CHAPTER 4
Hollow Mesoporous Zirconia Nanocontainers for Active Corrosion Protection

This chapter describes the fabrication of an active corrosion protection coating system with self-healing ability using inhibitor loaded hollow mesoporous zirconia nanocontainer. Zirconia nanocontainers with a hollow core/shell structure was synthesized through a hard templating approach and used as nanocontainers for loading 2-mercatobenzothiazole (2-MBT). A hybrid zirconia-silane sol-gel coating mixed with hollow mesoporous zirconia nanocontainers loaded with 2-MBT was deposited on modified 9Cr-1Mo. The corrosion protection performance of coatings with and without the addition of inhibitor loaded nanocontainers was investigated using electrochemical impedance spectroscopy (EIS). Further, artificial defects were made on the coatings in order to analyze the evolution of corrosion activity and unambiguously prove the active corrosion protection. It was found that the released inhibitor delayed the corrosion process and imparted active corrosion protection.

4.1 Introduction
Zirconium oxide is one of the widely used materials for various applications because of its interesting physical and chemical properties. Its application includes in refractories, pigments, piezoelectric devices, ceramic condensers, thermal barrier coatings, electrode and oxygen sensors, orthopedic implants and most importantly in catalysis [256]. Zirconia based materials with ordered mesopore structure and high surface area have been synthesized in the recent past [257-259]. Due to their large surface area and controllable pore size, mesoporous zirconia has opened many new possibilities for applications in catalysis, catalyst support and in drug delivery [260]. Due to the availability of interior cavity and highly permeable mesopore shells, hollow
mesoporous zirconia can be effectively used for loading guest species such as drug molecules or corrosion inhibitors and its controlled release. However, the synthesis of monodispersed hollow mesoporous spheres is a challenging task. To date, template assisted method is commonly used for the synthesis of hollow mesoporous structures. Typically, a template sphere is used and on which the latter shell is deposited [261-264]. These templates are later removed by either calcination or dissolution. Nevertheless, most of this template assisted methods results in the collapse of mesopore structure while removing the templates. The amorphous oxide structure crystallizes with increase in temperature and the resulting crystal growth leads to destruction of the pore structure and disappearance of high surface area and the spherical morphology. Both the spherical micelle templating and emulsion templating generally lacks the perfection of the spheres and having relatively broad size distribution [258, 265-267].

However, it is possible to synthesis hollow mesoporous spheres with very high degree of monodispersity and perfect spherical shapes that is typically not obtained through other methods by using oxidic template spheres instead of polymer templates. Solid silica spheres made by the Stober method can be used as templates for the synthesis of hollow mesoporous zirconia spheres because they are easily obtained in large scale, uniform morphology, and controllable size.

This chapter describes a new contribution to the design of nanocontainer for the encapsulation of corrosion inhibitor and utility of this new nanocontainer system for active corrosion protection. Hollow mesoporous zirconia (HMZ) nanocontainers with a hollow core/porous shell structure were synthesized through a hard template method [233-235]. Monodispersed solid silica nanoparticles were used as template for the synthesis of hollow mesoporous zirconia. The silica nanoparticles were coated with
zirconium oxide layer and later these silica templates were removed using sodium hydroxide. The HMZ were loaded with 2-MBT and this inhibitor nanocontainer system was mixed with hybrid coating. The incorporation of HMZ nanocontainers into sol-gel coatings was not studied earlier. The 2-MBT loaded HMZ were mixed with silane-zirconia hybrid sol and applied on modified 9Cr-1Mo ferritic steel by dip coating method. The corrosion protection efficiency of following four different coatings was studied and compared using EIS in order to ascertain the contribution of each component on the protective properties of silane-zirconia hybrid coating: (i) hybrid sol-gel coated modified 9 Cr-1Mo ferritic steel, (ii) inhibitor mixed hybrid sol-gel coated modified 9 Cr-1Mo ferritic steel, (iii) empty nanocontainer mixed hybrid sol-gel coated modified 9 Cr-1Mo ferritic steel and (iv) inhibitor loaded nanocontainer mixed modified 9 Cr-1Mo ferritic steel.

4.2 Experimental

4.2.1 Materials

Zirconium butoxide solution (80 wt. % in 1-butanol), tetraethoxysilane (TEOS), ethanol, concentrated ammonia solution (25 % NH₃ in water), sodium hydroxide (NaOH, Merck), and Brij 30 were used to synthesize hollow mesoporous zirconia nanospheres. 2-mercaptobenzothiazole (2-MBT) was used as corrosion inhibitor, acetone was used for inhibitor loading experiments and sodium chloride (NaCl) was used for releasing experiments.

