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**EFEITOS DE RECOBRIMENTOS ÓXIDOS MULTICOMPONENTES OBTIDOS POR
PEO NAS PROPRIEDADES ELETROQUÍMICAS DO TITÂNIO COMERCIALMENTE
PURO**

Sorocaba

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Dissertação apresentada como requisito para obtenção do título de Mestre em Ciência e Tecnologia de Materiais ao Programa de Pós-graduação em Ciência e Tecnologia de Materiais (POSMAT) da Universidade Estadual Paulista “Júlio de Mesquita Filho”, área de concentração Ciência de Materiais sob orientação do Prof. Dr. Nilson Cristino da Cruz.

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“Tão-somente esforça-te e tem mui bom ânimo, ...”

(Bíblia, Josué 1:7).

Deus seja louvado!

RESUMO

Titânio e suas ligas encontram aplicações militares e civis específicas devido a uma relação custo-benefício nem sempre interessante, apesar de possuírem extraordinárias propriedades químicas e físicas. Usinas nucleoeletricas de água pressurizada, por exemplo, constroem condensadores resfriados com água do mar e com tubulações de titânio comercialmente puro devido a resistência à corrosão e confiabilidade exigidas. Russos também já aplicaram titânio em cascos de submarinos por estes mesmos motivos aliados à resistência mecânica específica e à sua descrição magnética. Americanos o empregam nas estruturas de aeronaves de alto desempenho pela leveza e ponto de fusão superior ao do alumínio. Embora o titânio, protegido pela sua camada passiva, já possua elevada resistência à corrosão, modificações superficiais via oxidação eletrolítica assistida por plasma (PEO) podem ampliar esta resistência pelo espessamento da camada protetora, no entanto também aumentam a sua rugosidade e até promovem um comportamento superhidrofílico. O aumento da resistência à corrosão é interessante aos condensadores das usinas nucleoeletricas, mas o aumento da rugosidade e a superhidrofilicidade são inoportunas por favorecer a fixação de organismos marinhos e suas colônias. Contudo, este conjunto de novas características é especialmente interessante às aplicações biomédicas, pois a reação do organismo aos biomateriais implantados reduz o pH da área exposta ao ataque corrosivo, podendo evoluir a uma forma de corrosão localizada, como a formação de pites de corrosão. O risco deste tipo de degradação é minimizado pelo aumento da resistência eletroquímica da camada passiva nativa do titânio e a osseointegração é favorecida pela maior rugosidade e molhabilidade de uma superfície superhidrofílica. Neste trabalho foram produzidos por PEO filmes de óxidos sobre substrato de Ti-cp, a partir de diferentes composições de eletrólitos contendo: ZrO_2 , Ta_2O_5 , além da combinação destes dois óxidos. Uma vez obtidos, os filmes foram caracterizados por: FTIR, medição do ângulo de contato (molhabilidade), rugosidade, DRX, MEV, EDX, OCP, PDS e EIS. Destacamos os resultados obtidos com filmes produzidos com 6 g/L da mistura de óxidos, nos quais foi atingida a superhidrofilicidade e uma resistência à polarização seis vezes maior a do Ti-cp.

PALAVRAS-CHAVE: Titânio Comercialmente Puro, Zircônio, Tântalo, PEO, Corrosão.

ABSTRACT

Titanium and its alloys find specific military and civil applications due to a cost-benefit ratio that is not always interesting, despite having extraordinary chemical and physical properties. Pressurized water nuclear power plants, for example, build condensers cooled by seawater with commercially pure titanium pipes due to the corrosion resistance and reliability required. Russians have also applied titanium to submarine hulls for these same reasons, combined with specific mechanical strength and magnetic stealth. Americans use it in high-performance aircraft structures for its lightness and melting point higher than aluminum. Although titanium, protected by its passive layer, already has high resistance to corrosion, surface modifications via plasma electrolytic oxidation (PEO) can increase this resistance by thickening the protective layer, however they also increase its roughness and even promote a superhydrophilic behavior. The increase in resistance to corrosion is interesting for the condensers of nuclear power plants, but the increase in roughness and superhydrophilicity are inopportune because they favor the fixation of marine organisms and their colonies. However, this set of new characteristics is especially opportune for biomedical applications, as the body's reaction to the implanted biomaterials reduces the pH of the area exposed to corrosive attack, and may evolve to a form of localized corrosion, such as the formation of corrosion pits. The risk of this type of degradation is minimized by increasing the electrochemical resistance of the native passive layer of titanium and osseointegration is favored by the greater roughness and wettability of a superhydrophilic surface. In this work, oxide films on Ti-cp substrate were produced by PEO, from different electrolyte compositions containing: ZrO_2 , Ta_2O_5 , in addition to the combination of these two oxides. Once obtained, the films were characterized by: FTIR, contact angle measurement (wettability), roughness, XRD, SEM, EDX, OCP, PDS and EIS. We highlight the results obtained with films produced with 6 g/L of the oxide mixture, in which superhydrophilicity and a resistance to polarization six times greater than that of Ti-cp were achieved.

KEYWORDS: Commercially Pure Titanium, Zirconium, Tantalum, PEO, Corrosion.

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1. INTRODUÇÃO

No primeiro quartil do século XXI o uso do titânio evoluiu rapidamente à maturidade no ciclo de vida de produtos da indústria aeroespacial e também como biomaterial e componente náutico. A alta resistência à corrosão aliada a uma considerável resistência mecânica específica justificaram o emprego estratégico do titânio e de suas ligas pelas forças armadas de diversos países durante o século passado¹ e quiçá ao longo do próximo milênio também. Isto revela o potencial das pesquisas e desenvolvimentos que envolvem este metal. A resistência eletroquímica deste material destaca-se entre outros fatores, sendo em termos práticos o quinto elemento químico mais resistente à corrosão pela água do mar, superado apenas pela platina, pelo ouro, além do carbono e da prata². Superfícies de titânio expostas por 18 anos à água do mar apenas perderam a coloração original. Esta elevada resistência à corrosão é devida a uma fina película de dióxido de titânio impermeável e isolante, que se forma e regenera rápida e espontaneamente ao ar (O₂), todavia eventual ponto de falha nesta camada protetora, que não se recupere tempestivamente, pode iniciar o processo de corrosão puntiforme³. Tornar a camada passiva ainda mais inerte é o desafio para melhorar o desempenho do titânio em meios corrosivos contendo cloretos, como a água do mar, e a modificação superficial via oxidação eletrolítica assistida por plasma (PEO) revela-se um processo viável, rápido e econômico para este tratamento.

Os meios eletrolíticos empregados na PEO foram compostos por óxidos de zircônio e de tântalo, pois trabalhos anteriores relatam o aumento da resistência à corrosão em ligas de titânio pela modificação superficial e alguns estudos indicam o uso do zircônio ou do tântalo para promoção deste efeito⁴⁻⁷.

Com relação ao tântalo, estudos reportam sua contribuição positiva como elemento de adição às ligas de titânio, apesar de sua baixa resistência à corrosão em ambientes industriais com ácido fluorídrico. Por outro lado, em outros meios contendo ácido clorídrico ou sulfúrico, as ligas de tântalo com titânio balanceado, comparadas às comerciais Ti-cp, Ti-6Al-4V, Ti-6Al-7Nb, apresentam resistência à corrosão superior⁶.

O zircônio, por sua vez, é considerado uma boa alternativa a modificação superficial devido às suas propriedades mecânicas e alta resistência à corrosão^{4,5}. A resistência à corrosão do zircônio e de suas ligas também é devida a uma fina camada de óxido passivo que se forma espontaneamente sobre sua superfície, porém possui suscetibilidade à corrosão pontual quando em contato com eletrólitos halogenados⁴. Conforme já exposto, esta corrosão localizada é prejudicial por atravessar a barreira superficial e penetrar sem agredir a maior parte da superfície que permanece inalterada². Melhores desempenhos são interessantes e o espessamento e a modificação da camada superficial pode ser uma alternativa à obtenção de filmes protetores mais resistentes à corrosão puntiforme do titânio⁸.

As combinações do óxido de titânio com óxidos de zircônio e óxidos de tântalo revelaram-se efetivas para o aumento da resistência à corrosão da superfície do substrato de titânio comercialmente puro. Foram ensaiadas eletroquimicamente nove condições de tratamento superficial e uma do substrato Ti-cp como controle. Os resultados de medidas de potencial em circuito aberto (OCP), varredura potenciodinâmica direta (PDS) e a espectroscopia de impedância eletroquímica (EIS) referendaram os resultados positivos da modificação superficial. Destacaram-se as modificações produzidas pelo eletrólito com a mistura dos óxidos de zircônio e de tântalo sobre o substrato de titânio comercialmente puro, quando comparado aos resultados com óxidos isolados.

Além dos ensaios de corrosão, os ensaios de rugosidade e molhabilidade (ângulo de contato) foram igualmente relevantes para caracterização e estudo da viabilidade deste tratamento às tubulações dos condensadores de centrais nucleoeletricas resfriados com água do mar. Embora a PEO feita com eletrólito composto pela mistura de óxidos de zircônio e de tântalo tenha contribuído para um aumento na resistência à corrosão do titânio comercialmente puro, os resultados de rugosidade e molhabilidade não foram favoráveis às aplicações em trocadores de calor resfriados com água do mar. Nos filmes obtidos com 6 g/L de mistura de óxidos, por exemplo, houve um aumento significativo da rugosidade e as superfícies modificadas tornaram-se superhidrofílicas. Estas novas características favorecem a fixação de organismos marinhos e suas colônias; fenômeno extremamente

indesejável, pois além de promoverem a obstrução dos tubos dos trocadores de calor no médio e longo prazo também contribuem para o risco de corrosão induzida por microrganismos². Nestas condições rapidamente evoluem: a adsorção de aminoácidos, encadeamento de proteínas, crescimento de bactérias, estabelecimento de biofilmes, crescimento de macrorganismos até o domínio de uma biota própria do meio marinho⁹. Portanto a modificação superficial do titânio comercialmente puro, grau II, via PEO com eletrólito a base de óxido de tântalo e óxido de zircônio não é adequada às tubulações de trocadores de calor expostas a água do mar, embora melhore sua resistência à corrosão.

