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Effect of smooth, porous and fractal surface structure on the properties of an interface

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Recently, biomaterials research has focused on the creation of new materials. Mixing or doping of well-tried materials should aim to result in new physical or chemical properties, better tissue tolerability and improved long-term stability. We present another way of improving performance: the application of new technologies to well-known materials. The surface structure of a coating depends on the deposition technique. Hence, the transfer of, for example, sputtering technology to biotechnology may solve current problems with well-tried materials. This paper reports the influence of surface structure and area on the properties of pacemaker electrodes. Smooth electrodes were compared with porous electrodes produced by sintering and with fractal electrodes resulting from physical vapour deposition of iridium or titanium nitride. Micrographs revealed a slight enlargement of the surface area by sintering and an enormous enlargement with fractal coating. Analysis of electrochemical properties proved the advantages of fractal coating: the impedance spectra exhibited incomparable low impedances for frequencies down to 1 Hz and no after-potentials could be detected. Clinical results confirmed the superiority of fractal electrodes. The stimulation thresholds were significantly reduced, P-and R-wave amplitudes were increased, and ventricular evoked responses and monophasic action potentials were able to be measured with clarity unknown so far.

1. Introduction

The performance of an electrode is mainly determined by the properties of the boundary between the electrode and the tissue. This interface – the so-called phase boundary – is a complex system exhibiting non-ohmic behaviour. Therefore, a more detailed analysis is needed to clarify the physical mechanisms that form the basis of an electrode's characteristics.

The fundamental current transport mechanisms are different in an electrode and in an electrolyte such as the tissue liquid. Whereas in an electrode electrons are acting as charge carriers, the current in an electrolyte is due to the movement of solvated ions. The link between electronic and ionic current involves three different mechanisms competing for the interfacial charge transport. The first is a direct neutralization reaction between electrons leaving the electrode and ions close to the electrode's surface. However, on immersing the electrode in the electrolyte, the former is covered by a monolayer of adsorbed water molecules (Fig. 1). This monolayer hinders the direct electron transfer across the phase boundary. Furthermore, these direct reactions result in radicals, causing inflammation of the surrounding tissue, which must be avoided as it causes an increase in the pacing threshold.

The second mechanism is based on a reversible electrochemical reaction on the electrode's surface. The current flow is due to a change in the oxidation number of one of the participating materials. A well-known example is the Ag/AgCl electrode.

The third possibility for current transport across the phase boundary originates in the formation of the so-called Helmholtz double layer. Responding to the voltage applied to the electrode, solvated ions gather at the electrode's surface. The whole arrangement can be seen as a parallel plate capacitor, with the electrode and the solvated ions acting as the plates and the monolayer of absorbed water molecules as the dielectric. This kind of current is completely reversible and does not result in any toxic products, therefore exhibiting excellent biocompatibility.

Summarizing the main properties of the three mechanisms, the phase boundary can be represented by an equivalent circuit consisting of the faradaic resistance R_F and the Helmholtz capacitance C_H, where R_F gives rise to the irreversible part of the charge transport and C_H is responsible for the reversible current flow. R_F and C_H constitute an RC network with high pass filtering characteristics. C_H is closely related to the surface area:

$$C_H = \varepsilon\varepsilon_0 \frac{A}{d_{Hdl}}$$

where ε and ε_0 are the dielectric numbers and d_{Hdl} is the thickness of the Helmholtz double layer. Thus,

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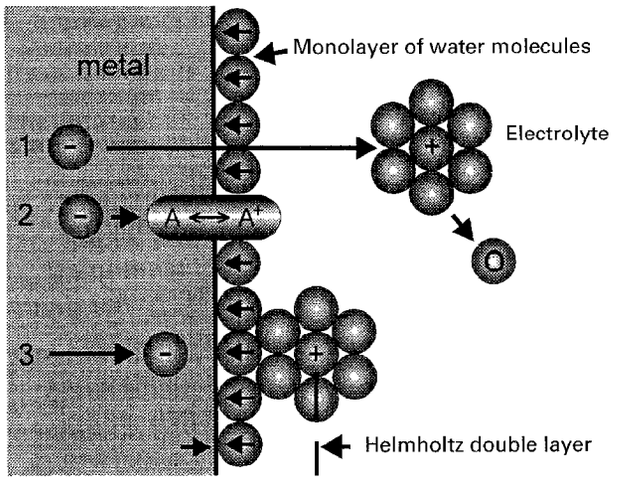

Figure 1 Diagram of the phase boundary – the interface between electrode and tissue liquid – with the possible charge transfer mechanisms: (1) direct neutralization reaction, (2) redox reaction, and (3) capacitive charge transfer.

