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Alternating Current Electrode Polarization*

H. P. Schwan

Electromedical Division, The Moore School of Electrical Engineering
University of Pennsylvania, Philadelphia, Pennsylvania

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This article attempts to summarize principles about electrode polarization as observed with alternating currents. The significance of alternating current electrode polarization in biological impedance work is discussed.

1. Definition of Electrode Polarization Impedance

Errors in determinations of biological impedances are frequently caused by electrode polarization phenomena which arise at the boundaries between the electrodes and the sample of interest. Electrode polarization is particularly disturbing in the case of highly conducting materials as presented by most biological samples and at low frequencies, which are of predominant interest in physiological research. It can also be disturbing in the case of measurement of biologically generated potentials (EEG, EKG, myography) even though high input impedance measuring equipment is used. A great deal of work has been and is performed without proper knowledge of electrode polarization, thus yielding erroneous results. The fundamentals of AC-electrode polarization are not generally known. Hence the following contribution is considered appropriate. It includes older work and more recent results from our laboratory.

If a metallic electrode is immersed in a solution or cellular suspension or inserted into tissue, a DC-boundary potential V_o is usually found to exist between the electrode and the fluid establishing contact with the electrode. Passage of a current will evoke a readjustment of the potential which is not instantaneous. Clearly, the readjustment can not anticipate the change in current and will follow it with a speed which is determined by the particular kinetics involved. If an alternating current i is passed through the electrode, the DC-polarization potential V_o becomes modulated with an alternating potential and the phase of the modulation potential $V(\sim)$ will lag that of the current, (Fig. 1). The modulation potential $V(\sim)$ is proportional to the alternating current, provided that the current is kept sufficiently small. This may be seen from the series development

$$V(\sim) = a_0 + a_1 i + a_2 i^2 + \ldots \tag{1}$$

where $a_0 = 0$ by definition of $V(\sim)$. Hence

$$V(\sim) = a_1 i + a_2 i^2 + \ldots = Z_p i \tag{2}$$

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with

$$Z_p = a_1\left[1 + \frac{a_2}{a_1} i + \ldots\right]. \tag{3}$$

We have observed that the condition "sufficiently small" is usually met if the modulation potential is small in comparison with the DC potential V_o (condition for "linearity"). Thus the alternating current aspect of electrode polarization is best characterized by a capacitive impedance Z_p or admittance. This applies at least in the range of linearity where the polarization impedance Z_p is practically independent of the current passing through the electrode.

The following topics cover various aspects of electrode polarization, as far as they are of practical interest in biological impedance work. They pertain primarily to platinum electrodes which are the best for alternating current work due to two

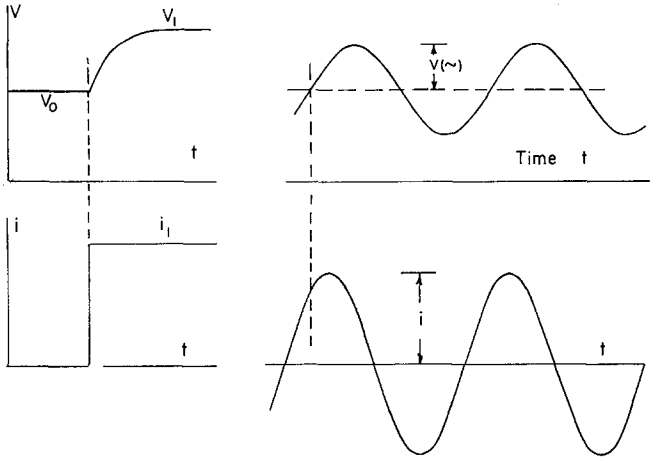

Fig. 1. Response of metal electrode boundary potential in the time domain (left) and frequency domain (right). For details see text

major advantages: Their polarization impedance is lower than that of electrodes made of other material and, perhaps even more important, they permit the application of a fine porous coat of platinum black, which reduces the polarization impedance of the electrode by up to four orders of magnitude ("black" electrodes). Platinum electrodes may be made out of solid platinum or may use a copper or brass base around which a sheet of platinum is wrapped, the latter procedure being cheaper. Following established practice, we shall characterize the polarization impedance $Z_p = R_p - j/\omega C_p$ by its components; namely, polarization resistance R_p and polarization capacitance C_p.

2. Linearity and Superpositioning Principle

The electrode polarization impedance is independent of current density only for small current densities. Limits of this linear behavior have been explored only quite recently (SCHWAN [*15*], SCHWAN and MACZUK [*19*]). Linearity of the impedance of platinum electrodes is maintained for current densities up to a "limit value" of very approximately 1 mA/cm² electrode surface at a frequency of about

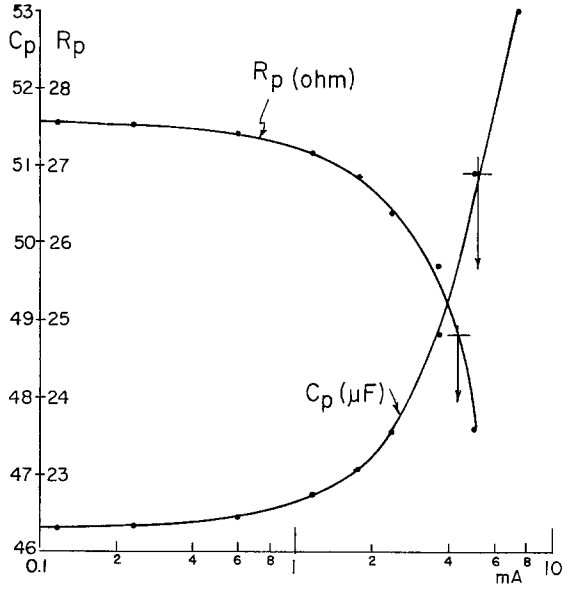

Fig. 2. Polarization capacitance C_p and resistance R_p as function of applied current. Uncoated platinum tip electrode against large reference electrode in 0.1 N KCl at 25 °C. Electrode area about 0.8 cm². Frequency 100 cps. The "limit current of linearity", is indicated by the arrows and here defined by a change of 10%. It is almost the same for the R_p- and C_p-curve. This is to be expected since tan δ changes much less with current than the polarization impedance

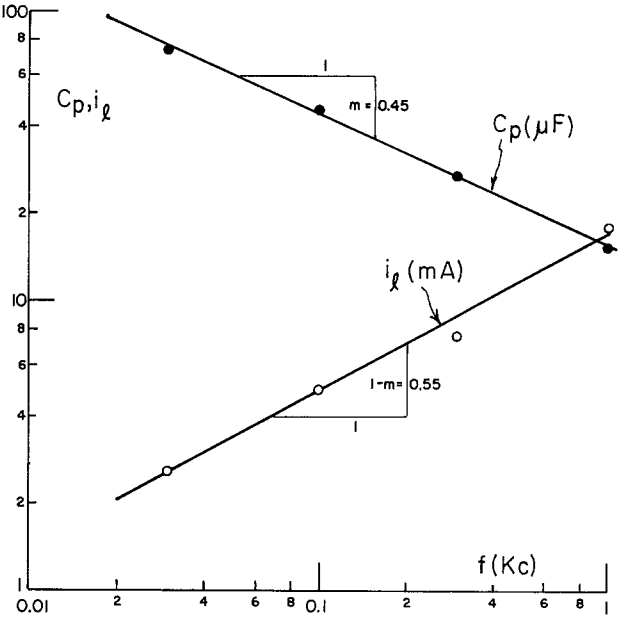

Fig. 3. Polarization capacitance C_p for low current density (closed circles) and limit current of linearity (open circles) as function of frequency. Same electrode and conditions as in Fig. 2. The slopes of the two curves add to 1 in agreement with Eq. (4)

