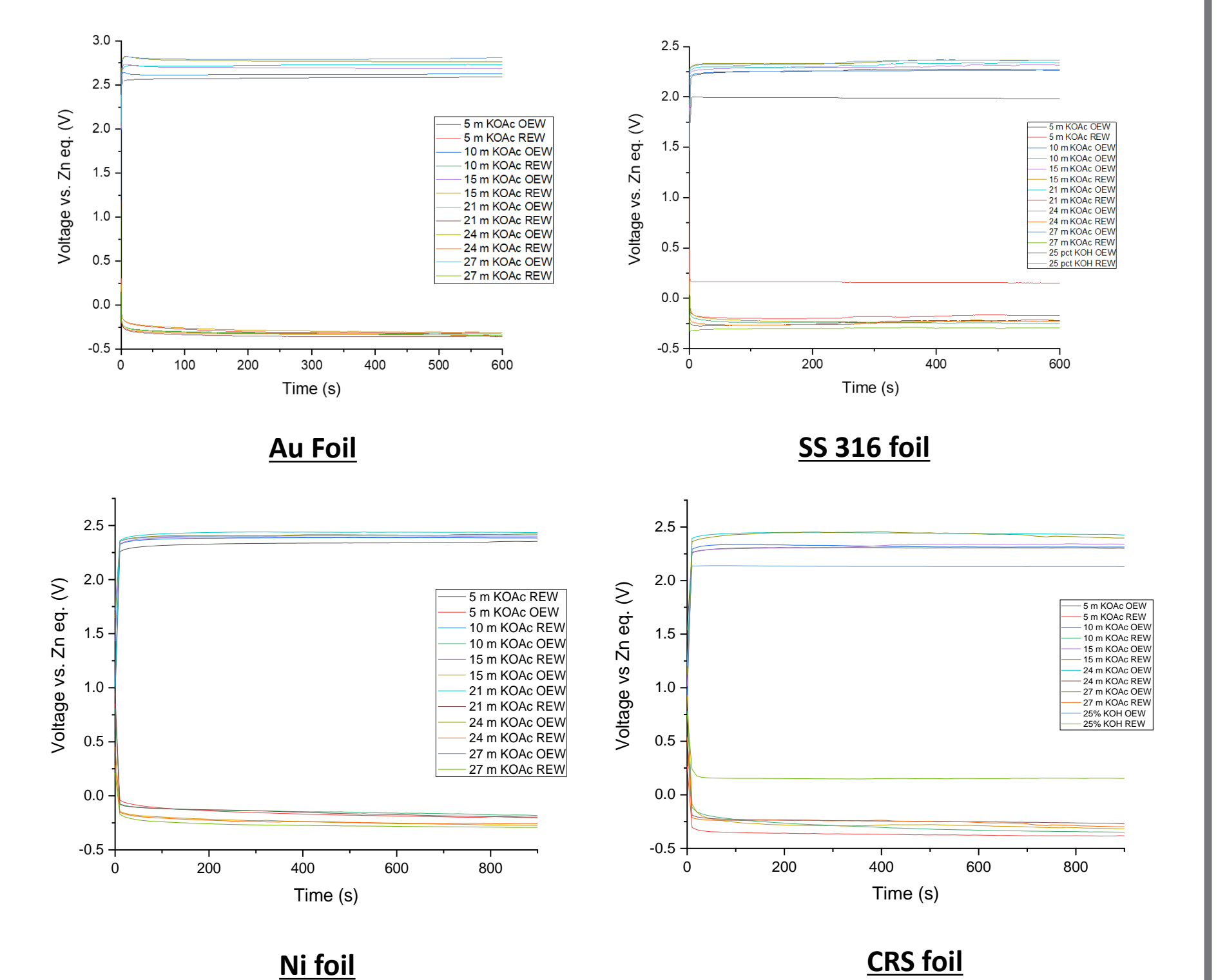


## Abstract

Grid scale batteries need to be inexpensive to manufacture, safe to operate, and non-toxic in composition. Thus, aqueous-based zinc aqueous (alkaline) batteries are ideal candidates for this end-use, but good cycle life and utilization of the zinc has proven difficult partly because zinc is susceptible to H<sub>2</sub> gas evolution in aqueous electrolytes. Additionally, the energy density of the battery gets limited by the aqueous nature of the electrolyte, which has a narrow electrochemical stability window. Water-in-salt electrolyte (WiSE) can address this shortcoming by lowering the activity of free water molecules in solution, thus reducing H<sub>2</sub> gas evolution. In this work, we show this extended stability window as well as reduced hydrogen gas evolution on a zinc electrode in various concentrated-acetate based electrolytes in comparison to 25% potassium hydroxide electrolyte solution.

