Mildly Acidic Acetate-Based Electrolytes for Zinc-Ion Batteries

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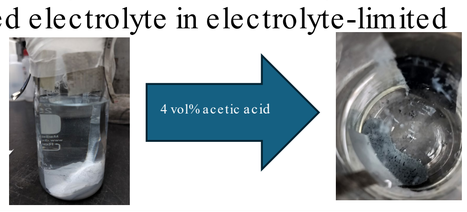
Project Overview

- Project Goal: Develop a low-cost and safe aqueous electrolyte for prospective high-voltage, energy-dense zinc-ion batteries. Mildly acidic, acetate electrolytes were previously shown to prevent passivating zinc oxide formation and have the potential to meet these goals.
- Current Practice: Most electrolytes used for zinc-ion batteries are sulfate-based and lead to low energy density and poor cycle life due to dissolution of the more attractive cathodes as well as formation of a zinchydroxysulfate blocking layer.
- Why CUNY Energy Institute: The institute has expertise in taking laboratory-scale research to commercial products.
- Innovation: There has been little work studying the acetate electrolyte chemistry. The high electrochemical window is attractive for higher voltage aqueous batteries.
- Impact: If successful, can lead to the production of low-cost, energy-dense zinc-ion batteries with higher operating voltages, a bottleneck that plagues aqueous batteries currently.
- Alignment: Low-cost Zn batteries can be made in the US from US sourced materials, consistent with OE's mission to maintain a reliable, affordable, secure, and resilient electricity delivery.

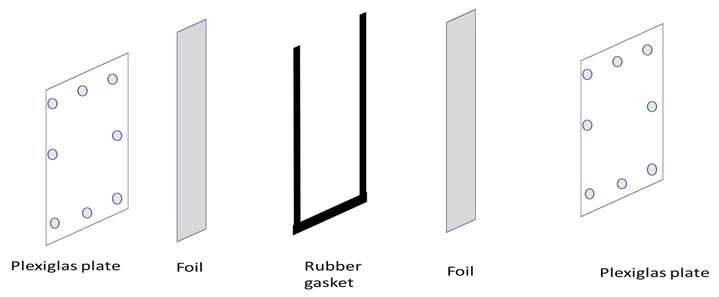
Background

- Previous work showed that lowering the concentration from 27 m to 5 m KOAc and mildly acidifying the electrolyte, through the addition of acetic acid, lead to successful zinc discharge at 5 mA/cm^2 without formation of irreversible zinc oxide formation.
- Work shown is a continuation of work pertaining to the electrolyte stability and zinc cyclability in this modulated acetate-based electrolyte in electrolyte-limited conditions.

