

Article

Deterioration of Novel Silver Coated Mirrors on Polycarbonate Used for Concentrated Solar Power

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Abstract: The lifetime of mirrors in outdoor conditions is crucial in the correct operation of any concentrating solar power (CSP) installation. In this work, the corrosion behavior of two types of metallized surfaces was studied. The first was made of a flexible polymer having a deposited reflective silver metallic film. The second was made of the same surface type with a dielectric SiO₂ protection coating by an atmospheric pressure plasma jet. Polycarbonate sheets were used as substrates on which metallic silver was deposited by the Dynamic Chemical Deposit technique. This electroless technique allowed producing the mirror finishing under environmental conditions by sequentially spraying; as aerosols projected towards the substrate surface, the activation and reducing-oxidizing solutions with rinsing after each one. The silver coatings were about 100 nm thick. Environmental and accelerated weathering degradation and salt and sulfide fogs were carried out. XPS analyses show that the corrosion products formed were Ag₂S, AgCl, and Ag₂O. It was observed that the tarnishing was initiated locally by the formation of Ag₂S columns as eruptions on the surface. Subsequently, the ions diffused through the protective layer and into the silver reflective layer, chemically reacting with the silver. The main atmospheric agents were H₂S, chloride particles, and HCl. High reflectance was initially obtained of about 95%. The obtained results suggest mechanisms for the degradation of exposed silver surfaces to moisturized atmospheres with corrosive compounds.

Keywords: solar; corrosion; silver; mirrors; APPJ; concentrated solar power



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1. Introduction

Concentrating solar power (CSP) is one of the leading technologies for converting energy from the sun into thermal energy and subsequently into electrical energy [1–5]. One of the main components that make up these technologies are solar reflectors, for which durability is one of the crucial factors in the correct operation of any CSP installation. They require satisfying many requirements, including profitability, having a high specular reflectance, and long-term environmental stability [1,2]. However, the performance of the reflectors depends mainly on the films deposited on the substrates [6,7]. Metal films such as silver, copper, and aluminum usually offer adequate performance for optical reflectors [8]. Silver (Ag) has some advantages as a thin film material, since it is considered because of its relatively high ionization potential, because it is a noble metal that has high conductivity, and because it has high reflectance within visible and infrared illumination [9–11].

Commercial mirrors are usually second-surface mirrors, meaning the reflective coating is placed on the bottom of a transparent substrate. They have a drawback because the total

solar reflectivity is reduced through absorption losses. On the other hand, a first-surface mirror has a reflective layer deposited on the front part of the substrate so that the light is reflected directly on the upper surface [10,12]. The disadvantage of silver as a top coating is that it tarnishes and corrodes with exposure to the atmosphere because of sulfur [13] and chloride [14,15]. Therefore, first-surface silver mirrors require a transparent protective layer or a multilayered coating with high adhesion between each layer and the substrate.

Most published studies that have been conducted in the field of CSP are based on phenomenological approaches. The characterization of degradation, which mainly considers the loss of reflectance, is rarely related to physical or chemical processes responsible for the degradation of properties [16]. The gained experience in CSP plants allows identifying stress factors responsible for solar glass mirror degradation, such as wind, dust, rain, dew, humidity, irradiation, and temperature. Depending on the placement surroundings, the constraints involve sand, saline fog, chemical pollutants from near industries, and so forth [17]. The modeling of humidity has been approached using empirical models, such as the Eyring-based model, Peck's model, and the Temperature ($^{\circ}\text{C}$) + Relative Humidity (%) correlation ($T + \text{RH}$) [16].

The weathering degradation of solar mirrors is usually related to their specular reflectance's decrement [18–22]. There are reports on mirror deterioration in environmental conditions, but mostly of glass substrates [17]. In the case of polymeric substrates, the deposition techniques are under vacuum conditions [23].

Considering that both silver and aluminum are prone to change their oxidation state, altering the surface specularity, several schemes have been developed to protect mirrors from corrosion during long-term environmental exposure [24–28]. These schemes frequently incorporate one or more coatings of protection in combination with a thin deposit for adhesion that holds them attached to the metallic layer.

The main environmental corrosion products of silver are silver sulfide (Ag_2S) and silver chloride (AgCl), although silver oxide (Ag_2O) and silver sulfate (Ag_2SO_4) also have been found [27–30]. These corrosion products result from electrochemical reactions of silver when exposed to small amounts of air pollutants in the environment. In addition, there is a synergistic effect of multiple contaminants, particularly in the presence of oxygen and moisture, which accelerates corrosion [15]. It is of particular interest to understand the possible corrosive degradation mechanisms and the sub-products formed in the metallic layers of the solar mirrors and develop methods and strategies to prevent such undesired changes in the future.

Accelerated aging techniques are commonly used to correlate the effects of laboratory tests and outdoor exposure. However, these mechanisms are irreversible, so many studies focus on classifying better materials and addressing different aspects, such as composition, environmental conditions, and the structure of mirrors, among others.

Limam et al. [31] studied the formation of channels that connect the surroundings of the silver layer, through the protective layer, with the surface pores, which allows the entry of H_2S and the growth of columns, causing surface tarnishing. Mishra et al. [32] investigated the behavior of multilayer degradation concerning reflectance in conditions of accelerated weathering degradation and low salt fog. These coatings showed higher reflectance and less deterioration in the accelerated weathering degradation and the salt fog environment. Garcia-Segura et al. [33] studied the degradation of reflective materials for CSP under accelerated aging tests to study the influence of H_2S , where they found different degradation patterns for reflectors.

In this work, we show a layered structure of SiO_2 /silver/polycarbonate that also could be used in applications such as electromagnetic shielding or electromagnetic interference suppressor, similar to other metacomposites with negative electromagnetic parameters [34–38], which have been used in zero-dimensional nanoparticles, one-dimensional wires, two-dimensional coatings, and three-dimensional composites.

Although coatings can help prevent the corrosion of mirrors, this remains a problem where air or moisture can penetrate protective layers, for example, because of mechanical

or chemical damage, manufacturing defects, or loss of adhesion. This work aims to evaluate the phenomenon of degradation of the silver mirror surfaces during natural weathering degradation and accelerated tests in a controlled environment and correlate the physicochemical changes in the surface with the loss of reflectance.

This study and its novelty yield using silver-coated polycarbonates by an aerosol-propelled electroless deposition (dynamical chemical plating, DCP) as mirrors for solar concentration, which were protected by a silica coating deposited using an atmospheric pressure plasma jet (APPJ) that was automated for control in its reproducibility and industrial use. Furthermore, the corrosion was studied in this system, since the silver layer did generate defects in specific spots by external or internal factors. Currently, the mirrors are made of glass with significant differences in cost, weight, shipping and handling, installation requirements, replacement procedure, cleaning, breakage, etc. Additionally, the use of coatings brings advantages and difficulties, but this option allows to have a first-surface mirror with increased reflectivity efficiency compared to putting the silver on the substrate back.

