Recent Approaches for Designing Nanomaterials-Based Coatings for Corrosion Protection

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Nedal Abu-Thabit and Abdel Salam Hamdy Makhlouf

Contents

Abstract

Nanotechnology-based coatings have shown remarkable growth in recent years in many strategic industries such as automotive, aerospace, petroleum, electronics, etc. The unique characteristics that can be offered from nanotechnology are one

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N. Abu-Thabit (✉)
Department of Chemical and Process Engineering Technology,
Jubail Industrial College, Jubail, Saudi Arabia
e-mail: abuthabit_nidal@yahoo.com

A.S.H. Makhlouf
Manufacturing Engineering Department, College of Engineering
and Computer Science, University of Texas Pan-American, Edinburg, TX, USA
e-mail: abdel.makhlouf@utrgv.edu

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of the main driving forces for the sharp innovation in coatings technology nowadays. Nanocoatings have recently been proposed to add functionalities to the materials to be coated such as anticorrosion self-healing, anti-icing, self-cleaning, etc. Different types of nanomaterials have been incorporated in anticorrosion coatings by adopting various approaches. The basic approach utilizes incorporation of inorganic nanomaterials with the traditional organic coatings to enhance certain functionality of the formulated nanocomposite coating. However, one of the recent trends in nanotechnology is to design nanomaterial-based coatings of multifunctionality. These include stimuli-responsive/smart coatings, self-healing coatings, organic/inorganic hybrid coatings, and electroactive coatings. This chapter highlights these emerging nanotechnologies and presents the most recent achievements in this area.

Keywords
Nanotechnology • Self-healing • Nanocoatings • Smart coatings • Corrosion protection

Introduction

Protective polymeric coatings are the most widespread approach for corrosion protection of metallic structures. They act as barrier to prevent or impede the interaction of corrosive species with the metallic substrates. However, there are some factors affecting the protection performance of the polymer such as temperature, humidity, and the presence of aggressive salts which result in the degradation of the polymer and deteriorate their barrier effect (Fig. 1a, b). Therefore, there is an increased demand for designing coatings with self-healing functionalities to provide long-term protection.

The sharp innovation in nanotechnology is one of the main reasons for the development of "smart" functional coatings which can be used for a variety of applications including antifogging [1] and anti-icing coatings [2–4], scratch-resistant coatings [5–7], anti-stain coatings [8, 9], moisture-resistant coatings [10–12], oil-repellent coatings [13, 14], self-cleaning coatings [15–17], antimicrobial coatings [18–22], UV protection coatings [23, 24], adhesive coatings [25], and anticorrosive self-healing coatings [26–37].

Self-healing coatings can be constructed by the adsorption of stimuli-responsive polymers on solid support materials. The stimuli-responsive polymers can be classified into two categories: (1) intrinsic polymers that are able to heal the cracks by themselves and (2) extrinsic polymers in which the healing agent has to be pre-embedded [38]. For example, thermally responsive reversible cross-linked polymers represent an important class of intrinsic self-healing polymers [39–41]. The mechanism of self-healing is based on Diels-Alder and *retro*-Diels-Alder reactions. However, in the case of extrinsic self-healing, the healing agent is encapsulated within a reservoir [42, 43]. The encapsulated healing agent contains liquid monomer that is able to polymerize at room temperature with the help of a

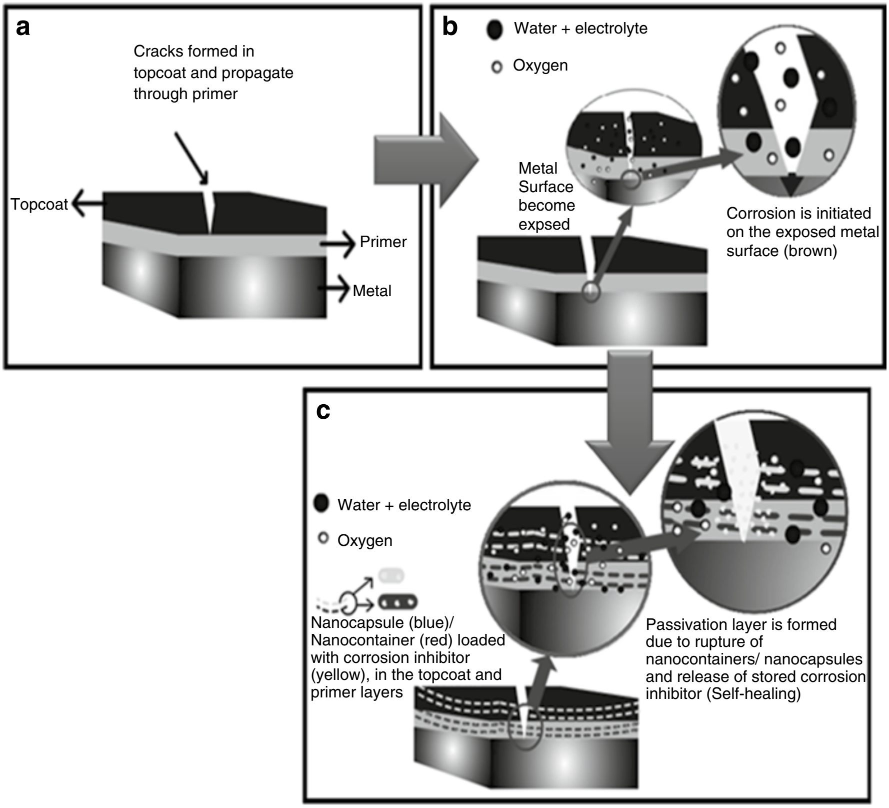

Fig. 1 Schematic illustration of self-healing anticorrosion coating (**a**) corrosion initiation at the topcoat layer, (**b**) corrosion penetrates to the metal surface, and (**c**) self-healing through the release of the encapsulated inhibitor that is embedded in the coating matrix

catalyst present in the composite matrix [44, 45]. However, there are some cases that the self-healing agent can polymerize without any catalytic support [46].

Smart self-healing coatings are designed to interact with the surrounding environment by responding to external physical or chemical changes induced by external stimuli such as temperature, pH, ionic strength, pressure, corrosion products, or light. This switching of the physiochemical properties will lead to the rupture of the self-healing container/capsule and eventually the release of the encapsulated corrosion inhibitor. Figure 1c illustrates the concept of self-healing-protective coating with autorepair functionality. The effective release of stored corrosion inhibitor from the encapsulated container provides a real triggering mechanism for spontaneous repair of small defects in a similar fashion to the toxic chromate coatings which maintain a passive layer of protective metal oxide through the intelligent release of chromate anions as illustrated in Eq. 1:

$$2\mathrm{Fe} + 2\mathrm{CrO}_4^{2-} + 4\mathrm{H}^+ \rightarrow \mathrm{Fe}_2\mathrm{O}_3 + \mathrm{Cr}_2\mathrm{O}_3 + 2\mathrm{H}_2\mathrm{O} \tag{1}$$

This chapter discusses the recent approaches for the design and preparation of anticorrosive coatings of self-healing functionality. These approaches include encapsulation of corrosion inhibitors, embedding corrosion inhibitors into nanocontainers and various inorganic microparticles, application of polyelectrolyte multilayers, and utilization of electrically conductive polymers as potential self-healing anticorrosive coatings.

