Sol–Gel Processing of Corrosion Barrier Coatings

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The sol–gel method produces glass and ceramic materials at lower temperatures than the corresponding products molded by melting. This method uses alkoxides, water, catalyst, and solvent. Depending on the relationship between alkoxide/water and the kind of catalyst, one can obtain a one-dimensional, two-dimensional, or three-dimensional network where one takes fibers, thin films, or bulk materials. Some years ago, scientists attempted to produce coatings on metals to protect against corrosion.

corrosion CBC Sol–Gel

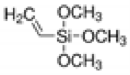
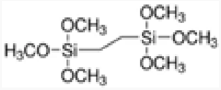
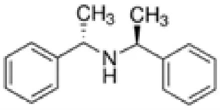
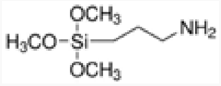
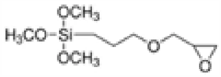
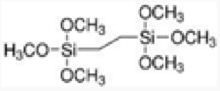
1. Brief Introduction of Sol–Gel Processing

Using a multiple immersion technique in the sol solution followed by a densification process, they deposited on copper, nickel, iron, and aluminum metals protective ZrO_2, SiO_2, TiO_2, and B_2O_3-$3SiO_2$ coatings. They were using the dip-coating method of metals in the sol solution, where they were first left to dry and next heat-treated slowly (5 °C/min) up to the temperature of 500 °C. The effectiveness of the sol–gel coatings against corrosion in the early studies was examined with weight loss measurements by exposing them to salt solutions. These studies revealed that the protection offered by the coating depends on its thickness. The increased thickness led to cracks during their thermal densification treatment or the alternating temperature during operation [1]. From the above studies, inorganic oxide coatings can protect metal substrates but do not significantly replace chromium-based corrosion barrier coatings (CBCs) [2]. One needs to reduce the densification temperature to 200 °C to avoid the metal's destruction and develop flexible coatings that will adapt their physical properties (e.g., anticorrosion protection, the thermal expansion coefficient of the coating) to the properties of the metal. To realize that requirement, one needs precursors consisting of two primary components, the one organic and the other inorganic, the one responsible for the flexibility of the CBC, and the other for the anticorrosion properties.

2. Silanes

Silanes are hybrid organic–inorganic compounds used to help alleviate the problem occurring in the traditional sol–gel technology. **Table 1** gives some chemical formulas of silanes/bis-silanes used to start the discussion [3]. These CBCs based on these precursors have proven effective in recent years [4]. Their hybrid structure maximizes their effectiveness against corrosion and their properties for primary technological needs.

Table 1. The structures of some silanes/bis-silanes.

Material	Structure
Vinyl trimethoxy silane	
Bis-l,2-(trimethoxysilyl) ethane	
Bis-[trimethoxysilylpropyl]amine	
(3-Aminopropyl)trimethoxysilane	
3-Glycidyloxypropyl- trimethoxysilane	
3-(Trimethoxysilyl)propyl methacrylate	
3-(2-Aminoethylamino)-propyldimethoxymethylsilane	
1,2-Bis(trimethoxysilyl)ethane	

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[4][5]

TSE [6][7]

[8]

