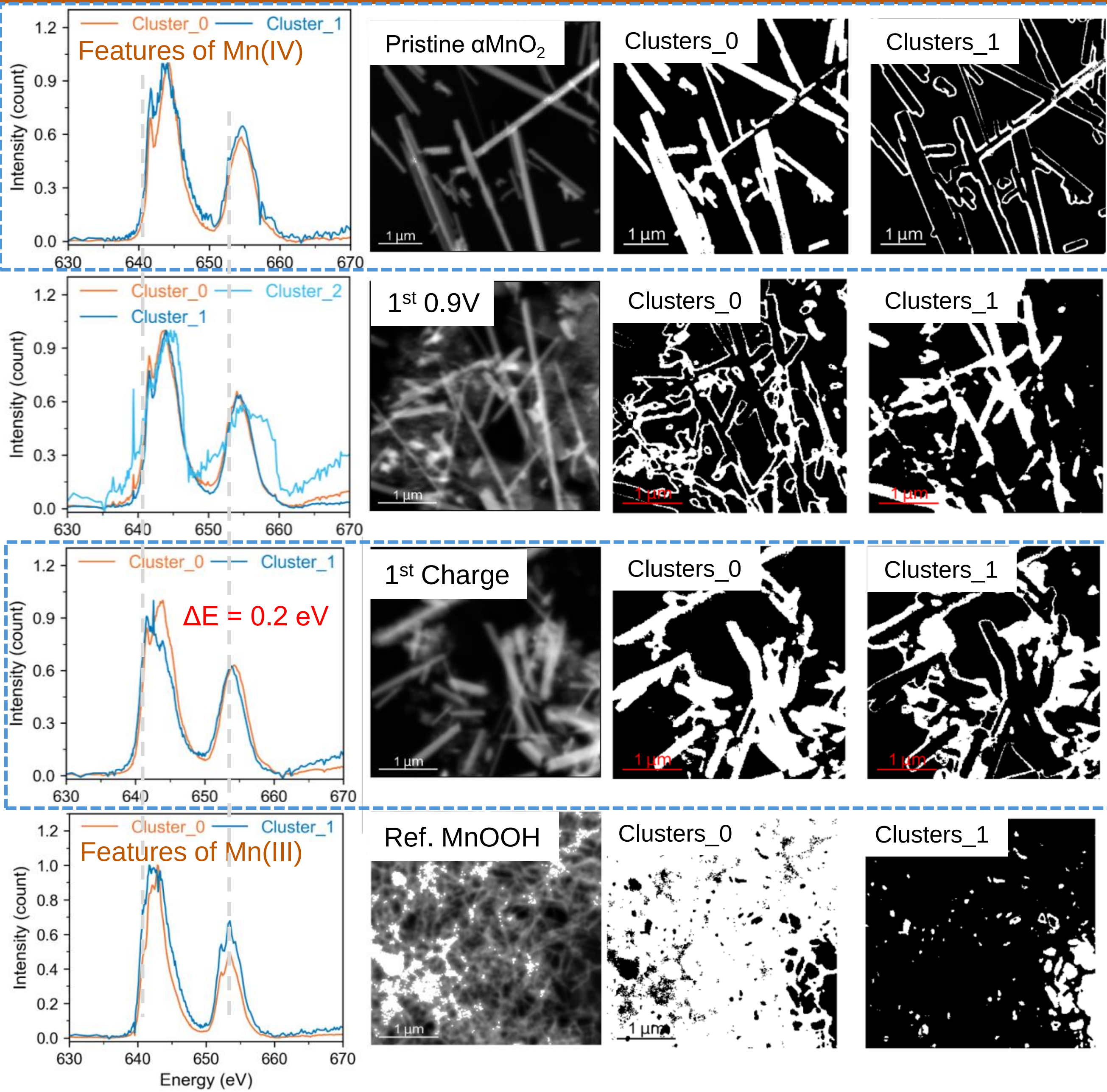
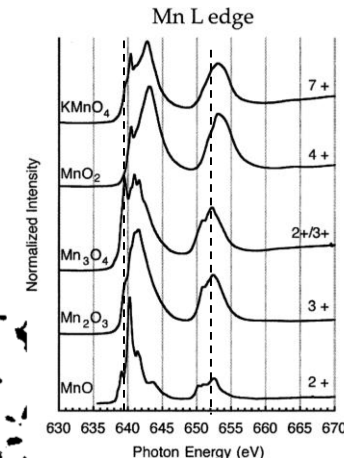
soft-TXM, Mn: Discoverable Mn(III)? - Cluster Analysis: No





