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Optimization of AC impedance test cell for accelerated evaluation of marine industrial coating in Kuwait

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ABSTRACT

In previous studies a new AC impedance test cell has been designed for the evaluation of coating systems. In the present work, the viability of the test cell has been investigated on a selection of commercial quality coating systems. This is made in order to achieve an accelerated evaluation and proper prequalification of marine industrial coating arriving at the desalination industry and off shore pipeline marine structure in the state of Kuwait. The AC impedance behavior of three coating systems, fusion bonded epoxy, high build epoxy (HBE), and polyurethane were examined under the new test cell in 5% NaCl solution. The same test was supported by salt spray fog test and QUV for 1,000 h at 35°C (ASTM B117). Triplicate samples of each coating system were retrieved from the salt fog cabinet for impedance measurements after 500, 750, and 1,000 h. The same specimens were also examined for gloss retention and FTIR. The overall results of impedance and capacitance obtained with the modified test cell showed typical AC impedance spectrums that have proven its importance as an accelerated quantitative testing cell when combined with salt spray cabinet testing. The screening program has indicated that HBE is the best performed coating for values of impedance $R_p = 8.53 \times 10^9\,\Omega$ and capacitance $C_c = 4.52 \times 10^{-12}$ F.

Keywords: AC impedance test cell; Marine industrial coating; Salt spray fog test; QUV test; AC impedance spectrum and high build epoxy

1. Introduction

Electrochemical impedance spectroscopy (EIS) method is one of the electrochemical methods that have been proven to be the best in delineation of degradation kinetics of metals coated by organic coating. Electrochemical methods are fast and quantitative and used in conjunction with accelerated tests to quantify coating integrity and long-term corrosion performance. [1] mentioned that EIS can measure corrosion rate under a paint film before it was clearly observed. In the impedance method, the electronic circuit is used to provide a qualified methodology for any coating system in an environment. This results in obtaining system characteristics such as durability, protectiveness, and other features [2]. The spectrum obtained from this technique was in the form of Nyquist and Bode diagrams frequency vs. modulus of impedance |Z| or plots related to phase shift (θ) vs. frequency (f) domain from 100 KHz to 10 MHz.

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A new cell has been erected [3] in order to facilitate measurement using electrochemical impedance instrument developed by Solartron. The new design of test cell was developed due to difficulties in conducting such tests using the traditional EIS test cell arrangement. The coated steel panels of size 7.5 × 12 cm in the old (traditional) cell arrangement is not suitable, because the EIS output signal will be dominated by edge effects and hence, the results will be inconsistent. This is due to the fact that the coated panels are dipped into electrolyte and the electrochemical signal will be associated with predominant higher corrosion tendency generated from specimen edges causing experimental errors and over estimation of corrosion tendency and signal scatter.

One way to avoid this edge factor as well as crevice corrosion attack is therefore to mask the edges with any nonconductive material or tape. However, this method introduces another problem of crevice corrosion possibility under the edges of the masking material. For this, a different cell arrangement is developed and used for EIS electrochemical testing at KISR laboratory and designed particularly to accommodate paint systems coated metal panels of size 7.5 × 115 cm [3]. The testing developed cell arrangement used for this project is shown in Fig. 4. This detrimental effect can be summarized as follows:

- The surface condition of the edges of any panel is different from that of the panel surface.
- Any metal sample has greater tendency toward corrosion at the edges than the body of the matrix because of the effect of the geometrical and electrostatic considerations.
- The thickness of paint film or coating on the edge is usually less than that of the surface.

2. Experimental method

Three different coating systems, fusion bonded epoxy (FBE); high build epoxy (HBE); and polyurethane (PU) were used in the experiment. They were coated at the manufacturer premises on carbon steel panels. These are typical representatives of the most common coating systems used for external protection of pipeline. FBE coating with an average thickness of 460.9 μm designed as a primer for the use in three-layer pipe coating systems. HBE is a single coating and it is 100% solid. This coat can repair and rehabilitate pipelines operating up to 95°C. It is a solvent-free epoxy and consists of two components and has an average thickness of 956.4 μm. PU is the high build solvent-free rapid cure two pack tar modified urethane. It can be applied at thickness ranges between 0.5 and 5.0 mm.

