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Electroactive coating of stimulating electrodes

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Electrophysiologic examinations as well as the electrotherapy of heart diseases require electrodes which distinguish themselves by outstanding sensing and pacing performance. Both, the sensing and the stimulation behaviour are determined by the interface between electrode and tissue. To avoid energy losses and distortions of heart signals having components down to 1 Hz, the interface's impedance has to be very small in the corresponding frequency range. Towards this goal a new coating has been developed: electrolytically deposited electroactive iridium oxide. On the electrode's surface iridium oxide forms a long-term stable reversible redox system which changes its oxidation state according to the applied potential. The decrease of impedance is demonstrated by impedance spectroscopy: the low-frequency limit is lowered by more than three orders of magnitude to a value of 0.4 Hz. The reason is the electroactivity of this material which is caused by reversible proton incorporation into the coating, as is proven by cyclic voltammetry. Due to the low interface impedance well below 1 Hz, the coated electrodes fulfil the requirements for medical applications. Outstanding sensing behaviour was shown by measuring the monophasic action potential in dogs, which is possible without any distortions.

1. Introduction

Progress in clinical diagnosis and electrotherapy of heart diseases has to result in lower stimulation thresholds and better sensing performance. To this goal the measurement of heart potentials such as ventricular evoked responses (VER) and monophasic action potentials (MAP) have become a topic of major interest for diagnosis as well as for physiological and automatic control of pacemakers. These tasks impose new requirements on leads: the ability of low energy stimulation and ameliorated measurement capabilities.

The most essential prerequisite is low impedance of the so-called phase boundary, the interface between electrode and tissue. From the physical point of view the phase boundary acts as a high-pass filter, hence causing disturbances of the measured signals. In order to avoid these distortions as far as possible the interfacial impedance must be very low, especially in the frequency range above 1 Hz, i.e. the lower cut-off frequency should be less than 1 Hz. This demand is usually fulfilled by enlarging the electrodes' active surface areas using techniques like sintering, etching or fractally coating [1]. Another way to reduce the impedance is by coating the electrode with electroactive materials.

An electroactive material forms a reversible redox system on the surface of an electrode. The change in oxidation number according to the applied potential is associated with a charge transfer across the phase boundary, thus resulting in an increased current flow which decreases the interfacial impedance. A well-known example is the silver–silverchloride electrode (Ag/AgCl) widely used for MAP measurements. However, in contact with biological tissue the silverchloride on the surface dissolves and causes inflammations of the myocardium due to its toxicity [2, 3].

In contrast to this, some metals of the platinum group such as rhodium (Rh), ruthenium (Ru) and iridium (Ir) combine electroactivity and excellent biocompatibility. As previous investigations have shown Rh and Ru coatings exhibit a very low impedance immediately after the coating process. However, the long-term stability is inadequate: the impedance of the phase boundary increases during electrochemical load [4].

Therefore this study presents results for electrodes which were coated with Ir or its oxides and hydroxides using electrolytic deposition. The coating process has been optimized with regard to the impedance of the phase boundary and the long-term behaviour under electrochemical loads, which are equivalent to the usual loads in electrostimulation. Investigations concerning the electrochemical properties of these coatings have been performed using cyclic and AC-voltammetry for different electrodes. Furthermore, electrodes coated with iridium oxide have been analysed for their abilities to measure MAPs.

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2. Materials and methods

2.1. The iridiumoxide coating process

As Fig. 1 shows, the elements of the platinum group have at least two different oxidation numbers. Therefore they exhibit electroactivity and are suitable for appropriate electrode coatings. However, platinum and palladium cannot take more than two different oxidation numbers and many osmium compounds are toxic. So Ir is the material preferred for electroactive coating [5]: it is exceptionally biocompatible and offers four different oxidation states. In the study presented this material has been electrolytically deposited on substrates made of either 316L-steel or platinum. These substances are widely applied in biomedical engineering and have proven their suitability for medical applications.

The first step in the manufacturing procedure is the electrolytic cleaning of the substrates which is done in the commercial basic solution Galvarol (DODUCO) with a current density of $-20\,A/dm^2$. Thereafter, oxide layers are dissolved in the acid solution Solvamet (DODUCO) using the same current density. 316L-substrates are additionally covered with a thin gold layer (Auromet, DODUCO) guaranteeing a high and uniform conductivity of the surface as well as a high adhesion of the iridium oxide coating. The electrolyte for the iridium oxide coating consists of iridium(IV)-chloride dissolved in water. As the oxides of the elements of the platinum group are hardly soluble in alkaline solution, using an alkalic medium for electrodeposition rises the process's efficacy. In order to avoid precipitation the iridium oxide dissolved has to be bonded in a stable complex. Therefore, oxalic acid is added to the solution resulting in a stable complex of iridium oxide. The pH value is adjusted to 10 by adding potassium carbonate.

