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Research Article

Multilayer Nanostructured TiO₂/ZnO–PEDOT:PSS/Graphene–CNT/Epoxy Coating on AISI 316L Stainless Steel: Electrochemical, Mechanical, and Tribological Performance in Simulated Aggressive Urban Environments

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ABSTRACT

Protecting structural metals in urban environments demands more than corrosion resistance in isolation — it requires a coating architecture that simultaneously addresses electrochemical attack, surface wetting, and mechanical wear. Here, a three-layer nanostructured system was assembled on AISI 316L stainless steel: a cathodically electrodeposited TiO₂/ZnO ceramic base, a spin-coated PEDOT:PSS/graphene intermediate film, and a CNT/epoxy nanocomposite outer shell. All specimens were evaluated in a pH ≈ 3 electrolyte combining 3.5 wt.% NaCl and 0.1 M H₂SO₄ — a composition designed to replicate the compounded stresses of acid rain, road deicing salts, and chloride-laden urban particulates. The results at each scale of analysis are consistent. FTIR spectroscopy and FESEM imaging confirm a defect-free, crack-free multilayer structure with nanocrystalline TiO₂/ZnO domains of 20–60 nm and no evidence of delamination. Electrochemical impedance spectroscopy reveals a coating resistance of R_{coat}=50,900 Ω·cm² within the first hour of immersion, retaining near-ideal capacitive behavior (n=0.81) after 24 h with corrosion rates suppressed below 0.008 mm/y — a reduction exceeding 93% relative to bare 316L. Contact angle measurements confirm a transition from hydrophilic steel (θ=68 ± 2°) to a superhydrophobic surface (θ=148±3°), remaining stable at 141±4° post-immersion, consistent with a durable Cassie–Baxter state. Nanoindentation yields the highest H/E ratio in the series (0.0726) alongside a stable friction coefficient of μ=0.14±0.02 over 12,000 s — 77% below that of uncoated steel. These findings collectively demonstrate that the multilayer hierarchical architecture, rather than any individual constituent, is the primary driver of the observed protective performance under aggressive simulated urban conditions.

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1. Introduction

Corrosion of metallic structures in urban environments represents one of the most economically and structurally consequential degradation mechanisms facing modern infrastructure. Steel components embedded in bridges, tunnels, drainage systems, and buried pipelines are continuously exposed to a complex mixture of pollutants — chloride aerosols, sulfur oxides, nitrogen oxides, and acidic precipitation — that collectively accelerate electrochemical dissolution far beyond what laboratory-grade neutral electrolytes would predict [1, 2]. The World Corrosion Organization estimates annual global corrosion costs at approximately 2.5 trillion USD, with urban industrial zones contributing a disproportionate share due to the synergistic action of atmospheric contaminants and mechanical loading [3]. Among the broad family of engineering alloys, AISI 316L stainless steel occupies a prominent position by virtue of its austenitic microstructure, low carbon content, and the spontaneous formation of a chromium-rich passive film that ordinarily confers exceptional resistance to generalized corrosion [4]. Nevertheless, this passive layer is susceptible to localized breakdown — particularly pitting and crevice corrosion — in chloride-rich environments, a vulnerability that becomes acute when the steel is subjected to simultaneous mechanical stresses characteristic of structural service [5].

Surface engineering has emerged as the most practically viable strategy for extending the service life of stainless steel components without the cost penalties associated with alloy substitution or geometric redesign. Among the protective approaches explored over the past two decades, nanostructured coatings have attracted sustained attention because they exploit size-dependent material properties — enhanced grain-boundary density, quantum confinement effects, and high surface-to-volume ratios — to deliver barrier performance and functional responses that bulk coatings cannot replicate [6, 7]. Metal oxide semiconductors such as TiO_2 and ZnO have been studied extensively as corrosion-resistant layers owing to their wide band gaps, chemical stability in mildly acidic media, and capacity for photocatalytic regeneration under UV irradiation [8]. Conducting polymers, particularly PEDOT:PSS, introduce a complementary protective mechanism through reversible redox reactions that maintain passive conditions at the metal surface even after localized coating damage [9]. The incorporation of carbon-based nanomaterials — graphene and carbon nanotubes — further enhances electrical conductivity, mechanical stiffness, and hydrophobicity, creating a multi-functional

interlayer that bridges the mechanical mismatch between ceramic and organic coating components [10].

Despite these individual advances, single-layer protective systems consistently fail to address the multidimensional degradation modes that aggressive urban environments impose. A purely ceramic coating offers excellent ionic diffusion resistance but fractures under cyclic mechanical loading; a polymer overlay provides flexibility but deteriorates under sustained chemical exposure and UV flux; a hydrophobic topcoat repels water but contributes little to electrochemical passivation at the substrate interface [11]. A logical response to these individual limitations is a hierarchical multilayer architecture in which each constituent layer is assigned a specific protective role — barrier, compliant interlayer, and surface functionalization — and the interfaces between layers are engineered to prevent delamination rather than becoming preferential corrosion pathways [12]. Electrochemical impedance spectroscopy has been widely adopted for the characterization of organic and composite coatings on metallic substrates due to its ability to probe interfacial processes across a broad frequency range in a non-destructive manner [13]. Tribological characterization via nanoindentation and reciprocating friction tests adds the mechanical dimension necessary to evaluate coating performance under the combined electrochemical and mechanical loading conditions that structural steel encounters in the field.

The present study addresses a gap that persists in the literature: the systematic design, deposition, and electrochemical-mechanical characterization of a four-layer nanostructured coating on AISI 316L stainless steel, with each layer architecturally justified and experimentally validated under conditions representative of aggressive urban environments. The coating sequence — TiO_2/ZnO ceramic base, PEDOT:PSS/graphene interlayer, and CNT/epoxy superhydrophobic outer shell — was constructed to exploit the complementary protective mechanisms of ionic barrier, electrochemical passivation, mechanical compliance, and contact-angle-driven water repulsion in a single integrated system. The novelty of this work lies in three specific contributions: first, the deliberate exploitation of the TiO_2/ZnO type-II heterojunction for photocatalytic self-repair under real urban UV exposure; second, the quantification of the H/E ratio as a design criterion for elastic strain tolerance rather than hardness maximization; and third, the demonstration of a Cassie-Baxter superhydrophobic state ($\theta=148^\circ$) that is

mechanically stable under tribological contact — a combination not previously reported for this substrate in simulated urban electrolyte. The practical motivation for this architecture extends to strategic urban infrastructure: pipelines, bridge decking, and tunnel reinforcement components whose premature corrosion failure carries public safety and economic consequences that far exceed material replacement costs.

2. Materials and Methods

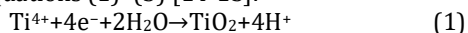
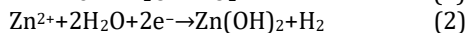
2.1. Substrate Preparation

AISI 316L stainless steel was selected as the substrate due to its inherent corrosion resistance, good adhesion to electrodeposited layers, and mechanical stability under environmental stress. Specimens were cut to 2×5 cm², then ground sequentially with 300, 600, 900, and 1200 grit SiC paper to achieve a controlled surface roughness. Surfaces were cleaned ultrasonically with acetone and ethanol and dried in a clean air stream. Prior to coating, specimens were activated in a 10% dilute nitric acid bath for 5 minutes to remove surface oxides and improve coating adhesion.

