

Article

Corrosion Resistance, Adhesion Strength, and Electrical Conductivity of 316L Bipolar Plates Treated with Combined Plasma Nitriding and TiN Coating

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Abstract

To enhance the corrosion resistance, adhesion strength, and electrical conductivity of bipolar plates for proton exchange membrane fuel cells (PEMFCs), a duplex surface treatment comprising plasma nitriding (PN) followed by arc ion plating of a TiN coating was applied to 316L stainless steel. The duplex coating exhibited a bilayer structure with a TiN top layer ($\sim 1.3 \mu\text{m}$) and a nitrided diffusion layer ($\sim 9.2 \mu\text{m}$). Compared with a single TiN coating, it showed superior corrosion resistance in both cathode and anode environments, with corrosion current densities of 0.069 and $0.422 \mu\text{A}\cdot\text{cm}^{-2}$, respectively, and maintained stable performance over $10,000$ s of potentiostatic polarization. Its interfacial contact resistance at $140 \text{ N}\cdot\text{cm}^{-2}$ was $7.84 \text{ m}\Omega\cdot\text{cm}^2$, below the Department of Energy (DOE) 2025 target of $10 \text{ m}\Omega\cdot\text{cm}^2$. The water contact angle also increased, benefiting water management. The nitrided interlayer substantially enhanced the adhesion strength of the TiN coating. These findings confirm that the sequential combination of plasma nitriding and TiN coating is an effective strategy for improving the corrosion resistance, electrical conductivity, and adhesion of stainless steel bipolar plates for PEMFC applications.

Keywords: PEMFC; 316L; plasma nitriding; TiN; arc ion plating; adhesion strength

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been widely studied as a zero-emission power source for automotive applications [1]. Bipolar plates constitute a critical component of PEMFCs in terms of weight, cost, and stack durability [2–4]. Metallic bipolar plates offer advantages over conventional graphite, including better formability, higher mechanical strength, and lower material cost [5]. Among various metallic materials, austenitic stainless steel [6] is one of the most extensively investigated bipolar plate substrates, yet its long-term service is limited by surface corrosion [2] in the aggressive PEMFC environment (acidic pH, fluoride ions, and temperature over 80°C) [7,8]. Corrosion not only degrades the plate itself but also increases the interfacial contact resistance (ICR) [9,10], directly reducing cell output [11]. Surface engineering is therefore required to achieve both corrosion resistance and electrical conductivity.

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In recent decades, several surface modification methods and coatings have been developed to protect metallic bipolar plates, with transition metal nitrides, carbon-based films, and conductive polymers being the most frequently investigated [6,12]. Several studies [13–16] on carbon-based films have demonstrated that, through approaches such as multilayer films (e.g., TiN/amorphous carbon double layers) or metal doping (e.g., with Cr and Ag), the ICR of amorphous carbon (a-C) coatings can be reduced to below 5 $\text{m}\Omega\cdot\text{cm}^2$, complying with the Department of Energy (DOE) standard ($\text{ICR} < 10 \text{ m}\Omega\cdot\text{cm}^2$). However, the poor adhesion between a-C coatings and stainless steel substrates due to thermal expansion mismatch remains a persistent challenge [6,17]. Conductive polymers have drawn much attention due to their low-cost synthesis and flexibility, but their commercial application is limited by their intrinsic porosity and limited long-term stability in acidic environments [18–20]. In contrast, transition metal nitride coatings have gained wider acceptance due to their balanced performance in conductivity, corrosion resistance, and cost [11,21]. Single-layer TiN or CrN deposited by physical vapor deposition (PVD) typically exhibits a corrosion current density of $0.85 \mu\text{A}\cdot\text{cm}^{-2}$ and an ICR of around $10 \text{ m}\Omega\cdot\text{cm}^2$ [22–24]; multilayered architectures, such as CrN/ZrN or TiN/TiAlN, can further reduce ICR to below $10 \text{ m}\Omega\cdot\text{cm}^2$ while improving durability [24–26]. Nevertheless, several critical shortcomings of nitride coatings have been identified. First, the intrinsic columnar growth morphology leaves pinholes, voids, etc., which act as fast diffusion paths for corrosive media, leading to localized corrosion [27,28]. Second, the presence of such inherent defects can also compromise the adhesion of PVD nitride coatings to the stainless steel substrate, making them prone to delamination under mechanical or thermal stress [29,30]. These limitations call for alternative surface engineering strategies that can overcome these inherent trade-offs and provide more robust protection for metallic bipolar plates.

Duplex surface treatments combining plasma nitriding (PN) with a conductive ceramic top coating (e.g., TiN and CrN) have been widely applied in wear-resistant tools and biomedical devices to enhance surface hardness, corrosion resistance, and biocompatibility [31–33]. Kao et al. [32] applied a low-temperature (390°C) PN process to AISI 316L followed by closed-field unbalanced magnetron sputtering of a TiN thin layer; the duplex treatment significantly improved the tribological properties and electrochemical resistance of the substrate in physiological solutions. Vaca et al. [34] applied PN treatment followed by cathodic arc deposition of Ti/TiN bilayers to 316L via plasma-based ion implantation and deposition; the duplex coatings exhibited improved adhesion compared to conventional PVD TiN, while corrosion resistance (3.5% NaCl solution) was enhanced in all coated samples. Using cathodic cage plasma nitriding combined with PVD TiN on AISI304 steel, Naeem et al. [35] demonstrated that the TiN layer remained adherent without detachment, and the pre-nitriding treatment effectively filled voids and cracks in the subsequent coating, substantially improving corrosion resistance (3.5% NaCl solution).

Despite the valuable insights provided by these prior studies, the potential of duplex coatings for PEMFC bipolar plates remains largely unexplored. The PEMFC environment is considerably more severe than the environments used in previous duplex coating studies. So far, no systematic investigation has been conducted on the corrosion performance of a plasma-nitrided and TiN duplex coating on 316L stainless steel specifically in simulated PEMFC cathode and anode environments. Moreover, previous studies have not performed a systematic evaluation of key parameters governing PEMFC performance—interfacial contact resistance (ICR), surface hydrophobicity, and adhesion strength. It is noteworthy that these prior studies focused on wear resistance or were conducted primarily in physiological environments (3.5% NaCl solution) rather than in the acidic, fluoride-containing electrolyte characteristic of PEMFCs.