Microcapsule-Based Self-healing Coatings

Definition and Limitations

The encapsulation process is considered as a key step for obtaining effective and functional self-healing coatings. The designed containers must possess strong shell walls, for long life durability, and impermeability to corrosive species such as atmospheric oxygen and water. Also, the containers should be able to supply the stored active content on demand upon certain triggering mechanism and consequently provide self-healing response.

The encapsulation process enables the self-healing coatings to provide superior performance over their traditional coating counterparts. In traditional coating systems, where the corrosion inhibitor is incorporated by direct mixing, possible interactions with the formulated coating can result in loss of inhibitor efficiency, coating degradation, or both [47]. However, in the case of smart-responsive coatings, the corrosion inhibitor is encapsulated in a variety of micro- or nanostructured materials such as microcapsules, nanocapsules, nanocontainers, and nanoreservoirs. Thus, the encapsulating container acts as a “host” for the corrosion inhibitor and also prevents the direct contact between the inhibitor and the coating, allowing for the controlled release of the stored active content at the time of corrosion initiation.

Synthesis and Preparation

Microcapsules can be designed and prepared by using different techniques including pan coating, spray drying, centrifugal extrusion, and emulsion-based methods [48]. Emulsion methods include emulsion polymerization, layer-by-layer assembly, internal phase separation, and coacervation. The efficient trigger-release performance of the prepared capsule depends on parameters such as shell wall thickness, permeability, mechanical integrity, and chemical functionality of the capsule shell wall as well as the capsule size.

Emulsion Polymerization

Emulsion polymerization process can be utilized for the preparation of capsules as illustrated in Fig. 2a. Emulsion is created by strong agitation or sonication of biphasic liquid, typically oil in water (emulsion) or water in oil (inverse emulsion) [49, 50]. Stirring or sonication creates droplets which become the core material of

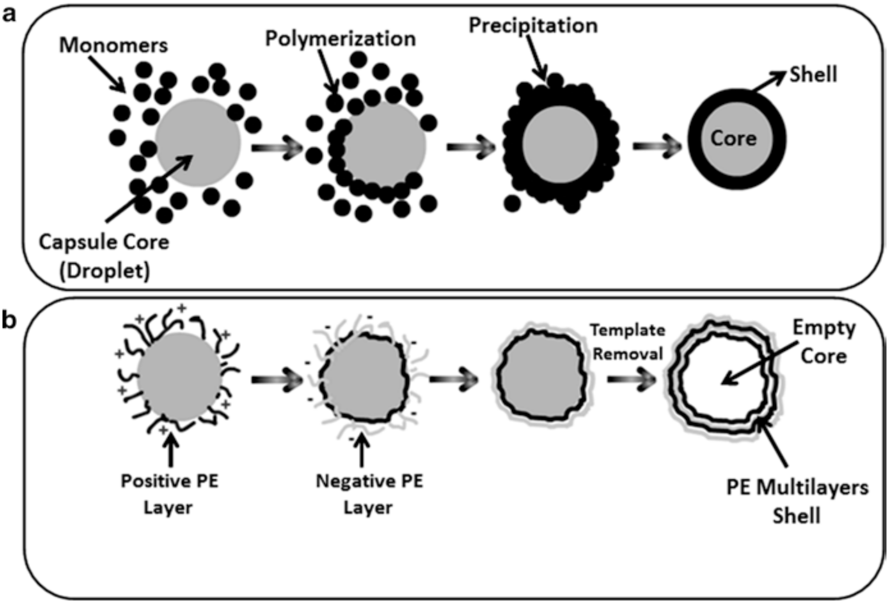

Fig. 2 Schematic illustration for microcapsule preparation (**a**) emulsion polymerization is used to create polymeric shell around the stabilized droplet, which become the core material, and (**b**) layer-by-layer deposition of polyelectrolytes onto metal oxide template, which is removed to create hollow and porous microcapsule

the capsule. The capsule shell wall is created by the polymerization at the aqueous/organic interface around these droplets. Polymers can be formed by condensation polymerization of two immiscible monomers at the aqueous/organic interface [44] or through in situ free radical polymerization reactions of vinyl monomers such as styrene, vinyl acetate, 1,3-butadiene, and isoprene [51].

Layer-by-Layer Assembly

In layer-by-layer (LBL) assembly, polyelectrolyte layers with alternating positive and negative charges are deposited on the capsule shell wall [47, 52, 53]. The thickness of capsule shell wall can be controlled by the number of deposited layers. Since polyelectrolytes are pH-responsive macromolecules, the trigger and release mechanism depends on the stability of the polyelectrolyte layers, which in turn is governed by the pH of the surrounding environment. Thus, the selection of weak/strong, acidic/basic ionizable groups allows for the optimization of trigger and release mechanism to occur at certain pH range.

Capsule fabrication using LBL method can be achieved via three stages as illustrated in Fig. 2b. The first stage represents the selection of suitable capsule core material such as metal oxide particles. Then, polyelectrolytes with alternating positive and negative charges are deposited on the capsule shell wall. The final stage includes the removal of the metal oxide core by acid treatment, leaving behind hollow, porous, and semipermeable capsules.

The porosity of the capsule shell wall enables the capsule core to be loaded and exchanged with a variety of molecules after the preparation process. However, the main disadvantage of this technique is the weakness of the created capsule shell wall due to the weak integrity of the layered polyelectrolytes shell wall, which often results in capsules that resemble deflated balloons after being dried.

In another approach, inverse emulsion polymerization was used to prepare epoxy-amine microcapsules, with diameter of 10–240 μm, which was embedded with 10 wt% magnesium sulfate solution as inhibitor [54]. Magnesium ions (Mg^{2+}) can react with hydroxide ions in alkaline medium, at $pH = 9.3$, to produce insoluble magnesium hydroxide as shown in the following equation:

$$Mg^{2+} + 2HO^{-} \rightarrow Mg(OH)_2 \qquad (2)$$

Nanocontainer-Based Self-healing Coatings

Compared to microcapsules, thin tubular nanocontainers are more attractive as they exhibit superior aero- and hydrodynamic properties and hence better processability. The modification of the inner and outer surfaces of the nanocontainers with well-defined functionality allows for designing nanocontainers with fine-tuned properties, for example, for varying hydrophobicity.

