Electrochemical Corrosion Behavior of Duplex Stainless Steel AISI 2205 in Ethylene Glycol-Water Mixture in the Presence of 50 W/V % LiBr

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ABSTRACT

The corrosion behavior of duplex stainless steel AISI 2205 was investigated in ethylene glycol-water mixture in the presence of 50 W/V % LiBr at different concentrations and different temperatures. Cyclic polarization, impedance measurements and Mott-Schottky analysis were used to study the corrosion behavior the semi conductive properties of the passive films. The results showed that with increasing in the ethylene glycol concentration to 10 V/V%, the corrosion rate of the steel alloy substrate increased. In higher concentrations of ethylene glycol, corrosion current of steel decreased. The results of scanning electron microscopy of electrode surface confirmed the electrochemical tests. Electrochemical experiment showed that duplex steel was stable for pitting corrosion in this environment. The increase in the ethylene glycol concentration led to increasing the susceptibility to pitting corrosion. The corrosion current increased as the temperature rise and also pitting potentials and repassivation potentials shifted towards the less positive values as the temperature increased. According to Mott-Schottky analysis, passive films of stainless steel at the different temperatures showed both n-type and p-type semiconductor behavior in different potential.

Keywords : Duplex stainless steel, Corrosion, Ethylene glycol, Impedance, Mott-Schottky.

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1. Introduction

Aqueous solutions containing high concentrations of lithium bromide are employed as absorbent solutions for almost all types of heating and refrigerating absorption systems that use natural gas or steam as energy sources [1,2]. Although LiBr possesses favorable thermo physical properties, it can cause serious corrosion problems on metallic components such as carbon steel, stainless steel, copper alloys and titanium in refrigeration systems and heat exchangers in absorption plants [3]. An alternative way to reduce some of these disadvantages of the water/LiBr mix-

ture is to add ethylene glycol to the system [4,5], because some thermo physical properties of the LiBr +water mixture, such as thermal conductivity, viscosity, maximum concentration etc. are improved [6].

Duplex austenitic-ferric stainless steels are vastly used in petroleum industries, particularly for submarine gas and oil lines and other offshore applications because of their reasonable cost, good mechanical and thermal properties, and resistance to stress corrosion and pitting [7]. Pitting corrosion of metals and alloys are a major cause of failure in different industrial media. Localized attack can be initiated when the passive film on the metal is disrupted. The

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aggressive anions, such as bromides can migrate to the actively corroding area and stabilize pitting corrosion [4,8]. It is known that the presence of alloyed elements such as Cr, Mo, and N improve the resistance to localized corrosion of the stainless steels [9]. Stainless steels represent the best candidates for structural materials under a wide variety of conditions. It is not always, however, the most corrosion resistant for many industrial environments, especially in the presence of chlorides and bromides [10].

Igual Munoz et al. [4], studied the corrosion behavior of three stainless steels EN 14311, EN 14429 austenitic stainless steels and EN 14462 duplex stainless steel in a commercial LiBr solution at different temperatures. Results showed that pitting corrosion resistance is improved by the EN 14462, which presented the highest pitting potential, and the lowest passivation current for the whole range of temperatures. Samient et al. [6], investigated the corrosion resistance of 1018 carbon steel, 304 and 316 type stainless steels in the LiBr (55 wt.%) + ethylene glycol + H₂O mixture. Results showed that, at all tested temperature, the three steels exhibited an active-passive behavior. Carbon steel showed the highest corrosion rate and most active pitting potential values was obtained for 1018 carbon steel.

The objective of the present work was to study the corrosion resistance and pitting corrosion behavior of duplex stainless steel AISI 2205 in the ethylene glycol and water mixture in the presence of LiBr. Electrochemical measurements were used in different concentrations and different temperatures.

2. Experiment

Material tested was duplex stainless steel AISI 2205 with chemical composition in Table 1. Samples for electrochemical experiments were cut in cubic dimensions by wire cut machine. Each sample was sealed by polyester resin so leaving an approximate area of 1 cm² to be exposed to the electrolyte. The exposed areas of the electrodes were mechanically abraded with 220, 400, 600, 800 and 1000 grades of emery paper, degreased with acetone and rinsed by distilled water before each electrochemical experiment.

Corrosion tests were carried out in 50 W/V% LiBr aqueous solution with different ethylene glycol concentration to simulate the automotive heat exchangers and heat transfer fluids. Electrochemical measurements were carried out in a conventional three electrode glass cell. Platinum electrode was used as a counter electrode and a saturated calomel electrode as the reference electrode. All electrochemical tests were performed by potentiostat/galvanostat model EG&G 2273 which controlled by power suite software. In all electrochemical experiment, before recording, the working electrode was maintained at its open circuit potential for 30 min until a steady state condition was obtained.

