Unraveling the Role of Layered ZHX Materials in Zn-Ion Battery Cycling

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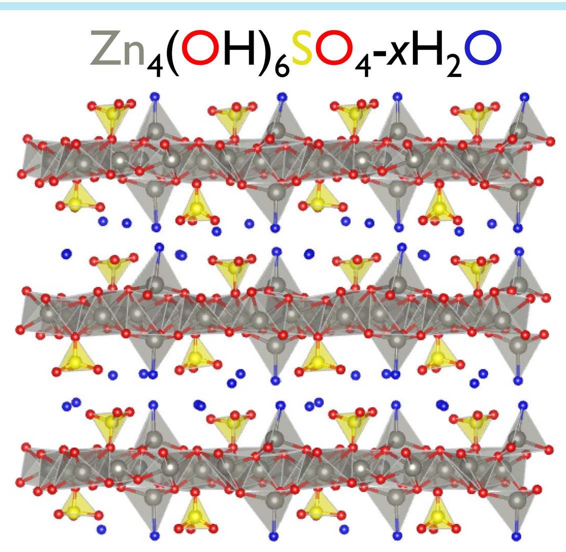
Background/Motivation

Project Goal: To gain insight on the mechanism by which Zn-ion batteries deliver electricity, identification of the mechanism-relevant zinc materials.
Current Practice: Underlying Li-ion mechanisms are commonly adapted to Zn-ion, but supporting evidence is limited.
Why SNL: Array of uncommon to near-unique instrumentation (e.g. TEM and cryo-PFIB SEM), critical for advancing new technologies (e.g. Zn-ion batteries).
Innovation: Leverages and expands on new capabilities (cryo-PFIB) to study the system in ways that were not previously possible.
Impact: Additional energy storage is needed to improve grid reliability & resilience, provide constant power for emerging technologies (e.g. AI), and high power for resource extraction. This work will aid in the development of Zn-ion batteries that store grid energy using safe, inexpensive, and US-sourced materials, components, and manufacturing.
Alignment: Zn-ion batteries as a grid-level storage system will improve the reliability and resilience of the grid using affordable and US-sourced materials and manufacturing.



Bear, I. J. *et al. Acta Crystallogr. Sect. B*, **1986**, *42*, 32.

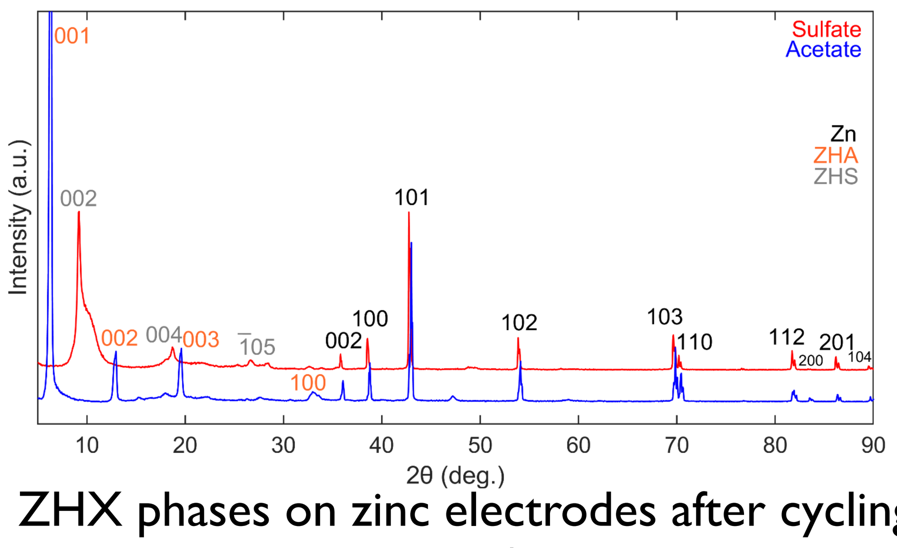
Mechanism in zinc-ion batteries is unclear:
- Redox mechanisms complex
- Layered ZHX phases can form
- By-product or part of mechanism?