Halloysite nanotubes, mesoporous silica containers, hydroxyapatite microparticles, and layered double hydroxides have been utilized as carriers and reservoirs for immobilization, storage, and controlled release of inhibitors that incorporated in self-healing anticorrosive coatings. In general, this can be achieved in three steps as illustrated in Fig. 3. The first step includes loading the organic or inorganic inhibitors into the target nanocontainer by the absorption of the inhibitor through the porous nanocontainers' structure, by encapsulation process utilizing emulsion polymerization, or by ion exchange with counter positive/negative ions in the corresponding nanocontainers. In the second step, the inhibitor-loaded nanocontainers are coated with pH-sensitive polyelectrolyte multilayers. Finally, the inhibitor-loaded nanocontainers are dispersed in suitable organic/inorganic polymeric matrix material.

Halloysite Nanocontainers

Nanocontainers can be made from different tubular materials such as carbon, polymeric, metal, and metal oxide nanotubes. Polymeric nanotubes can be templated by molecular sieves or cylindrical nanopores to form tubular structures [55]. Metal and metal oxide nanotubes are synthesized by employing polymeric or inorganic nanorods as scaffold template. The shortcoming of these types of nanotubes is the employment of template that needs to be prepared separately and requires extra post-synthesis removal steps, which is time-consuming and a costly process.

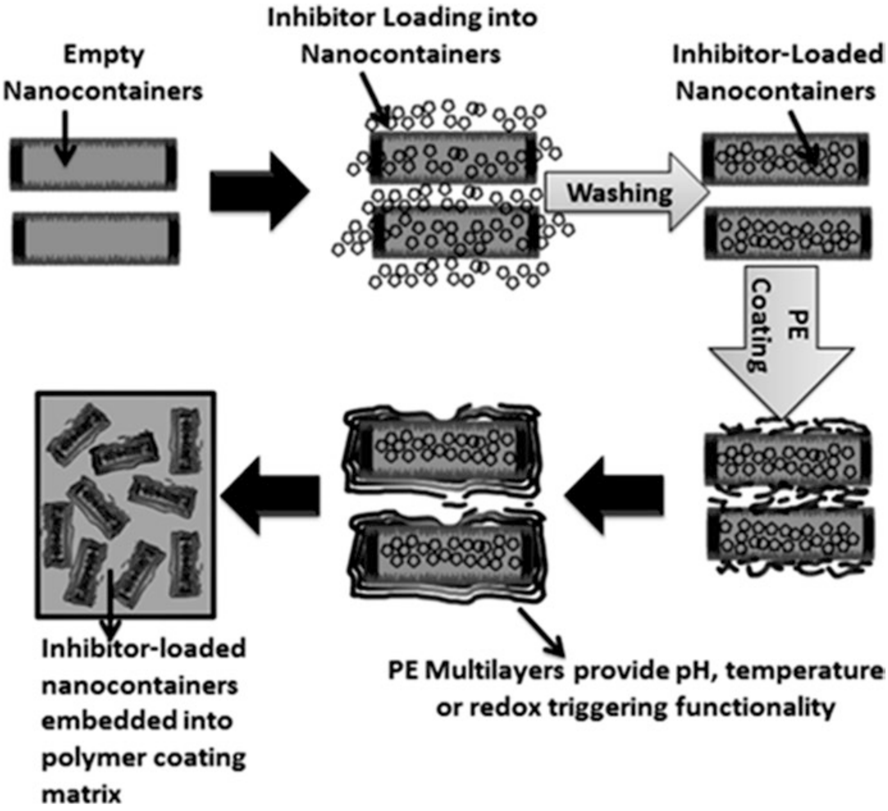

Fig. 3 Schematic illustration for preparation of inhibitor-loaded nanocontainers and their incorporation into coating matrix

One of the future prospective containers that can be industrially applicable is halloysite nanotubes. In comparison to the carbon nanotubes, halloysite is biocompatible and inexpensive nanocontainer ($4/Kg with annual production of 50,000 t per year) that can be used for a variety of applications including microencapsulation of biologically active molecules.

Halloysite is defined as a two-layered aluminosilicate with hollow tubular structure in the submicrometer range [56]. The adjacent alumina and silica layers create a packing disorder causing them to curve. The size of halloysite particles varies within 1–15 µm in length and 10–150 nm in inner diameter depending on the deposits. Thus, a variety of active agents such as drugs, corrosion inhibitors, and marine biocides can be entrapped within the halloysite inner lumen as well as within void spaces in the multilayered aluminosilicate shell. The entrapped and stored active agents are retained and released in a controlled manner for specific application. Both hydrophilic and hydrophobic agents can be entrapped after suitable pretreatment and conditioning of the halloysite [57–61].

A hybrid sol-gel film doped with halloysite nanotubes for controlled release of entrapped corrosion inhibitor on aluminum substrate has been proposed [62]. Initially, the halloysite nanocontainers were doped with 5 wt% 2-mercaptobenzothiazole inhibitor. In order to prevent the leakage of the doped inhibitor, the surface of the inhibitor-doped halloysite nanocontainers was coated with several alternating polyelectrolyte multilayers of (poly(styrene sulfonate)/poly(allylamine hydrochloride)). This step was essential to close the edges of the nanocontainers as well as to enable the controlled release of the doped 2-mercaptobenzothiazole inhibitor to the surrounding environment upon pH change. In a separate step, the organically modified hybrid sol-gel was prepared by using zirconium (IV) *n*-propoxide (TPOZ) and 3-glycidoxypropyltrimethoxysilane (GPTMS) precursors. Finally, the inhibitor-doped halloysite nanocontainers suspension was incorporated into the sol-gel solution prior to the dip coating of the AA2024-T3 samples. The prepared sol-gel films with the halloysite nanocontainers provided long-term corrosion protection in comparison with the undoped sol-gel film.

