Supporting Information

Enabling Corrosion-resistant of Magnesium through Cross-linking Polymerized Inorganic Sol–gel Coating

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Optimization of SiZr sol coating preparation

4.73 mL TEOS (19.76 mmol) was added into a mixed solvent composed of 2.5 mL ethanol and 2.5 mL isopropyl alcohol. Thereafter, 335.1 mg $ZrOCl_2$ (1.04 mmol, n(Si):n(Zr) = 5:95) was added until all solid substances were dissolved, which was followed by dropwisely transferring 374.4 μL HCl aqueous solution (20.8 mmol) and 3.96 mL GPTMS (15.7 mmol) into the clear solution. Finally, 20 mg Hmim (0.244 mmol) was added. Magnetic stirring was applied to all the procedures. The yielded solution was hydrolyzed and polymerised at RT for 1 h to achieve sol. Dip coating technique was employed to grow $SiO_2@ZrO_2$ (designated as SiZr hereafter) sol-gel coatings on the surface of Mg specimens. In brief, Mg pieces were placed in the sol for 10 s and vertically lift up through an electric-motor-driven arm at a speed of 1 cm/min. Thereafter, SiZr sol-covered Mg species were cured at 80 °C in oven for 4 h. To optimize the coating quality for corrosion resistance, two processing variables related to sol solution preparation, *i.e.* pH (1-4, HCl) and quantity of HCl (mole ratio of H_2O

in HCl:TEOS+ZrOCl$_2$, 1, 2, 4, and 6), were explored, respectively. In addition, GPTMS- and Hmim-free SiZr sol coatings were prepared as controls (SiZr-0).

When HCl is used as catalyst for reactions to sol solutions, acidity, *i.e.* pH, plays a key role in the catalytic performance of HCl. Reaction mechanism of SiZr sol is shown in Figure S1: under acidic conditions, hydrolysis of siloxane goes through a positively charged transition state. After -OR was protonated, electron cloud density around the central Si atom was reduced, its electrophilicity was enhanced and it was more vulnerable to attack by water molecules. Hence, in TEOS, ZrOCl$_2$ and GPTMS hydrolysis process, H$^+$ and water content decided to size of colloidal particles in sol, which affected porosity and density of SiO$_2$@ZrO$_2$ sol coating, ultimately affected corrosion resistance performance of SiO$_2$@ZrO$_2$ sol coating.

However, accurate pH measurements of EtOH- and isopropyl alcohol-containing sol solutions remain a challenge given the interference from a number of factors. As such, we attempted to define the acidity of sol solutions via measuring pH and volume of the added HCl (into sol) to effectively eliminate the interferences. To determine an optimal acidity and corresponding quantity of HCl for high-quality coating production, a set of sol coatings were prepared by an orthogonal strategy and their corrosion performance was evaluated via potentiodynamic polarization curves and EIS.

Firstly, original pH of HCl solution (varying from 1 to 4) was chosen as variable whilst a constant addition of HCl (which is indicated by means of mole ratio of H$_2$O in the HCl solution and TEOS+ZrOCl$_2$, 1:1) to prepare SiZr sol coatings for electrochemical evaluations. It is evident that acidity of sols imposes a slight difference

in suppressing the instant corrosion kinetics of the SiZr coatings on pure Mg in NaCl as indicated by the potentiodynamic polarization curves (Figure S2a) and the corresponding i_{corr} estimated through Tafel fitting extrapolation (Figure S2b), though all these coatings exhibit a passive region in the anodic branch. To reveal more information regarding the role of acidity of sol in passivity of the SiZr sol coatings, EIS plots were recorded and plotted in Figure S2c. Here, the $|Z|_{0.01 \, Hz}$ value is an important indicator for assessing corrosion resistance of materials, the larger $|Z|_{0.01 \, Hz}$ value indicates the better corrosion resistance of sample. It found that $|Z|_{0.01 \, Hz}$ value of coatings obtained under pH = 2 HCl solution was much larger than that of coatings prepared under other conditions, which revealed that the coating produced in sol with pH = 2 HCl exhibit the best corrosion performance in 0.1 M neutral NaCl.

