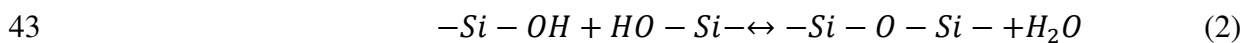
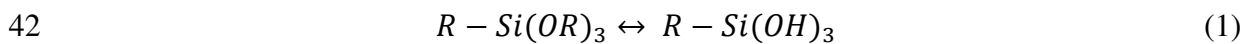


24 where the defect constitutes up to 52 % of total area. The protection offered in the
25 presence of a coloured pigment is delayed and it is proposed that the pigment restricts the
26 ability of Zn to couple with the underlying steel.

27 **1. Introduction**

28 The use of sol-gel coatings to provide corrosion protection has been a topic of interest for
29 the last few decades, ¹ and has been stimulated by the ongoing need for environmentally
30 friendly and non-toxic alternatives to chromate conversion coatings and pre-treatments. ²⁻
31 ⁴ Research has been focused on the use of sol-gel coatings as adhesion promoters when
32 applied between a metal substrate and an organic primer/topcoat. ⁵⁻⁶ Their ability to
33 provide effective corrosion protection has also been investigated on technologically
34 important metals such as Cu, ⁷⁻⁸ Al ^{7,9} alloys, Mg ¹⁰ and carbon steel. ¹¹

35 The production of sol-gel coatings occurs at low temperatures at which thermal
36 degradation and volatilization is minimised. The use of liquid alkoxysilane precursors
37 also means that sol gel technology can be used to over-coat surfaces of complex shapes.
38 ¹² Hydrolysis (Equation 1), and subsequent condensation (Equation 2) results in the
39 production of silanol groups and siloxane bonds respectively. As the polymer structures
40 agglomerate, networks extend into the liquid phase causing thickening and the production
41 of a gel. ¹²



44 Shrinkage occurs during the subsequent drying stage and the resultant coating can be
45 brittle for thicknesses > 100 μm. ¹³ At lower thickness values, porosity increases and the
46 performance is compromised. Research efforts have subsequently focused on the

47 production of hybrid sol-gel derived coatings which encompass the properties of both
48 organic polymeric materials and inorganic/ceramic constituents.¹⁴

49 However, sol-gel coatings are only able to provide barrier protection to the steel substrate
50 and are unable to provide active corrosion protection in the case that a large area of the
51 coating is breached. Several pieces of work have focused on the application of hybrid sol-
52 gel coatings, some of which have been doped with corrosion inhibitors, to hot dipped zinc
53 galvanized (HDG).¹⁵⁻¹⁷ Zn is more anodically active than steel and is therefore able to
54 provide cathodic protection to the substrate (in addition to the barrier protection offered
55 by the sol-gel). However, galvanizing primarily takes place via a hot dipping process
56 whereby steel components/structures are submerged within a molten bath of the coating
57 metal. This process cannot be completed at the point of use and is therefore associated
58 with substantial economic costs. One alternative to hot dip galvanising is the application
59 of Zn rich coatings, which consist of Zn particles dispersed in a binder. Such systems are
60 available in a liquid form and can be applied to steel substrates as a paint.

61 Addition of Zn particles or flakes can be made to both organic or inorganic binders and
62 Zn-rich primers have been made in this way for use on various steels.¹⁸⁻³⁰ Only Zn
63 particles which are in electrical contact with the steel substrate are able to contribute to
64 the sacrificial protection offered by such coatings, and the critical volume fraction must
65 therefore be higher than the percolation threshold.¹⁸⁻¹⁹ When the electrolyte reaches the
66 steel/coating interface the active Zn provides cathodic protection to the underlying
67 substrate for a period of time. Zn dissolution results in the loss of contact with the steel,
68 after which, corrosion product can form and eventually prevents galvanic coupling.^{18, 22}
69 At longer time periods the corrosion product must seal the pores to ensure adequate
70 protection.²⁰⁻²² Basic Zn salts, deposited at the substrate, have also been suggested to act

71 as corrosion inhibitors.²⁹⁻³² The ability of Zn sol-gel coatings to act sacrificially to a steel
72 substrate means that they are considered as suitable alternatives to HDG, especially for
73 cases where production levels and capital investment are low.

74 The chemical stability and enhanced oxidation and corrosion resistance afforded by sol-
75 gel coatings¹² also makes them viable candidates for coating of the advanced high
76 strength steel (AHSS) and ultra-high strength steel (UHSS) grades increasingly used for
77 automotive applications. To achieve the desired mechanical properties, steel parts are
78 press hardened at temperatures of up to 950 °C.³³ The oxidation resistance of
79 components is therefore of importance to avoid detrimental changes to both mechanical
80 properties and surface appearance. Thin, sol-gel coatings have previously been applied to
81 the boron-manganese steel alloy 22MnB5 with the aim of improving oxidation resistance.
82³³ The coatings were found to protect against oxidation up to 800°C and remained intact
83 during press hardening.³³ The absence of secondary phase intermetallics and residues
84 (which can form during the subsequent laser beam welding process) highlights the
85 suitability of sol-gel coatings to further industrial processing.³³ The corrosion properties
86 of 'higher abrasion resistant' sol-gel Zn-SiO₂ thin films have previously been
87 characterized using electrochemical impedance spectroscopy (EIS).³⁴ The films were
88 shown to behave differently to conventional sacrificial Zn based coatings (such as HDG),
89 and any enhanced corrosion protection was proposed to be a result the tendency of Zn to
90 react with Cl⁻ ions to form ZnCl₂ and meant that the coatings were deemed suitable for
91 use in marine environments. The question of whether Zn sol-gel coatings are able to
92 provide sacrificial protection to a steel substrate therefore remains largely unanswered.³⁴

93 The success of an active coating can be characterised by the distance over which the
94 system is able to protect a coating defect (throwing power), as well as the time before

95 coating failure. The barrier properties of the ‘binder’ material, alongside the
96 anode/cathode area ratio and geometry also play a role in influencing the galvanic
97 protection offered by such coatings. In the work described in this paper we make use of
98 an in situ scanning vibrating electrode technique (SVET) to study the ability of Zn rich
99 sol-gel composite coatings to provide sacrificial protection to steel. For active coatings,
100 the position and intensity of the net anodic and cathodic regions change with respect to
101 time. The spatial and temporal resolution of corrosion current density offered by the
102 SVET therefore provides advantages over conventional electrochemical techniques and
103 the technique has previously been used to analyse the ability of an Mg rich primer to
104 become the net anode in a Mg rich primer/ defect galvanic couple formed on unpolarised
105 AA2024-T3.³⁵ The aim of the present work is to semi-quantitatively assess the ability of
106 Zn sol-gel coatings to provide sacrificial protection to a steel substrate. As such, the size
107 of the defect is systematically changed and the total integrated anodic and cathodic
108 current density values associated with the defined regions, are calculated. Consumer
109 driven aesthetical requirements, especially in urban areas such as Singapore, have led to
110 the application of multiple layers which introduce colour into the system. Intermediate
111 layers enhance adhesion and layer compatibility, but result in greater economic costs and
112 overall corrosion resistance. The sacrificial protection afforded by coloured coatings, is
113 therefore compared to that provided by their uncoloured counterparts.

114 **2. Experimental**

115 *2.1 Coating Manufacture*

116 A sol-gel based binder was manufactured using a methodology described previously and
117 shown in Figure 1.³⁶ Briefly, Tetraethyl orthosilicate (TEOS, Sigma Aldrich) was used

118 as an alkoxy silane precursor. TEOS and (3-Glycidyloxypropyl) trimethoxysilane
119 (GLYMO, Sigma Aldrich) were mixed with molar ratio 3:2, and hydrolyzed in 0.5 M
120 itaconic acid ($\geq 99\%$, Sigma Aldrich) solution, with the presence of 5 wt.% LUDOX®
121 AS-40 colloidal silica (Sigma Aldrich). The mixture was stirred at 500 rpm for 72 to 120
122 hours to ensure complete hydrolysis before ageing. Basic coating additives (released
123 during curing) and Zn powder ($>98\%$ purity) were added and the mixture was
124 mechanically stirred for 10 minutes. A spray coating technique was used to apply the
125 coating to SA2.5 sand blasted (ISO 8501-1) A36 carbon steel.³⁷ The nominal chemical
126 composition of ASTM A36 is; carbon 0.25 - 0.29 %, copper 0.2%, manganese 0.8 – 1.2%,
127 phosphorous 0.04 %, silicon 0.15 -0.40%, sulfur 0.04% and the iron(balance). Curing
128 took place at 150 °C for 30 minutes.

129 *(Figure 1)*

130 In the case of coloured samples, a colouring blend was prepared by ball milling a
131 phthalocyanine based colourant (Heliogen Green L8605, BASF) to ~300 nm and
132 dispersing within ethanol. This colourant is widely used throughout the coating industry
133 and is highly stable and associated with desirable lightfastness properties.³⁸ The
134 colouring blend was added to sol-gel together with coating additives and Zn powder.
135 Three different coatings were investigated during this work; a coloured sol-gel coating
136 (CSG), a Zn rich sol-gel coating (ZnSG) and a coloured Zn rich sol-gel coating (CZnSG).
137 The thickness and composition of the dry coatings are shown in Table 1. It should be
138 borne in mind that the amount of Zn incorporated into the coatings is ~ 60 % (by volume)
139 and less than than typically used (~ 80 Vol. %) ^{21, 23, 28} It has previously been shown that
140 zinc rich coatings provide corrosion protection to steel for longer periods of time at
141 increased values of concentration.³⁹

142 *(Table 1)*

143 The coatings used throughout the work described in this paper are therefore composite
144 materials which can be physically, and electrically, represented by either three or four
145 components (given in the Table 1). All coatings comprise an electrically insulating matrix,
146 within which clusters of interconnecting pores exist. These pores can become filled with
147 electrolyte and may therefore exhibit ionic conductivity after periods of immersion.
148 ZnSG coatings contain clusters of electronically conducting Zn particles which are linked
149 ohmically. Green coloured pigments are also included in CSG and CZnSG coatings.

150 *2.2 Resistivity measurements*

151 Sheet resistance measurements were made using a CDE ResMAP 178 resistivity monitor
152 and then converted to conductivity. At least three readings were taken in each case.

