TiN\textsubscript{x} coated polycarbonate for bio-electrode applications

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\textbf{A B S T R A C T}

Titanium nitride (TiN\textsubscript{x}) thin films were deposited by PVD, in a wide range of compositions (0 < x < 0.99), on polycarbonate (PC) substrates, aiming at studying their potential application as bio-electrodes. The electrochemical study of the TiN films, performed in an isotonic sodium chloride solution, proved the very good chemical stability of all films in salt solution conditions. On the other hand, the electrochemical noise analysis showed that the electrical noise generated at the stoichiometric TiN/electrolyte interface is of the same magnitude as that generated by the traditional Ag/AgCl electrodes.

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1. Introduction

Electroencephalography (EEG) is the recording of the brain electrical activity along the scalp [1]. EEG is nowadays the most widely used brain imaging technique. It provides very good time-resolution of brain activity, and it offers significant advantages over competing state of the art technologies, such as MRI (magnetic resonance imaging) and CT (computerized tomography), both in terms of cost and space requirements. The conventional recording set-up generally involves the use of silver/silver chloride electrodes (Ag/AgCl) for signal transduction [1]. These are very reliable non-polarizable electrodes, with low skin-contact impedance values of the order of a few cm\textsuperscript{2} which are almost frequency independent [2]. However, skin preparation and gel paste application are needed before the exam in order to lower the skin/electrode impedance. This preparation is time consuming, uncomfortable to the patient and requires trained staff.

In order to overcome the drawbacks of the Ag/AgCl electrodes, a new class of devices is being investigated, for which no skin preparation or gel application are needed, the so-called “dry” electrodes. In these electrodes, the sensors are inert materials, either a metal or an insulator [3,4]. In a previous work [5] the authors investigated a dry electrode sensor, based in a titanium nitride (TiN) thin film deposited on a titanium substrate. TiN is an electrically conductive material, with a good chemical stability in most media and outstanding mechanical properties, used in a very broad range of applications, including in the biomedical area [6]. The influence of the N/Ti ratio on the structural, morphological and electrochemical properties of the TiN film in contact with synthetic sweat was studied, and it was concluded that the stoichiometric and slightly over-stoichiometric composition (N/Ti ≥ 1) were the most adequate for the applications envisioned [5].

In this work the titanium substrate was replaced by polycarbonate (PC), resulting in a potentially much cheaper and lighter electrode. These are two important advantages, particularly if 128 or even 256 electrodes are to be used for a single exam.

However, there are two important differences between using titanium or PC as substrates for the TiN PVD thin film deposition: (i) there is no chemical affinity between TiN and PC, so the PC surface must be activated before deposition in order to achieve good adhesion of the film to the polymeric substrate, and (ii) the deposition on PC cannot be performed at the high temperatures usual for metals [5], which limits the kinetic energy available to enhance interfacial adhesion and structural arrangements that help the film to reach a stable thermodynamic state.

In this work the structural, mechanical and electrochemical behaviour of titanium nitride (TiN\textsubscript{x}) thin-film coated polycarbonate (PC) was studied in order to optimize the deposition conditions for bio-electrode applications. A comparison with commercial silver/silver chloride (Ag/AgCl) electrodes was performed.

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2. Experimental details

TiN, films were deposited on PC (disks), on glass and on silicon (100) substrates, in a laboratory-sized reactive DC magnetron sputtering system. The PC disks, 20 mm in diameter and 4 mm thick, were pressed moulded from standard PC pellets (250 °C, 20 tons). The discs were: (i) wet abraded with SiC paper of decreasing grain sizes, (ii) polished with diamond pastes of 6 and 1 μm, (iii) cleaned in a sonicator with isopropanol (5 min) and (iv) distilled water (5 min) just before each deposition. Processes (iii) and (iv) were also used for the glass and Si substrates.

The films were prepared with the substrate holder positioned at 70 mm from the target, using a DC current density of 100 A m⁻² on the titanium target (99.96 at. % purity). A gas atmosphere composed of argon + nitrogen was used. The argon flow was kept constant at 60 sccm (Standard Cubic Centimetres per Minute, corresponding to 1 × 10⁻⁶ m³/s), which resulted in a partial pressure of 0.3 Pa for all depositions. The nitrogen flow varied from 0 to 5.5 sccm (corresponding to a partial pressure variation between 0 and 3.6 × 10⁻² Pa). The working pressure was approximately constant during the depositions, varying only slightly between 0.3 and 0.4 Pa. No bias voltage or external heating were used in order to avoid the polymeric substrates degradation. A thermocouple was placed close to the surface of the “substrate holder” on the plasma side (not in direct contact, since depositions were done in rotation mode), and the temperature was monitored during the entire film deposition time. A delay time of 5 min was used before positioning the surface of the samples in front of the Ti target in order to avoid film contamination resulting from previous depositions (which may have resulted in some target poisoning), and also to assure a practically constant deposition temperature during film growth.