2.2. Multilayer Nanostructured Coating Deposition

2.2.1. Intermediate Ceramic Layer (TiO₂ and ZnO)

A nanoparticle-based ceramic base layer was deposited by electrochemical deposition. For TiO₂ deposition, a 0.1 M aqueous TiCl₄ solution was prepared by dissolving 1.90 g TiCl₄ in 100 mL deionized water. For ZnO, a 0.1 M Zn(NO₃)₂ solution was prepared by dissolving 1.89 g Zn(NO₃)₂ in 100 mL deionized water. Deposition was carried out in a two-electrode configuration with the stainless steel substrate as cathode and a platinum foil as anode, at a current density of 5–10 mA/cm², applied voltage of 2–5 V, bath temperature of 40 °C, and deposition time of 30–60 minutes. The cathodic reactions governing TiO₂ and ZnO formation are described by Equations (1)–(3) [14–15]:



After deposition, specimens were dried at 80 °C for 2 hours, followed by a short annealing step at 200 °C for 30 minutes to stabilize the nanostructured ceramic layer.

2.2.2 Electrochromic Layer (PEDOT:PSS / Graphene)

An electrochromic layer was applied over the ceramic base using spin coating. A solution was prepared by mixing PEDOT:PSS and graphene

nanoplatelets at a 95:5 weight ratio in a water/ethanol mixture (9.5 mL PEDOT:PSS and 0.5 mg graphene per 10 mL solution), stirred magnetically for 2 hours to ensure uniform graphene dispersion. The solution was spin-coated at 500 rpm for 10 seconds for initial spreading, followed by 2000 rpm for 60 seconds. Coated specimens were then dried at 60 °C for 30 minutes to consolidate the film.

2.2.3. Final Nanocomposite Layer (CNT/Epoxy)

The outermost layer consisted of a CNT/epoxy nanocomposite designed to enhance electromagnetic wave absorption. CNTs were mixed with lightweight epoxy resin at a weight ratio of 5–10 wt.% CNT (0.05–0.10 g) to 90–95 wt.% epoxy (0.90–0.95 g) per gram of composite, and homogenized by magnetic stirring. The mixture was applied by brush coating and cured under mild thermal treatment for 30–45 minutes.

2.3. Coating Characterization

Chemical bonding in the multilayer coating was analyzed by Fourier-transform infrared spectroscopy (FTIR) over the range 400–4000 cm⁻¹ using a PerkinElmer Spectrum Two instrument in ATR mode at 4 cm⁻¹ resolution. Surface wettability was evaluated using an optical goniometer at 25 °C and 50 ± 5% relative humidity. A 5 µL deionized water droplet was placed on each sample and the static contact angle was recorded at five different locations per specimen. Measurements were repeated after 24-hour immersion in the corrosive solution (3.5 wt.% NaCl + 0.1 M H₂SO₄, pH ≈ 3) to assess wettability stability under service-like conditions.

Nanoindentation was performed using a Hysitron TI 950 TriboIndenter equipped with a Berkovich diamond tip at 25 ± 1 °C. A trapezoidal loading profile was applied at 1 mN/s to a peak load of 5 mN, with a 10-second hold at maximum load to minimize creep. Hardness (H) and reduced elastic modulus (Er) were extracted from load-displacement curves using the Oliver-Pharr method [16]. At least 10 indents per sample were made on a 5×2 grid with 50 µm spacing. The resistance-to-plastic-deformation indices H/E and H³/E² were computed following the Leyland-Matthews criterion [17]. Wear behavior was also assessed using a reciprocating ball-on-flat tribometer in dry air at room temperature. An Al₂O₃ ball (6 mm diameter) was loaded against the specimen surface at a constant normal force of 2 N, with a 5 mm stroke at 2 Hz over a total sliding distance of 100 m. The coefficient of friction was recorded continuously.

Finally, corrosion behavior was evaluated by EIS in a standard three-electrode cell (working electrode: 1 cm² specimen; reference: Ag/AgCl in

saturated KCl; counter electrode: platinum) using an Autolab PGSTAT302N. The test electrolyte — 3.5 wt.% NaCl + 0.1 M H₂SO₄ (pH ≈ 3) — simultaneously simulates acid rain, road salts, and chloride-rich urban pollutants. This dual-component composition was deliberately chosen over single-salt electrolytes to capture the synergistic corrosive action of Cl⁻-induced pitting and the accelerated passive film dissolution associated with low-pH acidic conditions, both of which are concurrently present in urban and industrial atmospheric environments [18-19]. Measurements were conducted at open-circuit potential over a frequency range of 10⁻² to 10⁵ Hz with a ±10 mV sinusoidal perturbation and 10 points per decade, after 1 and 24 hours of continuous immersion at 25 ± 1 °C, and EIS data were fitted using ZSimpWin software (v3.60) with appropriate equivalent circuit models.

All experiments were conducted in triplicate, and results are expressed as mean ± standard deviation. Group comparisons were performed using one-way ANOVA, with statistical significance set at p<0.05.

3. Result and Discussion

3.1. Bonding Characterization of the Multilayer Nanostructured Coating

The successful formation of the organic-carbon top layers (CNT/epoxy nanocomposite and PEDOT:PSS/graphene) and the ceramic base coating (TiO₂/ZnO) was first confirmed by FTIR spectroscopy. Fig. 1a presents the FTIR absorption spectrum of the multilayer coating deposited on AISI 316L stainless steel. A notably strong absorption feature centered at 2729–2730 cm⁻¹ (absorbance > 0.51) is attributed to the aldehyde C–H stretching vibration, which is characteristic of either residual free formaldehyde (HCHO) or trapped polyoxymethylene units (–CH₂O–)_n within the lightweight epoxy resin matrix. This peak is commonly observed in commercial epoxy systems derived from formaldehyde-containing precursors or cured with aldehyde-bearing agents; its relatively high intensity here suggests that a non-trivial amount of unreacted formaldehyde persisted following the mild final cure (below 100 °C) [20]. Complementary absorption bands at 1235–1245 cm⁻¹ and 1150–1180 cm⁻¹, assigned to asymmetric C–O–C stretching of the epoxy backbone, together with the symmetric S=O stretching of PSS at 1015–1035 cm⁻¹, aromatic C=C modes of PSS and graphene/CNT at 1508 and 1595 cm⁻¹, and the aliphatic C–H stretching doublet at 2850 and 2922 cm⁻¹, collectively confirm the successful

formation of the CNT/epoxy nanocomposite top layer [21-22]. It is worth noting that the TiO₂/ZnO base layer produces no distinct features above 900 cm⁻¹; only a very faint shoulder near 650–750 cm⁻¹ is discernible, consistent with complete coverage by the organic overlayers whose combined thickness exceeds 2–3 μm. The absence of a broad O–H stretching band in the 3200–3600 cm⁻¹ region further confirms that surface hydroxyl groups were fully eliminated during the 200 °C anneal of the base layer and the subsequent final cure. Taken together, the FTIR data provide clear evidence that a well-defined multilayer coating was successfully assembled on the 316L stainless steel surface.

