Proceedings of the 28th IEEE
EMBS Annual International Conference
New York City, USA, Aug 30-Sept 3, 2006

Long-Term Characterization of Electrode Materials for Surface Electrodes in Biopotential Recording

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Abstract—**The long-term electrical behavior of 16 different electrode materials was investigated by using continuous impedance spectroscopy over a period of 10 days. The materials included bare and electrolytically treated metals, metals coated with intrinsically conductive polymers, and polymers with conductive particles. Electrolytic treatment of metal electrodes yielded a significant impedance reduction. The lowest impedance values could be reached with the polymer-coated metal electrodes. The impedance behavior is an important aspect when choosing an electrode material, and has to be considered in signal processing. The choice of a material depends on the application of the electrode. Moreover, for long-term applications, the electrochemical stability of a material has to be considered.**

I. INTRODUCTION

ELECTRODES play an important role in biomedical technology. They are used for several applications, among them the recording of bioelectric potentials (ECG, EEG, EMG, ENG). Depending on their use, electrodes can have various sizes and designs. For superficial coupling to the body, electrodes with a surface area in the cm^2 range can be placed on the skin.

At the electrode interface, the electron current of the technical system is converted into an ion current flowing in the biological system, and vice versa. The electrochemical processes at the interface, and thus the electrical properties and the electrical behavior of the electrode, are strongly influenced by the materials present at the active surface, as well as by the surface area.

The electrical behavior of an electrode can be approximately described by an equivalent circuit diagram. The most common and most simple approach is shown in Fig. 1, various modifications can be found in the literature [1]. The Helmholtz capacitance C_H accounts for capacitive charging effects at the dielectric Helmholtz double layer, which is formed at the interface. The Faraday resistance R_F represents leakage currents penetrating this double layer, caused by reversible and irreversible Faraday reactions. The ohmic resistance of the electrolyte and the bulk material is considered by adding the resistance R_L. A dc voltage source V_S is included to account for the polarization voltage.

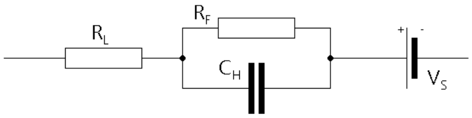

Fig. 1. Equivalent circuit diagram of an electrode.

Depending on the material, electrodes can be divided into polarizable and non-polarizable electrodes [2]. Bare metal electrodes are polarizable with a high polarization voltage that can be changes with repsect to a current flow. They are also called non-reversible electrodes and are characterized by a capacitive behavior. A non-polarizable electrode can be created by coating a metal electrode with a slightly soluble salt containing cations of the metal and anions also present in the electrolyte. A very popular example for this is the silver/silver chloride (Ag/AgCl) electrode.

Especially for recording electrodes, knowledge of the transition impedance of the material used as interface between a technical and a biological system is of crucial importance.

II. OBJECTIVE

Long-term stability is an important aspect for the evaluation of electrode materials, as many applications require the functionality of electrodes over several days, e.g. the monitoring of vital parameters with surface electrodes.

A means to determine the electrical properties of a material is the use of impedance spectroscopy [3]. With this technique, the complex impedance of an electrode is measured over a broad frequency spectrum. This is important as electrodes can be used within various frequency ranges, depending on the application.

In order to evaluate the suitability of potential electrode materials, there is need for a long-term characterization of the electrical properties of various materials for a period of at least 10 days.

III. MATERIALS AND METHODS

A. Electrode Materials

16 different materials were investigated, which could be divided into 5 groups:

- polarizable metals (silver, gold, platinum, iridium)

Manuscript received April 3, 2006. This work was supported by the MAVO InMuSens Project and the NEUROBOTICS Project (The fusion of NEUROscience and roBOTICS, IST-FET Project #2003-001917).

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- non-polarizable metals (galvanized and sintered Ag/AgCl, platinum black)
- polymer-coated metals (PEDOT (poly-3,4-ethylenedioxythiophene) on gold, iridium and platinum, polypyrrole on gold and iridium)
- conductive polymer paste (silver, carbon)
- nanoparticles in polysiloxane (silver, carbon, doped tin oxide)

14 electrodes were prepared from each material, the active electrode surface was a square with the area 1 cm^2. The materials were brought onto a glass carrier and contacted, except for the commercially available sintered silver/silver chloride electrodes (Golmed GmbH, Braunschweig), which were included for comparison.

B. Measurement Set-Up

The measurement set-up used in this work was described previously [4]. Impedance spectroscopy within a frequency range of 0.1 Hz – 100 kHz, with a measurement voltage of 50 mV was conducted. A 3-electrode set-up with a platinum counter electrode and an Ag/AgCl reference electrode was applied. Physiological saline (0.9 % NaCl) served as the electrolyte. 128 electrodes could be measured simultaneously. The measurements were performed continuously for a period of 10 days, at a constant temperature in an electromagnetically shielded environment.

