Electrochemistry and Safety

Brian M. Tackett
Assistant Professor of Chemical Engineering
Purdue University

P2SAC Fall 2025 Conference
December 2, 2025

PURDUE UNIVERSITY
Davidson School of Chemical Engineering

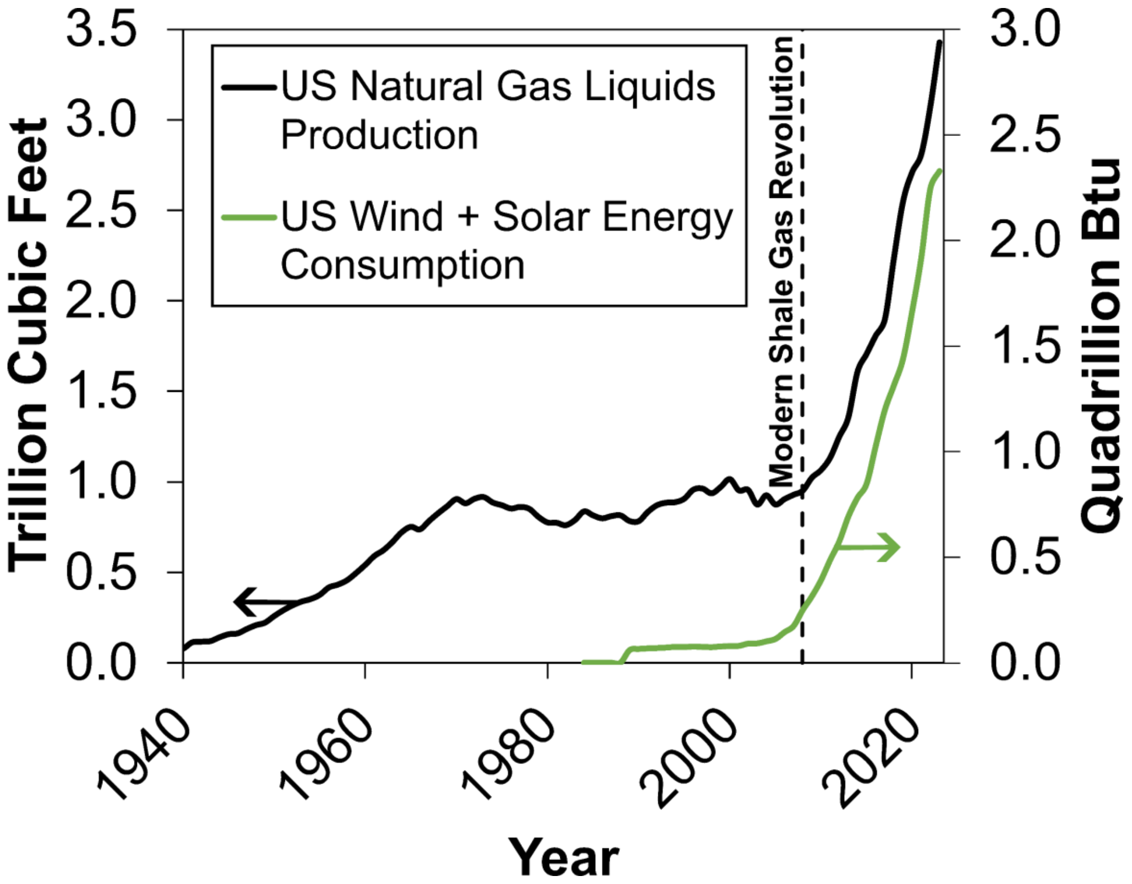
Motivation: Opportunity for Electrochemical Processes

*The **Energy Transition** + **Shale Gas Revolution** create unprecedented opportunities (and need) for electrochemical systems*

- Most chemical processes developed over the last ~100 years
  - **Energy only available in the form of heat** (combusting coal, oil, and gas)
- *Fuel → heat → electricity → industrial process* is inefficient, when electricity can just be cut out

For the first time in history, we have substantial energy in the form of electricity produced via wind & solar

- At the same time, US also has abundant feedstock to make essential chemicals
- **This allows us to reimagine a sustainable and electrified chemical industry**



A. Bhadouria, A. Biswas, B. M. Tackett. ***ACS Catalysis,*** 2025, 15, 6296-6314.

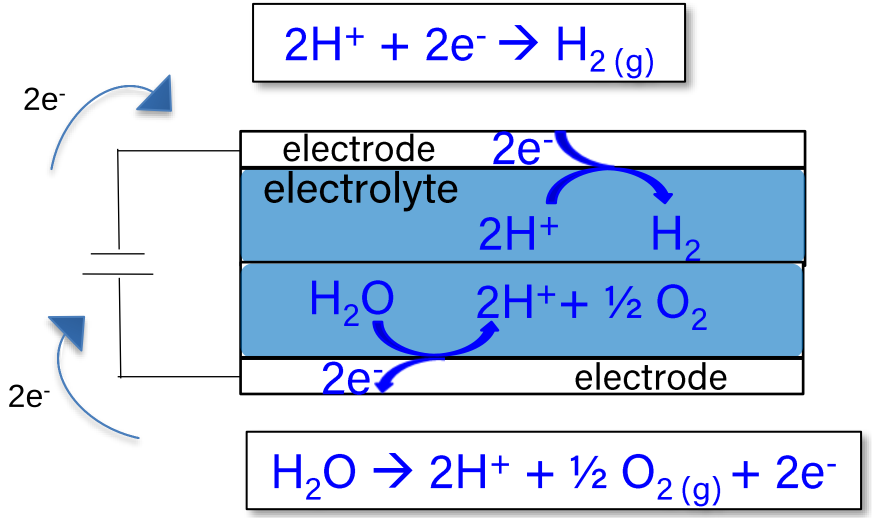
How do we ensure these electrochemical systems are safe?

Review: Electrochemical Reaction Fundamentals

3 elements of an electrochemical reaction:

1. Molecular transformation where an electron (e^-) is a reactant or a product
2. Inherently heterogeneous process with at least 2 phases
    - Electron conducting phase (electrode)
    - Ion conducting phase (electrolyte)
3. Contains 2 electrodes to maintain electroneutrality

- ***Current = reaction rate*** *(rate of flow of electrons)*
- ***Voltage = driving force*** *(impetus for electron flow)*



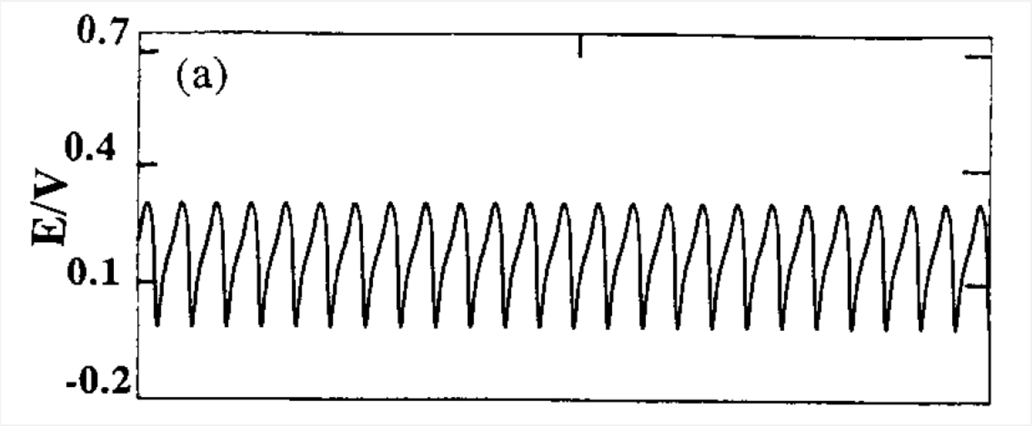
$2H^+ + 2e^- \rightarrow H_{2\,(g)}$

$H_2O \rightarrow 2H^+ + ½\ O_{2\,(g)} + 2e^-$

Let's leverage these principles to support a safe and electrified chemical industry

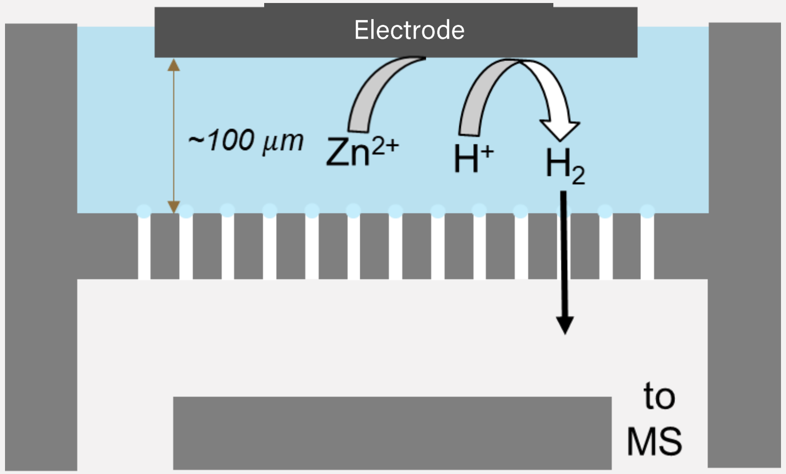
Two Examples

Electrochemical Manufacturing



- *Oscillatory instabilities can occur in almost any E-chem reactor, posing operation hazards*

