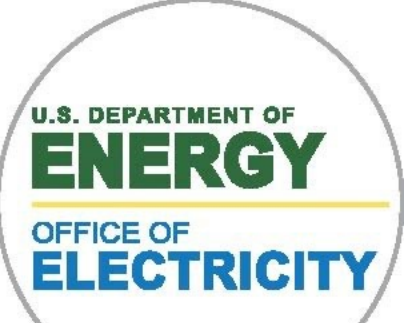


Practicality and electrochemistry of acetate water-in-salt electrolyte (WiSE) for zinc battery cycling

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Background

Water-in-salt electrolyte (WiSE) receives great attention recently as a method to boost the voltage stability of aqueous electrolyte batteries. Despite the many publications, practical or realistic battery testing is missing from the literature.

Here we test potassium acetate (K Ac) WiSE with a practical cell design and commercially-relevant coulombic areal capacity and current density. We also test the prevailing literature explanation for the physical reason for the increase of electrolyte voltage stability.

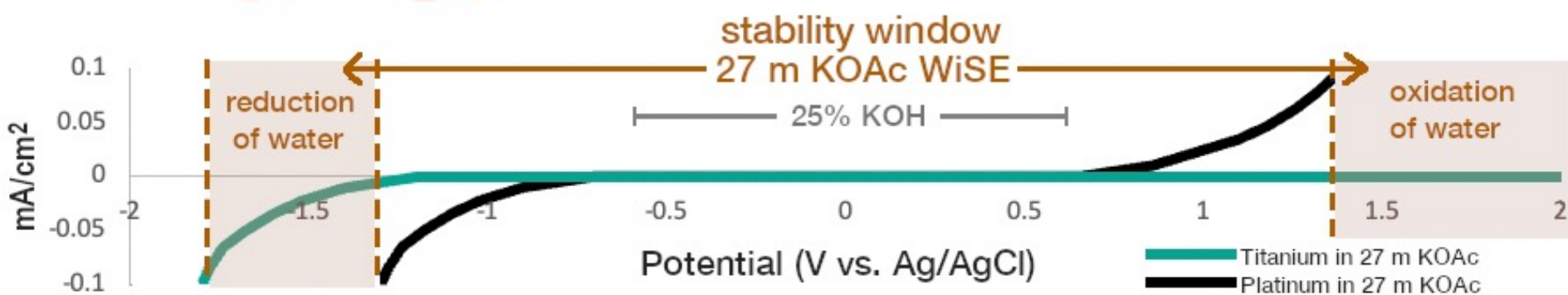
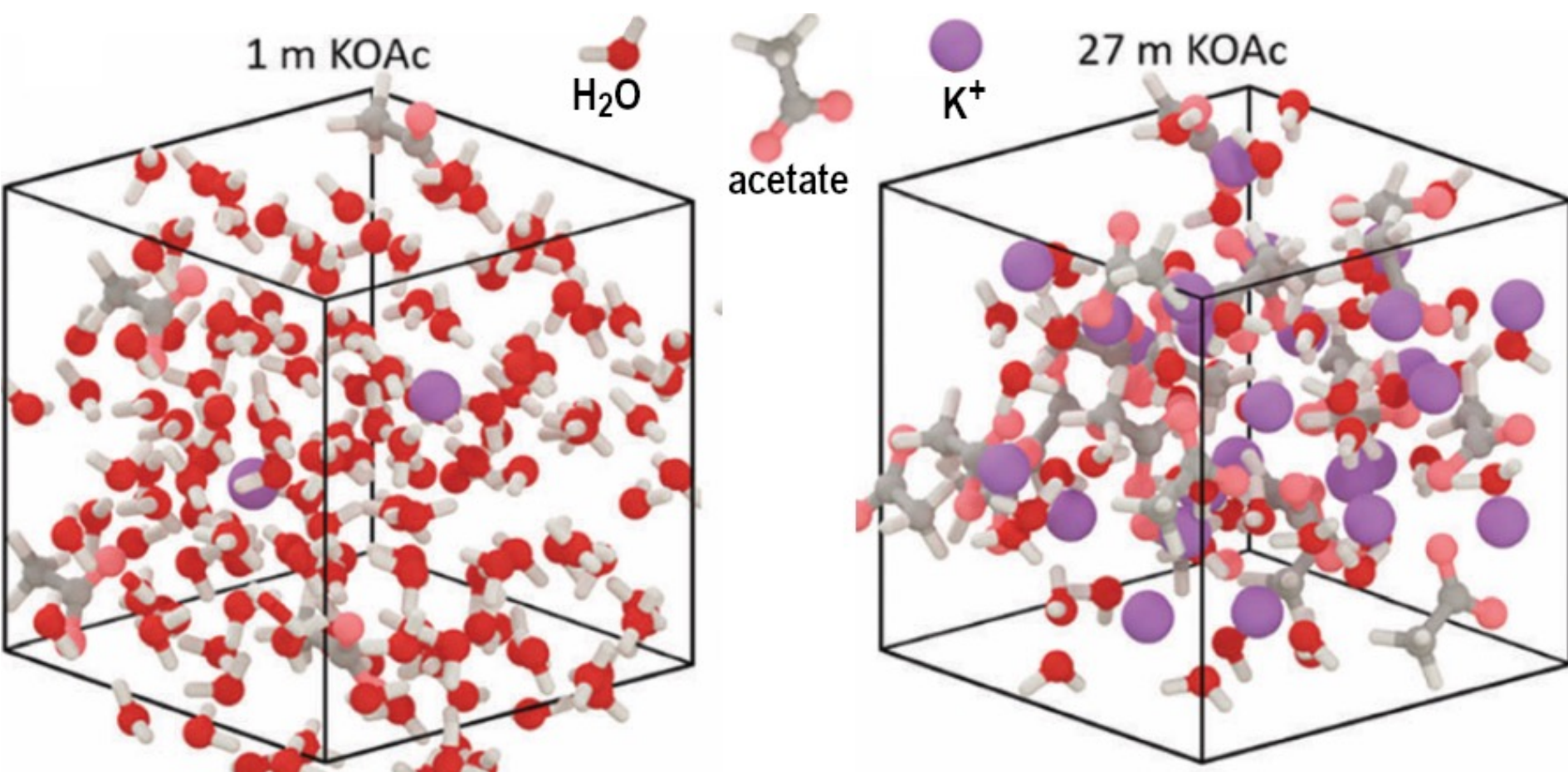
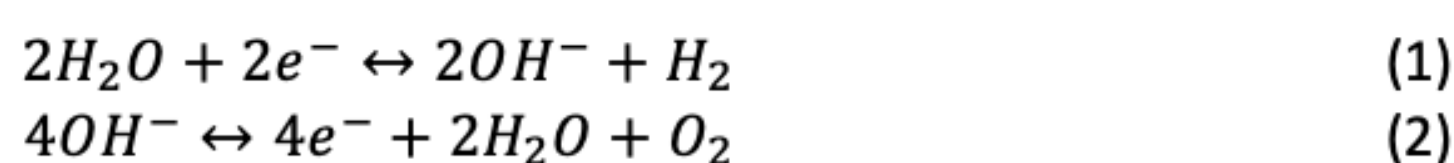