The atomic composition of the as-deposited samples was measured by Rutherford Backscattering Spectroscopy (RBS) using (1.4, 1.75) MeV and 2 MeV for the proton and 4 He beams, respectively. Two detectors were used, located at scattering angles 140 and 180° (annular detector). Measurements were made for two sample tilt angles, 0 and 30°. Composition profiles for the as-deposited samples were determined using the software NDF [7]. For the ¹⁴N, ¹⁶O and ²⁸Si data, the cross-sections given by Gurbich were used [8]. The area analyzed was about 0.5 × 0.5 mm². The uncertainty in the N concentrations is around 5 at. %.

The structure and phase distribution of the coatings were assessed by X-ray diffraction (XRD), using a Bruker AXS Discover D8 diffractometer, operating with Cu Kα radiation and in a Bragg–Brentano configuration. The XRD patterns were deconvoluted and fitted with a Voigt function to determine the structural characteristics of the films, such as the peak position (2θ), the full width at half maximum (FWHM) and the crystallite size.

Morphological features of the samples were probed by scanning electron microscopy (SEM), carried out in a Jeol JSM 6301F microscope operating at 10 keV. The adhesion level of the as-deposited TiN coatings to the polymeric substrates was assessed by the X-cut tape test, according to the ASTM D3359 standard. The samples were then analyzed by optical microscopy before and after test.

In the voltammetric experiments, the potential was scanned from −0.6 to 2.5 V at 1 mV/s (linear voltammetry), and from −0.4 to 0.4 V at 0.1 to 5 V/s (cyclic voltammetry). The experimental set-up consisted of a EG&G PAR 273A potentiostat, driven by the Zplot/Zview® software from Scribner. The three-electrode configuration was used with a saturated calomel electrode (SCE) and a Platinum wire as the reference and auxiliary electrodes, respectively. A 0.9% sodium chloride solution was used in all electrochemical studies, in order to simulate the sweat effect. Electrochemical impedance spectra (EIS) were acquired daily for a week, using a Solartron 1250 frequency response analyser and a EG&G PAR 273 potentiostat, driven by the Zplot/Zview® software from Scribner. The frequency was scanned from 20 kHz to 1 mHz, with a 7 mV (rms) amplitude ac signal. The Zview software was used for the simulations of the experimental spectra.

The electric noise measurements were performed with a Gamry G300 potentiostat driven by the ESA410 software. Several couples of similar samples, either Ag/AgCl (Easycap® sintered disc electrodes, 12 mm in diameter) or PC coated with TiN, were immersed in the sodium chloride solution and the open circuit potential difference acquired with a 500 Hz sampling rate for periods of 10 min. The electrochemical cell was kept inside a Faraday cage. Data analysis was performed by first applying a 20th order Butterworth bandpass filter (0.5–100 Hz). The first 10 s of each filtered data set were neglected to avoid including considerable filter artefact in subsequent evaluations. Then, successive segments of 30 s were considered for the calculation of the RMS values of noise and drift rate, over the total acquisition times. The power spectral density (Welch estimation) was calculated for 10 min segments, representative of all the Ag/AgCl commercial electrodes and TiN sample couples.

3. Results and discussion

3.1. Composition of the as-deposited samples

The evolution of the composition ratio (N/Ti) as a function of the nitrogen partial pressure is plotted in Fig. 1. The partial pressure of nitrogen, P₂, was monitored by the nitrogen flow rate, ϕ₂. No argon was detected by RBS analysis in the as-deposited samples, which means that its content should be less than ~3–5 at. %.