Por outro lado, estes resultados de corrosão, rugosidade e ângulo de contato são especialmente interessantes em aplicações biomédicas^{10,11}. O interior do corpo humano também é um meio eletroquímico naturalmente agressivo a corpos estranhos¹² e suas reações corrosivas podem gerar íons metálicos pelo ataque aos dispositivos biomédicos implantados¹³. Estes íons migram por todo organismo com alto risco de atingirem níveis de concentração tóxicos aos órgãos e tecidos¹⁴. Implantes metálicos, cujos principais representantes incluem: Ti e suas ligas, aço inoxidável e ligas de Cr e Co, possuem diferentes graus de resistências à corrosão e sofrem esta degradação em maior ou menor grau. Exames realizados em amostras de sangue e urina de pacientes submetidos a artroplastia revelaram concentrações de íons Cr, Ni e Ti superiores aos limites aceitáveis. Até mesmo o titânio e suas ligas, com sua camada passiva biocompatível, que o torna especialmente interessante como biomaterial, estão sujeitos à degradação, pois esta película protetiva não é completamente imune a tribocorrosão, por exemplo, quando o desgaste produzido pelo contato regular ao longo da vida útil de um implante ocorre simultaneamente ao ataque químico que tem origem nas diversas substâncias liberadas pelo metabolismo do ser vivo¹⁵. Outra condição agressiva às aplicações biomédicas ocorre imediatamente após a introdução de um implante em organismo vivo, quando inicia-se um complexo processo inflamatório como resposta a um procedimento cirúrgico invasivo ou à presença de qualquer corpo estranho⁴. Entre os vários efeitos desta reação, sucede a diminuição do pH local, pela presença de ácido hipocloroso (HOCl) e ácido láctico produzidos nos vacúolos dos fagócitos¹². Esta condição é desfavorável

à estabilidade do filme óxido protetor dos implantes na medida que facilita a penetração desta camada passiva nas posições mais suscetíveis da sua estrutura, podendo atingir e propagar o processo corrosivo pontual para regiões subjacentes à superfície¹⁰ e, mediante a uma eventual incapacidade de repassivação, até ao interior das peças². Nestas condições qualquer ganho na resistência à corrosão torna-se importante. Com relação ao aumento da rugosidade e redução do ângulo de contato, estas características são especialmente convenientes ao crescimento, à viabilidade celular e à osseointegração dos implantes de titânio^{16,17}.

As condições experimentadas por um implante in vivo são complexas e de difícil reprodução, todavia a caracterização in vitro é o início do desenvolvimento de qualquer biomaterial¹². Complementando esta etapa de desenvolvimento também foram realizadas as caracterizações FTIR, DRX e MEV/EDX para melhor compreensão das modificações obtidas.

2. METODOLOGIA

Foram realizadas as seguintes etapas nesta pesquisa:

1. Preparação de 30 amostras circulares de Ti-cp, com aproximadamente 3 mm de espessura, via corte de tarugo Ø 24 mm (10 unidades em cutoff e 20 unidades com eletroerosão a fio) e polimento progressivo das faces circulares com lixas d'água 80, 150, 240, 400 e 600.
2. Lavagem das amostras em três banhos de ultrassom: com tensoativo (100 mL água deionizada com 1 g de tensoativo), enxague com 100 mL de água deionizada e, por último, com álcool isopropílico (50 mL), durante 480 s em cada banho.
3. Secagem das amostras com ar quente, identificação individual e armazenamento em sacos plásticos com fecho hermético.

4. Produção de 1 L de eletrólito para cada carga de óxido (2, 4 e 6 g/L) com: 1 L de água deionizada, 2 g de hidróxido de potássio (KOH) e o respectivo óxido em suspensão. Este procedimento foi repetido para os três grupos de suspensão (ZrO_2 , Ta_2O_5 e mistura 50/50 de ZrO_2 e Ta_2O_5), totalizando 9 condições com diferentes eletrólitos e concentrações, conforme resumido na Tabela 1.

Tabela 1 - Agrupamento e identificação das amostras.

GRUPO / ÓXIDO	CONCENTRAÇÃO DO ELETRÓLITO ¹ (g/L)	IDENTIFICAÇÃO DAS AMOSTRAS	OBS.
CONTROLE ²	-	A00, A10 e A20	SEM OXIDAÇÃO
ZrO_2	2	A01, A02, A03	PEO: TENSÃO PULSANTE; EXCLUSIVAMENTE ANÓDICA; ONDA QUADRADA; PICO 500 V; f = 1000 Hz; CICLO DE TRABALHO = 50 %; DURAÇÃO 420 s.
	4	A04, A05, A06	
	6	A07, A08, A09	
Ta_2O_5	2	A11, A12, A13	
	4	A14, A15, A16	
	6	A17, A18, A19	
= ZrO_2 + Ta_2O_5 (50 / 50)	2	A21, A22, A23	
	4	A24, A25, A26	
	6	A27, A28, A29	

¹ Eletrólito: água deionizada, 2 g/L de KOH mais o respectivo óxido adicionado.

² Amostra base para PEO.

5. Ajuste dos parâmetros da PEO: diferença de potencial entre eletrodos 500 V, pulsados com frequência de 1 kHz, ciclo de trabalho 50% e duração de 420 segundos.

6. PEO de 27 amostras conforme Tabela 1.
7. Preservação de 3 amostras sem modificação superficial como controle.
8. Caracterização superficial das 27 amostras modificadas e das 3 amostras de controle através de ensaios não destrutivos: FTIR, perfilometria, molhabilidade, MEV/EDX e DRX.
9. Avaliação da resistência à corrosão em 3,5 % de NaCl com 5 medições de cada condição de PEO, por meio de medidas de Potencial em Circuito Aberto (OCP), Espectroscopia de Impedância Eletroquímica (EIS) e Varredura Potenciodinâmica Direta (PDS).

3. RESULTADOS E DISCUSSÃO

Os resultados deste trabalho e suas discussões estão apresentados na forma de artigo¹ publicado na revista *Metals* (ISSN: 2075-4701), classificada pela Qualis como A2 na área de Materiais e fator de impacto 2,6 pelo *Journal Citation Reports* (JCR).

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Article

Effect on the Electrochemical Properties of PEO Films Produced on Commercially Pure Titanium Using Multicomponent Oxide Coatings

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Abstract: Titanium has specific uses due to its cost, which is counterbalanced by its extraordinary chemical and physical properties. Submarine hulls and nuclear power plant pipes have been made of titanium since the last century due to its high corrosion resistance, and the aircraft industry has also exploited its remarkable properties, such as lightness and high melting point. Surface modifications by plasma electrolytic oxidation (PEO) may increase its corrosion resistance, roughness and wettability. Furthermore, greater corrosion resistance is a rather attractive property in nuclear power plant pipes, although the increased roughness and wettability are disadvantageous downsides as they favor the attachment of marine organisms. Nonetheless these new features are particularly interesting for biomedical applications. In this study, PEO films were produced on commercially pure titanium substrates using different electrolytes, one of which contains zirconium dioxide and the other consisting of tantalum pentoxide, in addition to a third one composed of a combination of the former two. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analyses were performed in addition to contact angle and roughness measurements, and electrochemical tests were carried out to comparatively characterize the different film compositions. The results revealed that excellent corrosion resistance was achieved by mixing oxides in the electrolyte.

Keywords: biomaterial; titanium; PEO; ZrO_2 ; Ta_2O_5 ; corrosion



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1. Introduction

Commercially pure titanium (CP-Ti) has enormous potential for advanced engineering applications due to its high strength-to-weight ratio and remarkable corrosion resistance resulting from its protective oxide layer [1]. It has been used in aerospace, marine engineering, chemical processing industries, as well as nuclear plants [2]. For instance, in nuclear power plants cooled by seawater, condenser tubes are typically made from materials offering excellent corrosion resistance and durability, given the harsh environment in which they operate [3]. Among the most used materials for manufacturing these condenser tubes, commercially pure titanium stands out owing to its performance in marine environments [4].

It is a biocompatible material, thus it is widely used in biomedical applications, although its corrosion resistance has limitations, particularly when in contact with strong acids or contaminants such as iron and chlorides at high temperatures, leading to localized corrosion cracking [5]. Furthermore, titanium is a very chemically reactive element [6] having a fairly negative standard electrode potential (-1.63 V) [7] and its corrosion protection is only provided by a thin and fragile native oxide layer [8]. Additional oxide coatings could enhance corrosion protection and provide functional properties, e.g., bioactivity behavior [6,9], not to mention the fact that there must be proper material and coating method selection to maximize titanium performance and durability [10].

Plasma electrolytic oxidation (PEO) is an efficient technique for enhancing the corrosion resistance of CP-Ti and other valve metals, improving their utilization in aggressive environments [11–13]. This conversion coating process can be resumed by developing an electric breakdown under a strong electric field within a system comprising the substrate, an oxide layer, a gas envelope, and the electrolyte [14]. The electric discharge in this system establishes a plasma state, wherein the surface substrate material is converted into a compound formed by the substrate itself under anodic polarization at high temperatures and pressures, in addition to the substrate alloy elements, of which oxygen is one, and the electrolyte components [15]. Film growth kinetics may vary depending on the substrate used, and also on some parameters defined by the electrical energy source, in addition to the composition, temperature and homogeneity of the electrolyte, resulting in changes in the characteristics and properties of the modified surfaces, such as the morphology, surface energy, crystalline structure, composition, and electrochemical response [16–19]. PEO allows the creation of a thick, dense, and adherent oxide layer on the titanium surface, surpassing the natural oxide film in both its durability and protective properties [20] despite producing rough surfaces that are not so interesting for corrosion resistance [21]. PEO coating may improve resistance to localized corrosion, such as pitting and crevice corrosion, in harsh conditions involving chlorides, acids, or high temperatures [22]. Additionally, it offers tailored surface properties, including increased hardness and wear resistance, thus further enhancing material performance in demanding applications [23]. By optimizing electrochemical stability and mechanical integrity, PEO ensures a longer service lifespan and reduces maintenance costs, particularly concerning titanium, which makes it a good choice for various applications [6,24,25].