Electrochemical Energy Storage

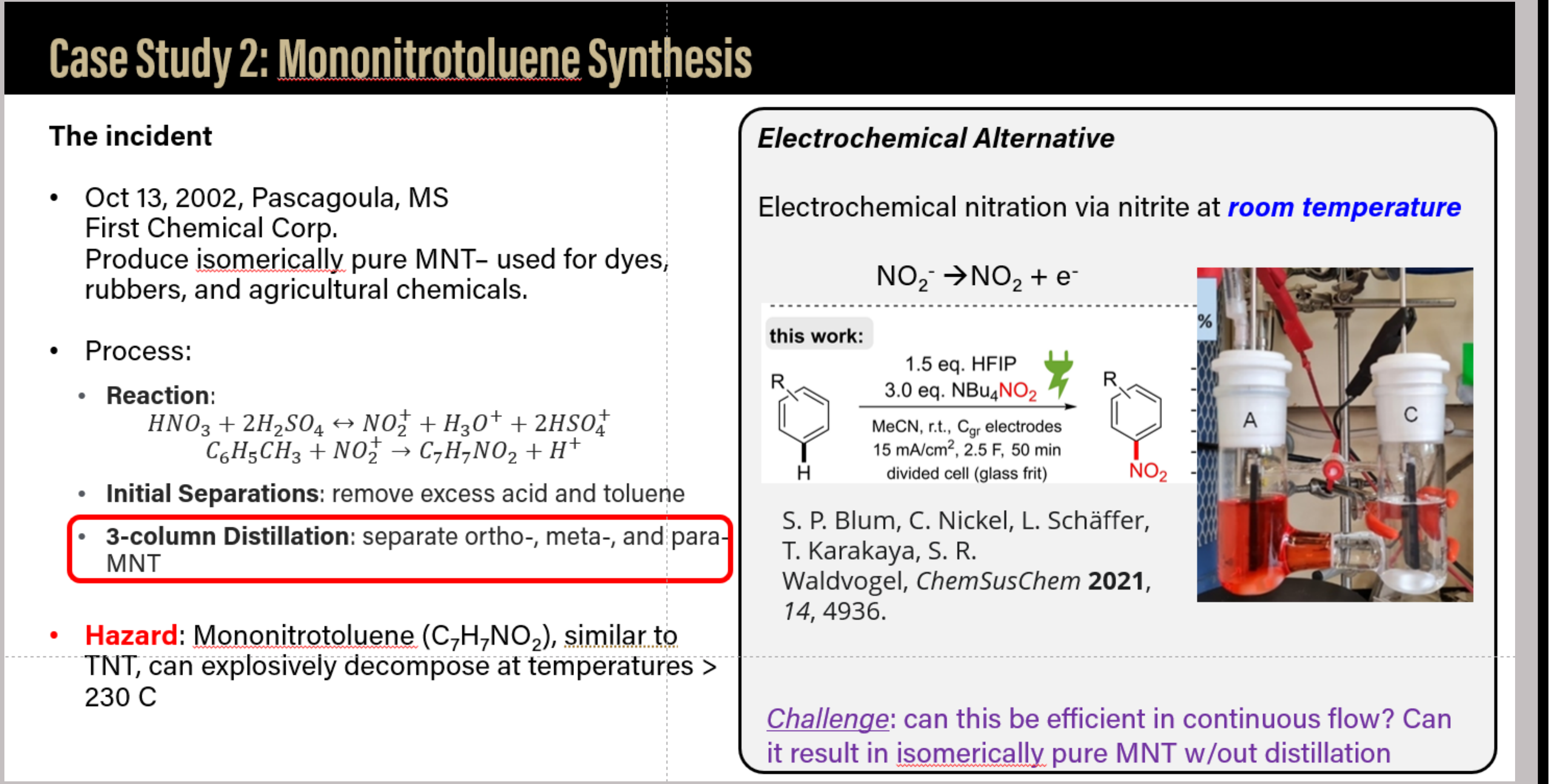


- *Aqueous batteries are inherently safe, but abundant water/H^+ causes issues with viability*

Manufacturing: safe(r) Echem alternatives

From P2SAC Spring ’25:

- We can come up with good ideas for electrochemical replacements for hazardous or inefficient process
- ***But what hazards will be associated with electrochemical reactors?***



Case Study 2: Mononitrotoluene Synthesis

The incident

- Oct 13, 2002, Pascagoula, MS
  First Chemical Corp.
  Produce isomerically pure MNT– used for dyes, rubbers, and agricultural chemicals.
- Process:
  - **Reaction**:
    $$HNO_3 + 2H_2SO_4 \leftrightarrow NO_2^+ + H_3O^+ + 2HSO_4^+$$
    $$C_6H_5CH_3 + NO_2^+ \rightarrow C_7H_7NO_2 + H^+$$
  - **Initial Separations**: remove excess acid and toluene
  - **3-column Distillation**: separate ortho-, meta-, and para-MNT
- **Hazard**: Mononitrotoluene ($C_7H_7NO_2$), similar to TNT, can explosively decompose at temperatures > 230 C

Electrochemical Alternative

Electrochemical nitration via nitrite at ***room temperature***

$$NO_2^- \rightarrow NO_2 + e^-$$

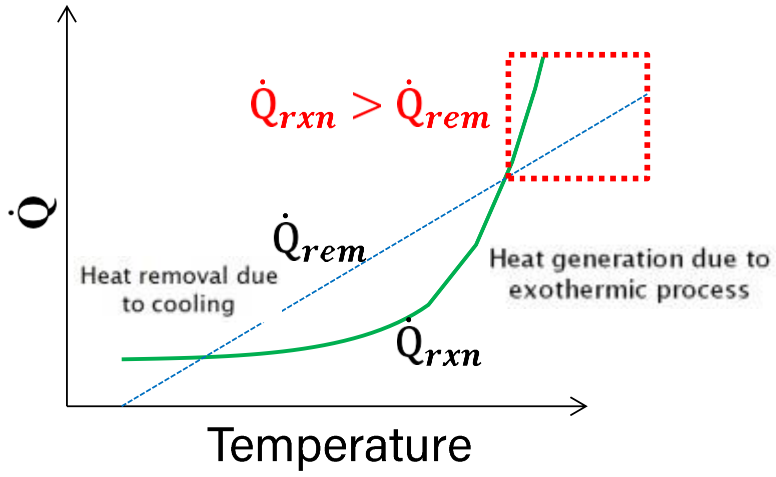
S. P. Blum, C. Nickel, L. Schäffer, T. Karakaya, S. R. Waldvogel, *ChemSusChem* **2021**, *14*, 4936.

Challenge: can this be efficient in continuous flow? Can it result in isomerically pure MNT w/out distillation

Reactivity Hazards for Continuous Reactors

Thermochemical Reactors

Runaway Reactions



- Heat generated via reaction exceeds heat removed via heat-exchange
- Hazardous scenarios understood by analyzing ***multiple steady states***

Electrochemical Reactors

Runaway Reactions?

- Echem rxns don't experience substantial T effects as result of reaction
- Energy of reaction manifests as electron potential, rather than heat

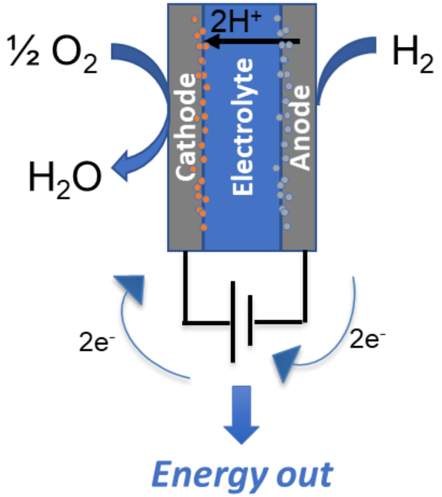
Ex)

$H_2 + ½ O_2 \rightarrow H_2O$

ΔH_{rx} = -242 kJ/mol

$\downarrow$

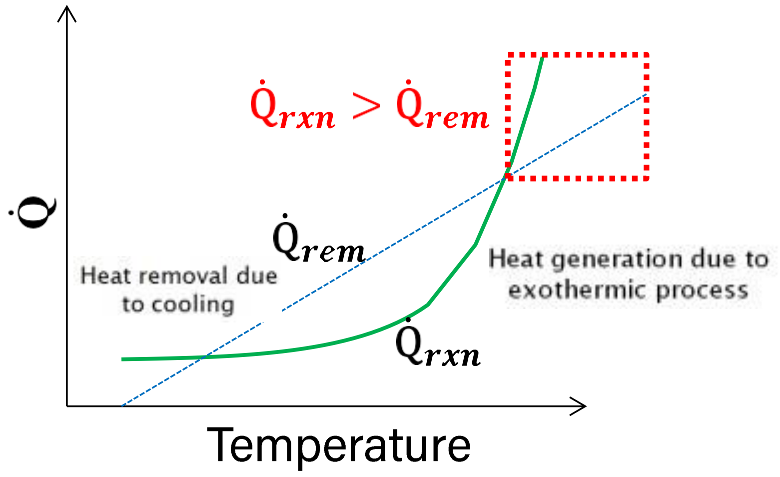
1.23 V @ 298K
in electrochemical reactor



Reactivity Hazards for Continuous Reactors

Thermochemical Reactors

Runaway Reactions

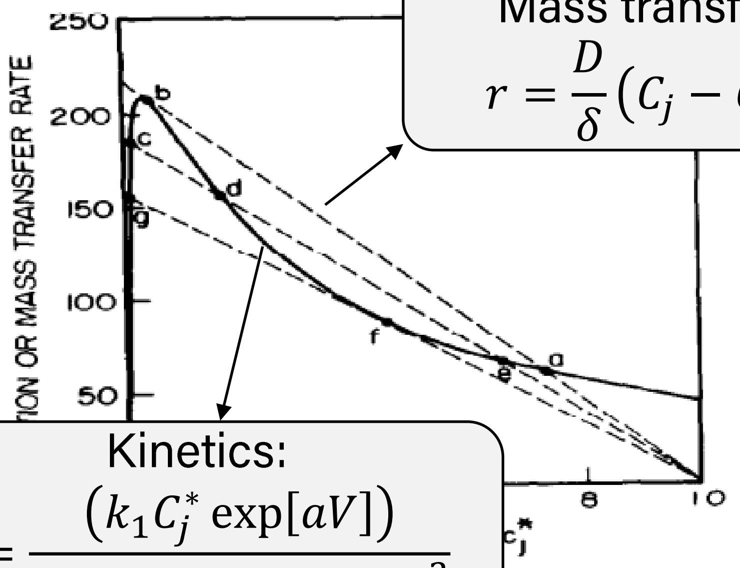


- Heat generated via reaction exceeds heat removed via heat-exchange
- Hazardous scenarios understood by analyzing ***multiple steady states***

Electrochemical Reactors

Runaway Reactions?