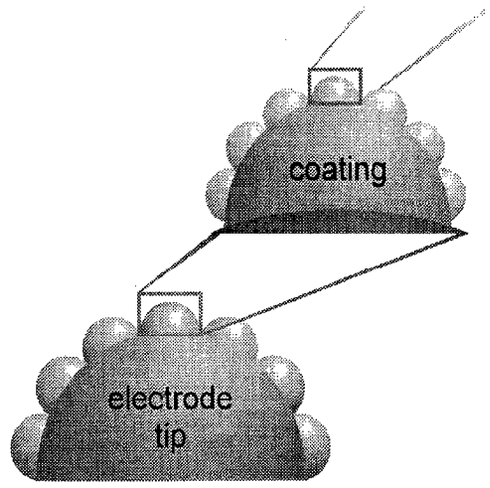

Figure 2 The principle of fractal coating. Repeatedly covering the surface with ever smaller hemispheres multiplies the surface area.

increasing the surface area leads to a larger Helmholtz capacitance.

Consideration of the high pass filtering by the electrode is of great importance with regard to transmission of pacing pulses as well as the electrode's measurement capabilities. As the results presented below show, a high cut-off frequency disables the electrode for measuring intracardiac signals like the monophasic action potential (MAP) or the ventricular evoked response (VER).

The last important aspect characterizing the electrode is the after-potential which disturbs every measurement directly following a stimulus. The delivery of a stimulus of length T charges the phase boundary according to the following equation:

$$U = \frac{1}{C_H}\int_0^T I_C(t)dt$$

where $I_C(t)$ is the current flowing during the pulse. As the formula shows, the after-potential can be minimized by enlarging C_H.

2. Methods and materials

As discussed above, a good electrode is characterized by a large surface area. However, increasing the surface area by simply enlarging the electrode is counterproductive, as the resulting electrode needs an increased amount of energy for effectively stimulating the surrounding tissue [5]. Hence, the problem which must be overcome is to integrate a surface area as large as possible on an electrode of limited size. To discuss this problem clearly in the following, we introduce two different attributes characterizing surface area: 'geometrical' means the area resulting directly from the tip's geometrical size, disregarding any surface structure, assuming an absolutely smooth surface. 'Active' means the actual interface area between electrode and electrolyte, considering roughness or porosity. It is the active surface area that counts for the Helmholtz capacitance. Hence, our problem is to increase the active surface area while leaving the geometrical area unaffected. One of the first techniques promising an enlargement of active surface area was sintering of spheres with a diameter of approximately 200 µm [1]. The resulting surface mainly consists of several layers of spheres covering the electrode, thus producing a porous electrode tip with an increased active surface area. However, most of the created area is an inner surface which does not allow adequate current densities.

Nevertheless, the idea of repeatedly covering the electrode's surface led to the procedure of fractal coating. Fig. 2 shows a detailed example. If the smooth tip is covered by hemispheres, the active area doubles. If on the surface of every hemisphere a new layer of smaller hemispheres is created, the active area again doubles. So N repetitions of this step with ever smaller hemispheres increases the active surface area by a factor of 2^N. The resulting tip shows a fractal structure with an enormous outer active surface area.

This type of coating can be produced using plasma-enhanced physical vapour deposition. In a high vacuum apparatus, argon ions from a plasma are accelerated by an outside electrical field towards the cathode made of the coating material. Single cathode atoms are sputtered away by the incident argon ions and are deposited on the electrode tips. To get excellent fractal surfaces this deposition process has to be diffusion limited. This sputtering technique can be applied to quite a variety of elements. Due to its well-known biocompatibility, iridium is a first choice material. By adding adequate gases to the argon atmosphere even combinations of elements can be deposited with a fractal structure, for example as was done with TiN.

3. Results and discussion

The evaluation of the different electrodes' performances covered several aspects. First of all, direct mapping of the surface using scanning electron microscopy (SEM), scanning tunnelling microscopy (STM) or atomic force microscopy (AFM) directly revealed the surface structure. Secondly, *in vitro*

investigations of impedance spectrum and after-potential or of long-term behaviour for different loads allowed differentiation of the electrodes prior to clinical use. Finally, clinical findings corroborated the conclusions drawn before.

