Influence of pH and Chloride Concentration on The Corrosion Behaviour of Cadmium Electrode

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The corrosion behaviour of cadmium electrode in NaCl solution at concentrations of 0.5-5.5% and at pH values of 4, 7 and 10 were investigated using potentiodynamic and cyclic polarization techniques. It was found that the anodic excursion characterized by three distinct region before oxygen evolution. Removed from critical potential, $E_{crit.}$, the electrode surface was covered with a porous non adherent layer of white $Cd(OH)_2$ and the passive state is due to formation black film of CdO.

From cyclic polarization data, the type of corrosion varies with pH value. General corrosion was observed at pH 4 and 7 while at pH 10 pitting corrosion occurs.

The inhibition effect of alanine and lactic acid for general and localized corrosion was examined.

Keywords: cadmium - polarization-inhibitor- pitting-sodium

Introduction

Cadmium, metal currently under scrutiny, has wide and varied uses from batteries to plastic pigments. Various investigators have noted and reported discrepancies in the actual and theoretical quantities of cadmium dissolving anodically in certain oxidizing electrolytes [1-4].

The corrosion phenomena of cadmium in aqueous NaCl solution were elucidated by taking into account the possibility of formation of different solid corrosion products and their irregular distribution on the surface [5].

One objective of the present work was to study the electrochemical behaviour of cadmium electrode in NaCl solution with different concentrations and pH. A second objective was to investigate the effect of alanine and lactic acid as inhibitors of cadmium corrosion.

Experimental Procedure

The material used in the present study was spectroscopically pure cadmium rod electrode (99.999%). A specimen holder was used to expose 1cm^2 surface area. The area shielded by the specimen holder was

then coated with a protective enamel to prevent crevice corrosion [40]. The exposed surface specimen was prepared by polishing with a sequence of emery paper (600,800 and 1200) grids, cleaning several times with deionized water and drying with acetone before immersing in the test solution. The cell was equipped with pt counter electrode and saturated calomel reference electrode (SCE). Curves were recorded potentiodynamically, by using Volta Lab PGZ301 Dynamic EIS Voltammetry, under aerated conditions beginning by one hour hold in test solution at open circuit.

Deionized water used to prepare solutions. All chemicals used are of reagent grade, the pH of the solutions were adjusted by using reagent grade sodium hydroxide (NaOH) and hydrochloric acid (HCl), for adjusting pH 7 less than 1 ml. phosphoric acid buffer (KH_2PO_4 + Na_2HPO_4) was used.

Results and Discussion

Fig.1 represents the potentiodynamic polarization curves of cadmium electrode in aerated NaCl of various concentrations ranging from 0.5 to 5.5% (pH = 4.8). The curves sweept from -200 to 2000 mV (SCE) at a scan rate of 5 mV/s.

On the positive going scan, the cathodic current decreases continually and change its sign at the corrosion potential $E_{corr.}$. The cathodic current density is due to the evolution of hydrogen gas according to the reaction:

$$2H^+ + 2e^- \rightarrow H_2$$
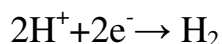
On the other hand, the anodic excursion characterized by three distinct regions: the first, which showed a slowly increase in current density, nearly constant and independent of potential up to certain potential E_{crit}. During the first region which ranged from -0.224V up to -0.163V the solution remained colorless. This could be explained as a result of anodic oxidation of hydrogen adsorbed at cadmium electrode during the cathodic reduction.

For potentials removed from $E_{crit.}$, the dissolution current density increases with the applied potential E, forming second potential region. The electrode was covered with a porous, non-adherent layer of white $Cd(OH)_2$. More increase of potential caused a gradual decrease of the current till the passive state was reached forming the third region, in which, the electrode was covered with black film of cadmium oxide, CdO,. Finally a transpassive potential starts to begin approximately at 1.176 V to 1.331 V and oxygen started to evolve with increasing in the current density on further increase in potential.

