

Review

Hybrid Sol-Gel Coatings: Smart and Green Materials for Corrosion Mitigation

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Abstract: Corrosion degradation of materials and metallic structures is one of the major issues that give rise to depreciation of assets, causing great financial outlays in their recovery and or prevention. Therefore, the development of active corrosion protection systems for metallic substrates is an issue of prime importance. The promising properties and wide application range of hybrid sol-gel-derived polymers have attracted significant attention over recent decades. The combination of organic polymers and inorganic materials in a single phase provides exceptional possibilities to tailor electrical, optical, anticorrosive, and mechanical properties for diverse applications. This unlimited design concept has led to the development of hybrid coatings for several applications, such as transparent plastics, glasses, and metals to prevent these substrates from permeation, mechanical abrasion, and corrosion, or even for decorative functions. Nevertheless, the development of new hybrid products requires a basic understanding of the fundamental chemistry, as well as of the parameters that influence the processing techniques, which will briefly be discussed. Additionally, this review will also summarize and discuss the most promising sol-gel coatings for corrosion protection of steel, aluminium, and their alloys conducted at an academic level.

Keywords: hybrid; coatings; sol-gel; corrosion; steel; green materials; aluminium; metallic

1. Introduction

The major degradation mechanism of metallic materials is corrosion (Figure 1). Corrosion can be generally defined as the reaction of a metallic material with its environment and the products of this reaction may be solid, liquid, or gaseous [1–4]. Both the physical and chemical properties of the products are important since they may influence the subsequent rate of reaction. In the case of steel, Cl^- , O_2 , and H_2O species, as well as electron transport, all play extremely important roles in the corrosion process [5–9].

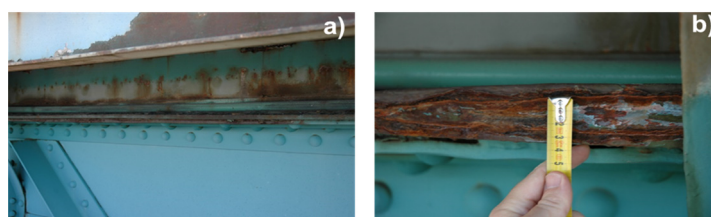


Figure 1. Corrosion of steel in a bridge: (a) general view; (b) detail of the thickness of the corrosion layer formed.

Corrosion prevention in a specific environment is usually performed using a corrosion resistant material, or at least one with exceptional lifetime. There are several methods for protection against corrosion that are based on electrochemical principles [9]. Alternatively, some of the methods adopt the obvious task of separating the metal from the environment. The success of this depends upon the chemical or electrochemical resistance of the protective layer. In particular situations it may be possible to adjust the environment in order to turn it less corrosive. Generally, corrosion prevention technology uses one or more of the following methods [2,5,7,8,10,11]:

1. Adopting metals with elements that enrich the surface with a corrosion-resistant component during the corrosion process;
2. Addition of aqueous inhibitors, which adsorb strongly on the metal surface and prevent the reaction with the oxidizing agent; and
3. Deposition of protective coatings.

The choice of the most effective method is not always simple and easy. This choice is partly governed by the actual environmental conditions and partly by economic considerations. The latter include not only the initial cost of application but also the replacement of corroded parts and, in some cases, renewal of the protecting medium. These are frequently the determining factors and the practicing corrosion engineer will use economic parameters as familiarly as scientific data in determining their choice (Figures 2 and 3).

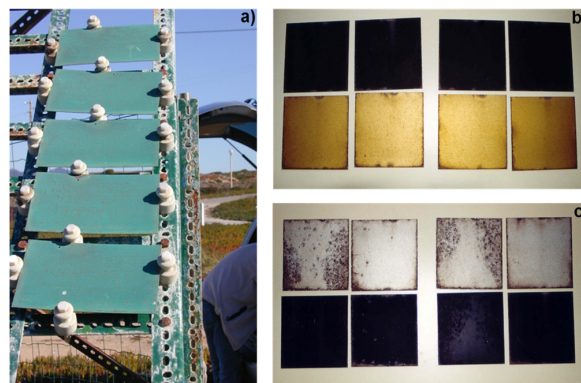


Figure 2. (a) *In situ* studies of coatings for steel protection in a marine environment; (b,c) anodized aluminium specimens after exposure in a natural industrial environment.

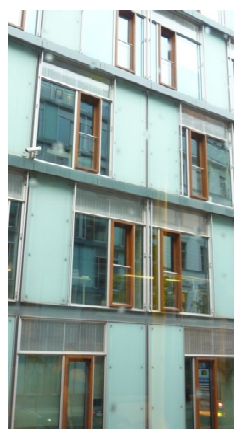


Figure 3. Aluminium components in a building façade.

Carbon steel is used in large amounts in the construction industry. By their nature of limited alloy content, usually less than 2% carbon of total weight, carbon steels are susceptible to very high corrosion

rates in aggressive solutions and atmospheres [11,12]. The traditional surface passivation treatment for steel is obtained by conversion coating, such as phosphating and chromating, which produces a layer of corrosion-protective products capable of resisting further chemical attack. Phosphate conversion coatings (phosphating) have found use in the passivation of steel surfaces. Phosphate films have a good adherence, are somewhat porous and, therefore, form an excellent basis for paints, lacquers, and rust-preventing oils and greases. The protective ability of the phosphate coating alone is insufficient, as phosphate films are formed at cathodic sites. Small, randomly-spaced anodic sites remain uncoated on the metal surface, resulting in the formation of pinholes. The presence of pinholes in phosphate conversion layers results in rapid film degradation under corrosive conditions, such as salt water contact. Chromate conversion coating (chromating) is a process resembling phosphating and often used as a passivating treatment after phosphating, but it is not used alone on steel. Chromating processes are rapid, cheap, and easily carried out. They all involve an oxidizing treatment of the metal surface in a bath containing chromic acid or chromates and accelerating anions. Formed layers containing chromates and chromium oxide are usually very thin, very dense and have a gel structure. Adherence is very good and the films form an excellent basis for painting [13–15].

