

Review

Sol-Gel Materials for Electrochemical Applications: Recent Advances

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Abstract: This review article emphasizes on the modern approaches to the types of sol-gel materials that are beneficial for electrochemistry, monitored by a report of recent advances in the numerous fields of sol-gel electrochemistry. Modified electrodes for sensors and supercapacitors as well as anti-corrosion are described. Sol-gel synthesis expands the capabilities of technologists to obtain highly porous, homogeneous, and hybrid thin-film materials for supercapacitor electrode application. The widespread materials are transition metal oxides, but due to their low conductivity, they greatly impede the rate capability of electrochemical supercapacitors. The way to optimize their properties is the production of complex oxides or different composites. Among the new materials, a special place is occupied by perovskites and materials with an olivine-type structure, which can be easily obtained by the sol-gel method. The sol-gel coating process has demonstrated excellent chemical stability to advance the corrosion resistance of the various metal alloy substrates. Furthermore, the sol-gel process is a user-friendly technique for applying a hybrid sol-gel coating to provide corrosion resistance. The hybrid sol-gel coating technique is the most attractive, easy to prepare at a lower temperature, and has shown the potential to swap Cr-based coatings. The hybrid sol-gel coating has exhibited promising properties of adherent and uses chemically inert to enhance the corrosion resistance of the metal and alloys. Hence, this review article emphasizes on the recent advances and approaches in the sol-gel coating processes that influence the belongings of its hybrid sol-gel coating for protecting metal substrates and their alloys from corrosion. In addition, the author discusses the current problem and challenges of hybrid anti-corrosion sol-gel coatings. Metal oxides and composites based on them are actively used to create electrochemical sensors. They synthesized, including the anhydrous and citrate sol-gel methods. Such materials are widely used as glucose biosensors and harmful gas sensors.



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1. Introduction

Sol-gel thin film technology has been around for more than six decades. The sol-gel process has been proposed as an alternative to traditional methods, such as sputtering, CVD, and plasma spray, for applying thin ceramic coatings. Sol-gel thin films are technically visible alternatives to these methods in several known as well as commercially viable alternatives [1–3]. The inorganic thin films obtained by the sol-gel method are successfully used in various fields [4,5]. For example, gas sensors based on sol-gel coatings have been investigated in the last 20 years. Several advantages can be expected in the development of sensitive gas sensors. In the context, of the sensors controlling the impurities via stoichiometry, low-temperature fabrication should provide better control over the structural morphology [6–12]. These factors contribute to low conductivity and high purity for excellent sensitivity. Finally, the high surface area materials and their porosity composed by sol-gel methods should increase sensitivity in mechanisms dominated by surface phenomena. Sol-gel is progressively enticing the consideration of the electrochemical

community as a versatile way to produce coatings for supercapacitors [13,14], electrochemical sensors [15], solid electrolytes [16], electrochromic devices [17], anti-corrosion protection [18,19], etc.

The hybrid sol-gel coating has attracted great attention due to its promising properties and insisting to explores a wide range of applications in a couple of decades. The combination of organic and inorganic materials in a single phase provides exceptional opportunities for electrochemical applications, anti-corrosion, opticals, and sensors. This no-holds-barred design concept has led to the development of hybrid coatings for diverse applications, such as highly optically transparent materials such as glass and glasses to protect the metal substrates from the penetrations of abrasion and corrosion.

In recent years, xerogels, aerogels, and even conductive hydrous gel applications have been produced and investigated. Many scientists have concluded that amorphous materials hold more promise than their crystalline nature, i.e., those that require rapid diffusions, such as Li batteries, electrolytes, and electrodes for supercapacitors.

Sol-gel chemistry is the production of inorganic or ceramics polymeric materials from solution by converting liquid precursors into sol and forming the gel network structure [20]. Traditionally, sol formation obtains via hydrolysis and is followed by condensation in the bottom-up approach. In this practice, the ultimate sol-gel products are made by the performance of several irreversible chemical reactions. There are several advantages of the sol-gel method due to its unique characteristics. [21]. Another important advantage is the possibility of joint deposition of several hydroxides or carbonates. Further heat treatment allows forming of complex oxides with particles of various shapes and sizes [22,23]. In addition, the sol-gel process makes it possible to obtain a highly dispersed homogenous composite with a high degree of purity [24]. The very important advantage of this method compared to conventional methods is the lower process temperature, which is the creation of metallic and ceramic nanomaterial in this process at various temperature ranges (70–320 °C) [25,26].

The last review on sol-gel materials for electrochemistry was published in 1997 [15]. Two new trends were noted: (1) the increased attention to amorphous gels; (2) the rapid spread of organic-inorganic hybrids in all areas of electrochemistry. A book [27] focused on the way to synthesize, assemble, and modify material that find use in the system designed for energy conversion and energy storage was published in 2012 and continues to be of great significant interest. The sol-gel process is used for various systems on the energy market.

This article is focused on the advances in the production of supercapacitor electrodes, electrochemical sensors, and anti-corrosion coatings by sol-gel method in the last 5 years. The types of sol-gel materials that are useful for electrochemistry are presented. Modified electrodes and corrosion-protecting coatings are described. Considerable interest has arisen in metal-oxide-based materials, perovskites, and carbon-based composite materials.

2. Sol-Gel Process

The sol-gel process describes the formation of a network of oxide layers through the condensation reaction of silane alkoxides and some metal precursors in the liquid phase. Sol-gel is usually made in two ways. The inorganic process contains the development of a network through the formation of sol suspensions of oxides and suspension of sol in the liquid phase. However, the most used method is the organic process, which normally begins with alkoxides or metalloid monomer precursors in organic solvents. The recent approach takes the gain of producing a hybrid material that combines the behavior of both the organic and inorganic process. The sol-gel formation generally takes place in four stages, i.e., hydrolysis, condensation, followed polymerization, and particle formation agglomeration, which spreads throughout the liquid medium and leads to coagulation by gelation. After the hydrolysis reaction, condensation reactions occur simultaneously and are followed by steps to form alcohol and water as by-products.

3. Sol-Gel Materials for Supercapacitors Application

A large specific surface area with high purity is required for the production of electrode materials for supercapacitors. Considering the advantages of the sol-gel method, it can be observed as a great potential process to prepare these materials. In general, tailor-made metal oxides and metal hydroxide-based electrodes follow a pseudocapacitance (redox) mechanism, whereas carbon-based electrodes store the charge via electric double-layer capacitance (EDLC). The materials to integrate both types of charge-storing mechanisms can be made using the universal process, which is a soft chemical approach. This is practiced to produce high porous metal oxides at adequate temperatures. The properties of supercapacitors depend on the electrochemical stability, conductivity, porosity, and structure features of the electrode materials for high specific capacitance at low resistance enables.

3.1. Olivine-Type Materials

Materials based on Li and metal phosphates of the d-block elements with the olivine structure LiMPO_4 (M = iron, manganese, cobalt, and nickel) stand out because of the high potential of the redox couple $\text{M}^{2+}/\text{M}^{3+}$ compared to lithium couple. This potential is 1.5–2.0 V higher than the potential of the corresponding metal oxides due to the inductive effect of M-O-P caused by the high covalency of the P-O bond in the phosphate (PO_4^{3-}) polyanion. This effect ensures the stabilization of the olivine structure and prevents the release of oxygen from the charged electrode material during cycling. In this regard, lithium and d-metal orthophosphates are safer compared to similar metal oxides. Mostly, this kind of material is used as a cathode electrode material for Li-batteries [28]. However, there are research papers where olivine-type materials are used for the production of hybrid batteries as more effective energy storage devices.

For example, a simple and time-efficient sol-gel process has been used to fabricate and tune the structural morphology of LiCoPO_4 without using any surfactants [29]. The authors also proved that the changing of pH has a major effect on the final product of the morphology, since pH affects the solubility, deposition rate of configurational ions, and nucleation of growth rate. Thus, it was shown the development of microspheres cluster to rods with submicronic nanoparticles has a positive consequence on the size of the particle and electrochemical properties (Figure 1).

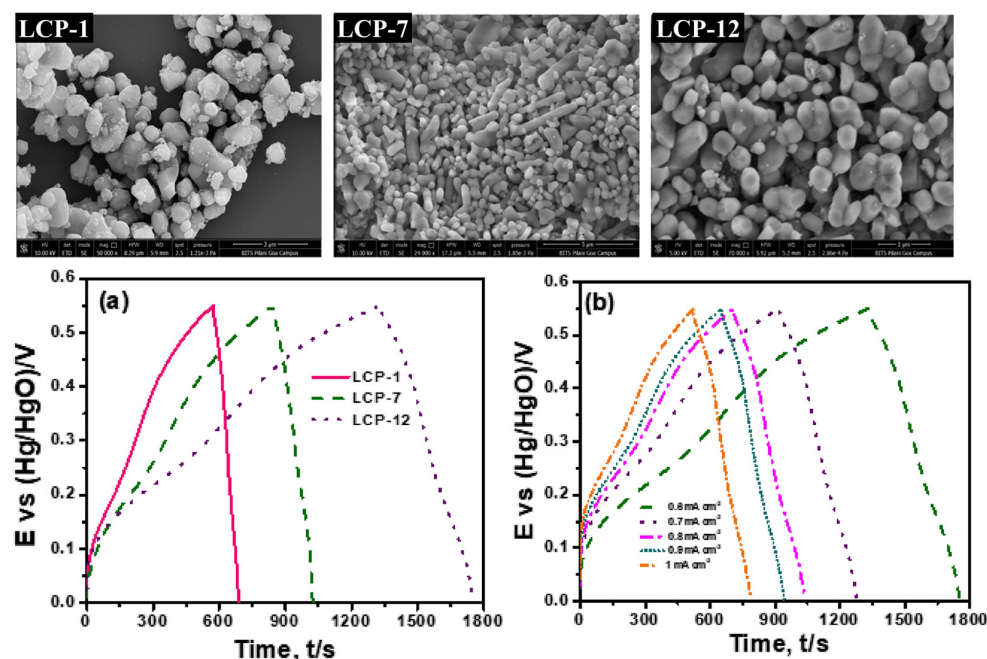


Figure 1. FE-SEM images of LCP-1, LCP-7, LCP-12; (a,b) galvanostatic charge-discharge capacitance comparison. LCP-1 fabricated from the solution with the pH = 1; LCP-7 fabricated from the solution with the pH = 7; LCP-12 fabricated from the solution with the pH = 12) [29].

The structural directing agents play a key role in the preparation of the sol-gel method, making homogeneously dispersed sol solution and accelerated particles to enhance electrochemical properties. N. Priyadharsini et al. [30] also preferred LiNiPO_4 as the potential electrode for hybrid capacitors. LiNiPO_4 nanoparticles were prepared with chelating agents (citric acid, L-ascorbic acid, and sorbitol) via the sol-gel process, and their materials were referred by LiNi-C, LiNi-A, and LiNi-S. Thus, particles with three different morphologies are formed (Figure 2).

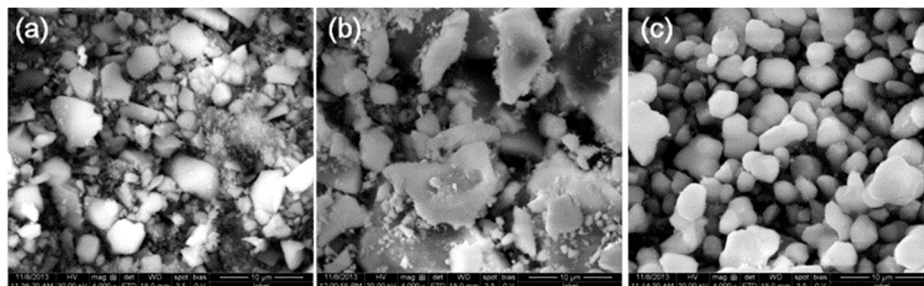


Figure 2. FE-SEM images of LiNi, (a) citric acid (LiNi-C); (b) L-ascorbic acid (LiNi-A); and (c) sorbitol (LiNi-S) [30].

Additionally, LiFePO_4 was prepared with different mole ratios of activated charcoal by the sol-gel method [31]. The LiFePO_4 combined with carbon composite materials reduces the crystalline grain size, and the shortened diffusion path facilitates fast ion transport and enhanced electrochemical performance.