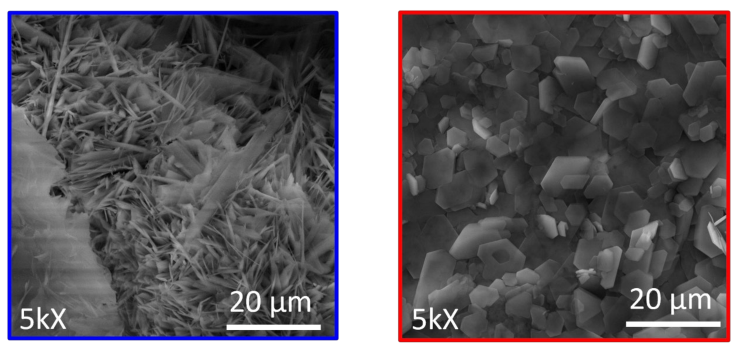
Here we investigate the role of ZHX:
- Typical $ZnSO_4$ electrolyte (**sulfate**)
- KOAc/HOAc electrolyte (**acetate**)
  - ↑molality → ↑conductivity/stability
  - Inexpensive, nontoxic materials.

ZHX Formation in Zn-Ion Cells

Cycled Zn electrodes from symmetric cells:
- Dull white appearance, ~1/3 less dense
- Likely electrolyte-derived phases (*i.e.* ZHX)
- $Zn \rightarrow Zn^{2+}$ may lead to ZHX either with OH^- (from HER) or H_2O (no HER)

$$5\,Zn_{(s)} + 8\,OH^-_{(aq)} + 2\,OAc^-_{(aq)} \rightarrow Zn_5(OH)_8(OAc)_{2(s)} + 10\,e^- \quad (1)$$
$$5\,Zn_{(s)} + 8\,H_2O_{(l)} + 2\,OAc^-_{(aq)} \rightarrow Zn_5(OH)_8(OAc)_{2(s)} + 8H^+_{(aq)} + 10\,e^- \quad (2)$$





ZHX phases on zinc electrodes after cycling:
- ZHS ($Zn_4(OH)_6SO_4$)[1] appears on zinc cycled in sulfate electrolyte
- ZHA ($Zn_5(OH)_8(OAc)_2$)[2] appears on zinc cycled in acetate electrolyte
- Micron-scale particles: ZHA blades & ZHS hexagonal platelets

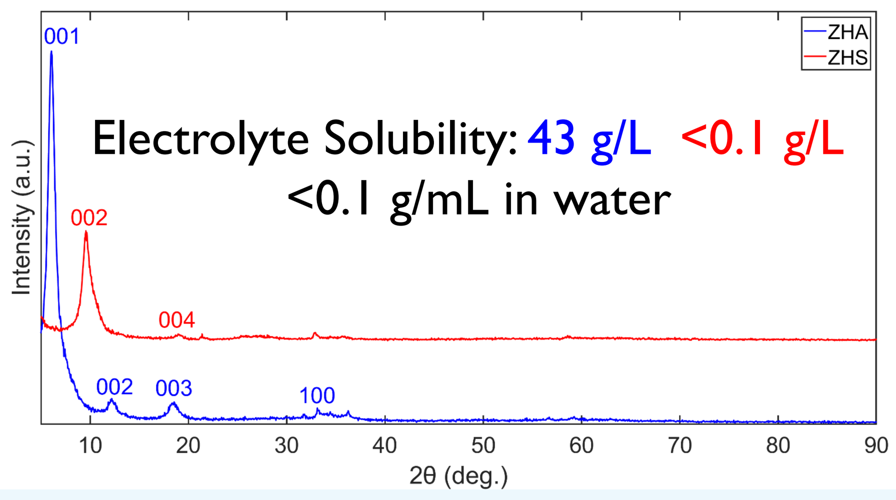
(1) Bear, I. J. *et al. Acta Crystallogr. Sect. B*, **1986**, *42*, 32. (2) Poul, L. *et al. Chem. Mater.* **2000**, *12*, 3123.

