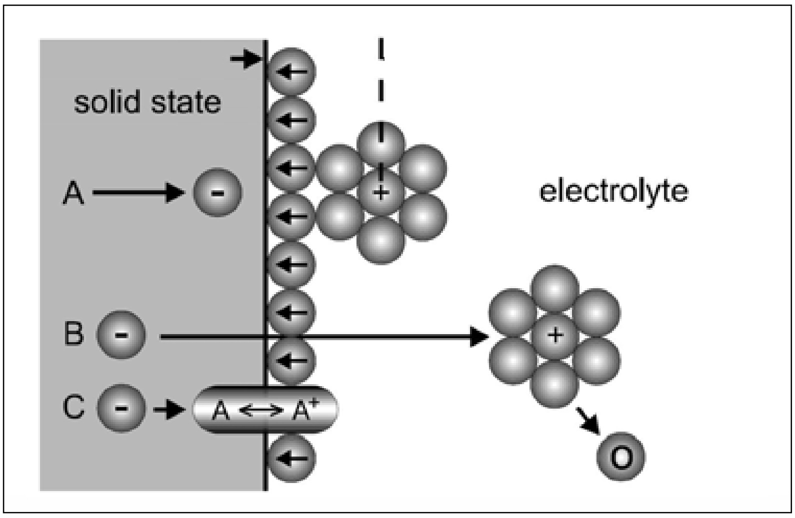
Electrodes

MB - JASS 09

Metal in electrolyte

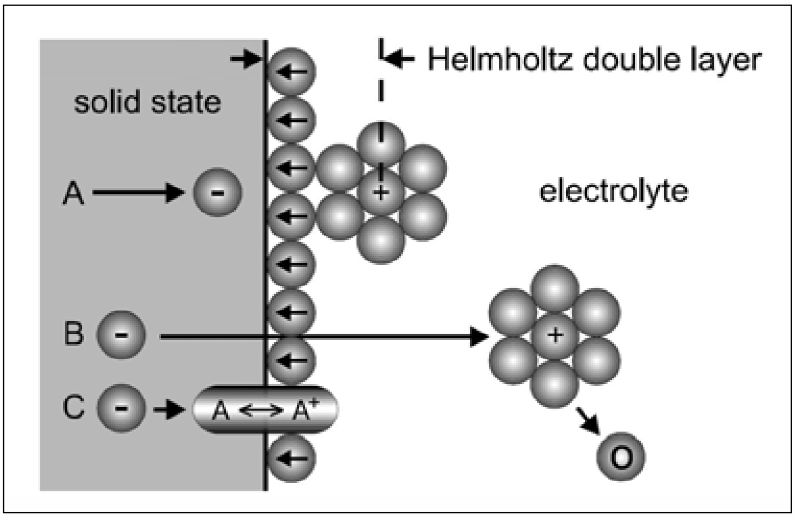


Helmholtz double layer (1)

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)

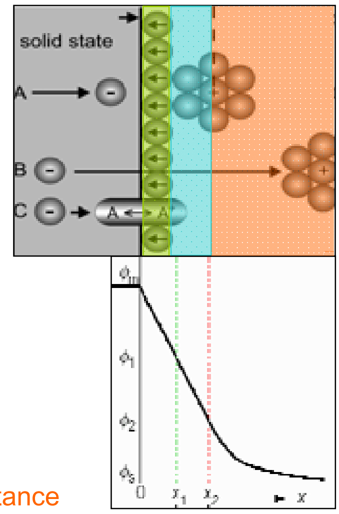


Helmholtz double layer (3)

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

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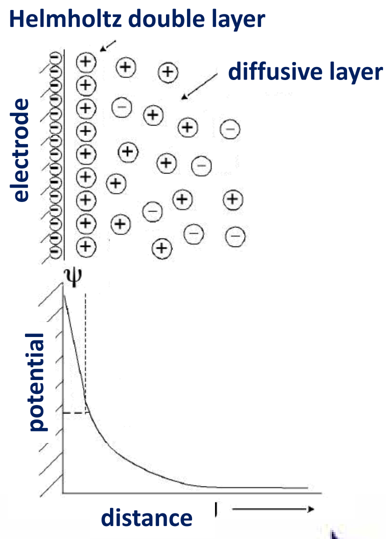
Model of Stern

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 → linear current reduction

$$I = \frac{U}{R}$$

  - Capacitor → storing charge

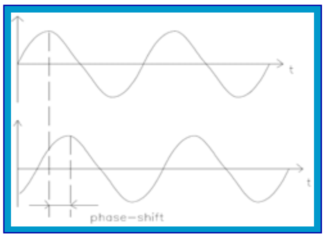
$$I = C\frac{dU}{dt}$$

  - Inductor → inducing current

$$\frac{dI}{dt} = \frac{U}{L}$$

Impedance – complex resistance

$U(t) = U(0)\sin(\omega t)$ → **Effector** → $I(t) = I(0)\sin(\omega t + \phi)$



Definition:

$$Z(\omega) = \frac{U(t)}{I(t)} = \frac{U(0)\exp(i\omega t)}{I(0)\exp(i(\omega t + \varphi))} = Z(0)\exp(-i\varphi)$$

