

# **Influence of 1% tin on the corrosion behaviour of Cu-30Zn brass in sulphide polluted 3.5% NaCl solution**

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## **Abstract**

The effectiveness of 1% tin (Sn) on preventing Cu-30Zn alloys from corrosion in sulphide polluted 3.5% NaCl solution was studied by AC and DC electrochemical techniques. The EIS results showed that a double-loop capacitive circuit could characterize the surface reactions. Moreover, corrosion resistance of surface layer formed on the alloy was remarkably less than the charge transfer resistance. Furthermore, increasing in Na<sub>2</sub>S concentration slightly increases the corrosion rate of alloy, confirming the potentiodynamic polarizations studies. Moreover, tin reduces the corrosion rate by forming SnO<sub>2</sub> as a protecting layer and by shifting corrosion potential toward positive values.

**Keywords: Brass, Tin, EIS, Polarization, Kinetic parameters**

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## 1. Introduction

Brass possesses attractive properties such as good corrosion resistance, good machinability, high thermal and electrical conductivity and better resistance to biofouling. Hence, it is used in water distribution systems, water treatment units, condensers, desalination, petrochemical and heat exchangers in oil and chemical industries, processing plants for electricity generation and desalination plants.

However, brass is susceptible to dezincification [1-4]. When dezincification occurs; regions of brass become replaced by a porous mass of copper, which has no strength. Generally, the preferential dissolution of Zn from Cu–Zn alloys occurs more predominantly with Zn rich than with Cu rich alloys [5].

The dezincification process leads to serious deterioration of the surface and mechanical properties of the remaining alloy. Thus studies on the mechanism of dezincification and the possible ways of preventing this type of corrosion failure have attracted many researchers. Selvaraj et al. [6] have recently reviewed the types of dezincification of brass, the effect of various pollutants, the mechanism of dezincification and its control. Alloying brass with elements like arsenic and/or phosphorous is reported to decrease the dezincification attack [7, 8].

Sulphide pollution of seawater at the coastal areas can occur from industrial waste discharge, biological and bacteriological process in seawater (seaweed, marine organisms or micro organisms, sulphide reducing bacteria), which promotes aqueous corrosion of copper and its alloys [9].

In principle, there are three different methods of preventing or minimizing dezincification: using  $\alpha$ -brass instead of  $(\alpha+\beta)$  brass (but it is expensive and less desirable), thermally treat two-phase brasses ( $\text{Zn}<39\%$ ) to transform them to the

single  $\alpha$ -phase, (again non-cost effective) and the third and presently most economic method to minimize dezincification is to add low levels of suitable elements to the alloy. These elements include arsenic, antimony, boron, phosphorus, tin and aluminium [10]. The effect of arsenic in inhibiting dezincification has two important limitations. First, it is restricted to the  $\alpha$ -brass. Secondly, even small traces of iron or manganese may result in the formation of brittle intermetallic compounds with arsenic. This causes a deterioration of the mechanical properties as well as a reduction in the efficiency of the inhibitor [10, 11]. Tin addition significantly increases the corrosion resistance of some brasses, especially resistance to dezincification [12]. In the present investigation, it is proposed to study the effectiveness of 1% tin (Sn) as the alloying element on the corrosion behaviour of brass in 3.5% NaCl with 50 and 200 mg/L of  $\text{Na}_2\text{S}$ . AC and DC electrochemical techniques including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were used to assess the inhibition efficiency of tin as the alloying element.

## 2. Experimental conditions

The electrodes used for corrosion studies were cut from blocks of Cu-30Zn and Cu-30Zn-1Sn alloys. They were abraded by 60, 220, 400, 600 grit silicon carbide paper respectively, degreased by acetone and rinsed by deionised water. The electrochemical measurements were performed using a potentiostat/galvanostat frequency response analyzer (ACM instruments, UK) and a flat cell. 3.5% NaCl solution was used as the electrolyte medium in which varying concentrations of  $\text{Na}_2\text{S}$  (50, 100 mg/L) were added to study the corrosion behaviour of brass. Only  $0.5 \text{ cm}^2$  of the brass electrode was exposed to the electrolyte solution. A graphite rod and

saturated calomel electrode (SCE) served as the counter and reference electrodes, respectively. All experiments were performed at  $25 \pm 1^\circ\text{C}$ .

LPR measurements were carried out by applying a small sweep from -10 to +10 mV around the rest potential at a scan rate of 1 mV/s after 30 minutes OCP condition. The polarization resistance ( $R_p$ ) and corrosion potential ( $E_{\text{corr}}$ ) values were calculated from this test.