Fig. 1. Molecular model of 1 molal KAc vs. 27 m KAc WiSE, and the resulting increase of electrolyte stability window, both modified from Lukatskaya et al. 2018 with permission from The Royal Society of Chemistry.

Theory of Electrolyte Voltage Stability

Development of high-voltage batteries requires a better understanding of the physical mechanisms of electrolyte voltage-stability. Recently WiSE electrolyte has attracted much research activity due to its expanded stability window. Many high profile publications claimed¹⁻⁷ a reduction of the water activity created expanded voltage stability, a hypothesis that assumes electrolyte voltage-stability is controlled by degradation of water via



where equilibrium occurs by balance of chemical μ and electron ϕ potentials

$$2\mu_{H_2O} - 2F\phi_{HER} = 2\mu_{OH^-} + \mu_{H_2} \quad (3)$$

$$4\mu_{OH^-} = -4F\phi_{OER} + 2\mu_{H_2O} + \mu_{O_2} \quad (4)$$

and where the values of ϕ are with respect to the same (arbitrary) reference potential used for μ_{OH^-} or μ_{H^+} . The stability window $\Delta\phi_{eW}$ is then

$$\Delta\phi_{eW} = \phi_{OER} - \phi_{HER} = -\frac{1}{2F}(\mu_{H_2O} - \mu_{H_2} - \frac{1}{2}\mu_{O_2}) \quad (5)$$

where the quantity in parentheses of (5) is commonly known as water's free energy of formation $\mu_{H_2O}^{form} = \mu_{H_2O} - \mu_{H_2} - \frac{1}{2}\mu_{O_2}$, yielding

$$\Delta\phi_{eW} = -\mu_{H_2O}^{form}/2F \quad (6)$$

The well-known value for free energy of formation of pure water at STP is $\mu_{H_2O}^{form} = 237.13$ kJ/mole, which when plugged into equation (6) calculates a stability window of 1.23 V for water, in agreement with experiment. Only blocking layers (e.g. SEIs) offer an alternative mechanism.

Here we show that WiSE do not gain voltage-stability from reduction of water activity, for which we present evidence from direct measurements of water activity in WiSE solutions. The true mechanism mediating electrolyte voltage-stability is likely solid-electrolyte blocking layers.

Water's molecular free energy (activity) in WiSE solution was measured via vapor pressure measurements at equilibrium in overlying gases. The variation in water's activity in WiSE vs. 25% KOH was less than 1% variation. Figure 2 shows the data and the lack of connection between H₂O activity and WiSE stability.

