Biopotential Electrodes

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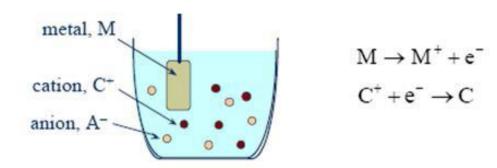
- In order to measure and record potentials and, hence, currents in the body, it is necessary to provide some interface between the body and the electronic measuring apparatus.
- Biopotential electrodes carry out this interface function.
- In any practical measurement of potentials, current flows in the measuring circuit.
- Ideally this current should be very small.
- However, in practical situations, it is never zero.
- Biopotential electrodes must therefore have the capability of conducting a current across the interface between the body and the electronic measuring circuit.

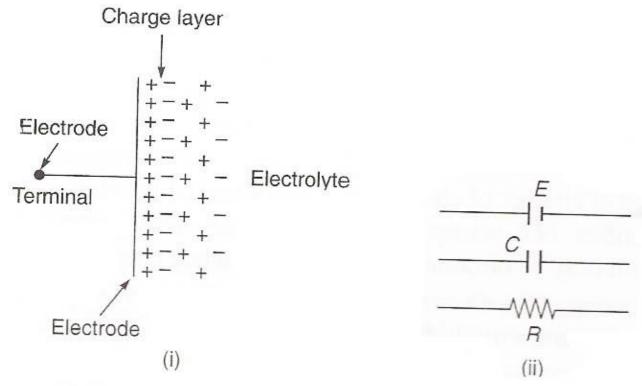
Biopotential Electrodes- (Cont.)

- The electrode actually carries out a transducing function, because in the body current is carried by ions, whereas in the electrode and its lead wire it is carried by electrons.
- Thus the electrode must serve as a transducer to change an ionic current into an electronic current.
- The interface required for the charge transfer is the electrode–electrolyte interface:
 - Electrode: some sort of metal with desired properties
 - Electrolyte: a conducting medium, specifically formulated electrode metal being used
- Classified as:
 - Noninvasive (skin surface)
 - Invasive (e.g. microelectrodes or wire electrodes)

The Electrode-Electrolyte Interface

- When a metal is placed in an electrolyte (i.e., an ionizable) solution, a charge distribution is created next to the metal/electrolyte interface.
- This localized charge distribution (charge gradient) causes an electric potential, called a half-cell potential, E which depends on
 - The metal,
 - Concentration of ions in solution and
 - Temperature
- Half cell potential cannot be measured without a second electrode.





- (i) Charge distribution at electrode-electrolyte interface
- (ii) Three components representing the interface

Table 5.1 Half-cell Potentials for Common Electrode Materials at 25 °C

The metal undergoing the reaction shown has the sign and potential E^0 when referenced to the hydrogen electrode

Metal and Reaction	Potential E ⁰ (V)	
$Al \rightarrow Al^{3+} + 3e^{-}$	-1.706	
$Zn \rightarrow Zn^{2+} + 2e^-$	-0.763	
$Cr \rightarrow Cr^{3+} + 3e^{-}$	-0.744	
$Fe \rightarrow Fe^{2+} + 2e^{-}$	-0.409	
$Cd \rightarrow Cd^{2+} + 2e^{-}$	-0.401	
$Ni \rightarrow Ni^{2+} + 2e^{-}$	-0.230	
$Pb \rightarrow Pb^{2+} + 2e^{-}$	-0.126	
$H_2 \rightarrow 2H^+ + 2e^-$	0.000 by definition	
$Ag + Cl^- \rightarrow AgCl + e^-$	+0.223	
$2Hg + 2Cl^{-} \rightarrow Hg_2Cl_2 + 2e^{-}$	+0.268	
$Cu \rightarrow Cu^{2+} + 2e^{-}$	+0.340	Electro
$Cu \rightarrow Cu^+ + e^-$	+0.522	
$Ag \rightarrow Ag^+ + e^-$	+0.799	for hyd
$Au \rightarrow Au^{3+} + 3e^{-}$	+1.420	for any
$Au \! \to \! Au^+ + e^-$	+1.680	the hy

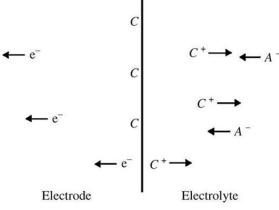
Standard Hydrogen electrode

Electrochemists have adopted the Half-Cell potential for hydrogen electrode to be zero. Half-Cell potential for any metal electrode is measured with respect to the hydrogen electrode.

