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Electrical characterization of titanium nitride surfaces for pacing electrodes

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TiN surfaces were obtained on platinum-10% iridium as well as titanium pacing electrodes by Arc Ion Plating and Ion Nitriding, under different experimental conditions. The electrical performances of the different electrodes obtained were compared using a normalized cell configuration. The electrical response of the system was further examined by analyzing the shape of the pulse response observed during the lead impedance determination, as well as, by using cyclic voltammetry and impedance spectroscopy. The increase in the electrode surface-to-geometric area ratio, associated with dark TiN coatings, resulted in substantially lower lead impedance values. The electrical characterization results obtained were related to the depolarization of the electrical interface when compared to the uncoated electrodes.

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1. Introduction

Biomedical devices used for tissue stimulation and to sense bioelectrical activity are currently used in a growing number of applications, such as pacemakers, muscle and nerve stimulation and control, etc. Considering that most of these devices are implanted, the lifetime of the power source is always a major concern, and a number of different approaches have been implemented to minimize energy consumption in these devices while providing suitable service [1].

An excitable tissue is adequately stimulated electrically by delivering a current density above the tissue threshold value [2, 3]. In general, it is customary to apply a constant voltage pulse of a given length to achieve suitable stimulation. The amount of energy used during stimulation is given by the product of the applied voltage and the value of the stimulation current, where the pacing impedance is defined by Equation 1:

$$Z = \frac{\int_0^{t_p} U(t)\,dt}{\int_0^{t_p} I(t)\,dt} \tag{1}$$

$$E_p = \frac{Z}{t_p} A_E^2 \left[\int_0^{t_p} J_E(t)\,dt \right]^2 \tag{2}$$

where Z is the pacing impedance (Ω), $U(t)$ is the applied voltage (V), t_p is the pulse time length (s), $I(t)$ is the current intensity (A), E_p is the pulse energy used, A_E is the electrode area (m^2), and J_E is the current density (A/m^2).

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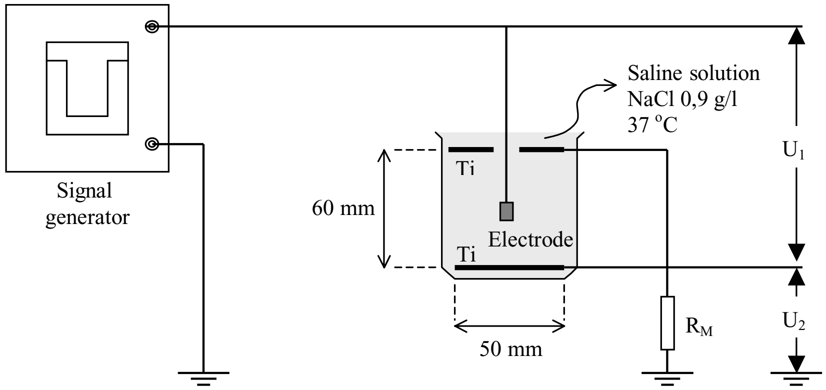

Figure 1 Standard *45502-2 (1996)* cell configuration for the determination of the pacing impedance.

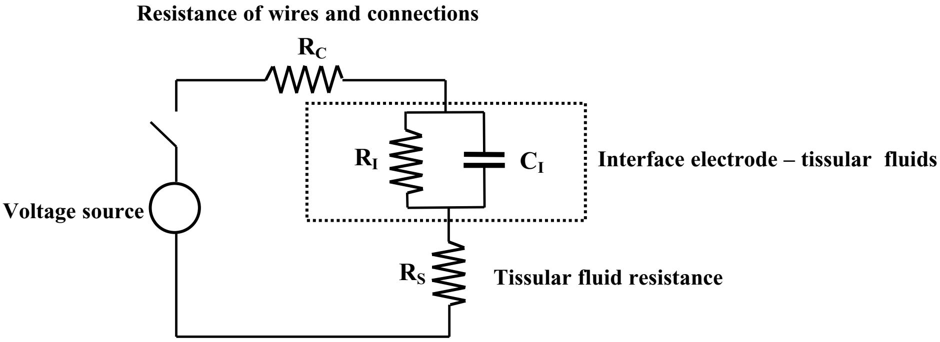

Figure 2 Tissue stimulation equivalent circuit.

