Self-Healing Coatings for Active Corrosion Protection: The Concept, Design, Evaluation and Challenges

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1 Introduction

Corrosion is a naturally occurring phenomenon and just like all-natural processes, corrosion of materials is spontaneous, and it drives the materials to its lowest possible energy states. Most of the metals and alloys have a natural tendency to combine with water and oxygen present in its environment and return to its most stable state. Iron and steel quite often interact with their environment return to their native and stable oxide states. Similar to any natural disasters such as earthquakes or severe weather changes, corrosion results in dangerous and expensive damage to everything from automobiles, home appliances, drinking water systems, gas and petroleum pipelines, bridges and buildings [1]. Various studies using different approaches have estimated that the cost of corrosion is equivalent to about 3–4% of each nation's gross domestic product (GDP). As per the estimation of National Association of Corrosion Engineers (NACE, USA), the annual cost of corrosion worldwide is estimated to be US$ 2.5 trillion. Further, studies arrived at a conclusion that savings of between 15 and 35% of the cost of corrosion could be achieved by employing appropriate corrosion control measures. NACE, USA estimated that the direct cause of corrosion in the USA was $ 276 billion in 1998, approximately 3.1% of GDP. However, by including the indirect losses of corrosion it was estimated to exceed $ 1 trillion [2, 3]. Our country India loses a staggering amount of $ 37 billion per year due to corrosion and related issues. Application of organic/polymeric coating system is one of the widely used strategies to combat corrosion of metals and alloys under service conditions [4]. Organic coatings act as relatively thin layer between the substrate materials and the environment. The terms organic protective coatings and paints are generally

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used interchangeably for both having an organic base. According to the definition of coating mentioned in the *Manuals for Coatings of Light Water Nuclear Plants*, "Coatings (paints) are polymeric materials that applied in fluid stage, cure to form a continuous film" [5, 6]. This is a general definition given very broadly and simply for both coatings and paints. However, as far as corrosion protection is concerned, it is necessary to define both these terms very specifically. "*Paint can be defined as any liquid material containing drying oils alone or in combination with natural resins and pigments which, when applied to a suitable substrate, will combine with oxygen from air to form a solid, continuous film over the substrate, thus providing a weather resistive decorative surface*" [5]. During its entire lifetime, a paint film continues to oxidize and slowly become porous to oxygen, water and other corrosive species, thus giving a less permanent protection against corrosion than the more sophisticated protective coating.

A protective coating is chemically a considerably different material from paint. It surpasses paint in adhesion, toughness and resistance to chemical, weather, humidity and water. "*A protective coating can be defined as any material composed essentially of synthetic resins or inorganic silicate polymers which, when applied to a suitable substrate, will provide a continuous coating that will resist industrial or marine environments and prevents serious breakdown of the basic structure in spite of abrasion, holidays, or imperfections in the coating*" [5]. In order to provide maximum protection, a protective coating should: (a) resist the penetration of ions from salts that are in contact with the coatings; (b) minimize the action of osmosis; (c) expand and contract with the underlying metal surface; and (d) retain the aesthetic appearance over a long period.

Generally, organic coatings offer all the aforesaid properties through ***passive protection*** by creating an effective barrier or physical layer to avoid the contact between the metallic substrates and water and other corrosive species present in the environment. However, organic coatings can offer adequate protection only if they are intact and devoid of any mechanical defects. Therefore, it is necessary to add some active agents to impart ***active protection***. In active corrosion protection methods, corrosion inhibitors are incorporated into protective barrier layers and this decreases the corrosion rate when the passive barrier layer starts deteriorating. Active and passive protection methods are the two main approaches currently used to prevent corrosion [7].

Active protection of metallic substrates from corrosion can be achieved by the introduction of inhibitors into the coating system. The corrosion inhibitors can be added into the different components of coating system: pre-treatment, or primer. Conventionally, substances containing lead, hexavalent (chromates) or trivalent chromium (dichromate) are used as corrosion inhibitive additives and this type of inhibitive species are found in pre-treatment layers. However, stringent environmental regulations and legislation lead to look for an alternative to these toxic inhibiting additives. Therefore, the introduction of environmentally friendly corrosion inhibitors for protective coatings is essential. Organic corrosion inhibitors are not harmful to the environment and very effective to control corrosion. In order to have the optimum corrosion control by the inhibitors, their solubility should be in

the right range in the corrosive medium. Very low solubility of inhibitors results in the deficit of inhibitive species to diffuse or migrate to the metal surface to protect it. On the other hand, very high solubility of inhibitors may give sufficient protection for a relatively short period since the active agents would be leached out. Moreover, higher concentration of inhibitors in the coating may have negative effects on the coating by either degrading its physical and mechanical properties or causing blistering and delamination of the coating [8, 9]. To overcome this, the inhibitors can be entrapped in some containers and thereby prevents the direct interaction of the inhibitive species to the coating matrix.

A novel strategy widely employed by corrosion scientists and engineers is the encapsulation of active agents in some micro/nanostructured reservoirs and disperse them uniformly into the coating systems. Based on this strategy, a new class of anticorrosion coatings that possess both passive barrier protection and active corrosion protection in response to any changes in the local environment has been developed by material scientists. The encapsulation of inhibitors into nanocontainers helps in the smart release of inhibitive species on demand in the right quantity. Active corrosion protection helps to restore the integrity of the coating when the passive coating matrix is broken, and corrosion of metallic substrates has instigated. The active corrosion protection is achieved by a self-healing mechanism.

2 The Concept of Self-Healing Coatings for Corrosion Protection

The term self-healing in material science implies the self-recovery of all the properties and functionalities of the materials after the detrimental action of the environment. This definition of self-healing can be applied to functional coatings also. Skorb et al. [10] stated that the partial recovery of main functionality of a material could also be considered as self-healing. In fact, there has been a difference in opinion about the definition of self-healing ability of functional coatings. One school of thought is focused on the recovery of the coating integrity after the destructive action of the external environment, i.e. the recovery at the structural level [11]. The restoration of the original barrier property of the coatings is considered as self-healing. The first of its kind is polymer-based self-healing coatings and the concept of this class of coating is as follows: Containers in the micrometre regimes are synthesized and filled with monomers similar to that of the polymer matrix and a suitable catalyst or ultraviolet sensitive agent to initiate the polymerization of the monomer. When any damages occurred on the coatings, the coating integrity would be disrupted and this in turn resulted in the release of the entrapped polymer. The released polymer would undergo polymerization in the presence of the catalyst and repair the coatings. The commonly used sealing agents are methyl methacrylate, 2-ethylhexyl methacrylate, tertiary butylaminoethyl methacrylate and lauryl methacrylate [12–16]. White et al. [16] first reported a structurally polymeric material having ability to automatically

heal cracks. In their work, the healing was accomplished by incorporating a microencapsulated healing agent and a catalytic chemical trigger within the epoxy matrix. Ruthenium-based Grubbs' catalyst was used to initiate the ring opening metathesis polymerization of dicyclopentadiene. Keller et al. [17] reported the development of poly (dimethyl siloxane)-based self-healing elastomeric polymer. Other authors argue that the recovery of the coating's properties for a specific application (e.g. anti-corrosion property) to which the coatings were prepared can be equally considered as self-healing coatings [18–20]. The argument of this category of self-healing coatings is as follows. The major function of a corrosion protective coating is to protect the underlying metallic substrates from corrosion, and it is not mandatory to recover all the properties of the coatings. The self-delaying and protection from corrosion activity of a defect causing corrosion in a coated material by any mechanism can be considered as "self-healing".

One of the approaches employed to achieve hybrid self-healing coatings is based on the use of inhibitors that can be released from the coating system. Since the direct addition of the inhibitor component into the protective coating system very frequently leads to either the deactivation of the corrosion inhibitor or degradation of the polymer matrix, it is ideal to entrap the corrosion inhibitor and avoid it's any direct interaction with coating matrix [21]. The most essential part of this second approach is to fabricate nanocontainers with good compatibility with the protective coating matrix. The nanocontainers should have a shell with permeable properties to load and release the active materials in response to external stimuli. The size of the nanocontainers should be less than 300–400 nm since nanocontainers of larger size can affect the integrity of the coating matrix and thereby reducing the passive protection of the coatings [21]. When the environment of the coating changes, these nanocontainers respond rapidly by releasing the entrapped active agents onto the metallic substrates and delay corrosion [19, 22, 23]. Various stimuli, which can induce the release of corrosion inhibitors from nanocontainers, are pH, temperature, redox, optical and magnetic field [24–32].

3   Design of Self-Healing Coatings for Active Corrosion Protection

In order to fabricate self-healing coatings with anticorrosion property, the following things are essential.

1. Corrosion inhibitor or active agents or self-healing material
2. Micro/Nanocontainers or capsules to encapsulate corrosion inhibitors/active agents/self-healing material
3. A polymeric/organic coating matrix to host the active agent-micro/nanocontainer system.

The selection of the proper nonmaterial which can act as a good container for loading inhibitors is the most important parameter for designing a self-healing
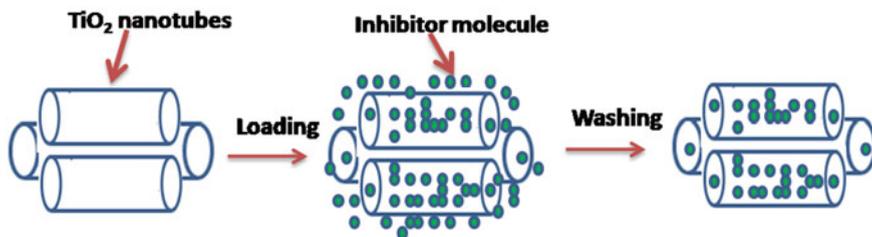
Fig. 1 Schematic drawing of the inhibitor loading into TiO$_2$ nanocontainers

coating. Moreover, the selected nanocontainers should be compatible with the organic matrix used as barrier coatings. The small size of the nanocontainers, generally less than 400 nm helps for homogeneous mixing of the nanocontainers in the coatings.