- **But** echem reactors can still experience ***multiple steady states***, creating potentially hazardous operating conditions



Mass transfer:

$$r = \frac{D}{\delta}\left(C_j - C_j^*\right)$$

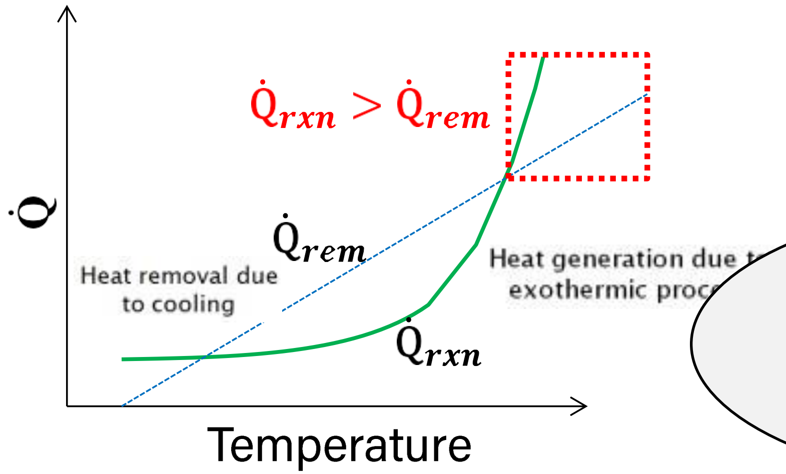
Kinetics:

$$r = \frac{\left(k_1 C_j^* \exp[aV]\right)}{\left(1 + k_2 C_j^* \exp[aV]\right)^2}$$

Reactivity Hazards for Continuous Reactors

Thermochemical Reactors

Runaway Reactions



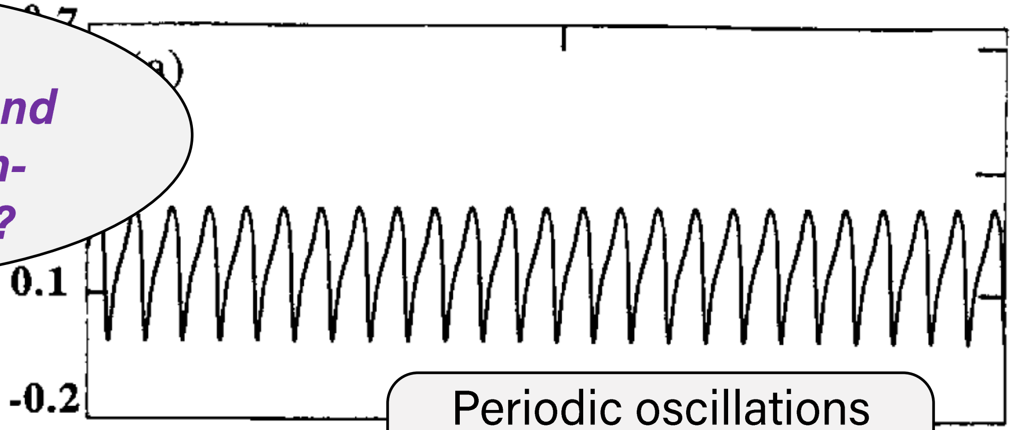
- Heat generated via reaction exceeds heat removed via heat-exchange
- Hazardous scenarios understood by analyzing ***multiple steady states***

How can we measure, model, and control these non-linear dynamics?

Electrochemical Reactors

Runaway Reactions?

- **And** echem systems often exhibit ***oscillatory behavior*** due to competing activator/inhibitor processes

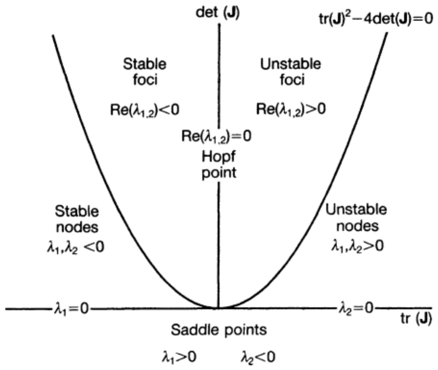


Periodic oscillations during electrochemical formate oxidation

Conditions for Electrochemical Oscillations

For a Single Reaction (O + e$^-$ → R):

Stability understood as interplay of kinetics and mass transport



Charge Balance

$$\frac{d\phi_{dl}}{dt} = \frac{U-\phi_{dl}}{RC_dA} - \frac{I_F}{C_dA} = f_1(C_o,\phi_{dl}) \qquad I_F = -nFAk_fC_o(0,t)$$

Mass Balance

$$\frac{dC_o(0,t)}{dt} = \frac{2D_o}{\delta^2}\left(C_o^{bulk} - C_o(0,t)\right) - \frac{2k_fC_o(0,t)}{\delta} = f_2(C_o,\phi_{dl})$$

$$\boldsymbol{J} = \begin{bmatrix} \dfrac{df_1}{d\phi_{dl}} & \dfrac{df_1}{dC_o} \\ \dfrac{df_2}{d\phi_{dl}} & \dfrac{df_2}{dC_o} \end{bmatrix}_{ss} \longrightarrow$$

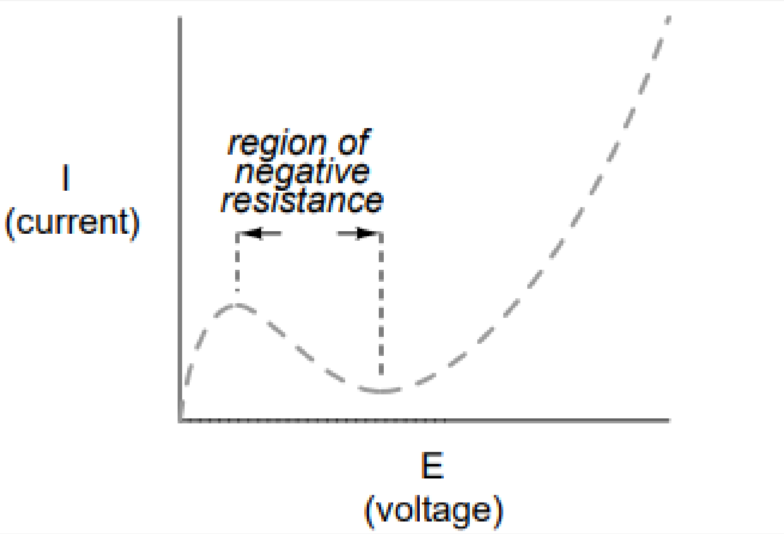
Both eigenvalues of $\boldsymbol{J}$ must be negative for the system to be stable

Prerequisite for oscillation:

$$\frac{\partial\phi_{dl}}{\partial I_F} < 0 \quad \& \quad R_s > \left|\frac{\partial\phi_{dl}}{\partial I_F}\right|$$

Negative Differential Resistance

Large "system" resistance



Conditions for Electrochemical Oscillations

For a Multiple Reactions / Multiple Pathways:

Oscillations can arise due to competing kinetics

- **Ex) electrochemical formate oxidation:**

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$$

Direct Pathway

$$HCOOH_{aq} + * \leftrightarrow *HCOOH$$

$$*HCOOH \rightarrow *COOH + H^+ + e^-$$

$$*COOH \rightarrow \boldsymbol{CO_2} + H^+ + e^-$$

Indirect Pathway

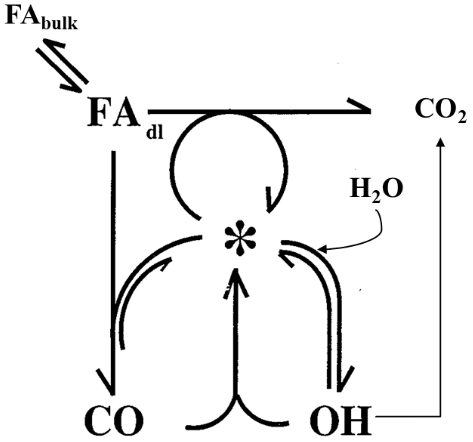
$$HCOOH_{aq} + * \leftrightarrow *HCOOH$$

$$*HCOOH \rightarrow *COOH + H^+ + e^-$$

$$*HCOOH \rightarrow \boldsymbol{*CO} + H_2O$$ **Poisoning of Surface**

$$H_2O + * \leftrightarrow *OH + H^+ + e^-$$ **Oxidation of Surface**

$$*CO + *OH \rightarrow CO_2 + H^+ + e^- + 2*$$ **Removal of Poison**

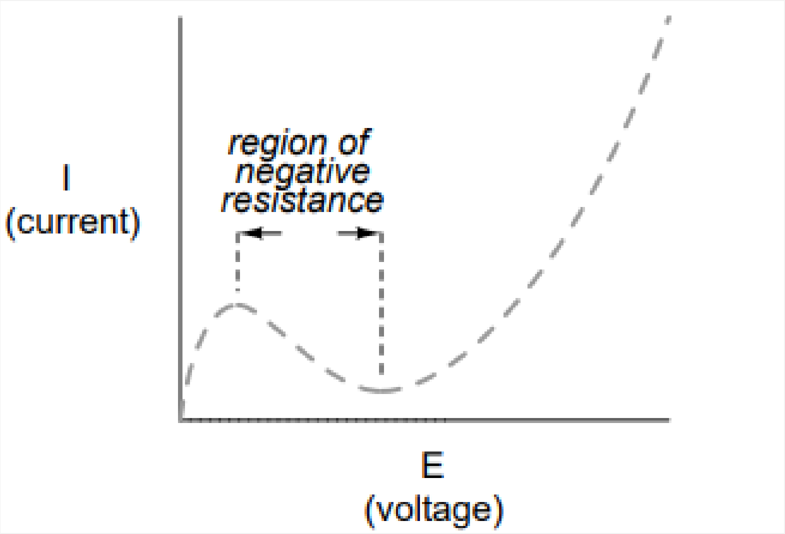


Prerequisite for oscillation:

$$\frac{\partial \phi_{dl}}{\partial I_F} < 0 \quad \& \quad R_s > \left| \frac{\partial \phi_{dl}}{\partial I_F} \right|$$

