The opportunity for electrochemistry to reduce reactivity hazards

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P2SAC Spring 2024 Conference
June 11, 2024

The opportunity for electrochemistry to reduce reactivity hazards & Reactivity hazards of electrochemical reactors

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Motivation: Opportunity for Electrochemical Processes

A large majority of industrial chemical processes are heat-driven

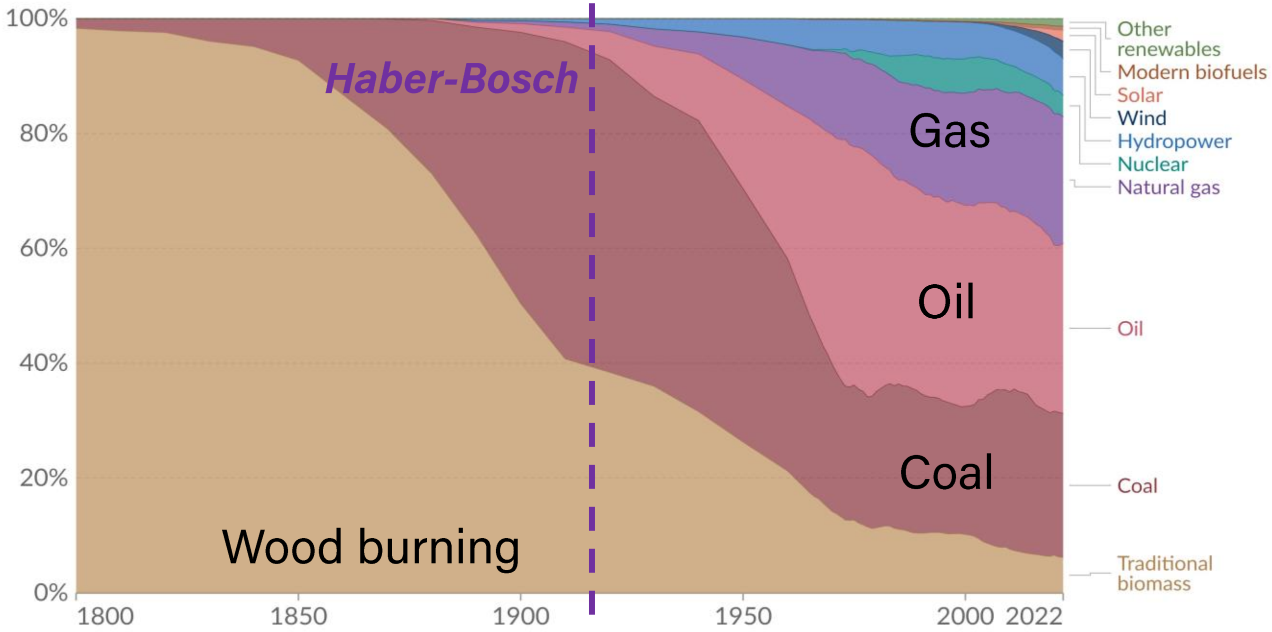
Why do we use fossil fuel heat to produce the chemicals we need?

- 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

Global primary energy consumption by source

Our World in Data

Primary energy is calculated based on the 'substitution method' which takes account of the inefficiencies in fossil fuel production by converting non-fossil energy into the energy inputs required if they had the same conversion losses as fossil fuels.



Data source: Energy Institute Statistical Review of World Energy (2023); Vaclav Smil (2017)
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Motivation: Opportunity for Electrochemical Processes

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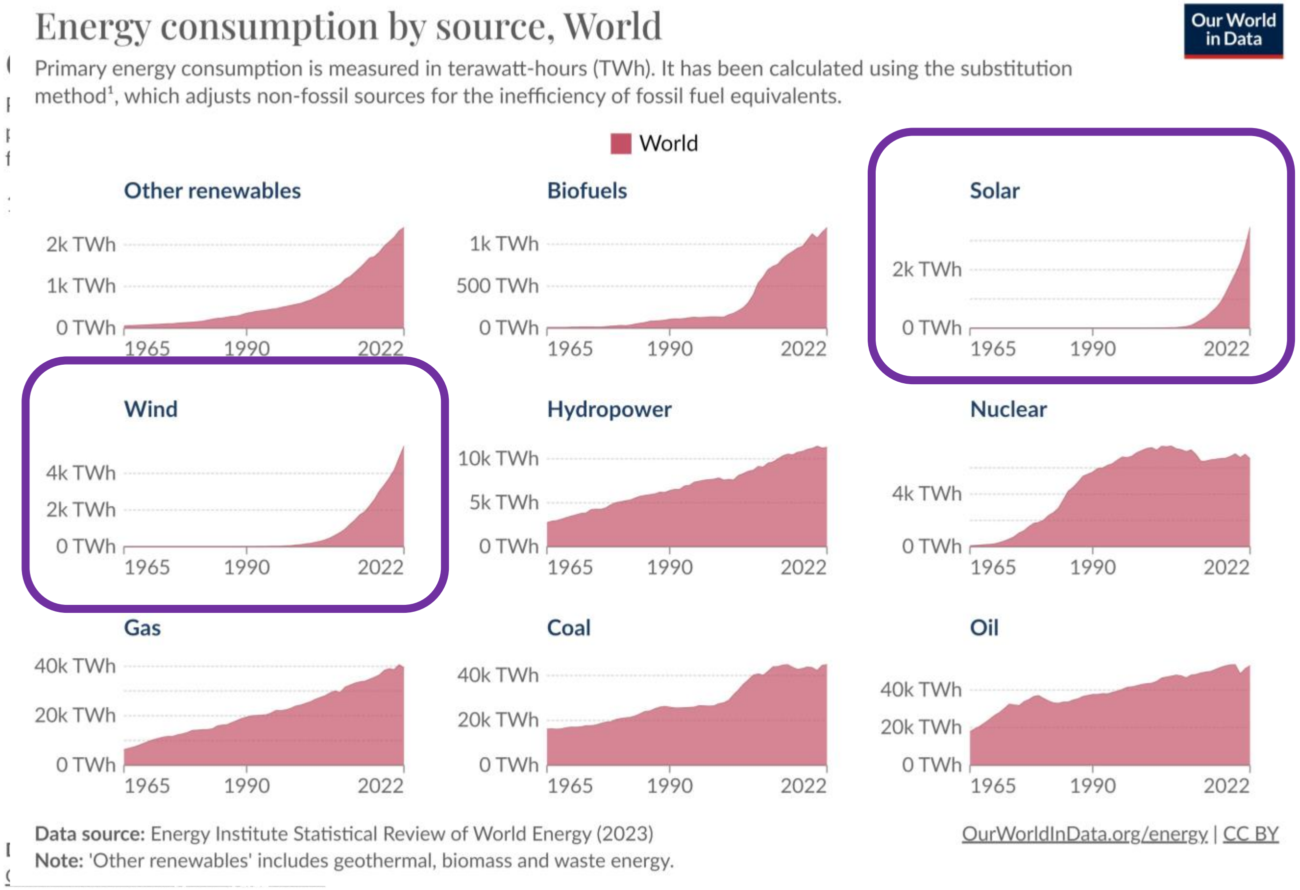
For the first time in history, we have substantial energy in the form of electricity produced via wind & solar