As it can be seen from Fig. 1, the increase of the nitrogen partial pressure strongly influences the atomic concentration of the chemical elements in the layers. Initially, from 0 to 2 × 10⁻² Pa, the evolution of the N/Ti atomic ratio is very smooth. At higher nitrogen partial pressures, from 2 × 10⁻² to 3.6 × 10⁻² Pa, a small increase in the nitrogen partial pressure leads to an abrupt and almost linear evolution of the N/Ti atomic ratio. At the highest N₂ partial pressures, nearly stoichiometric films were formed. No over-stoichiometric films were obtained, otherwise a third zone should appear, where the N/Ti atomic ratio evolution would stabilize [5].

The high amounts of Ti atoms that are sputtered from the target and the low nitrogen pressures inside the reactor up to ~2 × 10⁻²

Fig. 1. Plot of the nitrogen content in the films (x = N/Ti atomic ratio) as a function of the nitrogen partial pressure inside the sputtering chamber.
Pa create a high mean-free path for the Ti atoms. As no substrate bias voltage or external heating were used during the sputtering process, the low amount of nitrogen available cannot be easily absorbed in the growing films due to mobility constraints. As the amount of available nitrogen increases (with the increase of its partial pressure), its incorporation in the film is facilitated, thus explaining the rapid increase of the N/Ti ratio in this zone. When the nitrogen partial pressure is relatively high, the mean-free path starts to decrease, as well as the sputtering rate, due to a higher degree of nitrogen coverage of the cathode (target) and increasing secondary electron coefficient [5]. This may explain why the TiN film produced with the highest nitrogen partial pressure \(3.7 \times 10^{-2}\) Pa has a very similar value of the N/Ti atomic ratio to that of the film obtained at \(3.6 \times 10^{-2}\) Pa.

3.2. Structural and morphological characterization of the samples

Previous studies of sputtered TiN coatings on metallic substrates show that as N is added to Ti, the atomic lattice progressively changes from the hcp \(\alpha\)-Ti phase to the fcc \(\delta\)-TiN phase. This is due to the progressive increase of lattice distortions, as a result of the lattice size increment coming from N insertions [5].

Analysing the XRD diffraction patterns shown in Fig. 2, the overall tendency seems similar to what is observed for films deposited on metallic substrates [5]. However, a closer look reveals that the diffraction patterns can be clearly divided into distinct zones. Zone I comprehends the films prepared with the lowest nitrogen partial pressures, corresponding to highly sub-stoichiometric films, with N/Ti ratios up to 0.24. The films prepared within this zone revealed a set of diffraction patterns which are not easily indexed, since their angular position is situated between those of the fcc \(\delta\)-TiN (fcc – ICDD card no. 00-038-1420) and \(\alpha\)-Ti (hcp – ICDD card no. 00-038-1420). Nevertheless, and due to the low mobility and low N2 partial pressures some nitrogen is expected to be incorporated in interstitial positions within the Ti lattice, forming a kind of Ti(N) metastable solution. The nitrogen incorporation leads to the expansion of the Ti lattice observed in this first zone, demonstrated by the lower angular positions of the diffraction peaks when compared to the position of the (101) peak from the Ti lattice.

The titanium–nitrogen phase diagram is complex, but basically the Ti crystal is considered to be an “interstitial” crystal where N atoms fit into the gaps of the Ti structure. This structure evolves from hexagonal \(\alpha\)-Ti (space group P63/mmc), to face-centred-cubic \(\delta\)-TiN (space group Fm-3 m) as the amount of nitrogen is increased. The \(\alpha\)-Ti lattice can accept small amounts of nitrogen at octahedral sites [9], but since PVD is a thermodynamically non-equilibrium process, the \(\alpha\)-Ti lattice may be forced to accept more nitrogen atoms due to hindered mobility of the deposited particles [10]. Therefore, an oversaturated metastable solution of nitrogen in titanium is formed for the lower N contents. The shift in the diffraction lines revealed by Fig. 2 is thus a consequence of the N interstitials in octahedral \(\alpha\)-Ti sites, which causes lattice distortion. The fact that no significant variations are observed in peak positions is also consistent with the similar composition of the three films prepared within this zone.

A second major zone, zone II, can be indexed to the films prepared with the higher nitrogen partial pressures, corresponding to roughly stoichiometric films, with N/Ti ratios ranging from 0.85 up to 0.99. As one would expect from its particular close-stoichiometric condition, the films develop a fcc-type structure characteristic of stoichiometric-like TiN films. The fcc (111) peak is clearly visible and is placed in its expected angular position. An important note is that within this second zone the crystallinity of the films is particularly evident, as demonstrated by the sharpening of the diffraction peaks and their increased intensity. There is still a slight shift of the diffraction peaks, towards lower diffraction angles, which can be understood by the already mentioned stoichiometric or closely stoichiometric conditions of the films within this zone.