Finally, iridium oxide is electrolytically deposited at a temperature of 25°C with an anodic pulsed current. The pulses width is 0.2 s and the amplitude is $5\,A/dm^2$. No current flows during the 3 s between each pulse.

2.2. Measuring procedures

The electrochemical characteristics of the coated electrodes were analysed by potentiostatic methods such as potentiostatic impedance spectroscopy, cyclic voltammetry and AC-voltammetry. Topics of interest are the impedance of the phase boundary, the electroactivity and the mechanisms at the interface. Electroactivity and processes at the phase boundary are investigated by cyclic voltammetry: a triangular-shaped voltage with a slope of about 100 mV/s was applied and the current was measured in dependence of that voltage. The processes taking place at the interface were studied by changing the coreactants which are components of the electrolyte. For this purpose different electrolytes were used, e.g. the water free electrolyte acetonnitril (CH_3CN).

The reversibility of reaction is observed using AC-voltammetry. For that purpose an additional AC voltage with an amplitude of 10 mV and a frequency of 20 Hz was superimposed on the triangular-shaped voltage ramp. The AC current was measured separately using a look-in amplifier. This method corresponds to an impedance measurement at every point of the ramp. In the case of a reversible reaction the impedance values are independent of slope and polarity of the triangular voltage ramp. Therefore, performing one positive and one negative sloped ramp the resultant current–voltage diagram has to be symmetrical about the voltage reversal point.

The morphology of the surfaces was investigated by scanning electron microscopy (SEM), atomic force microscopy (AFM) and scanning tunnelling microscopy (STM). Finally, the MAP was measured in dogs using these iridium oxide coated electrodes.

	Platinum group		
Element Oxidation number	Ru Os	Rh Ir	Pd Pt
1⁺/2⁺	H K	K	O H Cl
3⁺	O H Cl K	O H Cl K	
4⁺	O Cl	O H Cl K	O H Cl
6⁺	O Cl K	O K	
7⁺	O H		
8⁺	O		

H Hydrate Cl Chloride

O Oxide K Complexe

Figure 1 Elements of the platinum group and their oxidation numbers.

3. Results

The iridium oxide deposition process is optimized with regard to the adhesion on the different substrate materials and to the impedance spectrum or the low-frequency limit, respectively. The iridium oxide coating distinguishes itself by excellent adhesion on platinum substrates. In contrast, satisfactory adhesion on 316L-electrodes can only be obtained by a thin intermediate gold layer deposited before the iridium oxide coating. The coatings are homogenous and initially of blue colour.

3.1. Morphology of the coating

The surface structure of the coatings was investigated by SEM, AFM and STM. Fig. 2 shows an AFM measurement of an electrode's surface covering an area of 3 µm × 3 µm. The coating has a wavy surface consisting of structures which look like hemispheres with diameters between 100 and 400 nm. A higher resolution (100 nm × 100 nm) shown in the STM micrograph in Fig. 3 reveals a nanocrystalline surface structure. The smaller objects extend over less than five nanometres.

3.2. Impedance of the interface

The impedance of the phase boundary is the most important criterion for the application of these coatings to stimulation as well as to sensing electrodes.

Fig. 4 compares the impedance spectra of the electrode–electrolyte interface of a coated and uncoated electrode immersed in phosphate buffered physiological saline. The high-pass characteristic of the phase boundary can be seen. The coated electrode exhibits a much smaller impedance in the frequency range below 1 kHz compared to the uncoated one. Whereas the uncoated substrate has a lower frequency limit of 1.5 kHz iridium oxide coating drastically reduces this value to 0.4 Hz. Due to the high-pass filter characteristic a capacity can be assigned to the phase boundary. For the uncoated electrode this capacity is determined as 6.6 $\mu F/cm^2$, and for the coated one, 36 mF/cm^2. The difference of more than three orders of magnitude in the lower frequency limit results in different suitability for medical applications. Whereas the uncoated electrode hinders current transfer during both stimulation and sensing, the iridium oxide coating allows stimulation and sensing without losses. Due to the very low cut-off frequency heart potentials having components down to 1 Hz can be measured without any distortions or losses.