4.2.2 Synthesis of Hollow Mesoporous Zirconia (HMZ) Nanocontainers

Hollow mesoporous zirconia nanocontainers with a hollow core/porous shell structure were synthesized through a hard templating method. Monodispersed silica nanoparticles were used as template for the synthesis of HMZ. Detailed procedure and
4.2.3 Characterization of Silica Nanoparticles and HMZ Nanocontainers

The high-resolution images of silica template and HMZ were taken using a JEOL JEM 2100 electron microscope operated at 200 kV. The powder samples were dispersed in ethyl alcohol under ultrasonication and few drops of the dispersed samples were placed on the sample holder and analyzed without further treatment. The phase analysis of HMZ was carried out using laser Raman spectroscopy (Lab RAM HR 800, HORIBA JOBIN YVON Raman spectrometer equipped with 1800 grooves/mm holographic grating). Nitrogen adsorption/desorption isotherms were recorded at 77 K on a Sorptomatic 1990.

4.2.4 Loading and Releasing of 2-MBT

100 mg of HMZ was mixed with 50 mL of 10 mg mL⁻¹ MBT solution. The mixture was then sonicated for 30 m and stirred further for 24 h in a glass vial. After 24 h of stirring of the mixture, the nanocontainers loaded with inhibitor molecules were taken out by centrifugation and cleaned with water. The MBT loaded HMZ was obtained by drying at room temperature. The filtrate was extracted from the vial and used for UV-visible spectroscopy studies to confirm the encapsulation of MBT. UV-visible spectroscopy (UV-2450, SHIMADZU make, Japan) was used for UV-vis analysis. Laser Raman spectroscopy (LRS) was also used to confirm the loading of 2-MBT into HMZ. A detailed description of loading of 2-MBT into HMZ is given in section 3.5.1 of chapter 3.

50 mg of MBT loaded HMZ 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. After the measurement, the solution was poured back immediately to the solution.

4.2.5 Development of Coatings on Modified 9Cr-1Mo

The modified 9Cr-1Mo ferritic steel substrates were cleaned and etched prior to the application of hybrid coating. The procedure employed for the pretreatment of modified 9Cr-1Mo is given in section 3.3.1 of chapter 3. A silane-zirconia hybrid coating was applied on the substrate as barrier coating and its detailed synthesis procedure is described in section 3.6.2 of chapter 3. Four different types of coatings were prepared. At first, coatings free of any inhibitor and nanocontainer were prepared and this is named as CS i.e. plain silane zirconia hybrid barrier coating. Secondly, inhibitors (2-MBT) were mixed directly with the hybrid coating was produced and named it as CS-I. Then the coatings incorporated with empty nanocontainers were prepared and it is referred as CS-N. Finally, coatings containing inhibitor loaded nanocontainers were prepared and it is referred as CS-NI. All the above mentioned three sol solutions were deposited on the modified 9Cr-1Mo steel by dip coating procedure, i.e., immersing a specimen in the hybrid sol-gel mixture for 100 s and thereafter, withdrawn at a constant lifting speed of 2 mm s⁻¹. The coated substrate was dried in air and then baked at 120 °C for 1 h.

4.2.6 Evaluation of Anticorrosion Efficiency of Coatings

Electrochemical impedance spectroscopy (EIS) was used to assess and compare the anticorrosion efficiency of the developed hybrid coatings on modified 9Cr-1Mo ferritic steel without and with artificial defect, during 1 week of immersion in 0.05 M NaCl solution and in 0.01 M NaCl solution, respectively. EIS measurements were carried out using Iviumstat. XRe. at open circuit potential, by applying a sinusoidal excitation of 10 mV in the frequency range of 100 kHz-10 mHz recording 10 points per decade of
frequency. A flat cell was used consisting of an Ag/AgCl reference electrode, platinum counter electrode and the coated modified 9Cr-1Mo ferritic steel of 1 cm$^2$ as working electrode. The morphology and composition of the coated substrates after immersion in 0.05 M NaCl solution was analyzed by scanning electron microscope and attached energy dispersive X-ray analysis (EDX) system.

4.3 Results and Discussion

4.3.1 Synthesis and Characterization of HMZ Nanocontainers

The five steps involved in the preparation of hollow mesoporous zirconia are described below.

1. Monodispersed silica template nanoparticles were synthesized using the well known Stober method [236].

2. The prepared monodispersed silica nanoparticles were then coated with amorphous layer of zirconium hydroxide during the hydrolysis of zirconium butoxide in the presence of Brij 30.

