Green Coatings
for Industrial Applications

R. Akid[1] *, H. Wang[1], M. Gobara[2], T.J. Smith[3] & J. Gittens[3]
[1] Materials and Engineering Research Institute, [3] Biomedical Research Centre,Sheffield Hallam University, Howard Street, Sheffield S1 1WB, UK. [2] Formally MERI, now at the Military Technical College, Cairo, Egypt.

(*corresponding author: r.akid@shu.ac.uk)

Abstract: Despite their 150 year history, sol-gel coatings have made little impact on the industrial coatings scene largely because of their inorganic nature which has limited systems to the need for very high cure temperatures, ca. 500°C +. Further issues such as; complicated processing, limited shelf life, lack of dry film thickness, restricted methods of applying the sol-gel coating system and poor adhesion to common engineering substrates have further limited the general application of this technology, being largely restricted to optical applications.

This paper describes the recent development of environmentally-compliant ‘Green” sol-gel coating systems for industrial applications, examples being; a water-based chrome-free system for coil coatings, aerospace/transportation chrome-free pre-treatment/primer replacements and antifouling coatings. The sol-gel coating systems are based upon an inorganic-organic alkoxysilane precursors formulated to allow the incorporation of additives such as inhibitors, conducting polymers, nanoparticles and in the case of antifouling coating, an active non-pathogenic biological component. The performance of these coating systems has been assessed using standard industrial tests, electrochemical methods and field trials.

1. Introduction

Sol-gel technology originates in the synthesis of inorganic gels, which has a long history dating back to 1846 by Ebelmen [1] who discussed the early developments with publications on the synthesis of silica gels from alkoxides. However, it was not until the 1970s that sol-gel technology began to gain industrial importance when monolithic inorganic gels were formed at low temperatures and converted to glasses without the need for a high temperature melting process. Conventional sol-gel materials are mostly oxides, in particular silica, alumina, aluminosilicates, titanium dioxide, zirconium dioxide and a long list of other oxide compositions. Since the 70’s, the synthetic technique of sol-gel processing has experienced tremendous development [2][3]. With the advent of "Hybrid organic–inorganic’’ systems, which are made of organic and inorganic components combined over length scales ranging from a few Angstroms to a few tens of nanometres has grown considerably. The development of these materials in the early 80's is mainly due to the development of soft inorganic chemistry processes, especially sol–gel processes, where mild synthetic conditions allow versatile access to chemically designed combinations of inorganic domains obtained via inorganic polymerization reactions with fragile entities such as organic or even bioactive molecules. By far the most extensively studied of these materials is that of the SiO_2-based sol-gel nanocomposites. Silica-based corresponding gels can easily be tailored to a large range of porous textures, network structures, surface functionalities and processing conditions. The pH, gelation time, shaping, transparency or hydrophobicity, for instance, can be adapted to a particular dopant or application.

Currently the greatest interest in hybrid sol-gels at Sheffield Hallam University is in that of coatings having specific properties for the protection of various metals against harsh environments. Recent environmental legislation has fuelled this interest, particularly given that sol-gels offer an opportunity to eliminate Cr-based pre-treatments and can be used to replace biocide-based coatings. In this paper the following potential application areas are considered:

1). A universal sol-gel pre-treatment or primer coating with the controllable released inhibitor to replace chromium (VI) based pre-treatment or primer coatings;
2). Sol-gel/conducting polymer hybrid coating having self- properties.
3). Bio-active functional coatings;

2. Sol -gel formulations and coating processes

SiO_2 based sol-gel formulations are typically achieved by the use of functional alkoxysilanes $[R_nSi(OR')_{4-n}]$, n = 1–3, R = organic group, R' = alkyl), in mixture with a tetraalkoxysilane $[Si(OR')_4]$ e.g. TEOS , as one or more of the precursors for the sol–gel reaction. The polymerization mechanism involves hydrolysis and co-condensation processes, leading to the following reactions for an initial 1: 1 mixture of alkoxysilane and organoalkoxysilane (eqns. 1–2):