Potentiodynamic polarization measurements were made at a potential scan rate of 60 mV/min. For cathodic polarization curves, the initial potential was shifted to more positive potential by 30–50 mV, and then scanned after about 30 minutes of stabilisation period toward more negative values. The anodic branches were obtained similarly by scanning toward more positive potentials. The corrosion potential ( $E_{\text{corr}}$ ) and corrosion current density ( $i_{\text{corr}}$ ) were determined by the Tafel extrapolation method. Electrochemical impedance (EIS) studies were carried out in the frequency range between 30,000 Hz and 0.01 Hz. The charge transfer resistance ( $R_{\text{ct}}$ ), passive layer resistance ( $R_{\text{pf}}$ ), double layer capacitance ( $C_{\text{dl}}$ ) and passive layer capacitance ( $C_{\text{pf}}$ ) were determined from the Nyquist plot by fitting the data using EIS spectrum analyser software. All the mentioned tests have been done after open circuit conditions to reach steady state.

### 3. Results and discussion

#### 3.1. LPR tests

From the LPR tests, the  $E_{\text{corr}}$  and polarization resistance values were obtained for two specimens in different solutions. Figure1 (a) and figure1 (b) present the variation of polarization resistance and  $E_{\text{corr}}$  respect to the various sulphide concentrations in 3.5% NaCl solution respectively. It is evident from Fig.1 that the addition of  $\text{Na}_2\text{S}$  shifted

the  $E_{\text{corr}}$  toward more negative values from -283 to -352 mV vs. SCE for Cu-30Zn

and from -256 to -281 mV vs. SCE for 1% Sn sample when the sulphide concentration changed from 0 to 200 mg/L. Moreover, the  $R_p$  values decreased from 4700 to 2532 ohm.cm<sup>2</sup> for Cu-30Zn alloy and from 6100 to 3106 ohm.cm<sup>2</sup> for 1% Sn sample when the sulphide concentration changed from 0 to 200 mg/L. The extent of shift in  $E_{\text{corr}}$  and the decrease in  $i_{\text{corr}}$  is found to be a function of the concentration of Na<sub>2</sub>S; higher concentration of Na<sub>2</sub>S leads to higher shift in  $E_{\text{corr}}$  and more decrease in  $R_p$  values. The potential shift towards more negative values may happen if the anodic dissolution of brass is accelerated by the action of sulphide as well as the decrease of the cathodic reaction [13].

Moreover, it is obvious from Fig.1 that 1% Sn specimen has greater  $R_p$  and more positive  $E_{\text{corr}}$  values than Cu-30Zn alloy in all solution.

### 3.2. Polarization curves

The cathodic and anodic polarization curves were plotted separately from a potential close to  $E_{\text{corr}}$  in absence and presence of various concentrations of Na<sub>2</sub>S. Figures 2 and 3 present the obtained results.

The corrosion potential ( $E_{\text{corr}}$ ) and corrosion current density ( $i_{\text{corr}}$ ) were calculated using the Tafel extrapolation method as given in Table1. It can be seen in Fig.2 (a) that the addition of sulphide decreased substantially the Tafel slope of Cu-30Zn sample but it didn't have significant effect on the 1% Sn sample (Fig.2 (b)).

The  $E_{\text{corr}}$  obtained from these curves are almost in agreement with the results that we obtained from LPR tests. It is evident from figures 2 and 3 that there is a decrease in  $E_{\text{corr}}$  values by increasing the amount of sodium sulphide. Moreover, Cu-30Zn alloy has lower  $E_{\text{corr}}$  values than 1% Sn sample in absence and presence of various

concentrations of Na<sub>2</sub>S. Figure 2 shows that the cathodic current density increased by addition of sodium sulphide, from 9 to 18  $\mu\text{A}/\text{cm}^2$  for Cu-30Zn alloy and from 6 to 11  $\mu\text{A}/\text{cm}^2$  for 1% Sn sample when the sulphide concentration changed from zero to 200 mg/L in 3.5% NaCl solution.

Fig. 3 presents the anodic branches of polarization curves of two specimens. The current maximum is explained as well by the formation of CuCl and Cu<sub>2</sub>O film that protects the brass from a further dissolution as the diffusion limiting current by CuCl<sub>2</sub><sup>-</sup> [13].

The current density increased slightly with addition of sodium sulphide, from 3.2 to 7  $\mu\text{A}/\text{cm}^2$  for Cu-30Zn alloy and from 1.9 to 4.6  $\mu\text{A}/\text{cm}^2$  for 1% Sn specimen when the sulphide concentration changed from zero to 200 mg/L in 3.5% NaCl solution.

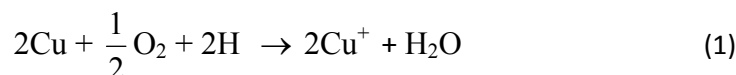
The sulphide added into the solution increased both cathodic and anodic current density, so both anodic and cathodic reactions are catalyzed by sulphide ions [14]; Moreover, 1% Sn sample has lower values of cathodic and anodic current density than Cu-30Zn alloy. Sn as the alloying element produces SnO<sub>2</sub> film [10] that may prevent 1% Sn sample from anodic dissolution and increases its corrosion potential toward noble values.