3.1. Morphology

The micrographs showed enormous differences between the surfaces of smooth, sintered and fractally coated electrodes. The active surface area of a smooth electrode is nearly identical to its geometrical area. An increase in active area was detected for the sintered electrodes. The tip was evenly covered with spheres, with pores in between leading to another layer with an identical structure deeper inside the tip. However, the surfaces of the spheres themselves were still smooth, i.e. exhibited no surface roughness or porosity [2]. Hence, the sintered electrode's active surface is less than the sum of the geometrical surface area of the spheres sintered to the electrode's tip. Therefore, the increase in surface area does not exceed a factor of 5 and the performance of the sintered electrodes is only slightly improved.

The fractally coated electrodes yielded quite different micrographs (Figs 3 and 4). The surface resembles a cauliflower and this appearance is nearly independent of the magnification chosen. This self-similarity verifies the fractality of the surface. Thus, an enormous active surface area is created which is directly accessible to the electrolytic charge carriers. Hence, such a surface favours the capacitive current transport mechanism to an incomparable degree.

3.2. Electrochemical properties

One of the most important aspects of an electrode is the impedance spectrum. Fig. 5 shows the spectra for three different electrodes: a smooth, a sintered and a fractally coated one. Despite the identical geometrical surface area of the tip ($10\,mm^2$), the three electrodes have different limiting frequencies: the larger the active surface area, the lower the cut-off frequency. The results from the smooth and the fractally coated tip differ by more than three orders of magnitude, reflecting the increase in the active surface area by a factor of at least 1000. If on the other hand the spectra of fractal TiN and Ir coatings are compared, the difference is much less pronounced (Fig. 6). This clearly proves the dominance of the surface structure over the surface material.

The lowering of the cut-off frequency has important consequences concerning the measurement of heart potentials with frequency components down to 1 Hz (e.g. MAP). The impedance spectra reveals that only the fractal coating guarantees their undisturbed and loss-free transmission.

The accurate measurement of intracardiac signals is also influenced by the after-potential. Figs 7 and 8 show these potentials after stimuli: whereas the smooth electrode exhibits a high after-potential disturbing every measurement, the fractally coated electrode does not show an after-potential at all.

Another important aspect which was investigated *in vitro* is the long-term stability of fractal Ir and TiN coatings depending on polarity and strength of the load. For cathodic pulses, no difference between the two materials could be found: both are stable in long-term. The results are quite different for anodic load: whereas Ir again proves to be stable in this situation, TiN coatings exhibit a severe decrease in capacitance (Fig. 9). Therefore, the application of TiN must be restricted to cathodic loads.

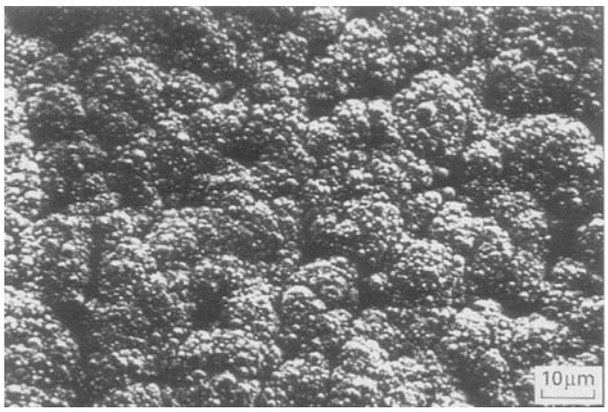

Figure 3 SEM micrograph of a surface fractally coated with iridium. The magnification of 1000 reveals a cauliflower-like structure.

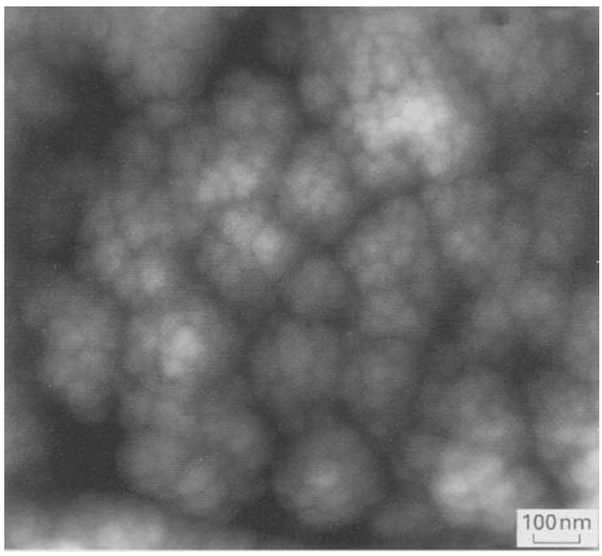

Figure 4 STM micrograph of the same surface as in Fig. 3, with a magnification of 16 000. The reoccurrence of the cauliflower structure clearly proves the self similarity and, hence, fractality of the surface.

