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# Modified sol-gel layer incorporating hexagonal boron nitride (h-BN) nanosheets for improved corrosion resistance in plasma electrolytic oxidation coatings on AA2024

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#### ABSTRACT

The sol-gel sealing method is widely recognized as a simple and effective technique for enhancing the protective performance of plasma electrolytic oxidation (PEO) coatings. While sol-gel coatings are already known for their reliability and corrosion resistance, incorporating nanoparticles has been shown to further improve their barrier properties. Our objective was to validate the positive impact of incorporating nanosheets and assess the influence of h-BN functionalization in the sol-gel/PEO coating system on AA2024. Specifically, as-received, oxidized, and functionalized nanopowders at two concentrations were added to the sol-gel solution. (3-Aminopropyl)triethoxysilane (APTES) was selected as the suitable candidate for h-BN functionalization, given that the sol-gel sealing comprises a combination of (3-glycidyloxypropyl)trimethoxysilane (GPTMS) and tetraethoxysilane (TEOS). Consequently, higher compatibility between the nanopowders and the sol-gel matrix was achieved, thereby improving the barrier properties. Various chemical techniques, such as zeta potential (ZP) measurement and Fourier Transform Infrared Spectroscopy (FTIR), were employed to confirm the successful oxidation and functionalization processes. Rheology evaluation further affirmed the influence of h-BN functionalization on its compactness and the viscosity of the network. The trace of nanosheets within the sol-gel coating on top of the PEO layer was visualized using Field Emission Scanning Electron Microscopy (FE-SEM). Finally, Electrochemical Impedance Spectroscopy (EIS) analysis reported that the modified sol-gel coating with functionalized h-BN exhibited the greatest corrosion resistance after exposure to 0.1 M NaCl electrolyte for 14 days.

# 1. Introduction

The AA2024 alloy is an ideal candidate for the aerospace field due to its outstanding ratio of weight to strength [1,2]. It contains two primary copper-rich phases: the S-phase (Al<sub>2</sub>CuMg) and the intermetallic particles (IMPs) composed of major elements (Al, Fe, Mn, and Cu) in the form of Al<sub>6</sub>(Cu, Mn, Fe). However, the vulnerability of AA2024 to localized corrosion is a significant drawback, primarily due to micro-galvanic coupling between the IMPs and the aluminum matrix [3–7] Specifically, the passive layer over the S-phase is not sufficiently resistant to corrosion, and any disturbance strips this layer away, exposing the underlying metal to corrosive electrolytes [8]. Among the various strategies to improve the corrosion resistance of AA2024, surface treatment stands out as particularly effective [9,10].

PEO [11], anodization [12], diffusion treatment [13], thermal

spraying [14], ion implantation [15], physical vapor deposition (PVD) [16], chemical vapor deposition (CVD) [17], and conversion coatings [18] are listed as various approaches to surface modification. PEO is widely recommended by scientists for the surface treatment of light alloys owing to its versatile and environmentally friendly characteristics [19,20]. This technique operates at a higher voltage compared to traditional anodizing, addressing plasma interactions, electrochemical processes, and species transport at the electrode surface. PEO is considered more environmentally friendly than anodizing, utilizing an aqueous alkaline (diluted) electrolyte [21–23]. Through the PEO procedure, numerous transient micro-arcs form on the metal, generating intense localized heat and pressure. These micro-discharges cause the oxide layer to repeatedly liquefy and solidify, resulting in the inclusion of electrolyte components into the oxide coating and facilitating the development of phases at high temperatures [24,25]. This leads to the

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creation of a ceramic coating that offers superior hardness, wear resistance, and anti-corrosion properties. However, the PEO coating applied to aluminum alloys typically consists of two layers: a porous outer layer and an internal sublayer, in which the porous one can negatively impact the protective effectiveness over the long term [26].

The intrinsic permeable structure of PEO layers may be blocked by low-soluble chemicals that are precipitated via a variety of posttreatments, including conversion coatings and hydrothermal treatments [27–29]. Nevertheless, applying a sol-gel sealing has emerged as a practical approach for surface post-treatments due to its adaptability, simplicity in formulation, and environmental friendliness [30–34]. The barrier properties of the sol-gel in the case of PEO/sol-gel case mostly define the performance and lifetime of the coating system [35].

Apart from reliable corrosion resistance properties, sol-gel coatings often include some drawbacks including low crosslinking density, micro or nano cracks, and micro-pores which provide diffusion pathways for aggressive elements [36]. In order to compensate for these flaws, the addition of nanomaterials has been strongly recommended by scientists [37–40]. Based on the structure of the nano additives, they can prolong the barrier properties by prolonging the diffusion pathways, consequently enhancing the coating lifetime. Numerous studies have been conducted in terms of the addition of nanomaterials such as graphene [41], CNT [30], clay [42], ceria [43], silica [44], and h-BN [45] into the sol-gel coating.

H-BN, having the chemical structure and molecular impermeability like graphene along with insulating properties, could enhance the barrier properties. Much research has been carried out in various coatings, such as PMMA [46], polyimide [47], PVA [48], and resin [49] to validate the positive influence of h-BN. To optimize the barrier effect of the nanocomposite, a comparatively high concentration of the h-BN is often needed [45]. According to research done by Cui et al., the optimal anticorrosion performance in water-borne epoxy coating was achieved at 1 wt% of h-BN [50]. However, because of the robust "lip-lip" interactions between adjacent layers, aggregation severely restricts the intake of relatively high concentrations of the pristine h-BN in many solvents [51]. This issue can be partially solved by the creation of chemically modified h-BN [52,53]. As documented in other resources, h-BN modified by GPTMS or subjected to a plasma treatment has demonstrated improved dispersibility in acrylic coatings for steel protection [54,55].