3.1 Encapsulation of Active Agents into the Micro/Nanocontainers

There are mainly two methods for loading the active agents or the self-healing molecules into the micro/nanocontainers. In the first method, the inhibitors are loaded after the successful synthesis of nanocontainers. Generally, inhibitor molecules were dissolved in ethanol or acetone at desired concentration. About 100 mg of nanocontainers was added to 50 mL of inhibitor solution, and the vial was sealed in order to avoid any evaporation of solvent and stirred electromagnetically for 24 h. A schematic of the loading of inhibitors into TiO$_2$ nanocontainers is depicted in Fig. 1 [33].

The loading process is generally carried out in the dark to prevent the photo degradation of organic inhibitor molecules if any. Nanocontainers loaded with inhibitor molecules can be collected by centrifugation and cleaned several times in ethanol to remove inhibitors adsorbed on the surface of the nanocontainer. The inhibitor-loaded nanocontainers were obtained by drying it in air at room temperature. In the second method reported by Tedim et al. the inhibitors were loaded in situ method while synthesizing the nanocontainers itself [11]. They reported the synthesis of a novel nanoreservoir based on silica nanocontainers loaded with corrosion inhibitor, 2-MBT in a one-stage process. The single-stage synthesis of silica nanocontainer and encapsulation of 2-MBT is depicted in Fig. 2.

3.2 Releasing of Inhibitors from the Nanocontainers

The continuous and sustained release of the inhibitor molecules from the nanocontainers on demand is the major functionality of the coatings to impart active corrosion
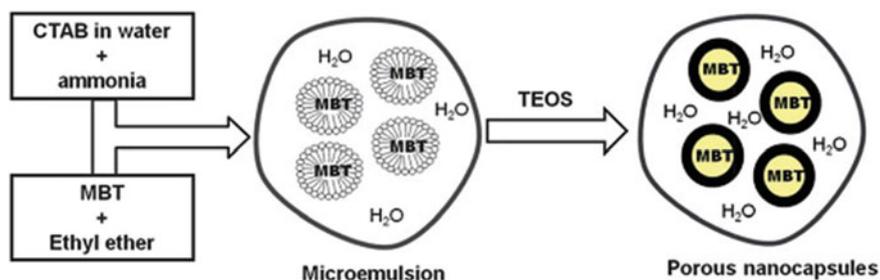
Fig. 2 Single-stage synthesis of silica nanocontainer and encapsulation of 2-MBT. Reproduced with permission [11]

protection. The presence of pore like channels on the surface and hollowness in the structure will facilitate the faster and sustained release of the inhibitor molecules. Hence, the nanocontainers having hollow core and porous shell structure are ideal materials for storing and releasing inhibitors. Chenan et al. [34] reported the use of hollow mesoporous zirconia nanospheres for sustained release of 2-MBT. Figure 3 shows the HRTEM image of hollow mesoporous zirconia.

The hollow core and porous channels are clearly visible in Fig. 3. These hollow mesoporous zirconia nanospheres were loaded with 2-MBT, and its sustained release property was demonstrated [34]. Figure 4 shows the release profile of hollow mesoporous zirconia nanocontainers. The releasing experiment was carried out as follows. 25 mg of MBT-loaded hollow mesoporous zirconia nanocontainers was dispersed in 150 mL of releasing medium (0.05 M NaCl) at different pH values of 3, 7 and 10 at room temperature, and the solution was stirred at a rate of 500 rpm using a magnetic stirrer. 1 mL of the solution was pipetted out at given time intervals for UV–visible analysis. In this experiment, pH is the trigger for the release of the inhibitor from the nanocontainers. During corrosion process, it is expected that the pH will be changed at local anodic and cathodic sites. Hence, in the real case, this change in pH can be used for the release of the inhibitors from the nanocontainers. When the releasing medium had infiltrated into the pores and channels of nanocontainers, the inhibitor

Fig. 3 HRTEM image of hollow mesoporous zirconia nanospheres
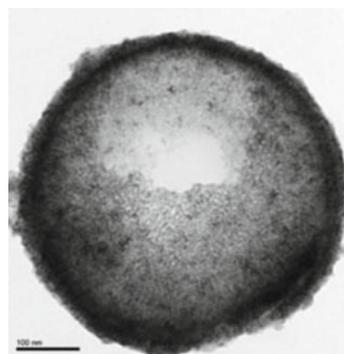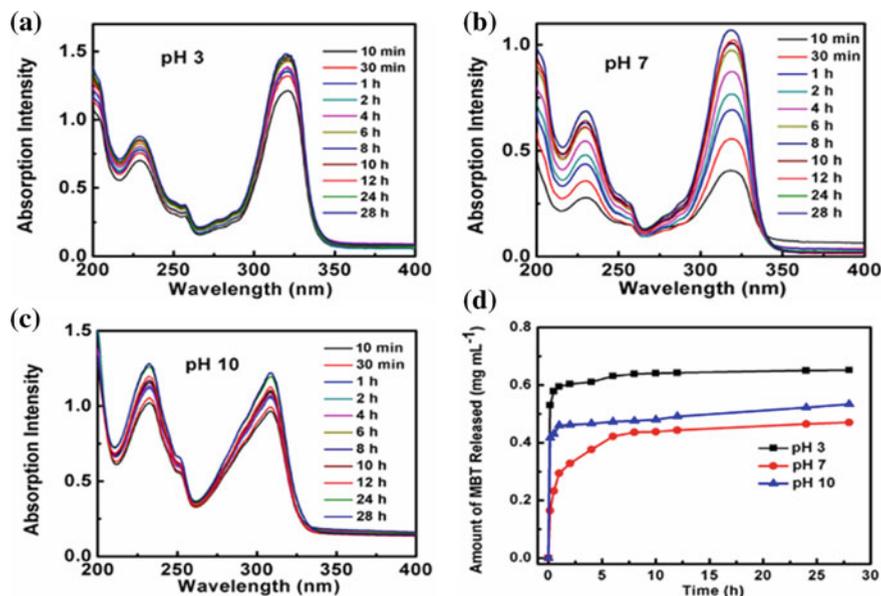
Fig. 4 UV–vis spectra at different times of the 0.05 M NaCl media in which 2-MBT was released from 2-MBT-loaded *hm*-ZrO$_2$ nanocontainers **a** at pH 3, **b** at pH 7, **c** at pH 10 and **d** corresponding pH-dependent releasing behaviour of 2-MBT from *hm*-ZrO$_2$-MBT system. Reproduced with permission [34]

molecules gets dissolved in the medium and released by diffusion through the pores along the aqueous pathways. The change in solubility of the inhibitors with a shift in pH from the neutral value helps in the faster release of inhibitor at higher amounts. In addition to this, at times the surface charge of the nanocontainers and the inhibitor molecules will be opposite when the pH changes from neutral value and this in turn results in the electrostatic repulsion between the nanocontainer and inhibitor molecules and hence results in faster release at acidic and alkaline pH. Chenan et al. [34] reported a faster release of 2-MBT from hollow mesoporous zirconia nanocontainers at alkaline and acidic conditions compared to neutral condition. Moreover, the release of MBT was levelled off and reached equilibrium in 4 h at pH 10. This study also reported that higher amount of 2-MBT was released from the hollow mesoporous zirconia nanocontainers at pH 3 and 10 compared to pH 7. This observation can be extrapolated to a corrosion process, as corrosion of metals is always accompanied by changes in local pH.

In another study, reported by Borisova et al. [22] fastest release of benzotriazole inhibitor from mesoporous silica nanocontainers was observed. In their study, the release profile was investigated by fluorimetrical analysis and they observed fastest release at pH 10, followed by pH 2. The maximum released amount was reached within 160 s at pH 10. Li et al. developed stimuli-responsive silica/polymer hybrid nanotubes for self-healing coatings. Their hybrid nanotubes loaded with inhibitor

molecules exhibited morphology-dependent release and pH, temperature, and redox-responsive release. Using surface graft polymerization technique, a pH-responsive PMMA outer wall, a temperature-responsive PANIPAM and redox-responsive PPEGMA polymer walls were made on the silica nanotubes [35].

3.3 Incorporation of Inhibitor-Loaded Nanocontainers into Coatings

After successful synthesis of nanocontainers and loading of the inhibitors into the nanocontainers, it is required to incorporate this inhibitor-nanocontainer system in some coatings. Generally, thin sol–gel coatings or other primer coatings based on epoxy or urethane resins act as a good host for this micro/nanocontainer loaded with active molecules. This host–guest coating matrix with both active and passive protection functionalities can be achieved by mixing the inhibitor-loaded nanocontainers with hybrid sol. The inhibitor-loaded nanocontainer mixed coatings are generally applied on the metallic substrates through various coating techniques such as spray coating, dip coating method, and spin coating or by using simple brush application [36–38].