153 *2.3 Adhesion Measurements*

154 Adhesion of the ZnSG and CZnSG coatings to the carbon steel substrates was assessed
155 by applying and removing pressure sensitive tape over cuts made in the coating according
156 to the test method specified by ASTM D3359 (Measuring Adhesion by Tape Test).⁴⁰

157 *2.4 Salt Spray*

158 Both scribed and unscribed coated coupons were exposed to an accelerated cyclic
159 corrosion test according to ISO 14993 (intermittent wet and dry conditions) to evaluate
160 the corrosion protective performance.⁴¹ For each test, three pieces of sample were
161 exposed as triplicates and representative images are shown.

162 *2.5 Open circuit potential*

163 A Solartron 1287 potentiostat was used to record the free corrosion potential (E_{corr})
164 values associated with intact coatings immersed in 0.86 M NaCl for 24 hours. A saturated
165 calomel reference electrode was used and. Three measurements were made for each
166 sample and representative data are shown.

167 2.6 EIS

168 Electrochemical impedance spectroscopy (EIS) was used to investigate the through pore
169 ionic conductivity of the coatings. EIS experiments were carried out using a Solartron
170 1287 electrochemical interface coupled with a 1255 frequency response analyzer. A
171 standard three-electrode cell was employed and incorporated a SG coated steel sample
172 coupon working electrode, a platinum gauze counter electrode and a saturated calomel
173 reference electrode. The input AC amplitude was 10 mV and the frequency range was
174 from 0.05 Hz to 100 kHz. Impedance spectra were obtained at 1 hour intervals. Two
175 measurements were made for each coating and representative data are shown.

176 2.7 SVET

177 Extruded PTFE tape (type 5490 HD supplied by 3 M) was used to expose a 9 mm x 9 mm
178 area in the centre of each coupon. Defects in the coating were created by mechanical
179 abrasion using a scalpel blade.

180 SVET is used to study aqueous corrosion and makes use of the ionic current flux that
181 exists in the electrolyte above a corroding sample. The inherent resistance of the
182 electrolyte results in the presence of an ohmically generated potential field.⁴²⁻⁴⁵ The
183 vibrating SVET microtip is able to sense an alternating potential at its vibration frequency.
184 The value detected by the SVET is then proportional to the potential gradient (or electric
185 field strength) in the direction of vibration and thus to the current.⁴²⁻⁴⁶

186 The SVET apparatus has been described in detail previously.⁴³ The SVET microtip is
187 comprised of a platinum microelectrode (125 μm) which is sealed in by a glass sheath
188 and has a total diameter of 250 μm . The probe was vibrated, via a pushrod, at a frequency
189 of 140 Hz using an electromagnetic driver. The probe vibration amplitude was 25 μm . μ
190 metal was used to enclose the electromagnetic driver and minimise electromagnetic flux
191 leakage. The wiring and pushrod were surrounded by an aluminium cylinder. Vibration
192 of the tip was constrained to the perpendicular direction by use of a bearing. A 2.5 cm x
193 2.5 cm chloridized low impedance silver chloride reference electrode was attached to the
194 cylinder at a distance of ca. 5 cm away from the probe.

195 Three stepper motors (Time and Precision Ltd) were used to move the SVET probe and a
196 Perkin Elmer 7265 lock-in amplifier was used to detect a SVET voltage signal.
197 Measurements of the peak-to-peak SVET probe vibration amplitude ($a_{pp} = 30 \pm 5 \mu\text{m}$)
198 were conducted in air using a stroboscope, in combination with a travelling microscope.

199 Ohm's law $V_{pp} = j_z (a_{pp}/K)$ can be used to relate the peak-to-peak SVET voltage signal
200 V_{pp} to the current flux density measured along the axis of probe vibration normal to the
201 sample surface (j_z). and the quantity a_{pp}/K is defined as the SVET calibration factor.⁴²⁻⁴⁶

202 A specially constructed two-compartment calibration cell was used. One of the
203 compartments consisted of a nylon beaker and contained a 1 cm^2 platinum electrode. The
204 other compartment was a 6 dm^3 tank which contained the experimental electrolyte. A 1
205 cm^2 platinum electrode was also present in the second compartment. Both silver chloride
206 electrodes were immersed within the electrolyte and the intra-electrode spacing was 10 –
207 20 cm. The compartments were connected by a 6 cm long, vertically orientated 0.5 cm
208 diameter tube. The SVET microtip was positioned in the tube and the current flux density
209 was assumed to be constant across the tube diameter meaning that current flux aligned

210 vertically (in a direction which was parallel with both the axis of the tube and the
211 direction of tip vibration). A battery powered galvanostat was used to pass currents (of
212 known value) through the tube. The SVET V_{pp} signal generated was recorded and a
213 calibration factor was calculated using the generated plots. This factor allowed SVET V_{pp}
214 signals to be converted to j_z values.

215 Following calibration, samples were securely attached to the bottom of the SVET tank.
216 Scans were conducted immediately following immersion in 0.86 M NaCl, and every 30
217 minutes thereafter for a 24-hour period. The SVET probe was scanned perpendicular to
218 the surface of the sample and the probe-sample spacing was 100 μm . The electrolyte was
219 unstirred at a temperature of 20 $^{\circ}\text{C}$.

220 Only the localized corrosion currents which arise from anodic and cathodic sites
221 separated by distances greater than the scan height (in this case 100 μm) can be
222 efficiently detected by SVET. For cases when the spacing is smaller than the scan height,
223 the current flux lines will no longer cross the plane of scan and will not be detected (or at
224 best inefficiently).^{42, 46} The SVET response peak for a point current source has a
225 theoretical width at half maximum (*whm*) of $1.53z$ (where z is the probe height).⁴⁷⁻⁴⁸ The
226 electrically sensitive part of the micro-tip has a finite width and peak broadening occurs.
227 The *whm* for the SVET used here has previously been listed as $\sim 260 \mu\text{m}$ when $z=100$
228 μm .⁴⁶

229 Surfer 8 (Golden Software) was used to plot SVET derived j_z data. Positive j_z values were
230 numerically integrated (via Equation 3) to obtain both the total anodic current ($I_{a(t)}$) and
231 area-averaged total anodic current density ($J_{a(t)}$) associated with each scan.

232
$$I_{at} = A \cdot J_{a(t)} = \int_0^X \int_0^Y [j_z(x,y,t) > 0] dx dy \quad (3)$$

233 where X and Y are the scan dimensions and A is the scan area. Similarly, negative j_z
234 values can be used to obtain total cathodic current ($I_{c(t)}$) and area-averaged total cathodic
235 current density ($J_{c(t)}$).

236 Faraday's law (Equation 4) can then be used to calculate the total amount of charge
237 density and mass loss associated with local anodes over the entire experimental time
238 period

$$239 \quad q = \frac{2Fm}{M} = \int_{t=0}^{t=t_{\max}} j_t dt \quad (4)$$

240 where q is the total charge density, m is the mass loss per unit area, M is the atomic
241 weight of Zn (65.38 Da), n is the valence of metal ions (2), F is the Faraday constant,
242 t_{\max} is the total immersion time. In all cases it is assumed that i_t remained constant
243 between scans.

244 **3. Results**

245 *3.1 Resistivity measurements*

246 The conductivity values associated with each type of coating are shown in Table 2. Data
247 intervals correspond to one standard deviation on the mean of three measurements. In the
248 absence of Zn, the conductivity of the coating was less than the lowest quantity which
249 could be measured by the available instrumentation. In comparison, a value of 250 S.m⁻¹
250 was obtained for ZnSG coatings, this falling to 170 S.m⁻¹ in the case of CZnSG.

251 **(Table 2)**

252 *3.2 Adhesion Measurements*

253 A rating of 5B (0 % coating removed) was recorded for ZnSG. Results for CZnSG varied
254 between 4B (less than 5% of the coating removed) and 3B (5% to 15% of the coating
255 removed).

256 *3.3 Salt spray*

257 The capability of coatings to provide corrosion protection to the steel substrate was
258 evaluated using accelerated corrosion exposure testing. During the 42 day period of
259 exposure, the coated samples were removed from the accelerated corrosion test chamber
260 for periodical evaluation. Photographs of the sample type after each time period are
261 shown in Figures 2-4.

262 The appearance of the CSG coating at various time intervals is shown in Figure 2. In the
263 case of unscribed samples (Figure 2a), brown Fe based corrosion product can be seen on
264 the sample surface within a few days and is assumed to form at defects in the coating, or
265 where the electrolyte has percolated through the coating. In the case of the scribed sample
266 (Figure 2b), red rust can be observed almost immediately and covers the entire surface
267 after 7 days.

268 Whilst the amount of white Zn corrosion product on ZnSG coatings increases with time
269 (Figure 3), substrate corrosion is not observed on un scribed (Figure 3a) or scribed
270 (Figure 3b) samples for the entire 42 day exposure period.

271 The appearance of the CZnSG coating at various time intervals is shown in Figure 4. The
272 corrosion protection capability (specially the sacrificial corrosion protection) is clearly
273 retained in the presence of coloured pigments. However, after several days of exposure in
274 the accelerated chamber, the formation of Zn corrosion products changes the aesthetics of
275 the coupons.

276 (Figure 2)

277 (Figure 3)

278 (Figure 4)

279 3.4 OCP Results

280 Figure 5 shows the free corrosion potential (E_{corr}) of coated steel samples, immersed in
281 0.86 M NaCl, as a function of immersion time. The E_{corr} measured for the A36 steel
282 substrate is ~ 0.45 V vs. SHE, and consistent with that expected for freely corroding steel.
283 In the case of CSG coatings (in the absence of Zn particles), E_{corr} is in the range of -0.4
284 vs. SHE, which indicates no cathodic protection⁴⁹⁻⁵² at all times and is similar to that
285 recorded for the bare steel substrate. For ZnSG and CZnSG coatings, E_{corr} remains below
286 -0.76 V vs. SHE for the 24 hour time period indicating cathodic protection of the
287 substrate.⁴⁹⁻⁵² Figure 5 also shows that E_{corr} values for both ZnSG coatings increase
288 approximately linearly with time after immersion, which is indicative of the gradual
289 dissolution of Zn.

290 (Figure 5)

291 3.5 EIS Results

292 Figure 6 shows the Bode plots obtained for a.) CSG and b.) CZnSG obtained after
293 immersion in 0.86 M NaCl for varying periods of time and Table 3 shows time dependent
294 low frequency impedance values obtained from Figure 6. For CSG coatings, the value of
295 $|Z|$ remains fairly uniform over the frequency range and decreases with immersion time.
296 The phase angle remains near zero ($\sim -10^\circ$) for the entire time of immersion (Figure 6a).

