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Electrode-electrolyte Interface Properties in Implantation Conditions

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Abstract—**A research was made on electrical properties of implantable electrodes. Materials used for this research were platinum (Pt), stainless steel (SS), gold (Au) and silver-silver chloride (Ag/AgCl) that was used as a reference electrode material although it is not suitable for implantation, Wetzig *et al.* [1]. The interface impedance of the electrode-electrolyte –interface in three different electrolytes, saline (0.9 m-% NaCl), SBF (Simulated Body Fluid) and PBS (Phosphate Buffered Saline), was measured. A Randles equivalent circuit was used to model the electrode-electrolyte –interface. The two independent components of the electric equivalent circuit of the interface were quantified for all materials in all electrolytes. Impedance of the electrode-electrolyte interface was measured by a slightly modified technique presented originally by Lario-García *et al.* [2].**

I. INTRODUCTION

Traditional surface potential measurements of ECG on the chest have many shortcomings: motion artefacts, possible power line interferences coupled to the measurement wires and time and place dependency to mention some. Time and place dependency of the measurement means that a skilled professional is needed to place the electrodes on the right places and to make the measurement at some definite time interval. The patient is encumbered by the measurement setup with electrodes and wires. Motion artefacts are a problem in any surface potential measurement, for example in ECG-measurements. This paper concentrates on measurement of the electrode characteristics and is based on a research project on implantable ECG-measurement devices.

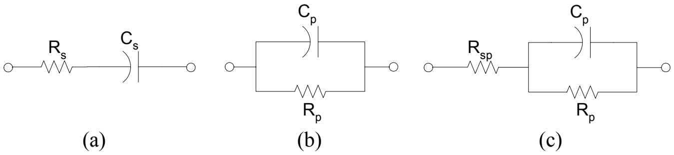
The electrode material plays an important role in the performance of the measurement system. It determines, together with the amplifier electronics, the detection limit and signal-to-noise ratio of the measurement signal. Therefore, much attention has to be paid on the choice of material to be used as implanted electrode. There are several different materials that are suitable for measurement purposes but some of these are not biocompatible, i.e. the material causes inflammation or even necrosis in the tissue.

Impedance model of the electrode-electrolyte interface and magnitude of the impedance are of scientific interest when designing a measurement system. The impedance of the interface creates an RC-filter at the input of the measurement amplifier which may limit the performance of the electrode measurement ability through filtering of the incoming biosignal in an unfavourable way.

In implantation condition electrodes are placed in a chemically rough environment. They are constantly at body temperature, 37 °C and achievable for attacks of different ions and proteins. Since the devices are implanted, they ought to be resistant to corrosion for long time periods.

II. THEORY

There are several different electrical equivalent circuit models for the electrode-electrolyte interface that can be found in the literature; the Warburg circuit equivalent [3], Fig. 1(a), modified Warburg model [3], Fig. 1(b), and a more comprehensive model with series resistor, Fig. 1(c), from [4].



(a) (b) (c)

Fig. 1. Various electrode-electrolyte interface circuit equivalents found in the literature.

Warburg equivalent presents the simplest model with series resistance and capacitance to present the dissipation and capacitive properties of the electrical double layer that forms on the interface. The major shortcoming of this Warburg model is that low frequency noise fluctuations are greatly attenuated due to the series capacitance. Therefore, usually a model with parallel resistance, Fig. 1(b), is used. Model with three components, Fig. 1(c), takes into account the interface dissipation for high frequency signals through the series connected resistor R_{sp}.

The last presented model is also the most accurate one so its use is encouraged. A theory for measuring the three independent components of the circuit equivalent is presented in [2]. The method assumes a two electrode system to be stimulated with square waves. A measurement resistor is connected in series with the signal path and the response is measured. From the response, the voltages of three separate time stamps are read. R_{sp}, R_p and C_p can be calculated from these values. The impedance of the interface is of interest since it determines the frequency range that is usable for measurement purposes.

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Using the basic formulas for resistance and capacitance, simple relationships between resistance, capacitance and area can be derived:

$$R = \rho \frac{l}{A} \propto \frac{1}{A} \quad (1)$$

$$C = \varepsilon \frac{A}{d} \propto A. \quad (2)$$

Equations above suggest that by doubling the effective area of the electrode, the resistance of the interface should drop to one half from that before and capacitance should behave inversely, i.e. capacitance should be doubled.