3.2. Sol-Gel Metal-Oxide-Based Materials

Various metal oxides pseudocapacitors (RuO_2 [32], MnO_2 [33], Fe_3O_4 [34], etc.) are widely reported as high-efficient electrode materials. However, individual oxides still suffer from low conductivity during a redox reaction, which greatly slows down the speed of electrochemical supercapacitors. The way to optimize their properties is the production of complex oxides or different composites.

3.2.1. Ni-Based Materials

NiCo_2O_4 nanosheets were synthesized oil-in-water emulsion system by a sol-gel method involving polyethylene glycol, dichloromethane, and water [24]. Metal precursors of nickel and cobalt were in an aqueous medium and then added to the emulsion. The synthesized NiCo_2O_4 electrodes had a honeycomb structure with high porosity as ion-buffering reservoirs. The NiCo_2O_4 showed a specific capacitance of ~ 140.1 mAh/g at a discharge current density of 0.5 A/g with 66.7% retention after 5000 cycles.

The main advantage of this work [35] is the comparison of the capacitance performance of the NiMn_2O_4 -MWCNT electrodes prepared in the sol-gel method under the solvothermal method. The investigated sol-gel material presented a lump-like structure with an uneven size, while when prepared by the solvothermal method, it displayed spherical morphology. The estimation of diffusion coefficients showed that solvothermal material is more promising for supercapacitor application than SG one. This fact was supported by the electrochemical investigations: solvothermal synthesis through preparing NiMn_2O_4 /MWCNT electrode materials gives better electrochemical performance than the sol-gel method.

NiO was prepared by reacting metal acetate sol-gel method in the water and methanol mixture, and consequently, the materials were annealed at 350 °C [36]. Then, the prepared NiO powder was mixed with carbon black and polyvinylidene difluoride binder for deposition onto the nickel foam with the following aged at 60 °C.

In this case, the morphology of NiO particles seems to be non-uniform and coarse, which is promising for electrochemical applications (Figure 3A). The fabricated NiO mesoporous material investigated the electrochemical performance and exhibited a high specific

capacitance of 871 F/g at 5 mV/s in 4.0 M KOH electrolyte solution with cyclic retention of 86.5% after 10,000 cycles.

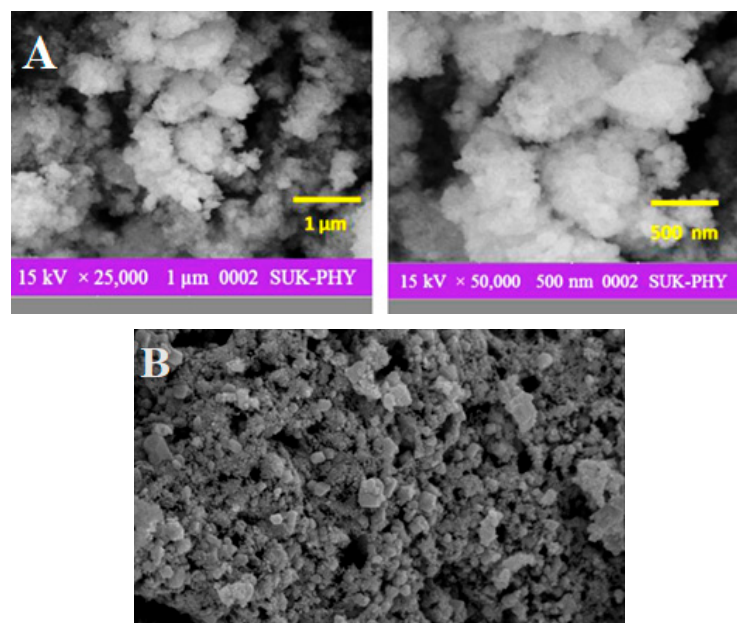


Figure 3. (A) FE-SEM micrographs of NiO NSs [36]; (B) SEM micrograph of NiCo₂O₄/CeO₂ sample [37].

NiCo₂O₄/CeO₂ nanomaterials were prepared with a different mole ratio of Ce (0.2 to 1.0) in an aqueous medium [37]. Glycine was used as a chelating agent. The SEM image of NiCo₂O₄/CeO₂ nanomaterials clearly showed spherical morphology (Figure 3B). CeO₂-doped NiCo₂O₄ shows a specific capacitance of 1355 F/g at a discharge current density of 5 A/g cyclic stability with 4.7% capacity loss at 10 A/g and retention of initial capacitance after 6000 cycles [37].

3.2.2. Mn-Based Materials

Manganese-based nanomaterials as a potential electrode can be measured as a promising candidate owing to being very cheap, naturally viable, and harmless, as demonstrated in [35,38,39]. In [38] NiMn₂O₄ nanomaterials were fabricated on tissue paper by a sol-gel process and the material demonstrated a high specific capacity of 303 F/g at the discharge current density of 0.5 A/g; furthermore, GCD studies show good cyclic stability after 5000 cycles. Conversely, in [39], the pure MnO₂ thin-film transparent electrodes prepared through the sol-gel route showed a specific capacity of 576 F/g. The main result of [39] is that the areal capacitance in the range of transparency was related to the thickness of the film.

In [40], nickel substituted porous ZnMn₂O₄ nanomaterial was synthesized by auto-combustion sol-gel process and followed by annealing at high thermal conditions. Precursors based on zinc, nickel, manganese nitrates, and fuel, such as glycine and urea, were used. Urea was initiated hydrolysis and glycine acted as a chelating agent, controlling morphology and reducing combustion temperature. It was shown that nickel substitution on ZnMn₂O₄ presented great impact on the structural morphology and their electrochemical performance. When the substitution contents increase, the grain size changes from 150 to 250 nm and the maximum value of specific capacity of 161.27 F/g is observed at 5 mV/s.

In some cases, Mn, like other transition metals, due to their low electric conductivity, do not reach its theoretically predicted value for capacitance. Thus, producing composite materials, as in [41], is promising. The MnO₂/activated carbon composite was prepared using the sol-gel technique at room temperature, while MnO₂ nanorods were synthesized by a hydrothermal treatment. The loading of MnO₂ into the activated carbon increased the specific capacitance from 166 to 213 F/g.

3.2.3. Others

Metal oxides are preferred as anode materials, because of their pseudocapacitive behavior, different oxidation states, lamellar structure, and very low cost. In [42], V_2O_5 nanorod@rGO nanocomposite was prepared by sol-gel method using ammonium meta vanadate and citric acid in an aqueous medium. The improved capacitance performance of the V_2O_5 @rGO composite is primarily endorsed to the rGO; the results showed a high specific capacitance of 289 F/g at a discharge current density of 0.01 A/g, and outstanding cyclic stability with 85% retention of the initial capacitance after 1000 cycles [42].

In [43], the sol-gel route was applied for synthesizing the 3D-graphene matrix from GO-GNs ink and the Fe_3O_4 /3D-graphene composite electrode was formed. The authors declared that 3D-graphene addition prevents the aggregation of Fe_3O_4 particles. The particle size of Fe_3O_4 in the composite is about 5 nm. The electrode demonstrates a maximum specific capacitance of 388.8 F/g at a discharge current density of 1 A/g and it maintained good cyclic stability with 88% retention of capacitance after 5000 cycles.

$BiFeO_3$ bismuth ferrite was synthesized with graphene by a sol-gel method, and the material was studied for supercapacitors' performance [44]. Loading of graphene boosted the electrochemical properties of the material. Bismuth ferrite electrode materials exhibit a capacitance of ~ 5.7 mF/cm², and the addition of graphene into BFO increases the capacitance value to ~ 11.35 mF/cm². The two-electrode cell exhibited good cyclic stability with a 5% loss in capacitance after 2000 cycles.

MCM-41 mesoporous silica material was prepared as support material using a sol-gel method, after which the material was annealed at 550 °C [45]. ZnO - TiO_2 was fabricated on the surface of the MCM-41 by the solvothermal method. The electrochemical studies show a high specific capacitance of 642.4 F/g. In addition, it displays excellent cyclic stability with 98.7% retention of capacitance after 5000 cycles.

3.3. Carbon Aerogels

In most works, xerogels are described due to their gel being destroyed when the solvent removes. After milling and heating discrete/clumps particles are obtained. If care is taken to remove the liquid by-products from the wet gel without collapsing the gel, the resulting material, called an aerogel, will have a continuous structure with a hierarchical combination of micropores and mesopores, with a large surface area (>200 m² g⁻¹). In general, aerogels contain nanodimension pores, low-density, and high surface area that make them good candidates for supercapacitors application. Sol-gel approaches deal with the opportunity to produce high pure bio-derived carbons with porous structural arrangement. Additionally, it exhibits good electrochemical performance, due to the reliable compositions of precursors [46–48].

The aerogel preparation process involves two stages, gel making (solvent penetration) and removal of solvents. In general, the term aerogel refers to the inner substance and not its constituent parts; hence, it is possible to prepare aerogels from a variety of material compositions [49–52] (Table 1).

The solid network of aerogels generally consists of both nanocrystalline and amorphous domains. Network formation depends on controlling gel bridging with terminal oxygen. In the alkoxide process, this condition can be met by changing the nature of the alkyl group and/or precursor concentration in the sol. For the Pechini method, the size and interconnectedness of particles are controlled by the choice and concentration of complexing and dispersing agents. It was demonstrated in [53] that aerogels suffer from low capacitance. Thus, doping with other atoms or producing composites with organic materials is promising.

The authors of [54] prepared nitrogen-doped porous carbon aerogels with a crosslink agent by the sol-gel method and investigated the supercapacitor performance of agar aerogels, as well as KOH-treated and urea/KOH-treated agar aerogels (Figure 4). Agar aerogels showed different structural morphologies. In this context, Agar- and KOH-treated aerogel consist of 3D microporous interconnected carbon networks, whereas urea/KOH-treated

agar aerogel consists of a porous carbon network, and the BET surface area is $2000 \text{ m}^2/\text{g}$. Additionally, the electrochemical performance exhibits a gravimetric capacitance of 400 F/g at a discharge current density of 0.5 A/g .

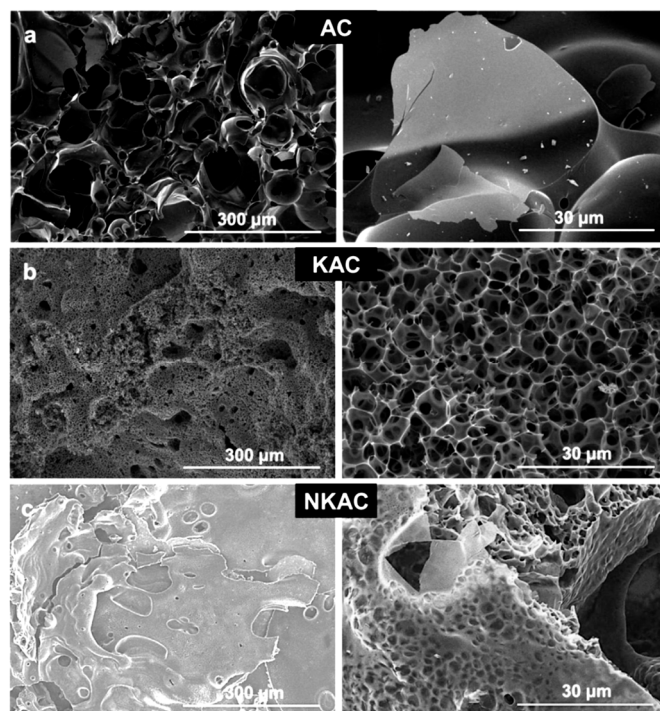


Figure 4. SEM images of agar aerogel (a), KOH-treated agar aerogel (b), and urea/KOH-treated agar aerogel (c) [54].

A simple and low-cost synthesized carbon aerogels/PPy composite material was obtained via a sol-gel process by the in situ polymerization method, and subsequently, the material was carbonized and activated with KOH [55]. The as-prepared aerogel materials showed a high specific capacitance of 433 F/g and a discharge current density of 0.5 A/g , while maintaining prolonged cyclic stability with $\sim 87.2\%$ retention of capacitance after 5000 cycles.