3. The silica core with the zirconia shell containing Brij 30 was aged in water for 3 days at room temperature.

4. Later the silica core with zirconia shell was calcined at 850°C to remove the organics and to achieve the crystallization of the shell.

5. Finally, the template, silica core was removed using NaOH (5 M) treatment for 48 h. The silica particles were leached out through the pores present in the zirconia shell. The removal of solid silica core particles resulted in the formation of hollow mesoporous zirconia nanocontainers.
Figure 4.1 depicts the HRTEM images of silica template particles having average diameter of 375 nm.

Figure 4.1: HRTEM images of solid silica nanoparticles at different magnifications

Figure 4.2 presents the HRTEM images of HMZ nanocontainers obtained after the removal of silica templates.

Figure 4.2: HRTEM images of HMZ nanocontainers at different magnifications
As presented in the HRTEM images, the average thickness of zirconia layer was 30 nm. The perfectly shaped spherical morphology of the zirconia nanocontainer was maintained after calcination and the removal of silica template with NaOH treatment (Figure 4.2). The porous structure of the shell helped the NaOH solution to access the core of the nanocontainer and dissolve the silica. The removal of silica particle from the interior confirmed that the zirconia nanocontainer had a porous structure. As shown in the HRTEM image (Figure 4.2d)) the hollowness was the most important structural feature of the as prepared zirconia nanospheres. Both the porous structure and hollowness are very essential for high loading capacity of the inhibitor molecules. During encapsulation, the pores on the shell facilitate the diffusion of the inhibitor molecules and the empty space inside the zirconia sphere facilitates the storage of inhibitor molecules. Moreover, the porous structure of the shell makes ease on demand release of the inhibitor molecules.

The phase of the as prepared hollow mesoporous zirconia was investigated using laser Raman spectroscopy. Figure 4.3 shows the Raman spectrum of hollow mesoporous zirconia.

![Raman spectra of as prepared HMZ nanocontainers](image)

**Figure 4.3: Raman spectra of as prepared HMZ nanocontainers**
As revealed by Figure 4.3, the characteristic phonon modes of tetragonal phase of zirconia were observed in the Raman spectra. Five Raman active modes of tetragonal phase were observed. The bands at 149 cm\(^{-1}\), 274 cm\(^{-1}\), and 463 cm\(^{-1}\) are assigned to the \(E_g\) mode of vibration of tetragonal phase [268]. The bands at 318 cm\(^{-1}\) and 648 cm\(^{-1}\) were of \(B_{1g}\) mode.

The mesoporosity of the sample was confirmed by \(N_2\) adsorption-desorption isotherm analysis presented in Figure 4.4.

![N\(_2\) adsorption-desorption isotherms of HMZ nanocontainers and pore size distribution (inset)](image)

**Figure 4.4:** \(N_2\) adsorption-desorption isotherms of HMZ nanocontainers and pore size distribution (inset)

The hollow zirconia particles showed a sorption isotherm of type IV with a hysteresis loop characteristic for materials with mesoporous structure. The hysteresis loop was due to the capillary condensation in mesopore structures. The type IV adsorption isotherm is a characteristic feature of mesoporous materials. The specific surface area of hollow zirconia products was obtained using the BET method and it was found to be
145.97 m² g⁻¹. Barrett- Joyner-Halenda (BJH) analyses revealed that the hollow zirconia products exhibited pore size centered at 3.9 nm and cumulative pore volume of 0.0993 cm³ g⁻¹. The high surface area, mesopore distributions and hollow structure of the nanocontainer are very important for inhibitor loading and controlled inhibitor release properties.

4.3.2 Inhibitor Loading and Releasing Properties of HMZ Nanocontainers

2-MBT was successfully loaded into HMZ nanocontainers by mixing HMZ nanocontainers with 2-MBT solution in acetone and followed by stirring for 24 h. Figure 4.5 presents the UV-vis spectra of 2-MBT solution before and after the interactions with HMZ nanocontainers.