1 Kc (Fig. 2). This limit-value increases with frequency. It appears from our data that the limit of linearity decreases to zero as the frequency approaches zero. Pertinent quantitative work is difficult. Hysteresis effects are observed as current values beyond the limit of linearity are applied, i.e., polarization impedance values do not only change with current density but are also dependent on previously applied currents. However, careful work using appropriate techniques to reduce such hysteresis effects has established the following simple law for the "limit current of linearity" i_l:

$$i_l = A f^{1-m} \qquad \text{with m defined by} \qquad C_p = B f^{-m} \tag{4}$$

f stands for frequency, A and B are constants, m however may vary with frequency. This law (4) has been shown to be a direct consequence of the fact that the evoked boundary potential $V(\sim)$ cannot surpass a frequency independent value (2). Its experimental verification is indicated by the typical example in Fig. 3.

Within the range of linearity the superpositioning principle may be expected to apply if stated as follows: The polarization impedance measured at a frequency f_1 is independent of the presence of other frequency components f_2, f_3, etc. of the current passing the electrode. Even though the polarization impedance changes with frequency, the superpositioning principle applies, as shown by WOLFF [*21*]. Thus, even the presence of strong harmonic content will not affect impedance determinations carried out at a fundamental frequency. This holds provided, of course, that the impedance measuring device is not responsive to harmonics, as may be achieved by use of appropriate filtering techniques.

3. Frequency Dependence of Electrode Impedance

The polarization impedance is traditionally expressed in terms of a series arrangement of a resistor (polarization resistance R_p) with a capacitor (polarization capacitance C_p). The choice of this equivalent circuit is not suggested by any polarization theory and hence is arbitrary. Polarization resistance and capacitance are functions of frequency. Investigations of this frequency dependence have been carried out in good part in the 1930's over various ranges of frequencies (MURDOCK and ZIMMERMANN from 0.05 to 3500 cps [*9*]; WOLFF from 0.2 to 200 Kc [*22*]; JOLIFFE from 0.1 to 2 Mc [*6*]). While each author states that the frequency dependence of the polarization capacitance is in a good approximation characterized by a power function of frequency, disagreement exists as to the value of the power factor. However, the published data fit together if a gradual change of the power factor with frequency is assumed. Electrode polarization affects biological impedance measurements up to more than 100 Kc. Hence it is desirable to present complete curves of R_p and C_p extending over the total frequency range from 10 cps up to 100 Kc. Such measurements have been carried out by the author with a variety of platinum electrodes of different sizes, both uncoated and coated with platinum black. The character of the frequency dependence generally observed is demonstrated by one typical example for both resistance R_p and capacitance C_p in the Fig. 4. The capacitance is usually proportional to $f^{-0.3}$ up to about 1 to 10 Kc. The power factor 0.3 increases then slightly to a value of about 0.5 near 100 Kc. The resistance behavior on the other hand is characterized by a power factor near 0.5 over most of the investigated frequency range. These data pertain

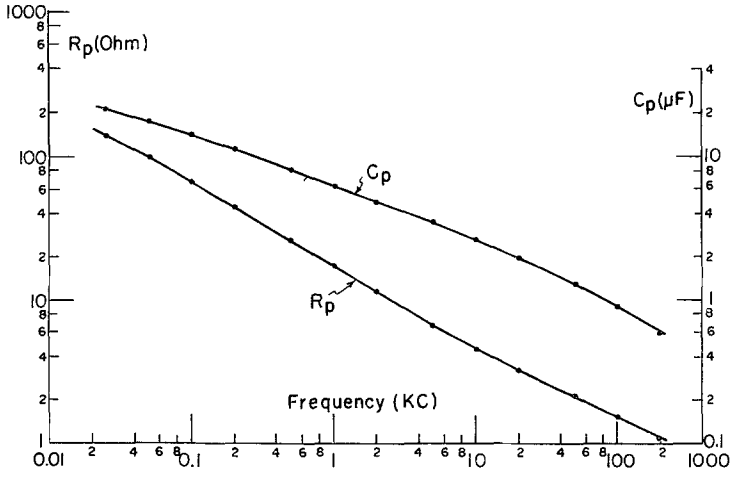

Fig. 4. Typical frequency dependence of C_p and R_p. Platinum electrode with medium cover of platinum black Area 1.4 mm², physiological saline solution

to electrodes with a surface area of more than 1 mm² and vary only moderately with degree of platinum black coating and electrolyte. Very small and micro-electrodes often display quite different characteristics, involving deviations of the power factor up to 50% and more from the values quoted above. However, polarization resistance and capacitance decrease with increasing frequency in any case and this decrease is best characterized by a power function of frequency, where the power factor itself may change with frequency more or less pronouncedly for a given electrode system.

Electrode polarization is characterized by an electrical phase angle δ which is frequency independent, provided that the electrode capacitance C_p changes exactly as a power function f^{-m} of frequency (Fricke, [4]). The Fig. 5 presents

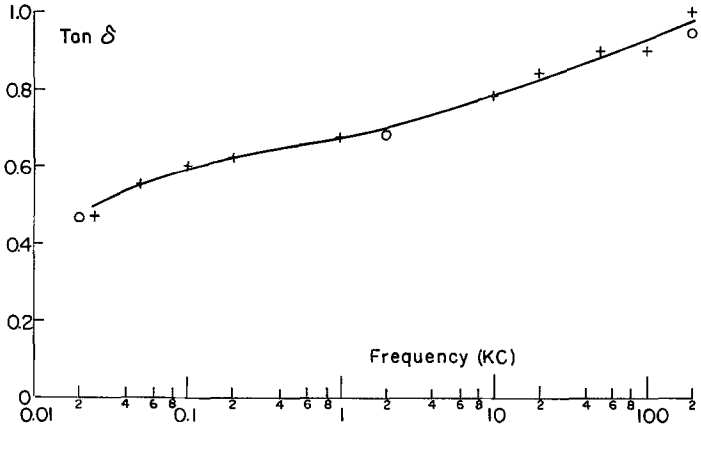

Fig. 5. The loss tangent tan δ as function of frequency for the electrode of Fig. 4. Crosses, experimental results. Circles, calculated from Eq. (5) using the slopes taken from the C_p-curve of Fig. 4

typical values of tan $\delta = R_p \omega C_p$. This quantity is indeed seen to be rather independent of frequency, varying only by a factor of about 2 as the frequency ranges over four decades. FRICKE derived, furthermore, the following relationship assuming frequency independence of m:

$$\delta = \mathrm{m} \frac{\pi}{2} \quad . \tag{5}$$

Since the frequency dependence of C_p is not exactly a power function of frequency, it is to be expected that FRICKE's law applies only approximately. In Fig. 5 experimental values of tan $\delta = R_p \omega C_p$ are compared with some calculated values using Eq. (5) (circles). The values calculated from FRICKE's law (5) are based on the slope of the C_p-curve taken from Fig. 4 at appropriate frequencies. While FRICKE's expression does not always apply exactly, it is seen to provide a rather good approximation for tan δ. Thus it is possible with the help of Eq. (5) to estimate polarization resistance from capacitance and vice versa. This is most useful in view of the often existing difficulty to determine either one of the two quantities R_p or C_p*.