III. MATERIALS

Electrode materials studied are gold (Au), platinum (Pt), stainless steel (SS) and silver-silver chloride (Ag/AgCl). Only three first of these are biocompatible. It is reported that an AgCl-coating will dissolve into the electrolyte in less than a week [5]. AgCl-coating is also toxic to tissue, as well as pure Ag, and therefore the Ag/AgCl-electrode should be coated with some biocompatible material before implanting it into living subjects. [1] Ag/AgCl is, however, the most used material in surface biopotential electrodes.

When the electrodes are coated with a biocompatible material, the measurement will turn into a capacitive measurement and there is assumable no big difference with the material used as electrode. The only demand for the electrode material in this case is that it is sufficiently good conductor, e.g. a region of n-doped Silicon could serve as electrode. The resistance of the electrode should not be higher than a few hundred ohms. The resistance has to be taken into account when designing the amplifier to ensure a non-loading measurement.

Together with electrode paste Ag/AgCl is very stabile material which shows only a little electrochemical noise compared with many other materials [6]. It also has a remarkably rapid stabilization time, i.e. time it takes for the electrochemical noise of the electrode to stabilize to the low long term level, when immersed into an electrolyte. This property among others makes it usable in sensitive and rapid surface biopotential measurements [7]. The Ag/AgCl-electrode was chosen to be the reference for the other electrode materials in terms of electrochemical noise.

Gold is found to be biocompatible material but it is not very commonly used as an electrode material. This is mainly because it is expensive and suffers from corrosion much more than other noble metals when it is used for stimulating purposes. As a recording electrode, it undergoes little or no corrosion. [8]

Platinum is widely used in electrodes, both in stimulating and recording ones. Platinum electrodes are found e.g. in cochlear implants and in pace makers as stimulating electrodes. They are found to be very biocompatible and suffer from corrosion only a little in both recording and stimulating use. [8]

Stainless steel (SS) is a common surgical material which is used e.g. in wires that close the sternum after a heart operation [9]. SS has an excellent corrosion resistance when used as passive implant as well as in stimulating purposes if only the voltage levels remain low. [8] SS is chosen as one of the materials to be tested due to its generality and relatively low price.

The materials differ in their electric behaviour so that Ag/AgCl is a nearly ideally non-polarisable material while Pt being nearly polarisable material. In a completely polarisable material there is no net transfer of charge over the electrode-electrolyte interface. Such a material can be regarded as a capacitor where there are two conducting surfaces, electrode and electrolyte, separated by an insulator, a double layer. Non-polarisable materials act contrary to polarisable materials: there is a net transfer of charge over the interface. Au and SS are located somewhere in between the two extremes.

Several different electrolytes were used in *in vitro* measurements. Saline, 0.9 m-% NaCl-solution, is commonly used although it is a quite simplified model of the electrochemical environment inside the human body. More complicated solutions have been constructed which simulate more accurately the various properties of the body fluids. Such solutions are among others, phosphate buffered saline (PBS) and simulated body fluid (SBF) whose pH is temperature dependent being 7.4 at 37^{o}C.

IV. METHODOLOGY

A. *Electrode preparation and setup*

Electrodes were ordered in two sizes, the others having twice the area of the others. The two different electrode sizes are used to be able to verify the area dependency of the interfacial properties. The electrodes with greater area have dimensions of 7 x 7 x 0.5 mm and the electrodes with smaller area have dimensions 7 x 3.5 x 0.5 mm. An electrode pair of same material was measured with separation between the midpoints of the electrodes being 55 mm.

B. *Interface impedance measurements*

The impedance of the electrode-electrolyte interface was measured by using the square wave driving method which is presented in [2].

Stimulation of the electrodes with square waves was performed with a signal generator. The amplitude of the input voltage was set to 1 V. The current I_U through the circuit was determined by measuring the output voltage over the measurement resistor R_{meas}, connected in the signal path, with a data acquisition card. Value of the measurement resistor was set to 995 Ω to obtain clearly detectable voltage. Input impedance of the measurement card is 100 GΩ in parallel with 100 pF capacitor which makes the input impedance at 350 Hz equal to 4.5 MΩ. The input impedance of the measurement card is sufficient to avoid distortion in the measurement signals since it is 4500 times greater than the resistor to be measured. [10]

The volume resistance of the electrolyte between the electrodes is calculated by using finite element method software FEMLAB®. Conductivities for the electrolytes have been measured with a four wire measurement setup at the laboratory.

C. *Analysis made on the measurement data*

The analysis on the measurement data was done with Matlab®. Measurement data was collected so that several voltage cycles were obtained which implies several analysis results, typically 2-5. The results were mean valued to obtain more reliable results and discard random deviations from the results.