The application of silane coupling agents to modify the surface of nanosheets has garnered significant interest as a viable means of achieving a satisfactory level of exfoliation and enhancing coating performance. GO nanosheets have been functionalized by Lee et al. [56] using various silane coupling agents containing alkyl, epoxy, and amine groups. They discovered that silanes could quickly form covalent bonds with the hydroxyl, epoxide, and carboxylic groups of GO. They claimed improved adhesive bonds at the interface with the steel substrate and appropriate dispersion of the functionalized GO nanosheets with silanes in the epoxy coating.

This study primarily aims to modify h-BN nanoparticles to produce oxidized h-BN (O/h-BN) and functionalized h-BN (F/h-BN). Additionally, it examines the effect of these nanoparticles, at two concentrations (1000 ppm and 2000 ppm), on the sealing behavior of a sol-gel coating applied to PEO-treated AA2024 alloy. TEOS, with its four hydrolyzable branches, plays a pivotal role in forming the sol-gel network. When combined with GPTMS, which contains three hydrolyzable branches and an epoxide functional group, the mixture facilitates the effective pore-filling of the PEO porous layer [57,58].

# 2. Materials and methods

#### 2.1. Materials

The substrate, a 9 cm<sup>2</sup> piece of AA2024 with a thickness of 0.16 cm, had a chemical composition of 0.03 % Zn, 0.12 % Fe, 0.61 % Mn, 1.41 % Mg, 4.5 % Cu, and Al balance (wt%). Before initiating the PEO, the alloy

Table 1

Summarized	01	different	coating	systems.

Name of the coating	h/BN incorporation into the sol-gel coating					
	Туре	Concentration (ppm)				
PEO	-	-				
PS	Neat sol-gel	-				
PS-N1	h-BN	1000				
PS-O1	O/h-BN	1000				
PS-F1	F/h-BN	1000				
PS-N2	h-BN	2000				
PS-O2	O/h-BN	2000				
PS-F2	F/h-BN	2000				

plates were cleaned in an ultrasonic bath containing acetone for 10 min. After being alkaline etched for 30 s using a solution of sodium hydroxide at 40  $^{\circ}$ C, the samples were acid-pickled for 30 s in a solution of nitric acid at room temperature.

A bipolar power source provided by Micronics Systems was applied to produce a square pulse pattern for 30 min at a frequency of 100 Hz, a duty cycle of 30 %, and an anodic current of 5 A in order to develop PEO coating. The RCQ parameter, which is set as 0.9, is the proportion of positive to negative charge (Qp/Qn) applied during a current pulse. KOH (1 g/L) and Na<sub>2</sub>SiO<sub>3</sub> (1.65 g/L), purchased from VWR, constituted the PEO electrolyte, which was kept below 40 °C in a jar attached to a cooling system [58,59].

The sol-gel solution was applied to cover the PEO specimens developed by combining GPTMS and TEOS precursors at 10 % and 20 % V/V, respectively, for one entire day in a solvent that included 60 % V/V distilled water and 10 % V/V ethanol, with the pH of 3 using acetic acid (all chemicals were purchased from VWR Co.). To enhance the protective features of the sol-gel coating, three different modes of h-BN nanopowders were introduced to the sol-gel coating, including asreceived h-BN, O/h-BN, and F/h-BN. The h-BN powders of 98 % purity and 1  $\mu$ m of average diameter were provided by Sigma-Aldrich Co. The way of modifications is explained below:

#### - Oxidation process of h-BN powders

To produce hydroxyl groups on h-BN nanosheets and edges, a relatively strong oxidation process was carried out. At first, 5 g of h-BN was added to a 200 mL concentrated solution in which the ratio of nitric acid to sulfuric acid had been set at 3:1, respectively. This solution was stirred for 10 h at room temperature followed by magnetic mixing at 80 °C in an oil bath for 72 h. Then, the centrifugation of the resulting solution was conducted during which the suspension was frequently washed to ensure the acidity of the powders was gone. Finally, the suspension was placed in an oven to dry at 60 °C over a night [60].

#### - Functionalization of O/h-BN procedure

The functionalization of O/h-BN was carried out using APTES as the sol-gel precursor. Initially, 2 g of O/h-BN was added to a solution consisting of 85 mL of ethyl alcohol, 5 mL of distilled water, and 6 mL of APTES. Acetic acid was then added to adjust the pH of the solution to 4.5, followed by stirring for 24 h at room temperature. Next, the pH of the solution was raised to 8–9 using a 5 wt% NaOH solution and the mixture was stirred in an oil bath at 80 °C for 2 h. The suspension underwent centrifugation six times, with each washing step involving a mixture of distilled water and ethanol in a 2:3 ratio. Finally, the suspension was placed in an oven at 60 °C overnight to obtain finely functionalized powders [61].

After obtaining various types of h-BN, 1000 ppm and 2000 ppm of each were added to the sol-gel solution at the initial moment of preparation for hydrolysis. Implementing a dip-coating technique via KSV Nima dip-coater equipment with a 100 mm/min withdrawal rate, sol-gel layers were coated on PEO panels. It was then cured for 1 h at 150  $^{\circ}$ C



Fig. 1. The FTIR spectra and schematic illustration of the pristine and modified h-BN nanopowders.

[57]. Various PEO coatings studied in this investigation were summarized in Table 1 where 'S' indicates the sol-gel system, 'N', 'O', and 'F' represent h-BN, O/h-BN, and F/h-BN, and the numbers 1 and 2 correspond to the 1000 ppm and 2000 ppm concentrations used.

