

Article

Formation of Single-Phase Ti–Au Intermetallic Coatings via Au Deposition and Annealing-Induced Diffusion: Microstructure and Electrochemical Performance

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Abstract

Ti–Au intermetallic compound (IMC) coatings have attracted considerable interest for biomedical devices and corrosion-protective surfaces owing to their excellent corrosion resistance, hardness, and biocompatibility. Although magnetron sputtering is widely used for high-performance functional coatings, conventional co-sputtering strategies tend to induce undesired secondary-phase formation in Ti–Au coatings, impairing phase stability and coating performance. In this work, Ti–Au IMC coatings were fabricated through a sequential Au-deposition/diffusion-annealing route, and the effects of annealing temperature and holding time on phase formation, phase selection, and microstructural evolution were systematically examined. Diffusion annealing produced a bilayered coating, with Ti₃Au preferentially formed in the inner layer, while the outer layer evolved successively from TiAu₂ to TiAu and then to Ti₃Au as diffusion proceeded. Under sufficient diffusion conditions, the coating was converted into a single-phase Ti₃Au intermetallic layer. Despite the limited durability of Ti–Au IMC coatings under the harsh PEMFC environment, electrochemical measurements in corrosive human body environments confirmed the corrosion resistance of the Ti–Au IMC coatings. The diffusion-mediated route via magnetron sputtering with annealing offers a practical means of tailoring Ti–Au IMC coatings for corrosion-stable biomedical and protective applications.

Keywords: Ti–Au alloy; intermetallic compound coating; annealing parameters; diffusion evolution; intermetallic compounds formation principle



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1. Introduction

Ti–Au alloys have been widely researched due to their high corrosion resistance, biocompatibility and specific strength. Ti–Au alloys can form dense passive oxide films (TiO₂) on their surfaces, providing effective protection to the Ti substrate under various conditions, especially in the presence of H and Cl ions [1,2]. In Ti–Au alloys, Au can function as a cathode, enhancing the corrosion resistance of Ti–Au alloys via selective dissolution [3]. In addition, the spontaneous buildup of an inert and stable oxide layer means that Ti alloys with non-toxic Au possess good biocompatibility [4]. Furthermore, Ti–Au alloys exhibit excellent mechanical properties [1,5]. These exceptional properties make them promising

candidates for corrosion-related applications, such as electrochemical devices and biomedical implants [6–11]. Recently, Ti–Au alloys have been extensively investigated to determine their corrosion resistance and biocompatibility in biomedical products [10]. Related studies are mainly on Ti containing 5–40 wt% Au [8,9,11,12]. By contrast, in the PEM field (PEMFC and PEMWE), Au is frequently used as the pure coating (1 μm) to modify Ti-based metal nitride coatings or in composite Ti/Au coatings [6,13,14], for which Ti–Au alloy coatings have tremendous research potential.

Currently, several methods for preparing Ti–Au alloys have been developed. For instance, through a small-scale resistance spot-welding process, Klimenov et al. [10] fused two titanium plates and a thin layer of gold foil to form a Ti–Au alloy. Fu et al. [15] produced Ti–Au (S)-sintered alloy by powder metallurgy. Takahashi et al. [9] fabricated 5%–40% Ti–Au cast alloys via argon gas-pressure casting. These methods mainly focus on alloy bulks in medical devices. To expand the application scope and reduce costs, Ti–Au alloy coatings have garnered increasing attention for surface-corrosive protection and biomedical applications. Hejazi et al. [16] fabricated Ti–Au gradient alloy layers (750 nm–2 μm) on a TiO_2 surface by sweeping (e.g., increasing or decreasing) the Au deposition rate during the cosputtering process. Lukose et al. [17] produced Ti–Au films (450–685 nm) on the Ti-6Al-4V through the cosputtering process. Klimenov et al. [18] prepared Ti–Au films (200 μm) on Ti-6Al-4V via the electron beam powder bed fusion method. Despite the advantages of the cosputtering process in preparing high-quality Ti–Au alloy coatings with controllable Ti/Au atomic ratios, the uncontrolled formation of Ti–Au intermetallic compounds (IMCs) [19] may negatively impact the film's composition and performance. Actively controlling the Ti–Au combination to form a Ti–Au IMC coating can fundamentally reduce the spontaneous formation of IMCs in Ti–Au alloys, while also enhancing the corrosion resistance and mechanical properties of Ti–Au alloys [11,19,20]. However, relevant research on actively controllable preparation is still limited.

To investigate the controllable preparation of Ti–Au IMC coatings, this study begins with the deposition of a pure and uniform Au coating (less than 1 μm) onto Ti substrate using magnetron sputtering. The subsequent annealing process promotes the interdiffusion of Au coating and Ti substrate, thereby forming a Ti–Au IMC phase with a consistent phase composition and structure. By controlling the annealing parameters, the synthesis of Ti–Au IMC layers can be effectively regulated, enabling the controllable preparation of different Ti–Au IMCs. This article focuses on the interdiffusion principle of Au coatings on a Ti substrate. Through the annealing process, which accelerates and controls the interdiffusion, a Ti–Au alloy coating with a controllable and stable Ti–Au IMC structure can be fabricated, offering a pathway to tailor the properties of coatings for various applications.

In this work, we demonstrate that the deposition of Au onto Ti, followed by thermal annealing, provides a feasible and controllable strategy for fabricating stable IMC-phase coatings. A clear temperature–time-dependent phase evolution rule was established, revealing how heat-treatment conditions regulate Ti–Au interdiffusion and govern IMCs' formation. Furthermore, relevant research has revealed the potential of Ti–Au IMC coatings due to their biocompatibility and hardness, but the research on the corrosion resistance of different IMC coatings is still limited. As Supplementary Materials, the corrosion resistance potential of these IMC coatings was explored in a PEMFC bipolar plate and dental instrument environments.

2. Materials and Methods

2.1. Coating Preparation

Bare Ti foils (Wengheng Metal Materials Trading Company, Hefei, China) were cut into 30 mm $\times$ 30 mm substrates, followed by ultrasonic cleaning with ethanol and ultrapure

water. After natural air-drying, the processed samples were transferred into the coating chamber. The deposition of the Au layer was conducted by a physical vapor deposition (PVD). A high-purity Au (99.99%) target (Zhongnuo New Materials, Shanghai, China) with a diameter of 50 mm was used. Based on the depositing rate (Figure S2), a target Au layer thickness of 600–800 nm was designed. This thickness range not only satisfies the cost requirements for the PEMFC and Dental applications [11,14], but also enables the effective regulation of elemental diffusion extent and the conduction of the structural analysis of the coating through SEM cross-section. A pure Au coating (687 nm shown in Figure S4) was prepared through magnetron sputtering with the direct current power of 30 W and a sputtering time of 1 h.

The Ti samples with pure Au coating were then subjected to annealing in an argon-protected annealing environment at 600 °C, 700 °C and 800 °C, respectively. The heating rate was 15 °C/min, followed by different holding times (1 h, 3 h, 5 h) to produce Ti–Au coatings with various IMCs. The schematic of the Ti–Au coating preparation is shown in Figure 1. Detailed experimental parameters are provided in Table 1, and these Ti–Au-coated samples were labeled according to the annealing parameters, as listed in Table 2.

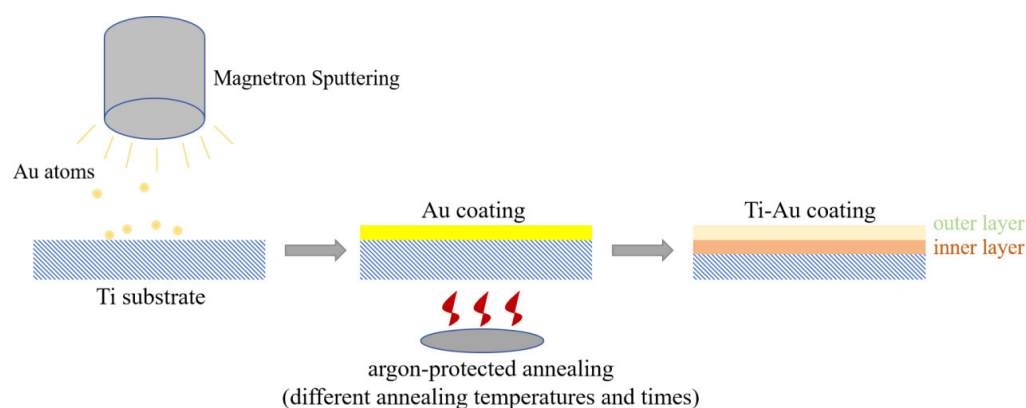


Figure 1. Schematic diagram of Ti–Au coating preparation.

Table 1. Detailed experimental parameters of Ti–Au coating preparation.

Progress	Parameter	
Preparation	Pressure	1.5 Pa
	Argon flow rate	60 Sccm
	Target-substrate distance	130 mm
	Rotation rate	5 rpm
	Direct current pulse power	30 W
	Deposition time	60 min
	Deposition temperature	25 °C
Annealing	Target temperature	600 °C, 700 °C, 800 °C
	Heating rate	15 °C/min
	Holding time	1 h, 3 h, 5 h
	atmosphere environment	Argon protection

Table 2. The exhibition of sample names based on annealing parameters' names.

Holding Time Annealing Temperature	1 h	3 h	5 h
600 °C	S _{600,1}	S _{600,3}	S _{600,5}
700 °C	S _{700,1}	S _{700,3}	S _{700,5}
800 °C	S _{800,1}	S _{800,3}	S _{800,5}

2.2. Microstructure and Composition Characterization

The crystalline structure of the coating samples was characterized using an X-ray diffraction (XRD) system, model number Miniflex 600, with a working voltage of 40 kV, employing Cu K α radiation (Rigaku, Takatsukishi, Japan). The measurements were conducted in continuous scanning mode within a 10° to 90° range, with a scan rate of 10° min^{−1}. The cross-sectional morphology, as well as its elemental distribution, was observed by a JSM-7800F cold field emission scanning electron microscope (SEM) with an energy dispersive X-ray spectroscopy (EDS) (JEOL Ltd., Akishima, Japan). The chemical state analysis of the coatings was conducted using a Thermo Scientific K-Alpha X-ray photoelectron spectroscopy (XPS) analyzer (Thermo Fisher, Waltham, MA, USA). The X-ray source employed was an Al K α micro-focus monochromator with a variable spot size. The energy range of the ion gun was between 100 and 4000 eV. The obtained spectra were analyzed using CasaXPS software 2.5, with calibration using the C 1 s peak at 284.8 eV as the standard charge calibration reference.