$Si(OR')_4 + R_nSi(OR')_{4-n} + (8 - n)H_2O\ ) \rightarrow Si(OH)_4 + R_nSi(OH)_{4-n} + (8-n)R'OH$.........(1)

$Si(OH)_4 + R_nSi(OH)_{4-n} \rightarrow (OH)_3Si–O–SiR_n(OH)_{(3-n)} + H_2O$ ....(2)

A wide spectrum of materials such as Nanoparticles (e.g. nanotubes), corrosion inhibitors or bioactive materials can be encapsulated, entrapped or embedded in a porous gel network therein creating new functional properties. Fig.1 shows a Typical sol-gel network structure showing incorporated functional materials. Further synthesis routes allow modification of the polymer groups to allow changes in the surface properties, such as hydrophobicity.

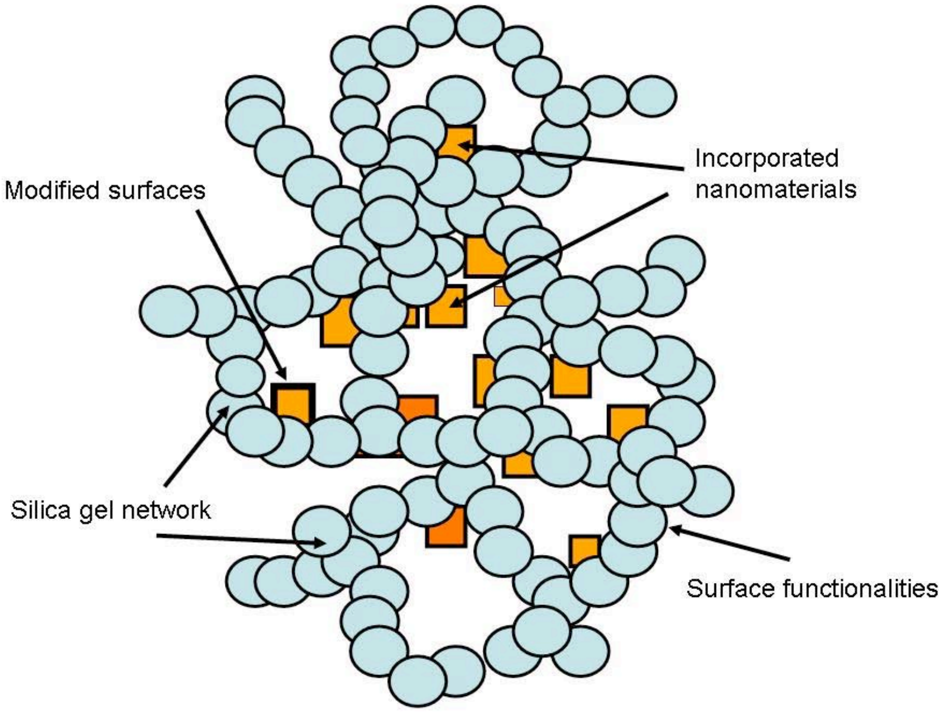
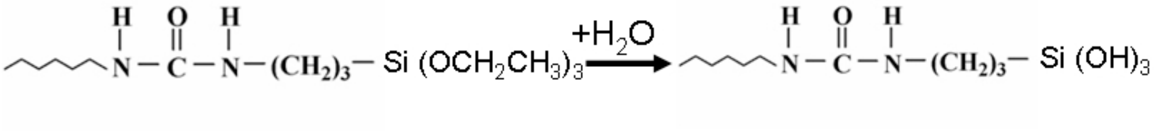


Figure 1. Schematic of a sol-gel network structure showing incorporated functional materials.