Cyclic polarization curves were obtained by polarizing the specimens at a scanning rate of 1 mV s⁻¹. Corrosion potential and corrosion current density values were calculated using Tafel extrapolation method. As applied potential values increased 100 mV more than E_{pit} , applied potential is reverse, in order to comparing cyclic polarization curves in different conditions. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency interval of 100 kHz to 1 mHz with AC amplitude of ± 10 mV. Fitting of experimental impedance spectroscopy data to the proposed equivalent circuit was done by means of a home written least square software based on the Marquardt method for the optimization of functions and Macdonald weighting for the real and imaginary parts of the impedance [11,12].

Mott-Schottky experiments were done by measuring the frequency response at 1 kHz. The surface morphology of the electrode surface was evaluated by scanning electron microscopy model VEGA, TESCAN at $\times 2000$ magnification.

3. Result and Discussion

3.1. Effect of ethylene glycol concentration

Cyclic polarization curves of duplex steel electrode measured in solutions at different concentrations of ethylene glycol are shown in Fig. 1. As can be seen, passivation and pitting corrosion behavior is observed in polarization diagrams. Cyclic polarization parameters are listed in Table 2, where E_{corr} , E_{pit} , E_{rp} , R_p , β_a ,

Table 1. Chemical composition of material tested.

Element	C max	Si max	Mn max	P max	S max	Cr	Ni	Mo	N
wt.%	0.03	1.0	2.0	0.03	0.015	22	5	3.2	0.18

β_c , and $C.R$ are the corrosion potential, pitting potential, repassivation potential, corrosion current density, polarization resistance, anode Tafel constant, cathode Tafel constant, and corrosion rate, respectively.

It can be seen from Fig. 1 and Table 2 that corrosion potentials shift to negative values with the increase in the ethylene glycol concentration. This is ascribed to the decrease in cathodic current in the presence of ethylene glycol. Ethylene glycol adsorbs on surface and decreases cathodic reactions. The anodic current shows no significant change due to the strong passivation of duplex stainless steel. With increasing in the ethylene glycol concentration to 10 V/V%, corrosion current of the steel alloy increases. The increase in corrosion current in this concentration is due to autoprotolysis of ethylene glycol caused by interactions between ethylene gly-

col and the water which leads to increasing production of ionic species [13]. With higher concentration of ethylene glycol, corrosion current of the steel alloy substrate decreases. The decrease in corrosion current of steel alloy is due to the increase in the degree of surface coverage.

Inspection of the curve reveals that the anodic scan exhibits the passive behavior prior to a certain critical breakdown potential E_{pit} . When the critical potential E_{pit} is exceeded, an increasing current is observed indicating breakdown of the passive film at local points. For $E > E_{pit}$, the current corresponds largely to the pitting corrosion of stainless steel. The increase in pitting susceptibility with increase in potential could be explained on the basis that an increase in the applied potential may increase the electric field across the passive film and therefore enhances the adsorption of the aggressive Br^- anions on the passive electrode surface [14]. In the course of a reverse potential sweep, the current decays slowly and remains higher than the current in the anodic sweep and a loop characteristic of pitting corrosion phenomena appears. This loop allows the repassivation or protection potential (E_{pro}) to be determined [15]. Protection potential corresponds to the potential value below which no pitting occurs and above which pit nucleation begins [15]. When the protection potential is reached, the anodic current density decreases very sharply and rapidly. The existence of a hysteresis loop in a cyclic polarization curve indicates a delay in repassivation of an existing pit when the potential is scanned cathodically. The area of the hysteresis loop is a measure of the pit propagation kinetics. The larger the hysteresis loop the more difficult it becomes to repassivate a pit and suggest lower pitting resistance.

According to Fig. 1, all concentration of ethylene

Fig. 1. Cyclic polarization curves of duplex steel alloy electrode in 50 W/V % LiBr and ethylene glycol-water solution at different concentrations of ethylene glycol: 1) 0; 2) 10; 3) 20; 4) 30; 5) 50; 6) 70 V/V %.

Table 2: Cyclic polarization parameters for the corrosion of duplex stainless steel 2205 in 50 W/V % LiBr and ethylene glycol-water solution with different concentrations of ethylene glycol.

