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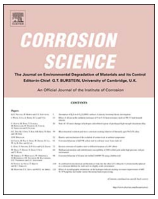

Sub-micrometer mesoporous silica containers for active protective coatings on AA 2024-T3

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ABSTRACT

In the present work, the sub-micrometer containers were prepared using mesoporous silica particles (SBA-15) with parallel channels as reservoir and 8-hydroxyquinoline as corrosion inhibitor. Layer-by-layer assembling was used to construct a shell of polyelectrolytes around the silica particles. Release of 8-hydroxyquinoline from sub-micrometer containers was studied in response to acidic or alkaline pH values. The results of electrochemical impedance spectroscopy (EIS) show the improvement of corrosion resistance of epoxy coatings containing sub-micrometer containers. Self-healing ability of the epoxy coatings was provided by sub-micrometer containers, as evidenced by the results of scanning vibrating electrode technique (SVET).

1. Introduction

Organic coatings are widely used for corrosion protection of metals (consisting over 60% of all protection methods). However, when organic coatings suffer cracks or defects, the metallic substrate is exposed to corrosive species and the direct corrosion attack takes place. The degradation of coatings often starts upon cracks or defects, leading to the ultimate failure of corrosion protection. Two main cases take place in the degradation process: one is the damage of the coatings (crack, scratch, etc.) and the other is the under-film corrosion [1]. In recent years, "active" self-healing coatings have attracted great interest in researchers. The self-healing ability is conducive to enhancing the service life of coatings, especially when the coatings suffer environmental impacts.

The automatic healing of cracks, scratches in the coatings can be achieved by the release of resin or low polymer contained in microcapsules [2–7]. In order to mitigate corrosion of metallic substrate, inhibitor pigments are usually incorporated into primers of coating system on metals. Chromates (VI) are high effective inhibitor pigments used in the primers. However, due to the toxicity of chromates, the use of chromates is prohibited or progressively banned in industries. The development of chromate-free epoxy coatings is an issue of prime importance for industrial applications [8–13]. Considering the combined properties of chromates (high inhibition efficiency, slow release and low solubility in aqueous solution), it is a big challenge to find new green inhibitor pigments [14]. Organic inhibitors are also very effective in corrosion inhibition. However, the direct introduction of organic inhibitors into organic coatings will raise a lot of problems, such as loss of integrity, deactivation of inhibitors or unexpected leakage of inhibitors to coating matrix. Therefore, the loading of organic inhibitors into containers and the controlled release of the organic inhibitors from the containers are crucial to develop self-healing coatings. Damages on coatings allow the release of organic inhibitors, which are delivered onto the exposed substrate, protecting the substrate against corrosion. So far, a lot of work has been done to develop active self-healing coatings by using organic inhibitors. The following materials have been used as carriers for organic inhibitors, such as layered double hydroxide nanocontainers [15–17], nano $CaCO_3$ [18], porous TiO_2 [19], cerium molybdate [20], carbon nanotubes [21,22], halloysite nanotubes [23–25], polymeric particles [26,27], and cellulose nanofibers [28,29]. For the purpose of controlling the release of organic inhibitors in a "smart" way, multilayer polyelectrolytes are used to construct shell of the containers to regulate the release of organic inhibitors triggered by corrosion of under-film metallic substrate [30,31]. The details of self-healing coatings with nano-containers can be found elsewhere [32–39]. The core materials of the containers can be silica armored polystyrene, porous silica nanoparticles, silica nanoparticles, etc. The organic inhibitors can be either loaded into the inner channels of porous materials or be adsorbed on the surface of solid materials. The polyelectrolyte layers were deposited on the core material to achieve the controlled release of the inhibitor in response to pH change of corrosive species. Layer-by-layer assembling is often used by alternatively depositing oppositely charged polyelectrolyte layers on the surface of the core material. Mesoporous particles possess large specific surface area and

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high loading ability for inhibitors and have been used for developing self-healing coatings. Especially, the nanometer mesoporous silica containers (diameter less than 100 nm) were used in sol-gel or water-based organic coatings to play self-healing effect [36–38].

Aiming to increase loading and release ability of organic inhibitors, thus to improve the self-healing ability of “active” organic coatings, our present work first focuses on SBA-15 material, a kind of commercial mesoporous silica with honeycomblike ordered hexagonal porous structure, consisting of hundreds of empty channels that are able to absorb or encapsulate organic molecules. SBA-15 has high stability and rigid framework. It is resistant to pH change, mechanical stress and heat. Additionally, SBA-15 possesses high pore volume and surface area. The channels inside SBA-15 are parallel in the direction of length and the openings of the channels are at the two ends of SBA-15 particles. The distribution of the channels in SBA-15 is different with that of the traditionally used spherical mesoporous silica particles, in which the random pores or diffused pores exist. The objective of using sub-micrometer mesoporous particles is to achieve self-healing effect with a small amount of sub-micrometer containers, in that less amount of sub-micrometer particles is able to load the same amount of inhibitor as compared to nanometer particles provided that their specific surface areas are similar. 8-hydroxyquinoline (8-HQ) was selected as the corrosion inhibitor because of its superior corrosion inhibiting properties [40–43]. The containers were characterized on the loading process and the release behaviour. The anticorrosive performance and self-healing effect of an epoxy coating loaded with the sub-micrometer containers on 2024-T3 aluminium alloy were studied by EIS and SVET.

2. Experimental

2.1. Preparation of mesoporous SBA containers

SBA-15 (SBA) was purchased from XF Nano Materials Tech Co., Nanjing, China. The length of the particles is from 0.5 to 1 μm and the width of the particles is from 0.2 to 0.5 μm. The diameter of mesochannels is about 6–10 nm and the specific surface area is about 550–600 m^2/g. Polyethyleneimine (PEI, molecular weight, Mw ≈ 75,000), poly-styrene sulphonate (PSS, Mw ≈ 70,000) and 8-HQ were purchased from Sigma-Aldrich.