Zirconia (ZrO_2) is recommended for protecting titanium surfaces against corrosion due to its excellent chemical stability, high hardness, and superior resistance to aggressive environments [26,27]. When applied as a coating material or incorporated into surface treatments, zirconia acts as a compact barrier and avoids the diffusion of corrosive agents within films, such as chloride ions, acids, and alkalis. Its compatibility with titanium and its ability to form dense uniform layers enhance the overall corrosion resistance of the substrate, even under extreme conditions such as high temperatures or marine environments. Furthermore, zirconia has demonstrated anticancer, antibacterial, and antioxidant effects in the human organism and, as a biocompatible and harmless metal oxide, its coatings are particularly valuable in medical and dental applications, because it safeguards titanium implants from corrosion-induced degradation while maintaining their mechanical integrity. By extending the durability and reliability of titanium, zirconia-based coatings contribute significantly to the performance and longevity of titanium components in various industrial and biomedical applications [17].

Another biocompatible element is tantalum (Ta), which has high mechanical and corrosion resistance, although with elevated cost. On the other hand, tantalum pentoxide (Ta_2O_5), which has a relatively low cost, is very stable even in corrosive solutions owing to its chemical stability, high dielectric strength, and a great ability to form dense, defect-free films [28–31]. Consequently, biocompatible Ta_2O_5 coatings are valuable for titanium

biomedical applications, since they are protected from corrosion-induced degradation while at the same time maintaining their functional properties [32]. Thus, by integrating Ta_2O_5 into surface treatments, performance and lifespan are significantly enhanced, benefiting industries such as aerospace, chemical processing, and medical devices [24,25,29].

The originality of this work lies primarily in the innovative use of oxide mixtures to create multicomponent coatings (TiO_2 , ZrO_2 , and Ta_2O_5) via PEO on CP-Ti grade 2 substrates. Its main objective was to evaluate the electrochemical behavior of these micrometric films in saline environments. Additionally, the topography, chemical and phase composition, roughness, and contact angle were thoroughly examined and correlated, providing valuable insights into the feasibility and potential applications of this technology across various sectors of society.

2. Materials and Methods

2.1. Surface Preparation

In this study, a total of 30 sample discs (24 mm in diameter) of CP-Ti grade 2 (Sandinox Biomaterials, Sorocaba, SP, Brazil) were used as metallic substrates to produce PEO films. Before the anodic oxidation, surfaces were polished using waterproof SiC sandpapers (80, 150, 240, 400 and 600 mesh, 3M DO BRASIL LTDA, Sumaré SP, Brazil). They were then cleaned in two sequential ultrasonic baths, first with surfactant (DET LIMP S32 CHEMCO, Hortolândia, SP, Brazil) and deionized water followed with an isopropyl alcohol (TOGMAX, Sorocaba, SP, Brazil) only bath; each one lasting for 480 s. Afterwards, they were dried in a hot air stream and stored in a desiccator until the beginning of PEO testing.

2.2. Surface Modification

PEO treatments were conducted in different electrolyte compositions of distilled water, potassium hydroxide (KOH, Exodo Científica, Sumaré, SP, Brazil), zirconia (ZrO_2 , SIGMA-ALDRICH BRASIL LTDA, Cajamar, SP, Brazil) and tantalum pentoxide (Ta_2O_5 , AMG Brasil S.A., São João del Rei, MG, Brazil). The corresponding concentrations of powders and the samples' nomenclature are shown in Table 1. Based on previous research [17], PEO treatments were performed in a pulsed MAO-30 power supply system (Plasma Technology Ltd., Hong Kong, China) operating at 500 V, 1 kHz, 50% for 420 s, with a water-cooled stainless steel reactor vessel set as a cathode, using the titanium sample as an anode. Three samples were kept as control without PEO.

Table 1. Sample test data.

Nomenclature	Electrolyte (g/L)		
	KOH	ZrO_2	Ta_2O_5
2 ZrO_2	2	2	-
4 ZrO_2		4	
6 ZrO_2		6	
2 Ta_2O_5	2	-	2
4 Ta_2O_5			4
6 Ta_2O_5			6
2 $ZrO_2 + Ta_2O_5$	2	1	1
4 $ZrO_2 + Ta_2O_5$		2	2
6 $ZrO_2 + Ta_2O_5$		3	3

2.3. Surface Characterization

Topographic details were examined using a scanning electron microscope coupled to an energy dispersive X-ray spectrometer (SEM/EDX; JEOL Ltd., Akishima, Tokyo, Japan) for

elemental analysis. Phase composition was evaluated by X-ray diffraction (XRD; Shimadzu XRD 6100 diffractometer, Kyoto, Japan) operating at 40 kV and 30 mA, measured using a thin film in continuous scan mode configuration with step size of 0.02° and collecting time of 1.2 s. Diffracted peaks were indexed using crystallographic datasheets from the International Centre for Diffraction Data (ICDD). Fourier transform infrared spectroscopy (FTIR-410; Jasco Co., Tokyo, Japan) identified the functional groups on the surface in transmittance mode, 4 cm^{-1} resolution and 128 scans. Average roughness (Ra) was measured by optical profilometry (Dektak 150 profilometer, Veeco Metrology, Tucson, AZ, USA), using a stylus radius of $12.5\text{ }\mu\text{m}$, scan length of $100\text{ }\mu\text{m}$ for 12 s and an applied force of $0.3\text{ }\mu\text{N}$. Surface wettability was verified using contact angle measurements (Ramé-hart Instrument Co., Succasunna, NJ, USA) and a distilled water droplet ($30\text{ }\mu\text{L}$) at room temperature.

2.4. Electrochemical Measurements

Electrochemical tests were carried out using an Autolab PGSTAT128N potentiostat/galvanostat (Metrohm AG, Herisau, Switzerland) connected to a three-electrode flat cell system. Each of the 30 samples representing the different experimental conditions of surface modification (as shown in Table 1), in addition to three CP-Ti control samples, was used as the working electrode, while a large-area platinum wire was used as the counter electrode and Ag/AgCl as the reference electrode. A 3.5 wt% NaCl solution was used as an electrolyte at room temperature to simulate the aggressiveness of marine environments. Open circuit potential (OCP) measurements were performed until reaching a steady state. Then, electrochemical impedance spectroscopy (EIS) was measured using 10 mV (rms) perturbation and frequencies ranging from 10 kHz to 100 mHz, 10 points per frequency decade. Polarization direct scanning (PDS) was conducted from -1 to $+2\text{ V}$, at a $1\text{ mV}\cdot\text{s}^{-1}$. Results were analyzed using the NOVA[®] software version 2.1.5 (Metrohm). Five replicate measurements were obtained for each test, and the results found for PEO films were compared with themselves and with those for the untreated sample (CP-Ti substrate).

3. Results and Discussion

3.1. Current-Time Curves

During the first minute of the PEO current was measured every 10 s. After this, the current was taken every minute until the end. These results are summarized in Figure 1. The PEO current started at relatively high levels and dropped, remaining at lower levels after the first minute, which already indicates the formation of an insulating layer, as had been observed in similar cases [24,29].

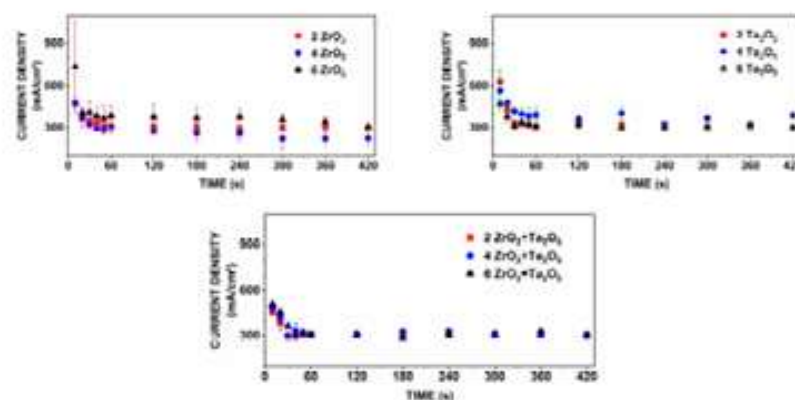


Figure 1. Current density vs. time graphs obtained during the PEO.

3.2. Morphological and Compositional Analysis

In Figure 2, some topographic details, such as small pores, clusters and plaques, are observed on the modified surfaces, but no remaining grooves from the original substrate were found. Pores are the result of electrical discharges occurring during the dielectric breakdown of the oxide layer [12], while agglomerates are probably particles absorbed from the electrolyte, assisted by the electrical field. The original morphology of the untreated substrate (control) completely disappeared after treatments, probably indicating complete coverage.

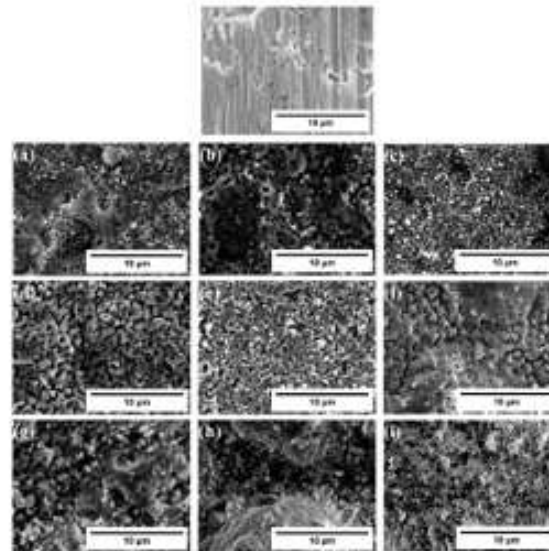


Figure 2. SEM images for the control (upper) and modified surfaces by PEO, sequentially: 2 ZrO₂ (a), 4 ZrO₂ (b), 6 ZrO₂ (c), 2 Ta₂O₅ (d), 4 Ta₂O₅ (e), 6 Ta₂O₅ (f), 2 ZrO₂ + Ta₂O₅ (g), 4 ZrO₂ + Ta₂O₅ (h), and 6 ZrO₂ + Ta₂O₅ (i).

Regarding the results in Figures 3–5, compared to the reference control substrate, a large increase in oxygen content was detected, clearly indicating the formation of layers of oxides (TiO₂, ZrO₂ and Ta₂O₅). The levels of Zr and Ta also increased exponentially, but non-gradually with respect to the electrolyte composition, which indicates that the treatment parameters are relevant for controlling the incorporation of different chemical elements as well. A recent work revealed that the conductivity and energy of the electrical discharges change by modifying the electrolyte composition, resulting in a removal of part of the oxide instead of the enrichment of chemical elements [25].