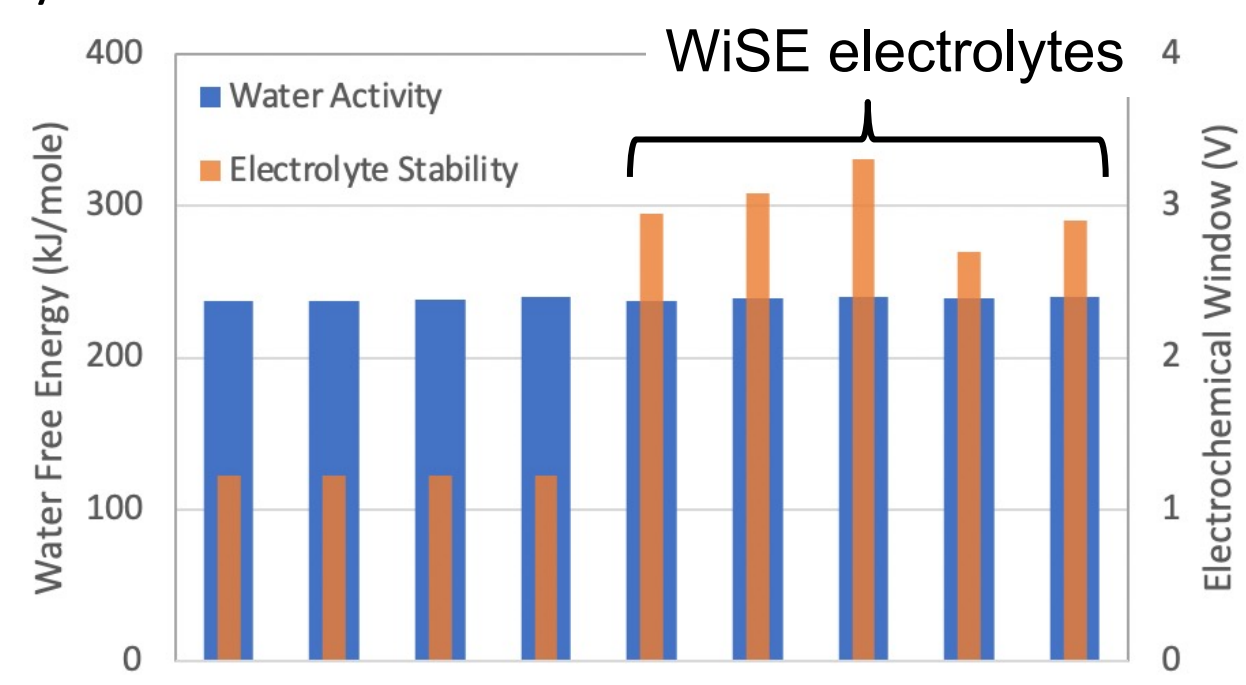


Fig. 2. Electrolyte voltage-stability (orange) does not correlate with H₂O activity (free energy) in WiSE solution.

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Electrochemistry of K-Acetate WiSE Electrolyte

