# THE EFFECT OF A COMPOSITE CHITOSAN/COPPER(II) ION COATING ON THE CORROSION RESISTANCE OF GRADE 4 TITANIUM IN SALINE: PRELIMINARY RESULTS

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### Abstract

In the present work, we successfully used electrophoretic deposition to produce a new composite chitosan-copper(II) [Cu(II]) ion coating on grade 4 titanium (Ti). We prepared the coating with an environmentally friendly in situ chemical reduction process from a 2% (v/v) aqueous acetic acid solution with 1 g dm<sup>-3</sup> chitosan and 10 g dm<sup>-3</sup> copper acetate at 20 V for 300 s at room temperature. We evaluated the relationship between physicochemical properties and corrosion resistance of the coatings with energy dispersive spectroscopy, Fourier-transform infrared spectroscopy, a scanning Kelvin probe, and electrochemical methods. The composite coating contained 2.1 ± 0.1 wt.% of Cu, which ensures antibacterial activity. We determined the mechanism and kinetics of the electrochemical corrosion of the composite chitosan–Cu(II) ion coating on grade 4 Ti in saline solution (0.9% sodium chloride) at 37°C. The surface modification makes grade 4 Ti a more attractive material for use in dentistry.

Keywords: chitosan, composite, copper, corrosion, electrophoretic deposition, titanium

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#### 1. Introduction

Biomaterials are one of the most studied groups of materials due to their high demand: their high quality and long lifetime have led to their use in aesthetic and biomechanical implants. Biomaterials have different compositions, structures, and properties and are distinguished by the fact that they are acceptable for use in the human body, and some of them can permanently connect with living tissue or participate in its regeneration [1]. With the development of reconstructive surgery, there is an increasing demand for biomaterials that can be used as implants to replace natural tissue, artificial organs that completely or partially replace the functions of internal organs, or prostheses placed in the body for a relatively short time to regenerate and restore the proper functioning of the body [2].

Many years of clinical experience have revealed metals and alloys that can be safely used in surgical practice. The distinguishing properties of metals and alloys intended for implantation include good corrosion resistance, appropriate mechanical properties, good metallurgical quality and homogeneity, non-toxicity and non-allergic reaction, resistance to abrasive wear, no tendency to promote clot formation, appropriate electrical properties, and acceptable production costs [1, 3–24]. The four basic groups of metallic biomaterials include austenitic steels [3, 4], shape memory alloys [5–8], cobalt-based alloys [9, 10], and titanium (Ti) [11–15] and its alloys [16–24]. Another classification of metallic biomaterials used for implants in medicine is based on how long they can be used safely in the patient's body [1, 2, 7, 15, 18].

The most important factor in the use of metals and their alloys in medicine is the properties that guarantee reliable cooperation of the implant-tissue-body fluid system. Many efforts have been made to improve the chemical composition, structure, and mechanical and physicochemical properties of metals and their alloys by modifying the surface to ensure biocompatibility and anti-corrosive performance [1, 3–24]. Moreover, surface layers accelerate osseointegration, limit the penetration of harmful compounds from the implant into the body, have anti-inflammatory properties, and can be intelligent drug carriers in targeted drug-delivery systems (DDS) [3, 5, 9, 20, 21].

Chitosan (CS) is one of the most promising biopolymers and has been proposed to improve the biocompatibility of metallic biomaterials, especially in regenerative medicine and tissue engineering [25-38]. CS is used in medicine as a component of dressing materials, as it stops bleeding; accelerates wound healing; and has antiinflammatory, analgesic, and antibacterial effects [27, 28]. This natural polymer has the ability to strongly adsorb to mucous membranes, which allows it to be used as a carrier in mucoadhesive drug-delivery systems (MDDS) to deliver drugs directly to mucous membranes [29]. CS also has the ability to create a variety of morphological structures such as films, membranes, nanoparticles, and hydrogels [25, 30-34]. It is very similar to the extracellular matrix of biological systems, biodegradable, bioactive, and does not show toxicity in the human body [35]. CS is characterised by high chemical resistance, thermal stability, antioxidant activity, anticancer activity, and good mechanical and antimicrobial properties [26, 27, 31, 35, 36]. It is used to immobilise copper (Cu) nanoparticles, ensuring long-term antibacterial properties of the CS-based composites [25, 28, 37]. Cu can be used in its ionic form [38, 39] or in nanoparticles [37] as antibacterial agents.