Aluminium alloys are extensively used in the construction industry, mainly in building components (Figure 3). Chromate and chromate-phosphate conversion coatings have also been widely used for several decades to provide improvement in corrosion resistance and paint adhesion on aluminium and its alloys, namely, of 5000 and 6000 series (for extruded products), and of 3000 series (for sheet products), which are used for different applications in building and construction.

The protection of metallic substrates with coatings has been an active area of materials science for many years [12–15]. Moreover, over the decades, changing regulation governing both environmental issues and human health concerns imposed severe restrictions on the use of hazardous compounds such as VOCs (Volatile Organic Compounds), HAPs (Hazardous Air Pollutants), and use of Cr(VI). Hexavalent chromium-containing compounds used in chromate conversion coatings are known to be toxic and carcinogenic; consequently, recent legislation imposes strong limitations in future use of chromium compounds yielding to a great effort in developing chromate-free coatings. These restrictions, and the lack of materials capable of accomplishing all technological needs, naturally, led to the development of new corrosion protective coating systems. Intense research efforts for the development of new smart and green systems for corrosion protection have been carried out in the last few decades. The paint industry is environmentally driven to pursue the reduction of the use of VOCs, such as solvents, resulting in an enormous attempt to find water-based alternatives. The developments of low-VOC, low-HAP, and non-toxic surface treatments, capable of providing effective corrosion protection, have been being chased and the sol-gel methodology is considered an adequate alternative to produce smart and green coatings.

The challenges for developing new coatings come from many areas of materials science. Metallurgy and electrochemistry are required in order to understand the alloy microstructure and corrosion process. Surface inorganic and polymer chemistries are needed for the design of the coating system and physics for the transport properties within the coating system.

This review presents a summary of the main research achievements in the development, using the sol-gel method, of hybrid sol-gel coatings for protection of steel and aluminium substrates against corrosion. A rational selection of the most relevant contributions was made in order to provide a reliable and a trustworthy analysis of the present consolidated know-how and perspectives to further development in this area. A comparative analysis between the potentialities of hybrid sol-gel coatings with the existing methods currently available in the mitigation of corrosion is also performed.

2. General Background of Sol-Gel Coatings for Corrosion Mitigation

The sol-gel process is a chemical synthesis method where an alkoxide network is created by progressive condensation reactions of molecular precursors from a liquid medium [16–18]. The process was initially used for the preparation of inorganic materials, such as glasses and ceramic. The sol-gel

process to produce hybrid coatings, compared to other methods, has several advantages. This process is often classified as a “green” technology since it uses compounds that do not introduce impurities into the end product (e.g., ceramic processing), is waste-free, excludes the stage of washing, and the processing temperature is generally low, frequently close to room temperature [19]. Additionally, materials with high specific porosity and specific surface area can be easily obtained by this method, which also allows the incorporation of substances, such as inhibitors. The low synthesis temperatures minimize the thermal volatilization and degradation of the entrapped species [16,18]. Additionally, the organic component, other additives, such as Ce(III), Ce(IV) or Cr(III) could be easily incorporated into the sol-gel system, increasing the corrosion resistance of the metal substrates. In addition to the corrosion inhibitors, sacrificial metal pigments, such as zinc, aluminium, magnesium, and their alloy particles, can also be included into the sol-gel coating formula according to the different metal substrates to be protected. As chemical precursors are predominantly in a liquid form, it is possible to cast coatings in complex shapes and to produce thin films without the need for machining or melting. There are several techniques for the deposition of coatings on metals, including physical vapor deposition, chemical vapor deposition, electrochemical deposition, plasma spraying, and the sol-gel process.

The first step to implement a synthesis through the sol-gel method is to select the chemical compounds, known as the *precursors* (Figures 4 and 5) that are combined forming a *sol*. This term designates a stable suspension of colloidal particles within a liquid [16,17]. This first step is a typical chemical transformation aiming the formation of a *sol* of colloidal particles or a solution of oligomers (small polymers). As *sol* is a fluid, it can be cast in a mold, or be applied on a surface using various shaping techniques, e.g., spraying on a surface, dipping, or spinning through a set of rotating nozzles (Figure 4). As the *sol* is a relatively stable solution it can be stored for a certain time before further casting, or applied by any of the above referred methods. Spraying and electrodeposition processes emerged recently and could be the major sol-gel coating application methods in the near future.

To achieve gelation, the chemical transformations of the *sol* in *gel* must be allowed to proceed until a single and interconnected network forms, only limited by the walls of the container and the mass of the reactive mixture. Another step in sol-gel art is drying, which is a very critical step. In many instances, a *dry gel* needs further thermal treatment to be densified [20]. The sol-gel process versatility allows incorporation of additional components that introduce material’s complementary functionalities, such as UV protection [21,22], anti-fouling [23,24], anti-reflection [25–29], moisture resistance [29–33], corrosion and adhesion protection [34–53], along with the enhancement of mechanical, thermal, and optical properties, opening a wide range of application in several fields of science. Furthermore, this method allows the control of several experimental conditions leading to a simple sequence that may be tuned to the nature, final shape, and desired function.

