

## The effect of halo-complex [copper (I) chloride] on corrosion behavior of 316 L stainless steel in 1M different halides solutions

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### Abstract

Aggressive halides environments (1M KCl and 1 M KBr solutions) were employed. Evaluation is based on results of scanning electron microscope (SEM), exposition immersion tests (weight loss measurements) and open-circuit potential measurements performed in 1M of different halides solutions (free of halo-complex) and in presence of different concentrations ( $5 \times 10^{-3} - 1 \times 10^{-2}$  M) of copper (I) chlorides (halo-complex). The results indicate that, the increase of halo-complex concentration leads to decrease corrosion rate and increases the IE% values. Examination of 316L stainless steel surface was conducted by using the scanning electron microscopes where it revealed that the presence of halo-complex inhibit the corrosion of 316 stainless steel in 1M halides solutions.

**Keywords:** Halo-complex, halides environments, 316L stainless steel

### 1- Introduction

Many passive metals, when exposed to the action of aggressive anions, undergo a type of localized corrosion known as pitting [1]. pitting corrosion of 316L stainless steel is of great practical interest, it can be a destructive form of corrosion in engineering structures if it causes perforation of equipment. Most equipment failures in stainless steel used by pitting corrosion, which is caused by chloride ions [2,3].

Stainless steel has found very wide applications both in modern chemical industries and other places such as desalination plants, construction materials, pharmaceutical industry thermal power plants, chemical cleaning and pickling

process due to high strength, workability and weld ability [4].

The anticorrosive properties of the stainless steel materials which a chromium contained higher than 12% are assigned to the spontaneous formation on the surface of a passive thin film layer, mainly composed of chromium and iron oxide/hydroxides [5].

Aggressive ions present in solution can penetrate through the weakened places of surface passive film and cause its local breakdown and initiation of the pitting corrosion [6]. Chloride are the most common aggressive anions present in industrial environments [7]. However, there are a few research conducting the behavior of stainless steel in iodide solution combined with varying of working temperature [8-14] and

their studies shows that the higher pitting potential of stainless steel alloys found in the  $\Gamma$  and  $\text{Br}^-$  ion compared to lower value in  $\text{Cl}^-$  containing solution with the fact that the more strong adsorption ability seem to be less aggressive anion. The aggressiveness of pitting corrosion caused by halide ion in terms of  $E_{\text{pit}}$  was in the order of  $\text{Cl}^- > \text{Br}^- > \Gamma$  under different experimental conditions and alloys composition was proved in several investigation [15-18].

Inhibitor is a keyword in the case of corrosion prevention by changing the chemistry of corrosive media. The use of inhibitors is one of the most practical methods for protection against corrosion especially in acidic conditions [19]. The adsorption of inhibitors depends of several factors such as type of acid, distribution of charge in molecule, nature and surface charge of metal and type of interactions between inhibitors and metallic surface [20, 21]. However, studies about metal complexes as corrosion inhibitor for steels in acid solution appeared in the literature are extremely limited [22, 23]. Abdel-Gaber *et al.* [24] proposed the corrosion inhibition through a bulky Co(III) Schiff base complex molecule could cover more than one active site, where carbon steel was immersed in  $\text{H}_2\text{SO}_4$  solution. Cobalt complexes as a corrosion inhibitor for 316 L stainless steel in  $\text{H}_2\text{SO}_4$  solution have been investigated [25].

The aim of the present work is the comparison of aggressiveness behavior of different halides solutions and the

investigation of the inhibition behavior of halo-complex [Cu(I) chloride] for 316 L stainless steel.

## 2- Experimental

### 2.1. Materials

Halo-complex [copper (I) chloride] was synthesis by reduction of copper (II) sulfate with sodium sulphite [26]. Different concentrations of [copper (I) chloride] were prepared ( $5 \times 10^{-3} - 1 \times 10^{-2}\text{M}$ ). 1M different halides solutions (KCl and KBr) were prepared from A.R. chemicals and de-ionized water. Freshly polished electrode used for each run. All solutions used under aerated condition and at room temperature. 316 L stainless steel with chemical composition listed in Table (1) was used as experimental metal.

