Industrial Electrochemistry
(Electrolysis: $\Delta G$ is positive, calculated $E$ is negative)

Why electrochemistry?
- clean and green (not always true!)
- often no or few byproducts
- electrons the cheapest redox “reagents”

Industrial electrochemical processes
- Primary metal production (electrowinning): Al, Mg, Na, and recently developed methods for Cu, Ni
- Metal refining: Cu, Ni – also electroplating
- Inorganic chemicals: Cl$_2}$/NaOH; H$_2$O$_2$ and other peroxy compounds; O$_3$; chromic acid; KMnO$_4$
- Organic compounds: adiponitrile
- Waste water purification and recycling

In North America:
- Al production = 10% of total electrical energy production
- Cl$_2$ production = 3% of total electrical energy production
Differences between laboratory set-up and industrial processes

- importance of mass transfer
  - stirred/unstirred solutions
  - batch vs continuous
  - planar vs 3-D electrodes

Mass transport occurs by:
  - diffusion = migration due to concentration gradient
  - migration of charged species due to potential gradient
  - convection (mechanical stirring or agitation)

Other issues
- undivided vs divided cells
- distance between electrodes
- potentiostatic vs amperostatic control
- importance of current efficiency
- what is the reaction at the other electrode?

Under laboratory conditions of electrochemical synthesis of a few grams of material, these issues are of minor importance. They are of immense importance industrially because of their impact on process costs, when thousands of kg – or even tonnes – of material are to be produced.
Mass transport and overpotential

The Tafel equation links (over)potential (a thermodynamic concept) with current (a kinetic concept)

For an anodic process:

$$\log i = \log i_0 + \alpha_A nF\eta/(2.303RT)$$

$$\alpha_A = \text{anode transfer coefficient}$$
$$\eta = \text{overpotential}$$
$$i_0 = \text{equilibrium exchange current density}$$

\[ i.e. \log i_{\text{exp}} \propto \eta \]

Eventually, the current (rate) levels off because of mass transport limitation (example: limiting currents in voltammetry) \(\rightarrow\) no benefit from further increase in cell potential

![Linear-scan voltammogram for the reduction of a hypothetical species A to give a product P.](image)
Optimizing mass transport therefore allows the use of applied potentials — higher current densities (faster reactions) before the limiting current is reached.

Note that the x axis here is overpotential

**Current efficiency, \( \phi \)** (expressed here as a fraction, not a %)

\[
\% \text{ yield} = \frac{n(\text{product})}{n(\text{reactant converted})}
\]

I am using \( n \) for moles of substance and \( n \) for moles of electrons

\[
\phi = \frac{\text{charge used to form product}}{\text{total charge passed}}
\]

\[
= \frac{n(\text{product}) \times (nF)}{\int i \, dt}
\]

for \( n \) moles of product

For constant-current conditions, this is

\[
\phi = \frac{n(\text{product}) \times (nF)}{i \cdot t}
\]
**Electrical energy consumption (EEC):**

\[
\text{EEC} = -nF \frac{E_{\text{cell}}}{\phi} \quad \text{per mole}
\]

\[
= -nF \frac{E_{\text{cell}}}{\phi M} \quad \text{per gram}
\]

EEC as defined above has the units J g\(^{-1}\). To convert to more practical units:

\[
\text{EEC (kW h/kg)} = \text{EEC (J/g)} \times (1000 \text{ g/1 kg}) \times (1 \text{ W s/1 J}) \times (1 \text{ kW/1000 W}) \times (1 \text{ h/3600 s})
\]

Thus EEC (kWh/kg) = \((2.78 \times 10^{-4}) \times \text{EEC(J/g)}\)

The objective is to minimize EEC

- **maximize** \(\phi\)
- **minimize** \(E_{\text{cell}}\)

What contributes to \(E_{\text{cell}}\)?