### 2.2. Methods

#### 2.2.1. Characterization analyses

FTIR technique was utilized to not only examine the chemical changes upon the nanosheet modification but also explore the probable interactions that may arise between the sol-gel matrix and the nanoparticles. To do this, with the IRTracer-100 (Shimadzu Co.) apparatus, finely dried droplets from various sol-gel nanocomposites were obtained in order to conduct the FTIR test in the interval of 650–4000 cm<sup>-1</sup> wavenumber. The crystalline structure of various nanoparticles was examined through the X-ray diffraction (XRD) test in the range of 20° to 80°. A Malvern Panalytical Empyrean X-ray diffractometer with CuK $\alpha$ 1 radiation ( $\lambda = 0.15$  nm),  $\theta$ - $\theta$  geometry, one-second step length, and

 $0.026^{\circ}$  incremental interval was utilized. The ZP of the nanoparticles was carried out in both acidic and basic media by Malvern Zetasizer Nano ZS equipment. The viscosity and flow properties of various sol-gels were evaluated using an Anton Paar instrument. Measurements of rheological behavior were conducted inside the DG-41 cylinder with shear rates ranging from 0 to 200  $s^{-1}$  at a controlled temperature of 26 °C. The PEO sol-gel nanocomposite coating system, both from the surface and cross-section of produced samples, as well as the form of nanoparticles, was demonstrated using FIB/FE-SEM (TESCAN, GAIA 3) equipped with an Energy Dispersive X-Ray Spectroscopy (Detector X-Max N 80, Oxford with Aztec software). Imaging was performed using secondary electrons with the standard Everhart-Thornley detector. To observe nanoparticles, a highly diluted electrolyte containing various h-BN nanoparticles was prepared. A few droplets of this solution were placed on glass slides, which were then left in an oven overnight at 50  $^\circ\text{C}$  , and a conductive coating was deposited to ensure they were ready for imaging.



Fig. 2. The XRD result of h-BN, O/h-BN, and F/h-BN nanoparticles.

# 2.2.2. Electrochemical examination

Implementing the EIS method, the protective qualities of several PEO/sol-gel nanocomposite coatings were examined for 14 days of exposure to a 0.1 M NaCl solution via BioLogic SP-300 instrument. The coated samples were used as the working electrodes, platinum was used as the auxiliary electrode, and Ag/AgCl/KCl (+197 mV/SHE) served as the reference electrode in a three-electrode configuration. An amplitude modulation of 10 mV from peak to peak in a sine wave was applied to gather EIS data over frequencies from 100 kHz to 100 mHz. The samples, each with an exposed area of  $1.0 \text{ cm}^2$ , were immersed in the corrosive medium. To ensure measurement precision, a minimum of two electrochemical tests were carried out for each sample at every time slot. To analyze the electrochemical aspects associated with corrosion, the data underwent fitting. This process was performed using the *ZView* software, where the most suitable electrical equivalent circuit (EEC) was applied.

#### 3. Results and discussion

#### 3.1. Nanoparticle characterization

#### 3.1.1. FTIR spectroscopy

The characteristics of various types of h-BN were analyzed by FTIR analysis, as shown in Fig. 1 along with a schematic illustration nanoparticle. The B-N backbone of nanoparticles is confirmed by peaks at 1278 cm<sup>-1</sup> and 740 cm<sup>-1</sup>, corresponding to in-plane stretching and outof-plane bending vibrations, respectively [62]. The h-BN particles underwent oxidation using a mixture of strong acids to improve wettability and enhance the chemical activity of surface groups. Specifically, H<sup>+</sup> ions were attracted to the lone pair electron of N atoms, activating the boron sites. The presence of additional peaks at 3460 and 1670  $\rm cm^{-1}$  for O/h-BN and F/h-BN cases revealed O—H and N—H<sup>+</sup> vibrations [60]. The N-H<sup>+</sup> peak may also represent the presence of an amine group over the h-BN nanopowder [63]. The shoulder at 912  $\text{cm}^{-1}$  related to the B-N-O band confirmed the successful oxidation process of h-BN nanopowders [64]. Several peaks/shoulders in the FTIR spectrum confirmed the APTES treatment after the oxidation process to obtain F/ h-BN powders. The symmetric and asymmetric stretching vibrations of CH<sub>2</sub> at 2891 cm<sup>-1</sup> and 2954 cm<sup>-1</sup>, respectively, illustrate the grafting of the organic skeleton of APTES onto the oxidized nanoparticles [64]. Additionally, a shoulder at 1161 cm<sup>-1</sup>, appearing exactly at the characteristic peak of Si-O-Si of silane coatings, indicates Si-O vibrations [61]. Consequently, two possible mechanisms explain the interaction of APTES with O/h-BN in the sol-gel solution: condensation reactions and hydrogen bonding coupled with electrostatic interactions. In the first mechanism, the silanol groups of APTES can condense with the hydroxyl groups on the oxidized h-BN surface, forming stable Si-O-B bonds. In the second mechanism, the NH2 groups of APTES can interact with hydroxyl (-OH) groups on the O/h-BN surface through hydrogen bonding, where the NH<sub>2</sub> group acts as a hydrogen bond donor, and the hydroxyl group serves as an acceptor. Additionally, under the acidic pH conditions of the sol-gel solution (pH  $\sim$  4), the NH<sub>2</sub> group can be partially protonated to NH<sub>3</sub><sup>+</sup>, facilitating electrostatic interactions with hydroxyl



Fig. 3. ZP analysis conducted in acidic and basic media (a) as well as FE-SEM observation of pristine and modified h-BN nanopowders (b).



Fig. 4. FTIR analysis of the neat and incorporated sol-gel solutions with nanoparticles in two different concentrations.

# groups [64-66].

#### 3.1.2. XRD test

The crystalline structure of h-BN, O/h-BN, and F/h-BN was examined by XRD analysis, as depicted in Fig. 2. Several characteristic peaks are identical in all types of nanopowders at  $2\theta = 26.6^{\circ}$ ,  $41.5^{\circ}$ ,  $43.7^{\circ}$ ,  $54.8^{\circ}$ , and  $75.8^{\circ}$ , corresponding to the (002), (100), (101), (004), and (110) planes, respectively (JCPDS card no. 34-0421) [67]. It can be concluded that no noticeable change in the crystallinity of h-BN powders was observed after oxidation and functionalization procedures. Nevertheless, the intensity of Bragg's peak at  $2\theta = 26.6^{\circ}$  slightly decreases in the F/h-BN sample, most probably due to the adsorption of APTES on the structure. Furthermore, no new peaks relating to any other contaminant were detected, indicating that the sample is pure. Similar to other investigations, no changes in XRD spectra after chemical modification suggested that the modification did not result in restacking of the few layers [68].