Upon inspection, Equation 2 indicates that for a current density fixed slightly above the tissue threshold value, decreasing the geometric area of the pacing electrode could lead to a better energy efficiency. However, the electrode size cannot be diminished beyond certain practical limits due to fabrication, manipulation, as well as implantation concerns [2]. Also, pacing electrodes are employed to passively sense the electrical activity of the heart in more modern demand pacemakers. Considering that the electrode sensing performance calls for large electrodes, a compromise in size must be reached. Henceforth, a higher energy efficiency could be achieved by lowering the pacing impedance.

The standard cell configuration shown in Fig. 1 is used for testing the electrical response of pacing electrodes [4], where a physiological salt solution at 37°C is employed to simulate the tissue fluids. The simplest appropriate electrical circuit to model the pacing impedance response is depicted in Fig. 2 [5, 6].

Based on the model of Fig. 2, and considering an applied voltage pulse of constant value and a certain time length, the value of the pacing impedance can be found to be:

$$Z = \frac{R_I + R_{CS}}{1 + \left(\frac{R_I \cdot \tau_I}{R_{CS} \cdot t_p}\right)\left(1 - e^{-t_p/\tau_I}\right)} \tag{3}$$

$$\tau_I = \frac{R_{CS} R_I C_I}{R_{CS} + R_I} \tag{4}$$

where R_I: interface resistance (Ω), C_I: capacitance of the interface double layer (F), R_{CS}: sum of the resistance of the connections plus the bulk resistance of the tissular fluids (Ω), and τ_I: circuit relaxation time constant (s).

R_{CS} is determined, for all practical purposes, by the bulk resistance of the tissular fluids since the resistance of the connections is negligible. The former depends on the concentration and mobility (temperature) of the ionic species present in solution, as well as the geometric shape of the stimulating electrode employed.

The solution of Equation 3 for different values of the interface resistance and capacitance is presented in Fig. 3, where R_{CS} was taken to be equal to 1 kΩ since this value is typically measured for the bulk resistance of the physiological salt solution used.

Upon inspection, Fig. 3 indicates that large interface capacitances exceeding a given value, i.e. about 10 μF in Fig. 3, can be expected to be capable of achieving almost full depolarization of the electrode-solution interface. The latter results in a marked decreased of the pacing impedance that reaches the limit value set by the solution resistance, for most practical purposes. Also, it should be noticed that there is no added benefit in increasing the interface capacitance above a certain value, since higher values have little effect on the pacing impedance modulus. Nonetheless, the latter is markedly dependent on the characteristics of the voltage pulse employed, and the minimum interface capacitance value required for full depolarization should increase significantly if longer pulses are used and vice versa.

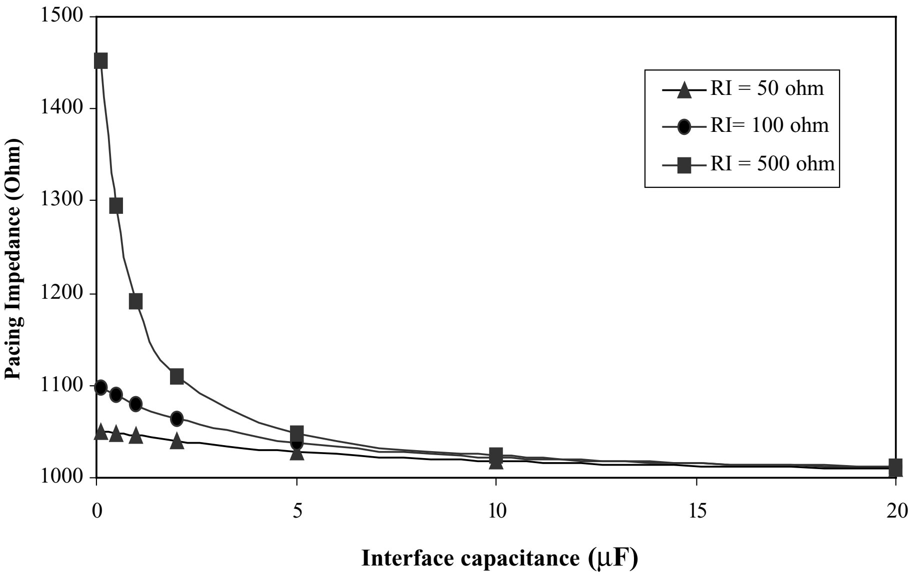

Figure 3 Pacing impedances calculated from Equation 3 as a function of the interface capacitance and resistance values resulting from an applied standard voltage pulse of 4.0 V and 0.5 ms where R_{CS} was taken to be 1 kΩ.