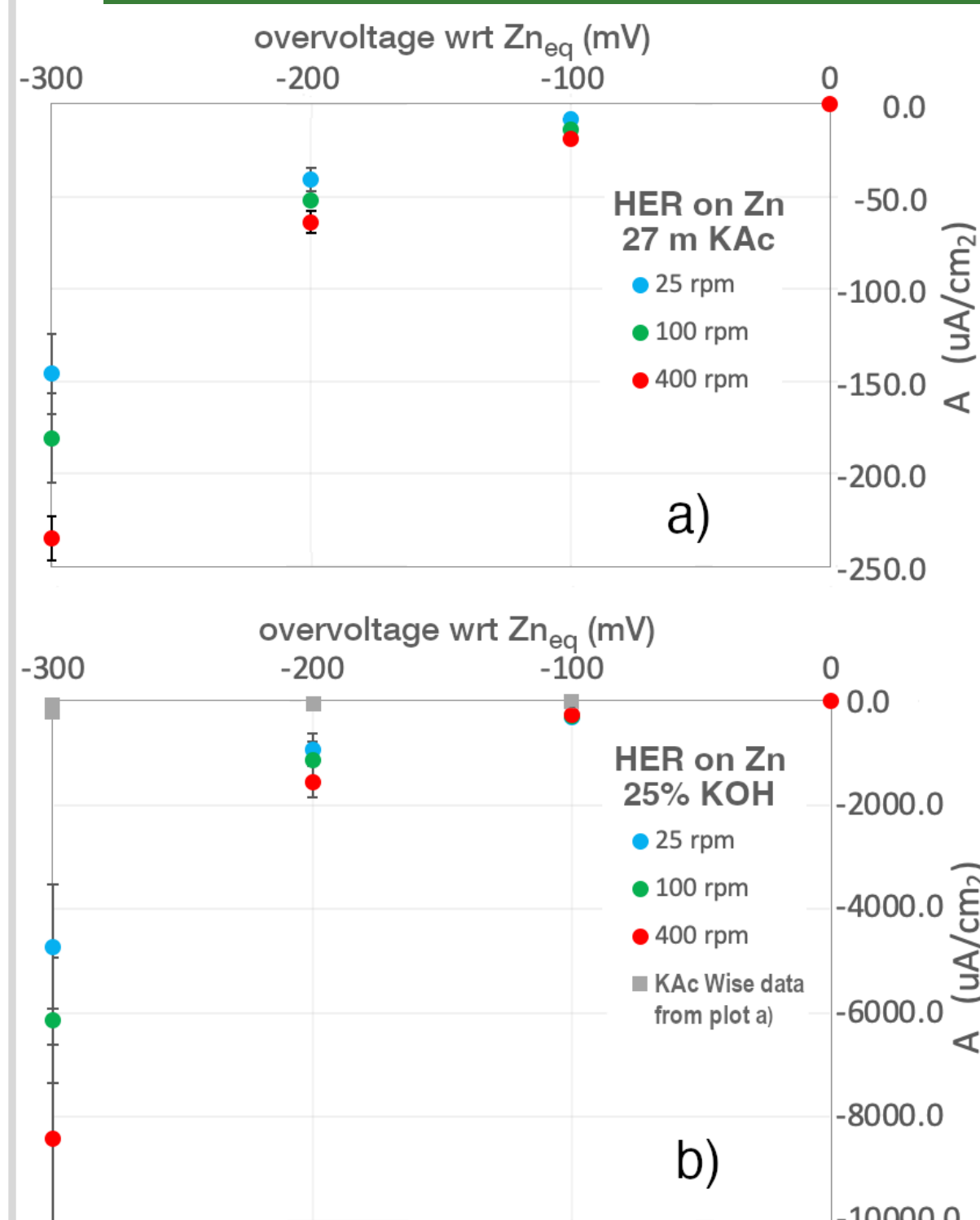


Fig. 3. Hydrogen evolution reaction via decomposition, 27 mKAc WiSE vs. traditional electrolyte (25% KOH).

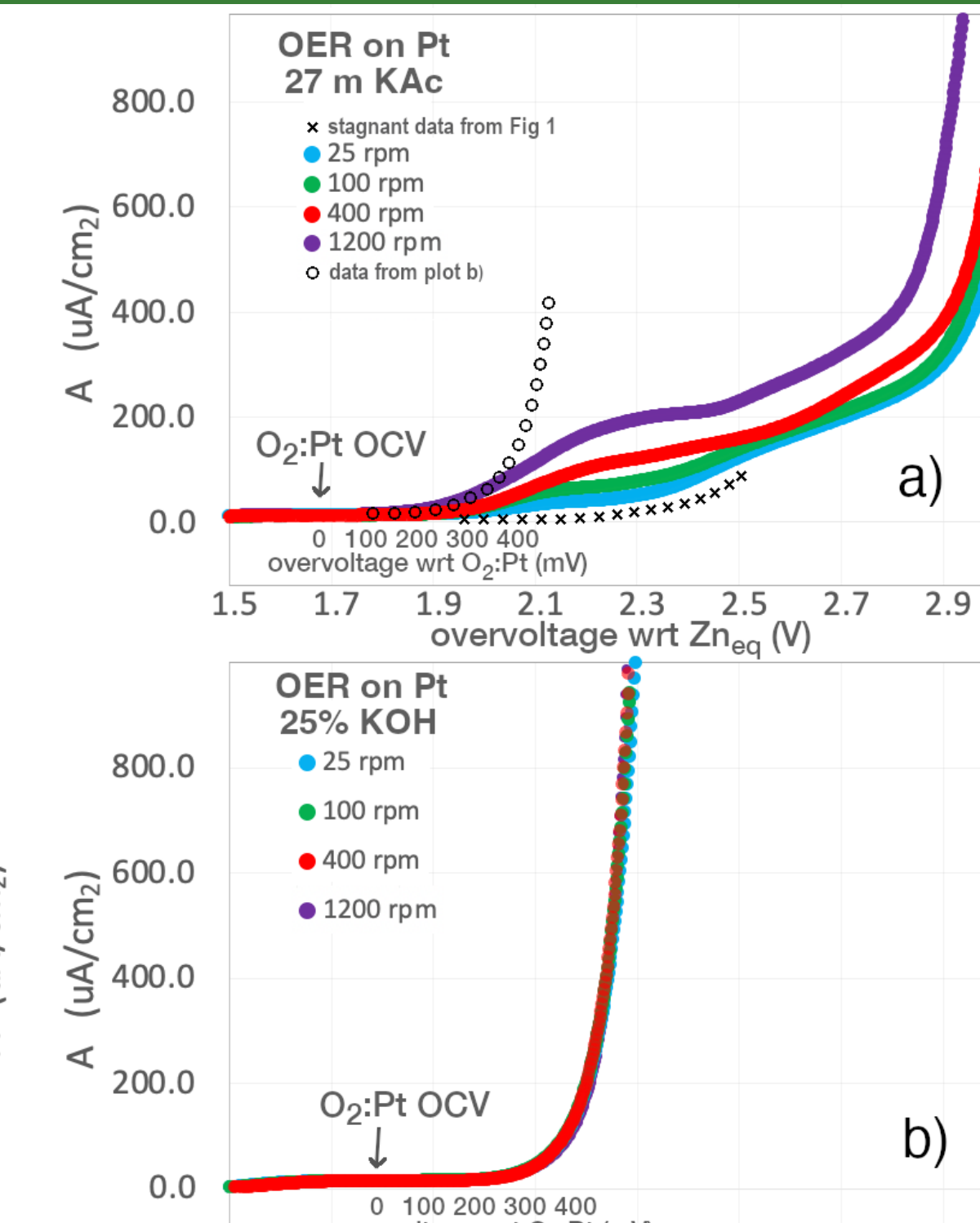


Fig. 4. Oxygen evolution reaction via electrolyte decomposition, 27 mKAc WiSE vs 25% KOH.

