

Article

Pulse-Reverse Electrodeposition of Thin Au Coatings on Ni-Coated Brass: Effects of Pulse Parameters on Microstructure and Corrosion Behavior

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Highlights

- Pulse-plated Ni provided a stable barrier for thin Au deposition.
- Response Surface Methodology (RSM) confirmed coupled effects among four pulse parameters.
- 800 Hz, 22%, 0.11 / $-0.004 \text{ A} \cdot \text{dm}^{-2}$ formed compact Au coatings.
- The thin Au coating reaches 0.3–0.6 μm , which can significantly reduce costs.
- Corrosion resistance improved by low roughness and fewer defect paths.

Abstract

Pulse-reverse electrodeposition was investigated as a route to reduce Au consumption while maintaining coating continuity and corrosion performance in thin Ni/Au finishes. A pulse-plated Ni barrier layer with an average thickness of approximately 4.45 μm was first prepared on brass, followed by Au deposition from a potassium dicyanoaurate-based electrolyte containing a cobalt additive. Pulse frequency, duty cycle, forward current density, and reverse current density were evaluated with respect to Au thickness, surface morphology, corrosion potential, roughness, and electrochemical impedance. The processing window was selected hierarchically by requiring an Au thickness of 0.3–0.6 μm , a relatively noble corrosion potential, a compact surface with few visible defects, low roughness, and a consistent impedance response; charge-transfer resistance was not treated as the sole criterion. Within the present bath, substrate, electrode geometry, and power-supply configuration, 800 Hz, 22% duty cycle, 0.11 $\text{A} \cdot \text{dm}^{-2}$ forward current density, and $-0.004 \text{ A} \cdot \text{dm}^{-2}$ reverse current density provided the most balanced overall response.

Keywords: pulse electrodeposition; cyanide gold plating; Ni/Au bilayer coating; corrosion resistance



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1. Introduction

Gold electrodeposition is widely used for electrical contacts because Au combines high electrical conductivity, low contact resistance, and resistance to corrosion and tarnishing [1–3]. Engineering specifications for electrodeposited Au coatings therefore emphasize coating thickness, composition, and service requirements rather than a single universally applicable deposition condition [4,5].

Reducing Au thickness is economically attractive, but a thinner finish places greater demands on coating continuity and defect control. In geometrically complex parts, non-uniform current distribution and incomplete coverage can create local pathways for electrolyte penetration and accelerate degradation of the underlying metallization [5–7]. These considerations motivate deposition strategies that reduce precious-metal use while preserving a continuous and electrochemically stable surface.

Pulse electrodeposition (PED) periodically modulates the applied current or potential. During the forward on-time (T_{on}), the instantaneous cathodic current can increase the nucleation rate; during the off-time (T_{off}) and reverse segment, the concentration boundary layer can partially recover and weakly bound surface features can be removed. Appropriate waveform control may therefore refine the deposit, improve coverage, and reduce visible surface defects relative to conventional direct-current plating [8–13].

The practical difficulty is that frequency, duty cycle, forward current density, and reverse current density are coupled: together they determine the pulse period, the absolute T_{on}/T_{off} durations, cathodic charge input, mass-transfer recovery, and anodic dissolution. Published studies often focus on single parameters, thicker deposits, or alloy systems, whereas connector-relevant thin Au layers deposited from commercial cyanide-based baths remain less systematically documented [14–16].

In Cu/Ni/Au contact finishes, the Ni underlayer is a functional barrier that retards Cu migration toward the Au surface and also defines the immediate substrate for Au nucleation [15,17]. Its thickness, continuity, and surface state can influence coverage of the subsequent thin Au layer. The present work therefore standardized the Ni layer before evaluating the Au pulse-deposition variables.

Recent studies on Ni-based finishes, Au/Ni contact coatings, and pulsed Au-alloy deposition show that crystallinity, visible defect density, roughness, and interfacial continuity affect corrosion and contact behavior [16,18,19]. The present study extends this work by combining single-factor experiments with response-surface analysis and by relating pulse parameters to Au thickness, surface morphology, roughness, phase constitution, and electrochemical response in a potassium dicyanoaurate-based commercial bath. The objective is to identify a practical processing window for the investigated system, not to claim a universal optimum or direct industrial qualification.

2. Experimental

2.1. Materials and Substrate Preparation

All conventional chemical reagents were of analytical-reagent grade and were used without further purification. Potassium dicyanoaurate, RONOVEL CM Make-up Additive, and RONOVEL CM Cobalt Concentrate were obtained from Rohm and Haas (Philadelphia, PA, USA). The two RONOVEL CM additives were proprietary commercial formulations and were used as received; their detailed compositions were not disclosed by the supplier. Sulfuric acid (98 wt.% H_2SO_4), hydrochloric acid (35–37 wt.% HCl), and acetone (AR) were supplied by Chongqing Chuandong Chemical Co., Ltd. (Chongqing, China). Ultrapure water was used throughout the experiments.

Brass sheets (65.00 mm × 50.00 mm × 0.20 mm) were used as substrates. Before electrodeposition, the substrates were ground sequentially with 600-, 800-, and 1000-grit SiC papers, ultrasonically degreased in acetone for 10–15 min, rinsed with ultrapure water, etched in 100–360 g·L^{−1} HCl for 1 min at room temperature, and activated in 200–300 g·L^{−1} HCl for 1–2 min. Electrodeposition was initiated immediately after rinsing.

2.2. Optimization of Pulse-Plated Ni Underlayer Parameters

A Ni barrier layer was deposited on brass to provide a reproducible substrate for the thin Au finish and to retard Cu migration. Preliminary pulse-plating results are provided in Section S1 of the Supplementary Materials (Figures S1–S5 and Table S1). The selected Ni condition was $0.75 \text{ A}\cdot\text{dm}^{-2}$ average current density, 80% duty cycle, 1000 Hz, and 8 min.

2.3. Pulse Electrodeposition of Gold

Potassium dicyanoaurate was used as the Au-ion source. The bath contained potassium dicyanoaurate ($5 \text{ g}\cdot\text{L}^{-1}$), RONOVEL CM Make-up Additive ($28 \text{ mL}\cdot\text{L}^{-1}$), and RONOVEL CM Cobalt Concentrate ($5 \text{ mL}\cdot\text{L}^{-1}$). The cobalt-containing commercial additive was used as a deposition modifier rather than as a target alloying source. Accordingly, the deposit is described as an Au coating, not an Au-Co alloy coating.

Au was deposited using a BP4610 high-speed bipolar power supply operated in pulse-reverse mode. A titanium plate (effective area 1.3 dm^2) and Ni-plated brass sheet (effective area 0.65 dm^2) served as the anode and cathode, respectively; the electrode spacing was 10 cm. All depositions were conducted at $50 \pm 3 \text{ }^\circ\text{C}$ for 7 min. Frequency (300–1000 Hz), duty cycle (10%–40%), forward current density (0.06 – $0.20 \text{ A}\cdot\text{dm}^{-2}$), and reverse current density (-0.002 to $-0.005 \text{ A}\cdot\text{dm}^{-2}$) were varied one at a time. When one parameter was varied, the other three were held at 800 Hz, 22%, $0.11 \text{ A}\cdot\text{dm}^{-2}$, and $-0.004 \text{ A}\cdot\text{dm}^{-2}$, as detailed in Table 1. The duty cycle δ was defined as

$$\delta = \frac{T_{\text{on}}}{T_{\text{on}} + T_{\text{off}}} \times 100\%$$

where T_{on} and T_{off} denote the forward-current duration and the remaining non-forward duration within one pulse period, respectively. Thus, $T_{\text{on}}/T_{\text{off}} = \delta/(100 - \delta)$. At 800 Hz, the total pulse period was 1.25 ms. The duty cycles of 10%, 15%, 22%, 30%, and 40% therefore corresponded to $T_{\text{on}}/T_{\text{off}}$ ratios of 0.111, 0.176, 0.282, 0.429, and 0.667, respectively.

Table 1. Single-factor experimental design for Au pulse electrodeposition.