industrial

rganisms can absorb. Thus, water-based chemistry was developed to alleviate the problem. The question arose whether both chemistries produce the same coatings. In an extensive study [5], the CBCs produced with and without methanol solutions were examined concerning the microstructure [9]. The aqueous chemistry yields more high molecular weight species, indicating that the aqueous solution BTSE is less reactive and newsworthy without health hazards. The resulting structures are similar in both cases. Another aspect of the silanes is their ability to be mixed with two or more substances, such as epoxy resins, polymers, and others. The procedure allows for economical upscaling. The silane CBC facilitates tiny pores allowing the diffusion of the electrolyte and the accumulation of corrosive species on the interface coating/substrate, resulting in corrosion. Researchers attempted to create a single layer with a larger thickness that was brittle, but the solution's stability during deposition was small [10]. It is worth noting that silanes are not electrochemically active substances in solution or solid-state and are not reduced or oxidized unless they have electrochemically active groups. Therefore, they act as barrier coatings. In summary, the silane coatings are hydrophobic and exhibit barrier properties. Their barrier properties prevent water, oxygen, and corrosive ions from reaching the metal substrate [11]. However, a silane film alone cannot effectively protect the metal from corrosion for a long time due to its small thickness, which quickly becomes saturated by the corrosive solution and thus ceases to act as a barrier [12]. This drawback has led to the search for complex systems such as metal/silane/organic coatings to reach greater efficiency and limit the migration of metal ions through the coating [13]. The resulting systems from these works resulted in protective coatings that were more stable with exposure to corrosive environments. The silane acts as a barrier to improve the adhesion between the metal and the organic coating, as in the case of epoxy resins [14], polyamides [15], and the mixture of epoxy/polyamide [16]. One research paper showed resistance to corrosion of metal AA2024-T3 silane-coated bis-[3-(triethoxysilyl)propyl] tetrasulfide (BTESPT). A water silane/DI/methanol solution equal to 4/5.5/90.5 vol% was used to immerse the metal. Afterward, blowing air at 120 °C for 40 min dried the coating. The same metal was pretreated with the standardized commercial (VI)-based TURCO^{TM} Accelagold used as a reference sample. Electrochemical studies were performed using a 0.1 N NaCl solution. The silane membrane protected the substrate better than the reference chromate pre-treatment offered. In addition, the adhesion of BTESPT to the metal was facilitated by sulfur in the silane molecule [17]. One study showed that the overlap of (3-Glycidyloxypropyl) trimethoxy silane (GPTMS)–tetraethyl orthosilicate (TEOS)–ammonium persulfate based on silanes showed good protective properties for steel [18]. Many researchers reported electrolytic polypyrrole (PPy) coatings being deposited on steel in the presence of oxalic acid with spectacular results for metals in the iron series [19][20][21][22][23][24]. Although it is not entirely clear, due to the interaction of metal and polymer through galvanic coupling and upward polarization of the substrate, PPy provides anticorrosion protection for steels [25][26][27][28]. Finally, it must be pointed out the difference between bis-silanes and silanes. Silanes have one Si atom per molecule, while bis-silanes have two Si atoms per molecule associated with three OR groups and six OR groups. Bis-silanes and silanes produce six SiOHs and three SiOHs per molecule during hydrolysis, respectively. After condensing the SiOH groups, bis-silanes create a denser network than do silanes.

3. ORMOSIL

a. *Precursors and Reactions*

ORMOSILs are prepared as organically modified silicate solutions that react with organic groups derived from an epoxy resin and a hardener. A series of solutions is prepared using the above ingredients in different proportions to select a suitable final product with the most satisfactory properties.

b. *Organically Modified Silane*

The reported silica alcohols or “silanes” are in the form of R’-Si(OR), where R’ is an organic group reacting with an organic polymer. In contrast, group R is an alkoxy group capable of participating in hydrolysis and condensation reactions. For example, a silane that can be used has the trade name Z 6020, while it is found as N-(2-aminoethyl)-3-(trimethyloxypyl) propylamine with a molecular weight of 222.

c. *Epoxy Resin*

Epoxy resins are compounds, which contain at least one epoxy ring (-CHOCH$_2$) as an essential component of their monomer, i.e., they consist of an organic root and an oxygen atom joined to two carbon atoms [29]. The ring mentioned above is very active and is responsible for the vast number of products resulting from its reaction with several hardening agents. There are three classes of epoxy resins that are cycloalephatic, where there are six-membered rings in the organic part. The epoxy oils contain inseparable fatty acids and glysidic resins, whereas the organic part is a combination of hydrogenic polybasic acids or poly-hydro phenols [29]. They belong to the category of thermosetting polymers, i.e., their original properties are altered irreversibly via heating above a specific temperature.