## Electrochemical stability window (ECSW) on current collectors



Voltage-time plots of electrochemical stability of various concentrations of acetate-based electrolytes (both dilute and concentrated) on gold (top left), stainless steel 316 (top right), nickel (bottom left) and cold-rolled steel (bottom right) substrates.

Constant current at 1 mA/cm<sup>2</sup> were used for these experiments. The plateaus correspond to reactions where electrolyte is degrading to form hydrogen or oxygen.

Electrolyte (m)	Reductive limit (V vs. Zn)	Oxidative limit (V vs. Zn)	Electrochemical Window
5 m KOAc	-0.31	2.59	2.9
10 m KOAc	-0.33	2.62	2.95
15 m KOAc	-0.31	2.69	3.0
21 m KOAc	-0.36	2.73	3.09
24 m KOAc	-0.35	2.77	3.12
27 m KOAc	-0.34	2.81	3.15

Summary of ECSWs of acetate-based electrolytes on Au foil. 25% KOH ECSW could not be measured due to its reactivity upon passage of current.

The data shows a slight rise in the window as the concentration of potassium acetate in water is increased.

Electrolyte Concentration (m)	Reductive limit (vs Zn.)	Oxidative limit (vs Zn.)	Electrochemical Window
5 m KOAc	-0.20	2.37	2.57
10 m KOAc	-0.18	2.38	2.57
15 m KOAc	-0.27	2.40	2.67
21 m KOAc	-0.29	2.43	2.72
24 m KOAc	-0.26	2.42	2.69
27 m KOAc	-0.30	2.42	2.72

Summary of ECSWs of acetate-based electrolytes on Ni foil

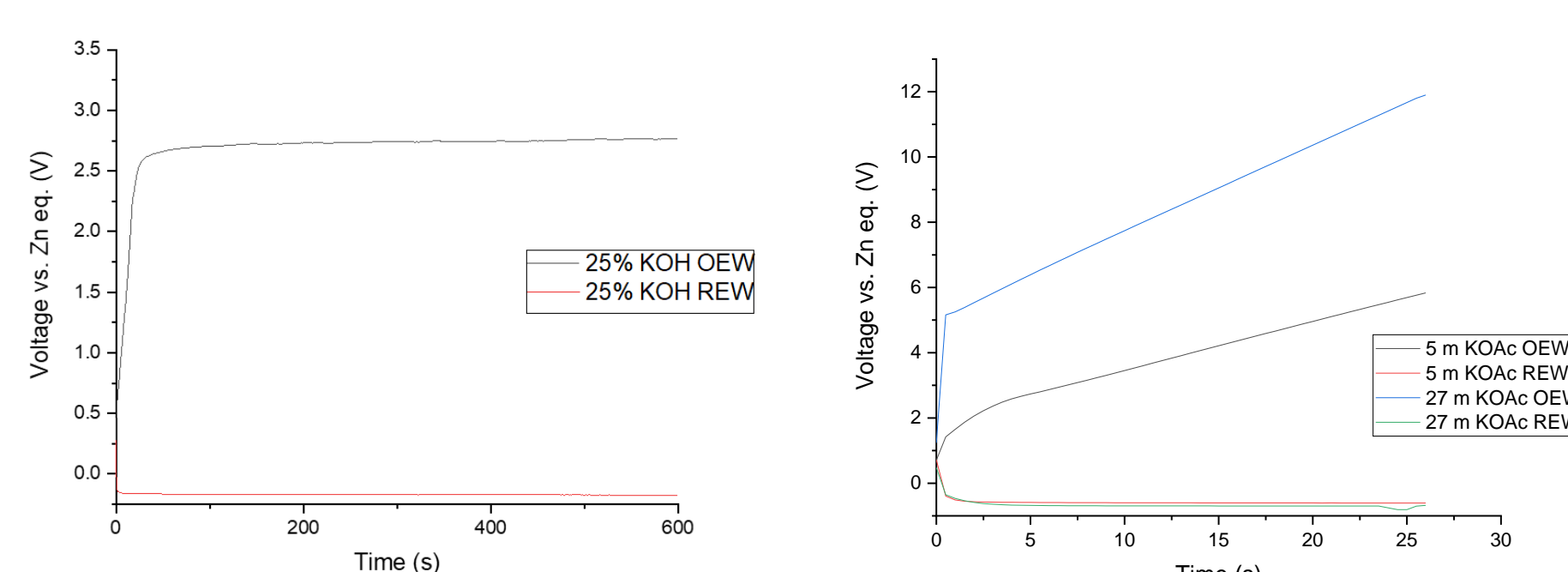
Electrolyte (m)	Reductive limit (V vs. Zn)	Oxidative limit (V vs. Zn)	Electrochemical Window
5 m KOAc	-0.22	2.24	2.46
10 m KOAc	-0.24	2.27	2.51
15 m KOAc	-0.28	2.28	2.56
21 m KOAc	-0.26	2.31	2.57
24 m KOAc	-0.24	2.36	2.6
27 m KOAc	-0.28	2.36	2.64
25% KOH	0.13	1.96	1.83