Ethylene glycol V/V %	0	10	20	30	50	70
E_{corr} / mV	-146	-123	-145	-346	-335	-375
I_{corr} / $\mu A\ cm^{-2}$	0.289	0.326	0.312	0.234	0.181	0.154
$R_p \times 10^{-6}$ / ohm	0.109	0.104	0.107	0.131	0.175	0.241
β_a / V dec ⁻¹	0.123	0.145	0.128	0.133	0.133	0.161
β_c / V dec ⁻¹	0.178	0.17	0.192	0.151	0.161	0.181
$CR \times 10^6$ / mm year ⁻¹	3363	3826	3594	2667	2087	1739
E_{pit} / mV	558	465	468	408	396	393
E_{rp} / mV	313	247	268	202	73	64

Table 3. Impedance parameters obtained in 50 W/V % LiBr solutions with different concentrations of ethylene glycol at open-circuit potential.

Ethylene glycol concentration V/V %	R_s / $\Omega \text{ cm}^2$	R_f / $\Omega \text{ cm}^2$	$Q_f \times 10^4$ / $\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$	n_f	$R_{ct} \times 10^{-5}$ / $\text{k}\Omega \text{ cm}^2$	$Q_{dl} \times 10^4$ / $\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$	n_{dl}
0	3.1	551	1	0.8	1.95	1.4	0.72
10	3.8	489	0.8	0.83	1.61	1.1	0.62
20	4.1	523	1.2	0.82	1.58	0.9	0.62
30	4.9	781	1.9	0.79	2.02	0.3	0.59
50	6.8	864	1.8	0.81	2.55	0.25	0.58
70	48	941	1.8	0.8	2.87	0.15	0.56

Fig. 2. Surface of duplex steel alloy electrode by metallographic microscope in 50 W/V % LiBr and ethylene glycol-water solution at different concentrations of ethylene glycol: a) 10; b) 30; c) 50; d) 70 V/V % ethylene glycol.

glycol exhibit hysteresis loop but in all concentrations, the susceptibility of duplex steel to pitting corrosion is very low due to the high value of ($E_{rp}-E_{pit}$). Therefore, duplex steel indicated stability in open circuit conditions. It can be seen from Table 3 that with increasing the ethylene glycol concentration, pitting potentials decreases. It may be concluded that the increase in ethylene glycol concentration leads to

increasing the susceptibility to pitting corrosion.

The morphologies of the electrode surface in different ethylene glycol-water solution in the presence of 50 W/V% LiBr are presented in Fig. 2. The images were obtained after holding the electrode at the potential +0.7 vs. open circuit for 600 s. The selected applied potential is higher than E_{rp} and therefore lead to pit initiation. From Fig. 2, it can be concluded that with

Fig. 3. a) Nyquist and b) Bode plots of duplex steel alloy electrode in 50 W/V % LiBr and ethylene glycol-water solution at different concentrations of ethylene glycol: 1) 0; 2) 10; 3) 20; 4) 30; 5) 50; 6) 70 V/V %.

the increase in the concentration of ethylene glycol, corrosion attack decreases. It is clear that, the surface is the smoothest in solutions containing 70 V/V% ethylene glycol.

In order to get more information about the corrosion phenomena, impedance measurements have been carried out in different concentration of ethylene glycol. The impedance plot for steel electrode in 50 W/V % LiBr solutions with different ethylene glycol concentrations at open circuit potential is shown in Fig. 3a and 3b.

The data revealed that impedance diagram consist of two overlapped capacitive semicircles which were depressed towards the real axis (Fig. 3a). The depressed semicircle in the low frequency region can be related to the combination of charge transfer resistance and the double layer capacitance. The high fre-

Fig. 4. Equivalent circuits compatible with the experimental impedance data in Fig. 3 for corrosion of duplex steel alloy electrode in ethylene glycol -water solution in the presence of LiBr.