2.1. Procedure for salt spray (fog) test

This test provides a controlled corrosive environment, which has been utilized to produce relative corrosion resistance information of the coating systems during exposure to the environment and it exhibits excellent correlation with underground environment. An automatic programmable salt fog cabinet from Heraeus-Votsch, Type HSN 400 Salt Spray Chamber, was used for the test. Specimens coated by the three different coating systems, (HBE, FBE, and PU) were exposed to salt spray experiments. These experiments were carried out according to ASTM B-117 for 1,000 h keeping samples exposed to a constant mist or spray of aerated 5% NaCl solution, near neutral pH (6.5–7.2) and the samples were collected at a rate of 24–48 ml per day at 35°C and 80% relative humidity. The desired concentration of the sodium chloride (NaCl) solution that was used in the salt spray test was prepared by dissolving 5 kg of the NaCl in 95 L of distilled water. Triplicate samples of each coating system in addition to two scribed samples were tested and evaluated. Performance evaluation included the determination of gloss retention combined with EIS technique and monitoring of any surface failure. The Fourier transform infrared (FTIR) finger printing technique was applied on fresh and exposed panels in order to investigate the change in the chemical structure of the polymer for both contaminated and non-contaminated samples. The FTIR results showed that there is hardly any change in the chemical structure of the FBE and HBE coatings.

However, this study will present only the results from AC impedance measurements and gloss retention values obtained after exposure to salt spray and QUV machine. The gloss retention values were measured before and after the exposure to salt spray chamber and QUV for 1,000 h at 35°C for the three systems of coatings. The gloss measurements were obtained at 20° and 60° according to ASTM D 523.

2.2. Procedure of EIS cell arrangement

The NaCl solution used in the EIS experiments was prepared in the laboratory by dissolving 30 g of NaCl to make 3% NaCl. The EIS measurements were applied on coated samples before the exposure to salt spray and after each period i.e. as received samples (0 h), 500, 750, and 1,000 h. A textile tape of narrow and long fabric (i.e. 100% cotton) is prepared. The middle part of the textile tape was pressed against the specimen's surface (working electrode) as shown in Fig. 1. The counter electrode (graphite plate), of the same size as the working electrode, was pressed against the textile tape on the other side. One end of the tape is immersed in a beaker with 3% NaCl solution and the other end was kept free inside an empty beaker to allow one-way lateral flow of the solution through the textile tape by the natural effect of capillary action. This method was applied in order to avoid any over estimation or increase in the concentration of the electrolyte. At this stage, the electrolytic solution contact was established. The reference electrode was connected with another textile tape of the same material. One section of this tape is pressed against the flow tape and the specimen surface and the other section was kept free in a third empty beaker. This arrangement was made to allow the electrolyte to flow into this beaker while avoiding the flow of the solution from the reference electrode to the specimen surface and to avoid evaporation of the electrolyte, which may have a detrimental effect on its concentration. The flow of the electrolyte was controlled by adjusting the ends of the textile tapes. The electrolyte level in the beaker was lower than specimen surface. The schematic arrangement of the EIS testing cell is shown in Fig. 1.

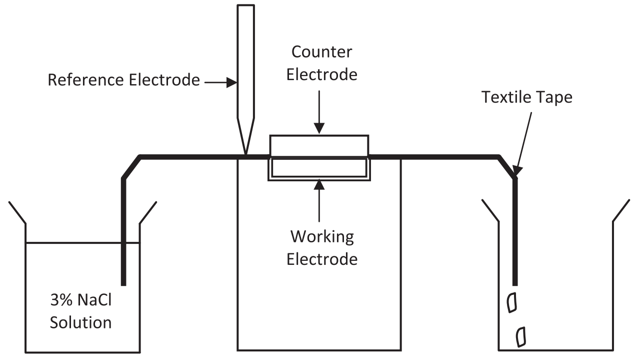

Fig. 1. Arrangement of the newly developed EIS cell.

3. Results and discussion

The results showed that the gloss retention values of HBE paint have not been affected during the course of the measurement even after 1,000 h of exposure. Unlike the other two coatings, the HBE kept the values of gloss retention before and after exposure for both the clean and contaminated cases as indicated in Table 1 and Figs. 2–5.

Each gloss retention value reported in Table 1 is an average of four measurements of triplicates samples given in percentage compared to a perfect mirror gloss of 100%. The results showed the significant decrease in the gloss retention values after the exposure to the salt spray tests for the two coating systems, FBE and PU.

However, for HBE the values remained constant indicating the protection behavior of this type of coating. The slight increase in the gloss retention values of the exposed coated samples of HBE is due to the use of arithmetic means in such comparison. The insignificant increase in gloss retention average shown in Table 1 and Fig. 2 does not mean any improvement in the HBE coating performance, but rather indicates the unchanged behavior. The outstanding behavior of this particular paint has been also noted with other diagnosis technique such as AC impedance which indicates a coherent and adherent paint system to the underlying substrate. Other paints, such as FBE and PU, show a significant decrease in the retention values after the 1,000 h exposure to the salt spray testing. The loss of gloss in these two paints, FBE and PU, can be attributed to the effect of temperature on the constituents of the polymeric material of these paints. The same findings are also reported elsewhere [4].

