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Scientific paper
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Corrosion behaviour of SS 316 L in artificial saliva in presence of electral

Corrosion resistance of three metals namely, SS 316L, mild steel (MS) and mild steel coated with zinc (MS-Zn) has been evaluated in artificial saliva in the absence and presence of electral. Potentiodynamic polarization study and AC impedance spectra have been used to investigate the corrosion behaviour these metals. The order of corrosion resistance of metals in artificial saliva, in the absence and also in the presence of electral was SS 316L > MS > MS-Zn.

Keywords: Artificial saliva, corrosion, metals, electral, dentistry, oral hygiene

INTRODUCTION

In dentistry, metallic materials are used as implants in reconstructive oral surgery to replace a single teeth or an array of teeth, or in the fabrication of dental prosthesis such as metal plates for complete and partial dentures, crowns, and bridges, essentially in patients requiring hypoallergenic materials. Due to its mechanical properties, good resistance to corrosion in biological fluids and very low toxicity, titanium was the most commonly selected material for dental implants and prosthesis. Corrosion of metallic implants was of vital importance, because it can adversely affect the bio compatibility and mechanical integrity of implants. Many metals and alloys have been used in dentistry. Their corrosion behaviour in artificial saliva have been investigated. Influence of pH and corrosion inhibitors such as citric acid, sodium nitrate and benzotriazole on the tribocorrosion of titanium in artificial saliva has been investigated [1]. Five non-precious Ni-Co based alloys have been analyzed with respect to their corrosion behaviour in artificial saliva [2]. The effect of eugenol on the titanium corrosion in artificial saliva enriched with eugenol at different concentrations has been investigated by [3]. The corrosion resistance of the commercial metallic orthodontic wires in simulated intra-oral environment has been evaluated by Ziebowicz et.al. [4]. Results of corrosion resistance tests of the CrNi, NiTi

and CuNiTi wires showed comparable data of parameters obtained in artificial saliva [4]. The effects of multi-layered Ti/TiN or single-layered TiN films deposited by pulse-biased arc ion plating (PBAIP) on the corrosion behaviour of NiTi orthodontic brackets in artificial saliva have been investigated [5]. Rajendran et al., have studied the corrosion behaviour metals in artificial saliva in presence of spirulina powder [6]. Corrosion behaviour of metals in artificial saliva in presence of D-glucose has been investigated [7].

The present work is undertaken

To study the corrosion behaviour of three metals, namely, mild steel, mild steel coated with zinc and SS316L in artificial saliva, in the absence and presence of electral, by polarization study and AC impedance spectra. Corrosion parameters such as corrosion potential, corrosion current, linear polarization resistance, charge transfer resistance and double layer capacitance have been derived from these studies. Electral is an oral rehydration salt. It is dissolved in water and taken orally. The main objective of the present study is to investigate how the oral intake of an aqueous electral solution affects the orthodontic wires used in dentistry. Hence the corrosion behaviour of three metals, in artificial saliva, in presence of electral is studied. The composition of commercially available electral is given in Tables 1 and 2. This electral powder is used in the present study.

Table 1: Composition of Electral Each Sachet (4.40g) contains

Sodium Chloride	IP	0.52 g
Potassium Chloride	IP	0.30 g
Sodium Citrate	IP	0.58 g
Dextrose anhydrous	IP	2.70 g
Excipients		Qs

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Table 2: Concentration of Electrolytes present in electrol

Electrolytes	MOs mole/litre
Sodium	75
Potassium	20
Chloride	10
Citrate	10
Dextrose	75
Total Osmolarity	24

MATERIALS AND METHODS

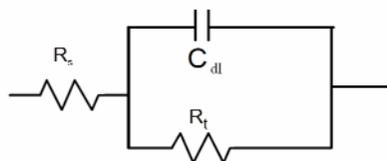
Three metal specimens, namely, mild steel, mild steel coated with zinc (commercial) and SS316L were chosen for the present study. The composition of mild steel is (wt%) 0.026 S, 0.06 P, 0.4 Mn, 0.1 C and balance iron [8]. The composition of SS316L is (wt%): 18 Cr, 12 Ni, 2.5 Mo, <0.03 C and balance iron [9]. The metal specimens were encapsulated in Teflon. The surface area of the exposed metal surface was 0.0875 cm². The metal specimens were polished to mirror finish and degreased with trichloroethylene. The metal specimens were immersed in Fusayama Meyer artificial saliva [3], whose composition is: KCl (0.4 g/l), NaCl (0.4 g/l), CaCl₂·2H₂O (0.906 g/l), NaH₂PO₄·2H₂O (0.690 g/l), Na₂S·9H₂O (0.005 g/l), urea (1 g/l). The pH of the solution was 6.5. [10]

In electrochemical studies, the metal specimens were used as working electrodes. AS was used as the electrolyte. The temperature was maintained at 37 ± 0.1°C.