J. Phys. Chem. A 2003, 107 (16), 2839–2847.

TEM-EDX

1. No obvious Mn(III) signals.
2. Cluster analysis could work.

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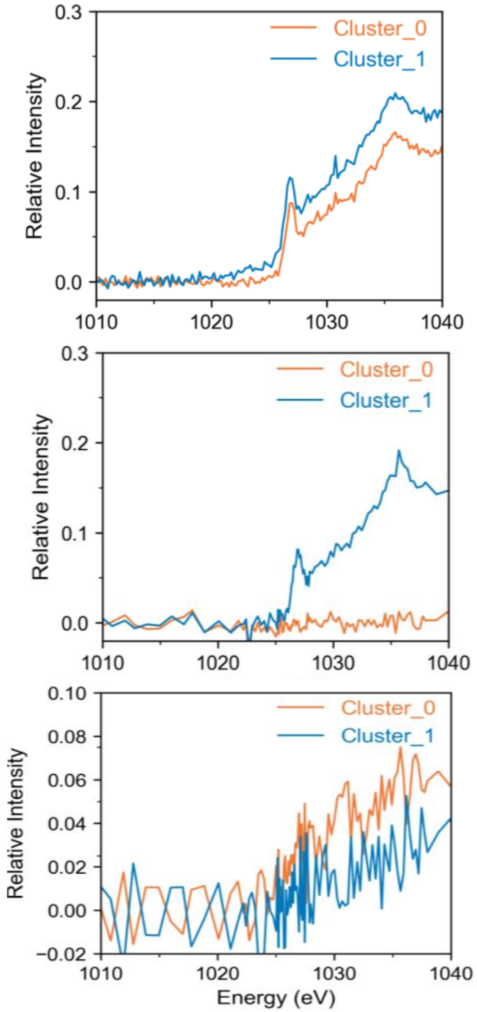
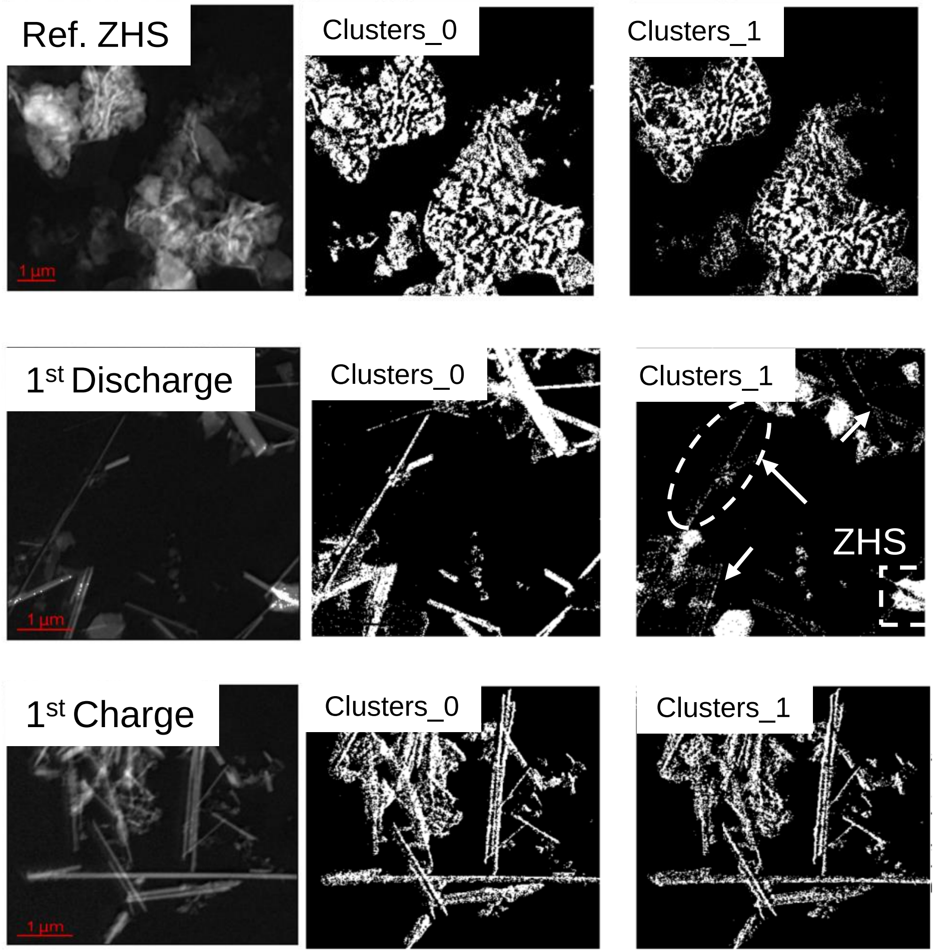
soft-TXM, Zn: Discoverable Zn? Yes!
- Cluster Analysis: On the surface