*It is NOT just \(E\) calculated by the Nernst Equation!!*

\[
E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad * - \quad \eta_{\text{cell}} \quad ** - \quad iR_{\text{cell}}
\]

* expressed as a reduction potential
** overpotentials beyond the equilibrium (calculated) potentials \(E\) for the individual anode and cathode reactions (different from the \(\eta\) needed to drive the reaction by inducing current through the cell)

Notice that all these terms make \(E_{\text{cell}}\) more negative, so a larger applied potential must be applied to drive electrolysis forward.
$iR_{\text{cell}}$ may have several components due to:

- resistance of the catholyte and anolyte solutions; minimized by small distance between anode and cathode
- resistance of the separator of a divided cell (e.g., ion exchange membrane); absent in an undivided cell
- resistance in the external circuit
- electrode materials and design

For an electrolytic process, $-E_{\text{cell}}$ is the smallest potential (voltage) that allows current to flow through the cell. To drive an electrolytic process, the applied potential must be greater than $E_{\text{cell}}$, i.e., there must be an overpotential $\eta$.

Eventually, if $\eta$ is too large, a competing reaction intervenes. Note the optimum $\eta$ is near $\eta_1$ on the diagram.

![Fig. 2.11 Schematic current versus overpotential curve for a cathodic reaction $O + ne^- \rightarrow R$, showing a mass transport controlled current $i_L$ as a plateau in the overpotential range $\eta_1 \rightarrow \eta_2$. At overpotentials more negative than $\eta_2$, an additional reaction, hydrogen evolution, takes place.](image-url)
% energy efficiency of the cell (%EE):

\[ \%EE = 100 \times \frac{(E_{\text{cathode}} - E_{\text{anode}})}{(E_{\text{cathode}} - E_{\text{anode}} - \eta_{\text{cell}} - iR_{\text{cell}})} \]

Both \( \eta_{\text{cell}} \) and \( iR_{\text{cell}} \) increase numerically with current density. Therefore high current density is a source of inefficiency BUT high current density increases the rate of formation of product (since \( q = i.t \))

**Heat transfer**

- \( iR_{\text{cell}} \) dissipates electrical energy as heat
- the need for heat to be vented may oppose the desire for a compact cell design

**Current and current density**

- current \( i \) is the measured current through the cell (amps)
- current density \( j \) is current per unit area of the electrode surface (A m\(^{-2}\))
- What really counts is \( j \) in terms of mass transport
- Hence the attraction of 3-D and other high-surface area electrodes such as carbon cloth and RVC, despite their physical fragility, tendency to plugging, inhomogeneous \( j \)
Electrode materials

- they should be cheap, long-lasting, free from fouling

<table>
<thead>
<tr>
<th>Cathodes</th>
<th>Anodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg, Pb, Ni</td>
<td>Pt, Pt/Ti, Ir/Ti, Pt–Ir/Ti (Pt/Nb, Pt/Ta)</td>
</tr>
<tr>
<td>Graphite and other forms of C</td>
<td>Graphite or other forms of C (treated)</td>
</tr>
<tr>
<td>sometimes treated thermally with</td>
<td>Pb in acid-sulphate media</td>
</tr>
<tr>
<td>organics or polymers (e.g. PTFE)</td>
<td></td>
</tr>
<tr>
<td>to modify porosity, density,</td>
<td></td>
</tr>
<tr>
<td>corrosion resistance, wettability</td>
<td></td>
</tr>
<tr>
<td>Steels</td>
<td>Ni in alkaline media</td>
</tr>
<tr>
<td>Stainless steels</td>
<td></td>
</tr>
<tr>
<td>Coatings of low-H₂ overpotential</td>
<td>Dimensionally stable anodes i.e. a</td>
</tr>
<tr>
<td>materials on steel, e.g. Ni, Ni/</td>
<td>mixed Ru-Ti oxide on Ti for Cl₂,</td>
</tr>
<tr>
<td>Al, Ni/Zn</td>
<td>IrO₂ on Ti for O₂</td>
</tr>
<tr>
<td>Hastelloys (Ni–Mo–Fe or Ni–Mo–Cr</td>
<td>Magnetite: Fe₃₋ₓO₄</td>
</tr>
<tr>
<td>alloys)</td>
<td></td>
</tr>
<tr>
<td>TiOₓ</td>
<td>Conducting ceramics e.g. Ti₄O₇</td>
</tr>
</tbody>
</table>
Types of electrochemical reactor

Recirculating systems are also used, especially (b)