Fundamental Effectors

- Effectors of charge transfer (electrical current)
  - Resistor → linear current reduction

$$I = \frac{U}{R} \qquad Z = R$$

  - Capacitor → storing charge

$$I = C\frac{dU}{dt} \qquad Z = \frac{1}{i\omega C}$$

  - Inductor → inducing current

$$\frac{dI}{dt} = \frac{U}{L} \qquad Z = i\omega L$$

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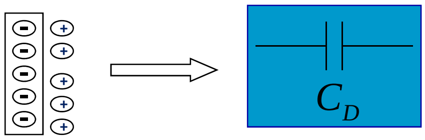
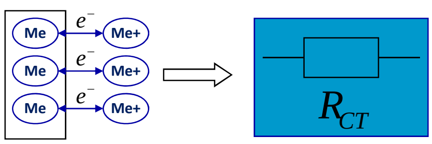
Equivalent circuit elements

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



- Charge Transfer Resistance
  - Redox-reaction on surface

$$R_{CT} \propto \frac{RT}{FI_{CT}}$$



F: faraday constant; R: gas constant; T: temperature; I_{CT} :exchange current density

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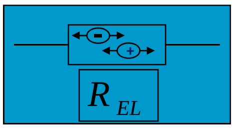
Equivalent circuit elements

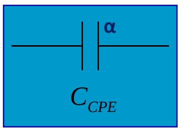
- Electrolyte Resistance
  - Depends on:
    - Ionic concentration, ion types
    - Temperature
    - Geometry of Current-Transport-Area
  - Conductivity κ:
    - Fitted by computer-models

$$R_{EL} = \frac{l}{\kappa \cdot A}$$

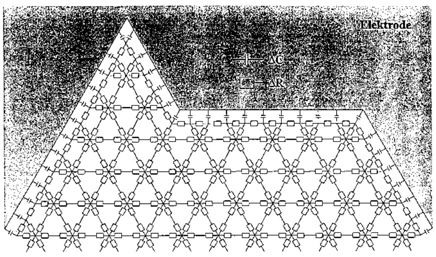


- Constant phase element
  - HDL is not an ideal capacitator
  - Current/Potential phase-shift
  - Empirical parameter α

$$Z = \frac{1}{(i\omega)^{\alpha} C}$$



Impedance of rough electrodes



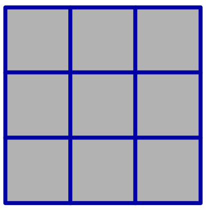
$$Y(\omega) = \frac{1}{Z(\omega)} = \sum_j \frac{i\omega C_j}{1 + i\omega R_j C_j}.$$

$$Y(r \cdot 1, \omega) = r^2 Y(1, \omega)$$

$$C_j(r \cdot 1) = r^{D_H} C_j(1)$$

$$R_j(r \cdot 1) = r^{-1} R_j(1)$$

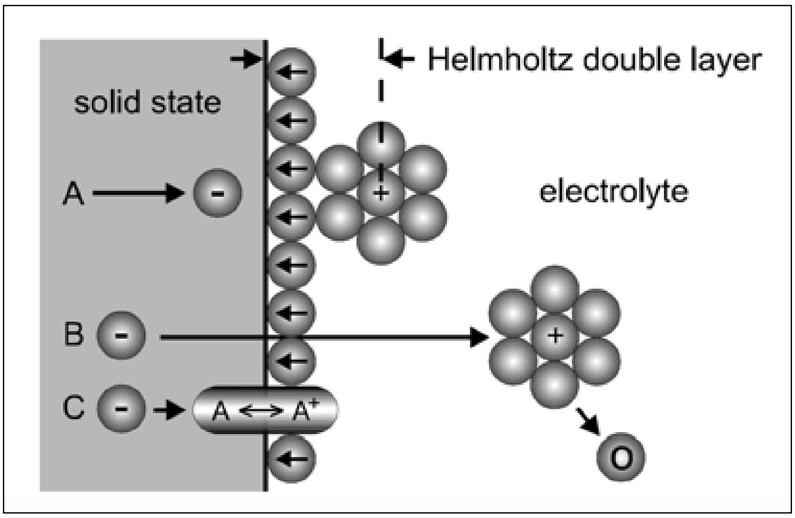
Hausdorff-Dimension $D_H = \dfrac{\log N(R)}{\log \frac{1}{R}}$