Commercially available electrol powder (composition given in Tables 1 and 2) was used in this study. 0.5 g of electrol was dissolved in 1 litre of artificial saliva.

Potentiodynamic polarization

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The working electrode was mild steel coated with zinc SS 316 L. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (anodic = b_a and cathodic = b_c) were calculated from Nyquist plots. Impedance, $\log(z/\text{ohm})$ values were calculated from bode plots; The equivalent circuit diagram is shown in Scheme 1.



Scheme 1. Equivalent Circuit Diagram: R_s – Solution resistance, R_t – Change transfer resistance, C_{dl} – Double layer capacitance

AC impedance spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell setup was also the same. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. Values of the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated.

RESULTS AND DISCUSSION

Analysis of potentiodynamic polarization curves

Corrosion behaviour of metals in artificial saliva. The corrosion parameters of various metals such as, mild steel, zinc coated mild steel and stainless steel 316L (SS), immersed in artificial saliva (AS) are given in Table 2. The potentiodynamic polarization curves are shown in Figs. 1 to 3.

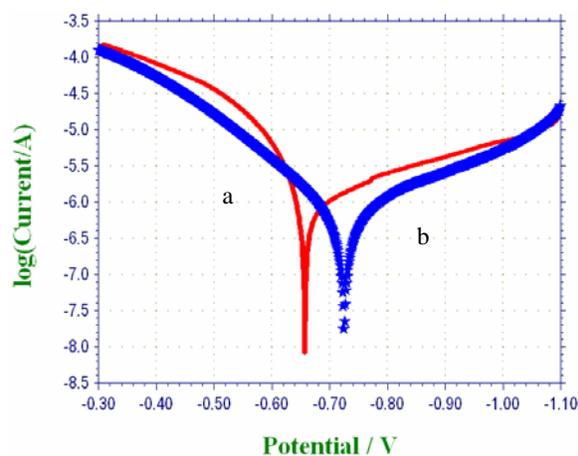


Figure 1. Polarization curves of MS immersed in various test solutions: a) AS, b) AS + electrol

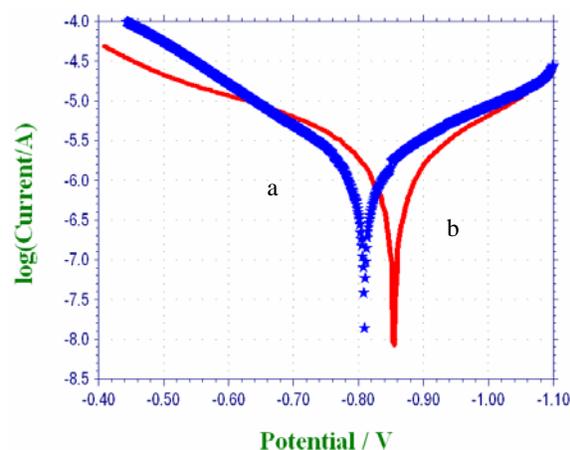


Figure 2. Polarization curves of MS-Zn immersed in various test solutions: a) AS, b) AS + electrol

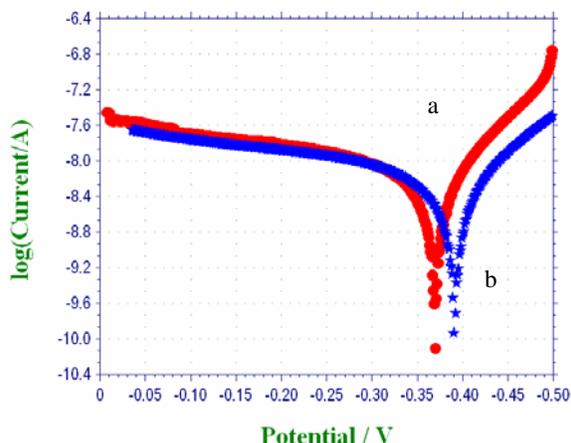


Figure 3. Polarization curves of SS 316L immersed in various test solutions: a) AS, b) AS + electral

When mild steel is immersed in artificial saliva (AS), the corrosion potential is -657 mV vs SCE (Fig.1a). The linear polarization resistance (LPR) is 2.06×10^4 ohm cm^2 and the corrosion current (I_{corr}) is 1.98×10^{-6} cm^2 .

When zinc coated mild steel is immersed in AS, the corrosion potential shifts to the cathodic side (Fig.2a). The LPR value increase to 4.34×10^4 ohm cm^2 and the corrosion current decreases to 9.98×10^{-7} cm^2 . These observations indicate that zinc coated mild steel is more corrosion resistant than mild steel itself. A protective layer is formed on the metal surface.