Abdullayev et al. reported an enhanced and strong anticorrosion self-healing effect caused by the sol-gel coating embedded with benzotriazole-doped halloysite nanocontainers in the cracked area of 2024 alloy [63]. In the same study, the corrosion protection performance of the industrial oil-based paint coating (ECS-34 True-Test) embedded with/without benzotriazole-doped halloysite nanotubes was investigated on scratched copper strips. After 10 days, immersion in highly corrosive environment, there was no evidence of visible rust in the scratched area, and the elemental analysis of the reacted corrosive solution did not show any copper content, whereas samples without halloysite nanocontainers were rusted, and their reacted corrosive solution was found to contain 128 ppm Cu(II) ions. These results demonstrate the self-healing functionality of the coating prepared by incorporation of the benzotriazole-loaded halloysite nanocontainers. The release rate of the benzotriazole was controlled by adapting two methods: (1) tube stopper formation and (2) layer-by-layer polyelectrolyte encapsulation for the inhibitor-embedded halloysite nanotubes. In the first method, the complexation reaction between loaded benzotriazole and transition metal ions was employed for the formation of stoppers at the tube ends. The best results were obtained when Cu(II) ions were employed for complex formation. It was found that the concentration of the Cu(II) ions has a direct and reverse effect on the release rate of the entrapped benzotriazole. In contrast, the polyelectrolyte multilayer shell (second method) did not slow down benzotriazole release from the encapsulated tubes. This finding was attributed to the low molecular weight of the benzotriazole inhibitor, which makes the diffusion through the polyelectrolyte multilayers more difficult to control.

In a later study, Abdullayev et al. [64] investigated the decrease in the release rate of the benzotriazole (BTA) through Cu-BTA complex at the tube ends based on the following reaction:

$$\underset{(\text{insoluble complex})}{\text{Cu}-\text{BTA}} + \underset{(\text{excess})}{\text{NH}_3} \rightarrow \underset{(\text{soluble/dissolved products})}{\left[\text{Cu}\left(\text{NH}_3\right)_4\right]^{2+} + \text{BTA}} \quad (3)$$

When ammonia solution was injected, a switch of the release rate of benzotriazole was observed, as was evident from the sharp increase in the concentration of both copper and benzotriazole in the treated solution. This result demonstrates that the stoppers can be diluted and the release rate can be restored with ammonia treatment.

Mesoporous Silica Nanocontainers (MSNs)

Monodisperse, mesoporous silica nanoparticles were loaded with organic corrosion inhibitor benzotriazole (BTZ) and embedded in hybrid sol-gel coating for corrosion protection of aluminum alloy AA2024 [65]. The reported mesoporous silica-BTZ system exhibited a number of interesting properties: (1) high surface area ($\approx 1000\ m^2\ g^{-1}$), (2) narrow pore size distribution ($d \approx 3$ nm), large pore volume ($1\ mL\ g^{-1}$), and high loading capacity of BTZ (41 wt%). The BTZ-doped silica nanocontainers were embedded in the sol-gel hybrid coating without further encapsulation steps (i.e., without using additional polyelectrolyte multilayer coating), which means that the trigger-release mechanism was entirely based on the corrosion process, providing a self-healing effect.

Li et al. investigated the synthesis and preparation of silica/polymer double wall hybrid nanotubes and their applications as stimuli-responsive nanocontainers in self-healing coatings [66]. The synthesis procedure started with the preparation of nickel hydrazine/silica core-shell rod templates, which were then surface modified by grafting methodology, using 3-(trimethoxysilyl) propyl methacrylate, for introducing carbon-carbon double bonds on silica surface. The thickness of the polymer coating was controlled by varying the feed ratio between monomer and nickel hydrazine/silica templates. Three different polymers were grafted on the surface of the silica: (1) the pH-responsive poly(methacrylic acid) (PMAA), (2) the temperature-responsive poly(N-isopropylacrylamide) (PNIPAM), and (3) the redox-responsive poly(poly(ethylene glycol)methacrylate) (PPEGMA). The final synthetic step was the selective etching of the nickel hydrazine/silica/polymer core-double shell rods in HCl solution. Then, the corrosion inhibitor benzotriazole (BTA) was encapsulated into the prepared SiO_2/polymer hybrid nanotubes, with 6–7 wt% loading capacity. The self-healing coating was prepared by dispersing BTA-loaded nanotube containers into SiO_x/ZrO_y hybrid films at room temperature. The anticorrosion agent BTA encapsulated in the hybrid nanotubes can be controlled to be released in the absence or presence of external stimuli. Silica/PMMA hybrid nanotubes showed pH-dependent release of BTA corrosion inhibitor, which was attributed to the swelling (at $pH = 12$) and shrinkage (at $pH = 2$) behavior of the grafted weak carboxylic acid moieties. Silica/PNIPAM hybrid nanotubes showed temperature-dependent release of BTA inhibitor due to the swelling and shrinkage of the PNIPAM outer wall at 25 and 50 °C, respectively. BTA-Silica/PPEGMA hybrid nanocontainers exhibited redox-dependent release of corrosion inhibitor due to the presence of the disulfide bonds in the grafted PPEGMA polymer networks.

Maia et al. reported one-stage process for the synthesis of porous silica nanocapsules (SiNC) loaded with 2-mercaptobenzothiazole (MBT) inhibitor for corrosion protection application [67]. The synthesized SiNCs have regular shape and a diameter in the range of 100–150 nm, with gradual mesoporosity. The encapsulation efficiency was 68 %, with MBT loading content of 10 wt%. Two samples were investigated for their corrosion protection performance. In the first sample, MBT-SiNCs were incorporated (2 wt%) in water-based epoxy coating, which was subsequently used to coat AA2024plates with a film of 30 μm thickness. The second sample was prepared with empty SiNC, and the MBT inhibitor was incorporated in the formulated coating matrix by direct addition. The active protection of MBT-SiNC was assessed by the introduction of two circular defects (spots) in each sample. The MBT release was triggered by changes in pH and concentration of chloride anion. The self-healing functionality of the MBT-SiNC was evident from the high value of the electrochemical impedance measurements and visual inspection after 30 days of immersion in aggressive solution. In comparison to coating prepared by direct dispersion of MBT inhibitor, the coating with MBT-encapsulated SiNCs exhibited better and controlled inhibitor release for longer periods.

Layered Double Hydroxides (LDHs)

Layered double hydroxides (LDHs), also known as anionic clays or hydrotalcite-like compounds, are anion exchange materials consisting of stacks of positively charged, mixed metal hydroxide layers between which anionic species and solvent molecules are intercalated [68, 69]. Due to their low toxicity, biocompatibility, and their ability to release active species in a controlled way, LDHs have been employed as nanocarriers for drug-delivery applications at cellular level [70–73]. Therefore, LDHs can be thought of as suitable nanocarrier substrates for immobilization and encapsulation corrosion inhibitor molecules. LDHs can be incorporated in corrosion-protective organic coatings to provide self-healing protection functionality through the release of the stored inhibitors. The anion exchange property of the LDHs is important for two reasons: (1) it allows the immobilization of negatively charged organic/inorganic inhibitor, and (2) it allows the entrapment of the corrosive anions such as, chloride and sulfate anions [74–78].