### 2.2. Methods and instruments

The morphology of stainless steel surface before and after immersion in the test solutions was examined by scanning electron microscope (JEOL-JSM-5500LV). Weight loss measurements were carried out in glass beaker containing  $50 \text{ cm}^3$  of corrosive solution with and without different concentrations of halo-complex [copper (I) chloride]. After an immersion time of 24 hours, the electrode was taken out and washed well with distilled water, dried and weighted accurately using digital balance (Analytical Balance Model FA 2104 A). The open circuit potentials of the metal immersed in the test solutions were motored using the electronic multimeter (DIGITAL MULTIMETER M-890C<sup>+</sup>).

**Table (1): Chemical composition of 316L stainless steel electrode (Weight %).**

| Element  | Si   | Cr    | Ni    | Mo   | Mn   | Fe    |
|----------|------|-------|-------|------|------|-------|
| Weight % | 0.56 | 17.28 | 10.57 | 2.62 | 1.14 | 67.83 |

Circular electrode with working surface area of  $1.76 \text{ cm}^2$  was used.

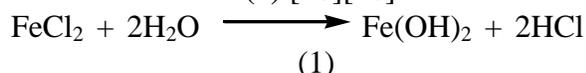
### 3- Results and Discussion

#### 3.1. Scanning electron microscope analysis

Microphotographs of 316L stainless steel surface before and after 24 hs. of immersion in blank solutions (1M KCl and 1M KBr) were obtained. Also the microphotographs of the surface of 316 L stainless steel in presence of highest concentration ( $1 \times 10^{-2}$ M) of copper (I) chloride in solutions containing 1M of KCl and 1M KBr were investigated.

Figure 1a shows the micrograph of an uncorroded freshly polished sample. Its surface is smooth and homogenous.

Figure 1(b-c) shows the surface of stainless steel after immersion time of 24 hours in 1M KCl and 1M KBr respectively. The samples have a gray appearance after treatment having lost its metallic color, showing presence of numbers of pits. The pits in case of 1M KCl depth than in case of 1M KBr. Thus  $\text{Cl}^-$  ions are aggressive enough to attack stainless steel and leads to a localized corrosion (e.g. pitting corrosion) due to small ion radius, which enable it to penetrate the oxide film under high electrical field present through the film [27] [16] [17]. The electrical neutrality and hydrolysis of the corrosion product inside the pit was enhanced by  $\text{Cl}^-$  ion migration cause pH dropped from 6 to 2 (acidification) facilitate the corrosion process as represented by the chemical reaction (1) [28][18]:



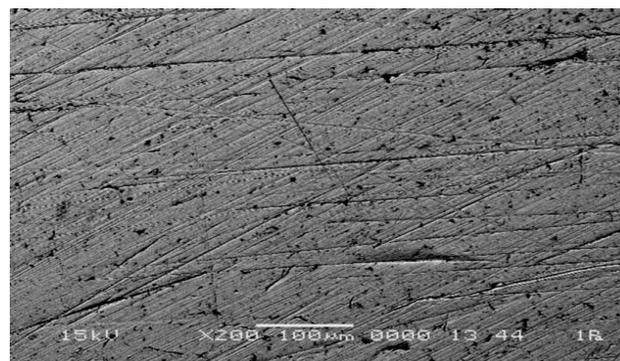
B.R. Tzaneva *et al.* [29] reported the same results in their studies and instructed the reason to the high reactivity of chloride ion with comparison to iodide ion. Decreasing the adsorption ability of the halide ion in the order  $\text{I}^- > \text{Br}^- > \text{Cl}^-$  with the resultant of lower electron injection to the oxide by iodide as well as the different stabilities of the halogen complex with metals.

Figures 1(d-e) represent the surface of stainless steel after exposed to 1M KCl

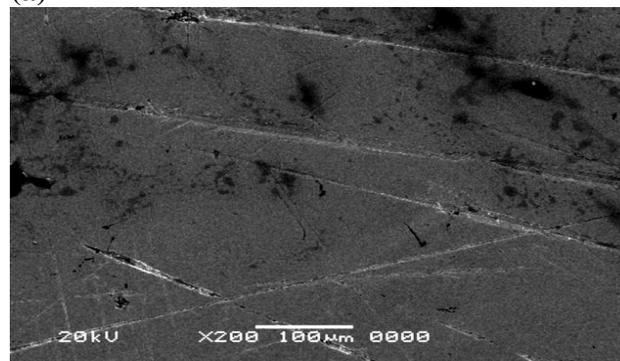
containing ( $1 \times 10^{-2}$ M) copper (I) chloride as inhibitor for 24 hs. immersion period and 1M KBr containing ( $1 \times 10^{-2}$ M) copper (I) chloride exposed for the same time of the immersion, respectively.