A basic resin used to create the ORMOSIL membranes can be the bisphenol A diglycidyl ether (DGEBA) condensed with epichlorohydrin. The result of condensation is the creation of an epoxy group at the end of each polymer. The trade name of the product is DGEBA ή Bisphenol A or GY-257, and the name found in the literature is phenol 4,4′-(1-methylethylidene) bis-, or phenol 4,4′ isopropylidenedi- and belongs to the third category of epoxy resins. The presence of the benzene ring in the DGEBA molecule confirms that the material becomes more rigid and stiffer in a short time when applied in a suitable environment.

d. Hardener

As its name suggests, the hardener is a substance that hardens some other compounds. For example, one can use diethylenetriamine as a hardener with triethylenetetramine (TETA) or HM 943.

e. Solvents

The solvents used to prepare this solution are a mixture of pure ethyl alcohol and acetone. The presence of both solvents ensures the proper dissolution of the precursors at the molecular level and ensures the necessary homogeneity. Therefore, the purity of solvents should be 99.9%.

f. Preparation of ORMOSIL

Figure 1 shows the mixing procedures of the components and their corresponding concentrations schematically.

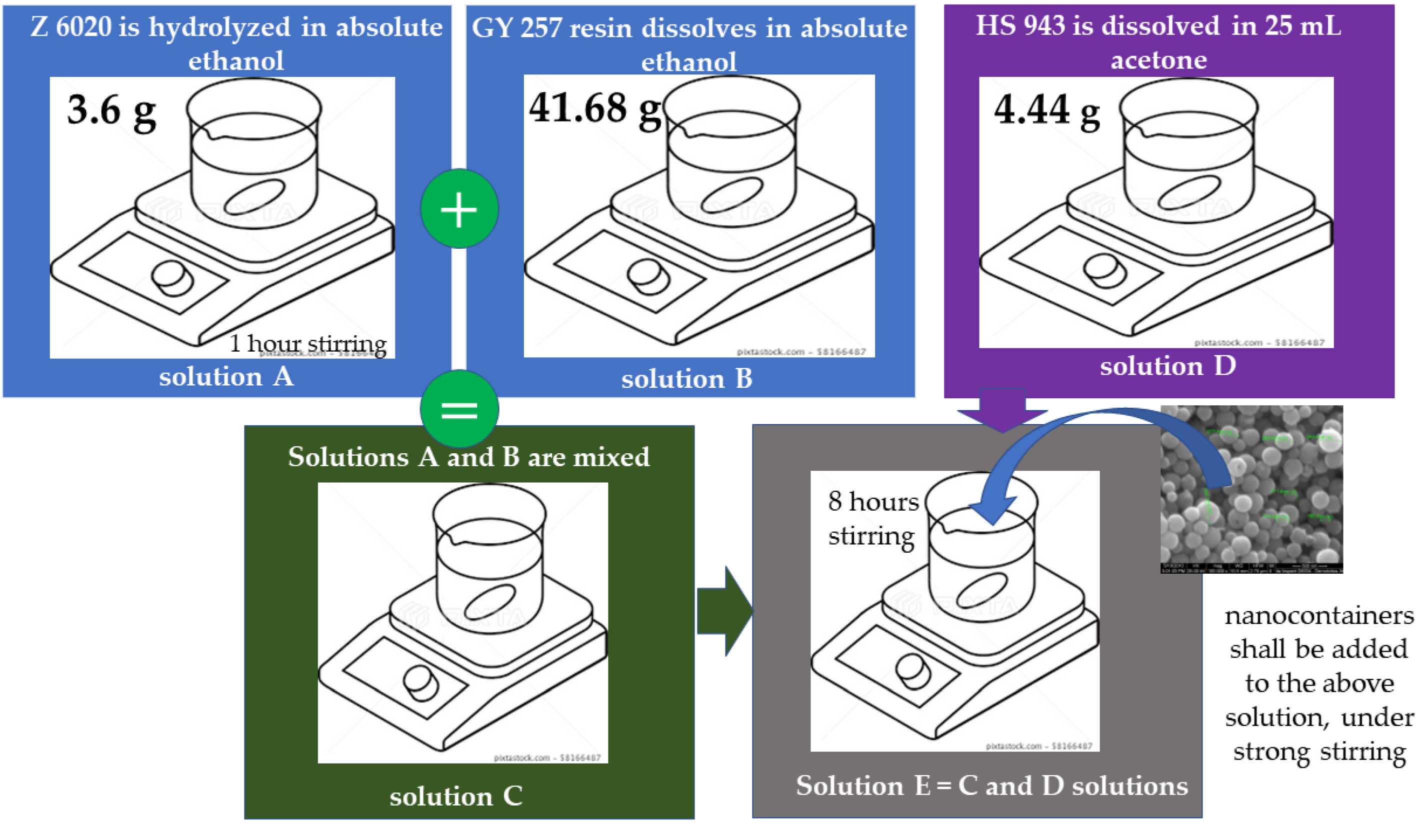

Figure 1. An example of CBC synthesis using the ORMOSIL method. Z 6020: N-(2-aminoethyl)-3-(trimethyloxypyl) propylamine, GY-257: phenol 4,4′-(1-methylethylidene) bis-, HM 943: triethylenetetramine.

Figure 2, **Figure 3** and **Figure 4** show the individual reactions.

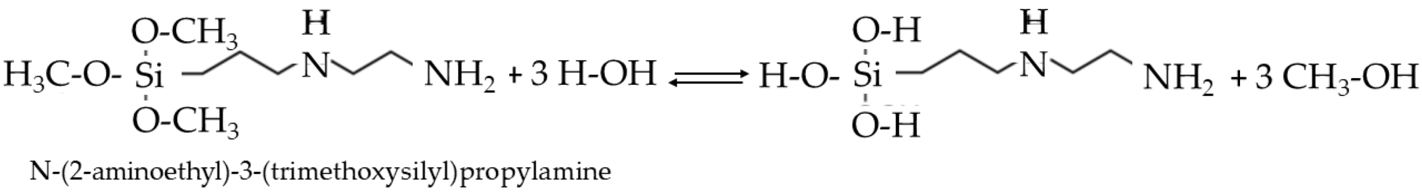

Figure 2. Hydrolysis of ORMOSIL.

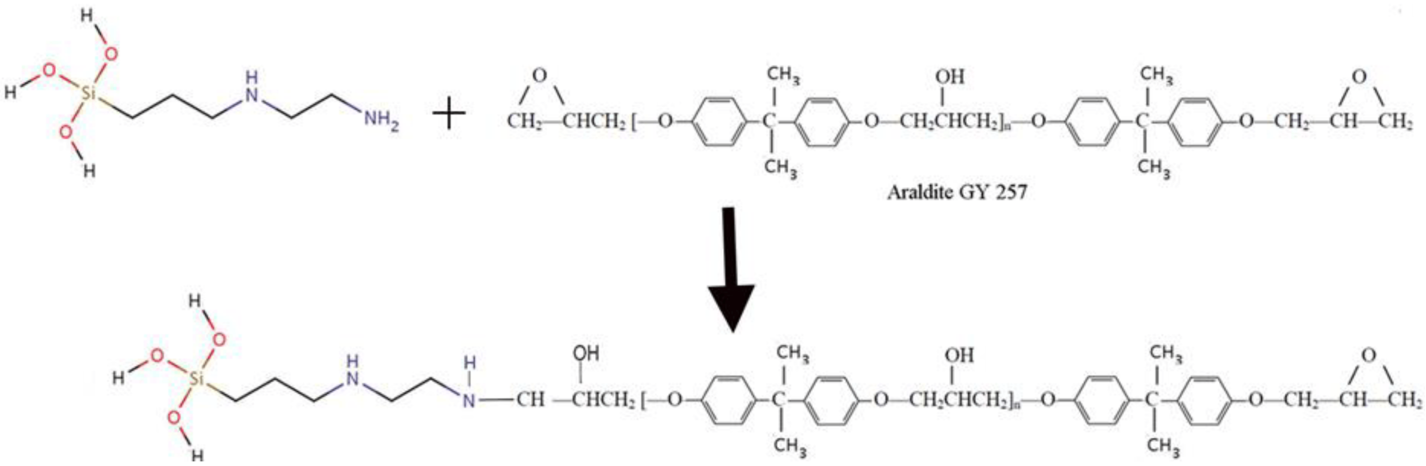

Figure 3. Epoxy group reaction with primary amine.