- **This allows us to reimagine a sustainable and electrified chemical industry**



Energy consumption by source, World

Primary energy consumption is measured in terawatt-hours (TWh). It has been calculated using the substitution method¹, which adjusts non-fossil sources for the inefficiency of fossil fuel equivalents.

Data source: Energy Institute Statistical Review of World Energy (2023)

Note: 'Other renewables' includes geothermal, biomass and waste energy.

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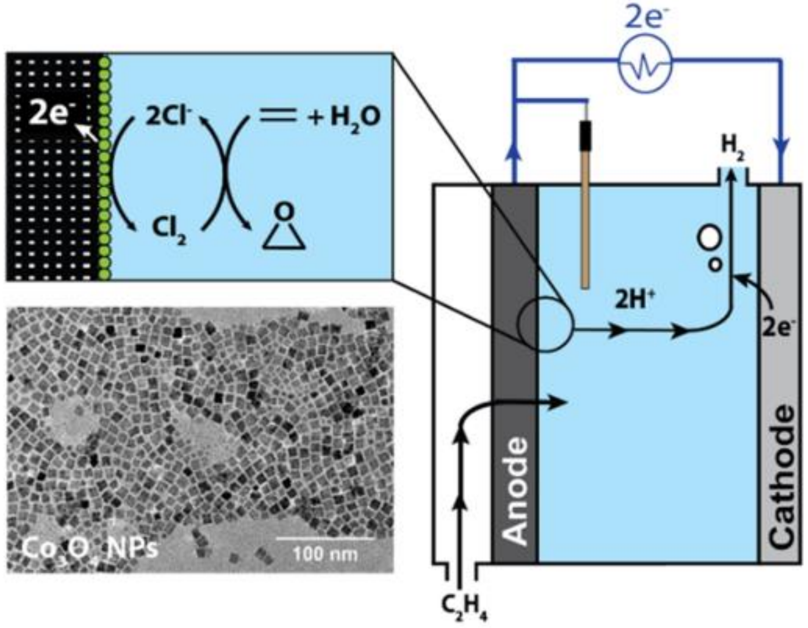
Motivation: Opportunity for Electrochemical Processes

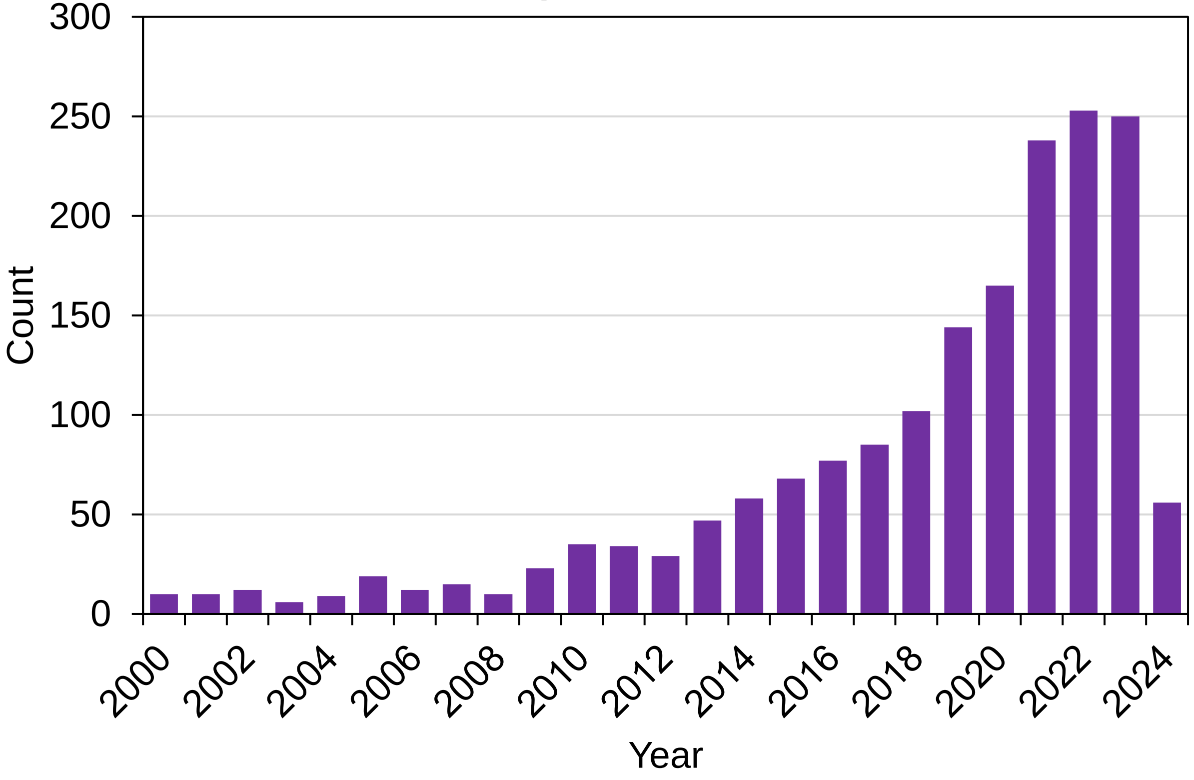
This has sparked interest in organic synthesis industries (e.g. pharma)

→ can leverage cheap/abundant electrons to:

- Replace toxic oxidants
- Reduce operating temperatures
- Achieve selective pathways with fewer steps



Web of Science results for “Electrochemical Synthesis” + “Pharmaceutical”



Motivation: Opportunity for Electrochemical Processes

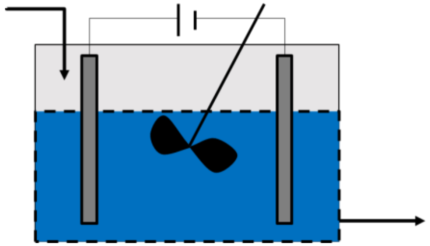
At the same time, there's a desire to move from batch to continuous processes

