

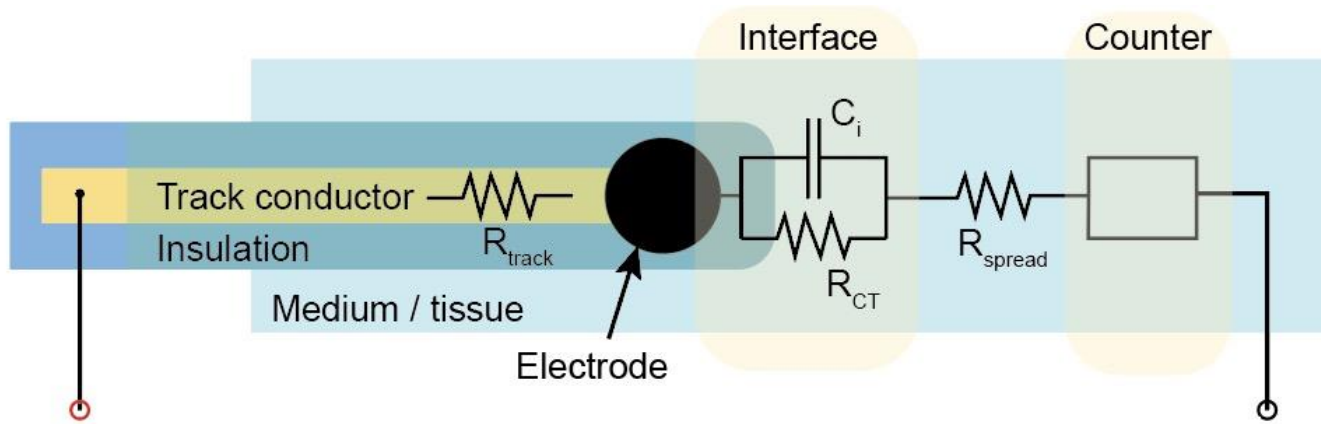
# Neural Interfaces

NX-422  
Electrochemical  
Characterisation

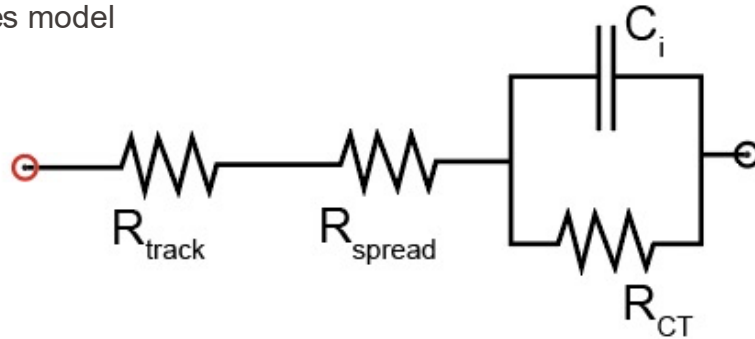
# Outline for the next 2 classes

- The nervous system
- Neural signals
- Neural electrodes
- **Electrochemistry of bioelectrodes**

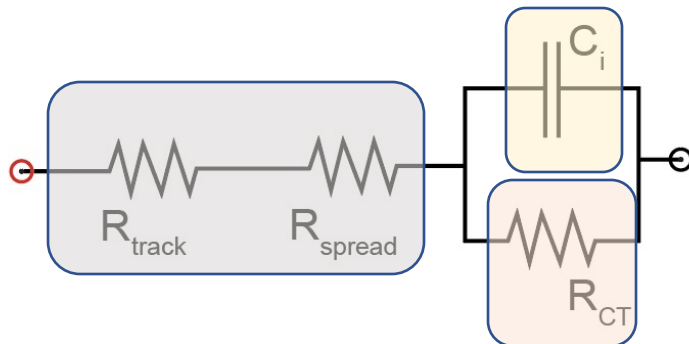
# Equivalent electrical model of an electrode



Randles model



# Equivalent electrical model of an electrode



$R_s$ : sheet resistance

$L, W$ : track length, width

$\rho$ : medium resistivity (0.6 – 3 Ohm m)

$r$ : electrode radius (10  $\mu\text{m}$  – 1 cm)

$t_{dl}$ : double layer thickness ( $\sim$  nm)

## Series resistance

- $R_{\text{track}} = R_s L / W$
- $R_{\text{spread}} = \frac{\rho_{\text{medium}}}{4r} \rightarrow$  depends on medium and electrode size

## Capacitive charge injection

$$|Z_i| \propto \frac{1}{2\pi f \cdot ESA}$$

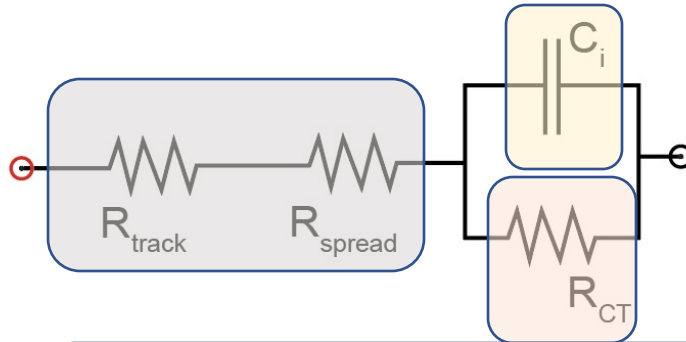
ESA: electrochemical surface area  
 $\rightarrow$  depends on process, coating roughness, electrode size

## Faradaic charge injection

$$R_{CT}$$

$\rightarrow$  depends on coating materials and electrode size  
 $\rightarrow$  the material affects the voltage onset of electrochemical reactions

# Equivalent electrical model of an electrode



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## Series resistance

- $R_{\text{track}} = R_s L / W$
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## Capacitive charge injection

- $C_i$  interface capacitance:  $C_H$  (double layer) //  $C_{GC}$
- $1/C_i = t_{dl} (\epsilon_0 \epsilon_r)^{-1} + \lambda_D (\epsilon_0 \epsilon_r)^{-1} (\cosh(z E_p / 2 V_t))^{-1}$ ;

Helmoltz (Parallel plate)

Gouy-Chapman  
V-dependent

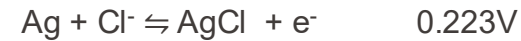
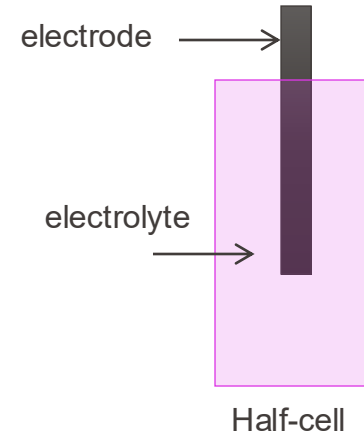
- $C_{dl} \rightarrow$  Constant Phase Element:  $Z_{CPE} = (j\omega C_i)^{-n}$ ;

## Faradaic charge injection

- $R_{ct}$  charge transfer resistance
  - From the Butler-Volmer equation (low overpotential approximation  $\rightarrow$  Ohm's law)
  - $R_{ct} = RT (z F J_0)^{-1}$
  - $J_0$  = equilibrium exch. Current  $\rightarrow$  from literature or measurable

## Metals used in physiological systems

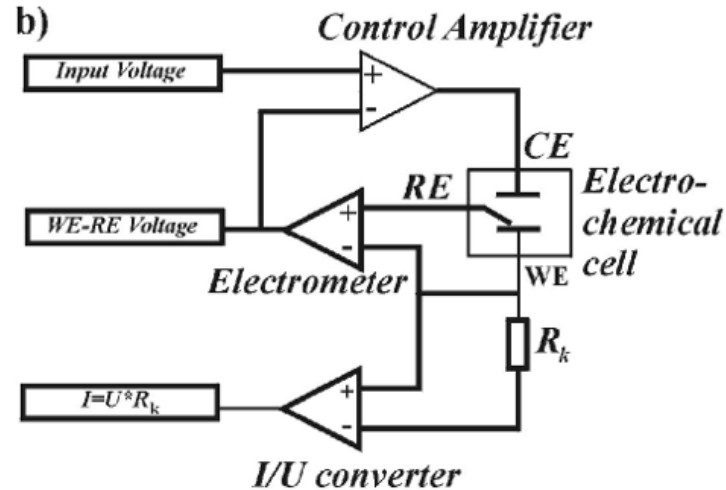
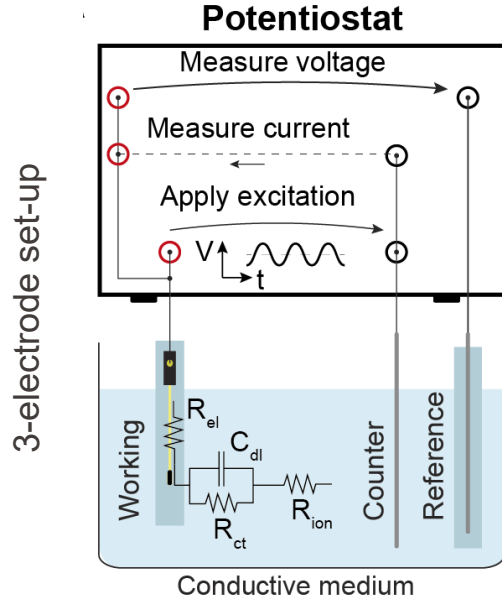
Metal / reaction	Potential $E_{hc}$ (V)
$Al \rightarrow Al^{3+} + 3e^{-}$	1.67
$2H^{+} + 2e^{-} \rightarrow H_2$	0 (reference)
$Ag \rightarrow Ag^{+} + e^{-}$	-0.799
$Pt \rightarrow Pt^{2+} + 2e^{-}$	-1.2
$Au \rightarrow Au^{3+} + 3e^{-}$	-1.42
$Au \rightarrow Au^{+} + e^{-}$	-1.68