![Figure 4.5: UV-visible spectra of 2-MBT before and after interaction with HMZ](image)

$\lambda_{\text{max}}$ for 2-mercaptobenzothiazole is at 325 nm. The UV-visible spectra (Figure 4.5) showed that, the absorption maxima for 2-MBT was decreased after the interaction of 2-MBT molecules with HMZ nanocontainers. Moreover, there were no new absorption bands and the position of the peaks was not changed. This decrease in the absorption intensity of 2-MBT after the interaction with HMZ nanocontainers confirmed the decrease of the 2-MBT concentration in the solution as well as the successful loading of the 2-MBT molecules in the pores and interiors of HMZ nanocontainers.
The loading of the organic inhibitor molecules in inorganic nanocontainers are made possible through weak non covalent interactions such as physical adsorption, electrostatic interaction, hydrogen bonding and \(\pi-\pi\) stacking [235]. The loading efficiency was calculated as follows:

\[
\text{Loading efficiency} = \frac{\text{Total amount of MBT} - \text{Free MBT in solution}}{\text{Total amount of MBT}} \times 100
\]  

(4.1)

The loading efficiency of 2-MBT in the HMZ nanocontainer was found to be 63\(\pm\)2\%. Furthermore, laser Raman spectroscopy confirmed the loading. Figure 4.6 depicts the Raman spectra of pure 2-MBT, HMZ and 2-MBT@HMZ.

![Figure 4.6: Raman spectra of HMZ, 2-MBT and 2-MBT loaded HMZ](image)

The characteristic peaks of both 2-MBT and zirconia were present in the spectra of 2-MBT@HMZ. The presence of the peaks of 2-MBT in 2-MBT loaded HMZ confirmed the loading of 2-MBT in HMZ. Five Raman active modes of tetragonal phase of zirconia were observed in the Raman spectra of HMZ. The bands at 149 cm\(^{-1}\), 274 cm\(^{-1}\), and 463 cm\(^{-1}\) are assigned to the \(E_g\) mode of vibration of tetragonal phase [268]. The
bands at 318 cm\(^{-1}\) and 648 cm\(^{-1}\) were of \(B_{1g}\) mode. All the major characteristic peaks and its assignments for 2-MBT are given in Table 4.1. The Raman spectra of MBT loaded HMZ showed the characteristic peaks of both MBT and zirconia and this confirmed the loading of 2-MBT in the HMZ nanocontainers [269-272].

### MBT Peak assignments in detail

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Approximate description of vibrations</th>
</tr>
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<tbody>
<tr>
<td>149 cm(^{-1})</td>
<td>SH bending</td>
</tr>
<tr>
<td>294 cm(^{-1})</td>
<td>CH bending</td>
</tr>
<tr>
<td>397 cm(^{-1})</td>
<td>CH bending</td>
</tr>
<tr>
<td>502 cm(^{-1})</td>
<td>Bz ring deformation</td>
</tr>
<tr>
<td>610 cm(^{-1})</td>
<td>CS stretching</td>
</tr>
<tr>
<td>667 cm(^{-1})</td>
<td>CS stretching</td>
</tr>
<tr>
<td>710 cm(^{-1})</td>
<td>CS stretching</td>
</tr>
<tr>
<td>766 cm(^{-1})</td>
<td>CH out of plane stretching</td>
</tr>
<tr>
<td>874 cm(^{-1})</td>
<td>CH out of plane bending</td>
</tr>
<tr>
<td>938 cm(^{-1})</td>
<td>CH bending</td>
</tr>
<tr>
<td>1035 cm(^{-1})</td>
<td>CN stretching</td>
</tr>
<tr>
<td>1081 cm(^{-1})</td>
<td>Bz ring or SCS antisymmetric stretching</td>
</tr>
<tr>
<td>1137 cm(^{-1})</td>
<td>CH in plane bending</td>
</tr>
<tr>
<td>1259 cm(^{-1})</td>
<td>NCS ring stretching</td>
</tr>
<tr>
<td>1277 cm(^{-1})</td>
<td>CC stretching</td>
</tr>
<tr>
<td>1431 cm(^{-1})</td>
<td>CC stretching</td>
</tr>
<tr>
<td>1466 cm(^{-1})</td>
<td>CC in plane stretching</td>
</tr>
<tr>
<td>1504 cm(^{-1})</td>
<td>CC stretching</td>
</tr>
<tr>
<td>1591 cm(^{-1})</td>
<td>CC in plane stretching</td>
</tr>
</tbody>
</table>

Table 4.1: Raman peak assignments for 2-MBT
The release behaviour of 2-MBT loaded HMZ was investigated by UV-visible analysis of NaCl (0.05 M) suspensions of 2-MBT loaded HMZ at different pH values. The absorption intensity at ca. 325 nm was measured at given time interval for 28 h and the results are shown in Figure 4.7.