Higher interface capacitance values can be readily achieved by increasing the electrode effective area. However it must be kept in mind that in order to achieve proper stimulation, the delivered current density must be kept above the tissue threshold value, thus the electrode geometric area must be maintained at a minimum. Therefore, high surface-to-area ratio electrodes should result in pacing devices with improved characteristics with respect to battery life and sensing capabilities, while maintaining proper tissue stimulation.

The scale of the electrode surface roughness, required to produce a significant effect on the electrical characteristics of the electrode, is rather small, since the electrode interfacial area required must be increased markedly. Thus, coatings and films of suitable biocompatible materials can be applied onto the electrode surface to produce the desired results if an adequate topography can be developed.

TiN offers a combination of properties—e.g., biocompatibility, excellent mechanical strength, high electrical conductivity, etc.—hard to match, as well as a number of plasma assisted surface modification and coating techniques are readily available to produce, in principle, the desired surface topographies.

TiN surfaces can be obtained by a number of different procedures, where Arc Ion Plating (AIP) [7, 8] and Ion Nitriding (IN) [9, 10], are of particular interest because of their different characteristics and capabilities. The object of this study was to characterize and model the electrical behavior of TiN surfaces applied by the two aforementioned techniques.

2. Experimental procedure

Titanium plates grade A of 20 × 10 × 0.5 mm, as well as platinum −10% iridium cylinders of 2 mm in diameter and 5 mm high, were coated by AIP under different processing conditions, with bias substrate potentials of 0 V, −20 V and −300 V, depositions times of 10 min, 30 min, and 60 min, distances to the arc of 14 cm and 24 cm, and orientations facing (front) and not facing (opposite) the arc. Detailed experimental conditions and results are offered elsewhere [11].

Titanium grade A plates of 20 × 10 × 0.5 mm with two different starting surface topographies, as received and sand blasted, were nitrided by IN varying the nitriding substrate temperature, i.e. 500°C and 600°C, and including or not a sputtering post treatment with Ar. Detailed experimental conditions and results are offered elsewhere [11].

Pacing impedance values for electrodes of 5.5 mm^2, were determined using the cell configuration presented in Fig. 1 following the standard procedure EN 45502−2 [4], with a solution temperature of 37 ± 2°C. A signal generator[1] was used to apply a 4.0 ± 0.1 V pulse with a total duration of 0.5 ± 0.05 ms, and the current response was determined by measuring the voltage drop across a known resistance (R_M) connected in series. U_1 and U_2 (see Fig. 1) were registered with a Vernier multipurpose lab interface.

Cyclic voltammetry was conducted in a 0.9 g/l NaCl solution at 37°C using a sufficiently large titanium counter-electrode, at 500 mV/s between −0.3 V and + 0.8 V vs. SCE (Saturated Calomel Electrode) with a potentiostat.[2]

Impedance spectroscopy[3] was carried out in the frequency range between 0.01 Hz and 10 kHz employing a 10 mV amplitude signal around the open circuit potential.

[1] BK precision 3011B.

[2] L.Y.P. Electrónica S.R.L. M5 potentiostat.

[3] ACM instruments GILL 8AC.

3. Results and discussion

Titanium nitride coatings obtained by AIP exhibited varying colorations and surface topographies ranging from smooth golden deposits, typical of those employed in mechanical applications, to dark deposits that exhibited in the as processed surface a large number of pyramids of about 0.1 μm in size [11] (see Fig. 4a). Inspection of the dark deposits obtained by AIP using SEM, XRD and XPS, revealed stoichiometric or nearly stoichiometric TiN strongly oriented in the (111) direction [11]. Examination under the SEM of fracture surfaces of the dark deposits, indicated that these type of coatings developed a columnar structure in which the columns are separated at least by high mismatch grain boundaries [11]. In contrast to this, IN did not produce surfaces with jagged topographies resulting only in smooth TiN golden layers, in spite of the different conditions employed [11] (see Fig. 4b).

