Definitions

- Ion: Charged particle (molecule / atom)
  - Cation: + Ion
  - Anion: - Ion

- Oxidation: Loss of e⁻ by molecule / atom / ion
- Reduction: Gain of e⁻ by molecule / atom / ion
- Electrolyte: Solution containing ions

Polarizable Electrodes

- No chemical reaction / electron / ion exchange
- Charge accumulates on surface of electrode like a capacitor

- High pass filter
- Biosignals: (high or low frequency?)
  - EKG: 150 Hz
  - EEG: 50 Hz
  - EMG: 20 Hz
Percutaneous Electrodes

- Polarizable
- Hook minimizes motion artifact
- Pull hard to remove

Non-Polarizable Electrodes

- Metal + neutral electrolyte (containing the metal)
  - Reaction due to concentration imbalance
    - Depends on type of metal, ionic concentration & temperature
    - Diffusion current
      - Ions: metal to gel
      - Electrons: gel to metal
    - Like a charged capacitor

- Half-cell Potential ($V_{hc}$)
  - Steady state charge at metal/electrolyte boundary
  - No net current
Table 5.1  Half-cell Potentials for Common Electrode Materials at 25 °C

<table>
<thead>
<tr>
<th>Metal and Reaction</th>
<th>Potential E°, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al → Al⁺⁺ + 3e⁻</td>
<td>-1.706</td>
</tr>
<tr>
<td>Zn → Zn²⁺ + 2e⁻</td>
<td>-0.763</td>
</tr>
<tr>
<td>Cr → Cr³⁺ + 3e⁻</td>
<td>-0.744</td>
</tr>
<tr>
<td>Fe → Fe³⁺ + 2e⁻</td>
<td>-0.409</td>
</tr>
<tr>
<td>Cd → Cd²⁺ + 2e⁻</td>
<td>-0.401</td>
</tr>
<tr>
<td>Ni → Ni²⁺ + 2e⁻</td>
<td>-0.230</td>
</tr>
<tr>
<td>Pb → Pb²⁺ + 2e⁻</td>
<td>-0.126</td>
</tr>
<tr>
<td>H₂ → 2H⁺ + 2e⁻</td>
<td>0.000 by definition</td>
</tr>
<tr>
<td>Ag + Cl⁻ → AgCl + e⁻</td>
<td>+0.223</td>
</tr>
<tr>
<td>2Hg + 2Cl⁻ → Hg₂Cl₂ + 2e⁻</td>
<td>+0.216</td>
</tr>
<tr>
<td>Cu → Cu²⁺ + 2e⁻</td>
<td>+0.340</td>
</tr>
<tr>
<td>Cu → Cu⁺ + e⁻</td>
<td>+0.522</td>
</tr>
<tr>
<td>Ag → Ag⁺ + e⁻</td>
<td>+0.799</td>
</tr>
<tr>
<td>Au → Au³⁺ + 3e⁻</td>
<td>+1.420</td>
</tr>
<tr>
<td>Au → Au⁺ + e⁻</td>
<td>+1.680</td>
</tr>
</tbody>
</table>

Source: Data from Handbook of Chemistry and Physics, 55th edition, CRC Press, Cleveland, Ohio, 1974–1975, with permission.

Current Carriers

- **Body**
  - Na⁺ ions
  - K⁺ ions
  - Cl⁻ ions
    - Present but not involved in nerve stimulation
- **Electric Circuit**
  - Electrons e⁻
  - Holes h⁺
- **Electrode**
  - Electron / ion transducer

To monitor
Over-potential

- Current dependent voltages
  - Concentration ($V_c$)
    - Ion distribution near interface affected by $I$
    - Like a current dependent component of half-cell potential
  - Activation ($V_a$)
    - Atoms must overcome energy barrier before oxidation/reduction occurs
    - Energy barrier different for oxidation & reduction
    - Dependent on direction of current

\[
V_{op}(I) = V_c(I) + V_a(\text{sgn}(I))
\]

Equivalent Circuit

- $V_{hc} = \text{half-cell potential}$
- $V_{op} = \text{over-potential}$
- $CJ = \text{junction capacitance}$
- $RJ = \text{junction resistance}$
- $RE = \text{electrolyte resistance}$
Measured Electrode Impedance

Fig 5.6 (MI): Experimentally Determined Impedance
Electrode Frequency Response

\[
Z(s) = \left( R_E + R_j \right) \frac{s}{R_E R_j C_J} \frac{1}{1 + \frac{s}{R_j C_J}} \\
Z(s) \approx R_j \frac{1}{R_E C_J} \frac{1}{1 + \frac{s}{R_j C_J}} \quad R_j \gg R_E
\]

EMG Electrodes

- NonPolarizable
  - Sweat reacts with electrolyte (AgCl)
  - Motion artifact

- Polarizable
  - Percutaneous (crosses skin boundary)
  - Invasive
  - Reduced motion artifact
  - SS, Platinum or Gold plated