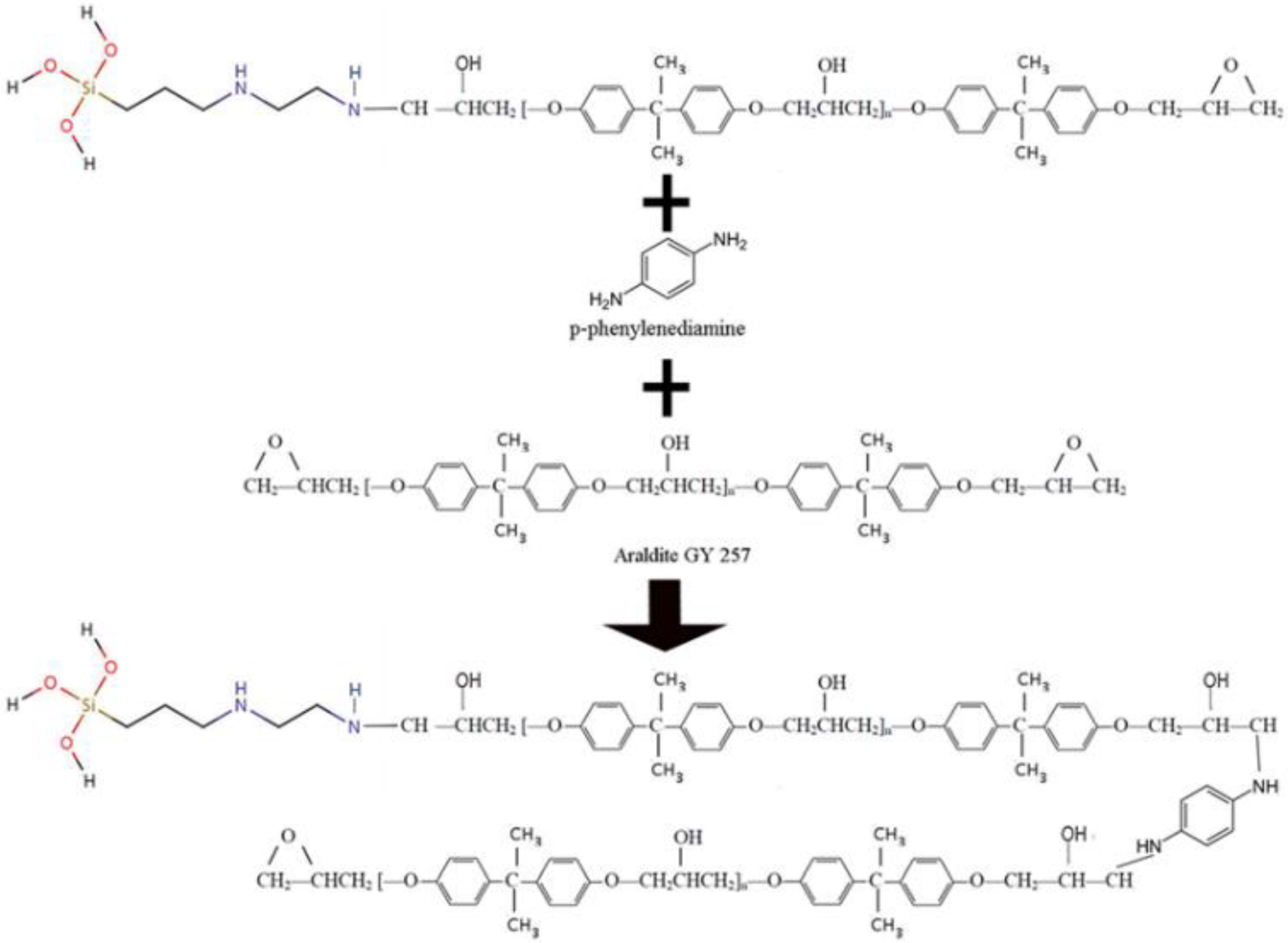

Figure 4. Synthesis of epoxy resin—ORMOSIL.