- *What reactivity hazards are specifically associated with flow electrochemistry?*
- *How can we address them?*

To understand, let's briefly review basic concepts of electrochemical reactions

Continuous Electrochemical Reactors

Electrochemical CSTR



$$S = \frac{(F_{A0} - F_A)n\mathcal{F}}{i}$$

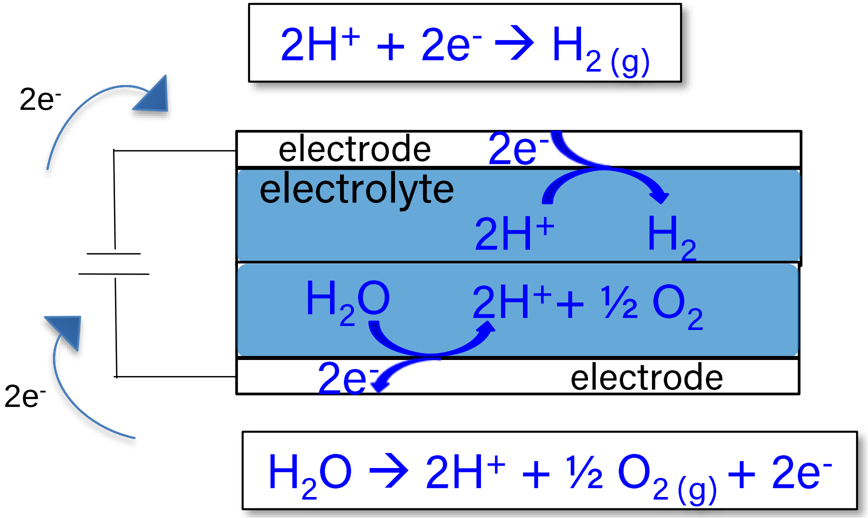
Electrochemical PFR

$$\frac{dC_A}{dx} = \frac{iS}{n\mathcal{F}Lv_0}$$

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


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

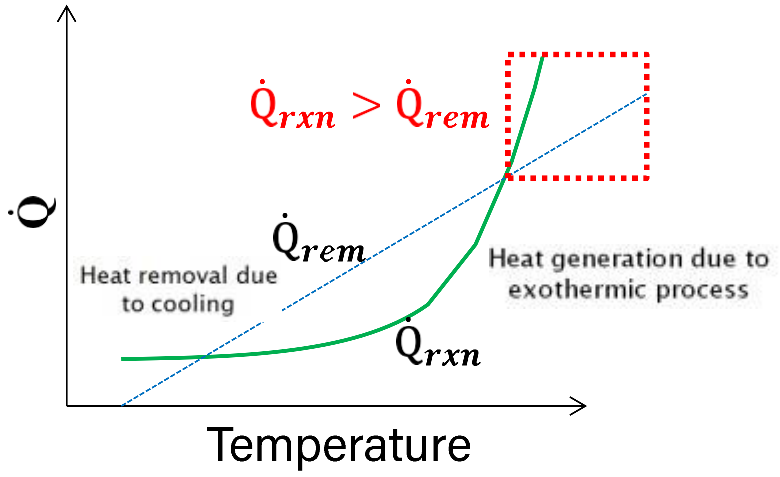
$H_2O \rightarrow 2H^+ + ½\, O_{2\,(g)} + 2e^-$

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

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

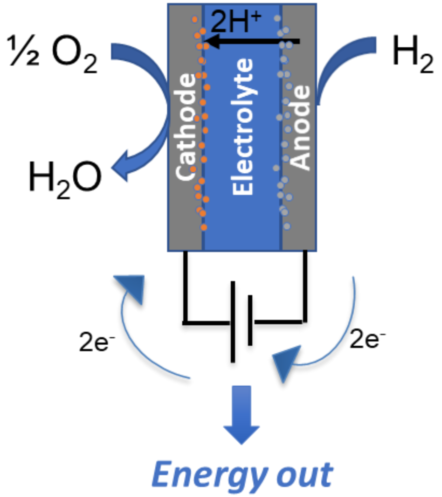
Ex)

$H_2 + ½ O_2 \rightarrow H_2O$

ΔH_{rx} = -242 kJ/mol

↓

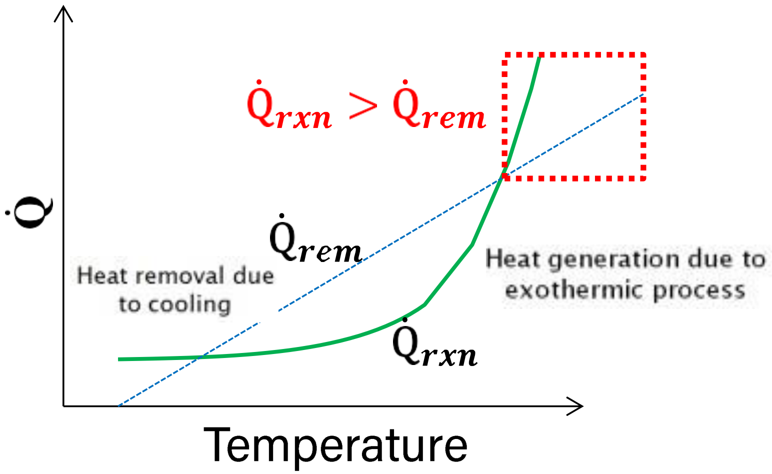
1.23 V @ 298K
in electrochemical reactor



