Tutorial: Design of Electrochemical Flow Reactors

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Assistant Professor of Chemical Engineering, Purdue

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Purdue University
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About Me

Education & Background

BS Chemical Engineering,
University of Pittsburgh *(2009 – 2013)*

PhD Chemical Engineering,
Columbia University *(2014 – 2019)*
Advisor: Jingguang Chen
(Electrocatalysis & Sustainability)

NRC Post-Doctoral Fellowship,
NIST *(2019 – Aug. 2021)*
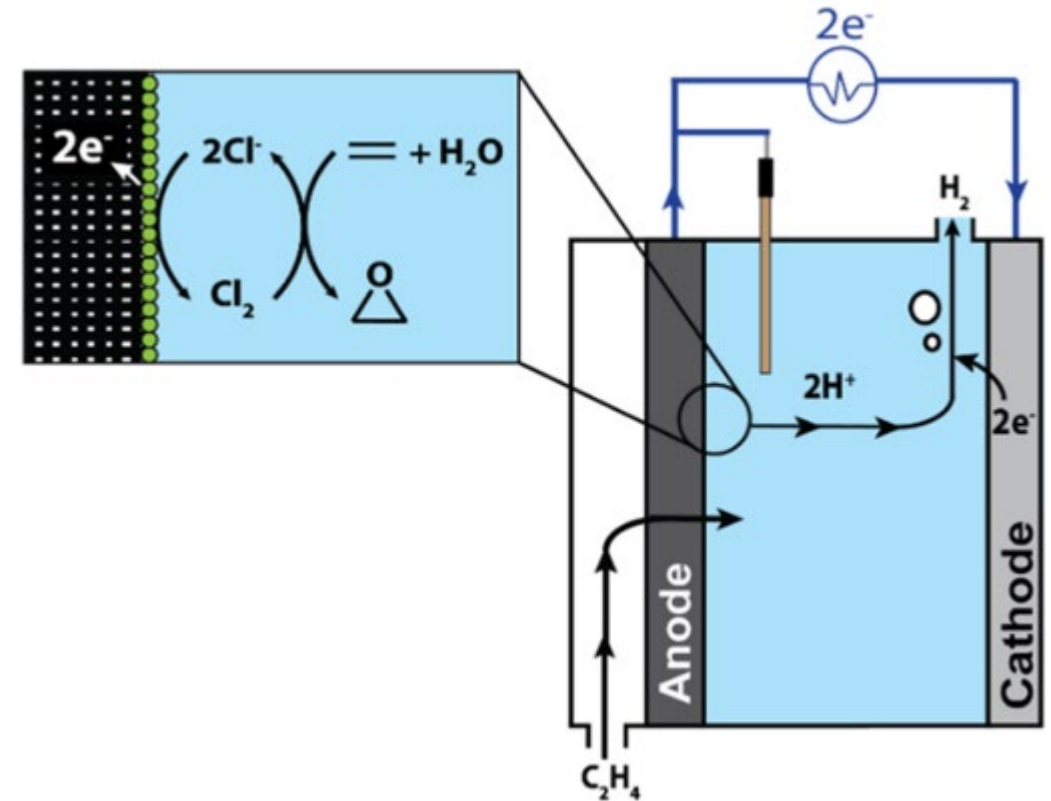*Advisor: Tom Moffat*
(Electrochemistry Fundamentals)

Asst. Prof. Chemical Engineering,
Purdue University *(Aug. 2021 –)*

"NIST is a sort of acropolis of the average"

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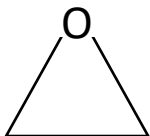
Tutorial Goals

- **<u>Why</u>** are we interested in electrochemical synthesis of chemicals?

  - *Identify key advantages and opportunities for E-chem synthesis*

- **<u>What</u>** are the basic elements of an electrochemical reaction?

  - *Describe components needed for E-chem synthesis*

- **<u>How</u>** do we leverage electrochemistry to produce chemicals in continuous flow reactors?

  - *Implement standard methodology for designing E-chem flow reactors*

Industrial organic syntheses are often hazardous

Case Study: Ethylene Oxide Synthesis

- Route 1: *Direct Oxidation*

  - $C_2H_4 + O_2 \rightarrow C_2H_4O$ $+ CO_2$
    (from over-oxidation/gas compression)

  - ~10% single pass conversion @ 200 – 260 C,
    ~20 bar
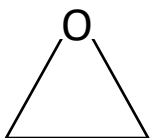
    - Higher T, above flammability limit