4. Preparation of Electrodes

Experience with the preparation of platinum black coated electrodes obtained in our laboratory is summarized in the following paragraph:

a) Optimal current density for platinum black application. The usual procedure to apply platinum black to platinum electrodes has been worked out by KOHLRAUSCH [*8*]: The electrode is inserted into a solution of 0.025 N hydrochloric acid, containing 0.3% platinum chloride and a trace of lead acetate (0.025%). A DC-current is then passed through the solution, utilizing platinum as a second electrode in order to avoid poisoning of the solution. Platinum is deposited at the electrode to be covered if the latter is arranged as cathode. The current density recommended by KOHLRAUSCH is 30 mA per cm² electrode surface. Pertinent measurements by MACZUK and SCHWAN [*19*] are summarized in the Fig. 6. They demonstrate that a smaller current density than suggested by KOHLRAUSCH achieves considerably higher polarization capacitance values, i.e., lower polarization electrode impedances than possible with KOHLRAUSCH's recipe. It is also recognized that the polarization capacitance passes an optimal value as a function of the amount of platinum deposited, the latter being expressed by the number of applied coulombs. This observation coincides with results reported by JONES and BOLLINGER [*7*]. These authors studied the effect of various amounts of platinum black on C_p and R_p, applying 0.4; 0.8; 1.7; 6; 12; 63 and 110 coulombs/cm² per electrode and using 30 mA/cm² current density. They found minimal polarization impedance in the 63-coulomb/cm² case, i.e., for a value somewhat higher than suggested by the results presented in Fig. 6.

Above stated results apply only for large electrodes. We have observed that electrodes with an effective surface area of less than about 1 mm² require heavier platinizing current densities in order to achieve optimal results. This statement

* In case of a resistance bridge, which does not provide calibrated variable capacitors, C_p can not be determined. In the case of a bridge which does not provide high resolution, R_p is often found to be so small in comparison with the sample resistance that it cannot be noticed.

may appear surprising in view of the seeming inability of any part of the electrode to take cognizance of anything but the current density it receives. But we suspect that factors other than current density, such as the decrease of the current density and field strength with increasing distance from the electrodes, are involved.

b) Stability of electrode impedance. If the current density is much smaller than the one indicated in the Fig. 6 for optimal coating, the platinum is no longer deposited in the finely granular and deep black colored form found desirable. The result is an unsatisfactory electrode from a polarization point of view. If the current density is, on the other hand, much larger, the deposit becomes rather

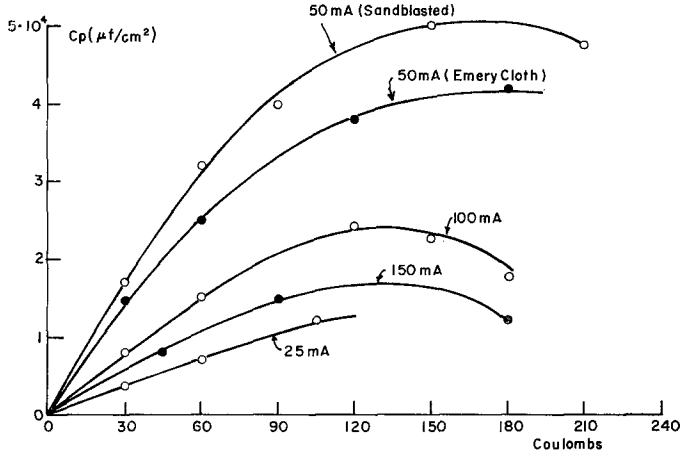

Fig. 6. Polarization capacitance C_p per cm² electrode area as function of platinization. The amount of platinum black applied to the electrodes is measured in terms of coulombs used during the coating process. Electrode area 5 cm². Frequency 20 cps. The data pertain to two identical electrodes in a cylindrical cell and separated by physiological saline solution. Parameter: Current used to apply Pt-black

coarse with a tendency of the black coating to flake off. In this case, the electrode usually deteriorates quite rapidly with use.

Storage of platinum black covered electrodes is best achieved by immersion of the electrodes in distilled water and by keeping them short circuited.

Platinum black covered electrodes always deteriorate with use. In tissue impedance work, the mere insertion of the electrode will often result in the removal of part of the soft platinum black due to friction. But even in the case of biological fluids such as blood or protein suspensions, deterioration results from use. The reasons for this are not clearly understood, but are probably related to the ability of macromolecular components to gradually enter into and thereby affect the porous surface of a platinum electrode covered with platinum black.

c) Cell design for platinization purposes. It is important to control the current flow in order to achieve a rather uniform current density over the total area of the electrode. This control of the electrical current may be achieved with a cell of the type depicted in Fig. 7, a type useful for the platinization of plane electrodes. However, WYATT [*23*] has recently pointed out that gravity may well effect the deposition of the platinum ions. In order to eliminate this effect, gradual rotation

of the electrodes about the cylinder axis is recommended for optimal results. The use of such techniques provides polarization impedances which are often less than half those which would result if the electrodes were merely hung into a large beaker filled with platinum chloride solution and using a large reference electrode as anode. In the latter case substantial variation of current density across the electrode to be covered exists, with consequent impossibility to fully realize optimal platinization in accordance with the data presented in Fig. 6.

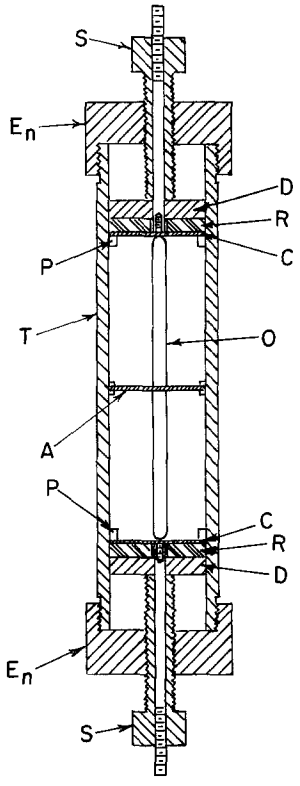

Fig. 7. Cell for application of Pt-black. *A* anode; *C* electrodes to be plated; *R* rubber gasket; *D* support for rubber gaskets and electrodes; *S* screw for pushing the electrodes *C* against three points *P* per electrode; E_n end caps; *T* tube containing platinum chloride solution; *O* gap on top of horizontally placed tube for gas escape. The arrangement shown serves to coat plane circular electrodes. Rotation of the electrodes about their axis is recommended for optimal results. All parts of the cell are made of insulating material with the exception of the electrodes and the metal rods running inside the screws *S* to the electrodes *C*

We wish also to point out the necessity to use fresh platinum chloride solution. The ability to deposit a suitably fine layer of platinum is reduced long before the platinum content of the platinum chloride solution is exhausted.

d) Aging and cleaning of electrodes. Both normal platinum electrodes and electrodes covered with a deteriorated coating should be thoroughly cleaned in order to achieve a good and reproducible coating. This cleaning is best achieved by immersion of the electrode into a solution of aqua regia followed by rinsing with clean water.