Yuelong Xu et al. [56] used a simple method to prepare a new starch-derived carbon aerogel. Starch was added in the sol-gel method with phloroglucinol, resorcinol, and formaldehyde, which provided oxygen-containing surface groups as a residue from carbonization. The as-prepared starch-derived carbon aerogel had a specific surface area of $734 \text{ m}^2/\text{g}$ and a specific capacitance of 147 F/g^{-1} at a discharge current density of 1.0 A/g .

Juan Xu et al. [57] have prepared lignin-derived carbon aerogels via polycondensation (lignin, resorcinol, and formaldehyde) through the sol-gel process under a microwave-assisted method. The as-obtained lignin-derived carbon aerogels show better performance than alkaline lignin. The lignin-derived carbon aerogels retained a specific capacitance of 96% after 2000 cycles; in addition, the material exhibited 195.3% of the specific capacitance compared to the carbon aerogels.

3.4. Perovskites

Perovskites are a new class of metal oxides with electronic structures and they have good thermal stability and ionic conductivity. Nanosized perovskite metal oxides with formula ABO_3 (A consists of lanthanides and B consists of a transition metal), which are considered to be replacement for individual oxides in a given application and are intensively studied for their use in catalysis, OER, capacitance (Table 1), and batteries [58–63].

The sol-gel method is advantageous for preparing perovskite-type materials for developing in a single-phase material with a relatively high surface area. In this process, the sol

effectively forms a gel. The disintegration of desiccated gel substance during calcination produces in the preferred perovskite [64].

Recently, one of the most popular sol-gel methods is Pechini for the synthesis of perovskites through polyesterification. It has become the most widely used process, owing to its flexibility in synthesizing perovskite membranes and deposition of dielectric films for the fabrication of capacitors [65,66].

Doped lanthanum perovskite manganites ($\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$) were obtained by the sol-gel method, and thus, electrode material was studied for the electrochemical performance of capacitance [67]. The Calcium -doped electrodes have shown increased capacitance, but poor stability is associated with the degree of irreversibility of pseudocapacitance response and severe leaching of cations. Thus, after 3000 cycles, the capacitance of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ electrode drastically declined (39% of capacitance) from 170 to 47 F/g.

The authors of [68] reported on the double perovskite $\text{PrBaCo}_2\text{O}_{5+\delta}$ oxide (PBCO) fabricated by the sol-gel method. The electrochemical tests showed that the PBCO electrodes exhibit a capacitance of 428.2 C/g at 1 mV/s. The capacitance retention was 93% after 2000 cycles.

Figure 5a shows the SEM images of various structures based on perovskites obtained by the sol-gel method.

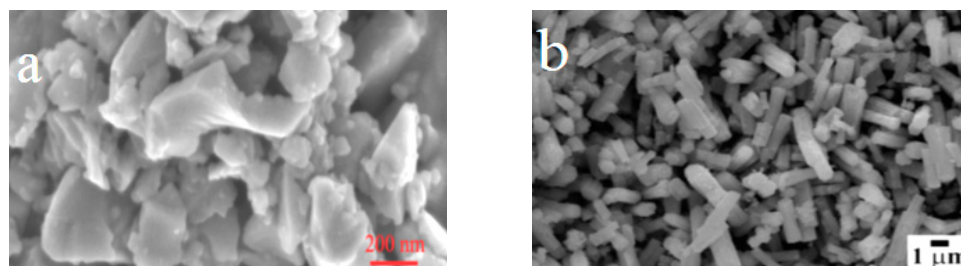


Figure 5. SEM images of different perovskites structures: (a) double perovskite $\text{PrBaCo}_2\text{O}_{5+\delta}$ [68]; (b) NiTiO_3 rods [59].

NiTiO_3 rods were synthesized through the sol-gel route and annealed at 600 °C for 2 h [59]. NiTiO_3 rods have a hexagonal morphology with coarse surfaces (Figure 5b). The hierarchical interlocking of NiTiO_3 nanoparticles with an increased textural boundaries offered a high surface area for considerably larger diffusion of OH^- ions, further additional leading to an increase in the specific capacitance of 542.26 F/g.

At the same time, $\text{SrCo}_{0.95}\text{V}_{0.05}\text{O}_3$ perovskite synthesized from the sol-gel process demonstrated a low specific capacitance of 0.04 F/g.

The authors of [62] reported on the $\text{SrCo}_{0.9}\text{Mo}_{0.1}\text{O}_{3-\delta}$ perovskite irregular clustered structures, providing good electrolytic mobility. The $\text{SrCo}_{0.9}\text{Mo}_{0.1}\text{O}_{3-\delta}$ perovskite showed a specific capacitance of 1223.34 F/g at a discharging current density of 1.0 A/g. Galvanostatic charge-discharge tests of $\text{SrCo}_{0.9}\text{Mo}_{0.1}\text{O}_{3-\delta}$ perovskite at a current density of 10 A g^{-1} was around 93.52% after 5000 cycles.

Table 1 shows the functional characteristics of supercapacitors based on materials acquired by the sol-gel process.

Table 1. Characteristics of some supercapacitor electrodes based on sol-gel materials.

Material	Electrode Capacitance	Current/Scan Rate	Stability, Cycles	Ref.
LiCoPO_4	631 F/g	0.6 mA/cm ²	5000 cycles (two electrode cells)	[29]
N-doped porous carbon aerogels	400 F/g	0.5 A/g	100,000 (96% retention)	[54]
V_2O_5 @rGO nanocomposite (V_2O_5 sol-gel)	289 F/g	0.01 A/g	1000 (85% retention)	[42]
NiCo_2O_4	140.1 mAh/g	0.5 A/g	5000 (66.7% retention)	[24]

Table 1. Cont.

Material	Electrode Capacitance	Current/Scan Rate	Stability, Cycles	Ref.
Fe ₃ O ₄ /3D-graphene (3D-graphene sol-gel route)	388.8 F/g	1 A /g	5000 (88% retention)	[43]
LiNiPO ₄	417 F/g	1 mA/cm ²	89% being retained after 2000 cycles (AC LiNiPO ₄ supercapacitor)	[30]
La _{1-x} CaxMnO ₃ , (perovskite)	170 F/g	1 A/g	Poor stability	[67]
N-doped carbon hollow microspheres	146 F/g (80 Mv/s)	-	-	[69]
NiMn ₂ O ₄	303 F/g	0.5 A/ g	5000 cycles	[38]
MnO ₂ nanorod-loaded activated carbon	213.1 F/g	1 A/g	5000 cycles (106% retention)	[41]
Zn _{1-x} NixMn ₂ O ₄ (x = 0.00, 0.25, 0.50, 0.75 and 1.00) nanospheres	161.27 F/g	5 mV/s	-	[40]
BiFeO ₃ ³⁻	64 F/g	20 mV/s	2000 (95% retention)	[44]
Graphene nanocomposite LiFePO ₄ + AC (LiFePO ₄ Sol-gel)	(two-electrode) 36 mA h/g	100 µA /cm ² .	-	[31]
NiO	871 F/g	5 mV/s	10,000(86.5% retention)	[36]
TiO ₂ -ZnO/MCM-41 (MCM-41 sol-gel)	642.4 F/g	2 A/g	5000 (98.7% retention)	[45]
MnO ₂	1.6 mF/cm ² (576 F/g)	0.1 mA/cm ²	-	[39]
NiCo ₂ O ₄ /CeO ₂	1355 F/g	5 A/g	6000 (4.7% capacity loss)	[37]
PrBaCo ₂ O _{5+δ}	428.2 C/g	1 mV/s	2000 (93% retention)	[68]
NiTiO ₃ rods	542.26 F/g	5 mV/s	2100 (91% retention)	[59]
LaMnO ₃	392 F /g	1 A/g	10,000 (90% retention)	[60]
Alumina-embedded SrCo _{0.95} V _{0.05} O ₃	0.4 F/g	25 mA/g	-	[61]
SrCo _{0.9} Mo _{0.1} O _{3-δ} ,	1223.34 F/g	1 A/g ¹	5000 (93.52% retention)	[62]
Aerogel/PPy	433 F/g	0.5 A/ g	5000 (87.2% retention)	[55]
starch-derived carbon aerogels	147 F/g	1 A/g	97.0% of the initial discharge capacity after 10,000 cycles.	[56]

4. Hybrid Sol-Gel Coating for Corrosion Resistance

The sol-gel coating has been performed on the metallic substrate in different ways, depending on microstructure, requirements and efficiency, and practical applications. In general, dip-coating and spin-coating are two commonly used methods for sol-gel coating. In addition, some other methods, SUCH AS PVD, CVD, ED, and spraying, have been used recently. In general, the sol-gel process through prepared colloidal materials under the development of the hybrid sol and tailor-made the formation of a gel network under mild conditions. For instance, alkoxysilane and metal alkoxides are used as precursors for the preparation of sols, such as tetraethylorthosilicate (TEOS), 3-glycidyloxypropyltrimethoxysilane (GPTMS), aluminum, titanium, and zirconium alkoxides, which are used in the sol-gel coating act as a protection agent and give a variety of properties that are used in many different areas, such as decorative, functional, photoactive, and wear- and corrosion-resistant coating. In this context, due to recent hybrid material coatings on metal alloys, researchers have started to develop a new hybrid coating with excellent barrier properties for anti-corrosion applications by combining competent and compatible metal surfaces for anti-corrosion applications. The combination of easily configurable properties of the inorganic and organic materials can refine the properties. Currently, there are many organic-inorganic hybrid materials with unique architectural features and significant properties that have been studied. In general, the hybrid organic-inorganic coating combines the advantages of the organic polymer, such as excellent impact resistance, good flexibility, and light weight, with

properties of the inorganic materials, such as high thermal stability, hardness, mechanical strength, chemical resistance, and excellent durability. It is difficult to combine a hydrophobic two-component organic molecule and an inorganic material, which is often hydrophilic, into an interconnected network. Therefore, to implement the interaction between them, it is necessary to apply special reaction conditions. Inorganic-organic hybrid sol-gel coatings represent a new generation of multifunctional materials with a wide range of convenient properties and a variety of protective applications. The sol-gel process has evolved as a flexible method of producing hybrid organic-inorganic coatings, which is an encouraging candidate for use as a corrosion-resistant coating because it can create a denser layer with strong adhesion. It was covalently attached to the metal substrate at a lower temperature. This hybrid coating is designed as an outcome of the hydrolysis and condensation of silanes with metal alkoxides and they are reported to have high corrosion resistance, as they combine the chemical and mechanical properties of hybrid coating composite to form strong, dense coatings with good visible bands and flexibility that strongly adhere to metal substrates. The hybrid sol-gel coating is the most environmentally friendly and low-cost process to resist corrosion in the studied metal substrates. Furthermore, the current review focuses mainly on the hybrid sol-gel coatings and their anti-corrosion on metallic substrates, as reported in the literature and summarized in detail [18,70–74].

4.1. Hybrid Sol-Gel Coating for the Corrosive Resistance of Al Alloys

Aluminum and its alloys have the most desirable properties: high thermal conductivity, high electrical conductivity, flexibility, ductility, mechanical stability, high strength-to-weight ratio, viability, lightweight, low cost, and excellent corrosion resistance properties. It is widely used in a variety of commercial applications, i.e., in electric wiring, automobile accessories, and mechanical engineering, and is particularly used in aerospace engineering. Due to their natural tendency to create passivating aluminum oxy-layers on the substrates, they find their main uses. However, the hexavalent chromium coating has very strong corrosion resistance behavior. Recently, researchers have been developing and studying their efficient hybrid sol-gel coating for the replacement of chromate conversion coating.

Costenaro H et al. [75] developed porous anodic aluminum oxide (AAO) on the AA2524 substrate and, subsequently, protected it with the TEOS/GPTMS hybrid sol-gel coating. Different types of AAO porous layers were developed by applying a different anodizing voltage to improve the protective layer thickness, pore tortuosity, and corrosive resistance of AAO with the compatibility of sol-gel coating (Figure 6). The GPTMS/TEOS hybrid coating on the TSA anodized 2524 provides good anti-corrosion performance for the long immersion time (42 days).