- Route 2: *Chlorohydrin Process*

  - $C_2H_4 +$ Cl_2 $+ H_2O \rightarrow$

   $Ca(OH)_2 \rightarrow C_2H_4O +$ $CaCl_2$ $+ H_2O$
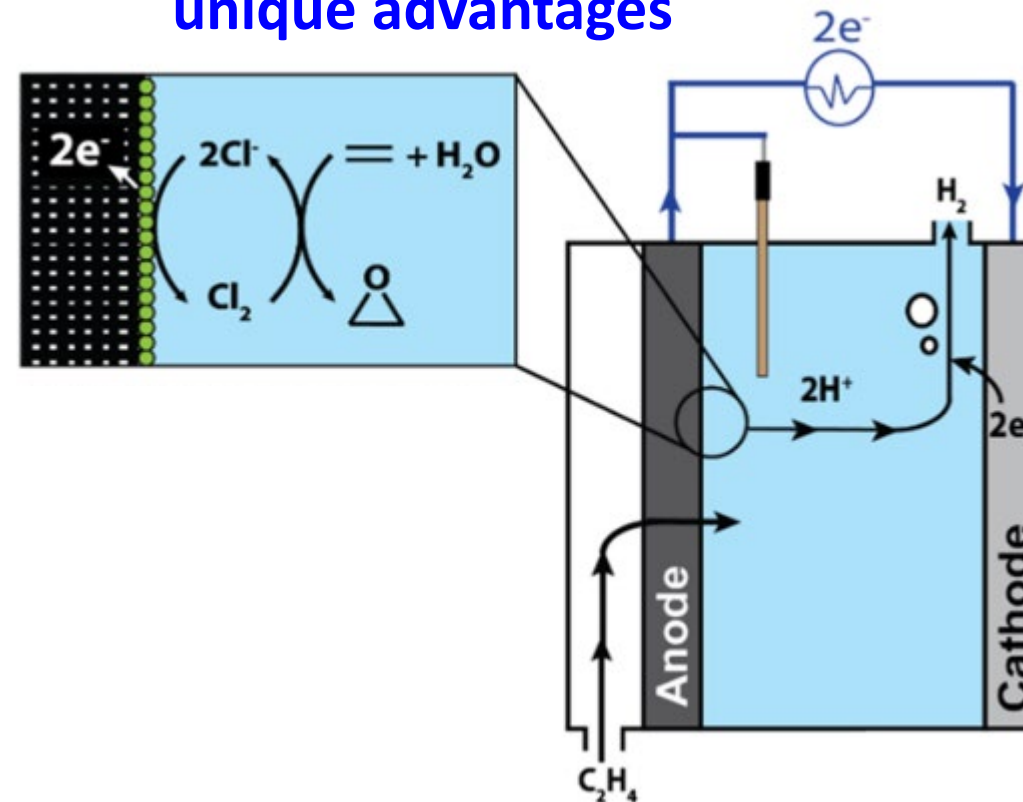
Industrial organic syntheses are often hazardous

Case Study: Ethylene Oxide Synthesis

- Cl_2 mediator is generated electrochemically at an electrode by electron transfer from aqueous Cl^- salt

  - *No bulk Cl_2 handling or processing*

- Cl_2 and H_2O transform ethylene to EO in the same manner as chlorohydrin process

- Resulting Cl^- ions are recycled and reinitiated as mediators

  - *No stoichiometric waste*

- Occurs @ 90 C

  - *No explosion hazard*

E-chem synthesis provides unique advantages

Why are we interested in E-chem synthesis?

Industrial organic syntheses are often **hazardous**

➡️ **E-chem synthesis provides** **unique advantages**

General Advantages of Electron-Driven Reactions

- Driving force for chemical reaction = electrochemical potential (i.e. voltage)

  - *Facilitates ambient T processes*

  - *Enables finer selectivity control*

- Electrodes are versatile

  - *Generate redox mediators in-situ*

  - *Catalyze reaction directly (enhance activity/selectivity)*

> *These enable selective reactions that can mitigate hazards and facilitate new synthetic pathways*
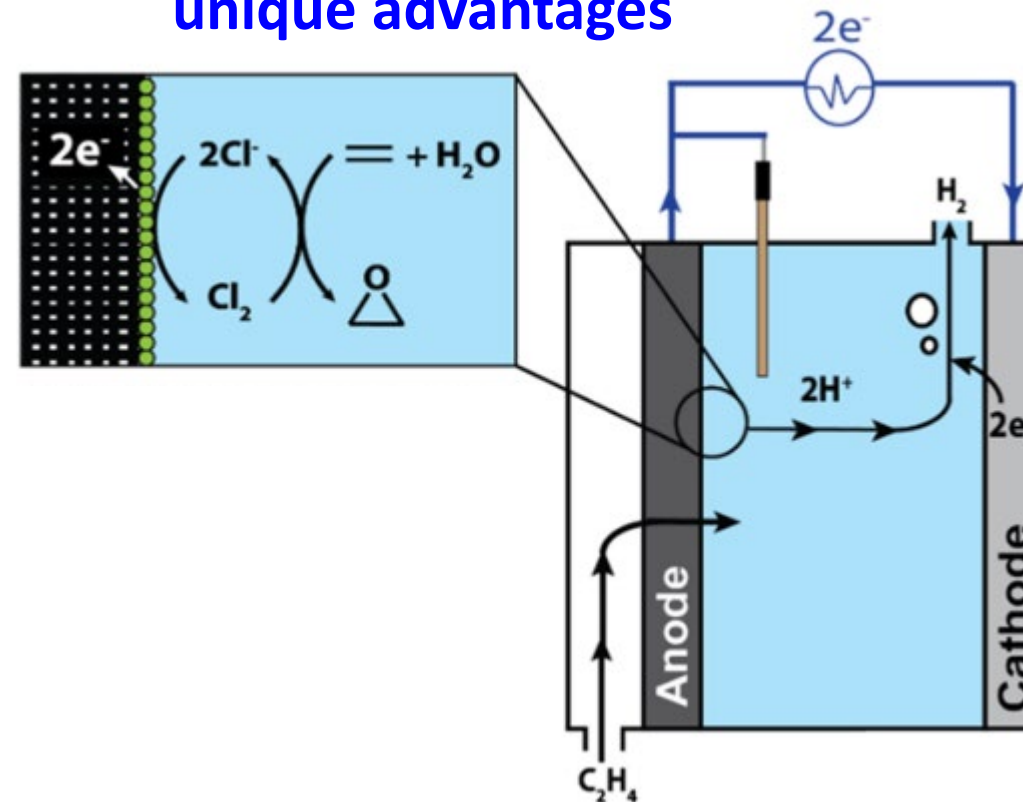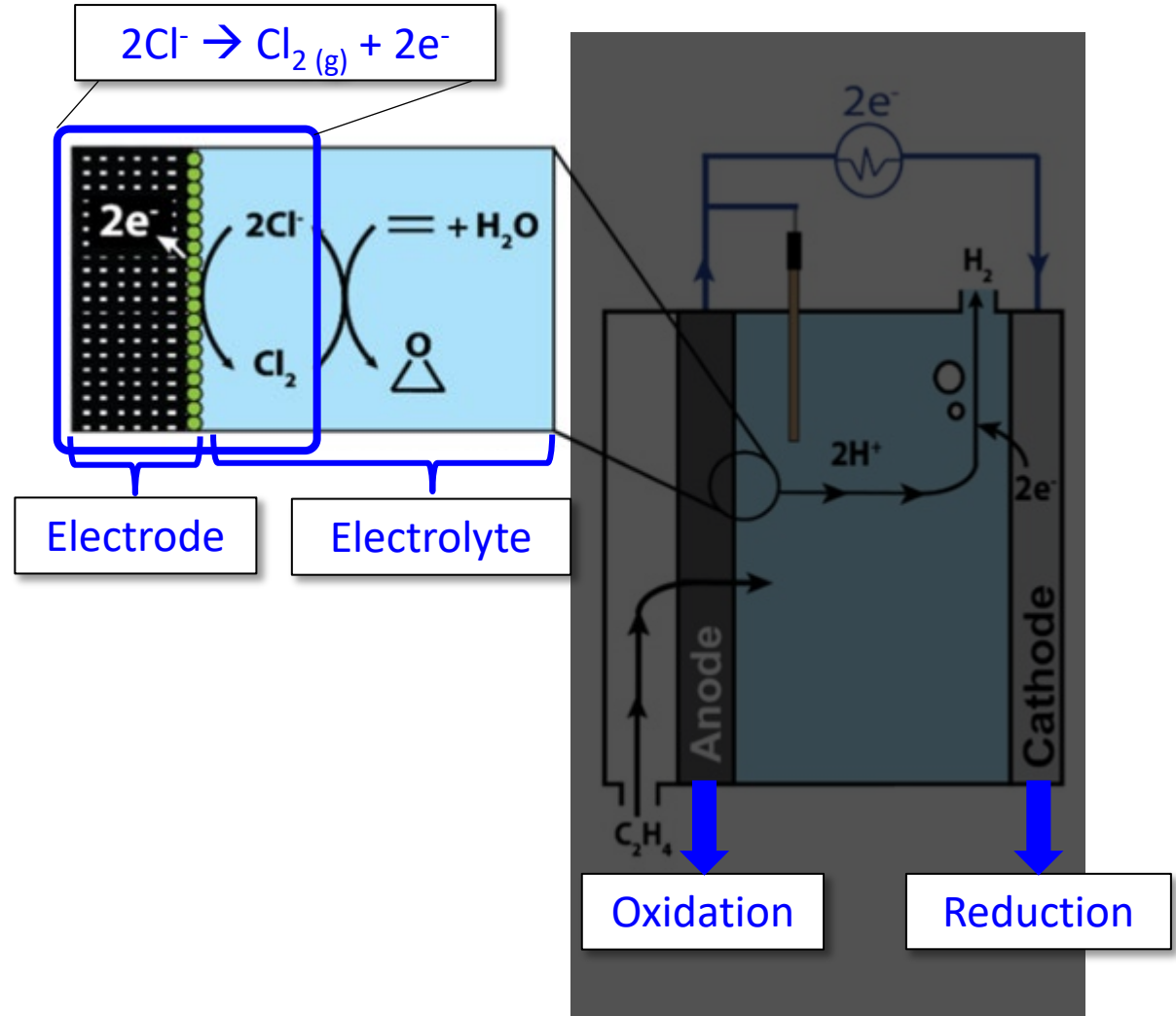
Three basic elements of an electrochemical reaction:

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

   - One for reduction half reaction (cathode)

   - One for oxidation half reaction (anode)

$2Cl^- \rightarrow Cl_{2\ (g)} + 2e^-$

Electrode

Electrolyte

Oxidation

Reduction

Anode

Cathode

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Chemical Engineering

How do we design E-chem reactors?

Translating Chemistry $\leftrightarrow$ Electrochemistry:

- Voltage/Potential is energy $\rightarrow$ $V_{cell} = -\dfrac{\Delta G_{rx}}{n\mathcal{F}}$

  $\mathcal{F}$ = 96485 C/(mol e): amount of charge in 1 mol e⁻

  n : (# mol e⁻) / (mol product)

- Current is reaction rate $\rightarrow$ $i = n\mathcal{F}r$

  r : rxn rate [mol m⁻² s⁻¹]

(Electro)Chemical Reaction Engineering:

1. **Mole Balance/Reactor Design Equation**
2. Rate Law
3. Stoichiometry
4. Combine
5. Evaluate (determine critical reactor parameters: *volume, concentration, flow rate, conversion, temperature, etc*)

How do we design E-chem reactors?

Mole Balance / Reactor Design Equation:

$$\text{In} \quad - \quad \text{Out} \quad + \quad \text{Gen.} \quad = \quad \text{Accumulation}$$

Apply this to any reactor type

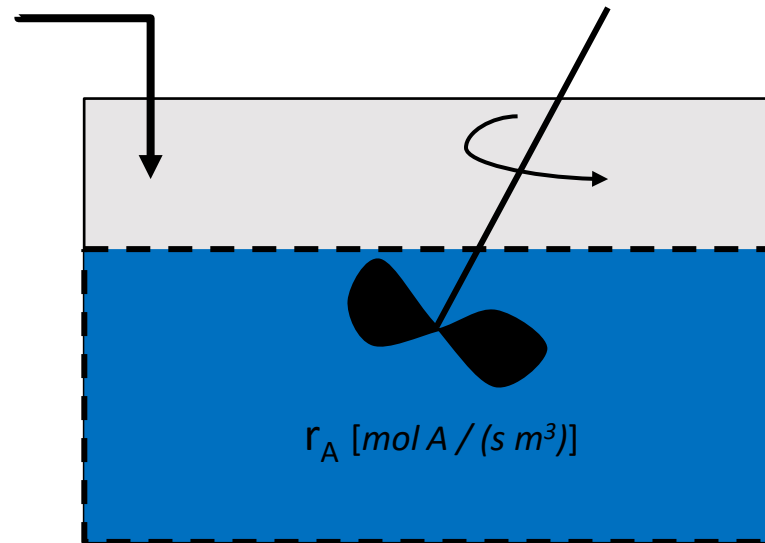Ex) Continuous Stirred Tank Reactor (CSTR): $A \rightarrow B + C$

$$F_{A0} \quad - \quad F_A \quad + \quad r_A * V \quad = \quad 0$$

*Assume perfect mixing (r_A the same everywhere)
*Assume steady state (no accum.)

