Glasses and Glass-Ceramics Prepared by Sol-Gel

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Introduction

For thousands of years, glass and ceramic materials have been produced using conventional melting and sintering processes that involve high temperature. Diverse alternative routes have been proposed, most of them focused on the reduction of the melting and sintering temperature ([Dimitriev *et al.*, 2008](#)). Between them, the “Sol-gel chemistry” constitutes a new and flexible non-traditional method for processing ceramic and glass materials at low temperatures since it is a wet-chemical technique. The possibility offered by Sol-gel technology to produce an extensive range of nano-/micro-structures combined with the good control of the properties makes it one powerful technique to fabricate materials ([Owens *et al.*, 2016](#)).

The first approach related to Sol-gel method appeared in the mid-nineteenth century (1846), when Ebelmen, a French chemist, observed how silicic esters hydrolyze slowly in the presence of humidity giving hydrated silica ([Ebelmen, 1846](#); [Schneller *et al.*, 2013](#)). However, the term “sol-gel” was first proposed by Graham in 1864 and almost 100 years later appeared in the first patent for Sol-gel dealing with the synthesis of SiO₂ and TiO₂ materials for optical applications ([Bahuguna *et al.*, 2016](#)). These compositions were re-formulated by [Schroeder \(1969\)](#) and further used in the fabrication of thin films on glass substrates by Sol-gel at industrial scale. In the same year, [Mazdiyasní *et al.* \(1969\)](#) prepared high-purity barium titanate powders.

In addition to the benefit of the low processing temperatures, Sol-gel process shows advantages as high homogeneity, molecular control of the composition and a wide variety of compositions with many different properties.

The importance of “*Sol-gel process*” became apparent in 1981, in the first “International Workshop on Glasses and Glass Ceramics from Gels” organized by Prof. Vittorio Gottardi and held in Padova, Italy. In this conference, the Sol-gel community, around 30 attendants mainly from glass research centers from Europe, opened the field to the industrial and academic world.

The first stage of the Sol-gel process is the preparation of a stable solution (sol), followed by a gelation and solvent evaporation resulting in the formation of a “gel”, densification and crystallization being the final stages. Even though there are several processing routes, two are the better established in the literature: the colloidal route and the polymeric route, represented in [Fig. 1](#). These routes have a common point the “gelification stage”, although the beginning is essentially different. In the colloidal route, the method starts from a colloidal suspension of small particles in a continuous liquid medium, where the gravitational forces are negligible. In the case of the polymeric route, the “sol” is obtained by controlled hydrolysis and condensation of metal-organic precursors (e.g., metal alkoxides or alkylalkoxides). In both cases, to incorporate a destabilizer or a catalyst increases the viscosity and transforms sol into gel, obtaining a continuous network that encloses the liquid phase. At this point, the gel maintains its shape. Drying and aging steps follow for removing the liquid phase (solvent).

Fig. 1 Colloidal and polymeric sol-gel routes.

alt-text: Fig. 1

The first materials prepared by Sol-gel were pure inorganic materials. However, in the eighties, [Schmidt \(1984\)](#) at the Fraunhofer Institute began to introduce organic groups in the inorganic networks, which had a big impact in the Sol-gel synthesis. The possibility to create novel materials allowed the expansion of the Sol-gel method to other areas. [Livage \(1997\)](#) explained the impact of synthesizing inorganic-organic hybrid materials that provide unique properties by combining the stability of the inorganic part with the flexibility and functionality of the organic part. This idea was linked to the concept of "chemie douce" referring to the processes of soft inorganic chemistry for creating tailored hybrid organic-inorganic materials. The versatility of blending inorganic with organic phases, gave rise to outlining different structures from ordered dispersions of inorganic bricks in hybrid matrix to highly controlled nano segregation of organic polymers within inorganic matrix ([Sanchez et al., 2001](#)). The structure and the properties depend on the nature of the inorganic and organic molecules as well as the synergy between them. [Sanchez et al. \(2003\)](#) classified these Sol-gel materials in four types depending on the degree of organization including from ordinary hybrid networks from organically modified metal alkoxides to the synthesis or mesostructured hybrid networks that combine nano-building blocks and self-assembly approaches ([Sanchez et al., 2010](#)).

[Yanagisawa et al. \(1990\)](#) and [Kresge et al. \(1992\)](#), Mobil and Japanese scientists turned the screw in this field thanks to the creation of the first mesoporous hybrid silicate, bringing the opportunity to create novel systems combining the pore size, shape and symmetry control with a tailored surface with amazing properties, in most cases, referred to optics.

The physical-chemical variables involved in the process are crucial to determine the final structure, morphology, and chemical composition of the products. The ability to design and control the different stages of the Sol-gel process allows new materials with enhanced and tailored properties to be prepared. The technique is compatible with many conventional material processing methods (e.g., casting, dip coating, spin coating, doctor blading, and spray coating), allowing the processing of sol-gel-derived materials in a variety of structural shapes, such as nanoparticles, supported thin films and coatings with controlled thicknesses, patterned surfaces, membranes, and monoliths. The potentiality and possibilities of designing original structures and compositions is reflected in the high impact in high-tech industries and optical fields of applications ([Green et al., 2003](#); [Soler-Illia and Innocenzi, 2006](#); [Fan et al., 2008](#); [Soller-Illia et al., 2011](#)) (Fig. 2).

Fig. 2 Critical aspects of sol-gel chemistry mesostructure assembly.

Reproduced from Boettcher, S.W., Fan, J., Tsung, C.-K., et al., 2007. *Harnessing the sol-gel process for the assembly of non-silicate mesostructured oxide materials*. *Accounts of Chemical Research* 40 (9), 784–792.

alt-text: Fig. 2

In this review, we present an insight on the advances in Sol-gel route, considering the physical and chemical aspects implicated in the process as well as an overview of the most important developments and applications. The better developed and used polymeric route is described in deeper detail.

Physical-Chemical Basis of the Process

Several papers appeared between 1846 and 1927 explaining the formation of hydrolyzed derivatives of silica. [King and Threlfall \(1928\)](#) deposited the first patent for partial hydrolyzed alkoxysilanes, describing the preparation of a solution of silica using a reaction between an ester of silicic acid and water. It was mentioned that the proportion of water must not exceed that required to convert the ester into an alcohol.

Although the discovery and the first developments on the formation of gel focused on silica as main element, a huge variety of metals can be used instead or mixed with silica. [Ray \(1934\)](#) from Carbon Chemical Corporation patented the hydrolysis and condensation processes for a generic metal that can be other than silicon. After specific studies and observations of [Roy and Osborn \(1954\)](#) the use of metal-organic precursors expanded a lot including a long list of metallic elements that can be prepared by Sol-gel.

Nowadays, many papers describe in detail the hydrolysis of alkoxides, especially metal alkoxides, using [Eq. \(1\)](#), in which M is a metal (Si, Al, In, Ti, Zr, Sn, Pb, Cr, Ta, etc.) and R an alkyl group. This reaction is followed and combined with the condensation ([Eqs. \(2\) and \(3\)](#)).

Hydrolysis:

Condensation can follow two routes, and usually both occur:

Metal-organic compounds are typically the most used precursors, especially tetra alkoxysilanes and tetra-methoxy-silanes. If the reactivity of the precursor is high, the reactions will occur so quickly to become difficult to control. The reactivity relates to the number of sites able to form Si-O-Si bonds. In case of alkoxides, this can be controlled by the modification of the group R: If the non-hydrolysable radicals increase, then the functionality decreases. Following this, alkoxides have a hydrolysis slower than alkyl-alkoxides.

[Villegas Broncano and Fernandez Navarro \(1987\)](#) reviewed the polycondensation reactions from monomeric units of the same specie as well as copolymerization of a mixture of different monomers. In this last case, it is important to control carefully the kinetics as they have different behavior.

With hydrolysis and condensation reactions, it is possible to create highly branched structures; when complete condensation takes place, compact oxides are produced. The structural differences depend on the basic equations (Eqs. (1) and (2)). Conditions such as the pH, catalyst and H₂O/alkoxide ratio affect the final structure. Chang and Ring (1992) explained the control of the reactions of hydrolysis and condensation deeply studying the aggregation of the species throughout the transition from the sol to the gel state.

Sakka and Kamiya (1982) described the relation between the hydrolysis of TEOS and the amount of HCl incorporated in the reaction. In the same decade, different publications confirmed that hydrolysis becomes more rapid by employing either basic or acid catalysts. The most used catalysts are mineral acids or ammonia but others, such as KOH, KF, HF are also known. Pope and Mackenzie (1986) studied the effect of a variety of catalysts on the hydrolysis and condensation of TEOS (Tetraethyl orthosilicate) and their relationship with the time needed for gelation, as shown in Fig. 3.

Fig. 3 Effects of catalyst on pH and gel times for TEOS hydrolyzed with 4 equivalents of water. The catalyst concentration is 0.05 mol: TEOS.

Modified from Pope, E., Mackenzie, J., 1986. Sol-gel processing of silica. II. The role of the catalyst. Journal of Non-Crystalline Solids (87), 185-198.

alt-text: Fig. 3

Chang and Ring (1992) exposed the relationship of reactions shown in Eqs. (1) and (2) with pH. In acid conditions, the hydrolysis is slower, the condensation rate increasing the aggregation of high-branched clusters forming a network. Under basic conditions a much-accelerated nucleophilic attack is involved. Larger structures have tendency to interact with smaller ones, exchanging OH⁻ and releasing OR groups. The size of the polymer formed is higher than those formed in acidic conditions and they show higher density.

