The Comparative Investigation of Corrosion and Passivation for X65 Carbon Steel in pH 1 to 5 HNO₃ Solutions without and with 0.01 mol L⁻¹ NaNO₂

Rongjiao Deng,a Pei Zhang,b Xiaoying Zhao,a Guanyu Cai,a Hui Liu,a Jinping Xiong,*a and Yong Zhou,*c

a State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, 100029 Beijing, China
b College of Chemistry and Food Science, Guangxi Key Laboratory of Agricultural Resources Chemistry and Biotechnology, Yulin Normal University, 537000 Yulin, China
c Key Laboratory for Green Chemical Process of Ministry of Education, Hubei Key Laboratory of Novel Reactor and Green Chemical Technology, Wuhan Institute of Technology, 430205 Wuhan, China

The influence of 0.01 mol L⁻¹ NaNO₂ addition on the corrosion and passivation of X65 carbon steel in pH 1 to 5 HNO₃ solutions was investigated and compared by electrochemical methods and microstructural techniques. In the pH 1 to 5 solutions without NaNO₂, the X65 steel presented the electrochemical characteristic of active dissolution, and the corrosion rate of X65 carbon steel decreased gradually with the raise of pH value. By contrast, with the addition of 0.01 mol L⁻¹ NaNO₂ in pH 1 to 5 HNO₃ solutions, the electrochemical characteristic of X65 carbon steel transferred from the active dissolution in the pH 1 to 5 solutions without NaNO₂ to the anodic passivation in the corresponding pH solutions with NaNO₂. For the X65 steel in the pH 1 to 5 solutions with NaNO₂, with the raise of pH value, the corrosion rate also decreased gradually but the passivation capability strengthened obviously. The corrosion and passivation of X65 carbon steel in pH 1 to 5 HNO₃ solutions without and with 0.01 mol L⁻¹ NaNO₂ were related to the cathodic reactions of H⁺ reduction, O₂ reduction and NO₂⁻/HNO₂ reduction.

Keywords: X65 carbon steel, HNO₃, NaNO₂, corrosion, passivation, electrochemical

Introduction

The application of carbon steels in production and living fields is wide and universal; however, the inevitability of corrosion and failure usually leads to the untimely damage of steel structure. The addition of inhibitors into environmental media is the one of main and important methods to decrease the corrosion rate of carbon steels in their service condition, which is attributed to the oxidation or the adsorption mechanism of inhibitors on the surface of carbon steels. NO₂⁻ is a kind of oxidation-type inhibitor and can promote the surface passivation of carbon steels due to the formation of surface passive film.

In alkaline and neutral environments, the related reports involving the passivation function of NO₂⁻ on the steel surface have been published repeatedly. Lee et al., Dong et al., Valcarce and Vazquez and Reffass et al. respectively reported the effectiveness of NO₂⁻ on the surface passivation of carbon steels in synthetic tap water (pH 7.2), in simulated carbonated concrete pore solution (pH 12.0), in mixed alkaline solution containing Cl⁻ (pH 13.9) and in mixed NaHCO₃ and NaCl solution (pH 8.3). The addition of NO₂⁻ into the above environmental media promoted the repassivation on the steel surface, and the mechanism of NO₂⁻ was mainly due to the following reaction:

\[ 2Fe^{2+} + 2OH^- + 2NO_2^- \rightarrow 2NO + \gamma-Fe_2O_3 + H_2O \] (1)

