Localized Electrochemical Impedance Spectroscopy Observation on Scratched Epoxy Coated Carbon Steel in Saturated $\text{Ca(OH)}_2$, with Various Chloride Concentration

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Abstract

The in-situ local corrosion behavior of scratched epoxy coated carbon steel is investigated in sat. $\text{Ca(OH)}_2$, with varying concentration of $\text{Cl}^-$ ions by localized electrochemical impedance spectroscopy (LEIS). The localized corrosion process and mechanism of coated steel (scratch area) is measured by LEIS plots and 3D topographic images. The LEIS responses measured at the defect are attributed to the pore impedance with defect in the high-frequency range and an interfacial corrosion reaction in the low-frequency range of corroding steel at the base of defect within 1-10 h immersion. The continuous decrease in $|Z|$ at the scratch is due to the higher extent of dissolution of Fe with increase of $\text{Cl}^-$ ion concentration. However, the resistance values of coated steel in sat. $\text{Ca(OH)}_2$, with each concentration of $\text{Cl}^-$ ions are not changed significantly with increase in immersion time from 1-10 h. On the other hand, LEIS Nyquist plots clearly showed that the measured impedance at high frequency is related to corrosion products formed at the defect which acts as anodic zones and the low frequency part are related to corroding of carbon steel with immersion of 1-5 days. 2D topographic images clearly showed that corrosion occurs at scratch and followed by coating degradation at scratch front as well as away from scratch due to cathodic reactions (reduction of $\text{O}_2$) leads to coating delamination. No significant change in corrosion resistance is observed for 0 and 0.0085 M/L of $\text{Cl}^-$ ions containing solution for 5 days of immersion as well as 1-10 h immersion. This is due the formation of better passive film on the steel surface (defect) in which the competition between the aggressive $\text{Cl}^-$ ions and the inhibitive $\text{OH}^-$ ions determines the rate of corrosion. A significant decrease in corrosion resistance is observed with higher concentration of $\text{Cl}^-$ ions ($0.17$ and $0.51$ M) due to the preferential adsorption of $\text{Cl}^-$ ions at the defect site.

Keywords: Carbon steel; Epoxy coating; Corrosion mechanism; Localized electrochemical impedance spectroscopy (LEIS); Saturated $\text{Ca(OH)}_2$; Chlorides

Introduction

Electrochemical impedance spectroscopy (EIS) has long been used to evaluate ability of coatings to resist corrosion of metals/alloys. The typical impedance spectra (Nyquist, Bode impedance and bode phase angle plots) being used to characterize the impedance parameters and the physical meaning of those parameters to determine the corrosion mechanism of steels under coating has been explored extensively [1,2]. However, the major limitation of this method is its inadequacy since the measured impedance values correspond to the electrochemical response of the whole electrode and it fails to reflect the averaged behavior of the macroscopic electrode having pinholes/defects. Hence, it is very difficult to extract complete quantitative information about the initial stages of corrosion and coating degradation. In recent years, verify of local electrochemical techniques have been developed to study local corrosion processes at initial stages and coating degradation at the microscopic level which includes Scanning Vibrating Electrode Technique (SVET), scanning reference electrode techniques (SRET), Scanning Kelvin Probe (SKP), Scanning Electrochemical Microscopy (SECM) and localized electrochemical impedance spectroscopy (LEIS), etc. [3-7]. LEIS measurements provide a promising alternative to investigate the coating degradation and localized corrosion of steel under coating. Moreover, the corrosion mechanism is a complex process in the scratched area of the epoxy coated carbon steel and depends on the type of metal/alloy, its chemical composition and ability to form a passive film, defect size, concentration of $\text{Cl}^-$ ions, transport phenomena and the nature of corrosion products [8-10]. In addition, LEIS could effectively separate the local impedance properties of the organic coating with defect when compared to the conventional EIS, in which it provides comprehensive understanding on the time of initiation of local corrosion and mechanism in aqueous environment.

