Electrochemistry for waste treatment

- **Positives:**
  - Potentially “green” – “only uses electrons”; does not “add a chemical to chase away another chemical”
  - Low cost of electricity (¢ per mole)
  - Most often applicable to oxidation
  - Treatment of wastes that are toxic or recalcitrant in biological processes
  - Well suited to aqueous wastes

- **Negatives:**
  - Must have a supporting electrolyte
  - Must avoid electrode fouling
  - Need for long-lived and cheap electrodes
  - Choice of reaction at counter electrode
  - Current efficiency declines as concentration falls
  - Must be engineered for high throughput

- **Metal ion removal:** variant of electrowinning only (a)
  - From aqueous solution (b) at low concentrations.

**Applications:**
- Primary leaching of low grade ores, or of tailings pile run-off
- Spent solutions from electroplating, catalysts, etching solutions, photographic fixing, batteries
- Cathode is generally the same metal as is being recovered; periodically removed
- High current density → H₂ evolution
Electrogenerated oxidants

- hydrogen peroxide, ozone, hypochlorite

**S** peroxide: difficulties of obtaining more than mM concentrations in a single pass. Recent developments include trickle bed reactors

Anode: $2\text{OH}^- \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^{-}$

Cathode: $\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^{-} \rightarrow \text{HO}_2^- + \text{OH}^-$

**Problems:** reverse of cathode reaction at the anode; further reduction of $\text{HO}_2^-$ to $\text{OH}^-$; catalytic decomposition of peroxide by transition metal ions, especially $\text{Fe}^{2+}$; requirement for strongly alkaline solutions
S  **ozone**: oxidation of water directly to $O_3$ (but problem of oxidation to $O_2$ instead)

\[
\begin{align*}
3H_2O & \rightarrow O_3 + 6H^+ + 6e \quad E^\circ = 1.51 \text{ V} \\
2H_2O & \rightarrow O_2 + 4H^+ + 4e \quad E^\circ = 1.23 \text{ V}
\end{align*}
\]

Essential to use anodes with high overvoltage for $O_2$

Anodes include PbO$_2$ and solid polymer electrolytes

Issue of explosive nature of $O_3$(g), whose solubility in water is not very high

S  **hypochlorite**: Oxidation of brine in a non-separated cell. Solution has disinfectant properties

**Cathode**: $2H_2O + 2e \rightarrow H_2 + 2OH^-$

**Anode**: $2Cl^- \rightarrow Cl_2 + 2e$

$Cl_2 + 2OH^- \rightarrow H_2O + ClO^- + Cl^-$

**Net**: $Cl^- + H_2O \rightarrow ClO^- + H_2$

Main applications are water purification for drinking and swimming *e.g.* on ships, for food processing; also for sterilization of treated sewage (superchlorination) at remote sites; disadvantage of organochlorine byproducts when organics are oxidized
Electrolytic methods for degradation of organics

- most methods are oxidative
- “electrochemical combustion” means complete conversion to CO$_2$ and H$_2$O
- electrochemical combustion usually undesirable (energy intensive); more often the objective is partial oxidation, and the treated product is then further degraded biologically
- probably the most serious problem is anode fouling by polymerized/oligomerized byproducts.

Example: phenols: serious drinking water problem because chlorophenols have very strong taste and odour

<table>
<thead>
<tr>
<th>Substituted phenol</th>
<th>Odour threshold, ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>2–</td>
<td>2</td>
</tr>
<tr>
<td>4–</td>
<td>250</td>
</tr>
<tr>
<td>2,4–</td>
<td>2</td>
</tr>
<tr>
<td>2,6–</td>
<td>3</td>
</tr>
<tr>
<td>2,4,6–</td>
<td>&gt; 1000</td>
</tr>
</tbody>
</table>

Simplest rationalization for oligomerization is:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{OH} \rightarrow & \quad \text{C}_6\text{H}_5\text{O}^+ + \text{H}^+ + \text{e} \\
\text{C}_6\text{H}_5\text{O}^+ + \text{C}_6\text{H}_5\text{OH} \rightarrow & \quad \text{dimer formation (still a radical) via C or O attack (aromatic substitution)}
\end{align*}
\]

More likely, the radical chemistry is initiated by attack of a hydroxyl radical (see below) on phenol
Steps in the development of an electrochemical remediation technology

Basic science
- voltammetry: at what potential does the substance oxidize (or reduce)? Direct oxidation possible, or electrocatalytic or mediated methods?
- does the waste stream contain ionic components, or must a supporting electrolyte be added?
- initial choice of electrode
- small scale electrolysis: what are the products and chemical yields? What is the mass balance?
- what is the current efficiency, and how does it vary with contaminant concentration?