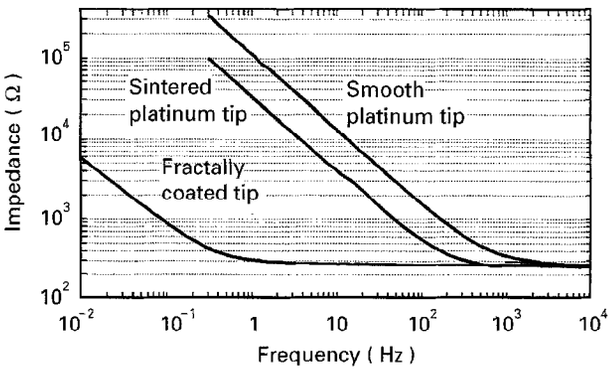

Figure 5 Comparison of the impedance spectra of a smooth, a sintered and a fractally coated electrode with the same geometrical surface area of $10\,mm^2$.

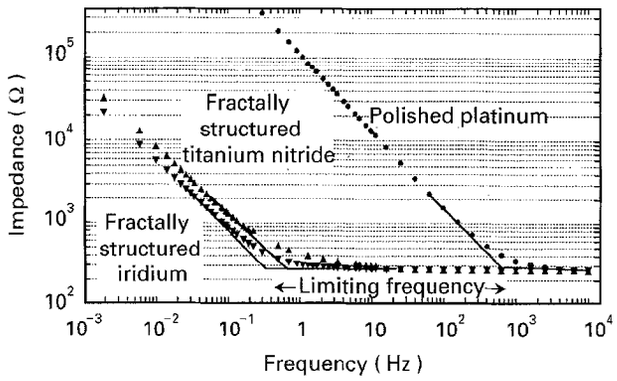

Figure 6 Comparison of the impedance spectra of two fractally coated electrodes, one coated with titanium nitride, the other with iridium, and a smooth platinum electrode.

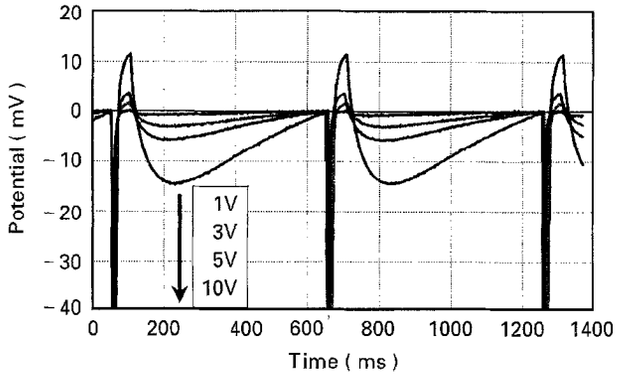

Figure 7 In vitro after-potentials of a smooth electrode dependent on the applied pulse voltage.

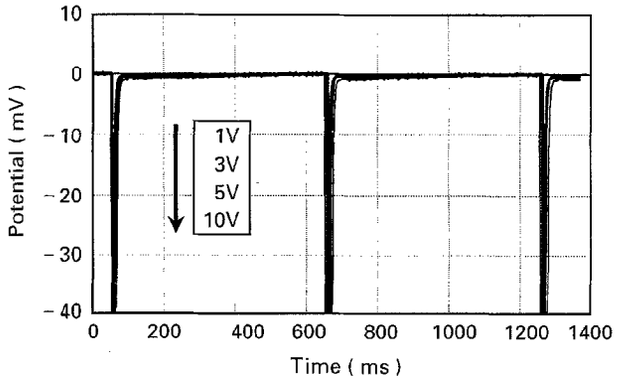

Figure 8 Same as Fig. 7, but for a fractally coated electrode.