2.3. Electrochemical Measurements

2.3.1. PEMFC Environment

The electrolyte used in the experiment was a dilute sulfuric acid (H₂SO₄) solution with a pH of 3, maintained at 80 °C, and supplemented with 2 ppm of sodium fluoride (NaF), with the effective exposed area of each test sample being 2 cm². Electrochemical tests were carried out using an Ametek VersaSTAT 3F electrochemical workstation (Ametek, Berwyn, PA, USA), employing a three-electrode system. The counter electrode (CE) was a platinum (Pt) sheet, while the reference electrode (RE) was an Ag/AgCl electrode with a saturated KCl-filled salt bridge. The sample under test served as the working electrode and was placed in a sample holder with a circular aperture of 2 cm² in area. To eliminate any gaps between the sample and the holder, and to prevent electrolyte leakage, a soft silicone O-ring gasket was installed.

Before proceeding with electrochemical impedance spectroscopy (EIS) or potentiodynamic polarization (PDP), the sample was held at open circuit potential (OCP) for 40 min to ensure stability. After achieving a stable OCP, EIS tests were performed with an alternating current (AC) amplitude of 10 mV, covering a frequency range from 10⁵ Hz to 10^{−2} Hz. The obtained EIS data were subsequently fitted using ZSimpWin software 3.6. For the PDP measurements, the potential was scanned from −0.35 V (relative to OCP) to 2.2 V (relative to Ag/AgCl) at a scan rate of 0.167 mV s^{−1}. The corrosion data, including corrosion potential (E_{corr}), corrosion current density (I_{corr}), pitting potential (E_{pitting}), and operation current density ($I_{0.6 \text{ V}}$), were obtained from the PDP curves. All electrochemical tests were repeated at least three times to guarantee data repeatability and reliability.

2.3.2. Human Body Environment

The electrolyte for the human body environment test was a 0.9 wt% NaCl solution at 37 °C, with the effective exposed area of the electrochemical test sample being 2 cm². Electrochemical tests were again performed using an Ametek VersaSTAT 3F electrochemical workstation (Ametek, Berwyn, PA, USA), with a three-electrode system. The CE was a Pt sheet, and the RE was an Ag/AgCl electrode with a saturated KCl-filled salt bridge. The sample to be tested served as the working electrode and was placed in a sample holder with a circular aperture of 2 cm². A soft silicone O-ring gasket was used to eliminate any gaps between the sample and the holder and prevent electrolyte leakage.

The sample was held at OCP for 40 min before both PDP and EIS to ensure stability. EIS tests were carried out with an AC amplitude of 10 mV, covering a frequency range from 10⁵ Hz to 10^{−2} Hz. The EIS data were fitted using ZSimpWin software. For the PDP tests,

the potential was scanned from -0.5 V (relative to OCP) to 1.5 V (relative to Ag/AgCl) at a scan rate of 0.167 mV s $^{-1}$. The corrosion data, including corrosion potential (E_{corr}), corrosion current density (I_{corr}), passivation current density (I_{pass}), and pitting potential (E_{pitting}), were obtained from the PDP curves. All electrochemical tests were repeated at least three times to guarantee data repeatability and reliability.

3. Results

3.1. Coating Characterization

3.1.1. The Composition of Ti–Au Coatings

Figure 2 displays the XRD patterns of $S_{600,1}$, $S_{600,3}$, $S_{600,5}$, $S_{700,1}$, $S_{700,3}$, $S_{700,5}$, $S_{800,1}$, $S_{800,3}$ and $S_{800,5}$, while Figure S1 presents the XRD spectra of bare Ti and pure Au-coated Ti for comparison. Since the coating thickness falls within the effective detection depth range of XRD ($1\text{--}10$ μm), all coated Ti samples exhibit weak Ti diffraction peaks originating from the substrate. Figure 2a shows the calibrated XRD spectra of $S_{600,1}$, $S_{600,3}$ and $S_{600,5}$. After annealing at 600 $^{\circ}\text{C}$, all these samples display prominent diffraction peaks corresponding to pure Au. Compared to Figure S1, the retention of Au diffraction peaks can be attributed to the fact that these annealed samples maintained most of the pure Au structure from the PVD Au coatings. In addition, these samples exhibit the TiO_x (primarily corresponding to TiO_2) and Ti_2Au peaks. As the holding time increased, the intensity of TiO_x peaks increased and characteristic Ti_3Au peaks gradually emerged. Figure 2b shows the XRD patterns of $S_{700,1}$, $S_{700,3}$ and $S_{700,5}$. After annealing at 700 $^{\circ}\text{C}$, distinct differences can be observed compared with Figure 2a. Au atoms in the coating no longer existed in the pure metallic Au state, but primarily reacted with Ti atoms to form Ti_3Au with less TiAu . With increasing holding time, the intensity of the Ti_3Au peaks gradually increased, while the intensities of the TiAu and TiO_x peaks decreased. Figure 2c exhibits the XRD patterns of $S_{800,1}$, $S_{800,3}$ and $S_{800,5}$. After annealing at 800 $^{\circ}\text{C}$, all diffraction peaks related to Au-containing phases correspond exclusively to Ti_3Au , with no occurrence of TiAu_2 or TiAu peaks compared with the spectra in Figure 2a,b. With increasing holding time, the TiO_x peaks were no longer detected, and the Ti_3Au peaks became more pronounced. Notably, Ti_3Au peaks are detected at all three annealing temperatures, probably due to Ti_3Au being the most stable phase in the Ti–Au IMC system [13]. Furthermore, except for $S_{800,3}$ and $S_{800,5}$, all annealed coated Ti samples exhibit the TiO_x peaks. This phenomenon can be attributed to the presence of trace amounts of oxygen, which could not be removed during the argon-protective process, as well as the high sensitivity of Ti to oxygen. The absence of oxide peaks in $S_{800,3}$ and $S_{800,5}$ can be tentatively ascribed to the formation of oxygen vacancies via the partial reduction of TiO_2 . Titanium oxide undergoes partial decomposition during argon-protected annealing at 800 $^{\circ}\text{C}$, generating oxygen vacancies in the lattice and decreasing the content of crystalline TiO_2 . Subsequently, some of the oxygen vacancies may be occupied by Au atoms, eventually forming Ti_3Au , which is more stable at high temperatures. The variation in the relative fraction of Ti^{3+} species detected by XPS offers indirect supporting evidence for this hypothesis [21,22]. It is worth noting that the above interpretation is a reasonable inference based on ex situ characterization results, and further in situ investigations are required to confirm the detailed evolution process.

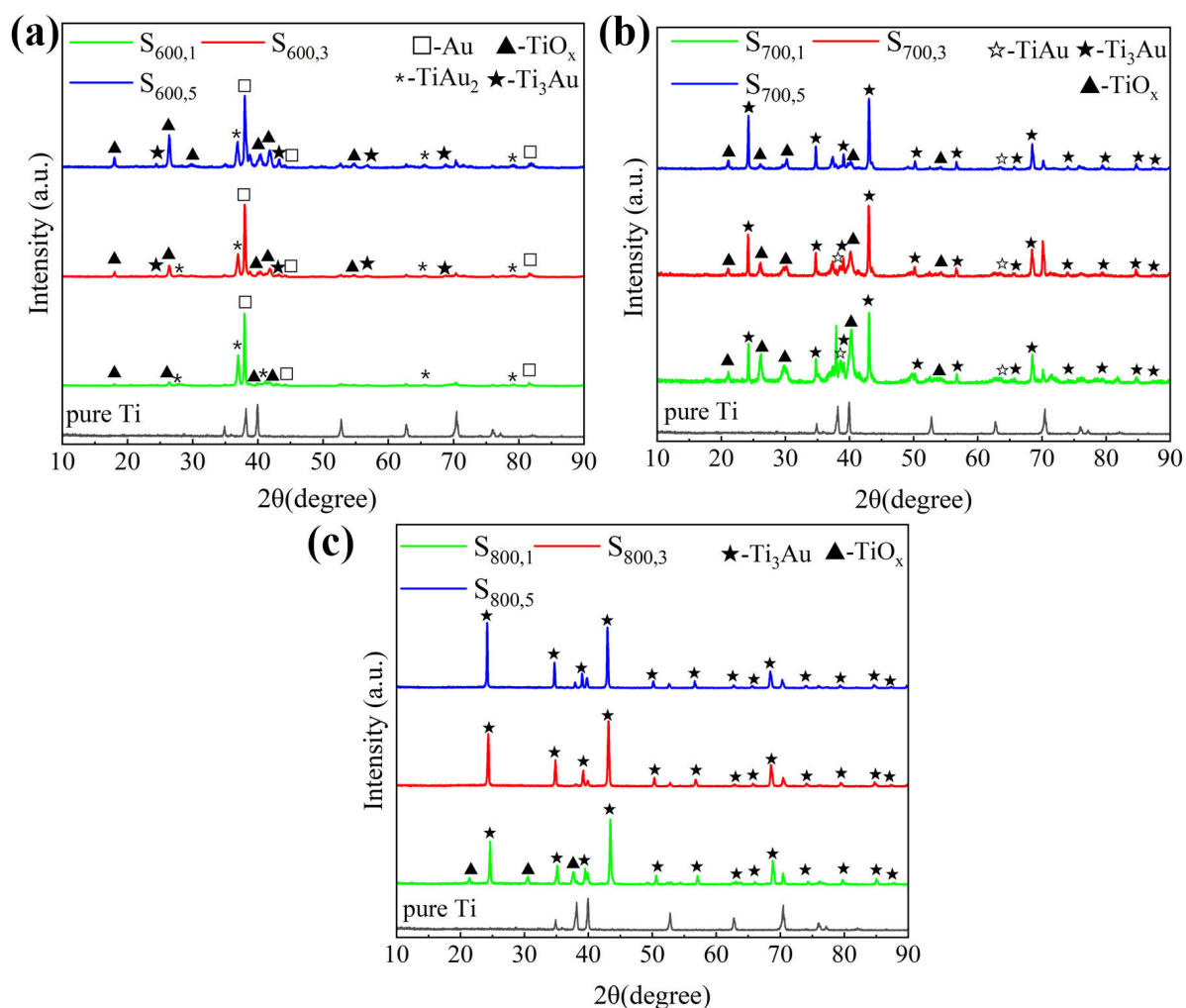


Figure 2. XRD patterns of the bare and Ti–Au-coated Ti samples in different annealing parameters: (a) 600 °C, (b) 700 °C and (c) 800 °C.