4 Self-Healing Anticorrosion Coating Using Micro/Nanocontainers Loaded with Corrosion Inhibitors

Various methods have been tried until now to develop micro and nanocontainers to host active agents. An essential requirement for a nanocontainer to be employed in a self-healing anticorrosion coating is to make the nanocontainer shell sensitive to corrosion process. The corrosion process and subsequent changes in external environment due to corrosion should trigger the release of the entrapped active agent (corrosion inhibitor). Initially, corrosion inhibitors were directly added into the coating matrix to achieve active corrosion protection based on self-healing ability. A hybrid sol–gel coating or an organic coating functions very well to host the active agents or reservoirs containing the active agents. From a corrosion perspective, the major function of the hybrid sol–gel film or polymeric film is a pre-treatment or primer layer for various metals and alloy surfaces and it works only as a physical barrier layer. These thin hybrid films could provide protection from corrosion for a short period of time due to the presence of cracks and pores in the coating. Most of the coatings are made up of amorphous polymeric film and these polymeric films have intrinsic free volume and cracks or pores which would provide pathways for corrosive species such as oxygen, water and other ions to access underlying metallic substrate. Employing corrosion inhibitors in the coating formulation either by directly adding or introducing as inhibitor-loaded reservoirs is one of the ways to enhance the

corrosion resistance of organic coatings when the barrier property of the coating is compromised. Zheludkevich et al. [39–42] reported an enhancement in the corrosion protective performance by the incorporation of corrosion inhibitors and addition of ZrO_2 nanoparticles into the sol–gel system. ZrO_2 nanoparticles were used as a reinforcement of hybrid sol–gel system and a reservoir for loading corrosion inhibitor [41]. $Ce(NO_3)_3$ was used as a corrosion inhibitor for loading ZrO_2 nanoparticles and prolonged release of Ce^{3+} ions was observed from the reservoir to ensure self-healing ability to the hybrid coatings.

Another strategy employed to provide self-healing ability to coatings was layer-by-layer (LbL) assembly method in the formation of nanocontainer shell [9, 18, 19]. A change in local pH around local anodic and cathodic site is the trigger for the release of corrosion inhibitor through the shells of the nanocontainer. One such nanocontainer system was fabricated using SiO_2 nanoparticles [9]. Using the LbL assembly method, charged species were coated on the surface of the nanoparticles. Here the charged nanoparticles would be the core of the smart container. The negatively charged silica nanoparticles were coated with a layer of positively charged poly(ethylene amine) (PEI), followed by the deposition of negatively charged poly(styrene sulfonate) (PSS). Then the positively charged corrosion inhibitor, benzotriazole was incorporated into the system. The inhibitor loading in the nanocontainer was increased by repeating the PSS/benzotriazole deposition [9]. LbL films made up of polyelectrolyte monolayers assembled on the surface of a nanoparticle have controlled permeability properties. Polyelectrolyte layers are permeable to small ions and organic molecules, and it can contain large organic molecules and nanomaterials. Moreover, with a change in pH, polyelectrolyte films would change their chemical composition since their degree of dissociation is pH sensitive [43]. From a corrosion protective coating perspective, polyelectrolytes have two major roles to play: (i) segregate the inhibitor molecules from the passive barrier coating matrix and thereby reducing the negative effect of the inhibitor on the integrity of the coatings, (ii) helps in the smart release of the corrosion inhibitors by controlling the permeability of polyelectrolyte layers in response to any changes in local pH, temperature, irradiation conditions and humidity [9]. Sonawane et al. [44] reported the fabrication of self-healing coatings based on inhibitor-loaded polyelectrolyte layers for corrosion protection of mild steel. In their approach, inhibitor molecules (benzotriazole) and oppositely charged polyelectrolyte layers were adsorbed on the surface of ZnO nanoparticles. Their corrosion results from Tafel plot and corrosion rate analysis confirmed that the 5 wt% loading of nanocontainers was useful and optimum for the sustained release of inhibitor for the applications in the marine coatings irrespective of the operating pH [44]. Even though LbL assembled nanocontainer-based coating system can provide active corrosion protection with self-healing ability, their complexity hinders their up scaling and industrial applications.

Another approach for the development of smart nanocontainers for active corrosion protection is based on the release of inhibitors by ion exchange. Bohm et al. reported ceramic corrosion inhibitor pigments containing Ce(III) and Ca(II) cation-exchanged bentonite to provide effective corrosion protection to organic-coated

galvanized steel [45]. The bentonite pigments were dispersed in polyester resin-based primer, and it was compared with two other primer systems containing Ca^{2+} exchanged silica pigments and strontium chromate dispersion. The corrosion protection performance of all the three different primer systems was investigated by measuring the rate of corrosion-driven organic coating delamination from the cut edge of samples during 1000 h of salt spray testing. Their results showed that Ce-bentonite pigment showed superior corrosion protection performance to that of strontium chromate pigments at all time during salt spray testing.

Layered double hydroxides (LDHs) are another type of ion-exchangers used for interacting with corrosion inhibitors. LDHs contain layers of positively charged mixed metal hydroxides stabilized by anions and solvent molecules between positively charged metal hydroxide layers. The corrosion protection using LDHs is achieved by the release of inhibitors in exchange of anions from the corrosive medium. They can function either by releasing anionic corrosion inhibitors or by entrapping corrosive anionic species like chloride ions. Moreover, the LDH layers are pH specific: at high pH the inhibitors can be exchanged with OH^- ions and at low pH entrapped inhibitors are released due to the dissolution of LDHs [46]. A work by Buchheit [47] and his colleagues demonstrated the active corrosion protection for Al alloys rendered by Al–Zn-decavanadate hydrotalcite pigments in amide cured bisphenol epoxy resin. The results showed that corrosion protection was achieved by the release of decavanadate from Al–Zn hydroxide-based hydrotalcite particles. Corrosion inhibition was realized by the release of both vanadates and Zn^{2+} which are anodic and cathodic inhibitors, respectively, for Al alloys. Moreover, the attacking chloride ion was exchanged for inhibiting decavanadate ion, and this was proved by XRD measurements.

Williams et al. [48] prepared hydrotalcite pigments incorporating various organic corrosion inhibitors (benzotriazole, ethyl xanthates and oxalates) and compared their filiform corrosion efficiency on AA 2024-T3. It was proved that the inhibitor efficiency was anion dependent and benzotriazole was most efficient anion for corrosion protection, but not as efficient as chromate. Zheludkevich et al. [49] prepared a new Mg/Al and Zn/Al LDH nanocontainers doped with divanadate anion as corrosion inhibitors for aluminium alloy 2024-T3. The results of their study showed that the coatings mixed with Zn/Al LDH nanocontainers conferred well-defined self-healing ability and their corrosion protection efficiency was superior to that of chromate-based systems. In another work reported by Poznyak et al. [50] from the same group organic corrosion inhibitors quinaldate and 2-mercaptobenzothiazole were incorporated into Zn–Al and Mg–Al LDH nanocontainers. The corrosion protection performance of LDH loaded with organic corrosion inhibitors toward AA 2024 aluminium alloy was studied using impedance spectroscopy, and a significant reduction in the corrosion rate was observed [50].

Tedim et al. [51] reported an enhancement in active corrosion protection using a combination of inhibitor-loaded nanocontainers. LDH nanocontainers were loaded with vanadates, phosphate and 2-mercaptobenzothiazole and the anticorrosion activity of these nanocontainers towards AA 2024 aluminium alloy was studied using

impedance spectroscopy. In order to understand the mechanism of corrosion inhibition, the bare alloy sample was immersed in chloride solution containing inhibitor-loaded LDH nanocontainers in addition to the incorporation of these nanocontainers in commercial coatings. Their results showed that the combination of various inhibitors can be effectively improving the active corrosion protection efficiency of the coatings. LDH can also be used as traps for aggressive corrosive species such as chlorides when no inhibitors are incorporated into LDH layers. In another work by Tedim et al. [52] Zn–Al-layered double hydroxides intercalated with nitrate anions were used as chloride nanotraps for protective organic polymeric coatings. They reported that the incorporation of nitrate anion intercalated LDH into polymeric coatings significantly decreased the infiltration of chloride ions through the protective coatings. Williams and McMurray also showed an anion exchange inhibition of filiform corrosion on organic-coated AA2024-T3 Aluminium alloy by hydrotalcite-based pigments [53]. Anions such as carbonates, nitrates and chromates were intercalated in LDH layers and successfully demonstrated as traps for chloride ions and thereby reducing the delamination rate of organic coatings.

The use of natural or artificially synthesized nanocontainer host for corrosion inhibitor is another approach for developing self-healing coatings for active corrosion protection. Naturally available halloysite clay nanotubes are a good container for storing active agents for controlled release. Many researchers [54–59] investigated the utility of halloysite nanotubes for active corrosion protection based on self-healing ability. Halloysite is naturally occurring alumina silicate clay with an outer diameter of $0.3\,\mu$m and a length of $3.0\,\mu$m. These nanocontainers are environmentally friendly and available in thousands of tons at very low price. The interaction of halloysite nanotubes with corrosion inhibitors is pH dependent [45].

Abdullayev et al. [55, 58] employed halloysite tubes as nanocontainers for anti-corrosion coating with benzotriazole (BTA) for 2024 aluminium alloy and copper alloy. They could achieve a maximum BTA loading of 5% by weight. Moreover, they could control the release rate of BTA by the formation of a metal (Cu)—BTA stoppers at the tube endings. This functionalization could enhance the loading efficiency of halloysite nanocontainers and ensure longer release time. Better loading of BTA in the nanocontainer was achieved through the formation of tube end stoppers by the successful complexation of leaking BTA with copper ions. Later, these BTA-loaded halloysite nanocontainers were mixed with paints, and its corrosion protection performance was assessed by monitoring the localized corrosion current density on the scratches in the coating.