With reference to hydrogen

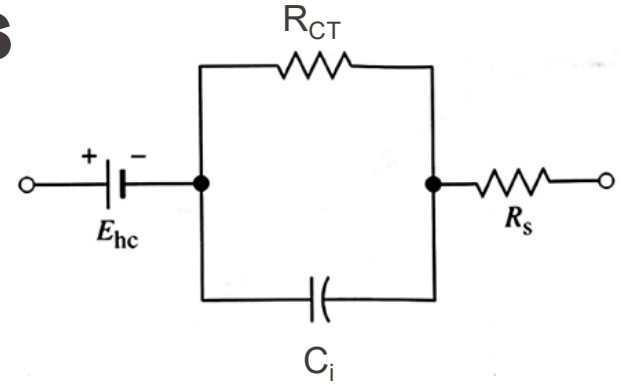
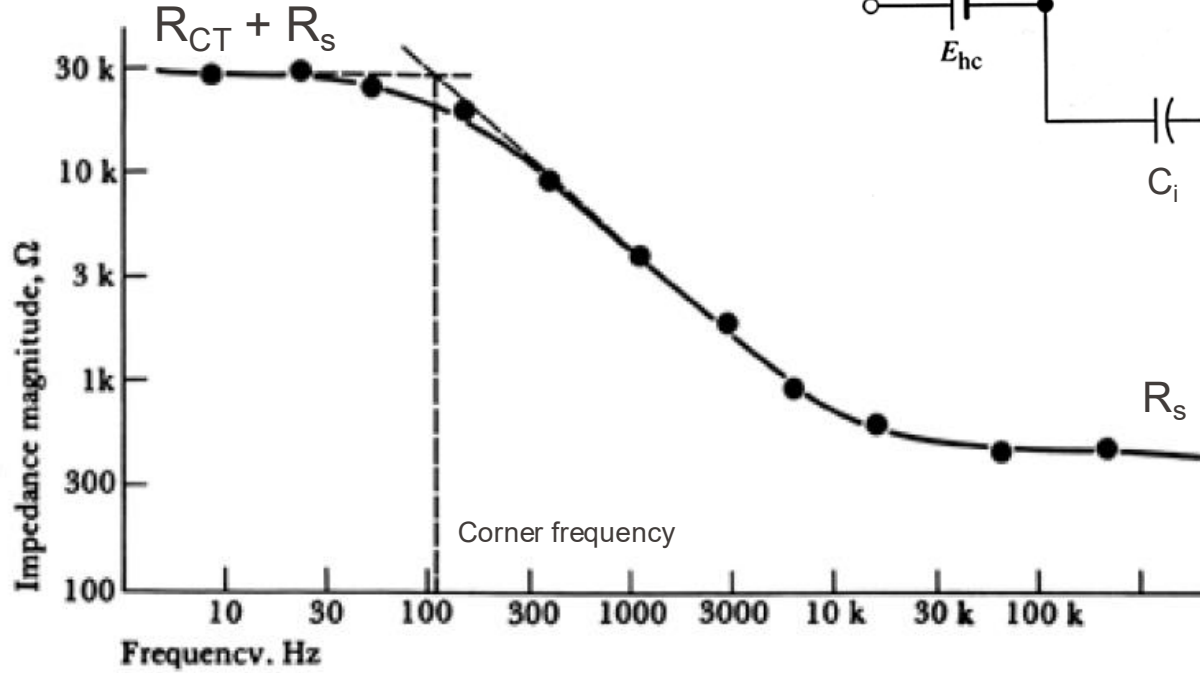
# Electrochemical impedance

- a measure of the reluctance of a component to current flow when subject to an AC stimulus

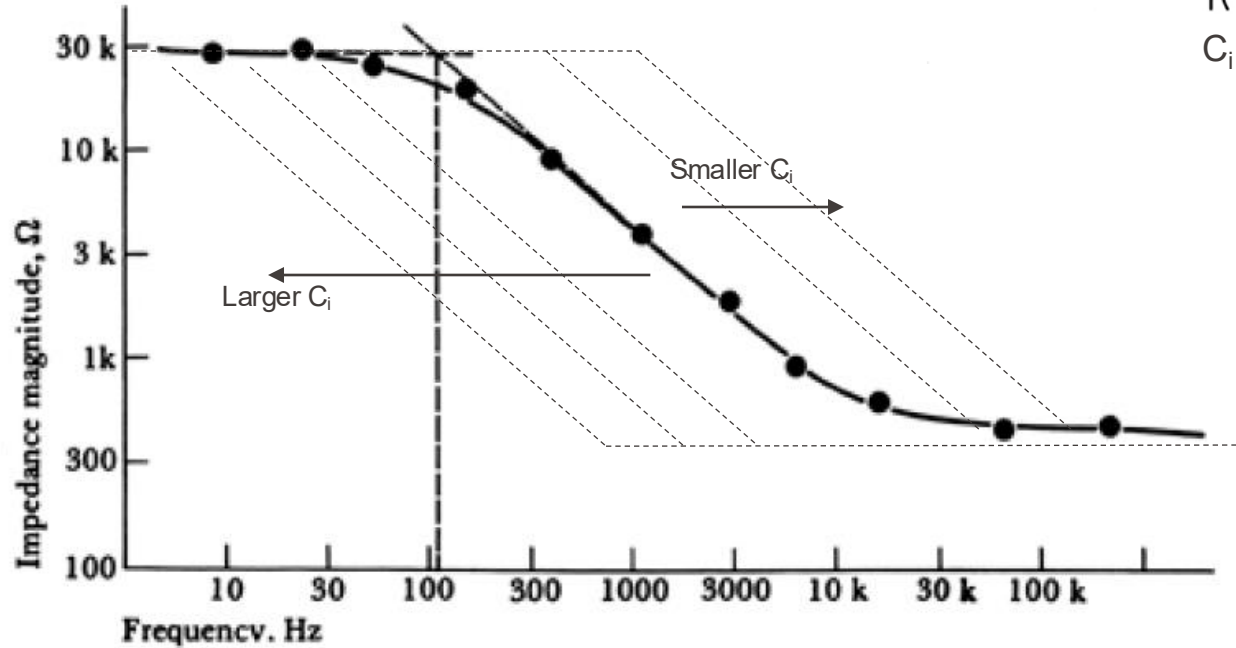
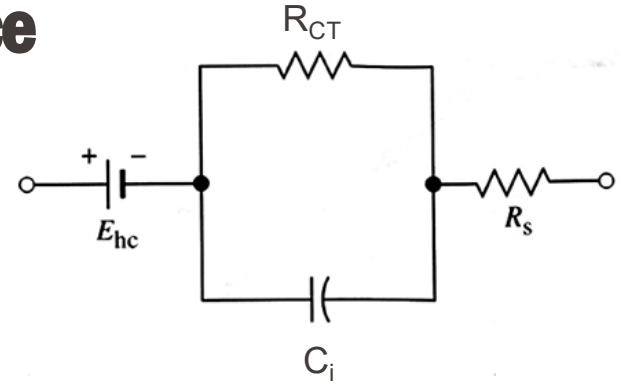


- AC domain → complex number notation
  - Any given sinusoidal stimulus can be expressed as
    - $V(t) = V_{max} e^{i\omega t}$  with  $\text{Re}(V)$  in phase with  $\text{Im}(V)$  at quadrature
  
- Resistor R:  $V = RI$ ,  $|Z| = \frac{V}{I} = R$  at any frequency
  
- Capacitor C:  $Q = CV$ ,  $|Z| = \frac{V}{I} = \frac{1}{\omega C}$ ,  $Z_{phase} = -90^\circ$  at any frequency
  - Capacitor impedance modulus has a  $f^{-1}$  and  $\text{Area}^{-1}$  dependency