3.1.2. The Phase-Structure of Ti–Au Coatings Cross-Section

Figure 3 shows the cross-sectional SEM images and EDS spectra of the Ti–Au-coated samples after annealing with different annealing parameters. Figure 3a–c display the SEM and EDS results of the coating section of $S_{600,1}$, $S_{600,3}$ and $S_{600,5}$. After annealing at 600 °C, Ti atoms successfully diffused into the entire Au coating, as shown in the EDS spectra of the Ti element. Meanwhile, two layers in the coating could be clearly observed in these samples. The outer layers of these three samples were thick, while the inner layers were relatively thin. As the holding time increased, these thin inner layers thickened in the direction of the substrates. Figure 3d–f exhibit the SEM and EDS results of $S_{700,1}$, $S_{700,3}$ and $S_{700,5}$. Compared with Figure 3a–c, the layering structure could be clearly observed without further magnification after annealing at 700 °C. When annealing for 1 h and 3 h, a dual-layer structure was still observed, with the outer layer being thinner and the inner layer thicker as holding time increased. Up until 5 h of annealing, the inner layer entirely covered the coating. Figure 3g–i present the SEM and EDS results of $S_{800,1}$, $S_{800,3}$ and $S_{800,5}$. After annealing at 800 °C for 1 h, the coating exhibited primarily one layer, with a few regions that differed from the layer contrast. With increasing holding time, these regions disappeared and an entire uniform layer formed.

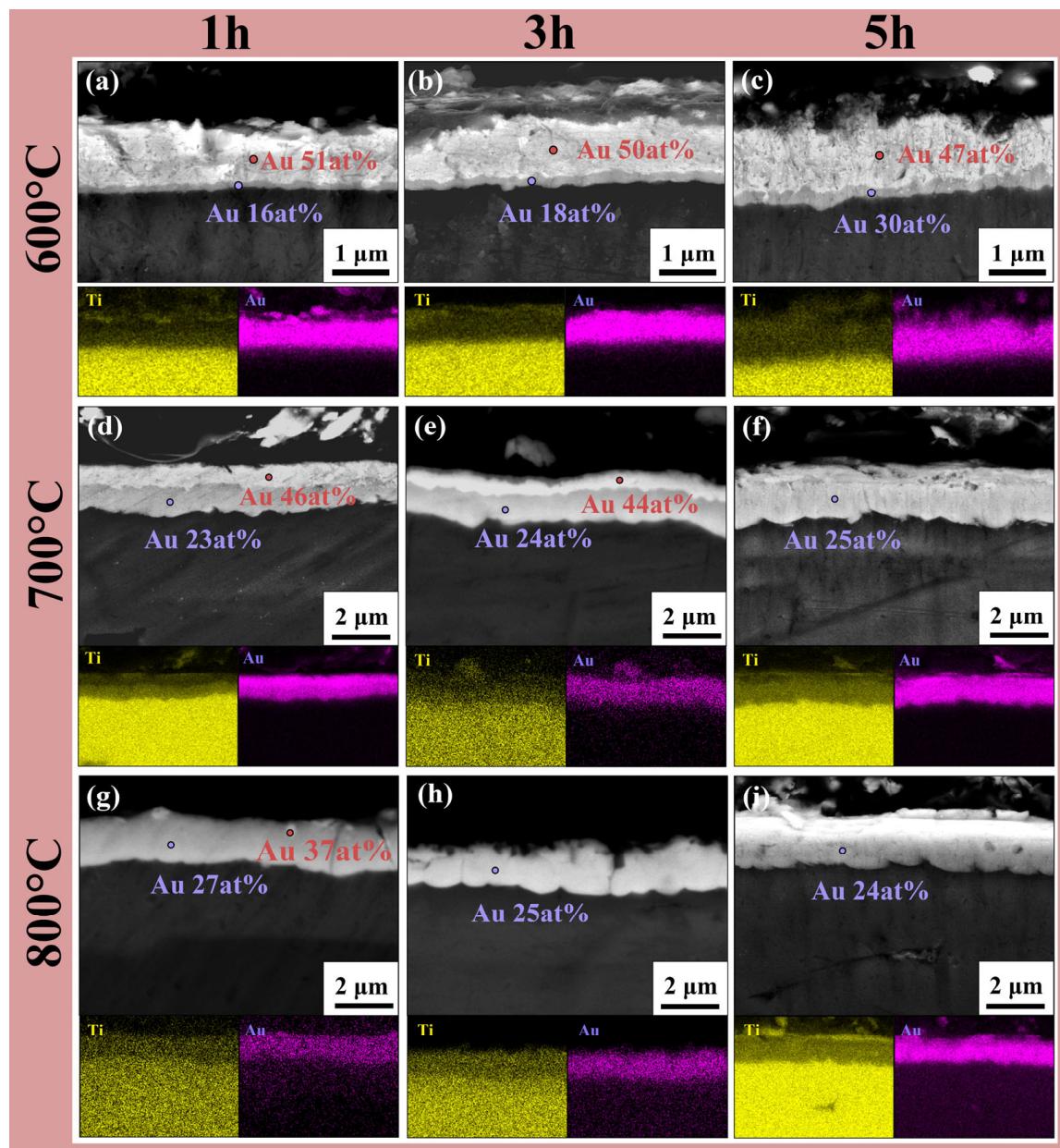


Figure 3. The cross-sectional SEM images and EDS spectra of the Ti–Au-coated samples under different annealing parameters: (a) $S_{600,1}$, (b) $S_{600,3}$, (c) $S_{600,5}$, (d) $S_{700,1}$, (e) $S_{700,3}$, (f) $S_{700,5}$, (g) $S_{800,1}$, (h) $S_{800,3}$ and (i) $S_{800,5}$.

Moreover, point scanning EDS analysis was performed on the cross-sectional SEM of $S_{600,1}$, $S_{600,3}$, $S_{600,5}$, $S_{700,1}$, $S_{700,3}$, $S_{700,5}$, $S_{800,1}$, $S_{800,3}$ and $S_{800,5}$. After annealing at 600 °C, the Au relative atomic contents (normalized to the total content of Ti and Au) in outer layers of $S_{600,1}$, $S_{600,3}$ and $S_{600,5}$ were 51%, 50% and 47%, respectively, while those of inner layers were 16%, 18% and 30%, respectively. With increasing holding time, the Au relative atomic contents of outer layers decreased, indicating that Ti diffused towards the outer layer. Meanwhile, the Au relative atomic contents of inner layers increased as the holding time increased, which can be attributed to the diffusion of Au towards the substrate and its combination with Ti to form the inner layer. This principle also explains the thickening of the inner layer mentioned above. After annealing at 700 °C, the Au relative atomic contents of outer layers in $S_{700,1}$ and $S_{700,3}$ were 46% and 44%, respectively, while those of inner layers were 23% and 24%, respectively. After annealing for 5 h, the Au relative atomic

content of the coating was 25%. The results suggest that not only the variation trends of Au relative atomic content in outer layers and inner layers, but also the Au relative atomic content in outer layers, are similar to those of the samples annealed at 600 °C. After annealing at 800 °C for 1 h, the regions that differed from the layer contrast exhibited a Au relative atomic content of 37%, while the Au relative atomic content of the coating layer was 27%. As the holding time increased, the Au relative atomic contents of the layers in $S_{800,3}$ and $S_{800,5}$ were 25% and 24%, respectively. Notably, compared to the variation trends in 600 °C and 700 °C annealing, the Au relative atomic contents of the layer in 800 °C annealing decreased as the holding time increased. This phenomenon can be attributed to the persistent inward diffusion of Ti atoms, which gradually dilute the Au concentration within the coating.

Based on the findings above, three specific Ti–Au-coated Ti samples were selected for further testing: $S_{600,3}$, $S_{700,3}$ and $S_{800,3}$. These samples were chosen because they exhibit the variation of Ti–Au IMCs in XRD and distinctly different layering results of various coatings in SEM. Such obvious structural and phase differences are straightforward and distinct for subsequent surface XPS and corrosion resistance measurements.

3.1.3. The Surface Characterization of Ti–Au Coatings

Figure 4 presents the XPS spectra for the surface analysis of $S_{600,3}$, $S_{700,3}$, and $S_{800,3}$, with detailed peak deconvolution summarized in Table 3. Figure 4a shows the Ti 2p spectrum of the three samples. According to the spin-orbit splitting (SOS) of the 2p spectrum, these peaks are categorized into Ti 2p_{3/2} in the low-binding-energy region and Ti 2p_{1/2} in the high-binding-energy region [23]. Combining the references [24–27] and the XRD results, these spectrum peaks were further deconvoluted into Ti–O peaks and Ti–Au peaks. The Ti–O state was attributed to the trace amounts of oxygen during the annealing process, while the Ti–Au state was a demonstration of the Ti–Au combination. For $S_{600,3}$, the spectrum is dominated by Ti–O peaks, which can be assigned to the Ti³⁺ and Ti⁴⁺ peaks by fitting. Ti⁴⁺ represents the TiO₂ and Ti³⁺ indicates the oxygen vacancies created by argon high-temperature annealing [21,22]. Additionally, the $S_{600,3}$ showed a weak Ti–Au peak in the lower-binding-energy region compared to its Ti–O peak. For $S_{700,3}$, a higher Ti–Au peak appeared compared to $S_{600,3}$, exhibiting an obviously asymmetric shape [24,28]. Therefore, two symmetric fitting peaks were applied to fit this Ti–Au peak. Notably, the Ti–Au peak shifted significantly to the right by 1.2 eV compared to $S_{600,3}$ (the 2p_{3/2} peak at 455.5 eV). For the $S_{800,3}$, the Ti–Au peak further shifted to the right by 1.1 eV compared to $S_{700,3}$ (the 2p_{3/2} peak at 454.7 eV). Meanwhile, such continuous peak displacement leads to spectral superposition, enabling $S_{800,3}$ to form an atypical odd-numbered peak profile.