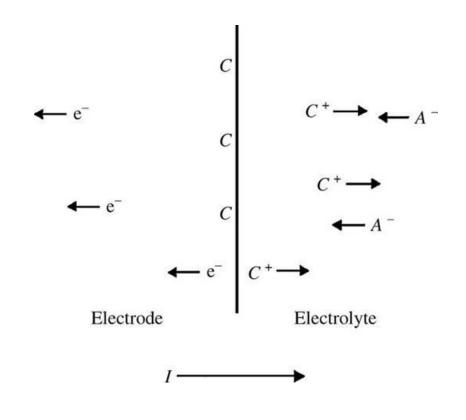
Source: Data from *Handbook of Chemistry and Physics*, 55th ed., Cleveland, OH: CRC Press, 1974–1975, with permission.

- The electrolyte represents the body fluid containing ions.
- A net current that crosses the interface, passing from the electrode to the electrolyte, consists of

- (1) electrons moving in a direction opposite to that of the current in the electrode,
- (2) cations (denoted by C⁺) moving in the same direction as the current,
- (3) anions (denoted by A⁻) moving in a direction opposite to that of the current in the electrolyte.



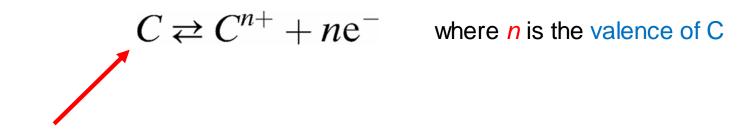
- The current crosses it from left to right.
- The electrode consists of metallic atoms C.
- The electrolyte is an aqueous solution containing cations of the electrode metal C⁺ and anions A⁻.



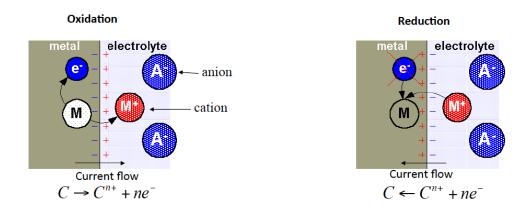
where n is the valence of C and m is valence of A

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

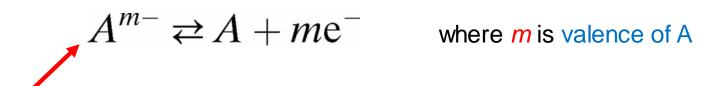
- For most electrode systems, the cations in solution and the metal of the electrodes are the same.
- This material in the electrode at the interface can become oxidized to form a cation and one or more free electrons.
- The cation is discharged into the electrolyte; the electron remains as a charge carrier in the electrode.



Current flow from electrode to electrolyte: oxidation

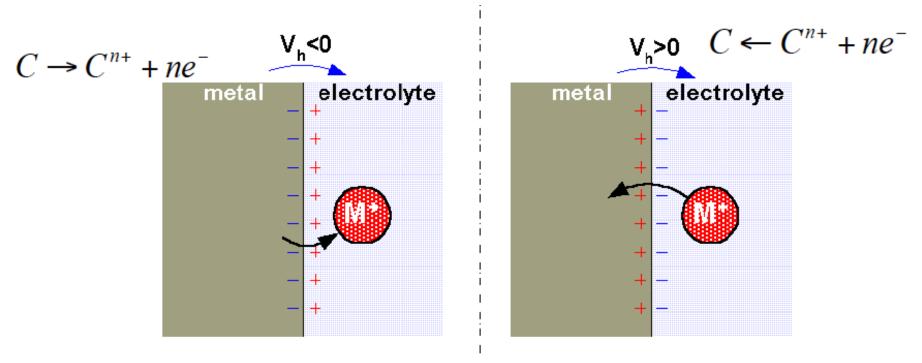


• An anion coming to the electrode–electrolyte interface can be oxidized to a neutral atom, giving off one or more free electrons to the electrode.



