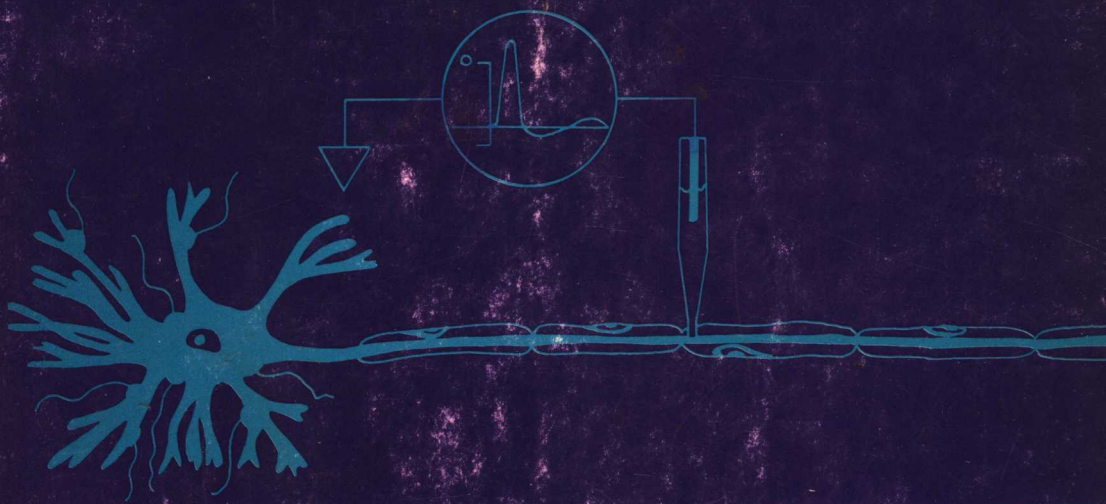
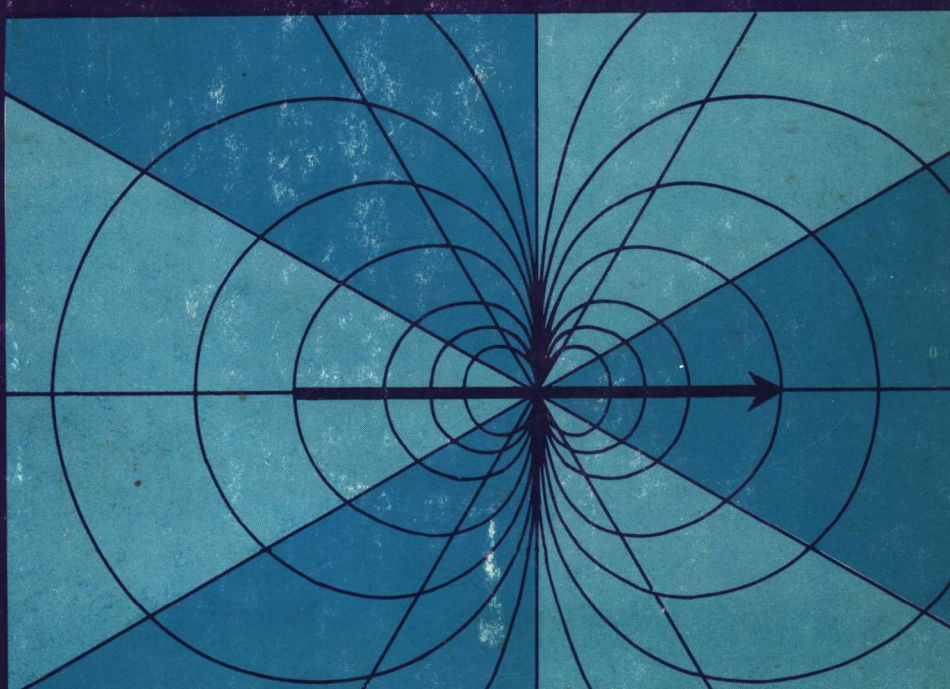
ELECTRODES AND THE MEASUREMENT OF BIOELECTRIC EVENTS