The gel point is defined as the moment at which the variation of the viscoelastic function with the vibration is at a minimum. The characteristics of the bonds define the final structure of the gels. Flory (1974) described the gel behavior where modulus of elasticity depends on the interlinking density of the network. Flory indicates that gelification is strongly dependent on the bonds, a main issue to control the network evolution through scale time. Once the polymeric network grows, the amount of clusters decreases and, so, the sol is not able to flow, becoming a viscous gel supporting a static load without floating. Rabinovich (1985) described the factors provoking the acceleration of the gelation point, in particular, the temperature, the increasing of the water ratio, a higher concentration of alkoxides and the increment of pH.

The obtained gel contains a high free energy because of its large surface area, high amount of chemically bound water and the final high volume. Orgaz-Orgaz (1988) studied the densification steps of the gel, which is an irreversible process in which the decrease in free energy proceeds along with a decrease in surface area, a reduction in pore size and volume.

Once the gel point is reached, the structures corresponding to fast gelation times are opened and porous, due to the lack of possibility to link further rearrangement. Vega and Scherer (1989) demonstrated by NMR that mobile and immobile polymers exist in the sol at the gelation point. At this moment, chemical reactions are still occurring and are crucial to define the properties as they affect the drying and sintering.

The following step to gelation point is aging. Polymerization is a main reaction involved in this step, increasing the connectivity by condensation reactions caused by the availability of hydrolyzed remaining groups. pH and temperature at which the gel is achieved govern the time necessary to complete the aging that goes from a few days to several months. Drying occurs after the aging with the transition from wet gel to a dry one by physical water and solvents desorption.

Scherer (1992) described the drying of gels in two consequent steps. The first one, called “Constant Rate Period” (CRP), is characterized by a constant evaporation rate, where part of the liquid evaporates by

capillary force. The wet gel shrinks continuously under compression, and the remaining liquid fills the pores. This initial period is critical for the control of the gel cracking because of the capillary tensions generated in the remaining liquid. It is possible to control cracking by adjusting the evaporation rate, the results being inversely proportional to the pore size: the higher the pore size the more reduced is the cracking. In the second step a small evaporation of the liquid still in the gel occurs, being the crucial phase in which cracking could appear. Preventive measures must be taken to avoid it, like lowering drying velocities from the beginning or by using hypercritical-drying condition (Bisson *et al.*, 2003).

A final homogeneous and dense glass or glass-ceramic results after a consolidation period that includes the thermal treatment of the gel. Numerous researchers explained that the gel densification and its properties depend on the sequential gelation, aging and drying parameters under which it was prepared.

Although Sol-gel steps are apparently sequential, in the case of coatings formation a competition is present between evaporation and condensation reactions. Brinker *et al.* (1992) explained how capillary forces influence the system promoting compaction during the evaporation and generating a resistance to it during condensation. They also described the effect of different balances between evaporation and condensation rates on the structure of the formed coating. In addition to the reaction rates and duration of each stage, other parameters need to be controlled to achieve a desired coating, and the method of deposition used strongly determines the final structure and is closely related to the specific applications.

Another important Sol-gel process relates to the preparation of monodispersed silica nanoparticles of controllable and uniform size, reported by Stöber and Fink (1968). It remains as the most used wet synthetic route to obtain silica nanoparticles. The synthesis takes place when a molecular precursor (typically tetraethylorthosilicate) reacts with water in an alcoholic medium in presence of ammonia as catalyst. Esquena *et al.* (1997) prepared silica particles with sizes above 1 μm by Sol-gel process. In this case, the reaction takes place in the aqueous medium in an acidic emulsion media using HCl. During the first minutes of reaction, the solution turns to a turbid suspension as evidence of the particle formation.

Li and Zhao (2013) proposed that during the Stöber process, a rapid burst of nuclei occurs, and the uniform particles grow without additional nucleation because of the attachment of constituent solutes in a kinetically controlled ambient. Following this idea, the Stöber process extended to obtain titanium nanoparticles, was more difficult to control due to its high reactivity. The preparation of core-shell nanoparticles combining SiO_2 or TiO_2 as shell and different compounds as core have gained interest in recent years (Kobayashi *et al.*, 2005; Yang *et al.*, 2013; Bai *et al.*, 2016).

Applications

The extensive possibilities of compositions able to be prepared by sol-gel, the inorganic, hybrid or organic precursors used in the different synthesis routes, and the multiples shapes of final products, from thick coatings to thin films, powders, monoliths or aerogels with amazing properties, allows this synthesis method to be applied in a variety of fields. The often-used materials, as metals, glasses, ceramics, or plastics, cover a traditional application, but these pure materials do not fulfill the requirements of many new innovative requirements or the design of multifunctional materials. The outbreak of hybrid synthesis by Sol-gel in the past decades made an enormous progress and lead to new materials with enhanced properties and cost-effective prices in many cases.

The objective of this section is to give a look and summarize the most important applications in the field of glasses and glass-ceramics, from biomaterials to optics, photo-catalysis or protective coatings. The goal is to describe the huge possibilities of this synthesis route and their applications and possibilities in the field of material science and technology.

The preparation of coatings is the most developed field of application of Sol-gel process. Large substrates with different shapes can be coated by cost-effective processes. Coatings are prepared from a single inorganic precursor, as well as by the combination of organic and inorganic materials. Single and multi-component oxide coatings are produced as monolayers or structures of films to provide different functionalization to glass and other substrates.

Deposition Methods for Sol-Gel Coating

Brinker and Scherer (1990) described the parameters implicated in the deposition process and highlighted that the rate of evaporation and condensation process determines the pore volume, pore size and surface area of the final films. A brief description of the most important methods used to prepare coatings is presented considering the factors involved in each method and the variety of applications.

Dip Coating Deposition

The dip-coating process involves the controlled vertical withdrawal of the substrate from the liquid at a specific velocity U_0 as shown in Fig. 4(a) (Brinker *et al.*, 1991). Scriven (1988) described the five stages of this coating process: immersion, followed by the start-up, deposition and drainage as simultaneous stages; evaporation as a final step occurs throughout the whole process.

Fig. 4 (a) Schematic of the dip coating process with sequential stages during the development of the structure. (b) Sol flow patterns during dip coating.

Modified from Brinker, C.J., Sehgalb, R., Hietalab, S.L., et al., 1994. Sol-gel strategies for controlled porosity inorganic materials. *Journal of Membrane Science* (94), 84–102.

alt-text: Fig. 4

During the immersion, while the substrate pulls the fluid going deep into the sol, two flow sol dynamic layers are generated (Streamline point “S”, Fig. 4(b)). As shown in Fig. 4(b), the outer layer (O), returns into the bath while the inner one (I) takes the substrate direction (Brinker and Hurd, 1994). The final thickness of the coatings strongly relates with the dynamics of these two layers and the position of S point (Scriven, 1988; Brinker et al., 1991).

Fig. 4(a) shows the parabolic shape provoked by the non-constant evaporation rate in the proximity of the drying line. The pore size is controlled by the structure, composition, rates of condensation and evaporation and the capillary pressure, which, as can be observed in Fig. 4(a), takes a different value in each part of the parabolic shape (Brinker et al., 1994).

Strawbridge and James (1986) described for the first time the different parameters that affect the final thickness. The equations were further modified to include new parameters that allow the most realistic behavior to be described. Brinker and Scherer (1990) advanced that the thickness variation depends on three important parameters, shown in Eq. (4), while the viscosity and density are constant. The relationship simplifies when considering that the lower the withdrawal rate, the thinner is the film, mainly due to an overlap between the deposition and drying stages (Thomas, 1994).

$$\text{thickness} \propto \frac{(\text{viscosity})(\text{withdrawal rate})^{1/2}}{(\text{density})} \quad (4)$$

Guglielmi and Zenezini (1990) proposed a new equation (Eq. (5)) that includes the measurable parameters of the sol, and fits well the evolution of film thickness in inorganic sols.

$$t_p = 10^{-3} \left(\frac{C_p}{\rho_p} \right) J \left(\frac{\eta U}{\rho g} \right)^{\frac{1}{2}} \quad (5)$$

Where t_p is the thickness of the heat-treated coating, C_p is the concentration of the solution expressed in grams of silica per litre, ρ_p is the density of the heat-treated coating expressed in $\text{gr}\cdot\text{cm}^{-3}$, η is the viscosity of the liquid, U is the withdrawal rate, ρ is the viscosity of the liquid and g is the gravitational acceleration.

During the evaporation step, the density of the coatings and the surface tension are constantly changing; this dynamic situation influences the drying profile which is also related to the ambient conditions as well as the specific characteristics of the sol and the substrate.

Brinker et al. (1994) described in detail how polymer or particle size, structure, reactivity, relative rates of reactions, liquid surface tension and the dipping withdrawals affect the final microstructure and thickness of the coating.

Spin Coating Deposition

Spin coating process is the simplest method to produce uniform thin films on flat substrates with thicknesses from nanometers to micrometers, (Sahu et al., 2009). Bornside et al. (1987) described the spin process consisting of four stages: deposition, spin up, spin off and evaporation of the solvents. Like the dip-coatings process, the evaporation overlaps with the other stages. The deposition begins when the sol falls on a rotating substrate, which is

accelerated up to the final speed. Secondly, a centrifugal force governs the spin up stage by letting the liquid flow radially and allowing the fluid to reach a uniform thickness. During the spin off stage, the excess of liquid on the surface flows to the perimeter. The evaporation of the solvent proceeds throughout all the steps governing the last stage, mainly when the vapor is overhead and saturated with volatile components. The rate of evaporation is a function of the partial pressure of the solvents and the amount of volatile components. The forced convection of the vapor above creates a mass transfer coefficient that is also uniform, generating a constant rate of evaporation.