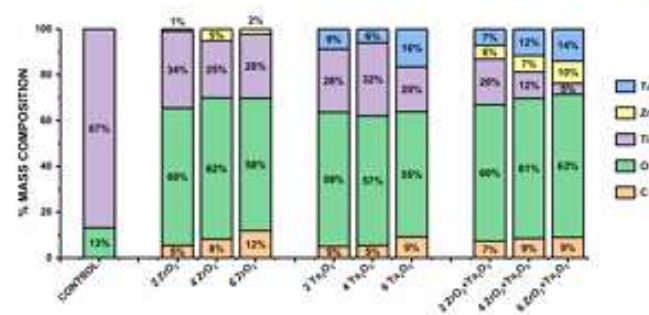


Figure 3. Semi-quantitative EDX analysis obtained for the control (CP-Ti) and modified surfaces in Figure 2.

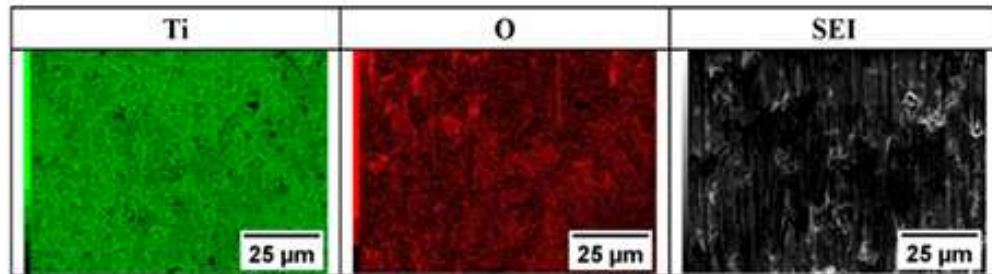


Figure 4. EDX mapping in the control unmodified surface.

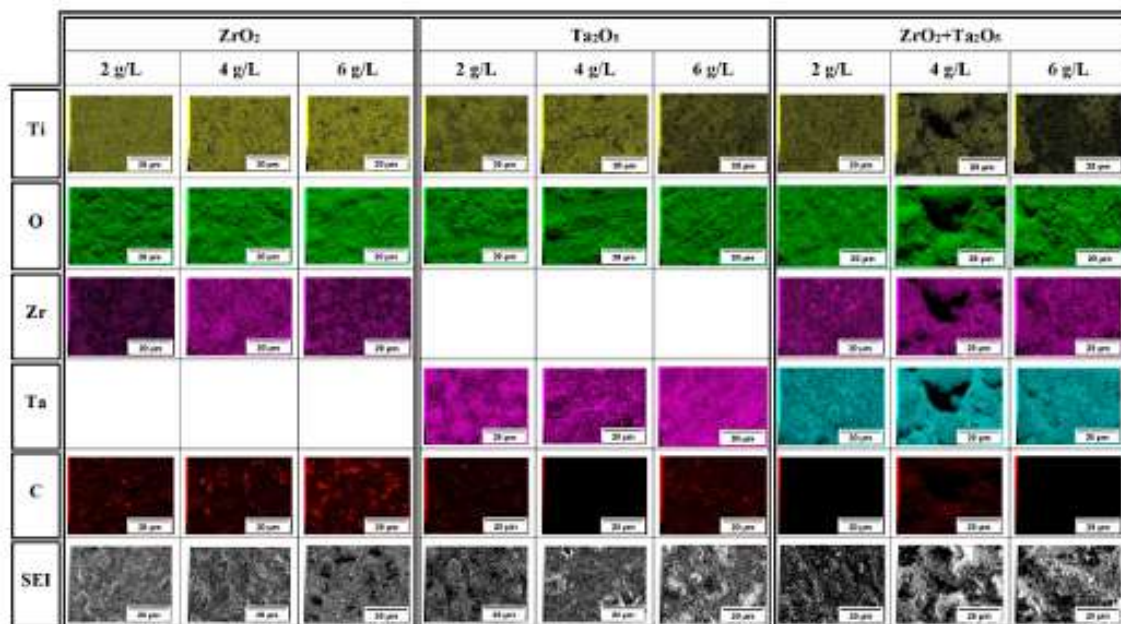


Figure 5. EDX mappings obtained for different films.

Figure 6, FTIR spectra, depicts O-H bonding presence at 3650 cm^{-1} frequency as stretching (ν) vibrations [33], probably originating from the electrolyte. Metal oxide surfaces can adsorb CO_2 from the environment and an asymmetric stretch band of CO_2 is characteristic, typically appearing in the region of 2340 cm^{-1} [34]. The bands at 1600 cm^{-1} are assigned to O-H bond bending (δ) [35] and at around 1350 cm^{-1} to C-H stretching (ν) vibrations [25]. Frequencies below 1000 cm^{-1} are related to metal-O bonding: 900 cm^{-1} were assigned to Ta-O-Ta vibration [36], 800 and 490 cm^{-1} to Ti-O vibration [37], and 600 cm^{-1} to Ta-O vibration [36,38]. Some regular ripples were identified in the range 1400 to 2400 cm^{-1} and probably are due to the optical phenomenon of Mie scattering [39]. Therefore, the results indicated that the ZrO_2 and Ta_2O_5 particles were successfully incorporated into the coatings during the PEO treatment, agreeing with the previous characterizations.

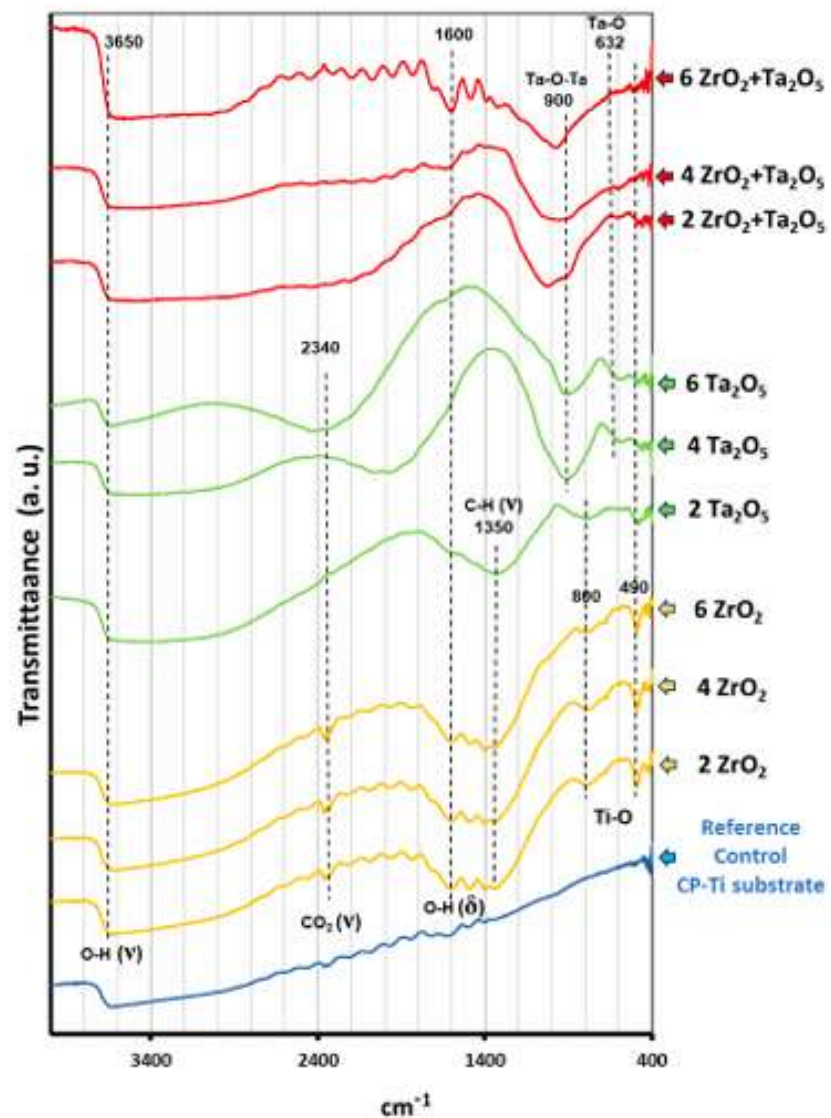


Figure 6. FTIR spectra for the control and modified surfaces of Figure 2.

According to the results in Figure 7, it was observed that the two variables, contact angle and roughness, are correlated since high contact angle values are associated with lower Ra values, and vice versa. Bharti et al. concluded that there should be another factor which influences wettability in addition to surface roughness and adsorbed OH polar groups on the surface tend to make it superhydrophilic [40], as found in $6 \text{ ZrO}_2 + \text{Ta}_2\text{O}_5$, where prominent OH presence was evidenced in previous FTIR spectra. The replacement of ZrO_2 by Ta_2O_5 does not substantially change roughness, most possibly because the major component on both surfaces (ZrO_2 or Ta_2O_5 at any concentration) is Ti (or its oxide, TiO_2). Thus, the incorporation of Zr or Ta in films only becomes more significant in the mixture of oxides ($\text{ZrO}_2 + \text{Ta}_2\text{O}_5$), which is in full agreement with the results shown in Figure 3.

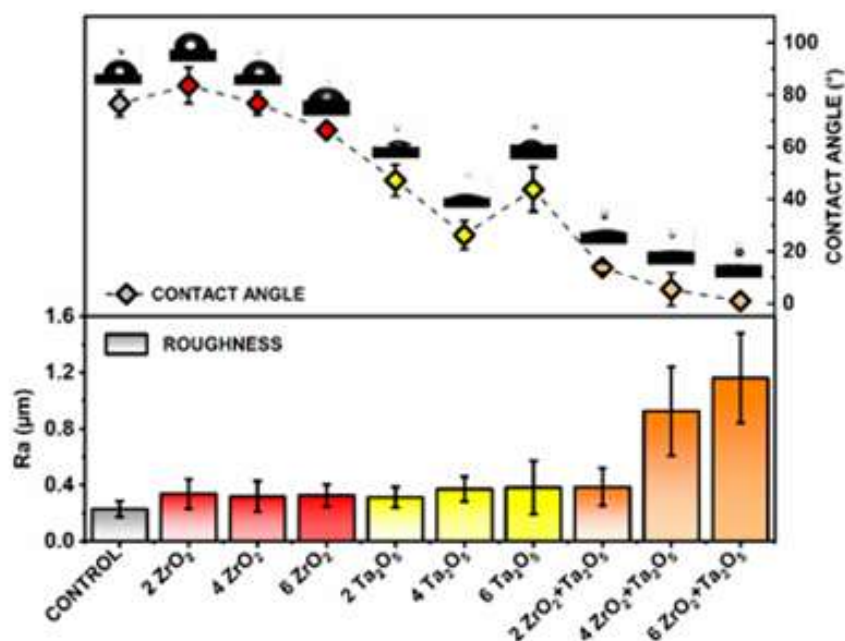


Figure 7. Contact angle, roughness and correlation values.