Zhong et al. [11-13] have studied the corrosion of steel under defected coating ($\sim200$ and $1000 \mu\text{m}$ diameter) in near-neutral $\text{pH}$ solution using LEIS. According to them, the LEIS response was dependent on the size of the defect. It was found that the $200 \mu\text{m}$ diameter was lost due to the blocking effect, which was mainly dominated by the diffusion process. On the other hand, the blocking effect was not experienced in the $1000 \mu\text{m}$ defect due to its relatively open geometry. Jorcin et al. [14] have explored the use of LEIS mapping to assess the delamination phenomena at the steel/epoxy-vinyl primer interface in $\text{NaCl}$ and identified that the delamination has originated from the artificial defects. Hence, LEIS is a promising alternative technique to explore the corrosion mechanism of coatings with defects at microscopic level to understand their degradation behavior as well as the localized corrosion behavior of steel in aqueous solutions.

Carbon steels are widely used as construction materials in many industries due to their low cost and ability to provide reasonably good mechanical properties besides being weldable. However, the structural

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components fabricated using carbon steels encounter failures during service, particularly due to surface related failures such as fatigue, wear and corrosion. Deterioration of concrete structures has become a serious problem and the deterioration caused by corrosion of the reinforcing steel is due to salt damage, since the total content of chlorides in freshly mixed concrete has been set at 0.3 kg/m³ or less [15]. Epoxy based protective coatings have been applied to the steel bars for many applications such as bridges, parking structures, pavements, marine structures etc., against corrosion for many years which acts as a physical barrier layer against corrosion and cost effective [16-18]. However, in real time all polymers are permeable to corrosive species such as oxygen, water and ions which could not be isolated from the metal substrate and the environment [19,20]. Further, the corrosion appeared to develop at imperfections in the coating, especially where the disbondment had taken place during the fabrication (bending)/processing of the rebar. Our previous study showed that the importance and understanding on the extent of local corrosion of scratched epoxy coated steel in sat. Ca(OH)₂, with or without 3% of Cl⁻ ions (added as NaCl) studied by EIS, SECM [21].

However, there is a limited published literature in higher pH solution by in-situ measurements on the understanding of local corrosion mechanism of steels [22-24]. In addition, the level of chloride ion concentration in sat. Ca(OH)₂ is one of the critical factors that determine the corrosion behavior of reinforcing steels in contact with concrete structures and depends on the dissolved oxygen concentration, pH and chloride binding, [Cl⁻]/[OH⁻] ratio and not a unique value due to the differences in the procedures [25,26]. It is important to study the corrosion mechanism of coated steels in sat. Ca(OH)₂, with varying concentration of Cl⁻ ions on the understanding of degradation of coating and local corrosion of steels in high pH solutions. The choice of concentration of NaCl preferred in the present study is (0.0085, 0.085, 0.17 and 0.51 M) based on our previous study. The concentration of NaCl is limited to 0 - 0.51 M (0-3%) because of change in corrosion behavior was significant at 0.5% NaCl [27]. Moreover, threshold level of chlorides in sat. Ca(OH)₂ on the corrosion of steel bars found to be below 3% NaCl [28]. Hence, in the present study, an attempt is made to understand extent of local corrosion process of scratched epoxy coated steel in sat. Ca(OH)₂ containing varying concentration of Cl⁻ ions with different time intervals by LEIS and LEIS mapping.

**Experimental Details**

**Preparation of specimens**

The chemical composition of the carbon steel specimen was given in a Table 1 as per JIS-SM (Japanese industrial standards-sheet metal). The specimen, with a surface area of 1.7 × 1.7 cm², was polished using silicon carbide (SiC) papers upto 800 grit. After polishing, the sample surface were rinsed with distilled water and dried with compressed air, and cleaned with ethanol before coating.

**Preparation of coatings and electrolyte solution**

The organic coating used in this investigation was commercially available fast drying epoxy. The liquid epoxy resin was a blended with multifunctional low molecular weight diluents and the diglycidyl ether of bis-phenol-A; the aliphatic amines were used as a curing agent. The weight ratio of the epoxy resin to the curing agent was 2:1. The epoxy resin was coated using a drawdown bar at a constant speed and then kept at room temperature for 24 h. This led to the formation of uniform coating with thickness of about ~40 µm. After coating, an artificial scratch in the epoxy coating was produced by using a driller to produce a scratch of 1000 µm width and length about 10 mm. The samples were then exposed to aerated aqueous solutions of saturated Ca(OH)₂ with varying concentration of Cl⁻ ions added as NaCl (0.0085, 0.085, 0.17 and 0.51 M). The test electrolyte was prepared using analytical grade chemicals then filtered using Whatman 42 filter paper.