L. A. GEDDES





ELECTRODES AND THE MEASUREMENT OF BIOELECTRIC EVENTS

L. A. GEDDES

Baylor College of Medicine
Houston, Texas

WILEY-INTERSCIENCE, a Division of John Wiley & Sons, Inc.
New York • London • Sydney • Toronto

Library of Congress Catalog Card Number: 75-180270

ISBN 0-471-29490-X

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

Preface

This book is written both for the life scientist and the physical scientist who are faced with the problems associated with the measurement of bioelectric events. Selecting the correct types of electrodes and knowing their characteristics is surely the starting point. Contained in the chapters that follow is a large amount of practical information relating to the fabrication of electrodes and their electrical characteristics. The electrodes described range in size from those used to record the electrocardiogram of a submerged whale to those small enough to record the transmembrane potential of a single living cell. In the application of theoretical principles, mathematical derivations are held to a minimum. Wherever possible, the stories told by mathematical expressions are presented graphically – a method that is most familiar to the life scientist and indeed is the method used by the physical scientist when dealing with complex systems in which it is difficult to define or measure all the underlying components.

There seems to be an aura of mystery surrounding the construction and electrical properties of electrodes; the author has sought to remove some of it by describing the properties of electrodes in quantitative terms wherever possible. Thus the book opens with a discussion of the properties of the common denominator in virtually all electrode systems, the electrode-electrolyte interface. Following this there is a description of the skin; then the various types of electrodes are discussed in detail. Insofar as possible, measured data are given for each type. Some of these data were already available to the reader and the author; where gaps were found to exist, the author has made an effort to fill them by measurements in his own laboratory. For the reader who wishes to consult original sources, an extensive bibliography has been included.

This book constitutes the first compilation of data on the electrodes presently used to measure bioelectric events. From the data presented, the reader should be able to construct electrodes of his own design and predict, with fair accuracy, their characteristics and properties.

Because there are many who desire to use and understand the properties of electrodes, the author has included six easily conducted experiments in an ap-

pendix. These experiments were selected on the basis of their fundamental importance to the measurement of bioelectric events. To the ingenious instructor they can serve as the starting point in the design of additional experiments.

This book derives its origin from the early and mid-1940s when the fields of clinical electromyography and electroencephalography were being developed; at this time the first transmembrane potentials were being measured with micropipets. Also at this time the author was fortunate enough to be working with Wilder Penfield and Herbert Jasper, two of the pioneers of applied and basic electrophysiology. This fortunate association, which lasted for a period of eight years, placed the author in contact with the many fascinating problems in electrophysiology and gave him ample opportunity to test his ideas for the solution of some of them. It also permitted the author to initiate courses for the fellows and residents who were conducting research in this field. From this initial exposure and that which followed during the years from 1952 to the present, when the author came under the guidance of Hebbel Hoff, the nature of bioelectric events and the absorbing problems connected with their measurement became clear. From these fortunate contacts, and because so many life and physical scientists now desire to measure bioelectric events, the author has collected the information and experience he has accumulated and has tried to present a logical and practical analysis of the problems encountered in the measurement of bioelectric events.

The electrodes from which data were obtained were fabricated by the author's team. Therefore, for all phases of measurement and data processing, special thanks and appreciation must go to A. G. Moore and J. Bourland who direct the activities of the mechanical and electronics laboratories in the Division of Biomedical Engineering. Supporting them with their considerable talents were M. Hinds, G. Cantrell, T. Coulter, J. Vasku, C. Martinez, and E. Arriga. Special thanks must go to Carter Jordan and Narvin Foster who were always ready to prepare the animals (no matter how large or small, docile or dangerous) needed for the studies. Recognition must also be accorded to Dr. Lee E. Baker, the author's collaborator in many of the studies and to Gary Wise and Dr. L. E. Geddes, who verified the experiments that appear in the appendix. Dr. G. Greeley of Texas A & M College of Veterinary Medicine is commended for his patience and skill in composing the frog drawings, made while the author demonstrated the various techniques. Dr. J. Bear of the Department of Chemistry of the University of Houston and Dr. Max Valentinuzzi of Baylor are hereby thanked for their reading of selected parts of the book. Special thanks must go to Miss Lucia Bonno, secretary to the Division of Biomedical Engineering, and to Diane Moffitt, her successor, who converted almost illegible notes and rough drafts into manuscript form which was considered worthy of publication.

