Zinc-Iron Flow Batteries with Common Electrolyte

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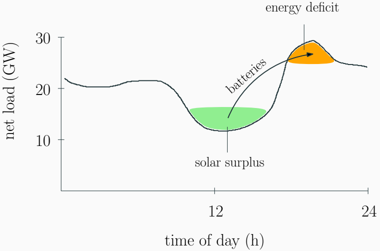
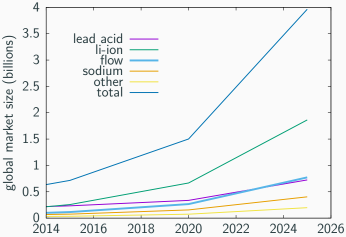
Motivation: Grid-Scale Energy Storage



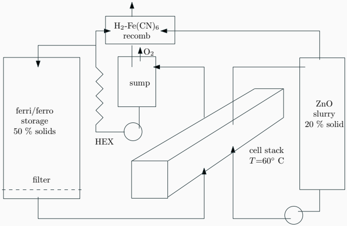


- Store solar energy during day, use at night [1]
- Replace peaker plants, enable micro-grids
- Need improvements in **cost and safety**

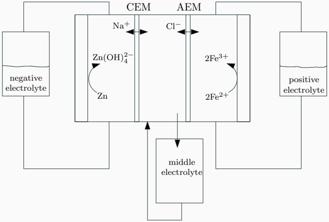
[1] Adapted from California Association of Independent System Operators (CAISO)

"Zinc-Iron" Flow Batteries

- Abundant, low-cost, readily-available materials
- Challenges include solids/slurry handling, ion-exchange membranes



(a)



(b)

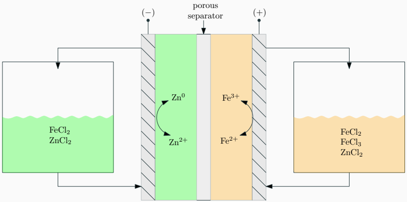
(a) Alkaline zinc-ferricyanide battery, adapted from Magnani et al.[1], and (b) a 2-membrane, 3-electrolyte battery, adapted from Gong et al.[2]

[1] N. Magnani et al., *Sandia Report*, SAND86-1266, (1987)
[2] K. Gong et al., *Energy Environ. Sci.* **8**, 2941 (2015)

Zinc-Iron Chloride: A New Approach[1]

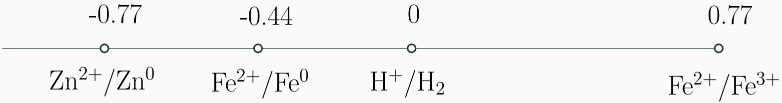
- Fe^{3+} is safer than Br_2 (positive redox electrode)
- Zn has higher performance than Fe (negative plating electrode)
- No ion-exchange membranes, no solids handling, no oil phase, no CN

name:	zinc - bromine	zinc - iron	all-iron
negative:	$Zn^{2+/0}$	$Zn^{2+/0}$	$Fe^{2+/0}$
positive:	Br^-/Br_2	$Fe^{2+/3+}$	$Fe^{2+/3+}$
cell:	1.84 V	1.53 V	1.21 V



[1] **S. Selverston** et al., *J. Electrochem. Soc.* **164**, 1069 (2017)

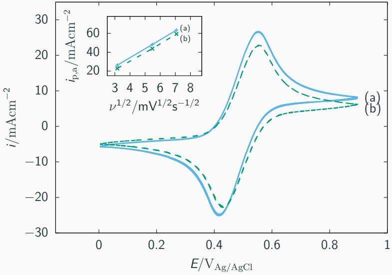
Can We Use a Mixed $ZnCl_2$-$FeCl_2$ Electrolyte?



- Thermodynamics would predict iron should be electroplated before zinc
- "Hydrogen evolution [on zinc] is greatly enhanced in the presence of impurities such as Fe..." (McBreen, 1984)
- "it is infeasible to use mixed electrolyte containing Zn and Fe as both the negative electrolyte and positive electrolyte" (Xie et al., 2016)
- Does Zn^{2+} affect the $Fe^{2+/3+}$ reaction?