The electrochemical parameters are given in Table1. It can be noted that, on increasing NaCl concentrations, the corrosion current $I_{corr.}$

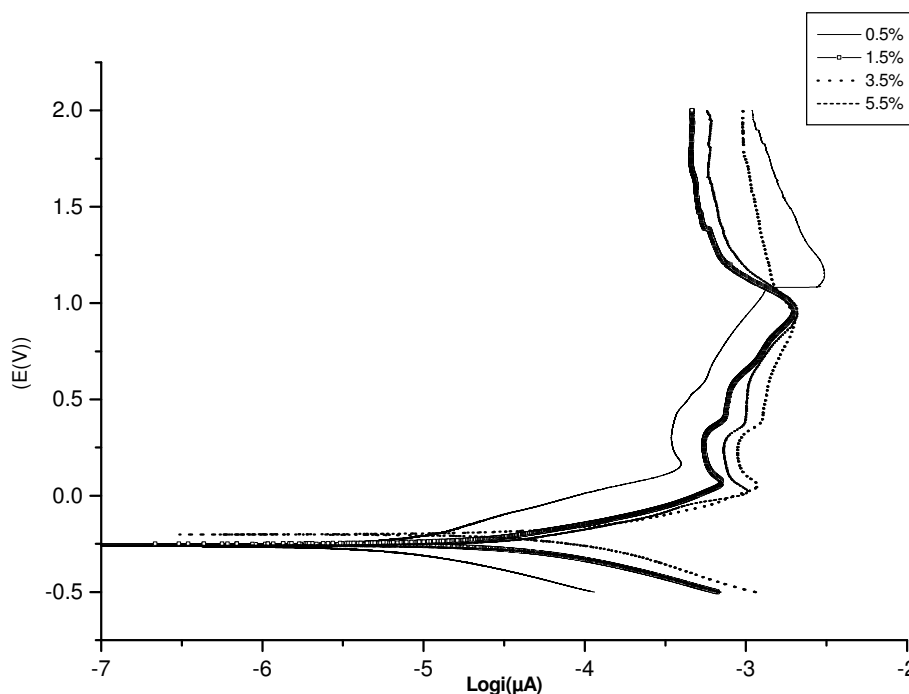and the corrosion rate increase while corrosion potential $E_{corr.}$ is almost constant.

Fig.(1) potentiodynamic polarization curves of cadmium electrode in different concentrtions of NaCl solution.

Table (1) electrochemical parameters of Cd electrode in NaCl solution.

Medium	Ecorr. mV	Icorr µA/cm²	Tafel Slopes Ba	Bc	Corrosion rate mm/year
0.5%NaCl	-260.9	8.6337	279.0	-216.5	100.9
1.5%NaCl	-250.3	53.5866	246.3	-228.4	626.7
3.5%NaCl	-261.2	86.7682	261.8	-278.1	633.014
5.5%NaCl	-262.6	62.9988	250.1	-233.3	736.8

In presence of aggressive anions, a local attack of passive metal occurs pitting was initiated by local breaking of the passive film by the anion in question. This circumstance gave rise to active-passive cells of limited anodic area, which in turn led to high rates of dissolution. The regeneration of the passive film did not take place because of the formation of a more acid microenvironment interior of the cavity as a result of the cation hydrolysis phenomena.

Fig.2 shows the cyclic polarization curves of cadmium electrode in 3.5% NaCl at pH values of 4, 7 and 10 respectively. The curves obtained

for pH 4 show that, the reverse scan came above the forward scan, indicating that the solution under these condition does not cause any pitting corrosion. By shifting pH value to 7, the reveres scan came below the forward scan forming a small loop, again the lack of hysteresis may be taken as an indication of an absence of pitting corrosion. Shifting pH to more alkaline value, at pH 10, the reveres scan formed a large hysteresis loop indicating of the electrode susceptibility to pitting corrosion.

From cyclic polarization data, the type of corrosion varies with pH. At pH 4 and 7, cadmium electrode was susceptible to general corrosion described as pitting initiation while at pH 10, as indicated from data in Table 2, the current density increased and pitting corrosion occurs. It is interesting to note that the difference between the type of corrosion found at pH 4 and 7(general) and at pH 10 (pitting) may be associated not only to the solution activity but also to the presence of film on the electrode surface [7, 8].