In the case of mild steel coated with zinc, the cathodic Tafel slope is 187 mV/decade and the anodic Tafel slope is 218 mV/decade. These values suggest that during anodic polarization, the rate of change of corrosion current with potential is high, and it is less during the cathodic polarization.

When SS 316L is immersed in AS, the corrosion potential is shifted to the noble side (-385 mV vs SCE). This suggests that a protective film is formed on the metal surface, when it is immersed in AS. The LPR value is very high 5.52×10^{-6} ohm cm^2 . The corrosion current decreases to a great extent. (8.55×10^{-9} cm^2). The values of Tafel slopes ($b_a = 430$, $b_c = 145$ mV/decade) indicate that the rate of change of current with potential is high during anodic polarization than during cathodic polarization. During cathodic polarization, current remains constant over a potential range.

A comparison of LPR values and corrosion current values of the three metals investigated reveals that SS 316 L is a better candidate to be used in dentistry.

Corrosion behaviour of metals in artificial saliva containing electral

Mild steel (MS): When mild steel was immersed in AS, containing electral, the corrosion potential was shifted to the cathodic side (when compared with the

behaviour of mild steel in AS) (Fig.1b). The cathodic Tafel slope (b_c) value was higher than that of the anodic Tafel slope value. This indicates that the change of current with the change of potential was high in the cathodic region than in the anodic region. This is due to the formation of a protective film on the anodic sites of the metal surface. This prevents the corrosion of metal. It was interesting to note that in the presence of electral, the LPR value increased and corrosion current decreased. It seems that a protective layer was formed on the metal surface which controlled the rate of corrosion of mild steel in AS, in the presence of electral [11-30].

Mild steel coated with zinc (MS-Zn): When mild steel coated with zinc was immersed in AS, containing electral the corrosion potential was shifted to -915 mV vs SCE (Fig.2b). That is corrosion potential was shifted to cathodic side in presence of electral (when compared to the corrosion potential in the absence of electral). The Tafels slopes were $b_c = 182$ mV/decade and $b_a = 239$ mV/decade. That is, rate of change of corrosion current in the cathodic region was less when compared with that in the anodic region. It is interesting to note that in the presence of electral, the LPR value decreased (from 4.34×10^4 to 1.902×10^4 ohms cm^2) and the corrosion current increased (from 9.976×10^{-7} to 2.359×10^{-6} A/ cm^2). That is, in the presence of electral, the corrosion resistance of mild steel coated with zinc decreased.

SS 316 L: In the presence of electral, the corrosion resistance of SS 316 L in artificial saliva decreased. This was revealed by the decrease in LPR value (from 5.518×10^6 to 2.966×10^6 ohm cm^2) and increase in corrosion current (from 8.55×10^{-9} to 1.656×10^{-8} cm^2). The corrosion potential was shifted from -385 to -312 mV vs SCE. The values of Tafel slopes were $b_c = 138$ mV/decade; $b_a = 626$ mV/decade. That is, the rate of change of current with potential was high in the anodic region that in the cathodic region.

Thus polarization study has led to the conclusion that in the presence of electral, the corrosion resistance of

- Mild steel in artificial saliva increased.
- Mild steel coated with zinc in artificial saliva decreased.
- SS 316 L in artificial saliva slightly decreased.

AC impedance spectra

AC impedance parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}) (derived from Nyquist plots) and impedance value $\log(z/\text{ohm})$ (derived from Bode plots), of various metals immersed in artificial saliva and artificial saliva containing electral are given in Table 4. The AC impedance spectra are shown in Figures 4 to 6 (Nyquist plots) and Figures 7 to 9 (Bode plots).

Table 3: Corrosion parameters of metals immersed in artificial saliva (SA) in the absence and presence of electral, obtained by polarization study

Metal	System	E_{corr} mV vs SCE	b_c mV/decade	b_a mV/decade	LPR ohm cm ²	I_{corr} A/cm ²
MS	AS	-657	278	142	2.057×10^4	1.983×10^{-6}
	AS + Electral	-761	199	167	1.025×10^5	3.843×10^{-7}
MS-Zn	AS	-855	187	213	4.340×10^4	9.976×10^{-7}
	AS + Electral	-915	182	239	1.902×10^4	2.359×10^{-6}
SS 316L	AS	-385	145	430	5.518×10^6	8.551×10^{-9}
	AS + Electral	-312	138	626	2.966×10^6	1.656×10^{-8}

Table 4: Corrosion parameters of metals immersed in artificial saliva (AS) in the absence and presence of electral obtained from AC impedance spectra