In this work, a duplex surface treatment comprising PN followed by cathodic arc ion plating (AIP) of a TiN top coating is applied to 316L stainless steel bipolar plates. This

study presents three key novelties: (i) It is the first systematic investigation of the specific process combination of PN and arc-ion-plated TiN on 316L bipolar plates for PEMFC applications. (ii) It provides a comprehensive evaluation of corrosion resistance in both simulated cathode and anode environments, together with ICR, surface hydrophobicity, and adhesion strength. These parameters are critical for PEMFC performance but have not been collectively assessed in previous duplex studies. Finally, (iii) it establishes a direct comparison between the duplex coating and a single TiN coating to identify the contribution of the nitrided interlayer to the overall performance enhancement. The corrosion resistance in simulated PEMFC cathode and anode environments, electrical conductivity, surface hydrophobicity, and adhesion property of the duplex coating are evaluated and compared with those of a bare 316L substrate and single TiN coating. Through systematic comparison and analysis, this study aims to investigate the enhancement effect of this duplex coating on the overall performance under PEMFC operating conditions and provide a feasible strategy to enhance the long-term durability of 316L bipolar plates, thereby supporting the practical application of PEMFC stacks.

2. Materials and Methods

2.1. Sample Preparation

Commercial 316L austenitic stainless steel plates with dimensions of 50 mm × 50 mm × 1 mm were employed as substrates, and their chemical compositions are shown in Table 1. Prior to surface treatment, the specimens were sequentially ground using SiC abrasive papers, followed by polishing, to achieve a surface roughness of $R_a \sim 0.4 \mu\text{m}$. Thereafter, the polished substrates were ultrasonically cleaned in analytical grade ethanol for 15 min and dried.

Table 1. Chemical composition of 316L stainless steel (wt%).

C	Si	Mn	P	S	Cr	Ni	Mo	Fe
0.0212	0.50	1.336	0.0289	0.0016	16.64	10.04	2.08	Balance

Plasma nitriding was conducted in a DC pulsed plasma nitriding reactor (LDMC-30F) using a pulsed DC power supply at a pulse voltage of 650 V and pulse frequency of 1 kHz. The specimens were first heated to 420 °C over 30 min and then treated at 420 °C for 3 h in a N_2/H_2 atmosphere (flow ratio 2:1) at a working pressure of 150 Pa. After nitriding, the specimens were cooled to room temperature within the chamber over a period of 2 h.

TiN coatings were deposited on both the nitrided 316L and original 316L by arc ion plating (AIP) using a 99.99% pure Ti target. The deposition process consisted of sequential stages: heating, etching, and deposition, followed by in-chamber cooling. Prior to deposition, the chamber was evacuated to a base pressure below 0.005 Pa, and the substrates were gradually heated to a working temperature of 420 °C over 30 min. The substrates were then etched by Ar^+ bombardment for 30 min to remove surface contaminants and promote coating adhesion. The main deposition parameters for both the etching and TiN deposition stages are summarized in Table 2. The total working pressure during deposition was maintained at 1.0 Pa. The coatings were applied to both sides of the specimens. The specimens coated with TiN on original and nitrided 316L were designated as “TiN” and “PN+TiN”, respectively. For reference, the original 316L substrate was designated as “316L”, and the nitrided specimen without a TiN coating was designated as “PN”.

Table 2. Deposition parameters for TiN coating.

Process	Gas Flow (sccm)	Time (min)	Bias (V)	Arc Current (A)	Temperature (°C)	Cool Time (min)
Etching	50 (Ar)	30	−200	60	420	/
TiN	200 (N ₂)	180	−100	80		120

2.2. Coating Characterizations

The phase composition was analyzed by X-ray diffraction (XRD, Panalytical X'Pert³) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 40 mA. The diffraction patterns were recorded over a 2θ range of 20° to 90° with a step size of 0.02° and a scan speed of $2^\circ/\text{min}$. A scanning electron microscope (SEM, ZEISS Sigma 300) equipped with energy-dispersive X-ray spectroscopy (EDS) was employed to investigate the cross-section morphology and coating thickness at 15 kV. EDS linear scanning was used to analyze the main elemental composition of the coatings.

The hydrophobicity of the coating surfaces was evaluated by static water contact angle measurements using a contact angle goniometer (SDC 350KS). Deionized water droplets (approximately $1 \mu\text{L}$ each) were deposited on each sample surface, and the contact angles were measured at five different positions per specimen to obtain an average value.

The adhesion strength of the coatings was assessed by scratch testing using a CSM REVETEST scratch tester. A Rockwell C diamond indenter ($200 \mu\text{m}$ radius) was drawn across the coating surface under a linearly increasing normal load from 100 mN to 20 N at a loading rate of $3.8 \text{ N}\cdot\text{min}^{-1}$ and a displacement speed of $1 \text{ mm}\cdot\text{min}^{-1}$.

2.3. Corrosion Studies and ICR Measurement

Corrosion tests were carried out using a three-electrode electrochemical workstation (CHI660F), with a platinum mesh electrode and a silver/silver chloride electrode (Ag/AgCl, saturated KCl) used as the counter-electrode and reference electrode, respectively. The working electrode was the test specimen with a circular exposed area of 1 cm^2 . All measurements were performed in an electrolyte consisting of 250 mL of an aqueous solution of H_2SO_4 ($\text{pH} = 3$) containing 0.1 ppm HF, maintained at 80°C using a circulating water bath. Prior to each test, the electrolyte was bubbled for 60 min with either hydrogen gas (H_2) to simulate the PEMFC anode environment or with air to simulate the cathode environment. The gas bubbling was maintained throughout the entire electrochemical measurement.

Potentiodynamic polarization tests were conducted separately in the simulated anode and cathode environments. The potential was scanned from -0.5 V to 0.9 V versus the open circuit potential (OCP) at a scan rate of 0.5 mV/s . The corrosion potential (E_{corr}) and the corrosion current density (i_{corr}) were determined by Tafel extrapolation of the polarization curves. Potentiostatic polarization tests were performed at -0.1 V (vs. SCE) for the simulated anode environment and at 0.6 V (vs. SCE) for the simulated cathode environment. The other test conditions were the same as those described for the potentiodynamic measurements. Electrochemical impedance spectroscopy (EIS) was also conducted to further evaluate the anticorrosion performance of the coatings in the simulated cathode environment. The frequency range was from 0.01 Hz to 100 kHz with an AC amplitude of 10 mV . Additionally, 30 min stabilization at the OCP was conducted before all potentiodynamic polarization and EIS tests.