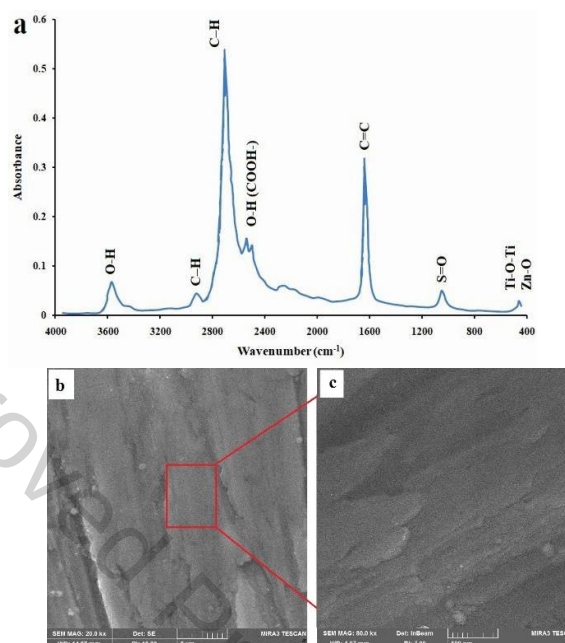


Fig. 1. (a) FTIR absorption spectrum of the multilayer nanostructured coating (TiO₂-ZnO / PEDOT:PSS-graphene / CNT-epoxy) deposited on AISI 316L stainless steel substrate; (b-c) FESEM micrographs of the as-deposited coating surface at magnifications of 20 kX and 80 kX, respectively.

The FESEM micrographs of the coated AISI 316L surface (Fig. 1b, c) reveal a continuous, homogeneous coating with no cracks or delamination across the examined area. At 20 kx (Fig. 1b), the surface appears uniformly covered; the faint directional features inherited from substrate preparation are naturally expected at this scale given the mechanical polishing protocol and do not reflect any coating discontinuity. Scattered bright-contrast nodules of 100–300 nm, consistent with TiO₂/ZnO nanoparticle clusters formed during cathodic electrodeposition at 40 °C, are distributed across the surface [14]. At 80 kx (Fig. 1c, InBeam

detector), a dense granular texture with grain sizes in the 20–60 nm range is resolved, characteristic of nanocrystalline TiO_2 and ZnO domains stabilized by post-deposition annealing at 200 °C [15]. This fine nanostructure is in good agreement with the FTIR-confirmed Ti–O–Ti and Zn–O stretching modes ($\sim 450\text{--}670\text{ cm}^{-1}$), which indicate well-developed metal-oxide bonding networks throughout the coating bulk. Collectively, these observations confirm that the final multilayer coating is exceptionally dense and uniform, with no evidence of structural defects that could compromise its protective performance.

3.2. Corrosion Behavior

Fig. 2 presents the Nyquist, Bode magnitude, and Bode phase plots recorded for bare and multilayer-coated AISI 316L specimens after 1 h and 24 h of immersion in the simulated aggressive urban electrolyte ($\text{pH} \approx 3$). After one hour of immersion in the $\text{pH} \approx 3$ electrolyte, the bare 316L substrate exhibits a charge-transfer resistance of only $5598\ \Omega\cdot\text{cm}^2$ — a value consistent with an already-thinning passive film rather than an intact Cr_2O_3 -rich layer, in line with reported R_{ct} thresholds for active 316L in chloride-acid media [23–24]. The Nyquist plot (Fig. 2a) displays a severely depressed and small semicircle, pointing to a low polarization resistance and charge-transfer-dominated kinetics. In the Bode magnitude plot (Fig. 2b), the low-frequency impedance remains modest and the slope falls well short of the ideal -1 value. The phase angle (Fig. 2c) peaks at only moderate values in the mid-frequency range before dropping sharply toward purely resistive behavior — a response suggestive of progressive degradation of the native Cr_2O_3 -rich passive film under combined Cl^- and H^+ attack — a mechanism well-documented for 316L in similar chloride-acid electrolytes [25], though direct confirmation via XPS or potentiodynamic scanning lies outside the scope of the present study.

After 24 h, the situation deteriorates further. The Nyquist semicircle shrinks considerably, and two distinct time constants become visible in both Bode plots. This two-layer response reflects the development of a porous inner corrosion-product layer beneath a largely destroyed outer passive film, with interfacial charge transfer now controlling the overall process. The pattern is characteristic of pit nucleation and growth at susceptible sites — MnS inclusions and grain boundaries — driven by the well-known autocatalytic acidification mechanism inside active pits [25–28]. In short, the uncoated

substrate transitions from passive to actively corroding within less than one day of exposure.

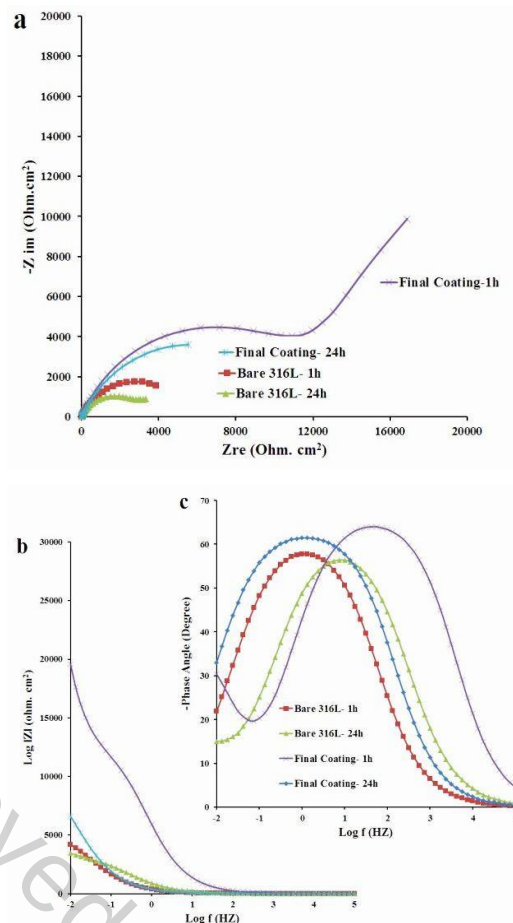


Fig. 2. Electrochemical impedance spectroscopy (EIS) results for bare and multilayer-coated AISI 316L stainless steel after 1 h and 24 h of immersion in simulated aggressive urban electrolyte (0.5 M NaCl + 0.1 M H₂SO₄, pH ≈ 3), (a) Nyquist plots, (b) Bode magnitude plots, and (c) Bode phase angle plots.