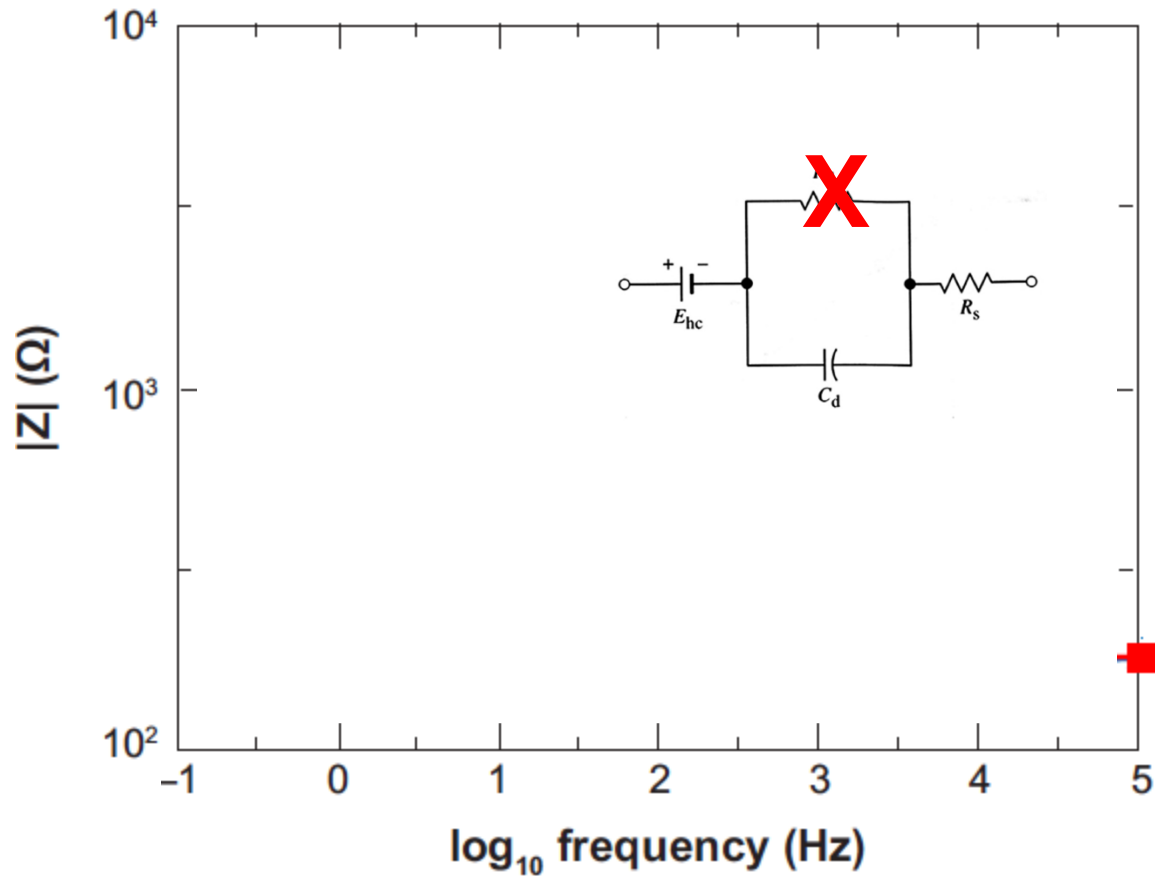
Bode plot



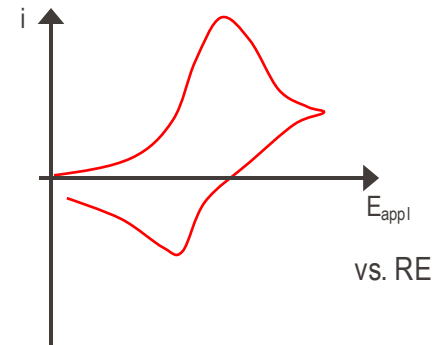
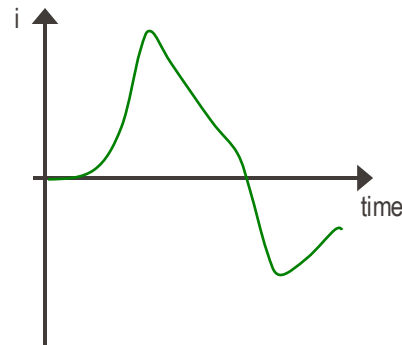
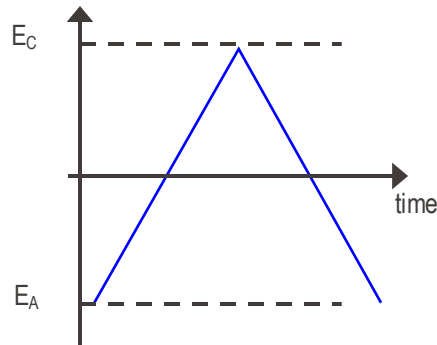
# How does the interface capacitance affect the impedance?



# Electrode impedance in the case of inert coatings

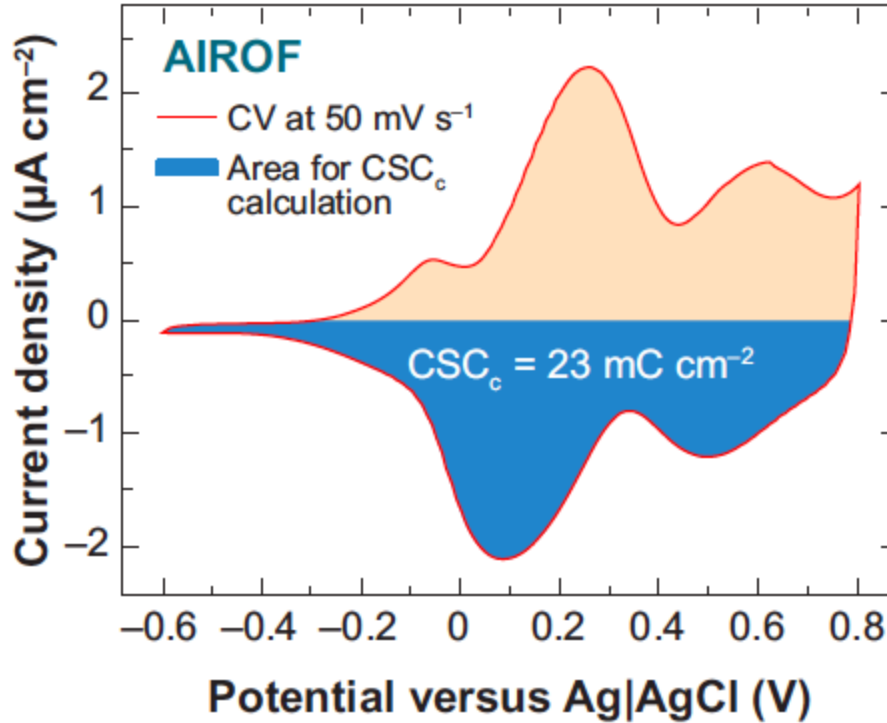


- « spectroscopy of the electrochemist »
- 3-electrode setup:
  - Sweep the potential of WE applied against CE and measured against RE
  - Measure the current at WE

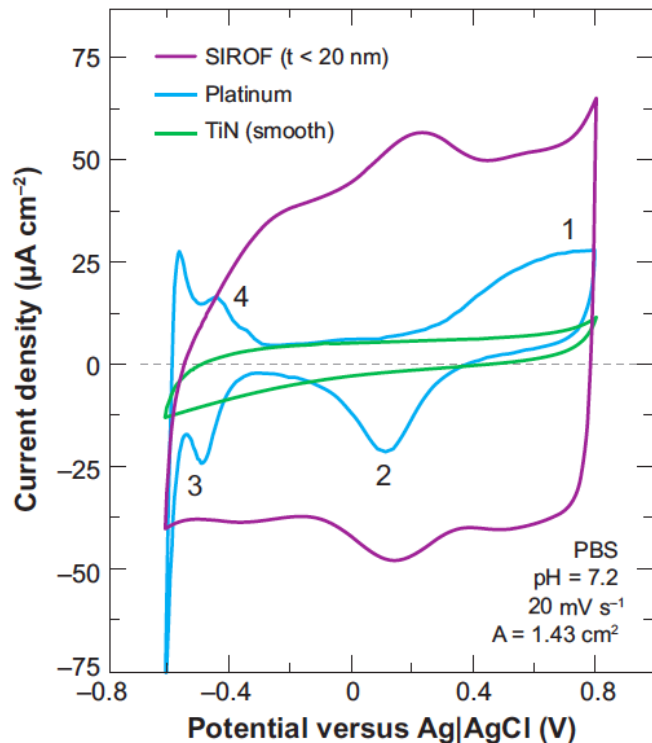


$E_A$  and  $E_C$  within the water window

# Cathodic storage capacity CSC



Slow voltage sweep  
10-1000mV/sec



Electrode material	CSC ( $\mu\text{C/cm}^2$ )
Gold	20
Stainless steel	50
Platinum	75
Titanium nitride	250
Iridium oxide	Up to 3,000