F_{A0} [*mol A / s*]

$$V = \frac{F_{A0} - F_A}{-r_A}$$

r_A [*mol A / (s m³)*]

Reactor volume: V [*m³*]

F_A [*mol A / s*]

How do we design E-chem reactors?

Mole Balance / Reactor Design Equation:

In	-	Out	+	Gen	=	Accumulation

Apply this to any reactor type

*Assume perfect mixing
*Assume steady state (no accum.)
Assume uniform rate across S

Ex) ***Electrochemical*** Continuous Stirred Tank Reactor (CSTR): A ***+ e$^-$*** $\rightarrow$ B + C

$$F_{A0} \quad - \quad F_A \quad + \quad \underline{r_A' * S} \quad = \quad 0$$

F_{A0} [*mol A / s*]
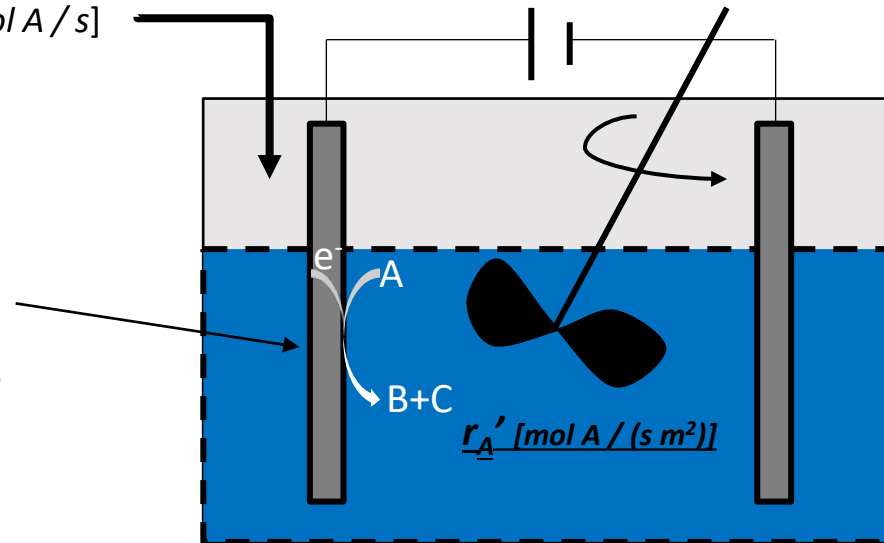
$$S = \frac{F_{A0} - F_A}{-r'_A} = \frac{(F_{A0} - F_A)n\mathcal{F}}{i}$$
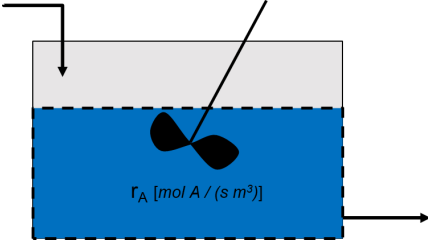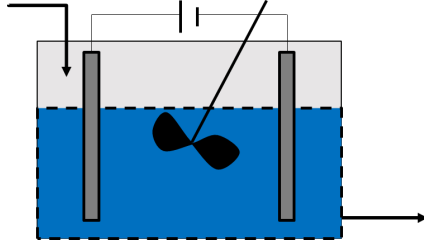
Electrode surface area: S [*m²*]

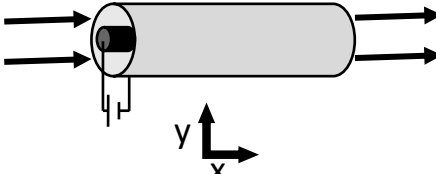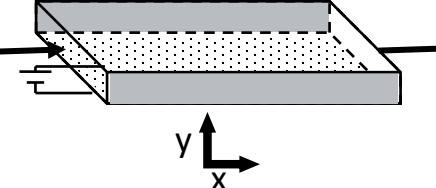*rxn ***only occurs*** on surface of electrode, so we normalize rate by surface area, rather than volume

e$^-$ A

B+C

$\underline{r_A'}$ [*mol A / (s m²)*]

Reactor volume: V [*m³*]

F_A [*mol A / s*]

How do we design E-chem reactors?

Mole Balance / Reactor Design Equation:

	Chem		E -chem	
CSTR		$$V = \frac{F_{A0} - F_A}{-r_A}$$		$$S = \frac{(F_{A0} - F_A)n\mathcal{F}}{i}$$
Plug Flow Reactor (PFR)		$$\frac{dF_A}{dV} = r_A$$	Concentric Cylinder	$$\frac{dC_A}{dx} = \frac{iS}{n\mathcal{F}Lv_0}$$
			Parallel Plate	$$\frac{dC_A}{dx} = \frac{iS}{n\mathcal{F}Lv_0}$$

r_A [mol A / (s m³)]

How do we design E-chem reactors?

Translating Chemistry ↔ Electrochemistry:

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  n : (# mol e⁻) / (mol product)

- Current is reaction rate → $i = n\mathcal{F}r$

  r : rxn rate [mol m⁻² s⁻¹]

(Electro)Chemical Reaction Engineering:
1. Mole Balance/Reactor Design Equation
2. **Rate Law** ⟶ *This is how we relate current to voltage*
3. Stoichiometry
4. Combine
5. Evaluate (determine critical reactor parameters: *volume, concentration, flow rate, conversion, temperature, etc*)

How do we design E-chem reactors?