Following the procedure reported in previous papers [36,37], the interfacial contact resistance (ICR) of the specimens was evaluated using an ST2921B bipolar plate resistance

testing system under compressive loads ranging from 10 to 160 N·cm⁻² at intervals of 10 N·cm⁻². During the measurement, the specimen was placed between two copper plates with a piece of carbon paper on each side. A constant current (I) was applied through the assembly, and the voltage drop (V) across the two copper plates was recorded. The total resistance (R_{total}) was then calculated as Equation (1),

$$R_{\text{total}} = \frac{V}{I/S} \quad (1)$$

where S is the contact area of the specimen. This measured resistance includes contributions from two specimen/carbon paper interfaces, two carbon paper/copper plate interfaces, and other resistances (e.g., bulk resistances of the carbon paper and copper plates), with the latter being relatively small and typically neglected. To isolate the resistance of a single sample/carbon paper interface, a reference measurement was performed without the specimen, using only one piece of carbon paper placed directly between the copper plates. The resistance obtained from this reference measurement (R_r) represents the sum of the two carbon paper/copper plate interfaces and other miscellaneous resistances. Therefore, the resistance of a single specimen/carbon paper interface ($R_{S/C}$) was then calculated as follows:

$$R_{S/C} = \frac{R_{\text{total}} - R_r}{2} \quad (2)$$

3. Results and Discussion

3.1. Morphology and Structure

XRD analysis was performed at the surface center of each specimen for phase identification purposes, primarily to confirm the successful formation of the TiN coating and the presence of the expected phases. Figure 1 shows the XRD patterns of the bare 316L substrate and the PN-, TiN-, and PN+TiN-coated specimens. For the PN specimen, distinct diffraction peaks corresponding to the expanded austenite phase (γ_N , also known as the S-phase) were observed. It is well established that, during plasma nitriding, nitrogen atoms diffuse into the austenite lattice. The TiN phase of the TiN and PN+TiN specimens exhibited a face-centered cubic (fcc) structure with a strong (111)-preferred orientation, which is consistent with previous reports on arc-ion-plated TiN films [38]. Notably, several weak γ peaks were also detected in the TiN specimen, whereas the PN+TiN specimen showed only TiN-related diffraction peaks, with no detectable signals from the underlying nitrided layer.

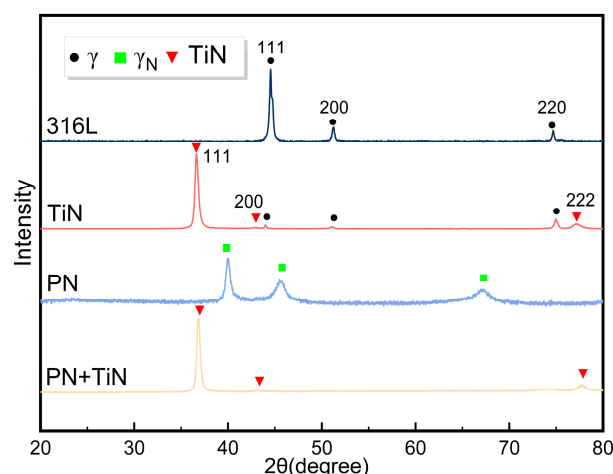


Figure 1. XRD patterns of the bare 316L substrate and the PN-, TiN-, and PN+TiN-coated specimens.

Figure 2 presents the cross-sectional SEM morphologies and EDS elemental depth profiles of the TiN- and PN+TiN-coated specimens. The 1000-times-magnified SEM images in Figure 2(a₀,b₀) reveal distinct surface and interfacial features between the two coatings. The TiN coating in Figure 2(a₀) exhibits a single compact layer of approximately 1.8 μm in thickness deposited directly on the 316L substrate. Numerous microdroplets and pinholes are visible on the coating surface, which are characteristic defects of AIP [27,28]. In contrast, the PN+TiN coating in Figure 2(b₀) shows a multilayer structure, with a TiN top layer of approximately 1.3 μm in thickness and a darker-contrast nitrified diffusion layer of about 9.2 μm beneath it. Notably, the surface of the PN+TiN coating is smoother and more uniform, with fewer microdroplets and pinholes observed. The high-magnification images in Figure 2(a₁,b₁) further reveal the interfacial quality of the two coatings. The TiN coating in Figure 2(a₁) shows the presence of microcracks and localized delamination at the coating/substrate interface. By contrast, the PN+TiN coating in Figure 2(b₁) exhibits a dense and intact interface, where cracks and delamination are rarely observed. The EDS line scans in Figure 2(a₂,b₂) provide the depth distribution of N, Ti, and Fe across the coating cross-sections. For the TiN specimen, the Ti and N signals drop sharply beyond approximately 2 μm in depth, accompanied by a rapid rise in the Fe content to the matrix level, indicating a sharp coating/substrate interface. In contrast, for the PN+TiN specimen, a significant N signal (approximately 10 wt%) persists from about 2 to 11 μm in depth, corresponding to the nitrogen-enriched diffusion layer observed in the cross-sectional SEM morphology.

