State of the Art and Recent Advances in Electrical Conductive Coatings by Sol-Gel Process

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Abstract

With the development of smart materials and the requirement of multifunctional systems, coatings were developed with the aim to improve and optimize many properties and especially in the electrical field (resistivity, conductivity, permittivity,..)

Relative to the electrical conductivity, the need is growing in many activity areas with the recent tendencies (green technology and energy). Recently, the sol-gel route to process coatings was investigated for its ability to develop innovative multifunctional coatings. Because the sol-gel matrix is known to be completely insulating, the conductivity can be brought by the development of a composite material, with the incorporation of conductive fillers into the insulating network.

The aim of this paper is to present an overview of the sol-gel coatings, dedicated to the electrical conduction, started in the 2000's. A rapid introduction will set the context including many "standard" applications of sol-gel coatings. Then, studies are gathered according to the fillers incorporated in the sol-gel formulation (Tables 1-3). Each coating is described in detailed. Correlations and tendencies are identified and discussed. The lowest surface electrical resistance is obtained using metallic fillers (145 m$\Omega_\square$), but the carbon fillers are very promising taking benefit of their various form factors.

After an exhaustive presentation of the state of the art in this field, some new quantitative examples of coatings recently developed are presented. Various systems and architectures are detailed with associated applications. The major results show a surface electrical resistance comparable to the best values listed in the literature (around 130 m$\Omega_\square$), but with carbon fillers against metallic fillers. Furthermore, the combination of carbon fillers and the capability to develop a sol-gel multi-layer is demonstrated. Finally, a key point is relative to the application of these conductive sol-gel coatings on a complex shape substrate.

Keywords: Electrical conductivity • Sol-gel coatings • Conductive fillers • Anticorrosion • Multifunctionnality • Connectors • Carbon black • Conductive organic polymers • Metal nanowires

Introduction

In surface engineering science developed to functionalize a large variety of materials and surfaces, among the very promising "soft chemistry" processes, the sol-gel approach plays a key role. It is a friendly environmental alternative with low temperature synthesis for a new generation of inorganic or hybrid materials [1]. The numerous advantages are mainly the following: a large choice of precursors depending on the wished required properties, a versatile and flexible process allowing a strict control of coating morphology, microstructure and thickness. Another great interest is the capability to shape multiscale coatings from some nanometers to one hundred micrometers thick, on various substrates. For example, the Organic-Inorganic Hybrid (OIH) coatings [2] are promising materials due to their multifunctionality with a broad spectrum of useful properties and a large potential application.

Historically, the sol-gel process starts with J.J. Ebelmen in 1845. He is interested in hydrated silica synthesis based on silicic ether in a wet atmosphere [3]. In 1860, T. Graham introduces terms colloids, sols, and gels, with the study of silicon and aluminium precursor's behaviours in water

and ethanol [4]. In the historical timeline (Figure 1), nearly a century after, in 1939, the German company Schott Glaswerke proposes a patent based on the sol-gel process for the glasses production of rear-view mirror [5].
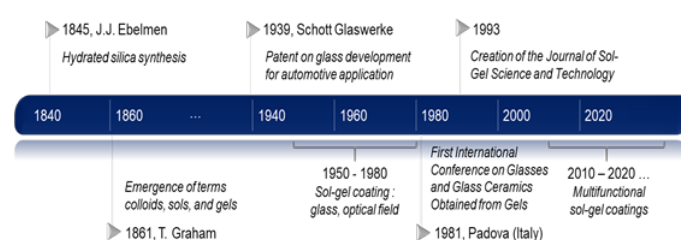

Figure 1. Sol-gel historical time line

The first sol-gel coatings found their application in the optical field with anti-reflective coatings, for the reflection, UV absorption or coloration [6,7]. From the 1980's until today, the sol-gel coatings are developed in a wide range of applications [8-10]. In the 1990's, there is the emergence of hybrid coatings, notably allowing the breakthrough of the anticorrosion and

protective coatings for metallic substrates [11-14].

A pie chart (Figure 2) lists main fields of sol-gel coatings since 1980. There are a lot of applications of sol-gel coatings: in optics [15-17] (reflection, UV-resistant, photochromic, …), mechanics [18,19] (abrasion, hardness, scratch resistant, …), electric field [20-22] (insulating, dielectric, electromagnetic, …), protection: anticorrosion [23-29], self-healing [30,31], self-cleaning [32,33], hydrophobicity [34], energy [35] or in bio-applications [36,37].
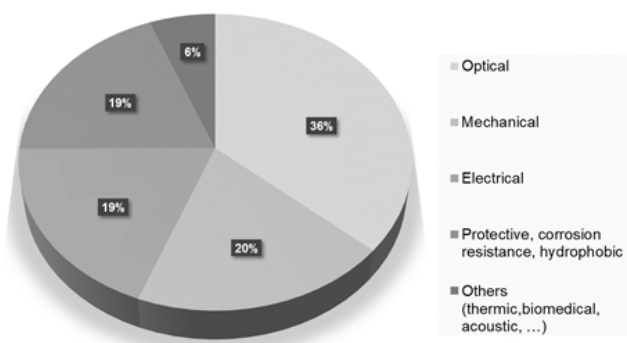
Figure 2. Sol-gel coating fields pie chart since 1980

Development of smart multifunctional coatings emerges few years ago. Many examples exist: superhydrophobic and superoleophilic [38], cleaning, anti-reflective and hydrophobic [39], anti-reflection and self-cleaning [40], antibacterial with self-cleaning [41], adherence and corrosion resistance [42] or again a combination of properties such as corrosion resistance and hydrophobicity [43].

All of these properties are addressed to a large variety of substrates: glasses [34,44,45], polymers [18,19], copper [46], magnesium alloys [47,48], zinc [24,42], aluminium alloys [23,26,28,43,49,50], steel [51,52], fabrics [53,54] or wood [55-57].

One of the real challenges among sol-gel coatings is to bring electrical conductivity property to networks, especially for the OIH network, which are naturally insulating. Indeed, few studies have been the subject of research and even less on dual properties such as electrical conductivity and anti-corrosion for instance.

The term sol-gel and electrical conductivity were historically associated with only the development of transparent fine layers in the optoelectronic field. Various authors proved the feasibility of ZnO thin layers (20-300 nm) [22,58-61], doped with aluminium and/or graphene oxide fillers [62-65]. These coatings show a surface electrical resistivity ranging from 200 $\Omega_\square$ to 5.10^5 $\Omega_\square$.

In the literature, there is a wide fillers range to bring electrical in insulating network. In the sol-gel coating field, there are few works based on metallic, polymeric and carbon fillers, with a surface resistivity ranging from 10^{-2} $\Omega_\square$ to 10^7 $\Omega_\square$. The results of these works will be detailed in a specific section of this review.

In the first part, part A, state-of-the-art of electrically conductive sol-gel coatings will be established. This part is built according to the filler's nature, completed by analysis and discussions of the results. The sol-gel matrices will be dissected at the same time of the major features. Some tendencies will be highlighted.

In part B, we make our contribution to this topic by adding recent and illustrative examples of some conductive sol-gel coatings developed in our researches from the elaboration, shaping step to the working characterization properties. The effect of multi-fillers, sol-gel architecture coatings, and application to complex items will be presented before concluding on future scientific challenges in this field.

Part A: State of the art on Sol-gel coatings for electrical conductivity

The electrical sol-gel coatings are applied on many different substrates. A literature survey of the two last decades shows that these coatings are mostly used to functionalize insulating substrates (glasses, polymers, or ceramics), 93%, against 7% for conductive substrate (metallic alloys or steels) (Figure 3a). There is a real tendency to provide an electrical conductivity to insulating substrates, goes along with other properties according to the final application.
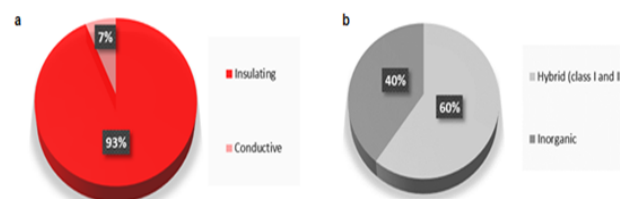

Figure 3. (a) Pie chart showing the substrates nature covered by electrical conductive sol-gel coatings and (b) pie chart showing the sol-gel network composition repartition

Usually, the electrical conduction is not the only property brought by these coatings. One of the most advantages of the sol-gel process is the possibility to combine different properties in the same coating, according to the application fields targeted. Mainly, electrical properties are combined with optics to form transparent conductive coatings [66-70] for the microelectronics or again the development of hybrid solar cells. There are applications on thermal field with heating diffusion [71,72]. Another characteristic studied is the provision of beneficial mechanical properties and especially with a high coating adhesion [73,74].

Recently, new properties are reached with hydrophobic behaviour on polymer [75] or cotton substrates [76]. Some works show sol-gel coatings with multi-properties. Indeed, Okada H. et al. [77] show the feasibility of electrically conductive coating with resistance properties to the temperature and humidity, where the electrical performance is preserved after thermal and humidity exposition. Vinogradov V.V. et al. [78] develop in their study the ability to combine electrical properties with mechanical (adhesion and flexibility) and optical (transparency) aspects.