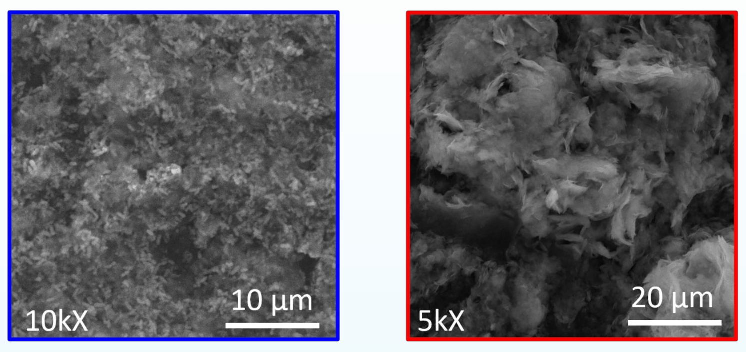
Synthesis of ZHX Materials

ZHA and ZHS can be synthesized by a RT aqueous precipitation reaction[1]

$$6\,NaOH_{(aq)} + 4\,ZnSO_{4(aq)} \rightarrow Zn_4(OH)_6SO_{4(s)} + 3\,Na_2SO_{4(aq)}$$
$$8\,NaOH_{(aq)} + 5\,Zn(OAc)_{2(aq)} \rightarrow Zn_5(OH)_8(OAc)_{2(s)} + 8\,NaOAc_{(aq)}$$

Aqueous NaOH and ZnX are combined, ZHX precipitates out





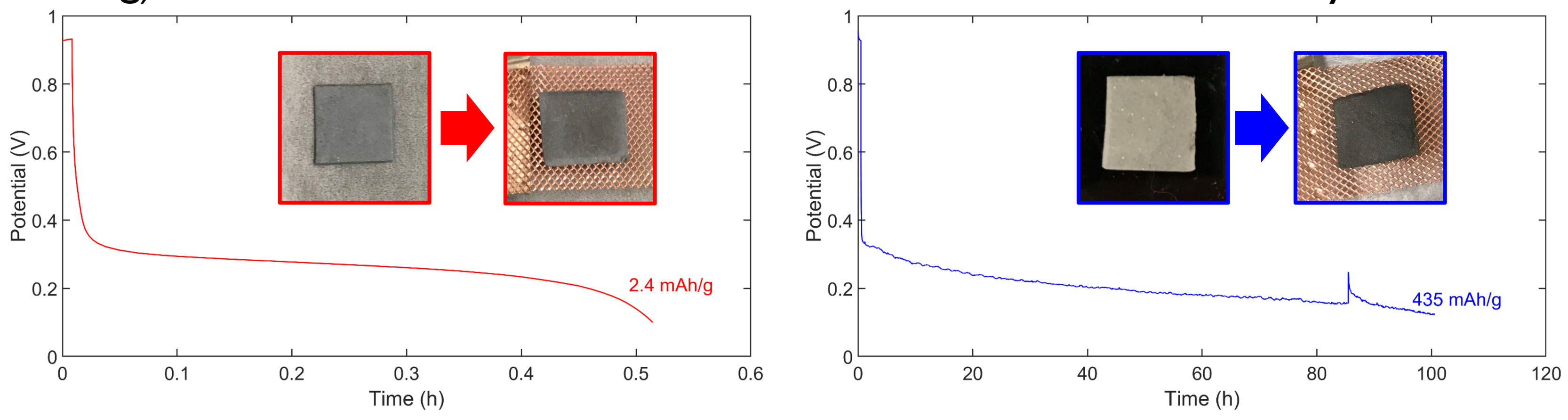
Materials are isostructural to ZHX formed *in situ*, morphologically are different:
- More finely divided particles, rice-like for ZHA, platelet-like for ZHS

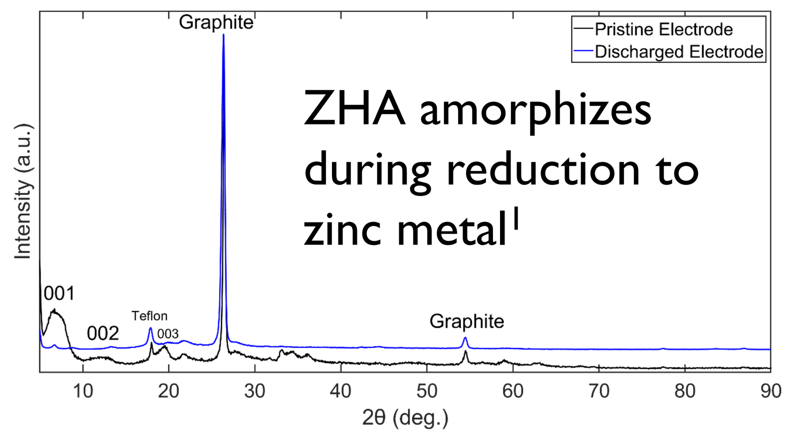
ZHA has significant solubility in electrolyte, which could facilitate reversibility

