Unique parameters in electrochemistry:
- Electrochemical cell: divided or undivided
- Current and potential: constant current (c.c.) or constant potential (c.p.)
- Electrolyte: various ammonium or alkali metal salts
- Electrodes: anode (oxidation), cathode (reduction)

Topics not discussed:
- Chemically modified electrodes
- Electrodes for inorganic and analytical electrochemistry

1. Electrode material

1-1. General Consideration
- Physical stability
- Chemical stability
- Overpotential
- Suitable physical form
- Cost and lifetime
- Electrical conductivity

1-2. Modes of action of electrodes
- Transfer electrons
- Absorb organic compounds
- Reactivity and product selectivity might be affected by electrode materials.
- Act as reagents
  - Sacrificial anode (source of electron for cathodic reduction)
  - NiOOH, PbO₂ anode
  - Ni and Pt cathode for hydrogenation

1-3. Overpotential
   Overpotential is the potential difference between a half-reaction's thermodynamically determined potential and the potential at which the redox event is experimentally observed.

   Thermodynamically defined potential:
   - Oxygen
     \[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad E^\circ_{\text{red}} = 1.23 \text{ (V)} \]  
   (vs SHE)
   - Hydrogen
     \[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad E^\circ_{\text{red}} = 0.00 \text{ (V)} \]

   Generally, material with large \( \text{O}_2 \) overpotential is used for anode and material with large \( \text{H}_2 \) overpotential is used for cathode.

1-4. Anode material
- Sacrificial anode: Al, Zn, Mg, steel etc.
- Non-sacrificial: Pt, carbon based material (graphite, glassy carbon, RVC, BDD)
Sacrificial anode  Source of electron for cathodic reduction

<table>
<thead>
<tr>
<th>Mg</th>
<th>Al</th>
<th>Zn</th>
<th>Fe</th>
<th>Ni</th>
<th>Sn</th>
<th>Pb</th>
<th>Cu</th>
<th>Hg</th>
<th>Ag</th>
<th>Au</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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</tr>
</tbody>
</table>
| Dissolve when used as anode material

Platinum
- Highly durable under oxidative conditions
- Wide potential range due to the large \( \text{O}_2 \) overpotential
- Most common anode material

Graphite
- Highly stable, but can be eroded under highly oxidative conditions.
- Wide potential range due to the large \( \text{O}_2 \) overpotential
- Absorption or intercalation of organic material may occur.
- Most common anode material

Glassy carbon (Vitreous carbon)
- Amorphous form of carbon
- Very hard (as hard as quartz)
- Good chemical stability and wide potential range

Reticulated Vitreous Carbon (RVC)
- Glassy carbon produced as a form
- Same chemical property as glassy carbon
- Large surface area

Boron-Doped Diamond (BDD)
- Highly durable under oxidative conditions
- Large \( \text{O}_2 \) overpotential (1.1 V) and \( \text{H}_2 \) overpotential (-1.1 V)
- Due to its large \( \text{O}_2 \) overpotential, OH radical and ozone can be generated under aqueous conditions.
- Used for waste-water treatment (complete mineralization of organic molecule using OH radical) and ozone generation.
- Recently introduced to electroorganic synthesis

Other anode material

- Large \( \text{O}_2 \) overpotential, wide potential range.
- Prepared by electrochemical deposition of \( \text{PbO}_2 \) onto conductive materials
- Used for production of inorganic oxidant such as perchlorate, periodate and ozone
- Electroorganic application is oxidation of alkenes, arenes and alcohols

- Prepared by forming \( \text{Ni(OH)}_2 \) on Ni plate
- Anodically stable only under basic conditions
- Oxidation of alcohol and amine proceeds by anodically generated Ni(III) on the electrode.

Carbon sulfide electrode  Review: Guillanton, Sulfur Reports. 1992, 12, 405.
- Sacrificial anode
- Used for thiolation of organic compounds
1-5. Cathode material

High H₂ overpotential

Carbon-based material, Pb, Sn, Hg, Cd, Zn
Useful for cathodic reduction of various organic molecules

Low H₂ overpotential

Pt, Ni, Cu, Ag, Fe(steelless steel)
These electrodes are used when H₂ evolution at cathode is desirable.