quency semicircle was related to capacitive behavior of the passive film, coupled with a resistance due to the ionic paths through the oxide film. Two distinguishable peaks in lower ethylene glycol and a broad peak in higher ethylene glycol concentrations are observed in the Bode plots corresponding to two overlapped semicircles in the Nyquist plot (Fig. 3b). The equivalent circuit compatible with the impedance diagrams was depicted in Fig. 4. In this electrical equivalent circuit, R_s , Q_{dl} and R_{ct} represent solution resistance, a constant phase element corresponding to the double layer capacitance and the charge transfer resistance of dissolution reaction. CPE_f and R_f are the electrical elements related to the resistance and capacitance of passive film. To obtain a satisfactory impedance simulation of duplex stainless steel, it is necessary to replace the capacitor (C) with a constant phase element (CPE) Q in the equivalent circuit. The most widely accepted explanation for the presence of CPE behavior and depressed semicircles on solid electrodes is microscopic roughness, causing an inhomogeneous distribution in the solution resistance as well as in the double-layer capacitance [16-18]. The simplest approach requires the theoretical transfer function $Z(\omega)$ to be represented by [19]:

$$Z(\omega) = R_s + \frac{R_f}{1 + \frac{1}{(Z_{ct}(\omega)/R_f)^{n_1}} + (i\omega)^{n_1} R_f Q_f}$$

$$Z_{ct}(\omega) = \frac{R_{ct}}{(i\omega)^{n_2} Q_{dl} R_{ct} + 1} \quad (1)$$

ω is the frequency in rad/s, $\omega = 2\pi f$ and f is frequency in Hz. To corroborate the equivalent circuit, the experimental data are fitted to equivalent circuit and the circuit elements are obtained. Table 3 illus-

Table 4. Polarization parameters for corrosion of duplex steel in 50 W/V % LiBr and %30 ethylene glycol-water solution at various temperatures.

Temperature / °C	E_{corr} / mV	E_{pit} / mV	E_{rp} / mV	I_{corr} / $\mu\text{A cm}^{-2}$	$CR \times 10^6$ / mm year ⁻¹
20	-346	408	202	0.23	2667
40	-44	381	185	0.65	7537
60	-41	230	-3	1.17	13566
80	-39	139	-111	2.19	25394

trates the equivalent circuit parameters for the impedance spectra of duplex steel corrosion in LiBr-ethylene glycol solution. From Table 3 with increasing the ethylene glycol concentration, the solution resistances (R_s) increase. Pure ethylene glycol has very poor electrical conductivity and is almost an insulator. Therefore the resistivity of ethylene glycol solution increases with the increase of the ethylene glycol content. In addition, the dilution by subjoining the water to solution may direct the action to facilitate the hydrolysis of the hydroxyl groups of ethylene glycol which lead to increasing electrical conductivity.

With increasing in ethylene glycol concentration to 10 %, the charge transfer and passive resistance decreases. Moreover, with higher concentration of ethylene glycol, the charge transfer and passive resistance increases. Higher R_f and R_{ct} values reflect the decrease in the porosity of passive film due to the protective properties of ethylene glycol film on surface.

Like most other organic compounds, ethylene glycol should be easily adsorbed on surface of electrode [20]. The double layer capacitance is a good indication of the adsorption of ethylene glycol on steel alloy surface. Q_{dl} can be easily calculated based on the equivalent circuit of the measured EIS. It appears that the double layer capacitance tends to decrease as the ethylene glycol concentration increases. This indicates a change at the steel alloy/solution interface. A decreasing interface capacitance can be caused by high dielectric water at the interface being replaced by some substance that is larger in molecular size. Ethylene glycol molecule is larger than water, so the adsorption of the ethylene glycol molecules at the surface of steel alloy can result in a lower Q_{dl} . When the concentration of ethylene glycol increases, more ethylene glycol will be adsorbed on the surface of electrode, leading to a lower Q_{dl} . In

Fig. 5. Cyclic polarization curves of duplex stainless steel electrode in 50 W/V % LiBr and %30 ethylene glycol-water solution at different temperatures.

other words, the steel alloy surface is more completely covered by ethylene glycol in a more concentrated ethylene glycol solution.

3.2. Effect of Temperature

Current-potential characteristics resulting from cyclic polarization curves of duplex stainless steel in 50 W/V% LiBr and 30 % ethylene glycol solution at various temperatures are shown in Fig. 5. The corresponding polarization parameters are listed in Table 4. It is found that with increase in temperature, under the same cathodic and anodic polarization potential, the cathodic and anodic current densities increases. Furthermore, the corrosion potentials shift to more positive values with increasing in the solution temperature which is related to the further increase of cathodic current in higher temperature in comparison with anodic reaction. The increasing solution temperature would accelerate both the cathodic reduction and anodic oxidation reaction [21]. In addition, an increase in the dissolution rate of passive films and a decrease in its thickness with increasing temperature

Table 5. Polarization parameters duplex stainless steel corrosion in 50 W/V % LiBr and ethylene glycol-water solution at different concentrations of ethylene glycol.