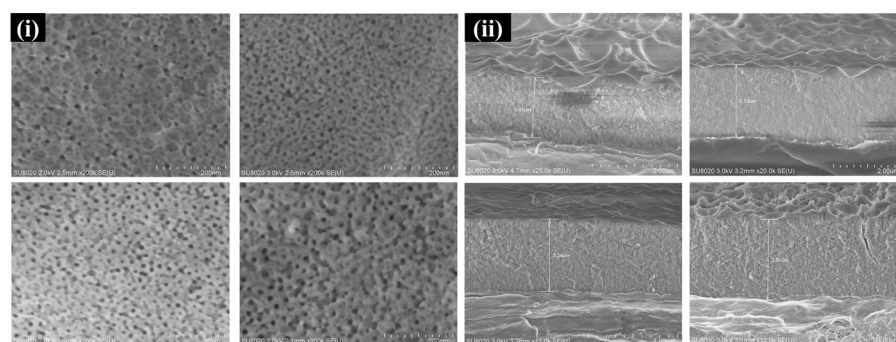


Figure 6. SEM images of anodic aluminum oxides by anodizing AA2524 (i) top surface microscopic image and (ii) cross-section images at different voltages at (8, 10, 14, and 16 V) [75].

Zhao X et al. [76] fabricated an LBL anodic composite film on the surface of 2A12 alloy by the sol-gel method. Primarily, an anodic porous oxide layer and a subsequent homogeneous aluminum sol-gel coating were created on the alloy substrate, after which the sol-gel composite film was self-assembled by LBL with PAA and PEI. The final self-assembled LBL composite was studied for corrosion resistance performance in a 3.5 wt%

NaCl solution. The SEM results of the anodization of 2A12 clearly show that the irregular surface of the aluminum alloy is covered by porous oxide, and becomes a non-uniform, homogenous surface with microporous arrangements, after the sol-gel coating. It is coated with a relatively uniform, dense, flawless, and improved anti-corrosion performance. PDS results show that the current density of LBL film was $0.00316 \mu\text{A}/\text{cm}^2$, which is two orders of magnitude lower than all other samples. The LBL film exhibited the best corrosion resistance performance with fewer defects.

Hussin M H et al. [77] developed a hybrid sol via hydrolysis over AA6061 alloy by mixing TEOS and APTES precursors and studied the corrosion resistance performance of the single TEOS and hybrid TEOS/APTES composite sol-gel coating. The corrosion resistance performance suggests that the hybrid silane coatings mitigate both the anodic and cathodic reactions simultaneously. These practices justify that the amalgamation of hybrid sol-gel improves the anti-corrosion properties of aluminum alloy.

Table 2 presents the results of the study on corrosion resistance using hybrid sol-gel coating on aluminum substrates.

Table 2. Studies on corrosion resistance using hybrid sol-gel coating on aluminum substrates.

Material Composition	Silane and Sol Sources	Substrate	Corrosion Medium	Ref.
Anodizing different voltage	TEOS, GPTMS	2524 Al alloy	-	[75]
Anodized Al alloy	Alumina sol	2A12 Al alloy	3.5% NaCl solution	[76]
LBL with PAA/PEI				
TEOS	TEOS, APTES	AA6061	3.5% NaCl solution	[77]
TEOS/APTES				
Zirconia benzotriazole	TMS	Al 2024	3.5% NaCl solution	[78]
GPTMS/TPOZ				
GPTMS/ASB	GPTMS, TPOZ, ASB	AA6061	5% NaCl solution	[79]
GPTMS/TPOZ/ASB				
nano-TiO ₂				
BTSE + GPTMS	BTSE, GPTMS	EN AC-43000	3.5% NaCl solution	[80]
BTSE + GPTMS/nano-TiO ₂		Al-Si alloy		
TiO ₂ nanosheets	KH750	AA2024-T3	3.5% NaCl solution	[81]
Chitosan/TiO ₂	TEOS, GPTMS	Al electrode	3.5% NaCl solution	[82]
rGO/APTES	APTMS, TEOS, GPTMS	2524 Al alloy	3.5% NaCl solution	[83]
MIL-53 MOF	TEOS, GPTMS	2524 Al alloy	Harrison's solution	[84]
Cerium oxide nanofiber	GPTMS, ASB	AA2024	3.5% NaCl solution	[85]
ZnAl-LDH				
Ce doped ZnAl-LDH	GPTMS, TPOZ	AA2024	0.05 M NaCl solution	[86]
ZnAl-LDH, Intercalated inhibitor (VO ₄ , MBZ, MoO ₄ , PA, 8HQ)	MPTS, PhTMS, APTMS, GPTMS	AA 2423-T3	3.5% NaCl solution	[87]
Inhibitors: L-cys, DGM, QUI, 2AP, GS, TiO ₂ -NPs	TEOS, MEMO	AZ61 Mg-Al alloy	-	[88]

Abbreviations: Tetraethylorthosilicate = TEOS, 3-glycidyloxypropyl-trimethoxysilane = GPTMS, amino-propyltrimethoxysilane = APTMS, trimethoxysilane = TMS, zirconium (IV) propoxide = TPOZ, aluminium tri-sec-butoxide = ASB, bis(triethoxysilyl) ethane = BTSE, gamma-aminopropyltriethoxysilane = KH750 (silane coupling agent), 3-aminopropyltriethoxysilane = APTES, tetra-n-propoxyzirconium = TPOZ, 3-methacryloxypropyltrimethoxy silane = MPTS, phenyltrimethoxy silane = PhTMS, 3-(trimethoxysilyl)propyl methacrylate = MEMO, Polyethyleneimine = PEI, polyacrylic acid = PAA, Vanadate = VO₄, 2-Mercaptobenzimidazole = MBZ, molybdate = MoO₄, phytic acid = PA, 8-hydroxyquinoline = 8HQ, L-cysteine = L-cys, dimethyl glyoxime = DMG, quinine = QUI, graphene sheets = GS, 2-amino pyridine = 2AP, Harrison's solution = 0.35% (NH₄)₂SO₄ + 0.05% NaCl.

Saeid Mersagh D et al. [78] made zirconia functionalized hybrid sol-gel protective coatings for the anti-corrosion properties of AA2024 aluminum alloy by the doping of benzotriazole, and the composite was studied by corrosion impedance studies in the 3.5% NaCl solution. EIS impedance results show that zirconia coating shows good resistance against corrosion, then after the incorporation of benzotriazole, the corrosion resistance is further increased. This result shows a positive effect of the anti-corrosive agent in

benzotriazole, due to the self-healing reactions beginning, benzotriazole being released from the coating, and a thin layer developing on cracks and defects.

Genet C et al. [79] prepared hybrid sol-gel coating by the incorporation of GPTMS, TPOZ, and ASB for the corrosion protection of the AA6061 Al alloy substrates. The corresponding by incorporating GPTMS, TPOZ, and ASB hybrid sol-gel matrices. GPTMS/TPOZ/ASB coating exhibits good corrosive resistance with higher resistance of 500 h duration. The GPTMS satisfied is sufficient to provide the consistency and flexibility required to produce crack-free and dense hybrid sol-gel coatings with a suitable barrier property against a corrosive environment.

Huang X et al. [80] deposited nano-TiO₂ doped hybrid sol-gel coating of BTSE and GPTMS on the surface of Al-Si alloy. The addition of nano-TiO₂ increased the protective coating on the EN-AC-43000 alloy. Furthermore, nano-TiO₂ has a significant impact on the structure and performance of the composite. The morphology of the hybrid composite coating demonstrates that dense and uniform protect substrates form an anti-corrosion coating and exhibit tremendous interfacial adherence with the substrate. The anti-corrosion coating could be effectively enriched by nano-TiO₂, which indicates reducing the corrosion and makes the positive corrosion potential. Likewise, the impedance modulus value reached 193 kΩ/cm².

Balaji J et al. [82] synthesized and studied the hybrid composites of chitosan-derived Hy/nano-TiO₂ in protecting the aluminum substrate from a corrosion environment. The self-assembled hybrid composite coating was prepared using the TEOS/GPTMS sol-gel method. The hybrid composite sol-gel coating established the formation of the Si-O-Si, Si-O-Ti, and Ti-O-Ti bands between the hybrid composite and chitosan to form a dense and stable layer that adheres to the Al substrate. The result of the hybrid composite inhibited the anodic process of the Al substrate and provided better corrosion performance than the self-assembled monolayer of the TiO₂ coating composite. An increase in the protective effect is described by the development of sol-gel coating on the substrate, which is confirmed by the resistance to charge transfer and inhibition efficiency of the hybrid composite.

Nezamdoust S et al. [83] investigated a hybrid GO/APTES composite silane-based sol-gel coating for AA2024. The rGO@APTES was prepared by mixing graphene oxides (GO) nanosheets, dicyclohexylcarbodiimide (DCC), and 3-aminopropyltriethoxysilane (APTES), and the final mixture was stirred for 24 h at 70 °C and dried. After that, rGO@APTES was prepared by the hydrolysis and condensation of silane precursors using tetraethylorthosilicate (TEOS) and 3-Glycidoxypropyltrimethoxysilane (GPTMS), followed by the addition of rGO@APTES. In this study, the ethoxy group of the rGO/APTES is easily hydrolyzed with silanes, which allows Si-O-Si formation for the chemical adhesion of functionalized nanoplates by hydrolysis of TEOS and GPTMS. The corrosion protection of EIS and PDS analyses of the prepared rGO/APTES nanocomposites coating with various concentrations of rGO@APTES (0, 50, 100, 200, and 500 ppm) nanoplates. The rGO/APTES sol-gel nanocomposites revealed high resistant polarization and better anti-corrosion than other composites. This is mainly due to the uniform dispersion of rGO nanosheets and is related to the formation of cross-linked and dense films by protecting the metal substrate.

Tarzanagha Y J et al. [84] incorporated MIL-53 MOF as a nanofiller in a sol-gel nanocomposite coating of TEOS and GPTMS and studied their effect of corrosive resistance on AA2524 alloy in Harrison's solution. The enhancement of the anti-corrosion by the dispersion of MIL-53 MOF into the sol-gel coating can be considered the chemical interaction between the MIL-53 MOF and the silane network. The hybrid MOF coating also significantly increased the resistance by forming a stable bond formation that confines the diffusion of the electrolyte on the substrate surface and by its better resistance between substrate and MOF with good distribution in the hybrid sol-gel nanocomposite. From the EIS plots presented in Figure 7, it can be seen that the low-frequency impedance modulus is around 6.9 kΩ/cm² for the pure alloy and increased to about 695 kΩ/cm² after the hybrid sol-gel. This result displays that the anti-corrosion of the AA2524 alloy is enriched by the sol-gel coating. The sol-gel/MOF coating was undamaged after 24 h of immersion,

indicating noble anti-corrosion behavior and better corrosion resistance due to the addition of the MOF nanoparticles.

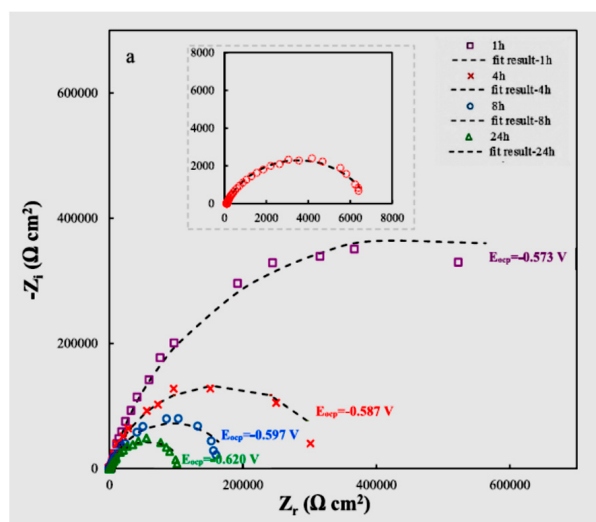


Figure 7. EIS and Nyquist plot for MIL-53 MOF sol-gel coating for different times of immersion [84].