297 For CZnSG coatings, the values of $|Z|$ recorded (Figure 6b) are ~3 times smaller than
298 those measured in the absence of Zn. The gradient of the $|Z|$ Bode plot tends toward -0.5
299 (Figure 6b) after longer periods of immersion. The phase angle values recorded at the
300 lowest frequencies during the initial times of immersion indicate that the overall circuit
301 impedance is dominated by resistive elements. The same is true at the high frequency
302 limit at which $|Z|$ tends toward the solution resistance (R_{solution}). The deviation away from
303 this behaviour at longer immersion times (20-24 hours) is likely to be a result of the
304 system becoming diffusion limited.

305 *(Figure 6)*

306 *(Table 3)*

307 *3.6 SVET Results*

308 **Intact coatings:** Figure 7 shows the SVET derived normal current density values
309 measured above CSG, ZnSG and CZnSG coatings immersed in 0.86 NaCl after various
310 periods of time. For CSG coatings (Figure 7a) the anodic (red) and cathodic (blue) j_z
311 values recorded are relatively small and spread evenly over the surface of the sample. The
312 j_z values recorded above ZnSG coated steel (Figure 7b) are an order of magnitude larger
313 than those observed for CSG coatings and in the region of those expected in the case that
314 electron transfer is not limited by an insulating coating. The cathodic current is spread
315 evenly across the surface and appears to dominate the sample surface. This effect has
316 previously been attributed to the vibration of the SVET probe which tends to increase the
317 transport of O_2 to the metal surface⁵³⁻⁵⁴ and which has previously been shown to increase
318 the oxygen reduction current by 3-4 times.⁵³ It is also worth considering that SVET
319 detects net current values and is only able to detect localized corrosion currents which

320 arise from anodic and cathodic sites separated by distances greater than the scan height
321 (in this case 100 μm). In the case of general corrosion the current flux lines will no longer
322 cross the plane of scan and will not be detected.^{42, 46} It is therefore possible that the
323 SVET is unable to resolve anodic areas present within the ‘net’ cathodic defect region

324 Small regions of localized anodic activity are also apparent. The ZnSG coatings are
325 porous and are therefore expected to become permeable with respect to the experimental
326 electrolyte, to some extent at least. However, red rust (indicative of anodic iron
327 dissolution) was not observed anywhere on the sample surface, even at the end of the 24
328 hour experimental time period. It therefore seems reasonable to assume that the anodic
329 current density regions detected by SVET arise from the sacrificial anodic dissolution of
330 zinc particles in the coating, and not from attack on the underlying steel substrate. In the
331 case of CZnSG coated steel slightly smaller current density values (~ 0.5 times those
332 measured for ZnSG) were recorded (Figure 7c). The net anodic area appears to increase
333 with immersion time. Figure 8a and 8b show that the corresponding integrated anodic
334 current density, and accumulated mass loss, obtained using Equation 3 and Equation 4
335 respectively, are higher in the case of CZnSG coatings, compared to ZnSG coatings.

336 *(Figure 7)*

337 *(Figure 8)*

338 **Sacrificial protection by ZnSG:** The ability of ZnSG coatings to provide sacrificial
339 protection to the underlying steel substrate was investigated by creating an artificial
340 coating defect by mechanical abrasion of the coating. Figure 9 shows the SVET derived
341 normal current density values measured above CSG, ZnSG and CZnSG coatings in the
342 presence of a 5 mm x 2 mm (12 % of total area) defect. As expected, for CSG (Figure 9a)

343 the coating is unable to offer any sacrificial protection. Immediately after immersion a net
344 cathodic area covers half of the sample, whilst the other half remains anodic. Fairly
345 rapidly a strong net anode is established in the defect region which is covered in red rust
346 following 24 hours of immersion. Lower j_z values are observed on the intact coating,
347 which acts as a partial barrier to electrolyte ingress. In comparison, for ZnSG coatings
348 (Figure 9b) the exposed steel remains cathodic with respect to the ZnSG surface.
349 Whereas the anodic j_z are distributed evenly over the surface of the intact coating, the
350 anodic j_z recorded for CZnSG coatings are localised at the defect edge during the first 4
351 hours of immersion. The anodic current becomes more evenly distributed as immersion
352 time increases. The re-distribution of anodic activity within the first few hours of
353 immersion can be seen more clearly in Figure 10 which shows the j_z values recorded
354 along the dotted lines in Figure 9c at various times of immersion. Values of up to ~ 1.3
355 A.m^{-2} are observed within the defect region during the initial scan. After just 2 hours this
356 value has fallen significantly and any remaining anodic activity ($\sim 0.3 \text{ A.m}^{-2}$) is localized
357 at the defect/coating interface. After 8 hours the anodic current density at the defect/
358 coating boundary is similar to that observed over the remainder of coated region of the
359 sample. Figure 11b shows j_z values recorded along the dotted lines shown in Figure 9c
360 during the later stages of CZnSG immersion. Between 12 and 20 hours the net cathodic
361 current density progressively decreases from $\sim 0.4 \text{ A.m}^{-2}$ to $\sim -0.2 \text{ A.m}^{-2}$ within the
362 defect region and there is some evidence that the same process occurs for ZnSG coatings.
363 When considering Figure 10 it should be borne in mind that the j_z values shown are only
364 taken from one scan line and resultantly the anodic and cathodic currents do not balance

365 For both ZnSG and CZnSG coatings the iron surface behaves as a net cathode for the 24
366 hour duration of the experiment and red rust is not observed on either surface following
367 24 hours of immersion.

368 *(Figure 9)*

369 *(Figure 10)*

370 Figure 11a and Figure 11b show the corresponding integrated anodic current density, and
371 accumulated mass loss, obtained using Equation 3 and Equation 4, respectively. As with
372 Figure 8, the reason for the higher values obtained for CZnSG coatings is, as yet,
373 unknown. Regardless, it is clear, from both Figure 9 and Figure 11, that ZnSG coatings
374 are able to provide sacrificial protection to the underlying substrate in the presence of the
375 green coloured pigment.

376 *(Figure 11)*

377 Having established the ability of ZnSG coatings to provide sacrificial protection to the
378 underlying substrate, the effect of defect area was investigated. Figure 12 shows the
379 SVET derived normal current density values measured above ZnSG coatings in the
380 presence of defects of varying size. In all cases the defect remained cathodic for the
381 entirety of the experiment time period (24 hours). For defects covering 25 % (Figure 13b)
382 and 52 % (Figure 12c) of the total area, small anodic regions are observed within the
383 cathodic defect region towards the end of the experiment. However, red rust was not
384 observed on the surface after 24 hours of immersion, even in the case of the largest defect
385 (covering 52 % of total area). Figure 13a and Figure 13b show the corresponding
386 integrated anodic current density, and accumulated mass loss, obtained using Equation 3
387 and Equation 4, respectively. In both cases the values recorded increase when the

388 exposed area increases from 12 % to 25 %. This increase in Zn dissolution is expected in
389 the case of a bigger cathode area. A decrease in both values are observed when the
390 exposed area is increased to ~52 % of the total area.

391 (*Figure 12*)

392 (*Figure 13*)

393 **4. Discussion**

394 *4.1 CSG coatings:* In the absence of Zn, CSG coatings provide barrier protection (and not
395 sacrificial protection) to the underlying substrate (Figure 5). This results in the low j_z
396 values recorded above an intact CSG coating immersed in NaCl (Figure 7a). The values
397 of total impedance $|Z|$ recorded upon initial immersion are low compared to those
398 previously reported for sol-gel coated steel (where coating thickness is comparable to, or
399 less, than that used here) ⁵⁵⁻⁵⁷ This suggests that sol-gel (used in isolation) is a poor
400 barrier coating ⁵⁸ and is consistent with the known inherent porosity associated with this
401 type of coating. ¹³ The low phase angles shown in Figure 6a indicate that the system is
402 dominated by resistive characteristics. The value of $|Z|$ is likely to tend toward that of the
403 coating resistance (R_{coating}), which is believed to originate from columns of electrolyte
404 which form within the porous structure of the organic polymer coating and allow limited
405 contact between the electrode and solution. As $|Z|$ tends to be dominated by, and have
406 characteristics of, the smallest individual impedance it follows that the capacitor
407 impedance be significantly higher than $\sim 1000 \Omega \cdot \text{cm}^{-2}$, even at a frequency of 100, 000
408 Hz. To check the plausibility of this statement the value of the coating capacitance was
409 calculated using Equation 5, where A is the coating area (in this case 1 cm^2), d is the
410 coating thickness ($\sim 30 \mu\text{m}$) and ϵ_0 is the permittivity of free space. The dielectric

411 constant of the CSG will vary with water content, but is, in the first instance, assumed to
412 be that of silica (~ 3.8)⁵⁹⁻⁶⁰. The calculated value (~ 0.1 nF) can be used in Equation 6 to
413 determine the capacitor impedance at a frequency (f) of 100, 000 Hz. The value obtained
414 ($10^4 \Omega.m^{-2}$) is an order of magnitude larger than the value of $|Z|$. This finding is
415 consistent with the system for which $|Z|$ is dominated by the resistive characteristics of
416 the coating. There is a slight decrease in the phase angle at the highest frequency which
417 may indicate that the capacitor impedance is becoming more dominant.

418
$$C = \frac{\epsilon_0 \epsilon A}{d} \quad (5)$$

419
$$Z = \frac{1}{2\pi f C} \quad (6)$$

420 The time dependent decrease in $|Z|$ (Figure 6a) is consistent with the gradual ingress of
421 electrolyte which, in time, reaches the steel substrate.

422 In the case that the coating is not fully intact, for example at pores in the coating (Figure
423 2a) or at artificial coating defects (Figure 2b) the CSG is unable to offer sacrificial
424 protection and anodic attack initially occurs within the defect (Figure 9a). As time
425 progresses, the electrolyte will ingress through pores in the CSG to the substrate and it is
426 predicted that a net anode and cathode would eventually divide the underlying steel (as is
427 the case on plain steel).