Rate Law:

Chem:
rate is exponential function of T

$\longleftrightarrow$
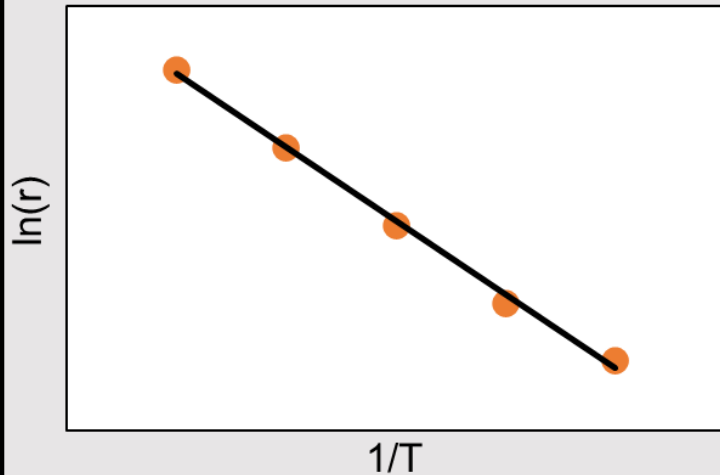
E-Chem:
rate is exponential function of V

$\longleftrightarrow$
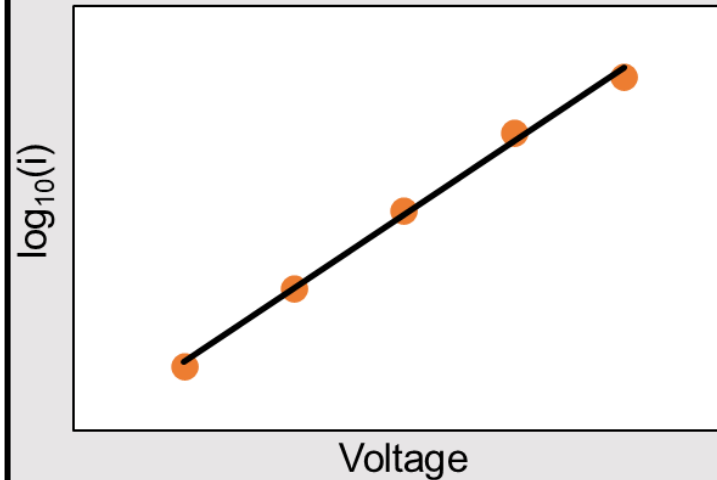
Mass-transfer limited:
rate is linear function of C_A

$r = kC_A^\alpha$
Arrhenius:

$$k = A \exp\left[-\frac{E_A}{RT}\right]$$

$i/(n\mathcal{F}) = r = kC_A^\alpha$
Tafel:

$$i = i_0 \exp\left[\frac{\alpha_a \mathcal{F}V}{RT}\right]$$

$i/(n\mathcal{F}) = r = k_c C_A$
MT coeff.:

$$k_c = \frac{D}{\delta}$$
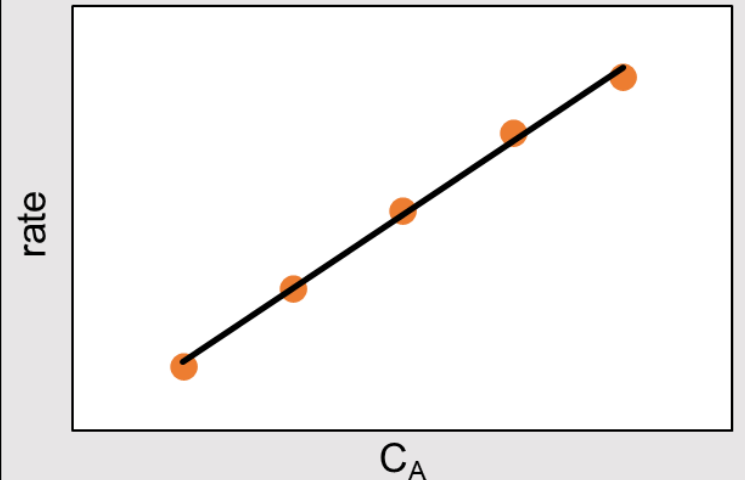
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  r : rxn rate [mol m⁻² s⁻¹]

(Electro)Chemical Reaction Engineering:

1. Mole Balance/Reactor Design Equation
2. Rate Law
3. Stoichiometry ——→ *(we will skip for now – useful for rxns with many components)*
4. **Combine** ——→ *This is where we set up solvable equations*
5. Evaluate (determine critical reactor parameters: *volume, concentration, flow rate, conversion, temperature, etc*)

Combine:

Ex) Echem CSTR operating under "mass-transfer limiting" conditions

Electrode surface area: S $[m^2]$

*rxn **only occurs** on surface of electrode, so we normalize rate by surface area, rather than volume

F_{A0} [mol A / s]

Reactor volume: V $[m^3]$

F_A [mol A / s]

MB: ✓

$$S = \frac{(F_{A0} - F_A)nF}{i}$$

RL:

$$i/(nF) = r = k_c C_A$$

To combine, write MB in terms of

$$C_A = \frac{F_A}{\upsilon_o} \leftarrow \left[\frac{m^3}{s}\right]$$

$$S = \frac{\upsilon_o (C_{Ao} - C_A) nF}{i} \Rightarrow \frac{S}{\upsilon_o} = \frac{C_{Ao} - C_A}{k_c C_A}$$

$$\frac{S}{\upsilon_o} = \frac{S}{V} \cdot \frac{V}{\upsilon_o}$$

$$= \sigma \hat{t}$$

$\uparrow$ $t_{space\ time}$

$$\boxed{\frac{C_A}{C_{Ao}} = \frac{1}{1 + \frac{S}{\upsilon_o} k_c} \qquad X_A = \frac{C_{Ao} - C_A}{C_{Ao}} = \frac{\frac{S}{\upsilon_o} k_c}{1 + \frac{S}{\upsilon_o} k_c}}$$

How do we design E-chem reactors?