2. Material and Methods

2.1. Deposition of the Metallic Layer

Polycarbonate sheets of 10×10 cm were used as a substrate on which metallic silver was deposited by the Dynamic Chemical Plating (DCP) technique with a coating thickness of approximately 100 nm. DCP has been used within automatized facilities (Figure 1). The importance of quality control for the layers of the mirror is emphasized. The automated facilities allowed the fabrication and reproducibility of mirrors in big areas, such as $1.2 \text{ m} \times 1.2 \text{ m} \times 0.0015 \text{ m}$ of mirrors for heliostats and $1.2 \text{ m} \times 2.4 \text{ m} \times 0.006 \text{ m}$ in the case of mirrors for parabolic trough solar concentrators. The surfaces were cleaned and pre-treated with a flame to improve adhesion between the metal layer and the substrate. The surface treatment with a flame was conducted to insert functional groups on the surface as an alternative, similar to corona electrical arc discharges and plasma surface pre-treatments. This was applied to all the pieces until homogenous wettability was obtained. This was conducted in the central section of the facilities shown in Figure 1.



Figure 1. Automated facilities to metallize and coat mirrors for CSP systems. The electroless metallization cabin (left side), entrance, and automatic polycarbonate sheets switching where the heat surface pre-treatment is applied (center), and APPJ cabin (right side).

2.2. Deposition of the Protective Layer

After the metallic layer deposition, two different coatings were deposited. For weathering degradation tests, a protective coating consisting of SiO_2 was applied. It was carried out by depositing hexamethyl disiloxane (HMDSO) reagent grade $\geq 98\%$ Sigma-Aldrich brand by the atmospheric pressure plasma jet (APPJ) technique [39–43]. Three applications were put on the metal substrate, allowing a coating thickness of about 600 nm. The process scheme for elaborating the substrate-silver-coating system is shown in Figure 2.

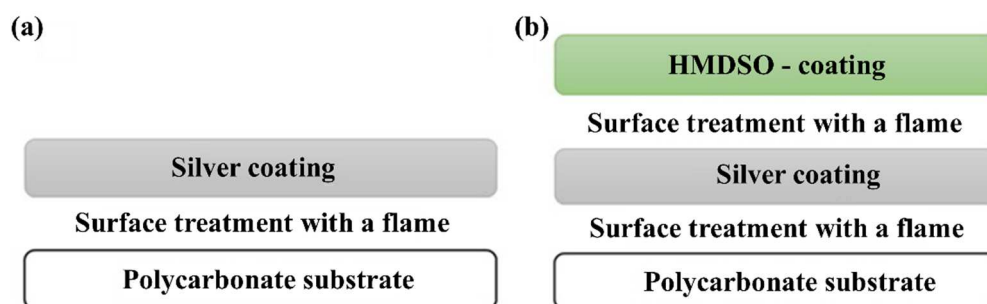


Figure 2. Process schemes for making a silvery mirror (a) without and (b) with a protective SiO_2 coating deposited using HMDSO.

In the case of electrochemical measurements, a protective layer of SiO_2 was applied [44,45]. It was deposited by the projection of an ultrasonic fog of tetraethyl orthosilicate (TEOS), reagent grade $\geq 98\%$ SIGMA-ALDRICH brand (San Luis, MO, USA), to the plasma zone of the APPJ.

The ultrasonic fog was obtained with a Yue-Hua brand ultrasonic nebulizer, model WH-2000. The distance between the plasma jet and the surface was 2 cm, and the time of exposition was 60 s with the projection to the plasma zone of the ultrasonic fog of TEOS. The coating thickness obtained was about 600 nm.

This type of coating has the characteristic of being continuous, homogeneous, dense, and adherent. The purpose of this layer was to serve as a physical barrier to the delay of corrosion. The process scheme for elaborating the substrate-silver-coating system is shown in Figure 2.

2.3. Weathering Degradation Tests

Samples of first-surface solar reflectors with and without protective coatings were tested after exposure to the environment for six months. Figure 3 shows the installed pieces on heliostats. Figure 3a shows the heliostat with sixteen sheets of mirrors and automatic sun-tracking. Figure 3b shows the assembling of mirror sheets with their aluminum frame on a steel structure.

Three replicas were used to guarantee representative test results. Some different parameters were recorded to monitor the conditions of natural exposure, which are important to influence the degradation of the coating and the substrate: temperature, wet weather (the time with condensed water on the surface of the coating), the total energy of solar radiation, and pollutants' content in the atmosphere (Cl, S, O, N, etc.). Table 1 shows the parameters of the conditions at the place where samples were installed, located at $20^{\circ}41'51''$ N, $100^{\circ}26'23''$ W with an altitude of 1895 m. As reported in the literature, a cross-shaped cut was made on each piece, penetrating the protective and reflective layers and exposing the metal directly to the corrosive atmosphere [33,46].



Figure 3. (a) Sixteen mirrors of solid polycarbonate conforming a heliostat. (b) Mirror sheets at the moment of being installed with aluminum frames.

Table 1. Parameters at the location where the tests were conducted (20°41′51″ N, 100°26′23″ W) after six months of exposure.

Parameter	Value
UV index	8.1 index (high)
Relative humidity (%)	45
Temperature (°C)	24
Solar radiation index	610 W/m ²

The behaviors of similar samples subjected to a series of accelerated aging tests based on salt fog and sulfur at high relative humidity were examined. The tests in a fog chamber were performed for 96 h under ASTM B117 [47]. Comparative studies were conducted on coated samples in a test atmosphere with controlled concentrations of 0.1 M H₂SO₄ [25] and 5% NaCl [47] at 28 °C and approximately 75% RH. Samples introduced into this test atmosphere fogged after 24 h of exposure. Subsequently, the morphology, structure, and chemical changes on the surfaces were evaluated.

2.4. Electrochemical Measurements

The samples with metallic coating and a barrier layer of SiO₂ by TEOS were electrochemically tested. The tests were conducted using H₂SO₄ because of predisposition of silver to oxidize in environments with hydrogen sulfide (H₂S) [48] and 0.5 M as the electrolyte, which was bubbled with nitrogen to remove the oxygen. The reference electrode used was SCE and platinum was the counter electrode. EIS measurements were performed at open circuit potential (OCP), with an amplitude of 10 mV and a frequency of 10⁵ to 0.01 Hz.