### 3.3. Pourbaix diagrams

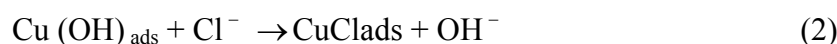
To compare the influence of sulphide ions and Sn on phase stability regions, thermodynamics calculations were performed and multi-component Pourbaix diagrams including chloride and sulphide species were drawn by Medusa (thermodynamic software) [15] as shown in Fig.4.

According to Pourbaix diagrams (Fig.4(a)), in the pH range between 7.5 to 8.5 (our experimental pH range) and the corrosion potential range of our specimens in 3.5% NaCl with sodium sulphide, main products of Cu are  $\text{Cu}_2\text{S}$  and  $\text{CuCl}_2^-$  formed by following reaction:

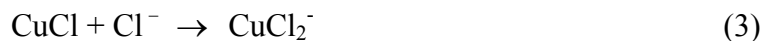
Copper can be oxidized in such a manner [16]:



$\text{Cu}^+$  can be present as  $\text{Cu}(\text{OH})_{\text{ads}}$  or  $\text{Cu}_2\text{O}$  and chloride ions can adsorb on the  $\text{Cu}(\text{OH})_{\text{ads}}$  film to form an adsorbed complex[16]:



When the activity of  $\text{CuCl}_2^-$  in the outer Helmholtz plane exceeds the solubility equilibrium, the following reaction occurs [16]:



In the present of  $\text{S}^{2-}$  we can have the following reactions [13]:



Considering the equations (1) and (4), following reaction can happen:

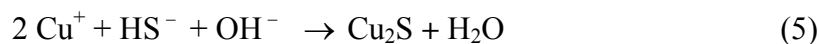


Figure 4(a) shows that lower  $E_{\text{corr}}$  values lead to higher amount of  $\text{Cu}_2\text{S}$  formed on the surface of the alloy and increase the corrosion rate. Moreover, Cu-30Zn alloy has more negative corrosion potential than 1% Sn sample so it has larger corrosion rate and this is in agreement with our results. Moreover, it is clear from Fig.4 (b) that in the pH range between 7.5 to 8.5 (our experimental pH range) and the corrosion



potential range of our specimens in 3.5% NaCl with and without sodium sulphide, Sn as the alloying element produces SnO<sub>2</sub> film [10] that may prevent 1% Sn sample from anodic dissolution and increases its corrosion potential toward noble values. Thus in presence of sulphide, corrosion rate and the amount of sulphide compound formed on the surface of 1% Sn sample are less than Cu-30Zn alloy.

### 3.4. Electrochemical impedance spectroscopy

The corrosion behaviour of brass in 3.5 % NaCl with and without various concentrations of Na<sub>2</sub>S was investigated by the AC impedance method at room temperature (25°C). Figure 5 presents Nyquist plot of impedance spectra of brass samples for different Na<sub>2</sub>S concentrations in 3.5% NaCl solution. The data collection was performed after 30 minutes of stabilisation time.

The equivalent circuits consist of solution resistance (R<sub>e</sub>) connected in series with two time constants R1 [P1 (R2P2)] presented in Fig5. The symbol P signifies the possibility of a non-ideal capacitance (CPE, constant phase element) with varying n. The impedance of the CPE is given by [17]:

$$P = Z_{CPE}(\omega) = [C_i \omega^n]^{-1} \quad (6)$$

For n = 1, the P element reduces to a capacitor with a capacitance C and, for n = 0, to a simple resistor. In the first process (R1P1) at higher frequencies in our solution, parameter P1 represents the capacitive behaviour at the electrolyte/metal interface (i.e. the double layer) and R1 represents the corresponding charge transfer resistance. In the second detected process, P2 represents the capacitive behaviour of the passive film formed, coupled with resistance due to ionic paths through oxide film R2.



In order to study the change in capacitance of the film formed and the double layer,

the capacitance was calculated from P using the equation  $C = [R^{1-n} P]^{1/n}$  [17]. The values of  $n_1$  and  $n_2$  were almost independent of solutions and were equal to 0.6 and 0.85 respectively. Moreover, solution resistance ( $R_e$ ) was approximately  $5 \Omega \cdot \text{cm}^2$  and the values of  $C_1$ ,  $R_1$ ,  $C_2$  and  $R_2$  were presented in Fig. 6.