# 3.1.3. ZP measurement

ZP analysis was conducted for h-BN, O/h-BN, and F/h-BN nanopowders in both acidic and basic media (pH ranging from 3 to 9), as reported in Fig. 3. Despite pristine h-BN not containing any functional groups, ZP values are observed across all pH ranges. At pH = 3, the concentration of H<sup>+</sup> is high, whereas the concentration of OH<sup>-</sup> dominates at pH = 9. Consequently, the ZP values become more negative from acidic to basic medium. After oxidation, the presence of oxygencontaining functional groups results in more negative values across the examined pH range due to the increased charge at the surface sites [69]. Another possible explanation for the more negative values in O/h-BN compared to h-BN is that the oxidation treatment may create defects in the h-BN skeleton. These defects could increase the active surface area available for interaction with ions in the electrolyte [70]. Interestingly, in F/h-BN nanopowder, the ZP becomes more positive at pH = 3 and more negative at pH = 9 compared to other nanopowders. The adsorbed amino groups on the h-BN body may protonate in acidic conditions to form positively charged (NH<sub>3</sub><sup>+</sup>). This protonation leads to an increase in the positive surface charge of the oxidized h-BN, resulting in a positive ZP. At pH = 9, deprotonation of amino groups on h-BN occurs [71], along with the presence of hydroxide ions diminished the ZP value of F/h-BN [72].

#### 3.1.4. FE-SEM observation

The stack of nanopowders was visualized using the FE-SEM technique, as shown in Fig. 3. It can be observed that while the morphology remains consistent, with the particle size of  $0.0725\pm0.0359~\mu\text{m}$ , variations in dispersion are evident. The agglomeration of nanoparticles was significantly reduced from h-BN to O/h-BN, most likely due to the electrostatic repulsive force between the oxidized particles, which induces a negative charge. However, silanization after oxidation resulted in the development of interactions and tendencies with the particles themselves, leading to enhanced agglomeration of O/h-BN after functionalization.

#### 3.2. Sol-gel coating examination

#### 3.2.1. FTIR analysis

The impact of various types of h-BN nanopowders on silane network formation was examined through FTIR analysis (Fig. 4). The stretching vibration of O-H and C-H peaks were attributed to peaks at 3331 and 2881 cm<sup>-1</sup>, respectively [73,74]. The peak at 1396 cm<sup>-1</sup> wavenumber is most probably related to the cyclic --CH bond, showing the trace of the epoxy group of GPTMS in the sol-gel sealing matrix [75]. It is generally known that the hydrolysis processes occur during the creation of the solgel network, converting alkoxy groups into hydrophilic silanol groups. After that, the hydrolyzed molecules find their way to either form a siloxane (Si-O-Si) network, which is more hydrophobic than silanol groups, or deposit on a metal surface (Si-O-M) [76]. The most noticeable peak in the spectra was related to the stretching vibration mode of Si-O-Si at 1022 cm<sup>-1</sup>, illustrating successful silane cluster formation in all types of sol-gel solutions [77]. The intensity of the Si-O-Si peak was magnified in the case of SF1 and SF2 compared to the neat sol-gel. The rationale behind the intensified Si-O-Si peak in

#### Table 2

The summary of the c	alculated ratio	of various tv	vpes of sol-gel solutions.
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Sample	S	SN1	SO1	SF1	SN2	SO2	SF2
[(Si—O—Si)/(Si—OH)]	1.86	1.67	1.87	2.34	1.43	1.75	2.42

these two solutions can be attributed to the formation of additional siloxane bonds between the silanol groups in the sol-gel matrix and the F/h-BN. The more pronounced Si-O-Si peak in the FTIR spectrum suggests that F/h-BN particles have been successfully incorporated into the sol-gel network. This incorporation occurs through covalent bonding, facilitated by the interaction of silanol groups on the sol-gel matrix with the functionalized F/h-BN surface. In other words, the presence of amino silane in the F/h-BN on the one hand and the silane matrix, comprised of TEOS and GPTMS, on the other hand led to establishing new bonds through the condensation reaction between the matrix and F/h-BN. To gain a clearer insight, the proportion of [(Si-O-Si)/(Si-OH)] was calculated and summarized in Table 2. The Si—OH bond is observed at the peak at 906  $cm^{-1}$ . The calculated values demonstrated that in both pristine h-BN concentrations, specifically in 2000 ppm, the hydrolysis and condensation reactions were hindered. causing a negative influence on network formation and subsequently its compactness. In SO1 and SO2, the ratio was almost the same as that of the neat sol-gel, exhibiting no significant change after incorporation. The highest evaluated ratio belongs to SF2, revealing that by heightening the concentration, the compatibility of F/h-BN to the sol-gel network was enhanced. The reaction between the epoxide group of GPTMS and the amine group of APTES can occur through the ring opening of the epoxide group, as depicted in the following reaction [78,79]:



Consequently, the integration of F/h-BN into the sol-gel matrix may be facilitated not only by condensation reactions between silane groups but also through the ring-opening mechanism of GPTMS induced by the amino group. This dual interaction mechanism likely contributes to the increased compactness and viscosity of the sol-gel system incorporating