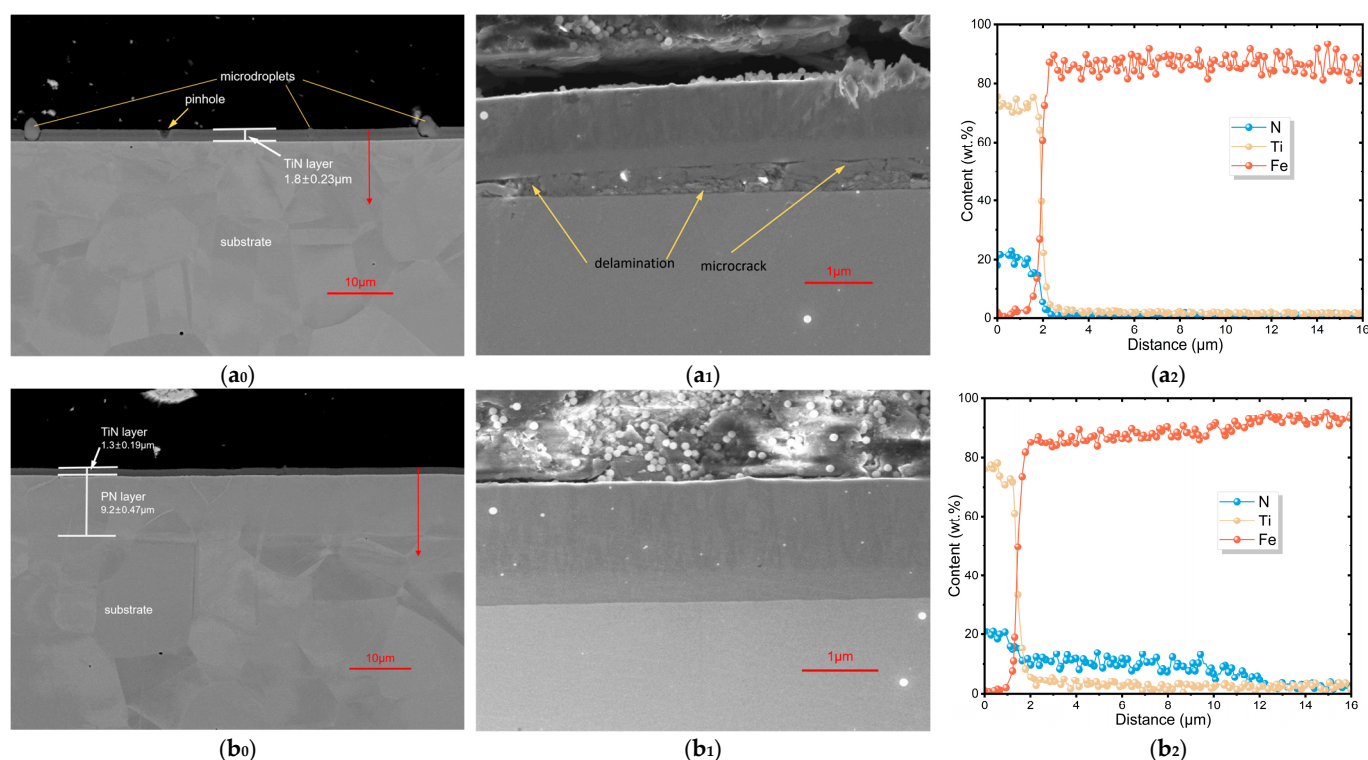


Figure 2. Cross-sectional SEM images of the TiN ((a₀), 1000×; (a₁), 10,000×) and PN+TiN ((b₀), 1000×; (b₁), 10,000×) specimens and EDS elemental depth profiles of the TiN (a₂) and PN+TiN (b₂) specimens.

Notably, the TiN top layer of the PN+TiN specimen (approximately 1.3 μm) is thinner than that of the single TiN specimen (approximately 1.8 μm). However, the PN+TiN coating exhibits significantly fewer defects: microdroplets, pinholes, microcracks, and interfacial delamination are all less frequently observed. This reduction in defect density is consistent with previous reports [33–35] stating that PN pretreatment can effectively reduce

voids and cracks in subsequently deposited PVD TiN coatings. It is also worth noting that, although the TiN coating has a greater thickness, it contains a higher density of structural defects than the PN+TiN coating. This observation suggests that the greater thickness of the TiN coating may be partly attributed to the increased presence of defects, which reduce the compactness and uniformity of the coating structure and may consequently affect the overall coating quality and subsequent performance. The differences in compactness and defect density between the two coatings may also explain why the XRD pattern of the thicker TiN coating still shows weak austenite peaks from the underlying substrate, whereas that of the PN+TiN specimen, despite having a thinner top layer, shows no detectable γ_N signals from the nitrified subsurface. These structural differences between the two coatings suggest that the presence of the nitrified interlayer may influence the subsequent TiN deposition and the resulting coating quality.

3.2. Corrosion Behavior

3.2.1. Potentiodynamic Polarization Tests

To evaluate the corrosion resistance of the specimens, potentiodynamic polarization tests were conducted in the simulated PEMFC cathode and anode environments. Figure 3 presents the potentiodynamic polarization curves of the bare 316L substrate, PN, TiN, and PN+TiN specimens in the simulated PEMFC cathode and anode environments, and the corresponding electrochemical parameters are summarized in Table 1. The protective efficiency (PE) was calculated using the following Equation (3):

$$PE(\%) = 100 \times \left(1 - \frac{i_{\text{corr}}}{i_{\text{corr}}^0}\right) \quad (3)$$

where i_{corr}^0 and i_{corr} are the corrosion current densities of the bare and treated 316L, respectively.

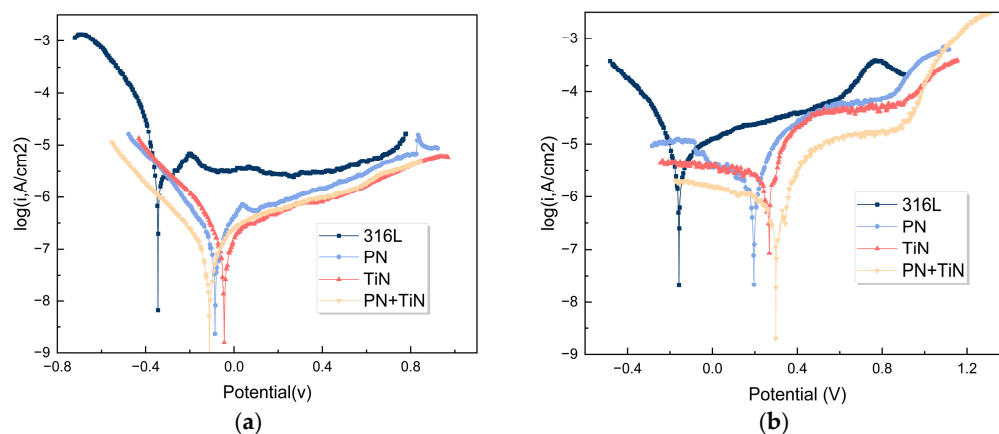


Figure 3. Tafel curves of untreated, PN, TiN, and PN+TiN 316L specimens in simulated PEMFC environment: (a) cathode (air bubbling); (b) anode (H₂ bubbling).

As shown in Figure 3 and Table 3, all specimens exhibited higher corrosion current densities in the anode environment than in the cathode environment, indicating that 316L BP is more susceptible to corrosion under anodic conditions, which is consistent with previous reports [39–41]. In the simulated cathode environment (Figure 3a), the polarization curve of the bare 316L substrate exhibited a distinct passive region, which is generally attributed to the presence of a surface oxide layer. However, as shown in Table 1, the corrosion current density of the bare 316L in the simulated PEMFC environment does not meet the DOE 2025 target ($i_{\text{corr}} < 1 \mu\text{A}\cdot\text{cm}^{-2}$). By contrast, all treated specimens showed a positive shift in corrosion potential and a pronounced decrease in corrosion current

density, reflecting improved corrosion resistance. The enhanced corrosion resistance of the PN specimen may be attributed to the formation of a compact expanded austenite (γ_N) layer, which acts as an effective diffusion barrier against corrosive species [42,43]. In the simulated cathode environment, the TiN specimen had an E_{corr} of -45.10 mV and i_{corr} of $0.116 \mu\text{A}\cdot\text{cm}^{-2}$, corresponding to a protective efficiency (PE) of 95.38% due to the dense columnar structure of the TiN coating, which physically blocks the ingress of the electrolyte [11,22]. Remarkably, the PN+TiN duplex coating delivered the lowest i_{corr} ($0.069 \mu\text{A}\cdot\text{cm}^{-2}$) among all specimens, despite presenting a slightly more negative E_{corr} (-105.07 mV) than both the PN and TiN specimens. In the anode environment (Figure 3b), the PN+TiN duplex coating achieved the best overall performance, with the highest E_{corr} (319.65 mV) and the lowest i_{corr} ($0.422 \mu\text{A}\cdot\text{cm}^{-2}$). In addition, in the simulated PEMFC environment, the PN+TiN coating exhibited the highest corrosion protective efficiency, reaching 97.22% for the cathode and 89.51% for the anode.

