

HANDOUT #3. ELECTRODES

1. METAL/ELECTROLYTE INTERFACE

A. Helmholtz double layer (Gouy-Chapman-Stern theory)

The flow of current in metal is carried by electrons whose flow is driven by electric fields, whereas in electrolyte it is carried by ions that are driven by both electric fields and concentration gradients (cf. Nernst-Planck equation). For metal electrodes placed in an electrolyte (this is referred to as an *electrode of the first kind*), the Gouy-Chapman-Stern theory describes the interrelationship between electrode potential, surface charge density, potential field in the electrolyte, and ion concentration (see Fig. 1).

Figure 1 [1]

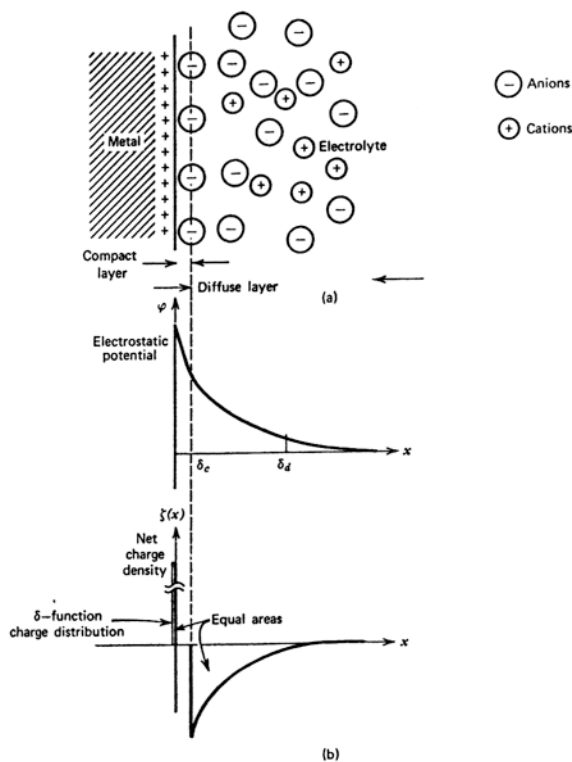


Figure 9.2. Structure of the double layer according to the model proposed by Stern (*Z. Elektrochem.*, 30, 508 [1924]): (a) ion distribution near the interface; (b) charge density and electrostatic potential. If δ_c ($\sim 2\text{\AA}$) is the closest distance of approach of an ion to the surface, the net charge density for $0 < x < \delta_c$ will be zero. For $x > \delta_c$ the electrostatic potential decays exponentially with distance. The "characteristic" distance δ_d for a univalent electrolyte $\approx 10\text{ \AA}$ for a $0.1M$ concentration and is $\approx 1000\text{ \AA}$ for a $10^{-5}M$ concentration.

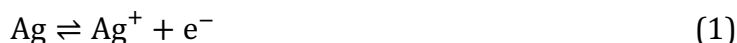
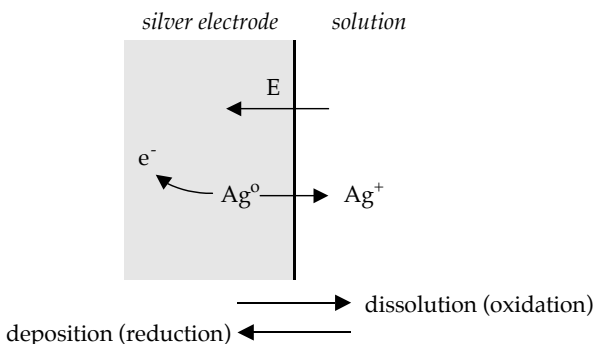
The charge distribution consists of a surface charge density on the electrode and a diffuse layer of opposite charge in the electrolyte, the total of which balances that on the electrode.

The two layers of charge are often referred to as the *Helmholtz electrical double layer*, and are analogous to the charges on a parallel plate capacitor.

B. Half-cell potential

With electrodes of the first kind, electrochemical reactions produce a potential difference between the metal and the electrolyte. This is illustrated below for a silver electrode.