For the natural passive film on the surface of carbon steels formed in atmosphere, \( \gamma-Fe_2O_3 \) repaired the defects in the film interiors and made the film rearrange a regular microstructure.
However, for the surface passivation of carbon steels in acidic environments, the effectiveness of NO$_2^-$ is very few reported, and the detailed mechanism of NO$_2^-$ is still not completely clear. Zhou et al.\textsuperscript{19-21} systemically investigated the influences of NaNO$_2$ addition and its concentration on the corrosion and passivation of Q235 carbon steel in CO$_2$ saturated solution (pH 3.7). The electrochemical behavior of Q235 carbon steel transferred from the activation in CO$_2$ saturated solution free of NaNO$_2$ to the passivation in the same solution containing NaNO$_2$\textsuperscript{19} with the increase of NaNO$_2$ concentration, the passivation capability of Q235 carbon steel was strengthened obviously until the NaNO$_2$ concentration was up to 0.05 mol L$^{-1}$;\textsuperscript{20} the mechanism of NO$_2^-$ on the surface passivation was very closely associated with the formation of Fe$_2$O$_3$ passive film under FeCO$_3$ corrosion product layer.\textsuperscript{21} Further, Zhou et al.\textsuperscript{22} also investigated the influence of NaNO$_2$ addition on the electrochemical behavior of Q235 carbon steel in pH 1 to 6 HCl solutions. Due to the absence of strong oxidability and the presence of Cl$^-$ in HCl solutions, the effectiveness of NaNO$_2$ on the surface passivation was very limited, and the occurrence of pitting corrosion was present when a high potential was applied. Besides, Zuo et al.\textsuperscript{23} and Garces et al.\textsuperscript{24} reported the influences of NaNO$_2$ on the corrosion and passivation for the X70 steel in acidic NaCl solution (pH 5.5) and for the corrugated steel bar in simulated pit solution (pH 1.46 to 6.38), respectively. Nevertheless, at present, the related mechanism of NO$_2^-$ on the surface passivation of carbon steels in acidic environments still needs to be further studied.

As summarized above, until by now, the reports involving the effectiveness of NO$_2^-$ on the surface passivation of carbon steels in CO$_2$ saturated solution (a weak and non-oxidizing acid environment)\textsuperscript{20} and in pH 1 to 6 HCl solutions (a strong and non-oxidizing acid environment)\textsuperscript{22} have been published. However, in strong and oxidizing acid environments, such as HNO$_3$ solutions, the related investigations are absent. Therefore, in this work, 0.01 mol L$^{-1}$ NaNO$_2$ is added in pH 1 to 5 HNO$_3$ solutions, and the electrochemical methods of open circuit potential (OCP) evolution, potentiodynamic polarization curve and electrochemical impedance spectroscopy (EIS) are carried out to investigate and compare the corrosion and passivation of X65 carbon steel in pH 1 to 5 HNO$_3$ solutions without and with 0.01 mol L$^{-1}$ NaNO$_2$.

**Experimental**

The investigated material was X65 carbon steel with the following chemical composition (wt.%): C, 0.030; Si, 0.170; Mn, 1.510; P, 0.024; S, 0.005; Mo, 0.160; Ni, 0.170; Cu, 0.040; Al, 0.020; Ti, 0.010; N, 0.006; Nb, 0.060; Fe, balance. Samples were manually abraded up to 1000 grit with SiC abrasive papers, rinsed with de-ionized water and degreased in alcohol.

The investigated solutions were pH 1 to 5 HNO$_3$ solutions without and with the addition of 0.01 mol L$^{-1}$ NaNO$_2$. After adding NaNO$_2$, the pH value of each solution was adjusted with the introduction of diluted HNO$_3$.

The electrochemical measurements of OCP evolution, potentiodynamic polarization curve and EIS were conducted using a CS310 electrochemical workstation (Wuhan Corrtest Instruments Corp., Ltd, China). A typical three electrode system was applied for all the electrochemical measurements. The system was composed of a saturated calomel electrode (SCE) as reference electrode (RE), a platinum sheet as counter electrode (CE) and an X65 sample as working electrode (WE). The sizes of CE and WE were 1.0 × 1.0 cm and 0.2 × 0.2 cm, respectively; WE was polished once again after each electrochemical test. According to the results of OCP evolution, the WE was immersed in the corresponding investigated solution for 10 min before the electrochemical tests of polarization and EIS were begun. In the OCP test, the recording frequency of potential was 5 Hz. In the polarization test, the potential scanning rate was 0.5 mV s$^{-1}$, and the potential scanning range was from $-0.2 \text{ V}_{\text{OCP}}$ to the potential value corresponding to the objective electrochemical characteristic. In the EIS test, a perturbation potential of 10 mV amplitude was applied in the frequency range from $10^4$ to $10^2$ Hz. The schematic diagram of electrochemical testing system was shown in Figure 1. All electrochemical measurements were performed at 25 °C, which was controlled with an electro-thermostatic water bath.