Lakshmi R V et al. [85] prepared a sol-gel coating based on aluminum-tri-sec-butoxides and GPTMS containing cerium to protect the AA2024 alloy and compared the sol-gel coating of cerium nanofiber with commercial ceria. They hybridized sol-gel coating by mixing ASB and GPTMS in different ratios and then cerium nanofibers were added into the solution mixture and then coated on the aluminum substrate (Figure 8). SEM and TEM images of hybrid composite morphology reveal that size of particles is ~25–30 nm, and the surface of the coating is smooth, uniform, and crack-free. The ceria nanofibers sol-gel coating shows good compatibility with the epoxy primer coating and it represents a potential alternative to conventional chromate pretreatment. Zhang Y et al. [86] described that ZnAl-LDH and Ce-doped ZnAl LDHs were synthesized and then integrated into a hybrid sol-gel anti-corrosion coating consisting of GPTMS and TPOZ for AA2024. It has been shown that Ce^{3+} ions partially replace Al^{3+} ions and are successfully integrated into LDH layers. The insertion of Ce (III) ions did not abolish the LDH layers. The impedance values of the embedded ZnAlCe-LDHs anti-corrosion coatings are higher than those of doped ZnAl-LDHs coating, particularly in the low-frequency range. Thus, it shows the positive effect of the adding cerium on corrosion protection processes. During immersion, the release of Ce^{3+} cations after LDH dissolution provides active protection of the alloy substrate and self-healing from localized corrosion attack by Ce atom. Similarly, Subasri R et al. [87] developed a ZnAl-LDH intercalated with different inhibitors (8HQ, MBZ, PA, MoO_4 , and VO_4) and investigated their corrosive resistance properties on AA2423-T3 alloy in 3.5 wt% NaCl. It was found that different inhibitors improve the overall corrosive resistance performance.

4.2. Hybrid Sol-Gel Coating for the Corrosive Resistance of Steel Substrates: Steel/Mild/Stainless/Low Carbon

Steel and its substrates are generally used in commercial applications. Alloy steel is an alloy formation with multiple elements (Mo, Mn, Ni, Cr, V, Si, and C) to enhance mechanical strength, hardness, toughness, and wear resistance. Even alloy steel is exposed to corrosion in an aggressive corrosive environment. Enduring present studies have established that the hybrid sol-gel coating on alloy steel substrates was broadly studied.

The corrosion resistance performance of the hybrid sol-gel coating on the steel substrate was studied and precise, as shown in Table 3.

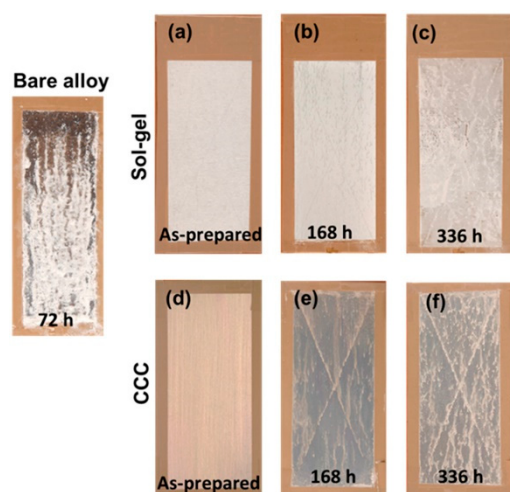


Figure 8. Corrosion resistance performance of AA2024, ceria nanofiber, and commercial ceria in the salt spray studies for sol-gel (a–c) and CCC (d–f) coating materials after 168 h and 336 h [85].

Table 3. Studies on the corrosion resistance using hybrid sol-gel coating on steel substrates.

Material Composition	Silane and Sol Sources	Substrate	Corrosion Medium	Ref.
-	TEOS, TMOMS	Mild steel	3.5% NaCl solution	[89]
-	GPTMS, TEOS, TETA	Low carbon steels	3.5% NaCl solution	[90]
SiO ₂	TEOS, GPTMS	S-46 (A1008 steel)	3.5% NaCl solution	[91]
TiO ₂ -SiO ₂	TBOT, TEOS	C45E steel	3.5% NaCl solution	[92]
TiO ₂ -SiO ₂	TTIP, TEOS	Mild steel		[93]
TiO ₂ hybrid sol	TBT, GPTMS	304 stainless steel	3.5% NaCl solution	[94]
Inhibitors: Ce, BTA, and 8H	TEOS, TMOS	Mild steel plate	-	[95]
ZnAl-MoO ₄ -LDH/SiO ₂	TMOMS, TEOS	Steel	3.5% NaCl solution	[96]
Zinc phosphate	γ-GPS, TEOS, MTES	Mild steel	0.1 M NaCl solution	[97]
Zinc acetylacetonate	g-GPS, TEOS, MTES	Mild steel	3.5% NaCl solution	[98]
NaX zeolite nanoparticles	TEOS, GPTMS	Mild steel	3.5% NaCl solution	[99]
Inhibitor: zinc nitrate, 2-mercaptobenzimidazole	TEOS, GPTMS	Treated Ti-Zr	3.5% NaCl solution	[100]
Meso porous silica	TEOS, GPTMS	S355 J2+N carbon steel	0.005 M NaCl solution	[101]
Inhibitor: ECBT	MTES, TEOS, TEPI, APTMS	Steel	3.5% NaCl solution	
La(4-OHCin) ₃				
GO, epoxy/polyamide				

Abbreviations: Tetraethylorthosilicate = TEOS, 3-glycidyloxypropyl-trimethoxysilane = GPTMS, aminopropyl-trimethoxysilane = APTMS, trimethoxymethylsilane = TMOMS, triethylenetetramine = TETA, tetra-n-butyl orthotitanate = TBOT, titanium (IV) isopropoxide = TTIP, tetra-n-butyl titanate = TBT, tetramethyl orthosilicate = TMOS, γ-glycidyloxypropyltrimethoxysilane = γ-GPS, methyltriethoxysilane = MTES, 3-(triethoxysilyl)propyl isocyanate = TEPI, Cerium = Ce benzotriazole = BTA, 8-hydroxyquinoline = 8H, Eriochrom Black T = ECBT, Lanthanum-4-hydroxy cinnamate = La(4-OHCin)₃, graphene oxide = GO.

Alibakhshi E et al. [89] prepared a hybrid silane coating of TEOS and TMOMS on the steel substrate. The prepared hybrid coating was immersed on the steel substrate and studied for corrosive resistance performance in 3.5% NaCl solution during various immersion times through electrochemical impedance spectroscopy (EIS) and salt spray tests. The resultant of TEOS/TMOMS (50/50 wt%) was hydrolyzed for 24 h and exhibits a lower degree of hydrophilicity of the coatings, and the denser Si-O-Si network provides the best corrosion resistance.

Perrin F X et al. [90] reported a hybrid coating of GPTMS and TMOS with TETA, where TETA acts as a cross-linker to interact with the GPTMS epoxy group and TETA amine group to form interconnected epoxyamino silicone networks. The final GPTMS/TEOS/TETA hybrid coating was applied to a mild steel substrate and the effective influence of the TETA on mild steel corrosion protection was studied. It was found that higher amine content and rapid condensation of silanol groups lead to the formation of Si-O-Si bridges. There are a

few silanol groups ready to react with the steel substrate, and a shortage of the binding site may develop, contributing to fast delamination after immersion in a NaCl-neutral solution. The hybrid composite with lower TETA offers balanced properties and the best corrosion resistance performance.

Vivar Laura M et al. [91] made a hybrid composite protective coating on a mild steel substrate by the incorporation of unfunctionalized and functionalized nanoparticles of silica (SiO_2). The result indicates that the addition of silica nanoparticles improves homogeneity and decreases cracking, thus leading to a development in the anti-corrosion coating matrix (Figure 9). However, silica nanoparticles have been functionalized with GPTMS, and the presence of the glycidyl group creates a stronger matrix of interfacial nanoparticles that suppresses agglomeration, reduces conductivity, and increases anti-corrosion, which is associated with an enhancement in the barrier properties of the hybrid composite.

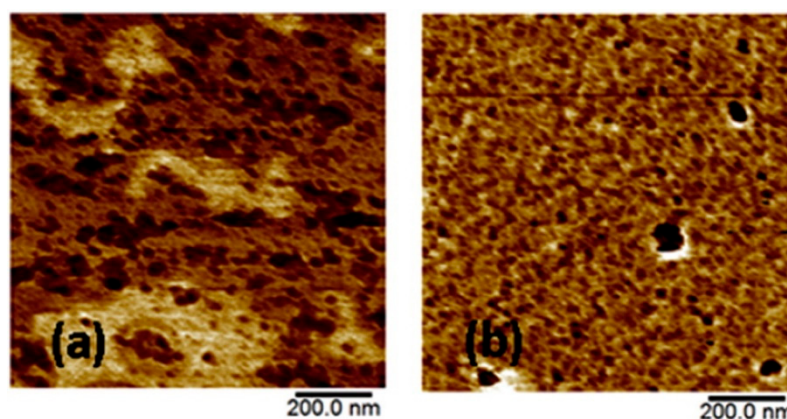


Figure 9. AFM images of hybrid nanocoating composite in 24 h salt spray studies for non-functionalized (a) and functionalized silica coating (b) [91].

Metal oxides and their hybrid composite coatings have been used to improve the mechanical properties, chemical stability, and corrosion resistance of steel. The TiO_2 coating has excellent chemical stability, heat resistance, low electron conductivity, low coefficient of thermal expansion, self-cleaning properties, photocatalyst properties, anti-oxidation protection, and acid-resistant whitening agent, making it an excellent anti-corrosion material. Recently, a combination of multi-component coatings was shown to have high thermal stability, excellent mechanical strength, and higher hardness and improve the corrosion resistance of the metallic substrate. Khosravi H S et al. [92] reported on TiO_2 - SiO_2 protective layer coating on a C45E steel substrate, and the effect of the amount of coating, and annealing temperature of corrosive resistance were investigated. The addition of the TiO_2 - SiO_2 hybrid sol-gel coatings and annealing at different temperatures enhance the corrosive resistance of the protective layer coating. Krishna V et al. [93] also reported that a TiO_2 - SiO_2 hybrid sol-gel coating was placed on the steel substrate and annealed at 410°C for 30 min. The resultant hybrid coating was thick and minimized defects, such as microcrack and delamination, and significantly enhanced oxidation resistance at elevated temperatures. Shanaghi A et al. [94] developed the hybrid organic-inorganic coating on 304 SS substrates by the sol-gel process to progress anti-corrosion. A hybrid sol-gel coating based on TiO_2 is imbued with three different encapsulated self-healing agents ((BTA, 8H, and Ce) and the corrosion resistance is studied. The hybrid BTA-inhibited TiO_2 coating was found to improve the corrosion resistance of the passive film. However, the hybrid coating contains Ce and 8H for 96 h of dipping in the 3.5% NaCl solution and it increases the defect, microcrack, and hole on the substrate.

Olyaa N et al. [95] synthesized molybdate intercalated ZnAl-Mo-LDH , further deposited it onto the SiO_2 sol-gel matrix, and applied it to mild steel to enhance corrosion protection properties. The deposited SiO_2 nanoparticles on the LDH show an essential role in the more controlled release of the intercalated molybdate anion and the formation of

a denser anti-corrosion coating barrier against aggressive species for a longer time. The results showed that the LDH(Mo)SS exhibited better barrier properties and offered an excellent active inhibition performance system with self-healing properties.

Ramezanzadeh B et al. [96] developed the anti-corrosion performance of zinc phosphate conversion coating (ZPCC), and the post-treated coating was established by combining TMOMS and TEOS. The hybrid silane coating resulted in dense, uniform, smooth, and crack-free coating on the ZPCC, reducing porosity and hydrophilicity. The final hybrid silane coating provides high barrier properties for the long immersion time, due to its unique formulation and curing time. Taheri M et al. [97] reported that the incorporation of ZAA as a corrosion inhibitor into the eco-friendly silane coating for enhanced anti-corrosion of 304L mild steel. The sol-gel hybrid protective coating was obtained by hydrolysis and condensation of silane precursors (γ -GPS, TEOS, and MTES) on the mild steel. The corrosion resistance of the hybrid sol-gel coating was functionalized with various concentrations of ZAA inhibitor (0.5, 1.0, and 2.0 mM) and studied for corrosion resistance performance. The results indicated that the presence of ZAA in the silane coating enhances anti-corrosion and causes less inhibition of the barrier protective effect.