428 **4.2 ZnSG:** ZnSG coatings are able to provide sacrificial protection to the underlying steel
429 substrate (Figure 5) and substrate corrosion was not observed on intact (Figure 3a) or
430 scribed coatings (Figure 3b) after 42 days of salt spray exposure. Coatings were able to
431 provide sacrificial protection to artificial coating defects (where the underlying steel
432 substrate was exposed) which covered up to 52 % of the total sample area for 24 hours of

433 immersion in 0.86 M NaCl and red rust is not observed following immersion (Figure 12).
434 The delay in the galvanic effect, and in the establishment of discrete anodic and cathodic
435 sites, increases with defect size. A similar time-dependent evolution of galvanic current
436 was observed during a scanning reference electrode technique (SRET) study into the
437 galvanic corrosion processes occurring in the region of coating defects and cut edges on
438 galvanised (Zn) steel ⁶¹⁻⁶² The build-up of galvanic current probably reflects a time-
439 dependent depassivation of the zinc surface and the establishment of stable sites of anodic
440 zinc (powder) dissolution. The stabilization and lateral spreading of anodic activity
441 occurs as a consequence of local changes in electrolyte composition at anodic sites. An
442 aggressive anolyte (with reduced pH and increased chloride activity) develops through a
443 combination of electro-migration (of Cl⁻) and hydrolysis (of Zn²⁺).⁶³⁻⁶⁴ The galvanic
444 current produces an alkaline catholyte by forcing the ORR onto the iron surface, leading
445 to the evolution of passivity (and suppression of anodic dissolution) on iron. This process
446 is visualized in Figure 9 and Figure 10 which show that the anodic current is initially
447 concentrated at the defect/coating interface. As time progresses Zn dissolution occurs
448 uniformly along the coating and a plateau in current density is observed.

449 The increase in SVET derived integrated anodic current density (Figure 13a), and
450 accumulated mass loss (Figure 13b) when the exposed area increases from 12 % to 25 %
451 of the total surface area is consistent with an increase in Zn dissolution which is expected
452 in the case of a larger cathode area. Figure 13b also shows that, between 4 and 12 hours,
453 the total anodic current recorded for a 25 % exposed area is ~ 2 x that measured in the
454 case that 12 % of the area is exposed. This indicates that the anodic current is directly
455 proportional to the exposed area and is consistent with efficient sacrificial protection of
456 the steel by the zinc based coating. The total cathodic current emerging from the defect

457 which covered 25 % of the total area was almost double that recorded when 12 % was
458 exposed. This finding implies that the individual cathodic j_z values (measured on the steel
459 defect) are independent of exposed area and supports the notion that the localised
460 corrosion observed is under cathodic control (i.e twice the anodic current is recorded
461 when doubling the defect area). The progressively decreasing current values with time is
462 likely to be a result cathodic deactivation through precipitation which inhibits the ORR
463 occurring on the steel surface. This ‘cathodic self-healing’ mechanism has been observed
464 previously during the study of cut edge corrosion occurring on Zn galvanised steel sheet.
465 ⁶⁵⁻⁶⁹ The zinc cations (at the anodic sites) interact with the hydroxide ions (produced at
466 cathodic sites) to form zinc based corrosion products on the active cathode. ⁶⁵⁻⁶⁹ This
467 process is controlled by the increase in interfacial pH and the precipitation of white zinc
468 based corrosion product formed on the region of exposed steel (scribe) in Figure 3 and
469 Figure 4 and within the defect area in Figure 9c.

470 This relationship appears to break down for a larger defect size (defects covering 52 % of
471 the total area). Small anodic regions are observed within the cathodic defect region
472 towards the end of the experiment (Figure 12c) and it is assumed that significant anodic
473 activity becomes co-located on the steel. It then seems plausible that subsequent decrease
474 in integrated anodic current density (Figure 13a), and accumulated mass loss (Figure 13b),
475 observed when the exposed area is increased to 52 % of the total area, is a consequence
476 of the limitations of the SVET to resolve localized corrosion. In the case that spacing is
477 smaller than the scan height, it is possible that current flux lines do not cross the plane of
478 scan and that the SVET is unable to resolve anodic areas present within the ‘net’ cathodic
479 defect region. ^{42, 46}

480 4.3 CZnSG; As demonstrated by the open circuit potential measurements shown in Figure
481 5, CZnSG coatings are able to provide sacrificial protection to the underlying steel
482 substrate and substrate corrosion is not observed on scribed coatings after 42 days of salt
483 spray exposure (Figure 4). Zn corrosion occurs over the entirety of the intact CZnSG
484 coating, which appear white after 24 hours of immersion (Figure 9c). Corrosion product
485 is also found to form within defects in the CZnSG coatings. This corrosion product build
486 up leads to the reduction in cathodic current density observed in Figure 10. The value of
487 CZnSG coating resistance (obtained using data given in Table 1 and Table 2) is low
488 ($\sim 1.8 \text{ m}\Omega$), and charge transfer resistance (R_{CT}) is thought to dominate at low frequency
489 values. The gradient of the $|Z|$ Bode plot tends toward -0.5 (Figure 6b) after longer
490 periods of immersion. This is consistent with finite diffusion control and a semi-infinite
491 Warburg diffusion characteristic which is believed to be a result of the more torturous
492 route of oxygen diffusion experienced in the presence of this corrosion product. The
493 reasons for the increase in SVET derived anodic j_z values and the associated accumulated
494 mass loss, recorded for CZnSG compared to ZnSG coatings, is unclear. However, given
495 the reduction in conductivity observed for CZnSG coatings (compared to ZnSG coatings),
496 it is plausible that the coloured pigments give some physical obstructions to Zn
497 connectivity. In the presence of an artificial defect emerging anodic current is focused on
498 the defect edges over the first 4 hours of immersion, and becomes more uniformly
499 distributed as immersion time increases. This is consistent with the notion that the
500 coloured pigment, present in CZnSG coatings, acts as a barrier which restricts the ability
501 of the Zn (present within the coating) to couple with the underlying steel substrate. The
502 defect edge presents a low resistance pathway through which the local galvanic cell
503 current can emerge. It is also plausible that increased porosity/defects exist in coloured

504 coatings due to the presence of the coating additive used to aid in pigment wetting and
505 dispersion.

506 Despite the decreased protection observed for CZnSG, the sacrificial protection offered is
507 deemed adequate for a single layer Zn rich coating.

508 **5. Conclusions**

509 An electrochemical investigation into the ability of zinc rich sol gel coatings to provide
510 sacrificial protection to steel substrates was conducted to show that;

- 511 • For CSG coatings the impedance remains uniform over the frequency range and
512 the coatings behave as resistors. The value of $|Z|$ decreases with immersion time.
513 For CZnSG coatings the gradient of the $|Z|$ Bode plot tends toward -0.5 after
514 longer periods of immersion and is consistent with a semi-infinite Warburg
515 diffusion characteristic which is believed to be a result of the more torturous route
516 of oxygen diffusion experienced in the presence of this corrosion product.
- 517 • For intact CSG coatings SVET derived j_z values are relatively small and
518 consistent with those expected in the case that limited electron transfer occurs.
519 CSG coatings are unable to offer any sacrificial protection in the presence of a
520 coating defect.
- 521 • For both ZnSG and CZnSG coatings the exposed steel remains cathodic with
522 respect to the coating for the entire 24-hour experimental time period. The SVET
523 derived integrated anodic current density, and accumulated mass loss values
524 obtained are higher for CZnSG coatings, compared to ZnSG coatings.
- 525 • ZnSG coatings are able to provide sacrificial protection (remains cathodic) for 24
526 hours in the presence of defects which cover up to ~ 52 % of the total sample area.

527 The SVET derived integrated anodic current density and accumulated mass loss
528 values increase when the exposed area increases from 12 % to 25 %.

529 It is proposed that;

530 • CSG coatings are only able to provide barrier protection (not sacrificial
531 protection) to the underlying substrate and anodic attack initially occurs locally
532 within any coating defects. As time progresses the electrolyte will ingress through
533 pores in the CSG and corrosive attack will be spread eventually over the substrate
534 surface.

535 • ZnSG coatings are able to provide sacrificial protection to the underlying steel
536 and an increase in defect size results in the increased dissolution of Zn and at
537 prolonged time periods anodic dissolution of the underlying substrate may occur.

538 • CZnSG coatings are able to provide sacrificial protection to the underlying steel
539 substrate. However, it is plausible that the presence of coloured pigments
540 physically obstruct Zn connectivity and act as barriers which restricts the ability
541 of the Zn to couple with the underlying steel substrate. Another possibility is that
542 increased porosity/defects exist due to the presence of the coating additive used to
543 aid in pigment wetting and dispersion.

544 **6. Acknowledgments**

545 Authors would like to thanks Building & Construction Authority (BCA), Singapore for
546 the support for this work through the MNDRF DfMA & BIM Grant Call. We thank
547 industrial collaborators; FRP Products Co Pte Ltd and ZINGAMETALL(S) Pte Ltd for
548 their support.

549 **7. Tables**

550 Table 1. Coating composition.

	Coloured SG	ZnSG	Coloured ZnSG
Thickness (μm)	38 \pm 5	31 \pm 5	30 \pm 5
Sol gel (Vol %)	91.5	37.3	36.9
Zinc (Vol %)	0	60.4	59.7
Silica (Vol %)	5.5	2.2	2.2
Green Pigment (Vol %)	3.0	0	1.2

551 Table 2. Coating conductivity Measurements.

	Conductivity (S.m^{-1})
ZnSG	250 \pm 47
Coloured ZnSG	170 \pm 32
SG	< 2 x 10 ⁻²

552 Table 3. EIS derived $|Z|$ at 0.1 Hz.

Immersion time (hours)	$ Z $ ($\Omega.\text{cm}^{-2}$)	
	CSG	CZnSG
1	1421	229
2	2822	237
3	1060	221
4	1025	219
5	1015	224
6	995	228
7	991	230
8	978	237
9	977	248
10	972	262
11	961	275
12	853	288
13	845	304
14	842	319
15	748	329
16	735	336
17	732	348
18	730	365
19	730	379
20	727	386
21	730	433
22	720	466
23	715	500
24	712	528

553

554 **8. Figure Legends**

555 Figure 1. A schematic representation the process followed during the manufacture of the
556 sol-gel based binder.

557 Figure 2. Optical images of scribed and un scribed CSG coatings after various times of
558 exposure to an accelerated cyclic corrosion test according to ISO 14993.

559 Figure 3. Optical images of scribed and un scribed ZnSG coatings after various times of
560 exposure to an accelerated cyclic corrosion test according to ISO 14993.

561 Figure 4. Optical images of scribed and un scribed CZnSG coatings after various times of
562 exposure to an accelerated cyclic corrosion test according to ISO 14993.

563 Figure 5. E_{corr} as a function of time for intact CSG, ZnSG and CZnSG coatings immersed
564 in 0.86 M NaCl for 24 hours.

565 Figure 6. Bode and Nyquist plots produced using data obtained during EIS investigations
566 of a.) CSG and b.) CZnSG coatings immersed in 5 % NaCl for 24 hours. The input AC
567 amplitude was 10 mV and the frequency range was from 0.05 Hz to 100 kHz.