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2. Price of Electrodes

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Quantity</th>
<th>Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt foil</td>
<td>Aldrich</td>
<td>1.5 g</td>
<td>$480</td>
</tr>
<tr>
<td></td>
<td>Alfa Aesar</td>
<td>0.025 mm × 25 mm × 25 mm</td>
<td>$107</td>
</tr>
<tr>
<td>Pt coated Ti</td>
<td>ebay</td>
<td>30 mm × 40 mm</td>
<td>$12.8</td>
</tr>
<tr>
<td>Graphite</td>
<td>many</td>
<td>1 lb</td>
<td>&lt;$10</td>
</tr>
<tr>
<td>Glassy carbon rod</td>
<td>Alfa Aesar</td>
<td>3 mm × 25 mm × 25 mm</td>
<td>$98</td>
</tr>
<tr>
<td>RVC</td>
<td>KRRaynolds</td>
<td>40 mm × 40 mm</td>
<td>$15</td>
</tr>
<tr>
<td>BDD</td>
<td>windson scientific</td>
<td>3 mm diameter</td>
<td>$305</td>
</tr>
<tr>
<td>Hg</td>
<td>Aldrich</td>
<td>1 kg</td>
<td>$422</td>
</tr>
<tr>
<td>Al, Mg, Ni, Cu, Pb, Sn, Fe, Zn</td>
<td>many</td>
<td>1 lb</td>
<td>&lt;$10</td>
</tr>
</tbody>
</table>

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3. Electrode Degradation

**Platinum anode** 

Pt is known to be corroded slowly in the presence of halide ion. (corrosion rate: 5mgA⁻¹h⁻¹ in the electrolysis of 8 M HCl for 80 h)

**Graphite anode** 

Generally, graphite is not tolerated under strongly oxidizing conditions or high voltage due to the formation of graphene oxide.

**Glassy carbon anode** 

OH radical can cause erosion of glassy carbon

Conditions: H₂O₂, Fe(NH₄)₂(SO₄)₂ and EDTA in 0.01 M acetate buffer

Micrographs of GC surface: before treatment (left), after 60 min (right)

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**BDD anode** 

BDD is also known to be eroded under harsh electrrchemical conditions.

Before electrolysis

After severe anodic polarization at 1Acm⁻² in 1 M HClO₄ for 576 h at 40 °C
4. Selected Electroorganic Reactions and Suitable Electrodes

4-1. Anodic oxidation

Oxidation of carboxylic acids (Kolbe reaction)  

\[
\text{RCOO}^- \xrightarrow{\text{anodic oxidation}} \text{R}^+ \xrightarrow{-\text{CO}_2} \text{R} \quad \text{MeOH, c.c., undivided cell}
\]

Anode: Pt (most common), Glassy carbon  
Cathode (not critical): Pt, carbon, Fe, Hg etc.

Heterocoupling  

\[
\text{COOH} \xrightarrow{\text{Pt anode}} \text{MeONa} \quad \text{MeOH, c.c., undivided cell}
\]

Steel cathode was chosen to avoid catalytic hydrogenation of the double bond.

Cascade cyclization  

\[
\text{Pt anode steel cathode} \quad \text{MeOH, c.c., undivided cell}
\]

Application to total synthesis  

\[
\text{Anode: Pt, graphite} \quad \text{ graphene anode graphite cathode} \\
\text{MeOH, KI, c.c., undivided cell}
\]

Regioselectivity of methoxylation is usually kinetic control, i.e., less substituted \(\alpha\)-position is functionalized preferentially.

Effects of anode material  

\[
\text{Pt cathode} \quad \text{MeOH, EtOH, c.c., undivided cell}
\]

Late-stage functionalization of polycyclic lactams  
Aubé, Angew. Chem. 2015, 127, 10701.

\[
\text{graphite anode graphite cathode} \quad \text{LiClO}_4, \text{MeOH} \text{ c.c. undivided cell}
\]

A mobile phone charger was used as a power supply.

A mobile phone charger was used as a power supply.
Electroorganic Chemistry: Choice of Electrodes

**Oxidation of peptides**


\[
\text{PhNHCO}_2\text{Me} + \text{Et}_4\text{NCl, MeCN/MeOH c.c., undivided cell} \rightarrow \text{MeCONHMeCO}_2\text{Me} 84\% (1.5:1 dr)
\]

Unusual oxidation


**Application to a natural product synthesis**


**C-H arylation**


**C-H amination**


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Oxidation of electron-rich \( \pi \)-system

Anode: Pt, graphite, RVC, BDD
Cathode: Pt, graphite

Proposed mechanism:

- **N-Br bond homolysis**
  - Hofmann-Loffler-Freytag

- **X+ MeOH**
  - NHTs

- **MeONa, MeOH c.c., undivided cell**
  - additive: KBr, KI
  - 30% 82%
  - 22%
  - -

- **carbon felt anode Pt cathode**
  - additive: \( \text{Bu}_4\text{NB(C}_6\text{F}_5\text{)}_4 \)
  - radical cation (1 eq.)
  - naphthalene
  - 73%
  - 9 other examples

- **carbon felt anode Pt cathode**
  - pyridine
  - piperidine
  - 99%
  - 12 other examples
Organocatalyzed oxidation  

\[
\text{R} + R'\text{OH} \rightarrow \text{ROR'}
\]

10 mol% cat., DBU, TBAB

\text{BF}_4^- \quad \text{c.p., undivided cell}

> 20 examples

Graphite cathode gave inferior effect due to the sluggish \( \text{H}_2 \) evolution.

Oxidation of other compounds

Though choice of electrodes varies, Pt is often the first choice for anode.