Ethylene glycol V/V %	$I_{\text{corr-293K}}$ / $\mu\text{A cm}^{-2}$	$I_{\text{corr-313K}}$ / $\mu\text{A cm}^{-2}$	$I_{\text{corr-333K}}$ / $\mu\text{A cm}^{-2}$	$I_{\text{corr-353K}}$ / $\mu\text{A cm}^{-2}$
10	0.33	1.1	1.74	2.84
30	0.23	0.65	1.17	2.19
50	0.18	0.35	0.88	1.82

are highly probable. As can be seen, polarization curves in all temperature exhibits hysteresis loop. Pitting potential and repassivation potentials shifts towards the negative values as the temperature increases. Passivation region decreases with increasing temperature. According to Fig. 5, in all temperature, the susceptibility of duplex steel to pitting corrosion is very low due to the high value of $(E_{rp}-E_{pit})$. But duplex stainless steel is more susceptible to pitting corrosion in higher temperature under applied anodic potential and repassivation of pit is more difficult.

The change of the corrosion current at different concentrations of the ethylene glycol and temperatures was studied in 50 W/V% LiBr-water solution and the results were listed in Table 5. At constant temperature, as the ethylene glycol concentration increases, corrosion current of steel alloy decreases due to the increase in the degree of surface coverage [19]. In contrast, at constant ethylene glycol concentration, the corrosion current increases as the temperature rise. To calculate activation thermodynamic parameters of the corrosion process, Arrhenius Eq. 2 and transition state Eq. 3 are used [22,23]

$$I_{\text{corr}} = K_a \exp\left(\frac{E_a}{RT}\right) \quad (2)$$

$$I_{\text{corr}} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{T}\right) \exp\left(-\frac{\Delta H_a}{RT}\right) \quad (3)$$

where E_a is the apparent activation energy of corrosion, R is the universal gas constant, K_a is the Arrhe-

Fig. 6. Typical Arrhenius plots of $\ln(I_{\text{corr}})$ vs. T^{-1} for duplex steel in 50 W/V % LiBr and ethylene glycol-water solution at different concentrations of ethylene glycol: 1) 10; 2) 30; 3) 50 V/V % ethylene glycol.

nus pre-exponential factor, h is the Plank's constant, N is the Avogadro's number, ΔS_a is the entropy of activation and ΔH_a is the enthalpy of activation.

Values of apparent activation energy of corrosion (E_a) for steel in the presence of various concentration of ethylene glycol were determined from the slope of $\ln(I_{\text{corr}})$ vs. T^{-1} plots (Fig. 6) and are shown in Table 6. Plots of $\ln(I_{\text{corr}} T^{-1})$ against T^{-1} (Fig. 7) give a straight line with a slope of $(-\Delta H_a R^{-1})$ and an intercept of $(\ln R N^{-1} h^{-1} + \Delta S_a R^{-1})$ from which the values of ΔH_a and ΔS_a are calculated and are listed in Table

Table 6. Thermodynamic parameters E_a , ΔH_a and ΔS_a for duplex steel corrosion in 50 W/V % lithium bromide and ethylene glycol-water solution at different concentrations of ethylene glycol.

Ethylene glycol V/V %	K_a / A cm^{-2}	E_a / kJ mol^{-1}	ΔH_a / kJ mol^{-1}	ΔS_a / $\text{kJ mol}^{-1}\text{K}^{-1}$	$RT=E_a-\Delta H_a$ / kJ mol^{-1}
10	87728	30.02	26.76	-0.159	3.26
30	113437	31.75	28.45	-0.154	3.3
50	168215	33.69	30.35	-0.150	3.34

Fig. 7. Transition state plots of $\ln(I_{corr} T^1)$ vs. T^{-1} for steel alloy in 50 W/V % LiBr and ethylene glycol-water solution at different concentrations of ethylene glycol: 1) 10; 2) 30; 3) 50 V/V % ethylene glycol.

6. It can be seen that E_a and ΔH_a values vary in the same way. This result permits to verify the known thermodynamic reaction between the E_a and ΔH_a as shown in Table 6 [24]:

$$\Delta H_a = E_a - RT \quad (4)$$

As can be seen, ΔS_a decreases with increasing ethylene glycol concentrations. The negative values of entropies imply that a decrease in disordering takes place on going from reactants to the adsorbed system [21]. The positive values of ΔH_a mean that the dissolution reaction is an endothermic process. An increase in ethylene glycol concentration leads to higher values of ΔH_a .