#### F/h-BN.

#### 3.2.2. Viscosity measurement

The rheology analysis (Fig. 5) illustrates the Newtonian behavior of sol-gel solutions with a variety of h-BN at two different concentrations. As expected, all incorporated sol-gel solutions had a higher viscosity than the neat one, and the higher the concentration of the introduced h-BN, the higher the viscosity. At each specific concentration, the viscosity follows the order SF > SO > SN, indicating that after each nanopowder treatment and introduction to the sol-gel, the compactness of the coating was enhanced. The higher the functional groups are present on the h-BN, the higher the possibility of chemical reaction with the sol-gel matrix. The presence of oxygen-functional groups led to the involvement of the O/h-BN nanopowders in hydrolysis and condensation reactions. For F/ h-BN, on the one hand, the functionalization was carried out by a silane precursor (APTES), and on the other hand, the coating itself is silane-based. Consequently, the compatibility of F/h-BN within the solgel network is higher than that of the other coating systems, which also confirms its higher viscosity and compactness. The presence of an active amine group on the h-BN surface enhances its ability to chemically interact with the sol-gel coating, thereby improving the compactness and barrier properties [80]. SF2, having the highest amount of F/h-BN, had the maximum viscosity not only because of the greater amount of nanopowders but also because of the more active nature of the obtained nanopowder. Moreover, the presence of the amine group on h-BN likely results in the ring opening of the epoxide group in the GPTMS molecule, consequently increasing the viscosity of the sol-gel solution. The viscosity enhancement originating from the ring opening of GPTMS by amine groups has been reported by other researchers [78,79].

#### 3.2.3. FE-SEM planar images

The planar view of the PEO samples coated with a sol-gel layer with/ without various types of h-BN particles was exhibited in Fig. 6. Recurrent oxide layer melting and solidification in a solution containing silicates throughout the PEO treatment produce distinctive porous patterns on aluminum alloys. Numerous holes and cracks appear haphazardly throughout the surface as a result of dispersed spark creation, plasma processes, and dielectric breakdown. Following the application of the sol-gel covering, pores and cracks were sealed, while some relatively larger ones could still be seen in the images. Higher magnifications provide a clearer insight into the PEO surface texture following the sol-



Fig. 5. Viscosity versus shear rate examination of sol-gel solutions in the presence of various types of nanoparticles.



Fig. 6. FE-SEM surface imaging in two magnifications of PEO (a1, a2), PS (b1, b2), PS-N1 (c1, c2), PS-O1 (d1, d2), PS-F1 (e1, e2), PS-N2 (f1, f2), PS-O2 (g1, g2), and PS-F2 (h1, h2).

gel application. Comparing PS with the rest of the sealed PEO layers, traces of nanopowders inside the sol-gel coating can be distinguished. Clearly, the higher the concentration, the more visible the particles over the PEO surface.

#### 3.2.4. Cross-section observations

FE-SEM pictures and EDS maps from the cross-sections of the PEO and PEO/sol-gel coatings are shown in Fig. 7. Due to the oxidation in the

silicate electrolyte, silicon (Si), aluminum (Al), and oxygen (O) elements appeared in the PEO coatings. It is widely recognized that greater coating thickness generally correlates with improved corrosion resistance properties. However, for PEO sublayers, the pore-filling capability of the top layer also plays a critical role [35]. The emergence of silicon inside the pores of the samples coated with PEO and sol-gel corroborated the capability of the sol-gel to fill the pores. No significant differences could be noted when comparing the sealed coatings. Although chemistry



Fig. 7. FE-SEM images plus EDS maps of various PEO/sol-gel coating systems.



Fig. 8. Nyquist diagrams of the PEO coated samples during two-week immersion in 0.1 M NaCl electrolyte.



Fig. 9. Bode spectra of coupons upon two-week exposure to the saline electrolyte.

and incorporation are not identical, some may be more condensed and compact than others, but the sealing ability of different kinds of incorporated sol-gel coatings was almost similar. As seen in the images, solgel sealing either deposits on the PEO coating (which is slightly happening) or diffuses through the cracks and pores. What matters concerning corrosion protectiveness is the quality of the barrier properties over the exposure time.

#### 3.2.5. Corrosion resistance evaluation

EIS was exploited to evaluate the corrosion resistance of PEO/sol-gel coatings with various types of h-BN incorporations. The Nyquist plots in

Fig. 8 and the Bode graphs in Fig. 9 respectively provide a visual representation of the EIS data for two weeks of immersion in a chloride solution. Furthermore, a collection of different EECs is presented in Fig. 10 to analyze the EIS outcome. Table 3 provides a summary of the electrochemical variables, which include  $R_{ct}$  (charge transfer resistance),  $R_{PEO}$  (PEO layer resistance), and  $R_{mix}$  (PEO/sol-gel mixed area resistance). Because of heterogeneity and roughness, no surface is an ideal interface. For this reason, the constant phase element (CPE) was employed rather than an ideal capacitor dictated by Eq. (2) [81].

$$Z_{CPE} = \left[\frac{1}{Y_0 (i\omega)^n}\right]$$
(2)



Fig. 10. Various employed EEC for the EIS fitting.

where *n* is the frequency dispersion factor with a domain of 0-1, denoting the ideality of the system as pure capacitance (1) or pure resistance (0). *Y*<sub>0</sub> represents the admittance of the CPE.

In the EIS spectra, experimental and fitting data are displayed as markers and solid lines, respectively. In that order, the PEO layer, double-layer, and PEO/sol-gel mixed area are the reasons for the terms CPE<sub>PEO</sub>, CPE<sub>dl</sub>, and CPE<sub>mix</sub>. It is worth mentioning that, following the application of the sol-gel top layer, the mixed region is composed of two distinct layers: an outer layer (R<sub>mix, out</sub> and CPE<sub>mix, out</sub>) containing the sol-gel precipitation and mostly the PEO outer layer, and an inner layer (R<sub>mix, in</sub> and CPE<sub>mix, in</sub>) consisting of the diffused sol-gel into the pores combined with the PEO inner layer.

