Miniature Bio-fuel Cell and Zn-Ag/AgCl Battery in Physiological Condition

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Basics in Electrochemistry, Batteries, Fuel Cells,...
What is electrochemistry?

- Branch of science relating chemical events and electricity:
  - Electron transfer or redox reactions through electrodes
  - Conversion between chemical energy and electrical energy
  - Scientific area relating electron transfer with electrical energy, chemical conversion, and electrical signal generation

  Chemical Energy, Chemical Transformation \[\xrightleftharpoons{\text{Galvanic, Electrolytic}}\] Electrical Energy, Electrical Signal

Galvanic - Fuel Cells, Batteries, Corrosions
Electrolytic – Electrolysis, Refining

- Related fields:
  Battery, Fuel cells, Sensors, Corrosions, Deposition/Plating/Coating, Display, Solar cells, Electronics, Neurosciences, etc
Meaning of Standard Electrode Potential ($E^o$)

- At more negative potential
  - Easily oxidizable
  - Good electron donor
  - Good reducing agent
  - Good anodic material

- At more positive potential
  - Easily reducible
  - Good electron acceptor
  - Good oxidizing agent
  - Good cathodic material

- Reference potential
  - $H^+/H_2$ 0.000

- Compare $E^o$s
  - Li/Li$^+$, K/K$^+$, Na/Na$^+$
  - F$_2$/F$^-$, Cl$_2$/Cl$^-$, Br$_2$/Br$^-$, I$_2$/I$^-$
  - Au, Ag, Cu

<table>
<thead>
<tr>
<th>Half-reaction</th>
<th>$E^o$, V vs. NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$ + e$^-$ → Li(s)</td>
<td>-3.040</td>
</tr>
<tr>
<td>K$^+$ + e$^-$ → K(s)</td>
<td>-2.924</td>
</tr>
<tr>
<td>Na$^+$ + e$^-$ → Na(s)</td>
<td>-2.713</td>
</tr>
<tr>
<td>Al$^{3+}$ + 3e$^-$ → Al(s)</td>
<td>-1.676</td>
</tr>
<tr>
<td>Zn$^{2+}$ + 2e$^-$ → Zn(s)</td>
<td>-0.763</td>
</tr>
<tr>
<td>Fe$^{2+}$ + 2e$^-$ → Fe(s)</td>
<td>-0.440</td>
</tr>
<tr>
<td>2H$^+$ + 2e$^-$ → H$_2$(g)</td>
<td>0.000</td>
</tr>
<tr>
<td>Cu$^{2+}$ + 2e$^-$ → Cu(s)</td>
<td>+0.340</td>
</tr>
<tr>
<td>I$_2$(s) + 2e → 2I$^-$</td>
<td>+0.535</td>
</tr>
<tr>
<td>Ag$^+$ + e$^-$ → Ag(s)</td>
<td>+0.800</td>
</tr>
<tr>
<td>Br$_2$(l) + 2e$^-$ → 2Br$^-$</td>
<td>+1.065</td>
</tr>
<tr>
<td>O$_2$(g) + 4H$^+$ + 4e$^-$ → 2H$_2$O</td>
<td>+1.231</td>
</tr>
<tr>
<td>Cl$_2$(g) + 2e$^-$ → 2Cl$^-$</td>
<td>+1.358</td>
</tr>
<tr>
<td>Au$^+$ + e$^-$ → Au(s)</td>
<td>+1.680</td>
</tr>
<tr>
<td>F$_2$(g) + 2e$^-$ → 2F$^-$</td>
<td>+2.866</td>
</tr>
</tbody>
</table>
Battery vs. Fuel Cell

- **Battery**
  - Primary battery – Zn/MnO$_2$…
  - Secondary battery – Li/Li$^+$, Pb/PbSO$_4$
  - Chemical form of energy is contained in a case

- **Fuel Cell**
  - H$_2$/O$_2$, Classification by the kind of electrolyte
  - Other possible fuels: methanol, hydrocarbon, glucose, organic acids, biomass…
  - Chemical form of energy is supplied from outside

- **Hybrid type**
  - Hybrid type - Al/Air, Zn/Air, …
\[
\begin{align*}
\text{Zn} + 2\text{OH}^- & \rightarrow \text{Zn(OH)}_2 + 2e^- & E_a &= -0.76 \text{ V} \\
2\text{MnO}_2(s) + \text{H}_2\text{O(l)} + 2e^- & \rightarrow \text{Mn}_2\text{O}_3(s) + 2\text{OH}^- & E_c &= +0.79 \text{ V}
\end{align*}
\]