Joshi et al. [59] reported an interfacial modification of clay nanotube for sustained release of corrosion inhibitors such as BTA, 2-MBT, 2-mercaptobenzimidazole for the corrosion protection of ASTM A366 steel plates. The clay nanotubes were modified with release stoppers urea–formaldehyde copolymer and copper-inhibitor complexation at the tube endings. These interfacial modified clay nanotubes were added into acrylic coating for corrosion protection, and the protection efficiency was investigated by microscanning the corrosion current on the scratch

made in the coatings. They found that the stopper formation with urea–formalde-hyde copolymer provided enhanced corrosion protection due to a longer release of corrosion inhibitors.

Shchukin and co-workers [60] developed active anticorrosion coatings with 2-mercaptobenzothiazole (2-MBT)-loaded halloysite nanotubes for 2024 aluminium alloys. Since the inhibitor-loaded nanotube has no desired releasing ability and loaded 2-MBT can be leached spontaneously due to the partial solubility in water, loaded halloysite nanotube surfaces were modified with polyelectrolyte layers. 2-MBT-loaded halloysite nanotubes were mixed with silane–zirconia hybrid sol–gel coatings, and active corrosion protection performance was studied using electro-chemical impedance spectroscopy [60]. Their study confirmed that the enhanced long-term corrosion protection for halloysite doped sol–gel coating compared to that of undoped sol–gel coating was due to the self-controlled release of the corrosion inhibitor from the halloysite nanocontainers in response to corrosion process. The major limitations of using halloysite nanotubes are its poorly defined composition, its particle size, the size of its inner hollow lumen, and the presence of 10–20% of dense, non-hollow material in the commercially available clay tubes. This limita-tion can be overcome by using artificially synthesized mesoporous and microporous nanomaterials as host for loading corrosion inhibitors [7].

Andreeva et al. [43] developed mesoporous SiO_2 nanoparticles-based coatings for active corrosion protection. Mesoporous SiO_2 nanocontainers loaded with corro-sion inhibitor, 2-(benzothiazol-2-ylsulfanyl)-succinic acid) were covered with poly-electrolyte layers to avoid any unwanted leakage of inhibitors. This nanocontainer system was incorporated into silane–zirconia hybrid films and applied over Al alloys using dip coating. The release of 2-(benzothiazol-2-ylsulfanyl)-succinic acid) from nanocontainer with polyelectrolyte was observed at pH 10. The self-healing ability of this coating was confirmed by Scanning Vibrating Electrode Technique (SVET) studies. Light-sensitive nanocontainers were also used so that the nanocontainer can be opened under the irradiation of light at specific wavelengths. One such nanocon-tainer system was developed using light-sensitive porous TiO_2 as nanocontainers for loading inhibitors [43]. This benzotriazole-loaded TiO_2 nanocontainer was covered with polyelectrolyte layers to avoid the spontaneous releasing of benzotriazole due to its solubility in water. The ultraviolet (UV)-activated opening of TiO_2 nanocon-tainers and the release of inhibitors to retard corrosion process was confirmed by SVET experiments.

Nanocapsules developed thorough LbL assembly of oppositely charged species and emulsion polymerization can be successfully overcome by using mesoporous inorganic nanoparticles as host materials for loading corrosion inhibitors. The biggest drawback of LbL-based nanocontainers is low amount of loaded inhibitors, complex design of the nanocontainer systems. This restricts their application for scaling up and long-term anticorrosion performance [7]. This disadvantage could be surmounted by using porous organic microcapsules formed by emulsion polymerization and nanoparticles stabilized polymer nanocontainers based on pickering polymerization [61, 62]. However, these nanocontainers are also having significant restrictions and limitations as far as corrosion protection is concerned [7]. The limitations suffered

by these nanocontainers are (i) deactivation of the inhibitors due to the negative interaction of inhibitors with the containers, (ii) loading efficiency of the container is limited to the solubility of the inhibitors in the emulsion oil phase forming the container core, (iii) uncontrolled shorter release of inhibitors affecting long-term corrosion protection. Recently, simpler mesoporous SiO_2 nanoparticles without any polyelectrolyte shell coverings were demonstrated to be effective nanocontainers for storage and sustained release of inhibitors [22]. Due to their high pore volume, surface area, and high inhibitor loading efficiency mesoporous silica can be used as nanocontainers for active corrosion protection. The incorporation of these nano-sized mesoporous containers would reinforce the sol–gel coating matrix and coating barrier property due to their mechanically stable and robust nature. Moreover, higher inhibitor loading was achieved using mesoporous nanoparticles as containers for corrosion inhibitors [22, 63, 64]. Borisova et al. studied protection efficiency of anti-corrosive coatings containing benzotriazole-loaded mesoporous silica nanoparticles [22]. Their study demonstrated pH-dependent controlled release of BTA from meso-porous silica nanoparticles without additional polyelectrolyte shells and suggested inhibitor release triggered by the corrosion process itself.

Maia et al. [11] prepared a novel self-healing protective coating with silica nanocontainers for long-term corrosion protection application. They reported a one-stage synthesis of 2-MBT-loaded silica nanocapsules (SiNC) through an oil-in-water microemulsion polymerization using cetyl trimethyl ammonium bromide (CTAB) as template-surfactant and ethyl ether as co-solvent. Their results showed that when SiNC loaded with 2-MBT was dispersed in NaCl solution, corrosion rate of aluminium alloy 2024 was reduced considerably. Moreover, when 2-MBT-SiNC nanocontainer system was mixed with conventional coatings, they performed better than coatings in which 2-MBT was added directly. Yasakau et al. reported the utility of cerium molybdate nanowires prepared via a new method based on a low-temperature, controlled rate mixing process for active corrosion protection on aluminium alloys [65]. They observed that the corrosion activity at local cathodic zones in aluminium alloys was inhibited by Ce and Mo oxide/hydroxide precipitates. In addition to that, the alloy surface was covered with a dense barrier layer mainly consisting of molybdenum oxides. Mekeridis et al. reported the development of a multilayer organic–inorganic coating containing TiO_2 nanocontainers for corrosion protection of AA2024-T3 [66]. TiO_2 nanocontainers were loaded with 8-hydroxyquinoline and incorporated into multilayer coatings made up of (3-Glycidyloxypropyl) trimethoxysilane (GPTMS) and epoxy resins. The enhanced corrosion resistance of inhibitor-loaded TiO_2 nanocontainer-doped coatings compared to that of undoped plain coating was demonstrated using electrochemical impedance spectroscopy.

Another study reported by Balaskas [38] of the same group showed improvement of corrosion protection efficiency of epoxy coating with TiO_2 nanocontainers loaded with 8-hydroxyquinoline. They observed a continuous increase in total impedance value with the time of immersion suggesting a possible self-healing effect due to the release of 8-hydroxyquinoline from TiO_2 nanocontainers. Kartsonakis et al. [36, 67, 68] incorporated cerium molybdate nanocontainers into the protective coatings for active corrosion protection of aluminium alloys 2024-T3, hot dip galvanized steel,

magnesium alloy ZK10. Li et al. [35] reported the utility of silica/polymer double-walled hybrid nanotubes as stimuli-responsive nanocontainers in self-healing coatings for carbon steel. The corrosion inhibitor BTA was encapsulated in the hybrid nanotubes. The BTA-loaded silica/poly (methacrylic acid) nanotube containers were doped into a silane-zirconia film to obtain a self-healing coating on carbon steel. A preliminary corrosion test of carbon steel coated with pure sol–gel silane zirconia coating and self-healing coating was carried out, and the results confirmed that self-healing coatings with BTA-loaded hybrid nanotube could hinder the corrosion process efficiently.

5 Self-Healing Anticorrosion Coating Using Micro/Nano Encapsulated Extrinsic Polymerizable Healing Agents

Here, the self-healing functionality is achieved by the ability of the coatings to repair their physical barrier integrity based on defect-filling effect. The micro/nano-encapsulated extrinsic polymerizable self-healing agent would be released upon any damage to physical integrity of the coating. When the physical barrier property of the coating is compromised owing to any mechanical damage, the capsules break and the released self-healing agent polymerize to form a protective film at the damaged site and thereby restore the barrier property of the coating. Generally, the polymerization of the released self-healing materials is realized by reacting with catalyst embedded in the coating itself or by reacting with air or moisture available and the resultant polymeric film fills the defect present on the coating.