IV. RESULTS

The measurement data was evaluated with respect to changes in the impedance over the measurement period. The figures 2-6 exemplarily show the results for a representative of each of the different material groups (iridium, platinum black, polypyrrole on gold, carbon polymer paste, and polysiloxane with silver nanoparticles). The results are displayed in 3D graphs, with the x-axis as the frequency, the y-axis as the absolute value of the impedance or the phase angle, respectively, and the z-axis as the time in days.

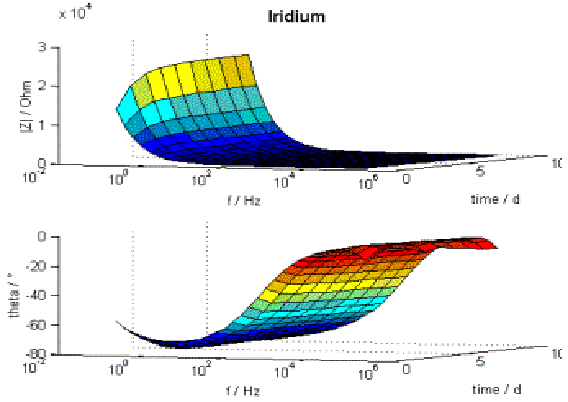


Fig. 2. Absolute impedance (top) and phase (bottom) of iridium vs. frequency over 10 days of measurement. The iridium layer was 200 nm thick and was sputtered on glass, with a 10 nm titanium layer as adhesion promoter.

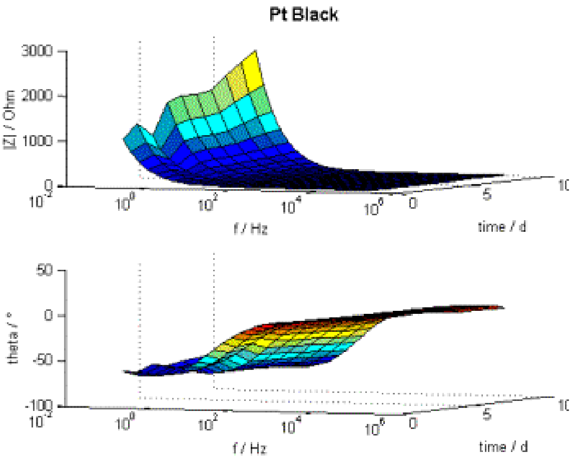


Fig. 3. Absolute impedance (top) and phase (bottom) of platinum black vs. frequency over 10 days of measurement. The platinum black layer was electroplated potentiostatically on a 200 nm platinum layer sputtered on glass, with a 10 nm titanium layer as adhesion promoter.

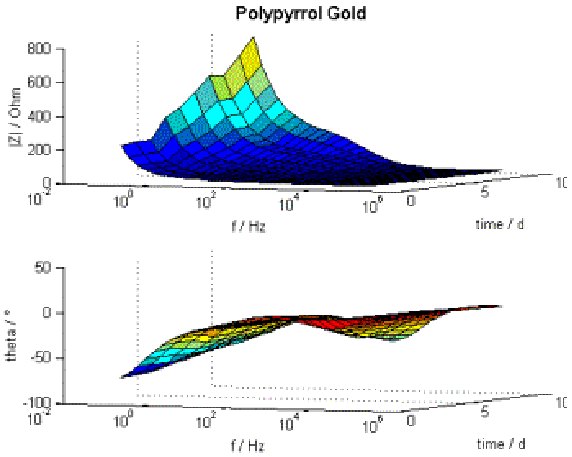


Fig. 4. Absolute impedance (top) and phase (bottom) of polypyrrole on gold vs. frequency over 10 days of measurement. The polypyrrole layer was electroplated galvanostatically on a 200 nm gold layer sputtered on glass, with a 10 nm titanium layer as adhesion promoter.

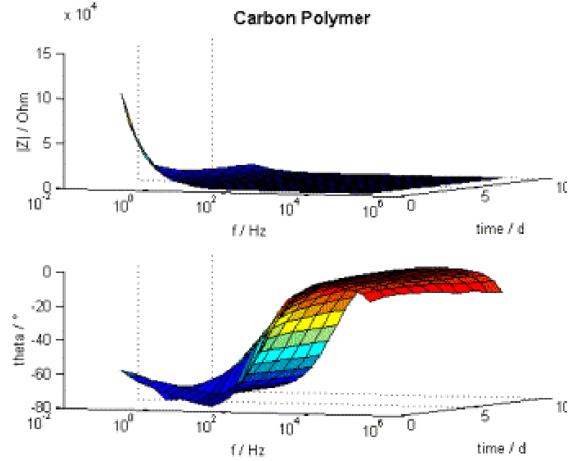


Fig. 5. Absolute impedance (top) and phase (bottom) of carbon polymer paste vs. frequency over 10 days of measurement. The polymer paste layer was brought on a glass substrate by a screen printing technique.