Pacing impedance values were found to be in the range of 750 Ω to 1,100 Ω for the different samples. The current response to an applied constant voltage pulse exhibited a marked decay from the initial value observed (see Fig. 5) for electrodes made either from the original substrates or coated with golden TiN obtained either by AIP or by IN. In contrast to this, the most favorable dark TiN deposits exhibited a constant current value under the same conditions, indicating that the lowest possible pacing impedance had been attained. It should be noticed that initial current value, observed immediately after the pulse is applied, is the same within experimental error for both type of electrodes (see Fig. 5), since this is determined by the solution resistance (see Fig. 2). As the interface progressively "charges up" during the application of the pulse, a current drop may be observed if the interface capacitance is not large enough. However, if the electrode surface is capable of developing a large interfacial capacitance, a constant value current should be observed, and the pacing impedance should be numerically equal to the solution resistance, i.e. $Z/R_S = 1$.

Differences in the geometric area of the electrodes must be taken into account in order to assess the performance of stimulus electrodes using pacing impedance values. For a given electrode geometry—e.g., disc, cylinder, sphere, etc.—the pacing impedance value observed is markedly influenced by the electrode geometric area. The impedance and the solution resistance values obtained for series of titanium electrodes with areas ranging from 3.5 mm^2 up to 25 mm^2 are presented in Fig. 6. The values observed for both quantities in this series of electrodes can be described by regressions in which, within experimental error, both are inversely proportional to the square root of the electrode area (see Fig. 6). The solution resistance was calculated using the initial current value attained, while the precision of the measurements was established by repeating the electrical measurements with a set of three electrodes prepared with the same area following the same fabrication procedure.

The solution resistance can be modeled considering the primary current distribution [12, 13] resulting from the

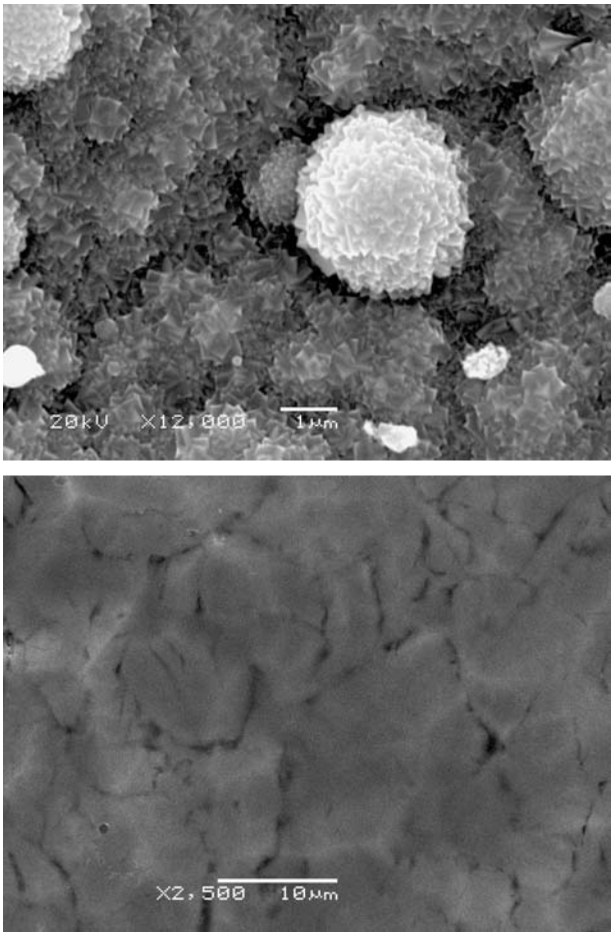

Figure 4. SEM micrographs (SE) of titanium nitride surfaces. (a) AIP coating obtained on titanium with the substrate at 24 cm and facing the arc, with zero d.c. bias, and 60 min processing time, 12,000 X. (b) Titanium nitrided surface by IN with a substrate temperature of 500°C, 12 h of processing time, sand blasted substrate, and post treated with Ar sputtering, 2,500 X.