Summary of ECSWs of acetate-based electrolytes compared to 25% KOH on SS 316 foil

Electrolyte Concentration (m)	Reductive limit (vs Zn)	Oxidative limit (vs Zn)	Electrochemical Window
5 m KOAc	-0.38	2.30	2.68
10 m KOAc	-0.35	2.31	2.66
15 m KOAc	-0.32	2.34	2.66
24 m KOAc	-0.27	2.43	2.70
27 m KOAc	-0.30	2.40	2.70
25% KOH	0.15	2.13	1.98

Summary of ECSWs of acetate-based electrolytes compared to 25% KOH on CRS foil

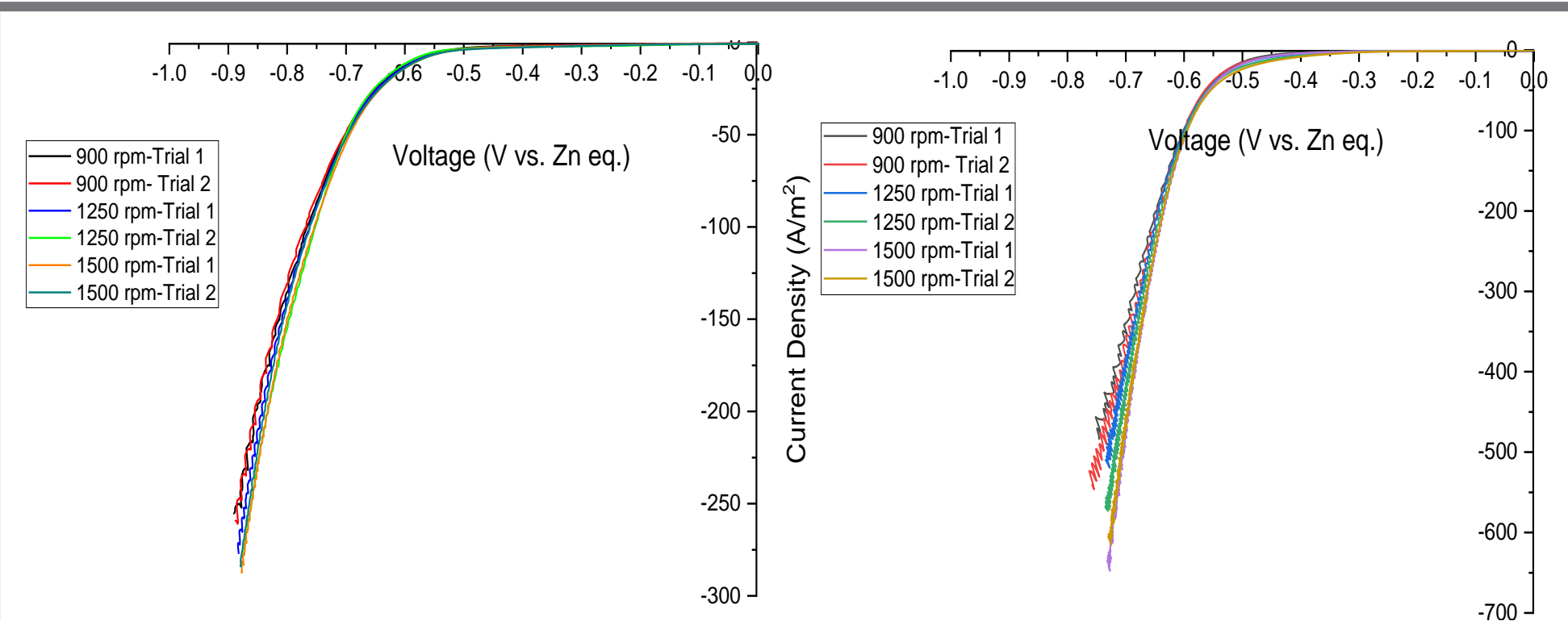
There is an obvious expansion in the electrochemical stability window when using acetate-based electrolytes over conventional, KOH-based electrolytes.