Figure 4.7 shows the release of 2-MBT and the increase of concentration of 2-MBT with time and attained equilibrium after 5 h. When the releasing medium had infiltrated into the pores and channels of HMZ nanocontainers, the inhibitor molecules (2-MBT) gets dissolved in the medium and released by diffusion through the pores along the aqueous pathways. The releasing of 2-MBT from HMZ followed similar release
kinetics at different pH values. A faster release was observed under alkaline and acidic conditions compared to neutral condition. The release of 2-MBT was leveled off and reached equilibrium in 4 h at pH 10.

It was observed that higher amount of 2-MBT was released from the HMZ at pH 3 and 10 compared to pH 7. The amount of 2-MBT released after 28 h under acidic and alkaline conditions were 0.66 mg mL\(^{-1}\) and 0.53 mg mL\(^{-1}\) respectively, while in neutral conditions it was 0.45 mg mL\(^{-1}\) only. The difference in the release rate and quantity of 2-MBT released from HMZ can be explained by the variation of solubility of 2-MBT and the differences in the surface charge of both 2-MBT and zirconia particles with pH. The solubility of 2-MBT is low in neutral pH, but relatively higher in alkaline and acidic conditions [172]. Both the zirconia particles and the inhibitor molecules have the same surface charge when the pH values vary from neutral pH values. Under acidic pH conditions, zirconia particles have positive surface charge whereas; at alkaline pH zirconia particles acquire negative surface charge [273]. At acidic pH, 2-MBT could be protonated due to the presence of a lone pair of electrons on the N atom and carries a positive charge [274, 275]. Thus under acidic conditions, both the zirconia particles and 2-MBT had positive charge and this led to larger electrostatic repulsion between them, thereby facilitating faster release of 2-MBT from HMZ nanocontainers in high amount. Similarly, under alkaline conditions, 2-MBT exists in ionized form with a negative charge on the S atom and thus the 2-MBT molecules carry negative surface charge [276]. It is clear from Figure 4.7(c) that the absorption band at 325 nm is shifted to 309 nm since in basic medium (pH >9) 2-MBT exists in ionized form with negative charge on the sulfur atom. Again this led to electrostatic repulsion between the HMZ nanocontainers and 2-MBT, thereby facilitating the diffusion of 2-MBT through the pores of HMZ nanocontainers and faster release under alkaline condition. Hence, it
could be stated that the release of loaded 2-MBT from HMZ nanocontainers was pH specific since when the pH was shifted from neutral value, the amount of 2-MBT release was more. This dependency of inhibitor release on pH confirmed the stimuli responsive intelligent releasing property of HMZ nanocontainers. This observation can be extrapolated to a corrosion process, as corrosion of metals is always accompanied by changes in local pH. Thus, the above-mentioned results are encouraging for the use of inhibitor loaded HMZ nanocontainers in anticorrosive active coating systems with self-healing ability.

4.3.3 Anticorrosion Efficiency of Various Hybrid Coatings on Modified 9Cr-1Mo Ferritic Steels

Corrosion protection efficiency of various coatings produced on modified 9Cr-1Mo was investigated using electrochemical impedance spectroscopy (EIS) studies and scanning electron microscopy (SEM) analysis. All the coated modified 9Cr 1Mo steel specimens were immersed in 0.05 M NaCl solution and their impedance response were recorded at regular intervals of time. Figure 4.8 shows the impedance spectra of BS (uncoated modified 9Cr 1Mo specimen), CS (hybrid coating), CS-I (inhibitor mixed hybrid coating), CS-N (nanocontainer impregnated hybrid coating) and CS-NI (inhibitor loaded nanocontainer impregnated hybrid coating) after 1 h of immersion in 0.05 M NaCl solution. As revealed in Figure 4.8, all the coated substrates (CS, CS-N, and CS-NI) performed better than the uncoated modified 9Cr 1Mo ferritic steel (BS) after 1 h of immersion in 0.05 M NaCl solution. The order of corrosion protection efficiency after 1 h of immersion is as follows, CS-NI> CS-I> CS-N> CS> BS. The impedance spectrum of BS was characterized by the combination of a resistive response and a double layer capacitive response.
Figure 4.8: EIS behaviour of BS, CS, CS-I, CS-N, CS-NI after 1 h of immersion in 0.05 M NaCl solution

CS, CS-I, and CS-N showed three time constants after 1 h of immersion. The first time constant was attributed to the barrier property of the coating, the second time constant to the oxide layer and the third time constant to redox reactions at the underlying metal surface due to corrosion. Impedance response due to corrosion activity was evident at low frequency region in the spectra of CS, CS-I and CS-N even after 1 h of immersion. However, impedance spectrum of CS-NI developed only two time constant after 1 h of immersion in 0.05 M NaCl solution. The time constant at high frequency was attributed to the barrier property of the coatings. The second time constant, which was not developed fully, could be attributed to the response of the oxide film.