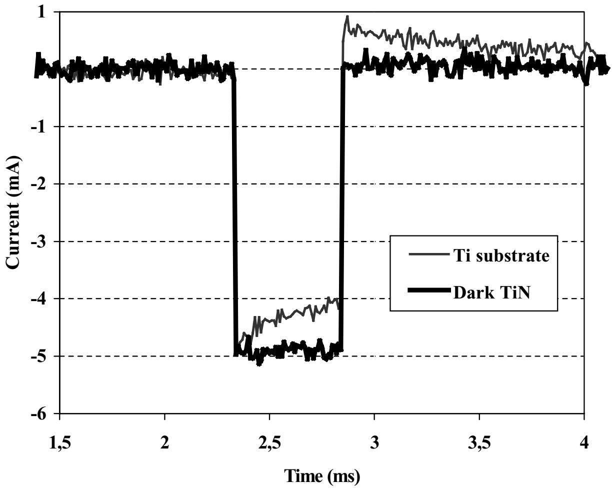

Figure 5. Current responses observed during pacing impedance determinations for a Ti substrate and a dark TiN coating obtained by AIP on Ti at 24 cm and opposite to the arc, with zero bias, and 60 min processing time.

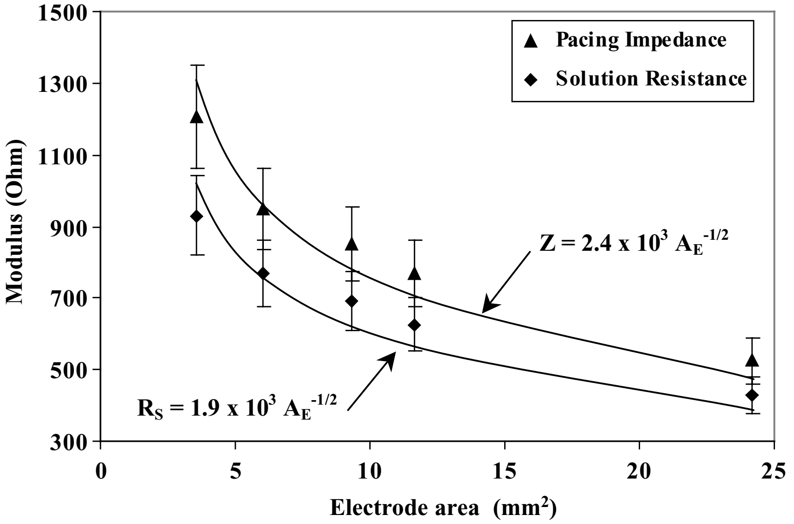

Figure 6 Pacing impedance and solution resistance values observed for Ti electrodes of increasing area for an applied voltage pulse of 4.0 V and 0.5 ms.

applied electric field with a counterelectrode of infinite area. Under these conditions, the value of the resistance of the solution for a disc electrode is found to be:

$$R_S = \frac{\sqrt{\pi}}{4} \cdot \frac{1}{\kappa\sqrt{A_E}} \qquad (5)$$

where R_S: solution resistance (Ohm), A_E: geometric electrode area (m^2), κ: solution conductivity (S m^{-1}). A similar dependence, e.g., $R_S \propto (A_E)^{-1/2}$, can be derived for other simple geometries [12 , 13].

Using Equation 5 for the experimental conditions employed, i.e. a 0.9 g/l NaCl solution at 37°C, a dependence of the solution resistance with the electrode area of $R_S = 1.8 \times 10^3 (A_E)^{-1/2}$ can be calculated, a result that matches within 5% the experimental regression estimated.

The experimental as well as the model results indicate that the solution resistance and the pacing impedance behave similarly with respect to the electrode geometric area even for relatively high polarized interfaces, since for fully depolarized interfaces both are numerically equal, i.e. $Z/R_S = 1$. Considering this, it results advantageous to compare the performance of the different electrode surfaces by assessing the ratios of the pacing impedance to the solution resistance, i.e. Z/R_S, since the use of this normalized variable eliminates slight differences in the electrode area and geometry. The normalized pacing impedance results are presented in Table I for different electrode surfaces.

TABLE 1 TiN surfaces normalized pacing impedance values, interface capacitance and interface resistance values measured by cyclic voltammetry. The pacing impedances are expressed as their ratio to the solution resistance.