Metal	System	Nyquist plot		Bode plot
		R_t ohm cm ²	C_{dl} F/cm ²	Impedance log(z/ohm)
MS	AS	779	6.54×10^{-9}	2.92
	AS + Electral	847	6.023×10^{-9}	3.014
MS-Zn	AS	650	7.84×10^{-9}	2.82
	AS + Electral	564	9.045×10^{-9}	2.81
SS 316L	AS	29577	0.17×10^{-9}	4.72
	AS + Electral	60090	8.48×10^{-11}	4.993

Mild steel (MS)

When mild steel was immersed in AS, (Figure 4a) the charge transfer resistance was 779 ohm cm². The double layer capacitance was 6.54×10^{-9} F/cm². The impedance value [log(z/ohm)] was 2.92 (Figure 7a). In presence of electral, (Fig.4b), R_t value increased and C_{dl} value decreased. There was increase in the value of impedance [log(z/ohm)] (Figure 7b). These observations indicated that in the presence of electral in artificial saliva, the corrosion rate of mild steel was reduced, due to the formation of protective film formed on the metal surface. The protective film, probably, consisted of oxides of iron and iron complexes of the active principles present in electral.

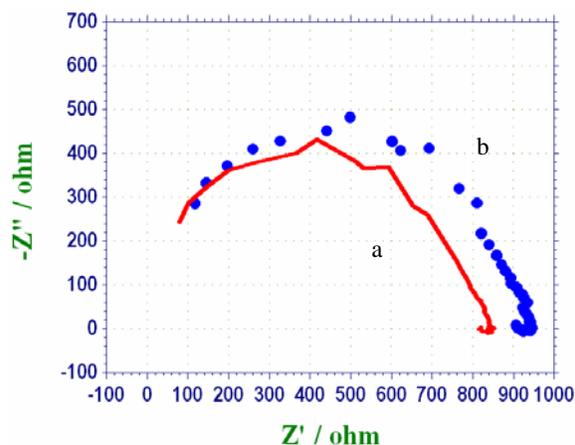


Figure 4. AC impedance spectra (Nyquist plots) of MS immersed in various test solutions: a) AS, b) AS + electral

Mild steel coated with zinc (MS-Zn)

When mild steel coated with zinc was immersed in AS, the charge transfer resistance was 650 ohm cm² (Fig.5a). The double layer capacitance was 7.84×10^{-9} F/cm². The impedance value log(z/ohm) was 2.82.

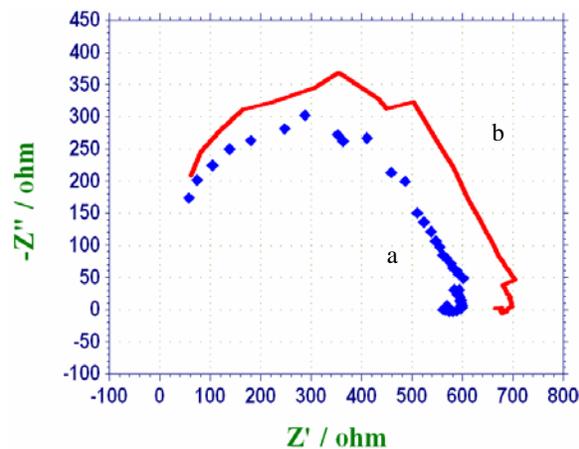


Figure 5. AC impedance spectra (Nyquist plots) of MS-Zn immersed in various test solutions: a) AS, b) AS + electral

When these values are compared with the values of mild steel, it was observed that mild steel coated with zinc was less corrosion resistant (in artificial saliva) than

mild steel. That is the protective film formed on the metal surface was less stable and easily broken by the ions present in AS.

Similar observation was made when mild steel coated with zinc was immersed in AS containing electral (Figure 5b). The R_f value decreased from 650 to 564 ohm cm^2 ; the C_{dl} value increased from 7.84×10^{-9} to 9.045×10^{-9} F/cm²; and the impedance value, $\log(z/\text{ohm})$, decreased from 2.82 to 2.81. This observation suggested that the film formed on mild steel coated with zinc in AS, in the presence of electral was less stable and easily broken by the ions present in AS.