Contact angle and roughness analyses are relevant for industrial and biomedical applications. Although PEO can increase the corrosion resistance of commercially pure titanium, roughness and contact angle results were unfavorable to seawater applications. For instance, in Figure 7, 6 ZrO₂ + Ta₂O₅ samples had increased roughness and reached superhydrophilicity simultaneously. This fact improves the risk of marine organism attachment, leading to amino acid adsorption, protein chaining and the establishment of biofilms that could rapidly evolve to the domination of a marine biota [41], in addition to the undesirable corrosion induced by microorganisms [42]. On the other hand, enhanced corrosion resistance, increased roughness and superhydrophilicity are especially attractive for biomedical purposes [43].

Figure 8 depicts XRD diffractograms for the control (CP-Ti without PEO treatment taken as reference) and the samples modified by PEO. The control peaks at 35.0°, 38.4°, 40.2° and 53.0° corresponded to the ICDD card 44-1294 for the hexagonal close-packed structure of metallic titanium [17]. The modified samples still indicated metallic Ti peaks as well. All PEO-treated samples indicated the presence of TiO₂ in both anatase and rutile phases resulting from the PEO process. For the samples modified with ZrO₂, only the sample with an added 6 g/L indicated baddeleyite presence at 30.3°, while the sample reaching the largest Zr mass% according to the EDX analysis (5%) for 4 ZrO₂, did not indicated the same increase in the diffractogram. The samples modified with Ta₂O₅, having a higher oxide concentration (4 and 6 g/L), indicated the presence of orthorhombic Ta₂O₅ at 26.7°, 28.3°, 36.6°, and 55.4°, visible on the ICDD card 25-922. As for the EDX analysis of those samples, both revealed the presence of Ta on the surface, having 6 and 16 mass %, respectively. Ultimately, all samples modified with both oxides (ZrO₂ plus Ta₂O₅) indicated the presence of baddeleyite at 30.3°.

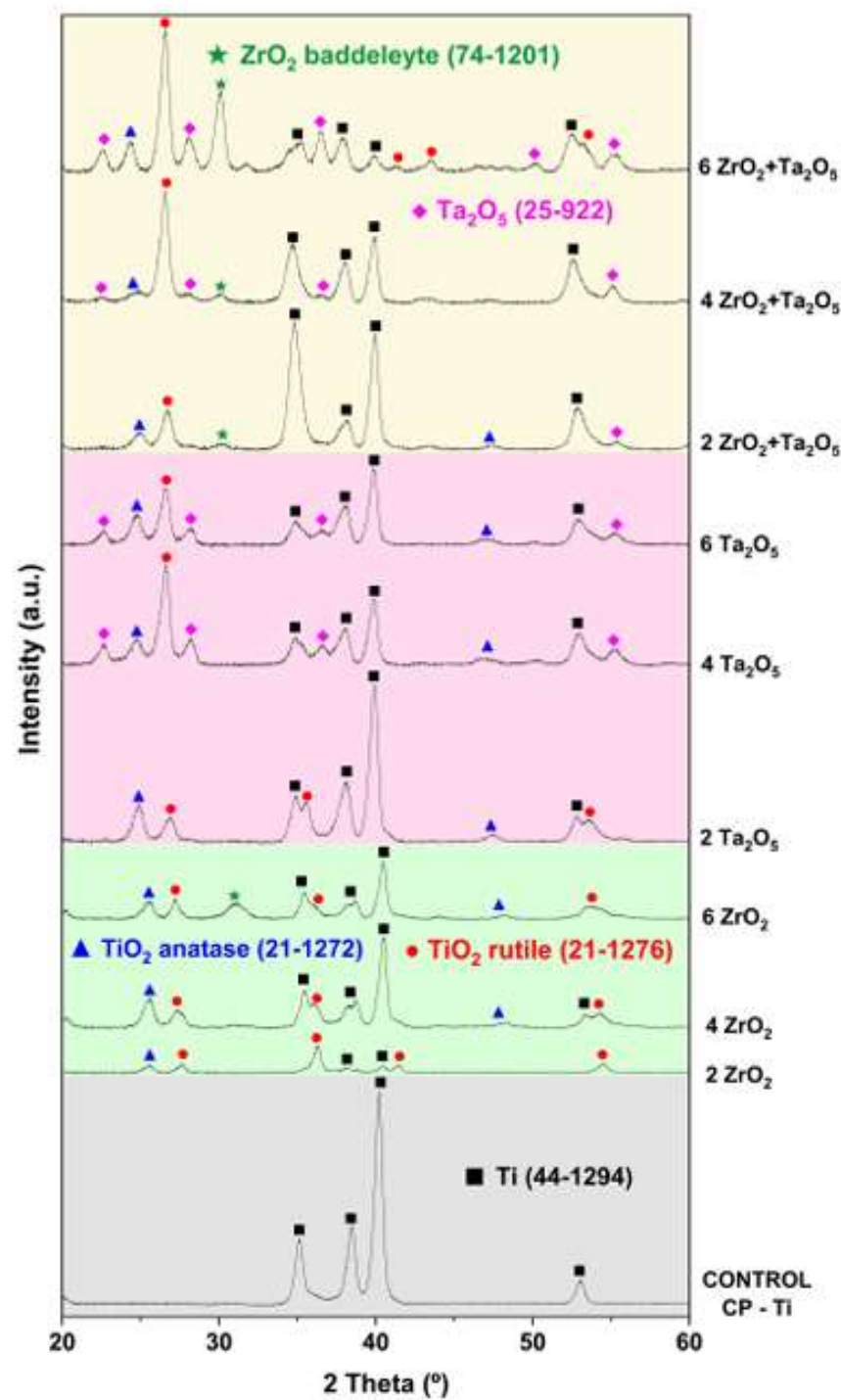


Figure 8. XRD patterns for the modified surfaces in Figure 2.

3.3. Electrochemical Analysis

3.3.1. Open Circuit Potential — OCP Measurements

Figure 9 shows the OCP graphs for the control group and the films obtained by PEO in different experimental conditions. It was observed that the largest dispersions between curves corresponded to the lowest oxide concentrations, 2 and 4 g/L, both for ZrO_2 and Ta_2O_5 , while it seems that the mixture $\text{ZrO}_2 + \text{Ta}_2\text{O}_5$ was not significantly affected by changes in concentration. Both ZrO_2 and Ta_2O_5 were at concentrations of 2 and 4 g/L, although the dispersions between curves were the largest. This change tends to be increasingly positive OCP values, while in the remaining film compositions, fluctuations in the potential are closer to those found for the control group, which might be a consequence of partial coverage of the substrate.

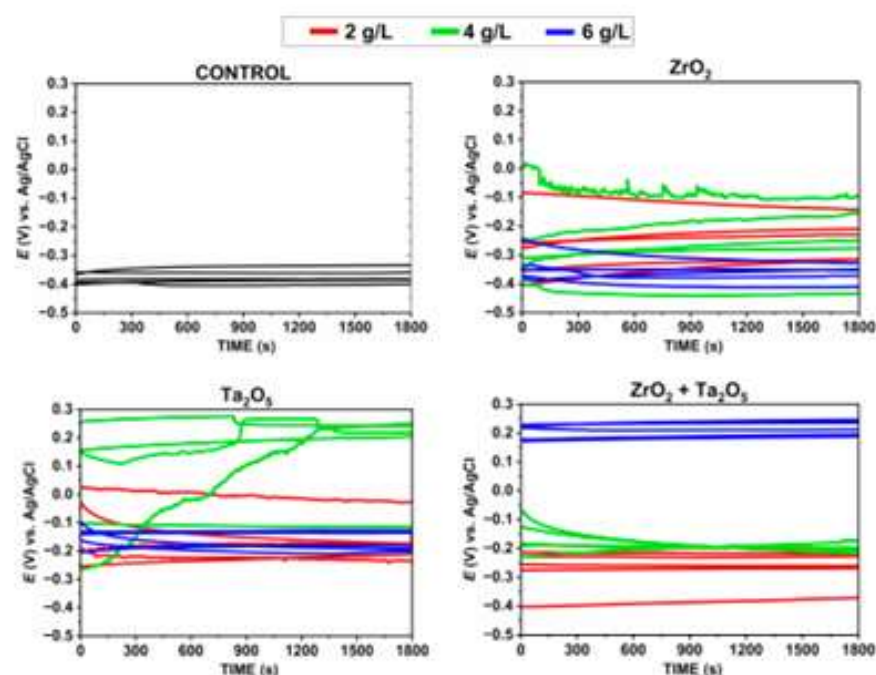


Figure 9. Open circuit potential measurements, OCP (V) found for the control group and different compositions of films.

To further this analysis, the OCP values found in the steady state (last point of each curve) of the five repetitions of each test were collected to devise a scatter diagram instead of average values. This considered that, in a few cases, dispersions were so great that they could be attributed to the heterogeneity of the films themselves, so that the analysis of average values could lead to a misinterpretation of data.

According to the OCP values in Figure 10, it was observed that the slightest dispersion between points occurred for the control group, in which all replicate measurements were below -0.3 V (Ag/AgCl), which can be explained by the formation of a native uniform film resulting from the oxidation of titanium, making the surface less active to corrosive attack by chloride ions. Comparatively, the dispersions obtained for different film compositions were significantly greater, so that, for a single composition, the OCP may vary widely, from values lower than -0.4 V to approximately -0.1 V, as can be observed for 4 ZrO_2 (4 g/L). Such a significant difference may be due to the heterogeneous nature of films formed by PEO, non-uniform distribution in the metal substrate coverage, or even the

presence of defects or porosities in the films, as had also been attested by other authors in related works [6,44]. Furthermore, for most film compositions, although OCP values are more often positive than for those obtained for CP-Ti (control), values as negative as those found for the control samples were observed at times, which is another indication of a few discontinuities in PEO films.