Table 3. Corrosion properties of specimens in simulated PEMFC cathode and anode environments.

Environment	Specimen	E_{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (V/dec)	β_c (V/dec)	R_p ($\text{k}\Omega\cdot\text{cm}^2$)	PE (%)	P (%)
Cathode	316L	-276.48	2.504	0.1099	0.1070	5.85	/	/
	PN	-75.89	0.132	0.2230	0.2467	37.74	94.71	15.5
	TiN	-45.10	0.116	0.1404	0.3745	22.50	95.38	25.0
	PN+TiN	-105.07	0.069	0.0802	0.3467	68.45	97.22	8.54
Anode	316L	-155.16	4.024	0.1840	0.1052	11.60	/	/
	PN	20.99	1.348	0.1533	0.2079	289.16	66.50	4.01
	TiN	237.91	1.971	0.1805	0.1078	253.06	51.02	4.59
	PN+TiN	319.65	0.422	0.2105	0.1826	611.90	89.51	1.90

To further quantify the effect of the nitrided interlayer on coating integrity, the electrochemical equivalent porosity (P) of the coated specimens was estimated from the potentiodynamic polarization data using the method reported in [44,45]. This parameter represents the fraction of the coating surface that is electrochemically connected to the substrate through defects such as pores, pinholes, or microcracks, rather than being a direct geometric measure of physical voids. It serves as an indirect but useful indicator of the coating's structural integrity and defect density, reflecting the extent to which the coating can effectively isolate the substrate from the corrosive environment. It was calculated as

$$R_p = \frac{\beta_a \cdot |\beta_c|}{2.303 \cdot i_{\text{corr}} \cdot (\beta_a + |\beta_c|)} \quad (4)$$

$$P(\%) = \frac{R_{\text{ps}}}{R_{\text{pc}}} \times 10^{\frac{|\Delta E_{\text{corr}}|}{\beta_{\text{as}}}} \times 100\% \quad (5)$$

where R_p is the polarization resistance ($\Omega\cdot\text{cm}^2$), and β_a and β_c are the anodic and cathodic Tafel slopes (V/dec), respectively. In Equation (5), R_{ps} and R_{pc} represent the polarization resistance of the bare substrate and coated specimen, respectively; ΔE_{corr} is the difference in the corrosion potential between the uncoated substrate and coated sample; and β_{as} denotes the anodic Tafel slope of the bare 316L substrate. $P(\%)$ is the electrochemical equivalent porosity, reflecting the relative fraction of coating defects connected to the substrate.

The significance of porosity in corrosion protection lies in its direct relationship with the defect structure of the coating. In general, pores, pinholes, and microcracks act as preferential pathways for the ingress of corrosive electrolyte towards the underlying substrate. A higher electrochemical equivalent porosity indicates a more defective coating structure,

which leads to a larger effective area of exposed substrate and, consequently, a higher corrosion current density. Conversely, a lower P value implies a denser coating with fewer penetration pathways. In the present study, the substantial reduction in P for the PN+TiN coating compared to the single TiN coating (8.54% vs. 25.0% in cathode; 1.90% vs. 4.59% in anode) correlates well with its superior corrosion performance. This result is corroborated by the SEM observations (Figure 2), which reveal that the nitrified interlayer significantly reduces the defect density of the TiN top coating, including pinholes, microdroplets, and interfacial microcracks.

These results clearly demonstrate that the PN+TiN duplex coating has a positive effect on the corrosion resistance of 316L stainless steel, outperforming both the single PN and single TiN coatings in both simulated PEMFC environments, while its corrosion current densities in both environments meet the DOE 2025 target. This excellent performance may be explained by the complementary roles of the two layers: the TiN top layer serves as the primary physical barrier, while the PN subsurface reduces pinhole defects in the TiN coating and provides an additional γ_N diffusion barrier.

3.2.2. Potentiostatic Polarization Tests

To evaluate the stability of the different coatings under prolonged potentiostatic polarization under simulated PEMFC operating conditions, potentiostatic polarization measurements were conducted at +0.6 V (vs. SCE) in the cathode environment with air bubbling and at −0.1 V (vs. SCE) in the anode environment with H₂ bubbling for 10,000 s, and the results are shown in Figure 4. In the case of the bare 316L sample, when in the cathode environment (Figure 4a), the current density dropped rapidly from a relatively high value within the first 100 s and then gradually stabilized at approximately 1.4 $\mu\text{A}\cdot\text{cm}^{-2}$. This rapid decrease was caused by passive film formation on the stainless steel surfaces under polarization. When in the anode environment (Figure 4b), a similar rapid decrease occurred during the initial 100 s, after which the current density stabilized at around 0.1 $\mu\text{A}\cdot\text{cm}^{-2}$. In both cases of the TiN sample and the PN+TiN sample, when in the cathode environment (Figure 4a), the current densities stabilized at approximately 0.1 and 0.3 $\mu\text{A}\cdot\text{cm}^{-2}$, respectively, both significantly below the DOE 2025 target of 1 $\mu\text{A}\cdot\text{cm}^{-2}$ [3]. When in the anode environment, both coated specimens experienced a sharp drop to a negative value within the first 10 s, followed by a gradual increase over the next several hundred seconds to their respective stable values of 0.1 and −0.2 $\mu\text{A}\cdot\text{cm}^{-2}$. The negative current density recorded for the PN+TiN coating in the anode environment indicates that the coating is under cathodic protection [9] and thus shows better corrosion resistance. The results shown in Figure 4 confirm that the PN+TiN coating possesses high stability in a working PEMFC environment.

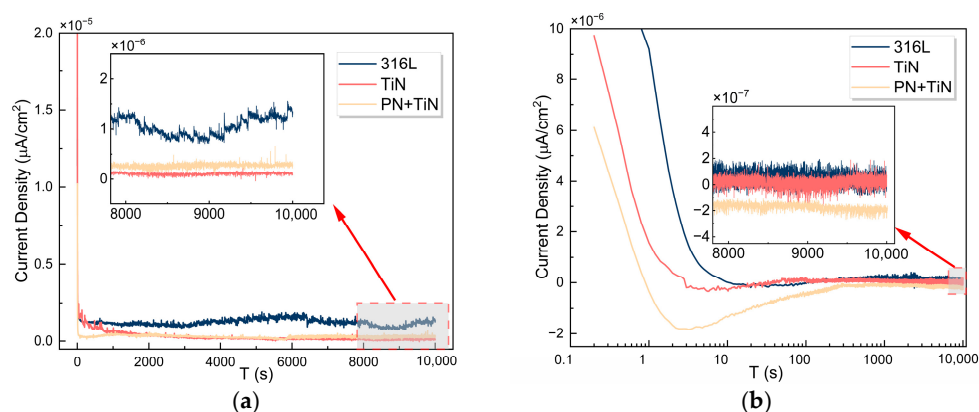


Figure 4. Potentiostatic polarization curves of bare 316L, TiN, and PN+TiN specimens in simulated PEMFC environments: (a) 0.6 V (vs. SCE) in cathode environment with air bubbling; (b) −0.1 V (vs. SCE) in anode environment with H₂ bubbling.