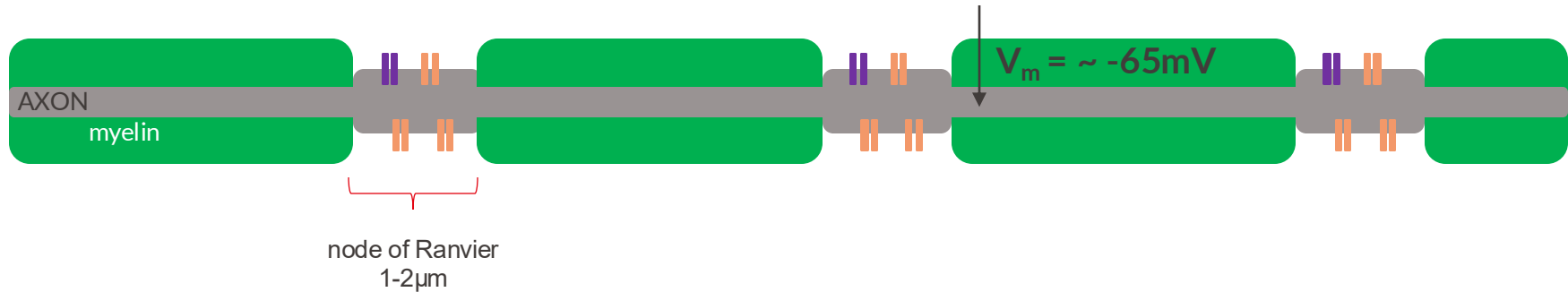
1,2 Pt oxidation and reduction  
 3,4 H plating and stripping from Pt

- EIS as a tool to understand the mechanisms of charge transduction
- The Bode plot of the impedance modulus
- Components of the impedance spectra and parameters affecting them
  
- Cyclic voltammetry: useful especially for electrochemical reactions (peaks distributed across voltage spectrum)
- CSC: a benchmarking metric

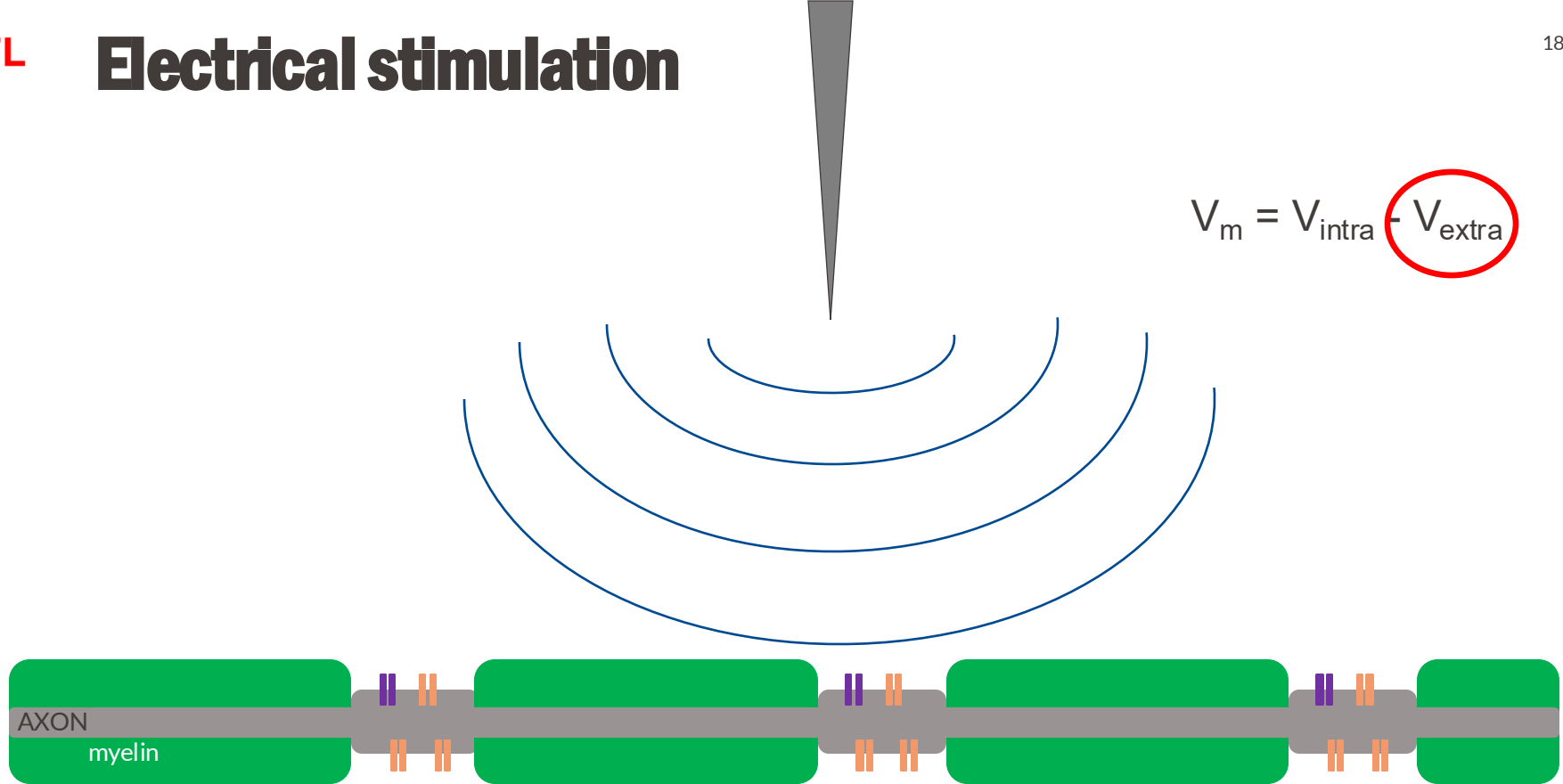
# Neural stimulation neuromodulation

- Current flowing between 2 electrodes will  
**stimulate** the tissue at the **cathode** (negative electrode)  
**resist** excitation at the **anode** (positive electrode)
- Cathodic stimulation: depolarization of the cell membrane  
i.e. generation of an action potential

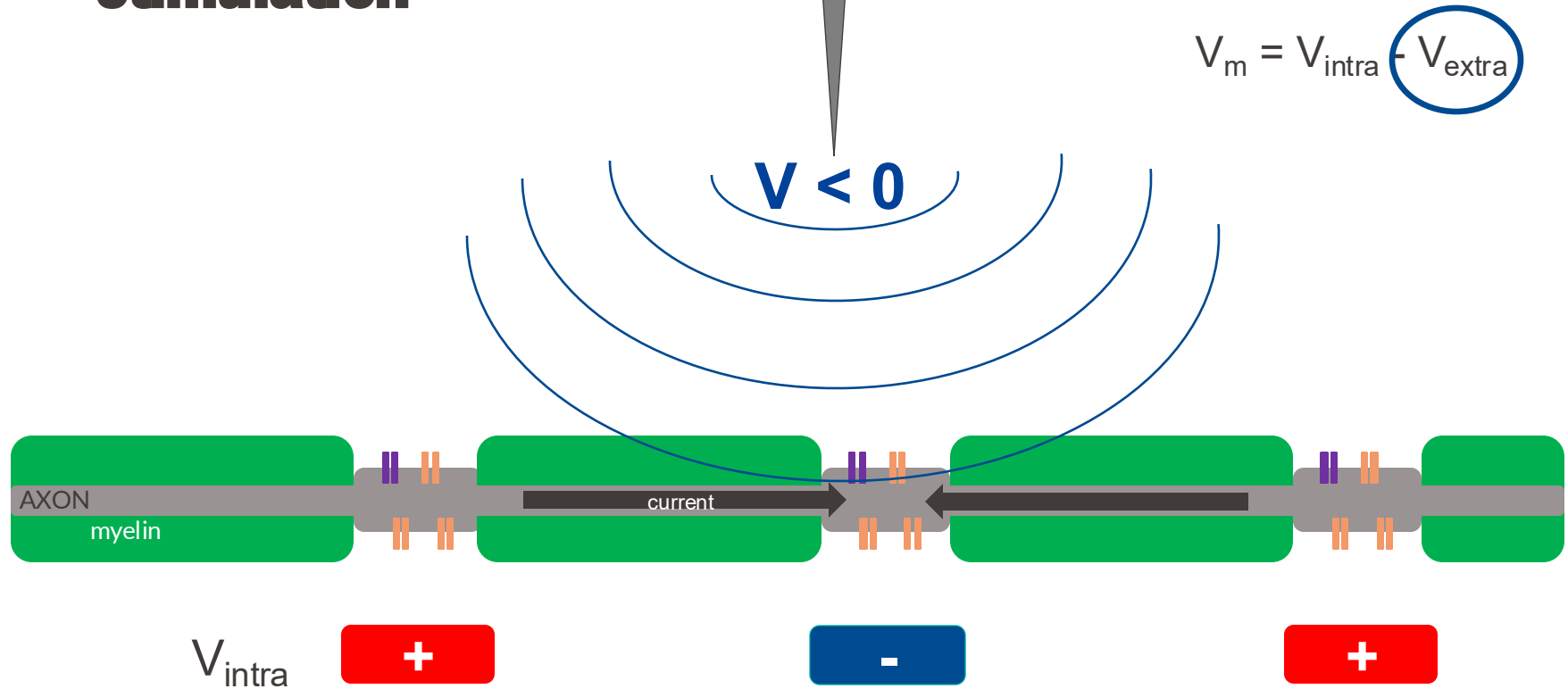
$$V_m = V_{\text{intra}} - V_{\text{extra}}$$