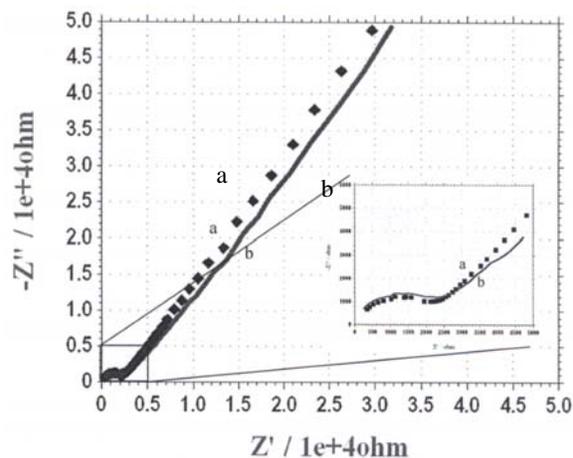


Figure 6. AC impedance spectra (Nyquist plots) of SS 316L immersed in various test solutions: a) AS, b) AS + electral

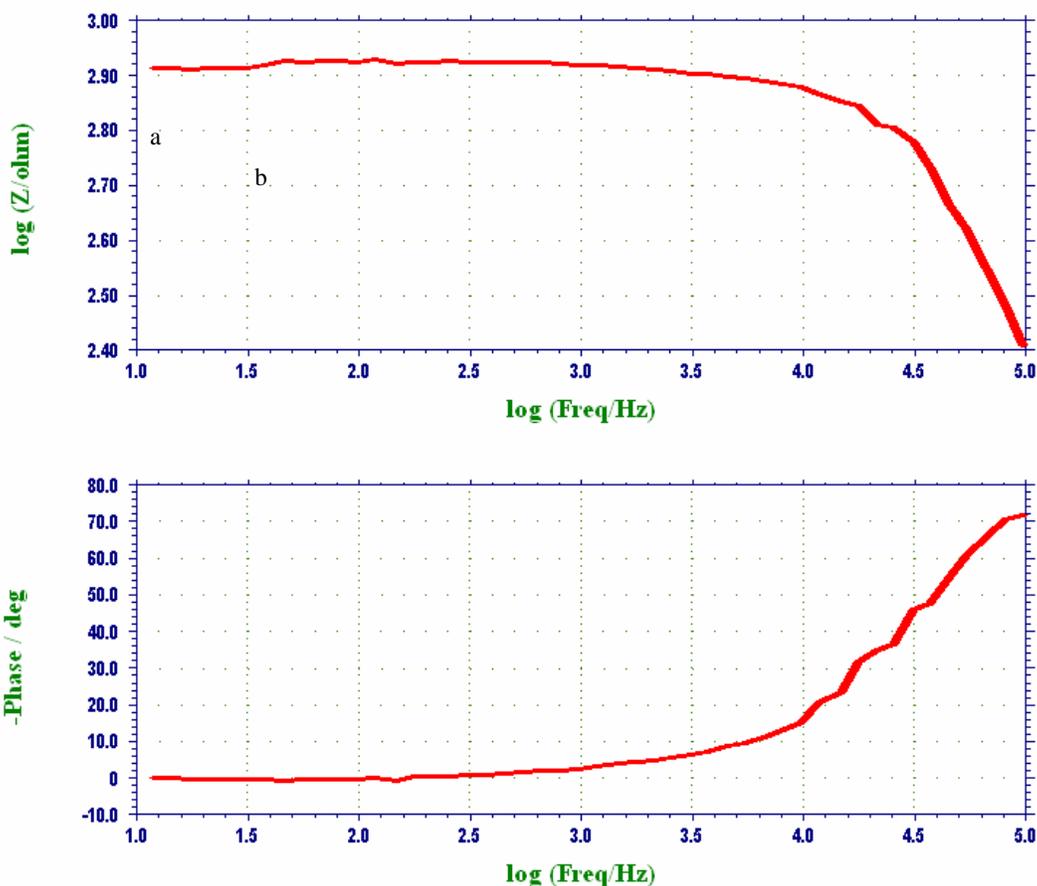


Figure 7. AC impedance spectra (Bode plots) of MS immersed in various test solutions: a) Artificial Saliva