Secondly, electrochemical behavior of the SiZr sol coatings prepared for varying addition of HCl was studied. Taking total mole of TEOS and $ZrOCl_2$ as reference and a set of H_2O in added HCl, *i.e.*, one-fold (SiZr1W), two-fold (SiZr2W), four-fold (SiZr4W) and six-fold (SiZr6W) was employed. As shown in Figure S2d-S2f, similar to those of the previous cases, the variation in mole ratio of H_2O in HCl, and TEOS and $ZrOCl_2$ contributes slightly to the passive function of the resulting SiZr sol coatings in inhibiting instant anodic kinetics of the pure Mg substrates in NaCl. In contrast, a dramatic influence on the interfacial reactions between of SrZr sol coatings is evident in EIS plots. SiZr1W holds a promising potential for corrosion resistance in comparison to other coating counterparts.

It is striking that adhesion strength (Figure S3) of all the SiZr sol coatings on Mg plates was ascertained as 5B, which is the highest adhesion level of coating through GB/T 9286-1998 standards. However, approximate 30% of SiZr4W coating was peeled off after curing process and prior to such adhesion testing. It was found that there was a balance problem with acidity and addition of HCl solution: a) when the amount of HCl solution increased, the content of H^+ in the sol would increase. In this case, it was easily made coating into peel-off that H_2 gas was caused by the reaction between metal and H^+ (Reaction 1) in the process of forming the coating with metal substrate, *e. g.* SiZr4W. b) Increasing H_2O in the added HCl solution to preparation sols led to some larger clusters that were formed into sol. As such, corrosion resistance of the resulting coating, *e.g.* SiZr6W, could be increased owing to the compact packing of clusters.

$$Mg + H^+ + H_2O \rightarrow Mg(OH)_2 + H_2\uparrow \qquad\qquad (1)$$

In conclusion, an optimal set of processing conditions for SiZr sol coatings preparation was identified as follows: TEOS and $ZrOCl_2$ were added in a mixed solvent composed volume ratio of ethanol to isopropanol was 1, thereafter HCl solution (pH = 2, mole ratio of H_2O in HCl:TEOS+$ZrOCl_2$ is 1:1) was added to sol solution form an acid environment for hydrolyzing process of GPTMS and $SiO_2@ZrO_2$ clusters, thereafter GPTMS and Hmim were added successively, at last, Mg pieces were dip-coated and cured at 80 °C in oven for 4 h. Under the condition, SiZr coating prepared would not negative to affect adhesion of coating, but obtain excellent anti-corrosive effect, which will be used in the following study and SiZr1W sol coating is designated as SiZr sol coating hereafter.
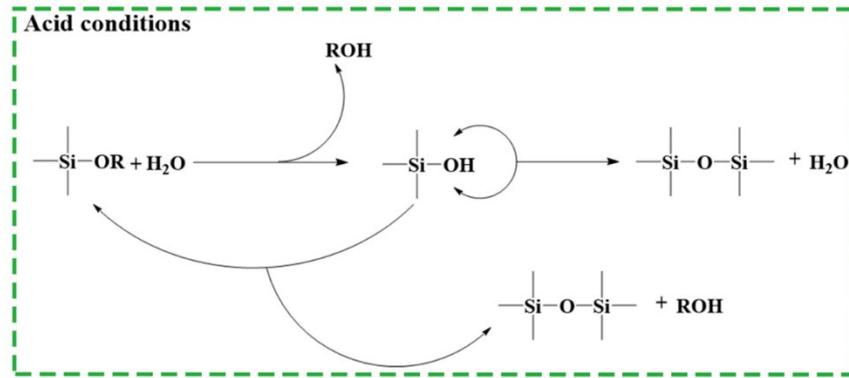
Figure S1. Schematic illustrations of reaction mechanism of SiO_2 sol.
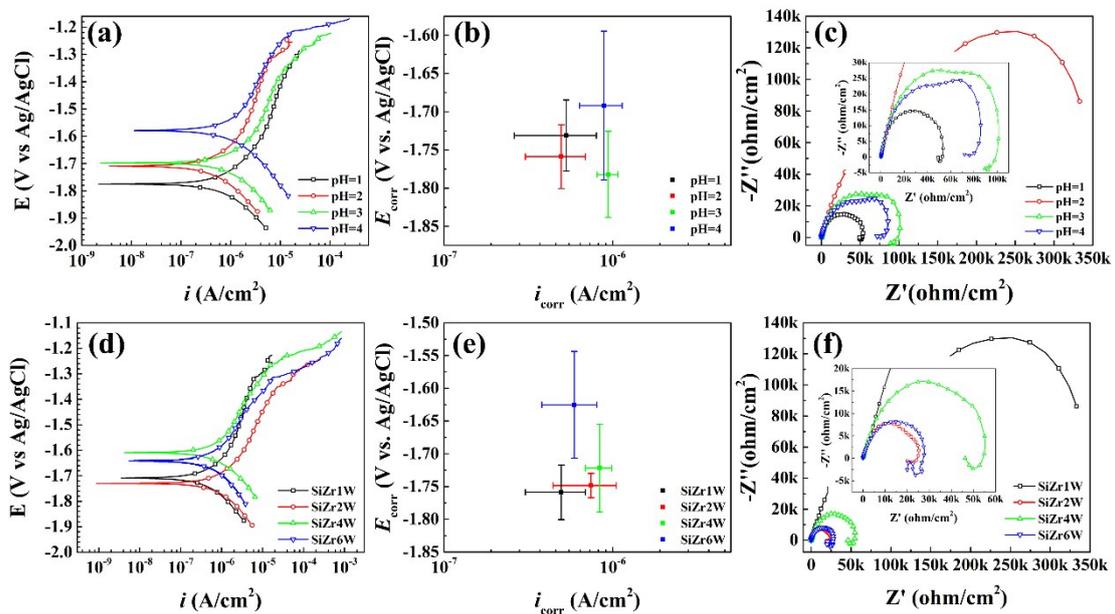
Figure S2. Electrochemical analysis of the SiZr sol coatings as a function of (a-c) pH of HCl into sol solution with constant mole ratio of H_2O in HCl solution and TEOS+$ZrOCl_2$ (1:1). (a) Potentiodynamic polarization curves recorded in 0.1 M NaCl at a sweep rate of 1 mV/s (n = 5); (b) Estimated average values of E_{corr} and i_{corr} through Tafel fitting extrapolation via CHI 16.06 software; and (c) Nyquist plots obtained in 0.1 M NaCl with a frequency range from 100 kHz to 10 mHz. Electrochemical analysis of the SiZr sol coatings as a function of (d-f) volume of H_2O in HCl solution and TEOS+$ZrOCl_2$ with a constant pH 2 of added HCl into sol solutions. (d)

