Electrochemical reaction engineering: a lost (and found) art

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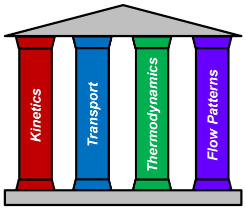
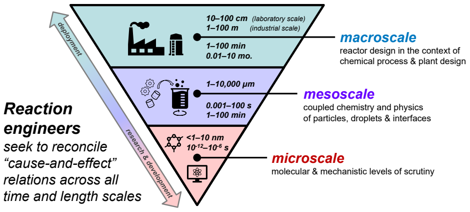
What is reaction engineering?





macroscale
reactor design in the context of chemical process & plant design

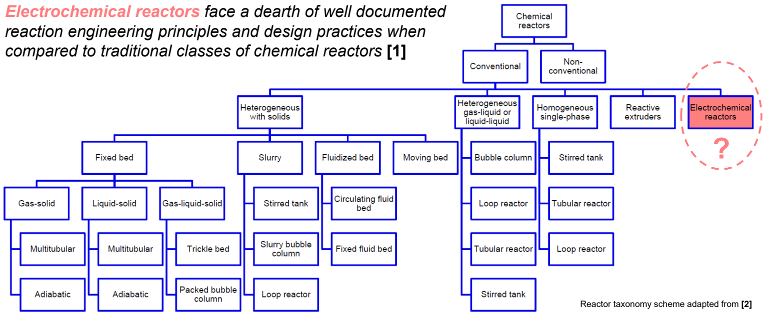
mesoscale
coupled chemistry and physics of particles, droplets & interfaces

microscale
molecular & mechanistic levels of scrutiny

Reaction engineers *seek to reconcile "cause-and-effect" relations across all time and length scales*

Reactor taxonomy

Electrochemical reactors face a dearth of well documented reaction engineering principles and design practices when compared to traditional classes of chemical reactors **[1]**



Reactor taxonomy scheme adapted from **[2]**

Applying chemical engineering fundamentals

Mass balance

$$\begin{pmatrix}\text{rate of}\\\text{mass input}\end{pmatrix}-\begin{pmatrix}\text{rate of}\\\text{mass output}\end{pmatrix}+\begin{pmatrix}\text{rate of mass}\\\text{production}\end{pmatrix}=\begin{pmatrix}\text{rate of mass}\\\text{accumulation}\end{pmatrix}$$

$$\boxed{\frac{dm_j}{dt}=\Delta\Phi_j+M_jR_jV+\frac{M_jI(FE)_{\text{overall}}}{n_jF}}$$

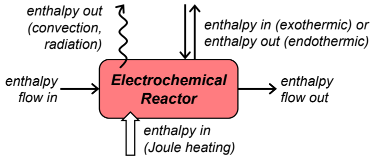
Definitions applicable to any volume V of interest, such as a single electrode, a single electrochemical reactor, a reactor plus a separator, or a complete process. **[1]**

- m_j = mass of species *j* in the system
- $\Delta\Phi_j$ = net input of *j* into the system
- M_j = molar mass of *j*
- M_jR_j = net mass rate of production of *j* per unit volume *V* by non-electrochemical reaction
- $\frac{M_jI(FE)_{\text{overall}}}{n_jF}$ = net mass rate of production of *j* by electrochemical reaction

Energy balance

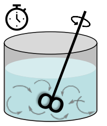
$$\begin{pmatrix}\text{accumulation of}\\\text{thermal energy}\end{pmatrix}=\begin{pmatrix}\text{enthalpy flow}\\\text{into the reactor}\end{pmatrix}-\begin{pmatrix}\text{enthalpy flow}\\\text{out of the reactor}\end{pmatrix}$$

$$\boxed{\sum m_jC_{Pj}\frac{dT}{dt}=I^2R_e-\sum R_j\Delta H_j+\sum W_jC_{Pj}[T_i-T]-Q_L}$$

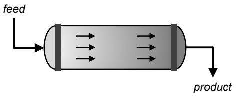


- $\sum m_jC_{Pj}\frac{dT}{dt}$ = accumulation of energy in the system
- I^2R_e = Joule (i.e., resistive) heat input
- $\sum R_j\Delta H_j$ = enthalpy change due to all reactions
- Q_L = enthalpic heat losses within the system
- $\sum W_jC_{Pj}[T_i-T]$ = enthalpy change from inlet to outlet for all components *j* with mass flow W_j, inlet temperature T_i and system temperature *T* **[1]**

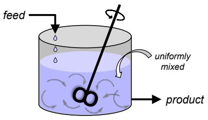
Idealized chemical reactor archetypes



Batch reactor



Plug flow reactor (PFR)



Continuously stirred tank reactor (CSTR)

Illustrative design case: electrochemical CSTRs

Design equation for an eCSTR

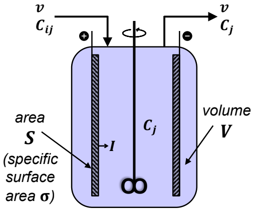
$$\boxed{A+n_1e^-\rightleftharpoons B}$$