Figure 4.9 shows the EIS response of CS, CS-I, CS-N and CS-NI after 1 day of immersion in 0.05 M NaCl solution. Both the CS and CS-N exhibited two time constants. After one day of immersion, for both CS and CS-N, the resistive response in the low frequency region was well evolved and resistance from the oxide layer was
absent, indicating that the coatings developed conductive pathways for electrolyte. The first time constant at high frequency was attributed to the response of the barrier property of the coatings for CS, CS-I, CS-N and CS-NI.

Figure 4.9: EIS behaviour of CS, CS-I, CS-N, and CS-NI after 1 day of immersion in 0.05 M NaCl

The second time constant at lower frequency was attributed to the impedance response of the double layer for CS and CS-N. However, the second time constant for CS-NI was attributed to the impedance response of the oxide layer interface, since no signs of corrosion activity were observed in the EIS spectra of CS-NI. As shown in Figure 4.9, the coating barrier property of both CS and CS-N were reduced compared to that CS-I and CS-NI. However, for CS-NI, no clear resistive plateau was observed revealing that the underlying metal surface was protected.

Figure 4.10 shows the EIS response of CS, CS-I, CS-N and CS-NI after 1 week of immersion in 0.05 M NaCl solution. As revealed by Figure 4.10, the barrier property of both CS, CS-I, and CS-N were deteriorated considerably and it was evidenced by the disappearance of capacitive slope in the first time constant at high frequency.
Figure 4.10: EIS behaviour of CS, CS-I, CS-N, and CS-NI after 1 week of immersion in 0.05 M NaCl solution

A time constant associated with mass transport of species participating in the redox reactions at the metal surface was also observed for CS. However, CS-NI still had a time constant due to the barrier property of the coatings at high frequency consisting of a capacitive slope and a resistive plateau. The impedance at low frequency can be considered as a measure of the polarization resistance of the coatings and hence can be used to examine the corrosion protection efficiency. The value of modulus of impedance for CS, CS-I, and CS-N was very low compared to CS-NI. Moreover, the value of modulus of impedance at low frequency for CS-NI remains almost unchanged even after 1 week of immersion and this indicates the active corrosion protection rendered by the release of inhibitor molecules from zirconia nanocontainers.

Figure 4.11 shows the evolution of impedance behaviour of CS-NI during 1 week of immersion in 0.05 M NaCl solution. All the impedance spectra have two time constants. The high frequency part of the spectrum is related to the barrier property of the coating and the time constant at lower frequency is attributed to the response of the
oxide film. No time constant due to any redox reactions at the underlying metal surface was observed.

**Figure 4.11: EIS response of CS-NI during 1 week of immersion in 0.05 M NaCl**

Moreover, the second time constant was capacitive in nature since the oxide resistive plateau was not well evolved. It is observed that the resistive plateau corresponding to the coating resistance decreased continuously as the immersion progressed. These results reflect that the coating had conductive pathways for the electrolyte. Nevertheless, the value of modulus of impedance at low frequency remained almost unchanged from 1 day of immersion to 1 week of immersion. The resistance of this oxide interlayer positioned at lower frequency is very important for protecting the underlying metal surface from corrosion, since it is the last barrier for the electrolyte before accessing the metal surface. Even though the barrier property of the coating decreased for CS-NI within 1 day of immersion, the coating resistive plateau remains almost same from 3 day of immersion to 1 week of immersion.

The capacitive slope of second time constant was also did not change with immersion from 1 day to 1 week. However, CS, CS-I, and CS-N did not show this type of behaviour. The impedance response of the oxide layer did not last more than 1 day for
both CS and CS-N. After 1 day of immersion, the time constant due to oxide layer was disappeared from the EIS spectra and corrosion process started on the underlying metal surface (Figure 4.9). This result reflects the hindering of redox reactions due to the action of active agents (inhibitive species) released from the containers and thus providing active corrosion protection to the underlying metal surface for CS-NI. This corrosion protection performance of CS-NI is related to the fact that corrosion inhibitor is released from the nanocontainer mixed in the coating, since CS, CS-I, and CS-N do not show this behaviour.

SEM analysis and photographs of coated modified 9Cr 1Mo ferritic substrates support the above-mentioned EIS analysis after 1 week of immersion in 0.05 M NaCl solution. Figure 4.12 shows the photographs of the coated samples after 1 week of immersion.