$$V_m = V_{\text{intra}} - V_{\text{extra}}$$

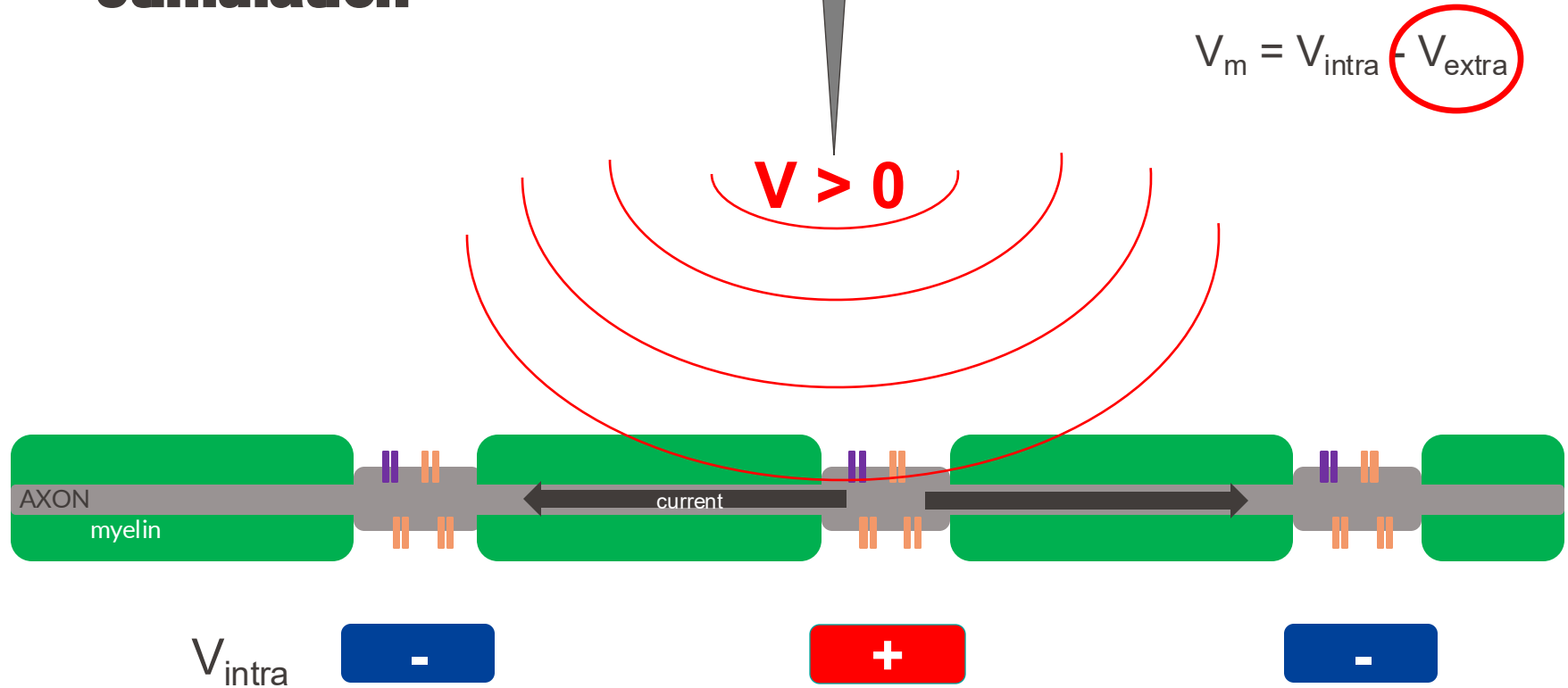


# Cathodic electrical stimulation



inward current enters the node → Membrane depolarisation → Triggered action potential

# Anodic electrical stimulation

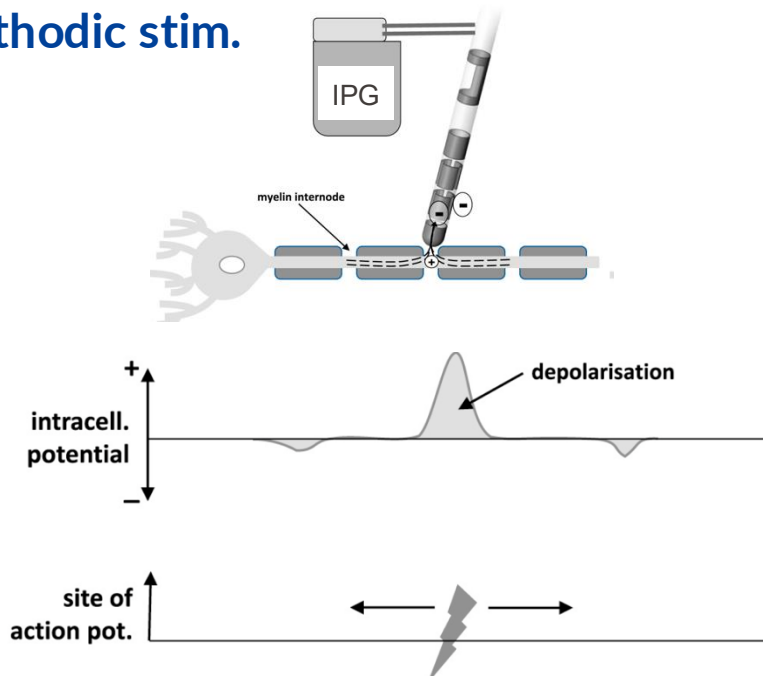


Inward currents enter neighboring nodes → Depolarised membrane in the lateral nodes

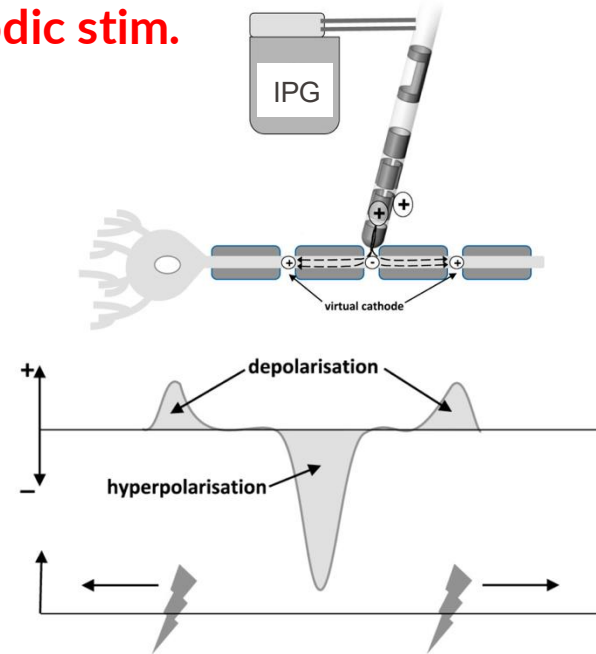
→ triggered action potential

# Cathodic vs anodic stimulation

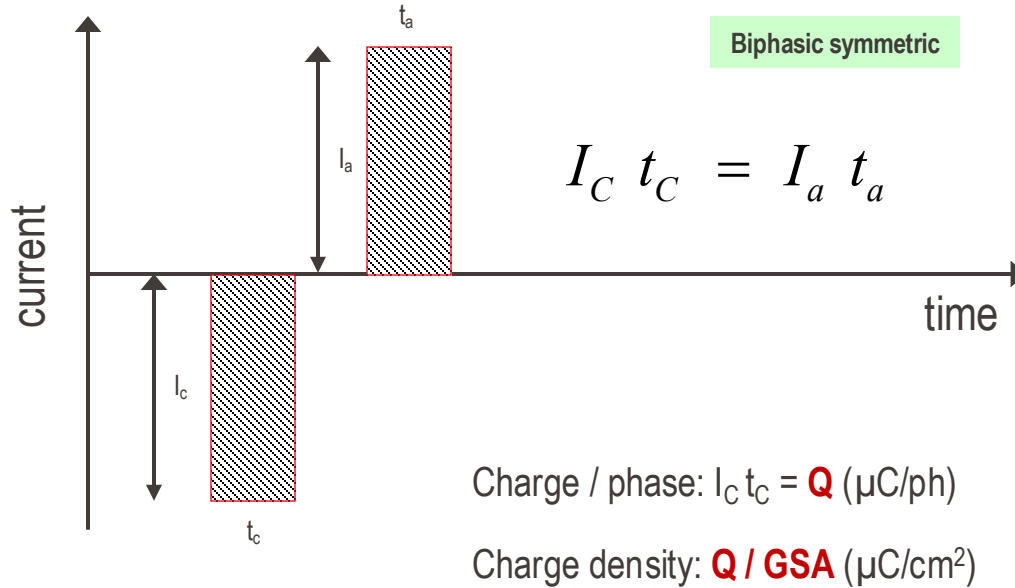
## Cathodic stim.