After a platinum electrode has been coated with platinum black, its polarization impedance is observed to first rapidly and then more slowly change with time. In order to "age" the electrode system, the freshly coated electrodes are best immersed in distilled water or an electrolytic solution similar to the one involved in the impedance measurements eventually intended (such as physiological saline solution). The electrodes ought to be externally short-circuited. After about a day the polarization impedance is found to be stable. A more rapid aging procedure has been proposed by MURDOCK and ZIMMERMANN [9]. It involves repeated cycling of the electrode system through a temperature range from 0 °C to near the boiling point.

5. Effect of Electrode Polarization on Biological Impedances

The sum of polarization and biological impedance may be erroniously identified with the latter in the absence of any knowledge about electrode polarization. Indeed, a substantial amount of biological impedance data continues to be in error

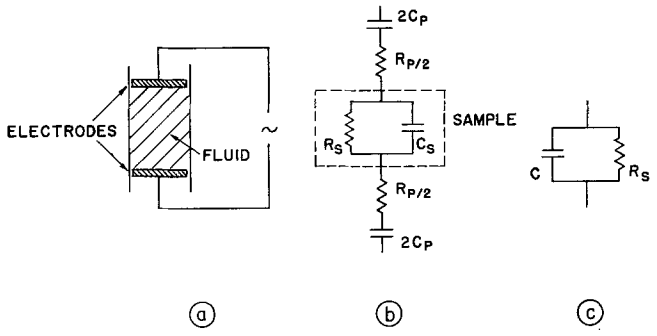

Fig. 8 a—c. a) Cell with electrolyte exhibiting electrode polarization at the interface between electrodes and test solution; b) Equivalent electrical circuit depicting the polarization impedance (R_p, C_p) in series with the sample (R_s, C_s); c) Total observed capacitance C and resistance R in terms of an equivalent parallel circuit

and reflects confusion about the relative contribution of electrode polarization and tissue or biological sample polarization to the total impedance observed. An analysis of this situation has been given by us in another article (SCHWAN, [*13*]) and is indicated in the Fig. 8. The electrode polarization impedance is in series with the biological impedance (Fig. 8 a, b). The total impedance thus observed is

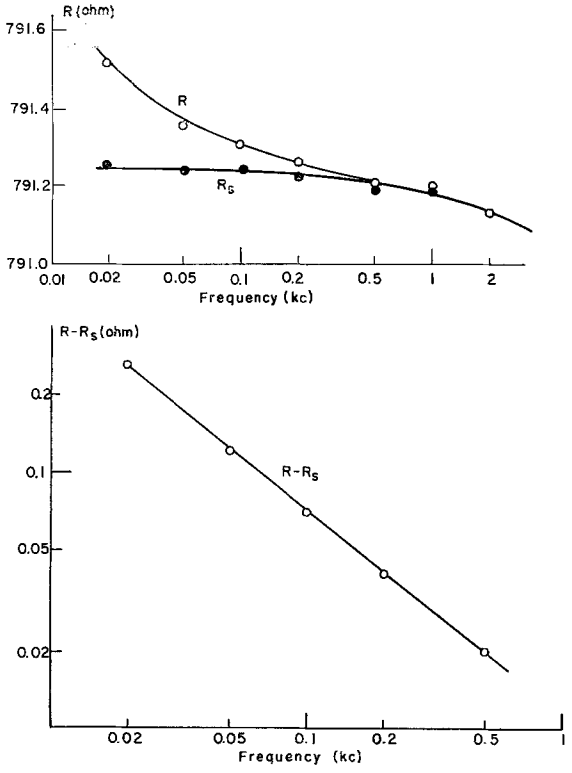

Fig. 9. Typical frequency dependence of the resistance R of a sample of blood if placed in a cell with small electrode polarization. R is the correct blood sample resistance, R-R_s is largely caused by electrode polarization and nearly equal to R_p. Electrode distance 8 cm, heavily coated Pt-electrodes

traditionally noted in terms of an equivalent parallel R-C combination as indicated in the Fig. 8 c. By equating the circuits b and c it can be shown that

$$R = [1 + (R\omega C)^2]\left[R_p + \frac{R_s}{1 + (R_s\omega C_s)^2}\right] \tag{6}$$

$$\frac{1}{\omega C} = \left[1 + \frac{1}{(R\omega C)^2}\right]\left[\frac{1}{\omega C_p} + \frac{1/\omega C_s}{1 + (1/R_s\omega C_s)^2}\right] . \tag{7}$$

This reduces for most practical purposes of interest here to the following relations:

$$R = R_s + R_p + (R\omega C)^2 \cdot R_s \tag{8}$$

$$C = C_s + 1/\omega^2 R^2 C_p . \tag{9}$$

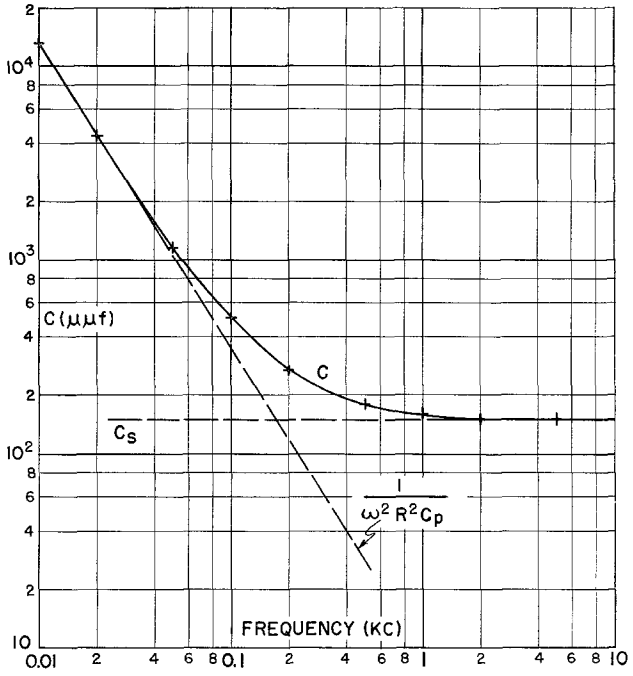

Fig. 10. Frequency dependence of the apparent capacitance C of a sample of blood in a cell of small electrode polarization. The observed capacitance C is the sum of the true capacitance C_s and a frequency dependent term $1/\omega^2 R^2 C_p$ caused by electrode polarization. If the sample cell is not designed carefully, the term $1/\omega^2 R^2 C_p$ is much larger than demonstrated, making it impossible to determine the dielectric constant of blood. Electrode distance 8 cm, heavily coated Pt-electrodes

These equations are approximations which are based on the assumptions

$$R\omega C < 1; \quad R_p < R_s . \tag{10}$$

They are found to apply in most biological impedance work unless an inadequate electrode system choice is made as may be recognized from the following:

If C compares with C_s, the condition $R\omega C < 1$ is identical with the statement $R_s\omega C_s < 1$, in view of the additional condition $R_p < R_s$. $R_s\omega C_s < 1$ holds for most biological material for the low frequency range where polarization is likely to be a problem, i.e., below 10 Kc to 1 Mc, depending on circumstances.

If on the other hand C is much larger than C_s, then from Eq. (9), $R\omega C = 1/R\omega C_p$ and the statement $R\omega C < 1$ is identical with the demand that $1/\omega C_p < R$. Since $1/\omega C_p$ is comparable with R_p, the phase angle of polarization impedance being not too different from 45°, this latter statement is identical with the demand $R_p < R$. Thus the conditions formulated by the Eq. (10) are shown to be identical with the demand that the electrode system under consideration displays polarization impedance values which are smaller than those of the sample under investigation.