Figure 6(a) shows that 1% Sn sample has higher values of  $R_1$  than Cu-30Zn in all solution.  $R_1$  values decreased from  $5949 \text{ ohm} \cdot \text{cm}^2$  in absence of sulphide to  $2600 \text{ ohm} \cdot \text{cm}^2$  in the present of 200 mg/L sulphide concentration for 1% Sn sample and from  $4378 \text{ ohm} \cdot \text{cm}^2$  in absence of sulphide to  $2273 \text{ ohm} \cdot \text{cm}^2$  in the present of 200 mg/L sulphide concentration for Cu-30Z alloy. Moreover,  $C_1$  values increased from  $68 \mu\text{F} \cdot \text{cm}^{-2}$  in absence of sulphide to  $254 \mu\text{F} \cdot \text{cm}^{-2}$  in the present of 200 mg/L sulphide concentration for 1% Sn sample and from  $89 \mu\text{F} \cdot \text{cm}^{-2}$  in absence of sulphide to  $298 \mu\text{F} \cdot \text{cm}^{-2}$  in the present of 200 mg/L sulphide concentration for Cu-30Z (Fig.6 (b)).  $\text{Cu}_2\text{S}$  is an electronic conducting species, thus gives rise to a double layer capacitance [13]. The sulphide ions actually increased the corrosion current density. Moreover, it is found from Fig.6(c) that  $R_2$  values increased with sulphide concentration from  $137 \text{ ohm} \cdot \text{cm}^2$  in absence of sulphide to  $600 \text{ ohm} \cdot \text{cm}^2$  in the present of 200 mg/L sulphide concentration for 1% Sn sample and from  $196 \text{ ohm} \cdot \text{cm}^2$  in absence of sulphide to  $549 \text{ ohm} \cdot \text{cm}^2$  in the present of 200 mg/L sulphide concentration for Cu-30Z alloy. Higher sulphide concentration leads to higher amount of corrosion products accumulated on the surface of electrode and increases the thickness of film formed and grows  $R_2$  values and considering the equation  $C_{ct} = \frac{\epsilon_o \epsilon}{d} S$  [18] (where  $d$  is the thickness of the surface film,  $S$  is the

surface of the electrode,  $\epsilon_o$  is the permittivity of air and  $\epsilon$  is the local dielectric

constant ) decreases C2 values from 98 to 51  $\mu\text{F.cm}^{-2}$  for 1% sample and from 79 to 40  $\mu\text{F.cm}^{-2}$  for Cu-30Z alloy when the sulphide concentration changed from 0 to 200 mg/L (Fig.6(d)). However, growing R2 values dose not have significant effect on corrosion rate due to low values of R2 in comparison to R1 values.

#### 4. Conclusions

The corrosion rate of Cu-30Zn alloys in 3.5% chloride solution rises as the sulphide concentration increases and the corrosion potential is shifted toward more active values.

The presence of Sn in the Cu-30Zn alloys decreases the corrosion rate slightly and shifts corrosion potential toward more noble values.

According to Pourbaix diagrams, in the presence of Sn, the amount of sulphide compound decreases on the surface of Cu-30Zn-1Sn alloy and  $\text{SnO}_2$  compound formed on the surface of Cu-30Zn-1Sn alloy may prevent 1% Sn sample from anodic dissolution and increases its corrosion potential toward noble values.

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Figure 1 (a) Polarization resistance and (b).  $E_{\text{corr}}$  values for Cu-30Zn and Cu-30Zn-1Sn alloys in 3.5% NaCl solution with 50 and 200 mg/L of  $\text{Na}_2\text{S}$

Figure 2 Cathodic polarization curves for Cu-Zn alloys in 3.5% NaCl in presence of different concentration of  $\text{Na}_2\text{S}$  (a) Cu-30Zn, (b) Cu-30Zn-1Sn

Figure 3 Anodic polarization curves for Cu-Zn alloys in 3.5% NaCl in presence of different concentration of  $\text{Na}_2\text{S}$  (a) Cu-30Zn sample, (b) Cu-30Zn-1Sn sample

Figure 4 Pourbaix diagrams of (a) Cu in 3.5% NaCl with 50 and 200 mg/L  $\text{Na}_2\text{S}$  (in both cases the diagram is the same) and (b) Sn in 3.5% NaCl with 0, 50 and 200 mg/L of  $\text{Na}_2\text{S}$  (in all three cases the diagram is the same),  $T=25^\circ\text{C}$

Figure 5 Nyquist plots recorded for Cu-30Zn and Cu-30Zn-1Sn in 3.5% NaCl in addition of sulphide at different concentrations after 30 min of stabilisation time at the open circuit conditions

Figure 6 Effect of sulphide concentration on the elements of (a) charge transfer resistance, (b) double layer capacitance, (c) passive layer resistance and (d) passive layer capacitance of Cu-30Zn and Cu-30Zn-1Sn

Table 1 Corrosion parameters of samples in 3.5% NaCl in presence of different sulphide concentrations obtained from polarisation curves

Sample	Na <sub>2</sub> S (mg/L)	Cathodic		Anodic	
		E <sub>corr</sub> (mV) vs.SCE	i <sub>corr</sub> (μA/cm <sup>2</sup> )	E <sub>corr</sub> (mV) vs.SCE	i <sub>corr</sub> (μA/cm <sup>2</sup> )
Cu-30Zn	0	-288	9	-290	3.2
	50	-368	14	-407	3.8
	200	-301	18	-331	7
Cu-30Zn-1Sn	0	-221	6	-255	1.9
	50	-237	8	-277	2.7
	200	-267	11	-289	4.6