(at pH = 14.0)

\[
\begin{align*}
\text{Zn(s)} + 2\text{OH}^-(\text{aq}) & \rightarrow \text{Zn(OH)}_2(s) + 2e^- & E_a &= -0.76 \text{ V} \\
2\text{MnO}_2(s) + \text{H}_2\text{O(l)} + 2e^- & \rightarrow \text{Mn}_2\text{O}_3(s) + 2\text{OH}^- & E_c &= +0.79 \text{ V}
\end{align*}
\]

\[
\text{Zn(s)} + 2\text{MnO}_2(s) + \text{H}_2\text{O(l)} \rightarrow \text{Zn(OH)}_2(s) + \text{Mn}_2\text{O}_3(s) & \quad E_{\text{rxn}} = 1.55 \text{ V}
\]
\[ \text{H}_2-\text{O}_2 \text{ Fuel Cell} \]

\[ 2\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \quad \text{E}_a = 0.00 \text{V} \]

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad \text{E}_c = +1.23 \text{V} \]

(at pH = 0.0)

\[ 2\times (\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-) \quad \text{E}_a = 0.00 \text{ V} \]

\[ \text{E}_{\text{rxn}} = +1.23 \text{ V} \]
Basic Components of Electrochemical Cells

- Components of the cell
  - Electrodes
    - Anode
    - Cathode
  - Solution
    - Electroactive species
    - Supporting electrolyte
    - Solvent
  - Separator
  - Wire
  - Case

(Note!) Electron transfer (or redox reaction) always accompanies ion transfer.

Daniel Cell
Zn(s)/ZnSO₄(1 M)//CuSO₄(1 M)/Cu(s)
## Redox Potentials of Biologically Important Reagents and Enzymes

<table>
<thead>
<tr>
<th>Redox Couple (Ox/Red)</th>
<th>$E^\circ$ (mV vs. NHE, pH = 7.0)</th>
<th>Redox Couple (Ox/Red)</th>
<th>$E^\circ$ (mV vs. NHE, pH = 7.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Succinate + CO$_2$ / α-KG</td>
<td>-670</td>
<td>FAD / FADH$_2$</td>
<td>-220</td>
</tr>
<tr>
<td>Acetate / Acetaldehyde</td>
<td>-600</td>
<td>Pyruvate / Lactate</td>
<td>-190</td>
</tr>
<tr>
<td>CO$_2$/formate</td>
<td>-580</td>
<td>FMN / FMNH$_2$</td>
<td>-190</td>
</tr>
<tr>
<td>CO$_2$/CO</td>
<td>-520</td>
<td>Dehydro- / Ascorbate</td>
<td>+80</td>
</tr>
<tr>
<td>Gluconate / Glucose</td>
<td>-440</td>
<td>Cytochrome c</td>
<td>+220</td>
</tr>
<tr>
<td>2H$^+$ / H$_2$</td>
<td>-414</td>
<td>O$_2$/H$_2$O$_2$</td>
<td>+281</td>
</tr>
<tr>
<td>CO$_2$/CH$_3$OH</td>
<td>-380</td>
<td>p-Phenylenediamine (PPD)</td>
<td>+356</td>
</tr>
<tr>
<td>Cystine / Cysteine</td>
<td>-340</td>
<td>L-DOPA</td>
<td>+380</td>
</tr>
<tr>
<td>NAD(P)$^+$ / NAD(P)H</td>
<td>-320</td>
<td>Ferri / Ferrocyanide</td>
<td>+430</td>
</tr>
<tr>
<td>CO$_2$/acetate</td>
<td>-290</td>
<td>ABTS (-N=N-)</td>
<td>+677</td>
</tr>
<tr>
<td>CO$_2$/CH$_4$</td>
<td>-240</td>
<td>Laccase (P. versicola)</td>
<td>+780</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O$_2$ / H$_2$O</td>
<td>+820</td>
</tr>
</tbody>
</table>
\[ P \text{ (W)} = E_{cell} \text{ (V)} \times I \text{ (A)} \]

- Power \((W = J/s = V \cdot I)\)
- \(E_{cell} = E_c - E_a : \text{Choice of } E_a \text{ and } E_c\)
- \(I : \text{Electron transfer reaction rate}\)
  \((\text{Fast ET, MT, Increase Area})\)
Factors Affecting Electrode Reaction Rate, i.e. Current

Electron Transfer (Chemical Reactions) Mass Transfer

Mediated Electron Transfer (MET) vs. Direct Electron Transfer (DET)

\[ \text{Cat} \quad +e^- \text{ or } -e^- \quad \text{Product} \quad +e^- \text{ or } -e^- \\
\text{Cat}^* \quad \text{Substrate} \]

\[ \text{Med} \quad +e^- \text{ or } -e^- \quad \text{Enzyme}^* \quad +e^- \text{ or } -e^- \quad \text{Substrate} \]

\[ \text{Med}^* \quad \text{Enzyme} \quad \text{Product} \quad +e^- \text{ or } -e^- \]
**Electrical Communication between Electrode and Enzyme**