Experimental Series	Varied Parameter	Values Tested	Parameters	Conditions	Purpose
Frequency series	Frequency, f (Hz)	300, 500, 800, 1000	duty = 22% $j_p = 0.11 \text{ A}\cdot\text{dm}^{-2}$ $j_r = -0.004 \text{ A}\cdot\text{dm}^{-2}$	$T = 50 \pm 3 \text{ }^\circ\text{C}$ $t = 7 \text{ min}$ electrode spacing = 10 cm	Effect of pulse period
Duty-cycle series	Duty cycle (%)	10, 15, 22, 30, 40	$f = 800 \text{ Hz}$ $j_p = 0.11 \text{ A}\cdot\text{dm}^{-2}$ $j_r = -0.004 \text{ A}\cdot\text{dm}^{-2}$	$T = 50 \pm 3 \text{ }^\circ\text{C}$ $t = 7 \text{ min}$ electrode spacing = 10 cm	Effect of $T_{\text{on}}/T_{\text{off}}$ ratio
Forward-current series	j_p ($\text{A}\cdot\text{dm}^{-2}$)	0.06, 0.08, 0.11, 0.15, 0.20	$f = 800 \text{ Hz}$ duty = 22% $j_r = -0.004 \text{ A}\cdot\text{dm}^{-2}$	$T = 50 \pm 3 \text{ }^\circ\text{C}$ $t = 7 \text{ min}$ electrode spacing = 10 cm	Effect of cathodic charge input
Reverse-current series	j_r ($\text{A}\cdot\text{dm}^{-2}$)	-0.002 , -0.003 , -0.004 , -0.005	$f = 800 \text{ Hz}$ duty = 22% $j_p = 0.11 \text{ A}\cdot\text{dm}^{-2}$	$T = 50 \pm 3 \text{ }^\circ\text{C}$ $t = 7 \text{ min}$ electrode spacing = 10 cm	Effect of anodic dissolution

2.4. Response Surface Design of Coupled Pulse Parameters

To further evaluate the coupling among pulse frequency, duty cycle, forward current density, and reverse current density, response surface methodology (RSM) was conducted

using the corrosion potential of the Au coating as the response value. A four-factor, three-level Box–Behnken design was generated using Design-Expert 13. The four independent variables were pulse frequency (A, f), duty cycle (B, duty), forward current density (C, j_p), and reverse current density (D, j_r). The factor levels were selected according to the favorable ranges obtained from the single-factor experiments. The factor levels, experimental matrix, and response values are provided in Section S3 of the Supplementary Materials.

2.5. Coating Characterization

All Au-coated specimens used for the corrosion tests were deposited on the same pulse-plated Ni underlayer prepared at an average current density of $0.75 \text{ A} \cdot \text{dm}^{-2}$, a duty cycle of 80%, a frequency of 1000 Hz, and a deposition time of 8 min. Electrochemical measurements (Tafel polarization and electrochemical impedance spectroscopy, EIS) of the Au coatings deposited under different conditions were performed using an Interface 1010E electrochemical workstation (Gamry Instruments, Warminster, PA, USA). A 3.5 wt.% NaCl solution was used as the corrosive medium. After stabilization of the open-circuit potential (OCP), measurements were conducted in a conventional three-electrode cell, with the coated specimen as the working electrode (exposed area: 1 cm^2), a saturated calomel electrode as the reference electrode, and a platinum sheet as the counter electrode. Polarization curves were recorded from -0.75 to 0.35 V (vs. SCE) at $10 \text{ mV} \cdot \text{s}^{-1}$. E_{corr} was obtained by fitting the Tafel regions. EIS was measured at the stabilized OCP using a 5 mV AC perturbation over 10^{-2} – 10^5 Hz .

The impedance spectra were fitted by modulus-weighted complex nonlinear least squares using the finite-length-diffusion circuit R_s –[constant phase element (CPE)] $[(R_{ct} + W_s)]$ [20,21]. The CPE admittance was defined as $Y_{\text{CPE}} = Q(j\omega)^n$. The finite-length transmissive (short-circuit) Warburg element was defined as $Z_W = R_W \tanh[(j\omega T_W)^{1/2}] / (j\omega T_W)^{1/2}$, where R_W ($\Omega \cdot \text{cm}^2$) is the finite diffusion resistance and $T_{W(s)}$ is the characteristic diffusion time. High-frequency points with positive Z'' , attributed to lead/fixture inductance and not represented by this circuit, were excluded from the nonlinear regression and are identified in Figure 7. Local 95% confidence intervals were estimated from the Jacobian covariance matrix. The complete confidence intervals, Bode fits, and normalized residuals are provided in Section S4 of the Supplementary Materials.

The thickness of each Ni/Au coating was measured using an FISCHERScope X-RAY XDV-SDD (XRF) coating-thickness instrument (Helmut Fischer GmbH, Sindelfingen, Germany). Five sites were measured for each sample; the thickness of the Ni coating was $4.45 \mu\text{m}$, while the Au coating thickness is presented in Table 2 as the mean $\pm$ standard deviation. The atomic force microscopy (AFM) measurements reported in this work characterize the Au-coated surfaces only; quantitative roughness data for the uncoated brass substrate and the Ni underlayer were not available and are therefore not compared.

Surface morphology was examined by field-emission scanning electron microscopy (FE-SEM; MIRA LMS, TESCAN Group, Brno, Czech Republic). Elemental composition was measured by energy-dispersive X-Ray spectroscopy (EDS). Representative elemental maps and the quantitative composition for the selected combined pulse condition are provided in Figure S6 and Table S3 of the Supplementary Materials. Surface roughness of the Au-coated specimens was measured by atomic force microscopy using an MFP-3D Origin+ instrument (Asylum Research, Oxford Instruments, Santa Barbara, CA, USA) in static mode using a silicon nitride probe. Crystal structure was analyzed by grazing-incidence X-Ray diffraction using a Rigaku SmartLab XE diffractometer (Rigaku Corporation, Tokyo, Japan) equipped with a D/teX 250 detector and Cu K α radiation ($\lambda = 0.15406 \text{ nm}$). Measurements were conducted at 40 kV and 150 mA with a fixed incidence angle of 0.2° . Patterns were recorded over $2\theta = 5$ – 90° using a 0.01° step and a scanning rate of $5^\circ \cdot \text{min}^{-1}$. The Au(111)

envelope was fitted with a pseudo-Voigt function, and the apparent coherent-domain size was estimated using the Scherrer equation, $D = K\lambda/(\beta\cos\theta)$, with $K = 0.9$ and β equal to the fitted FWHM in radians. No instrumental-broadening correction was applied; therefore, the reported sizes are comparative apparent values rather than absolute crystallite sizes.

Table 2. Corrosion potential and Au coating thickness of samples prepared under different single-factor pulse-parameter series.

Varied/Fixed Pulse Parameters	Parameter Value	E_{corr} (V vs. SCE)	Au Thickness (μm)
f varied duty = 22% $j_p = 0.11 \text{ A}\cdot\text{dm}^{-2}$ $j_r = -0.004 \text{ A}\cdot\text{dm}^{-2}$	300 Hz	−0.130	0.45 ± 0.02
	500 Hz	−0.120	0.40 ± 0.01
	800 Hz	−0.102	0.45 ± 0.02
	1000 Hz	−0.107	0.46 ± 0.03
duty varied f = 800 Hz $j_p = 0.11 \text{ A}\cdot\text{dm}^{-2}$ $j_r = -0.004 \text{ A}\cdot\text{dm}^{-2}$	10%	−0.126	0.25 ± 0.02
	15%	−0.123	0.34 ± 0.03
	22%	−0.103	0.45 ± 0.02
	30%	−0.116	0.61 ± 0.01
	40%	−0.134	0.61 ± 0.01
j_p varied f = 800 Hz duty = 22% $j_r = -0.004 \text{ A}\cdot\text{dm}^{-2}$	$0.06 \text{ A}\cdot\text{dm}^{-2}$	−0.129	0.27 ± 0.02
	$0.08 \text{ A}\cdot\text{dm}^{-2}$	−0.118	0.37 ± 0.01
	$0.11 \text{ A}\cdot\text{dm}^{-2}$	−0.102	0.44 ± 0.02
	$0.15 \text{ A}\cdot\text{dm}^{-2}$	−0.122	0.65 ± 0.03
j_r varied f = 800 Hz duty = 22% $j_p = 0.11 \text{ A}\cdot\text{dm}^{-2}$	$0.20 \text{ A}\cdot\text{dm}^{-2}$	−0.118	0.83 ± 0.04
	$-0.002 \text{ A}\cdot\text{dm}^{-2}$	−0.110	0.51 ± 0.01
	$-0.003 \text{ A}\cdot\text{dm}^{-2}$	−0.133	0.41 ± 0.01
	$-0.004 \text{ A}\cdot\text{dm}^{-2}$	−0.103	0.45 ± 0.02
	$-0.005 \text{ A}\cdot\text{dm}^{-2}$	−0.107	0.38 ± 0.03

3. Results and Discussion

3.1. Combined Effects of Pulse Parameters on the Morphology and Corrosion Resistance of the Ni Underlayer

Before discussing the Au pulse-electrodeposition results, the Ni underlayer needs to be briefly considered because it serves as the immediate substrate for all subsequent Au deposition. In the present Ni/Au bilayer system, the Ni layer functions not only as a diffusion barrier against Cu migration from the brass substrate, but also as an interfacial layer whose continuity and surface state can affect the nucleation and coverage of the thin Au overlayer. Therefore, the optimization of the Ni underlayer was treated as a necessary preliminary step to ensure interfacial stability and comparability in the subsequent evaluation of pulse-plated Au coatings.

The selected Ni layer was deposited at $0.75 \text{ A}\cdot\text{dm}^{-2}$ average current density, 80% duty cycle, 1000 Hz, and 8 min. Its average thickness, determined from five positions, was approximately $4.45 \mu\text{m}$. Figure 1 shows the surface before and after 196 h immersion in 3.5 wt.% NaCl. No severe macroscopic corrosion features are visible after immersion. The images support the use of this Ni layer as a reproducible substrate for the Au experiments; they do not, by themselves, quantify total coating porosity or prove complete suppression of Cu diffusion.