Figure 1(a) Polarization resistance and (b)  $E_{\text{corr}}$  values for Cu-30Zn and Cu-30Zn-1Sn alloys in 3.5% NaCl solution with 0, 50 and 200 mg/L of  $\text{Na}_2\text{S}$

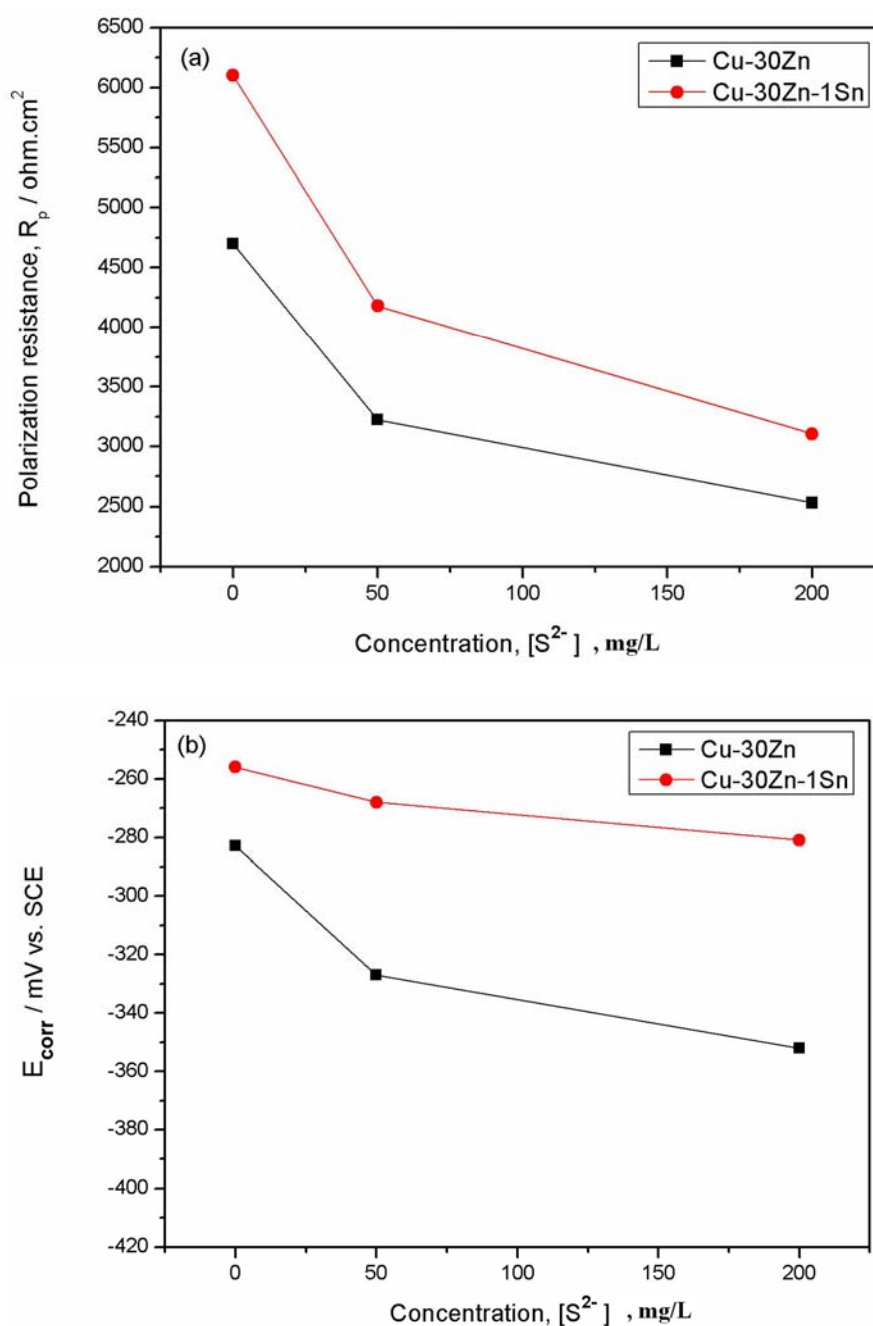




Figure 2 Cathodic polarization curves for Cu-Zn alloys in 3.5% NaCl in presence of different concentrations of  $\text{Na}_2\text{S}$  (a) Cu-30Zn, (b) Cu-30Zn-1Sn