Reactivity Hazards for Continuous Reactors

Thermochemical Reactors

Runaway Reactions



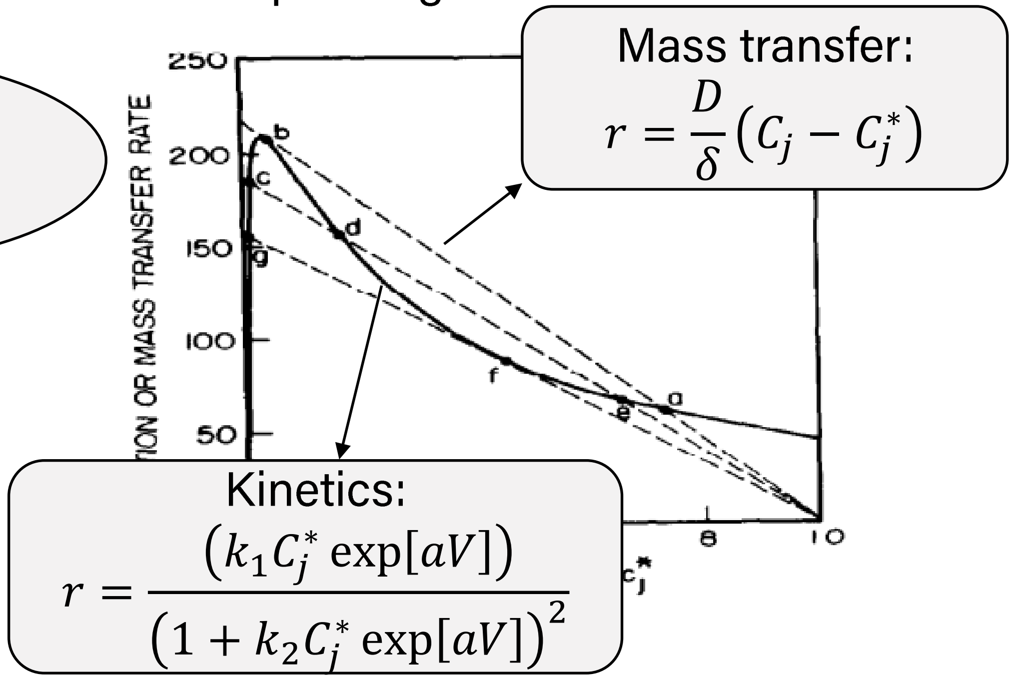
- Heat generated via reaction exceeds heat removed via heat-exchange
- Hazardous scenarios understood by analyzing ***multiple steady states***

What are the hazards?

Electrochemical Reactors

Runaway Reactions?

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



Mass transfer:

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

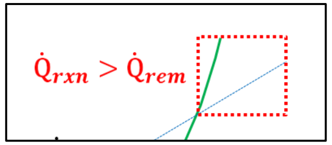
Kinetics:

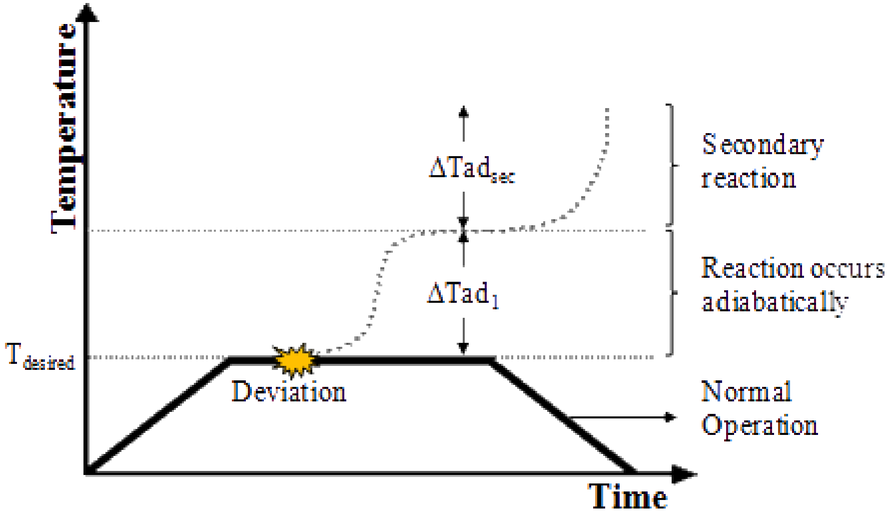
$$r = \frac{\left(k_1 C_j^* \exp[aV]\right)}{\left(1 + k_2 C_j^* \exp[aV]\right)^2}$$

Reactivity Hazards for Continuous Reactors

Thermochemical Reactors

Hazards during runaway conditions



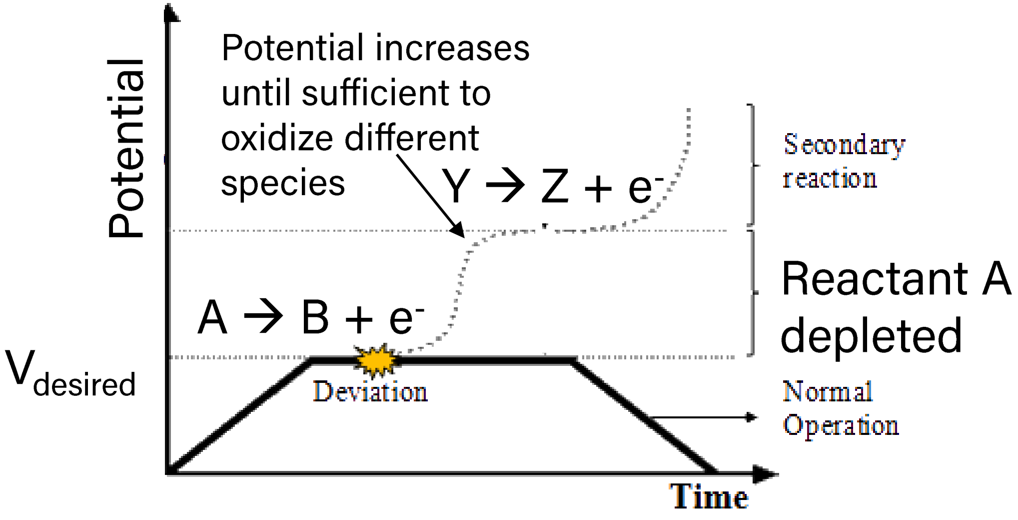


- High T exceeds reactor specs
- **High T initiates secondary rxn**
  - Gas generation/pressure increase
  - Hazardous/undesired chemicals

Electrochemical Reactors

Hazards during "runaway" conditions

Constant current operation

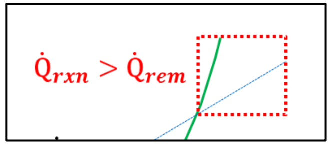


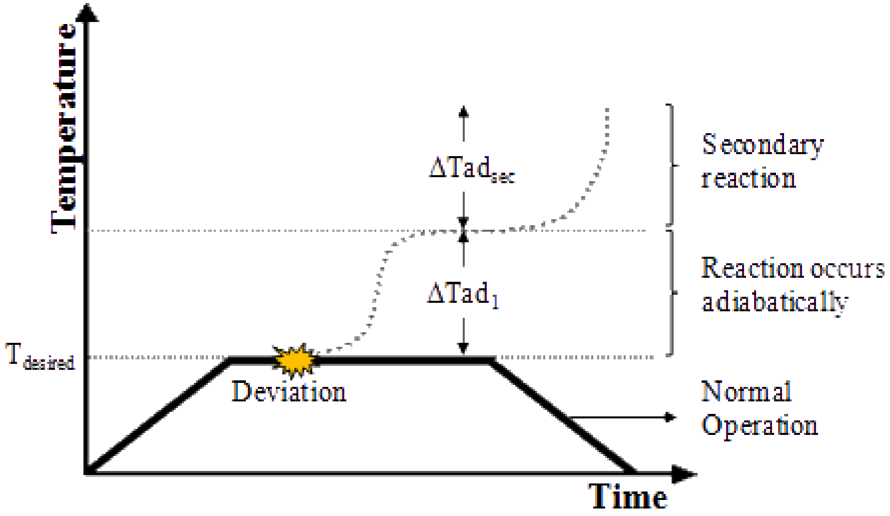
- Depletion of reactant initiates secondary rxn
  - Solvent/electrode decomposition
  - H_2/O_2 generation
  - Polymerization
  - ***Higher T due to increased Joule heating***