Spin coating has an evident advantage due to the higher layer uniformity in comparison with others deposition techniques (Strawbridge and James, 1986). Ideally, the thickness is inversely proportional to the square root of the rotation speed (Thomas, 1994). Although, it is overly sensitive to the spin speed, the viscosity of coating solution, and roughness of the substrate.

However, the dip-coating and spin-coating processes present important limitations, the most important related with the maximum thickness obtained (Castro *et al.*, 2004). To solve this aspect, and other limitations, many efforts were developed to produce Sol-gel coatings with other techniques, such as EPD deposition.

Electrophoretic Deposition

Since dip-coating and spin-coating techniques focus on flat substrates and thin thicknesses, electrophoresis deposition was proposed as good alternative method to Sol-gel coating (Sheffer *et al.*, 2003; Castro *et al.*, 2004).

Clark *et al.* (1988) defined the electrophoresis as the movement of charged particles in a fluid (suspension) due to the application of an external electric field. According to Van der Biest and Vandeperre (1999), electrophoretic deposition is a combination of two processes, electrophoresis, and deposition. The electrophoresis involves the motion of charged particles in a stable suspension under an electric field, while the deposition is the result of the impact of these particles against the electrode of opposite sign. The rate of migration depends on many factors including size and shape of particles, physical and chemical characteristics of the support medium, the strength of the electromotive force and the ionic strength of the buffer. The power supply also plays an important role and a constant voltage or constant current can be used, although constant current is preferred with longer electrophoresis times.

On the other hand, the deposited mass is a function of different parameters such as particle concentration, electrophoretic mobility, area of the substrate, applied field and deposition time.

Spray Coating

In many cases, spray coating is chosen because of its suitability to cover surfaces without limits of geometry or dimensions, and the simplicity of the equipment needed. Chen *et al.* (1999) defined the process as the atomization/spraying of a suspension of droplets of the order of tens to hundreds of micrometers, followed by a drying process to produce a continuous surface of solid particles. To generate droplets, the liquid can be atomized by rotary disks, two-fluid nozzles or ultrasonic nebulizers, depending on the droplet size required. Larger particles arrive first to the substrate surface, creating a coating with different particle sizes, and porosity.

Different physicochemical parameters such as pH, viscosity or temperature affect the structure of the coating.

Applications of Sol-Gel Coatings

Optical and Photonics Applications

Inorganic and organic-inorganic hybrid Sol-gel coatings showed important optical applications due to their emissions, luminescence, optical nonlinearity and sensing properties, which modify the reflectance, transmission or absorption of the substrate. Moreover, Sol-gel process allows the incorporation of optically active particles or molecules into the Sol-gel matrix, and the possibility to dope them.

For many years, different oxides as Sol-gel layers for photovoltaic cells, especially TiO₂ with SiO₂ in different configurations, proved successful, improving the solar cells efficiency (Pettit *et al.*, 1985; Lee *et al.*, 2003; Faustini *et al.*, 2010). Other oxides such as ZnO are also developed for similar applications. The review of Znaidi (2010) deeply describes the preparation and characterization of ZnO Sol-gel coatings.

Light emitting diodes reached unique results for highly condensed films. Shi *et al.* (2015) studied the photo-activation of hybrid Sol-gel coatings for its use as diodes and, Yilmaz *et al.* (2015) described the preparation of *n*-ZnO films on p-Si substrates diodes by dip-coating. Many papers report the use of white light emitting diodes (Kim *et al.*, 2009; Keskenler *et al.*, 2013; Fu *et al.*, 2013; Nayak *et al.*, 2009). Although Schottky-prepared diodes combining different precursors and layers showing many advances, there still exists the need for the development of novel phosphor materials to increase down-conversion efficiencies (Gouveia-Neto *et al.*, 2012; Righini *et al.*, 2019).

Particular attention was paid to the preparation of oxyfluoride glass-ceramics (OxGCs) for photonic applications after the pioneering work of Wang and Ohwaki (1993) (de Pablos Martín *et al.*, 2002).

The Sol-gel route appears as a promising alternative to prepare OxGC films and bulk materials avoiding the limitation of melt-quenching (MQ) such as the loss of fluoride content. OxGCs are polycrystalline materials containing active lanthanide-fluoride nano-crystals (NCs) that crystallize in a glass matrix. The doping of nanocrystal with rare earth allows the optical properties to be improved (Gorni *et al.*, 2018a,b; Zhou *et al.*, 2018). The incorporation of active nano-crystalline phases into a silica glass matrix combines the low phonon energies of fluoride nanocrystals (250–450 cm⁻¹) with the excellent thermal, mechanical, and chemical stability of oxide glass matrices. The low phonon energy

can reduce the non-radiative de-excitation probability of the luminescent RE ions by the multi-phonon relaxation (Gorni *et al.*, 2018a,b). Gorni *et al.* (2017a,b) prepared crack-free 80SiO₂-20LaF₃ coatings doped with 3%Nd³⁺ and Er³⁺, confirming the incorporation of the dopants in the NC and including up to 18%wt of LaF₃, the highest crystalline fraction ever reported (Gorni *et al.*, 2019), Fig. 5.

Fig. 5 (a) Normalized emission spectra of Nd³⁺ in the 80SiO₂-20LaF₃ Sol-gel supported layer treated at 650°C for 3 h doped with 3% Nd³⁺ obtained by exciting at 786 nm (blue line) and 806 (red line). Data correspond to 9K. (b) Quantitative Rietveld refinement of the LaF₃ crystalline fraction with NaF as internal standard for 80SiO₂-20LaF₃ 0.5Er³⁺ bulk GC treated at 550°C for 1 min.

Reproduced from Gorni, G., Balda, R., Fernández, J., *et al.*, 2017a. Oxyfluorideglass-ceramic fibers doped with Nd³⁺ structural and optical characterization. *CrystEngComm - Royal Society of Chemistry* (19), 6620-6629. Gorni, G., Balda, R., Fernández, J., *et al.*, 2017b. 80SiO₂-20LaF₃ oxyfluoride glassceramic coatings doped with Nd³⁺ for optical applications. *International Journal of Applied Glass Science*, 1-10. Gorni, G., Velázquez, J.J., Mosa, J., *et al.*, 2019. Transparentsol-gel oxyfluoride glass-ceramics with high crystalline fraction and study of RE incorporation. *Nanomaterials* (9), 1-16.

alt-text: Fig. 5

In particular, doped SiO₂-LaF₃ materials are interesting for optical and photonic applications such as photovoltaic devices where the efficiency of solar cells could be improved by modifying and widening the solar spectrum range able to be used, and as dielectric ceramics used in resonators, for planar integrated photonic applications, etc. Lanthanide-doped GdF₃ is considered a promising host because Gd³⁺ ions can act as a sensitizer for other Ln³⁺ ions and enhance the luminescence processes (Chen *et al.*, 2008). On the other hand, SiO₂-NaGdF₄ or SiO₂-GdF₃ matrix may be suitable for infrared and tunable phosphors, sensing, solar cells, plasma display panels, biomedical imaging, and others (Yin *et al.*, 2012). YF₃-based sol-gel nano-glass-ceramics are good candidates for photovoltaic applications such as efficient phosphors due to the wide band gap (4.10 eV) and the fact that Y³⁺ sites can be substituted by some trivalent RE ions. The preparation of these materials as coatings is gaining more and more interest because new and novelty applications are possible, such as displays or smart windows.

Protective Coatings

The use of Sol-gel coatings is a good alternative to improve the resistance to corrosion or abrasion of metal substrates reducing the contact between substrate and aggressive medium.

Durán *et al.* (2018) classified Sol-gel protective coatings in three groups:

- (Put smaller points in the three lines) Inorganic and organic-inorganic hybrid coatings with low content of organic groups with sintering temperature between 400°C and 500°C.
- Organic-Inorganic hybrid coatings with high organic content cured under 200°C.
- Inorganic and hybrid coatings with corrosion inhibitors.

Inorganic coatings provide good corrosion protection against oxidation and nitridation in anhydrous media of stainless steels (Shane and Mecartney, 1990; Atik and Aegerter, 1992; de Sanctis *et al.*, 1995; de Damborenea *et al.*, 1995; Voevodin *et al.*, 2001). SiO₂ and SiO₂-ZrO₂ Sol-gel coatings are the most studied compositions, but others were also considered such as ZrO₂, B₂O₃, SiO₂-B₂O₃, SiO₂-ZrO₂, SiO₂-TiO₂, ZrO₂-Y₂O₃, ZrO₂-CeO₂. Inorganic coatings of SiO₂ constitute an efficient protection of surface mirrors for solar collectors (Morales and Durán, 1997). However, the sensitivity to corrosion in electrolytic media is high due to the presence of micro-cracks or defects in the pure inorganic coatings. The incorporation of low amounts of organic groups allows reductions in the penetration of the electrolyte compared to pure inorganic films, offering better electrochemical behavior as well as increased ductility and thickness (Gallardo *et al.*, 2003). These hybrid coatings are demonstrated to be also suitable for biological applications when bioactive powders are incorporated, inducing the formation of hydroxyapatite when in contact with physiological solutions (Gallardo *et al.*, 2001; Garcia and Durán, 2006).

