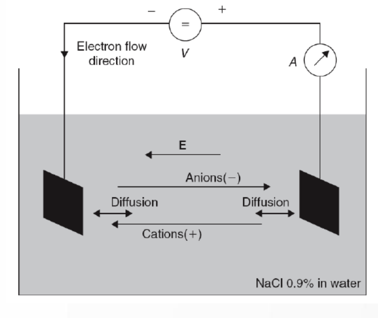
BIOELECTRODES

Lecture Notes

Ahmet Ademoglu, *PhD*
Bogazici University
Institute of Biomedical Engineering

Electrolytic Experiment



$C \rightleftharpoons C^{n+} + ne^-$ $\quad$ $A^{m-} \rightleftharpoons A + me^-$

n: valence of C $\quad$ m: valence of A

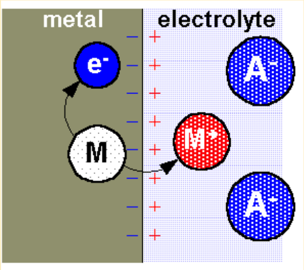
The basic electrolytic experiment, shown with material transport directions.

The dominating reaction can be inferred from the following

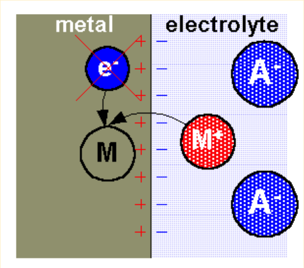
Current flow from electrode to electrolyte : Oxidation (Loss of e-)

Current flow from electrolyte to electrode : Reduction (Gain of e-)

Metal cation leaving into the electrolyte or joining the metal



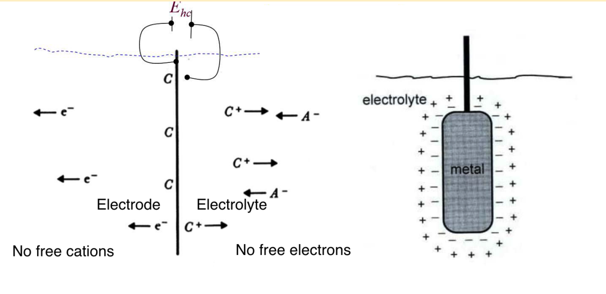
One atom M out of the metal is oxidized to form one cation M^+ and giving off one free electron e^- to the metal.
Current flow from electrode to electrolyte (Oxidation)



One cation M^+ out of the electrolyte becomes one neutral atom M taking off one free electron from the metal.
Current flow from electrolyte to electrode (Reduction)

Electronic Current vs Ionic Current

Electrode-Electrolyte Interface



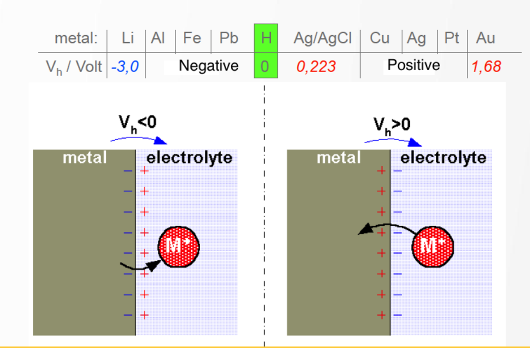
1. Electrons move opposite to the direction of current
2. Cations (C^+) move in the direction of current
3. Anions (A^-) move in the opposite direction of current

Electrode is made up of atoms of the same material as cations Ag/AgC.

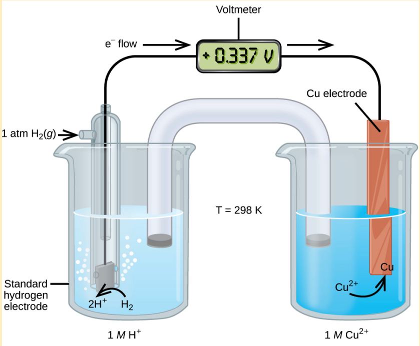
Half-Cell Potential

When metal C contacts electrolyte, oxidation or reduction begins immediately. Local concentration of cations at the surface changes. Charge builds up in the regions. Electrolyte surrounding the metal assumes a different electric potential from the rest of the solution. A characteristic potential difference established by the electrode and its surrounding electrolyte builds up which is called *half-cell potential* E^o.