Effect of Zinc on $Fe^{2+/3+}$

- Iron redox kinetics not strongly affected[1] by Zn^{2+}

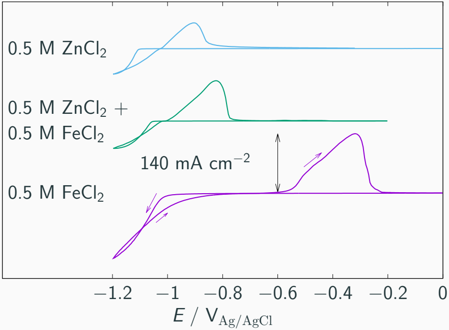


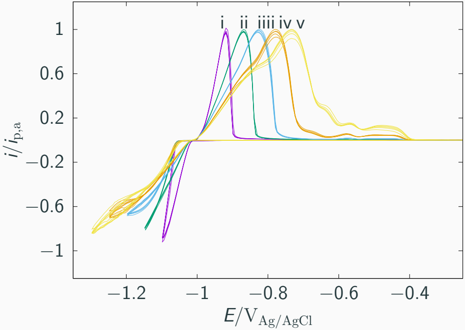
Effect of $ZnCl_2$ on Fe (II)/(III) redox reaction on graphite electrode with 1 M NH_4Cl at pH=1 at $\nu = 10$ mV s^{-1}. Initial electrolyte (a) contained 0.2 M Fe(II) and 0.2 M Fe(III), and the modified electrolyte (b) contained 0.8 M Zn(II).

[1]**S. Selverston** et al., *J. Electrochem. Soc.* **164**, 1069 (2017)

Using "Anomalous Codeposition (ACD)" to our Advantage

- Iron electrodeposition is strongly inhibited in the mixed electrolyte
- Deposition and stripping from mixed $ZnCl_2$-$FeCl_2$ almost the same as $ZnCl_2$-only electrolyte [1]

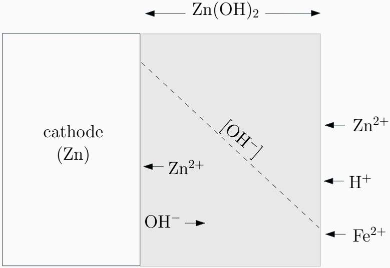


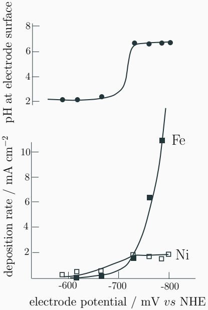


[1]**S. Selverston** et al., *J. Electrochem. Soc.* **164** 1069 (2017)

Hydroxide Suppression Mechanism (HSM)

- Proposed in 1965 for Ni-Fe [1,2]





$$Zn(OH)_2 + 2e \longrightarrow Zn + 2OH^-$$

[1] H. Dahms, I. Croll, *J. Electrochem. Soc.* **112** (1965)
[2] H. Yan, et al., *J. Electrochem. Soc.* **43**, 1577 (1996)

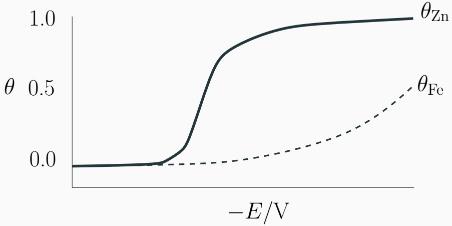
Competitive Adsorption

- Emphasis on kinetics rather than thermodynamics[1]

$$\mathrm{M(II)} + e^- \xrightarrow{k_{1,M}} \mathrm{M(I)_{ads}} \quad (1)$$

$$\mathrm{M(I)} + e^- \xrightarrow{k_{2,M}} \mathrm{M} \quad (2)$$

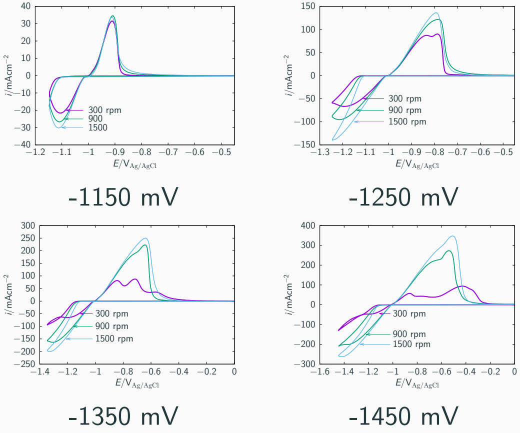
$$k_{1,M} = k^{o}_{1,M} \exp(b_{1,M} V) \quad (3)$$