$$Y(\omega) = 1/Z(\omega) = Y_0 (i\omega)^{\alpha}$$

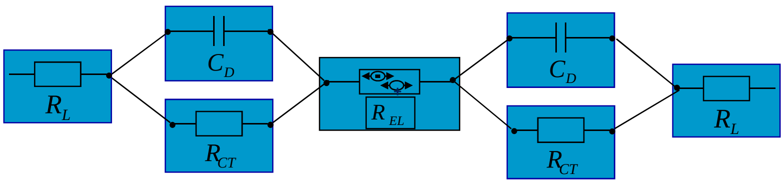
$$\alpha = \frac{1}{D_H - 1}$$

Helmholtz double layer

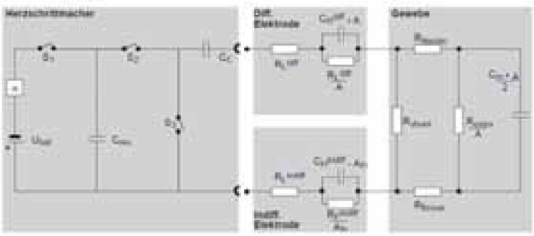


Circuit Model

- Basic Model

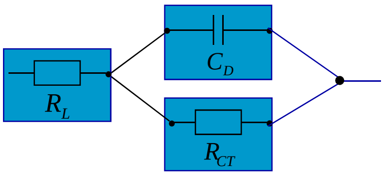


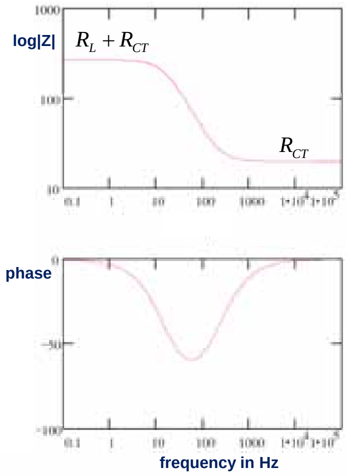
- Advanced Pacemaker Model



Impedance of Electrochemical-Cells

- Randles-Cell
  - Schematic



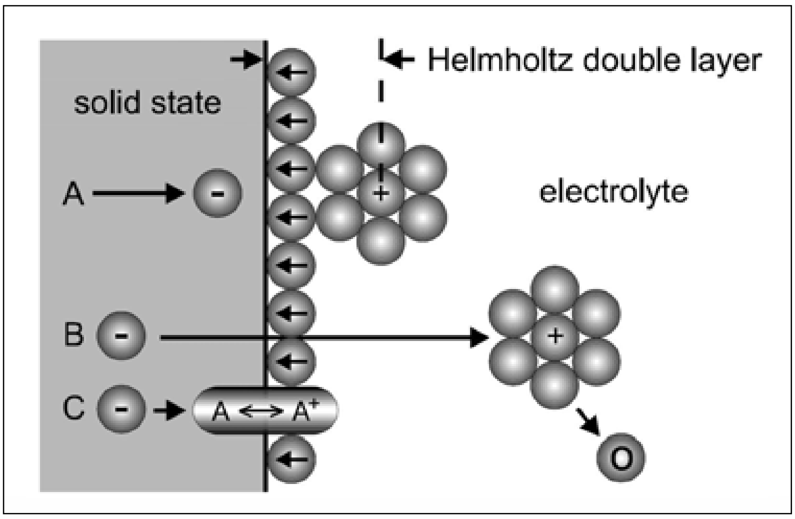


  - Overall Impedance

$$Z = R_L + \frac{R_{CT} \cdot \frac{1}{i\omega C_D}}{R_{CT} + \frac{1}{i\omega C_D}}$$

    - ω → 0: infinite charge-time
    - ω → ∞: short circuit

Electrochemical Impedance



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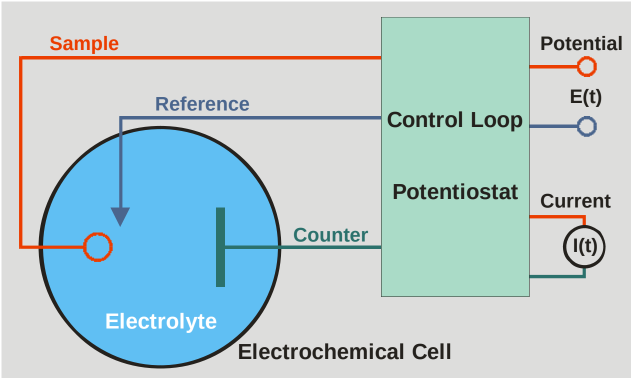
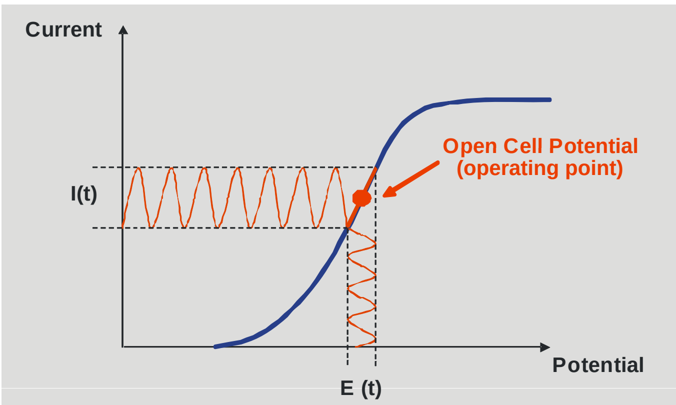
Experimental setup



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

Experimental setup

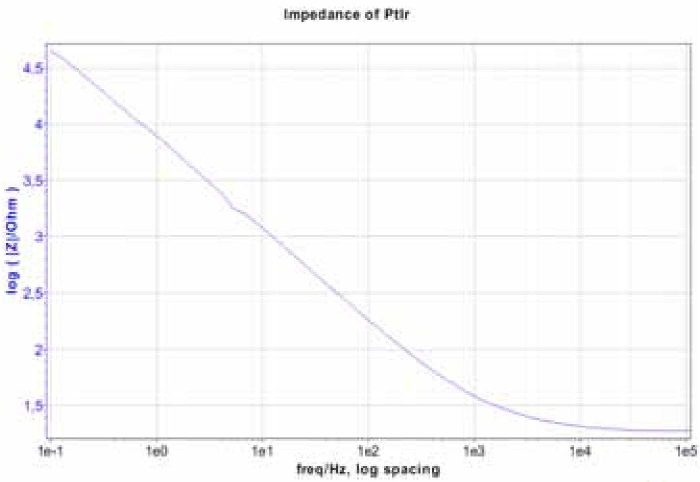


Small disturbance away form the open cell potential (point of equilibrium)

