

EFFECTS OF CHLORIDE IONS ON THE CORROSION RESISTANCE OF CONDUCTING POLYPYRROLE COATED STEEL IN SIMULATED CONCRETE PORE SOLUTION

Hema MUNOT¹, Pravin DESHPANDE², Chetankumar MODHERA³

Epoxy based paint containing conducting polypyrrole as a pigment was applied on low carbon steel sample. By using Tafel polarization technique, corrosion rates of uncoated low carbon steel sample and painted low carbon steel sample, in 3.5 wt% NaCl were determined. The corrosion rate of conducting polypyrrole coated low carbon steel sample was found to be 0.09 mpy which is about 81 times lower than that of uncoated steel sample. A shift of 186 mV in the value of the corrosion potential in the positive direction indicates that the polypyrrole coating imparts corrosion protection by anodic protection. The uncoated and painted steel samples were immersed in simulated concrete pore solution and electrochemical studies were carried out. It was found that the passive film generated on uncoated low carbon steel sample in pore solution gets damaged with addition of chloride ions. As compared to uncoated low carbon sample, polypyrrole coated low carbon steel sample exhibits higher impedance (Z_{mod}) \sim 6340 K Ω -cm 2 , higher coating resistance (R_C) \sim 1778 K Ω -cm 2 and lower capacitance (C_C) \sim 11.66x10 6 μ F just after immersion, in pore solution without chloride contents. Polypyrrole coated steel sample was able to protect low carbon steel for up to 240 hours of immersion in the pore solution containing no chlorides and in the pore solution containing 0.25M NaCl. However, at 0.5M NaCl & higher concentrations, the self healing ability of polypyrrole coating was no longer operating to protect steel sample from corrosion. The novelty of the paint coatings formulated by using polypyrrole pigments is that in case of damage of paint coating in service or handling, a passive film gets generated and protects the underlying metal from further corrosion. Findings in these investigations revealed possibility of using conducting polypyrrole based paint coating system for the protection of rebar in concrete.

Keywords: Conducting polypyrrole, Chloride ions, Concrete pore solution, Rebar

¹ PhD Research scholar, Sardar Vallabhbhai National Institute of Technology, Surat (Gujarat), India

² Prof, Department of Metallurgy and Material Science, College of Engineering, Pune, India, e mail- pravinpd@hotmail.com

³ Prof, Applied Mechanics, Sardar Vallabhbhai National Institute of Technology, Surat (Gujarat), India

1. Introduction

Concrete is a composite material composed of coarse and fine aggregates embedded in a matrix of hardened hydrated cement. The aggregate is generally impermeable and chemically inert. On the other hand, the hardened cement is porous and contains pore solution. After several days of hydration, the pore solution contains alkali ions such as potassium, sodium and hydroxide ions in relatively large amounts along with much smaller concentration of calcium and sulphate ions and other ions. High alkalinity (pH ~ 13), due to large hydroxide concentration, of the concrete pore solution is responsible for passive film formation on reinforced steel sample [1]. However, break down of passive film can occur due to chloride attack or carbonation. Chloride induced corrosion takes place when chloride ions diffuse through the pore network of the concrete or cracks and attack the reinforcement. The process of chloride penetration into the pore space of concrete is complex but can be simplified as follows: If the surface of concrete gets in contact with sea water or chlorides containing water, the aqueous solution is first absorbed quickly by capillary action. When the rate of capillary absorption becomes negligible, chlorides get transported deeper into the concrete by a slow diffusion process [2]. The use of chloride contaminated aggregates and the exposure to sea water are the main sources for chloride ions in concrete and thereby corrosion. However, to reduce the rate of corrosion, various methods have been tried, like use of high performance concrete, low water/cement ratio, optimum thickness of concrete cover, use of corrosion inhibitors, application of cathodic protection and use of galvanized and epoxy coated rebars [3]. For example, C. Lin et al. investigated corrosion behaviour of epoxy/zinc duplex coated rebar embedded in concrete in ocean environment [4]. R. Selvaraj et al. used epoxy silicone- polyamide, polyester polyol-aromatic isocyanate and acrylic polyol-aromatic isocyanate with titanium dioxide and zinc phosphate as the main pigment to formulate organic coatings for rebars. In this work, it has been found that the epoxy silicone polyamide resin based coating exhibited good barrier protection to the steel rebar [5]. G. Chen et al. studied corrosion resistance and mechanism of steel rebar coated with pure enamel, an enamel mixed with 50% calcium silicate and a double enamel with an inner layer of pure enamel and an outer layer of the mixed enamel. Their corrosion resistance was compared with commonly used fusion bonded epoxy coating in 3.5 wt % NaCl. It was found, in these investigations, that the pure and double enamel coatings can protect the steel rebar better than the mixed enamel coating due to their denser microstructure with isolated pores and the intact epoxy coatings offered better corrosion protection than the enamel coatings [6]. Unfortunately, coated rebars are prone to mechanical damage during handling and installation and subsequent corrosion. Recently, conducting polymers such as polyaniline and polypyrrole have been emerged as