The surface-cleaned metals are immersed in the finished solution with or without the nano-containers six times at, e.g., a 32 cm/min speed and remain in the diathesis for one minute. Then, the coatings are heated at 70 °C for four days. **Figure 5** shows the reactions occurring in this process.

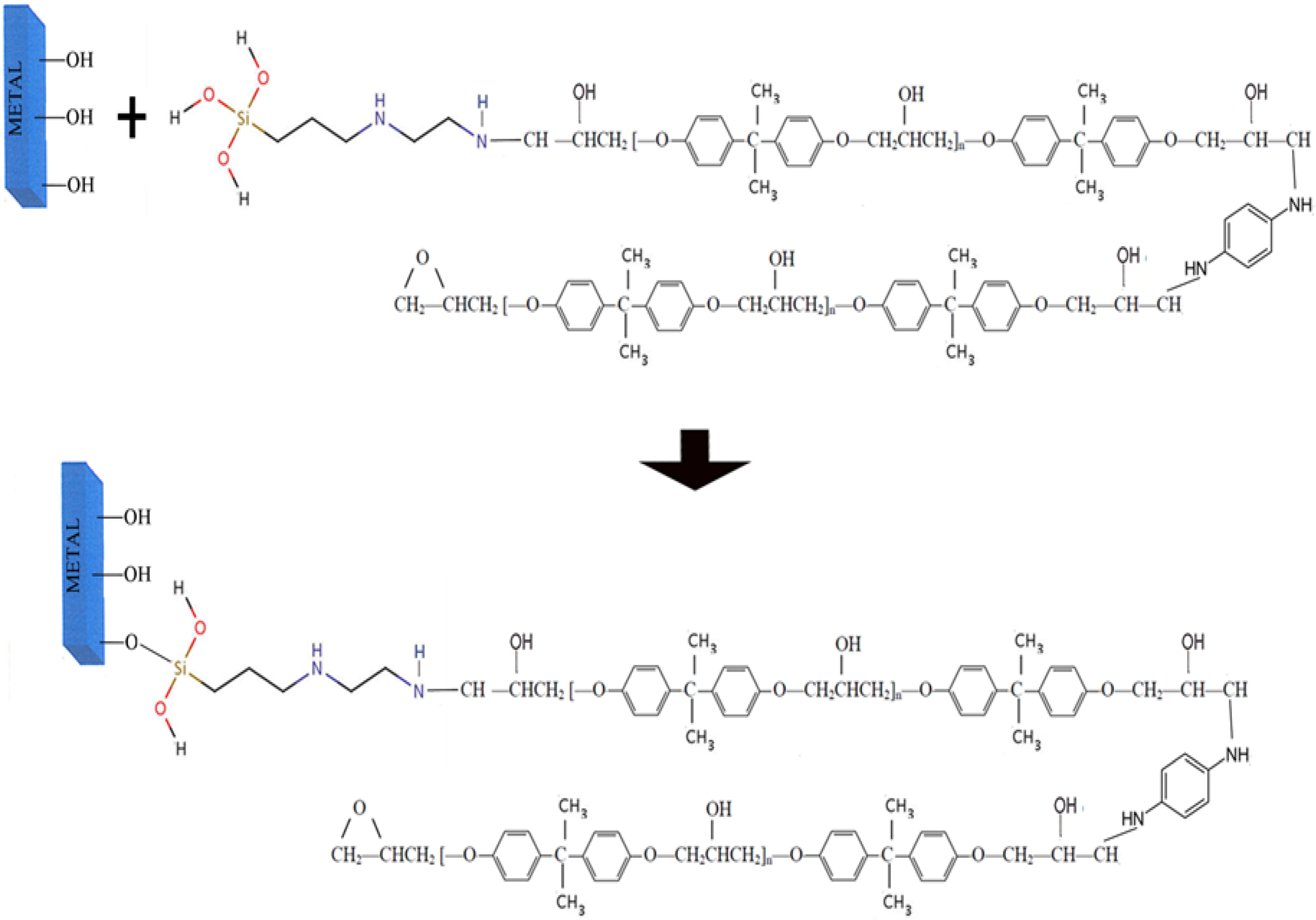

Figure 5. Attachment of a hybrid coating to the surface of the metal.