Inorganic-organic hybrid coatings with high organic contents are appropriate for protecting light alloys such as aluminum, magnesium, or their alloys, widely used in automotive, aeronautic and aerospace industries. [Conde et al. \(2002\)](#) demonstrated that corrosion resistance of aluminum alloys improves when polymeric sols are prepared with the addition of colloidal suspension. This type of coating is quite interesting because it combines the properties of organic compounds (flexibility, high density, [Rosero-Navarro et al., 2009a,b](#)) and compatibility with the paint system) with those of inorganic components (scratch resistance, durability, etc.).

The most recent trend in corrosion protection is the incorporation of inhibitors in hybrid Sol-gel coatings, the third group. Protective coatings with inhibitors permit repair of damages without external intervention, the so-called *self-healing effect*. Two different types of coatings are considered: (1) conversion coatings obtained from rare earths and inorganic coatings of pure inhibitors produced by Sol-gel ([Fahrenholz et al., 2002](#); [Conde et al., 2008](#); [Rosero-Navarro et al., 2011](#)); (2) coatings obtained by incorporation of inhibitors to hybrid coatings ([Rosero-Navarro et al., 2009a,b](#); [Carvalho et al., 2014](#)). These films can be further coated with epoxy paints for use in the aircraft industry ([Durán et al., 2018](#)).

In other approaches, a number of organic compounds such as triazole and thiazole derivatives, 8-hydroxyquinoline and phosphonate-containing compounds or nano-reservoirs or nano-containers are also investigated as alternative corrosion inhibitors, associated with their good compatibility with hybrid coatings ([Borisova and Schkukin, 2013](#); [Chen and Fu, 2012](#)). However, it is difficult to control the release of the inhibitor to ensure a continued delivery to corrosion sites.

Last approaches focus on the combination of protective layers to arrive to an effective long-lasting corrosion protection ([Castro et al., 2020](#)). [Fig. 6](#) provides a schematic of the protective structure consisting of a first anodizing layer cover with a pure glass-like CeO_2 inhibiting layer finally protected with a thick hybrid SiO_2 layer.

Fig. 6 Schematic illustration of the combined system and protective mechanism of A3-Ce-GTL integrated system.

Reproduced from Castro, Y., Ozmen, E., Durán, A., 2020. Integrated self-healing coating system for outstanding corrosion protection of AA2024. *Surface & Coatings Technology* 387 (125521).

alt-text: Fig. 6

Porous Coatings for Sensors, Biosensors and Photo-Catalysis

It is possible to control the porosity (pore volume and pore size) of inorganic coatings obtained by Sol-gel by adjusting the rate of condensation and evaporation and using structure-directing agents (surfactants) ([Brinker et al., 1994](#)). These porous materials present high surface area and intrinsic porosity, showing unique structures. Due to their special characteristics, they find many applications as sensors, biosensors and photocatalysts.

Photo-catalytic activity of mesoporous TiO_2 coatings attracted high attention. [Fujisjima et al. \(2008\)](#) intensely studied the photocatalytic behavior of TiO_2 coatings, concluding that their super-hydrophilicity constitutes a great advantage for this application ([Sharma et al., 2006](#)). The Dionysiou group ([Antoniu and Dionysiou, 2007](#); [Quici et al., 2010](#)) is a key reference in this field. On the other hand, [Arconada et al. \(2011, 2010, 2009\)](#) described the photocatalytic activity of multilayer mesoporous TiO_2 films in aqueous solution (methyl orange) and in gas phase (trichloroethylene, hydrogen sulfide and methyl ethyl ketone). The control of crystallinity and the structural and textural properties of the semiconductor, such as the specific surface area, porosity, volume and distribution of the pore size are crucial to improve the photocatalytic behavior. In general, the addition of surfactants increases the thickness of the coatings generating catalysts with high meso-porosity and specific surface area, suggesting a higher contact surface between pollutant and semiconductor, and higher photocatalytic activity ([Castro and Durán, 2015](#)).

Other important application of mesoporous TiO_2 coatings involves the combination of biocidal activities with self-cleaning properties. [Roldán et al. \(2015\)](#) described the preparation of different systems consisting of a layer of SiO_2 followed by a mesoporous or dense layer, doped with silver nanoparticles (Ag NPs) ([Fig. 7](#)). The authors reported the preparation of dense and mesoporous $\text{SiO}_2/\text{TiO}_2$ coatings doped with Ag nanoparticles and found very high and synergic photocatalytic and bactericidal activities. The best photocatalytic activity appears when Ag nanoparticles situate in the SiO_2 layer, whereas the best bactericidal property is reached when the Ag nanoparticles are in the TiO_2 layer.

Photocatalytic degradation of methyl orange (MO)
 $c=3\text{mg/L}$, UV-irradiation, 50 cm^2

Fig. 7 Photocatalytic degradation of MO by different $\text{SiO}_2/\text{TiO}_2$ nanostructured coating systems doped with silver nanoparticles (Ag NPs).

Modified from Roldán, M.V., Castro, Y., Pellegrini, N., Durán, A., 2015. Enhanced photocatalytic activity of mesoporous $\text{SiO}_2/\text{TiO}_2$ sol-gel coating doped with Ag nanoparticles. *Journal of Sol-Gel Science and Technology* 76, 180–194.

alt-text: Fig. 7

Although TiO_2 is the most widely used semiconductor for photocatalytic applications, other oxides, such as SiO_2 , Al_2O_3 , ZnO or their combinations are also utilized (Pal and Sharon, 2002). A high porosity and specific surface area is necessary to promote an extensive contact between the organic compounds and the semiconductor surface (Haas-Santo *et al.*, 2001).

Sol-gel coatings also have an extensive field of applications as optical sensors to determine pH, ionic species or solvents as well as gas sensors and biosensors (Jerónimo *et al.*, 2007). The films change their optical behavior as response to environmental changes (Jeon *et al.*, 2013). pH sensitive dyes can be immobilized in Sol-gel films to be used as indicators. Absorption, fluorescence, and luminescence are used for detection. Depending on the indicator and Sol-gel precursors used the response time changes from less than 1 s to more than 4.5 min (Nguyen *et al.*, 1999; Ertekin *et al.*, 2003). Lifetime and stability can also vary from hours to months (Lobnik *et al.*, 2001; Wang *et al.*, 2003). Sensitive systems for gas detection based on Sol-gel coatings were also widely developed as the nano porosity of the Sol-gel matrix is used as a path for gas molecules where functional particles can be embedded and films show a reversible change in optical transmittance when exposed to certain gases, providing detection limits of 10 ppm (Martucci *et al.*, 2003). Based on the immobilization of reagent of colored complexes, thin films for ionic species detection are extensively used with detection limits above 1 ppm (Wallington *et al.*, 1997).

The availability of transparent coatings with a wide variety of matrices, along with the possibility to entrap biomolecular dopants, opened the door to the development of biosensors from Sol-gel coatings (Jerónimo *et al.*, 2007). The immobilized biomolecules maintain their biological functions and structures inside the Sol-gel matrix. Blyth *et al.* (1995) developed the first biosensor by Sol-gel for nitrogen monoxide and carbon monoxide detection, revealing that thin films are more efficient for bio-detection than monoliths. Enzymes like oxidoreductases and glucose oxidases remains active within the Sol-gel matrix and different sensing systems are still being developed (Ramanathan *et al.*, 1997).

Biomaterials Made by Sol-Gel

Sol-gel materials have been extensively studied for biomedicine and biomedical applications, including the design of materials in bio-sensing and bio-production (Avnir *et al.*, 2006). Nowadays, Sol-gel biomaterials are used in bio-encapsulation and drug release applications and as innovative bioactive materials. The behavior of a specific biomolecule in the inorganic, organic or hybrid nanocomposite material environment, determines the possibilities of these biomolecules to keep their native properties (Jin and Brennan, 2002).

Enzyme-based biosensors are an important field under development. Fukushima *et al.* (1988) and Jin and Brennan (2002) reported the immobilization of cells and enzymes using Sol-gel, demonstrating the good efficiency. Different compositions and hybrid organic-inorganic sol gel materials are reported for reducing the denaturalization of the enzymes during the aging of the inorganic network (Ellerby *et al.*, 1992; Gill and Ballesteros, 2000; Livage *et al.*, 2001).

Tan *et al.* (2005) stated for the first time a hybrid composite made with chitosan/silica, one of the most studied composites nowadays (Zhou *et al.*, 2015; Spirk *et al.*, 2013; Budnyak *et al.*, 2014). Hybrid chitosan and silica are suitable for cholesterol oxidase, amylase, urease, catalase and invertase. Similar hybrid systems are used for cell encapsulations. Sol-gel is a rapid process for immobilizing cells into a stable biomatrix; (Alvarez *et al.*, 2007)

demonstrated the high activity and longevity of cells entrapped in silica matrix.

On the other hand, porous Sol-gel materials with cationic amino groups that interact with alginate are demonstrated to be suitable for proliferation and insulin secretion both in vivo and in vitro. [Sakai et al. \(2001\)](#) designed a Sol-gel synthesis route for preparing microcapsules with double layer of alginate used in bio-artificial pancreas. These organic-inorganic microcapsules derived from Sol-gel are thus suitable for use in the field of bio-artificial organs.