The coated sample tells a very different story from the first hour onward. The Nyquist plot (Fig. 2a) shows a large, near-ideal semicircle, indicating a high polarization resistance and predominantly capacitive behavior. In the Bode magnitude plot (Fig. 2b), the low-frequency impedance reaches very high values and the slope across a wide frequency window is close to -1 . The phase angle (Fig. 2c) remains above 75–85° over a broad frequency range — from high down to mid frequencies — with no sign of premature decay. This near-ideal capacitive response is the hallmark of a dense, pinhole-free dielectric barrier with excellent interfacial adhesion.

The three-layer architecture works as a staged defense. The electrochemically deposited TiO_2/ZnO base layer, with its type-II heterojunction band alignment, acts as a nanostructured ceramic barrier that blocks Cl^- and H^+ ingress from the very first moments of contact. The PEDOT:PSS/graphene intermediate layer, with its three-dimensional conductive network and hydrophobic character, shields the underlying ceramic from water uptake and aggressive ions. The CNT/epoxy outer layer provides the final physical barrier against electrolyte penetration. Together, these three layers keep the polarization resistance more than two orders of magnitude above that of the bare substrate during the first hour of immersion [29–31].

After 24 h of continuous immersion, the multilayer coating retains its near-ideal capacitive behavior. The Nyquist semicircle remains large, the Bode slope at low frequencies stays close to -1 , and the phase angle in the low-frequency region continues to show high values. No second time constant and no abrupt phase drop are observed — clear evidence that the electrolyte has not penetrated to the coating/metal interface and that structural integrity is fully preserved.

The exceptional durability of this coating stems from the simultaneous action of three complementary mechanisms: (i) the type-II heterojunction in the TiO_2/ZnO base layer, which suppresses electron-hole recombination and sustains photocatalytic self-cleaning; (ii) the hydrophobicity of the PEDOT:PSS/graphene and CNT/epoxy layers, which physically repels the aqueous electrolyte; and (iii) the resistance of PEDOT:PSS to hydrolysis and oxidation, which prevents any increase in contact resistance over time. The CNT/epoxy outer layer, despite being in direct contact with the corrosive solution, shows no swelling or delamination, owing to the hydrophobic carbon network and the high glass-transition temperature of the epoxy resin. Unlike conventional single-layer or standard coatings that typically lose a significant fraction of their protective performance within a few hours, the proposed multilayer system remains a fully intact barrier even after 24 h of uninterrupted exposure [29–33].

Given the demanding service conditions faced by critical and strategic infrastructure — where long-term surface integrity directly determines operational reliability — this level of corrosion resistance is particularly meaningful. Localized coating failure, spalling, or the accumulation of corrosion products on exposed structural components not only compromises mechanical integrity but also alters surface morphology and dielectric properties in ways that are difficult to

reverse. The fact that the multilayer coating maintains near-ideal capacitive behavior throughout the entire 24-hour test confirms that surface morphology, roughness, and the dielectric character of each layer remain essentially unchanged under aggressive urban conditions. To extract quantitative parameters, the equivalent circuits shown in Fig. 3 were fitted to the EIS data using ZSimpWin; the results are summarized in Table 1.

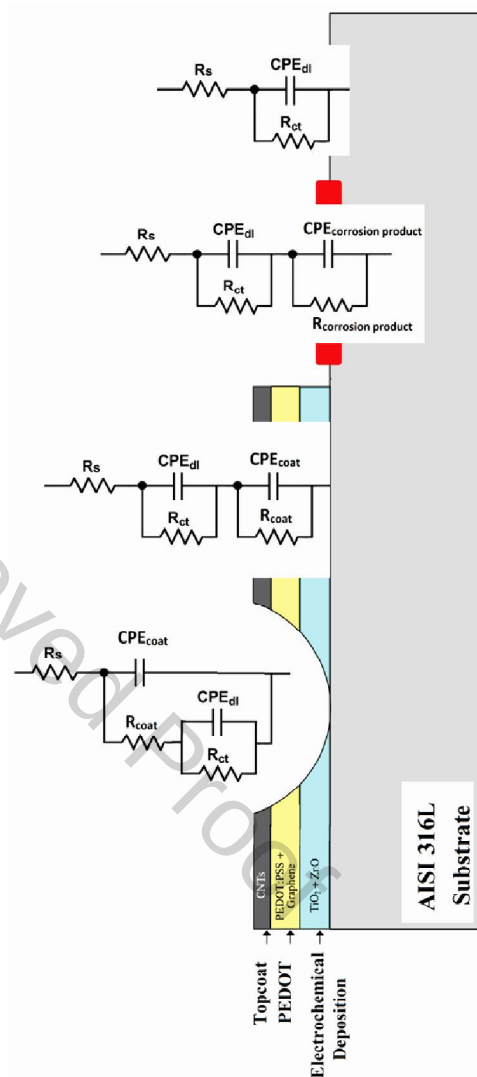


Fig. 3. Electrochemical impedance spectroscopy (EIS) results for bare and multilayer-coated AISI 316L stainless steel after 1 h and 24 h of immersion in simulated aggressive urban electrolyte (0.5 M NaCl + 0.1 M H_2SO_4 , pH $\approx$ 3), (a) Nyquist plots, (b) Bode magnitude plots, and (c) Bode phase angle plots.

Table 1. Equivalent circuit parameters extracted from ZSimpWin fitting of EIS data for bare and multilayer-coated

AISI 316L stainless steel after 1 h and 24 h of immersion in simulated aggressive urban electrolyte (pH ≈ 3).

Sample	Immersion time (h)	R_{sol} ($\Omega \cdot \text{cm}^2$)	R_{coat} or cp ($\Omega \cdot \text{cm}^2$)	CPE_{coat} or cp ($\mu\text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{n-1}$)	n_{coat} or cp	R_{ct} ($\Omega \cdot \text{cm}^2$)	CPE_{dl} ($\mu\text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{n-1}$)	n_{dl}	Chi-Squared
Bare 316L	1	29	-	-	-	5598	77.01	0.71	0.00012
	24	24	3759	82.99	0.68	2987	26.99	0.74	0.00037
Coated 316L	1	25	50900	8.11	0.82	12273	32.48	0.86	0.00048
	24	11	2574	6.27	0.81	8789	77.36	0.78	0.00031

Rs: solution resistance; Rcoat: coating resistance; Rct: charge-transfer resistance; Rcp: corrosion-product layer resistance; CPE: constant phase element admittance (Y_0 , $\mu\text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{n-1}$); n: CPE exponent ($0 < n \leq 1$). Chi-squared (χ^2) values confirm goodness of fitting.