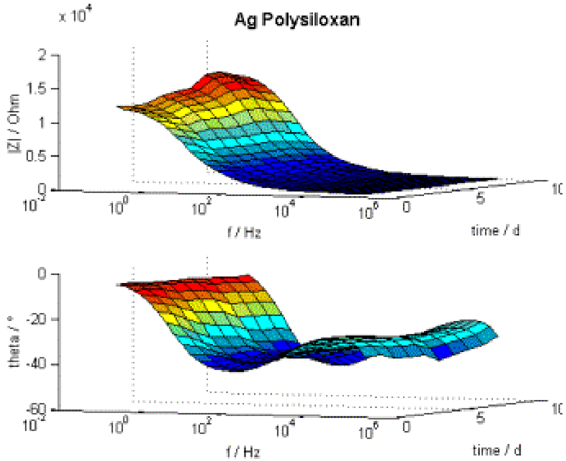
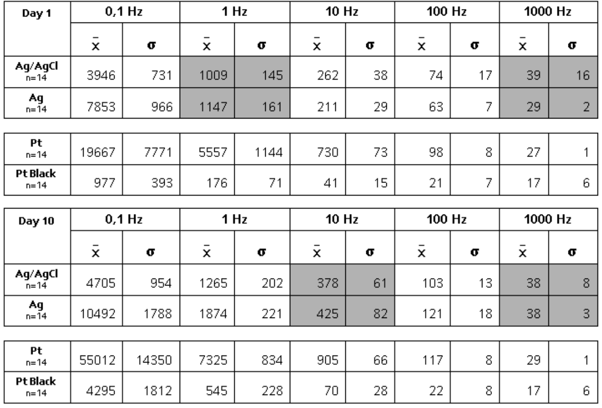


Fig. 6. Absolute impedance (top) and phase (bottom) of polysiloxane with silver nanoparticles vs. frequency over 10 days of measurement. The polysiloxane layer was brought on a glass substrate by a screen printing technique.



Day 1	0,1 Hz		1 Hz		10 Hz		100 Hz		1000 Hz	
	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
Ag/AgCl n=14	3946	731	1009	145	262	38	74	17	39	16
Ag n=14	7853	966	1147	161	211	29	63	7	29	2

Pt n=14	19667	7771	5557	1144	730	73	98	8	27	1
Pt Black n=14	977	393	176	71	41	15	21	7	17	6

Day 10	0,1 Hz		1 Hz		10 Hz		100 Hz		1000 Hz	
	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
Ag/AgCl n=14	4705	954	1265	202	378	61	103	13	38	8
Ag n=14	10492	1788	1874	221	425	82	121	18	38	3

Pt n=14	55012	14350	7325	834	905	66	117	8	29	1
Pt Black n=14	4295	1812	545	228	70	28	22	8	17	6

Fig. 7. Statistical comparison between silver and silver/silver chloride, and platinum and platinum black, respectively, on day 1 and day 10. Grey: no significant difference, white: significant difference between the mean values at a significance level of 0.01.

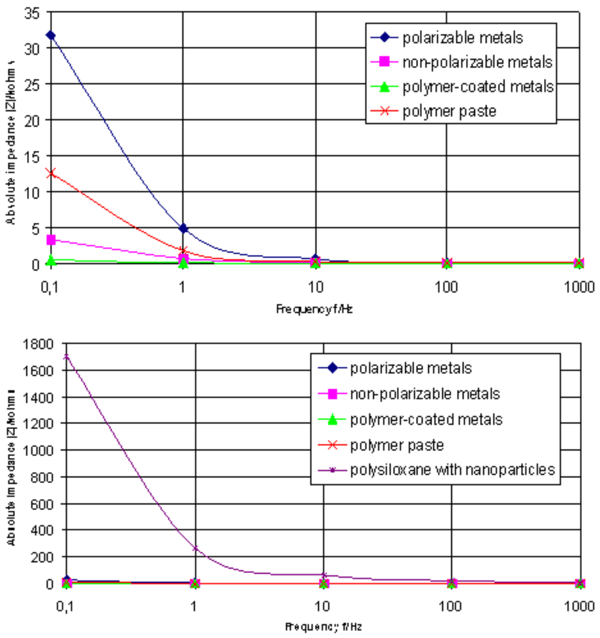


Fig. 8. Absolute impedance versus frequency, average results for the 5 different material groups. The values are averaged over 10 days.