Ever since the publication in 2001 of a study on the microencapsulation of dicyclopentadiene to fabricate a self-healing composite by White and Sottos [16], the research papers in self-healing coatings based on extrinsic polymerizable healing agents have been increased dramatically. The common polymerizable components encapsulated in the containers are dicyclopentadiene and epoxy [69–75]. Scott R. White's group in the University of Illinois has carried out pioneering work in developing self-healing coating based on polymeric nanocapsules [16, 70–74]. White et al. [16] first reported a structurally polymeric material having ability to automatically heal cracks by the utilization of polyurea-formaldehyde microcontainers loaded with dicyclopentadiene (DCPD). In their work, the healing was accomplished by incorporating a microencapsulated healing agent and a catalytic chemical trigger within the epoxy matrix. Ruthenium-based Grubbs' catalyst was used to initiate the ring opening metathesis polymerization of DCPD. Other than DPCD, materials such as epoxy, 1H, 1H′, 2H, 2H′-perfluorooctyl triethoxy silane, have also been encapsulated in PUF microcontainers [74–76]. Similarly, drying oils such as linseed oil and tung oil have also been encapsulated in microcontainers to heal the crack in coating for corrosion protection [77–79]. Garcia et al. reported another promising healing agent, silyl ester, which is a catalyst free polymerizable healing agent, and it is capable of reacting with water/humidity and form a protection layer on the metallic

substrate when damage occurs to the coating [80]. Recently, Sun et al. reported a self-healing coating mixed with double-layered microcapsules containing hexamethylene diisocyanate as the self-healing material [81]. Furthermore, polymers with intrinsic microporosity were also used for loading benzotriazole as inhibitors for the protection of aluminium alloys [82]. Most of these smart coatings rendered their self-healing ability by the passivation of the metal surface or by forming a new physical barrier layer by the corrosion inhibitors or active agents released from the micro/nanocontainers. Mohwald et al. [83] reported a novel self-healing anticorrosion mechanism by using an organofunctional silane as healing agent encapsulated in polyurethane microcapsule [83]. Similarly, there have been attempts made by researchers to create polyurethane/polyurea-formaldehyde bi-layer microcontainers to improve the property of the microcontainers to single polyurethane or polyurea-formaldehyde walls. This strategy has been adopted to improve the encapsulation capacity and robustness of the capsule shell walls [84].

Kumar et al. [15] investigated the efficacy of self-healing corrosion protection system using urea–formaldehyde microcapsules loaded with Tung oil. Their study showed that the application of microcapsules as an intermediate layer between two coats of standard primer coating could provide sufficiently long self-healing. Leal et al. [85] reported the preparation of a dual stimuli-responsive microcapsules by loading linseed oil in poly(urea–formaldehyde) microcapsules and subsequently coated it by benzotriazole inhibitors sandwiched by polyelectrolyte layers using layer-by-layer coating technique. Linseed oil was encapsulated in poly(urea–formaldehyde) microcapsules using in situ emulsion polymerization technique, and the linseed oil would be released upon any mechanical damage to the capsules. At the same time, the release of benzotriazole was realized by any local change in pH owing to the onset of corrosion. The structure of the microcapsule system containing two payloads is depicted in Fig. 5.
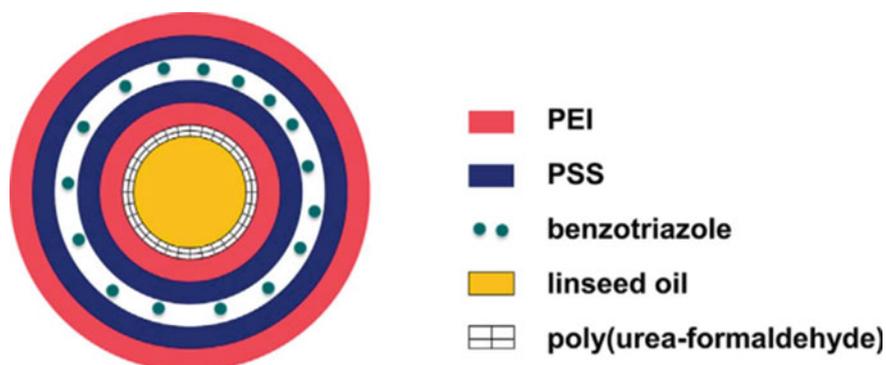

Fig. 5 Schematic representation of microcapsule containing two payloads. Reproduced with permission [85]

6 Evaluation of Active Corrosion Protection Based on Self-Healing Ability

Various electrochemical techniques have been used for the evaluation of the active corrosion protection based on self-healing ability since corrosion process is electrochemical in nature. In addition to this, real-time environmental corrosion tests, immersion tests in salt solution, and accelerated corrosion tests like salt spray test was employed for the same [35, 41, 68, 86–91]. All these techniques or tests are carried out in ambient atmospheric conditions or in solutions containing corrosive species. The techniques which are making use of the principles of aqueous corrosion can be carried out locally on a particular point or area of the coated surface or in bulk solutions involving all the area of the coated surface. The availability of various small probes made it possible to investigate the corrosion process in micro world. Techniques such as scanning vibrating electrode technique (SVET), scanning electrochemical microscopy (SCEM) and localized electrochemical impedance spectroscopy (LEIS) are some of the localized electrochemical techniques used for microlevel corrosion analysis. The traditional electrochemical techniques such as open-circuit potential (OCP) measurements, potentiodynamic polarization (PP) method and electrochemical impedance spectroscopy can also be successfully used to evaluate self-healing corrosion protection.

Cho et al. [86] used a simple electrochemical technique to demonstrate self-healing property of polymer coatings. In their experiments, the coated metal substrate was acted as working electrode in a simple electrochemical cell. They measured the steady-state current between the coated metal working electrode and platinum counter electrode when a constant potential of 3 V was applied in 1 M NaCl solution. Figure 6 shows the experimental set-up for the electrochemical test and the current vs. time plot obtained after the experiment.
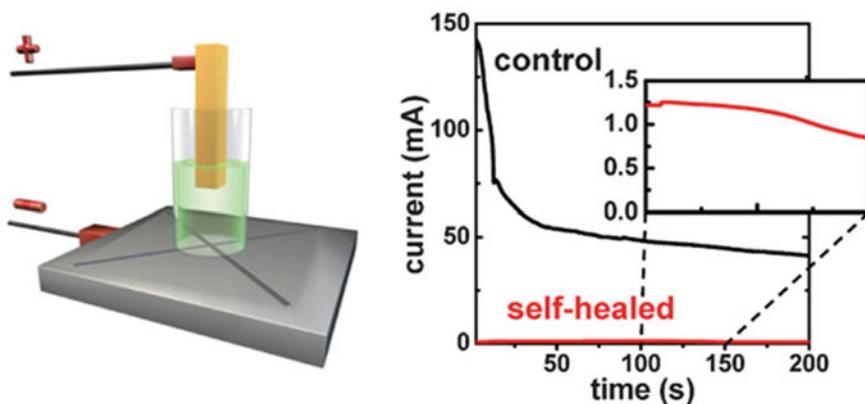

Fig. 6 Schematic diagram for the electrochemical test and the current versus time for the scribed control and self-healing coatings. Reproduced with permission [86]

They reported that before scribing the coatings, the current passing through both the control and self-healing coatings were identical (roughly around 0.34 μA cm^{-2}). However, after making scratch on the coatings, both the coatings behaved differently when kept in the electrochemical cell. The current passed through the scratched control coating was quite large compared to that of undamaged control coating (26.6–58.6 mA cm^{-2} for three samples). However, the current produced when the self-healing coated samples were connected was considerably low (12.9 μA cm^{-2}– 1.4 mA cm^{-2} for four samples). Moreover, they could observe the evolution of gas bubbles from the scratched area of the control coatings, however, no such bubbling of gas was observed from the scribbled area of the self-healing coated sample.

Jafari et al. [87] used potentiodynamic polarization method to evaluate the self-healing property of the coatings. They investigated the corrosion protection of copper with three types of nanocapsules which can render active corrosion protection. They loaded benzotriazole inhibitors in Polyelectrolyte Nanocapsules (PNC), and the effectiveness of the release of the benzotriazole inhibitor from the PNC container was investigated using potentiodynamic polarization method. Figure 7 shows the polarization curves for copper electrode in 0.5 M NaCl solution containing polyelectrolyte nanocapsules (PNC). They observed that as seen in Fig. 7, the corrosion process reduced with time and this showed the release of benzotriazole inhibitor from the nanocontainers. They reported that i_{corr} value was decreased with time as well as the E_{corr} value shifted to more positive side during immersion in salt solution containing benzotriazole-loaded nanocapsules. This clearly demonstrated the release of benzotriazole from the nanocapsules and protected the copper metal from corrosion. Aramaki et al. [88] prepared a self-healing protective coating based on cerium nitrate on zinc electrode, and the self-healing property was studied using potentiodynamic polarization studies.

Fig. 7 Polarization curves for copper electrode in 0.5 M NaCl solution containing polyelectrolyte nanocapsules (PNC) after different times of immersion. Reproduced with permission [87]
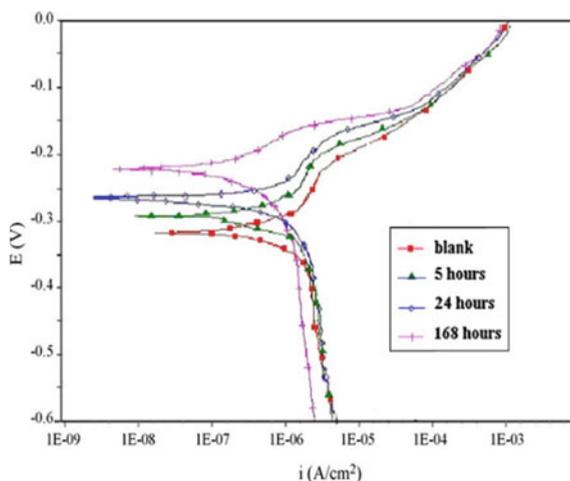
The surface of both the coated and uncoated zinc electrode was scratched and immersed in 0.5 M NaCl solution, and they showed using Tafel plot that the coated film was highly protective and self-healing against corrosion of scratched Zinc.