**LEIS measurements**

The LEIS measurements were performed using Model 470 scanning electrochemical work station, which comprises a Potentiostate/ Galvanostate/FRA (model 3300) with lock-in amplifier, environmental tri-cell system, a video microscope system to position the 7×7 mm² area of the scratched epoxy coated steel was a 7×1 mm² over the working electrode (WE). The schematic of the electrode installation and experimental set-up of LEIS is shown in Figure 1 [27]. Scratched epoxy coated carbon steel was a working electrode (WE) while saturated calomel electrode (SCE) and a graphite rod were used as the reference and auxiliary electrodes, respectively. The relative location of the microprobe to the WE was monitored by the camera system, which can be adjusted by a stepper motor in the x, y, z directions. The scanning microprobe was operated in two modes. The first mode was used for LEIS measurements. The microprobe having a 5-6 µm tip was set directly above the scratched epoxy coated carbon steel to measure the typical impedance response. The distance between the tip of the microprobe and the surface of the WE was ~50 µm, which was adjusted and monitored with the help of a video camera TV system, supplied along with the workstation. During LEIS measurements, an AC amplitude signal of 30 mV was applied to the electrode system. The frequency range used for the study was 20,000 to 0.1 Hz. The second mode was used for LEIS mapping at a fixed frequency of 10 Hz. The tip of the microprobe was stepped over a designated area of the electrode surface. The scanning was performed by the moving of the tip of the microprobe in the x-y axis while the x-y scales were set as a 7×1 mm². The step size (100 × 200 µm in x-y direction) was controlled to obtain a plot of 71 lines × 6 lines. The 3D plots were obtained from 3D Isopleot software. Specimens were mounted horizontally facing upwards. Before all experiments, the scratched epoxy coated carbon steels (WE) was kept at open-circuit potential (OCP) in the test solution for 1800 s and LEIS measurements were made at their respective OCP’s for different time intervals for 1-10 h and 1-5 days of immersion.

**Results and Discussion**

**LEIS measurements for 1-10 h immersion**

LEIS measurements performed on scratched epoxy coated carbon steel in sat. Ca(OH)₂, and sat. Ca(OH)₂ with 0.0085, 0.085, 0.17 and 0.51 M for 1-10 h. LEIS Nyquist plots of scratched epoxy coated carbon steel in sat. Ca(OH)₂ with varying concentration of Cl⁻ ions for 5 h are shown in Figure 2a. The corresponding Bode impedance and Bode phase angle plots are shown in Figure 2b and 2c. It is evident from Figure 2a that the capacitive part at high frequency range is associated with the pore resistance and its corresponding capacitance at the defect of steel surface. The capacitive part in the low frequency region is related to the double layer capacitance and charge-transfer resistance of corroding steel at the defect of base metal. Since, the LEIS is measured at single point at the defect site, the measured impedance at high frequency corresponds to the pore impedance during 1-10 h immersion [13]. The proposed electrical circuit model is shown in Figure 3. In this model, R₂ represents the solution resistance while Rₚ and CPEₚ correspond to the pore resistance and the corresponding pore capacitance, while Rₚ and CPEₚ are the charge transfer resistance and double layer capacitance of the system, respectively. The impedance of CPE is given by Zₚ=1/Q(ω)°, Where ‘n’ is the CPE exponent. The capacitance element Q(CPE) will be pure capacitance when n=1 while
Figure 1: The schematic of the electrode installation and experimental set-up of LEIS, from Ref. [27].