Before discussing the fitted parameters, it is worth clarifying the physical meaning of the double-layer capacitance term and how it is extracted from the CPE element used in the equivalent circuits (Fig. 3). Because real electrode surfaces are heterogeneous and rough, a pure capacitor poorly describes the frequency-dependent response at the electrode-electrolyte interface; a constant phase element (CPE) is therefore substituted, with admittance, Eq. 4:

$$Y_{CPE} = Y_0(j\omega)^n \quad (4)$$

where Y_0 ($\mu\text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{n-1}$) is the CPE magnitude, ω is the angular frequency ($\text{rad} \cdot \text{s}^{-1}$), $j = \sqrt{-1}$, and n is the CPE exponent ($0 < n \leq 1$; $n = 1$ recovers an ideal capacitor, $n = 0.5$ represents a Warburg diffusion element). The effective double-layer capacitance C_{dl} is recovered from the CPE parameters using the Brug formula, which accounts for surface-distributed time constants [34]:

$$C_{dl} = Y_0 \left(\frac{1}{R_{sol}} + \frac{1}{R_{ct}} \right)^{n-1} \quad (5)$$

where R_{sol} is the solution resistance and R_{ct} is the charge-transfer resistance, both taken from the same equivalent circuit. For the coating circuit an analogous expression applies with R_{coat} replacing R_{ct} and CPE_{coat} replacing CPE_{dl} . For the bare substrate, the charge-transfer resistance R_{ct} starts at only $5598 \Omega \cdot \text{cm}^2$ after 1 h and falls to $2987 \Omega \cdot \text{cm}^2$ by 24 h. The simultaneous appearance of a second time constant — associated with a corrosion-product resistance of $3759 \Omega \cdot \text{cm}^2$ and a capacitance of $26.99 \mu\text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{n-1}$ — confirms the rapid build-up of a porous, unstable corrosion-product layer. The CPE exponent n drops from 0.71 to 0.68, reflecting a marked increase in surface heterogeneity and the progression of localized attack at MnS inclusions and grain boundaries. This behavior is entirely expected for 316L steel in a strongly acidic chloride medium (pH 3) and confirms that the native Cr_2O_3 -rich passive film is fully destroyed within 24 h [26–28].

The coated specimen behaves very differently. At 1 h, the coating resistance R_{coat} reaches $50,900 \Omega \cdot \text{cm}^2$ — more than nine times the charge-transfer resistance of the bare steel at the same time — and $n=0.82$, indicating near-ideal capacitive behavior and a uniform, defect-free surface. After 24 h, R_{coat} decreases to $2574 \Omega \cdot \text{cm}^2$; this is a notable drop, yet the value still approaches the R_{ct} of the bare substrate ($2987 \Omega \cdot \text{cm}^2$) at the same immersion time, and no second time constant appears. The n value shifts only marginally from 0.82 to 0.81, confirming that the dielectric character of the coating is essentially preserved.

The reduction in coating capacitance from $8.11 \mu\text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{n-1}$ at 1 h to $6.27 \mu\text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{n-1}$ at 24 h is, perhaps counterintuitively, a positive sign: it indicates that water and ion uptake into the outer polymer layers actually decreased over time, consistent with gradual densification of the coating rather than progressive degradation. The resistance drop itself is attributed primarily to limited ion diffusion into the outer polymeric-carbon layers and partial saturation of microscopic pores — a process largely offset by the photocatalytic self-repair activity of the TiO_2/ZnO base layer and the hydrophobic

character of the PEDOT:PSS/graphene and CNT/epoxy overlayers [24–28].

Maintaining a polarization resistance of 2574 $\Omega \cdot \text{cm}^2$ after 24 h of direct contact with the aggressive electrolyte limits the corrosion rate to below 0.008 mm/y — a reduction of more than 93% relative to the uncoated substrate — while preserving the surface morphology and overall coating integrity that are essential for reliable long-term performance in harsh urban environments.

These results gain additional weight when considered alongside published data on structurally comparable systems. In recent investigations of PEDOT-based nanocomposite coatings deposited on steel substrates and evaluated in acidic chloride media, coating resistance values in the range of 15,000–30,000 $\Omega \cdot \text{cm}^2$ have been reported, with measurable impedance loss observed beyond the first few hours of immersion. Epoxy films reinforced with reduced graphene oxide have similarly been shown to reach resistances on the order of 20,000–40,000 $\Omega \cdot \text{cm}^2$ under analogous electrolyte conditions, though again with declining barrier efficiency over prolonged exposure [29–34]. In both cases, the protective response depends on a single dominant mechanism — electrochemical passivation or physical diffusion resistance — without the architectural redundancy that a multilayer design provides. The R_{coat} of 50,900 $\Omega \cdot \text{cm}^2$ recorded here after one hour of immersion exceeds both reference classes by a factor of roughly two to three, and the near-ideal capacitive character retained after 24 h ($n = 0.81$) reflects the compounded barrier contributions of three compositionally distinct layers acting in series, a level of durability that no single-component system in the cited literature has demonstrated under comparably aggressive conditions.

The contact angle data (Table 2), reveal a systematic progression in surface wettability that directly reflects the layered architecture and chemical composition of the multilayer coating. The bare 316L substrate exhibits a hydrophilic character ($\theta = 68 \pm 2^\circ$), which decreases further to $52 \pm 3^\circ$ after immersion, consistent with oxide dissolution and increased surface energy under aggressive conditions [35]. Incorporation of the TiO_2/ZnO layer shifts the surface toward semi-hydrophobic behavior ($\theta = 78 \pm 3^\circ$, rising to $85 \pm 2^\circ$ post-immersion), a response attributable to photocatalytic restructuring of surface hydroxyl groups — an interpretation corroborated by the FTIR bands near $450\text{--}670 \text{ cm}^{-1}$ confirming Ti–O–Ti and Zn–O network formation.

Table 2. Water contact angle measurements of the bare 316L stainless steel substrate and each coating layer, before

and after 24 h immersion in the test electrolyte (3.5 wt.% NaCl + 0.1 M H_2SO_4 , pH ≈ 3).

Sample	Contact Angle Before Immersion ($^\circ$)	Contact Angle After 24h Immersion ($^\circ$)
Bare 316L substrate	68 ± 2	52 ± 3
TiO_2/ZnO	78 ± 3	85 ± 2
PEDOT:PSS/Graphene	105 ± 4	98 ± 3
Final coating (CNT/Epoxy)	148 ± 3	141 ± 4

The PEDOT:PSS/Graphene interlayer further elevates hydrophobicity ($\theta = 105 \pm 4^\circ$), as the conjugated aromatic backbone of graphene reduces polar surface interactions, consistent with the C=C stretching signatures observed at $\sim 1580 \text{ cm}^{-1}$ in the FTIR spectrum. The outermost CNT/Epoxy layer achieves a superhydrophobic state ($\theta = 148 \pm 3^\circ$, retained at $141 \pm 4^\circ$ after 24 h immersion), which mechanistically impedes electrolyte penetration to the metal interface, thereby suppressing both anodic dissolution and cathodic oxygen reduction — a direct correlation with the significantly reduced corrosion current densities recorded for the final coating system. This retained superhydrophobicity under immersion conditions confirms the structural robustness of the coating and its capacity to maintain a stable air-entrapping Cassie–Baxter wetting state even in a highly corrosive medium (3.5 wt.% NaCl + 0.1 M H_2SO_4 , pH ≈ 3) [36].