Figure 6 shows the EIS diagram of the bare sample (Sample 1), ORMOSIL coated (Sample 2), ORMOSIL coated + CeO_2 (Empty) (Sample 3), and ORMOSIL coated + CeO_2(5-ATDT) (Sample 4) [30][31]. The measurement showed that the ORMOSIL coating offered protection to the HDG metal. The metal had an $\mathbf{R}_p$ = 1.73 E^{+03} Ohm cm^2, while the metal protected with ORMOSIL had a protected metal with ORMOSIL $\mathbf{R}_p$ = 1.55 E^{+04} Ohm cm^2. When CeO_2 (empty) nano-containers were added to ORMOSIL, $\mathbf{R}_p$ = 9.32 E^{+04} Ohm cm^2 and increased to $\mathbf{R}_p$ = 3.05 E^{+05} Ohm cm^2 when the nanocontainers were loaded with 5-ATDT corrosion inhibitor [30][32]. The effect of coating the metal with ORMOSIL + CeO_2 (5-ATDT) was the increase of R_p in this sample by 1033.60, 109.21, and 7.76 from the steel samples HDG, HDG-ORMOSIL, and HDG-ORMOSIL + CeO_2 (EMPTY), respectively. This sample exhibited the “self-healing” phenomenon [32].

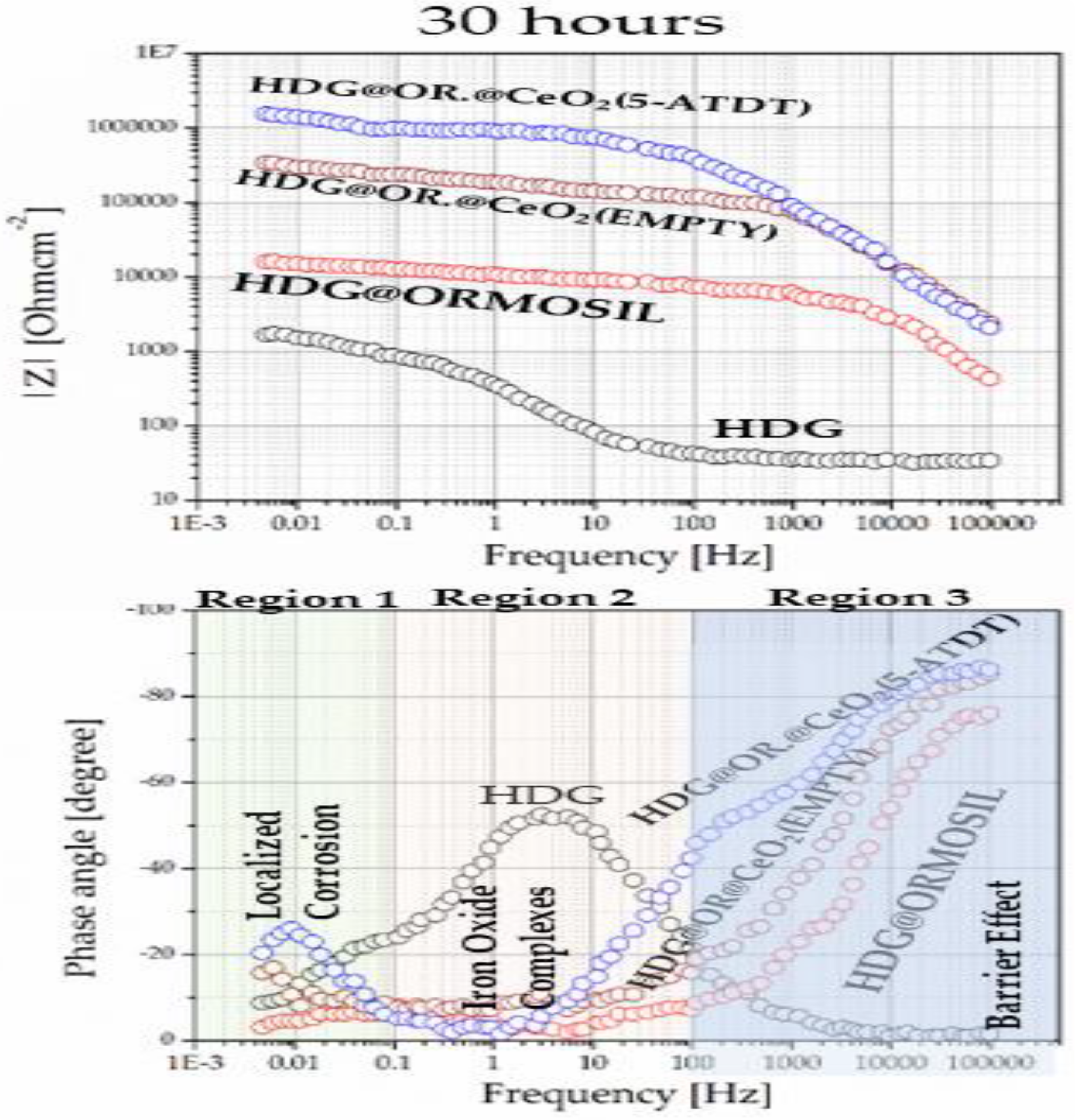

Figure 6. FRA of the samples HDG, HDG@ORMOSIL, HDG@ORMOSIL@CeO$_2$ (EMPTY), and HDG@ORMOSIL@CeO$_2$ (5-ATDT) exposed to a 0.5 M NaCl corrosive environment at ambient temperature [32].

The thickness, structure, and corrosion resistance were investigated concerning the type and concentration of the solvent for which they were produced by mixing 11.2 mL of tetraethyl orthosilicate (TEOS), 15.2 mL vinyltrimethoxysilane (VTMOS), and 4.0 mL 3-(trimethoxysilyl) propyl methacrylate (MEMO) with 19.6 mL 0.05 M HNO$_3$ [33]. Solvent concentrations ranged between 28.5 and 66.5 vol.% and were non-polar solvents (hexane, heptane), aprotic polar solvents (acetone, MEK), primary alcohols (methanol, ethanol, isopropanol, 2-methoxy ethanol, 2-ethoxyethanol, 2-methyl-1-butanol, 3-methyl-1-butanol), secondary alcohols (1-methoxy-2-propanol), and tertiary alcohols (t-amyl alcohol). In summary, corrosion resistance