non toxic and anti corrosive pigments. The coating based on these polymers can impart corrosion protection by one or combination of the simultaneously operating mechanisms - It can act as a physical barrier or active electronic barrier, it can be self healing agent, it can displace oxygen reduction or it can be mediator /catalyst for the formation of corrosion products. The novelty of the paint coatings formulated by using these pigments is that, in case of damage, a passive film gets generated and protects the underlying metal from further corrosion [7]. Recently, A. H.El-Shazly et al. investigated the possibility of improving the corrosion resistance of reinforced concrete against chloride ions and sulphate ions by using polyaniline coatings. In this work, it was found that polyaniline coating had improved the corrosion resistance of reinforced concrete against chloride ions by a factor ranging from 1.10 to 1.90 and by a factor ranging from 1.3 % to 1.6% against sulphate ions compared to uncoated steel samples [8]. A.H.El-Shazly et al. checked the possibility of improving the corrosion resistance of buried pipe line by electro depositing polyaniline layer on it. It was observed that polyaniline improved corrosion resistance against NaCl , H_2SO_4 and water by factors up to 1.88, 1.89 and 1.54 respectively [9]. To the best of our knowledge, there are no reports in the literature regarding use of polypyrrole based paint coatings for the protection of reinforced concrete bar. In the present work, therefore, we synthesized polypyrrole pigments and polypyrrole coating painted steel sample was tested against attack of chloride ions in pore solution. Cement paste takes at least thirty minutes to set initially, three days and seven days to achieve 50% and 66% desired strength respectively from construction point of view. Hence testing of the coated steel samples immersed in pore solutions was carried out at these time periods and beyond.

2. Experimental procedure

2.1 Conducting polypyrrole based paint preparation

Conducting polypyrrole was synthesized by the method adapted by V. Truong et al [10] and conducting polypyrrole based paints were prepared by the method described by P. Deshpande et al [11] and elaborated as follows. Conducting polypyrrole (2 g) as a pigment, 12 g of Xylene, 8 g of titanium dioxide (TiO_2) and 8 g of bis-(2-ethylhexyl) phthalate (dioctyl phthalate: DOP) were added to the solution of 70 g of epoxy resin (GY 250 supplied by Huntsman Advanced Materials (India) Pvt Ltd. Andheri (East), Mumbai- 400093, India). The mixture was ball milled for 16h (Ball Mill supplied by Indo German Industries, Daman, India. Drive motor: Crompton Make - 2HP, 1440 rpm, 415 V, 50 Hz). The purpose of adding titanium dioxide and Di-octyl phthalate in epoxy resin was to improve viscosity and elastic properties of paint. Xylene was used as a solvent for paint formulation. The paint was filtered through fine cotton and applied on the low carbon steel samples (AISI 1015 supplied by Rajasthan steels, Pune, India) by

film applicator to keep paint thickness - 60 μm uniform on the entire surface. Finally, the painted low carbon steel samples were cured in air at ambient temperature for 24 hours.

2.2 Preparation of simulated pore solution

The electrolyte used for immersion should be an exact representative concrete pore solution with Ca^+ , K^+ , and Na^+ ion additions [12]. Chemical composition of the simulated concrete pore solution, therefore, is designed as shown in Table 1. One solution without chloride content and three solutions containing increasing chloride contents - 0.25M NaCl, 0.5M NaCl and 1M NaCl were prepared.

Table 1

Chemical composition of the simulated concrete pore solution

Compound	Mol.L ⁻¹	Weight in grams per 100 ml of water
NaOH	0.1	0.4
KOH	0.3	1.68
$\text{Ca}(\text{OH})_2$	0.03	0.22
$\text{CaSO}_4 \cdot \text{H}_2\text{O}$	0.002	0.03

2.3 Corrosion studies

A corrosion cell having three electrode geometry of paint coated samples as working electrode

(8 cm^2), platinum as counter electrode and saturated calomel electrode (SCE: pH Products, Hyderabad, India) as a reference electrode was used. The cell was coupled with Gamry reference system1000 (Wilmington, USA) for electrochemical impedance measurements. All measurements were carried out five times to obtain good reproducibility of the results.

3 Results and discussion

3.1 Potentiodynamic polarization

Polarization curves were obtained by applying potential ± 250 mV with respect to open circuit potential for uncoated low carbon steel sample and epoxy based polypyrrole coated low carbon steel sample in 3.5 wt % NaCl solution as shown in Figs 1 and 2 and the values obtained are recorded in Table 2. Corrosion rate was found out using Echem Analyst software (ASTM G 102-89 reapproved 1994:- Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements)