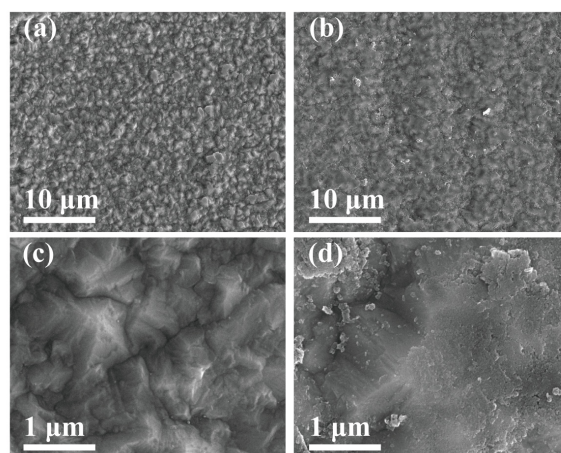


Figure 1. FE-SEM surface morphology of the Ni coating deposited under the selected Ni-plating parameters ($0.75 \text{ A}\cdot\text{dm}^{-2}$, 80% duty cycle, 1000 Hz, and 8 min): (a,c) before immersion and (b,d) after 196 h immersion in 3.5 wt.% NaCl solution. Panels (c,d) are high-magnification images of (a,b), respectively.

3.2. Effects of Pulse Parameters on Au Coating Thickness and Corrosion Potential

Frequency, duty cycle, forward current density, and reverse current density jointly determine the pulse period, the absolute $T_{\text{on}}/T_{\text{off}}$ durations, cathodic charge input, diffusion-layer recovery, and anodic dissolution. The single-factor experiments therefore identify dominant trends under the fixed conditions in Table 1. The selected processing window was defined using a hierarchical criterion: (i) the Au thickness had to remain within the intended $0.3\text{--}0.6 \text{ }\mu\text{m}$ range; (ii) E_{corr} was used as the primary electrochemical screening response; (iii) the surface had to remain comparatively uniform without pronounced nodules or visible surface openings in FE-SEM; and (iv) roughness and EIS parameters were used as supporting criteria. R_{ct} was not maximized independently because it is affected by thickness and interfacial heterogeneity.

Table 2 reports E_{corr} and Au thickness for every single-factor series. Thickness is given as the mean $\pm$ standard deviation from five XRF positions. The fixed pulse parameters for each series are stated directly in the first column so that the data can be interpreted without referring back to Table 1.

Within the frequency series, Au thickness remained in a narrow range of $0.40\text{--}0.46 \text{ }\mu\text{m}$. E_{corr} shifted from -0.130 V at 300 Hz to -0.102 V at 800 Hz and then to -0.107 V at 1000 Hz. Because the thicknesses are comparable, this series provides the clearest evidence that waveform timing, rather than thickness alone, affects the corrosion response. At 800 Hz, repeated nucleation and partial diffusion-layer recovery produced the most balanced response in this series. Increasing duty cycle increased the deposited amount, and the 30% and 40% coatings both had an average thickness of $0.61 \text{ }\mu\text{m}$. Despite their identical average thickness, their E_{corr} values differed (-0.116 and -0.134 V , respectively), showing that thickness alone cannot explain the electrochemical trend. The 22% condition retained an Au thickness of $0.45 \pm 0.02 \text{ }\mu\text{m}$ and gave the most noble E_{corr} in this series. with the explicit value $T_{\text{on}}/T_{\text{off}} = 0.282$ provided sufficient cathodic deposition while retaining time for concentration recovery.

Forward current density produced the largest thickness variation, from $0.27 \pm 0.02 \text{ }\mu\text{m}$ at $0.06 \text{ A}\cdot\text{dm}^{-2}$ to $0.83 \pm 0.04 \text{ }\mu\text{m}$ at $0.20 \text{ A}\cdot\text{dm}^{-2}$. The increase in R_{ct} at high current density must therefore be interpreted partly as a thickness effect. Nevertheless, the most noble E_{corr} occurred at $0.11 \text{ A}\cdot\text{dm}^{-2}$, where the Au thickness was $0.44 \pm 0.02 \text{ }\mu\text{m}$ and the FE-SEM surface was comparatively uniform. Higher current densities increased the deposition rate but also promoted concentration polarization and nodular growth. For the reverse-current

series, thickness varied from 0.38 to 0.51 μm and E_{corr} changed non-monotonically. At $-0.004 \text{ A}\cdot\text{dm}^{-2}$, mild anodic dissolution and subsequent cathodic renucleation produced the most noble E_{corr} while maintaining an average Au thickness of $0.45 \pm 0.02 \mu\text{m}$. The stronger $-0.005 \text{ A}\cdot\text{dm}^{-2}$ reverse segment reduced thickness and was associated with more visible surface heterogeneity.

These data show that Au thickness is an important covariate but not a sufficient predictor of corrosion behavior. The selected condition—800 Hz, 22% duty cycle, $0.11 \text{ A}\cdot\text{dm}^{-2}$ forward current density, and $-0.004 \text{ A}\cdot\text{dm}^{-2}$ reverse current density—satisfied the target thickness range and provided the most balanced combination of E_{corr} , surface morphology, roughness, and impedance response. It is therefore described as a favorable processing window for this system rather than a global optimum.

3.3. Effect of Pulse Frequency on the Surface Morphology of Au Deposits

Figure 2 compares the surface morphologies of pulse-electrodeposited Au coatings obtained at 300, 500, 800, and 1000 Hz. The surface becomes progressively more uniform from 300 to 800 Hz, whereas localized coarsening and agglomeration reappear at 1000 Hz. The features observed by SEM are described as surface particles or morphological features; they are not assumed to be identical to the XRD coherent-domain size discussed in Section 3.9.

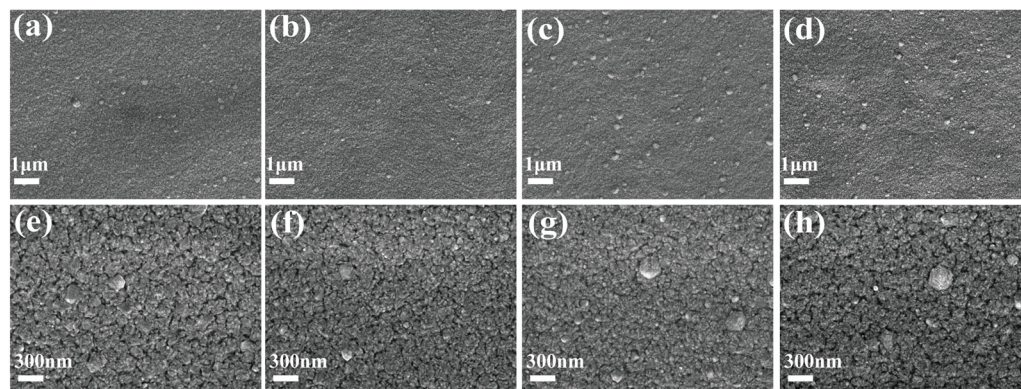


Figure 2. FE-SEM surface morphology of Au coatings deposited at (a,e) 300 Hz, (b,f) 500 Hz, (c,g) 800 Hz, and (d,h) 1000 Hz; panels (a–d) and (e–h) are low- and high-magnification images, respectively. Duty cycle, j_p , and j_r were fixed at 22%, $0.11 \text{ A}\cdot\text{dm}^{-2}$, and $-0.004 \text{ A}\cdot\text{dm}^{-2}$. Representative EDS maps for the selected combined condition are provided separately in Figure S6.

At 300 Hz (Figure 2a,e), the surface shows pronounced hill-like topography, relatively large particles, and heterogeneous coverage. The longer pulse period and cathodic on-time can increase the extent of uninterrupted growth and local concentration gradients, which is consistent with the coarse, non-uniform surface observed under this condition [8,14,22].

At 500 Hz (Figure 2b,f), the characteristic surface features become smaller and the distribution is more uniform, with fewer interparticle depressions. The shorter pulse period can increase the frequency of nucleation events and permit more frequent diffusion-layer relaxation [8,14,23]. The fitted R_{ct} is also larger than at 300 Hz; however, this electrical response is interpreted together with thickness and morphology and is not used as evidence of coating density.

At 800 Hz (Figure 2c,g), the surface features are comparatively fine and equiaxed, and the coverage is more uniform with fewer visible surface openings than at 300 and 500 Hz. This morphology is consistent with a balance between repeated nucleation and diffusion-layer recovery. However, the SEM images provide only surface-morphology evidence and do not quantify coating density or through-porosity.

At 1000 Hz (Figure 2d,h), localized agglomeration becomes more evident and some feature boundaries are less distinct. The shortened pulse intervals may limit complete interfacial relaxation and ion replenishment, leading to less uniform surface development. Although the refitted EIS data give a larger R_{ct} at 1000 Hz than at 800 Hz, the morphological and polarization results are less favorable; therefore, 800 Hz is retained as the more balanced frequency within the tested range.

In summary, pulse frequency affects Au surface development through the time scale of cathodic growth, repeated nucleation, diffusion-layer recovery, and reverse-pulse reactivation. Low frequency favors longer uninterrupted growth, whereas very high frequency can provide insufficient time for interfacial relaxation [8–10,13–16,24]. Within the investigated range, 800 Hz gives the most uniform surface morphology under the fixed background conditions, but it does not maximize every EIS parameter.