Table 1
Average of gloss retention values for various coatings before and after exposure to salt spray for 1,000 h at 35˚C

Coating Type		Before exposure		After exposure	
		20˚	60˚	20˚	60˚
FBE	Clean	33.75	73.95	6.61	28.07
	Contaminated	24.47	68.96	5.73	25.77
HBE	Clean	5.39	32.89	5.87	34.70
	Contaminated	1.64	11.80	1.63	11.54
PU	Clean	26.34	71.56	0.98	9.14
	Contaminated	36.08	86.01	2.41	19.72

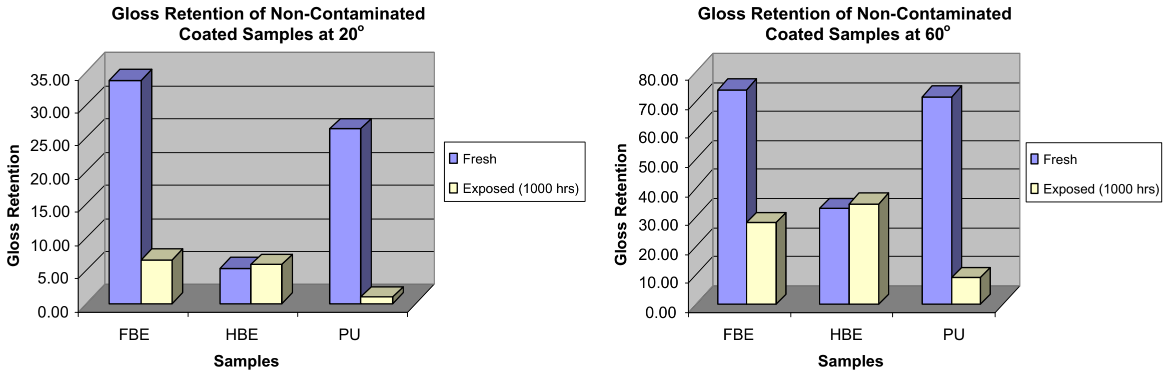

Fig. 2. Gloss retention value of noncontaminated coated samples at 20 and 60˚C.

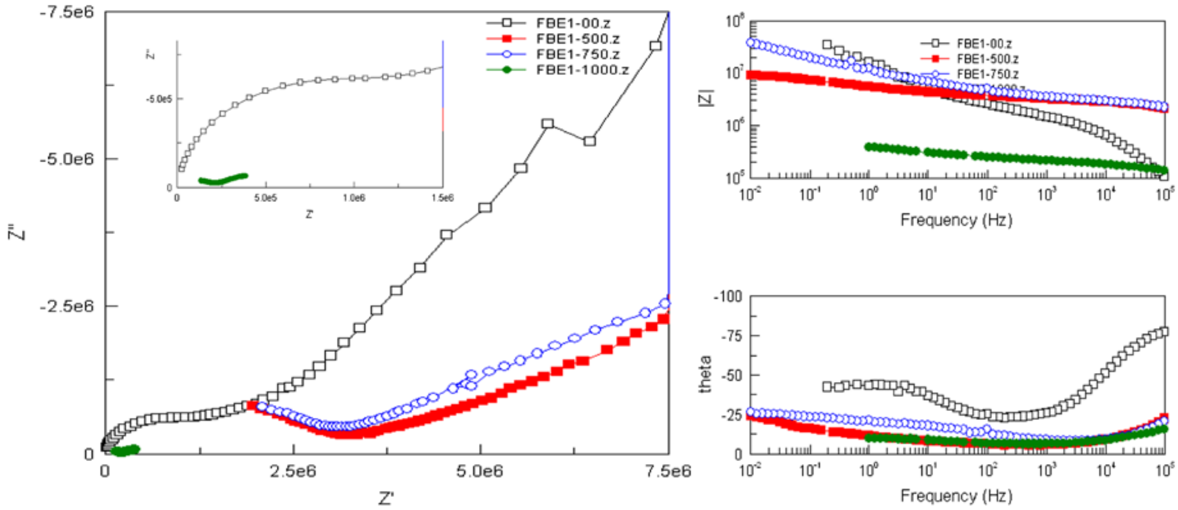

Fig. 3. Nyquist and Bode plots for noncontaminated FBE coated steel.