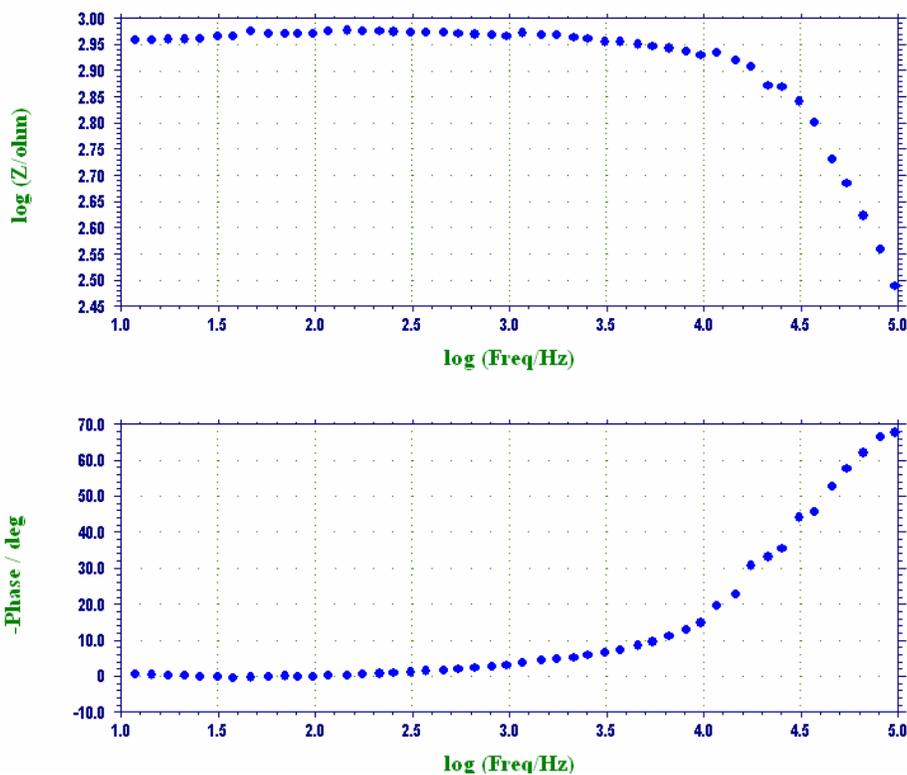


Figure 7. AC impedance spectra (Bode plots) of MS immersed in various test solutions: b) AS + electrical

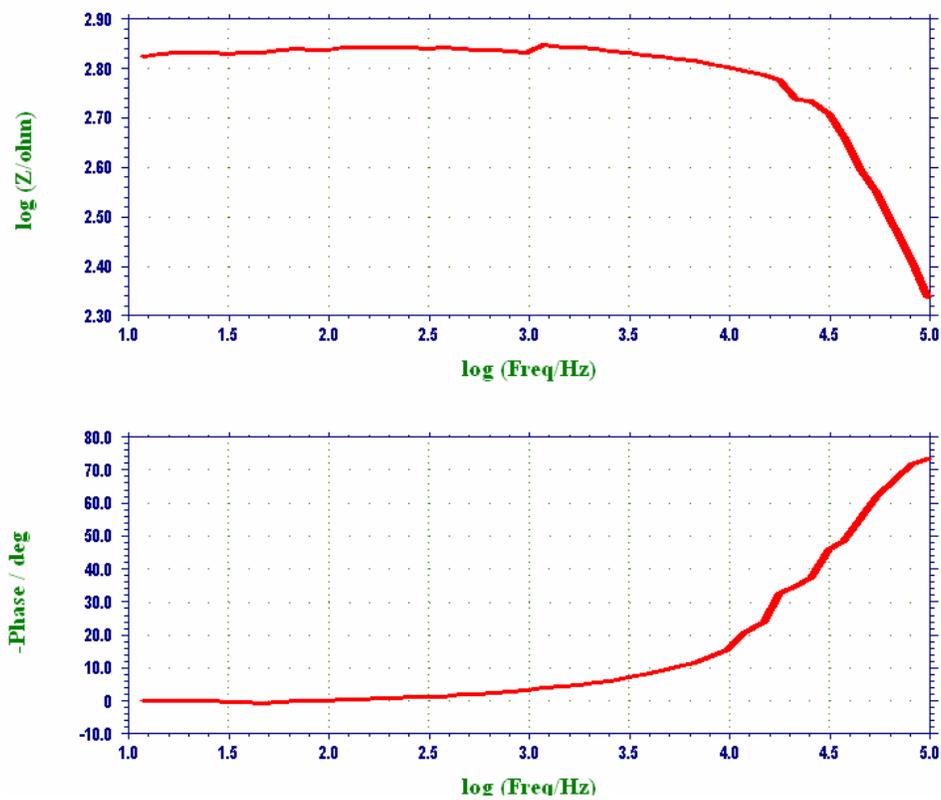


Figure 8. AC impedance spectra (Bode plots) of MS-Zn immersed in various test solutions: a) Artificial saliva (AS)