Perhaps the greatest appreciation should go to the many students with genuinely inquiring minds with whom the author has been fortunate enough to

be associated; for it was mainly their desire for knowledge that prompted the author to seek out pertinent information wherever it could be found. Without the contributions of all the persons mentioned, there would have been no book and no experiments.

Houston, Texas
September 1971

L. A. GEDDES

Contents

Introduction

Interest in electrodes originated with Galvani's three frog-muscle contraction experiments* (ca. 1800); the first dealt with stimulation by electrostatic induction, the second with stimulation by electrode potentials and the third truly demonstrated bioelectricity. It was the research carried out by Volta, because of Galvani's explanation of his second experiment, that resulted in the discovery of current electricity produced by what is now known as the galvanic or voltaic cell, consisting of two dissimilar metal electrodes in an electrolyte. Physical scientists devoted their attention to the design of electrodes to obtain the maximum amount of electrical energy from such cells; electrophysiologists concerned themselves with developing electrode pairs that produced no potential difference so that the voltage measured between electrodes encompassing living cells was biological in origin.

In the measurement of a bioelectric event (except when insulated electrodes are used), the two electrodes are always in contact with electrolytes; for this reason it is necessary to know the nature and properties of an electrode-electrolyte junction in order to interpret correctly, with an instrument of known properties, the potential difference measured between the electrode terminals. Therefore, considerable attention is devoted to an accurate description of this junction as it participates in the measurement of bioelectric signals.

Despite the many different configurations and names applied to electrodes used to measure bioelectric events, there are basically only two functional types, extracellular and intracellular. Extracellular electrodes, which take the form of plates or screens, are placed on the integument or on tissues; in the form of probes they are inserted below the integument to establish better contact or to bring the electrode closer to the source of the biopotential, the ionic gradient that exists across all cell membranes. Extracellular electrodes are large and usually distant with respect to the dimensions of the cells on which

* See Geddes and Hoff 1971.

the measurements are made. Intracellular electrodes are much smaller than the cells under study and hence can be advanced through cell membranes without damage. In practice, intracellular electrodes (very slender pointed needles of metal or glass micropipets) usually have diameters in the range of 0.5 to 1.5 μ (microns). In the following chapters, the various electrodes used for the measurement of bioelectric events are described and insofar as possible, their electrical properties are presented. From these data the reader should be able to estimate the appropriateness of an electrode type and a measuring instrument for the measurement of a bioelectric event.