Table 3. The specific peak position of XPS of the coatings annealed for 3 h at 600 °C, 700 °C and 800 °C.

Sample	$S_{600,3}$		$S_{700,3}$		$S_{800,3}$	
Binding Energy /eV	Ti 2p _{3/2}	Ti 2p _{1/2}	Ti 2p _{3/2}	Ti 2p _{1/2}	Ti 2p _{3/2}	Ti 2p _{1/2}
Ti ³⁺	457.63	462.01	457.40	462.85	457.61	462.10
Ti ⁴⁺	458.66	463.38	458.36	463.91	458.58	464.31
Ti–Au	455.08	460.24	454.58	460.41	453.55	459.65
	/	/	455.57	461.31	454.55	460.28
	Au 4f _{7/2}	Au 4f _{5/2}	Au 4f _{7/2}	Au 4f _{5/2}	Au 4f _{7/2}	Au 4f _{5/2}
Au	83.86	87.54	/	/	/	/
Ti–Au	84.17	87.81	84.22	87.88	84.36	88.04

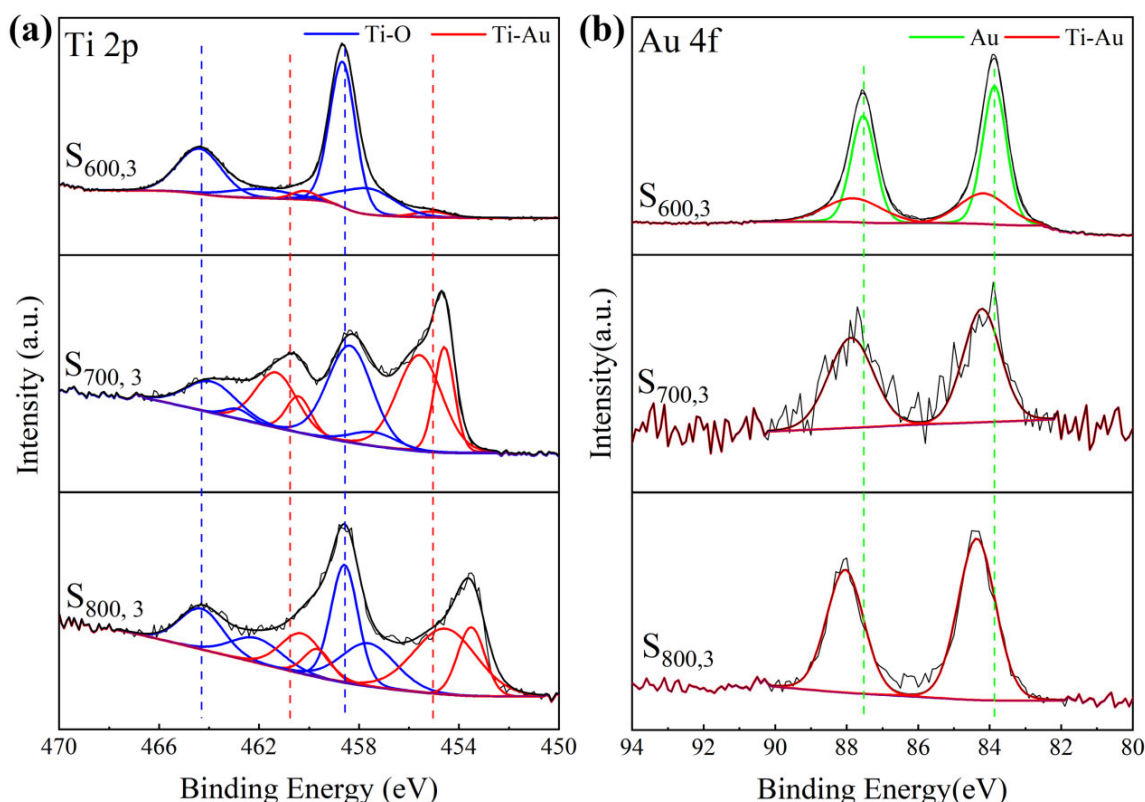


Figure 4. The XPS spectrum of the coatings annealed for 3 h at 600 °C, 700 °C, 800 °C: (a) Ti 2p and (b) Au 4f.

Figure 4b presents the Au 4f spectrum of $S_{600,3}$, $S_{700,3}$, and $S_{800,3}$. Based on the SOS of the 4f spectrum, these peaks are categorized into Au 4p_{7/2} in the low-binding-energy region and Au 4p_{5/2} in the high-binding-energy region. Combining the references [24] and the SEM results, these spectrum peaks were categorized into Au peaks and Ti–Au peaks. Based on the peak fitting results, $S_{600,3}$ exhibits the pure Au and Ti–Au peaks, with pure Au occupying a larger peak area proportion. By contrast, $S_{700,3}$ only exhibits the Ti–Au peak without a pure Au peak, and the Ti–Au peak shifted to the left compared to $S_{600,3}$. For $S_{800,3}$ the Ti–Au peak further shifted to the left.

As reported by A. Bzowski et al. [24], these continuous displacements in both Ti 2p and Au 4f can be attributed to the decrease in Au content in the Ti–Au structure as the annealing temperature increases. Since Au is more electronegative than Ti, charge transfer from Ti to Au is anticipated. Therefore, the lower the relative content of Au, the less the charge is lost in Ti, which promotes a negative binding energy shift of the core levels in Ti 2p peaks. By contrast, it promotes the Au core levels to shift toward a positive binding energy in the Au 4f spectrum. Therefore, the Au content of the Ti–Au phase followed the sequence $S_{600,3} > S_{700,3} > S_{800,3}$. Combined with the EDS point scan results in Figure 3a–f, it is demonstrated that similar overall Au atomic contents do not guarantee identical IMCs across coating surfaces, which is analyzed in the discussion section.

3.2. The Corrosion Behavior of Ti–Au Coatings in PEMFC Environment

Figure 5a illustrates the PDP curves of $S_{600,3}$, $S_{700,3}$ and $S_{800,3}$ measured in a simulated PEMFC environment, with the fitted electrochemical parameters listed in Table 4. A similar current density response was displayed in the selected Ti–Au-coated Ti samples during polarization testing. Notably, the PDP curves for these samples were primarily divided into three distinct regions with increasing potential [28–30], as follows: (i) The

active dissolution region, where the current density increases due to the dissolution of the coating surface. When reaching a critical passivation potential, a passivation film starts to form on the surface, reducing the current density. (ii) The stable passivation region, where the passivation film progressively covers the surface, decreasing the metal dissolution rate. During this stage, the current density remains almost constant with the increasing potentials, and this current density is referred to as the passivation current density. (iii) The pitting region, where samples with weaker pitting resistance exhibit a sharp increase in current density at a specific threshold potential, indicating the occurrence of pitting corrosion.

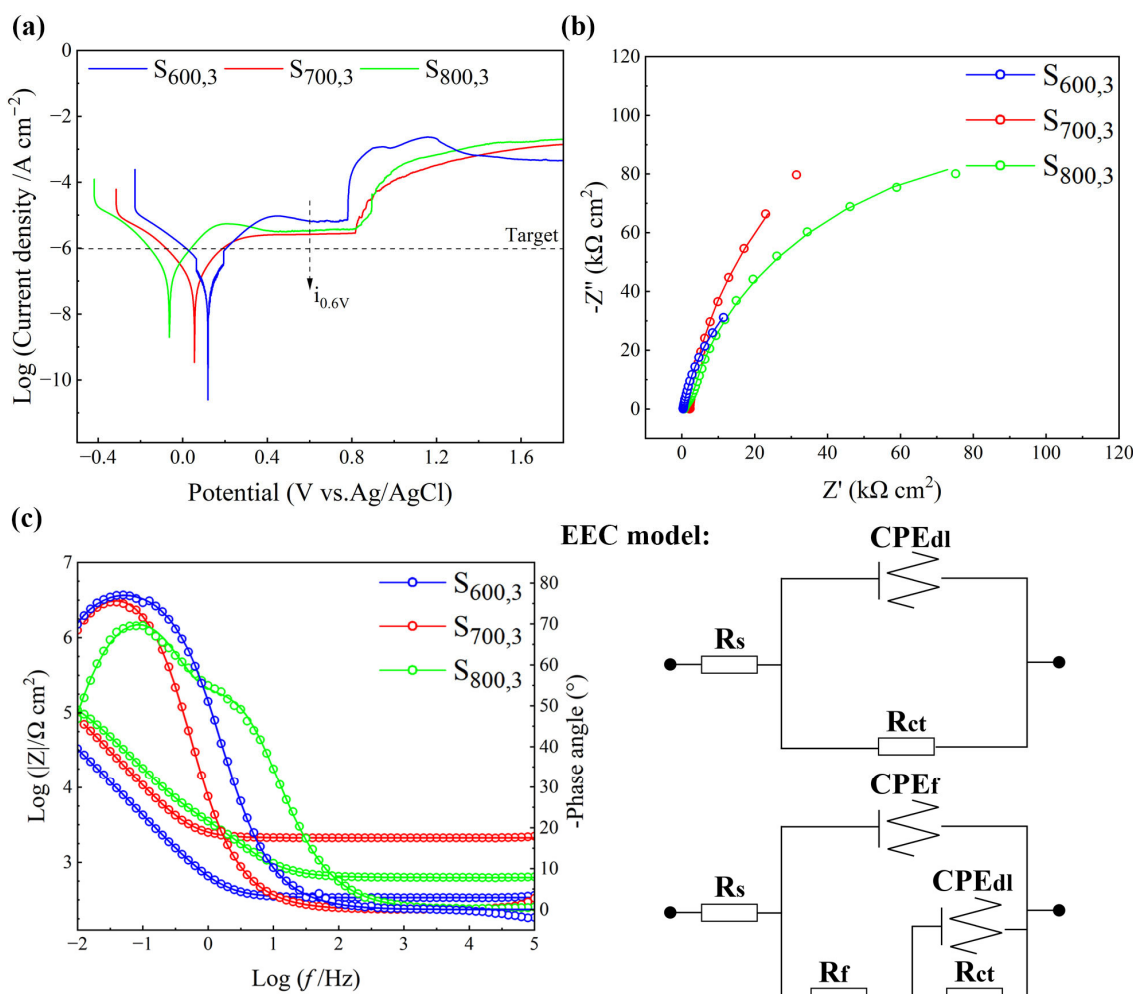


Figure 5. (a) The potentiodynamic polarization curves of the coatings annealed for 3 h at 600 °C, 700 °C and 800 °C in a simulated PEMFC anodic environment. The EIS spectrum of these samples: (b) Nyquist plots. (c) Bode plots.