## Anodic stim.

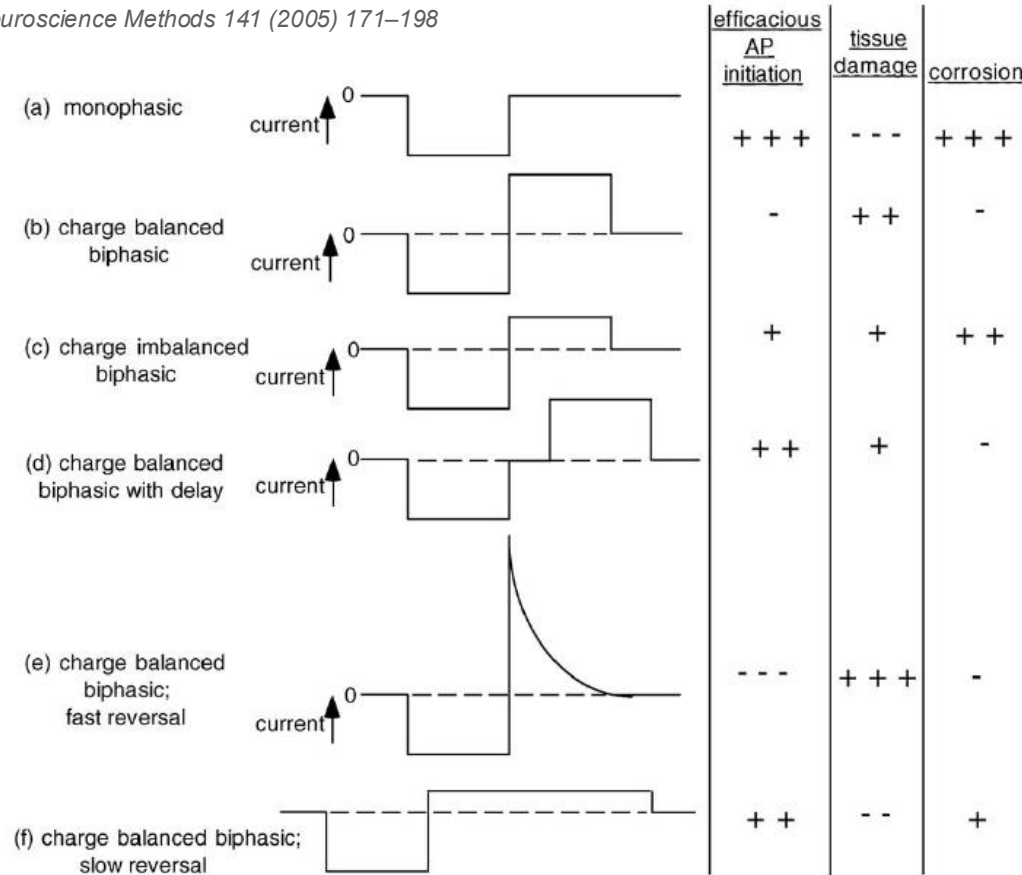


# Constant current pulses

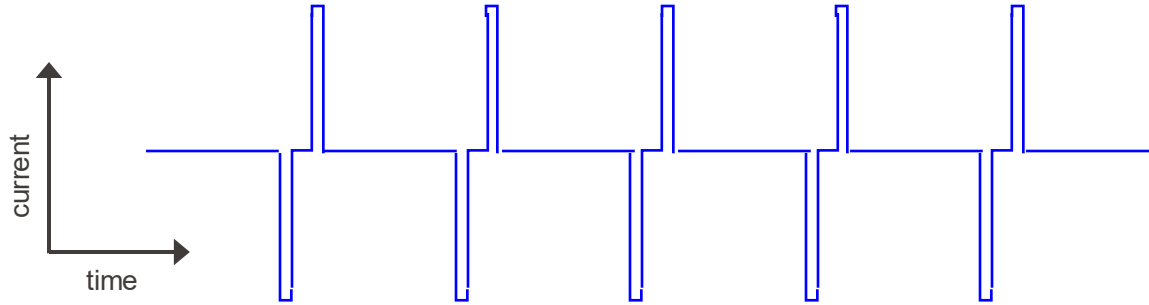


GSA: geometric surface area

*Journal of Neuroscience Methods 141 (2005) 171–198*



- Applying a train of current pulses to the target tissue



**Challenge:** produce reversible charge-injection chronically

Reversible = {  
no electrode damage (corrosion)  
no tissue damage

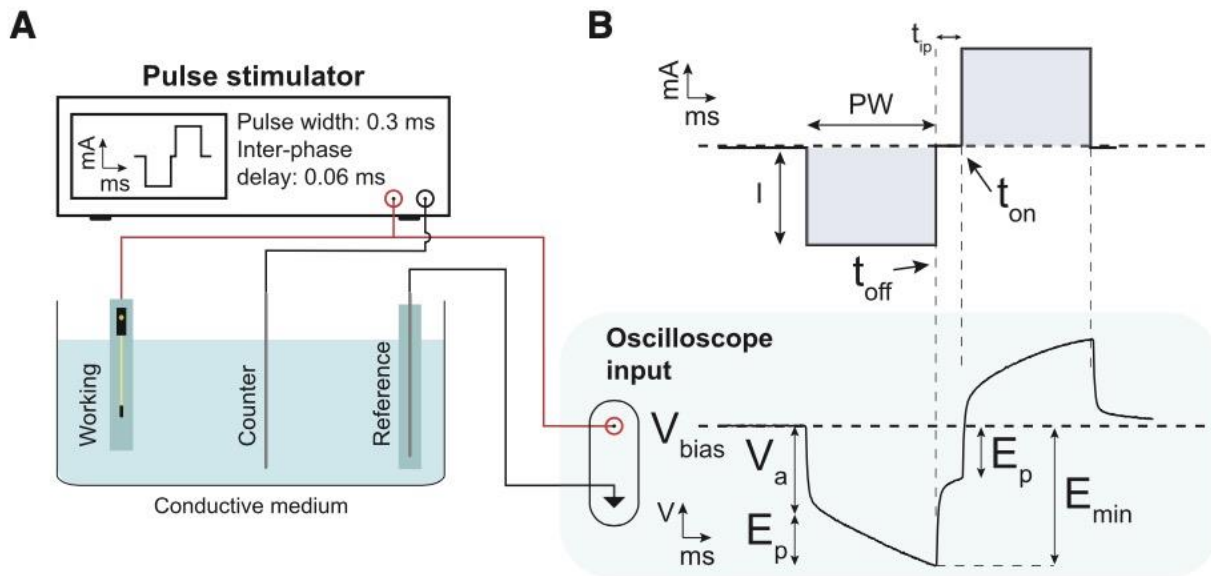
# Voltage transient measurements

- Estimate the maximum charge that can be injected in a current-controlled stimulation pulse
- 3-electrode setup (in vitro)
  - Determine maximum polarization (most negative and positive potentials)
  - Safe boundaries: water window and reduction potentials