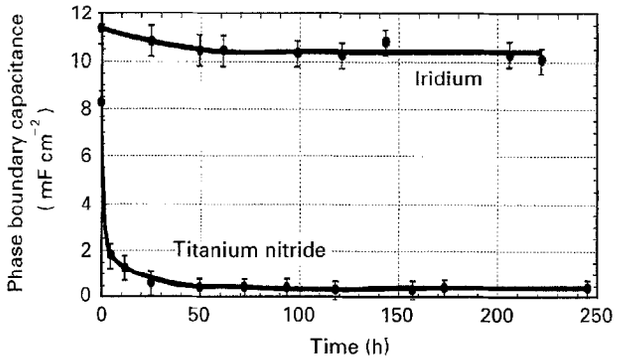

Figure 9 Influence of anodic load on the phase boundary capacitance of fractal iridium and titanium nitride surfaces.

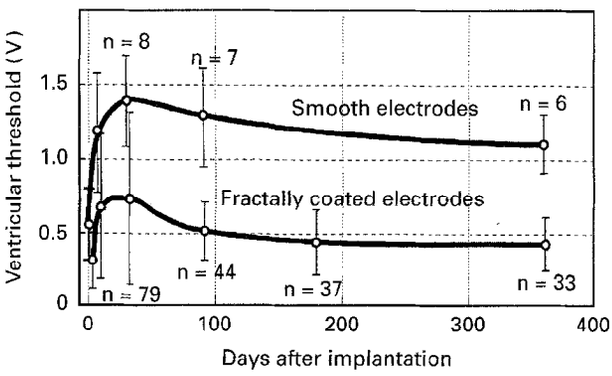

Figure 10 Thresholds for ventricular stimulation with smooth and fractally coated electrodes.

3.3. Clinical findings

The *in vitro* evaluation showed that, of the two possibilities studied for ameliorating an electrode's performance, fractal coating is definitely superior to sintering. Therefore, this section only compares the clinical findings for electrodes fractally coated with Ir with those for smooth electrodes.

The first important aspect is the threshold for ventricular stimulation. As Fig. 10 shows, fractal electrodes exhibited less than half the threshold values of smooth electrodes, in the short- as well as in the long-term. This threshold reduction is due to an increase in active surface area, an intrinsic, time-independent property of the fractal electrode. Therefore, the disadvantage of a limited steroid reservoir is avoided [3]. A further gain is the identical threshold for unipolar and bipolar pacing. Normally, the use of a small ring electrode instead of the large pacemaker case results in an increased threshold for the bipolar mode. However, the enormous active surface area of the fractal electrode compensates for the decrease in geometric size [4].

Another important characteristic is a high sensing amplitude. Again the fractally coated electrodes exhibited exceptional properties. The excellent P-wave sensing allowed the reliable establishment of a physiological rhythm and the long-term R-wave amplitude measured in the ventricle was nearly two times higher than that of smooth electrodes [4].

Closely related to the sensing properties is the detection of the VER. The smooth electrodes were nearly unable to transmit the VER signals: the enormous polarization artefact was superimposed on the signal's amplitude (Fig. 11). For fractal electrodes the situation was quite different (Fig. 12): the VER was correctly detected and the preceding stimulus did not disturb the measurement at all.

The situation was even more impressive concerning the MAP. The smooth electrodes were totally unable to detect the MAP due to their awkward impedance spectra. Fig. 13 shows an MAP detected by a fractally coated electrode: all the important features are clearly visible. Therefore, fractal coatings enable long-term stable MAP measurements of excellent quality to be made using the pacing electrodes. Thus, the immense

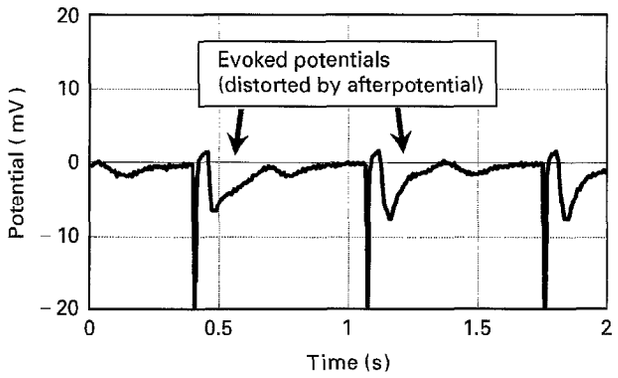

Figure 11 VER for a smooth electrode.