3.4. Effect of Duty Cycle on the Surface Morphology of Au Deposits

As shown in Figure 3, the surface morphology changes non-monotonically as the duty cycle increases from 10% to 40%, evolving from relatively uneven coverage at low duty cycle to a more uniform surface at 22% and then to renewed nodular roughening at 30%–40%. At 10%–15%, the short T_{on} limits the deposited charge per cycle and produces heterogeneous surface development. These observations are interpreted as surface-morphology trends rather than a quantitative measure of coating density.

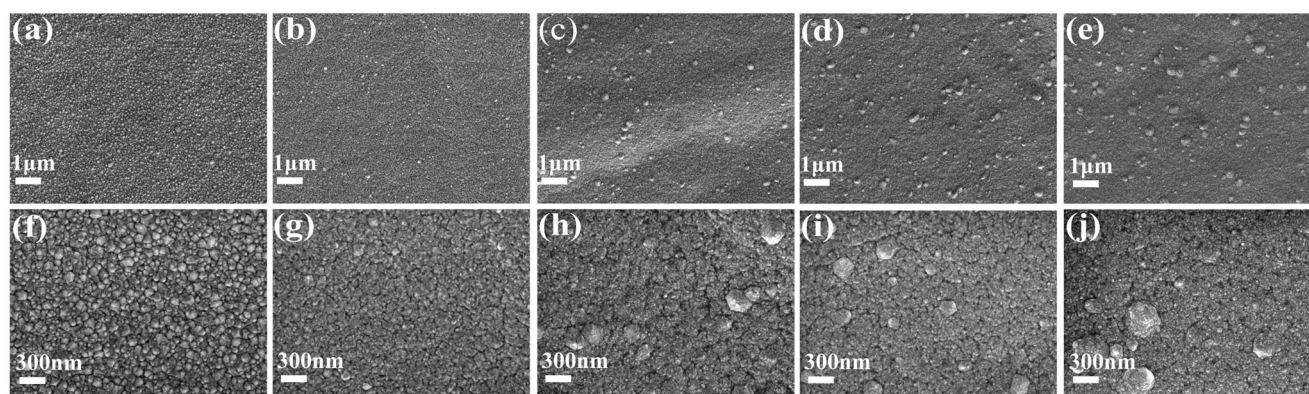


Figure 3. FE-SEM surface morphology of Au coatings deposited at (a,f) 10%, (b,g) 15%, (c,h) 22%, (d,i) 30%, and (e,j) 40% duty cycle; panels (a–e) and (f–j) are low- and high-magnification images, respectively. Frequency, j_p , and j_r were fixed at 800 Hz, $0.11 \text{ A} \cdot \text{dm}^{-2}$, and $-0.004 \text{ A} \cdot \text{dm}^{-2}$.

At a duty cycle of 22%, the coating shows the most uniform surface within this series, with finer features and fewer visible nodules and depressions. The intermediate T_{on}/T_{off} ratio provides sufficient cathodic charge while retaining relaxation time for replenishment of $[\text{Au}(\text{CN})_2]^-$ near the cathode [25,26]. This condition also gives the most noble E_{corr} and the largest R_{ct} within the duty-cycle series, supporting its selection under the investigated background parameters. At duty cycles of 30%–40%, the extended T_{on} and shorter T_{off} limited diffusion-layer recovery. The surfaces became rougher and visible nodular features reappeared. These morphological changes are considered together with the EIS results in Section 3.8; they are not interpreted as a direct quantitative measurement of total porosity.

The duty cycle regulates the deposited charge during T_{on} and the time available for diffusion-layer recovery during T_{off} . Considering the thickness, E_{corr} , FE-SEM morphology, and EIS response together, 22% is identified as the favorable duty cycle for the present system. This conclusion is limited to the tested background parameters and does not imply a direct measurement of residual stress or coating density.

3.5. Effect of Forward Current Density on the Surface Morphology of Au Deposits

As shown in Figure 4, increasing the forward current density from 0.06 to 0.20 A·dm^{−2} produces a non-linear change in surface morphology. At 0.06 A·dm^{−2}, the surface consists of fine but relatively loosely distributed features, with local depressions and incomplete-looking coverage. This is consistent with a low cathodic driving force and a limited deposition rate under the fixed plating time. At 0.11 A·dm^{−2}, the surface is comparatively smooth and uniform, with equiaxed features and fewer visible nodules than at the lower and higher current densities. The corresponding EDS map shows a spatially continuous Au signal over the analyzed area. The morphology suggests a useful balance between cathodic nucleation and ion supply, but it does not constitute a direct measurement of total porosity or coating density. When the forward current density is increased to 0.15–0.20 A·dm^{−2}, larger nodules and multi-level surface features become more pronounced. The higher cathodic charge increases the Au deposition rate and coating thickness, while local mass-transfer limitation can promote non-uniform growth [22,24]. Correspondingly, the increase in at high current density cannot be separated from the barrier contribution of the thicker Au layer.

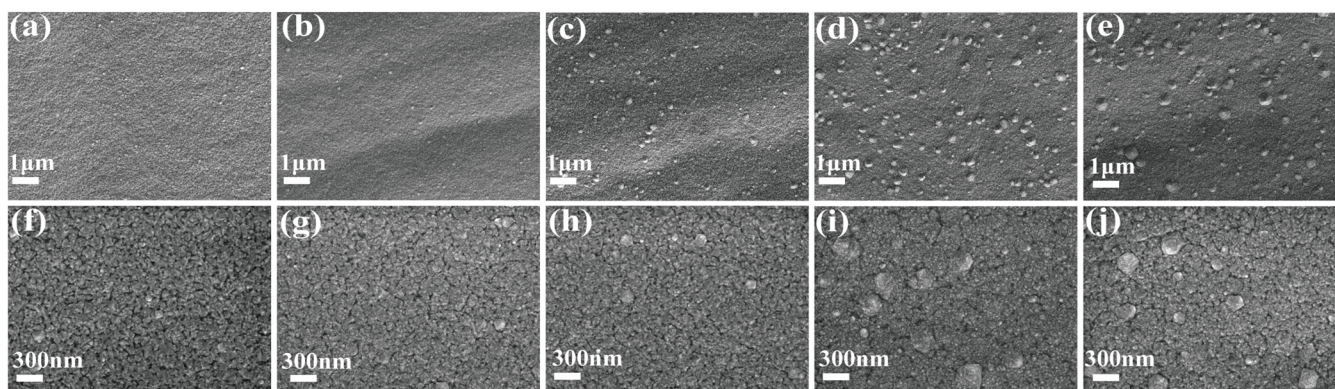


Figure 4. FE-SEM surface morphology of Au coatings deposited at (a,f) 0.06, (b,g) 0.08, (c,h) 0.11, (d,i) 0.15, and (e,j) 0.20 A·dm^{−2} forward current density; panels (a–e) and (f–j) are low- and high-magnification images, respectively. Frequency, duty cycle, and j_r were fixed at 800 Hz, 22%, and -0.004 A·dm^{−2}.

Within the intended Au thickness range, 0.11 A·dm^{−2} provides the most balanced combination of surface uniformity, E_{corr} , and coating thickness. Lower current density gives less complete-looking coverage, whereas higher current density increases thickness and R_{ct} but also produces more nodular surface development. The selected value is therefore a multicriteria processing condition rather than the current density that maximizes a single electrochemical parameter.

The forward-current-density series demonstrates that coating morphology and impedance are jointly influenced by cathodic driving force, mass transport, and deposited thickness. Because thickness increases with current density, the present single-factor data do not permit the intrinsic interfacial effect of current density to be isolated completely.

3.6. Effect of Reverse Current Density on the Surface Morphology of Au Deposits

As shown in Figure 5, increasing the reverse current density (anodic segment) from -0.002 to -0.005 A·dm^{−2} markedly intensifies the competition between anodic dissolution and cathodic renucleation during pulse-reverse deposition, giving rise to a characteristic “improvement followed by deterioration” in the microstructure and interfacial characteristics of the Au deposit.

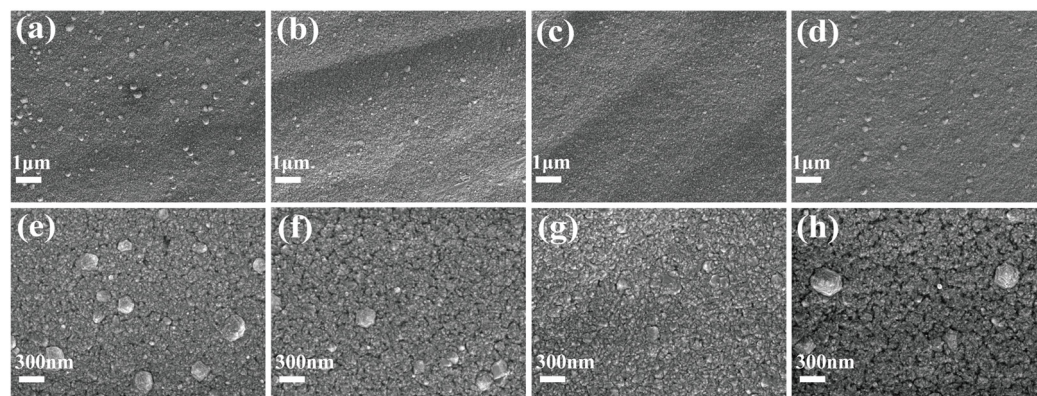


Figure 5. FE-SEM surface morphology of Au coatings deposited at (a,e) -0.002 , (b,f) -0.003 , (c,g) -0.004 , and (d,h) -0.005 $\text{A}\cdot\text{dm}^{-2}$ reverse current density; panels (a–d) and (e–h) are low- and high-magnification images, respectively. Frequency, duty cycle, and j_p were fixed at 800 Hz, 22%, and 0.11 $\text{A}\cdot\text{dm}^{-2}$.