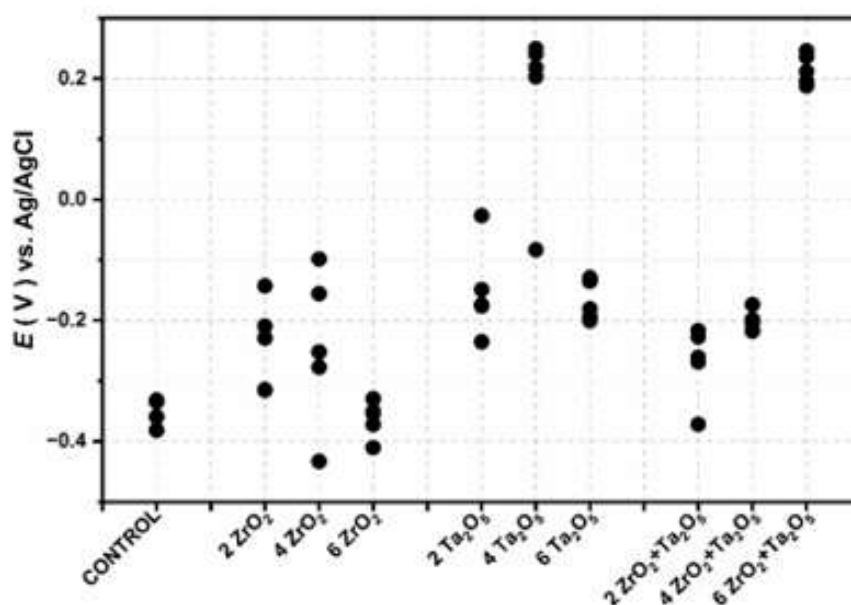


Figure 10. Scatter diagram ($n = 5$) shows the OCP values at steady state (1800 s).

Aliofkhazraei et al. (2021) proposed an alternative way to minimize this problem by increasing film thickness to hinder the access of chloride ions to the metal substrate, thus limiting the number of anodic sites located on the surface [6]. Compositional changes have also been investigated for the same purpose. For instance, Babaei et al. (2015) demonstrated that increasing the content of Zr in films produced by PEO leads to a significant increase in OCP values, but such an increase was only observed after 10 h of film immersion in an aqueous medium containing chloride ions [44]. Therefore, the kinetic effects on the formation of secondary oxides during the period of exposure to the electrolyte must also be considered [6,44].

Furthermore, it is worth mentioning that, with respect to the three compositions, from 2 to 6 g/L, represented by a mixture of oxides, $ZrO_2 + Ta_2O_5$, the higher the concentration, the greater the OCP values. Moreover, all replicate measurements resulted in OCP values greater than +0.1 V (Ag/AgCl) at 6 g/L, indicating that a mixture of oxides, at the highest concentration tested, should produce a synergistic effect to protect the substrate, which can be better elucidated in a further step through surface analysis at a nanometric scale. From a compositional standpoint, it is assumed that a mixture of oxides might form more corrosion-resistant phases.

3.3.2. Polarization Direct Scanning—PDS Measurements

PDS curves for CP-Ti substrates and PEO films are shown on Figure 11. Regarding the dispersions among the five replicates of the PDS measurements, the same behavior observed in OCP is found in the polarization curve profiles, with the smallest differences for the control group compared to PEO films. This is probably owing to the multiphase or heterogeneous characteristic of PEO films compared to the native TiO_2 film grown on the

surface of control samples. The five replicates exhibited a pseudopassive behavior for CP-Ti in chloride medium, indicated by a slight increase in current with increasing potential, within potentials ranging from -0.5 to 0 V (Ag/AgCl). Yerokhin and colleagues obtained a similar behavior in their studies, which was explained by the tendency to depassivation due to the instability of the TiO_2 film in a chloride medium; therefore, leading to native oxide dissolution and the formation of soluble complexes [7]. The difference in corrosion potential, E_{corr} , between the five replicate measurements, precisely at the inflection point of each curve, the control in Figure S1, may be related to the native film growth occurring continuously on the surface of samples, which becomes increasingly thicker with the aging of samples. After the formation of PEO films, this difference between replicates in OCP values remained and, in a few cases, it has even increased, probably since these films are not uniform along the metal substrate coverage. On the other hand, one outstanding result is that, for all compositions investigated herein, the pseudopassive behavior characteristic of CP-Ti in a chloride medium was thoroughly eliminated, i.e., in the passive section of PDS curves, the current remained constant or even decreased from an increase in potential at times, thus indicating that the constituent oxides of PEO films are more stable in a chloride medium, compared to those of the native TiO_2 film. Furthermore, corrosion currents were lower than $1 \mu\text{A}$ for all replicates of CP-Ti, and even lower by several orders of magnitude for PEO films. Regarding the passivation current density, for the control samples, these values oscillated around $1 \text{ mA}/\text{cm}^2$, while for the three PEO film compositions, these values varied between 0.1 and $1 \mu\text{A}/\text{cm}^2$, regardless of their respective concentrations. Furthermore, none of the PEO film samples showed a transpassive section; thus, no film rupture is expected since the potential sweep in the anodic branch of the curves indicates only the passivation film thickening in the chloride medium.

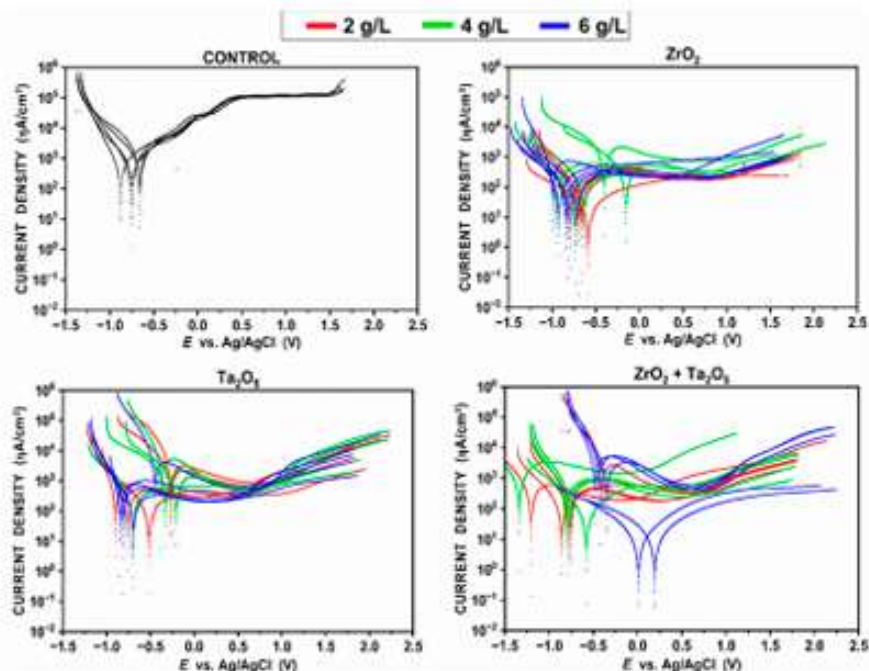


Figure 11. PDS curves for the CP-Ti substrate (control) and other film compositions. Five replicate measurements for each experimental condition were taken.

3.3.3. Electrochemical Impedance Spectroscopy—EIS Measurements

The EIS spectra obtained in complex plane format for the control group exhibited a single distorted semicircle in the frequency range investigated, and experimental results were fitted using the equivalent electrical circuit model inserted in the graph shown in Figure 12. The control is composed of the solution resistance, R_s , and a parallel association of the polarization resistance, R_p , with the electric double layer capacitance which was better modeled by a constant phase element, CPE, in order to emphasize a non-ideal capacitance, thus considering the angular frequency exponent, n , associated with the deviation from ideality used to represent a non-uniform current distribution related to surface heterogeneities, such as roughness and porosity. On the other hand, the EIS spectra of all other film compositions in Figure 12 were better fitted by the circuit composed of the solution resistance, R_s , followed by the film capacitance (semicircle obtained at high frequencies), which was better modeled by a CPE in parallel with the film polarization resistance, R_p , in addition to the Warburg element, W , inserted to fit the straight line component at low frequencies in the complex plane, representing diffusional phenomena at the metal/film/electrolyte interface.

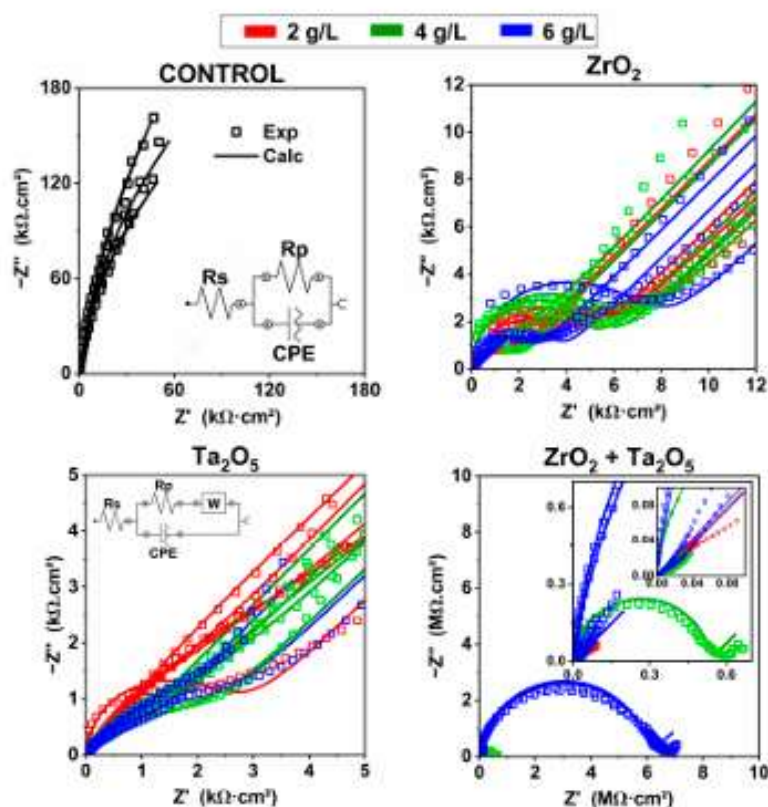


Figure 12. EIS spectra in the complex plane obtained for the control group and other film compositions. Insertion: equivalent electrical circuit models used to fit EIS spectra.