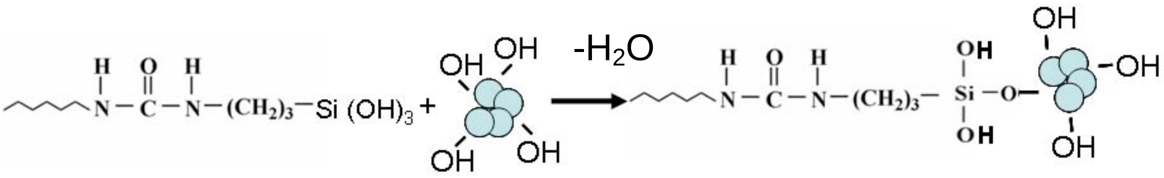
The typical hydrolysis and condensation processes that can take place during synthesis are shown below:

Hydrolysis:



$$\sim\sim\sim\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_3-Si\,(OCH_2CH_3)_3 \xrightarrow{+H_2O} \sim\sim\sim\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_3-Si\,(OH)_3$$

Condensation:



$$\sim\sim\sim\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_3-Si\,(OH)_3 + \text{particle}(OH)_4 \xrightarrow{-H_2O} \sim\sim\sim\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_3-\underset{OH}{\overset{OH}{Si}}-O-\text{particle}(OH)_3$$

The sol can be applied onto the metal substrate by dip, spray, roller, or other adaptable techniques used within industry and the coating is subsequently cured at a designated temperature. Removal of volatile compounds such as water and alcohol causes shrinkage of the network until a dry film is formed. This last process has been one of the major obstacles to the development of crack-free coatings.

The chemistry of the sol-gel formulation is critical in determining whether or not the sol-gel reacts with the surface onto which it is applied. In the case of the SHU anti-corrosion systems two layers are formed, see Fig 2. Here a distinct inner ‘conversion’ layer of nano-size dimensions is formed. Analysis of this has proven that a chemical change occurs at this interface [4]. The total thickness of the coating in Fig.2 is about 15 microns while the thickness of the inner layer is less than 50nm. Analysis of the EIS data for the Al alloy and the mild steel tests also revealed corrosion protection behaviour consistent with the presence of inner and outer layers within the sol-gel [5-7].

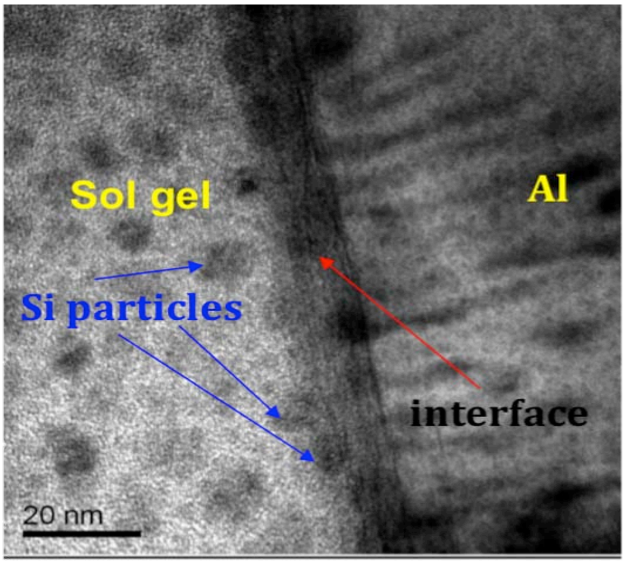


Figure 2. Transmission Electron Microscope section through a sol-gel coating applied to an aluminium alloy AA2024 substrate.