Voltage-time plots of electrochemical stability of 25% KOH (left) and 5 and 27 m KOAc (right) on titanium foil

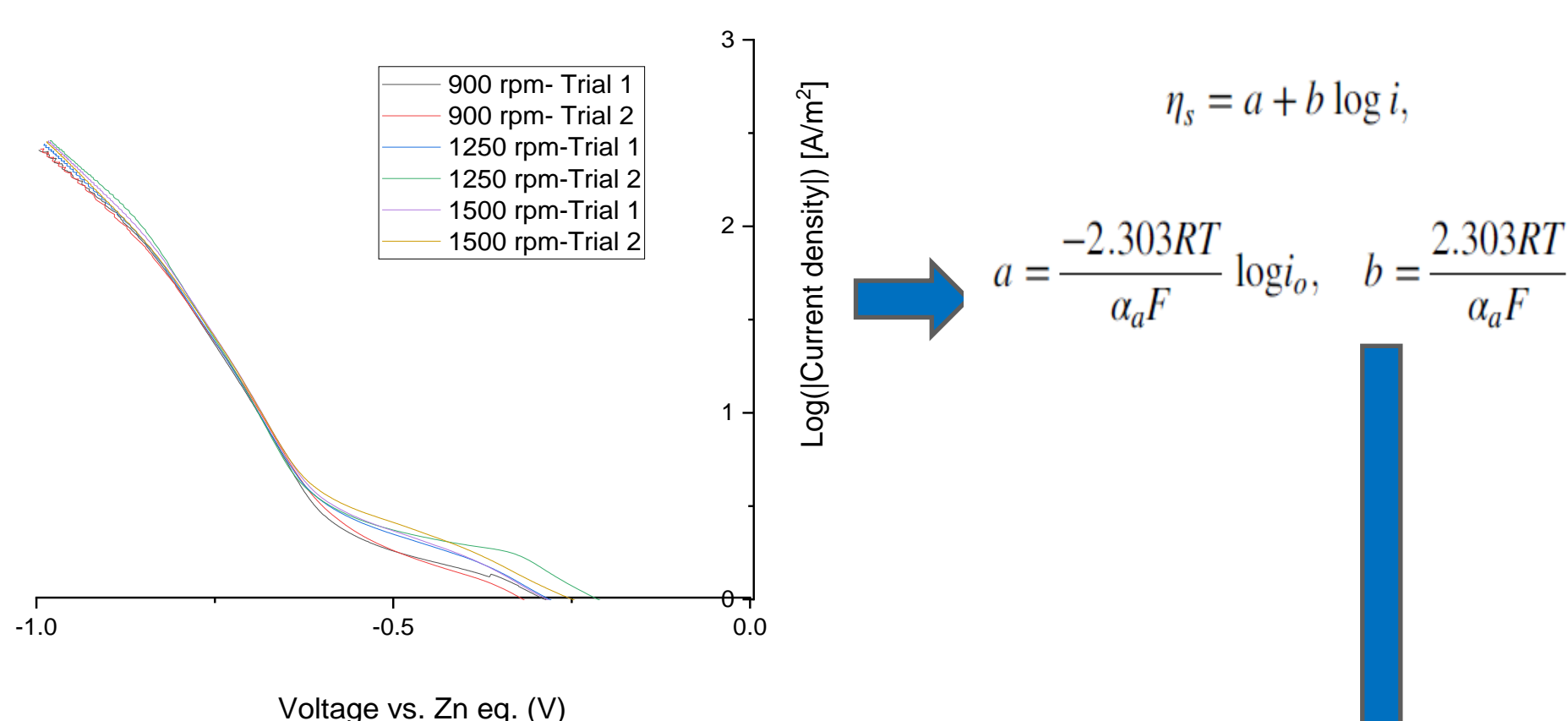
The oxidative stability window of 25% KOH is remarkably improved on Ti foil. Additionally, no oxygen evolution is measured on Ti for all concentrations of acetate-based electrolytes!