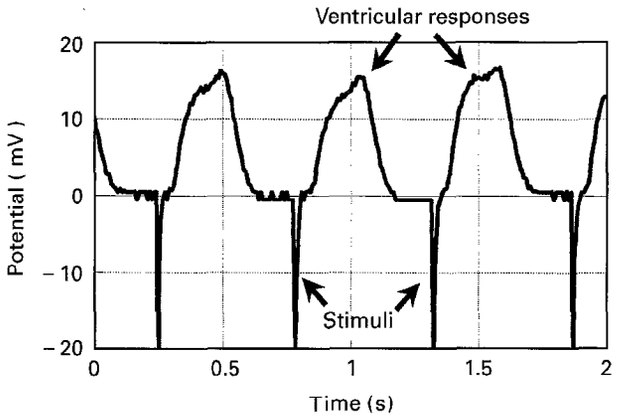

Figure 12 VER for an electrode fractally coated with iridium.

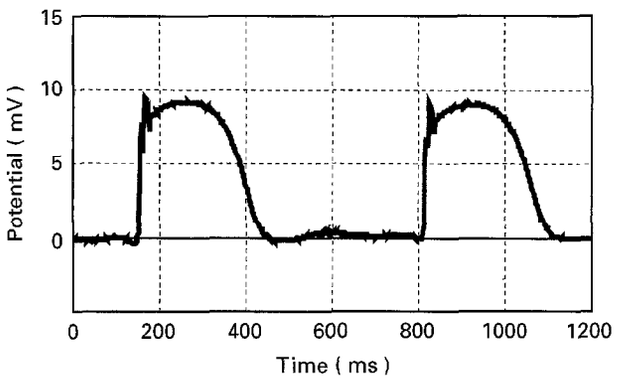

Figure 13 MAP measured by a fractally coated electrode.

amount of information contained in the MAP becomes directly available for application in the electrotherapy of the heart.

4. Summary and conclusion

The results presented conclusively show that the surface structure of medical implants has great influence on the devices' characteristics. Especially for pacemaker electrodes, the important role the active surface area plays has been proven by comparing the pacing and sensing abilities of smooth, porous sintered and fractal electrodes. Whereas the slight enlargement of the active surface by sintering ameliorates the electrode's capabilities only to a small degree, fractally coating with Ir or TiN results in an increase in area of more than three orders of magnitude. The fractal surface structure can directly be seen in SEM, STM or AFM micrographs. In *in vitro* investigations this increase was paralleled by a lowered cut-off frequency in the impedance spectrum and by the absence of a polarization artefact. It was also shown that the application of TiN coatings must be limited to cathodic loads, whereas Ir exhibits perfect long-term stability for all relevant pacemaker loads. The area enlargement leads to *in vivo* pacing and sensing performances of an excellence unknown so far: pacing thresholds are significantly reduced, R- and P-wave amplitudes are increased and VERs and MAPs are measured with exceptional quality. This multiplies the lifespan of pacemakers, extends their reliability and makes new important information available for the electrotherapy of the heart.

From a more general point of view the dominance of structure over material encourages the application of techniques such as physical vapour deposition, which are widely used, for example, in manufacturing of integrated circuits, in biotechnology. Thus, materials well known for their good biocompatibility may gain different properties, allowing their use for new devices. Requirements that cannot be met so far may be fulfilled not by new materials, but by well-tried materials with new surface structures.

References

1. M. S. HIRSHORN, L. K. HOLLEY, M. SKALSKY, C. R. HOWLETT and E. MUSGROVE, *PACE* **6** (1983) 525.
2. G. RAO, in "Euro-Pace '93", edited by A. E. Aubert, H. Ector and R. Stroobandt (Monduzzi Editore, Bologna, 1993) p. 451.
3. G. TAUBERT, A. GEBAUER, F. LÜNNINGHAKE, A. BRANDES, J. POTRATZ and U. STIERLE, in "Euro-Pace '93", edited by A. E. Aubert, H. Ector and R. Stroobandt (Monduzzi Editore, Bologna, 1993) p. 441.
4. A. BOLZ, "Die Bedeutung der Phasengrenze zwischen alloplastischen Festkörpern und biologischen Geweben für die Elektrostimulation" (Fachverlag Schiele & Schön, Berlin, 1995).
5. K. B. STOKES, in "The 92 scenario on cardiac pacing, III. Symposio Meridionale di Cardiostimolzione", edited by E. Adornato and A. Galassi (Edizione Luigi Pozzi, Rom, 1992) p. 505.

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