Figure 2: LEIS Nyquist (a) and Bode (b, c) plots of scratched epoxy coated carbon steel in sat. Ca(OH)₂ with varying concentration of Cl⁻ ions at their respective open circuit potentials.
observed for higher concentration of Cl- ions (0.17 and 0.51M). The presence of Cl- ions in sat. Ca(OH)2 promotes preferential adsorption of Cl- ions on the electrode surface and enhances the corrosion rate of steels [30,31]. In sat. Ca(OH)2, the average [Z] measured at zone H is above ~ 1 × 10^8 ohm.cm^2 whereas it decreased to ~ 6 × 10^6 ohm.cm^2 in zone L in a sat. Ca(OH)2, while the impedance values are maintained with immersion time for 1-10 h. By the addition of Cl- ions to the sat. Ca(OH)2, the average [Z] starts to decrease both at the H zone as well as at the L zone from 1 × 10^8 to 1 × 10^6 ohm.cm^2 and 4.76 × 10^7 to 2.88 × 10^7 ohm.cm^2 respectively. These inferences indicate that the local corrosion process is enhanced by the Cl- ions due to the dissolution of Fe from the scratch area. However, the addition of 0.0085 M of Cl- ions in sat. Ca(OH)2 does not show any significant change in impedance values at L zone. The observed results are in line with our previously reported results [27].

![Figure 3: Equivalent circuit diagram (LEIS) for scratched epoxy coated carbon steel under immersion in sat. Ca(OH)2 containing varying concentration of Cl ions for 1-10 h.](image)

The corresponding LEIS line profiles are shown in Figure 6, which clearly indicates the decrease in [Z] in the L-zone due to the higher dissolution of Fe at the scratched area with increase in concentration of Cl ions. The [Z] measured at the L zone as a function of concentration of Cl ions is plotted in Figure 7. It is evident from the Figure 7 that an increase in concentration of Cl ions has led to an increase in the rate of corrosion of scratched epoxy coated steel at the L zone. The shape of the curves in Figure 6 further confirms the inferences made from Figure 5 that at higher concentration of Cl ions, the extent dissolution of Fe at scratched area becomes higher. Further, the continuous decrease in [Z] over the coating and the scratched area indicates that a continuous dissolution of Fe and the easy availability of corrosive intermediate species (containing Fe(II)/Fe(III) compounds) near the scratched area which could be deposited over the coating due to the higher pH from the bulk solution [32]. However, there is no sign of additional defects over the coating that has been observed from the LEIS maps with the addition of Cl- ions to the sat. Ca(OH)2. On the other hand, the decrease in [Z] over the coating might be due to the water uptake of the epoxy coating [10,33]. Further, the experiments have been conducted by long term immersion for 1-5 days on the better understanding of local corrosion process at scratch and coating area of scratched epoxy coated carbon steel in varying concentration of Cl ions.

**LEIS measurements for 1-5 days of immersion**

LEIS Nyquist plots of scratched epoxy coated carbon steel in sat. Ca(OH)2 with 0.51 M Cl- ions for 5 days of immersion are shown in Figure 8a. The corresponding Bode impedance and Bode phase angle plots are shown in Figures 8b and 8c. It is evident from Figure 8a that the capacitive part at high frequency range is associated with the corrosion product layer at scratch, the inductive loop at intermediate frequencies is due to the adsorption of corrosion species involved in the local corrosion process and, the capacitive part in the low frequency region is related to the double layer capacitance and charge transfer resistance of corroding steel [34,35]. The proposed electrical circuit model and fittings values are shown in Figures 9 and 10 for sat. Ca(OH)2 with varying concentration of Cl ions respectively. In this model, R_s represents the solution resistance while R_corpor product layer and CPE_corpor product layer correspond to the resistance of corrosion product layer and the corresponding capacitance of the corrosion product layer, respectively. L is the inductance of adsorbed intermediate corrosive species involved in the local corrosion process while R_n and

| Sample | Elements (mass %) |
|--------|------------------|
| Carbon steel | C | Si | Mn | P | S | Al | N | O | Fe |
| | 0.10 | 0.30 | 0.70 | 0.01 | 0.003 | 0.03 | 0.003 | 0.002 | Bal. |

Table 1: Chemical composition of carbon steel specimen.
Figure 4: Local impedance values of (a) $R_{pore}$, (b) CPE$_{pore}$, (c) $R_{ct}$ and (d) CPE$_{dl}$ for scratched epoxy coated carbon steel after wet/dry cycles test in sat. Ca(OH)$_2$ with varying concentration of Cl$^-$ ions recorded at their respective OCPs for 1-10 h.