Between these two major zones, one can define a transition zone, zone T, comprehending the films that exhibit intermediate N/Ti ratios – from 0.34 to 0.75. The diffraction patterns of this zone T suggest the existence of a transition between the results obtained for the films indexed to the previous two major zones, evidenced by the progressive shift towards lower diffraction angles, consistent with the change from the two previous crystalline phases (hcp Ti and fcc TiN).

While in the films from zone I a growing crystallinity was observed (increasing peak definition and intensity), in zone T the films are quasi-amorphous, as demonstrated by the significant peak broadening and low intensity of the diffraction pattern. This behaviour is not surprising due to the particular composition of the samples: relatively high amounts of N if regarded from a hcp, \(\alpha\)-Ti like structure in which they would occupy interstitial positions, but relatively low from a TiN-like phase, in which a significant amount of N vacancies would be developed. The exact nature of the poor crystallinity is difficult to ascertain unequivocally, but it seems to be rather close to that of fcc-TiN. In fact, the correspondent phase diagram [11–13] shows that the \(\delta\)-TiN phase can occur already for atomic concentrations of N as low as 30 at. % which is the case of the samples prepared within this transition zone. Moreover, the large lattice deformations that result from the formation of the cubic lattice in these high sub-stoichiometric conditions (resulting from extensive N vacancies), leads to the development of crystalline structures with extensive lattice defects, and thus to the poor crystallinity observed in these films. As the N/Ti atomic ratio increases, the higher amounts of N2 can compensate the lack of mobility in the system, thus being inserted within the lattice of TiN (fcc), giving rise to a less vacant lattice. As a result, the diffraction peak shifts continuously towards lower

![Fig. 2. Evolution of the XRD patterns of the films as a function of N/Ti atomic ratio (x).](image-url)
diffraction angles, approaching the expected position of the (111) peak from TiN. This explains the observed behaviour of the films indexed to this zone. For \( x = 0.75 \), the (200) diffraction peak of \( \delta \)-TiN can also be found, as a broad and low intensity peak around \( 2\theta \approx 42.5^\circ \), reinforcing the assignment of these films to the fcc TiN-type structure.

Further evidence of these different groups of samples within the whole set of prepared films can be seen in Fig. 3, where the grain sizes were obtained after the XRD peaks deconvolution. The values of grain size within the transition zone should be seen with care since the diffraction patterns are difficult to deconvolute. It is important to note that the results correlate very well with the diffraction patterns, given that the films crystallinity is clearly higher in zones I and II.

The films from zones I and T give rise to grains (values around \( \sim 15 \text{ nm} \)) that seem to be predominantly smaller than those of zone II (above 25 nm). This tendency towards smaller grain sizes is typical of highly saturated metal–metalloid compounds, and can be described by the Gibbs–Thomson equation [14]. Looking closely into zone I, there seems to be a tendency to have a small increase of grain size with increasing N/Ti atomic ratios, which may be due to the increase of the films crystallinity, as shown above in Fig. 2.

When the transition zone is reached, there is a large peak shift towards lower diffraction angles, which suggests that nitrogen is being inserted in the Ti lattice, thus exhibiting small grain size predominance. It is known that the introduction of nitrogen into Ti lattices implies that the grain growth is inhibited, causing the formation of more grain boundaries and distortion of the lattices (large micro strains are developed) with the nitrogen interstitial sites [5].

In zone II, the small grain size tendency is changed, as the growth is highly (111) textured and a high level of crystallinity is attained, which is usually associated with a grain growth phenomena [15]. These results of grain size evolution induce, again, the existence of two major types of films, where the first two zones have lower grain sizes when compared to the samples indexed to zone II, where the films present relatively larger grains.

Fig. 4 shows the SEM micrographs of the main types of morphologies observed for the set of TiN films that were prepared. The plan view is shown on the micrographs of Fig. 4. Two main types of morphological arrangements are revealed, showing a good correlation with the compositional and structural analysis. The films from both zones I and T display dense, rough and granular-like structures (Fig. 4a and b), where the discontinuities observed are related with the initial polishing features. On the other hand, the films from zone II display grains with a pyramidal shape and a
porous structure. The existence of porous films when high N/Ti ratios are used was already observed for TiN films deposited on titanium and silicon \([5,15]\) and it is related with the strong internal stresses generated on passing from the \(\alpha\)-Ti to the \(\delta\)-TiN lattice \([16,17]\). According with our previous studies on titanium, a columnar growth of the films is expected, with the pyramidal grain shape corresponding to the column tops and the pores are ascribed as intercolumnar spacing \([5]\).