Table 4. The Potentiodynamic polarization curves data of the coatings annealed for 3 h at 600 °C, 700 °C and 800 °C in a simulated PEMFC anodic environment.

Sample	S _{600,3}	S _{700,3}	S _{800,3}
E_{corr} (mV)	119.0	55.51	−63.18
I_{corr} ($\mu\text{A cm}^{-2}$)	0.3270	0.0984	0.2022
E_{pitting} (mV)	779.9	816.5	803.9
$I_{0.6\text{ V}}$ ($\mu\text{A cm}^{-2}$)	6.516	2.617	3.321

The E_{corr} of $S_{600,3}$, $S_{700,3}$ and $S_{800,3}$ were 119.0, 55.51, -63.18 mV, respectively, demonstrating that $S_{600,3}$ and $S_{700,3}$ exhibited good thermodynamic stability against corrosion. Moreover, $S_{600,3}$ exhibited the highest I_{corr} of $0.327 \mu\text{A cm}^{-2}$, compared to the I_{corr} of $S_{700,3}$ and $S_{800,3}$ at 0.0984 and $0.2022 \mu\text{A cm}^{-2}$, respectively. A lower I_{corr} corresponds to the formation of a denser passive film and superior anti-corrosion performance in corrosive environments. Considering that the operational potential of PEMFC is 0.6 V, the $S_{600,3}$ also exhibits the highest $I_{0.6 \text{ V}}$ of $6.516 \mu\text{A cm}^{-2}$, compared to the $I_{0.6 \text{ V}}$ of $S_{700,3}$ and $S_{800,3}$ at 2.617 and $3.321 \mu\text{A cm}^{-2}$, respectively.

Additionally, the E_{pitting} of the three at approximately 0.8 V is considered to represent the pitting potential. As summarized in Table 4, the E_{pitting} follows the order: $S_{700,3} > S_{800,3} > S_{600,3}$. These results suggest that all three samples underwent pitting corrosion in high potentials, leading to a rise in current density. $S_{600,3}$ exhibited the weakest pitting resistance among the three samples, and its pitting current density increased rapidly compared to $S_{700,3}$ and $S_{800,3}$.

Figure 5 illustrates the EIS for $S_{600,3}$, $S_{700,3}$ and $S_{800,3}$ obtained in a simulated PEMFC anodic environment under OCP conditions with fitting results. Figure 5b,c display the Nyquist plots and Bode plots for $S_{600,3}$, $S_{700,3}$, and $S_{800,3}$, respectively. The Nyquist plots of $S_{600,3}$, $S_{700,3}$, and $S_{800,3}$ in Figure 5b were all characterized as single capacitive semi-circles that were suppressed over time. A larger diameter of the semicircular arcs in the Nyquist plot indicates a lower corrosion rate of the coating. The $S_{700,3}$ exhibited the largest arc radius, which suggests that it possessed the best electrochemical impedance performance compared to $S_{600,3}$ and $S_{800,3}$. In the Bode plot (phase degree vs. log frequency), for $S_{600,3}$, a narrow peak spanning from 10 Hz to 10^{-2} Hz was observed, indicating a capacitive element in its equivalent circuit (EEC) model. For $S_{700,3}$, its Bode plot shows that the capacitive peak of $S_{700,3}$ was narrower than that of $S_{600,3}$, indicating that it also adopted a capacitive element in its EEC model. The Bode plot of $S_{800,3}$ shows that two narrow peaks spanning from 10^2 Hz to 10^{-2} Hz were observed, indicating two capacitive elements in its EEC model.

The fitting for EIS of $S_{600,3}$ and $S_{700,3}$ utilized the EEC model with one time-constant: R_s (CPE_{dl} R_{ct}), while for $S_{800,3}$, the EEC model R_s (CPE_f (R_f (CPE_{dl} R_{ct}))) was used. The $S_{800,3}$ used a different equivalent circuit compared to $S_{600,3}$ and $S_{700,3}$, due to the presence of two capacitive peaks of $S_{800,3}$ in the Bode plots and one capacitive peak of $S_{600,3}$ or $S_{700,3}$ by contrast. Therefore, a constant phase element (CPE_f) and a resistor (R_f) were added in the fitting equivalent circuit for $S_{800,3}$. This EEC model indicates that the coating of $S_{800,3}$ was unable to protect its substrate from corrosion. The fitting results are detailed in Table 5. R_s represents the solution resistance, R_f and CPE_{dl} are the coating resistance and double-layer capacitance, respectively; R_{ct} denotes the charge transfer resistance at the electrolyte/material interface, CPE_f represents the coating capacitance, and n (defined as the CPE power) is an adjustable parameter that always lies between 0.5 and 1 [29,31]. Notably, the R_{ct} values shown in Table 5 are related to the diffusion resistance of corrosive ions, and indicate the ability to prevent the dissolution of metal ions. Meanwhile, due to the significant numerical disparity between R_{ct} and R_s or R_f (approximately three orders of magnitude), the R_{ct} values can be considered decisive factors in determining the corrosion resistance. The R_{ct} values follow the order $S_{700,3} > S_{800,3} > S_{600,3}$, indicating that the $S_{700,3}$ exhibited the best corrosion resistance among the three.

Table 5. The EIS data of the coatings annealed for 3 h at 600 °C, 700 °C and 800 °C in PEMFC.

Sample	R_s (Ω cm ²)	CPE_f ($10^{-5} \Omega^{-1} \text{cm}^{-2} \text{s}^n$)	n_1	R_f (Ω cm ²)	CPE_{dl} ($10^{-5} \Omega^{-1} \text{cm}^{-2} \text{s}^n$)	n_2	R_{ct} ($10^4 \Omega$ cm ²)
S _{600,3}	333.9	/	/	/	36.19	0.9118	16.63
S _{700,3}	2118	/	/	/	15.01	0.9442	31.03
S _{800,3}	627.7	4.19	0.8513	9421	2.826	0.9683	20.19

3.3. The Corrosion Behavior of Ti–Au Coatings in a Human Body Environment

Figure 6 presents the PDP curves of S_{600,3}, S_{700,3} and S_{800,3} obtained in a simulated human body environment (0.9 wt% NaCl, RT), with the PDP curve data summarized in Table 6. The PDP curves can also be divided into three distinct regions with increasing potentials, similar to the PDP curves in PEMFC. Unlike the electrochemical response in the PEMFC environment, a different current density response was displayed in the selected Ti–Au-coated Ti samples for the human body environment. The S_{800,3} exhibited a relatively narrow region between the E_{corr} and critical passivation potential compared to other samples. This difference indicates that the coatings of S_{800,3} were more sensitive to the potential alteration, promoting the release the Ti atoms to carry out the passivation reaction.