Figure 5: The 3D LEIS maps measured over a scanning area of 7 mm × 1 mm (x-y scale) over the scratched epoxy coated carbon steel in sat. Ca(OH)$_2$ with varying concentration of Cl$^-$ ions for 1-10 h immersion. Scale: 7 mm × 1 mm in x and y directions, vertical direction is $|Z|$.
Figure 6: LEIS line profile measured at L zone of scratched epoxy coated carbon steel in sat. Ca(OH)$_2$ containing varying concentration of Cl$^-$ ions for 1-10 h: (a) 0 M, (b) 0.0085 M, (c) 0.085 M and (d) 0.51 M.

Figure 7: Impedance measured at L zone ($|Z|_{10\text{Hz}}$) over scratched epoxy coated carbon steel in sat. Ca(OH)$_2$ with varying concentration of Cl$^-$ ions. CPE$_{dl}$ are the charge transfer resistance and double layer capacitance of the system, respectively. It is evident from Figure 10, the resistance of corrosion product layer is decreased from $1.01 \times 10^5$ to $1.24 \times 10^4$ ohm.cm$^2$ (one fold decrease) by the addition 0.51 M Cl$^-$ ions from 1$^{st}$ to 3$^{rd}$ day of immersion. With increase in immersion time from 3$^{rd}$ to 5$^{th}$ day, resistance of corrosion product layer is slightly increased to $2.66 \times 10^4$ ohm.cm$^2$. This is due to the formation of corrosion products that makes difficulty in charge transfer at the interface of corrosion product layer and bare steel interface. However, the charge transfer is not completely restricted due to the formation of intermediate corrosion products [21]. The resistance of the corrosion product layer formed on scratched area is higher ($9.47 \times 10^5$ to 1.49 $\times 10^7$ ohm.cm$^2$) in sat. Ca(OH)$_2$ for 1-5 day of immersion. In the presence of 0.085 M Cl$^-$ ions, the resistance of the corrosion product layer is initially increased from $9.95 \times 10^5$ to $3.57 \times 10^6$ ohm.cm$^2$ then it is decreased from $3.57 \times 10^6$ to $1.81 \times 10^5$ ohm.cm$^2$ with increase in immersion time for 1-5 days. On the other hand, the resistance of R$_{\text{corr product layer}}$ is higher in sat. Ca(OH)$_2$, ($1 \times 10^7$ to $1.40 \times 10^7$ ohm.cm$^2$) as compared to 0.0085 M Cl$^-$ added solution ($4.85 \times 10^6$ to $7.66 \times 10^6$ ohm.cm$^2$) for 1-5 days of immersion. In this case, the R$_{\text{corr product layer}}$ is increased with immersion time for 0 and 0.0085 M Cl$^-$ ions as compared to other concentration of Cl$^-$ ions added solutions. These inferences clearly indicate that R$_{\text{corr product layer}}$ depends on Cl$^-$ion concentrations and the corresponding chemical compositions of corrosion product layers [23,36]. Moreover, Cl$^-$ to OH$^-$ ion concentration is also important factor that determines the chemical compositions of the corrosion product layers [23]. The charge transfer resistance, R$_{ct}$ of corroding steel is increased from $1.29 \times 10^6$ to $1.28 \times 10^7$ ohm.cm$^2$ 1-2 days of immersion time and it retained at $7.93 \times 10^6$ ohm.cm$^2$ in immersion time in the absence of Cl$^-$ ion solution. Similarly, the R$_{ct}$ values are increased from $1.05 \times 10^6$ to $6.49 \times 10^6$ for 1$^{st}$ day of immersion and then sustained in the resistance values ($2.90 \times 10^6$)
Figure 8: LEIS Nyquist (a) and Bode (b, c) plots of scratched epoxy coated carbon steel immersed in sat. Ca(OH)2 with 0.51 M Cl- ions for 1-5 days at their respective open circuit potentials.