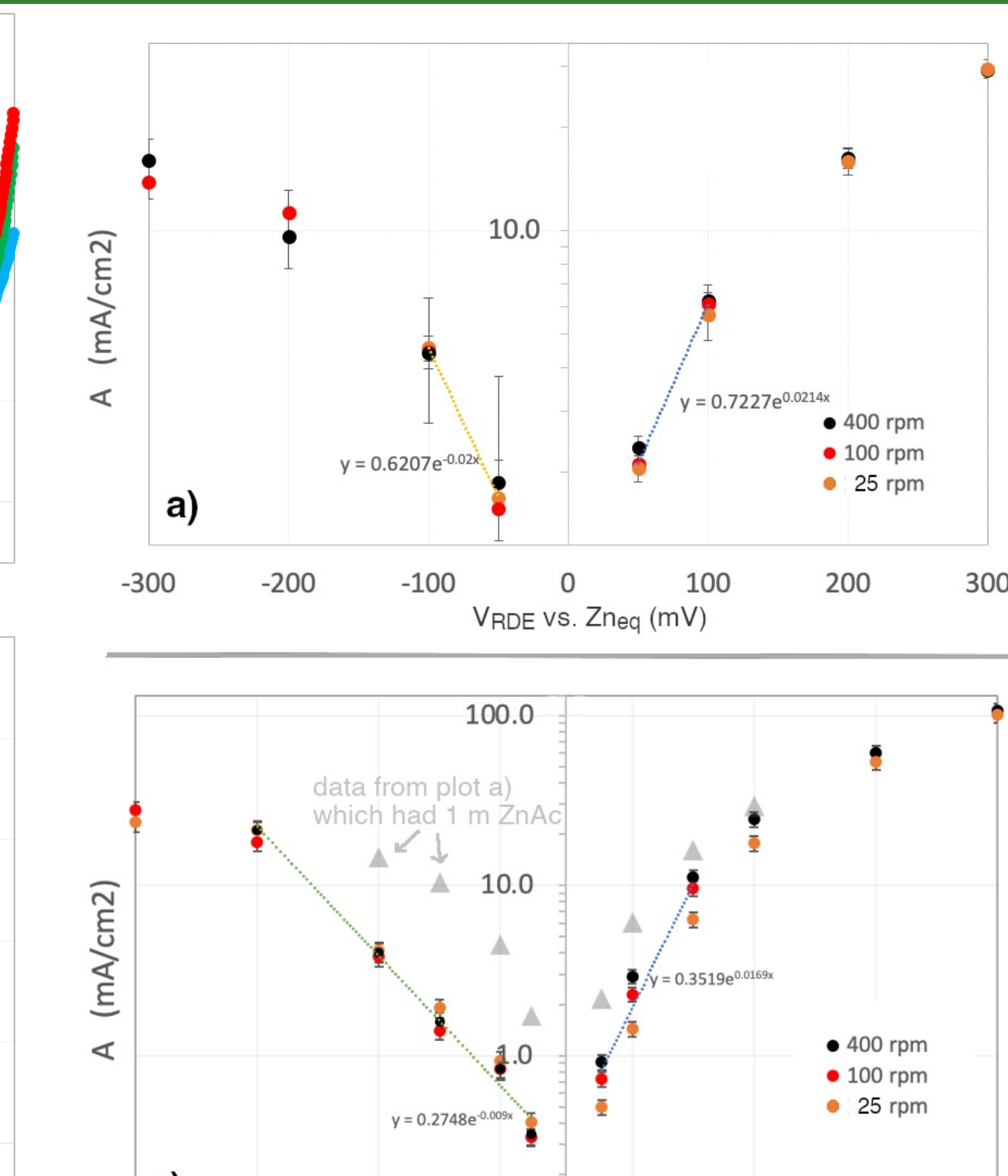


Fig. 5. Zn plating/deplating in 27 mKAc WiSE.

Hydrogen evolution in KAc WiSE (Fig 3) shows a ~100 mV shift of onset and is 40x lower than in 25% KOH, and although the mechanism for this reduction is unknown a leading hypothesis is that higher OH⁻ concentration speeds up the rate-limiting step of converting adsorbed H to H₂. Oxygen evolution in KAc WiSE electrolyte (Fig 3) shows a 400 mV shift of onset voltage but this shift can be eliminated by stirring (RDE rotation), thus the voltage-stability mechanism seems to be a SEI-like blocking layer. Zinc plating/deplating in WiSE occurs with a ~20x lower Tafel slope than in 25% KOH⁸, likely also due to blocking layers.