Comparison of these photographs reveals that, the surface does not appear corrected in several zones. From the observation, found that, the stainless steel surface protects after adding highest concentration of copper (I) chloride.

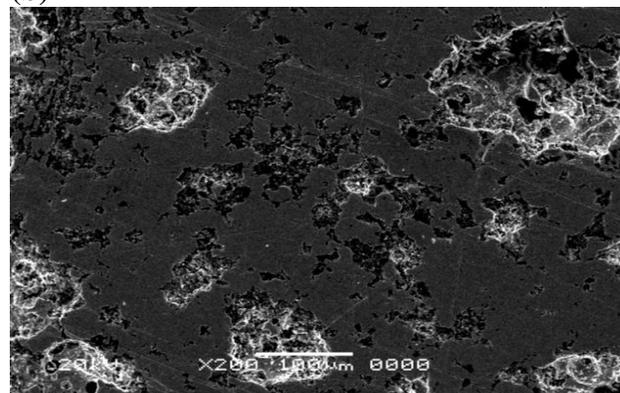
These results are in agreement with the other techniques



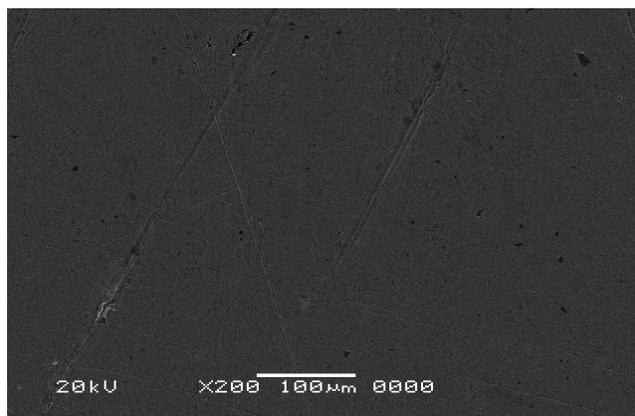
(a)



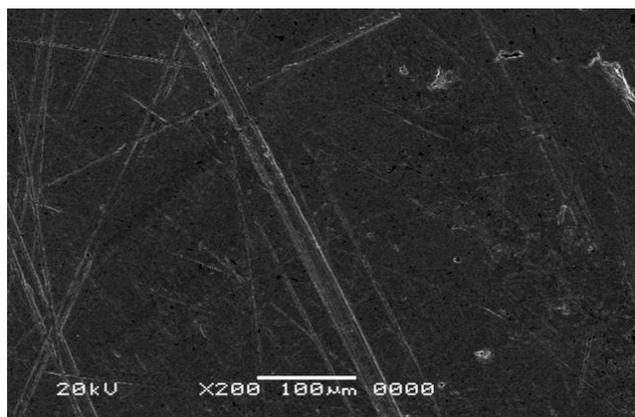
(b)



(c)



(d)



(e)

**Fig. (1):** Microphotographs of 316L stainless steel surface at 200 magnification (a) polished surface, (b) stainless steel surface after immersion 24 hr. in 1M KCl, (c) stainless steel surface after immersion 24 hr. in 1M Br, (d) stainless steel surface after immersion 24 hr. in 1M KCl containing ( $1 \times 10^{-2}$ M) of halo-complex, (e) stainless steel surface after immersion 24 hr. in 1M KBr containing ( $1 \times 10^{-2}$ M) of halo-complex.

### 3.2. Weight loss measurements

#### 3.2.1. In case of 1M halides solutions free of copper (I) chloride.

The weight loss study 316L stainless steel in different halides solutions (1M KCl and 1M KBr) has been performed at room temperature.

Table 2, illustrate comparison of the weight loss values in different aggressive solutions

(1M KCl and 1M KBr). From the results, found that the weight loss in case of chloride solution more than in case of bromide solutions [15-18].

**Table (2):** Weight loss values of 316 L stainless steel in 1M different halides solutions free of copper (I) chloride.

| Solutions        | 1M                  |                     |
|------------------|---------------------|---------------------|
|                  | KCl                 | KBr                 |
| Weight loss (gm) | $39 \times 10^{-4}$ | $25 \times 10^{-4}$ |

#### 3.2.2. In case of presence of different concentrations of halo-complex [copper (I) chloride] as corrosion inhibitor for 316L stainless steel.