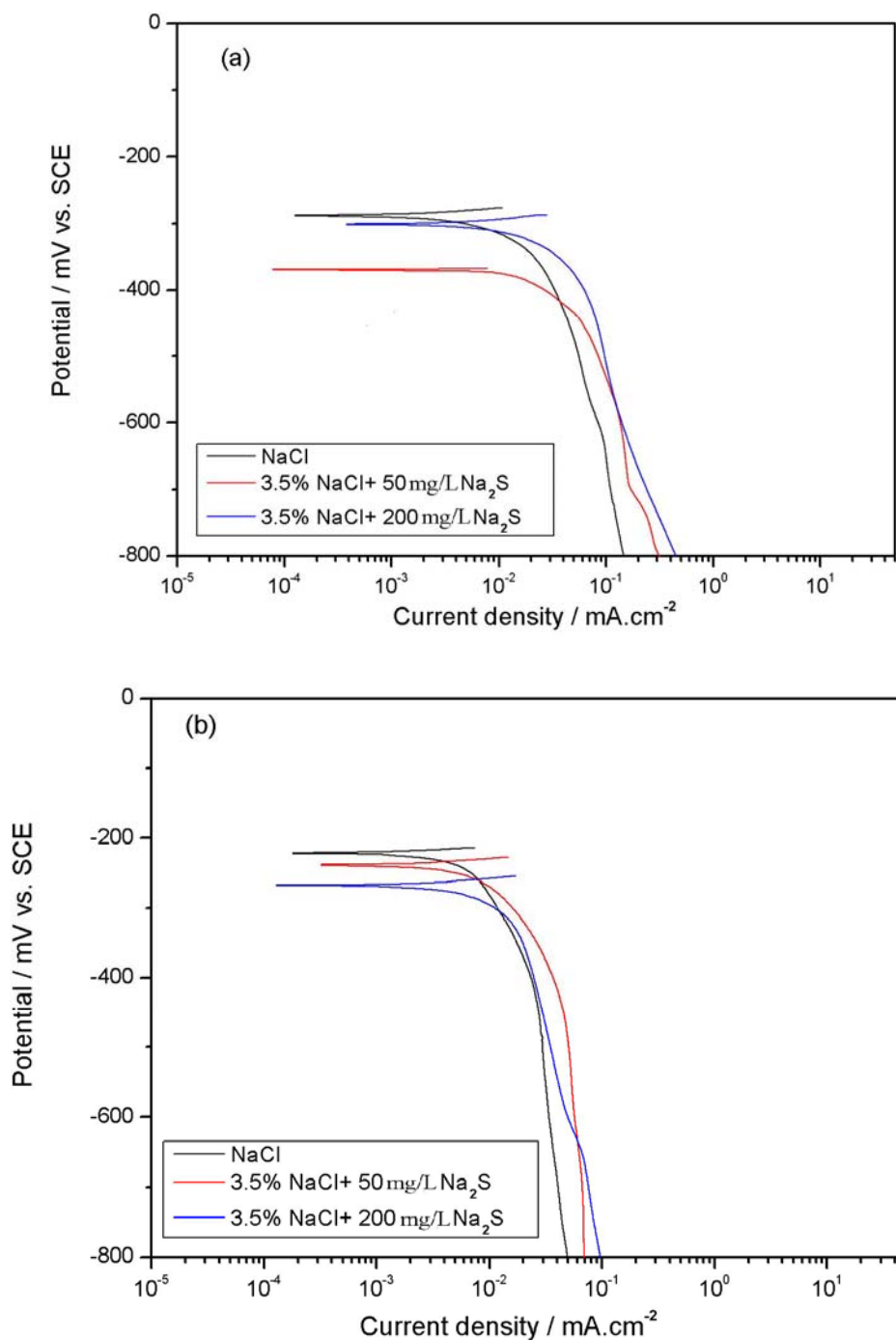


Figure3 Anodic polarization curves for Cu-Zn alloys in 3.5% NaCl in presence of different concentrations of  $\text{Na}_2\text{S}$  (a) Cu-30Zn, (b) Cu-30Zn-1Sn