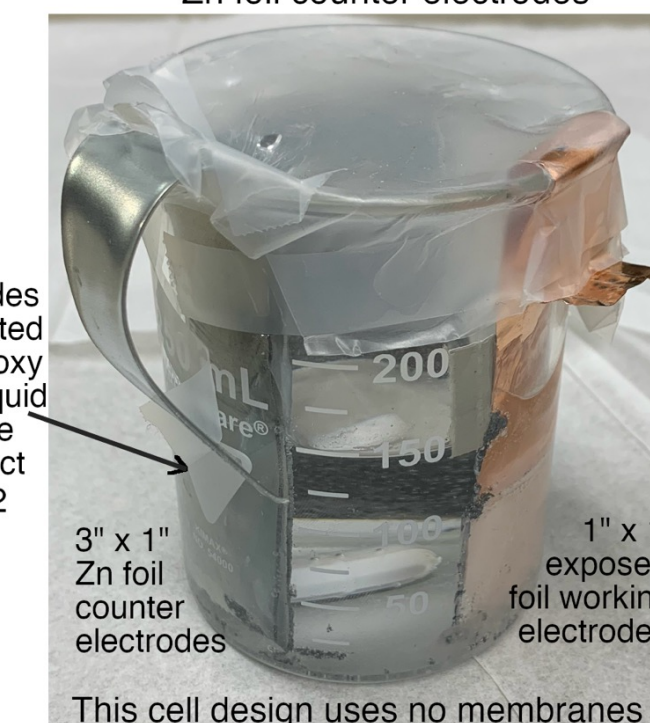
Practical Cell Design Cycle Testing

Cell Design: Tightly-Packed Industrial
1.5 mL of electrolyte per 100 mAh cycled attempted to cycle 27 mAh cm⁻² Zn foil counter electrodes



Cell Design	Electrolyte	Current Density	Performance
3 layers of cellophane	27:1 m K:Zn Ac WiSE	1 mA cm ⁻²	fail: >1V
Zn foil			fail: >1V
2 g Zn pow. w. 3% PFTE			fail: >1V
3 layers of celguard	27:1 m K:Zn Ac WiSE	1 mA cm ⁻²	fail: >1V
Zn foil			fail: >1V
2 g Zn pow. w. 3% PFTE			fail: >1V
1 layer of cellophane	5:3 m K:Zn Ac WiSE	1 mA cm ⁻²	fail: >1V
Zn foil			fail: >1V
Zn pow. w. 3% PFTE			fail: >1V
Zn mesh			fail: >1V
1 layer of cellophane	12:5 m K:Zn Ac WiSE	1 mA cm ⁻²	fail: >1V
Cu foil vs. Zn foil			fail: >1V
25% w% KOH electrolyte	25% w% KOH electrolyte	1 mA cm ⁻²	7~5 mV, c.e. ~99%

Cell Design: Excessive Volume and Electrolyte
90 mL of electrolyte per 100 mAh cycled attempted to cycle 27 mAh cm⁻² Zn foil counter electrodes



Cell Design	Electrolyte	Current Density	Performance
no membrane, 2 cm gap, unstirred	27:1 m K:Zn Ac WiSE	1 mA cm ⁻²	fail: c.e.~60%
Cu foil vs. Zn foil			fail: c.e.~40%
Ni foil vs. Zn foil			fail: c.e.~40%
Ti foil vs. Zn foil			fail: c.e.~40%
Sn foil vs. Zn foil			fail: c.e.~40%
no membrane, 2 cm gap, stirred	27:1 m K:Zn Ac WiSE	1 mA cm ⁻²	fail: c.e.~80%, chaotic
Cu foil vs. Zn foil			fail: c.e.~70%, chaotic
Ni foil vs. Zn foil			fail: c.e.~60%, chaotic
Ti foil vs. Zn foil			fail: c.e.~50%, chaotic
Sn foil vs. Zn foil			fail: c.e.~50%, chaotic
no membranes, 2 cm gap, unstirred	5:3 m K:Zn Ac WiSE	1 mA cm ⁻²	fail: c.e.~80%, chaotic
Cu foil vs. Zn foil			fail: c.e.~75%, chaotic
no membranes, 2 cm gap, stirred	5:3 m K:Zn Ac WiSE	1 mA cm ⁻²	c.e.~98%
Cu foil vs. Zn foil		2 mA cm ⁻²	c.e.~95%
no membranes, 2 cm gap, unstirred	12:5 m K:Zn Ac WiSE	1 mA cm ⁻²	fail: c.e.~70%
Cu foil vs. Zn foil			fail: c.e.~80%
no membranes, 2 cm gap	25% w% KOH electrolyte	1 mA cm ⁻²	7~10 mV, c.e.~95%

Fig. 6. WiSE performs poorly with an industrial cell design and practical coulombic areal capacity.

Testing of KAc WiSE in practical cell design and industrial coulombic areal capacity (Fig 6 and Fig 7) shows poor performance due to excessive overvoltage from the WiSE, due to slow ionic mass transfer. Only stirred solutions show capability to cycle.

Zinc concentration in the WiSE can be boosted by ionic interaction with dissolved KAc (Fig 8) and this allows for a 5:2 K:Zn WiSE to be formulated without risk of solids precipitation. This aids ionic mass transfer and is the only formula that cycles well in our testing.

Dendrite growth (Fig 7 c) through f) shows much shorter dendrites in WiSE as compared to 25% KOH, which could be the one "silver lining" benefit of SEI blocking layers in WiSE.