3.3. Mechanical Properties and Tribological Behavior

Fig. 4 presents the load–displacement curves and coefficient of friction (COF) profiles obtained for all tested configurations, with the corresponding mechanical and tribological parameters summarized in Table 3. The load–displacement curves obtained from nanoindentation testing (Fig. 4a) reveal a pronounced and systematic shift in mechanical response as additional functional layers are introduced onto the substrate. The bare AISI 316L stainless steel exhibits a penetration depth of approximately 300 nm under a peak load of 5000 μN , yielding $H = 2.2 \pm 0.1 \text{ GPa}$ and $E = 190 \pm 5 \text{ GPa}$ —values fully consistent with the established mechanical profile of austenitic stainless steel [16–17]. The TiO_2/ZnO ceramic bilayer produces the shallowest penetration depth ($\sim 170 \text{ nm}$) at

the same load, reaching the highest hardness in the series at $H=9.4\pm0.5$ GPa and $E=151\pm6$ GPa. This remarkable stiffening is rooted in the nanocrystalline grain structure that develops during low-temperature annealing, where grain-boundary strengthening and the ionic nature of metal-oxygen bonds collectively resist plastic deformation [37]. The PEDOT:PSS/Graphene intermediate layer, on the other hand, penetrates to roughly 600 nm under the same load, with $H=0.8\pm0.1$ GPa and $E=12\pm2$ GPa, reflecting the viscoelastic character of its conjugated polymer matrix. For the complete multilayer coating, the indenter reaches ~ 830 nm—the deepest displacement recorded—confirming that the CNT/epoxy outer shell acts as a compliant cushion that absorbs and redistributes contact energy before the load reaches the harder sublayers. The relatively steep and smooth unloading segments across all coated specimens signal a high fraction of elastic recovery, which fundamentally limits irreversible damage accumulation under repetitive mechanical contact.

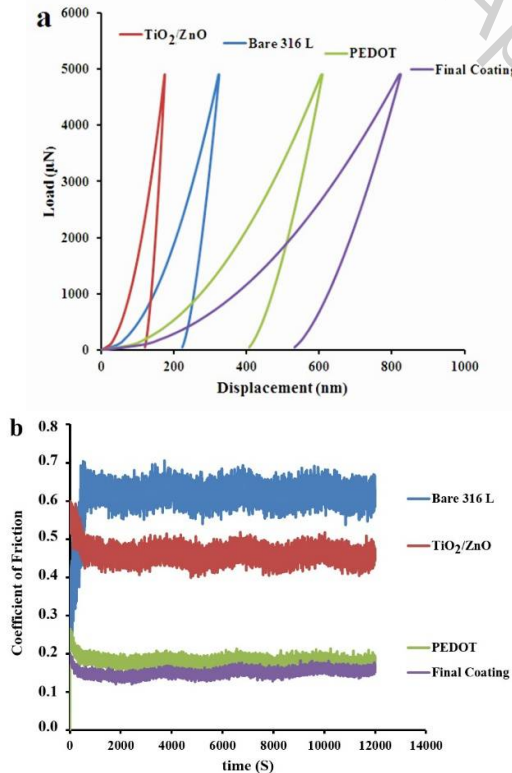


Fig. 4. (a) Load–displacement curves obtained from nanoindentation measurements, and (b) Coefficient of friction (COF) as a function of sliding time for bare AISI 316L stainless steel substrate and each coating layer.

Table 3. Mechanical and tribological properties of bare AISI 316L stainless steel and coating layers.

A more discriminating measure of wear

Sample	H (GPa)	E (GPa)	H/E	Coefficient of Friction (COF)
Bare AISI 316L	2.2 ± 0.1	190 ± 5	0.0113	0.62 ± 0.05
TiO ₂ /ZnO	9.4 ± 0.5	151 ± 6	0.0623	0.46 ± 0.04
PEDOT:PSS/Graphene	0.8 ± 0.1	12 ± 2	0.0667	0.18 ± 0.03
Final Coating	0.45 ± 0.05	6.2 ± 0.8	0.0726	0.14 ± 0.02

performance emerges when hardness is normalized against elastic modulus. The H/E ratio captures the material's capacity to store elastic strain energy without yielding, and it correlates more directly with practical wear resistance than absolute hardness values alone [17]. Among all tested configurations, the final multilayer coating achieves the highest H/E of 0.0726, despite having the lowest absolute hardness in the series. This apparent paradox is resolved by recognizing that the very low elastic modulus of the CNT/epoxy outer layer ($E=6.2\pm0.8$ GPa) disproportionately elevates the ratio, enabling the coating surface to deform elastically over a wider strain range before the onset of plastic flow. The TiO₂/ZnO layer yields $H/E=0.0623$, which also surpasses the PEDOT:PSS/Graphene value of 0.0667 only marginally, yet both far exceed the bare substrate's ratio of 0.0113. These results indicate that each deposited layer contributes an incremental but meaningful improvement to the overall tribological architecture, and the hierarchy of mechanical properties across the multilayer cross-section is not incidental but functionally optimized.

The significance of these H/E values is clarified by comparison with established nanocomposite benchmarks. Leyland and Matthews identified $H/E \approx 0.05\text{--}0.07$ as the practical lower bound for coatings capable of resisting plastic deformation under cyclic contact without requiring high absolute hardness [17]; at 0.0726, the multilayer system reported here sits above that threshold, reaching this position through the exceptionally low elastic modulus of the CNT/epoxy outer layer ($E = 6.2 \pm 0.8$ GPa) rather than through hardness maximization. Hard ceramic coatings such as TiN and CrN, which are widely reported at hardness values of

18–25 GPa, typically achieve H/E ratios of only 0.040–0.060 because their large elastic moduli dominate the ratio, leaving them susceptible to cracking under variable mechanical loading despite their surface hardness [37]. The multilayer architecture thus occupies a more favorable position in the H/E design space than conventional hard ceramic systems, and the sustained friction coefficient of $\mu = 0.14 \pm 0.02$ recorded over 12,000 s is a direct consequence of this elastic compliance rather than of hardness alone.

The friction evolution data presented in Fig. 4b consolidate this mechanical picture with direct tribological evidence. Bare 316L sustains a high and unstable coefficient of friction throughout the entire 12,000 s sliding interval ($\mu=0.62\pm0.05$), with persistent noise and erratic fluctuations that are characteristic signatures of adhesive wear, metallic ploughing, and intermittent junction formation at the contact interface. The TiO_2/ZnO interlayer reduces friction to 0.46 ± 0.04 through the hardness-dominated suppression of asperity interlocking, yet the signal retains notable scatter, suggesting that oxide film delamination events still occur under sustained sliding. The PEDOT:PSS/Graphene layer brings a qualitative change in friction character: the COF drops sharply to 0.18 ± 0.03 and stabilizes almost immediately, reflecting the well-known ability of graphene basal planes to shear at low stress and form a lubricious transfer film. The stabilization observed at this stage is attributed not only to the intrinsic low shear strength of graphene but also to the viscoelastic compliance of the PEDOT:PSS matrix, which is understood to accommodate micro-asperity contacts and redistribute local contact stresses more uniformly across the sliding interface. It has been reported that such polymer–nanocarbon hybrid interlayers are capable of suppressing stick-slip transitions that would otherwise manifest as high-frequency COF oscillations under reciprocating contact conditions. Furthermore, the conductive nature of this layer is considered to facilitate the dissipation of any triboelectrically generated charge, a mechanism that has been associated with a reduction in adhesive friction components in polymer-coated metallic systems. The progressive reduction in friction amplitude from the TiO_2/ZnO to the PEDOT:PSS/Graphene layer therefore reflects a transition in dominant dissipation mechanism—from plastic deformation and brittle oxide fracture toward viscoelastic damping and interfacial shear of ordered nanoplatelet assemblies. This mechanistic transition sets the stage for the final surface layer to operate under already-reduced