Figure 2



With the reaction going to the right, the atomic silver in the electrode is dissolved and enters the solution as a free ion. An electric field develops, opposing the flux of Ag into the solution, until an equilibrium is reached. The equilibrium potential is referred to the *half-cell potential*, E_{hc} , of the metal. E_{hc} cannot be measured directly -- only with respect to another electrode which by convention is the *hydrogen electrode*. E_{hc} can be expressed as the sum of a *standard electrode potential*, E^0 , plus a term dependent on a , the activity of the metal ion.

$$E_{hc} = E^0 + \frac{RT}{F} \ln a \quad (2)$$

Table 1 tabulates E^0 for a number of common metal electrode materials.

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
$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$	-1.706
$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	-0.763
$\text{Cr} \rightarrow \text{Cr}^{3+} + 3\text{e}^-$	-0.744
$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$	-0.409
$\text{Cd} \rightarrow \text{Cd}^{2+} + 2\text{e}^-$	-0.401
$\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$	-0.230
$\text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}^-$	-0.126
$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	0.000 by definition
$\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + \text{e}^-$	+0.223
$2\text{Hg} + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{e}^-$	+0.268
$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$	+0.340
$\text{Cu} \rightarrow \text{Cu}^+ + \text{e}^-$	+0.522
$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$	+0.799
$\text{Au} \rightarrow \text{Au}^{3+} + 3\text{e}^-$	+1.420
$\text{Au} \rightarrow \text{Au}^+ + \text{e}^-$	+1.680

Table 1 [2]

C. Equivalent circuit model

An electrode can be modeled by a circuit (Fig. 3) that includes a battery representing the half-cell potential, a capacitor representing the electrical double layer, and resistors that represents the flow of Faradic (non-capacitive) current across the electrode-electrolyte interface and in the electrolyte.

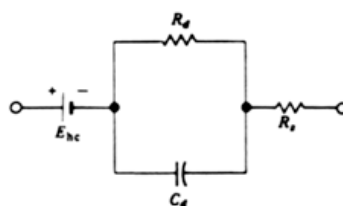


Figure 3
[2]

Figure 5.9 Equivalent circuit for a biopotential electrode in contact with an electrolyte E_{hc} is the half-cell potential, R_d and C_d make up the impedance associated with the electrode-electrolyte interface and polarization effects, and R_s is the series resistance associated with interface effects and due to resistance in the electrolyte.

With this model, one predicts the following frequency-dependence for the electrode impedance. Thus, electrode impedance drops at high frequencies.

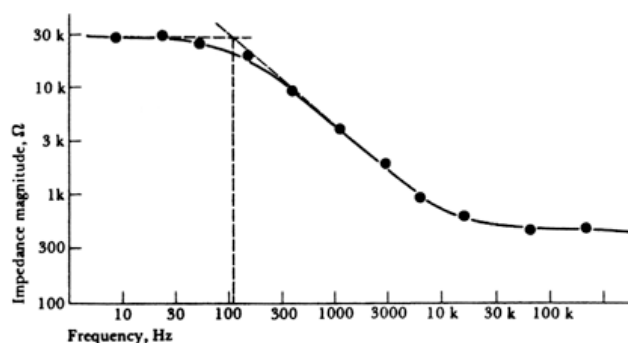


Figure 4
[2]

Figure E5.1 Experimentally determined magnitude of impedance as a function of frequency for the electrode system of Example 5.4.

Other circuit models of the electrode with varying complexity are shown in Fig. 5.

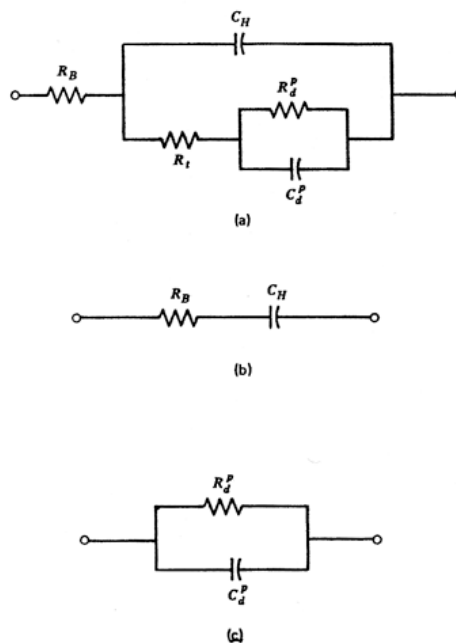


Figure 5 [1]

Figure 10.2. Model of Figure 10.1 including resistance polarization effects: (a) complete model; (b) high-frequency approximation; and (c) low-frequency approximation.