Sol-gel process is also applied in the biomedical field as implants and sensors where a molecular control of hydroxyapatite incorporation is required, together with the biological behavior of proteins and cells ([Hench, 1997](#)). These materials do not provoke rejection by the human body and over time, they are partially reabsorbed and replaced by natural bone.

Bioactive Sol-gel materials shaped as coatings, monoliths or powders are used to obtain an efficient bond to bone by chemical reactions occurring at the interface of the bone tissue that improve the nucleation of the hydroxyapatite. These bioactive Sol-gel materials promote hydroxyapatite multilayer formation on the bone tissue, both in vivo and in vitro. [Pereira and Hench \(1996\)](#) described the mechanism of hydroxyapatite formation on different gel silica substrates. [Sepulveda et al. \(2001\)](#) made a full comparison between bioactive glasses made by melt quenching and by Sol-gel, obtaining remarkable differences in the surface area. The biocompatibility of the implant is determined not only by the availability of growth of the apatite, but also by the capacity to absorb proteins ([Lobel and Hench, 1996](#)).

There is a clinical need for materials to stimulate the repair of bone by kindling the body's own healing mechanisms. Bone can heal itself if the defect is small, but needs assistance if the defect is over a critical size. Temporary templates (scaffolds) act as guides and stimulus for vascularised bone growth. Inherently brittle materials cannot be used in applications that experience cyclic loads, the current bioactive materials needing toughness and plasticity. The obvious way to improve toughness is to make a composite material, using a bioactive ceramic or glass as the inorganic phase within a biodegradable polymer as the organic matrix. The degradation can be made more congruent by careful polymer selection and manipulation or by developing specialized types of nanocomposites. [Jones and Valliant \(2011\)](#) and Martin and Jones (2012) tried to understand how each property of the glass and hybrid scaffolds affects cellular response to optimize the materials and ensure long-term success and clinical products. They focused on the characterization of the hierarchical structures of Sol-gel glasses and hybrids, from atomic-scale amorphous networks, through the covalent bonding between components in hybrids and nanoporosity, to quantifying open macroporous networks of the scaffolds. Nondestructive in situ monitoring of degradation and bioactivity mechanisms of the materials are also included ([Fig. 8](#)).

Fig. 8 X-ray microtomography images of (a) bioactive glass foam scaffold and (b) trabecular bone.

Reproduced from Martin, R.A., Yue, S., Hanna, J.V., et al., 2012. Characterizing the hierarchical structures of bioactive sol-gel silicate glass and hybrid scaffolds for bone regeneration. *Philosophical Transactions of the Royal Society A-Mathematical Physical and Engineering Sciences* 370 (1663), 1422-1443.

alt-text: Fig. 8

[Boccaccini and Zheng \(2017\)](#) reviewed silicate-based bioactive glass nanoparticles (BGN) with unique properties in biomedical applications. Sol-gel synthesis of BGN is drawing widespread attention, because the convenience and versatility it offers to tune the properties of BGN. Considering the importance of the BGN morphology and composition to their biomedical applications, strategies to control the size, shape, pore structure and composition of BGN are relevant. BGN are particularly interesting biomaterials for bone related applications, but they also have potential for other biomedical applications, e.g., in soft tissue regeneration/repair.

Other Applications

Sol-gel process permits ([Boccaccini and Zheng, 2017](#)) preparation of a wide range of outstanding products; some of them gave rise to special fields of research inside the Sol-gel community.

Aerogels have unique properties due to the possibility of controlling the shape and size of pores at low processing temperatures. The extremely low density of these materials explains their amazing thermal and acoustic insulation properties. Aerogels are used as composites (Shajesh *et al.*, 2009; Moner-Girona *et al.*, 2002), absorbents (Rao *et al.*, 2007) and sensors, and have a huge variety of possible science and technology applications (Gurav *et al.*, 2010).

Brinker and Scherer (1985) reported the fabrication of fibers as a new field of applications of Sol-gel materials. Fibers prepared by Sol-gel can be used for reinforcement, superconducting, electrolytic or optical applications, as well as for improving chemical durability (Russel-Flores *et al.*, 1993; Sakka, 1990).

Different Sol-gel routes continue to be active for preparing Fe₂O₃-C fibers for anodes in Li-ion batteries (Changbin *et al.*, 2018) and PES-TiO₂ hollow fiber hybrid membranes were recently reported by Lu *et al.* (2017). Sol-gel xerogels are applied as sensors and fuel cells taking advantage of the elevated controlled porosity (Grattan *et al.*, 1991; Li *et al.*, 2011).

In the field of optical applications, bulk gels and monoliths are essential parts of fiber optics, lenses, glasses with graded refractive index, etc. (Grant and Glass, 1997).

Uncited References

Amauri *et al.*, 2012; Dalzell and Clark, 1986; Hench *et al.*, 1971; Jones, 2013; Jonschker *et al.*, 1998; Kecht *et al.*, 2008; Li *et al.*, 2017; Livage, 1977; Potanin, 1992; Reis *et al.*, 1997; Roldán *et al.*, 2014; Zhang *et al.*, 1992.

References

Alvarez G.S., Desimone M.F. and Diaz L.E., Immobilization of bacteria in silica matrices using citric acid in the sol-gel process, *Applied Microbiology and Biotechnology* **73** (5), 2007, 1059–1064.

~~Amauri P.J., Montoro L.A., Souza G.S. and Alves O.L., Towards long term colloidal stability of silica-based nanocarriers for hydrophobic molecules: Beyond the Stöber method, *Chemical Communications* **48**, 2012, 591–593.~~

Antoniou M.G. and Dionysiou D.D., Application of immobilized titanium dioxide photocatalysts for the degradation of creatinine and phenol, model organic contaminants found in NASA's spacecrafts wastewater streams, *Catalysis Today* **124**, 2007, 215–223.

Arconada N., Castro Y. and Durán A., Photocatalytic properties in aqueous solution of porous TiO₂-anatase films prepared by sol-gel process, *Applied Catalysis A: General* **385**, 2010, 101–107.

Arconada N., Castro Y., Duran A. and Hequet V., Photocatalytic oxidation of methyl ethyl ketones over sol-gel mesoporous and meso-structured TiO₂ films obtained by EISA method, *Applied Catalysis B: Environmental* **107**, 2011, 52–58.

Arconada N., Durán A., Suárez S., et al., Synthesis and photocatalytic properties of dense and porous TiO₂-anatase thin films prepared by sol-gel, *Applied Catalysis B: Environmental* **86**, 2009, 1–7.

Atik M. and Aegerter M.A., Corrosion resistant sol-gel ZrO₂ coatings on stainless steel, *Journal of Non-Crystalline Solids* **147-148**, 1992, 813–819.

Avnir D., Coradin T., Lev O. and Livage J., Recent bio-applications of sol-gel materials, *Journal of Materials Chemistry* **16**, 2006, 1013–1030.

Bahuguna G., Mishra N.K., Chaudhary P., et al., Thin film coating through sol-gel technique, *Research Journal of Chemical Sciences* **6** (7), 2016, 65–72.

Bai A.B., Song H., He G., et al., Facile synthesis of core-shell structured ZrO₂@SiO₂ via a modified Stöber method, *Ceramics International* **42** (6), 2016, 7583–7592.

Bisson A., Rigacci A., Lecomte D., et al., Drying of silica gels to obtain aerogels: Phenomenology and basic techniques, *Drying Technology* **21** (4), 2003, 593–628.

Blyth D.J., Aylott J.W., Richardson D.J. and Russell D.A., Sol-gel encapsulation of Metalloproteins for the development of optical biosensors for nitrogen monoxide and carbon monoxide detection, *Analyst* **120**, 1995, 2725–2730.

Boccaccini A.R. and Zheng K., Sol-gel processing of bioactive glass nanoparticles: A review, *Advances in Colloid and Interface Science* **249**, 2017, 363–373.

Borisova D.M.H. and Schukin D.G., Influence of embedded nanocontainers on the efficiency of active anticorrosive coatings for aluminum alloys part II: Influence of nanocontainer position, *Applied Materials & Interface* **5**, 2013, 80–87.

Bornside D.E., Macosko C.W. and Scriven L.E., Modeling of spin coating, *Journal of Imaging Technology* **13** (4), 1987, 122–130.

Brinker J.C. and Scherer G.W., Film formation, Sol-Gel Science, 1990, Elsevier, Oxford, 787–836.

Brinker C.J., Frye G.C., Hurd A.J. and Ashley C.S., Fundamentals of sol-gel dip coating, *Thin Solid Films* **201**, 1991, 97–108.

Brinker C.J. and Hurd A., Fundamentals of sol-gel dip-coating, *Journal de Physique III, EDP Science* **4** (7), 1994, 1231–1242.

Brinker C.J., Hurd A.J., Schunk P.R., et al., Review of sol-gel thin film formation, *Journal of Non-Crystalline Solids* **147**, 1992, 424–436.

Brinker C.J. and Scherer C.W., Sol-gel-glass: I. Gelation and gel structure, *Journal of Non-Crystalline Solids* **70**, 1985, 301–322.

Brinker C.J., Sehgalb R., Hietalab S.L., et al., Sol-gel strategies for controlled porosity inorganic materials, *Journal of Membrane Science* **94**, 1994, 84–102.

Budnyak T.M., Tertykn V.A. and Yanovska E.S., Chitosan immobilized on saponite surface in extraction of V(V), Mo(VI) and Cr (VI) oxoanions, *Chemistry, Physics and Technology of Surface* 2014, 445–453.