Translating Chemistry ↔ Electrochemistry:

- Voltage/Potential is energy → $V_{cell} = -\dfrac{\Delta G_{rx}}{n\mathcal{F}}$

  $\mathcal{F}$ = 96485 C/(mol e): amount of charge in 1 mol e$^-$

  n : (# mol e$^-$) / (mol product)

- Current is reaction rate → $i = n\mathcal{F}r$

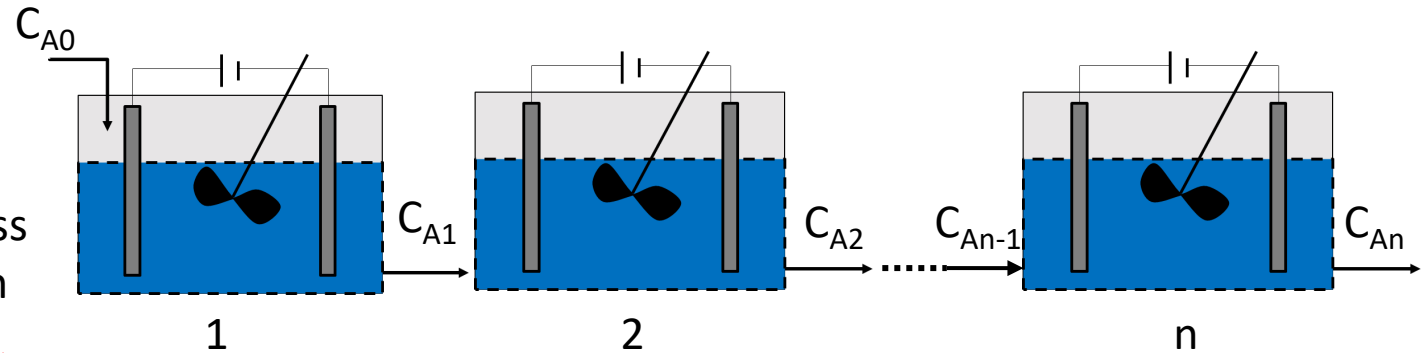 r : rxn rate [mol m^{-2} s^{-1}]

(Electro)Chemical Reaction Engineering:
1. Mole Balance/Reactor Design Equation
2. Rate Law
3. Stoichiometry
4. Combine
5. **Evaluate** (determine critical reactor parameters: *volume, concentration, flow rate, conversion, temperature, etc*)

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Evaluate:

Ex) How many Echem CSTRs in series are needed to achieve >99% conversion if each operates under mass transfer limiting current? What is the current of each reactor?

$v_0 = 8.3 \times 10^{-5} \frac{m^3}{s}$

$C_{A0} = 100 \; ppm$

$S = 1.7 \; m^2$

$k_c = 1.62 \times 10^{-4} \frac{m}{s}$

$MW_A = 65 \frac{g}{mol}$

$n = 2 \frac{mol \; e^-}{mol \; A}$

use previous combined MB/BL,

for any reactor n

$$\frac{C_{An}}{C_{An-1}} = \frac{1}{1 + \frac{S}{v_0}k_c}$$

To eval. for whole series

$$\frac{C_{An}}{C_{A0}} = \frac{C_{An}}{C_{An-1}} \cdot \frac{C_{An-1}}{C_{An-2}}, \; \ldots \; \frac{C_{A1}}{C_{A0}} = \frac{1}{\prod_1^n \left(1 + \frac{S}{v_0}k_c\right)} = \frac{1}{\left(1 + \frac{S}{v_0}k_c\right)^n}$$

Evaluate:

Ex) How many Echem CSTRs in series are needed to achieve >99% conversion if each operates under mass transfer limiting current? What is the current of each reactor?

C_{A0}

C_{A1} C_{A2} C_{An-1} C_{An}

1   2   n

$$v_0 = 8.3 \times 10^{-5} \frac{m^3}{s}$$

$$C_{A0} = 100 \, ppm$$

$$S = 1.7 \, m^2$$

$$k_c = 1.62 \times 10^{-4} \frac{m}{s}$$

$$MW_A = 65 \frac{g}{mol}$$

$$n = 2 \frac{mol \, e^-}{mol \, A}$$

for $X = 0.99$

$$\frac{C_{An}}{C_{A0}} = 0.01 = \frac{1}{\left(1 + \frac{S}{v_0} k_c\right)^n} \Rightarrow n = \frac{\ln(100)}{\ln(4.3)} = 3.15$$

4.3

 # need 4 reactors

How do we design E-chem reactors?

Evaluate:

Ex) How many Echem CSTRs in series are needed to achieve >99% conversion if each operates under mass transfer limiting current? What is the current of each reactor?