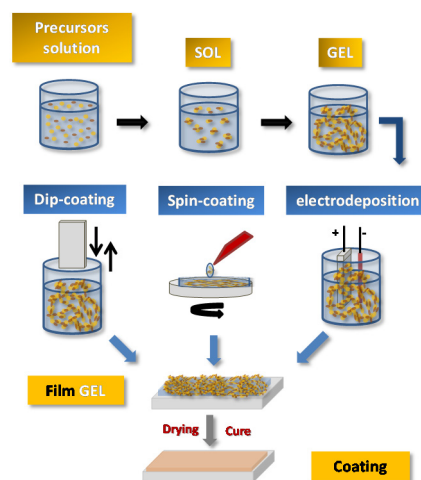


Figure 4. Examples of processing routes to obtain sol-gel coatings. Adapted from [54].

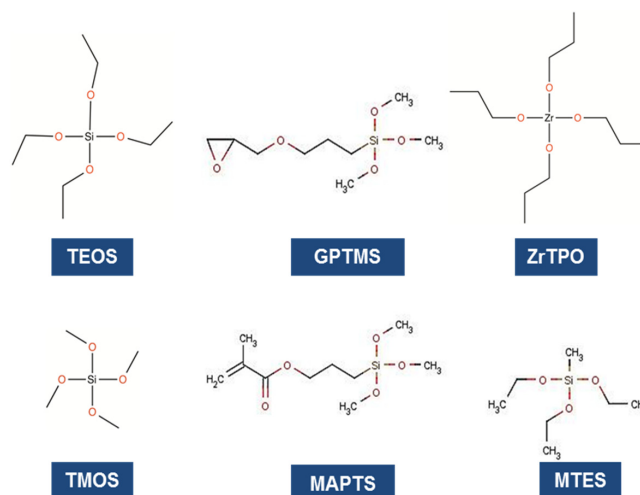
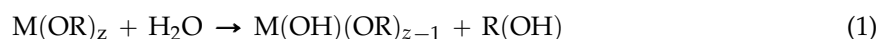


Figure 5. Examples of precursors used in the synthesis of hybrid materials.

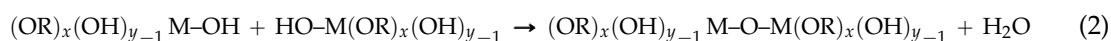
There are two main methods to prepare sol-gel coatings: the inorganic method and the organic one. The first method involves the evolution of networks through the formation of a colloidal suspension (habitually, oxides) and gelation of the *sol* (colloidal suspension of very small particles that may vary from 1 to 100 nm) to form a network in a continuous liquid phase [16]. The most commonly used method to prepare sol-gel coatings is the organic one, which normally starts with a solution of monomeric metal or metalloid alkoxide precursors $M(OR)_n$ in an alcohol or other low-molecular weight organic solvent. M represents a network-forming element, such as Si, Ti, Zr, Al, Fe, B, *etc.*, and R is typically an alkyl group (C_xH_{2x+1}). This later approach has the advantage of obtaining organic-inorganic hybrid materials combining the behavior of the organic component (polymeric) with the stiffness of the inorganic (alkoxide) backbone [55].

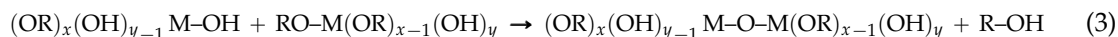
Generally, the sol-gel method used to obtain hybrid materials (organic method) occurs in four stages: (i) a hydrolysis reaction of the metal alkoxide groups ($-OR$) are replaced by the hydroxyl groups ($-OH$) (Equation (1)); (ii) condensation and polymerization of monomers to form chains and particles; (iii) growth of the particles; and (iv) agglomeration of the polymer structures followed by the formation of networks that extend throughout the liquid medium resulting in a *gel*. Indeed, both the hydrolysis and condensation reactions occur at the same time once the hydrolysis reaction has been initiated. Both the hydrolysis and condensation steps produce low molecular weight by-products, such as alcohol and water.



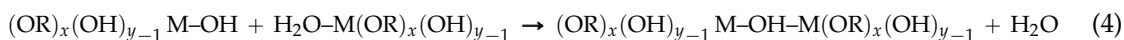
The mechanism of Equation (1) involves the nucleophilic attack of the negatively-charged hydroxyl group ($HO^{\delta-}$) to the positively-charged metallic atom ($M^{\delta+}$). Hydroxyl groups are produced followed by the transference of one proton (H^+) and breaking of the $M-OR$ bond and formation of an alcohol $R-OH$ [16]. This process repeats successively until all the alkoxide groups are replaced. Subsequently, the condensation reactions of the resulting hydroxyl groups takes place, in which the hydrolyzed species $M(OR)_x(OH)_y$ ($x = 0, 1, \dots, z-1$; $y = z-x$) give birth to the formation of a three-dimensional network [16]. The condensation process may occur via oxolation or ololation reactions [16]. In the oxolation two hydrolyzed species react forming “oxo” bonds $M-O-M$ (Equations (2) and (3)) and in ololation (Equation (4)) one of those species is protonated, generating $M-OH-M$ bonds [16].

Oxolation:





Olation:



Upon drying, these small molecules are driven off and the network shrinks as further condensation may occur. These processes are fundamentally affected by the initial reaction conditions, such as temperature, pH, molar ratios of reactants, and solvent composition, among others. Cracks are easy to form if the film formation conditions are not carefully controlled [16,55].