3. Sol-gel systems

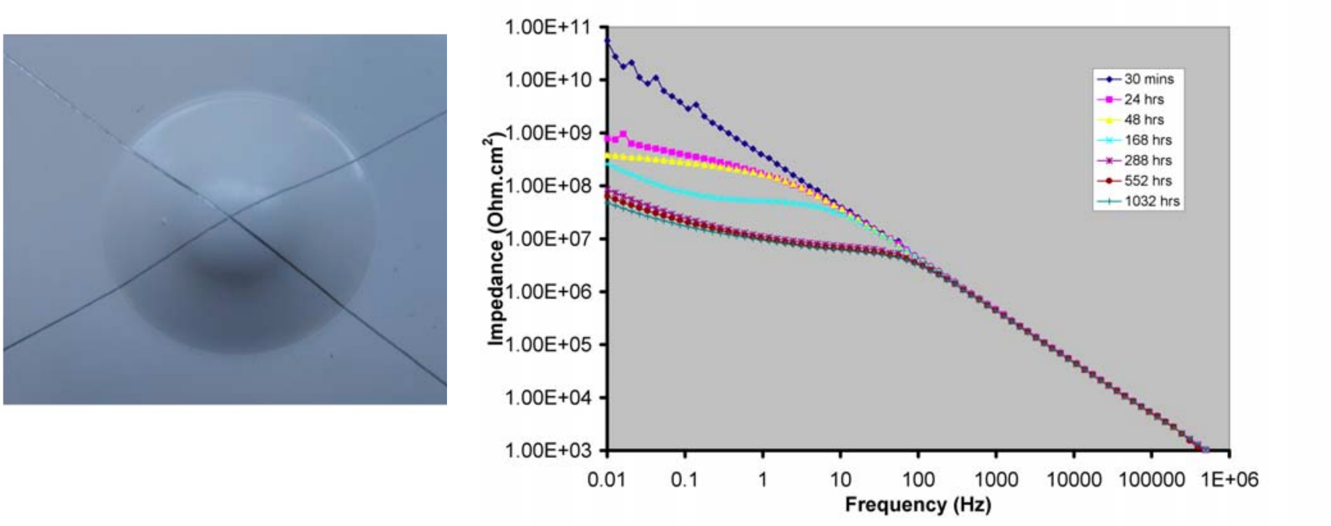
A brief discussion on the following specific sol-gel systems being developed at Sheffield Hallm will follow;

a. *Water-based pre-treatment/primer*
b. *Self-healing sol-gel/conducting polymer coating*
c. *Biocide-free antifouling coating*

Water-based pre-treatment/primer for coil coating applications

One of the main challenges set in the coil coating industry is to coat and cure the reactive steel, hot-dip galvanized steel or aluminium strip surface at high line speeds. Typically it may be necessary to cure a coating within 10 seconds. This is achieved on a daily basis using solvent-based coating systems but a future goal of the industry is to use the existing coil coating production lines but replace typical solvent based pre-treatments with water-based Cr-free systems.

Fig. 3 presents the mechanical (adhesion) properties of a water based sol-gel top coated with polyester, following an Erichson cupping test and exposure to boiling water for 30 minutes and electrochemical impedance spectroscopy (EIS) results of a water based sol-gel coated steel strip cured using infra-red lamps. The time/temperature cure profile is shown in Fig. 4.



(a) (b)

Figure 3 (a) Adhesion performance and (b) EIS response in 3.5% NaCl solution

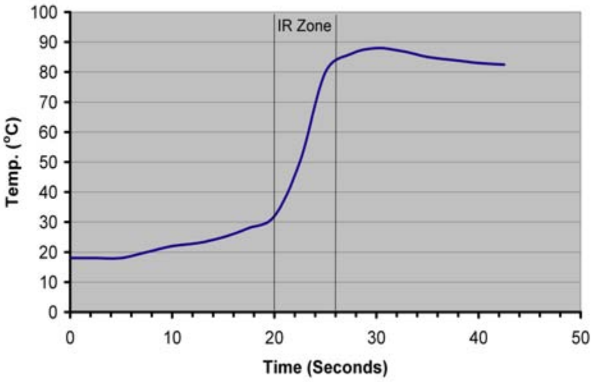


Figure 4 Time/temperature profile during IR curing

The coating exhibits good adhesion and high impedance (>10^8 ohms.cm^2) for over 1000 hours immersion in the chloride environment.

Self-healing sol-gel/conducting polymer coating

Conducting polymers (CPs) such as polyaniline (PANI) and polypyrrole (PP) have been recognised as potential ingredients for anti-corrosion coatings for many years [8]. However, historically, much of the research work has been focused on the protection of mild steel. Although these types of coating offer a number of benefits, notably the ability to form a passive layer and the ability to transfer charge within the coating, there are issues such as lack of coating flexibility and substrate adhesion that have limited their industrial use.