1

The Electrode-Electrolyte Interface

When a metallic electrode is placed in an aqueous solution, there is a tendency for the metal ions to enter into solution; there is also a tendency for ions in the solution to combine with the electrode. Although details of the reaction may be complex in a given situation, the net result is a charge distribution at the electrode-electrolyte interface and its spatial arrangement depends on the way in which the electrode metal reacts with the electrolyte. Several forms of charge distribution are possible; the simplest was conceived by Helmholtz (1879), who described the electrical double layer, later called the Helmholtz layer. He proposed the arrangement (Fig. 1-1*a*) which represents a layer of ions tightly bound to the surface of the electrode and an adjacent layer of oppositely charged ions in the solution; with such a simple arrangement the potential distribution would be as shown. Because of the thermal motion of ions, it was believed that the simple Helmholtz electrical double layer was not adequate to describe the environment of an electrode, Gouy (1910) suggested another charge distribution in which the fixed (Helmholtz) layer of negative charge was not enough to balance the positive charge of the electrode. To satisfy this requirement, he proposed the existence of a diffuse charge distribution adjacent to the Helmholtz layer. Gouy's arrangement of a fixed and diffuse layer and the accompanying potential distribution appear in Fig. 1-1*b*. Stern (1924) believed that the fixed layer could contain more negative charges than are required to balance the positive charges on the electrode. This situation, in combination with the diffuse Gouy layer, is presented in Fig. 1-1*c*, along with the expected potential distribution. Either combination of a fixed and diffuse layer is called a Stern layer. It is also possible for the charge distribution to consist entirely of a diffuse Gouy layer and to exhibit the potential distribution in Fig. 1-1*d*. As stated previously, the particular charge distribution that exists depends on the species of metal used for the electrode and the type of electrolyte. It is the ionic distribution that endows an electrode with its properties.

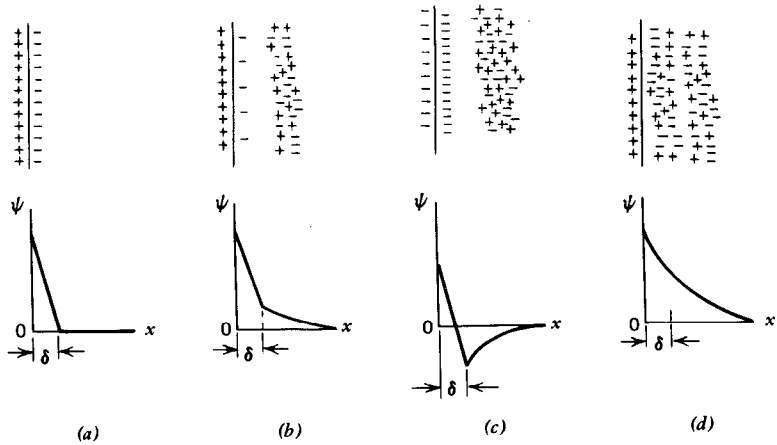


Fig. 1-1. Various configurations of charge and potential distribution at an electrode-electrolyte interface: (*a*) Helmholtz (1879); (*b*) Gouy (1910); (*c*) Stern (1924); (*d*) pure Gouy.

Parsons (1964) described electrodes in terms of the reactions at the double layer. Electrodes in which no net transfer of charge occurs across the metal-electrolyte interface were designated by him as perfectly polarized. Those in which unhindered exchange of charge is possible are called perfectly non-polarizable. Real electrodes have properties that fall between these idealized limits. It should be apparent by this definition that a truly polarized electrode has all the characteristics of a capacitor. MacInnes (1961) stated that the term "electrode polarization" is used in two ways: as previously, and to refer to the condition when an electrode-electrolyte potential is altered by the passage of a current.

Electrode Potential

As a result of the particular charge distribution that occurs when an electrode contacts an electrolyte, the electrode acquires a potential. Because it is not possible to measure the potential of a single electrode with respect to a solution, and because it is impractical to tabulate the various potential values attained between electrodes of different metals in a variety of electrolytes, electrode potentials are measured with respect to a standard electrode that is easily reproduced in the laboratory; such an electrode is the standard hydrogen electrode (SHE). Although choice of a particular reference electrode fixes electrode potentials with respect to it, it does not effect the difference in potential measured between two electrodes in an electrolyte; in fact it permits calculation of the potential difference by subtraction of the individual potentials measured with respect to the SHE.