When compared with the TiN films grown at higher temperatures on metallic substrates \([5]\), some significant differences exist. In fact, although both the high (deposited on titanium) and low temperature (deposited on PC substrates) films show the same structural evolution with the nitrogen content, such evolution is clearly delayed in terms of composition for the low-temperature films. For example, for \(N/ Ti = 0.7\) the high temperature film already displays a well-defined \(\delta\)-TiN structure \([5]\), whereas for the film with the approximately same composition deposited on PC (\(N/ Ti = 0.75\)) the structure is still essentially amorphous. Also, the columnar structure of the \(\delta\)-TiN phase is better defined in the case of the high temperature films.

### 3.3. TiN adhesion behaviour to PC

In order to test the adhesion level of the as-deposited TiN coatings to the PC substrate, the X-cut tape test (ASTM standard D3359-08) was performed on samples from zone I (\(N/ Ti = 0.24\)) and zone II (\(N/ Ti = 0.95\)). Samples from zone T were not tested because they have morphology similar to the zone I samples.

Fig. 5 presents the surface aspect of the TiN coated PC samples from zones I and II before removal of the tape (a and b), and zones I and II after the removal of the tape (c and d). Major differences in terms of adhesion are apparent from the after test photos, (Fig. 5c and d), where a much stronger delamination is apparent in the under-stoichiometric sample. The distorted lattice with strong internal stresses of zone I samples leads to an as-deposited coating that is already severely cracked due to the cutting procedure (Fig. 5a), giving rise to a very poor adhesion level, rated as 0A – removal beyond the area of the X (Fig. 5c). On the other hand, the as-deposited sample from zone II (Fig. 5b) presents only some initial scratches due to the polishing procedure and no further cracking of the coating is visible. Consequently, the adhesion behaviour of the sample from zone II is much better than the one from zone I, being rated as 4A – trace peeling or removal along incisions or at their intersection. In conclusion, zone I samples seem unsuitable for electrode application, where repeated skin contact and cleaning would most likely lead to a rapid damaging of the coatings.

### 3.4. Electrochemical studies in sodium chloride solutions

#### 3.4.1. Open circuit potential

The open circuit potentials (OCP) for the TiN samples are shown in Fig. 6. The results indicate that there is a stabilization period of about 10–15 min, common to all samples, after which a continuous and smooth potential decrease takes place, tending to a plateau. The Ti-rich samples consistently display less noble OCP values. This lower thermodynamic stability may be related with the fact that, as described in section 3.2, these samples display either amorphous or highly distorted and metastable structures, and therefore higher reactivity than the stoichiometric, well-crystallized ones. Also, the Ti-rich films have non-oxidized free titanium within their structures, which is much more reactive towards oxygen than stoichiometric or close-stoichiometric titanium nitride. Finally, a different surface charge contribution effect also cannot be discarded to help explaining the observed differences.

#### 3.4.2. Potentiodynamic analysis

The cyclic voltammetry (CV) curves show a capacitive behaviour extending from about \(-0.25\) to \(-0.25\) \(V\) for films from zone I and zone II at low sweep rates, see Fig. 7. However, for zone II films, at the highest sweep rates, the behaviour tends to incorporate a resistive component, as shown in Fig. 7B. This behaviour is characteristic of a porous electrode \([15]\), which corroborates the SEM results.
displayed in Fig. 4c. Similar behaviour was previously observed by the authors for stoichiometric TiN films deposited on titanium substrates at high temperatures [5].

The double layer capacitances were calculated for all film stoichiometries from the slope of the line defined by the capacitive current at 0 V (well within the double charging region) vs sweep rate. Only the sweep rates where the capacitive behaviour was observed were considered for the calculations. In these conditions, the evolution of the double layer capacitance values reflects the evolution of the real area of the samples, thus showing how the morphologies of the films change with the N/Ti ratio, Fig. 8. The same three regions already identified in the XRD spectra, Fig. 2, can be seen, showing that the transition from zone I to zone T films takes place with only a slight area increase, whereas the transition from zone T to zone II films involved an important area increase that should be essentially ascribed to the development of the porous structure, following the thin film crystallization in the γ-TiN structure.

