Electrodes

MB - JASS 09

Metal in electrolyte

solid state

A

B

C

electrolyte

1
Helmholtz double layer (1)

Helmholtz double layer: simplest approximation
→ surface charge is neutralized by opposite signed counterions placed away from the surface

- How is Helmholtz double layer described?
  - electrical double layer of positive and negative charges
  - describes the variation of electric potential near a surface
  - one molecule thick

- Where does the Helmholtz double layer occur?
  → at surfaces of a metal immersed in a dissociating solvent

Helmholtz double layer (2)

The diagram illustrates the Helmholtz double layer at a solid state interface. The solid state is shown on the left, with charged ions A, B, and C. The electrolyte is shown on the right, with counterions A'. The double layer is depicted as a region of neutral charge between the solid state and the electrolyte, maintaining electrostatic equilibrium.
Helmholtz double layer (3)

The 2 constituents of the double layer

1. inner Helmholtz layer
   → potential changes linearly with the distance
   → it comprises the absorbed water molecules

2. outer Helmholtz layer
   → potential varies linearly with the distance
   → it comprises hydrated (solvated) cations

additional:

3. outer diffuse layer (Gouy-Chapman layer)
   → potential varies exponentially with the distance
   → contains excess cations or anions distributed in a diffuse layer

Helmholtz double layer - limitations

Helmholtz does not account for

- diffusion/mixing in solution
- possibility of absorption on to the surface
- interaction between solvent dipole moments & electrode

New model by Stern addresses some of these limitations:

- ions are assumed to be able to move in solution

→ electrostatic interaction in competition with Brownian motion
Model of Stern

Combination of

→ Helmholtz-model = double layer

and

→ Gouy-Chapman-model = diffusive layer

How to model the Helmholtz-layer?

- Charge Transfer by Ions
  - Diffusion
  - Adsorption
  - Redox reactions

- Charge Transfer by Electrons
  - Surface polarisation
  - Redox reactions

\[ I = \frac{dQ}{dt} \]

Equivalent electric circuit model
Fundamental Effectors

- Effectors of charge transfer (electrical current)
  - Resistor $\rightarrow$ linear current reduction
    \[ I = \frac{U}{R} \]
  - Capacitor $\rightarrow$ storing charge
    \[ I = C \frac{dU}{dt} \]
  - Inductor $\rightarrow$ inducing current
    \[ \frac{dI}{dt} = \frac{U}{L} \]

Impedance – complex resistance

Definition:
\[ Z(\omega) = \frac{U(t)}{I(t)} = \frac{U(0)\exp(i\omega t)}{I(0)\exp(i(\omega t + \phi))} = Z(0)\exp(-i\phi) \]
Fundamental Effectors

- **Effectors of charge transfer (electrical current)**
  - **Resistor** → linear current reduction
    \[ I = \frac{U}{R} \]
    \[ Z = R \]
  - **Capacitor** → storing charge
    \[ I = C \frac{dU}{dt} \]
    \[ Z = \frac{1}{i \omega C} \]
  - **Inductor** → inducing current
    \[ \frac{dl}{dt} = \frac{U}{L} \]
    \[ Z = i \omega L \]

Equivalent circuit elements

- **Double layer capacitance**
  - Charge separation (Å-scale)
  - Depends on:
    - Temperature
    - Ionic concentrations
    - Oxide layers
    - Electrode roughness etc.

- **Charge Transfer Resistance**
  - Redox-reaction on surface
  \[ R_{CT} \propto \frac{RT}{F I_{CT}} \]

\( F \): faraday constant; \( R \): gas constant; \( T \): temperature; \( I_{CT} \): exchange current density
Equivalent circuit elements

- **Electrolyte Resistance**
  - Depends on:
    - Ionic concentration, ion types
    - Temperature
    - Geometry of Current-Transport-Area
  - Conductivity $\kappa$:
    - Fitted by computer-models

- **Constant phase element**
  - HDL is not an ideal capacitor
  - Current/Potential phase-shift
  - Empirical parameter $\alpha$

Impedance of rough electrodes

- Hausdorff-Dimension $D_H = \frac{\log N(R)}{\log \frac{1}{R}}$

- $Y(\omega) = \frac{1}{Z(\omega)} = \sum\frac{\alpha C}{1+i\omega R C}$

- $Y(r \cdot 1, \omega) = r^\alpha Y(1, \omega)$
- $C_j(r \cdot 1) = r^\alpha C_j(1)$
- $R_j(r \cdot 1) = r^\alpha R_j(1)$

- $Y(\omega) = \frac{1}{Z(\omega)} = Y_0(1) \alpha^\alpha$

- $\alpha = \frac{1}{D_H - 1}$
Helmholtz double layer

- Basic Model

- Advanced Pacemaker Model

Circuit Model
Impedance of Electrochemical-Cells

- **Randles-Cell**
  - Schematic
  - Overall Impedance
    \[
    Z = R_L + \frac{1}{\omega C_D} + \frac{R_{CT}}{\omega C_D} + \frac{1}{\omega C_D}
    \]

  - \( \omega \to 0 \): infinite charge-time
  - \( \omega \to \infty \): short circuit

Electrochemical Impedance
Experimental setup

- Three electrode setup
- System in equilibrium
- Current between sample & counter electrode
- Potential reference electrode