8-HQ was first dissolved into 75% ethanol solution. The SBA particles were added into the solution and stirred for 10 min. The mixed solution was placed in beaker and was evacuated using a vacuum pump at room temperature so that 8-HQ can be sucked into the channels of the SBA particles. The vacuum cycle was repeated for three times to obtain the maximum loading of 8-HQ, and then the particles were filtered out. To produce the SBA containers (SBA-8HQ), 0.02 g of dry SBA particles loaded with 8-HQ was dispersed into 10 mL of water and then treated by ultrasonic vibration for 5 min. PEI and PSS were added in purified water and the concentration of PEI and PSS is 2 mg/mL. The obtained SBA-8HQ solution was mixed with 3 mL of 2 mg/mL PEI solution for 10 min. Then, the SBA/8-HQ/PEI sample was washed three times with purified water and separated by centrifugation. The deposition of PSS was performed by mixing 3 mL of 2 mg/mL PSS solution with the centrifuged SBA/8-HQ/PEI sample. Then, the SBA/8-HQ/PEI/PSS sample was washed three times with purified water and centrifuged. Finally, the sample was dried in the air and ready for use. The concentration of 8-HQ in aqueous solution during loading and release experiments was monitored using UV2100 UV–vis spectrophotometer. The release percentage of 8-HQ at pH 0, 2, 4, 6, 7, 8, 10, 12 and 13.5 was calculated. In order to obtain the release percentage of 8-HQ from the SBA-8HQ, 0.02 g SBA-8HQ was dispersed in 200 mL of purified water adjusted to the above-mentioned pHs. After 2 and 12 h of incubation under stirring, the SBA-8HQ were filtered and the concentration of 8-HQ in the supernatant was measured and then the release percentage was calculated.

Table 1
Composition of AA 2024-T3 (wt.%).

	Al	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
AA 2024-T3	balance	0.06	0.17	4.54	0.63	1.51	0.01	0.08	0.03

2.2. Characterization of mesoporous SBA containers

Zeta potentials of the original SBA, SBA/8-HQ, SBA/8-HQ/PEI and SBA/8-HQ/PEI/PSS were measured in triplicate at room temperature using the Zetasizer (Nano-ZS90, Malvern Instruments, UK). Fourier transform infrared spectra (FT-IR) were performed using a Nicolet 470 spectrometer from Brucker with KBr pellets. The spectra between 500 and 4000 cm^{-1} were recorded with 1 cm^{-1} resolution in transmission mode. The surface morphologies of SBA, SBA/8-HQ, SBA/8-HQ/PEI/PSS were observed using XL30 type scanning electronic microscope (SEM) from Philips and a Jeol JEM 2010F transmission electron microscopy (TEM).

2.3. Analysis of barrier effect and self-healing ability of epoxy coatings

Aluminium alloy 2024-T3 was used as substrate, which was purchased from Q-lab Corporation, USA. The composition of AA 2024-T3 is shown in Table 1. Three types of coatings were applied. One was epoxy varnish prepared by mixing epoxy resin and polyamide resin with the ratio 2.5:1. The other two coatings were obtained by incorporating 3% SBA or 3% SBA-8HQ into the epoxy resin. The epoxy resin was mixed with SBA or SBA-8HQ using high-speed dispersion machine at a speed of 1200 revolutions per min for 30 min to ensure the uniform mixing of SBA or SBA-8HQ in the epoxy resin. After curing with polyamide resin, the epoxy matrix with SBA or SBA-8HQ was dispersed at a speed of 1200 revolutions per min for 10 min. Then, the epoxy coatings were applied on AA 2024-T3 substrate using air spraying. The thickness of the dry film was approximately 42 ± 2 μm.

Electrochemical impedance spectroscopy (EIS) measurements were employed to evaluate the barrier effect of the three types of coated samples, which were immersed in 0.005 M NaCl at room temperature. The low concentration of NaCl was chosen in order to better examine the difference in protection ability of the epoxy coatings. EIS measurements were carried out using an EG & G 273 Potentiostat/Galvanostat and EG & G 5210 lock-in amplifier connected to a computer. The working electrodes were exposed in 0.005 M NaCl for 20 min prior to the tests. Before the EIS measurements, open circuit potentials of the samples were recorded. The exposed area of the working electrodes to 0.005 M NaCl is 12.56 cm^2. The test system consisted of a three-electrode cell, in which a saturated calomel electrode (SCE), a platinum foil electrode and a coated sample were used as reference, counter and working electrode, respectively. EIS spectra were acquired in a frequency range from 100 kHz to 10 mHz with 20 mV amplitude perturbing signal. The EIS data were analyzed using Zsimpwin software. For EIS measurements, three parallel samples were tested to verify the reproducibility of the results.

A commercial SVET equipment from Applicable Electronics, controlled by the Sciencewares ASET program, was used to perform the SVET measurements. Just before SVET measurements, two artificial defects were prepared on each coated sample by drilling with a metallic needle. The defects were made until the epoxy coatings were completely penetrated. The exposed area of the samples to the corrosive solution is approximately 9 mm^2. For SVET measurements, the Pt-Ir probes (Microprobe, Inc.) were platinized to form a small, 30 μm diameter, ball of platinum black at the tip. The frequency of probe vibration in perpendicular direction to the sample surface was 325 Hz. The measurements were taken at open-circuit potential. The time of acquisition for each SVET data point was 0.6 s. The local ionic current densities were mapped on a 50 × 50 grid (generating 2500 grid points)