## HER: Gassing rates and kinetic parameters



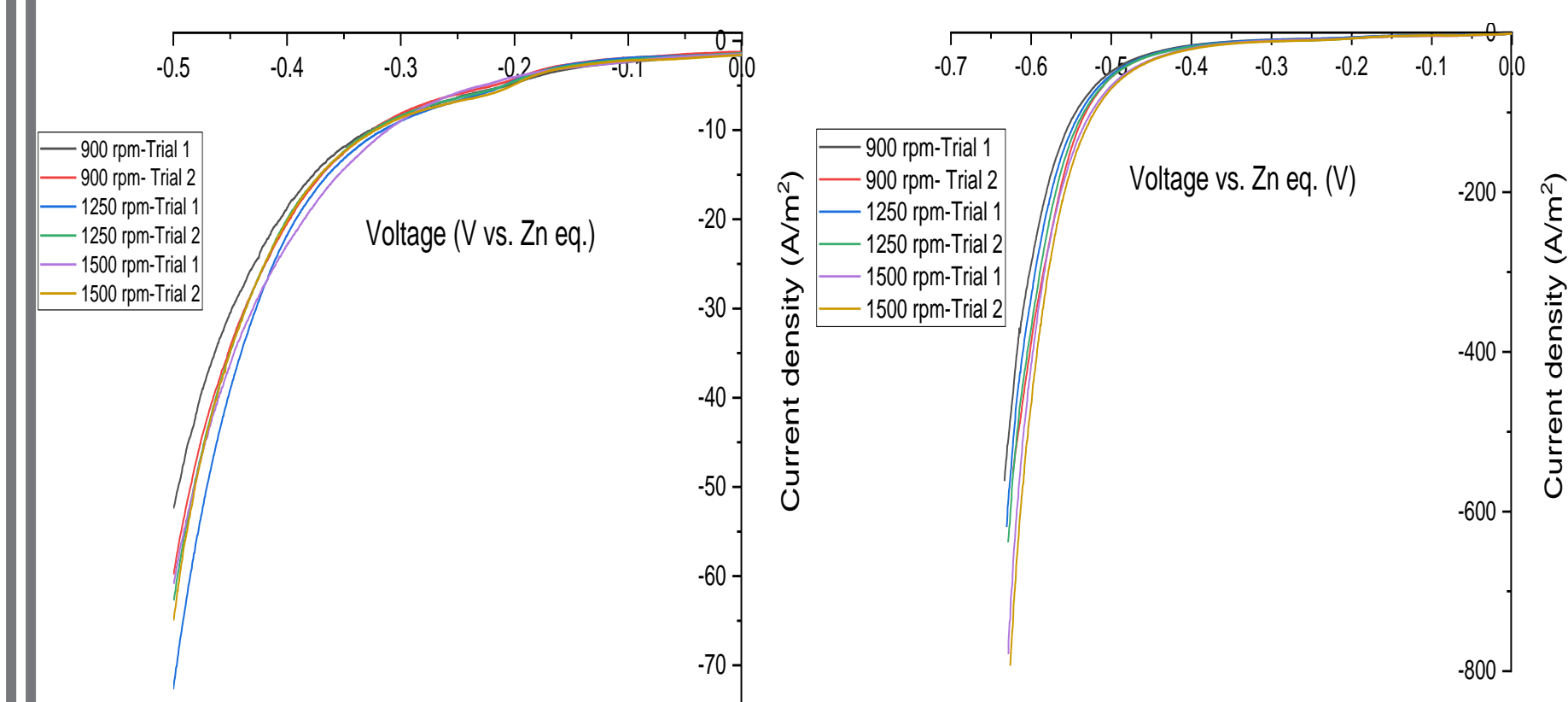
Volammetric curves for HER on a glassy carbon [GC] (top) and zinc (bottom) rotating-disk electrode (RDE) in 27 m KOAc at 900, 1250 and 1500 rpm rotation rates