Negative Differential Resistance

Large "system" resistance

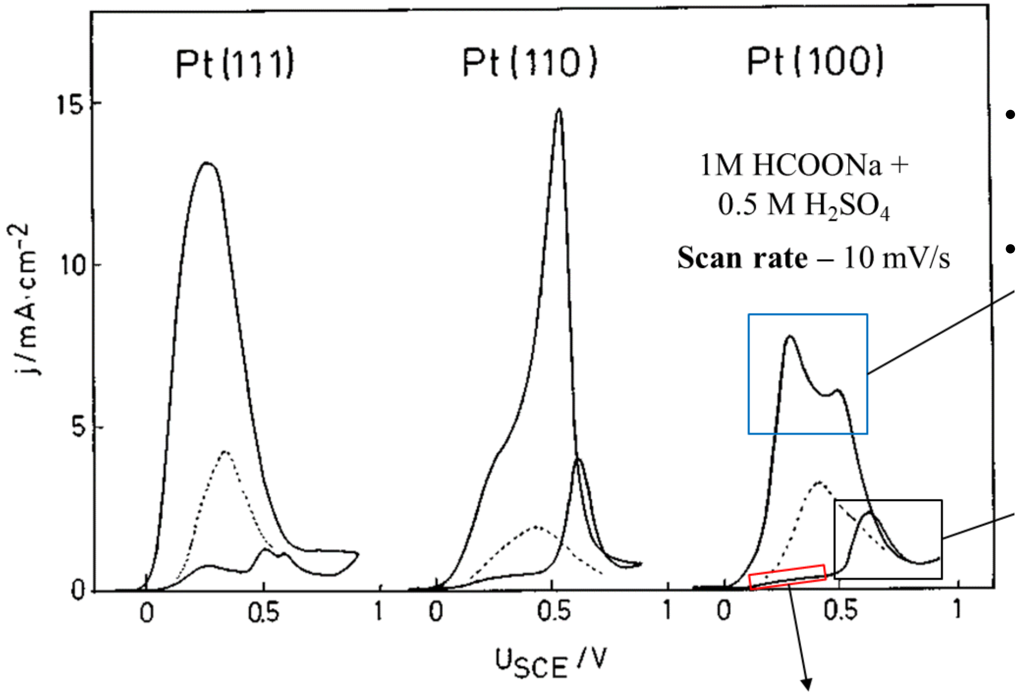


Conditions for Electrochemical Oscillations

For a Multiple Reactions / Multiple Pathways:

Oscillations can arise due to competing kinetics

- **Ex) electrochemical formate oxidation:**
  @ low solution resistance (R_s)



Catalyst surface covered wi
CO (poison), hence low rat

- Reverse scan **<0.7V**- Desorption of OH and FA oxidation.
- **0.5 – 0.3 V**- CO is slow to poison, direct FA oxidation

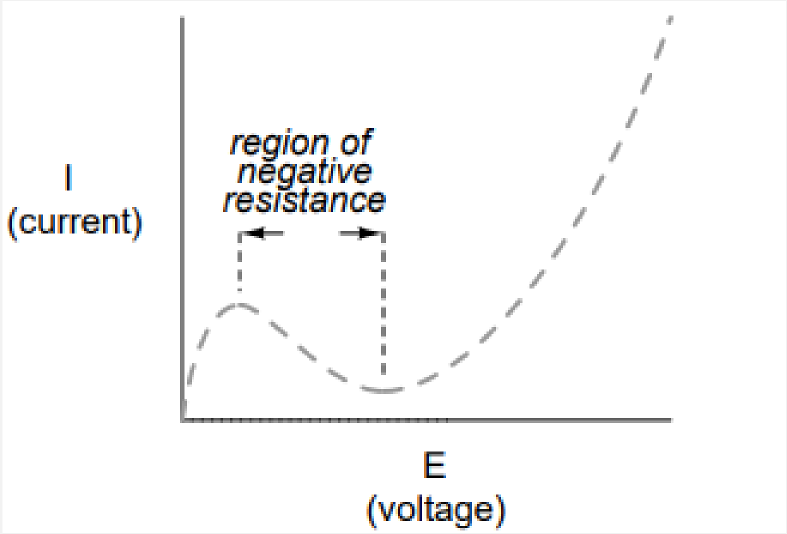
- **0.5-0.7 V**- Poisoned CO removed by adsorbed OH
- **> 0.7 V** - Adsorbed OH acts as a poison

Prerequisite for oscillation:

$$\frac{\partial \phi_{dl}}{\partial I_F} < 0 \quad \& \quad R_s > \left|\frac{\partial \phi_{dl}}{\partial I_F}\right|$$

Negative Differential Resistance

Large "system" resistance

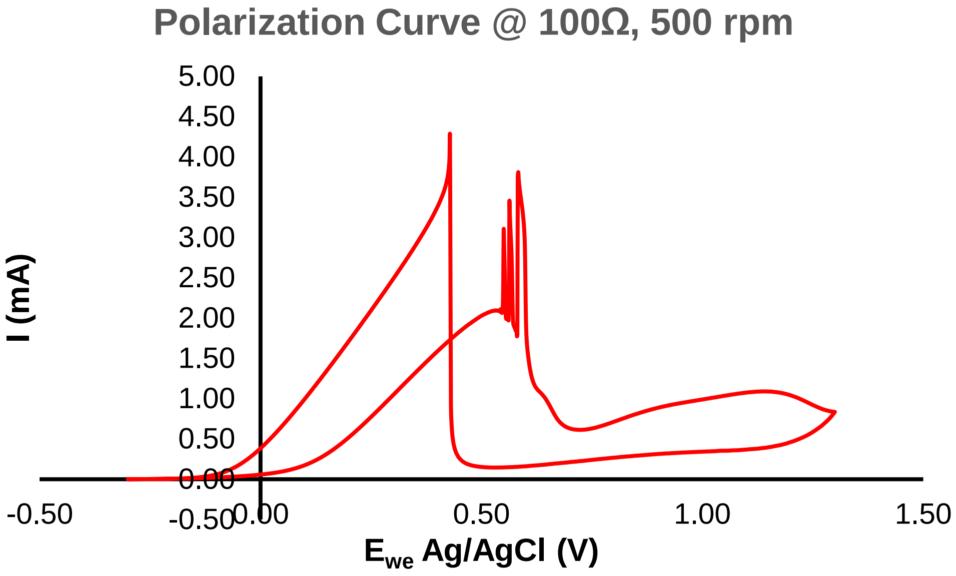


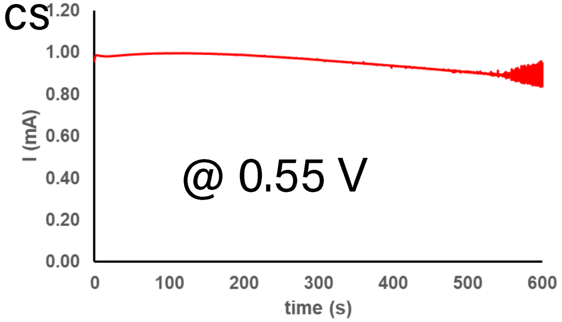
Conditions for Electrochemical Oscillations

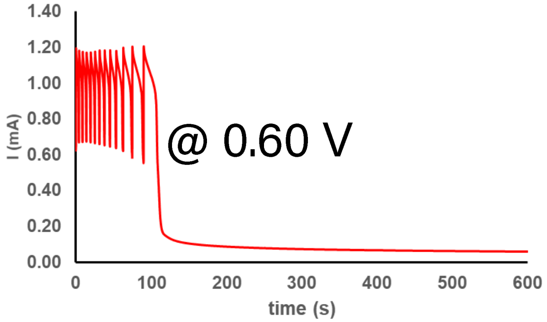
For a Multiple Reactions / Multiple Pathways:

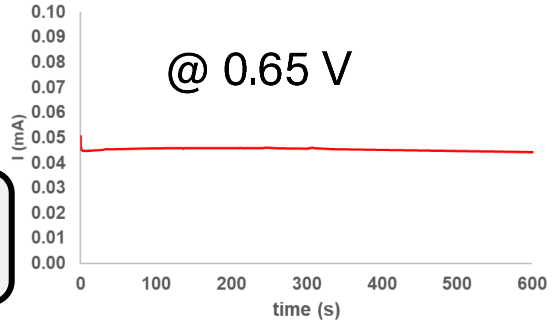
Oscillations can arise due to competing kinetics

- **Ex) electrochemical formate oxidation:**
  @ 100 Ω resistance (R_s)









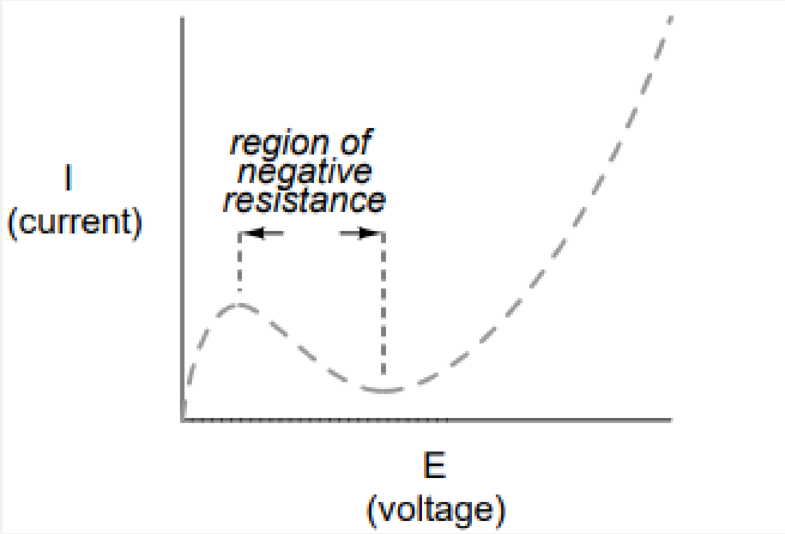
Current is rate – so what is happening chemically when current oscillates?