A graphical demonstration of the Eqs. (8) and (9) is given in the Figs. 9 and 10, pointing out the fact that both R_p and C_p are approximated by power functions of frequency. As demanded by Eq. (9), the total capacitance C predominantly reflects the true sample capacitance at high frequencies or is due to electrode polarization at low frequencies. The change from the one to the other condition occurs within about one frequency decade, with a center frequency characterized by the equation

$$\omega_c \, R\sqrt{C_s C_p} = 1 \, . \tag{11}$$

The effect of electrode polarization on the resistive part of the total impedance is in most cases a minor one in comparison with that on the capacitance. The ratio of the resistive to capacitive relative error due to electrode polarization has been shown to be approximately C_s/C_p (SCHWAN, [*11*]). This ratio is for typical C_p values in the μF-range and for biological impedance values in the pF-range, indeed very small. The examples in Figs. 9 and 10 illustrate this situation. However, this does not necessarily permit one to neglect electrode polarization effects on the resistance. Investigations of dielectric relaxation phenomena at low frequencies, for example, involve often very small changes of the resistance of biological suspensions, even though associated capacitance changes may be very large. Thus the determination of significant resistive changes with frequency is often just as disturbed by electrode polarization as that of capacitive changes with frequency.

6. Effects of Biological Matter on Electrode Polarization

The following procedure has sometimes been suggested to correct for the effects of electrode polarization:

a) Measure the impedance Z of the biological sample.

b) Replace the biological sample by the "contact" solution which established in step a) intimate contact between electrodes and biological sample (i.e., physiological saline, etc.) and again measure the total impedance.

c) Determine from the latter reading both polarization quantities R_p and C_p by appropriate use of the Eqs. (6) and (7) or (8) and (9).

d) Subtract the polarization impedance $Z_p = R_p - \frac{j}{\omega C_p}$ from the measured impedance Z in order to obtain the correct biological sample impedance.

The validity of this technique is based on the assumption that the polarization impedances involved in the measurements with biological sample and with contact fluid alone are identical. This is not necessarily so as shown by pertinent investigations (SCHWAN, [*11*]; BOTHWELL and SCHWAN, unpublished). A typical result of such investigations is shown in Fig. 11. It demonstrates that the polarization impedance is a strong function of the amount of erythrocytes in blood. This fact

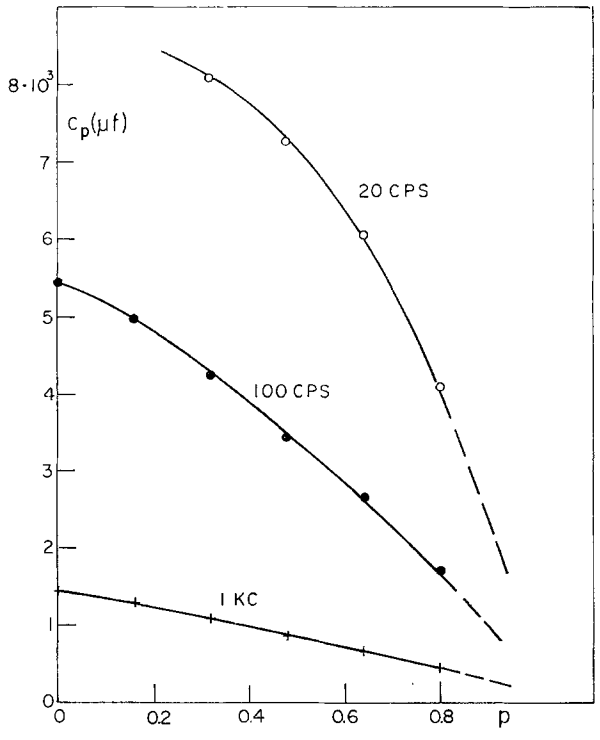

Fig. 11. Electrode polarization capacitance as function of erythrocyte concentration p of blood samples between the electrodes. Note that all curves appear to intersect the abscissa at p near 1

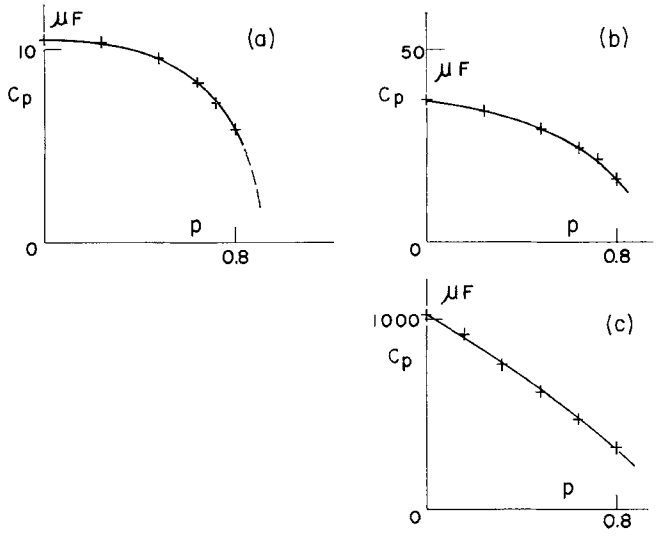

Fig. 12. Polarization capacitance as function of erythrocyte concentration p. The strongly curved plot characterizes a platinum electrode free of platinum black, the straight plot represents the same electrode heavily coated with Pt-black, and the slightly curved plot a medium black cover

may be readily explained by the "shadow" which the biological cells near the electrodes cast on the latter. The cells are very poor conductors at low frequencies and therefore force the electrical current to bypass them. Thus the polarization impedance is increased, being inversely proportional to the total electrode area reached by the current. However, starting details remain still unexplained. Thus we are not yet able to account for the experimentally observed fact that the shape of the plot of either C_p or R_p against particle volume concentration depends strongly on the electrode preparation itself (Fig. 12).

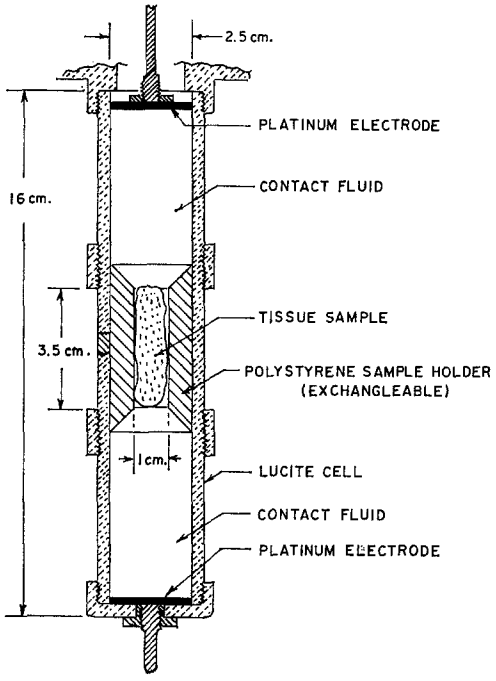

Fig. 13. Electrolytic cell for the determination of tissue impedance. Exchangeable sample holder sleeves permit the investigation of tissue samples of different dimensions

If the biological sample is kept at such a distance from the electrodes that the cellular "shadows" do not reach the electrodes, the correction technique outlined in the beginning of this paragraph is not objectionable. The technique is particularly applicable to solid samples and tissues and is illustrated in Fig. 13 (SCHWAN, [12]). Here the electrodes are separated from the unknown sample to be investigated by a contact fluid such as Ringers or physiological saline solution. After the unknown sample has been investigated it is replaced by the contact fluid and the latter measured alone. In both measurements electrode polarization enters in the same manner, the biological sample being sufficiently far removed from the electrodes so as not to affect the electrode polarization impedance. Hence, in converting all measured values into impedances and subtracting the impedances obtained with the sample from the impedances obtained with the contact fluid alone, values are obtained which are independent of electrode polarization. Since

the impedance of that part of the contact fluid which occupied the volume taken by the unknown sample is usually easily determined from geometrical dimensions and specific admittance of contact fluid, the unknown sample impedance can be calculated.