No Zn intercalation into nano-wires MnO_2. But coating on the surface.

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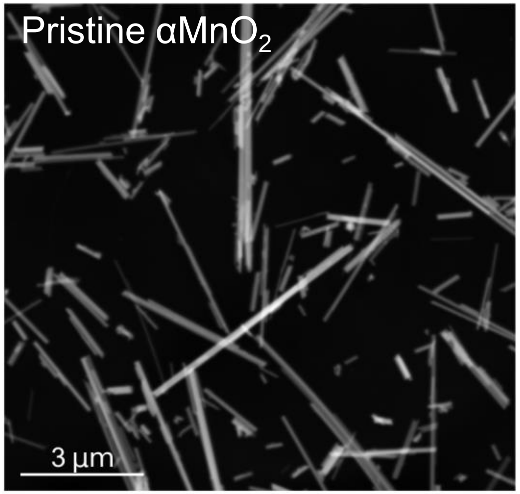
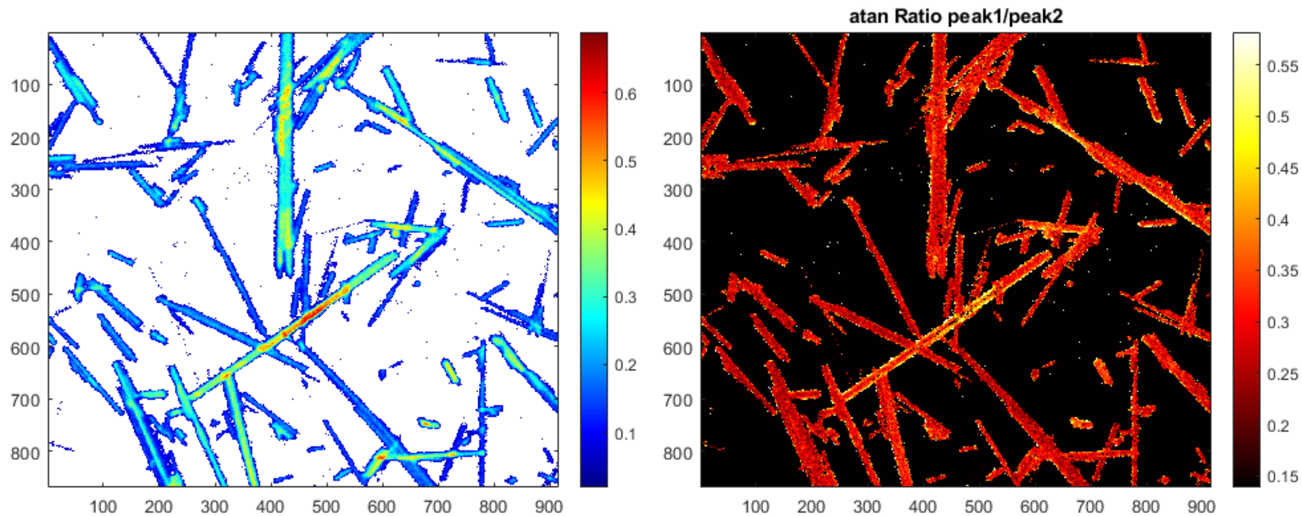
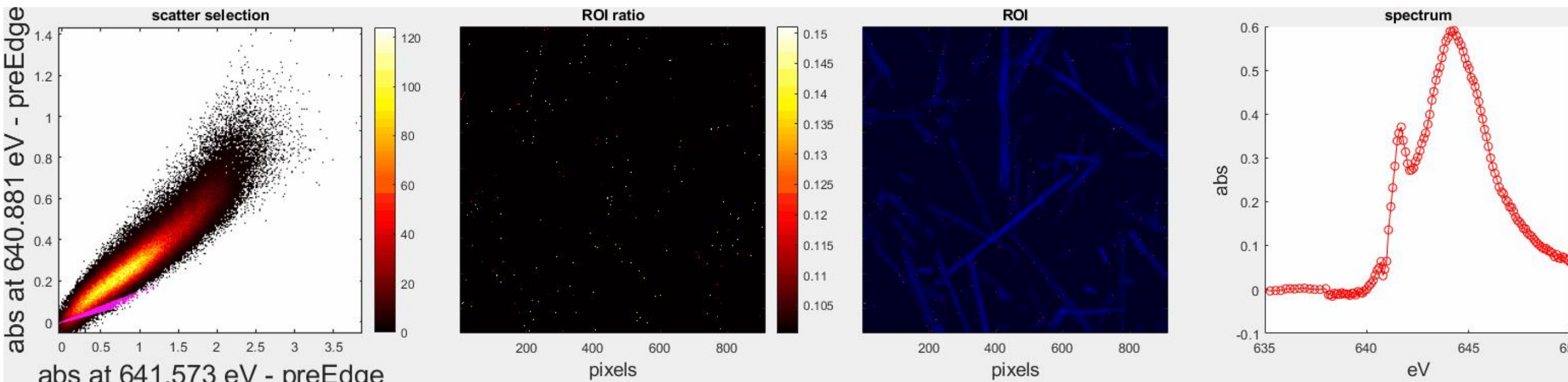
soft-TXM, Mn: Discoverable Mn(III)? Yes - Phase Mapping[1]