contact severity, which is considered essential to the durability of the outermost CNT-reinforced epoxy film. Most significantly, the complete multilayer coating achieves and sustains the lowest friction throughout the test at $\mu=0.14\pm0.02$, with negligible transient excursions from the very first moments of sliding. This behavior confirms that the hierarchical design—where a hard ceramic foundation carries load, an intermediate conductive-polymer layer provides interfacial compliance, and a CNT-reinforced epoxy surface supplies lubricity—acts synergistically to deliver a tribological performance that no individual constituent could achieve in isolation.

4. Conclusion

The multilayer coating developed in this study outperforms bare 316L stainless steel and any individual constituent layer by a margin that cannot be attributed to chance or incremental improvement. The impedance data for bare 316L — a declining R_{ct} from 5598 to 2987 $\Omega\cdot\text{cm}^2$ and the emergence of a second time constant by 24 h — are consistent with progressive passive film degradation and corrosion-product accumulation in aggressive chloride–acid media, pointing toward conditions favorable for localized attack. The multilayer architecture intercepts this degradation pathway at three mechanistically distinct levels. The TiO_2/ZnO ceramic base acts as a diffusion barrier against chloride and proton ingress while its type-II heterojunction enables partial photocatalytic self-repair under sustained electrochemical exposure. The PEDOT:PSS/graphene interlayer introduces interfacial compliance and shifts wettability toward hydrophobic behavior, preventing stress-driven delamination at the ceramic–polymer boundary. The CNT/epoxy outer shell finalizes the protection by establishing superhydrophobic character and delivering tribological stability — a friction coefficient of $\mu=0.14\pm0.02$ maintained over 12,000 s — that neither ceramic nor polymer coatings alone can sustain. The H/E ratio of 0.0726, the highest in the series despite the lowest absolute hardness, captures the defining quality of this system: it deforms elastically under contact rather than fracturing, making it resilient where conventional hard coatings are brittle. For urban infrastructure subjected to compounded acid, chloride, and mechanical loading over extended service lives, this result carries direct practical relevance.

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Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper. No financial, personal, or professional relationships with other people or organizations have influenced the work reported in this manuscript. All funding sources for this research have been disclosed in the Acknowledgments section.

Authors' Contribution Statement

Amir Farrokhi: Conceptualization; Data Curation; Formal Analysis; Investigation; Supervision; Validation; Writing – Original Draft; Writing – Review & Editing, etc.

Ali Shanaghi: Conceptualization; Methodology; Project Administration; Software; Supervision; Validation; Writing – Original Draft; Writing – Review & Editing.

References

- [1] Koch, G., Varney, J., Thompson, N., Moghissi, O., Gould, M., & Payer, J. (2016). International measures of prevention, application, and economics of corrosion technologies study. NACE International.
- [2] Hou, B., Li, X., Ma, X., Du, C., Zhang, D., Zheng, M., Xu, W., Lu, D., & Ma, F. (2017). The cost of corrosion in China. *npj Materials Degradation*, 1(1), 4. <https://doi.org/10.1038/s41529-017-0005-2>
- [3] Revie, R. W., & Uhlig, H. H. (2008). Corrosion and corrosion control: An introduction to corrosion science and engineering (4th ed.). Wiley-Interscience.
- [4] Pardo, A., Merino, M. C., Coy, A. E., Viejo, F., Arrabal, R., & Matykina, E. (2008). Pitting corrosion behaviour of austenitic stainless steels — combining effects of Mn and Mo additions. *Corrosion Science*, 50(6), 1796–1806. <https://doi.org/10.1016/j.corsci.2008.03.001>
- [5] Shahryari, A., Omanovic, S., & Szpunar, J. A. (2008). Electrochemical formation of highly pitting resistant passive films on a biomedical grade 316LVM stainless steel surface. *Materials Science and Engineering: C*, 28(1), 94–106. <https://doi.org/10.1016/j.msec.2007.09.002>
- [6] Ganesh Babu, S., Vinoth, R., Narayana, P. S., Bahnemann, D., & Neppolian, B. (2015). Reduced graphene oxide wrapped Cu₂O supported on C₃N₄: An efficient visible light responsive semiconductor photocatalyst. *APL Materials*, 3(10), 104415. <https://doi.org/10.1063/1.4928286>
- [7] Voevodin, N. N., Balbyshev, V. N., Khobaib, M., & Donley, M. S. (2003). Nanostructured coatings approach for corrosion protection. *Progress in Organic Coatings*, 47(3–4), 416–423. [https://doi.org/10.1016/S0300-9440\(03\)00131-0](https://doi.org/10.1016/S0300-9440(03)00131-0)
- [8] Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K., & Taga, Y. (2001). Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science*, 293(5528), 269–271. <https://doi.org/10.1126/science.1061051>
- [9] Gelling, V. J., Wiest, M. M., Tallman, D. E., Bierwagen, G. P., & Wallace, G. G. (2001). Electroactive-conducting polymers for corrosion control. *Progress in Organic Coatings*, 43(1–3), 149–157. [https://doi.org/10.1016/S0300-9440\(01\)00182-5](https://doi.org/10.1016/S0300-9440(01)00182-5)
- [10] Tiwari, A., & Turner, A. (2012). Intelligent nanomaterials. Wiley. ISBN 978-0-470-93879-9
- [11] Hamdy, Abdel Salam and Butt, D. P.. (2007). "Novel Anti-Corrosion Nano-Sized Vanadia-Based Thin Films Prepared by Sol-Gel Method for Aluminum Alloys". *Journal of Materials Processing Technology*, 181(1-3), 76-80. <https://doi.org/10.1016/j.jmatprotec.2006.03.042>
- [12] Zha, J. and Roggendorf, H. (1991), Sol-gel science, the physics and chemistry of sol-gel processing, Ed. by C. J. Brinker and G. W. Scherer, Academic Press, Boston 1990, xiv, 908 pp., bound—ISBN 0-12-134970-5. *Advanced Materials*, 3: 522-522. <https://doi.org/10.1002/adma.19910031025>
- [13] Orazem, M. E., & Tribollet, B. (2017). Electrochemical impedance spectroscopy (2nd ed.). Wiley. ISBN: 978-1-118-52739-9
- [14] Karuppuchamy, S., Amalnerkar, D. P., Yamaguchi, K., Yoshida, T., Sugiura, T., & Minoura, H. (2002). Cathodic electrodeposition of oxide semiconductor