Substrate	Processing conditions AIP	Surface aspect	Z/Rs	C_I (μF)	R_I (Ohm)
Ti	reference	Grey	1.24	1.8	64.0
Ti	−300 V, 10 min, 14 cm Opposite	Golden–lustrous	1.24	2.0	51.1
Ti	−20 V, 30 min, 14 cm, Opposite	Golden−matte	1.12	10.9	32.3
Ti	0 V, 10 min, 14 cm, Opposite	Dark gold	1.08	59.8	3.8
Ti	0 V, 10 min, 24 cm, Opposite	Golden−gray	1.10	27.6	11.1
Ti	0 V, 30 min, 14 cm, Front	Yellow-matte	1.10	46.2	8.9
Ti	0 V, 30 min, 14 cm, Opposite	Brown	1.06	94.8	6.9
Ti	0 V, 30 min, 24 cm, Opposite	Black	1.04	160	4.0
Ti	0 V, 60 min, 14 cm, Opposite	Brown	1.01	383	3.2
Ti	0 V, 60 min, 24 cm, Front	Brown	1.04	289	2.3
Ti	0 V, 60 min, 24 cm, Opposite	Black	0.98	619	1.7
Pt-Ir	0 V, 60 min, 24 cm, Opposite	Black	1.07	315	2.2
Substrate	**Process Conditions IN**	**Surface Aspect**	**Z/Rs**	**C_I (μF)**	**R_I (Ohm)**
Ti as received	reference	Grey	1.18	3.3	38.2
Ti sand blasted	reference	Grey	1.13	3.5	9.9
Ti	500°C	Golden	1.20	2.7	94.8
Ti	500°C, Ar sputtered	Golden	1.26	2.7	86.5
Ti	600°C	Golden	1.23	2.4	233
Ti	600°C, Ar sputtered	Golden	1.18	1.7	60.3

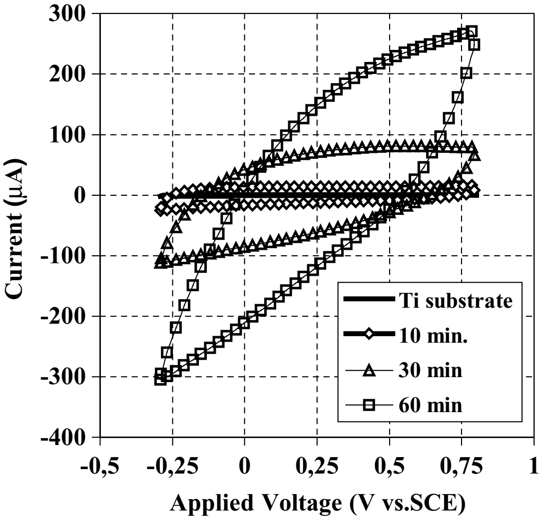

Figure 7 Cyclic voltammograms of TiN coatings obtained by AIP on titanium with the substrate at 24 cm and opposite to the arc, with zero d.c. bias, and increasing processing times and thicknesses, e.g. 10 min—0.8 μm, 30 min—1.8 μm, 60 min—5.0 μm[11].

Metal-solution interface polarization effects can be assessed through cyclic voltammetry [14], by cycling through alternatively increasing and decreasing potentials at constant speed between two given potentials referred to a normalized electrode (SCE). In principle, the interface capacitance is directly proportional to the interface effective area, while the interface resistance is inversely proportion to the latter [14]. The interface capacitance and resistance values estimated from the voltammograms are presented in Table 1.

Electrodes with golden TiN surfaces, obtained either by AIP or by IN, exhibited markedly low interface capacitances similar to those of the original substrates (see Table I). According to the simple model presented in Fig. 2, these electrodes should exhibit higher pacing impedance values, in agreement with the observations made during the determination of the pacing impedance. This distinctly indicates that the mere presence TiN on the electrode surface does not result in improved electrical characteristics, unless an adequate topography has been achieved through proper processing. In contrast to this, increasingly darker TiN coatings exhibit improved interface characteristics, i.e. large capacitance and low resistance, resulting in a marked decrease of the pacing impedance values observed.

In general for coatings obtained by AIP, the substrate bias had a critical influence on the electrode electrical characteristics, while for a given processing time, the best results were obtained with the substrate far and not facing the arc [11]. Longer processing times for AIP coatings resulted in similar topographies (see Fig. 4a), but the deposits were found to be increasingly thicker, ranging from about 1 μm for 10 min of run time to about 5 μm for 60 min of deposition time [11].

The voltammograms of dark TiN coatings processed under identical conditions but with increasingly longer deposition times indicate that markedly larger interface capacitances are found in thicker coatings (see Fig. 7 and Table I). The surface topography in these deposits resulted to be very similar [11], however increasingly thicker deposits exhibited markedly larger electrode effective areas. These facts suggest that this type of coating has a fairly open structure that results in an added capacitance on top of the one derived from the electrode topography.