4. Electrochemical impedance spectroscopy (EIS)

The Nyquist and Bode plots for chloride-contaminated and noncontaminated sample coated with the three coating systems are shown in Figs. 3–8, using the developed test cell.

The changes of the impedance during exposure to 5% NaCl solution for coated steel are given below. Fig. 3 shows that FBE coating is not capacitive and indicates the poor quality of the coating. Fig. 3 indicates two-time constant with one semicircle at high frequency and diffusion control known as Warburg diffusion in the second low frequency semicircle resulting in corrosion occurrence with time.

The coating behaves as a porous membrane in this manner since it is not compact and porous. This behavior can be clearly seen at the Nyquist and Bode spectrum of this paint at 1,000 h. The values of R_Ω and C are 3.48×10^5 ohms and 2.07×10^{-12} farads, respectively. For HBE coating, Fig. 4 illustrates the capacitive behavior of the coating at 0, 500, 750, and 1,000 h. At 0 h, it shows that this coating is very compact and adherent to the steel substrate, i.e. no water uptake within the coating. But at 500 h the behavior changed drastically due to high diffusion of water resulted in localized microcorrosion that was not visible to the naked eyes. At 1,000 h the plot shows one-time constant with complete semicircle, where the paint material reaches passive–active transition at a faster rate. The above hypothesis can be reflected in both types of Bode plots as an alternative presentation of the curve.

Fig. 5 shows degradation of PU coating with time at the as received conditions. Then it modifies its performance, at 1,000 h, presenting two-time constant with one semicircle at the paint-solution interface and another curvature at the metallic corrosion interface.

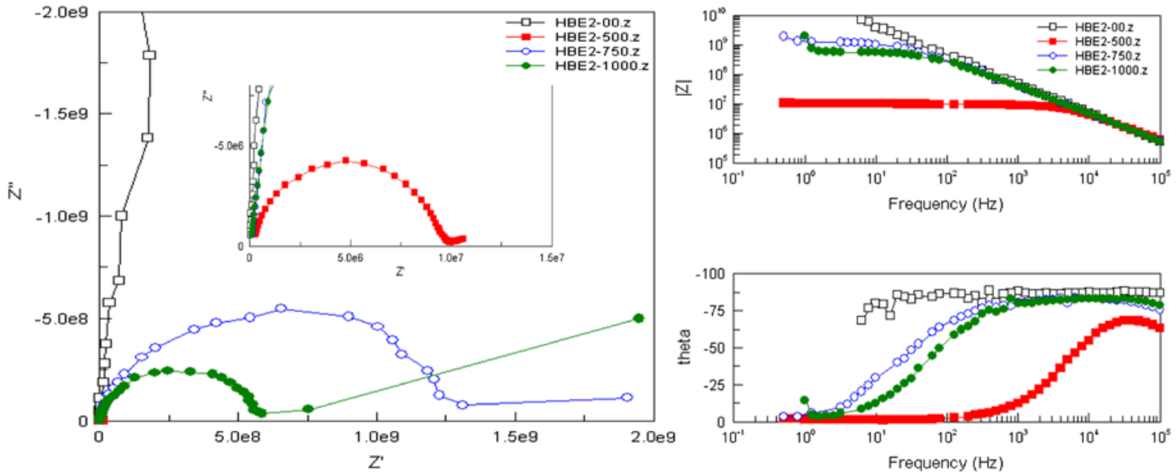

Fig. 4. Nyquist and Bode plot for noncontaminated HBE coated steel.