3.2.3. EIS Tests

To further evaluate the corrosion protection performance of the coatings, electrochemical impedance spectroscopy (EIS) was conducted in the simulated PEMFC cathodic environment. Figure 5a,b present the Nyquist and Bode plots for the bare 316L, TiN, and PN+TiN specimens recorded in the simulated PEMFC cathodic environment. In the Nyquist plot shown in Figure 5a, all three specimens exhibit a single capacitive semicircle but with different diameters. The diameter of the capacitive arc corresponds to the charge transfer resistance (R_{ct}) at the electrode/electrolyte interface; a larger diameter indicates a higher R_{ct} and thus greater corrosion resistance [13,30]. The arc diameter of both coated specimens is significantly larger than that of the bare 316L, and the PN+TiN duplex coating exhibits the largest arc diameter, indicating its superior anticorrosion performance. The Bode plots in Figure 5b further support this trend. The phase angle curves of the coated specimens exhibit a broad plateau of high phase angles (approximately -80°) over a wider frequency range compared to the curve of the bare substrate, which is indicative of a more capacitive and protective surface layer [45,46].

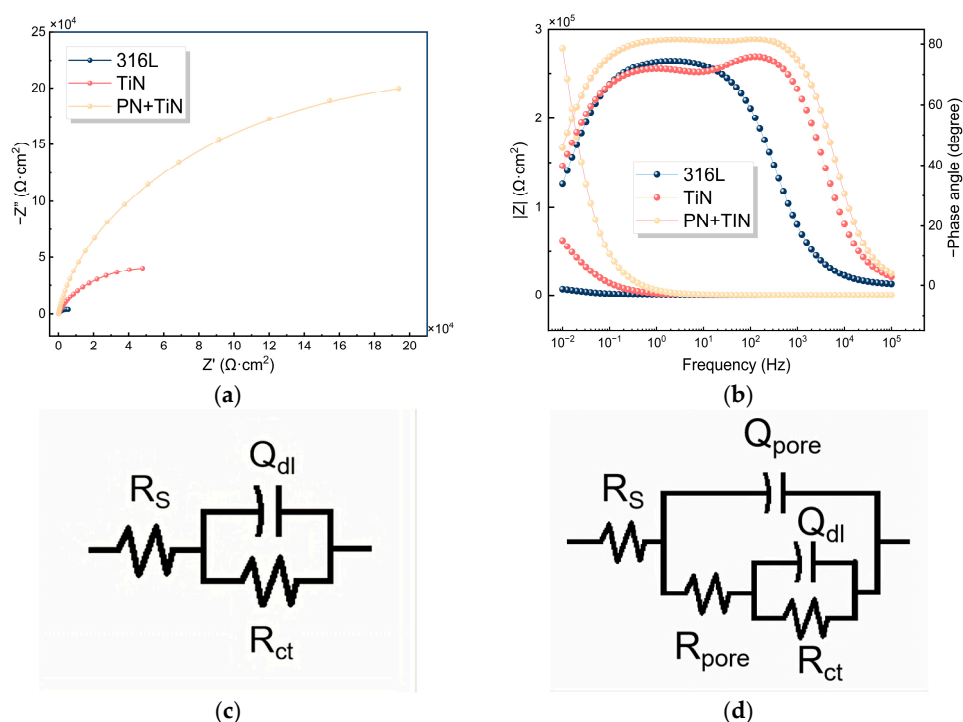


Figure 5. EIS results of 316L, TiN, and PN+TiN specimens for simulated PEMFC environments: (a) Nyquist plot; (b) Bode plot; (c) equivalent circuits of bare 316L; (d) equivalent circuits of coated 316L.

The EIS data were fitted using the equivalent circuit models proposed by Pugal Mani et al. [46], as shown in Figure 5c,d, and the fitting parameters are presented in Table 4. In these models, R_s represents the solution resistance; Q_{dl} is the constant phase element corresponding to the double-layer capacitance; Q_{pore} denotes the coating capacitance; and R_{pore} corresponds to the ionic transport resistance through pores and defects within the coating. The chi-square (χ^2) values in Table 4 were used to evaluate the goodness of fit of the EIS data. The χ^2 values of all specimens are below 10^{-3} , indicating good agreement between the experimental data and the equivalent circuit models. The R_{pore} value provides an electrochemical indication of the coating porosity. Fewer or smaller pores lead to higher ionic transport resistance, whereas a more porous coating allows electrolyte penetration through the pores, enabling direct ionic migration to the substrate and resulting in

a lower R_{pore} value. In the present study, the R_{pore} of the PN+TiN coating ($1526 \Omega \cdot \text{cm}^2$) is substantially higher than that of the single TiN coating ($678 \Omega \cdot \text{cm}^2$), indicating a lower porosity and defect density in the PN+TiN coating.

Table 4. Fitting parameters of 316L, TiN, and PN+TiN specimens extracted from the Nyquist plot.

Specimen	$R_s (\Omega \cdot \text{cm}^2)$	$Q_{\text{pore}} (\mu\text{F} \cdot \text{cm}^{-2})$	n_1	$R_{\text{pore}} (\Omega \cdot \text{cm}^2)$	$Q_{\text{dl}} (\mu\text{F} \cdot \text{m}^{-2})$	n_2	$R_{\text{ct}} (\times 10^4 \Omega \cdot \text{cm}^2)$	$X^2 (\times 10^{-4})$
316L	1.71	-	-	-	877.3	0.84	0.984	9.16
TiN	2.08	52.90	0.91	678	52.07	0.74	10.93	3.31
PN+TiN	1.90	24.05	0.94	1526	7.96	0.79	48.14	8.06

To evaluate the overall corrosion resistance of the coating systems, the total polarization resistance R_p was defined as the sum of R_{ct} and R_{pore} . A higher R_p value indicates better corrosion resistance. The R_p of the PN+TiN duplex coating is more than one order of magnitude higher than that of the bare 316L substrate, and it is also substantially higher than that of the single TiN coating, confirming that the duplex system offers the highest resistance to electrochemical corrosion. Furthermore, the total coating capacitance, defined as $Q_{\text{total}} = Q_{\text{pore}} + Q_{\text{dl}}$, was used to evaluate the compactness of the coating structure. The presence of pores provides pathways for electrolyte penetration through the coating, which significantly increases the effective dielectric constant and the effective surface area, thereby raising the overall capacitance [13,45]. The Q_{total} values of TiN and PN+TiN are $112.97 \mu\text{F} \cdot \text{cm}^{-2}$ and $32.01 \mu\text{F} \cdot \text{cm}^{-2}$, respectively. The significantly lower Q_{total} of the PN+TiN duplex coating indicates that the nitrided interlayer effectively reduces the porosity and defect density of the coating system and reinforces the barrier function of the coating. These EIS results are in good agreement with the potentiodynamic and potentiostatic polarization data, collectively confirming that the PN pretreatment substantially enhances the corrosion protection performance of the TiN coating.