The electrochemical potential was also swept at low speed (1 mV/s) in a much wider potential range (−0.75–2.5 V), Fig. 9. Similar curves are displayed by all films, with a small plateau ranging from 0.07 to 0.2 V corresponding to the formation of oxynitrides, and a current peak around 1.5 V ascribed to further oxidation of the oxynitrides, with the formation of titanium oxide and of nitrogen gas [5]. These curves also show that all TiN films are chemically stable around their OCP’s, as their dissolution currents are in the sub-micro A/cm² range. The higher passivation currents observed for titanium and the Ti-rich films are most likely related with the titanium oxidation. We note that the real area of the films was taken into account in the curves, according with the double layer calculations of Fig. 8.

3.4.3. Electrochemical impedance spectroscopy

The Bode spectra for three samples representative of all stoichiometries are shown in Fig. 10. The impedance modulus is clearly lower for the zone II TiN sample, as expected from the associated morphologic changes seen in Fig. 4. The phase vs frequency plot for titanium and the zone II films display a quite simple structure that is indicative of a single time constant. On the other hand, the spectrum for the zone I films seems to indicate the presence of more than one time constant.

Based on these observations, and taking into account the well-known self-passivating behaviour of titanium, the electrical circuit displayed in Fig. 11 was chosen to describe the interfacial behaviour of the thin films. All capacitive elements were first replaced by constant phase elements (CPE), in order to account for roughness and other surface inhomogeneities or relaxation processes. Following the simulations one of the capacitive elements showed “p” values consistently around 1, so a simple capacitor was finally used. The impedance of a CPE can be defined by Eq. (1):

$$Z_{\text{CPE}} = 1/(T(j\omega)^p)$$  \hspace{1cm} (1)

where “T” and “p” are the CPE parameters and $\omega$ stands for the angular frequency [18].
In the electric circuit of Fig. 11, \( R_s \) stands for the electrolyte resistance and the upper and lower branches of the parallel circuit account for the non-Faradic and Faradic interfacial processes respectively. \( CPE_{el} \) simulates the double-layer capacitive behaviour of the TiN/electrolyte interface; the resistance to electronic charge transfer (that should be in parallel with \( CPE_{el} \)) was considered infinite as no redox reactions are supposed to take place, given the OCP of the interface (see Fig. 6).

In the lower branch, \( W_r \) stands for the ionic diffusion through the oxide/oxynitride, which was simulated with a semi-infinite Warburg diffusion element \((p = 0.5 \text{ in Eq. (1)})\). The Warburg diffusion coefficient, \( \sigma \), relates with \( T_w \) value through Eq. (2) [5]:

\[
\sigma = 1/(\sqrt{2}T_w)
\]

In fact, TiN is often used in electronics for its atomic diffusion blocking effects. The terms \((CPE, R_t)\) stand for the interfacial capacitance and charge transfer resistance due to the titanium oxide/oxynitride related electrochemical processes.

The simulations are in very good agreement with the experimental spectra, as shown in Fig. 10 and Table I. Titanium displays a \( p \) for the \( CPE_{el} \) not far from 1, an indication of an essentially capacitive behaviour of the titanium oxide film, which was formed in contact with atmospheric oxygen. The high \( T_w \) value should be ascribed to a very thin and hydrated oxide film, thus with poor blocking ability. After the insertion of a small amount of nitrogen the blocking character of the film increases (lower \( T_w \)) and the charge transfer resistance increases. On the other hand, the high \( CPE \) calculated for the stoichiometric TiN is an area effect related to porosity and was also observed by Norlin et al. [15]. In the case of the stoichiometric film both the high roughness and porosity should be responsible for the deviation from the ideal capacitor behaviour \((p = 0.82)\). The charge transfer resistance is high for all films, corroborating the results of the very low dissolution currents observed in the neighbourhood of the OCP, Fig. 9. They are of the same order of magnitude as those obtained for the high temperature TiN films [5], meaning that the deposition temperature plays an important role on the structure of the films but not in their chemistry.