Half-cell Potentials for Common Electrodes



Measuring Half-Cell Potential



Half cell potential cannot be measured without a second electrode. By convention, the hydrogen electrode is chosen as the reference. Other half cell potentials are expressed as a potential difference with this electrode.

Polarization

The half-cell potential is established when no electric current exists between the electrode and electrolyte. When there is a current, the observed half-cell potential is altered as to oppose the current. The extent of the potential change caused by the current is known as *polarization*. The difference between the observed half-cell potential and the zero-current half-cell potential is called *overpotential*.

Components of overpotential

1. **ohmic overpotential** : arising from the resisitivity of the electrolyte current
2. **concentration overpotential** : due to the difference between the rates of oxidation and reduction at the interface
3. **activation overpotential** : a voltage difference that occurs when a current exists and either a reduction or oxidation predominates

Polarization Potential

$$V_p = E^o + V_r + V_c + V_a$$

V_p : Polarization potential
E^o : Standard half-cell potential
V_r : Ohmic overpotential
V_c : Concentration overpotential
V_a : Activation overpotential

Potential across a membrane between two ionic solutions

$E = -\frac{RT}{nF} \ln \frac{a_1}{a_2}$, a_1 and a_2: activities of ions on each side of the membrane

E^o is determined at standard temperature when electrode is placed in electrolyte with cations of the electrode material having unity activity. As activity changes from unity,

$$E = E^o + \frac{RT}{nF} \ln(a_{C^{n+}}),$$

E : Half-cell potential, $a_{C^{n+}}$: Activity of cation C^{n+}

Polarizability and Electrodes

Perfectly Polarizable Electrodes

No charge crosses the electrode when current is applied.

Noble metals are closest (like platinum and gold); they are difficult to oxidize and dissolve.

Current does not cross, but rather changes the concentration of ions at the interface.

Behave like a capacitor.

Perfectly Non-Polarizable Electrodes

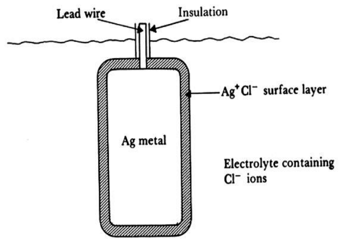
All charge freely crosses the interface when current is applied.

No overpotential is generated.

Behave like a resistor.

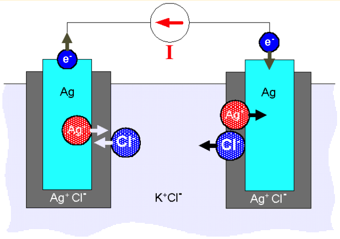
Silver/silver-chloride is a good non-polarizable electrode.

The Classic Ag/AgCl Electrodes



Practical electrode, easy to fabricate.
Metal (Ag) electrode is coated with a layer of slightly soluble ionic compound of the metal and a suitable anion (Cl).
Reaction 1: $Ag \rightleftharpoons Ag^{+} + Cl^{-}$
Silver oxidizes at the Ag/AgCl interface
Reaction 2: $Ag^{+} + Cl^{-} \rightleftharpoons AgCl$
Silver C^{+} combine with chloride A^{-}.
AgCl is only slightly soluble in water.
It precipitates onto the electrode to form a surface coating.

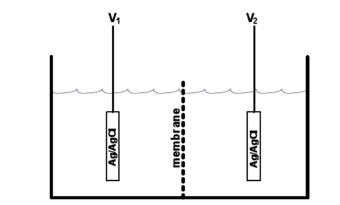
Its Fabrication



Electrolytic process
Ag/AgCl electrode serves as cathode.
Ag electrode serves as the anode.
A 1.5 volt battery is the energy source.
A resistor limits the current.
A milliammeter measures plating current.
Reaction has an initial surge of current.
When current approaches a steady state (about 10 μA), the process is terminated.