![Figure 1. Schematic diagram of electrochemical testing system.](image-url)
dispersion X-ray spectroscopy (EDS) instrument attached on the SEM system.

**Results and Discussion**

Figure 2 shows the OCP evolutions and the potentiodynamic polarization curves of X65 samples in pH 1 to 5 HNO₃ solutions without 0.01 mol L⁻¹ NaNO₂. From Figure 2a, in the different pH solutions, OCP stabilizes gradually with the extensive immersion time and shows the stable value when the immersion time is up to 10 min. Therefore, in the following electrochemical tests of polarization and EIS, all the X65 samples were immersed in the corresponding solutions for 10 min before the polarization and EIS tests were begun.

In the pH 1 to 3 solutions without NaNO₂, the stable OCP value decreases with the raise of pH value, as shown in Figure 2a. Similar result is also observed on the potentiodynamic polarization curves shown in Figure 2b: corrosion potential (Ecorr) moves to the negative direction with the raise of pH value from 1 to 3. The above influences of pH values on OCP and Ecorr suggest that the dominated cathodic reaction occurred on the X65 surface in the pH 1 to 3 solutions without NaNO₂ is the H⁺ reduction with the standard potential (E₉₅₂) of 0 V SHE (SHE: standard hydrogen electrode):

\[ 2H^+ + 2e \rightarrow H_2 (E_{SE} = 0 \text{ V SHE}, \text{ pH 0}) \]  

In very acidic environments, the influence of pH value on the equilibrium potential (E_eq) of H⁺ reduction (equation 2) can be described as follows:\(^{25}\)

\[ E_{eq} (H^+/H_2) = -0.059 \text{ pH} \]  

In the pH 1 to 3 solutions without NaNO₂, with the raise of pH value, the E_eq(H^+/H₂) value decreases, so the stable OCP and the Ecorr move to the negative direction.

Further, in the pH 3 to 5 solutions without NaNO₂, the stable OCP and the Ecorr move to the positive direction with the raise of pH value. From Figure 2b, on the one hand, the value of corrosion current density (i_corr) for the X65 steel in the pH 4 to 5 solutions without NaNO₂ are in the order of magnitudes between 10⁻⁶ and 10⁻⁵ A cm⁻². On the other hand, the corrosion rate of X65 carbon steel in the pH 4 to 5 solutions is obvious lower than that in the pH 1 to 3 solutions. The above two aspects suggest that the O₂ reduction has become the dominated cathodic reaction occurred on the X65 surface in the pH 4 to 5 solutions without NaNO₂:

\[ O_2 + 2H_2O + 4e \rightarrow 4OH^- (E_{SE} = 1.220 \text{ V SHE}, \text{ pH 0}) \]  

At the same time, the influence of pH value on the E_eq of O₂ reduction (equation 4) can be described as follows:\(^{25}\)

\[ E_{eq} (O_2/\text{OH}^-) = 1.228 - 0.059 \text{ pH} \]

In the pH 4 to 5 solutions without NaNO₂, the stable OCP and the Ecorr move to the positive direction with the raise of pH value, which may be attributed to the influences of pH values on the electrode reactions of O₂ reduction and Fe oxidation. The Fe oxidation is the main anodic reaction occurred on the surface of carbon steels in acidic environments:

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e (E_{SE} = -0.441 \text{ V SHE}, \text{ a}_{\text{Fe}^{2+}} = 1 \text{ mol L}^{-1}) \]