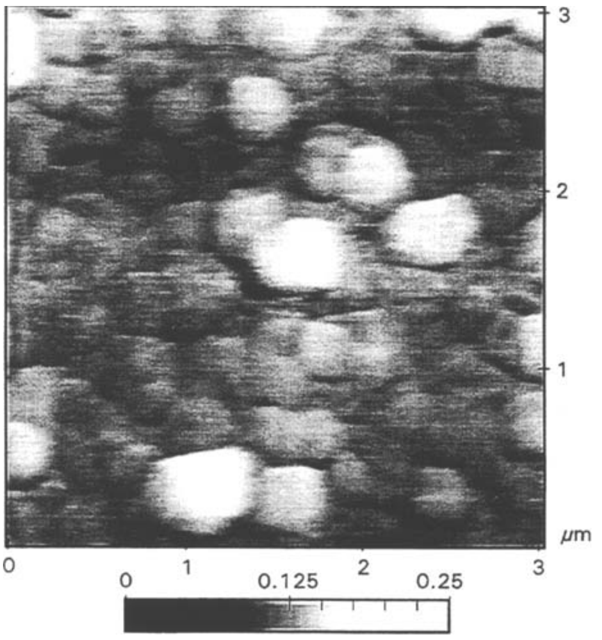

Figure 2 AFM micrograph of an iridium oxide coated electrode (3 µm × 3 µm).

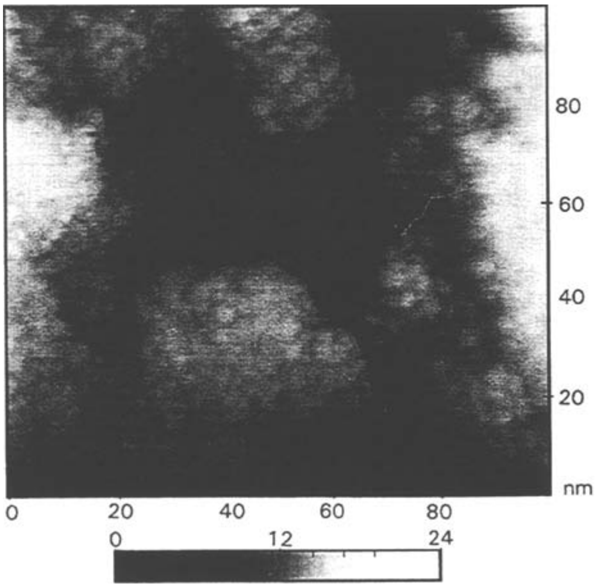

Figure 3 STM micrograph of the nanocrystalline structure of the iridium oxide coating (100 nm × 100 nm).

3.3. Long-term behaviour

The long-term behaviour of the iridium oxide coatings were investigated for different loads. Anodic and cathodic pacemaker pulses (voltage: 10 V, pulse width: 1 ms, frequency: 2 Hz) were applied for 4 weeks. During the first 24 h the impedance curve is negligibly changed by the electrochemical load. However, following this the coating distinguishes itself by a perfect long-term stability, as is shown in Fig. 5 for anodic loads. In the case of cathodic loads the coating has a similar behaviour. Furthermore, the electrochemical properties of iridium oxide aren't altered by storage in physiological saline or in air.

3.4. Electroactivity of the iridium oxide coating

The decrease in the cut-off frequency by more than three orders of magnitude cannot be explained by an

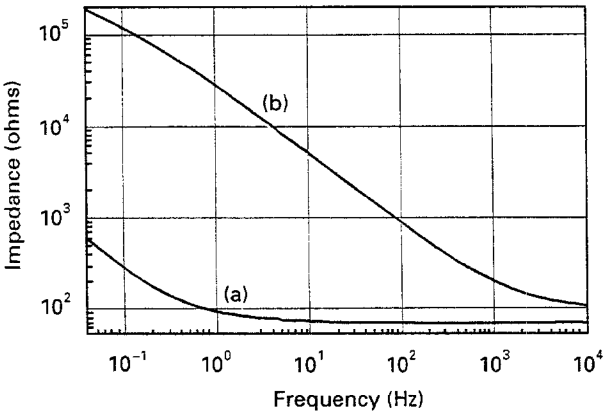

Figure 4 Impedance spectrum of an iridiumoxide coated (a) and an uncoated (b) electrode made of 316L-steel.