Current flow from electrolyte to electrode: reduction

- Both reactions are often reversible and that reduction reactions (going from right to left in the equations) can occur as well.
- As a matter of fact, when no current is crossing the electrode–electrolyte interface, these reactions often still occur. But the rate of oxidation reactions equals the rate of reduction reactions, so the net transfer of charge across the interface is zero.
- When the current flow is from electrode to electrolyte, the oxidation reactions dominate.
- When the current is in the opposite direction, the reduction reactions dominate.



Certain mechanism separate charges at the metal-electrolyte interface results in one type of charge is dominant on the surface of the metal and the opposite charge is concentrated at the immediately adjacent electrolyte.

Polarization

- When no electric current flows between an electrode and the electrolyte the potential observed should be the half-cell potential. If, however, there is a current, these potentials can be altered.
- The difference between the potential at zero current and the measured potentials while current is passing is known as the *over voltage* (*overpotential*) and is the result of an alteration in the charge distribution in the electrolyte in contact with the electrodes. This effect is known as polarization.
- The overpotential can be separated into three components:
 - the ohmic
 - the concentration
 - the activation over potentials.

- The ohmic overpotential is a direct result of the resistance of the electrolyte.
- When a current passes between two electrodes immersed in an electrolyte, there is a voltage drop along the path of the current in the electrolyte as a result of its resistance.
- This drop in voltage is proportional to the current and the resistivity of the electrolyte.

- The concentration overpotential results from changes in the distribution of ions in the electrolyte in the vicinity of the electrode—electrolyte interface.
- Recall that the equilibrium half-cell potential results from the distribution of ionic concentration in the vicinity of the electrode–electrolyte interface when no current flows between the electrode and the electrolyte.
- Under these conditions, the rates of oxidation and reduction at the interface are equal.
- When a current is established, this equality no longer exists. Thus it is reasonable to expect the concentration of ions to change.
- This change results in a different half-cell potential at the electrode.
- The difference between this and the equilibrium half-cell potential is the concentration overpotential.

- Charge transfer in the oxidation-reduction reaction at the interface is not entirely reversible.
- For metal ions to be oxidized, they must overcome an energy barrier.
- If the direction of current flow is one way, then either oxidation or reduction dominates, and the height of the barrier changes.
- This energy difference produces a voltage between the electrode and the electrolyte, known as the activation overpotential.

These three mechanisms of polarization are additive. Thus the net overpotential of an electrode is given by

$$V_p = E_0 + V_r + V_c + V_a$$

where

 E_0 : half-cell potential

 V_p : total potential, or polarization potential, of the electrode

 V_r : ohmic overpotential

 V_c : concentration overpotential

 V_a : activation overpotential

When an ion-selective semipermeable membrane separates two aqueous ionic solutions of different concentration, an electric potential exists across this membrane. It can be shown (Plonsey and Barr, 2007) that this potential is given by the Nernst equation

$$E = -\frac{RT}{nF} \ln \left[\frac{a_1}{a_2} \right]$$

Where

 a_1 and a_2 are the activities of the ions on each side of the membrane.

- The half-cell potentials listed in Table 5.1 are known as the standard halfcell potentials because they apply to standard conditions. When the electrode–electrolyte system no longer maintains this standard condition, half-cell potentials different from the standard half-cell potential are observed.
- The differences in potential are determined primarily by temperature and ionic activity in the electrolyte.
- Ionic activity can be defined as the availability of an ionic species in solution to enter into a reaction.

- The standard half-cell potential is determined at a standard temperature; the electrode is placed in an electrolyte containing cations of the electrode material having unity activity.
- As the activity changes from unity (as a result of changing concentration), the half-cell potential varies according to the Nernst equation:.

$$E = E^0 + \frac{RT}{nF} \ln(a_{c^{n+}})$$

where

E: half-cell potential

E⁰: standard half-cell potential

n : valence of electrode material

 $a_{c^{n+}}$: activity of cation C^{n+}

- Example: A Zn electrode and Ag electrode coated with AgCl are placed in a 1M ZnCl₂ solution (activities of Zn and Cl are approximately unity) to form an electrochemical cell. The solution is maintained at a temperature of 25°C.
- a) What chemical reactions might you expect to see at these electrodes?
- b) If a very high input impedance voltmeter were connected across these electrodes, what would it read?
- c) If the lead wires from the electrodes were shorted together, would a current flow? How would this affect the reactions at the electrodes?
- How would you expect the voltage between the electrodes to differ from the equilibrium open circuit voltage of the cell immediately following removal of the short circuit?

a)

- Zinc is much more chemically active than Ag, so the atoms on its surface oxidize to Zn²⁺ ions according to the reaction: Zn ≠ Zn²⁺ + 2e⁻, which according to Table 5.1 has an E0 of -0.763 V.
- At the Ag electrode, Ag can be oxidized to form Ag⁺ ions according to the reaction: $Ag \rightleftharpoons Ag^+ + 1e^-$. These ions immediately react with the Cl ions in solution to form

$$Ag^+ + Cl^- \rightleftarrows AgCl$$
.