Self Study Question

A membrane separates a container into two compartments as shown below. The first compartment contains a solution of 10 mmol of NaCl and 1 mmol of KCl in 1 L of water. The second compartment contains a solution of 1 mmol of NaCl and 10 mmol of KCl in 1 L of water. Two identical Ag/AgCl electrodes are immersed, one in each compartment. The voltage between the electrodes is measured with a voltmeter of infinite input impedance.



a) Find the concentrations of Na^+, K^+ and Cl^- in the first and second compartments.
Using Goldman-Hodgkin-Katz equation:

$$E = \frac{RT}{F} \ln \left\{ \frac{P_K[K^+]_o + P_{Na}[Na^+]_o + P_{Cl}[Cl^-]_i}{P_K[K^+]_i + P_{Na}[Na^+]_i + P_{Cl}[Cl^-]_o} \right\} \text{ where } \frac{RT}{F} = 26mV$$

$i \rightarrow 1$

$o \rightarrow 2$

1: 10 mmol $NaCl$ + 1mmol KCl in liter $\rightarrow [Na^+]_1 = 10,\ [K^+]_1 = 1,\ [Cl^-]_1 = 11\ \frac{mmol}{liter}$

2: 1 mmol $NaCl$ + 10mmol KCl in liter $\rightarrow [Na^+]_2 = 1,\ [K^+]_2 = 10,\ [Cl^-]_2 = 11\ \frac{mmol}{liter}$

b) Assume that the membrane is permeable to Cl^- only. Find $V_1 - V_2$ at rest.

$V_1 - V_2 = \frac{RT}{F} \ln \frac{[CL^-]_1}{[CL^-]_2} = \frac{RT}{F} \ln 1 = 0.$

c) Assume that the membrane is equally permeable to Cl^- and Na^+. Find $V_1 - V_2$ at rest.

$V_1 - V_2 = \frac{RT}{F} \ln \frac{[Na^+]_2+[CL^-]_1}{[Na^+]_1+[CL^-]_2} = \frac{RT}{F} \ln \frac{12}{21} = -14.6mV.$

d) Assume that the membrane is equally permeable to Cl^- and K^+. Find $V_1 - V_2$ at rest.

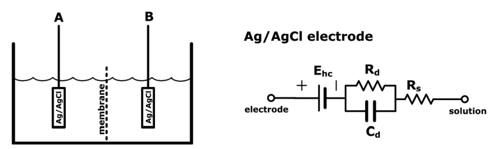
$V_1 - V_2 = \frac{RT}{F} \ln \frac{[K^+]_2+[CL^-]_1}{[K^+]_1+[CL^-]_2} = \frac{RT}{F} \ln \frac{21}{12} = 14.6mV.$

e) Assume that the membrane is equally permeable to all ions. Find $V_1 - V_2$ at rest.

$V_1 - V_2 = \frac{RT}{F} \ln \frac{[K^+]_2+[Na^+]_2+[CL^-]_1}{[K^+]_1+[Na^+]_1+[CL^-]_2} = \frac{RT}{F} \ln \frac{22}{22} = 0.$

Self Study Question

A membrane separates a container into two compartments as shown below. The inside compartment (A) contains a solution of 100 mmol of NaCl and 10 mmol of KCl in 1 L of water. The outside compartment (B) contains a solution of 1 mmol of NaCl and 10 mmol of KCl in 1 L of water. Two identical Ag/AgCl electrodes are immersed, one in each compartment. For each Ag/AgCl electrode, the half cell potential E_{hc} is $0.223V$, and the impedance parameters are $R_d = 320k\Omega$, $C_d = 10pF$, and $R_s = 10k\Omega$. The membrane has equal permeabilities to all three ions.



a) Find the Nernst potential of Na^+, K^+ and Cl^-.

$E_{K^+} = 26 \ln \frac{10}{10} = 0mV$, $E_{Na^+} = 26 \ln \frac{1}{100} = -120mV$, $E_{Cl^-} = 26 \ln \frac{110}{11} = 60mV$

b) Derive the voltage between nodes A and B at rest.

$$V_A - V_B = \underset{A-Ag/AgCl}{E_{HC}} + E_{GHK} - \underset{Ag/AgCl-B}{E_{HC}} = 26 \ln \frac{10+1+110}{10+100+11} = 26 \ln \frac{121}{121} = 0mV$$

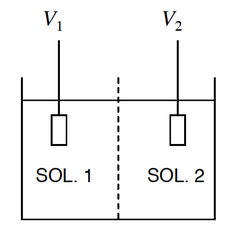
c) Derive and sketch the impedance $Z(j\omega)$ between nodes A and B as a function of ω. You may assume that the resistance for ion transport across the membrane R_{mem} is $1M\Omega$.