Another electrochemical technique which has been successfully employed for the evaluation of self-healing coating is electrochemical impedance spectroscopy. Zheldkevich et al. [41] demonstrated the possibility of using electrochemical impedance spectroscopy is an ideal technique to investigate active corrosion protection based on self-healing of defects in a coating. His experiments proved that an increase of low frequency impedance during immersion in a corrosive medium can be related to the inhibition of active corrosion process and self-healing of the corroded area of the coating. Moreover, in his study, he concluded that impedance method can be routinely used for the investigation of the self-repairing of coatings. The 2024 Aluminium alloy was coated with hybrid sol–gel film, and it was used as a model-coated system to study the healing of an artificial system by corrosion inhibitor 8-hydroxyquinoline. In their work, they tried to prove that the increase in low frequency impedance was conferred by the self-healing due to the release of a corrosion inhibitor.

They obtained an increase in the low frequency impedance when an aluminium alloy coated with hybrid sol–gel film containing benzotriazole inhibitor during immersion in salt solution. Figure 8 given below showed that after an initial drop in the low frequency impedance, it started increase to the initial value. However, in the case of undoped sol–gel film, the low frequency impedance was decreasing continuously with immersion without showing any sign of recovery. The better performance of the inhibitor-doped hybrid sol–gel coatings was attributed to the release of the corrosion inhibitor to the damaged part of the coating since the undoped coating did not show this effect.

Fig. 8 Impedance spectra during immersion in 0.5 NaCl for inhibitor containing double-layer sol–gel film (**a**) and undoped single-layer sol–gel film (**b**) before and after defect formation. Reproduced with permission [41]
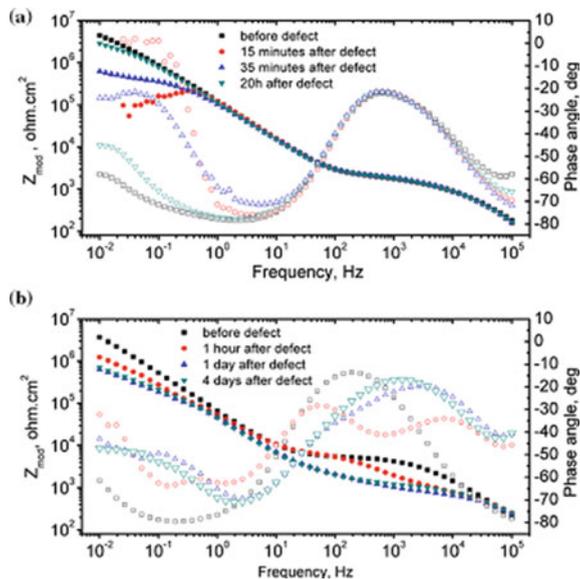
In another work reported by Kartsonakis et al. [68], 2-MBT-loaded cerium molybdate nanocontainers were added into organic–inorganic hybrid epoxy-based coatings and their effect on the corrosion protection of hot-dipped galvanized steel was studied. The improved corrosion resistance of the inhibitor-loaded nanocontainer mixed hybrid coating was demonstrated using electrochemical impedance spectroscopy. In order to understand the self-healing ability of the coatings and the evolution of corrosion process on the damaged site of the coatings, artificial defects of 1 mm were made on the surface of the coatings and exposed to 5 mM NaCl solution. During one week of immersion, they observed that initially the impedance value at low frequency has decreased continuously; however, after sixth day, low frequency impedance value increased. This increase in low frequency impedance was attributed to the recovery of the coating characteristics (corrosion protection) due to the release of the inhibitors from the nanocontainers.

Localized electrochemical techniques are very good to study local corrosion inhibition and self-healing ability of coatings. Snihirova et al. [89] used Local Electrochemical Impedance Spectroscopy (LEIS) to study the active corrosion protection rendered by a water-based epoxy coating containing inhibitor-loaded $CaCO_3$ nanocontainers. Figure 9 shows the LEIS map of aluminium alloy coated with both reference coating and nanocontainer-based coatings after making artificial defects. The figure depicts the evolution of admittance across a line perpendicular to the defect in both the reference and nanocontainer containing coatings after 1, 8 and 46 h of immersion in salt solution. The admittance maximum or lower impedance denotes the defect on the coating, and the remaining area of the intact coating is represented by lower admittance value. They observed that the reference coatings
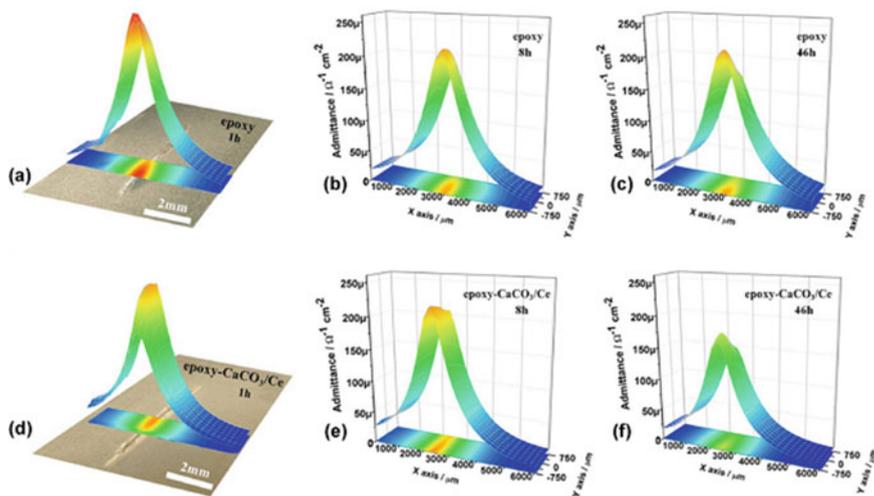

Fig. 9 LEIS map of the AA2024 coated with the water-based reference epoxy coating (**a–c**) and coating loaded with CaCO₃/Ce microbeads (**d–f**) over artificial defects. Reproduced with permission [89]

showed highest admittance value during initial immersion time compared to that of the coating modified with $Ce/CaCO_3$ microbeads and the admittance of the reference coatings remained the same during the test period. However, their results showed a different behaviour for coatings modified with $Ce/CaCO_3$ microbeads during the course of immersion in salt solution. A continuous decrease of admittance with time was observed for the coatings modified with $Ce/CaCO_3$ microbeads. This decrease in corrosion activity at the defect was attributed to the released Ce ions from the $CaCO_3$ microbeads with immersion. In another work published by Plawecka et al. [90], LEIS mapping was carried out to evaluate the self-healing ability of epoxy-based coating modified with nanocapsule-loaded 2-MBT applied over both AA5083 and galvanized steel substrates. In order to expose the metal surface to the electrolyte solution and the commencement of the corrosion immediately after the start of the immersion, a defect of 7 mm long was made on the coating. Figure 10 shows the LEIS mapping of both blank coating and coating modified with nanocapsules containing inhibitors after various times of immersion in salt solution. They observed that during the initial hours of immersion test, the modified coatings had higher values of admittance compared to that of the blank coatings. However, as the experiments proceeded further, it was observed that the electrochemical activity was increased for the blank sample and even signs of multiple active spots were visible in the LEIS mapping. On the other hand, the admittance value decreased for coatings modified with nanocapsules containing inhibitors and this according to authors due to the release of the inhibitors from the nanocapsules as the immersion time progressed. This clearly demonstrated the self-healing ability of the coatings modified with nanocapsules containing inhibitors.

Scanning Vibrating Electrode Technique is another localized technique used to map the localized electrochemical activity spatially. M.L. Zheldukevich used SVET to demonstrate the self-healing effect of bi-layer protective coatings applied over aluminium alloy 2024 [91]. Their coating constitutes a cerium ion containing chitosan layer and a hybrid silica zirconia barrier layer. The chitosan-based layer acts as a reservoir for the release of the corrosion inhibitors. They used SVET to study the local current density in the microconfined defects on the protective coatings. Figure 11 shows the SVET maps and current profile of the micro defects in the protective bi-layer coatings with corrosion inhibitors during immersion in 0.05 M NaCl solution.

Two artificial defects of size 200 μm were made on the coatings for simulating the situation of coating damage during service life and immersed in 0.5 M NaCl solution. Their results showed that anodic current densities diminished with immersion time and only wide inactive cathodic zones were detected after 70 h of immersion in salt solution. They reported that the relatively low anodic current values were due to the healing of the localized defect, and the appearance of only cathodic current at the defect site could be due to the release of the Ce^{3+} ions. Further, they also reported a different response from the undoped bi-layer coatings. A continuous increase in the corrosion activity was observed during two days of immersion.