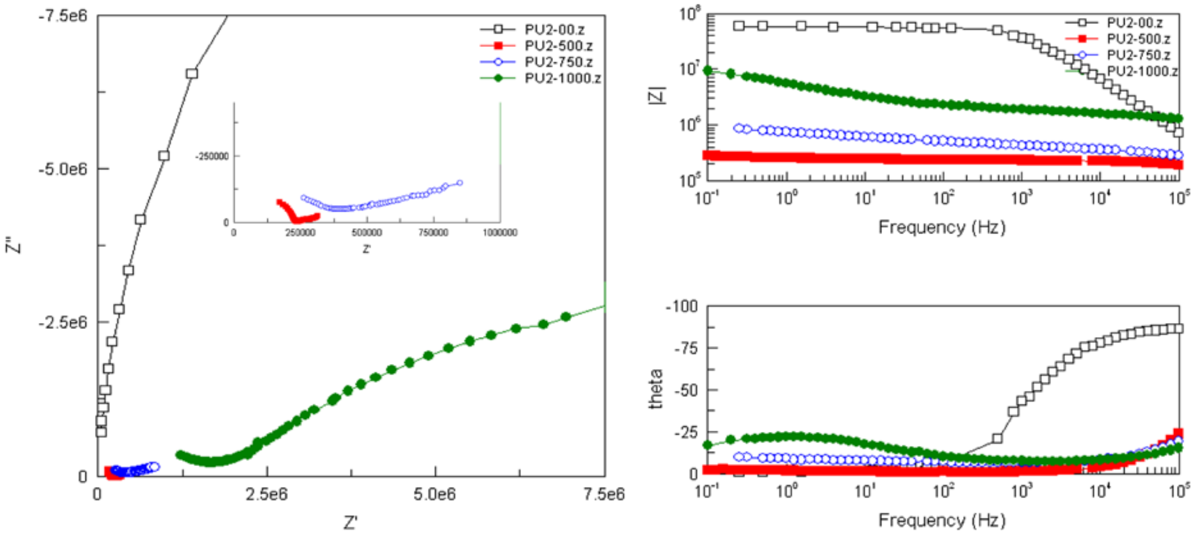

Fig. 5. Nyquist and Bode plots for noncontaminated PU coated steel.

Coating impedance of 1.2×10^6 ohms has been attained and the capacitance is 2.68×10^{-12} farads after 1,000 h of exposure.

4.1. *AC impedance results of coated samples with NaCl contamination*

The changes of the impedance during exposure to 5% NaCl solution for coated steel contaminated with fine mist of 3% NaCl solution are given below. Fig. 6 presents the behavior of FBE coating. Fig. 6 shows two-time constant with one semicircle at high frequency and a diffusion control tail known as Warburg diffusion. This may be caused by corrosion product precipitation at the bottom of the pores preventing interdiffusion of chloride species toward the metal substrate (through the protective oxide film of corrosion product). This can be seen clearly at the spectrum of this paint at 1,000 h. The values of R_{po} and C are 7.62×10^5 ohms and 5.42×10^{-13} farads, respectively. Bode plot, Fig. 6, confirms the analysis since the plot shows two directions.

Fig. 7 indicates an incomplete capacitive behavior most probably caused by salt contamination. As this can be also seen in Fig. 7 where in HBE coating, chloride contamination causes deterioration of the coating at faster rate due to the presence of chloride species beneath the coating. It also enhanced the interdiffusional behavior of water and migration of sodium chloride species with increasing wetability of the

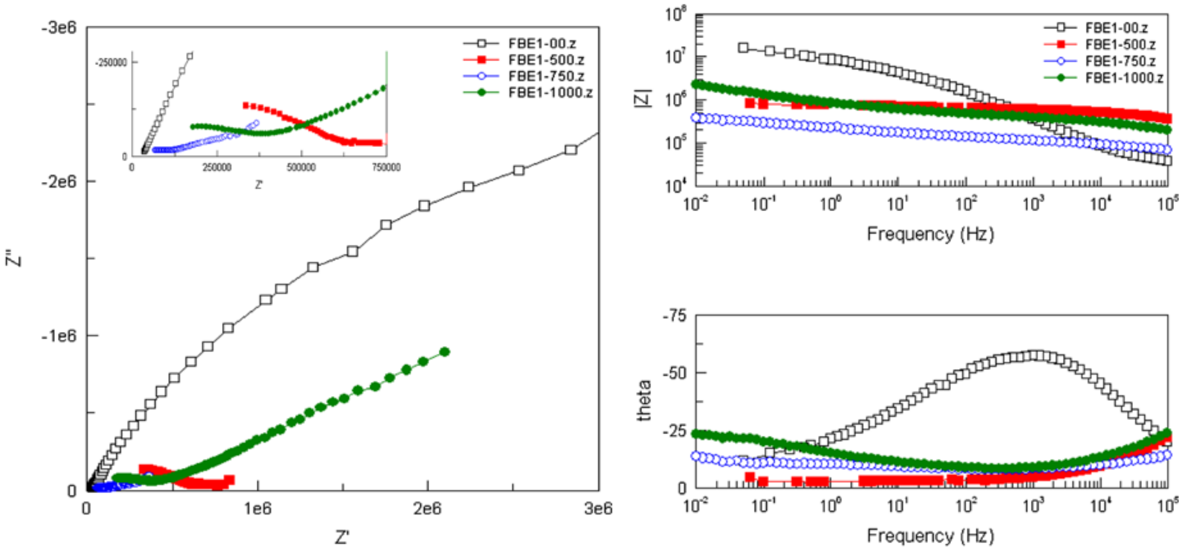

Fig. 6. Nyquist plot for chloride contaminated FBE coated steel.