568 Figure 7. SVET derived surface maps showing the distribution of normal current density
569 j_z above intact a.) CSG, b.) ZnSG and c.) CZnSG samples freely corroding in near neutral
570 0.86 M NaCl after various immersion times.

571 Figure 8. SVET derived a.) integrated anodic current density and b.) accumulated mass
572 loss as a function of time in the case of intact CSG, ZnSG and CZnSG coatings immersed
573 in 0.86 M NaCl for 24 hours.

574 Figure 9. SVET derived normal current density values measured above CSG, ZnSG and
575 CZnSG coatings in the presence of a 5 mm x 2 mm (12 % of total area) defect after
576 various times of immersion in 0.86 M NaCl. The optical images show the surface
577 appearance of each sample following immersion in 0.86 M NaCl for 24 hours.

578 Figure 10. A plot of the j_z values recorded along a.) the dotted lines shown in Figure 9
579 after various immersion times shown along with schematics showing the mechanism by
580 which coatings are believed to provide sacrificial protection to the steel substrate at
581 coating defects.

582 Figure 11. SVET derived a.) integrated anodic current density and b.) accumulated mass
583 loss as a function of time in the case that 5 mm x 2 mm (12 % total area) artificial defect
584 is created in the CSG, ZnSG and CZnSG coatings which are then immersed in 0.86 M
585 NaCl for 24 hours.

586 Figure 12. SVET derived normal current density values measured above ZnSG coatings
587 in the presence of a a.) 5 mm x 2 mm (12 % of total area), b.) 5 mm x 4 mm (26 % of

588 total area), c.) 7 mm x 6 mm (52% of total area) defect after various times of immersion
589 in 0.86 M NaCl.

590 Figure 13. SVET derived a.) integrated anodic current density and b.) accumulated mass
591 loss as a function of time in the case that artificial defects of varying size are created in
592 ZnSG coatings which are then immersed in 5 % NaCl for 24 hours.

593 9. References

- 594 1. M. Guglielmi, Journal of Sol–Gel Science and Technology. **8**, 443 (1997).
- 595 2. D. Wang, G. P. Bierwagen, Progress in Organic Coatings. **64**, 327 (2009).
- 596 3. D. Balgude, A. Sabnis, Journal of Sol-Gel Science and Technology. **64**, 124
597 (2012).
- 598 4. R. Kasemann, H. Schmidt, New Journal of Chemistry. **18** 1117 (1994).
- 599 5. M. Fedel, F. Deflorian, S. Rossi, in *Green corrosion chemistry and engineering:
600 opportunities and challenges*, 1st ed, S. K. Sharma, Editor, p. 181, Weinheim:
601 Wiley-VCH Verlag GmbH & Co. (2012).
- 602 6. J. Kron, K. J. Deichmann, K. Rose, in *Self-Healing Properties of New Surface
603 Treatments (EFC 58)*, L. Fedrizzi, W. Fürbeth, F. Montemor, Eds., p.105, Leeds:
604 Institute of Materials, Minerals and Mining (2011).
- 605 7. Y-S. Li, W. Lu, Y. Wang, T. Tran, Spectrochimica Acta A. **73**, 922 (2009).
- 606 8. L. K. Tan, A. M. Soutar, Thin Solid Films. **516**, 5706 (2008).
- 607 9. Z. Feng, Y. Liu, G. E. Thompson, P. Skeldon, Electrochimica Acta. **55**, 3518
608 (2010).
- 609 10. A.L.K. Tan, A. M. Soutar, I. F. Annergren, Y. N. Liu, Surface and Coatings
610 Technology. **198**, 478 (2005).
- 611 11. N. Norzita, M. Haziq, M. Zurina, International Journal of Chemical and
612 Environmental Engineering. **3**, 267 (2012).
- 613 12. G. Parashar, D. Srivastava, R. Kumar, Progress in Organic Coatings. **42**, 1 (2001).
- 614 13. P. Zarras, J. D. Stenger-Smith, in *Intelligent Coatings for Corrosion Control*, A.
615 Tiwari, J. Rawlins, L. H. Hihara, Eds., p. 59, Butterworth Heinemann (2015).
- 616 14. T. L. Metroke, R. L. Parkhill, E. T. Knobbe, Progress in Organic Coatings. **41**,
617 233 (2001).
- 618 15. R. B. Figueira, C. J. R. Silva, E. V. Pereira, Surface and Coatings Technology.
619 **265**, 191 (2015).

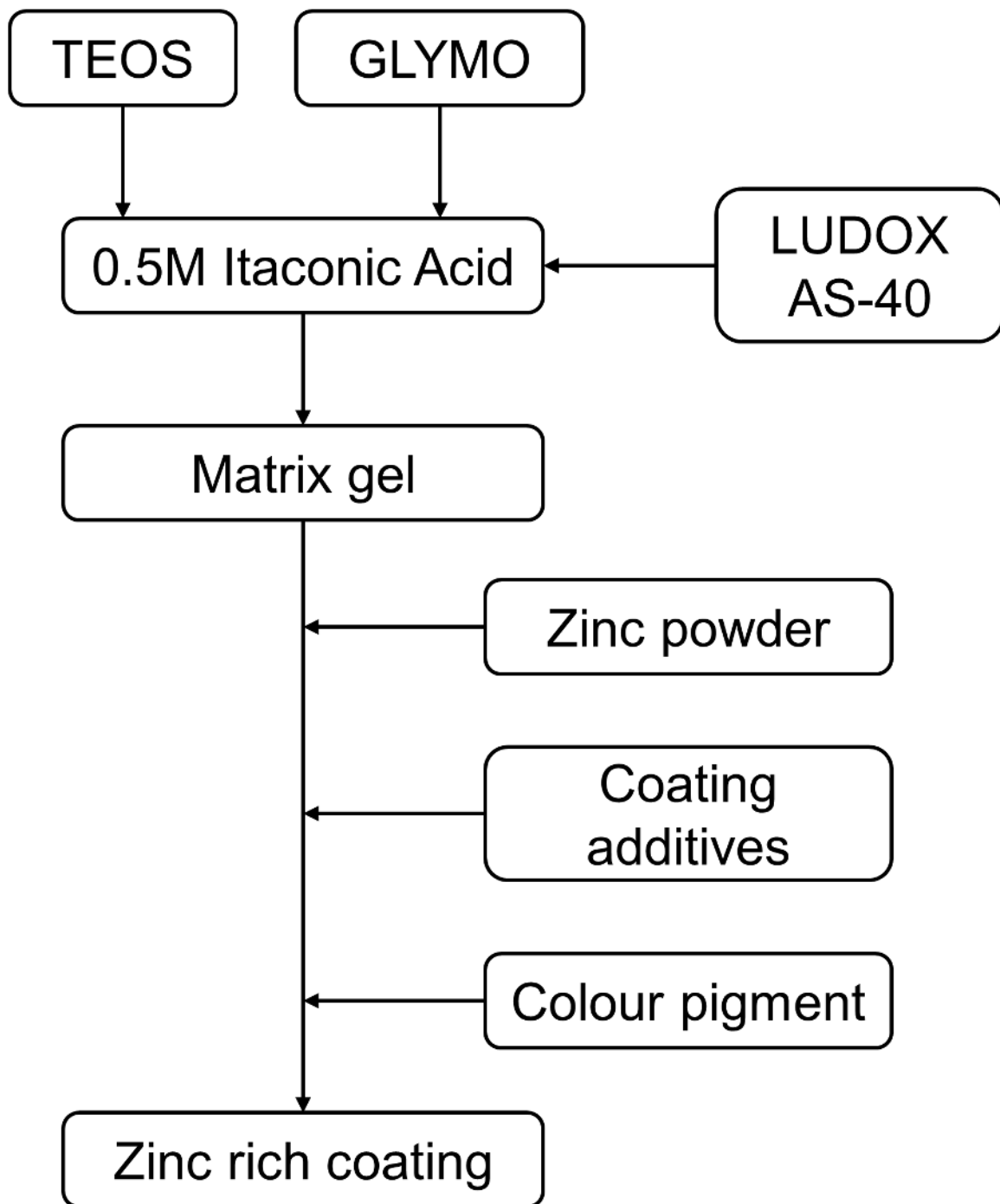
- 620 16. C. A. Sáenz, E. Martin-Ugarte, J. B. Jorcín, G. Imbuluzqueta, P. S. Coloma, U.
621 Izagirre-Etxeberria, *Journal of Sol-Gel Science and Technology*. **89**, 264 (2019).
- 622 17. P. Savignac, M. J. Menu, M. Gressier, B. Denat, Y. El Khadir, S. Manov, F.
623 Ansart, *Molecules*. **23**, 1079 (2018).
- 624 18. C. M. Abreu, M. Izquierdo, P. Merino, X. R. Novoa C. Perez, *Corrosion*. **55**, 1173
625 (1999).
- 626 19. R. Barajas, M. Morcillo, J.M. Bastidas, S. Feliú, *Pinturas y Acabados*. **33**, 55
627 (1991).
- 628 20. . S. Feliú, R. Barajas, J.M. Bastidas, M. Morcillo, *Journal of Coatings Technology*.
629 **61**, 63 (1989).
- 630 21. R. A. Armas, C. A. Gervasi, A. Disarli, S. G. Real, J. R. Vilche, *Corrosion*. **48** (5),
631 379 (1992).
- 632 22. F. Theiler, *Corrosion Science*. **14**, 405 (1974).
- 633 23. D. Pereira, J. Scantlebury, M. Ferreira, M. Almeida, *Corrosion Science*. **30**, 1135
634 (1990).
- 635 24. S. Lindquist, L. Meszaros, L. Svenson, *Journal of the Oil and Colour Chemists’*
636 *Association*. **68**, 10 (1985).
- 637 25. R. Fernandez-Prini, S. Kapusta, *Journal of the Oil and Colour Chemists’*
638 *Association*. **62**, 93 (1979).
- 639 26. O. O. Knudsen, U. Steinsmo, M. Bjordal, *Progress in Organic Coatings*. **54**, 224
640 (2005).
- 641 27. H. Marchebois, M. Keddám, C. Savall, J. Bernard, S. Touzain, *Electrochimica*
642 *Acta*. **49**, 1719 (2004).
- 643 28. M. Morcillo, R. Barajas, S. Feliu, J. M. Bastidas, *Journal of Materials Science*. **25**,
644 2441 (1990).
- 645 29. J. E. O. Mayne, U. R. Evans, *Soc. Chem. Ind. Rev.* **22**, 109 (1944).
- 646 30. J. E. O. Mayne, *Soc. Chem. Ind. Rev.* **66**, 93 (1947).
- 647 31. T. K. Ross, J. Wolstenholme, *Corrosion Science*. **17**, 341 (1977).
- 648 32. S. E. Faidi, J. D. Scantlebury, P. Bullivant, N. T. Whittle, R. Savin, *Corrosion*
649 *Science*. **35**, 1319 (1993).
- 650 33. M. Yekehtaz, C. Klesen, S. Benfer, W. Bleck, W. Fürbeth, *Materials and*
651 *Corrosion*. **63**, 940 (2012).