The natural source of CS is chitin, which is a structural element in the exoskeleton of sea crustaceans including red crabs, shrimp (e.g., *Pandalus borealis*), and krill, pictured in Figure 1 [40]. CS is commonly produced as a result of chemical or enzymatic deacetylation of chitin. This process involves removing some or all of the acetyl groups from the acetylamino groups of chitin. Chemical deacetylation is carried out in several

stages. Initially, mineral salts and lipids are removed from the shells of crustaceans by immersing them for 90 min in 5% hydrochloric acid (HCl). Then the proper deacetylation of chitin is carried out in 50% sodium hydroxide (NaOH) [25, 40].



Figure 1. Schematic illustration of chitosan structure obtained from chitin deacetylation.

The reactions to obtain CS from chitin are usually carried at 90–140°C for 30–180 min. The obtained CS has different properties, degrees of deacetylation, molecular weights, and viscosities. A temperature of 100°C can yield CS with a lower degree of acetylation and better properties. However, the use of such conditions may result in degradation of the CS chain, and thus also reduce the molecular weight of the resulting polymer. Enzymatic deacetylation of chitin is used when medical or agricultural conditions require the use of material characterised by low molecular weight, high solubility in water, and low viscosity. It can be carried out using enzymes such as chitanase and chitosanase. This entire process does not alter the structure of the resulting biopolymer and can be easily controlled.

From a chemical point of view, CS is a natural cationic polysaccharide composed of randomly distributed  $\beta$ -(1 $\rightarrow$ 4)-linked D-glucosamine (deacetylated unit) and *N*acetyl-D-glucosamine (acetylated unit). The two-dimensional (2D) structure of CS is shown in Figure 1. CS is very difficult to dissolve in water, alkaline solutions, or common organic solvents due to the formation of intermolecular hydrogen bonds of its molecules. However, this biopolymer is soluble in dilute aqueous acidic solutions with a pH below 6.5, which can convert glucosamine units into soluble form R – NH<sub>3</sub><sup>+</sup>. This is mainly due to the presence of amino groups in its molecular structure, which are protonated in the aqueous acid solution, rendering CS soluble. Due to the negligible solubility of CS in solutions with a neutral pH, deposition is carried out only from acidic solutions [25, 30–34, 37, 38].

The main objective of this work was to determine the effect of the novel CS–Cu(II) ion coating obtained via *in situ* deposition by electrophoretic deposition (EPD) on the corrosion resistance of grade 4 Ti used in implant prosthetics in physiological saline solution (0.9% sodium chloride [NaCl]). After obtaining the coated Ti samples, we performed initial *in vitro* corrosion resistance tests by using electrochemical impedance spectroscopy (EIS) to determine the mechanism and kinetics of electrochemical corrosion. We chose Cu as a component of the composite because it is highly resistant to corrosion and has antimicrobial activity: in *in vitro* assays it kills 99.9% of microorganisms within 2 h of contact [39].

#### 2. Materials and Methods

#### 2.1. EPD Conditions

The material of the study was Ti with purity grade 4 (Ti G4) in the form of a rod (Bibus Metals Ltd., Poland). Ti G4 samples were prepared as discs with a diameter of 10 mm and a height of 5 mm. Disc-shaped Ti G4 samples were ground with 80# to 5000# grit silicon carbide paper and mechanically polished using the 0.01  $\mu$ m alumina powder (Struers Inc., USA) and a metallographic grinding and polishing machine (Forcipol 102, Metkon Instruments Inc., Turkey). The polished samples were ultrasonically cleaned for 20 min using acetone and ultra-pure water with a resistivity of 18.2 M $\Omega$  cm at 25°C (Milli-Q Advantage A10 Water Purification System, Millipore SAS, France). The cleaning procedure was then repeated.