Done by Andrea Sorrentino

Sample	Batch1, α-MnO_2
K (wt.% (p/p))	4.9
Mn (wt.% (p/p))	62.0
Ratio (K/Mn)	0.111(4)

1. More sensitive to thickness effect.
2. Features are same with that of Mn(IV)

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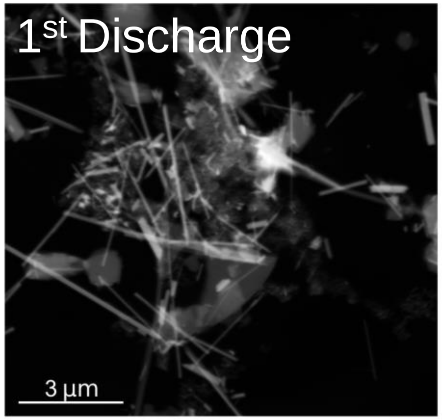
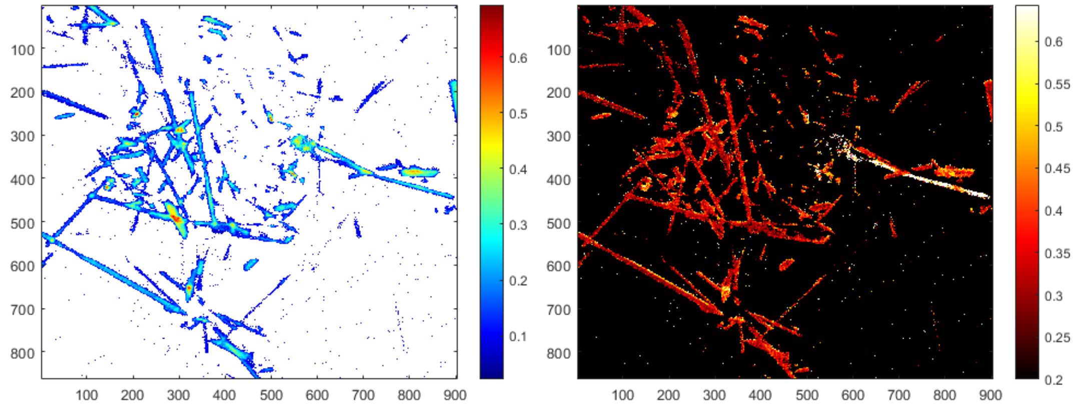
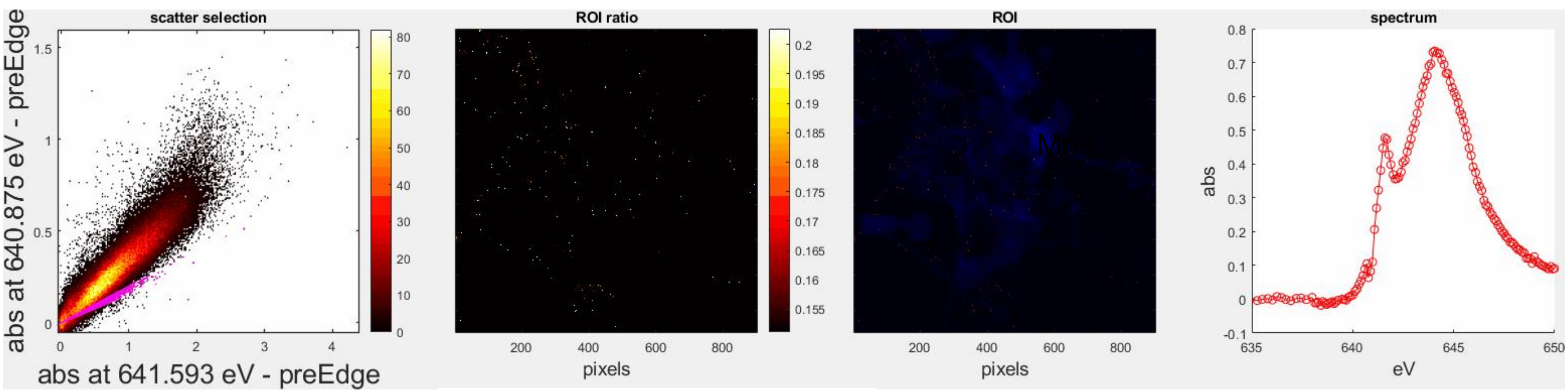
[1] Applied Sciences **2021**, 11 (6), 2791.