The production process of so-called low-bulk density silica involving the hydrolysis of tetraethoxysilane (TEOS) (Figure 5) in the presence of cationic surfactants was patented in 1971, and the organic-inorganic hybrid materials prepared by the sol-gel process started in the middle of the 1980s. Several inorganic coatings have been studied for corrosion protection, specifically oxide coatings obtained by sol-gel processing. In spite of all the advantages of sol-gel processing, sol-gel oxide coatings suffer from several disadvantages. Generally, they are highly porous with low mechanical integrity, so annealing or sintering at high temperatures is required in order to achieve a dense microstructure. Consequently, sintering at high temperatures might introduce cracks and/or delamination into the sol-gel coatings due to a large mismatch of thermal expansion coefficients and possible chemical reactions at the interface. High temperatures also limit the application of sol-gel coatings on temperature-sensitive substrates and devices. One viable approach to dense, sol-gel-derived coatings without post-deposition annealing at elevated temperatures is to synthesize hybrid coatings. When appropriate chemical composition and processing conditions are applied, relatively dense and non-porous hybrid coatings can be developed. These materials can combine density, flexibility, hardness, and easy processing of the organic component with the hardness, chemical, and weather resistance of the inorganic component, thereby exhibiting multifunctional behavior.

In the first attempt to implement a classification of hybrid materials obtained by sol-gel, the hybrid networks were divided into two general classes: class I and class II. This classification was established considering the interaction between the inorganic and organic components and the first detailed report on this topic was made in 1994 [56]. The initial work concerning corrosion protection offered by sol-gel coatings was conducted using class I hybrids, in which the inorganic and organic components are bonded by van der Waals forces. Messadeq *et al.* [57] proved that the corrosion resistance of stainless steel (SS) could be increased by a factor of 30 using hybrid coatings (class I) prepared by the dispersion of poly(methyl methacrylate), into a zirconia sol. Nevertheless, phase separation and subsequent delamination caused long-term failure of the film. The use of class II hybrids, in which the organic and inorganic components are linked by covalent bonds, could reduce the phase separation and delamination as well as increase resistance. Thereby, the research in this area headed to organo-functional alkoxysilanes which have been extensively used in the last decade to prepare hybrid coatings. Mainly due to their adhesive and coupling nature with other molecules and substrates, and by the increased resistance obtained with these materials. The studies concerning protection of metals using siloxane-based films have consistently demonstrated that siloxanes, a group of environmentally-compliant chemicals, could efficiently protect metals against different forms of corrosion. A large variety of chemical species could be incorporated and the wide range of available chemical precursors for the sol-gel process would allow the production of a diversity of economical hybrid coating materials at mild synthesis conditions. Furthermore, hybrid materials could be produced by low-cost and high-efficiency common spray, spin, and dip-coating methods (Figure 4), which enhances the production of layers with adjusted chemical and physical properties. These materials can be potentially used as eco-friendly corrosion protection systems providing an improved level of performance compared to the traditional organic coating systems showing superior weatherability. Several review papers about the progress and development of sol-gel coatings on metal substrates have been published. The most significant contribution was given by Wang and Bierwagen in 2009 [55], where the progress of sol-gel protective coatings was

discussed and the most significant advances until 2007 were reported. Later in 2012, Balgude and Sabnis [19] discussed the potential of hybrid sol-gel coatings for the production of multifunctional pre-treatments for metallic substrates. One year later, Abdolah *et al.* [34] discussed the most relevant works published on sol-gel coatings with self-healing properties. In 2014 Figueira *et al.* [58] published a review of the most recent and relevant achievements on the development of hybrid sol-gel coatings for corrosion mitigation of metallic substrates. The general consensus of these studies revealed that these materials have a good corrosion resistance and could be effective alternatives to the traditional organic-based coating systems.

2.1. Corrosion Protective Sol-Gel Coatings in Steel Substrates

Steel is a common and versatile substrate with several applications. By definition, steel must be at least 50% (*w/w*) iron and must contain one or more alloying element. These elements include carbon, manganese, silicon, nickel, chromium, molybdenum, vanadium, titanium, niobium, and aluminum [12]. Generally, these substrates are passivated by the use of chemical conversion layers (chromating and phosphating). Several studies were found on developing hybrid sol-gel coatings for application on iron-based alloy surfaces. Nevertheless, only the most representative published in the last decade, will be referred. Several iron-based substrates have been studied, such as carbon steel [46,59–63], 304, and 316 stainless steel [47,64–69]. Chou *et al.* [70] in 2003 produced hybrid coatings by copolymerizing TEOS and 3-methacryloxypropyltrimethoxysilane (MAPTS) (Figure 5) in a two-step acid-catalyzed process. The obtained coatings were uniform, defect-free with excellent adhesion and flexibility that enhanced the corrosion protection of 304 and 316 stainless steel substrates. Gunji *et al.* prepared polysilsesquioxanes through acid-catalyzed hydrolytic polycondensation of methyltriethoxysilane (MTES) (Figure 5) and tri-isopropoxy(methyl)silane [71]. Castro *et al.* obtained by dipping and by electrophoretic deposition (EPD) homogeneous and crack-free coatings prepared under basic catalysis of TEOS and MTES. The EPD method produced thicker coatings with enhanced corrosion resistance of the AISI 304 stainless steel [72]. Recently sol-gel coatings synthesized from MTES and TEOS for stainless steel AISI 316-L with different MTES:TEOS molar ratios were also reported [73]. Jianguo *et al.* studied a hybrid SiO₂ gel/Dacromet composite coating under acid-catalyzed hydrolysis with TEOS and MAPTS in ethanol. This system enhanced the erosion-corrosion resistance of Dacromet markedly in the carbon steel [74].