Cyclic potentiodynamic polarization (CPP) measurements were studied at 10 mV/s from −0.3 V vs. OCP to 0.6 V vs. OCP, and the final potential was 0 V vs. the starting potential. The corrosion rate (CR), corrosion current (*I*_{corr}), and corrosion potential (*E*_{corr}) were determined with Tafel slopes, extrapolating the anodic and cathodic slopes. This was calculated with Equation (1), where CR is the corrosion rate in mm/year, K is 3272 mm/cm per year, *I*_{corr} is the corrosion current [A], EW is the equivalent weight [g/MEq] (107.86 g/MEq for Ag), ρ is the density [g/cm³] (10.49 g/cm³ for Ag), and A is the geometric area [m²] (2 cm² for the electrochemical cell used).

$$CR = K \frac{i_{\text{corr}} EW}{\rho A} \quad (1)$$

2.5. Characterization

A combination of several analytical techniques sensitive to the surface was used to characterize the defects that occur on the reflective surfaces. The samples were gently rinsed with deionized water before the characterizations. The surface characterization was conducted by digital optical microscopy, X-ray emitted Photoelectron Spectroscopy (XPS), and reflectance.

The characterization of XPS was performed with a Thermo Scientific TM K-AlphaTM+ Spectrometer, an operating pressure of about 10^{-9} mBar, using an Al K α monochromatized X-ray source ($h\nu = 1486.6$ eV), with a spot size of 400 μm , step energy of 20.0 eV, with a total of 10 scans. All acquired spectra were processed by the Advantage software, using a Shirley-type background, and referenced to the C1s bond at 284.8 eV (NIST Standard Reference Database 20, Version 4.1). High-resolution spectra by XPS were taken from the core-level regions C1s, O1s, S2p, Ag3d, and Cl2p.

The digital optical microscopy was conducted using a Keyence VHX-5000 with an optical objective of 5000X, model VH-Z500R/Z500T with a numeric aperture N.A. = $N \sin \theta = 0.82$ (N refraction index around the objective/ $N \sim 1$ for air). A value close to 1 implies a higher resolution and a clearer image. The quantification of the detached area was conducted with the software of the microscope.

The reflectance measurements were performed with an Ocean Optics USB2000+ spectrophotometer having an integrating sphere with an internal white light source, using a 200 μm optical fiber. The measurements were performed in a range of 400–800 nm wavelengths. Three different areas were measured in each sample, with three repetitions in the areas of the cut to obtain representative results. The spectra were taken using an aluminum standard of Ocean Optics as the white reference (100% luminance), with metallic mirror finishing and high optical quality, and a cavity as the dark reference (0% luminance). The usual spectrum of silver increases at higher wavelengths because the white reference for calibration is something white such as Teflon. Nonetheless, such white references are weak in reflectance, even using an integrating sphere. The reflectance of a mirror can give values of 300–400% using such references, which can be normalized and set to 100%.

3. Results and Discussion

Square pieces of mirrors on polycarbonate substrates were successfully created by the DCP technique, which is an electroless metallization using an aerosol instead of dipping into a bath solution. Figure 4 shows two kinds of panels (1.2 m $\times$ 1.2 m), solid and twin wall sheets. This study makes no difference between them, since the tests were conducted on the silvery or silver/top coating regardless of the substrate type.

The following is an evaluation of the degradation of silver reflective surfaces exposed to environmental and accelerated weathering degradation. Reflectance is a parameter to quantify the optical quality of reflective surfaces for solar concentrators. In Figure 5, the reflectance curves of the samples that were exposed to controlled corrosive atmospheres are shown. Figure 5a shows the behavior of the reflectivity of the silver surfaces with and without coating in a 5% NaCl medium. The lowest percentage of reflectivity (36%) was that of the exposed surface without any coating compared to the coated surface, where an average of 62% was obtained. According to the optical images, a thinning was visualized in the metal layer, where moisture began to seep through the borders, and it began to degrade the silver layer. Similarly, black spots and tiny pores started to form on both surfaces, which caused the reflectivity percentage to decrease compared to the clean silver surface, which had 95% (black line).

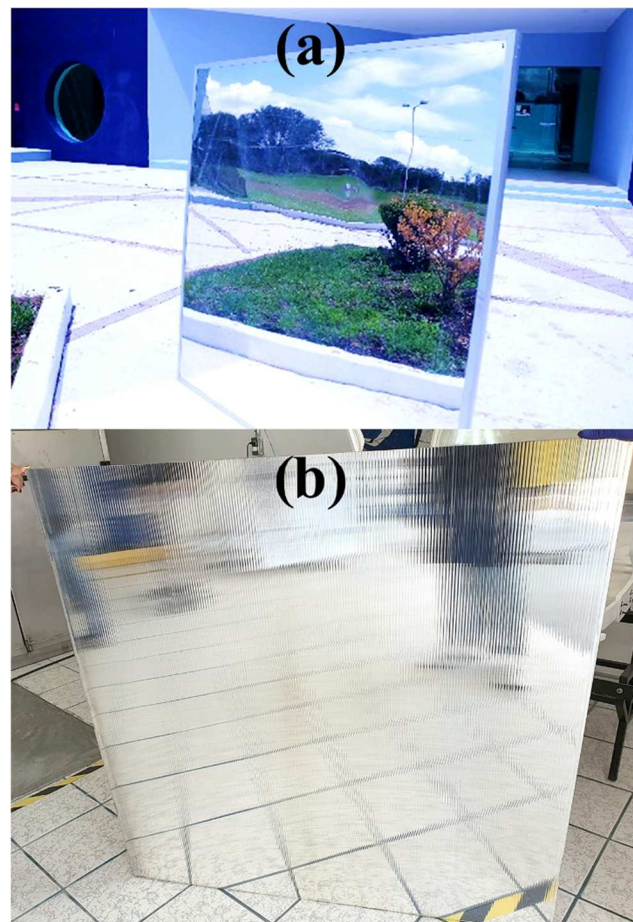


Figure 4. Plated polycarbonate mirrors using (a) solid and (b) twin wall sheets.

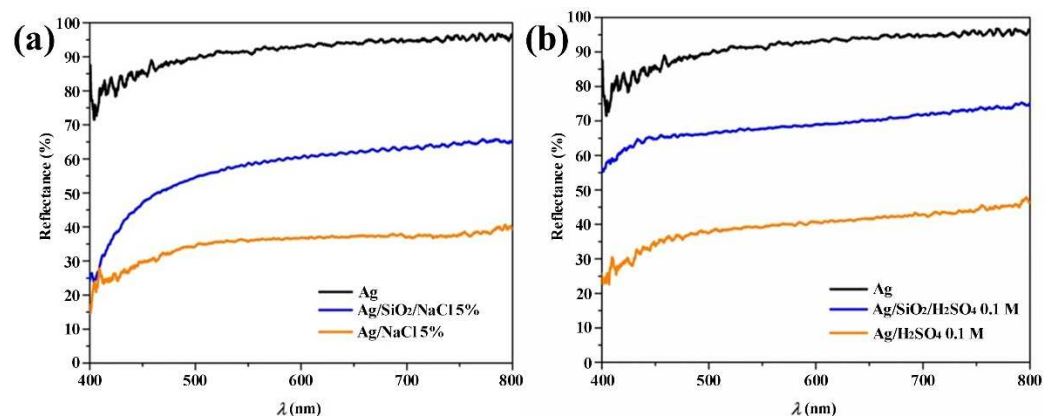


Figure 5. Reflectance curves of the accelerated weathering degradation tests of three different surfaces, bare silver, silver, and SiO_2 /silver, after exposure to a corroding medium, with two kinds of ion sources: (a) NaCl 5% and (b) H_2SO_4 0.1 M. The spectra were taken using an aluminum standard as a white reference.