In 2016, a patent reports an application on aluminium alloys [79]. In these patents, the aim is to replace the Alodine 1200 conversion coating. There is a demand for a new multi-properties concept with both electrical conductivity and corrosion resistance properties, which are in a first approach, antagonist properties.

The conduction is characterized by a charge transport phenomenon. This transport can occur under an electrical field with a charge transfer (electrons for metallic or semiconducting materials or ions for ionic compounds). In the case of sol-gel materials, obtained after sol-gel chemical reactions (hydrolysis and condensation), their matrix can be only inorganic or hybrid, combining organic and inorganic moieties. This depends on the precursors' composition (Figure 4). Commonly metal salts or metal alkoxides are used to produce inorganic matrix whereas organic surfactants as structuring agent or organosilanes are introduced to produce hybrid materials. These later are classified in two classes according the interaction between the organic and the inorganic part. For hybrid Class I weak interaction (Van der Waals strength or hydrogen bonding) exists between both parts whereas strong like (covalent bonding) is created between the organic and inorganic parts for hybrid Class II. A combination of the two classes is possible in the same matrix.
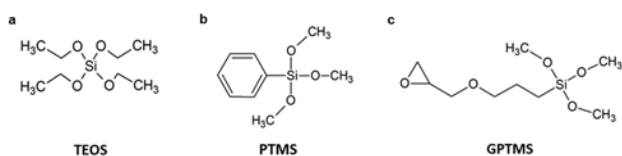
Figure 4. Example of silane sol-gel precursors to obtain inorganic (a) or class II hybrid (b, c) matrix

The literature shows a majority of hybrid sol-gel networks used in electrical conduction application, 60%, against 40% of networks composed of inorganic structures (Figure 3b). The advantages of these hybrid precursors are multiple including an increase of network flexibility, better adhesion properties to the substrates, or also cracking reduction after thermal treatment. The organic networks are less numerous, and the fully inorganic networks are used to obtain ceramic coatings.

In all cases, their chemical composition and structure induce an electrical insulating behaviour. To bring these conduction properties, the way consists of incorporating fillers with a high electrical conductivity level. Figure 5 shows the materials able to reach this objective. Firstly, metals exhibit a high level of electrical conductivity in the range 10^7 to $10^9 S.m^{-1}$.
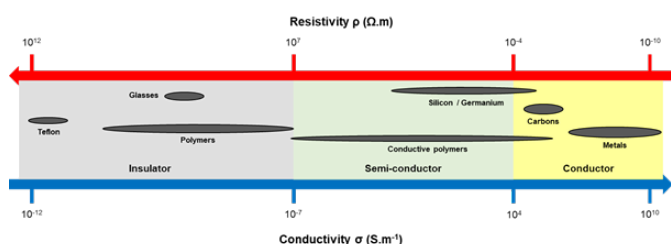
Figure 5. Conductive/resistive properties of different classes of materials

Then, carbon and its derivatives (carbon black, carbon nanotubes, …) are a solution with a conductivity in the range 10^5-10^6 $S.m^{-1}$. Finally, some classes of polymers can be conductive in some conditions, such as PEDOT or PAni (10^{-5} to 10^5 $S.m^{-1}$).

To confer electrical properties to insulating materials, the addition of well-chosen fillers can be interesting especially when they exhibit a high shaping factor. A literature analysis on the period 2000 to 2020 (corresponding to 26 publications) proves the various possibilities of incorporated fillers into the sol-gel network: organic conductive polymer, metallic and carbon fillers. These fillers can be commercially found or various synthesis processes exist in the literature (for metallic nanowires for example). As shown in Figure 6, carbon fillers part corresponds to 58% in the conductive sol-gel coating. For the other fillers, 23% is composed of metallic fillers and 19% for organic conductive polymer fillers. Two levels are identified to bring electrical conductivity: with organic polymer which induces a chemical reaction with the sol-gel network and with the addition of solid fillers, inert towards the network. In this second approach, the electrical percolation threshold will be an important notion and will impact the filler quantity to achieve a conductive state.
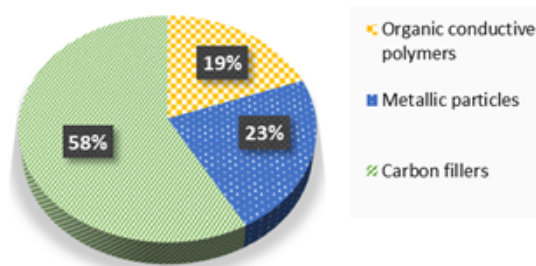
Figure 6. Pie chart showing the different fillers repartition in the sol-gel networks

The Figure 7 shows the surface resistances indexed in the literature between 2000-2020. It gathers all values together and they are classified by the filler nature. The surface resistances vary on a large range ($m\Omega_\square$ to $M\Omega_\square$).
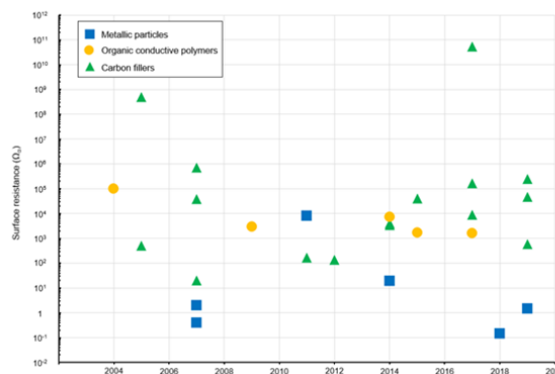
Figure 7. Representation in time of surface resistance values as a function of fillers added in the sol-gel network

Unsurprisingly, the most conductive coatings are obtained using metallic fillers. For the conductive polymer fillers, the surface resistance is relatively high, and these fillers can complicate the chemical structuration of the sol-gel network by chemical reactions. The carbon fillers appear as an interesting compromise between the large choice of morphology and shaping factors (1D, 2D, or 3D) and the surface resistance level, which is around 100 $\Omega_\square$ for the best formulations.

In the following, a table for each filler type (organic conductive polymers-Table 1, metallic particles-Table 2, and carbon fillers-Table 3) is presented to summarize the characteristics of the corresponding sol-gel conductive coatings. For each coating chemical nature of the filler, the network and, the substrate are given, the thermal treatment justifying the nature, hybrid or ceramic, of the matrix is also noted. A specific attention has been brought to the thickness coating and the surface resistances, for the latter two values are reported, the referenced data and a calculated value expressed in $\Omega_\square$, for comparative purposes. This parameter corresponds to the electrical resistivity divided by the coating thickness. In some papers, the surface resistance is already indicated and in other works, some information are missing to determinate the resistance $\Omega_\square$. These tables help to highlight some tendencies about fillers performance on sol-gel conductive coatings. In the 2000's, there are few works, and then there is an increase of this thematic around 2014 with the development of the sol-gel coatings.

Filler	Filler description	Network	Substrate	Thermal Treatment	Thickness	Original data given	Surface Resistance	Year [Ref.]
PEDOT	3,4-ethylenedioxythiophene (EDOT)	Inorganic	PET	120°C / 30 min	1 µm	3 kΩ/□	$3.10^3 \Omega_\square$	2009 [80]
PEDOT:PSS	PEDOT:PSS pellets	Hybrid (I)	Glass or PA	85°C / 30 min	≈ 24 µm	1.7 kΩ/□	$1,7.10^3 \Omega_\square$	2015 [70]

PEDOT:PSS	PEDOT:PSS pellets	Hybrid (II)	Glass or PA	80 - 90°C 30 min	0.05 – 0.2 µm	0.8 to 3 kΩ/sq	$1.6.10^3 \ \Omega_\square$	2017 [81]
PAni	PAni particles (37 wt.% PAni and 63 wt.% silica)	Hybrid (II)	Glass ou PP	80°C 2h and	50-500 µm	$3.8.10^{-4}$	$1.10^5 \ \Omega_\square$	2004 [74]
	Diameter = 430 nm			105°C 1h		S.cm^{-1}		
PPy	Pyrrole (98%)	Inorganic	304L steel	t°amb	≈ 0.16 µm	/	/	2013 [82]
				under N2				
TTF, TCNQ	Tetrathiafulvalene (TTF) and	Hybrid (I)	PP	60°C 48h	150 µm	$9.36.10^{-3}$ S.cm^{-1}	$7.10^3 \ \Omega_\square$	2014 [77]
	7,7,8,8-tetracyanoquinodi-methane (TCNQ)							
	TTF-TCNQ complex with black coloration at 32wt.%.							