Prerequisite for oscillation:

$$\frac{\partial \phi_{dl}}{\partial I_F} < 0 \quad \& \quad R_s > \left|\frac{\partial \phi_{dl}}{\partial I_F}\right|$$

Negative Differential Resistance

Large "system" resistance

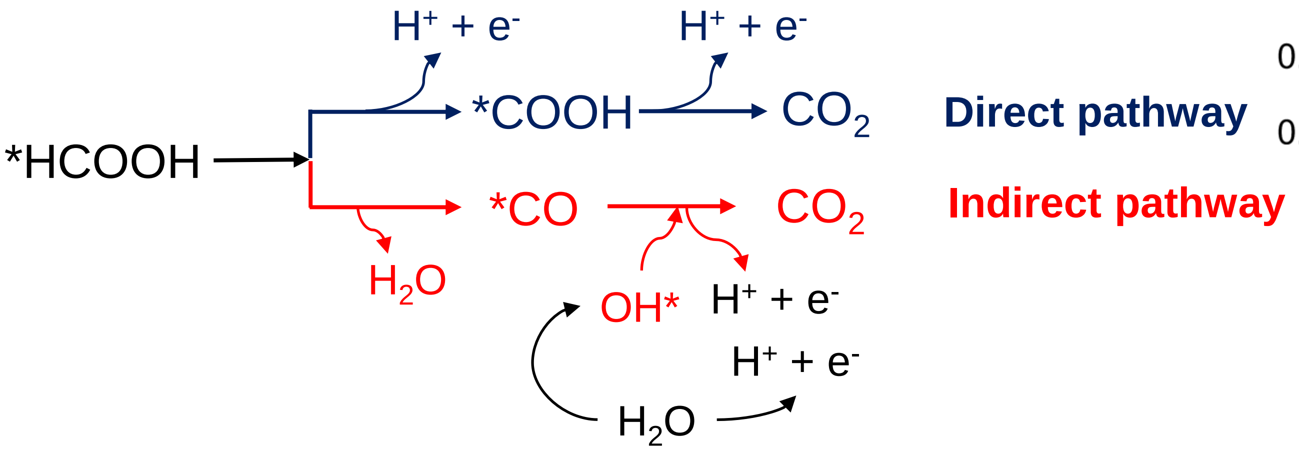


Implications of Electrochemical Oscillations

For a Multiple Reactions / Multiple Pathways:

Oscillations can arise due to competing kinetics

- **Ex) electrochemical formate oxidation:**

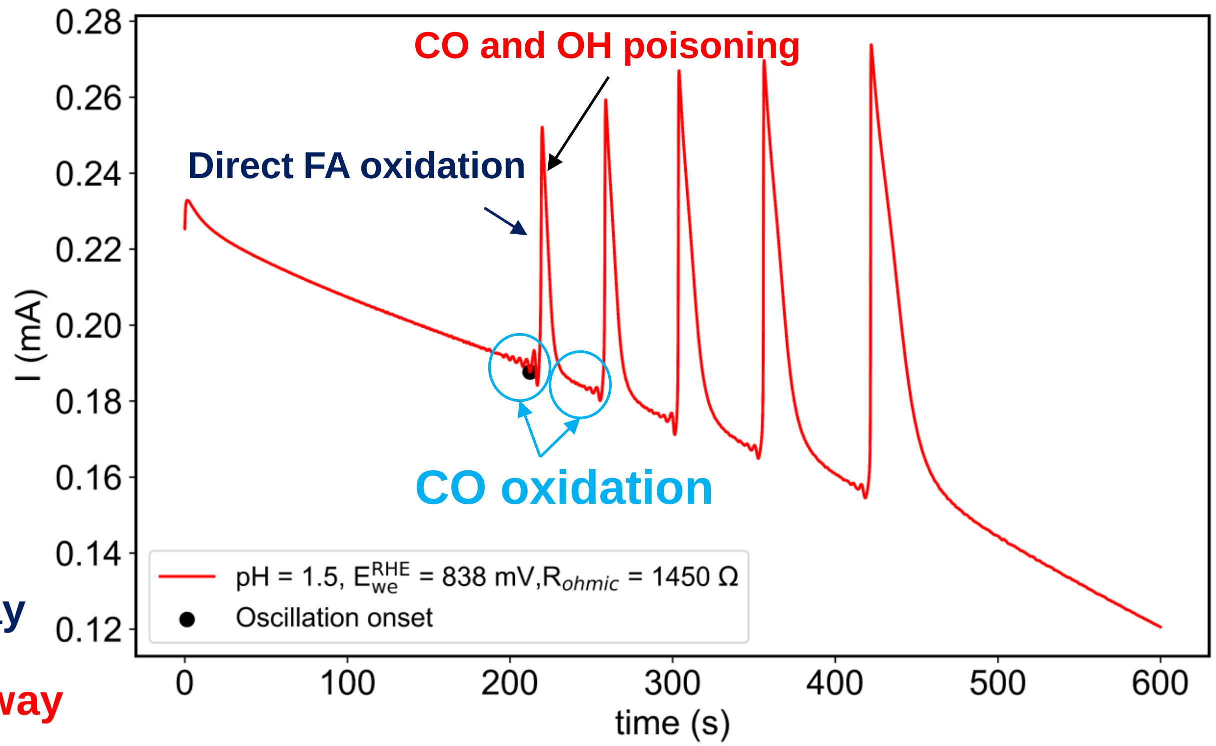


$*HCOOH \rightarrow *COOH + H^+ + e^- \rightarrow CO_2 + H^+ + e^-$ **Direct pathway**

$*HCOOH \rightarrow *CO + H_2O$; $*CO + OH^* \rightarrow CO_2 + H^+ + e^-$ **Indirect pathway**

$H_2O \rightarrow OH^* + H^+ + e^-$

Capon, Andrew, and Roger Parsons. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*. **1973**, 45.2: 205-231.