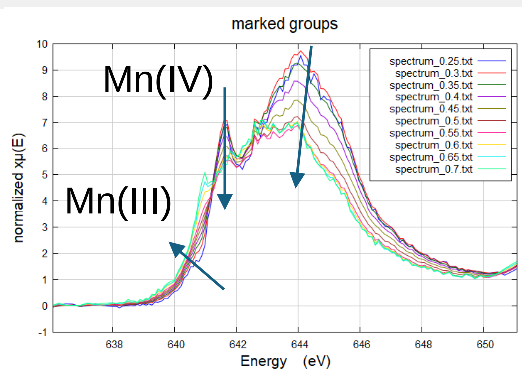
soft-TXM, Mn: Discoverable Mn(III)? Yes - Phase Mapping[1]







Done by Andrea Sorrentino



1. Features are CHANGED
2. Discoverable Mn(III)? Yes

[1] Applied Sciences **2021**, 11 (6), 2791.

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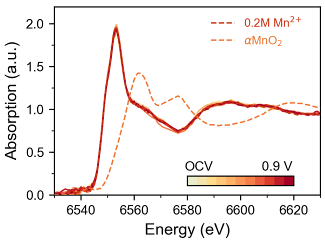
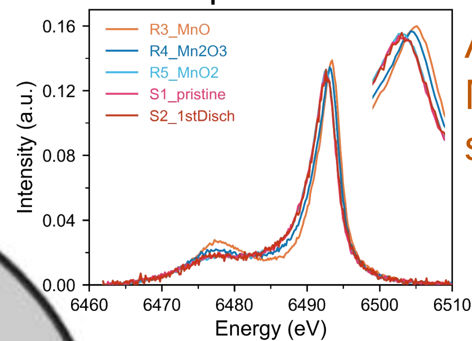
Conclusion: Proposed Mechanism of αMnO_2

αMnO_2 dissolution with Mn(III) transformation, Capacity limited by surface passivation of Zn.

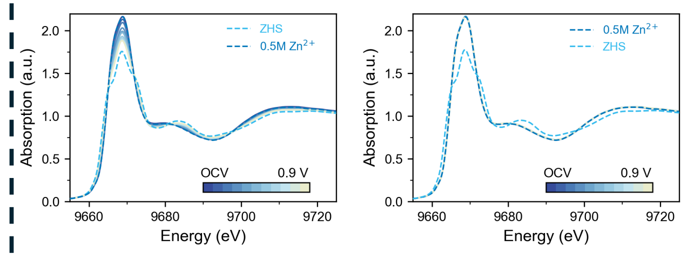


No soluble Mn(III)