![Figure 4.12: Optical photographs of the coated samples after 1 week of immersion in 0.05 M NaCl solution. The drawn circles indicate the exposed area of the coatings](image)

It is very clear from the figure that both CS and CS-I were badly damaged and the underlying metal surface was visible. Moreover, brown colored corrosion product was also appeared on the coating surface. For CS-N, it is observed that blistering of coatings occurred and corrosion products settled in some areas. However, CS-NI was not
attacked visibly by corrosion. Neither the delamination of coating nor the deposition of corrosion products were observed on the surface of CS-NI. This observation supports the results obtained from EIS analysis of various coatings during 1 week of immersion. Figure 4.13 shows the SEM images of various coated substrates after 1 week of exposure to 0.05 M NaCl solution.

Figure 4.13: SEM images and its corresponding EDX spectrum of various coated substrates after 1 week of exposure to 0.05 M NaCl solution

The SEM analysis of the coated substrates after immersion presented similar results obtained from EIS and photographs. Coatings were delaminated and flakes were visible for CS, CS-I, and CS-N. Corrosion products were also visible in the magnified view of the micrograph of CS, CS-I, and CS-N. However, uniform and damage free coating surface was observed for CS-NI after 1 week of immersion. EDX spectrum revealed that chlorine was present on the surface of the coating and Si and Zr peaks were not
observed for both CS and CS-I. Peaks of Si and Zr were present and no peak for Cl was observed for CS-NI.

In order to investigate the active corrosion protection, the coated specimens (CS and CS-NI) were exposed to 0.01 M NaCl solution after making artificial defect on it and impedance response was recorded at given intervals of time. The idea is to destroy the integrity and barrier effect of the coating and to evaluate the corrosion process on the underlying metal surface.

Figure 4.14 shows the evolution of the impedance response of scratched CS for 1 week while immersing in NaCl solution.

![Figure 4.14: EIS spectra of CS during immersion in 0.01 M NaCl solution after making an artificial defect](image)

After 1 hour of immersion, scratched CS had three time constant. The first time constant at high frequency is due to the barrier property of the coatings. The second time constant at mid frequency is due to the intermediate oxide layer and third time constant at lowest frequency is due to the corrosion activity. After 3 days of immersion it was observed that the time constant for oxide layer was not identified on the Bode plot and the low frequency impedance value has decreased. Moreover, after 1 week of
immersion, the time constant at high frequency was not present on the Bode plot suggesting that CS completely lost its barrier property. These observations suggested that scratched CS was corroding continually during immersion in NaCl solution.

Figure 4.15 shows the evolution of impedance response of scratched CS-NI for 1 week during immersion in 0.01 M NaCl solution.

![EIS spectra of CS-NI during immersion in 0.01 M NaCl solution after making an artificial defect](image)

**Figure 4.15: EIS spectra of CS-NI during immersion in 0.01 M NaCl solution after making an artificial defect**

The impedance response after 1 h of immersion had two time constants; one at high frequency was due to the barrier property of the coatings and the second time constant at middle frequency due to the oxide film. No corrosion activity at low frequency was observed. After 1 day of immersion, it was observed that the low frequency impedance value was decreased as identified on the Bode plot. However, the barrier property of the coating remained almost constant. During 1 week immersion, from 24 h to 168 h the low frequency impedance remains unchanged there in suggesting active corrosion protection. For CS-NI, the low frequency time constant was not fully evolved. The resistive plateau was not observed, only the capacitive slope was present in the Bode plot. The abovementioned experiment undoubtedly confirms that the highest value of
low frequency impedance module for CS-NI can be related to the healing of the defect by the inhibitor released from the nanocontainer embedded in the coating, since the coating without inhibitor loaded nanocontainer impregnated coatings did not show this effect.

In order to get a quantitative estimation of corrosion resistance, experimentally obtained impedance spectra for scratched CS-NI and CS were fitted using equivalent circuit (EC) models. The ECs used to fit the impedance spectra were depicted in Figure 4.16.

![Figure 4.16: Equivalent circuits used to fit the experimental EIS data of scratched CS and CS-NI during 1 week of immersion in 0.01 M NaCl solution](image)