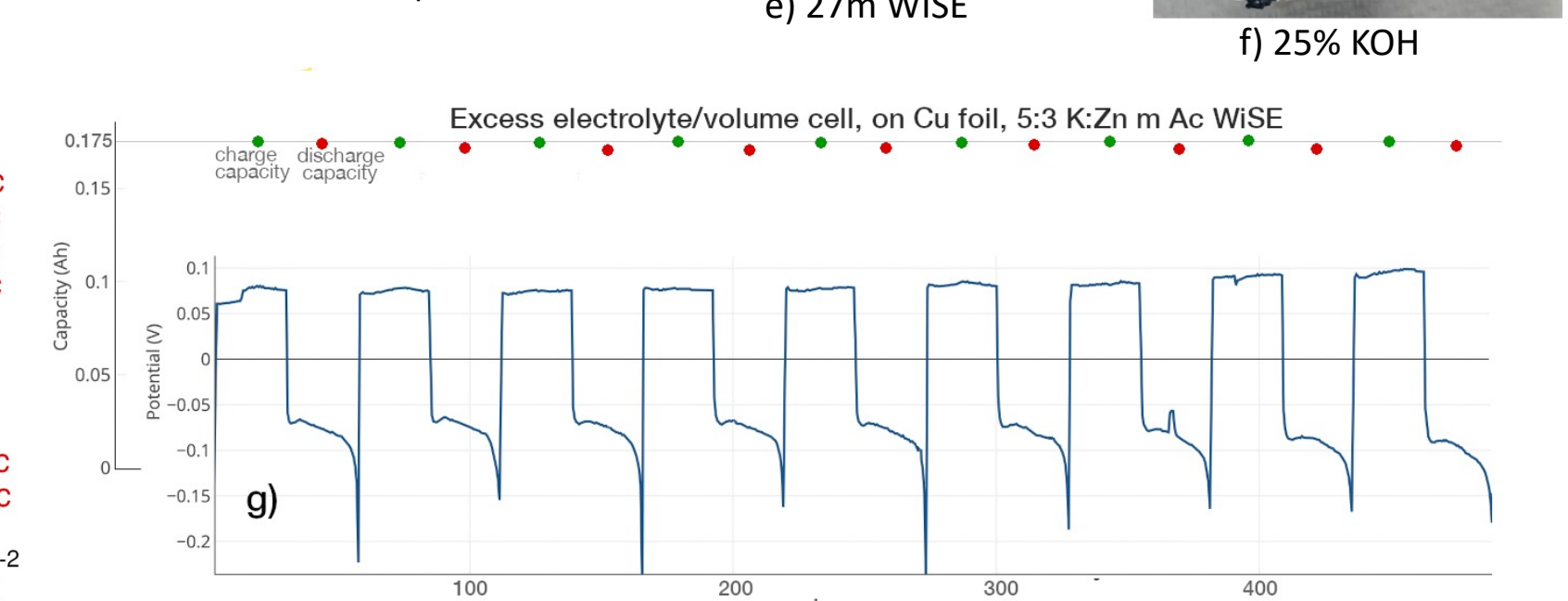
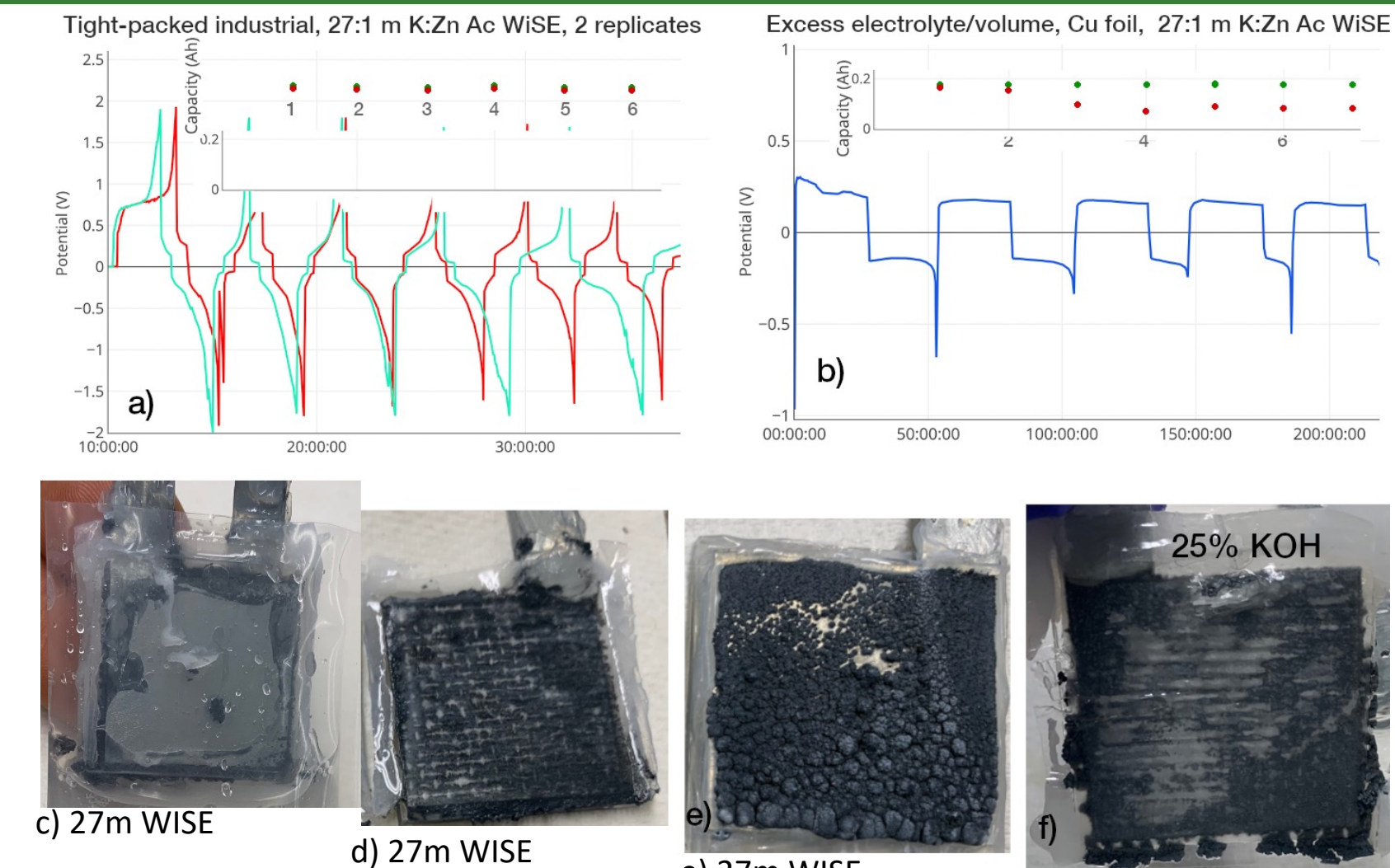


