Electrochemical study of electrode behaviour during bioelectric impedance measurements

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I. Introduction

As a part of multidisciplinary research on the electric stimulation of living tissues, an attempt to develop an accurate experimental technique to measure biological impedances has been undertaken (de Fraiteur, 1978 ; Pegoff, 1979).

Schematically, this technique uses two stimulating electrodes to impose a step current signal to the sample and two measurement electrodes to measure the potential difference between two given points of this sample. The complex impedance is calculated from these values.

The two aims of this work were to define convenient kinds of electrodes and to estimate their influence on the measurements. Experimental measurements were performed in NaCl solutions and in biological tissues to investigate the interferences at the electrode-biological medium interfaces.

II. Experimental procedure

Polarization measurements on titanium electrodes were carried out, at room temperature, in 0. 11N NaCl solution and, « in vivo », in muscles from the posterior limb of a rabbit under general anaesthesia. The potentiostatic method was used with a scanning speed of 1 V/min. The potentiostat, Tacussel type PRT 20-2X, was piloted by a Tacussel Ser-

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vovit 12 Pilot Scanner. A Tacussel electronic millivoltmeter type Aries 10000 and an X-Y recorder completed the equipment.

III. Results. Discussion

1. Choice of the electrodes.

a) *Stimulating electrodes.*

The following properties of Ti justify its use as stimulating electrodes.

The voltage-pH diagram of the system Ti/H_2O at 25°C (Pourbaix, 1963), shows that Ti, in aqueous solutions, without complexing ions, is easily passivated by an oxide film, probably TiO_2, the thermodynamically stable oxide in water.

This oxide film protects Ti from corrosion in physiological media (like 0.9 % aqueous solution of NaCl). Fraker (1973), and Levy (1973), by measuring the open circuit potential of Ti versus time, in physiological solutions (Ringer, Hanks), obtained curves exhibiting no apparent interruption in the formation of the film which remains intact. Moreover, polarization measurements, made by the latter showed that the breakdown potential of Ti was much more positive than the highest potential observed during long term isolated exposure, and concluded that « breakdown of isolated specimens and onset of pitting are quite unlikely, even after very long exposure ». The polarization curves in 0.11N NaCl solution (fig. 1), and in a living muscle of rabbit (fig. 2), present Ti as an ideally polarized electrode with a range of passivity of more than 1 V in both cases. The double-layer capacity allows a periodic current to pass in this passive area while the faradic current is reduced : in the case of the living muscle, for instance, the faradic current is approximatively 6 $\mu A/cm^2$.

b) *Measurements electrodes.*

Ti is an ideally polarized electrode :

— Its potential can be defined by some redox equilibrium of ions present in the sample, especially by oxygen. In these conditions Ti could not present a reproducible potential.

Experimentally, a continuous drift of the open circuit potential of Ti in saline solution, probably due to the oxide film formation, has been observed at every test.

— A very small current can produce a jump of its potential and Ti, because of its polarizability, needs a long time to recover its initial state.

Therefore Ti has been replaced, for the measurement electrodes, by reference electrodes of the Ag/AgCl type, consisting of a silver chloride plated silver wire introduced by means of a glass capillary into the sample.

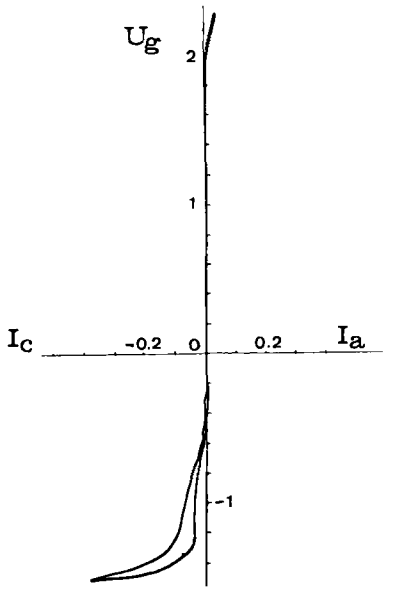

FIG. 1.

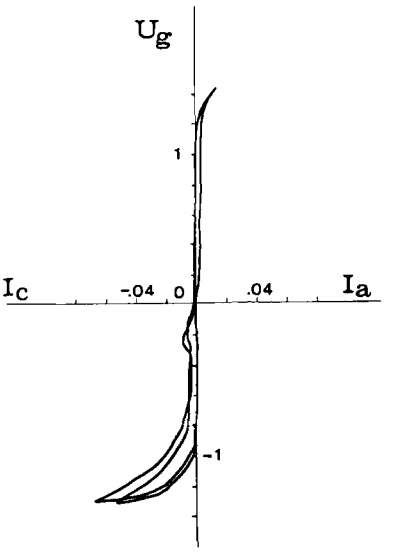

FIG. 2.

FIG. 1. — Ti in 0.11 N NaCl solution, aerated and unstirred, 20° C.
Speed of scanning : 1 V/min.
Scales : U_g : 0.2 V/division.
I_a, I_c : 0.1 mA/division.
Reference : saturated calomel electrode (SCE).