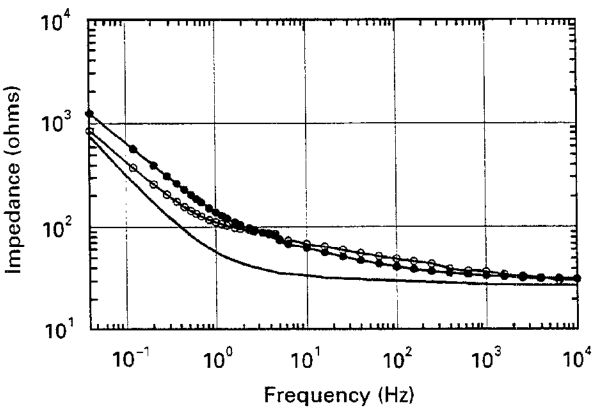

Figure 5 Long-term behaviour under anodical loads in physiological saline: — no load; —○— anodic load, 1 day; —●— anodic load, 32 days.

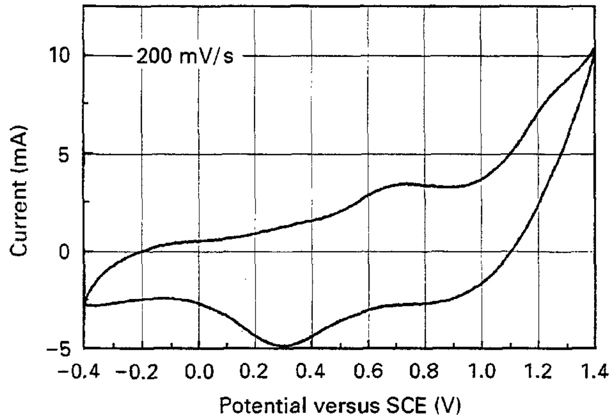

Figure 6 Cyclic voltammogram of a coated electrode in phosphate buffered physiological saline.

enlargement of the surface area by the nanocrystalline structure. The main reason is the electroactivity of the material used: Fig. 6 displays a voltammogram of a coated electrode: the applied voltage ramp has a minimum value of -0.4 V, a maximum of 1.4 V and a slope of 200 mV/s. The peaks or shoulders visible in the current–voltage diagram around 1.25 V, 0.7 V and 0.3 V are due to chemical reactions. These reactions are connected to a change in oxidation number of iridium and, hence, to a charge transfer across the phase boundary, thus lowering the impedance. Therefore, the electroactivity of the material leads to an additional current flow which is responsible for the observed decrease of the low-frequency limit.

As a comparison with an electrochemically activated iridium surface shows [6], the peaks observable in the voltammogram can be assigned to the following surface reactions:

$$Ir(OH)_4 + H^+ + e^- \Leftrightarrow Ir(OH)_3 \cdot H_2O$$

$$Ir(OH)_3 \cdot H_2O + H^+ + e^- \Leftrightarrow Ir(OH)_2 \cdot 2H_2O$$

$$Ir(OH)_2 \cdot 2H_2O + H^+ + e^- \Leftrightarrow Ir(OH) \cdot 3H_2O$$

3.5. Reversibility of the reactions

Fig. 7 shows a result of the AC voltammetry. The AC current–voltage curve is symmetrically related to 0.9 V in the negative sloped ramp. The small shift of the curve to the right is caused by the high slope of 50 mV/s. Consequently, the impedance at any point of the ramp with positive slope is equal to the corresponding point in the negative ramp. Therefore, the reactions are perfectly reversible which is a decisive prerequisite for medical application.

3.6. Proton storage as the fundamental process

The electroactivity of iridium oxide is due to a reversible incorporation of protons (H^+) into the coating during electrochemical reactions. This has been proven by cyclic voltammetry using acetonnitril (CH_3CN) as electrolyte – a water-free solution that does not contain protons or OH^- ions. The voltammogram displayed in Fig. 8 shows a negligible current flow of less than 0.01 mA and no peaks are visible. Therefore, the coating does not exhibit electroactivity in this electrolyte. The reason is the absence of coreactants necessary for the electrochemical surface reactions. The addition of lithiumperchlorate ($LiClO_4$) into the acetonnitril provokes a strong increase of the current by two orders of magnitude and peaks appearing in the voltage–current curve demonstrate the regained electroactivity of the coating (Fig. 9). In this case lithium ions act as proton donators. In contrast

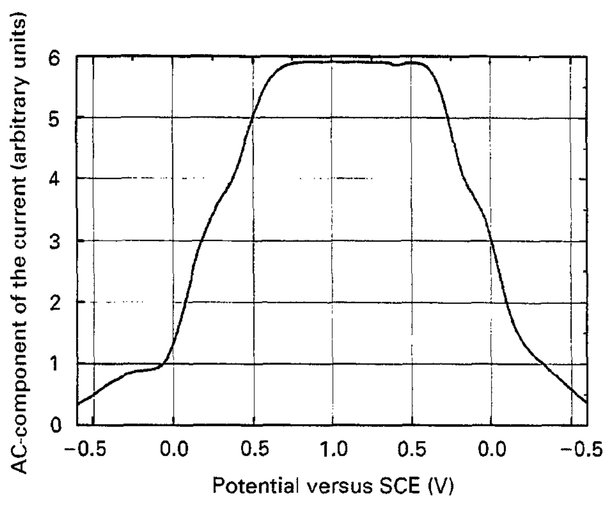

Figure 7 AC-voltammogram of a coated electrode in phosphate buffered physiological saline: AC current; 10 mV, 20 Hz; slope 50 mV/s.