Figure 5b shows the reflectance curves for the samples exposed to a corrosive atmosphere of H_2SO_4 0.1 M. The uncoated silver surfaces had the lowest percentage of reflectivity (40% average). The samples with coating had a percentage of reflectivity of 70% after the test. A decrease of 58% was observed on the uncoated surface and 26% on the coated surface compared to the clean silver surface (95%). The optical images showed that a sulfide layer began to form, which caused mechanical stress that broke the protective layer and caused detachments. Similarly, there were problems with adherence in some areas.

The water that reached the inner silver surface came through the silica (SiO_2) film pores or the interfaces, acted as a medium for the access of ions or molecules for the subsequent chemical reactions, and caused the dissolution of corrosion products [29].

The results from the characterization showed that the silver reflective layer was significantly changed by the corrosive atmospheres of NaCl and H_2SO_4 . The reflectivity losses of the two surfaces tested in the salt fog were more significant than those of the tests with sulfate. The process of forming AgCl and dissolving it, which was visualized as a thinning of the silver layer, resulted in a more significant change in similar periods. The roughness change and the thickness reductions had more influence than an Ag_2S layer formation. The silver thickness of these samples, usually about one hundred nanometers, reduces signifying, increasing the transmittance, considering that silver layers below about forty nanometers are transparent to the naked eye.

Figures 6a–d and 7a–d show the reflectance as a function of time and wavelength, respectively, for a silver surface without and with a SiO_2 protective coating. In these graphs, there were decrements in reflectivity with values of about 30% after 50 h. The protective coatings were composed of particles instead of continuous layers, which caused nearly similar behaviors to uncoated silver. The continuous and particulate coating made by APPJ using HMDSO depends on the process parameters, such as deposition rate, nozzle aperture, and distance to the substrate.

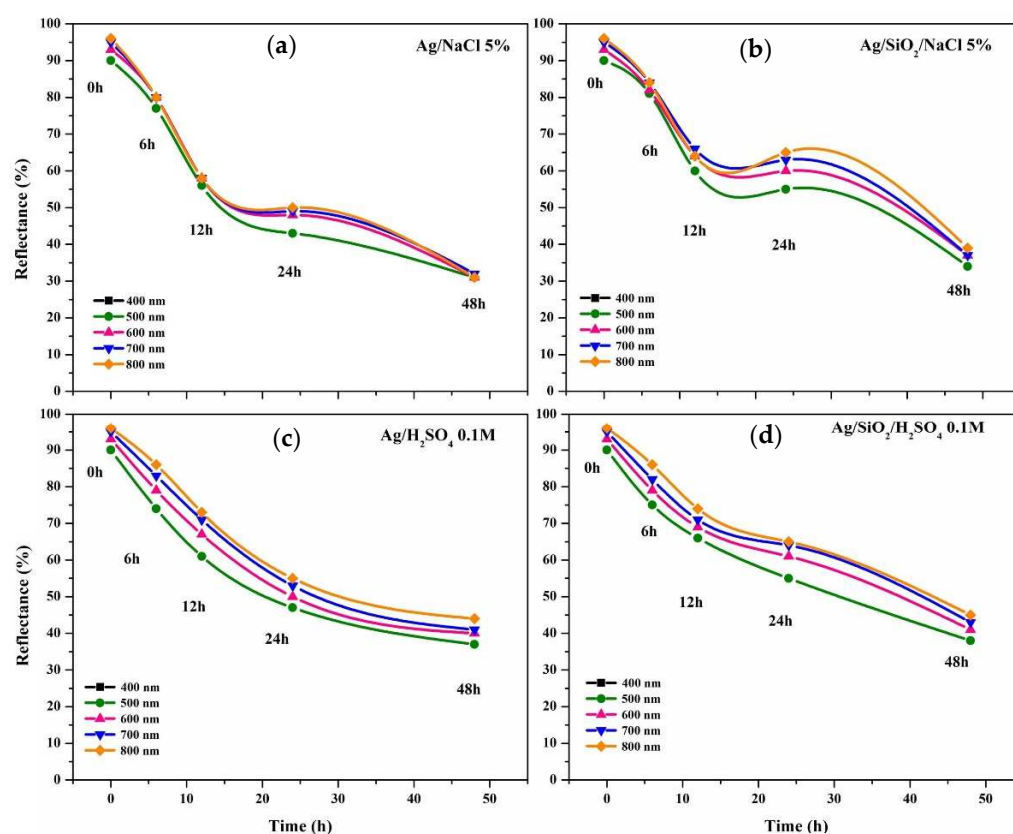


Figure 6. Reflectance curves vs. time of the accelerated weathering degradation tests of bare silver and silver with a SiO_2 protective coating in two kinds of ion sources: (a,c) NaCl 5% and (b,d) H_2SO_4 0.1 M, respectively.