Later, Wang and Akid showed that a multi-layer hydrophobic coating with a doped cerium nitrate/hydrophobic layer provided good corrosion resistance to mild steel [75]. Quian *et al.* tested hybrid coatings cured with pre-hydrolyzed amino-siloxane on carbon steel, which exhibited good corrosion resistance against alkaline, acidic and saline conditions [62]. Kannan *et al.* [76] produced coatings in a two-step reaction process by copolymerizing 2-methacryloyloxyethyl-phosphate containing a polymerizable methacrylate group and a functional group with MAPTS. It was concluded that this hybrid gel coatings improved corrosion resistance of mild steel in comparison with the uncoated samples. The presence of strong interfacial interaction was attributed to the interaction of phosphate group with the metallic substrate. Guin *et al.* [77] prepared hybrid nanotitania-silica composite coating from polycondensation of titanium-isopropoxide and N-phenyl-3-aminopropyltriethoxysilane. These coatings offered hydrophobic surface with good corrosion protection to steel sheets. Recent studies have reported the use of aqueous hybrid silica coatings on mild steel using GPTMS and aminopropyltriethoxysilane (APTES) sols [78] and TEOS and GPTMS together with various quantities of colloidal silica suspension [60]. Sol-gel coatings prepared from condensation and polymerization of TEOS and MAPTS, TEOS and MTES, TMOS and MAPTS, or TMOS and MTES mixtures in three molar ratios were also reported by Criado *et al.* [79,80]. For carbon steel, hybrid sol-gel coatings prepared from 3-(trimethoxysilyl) propyl methacrylate and bis [2-(methacryloyloxy) ethyl] phosphate via the sol-gel process [81] were applied. Generally, the recent publications, from 2013 to 2015 are following a tendency found previously [58], where the majority of the reported papers on this substrates use TEOS; GPTMS, MAPTS, and MTES.

2.2. Corrosion Protective Sol-Gel Coatings in Aluminium Substrates

Aluminum has a wide range of applications particularly in construction, transport, packaging, and engineering (Figure 6). However, it is in the transport sector, particularly the aviation industry, that these substrates find their main uses [82]. This may explain the strong research efforts on searching for efficient coatings and pre-treatments to replace the use of hexavalent chromium-based surface treatments [58].

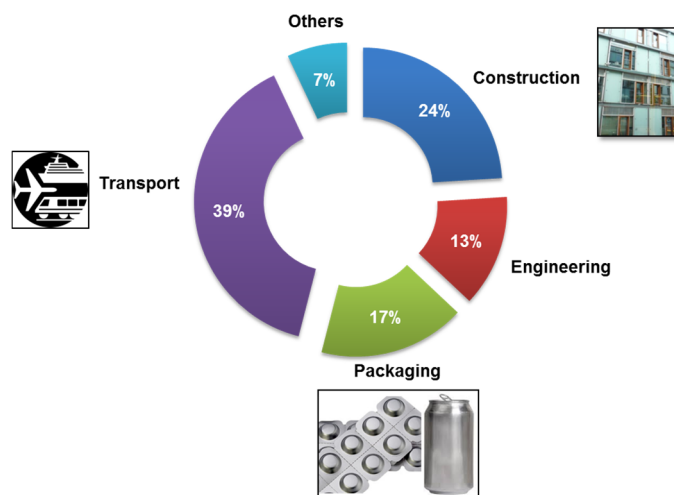


Figure 6. Main end-uses for aluminum products in Europe (data from 2013). Adapted from [82].

Sol-gel coatings have been extensively studied as a promising environmental friendly alternative for replacement of hexavalent chromium-based surface treatments of aluminium alloys [58]. This is not an easy task since these conversion coatings are very effective in promoting both adhesion and corrosion protection due to the active corrosion-inhibiting effect of Cr(VI) ions present in the film, besides the physical barrier induced by the film itself.

Solely inorganic sol-gel coating systems are porous and require densification with high curing temperatures (above 300 °C) which can induce sensitisation as well as the loss of mechanical properties of the aluminium alloy substrate [83], making them unsuitable for corrosion protection of these alloys. However, hybrid sol-gel coatings, due to the presence of the organic component, which increases flexibility and density, require much lower curing temperatures (below 150 °C) to achieve the desired barrier properties making them more interesting and suitable for aluminium corrosion protection (Figure 7). Additionally, they have the ability to incorporate additives, such as inhibitors and nanoparticles, *etc.*, which further enhance corrosion and mechanical resistance of these types of coatings [55,84].

In 2001, Parkhill *et al.* [85] prepared epoxy-silica sol-gel films on 2014-T3 aluminium alloy. These results showed excellent barrier properties and enhanced corrosion resistance in salt spray test in comparison to the chromate conversion pre-treatment conventionally applied to aircraft alloys. From this point forward, several types of organically-modified sol-gel coatings have been studied for the corrosion protection of aluminium alloys [86–94]. Most of them are based on organo-alkoxysilane precursors containing organo-functional groups, like epoxy [84,92,93,95–107], methacrylic [36,108], or vinyl [15] that can be polymerized further increasing the coating's density, and thus improving its barrier effect [84]. This shows better anticorrosive properties in comparison to hybrid sol-gel coatings based on non-functional organosilanes. Some other functional groups could be present, like phenyl [68,109], which is used to increase coatings hydrophobicity or phosphonate [55,110,111], which is used to improve bonding to the substrate. Therefore, the different organic groups are used to achieve tailored properties of the sol-gel coatings including compatibility with organic paints systems.