Table 1. Sol-gel coatings with electrical conducting polymers

Filler	Filler description	Network	Substrate	Thermal Treatment	Thickness	Original datas given	Surface Resistance	Year [Ref.]
Nickel powder	Particles size: 1-5 µm	Inorganic	304L steel + alumina/silica col-gel coating	300 - 500°C	/	2 Ω.sq^{-1}	$2 \ \Omega_\square$	2007 [83]
Zinc nanoparticles	Nano Amor	Hybrid (I)	Silicon wafer	t°amb. 130°C 2h	1.7 µm	0.71 (Ω.cm^{-1})	$8.3.10^3 \ \Omega_\square$	2011 [86]
	Average size: 130 nm							
Silver powder	Particles size: 1-5 µm	Inorganic	304L steel + alumina/silica col-gel coating	300 - 500°C	/	0.4 Ω.sq^{-1}	$4.10^{-1} \ \Omega_\square$	2007 [83]
Silver nanoparticles	Synthesis of Ag-silica nano-composite from AgNO3 and TEOS	Inorganic	Glass	80°C 5h et 500°C 3h	≈ 10 µm	6871 S.cm^{-1}	$1.45.10^{-1} \ \Omega_\square$	2018 [84]
Silver nanow-ires	Obtained from the polyol process	Inorganic	PET	t°amb. 24h	≈ 0.4 µm	19 Ω.sq^{-1}	$19 \ \Omega_\square$	2014 [78]
	Diameter = 50-150 nm							
	Length = 10 µm							
Silver nanow-ires	Obtained from the polyol process	Hybrid (II)	Al, Mg alloys	80°C < t < 120°C	0,5 - 5 µm	/	/	2016 [79]
	Shape factor 1 - 100							
Silver nanow-ires	Obtained from polyol process	Hybrid (II)	Glass	105°C 30 min	/	1.5 Ω.sq^{-1}	$1,5 \ \Omega_\square$	2019 [85]
	Diameter: 40-80 nm							
	Length: 30-80 µm							
	Dispersed in isopropanol							

Table 2. Conductive sol-gel coatings incorporating metallic fillers

Filler	Filler description	Network	Substrate	Thermal Treatment	Thickness	Original datas given	Surface Resistance	Year [Ref.]
Carbon black	Carbon black: Degussa Purex HS 55	Inorganic	Ceramic (tile)	400°C 1h	≈ 0.5 µm	7.10^{-5} Ω.m	$1,4.10^2 \ \Omega_\square$	2012 [90]
	1.4-1.7 µm agglomerates							
Carbon black	Carbon black: Degussa XE-2B and L6, and, RUF IN-1 and IN-2	Hybrid (II)	Alumina or glass	200°C 15 min	10 to 30 µm	10^4 to 10^8 Ω.cm	5.10^7 to $5.10^{11} \ \Omega_\square$	2005 [71]
	Size: 30 to 500 nm							
Carbon black and carbon nanofibers	Carbon black: Degussa Purex HS 55 Size: 1.4-1.7 µm agglomerates Carbon fibers: Grupo Antolin S.A.	Inorganic	Ceramic (tile)	400°C 1h	≈ 0.5 µm	2.10^{-3} Ω.m	$4.10^3 \ \Omega_\square$	2014 [72]

	Size: Diameter = 30-300 nm Length = ≥ 30 µm							
Graphite	Graphite flakes 10 µm	Inorganic	304L steel + alumina/ silica sol-gel coating	300°C - 500°C	200 µm	20 Ω.sq^{-1}	2.10^1 Ω$_\square$	2007 [83]
Exfoliated graphite oxide	Prepared via the Hummers method	Inorganic	Glass	100°C 3h - 400°C	≈ 0.03 µm	0.45 S.cm^{-1}	$7.4.10^5$ Ω$_\square$	2007 [66]
Reduced graphene oxide (rGO)	Nano Carbon	Hybrid (II)	Cotton (cellulose)	100°C 15 min	≈ 0.01 µm	$5.3.10^{10}$ Ω	$5.3.10^{10}$ Ω$_\square$	2017 [54]
Graphene	Graphene Laboratories Thickness = 8 nm (20-30 monolayers) Lateral size = 550 nm	Hybrid (II)	Cotton (cellulose)	100°C 15 min	≈ 0.01 µm	$1.7.10^5$ Ω	$1.7.10^5$ Ω$_\square$	2017 [54]
Graphene	MExplorer Water disperse graphene paste	Hybrid (II)	Glass	105°C 30 min	/	600 Ω.sq^{-1}	6.10^2 Ω$_\square$	2019 [85]
Graphene	Graphene Laboratories Thickness = 8 nm (20-30 monolayers) Lateral size = 550 nm	Hybrid (II)	PP	105°C 20 min	≈ 0.01 µm	$4.82.10^4$ Ω	$4.82.10^4$ Ω$_\square$	2019 [91]
Graphene	Graphene Laboratories Thickness = 8 nm (20-30 monolayers) Lateral size = 550 nm	Hybrid (II)	PET	105°C 20 min	≈ 0.01 µm	$2.53.10^5$ Ω	$2.53.10^5$ Ω$_\square$	2019 [91]
Carbon nanofibers	Carbon nanofibers: Applied Sciences INC, Pyrograff III Size: Diameter = 70-300 nm Length = 30-150 µm	Hybrid (II)	Alumina or glass	200°C 15 min	10 to 30 µm	1 Ω.cm	5.10^2 Ω$_\square$	2005 [71]
Single-wall carbon nanotubes	Diameter = 2 nm	Hybrid (I)	Glass	150°C 1h	0.3 µm	174.1 Ω.sq^{-1}	$1,74.10^2$ Ω$_\square$	2011 [68]
Multi-wall carbon nanotubes	/	Hybrid (II)	Glass or polycarbonate	40°C 10 min, 130°C 30 min	0.085 µm	3.10^2 (Ω.m)$^{-1}$	39.10^3 Ω$_\square$	2007 [67]
Multi-wall carbon nanotubes	Nanostructured and Amorphous Materials Size CNT1: Diameter = 10-30 nm Length = 1-10 µm Size CNT2 : Diameter = 10-20 nm Length = 10-30 µm	Hybrid (I)	Glass	RT. 48h et 65°C 48h	300 µm	≈ 10^{-3} (Ω.cm)$^{-1}$	$3.3.10^3$ Ω$_\square$	2014 [92]
Multi-wall carbon nanotubes	Nanolab Size: Diameter = 10-20 nm (outside) 5-10 nm (inside) Length = 10-30 µm	Inorganic	Cotton (cellulose)	/	/	40 kΩ.cm^{-2}	40.10^3 Ω$_\square$	2015 [76]

Multi-wall carbon nano-tubes	Alfa Aesar, pristine multi-wall carbon nanotubes	Inorganic	PET	/	/	9.10^3 Ω.sq^{-1}	9.10^3 Ω$_\square$	2017 [75]

Table 3. Sol-gel coatings incorporating carbon based fillers

Organic conductive polymers containing coatings

Very few examples of sol-gel conductive coatings incorporating organic conductive polymers have been reported. The pie chart, Figure 8, shows that the main conductive polymer used is the PEDOT [70,80,81] (polyethylenedioxythiophene). Only one example involving PAni [74] (polyaniline), PPy [82] (polypyrrole) and TTF-TCNQ complex [77] are reported.
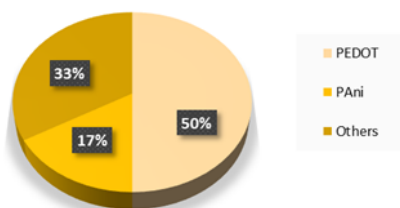
Figure 8. Pie chart showing the conductive polymer fillers repartition in the sol-gel network

Because of chemical affinity, these coatings are for the most part obtained with hybrid organic/inorganic sol-gel precursors. The organic character of fillers and the hybrid matrix imply doing a thermal treatment at relatively low temperatures to preserve the chemical integrity and benefits of the addition of the filler. These sol-gel formulations are mainly performed on insulating substrates (glasses or polymers-83%) and the coatings thicknesses are between 5.10^{-2} to 2.10^2 µm. regarding the surface resistance, it varies from $1.6.10^3$ to 1.10^5 Ω$_\square$.

Špírková M. et al. [74] and Wang H. [81] works are based on hybrid class II precursor (GPTMS) with respectively the PAni or the PEDOT:PSS as the conductive fillers. Nevertheless, the surface resistances are relatively high, in the order of 1 to 3 kΩ$_\square$ for thicknesses between 0.05 to 0.2 µm [81]. The lower resistance is described by Wang H. [81] in a patent, with the incorporation of a PEDOT:PSS in a sol. After thermal treatment (85°C-30 min), the coating thickness is in the order of 0.05 to 0.2 µm with the variation of the surface resistance between 0.8 to 3 kΩ$_\square$.

It is difficult to find some correlation between all of these works, but it is possible to extract two different behaviours with the incorporation of organic conductive polymer. Firstly, Špírková M. et al. [74] use the PAni as conductive polymer but without chemical reaction with sol-gel precursors. It is used as an additional filler to create a conductive network interlocked with the sol-gel matrix.

Secondly, Wang H. et al. [70,81] and Choi J.S. et al. [80], use the PEDOT to bring electrical properties and explain that the PEDOT reacts chemically with the sol-gel precursors. Choi J.S. et al.[80] show the reactions to functionalise EDOT with silicon-based inorganic precursors and then how this functionalised precursor reacts with PEDOT.

Okada H. et al. [77] report a condensation of the electrical conductive TTF-TCNQ complex at the surface of the hybrid matrix, by the UV-vis and XRD characterizations, which improve intrinsically the conductivity of the matrix.