Reactivity Hazards for Continuous Reactors

Thermochemical Reactors

Hazards during runaway conditions



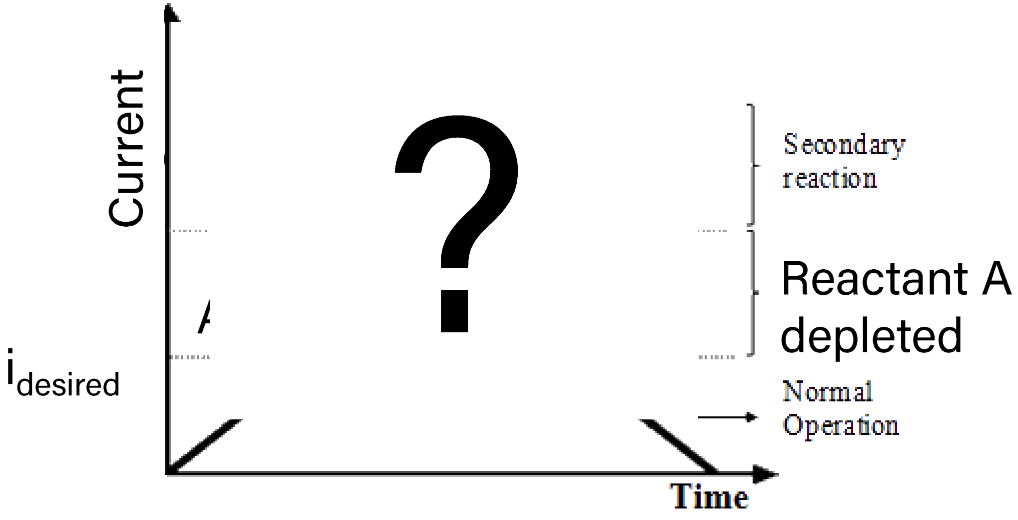


- High T exceeds reactor specs
- **High T initiates secondary rxn**
  - Gas generation/pressure increase
  - Hazardous/undesired chemicals

Electrochemical Reactors

Hazards during "runaway" conditions

Constant potential operation

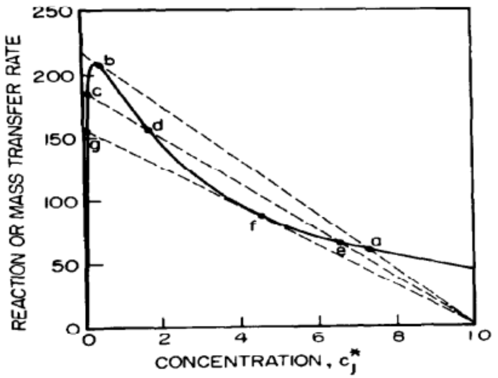


- Unpredictably high/low current (reaction rate)
  - Could lead to oscillation/control issues

Analyzing Unstable Steady States in Electrochemistry

Challenges for addressing reactivity hazards related to multiple steady states:

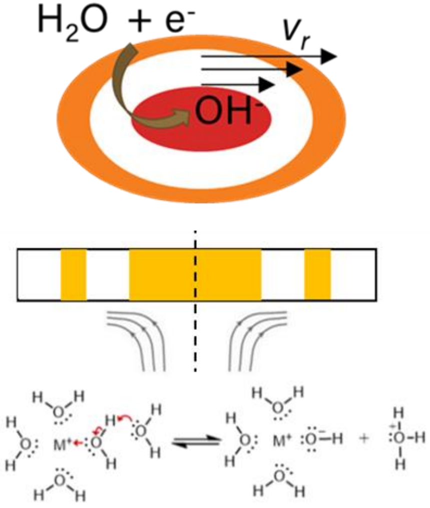
- Electrochemical multiple steady states arise as solutions to coupled equations of
  - Kinetics
  - Mass transport
  - Electric field
- There is no existing experimental exploration of electrochemical multiple steady states



Sakellaropoulos and Volintine. *Chemical Engineering Science*, 1980, 35: 396–404.

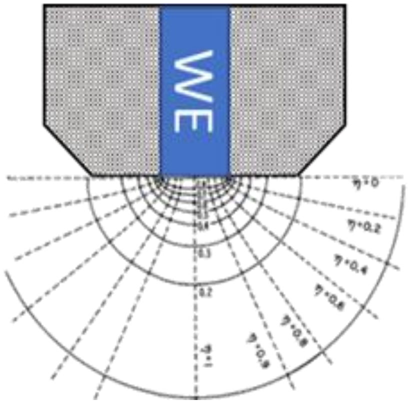
Experimental analysis must simultaneously account for kinetics, MT, & potential @ steady state

Rotating Ring-Disk Electrode



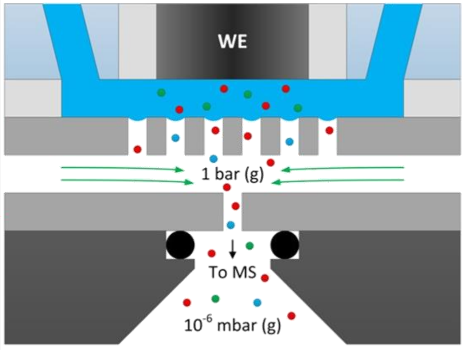
- Well defined hydrodynamics
- Product sensing via ring