PEO coatings are typically defined by the presence of two separate layers: an inner layer and an outer layer. [82]. The porous layer is perceived to have a negative long-term effect as it allows the corrosive medium to diffuse through it and reach the substrate. A clear distinction between these two layers emerged after 6 h of immersion in the EIS outcome. The resistance of the inner layer (referred to as RPEO, in) was notably higher than that of the outer layer (referred to as R<sub>PEO, out</sub>), suggesting that the dense inner layer predominantly contributes to short-term protection [83]. Coating degradation begins after 24 h, prompting adjustments to the time constants to contain both substrate reactions and the entire coating, including both inner and porous layers. As some pores expanded or formed, pathways for corrosive medium to diffuse were created [84]. The applied EEC was therefore changed from Fig. 10a to b, illustrating that the sequence of permeation was divided into two levels by using a series circuit with two-time constants [85]. According to the EEC in Fig. 10b, CPE<sub>dl</sub>, and R<sub>ct</sub> show the substrate response, while RPEO and CPEPEO represent the PEO layer. This suggests that, during a 24-hour immersion period, a reduction in barrier qualities caused the emergence of some holes that are sufficiently deep for

accessing the substrate. Following that, throughout the two-week immersion period, the PEO sample kept exhibiting this electrochemical activity.

3.2.5.1. PEO/sol-gel case. Upon application of the sol-gel coating, the electrochemical behavior of the PEO shifts according to the EEC shown in Fig. 10c. The enhancement in the corrosion resistance of the PEO layer, following each sol-gel sealing, was confirmed by an increase in the impedance modulus in the Bode diagrams. Additionally, the EEC (Fig. 10c) indicates that the aggressive electrolyte does not reach the substrate within the first 48 h of immersion in the PS sample. However, as immersion time progresses, the narrowing phase diagram reveals a gradual penetration of the electrolyte through pathways. This leads to the appearance of a new time constant, as shown in the EEC in Fig. 10d. In the EEC (Fig. 10d), the PEO and sol-gel layers appear to coexist within the middle-frequency range, with the sol-gel layer dominating the higher frequencies. Comparing the values of Rmix, out and Rmix, in suggests that the inner part of the mixed region primarily contributes to corrosion resistance improvement. This observation highlights the effective penetration of the sol-gel into the porous structure of the PEO coating, accompanied by a slight surface precipitation over the PEO layer.

Fabrication of sol-gel layers incorporated with h-BN nanosheets, depending on the modification type and the concentration, brought about various protection performances for two weeks of exposure.

*3.2.5.2. PEO/sol-gel/pristine h-BN.* The Nyquist and Bode plots indicate that the protecting function of the coating set-up is reduced in both PS-N1 and PS-N2 compared to PS. Not only did the nanosheet fail to enhance anti-corrosion performance, but it also had a detrimental influence. Specifically, in the short immersion test (6 h), PS-N1 displayed

#### Table 3

Summarized data following the fitting procedure of various PEO coating systems with the appropriate EEC.

Sample	Immersion time in an	Employed EEC	$R_{mix, out}$ (k $\Omega$	CPE <sub>mix, out</sub>		$R_{\text{mix, in}}$ or	$CPE_{mix, in}$ or $CPE_{PEO}$		$R_{ct}$ (k $\Omega$	CPE <sub>dl</sub>	
	hour (h) and week (w)	from Fig. 10	cm²)	$Y_0 (n\Omega^{-1} cm^{-2} s^n)$	n	$R_{PEO}$ (k $\Omega$ cm <sup>2</sup> )	$Y_0 (n\Omega^{-1} cm^{-2} s^n)$	n	cm²)	$Y_0 (n\Omega^{-1} cm^{-2} s^n)$	n
PEO	6 h	а	_	-	_	75	3593	0.79	293	16,051.00	0.96
	24 h	b	-	-	-	36	72,787	0.64	20	8757.00	0.91
	48 h	b	-	-	-	37	49,143	0.79	10	21,241.00	0.90
	72 h	b	-	-	-	23	64,442	0.89	7	33,149.00	0.92
	1w	b	-	-	-	41	119,420	0.91	5	66,165.00	0.90
	2w	b	-	-	-	32	149,470	0.97	6	86,905.00	0.91
PS	6 h	с	1187.50	2.33	0.96	212,600	33.91	0.57	-	-	-
	24 h	с	752.21	2.74	0.95	23,424	48.90	0.59	-	-	-
	48 h	с	960.70	3.10	0.94	26,577	48.12	0.66	-	-	-
	72 h	d	276.12	2.53	0.96	4088	55.39	0.51	20,966	15.57	0.93
	1w	d	448.51	3.87	0.94	4412	22.75	0.74	25,744	198.94	0.52
	2w	d	59.61	5.04	0.92	4021	32.62	0.84	23,820	200.65	0.70
PS-N1	6 h	с	791.91	2.44	0.94	9781	72.61	0.59	-	-	-
	24 h	d	190.04	4.14	0.91	501	155.18	0.76	2627	130.95	0.89
	48 h	d	113.61	5.29	0.89	468	407.89	0.59	1638	295.59	0.98
	72 h	d	62.58	5.73	0.89	408	484.83	0.62	935	752.61	0.93
	1w	d	31.15	7.16	0.88	751	364.28	0.74	386	7058.2	0.91
	2w	d	21.80	10.62	0.80	401	512.42	0.75	375	8305.88	0.94
PS-O1	6 h	с	775.46	2.02	0.94	11,612	46.58	0.67	_	-	-
	24 h	d	518.92	2.35	0.94	924	30.87	0.70	17,362	52.02	0.74
	48 h	d	100.90	2.67	0.93	1691	153.69	0.64	6376	53.65	0.96
	72 h	d	107.10	2.79	0.93	1230	137.73	0.67	6124	116.91	0.96
	1w	d	50.17	6.62	0.79	458	311.08	0.93	2622	386.07	0.97
	2w	d	17.90	10.09	0.85	940	440.53	0.78	670	1260.1	0.92
PS-F1	6 h	с	5682.30	1.30	0.96	338,900	1.50	0.61	_	-	-
	24 h	с	5330.30	1.41	0.96	229,700	1.79	0.57	_	-	-
	48 h	с	9558.40	1.68	0.95	22,247	15.00	0.91	_	-	-
	72 h	d	1800.40	1.94	0.94	3252	8.37	0.90	14,808	55.31	0.92
	1w	d	459.36	3.63	0.91	1549	29.59	0.82	17,538	70.70	0.95
	2w	d	136.74	7.52	0.86	287	32.41	0.91	7778	86.86	0.87
PS-N2	6 h	d	323.62	2.00	0.94	3645	17.23	0.65	14,287	8.89	0.85
	24 h	d	254.92	3.14	0.91	2242	43.57	0.78	3752	66.12	0.92
	48 h	d	239.34	5.53	0.88	476	101.49	0.76	2686	150.63	0.93
	72 h	d	200.20	7.18	0.86	326	159.88	0.71	2457	278.77	0.93
	1w	d	91.94	62.38	0.70	288	626.58	0.65	632	1057.50	0.93
	2w	d	5.72	963.82	0.61	195	922.42	0.81	241	3106.40	0.84
PS-O2	6 h	с	1956.50	2.77	0.92	50,861	5.54	0.69	-	-	-
	24 h	с	1067.10	2.42	0.93	12,047	16.32	0.86	-	-	-
	48 h	с	953.34	2.54	0.93	18,827	14.79	0.84	_	-	-
	72 h	с	811.84	3.75	0.91	18,295	15.72	0.81	_	-	-
	1w	с	46.47	3.30	0.92	50	44.57	0.87	3118	81.45	0.84
	2w	с	32.64	2.99	0.93	18	76.85	0.88	2668	161.40	0.79
PS-F2	6 h	с	12,843.00	1.35	0.97	733,300	2.36	0.55	-	-	-
	24 h	с	12,776.00	1.41	0.97	717,000	2.67	0.53	-	-	-
	48 h	с	7867.50	1.46	0.97	557,100	3.39	0.51	-	-	-
	72 h	с	5788.00	1.47	0.97	454,300	3.67	0.52	-	-	-
	1w	с	1577.60	1.86	0.95	73,125	9.99	0.88	-	-	-
	2w	с	395.64	2.20	0.94	53,283	23.12	0.88	-	-	-