Poznyak et al. reported the preparation of nanocrystalline LDHs, with platelike morphology, as novel inorganic host materials intercalated with guest organic inhibitors for anticorrosion applications [79]. Two different organic inhibitors were used, 2-mercaptobenzothiazolate (MBT) and quinaldate (QA). The anion exchange reaction of the nitrate-loaded LDHs precursors was utilized for creation of organic inhibitor containers. The release of the negatively charged organic inhibitors was found to occur by an exchange mechanism (i.e., release of inhibitor and entrapment of the aggressive anions) and sequential release of the anions, providing active feedback for corrosion protection control. The corrosion protection performance of the prepared LDHs was investigated by electrochemical impedance spectroscopy (EIS) technique on a bare AA2024 aluminum alloy for two weeks. The AA2024 samples were placed in contact with LDH suspensions in a 0.05 M NaCl solution. After 24 h immersion time, EIS showed a small anticorrosion activity of these systems. This observation was attributed to the local alkalization of the solution in the presence of hydroxide-rich LDHs particles, which causes a decrease in the inhibition efficiency of MBT and QA inhibitors. However, the corrosion process was inhibited after long immersion times due to the formation of a protective film, with enhanced performance in case of MBT inhibitor.

Tedim et al. utilized the anion exchange reaction to prepare Zn-Al LDHs intercalated with phosphate, vanadate, and 2-mercaptobenzothiazolate inhibitors [80]. The corrosion protection assessment was performed on AA2024 substrate. The AA2024 samples were treated with a thin layer (2 μm) of hybrid sol-gel, followed by over-painting with non-inhibited water-based epoxy primer (25 μm), and finally, a 30 μm topcoat layer was introduced. Both primer and sol-gel formulations were loaded with 10 wt% LDHs nanocontainers in dry paint film. The developed coating showed well-defined active corrosion protection toward AA2024 substrates. The best results were obtained with a combination of sol-gel film (pretreatment layer) doped with LDH-MBT and primer doped with LDH-VO_x. It was concluded that the MBT anions were available in a very short time scale for protection of the interface layer between the aluminum substrate and the sol-gel film, whereas the long-term protection was conferred by vanadate anions released from LDH nanocontainers added to the primer. The results proved that the combination of different types of nanocontainers in the same or in different functional coating layers is an effective way to design active corrosion protection systems with enhanced and superior performance.

Guo et al. proposed a simple one-step hydrothermal synthesis method for the direct fabrication of zinc-aluminum layered double hydroxide (ZnAl-LDH)/alumina bilayer film on an aluminum substrate [81]. The resulted film was found to exhibit strong, compact, and uniform adhesion to the aluminum substrate. Coated aluminum substrates were immersed in 3.5 % NaCl aqueous solution for the assessment of the corrosion protection performance. Polarization measurements showed that the bilayer film was able to provide an effective corrosion protection for the coated substrates, as revealed from the low corrosion current density value (10^{-8} A/cm^2). EIS showed that the impedance of the bilayer was as high as 16 MΩ, which means that the film was able to provide a protective passive layer with high charge transfer resistance.

Hydroxyapatite (HAP) Microparticles

Hydroxyapatite (HAP) microparticles, which is a calcium phosphate-based clay ($Ca_{10}(PO_4)_6(OH)_2$), possess a number of features that make them suitable carriers for corrosion inhibitors. These features include crystallinity, insolubility in water, submicrometer size, high surface area, and chemical dissolution at acidic pH range. The dissolution of HAP microparticles in the acidic medium provides a pH-dependent triggering mechanism for the release of stored inhibitors, whereas their high surface area enables a high loading capacity.

Snihirova et al. investigated the incorporation of inhibitor-doped HAP microparticles into a hybrid sol-gel coating as new feedback-active anticorrosion system [82]. Cerium (Ce^{3+}) and lanthanum (La^{3+}) cations, salicylaldoxime (Sal), and 8-hydroxyquinoline (8HQ) were used as the dopants in the HAP microparticles. Inorganic cationic inhibitors were incorporated by cation exchange with Ca^{2+}, and the organic inhibitors were adsorbed on the surface of HAP microparticles. This resulted in 22, 20, 9.3, and 0.54 wt% loadings for (Ce^{3+}), (La^{3+}), (8HQ), and (Sal), respectively. AA2024-T3 was coated with thin films of the formulated coating that contains 0.2 wt% inhibitor-doped HAP microparticles, by employing dip coating technique. The release of doped inhibitors occurred at pH below 6, with an acceleration of Ce^{3+} and La^{3+}release when the pH falls below 3.1. The local acidification down to pH = 3.65 was attributed to the anodic dissolution of Al (Eq. 4), as revealed from localized pH measurements that was conducted using pH-selective microelectrodes.

$$\mathrm{Al}^{3+}\left(\mathrm{aq}\right)+\mathrm{H_2O}\leftrightarrow\left[\mathrm{Al}\left(\mathrm{OH}\right)\right]^{2+}\left(\mathrm{aq}\right)+\mathrm{H}^{+}\left(\mathrm{aq}\right) \tag{4}$$

Thus, the HAP microparticles were able to sense the corrosion onset (local acidification) and release the stored inhibitors on demand. Also, the dissolution of HAP microparticles contributed to corrosion protection by pH buffering mechanism, as conferred from the delayed corrosion of the AA2404-treated substrates with sol-gel coating embedded with blank HAP microparticles (i.e., undoped with inhibitor).

Layer-by-Layer Approach for Designing Self-healing Coatings

Polyelectrolytes multilayers with alternating charges can be deposited on metal substrate, and the low molecular weight corrosion inhibitors can be embedded between the deposited polyelectrolyte layers as shown in Fig. 4. The key parameters for controlling the growth of the multilayers are the pH and the ionic strength (degree of ionization/dissociation) of certain polyelectrolyte. These factors affect the conformations of the deposited polyelectrolytes and, consequently, the thickness of the multilayers [83–90]. The conformation of the polyelectrolytes can be altered by changing the pH or by the addition of salt. The presence of salt in the deposited layers allows for polymeric chains to collapse and converts the expanded chains into the coil conformation. Deposition of the weak polyelectrolytes can be easily affected by the pH of the polymeric solution. At certain pH range, the polyelectrolyte is completely dissociated, and, as a result, the maximum charge density can be achieved at that pH range.