Rassouli L et al. [98] prepared organic and inorganic corrosion inhibitors (2-Mercaptobenzimidazole and zinc) individually doped with NaX zeolite particles in the hybrid sol-gel system to increase the anti-corrosion coating performance. The hybrid sol-gel coating was made from MTES, TEOS, and g-GPS, and the evaluation of its corrosion protection on a mild steel substrate. The doped NaX zeolite particles became release inhibitors (2-Mercaptobenzimidazole and zinc cations) at the interface of the formed protective layer with a silane coating on the substrate surface and reduced corrosion when immersed for one day in 3.5% NaCl solutions (Figure 10), probably in the composition of zinc hydroxide, organic inhibitor, and its complex. It has been found that zeolite particles, which prevent electrolyte contact with the interface, boost the barrier properties.

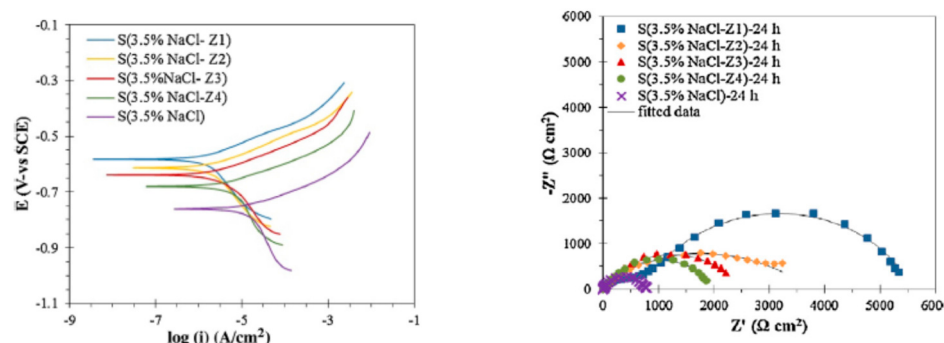


Figure 10. The polarization curves and AC impedance spectra of stainless steel coated with inhibitor doped zeolites after one-day immersion in 3.5% NaCl solutions [98].

Ashrafi-Shahr S M et al. [99] have prepared functionalized mesoporous silica nanoparticles with Eriochrom Black T and their mesoporous silica was dispersed into the sol-gel coating to provide an intelligent corrosion barrier system for the mild steel substrate. Increasing corrosion resistance is associated with the release of ECBT molecules from functionalized nanoparticles on the sol-gel coating. By incorporating ECBT functionalized mesoporous silica into the MS/ECBT sol-gel coating, that composite provides better corrosion protection for long immersion times and adhesive strength.

Suárez Vega A et al. [100] investigated lanthanum 4-hydroxy cinnamate [$La(4-OHCin)_3$] as an inorganic corrosion inhibitor for the carbon steel substrate extensively. Two different silane coatings Si-based and Si-Ti based were prepared by the sol-gel method and anti-corrosion performance was examined by incorporating the corrosion inhibitor $La(4-OHCin)_3$ in different concentrations into the sol-gel coating. Because of the synergistic properties of the La ion and carboxylate ions, $La(4-OHCin)_3$ performed better in lower concentrations. Initially, the carboxylate ion shifted the reaction to the anode site, giving a positive corrosion potential and reducing current density. After prolonged exposure, La

ion reacts to the cathode side, changing corrosion potential less and maintaining a lower current density. The high concentration results in a more porous coating with aggregation causing water uptake. They are less protective and have higher porosity, which directly affects corrosion protection.

Parhizkar N et al. [101] described GO and functionalized GO, developed in the sol-gel anti-corrosion coating on the steel substrate. The GO was synthesized by the modified Hummer's method and the prepared GO was covalently functionalized with TEPI (IGO) and APTES (AGO) silanes, which were used as nanofiller in a sol-gel coating of TEOS and MTES, and their corrosive resistance behavior and adhesion properties were studied. The corrosion studies revealed that AGO and IGO for silane coating notable enhancement in the corrosive resistance due to the epoxy coatings giving better compatibility with the silane matrix and blocking surface porosity through covalently bonded silane and functionalized GO.

4.3. Hybrid Sol-Gel Coating for the Corrosive Resistance of Steel Substrates: Mg Substrates

Magnesium alloys are materials with the most interesting properties: low density, better mechanical stability, high strength-to-weight ratio, excellent thermal conductivity, low specific gravity, and excellent corrosion resistance, which are of recent interest for commercial applications. However, Mg alloys are extremely vulnerable to corrosion environments, which limits their applications. Recent research into the fabrication of the hybrid sol-gel coating on the Mg alloys has been studied (Table 4).

Table 4. Studies on corrosion resistance using hybrid sol-gel coating on magnesium substrates.

Material Composition	Silane and Sol Sources	Substrate	Corrosion Medium	Ref.
-	TEOS, GPTMS	AZ31B	Harrison's solution	[102]
Ce-V	TEOS, GPTMS	AM60B	Harrison's solution	[103]
Ti-Zr-hybrid (TEOS+GPTMS)	TEOS, GPTMS, PTMS	AM60B	0.05 M NaCl solution	[104]
Ti-Zr-PTMS				
Halloysite nanotube	GPTMS	AZ91D	3.5% NaCl solution	[105]
Ce-Zr	TEOS, GPTMS	AM60B	3.5% NaCl solution	[106]
C-60	PTMS	AM60B alloy	3.5% NaCl solution	[107]
OH-MWCNTs				
MMT				
Inhibitors: L-glutamine, L-methionine, L-alanine	TEOS, MTES	AZ91	3.5% NaCl solution	[108]
Inhibitors: QDA, BET, DOP, and DZU	GPTMS, TMSPED	AZ31B	3.5% NaCl solution	[109]

Abbreviations: Tetraethylorthosilicate = TEOS, 3-glycidyloxypropyl-trimethoxysilane = GPTMS, methyltriethoxysilane = MTES, phenyl-trimethoxysilane = PTMS, N-[3-(trimethoxysilyl) propyl] ethylenediamine = TMSPED, fullerene = C-60, multiwalled carbon nanotubes = MWCNTs, hydroxylated multiwalled carbon nanotubes = OH-MWCNTs, montmorillonite = MMT, L-glutamine = L-glu, L-methionine = L-met, L-alanine = L-ala, quinaldic acid = QDA, betaine = BET, dopamine hydrochloride = DOP, diazolidinyl urea = DZU, Harrison's solution = 0.35% (NH₄)₂SO₄ + 0.05% NaCl.

Qian Z Q et al. [102] prepared a silica-based hybrid sol-gel coating to progress the corrosion resistance of Mg AZ31B in Harrison's solution. TEOS and GPTMS were subjected to hydrolyzed acid, and after complete hydrolysis, TETA was added. Then, the final hybrid sol-gel coating was fabricated onto the Mg substrate by a dip coating method. SEM displayed that the surface of the hybrid coating was highly homogenous and crack-free. The compact hybrid silane coating with a smooth thickness was formed on the substrate. This hybrid coating provides better corrosion resistance compared to untreated substrates.

Nezamdoust S et al. [103] investigated the Ce-V conversion coating and the hybrid sol-gel coating on AM60B Mg alloy. The hybrid sol-gel coating was prepared through the hydrolysis of TEOS/GPTMS. The resultant coating was entirely sealed by a thin, compact, and defect-free hybrid sol-gel film and provided the high-level corrosion resistance of an Mg alloy. Additionally, the same group [104] reported that Ti-Zr conversion coating was deposited and followed by two different sol-gel coatings that were applied to increase the

anti-corrosion of AM60B Mg alloy. In this context, two different hybrid sol-gel conversion coatings were prepared using Ti-Zr pre-treated Mg alloy, which is a silane sol-gel conversion coating with the hydrolysis of silane precursors TEOS+GPTMS and PTMS. The corrosion resistance studies revealed that the Ti-Zr/hybrid and Ti-Zr/PTMS sol-gel coatings provided good protection for the Mg substrate compared to another sol-gel coating.

Adsul S H et al. [105] examined the effect of doping inorganic inhibitors ($\text{Ce}^{3+}/\text{Zr}^{4+}$) encapsulated HNT on the corrosion barrier of the hybrid sol-gel coating on the AZ91D. The potentiodynamic polarization studies confirm that the hybrid coating had good corrosion protection properties, and cationic inhibitors can also control release to change pH in the defective area, which provides self-healing properties for localized corrosion attack in an aggressive environment. The nanoclay material has greater potential for replacement than conventional chromate coating.

Samadianfard R et al. [106] oxidized fullerene-TEOS-GPTMS hybrid coating was deposited on the AM60B Mg alloy by a dip coating method. The influence of the incorporation of different concentrations of oxidized fullerene nanoparticles in the sol-gel coating was investigated in corrosion resistance and surface morphology coatings. The EIS results clearly showed that incorporation of the oxidized fullerene nanoparticles into the sol-gel coating significantly enhanced the corrosion resistance in 3.5 wt% NaCl solution and that was attributed to the crack free of chemical interaction. Similarly, Nezamdoust S et al. [107] incorporated different concentrations of OH-MWCNTs into PTMS sol-gel coating on the AM60B and studied corrosion resistance of the OH-MWCNTs incorporated PTMS sol-gel coating in Harrison's corrosive solution at different immersion times along with hydrophobicity properties. The EIS results confirmed that the corrosion resistance of the PTMS sol-gel coating was increased with the concentration of OH-MWCNTs.

Ashassi-Sorkhabi H et al. [108] studied the effect of montmorillonite clays (cloisite Na+, cloisite 20A, and cloisite 30B) and amino acids (L-glutamine, L-methionine, and alanine) on the corrosion resistance of the hybrid TEOS-MTES sol-gel coating on an AZ91 Mg alloy. The results showed that among them, cloisite Na+ ($R_{\text{total}} = 40 \text{ k}\Omega/\text{cm}^2$) MMT nanoparticle and L-methionine ($R_{\text{total}} = 47 \text{ k}\Omega/\text{cm}^2$) amino acid have good barrier properties. In addition, the combination of cloisite Na+ and L-methionine to the hybrid TEOS-MTES sol-gel coating amplified its corrosion resistance intensely ($R_{\text{total}} = 430 \text{ k}\Omega/\text{cm}^2$) due to the synergistic effect.

Upadhyay V et al. [109] evaluated the incorporation of various inhibitors (BET, DOP, DZU, and QDA) on the corrosion resistance of the sol-gel coating of GPTMS and TMSPED on the AZ31B. The resultant of sol-gel coatings have been found to provide a good barrier to the substrate and afford some defense even without the presence of inhibitors. Finally, when the properties of the inhibitors were compared, the QDA-doped sol-gel was able to contain the corrosion in the defect.

5. Sol-Gel Technologies in Electrochemical Sensors

Electrochemical sensors are a class of chemical sensors in which an electrode is used as a transducer element in the presence of the analyte. Modern electrochemical sensors use several properties to determine various parameters in our daily life, whether physical, chemical, or biological parameters. In this regard, they are very widely applicable. Some examples are sensors for monitoring the environment, health, and appliances, as well as sensors related to machines such as cars, airplanes, mobile phones, and technological media. Currently, new materials, production methods, and strategies are actively used in the development of electrochemical sensors to increase selectivity and detection limits. Sol-gel matrices are useful in the production of electrochemical sensors due to their chemical inertia, mechanical stability, biocompatibility, and high specific surface area provided by porous grids with an open frame. All these features allow sol-gel nanocomposite sensors to demonstrate increased sensitivity and low detection limits about a wide range of target analytes [110]. The sol-gel method is most applicable in the formation of sensitive materials based on oxides, complex oxides, and their composites.

5.1. Oxide Materials and Materials Based on Them

Materials based on oxides of various metals obtained by the sol-gel method are most actively used in electrochemical sensors.

Zinc oxide-based materials are very popular. Golli, A.E et al. [111] reported the preparation of ZnO nanoparticles by the sol-gel method. Zinc acetate was dissolved in methanol at room temperature with constant stirring for 2 h, then copper chloride was added into the mixture, and the resultant product dried to get aerogel nanomaterial and the final product was annealed. The SEM image of fabricated Cu/ZnO showed spheroid-like spherical nanoparticles (Figure 11).