Electrochemical aziridination  

\[
\text{N}=\text{NH}_2 + \text{HNEt}_3\text{OAc, MeCN c.p., divided cell} \rightarrow \text{Phth}\text{=N} \quad 85\%
\]

13 other examples

This reaction didn't work with graphite anode due to competing alkene oxidation on graphite.

Coupling of phenols on BDD  

\[
\text{BDD anode} \quad \text{Ni cathode} \quad [\text{Et}_3\text{NMe}]\text{O}_3\text{SMe} \quad \text{H}_2\text{O}, 70^\circ \text{C} \quad \text{c.c., undivided cell} \rightarrow \text{Me} \quad \text{HO} \quad \text{Me} \quad 49\%
\]

was obtained with Pt anode.

Oxidation of phosphorus  

\[
\text{graphite anode} \quad \text{graphite cathode} \quad 3 \text{ eq. } \text{nBu}_3\text{P} \quad 2 \text{ eq. } \text{MeSO}_3\text{H} \quad \text{BnNEt}_3\text{Cl}, \text{CH}_2\text{Cl}_2 \quad \text{undivided cell, c.c.} \rightarrow \text{6} \quad 63\% \quad (\text{trans:cis}=81:19)
\]

6 other examples

Effects of anode material  

\[
\begin{align*}
\text{Me} & \quad \text{Pt cathode} \\
\text{Me} & \quad \text{Pt anode} \\
\text{Me} & \quad \text{Glassy carbon}
\end{align*}
\]

anode:

\[
\begin{align*}
\text{anode:} & \quad \text{Pt} \\
\text{anode:} & \quad \text{Glassy carbon}
\end{align*}
\]

3/4 = 4.4 (19% yield)

3/4 = 21 (35% yield)


Generation of MeO\(^*\) was confirmed in the case of Pt and BDD as anode.
Mechanism:

- Oxidation of sulfur

- Reduction of esters

- Reduction of amides

**4.2. Cathodic reduction**

**Reduction of carbonyl group**
- Anode: Pt, graphite, sacrificial anodes
- Cathode: Hg, Sn, Mg, Pb, Pt, graphite

**Reductive cyclization of ketones**

- 6-membered & piperidine ring formation and transannular cyclization were also demonstrated.
**Reduction of alkenes and conjugated alkenes**

Anode: Pt, graphite, sacrificial anodes

Cathode: Hg, Sn, Mg, Pb, Zn, Pt, graphite

**Reduction of dienes**


\[
\text{Mg anode} \quad \text{Mg cathode} \quad \text{LiClO}_4, \text{THF} \quad \text{c.c., undivided cell} \quad \text{intermediate} \]

62%

Pt, Al, Zn, Ni, Cu, Pb as cathode • • 0%

**Reduction of unsaturated esters**

- Dimerization

\[
\text{Pt anode} \quad \text{Cu cathode} \quad \text{TBAOTs, DMF} \quad \text{c.p. divided cell} \]

76%

**Natural product synthesis**


**An example of notable anode effect**


\[
\text{Al anode steel cathode} \quad \text{NBu}_4\text{BF}_4, \text{NBu}_4\text{I} \quad \text{NMP}, \text{c.c.} \quad \text{undivided cell} \]

50%

Mg, Zn anode • • • yield <10%

**Reduction of other compounds**

Anode: Pt, graphite, sacrificial anodes

Cathode: Materials with large H\textsubscript{2} overpotential

**Reductive carbon-halogen bond cleavage**


**Birch reduction**


**Electrochemical transition-metal catalysis**

Mechanism:

\[ \text{NiBr}_2(bpy) \rightarrow \text{Ni}(0) \rightarrow \text{Ni-Ph} \rightarrow R-Cl \rightarrow R-\text{Ph} \]  
\[ \text{Ph}^{\text{II}} \rightarrow \text{Ni-Ph} \rightarrow R-\text{Cl} \rightarrow \text{cathodic reduction} \]

This step might be similar to Weix’s system.


Summary

Anode material

Do you use sacrificial anode?

- Yes
  - Al, Zn, Mg, Fe etc.
  - Pt, carbon based material
- No: I don’t know

Cathode material

Is your target reaction reduction?

- Yes
  - \( R-\text{Cl} \rightarrow R-\text{Ph} \)
- No: I don’t care

Is \( H_2 \) evolution OK?

- Yes
  - Whatever conductive
  - Pt, Ni, Fe and other material with small \( H_2 \) overpotential
- No
  - carbon based material and other material with large \( H_2 \) overpotential

Useful material for electroorganic synthesis

- Redox potential of organic compounds  
  Nicewicz, Synlett, 2016, 27, 714.

Reviews for further study

- Indirect (mediated) electrolysis

- Application to complex molecule syntheses
  (b) Moeller, Tetrahedron, 2000, 56, 9527.

- Electrochemical halogenation

- Electrochemistry with transition-metal catalysis