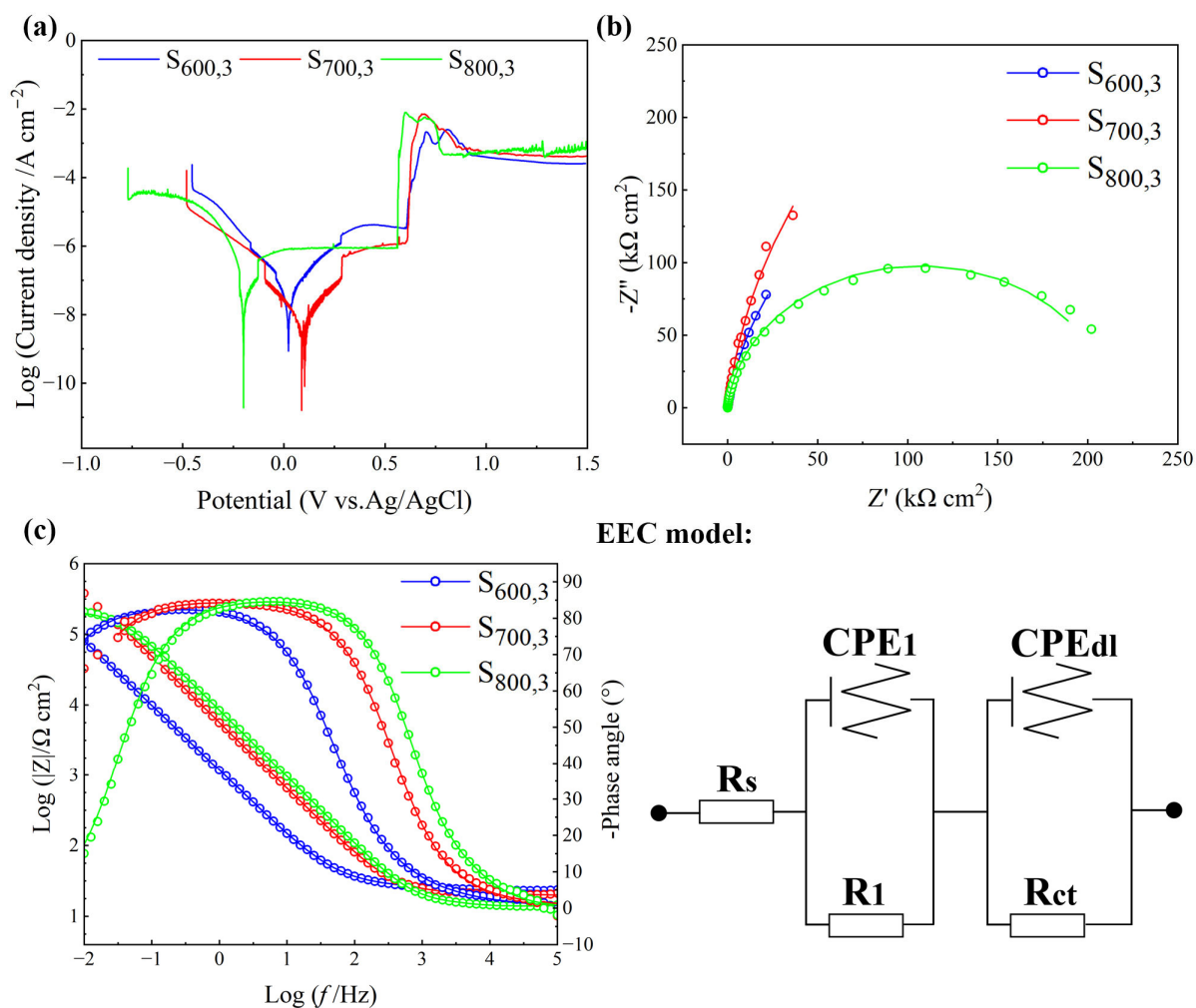


Figure 6. (a) The potentiodynamic polarization curves of the coatings annealed for 3 h at 600 °C, 700 °C and 800 °C in a simulated human body environment. The EIS spectra of these samples: (b) Nyquist plots. (c) Bode plots.

Table 6. The potentiodynamic polarization curve data of the coatings annealed for 3 h at 600 °C, 700 °C and 800 °C in a simulated human body environment.

Sample	S _{600,3}	S _{700,3}	S _{800,3}
E_{corr} (mV)	23.00	88.03	−199.4
I_{corr} ($\mu\text{A cm}^{-2}$)	0.0851	0.0089	0.0356
$E_{pitting}$ (mV)	598.4	607.3	561.0
I_{pass} ($\mu\text{A cm}^{-2}$)	3.309	0.529	0.861

The E_{corr} values of S_{600,3}, S_{700,3} and S_{800,3} were 23.00, 88.03 and −199.4 mV, respectively, demonstrating that S_{700,3} exhibited excellent thermodynamic stability against corrosion among the three. In addition, S_{600,3} exhibited the highest I_{corr} of 0.0851 $\mu\text{A cm}^{-2}$ compared to the I_{corr} of S_{700,3} and S_{800,3} at 0.0089 and 0.0356 $\mu\text{A cm}^{-2}$, respectively. Furthermore, the $E_{pitting}$ of the three at approximately 0.6 V is considered to represent the pitting potential, and the $E_{pitting}$ follows the order (Table 6) S_{700,3} > S_{800,3} > S_{600,3}. These results suggest that the three samples underwent pitting corrosion in the human body environment, resulting in a sharp rise in current density, and the S_{700,3} exhibited the best pitting resistance.

Figure 6 presents the EIS results for S_{600,3}, S_{700,3}, and S_{800,3} obtained in a simulated human body environment under OCP conditions with fitting results. Figure 6b,c display the Nyquist and Bode plots for these samples, respectively. From the Nyquist plot, the S_{700,3} in Figure 6b exhibits the largest capacitive arc radius, suggesting that the S_{700,3} coating possessed the best electrochemical impedance performance compared to S_{600,3} and S_{800,3}. In the Bode plot, S_{600,3} exhibited a broadened peak spanning from 10³ Hz to 10^{−2} Hz, indicating at least two capacitive elements in its equivalent circuit model. For S_{700,3}, compared to S_{600,3}, the capacitive peak was similar but broader than that of S_{600,3}, indicating its equivalent circuit model was the same as that of S_{600,3}. For S_{800,3}, a capacitive peak spanning from 10^{−1} Hz to 10⁴ Hz was observed. Similar to S_{600,3} and S_{700,3}, there were at least two capacitive elements in its equivalent circuit model. Notably, the spanning region of S_{800,3} shifted to the high-frequency region, with the phase angle frequency ranges in the order of S_{700,3} > S_{600,3} > S_{800,3}.

The fitting for EIS of S_{600,3}, S_{700,3}, and S_{800,3} utilized the equivalent circuit model R_s ($CPE_1 R_1$) ($CRE_{dl} R_{ct}$), with the fitting results detailed in Table 7. The fitting CPE_1 and R_1 are assigned to the interfacial defects. These samples used the equivalent circuit with two time constants, as the widths of the capacitive peaks of these samples in Bode plots were broad enough. The broad capacitive peak was generally seen because of the overlap of at least two capacitive peaks. Notably, the S_{700,3} exhibited the highest R_{ct} of 85.5 10⁴ $\Omega \text{ cm}^2$, compared to the R_{ct} of S_{600,3} and S_{800,3} at 49.54 and 21.43 10⁴ $\Omega \text{ cm}^2$, respectively. It can be concluded that S_{700,3} exhibited the best corrosion resistance among the three.

Table 7. The EIS data of the coatings annealed for 3 h at 600 °C, 700 °C and 800 °C in a human body environment.

Sample	R_s ($\Omega \text{ cm}^2$)	CPE_1 (10 ^{−5} $\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	n_1	R_1 ($\Omega \text{ cm}^2$)	CPE_{dl} (10 ^{−5} $\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	n_2	R_{ct} (10 ⁴ $\Omega \text{ cm}^2$)
S _{600,3}	22.66	311.9	0.4953	13.75	15.51	0.9260	49.54
S _{700,3}	19.24	2377	0.295	6389	3.12	0.9449	85.5
S _{800,3}	13.91	3.193	0.9749	1.603	2.069	0.9488	21.43

4. Discussion

4.1. Changes in Coating Composition and Structure

The SEM results reveal that annealing temperature and holding time govern the layered structure of a coating, accompanied by varying Au relative atomic contents in Ti–Au-coated Ti samples. Combined with the XRD results, XPS analysis and Ti–Au phase diagram [5], we identified the Ti–Au components of each layer in each sample (Figure 7a). After annealing at 600 °C, the Au contents of outer layers were nearly 50%. As the Ti–Au phase was not observed in the XRD results under 600 °C annealing, the Au atoms in outer layers are assumed to primarily form a pure Au structure with fewer TiAu_2 , which could be supposed by the two Au 4f peaks of $S_{600,3}$ in XPS (Figure 4b). Meanwhile, the inner layers consisted of Ti_3Au . This can be attributed to the emergence of Ti_3Au diffraction peaks in XRD and the increase in Au contents to nearly 25% as the inner layers thickening towards the substrate (as shown in Figures 2a and 3a–c). After annealing at 700 °C, the Au contents of outer layers in $S_{700,1}$ and $S_{700,3}$ were also nearly 50%, while those of inner layers were nearly 25%. This indicates that the outer layers were Ti–Au and the inner layers were Ti_3Au , which can be demonstrated by XRD result. As the holding time increased, the Ti–Au layer continuously transformed to the Ti_3Au layer. When annealing for 5 h, the Ti–Au layer totally transformed to the Ti_3Au layer. After annealing at 800 °C, the Au contents of layers in $S_{800,1}$, $S_{800,3}$ and $S_{800,5}$ were nearly 25%, indicating that the layers were single-phase Ti_3Au . These results regarding Ti–Au IMCs types were further demonstrated by the peaks' displacement in XPS. Notably, local regions with dissimilar contrast exhibited an Au atomic content of 37%. Combined with the above analysis of the transformation of Ti–Au under 700 °C annealing, these regions were probably at the stage of Ti–Au transforming into Ti_3Au . Due to the clearly defined layered structures seen in the cross-section, the SEM represents distinctly different phase structures, and given the limitations of the characterization conditions, etched-depth XPS measurements were not performed in the present work. Follow-up research will adopt more advanced characterization techniques to further reveal the microscopic mechanisms of interface diffusion through deeper characterization.

As shown in Figure 7a, Ti_3Au directly formed at the substrate/coating interface for all Ti–Au-coated Ti samples. This preferential formation can be attributed to Au's diffusion towards the Ti substrate, with the schematic diagram shown in Figure 7b. As illustrated by the inner layer reaction, the initial formation of Ti_3Au at the substrate/coating interface during the annealing process is primarily influenced by the activation energy of components. Due to the weak diffusion of Au [32], the substrate-side interface mainly consists of Ti with less Au at the onset of annealing. This significant disparity between the Ti and Au components reduces the activation energy required for the transformation of Ti and Au atoms into the Ti_3Au phase, directly forming the most stable Ti_3Au (with the lowest cohesive energy shown in Table 8 [12]), regardless of these annealing temperatures. As the Ti_3Au phase emerges and increases, the inner layer forms then thickens. In contrast, the high diffusion ability of Ti [32] towards the coating hinders the component-driven element, meaning the Ti–Au IMCs' formation in the outer layer reaction is mainly influenced by the thermal-driven activation energy (Figure 7b). Once the required activation energy is satisfied, the Ti's diffusion towards the coating allows the formation of the corresponding Ti–Au IMCs, finally constructing the outer layer.