Figure 9: Equivalent circuit diagram for scratched epoxy coated carbon steel under immersion in sat. Ca(OH)2 containing varying concentration of Cl- ions for 1-5 days.

with increase in immersion time in 0.0085 M Cl- ion solution. The $R_{ct}$ values (absence of Cl- ions) are comparable with $R_{ct}$ values of 0.0085 M Cl- ions increase in immersion time. The increase in concentration of Cl- ions in to 0.085 M, the $R_{ct}$ values are increased initially from $4.20 \times 10^5$ (day 1) to $1.16 \times 10^6$ ohm.cm$^2$ (day 2) and then start to decrease with immersion time from $1.16 \times 10^6$ to $1.01 \times 10^5$ ohm.cm$^2$. However, in case of sat. Ca(OH)$_2$ with 0.51 M Cl, the $R_{ct}$ values start to decrease from $1.24 \times 10^5$ to $1.12 \times 10^6$ ohm.cm$^2$ for 1st to 2nd day of immersion then starts to increase slightly from $1.12 \times 10^6$ to $3.18 \times 10^4$ ohm.cm$^2$ with increase in immersion time.

The various concentrations of chloride threshold levels on the corrosion resistance of steels have been reported by various researchers [28,37,38]. Li and Sagues [37] studied the chloride threshold level in saturated Ca(OH)$_2$ was found to be 0.01-0.04 M. Gouda [38] has been reported that the 0.007 M could be the chloride threshold level (added as NaCl) in a saturated Ca(OH)$_2$ solution, which did not affect the passivity of the steel. Moreno et al. [28] have been reported that the 0.02% Cl (0.0034 M) addition in to the sat. Ca(OH)$_2$ solution has no appreciable change in anodic behavior of steel and it was observed that Cl- ion concentration equal to or higher than 0.05% (0.0085 M) induce pitting of the steel. However, the epoxy-coated steel can gave a good protection; long term performance even on severe exposure to chloride conditions have been reported with considering properly coated and handled steels [39,40]. Al-Amoudi et al. [40] found that the chloride threshold level of epoxy-coated steel with various degrees of coating damage (1 and 2%) and the chloride threshold level was about 2 and 0.4% (0.35 and 0.068 M) by weight of cement respectively. In the present...
Figure 10: Local Impedance values of (a) $R_{\text{corr\_protect\_layer}}$, (b) $\text{CPE}_{\text{corr\_protect\_layer}}$, (c) $R_{\text{ct}}$, (d) $\text{CPE}_{\text{ct}}$ and (e) $L$ for scratched epoxy coated carbon steel under immersion in sat. Ca(OH)$_2$ with varying concentration of Cl$^-$ ions recorded at their respective OCPs for 1-5 days.
Figure 11: 2D LEIS maps measured over a scanning area of 7 mm × 1 mm (x-y scale) over the scratched epoxy coated carbon steel in sat. Ca(OH)₂ with 0.51 M of Cl⁻ ions: (a, b and c) at scratch area, (d, e and f) over coating area for 1, 3 and 5 days of immersion respectively; different color shades indicates difference in |Z| at different zones.
study, 0.0085 M of Cl ions in sat. Ca(OH)$_2$ is found to be comparable with absence of Cl$^-$ ions (Figures 4, 7 and 10), beyond 0.0085 M of Cl$^-$ ions led to the significant decrease in corrosion resistance of scratched epoxy coated carbon steel.

The 2D LEIS maps acquired at scanning area of 7 mm × 1 mm (x-y scale) over the scratch and coated area of carbon steel in sat. Ca(OH)$_2$ with 0.51 M of Cl$^-$ ions for 1, 3 and 5 days of immersion are shown in Figure 11. In Figure 11, the different color shades represents the measured impedance, |Z| distribution along the x-y axis. It is evident from (Figure 11a, 11b and 11c) shows the measured impedance over the scratch area, while the Figure 11d, 11e and 11f shows the measured impedance over the coated area. The significant decrease in impedance at scratch is observed with increase in immersion time from 1$^{st}$ day to 3$^{rd}$ day (2.5 × 10$^5$ to 3.5 × 10$^4$ ohm.cm$^2$) and then slightly increased at 5$^{th}$ day (5 × 10$^4$ ohm.cm$^2$) at scratch area. In addition, the corrosion at scratch area is broadened in 3$^{rd}$ day of immersion due to direct penetration of electrolyte (arrow marks in Figure 11b), while the additional corrosion spots could be found in over the coated area (arrow marks shown in Figure 11e). The corrosion at scratch area is restricted due to the formation corrosion products with increase in immersion time to 5$^{th}$ day (Figure 11c). The additional corrosion spots at scratch front and away from the scratch could be extended with larger corrosion spots (Figure 11e and 11f). This is mainly due to the formation of corrosion products at the scratch area (at high pH solutions) eventually corrosion starts at some other places (around the corrosion spots) [21]. The observed results are in line with LEIS parameters (Figure 10) for 0.51 M Cl$^-$ ions containing solution.