In addition to electrochemical techniques, real-time tests also employed by various research groups to study the self-healing properties of coatings. Simple immersion in
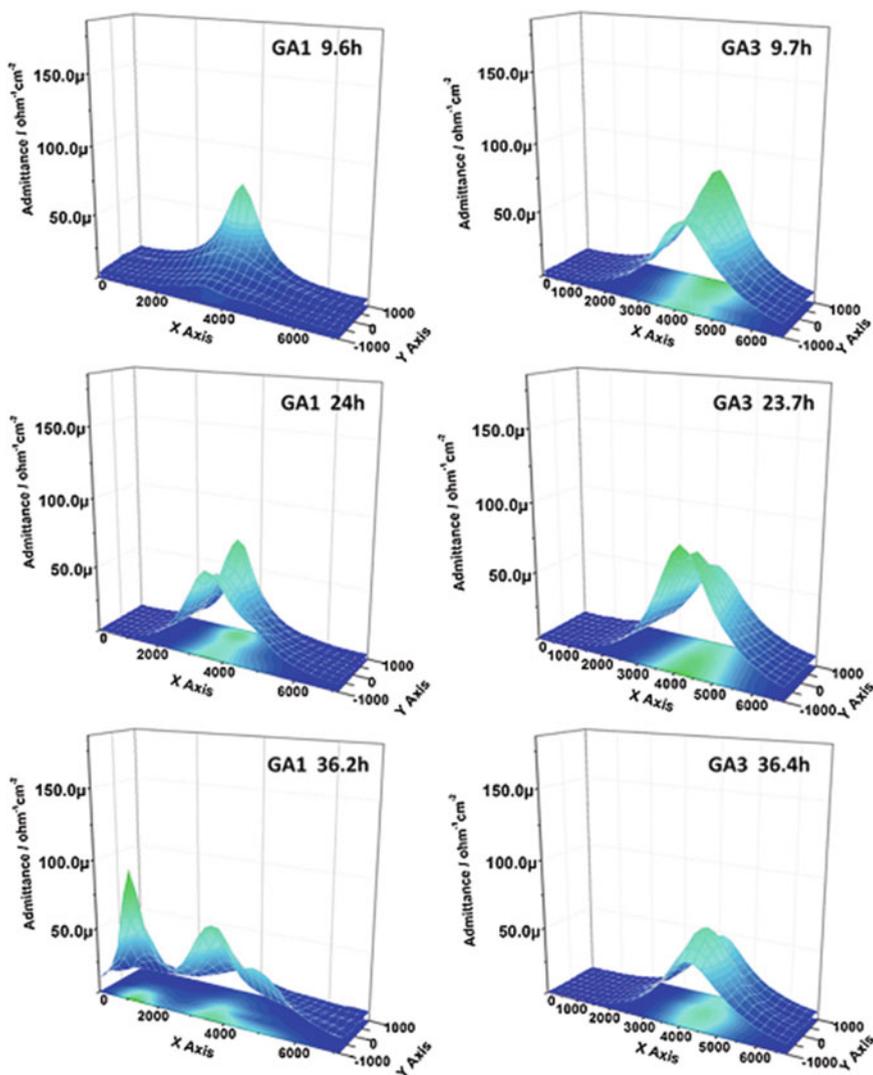
Fig. 10 LEIS maps for the blank coating (GA1) and for coating modified with nanocapsules (GA3) applied on galvanized steel for different immersion times in 0.005 M NaCl. Reproduced with permission [90]

salt solution is one of the easy tests for investigating the active corrosion protection property. Li et al. produced benzotriazole-loaded silica/polymer nanotube-doped silane–zirconia self-healing coatings over carbon steel and compared its corrosion protection efficiency with pure silane–zirconia coatings [35]. They immersed both the reference coatings and inhibitor-loaded nanocontainer impregnated hybrid coatings in salt solutions. They found that the coating with inhibitor-loaded nanocontainers
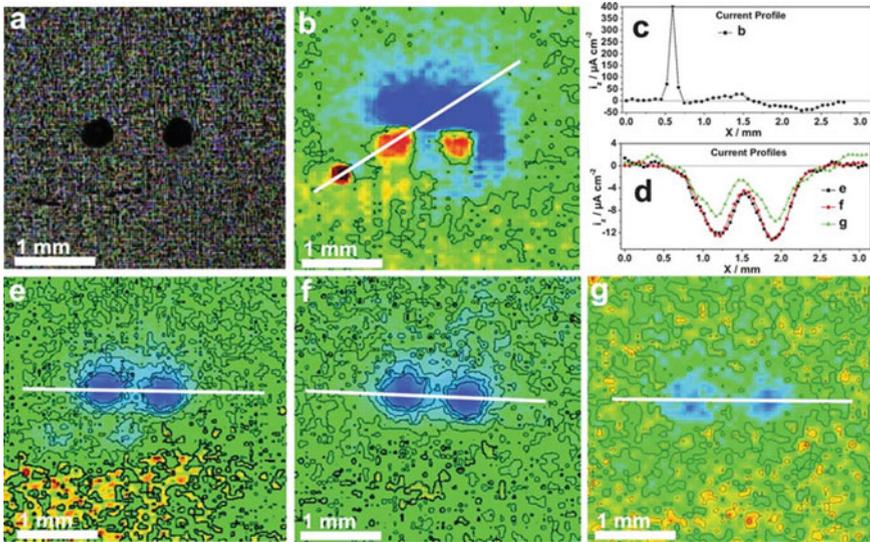
Fig. 11 Optical micrograph (**a**) and SVET maps obtained on AA2024 coated with Ce-containing chitosan and sol–gel after different immersion times in 0.05 M NaCl solution: 1.5 h (**b**), 5 h (**e**), 40 h (**f**) and 70 h (40 h in 0.05 M NaCl + 30 h in 0.5 M NaCl) (**g**). Selected current profiles for map b (**c**) and maps e, f and g (**d**). Reproduced with permission [91]

could stop and delay corrosion compared to coatings without any inhibitors when tested in 0.1 M NaCl solution for 48 h. Figure 12 shows the carbon steel coupons after 48 h of corrosion testing in 0.1 M NaCl solution. The part B of the figure explains the corrosion protection mechanism of the coating. When the coating was attacked by the corrosive species, the coating was disrupted, and corrosion started. However, inhibitor gets released from the broken nanotubes, and this release was faster when the pH changed due to corrosion and thereby delayed corrosion and provided protection to the carbon steel surface.

Huang et al. employed corrosion immersion test for steel panels coated with self-healing anticorrosion coatings loaded with polyurethane microcapsules containing hexamethylene diisocyanate (HDI). In their coating, they integrated microcapsules containing active agents into the epoxy resin and preliminary self-healing corrosion test was carried out, and the results are shown in Fig. 13 [92].

The steel panel coated with the self-healing epoxy coating was not affected by corrosion at all, whereas the control epoxy coating corroded freely when immersed in 10% NaCl solution for two days.

Systematic long-term neutral salt spray test was another real time corrosion testing employed for protective coatings. Chenan et al. used salt spray test according to ASTM B117 to test the self-healing ability of 2-MBT-loaded TiO_2 impregnated hybrid epoxy coatings on modified 9Cr-1Mo ferritic steels [93]. The epoxy coating containing inhibitor-loaded nanocontainer was tested along with a reference coating. Both the Epoxy Nanocontainer Coating (ENC) and reference coating (Plain epoxy
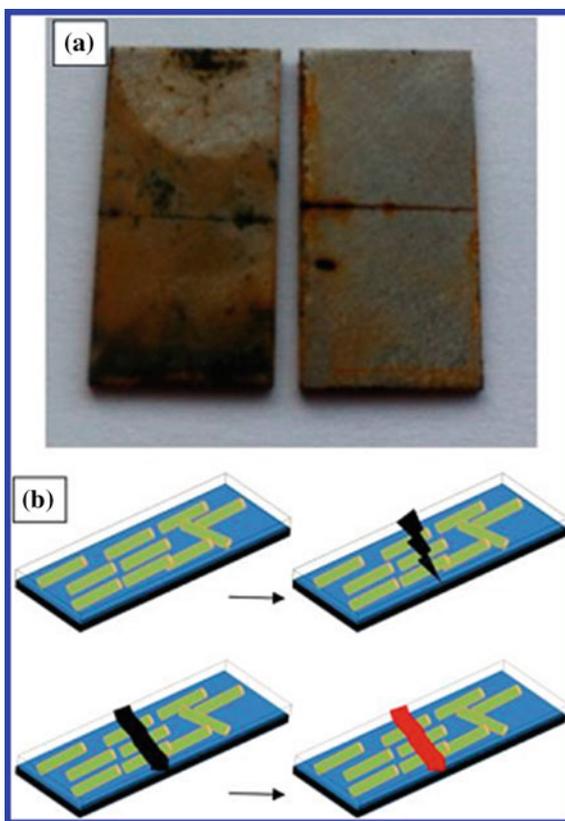
coating, PEC) were exposed to 1000 h of salt spray test. Two sets of coated specimens were exposed to salt spray test. Blistering of the coatings and under coat corrosion was clearly visible in the case of PEC after 1000 h of salt spray exposure. Moreover, a small flake of the coating was peeled off due to the loss of adhesion to the metallic substrate (Fig. 14a). Conversely, no delamination of coatings was observed for ENC. Insignificant rust markings appeared on one side in the scratched area of the coating (Fig. 14a). However, in the second set of tested samples, such rust markings were not observed on the scratched area (Fig. 14b). The salt spray chamber test showed sufficient protection even after 1000 h of exposure for inhibitor-loaded nanocontainer mixed epoxy coating compared to that of reference (plain top epoxy) coating.
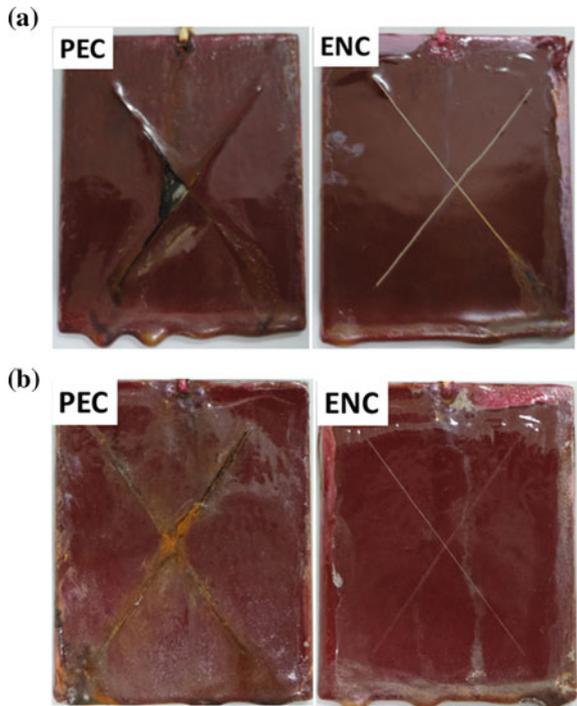
7 Limitations of Self-Healing Coatings