Carvalho J.B., Silva R.S., Cesarino I., et al., Influence of the annealing temperature and metal salt precursor on the structural characteristics and anti corrosion barrier effect of CeO₂ sol-gel protective coatings of carbon steel, *Ceramics International* **40**, 2014, 13437–13446.

Castro Y. and Durán A., Sol-gel TiO₂ materials and coatings for photocatalytic and multifunctional applications, In: Levy D. and Zayat M., (Eds.), *The Sol-Gel Handbook*, 2015, Wiley-VCH, 911–928.

Castro Y., Ferrari B., Durán A. and Moreno R., Effect of rheology and processing parameters on the EPD coatings of basic sol-gel particulate sol, *Journal of Materials Science* **39**, 2004, 845–849.

Castro Y., Ozmen E. and Durán A., Integrated self-healing coating system for outstanding corrosion protection of AA2024, *Surface & Coatings Technology* **387** (125521), 2020.

Changbin S., Sihao C. and Zhen L., Controllable synthesis of Fe₂O₃-carbon fiber composites via a facile sol-gel route as anode materials for lithium ion batteries, *Applied Surface Science* **427**, 2018, 476–484.

Chang S.Y. and Ring T.A., Map of gel times for three phase region tetraethoxysilane, ethanol and water, *Journal of Non-Crystalline Solids* **147/148**, 1992, 56–61.

Chen C.H., Emond M.H.J., Kelder E.M., et al., Electrostatic sol-spray deposition of nanostructured ceramic thin films, *Journal of Aerosol Science* **30** (7), 1999, 959–967.

Chen D., Wang Y., Yu Y. and Huang P., Structure and optical spectroscopy of eu-doped glass ceramics containing GdF₃ nanocrystals, *Journal of Physical Chemistry* **112**, 2008, 18943–18947.

Chen T. and Fu J., An intelligent anticorrosion coating based on pH-responsive supramolecular nanocontainers, *Nanotechnology* **23** (50), 2012.

Clark D.E., Dalzell W.J. and Folz D.C., Electrophoretic alumina sol-gel coatings on metallic substrates, *Ceramic Engineering and Science Proceedings* **9**, 1988, 1111–1118.

Conde A., Arenas M.A., de Frutos A. and de Damborenea J., Effective corrosion protection of 8090 alloy by cerium conversion coatings, *Electrochimica Acta* **53** (26), 2008, 7760–7768.

Conde A., Durán A. and de Damborenea J., Protección contra la corrosión de aleaciones de aluminio mediante recubrimientos sol-gel, *Boletín de la Sociedad Española de Cerámica y Vidrio* **41** (3), 2002, 319–323.

Dalzell W.J. and Clark D.E., Thermophoretic and electrophoretic deposition of sol-gel composite coatings, In: Smothers W., (Ed), *Proceedings of the 10th Annual Conference on Composites and Advanced Ceramic Material: Ceramic Engineering and Science Proceedings 7*, 1986, The American Ceramic Society, Inc., 1014–1026.

de Damborenea J., Pellegrini N. and Durán A., Electrochemical behaviour of SiO₂ sol-gel coatings on stainless steel, *Journal of Sol-Gel Science and Technology* **4**, 1995, 239–244.

de Sanctis O., Gómez L., Pellegrini N. and Durán A., Behaviour in hot ammonia atmosphere of SiO₂-coated stainless steels produced by sol-gel procedure, *Surface and Coatings Technology* **70** (2–3), 1995, 251–255.

Dimitriev Y., Ivanova Y. and Iordanova R., History of sol-gel science and technology, *Journal of the University of Chemical Technology and Metallurgy* **43** (2), 2008, 181–192.

Durán A., Castro Y., Conde A. and Damborenea J.J., Sol-gel protective coatings, *Handbook of Sol-Gel Science and Technology*, 2018, Springer International Publishing, 2369–2433.

Ebelmen M., Sur les combinaisons des acides borique et silicique avec les éthers, *Annales de Chimie et de Physique* **25**, 1846, 129–166.

Ellerby L.M., Nishida C.R., Nishida F., et al., Encapsulation of proteins in transparent porous silicate glasses prepared by the sol-gel method, *Science* **255** (5048), 1992, 1113–1115.

- Ertekin K., Alp S., Yenigul B., et al., Photophysical and photochemical characteristics of an azlactone dye in sol-gel matrix; a new fluorescent pH indicator, *Dyes and Pigments* **56**, 2003, 125–133.
- Esquena J., Pons R., Azemar N., et al., Preparation of monodisperse silica particles in emulsion media, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **123-124**, 1997, 575–586.
- Fahrenheit W.G., O'Keefe M.J., Zhou H. and Grant J.T., Characterization of cerium-based conversion coatings for corrosion protection of aluminum alloys, *Surface and Coatings Technology* **155** (2–3), 2002, 208–213.
- Fan J., Boettcher S.W., Tsung K.-C., et al., Field-directed and confined molecular assembly of mesostructured materials: Basic principles and new opportunities, *Chemistry of Materials* **20**, 2008, 909–921.
- Faustini M., Nicole L., Boissière C., et al., Hydrophobic, antireflective, self cleaning and antifogging sol-gel coatings: An example of multifunctional nanostructured materials for photovoltaic cells, *Chemistry of Materials* **22**, 2010, 4406–4413.
- Flory P.J., Introductory lecture, *Faraday Discussions of the Chemical Society* **57**, 1974, 7–18.
- Fujisjima A., Zhang X. and Tryk D.A., TiO₂ photocatalysis and related surface phenomena, *Surface Science Reports* **63**, 2008, 515–582.
- Fukushima Y., Okamura K. and Imai K., A new immobilization technique of whole cells and enzymes with colloidal silica alginate, *Biotechnology and Bioengineering* **32** (5), 1988, 584–594.
- Fu Q., Chen J., Shi C. and Ma D., Room-temperature sol-gel derived molybdenum oxide thin films for efficient and stable solution-processed organic light emitting diodes, *Journal American Chemical Society* **5** (13), 2013, 6024–6029.
- Gallardo J., Durán A., Garcia C.C., et al., Effect of sintering temperature on the corrosion and wear behaviour of protective SiO₂-based sol gel coating, *Journal of Sol-Gel Science and Technology* **27** (2), 2003, 175–183.
- Gallardo J., Galliano P. and Durán A., Bioactive and protective sol-gel coatings on metals for orthopaedic prostheses, *Journal of Sol-Gel Science and Technology* **21**, 2001, 6574.
- Garcia C.C. and Durán A., Bioactive coatings deposited on titanium alloys, *Journal of Non-Crystalline Solids* **352** (32–35), 2006, 3488–3495.
- Gill I. and Ballesteros A., Bioencapsulation within synthetic polymers (Part 1): Sol-gel encapsulated biologicals, *Trends in Biotechnology* **18**, 2000, 282–297.
- Gorni G., Balda R., Fernández J., et al., Oxyfluoride glass-ceramic fibers doped with Nd³⁺ structural and optical characterization, *CrystEngComm – Royal Society of Chemistry* **19**, 2017a, 6620–6629.
- Gorni G., Balda R., Fernández J., et al., 80SiO₂-20LaF₃ oxyfluoride glass ceramic coatings doped with Nd³⁺ for optical applications, *International Journal of Applied Glass Science* 2017b, 1–10.
- Gorni G., Balda R., Fernández J., et al., Effect of the heat treatment on the spectroscopic properties of Er³⁺-Yb³⁺ doped transparent oxyfluoride nano-glass-ceramics, *Journal of Luminescence* **193**, 2018a, 51–60.
- Gorni G., Velázquez J.J., Mosa J., et al., Transparent glass-ceramic produced by sol-gel: A suitable alternative for photonic materials, *Materials* **11** (212), 2018b, 1–30.
- Gorni G., Velázquez J.J., Mosa J., et al., Transparent sol-gel oxyfluoride glass-ceramics with high crystalline fraction and study of RE incorporation, *Nanomaterials* **9**, 2019, 1–16.
- Gouveia-Neto A., da Silva A., Bueno L.A. and da Costa E.B., Luminescent features of sol-gel derived rare earth multi-doped oxyfluoride nano-structured phosphors for white LED application, *Journal of Luminescence* **132**, 2012, 299–304.
- Grant S. and Glass R.S., A sol-gel based fiber optic sensor for local blood pH measurements, *Sensors and Actuators B* **45**, 1997, 35–42.
- Grattan K.T., Badini G.E. and Palmer A.W., Use of sol-gel techniques for fibre-optic sensor applications, *Sensors and Actuators A* **25-27**, 1991, 483–487.
- Green D.L., Lin J.S., Lam Y.-F., et al., Size, volume fraction, and nucleation of Stober silica nanoparticles, *Journal of Colloid and Interface Science* **266**, 2003, 346–358.
- Guglielmi M. and Zenezini S., The thickness of sol-gel silica coatings obtained by dipping, *Journal of Non-Crystalline Solids* **121** (1–3), 1990, 303–309.
- Gurav J.L., Jung I.-K., Park H.-H., et al., Review article: Silica aerogel: Synthesis and applications, *Journal of Nanomaterials* **2010**, 2010, 1–12.
- Haas-Santo K., Fichtner M. and Schubert K., Preparation of microstructure compatible porous supports by sol-gel synthesis for catalyst coatings, *Applied Catalysis A: General* **220**, 2001, 79–92.
- Hench L.L., Sol-Gel Materials for Bioceramic Applications, 1997, Department of Materials, Imperial College of Science Technology and Medicine, London.