Apply a mass balance under limiting current density:

$$v(C_{Ai}-C_A)=\frac{i_1S}{n_1F}\qquad \tau=\frac{V}{v}\quad \textit{residence time } \tau$$

$$C_{Ai}-C_A=\frac{\sigma\tau i_1}{n_1F}\qquad i_1=i_L=n_1Fk_{LA}C_A$$

$$C_{Ai}-C_A=\sigma\tau k_{LA}C_A$$



Finally, solve for the exit concentration C_A and the fractional conversion X_A:

$$\boxed{\frac{C_A}{C_{Ai}}=\frac{1}{1+\sigma\tau k_{LA}}}\qquad\boxed{X_A=1-\frac{C_A}{C_{Ai}}=\frac{\sigma\tau k_{LA}}{1+\sigma\tau k_{LA}}}$$

Three important reactor parameters *influence the performance of an eCSTR:*

1. Specific electrode area σ
2. Residence time τ
3. Mass transfer coefficient of A, k_{LA}

Characteristic mixing timescales

Ideal mixing is achieved when the mixing time t_c is much smaller than the residence time τ **[1]**

Electrolyte recirculation time

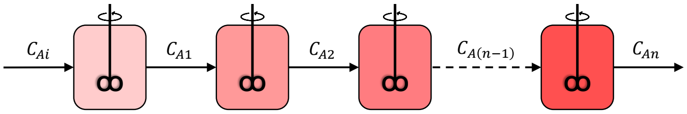
$$t_c=\frac{T_cd_v^2}{n_id_i^2}$$

Ideal mixing criterion

$$\tau>\frac{100d_v^2}{n_id_i^2}$$

- t_c = electrolyte recirculation (mixing) time
- T_c = impeller coefficient (= 1 for turbine type)
- d_v = inner diameter of vessel
- d_i = outer diameter of impeller
- n_i = rotational speed of impeller

Cascades of eCSTRs



For Tafel reactions occurring in equal-size eCSTRs and operating at identical electrode potentials:

$$\frac{C_{An}}{C_{A(n-1)}}=\frac{1}{\left(1+\frac{\sigma\tau k_f}{(1+Da)}\right)}\qquad\frac{C_{An}}{C_{Ai}}=\frac{C_{An}}{C_{A(n-1)}}\cdot\frac{C_{A(n-1)}}{C_{A(n-2)}}\cdots\frac{C_{A1}}{C_{Ai}}\qquad\boxed{\frac{C_{An}}{C_{A(n-1)}}=\left(1+\frac{\sigma\tau k_f}{(1+Da)}\right)^{-n}}$$

where: $$Da=\text{Damköhler number}=\frac{\text{surface reaction rate}}{\text{diffusive mass transfer rate}}\ \Rightarrow\ Da=\frac{k_{\text{forward}}}{k_{LA}}$$

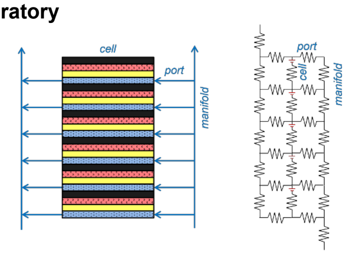
Engineering challenges beyond the laboratory

Stacks are multiple electrochemical cells configured to be electrically in series, but hydraulically in parallel **[2]**

- Require highly uniform distribution of liquid electrolyte, gaseous reactants and current to reconcile performance with lab cells

Shunt currents may pose integrity, efficiency and corrosion issues within an overall process **[2]**

- Ionically-conductive route(s) allow bypassing of reactive region
- Highly likely for electrolyte-based heat management strategies



Five-step methodology for electrochemical reactor scale-up

1. **Perform a single-cell mass balance**
   - Do mass balances inversely track with reactant conversion?
   - Are expected stoichiometries preserved (including e⁻)? **[2]**
2. **Fundamental electrochemical measurements**
   - Validate thermodynamics (three-electrode cell, coulometry)
   - Measure intrinsic kinetics (rotating ring-disc electrode)
   - Propose and quantify a complete reaction network
   - Evaluate the adiabatic temperature rise (*crucial for safety!*)
3. **Quantify single-cell performance**
   - What is the per-pass conversion of the primary reactant?
   - What does the polarization curve look like?
     - Incorporate [ohmic losses] + [mass transfer losses] **[2]**
   - Develop a mathematical model of cell performance
4. **Validate performance across large-format single cells and miniature stacks**
   - Check for corrosion, particularly at electrode edges! **[2]**
   - Do product formation rates scale with total electrode area?
   - Develop coupled continuum models to link kinetics, transport phenomena and hydrodynamics of each system
5. **Model and validate large stack performance**
   - Re-evaluate cell model in an iterated repeat call routine **[2]**
   - Add shunt current losses and estimate overall efficiency
   - Optimize reactor inputs for a fixed design geometry
     - Current density (and Δ*V* between end cells)
     - Number of cells (total electrode area)
     - Flow rates and recycle ratios
     - Coolant flow rates (heat exchange requirements)

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[1] Scott, K., Electrochemical Reaction Engineering, Academic Press, London, 1991.
[2] Barton, J. L., Dow Industrial Reaction Engineering Course, Lecture 11, NSF CISTAR Exclusive Professional Development, The Dow Chemical Company. Accessed 16 April 2021.