- thin films and their application to dye-sensitized solar cells. *Solid State Ionics*, 30(1), 19–27. [https://doi.org/10.1016/S0167-2738\(02\)00599-4](https://doi.org/10.1016/S0167-2738(02)00599-4)
- [15] Peulon, S., & Lincot, D. (1996). Cathodic electrodeposition from aqueous solution of dense or open-structured zinc oxide films. *Advanced Materials*, 8(2), 166–170. <https://doi.org/10.1002/adma.19960080216>
- [16] Oliver, W. C., & Pharr, G. M. (1992). An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *Journal of Materials Research*, 7(6), 1564–1583. <https://doi.org/10.1557/JMR.1992.1564>
- [17] Leyland, A., & Matthews, A. (2000). On the significance of the H/E ratio in wear control: a nanocomposite coating approach to optimised tribological behaviour. *Wear*, 246(1–2), 1–11. [https://doi.org/10.1016/S0043-1648\(00\)00488-9](https://doi.org/10.1016/S0043-1648(00)00488-9)
- [18] Parichehr, R., Dehghanian, C., & Nikbakht, A. (2021). Preparation of PEO/silane composite coating on AZ31 magnesium alloy and investigation of its properties. *Journal of Alloys and Compounds*, *876*, 159995. <https://doi.org/10.1016/j.jallcom.2021.159995>
- [19] Feng, Z., Liu, Y., Hashimoto, T., Thompson, G.E., Zhou, X. and Skeldon, P. (2013). Influence of surface pretreatments on the corrosion protection of sol–gel coated AA2024-T3 aluminium alloy. *Surf. Interface Anal.*, 45: 1452–1456. <https://doi.org/10.1002/sia.5216>
- [20] Smith, A. L. (1960). Infrared spectra-structure correlations for organosilicon compounds. *Spectrochimica Acta*, 16(1–2), 87–105. [https://doi.org/10.1016/0371-1951\(60\)80074-4](https://doi.org/10.1016/0371-1951(60)80074-4)
- [21] Lee, Y. and Ahn, J.H. (2011). Erratum: Graphene-based transparent conductive films. *Nano*, 10 (1), 1592001. <https://doi.org/10.1142/S1793292015920010>
- [22] Groenendaal, L., Jonas, F., Freitag, D., Pielartzik, H. and Reynolds, J.R. (2000). Poly(3,4-ethylenedioxythiophene) and Its Derivatives: Past, Present, and Future. *Adv. Mater.*, 12: 481–494. [https://doi.org/10.1002/\(SICI\)1521-4095\(200004\)12:7<481::AID-ADMA481>3.0.CO;2-C](https://doi.org/10.1002/(SICI)1521-4095(200004)12:7<481::AID-ADMA481>3.0.CO;2-C)
- [23] Kou, Y., Liu, X., & Li, Q. (2026). The Impact of pH Value on Corrosion Behavior of 316L, 2507 and TA2 Alloys. *Materials*, 19(13), 2863. <https://doi.org/10.3390/ma19132863>
- [24] Zanotto, F., Grassi, V., Balbo, A., Monticelli, C., & Zucchi, F. (2018). Stress-Corrosion Cracking Behaviour of Lean-Duplex Stainless Steels in Chloride/Thiosulphate Environments. *Metals*, 8(4), 237. <https://doi.org/10.3390/met8040237>
- [25] Frankel, G. S. (1998). Pitting corrosion of metals: a review of the critical factors. *Journal of The Electrochemical Society*, 145(6), 2186–2198. <https://doi.org/10.1149/1.1838615>
- [26] Szklarska-Smialowska, Z. (1999). Pitting corrosion of aluminum. *Corrosion Science*, 41(9), 1743–1767. [https://doi.org/10.1016/S0010-938X\(99\)00012-8](https://doi.org/10.1016/S0010-938X(99)00012-8)
- [27] Strehblow, H.-H. (2002). Mechanisms of pitting corrosion. In P. Marcus (Ed.), *Corrosion Mechanisms in Theory and Practice* (2nd ed., pp. 243–285). Marcel Dekker. <https://doi.org/10.1201/b11020-8>
- [28] Laycock, N. J., & Newman, R. C. (1997). Localised dissolution kinetics, salt films and pitting potentials. *Corrosion Science*, 39(10–11), 1771–1790. [https://doi.org/10.1016/S0010-938X\(97\)00049-8](https://doi.org/10.1016/S0010-938X(97)00049-8)
- [29] Ali RM, Hermas AA, Elnady AM, Mansoure TH (2026);, "Corrosion resistance behavior of PEDOT nanocomposite coatings for steel material". *Anti-Corrosion Methods and Materials*, 1-13. Article in press. <https://doi.org/10.1108/ACMM-09-2025-3397>
- [30] Forouzesh, S., Jafari, H. & Sadeghzadeh, A. Effect of reduced graphene oxide produced by plant extract on anti-corrosion behaviour of epoxy coating. *J. Cent. South Univ.* 32, 820–836 (2025). <https://doi.org/10.1007/s11771-025-5920-8>
- [31] Roselli, S. N., Romagnoli, R., & Deyá, C. (2017). The anti-corrosion performance of water-borne paints in long term tests. *Progress in Organic Coatings*, 109, 172–178. <https://doi.org/10.1016/j.porgcoat.2017.04.031>
- [32] Deflorian, F., & Rossi, S. (2006). An EIS study of ion diffusion through organic coatings. *Electrochimica Acta*, 51(8–9), 1736–1744. <https://doi.org/10.1016/j.electacta.2005.02.145>

- [33] Macdonald, D. D. (2006). Reflections on the history of electrochemical impedance spectroscopy. *Electrochimica Acta*, 51(8-9), 1376-1388. <https://doi.org/10.1016/j.electacta.2005.02.107>
- [34] Brug, G. J., van den Eeden, A. L. G., Sluyters-Rehbach, M., & Sluyters, J. H. (1984). The analysis of electrode impedances complicated by the presence of a constant phase element. *Journal of Electroanalytical Chemistry*, 176 (1-2), 275-295. [https://doi.org/10.1016/S0022-0728\(84\)80324-1](https://doi.org/10.1016/S0022-0728(84)80324-1)
- [35] Boinovich, L. B., & Emelyanenko, A. M. (2008). Hydrophobic materials and coatings: principles of design, properties and applications. *Russian Chemical Reviews*, 77(7). <https://doi.org/10.1070/rc2008v077n07a beh003775>
- [36] Ragesh, P., Anand Ganesh, V., Nair, S. V., & Nair, A. S. (2014). A review on 'self-cleaning and multifunctional materials.' *Journal of Materials Chemistry A*, 2(36), 14773-14797. <https://doi.org/10.1039/C4TA02542C>
- [37] Musil, J. (2000). Hard and superhard nanocomposite coatings. *Surface and Coatings Technology*, 125(1-3), 322-330. [https://doi.org/10.1016/S0257-8972\(99\)00586-1](https://doi.org/10.1016/S0257-8972(99)00586-1)

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