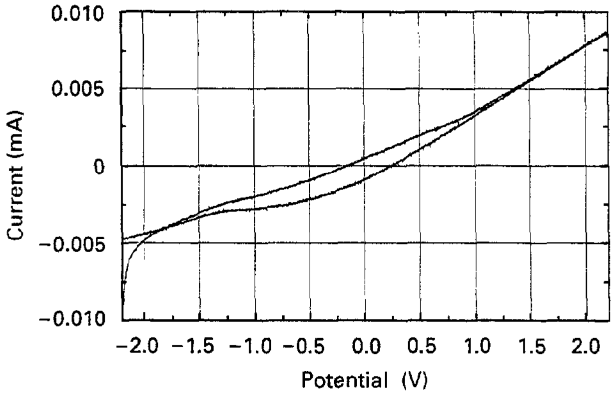

Figure 8 Cyclic voltammogram of a coated electrode in acetonnitril.

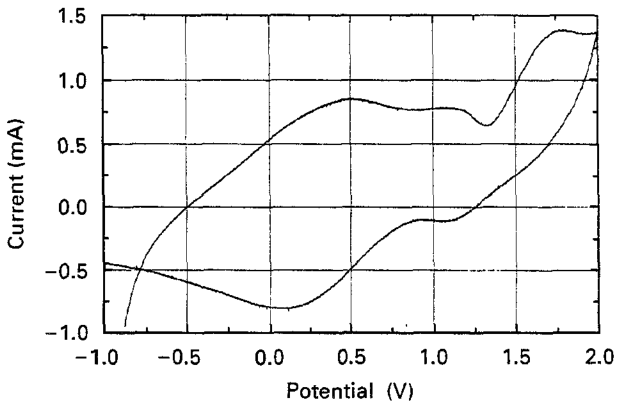

Figure 9 Cyclic voltammogram of a coated electrode in acetonnitril following the addition of $LiClO_4$.

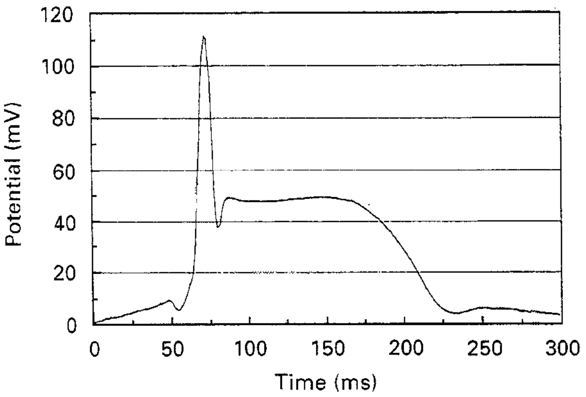

Figure 10 MAP measured in dogs using iridium oxide coated electrodes.

to this, adding potassium hydroxide only leads to a negligible increase in current flow. Summarizing these results, the electroactivity of iridium oxide coatings in aqueous electrolytes is based on the incorporation of protons into the iridium oxide layer, whereas hydroxide ions play only a minor role for electroactivity.

3.7. Measurement of the MAP

Following the development of the new coating and the *in vitro* characterization of its electrochemical properties the focus shifted towards a more medical application: MAP measurement. Conventional temporary electrodes for electrophysiological investigations (Multicath 4, BIOTRONIK) were coated with iridium oxide as described above. Using these electrodes MAP measurements were performed in dogs. As expected according to the results of the impedance spectroscopy, the new electrodes allow the measurement of undistorted MAP signals (Fig. 10)

4. Conclusions

The results presented above prove that electrochemically deposited iridium oxide coatings lower the interfacial impedance very significantly and exhibit excellent long-term stability. Therefore, these coatings show exceptional electrochemical performances combining low threshold stimulation and ideal sensing behaviour. The possibility of measuring the MAP with long-term stable and biocompatible electrodes offers a multitude of applications in medical diagnosis and in electrotherapy of heart diseases.

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