C_{A0}

1   2   n

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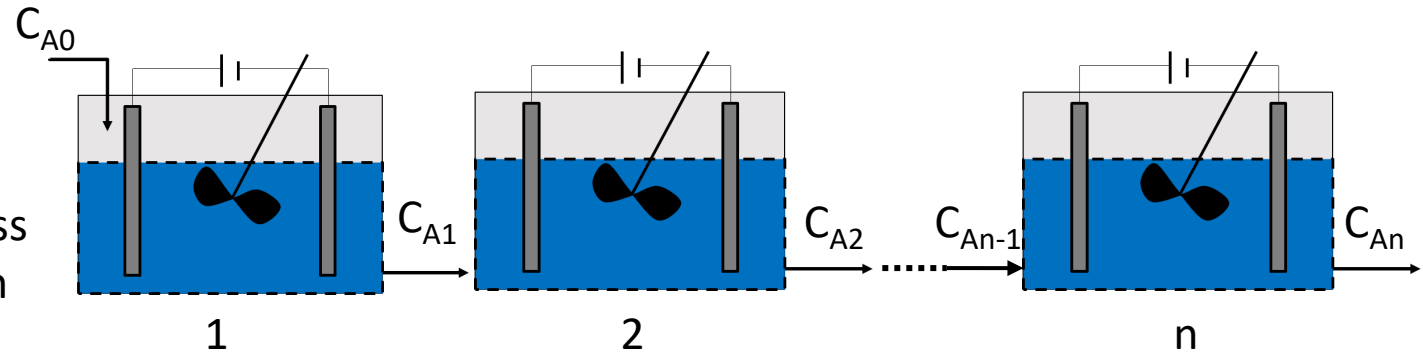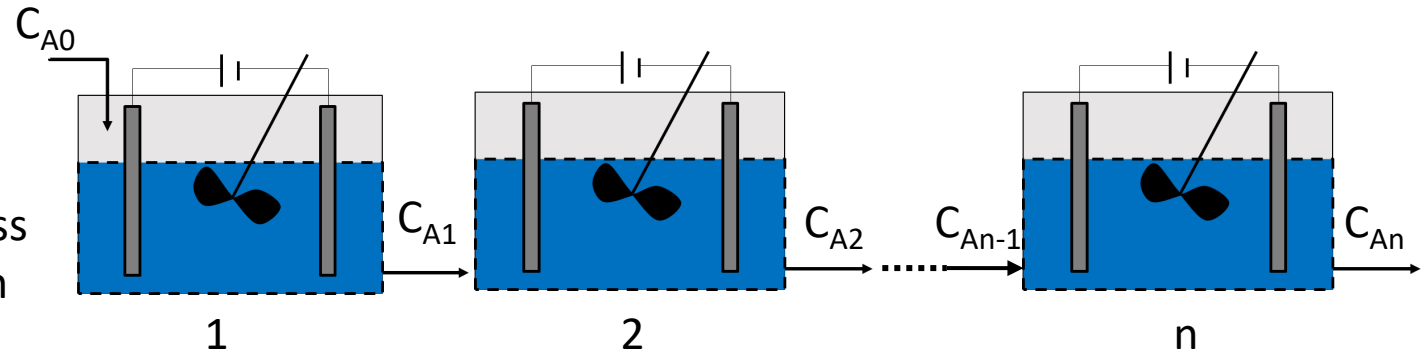$MW_A = 65 \frac{g}{mol}$

$n = 2 \frac{mol \; e^-}{mol \; A}$

to obtain i for each, recall

$$\frac{i}{nF} = k_c C_{An}, \quad \text{where } C_{An} = \frac{C_{A0}}{\left(1 + \frac{S}{v_0} k_c\right)^n}$$

n	C_{An} [mol/m³]	i [A/m²]
1	0.358	11.2
2	0.0832	2.60
3	0.0194	0.60
4	0.0045	0.14

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Tutorial Goals

- **Why** are we interested in electrochemical synthesis of chemicals?

  - *Identify key advantages and opportunities for E-chem synthesis*

- **What** are the basic elements of an electrochemical reaction?

  - *Describe components needed for E-chem synthesis*

- **How** do we leverage electrochemistry to produce chemicals in continuous flow reactors?

  - *Implement standard methodology for designing E-chem flow reactors*

- **When** do you reach out to the Tackett Research Group to help improve your E-chem system?
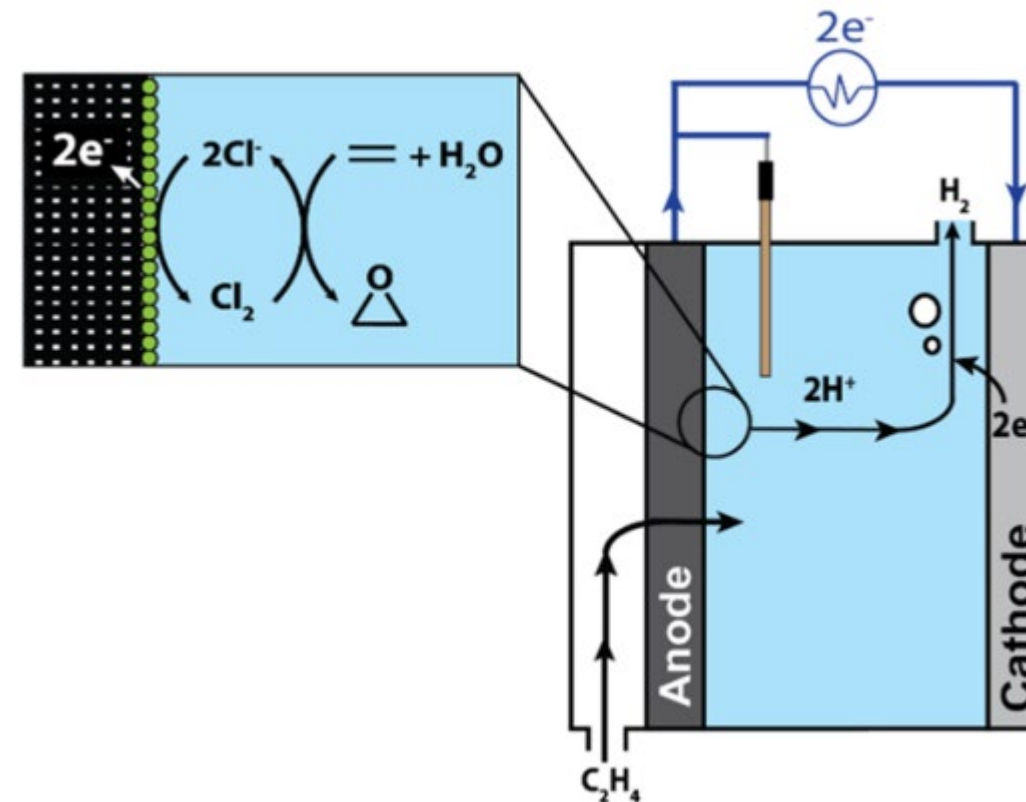
Tackett Research Group

- Our lab has a unique combination of characterization techniques that enable fundamental study of a wide array of electron-driven chemical reactions

What is the E-chem rate law/mechanism?