The “\( R_t \)” and the Warburg diffusion parameter \( \sigma \) vs composition obtained from the EIS spectra simulations are reported in Fig. 12. The
evolution of $r$ with composition shows that ionic diffusion is important only for zone I films and the steep $r$ decrease roughly accompanies the transition from zone I to zone T films. As stated before, it should be related with the decrease of crystalinity of the titanium lattice and the formation of a large number of vacancies that provide the necessary paths for ionic diffusion. We note that such high “$r$” drop cannot be explained by simple area change effects. The $R_t$ values, which are related with the Faradic dissolution processes taking place at the interface, increase with the N/Ti ratio, in agreement with the higher reactivity of titanium that exists in the non-combined form in the Ti-rich films. As long as it combines with nitrogen, its reactivity decreases with the consequent increase of $R_t$. This trend is in good agreement with the voltammograms shown in Fig. 9.

The evolution of the electrical behaviour of the TiN$_x$ films with the immersion time was also assessed. All films displayed a very stable behaviour and no significant evolution was observed in the EIS curves except for a slight tendency for $R_t$ to increase.

3.4.4. Electrical noise measurements

A main requirement for a material to be used as a bio-electrode is its transparency to the bio-signal, meaning that it should not generate any noise that would mask the signal to be recorded. Thus, if one imagines that a layer of sweat forms between the electrode and skin, the electric noise developed at such an interface should be significantly lower than the ECG signal (≈1 mV) or the EEG signal (≈50 μV) being recorded.

The power spectral density (PSD) of noise for a stoichiometric TiN/TiN couple is reported in Fig. 13, together with the same plot for a Ag/AgCl/Ag/AgCl, commercial electrode couple. It is apparent that the noise generated by both couples is very similar over all the EEG frequency range as well as the corresponding RMS noise values: 3.23 ± 0.03 μV (TiN) and 2.80 ± 0.02 μV (Ag/AgCl) (vs SCE).

There is an increase of the noise for lower frequencies, a typical behaviour already reported by other authors [19].

The electrochemical potential drift rate and stabilization time are also important parameters to take into account, particularly when dealing with low frequency and/or small amplitude signals that may easily be masked if important drift rates are present. Concerning the Ag/AgCl electrodes, drift is practically inexistent and potential stabilization is almost instantaneous, as shown in Fig. 14. A much higher electrochemical potential irreproducibility exists among TiN couples. This was expected given that there is not a well-defined electrochemical process taking place at the interface to “lock” the electrochemical potential. However, the drift rate

![Fig. 12. Charge transfer resistance ($R_t$) and Warburg coefficient ($\sigma$) vs thin film composition, as calculated from the simulations of the EIS spectra.](image1)

![Fig. 13. Noise power spectral density (PSD) spectra for commercial Ag/AgCl and stoichiometric TiN electrode couples immersed in isotonic NaCl solution and RMS values of electric noise (SCE).](image2)

![Fig. 14. Electrochemical potential drift rates (vs SCE) for commercial Ag/AgCl and stoichiometric TiN electrode couples immersed in isotonic NaCl solution.](image3)
decreases to acceptable values within 5–10 min, ensuring that low bio-potential values will be able to be measured.

4. Conclusions

In this work, TiN$_x$ thin film coated PC samples were studied in a wide range of compositions, aiming at selecting the best coating composition on PC for dry electrode applications. XRD analysis showed three different zones for the diffraction patterns of TiN$_x$, namely a distorted a-Ti lattice for N/Ti < 0.24 (zone I), a well crystallized d-TiN structure for N/Ti > 0.85 (zone II) and a transition zone (zone T) between the two mentioned compositions, characterized by an essentially amorphous structure. The films in zones I and T are granular and compact whilst the films formed in zone II display granules with a pyramidal shape and a porous morphology.

All films proved to have a good chemical resistance in the presence of isotonic sodium chloride, independently of their composition. Passive dissolution currents densities below 1 $\mu$A/cm$^2$ were found in all cases, decreasing for higher N/Ti values. The EIS data showed significantly lower impedance values for the zone II films, what will facilitate bio-signal transfer in the presence of a sweat layer.

The adhesion tests proved that the coatings in zone II exhibit a clearly better adhesion than those from zone I, which was ascribed to a more stable and stress-free lattice.

Finally, electrochemical noise tests carried out in sodium chloride solution showed that zone II TiN$_x$ films display RMS noise values of the order of those measured for the classic Ag/AgCl electrodes but higher drift rates and potential irreproducibility. However, electrochemical potential reaches acceptable values within 5–10 min, making zone II TiN$_x$ films on PC suitable for dry electrode applications.

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