By incorporating a conducting polymer into a sol-gel coating, a novel hybrid coating is formed which has the advantage of flexibility and good adhesion from the sol-gel while simultaneously providing excellent corrosion resistance through the presence of the CP. This type of coating has been applied to the aerospace AA2024 grade. Fig. 5 presents the results of a comparison between sol-gel ‘only’ and hybrid sol-gel/CP coatings that have been scribed and subject to Neutral Salt Spray testing in 5% NaCl at 35°C. As can be clearly seen the sol-gel coating alone offers little corrosion protection, showing extreme pitting and delamination at the scribe. Conversely, little corrosion is observed on the sol-gel/CP coating. Further evidence of the corrosion resistance and self-healing capability of the hybrid system is shown in Fig. 6, which presents a scanning vibrating electrode (SVET) scan over a scribed coating on AA2024. Here it can be seen that there is activity at the scribe in the first few hours of immersion. Eventually this activity ceases after around 16 hours.

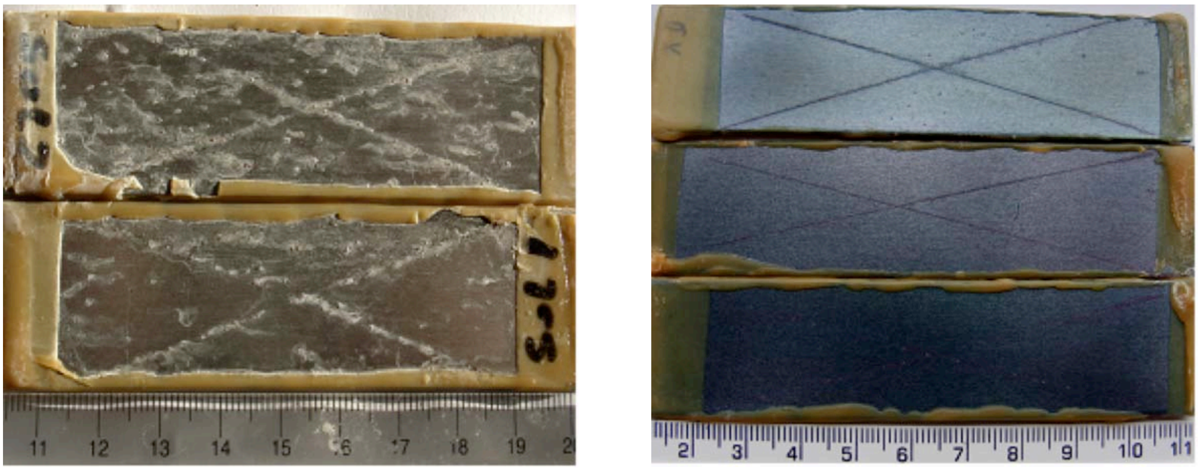

(a) (b)

Figure 5 Salt spray test results on scribed AA2024; (a) sol-gel only (168 hrs) and (b) sol-gel/CP (500 hrs)

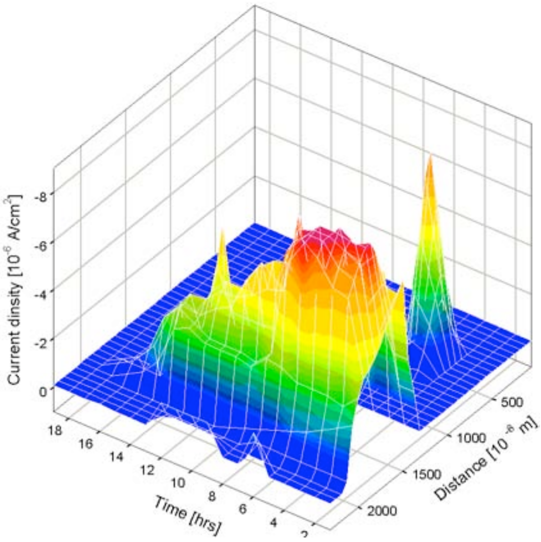


Figure 6 SVET area scan over a scratched sol-gel/CP coating. Test conducted in 3.5 %NaCl solution.