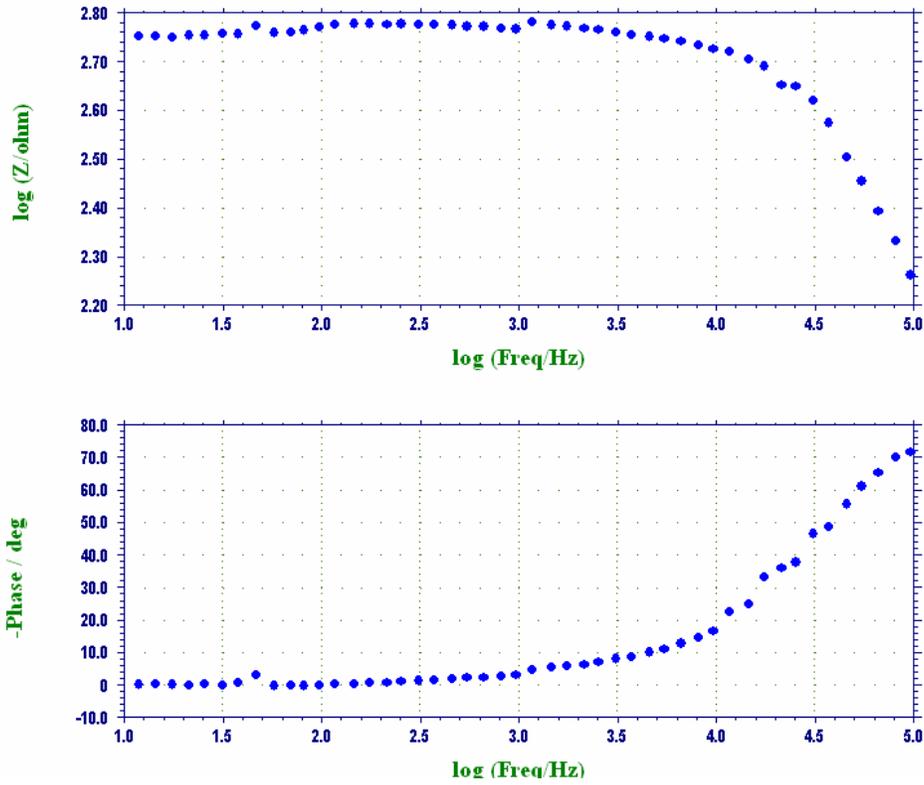


Figure 8. AC impedance spectra (Bode plots) of MS-Zn immersed in various test solutions: b) AS + electrol

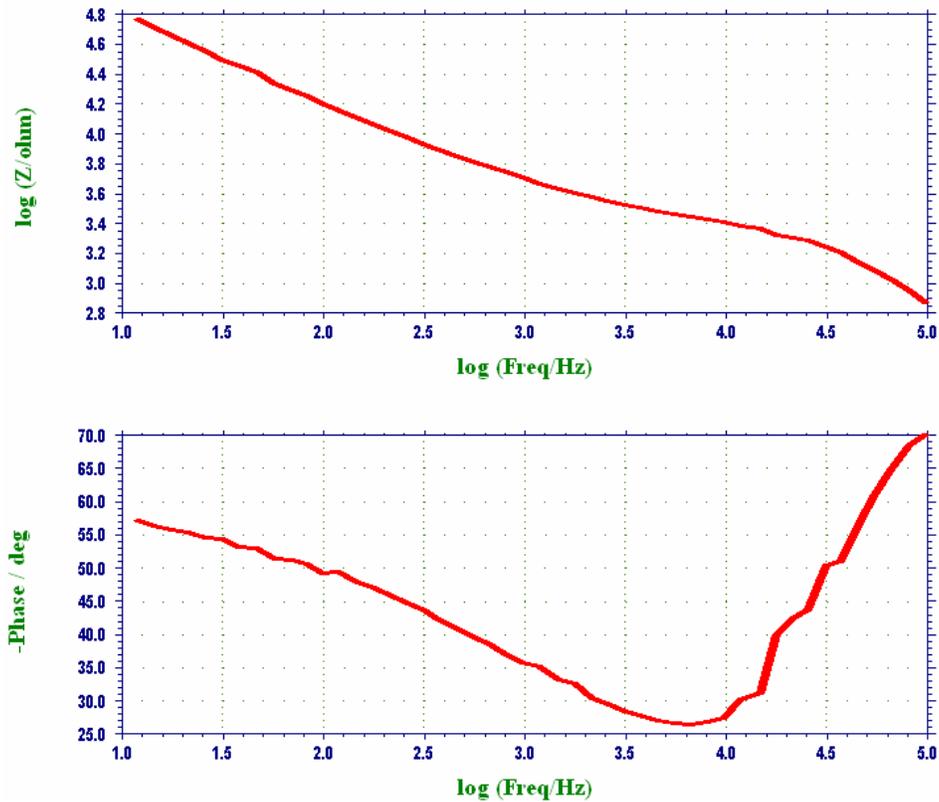


Figure 9. AC impedance spectra (Bode plots) of SS 316L immersed in various test solutions: a) Artificial Saliva