7. Techniques to Correct for Electrode Polarization

Many techniques can be used to correct for the electrode polarization contribution to the total observed impedance. The best choice must be adapted to the particular measurement problem involved and the accuracy of the final result desired. We will summarize here some of the principal techniques.

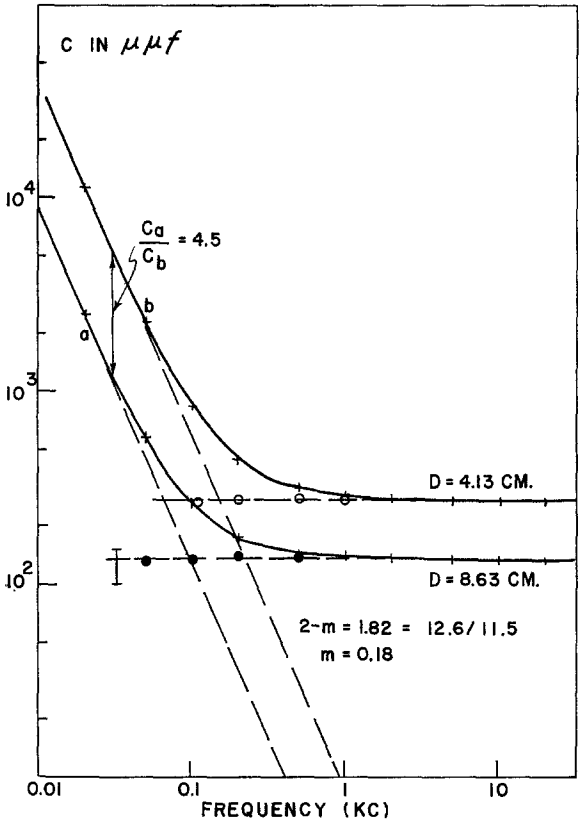

Fig. 14. Frequency dependence of the apparent capacitance of two samples of blood in the same cell, but for different electrode spacings d

a) Electrode distance variation technique. A prerequisite for the applicability of this technique (FRICKE, [5], COLE, [1]) is the possibility to vary the cell constant of the electrode system used. For two different electrode placements the following equations apply (s sample, p polarization, o observation),

$$Z_1(\mathrm{s}) + Z(\mathrm{p}) = Z_1(\mathrm{o}) \tag{12}$$

$$Z_2(\mathrm{s}) + Z(\mathrm{p}) = Z_2(\mathrm{o}) \tag{13}$$

from which, by subtraction

$$Z_1(s) - Z_2(s) = Z_1(o) - Z_2(o) \tag{14}$$

which is independent of electrode polarization impedance. The difference $Z_1(s) = Z_2(s)$ is identical with the product of the cell constant corresponding to the change in electrode distance [i.e., with $(d_1 - d_2)/$ cross section A for a cylindrical cell] and the specific impedance $1/(\varkappa + j\omega\varepsilon\varepsilon_r)$. The technique is usually rigorous and accurate. However, constancy of the polarization impedance is necessary as the electrode spacing is varied. In practice it is found desirable to follow the change in electrode placement by a return to the original electrode position in order to check if the original total impedance reading can be repeated. The extent to which this can be achieved reflects on the accuracy with which the sample impedance can be

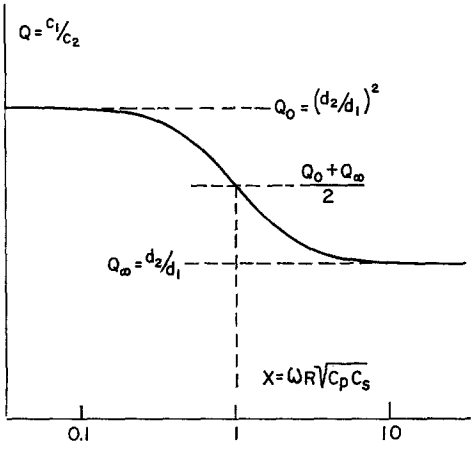

Fig. 15. The ratio $Q = C_1/C_2$ of two apparent capacitance readings is plotted against the parameter $x = \omega R\sqrt{C_p C_s}$ (C_s sample capacitance, C_p polarization capacitance). The apparent capacitance C observed at small electrode distances is inversely proportional to the square of the electrode distance d and for large distances proportional to $1/d$

determined. Limitation of the technique: The polarization impedance Z_p becomes large in comparison with the sample impedances $Z_1(s)$ and $Z_2(s)$ at low frequencies. Minor errors in the determination of $Z(o)$ reflect then in large relative errors of $Z(s)$. A more detailed analysis shows that the technique often permits a downward extension of the frequency range of successful determination of biological sample impedances by about one additional decade.

b) Large electrode distance. A simple technique to check on the presence of electrode polarization contributions to the capacitance is possible. It takes cognizance of the fact that the first term of Eqs. (8) and (9) changes linearly with d or $1/d$ respectively while the disturbing polarization term changes not at all or with $1/d^2$ respectively, provided that the sample impedance is proportional to the electrode distance d. This means that the relative contribution of electrode polarization can be minimized by use of large electrode separation. A linear dependence of C with $1/d$ obviously indicates that polarization is not disturbing, while an inverse dependence of C with d^2 is indicative of predominant polarization influence (Fig. 14). In Fig. 14 are plotted C-data obtained at two electrode distances which

illustrate these facts. The frequency $\omega = 1/R\sqrt{C_s C_p}$, which characterizes the change from the one to the other state, is inversely proportional to the square root of d (Fig. 15). Hence, for lower frequencies rapidly increasing d-values are needed to avoid disturbing electrode polarization contributions to C.

c) Graphical technique. A graphical technique to obtain correct capacitance values is as follows: Measure C at two electrode distances, one of them being so small that C is largely caused by electrode polarization; shift the curve for large C