 Most of this precipitates out of solution due to this salt's low solubility. This reaction has an E⁰ of 0.223 V at 25 °C. b)

When no current is drawn from or supplied to either electrode, and the concentration of ions is uniform throughout the solution, the difference in voltage between the electrodes is the difference between the half-cell potentials:

$$V = E_{\rm Zn}^0 - E_{\rm Ag}^0 = -0.763 \,\text{V} - 0.233 \,\text{V} = -0.986 \,\text{V}$$

Because Zn oxidizes at a higher potential, the electrons remaining in it are at a higher energy than those in the Ag. Thus the Zn electrode has a negative voltage with respect to the Ag electrode.

c)

There is a potential difference between the two electrodes, so there will be a current when they are shorted together. The flow of electrons is from the Zn to the Ag, because the Zn electrons are at a higher energy. Thus Zn is consumed and yields electrons, and AgCl absorbs electrons and plates out metallic Ag. d)

- When the electrodes are connected, they must be at the same potential at the point of connection. Thus the 0.986 V half-cell potential difference must be opposed by polarization overpotentials and ohmic losses in the electrodes and connecting wires.
- When the connection is broken and the current stops, the ohmic overpotential and electrode losses become zero, but the concentration overpotential remains until the gradient of the ionic concentration at the electrode surfaces returns to its equilibrium value for zero current.
- Thus the difference in voltage between the two electrodes is less than 0.986 V when the circuit is opened but rises to that value asymptotically with time.

Polarizable and Nonpolarizable Electrodes

- Perfectly polarizable electrodes <u>pass a current</u> between the electrode and the electrolytic solution <u>by changing the charge distribution</u> within the solution near the electrode. This current is a displacement current and electrode behaves like a capacitor. (Example: Platinum electrode)
- Perfectly polarisable electrodes have an disadvantage of motion artefact therefore <u>used only for stimulation</u>.
- Perfectly nonpolarised electrodes, however, allow the current to pass freely across the electrode-electrolyte interface without changing the charge distribution in the electrolytic solution adjacent to the electrode. (Example: Ag/AgCl Electrode)



Perfectly non polarisable electrodes <u>used for recording</u>.

The Silver/Silver Chloride Electrode

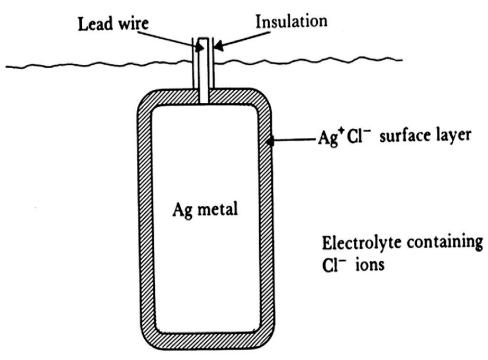


Figure 5.2 A silver/silver chloride electrode, shown in cross section.

<u>Features:</u>

- 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: silver oxidizes at the Ag/AgCl interface

$$Ag \Rightarrow Ag^+ + e^-$$

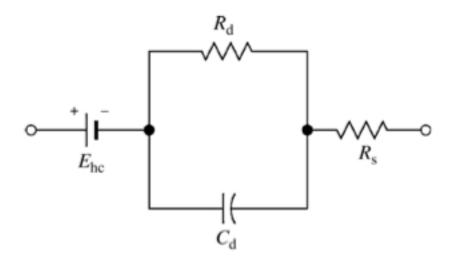
Reaction 2: silver cations combine with chloride anions

$$Ag^+ + Cl^- \Leftrightarrow Ag Cl$$

AgCl is only slightly soluble in water so most precipitates onto the electrode to form a surface coating.