Engineering aspects
- should batch, flow, recirculating batch cells ... be used?
- divided or (much preferred) undivided cell?
- can the process meet regulatory effluent standards?
- potentiostatic or (much preferred) amperostatic operation?
- cell design and electrode design
**Oxidation**: Anodes

- Metal anodes favour direct electron transfer at the electrode

\[
P \rightarrow P^{\ds} + e
\]

**Disadvantage**: many organic pollutants have very high oxidation potentials, and so water is oxidized in preference to the contaminant of interest

- Work of Comninellis on different mechanisms of oxidation for metal oxide type anodes. These electrodes are essentially electrocatalytic, in that they do not require the loss of an electron from the substrate

**Type 1**: form OH radicals: PbO₂ and Ti/SnO₂ type DSAs

\[
\begin{align*}
MO_x + H_2O & \rightarrow MO_x(OH_{ads}) + H^+ + e \\
MO_x(OH_{ads}) + P & \rightarrow MO_x + "P-OH"
\end{align*}
\]

P is oxidized by adsorbed or free (dissociated) OH, which is a very powerful oxidant

**Type 2**: form higher metal oxides: Ti/IrO₂ type DSAs

\[
\begin{align*}
MO_x + H_2O & \rightarrow MO_x(OH_{ads}) + H^+ + e \\
MO_x(OH_{ads}) & \rightarrow MO_{x+1} \\
MO_{x+1} + P & \rightarrow MO_x + "PO"
\end{align*}
\]

the higher oxide is the oxidizing agent
Applications foreseen:

- food industry
- textiles and leather
- landfill leachates
- chemical industry wastes
**Boron-doped diamond (BDD) electrodes** (Comninellis, *Electrochemistry Forum*, 2002)

Prepared by vapour deposition, *e.g.*, 1% CH$_4$ + 3 ppm Me$_3$B in H$_2$ onto a substrate such as Ti. Allow very high oxidation potentials to be used, but to date the films are (a) expensive to prepare (b) unacceptably fragile.

Applications foreseen for BDD are waste treatment and the electrosynthesis of compounds that require high oxidation potentials.

![Comparison between Pt and BDD](image)

Comninellis, 2002
BDD electrode for oxidation of 4-chlorophenol
Rodrigo et al., J. Electrochem. Soc, 148, D60-D64 (2001)

- objective was electrochemical combustion
- electrode fouling (deposition) avoided by excursions to highest anodic polarization possible
- oxidation involves both direct oxidation of substrate to phenoxy radicals and benzoquinone and also attack by OH radicals

![Graph](image-url)

**Figure 11.** Concentration trends, expressed as mg C dm$^{-3}$, during 4-CP oxidation in 1 M $\text{H}_2\text{SO}_4$ at BDD anode: (●) 4-chlorophenol, (×) 1,4-benzoquinone, (□) maleic acid, (−) other intermediate compounds, and (△) carbon in solution transformed to CO$_2$. 4-CP concentration 15.6 mM, $i$ = 30 mA cm$^{-2}$, $T$ = 25°C.
Mediated electrolysis: Example, Ag(II)

The “mediator” is the substance oxidized (or reduced), and this is the only electrochemistry in the system; the oxidized (reduced) form of the mediator then reacts chemically with the contaminant

\[
\begin{align*}
\text{Ag}^+ & \rightarrow \text{Ag}^{2+} + e \\
\text{Ag}^{2+} + \text{H}_2\text{O} & \rightarrow \text{Ag}^+ + \text{H}^+ + \text{OH} \text{ (radical)} \\
\text{OH} + P & \rightarrow \text{oxidation of } P
\end{align*}
\]

Recall that characteristic OH chemistry is abstraction of hydrogen or addition to multiple bonds.

Example of destruction of aromatics by mediated Ag$^+$ oxidation. Solution should not contain Cl$^-$, else AgCl will precipitate. Ag$^+$ is needed only in catalytic amounts.

Other oxidations systems: Ce(III)/Ce(IV)

Reduction systems: Co(III)/Co(II); Cr(III)/Cr(II)

- the objective is to produce a higher (lower) oxidation state that is close to the most reactive that can be formed in aqueous solution
**Electrocoagulation technologies**

- Use of sacrificial metal anodes (usually iron)
- Combination of electrochemistry and precipitation. Usually this involves co-precipitation of Fe(OH)$_3$ or the related phase hydrated FeOOH along with the contaminant
- In combination with H$_2$O$_2$, OH radicals are formed: electro-Fenton reaction
  Fenton reaction: $\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O} + \text{OH}$

**Application of electrocoagulation to the removal of arsenic (J. Wang, unpublished)**

- As is present as As(III) and As(V). As(V) coprecipitates readily with Fe(OH)$_3$ at pH 5–8
- Oxidation at Fe anode has several functions:
  - oxidation of As(III) to As(V)
  - oxidation of Fe to Fe$^{2+}$
  - oxidation of water to (e.g.) H$_2$O$_2$ and OH, which oxidize As(III) and also Fe$^{2+}$ to Fe$^{3+}$
  - at the pH of drinking water Fe(OH)$_3$ precipitates along with As(V) $\equiv$ H$_2$AsO$_4^-$
- WHO limit of 10 ppb for As is achievable