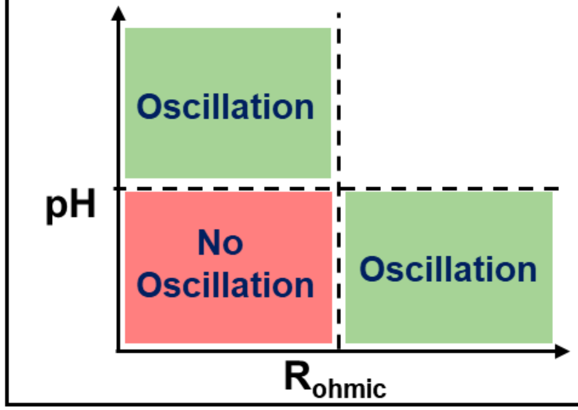


Many factors can influence these unstable behaviors

Implications of Electrochemical Oscillations

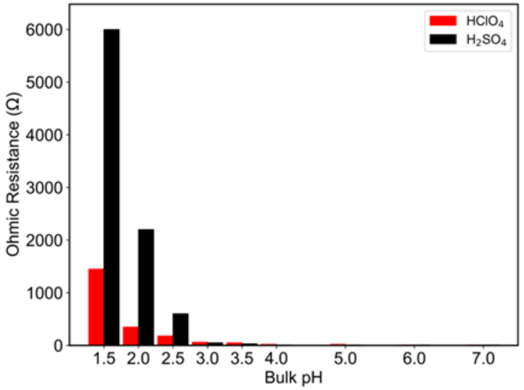
Anion affecting *OH binding energy

$$BE_{*OH^{(aq)}} = BE_{*OH^{(g)}} + \Delta E_{solvation(*OH)} - e\phi$$

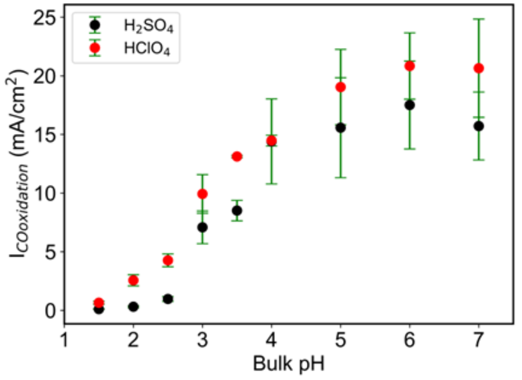


Binding Energy threshold

Anion hydration effect on R_{ohmic} and $I_{CO\ ox.}$

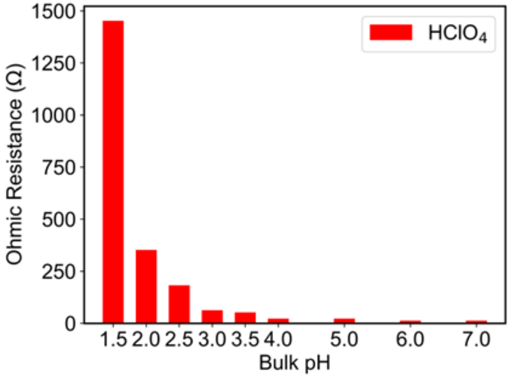


Strong hydration, high R_{ohmic}

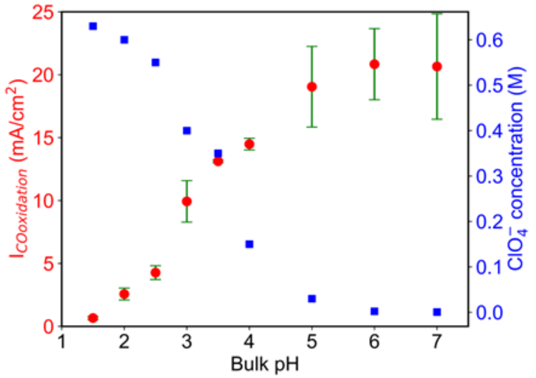


Strong hydration, low $I_{CO\ ox.}$

Anion concentration effect on R_{ohmic} and $I_{CO\ ox.}$



High C_{anion}, high R_{ohmic}



High C_{anion}, low $I_{CO\ ox.}$

Future Work

Estimating *OH binding strength

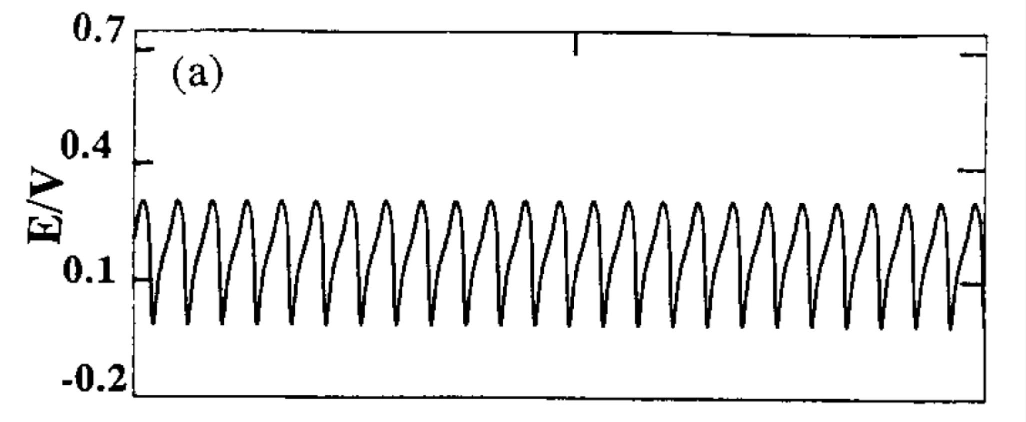
- CO displacement experiments with different anion concentrations.
- CO displacement experiments with anions of varying hydration.

pH-dependent microkinetic model

- Approximating the rate coefficients as a function of pH.

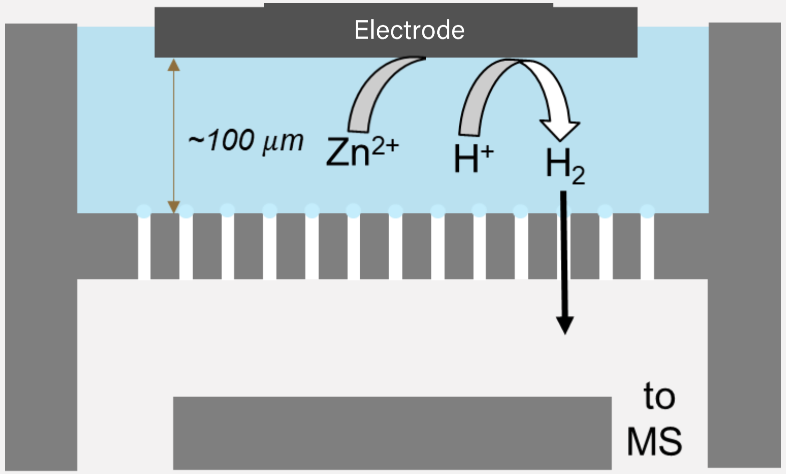
Two Examples

Electrochemical Manufacturing



- *Oscillatory instabilities can occur in almost any E-chem reactor, posing operation hazards*

Electrochemical Energy Storage



- *Aqueous batteries are inherently safe, but abundant water/H^+ causes issues with viability*

Electrochemical Energy Storage: Enabling Zn metal batteries

Zn metal batteries can support grid-level storage

- *Zn is cheap, abundant,* ***non-hazardous***

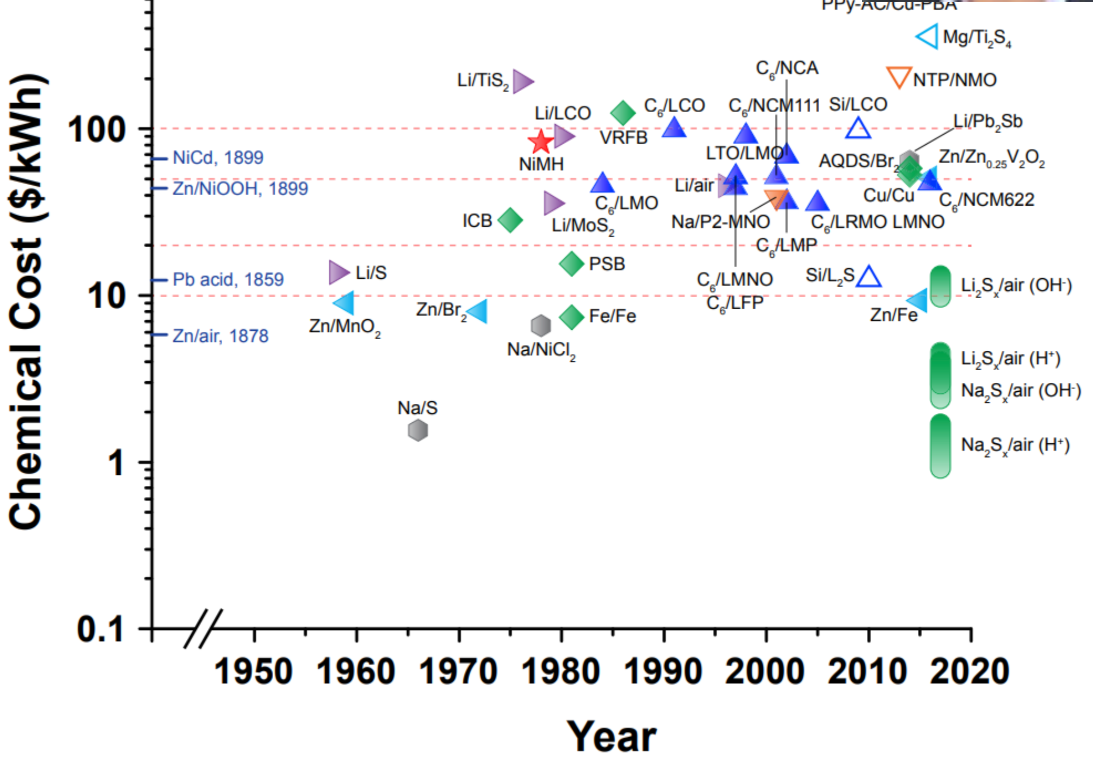
- Anode reaction is simple aqueous electrodeposition

$$Zn^{2+} + 2e^- \rightarrow Zn^0$$

Uneven Zn plating hinders battery stability

- **Electrocatalytic** hydrogen evolution reaction (HER) is undesired and contributes to uneven Zn deposition/instability

$$2H^+ + 2e^- \rightarrow H_2$$



Y.-M. Chiang, et al. *Joule*, 2017, 1: 306–327.

Electrochemical Energy Storage: Enabling Zn metal batteries

Zn metal batteries can support grid-level storage

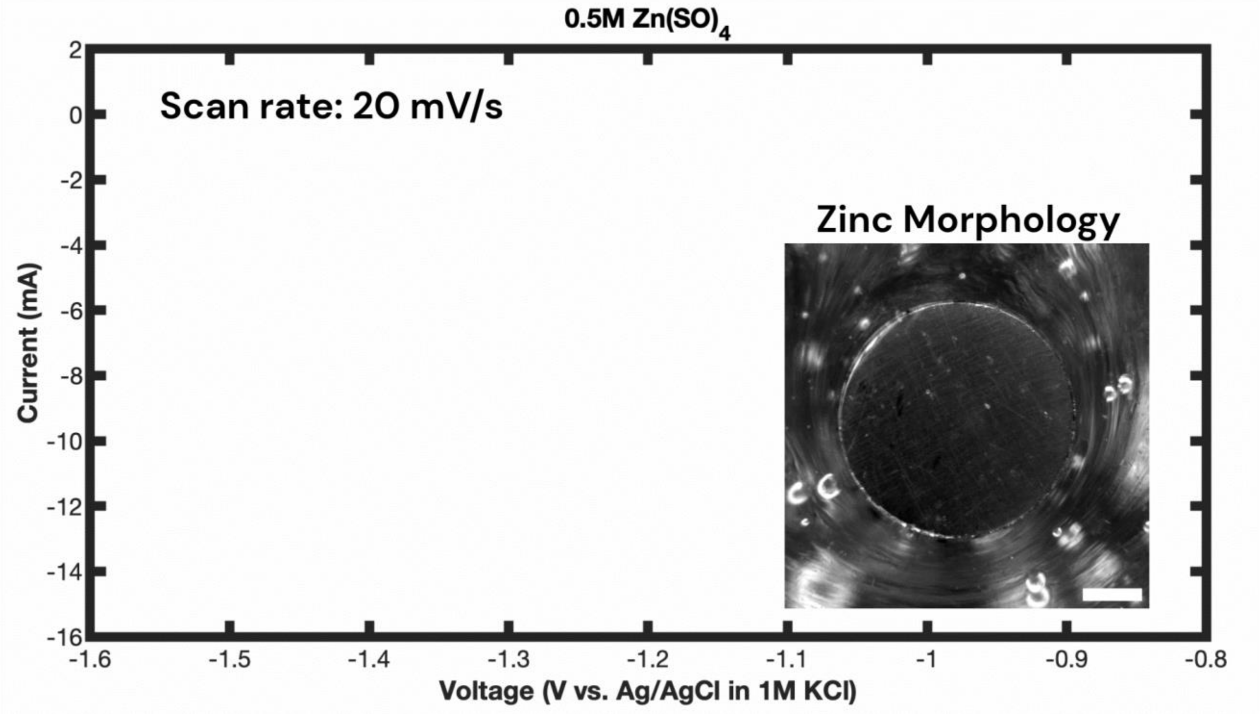
- *Zn is cheap, abundant, non-hazardous*
- Anode reaction is simple aqueous electrodeposition