D. Warburg impedance (diffusional effects)

The current that flows across from electrode to solution depends not only on the flux of current across the electrode interface (e.g., Eq. 1), but also on the rate of diffusion of ions within the solution to and from the interface. If diffusion is the rate-limiting step, theory suggests that the resistance and reactance of the electrode impedance are frequency-dependent, varying as $f^{0.5}$ (actually, $1/f^{0.5}$). The Warburg impedance appears as the parallel combination of R_d^P and C_d^P in panel *a* of Fig. 5. The Warburg impedance can also be represented by a series combination of R and C , both of which again depend on $f^{0.5}$. Measurements of series R and C show that they are indeed, frequency-dependent, and for the case of a stainless-steel electrode placed in saline (Fig. 6), the frequency dependence is close to $f^{0.5}$.

Figure 6 [3]

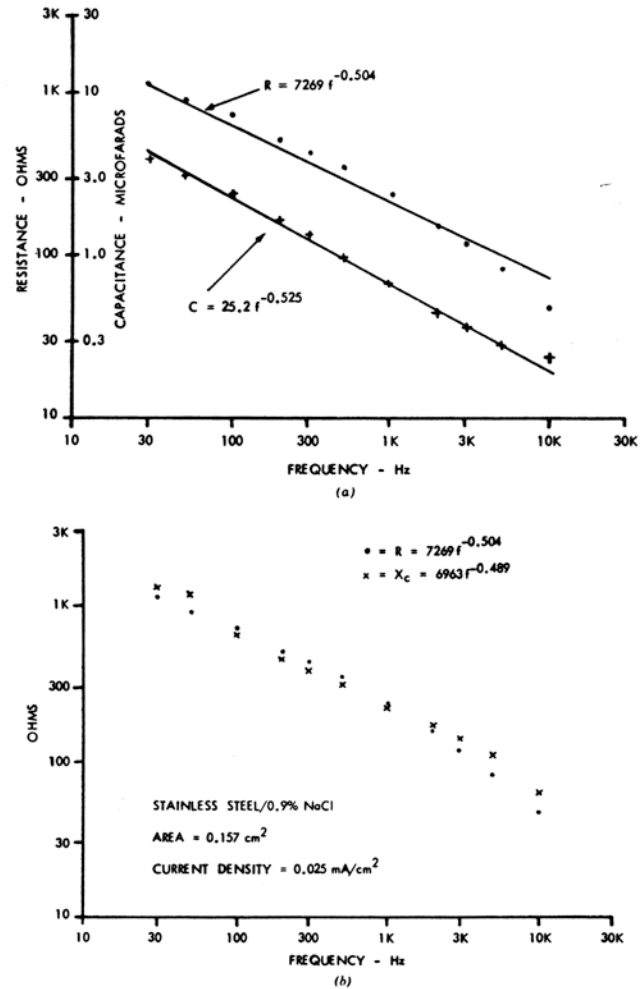


Figure 12 Stainless steel 0.9% saline electrode-electrolyte interface measured with a current density of 0.025 mA/cm² over a frequency range from 20 Hz to 20 kHz. (a) Series-equivalent resistance R and capacitance C ; (b) series-equivalent resistance R and reactance $X = \frac{1}{2} \pi f C$. [From L. A. Geddes et al., *Med. Biol. Eng.* 9:511-521 (1971). By permission.]

E. Impedance varies with current density

Complicating the picture further is that electrode impedance varies with the magnitude of current passing across the electrode. Shown in Fig. 7 are measurements of R and C for a series RC representation of a stainless steel electrode in saline, as a function of current density and frequency. At high currents, R decreases whereas C increases, so that both resistance and reactance decrease at high current densities.