Based on the inferences made in the present study, a pictorial model is proposed to explain the corrosion mechanism of scratched epoxy coated carbon steel in sat. Ca(OH)$_2$ containing varying concentration of Cl$^-$ ions.

Conclusion

The influence of varying concentration of chloride ions on the local corrosion behavior of scratched epoxy coated carbon steel in sat. Ca(OH)$_2$ is investigated by in-situ manner using LEIS. The LEIS responses measured at the defect are attributed to the pore impedance in the high-frequency range and an interfacial corrosion reaction in the low-frequency range of corroding steel within 1-10 h immersion. The pore resistance, $R_p$ of scratched epoxy coated carbon steel is decreased from the range of 3.93 × 10$^6$ to 2.75 × 10$^5$ ohm.cm$^2$, the charge transfer resistance; $R_t$ is also decreased from 6.38 × 10$^5$ to 2.84 × 10$^4$ ohm.cm$^2$ with increase in concentration of Cl$^-$ ions from 0-0.51 M. The LEIS maps acquired at 10 Hz provides a better recognition of anodic and cathodic areas on the local corrosion process of scratched epoxy coated carbon steel. The decrease of change in |Z| range from 6.27 × 10$^6$ to 4.85 × 10$^5$ ohm.cm$^2$ is marginal by the addition of 0.0085 M Cl$^-$ ions into the sat. Ca(OH)$_2$, whereas it decreased from 4.85 × 10$^5$ to 2.88 × 10$^4$ ohm.cm$^2$ with increase in concentration of Cl$^-$ ions from 0.0085 to 0.51 M. The [Z] measured by LEIS reveals a continuous decrease in impedance at the scratch due to the higher dissolution of Fe with an increase in concentration of Cl$^-$ ions, which is further validated by the variation in [Z] by LEIS maps. This clearly indicates that an increase of NaCl concentration leads to the significant increase in the corrosion rate of the scratched epoxy coated carbon steel due to preferential adsorption of Cl$^-$ ions on the electrode.

On the other hand, LEIS Nyquist plots clearly showed that the measured impedance at high frequency is related to resistance of corrosion product layer ($R_p$ for product layer) formed at the defect which acts...
as anodic area and the low frequency part are related to corroding of carbon steel with immersion of 1-5 days. The resistance of corrosion product layer is decreased from 1.01 × 105 to 2.4 × 104 ohm.cm² (one fold decrease) by the addition of 0.51 M Cl⁻ ions from 1st to 5th day of immersion. With increase in immersion time from 3rd to 5th day, resistance of corrosion product layer is slightly increased to 2.66 × 10⁴ ohm.cm². This is due to the formation of corrosion products that makes difficulty in charge transfer at the interface of corrosion product layer and bare steel in which the charge transfer is not completely restricted due to the formation of intermediate corrosion products. The R_corr values are much higher in sat. Ca(OH)₂ and with 0.0085 M Cl⁻ ions as compared to 0.085 and 0.51 M Cl⁻ ions and it varied slightly higher/lower impedance values. These inferences indicate that R_corr depends on Cl⁻ ion concentrations and the corresponding chemical compositions of corrosion product layers. This has been clearly indicated in the 2D topographic images that corrosion occurred at scratch along with scratch front as well as from the scratch with increase in immersion time. The different color zone at scratch area revealed that the formation of corrosion products followed by the localized corrosion due to the porous nature of the passive layer. The 2D topographic image results are well agreement with LEIS parameters for 1-5 days of immersion. No significant reduction in LEIS values at 1-10 h immersion. [Z] values at 1. Z, LEIS in 1-5 days of immersion in 0 and 0.0085 M Cl⁻ ions. This is due to the presence of sufficient concentration of inhibitive OH⁻ ions in solution. The inferences made in the present study points out that beyond 0.0085 M NaCl is likely to increase the corrosion rate of scratched epoxy coated carbon steel.

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