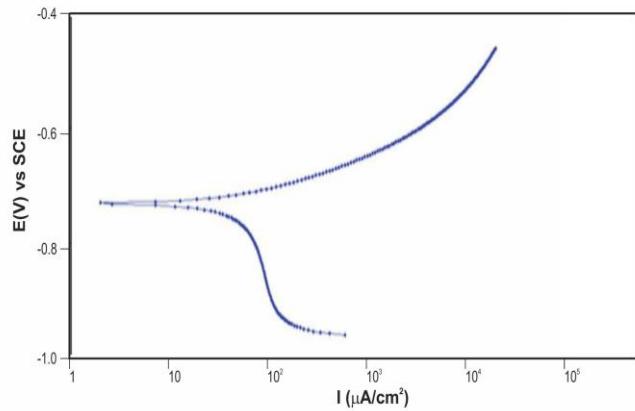


Fig.1: Tafel plot for low carbon steel sample in solution with 3.5 wt% NaCl

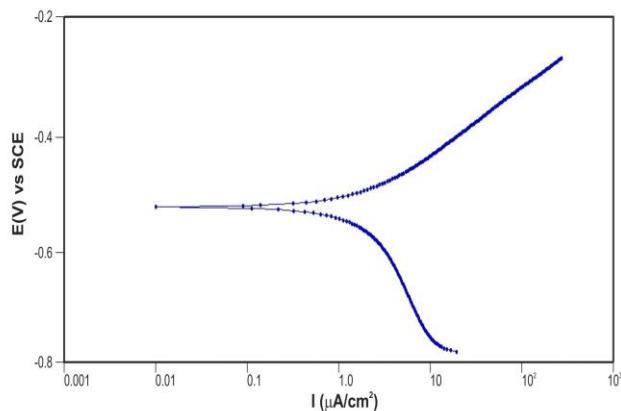


Fig.2: Tafel plot for epoxy based polypyrrole coated low carbon steel sample in solution with 3.5 wt% NaCl

Table 2
Corrosion rates for uncoated low carbon steel sample and epoxy polypyrrole coated low carbon steel sample in solution containing 3.5 wt% NaCl.

Sample	E_{corr} (mV)	I_{corr} ($\mu A cm^{-2}$)	Corrosion Rate (mpy)
Uncoated or bare low carbon steel sample	-731	63.5	7.2
Polypyrrole coated low carbon steel sample	-545	1.83	0.09

Corrosion potential increased from -731 mV for uncoated low carbon steel sample to -545 mV for conducting polypyrrole painted steel sample. It should also be noted the corrosion rate is substantially reduced due to the decrease in current density from $63.5 \mu\text{A cm}^{-2}$ to $1.83 \mu\text{A cm}^{-2}$. The corrosion rate of conducting polypyrrole coated low carbon steel sample is found to be 0.09 mm per year which is about 81 times lower than that of unpainted low carbon steel sample. A shift of 186 mV in the value of the corrosion potential in the positive direction indicates that the coating imparts corrosion protection by preventing cathodic reduction process i.e. by anodic protection.

3.2 Open circuit potential measurements

The open circuit potential was monitored for uncoated and polypyrrole coated samples immersed in chloride free concrete pore solution and concrete pore solution containing fixed amounts of chlorides. The results are recorded in the table 3 and 4.

Table 3

Open Circuit Potential measurements: Uncoated steel sample

Sr. No.	Sodium chloride addition in pore solution	Open circuit Potential, mV			
		Immersion Time , hours			
		0	72	168	240
1	0M NaCl	-455	-430	-401	-230
2	0.25M NaCl	-455	-428	-398	-235
3	0.5M NaCl	-455	-460	-480	-495
4	1M NaCl	-455	-510	-490	-515

The open circuit potential was monitored for polypyrrole coated samples immersed in chloride free concrete pore solution and concrete pore solution containing fixed amounts of chlorides and the results are recorded in table 4.

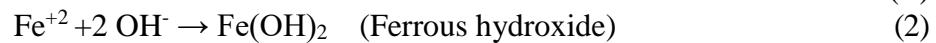
Table 4

Open Circuit Potential measurements: Polypyrrole coated sample

Sr. No.	Sodium chloride addition in pore solution	Open circuit Potential, mV			
		Immersion Time , hours			
		0	72	168	240
1	0M NaCl	-385	-302	-284	-139

2	0.25M NaCl	-385	-372	-311	-283
3	0.5M NaCl	-385	-396	-344	-317
4	1M NaCl	-385	-487	-460	-331

It is observed that just after immersion in the pore solution, the open circuit potential for uncoated steel sample immersed in pore solution, the initial potential was -455 mV. Subsequently, open circuit potential was found to be decreased from -455 mV to -430 mV within 72 hours of immersion in the case of uncoated steel sample in chloride free pore solution. This shift in potential, in positive direction, can be assigned to the formation of passive film on the uncoated steel sample in chloride free pore solution. Formation of passive film in pore solution takes place in two stages as follows:



The passive film that develops initially on uncoated steel sample is ferrous. Over time the ferrous hydroxide gets converted to the more stable ferric oxide – γ Fe OOH [1]. Beyond 168 hours of immersion significant variations are noted in the open circuit potentials and it attained the values of -401 mV and -230 mV by the end of 168 and 240 hours of immersion respectively. This indicates full passivity stage of steel sample in pore solution due to ferric oxide film formation. These results are in good agreement with recent work [13]. Uncoated low carbon steel sample was able to remain in passive state even after addition of 0.25M NaCl to the pore solution. However, with further increase of chloride contents in the pore solution that is, at concentrations of 0.5M NaCl and 1M NaCl, the steel sample was no longer able to show passivity with time. In case of polypyrrole coated steel samples, the initial potential observed just after immersion was -385 mV. When there was no addition of chlorides to the pore solution, the open circuit potential for the Polypyrrole coated steel sample increased to -302 mV, -284 mV and -139 mV after 72 hours, 168 hours and 240 hours of immersion respectively. With increasing chloride contents in the pore solution, the potentials attained the values of -283 mV, -317 mV and -331 mV respectively after 240 hours of immersion. However, these values are significantly less than that of uncoated steel sample. This reveals the relative immunity of polypyrrole coated steel samples to chloride attack as compared to uncoated steel samples immersed in pore solution. Barrier effect of polypyrrole coating suppress active dissolution of the steel and oxidative property of polypyrrole shifts the potential into the passive state [14]. But the protective ability of polypyrrole coating decreases when chloride contents increase to 0.5M NaCl and

beyond, in the pore solution.

3.3 Electrochemical Impedance measurements

Electrochemical impedance measurements (Table 5) were carried out for the uncoated and polypyrrole coated low carbon steel samples immersed in chloride free concrete pore solution and concrete pore solution containing fixed amounts of chlorides.

Table 5

Impedance parameters	
Initial Frequency	100,000 Hz
Final Frequency	0.1 Hz
Initial Delay	1800 sec
AC Voltage	10 mVrms

The results of these studies are reported here in terms of Bode plots, depicted in Figs. 3 to 6. These plots are analyzed using equivalent circuit shown in Fig. 7 and the impedance (Z_{mod}), the coating resistance (R_C) and the coating capacitance (C_C) values, except solution resistance (R_U), obtained by modelling these figures are recorded in tables 6, 7 and 8. The equivalent circuit shown in Fig. 7 is Randles circuit. Randles circuit, a combination of resistor and capacitor can be used to model non coated metals as well as coated metals. When this circuit is used to model electrochemical processes in the case of non coated steel, the resistance of the metal to polarization and capacitance associated with the formation of double layer are expressed in terms of polarization resistance (R_p) and double layer capacitance(C_{dl}) respectively. In the case of coated steel, modeled using the same circuit, these terms are replaced by coating resistance (R_c) and coating capacitance (C_c) respectively [15]. Fig. 3 shows Bode plot of the uncoated low carbon steel sample just after the immersion in pore solution and Fig. 4 depicts Bode plot of the uncoated low carbon steel sample for 72 hours immersion in pore solution as a function of NaCl concentration.

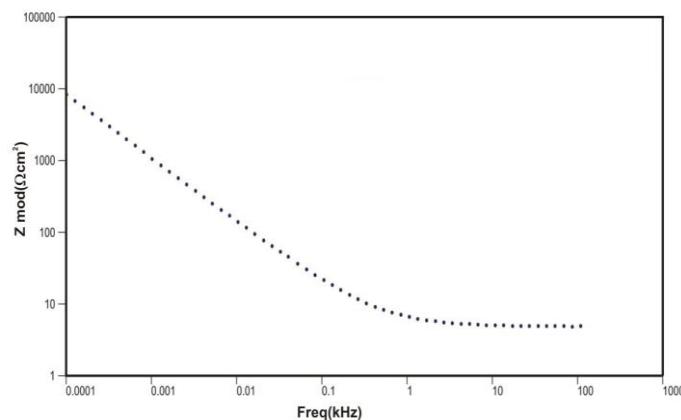


Fig 3: Bode plot of uncoated steel sample just after immersion in pore solution.

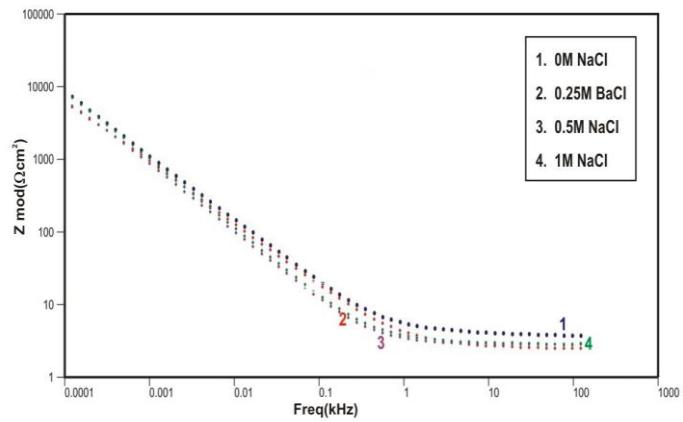


Fig. 4: Bode plot of uncoated steel sample immersed for 72 hours in pore solution.

Fig. 5 and Fig. 6 show Bode plots of the uncoated steel sample for 168 hours and 240 hours of immersion in the pore solution respectively, as a function of NaCl concentration.