Figure 7 [2]

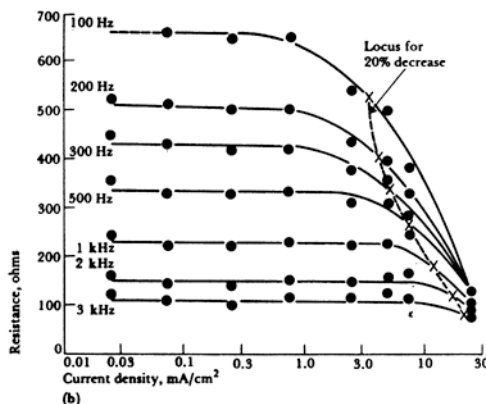
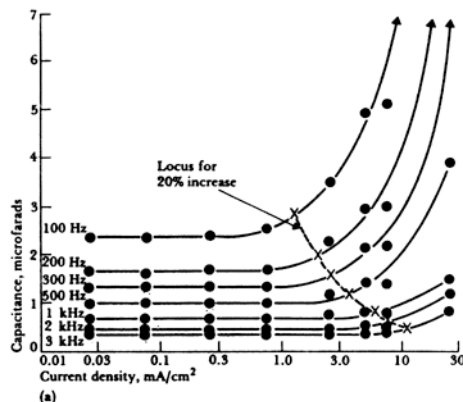


Figure 5.8 (a) Dependence of capacitance value on current density and frequency, given that the impedance of a stainless steel electrode in contact with physiological saline is represented as a series RC circuit. (b) Relationship among series resistance, frequency, and current density for the electrode of part (a). (From L. A. Geddes, C. P. DaCosta, and G. Wise, "The Impedance of Stainless Steel Electrodes," *Medical and Biological Engineering*, 1971, 9, pp. 511–521.)

2. NON-POLARIZABLE (REVERSIBLE) ELECTRODES

A. Non-polarizable vs polarizable electrodes

Let's go back to our diagram of the metal/electrolyte interface for electrodes of the first kind.

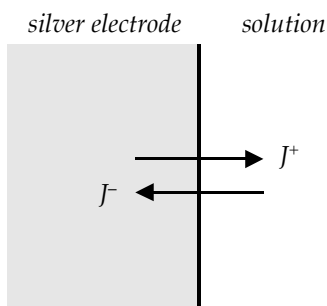
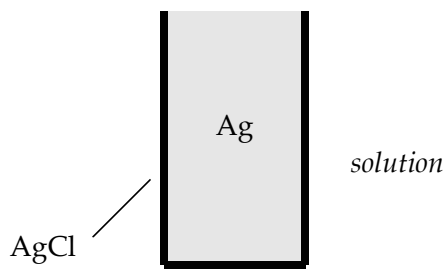


Figure 8

Here, J^+ and J^- refer to the unidirectional currents associated with electrochemical fluxes across the interface. At equilibrium, with no net current across the interface, J^+ and J^- are equal to each other (call it J_0). If J_0 is small, then little or no ion flux can occur across the interface, and charge is transferred primarily as displacement (capacitive) current. As a consequence, large changes can occur in the diffuse charge layer of the electrolyte next to the electrode, and the half-cell potential of the electrode is unstable. On the other hand, if J_0 is large, then Faradic current passes freely across the interface without greatly affecting the electrical double layer, and the half-cell potential is highly stable. The former situation is associated with a *polarizable electrode*, whereas the latter is associated with a *non-polarizable electrode*.

An example of a non-polarizable electrode is an *electrode of the second kind*. This electrode consists of a metal immersed in an electrolyte which forms a salt consisting of a metal cation and an electrolyte anion on the surface of the electrode. The most commonly used electrode of the second kind is a Ag/AgCl electrode (Fig. 9). Another electrode of the second kind is the calomel electrode, which consists of Hg/Hg₂Cl₂.

Figure 9



The AgCl coating is porous and allows the flow of current through it. The electrochemical reactions at the interface are now,



The half-cell potential is given by,

$$E_{hc} = E_{\text{Ag}/\text{Ag}^+}^0 + \frac{RT}{F} \ln a_{\text{Ag}^+} \quad (4a)$$