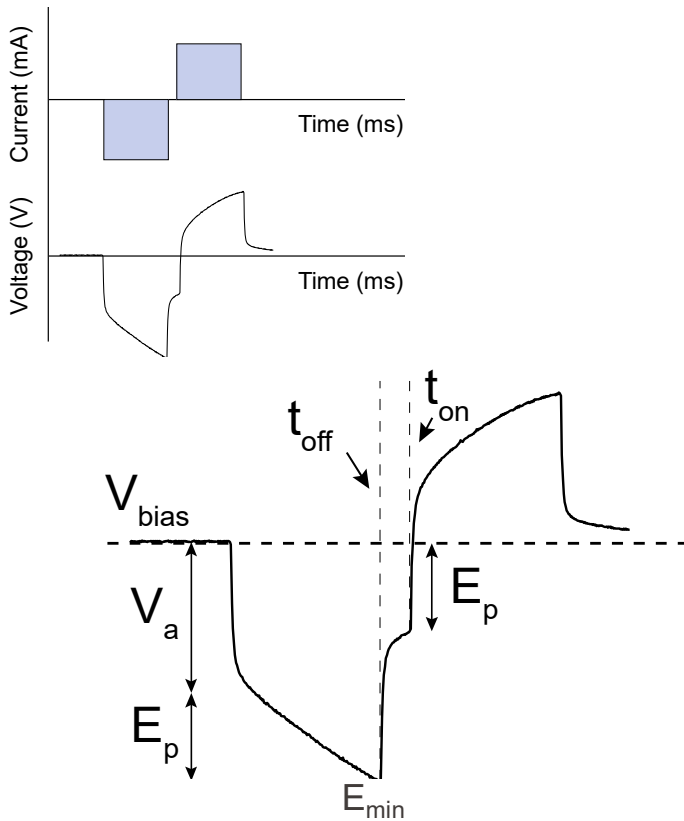
$$\Delta V = i_c R_i + \eta_c + \eta_a + \Delta E_0$$

$R_i$	electrolyte resistance
$\eta_c$	concentration overpotential
$\eta_a$	activation overpotential
$\Delta E_0$	shift in the equilibrium potential

# Voltage transient measurements



# Voltage transient in response to a biphasic current pulse



- $V_{\text{bias}}$ : equilibrium potential (half-cell potential)
- $V_a$ : Access voltage (ohmic drops)
  - IR drop in the interconnect
  - IR drop in the tissue/electrolyte
  - Concentration overpotential  $\eta_c$
- $E_p$ : Electrode polarisation at the interface
  - Activation overpotential  $\eta_a$
  - Potential equilibrium shift  $E_0$
- **$E_{\text{min}}$ : Minimum cathodic excursion =  $V_a + E_p$**

$$E_{\text{min}} = \underbrace{IR + \eta_c}_{V_a} + \underbrace{E_0 + \eta_a}_{E_p}$$

Away from the electrode                      At the interface

- If there is a current flowing from the electrode to the electrolyte, the potential is altered,  $E = E_{hc} + i_F R_F$

$$\text{Overpotential: } \eta = |E - E_{hc}|$$

- **Perfectly polarizable electrodes**



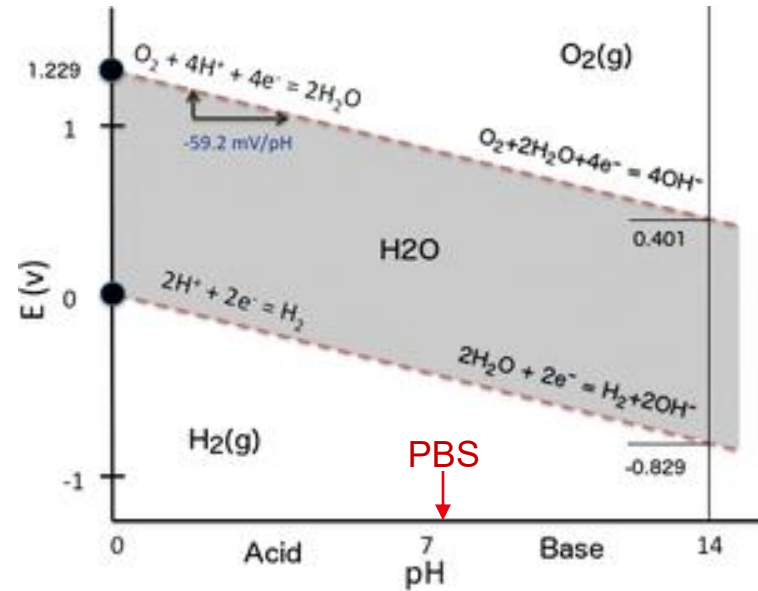
- No actual charge crosses the interface when a current is applied
- The current across the interface is a **displacement current**
- e.g. TiN

- **Perfectly non polarizable electrodes**



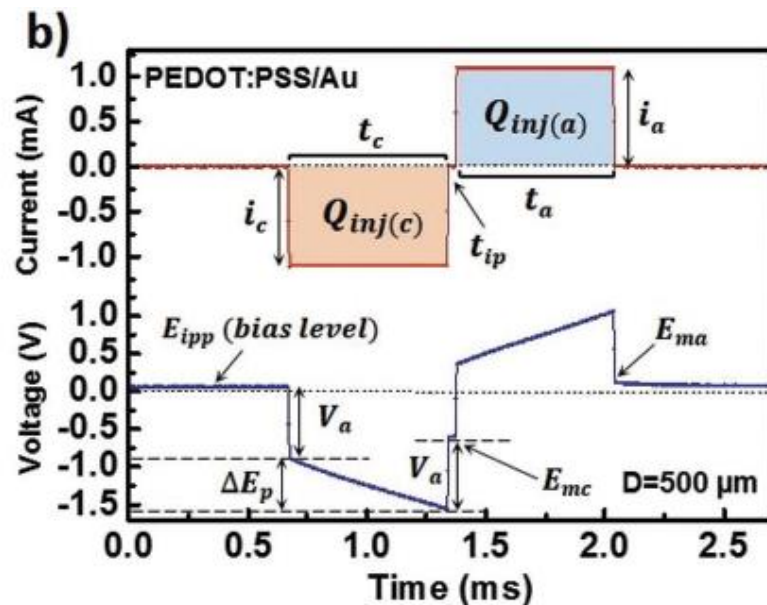
- Current passes freely across the interface, requiring energy to make the transition
- e.g. Ag/AgCl

- Electrochemical window within which the electrode material is neither oxidized nor reduced.
- The electrolyte, the solvent and the nature of the working electrode influence the potential window
- Water electrolysis requires 1.23V (potential across 2 inert electrodes)
  - -0.6V - +0.8V



# Charge Injection Capacity CIC

- $E_{mc}$ :
  - maximum cathodal electrochemical potential excursions calculated by subtracting  $V_a$  from the maximum negative voltage transients or the electrode potential immediately, (when  $V_a$  is zero)
- $E_{ma}$ :
  - maximum anodic electrochemical potential excursions
- Total charge:  $Q_{inj} = Q_{inj(c)} - Q_{inj(a)}$
- CIC:
  - total charge density at which either  $E_{mc}$  reaches water reduction potential (cathodal limit) and/or  $E_{ma}$  reaches water oxidation potential (anodal limit).



$$CIC = Q_{inj,c} / GSA$$

# EPFL Take home messages on VT – key information

- Max potential excursions: how much voltage we need to drive the current we want through the electrode interface
  - → Constraints on batteries / V supply
  - → Voltage- (energy-) efficient stimulation
- Cathodic and Anodic interface polarisation
  - → Range for electrochemically safe stimulation → CIC
- All these metrics vary with the waveform design.
  - For a given Q, Longer PW reduces excursions

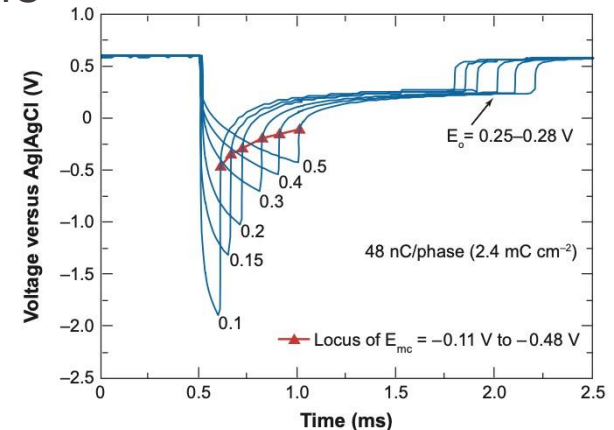


Figure 14

Comparison of voltage transients of an AIROF microelectrode pulsed at  $48 \text{ nC phase}^{-1}$  at pulsewidths from 0.1–0.5 ms.