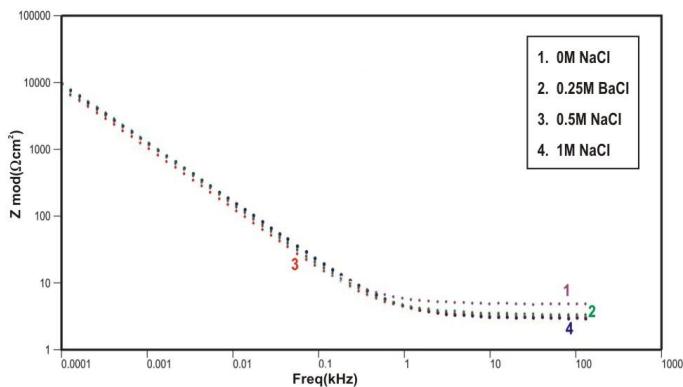


Fig. 5: Bode plot of uncoated steel sample immersed for 168 hours in pore solution.

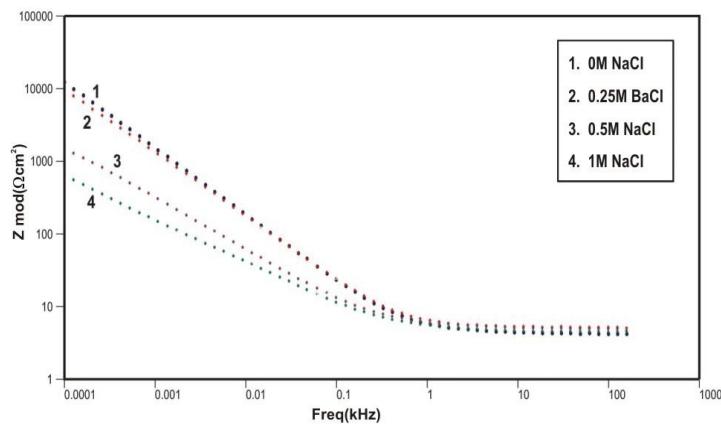


Fig. 6: Bode plot of uncoated steel sample immersed for 240 hours in pore solution.

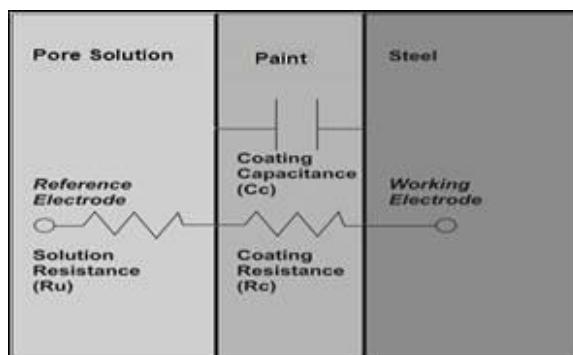


Fig 7: Equivalent circuit used for modelling impedance behaviour

Table 6

Uncoated steel sample: Impedance values

Sr. no	Sodium chloride Concentration	Z _{mod} (KΩ-cm ²)			
		Immersion time			
		0 hrs	72 hrs	168 hrs	240 hrs
1	Without NaCl	6.55	6.82	7.33	8.55
2	0.25 M NaCl	6.55	5.36	7.30	6.75
3	0.5 M NaCl	6.55	5.01	5.77	1.14
4	1 M NaCl	6.55	4.16	4.33	0.50

Table 7

Uncoated steel sample: Coating resistance

Sr. no	Sodium chloride Concentration	Rc (KΩ – cm ²)			
		Immersion time			
		0 hr	72 hrs	168 hrs	240 hrs
1	Without NaCl	8.13	12.85	15.36	27.14
2	0.25 M NaCl	8.13	8.01	13.47	10.97
3	0.5 M NaCl	8.13	5.76	11.25	0.81
4	1 M NaCl	8.13	5.20	5.15	0.22

Table 8

Uncoated steel sample: Coating Capacitance

Sr. N. o	Sodium chloride Concentration	Cc (μF)			
		Immersion time			
		0 hr	72 hrs	168 hrs	240 hrs
1	Without .NaCl	156.7	148.2	130.3	120.2
2	0.25 M NaCl	156.7	158.1	128.3	126.4
3	0.5 M NaCl	156.7	160.3	148.4	520.4
4	1 M NaCl	156.7	158.4	240.2	790.3

All the Bode plots reveal two characteristic segments of the straight line. At lower frequencies, the straight line bends so as to become a line parallel to the abscissa: that is, the impedance is independent of frequency at low frequencies, indicating a gradual transition from capacitive to resistive behaviour. In the case of uncoated steel sample, the impedance (Z_{mod}) increased from $6.55 \text{ K}\Omega\text{-cm}^2$ to $8.55 \text{ K}\Omega\text{-cm}^2$ from just after immersion to the end of 240 hours of immersion in pore solution without NaCl contents. However, for the uncoated steel sample, the impedance values (Z_{mod}) decreased from $6.55 \text{ K}\Omega\text{-cm}^2$ to $5.36 \text{ K}\Omega\text{-cm}^2$, $5.01 \text{ K}\Omega\text{-cm}^2$ and $4.16 \text{ K}\Omega\text{-cm}^2$ from just after immersion to the end of 72 hours of immersion, in pore solution with increasing chloride contents from 0.25M NaCl to 1M NaCl respectively. The impedance again increased beyond 72 hours of immersion to 168 hours of immersion, up to $7.3 \text{ K}\Omega\text{-cm}^2$, $5.77 \text{ K}\Omega\text{-cm}^2$ and $4.32 \text{ K}\Omega\text{-cm}^2$.