-> Linear system response

Impedance Measurement(1)

Electrode ring made of platinum-iridium



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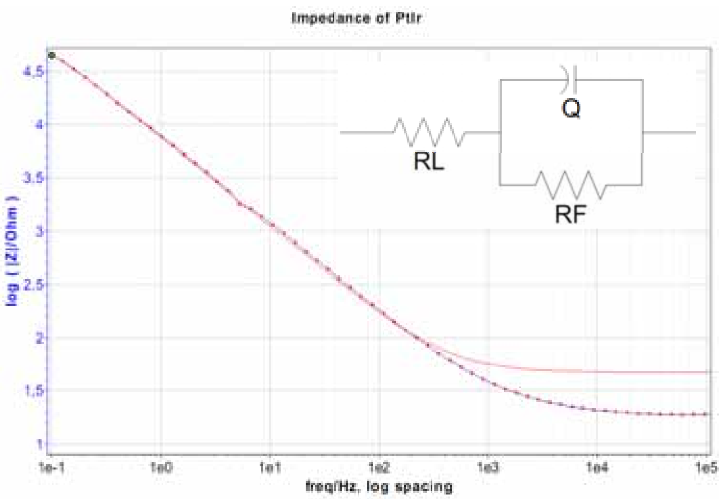
Impedance Measurement(2)



$$Z_Q = \frac{1}{(i\omega)^\alpha C}$$

Fit:

R_L = 47 Ohm

R_F = 0.1 MOhm

C_q = 27e-6 F

a = 0.85

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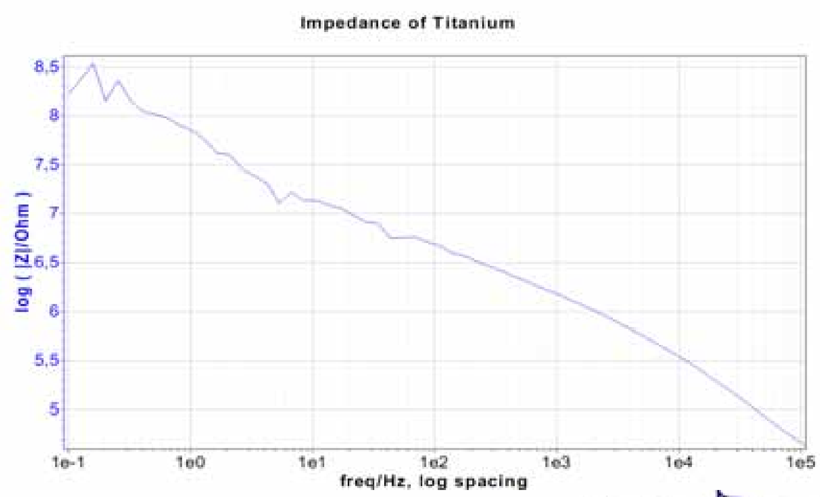
Impedance Measurement (3)

Electrode tip made of Titanium



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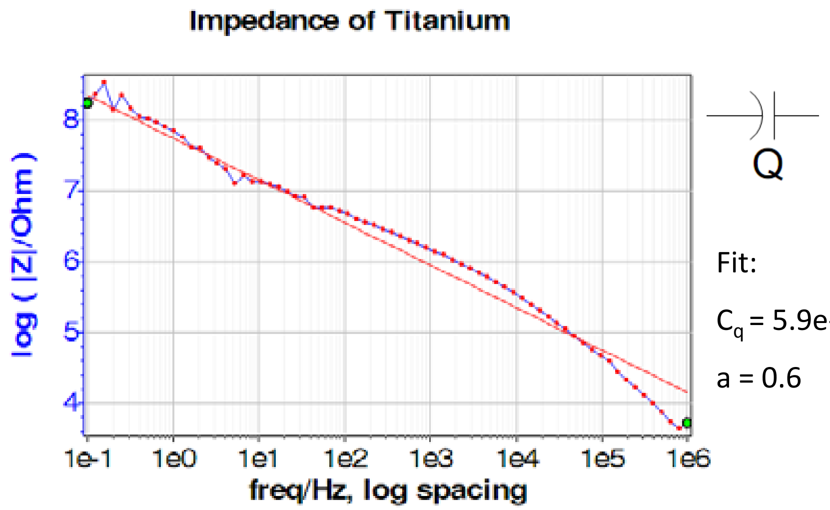
Impedance Measurement(4)



Fit:

C_q = 5.9e-9 F

a = 0.6

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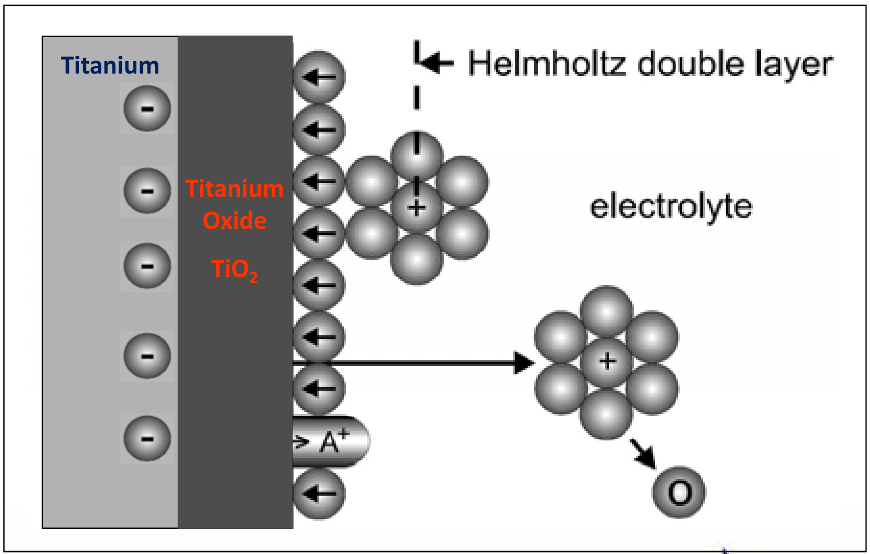
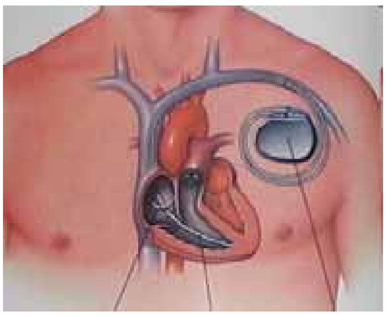
Titanium



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

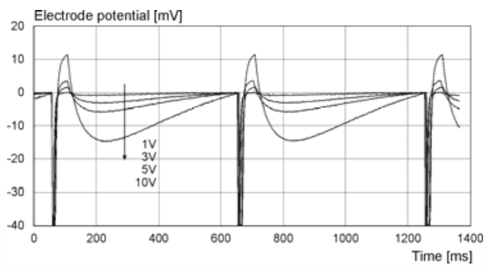


Challenges in cardiac pacing (2)

- 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 $U = Q_{st} / (A\ C_p)$
    → 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

- Small electrodes

→ Sets limits to the capacitance of the Helmholtz double layer

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

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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

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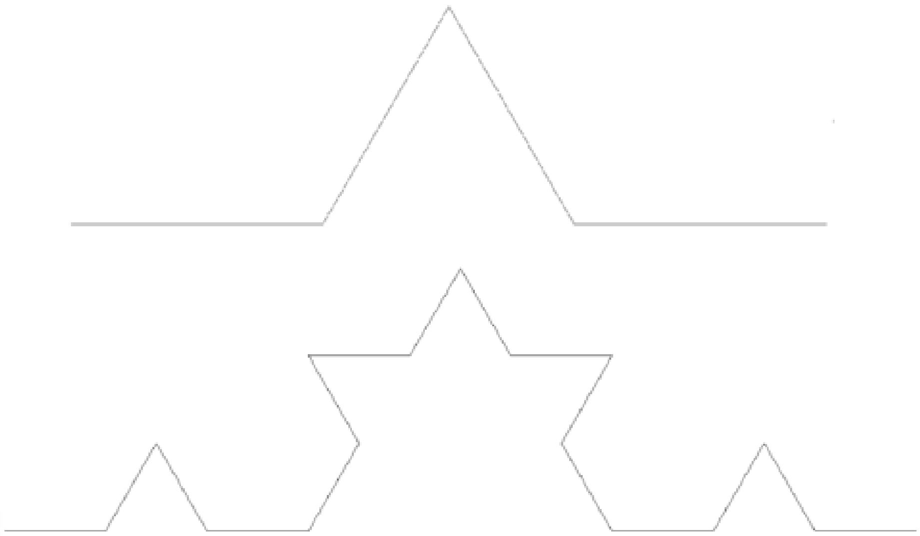
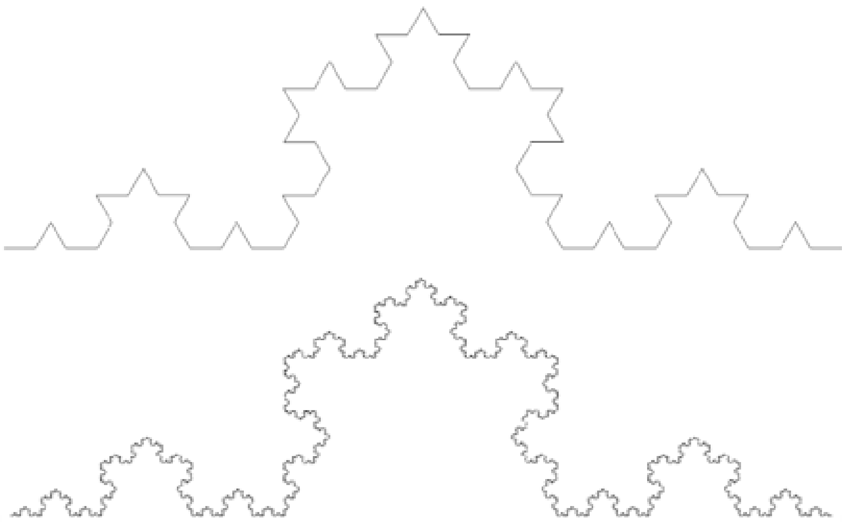
Fractal → Koch-curve (1)