Layer-by-layer (LBL) deposition can be achieved by three different methods: spraying, spin coating, and dip coating. The dip coating technique includes the following steps: (1) the substrates are immersed in the dipping solution, (2) equilibrium time of 10–20 min, and (3) washing the substrate with suitable solvent to

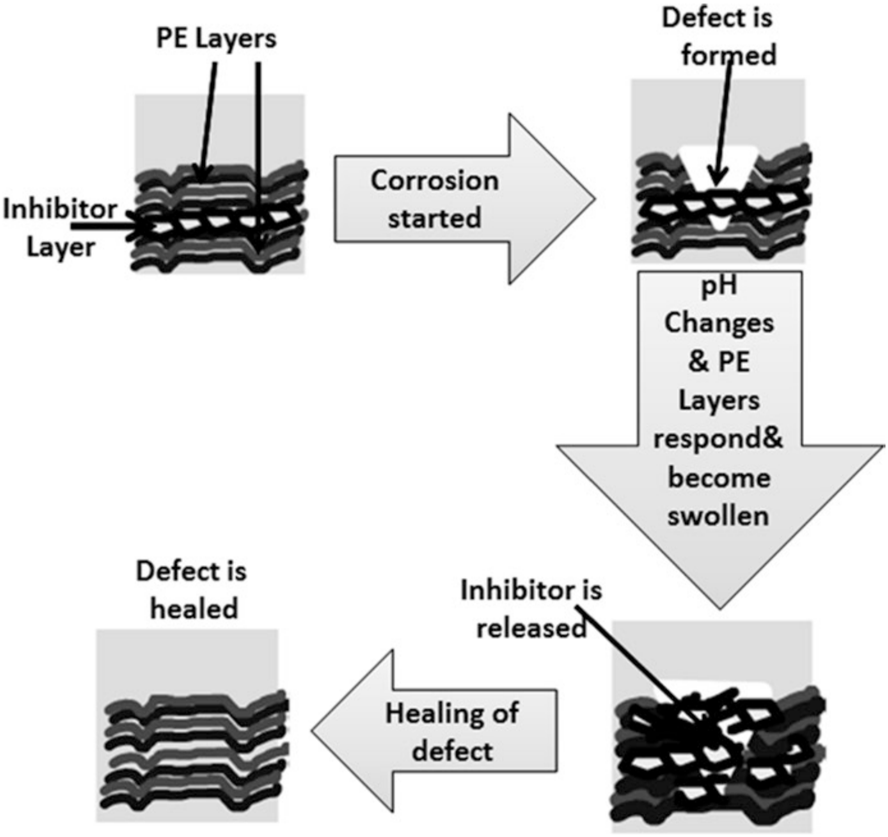

Fig. 4 Schematic illustration for using polyelectrolyte multilayers, embedded with corrosion inhibitor layer, for preparation of self-healing coating

remove the excess polyelectrolyte. This method is time-consuming and requires relatively large amount of material for each deposition. However, this is the only method that can be used for the formation of polyelectrolyte capsules and deposition of LBL films on spheres, microcapsules, and nanocontainers, as discussed previously in Sections 2 and 3.

In case of spraying technique, the procedure involves the following steps: (1) two spraying sequences per single layer, (2) waiting time interval for the removal of excess polyelectrolyte solution, (3) spraying with the rinsing solution, and (4) another waiting time interval for the removal of the excess rinsing solution. The key advantage of the spraying technique is the time reduction for the multilayers formation.

Spin coating technique requires excess polyelectrolyte solution to be applied to the metal substrate before spinning. Next, the solvent is expelled from the substrate surface, and the dissolved component forms a layer. The spinning time and rate can be varied for particular system. This technique is very fast and does not require equilibration time. However, this technique can be only applied to planar surfaces.

The thickness and roughness of the prepared layer-by-layer films depend on the used coating technique. The self-healing ability of the deposited polyelectrolyte layers is strongly affected by the ionic strength of the used polyelectrolytes. For example, when the scratched metal substrate was coated with two weak polyelectrolytes, polyethylenimine (PEI) and poly(acrylic acid) (PAA), and immersed in 0.1 M NaCl solution, the (PEI/PAA) system was able to stop the initiation of the corrosion [52]. The self-healing mechanism was attributed to the high mobility of the nanolayers that facilitate the water penetration through the polyelectrolyte multilayers and trigger the release of the embedded inhibitor. In comparison with the above "weak-weak" polyelectrolytes, the two strong polyelectrolytes, poly (diallyldimethylammonium) chloride (PDADMAC) and polystyrene sulfonate (PSS), did not show self-healing property. In this case, the high charge density of the two strong polyelectrolytes cannot be altered by pH change.

Grigoriev and coworkers prepared a series of polyelectrolyte/inhibitor complexes by employing different LBL deposition procedures [91]. The polyelectrolyte/inhibitor complexes have two main advantages: (1) they will help to build up more thick and protective multilayers and, thus, reduce the permeability of polyelectrolyte multilayers that may lead to the undesired fast release of the stored inhibitor and (2) the polyelectrolyte/inhibitor complex is formed through interlayer bonds that enable the coating to respond more effectively to the aggressive factors. The thickness of the multilayers formed between polyethylene imine (PEI), poly(allylamine hydrochloride) (PAH), and 2-(benzothiazole-2-ylsulfanyl) succinic acid inhibitor (BYS), $\mathrm{PEI(BYS/PAH)_{10}}$, showed a pH dependence, with a distinct maximum at pH 7. At acidic or basic conditions, the thickness of the multilayers decreases, allowing for partial release of the bonded inhibitor and hence providing the self-healing functionality of the coating. Similarly, the protective coating with embedded 8-hydroxyquinoline (8HQ) in the $\mathrm{PSS/(8HQ/PSS)_n}$ multilayers demonstrated a very effective mechanism for corrosion suppression. Thus, the inhibitor release provided an active feedback for effective termination of corrosion.

In addition, the above study [91] reported the utilization of SiO_2 mesoporous microcontainers filled with benzotriazole (BTA) inhibitor and plugged by the (PSS/BTA) complex into a sol-gel coating for protection of aluminum alloy AA2024. The stiff inorganic SiO_2 carriers provided the integrity for the microcontainers, and their charged shells improve their dispersion in the coating matrix. The results of the scanning vibrating electrode (SVET) for the anticorrosion efficiency in 0.1 M NaCl revealed that the protective coating with incorporated nanocarriers exhibited an excellent self-healing performance. Anodic activity was developed after 42 h of the total immersion time. However, after another 18 h (i.e., after 60 h of the total immersion time in NaCl solution), almost complete suppression of the corrosion process was detected, with anodic activity less than 2 $\mu A\ cm^{-2}$, demonstrating the self-healing response of the coating for the corrosion process.

Electrically Conductive Polymers for Self-healing Coatings

Electrically conductive polymers (ECPs) belong to those classes of polymers which have π conjugation along the polymer backbone such as polyaniline (PANi), polypyrrole (PPy), and polythiophene (PTh), as shown in Fig. 5. ECPs are known for their ability to undergo oxidation-reduction reactions by gaining or loosing electrons from the surrounding environment. Due to this interesting property, ECPs have been utilized as novel corrosion-protective coatings for a variety of metals and alloys [92–94].