$\text{K}\Omega\text{-cm}^2$ and subsequently decreased up to $6.75 \text{ K}\Omega\text{-cm}^2$, $1.14 \text{ K}\Omega\text{-cm}^2$ and $0.5 \text{ K}\Omega\text{-cm}^2$ up to 240 hours of immersion respectively. Maximum coating resistance (R_C) $\sim 27.14 \text{ K}\Omega\text{-cm}^2$ and minimum coating capacitance (C_C) $\sim 0.22 \mu\text{F}$ is observed in case of the steel sample dipped in pore solution having no chloride contents for 240 hours duration. Increase in coating capacitance as a function of time can be assigned to the penetration of water molecules and corrosion species into the passive film on steel sample (Table 8). Electrochemical impedance results therefore support changes in open circuit potential values of the steel samples. The Bode plots for the Polypyrrole coated steel sample immersed in the pore solution for just after immersion in pore solution, after 72 hours, after 168 hours and after 240 hours of immersion are shown in Figs. 8 to 11.

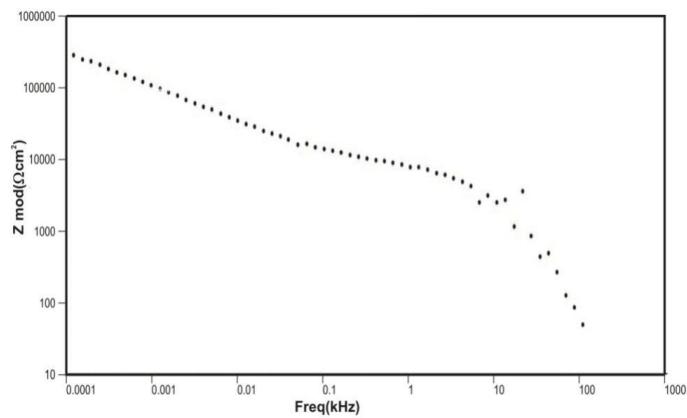


Fig. 8: Bode plot of Polypyrrole coated steel sample just after immersion in pore solution.

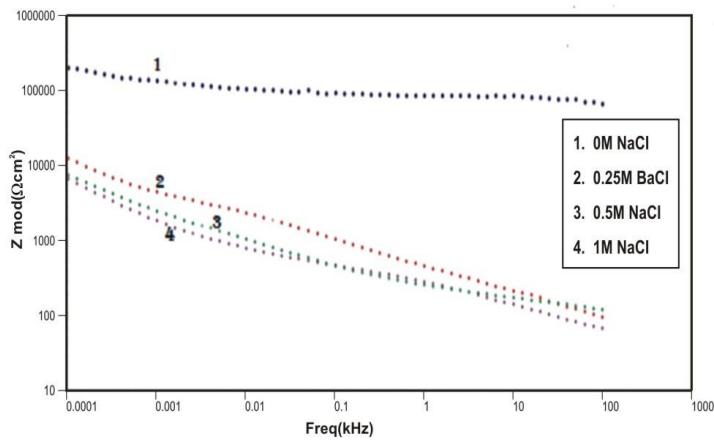


Fig. 9: Bode plot of Polypyrrole coated steel sample after being immersed for 72 hours in pore solution.

The impedance values (Z_{mod}), coating resistance (R_C) and coating capacitance (C_C) are obtained by using equivalent electrical circuit shown in Fig. 7

and recorded in tables 9, 10 and 11 respectively. Fig 8 and Fig 9 show impedance values of the coated steel sample just after immersion in pore solution and after 72 hours of immersion in the pore solution respectively, as a function of NaCl concentration.

Fig. 10 & Fig. 11 show impedance values of the coated steel sample after 168 and 240 hours' immersion in the pore solution respectively, as a function of NaCl concentration.

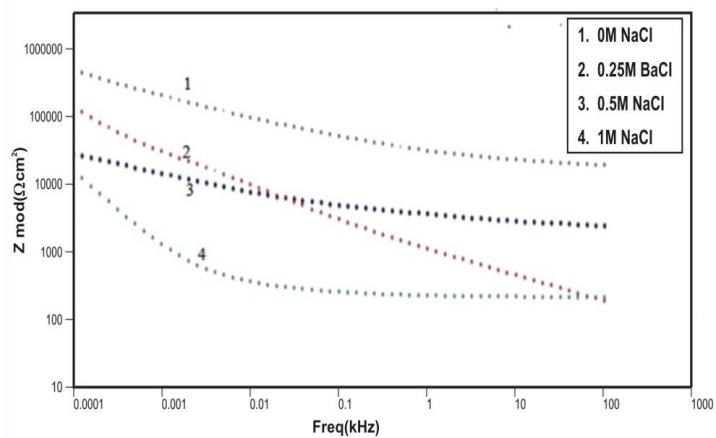


Fig. 10: Bode plot of Polypyrrole coated steel sample after being immersed for 168 hours in pore solution.