$$Zn^{2+} + 2e^{-} \rightarrow Zn^{0}$$

Uneven Zn plating hinders battery stability

- **Electrocatalytic** hydrogen evolution reaction (HER) is undesired and contributes to uneven Zn deposition/instability

$$2H^{+} + 2e^{-} \rightarrow H_2$$



Strategy: *Use an electrode/electrolyte that disfavors catalytic H_2 formation without hindering Zn plating*

Challenge: *Both reactions contribute to current simultaneously*

K. Roy, A. Rana, J. N. Heil, B. M. Tackett, J. E. Dick. ***Angew. Chem. Int. Ed.***, 2024, 63: e202319010.

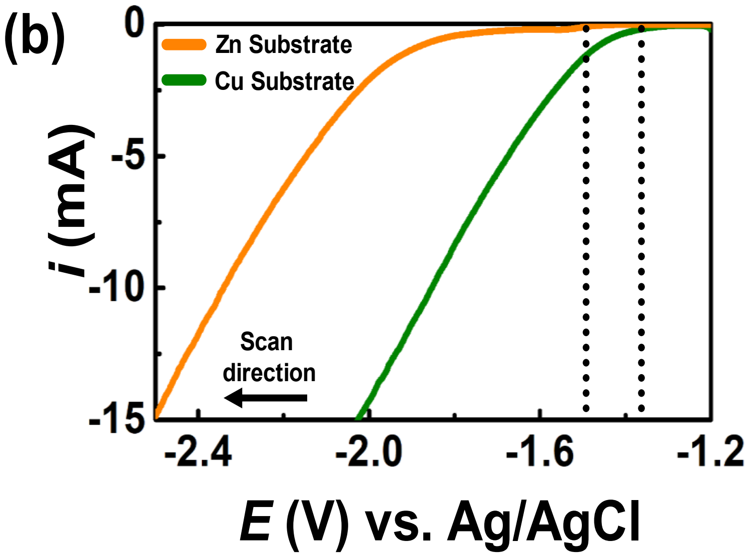
EC-MS Analysis of Zn plating and HER

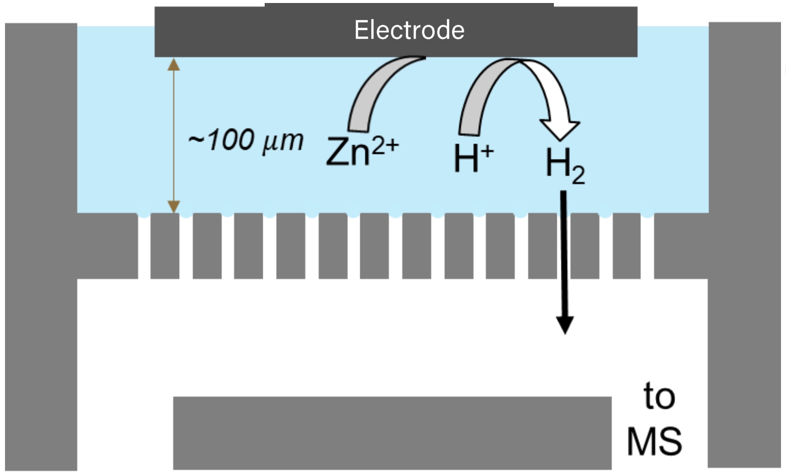
Typical Approach: Measure catalytic HER in the absence of Zn^{2+} to isolate kinetics of unwanted reaction

- In the **absence of Zn^{2+}**, HER onset is:
  - ~-1.35 V on Cu electrode
  - ~-1.50 V on Zn electrode

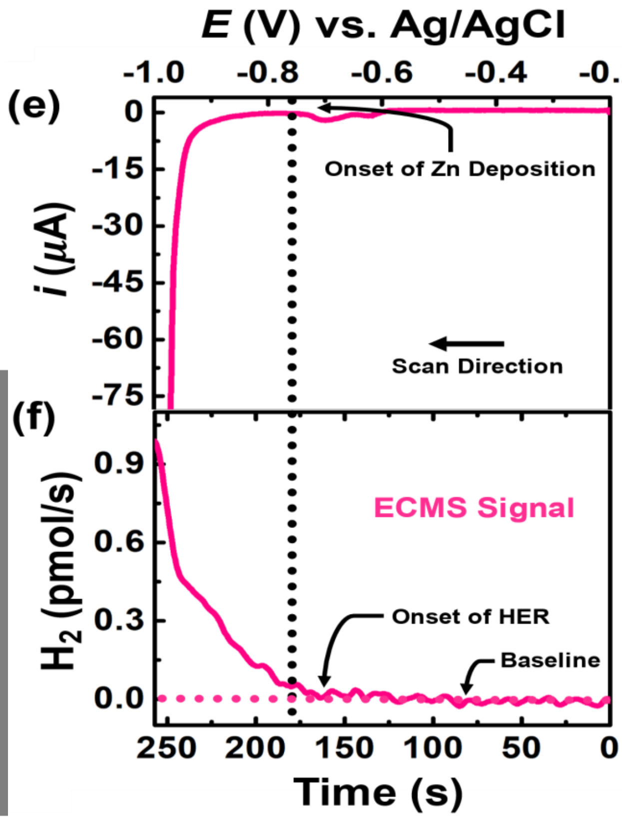
Our Approach: Measure HER partial current with EC-MS in the presence of Zn^{2+}

- In the **presence of Zn^{2+}**, HER onset is:
  - ~-0.8 V on Cu electrode
  - *Coincident with onset of Zn^{2+} reduction*





HER appears to originate from ***water solvating Zn^{2+}***



A. Rana, K. Roy, J. N. Heil, J. H. Nguyen,, C. Renault, B. M. Tackett, J. E. Dick. ***Adv. Energy Mater.*** 2024, 14, 2402521.

EC-MS Analysis of Zn plating and HER

Typical Approach: Measure catalytic HER in the absence of Zn^{2+} to isolate kinetics of unwanted reaction

- In the **absence of Zn^{2+}**, HER onset is:
  - ~-1.35 V on Cu electrode
  - ~-1.50 V on Zn electrode

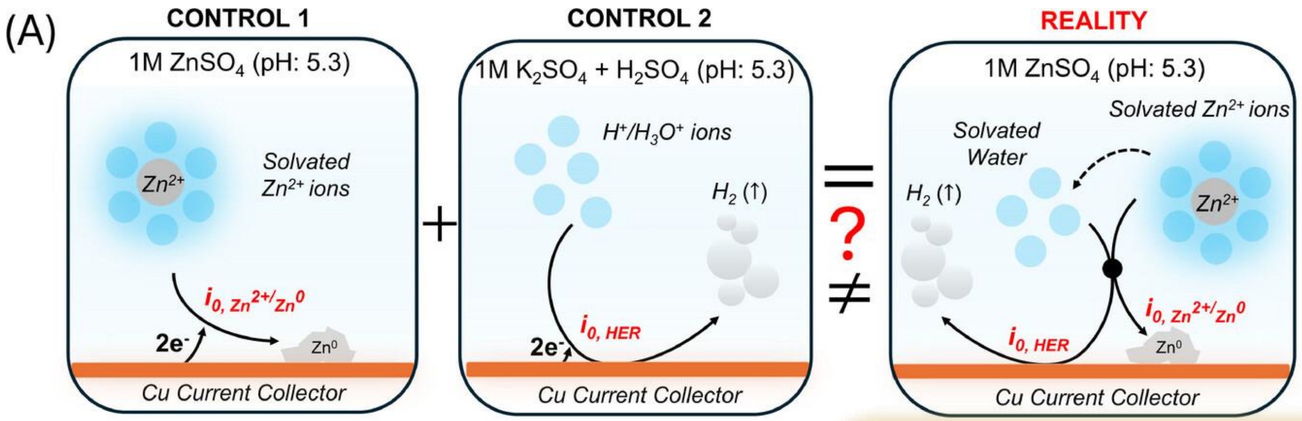
Our Approach: Measure HER partial current with EC-MS in the presence of Zn^{2+}

