



Enhancing water repellency and anticorrosion properties of a hybrid silica coating on mild steel



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ABSTRACT

In this study, a sol–gel route has been designed for the synthesis of a hydrophobic organic–inorganic polymer network used to protect mild steel substrate against corrosion in 3.5 wt% NaCl solution. The underlined protective hybrid coating is prepared using tetraethoxysilane (TEOS) and 3-glycidoxypropyltrimethoxysilane (GPTMS) with dimethoxymethyl octadecylsilane (DMOMS), bearing a C18 alkyl group, added at room temperature in order to provide a water repelling property to the coating. The superior protective property of this coating matrix has been found to be related to high water contact angle (θ_w) values, even after modification with surface active zinc-based corrosion inhibitor pigments. Insight into the protection mechanisms of these hybrid coatings (modified and unmodified) on the mild steel electrodes has been explained using electrochemical impedance spectroscopy. Results from electrochemical and SEM surface analyses reveal prolonged corrosion protection with better performance obtained for the modified coating matrices due to their reticulated make-up and effective barrier properties against the diffusion of aggressive species. The presence of corrosion inhibitors in this rigid anticorrosive silica network offers superior surface and bulk properties to the modified sol–gel coatings, and hence, fosters greater impedance against ionic current of corrosive species. The reduced protection on prolonged immersion must have been due to higher coating permeability via conductive pathways to the metal surface, and this is associated with the bulk pores on the sol–gel coating. Nuclear magnetic resonance (NMR) and Fourier transform infra-red (FTIR) spectroscopies have been employed to probe the extent of hydrolysis/condensation, and to ascertain the presence of the chemical group offering the needed hydrophobicity to the coating matrix.

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1. Introduction

Modern applications of hydrophobic and superhydrophobic engineering surfaces include, but are not limited to, water purification and desalination membranes, anti-bacterial and anti-corrosion coatings, oil–water separation, catalysis, sensor and battery-manufacture [1]. The study of surface hydrophobicity and associated interfacial phenomena has attracted a great deal of interest in theoretical and experimental scientific and engineering research; the Wenzel and Cassie–Baxter state models being some of the most widely studied theoretical models for qualitatively predicting contact angles (θ_w) of these surfaces and their

wettability [2,3]. Many processes accompanying engineering modifications, though with some limitations in this regard, are designed to bio-mimic the naturally-occurring “lotus effect” from *Nelumbo nucifera* (Lotus) leaf surfaces with high contact angles [1–3]. Apart from the lotus leaf, there are an abundance of flora with similar water repelling and self-cleaning properties. However, since a substrate’s wettability property is a surface characteristic widely influenced by its morphology and chemical composition, synthesis designs of organic coatings for metal protection are not without appropriate bulk modification [4], careful choice of appropriate precursors and process routes. Among useful sol–gel additives and precursors offering hydrophobic properties, Mahltig et al. [4] has mentioned polysiloxanes with increasing chain-length of alkyl groups, monomeric alkylsilanes, as well as fluorinated compounds, for metallic and non-metallic (e.g. functionalized textiles) substrates. Having a hydrophobic protective coating with low

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wettability reduces the initial approach and subsequent passage of water molecules and other corrosive species to the metal surface, and the protective property of the coating is hugely enhanced.

Sol–gel films exhibit enhanced potential as protective coatings, as they remain viable substitutes for chromate-based surface pre-treatments and coatings that can impact upon the environment and human health [5,6]. The synthesis of organic–inorganic hybrid coatings via the sol–gel method has been widely reported for large area substrate applications [7–10], and the success of this unique process has been linked with its ease of application, control of process variables [11], and the relative abundance of precursors employed for making protective sol–gel coatings with desirable characteristics [12]. Widely used in reducing processes accompanying anodic dissolution, recent researches [13–16] have proposed that anticorrosive sol–gel coatings can be functionalized to yield better and improved multifunctional properties by adequate choice of inhibitors and reaction conditions. Most sol–gel coatings synthesized from simple monomers such as alkoxides of silicon and other metals (e.g. Ce, Zr, Sn, Al and Ti) are susceptible to minor damage and persistent defects thereby allowing easy access of ions to the metal substrate resulting in cavitation and pitting corrosion [17]. These cracks are not restricted to protective coatings with uneven bulk particles but also those with the presence of micro and nano-pores in the bulk of their matrices [18]. However, by chemical and/or morphological modification of coatings containing relatively low surface energy (LSE) additives and materials, hydrophobic properties may be combined with barrier corrosion resistance characteristics [19], thereby limiting the initial approach of water to their bulk surfaces. The use of graphene [21], TiO₂/multiwall carbon nanotubes (MWCNT) [20,24], alumina [23], and nanoparticles [22] in this regard has also been reported. Ansari et al. [25] have recently successfully incorporated nanosized clay into a sol–gel coating for the corrosion protection of stainless steel 304 L in NaCl solution. The contact angle varied with the amount of clay in the bulk of the coating ($\theta_w = 68\text{--}72^\circ$). They synthesized the protective sol–gel coating from methyltriethoxysilane (MTES), gamma-glycidoxypropyltrimethoxysilane (γ -GPS) and TEOS via the sol–gel method, and the optimum amount of incorporated clay in the coating on steel was evaluated with electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) analyses. Authors recorded improved electrochemical impedance and noise resistance in the presence of the nanoclay, with 1000 ppm nanoclay content contributing to the optimum protective performance of the sol–gel coating. Wang et al. [26] have reported the effect of multilayered polytetrafluoroethylene (PTFE) functionalized sol–gel coating on canvas with enhanced hydrophobic and self-cleaning ability. Its improved water impact resistance was linked with surface superhydrophobicity ($\theta_w = 140\text{--}155^\circ$), strength and weatherability of the canvas substrate. Authors also related the improved water impact endurance of this PTFE-coated canvas to the presence of hydrophobic $-\text{CH}_3$ and $-\text{CF}_2$ groups at the surface of the protective coating. Zheludkevich et al. [27] have investigated the effect of pre-layer deposition of chitosan on a protective hybrid sol–gel barrier film for aluminium alloy 2024 corrosion inhibition in 0.05 M NaCl. This modification had remarkable surface influence on the localized corrosion of the substrate. Localized electrochemical results also showed some micro-confined defects in the coating having been self-healed in the presence of cerium-doped biopolymer on AA2024 immersed in the saline electrolyte. Tiwari et al. [28] have reported the performance of yttria-stabilized and alumina stabilized zirconia hybrid sol–gel coatings for mild steel against surface corrosion in 3.5 wt% NaCl and non-protective rust. The improved barrier protection for these sol–gel type coatings was linked to their enhanced wear and corrosion inhibition as well their mechanical strength and thermal stability. Sol–gel process has also been deployed in preparing epoxy–NiO