# Note: CIC and CSC are very different metrics

Same units (charge density), but:

- Different regimes (slow/fast sweeps in CV vs. onset/plateau in stim)
- Both must be accompanied by the measurement parameters (CV speed and limits, stim waveforms)
- Choice of metric depends on relevance to the application, and against which other electrode you are benchmarking

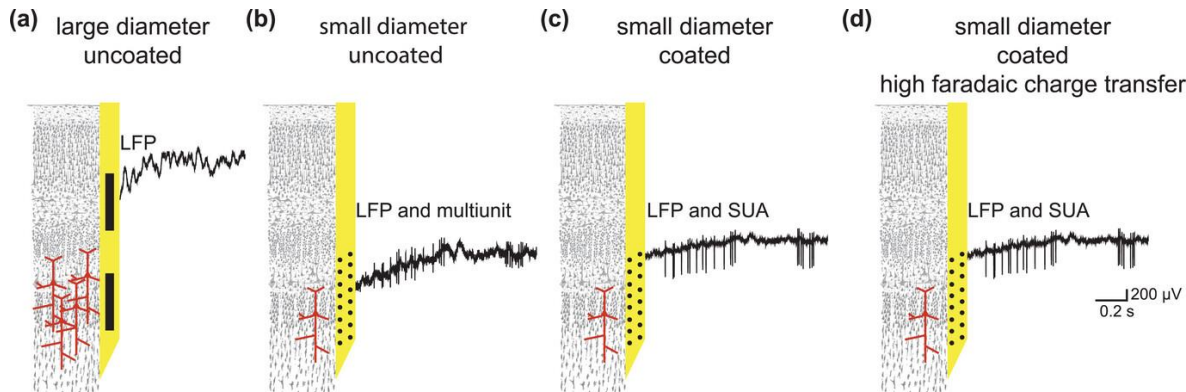
- **Extracellular signals** have an amplitude in the 10 $\mu$ V to 1mV
  - Very low-level input signals
- System noise = electrode noise + preamp noise
- Thermal noise (electrode)

$$U_N = \sqrt{4 k T R \Delta f} \text{ (in volts)}$$

Important for  
recording electrodes

- Electrochemical/biological noise or 1/f noise
- Low impedance prevents shunting through parasitics

# Recording Quality Is Related to Impedance



(e)

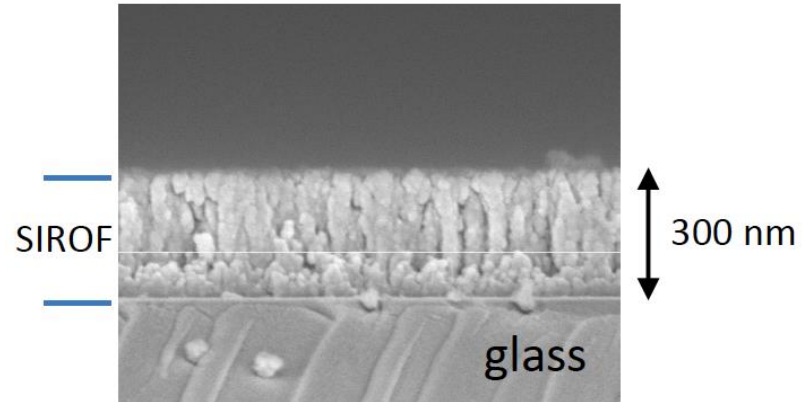
electrode	profile	coating	effective surface area	impedance	double layer capacitance	other capacitance	spatial resolution	low freq SNR	high freq SNR	yield	Recording quality
○		none	↑	↑	↓	↓	↓	↑	↓	↓	Better Worse
○		none	↓	↓	↓	↓	↑	↓	↓	↓	
●	⋮	metallic	↑	↑	↑	↓	↑	↑	↑	↑	
●	⋮	polymer/SiROF	↑	↑	↑	↑	↑	↑	↑	↑	

- « pseudo-capacitive » interface (surface redox process)
- Modest charge-injection capacity:  $< 100\mu\text{C} / \text{cm}^2$
- « the » clinical electrode material

# Materials - Iridium oxide

- Most charge injection is by redox processes
- Fabrication
  - Electrodeposition
  - Sputtering
  - Thermal deposition

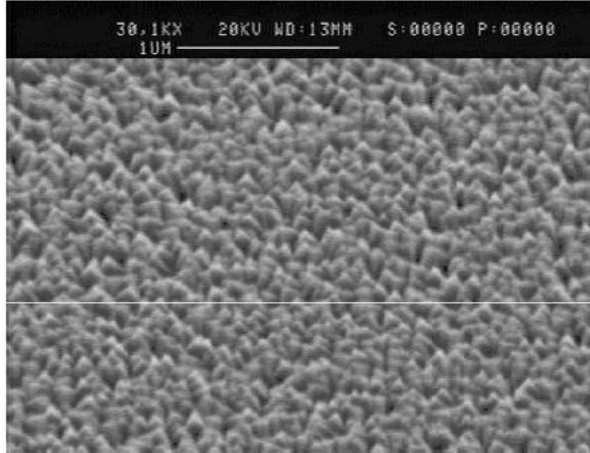
→ Requires activation



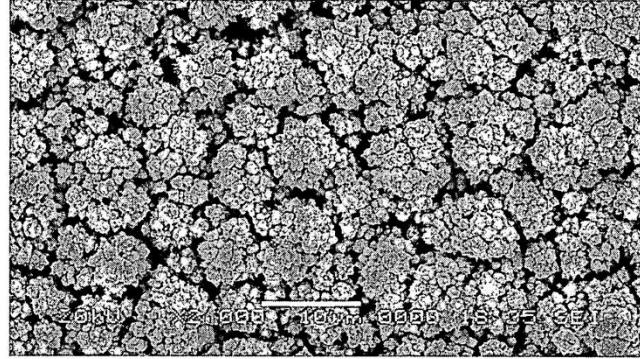
- Charge injection: 1-8mC/cm<sup>2</sup>

# Porous - Rough structures

TiN



Platinum grey

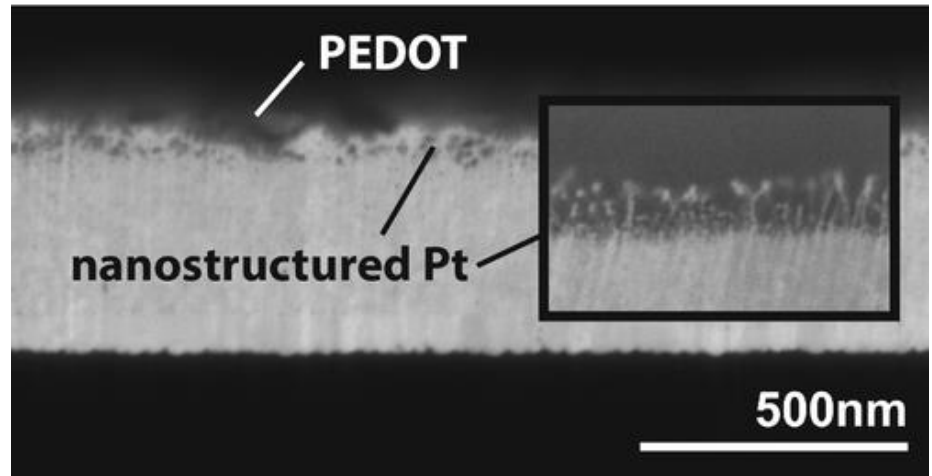
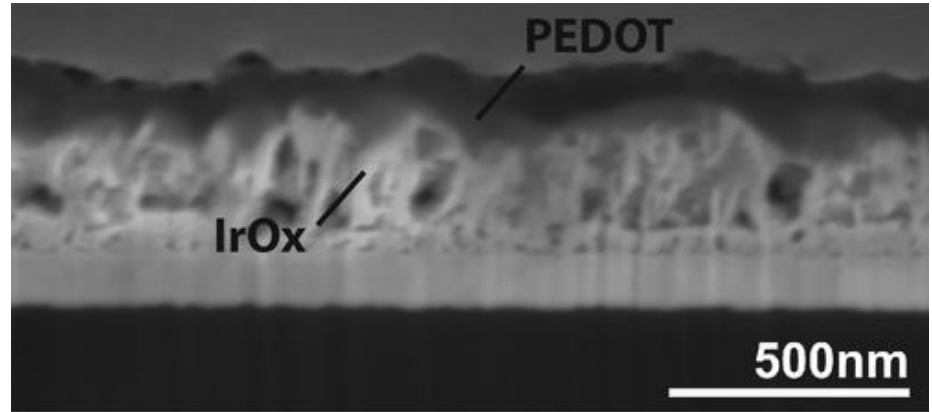


Electrode material	$Q_{inj}$ (mC/cm <sup>2</sup> )	Water window
Platinum	0.1-0.2	-0.6 to 0.8V
Titanium nitride	1	-0.9 to 0.9V
Platinum black	1	-0.6 to 0.8V

CP coatings for neural microprobes due to superior electrochemical performance vs. metals:

- **Small electrodes, big performance:** Low impedance and **high charge-injection capacity**
- **Typified by PEDOT** (poly(3,4-ethylenedioxythiophene)). Mixed conduction (electronic+ionic) polymer
- **Simple fabrication by Electrodeposition** of thin films onto metallized probes—low-cost and scalable.
- **Customizable interface:** Easy tuning/functionalization .

Boehler 2016



# Take-home messages

## The « optimal » electrode

- Low energy consumption for stimulation
- Effective charge injection at geometrically small electrode sites
- High reversible charge injection limits
- Low and stable impedance
  
- Low frequency dependence of the impedance
- Low electrochemically induced noise
  
- Long term stability over decades in the body
- Biotolerance of the materials