At -0.002 $\text{A}\cdot\text{dm}^{-2}$, the anodic segment is weak and the surface retains non-uniform nodules and local depressions. At -0.003 $\text{A}\cdot\text{dm}^{-2}$, the nodular features are reduced and the distribution becomes more uniform, consistent with a moderate leveling/reactivation effect during the reverse pulse [9,12,27]. These observations describe visible surface features only and should not be interpreted as a quantitative measurement of coating porosity.

At -0.004 $\text{A}\cdot\text{dm}^{-2}$, the coating exhibits the most uniform and comparatively smooth surface in the reverse-current series, with fewer visible nodules and openings. This morphology is consistent with moderate anodic leveling followed by renewed cathodic nucleation. The refitted EIS results, however, give $R_{ct} = 423.3$ $\Omega\cdot\text{cm}^2$ at -0.004 $\text{A}\cdot\text{dm}^{-2}$, whereas -0.005 $\text{A}\cdot\text{dm}^{-2}$ gives the largest R_{ct} (770.4 $\Omega\cdot\text{cm}^2$). The latter condition also shows more pronounced surface roughening and agglomeration. Thus, the larger R_{ct} at -0.005 $\text{A}\cdot\text{dm}^{-2}$ does not by itself establish the most favorable overall coating response. The -0.004 $\text{A}\cdot\text{dm}^{-2}$ condition was selected from the combined evidence of E_{corr} , target thickness, surface morphology, and impedance behavior, rather than from R_{ct} alone.

Taken together, Figures 2–5 show that the favorable parameter window produces a finer and more continuous Au surface with fewer visible nodules and surface openings. Frequency and duty cycle regulate the pulse period and T_{on}/T_{off} durations, the forward current density controls cathodic charge input, and the reverse current density controls anodic dissolution. These observations are limited to surface morphology: neither FE-SEM nor the available AFM data provide a direct measurement of coating density or total porosity.

3.7. Response Surface Analysis of Coupled Pulse Parameters

To further evaluate the coupling among pulse frequency, duty cycle, forward current density, and reverse current density, RSM was performed using corrosion potential as the response value. The experimental results were fitted by multiple regression analysis using Design-Expert 13. In the regression model, A, B, C, and D are dimensionless coded variables corresponding to pulse frequency, duty cycle, forward current density, and the magnitude of reverse current density, respectively. Their actual values at the coded levels of -1 , 0 , and $+1$ are listed in Table S4. The second-order regression equation in terms of coded factors was obtained as follows:

$$Y = -0.1038 - 0.0001A + 0.0008B + 0.002C - 0.0001D - 0.0005AB - 0.0011AC \\ - 0.0003AD - 0.0004BC - 0.001BD + 0.0006CD - 0.0124A^2 - 0.0131B^2 \\ - 0.0147C^2 - 0.014D^2$$

Because A, B, C, and D are dimensionless, all coefficients in the coded regression equation have the same unit as E_{corr} , i.e., V vs. SCE.

The reliability and accuracy of the regression model were evaluated by analysis of variance (ANOVA) using Design-Expert 13. The ANOVA results for the corrosion-potential model are presented in Table 3. The coefficient of determination, R^2 , was used to evaluate the agreement between the predicted and experimental values. The value of R^2 ranges from 0 to 1, with a value closer to 1 indicating a smaller deviation between the fitted model and the experimental results. The R^2 value of the present model was 0.9872, demonstrating excellent agreement between the predicted and experimental corrosion potentials. The model therefore adequately describes the relationship between the corrosion potential of the coating and the investigated pulse parameters. The p value was used to evaluate the statistical significance of the model and individual model terms. A smaller p value indicates a stronger statistical relationship between the corresponding factor and the response. A model term is generally considered statistically significant when $p < 0.05$, whereas a value of $p > 0.05$ indicates that the term is not statistically significant.

Table 3. Analysis of variance for the corrosion-potential regression model.

Scheme	Sum of Squares	df	Mean Square	F-Value	p -Value	
Model	0.0020000000	14	0.0001000000	66.18	<0.0001	significant
A, f	0.00000005333	1	0.00000005333	0.0241	0.0380	-
B, duty	0.00000705300	1	0.00000705300	3.19	0.0094	-
C, j_p	0.00000000000	1	0.00000000000	22.43	0.0005	-
D, j_r	0.00000027000	1	0.00000027000	0.1221	0.0329	-
AB	0.00000121000	1	0.00000121000	0.5471	0.4737	-
AC	0.00000529000	1	0.00000529000	2.39	0.1479	-
AD	0.00000036000	1	0.00000036000	0.1628	0.6937	-
BC	0.00000056250	1	0.00000056250	0.2543	0.6232	-
BD	0.00000380200	1	0.00000380200	1.72	0.2143	-
CD	0.00000132200	1	0.00000132200	0.5979	0.4543	-
A^2	0.00080000000	1	0.00080000000	370.51	<0.0001	-
B^2	0.00090000000	1	0.00090000000	411.96	<0.0001	-
C^2	0.00110000000	1	0.00110000000	518.99	<0.0001	-
D^2	0.00100000000	1	0.00100000000	474.02	<0.0001	-
Residual	0.00000000000	12	0.00000221200	-	-	-
Lack of Fit	0.00000000000	10	0.00000265400	796.05	0.5379	not significant
Pure Error	0.00000000666	2	0.00000000333	-	-	-
Cor Total	0.00210000000	26	-	-	-	-

As shown in Table 3, the overall regression model was highly significant ($p < 0.0001$), whereas the lack-of-fit term was not significant ($p = 0.5379$). The non-significant lack of fit indicates that the discrepancy between the fitted model and the experimental data was not significant relative to the pure experimental error. In addition, the Adeq Precision value was 28.3716, which was considerably higher than the recommended minimum value of 4, indicating an adequate signal-to-noise ratio. These statistical results confirm that the regression equation established using corrosion potential as the response is reliable and suitable for navigating the investigated design space. Among the linear terms, factor C was highly significant, with a p value substantially lower than 0.05. Factors A, B, and D were also statistically significant, with p values of 0.0380, 0.0094, and 0.0329, respectively. Based on the relative statistical significance of the linear terms, the influence of the four pulse parameters followed the order:

$$C > B > D > A$$

where A, B, C, and D represent frequency, duty cycle, forward current density, and reverse current density, respectively.

Figure 6 shows the response surface plots for the pairwise interactions among the four pulse parameters. All response surfaces exhibit a dome-like profile, indicating that the corrosion potential does not vary monotonically with any single parameter. Instead, a more favorable corrosion response is obtained within an intermediate parameter region. As shown in Figure 6a, when the forward and reverse current densities were fixed, the corrosion potential first shifted in the noble direction and then shifted negatively with increasing frequency and duty cycle. This indicates that an appropriate pulse period and $T_{\text{on}}/T_{\text{off}}$ ratio are necessary to balance cathodic nucleation and diffusion-layer recovery. At low frequency or low duty cycle, insufficient nucleation or incomplete surface coverage may occur, whereas excessively high frequency or duty cycle may restrict ion replenishment and promote concentration polarization. Similar non-monotonic trends are observed for the interactions of duty cycle with forward and reverse current density (Figure 6b,c). A moderate forward current density can increase the cathodic nucleation rate, whereas excessive cathodic current intensifies local $[\text{Au}(\text{CN})_2]^-$ depletion. A moderate reverse segment can contribute to surface leveling and reactivation, while a stronger anodic segment can increase dissolution and surface heterogeneity. Because E_{corr} was the sole RSM response, these mechanistic interpretations are considered together with the independently measured thickness and FE-SEM results rather than inferred from the response surface alone.