[1] M. Matlosz, *J. Electrochem. Soc.* **140**, 2272 (1993)

Negative Scan Limit and RPM on Glassy Carbon

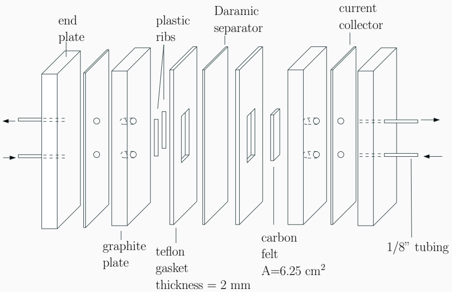
- Increasing rotation rate *enhances* ACD, contrary to HSM[1]
- 0.5 M $ZnCl_2$, 0.5 M $FeCl_2$, 1 M NH_4Cl, $\nu = 50$ mV s^{-1}, bulk pH=1

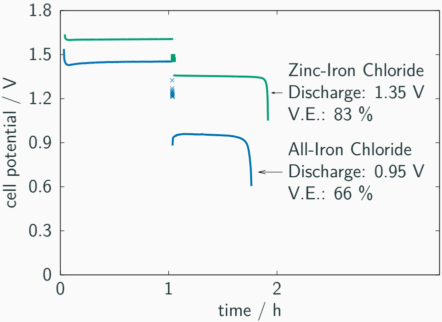


[1]**S. Selverston** et al., *J. Electrochem. Soc.* **164** 1069 (2017)

Battery Proof-of-Concept

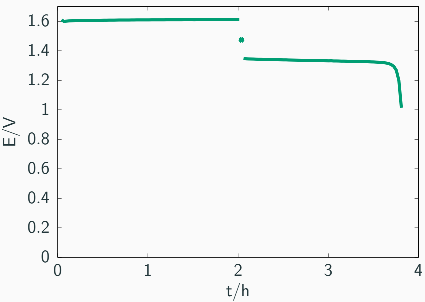
- 42 % relative gain in discharge voltage, 26 % relative gain in voltaic efficiency compared to all-iron at ± 25 mA cm^{-2}
- Consistent with selective zinc plating via anomalous codeposition (ACD)

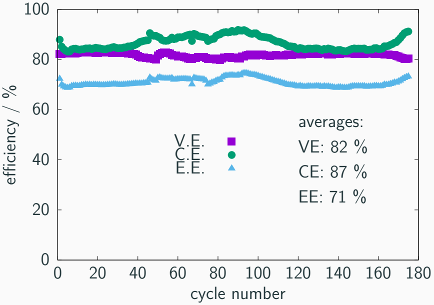




Accelerated Lifetime Testing

- 30-days, 175 continuous cycles achieved without replacing electrolyte
- Room-temperature, no flow fields, no dendrite suppressors used
- Two-hour charges at 25 mA cm^{-2} (loading = 50 mAh cm^{-2})





Conclusions

- First demonstration of a zinc-iron hybrid flow battery based using mixed electrolytes, microporous separators
- Based on anomalous codeposition of zinc; probably not HSM
- Demonstrated 30 days of cycling with over 70 % energy efficiency
- Extraordinary balance between cost, safety and performance

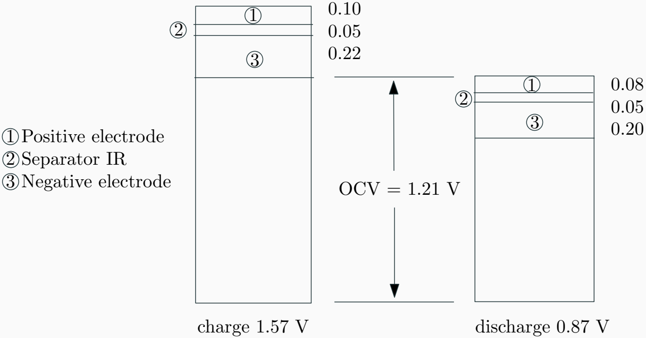
I would like to thank:

- My advisors: Prof. Robert Savinell and Prof. Jesse Wainright
- My colleagues in the EEEL Lab
- The project sponsors: US DOE-OE, PNNL

Thank you!