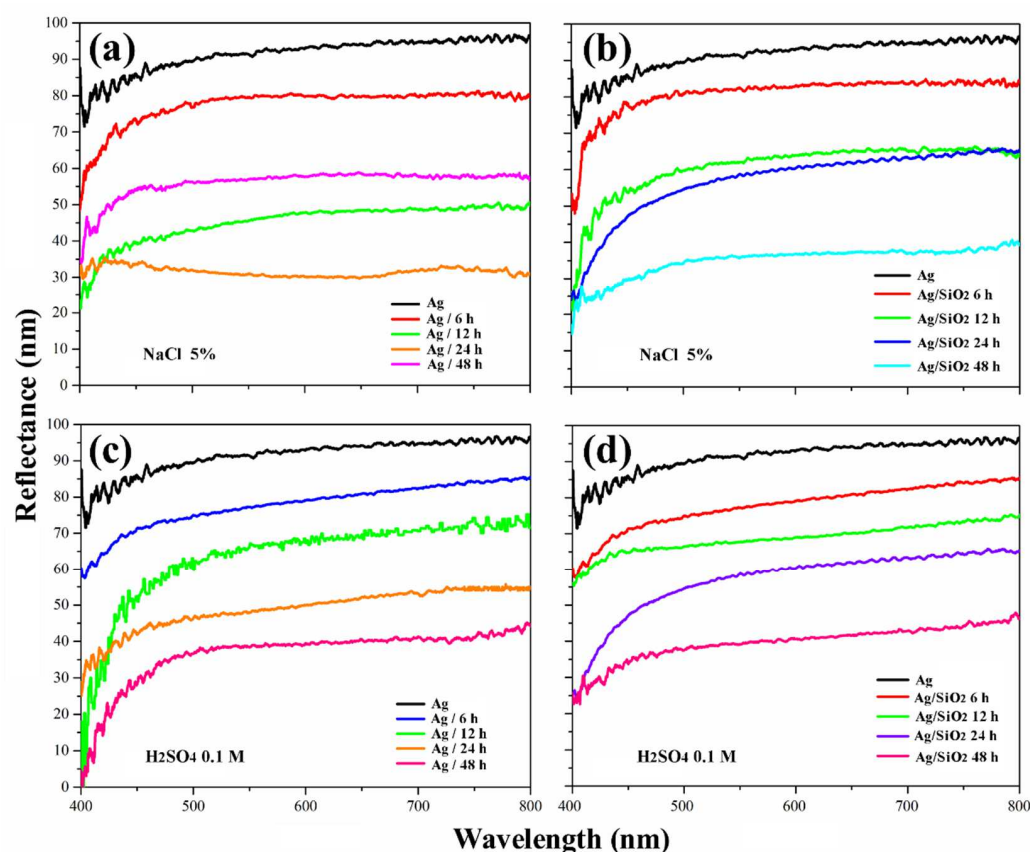


Figure 7. Reflectance curves vs. wavelength of the accelerated weathering degradation tests of bare silver and silver with a SiO₂ protective coating in two kinds of ion sources: (a,c) NaCl 5% and (b,d) H₂SO₄ 0.1 M, respectively.

In addition to the reflectance changes using NaCl and H₂SO₄ fogs, the silver layer reflectance detriment with time is also affected by salt concentration, original silver coating thickness, temperature, and dry/wet alternating periods.

The conducted tests showed that airborne particles could lead to the corrosion of silver, even with protective layers. It was found that airborne particles combined with water condensation (dew) on the protective coating of silver became a source of S/Cl and extended the moisture time on the surface. In this way, a solution containing S or Cl can be formed on the protective layer. This solution first damages the protective layer, then permeates the layer, and finally damages the silver. This mechanism is demonstrated by evaluating experiments with bare silver and silver coated with a SiO₂ layer [31]. Subsequently, water vapor penetrates the interface between the silver film and the substrate along the edges of the coating or through permeable defects, which causes delamination and blistering of the coating. The loss of reflectance was partly because of the scattered light of these blisters on the surface of the silver film.

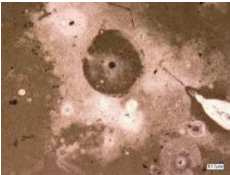
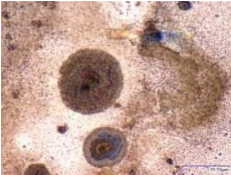
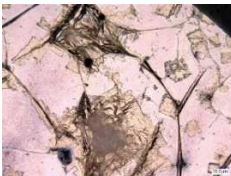
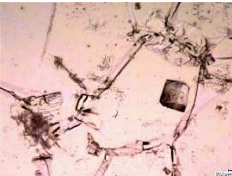
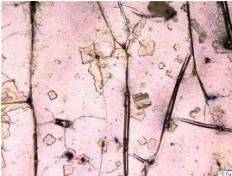
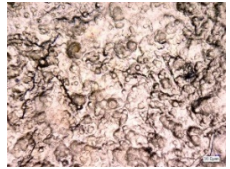
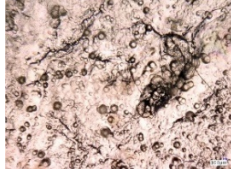
Table 2 is a general description of the most significant degradation characteristics found in the reflective layer with and without protection at the end of each test with corrosive fog.

For the surfaces that were exposed to the outdoor ambient atmosphere, it is observed that the tarnished layer on the uncovered surface appeared as dark gray circular points on a light brown background. On the other hand, the tarnish on the silver film coated with SiO₂ was mainly light brown.

The corrosion reactions of the silver exposed to the salt mist involve the dissolution of silver on the surface layer, which carried out the precipitation of AgCl on the surface. The migration and agglomeration of the silver atoms induced by Cl[−] ions weaken the adhesion

between the silver layer and the protective layer, which causes cracking and delamination of the latter.

Table 2. Analysis of microscopic degradation of reflective surfaces with and without a protective coating, in different accelerated weathering degradation tests (after 96 h) and environmental tests (after six months), where coating defects are observed. The scale bars are shown as blue lines representing 10 or 20 μm .

	Samples with a Protective Coating		Samples without Coating	
Environmental weathering degradation				
Accelerated weathering degradation (NaCl 5%)				
Accelerated weathering degradation (H ₂ SO ₄ 0.1 M)				

In an aqueous medium, Cl^- ions begin to react with the surface, causing cracks to originate on the silver–substrate interface and extending toward the top coating. This leads to the formation of corrosion products on the coating surface in the form of AgCl (Figure 8a, Equation (2)). Meanwhile, evolutionary ions occur in the cathodic hydrogen reaction (Equation (3)), as reported elsewhere [27]. As chloride ions penetrate the coating and even the metal layer through minor imperfections, they create small channels that make pores on the surface.

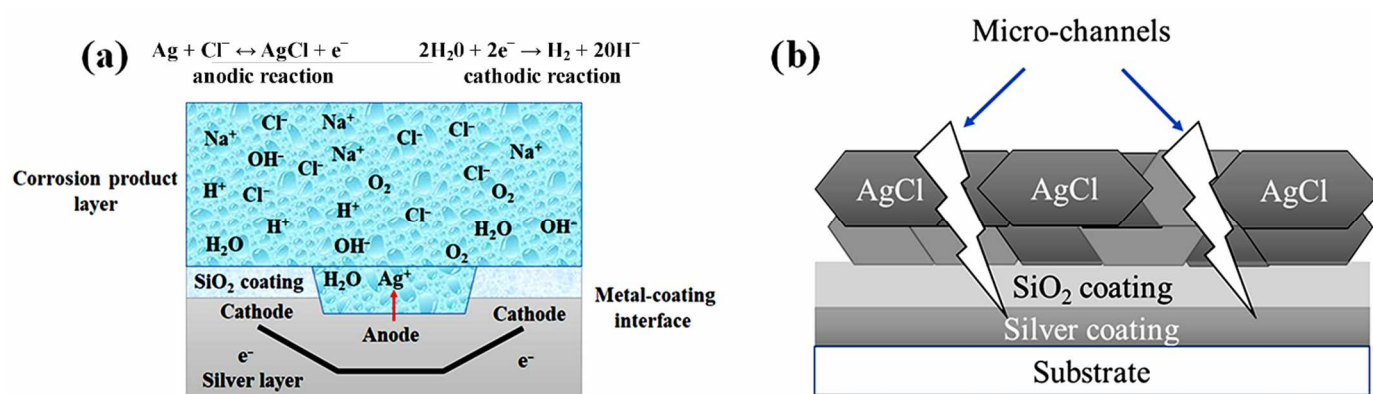


Figure 8. (a) Proposed degradation path for a silver surface coated in a NaCl medium. (b) Scheme of the growth of corrosion compounds through micro-channels and the evolution on the coating surface to the metal layer in a NaCl medium.