Electrode Behavior and Circuit Models

 We will only consider low current densities, and consequently the electrode-electrolyte interface can be modeled as a linear system with an equivalent circuit composed exclusively of linear components.



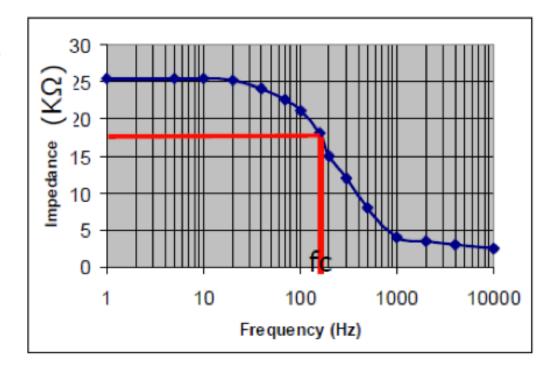
- E_{hc} is the half-cell potential
- C_d is the capacitance of the electric double layer (polarizable electrode properties).
- R_d is resistance to current flow across the electrodeelectrolyte interface (nonpolarizable electrode properties).
- R_s is the series resistance associated with the conductivity of the electrolyte.

The impedance of electrode-electrolyte interface

$$Z = R_{s} + \frac{\frac{R_{d}}{j2\pi fC_{d}}}{R_{d} + \frac{1}{j2\pi fC_{d}}} = R_{s} + \frac{R_{d}}{1 + j2\pi fC_{d}R_{d}}$$

- At very high frequencies, the impedance of the capacitor is negligible versus R_d , so the net impedance remains constant at R_s .
- At very low frequencies, the impedance of the capacitor is much greater than R_d so the net impedance remains constant, $R_s + R_d$.
- At frequencies between these extremes, the electrode impedance is frequency dependent.

An example of biopotential electrode impedance magnitude as a function of frequency. Characteristic frequencies will be somewhat different for electrode different geometries and materials.



The magnitude of the impedance of a single metal surface electrode immersed in an electrolyte is given the Figure. Half-cell potential is measured as -0.583V. From this graphical data, compute the equivalent circuit elements as defined in the equivalent circuit: R_d , C_d and R_s .

The magnitude of the impedance of a single metal surface electrode immersed in an electrolyte is given the Figure. Half-cell potential is measured as -0.583V. From this graphical data, compute the equivalent circuit elements as defined in the equivalent circuit: R_d , C_d and R_s .

From the Figure we see that the impedance |Z| is constant both at low and high frequencies.

At low frequencies
$$|Z| = R_d + R_s$$

At high frequencies
$$|Z| = R_s$$

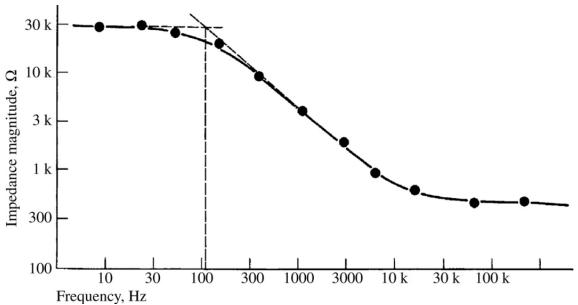
Thus from the Figure
$$R_s = 400\Omega$$
 and $R_d = 25.4 - 0.4 = 25k\Omega$

At the critical frequency f_c (R_c can ve neglegted) $C_d = 1/2\pi f_c R_d$

Thus from the Figure
$$f_c = 159Hz$$
 $C_d = 4 \times 10^{-8} F$

Example:

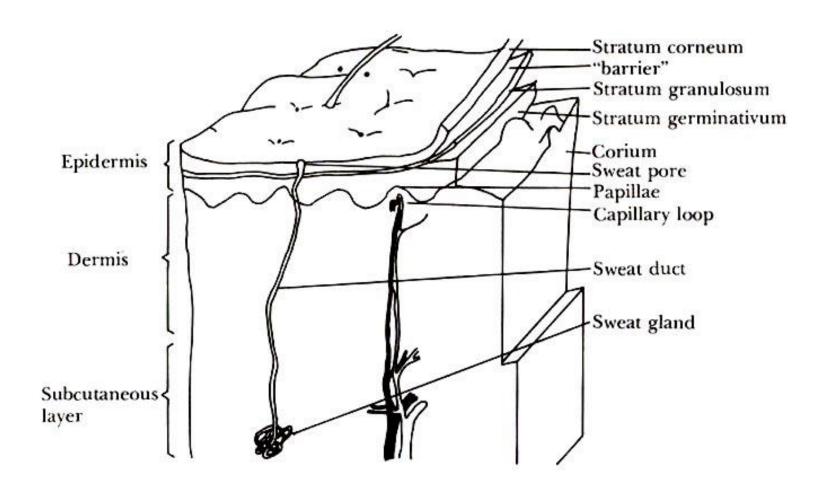
• We want to develop an electrical model for a specific biopotential electrode studies in the laboratory. The electrode is characterized by placing it in a physiological saline bath in the laboratory, along with an Ag/AgCl electrode having a much greater surface area and a known half-cell potential of 0.233 V. The dc voltage between the two electrodes is measured with a very-high-impedance voltmeter and found to be 0.572 V with the test electrode negative. The magnitude of the impedance between the two electrodes is measured as a function of frequency at very low currents; it is found to be that given in the following figure. From these data, determine a circuit model for the electrode.



ANSWER The very large surface area of the Ag/AgCl reference electrode makes its impedance very small compared to that of the test electrode, so we can neglect it. We cannot, however, neglect its half-cell potential, which is unaffected by surface area. The half-cell potential of the test electrode is $E_r^0 = 0.223 \text{ V} - 0.572 \text{ V} = -0.349 \text{ V}$.

At frequencies above about 20 kHz, the electrode impedance is constant because $C_{\rm d}$ in Figure 5.4 is short-circuited. Thus $R_{\rm s} = 500\,\Omega$. At frequencies less than 50 Hz, the electrode impedance is constant because $C_{\rm d}$ is open-circuited. Thus $R_{\rm s} + R_{\rm d} = 30\,{\rm k}\Omega$. Thus $R_{\rm d} = 29.5\,{\rm k}\Omega$. The corner frequency is 100 Hz. Thus $C_{\rm d} = 1/(2\pi f R_{\rm d}) = 1/(2\pi 100 \times 29500) = 5.3 \times 10^{-8}\,{\rm F}$.

Skin Anatomy



The Electrode-skin Interface And Motion Artifact

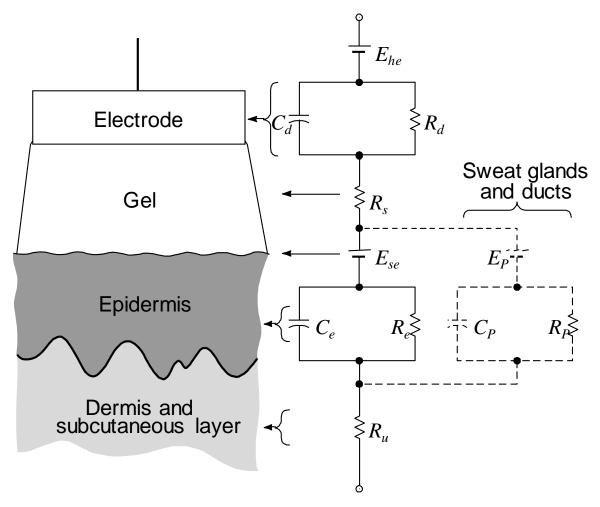


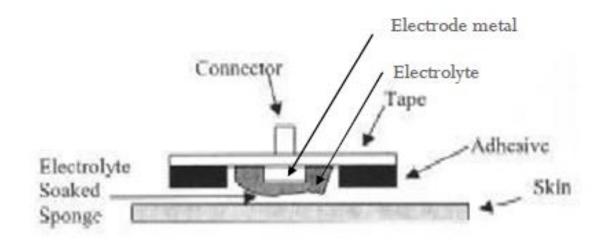
Figure 5.8 A body-surface electrode is placed against skin, showing the total electrical equivalent circuit obtained in this situation. Each circuit element on the right is at approximately the same level at which the physical process that it represents would be in the left-hand diagram.

The Electrode—skin Interface And Motion Artifact- (cont.)