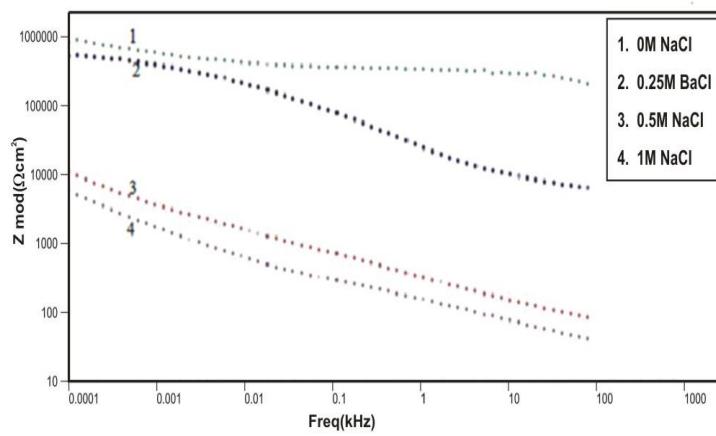


Fig. 11: Bode plot of Polypyrrole coated steel sample after being immersed for 240 hours in pore solution.

Table 9

Polypyrrole coated steel sample: Impedance values

Sr. no	Sodium chloride Concentration	Z _{mod} KΩ·cm ²			
		Immersion time			
		0 hrs	72 hrs	168 hrs	240 hrs

1	Without NaCl	6340	232	25.94	450.6
2	0.25 M NaCl	6340	13.44	10.51	276
3	0.5 M NaCl	6340	8.09	3.27	7.15
4	1M NaCl	6340	7.26	2.19	3.87

Table 10

Polypyrrole coated steel sample: Coating resistance

Sr. no	Sodium chloride Concentration	R _c KΩ-cm ²			
		Immersion time			
		0 hrs	72 hrs	168 hrs	240 hrs
1	Without NaCl	1778	85.54	9.96	177.4
2	0.25 M NaCl	1778	2.31	1.84	128.9
3	0.5 M NaCl	1778	1.98	1.44	5.42
4	1 M NaCl	1778	0.43	0.27	0.95

Table 11

Polypyrrole coated steel sample: Coating capacitance

Sr. no	Sodium chloride Concentration	C _c (μF)			
		Immersion time			
		0 hrs	72 hrs	168 hrs	240 hrs
1	Without NaCl	11.66x10 ⁻⁶	0.4	1.07	0.03
2	0.25 M NaCl	11.66x10 ⁻⁶	1.13	3.82	0.3
3	0.5 M NaCl	11.66x10 ⁻⁶	1.97	22.90	1.81
4	1 M NaCl	11.66x10 ⁻⁶	10.54	584	1.98

As compared to uncoated low carbon steel sample, polypyrrole coated low carbon steel sample exhibits higher impedance (Z_{mod}) \sim 6340 KΩ-cm², higher coating resistance (R_c) \sim 1778 KΩ-cm² and lower capacitance (C_c) \sim 11.66x10⁻⁶ μF just after immersion in pore solution without chloride contents. Higher values of impedance, higher coating resistance and lower coating capacitance can be

attributed to protective nature of conducting polypyrrole as a pigment [7,14-16]. Water molecules and corrosion species penetrate into the coating as a function of immersion time. This is reflected in the lowering of impedance and coating resistance values with associated increase in coating capacitance as a function of time during immersion in pore solution up to 168 hours. Subsequently, impedance (Z_{mod}) and coating resistance (R_C) gets increased to the level of $\sim 450.6 \text{ K}\Omega\text{-cm}^2$ and $177.4 \text{ K}\Omega\text{-cm}^2$ respectively by the end of 240 hours of immersion. However, it must be noted that the impedance values (Z_{mod}) and coating resistance (R_C) decreased and coating capacitance (C_C) increased with increasing chloride contents up to 0.25M NaCl during 168 hours of immersion. The impedance values (Z_{mod}) and coating resistance (R_C) exhibited subsequent increase and coating capacitance (C_C) decreased between 168 to 240 hours of immersion in pore solution (Tables 9, 10 and 11). This significant increase therefore, can be assigned to the self healing effect of conducting polypyrrole as a pigment [7,14,16]. However, at 0.5M NaCl and beyond, a significant decrease in impedance and coating resistance and an increase in coating capacitance is noted. Thus, 0.5M NaCl can be taken as critical concentration even for polypyrrole coated steel samples. Electrochemical impedance results support and validate changes in open circuit potentials of the samples immersed in pore solution (Table 4).