These pores are joined, causing the metal layer detachment. Compared to the uncoated metal surface, the metal layer was removed more quickly with a NaCl solution. The micro-channels formed through the AgCl layer are likely the main conduction path at this stage. The representative scheme of the growth of corrosion compounds is visualized in Figure 8b.

The transport of ions through the corrosion product layer is essential for corrosion [49]. However, in the case of AgCl formation, the dominant load carrier within the AgCl layer is still controversial. Some researchers state that Ag^+ is the leading charge carrier inside the micro-channels through the AgCl layer [50], while others suggest that Ag^+ and Cl^- contribute to the transport process.

In the test of accelerated weathering degradation of the coated silver surface with sulfate fog, the sulfide was deposited as a brown cover layer and caused the detachment of both the metallic deposit and the coating. In the case of the sulfate medium, the micrographs show that a similar mechanism produces the beginning of tarnishing to that of the medium with chlorides, which involves different paths that interconnect the protective layer and allow the entry of corrosive compounds into the silver layer. It is suggested that these permeation pathways are of microstructural origin and could correspond to the intergranular boundaries of the SiO_2 layer.

Optical microscope images show that blisters form, having cracks connecting them. Subsequently, these blisters cause detachment of the metallic and protective layers. In the case of the outdoor ambient atmosphere, it can be deduced that the blisters were formed due to a reaction of silver and chemical species that permeate, forming compounds which have a higher volume than the original metal and finally breaking, creating the crack. As a result, the blisters become permeable to moisture and increase the local corrosion rate.

Figure 9 shows examples of typical failures that cause degradation of the reflective layer of the silver mirrors after exposure to environmental and accelerated weathering degradation obtained with the digital optical microscope. The evolution of the points was monitored over time, showing a small growth of specific points. Significant corrosion points or a large number of small points, smaller than $100\text{ }\mu\text{m}$, cause the reflectance loss in this type of surface.

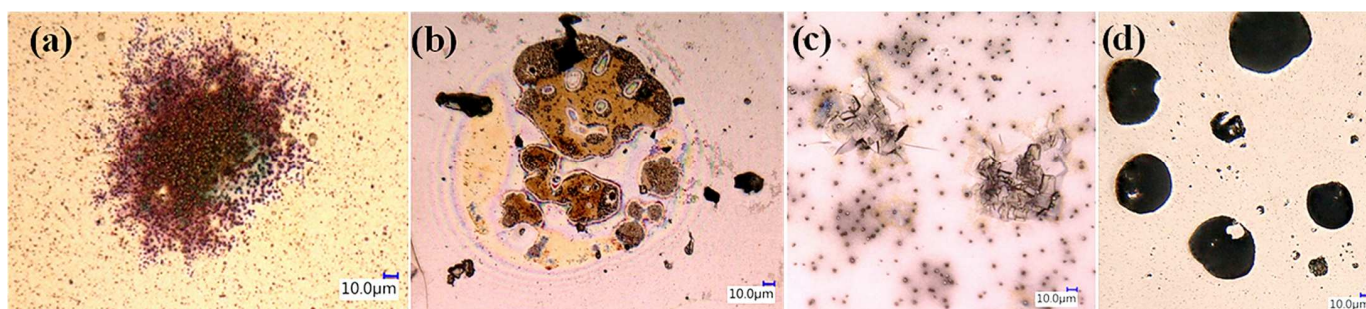


Figure 9. Optical microscope images of the most common corrosion points on silver reflective surfaces after 96 h of accelerated weathering degradation and after six months of environmental weathering degradation: (a) reflective surface exposed to the environment, (b) reflective surface with coating exposed to the environment, (c) reflective surface with coating in NaCl 5% aqueous solution, (d) reflective surface with coating in a H_2SO_4 0.1 M aqueous solution. The scale bars in blue lines represent $10\text{ }\mu\text{m}$.

Figure 10 shows the results of the XPS analysis for bare and coated silver samples exposed to accelerated weathering degradation conditions in NaCl 5% and H_2SO_4 0.1 M. The XPS $\text{Ag}3\text{d}$ core-level spectra (Figure 10a) show two peaks assigned to the $3\text{d}_{5/2}$ – $3\text{d}_{3/2}$ spin-orbit doublet (blue line), with the main peak at 368.2 eV. Likewise, the silver peaks of samples exposed to sulfate and chloride media were found at 367.8 eV and 374.1 eV, with

shifts in the peak energy levels of about ± 0.4 eV. These energy shifts were attributed to the formation of Ag_2O on the surface [28].