Fractal → Koch-curve (2)



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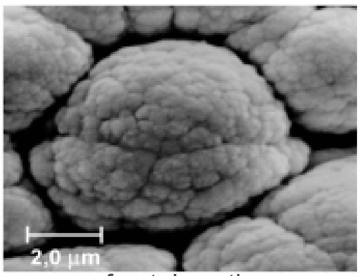
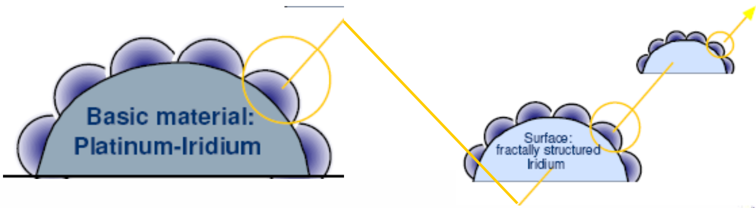
Fractal coating (2)

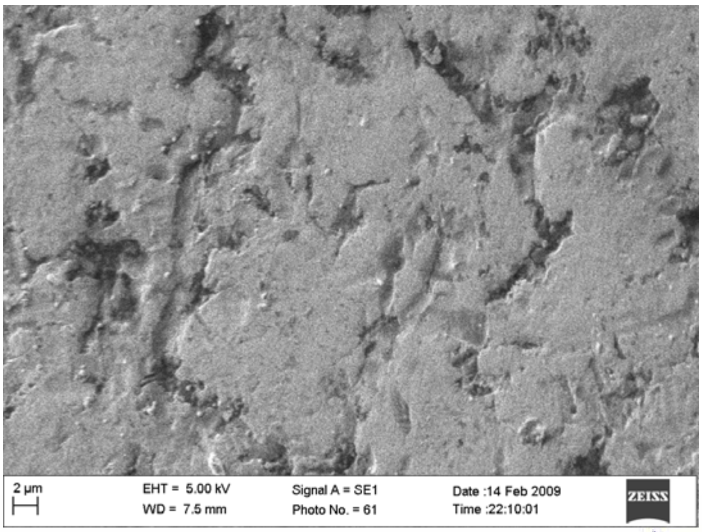
fractal surface in nature (romanesco)



fractal coating



SEM of Pt-Ir (1)



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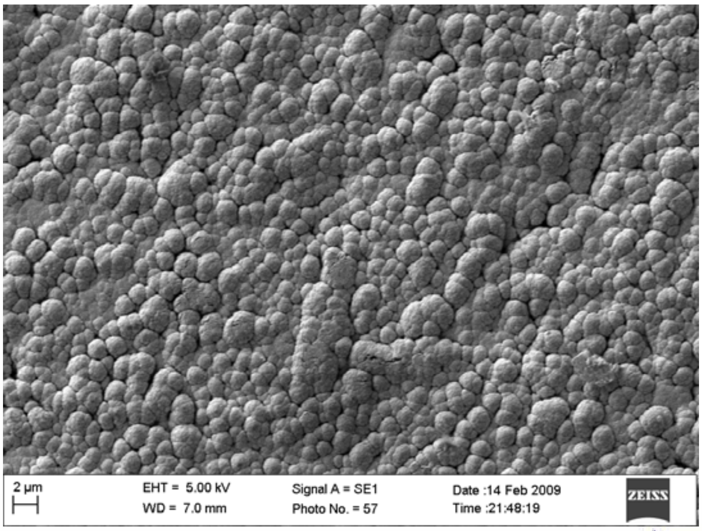
SEM of Ir-fractal (1)



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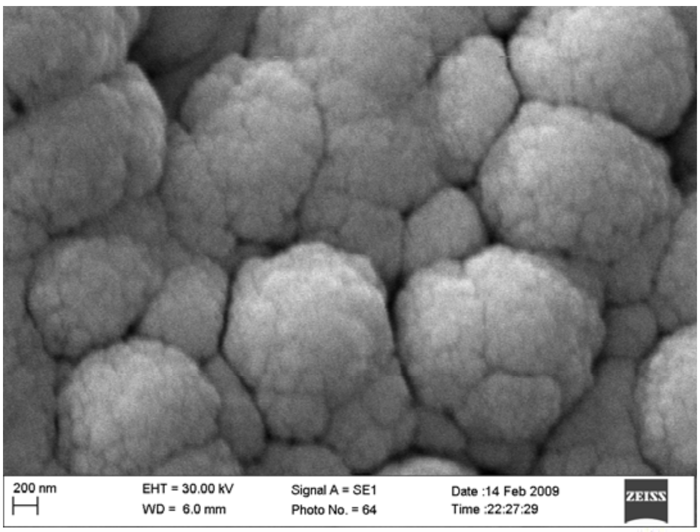
SEM of Ir-fractal (2)