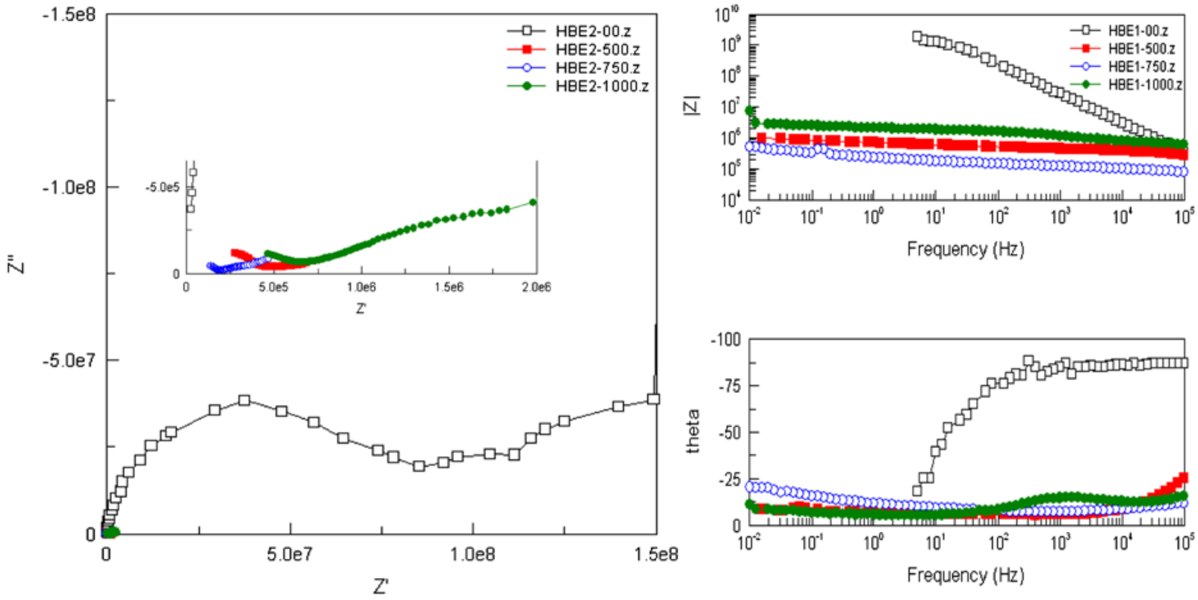

Fig. 7. Nyquist and Bode plots for chloride contaminated HBE coated steel.

coating. It is believed that chloride species have been presented as crystalline elements at the interface having very high affinity for water which resulted in the formation of pocket microcorrosion cell at a different rates on the surface of the steel at the junction between the coating and steel substrate.

PU coating indicates that it is more tolerable to chloride contamination than other coatings. Fig. 8 clearly shows degradation in the performance of the contaminated paint after immersion in NaCl with time. It shows more than one-time constant with triple semicircles at 500, 750, and 1,000 h control at low frequency presented by Warburg diffusion tail that inclined toward 45° angle.

PU has been deformed due to chloride contamination and it showed a clear behavior of diffusion at 500 h, the coating showed very high impedance then it decreases with time reaching impedance values of R_Ω ohms and C equal to 4.6×10^3 ohms and 2.52×10^{-10} farads, respectively. However, after 1,000 h of exposure in salt spray chamber, it has been drastically reduced to values of 4.23×10^2 ohms and 4.51×10^{-8} farads.

The impedance plots presented in this work indicated that only HBE coating gave the best performance, while FBE and PU showed the opposite performance. In this respect, it can be said that the water uptake (diffusion) in HBE is much lesser than the other two coatings, leading to less chance of corrosive entrance or attack at the interface between coating and substrate. This can be also seen from Warburg diffusion tail mostly dominated with the spectrum of this paint. Although HBE became brittle and fragile when over time exposed to atmospheric weather, it did not degrade easily when covered with sand particles at a depth of 2–4 m. If presented in the open atmosphere, it would suffer from ultraviolet (UV) radiation that causes severe destruction of the polymeric material constituents of the weaker paint material. In many cases, this can be overcome by the use and addition of UV stabilizer with the paint constituents [5].

