Focus of today’s lecture

- Electroreduction and indirect oxidation processes, and their use for groundwater treatment
- Electrosorption: Salts removal for water desalination (process called Capacitive Deionization or CDI) and organics removal
Part 1

PROCESSES DRIVEN BY FARADAIC REACTIONS AT THE CATHODE

Faradaic reactions

Occur when charges (e.g., electrons) are transferred across the metal-solution interface. Electron transfer causes oxidation or reduction to occur (these are governed by Faraday Law’s).

Give few examples?

When it comes to electrochemical transformation/removal of water pollutants...
Direct and indirect degradation processes induced by Faradaic reactions

**Oxidation**
- Direct (electrolysis) at the anode
- Indirect mediated by anode
- Indirect mediated by cathode

**Reduction**
- Direct (electrolysis) at the cathode
- Indirect mediated by cathode
- Indirect mediated by anode

**INDIRECT REDUCTION MEDIATED BY CATHODE**
Hydrodechlorination or HDC

- e.g. tetrachloroethylene, trichloroethylene, chlorophenol, chlorobenzene

Electrochemical reduction through hydrodechlorination (HDC) occurs at the cathode due to water electrolysis (hydrogen evolution reaction or HER).

Step 1: Process starts with electrochemical hydrogen adsorption (Volmer reaction) where atomic hydrogen ($H_\text{a}$) is chemically adsorbed on active site of the electrode surface (M)

\[ H^+ + M + e^- \rightleftharpoons M-H^* \text{ (acid solution)} \]

\[ H_2O + M + e^- \rightleftharpoons M-H^* + OH^- \text{ (alkaline solution)} \]
Hydrodechlorination or HDC

Electrochemical reduction through hydrodechlorination (HDC) occurs at the cathode due to water electrolysis.

**Step 2:** The $H_2$ further involves in electrochemical desorption (Heyrovsky reaction)

$$M - H^x + H^+ + e^- \rightleftharpoons M + H_2 \text{ (acid solution)}$$

$$M - H^x + H_2 O + e^- \rightleftharpoons M + OH^- + H_2 \text{ (alkaline solution)}$$

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Hydrodechlorination or HDC

Electrochemical reduction through hydrodechlorination (HDC) occurs at the cathode due to water electrolysis.

**Step 2:** OR chemical desorption (Tafel reaction) to create hydrogen gas or interacts with the reducible molecules like chlorinated substances, which leads to HDC.

$$2 \text{M} - H^x \rightleftharpoons 2 \text{M} + H_2 \text{ (both acid and alkaline solutions)}$$
Influence of cathode material

The good HDC catalyst should have strong bond with H₂ to allow proton-electron transfer process but weak enough to ensure the bond breaking and the product release.

If the hydrogen-metal surface (H₂-M) binding energy is too high, adsorption is slow and limits the overall rate but if it is too low, desorption is slow.

Trassati’s volcano plot for the HER in acid solutions. $j_{00}$ denotes the exchange current density, and $E_{MH}$ the energy of hydride formation

Modern “Volcano” plots

There is a clear separation into three groups: sp metals, which are the worst catalysts, coinage metals, which are intermediate, and the d metals, which contain the best catalysts, but also Ni and Co, which are mediocre.
What has major effect on HDC?

Same cathodes and process but for different contaminant removal?
PRACTICAL APPLICATIONS

Approach 1
Approach 2
Results

Anode: \( \text{C}_2\text{HCl}_3 + 13\text{H}_2\text{O} \rightarrow 2\text{CO}_2(\text{aq}) + 6\text{e}^- + 3\text{Cl}^- + 9\text{H}_3\text{O}^+ \)

Cathode: \( \text{C}_2\text{HCl}_3 + 10\text{e}^- + 7\text{H}_2\text{O} \rightarrow 2\text{CH}_4(\text{aq}) + 3\text{Cl}^- + 70\text{H}^- \)

Over 90% degradation of TCE can be achieved without formation of DCE or VC

Another effect on HDC?

Competitive reactions: \( \text{O}_2 \) reduction!
INDIRECT OXIDATION MEDIATED BY CATHODE

Indirect oxidation processes

Cathodes can support formation of H$_2$O$_2$ via 2-electron O$_2$ reduction reaction (2e ORR)
Cathode material

**Activated Carbons**
- Powder
- Granular
- Pellets

Cathode material

- Carbon black
- Acetylene black
- Carbon nanotubes (CNTs)
- Graphene

Introducing other active carbon materials

- Chemical oxidation
  (H₂O₂, Fenton reagent, HNO₃, etc.)