In addition, from Figure 2b, for the X65 steel in the
pH 1 to 5 solutions without NaNO₂, the anodic current density continuously increased with the positive shift of applied potential, indicating the electrochemical characteristic of active dissolution. It is prominent for the influence of pH value on the corrosion rate of X65 carbon steel: the $i_{corr}$ value decreases obviously with the raise of pH value. This rule can be explained as follows. It is assumed that there is no influence of pH value on the anodic reaction of Fe oxidation (equation 6). With the raise of pH value, the chemical equilibrium of H⁺ reduction (equation 2) and O₂ reduction (equation 4) will move to the left direction: the higher pH value, the stronger is the movement. The cathodic reactions are restrained, resulting in the $i_{corr}$ decrease. However, from Figure 2b, it is noteworthy that the increasing rate of anodic current density with the applied potential is not prominent, particularly that in the pH 3 to 5 solutions, suggesting the deposition and protection of corrosion product on the surface of X65 carbon steel. Figure 3 shows the surface SEM morphologies of X65 samples polarized to 0.5 V SCE in the pH 3 HNO₃ solution without 0.01 mol L⁻¹ NaNO₂. From the low-magnification SEM morphology shown in Figure 3a, corrosion product is present on the sample surface and is composed of Fe, N and O by EDS analysis. Further, from the high-magnification SEM morphology shown in Figure 3b, the presence of cracks and pores is observed on the corrosion product, indicating the limited protection for the X65 substrate. The surface SEM morphologies of X65 samples in the other four solutions are similar to those in the pH 3 solution without NaNO₂.

Figure 4 shows the OCP evolutions and the potentiodynamic polarization curves of X65 samples in pH 1 to 5 HNO₃ solutions with 0.01 mol L⁻¹ NaNO₂. Comparing Figure 4b with Figure 2b, the influence of 0.01 mol L⁻¹ NaNO₂ addition on the electrochemical behavior of X65 carbon steel in pH 1 to 5 HNO₃ solutions is very prominent. In the pH 1 to 4 solutions with NaNO₂, the X65 steel presented the electrochemical characteristic of anodic passivation, and the active region, the active-passive transition region, the passive region and the transpassive region can be observed on the four polarization curves; in contrast, in the pH 5 solution with NaNO₂, the X65 steel presented the electrochemical characteristic of self-passivation. With the addition of 0.01 mol L⁻¹ NaNO₂ in pH 1 to 5 HNO₃ solutions, the obvious variation of electrochemical characteristic indicates the effectiveness of NO₂⁻ on the surface passivation of X65 carbon steel.

For the X65 steel, when the applied potential is at the vicinity of OCP, the influences of pH values on $E_{corr}$ and $i_{corr}$ in the pH 1 to 5 solutions with NaNO₂ are similar to those in the corresponding pH solutions without NaNO₂, which has been explained in the previous discussion. At the same time, by SEM observation, corrosion product is also present on the surface of X65 carbon steel when the X65 steel was polarized to the active-passive transition potential ($E_{trans}$) in the pH 1 to 5 solutions with NaNO₂. However, with the positive shift of applied potential, the passive region is present on the polarization curves, as shown in Figure 4b. It is generally accepted and confirmed that the surface passivation of carbon steels is very closely related to the generation of Fe³⁺, which is the main component of surface passive film. Therefore, the anodic reaction of Fe²⁺ oxidation is essential for the passivation of X65 carbon steel:

$$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e \quad (E_{st} = 0.771 \text{ V SHE}, \quad a_{\text{Fe}^{3+}} = 1\text{ mol L}^{-1})$$

However, the $E_{st}$ of Fe²⁺ oxidation (equation 7) is more greatly positive than that of H⁺ reduction (equation 2) or O₂

![Figure 3. Surface SEM morphologies of X65 samples polarized to 0.5 V SCE in pH 3 HNO₃ solutions without 0.01 mol L⁻¹ NaNO₂.](image)
reduction (equation 4), resulting in the absence of surface passivation for the X65 steel in pH 1 to 5 HNO₃ solutions without 0.01 mol L⁻¹ NaNO₂.