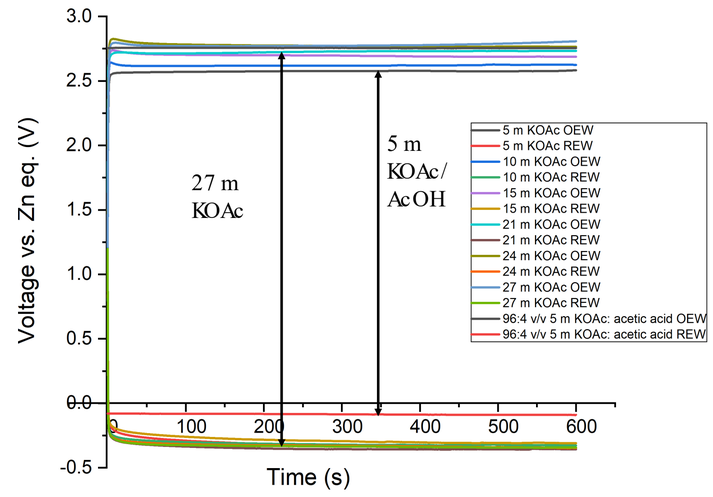


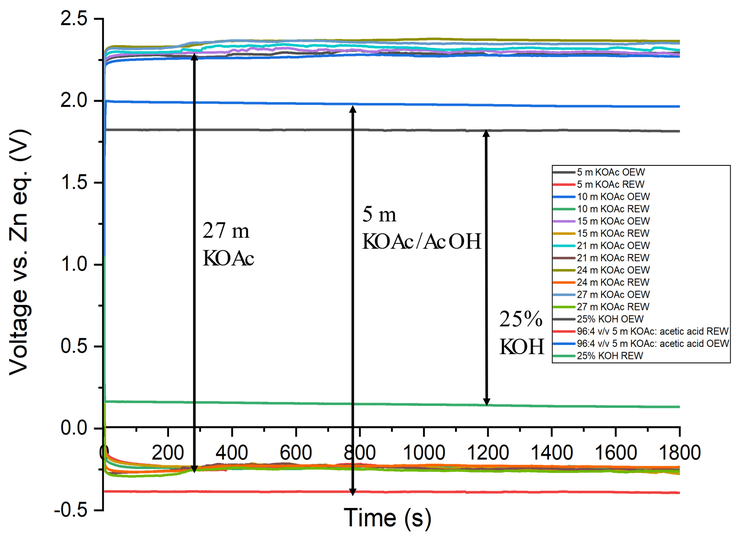
Electrolyte Electrochemical Stability Studies

Objective: Assess concentration-dependent electrolyte electrochemical stability and compare to 25% KOH when possible.



In-house apparatus used to study electrolyte stability windows. Constant current at a current density of 1 mA/cm^2 was applied. Zinc wire was used as the reference electrode for these experiments.



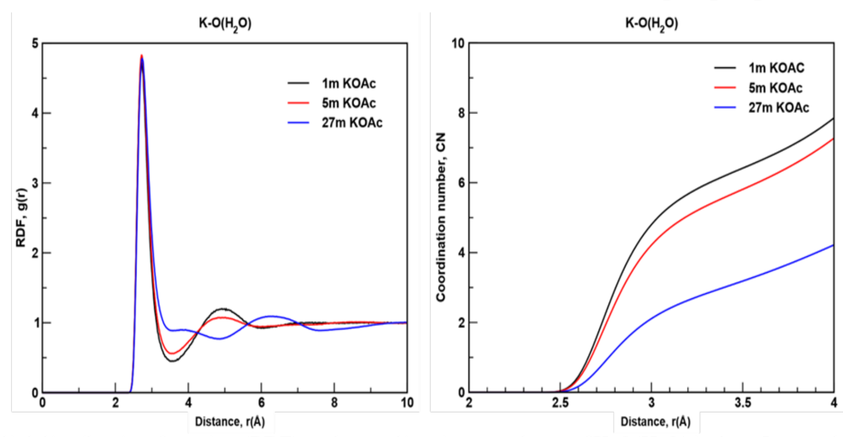


Electrochemical stability windows of KOAc electrolytes as a function of concentration on gold (top) and SS316L (bottom)

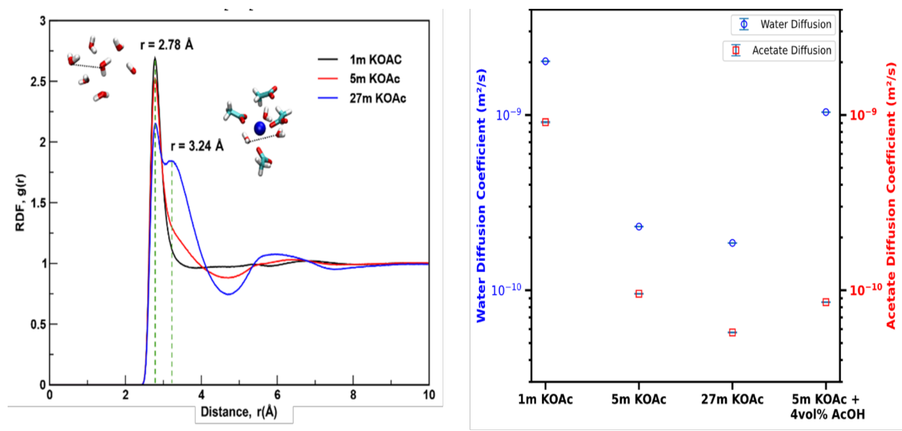
- 27 m KOAc has the highest electrochemical window (ECW) of 3.3 V on Au foil.
- Dilute concentrations of KOAc have similar stability windows.
- Acidifying the electrolyte leads to a reduction in the overall electrochemical stability due to reduced oxidative potential.
- The mildly acidic electrolyte has higher electrochemical window than 25% KOH.

Solvation structure of electrolyte

Objective: Investigating how ion coordination and local water environments evolve from dilute to highly concentrated electrolytes, and how these molecular interactions influence macroscopic properties.