The measurement principle is purely based on AC-current flow between the electrodes. A combined DC- and AC-current would be a better choice to find out the impedance of the network [11]. In [11], they have also suggested a power relationship between the interface properties and frequency. These relationships are expressed in mathematical form in (3) and (4) as

$$R_p \propto f^{-l} \tag{3}$$

$$C_p \propto f^{-m}. \tag{4}$$

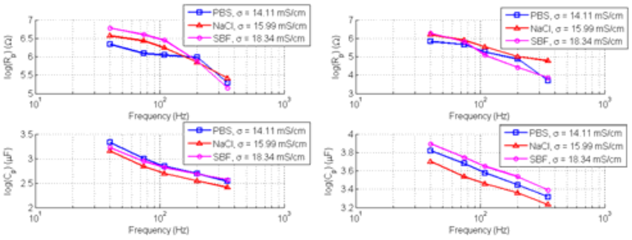
The power l remains constant at +0.5 on frequency band 20 Hz to 200 kHz and power m varies between +0.3 and +0.5 at the same interval.

V. RESULTS

Impedance of the electrodes in a specific electrolyte was determined according to procedure explained in part II. The measurements were performed after the electrode pair had been immersed into the electrolyte and let stabilize for a few minutes. Interface impedance was measured at five different frequencies: 40, 75, 110, 200 and 350 Hz.

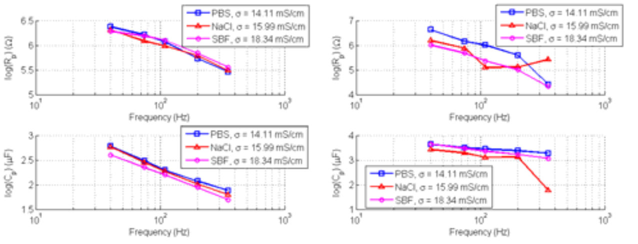
In the analysis of the measurement results, the modified Warburg circuit equivalent was used; see Fig. 1(b). This was because the analysis is very sensitive to accuracy of the measurement result and erroneous results, e.g. complex numbered resistances, were obtained when the most complex circuit equivalent was used. These false results were due to measurement noise in the DAQ-card combined with small resistance values.

The analysis results are presented in Figs. 2-5.



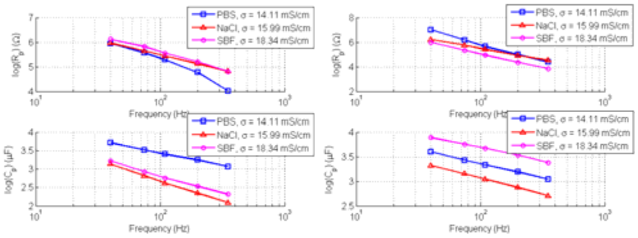
(a) (b)

Fig. 2. Au-electrodes, (a) electrode size 3.5 x 3.5 x 0.5 mm^3, (b) electrode size 7.0 x 7.0 x 0.5 mm^3.



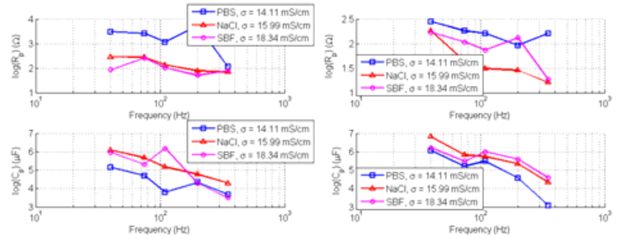
(a) (b)

Fig. 3. Pt-electrodes, (a) electrode size 3.5 x 3.5 x 0.5 mm^3, (b) electrode size 7.0 x 7.0 x 0.5 mm^3.



(a) (b)

Fig. 4. SS-electrodes, (a) electrode size 3.5 x 3.5 x 0.5 mm^3, (b) electrode size 7.0 x 7.0 x 0.5 mm^3.



(a) (b)

Fig. 5. Ag/AgCl-electrodes, (a) electrode size 3.5 x 3.5 x 0.5 mm^3, (b) electrode size 7.0 x 7.0 x 0.5 mm^3.