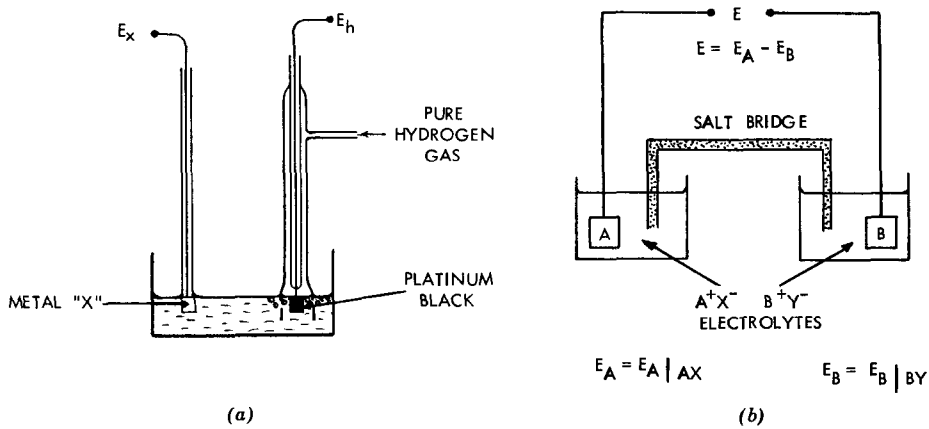


Fig. 1-2. Electrode potential: (*a*) measurement of electrode potential with the standard hydrogen electrode; (*b*) the Galvanic (Voltaic) cell.

The standard hydrogen electrode (Fig. 1-2*a*)* consists of a platinum-black electrode in contact with a solution (usually HCl) containing hydrogen ions of unit activity and dissolved molecular hydrogen; the activity of the latter is specified by requiring it to be in equilibrium with hydrogen at 1 atmosphere in the gas phase. The platinum black has a large capacity for absorbing hydrogen and probably acts as a catalyst to convert the hydrogen to its ionic form. The hydrogen gas is bubbled over the electrode and the cell is operated at 1 atmosphere. The potential of such an electrode is defined as zero at all temperatures, a fact that is contrary to physical reality but can be circumvented by identifying the temperature at which the measurement of electrode potential is made.

If an electrode of element X is placed in the electrolyte (of unit activity) with the SHE, a galvanic or voltaic cell is created and a potential difference can be measured; the potential will, of course, be relative to that of the hydrogen electrode. Because the potential of the latter is defined as zero, potential measured is called the electrode potential (E_X^0) for the metal X; Table 1-1 lists the electrode potentials for a variety of metals used as electrodes.

If a second electrode X′ of the same metal (X) is placed in the electrolyte, the same potential will be measured between the hydrogen electrode; that is $E_{X'}^0 = E_X^0$. If the potential is measured between electrodes X and X′, the value obtained will be zero.

When two electrodes of different metals X, Y are placed into any electrolyte,

* The first practical hydrogen electrode was introduced by Hilderbrand, who described its properties in 1913; it later became the standard hydrogen electrode.

Table 1-1 Electrode Potentials for Commonly used Materials in Electrodes[a] (E^0 values)

Metal and Reaction	Potential ($E^0_{25°C}$) (V)	Temperature Coefficient (mV/°C)
$Al = Al^{3+} + 3e^-$	−1.662	+1.375
$Zn = Zn^{2+} + 2e^-$	−0.7628	+0.962
$Zn\ (Hg) = Zn^{2+} + Hg + 2e^-$	−0.7627	—
$Cr = Cr^{3+} + 3e^-$	−0.744	+1.339
$Fe = Fe^{2+} + 2e^-$	−0.4402	+0.923
$Cd = Cd^{2+} + 2e^-$	−0.4029	+0.778
$Ni = Ni^{2+} + 2e^-$	−0.250	+0.93
$Pb = Pb^{2+} + 2e^-$	−0.126	+0.420
$Pt(H_2)H^+$	0	—
$Ag + Cl^- = AgCl + e^-$	+0.2225[b]	+0.213
$Cu = Cu^{2+} + 2e^-$	+0.337	+0.879
$Cu = Cu^+ + e$	+0.521	+0.813
$2\ Hg = Hg_2^{2+} + 2e^-$	+0.788	—
$Ag = Ag^+ + e^-$	+0.7991	−0.129
$Pt = Pt^{2+} + 2e^-$	+1.2 approx.	—
$Au = Au^{3+} + 3e^-$	+1.498	—
$Au = Au^+ + e^-$	+1.691	—