Radial distribution function (RDF) and coordination numbers of K–O(H$_2$O) in 1m, 5m, and 27m KOAc electrolytes (figure above, left and right respectively)

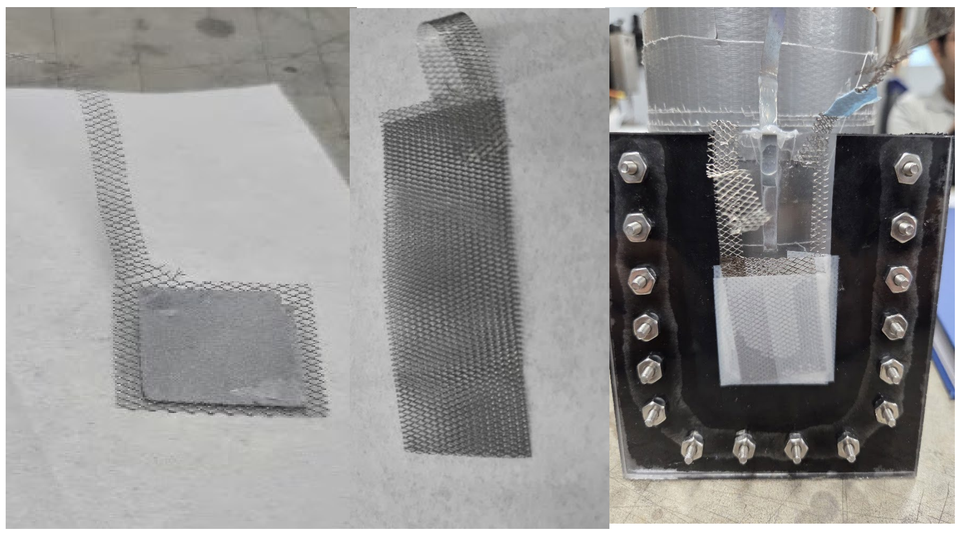


RDF illustrating water–water interactions in all electrolyte compositions (figure above, left) and water and acetate diffusion coefficients measured by ^{1}H PFG-NMR in 1m, 5m, and 27m KOAc, as well as 5m KOAc + 4 vol% acetic acid (figure above, right)

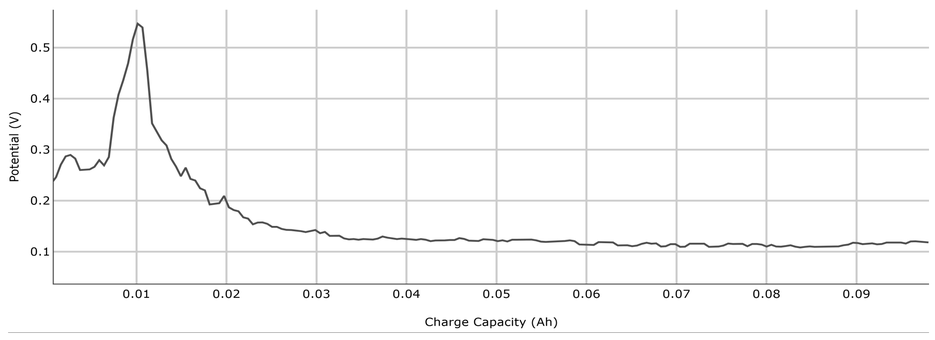
- As salt concentration increases, a depletion of free water molecules is observed, indicating a transition from a water-rich to an ionically coordinated environment.
- Addition of acetic acid increases water diffusion fivefold, implicating the presence of free water molecules in limiting the electrochemical window.

Zinc Single Discharge Study in 96:4 v/v 5 m KOAc: acetic acid: Electrolyte-Lean Conditions

Objective: Observe Zn stripping behavior from a powder electrode in a cell format and electrolyte volume that resembles practical conditions. Aimed at 10% Zn utilization.



95/5 Zn/PTFE powder electrode pressed onto a Ti mesh that was used as the current collector electrode (left) and picture of the prismatic-type cell format used (right). Zn foil was used as the reference electrode, oversized titanium mesh was used as the counter electrode (center) and the electrolyte volume used was ~3 mL, corresponding to ~ 0.003 mL/mAh. Active mass loading of 176.7 mg/cm^2.