Potentiodynamic polarization curves recorded in 0.1 M NaCl at a sweep rate of 1 mV/s ($n = 5$); (e) Estimated average values of E_{corr} and i_{corr} through Tafel fitting extrapolation; and (f) Nyquist plots obtained in 0.1 M NaCl with a frequency range from 100 kHz to 10 mHz.
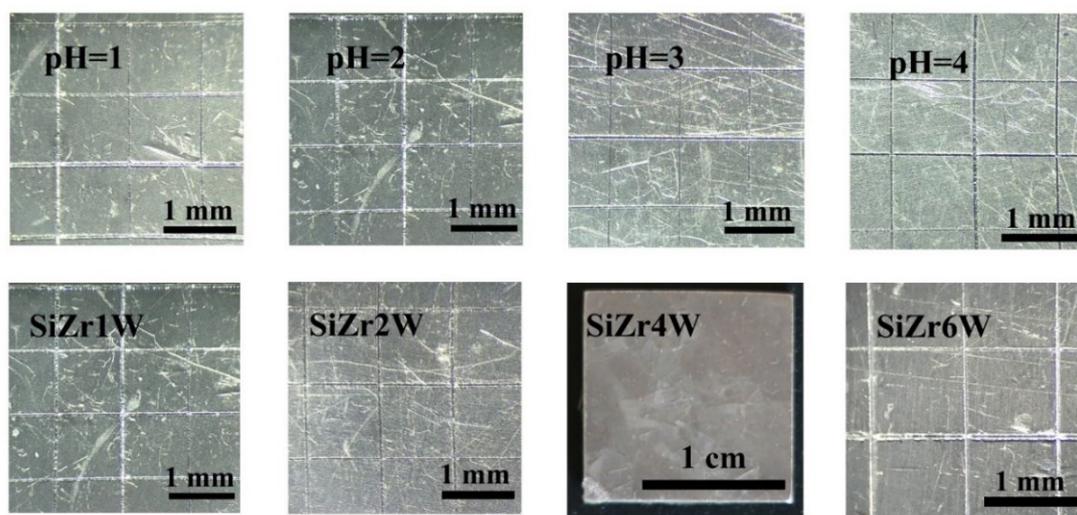
Figure S3. Characterisation of adhesion strength of various SiZr sol coatings on pure Mg substrate via Photograph Crossing method according to Chinese National Standards of GB/T 9286-1998.