Even though there are reports in literature about the advantages on the use of self-healing coatings for active corrosion protection for metals and alloys, these types
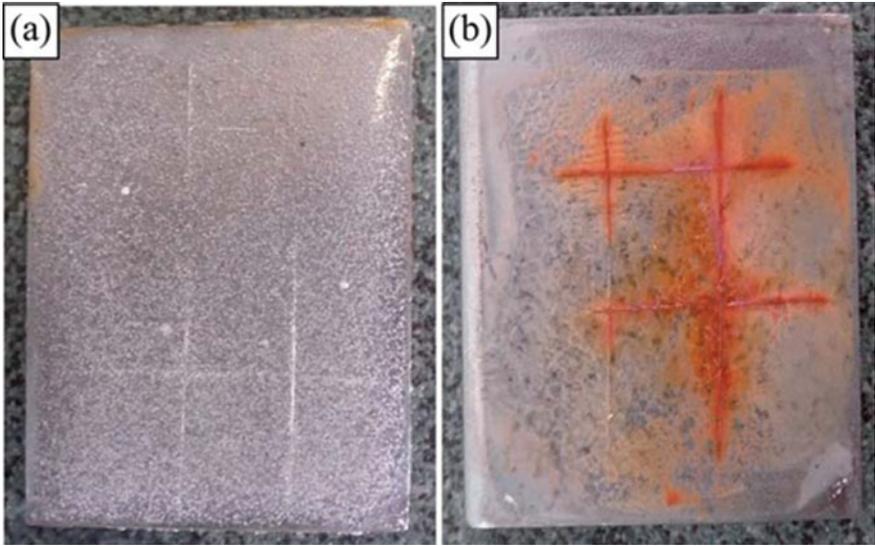
Fig. 13 Corrosion test results for steel panels coated with **a** epoxy coating mixed with 10 wt% of prepared HDI-filled microcapsules; **b** control epoxy coating. The panels were immersed in 10% NaCl solution for 48 h. Reproduced with permission [92]

Fig. 14 Photographs of the Epoxy Nanocontainer Coating (ENC) and reference coating (plain epoxy coating, PEC) after 1000 h of exposure to neutral salt spray test; **a** first set, **b** second set. Reproduced with permission [93]

of coatings have their own limitations. Except a few, coatings with self-healing functionalities have not entered the markets for industrial use. There are doubts about the long-term efficacy of the "self-healing" protection offered by these new classes of coatings. As described in the preceding sections of this book chapter, for effective healing of the defect to occur, the encapsulated healing agent should have compatible chemical composition and satisfactory mechanical strength to that of the applied coating matrix. Since epoxy-based healing agents satisfied the aforesaid criteria, epoxy and its curing agents are widely used for encapsulation. These two-part healing materials have to be stored separately in the microcapsules to avoid unwanted cross-linking between the healing materials. Further, the healing process would take place only when both epoxy and curing agent gets released from the capsules upon mechanical damage. The distribution of microcapsules in the coating should be uniform for immediate availability of the healing agent when mechanical damage occurs. Furthermore, the catalyst used in many self-healing coating systems to aid the polymerization is costly, and hence, the complete self-healing design would not be cost-effective. Similarly, self-healing achieved by using water reactive self-healing chemicals such as silanes and liquid isocyanate lacks long-term protection and self-healing ability. Wang et al. while assessing the self-healing ability of a scratched alkyd varnish coating containing PUF microcapsule with isophorone diisocyanate as core material observed that self-healing functionality was not achieved when the width of the scratch was more than 30 microns. Further research is required to assess the width or the dimension of the defect which should be effectively healed by the self-healing materials available in the coating [94].

The self-healing ability of a coating depends on the size of the capsules, and the quantity of the capsules present in the coating in addition to its chemical and physical properties. The capsule wall should not be too strong or weak. The capsule wall should be brittle enough to break when the mechanical integrity of the bulk coating is breached. At the same time, the capsule wall should be strong to avoid any unwanted leakage of the core material having self-healing ability. Moreover, many of the reported microcapsules have very large size in hundreds of microns, and hence, it would be difficult to load these larger microcapsules in thin pre-treatment layers such etch primers or sol–gel coatings. The large sized microcapsules itself can cause problems to the barrier property of the coatings. In order to heal the entire defect along its length or breadth, large quantity of healing agents should be released from the broken capsules [95–97].

The biggest drawback of inhibitor-loaded nanocontainers for self-healing corrosion protection is that these types of system do not ensure the complete recovery of the physical barrier property of the bulk coating [95]. They are working at functional level; not structural as far as the corrosion protection is concerned. In most of the cases, a stimulus is needed for the release of the corrosion inhibitors from the nanocontainer. Here, the local pH changes in response to corrosion process itself are the stimuli for the release of corrosion inhibitors. Prior to the release of the inhibitors, the physical barrier property is broken, and corrosion process starts. The corrosion inhibitor-loaded nanocontainer system is generally introduced into thin sol–gel coating as a primer or pre-treatment layer for the immediate availability of corrosion

inhibitors at the coating/metal interface on the onset of corrosion. Uniform distribution of the inhibitor-loaded nanocontainers, high loading capacity of the container and good corrosion inhibition performance of the loaded inhibitors are essential for self-healing corrosion protection. Further, the long-term efficacy of corrosion inhibitors inside the coating matrix is also not clear. When a scratch is made on the coatings, the large corrosion inhibiting molecules must compete with instantaneously reacting corrosive molecules such as oxygen, water and chloride ions. This is a challenge as the adsorption of organic molecules would take more time than that of simple oxygen reduction reaction. Further, inhibitors are less effective once corrosion has started, and releasing of corrosion inhibitors is not sufficient for sustained self-healing property. Similarly, the use of larger concentrations of nanocontainers are not advisable, since higher the concentration of nanocontainers, higher the stress formation and affects the integrity of the sol–gel coating itself. The challenge is to preserve the desirable properties of the coatings to achieve effective self-healing with minimum loading of nanocontainers or microcapsules.

A recent study published by Wang and Zhou discusses the long-term efficacy of the self-healing protection offered by linseed oil encapsulated self-healing anti corrosive coating [98]. They have carried out a systematic evaluation and failure analysis of self-healing epoxy-polyamine coating matrix using electrochemical impedance spectroscopy. They mainly investigated the influence of linseed oil encapsulated PUF microcapsules on the barrier property of the intact epoxy coating. They argued that no relevant study had been published on the influence of linseed oil encapsulated PUF microcapsules on the anticorrosive property of the intact epoxy coatings. They reasoned that the addition of linseed oil encapsulated PUF microcapsules negatively affect the barrier property of the intact epoxy coating by two ways. The PUF microcapsule may absorb more water than that of epoxy due to the presence of enriched hydrophilic amine and carbonyl groups on PUF shells. Moreover, uncured linseed oil might be a vulnerable spot for the diffusion of corrosive species to the metal surface compared to that of highly cross-linked epoxy moiety. In their study, it was found that the addition of 10 wt% linseed oil encapsulated PUF microcapsules into the epoxy coating resulted in the increase of the absorption of water; however, the anticorrosive property of the self-healing coating was as good as the pure epoxy coating. Even though the self-healing coating could heal the micro crack when scratched and exhibit self-healing ability and corrosion inhibition, the anticorrosive performance of scratched self-healing coating is not comparable with the intact epoxy coating. At the micro crack, the self-healing coating lost its barrier property within 1 day of immersion in 3.5 wt% NaCl solution and the rapid failure might be due to unstable interaction of linseed oil coating with epoxy coating matrix under immersion condition. Their study further put forward that the stability of the interaction between the healing material and the coating matrix and/or the microcapsule shell material should be given more consideration while designing novel microcapsule-based self-healing anticorrosive coating systems in the future.

8 Summary and Scope for Future Works

This chapter provides a comprehensive review of the self-healing coatings for active corrosion protection. With the advancement in nanotechnology, various nanocontainers and microcontainers were used to encapsulate corrosion inhibitors as well as self-healing materials. The design of a self-healing system requires nano/microcapsules to load corrosion inhibitors or self-healing molecules and a compatible coating matrix. The release of appropriate quantity of inhibitor should occur in response to corrosion and the release should be continuous and sustained for long-term self-healing effect. Further, the choice of the inhibitors is substrate specific as inhibitors that work for Al alloys may not be effective for steel. The released inhibitor should not affect the coating matrix also. The self-healing coating should be smarter to heal large macrocracks on the bulk coating. Research should be carried out to find out the use of self-healing-based active corrosion protection along with galvanic protection to use the synergistic effect of sacrificial protection and self-healing effect. Similarly, the interaction between the released healing materials and bulk coating matrix should be understood prior to the design of the self-healing coating system. It is also required to prepare coatings with multiple functionalities to protect structural materials from corrosion in different environments. The following are some of the works to be carried out for the aforesaid purpose. Additional studies are required to investigate the kinetic and structural properties of the nanocontainers and the diffusion of the released inhibitor inside the coating matrix.

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