In fact, the passive films of the metals are substantially made up of metallic oxides or hydroxides which are envisaged as semiconductors. Therefore, semiconducting properties are often observed on the passive films. Passivity of stainless steel is usually attributed to the formation of a mixture of iron and chromium oxide film with semiconducting behavior [25]. Mott-Schottky analysis has been extensively used to study the semiconducting properties of the passive films. The charge distribution at the semiconductor/solution is usually determined based on Mott-Schottky relationship by measuring electrode capacitance as a function of electrode potential E [26-28]:

$$\frac{1}{C} = \frac{2}{\varepsilon \varepsilon_0 e N_D} \left(E - E_{fb} - \frac{kT}{e} \right) \text{ for n-type semiconductor} \quad (5)$$

Fig. 8. Mott-Schottky plots of the capacitance behavior measured in 50 W/V % LiBr and %30 ethylene glycol-water solution at different temperatures.

$$\frac{1}{C} = \frac{-2}{\varepsilon \varepsilon_0 e N_A} \left(E - E_{fb} - \frac{kT}{e} \right) \text{ for p-type semiconductor} \quad (6)$$

Where ε is the dielectric constant of the passive film, usually taken as 12 [29], ε_0 the permittivity of vacuum (8.854×10^{-12} F/m), e the electron charge, N_D the donor density for n-type semiconductor and the acceptor density for p-type semiconductor, E_{fb} the flat band potential, k the Boltzmann constant and T is the absolute temperature. According to Eqs. 5-6, N_D and N_A can be determined from the slope of the experimental $1/C^2$ versus E plots, and E_{fb} from the extrapolation of the linear portion to $1/C^2 = 0$.

Fig. 8 displays the C^2 vs. E for 2205 duplex stainless steels formed in different solution temperatures in 50 W/V% LiBr and %30 ethylene glycol-water solution. The results show both n-type and p-type semiconductive behavior. A peak appeared in Mott-Schottky plots for all films, which indicated an inversion from n-type to p-type semiconductor. Linear relationship can be observed between C^{-2} and E in all temperature. The positive slopes shows n-type semiconductor behavior in all the passive films formed on stainless steel and also negative slopes shows a p-type semiconductor behavior [30]. For duplex stainless steels, it is assumed that the semiconducting behavior reflects the duplex character of their surface films, with an inner region essentially formed of Cr_2O_3 and an outer region mainly composed of Fe_2O_3 [31]. Thus, the positive slope reveals that the oxide films behave as a n-type semiconductor with characteristic of Fe_2O_3

Table 7. Mott-Schottky analysis of passive film of duplex steel in 50 W/V% LiBr and %30 ethylene glycol-water solutions at different temperature.

Temperature /°C	$N_D / 10^{20} \text{cm}^{-3}$	$N_A / 10^{19} \text{cm}^{-3}$	E_{fb-n} / V	E_{fb-p} / V
20	3.93	2.36	-0.619	0.375
40	13.11	3.93	-0.583	0.173
80	14.75	19.67	-0.405	-0.014

and the negative slope can be interpreted as p-type semiconductor behavior of Cr_2O_3 [32,33].

Table 7 shows Mott-Schottky analysis of passive film of duplex steel in different temperatures. According to these results, it can be concluded that with increasing in solution temperature, the donor density for n-type semiconductor and the acceptor density for p-type semiconductor increases. An increase in N_D and N_A values lead to an increase in electric conductivity of passive films and therefore the corrosion resistance decreases.

4. Conclusion

The corrosion behavior of duplex stainless steel AISI 2205 was investigated in different ethylene glycol-water mixtures in the presence of 50 W/V% LiBr and different temperatures. Mott-Schottky analysis has been used to study the semiconducting properties of the passive films. According to electrochemical experiments, with increasing in the ethylene glycol concentration to 10 V/V%, corrosion current of the duplex steel increased. With higher concentration of ethylene glycol, corrosion current of the steel alloy substrate decreased and pitting potentials shifted to negative potentials. In all concentrations of ethylene glycol, the susceptibility of duplex steel to pitting corrosion was very low due to the high value of $(E_{rp}-E_{pit})$ and duplex steel showed stability in open circuit conditions.

The corrosion current increases as the temperature raised and also pitting potentials and repassivation potentials shifted towards less positive values. The positive values of H_a mean that the dissolution reaction is an endothermic process. According to Mott-Schottky analysis, there were both n-type semiconductor and p-type semiconductor behavior. It can be concluded that with increase solution temperature consequently the donor density for n-type semiconductor and the acceptor density for p-type semiconductor increased which led to decreasing corrosion resistance of passive film.

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