Micro Electrode



- Access steady state in quiescent media

Electrochemical Mass Spec

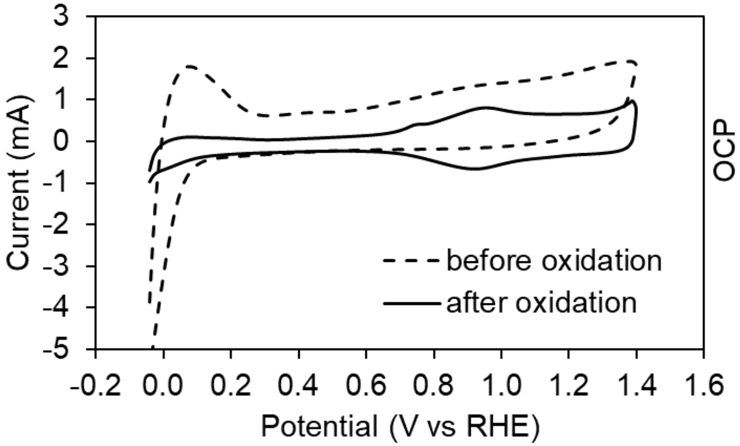


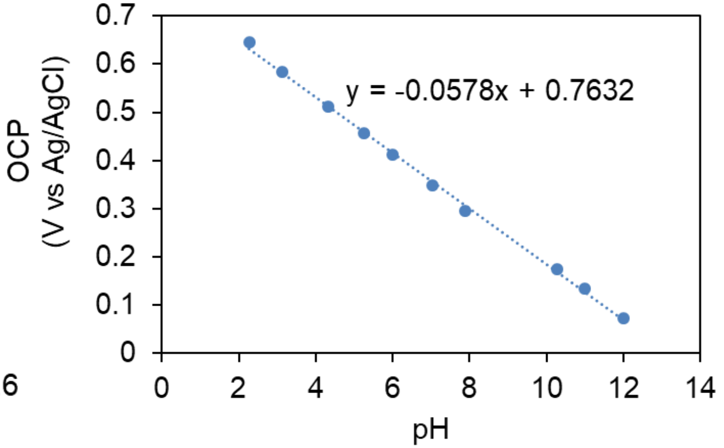
- Defined 100µm BL for gaseous reactants
- Product speciation

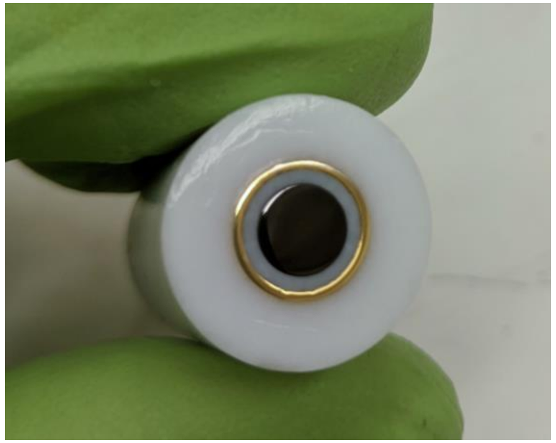
Iridium Oxide pH Sensor on RRDE

- Iridium oxide pH sensor can help
  - Potentiometric
  - Reaction agnostic
  - Fabrication flexible (e.g. RRDE)

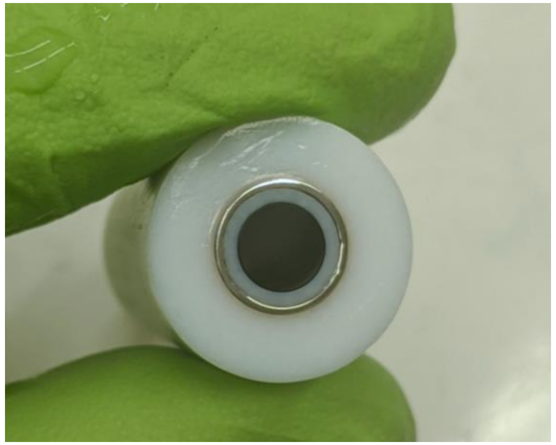
$$2IrO_2 + 2H^+ + 2e^- \rightleftharpoons Ir_2O_3 + H_2O$$



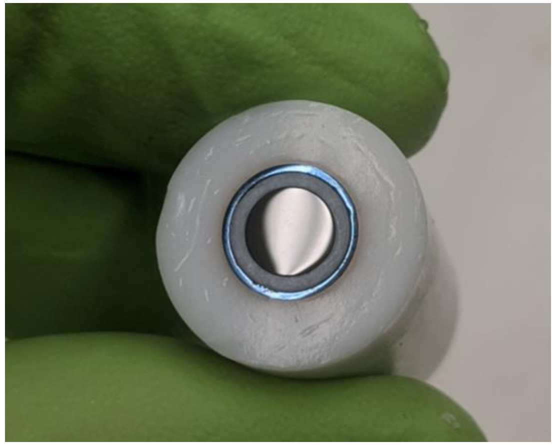




Gold



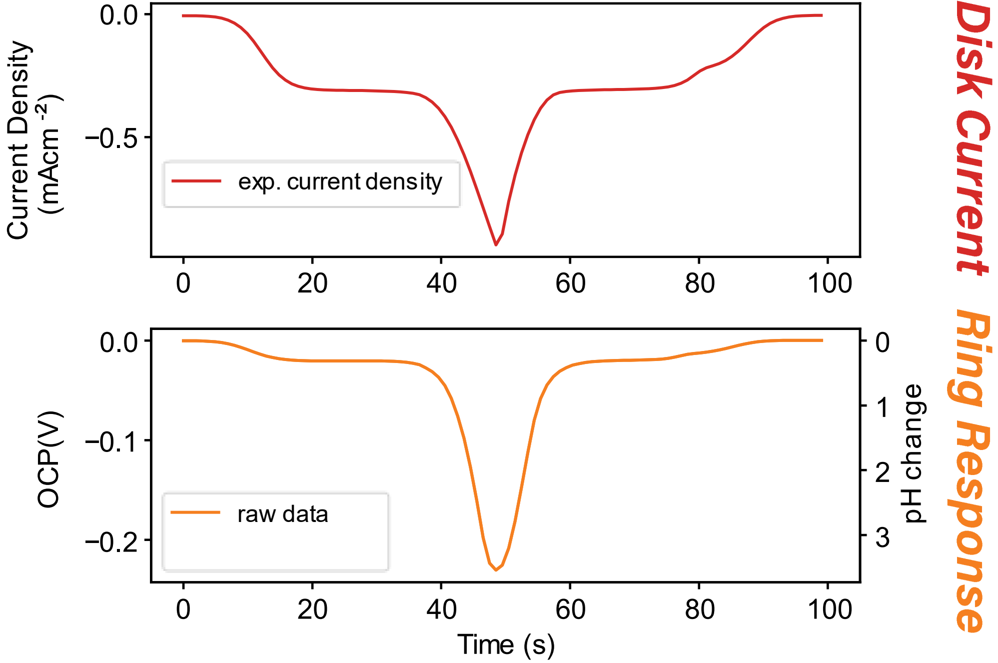
Iridium



Iridium oxide

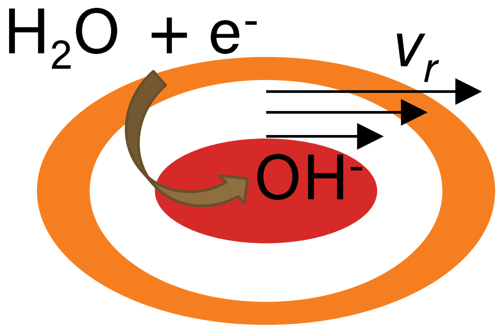
Sensing pH with Rotating Ring-Disk Electrode (RRDE)

How do we determine disk pH based on ring pH?