depends on the type and concentration of the solvent. They found that high solvent concentrations lead to coatings with enhanced resistance to corrosion using aprotic solvents. Minor alcohols yield enhanced corrosion protection at low diluent concentrations. High concentrations of large alcohol diluents degrade the corrosion resistance of the ORMOSIl membrane. This work offered a benchmark between structure–corrosion–the type of solvent–the solvent quantity that is useful for a researcher [33]. ORMOSILS were prepared with 3-glycidoxypropyltrimethoxysilane (GLYMO)–TEOS through the sol–gel method using nitric acid for the complexation of GLYMO and TEOS. As a result, a solid state of -^{1}H–^{13}C and ^{1}H–^{29}Si CP/MAS NMR led to the organic content determining the microstructure, and thus the anti-corrosion capacity of ORMOSIl. Moreover, the microstructure of ORMOSIL and the method of deposition affects the structure and, consequently, the anti-corrosive performance characteristics [34].

4. Water-Based Commercial Sol-Gel CBCs

Chemetall GmbH developed the product OXSILAN AL-0500 based on silane for 2024, 2219, 5083, and 7075 aluminum [35]. These panels underwent multiple coatings with a solvent-free epoxy primer type MIL-DTL-53022, an epoxy primer without water type mil-DTL-53030, and a coating of polyurethane lymphatic type MIL-PRF-85285. As a result, the effects of accelerated corrosion were acceptable in some cases [35].

Boeing developed an anticorrosive sol–gel CBC using Zr(IV) n-isopropoxide and 3-glygodopropyltrimmethoxysilane (GLYMO) as organosilane compounds. Acetic acid was the catalyst. The anticorrosive sol–gel CBC exhibited excellent adhesion to the metal. Accordingly, the CBC with the trade name “Boegel” provides exceptional barrier properties to the metal without needing a further anticorrosive layer [36].

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