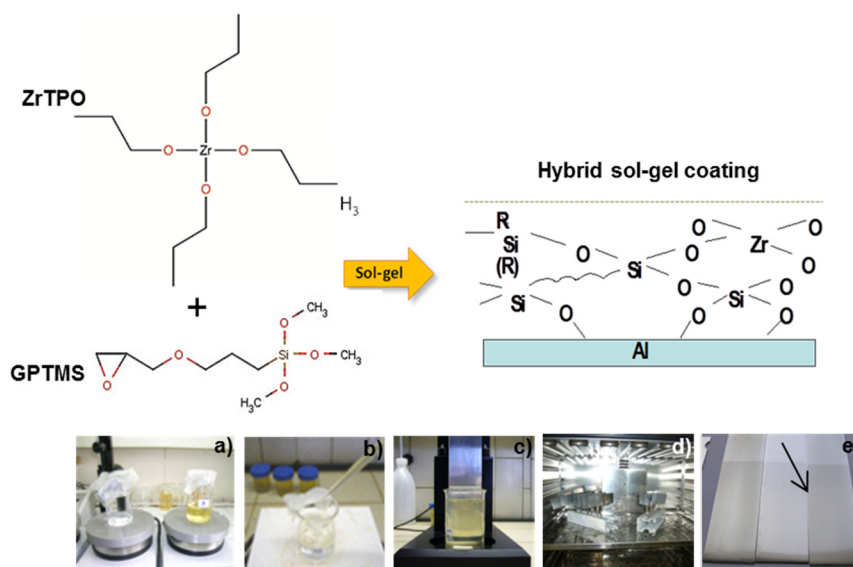


Figure 7. Hybrid sol-gel coating synthesis and deposition steps in the laboratory: (a) separate hydrolysis of precursors (GPTMS and ZrTPO); (b) mixing sols; (c) dipping; (d) curing of aluminium substrates; and (e) visual aspect of sol-gel coated samples.

The amino groups have the ability to react with the epoxy groups and provide compatibility with organic polymer paint systems. Hence, the inclusion of amine-derived cross-linking agents in the sol-gel synthesis of epoxy-silica based hybrid coatings allows the promotion of the organic network formation at low temperature [112], with inherent energy savings. Moreover, the process is essentially water-based which is also environmentally benign. However, the amino-cured hybrid sol-gel coatings developed at room temperature show reduced barrier properties in water with time due to low hydrolytic stability [113,114]. The corrosion behaviour of low temperature amine-cured epoxy-silane sol-gel coatings has been studied by Vreugdenhil *et al.* [115] and by Davis *et al.* [112] using diethylenetriamine (DETA). DETA is one of the most common epoxy crosslinkers resulting in obtaining a dense protective coating able to provide aluminum corrosion protection. Khramov *et al.* [116] also studied epoxy-silane sol-gel coatings crosslinked with amino-silanes and found significant improvement in these coating's corrosion performance in comparison to those of DETA crosslinked ones. The amino-silanes show the advantage of contributing also to the inorganic network formation. In addition to amino-silanes, other amines have been studied as alternative to DETA like di-amines of longer carbon chain [97] or branched amines [117,118], the resultant coatings showed improved corrosion protection properties compared to those derived from formulations containing DETA. Without the addition of amine or other crosslinking agents, epoxy-silane-based sol-gel coatings require thermal curing at temperatures above 100 °C to complete organic network formation. The introduction of organic components in sol-gel films results in thicker crack-free coatings with improved corrosion protection properties. However, it also decreases wear resistance and mechanical properties, making them prone to physical damage. To overcome this drawback several strategies have been studied, such as the addition of inorganic nanoparticles of silica, aluminium oxide, and other oxides to the sols [83,84,113,119], or the formation of nanostructured films or particles achieved by *in situ* synthesis during the sol-gel process through controlled hydrolysis/condensation of sol-gel precursors [84,98,116,120–122]. The latter process has the advantage of providing chemical bonds between a hybrid matrix and nanoparticles. Examples of such coatings are those obtained by Donley *et al.* [116] through the self-assembled nanophase particle process using tetramethoxysilane (TMOS) and GPTMS. Furthermore, hybrid coatings with incorporated zirconia nanoparticles prepared first by Zheludkevich *et al.* [121] from GPTMS, TEOS, and ZrTPO, and later by Fontinha [123] with the same precursors (excepting TEOS) (Figure 8), and the epoxy-zirconia-silica-based sol-gel film

prepared by Lamaka *et al.* [122] from GPTMS, ZrTPO, and titanium(IV) iso-propoxide, (containing a nanostructured porous TiO₂ interlayer) also revealed that the incorporation of nanostructured components into the hybrid sol-gel films leads to the improvement of their barrier and mechanical properties. Recently, Rodič *et al.* reported the use of ZrTPO and methacrylic acid (MAA), following their combination with sol synthesized from TEOS and 3-methacryloxypropyl trimethoxysilane. The various molar contents of ZrTPO of MAA were studied and the coatings offered high corrosion protection to aluminum substrates under simulated aircraft conditions [108,124].

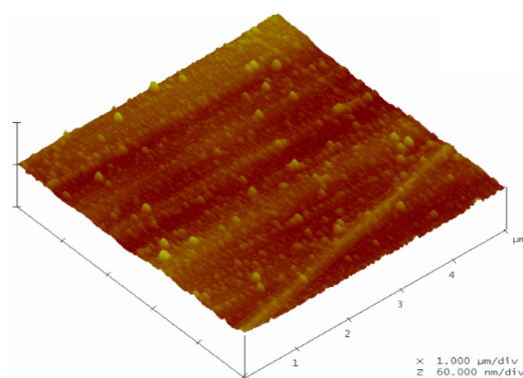


Figure 8. AFM image of an epoxy-zirconia-silica hybrid sol-gel coating surface topography with nanosized particles incorporated in the matrix [123].