- Mediated Electron Transfer by Osmium Redox Polymer

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E^0$ (mV Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVI-[Os-(diamine-bpy)$_2$Cl]</td>
<td>-170</td>
</tr>
<tr>
<td>PAA-PVI-[Os(dme-py)$_2$]</td>
<td>+ 100</td>
</tr>
<tr>
<td>PAA-PVI-[Os(bpy)$_2$Cl]</td>
<td>+ 200</td>
</tr>
<tr>
<td>PVI-[Os(bpy)$_2$Cl]</td>
<td>+ 200</td>
</tr>
<tr>
<td>PAA-PVP-[Os(bpy)$_2$Cl]</td>
<td>+ 300</td>
</tr>
<tr>
<td>PAA-PVI-[Os(dCl-bpy)$_2$Cl]</td>
<td>+ 350</td>
</tr>
<tr>
<td>PVI-[Os(dCl-bpy)$_2$Cl]</td>
<td>+ 350</td>
</tr>
<tr>
<td>PVP-[Os(dCl-bpy)$_2$Cl]</td>
<td>+ 400</td>
</tr>
<tr>
<td>PVI-[Os(tpy)(dme-py)]</td>
<td>+ 550</td>
</tr>
</tbody>
</table>

A redox-enzyme electrically ‘wired’ to an electrode surface by flexible polymer chains functionalized with redox-mediator groups and surrounding the enzyme at the electrode surface.


Glucose/O₂ Bio-fuel Cell
Glucose/O$_2$ Bio-fuel Cell

Oxidation of Glucose

Glucose $\rightarrow$ Gluconolactone $+ 2H^+$

$2e^-$

Reduction of Oxygen

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

$E_a = -0.44$ V vs. NHE

$2 \times (Glucose + H_2O \rightarrow Gluconolactone + 2H^+ + 2e^-)$

$E_c = +0.82$ V vs. NHE

$2$ Glucose $+ O_2 \rightarrow 2$ Gluconolactone

$E_{cell} = 1.26$ V
Enzymes and Mediators Are Essential for Bio-fuel Cell

\[ \text{Glucose} \xrightarrow{\text{GOx}} \text{Os(II)} \xrightarrow{\text{H}^+} \text{Os(III)} \xrightarrow{\text{Laccase}} 2\text{H}_2\text{O} \]

\[ 2\text{H}^+ + \frac{1}{2}\text{O}_2 \]

\[ \xrightarrow{\text{anode}} \]

\[ \text{Gluconolactone} \]

\[ \xrightarrow{\text{cathode}} \]

\[ \rightarrow \text{Membraneless, Caseless Possible} \]
A redox-enzyme electrically ‘wired’ to an electrode surface by flexible polymer chains functionalized with redox-mediator groups and surrounding the enzyme at the electrode surface.
Osmium Polymers for GOx

For GOx
PVI-[Os-(diamine-bpy)_2Cl]^{+2+}
$E^0 = -170 \text{ mV vs. Ag/AgCl}$

For GOx
PVP-[Os-(dimethyl-bis-imidazole)_2Cl]^{2+3+}
$E^0 = -190 \text{ mV}$
Osmium Polymers for BOD and Laccase

For BOD
PAA-PVI-[Os(dCl-bpy)$_2$Cl]$^{+/2+}$
$E^0 = +350$ mV

For Laccase
PVI-[Os(tpy)(dme-py)]$^{2+/3+}$
$E^0 = +500$ mV
Glucose/O$_2$ Miniature Bio-fuel Cell – under Air, GOx/Lc

Redox polymers $I$ and $II$ respectively “wire” glucose oxidase (GOx) and bilirubin oxidase (BOD), selective and non-leachable electrocatalysts.
2.4 µW Power from a “Wired” Enzyme Glucose- O$_2$ Micro-fuel Cell Operating in a Grape


7 µm carbon fibers. Drawn, as the fibers are too fine to be photographed.
* The cell consists of two 13 μm diameter, 2 cm long, “wired” enzyme-coated carbon fibers. Their combined footprint is 0.53 mm² and their combined volume is 0.0052 mm³
• Possible Candidates of Fuels from Body:
  • **Sugar**: Sucrose, Glucose, Fructose,…
  • **Organic Acids**: Formic, Acetic, Citric,…

Sucrose
(α-d-Glucopyranosyl-(1→2)-β-d-fructofuranose)