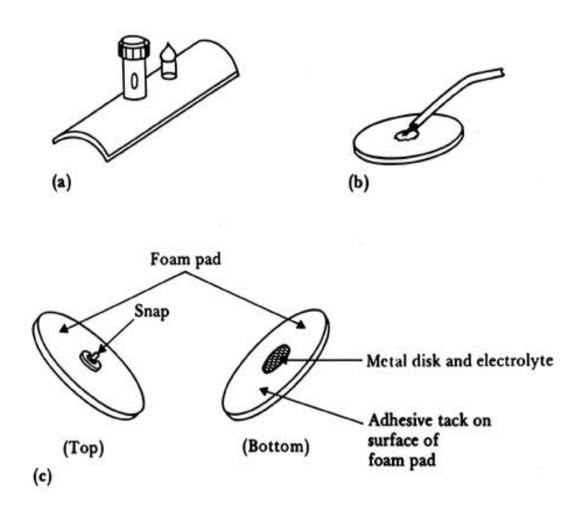
- When polarizable electrode is in contact with an electrolyte, a double layer of charge forms at the interface.
- Movement of the electrode will disturb the distribution of the charge and results in a momentary change in the half cell potential until equilibrium is reached again. This change is known as motion artifact.

Body-surface Recording Electrodes

- Body surface recording electrodes (commonly used)
 - Metal Plate Electrodes
 - Suction Electrodes
 - Floating Electrodes
 - Flexible Electrodes

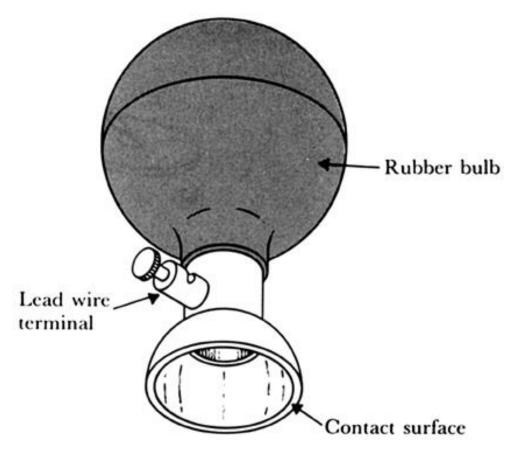


➤ Metal-Plate Electrodes



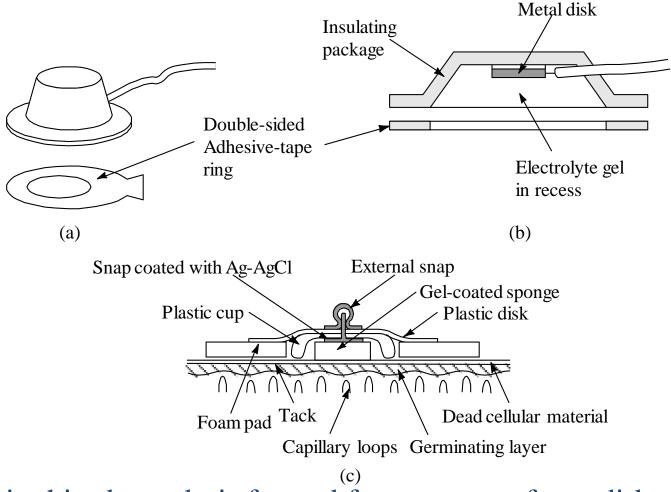
Body-surface biopotential electrodes (a) Metal-plate electrode used for application to limbs. (b) Metal-disk electrode applied with surgical tape. (c) Disposable foam-pad electrodes, often used with electrocardiograph monitoring apparatus.

> Suction Electrodes



A metallic suction electrode is often used as a precordial electrode on clinical electrocardiographs. **No need for strap or adhesive** and can be **used frequently**. **Higher source impedance** since the contact area is small

> Floating Electrodes

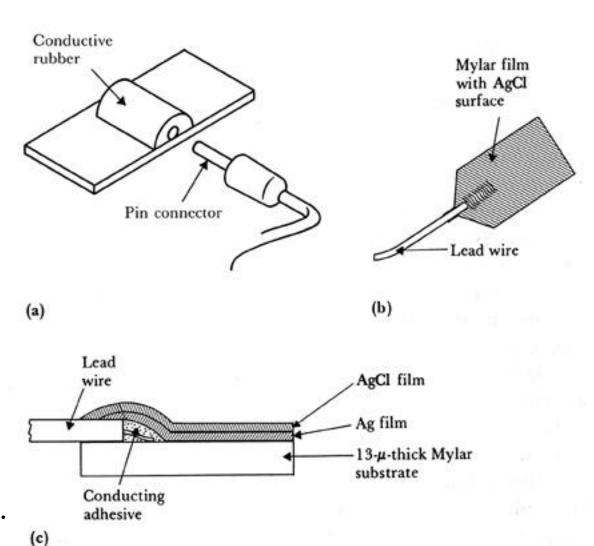


The recess in this electrode is formed from an open foam disk, saturated with electrolyte gel and placed over the metal electrode. **Minimize motion artifact**