Additionally, these nanostructured components can be used to introduce corrosion inhibitors within the sol-gel structure.

Doping the hybrid sol-gel coatings with corrosion inhibitors in order to reproduce a corrosion self-healing ability of chromate conversion layers is another way to improve sol-gel coatings' corrosion performance aiming at the replacement of the toxic Cr(VI) surface treatments. Some of the most effective and environmentally friendly inhibitors are derived from cerium salts [119,125–127]. Good results have also been reported with aluminum polyphosphate [128]. Organic inhibitors derived from thiazole [103,107,122,129] have also shown quite good results. However, it has been reported that the presence of inhibitors within the sol-gel coating, namely, when freely dispersed in the hybrid matrix, above a certain limit, has a detrimental effect in the long-term chemical stability and barrier properties of the coatings [43,44,121]. Consequently, several research efforts in this field have been focused on the development of micro- and nanocontainers compatible with hybrid sol-gel coatings that can be used for the controlled storage and release of the corrosion inhibitor (Figure 9) [39,40,130–141]. Some examples of this strategy include the incorporation of cerium salts in nanostructured hybrid sol-gel coating's components synthesized *in situ* like the above mentioned, or the complexation of organic inhibitors with cyclodextrins [142].

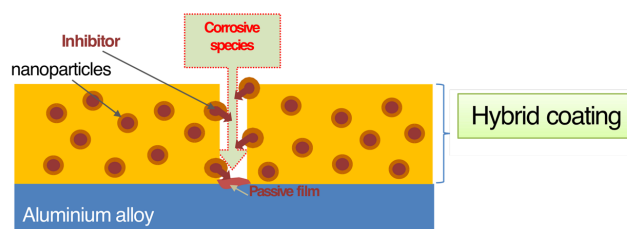


Figure 9. Generic scheme showing the corrosion healing mechanism of a hybrid sol-gel coating containing inhibitor loaded nanoparticles [123].

Other approaches to solve the problems related to long-term storage of inhibitors involve their incorporation in “smart” micro- and nanocontainers embedded in the hybrid matrix. Such as

functionalization of silica nanoparticles loaded with benzotriazole by a layer-by-layer (LbL) deposition technique coated with poly(ethyleneimine)/poly(styrene sulfonate) (PEI/PSS) polyelectrolyte layers that respond to pH change [143,144]. Similarly, natural halloysite nanotubes coated with polyelectrolyte shells by LbL were used to host the inhibitor 2-mercaptobenzothiazole [39]. In both cases a significant increase in corrosion resistance of the doped hybrid coatings was achieved in comparison to the undoped ones. Another type of “smart” reservoirs for corrosion inhibitors are those based on ion-exchange, like the layered double hydroxides (LDHs). LDHs (also known as anionic clays or hydrotalcite-like compounds) consist of stacks of mixed-metal hydroxides, positively-charged, stabilized by anions and solvent molecules located between the positive layers. The release of species from LDHs is based on an anion-exchange mechanism. From the corrosion protection point of view, LDHs have a double role: (i) release of anionic corrosion inhibitors and (ii) entrapment of aggressive anionic species such as chlorides. Furthermore, the release of inhibitors can also be indirectly triggered by pH changes: at very high pH the inhibitors can be exchanged with hydroxyl anions, whereas at very low pH the LDHs dissolve releasing the entrapped inhibitors [39]. Álvarez *et al.* [102] incorporated different concentrations of hydrotalcite compounds into hybrid ZrTPO-GPTMS sol-gel coatings, the doped films showed increased adherence and corrosion resistance. In two other studies, concerning the incorporation of stimuli-response particles into hybrid epoxy-zirconia-silica sol-gel coatings, calcinated red mud particles were used showing inhibitive action, and modified zeolites were used to host cerium (III) compounds, improving the protective performance of the hybrid coatings applied on AA 2014-T3 alloy [101,145]. Another strategy to incorporate and stabilize inhibitor species within hybrid sol-gel coatings is the use of multi-layered coatings. Rosero-Navarro *et al.* [146] developed an active sol-gel coating by sandwiching a Ce(III)-doped layer between two hybrid undoped layers synthesized from TEOS, MAPTS, ethylene glycol dimethacrylate, and glycidyl methacrylate. The corrosion performance between a three-layered inhibiting system was compared with a passive undoped bi-layered system. The former revealed enhanced corrosion properties when compared to the latter. According to the authors, this coating system was developed aiming to be employed either as a complete corrosion protection system without a top coat or as primer for successive application of water-based top-coats. Recently, Ferreira *et al.* [147] reported the synthesis of polyurea microcapsules loaded with corrosion inhibitor 2-mercaptobenzothiazole (MBT) for corrosion protection of 2024 aluminum alloy. The microcapsules were prepared by interfacial polycondensation and added to a hybrid sol-gel coating. The authors showed that results obtained indicate that capsules loaded with MBT do not affect the barrier properties of the coatings, and enhanced the adhesion to the metallic substrate. Baraka *et al.* [106] extracted collagen powder and dissolved it within a hybrid silica sol-gel to produce an environmental friendly (green) coating. The authors reported that the collagen improved the corrosion resistance of the coated AA2024 and did not compromise the mechanical properties of the coating. For aluminium substrates, more precursors have been tested than for steel alloys, however the reported data shows that the most used precursors are TEOS, GPTMS, TMOS, and ZrTPO which is according to the tendency found until 2013 [58].