3.3. Contact Angle Measurements

The surface wettability of the bipolar plate plays a critical role in water management within PEMFC stacks. A hydrophobic surface is therefore desirable to facilitate rapid water removal and to improve the performance of PEMFC. As shown in Figure 6, the average water contact angle of the 316L substrate is about 79° , which indicates low hydrophobicity. After TiN coating and PN+TiN duplex coating deposition, the contact angles increased to 92.60° and 97.69° , respectively. The increased angles of the coated specimens can be primarily attributed to the metal nitride surface having a lower polarity than the oxide layer on the bare 316L substrate. It is well established that oxide surfaces show higher electronegativity [25] and thus stronger affinity for water molecules. The similar contact angles observed for the TiN and PN+TiN coatings fall within expectations, as both specimens have a nearly identical phase composition and (111)-preferred orientation, as confirmed by the XRD results (Figure 1). The slight increase of approximately 5° for the PN+TiN sample may be attributed to the reduced density of surface defects, such as microdroplets and pinholes, which are commonly generated during arc ion plating. The underlying nitrided layer improves the surface quality of the subsequently deposited TiN coating, thereby reducing surface roughness and promoting a more hydrophobic surface state.

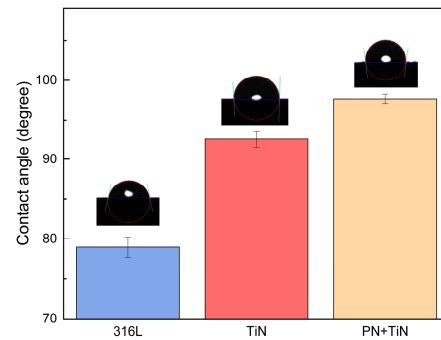


Figure 6. Static water contact angles of deionized water on the bare 316L, TiN, and PN+TiN samples.

3.4. ICR Measurements

The ICR between the bipolar plate and the gas diffusion layer (GDL) is a critical parameter that directly influences the overall ohmic loss and power output of a PEMFC stack. The DOE has also set a target ICR of less than $10 \text{ m}\Omega\cdot\text{cm}^2$ at a compaction force of $140 \text{ N}\cdot\text{cm}^{-2}$ for bipolar plates. To evaluate the electrical conductivity of the coated specimens, the ICR between each sample and carbon paper was measured as a function of compaction force ranging from 10 to $160 \text{ N}\cdot\text{cm}^{-2}$, and the results are presented in Figure 7. For the bare 316L substrate, the ICR decreased sharply from $2942.9 \pm 243.7 \text{ m}\Omega\cdot\text{cm}^2$ at $10 \text{ N}\cdot\text{cm}^{-2}$ to $21.4 \pm 2.7 \text{ m}\Omega\cdot\text{cm}^2$ at $160 \text{ N}\cdot\text{cm}^{-2}$. The consistently high ICR values across the entire compaction force range can be attributed to the presence of a native insulating oxide layer, which severely impedes electron transfer between the bipolar plate and the GDL. In contrast, both the TiN and PN+TiN specimens exhibited significantly lower ICR values. At a compaction force of $140 \text{ N}\cdot\text{cm}^{-2}$, the ICR of the TiN was $9.56 \pm 2.63 \text{ m}\Omega\cdot\text{cm}^2$, while that of the PN+TiN was $7.84 \pm 2.10 \text{ m}\Omega\cdot\text{cm}^2$, both meeting the DOE 2025 target. At this standard compaction force, the PN+TiN coating exhibited the lowest ICR among all specimens, outperforming the single TiN coating.

This performance gap under the DOE standard condition directly points to the role of the nitrided interlayer. The ICR is governed by two factors: the intrinsic conductivity of the coating material and the effective contact area between the coating and the GDL. While both TiN top layers have the same high conductivity, their effective contact areas differ. In the single TiN coating, inherent defects of arc ion plating, including microdroplets, pinholes, and surface roughness, reduce the real contact area. The nitrided interlayer addresses this through two complementary mechanisms. First, by modifying the substrate surface prior to TiN deposition, the nitrided subsurface promotes more uniform coating growth, resulting in a smoother surface with fewer defects and thus a larger real contact area with the GDL. Second, the PN treatment itself improves the surface conductivity of the stainless steel substrate by forming a conductive γ_N layer. The lower ICR of the PN+TiN coating under the DOE standard condition is therefore a direct result of the nitrided interlayer simultaneously improving surface quality and interfacial conductivity. It should be noted that systematic surface roughness measurements were not performed in this study. Nevertheless, the SEM morphology and the ICR results presented in this section collectively provide complementary evidence of the surface quality differences between the two coated specimens.

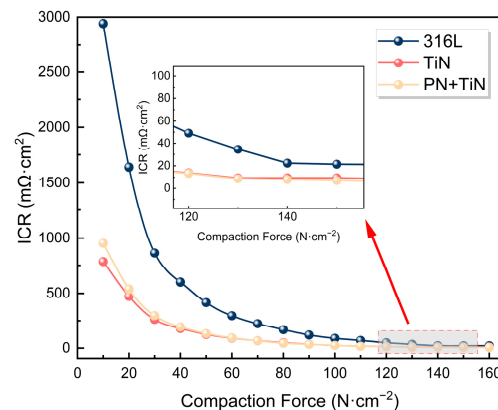


Figure 7. ICR of the 316L, TiN, and PN+TiN specimens under various compaction forces.

3.5. Adhesion Measurements

To evaluate the adhesion strength between the coatings and the 316L substrate, scratch testing was performed, during which tangential force (F_t), acoustic emission (AE) signals, and the corresponding scratch track morphologies were recorded and are shown in Figure 8. Three characteristic critical loads were identified based on the combined analysis of AE signal evolution and scratch track morphology: Lc1 for initial microcracking, Lc2 for partial delamination, and Lc3 for total delamination of the coating. Lc1, determined from the first AE peak in Figure 8, was 1.15 N for the TiN coating and 1.97 N for the PN+TiN coating. This significant increase indicates that the duplex coating exhibits substantially higher resistance to the initiation of microcracking. Total delamination occurred at 8.17 N for the PN+TiN specimen, which was higher than that of the TiN coating (6.51 N). Furthermore, chipping was observed near the scratch edge of the TiN specimen, even within the load range exceeding Lc3, whereas no such damage occurred for the PN+TiN coating within the corresponding range.