ECPs function as corrosion-protective coatings by one or more of the following three mechanisms [95]. First, ECPs can provide barrier protection by isolating the metal surface from the surrounding environment. This can be achieved by using the ECPs as primers or as a component of the barrier layer [96–101]. Second, ECPs can provide anodic protection through the formation of passive layer of metal oxide (ennobling mechanism) [102, 103]. In this case, ECPs act as oxidizing agent for the leached metal ions, maintaining the metal in the passive domain by providing a thin layer of metal oxide.

In the third protection mechanism, Kendig [104] proposed that ECPs can provide self-healing functionality for the coated metal substrates through storage and immobilization of the doped corrosion inhibitor anions as illustrated in Fig. 6 [105]. The release of the stored inhibitor anions to the corroded areas is triggered by the electrochemical reduction of the ECP. Different organic/inorganic dopants (Fig. 7) can be immobilized on the polymeric backbone of ECPs [106–114]. This can be achieved during polymerization process of the ECP, through doping process (Eq. 5), or by ion exchange reaction with negatively charged inhibitor anions (Eq. 6).

$$\underset{(\text{Undoped})}{\text{ECP}} + \underset{(\text{Dopingacid})}{\text{H}^{+}\text{A}^{-}} \underset{\text{Doping Process}}{\rightarrow} \underset{\left(\text{Doped with inhibitor A}^{-}\right)}{\left(\text{ECP}-\text{H}^{+}\right)\text{A}^{-}} \tag{5}$$

$$\underset{\text{Doped with A}^{-}}{\left(\text{ECP}-\text{H}^{+}\right)\text{A}^{-}} + \underset{(\text{Doping inhibitor})}{\text{B}^{-}} \underset{\text{Ion}-\text{exchange}}{\rightarrow} \underset{\left(\text{Doped with inhibitor B}^{-}\right)}{\left(\text{ECP}-\text{H}^{+}\right)\text{B}^{-}} \tag{6}$$

Polyaniline doped with 2,5-dimercapto-1,3,4-thiadiazole (DMcT) was tested, in solvent-borne epoxy, as anticorrosion coating for aluminum alloys (AA2024-T3 and 7075-T6) [115]. The results showed that DMcT-doped PANi epoxy primer

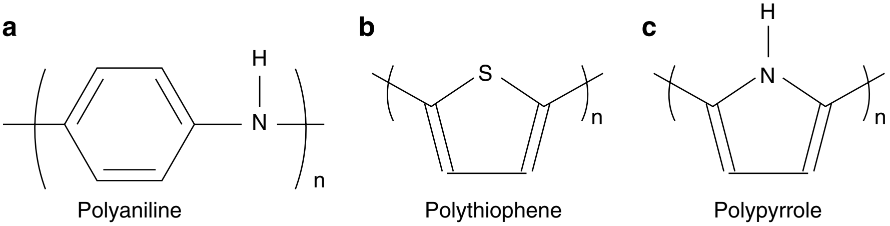

Fig. 5 Chemical structure of common electrically conductive polymers

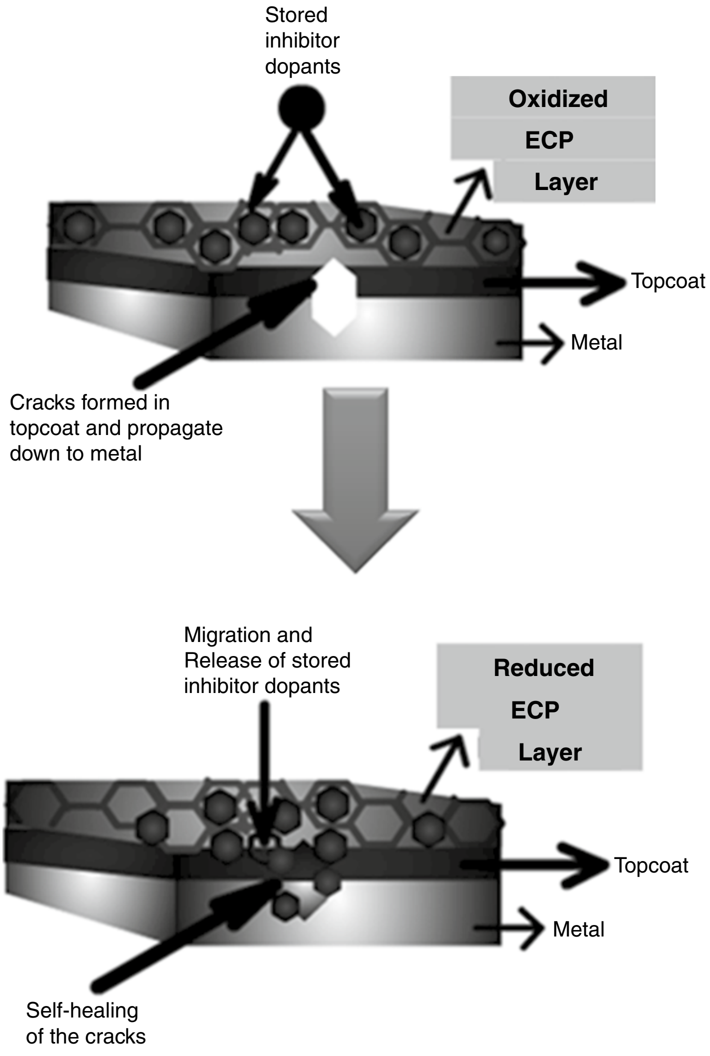

Fig. 6 Schematic illustration of self-healing functionality of an electrically conductive polymer (ECP)

coating was able to provide similar protection performance to that of strontium chromate coating for a period of 2,000 h in corrosive media. The enhanced anticorrosion performance was attributed to the effective release of the anionic organic inhibitor (DMcT) from the reduced polyaniline which suppresses the oxygen reduction reactions and consequently delayed the corrosion process.