The ac-current density at the electrodes varied from 850 µA/cm^2 to 2000 µA/cm^2. The current density varies from measurement to measurement because the voltage between the electrodes was kept constant and current varied according to the separation and the area of the electrodes. According to [11], stimulation solely with ac-voltage produces somewhat different values for interface impedance than combined dc- and ac-stimulation. With ac-current densities used in this research one obtains somewhat greater absolute values for R_p and C_p and steeper slope of the f-R,C –graph than with a decade lower ac-current density. [11]

VI. DISCUSSION

The impedance of the electrode-electrolyte interface was measured using technique presented in [2] and shortly revised in section IV. The technique was applied successfully yet Ag/AgCl seemed to behave little differently than the other materials. Ag/AgCl is almost a perfectly non-polarisable electrode material while the others are more polarisable. The interface resistance and capacitance of Ag/AgCl, Fig. 5, do not follow the power law suggested in [11] and the capacitance values are higher than for any other material. This would indicate that Ag/AgCl is a polarisable material which it is not. However, the raw data of the measurements clearly indicate that capacitive behaviour seen in response is much greater for platinum, gold and stainless steel than for Ag/AgCl. This proposes that the analysis used to solve the interface impedance is not applicable in case of non-polarisable materials. What comes to the interface capacitance of Ag/AgCl, the results have to be neglected as false results. Due to correlation between resistance and capacitance in the analysis, see [2], false results for the interface capacitance imply false results for the resistance. It can be therefore stated that the use of interface impedance measurement method presented in [2] is limited to contain only electrode materials that are sufficiently different from the non-polarisable materials. This, in general, is not very restrictive condition since not many materials are so close to being non-polarisable.

The power law for behaviour of interface resistance and capacitance mentioned in section IV, (3)-(4), was verified in the research. It can be clearly seen in Figs. 2 to 4 that when plotted on log-log scale, the behaviour of the interface properties is linear. The power for slope of interface resistance for these materials (Pt, Au and SS) was calculated to be between -0.70 and -0.95 for 7 x 7 x 0.5 mm electrodes and from -0.43 to -0.54 for 3.5 x 7 x 0.5 mm electrodes. The corresponding powers for interface capacitance were between -0.16 and -0.26 for electrodes with greater area and -0.34 and -0.48 for electrodes with smaller area. It is interesting to note that the slope of the exponential curve depends on the area of the electrode.

The theoretical relation that is assumed between the interface resistances and capacitances of the electrodes of different area is expressed in (1) and (2). The ratio of the areas of the electrodes was 1.98 which on logarithmic scale corresponds to absolute difference of 0.68 between the values. It can be seen in Fig. 2 to Fig. 4 that the difference in the interface properties is typically between approximately 0.5 and 1.0 except for some discrepancies. It can be said that the measurement results follow the theory presented in section IV quite well. Deviances in Fig. 2(a) and Fig. 4(b) for PBS are probably due to contamination of the PBS solution which has led to erroneous measurement results.

VII. CONCLUSIONS

Electrode-electrolyte interface impedance measurements were performed with a fairly new measurement method presented in [2] and slightly modified in this paper. The method seemed to work out well for electrode materials which are polarisable but not for non-polarisable materials, e.g. Ag/AgCl. Analysis results show that theoretical dependency of the interface properties on the area of the electrode is approximately as estimated in (1) and (2).

Stainless steel is not commonly used as electrode material but according to results gained in this research, its use as electrode material in implantable conditions is strongly encouraged.

Future considerations include measurements of the interfacial impedance of textile electrodes. Interface impedance measurement method as introduced in this article will be utilized with slight modifications, mainly regarding the value of the measurement resistor. Measurements of the interface impedance will be performed with both wet and dry textile electrodes placed on the properly prepared human arm.

Preliminary measurements with dry textile electrodes indicate that the measurement accuracy with the proposed method is not too good due to weak signal obtained with the electrodes. It is, however, possible to obtain reasonable results with the method by modifying the measurement apparatus to better meet the different measurement environment. By adjusting the value of the measurement resistor to an optimal level and driving a greater voltage (current) to the electrodes, the response can be made better. The areas of the textile electrodes that were tested were approximately four times the area of the electrodes thus higher current can be driven through the electrodes without affecting the current density at the electrode.

In the future, capacitive electrodes meant for implantation conditions will also be studied. The electrode material will be coated with a very thin layer of biocompatible material, e.g. parylene or TiO_2. Au-electrodes that were coated with a 3 μm parylene layer have been measured and results show that 3 μm of insulator is too thick a layer. The 3-dB frequency raised from 530 mHz up to over 100 Hz with this layer thickness. TiO_2 can be applied in layer thicknesses down to 200 nm which is obviously a clear improvement.

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