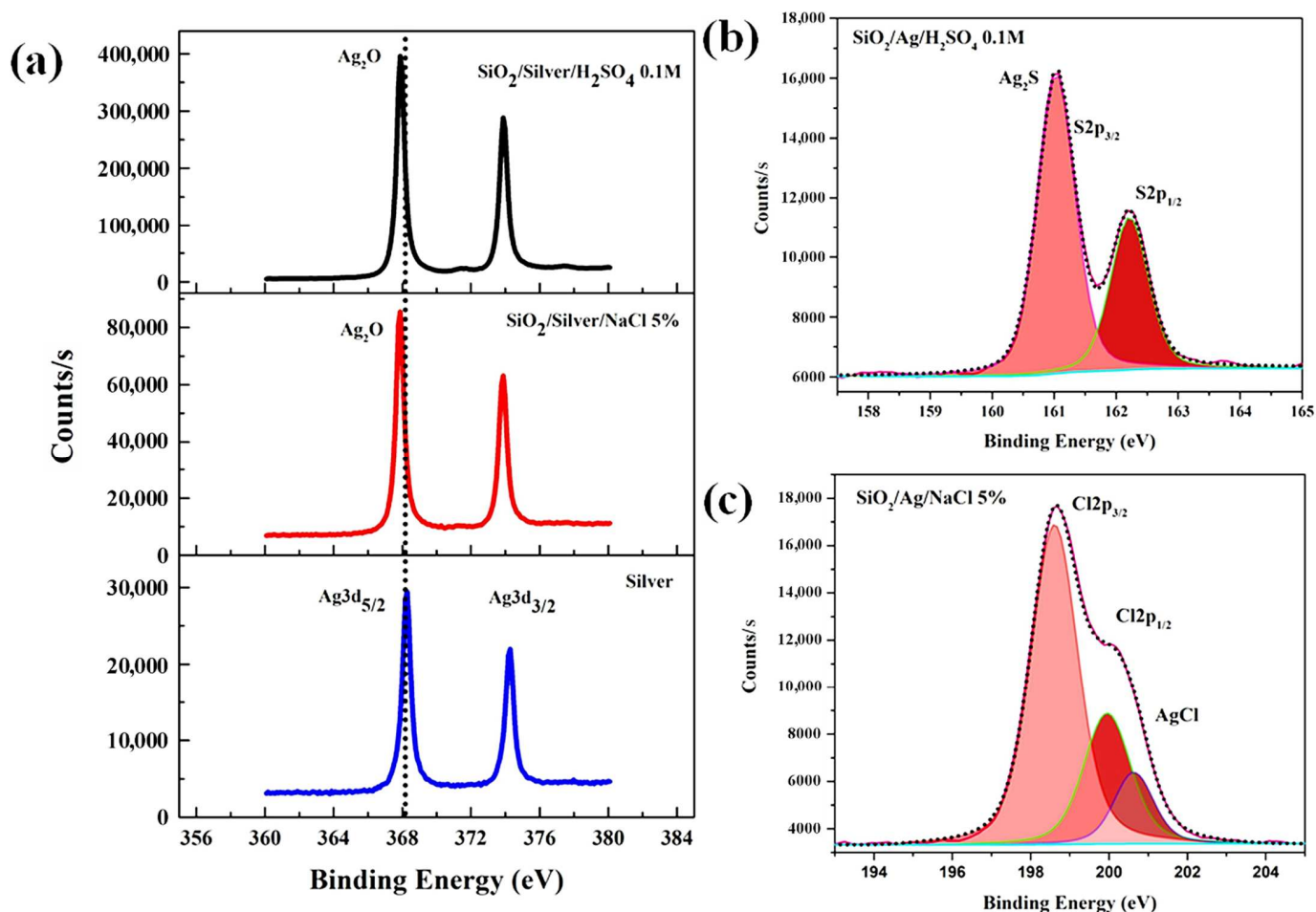


Figure 10. High-resolution XPS spectrum of (a) $\text{Ag}3d$, (b) $\text{S}2p$, and (c) $\text{Cl}2p$ of metallic surfaces with protective coatings tested in accelerated environments of 5% NaCl and 0.1 M H_2SO_4 .

Figure 10b,c show the high-resolution spectra of $\text{Cl}2p$ and $\text{S}2p$, respectively. Concerning the chlorine spectrum, the peak corresponding to the formation of AgCl with binding energy at 200.6 eV was observed. This can be corroborated in the optical microscope images, where the formation of a thick silver chloride layer was observed on the surface. Silver sulfide is a black corrosion product called tarnish, responsible for the loss of silver. After 48 h of exposure, the sulfide columns, consisting of Ag_2S as shown by XPS (Figure 10c), have grown from the silver layer and through the protective layer and emerged locally above the surface. Sulfur stains initially grow on the periphery of the pores, which can be attributed to the imperfect seal of the protective layer. The generated cracks open new routes for the entrance of H_2SO_4 that can supply ions for the more significant growth of Ag_2S . The silver layer began to be removed except in the pores where the silver was sulfide.

Figure 11 shows the results of the cyclic potentiodynamic polarization measurements and Table 3 shows the numerical values. In the case of the corrosion potential (E_{corr}), it shifts to a lower potential, from 63.25 mV to 8.42 mV. The corrosion current (i_{corr}) was determined by extrapolation of anodic (β_a) and cathodic (β_c) Tafel slopes. It decreases in the sample with the SiO_2 coating. The pitting potential (E_{pitt}) is the potential at which there is a change in the slope of the anodic zone, and this increase in current is attributed to the propagation of corrosion. It is higher in the sample coated with SiO_2 , which indicates that the pitting takes longer to propagate in that sample. These current and potential results

indicate that the coated piece is less prone to corrosion. While the corrosion rate is slower and decreases by 2.28 times in the coated sample, this is due to the protective barrier effect of the SiO₂ layer.

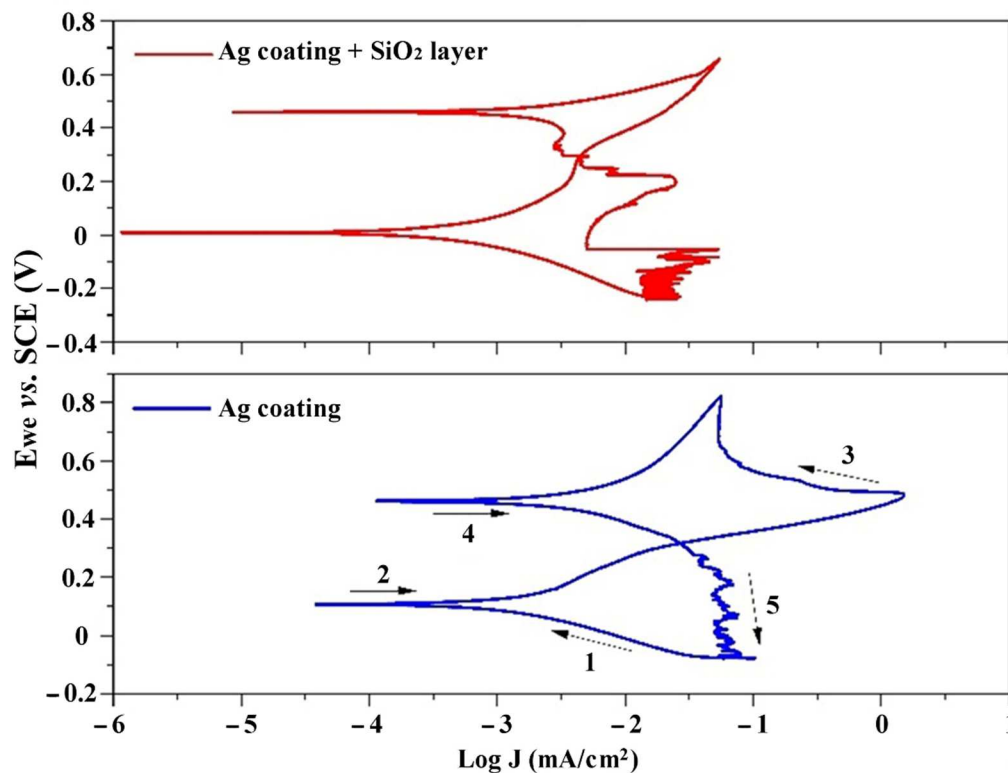


Figure 11. Cyclic potentiodynamic polarization results conducted in H₂SO₄ 0.5 M.

Table 3. Analysis of Tafel slopes.