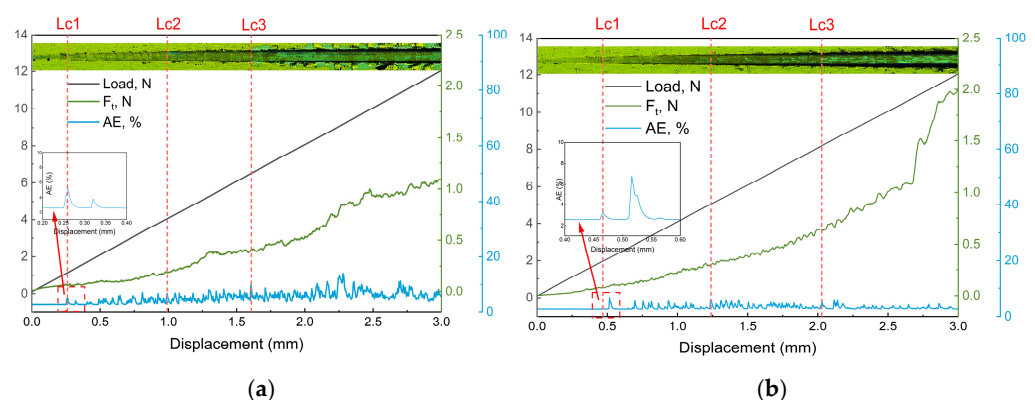


Figure 8. Scratch adhesion characteristics of TiN (a) and PN+TiN (b) specimens.

The improvement in adhesion strength following PN pretreatment is attributed to two primary mechanisms. First, PN increases the substrate hardness through the formation of a nitrogen diffusion zone consisting of expanded austenite (γ_N). The critical load of adherence for hard thin films varies linearly with the substrate hardness. A harder substrate provides stronger mechanical support to the coating during scratching, delaying the onset of plastic deformation and cohesive failure. Second, the nitrided subsurface creates a compositional and mechanical gradient between the soft steel substrate and the hard TiN coating, reducing the sharp discontinuity in properties at the interface [47]. This gradient transition zone distributes shear stress over a broader region, increasing the

resistance to interfacial delamination [48]. In addition, PN treatment prior to PVD coating has been shown to promote stronger chemical bonding at the interface [47]. The synergistic effect of improved substrate support and enhanced interfacial bonding explains the higher Lc1, Lc2, and Lc3 values of the PN+TiN coating.

4. Conclusions

In this work, a duplex surface treatment comprising plasma nitriding (PN) followed by arc ion plating (AIP) of a TiN top coating was successfully applied to 316L stainless steel bipolar plates. The corrosion resistance, electrical conductivity, surface hydrophobicity, and adhesion strength of the duplex coating were systematically evaluated and compared with those of a bare 316L substrate, single PN layer, and single TiN coating. The following conclusions can be drawn:

- The PN+TiN duplex coating exhibited a bilayer structure with a TiN top layer of approximately 1.3 μm and a nitrided diffusion layer of about 9.2 μm . Compared with the single TiN coating (1.8 μm), the PN+TiN coating was thinner but significantly denser and more uniform, with substantially fewer microdroplets, pinholes, and microcracks and less interfacial delamination. XRD analysis confirmed the expanded austenite (γ_{N}) phase in the nitrided layer, and both TiN and PN+TiN coatings exhibited a strong (111)-preferred orientation.
- The PN+TiN duplex coating demonstrated superior corrosion resistance in both simulated PEMFC cathode and anode environments. It achieved the lowest corrosion current densities (0.069 $\mu\text{A}\cdot\text{cm}^{-2}$ in cathode and 0.422 $\mu\text{A}\cdot\text{cm}^{-2}$ in anode) and protective efficiencies of 97.22% and 89.51%, meeting the DOE 2025 target. The electrochemical equivalent porosity of the PN+TiN coating was significantly lower than that of the single TiN coating (8.54% vs. 25.0% in cathode; 1.90% vs. 4.59% in anode). Potentiostatic polarization confirmed its excellent stability over 10,000 s. EIS analysis revealed the highest charge transfer resistance ($48.14 \times 10^4 \Omega\cdot\text{cm}^2$), lowest coating capacitance (32.01 $\mu\text{F}\cdot\text{cm}^{-2}$), and substantially higher pore resistance (1526 $\Omega\cdot\text{cm}^2$) than the single TiN coating (678 $\Omega\cdot\text{cm}^2$), confirming the reduced defect density of the duplex coating.
- The PN+TiN duplex coating achieved a low interfacial contact resistance of 7.84 $\text{m}\Omega\cdot\text{cm}^2$ at 140 $\text{N}\cdot\text{cm}^{-2}$, meeting the DOE 2025 target. This reduction is attributed to the dual role of the nitrided interlayer: promoting uniform TiN growth with fewer defects to increase the real contact area and forming a conductive γ_{N} layer that improves the surface conductivity of the substrate.
- The PN+TiN coating exhibited enhanced hydrophobicity (97.69° vs. 92.60° for TiN and 78.97° for 316L) and significantly improved adhesion strength, with the critical load for complete delamination (Lc3) increasing from 6.51 N for TiN to 8.17 N for PN+TiN. The improved adhesion is attributed to the gradient transition zone formed by the nitrided subsurface.

In summary, the sequential combination of PN and TiN coating is an effective strategy for improving the corrosion resistance, electrical conductivity, surface hydrophobicity, and adhesion of stainless steel bipolar plates for PEMFC applications. The nitrided interlayer plays a critical role by reducing defect density, enhancing interfacial integrity, and providing a conductive subsurface.

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Abbreviations

The following abbreviations are used in this manuscript:

PEMFC	Proton exchange membrane fuel cell
TiN	Titanium nitride
γ^N	Expanded austenite
ICR	Interfacial contact resistance
a-C	Amorphous carbon
DOE	Department of Energy
PVD	Physical vapor deposition
PN	Plasma nitriding/plasma-nitrided
AIP	Arc ion plating
XRD	X-ray diffraction
SEM	Scanning electron microscopy
EDS	Energy-dispersive X-ray spectroscopy
SCE	Saturated calomel electrode
EIS	Electrochemical impedance spectroscopy
OCP	Open circuit potential
PE	Protective efficiency
GDL	Gas diffusion layer
AE	Acoustic emission
Lc	Critical load

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