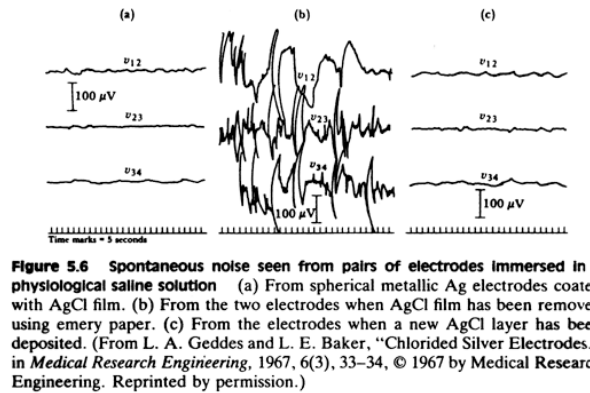
$$= E_{\text{Ag}/\text{Ag}^+}^0 + \frac{RT}{F} \ln K_s - \frac{RT}{F} \ln a_{\text{Cl}^-} = 0.224\text{V} - \frac{RT}{F} \ln a_{\text{Cl}^-} \quad (4b)$$

where K_s is the solubility product relating the activity of Ag^+ to that of Cl^- . Because electrodes of the second kind have stable half-cell potentials, they are often used as reference electrodes.

B. Ag/AgCl electrodes are less noisy compared with bare Ag electrodes

The greater stability of the half-cell potential of electrodes of the second kind compared with that of electrodes of the first kind is illustrated in Fig. 10.

Figure 10 [2]



C. Ag/AgCl electrodes exhibit less motion artifact compared with Ag electrodes

Electrode motion can greatly perturb the diffuse charge layer of metal anions associated with electrodes of the first kind, whereas with electrodes of the second kind the half-cell potential depends on the anion concentration in solution (which remains constant with motion) and not metal cation concentration. Thus, electrodes of the second kind are much less noisy compared with electrodes of the first kind.

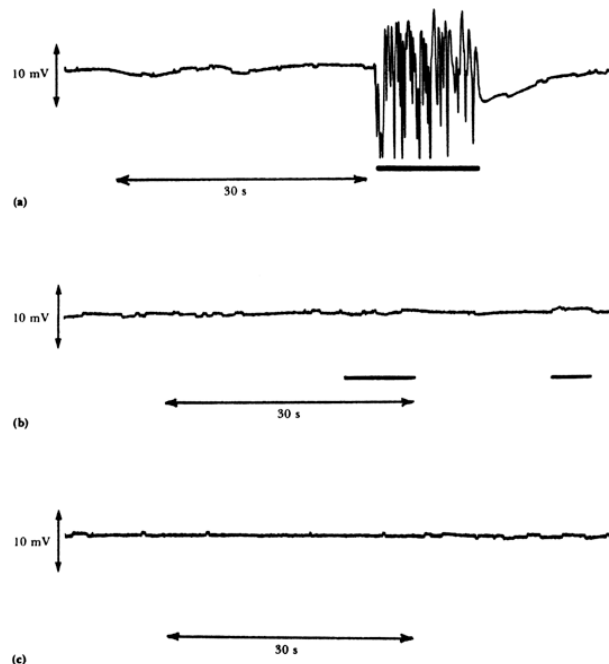


Figure 11 [2]

D. Ag/AgCl electrodes have lower impedance at higher frequencies

Figure 12 [2]

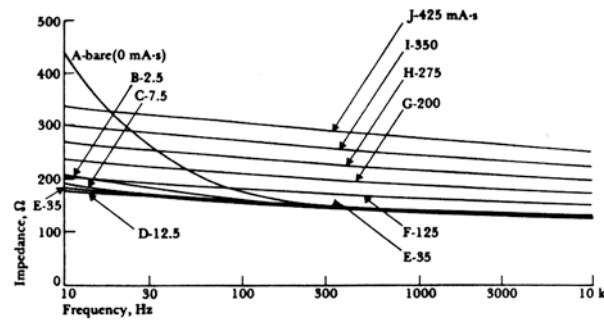


Figure 5.10 Impedance as a function of frequency for Ag electrodes coated with an electrolytically deposited AgCl layer. The electrode area is 0.25 cm^2 . Numbers attached to curves indicate number of mA·s for each deposit. (From L. A. Geddes, L. E. Baker, and A. G. Moore, "Optimum Electrolytic Chloriding of Silver Electrodes," *Medical and Biological Engineering*, 1969, 7, pp. 49–56.)