- 652 34. O. Razavizadeh, M. Ghorbani, *Journal of Sol-Gel Science and Technology*. 79
653 (2016) 133.
- 654 35. B. Kannan, C. F. Glover, H. N. McMurray, G. Williams, J. R. Scully, *Journal of*
655 *the Electrochemical Society*. **165**, C27 (2018).
- 656 36. L.Y.L. Wu, E. Chwa, Z. Chen, X.T. Zeng, *Thin Solid Films*. 516, 1056 (2008).
- 657 37. ISO 8501-1: 2007. Preparation of steel substrates before application of paints and
658 related products- Visual assessment of surface cleanliness- Part 1: Rust grades and
659 preparation grades of uncoated steel substrates and of steel substrates after overall
660 removal of previous coatings. Geneva, ISO Copyright Office (2007).
- 661 38. G. Löbber, in *Ullmann's Encyclopedia of Industrial Chemistry (Vol. 27)*, F.
662 Ullman, Ed., p. 181-213, Wiley-VCH (2011).
- 663 39. C.A. Gervasi, A.R. Di Sarli, E. Cavalcanti, O. Ferraz, E.C. Bucharsky, S.G. Real,
664 J.R. Vilche, *Corrosion Science*. **36**, 1963 (1994)
- 665 40. ASTM D3359-17, Standard Test Methods for Rating Adhesion by Tape Test,
666 ASTM International, West Conshohocken, PA (2017).
- 667 41. ISO 14993:2001. Corrosion of metals and alloys - Accelerated testing involving
668 cyclic exposure to salt mist, "dry" and "wet" conditions. Geneva, ISO Copyright
669 Office (2001).
- 670 42. G. Williams, H. N. McMurray, *J. Electrochem. Soc.*, **155**, C340 (2008).
- 671 43. S. Bohm, H. N. McMurray, S. M. Powell, D. A. Worsley, *Electrochimica Acta*, 45,
672 **2165** (2000).
- 673 44. D. Worsley, H. N. McMurray, A. Belghazi, *Chem. Commun.*, **24**, 2369 (1997).
- 674 45. S. M. Powell, D. A. Worsley, *British Corrosion Journal*, **36**, 42 (2001).
- 675 46. G. Williams, H. N. McMurray, R. Grace, *Electrochimica Acta*, **55**, 7824 (2010).
- 676 47. H. S. Isaacs, G. Kissel, *J. Electrochem. Soc.* **119**, 1628 (1972).
- 677 48. H. S. Isaacs, *J. Electrochem. Soc.*, **138**, 722 (1991).
- 678 49. BS EN 15112:2006
- 679 50. National Association of Corrosion Engineers SP0169-2013
- 680 51. National Association of Corrosion Engineers SP 05 75- 2007
- 681 52. National Association of Corrosion Engineers SP0176-2007

- 682 53. H. N. McMurray, D. Williams, D. A. Worsley, *Journal of the Electrochemical*
683 *Society*. **150**, B567 (2003)
- 684 54. A. C. Bastos, M. C. Quevedo, M. G. S. Ferreira, *Corrosion Science*. **92**, 309
685 (2015).
- 686 55. T. Lutzler, T.V.J. Charpentier, R. Barker, S. Soltanahmadi, W. Taleb, C. Wang,
687 A. Alejo-Rodriguez, E. Perre, H. Schneider, A. Neville, *Materials Chemistry and*
688 *Physics*. **216**, 272 (2018).
- 689 56. L. Claire, G. Marie, G. Julien, S. Jean-Michel, R. Jean, M. Marie-Joëlle, R.
690 Stefano, F. Michele, *Progress in Organic Coatings*. **99**, 337 (2016).
- 691 57. L. Vivar Mora, S. Naik, S. Paul, R. Dawson, A. Neville, R. Barker, *Surface and*
692 *Coatings Technology*. **324**, 386 (2017).
- 693 58. G. P. Bierwagen, L. Hi, J. Li, L. Ellingson, D. E. Tallman, *Progress in Organic*
694 *Coatings*. **39**, 67 (2000).
- 695 59. R. A. Serway, J. S. Faughn. *College Physics*. 6th edition. P. 519 Canada:
696 Thomson Learning (2003).
- 697 60. G. Chandrashekhar, M. Shafer, *MRS Proceedings*. **73** (1986) 705.
- 698 61. H. N. McMurray, S. R. Magill, B. D. Jeffs, *Ironmaking and Steelmaking*. **23**, 183
699 (1996).
- 700 62. H. N. McMurray, D. A. Worsley, in *Research in Chemical Kinetics Vol. 4*, R. G.
701 Compton, G. Hancock, Eds., p.149, Blackwell Science, Oxford UK (1997).
- 702 63. N. Wint, K. Khan, J. H. Sullivan, H. N. McMurray, *Journal of The*
703 *Electrochemical Society*, **166**, C3028 (2019).
- 704 64. N. Wint, N. Cooze, J. R. Searle, J. H. Sullivan, G. Williams, H. N. McMurray, G.
705 Luckeneder, C. Riener, *Journal of the Electrochemical Society*, **166**, C3147
706 (2019).
- 707 65. K. Ogle, V. Baudu, L. Garrigues, X. Philippe, *Journal of the Electrochemical*
708 *Society*. **147**, 3654 (2000).
- 709 66. K. Ogle, S. Morel, D. Jacquet, *Journal of the Electrochemical Society*. **153**, B1
710 (2006).
- 711 67. R. Krieg, M. Rohwerder, S. Evers, B. Schuhmacher, J. Schauer-Pass, *Corrosion*
712 *Science*. **65**, 119 (2012).
- 713 68. F. Thébault, B. Vuillemin, R. Oltra, K. Ogle, C. Allély, *Electrochimica Acta*. **53**
714 (2008) 5226.
- 715 69. F. Thébault, B. Vuillemin, R. Oltra, C. Allély, K. Ogle, *Electrochimica Acta*. **56**
716 (2011) 8347.

717

718



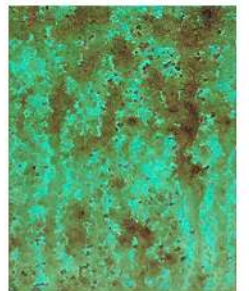
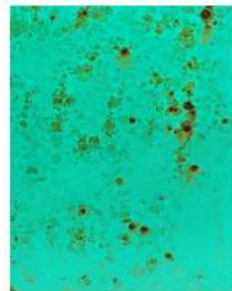
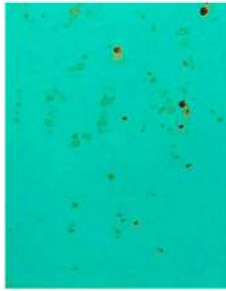
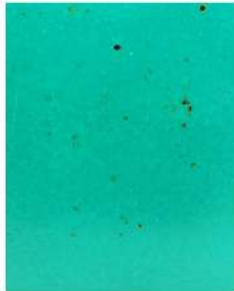
1 day

2 days

3 days

4 days

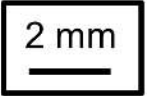
7 days



a.)



b.)



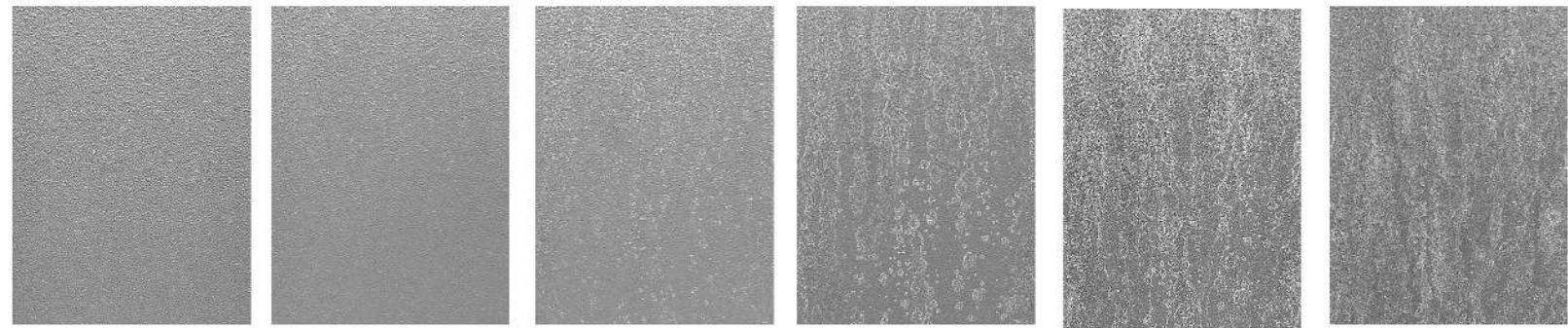
5 days

10 days

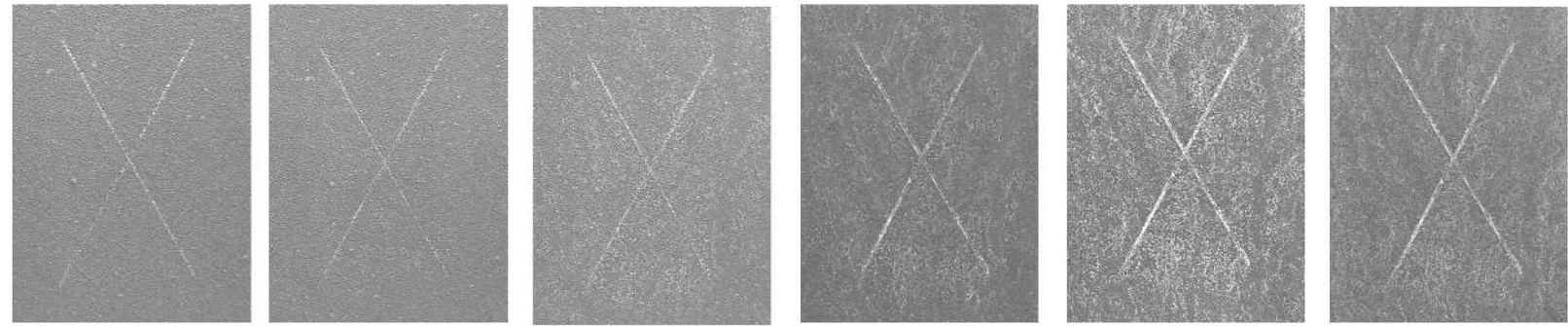
20 days

30 days

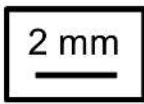
42 days



a.)



b.)