For EPD, electrodes were prepared from the polished samples. An insulated Cu wire was attached to one side of the samples using epoxy resin (Electrodag 915 silver paint, TAAB Laboratories Equipment Ltd., UK), which provided electrical contact. The back side of the samples and the side walls were protected with a chemically resistant, two-component epoxy resin (Distal Classic, Libella Ltd., Poland). The electrodes were sonicated first in acetone and then in ultrapure water.

CS was deposited on the Ti G4 substrate by cataphoresis from a 2% (v/v) aqueous solution of acetic acid (CH<sub>3</sub>COOH), in which 1 g dm<sup>-3</sup> CS was dissolved. Milli-Q water was used as a solvent. The solution was subjected to magnetic stirring at 300 rpm for 24 h to ensure complete dissolution of CS. The molecular weight of CS was 80 kDa and the degree of deacetylation was 75–85%. All chemicals were purchased from Sigma-Aldrich (USA). For the composite CS–Cu(II) ion coating, a 2% (v/v) aqueous solution of CH<sub>3</sub>COOH containing 1 g dm<sup>-3</sup> CS and 10 g dm<sup>-3</sup> Cu(CH<sub>3</sub>COO)<sub>2</sub> with pH 5.0 ± 0.1 was prepared. Then, the solution was sonicated for 30 min at 25°C. The CS and composite CS–Cu(II) ion coatings was deposited at a voltage of 20 V for 300 s at room temperature using a PWR800H high-current power supply (Kikusui Electronics Corporation, Japan). A two-electrode electrolytic cell was used for EPD. The distance between the Ti G4 cathode and the anode (platinum foil) was 1.5 cm. The electrodes were parallel to each other and the walls of the electrolyte cell. After EPD, the working electrodes were carefully rinsed with Milli-Q water, dried for 24 h at ambient temperature, and the weight gain was determined gravimetrically.

#### 2.2. Material Characterisation Methods

The local chemical composition of the investigated materials was determined using a Hitachi TM4000 Benchtop scanning electron microscope (Hitachi, Japan) with a tungsten cathode, which was equipped with an energy dispersive spectroscopy (EDS) detector by Oxford Instruments (UK) and AZtecOne analytical software. EDS spectra were recorded form various homogeneous microregions on the surface of the samples. Each scan area was  $10 \times 10 \ \mu m^2$ .

The functional groups of the studied materials were determined with attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR). An IR Trace-100 spectrophotometer (Shimadzu, Japan) was used to record the ATR-FTIR absorption spectra; it was equipped with an ATR diamond attachment for testing solids. The measurements were performed by maintaining contact between the crystal and the material in the spectral region of  $4000-400 \text{ cm}^{-1}$  at 100 scans per sample at  $21 \pm 1^{\circ}$ C.

#### 2.3. Scanning Kelvin Probe (SKP) Measurements

The surface topography and contact potential difference (CPD) maps of TI/CS, Ti/CS–Cu(II), and the uncoated Ti G4 substrate were evaluated with a SKP using a Scanning

Electrochemical Workstation M370 device (Princeton Applied Research, USA) equipped with a tungsten Kelvin probe (KP,  $\emptyset = 500 \ \mu m$ , Princeton Applied Research). The scanned area was  $2.5 \times 2 \ mm$ , and the distance between the sample and the Kelvin probe was ca. 100  $\mu m$  [41]. The Kelvin probe passed over the sample surface in a sweep scan mode with a velocity of 20  $\mu m \ s^{-1}$ . The Scanning Electrochemical Work Station M370 Version 2.45 software was used.