an electrochemical response with two-time constants, as depicted in Fig. 10c, whereas PS-N2 exhibited a three-time-constant EEC (shown in Fig. 10d) across all EIS measurement intervals. It is important to note that as-received h-BN lacks functional groups, preventing its direct involvement in the formation of the sol-gel network. Consequently, although the diffusion routes for the electrolyte were extended, the solgel/h-BN interface may still degrade upon exposure to the saline environment. The higher intake of as-receive h-BN resulted in increased interface vulnerability which is why the employed EEC demonstrates the access of the electrolyte at the beginning of the EIS test. Furthermore, the FTIR analysis revealed the detrimental impact of as-received h-BN on the formation of the sol-gel network, particularly at a concentration of 2000 ppm, which subsequently reduces the compactness of the sol-gel sealing. Fig. 12 illustrates that PS-N2 exhibited higher corrosion resistance than PS-N1 up to 72 h of exposure; however, PS-N1 displayed superior barrier properties from that point onward until the end of the analysis. The rate of corrosion degradation was higher in PS-N2 than in PS-N1, likely due to the increased vulnerability of the h-BN/sol-gel interface to diffused electrolyte as well as lower barrier characteristics,

even though higher concentrations of pristine h-BN result in longer diffusion pathways.

3.2.5.3. PEO/sol-gel/oxidized h-BN. The electrochemical examination revealed that the barrier properties of PS-O1 are greater than those of PS-N1 but still lower than PS. Interestingly, PS-O2 exhibited higher protection than PS for up to 72 h, after which both displayed almost identical behavior. The generation of hydroxyl groups on the h-BN surface could facilitate the incorporation of the nanosheets into the network formation, although perhaps not to a significant extent at a 1000 ppm intake. However, increasing the utilization of O/h-BN to 2000, along with improved dispersion, led to an enhancement in corrosion resistance. This observation aligns with the employed EEC type (Fig. 10c), which illustrates the presence of only two distinct mixed layers in the PS-O2 coating system up to 72 h of immersion. Beyond this duration, as the aggressive environment reached the substrate, an additional time constant emerged (Fig. 10d), indicating the evolving electrochemical response due to substrate exposure.



Fig. 11. The impedance modulus at low frequency (a), effective capacitance (b), and resistance (c) of the PEO coating without a sol-gel top layer.

3.2.5.4. PEO/sol-gel/functionalized h-BN. Through the chemical modification of O/h-BN by APTES, it could be expected to have chemical interactions between F/h-BN and the sol-gel matrix. This is why PS-F1 and PS-F2, among all types of sol-gel nanocomposites, demonstrated superior protective characteristics. Comparing PS-F1 and PS-F2, it can be observed that initially, during the EIS test, they exhibited similar behavior, while after 48 h, the decrease in barrier properties of PS-F1 was significantly higher than that of PS-F2. This substantial drop in barrier properties could have resulted from the insufficient amount of F/ h-BN to act as a barrier against the aggressive electrolyte. Specifically, PS-F2 demonstrated the most protectivity among all PEO/sol-gel coating systems, indicating that by increasing the concentration of F/h-BN, the integration and compatibility with the sol-gel matrix were enhanced along with the improvement in barrier properties. In other words, the combination of F/h-BN and the sol-gel network created a dense medium with superb corrosion resistance, which could also seal the PEO pores. Moreover, the PS-F2 coating system consistently conformed to the EEC model shown in Fig. 10c across the entire immersion period, indicating that the aggressive electrolyte did not reach the substrate even after two weeks of exposure. The highest values of  $R_{mix, out}$  and  $R_{mix, in}$  observed in the PS-F2 sample underscore the critical importance of sol-gel sealing compactness in enhancing the protective characteristics of the PEO



Fig. 12. The evolution of EIS parameters over two weeks of immersion in the aggressive electrolyte through the low-frequency impedance (a), the effective capacitance of the mixed region in the outer layer (b), and the resistance of the mixed region in the outer (c) and inner (d) layers.