A similar self-healing response has been found when using EIS measurements on ‘initially-intact’ and then ‘scribed in solution’ samples. Initially the impedance value drops and then as the CP is activated the impedance value recovers [9].

The self-repair behaviour properties of the coating are based upon the ability of the CP to undergo a reversible redox reaction from the emeraldine base to the lecomeraldine form allowing an electron transfer reaction when N=C is reduced to N-C [10].

Biocide-free antifouling coating

Subject to the nature and type of nutrients, microorganisms can rapidly colonise a surface which is immersed in an aqueous environment. The attachment of micro/macrofouling has enormous economic consequences for many applications such as marine shipping, oil pipeline structures, heat exchangers etc. For example, 5% biofouling of a ship’s hull can lead to an increase in drag that contributes to a 10% fuel loss, the added frictional forces that contribute to this loss steadily increase in magnitude with an increase in the degree of biofouling.

Furthermore, the development of a bio-film can lead to subsequent colonization of bacterial types that ultimately generate aggressive environments, notably sulphate reducing bacteria (SRB). Here the formation of sulphide and hydrogen sulphide can lead to rapid localised corrosion, especially ferrous-based materials.

As stated, a primary benefit of the hybrid sol-gel system is that it allows a variety of additives to be incorporated into the matrix, therein enhancing the functionality of the coating system. One

specific aspect that has been developed at Sheffield Hallam is that of the encapsulation of a bio-active components selected to prevent biofouling and microbially induced corrosion.
Following a ‘proof of concept’ study it was realised that endospores and vegetative cells could be encapsulated within the sol gel matrix [6]. An initial concern was that of maintaining the viability of the endospores when added to the sol-gel, particularly given the high solvent levels (up to 50%) and low pH levels (down to 2) of the sol-gel. To assess the survivability of the endospores a series of experiments was carried out to determine the number of colonies formed on the surface as a function of solvent concentration and pH. Fig 7 presents the results of this study showing high viability of the endospores at different levels of solvent and pH [11].

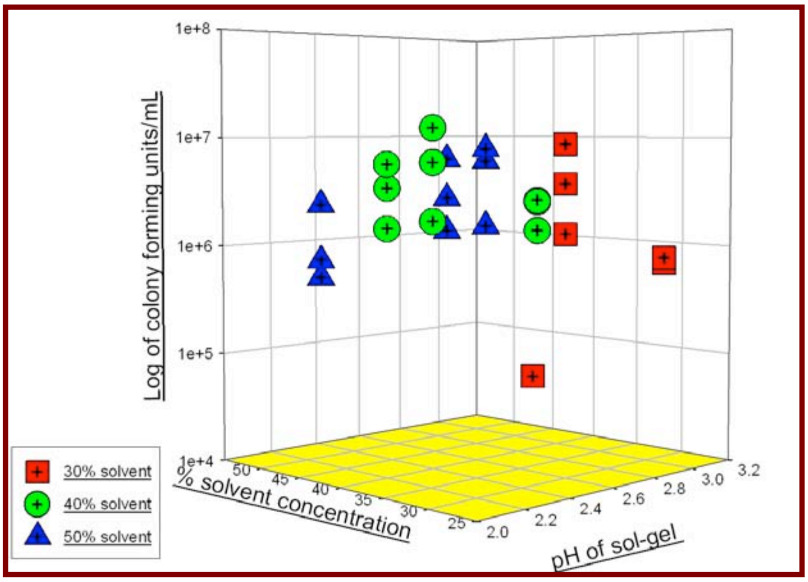


Figure 7 Viability of *Paenabacillus polymyxa* endospores in sol-gel formulations of varying solvent concentration and pH.

Further proof of the ability of the spores to survive in the sol-gel environment is shown by evaluating whether or not the bacteria colonise the surface on exposure to suitable nutrients. Fig. 8 presents fluorescence microscopy images of an abiotic (bacteria-free) and biotic (added bacteria) coatings after immersion in nutrient rich artificial seawater. Here it can be seen that viable (living) microorganisms are evident in the coating within 24 hours of exposure to the solution.