Inorganic inhibitors such as MoO_4^{2-}, PO_4^{3-}, and WO_4^{2-} can be immobilized and stored as dopant anions into the ECP matrix. Molybdate-doped polyaniline was investigated as self-healing anticorrosive coating [116]. $PANi-MoO_4^{2-}$ film was

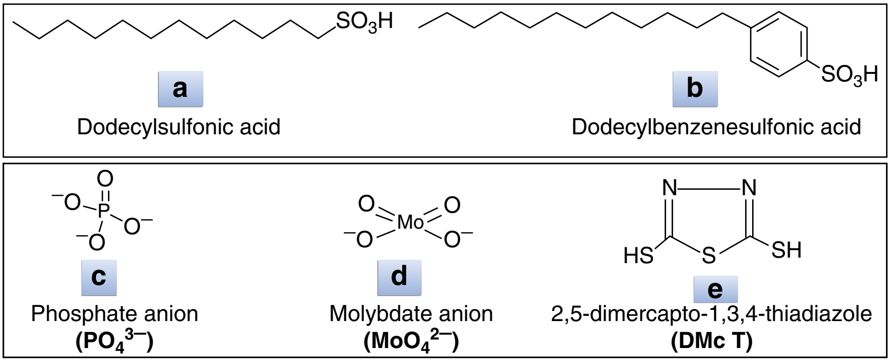

Fig. 7 Chemical structure of organic doping acids (**a** and **b**), inorganic inhibitor dopants (**c** and **d**), and organic inhibitor dopant (**e**)

deposited on mild steel substrate by in situ electrochemical polymerization in the presence of oxalic acid solution. $\mathrm{PANi}-\mathrm{MoO}_4^{2-}$ coating system showed superior anticorrosion performance to that of pure PANi due to the formation of iron-molybdate complex along with the passive film as shown in the following equations:

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{3+} + 3\mathrm{e}^- \tag{7}$$

$$2\mathrm{Fe}^{3+} + 3\mathrm{MoO}_4^{2-} \rightarrow \mathrm{Fe}_2\left(\mathrm{MoO}_4\right)_3 \tag{8}$$

Steel substrates coated with molybdate-doped polypyrrole film were protected in chloride-containing solution even when the coating has defects [117]. This was attributed to the migration of molybdate anions through the polypyrrole film in a short time and subsequent formation of passive layer at the defected sites.

Polypyrrole doped with larger molecular size phosphomolybdate anion $[\mathrm{PMo}_{12}\mathrm{O}_{40}]^{3-}$ has also been investigated and showed significant self-healing corrosion protection performance [118, 119]. Responsive release of the inhibitor $[\mathrm{PMo}_{12}\mathrm{O}_{40}]^{3-}$ occurs only when the potential at the metal-polymer interface decreases at an active defects.

Kowalski et al. investigated bilayered polypyrrole coating composed of molybdate-doped internal layer and dodecyl sulfate-doped external layer [120]. The immobile and bulky counter anion (dodecyl sulfate) prevents the penetration of small aggressive anions through anion exchange reaction, whereas the internal layer provides the self-healing functionality through the controlled release of the molybdate anions. The above duplex coating was applied to steel substrate and provided corrosion protection for 190 h in chloride-containing solution. However, steel substrate coated with similar thickness of dodecyl sulfate-doped polypyrrole monolayer was able to provide corrosion protection for only 10 h. It was concluded that the molybdate-doped internal layer was able to maintain the metal substrate in the passive domain for longer period, which is attributed to the formation of salt layer of ferric molybdate complex at the defect site [121].

Chen et al. prepared polyaniline (PANi)-containing coating for waterborne corrosion protection applications by using oxidative dispersion polymerization of aniline monomer in the presence of partially phosphorylated polyvinyl alcohol (P-PVA) [122]. The resulted PANi nanoparticles were stabilized by P-PVA with uniform diameters in the range of 60–100 nm. The coating was prepared by using waterborne epoxy resin as matrix, with a dry film thickness of ≈90 μm. Mild steel samples were dip coated with the waterborne PANi/P-PVA-containing coating and exposed to 3.0 wt% NaCl solution. The corrosion protection performance was evaluated by the measurement of OCP versus time of exposure and EIS. After 30 days of salt spray tests, samples coated with 2.5 wt% PANi/P-PVA content, the measured impedance values were higher than $1\times10^7\ \Omega\ \mathrm{cm}^2$, which showed that the PANi/P-PVA coating was able to provide superior corrosion protection for long period.

Conclusions and Future Remarks

Development of self-healing coatings for corrosion protection applications can be considered as one of the future emerging nanotechnology fields. Nowadays, there is a lot of scientific research interest in this fast growing area. The main advantage of self-healing coatings is their autoresponse to the corrosion phenomena. The *responsive* self-healing coatings are characterized by their ability to provide instantaneous feedback upon corrosion initiation. The criterion for automatic feedback depends on the design of the self-healing coating as well as the surrounding environment.

Different materials with nano and microscale dimensions have been utilized for the preparation of self-healing agents prior to their embedding and incorporation into the polymeric coating matrix. The selection and design of specific self-healing agent can provide specific triggering mechanism for the effective release of the encapsulated active corrosion inhibitor molecules. Since corrosion is an electrochemical process accompanied with pH change, *redox*-dependent and *pH-dependent* triggering mechanisms are suitable for providing active feedback in case of corrosion initiation.

Different approaches have been investigated for the design, synthesis, and preparation of self-healing coatings. The first approach employs different types of inorganic *nanocontainers* and microparticles as carriers/reservoirs for storage and immobilization of corrosion inhibitor molecules. These carriers include halloysite nanotubes, mesoporous silica nanotubes, hydroxyapatite microparticles, and layered double hydroxides nanotubes. Corrosion inhibitors are incorporated by simple adsorption or by cationic/anionic exchange with unbound cations/anions, like in the case of hydroxyapatite and layered double hydroxide microparticles.

The second approach utilized layer-by-layer polyelectrolyte assembly for the preparation of thin-responsive coating films. Corrosion inhibitor layers are sandwiched between the alternating positive and negative polyelectrolyte multilayers. The effective release of the corrosion inhibitor and the self-healing functionality of the polyelectrolyte multilayer depend on the type of the used polyelectrolytes (weak/strong), the ionic strength of the polyelectrolyte solution, and the conformation of the polyelectrolyte multilayers (coiled/expanded).

The third approach utilized the electrically conductive polymers (ECPs) as potential class of the self-healing anticorrosive polymeric coatings. ECPs are redox-active polymers and have the ability to sense the corrosion process by the accompanied oxidation-reduction reactions. ECPs can immobilize the anionic corrosion inhibitors through doping/de-doping process. When corrosion is initiated, the metal substrate is oxidized at the defected site, and consequently, the ECP gains the released electrons and became the reduced state. As a result, the stored anionic inhibitor migrates to the defected site and provides a self-healing action.

Properties of certain self-healing coatings can be designed and fine-tuned by using a combination of the above discussed approaches. However, the development in the area of nanomaterial-based anticorrosive self-healing coatings is still in its early stage, and multidisciplinary collaboration is required to overcome both economic and technical challenges for commercialization of this type of coatings. The applicable environmental conditions and the cost are very important criteria for marketing self-healing coatings. The technical challenges such as mechanical properties, adhesion, durability, and coating lifetime are essential factors for future investigation and improvement in this area.

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