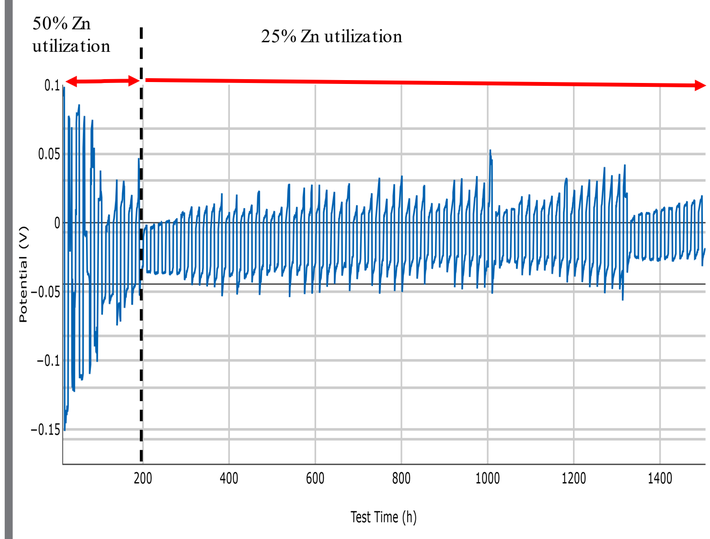
Voltage-Capacity curve of a representative Zn//Ti cell. Achieves 10% of Zn capacity!

Initial zinc mass pre-cycling (g)	Final zinc mass post-cycling @ 10% Zn utilization (g)	Mass difference	Zn utilization
1.14	1.026	0.114	10%

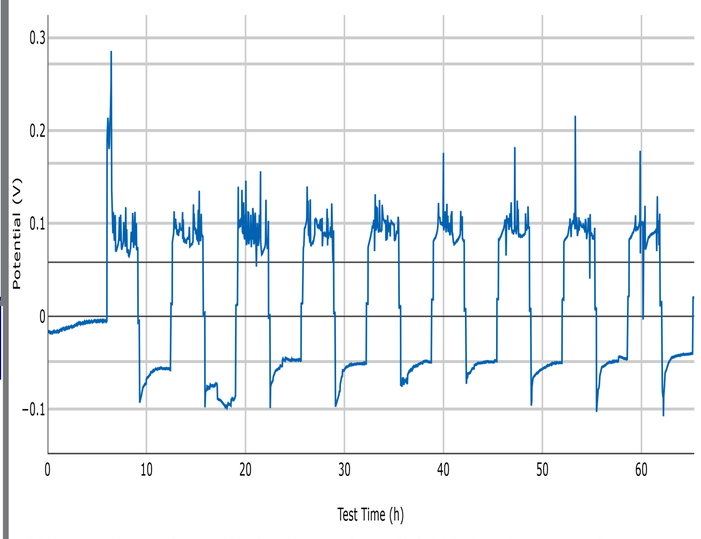
- Mass balance matches discharged capacity based on a single discharge.
- Can discharge zinc at a high areal capacity of ~14.5 mAh/cm^2.

Zinc cycling at 5 mA/cm^2

Objective: Test zinc reversibility in this electrolyte in both symmetric Zn//Zn and asymmetric Zn//Ti cells at 5 mA/cm^2.



Voltage-time curve of Zn//Zn foil prismatic, 3-electrode cell in 96:4 v/v% 5 m KOAc: acetic acid at 5 mA/cm^2. The first 5 plating-stripping cycles were based on 50% DOD, whereas subsequent cycling was based on 25% DOD. The reference electrode is Zn wire.



Voltage-time plots of a 3-electrode cell 95/5 Zn/PTFE powder electrode as the working electrode, Zn foil as the reference electrode and oversized titanium mesh as the counter electrode. 0.1 m zinc acetate was added to the electrolyte. Cells run at 5 mA/cm^2 with a capacity limitation of ~14.5 mAh/cm^2

- This mildly acidic electrolyte was successful in cycling Zn//Zn foil symmetric cell at 25% utilization for ~75 cycles.
- In Zn//Ti cells, we are able to get 10% utilization of Zn for 10 cycles (cells still cycling)

Future Work

- Zn//Zn and Zn//Ti cells show promise of zinc cyclability at 5 mA/cm^2 in the acetate electrolyte.
- Current and future work will focus on the improving Zn cycling efficiency and testing of cathodes in this electrolyte.

Acknowledgements

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