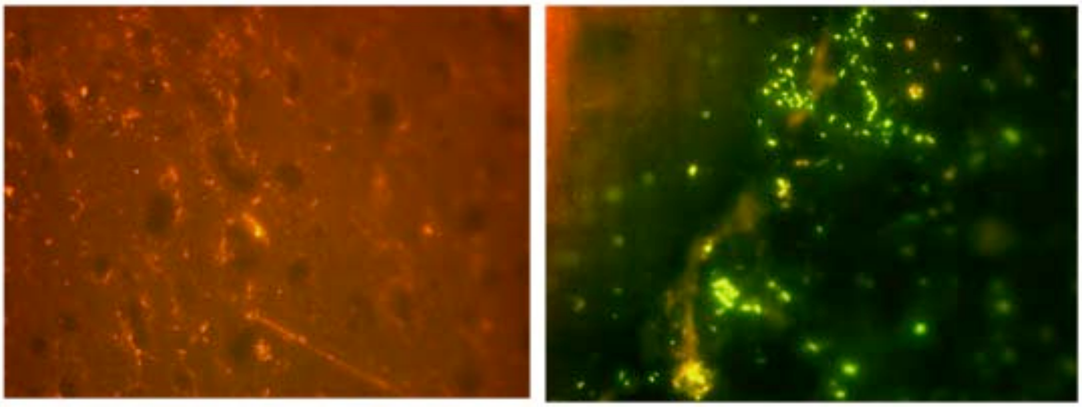


Figure 8 Images of abiotic (left) and biotic (right) sol-gel coating on Al 2024-T3 after staining with BacLight kit following 24 hours immersion in Nutrient Broth. Viable (living) bacteria fluoresce green.

Effectiveness of the coating to prevent fouling is shown in Fig.9 which presents images of panels subject to constant immersion over a 29 week period at Whiby Harbour, a site on the east coast of the UK. It can be clearly seen that the surface of biotic coating is unattractive for the settlement of barnacles.

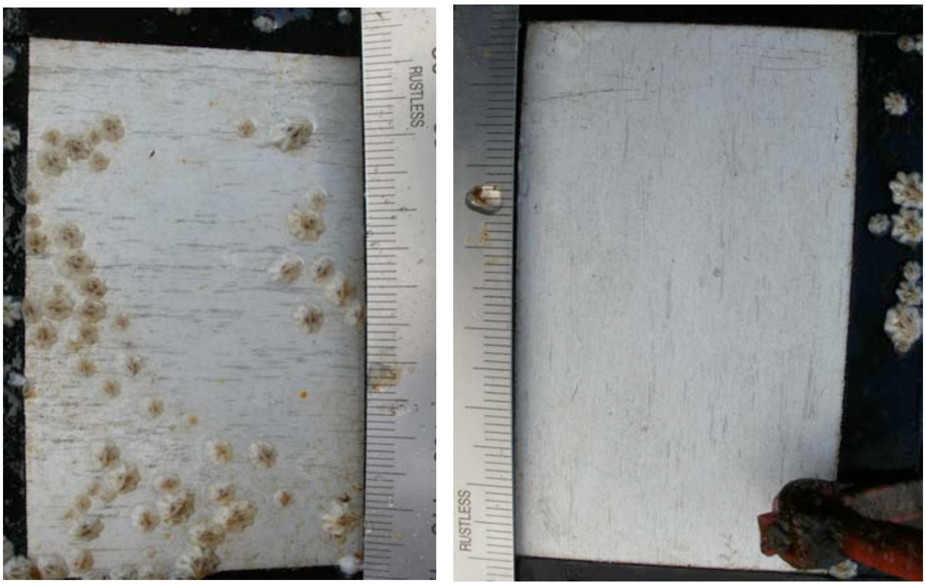


Figure 9. Comparison of barnacle settlement on sol-gel surfaces, abiotic (left) and biotic (right).