E. Ag/AgCl electrodes are light sensitive

Silver halides such as AgCl are light sensitive, and undergo a reduction reaction with light energy, resulting in the formation of atomic Ag. This process results in a dark spot and is the basis of photographic film. The same reaction results in a change in the electrode potential of Ag/AgCl electrodes and thus, produces light artifacts.

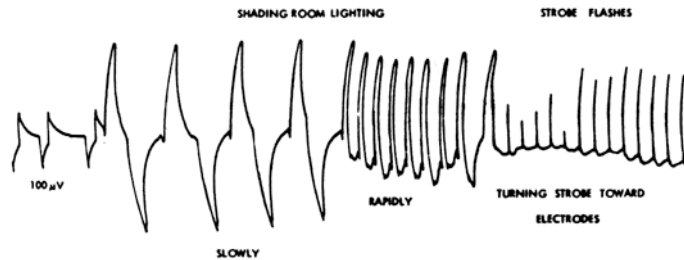


Figure 13 [3]

Figure 7 The photosensitivity of a pair of chlorided silver electrodes in 0.9% saline in a lighted room. After the $100 \mu\text{V}$ calibration, the electrodes were shaded and exposed to light by slowly and rapidly casting a shadow on them by placing the hand above them. Then the light from a flashing stroboscope was directed toward the electrodes to evoke a similar photovoltaic effect due to the action of light on the electrode-electrolyte double layer of charge. [From L. A. Geddes, *Am. J. EEG Technol.* 13:195–203 1973. By permission.]

3. SKIN ELECTRODES

A. Skin section

Skin has a multilayered structure, including the epidermis, dermis and subcutaneous layer as shown in Fig. 14. This results in a tissue with electrical properties that can be represented by the equivalent circuit shown in the next section.

Figure 14 [2]

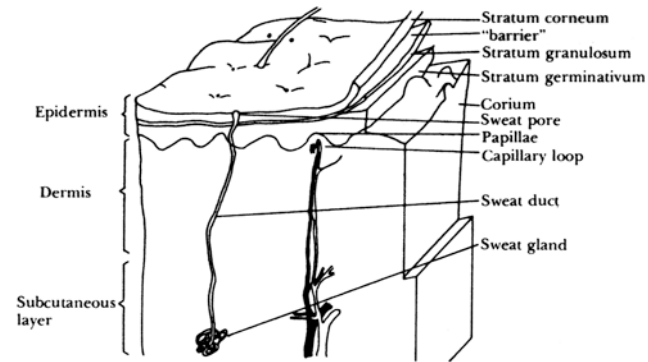


Figure 5.11 Magnified section of skin, showing the various layers (Copyright © 1977 by The Institute of Electrical and Electronics Engineers. Reprinted, with permission, from *IEEE Trans. Biomed. Eng.*, March 1977, vol. BME-24, no. 2, pp. 134–139.)

B. Equivalent circuit

Shown in Fig. 15 is the total equivalent circuit for a skin electrode. There are separate sections that represent the electrode, electrode gel (used to moisten the skin and reduce the epidermal impedance, and reduce motion artifact), epidermis, and subcutaneous layer.

Figure 15 [3]

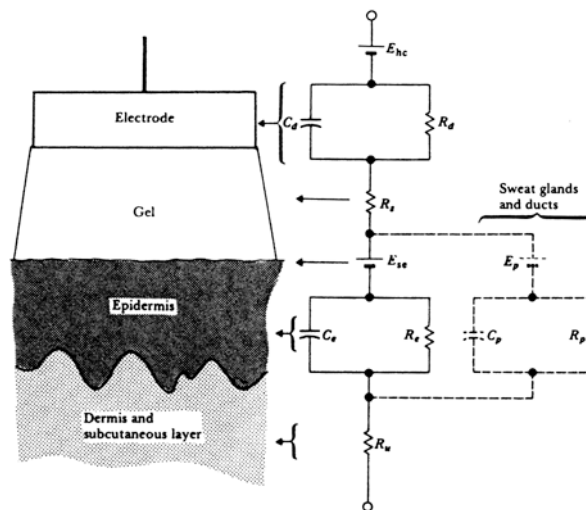


Figure 5.12 A body-surface electrode is placed against skin, showing the total electrical equivalent circuit obtained in this situation. Each circuit element on the right is at approximately the same level at which the physical process that it represents would be in the left-hand diagram.