Table 2 shows fitting results corresponding to the control group. As expected, R_p values varied between approximately 0.5 and $1 \text{ M}\Omega \cdot \text{cm}^2$ for all replicates, indicating a highly corrosion-resistant surface due to the formation of the native TiO_2 film. CPE-Y0 values are consistent with the electrochemical response of a metal surface in contact with an oxidizing aqueous medium, and CPE- n with $n \cong 1$ agrees with the single large-diameter

semicircle. Interestingly, the R_p values corresponding to PEO films, Tables 3–5, vary in several orders of magnitude, and are even significantly lower than those calculated for CP-Ti substrates in a few cases, which may be due to the accumulation of electrolyte within the pores of films, thus increasing the local chloride concentration and producing a localized corrosion phenomenon as a consequence by restricting the ionic mobility within the film at its interface with the metallic substrate. The EIS spectra, obtained in Bode format (Figures S1 and S2 above, found in the Supplementary Material), exhibit a second maximum of the phase angle at low frequencies in some cases, narrower than 30° , which is consistent with the diffusion inside pores [45]. Furthermore, the large dispersions between measurements reveal the native heterogeneity of PEO films [46]. CPE-Y0 values smaller than $10^{-8} \text{ S}\cdot\text{s}^n\cdot\text{cm}^{-2}$ are consistent with those expected for passive or protective films [47].

Table 2. Fitting results of EIS spectra for the control group in a 3.5 wt% NaCl solution.

Control	EIS Measurement Replicates				
	1	2	3	4	5
R_s ($\Omega\cdot\text{cm}^2$)	10.96 (0.6)	8.99 (0.6)	10.21 (0.6)	12.61 (0.9)	11.58 (0.7)
R_p ($\Omega\cdot\text{cm}^2$)	4.79×10^5 (4.4)	6.33×10^5 (4.5)	5.22×10^5 (4.7)	1.06×10^6 (12.9)	1.03×10^6 (8.2)
CPE-Y0 ($\text{S}\cdot\text{s}^n\cdot\text{cm}^{-2}$)	9.29×10^5 (0.4)	7.69×10^5 (0.4)	9.61×10^5 (0.3)	8.29×10^5 (0.6)	7.52×10^5 (0.4)
CPE-n	0.93 (0.1)	0.92 (0.1)	0.91 (0.1)	0.92 (0.2)	0.92 (0.1)

Table 3. Fitting results of EIS spectra for ZrO_2 films in a 3.5 wt% NaCl solution.

ZrO_2		EIS Measurement Replicates				
		1	2	3	4	5
R_s ($\Omega\cdot\text{cm}^2$)	2 ZrO_2	10.87 (fixed)	10.87 (fixed)	21.40 (23.5)	10.87 (fixed)	10.87 (fixed)
	4 ZrO_2	10.87 (fixed)	10.87 (fixed)	22.50 (14.5)	10.87 (0.1)	10.87 (0.1)
	6 ZrO_2	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)	22.24 (7.0)
R_p ($\Omega\cdot\text{cm}^2$)	2 ZrO_2	6.64×10^3 (4.5)	2.12×10^5 (5.6)	1.29×10^3 (2.9)	5.12×10^3 (2.0)	4.27×10^3 (1.4)
	4 ZrO_2	5.54×10^3 (1.9)	4.56×10^3 (1.6)	3.34×10^3 (14.6)	1.48×10^3 (2.0)	5.20×10^3 (1.9)
	6 ZrO_2	7.13×10^3 (2.3)	2.24×10^3 (2.5)	1.27×10^4 (3.1)	3.39×10^3 (3.8)	3.96×10^3 (22.5)
CPE-Y0 ($\text{S}\cdot\text{s}^n\cdot\text{cm}^{-2}$)	2 ZrO_2	7.6×10^{-8} (28.5)	6.0×10^{-9} (23.8)	9.8×10^{-10} (20.7)	2.0×10^{-9} (21.1)	1.8×10^{-9} (16.3)
	4 ZrO_2	4.2×10^{-10} (17.8)	3.0×10^{-10} (15.9)	1.4×10^{-5} (13.3)	6.4×10^{-10} (27.0)	5.6×10^{-10} (20.7)
	6 ZrO_2	8.8×10^{-10} (26.0)	1.0×10^{-9} (29.9)	2.3×10^{-8} (25.9)	1.5×10^{-9} (27.6)	2.2×10^{-3} (9.0)
CPE-n	2 ZrO_2	0.69 (3.3)	0.74 (2.8)	1.04 (1.4)	0.91 (1.8)	0.93 (1.4)
	4 ZrO_2	1.02 (1.3)	1.05 (1.1)	0.66 (2.4)	1.05 (2.0)	1.03 (1.6)
	6 ZrO_2	0.96 (2.1)	1.00 (2.3)	0.89 (2.3)	0.96 (2.0)	0.62 (1.6)
W-Y0 ($\text{S}\cdot\text{s}^{1/2}\cdot\text{cm}^{-2}$)	2 ZrO_2	6.1×10^{-6} (3.4)	5.9×10^{-7} (4.7)	5.2×10^{-8} (1.3)	2.7×10^{-6} (1.0)	3.3×10^{-6} (0.6)
	4 ZrO_2	2.5×10^{-6} (1.2)	3.1×10^{-6} (1.3)	5.2×10^{-3} (3.8)	5.1×10^{-6} (0.8)	4.1×10^{-6} (2.2)
	6 ZrO_2	2.7×10^{-6} (1.6)	3.9×10^{-6} (1.0)	2.0×10^{-8} (2.2)	5.4×10^{-6} (2.3)	4.0×10^{-3} (17.2)

Table 4. Fitting results of EIS spectra for Ta₂O₅ films in 3.5 wt% NaCl solution.

Ta ₂ O ₅		EIS Measurement Replicates				
		1	2	3	4	5
R_s ($\Omega \cdot \text{cm}^2$)	2 Ta ₂ O ₅	10.87 (fixed)	26.68 (8.5)	24.01 (11.8)	21.01 (12.2)	25.09 (8.1)
	4 Ta ₂ O ₅	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)
	6 Ta ₂ O ₅	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)
R_p ($\Omega \cdot \text{cm}^2$)	2 Ta ₂ O ₅	2.40×10^3 (3.9)	2.17×10^4 (29.0)	3.92×10^3 (17.6)	4.65×10^3 (7.6)	6.47×10^3 (4.9)
	4 Ta ₂ O ₅	1.54×10^3 (5.9)	4.96×10^2 (3.2)	2.30×10^3 (2.8)	2.65×10^3 (4.5)	4.19×10^2 (5.2)
	6 Ta ₂ O ₅	2.28×10^3 (3.5)	2.30×10^5 (7.6)	2.63×10^3 (6.0)	1.06×10^3 (11.1)	3.65×10^3 (7.2)
CPE-Y0 ($\text{S} \cdot \text{s}^n \cdot \text{cm}^{-2}$)	2 Ta ₂ O ₅	1.4×10^{-9} (23.5)	1.5×10^{-3} (5.8)	1.2×10^{-3} (11.4)	9.6×10^{-6} (6.7)	1.0×10^{-3} (4.2)
	4 Ta ₂ O ₅	3.8×10^{-6} (10.8)	5.4×10^{-6} (1.0)	9.4×10^{-8} (5.9)	2.6×10^{-6} (7.3)	2.1×10^{-8} (22.3)
	6 Ta ₂ O ₅	9.4×10^{-10} (29.9)	3.0×10^{-6} (15.7)	6.3×10^{-8} (6.0)	7.7×10^{-6} (17.9)	9.6×10^{-6} (5.4)
CPE-n	2 Ta ₂ O ₅	0.99 (1.7)	0.59 (1.1)	0.65 (2.0)	0.68 (1.2)	0.66 (0.8)
	4 Ta ₂ O ₅	0.70 (1.5)	0.24 (2.4)	0.61 (1.0)	0.68 (1.0)	0.92 (1.7)
	6 Ta ₂ O ₅	1.02 (2.2)	0.70 (2.1)	0.65 (0.9)	0.65 (2.5)	0.57 (0.9)
W-Y0 ($\text{S} \cdot \text{s}^{1/2} \cdot \text{cm}^{-2}$)	2 Ta ₂ O ₅	4.8×10^{-6} (2.6)	1.3×10^{-3} (20.6)	2.9×10^{-5} (4.6)	3.9×10^{-5} (2.2)	4.0×10^{-3} (1.8)
	4 Ta ₂ O ₅	5.1×10^{-5} (2.3)	2.3×10^{-6} (1.5)	1.1×10^{-4} (1.9)	2.6×10^{-5} (1.7)	1.3×10^{-3} (1.3)
	6 Ta ₂ O ₅	3.1×10^{-6} (1.9)	7.5×10^{-3} (5.4)	3.6×10^{-5} (3.9)	7.5×10^{-5} (4.6)	2.8×10^{-3} (5.3)

Table 5. Fitting results of EIS spectra for ZrO₂ + Ta₂O₅ films in a 3.5 wt% NaCl solution.