Small disturbance away form the open cell potential (point of equilibrium)

-> Linear system response
Impedance Measurement(1)

Electrode ring made of platinum-iridium

Impedance of PtIr

$\log \left( \frac{Z}{\text{Ohm}} \right)$ vs. freq/Hz, log spacing

Impedance Measurement(2)

$Z_0 = \frac{1}{(i \omega)^{n} C}$

Fit:

$R_L = 47 \text{ Ohm}$

$R_F = 0.1 \text{ MOhm}$

$C_q = 27e-6 \text{ F}$

$a = 0.85$
Impedance Measurement (3)

Electrode tip made of Titanium

![Graph showing impedance of Titanium](image)

**Fit:**

\[ C_q = 5.9 \times 10^{-9} \text{ F} \]
\[ a = 0.6 \]

Impedance Measurement (4)
Challenges in cardiac pacing (1)

Two main task of cardiac pacemakers:
- Sensing the intra-cardial ECG, i.e. detecting heartbeats, fibrillation, arrhythmia
- Electric stimulation of heart muscles when necessary without interference to sensing
Challenges in cardiac pacing (2)

- Requirements for accurate ECG measurements
  - Frequency independent damping of ECG signals → low distortion in ECG waveforms
  - Low damping of ECG signals → good signal transmission
  - Small electrodes lead to better electrical contact to myocardium

Challenges in cardiac pacing (3)

- Requirements for efficient pacing
  - Low damping → reduces power dissipation → longer battery lifetime
  - Low polarization artifact voltage \( U = \frac{Q_{st}}{A C_p} \) → gives the possibility to pace and sense via the same electrode
Challenges in cardiac pacing (4)

Conflicts in the previous requirements

- Low damping
- Frequency independent damping
- Low polarization artifact voltage

→ Low impedance required
→ High Helmholtz capacity required

→ Sets limits to the capacitance of the Helmholtz double layer

Solution: Increase the specific Helmholtz capacity between electrode surface & electrolyte

Fractal coating (1)

Definition: Fractal

- rough or fragmented geometric shape that can be split into parts, each of which is (at least approximately) a reduced-size copy of the whole

- A mathematical fractal is based on equations that undergo iteration based on recursion

Fractal → characteristic features:
- fine structure at arbitrarily small scales
- too irregular to be easily described in traditional geometric language
- self-similar
- recursive
Fractal $\rightarrow$ Koch-curve (1)

Fractal $\rightarrow$ Koch-curve (2)
Fractal coating (2)

fractal surface in nature (romanesco)  
fractal coating

Basic material: Platinum-Iridium

SEM of Pt-Ir (1)

2.0 μm

EM = 5.00 kV  
WD = 7.5 mm  
Date: 14 Feb 2009  
Time: 22:10:01
Modern Pacemaker Electrode

Fractal coated electrode:
1 → sealing
2 → fractal coating
3 → steroid

Advantages:
- 1000 time enlargement of the electrical active surface compared to the normal geometric size
- Reduction of depolarization effects
- Increasing long time stability

Diffusion limited aggregation

**Random Walks** (Brownian motion etc.)
- space/time discrete processes
- continuous formulation
Impedance measurement of Ir-fractal (1)

Fit:
\[
R_L = 26 \text{ Ohm} \\
R_F = 5 \text{ kOhm} \\
C_q = 2e^{-3} \text{ F} \\
a = 0.83
\]

Impedance measurement of Ir-fractal (2)

Fit:
\[
R_L = 48 \text{ Ohm} \\
R_F = 32 \text{ kOhm} \\
C_q = 2e^{-3} \text{ F} \\
a = 0.77
\]
Increasing Helmholtz capacity

Methods to increase the specific Helmholtz capacity of the electrode electrolyte boundary layer (i.e. the capacity per geometric surface):

- **Fractal electrode surface**
  - Increasing effective electrode surface without increasing the geometric dimensions

- **Electro-active surface**
  - Electrochemical enhancement of specific capacity

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**Electro-active surfaces**

- Revision: Faraday resistance $R_F$
  - Charge transport via irreversible chemical reactions

![Diagram of electro-active surfaces](image)
Electro-active surfaces

- Reversible redox reaction
  \[ \text{e}^- + \text{H}_2\text{O} + \text{Me}_4^+\text{O}_2 \leftrightarrow \text{Me}_3^+\text{OOH} + \text{OH}^- \]

- Acts as charge/energy storage
  \[ \rightarrow \text{Impedance characteristics like a capacitor} \]

Electro-active surfaces

- Reversible reactions act as energy/charge storage
  - Requirements: - Reactants/products need to remain at the boundary layer
  - non-toxic substances, e.g. iridium oxide

\[ R_F \]
\[ R_L \]
\[ C_{HDL} \]
\[ C_{EAS} \]
Stimulating Experiment

- Petri dish with
  - 100 mM Fe(II)SO₄
  - 100 mM KSCN (potassium thiocyanate)

- Anodic pulses via coated/uncoated electrodes
  - 10V, 1ms, 100bpm

Fe³⁺ and thiocyanate (N≡C-S⁻) form a deeply red complex

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^{-}
\]

\[
\text{Fe}^{3+} + \text{SCN}^{-} + 5\text{H}_2\text{O} \rightarrow \text{Fe}\text{(SCN)(H}_2\text{O)}_5^{2+}
\]