C. Foam pad and flexible electrodes

A variety of body-surface electrodes used for biopotential measurements is shown in Fig. 16. Perhaps the most familiar are the disposable foam-pad electrodes, which are used for measurements of the electrocardiogram.

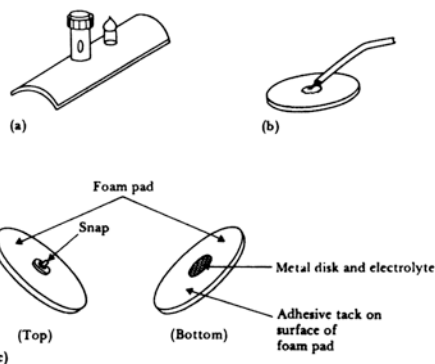


Figure 16 [2]

Figure 5.14 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 electrocardiographic monitoring apparatus.

X

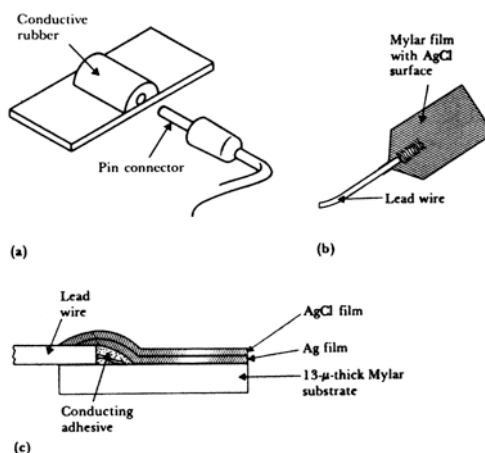


Figure 17 [3]

Figure 5.17 Flexible body-surface electrodes (a) Carbon-filled silicone rubber electrode. (b) Flexible thin-film neonatal electrode (after Neuman, 1973). (c) Cross-sectional view of the thin-film electrode in (b). [Parts (b) and (c) are from International Federation for Medical and Biological Engineering, *Digest of the 10th ICMBE*, 1973.]

D. Percutaneous electrodes

Percutaneous electrodes (which cross the skin) are used record biopotentials from the underlying skeletal muscle (Fig. 18). In one variant, the electrode is inserted into the bore of a hypodermic needle (which is used for insertion), and contains a barbed tip to hold the electrode in place when the needle is withdrawn. The electrode wire is often coiled to increase electrode flexibility.

Figure 18 [2]

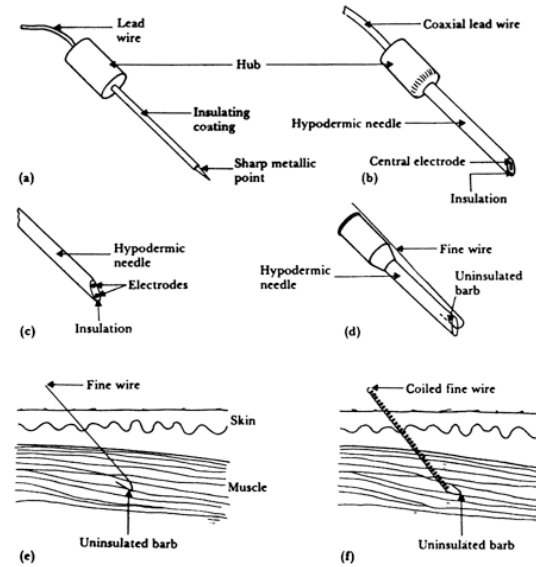


Figure 5.19 Needle and wire electrodes for percutaneous measurement of biopotentials (a) Insulated needle electrode. (b) Coaxial needle electrode. (c) Bipolar coaxial electrode. (d) Fine-wire electrode connected to hypodermic needle, before being inserted. (e) Cross-sectional view of skin and muscle, showing fine-wire electrode in place. (f) Cross-sectional view of skin and muscle, showing coiled fine-wire electrode in place.

References

1. Cobbold, R. S. C. Tranducers for Biomedical Measurements: Principles and Applications. Chaps. 9, 10. John Wiley & Sons, New York, 1974.
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3. Neuman, M. R. Biopotential electrodes. In: Medical Instrumentation Application and Design, J. Webster, ed. Chap. 5. Houghton Mifflin Co., Boston. 1992.