The chloralkali process

\[ 2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{Cl}_2 + \text{H}_2 \]

Economics of equal masses of NaOH and Cl\(_2\) being produced; reintroduction of soda ash process for NaOH

**Electrolysis:** Anode reaction

\[ \text{Cl}^- (\text{aq}) \rightarrow \frac{1}{2}\text{Cl}_2 + e^- \]

at a graphite anode (old style cells) or Ti/IrO\(_2\) (newer cells)

Cathode reaction: old style mercury cell

\[ \text{Na}^+ (\text{aq}) + e^- \rightarrow \text{Na/Hg} \]

\[ \text{Na/Hg} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2} \text{H}_2 \]

separate reaction
• Advantage of the old style cell: H₂ and Cl₂ formed in separate steps

• Disadvantage: cost of Hg and losses of Hg to the environment —> high concentrations of Hg in fish —> phase-out of this technology

• Newer technology: diaphragm or membrane separated cells to separate the H₂(g) and Cl₂(g) streams: use of Nafion as a cation exchange membrane (cations pass through; neutrals and anions are repelled). Mercury free!

Anode reaction
\[ \text{Cl}^- (\text{aq}) \rightarrow \frac{1}{2}\text{Cl}_2 (\text{g}) + e^- \]

Cathode reaction
\[ \text{H}^+ (\text{aq}) + e^- \rightarrow \frac{1}{2}\text{H}_2 (\text{g}) \]
The asbestos diaphragm cell gives a lower quality NaOH; contaminated with NaCl because the diaphragm is not selectively permeable.

The Nafion membrane overcomes this limitation

\[ \sim(CF_2–CF_2)_x–(CF_2–CF)\sim ~ \times \]
\[ (OCF_2–CF(CF_3))_y–OCF_2CF_2–SO_3^- \ H^+ \]

- NaOH forms because Na\(^+\) ions cross the ion exchange membrane to restore charge balance due to loss of H\(^+\); important property of ion exchange membranes

**Cell potential**

For: \( 2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{Cl}_2 + \text{H}_2 \)

\( \text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + e^- \ \ E^\circ = -1.36 \text{ V} \)

\( \text{H}_2\text{O} + e^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^- \ \ E^\circ = -0.83 \text{ V} \)

Overall \( E^\circ(\text{cell}) = -2.19 \text{ V} \)

Suppose you could use as the cathode:

\( \text{O}_2 + 4e^- + 4\text{H}^+ \rightarrow 4\text{OH}^- \ \ E^\circ = +0.40 \text{ V} \)

Then the overall cell reaction would be:

\( 2\text{NaCl} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{Cl}_2 \)

and the overall \( E^\circ(\text{cell}) \) would be reduced to \(-0.96 \text{ V} \)
Energy costs

- The $V$ vs $j$ curves are linear because the major inefficiency in all cell types is due to $iR_{cell}$. The diaphragm has higher resistance than the Nafion membrane.

- The mercury cell, for which the cathode reaction is:
  \[ \text{Na}^+ + e^- \rightarrow \text{Na/Hg} \quad E = -1.85 \text{ V} \]
  hence $E$ at $j = 0$ is $-3.2 \text{ V}$

- Recall that energy costs scale linearly with $V$, but that high $j \rightarrow$ greater rate of production. Compromise between throughput (return on capital) and operating costs.
- \( E_{\text{cell}} > E^\circ \text{(calc)} \) of 2.19 V

- high purity NaOH and better energy efficiency of membrane cell

- membrane cell requires higher purity NaCl to avoid membrane fouling: *always a problem with divided cells*

- Ti/IrO\(_2\) anodes (superior to carbon) resist corrosion by Cl\(_2\); a “dimensionally stabilized anode” (DSA)

<table>
<thead>
<tr>
<th></th>
<th>Mercury cell</th>
<th>Diaphragm cell</th>
<th>Membrane cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell voltage/V</td>
<td>-4.4</td>
<td>-3.45</td>
<td>-2.95</td>
</tr>
<tr>
<td>Current density/A cm(^{-2})</td>
<td>1.0</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Current efficiency for Cl(_2)/%</td>
<td>97</td>
<td>96</td>
<td>98.5</td>
</tr>
<tr>
<td>Energy consumption/kWh per ton of NaOH</td>
<td>3150</td>
<td>2550</td>
<td>2400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Electrolysis only</td>
<td>3150</td>
<td>2550</td>
<td>2400</td>
</tr>
<tr>
<td>(b) Electrolysis + evaporation to 50% NaOH</td>
<td>3150</td>
<td>3260</td>
<td>2520</td>
</tr>
<tr>
<td>Purity Cl(_2)/%</td>
<td>99.2</td>
<td>98</td>
<td>99.3</td>
</tr>
<tr>
<td>Purity H(_2)/%</td>
<td>99.9</td>
<td>99.9</td>
<td>99.9</td>
</tr>
<tr>
<td>O(_2) in Cl(_2)/%</td>
<td>0.1</td>
<td>1–2</td>
<td>0.3</td>
</tr>
<tr>
<td>Cl(^-) in 50% NaOH/(%)</td>
<td>0.003</td>
<td>1–1.2</td>
<td>0.005</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>concentration prior to evaporation/(%)</td>
<td>50</td>
<td>12</td>
<td>35</td>
</tr>
<tr>
<td>Mercury pollution</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>considerations</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Requirement for brine purification</td>
<td>Some</td>
<td>More stringent</td>
<td>Very extensive</td>
</tr>
<tr>
<td>Production rate per single cell/tons NaOH per year</td>
<td>5000</td>
<td>1000</td>
<td>100</td>
</tr>
<tr>
<td>Land area for plant, of 10(^5) tons NaOH per year/m(^2)</td>
<td>3000</td>
<td>5300</td>
<td>2700</td>
</tr>
</tbody>
</table>
Aluminum production: an example of electrowinning