The corrosion rate of 316 L stainless steel in 1M KCl and 1M KBr in presence of different concentrations ( $5 \times 10^{-3}$ - $1 \times 10^{-2}$ M) of copper (I) chloride has been investigated Table (3), illustrate the corrosion rate values in presence and absence different concentrations of copper (I) chloride. It was observed from the data, a continuous decrease in the corrosion rate with increase in the amount of copper (I) chloride in the solutions. Figure(2), illustrate the variation of inhibition efficiency with the concentration of copper (I) chloride at room temperature. Table (3), illustrated also the inhibition efficiency in presence of different concentrations of halo-complex, the inhibition efficiency (IE %) and corrosion rate values were calculated from the following equations (1) and (2) respectively [29] [30]:

$$W = \frac{\Delta m}{st} \quad (1)$$

where  $\Delta m$  (gm) is the mass loss, S ( $\text{cm}^2$ ) is the area, t (h) is the immersion period and W( $\text{gm cm}^{-2}/\text{h}$ ) is the corrosion rate.

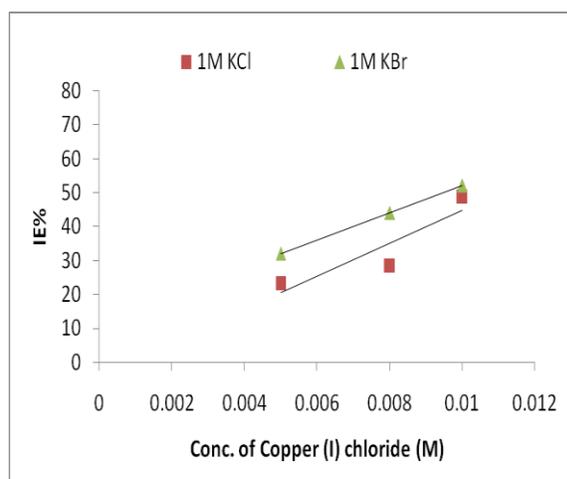
$$\% \text{ IE} = 100 \times \left[ 1 - \frac{\Delta W_{inh.}}{\Delta W_{free}} \right] \quad (2)$$

where  $\Delta W_{\text{free}}$  the mass loss in absence of inhibitor and  $\Delta W_{\text{inh.}}$  the mass loss in

presence of different concentrations of halo-complex [copper (I) chloride].

**Table (3): Weight loss values and IE% values of 316L stainless steel in presence and absence different concentrations of copper (I) chloride.**

| Solutions      | Concentration of halo-complex (copper (I) chloride) (M) | Weight loss (gm)    | Corrosion rate (gm cm <sup>-2</sup> /h) | Inhibition Efficiency (IE%) |
|----------------|---|---------------------|---|-----------------------------|
| 1M KCl (Blank) | --  | $39 \times 10^{-4}$ | $9.23 \times 10^{-6}$                   | --                          |
|                | $5 \times 10^{-3}$                                      | $30 \times 10^{-4}$ | $7.10 \times 10^{-6}$                   | 23.1                        |
|                | $8 \times 10^{-3}$                                      | $28 \times 10^{-4}$ | $6.62 \times 10^{-6}$                   | 28.3                        |
|                | $1 \times 10^{-2}$                                      | $20 \times 10^{-4}$ | $4.73 \times 10^{-6}$                   | 48.7                        |
| 1M KBr (Blank) | --  | $25 \times 10^{-4}$ | $5.91 \times 10^{-6}$                   | --                          |
|                | $5 \times 10^{-3}$                                      | $17 \times 10^{-4}$ | $4.02 \times 10^{-6}$                   | 32                          |
|                | $8 \times 10^{-3}$                                      | $14 \times 10^{-4}$ | $3.31 \times 10^{-6}$                   | 44                          |
|                | $1 \times 10^{-2}$                                      | $12 \times 10^{-4}$ | $2.84 \times 10^{-6}$                   | 52                          |



**Fig. (2): The variation of inhibition efficiency (IE%) with the concentrations of copper (I) chloride in different halides solutions at room temperature**

From the results, found that the increase of inhibitor concentration leads to an increase in inhibition efficiency which may be due to the blocking effect of the surface by both adsorption and film formation mechanism which decreases the effective area of attack. Amin Rabiei *et al.* [25], illustrate the