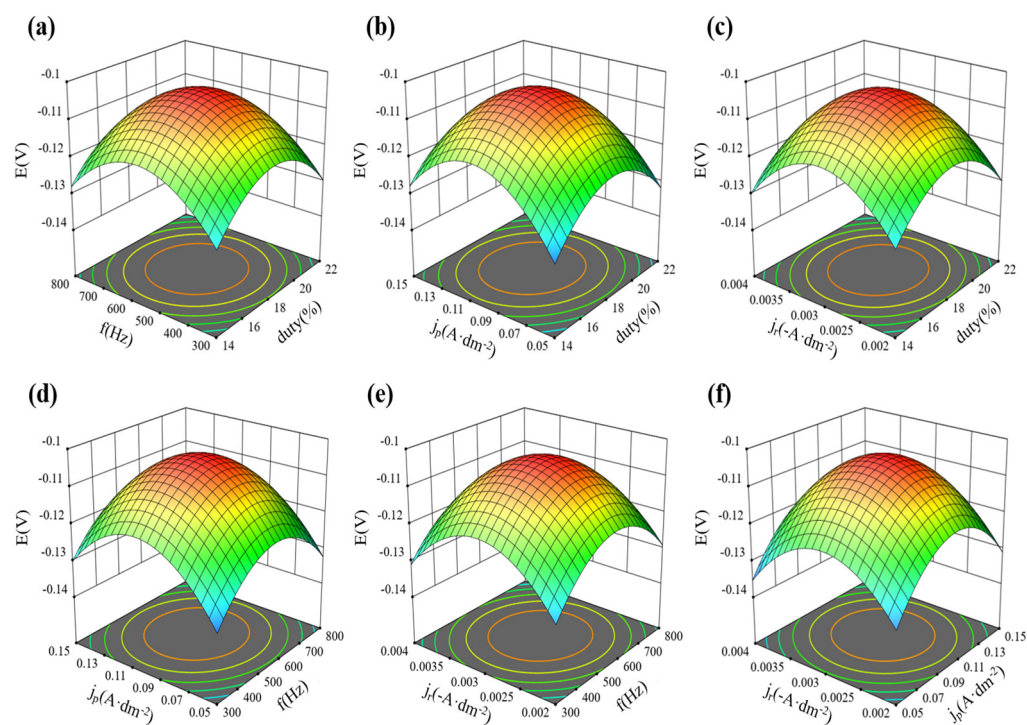


Figure 6. Response-surface plots for E_{corr} (V vs. SCE): (a) f (Hz)–duty (%), (b) j_p ($\text{A}\cdot\text{dm}^{-2}$)–duty (%), (c) j_r ($-\text{A}\cdot\text{dm}^{-2}$)–duty (%), (d) j_p ($\text{A}\cdot\text{dm}^{-2}$)– f (Hz), (e) j_r ($-\text{A}\cdot\text{dm}^{-2}$)– f (Hz), and (f) j_r ($-\text{A}\cdot\text{dm}^{-2}$)– j_p ($\text{A}\cdot\text{dm}^{-2}$). In each panel, the two unplotted factors were fixed at their center levels.

Based on the RSM optimization, the favorable pulse condition was predicted to be 850 Hz frequency, 22% duty cycle, $0.12 \text{ A}\cdot\text{dm}^{-2}$ forward current density, and $-0.004 \text{ A}\cdot\text{dm}^{-2}$ reverse current density. This predicted condition is close to the selected combined pulse condition obtained from the single-factor experiments, i.e., 800 Hz, 22%, $0.11 \text{ A}\cdot\text{dm}^{-2}$, and $-0.004 \text{ A}\cdot\text{dm}^{-2}$. For practical operation and consistency with the experimentally tested parameter levels, 800 Hz, 22%, $0.11 \text{ A}\cdot\text{dm}^{-2}$, and $-0.004 \text{ A}\cdot\text{dm}^{-2}$ were

selected for subsequent structural and electrochemical characterization. The RSM results therefore support the interpretation that the favorable corrosion response originates from a coupled pulse window rather than from an isolated single-parameter effect.

3.8. Effect of Pulse Parameters on the EIS Response of Au Coatings

For the frequency series (Figure 7a), R_{ct} was 419.3, 778.9, 423.3, and 874.6 $\Omega \cdot \text{cm}^2$ at 300, 500, 800, and 1000 Hz, respectively. The relatively low value at 300 Hz is consistent with prolonged growth and heterogeneous coverage. The larger values at 500 and 1000 Hz indicate slower apparent charge transfer, but the 1000 Hz surface showed more pronounced agglomeration. Therefore, R_{ct} alone does not identify 800 Hz as the best frequency; 800 Hz was retained because its morphology and E_{corr} provided a more balanced response within the investigated range. As summarized in Table S6, R_s remained within a relatively narrow range of 4.16–4.96 $\Omega \cdot \text{cm}^2$, while the CPE exponent n varied from 0.797 to 0.869, indicating comparable solution resistance and a similarly non-ideal capacitive response across the frequency series. In contrast, both R_{ct} and R_W were substantially higher at 500 and 1000 Hz than at 300 and 800 Hz, showing that pulse frequency affected both the apparent charge-transfer process and the finite-diffusion contribution, although neither parameter alone determined the selected frequency.

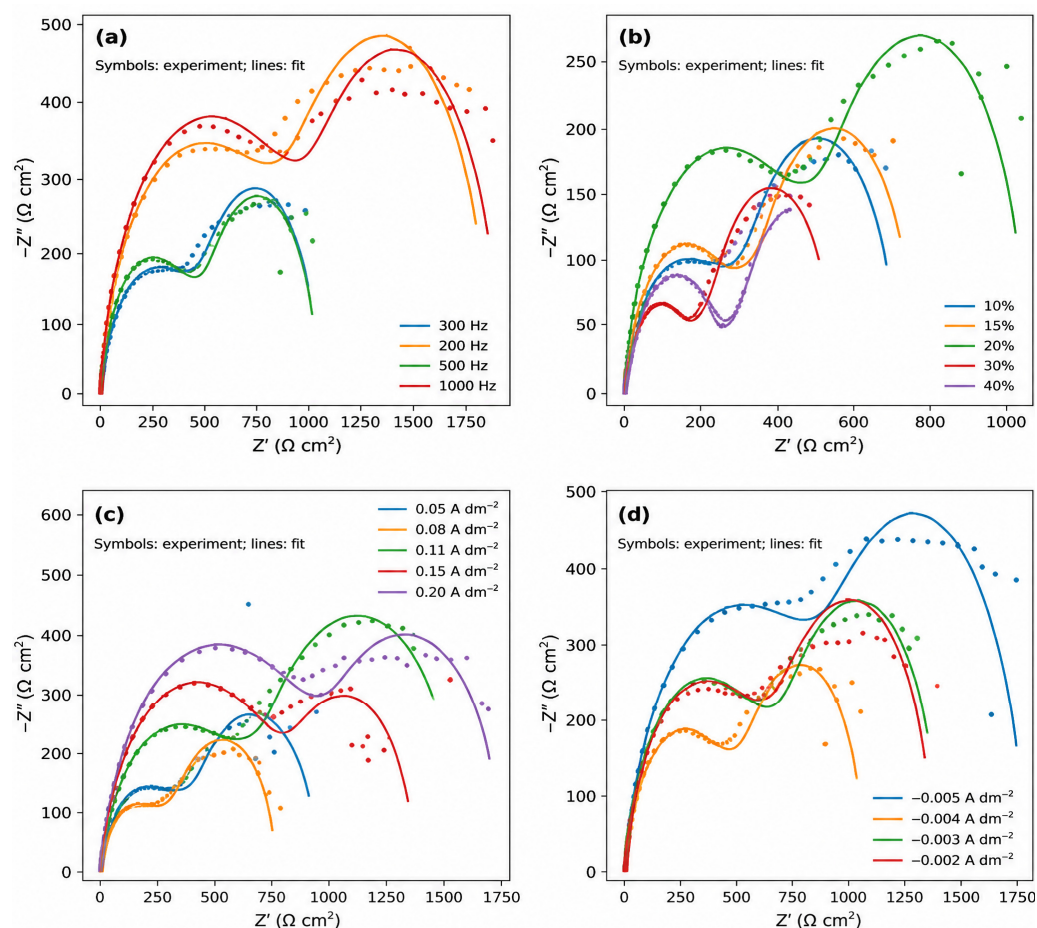


Figure 7. Experimental Nyquist spectra (open symbols) and fitted curves (solid lines) for Au coatings deposited under different (a) pulse frequencies, (b) duty cycles, (c) forward current densities, and (d) reverse current densities. The spectra were fitted with $Rs-[CPE||(R_{ct} + W_s)]$.

For the duty-cycle series (Figure 7b), R_{ct} increased from 252.2 and 271.6 $\Omega \cdot \text{cm}^2$ at 10% and 15% to 423.3 $\Omega \cdot \text{cm}^2$ at 22%, then decreased to 161.2 and 246.3 $\Omega \cdot \text{cm}^2$ at 30% and 40%. This non-monotonic behavior supports an intermediate T_{on}/T_{off} window: low duty

cycles provide limited cathodic charge, whereas high duty cycles shorten diffusion-layer recovery and intensify concentration polarization. In this series, the electrochemical and morphological criteria converge at 22%. Table S7 shows a pronounced non-monotonic dependence of the fitted parameters on duty cycle. The coating deposited at 22% exhibited the largest R_{ct} and R_W together with the highest n value, whereas the 40% condition showed the lowest n and a markedly longer T_W , consistent with increased interfacial heterogeneity and slower low-frequency relaxation at an excessive duty cycle.