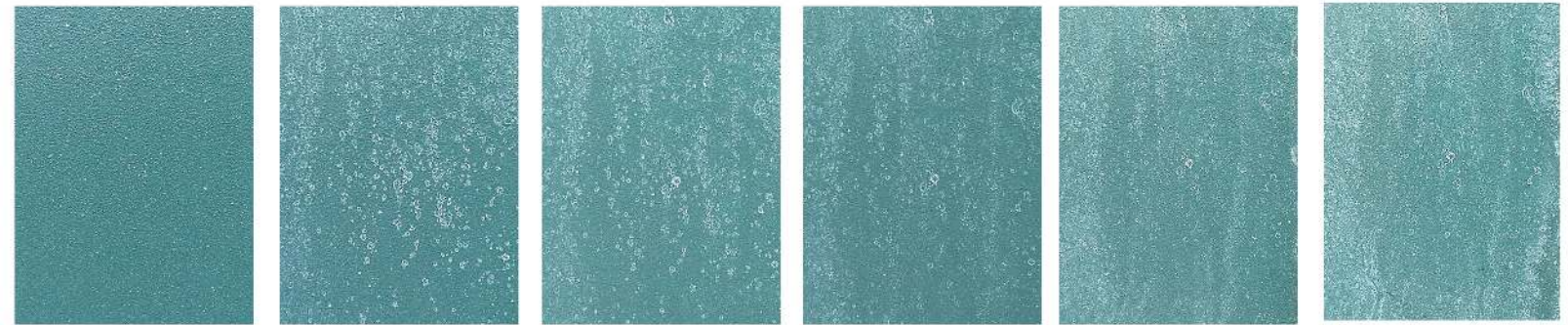
5 days

10 days

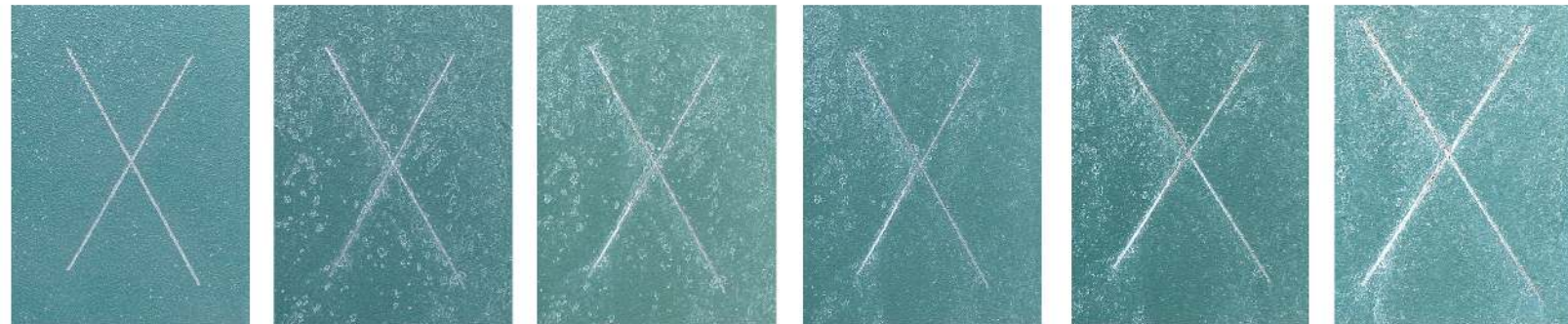
20 days

30 days

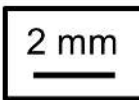
42 days

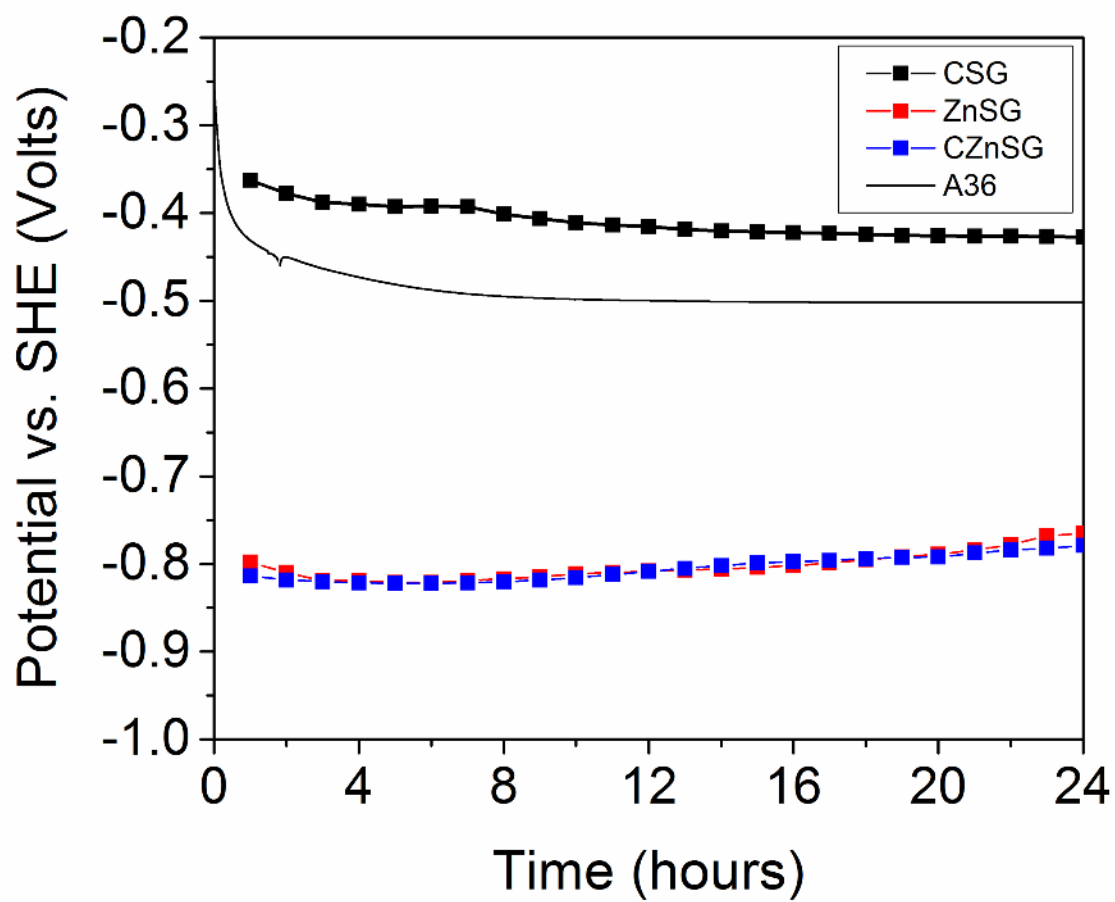


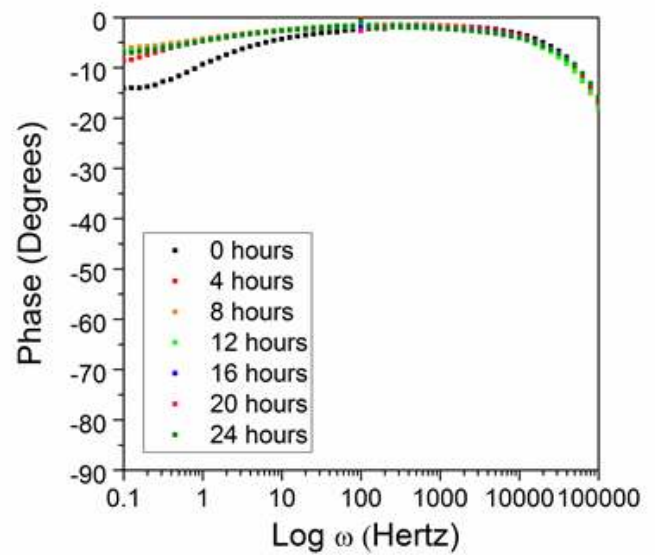
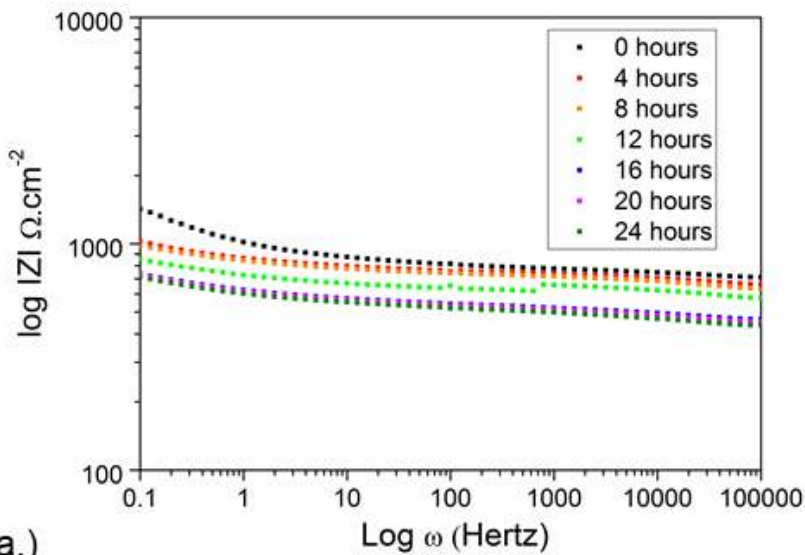
a.)