Fig. 7. Overvoltage and coulombic efficiency in (a), (b), and (g) show improvement with added H₂O. Photographs of dendrite formation in (c), (d), (e), (f) show shorter dendrites in KAc WiSE.

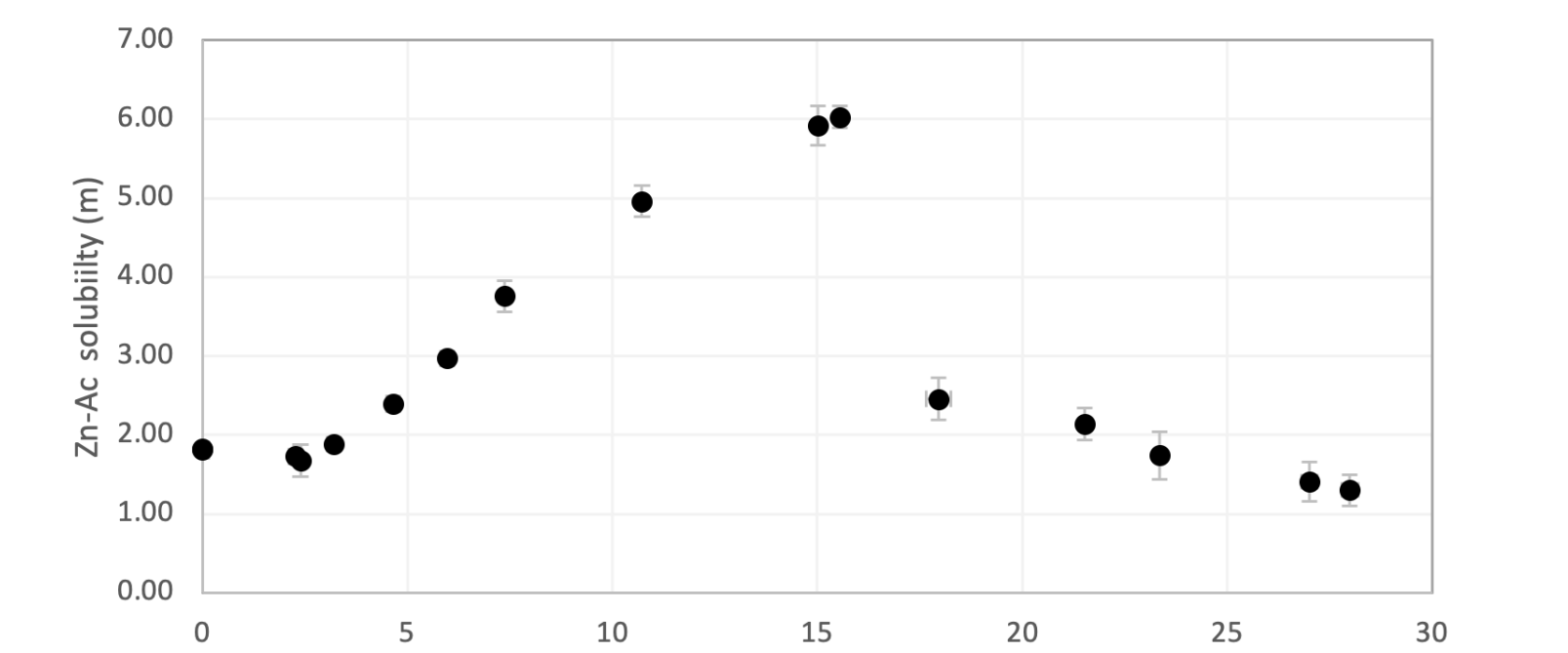


Fig. 8. Zn Ac solubility is boosted by interaction with K Ac.

Conclusions

Electrolyte voltage stability in WiSE is improved compared to traditional KOH electrolyte, but is not controlled by H₂O activity as claimed often in literature. Rather, reaction kinetics and SEI layers control voltage stability. Zn plating/deplating is too slow in nominal KAc WiSE for commercially-relevant current density. Dilution of WiSE improves mass transfer but reduces voltage stability. Zn dendrites are reduced in KAc WiSE. Future research aims to improve Zn plating/deplating in KAc WiSE without reducing voltage-stability.

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