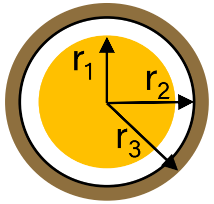
Contributions to ring response:

- ***Ohmic drop induced by potential distribution***
- ***Boundary layer pH changes induced by disk reaction***
    - Well-described by RRDE convection-diffusion
    - Influenced by homogeneous buffers



Ohmic Drop at Ring

- Current flowing to the disk induces potential change at the ring, regardless of pH change



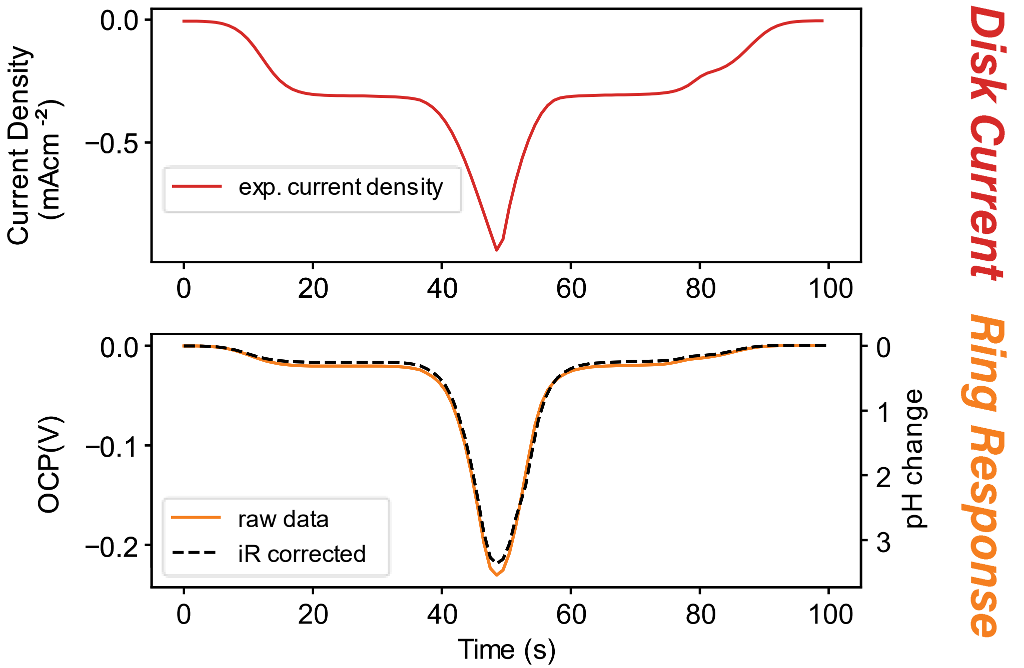
$$\frac{\phi}{I} = \frac{\left(\frac{\phi}{\phi_0}\right)}{4\kappa r_1}$$

Ring potential induced by disk current

$$\frac{\phi}{\phi_0} = \underbrace{\kappa r_3 R_{rd}}_{} \frac{4r_1}{r_2}$$

Tabulated by Miksis and Newman[1]

- Provides the **upper limit** for ohmic drop at ring, corresponding to **primary current distribution**[1,2]



1. J. J. Miksis and J. Newman, *J. Electrochem. Soc.*, 1976, **123**, 1030.
2. S. Hessami and C. W. Tobias, *AIChE J.*, 1993, **39**, 149–162.

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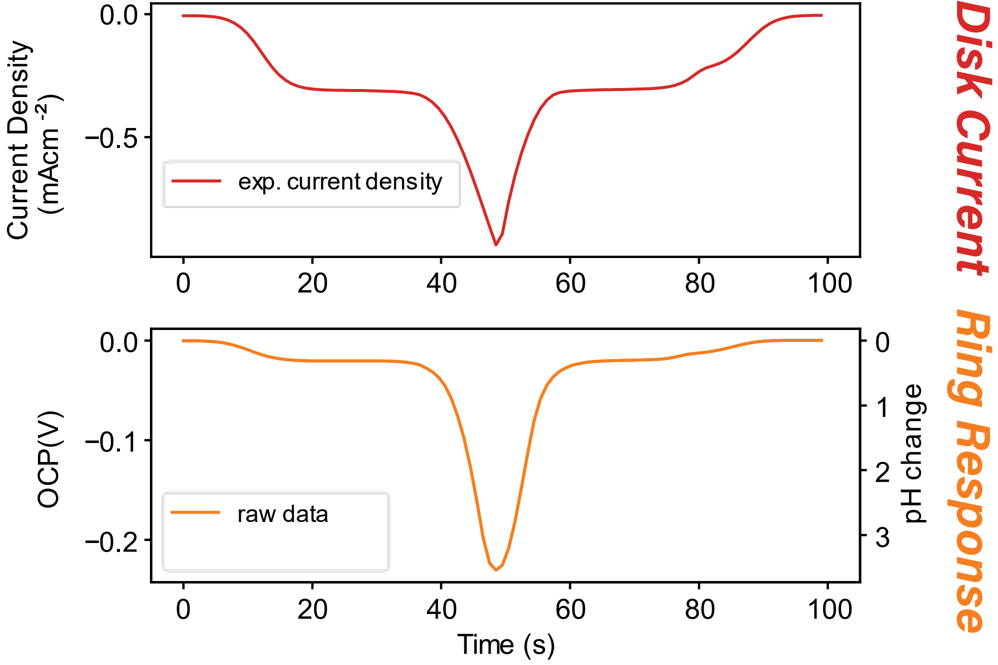