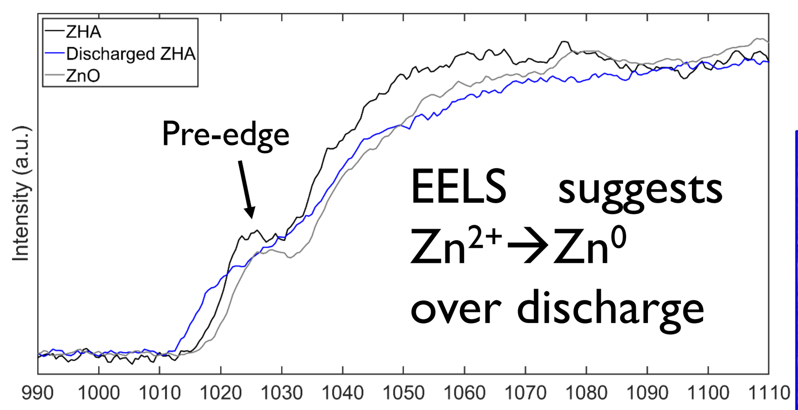
Modified from (1) Hedberg, J. *et al. J. Electrochem. Soc.* **2010**, *157*, C363.

Can ZHX be Reduced?

ZHA (435 mAh/g) cathode can be fully reduced in a zinc battery while ZHS (467 mAh/g) cannot = ZHA formation is reversible; ZHS formation is likely irreversible

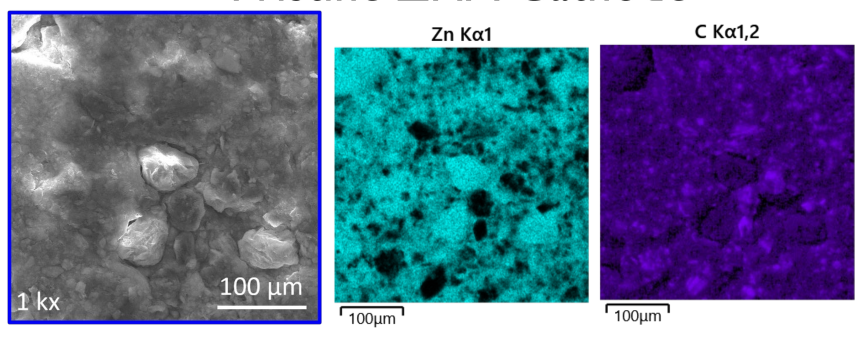




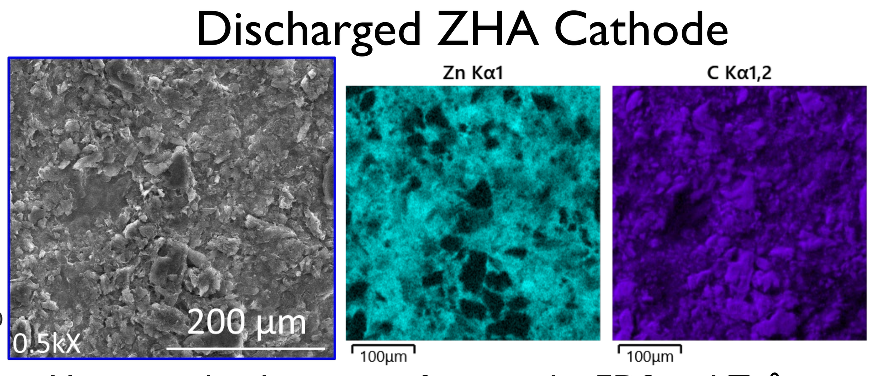


After discharge, electrode is coated in finely divided zinc with graphite visible