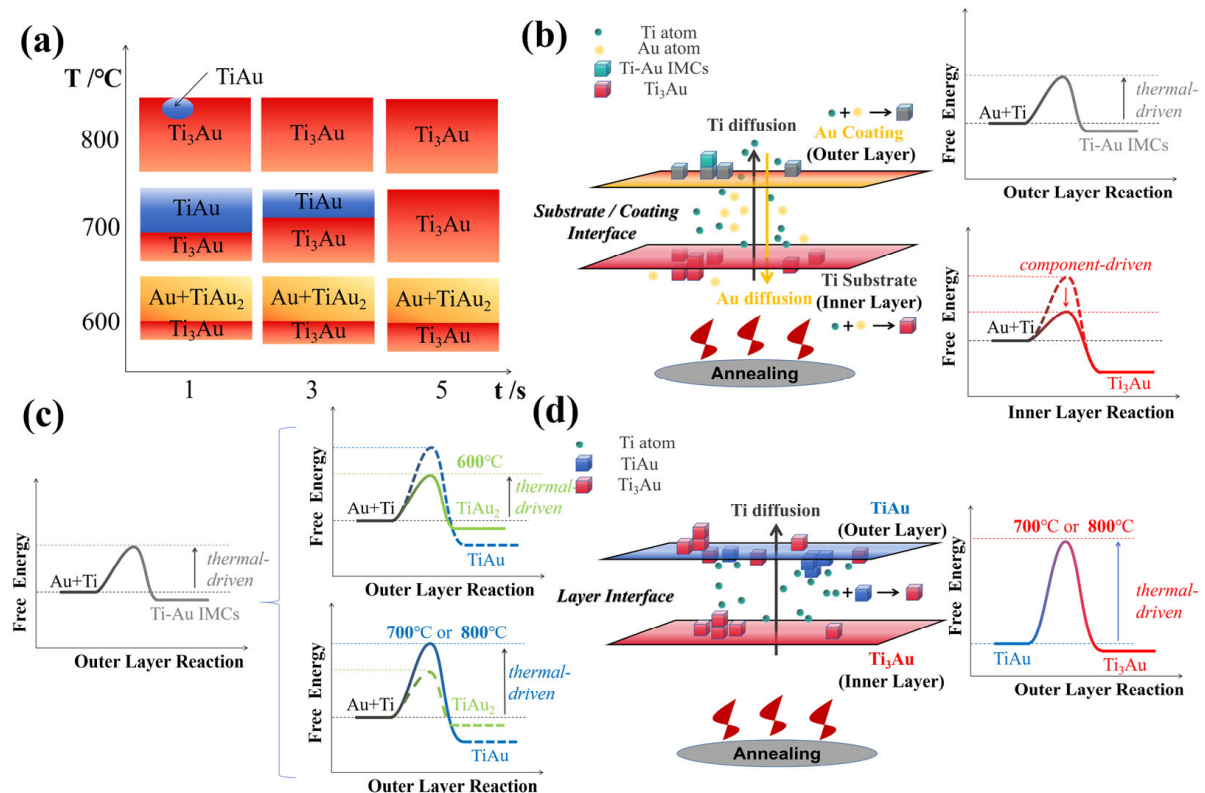


Figure 7. (a) The Ti–Au components of each layer in each sample under different annealing processes. (b) The schematic diagram of Ti and Au diffusion and their reaction at the substrate/coating interface. (c) The activation energy principle of various Ti–Au IMCs' formation in the outer layer. (d) The schematic diagram of Ti–Au's transformation into Ti_3Au in the layer interface.

Table 8. The actual formation enthalpy and cohesive energy of Ti–Au IMCs.

Ti–Au IMC	Formation Enthalpy (eV/Atom)	Cohesive Energy (eV/Atom)
TiAu_2	−0.436	−4.217
TiAu	−0.33	−4.511
Ti_3Au	−0.366	−5.148

The evolution of Ti–Au IMCs in the outer layer is further illustrated in Figure 7c. Notably, a transition temperature (threshold) was found between 600 °C and 700 °C. When the annealing temperature exceeded this threshold, the Ti–Au IMC in the outer layer transformed from the TiAu_2 at 600 °C to the TiAu at 700 °C. By contrast, below this threshold, even if the diffusing Ti reached the composition range according to the phase diagram (Figure 3a–c), TiAu could not be observed within the selected holding time. The underlying principle can be explained through thermodynamic considerations. As shown in Figure 7c, only the higher annealing temperature that can provide enough thermal-driven energy to overcome the energy barrier facilitates the transformation of Ti and Au atoms into TiAu instead of TiAu_2 . According to the formation enthalpy and cohesive energy data provided by Liu et al. [12] (Table 8), TiAu_2 possesses a more negative formation enthalpy than TiAu, and thus forms more spontaneously at 600 °C. Nevertheless, its less negative cohesive energy leads to a less stable structure, meaning that higher annealing temperatures such as 700 °C tend to promote the formation of a more stable Ti–Au while hindering the formation of TiAu_2 . TiAu_4 is an equilibrium IMC in the Ti–Au binary system, and can coexist with the Au or TiAu_2 phase in the equilibrium phase diagram. However, under the solid-state diffusion annealing conditions of this study, this phase was not detected.

This absence can be reasonably explained via both the thermodynamic intrinsic properties and the diffusion kinetics characteristics. From the thermodynamic properties, the first-principles calculation results of Fan et al. indicate that the TiAu_4 phase has a more positive formation enthalpy (-0.289 eV/atom) and cohesive energy (-3.750 eV/atom), and the energy barrier that needs to be overcome for its nucleation is significantly higher than that of TiAu_2 , TiAu , Ti_3Au and other Ti–Au IMCs. In non-equilibrium solid-state diffusion reactions, it is inherently difficult for it to preferentially nucleate and maintain stability. From the diffusion kinetics characteristics of this system, pure Ti foil serves as the substrate, and the outward flux of diffusing Ti atoms far exceeds the inward flux of diffusing Au atoms during annealing. A sufficient local enrichment of Ti around Au atoms would be more likely to generate TiAu_2 rather than TiAu_4 with the lowest formation enthalpy.

Furthermore, as the holding time extended or the annealing temperature increased, the thickness of the inner layer continuously increased towards the coating surface until the outer layer disappeared (Figure 7a). This phenomenon can be illustrated by the formation mechanism of Ti_3Au and the diffusion and reaction kinetics. For the formation of Ti_3Au , as the annealing temperature reaches 700°C or 800°C , the inward-diffusing Au atoms utilize the component-driven effect to form the inner layer of Ti_3Au , and the remaining Au atoms in the outer layer form Ti–Au via a thermal-driven action, as shown in Figure 7b,c. As the holding time extended, the diffusing Ti preferentially combines with the TiAu at the inner layer/outer layer surface to transform to Ti_3Au , as shown in Figure 7d, leading the layer interface to displace towards the surface. For the diffusion and reaction kinetics, according to the Arrhenius equation of diffusion or reaction, the diffusion and reaction rates are positively correlated with the diffusion coefficient (D) and reaction rate constant (k), respectively, and they are expressed as [33,34]

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (1)$$

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where D_0 is the prefactor (m^2/s), and it is generally regarded as a material constant. Q is the activation energy for diffusion (J/mol). R is the gas constant ($8.314 \text{ J/mol}\cdot\text{K}$). T is the temperature. A is the prefactor (frequency factor); it represents the frequency of the reaction or the probability of collision. E_a is the activation energy required for the reaction (J/mol). Based on these above equations, an elevated annealing temperature enhances the Ti–Au atoms' diffusion and Ti–Au IMCs' transformation rates, thereby accelerating the formation and transition of Ti–Au IMCs. Consequently, as the annealing temperature increases, the mutual diffusions of Au and Ti are accelerated, and then the formation of Ti_3Au is expedited, promoting the inner layer to thicken and cover the entire coating.

Based on the above analysis, the full process can be illustrated and explained via the phase diagram shown in Figure 8. During the annealing process, Ti and Au atoms diffuse mutually at the substrate/coating interface, Ti moves towards the coating and Au moves towards the substrate. Due to the component-driven effect, the Ti_3Au phase directly forms at the surface closer to the Ti substrate, and continuously increases and reaches the maximum thickness. This principle is also shown in the Fe–Al coating preparation [35]. Meanwhile, the thermal-driven mechanism plays a significant role in forming Ti–Au IMCs in the Au coating.

When annealed at 600°C , the samples exhibit a low formation rate of Ti–Au IMCs and hinder the Ti_2Au phase's transform to Ti–Au. Thereby, the outer layers retain the most pure Au structure, and less Ti_2Au . As the annealing temperature exceeds the threshold, TiAu_2 can transform into Ti–Au with a higher formation rate compared to the samples annealed

at 600 °C. Moreover, as the annealing temperature exceeds the threshold, more diffusing Ti combines with Au or TiAu at the inner/outer layer interface, thickening the inner layer of Ti₃Au towards the surface. Eventually, all the Au atoms are completely transformed into single-phase Ti₃Au.

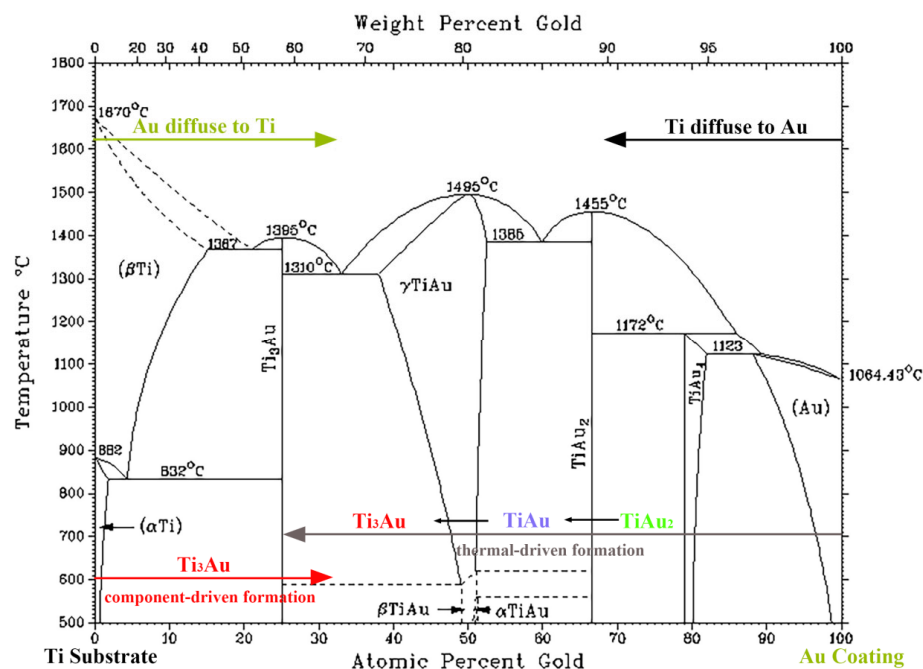


Figure 8. The Ti–Au mutual diffusion and the Ti–Au IMCs’ formation in the phase diagram.