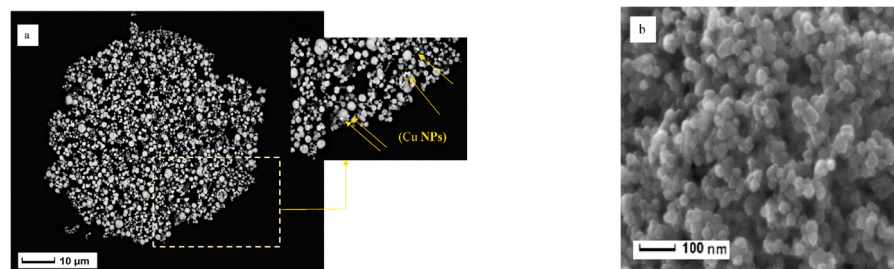


Figure 11. (a) FE-SEM image of a ZnO on Cu NPs. (b) High-resolution image of aggregated ZnO [111].

The resulting material was used in an amperometric glucose sensor and showed a high reaction and selectivity.

Haque, M et al. [112] reported that copper-doped zinc oxide was prepared via the implementation method of the sol-gel process. At first, zinc acetate was dissolved in 0.1 M sodium hydroxide and stirred at 60 °C for 30 min; then, copper acetate was added dropwise into the solution, and the resultant mixture was stirred at 80 °C. SEM images of the ZnO and Cu-doped ZnO nanoparticles showed ~20 nm spherical nanoparticles. Electrochemical sensing of myoglobin was studied in blood using Cu-ZnO nanoparticles, myoglobin was detected in the range of 3–15 mM with 0.46 nM myoglobin detection limit at high sensitive $10.14 \mu\text{A nM}^{-1}\text{cm}^{-2}$.

Zhan, B et al. [113] prepared ZnO with the sol-gel method, $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ was dissolved in ethanol, then a stabilizer of ethanolamine was added in the above solution, and finally, the mixture was stirred to form transparent homogenous at 70 °C for one hour, after which it was left undisturbed for 48 h. Similarly, ZnO was prepared with different solvents, i.e., isopropyl alcohol, ethylene glycol, and methyl ether, respectively. SEM images of the ZnO (ZnOeth, ZnOme, and ZnOgme) showed that the crystal growth depends on solvents, which controlled the shape and size of ZnO particles. Electrochemical sensing of clenbuterol was studied using ZnO nanoparticles; clenbuterol was detected in the range 0.3–1000 ng/mL, with a low detection limit of 0.12 ng.

There is research on the production of electrochemical sensors based on tin oxide [114–119]. In these works, electrochemical sensors are used to detect various harmful substances. They have different principles of operation. These works are united by the fact that the sensitive material is obtained by various variations of the sol-gel method. Lete, C et al. [115] prepared tin oxide in the sol-gel method by dissolving Sn(II) 2-ethyl hexanoate in absolute alcohol and triethanolamine. The resulting mixture solution was deposited a multilayer film at 450 °C and thermally treated at 600 °C for 1 h. AFM topographical images of SnO_2 film display a very smooth surface with $\text{RMS} > 3 \text{ nm}$, with 30 nm deep, and a diameter of 100 nm (see Figure 12).

Tin oxide films were used in the sensor platform to detect nitrites in milk, mineral water, and beer by impedance and conductometric methods. There is also research on the production of electrochemical sensors based on oxides and titanium and tungsten [120–123]. The preparation of tungsten trioxide [121] and its morphology is shown in Figure 13. Using fabricated WO_3 were studied for dopamine sensing vby cyclic voltammetry analysis, and the material showed better sensing of dopamine with excellent stability.

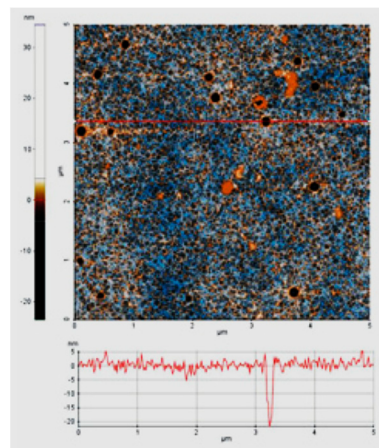


Figure 12. AFM image of SnO_2 films [115].

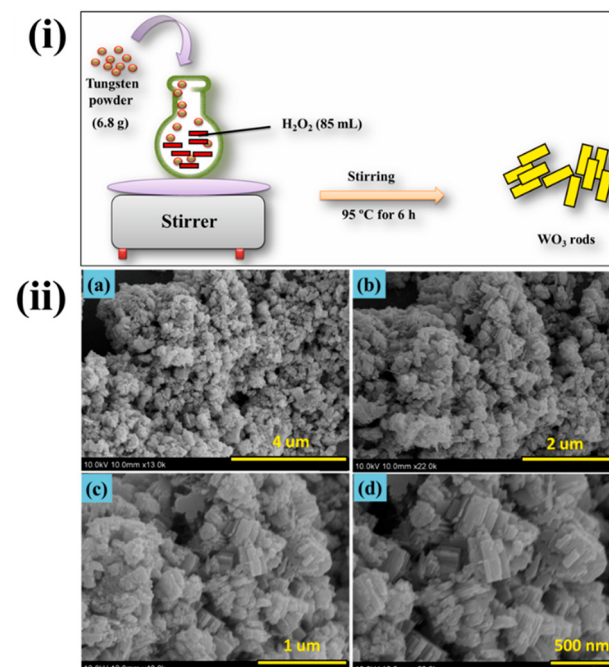


Figure 13. Schematic representation of the synthesis of WO_3 rods. (i) SEM image of WO_3 rods at different magnifications (a–d) (ii) [121].

Composite materials based on oxides are also obtained by the sol-gel method for subsequent use in electrochemical sensors. Abdullah M. M et al. [124] have prepared $\alpha\text{-Fe}_2\text{O}_3$ doped CdSe in ultra-sonication method and examined the material for methanol detection. The SEM image of the $\alpha\text{-Fe}_2\text{O}_3$ -doped CdSe nanoparticles showed ~ 15 nm rod-like morphology. As prepared $\alpha\text{-Fe}_2\text{O}_3$ -doped CdSe nanoparticles were studied for methanol sensing, showing good methanol sensing performance with greater sensitivity.

Tareen, A.K et al. prepared [125] MnO-CrN composite via the ammonolysis process, and performed chromium and manganese nitrate ammonolysis at 800°C for 8 h. SEM and TEM images of MnO-CrN show nanoparticles with aggregation with an average particle size of about ~ 10 nm.

Naikoo, G.A et al. [126] prepared monoliths based on NiO using the sol-gel method, and fabricated $\text{NiO}@\text{Si-NPs}$ monolith on silica nanoparticles calcinated at 650°C . The SEM image of the $\text{NiO}@\text{Si-NPs}$ showed nanocube-like morphology and the resulting material was studied with glucose sensing in the range of $10\text{--}100$ mV/s. Paramparambath, S et al. [127] have prepared CuO-MgO composition by the sol-gel method in the aqueous

medium, which was then calcined at 500 °C for 4 h. SEM images of CuO-MgO NC showed highly aggregated morphology of nanoparticles in the range of 200–500 nm. As-prepared CuO-MgO NC was studied dopamine sensing, and the material shows good sensitivity to dopamine with a sensitivity of $69 \mu\text{Acm}^{-2}\text{mM}^{-1}$.

Lu, Q et al. [128] have prepared FeVO_4 and modified FeVO_4 with a different mole ratio of metal oxides (NiO , SnO_2 , WO_3) by the sol-gel method in the aqueous medium and obtained the material calcined at 800 °C for 2 h. Finally, FeVO_4 and modified FeVO_4 materials were studied using ammonia sensors in the YSZ electrolyte. SEM images of FeVO_4 nanoparticles showed rod-like morphology with an irregular structural arrangement. FeVO_4 modified with NiO nanoparticles detected ammonia in the range of 53–83 mV.

5.2. Materials Based on Complex Oxides

Double and triple oxides of semiconductor metals are a popular object of research in electrochemical sensors. This is due to their high conductivity and stability of chemical properties. Oftentimes, such materials are obtained using the sol-gel method.

Peng S et al. [129] prepared cadmium indium oxides using the sol-gel method in the aqueous medium and studied glucose biosensors. SEM images of nickel-coated CdIn_2O_4 showed multilayer stacked nanoplates, and it shows good selectivity of glucose.

Similarly, Shu, H et al. [130] prepared CdIn_2O_4 with iron modification by sol-gel method in the aqueous medium and examined glucose biosensors. SEM images of iron-modified CdIn_2O_4 showed aggregated nanoparticles (Figure 14) and it provides good electrochemical conductivity to the detection of glucose.

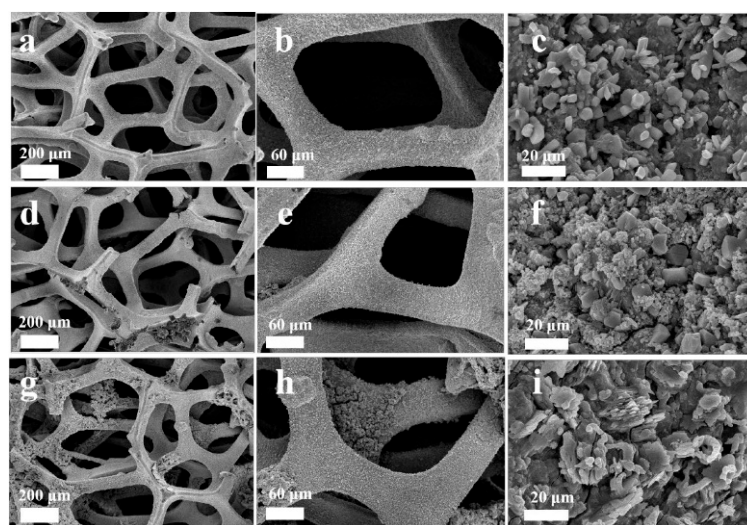


Figure 14. SEM images of $\text{Fe-CdIn}_2\text{O}_4$ on nickel foam. (a–c) 25%; (d–f) 30%; and (g–i) 35% [130].

Petruleviciene, M et al. [131] prepared BiVO_4 thin films on fluoride-doped tin oxide substrates by the sol-gel method in the aqueous medium. Fabrication of BiVO_4 thin film, urea, and polyvinyl alcohol was used as a stabilizer and the layer deposition was annealed at 450 °C for 2 h. SEM images of BiVO_4 thin films revealed that morphology, the influence of PVA additive on the urea-PVA treated coating, and nanoparticles are interconnected to BiVO_4 thin films (Figure 15). PVA-modified coating BiVO_4 thin films have a greater affinity to glucose adsorption.

The MnFe_2O_4 nanoparticles and the MnFe_2O_4 nanoparticles modified carbon electrode paste (CPE) were prepared via the sol-gel process [132]. The AuNPs were formed onto the MnFe_2O_4 /CPE surface by electrodeposition of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$. The SEM image indicates a nanostructure layer of the AuNPs onto the modified CPE/ MnFe_2O_4 NPs surface. This sensor showed good sensitivity to flunitrazepam.

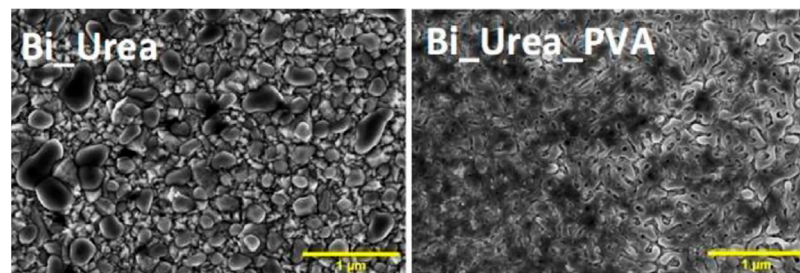


Figure 15. SEM images of Bi_Urea and Bi_Urea_PVA coatings [131].

MWCNTs/CuFe₂O₄ (carbon nanotubes in combination with copper ferrite) nanocomposite was successfully fabricated by the sol-gel method [133]. After the preparation of CuFe₂O₄, citric acid was added to the mixture and stirred at 80 °C for 3 h. Then, MWCNTs were added and ultra-sonicated at 80 °C for 1 h. The resultant material was calcined at 400 °C for 4 h. The SEM images of MWCNTs/CuFe₂O₄ nanoparticles showed tubular-like spherical morphology with a diameter of 32 nm (Figure 16). As a result, CuFe₂O₄ loading on MWCNTs reduces the particle size, which exposes more active centers in the nanocomposite. This feature of the morphology of the material, according to the authors of the work, contributes to a better sensitivity to bisphenol A.