[a] From A. J. de Bethune, in *Handbook of Electrochemistry*, C. A. Hampel, Ed., New York: Reinhold, 1964.
[b] MacInnes (1939).

a galvanic cell is created whose potential depends on four factors: the difference in the potentials of the individual electrodes (E_X^0, E_Y^0 in Table 1-1), the temperature, the concentration of the electrolyte, and the manner in which the electrode metals react with the electrolyte. Although the potential of a galvanic cell is sometimes quite difficult to calculate, the underlying principles can be illustrated by a simple model. Consider a galvanic cell consisting of two metal electrodes A and B, each dipping into an electrolyte which is a salt of each metal (Fig. 1-2*b*); connection between the two electrolytes is established by a salt bridge (see p. 18) to avoid the creation of a liquid-junction or diffusion potential. Thus the galvanic cell consists of the two following half-cells:

$$E_{1/2A} = E^0_{A^{n+}} - \frac{RT}{nF} \ln A_{A^{n+}}$$

$$E_{1/2B} = E^0_{B^{n+}} - \frac{RT}{nF} \ln A_{B^{n+}}$$

In these expressions, the E^0 values are the standard electrode potentials measured with respect to the hydrogen electrode (Table 1-1), T is the absolute temperature, R is the gas constant, n is the valence, A is the activity of the

metal ions in the electrolyte, and F is the faraday; the activity is, of course, proportional to the concentration.

The potential difference E_{AB} of such a voltaic cell is the difference between the two half-cell potentials $E_{1/2A}$ and $E_{1/2B}$; therefore

$$\begin{aligned} E_{AB} &= E_{1/2A} - E_{1/2B} \\ &= E^0_{A^{n+}} - E^0_{B^{n+}} - \frac{RT}{nF} \ln \frac{A_{A^{n+}}}{A_{B^{n+}}} \end{aligned}$$

Note that the potential of the voltaic cell is composed of two parts: one (usually the larger) that is the difference in the half-cell potentials of the metals measured with respect to the hydrogen electrode and a second (usually smaller) that is due to the concentrations (strictly activities) of the metal ions in solution. (It should be recalled that in this simple example, a liquid-junction potential was eliminated by the use of a salt bridge.)

When electrodes are applied to a subject to measure a bioelectric event, a galvanic cell is created because each electrode is in contact with an electrolyte, which may be electrode paste, saline solution, or tissue fluids. Therefore, the actual potential measured between the electrode terminals will have several origins, and the magnitude of each may be difficult to establish accurately in a particular situation. Nonetheless it should be remembered that there exist two electrode potentials between the electrode terminals, and these potentials may not be equal. Obviously if electrodes of the same metal contact the same electrolyte, the net electrode potential will be zero. There will, however, be a net electrode potential if the same metals are in contact with solutions of differing concentrations or if different metals are in contact with the same electrolyte. If different metals are in contact with different electrolytes, there may be a liquid-junction potential in addition to the electrode potentials.

The best way of minimizing the existence of an electrochemical potential difference between the electrodes is to use electrodes made from the same metal, arranging to have them in contact with the same electrolyte. Even when this precaution is taken, there is often a small residual potential difference which is not always stable. The residual potential is probably due to differences in surface contamination of the two electrodes or to slight differences within the electrode metal. Usually a residual potential difference can be tolerated and canceled with an opposing voltage. When capacitively coupled recording systems are used, a residual potential is not coupled into the measuring instrument. However, residual potentials are not always stable and they fluctuate randomly, adding artifact to the record of the bioelectric event. It should be emphasized that in most instances the biopotentials measured, especially with extracellular electrodes, are of the order of a few millivolts. This requires that random variations in electrode potentials be small with respect to the magnitude of the biopotential.