> Flexible Electrodes

Flexible body-surface electrodes (a) Carbon-filled silicone rubber electrode. (b) Flexible thin-film neonatal electrode.

(c) Cross-sectional view of the thin-film electrode in (b).



Used for newborn infants.

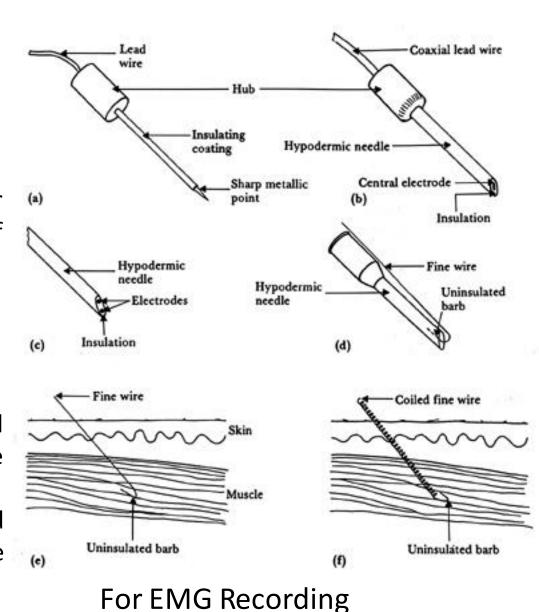
Compatible with X-ray

Electrolyte hydrogel material is used to hold electrodes to the skin.

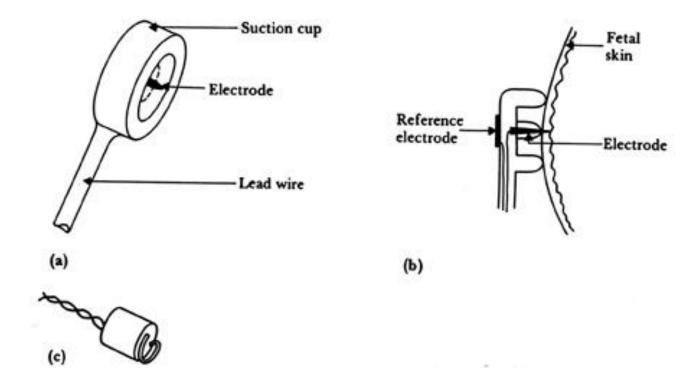
➤ Internal Electrodes

No electrolyte-skin interface

- 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.

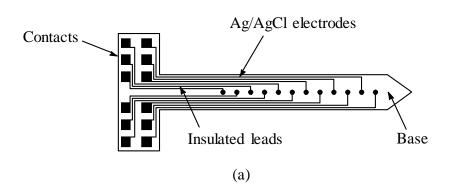


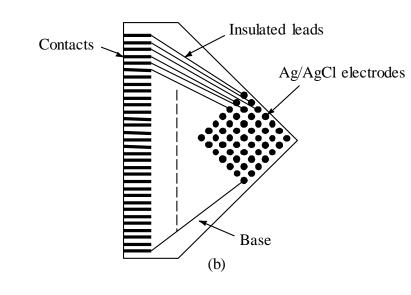
> Fetal ECG Electrodes



Electrodes for detecting fetal electrocardiogram during labor, by means of intracutaneous needles (a) Suction electrode. (b) Crosssectional view of suction electrode in place, showing penetration of probe through epidermis. (c) Helical electrode, which is attached to fetal skin by corkscrew type action.

> Electrode Arrays





(a) One-dimensional plunge electrode array 10mm long, 0.5mm wide, and 125μm thick, used to measure potential distribution in the beating myocardium (b) Two-dimensional array, used to map epicardial potential and (c) Three-dimensional array, each tine is 1,5 mm