HCOOH
CH₃COOH
Citric Acid
(HOOCCH₂C(OH)(COOH)CH₂COOH)
CH₃OH
,…

α-d-Glucopyranose

α-d-Fructofuranose
(a cyclic form of fructose)
Zn Anode for Miniaturized Power Source in Physiological Conditions

\[
\begin{align*}
Zn(s) & \rightarrow Zn^{2+} + 2e^- & E_a = -0.76 \text{ V vs. NHE} \\
AgCl(s) + e^- & \rightarrow Ag(s) + Cl^- & E_c = +0.20 \text{ V vs. NHE} \\
\hline
Zn(s) + 2 AgCl(s) & \rightarrow Zn^{2+} + Ag(s) + Cl^- & E_{rxn} = 0.96 \text{ V}
\end{align*}
\]

Physiological Condition

PBS (Phosphate Buffered Saline):
20 mM phosphate buffer, pH = 7.4, 0.15 M NaCl

Serum
PBS + others (proteins, ascorbate, urate,...)
Motivation - Anodic Potential Limit of Glucose/O₂ Bio-fuel Cell

$E^\circ$ (glucose/gluconate) = -0.64 V vs. Ag/AgCl (at pH=7)

$E^\circ$ (FADH₂/FAD) = -0.42 V

$E^\circ$ (GOx) = -0.2 ~ -0.4 V

$E^\circ$ (mediator or polymer) = 0.0 ~ -0.2 V

cf. $E^\circ$ (Zn/Zn²⁺) = -0.963 V vs. Ag/AgCl
Preparation of Zn Anode

- Zinc deposition and Nafion coating on 2 cm long, 76 µm diameter Pt wire electrode
Zn Anode for Implantable Power Source

Hopeite Growth on Nafion coated Zn anode

Discharge Curves (13 mA·cm⁻²)

Initial stages of discharge

After completion of discharge (1.6 C)

4 mC 250 mC 430 mC

Formation of highly Zn²⁺ conductive and O₂ blocked layer formation upon discharging in PBS condition → Made Zn anode working in neutral solution

(1) in pH 7.4, 20 mM phosphate buffer + 0.15 M NaCl
(2) in pH 7.4, 20 mM phosphate buffer
(3) in 0.15 M NaCl solution
(4) in serum

Heller, A; Shin, W., US Pat. 20070125644
Microscopic and SEM Images after Finishing Discharge

pH 7.4, 20 mM phosphate buffer (containing 0.15 M NaCl)

0.15 M NaCl solution

pH 7.4, 20 mM phosphate buffer
**Miniaturization of Zn Anode**

5 mm disc: $R = 50 \, k\Omega$, $I = 20 \, \mu A$

Discharge Efficiency $\sim 80\%$

![5 mm disc image]

152 $\mu$m disc: $R = 48 \, M\Omega$, $I = 20 \, nA$

Discharge Efficiency $\sim 60\%$

![152 $\mu$m disc image]

Electrodeposition on 10 $\mu$m disk: $9.9 \times 10^{-6} \, C$ (50 nA x 1980 s)

21 $\mu$m disc: $I = 1.4 \, nA$ constant oxidation

Discharge Efficiency $\sim 25\%$

![21 $\mu$m disc image]

1.4 nA x 1.0 V = 1.4 nW

Shin, W; Lee, J.; *Unpublished.*
The Potentially Implantable Zn–AgCl Cell

Projected scheme

Ag/AgCl cathode-coated with biocompatible hydrogel allowing the out-diffusion of Cl- ->should be safe to implant

Fig. Schematic diagram of a caseless miniature Zn(Nafion)–AgCl battery operating in the subcutaneous interstitial fluid

<table>
<thead>
<tr>
<th>Cell</th>
<th>Li-MnO₂</th>
<th>Zn-air</th>
<th>Zn-MnO₂</th>
<th>Zn-AgCl (proj.)</th>
<th>Zn-O₂ (proj.)</th>
<th>Glucose-air (proj)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Availability</strong></td>
<td>Now</td>
<td>Now</td>
<td>Now</td>
<td>Lab</td>
<td>Lab</td>
<td>Lab</td>
</tr>
<tr>
<td><strong>Case</strong></td>
<td>Steel</td>
<td>Steel</td>
<td>Steel</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>Organic</td>
<td>KOH</td>
<td>KOH</td>
<td>Serum</td>
<td>Physiological</td>
<td>Physiological</td>
</tr>
<tr>
<td><strong>Min. size, mm³</strong></td>
<td>200</td>
<td>50</td>
<td>200</td>
<td>0.1</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>W/L</strong></td>
<td>300</td>
<td>150</td>
<td>200</td>
<td>50</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td><strong>Wh/L</strong></td>
<td>650</td>
<td>1800</td>
<td>600</td>
<td>500</td>
<td>5000</td>
<td>50,000</td>
</tr>
<tr>
<td><strong>Life at 37°C</strong></td>
<td>3 years</td>
<td>1 month</td>
<td>1 year</td>
<td>1 month</td>
<td>2 weeks</td>
<td>2 weeks</td>
</tr>
</tbody>
</table>