Hench L.L., Splinter R.J. and Allen W.C., Bonding mechanisms at the interface of ceramic prosthetic materials, *Journal of Biomedical Materials Research* **1971**, 117–141.

Jeon D., Yoo W.J., Seo J.K., et al., Fiber-optic pH sensor based on sol-gel film immobilized with neutral red, *Optical Review* **20** (2), 2013, 209–213.

Jerónimo P.C., Araújo A.N., Conceição M. and Montenegro B., Optical sensors and biosensors based on sol-gel films, *Talanta* **72**, 2007, 13–27.

Jin W. and Brennan J.D., Properties and applications of proteins encapsulated within sol-gel derived materials, *Analytica Chimica Acta* **461** (1), 2002, 1–36.

Jones J.R., Review of bioactive glass: From Hench to hybrids, *Acta Biomaterialia* **9**, 2013, 4457–4486.

Jones J.R. and Valliant E.M., Softening bioactive glass for bone regeneration: Sol gel hybrid materials, *Soft Matter* **7** (11), 2011, 2083–5095.

Jonschker, G., Mennig, M., Schmidt, H., 1998. Europe, Patent No. EP0973958.

Kecht J., Schlossbauer A. and Bein T., Selective functionalization of the outer and inner surfaces in mesoporous silica nanoparticles, *Chemistry of Materials* **20**, 2008, 7207–7214.

Keskenler E.F., Tomakin M., Doğan S., et al., Growth and characterization of Ag/n-ZnO/p-Si/Al heterojunction diode by sol-gel spin technique, *Journal of Alloys and Compounds* **550**, 2013, 129–132.

Kim K., Song Y.W., Leem J., et al., Preparation and analysis of schottky diodes with Au and sol-gel-processed ZnO thin films, *Journal of the Korean Physical Society* **55** (1), 2009, 140–143.

King, G., Threlfall, R., 1928. Material for Forming Coatings, for the use as Impregnating Agents or for Like Purposes. United States, Patent No. 1.809.755.

Kobayashi Y., Katakami H., Mine E., et al., Silica coating of silver nanoparticles using a modified Stöber method, *Journal of Colloid and Interface Science* **283** (2), 2005, 392–396.

Kresge C.T., Leonowicz M.E., Roth W.J., et al., Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, *Nature* **359**, 1992, 710–712.

Lee S.-C., Lee J.-H., Oh T.-S., Kim Y.-H. and Lee J.H., Fabrication of tin oxide film by sol-gel method for photovoltaic solar cell system, *Solar Energy Materials & Solar Cells* **74** (3–4), 2003, 481–487.

Li F., Huang X. and Zhang G. J., Preparation of ultra-high temperature ceramics-based materials by sol-gel routes, In: *Recent Applications in Sol-Gel Synthesis*, 2017, Intech Open, 39–61.

Li H., Jin D., Yu Q. and Tu H., Optical humidity sensing proton-conducting sol-gel glass monolith, *Journal of Power Sources* **196**, 2011, 3836–3840.

Livage J., Vers une chimie écologique. Quand l'air et l'eau remplacent le pétrole, *Le Monde* **26**, 1977.

Livage J., Sol-gel processes, *Current Opinion in Solid State and Materials Science* **2** (2), 1997, 132–138.

Livage J., Coradin T. and Roux C., Encapsulation of biomolecules in silica gels, *Journal of Physics Condensed Matter* **13** (33), 2001, 673–691.

Li W. and Zhao D., Extension of the Stöber method to construct mesoporous SiO₂ and TiO₂ shells for uniform multifunctional core-shell structures, *Advanced Materials* **25**, 2013, 142–149.

Lobel K.D. and Hench L.L., In-vitro protein interaction with a bioactive gel-glass, *Journal of Sol-Gel Science and Technology* 1996, 69–76.

Lobnik A., Majcen N., Niederreiter K. and Uray G., Optical pH sensor based on the absorption of antenna generated europium luminescence by bromothymolblue in a sol-gel membrane, *Sensors and Actuators B* **74**, 2001 200–206.

Lu S.-H., Liu M. and Xu Z.-L., A novel PES-TiO₂ hollow fiber hybrid membrane prepared via sol-gel process assisted reverse thermally induced phase separation (RTIPS) method, *Journal of Membrane Science* **528**, 2017, 303–315.

Martin R.A., Yue S., Hanna J.V., et al., Characterizing the hierarchical structures of bioactive sol-gel silicate glass and hybrid scaffolds for bone regeneration, *Philosophical Transactions of the Royal Society A-Mathematical Physical and Engineering Sciences* **370** (1963), 2012, 1422–1443.

Martucci A., Sartori S., Muffato A., et al., Sol-gel synthesis of -Na₂O.xAl₂O₃ films, *Journal of the American Ceramic Society* **86** (11), 2003, 1965–1968.

Mazdiyasn K.S., Dolloff R.T. and Smith J.S., Preparation of high-purity submicron barium titanate powders, *The American Ceramic Society* **52** (10), 1969, 523–526.

Moner-Girona M., Martinez E., Esteve J., et al., Micromechanical properties of carbon-silica aerogel composites, *Applied Physics A* **74**, 2002, 119–122.

Morales A. and Durán A., Sol-Gel protection of front surface silver and aluminium mirrors, *Journal of Sol-Gel Science and Technology* **8**, 1997, 451–457.

Nayak P.K., Yang J., Kim J., et al., Spin-coated Ga-doped ZnO transparent conducting thin films for organic light-emitting diodes, *Journal of Physics D: Applied Physics* **42**, 2009, 1–6.

Nguyen T., McNamara K.P. and Rosenzweig Z., Optochemical sensing by immobilizing fluorophore-encapsulating, *Analytica Chimica* **400**, 1999, 45–54.

Orgaz-Orgaz F., Gel to glass conversion: Densification kinetics and controlling mechanisms, *Journal of Non-Crystalline Solids* **100**, 1988, 115–141.

Owens G.J., Singh R.K., Foroutan F., et al., Sol-gel based materials for biomedical applications, *Progress in Materials Science* **77**, 2016, 1–79.

de Pablos Martín A., Durán A. and Pascual M.J., Nanocrystallisation in oxyfluoride systems: Mechanisms of crystallisation and photonic properties, *International Materials Reviews* **57** (3), 2002, 165–186.

Pal B. and Sharon M., Enhanced photocatalytic activity of highly porous ZnO thin films prepared by sol-gel process, *Materials Chemistry and Physics* **76** (1), 2002, 82–87.

Pereira M.M. and Hench L.L., Mechanisms of hydroxyapatite formation on porous gel-silica substrates, *Journal of Sol-Gel Science and Technology* **7**, 1996, 59–68.

Pettit R.B., Brinker C.J. and Ashley C.S., Sol-gel double layer antireflection coatings for silicon solar cells, *Solar Cells* **15** (3), 1985, 267–278.

Pope E. and Mackenzie J., Sol-gel processing of silica. II. The role of the catalyst, *Journal of Non-Crystalline Solids* **87**, 1986, 185–198.

Potatin A.A., Macro- and microrheological modeling of spin coating, *Chemical Engineering Science* **47** (8), 1992, 1871–1879.

Quici N., Litter M., Vera M., et al., Effect of key parameters on the photocatalytic oxidation of toluene at low concentrations in air under 254 + 185 nm UV irradiation, *Applied Catalysis B: Environmental* **95**, 2010, 312–319.

Rabinovich E.M., Review: Preparation of glass by sintering, *Journal of Materials Science* **20**, 1985, 4259–4297.

Ramanathan K., Kamalasanan M.N., Malhotra B.D., et al., Immobilization and characterization of lactate dehydrogenase on TEOS derived sol-gel films, *Journal of Sol-Gel Science and Technology* **10**, 1997, 309–316.

Rao V.A., Hegde N.D. and Hirashima H., Absorption and desorption of organic liquids in elastic superhydrophobic silica aerogels, *Journal of Colloid and Interface Science* **305**, 2007, 124–132.

Ray, A.B., 1934. Method of Depositing Silica on Material. United States, Patent No. 2.027.931.

Reis R.L., Cunha A.M., Fernandes M.H. and Correia R.N., Treatments to induce the nucleation and growth of apatite-like layers on polymeric surface and foams, *Journal of Materials Science: Materials in Medicine* **8**, 1997, 897–905.

Righini G.C., Enrichi E., Zur L. and Ferrari M., Rare Earth doped glasses and light managing in solar cells, *Journal of Physics* **1221**, 2019, 1–5.

Roldán M.V., Castro Y., Pellegrini N. and Durán A., Enhanced photocatalytic activity of mesoporous SiO₂/TiO₂ sol-gel coating doped with Ag nanoparticles, *Journal of Sol-Gel Science and Technology* **76**, 2015, 180–194.

Roldán M.V., de Oña P., Castro Y., et al., Photocatalytic and biocidal activities of novel coating systems of mesoporous and dense TiO₂ anatase containing silver nanoparticles, *Materials Science and Engineering C* **43**, 2014, 630–640.

Rosero-Navarro N.C., Curioni M. and Castro Y., Glass-like CexOy sol-gel coatings for corrosion protection of aluminium and magnesium alloys, *Surface & Coatings Technology* **206** (2–3), 2011, 257–264.

Rosero-Navarro N.C., Pellice S. and Castro Y., Improved corrosion resistance of AA2024 alloys through hybrid organic-inorganic sol-gel coatings produced from sols with controlled polymerization, *Surface & Coatings Technology* **203** (13), 2009a, 1897–1903.