Table 2 summarizes comparison obtained from AC impedance results. Drastic change in AC impedance spectrum has been considered as an indication of water uptake when it was changed from larger to smaller diameter of the semicircle. The coating resistance of HBE was highest, followed by PU, and then by FBE for noncontaminated condition (HBE > FBE > PU). However, the resistance sequence of these coatings had changed to HBE > FBE > PU when contaminated with 3% NaCl. This indicates performance of the excellent behavior of HBE in both cases.

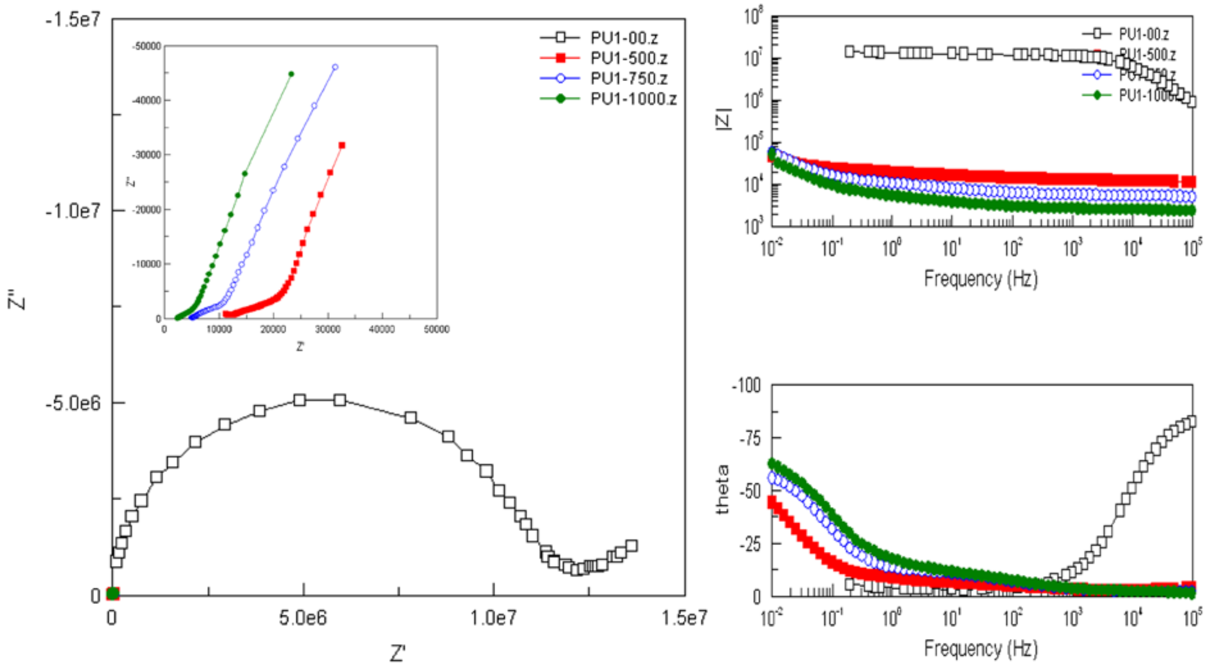

Fig. 8. Nyquist and Bode plots for chloride contaminated PU coated steel.

Table 2
Summary of AC impedance results

	Noncontaminated panels			Chloride contaminated panels		
	FBE	HBE	PU	FBE	HBE	PU
Performance	Poor	Excellent	Poor	Poor	Good	Poor
Water uptake	High	Rare	Poor	High	Poor	High
R (ohms)	3.48×10^5	8.53×10^9	1.2×10^6	7.62×10^5	4.99×10^8	4.23×10^2
C (farads)	2.07×10^{-12}	4.52×10^{-12}	2.68×10^{-12}	5.42×10^{-13}	7.43×10^{-12}	4.51×10^{-8}

Referring to Fig. 9, we can observe that the gloss retention values of HBE coated samples did not significantly change as the other two coatings did. The gloss results supported the AC impedance results that HBE has the best resistance behavior. FTIR finger printing also confirmed the excellent performance of HBE. Furthermore, no significant changes were observed in the spectra of HBE and FBE coatings. The only visible change was in the noncontaminated PU, as seen in Fig. 10, coating. HBE is categorized as coating based on epoxy type resin. Such coatings have gained significant value in different industrial applications. Coatings based on epoxy resins are easy to process and also safe, and have good mechanical and chemical properties [6]. Furthermore, in order to compare paint performance on substrates, sodium chloride contamination was applied to a set of steel panels. This was done to study different methods of coating application as well as to accelerated paint deterioration.