Supplementary Material

All-Fe Losses

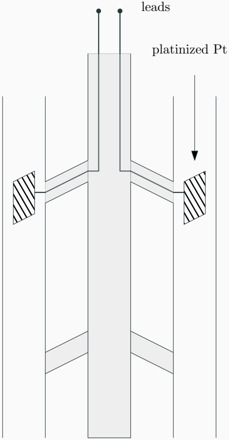


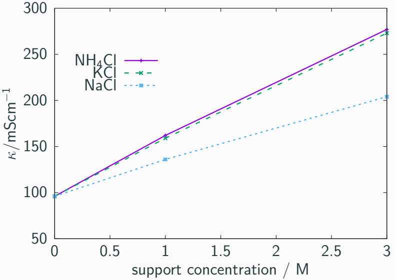
- Adapted from 1981 study[1]

[1] Hruska and Savinell, J. Electrochem. Soc. **128**, 18 (1981)

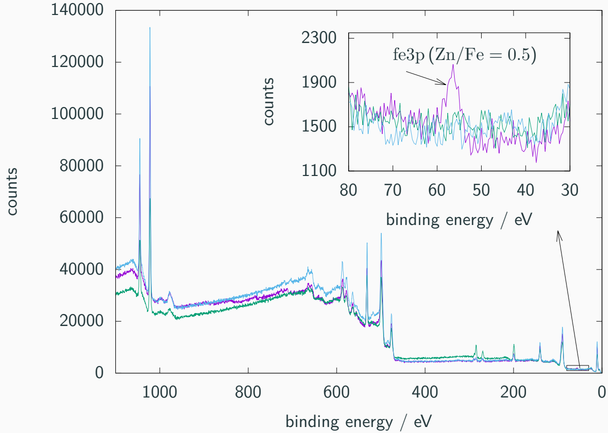
Zinc-Iron Chloride Conductivity

- Sufficiently high conductivity, similar to all-iron chloride battery



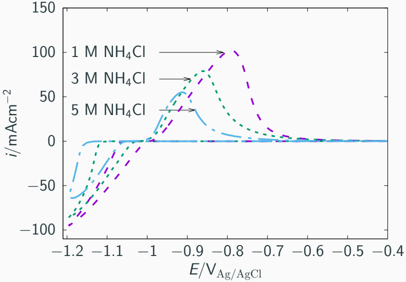


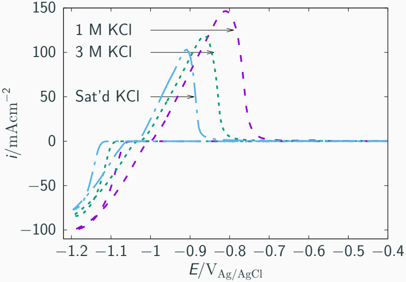
XPS Analysis



XPS analysis of three samples deposited at *p*H=2. The sample with Zn/Fe=0.5 showed a pronounced Fe3p peak and an estimated 10 $\%_{\mathrm{at}}$ iron.

Supporting Electrolyte Effects

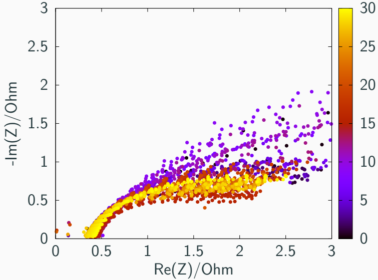


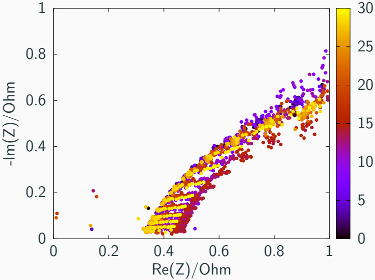


Effect of supporting electrolyte cations on the deposition and dissolution (Zn/Fe=4, pH=1). Total metal ion concentration $C_{\mathrm{Me}^{2+}} = 1$ M. Titanium sheet substrate. Room-temp, unstirred.

EIS during Lifetime Testing

- Color shows number of days
- Oscillating resistance- not linearly increasing with time





Electrochemical impedance spectroscopy (EIS) of zinc-iron chloride cell over 30 days of operation. Scans were carried out from 10 kHz to 10 Hz after charging.