As shown in Figure 9, three mechanisms are conceivable with organic conductive polymers: as additional filler (1) without chemical bonding between both parts resulting in two polymeric networks imbricated; conductive polymer is involved in chemical reaction with the sol-gel network (2) giving rise to a covalent mixed network; the third possibility lies in the combination of these two first (3). In all cases, the level of the surface resistance is relatively high, and the use of other fillers natures is necessary to enhance the conductivity.
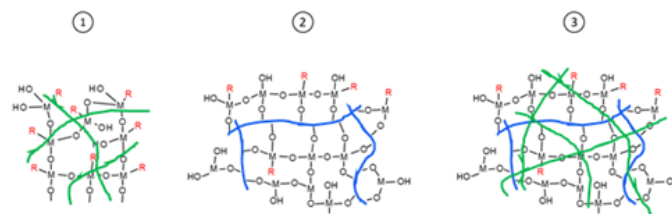

Figure 9. Different conceivable mechanisms with organic conductive polymers with sol-gel network.

Metallic particles containing coatings

Because of its high level of conductivity, introduction of metallic particles in sol-gel formulations to obtain conductive coatings has been investigated. Figure 10, shows that silver [78,79,83-85] is mainly used (86%) as nanomaterial, as well as nickel [83] or zinc [86] fillers. For chemical affinity, the sol-gel network was first based on inorganic dol-gel precursors (50%) and coating was deposited on steel substrate allowing retaining the conductivity of the bare substrate. More recently a patent describes the feasibility to deposit a sol-gel conductive coating incorporating silver nanowires on aluminium alloys [79]. In this latter case an organic-inorganic hybrid matrix embedded the conductive nanomaterial.
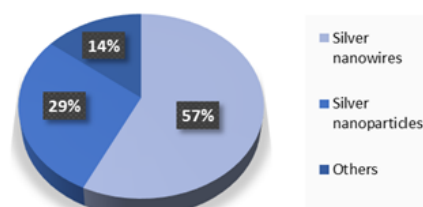

Figure 10. Pie chart showing the metallic fillers repartition in the sol-gel network

The insulate substrates such as glasses, polymers or ceramics have been also investigated with success. With the use of inorganic precursors, the thermal treatments can be higher than 150°C-200°C and ceramic coatings are formed. For the formulation containing hybrid precursors, the thermal treatment does not generally exceed 130°C. The coating thicknesses are relatively low and comprised between 0.4 and 10 µm.

Concerning the surface resistances, the conductivity threshold reached is lower than that of the coatings incorporating conductive polymer due to the intrinsic electrical conductive properties of metallic fillers. The surface resistances are in the range $1.45.10^{-1}$ and $8.3.10^3$ Ω$_\square$. Furthermore, the fillers with a high shaping factor (nanowires) are preferred to improve the electrical conductivity.

Factor (longest dimension In this table, despite the use of metallic nanoparticles, Xie J et al. [86], report a high surface resistance. This can be explained by the relatively thin conductive coatings (≈ 1.5 µm) applied on relatively insulating substrates (silicon wafer). The fillers nature is not the only parameter to bring electrical conductivity, the layer thickness and the fillers shaping factors are key parameters to ensure an efficient conduction and to achieve the percolation threshold.

The filler's geometry and especially the shaping on the smallest) will determine the ease of reaching the electrical percolation threshold. Many statistical models exist to describe this phenomenon, and for the electrical conduction, Kirkpatrick S. [87], Balberg I. [88], and Garboczi E.J. [89] suggested models taking into account the fillers geometry. Higher is the shaping factor, lower is the fillers concentration, for a transition from insulating to the conductive state. This is illustrated in Figure 11, the percolation threshold with a filler of a high shaping factor (as nanowires; 1D) will be achieved easier for a lower filler concentration, 2 vol.%, towards 5 vol.% and 9 vol.% for 2D and 3D particles, respectively.
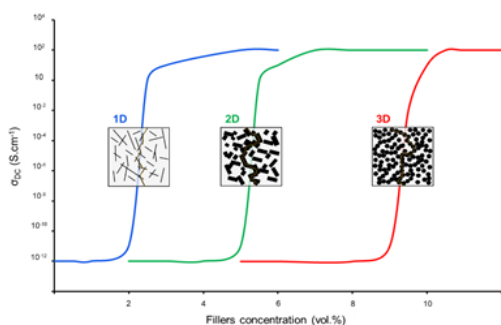
**Figure 11.** Electrical conductivity σDC in function of fillers concentration by aspect ratio

In the same idea, Li X. et al. [85] reported an hybrid sol-gel coating with incorporation of Ag nanowires to achieve a low surface resistance, of 1,5 $\Omega_\square$. Recently, Ma Z. et al. [84] reported a silica/silver nanoparticles based conductive composite coating deposited on glass. The silver nanoparticles are synthesized insitu, from silver nitrate, during the sol-gel reaction. The coating thickness is around 10 μm with a surface resistance of 145 m$\Omega_\square$, which is the lowest value reported at our knowledge.

The metallic nanoparticles are very interesting because of their conduction level, especially with application on chemically inert and insulating substrates. Deposit on metals or metallic, can generate a detrimental galvanic coupling. For this reason, carbon based fillers have been investigated.

Carbon fillers

The main part, reported in the literature of the sol-gel conductive coatings is based on carbon fillers.

They have different advantages and especially a wide range of morphologies and shaping factors: carbon black (1D) [71,72,90], graphite/graphene (2D) [54,66,83,85,91], and carbon fibres/nanotubes (3D) [67,68,71,72,75,76,92]. Figure 12 exhibits the filler repartition in the sol-gel networks at a quite similar proportion.
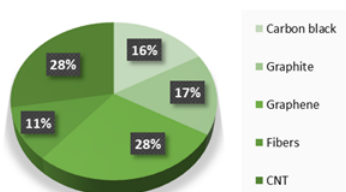

Figure 12. Pie chart showing the carbon fillers repartition in sol-gel network

For the sol-gel networks, 70% of coatings are composed of hybrid precursors. The coatings are quite always deposited on insulating substrates (glasses, polymers, or ceramics). As previously mentioned, the thermal treatment will depend on the organic or inorganic network nature.

The coating thicknesses are variable in the range of 1.10^{-2} to 3.10^2 μm.

At first glance, it is difficult to correlate the surface resistances values with the filler's constitution, their morphology, or with the sol-gel network composition. The resistance range is comprised between 2.10^1 and $5.3.10^{10}$ $\Omega_\square$. These results can be reorganized by the fillers nature to extract some tendencies. Figure 13 gathers these data.
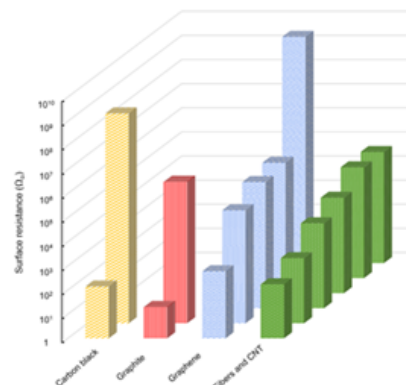
Figure 13. Surface resistance of sol-gel coatings incorporation different carbon based fillers

According the nature of the carbon fillers, it is clearly identifiable that the fillers with a high shaping factor are mostly used. During the last decades, many works are reported with the incorporation of carbon nanotubes. The thicknesses are comprised between 0.085 to 300 μm with a ceiling of the surface resistance at 10^2 to 10^3 $\Omega_\square$. Then, recently, the graphene was added to sol-gel formulations for applications on cotton [54,91], with very thin layers and high surface resistances. So, the use of filler with a small size and a high shaping factor is not the solution to bring an efficient electrical conductivity. Indeed, from Barnes H.A. [93], the shaping factor will impact the formulation of sol with fillers, by inducing an overload in the solution due to a higher effective volume. The friction between fillers will increase and it will lead to an increase of the sol viscosity [93,94] as shown in Figure 14.
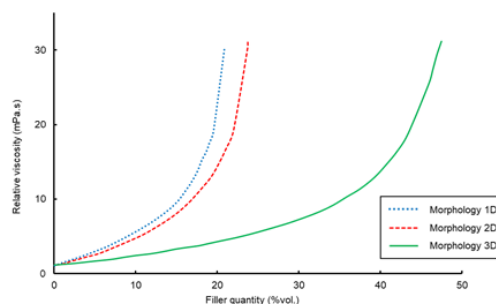
Figure 14. Evolution of the relative viscosity as a function of the filler's morphology

With this partial conclusion, with the use of 1D morphology (carbon black and graphite), it will be easier to develop coating with higher electrical conductivity. Indeed, the first works published (between 2005 to 2012) show an enhancement of the surface resistance. The coatings thickness is variable (0.03 to 200 μm), with the lowest surface resistances near from 100 $\Omega_\square$ [83,90].

Enriquez E. et al. [90] obtained a coating with a surface resistance of 140 $\Omega_\square$. The coatings are deposited by spraying technique with a thickness of around 0.5 μm. The thermal treatment is relatively high (400°C-500°C

during 60 min), compatible with the sol-gel network, which is fully inorganic, based on silica with carbon black. From a carbon black content of 50 wt.%, the surface resistance stabilizes around a hundred square ohm. To try to improve this result, the incorporation of carbon black (20 wt.%) combined with carbon fibers (1 wt.%) [72] is studied. The combination enables a reduction of carbon black concentration and allows achieving a surface electrical resistance slightly higher. This concept of incorporation of fillers with different morphologies is interesting to control the sol viscosity and to enhance the capability to reach the percolation threshold.