Hint : $Z(j\omega) = R_{mem} + 2R_s + 2\frac{R_d \cdot 1/j\omega C_d}{R_d + 1/j\omega C_d} = 1.02 \cdot 10^6 + \frac{640 \cdot 10^3}{1 + j\omega/(31 \cdot 10^3)}$

Self Study Question

Consider an electrochemical cell at room temperature, with two compartments of ionic solutions each containing KCl and NaCl with concentrations given in the table below. The two compartments are separated by a membrane that is equally permeable to all ion types, K^+, Na^+ and Cl^-. Two identical Ag/AgCl electrodes are inserted, one in each compartment.

a) Find the voltage $V_2 - V_1$ between the electrodes measured by a voltmeter with infinite input impedance.



	SOL. 1	SOL. 2
KCl	1000 mmol/L	10 mmol/L
NaCl	90 mmol/L	10 mmol/L

$$V_2 - V_1 = E_{HC} + 26 \ln \frac{P[K^+]_1 + P[Na^+]_1 + P[CL^-]_2}{P[K^+]_2 + P[Na^+]_2 + P[CL^-]_1} - E_{HC} =$$

$$26 \ln \frac{[KCl]_1 + [NaCl]_1 + [NaCl]_2 + [KCl]_2}{[KCl]_2 + [NaCl]_2 + [NaCl]_1 + [KCl]_1} = 26 \ln 1 = 0$$

b)The two electrodes each have $0.1 mmol$ of $AgCl$ deposited on the surface of their Ag core, when they are brand new. For how much total time can you drive a current of $100mA$ through the electrochemical cell before the electrodes malfunction? Does the polarity of this current matter? Faradays constant F is approximately $100,000 C/mol$.

Either of both electrodes malfunctions when the $AgCl$ layer becomes completely depleted, *i.e.*, 0.1 mmol of $AgCl$ dissociates.
$T_{Total} = F \cdot 0.1\ mmol/I = 100 \cdot 0.1/0.1 = 100s$
Polarity determines which of the two electrodes will malfunction.

Self Study Question

Consider two identical electrodes inserted in a Petri dish containing a biological cell culture preparation at room temperature. The cells are in a physiological saline environment of $0.15 mol/L$ NaCl in distilled water. Assume the cells are impermeable to K^+ and any other ion types except Na^+ and Cl^-.

a) Assume both electrodes are in the extracellular saline environment, without penetrating any cell. What voltage do you expect to measure by a voltmeter with infinite input impedance between the electrodes, and why?

Since the two half cell potentials are the same
and the voltage drop across the saline environment is zero at zero current,
the voltage measured will be zero.

b) Now one of the two electrodes is inserted in one of the cells in the culture. When a pharmacological agent is introduced to block all sodium channels, the voltage measured between this electrode and the other electrode remaining in the saline environment is $V_{cell} - V_{saline} = -60mV$. What does that tell about Nernst potentials of the cell, and ion concentrations inside the cell? Explain.

Cells are impermeable to $K^+ \rightarrow P_K = 0$

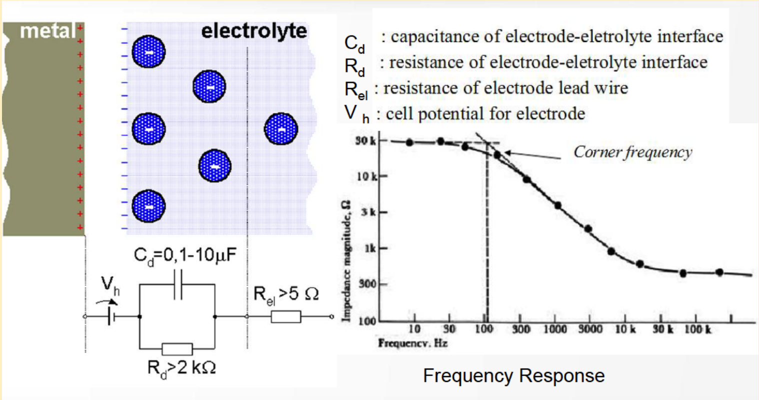
All Na channels are blocked $\rightarrow P_{Na} = 0$