ZrO ₂ + Ta ₂ O ₅		EIS Measurement Replicates				
		1	2	3	4	5
R_s ($\Omega \cdot \text{cm}^2$)	2 ZrO ₂ + Ta ₂ O ₅	8.51 (27.8)	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)
	4 ZrO ₂ + Ta ₂ O ₅	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)	13.14 (20.9)	10.87 (fixed)
	6 ZrO ₂ + Ta ₂ O ₅	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)	10.87 (fixed)
R_p ($\Omega \cdot \text{cm}^2$)	2 ZrO ₂ + Ta ₂ O ₅	5.85×10^2 (3.9)	2.05×10^3 (5.2)	6.35×10^4 (25.2)	1.85×10^4 (12.5)	2.75×10^3 (10.7)
	4 ZrO ₂ + Ta ₂ O ₅	5.32×10^3 (1.2)	1.09×10^4 (5.0)	1.32×10^4 (5.8)	4.04×10^4 (3.9)	5.06×10^3 (4.7)
	6 ZrO ₂ + Ta ₂ O ₅	4.55×10^3 (7.8)	8.74×10^3 (9.9)	2.79×10^3 (23.8)	6.07×10^6 (1.3)	6.05×10^6 (1.3)
CPE-Y0 ($\text{S} \cdot \text{s}^n \cdot \text{cm}^{-2}$)	2 ZrO ₂ + Ta ₂ O ₅	2.9×10^{-9} (24.2)	1.8×10^{-9} (28.4)	1.5×10^{-5} (5.7)	4.5×10^{-6} (10.6)	3.9×10^{-6} (9.9)
	4 ZrO ₂ + Ta ₂ O ₅	2.9×10^{-9} (5.6)	6.5×10^{-7} (12.6)	1.1×10^{-8} (10.2)	1.0×10^{-5} (1.4)	3.1×10^{-3} (4.6)
	6 ZrO ₂ + Ta ₂ O ₅	4.6×10^{-6} (7.5)	7.9×10^{-7} (15.3)	5.25×10^{-8} (20.6)	3.3×10^{-9} (3.4)	2.5×10^{-9} (3.7)
CPE-n	2 ZrO ₂ + Ta ₂ O ₅	1.01 (1.7)	1.00 (2.0)	0.45 (1.3)	0.58 (1.8)	0.77 (1.3)
	4 ZrO ₂ + Ta ₂ O ₅	0.94 (0.7)	0.74 (1.7)	0.74 (1.4)	0.51 (0.3)	0.51 (1.0)
	6 ZrO ₂ + Ta ₂ O ₅	0.65 (1.1)	0.73 (2.0)	0.67 (2.8)	0.90 (0.5)	0.93 (0.5)
W-Y0 ($\text{S} \cdot \text{s}^{1/2} \cdot \text{cm}^{-2}$)	2 ZrO ₂ + Ta ₂ O ₅	8.3×10^{-6} (1.0)	5.3×10^{-6} (2.4)	9.1×10^{-8} (13.4)	2.2×10^{-5} (7.9)	3.5×10^{-3} (3.9)
	4 ZrO ₂ + Ta ₂ O ₅	8.6×10^{-6} (12.1)	4.3×10^{-5} (7.6)	3.3×10^{-5} (6.1)	1.0×10^{-5} (1.7)	1.5×10^{-4} (3.8)
	6 ZrO ₂ + Ta ₂ O ₅	1.9×10^{-5} (1.9)	1.3×10^{-3} (2.9)	2.4×10^{-5} (4.6)	3.3×10^{-6} (17.5)	3.7×10^{-6} (20.1)

Variations in the chemical composition of electrolytes may result in remarkable differences in the phase formation and morphology of films produced by anodic oxidation [48]. Several authors found R_p values for films obtained by PEO which are higher than those corresponding to the metallic substrate (usually CP-Ti) in several orders of magnitude. Therefore, they have suggested equivalent electrical circuit models representing an anodic film consisting of two layers, i.e., one being internal and compact, the other an external and porous layer [48–50]. However, R_s values herein calculated for the PEO films were generally lower than those determined for CP-Ti substrates, and this fact was attributed to the presence of large pores enabling the electrolyte diffusion inside the film, as in Tables 2–5, where values in parentheses represent the percentage error of each circuit element and

$\chi^2 < 0.1$ for all fitted spectra. A decrease in the phase angle accompanied by an increase in capacitance and a longer exposure time of films to the corrosive medium is generally associated with the presence of pores in films [44].

Capacitance values determined by fitting EIS spectra are consistent with those expected for a metal covered with a protective and compact barrier-type film. Therefore, there is no evidence of corrosion on the metal substrate [47]. Zehra et al. (2021) produced highly corrosion-resistant films in a 3.5 wt% NaCl solution after PEO treatment on titanium substrates. R_p values, according to the authors, were higher by two orders of magnitude, compared to those obtained for the metallic substrate which was attributed to the formation of a hybrid film composed of TiO_2 , MoO_2 and SiO_2 [50]. On the other hand, Sowa et al. obtained low impedance values for some films produced by PEO on tantalum substrates. The authors attributed it to pores and lower resistance to diffusion phenomena at low frequencies [49].

3.4. General Considerations

The semiquantitative analysis using EDX demonstrated that the oxide mixture was the experimental condition that most effectively facilitated the incorporation of Zr and Ta. The concentration of these elements in the films increased proportionally with the addition of ZrO_2 and Ta_2O_5 oxides to the PEO electrolytes. Although the underlying mechanism remains unclear, it is assumed that the oxide mixture promotes the formation of TiO_2 , ZrO_2 , and Ta_2O_5 phases on the substrate surface, while also obscuring the presence of metallic Ti in XRD analyses.

According to the contact angle measurements, the 6 $\text{ZrO}_2 + \text{Ta}_2\text{O}_5$ condition exhibited the best wettability, which may be linked to the increased presence of TiO_2 , ZrO_2 , and Ta_2O_5 phases in XRD. These phases likely act as OH receptor sites during intense PEO discharges, a hypothesis consistent with the strong presence of this polar group in the FTIR spectrum.

Furthermore, the mixing of ZrO_2 and Ta_2O_5 oxides into the electrolyte resulted in more heterogeneous and better-sealed surfaces with fewer pores under SEM. This structural modification may have influenced the electrochemical response, leading to remarkably strong outcomes for these experimental conditions, both in terms of potential measurements and R_p magnitude.

Therefore, based on these findings, an effective strategy may be one that enhances heterogeneity and compositional diversity, optimizing the incorporation of various metal oxides in films produced via PEO.

4. Conclusions

Different films were investigated herein with respect to morphology, composition, presence of phases, electrochemical behavior and hydrophilic properties. Although films produced by PEO are quite heterogeneous and have a very irregular topography, in addition to being characterized by the presence of a large number of micrometric pores among the compositions under evaluation, it is noteworthy that the mixture of oxides ($\text{ZrO}_2 + \text{Ta}_2\text{O}_5$) seems to produce a synergistic effect in terms of wettability, which also becomes less susceptible to spontaneous corrosion (due to having presented the highest OCP values), in addition to a distinct behavior in PDS curves and EIS results, due to larger capacitive arcs.

Regarding the electrochemical analysis, a remarkable result is clear in PDS profiles, which was the fact that PEO films were more stable in the chloride medium compared to the native film, even though they are still characterized by the presence of large pores that may constrain their protective properties. To avoid such a problem, a set of sequential PEO tests should be implemented in a further step, aiming to create a multilayer film so that the pores of an underlying layer could be filled with a superposition of a new oxide layer. In

general, the results obtained in this study indicate that the two highest concentrations of $\text{ZrO}_2 + \text{Ta}_2\text{O}_5$ mixture should be further explored in a subsequent step of this work.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/met15060658/s1>, Figure S1: Bode diagrams, impedance module obtained measurements (Exp) and fitted values (Calc) for the control group and other film compositions; Figure S2: Bode diagrams, phase angle—obtained measurements (Exp) and fitted values (Calc) for the control group and other film compositions.

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Abbreviations

The following abbreviations are used in this manuscript:

MDPI	Multidisciplinary Digital Publishing Institute
CP-Ti	Commercially pure titanium
PEO	Plasma electrolytic oxidation
SEM	Scanning electron microscope
EDX	Energy dispersive X-ray spectroscopy
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
MAO	Micro-arc oxidation
SP	São Paulo
MG	Minas Gerais
AZ	Arizona
NJ	New Jersey
USA	United States of America
PGSTAT	Potentiostat/galvanostat
AG	Corporation (Aktiengesellschaft)
OCP	Open circuit potential
EIS	Electrochemical impedance spectroscopy
PDS	Polarization direct scanning
ICDD	International center for diffraction data
E_{corr}	Corrosion potential
R_s	Solution resistance
R_p	Polarization resistance
CPE	Constant phase element
W	Warburg element
AMG	Advanced Metallurgical Group

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4. CONCLUSÕES

O recobrimento óxido multicomponente feito através da oxidação assistida por plasma eletrolítico sobre o substrato de titânio comercialmente puro pode aumentar significativamente a resistência de polarização da superfície deste material e consequentemente sua resistência à corrosão em meios salinos como a água do mar. Os melhores resultados foram obtidos com a mistura 50/50 de óxidos de zircônio com óxidos de tântalo em suspensão no eletrólito na concentração total de 6 g/L. Este mesmo grupo de amostras apresentou o maior aumento de rugosidade superficial e o menor ângulo de contato, tendo atingido o comportamento superhidrofílico. Este conjunto de novas propriedades é especialmente interessante às aplicações biomédicas que requerem uma superfície com maior resistência à corrosão aliada a uma melhor afinidade biológica.

O processo de oxidação assistida por plasma eletrolítico, da forma como foi realizado, produziu uma variação muito grande nas medições da análise eletroquímica e precisa ser mais bem estudado e definido para redução desta distribuição e consequente reprodutividade de resultados.

5. SUGESTÕES DE TRABALHOS FUTUROS

O desenvolvimento desta pesquisa estimula e indica o caminho para continuidade de um trabalho que possa explorar as oportunidades de melhoria identificadas e ampliar as conclusões sobre o emprego do titânio comercialmente puro modificado superficialmente via PEO com as seguintes sugestões:

- Partir da mistura de óxidos de zircônio e óxidos de tântalo na concentração 6 g/L para o eletrólito da nova PEO, mantendo tensão, ciclo de trabalho e duração do tratamento;
- Produção de amostras via PEO com agitação do eletrólito;
- Refinamento e controle de uma granulometria homogênea dos óxidos particulados em suspensão no eletrólito da PEO;

- Medir a condutividade dos eletrólitos antes e depois da PEO para maior controle do processo;
- Repetir as análises FTIR, Rugosidade, Ângulo de Contato, DRX, MEV e EDX;
- Análise do comportamento eletroquímico em solução de fluido corpóreo simulado (SBF);
- Análise das curvas de Tafel separando os ramos anódicos dos catódicos;
- Análise com voltametria cíclica (VC) para caracterização do potencial de pite;
- Análises eletroquímicas separadas sem encadeamento de medições OCP, EIS, Tafel e VC;
- Medir resistência ao desgaste conforme ensaio padrão da Fatec Sorocaba;
- Avaliar secções transversais das amostras obtidas por PEO;

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