Sample	β_a	β_c	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{pitt} (V)	Corrosion Rate (mmpy)
Ag Coating	174.167 ± 36	120.3 ± 32	63.25 ± 37.33	1.24 ± 0.59	0.13 ± 0.02	0.0208 ± 0.01
Ag Coating + SiO ₂ layer	185.5 ± 26	150.3 ± 29	8.42 ± 12.78	0.54 ± 0.13	0.21 ± 0.06	0.0091 ± 0.003

A Warburg element was added in both equivalent circuits in Figure 12 since the exchange current of Ag oxidation is very large. Therefore, the diffusion of Ag ions from the metal surface is the limiting stage of silver dissolution [51].

The results of electrochemical impedance spectroscopy are shown in Figure 12. The spectra of both samples approach capacitive semicircles. The largest corresponds to the sample with the protective coating, which is attributed to better resistance to corrosion through the barrier layer. The silver-coated sample was adjusted using a three-component equivalent circuit. In contrast, the silver-coated sample plus the protective SiO₂ coating was adjusted using a five-component equivalent circuit due to the contribution of the second layer. The equivalent circuits are composed of the resistance of the electrolytic solution (R_s), constant phase element (CPE), and capacitor (C), attributed to the electrochemical double layer, the internal resistance of the coating (R_s), and the resistance to charge transfer (R_{ct}), which is the value that indicates how easy it is for electrons to flow in the system and therefore is directly related to corrosion resistance. The corrosion rate of silica top coatings is 229% smaller for samples with silica layer protection against corrosion.

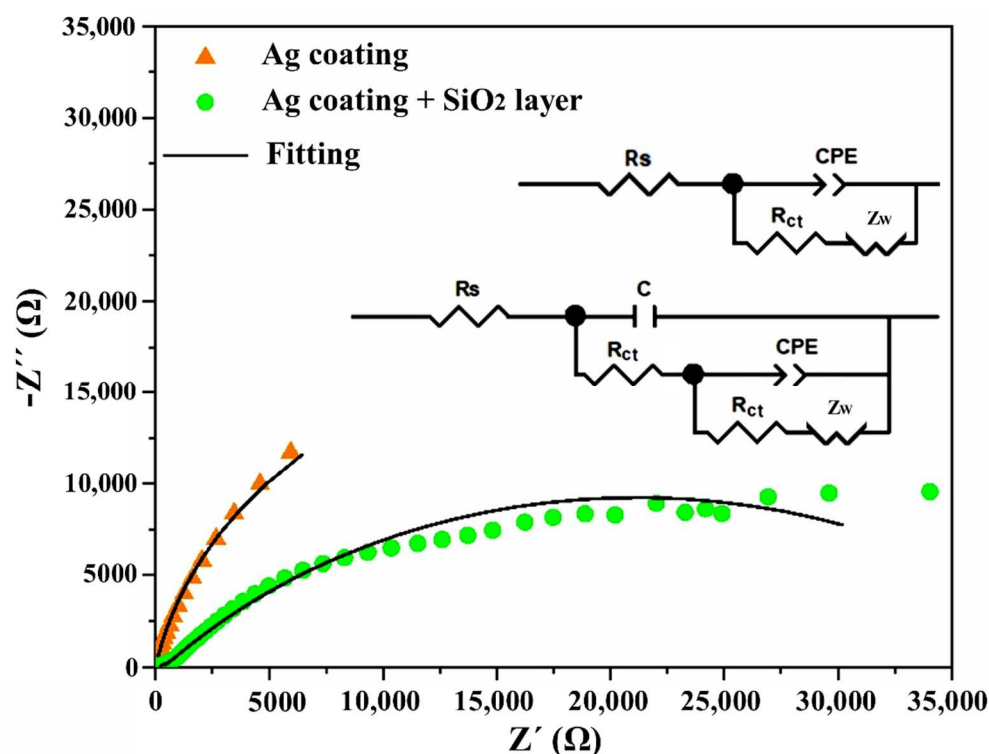


Figure 12. EIS measurements and equivalent circuits conducted in H_2SO_4 0.5 M.

Table 4 shows the results of the equivalent circuits of both systems. Solution resistance and charge transfer resistance are increased in the sample with the SiO_2 protective coating due to the inert protective layer that functions as a protective barrier. Therefore, the sample with the SiO_2 coating is protected against corrosion by this barrier.

Table 4. EIS results for surfaces of Ag coating and Ag coating + silica layer.

Sample	R_s (Ω)	C (F)	R_{ct} (Ω)	CPE-T ($\text{F.s}^{(n-1)}$)	CPE-P ($\text{F.s}^{(n-1)}$)	R_{ct} (Ω)
Ag Coating	25.52 ± 10.13	-	-	0.000544 ± 0.0003	0.8437 ± 0.059	$30,937.5 \pm 13,408$
Ag Coating + SiO_2 layer	210.2 ± 8.20	7.24×10^{-8}	205.12 ± 11.71	$4.81 \times 10^{-5} \pm 1.2 \times 10^{-5}$	0.0061 ± 0.002	$41,527.93 \pm 1572$

The R_{ct} was 134% higher for samples with silica layer protection against corrosion. Comparing the corrosion rates (Table 3) with the R_{ct} (Table 4), both indicate that the silica top coating acted as a physical barrier.

4. Conclusions

Silver mirrors on polycarbonate substrates were successfully made and tested, with a size of $1.2 \text{ m} \times 1.2 \text{ m}$. These mirrors are considered novel because (a) they were made on solid and twin wall polycarbonate sheets as substrates, (b) they were made by aerosol spraying of the reactants by the Dynamic Chemical Plating technique under environmental conditions, (c) atmospheric pressure plasma et coatings were deposited on the silver layer for protection, and (d) they were made using an automatized process.

After both environmental and accelerated weathering degradation tests, it was observed that the percentage of reflectance was decreasing on both surfaces with and without a protective coating. The accelerated weathering degradation tests evaluated the deterioration of the metal surface, which allowed proposing mechanisms for such deterioration behavior. The most common defects were silver sulfate spots on the reflector. These grow around the pores, which can be attributed to the imperfect seal of the protective layer and the formation of cracks, resulting in moisture diffusion into the metal–coating interface.

Other defects were the detachment of the reflective surface of the polymer substrate, blisters, and holes. It was shown that the degradation of the reflective surface resulted in the occurrence of absorption and spreading mechanisms.

The accelerated weathering degradation tests in H_2SO_4 and NaCl led to the failure of the optical performance of the coated silver samples. However, the decrement of reflectance is not as significant as in the bare silver samples, where a significant loss in reflectance was observed after exposure, which was caused by the development of sulfide and silver chloride stains.

The main defects revealed a degradation mechanism similar to the mechanism of Ag_2S column growth through the protection layer but involving different paths that pass through the protection layer and allow H_2S to enter the silver layer. It was proposed that these pathways were of microstructural origin and could correspond to the incompletely fused intergranular boundaries of the SiO_2 layer.

In the outdoor-exposed samples, pitting was found on the upper coating associated with silver corrosion points. Therefore, additional accelerated aging tests that simulate aggressive industrial environments would be significant.

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