#### coating.

As low-frequency impedance is a criterion for assessing protection performance, Fig. 12a. provides a clearer comparison between the PEOcoated samples. This value is significantly higher in all PEO layers coated with the sol-gel, while the response of their barrier characteristics varies during exposure. It is worth mentioning that PS-N1, PS-O1, PS-N2, and PS-O2 samples had lower impedance modulus at the end of the examination than PS, indicating a potential reduction in the protecting qualities of the neat sol-gel coating after the introduction of nanoparticles. While it is not common to observe such a controversy, as nanomaterials typically extend diffusion pathways and enhance barrier characteristics, the sol-gel/h-BN nanosheets present a unique case. The most and least effective sol-gel sealing layers belong to PS-F2 and PS-N2, respectively. Additionally, considering the interface between the sol-gel and h-BN nanosheets, coagulation of h-BN is feasible at higher concentrations, such as 2000 ppm. Consequently, the sol-gel sealing becomes less corrosion-resistant, as observed in the PS-N2 sample.

Identifying distinct mixed layers within these coating systems is challenging due to their potential overlap. Given the pore-filling capability of the sol-gel coating for the PEO pores as well as the "*n*" values of the CPE<sub>mix, out</sub> is closer to 1 which indicates more ideality, to effectively compare the performance of different sol-gel sealings, we focus specifically on the outer part of the mixed region for comparative analysis. This consideration provides more meaningful and interpretable outcomes, as it allows for the determination of the barrier properties of the top layer in the upper section of the mixed region and its role in water uptake, given that the sealing ability of this sol-gel has been previously corroborated [10,35,57,58]. To acquire a more profound understanding of the sealing properties of several modified sol-gel layers for the PEO coating, the effective capacitance was calculated according to the formula below and brought up in Fig. 12b [81,86].

$$C_{\text{mix,out}} = Y_{0,\text{mix,out}}^{1/n} R_{\text{mix,out}}^{(1-n)/n}$$
(3)

Based on the eq.  $C = \varepsilon \varepsilon_0 A/d$ , the coating thickness and capacitance have an opposite correlation. Therefore, when coating permittivity is enhanced by water diffusion, it brings about an increase in coating capacitance. The easy penetration of electrolytes into the PEO layer leads to a significant rise in capacitance shortly after immersion. However, a notable decrease in capacitance was observed in the PEO sample after applying the sol-gel coating, as shown in Fig. 11b and Fig. 12b. Due to the micrometer-scale variations in the thickness of the mixed layer, lower capacitance values are expected. Across all coating systems, an increasing trend in capacitance is noted after two weeks of immersion in the saline electrolyte. The rising trend is more intense in some coatings, including PS-N1 and PS-N2, due to their relatively poorer corrosion resistance. To provide some quantification, the effective capacitance (Ceff. mix. out) of PS-N2 reaches 34.67 nF·cm<sup>-2</sup> upon completion of the EIS test; however, this parameter is only 1.40  $nF \cdot cm^{-2}$  for the PS-F2 sample. The dense and protective properties of the PS-F2 coating hindered the ingress of the corrosive solution, resulting in the lowest water uptake.

 $R_{mix, \ out}$  and  $R_{mix, \ in}$  (Fig. 12c and d) whose values are considerably greater than  $R_{PEO}$ , might be used to validate the role of the sol-gel sealing for the PEO layer. Fig. 12d illustrates that the  $R_{mix, \ in}$  value of PS was higher than that of PS-N1, PS-O1, and PS-N2 at all immersion times. Regardless of the type of modification, the  $R_{mix, \ in}$  values are greater in cases using 2000 ppm of nanosheets. The  $R_{mix, \ in}$  value of PS-F1 was relatively high initially, but it dropped drastically after 24 h, most probably due to an inadequate number of nanoparticles in the sol-gel formulation. Similarly, the  $R_{mix, \ in}$  value for the PS-O2 was significantly higher than that for PS-O1; however, like PS-F1, it declined considerably upon immersion. The resistance properties of PS-F2 and its sealing properties made it the best PEO/sol-gel coating in this investigation. Not only did it have the highest  $R_{mix, \ in}$  and  $R_{mix, \ out}$  values, but  $R_{mix, \ in}$  also remained almost constant up to 72 h immersion. After one week of immersion, a drastic decrease in  $R_{mix, \ in}$ 

the value reached  $5.33\times 10^7~\Omega\cdot cm^2$  which is the highest in PEO/sol-gel coated samples.

#### 4. Conclusion

On the AA2024 substrate, the sealing of the PEO coating was achieved by fabricating sol-gel nanocomposite coatings. In this process, pristine h-BN nanopowders underwent an oxidation process followed by APTES functionalization, which was validated by FTIR, XRD, and ZP tests. The integration and compatibility of the nanopowders within the sol-gel matrix significantly enhanced after the functionalization process, resulting in higher barrier properties. The incorporation of nanoparticles was conducted in two concentrations, 1000 ppm and 2000 ppm, revealing that this factor plays a key role in the corrosion resistance of the whole coating system. In the case of pristine h-BN, increasing concentration led to a decrease in corrosion resistance; however, improvement was reported for the rest of the coupons. For pristine h-BN, agglomeration and coagulation inside the sol-gel network could be the most possible reason for its detrimental influence on corrosion resistance properties. The compactness of the sol-gel sealing and, accordingly, the protection performance increased as the concentration of F/h-BN increased, thanks to more interactions of the functionalized nanoparticles with the sol-gel network. PS-F2 and PS-N2 were nominated as the most and the least protective coating systems, respectively.

## CRediT authorship contribution statement

Sajjad Akbarzadeh: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis. Zorigtbaatar Batjargal: Methodology, Investigation. Vedi Ölmez: Validation, Investigation. Marie-Georges Olivier: Writing – review & editing, Validation, Supervision, Methodology, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Sajjad Akbarzadeh reports financial support was provided by Fédération Wallonie-Bruxelles. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Data availability

Data will be made available on request.

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