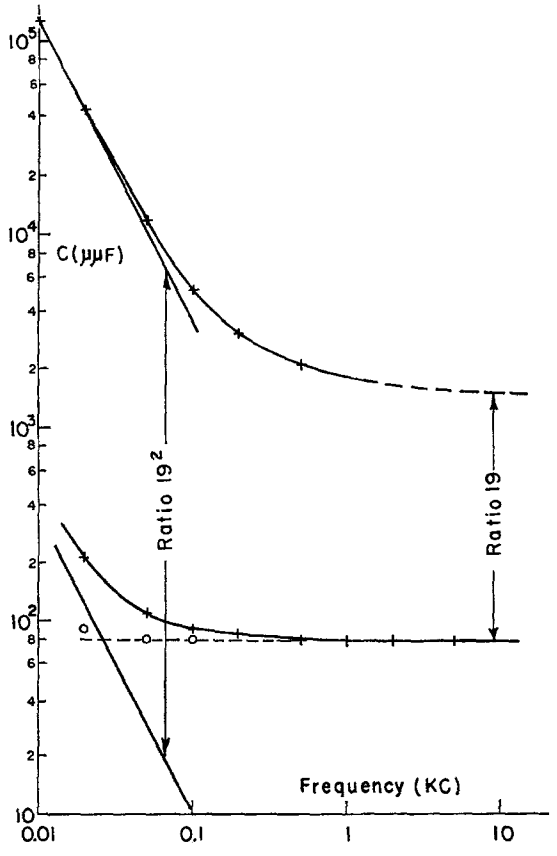

Fig. 16. Frequency dependence of the apparent capacitance C of a sample of blood for a large and a rather small electrode distance. The resistance ratio is 19 and equal to the capacitance ratio approached at high frequencies where polarization does not disturb. The straight line approached at low frequencies by the upper curves is shifted downwards by a factor of 19^2. The shifted curve is subtracted from the C-values obtained for large distance (lower curve) in order to obtain correct C_s-data (open circles)

downwards by the R^2-ratio which is given by the resistance values for the two distances; subtract the shifted curve from the one obtained at the larger distance in order to obtain true sample capacitance data. An example is given in Fig. 16. The validity of this procedure is readily derived from Eq. (9).

A variety of techniques are available in case that the electrode spacing cannot be varied. Two typical examples are listed:

d) Substitution technique. The sample with unknown impedance properties is replaced by a sample with known impedance properties. The latter is chosen to approximate similar electrode polarization values as exist with the unknown and serves to determine R_p and C_p from Eqs. (6) and (7) or (8) and (9). Typical examples are the replacement of blood by plasma, the replacement of a protein solution by an electrolyte of similar or identical ionic composition as present in the medium surrounding the proteins. The technique is reasonably successful if the elements which give rise to unknown impedance properties (blood cells and protein molecules in the examples quoted) are of sufficiently low volume concentration to reduce previously described "shadow" effects (section 6) to an insignificant level. If this is not possible, the substitution technique is still useful provided that cognizance is taken of the "shadow" effect, i.e., by appropriate increase of Z_p (electrolyte) before identifying it with Z_p (biological sample).

e) Frequency variation technique. Consider Eq. (9) as represented by a typical example in Fig. 10. We assume that C_p is a power function of frequency f^{-m}. Then the capacitance data at low enough frequencies to assure that the polarization term is large in comparison with the sample capacitance C_s, are expressed by a function $f^{(-2-m)}$ (dashed line in Fig. 10). Subtraction of the data represented by the dashed line from the experimentally observed curve yields the true sample capacitance. Errors which are due to gradual changes in m with frequency can often be neglected. They can be taken into account if more precise results are desired and m can be determined over the frequency range of interest in separate runs with the suspending medium.

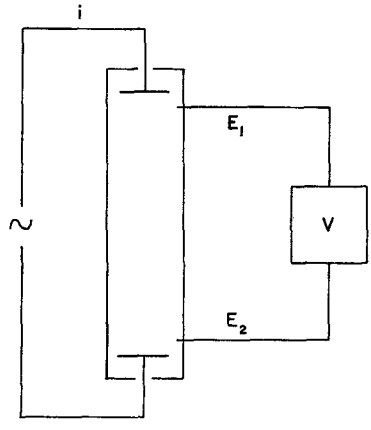

Fig. 17. Principle of 4-electrode technique. The use of two sensing electrodes E_1 and E_2 permits the registration of the potential across the sample undisturbed by electrode polarization (see text)

Other frequency variation techniques which have been used will not be summarized here. We particularly refer to a technique useful for protein work as used by FERRY and ONCLEY [*3*] and ONCLEY [*10*]. Techniques applicable to tissue impedance measurements *in situ* have been developed by SCHWAN and KAY [*17, 18*].

f) Four-electrode technique. Consider the diagram in Fig. 17. We assume that it is possible to measure the potential between the pick-up electrodes E_1 and E_2 without drawing current. This condition may be approximated by use of a voltmeter with very high input impedance. Then, due to the linear relationship between electrode polarization potential and current passing through the electrode, the registered potential will be uninfluenced by polarization phenomena. The ratio of the observed potential and the current which passes through the sample is identical with the impedance of the sample and independent of the polarization impedance of the current electrodes. Refinements of this principle have been presented before [*14, 16*].

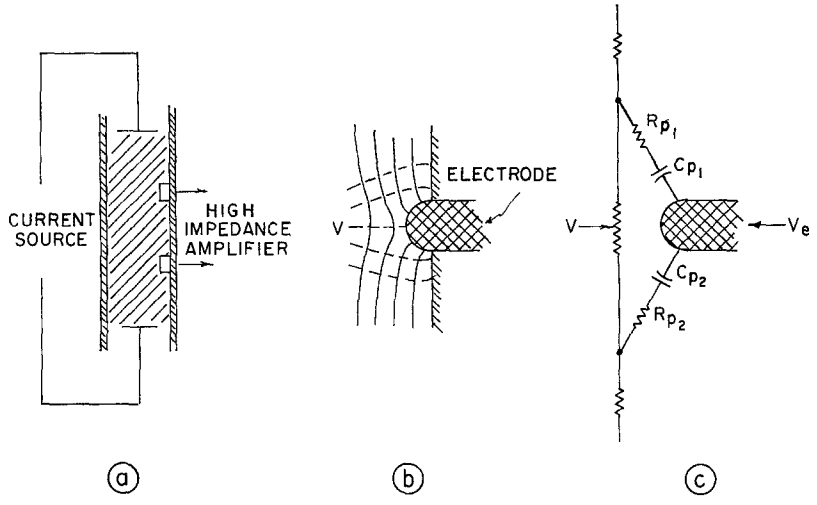

Fig. 18 a—c. a) and b) Illustration of a sensing potential electrode exposed to an electrical field. The dashed lines indicate equipotential surfaces. c) Electrical equivalent of the situation shown in a) and b). The polarization elements R_p and C_p, associated with different parts of the electrode surface, are not necessarily of equal value. Hence the potential V_e, which is registered by the sensing electrode, is not likely to be identical with the potential of interest V

The four-electrode technique aids in eliminating electrode polarization contributions to the sample impedance under investigation. However, in practical work with this technique care has to be taken that electrical currents do not enter and leave the potential electrodes as indicated in the Fig. 18, thereby creating a net polarization potential. This problem arises from the difficulty to construct electrodes with a uniform distribution of specific polarization impedance (polarization impedance per unit area surface) over the entire electrode surface. Nonuniformity of polarization will place the electrode on a potential level different from the one it ought to register [*14*, *13*]. This is indicated schematically in the diagram in Fig. 18. The potential polarization at the electrodes can be minimized by use of "fluid" electrodes, which in turn contact the metal electrode at a point not reached by the current passing through the sample (Fig. 19). It is furthermore advisable to use large potential electrodes with resultant small polarization impedance and a large input impedance to the voltage measuring device. This will minimize polarization caused by current flow through the voltmeter circuit.