Impedance spectroscopy revealed that once again there are little electrical differences between electrodes surfaces made from Pt-10%Ir, Ti, and golden TiN, while dark TiN clearly separates from the rest. At relatively high

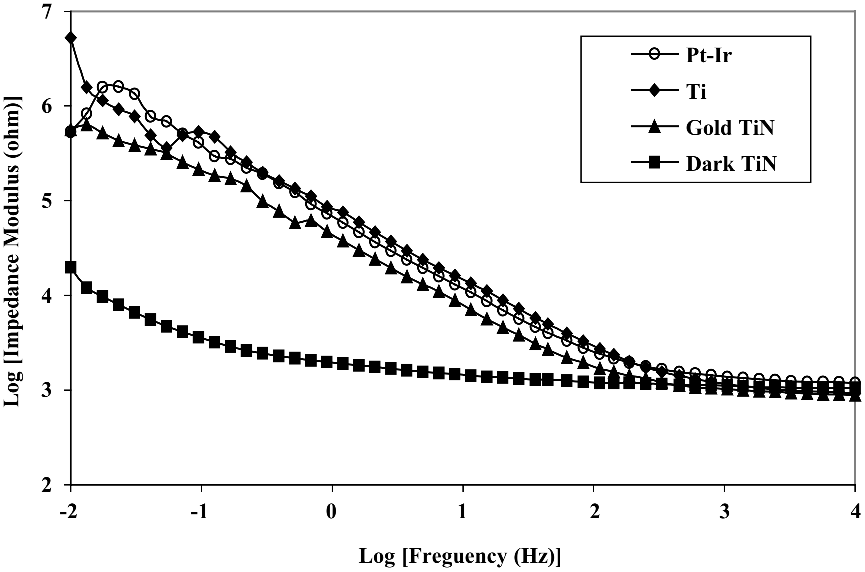

Figure 8 Impedance spectroscopy of 5.5 mm^2 electrodes of the original substrates compared to TiN coatings obtained by AIP—Golden TiN: d.c. substrate bias—300 V, Ti substrate placed at 14 cm opposite to the arc for 10 min—Dark TiN: zero substrate bias, Ti substrate placed at 24 cm opposite to the arc, for 60 min.

frequencies, e.g., from about 300 Hz to 10 kHz, all electrodes behave almost identically exhibiting impedance moduli around 1 kΩ (see Fig. 8) and almost zero capacitive phase angle (not shown), indicating a resistive behavior fairly close to the solution resistance. At lower frequencies however, the electrode interface polarization effects begin to increase significantly the impedance modulus and the capacitive phase angle for all the electrode surfaces except for those coated with dark TiN.

4. Conclusions

1. In agreement with the simple model employed, the use of electrodes capable of developing high interfacial capacitances at the electrode-fluid interface resulted in markedly lower pacing impedances.

2. The pacing current response of dark TiN coatings applied by AIP with the best topographies was observed to be almost constant, with the electrode attaining an almost purely resistive behavior for the conditions tested.

3. The pacing impedance as well as the resistance of the solution, for the simple geometry employed, were found to vary inversely proportional to the square root of the electrode area within experimental error. This result was found to be in agreement with a resistance model that considered the primary current distribution in the solution resulting from the applied pulse.

4. The ratio of the pacing impedance modulus to the resistance of the solution was employed to better assess the performance of the different electrode surfaces to eliminate slight differences in area and geometry between the electrodes.

5. Golden TiN deposits obtained either by AIP or by IN exhibited low interface capacitances and high impedance values, in contrast to dark TiN coated electrodes that resulted in electrodes with high surface-to-area ratios.

6. The mere presence of a TiN layer onto the electrode surface did not improve the electrical characteristics of the electrodes unless a suitable topography was developed through proper processing conditions.

7. The increase in the interface capacitance confirmed by cyclic voltammetry for dark TiN coatings obtained by AIP with longer deposition times suggests that the structure of the deposits has a fairly open nature contributing to the interfacial capacitance with an added component besides that of the topography.

8. Impedance spectroscopy results were consistent with the simple model proposed to explain the system electrical behavior, and in agreement with cyclic voltammetry as well as pacing impedance results.

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