To show the effect of electrolytic treatment, a statistical comparison (t test) between the materials silver and silver/silver chloride on the one hand, and platinum and platinum black on the other hand was done. The results of this evaluation are depicted in Fig. 7. The grey fields show the points with no significant difference, the white fields the points with significant difference between the mean values at a significance level of 0.01.

For each material, the average value of all measurements within the period of 10 days was calculated at 5 different frequencies (0.1 Hz, 1 Hz, 10 Hz, 100 Hz and 1 kHz). Moreover, the total average values over all representatives of the 5 different material groups was calculated. These values are presented in Fig. 8.

V. DISCUSSION

For all materials, the absolute value of the impedance decreases strongly with increasing frequency, as expected from theory (cf. Fig. 1).

For small frequencies, the materials from the group of polysiloxane with nanoparticles show by far the highest impedance. These materials exhibit a more capacitive character. Electrodes made from polysiloxanes with nanoparticles are suitable for dry measurement of biosignals, without the requirement of electrolyte gels on the skin, as the potentials are recorded by capacitive coupling.

The transition from polarizable metals to non-polarizable metals by surface treatment yields a significant impedance reduction (Fig. 2 and Fig. 8), which corresponds to theory [2] and experiments in the literature [5], [6].

The results for the polymer pastes are between the polarizable and non-polarizable metals. The impedance of the silver polymer paste is lower than that of the sputtered silver, although silver is the conducting material in both cases. This might be explained by the rough surface of the polymer paste, yielding an enlarged surface area.

The best results are obtained with the electrodes coated with a layer of a conductive polymer. Polypyrrole as well as PEDOT can be used to significantly lower the impedance of an electrode. This is considered to be due to the surface enlargement caused by the porous polymer layer [7].

Material-dependent differences can also be seen in the phase diagrams (figures 3-7). Most of the materials exhibit a typical phase behavior: the absolute phase angle is small for high frequencies, and rises for lower frequencies. This phase angle rise is shifted to lower frequencies by surface treatment (coating with silver chloride, platinum black or intrinsically conductive polymers).

The rise of the phase angle corresponds to the increase of the absolute impedance for decreasing frequencies. In the equivalent circuit diagram in Fig. 1, the influence of the capacity reactance becomes stronger, and less charge can be transmitted by the Helmholtz capacitance. For a frequency of zero, current can only flow through the Faraday resistance R_F. Thus, the absolute impedance at very low frequencies is an approximation to R_F. The Faraday resistance can also be directly measured by applying a constant current in combination with a potential-sensing electrode [8]. R_F is however dependent on the current density. For platinum, literature yields a value of 30.3 kΩ (extrapolated to a current density of zero). Our measurements resulted in an impedance of 55.1 kΩ for platinum at 0.1 Hz, at a current density of $\approx 10^{-3}$ mA/cm^2.

High absolute phase angles induce a phase shift of the recorded signals. This effects especially low-frequency signals, as the absolute time shift for a given phase angle is inversely proportional to the frequency. The phase shift has to be considered during the design of the signal processing unit for the system, in order to obtain undistorted signals.

Long-term stable surface electrodes are essential for the continuous monitoring and recording of biopotentials. So far, this problem has not been solved satisfactorily [9]. Thus, the integration of stability investigations is important in an evaluation of electrode materials.

Over the time, most materials from the study showed an increase in impedance during the first days. After this initial rise, the impedance remained relatively constant. However, for some materials, the impedance dropped with progressing time. This was the case for the carbon polymer paste and the materials from the group "nanoparticles in polysiloxane".

While the impedance of the sintered Ag/AgCl electrodes remained almost constant over 10 days, a significant impedance increase was visible for the Ag/AgCl electrodes prepared by galvanization. This underlines that not only the material itself, but also its structure strongly influences the electrical stability of an electrode.

Concerning the group of metals coated with intrinsically conducting polymers, PEDOT is considered to have a better long-term stability than polypyrrole [10]. This could be confirmed by the measurements. While the impedance of the PEDOT-coated electrodes remained almost constant, polypyrrole showed an increase in the absolute impedance.

VI. CONCLUSION

In this work, long-term impedance spectroscopy measurements on 16 potential electrode materials have been conducted. The materials could be allocated to five groups with similar electrochemical behavior. Continuous measurement data was obtained for a period of 10 days.

The effect of electrolytic treatment, yielding coating layers of different kinds, on the electrochemical properties of electrode materials could be successfully demonstrated.

The electrochemical stability and the electrical properties of an electrode depend on the used material. When choosing a material for an electrode, the intended field of application has to be considered.

ACKNOWLEDGMENT

We would like to thank our partners in the MAVO InMuSens Project and the NEUROBOTICS Project.

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