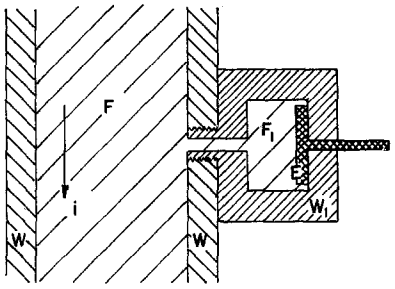

Fig. 19. Design of a potential sensing electrode. The design minimizes the effects of electrode polarization illustrated in Fig. 18 by moving the electrode out of the field. A fluid coupling is used to establish contact with the point whose potential is to be measured. The electrode itself is of large size to further minimize polarization. The point of contact with the main vessel containing the sample of interest is small in order to permit registration of a well defined potential. F material to be investigated; F_1 contact fluid; W wall of main sample cell; W_1 wall of electrode housing; E electrode

8. Transient Response of Electrodes

It has been pointed out above that the electrical behavior of electrodes is best characterized by their polarization potential in the case of DC-measurements and

by their polarization impedance in the case of small AC-currents. For large current densities, the AC-behavior of electrodes has been studied recently and it appears that in this case the electrode is characterized by a constant AC potential rather than impedance (SCHWAN, [*19*]). The limit of linearity law stated in Eq. (4) enables us to readily understand the transition from the linear AC case to the DC case: The limit current for linearity simply reduces to zero as the frequency is lowered to zero, i.e., a linear DC impedance could only be observed with zero current, i.e., is nonobservable.

We consider now electrode behavior in transient experiments where one studies the response evoked by a step function current or step function potential across the sample (voltage clamp). The prediction of the electrode's behavior is readily possible from known AC-electrode properties provided that:

a) The frequency spectrum of the current passed through the electrode is known or can be determined.

b) No DC components are present.

c) No Fourier component taxes the electrode beyond its linear limits.

Under such circumstances linearity of the electrode characteristics prevails, the superposition principle can be applied and established transform techniques can be used to make the transformation from the time to the frequency domain. However, in many cases some of the above stated assumptions are not valid and the transformation to the frequency domain is no longer possible. Under such circumstances the electrode behavior can be very complex. It is unfortunate that a great deal of work has been carried out during the past decades with transients and without apparent realization of the principles stated above. As a consequence electrical characteristics have been claimed for the biological structure under study which are at least in part caused by the electrode response. The only detailed study of electrode polarization in the presence of transients, known to us, is the one by WEINMAN and MAHLER [*20*].

9. Microelectrodes

A large percentage of all biological work is carried out with microelectrodes. Much of this work is conducted with transients and AC steady state considerations have to be taken into account just as well as DC-polarization as pointed out above. One usually observes that a great deal of attention is dedicated to obtain "non-polarizable" electrodes. Electrodes which are "nonpolarizable", i.e., have a low DC-potential, are not necessarily "nonpolarizable" from an AC point of view. For example, while the silver-silverchloride electrode is superior to the platinum electrode for DC work, it is inferior for AC- purposes. Since most transient work involves a mixture of DC- and AC-components, a most appropriate choice should not be based on DC-considerations alone. The only proposal known to us of an electrode which combines low DC-polarization with more adequate AC-characteristics is the platinum covered silver-silverchloride electrode proposed by COLE and KISHIMOTO recently [*2*].

Electrode size is critically related to its performance. It is of obvious interest to use electrodes as small as possible in order to minimize the traumatic effects of electrode insertion into biological materials such as tissues or biological cells. However, several factors limit the usefulness of small electrodes:

a) Experiments have been conducted by SCHWAN and KAY to determine the effects of fluid accumulation around the tip of small electrodes inserted into tissue [*17*]. It was observed that the relative error which is caused by fluid accumulation is the more pronounced, the smaller the electrode. This effect can be readily understood if one makes the reasonable assumption that the linear dimensions of the fluid volume around the electrode depend less than proportionally on the effective of the electrode tip. If the electrode size is reduced, an increasingly large portion of the potential gradient will be placed in fluid accumulated around the tip and the impedance observed will increasingly reflect the fluid medium rather than the tissue.

b) The total impedance of a small tip electrode represents largely its polarization impedance. Consider a tip electrode of spherical shape. Then the impedance caused by the sample is given by

$$Z \text{ (sample)} \sim \frac{\mathrm{K}}{r} \tag{15}$$

where r is the radius of the electrode and K reflects the specific impedance properties of the medium surrounding the electrode. The polarization impedance of the electrode, however, is inversely proportional to its area and to the polarization impedance per unit electrode area $Z_o(\mathrm{p})$

$$Z(\mathrm{p}) = \frac{Z_0\,(p)}{r^2}\ . \tag{16}$$

Hence the ratio between polarization impedance and impedance to be sampled is given by

$$Z(\mathrm{p})/Z \text{ (sample)} \sim 1/r \tag{17}$$

i.e., increases with $1/r$. Typically for nominal polarization values and impedance values characteristic of tissues, and for electrodes in the μ-range, $Z(\mathrm{p})$ is much larger than Z (sample) at low frequencies. Thus many tissue impedance data have been published during recent years which are suspected to partially reflect electrode behavior. A simple method to check whether or not electrode polarization affects observed capacitance values is suggested by Eq. (9). In the presence of strong polarization the second term of this equation will be large and C changes with $1/R^2$. Thus, if R changes by x%, C must change by 2 x%. Indeed, many cortical impedance data have been published which follow exactly this behavior. Another check is implied by Eq. (5). According to this equation R_p and $1/\omega C_p$ are comparable. Thus, if impedance data are obtained where resistance and reactance are of comparable magnitude, polarization might be suspected not only to explain observed C-values, but also R. For most tissues R, if not affected by electrode polarization, is considerably larger than $X = 1/\omega C$ (SCHWAN, [*14*], Fig. 3). Clearly then, extreme caution must be exercised in the use of small electrodes in biological impedance studies.

Electrode polarization is a major nuisance in biological impedance work with low frequencies. It requires careful consideration in order to eliminate its effects on biological impedances. It is also obvious that successful elimination or correction for existing polarization difficulties is only possible with alternating current steady state techniques. In the case of transient techniques, the strong frequency dependence of the polarization impedance will cause a rather complicated transient

response of the electrode. Its separation from transients due to the biological material is very difficult. With this in mind we urge careful evaluation of a good part of the work done in electrobiology with transient techniques. This statement applies also to a somewhat lesser extent for cases where multielectrode systems, involving pairs of current and voltage electrodes, have been used for the reasons formulated above.

Summary

This article summarizes principles of alternating current electrode polarization. The importance of alternating current electrode polarization in biological impedance studies is discussed. The following topics are treated in detail: Definition of Electrode Polarization Impedance; Linearity and Superpositioning Principle; Frequency Dependence of Electrode Impedance; Preparation of Electrodes (Optimal current density for platinum black application, Stability of electrode impedance, Cell design for platinization purposes, Aging and cleaning of electrodes); Effect of Electrode Polarization on Biological Impedances; Effects of Biological Matter on Electrode Polarization; Techniques to Correct for Electrode Polarization (Electrode distance variation technique, Large electrode distance, Graphical technique, Substitution technique, Frequency variation technique, Four-electrode technique); Transient Response of Electrodes; Microelectrodes.

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Prof. H. P. Schwan
Electromedical Division
The Moore School of Electrical Engineering
University of Pennsylvania
Philadelphia 4, Pa, USA