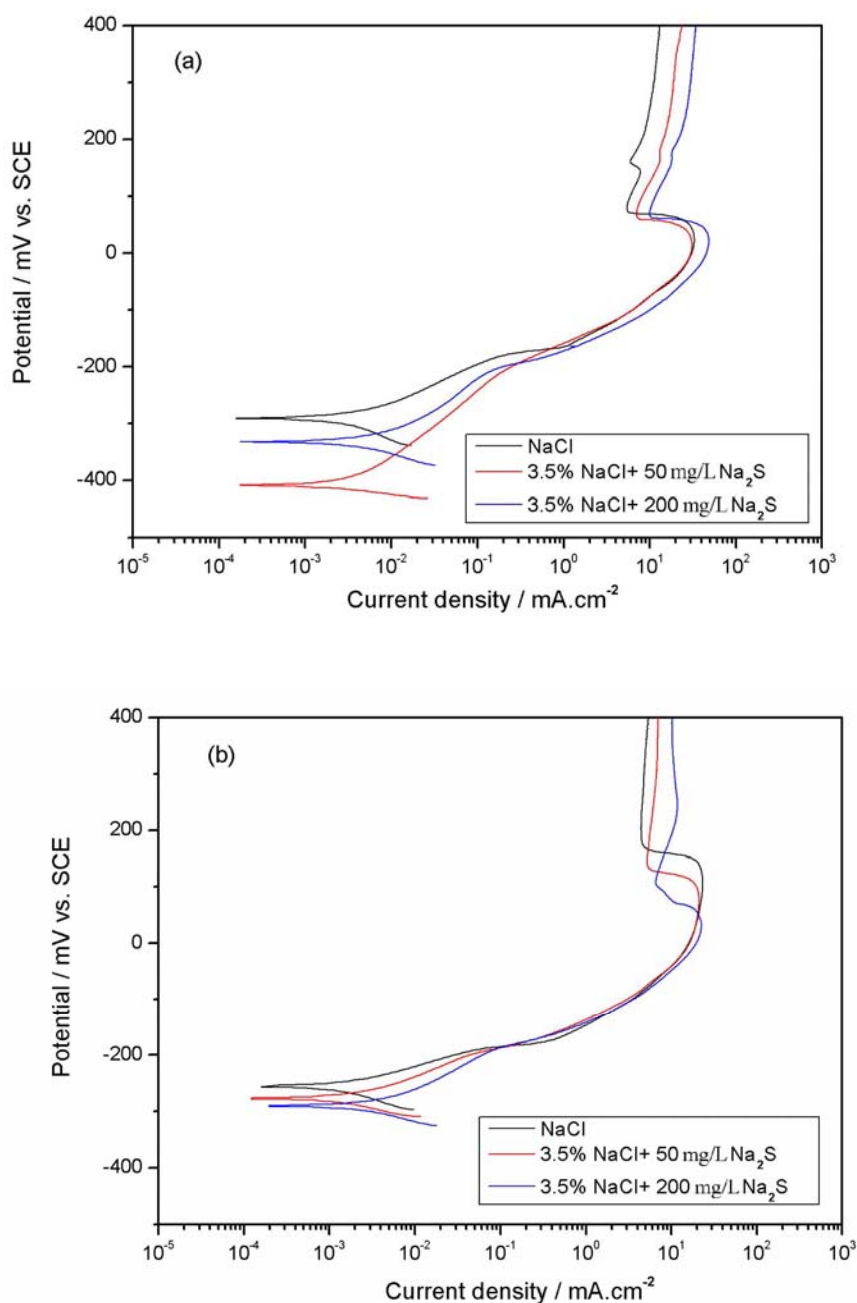


Figure 4 Pourbaix diagrams of (a) Cu in 3.5% NaCl with 50 and 200 mg/L  $\text{Na}_2\text{S}$  (in both cases the diagram is the same) and (b) Sn in 3.5% NaCl with 0, 50 and 200 mg/L of  $\text{Na}_2\text{S}$  (in all three cases the diagram is the same),  $T=25^\circ\text{C}$ .