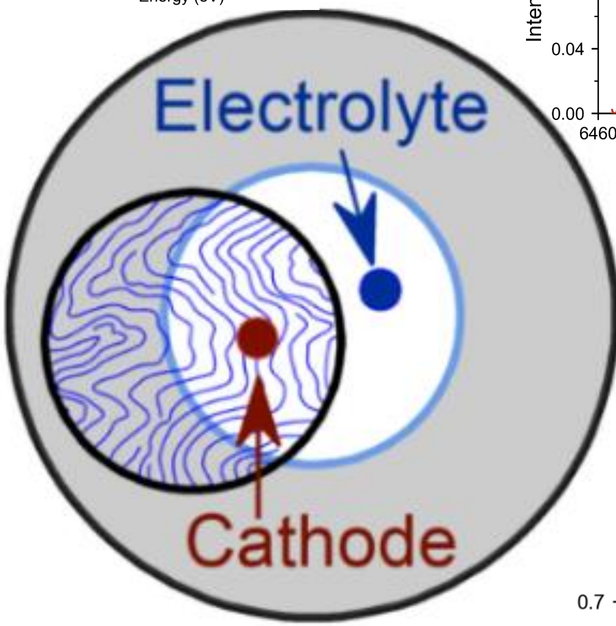
Kβ-XES



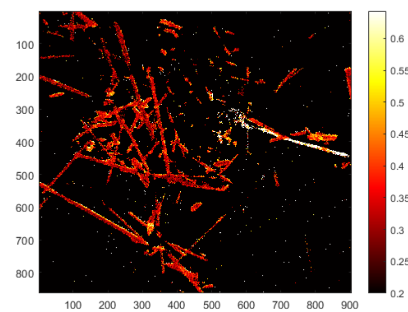
Averaged Mn is not shifted

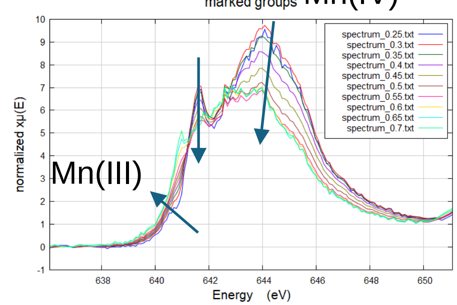


ZHS as pH buffer



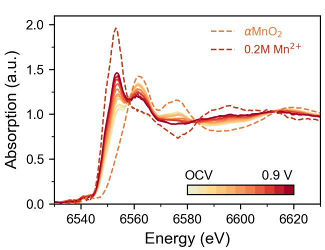
Phase mapping, soft-TXM





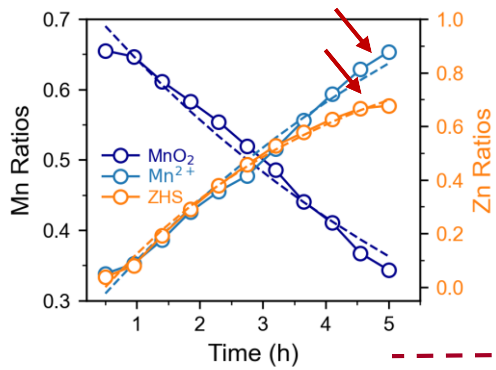
Mn(IV) is converting to Mn(III)

Mn XANES



αMnO_2 to Mn(II, aq)

MCR-ALS, XANES



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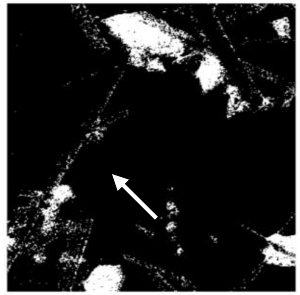
Clusters, soft-TXM



Unknown Zn coating on αMnO_2 surface

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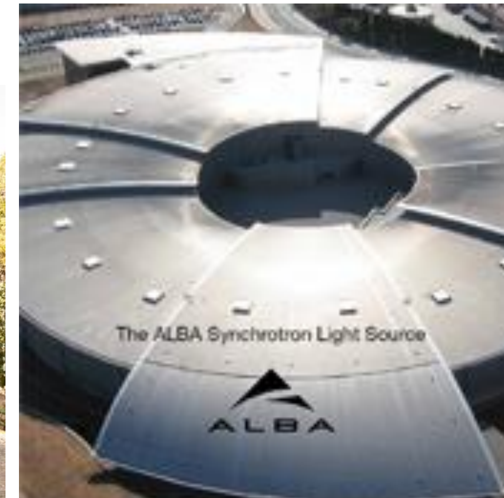

Thank you for your attention!

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