The lowest surface resistance is obtained for a sol-gel formulation based on inorganic precursors with graphite fillers [83]. The coating is formed after spray deposition on a substrate, composed of a steel 304 L with an alumina-silica sol-gel coating. The thickness of the conductive coating with graphite is around 200 µm. The surface resistance reported is 20 $\Omega_\square$, the lower with using carbon fillers to our knowledge.

To conclude on this first part, the initial conductivity state will be the value of the electrical conductivity of the sol-gel matrix without filler, and the final conduction state will depend on the filler characteristics. Indeed, the final conductivity value will be function of the filler nature, its purity and/or defects, and its dispersion capability into the insulating sol-gel network. The shaping factor is not the only parameter to consider for the development of a coating with a high electrical conduction level. The fillers behaviour into the sol with their effects on the viscosity and on the thickness are also important parameters. So, many parameters need to be identified and controlled, for the development of a coating with all the electrical properties requested.

This state of the art about electrical conductive sol-gel coatings can be an interesting base for the development of new sol-gel multi functionalized coatings. In comparison with the different works published and the performances obtained, the carbon fillers are good candidates with a lot of advantages (shaping factor, morphology, availability, cost…). In the field of such innovative and multifunctional materials, in the next part below, different sol-gel architectures will be presented, with the use of multi-fillers to achieve multi-properties as electrical conductivity, corrosion resistance or coloration. A focus will be done on the sol-gel coating application on complex items.

Part B: Some advances

Carbon based fillers present many different shaping factors (φ). In the following examples, the sol-gel conductive coating was mainly based on carbon black fillers from IMERYS company (φ ≈ 1) even if other carbon fillers were investigated such as graphene from Graphene Production (φ=10-100) or carbon fibers from CAR FiberTec (φ=500). The sol-gel matrix is a class II organic-inorganic hybrid network involving the (3-glycidyloxipropyl) trimethoxisilane (GPTMS; ≥ 98%, MERCK) and zirconium (IV) propoxide (TPOZ; 70 wt.% in 1-propanol, MERCK) as precursors. Glacial acetic acid (VWR) and deionized water are used as chelating agent and solvent respectively. As indicated above, different carbon fillers are used as conductive species: carbon black (with the acronym CB), graphene (Gr), and carbon fibers (CF).

The sols were deposited onto the substrates by the dip-coating method using the equipment RDC 21-K Dip Coater (Bungard Elektronik GmbH and Co.) with a controlled withdrawal speed in the range 50 to 600 mm.min^{-1}.

The characterizations were mainly focused on the coatings morphology and on the surface electrical resistance and/or corrosion resistance properties. The morphology was observed from a cross-section using the FIB technique (SEM Helios 600 i (FEI)). The surface electrical resistance was measured by a two-point probe method with copper electrodes on the sample and a high-precision multimeter (model 2110 5½ Digit Multimeter-Keithley). A minimum of six measurements on two samples was realized.

In the following, several examples will be presented, and the effect of the fillers (morphology, concentration) will be discussed. Various substrates were used and brought much information on the targeted electrical conductivity property.

Finally, an example of a sol-gel conductive coating with carbon fillers will be presented on a complex item which is an industrial electrical connector (from Amphenol Socapex Company).

A first example is based on a sol-gel coating composed only of carbon black fillers (CB). This filler has a 3D shape, circular, with a unit size 60 nm. The sol is deposited onto metallic alloy substrate by dip-coating. The criteria for this coating are to preserve the electrical conductivity to the system, and to add dark coloration, to minimize the shining metallic aspect. Figure 15 shows the coating homogeneity after deposition and thermal treatment, with no macroscopic defect is visible.
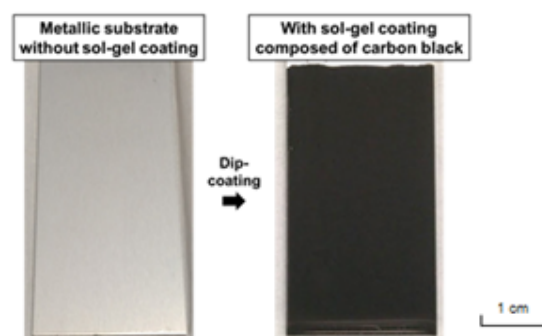
Figure 15. Sol-gel coating with carbon black fillers on metallic substrate by dip-coating process

The cross-section view on the Figure 16 brings information about the coating morphology. Indeed, the analysis reveals that porosity at different sizes is visible in the whole volume (Figure 16a). The coating thickness is around 3.5 µm. At a higher magnification, the interface between the sol-gel coating and the substrate is clearly identifiable (Figure 16b). There is both a good affinity and matter continuity with the metallic alloy. The presence of carbon black is proved with some spherical particles inside the sol-gel network (encircled on the cross-section).
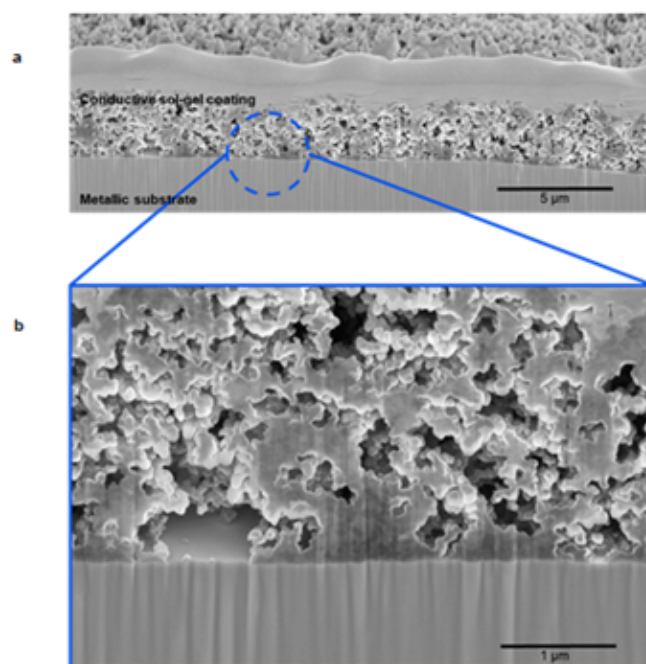
Figure 16. SEM observation of the cross-section after FIB preparation of sol-gel coating with carbon black on metallic substrate at two different magnifications ((a) x5000 and (b) x25 000)

Regarding the electrical properties, the surface electrical resistance is evaluated at 130 m$\Omega_\square$ (±10). Do not forget that without carbon black, the sol-gel network leads to a fully insulating coating. So, the obtained value corresponds to the surface electrical resistance of the metallic substrate (100 m$\Omega_\square$). This level of resistance is comparable with the value obtained by Ma. Z. et al. [84], for Ag/silica sol-gel coating with metallic fillers.

Other works, from Hübert T. et al. [71] also demonstrated a high surface resistance (3.3.10^3 $\Omega_\square$) with hybrid sol-gel coating based on carbon black on ceramic or glass substrates.

This difference can be explained by the substrate effect. Indeed, in our configuration the substrate is electrically conductive (metallic alloy) and in the work reported, the substrate is insulating (ceramic). There is an influence of the substrate nature on the electrical conduction, especially according to the Z axis.

In this other case, the sol-gel coatings were deposited onto insulating substrates to study the influence of the only fillers on the electrical conduction properties and the facility to achieve the percolation threshold. The sol-gel formulations were composed of mixtures: carbon black+graphene (CB+Gr) and carbon black+carbon fibers (CB+FC). Nevertheless, graphene and carbon fibers were added in a lower content than carbon black. Formulations are composed of 75 wt.% of CB with 6 wt.% of Gr and 75 wt.% of CB with 25 wt.% of FC.

Figure 17 shows the surface microscopic analysis of the coatings. For the CB+Gr based coating, the graphene is detected on the surface (zoom on the cross-section Figure 17a). It is chemically linked with the sol-gel network and the carbon black. With the incorporation of carbon fibers, a preferential orientation is proved (Figure 17b). This can be due to the dip-coating process where the fibers orientate alongside the substrate during the withdrawal step.
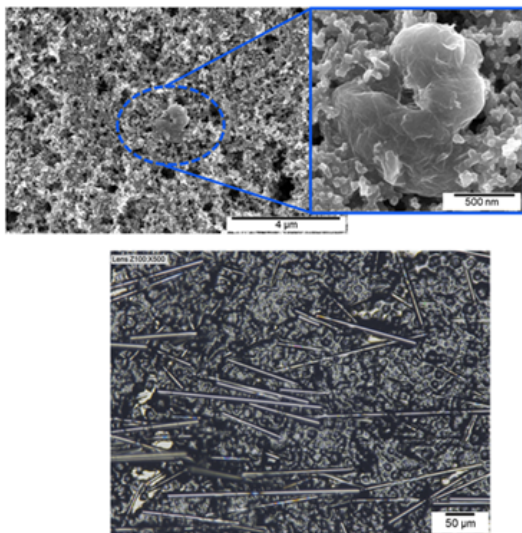
Figure 17. Surface analysis and optical microscopy on sol-gel coating with multi-fillers ((a) carbon black + graphene CB+Gr and (b) carbon black + carbon fibers CB+FC)