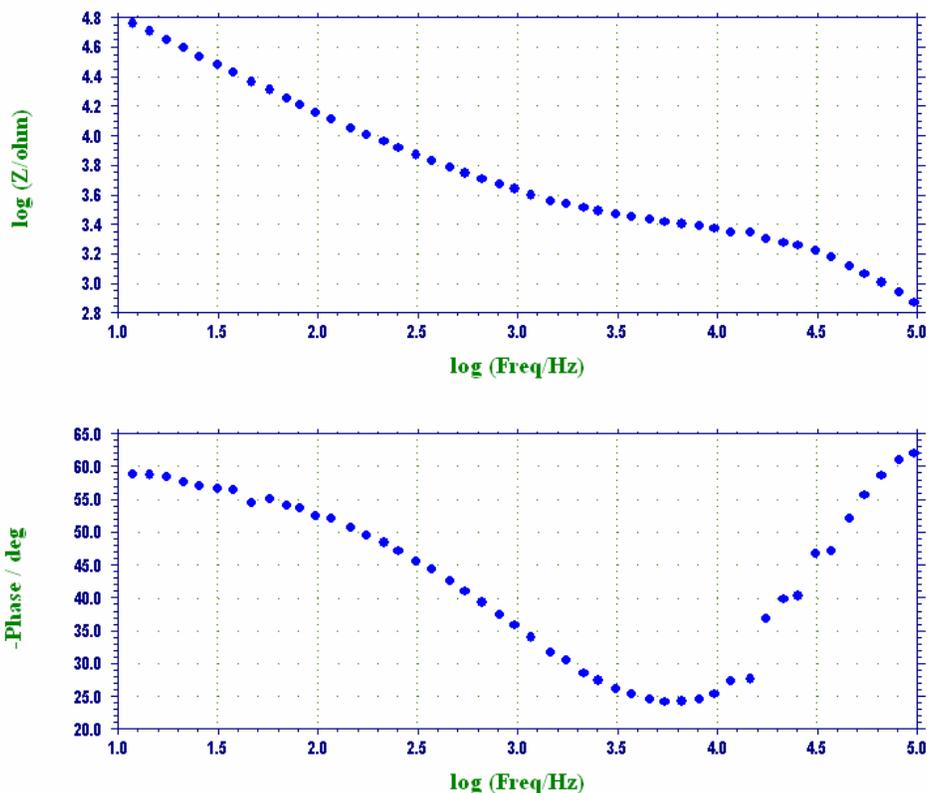


Figure 9. AC impedance spectra (Bode plots) of SS 316L immersed in various test solutions: b) AS + electral

SS 316L

When SS 316L was immersed in AS, the charge transfer resistance was very high, 29577 ohm cm^2 . The double capacitance was very low, $0.17 \times 10^{-9} \text{ F/cm}^2$; and the impedance value $\log(z/\text{ohm})$ was high, 4.72. These observations suggest that the protective film formed on SS 316L was more stable. It was able to withstand the attack of aggressive ions present in AS. SS 316L is a better candidate in artificial saliva, since it is more corrosion resistant, when compared with mild steel and mild steel coated with zinc.

When SS 316L was immersed in AS containing electral the R_t value was 29577 to 60090 ohm cm^2 ; the C_{dl} value decreased from 0.17×10^{-9} to $8.48 \times 10^{-11} \text{ F/cm}^2$; and impedance value increased from 4.72 to $4.993 \log(Z/\text{ohm})$. These values suggested that in the presence of electral in AS, the corrosion resistance of SS 316L increased.

It is interesting to note that as per polarization study SS 316 L is less corrosion resistant in presence of electral in artificial saliva. This can be explained by the fact the protective film formed on the metal surface is more compact the film is more stable it does not allow the electron transfer from metal surface to the bulk of the solution. So the charge transfer resistance increased from 29577 to 60090 ohm cm^2 and the double layer

capacitance decreased from 0.17×10^{-9} to $8.48 \times 10^{-11} \text{ F/cm}^2$.

CONCLUSIONS

The corrosion behaviour of three metals namely, mild steel (MS), mild steel coated with zinc (MS-Zn) and SS 316L have been studied in artificial saliva in the absence and presence of electral. Polarization study has led to the following conclusions.

In the absence of electral, the order of corrosion resistance was:

$$\text{SS 316L} > \text{MS} - \text{Zn} > \text{MS}$$

In the presence of electral, the order of corrosion resistance was :

$$\text{SS 316 L} > \text{MS-Zn} > \text{MS}$$

- SS 316L was less corrosion resistant in the presence of electral than in its absence.
- MS was more corrosion resistant in the presence of electral than in the absence of electral.
- MS-Zn was more corrosion resistant in the absence of electral than in the presence of electral.

AC impedance spectra has led to the following conclusions:

In the absence of electrical, the order of corrosion resistance was:

SS 316L > MS > MS-Zn

In the presence of electrical, the order of corrosion resistance was

SS 316 L > MS > MS -Zn

- SS 316L was more corrosion resistant in the presence of electrical than in the absence of electrical.
- MS was more corrosion resistant in the presence of electrical than in the absence of electrical.
- MS-Zn was more corrosion resistant in the absence of electrical than in the presence of electrical.

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