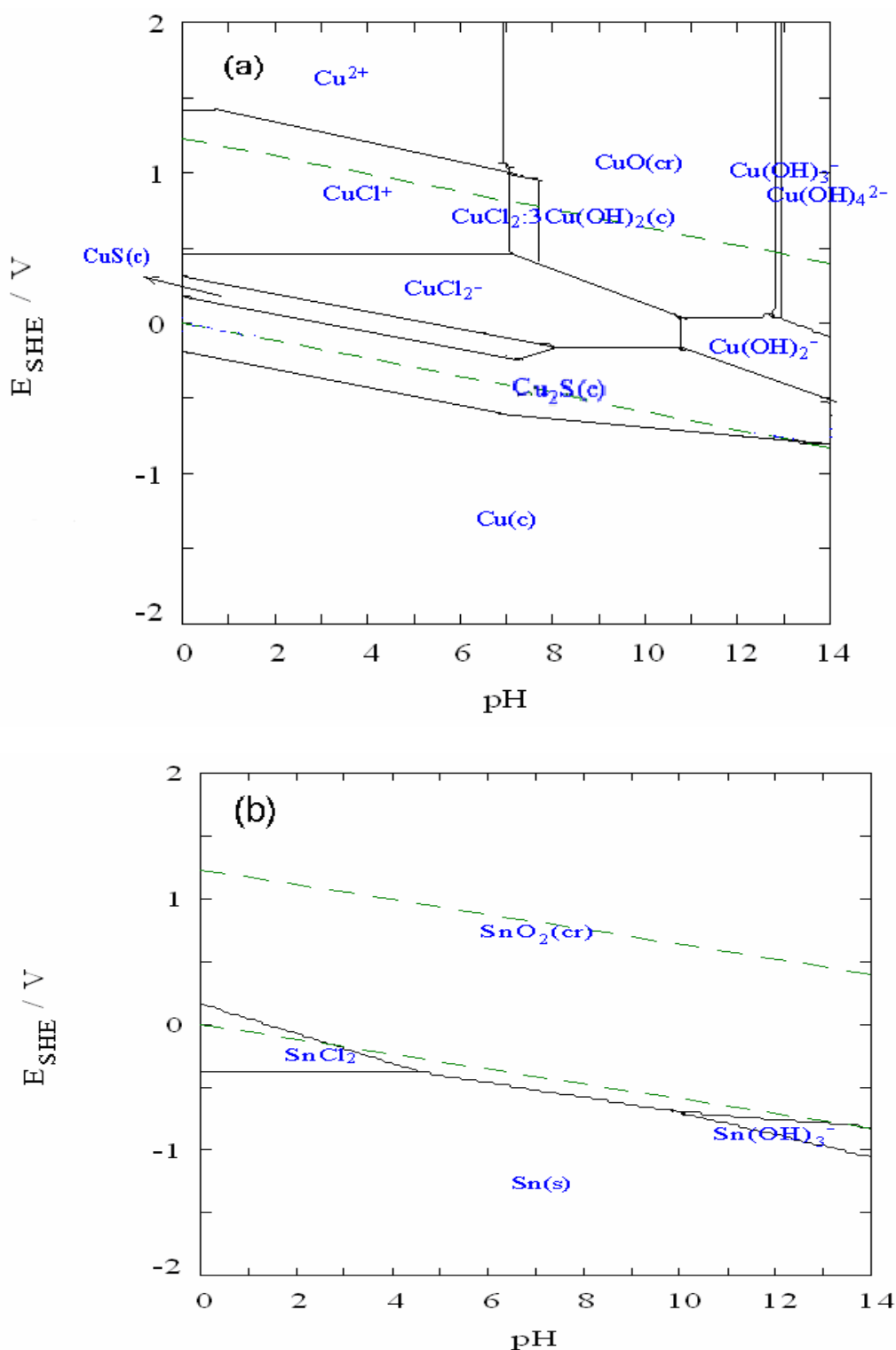


Figure 5 Nyquist plots recorded for Cu-30Zn and Cu-30Zn-1Sn in 3.5% NaCl in addition of sulphide at different concentrations after 30 minutes of stabilisation time at the open circuit conditions.

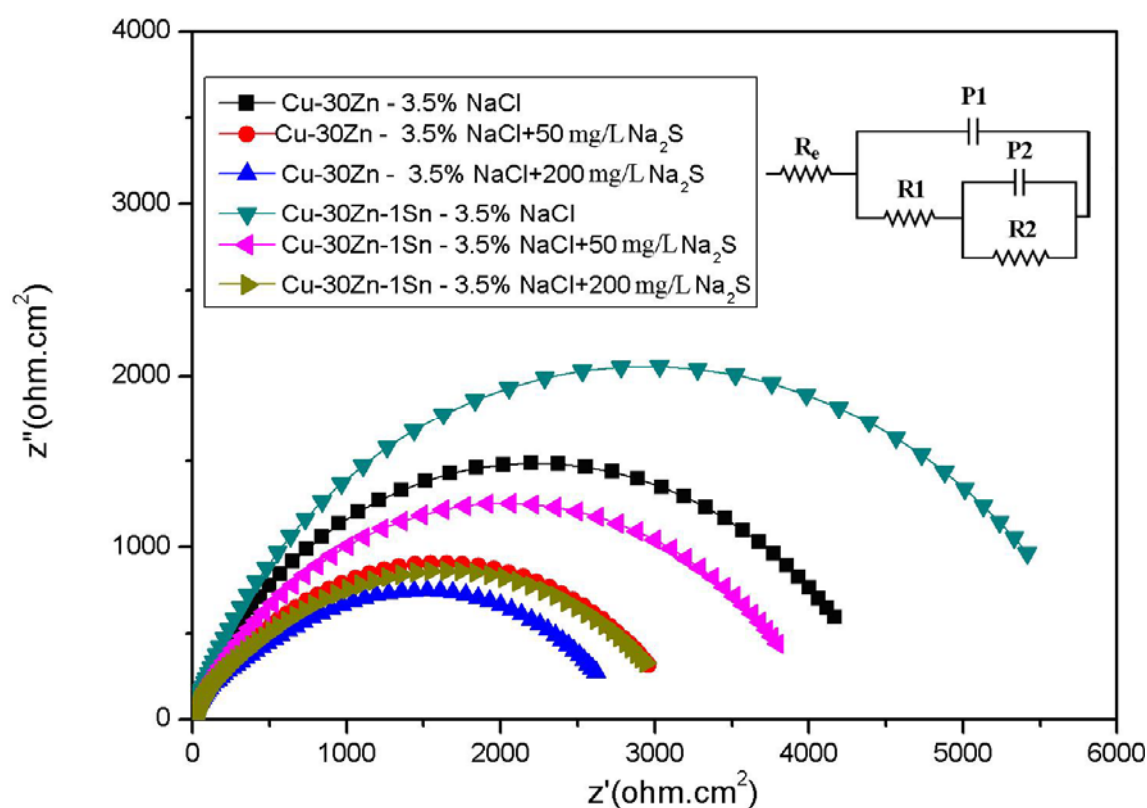


Figure 6 Effect of sulphide concentration on the (a) charge transfer resistance (b) double layer capacitance (c) passive layer resistance and (d) passive layer capacitance of Cu-30Zn and Cu-30Zn-1Sn alloys