Doping with hetero-atoms

- S-doping
- N-doping
- F-doping
- O-doping

Introducing metal oxides

- MnO₂
- TiO₂
- V₂O₅
- Cr₂O₃

...
Cathode material

Modifications: heteroatom-doping (i.e. oxygen-containing functional groups)

Hydrogen peroxide generation

\[ \text{AC} + \text{H}_2\text{O}_2 \rightarrow \text{AC}^+ + \text{OH}^- + \cdot \text{OH} \]
\[ \text{AC}^+ + \text{H}_2\text{O}_2 \rightarrow \text{AC} + \text{H}^+ + \text{HO}_2^- \]
ELECTROSORPTION: SALTS REMOVAL FOR WATER DESALINATION (PROCESS CALLED CAPACITIVE DEIONIZATION OR CDI) AND ORGANICS REMOVAL
Electrosorption

- Charge separates across the interface, resulting in the formation of strong electrical double layers (EDL) near the high conductivity and high surface area surfaces. When the electrode is charged and put into a solution with ions, the interface of the charged electrode and ions rich solution will be occupied with counter ions as a result of the Coulomb force, forming EDL.
- Under some conditions, a given electrode-solution interface will show a range of potentials where no charge-transfer reactions occur because such reactions are thermodynamically or kinetically unfavorable. Charge does not cross the interface but external currents can flow!

Electrosorption

<table>
<thead>
<tr>
<th>Adherent/precursor</th>
<th>Adsorbate</th>
<th>Maximum adsorption capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon fibers (commercial)</td>
<td>Acid Orange 7 dye</td>
<td>645.59</td>
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<tr>
<td>Polyacrylonitrile resin</td>
<td>Phenol</td>
<td>225.86</td>
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<tr>
<td>Activated carbon fibers (commercial)</td>
<td>Naphtaleneisulfonic acid</td>
<td>320.10</td>
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<tr>
<td></td>
<td>Benzyl alcohol</td>
<td>210.00</td>
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<tr>
<td>Activated carbon cloth (commercial)</td>
<td>Naphtolic acid</td>
<td>200.00</td>
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<tr>
<td>SpectraCarb 2225 (commercial)</td>
<td>Bencodine</td>
<td>501.47</td>
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<tr>
<td>Activated carbon fibers (commercial)</td>
<td>Chromium (VI)</td>
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<tr>
<td></td>
<td>Phenoloxide ions</td>
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<td></td>
<td>p-Nitrophenol</td>
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<tr>
<td>Activated carbon fibers (commercial)</td>
<td>Sodium dodecylsulfonate</td>
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<td>Urotropia</td>
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<td>Polyacrylonitrile resin</td>
<td>Antline</td>
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<td>Polyacrylonitrile resin</td>
<td>Butanol</td>
<td>307.68</td>
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<td>MIFEN 2985 (commercial)</td>
<td>Metabolism pesticide</td>
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<tr>
<td>SpectraCarb 2225 (commercial)</td>
<td>Nitrate</td>
<td>142</td>
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<td></td>
<td>Nitroxide</td>
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<td>Coconut charcoal</td>
<td>Phenol</td>
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<tr>
<td>SpectraCarb 223 (commercial)</td>
<td>Ethyl acetate</td>
<td>1182.52</td>
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<td></td>
<td>Thiohydantoin</td>
<td>833.25</td>
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</tbody>
</table>
Electrosorption

Accelerating the adsorption rate

Ability for regeneration

Anionic dye removal efficiency (%)

Flow rate (m3/h)

Electrosorption

Electrosorption

Pot. E/mV vs Ag/AgCl

Loading, s/mol g⁻¹ (q)

CH₃OH

SO₃⁻

CO₂⁻

CH₃

uncharged species

cations (+)

anions (−)

E₀EC

potential (E)
Capacitive deionization or CDI

Upon applying a voltage difference between two porous carbon electrodes, ions are attracted to the oppositely charged electrode.

As a result, desalinated water is produced.

Mechanism

Capacitive ion storage is the phenomenon of the formation of an electrical double layer (EDL), where upon applying a charge, ions are captured electrostatically and stored capacitively in the diffuse layer formed next to the carbon interface.

The formation of the capacitive EDL is the heart of the CDI process.
Types of reactors

(a) Feed water (b) Feed water
Freshwater Freshwater

(c) Feed water Concentrate

(d) Freshwater Concentrate

References

• Rajic et al., The influence of cathode material on electrochemical degradation of trichloroethylene in aqueous solution, Chemosphere 147 (2016) 98-104
• Porada et al., Review on the science and technology of water desalination by capacitive deionization, Progress in Materials Science 58 (2013) 1388-1442
• Bayram & Ayranci, Electrosorption based waste water treatment system using activated carbon cloth electrode: Electrosorption of benzoic acid from a flow-through electrolytic cell, Separation and Purification Technology 86 (2012) 113–118
• Koparal et al., Electroadsorption of Aclan Blau dye from textile effluents by using activated carbon-perlite mixtures, Water Environment Research 74(4) (2002), 521-525