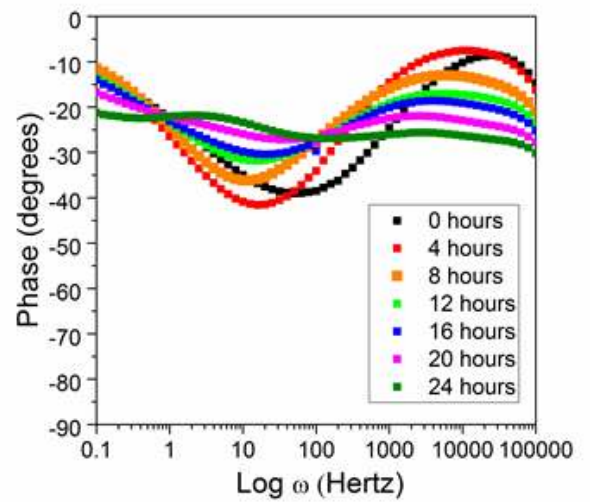
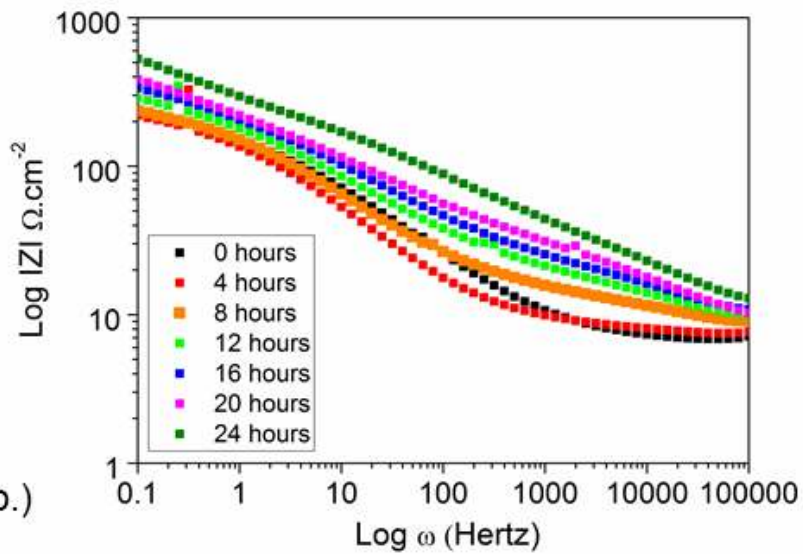
b.)



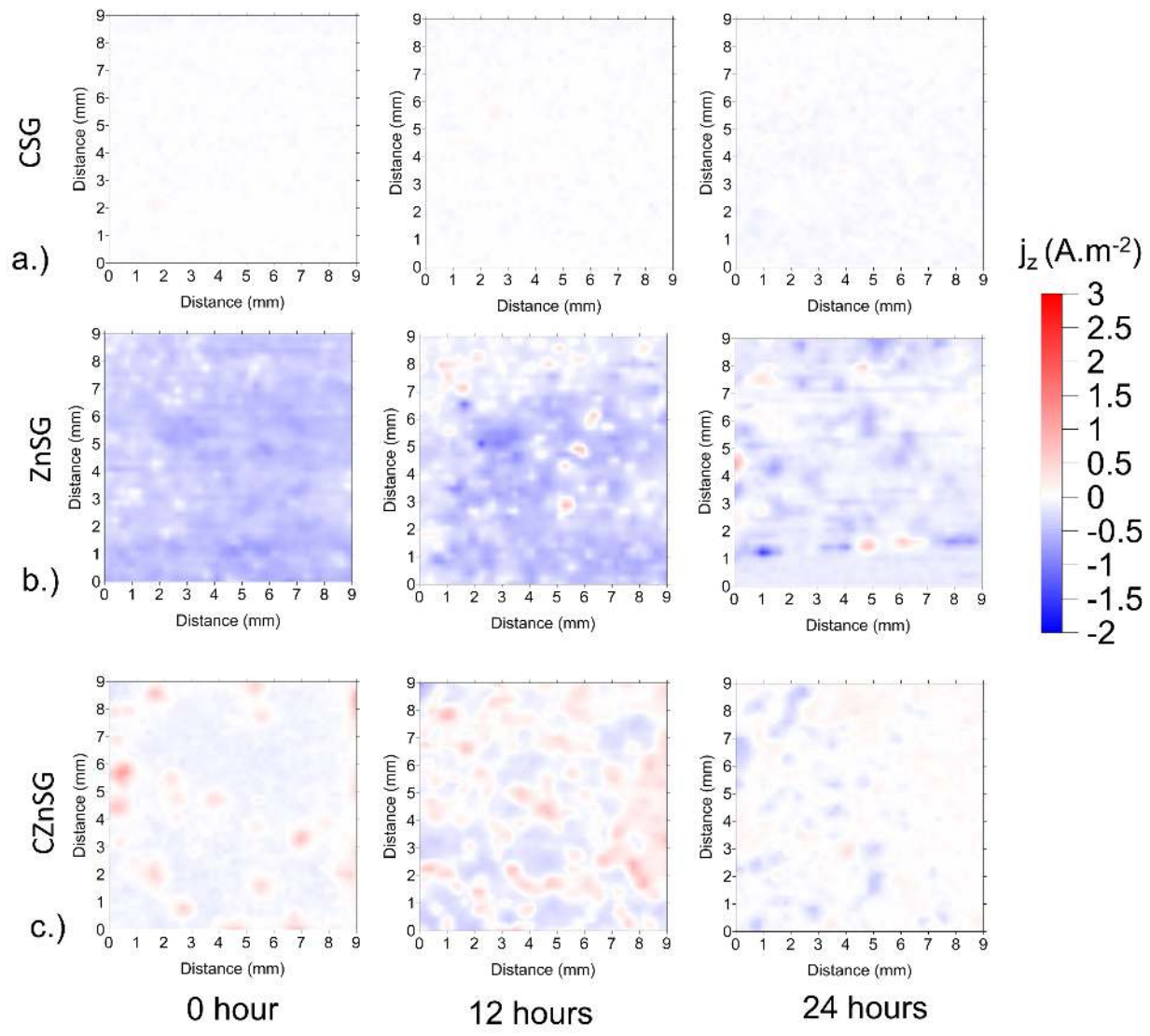


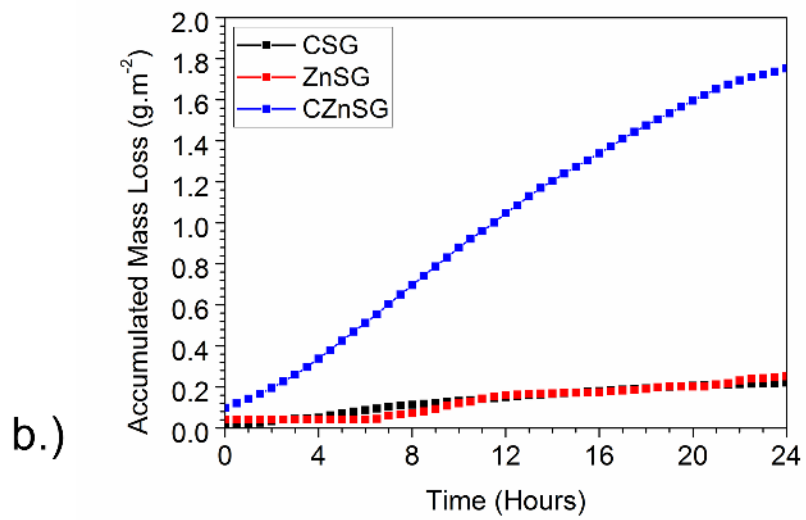
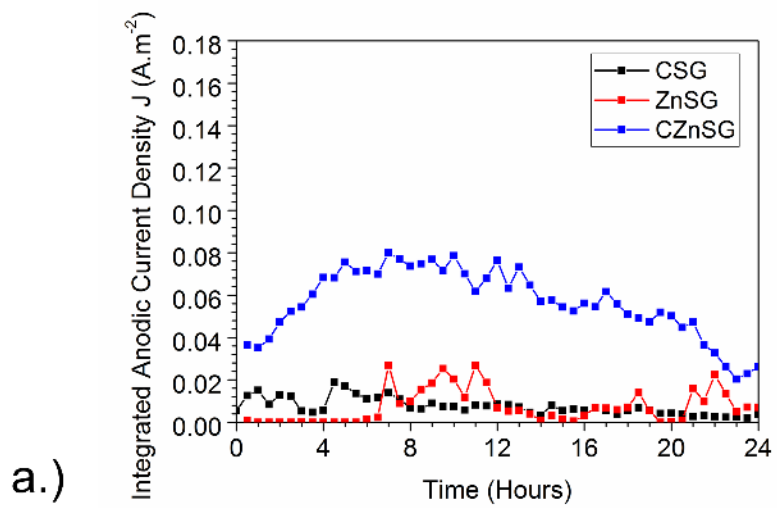


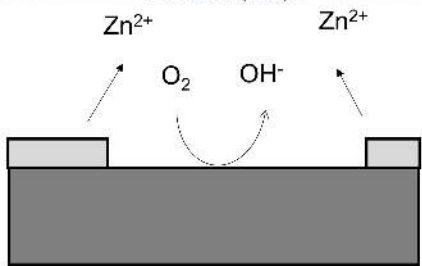
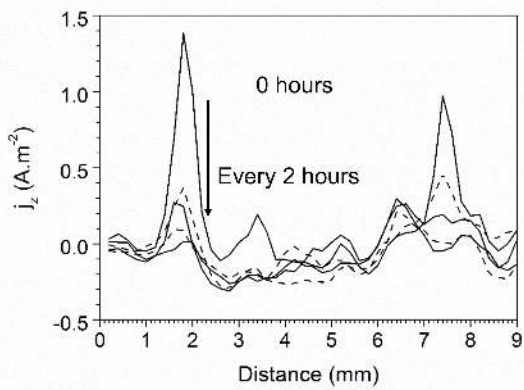
a.)



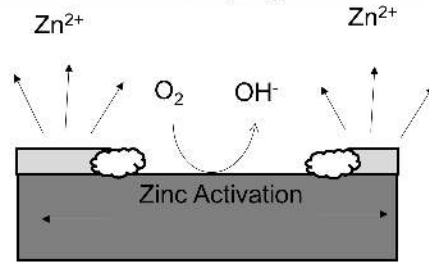
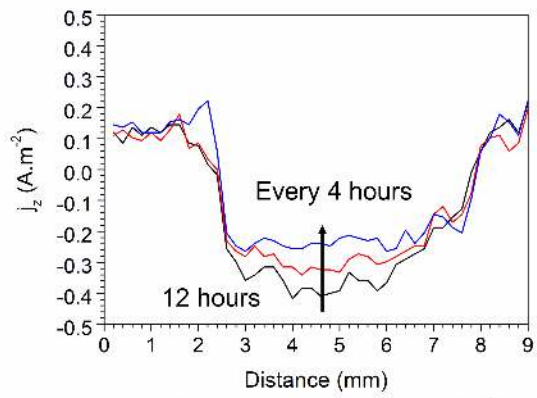
b.)







a.)



b.)