Cadmium has large hydrogen overpotential, for a current density of $1 Adm^{-2}$ this is 1.134 [9], it is expected that the dissolved oxygen has an influence on the corrosion rate [10]. In acidic and neutral media cadmium will dissolve as Cd^{+2}, which convert into white hydroxide [11]. Inactive $Cd(OH)_2$ is thermodynamically the most stable form of all oxide, anhydrous and hydrated forms [9]. An increase in the pH value lead to a pronounced dissolution of cadmium due to the predominance of the soluble colorless bi-cadmite ion $HCdO_2^-$ which has a minimum solubility [11].
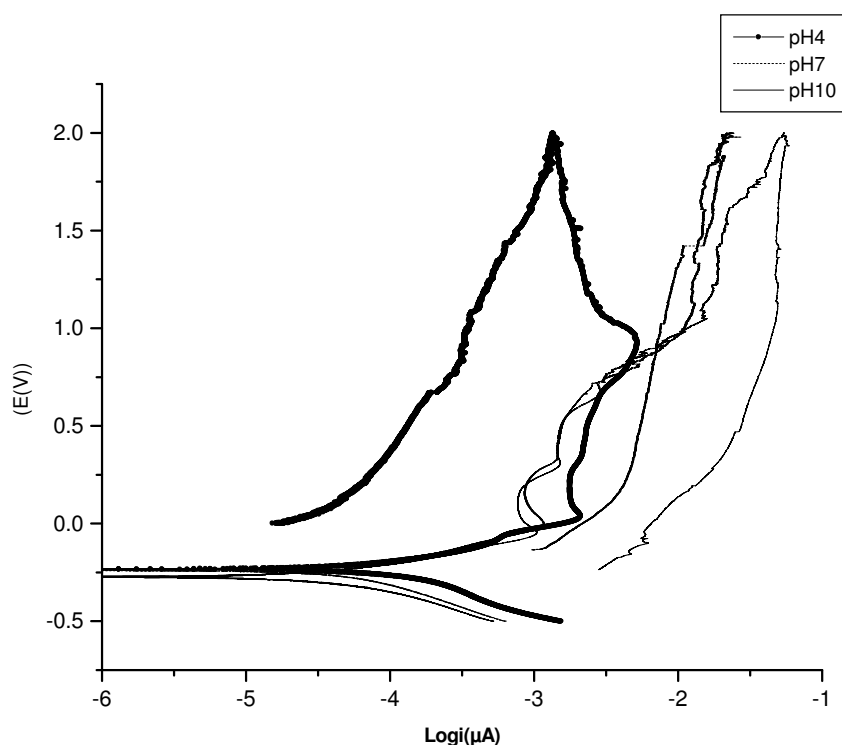
Fig.(2) Cyclic anodic polarization curves of cadmium electrodein 3.5% NaCl solution at pH values of 4, 7 and 10.

Amino acids and hydroxy carboxylic acids are biodegradable and might accommodate at least some of the environmental restriction [12].

The inhibition effect of alanine and lactic acid for general and localized corrosion of cadmium electrode in aqueous solution of 3.5% NaCl at pH 4,7 and 10 respectively was studied. Table (2) summarized the results of electrochemical parameters obtained from potentiodynamic polarization curves of cadmium electrode in aerated 3.5% NaCl solution containing 10^{-2}M alanine and also 10^{-2}M lactic acid at pH 4,7,10.

As is seen from the data mentioned in table (2), the values of the corrosion current density, $I_{corr.}$, decreased associated by notable decrease in corrosion rate.

Fig.(3) represent the cyclic polarization curves for cadmium electrode in 3.5% NaCl solution containing 10^{-2}M alanine and also 10^{-2}M lactic acid at pH 10. It was found that the hysteresis loop observed during the reveres anodic scan, which indicates the possibility of pitting corrosion, was diminished for both alanine and lactic acid.

Depending on the pH value of the medium, percent amount of dominate form of the amino acids differs. At the isoelctric point, amino acids are in the form of Zwitter ion. For this reason at pH values around isoelctric point, pH6, inhibition effect of alanine are minimum and away from it, the inhibition effect are greater [13]. Respectively in neutral and slightly basic solution, percent of ionized form of the hydroxyl carboxylic

acid is higher than non-ionized form. The ionized form of the lactic acid can be strongly adsorbed on the surface.

Table (2) Electrochemical parameters of Cd electrode in 3.5% NaCl solution at pH values of 4, 7 and 10 containing 10^{-2}M alanine and 10^{-2}M lactic acid.