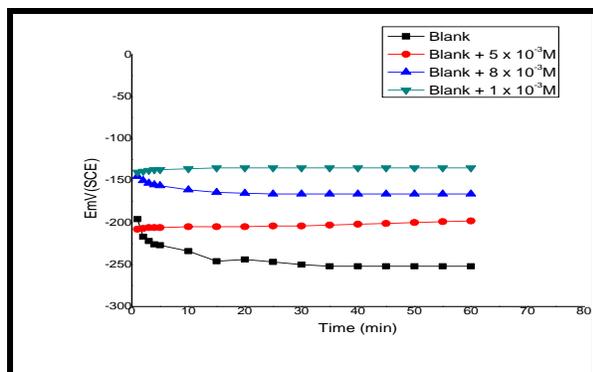
corrosion inhibitory effects of Co complexes and their respective ligands and to elucidate a possible mechanism for the corrosion inhibition of ligand their respective complexes.

### 3.3. Open – circuit potential measurements

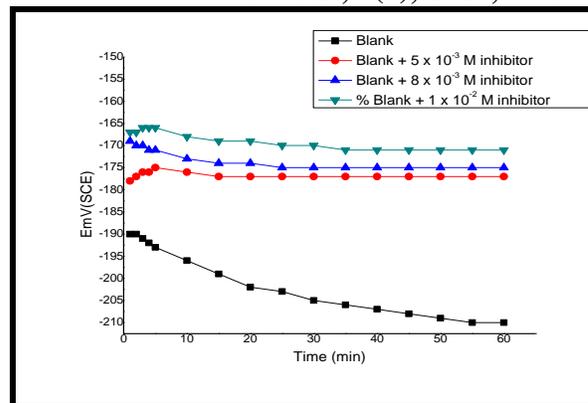
One of the simplest qualitative methods to study the corrosion behavior of metals is the measurements of open-circuit potential (OCP) in the time. The open circuit potentials of stainless steel electrode as a function of time in aerated solutions of 1M KCl and 1M KBr containing different concentrations of [copper (I) chloride] are followed till the steady state values ( $E_{s,s}$ ) are reached. A rise in potential in the positive direction indicates the formation of passive film, and a steady potential indicated that the film remains protective.

Some authors, found that, the passive layer formed on 316L stainless steel in aqueous NaCl solutions consists of  $Fe_2O_3$ ,  $Cr_2O_3$  and  $FeCl$  [31] [32].

Figures (3-4) illustrate the variation of OCP of stainless steel electrode as a function of time in 1M KCl and 1M KBr containing different concentrations ( $5 \times 10^{-3} - 1 \times 10^{-2}$ ) of copper (I) chloride.

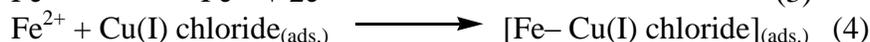
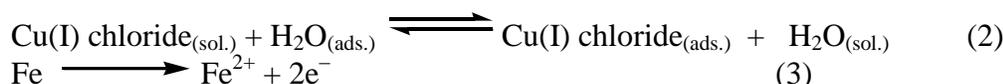


**Figure (3): The variation of open-circuit potentials of 316 L stainless steel in 1M KCl in presence and absence of ( $5 \times 10^{-5} - 1 \times 10^{-2}$ ) halo-complex at room temperature as a function of time**



**Figure (4): The variation of open-circuit potentials of 316 L stainless steel in 1M KBr in presence and absence of ( $5 \times 10^{-3} - 1 \times 10^{-2}$ ) halo-complex at room temperature as a function of time.**

Generally the mechanism of corrosion inhibition of copper (I) chloride can be associated with electrostatic interaction between charged metal surface and the inhibitor molecules to form a coordinate covalent bond [5]. It is generally accepted that the first step in the adsorption of halo-complex [copper (I) chloride] on the stainless steel surface usually involves the replacement of one or more water molecules adsorbed at the metal surface [equation (2)].



The inhibitor may then combine with freshly generated  $\text{Fe}^{2+}$  ions on the stainless steel surface, forming metal inhibitor complex [equation (4)] [5].

#### 4. Conclusions

Based on the results of performed experiments can be concluded.

A surface of 316 L stainless steel was attacked by local pitting corrosion during immersion period in different halides while the stainless steel surface repair in presence of halo-complex.

Observed corrosion attack was reflected in mass losses during immersion tests. Corrosion rates were calculated from mass

losses decreased with increase of halo-complex content in solution.

The corrosion inhibitory effect of halo-complex may be due to the adsorption of halo-complex on the stainless steel surface.