It should be noted that this work adopts conventional XRD for phase characterization, which collects superimposed phase signals from the full depth of the coating. This method cannot accurately quantify the relative fraction of phases at different depths, and the diffraction signal intensity of surface phases will be relatively higher. To further reveal the phase evolution law along the depth direction, depth-resolved phase analysis can be undertaken via grazing incidence XRD with incident angle tuning, and related detailed characterizations will be carried out in future work.

In Figure 8, the arrows in the upper part of the figure represent the diffusion tendency of Ti and Au atoms, and the arrows in the lower part of the figure represent the formation tendency of Ti–Au IMCs.

4.2. The Corrosion Resistance of Coating

The EIS and PDP results demonstrate that the selected Ti–Au-coated Ti samples exhibited different performances. Through the PEMFC and human body environment tests, it could be found that the coating performance exhibited certain similarities and differences in the two H⁺ and Cl[−] corrosion environments.

Notably, S_{700,3} demonstrated the best R_{ct} and $I_{0.6\text{ V}}$ compared to S_{600,3} and S_{800,3} in both corrosion environments. Combining the coating compositions (Figure 7a), it can be noted that the surface of S_{700,3} is entirely TiAu, and the inner layer is Ti₃Au, which can be regarded as a TiAu/Ti₃Au double-layer coating. This indicates that the TiAu/Ti₃Au double-layer coating possessed the most superior corrosion resistance, and the Au coating with a small amount of TiAu₂ exhibited the worst corrosion resistance. The lower $I_{0.6\text{ V}}$ of the TiAu/Ti₃Au double-layer or Ti₃Au single-phase layer compared to the Au + Ti coating with a small amount of TiAu₂ is due to the fact that the single-phase layer can form a relatively uniform and stable oxide film during corrosion. By contrast, the mixture of Au

and fewer TiAu₂ leads to a strong galvanic cell reaction, accelerating TiAu₂ dissolution and damaging the coating structure [6].

All three Ti–Au-coated Ti samples exhibited similar pitting corrosion potential in the PDP curves, while the pitting corrosion potentials varied in different corrosion environments. This behavior was due to the Ti–Au IMCs exhibiting a dissolution potential [8,9]. When the potential reaches the dissolution potential, the Ti–Au IMC will dissolve, forming a non-uniform surface that leads to the occurrence of pitting corrosion, and the current density rises rapidly. The differences in pitting potentials under different corrosive environments and the more sharp pitting current density curves' change reveal that Cl[−] ions have a greater ability to destroy pitting corrosion than H⁺. In addition, Cl[−] ions exhibit a higher erosional ability than H⁺, as indicated by the double capacitive elements of the EEC model in the human body environment.

As regards commercial application, the corrosion resistances of the Ti–Au coating were not sufficient to meet the PEMFC, due to the $I_{0.6\text{ V}}$ of 2.639 $\mu\text{A cm}^{-2}$, which is lower than the requirement ($I_{0.6\text{ V}}$ of 1 $\mu\text{A cm}^{-2}$ for PEMFC). Compared to other coatings and the Ti substrate, as discussed in the relevant literature shown in Table 9, the Ti–Au IMC coatings do not reach the commercial standard for PEMFC. The operating environment of the bipolar plates in PEMFC is extremely harsh (80 °C temperature, strong acidic medium, containing F[−] passivating ions), which imposes extremely high requirements on the corrosion resistance stability of the materials. The equilibrium dissolution potential of the Ti–Au intermetallic compound lies between Ti and Au, which may lead to a significant increase in the dissolution tendency of multi-atoms (Ti, TiAu, Au) under strong corrosive conditions. Despite the insufficient performance in harsh PEMFC, the Ti–Au IMC coatings exhibit the best corrosion resistance in dental applications (human body) compared to Au and Ti and other reported coatings in Table 10. In particular, compared to the TiAu/Ti₃Au prepared by electroplating assisted by laser [11], a protective structure with good corrosion resistance (lower I_{corr}) can be achieved through magnetic control sputtering and thermal treatment. Moreover, compared with cast Ti–40Au alloys (with a small amount of Ti₃Au) [8], this further proves that the multiphase IMC suffers from preferential interfacial dissolution, leading to a decrease in corrosion resistance, while the preparation of single-phase IMC layers can achieve superior corrosion resistance.

Table 9. The comparison of coating performance in the PEMFC environment.

Coating	Substrate	Environment	$E_{\text{corr}}(\text{mV})$ - Ag/AgCl	$I_{0.6\text{ V}}$ ($\mu\text{A cm}^{-2}$)	References
standard	/	/	/	1	2025 DOE target [36]
TiAu/Ti ₃ Au	Ti	80 °C, 0.0005 M H ₂ SO ₄ + 2 ppm F [−]	55.51	2.617	/
Au coating (in Figure S5)	Ti	80 °C, 0.0005 M H ₂ SO ₄ + 2 ppm F [−]	196.9	0.1821	/
/	Ti (in Figure S5)	80 °C, 0.0005 M H ₂ SO ₄ + 2 ppm F [−]	−19.13	0.9592	/
Au/TiN	Ti	80 °C, 0.0005 M H ₂ SO ₄ + 1 ppm F [−]	165	2.313	[7]
CrN	Ti	80 °C, 0.5 M H ₂ SO ₄ + 5 ppm F [−]	316	0.594	[37]
TiCr/TiCrN	Ti	80 °C, 0.5 M H ₂ SO ₄ + 2 ppm F [−]	−219	0.22	[38]

Table 10. The comparison of coating performance in the human body environment.

Coating	Substrate	Environment	$E_{\text{corr}}(\text{mV})$ - Ag/AgCl	I_{corr} ($\mu\text{A cm}^{-2}$)	References
Au + Ti ₂ Au/Ti ₃ Au	Ti	0.9 wt% NaCl, 37 °C	23.00	0.0851	/
TiAu/Ti ₃ Au	Ti	0.9 wt% NaCl, 37 °C	88.03	0.0089	/
Ti ₃ Au	Ti	0.9 wt% NaCl, 37 °C	−199.4	0.0356	/
TiAu/Ti ₃ Au	Ti	250 mL of ringer's solution (0.86 wt% NaCl)	88	0.046	[11]
Au	Ti	250 mL of ringer's solution (0.86 wt% NaCl), 37 °C	−35	0.440	[11]
/	Ti	250 mL of ringer's solution (0.86 wt% NaCl), 37 °C	−90	0.639	[11]
/	Ti-5Au	0.9 wt% NaCl, 37 °C	−418.67	0.29	[8]
/	Ti-40Au	0.9 wt% NaCl, 37 °C	−381.73	7.78	[8]

5. Conclusions

Based on diffusion annealing after gold plating, this study systematically investigated the influence of annealing parameters (temperature and time) on the diffusion behavior and phase composition of Ti–Au IMC coatings. A clear temperature–time-dependent phase evolution relationship was established, revealing how heat treatment conditions regulate Ti–Au interdiffusion and dominate the formation of Ti–Au IMCs. Furthermore, the corrosion resistance of the Ti–Au IMC coatings was investigated to extend the evaluation of their potential application performance. The key findings and conclusions are summarized as follows:

1. A single-phase Ti₃Au coating can be prepared through the PVD followed by the annealing process. In contrast, a single-phase TiAu or TiAu₂ coating cannot be formed under these process parameters. This is because Ti₃Au always forms directly at the interface, as governed by the diffusion of Au towards the substrate;
2. The annealing temperature influences not only the formation of Ti–Au IMCs as governed by the activation energy principle, but also the diffusion and formation rates. For 600 °C-annealed samples, the IMCs in the outer layer were TiAu₂ even when the Au relative content reached 50%. For 700 °C-annealed samples, the IMCs of TiAu₂ transformed to Ti–Au. As the temperature increased, the inner layer of Ti₃Au thickened and covered the entire coating;
3. The holding time primarily influences the continuous diffusion of Ti and Au. As the holding time increased, the Ti diffusion mainly promoted the thickening of Ti₃Au layer towards the surface, while the Au diffusion promoted that towards the substrate;
4. The Ti–Au coating prepared via 700 °C annealing for 3 h exhibited the highest corrosion resistance. In the PEMFC environment, this coating was characterized by the lowest $I_{0.6\text{ V}}$ of 2.617 $\mu\text{A cm}^{-2}$, which still failed to meet the requirements of PEMFC. In the human body environment, it displayed the lowest I_{corr} of 0.0089 $\mu\text{A cm}^{-2}$. Compared with the Ti–Au alloys in other studies, the Ti–Au coatings fabricated via this route exhibited superior corrosion resistance.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/coatings16080932/s1>, Figure S1: XRD patterns of the bare and Au-coated Ti samples. Figure S2: the AFM diagram and thickness of Au coating for depositing at different powers for 5 min: (a) 10 W; (b) 20 W; (c) 30W. Figure S3: The deposition rate of Au. Figure S4: The thickness of SAu deposited at 30 W for 1 h. Figure S5: The potentiodynamic polarization curves of bare Ti substrate and pure Au coatings in a simulated PEMFC environment. Table S1: The

potentiodynamic polarization curves' data of bare Ti substrate and pure Au coatings in a simulated PEMFC environment.

Author Contributions: Conceptualization, B.D.; methodology, B.D. and G.Z.; software, M.Z.; validation, Z.Y. and W.L.; formal analysis, B.D. and H.X.; investigation, Z.Y. and G.Z.; resources, Z.Y. and G.Z.; data curation, W.L.; writing—original draft preparation, X.L.; writing—review and editing, X.L.; visualization, Z.Y.; supervision, W.F.; project administration, G.Z.; funding acquisition, B.D. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The raw data required to reproduce these findings cannot be shared at this time as the data also form part of an ongoing study.

Conflicts of Interest: The authors declare no conflicts of interest.

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