#### 2.4. In Vitro Corrosion Resistance Measurements

In vitro evaluation of the corrosion resistance of the obtained electrodes was performed in physiological saline solution of pH 7.4  $\pm$  0.1 at 37  $\pm$  1°C in accordance with ISO 10271:2021–02 [42]. Immediately before the electrochemical measurements, freshly prepared solutions were deaerated with argon (99.999% purity) for 30 min. The tests began with the measurement of the open-circuit potential (E<sub>oc</sub>) for 2 h with a sampling frequency of 10 s. Each measurement was repeated three times and the results are presented as the mean and the standard deviation. An ECO CHEMIE Autolab/PGSTAT30 electrochemical system (Metrohm Autolab B.V., The Netherlands) was used, which consisted of a potentiostat/galvanostat and a data acquisition system with one software package. The General Purpose Electrochemical System (GPES) for Windows (version 4.9) software was used to record the Direct Current (DC) electrochemical measurements and to analyse the results.



Figure 2. Frequency Response Analyzer diagram for the Autolab/PGSTAT30 electrochemical system.

EIS of the interfacial properties of the obtained electrodes was carried out in potentiostatic conditions at the stabilised  $E_{\rm OC}$  in the frequency range from 50 kHz to 1 mHz with a frequency resolution of 0.003%. Ten frequencies per decade were scanned using a sine wave drive signal with an amplitude of 10 mV. Kramers-Kronig relations were used to assess the correctness of the obtained EIS data [43]. The experimental EIS spectra were analysed based on the concept of electric equivalent circuits, considering the physical meaning of the circuit elements used. The response simulation of the equivalent electrical circuits and the fit of the circuit parameters to the recorded EIS data were determined with the EQUIVCRT program with the circuit description code defined by Boukamp using the complex non-linear least squares (CNLS) method [44]. The F statistical test was used to check the significance of the parameters of the equivalent electrical circuits used. The Frequency Response Analyzer (FRA) for Windows (version 4.9) software was used for EIS measurements and analysis of the results. A diagram of the FRA used in the Autolab/PGSTAT30 electrochemical system is shown in Figure 2.

It consisted of a digital-to-analogue converter (DAC), a multiplying digital-to-analogue converter (mDAC), a digital signal generator (DSG), a signal conditioning unit (SCU), and a fast analogue-to-digital converter (ADC).

#### 3. Results and Discussion

# **3.1.** Surface Topography and Electronic Properties of the Composite CS/Cu(II) Ion Coating

Statistical analysis of the obtained surface topography and corresponding CPD maps shown in Figure 3 allowed us to determine the height parameters that quantitatively characterise the surface properties of the investigated materials.



Figure 3. Surface topography maps with the corresponding contact potential difference map for (a) the titanium (Ti) substrate, (b) Ti with a chitosan (CS) coating, and (c) Ti with the composite CS-copper(II) [Cu(II)] ion coating.

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On the surface topography maps registered for Ti/CS and Ti/CS–Cu(II), there are characteristic bulges with a diameter of 500–1000  $\mu$ m. The observed bulges are the result of the evolution of hydrogen gas bubbles due to electrolytic hydrogen evolution that accompanies EPD. Compared with the uncoated Ti substrate, the maximum peak height is about 6 times higher for Ti/CS and about 3 times higher for Ti/CS–Cu(II). The maximum height for Ti, Ti/CS, and Ti/CS–Cu(II) is 4.2, 24.6, and 12.9  $\mu$ m, respectively. This means that embedding Cu(II) into the CS matrix reduces the height of the observed bulges. The mean difference in height from the mean plane is 1.3, 3.8, and 3.4  $\mu$ m for Ti, Ti/CS, and Ti/CS–Cu(II), respectively. Deposition of the CS coating and the addition of Cu(II) increase the heights of peaks and valleys by about 2.8 and 2.5 times, respectively, compared with pure Ti.

Pure Ti has the smallest arithmetic mean of CPD (CPD<sub>av</sub>), approximately -1 V. Cataphoretic deposition of CS increases the CPD<sub>av</sub> by about 0.1 V (about 10%), which means that CS forms a protective coating in air. The addition of Cu(II) increases CPD<sub>av</sub> by about 0.4 V (about 40%) compared with uncoated Ti. This means that deposition of CS and the addition of Cu(II) reduce the activity of the Ti substrate in air. The mean difference in CPD values from the mean plane for Ti, Ti/CS and Ti/CS–Cu(II) is 23, 28, and 27 mV, respectively. It follows that the CS and Cs–Cu(II) coatings only slightly increase the magnitude of CPD peaks and valleys (about 1.1–1.2 times).