$V_{cell} - V_{saline} = 26 \ln \frac{[Cl^-]_{cell}}{[Cl^-]_{saline}} = E_{Cl} = -60mV$

$[Cl^-]_{cell} = \frac{1}{10}[Cl^-]_{saline} = 0.015m/liter$ for Cl^-.

Nothing can be said for Na^+ and K^+.

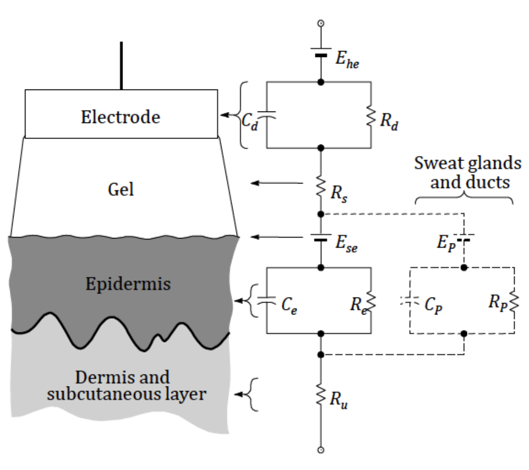
Electrode Behavior and Circuit Models



At low frequencies: $R_d + R_{el}$

At high frequencies: R_{el}

Electrode-Skin Interface Model



For 1 cm^2, skin impedance reduces from approximately 200 KΩ at 1 Hz to 200Ω at 1MHz. Transparent electrolyte gel containing Cl^- is used to maintain good contact between the electrode and the skin.

Motion Artifact

- When the electrode moves with respect to the electrolyte, the distribution of the double layer of charge on polarizable electrode interface changes. This changes the half cell potential temporarily.
- If a pair of electrodes is in an electrolyte and one moves with respect to the other, a potential difference appears across the electrodes known as the motion artifact.This is a source of noise and interference in biopotentialmeasurements.
- Signal due to motion has low frequency so it can be filtered out when measuring a biological signal of high frequency component such as EMG or axon action potential. However, for ECG, EEG and EOG whose frequencies are low it is recommended to use nonpolarizable electrode to avoid signals due to motion artifact.

Self Study Problem

Consider the skin-electrode model with
$E_{hc} = 200mV$, $R_s = 1k\Omega$, $C_d = 1pF$, $C_e = 10pF$, $C_p = 0$ $E_{sc} = 430mV$,
$R_u = 100k\Omega$, $R_d = 1M\Omega$, $R_e = 10M\Omega$, $R_p = \infty$

a) Find the expression for the impedance of the circuit when the subject is not sweating, that is, disregarding the sweat glands and ducts contribution.

$$Z_{Total}(dry) = \frac{R_d/j\omega C_d}{R_d+1/j\omega C_d} + R_s + \frac{R_e/j\omega C_e}{R_e+1/j\omega C_e} + R_u$$

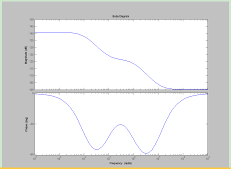
b) Find the expression for the impedance of the circuit when the subject is sweating, that is, including the sweat glands and ducts contribution.

$$Z_{Total}(wet) = \frac{R_d/j\omega C_d}{R_d+1/j\omega C_d} + R_s + \frac{R_e/j\omega C_e}{R_e+1/j\omega C_e} // \frac{R_p/j\omega C_p}{R_p+1/j\omega C_p} + R_u$$

c) Using the following parameter values sketch (or plot) the magnitude of the impedance as a function of frequency, from $0.1Hz$ to $100Hz$ on a log-log scale. Make sure to properly label your plot with values and units.