Electrochemical Mass Spectrometer (EC-MS)

- Fast (~1 s) and sensitive (100% product collection) gaseous product analysis
- Inert or reactive gas dosing capabilities

Ideal for fundamental studies of desorbed species

Surface Enhanced Infrared Absorption Spectroscopy (SEIRAS)

- Plasmon-enhanced vibrational spectroscopy captures near-surface signals
- Compatible with deposited film electrodes

Ideal for fundamental studies of adsorbed species

Is the reaction MT-limited?

pH-Sensing Rotating Ring Disk Electrode (RRDE)

- RRDE system provides well-defined hydrodynamics for accurate reaction-convection-diffusion model
- IrO_x functionalized ring is a fast, robust pH sensor

Ideal for detecting local pH changes on planar electrodes

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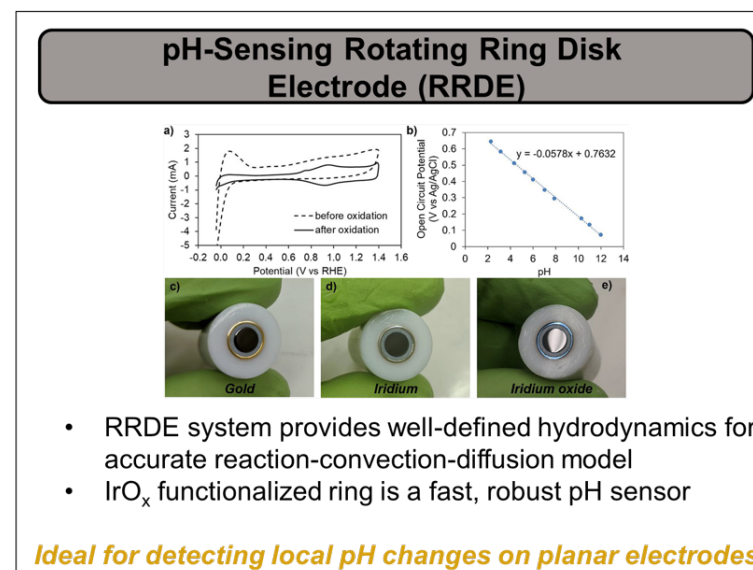Davidson School of Chemical Engineering
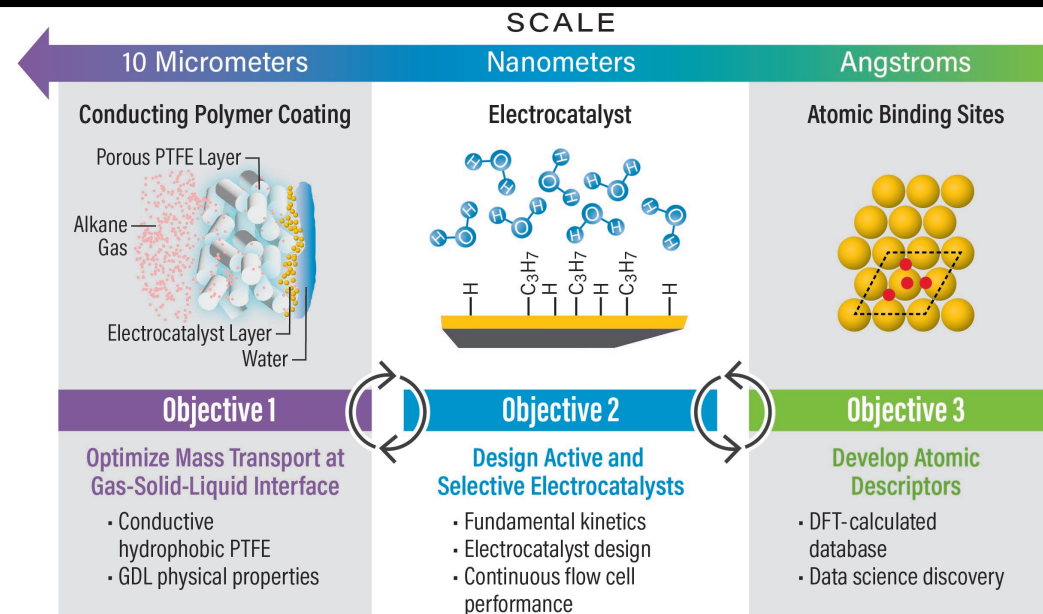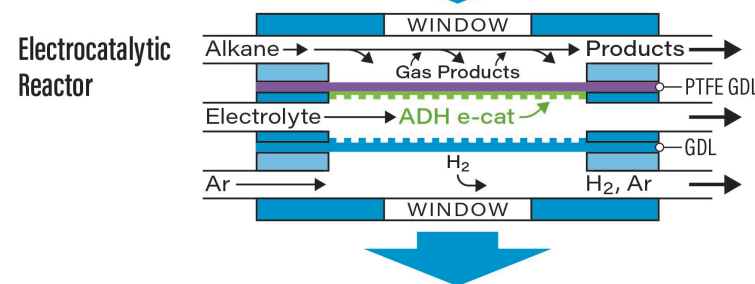
Tackett Research Group

- Our lab has a unique combination of characterization techniques that enable fundamental study of a wide array of electron-driven chemical reactions

- Our department has collaborative and complementary faculty that enable multi-scale electrochemical reactor studies

How could the product yield be improved?

SCALE

10 Micrometers	Nanometers	Angstroms
Conducting Polymer Coating	Electrocatalyst	Atomic Binding Sites
Objective 1	**Objective 2**	**Objective 3**
Optimize Mass Transport at Gas-Solid-Liquid Interface	Design Active and Selective Electrocatalysts	Develop Atomic Descriptors
• Conductive hydrophobic PTFE • GDL physical properties	• Fundamental kinetics • Electrocatalyst design • Continuous flow cell performance	• DFT-calculated database • Data science discovery

Electrocatalytic Reactor

Fundamental Scientific Insights for Aqueous Electrocatalytic Alkane Dehydrogenation from Nano-Scale to Device-Scale

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