#### 3.2. Chemical Composition of the Composite CS/Cu(II) Ion Coating

We analysed the local chemical composition in selected micro-areas to confirm the deposition of the composite CS–Cu(II) ion coating on the surface of Ti G4. Figure 4 shows a representative EDS spectrum of the Ti/CS–Cu(II) surface.



Figure 4. A representative energy-dispersive spectrum for the composite chitosancopper(II) ion coating on the grade 4 titanium substrate.

The EDS spectrum shows carbon (C), Cu, oxygen (O), and Ti peaks. Analysis of the local chemical composition revealed the presence of C as the main element of CS. The high intensity of the C peak indicates the presence of a CS matrix. The recorded spectral lines from Cu confirm the presence of this metal as a component of the obtained composite coating. We determined that the Cu content in the CS–Cu(II) coating was  $2.1 \pm 0.1$  wt.%, which is the threshold amount to ensure the obtained CS-based coating would have effective antimicrobial activity. We also noted the presence of peaks originating from the Ti G4 substrate, but their occurrence is related to the depth of penetration of the electron

beam. The low-intensity O peak is associated with the presence of a self-passive oxide film on the surface of the Ti G4 substrate. We did not consider the presence of O as a light element in the quantitative microanalysis. Based on the scanning electron microscopic observations of cross-sections, the obtained composite Ti/CS–Cu(II) ion coating was thicker, at  $34 \pm 8 \mu m$ , compared with the CS coating, at  $21 \pm 6 \mu m$ .

The ATR-FTIR spectroscopy results allowed us to verify the presence of the CS and composite CS–Cu(II) ion coatings on the Ti G4 substrate, to determine the characteristic functional groups in the obtained coatings, and to examine whether the investigated coatings were degraded during EPD. Figure 5 shows representative ATR-FTIR absorption spectra of the CS powder, Ti/CS, and Ti/CS–Cu(II).



**Figure 5.** Attenuated total reflectance Fourier-transform infrared spectra collected for (a) chitosan (CS) powder, (b) titanium (Ti) with the CS coating, and (c) Ti with the CS-copper(II) [Cu(II)] ion coating.

The ATR-FTIR absorption spectrum of CS powder shows a peak at 3556 cm<sup>-1</sup>, which indicates symmetric vibrations for O–H and N–H stretching of the amine [45]. The high-intensity peak at 2631 cm<sup>-1</sup> indicates the presence of NH<sub>2</sub> bonds characteristic of CS. The bands at 1651 and 1025 cm<sup>-1</sup> are attributed to stretching vibrations of C=O in amide I and asymmetric stretching of the C–O–C bond in the polysaccharide ring, respectively [46, 47]. In addition, there are peaks of the amide bands characteristic of CS. The peak at 1540 cm<sup>-1</sup> corresponds to the bending vibrations of the N–H bond, and the peak at 1420 cm<sup>-1</sup> is related to the deformation of the CH<sub>3</sub> bond. Ti with the CS/CS–Cu(II) coating shows peaks characteristic of CS in the initial state, which confirms the deposition of CS on the Ti surface. It also shows a peak at 608 cm<sup>-1</sup>, which confirms Cu(II) has been embedded into the CS matrix [48].

CS is a biopolymer with high adsorption properties and the ability to chelate transition metal cations due to the presence of free amine groups in its structure [35]. EPD of CS/Cu(II) on the Ti G4 substrate is based on the chelation of Cu(II) ions by CS, which proceeds in two stages. CS amino groups protonation is required in the first stage to obtain a positive charge by macromolecules of CS in a 2% (v/v) aqueous solution of CH<sub>3</sub>COOH at pH < 6.5 [25, 30–34]. In these conditions, CS can become a cationic polyelectrolyte as follows:

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$$CS - NH_2 + H^+ \rightarrow CS - NH_3^+.$$
(1)

The interaction between protonated CS and Cu(II) in the solution leads to the formation of CS– $NH_2Cu^{2+}$  complexes:

$$CS - NH_3^+ + Cu^{2+} \rightarrow CS - NH_2Cu^{2+} + H^+.$$
 (2)

A dense, stable, and positively charged hydrogel coating is obtained on the cathode surface using EPD.