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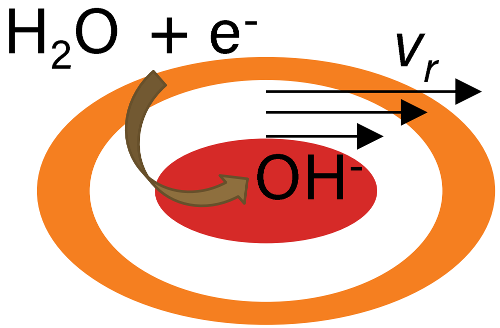


Modeling pH change during HER in unbuffered pH 4 acid

2-step HER in mild acid:

$$\boldsymbol{H^+ + H_2O + 2e^- \rightleftharpoons H_2 + OH^-}$$

Analytical solution for proton concentration on disk surface:

$$c_{d,H} = K_5^{\frac{1}{2}} \left[\frac{\bar{c} + \sqrt{\bar{c}^2 + \theta(-\alpha)\theta(2-\alpha)}}{\theta(-\alpha)} \right]$$

$$\theta(b) = 2K_5^{\frac{1}{2}} \left[1 + 2k \frac{\delta_N}{D} K_5^{\frac{-b}{2}} \exp\left(\frac{FEb}{RT} \right) \right]$$

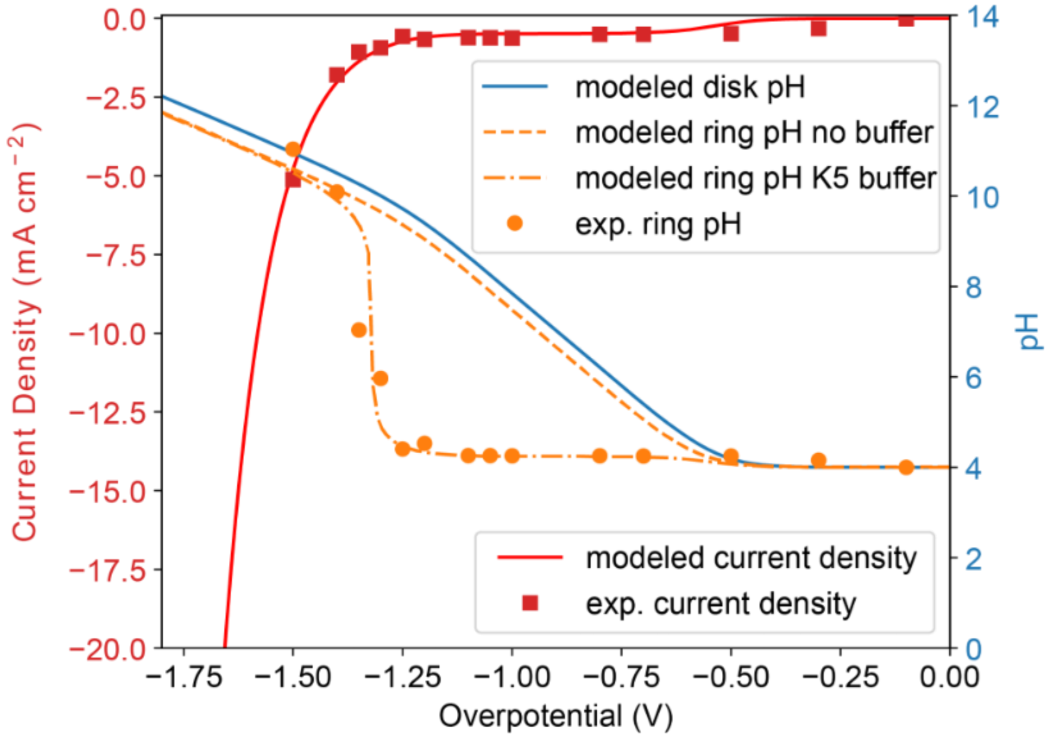
Model validated by Broekmann et al.[1] K_5 ➔ water autoprotolysis equil.

Equation for ring concentration:

$$(\bar{\boldsymbol{c}}_{\boldsymbol{ring}} - \bar{\boldsymbol{c}}_{\boldsymbol{bulk}}) = \boldsymbol{N_D}(\bar{\boldsymbol{c}}_{\boldsymbol{disk}} - \bar{\boldsymbol{c}}_{\boldsymbol{bulk}})$$

N_D = RRDE ***detection efficiency***

$\bar{c} = c_H - c_{OH}$



RRDE accurately captures large pH change in unbuffered acid

B. M. Tackett, D. Raciti, N. W. Brady, N. L. Ritzert, T. P. Moffat. ***J. Phys. Chem. C****, 2022, 126, 7456.*

[1] Gálvez-Vázquez, M. D. J., Grozovski, V., Kovács, N., Broekmann, P., & Vesztergom, S. (2020). *J. Phys. Chem. C*, 2020, *124,* 3988–4000.

Summary and outlook

Electrochemical processes can inherently mitigate reactivity hazards:

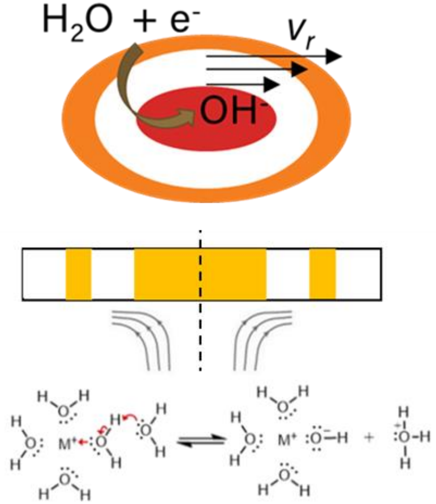
- Ambient T operation
- Substitution of toxic oxidants
- Simplified reaction schemes

But continuous electrochemical reactors can experience analogous reactivity hazards due to *multiple steady states*

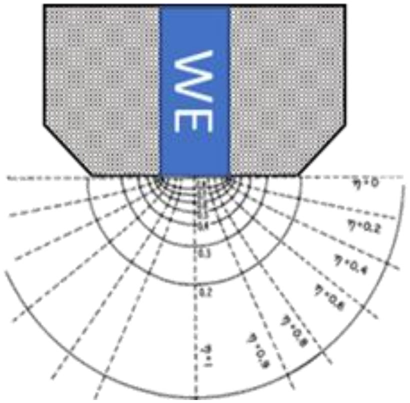
- Secondary reactions
- Unpredictable oscillations

The first step to addressing such hazards is experimental exploration of multiple steady state behavior

Rotating Ring-Disk Electrode



Micro Electrode



Electrochemical Mass Spec