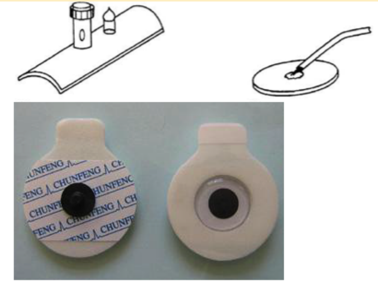
$$Z_{Total}(dry) = R_s + R_u + \frac{R_d}{1+j\omega R_d C_d} + \frac{R_e}{1+j\omega R_e C_e}$$

$$Z_{Total}(wet) = R_s + R_u + \frac{R_d}{1+j\omega R_d C_d} + \frac{R_e R_p/R_e+R_p}{1+j\omega(R_e R_p/R_e+R_p)(C_e+C_p)}$$



$$Z_{Total}(dry) = Z_{Total}(wet)$$

Body-surface biopotential electrodes



Metal plate electrodes

Large surface: Traditional, still used (ECG)

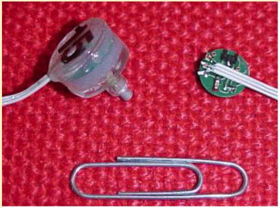
Metal disk with stainless steel: platinum or gold coated (EMG), (EEG)

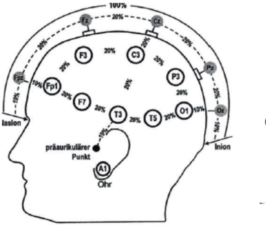
Disposable foam-pad: smaller diameters, motion artifacts, (ECG)

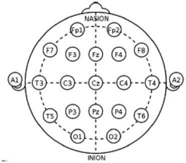
Metal Suction Electrodes

A paste is introduced into the cup.
The electrodes are then suctioned into place.
Ten of these can be used for clinical ECG as limb and precordial (chest) electrodes.