Pristine ZHA Cathode



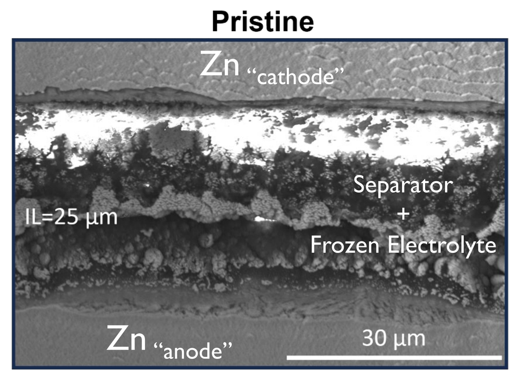
Discharged ZHA Cathode

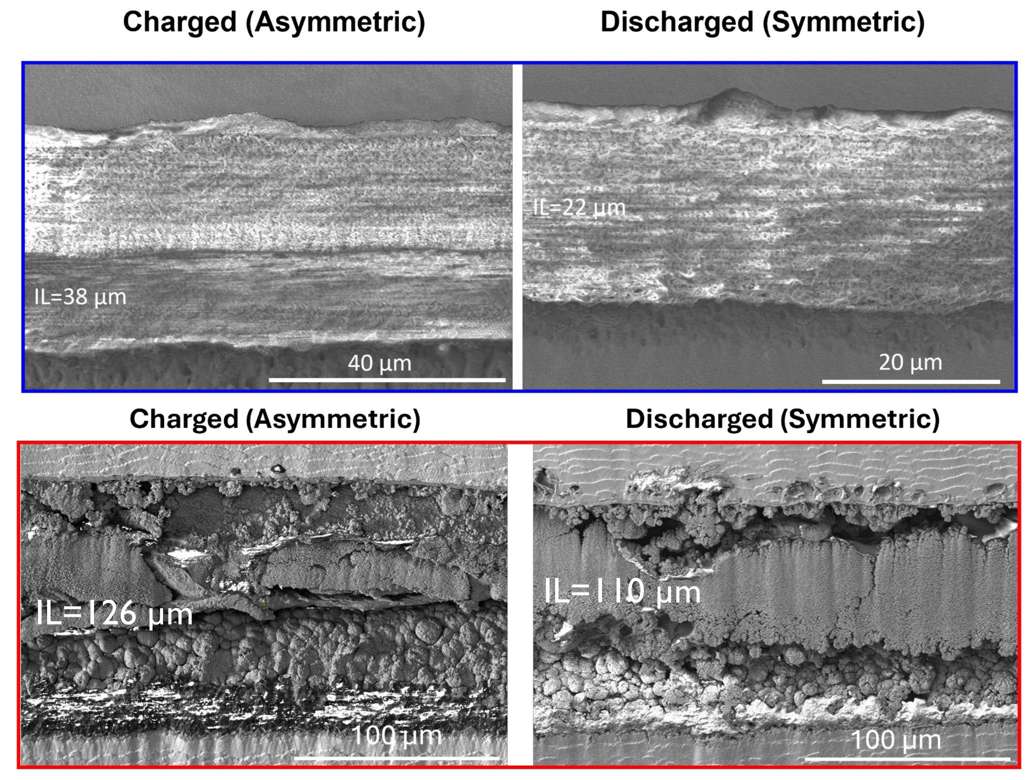


[1]Dissolution is an alternative possibility to amorphization. However, the detection of zinc in the EDS and Zn^0 in the EELS confirms that reduced, amorphous zinc is in fact present.

How Much ZHX is Formed?

Cryogenic laser ablation was used to expose the interphase of the cells at ~-100 °C *in vacuo*. To the best of our knowledge this is the 1st time that this recently developed technique (at SNL)[1] has been applied to aqueous batteries. [1]Jungjohann, K. L. *et al. ACS Energy Lett.* **2021**, *6*, 2138.





After 10 cycles, a layer of ZHA (Zn,C,O by EDS) is observed to reversibly form at the interface.

In contrast, a much thicker ZHS layer (Zn,S,O by EDS) forms in the sulfate cells and reversibility appears to be minimal.

Corrosion is also seen in the bulk of the zinc electrode with $ZnSO_4$.

Conclusions

Reversibility of ZHX species does occur but is electrolyte dependent
- ZHA (acetate-based electrolytes) can form reversibly
- ZHS (sulfate-based electrolytes) forms irreversibly

Mechanistic considerations (critical for battery development) must take electrolyte into account
- Some electrolytes lead to reversible formation of ZHX species which suggests that their formation is part of the overall redox mechanism

Electrolytes that form soluble, reducible ZHX species may be preferable for use in Zn-ion batteries
- The commonly used sulfate may be less-than-ideal due to irreversible ZHS formation and bulk corrosion

Research into the complex mechanism of mildly acidic zinc and optimizing battery performance is ongoing

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