The enormous number of studies performed with hybrid sol-gel coatings showed the effective ability of these coatings to protect aluminum alloys from corrosion. However, very few involved testing their performance with industrial organic paints [113,117,123,148] in order to assess the compatibility of both systems and with the industrial requirements (Figure 10) that generally are only partially fulfilled.

The introduction of organosilane based hybrid coatings on an industrial scale is still in an early stage of development due to economic reasons and to the limitations imposed for the industrial use of these products related to the long-term stability of the sols. Additionally, some of the higher performing solutions involve complex formulations and conditions of preparation that might be difficult to achieve in large-scale industrial applications. Future demands will involve the development of integrated solutions where hybrid coatings are mixed with conventional components to create coatings that will combine functions of conversion coatings, primer, and topcoat, and of course, with self-healing ability.

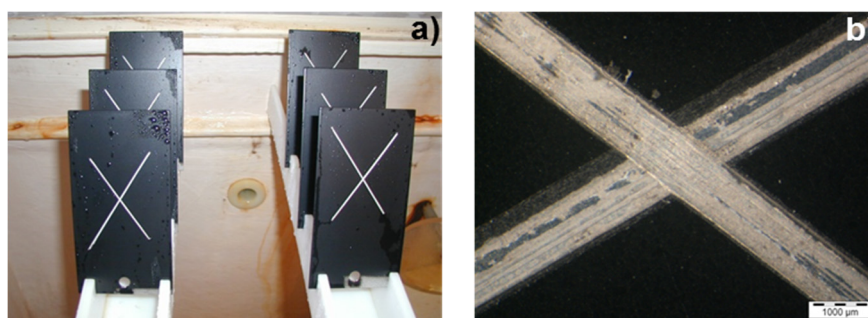


Figure 10. (a) Polyester powder coated aluminum alloy 6063 sheets pre-treated with a hybrid sol-gel doped with Ce(III) inhibitor after 1000 hours salt spray (NSS) test (ISO 9227); (b) Neither signs of aluminum corrosion outside the scribe, nor signs of blistering or infiltration over the scribe length, were visible on the coating [123].

3. Future Hybrid Coating Systems and Approaches

It is undeniable that the future applications and research will be focused primarily on the investigation of more environmental friendly precursors/reagents or industrial colloid particles to replace the traditional precursors in the formation of sol-gel protective coatings without changing the general properties. Combined systems will be also developed in order to achieve the best protection possible against corrosion, such as metal-rich sol-gel coatings, containing zinc or magnesium particles, or other inhibitor particles, which combine the barrier properties of sol-gel layer and cathodic protection of sacrificial particles; multilayer systems, such as the one proposed in Figure 11 in which a pre-emptive behavior is considered. This system combines different sol-gel layers with different functions, which is a very promising area to explore.

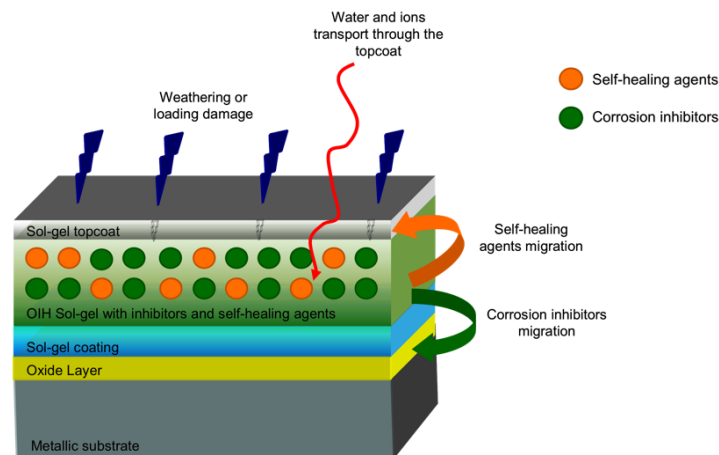


Figure 11. A possible schematic illustration of a three-layer system based on hybrid sol-gel coatings and the illustration of how the pre-emptive healing system works. Water and electrolyte diffusion through the sol-gel topcoat can generate corrosion reactions at the metal-oxide interface. Pre-emptive healing could occur through the trapping of water and corrosives and/or the release of inhibitors from the hybrid sol-gel, which targets the corrosion reactions and shuts them down. Self-healing agents also heal the top-coat from the effects of weathering and/or other damage.

The properties of sol-gel coatings, such as delamination, crackability, and adhesion, are crucial factors to ensure the quality of coatings for corrosion mitigation. However, a systematic theory and procedure on how to evaluate the viability, efficiency and stability of these coatings has not been implemented yet. Nevertheless, to guarantee the achievement of efficient sol-gel coatings for corrosion mitigation, these procedures must be considered and applied. Hybrid sol-gel materials

synthesized and found in the literature demonstrated market viability either due to unique properties that allow new end-use applications or show a significantly enhanced cost/performance relationship compared to the available materials in the marketplace. However, it must be emphasized that there are many anti-corrosive epoxy coatings commercially available and the continuous research for contemporaneous hybrid polymers has been gaining market niches, leading us to believe that these are the directions for future success. On the other hand, it was also shown that some hybrid materials already exist with significant commercial potential; however, these have not yet reached commercial status. Like all innovative materials, these are facing many difficulties and challenges for large-scale industrial production since a number of factors, including capital investment, ease of manufacturing, coating performances, and environmental issues need to be considered when developing a coating process for industrial application. Therefore, future trends for hybrid sol-gel coatings are predicted to be towards low cost, pollution-free, ease of synthesis, and effective in corrosion control. These obstacles and difficulties should be easily overcome by establishing a direct connection between the industry, the users/customers and the scientists, creating a synergy in which everyone wins.

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