The HER is observed to be controlled by both mass-transfer and kinetic effects on a GC electrode except at overpotentials of 630-820 mV, where kinetics dominate, evidenced by no change in current in this potential range.



Tafel plot of HER in 27 m KOAc on GC RDE

Tafel slope (mV/dec)	Exchange Current density $i_0$ (A/m <sup>2</sup> ) [x 10 <sup>-9</sup> ]
71.5 ± 2.3	6.03 ± 3.85



Volammetric curves for HER on a GC (left) and zinc (right) rotating-disk electrode (RDE) in 25% KOH at 900, 1250 and 1500 rpm rotation rates

Not possible to decouple the effects of mass-transfer vs. kinetics for the HER in 25% KOH.

## H<sub>2</sub> Gassing Rates in 25% KOH H<sub>2</sub> Gassing Rates in 27 m KOAc

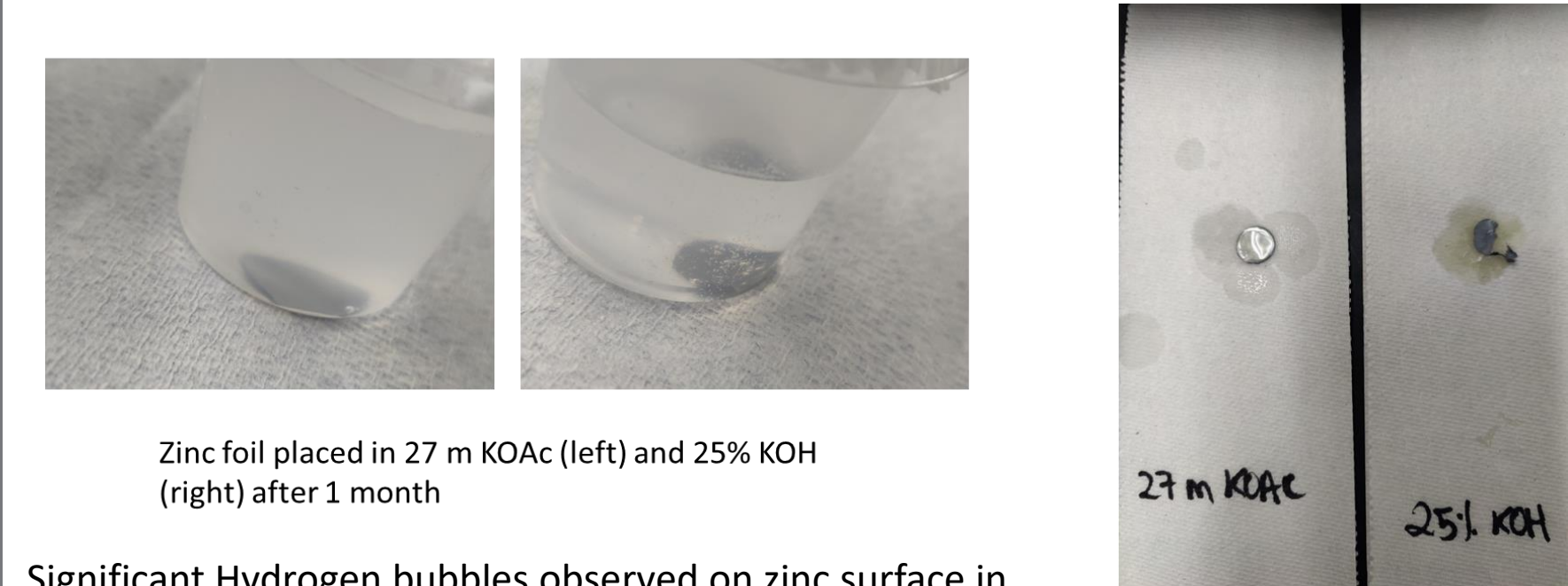
Overpotential vs. Zn eq. (mV)	Average molar H <sub>2</sub> rates @ 900 rpm (mol/cm <sup>2</sup> ) x 10 <sup>3</sup>	Average molar H <sub>2</sub> rates @ 1250 rpm (mol/cm <sup>2</sup> ) x 10 <sup>3</sup>	Average molar H <sub>2</sub> rates @ 1500 rpm (mol/cm <sup>2</sup> ) x 10 <sup>3</sup>
100	1.11 ± 0.17	1.04 ± 0.01	1.18 ± 0.01
200	2.36 ± 0.17	2.34 ± 0.01	2.31 ± 0.30
300	4.29 ± 0.06	4.52 ± 0.21	4.58 ± 0.12
400	10.21 ± 0.7	10.9 ± 0.4	11.2 ± 0.1
500	29.3 ± 1.2	35.3 ± 3.5	32.8 ± 1.7