#### References

- [1] W. Schenk, Corrosion 20, (1964) 129.
- [2] M. G. Fontana and N.D. Greene, Corrosion Engineering, New York, McGraw-Hill, 51, (1967).
- [3] M. E. Curley-Fiorino and G. M. Schmid, Corrosion Science 20, (1980) 313.

- [4] P. Selrakumar, B. B. Alange and O. Thangavelu, *Research Journal of Chemical Science* 3(4), (2013) 87.
- [5] A. Wisal Isa and S. Marwa Hussain, Ibn Al-Haitham, *Journal for Pure & Appl. Sci.* 28(1), (2015) 113.
- [6] B. Hadzima and T. Liptakova, Žilina, *EDIS-Žilinská Univerzita* 116, (2008).
- [7] F. Heravi, M. H. Moayed and M. Mokhber, *Journal of Dentistry of Tehran* 12(1), (2015) 49.
- [8] Y. L. Chou, Y. C. Wang, J. W. Yeh and H. C. Shih, *Corrosion Sci.* 52, (2010) 3481.
- [9] D. S. Azambuja, E. Martini and I. L. Müller, *Journal of the Brazilian Chemical Society* 14, (2003) 570.
- [10] Z. Szklarska – Smialowska and ZS-Smialowska, *NACE International, Houston, TX* 88, (2005).
- [11] A. U. Malik, M. Kutty, N. A. Siddiqi, I. N. Andijani and S. Ahmad, *Saline water conversion Corp., Saudi Arabia* (1990).
- [12] J. R. Galvele, R. M. Torresi and R. M. Cavanza, *Corrosion Science* 31, 563 (1990) 563.
- [13] E. A. El Meguid and A. A. El Latif, *Corrosion Science* 49, (2007) 263.
- [14] S. U. Lee, J. C. Ahn, D. H. Kim, S. C. Hong and K. S. Lee, *Materials Science and Engineering A* 434, (2006) 155.
- [15] G. S. Frankel, L. Stockert, F. Hunkeler and H. Boehni, *Corrosion* 43, (1987) 429.
- [16] M. Kaneko and H. S. Isaacs, *Corrosion Science* 42, (2000) 67.
- [17] R. C. Newman, M. A. A. Ajjawi, H. Ezuber and S. Turgoose, *Corrosion Science* 28, (1988) 471.
- [18] Y. T. Sutsumi, A. Nishikata and T. Tsuru, *Corrosion Science* 49, (2007) 1394.
- [19] S. Issaadi, T. Douadi, A. Zouaoui, S. Chafaa, M. A. Khan and G. Boue, *Corrosion Science* 53, (2011) 1484.
- [20] M. Abdallah, *Corros. Sci.* 46, (2004) 1981.
- [21] H. Ashassi, Zighasem and D. Seifzadeh, *App. Surf. Sci.* 249, (2005) 408.
- [22] S. Rangelov and V. Mircheva, *Corrosion Science* 38, (1996) 301.
- [23] K. F. Khaled, K. Babic – Samardzija and N. Hackerman, *Corrosion Science* 48, (2006) 3014.
- [24] A. M. Abdel-Gaber, M. S. Masoud, E. A. Khalil and E. E. Shehata, *Corrosion Science* 51, (2009) 3021.
- [25] Amin Rabiei Baboukani, Ehsan Sharifi, Saeid Akhavan and Ahmad Saatchi, *Journal of Materials Science and Chemical Engineering* 4, (2016) 28.
- [26] [http://www. Chem. Uwimona, edu.jm>Lab\\_manuals](http://www.Chem.Uwimona.edu.jm>Lab_manuals).
- [27] N. Ebrahimi, M. Momeni, M. H. Moayed and A. Davoodi, *Corrosion Science* 53, (2011) 637.
- [28] Z. Ahmad, *El-Servier Science & Technology Books Publisher/ BH.* (2006).
- [29] M. Scendo, *Corros. Sci.* 49, 373 (2007) 373.
- [30] M. A. Quraishi, A. Singh, V. K. Singh, D. K. Yadav and A. K. Singh, *Mater. Chem. Phys.* 122 (1), (2010) 114.
- [31] S. Zhou, M. M. Stack and R. C. Newman, *Corros. Sci.* 38, 1071 (1996) 1071.
- [32] A. C. West, *J. Electrochem. Soc.* 140, (1993) 403.