Rosero-Navarro N.C., Figiel P., Jedrzejewski R., et al., Influence of cerium concentration on the structure and properties of silica-methacrylate sol-gel coatings, *Journal of Sol-Gel Technology* **54**, 2009b, 301–311.

Roy R. and Osborn E.F., The system Al₂O₃-SiO₂-H₂O, *American Mineralogist* **39**, 1954, 853–885.

- Russel-Floys R.S., Harris B., Cooke R.G., et al., Application of sol-gel processing techniques for the manufacture of fiber-reinforced ceramics, *Journal of the American Ceramic Society* **76** (10), 1993, 2635-2643.
- Sahu N., Parija B. and Panigrahi S., Fundamental understanding and modeling of spin coating process: A review, *Indian Journal of Physics* **83** (4), 2009, 493-502.
- Sakai S., Ono T., Ijima H. and Kawakami K., Synthesis and transport characterization of alginate/aminopropyl silicate/alginate microcapsule: Application to bioartificial pancreas, *Biomaterials* **2001**, 2827-2834.
- Sakka S., Sol-gel processing of insulating electroconducting and superconducting fibers, *Physical and Chemical Properties of Shaped Materials: (e) Fibers* **121**, 1990, 417-423.
- Sakka S. and Kamiya K., The sol-gel transition in the hydrolysis of metal alkoxides in relation to the formation of glass fibers and films, *Journal of Non-Crystalline Solids* **48** (1), 1982, 31-46.
- Sanchez C., Rozes L., Ribot F., et al., "Chimie douce": A land of opportunities for the designed construction of functional inorganic and hybrid organic-inorganic nanomaterials, *Compte Rendus Chimie* **13**, 2010, 3-39.
- Sanchez C., de A.A. Soler-Illia G.J., Ribot F., et al., Designed hybrid organic-inorganic nanocomposites from functional nanobuilding blocks, *Chemistry of Materials* **13** (10), 2001, 3061-3083.
- Sanchez C., de A.A. Soler-Illia G.J., Ribot F. and Grosso D., Designing of functional nano-structured materials through the use of controlled hybrid organic-inorganic interfaces, *Compte Rendus Chimie: Nanomaterials and Their Physical Properties* **6**, 2003, 1131-1151.
- Scherer W.G., Recent progress in drying of gels, *Journal of Non-Crystalline Solids* **147**, 1992, 363-374.
- Schmidt, H., 1984. Organically modified silicates by the sol-gel process. In: MRS Proceedings, vol. 32, p. 327. Fraunhofer.
- Schneller T., Waser R., Kosec M. and Payne D., (Eds.), *Chemical Solution Deposition of Functional Oxide Thin Films*, 2013, Springer.
- Schroeder H., Oxide layers deposited from organic solutions, *Physics of Thin Films* **5**, 1969, 87-141.
- Scriven L.E., Physics and applications of dip coating and spin coating, *Materials Research Society Proceedings* **121**, 1988, 717-729.
- Sepulveda P., Jones J.R. and Hench L.L., Characterization of Melt Derived 45S5 and sol-gel-derived 58S Bioactive Glasses, *Journal of Biomedical Materials Research* **58** (6), 2001, 734-740.
- Shajesh P., Smitha S., Aravind P.R. and Warriar K.G.K., Effect of 3-glycidioxypropyltrimethoxysilane precursor on the properties of ambient pressure dried silica aerogels, *Journal of Sol-Gel Science and Technology* **50**, 2009, 353-358.
- Shane M. and McCartney M.L., Sol-gel synthesis of zirconia barrier coatings, *Journal of Materials Science* **25**, 1990, 1537-1544.
- Sharma S.D., Singh D., Saini K.K., et al., Sol-Gel-derived super-hydrophilic nickel doped TiO₂ film as active photo-catalyst, *Applied Catalysis A: General* **314**, 2006, 40-46.
- Sheffer M., Groysman A. and Mandlet D., Electrodeposition of sol-gel films on Al for corrosion protection, *Corrosion Science* **45**, 2003, 2893-2904.
- Shi S., Allonas X., Croutxé-Barghorn C. and Chemtob A., Activation of the sol-gel process by visible light-emitting diodes (LEDs) for the synthesis of inorganic films, *New Journal of Chemistry* **39**, 2015, 5686-5693.
- Soler-Illia G.J. and Innocenzi P., Mesoporous hybrid thin films: The physics and chemistry beneath, *Chemistry-A European Journal* **12**, 2006, 4478-7794.
- Soller-Illia G.J., Angelomé P.C., Fuertes M.C., et al., Mesoporous hybrid and nanocomposite thin films. A sol-gel toolbox to create nanoconfined systems with localized chemical properties, *Journal of Sol-Gel Science and Technology* **57**, 2011, 299-312.
- Spirk S., Findenig G., Doliska A., et al., Chitosan-silane sol-gel hybrid thin films with controllable layer thickness and morphology, *Carbohydrate Polymers* **2013**, 285-290.
- Stöber W. and Fink A., Controlled growth of monodisperse silica spheres in the micron size range, *Journal of Colloid and Interface Science* **26**, 1968, 62-69.
- Strawbridge I. and James P.F., The factors affecting the thickness of sol-gel derived silica coatings prepared by dipping, *Journal of Non-Crystalline Solids* **86**, 1986, 381-393.
- Tan X., Tian Y. and Cai P., Glucose biosensor based on glucose oxidase immobilized in sol-gel chitosan/silica hybrid composite film on Prussian blue modified glass carbon electrode, *Analytical and Bioanalytical Chemistry* **381**, 2005, 500-507.

Thomas I.M., Optical coating fabrication, In: Klein L.C., (Ed), *Sol-Gel Optics Processing and Applications*, 1994, Kluwer Academic Publishers, Livermore, California, 141–168.

Van der Biest O.O. and Vandeperre L.J., Electrophoretic deposition of materials, *Annual Review of Materials Science* **29**, 1999, 327–352.

Vega A.J. and Scherer G.W., Study of structural evolution of silica gel using ^1H and ^{29}Si NMR, *Journal of Non-Crystalline Solids* **111**, 1989, 153–166.

Villegas Broncano M.A. and Fernandez Navarro J.M., Preparacion de vidrios de silicatos alcalinos por el método sol-gel, *Boletin Sociedad Española de Cerámica y Vidrio* **26** (2), 1987, 99–108.

Voevodin N.N., Grebasch N.T., Soto W.S., et al., An organically modified zirconate film as a corrosion-resistant treatment for aluminium 2004-T3, *Progress in Organic Coatings* **41**, 2001, 287–293.

Wallington S.-A., Labayen T., Poppe A., et al., Sol-gel entrapped materials for optical sensing of solvents and metal ions, *Sensors and Actuators B* **38-39**, 1997, 48–52.

Wang E., Chowa K.-F., Kwan V., et al., Fast and long term optical sensors for pH based on sol-gel, *Analytica Chimica Acta* **495**, 2003, 45–50.

Wang Y. and Ohwaki J., New transparent vitroceramics codoped with Er^{3+} and Yb^{3+} for efficient frequency upconversion, *Applied Physics Letters* **63**, 1993, 3268–3270.

Yanagisawa T., Shimizu T., Kuroda K. and Kato C., The preparation of Alkyltrimethylammonium-Kanemite complexes and their conversion to microporous materials, *Bulletin of the Chemical Society of Japan* **63** (4), 1990, 988–992.

Yang T., Liu J., Zheng Y., et al., Facile fabrication of core-shell-structured Ag@carbon and mesoporous yolk-shell-structured Ag@carbon@silica by an extended Stöber method, *Chemistry-A European Journal* **19**, 2013, 6942–6945.

Yilmaz M., Caldiran Z., Deniz A.R., et al., Preparation and characterization of sol-gel derived n-ZnO thin film for Schottky application, *Applied Physics A Materials Science & Processing* **119**, 2015, 547–552.

Yin W., Zhao L., Zhou L., et al., Enhanced red emission from $\text{GdF}_3\cdot\text{Yb}^{3+}$, Er^{3+} upconversion nanocrystals by Li^+ doping and their application for bioimaging, *Chemistry-A European Journal* **18**, 2012, 9239–9245.

~~Zhang Y., Brinker C.J. and Crooks R., Electrophoretic deposition of sol-gel derived ceramic coatings, *Better Ceramics Through Chemistry V* **271**, 1992, 465–470.~~

Zhou H.Y., Jiang L.J., Cao P.P., et al., Glycerophosphate-based chitosan thermosensitive hydrogels and their biomedical applications, *Carbohydrate Polymers* **117**, 2015, 524–536.

Zhou J., Leño J.L., Jr., Liu Z., et al., Impact of lanthanide nanomaterials on photonic devices and smart application, *Small* **14**, 2018, 1–29.

Znaldi L., Sol-gel deposited ZnO thin films: A review, *Materials Science and Engineering B* **174**, 2010, 18–30.

Abstract

This review presents an insight on the advances in the Sol-gel route for preparation of glasses and glass-ceramics, considering the physical and chemical aspects governing the process. An overview of the most important developments and applications including Sol-gel coatings, appearing as the main technique used in optical as well as protective or photocatalytic applications. Biomaterials prepared by Sol-gel are also highlighted.

Keywords: Biomaterials; Coating deposition methods; Glass-ceramics; Glasses; Mesoporous materials; Optical applications; Photocatalytic coatings; Protective coatings; Sol-gel coatings; Sol-gel fibers

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