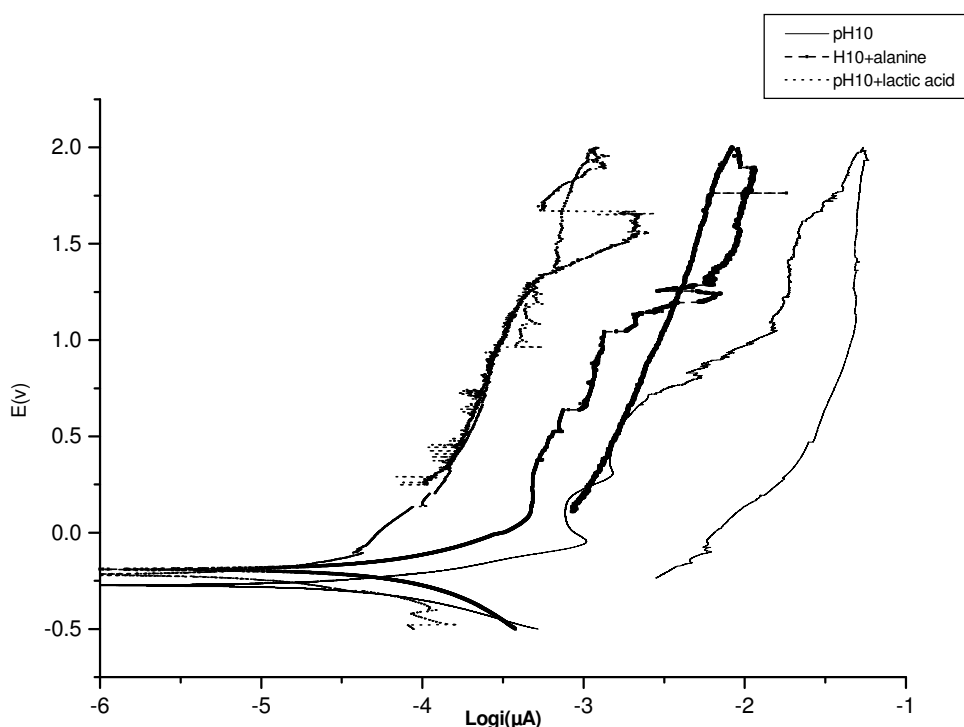| Medium	Ecorr. mV	Icorr µA/cm²	Tafel Slopes Ba	Bc	Corrosion rate mm/year
pH4	-232.7	25.0714	450.2	-366.7	311.018
alanine	-245.8	5.5380	45.4	-81.8	64.77
lactic	-221.5	18.7708	42.8	-386.6	219.5
pH7	-240.4	53.7322	216.0	-254.9	628.4
alanin	-218.9	30.7423	936.1	-293.3	359.5
lactic	-191.4	45.6404	328.1	-419.0	431.4
pH10	-239.8	56.2917	163.5	-253.6	658.4
alanine	-195.2	38.8860	330.1	-343.1	454.8
lactic	-238.5	10.18	176.0	-320.9	1.191

Fig.(3) Cyclic anodic polarization curves of cadmium electrode in 3.5% NaCl solution at pH10 with 10^{-2}M alanine and Lactic acid.

SEM

From the examination of SEM micrographs the following observation could be obtained which are in agreement with cyclic anodic polarization experiments:

- 3.5% NaCl solution at pH4: cadmium specimens were corroded uniformly indicating that the uniform corrosion is the reason for degradation fig. (4a).
- 3.5% NaCl solution at pH10: extensive pits over the entire alloy surface are observed indicating that pitting corrosion is the mode of degradation fig. (4b).
- 3.5% NaCl solution containing 10^{-2} alanine at pH4: smooth electrode surface was observed with improving for the surface condition fig. (4c).
- 3.5% NaCl solution containing 10^{-2} lactic acid at pH10: only a few numbers of pits with small size are observed fig. (4d).
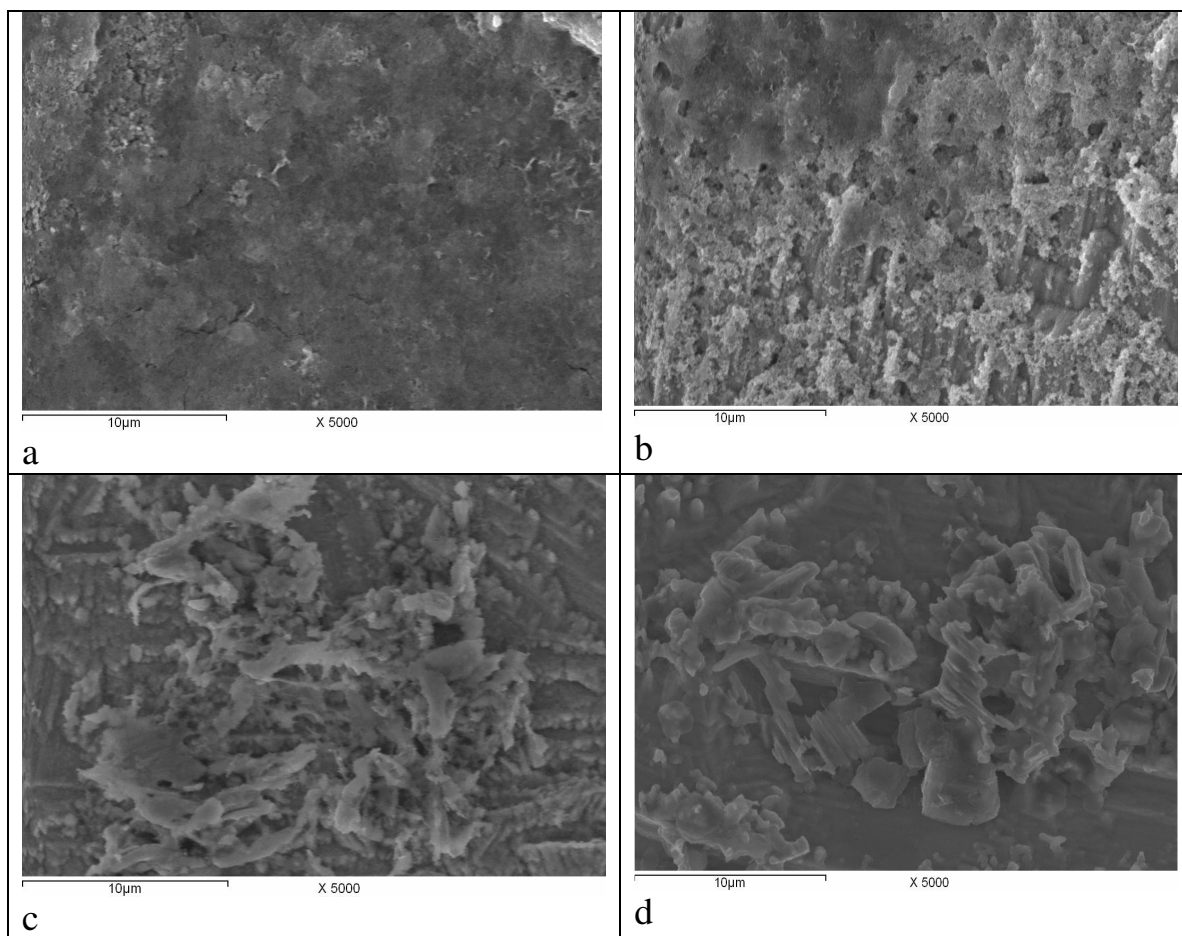

Fig.(4) SEM micrographs of a Cd specimen in 3.5% NaCl solution (a) pH4, (b) pH10, (c) with 10^{-2} alanine at pH4, (d) with 10^{-2} lactic acid at pH10.

Conclusion

The corrosion behaviour of cadmium electrode in NaCl solution showed that, the cathodic current density is due to the hydrogen evolution. On the other hand , the anodic curves indicated three regions. Increasing the NaCl concentration shifted the current density and corrosion potential to active direction.

Cyclic polarization curves showed that , at pH 4 and 7 cadmium electrode susceptible to general corrosion described as pitting initiation, while at pH 10 the current density increased and pitting corrosion occurs. Shifting pH value to more alkaline ranges lead to pronounced dissolution of cadmium electrode due to the formation of soluble bi-cadmite ion $HCdO_2^-$ which has a minimum solubility.

Alanine and lactic acid have an inhibition effect for both general and localized corrosion of cadmium electrode. Alanine showed the greater inhibition effect away from their isoelectric point.

Acknowledgement

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