- **R<sub>sol</sub>** is the solution resistance; **R<sub>coat</sub>, R<sub>ox</sub>** and **R<sub>p</sub>** are respectively the pore resistance of the sol-gel barrier coating, intermediate oxide layer and polarization resistance. **Q<sub>coat</sub>, Q<sub>ox</sub>, Q<sub>dl</sub>** are the constant phase elements of sol-gel hybrid coating, intermediate oxide layer and double layer respectively. Instead of pure capacitance, constant phase elements were used since the phase angle is not equal to -90°. For scratched CS-NI, in the beginning of the immersion test, two time constants completely appeared in the
impedance spectra and the third time constant at the low frequency was not evolved completely. Hence the impedance spectrum of CS-NI after 1 h of immersion was fitted using EC depicted in Figure 4.16(a). The EC shown in Figure 4.16(b) was used to fit impedance spectra of both scratched CS-NI during immersion of 24 h to 168 h and CS during immersion of 1 h to 24 h. Impedance spectra of CS during immersion of 48 h to 144 h was fitted using EC shown in Figure 4.16(c). Figure 4.16(d) was used to fit the impedance spectra of CS after 168 h of immersion. The error of fitting $\chi^2$ was less than or equal to $10^{-3}$ for all the spectra.

Figure 4.17 shows the evolution of $R_{\text{coat}}$ during immersion in 0.01 M NaCl solution.

![Figure 4.17: Evolution of hybrid barrier coating resistance ($R_{\text{coat}}$) during 1 week of immersion in 0.01 M NaCl solution.](image)

The pore resistance of sol-gel barrier coating depends on the porosity, cracks and the amount of water absorbed during immersion in salt solution. For CS-NI, the pore resistance of the coating almost remained constant and the value of $R_{\text{coat}}$ was almost 6 times more compared to that of CS. The presence of this high frequency time constant even after 1 week of immersion for scratched CS-NI in a corrosive environment shows that CS-NI preserves its barrier property. After 144 h of immersion, $R_{\text{coat}}$ value of CS
could not be extracted from the impedance spectra and this indicated the complete disruption of the barrier property of CS.

The polarization resistance ($R_p$) is the parameter, which can be directly correlated to the active corrosion protection rendered by corrosion inhibitors [172]. Figure 4.18 presents the evolution of $R_p$ during immersion.

![Figure 4.18: Evolution of polarization resistance of (a) CS-NI, (b) CS during 1 week of immersion in 0.01 M NaCl solution.](image)

The polarization resistance of CS decreased continuously during 1 week of immersion (Figure 4.18(b)). However, for CS-NI, $R_p$ value decreased from 24 h to 96 h and from 96 h onwards the value of $R_p$ increased and showed a stable behaviour (Figure 4.18(a)). The final $R_p$ value of CS-NI was about three orders of magnitude higher than CS. This may be attributed to the release of 2-MBT from ZrNC and thus provided active corrosion protection to the underlying metal surface.
Figure 4.19 presents the photograph of scratched CS-NI and CS after 1 week of immersion in 0.01 M NaCl solution.

Figure 4.19: Optical photographs of scratched CS-NI and CS after 1 week of immersion in 0.01 M NaCl solution. The drawn circles indicate the exposed area of the coatings

Corrosion products appeared on the scratched area and pits were developed on the surface of CS. However, corrosion products were not appeared on the scratched area of CS-NI and the surface was not attacked by corrosion. These observations are in good agreement with the EIS results.

With the aid of the aforementioned results a probable mechanism for active corrosion protection based on the self-healing is depicted in Figure 4.20. When the integrity of the coating is lost due to corrosion or some inherent defects in the coating, it could not function as a barrier against the permeation of any corrosive species. However, the hybrid coating containing inhibitor loaded nanocontainers could effectively delay the corrosion process by releasing the loaded inhibitor molecules. The nanocontainers could release inhibitors around the attacked or scratched region in response to pH
changes. The released inhibitor can delay the corrosion process either by forming a thin layer or by complexing with the metal ions.

Figure 4.20: Self-healing mechanism of active corrosion protection

4.4 Summary

- Hollow mesoporous zirconia nanocontainers with uniform spherical shape and average diameter of 375 nm were synthesized using a hard templating method. Solid silica nanoparticles were used as the template.
- Subsequently, HMZ nanocontainers were loaded with 2-MBT molecules and the loading efficiency was found to be 63%. The successful loading of 2-MBT into HMZ was confirmed by laser Raman spectroscopy.
- The pH specific release of 2-MBT from HMZ was observed and it was found that the release of 2-MBT was faster and higher in amount when the pH was shifted from neutral values.
The enhanced corrosion resistance of 2-MBT loaded HMZ impregnated hybrid coating was established using EIS, SEM and visual inspection.

EIS was employed as a useful technique for the study of active anticorrosion performance of 2-MBT loaded HMZ mixed coatings after creating artificial defects on the coating surface. The increase in the low frequency impedance of CS-NI during the immersion is due to the self-healing effect achieved by the releasing of loaded inhibitor from the nanocontainers.