For the forward-current-density series (Figure 7c), R_{ct} was 332.1, 245.9, 568.1, 734.5, and 878.4 $\Omega \cdot \text{cm}^2$ from 0.06 to 0.20 $\text{A} \cdot \text{dm}^{-2}$. The increase above 0.08 $\text{A} \cdot \text{dm}^{-2}$ partly follows the measured increase in Au thickness and therefore cannot be attributed solely to a change in intrinsic interfacial kinetics. At 0.11 $\text{A} \cdot \text{dm}^{-2}$, the coating combines a relatively noble E_{corr} with a comparatively uniform surface and a moderate thickness, whereas the higher-current coatings have larger R_{ct} values together with thicker and more nodular deposits. As shown in Table S8, R_{ct} increased from 245.9 $\Omega \cdot \text{cm}^2$ at 0.08 $\text{A} \cdot \text{dm}^{-2}$ to 878.4 $\Omega \cdot \text{cm}^2$ at 0.20 $\text{A} \cdot \text{dm}^{-2}$, while Q generally decreased with increasing forward current density. Because the Au thickness also increased substantially in this series, the larger R_{ct} values at 0.15–0.20 $\text{A} \cdot \text{dm}^{-2}$ cannot be attributed solely to improved intrinsic interfacial kinetics, and the non-monotonic variations in R_W and T_W further indicate concurrent changes in the diffusion-related response.

For the reverse-current-density series (Figure 7d), R_{ct} was 561.3, 578.4, 423.3, and 770.4 $\Omega \cdot \text{cm}^2$ at -0.002 , -0.003 , -0.004 , and -0.005 $\text{A} \cdot \text{dm}^{-2}$, respectively. The largest R_{ct} at -0.005 $\text{A} \cdot \text{dm}^{-2}$ does not coincide with the most favorable morphology or E_{corr} . The -0.004 $\text{A} \cdot \text{dm}^{-2}$ condition was selected because moderate anodic reactivation produced a more uniform surface without the stronger roughening observed at -0.005 $\text{A} \cdot \text{dm}^{-2}$. This result again shows that R_{ct} should be interpreted together with thickness, morphology, and polarization behavior. Table S9 shows that Q and n varied within relatively narrow ranges, whereas R_{ct} and R_W changed markedly with reverse current density. The -0.005 $\text{A} \cdot \text{dm}^{-2}$ condition gave the largest R_{ct} and R_W , but its less favorable surface morphology and E_{corr} indicate that this electrical maximum does not represent the most balanced coating response; therefore, -0.004 $\text{A} \cdot \text{dm}^{-2}$ was retained on the basis of the combined electrochemical and morphological evidence.

The Nyquist spectra contain overlapping depressed features and a low-frequency turnover, indicating coupled interfacial charge transfer, non-ideal capacitance, and finite diffusion [20,21]. The $R_s-[CPE||(R_{ct} + W_s)]$ circuit reproduced the dominant response with reduced weighted χ^2 values of 1.98×10^{-4} – 1.95×10^{-3} and weighted RMSE values of 1.37%–4.31%.

An independently prepared specimen tested under the same nominal center condition (800 Hz, 22% duty cycle, 0.11 $\text{A} \cdot \text{dm}^{-2}$, and -0.004 $\text{A} \cdot \text{dm}^{-2}$) yielded $R_{ct} = 568.1$ $\Omega \cdot \text{cm}^2$, compared with 423.3 $\Omega \cdot \text{cm}^2$ for the center-condition specimen shared across the frequency, duty-cycle, and reverse-current series. The repeated appearance of the latter spectrum in those three series represents reuse of the same center-condition measurement for within-series comparison rather than three independent replicates. The difference between the two independently prepared specimens indicates measurable specimen-to-specimen variability and further supports interpreting morphology, thickness, E_{corr} , and EIS together rather than R_{ct} alone.

Overall, the refitted spectra do not identify a condition that maximizes every electrical parameter. The selected combination of 800 Hz, 22%, 0.11 $\text{A} \cdot \text{dm}^{-2}$, and -0.004 $\text{A} \cdot \text{dm}^{-2}$ should therefore be described as a multicriteria processing window, not as the condition with the universally highest R_{ct} . The finite-length Warburg parameters further indicate that the low-frequency response varies with both diffusion resistance and characteristic

diffusion time, consistent with changes in coating thickness, defect pathways, and access of the electrolyte to the Ni/Au interface [20,28].

3.9. Coating Structure and Roughness Under the Selected Combined Pulse Condition

Figure 8 compares grazing-incidence XRD patterns from six representative pulse conditions. The reflections near 38.2° , 44.4° , 64.6° , 77.5° , and 81.7° correspond to fcc Au (111), (200), (220), (311), and (222), respectively (Au PDF No. 98-000-0062). The weak feature near 51.8° is assigned to fcc Ni(200) from the $4.45\text{ }\mu\text{m}$ Ni underlayer (Ni PDF No. 04-0850). In addition, Au(200) overlaps with Ni(111) near $44.4\text{--}44.5^\circ$, and Au(311) partially overlaps with Ni(220) near $76.4\text{--}77.5^\circ$. No additional crystalline Au–Co or intermetallic phase was detected within the sensitivity of the measurement.

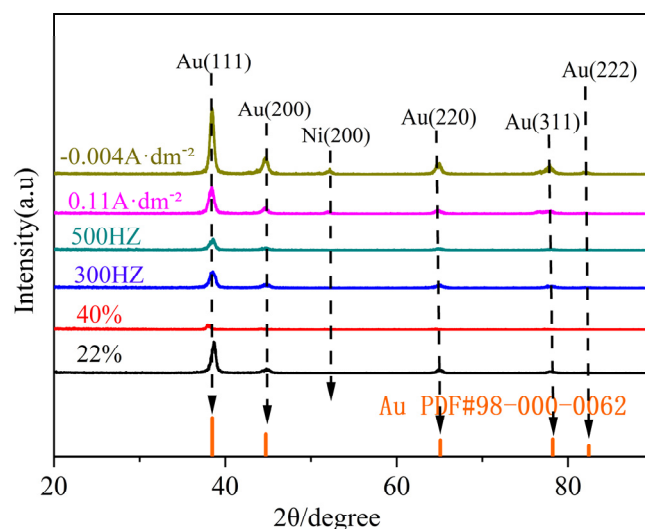


Figure 8. Grazing-incidence XRD patterns of representative Au coatings deposited at 22% and 40% duty cycle, 300 and 500 Hz, $0.11\text{ A}\cdot\text{dm}^{-2}$ forward current density, and $-0.004\text{ A}\cdot\text{dm}^{-2}$ reverse current density. Dashed lines identify fcc Au reflections.

Although most of the representative Au coatings had comparable thicknesses, their diffraction intensities differed. Diffraction intensity is governed not only by coating thickness but also by preferred orientation, coherent-domain structure, surface morphology, grazing-incidence alignment, and the fraction of crystallites satisfying the diffraction condition. In addition, the Au(200) and Au(311) reflections partly overlap with the Ni(111) and Ni(220) reflections from the underlayer. Therefore, the absolute peak intensities were not quantitatively compared, and the present analysis focuses on phase identification and the width of the Au(111) reflection.

Pseudo-Voigt fitting of the Au(111) envelope gave uncorrected FWHM values of $0.551\text{--}0.800^\circ$ and apparent D_{111} values of $10.5\text{--}15.3\text{ nm}$ (Table S10 and Figure 9). The $-0.004\text{ A}\cdot\text{dm}^{-2}$ specimen had the narrowest Au(111) envelope and the largest apparent coherent-domain size (15.3 nm), whereas the 300 and 500 Hz specimens gave values near $10.5\text{--}10.6\text{ nm}$. Thus, the selected corrosion-resistant condition does not correspond to the smallest coherent domain, and its performance should not be attributed to crystallite refinement alone. SEM particle dimensions and XRD coherent-domain size describe different structural scales [29]. Quantitative residual stress was not calculated because no internal standard or instrumental-broadening reference was measured and the GIXRD peak positions are susceptible to sample-height/zero-shift effects and Au/Ni peak overlap.

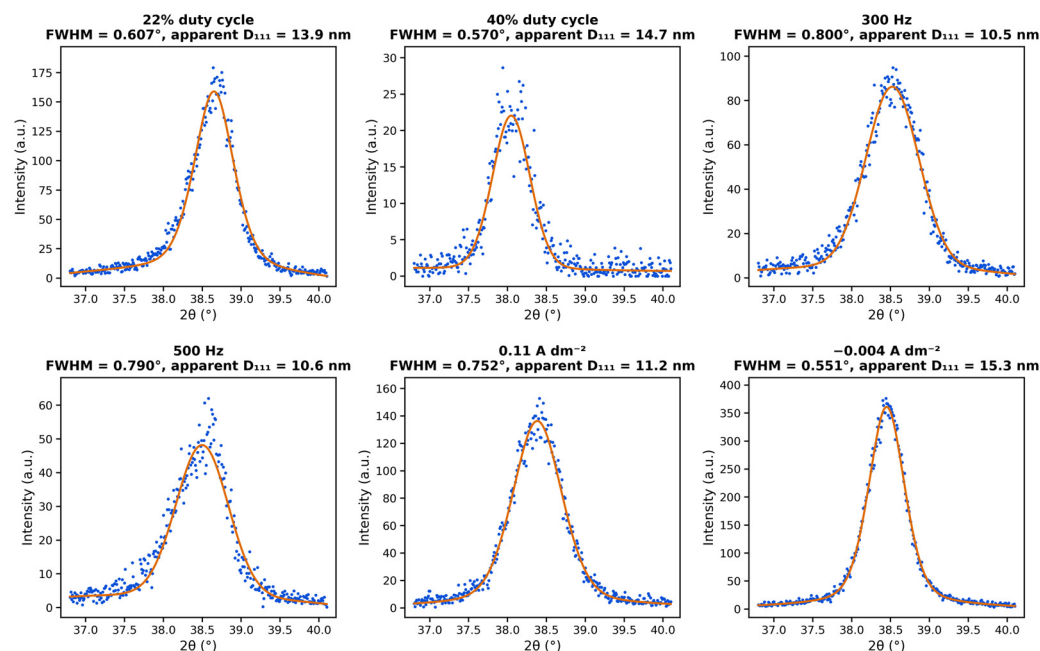


Figure 9. Pseudo-Voigt fits of the Au(111) envelope for the six representative pulse conditions. Open symbols are experimental data and solid lines are fitted envelopes.