#### 3.3. In Vitro Corrosion Resistance of the Composite Ti/CS-Cu(II) Ion Coating

We performed EIS to determine the mechanism and kinetics of the electrochemical corrosion process along with the capacitive characteristics of Ti/CS-Cu(II). Figure 6 presents the results of EIS measurements at  $E_{oc}$  in the form of Bode diagrams obtained for the Ti electrode before and after surface modification in physiological saline solution at 37°C. For all investigated electrodes, there is only one semicircle visible in the frequency range from 50 kHz to 1 mHz. The Ti/CS electrode shows the largest semicircle diameter, while the Ti/CS-Cu(II) electrode shows the smallest diameter. The experimental EIS spectra marked with symbols in Figure 6 were approximated by an electrical equivalent circuit of a modified Randle's cell with the Boukamp description code  $R_1(R_2Q_1)$  and the CNLS method [44]. The  $R_1(R_2Q_1)$  model represents the physical model of the Ti electrode, coating, and saline solution system. The parameter  $R_1$  in this model is assigned to the resistance of the solution,  $R_2$  represents the charge transfer resistance  $(R_{ct})$  through the coating-solution interface, and the double layer capacitance parameter  $(C_{dl})$  corresponds to an ideal capacitor. In the CNLS fitting, we used a constant phase element (CPE) described in the Boukamp code as Q instead of a capacitor [44]. The CPE impedance  $(\hat{Z}_{CPF})$  is described by Equation 3, where T is the capacitance parameter (in F cm<sup>-2</sup> s<sup> $\phi$ -1</sup>) and  $\phi \leq 1$  is a dimensionless CPE exponent associated with the constant phase angle,  $\alpha = 90^{\circ}(1-\phi)$  [43]:

$$\hat{Z}_{\rm CPE} = \frac{1}{T(j\omega)^{\phi}}.$$
(3)



**Figure 6.** Experimental (symbols) and simulated (line) Bode diagrams showing the (a) magnitude and (b) phase angle for the titanium (Ti) electrode before and after depositing the chitosan (CS) and composite CS-copper(II) [Cu(II)] ion coatings in physiological saline solution (0.9% sodium chloride) at 37°C.

The magnitude Bode diagrams reveal a linear dependence of log |Z| on log *f* with a slope close to -1 at the intermediate frequency range (Figure 6a). In Figure 6b, there is only one time constant and a near-capacitive response in all EIS spectra, suggesting a one-step mechanism for the electrochemical corrosion that occurs. The maximum values of the phase angle for the Ti electrode with and without the CS coating are above  $-80^\circ$ . For the Ti/CS–Cu(II) electrode, the maximum values of the phase angle are below  $-60^\circ$ . The decrease in the phase angle is caused by the increase in the conductivity of the electrode with the deposited composite CS–Cu(II) ion coating. The parameters obtained using the  $R_1(R_2Q_1)$  model shown in Figure 6a to fit the experimental EIS data for the Ti electrode before and after EPD in physiological saline solution at 37°C are shown in Table 1.

**Table 1.** The parameters of the  $R_1(R_2Q_1)$  electrical equivalent circuit with their standard deviations obtained as a result of the complex non-linear least squares fitting procedure of the experimental electrochemical impedance spectroscopy data for the titanium (Ti) electrode before and after electrophoretic deposition in physiological saline solution at 37°C.