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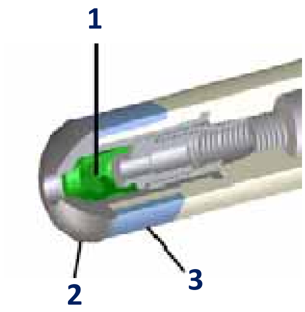
Modern Pacemaker Electrode

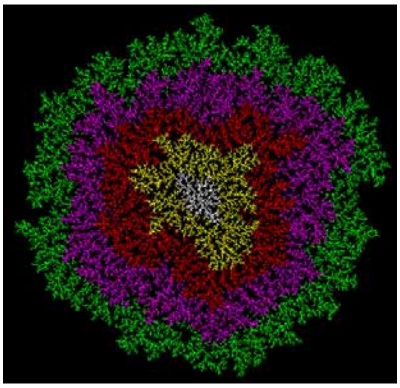
Fractal coated electrode:
1 → sealing
2 → fractal coating
3 → steroid



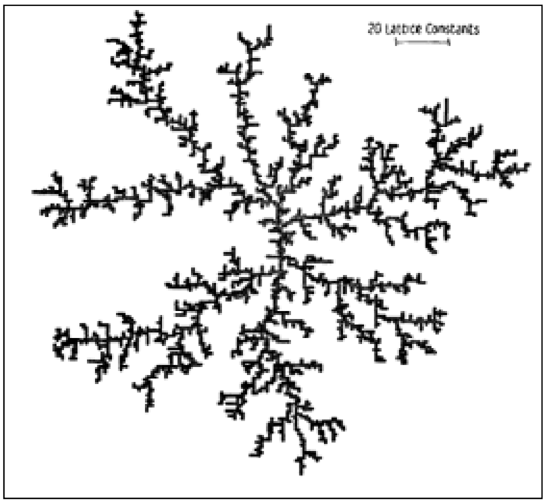
Advantages:
- 1000 time enlargement of the electrical active surface compared to the normal geometric size
- Reduction of depolarization effects
- Increasing long time stability

Diffusion limited aggregation

Random Walks (Brownian motion etc.)
→ space/time discrete processes
→ continuous formulation

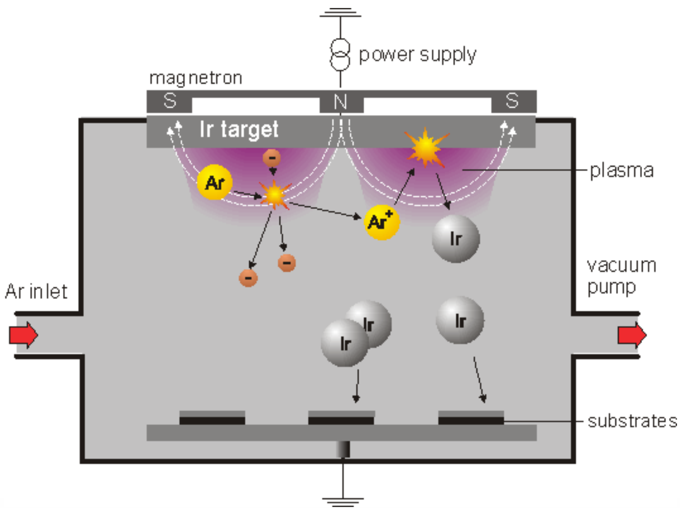


DLA – random aggregation of particles



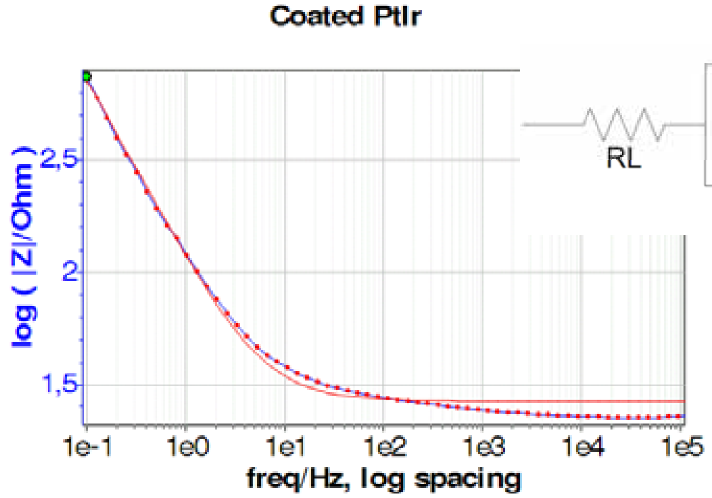
Physical Review Letters; Vol. **47**, Nr.**19**; 1981

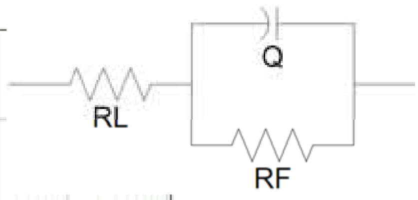
Diffusion limited aggregation – PVD



Progress in Biomedical Research; M. SCHALDACH; 1997

Impedance measurement of Ir-fractal(1)





Fit:

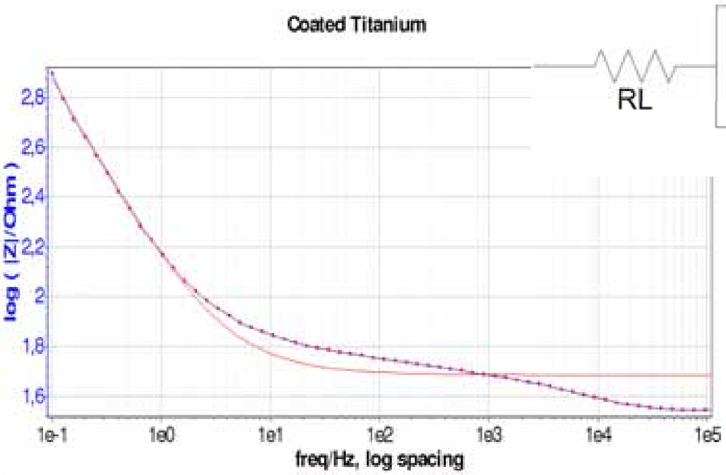
R_L = 26 Ohm

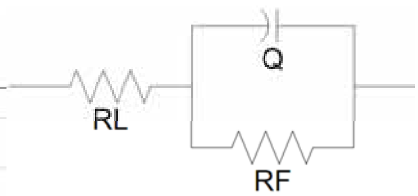
R_F = 5 kOhm

C_q = 2e-3 F

a = 0.83

Impedance measurement of Ir-fractal(2)





Fit:

R_L = 48 Ohm

R_F = 32 kOhm

C_q = 2e-3 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

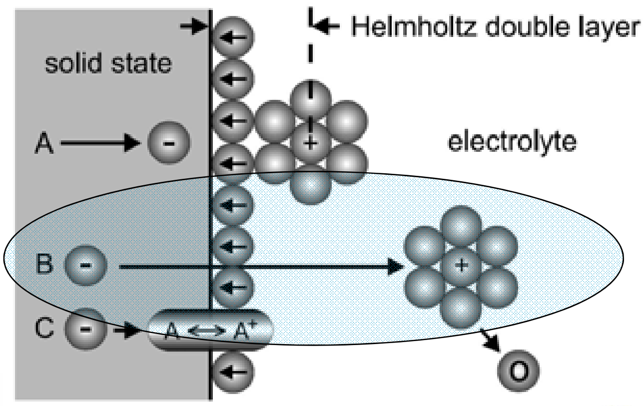
Increasing effective electrode surface without increasing the geometric dimensions

Electro-active surface

Electrochemical enhancement of specific capacity

Electro-active surfaces

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



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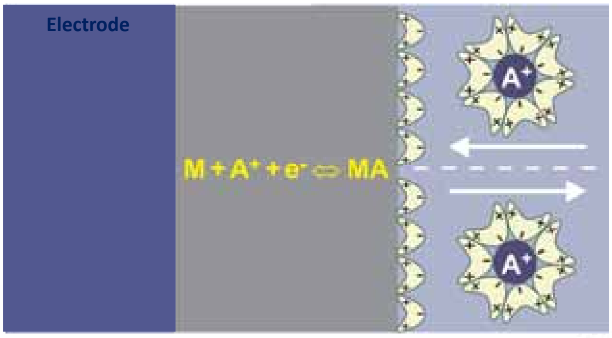
Electro-active surfaces

- Reversible redox reaction

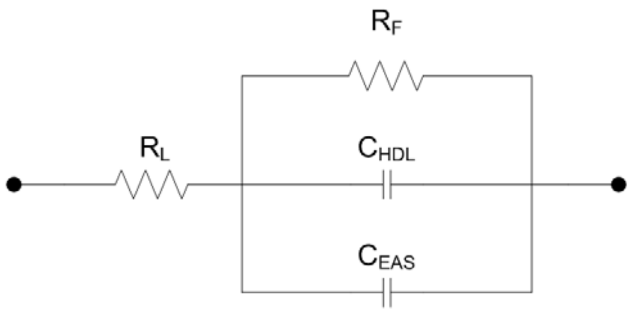
$$e^- + H_2O + Me^{4+}O_2 \leftrightarrow Me^{3+}OOH + OH^-$$

- Acts as charge/energy storage
  → Impedance characteristics like a capacitor

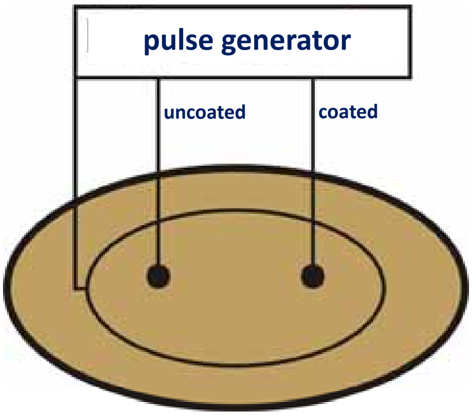


Electro-active surfaces

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



Stimulating Experiment



Petri dish with

-100 mM Fe(II)SO_4

- 100 mM KSCN (potassium thiocyanate)

Anodic pulses via coated/uncoated electrodes

- 10V, 1ms, 100bpm

Fe^{3+} and thiocyanate ($N \equiv C\text{-}S^-$) form a deeply red complex

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

$$Fe^{3+} + SCN^- + 5H_2O \rightarrow Fe(SCN)(H_2O)_5^{2+}$$

Stimulating Experiment