A cross-section of the coating with CB+FC is presented in Figure 18. Carbon fibers are visible in both the bulk and the surface. The thickness of the coating is around 7 μm. Efficient chemical links are identifiable between carbon fibers, carbon black, and the sol-gel network (dotted square on the cross-section-Figure 18). The surface resistance was measured in each case. With CB+Gr, the resistance value is around 85 $\Omega_\square$ (± 6) and for the coating with CB+FC, two different surface resistances were determined. Indeed, a heterogeneity in the electrical conduction distribution was proved because of the fibers orientation during the withdrawal step. In the direction of the deposit, the surface resistance is 60 $\Omega_\square$ (±7) and perpendicularly to

the deposit the resistance is 110 $\Omega_\square$ (± 6).
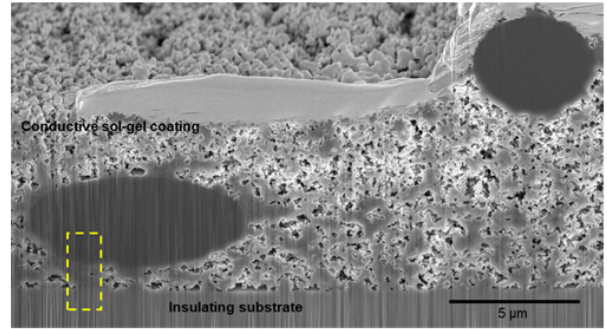
Figure 18. SEM view of the cross-section after FIB preparation of two sol-gel layers

In the literature, no study is reported dealing with a sol-gel coating composed of both carbon black and graphene. For a mixture of carbon black and carbon fibers, a work from Enriquez E. et al. [72] is found. The surface electrical resistance obtained is of 4.10^3 $\Omega_\square$ for a thickness coating of 0.5 μm. The substrate is also insulating, but the difference with our work can be explained by the fillers ratio in the sol-gel network (75 wt.% of CB plus 25 wt.% of CF against 20 wt.% of CB plus 1 wt.% of CF in their case).

One of the major advantages of the sol-gel process is the possibility to adjust the sol formulation in order to combine different properties in the same material. For coatings exhibiting electrical properties, other additional properties are often associated, as previously indicated: electrical and thermal [71,72], electrical and optical [66-68,70], or electrical and mechanical properties [74,78] for instance.

As presented below, sol-gel coatings can be developed with electrical conduction properties combined with other physical properties. In the next paragraphs two systems based on two sol-gel layers will be presented.

The first architecture is composed of a porous sol-gel coating only loaded with carbon black CB and with a sol-gel top-coat with graphene Gr fillers. The aim of this architecture is to create electrical conductive paths by the first deposit and to fill the porous CB layer to reinforce the mechanical properties. Also, it is interesting to bring graphene fillers in the final top-coat. The Figure 19 exhibits the effect of the top-coat application by dip-coating process. The infiltration is completed without formation of an extra thickness (still 3.5 μm). For the surface electrical resistance, the graphene fillers preserve a low resistance, with a value of 150 m$\Omega_\square$.
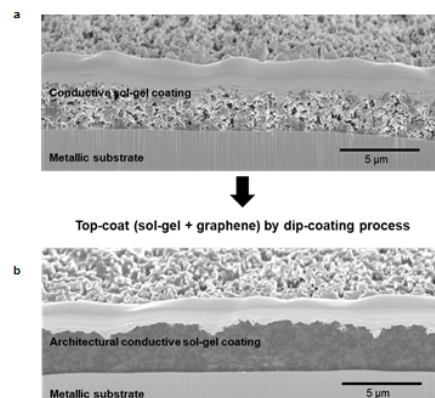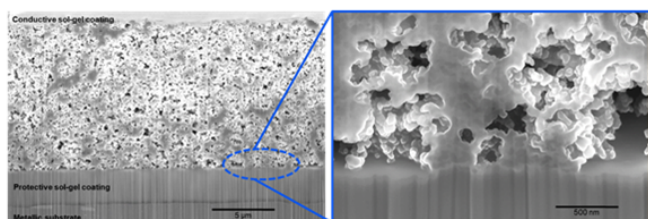

Figure 19. SEM Cross-section after FIB preparation of the sol-gel coating with carbon black only (a) and the sol-gel CB coating with sol-gel Gr top-coat (b)

The graphene is known in the literature to bring several other interesting properties [95-97]. Here, in addition to the electrical conductivity, the graphene is incorporating for mechanical (lubrication) and hydrophobic

properties.

The second architecture is composed of two sol-gel layers, in the aim to protect the metallic substrate against corrosion and to bring additional electrical conduction properties. The challenge is here to merge two antagonist properties. The architecture is presented in the Figure 20 highlighting the intime interface of the two sol-gel layers. The first layer was applied by the dip-coating process directly onto the metallic substrate. This sol-gel coating was characterized alone in previous works [50] for their corrosion resistance properties (500 h to BSN exposure). It is a fully electrical insulating coating 4 µm thick. The second layer, 15 µm thick, is based on both black carbon CB and graphene Gr fillers to confer surface conductivity. A key point is to underline that strong chemical bonds are identified between the two layers, which can be possible by the sol-gel matrix precursors which are of the same chemical family involving an zirconium and silicon mixed matrix.

Figure 20. SEM view of the cross-section after FIB preparation of two sol-gel layers

The electrical surface resistance is 70 $\Omega_\square$, in the same range of the values listed in the literature on insulating substrate.

Here, the architecture exhibits a new concept with a combination of two antagonist properties. Indeed, the electrical conduction and corrosion resistance are both ensured even though the conductive materials are known to have a low anti-corrosion performance, with the charge transfer. A BSN exposure test was realized with this coating, and a very promising durability of 168 h ($\approx$ 1 week) was obtained.

A final point detailed in this paper is the development of these electrical conductive sol-gel coatings on a very complex in shape substrates. Indeed, the final targeted application is to deposit functional coatings onto an electrical connector, from Amphenol Socapex Company, for the aerospace and military field. These connectors present a particularly complex shape and uneven geometry with holes, screw threads and gears.

The sol-gel architecture with successively the porous CB layer and the Gr top-coat was deposited on the metallic connector by dip-coating process. Figure 21 shows the coated connectors with an efficient covering of the coating on all parts of the connector. The dip-coating technique is very promising and seems well adapted to sol-gel coating applications on complex items, even if some improvements have to be done to limit the formation of over thicknesses, partially observed, due to the gravitational flow during the withdrawal step. On the flat surfaces there is 4 µm of conductive sol-gel coatings but on uneven parts, the thickness can be reach 15-20 µm.

Figure 21. Sol-gel coating on Amphenol Socapex's connectors by dip-coating process

Another characterization was investigated on the connector with the conductive sol-gel coating, in order that to determine the electrical continuity when it is assembled. This test was executed according to a military standard MIL-DTL-38999. After assembly, a current of 1 volt under 1 ampere was applied and a voltage drop is measured in mV. To be complied with the standard a maximum value of 2.5 mV must be expected, with the sol-gel conductive architecture, an electrical continuity of 0.1 mV was measured. This confirms the electrical conductivity performance achieve with the carbon based fillers formulations.

Conclusion

The conductive sol-gel coatings constitute an innovative development field which can present a great interest in many application fields.

This paper summarizes the different developments of electrically conductive sol-gel coatings reported in the literature these last years. These coatings may be applied on many different substrates as, polymers, glasses, ceramics,… The choice of filler nature depends on the application aimed. For example, organic conductive polymers are an efficient alternative for electronic devices with the requirement of high flexibility (smartphone or computer with new smart screen). For the optical field, graphene or carbon nanotubes are preferentially used for their transparency properties combined with electrical conduction. Nevertheless, the sol-gel process is characterized by the possibility to modify a lot of parameters to achieve the required coating. Indeed, after the filler nature is chosen, the filler concentration, the sol viscosity, the coating thickness, the deposit technique and, the thermal treatment are many parameters to control.

Very promising results are obtained with electrical performances equivalent or even better than coatings found in the literature. The investigation field is really large with a combination of multiparameters. Indeed, here only sol-gel coatings with carbon fillers were presented, but it is conceivable to combine fillers with different natures, as metallic and carbon based fillers for instance. Furthermore, the feasibility to combine multi-properties with a new concept of antagonist criteria such as electrical conduction and corrosion resistance has been demonstrated.

In the future, it will be interesting to develop "all-in-one" coating in one step, confering these multiproperties.

Conflict of Interest Statement

The authors declare no conflicts of interest.

References

1. Brinker, CJ and Scherer GW. "The physics and chemistry of sol-gel processing." *Sol-Gel Science* (1990).

2. Judeinstein, P and Sanchez C. "Hybrid organic–inorganic materials: a land of multidisciplinarity. "*J Mat Chem* (1996) 6: 511.

3. Ebelmen, JJ. "Chimie sur une production artificielle de silice diaphane." *Comptes-rendus de l'Académie des Sciences. (*1845) 21: 502-507.

4. Graham, T. "X. Liquid diffusion applied to analysis."*Philosophical Transactions of the Royal Society of London*. (1861) 151:183.

5. Geffcken, W and Berger E. " p. Jenaer Glaswerke Schott & Gen., Jena." Deutsches Reichspatent . (1939) 736411.

6. Uhlmann, DR, Motakef S, Suratwala T and Wade R, et al." Ceramic films for optical applications." *J. Sol-Gel Sci. Technol.* (1994) 2: 335.