Electrode type	$\frac{R_1}{[\Omega \text{ cm}^2]}$	$\frac{R_2}{[\Omega \text{ cm}^2]}$	$Q_1 - T$ [F cm <sup>-2</sup> s <sup>-1</sup> ]	Q <sub>1</sub> - <i>φ</i>
Ti	$5.25\pm0.20$	$(1.18 \pm 0.32) \times 10^{6}$	$(4.05 \pm 0.77) \times 10^{-5}$	$0.925\pm0.004$
Ti/CS	$3.50\pm0.20$	$(7.97 \pm 0.14) \times 10^{6}$	$(1.26 \pm 0.20) \times 10^{-5}$	$0.949\pm0.003$
Ti/CS–Cu(II)	$15.90\pm0.20$	$(4.36 \pm 0.9) \times 10^3$	$(3.04 \pm 0.45) \times 10^{-4}$	$0.683\pm0.003$

Note. CS, chitosan; Cu(II), copper(II).

The CNLS fitting results obtained for all tested electrodes revealed that the Ti/CS has the highest *in vitro* corrosion resistance in saline solution: it has the highest  $R_{2^{2}}$  (7.97  $\pm 0.14$ ) × 10<sup>6</sup>  $\Omega$  cm<sup>2</sup>, and at the same time the lowest value of the capacitive parameter  $Q_1-T$ , namely (1.26  $\pm 0.20$ ) × 10<sup>-5</sup> F cm<sup>-2</sup> s<sup>-1</sup> (Table 1). It is worth emphasising that the  $R_2$  kinetic parameter for the self-passive Ti electrode is nearly 7 times lower compared with the highly corrosion-resistant Ti/CS. The composite CS–Cu(II) ion coating with antimicrobial properties does not improve the corrosion resistance of the Ti electrode, as evidenced by the lowest  $R_2$  value of (4.36  $\pm 0.9$ ) × 10<sup>3</sup>  $\Omega$  cm<sup>2</sup>. Along with the increase in *in vitro* corrosion resistance, there is a decrease in  $Q_1-T$ . Moreover, the Ti/CS and Ti/CS–Cu(II) coatings are hydrogel materials and absorb water in saline solution. The absorbed water accelerates the gradual biodegradation of the CS coating, a phenomenon that is essential in drug delivery systems [35]. The  $Q_1-\phi$  parameter is empirical and for all investigated electrodes shows a strong deviation from 1 (Table 1), which is a consequence of the presence of physical, chemical, or geometric inhomogeneities on the electrode surface [43].

The mechanism by which the CS–Cu(II) ion coating degrades is based on water absorption, which causes the hydrolysis of bonds in CS and the tearing of polymer chains. In the biological milieu, the obtained coatings also absorb enzymes, which leads to enzymatic degradation. As the coating degrades, Cu(II) ions are released into the biological milieu. Corrosion of the Ti G4 substrate in the biological milieu has an electrochemical nature. Oxidation of Ti atoms and release of the corrosion products in the ionic form to a solution has been described previously [11].

# 4. Conclusions

The results confirm that the composite CS-Cu(II) ion coating can be successfully deposited on the Ti G4 substrate by EPD using the proposed conditions. The chemical characterisation of the obtained composite coating by EDS and ATR-FTIR proved that Cu(II) ions are embedded in the CS matrix. The EDS microanalysis revealed a Cu content of  $2.1 \pm 0.1$  wt.%. in the obtained composite coating; this content is sufficient for high antibacterial activity. The thickness of the CS coating was  $21 \pm 6 \,\mu$ m, and after embedding Cu(II) ions into the CS matrix, the thickness of the composite coating increased to  $34 \pm$ 8 μm. The surface topography study of the obtained coatings by the SKP method showed that bulges with a diameter of  $500-1000 \,\mu\text{m}$  are formed during EPD due to the electrolytic hydrogen evolution reaction. The surface modification changed the electronic properties of the Ti G4 substrate. The CS and composite CS-Cu(II) ion coatings reduce the activity of the Ti in air. In vitro corrosion resistance parameters of the tested materials determined in physiological saline solution at 37°C using EIS at the  $E_{0C}$  proved that the surface modification by the deposition of the CS coating increases anti-corrosion performance of the Ti electrode. The EIS characteristics of the interfacial properties revealed capacitive behaviour for all of the investigated materials. We found that there is only one time constant in the circuit, which indicates a one-step mechanism for the electrochemical corrosion process with the slowest kinetics for the Ti/CS electrode.

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