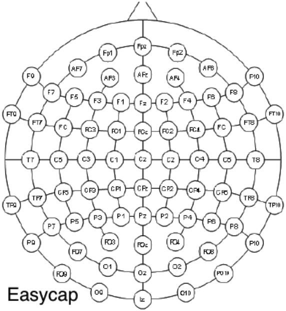
Surface EEG Electrodes







10-20 Electrode System



Easycap

EMG Electrodes

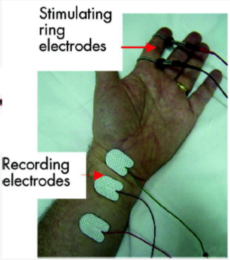
Surface

Subcutaneous

EMG Electrodes

- **Clips electrodes**

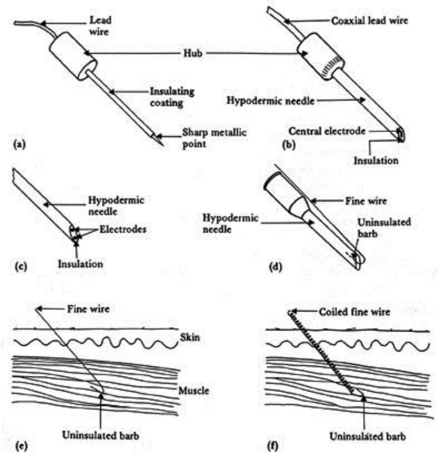
- **Ring electrodes**



- **Bipolar Felt Pad Stimulator/Electrode**

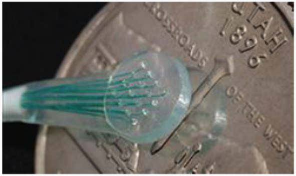
- **Bar electrodes**

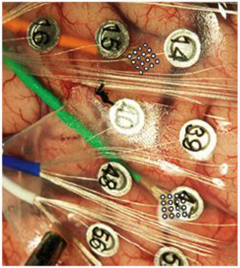
Percutaneous Electrodes

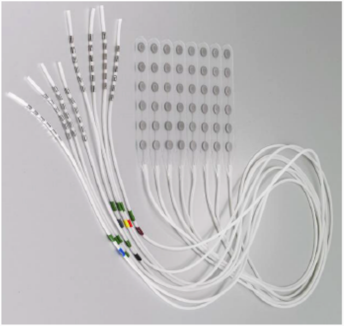


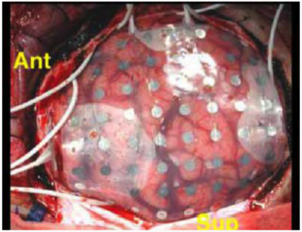
Needle and wire electrodes for percutaneous measurement of biopotentials.
(a) Insulated needle electrode.
(b) Coaxial needle electrode.
(c) Bipolar coaxial electrode.
(d) Fine-wire electrode connected to hypodermic needle, before being inserted.
(e) Cross-sectional view of skin and muscle, showing coiled fine-wire electrode in place.

Electrocorticographic Electrodes



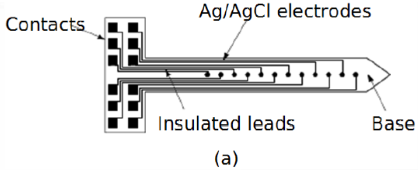


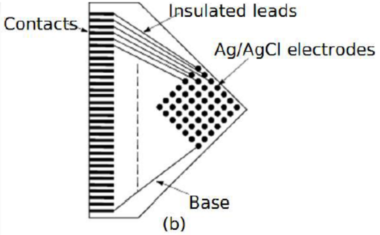


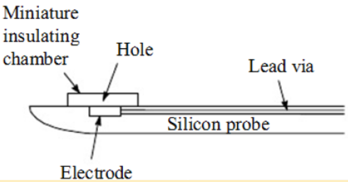


Micro-electrocorticographic Grid

Electrode Arrays



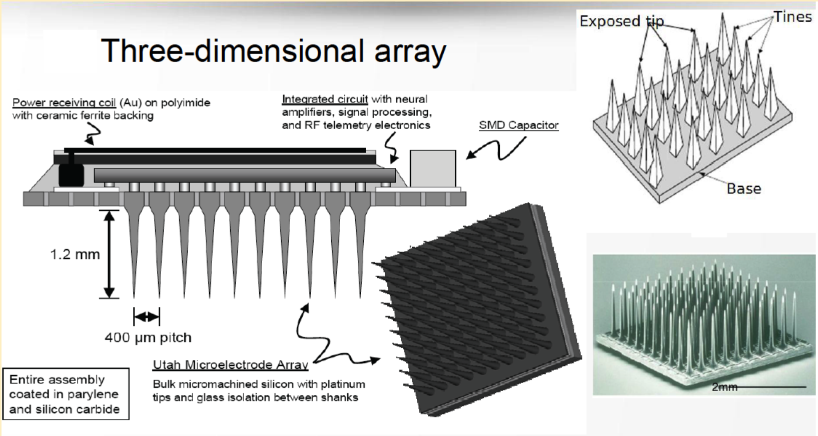




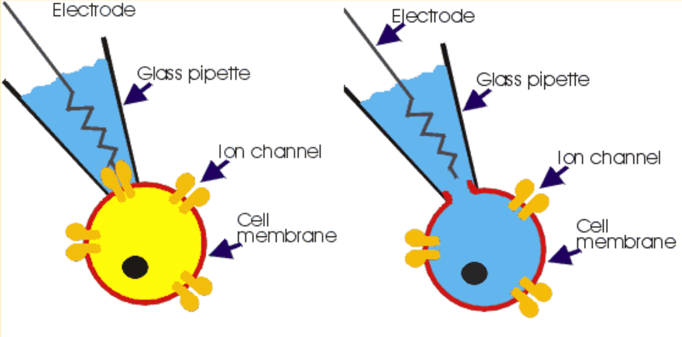
(a) One-dimensional plunge electrode array.

(b) Two-dimensional array

Electrode Arrays



Microelectrodes measure potential difference across cell membrane



Cell attached recording
Pipette touching the membrane and forming a high-ohmic junction ($\sim 1G\Omega$).
Tip diameter: 0.05-10 μms.

Whole cell recording
By suction through a pipette the membrane breaks solution in the pipette and inside of the cells become uniform.