Overpotential vs. Zn eq. (mV)	Average molar H <sub>2</sub> rates @ 900 rpm (mol/cm <sup>2</sup> ) x 10 <sup>3</sup>	Average molar H <sub>2</sub> rates @ 1250 rpm (mol/cm <sup>2</sup> ) x 10 <sup>3</sup>	Average molar H <sub>2</sub> rates @ 1500 rpm (mol/cm <sup>2</sup> ) x 10 <sup>3</sup>
100	3.51 ± 0.55	4.43 ± 0.81	4.17 ± 0.49
200	5.24 ± 0.51	7.05 ± 1.70	6.12 ± 0.53
300	7.37 ± 0.29	9.58 ± 0.96	9.48 ± 0.64
400	9.64 ± 0.10	12.1 ± 0.42	13.0 ± 0.95
500	16.6 ± 1.09	18.3 ± 0.07	19.6 ± 0.96

The results show up to 4 orders of magnitude decrease in gas generation on zinc in 27 m KOAc vs. 25% KOH.

## Zinc corrosion in 25% KOH vs. WiSE



Zinc foil placed in 27 m KOAc (left) and 25% KOH (right) after 1 month

Significant Hydrogen bubbles observed on zinc surface in 25% KOH!

## Conclusions and Future Work

- The acetate-based "water-in-salt" electrolyte show tremendous promise as a low-cost, eco-friendly strategy to bolster the electrochemical stability of aqueous-based electrolytes, displaying the highest electrochemical window of 3.15 V on a gold surface.
- The electrochemical stability of several WiSE solutions were measured on several practical current collector surfaces and compared with 25% KOH.
- The gassing rates of hydrogen evolution were compared in 27 m KOAc and KOH and show up to ~ 10000 times reduced H<sub>2</sub> generation.
- Zinc shows no signs of corrosion in the KOAc-WiSE when compared to 25% KOH after exposed for 1 month, which is advantageous for long-term storage of the zinc anode.
- Future work will focus on:
  - Zinc electroplating/stripping studies at realistic current densities
  - Finding strategies to reduce the viscosity of the WiSE electrolytes in order to improve ionic conductivity
  - Continued testing of cathode materials in these acetate-based electrolyte systems to achieve a higher discharge potential than manganese-dioxide based cathodes
  - Using non-aqueous solvents as supporting electrolytes
  - Hybrid KOH/acetate WiSE electrolytes

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