7. Livage, J. "Sol-gel Chemistry in Medicinal Science." *Rev. Verre* . (2000) 6.

8. Sakka, S. "Preparation and properties of sol-gel coating films." *Journal of Sol-Gel Science and Technology*. (1994) 2: 451.

9. Aegerter, MA, Almeida R, Soutar A and Tadanaga K, et al. "Coatings made by sol–gel and chemical nanotechnology." *J. Sol-Gel Sci. Technol.* (2008) 47: 203.

10. Minami, T. "Advanced sol–gel coatings for practical applications." *J. Sol-Gel Sci. Technol.* (2013) 65: 4.

11. Kato, K. "Enhancement of the corrosion resistance of substrates by thin SiO2 coatings prepared from alkoxide solutions without catalysts." *J. Mater. Sci.* (1993) 28: 4033.

12. de Lima Neto, P, Atik M, Avaca LA and Aegerter MA. "Sol-gel coatings for chemical protection of stainless steel." *J. Sol-Gel Sci. Technol.* (1994) 2: 529.

13. Guglielmi, M. " Sol-Gel Coatings on Metals." *J. Sol-Gel Sci. Technol.* (1997) 8: 443.

14. Mackenzie, JD and Bescher E. "Physical Properties of Sol-Gel Coatings."*J. Sol-Gel Sci. Technol.* (2000) 19: 23.

15. Pénard, AL, Gacoin T and Boilot JP. "Functionalized Sol–Gel Coatings for Optical Applications." *Acc. Chem. Res.* (2007) 40: 895.

16. Rose, K, Dzyadevych S, Fernández-Lafuente R and Jaffrezic N, et al. "Hybrid coatings as transducers in optical biosensors."*J. Coatings Technol. Res.* (2008) 5: 491.

17. Biswas, PK." Sol–gel thin films for optics and photonics." *J. Sol-Gel Sci. Technol.* (2011) 59: 456.

18. Schottner, G, Rose K and Posset U. " Scratch and Abrasion Resistant Coatings on Plastic Lenses-State of the Art, Current Developments and Perspectives." *J. Sol-Gel Sci. Technol.* (2003) 27: 71.

19. Lee, TH, Kang ES and Bae BS. "Catalytic effects of aluminum butoxyethoxide in sol-gel hybrid hard coatings."*J. Sol-Gel Sci. Technol.* (2003) 27: 23.

20. Olding, T, Sayer M and Barrow D. "Ceramic sol–gel composite coatings for electrical insulation."*Thin Solid Films* (2001) 398–399: 581.

21. Shilova, OA, Hashkovsky SV and Kuznetsova LA. "Sol-Gel preparation of ceramic coatings for electrical, laser, space engineering and power."*J. Sol-Gel Sci. Technol.* (2003) 26: 687.

22. Znaidi, L." Sol–gel-deposited ZnO thin films: A review." *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* (2010) 174: 18.

23. Esteban, J. "Développement par procédé sol-gel de revêtements anti corrosion d'alliages d'aluminium à usage aéronautique: de l'effet barrière à l'auto-cicatrisation." *Thèse de l'Université de Toulouse 3 - Paul Sabatier.* (2011).

24. Meiffren, V. "Développement de nouveaux revêtements anti-corrosion sur alliages de zinc par des voies sol-gel en milieu aqueux ou faiblement solvanté." *Thèse de l'Université de Toulouse 3 - Paul Sabatier.* (2011).

25. Cambon, JB. "Elaboration et caractérisation de revêtements anti-corrosion par voie sol-gel sur l'acier inoxydable martensitique X13VD." *Thèse de l'Université de Toulouse 3 - Paul Sabatier.* (2012).

26. Jaubert, O. " Revêtements hybrides multifonctionnels élaborés par voie sol-gel pour la protection d'alliages d'aluminium pour l'aéronautique (AA2024-T3)." *Thèse de l'Université de Toulouse 3 - Paul Sabatier.* (2012).

27. Figueira, RB, Silva CJR and Pereira EV. "Organic–inorganic hybrid sol–gel coatings for metal corrosion protection: a review of recent progress."*J. Coatings Technol. Res.* (2015) 12: 1.

28. Noiville, R. " Revêtements hybrides autocicatrisants pour la protection contre la corrosionde l'alliage d'aluminium 2024-T3: Introductionde nanoréservoirs d'inhibiteur de corrosion." *Thèse de l'Université de Toulouse 3 - Paul Sabatier.* (2016).

29. Figueira, RB. "Hybrid sol–gel coatings for corrosion mitigation: A critical review."*Polymers (Basel). (*2020) 12: 689.

30. AbdolahZadeh, M, van der Zwaag S and Garcia SJ. "Self-Healing Corrosion-Protective Sol–Gel Coatings Based on Extrinsic and Intrinsic Healing Approaches." *Adv. Polym. Sci.* (2016) 273: 185.

31. Silva, ACM, Moghadam AD, Singh P and Rohatgi PK. "Self-healing composite coatings based on in situ micro nanoencapsulation process for corrosion protection." *J. Coatings Technol. Res.* (2017) 1.

32. Ganbavle, VV, Bangi UKH, Latthe SS and Mahadik SA, et al." Self-cleaning silica coatings on glass by single step sol–gel route." *Surface and Coatings Technology*. (2011) 205: 5338.

33. Power, AC, Barrett A, Abubakar J and Suarez LJ, et al." Versatile self-cleaning coating production through sol–gel chemistry." *Adv. Eng. Mater.* (2016) 18: 76.

34. Hata, S, Kai Y, Yamanaka I and Oosaki H, et al. "Development of hydrophilic outside mirror coated with titania photocatalyst." *JSAE Rev.* (2000) 21: 97.

35. Pettit, RB and Brinker CJ. "Use of sol-gel thin films in solar energy applications."*Sol. Energy Mater.* (1986) 14: 269.

36. Böttcher, H. "Bioactive Sol-Gel Coatings."*J. Für Prakt. Chemie.* (2000) 342: 427.

37. Gollwitzer, H, Haenle M, Mittelmeier W and Heidenau F, et al." A biocompatible sol–gel derived titania coating for medical implants with antibacterial modification by copper integration." *AMB Express.* (2018) 8.

38. Mahadik, SA, Pedraza FD, Relekar BP and Parale VG, et al. "Synthesis and characterization of superhydrophobic–superoleophilic surface."J. *Sol-Gel Sci. Technol.* (2016) 78: 475.

39. Dey, T and Naughton D." Cleaning and anti-reflective (AR) hydrophobic coating of glass surface: A review from materials science perspective." *J. Sol-Gel Sci. Technol.* (2016) 77: 1.

40. Sarkın, AS, Ekren N and Sağlam Ş. "A review of anti-reflection and self-cleaning coatings on photovoltaic panels."*Sol. Energy.* (2020) 199: 63.

41. Estekhraji SAZ and Amiri S. "Sol–gel preparation and characterization of antibacterial and self-cleaning hybrid nanocomposite coatings." *J. Coatings Technol. Res.* (2017) 14: 1335.

42. Savignac, P, Menu MJ, Gressier M, and Denat B, et.al. "Improvement of Adhesion Properties and Corrosion Resistance of Sol-Gel Coating on Zinc."Molecules (2018) 23: 1079.

43. Maeztu, JD, Rivero PJ, Berlanga C and Bastidas DM, et al., "Effect of graphene oxide and fluorinated polymeric chains incorporated in a multilayered sol-gel nanocoating for the design of corrosion resistant and hydrophobic surfaces."*Appl. Surf. Sci.* (2017) 419: 138.

44. Mennig, M, Schmitt M and Schmidt H. "Synthesis of Ag-Colloids in Sol-Gel Derived SiO2-Coatings on Glass."*J. Sol-Gel Sci. Technol. (*1997) 8: 1035.

45. Hattori, A and Tada H. "High photocatalytic activity of f-doped tio2 film on glass."J. Sol-Gel Sci. Technol. (2001) 22: 47.

46. Nikkola, J, Mannila J, Mahlberg R and Siivinen J, et al." Sol–gel based protective coatings for copper products." *J. Coatings Technol. Res.* (2008) 5: 335.

47. Upadhyay, V, Bergseth Z, Kelly B and Battocchi D. "Silica-Based Sol-Gel Coating on Magnesium Alloy with Green Inhibitors."*Coatings* (2017) 7.

48. Nezamdoust, S, Seifzadeh D and Rajabalizadeh Z. " Application of novel sol–gel composites on magnesium alloy." *J. Magnes. Alloy.* (2019) 7: 419.

49. Cambon, JB, Esteban J, Ansart F and Bonino JP, et al. "Effect of cerium concentration on corrosion resistance and polymerization of hybrid sol–gel coating on martensitic stainless steel." *Progress in Organic Coatings*. (2012) 47: 3170.

50. Genet, C, Menu MJ, Gavard O and Ansart F, et al. " Innovative formulation combining al, zr and si precursors to obtain anticorrosion hybrid sol-gel coating." *Molecules.* (2018) 23: 1135.

51. Galliano, P, De Damborenea JJ, Pascual MJ and Durán A. "Sol-Gel Coatings on 316l steel for clinical applications."*J. Sol-Gel Sci. Technol.* (1998) 13: 723.