In addition to the antifouling properties of the coating laboratory and field trials have shown that the bioactive coating has a higher corrosion resistance than that of an equivalent abiotic coating. Figure 10 presents electrochemical impedance data obtained from two different types of biotic coating compared to an abiotic coating.

As can be seen by the size of the semicircles in the Nyquist plot, Fig 10a, (which represent coating resistance, that is, large diameter equates to high resistance) there is a significant improvement in corrosion resistance when bacteria are incorporated into the coating. Linear polarization resistance (R_p) data also shows that, compared to bacteria encapsulation in the coating, the corrosion resistance of an abiotic coating, with or without the addition of dead bacterial endospores, was on average lower than the biotic sample.

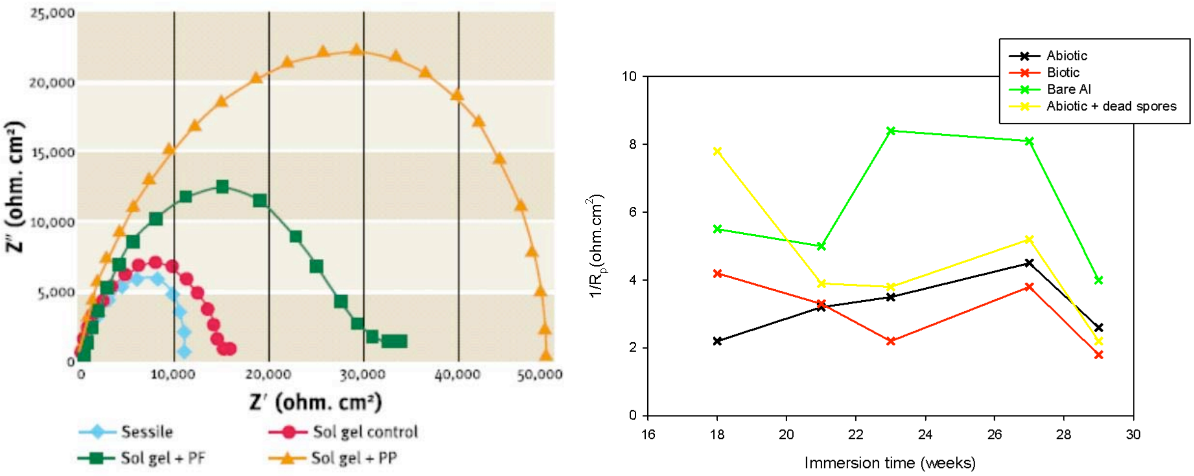


Figure 10 Corrosion resistance measurements made of abiotic and biotic coatings (a) Laboratory EIS results and (b) Field trial Linear Polarisation resistance results.

6. Conclusions

A non-toxic, environmentally-friendly Si-based hybrid sol gel platform coating system has been developed for use as a pre-treatment/primer or as a stand-alone coating for a variety of metal substrates, namely steel, Al, Zn and Mg. These systems are currently showing good corrosion resistance performance and have viable potential to replace traditional chromate pre-treatments/primers. The sol-gel system has the advantage of variable cure times and temperatures from room temperature up to around 200°C depending upon the sol-gel formulation and type of substrate being coated. A rapid cure system has been developed that can be cured in less than 10 seconds at peak metal temperatures less than 100°C. Coating thickness can vary up to 20 μm, subject to formulation chemistry and multilayer coatings can be applied using these systems. The sol-gel coating system has also proven to be an acceptable surface for subsequent organic topcoat treatments. Self-healing f these coatings can be achieved either by the incorporation of controlled-release inhibitors or by the addition of a conducting polymer. The ability to tailor the chemistry of these systems to allow the incorporation of bacteria, thus providing antifouling functionality and improved corrosion resistance is a unique aspect currently not found with any other sol-gel system. Finally, although not reported here, carbon nanotubes may also be incorporated into the sol-gel to provide the functionality of ‘scratch resistance’ whilst also maintaining high resistance to localised corrosion.

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