- ore is bauxite $\text{Al}_2\text{O}_3$ which is purified, then electrolyzed using cryolite $\text{Na}_3\text{AlF}_6$ as the supporting electrolyte (Heroult-Hall process); 15 wt%, 1000°C
- Carbon anodes (powdered anthracite/pitch; compressed and baked); carbon cathodes (though they actually get covered with liquid Al metal)

- overall chemistry:
  \[
  2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2
  \]
  exact Al species are not known

- pollution problems: HF; polycyclic aromatic hydrocarbons
Energetics and costs

- very high electricity requirement; ~ 15,000 kWh per tonne Al

- most Al reduction plants have their own hydroelectric supply (e.g., Kitimat)

- thermodynamic cell potential is −1.18 V (it would be −2.2 V if O₂ were produced at the anode instead of CO₂)

  Contributions to $E_{\text{cell}}$: 1.18 V
  - anode/cathode overvoltages 0.5 V (all at anode)*
  - $iR$ drops (anode, cathode) 1.1 V
  - $iR$ drop (electrolyte) 1.5 V
  - Total 4.3 V

* typical problem when a gas is evolved; ohmic resistance of gas bubbles that have not disengaged the surface

- costs:
  - purified bauxite 30%
  - electricity 23
  - capital 17
  - labour 16
  - carbon anodes 7
  - other materials 7
  - Total 100%
Monsanto’s adiponitrile process

- adiponitrile as an intermediate in the production of nylon[6,6], affording both adipic acid and hexamethylenediamine

- \[2\text{CH}_2=\text{CH–C}≡\text{N} + 2\text{H}^+ + 2e^- \rightarrow \text{N}≡\text{C–(CH}_2)_4–\text{C}≡\text{N}\]

- mechanism is known in general outline, but not in every step
  \[\text{CH}_2=\text{CH–C}≡\text{N} + e^- \rightarrow [\text{CH}_2=\text{CHCN}]^-\] occurs first

what is not clear is:
1) the order of protonation and electron transfer steps
2) whether electron transfer occurs from the cathode or from anionic intermediates in solution
3) at what point the new C–C bond is formed. Here is one possibility

\[\text{CH}_2=\text{CHCN}^- + \text{CH}_2=\text{CH–CN} \rightarrow \text{NC}–\text{CH}·\text{CH}_2\text{CH}_2\text{CH}·\text{CN} \]

\[\downarrow \text{H}^+; e^- \]

\[\text{N}≡\text{C–(CH}_2)_4–\text{C}≡\text{N}\]

- Original adiponitrile process (Monsanto, 1965) used Pb cathode, PbO2/AgOanode; cation exchange membrane; supporting electrolyte Et$_4$N$^+$ EtOSO$_3$$. The anode reaction was O$_2$ evolution from 5% H$_2$SO$_4$. Catholyte feed is acrylonitrile, which is 7% soluble in aq phase (adiponitrile dissolves into the excess acrylonitrile)
• More recent developments:
  S undivided cell (cheaper, simpler, easier extraction of products)
  S carbon steel anodes + corrosion inhibitors. Anode reaction is again \( \text{O}_2 \) evolution
  S Cd-plated carbon steel cathodes
  S in practice, there is a series of parallel carbon steel plates, one face of which is Cd plated. EDTA in the supporting electrolyte is found to suppress \( \text{H}_2 \) formation as a competing cathode reaction
  S 15% \( \text{Na}_2\text{HPO}_4 \) as the supporting electrolyte (+ 0.4% of a complex quaternary ammonium salt)

• Energy aspects and costs

<table>
<thead>
<tr>
<th></th>
<th>Old style cell</th>
<th>New style cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>( j, \text{A cm}^{-2} )</td>
<td>0.45</td>
<td>0.20</td>
</tr>
<tr>
<td>Voltages</td>
<td></td>
<td></td>
</tr>
<tr>
<td>reversible cell potential, V</td>
<td>–2.50</td>
<td>–2.50</td>
</tr>
<tr>
<td>overpotentials</td>
<td>–1.22</td>
<td>–1.87</td>
</tr>
<tr>
<td>electrolyte ( iR )</td>
<td>–6.24</td>
<td>–0.47</td>
</tr>
<tr>
<td>membrane ( iR )</td>
<td>–1.69</td>
<td>–</td>
</tr>
<tr>
<td>Total</td>
<td>–11.65</td>
<td>–3.84</td>
</tr>
<tr>
<td>Energy, kWh t(^{-1})</td>
<td>6700</td>
<td>2500</td>
</tr>
</tbody>
</table>
Paired electrolysis: an electrochemist’s dream

- The concept: to produce a useful product at each electrode \(i.e.,\) couple an oxidative reaction with a reductive reaction

- Better yet: use an undivided cell — therefore the product of reduction must not be reoxidizable and the product of oxidation must not be reducible

- The BASF process for phthalide and t-butylbenzaldehyde (agrochemical intermediates)

- Oxidative process: \(p\)-tert-butyltoluene → \(p\)-tert-butylbenzaldehyde dimethylacetal

- Reductive process: phthalic anhydride → phthalide