Visual deterioration of the samples' condition was represented by rusting and blistering and impedance response as seen in the impedance plots gave evidences that chloride has a significant effect on the accelerated deterioration of coated samples. The contamination with fine mist of 3% NaCl solution caused considerable decrease in the resistance of the three coatings as shown in Figs. 6 and 8. Coatings' capacitance increased with time due to water uptake of the polymeric material of the paints. This effect of Cl will enhance the conductive nature of the dielectric property of paints. Visual examination of all three coatings after salt spray exposure for 1,000 h confirms the outstanding performance of HBE coating when comparing with two other coatings, such as FBE and PU. FBE is low-quality paint since it suffered from rust tearing and blistering effect after the exposure to salt spray testing. For PU coating, it showed rust tearing due to the absence of inhibitive primer to protect the substrate.

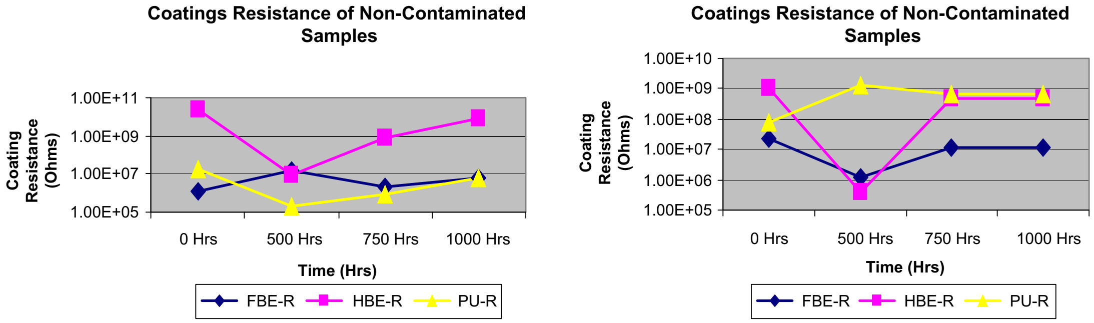

Fig. 9. Resistance change of the three noncontaminated coated panels with time.

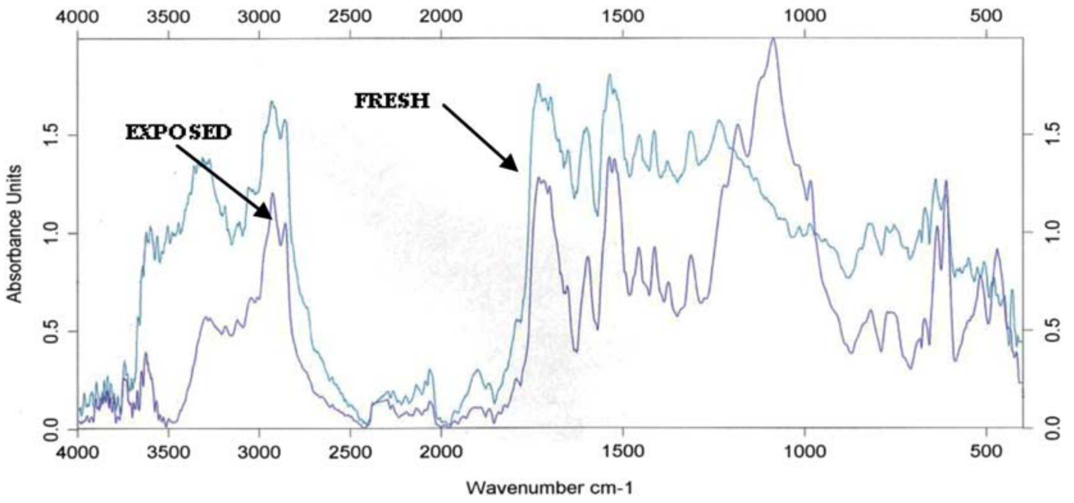

Fig. 10. FTIR spectra of **PU** coated panels for fresh and exposed samples for 1,000 h.

5. Conclusion

- The modified AC impedance test cell utilized in this study has proved its importance as an accelerated testing cell when combined with salt spray weathering cabinet.
- AC impedance technique with the developed test cell has proved its viability as a powerful tool for studying coating durability, degradation, and screening.
- The decrease in coating film impedance with time suggests that the solution ingress permanently damages the coating film locally at discrete pathways, increases with time.
- Exposure to salty environment may cause decomposition or restructuring of some hydrocarbon groups as the disappearance of ether group in PU coated samples.
- According to AC impedance measurements in conjunction with other diagnostic testing techniques such as gloss retention, FTIR, and visual examination, the following screening of the commercially applied coating systems is in the order: HBE > FBE > PU.

Acknowledgments

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