nanocomposite materials and used in studying salt spray resistance on mild steel by Madhup et al. [29]. Better protection of the substrate as per corrosion resistance was attributed to reduced NiO nanoparticles in the coating. NiO nanoparticles was also reported to enhance the abrasion and wear strength of the epoxy coating. The protective property of TiO₂–SiO₂ enamel sol–gel has been investigated for stainless steel. The barrier protection was reported to be influenced by the coating thickness, mechanical strength and numbers of layers of the coating on the substrate, as well as heat treatment. A 470 nm thick triple layer coating was obtained after characterization, and stainless steel corrosion tests were conducted in boiling 3% oxalic acid and 1 N NaOH at 95 °C and 80 °C, respectively [30]. A hybrid organic–inorganic sol–gel synthesized from silica nanoparticles, tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) precursors has been reported for surgical grade stainless-steel implants corrosion protection [31]. Effect of strontium known to stimulate bone formation around the steel implant was also investigated. Coated implants were found to resist degradation induced by aggressive simulated body fluids after a month immersion. Corrosion and bioactivity tests were conducted in vitro in order to analyze bone formation on the implants.

In the present work, we introduce an approach for obtaining hydrophobic sol–gel surfaces with prolonged anticorrosive and protective properties based upon TEOS silica, doped with micro-sized zinc aluminium polyphosphate and zinc molybdate for mild steel in 3.5 wt% NaCl. This new sol–gel coating is synthesized by an alcohol-assisted sol–gel process with TEOS and GPTMS as the colloidal silica network and adhesion promoter, respectively, alongside an LSE precursor with a long alkyl (C18) group (dimethoxymethyl octadecylsilane). This new protective coating is found to exhibit improved hydrophobicity ($\theta_w \gg 100^\circ$) and protective performance due to the presence of the unreacted C18 alkyl group in the sol–gel network. The present sol–gel route produces enhanced protective silica coating with hydrophobic surfaces and reduced bulk wettability as against the usual practice of surface treatments of coatings to achieve water repellency [11]. Although the inorganic networks of most sol–gel coatings possess high crack-forming resistance upon prolong curing on metal substrates, the incorporation of organic components leads to thicker hybrid coating matrices with improved flexibility, abrasion resistance, stability, compatibility and potential for more modification [32]. Typically such organic components in sol–gels are derived from precursors like the organoalkoxysilanes, $\text{SiR}'_x(\text{OR})_{4-x}$. The bulk presence of harder fillers and anticorrosive pigments also reduce the possibility of formation of these cracks by lowering the porosity of the organic–inorganic hybrid sol–gel systems, hence, increasing their corrosion protection properties and mechanical strength. On this note, the incorporation of surface active zinc molybdate and zinc polyphosphate was selected as candidate the bulk modification method for this study. Metal pigments of this class have been previously reported [33,34] to spontaneously form passive layers of oxides on substrate surfaces thereby limiting the transport of corrosive ions across the substrate–solution interface [35].

2. Experimental details

2.1. Materials

Analytical-grade isopropyl alcohol (IPA) and the silane precursors were purchased from Sigma–Aldrich (US), and were used without further purification. The silane precursors (Sigma–Aldrich, US) include a tetrafunctional alkoxide, tetraethoxysilane (TEOS), and two organoalkoxysilanes (3-glycidoxypropyltrimethoxysilane (GPTMS) and dimethoxymethyl octadecylsilane (DMODS))

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