4. Conclusions

Passive film generated on low carbon steel sample in concrete pore solution gets damaged with addition of chloride ions to the simulated pore solution. The corrosion rate of conducting polypyrrole coated low carbon steel sample was found to be 0.09 mpy, about 81 times lower than that of unpainted low carbon steel sample. A shift of 186 mV in the value of the corrosion potential in the positive direction indicates that the polypyrrole based coating imparts corrosion protection by preventing cathodic reduction process i.e. by anodic protection. As compared to uncoated low carbon steel sample, polypyrrole coated low carbon steel sample exhibits higher impedance (Z_{mod}) $\sim 6340 \text{ K}\Omega\text{-cm}^2$, higher coating resistance (R_C) $\sim 1778 \text{ K}\Omega\text{-cm}^2$ and lower capacitance (C_C) $\sim 11.66 \times 10^{-6} \mu\text{F}$, just after immersion in pore solution, without chloride contents. Polypyrrole coated steel sample was able to protect low carbon steel for up to 240 hours of immersion in the pore solution containing no chlorides and in the pore solution containing 0.25M NaCl. However, at 0.5M NaCl & higher concentrations, the self healing ability of polypyrrole coating is no longer applicable to protect steel sample from corrosion.

The novelty of the paint coatings formulated by using polypyrrole pigments is that in case of damage of paint coating in service or handling, a passive film gets generated and protects the underlying metal from further corrosion. Findings in these investigations revealed possibility of using conducting polypyrrole based paint coating system for the protection of rebar in concrete.

Acknowledgments

The Authors thank Prof. N.B. Dhokey, Head, Department of Metallurgy and Materials Science, College of Engineering, Pune, (M.S.) for providing facilities and Prof. B. B. Ahuja, Director, College of Engineering, Pune, (M.S.) for his encouragement.

R E F E R E N C E S

- [1] *A. Bentur, S. Diamond and N. S. Berke* " Steel corrosion in concrete: Fundamentals and Civil Engineering Practice ", E and FN Spon, London, First edition, 1997, p 16.
- [2] *P.K. Mehata and P. J.M. Monteiro*" Concrete Microstructure, properties and materials", Tata McGraw- Hill, New Delhi, Third edition, 2006, pp 21- 47.
- [3] *V. Kumar* " Protection of steel reinforcement for concrete: A review ", Corrosion Reviews, **Vol. 16**, 1998 pp 318-358.
- [4] *S. Dong, B. Zhao, C. Lin, R. Du, R. Hu, G. Hu and G. Zhang*," Corrosion behavoir of epoxy/zinc duplex coated rebar embedded in concrete in ocean environment ", Construction and Building Materials, 28, 2012, pp 72- 87.
- [5] *R. Selvaraj and B. Chuvaneshwari*, "Characterization and Development of organic coatings for steel rebars in concrete", Portugaliae Electrochimica Acta, 27, 2009, pp 657- 670.
- [6]. *F. Tang, G.Chen, R. Brow, J. Volz, M. Koenigstein*, " Corrosion resistance and mechanism steel rebar coated with three types of enamel" Corrosion Science, 59, 2012, pp 157-168.
- [7] *P. Deshpande and D. Sazou* "Corrosion protection of Metals by Intrinsically Conducting Polymers" CRC Press, Boca Raton, First edition, 2015, pp 1- 17.
- [8] *A. El Shazly and H. Al Turaif* " Improving the corrosion resistance of buried steel by using polyaniline coating " Int. J. Electrochem. Sci., **Vol. 7**, 2012, pp 211-221.
- [9] *A. El Shazly, A. Wazzan and T. Radain* " Investigations for the possibility of improving the reinforced concrete corrosion resistance using polyaniline coated steel " Int. J. Electrochem. Sci., **Vol. 7**, 2012, pp 2416-2429.
- [10] *V. Truong, P. Lai, B. Moore, R. Muscat and M. Russo* " Corrosion protection of magnesium by electro active polypyrrole / paint coatings " Synth. Metals, **Vol. 110**, 2000, pp 7- 15.
- [11] *P. Deshpande, S. Vagge, S. Jagtap, R. Khairnar and M. More* " Conducting polyaniline based paints on low carbon steel for corrosion protection " Protection of Metals and Physical Chemistry of Surfaces **Vol. 48**, 2012 pp 356- 360.
- [12] *A. Poursaei*, " Corrosion of steel bars in saturated Ca(OH)₂ and concrete pore solution " Concrete Research Letters, **Vol 1**, 2010, p 90.
- [13] *J. Williamson and O. B. Isgor* " The effect of simulated concrete pore solution composition and chlorides on the electronic properties of passive film on carbon steel rebar" Corrosion Science, 106, 2016, pp 82- 95.
- [14] *T. Ohsuka*, " Corrosion protection of steels by conducting polymer coatings" International Journal of Corrosion, 2012, p4
- [15] *D. Loveday, P. Peterson, B. Rodgers*, " Evaluation of organic coatings with electrical impedance spectroscopy Part I, Journal of Coating Technology,2004, p 48.
- [16] *M. Selvaraj, S. Palraj, K. Maruthan, G. Rajagopal, G. Venkatachari* " Polypyrrole as a protective pigment in organic coatings" Synthetic Metals, 158, 2008, pp 888- 899.