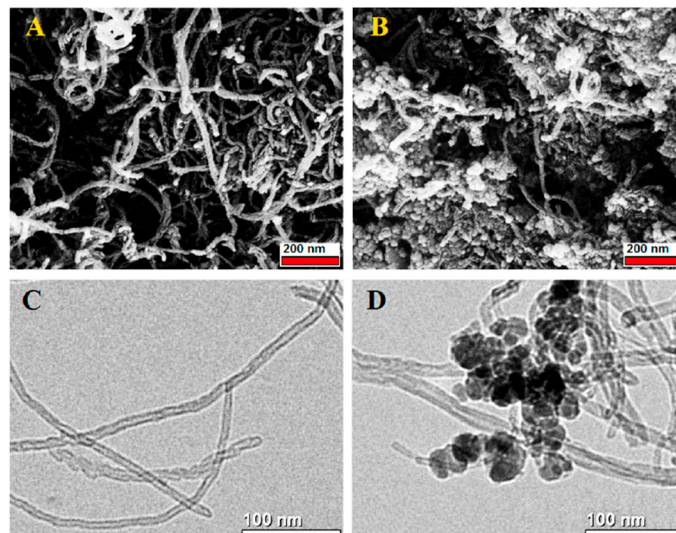


Figure 16. SEM (A,B) and TEM (C,D) images of MWCNTs and MWCNTs/CuFe₂O₄ nanocomposite [133].

Zhang, Y et al. [134] prepared La₂NiFeO₆ by the sol-gel method, and citric acid was used as a complexing agent. The resulting material was annealed at 400 °C for 4 h and the final materials were sintered at 1000 °C, 1100 °C, and 1200 °C respectively. The SEM images of La₂NiFeO₆ materials exhibit particle average size of 300 nm (sintered at 1000 °C) and 500 nm (sintered at 1100 °C), whereas materials sintered at 1200 °C show a slightly agglomerated average size of 1 micron (Figure 17).

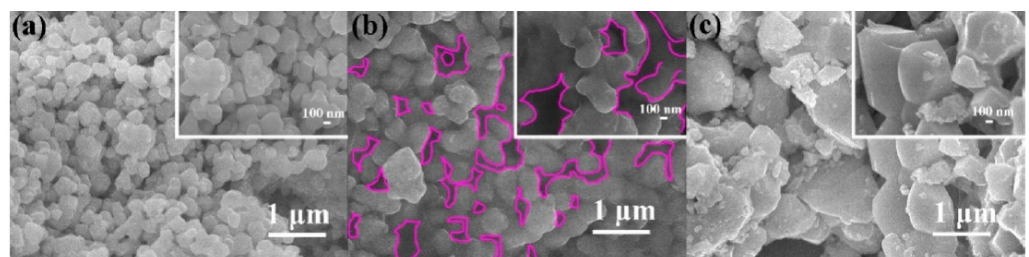


Figure 17. SEM image of La₂NiFeO₆ (sintered at three different temperatures; (a) 1000, (b) 1100, and (c) 1200 °C) [134].

Usually, the structures of complex oxides are used in the creation of electrochemical biosensors. In most of the works presented, they are detectors of complex organic substances in standard solutions of electrolytes: red blood salt and potassium chloride. However, there are also works in which the obtained materials are used to detect inorganic substances and organic gases.

Similarly, Hao X et al. [135] have prepared La_2NiO_4 by sol-gel method, and citric acid is used as a complexing agent. The resulting material was thermally treated at 80°C for 2 h and followed by sintering at 1000°C for 2 h. The fabricating La_2NiO_4 material has potential electrochemical sensors for sub-ppm H_2S detection.

Wang, J et al. [136] prepared CdTiO_3 by sol-gel method. Subsequently citric acid was injected and stirred at room temperature for 3 h. The resulting final material was calcined at 1000°C for 3 h. The SEM images of CdTiO_3 nanoparticles showed irregularly arranged multilayered structures with a porous inner channel (Figure 18). The resultant CdTiO_3 nanoparticles quickly detect the acetylene gas.

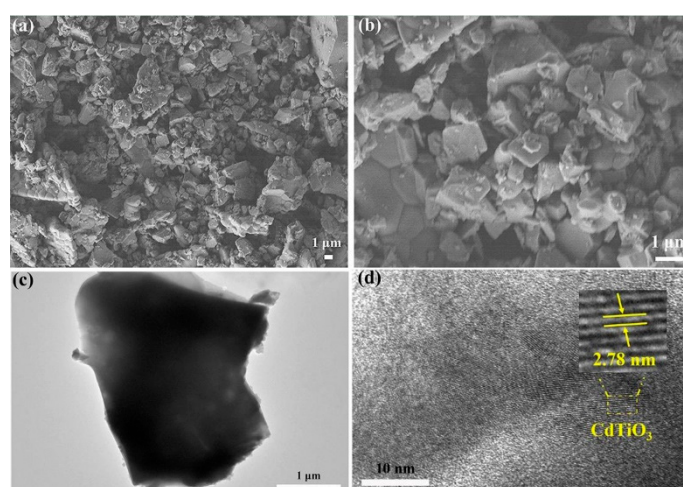


Figure 18. (a,b) SEM and (c,d) TEM images of CdTiO_3 [136].

La_2CuO_4 nanocrystals were synthesized by the sol-gel process and utilized for hydrogen peroxide detection [137]. The components of the gel-forming solution were mixed in deionized water. Then, the temperature treatment of the resulting gel took place. The sensitivity of the resulting gel for hydrogen peroxide reached 100%.

The functional features of the materials considered are presented in Table 5.

Table 5. Characteristics of some electrochemical sensors based on sol-gel materials.

Sol-Gel Material	Detectable Substance	Maximum Gas Sensitivity	Linear Range	Ref.
Cu/ZnO nanocomposite	glucose	$36.641 \mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$	0.01–1, 1–7 mM	[111]
Cu-doped ZnO nanoparticles	myoglobin	$2.13\text{--}10.14 \mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$	3–15 nM	[112]
ZnO nanoparticles	clenbuterol	-	0.3–1000 ng/mL	[113]
$\text{SiO}_2/\text{Al}_2\text{O}_3/\text{C}$	nitrite	$410 \mu\text{A}\mu\text{M}^{-1}$	0.2–280 μM	[114]
SnO_2 coatings	nitrite	$22.56 \mu\text{A}\mu\text{M}^{-1}$	10–400 μM	[115]
Pt- SnO_2 nanoparticles	hydrogen	-	0.08–500 ppm	[116]
Au- SnO_2 nanoparticles	vitamin B ₁₂	$110.843 \mu\text{A}\mu\text{M}^{-1}$	0–1500 pM	[117]
Cu-doped SnO_2 nanoparticles	ethyl acetate	$4.8 \mu\text{A/ppb}$	1–20 ppb	[118]
CuNPs on the C/ SiO_2 working electrode	glucose	-	53–670 mg/L O_2	[119]
p- TiO_2 nanoparticles	ethanol	~50%	1–100 ppm	[120]
WO_3 rods	dopamin	$3.66 \mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$	1–250 μM	[121]

Table 5. Cont.

Sol-Gel Material	Detectable Substance	Maximum Gas Sensitivity	Linear Range	Ref.
Nitrogen-doped carbon sheets wrapped in SnO ₂ nanoparticles	glucose	215 nAμM ⁻¹ cm ⁻²	0.05–10 μM	[122]
α-Fe ₂ O ₃ doped CdSe	aqueous methanol	0.2744 μAmM ⁻¹ cm ⁻²	0.2–48 mM	[123]
MnO–CrN nanocomposite	hydrogen peroxide	2156.25 μAmM ⁻¹ cm ⁻²	0.33–15 000 μM	[125]
NiO nanoporous materials	glucose	445 μAm ⁻¹ cm ⁻²	-	[126]
CuO–MgO composite	dopamine	69 μAmM ⁻¹ cm ⁻²	10–100 μM	[127]
WO ₃ @SnO ₂ -20	ammonia	-	5–50 ppm	[128]
CdIn ₂ O ₄ nanoparticles	glucose	3292.5 μAmM ⁻¹ cm ⁻²	1.0 μM–1.0 mM	[129]
Fe–CdIn ₂ O ₄ nanoparticles	glucose	8992 μAmM ⁻¹ cm ⁻²	0.01–1 mM	[130]
BiVO ₄	glucose	-	1–35 mM	[131]
MnFe ₂ O ₄	flunitrazepam	-	0.1–100 μM	[132]
Multiwalled carbon nanotubes	bisphenol	0.355 μAμM ⁻¹	0.01–120 μM	[133]
CuFe ₂ O ₄	triethylamine	-	0.5–200 ppm	[134]
La ₂ NiFeO ₆	hydrogen sulfide	–70 mV	0.05–2 ppm	[135]
K ₂ NiF ₄ -type oxides La ₂ NiO ₄	acetylene	–91 mV	5–100 ppm	[136]
CdTiO ₃	hydrogen peroxide	-	0.50–15.87 μM	[137]
Ln ₂ CuO ₄ nanocrystals				

As can be seen from the table, the materials considered are used to detect a wide range of substances. However, they are most applicable as biomarkers. When they are used in this capacity, the boundaries of the definition of the detected substance are at the level of mM or μM. When detecting gases, the lower detection limit is below 1 ppm. All the materials considered are characterized by a relatively high sensitivity to the substance being determined. Glucose sensors are characterized by the highest sensitivity. Thus, when obtaining materials for electrochemical sensors, three varieties of sol-gel methods are mainly used: anhydrous, aqueous, and citrate. As a result of using these methods, it is possible to obtain sensors that are more highly sensitive than their analogs. These electrochemical sensors are most often used to detect complex organic substances in liquid media. The most popular detectable substance is glucose.

6. Conclusions

The hybrid sol-gel coating on various metallic substrates enhances their long-term corrosion resistance in high-corrosion environments and commercial industrial applications. Future research and development will mainly focus on investigating smarter and more functionally advanced materials to replace the traditional chromate or phosphating coating. To achieve the best possible protection against corrosion, smart materials have been developed that respond to react with pH, temperature, and humidity conditions. In general, hybrid organic-inorganic coating with nanodimensional materials provides better corrosion resistance and has high resistance to oxidation, abrasion resistance, water resistance, and many other properties. The above functional properties combined with smart materials are a very promising area to explore. All advanced functional and smart materials face many more challenges in their business operations. From this perspective, when developing an intelligent coating material for the industrial process, many factors need to be considered, such as ease of manufacturing, coating efficiency, and environmental aspects. Therefore, the development of smart materials for corrosion resistance will certainly achieve a breakthrough soon.

In the fabrication of supercapacitors, the sol-gel process propositions control the particle size and morphology at adequate temperatures. During the preparation, metal precursors are added in the gel form, and the final materials were prepared without long-range diffusion. Recent reports show how the composition of supercapacitor materials can be varied by altering the proportion of the metal precursors. The choice of complexing and dispersing agents affects influence the particle size, shape, and porosity. In addition, the

final porous aerogels materials enhance conductivity, and retains amorphous morphology. Among sol-gel materials for supercapacitor application, metal-oxides and their composites are still of great interest. The new trend of recent years is the perovskite materials due to the sol-gel method allowing the production of materials with comparatively high surface area and great uniformity. Since the last century, carbon aerogels are promising materials for supercapacitor electrode applications.

Metal oxides and composites based on them are most actively used to create electrochemical sensors. They will be obtained, including the anhydrous and citrate sol-gel method. Such materials are widely used as glucose biosensors. They can also be used as sensors for harmful gases. The choice of a particular method largely determines the morphological features of the materials obtained. The materials obtained by the sol-gel method are widely used as glucose biosensors and other biomarkers. They can detect substances in the smallest concentrations while achieving relatively high sensitivity. Sol-gel materials can also be used as sensors for harmful gases and vapors of organic substances. The lower limit of detection of electrochemical sensors based on them in most cases does not exceed 1 ppm. Thus, the sol-gel method plays an important role in obtaining new highly sensitive electrochemical sensors.

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