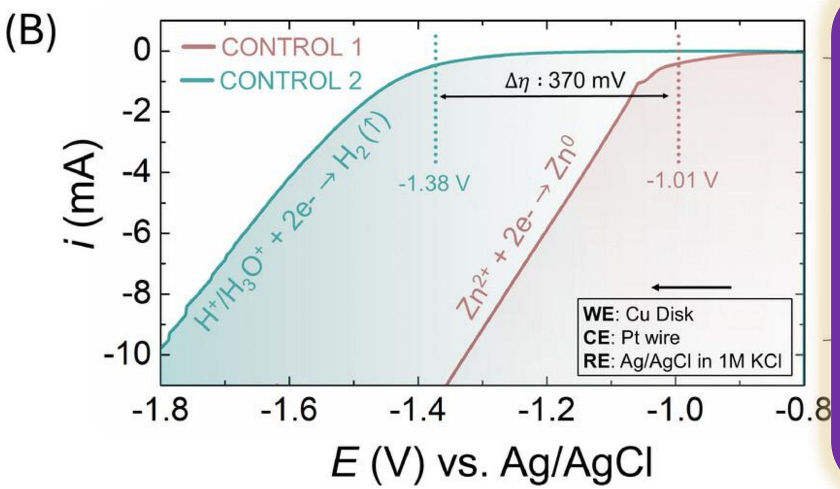
- In the **presence of Zn^{2+}**, HER onset is:
  - ~-0.8 V on Cu electrode
  - *Coincident with onset of Zn^{2+} reduction*

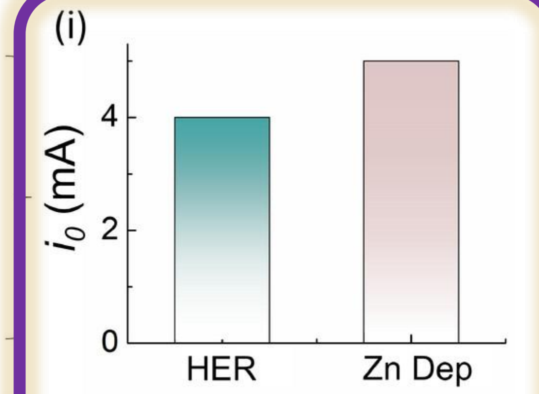
A. Rana, S. Paul, A. Bhadouria, A. Bano, J. H. Nguyen, Md. A. Faisal, K. Roy, B. M. Tackett, J. E. Dick. ***Adv. Energy Mater.*** 2025, e03155.

What is implication for intrinsic kinetics?

$$i = i_0 \, exp\left[\frac{\alpha F V}{RT}\right] \rightarrow i_0 \approx k$$







Are they really similar?

EC-MS Analysis of Zn plating and HER

Typical Approach: Measure catalytic HER in the absence of Zn^{2+} to isolate kinetics of unwanted reaction

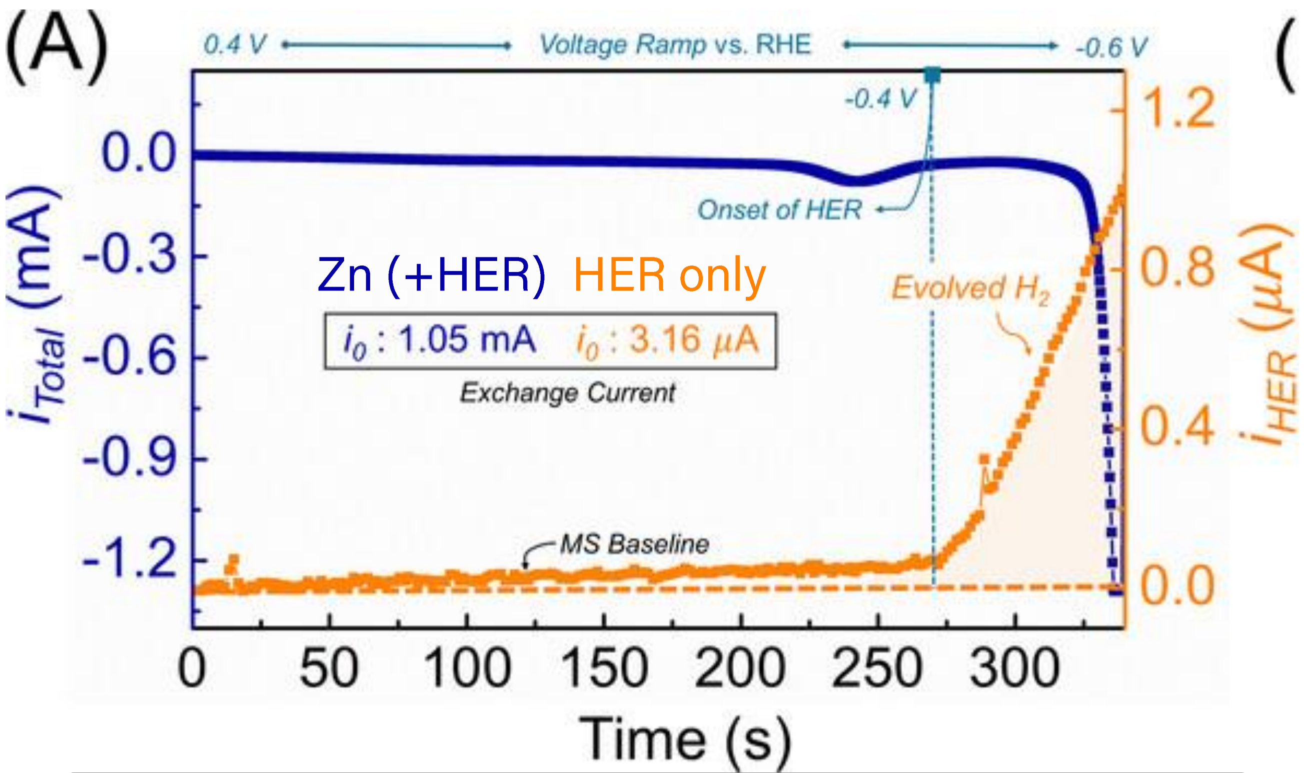
- In the **absence of Zn^{2+}**, HER onset is:
  - ~-1.35 V on Cu electrode
  - ~-1.50 V on Zn electrode

Our Approach: Measure HER partial current with EC-MS in the presence of Zn^{2+}

- In the **presence of Zn^{2+}**, HER onset is:
  - ~-0.8 V on Cu electrode
  - *Coincident with onset of Zn^{2+} reduction*

What is implication for intrinsic kinetics?

$$i = i_0\, exp\left[\frac{\alpha F V}{RT}\right] \rightarrow i_0 \approx k$$

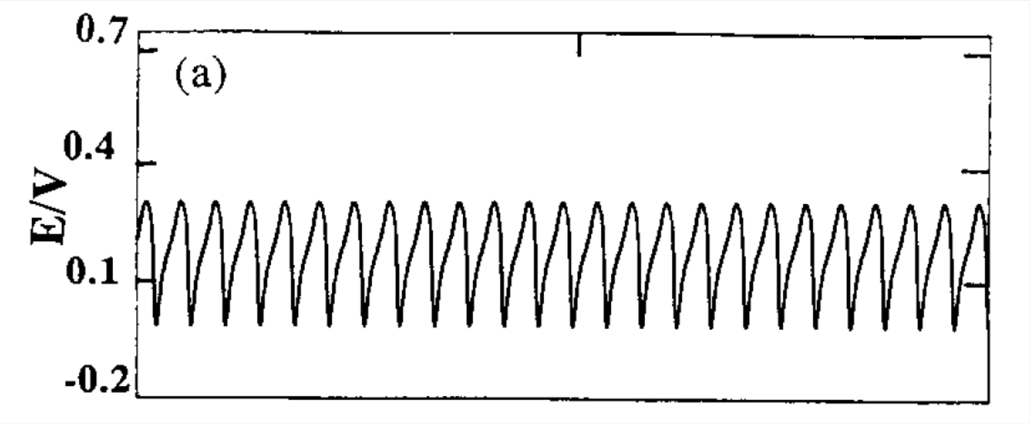


A. Rana, S. Paul, A. Bhadouria, A. Bano, J. H. Nguyen, Md. A. Faisal, K. Roy, B. M. Tackett, J. E. Dick. ***Adv. Energy Mater.*** 2025, e03155.

*If we use current **plus** MS, we can determine relevant kinetics for rational improvement*

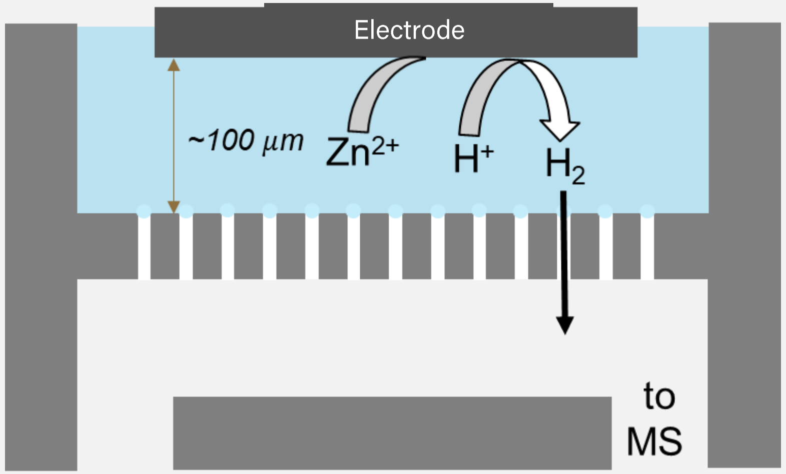
Two Examples

Electrochemical Manufacturing



- *Oscillatory instabilities can occur in almost any E-chem reactor, posing operation hazards*

Electrochemical Energy Storage



- *Aqueous batteries are inherently safe, but abundant water/H^+ causes issues with viability*

Acknowledgements

- Piyush Sharma (oscillations & instabilities)
- Prof. Can Li
- Esin Aydemir (aqueous Zn batteries)

- Prof. Jeffrey Dick (Purdue Chemistry)
- Ashutosh Rana

P²SAC
Purdue Process Safety & Assurance Center