The average thickness of the Ni underlayer, independently determined by five-position XRF measurements, was approximately 4.45 μm . The Ni underlayer therefore provided a continuous intermediate layer between the brass substrate and the Au coating in the examined specimens. However, the present cross-sectional observations do not directly quantify elemental interdiffusion, coating density, or total porosity. The two-dimensional AFM height maps provide a more direct comparison with the top-view SEM images. The four independently prepared specimens deposited under the nominally selected pulse condition exhibited an average R_q of 15.23 ± 3.10 nm ($n = 4$, mean $\pm$ standard deviation) ($n = 4$, indicating four sample groups), indicating moderate specimen-to-specimen variation in nanoscale surface roughness. The moderate variation among the specimens indicates a generally reproducible nanoscale surface roughness, although localized protrusions remained visible in several regions. Because the roughness of the untreated brass substrate and the Ni-only underlayer was not measured, the present AFM results are limited to comparisons among the Au-coated specimens and do not demonstrate a quantitative reduction in roughness relative to the substrate.

Figure 10 compares the top-view morphology, cross-sectional structure, and two-dimensional surface topography of the coatings obtained at the selected levels of the four single-factor series. The cross-sectional SEM images reveal a continuous Au layer on the Ni underlayer, with local Au-layer thicknesses of approximately 0.44–0.45 μm . No obvious through-thickness cracks or interfacial delamination were observed within the examined regions.

The comparatively low roughness under the selected condition is consistent with the coordinated influence of cathodic deposition, diffusion-layer recovery, and reverse-pulse dissolution. At 800 Hz and 22% duty cycle, the waveform retains both a cathodic deposition interval and an off-time for ion replenishment. The forward current density of $0.11 \text{ A} \cdot \text{dm}^{-2}$ provides sufficient cathodic driving force without the pronounced nodular development observed at higher current density, while the $-0.004 \text{ A} \cdot \text{dm}^{-2}$ reverse segment can remove protruding material and reactivate the surface. These interpretations are consistent with the reduced surface-height variation, but the present data do not directly resolve nucleation density, grain-boundary structure, or through-porosity [9,12,27].

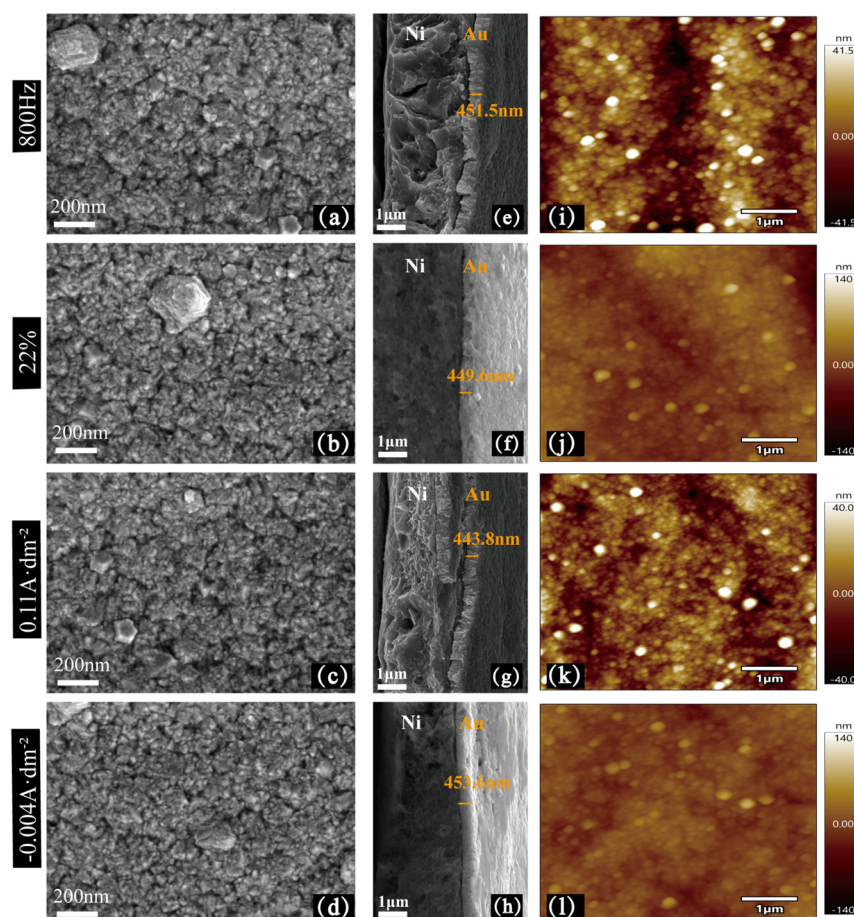


Figure 10. Top-view FE-SEM images (a–d), cross-sectional FE-SEM images (e–h), and two-dimensional AFM height maps (i–l) of four independently prepared Au coatings deposited under the same nominal pulse condition: 800 Hz frequency, 22% duty cycle, $j_p = 0.11 \text{ A} \cdot \text{dm}^{-2}$, and $j_r = -0.004 \text{ A} \cdot \text{dm}^{-2}$. The rows correspond to specimens originating from the frequency, duty-cycle, forward-current-density, and reverse-current-density series, respectively. The local Au-layer thicknesses are indicated in panels (e–h). The AFM scan area was $25.6 \mu\text{m}^2$, and the color bars show the surface-height coordinate, z , in nanometers.

The AFM and SEM observations are consistent with a comparatively smooth and continuous surface under the selected condition. This morphology can reduce the number of visible defect pathways and localized active sites, but the present measurements do not quantify coating density or total through-porosity.

3.10. Structure-Corrosion Relationship of the Pulse-Plated Au Coatings

The corrosion response of the thin Au coating reflects the combined influence of thickness, surface morphology, roughness, crystallographic phase, coating continuity, and impurity incorporation [28,30–32]. Thickness provides a barrier contribution, but the duty-cycle data show that coatings with the same average thickness can exhibit different E_{corr} values. FE-SEM and AFM indicate that the selected condition produces a comparatively uniform surface with fewer visible nodules. XRD identifies metallic Au as the dominant crystalline phase, and EDS does not detect Co at the measurement limit. The improved response is therefore attributed to the combined effects of adequate Au thickness, surface continuity, reduced roughness, and fewer visible defects rather than to an Au–Co alloy or to thickness alone.

The scope of the conclusions is limited by the available measurements. The selected condition is also specific to the present bath composition, brass/Ni substrate, electrode

geometry, temperature, and power supply. Changes in these factors may shift the favorable pulse window.

4. Conclusions

This study establishes a system-specific pulse-reverse deposition window for producing thin Au coatings on a standardized Ni barrier layer. Across the tested conditions, corrosion behavior was governed by the combined effects of Au thickness, waveform-dependent surface development, and interfacial response rather than by any single pulse parameter.

1. The selected Ni underlayer had an average thickness of approximately 4.45 μm . For the Au layer, 800 Hz, 22% duty cycle, 0.11 $\text{A}\cdot\text{dm}^{-2}$ forward current density, and $-0.004 \text{ A}\cdot\text{dm}^{-2}$ reverse current density satisfied the target 0.3–0.6 μm thickness range and provided the most balanced E_{corr} , surface morphology, roughness, and impedance response. This condition did not maximize R_{ct} in every series, confirming that R_{ct} alone is not an appropriate optimization criterion when coating thickness varies.
2. The response-surface analysis supports interaction among the four pulse variables, while XRD and EDS identify metallic Au as the principal phase and show no detectable Co incorporation. AFM measurements on four independently prepared coatings gave an average R_{q} of $15.23 \pm 3.10 \text{ nm}$.
3. These findings provide process guidance for the investigated bath and electrode configuration. They do not establish a universal optimum, directly quantify coating density or total porosity.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/coatings16080926/s1>, Section S1: Ni-underlayer preparation, thickness, morphology, and corrosion potential; Section S2: Representative EDS maps and quantitative compositions; Section S3: Response-surface design and statistical outputs; Section S4: Complete EIS fitting parameters, confidence intervals, Bode fits, and residuals; Section S5: Au(111) peak fitting and apparent coherent-domain size.

Author Contributions: Conceptualization, X.O. and F.S.; methodology, X.O.; investigation, X.O.; writing—original draft preparation, X.O.; writing—review and editing, F.S.; supervision, F.S., Y.S. and H.L.; funding acquisition, F.S. All authors have read and agreed to the published version of the manuscript.

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