FIG. 2. — Ti in posterior limb of rabbit under anaesthesia.
Speed of scanning : 1 V/min.
Scales : U_g : 0.2 V/division.
I_a, I_c : 0.02 mA/division.
Reference : SCE.

2. **Influence of the electrodes.**

a) *Stimulation electrodes.*

A voltage generator produces a voltage step signal which is transformed into a current signal by means of a resistance R. The current signal will

remain a perfect step if R is much more important than Z, the total impedance of the stimulating electrodes and of the sample, and r_i, the internal resistance of the generator.

b) *Measurement electrodes.*

The complete interpretation of the impedances measured is not possible. Experimental measurements in NaCl solutions and in biological tissues were performed (Pegoff, 1979 ; Georges, 1979). All of them gave complex parts of the impedance corresponding to capacitive phenomena. A primordial question would be to know which part of these capacities could come from the electrodes or from another origin.

In the case of an influence of the electrodes, we distinguished between an electrochemical influence and a simple electrostatic influence.

By electrochemical influence, we mean the fact that the polarization impedance of the measurement electrodes, due to the double-layer capacity and interfacial phenomena of absorption could produce a potential difference involved in the potential difference measured, if sufficient current flows through its interface with the sample.

We considered the hypothesis that the current lines in the cell go around the measurement electrodes without entering them.

This hypothesis is supported by the fact that the energy necessary to transform, through chemical reactions, the ionic current in the sample into an electronic current in the metallic electrode, at the sample/electrode interface, and conversely at the electrode/sample interface, is not available :

— either in the surrounding solution, where the potential difference due to the ohmic drop, is too small ;

— or in the metallic electrode, where all the points lie approximately at the same potential.

The last possibility for a current to flow through the metallic interface would be to pass through the external electric circuit of measurement. This current can then be reduced by the use of a sufficiently great input impedance of the measurement apparatus. In our case, this impedance is of 10^{10} ohms.

For these reasons, we assume that the polarization impedance of the measurement electrodes gives a negligible potential difference and that it has no effect on the measurements. However, it does not mean that the potential difference measured can be attributed only to the sample.

Indeed, electrostatic influences and side effects in the cell are still able to create interferences. Among possible parasitic effects, one can retain :

— An electrostatic influence of the materials of the measurement electrodes, or of the plexiglass cell. In the case of the electrodes, for instance, the presence of the glass capillary used to drive the silver wire electrode into the sample could produce at sufficiently high frequencies, a parasitic capacity.

— The appearance of a capacity between two cylindric conductors in a given solution. The calculation (Georges, 1979) based on the dielectric constant of the NaCl solution gives a negligible contribution to the total capacity.

— Parasitic capacities from the measurement apparatus which need special protection (Pegoff, 1979).

IV. **Conclusions**

The first part of this work consisted in the choice of the best kind of electrodes for a measurement of bioelectric impedances (technique with four electrodes).

Ti, presenting favourable properties, was retained for the stimulating electrodes. It can indeed conduct a periodic current through its double-layer capacity and presents, on its surface, in a physiological environment, an oxide film which prevents it from corrosion. These properties also justify its use as stimulating electrodes in clinical treatments.

On the contrary, Ti as an ideally polarized electrode does not present the reference characteristics necessary for the measurement electrodes and is therefore replaced by reference electrodes of the type Ag/AgCl.

The second part of the work was principally an approach to the influence on the measurements of the measurement electrodes. From a theoretical point of view, we assumed that the measurement electrodes do not create electrochemical interferences on the measurements if a sufficient impedance exists in the external electric circuit, but that they could, like other material present in the cell, create some electrostatic influences which have not yet been fully analysed.

BIBLIOGRAPHY

FRAITEUR M. (de), DUBOIS T. Etude d'un membre *in vivo* soumis à des stimulations électriques. *Travail de fin d'études*, FSA, ULB, 1977-1978.

FRAKER A.C., RUFF A.W., YEAGER M.P. Corrosion of Ti alloys in physiological solutions. In : Jaffee R, Burte H. *Titanium, science and technology*. Plenum Press, New York, London, 1973, *4*, 2447.

GEORGES B. Contribution à l'étude de la stimulation électrique de tissus vivants. *Travail de fin d'études,* FSA, ULB, 1978-1979.

LEVY M., DAWSON D.B., SKLOVER G.N., SEITZ D.W. jr. The corrosion behaviour of Ti alloys in chloride solutions : materials for surgical implants. In : Jaffee R., Burte H. *Titanium, science and technology.* Plenum Press, New York, London, 1973, *4,* 2459.

PEGOFF S. Contribution à l'étude de la stimulation électrique de tissus vivants. *Travail de fin d'études,* FSA, ULB, 1978-1979.

POURBAIX M. *Atlas d'équilibres électrochimiques à 25° C.* Gauthier-Villars, Paris, 1963.