52. Lavollée, C. "Revêtements hybrides architecturés élaborés par voie sol-gel pour la protection anticorrosion et anti-usure de l'acier DC04." *Thèse de l'Université de Toulouse 3 - Paul Sabatier*. (2015).

53. Ismail, WNW. " Sol–gel technology for innovative fabric finishing-A Review." J. Sol-Gel Sci. Technol. (2016), 78: 698.

54. Kowalczyk, D, Fortuniak W, Mizerska U and Kaminska I, et al. "Modification of cotton fabric with graphene and reduced graphene oxide using sol–gel method."*Cellulose* (2017) 24: 4057.

55. Tshabalala, MA and Sung LP. "Wood surface modification by in-situ sol–gel deposition of hybrid inorganic organic thin films."*J. Coatings Technol. Res.* (2007) 4: 483.

56. Subasri, R, Reethika G and Soma Raju KRC. "Multifunctional sol-gel coatings for protection of wood." *Wood Mater. Sci. Eng.* (2013) 8: 226.

57. Tsvetkova, IN, Krasil'nikova LN, Khoroshavina YV and Galushko AS, et al. "Sol-gel preparation of protective and decorative coatings on wood."J. *Sol-Gel Sci. Technol.* (2019) 92: 474.

58. Tsuchiya, T, Emoto T and Sei T. "Preparation and properties of transparent conductive thin films by the sol-gel process."*J. Non. Cryst. Solids*. (1994) 178: 327.

59. Tang, W and Cameron DC. "Aluminum-doped zinc oxide transparent conductors

deposited by the sol-gel process."T*hin Solid Films*. (1994) 238: 83.

60. Nishio, K, Miyake S, Sei T and Watanabe Y, et al. "Preparation of highly oriented thin film exhibiting transparent conduction by the sol-gel process."*J. Mater. Sci.* (1996) 31: 3651.

61. Ohyama, M, Kozuka H and Yoko T. "Sol-Gel preparation of transparent and conductive aluminum-doped zinc oxide films with highly preferential crystal orientation."*J. Am. Ceram.* (1998) 8: 1622.

62. Valle, GG, Hammer P, H. Pulcinelli S and Santilli CV. "Transparent and conductive ZnO:Al thin films prepared by sol-gel dip-coating."*J. Eur. Ceram. Soc.* (2004) 24: 1009.

63. Rydzek, M, Reidinger M, Arduini-Schuster M and Manara J. "Comparative study of sol–gel derived tin-doped indium- and aluminum-doped zinc-oxide coatings for electrical conducting and low-emitting surfaces."*Prog. Org. Coatings* (2011) 70: 369.

64. Schellens, K, Capon B, De Dobbelaere C and Detavernier C, et al. "Solution derived ZnO:Al films with low resistivity." *Thin Solid Films*. (2012) 524: 81.

65. Yu, X, Xu J, Lu H and Fang G. "Sol-gel derived Al-doped zinc oxide Reduced graphene oxide nanocomposite thin films." *J. Alloys Compd*. (2017) 699: 79.

66. Watcharotone, S, Dikin DA, Stankovich S and Piner R, et al. "Graphene–Silica Composite Thin Films as Transparent Conductors."*Nano Lett.* (2007) 7: 1888.

67. Al-Dahoudi, N. "Formation of a conductive nanocomposite on plastic and glass substrates through wet chemical deposition of well dispersed carbon nanotubes."*AIP Conf. Proc.* (2007) 929: 100.

68. Jeon, J, Il Lee T, Choi JH and Oh HS, et al. "Enhanced stability of carbon nanotube transparent conductive film with sol-gel silica layer."*Electrochem. Solid-State Lett.* (2011) 14: K28.

69. Senani, S, Campazzi E, Villatte M and Druez C. "Potentiality of UV-cured hybrid sol–gel coatings for aeronautical metallic substrate protection."*Surf. Coatings Technol.* (2013) 227: 32.

70. Wang, H and Kumar V. "Transparent and conductive polysiloxanes/ PEDOT:PSS nanocomposite thin films with a "water-impermeable" property to significantly enhance stability of organic inorganic hybrid solar cells." *RSC Adv*. (2015) 5: 9650.

71. Hübert, T, Shimamura A and Klyszcz A. *Mater. Sci. Pol.* (2005) 23: 61.

72. Enríquez, E, de Frutos J, Fernández JF and de la Rubia MA. "Conductive coatings with low carbon-black content by adding carbon nanofibers." *Compos. Sci. Technol.* (2014) 93: 9.

73. Wei, Y, Yeh JM, Jin D, and Wang J, et al." Composites of Electronically Conductive Polyaniline with Polyacrylate-Silica Hybrid Sol-Gel Materials." *Chem. Mater.* (1995) 7: 969.

74. Špírková, M, Stejskal J and Prokeš J. "Hybrid organic-inorganic coatings and films containing conducting polyaniline nanoparticles."*Macromol. Symp.* (2004) 212: 343.

75. Yao, W, Bae KJ, Jung MY and Cho YR. "Transparent, conductive and superhydrophobic nanocomposite coatings on polymer substrate.*"J. Colloid Interface Sci. (2017) 506: 429.*

76. Nasirizadeh, N, Dehghani M and Yazdanshenas ME. "Preparation of hydrophobic and conductive cotton fabrics using multi-wall carbon nanotubes by the sol gel method.*" J. Sol-Gel Sci. Technol.* (2015) 73: 14.

77. Okada, H, Tanaka K and Chujo Y. "Preparation of environmentally resistant conductive silica-based polymer hybrids containing tetrathiafulvalene tetracyanoquinodimethane charge-transfer complexes." *Polym. J. (*2014) 46: 800.

78. Vinogradov, VV, Agafonov A and Avnir D." Conductive sol–gel films." *J. Mater. Chem. C* (2014) 2: 3914.

79. Cambon, JB, Esteban J, Mafouana R and Rodriguet JP. "Elaboration d'un traitement anti-corrosion par voie sol-gel." *Ruetsch.* (2016) FR3047491-A1.

80. Choi, JS, Jeon JK, Ko YS and Park YK, et al. "Electrical and physicochemical properties of Poly(3,4-ethylenedioxythiophene)-based organic inorganic hybrid conductive thin films."*Thin Solid Films* (2009) 517: 3645.

81. Wang, H. "US 2017/0037259." Electrically conducting PEDOT sol-gel derived coating, (2017)

82. Raveh, M, Liu L and Mandler D. "Electrochemical co-deposition of conductive polymer–silica hybrid thin films."*Phys. Chem. Chem. Phys.* (2013) 15:10876.

83. Barrow, M. "Sol-gel derived resistive and conductive coating." *EP1370497-B1*. (2007).

84. Ma, Z, Jiang Y, Xiao H and Jiang B, et al. "Sol-gel preparation of Ag-silica nanocomposite with high electrical conductivity."*Appl. Surf. Sci.* (2018) 43: 732.

85. Li, X, Kim N, Youn S and An TK, et al. "Sol–Gel processed organic–inorganic hybrid for flexible conductive substrates based on gravure-printed silver nanowires and graphene." *Polymers* (Basel). (2019) 11: 1.

86. Xie, J, Guo W and Wang J. "Sol-gel-derived hybrid conductive films for electromagnetic interference (EMI) shielding." *J. Wuhan Univ. Technol. Mater. Sci. Ed.* (2011) 26: 216.

87. Kirkpatrick, S. "Percolation and conduction."*Rev. Mod. Phys.* (1973) 45: 574.

88. Balberg, I, Binenbaum N and Wagner N. "Percolation thresholds in the three-dimensional sticks system." *Phys. Rev. Lett.* (1984) 52: 1465.

89. Garboczi, EJ, Snyder KA and Douglas JF. "Geometrical percolation threshold of overlapping ellipsoids."*Phys. Rev.* (1995) 52: 819.

90. Enríquez, E, Fernández JF and De La Rubia MA. "Conductive coatings with low carbon-black content by adding carbon nanofibers."*Carbon N. Y.* (2012) 50: 4409.

91. Kowalczyk, D, Brzezinski S, Kaminska I and Wrobel S. "Elemental segregation in an AlCoCrFeNi high-entropy alloy A comparison between selective laser melting and induction melting." *J. Alloys Compd. (*2019) 784: 22.

92. Pokrass, M, Azulay D, Balberg I and Atar N, et al." Electrical properties study of multi-walled carbon nanotubes/hybrid-glass nanocomposites." J. *Sol-Gel Sci. Technol.* (2014) 70: 517.

93. Barnes, HA. "Institute of non-newtonian fluid mechanics." A Handbook of elementary rheology University of Wales. (2000).

94. Genovese, DB. "Shear rheology of hard-sphere, dispersed and aggregated suspensions and filler-matrix composites."*Adv. Colloid Interface Sci.* (2012) 171–172 : 1.

95. Singh, V, Joung D, Zhai L and Das S. "Graphene based materials: Past, present and future."*Prog. Mater. Sci.* (2011) 56: 1178.

96. Bohm, S. "Siva Böhm discusses how graphene can be used to prevent corrosion of metals such as steel."*Nat. Nanotechno*l. (2014) 9: 741.

97. Pourhashem, S, Ghasemy E, Rashidi A and Vaezi MR. "Exploring corrosion protection properties of solvent based epoxy-graphene oxide nanocomposite coatings on mild steel."*J. Coatings Technol. Res.* (2017) 78: 92.