With the addition of 0.01 mol L⁻¹ NaNO₂ in pH 1 to 5 HNO₃ solutions, the presence of NO₂⁻ makes the following cathodic reactions available:²⁶-²⁸

\[
2\text{NO}_2^- + 8\text{H}^+ + 6\text{e}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O} \quad (E_{\text{st}} = 1.188 \text{ V SHE}) \quad (8)
\]

\[
2\text{HNO}_2 \rightarrow \text{N}_2\text{O}_4 + 2\text{H}^+ + 2\text{e}^- \quad (E_{\text{st}} = 1.070 \text{ V SHE}) \quad (9)
\]

\[
2\text{NO}_2^- + 6\text{H}^+ + 4\text{e}^- \rightarrow \text{N}_2\text{O}_4 + 3\text{H}_2\text{O} \quad (E_{\text{eq}} = 0.972 \text{ V SHE}) \quad (10)
\]

\[
\text{HNO}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 3\text{H}^+ + 2\text{e}^- \quad (E_{\text{eq}} = 0.940 \text{ V SHE}) \quad (11)
\]

Because the E_{eq} of above reduction reaction concerning NO₂⁻/HNO₂ (equation 8 to 11) is more positive than that of Fe^{2+} oxidation (equation 7), the anodic reaction of Fe^{2+} oxidation (equation 7) is possible if one or more of equations 8 to 11 occur on the X65 surface when a high potential was applied. However, the kinetic investigations and the E_{eq} calculations are necessary to verify the real cathodic reactions of NO₂⁻/HNO₂ reduction, which will be carried out in the future investigations. In this work, the effectiveness of NO₂⁻ on the surface passivation of X65 carbon steel in pH 1 to 5 HNO₃ solutions is certain, which can provide a degree of theoretical basis to the engineering application, similar to that of anodic protection.

Further, from Figures 2b and 4b, the influences of NaNO₂ addition and pH value on the corrosion and passivation parameters, including E_{corr}, i_{corr}, E_{trans}, critical passive current density (i_{crit}) and maintaining passive current density (i_{main}), are very obvious. In this work, the CVIEW software was applied to analyze the results of potentiodynamic polarization curve. Table 1 lists the calculated results of E_{corr}, i_{corr}, E_{trans}, i_{crit} and i_{main}.

It is similar the influences of pH values on E_{corr} and i_{corr} both in the pH 1 to 5 solutions without and with NaNO₂, which has been explained in the previous discussion. In the pH 1 to 4 solutions with NaNO₂, the X65 steel presented the electrochemical characteristic of anodic passivation, and it is worth noting that both the E_{corr} and i_{corr} values decrease obviously with the raise of pH value, indicating that the surface passivation in the high pH solutions is easier than that in the low pH solutions. Further, this result also suggests the cathodic reactions of equations 9 and 11 are more possible than those of equations 8 and 10. In the pH 5 solution.

<table>
<thead>
<tr>
<th>pH</th>
<th>Without NaNO₂</th>
<th>With NaNO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E_{corr} / V_SCE</td>
<td>i_{corr} / (A cm⁻²)</td>
</tr>
<tr>
<td>1</td>
<td>−0.42</td>
<td>3.27 × 10⁻²</td>
</tr>
<tr>
<td>2</td>
<td>−0.57</td>
<td>2.52 × 10⁻³</td>
</tr>
<tr>
<td>3</td>
<td>−0.67</td>
<td>3.75 × 10⁻⁴</td>
</tr>
<tr>
<td>4</td>
<td>−0.37</td>
<td>6.59 × 10⁻⁵</td>
</tr>
<tr>
<td>5</td>
<td>−0.23</td>
<td>1.30 × 10⁻⁵</td>
</tr>
</tbody>
</table>

E_{corr}: corrosion potential; i_{corr}: corrosion current density; E_{trans}: active-passive transition potential; i_{crit}: critical passive current density; i_{main}: maintaining passive current density.
The Comparative Investigation of Corrosion and Passivation for X65 Carbon Steel


with NaNO₂, the X65 steel presented the electrochemical characteristic of self-passivation, and the absence of active-passive transition suggests the relatively high passivation capability. Besides, the influence of pH value on the \( i_{\text{corr}} \) value is not obvious in the pH 1 to 5 solutions with NaNO₂.

At the same time, from Table 1, the \( i_{\text{corr}} \) value in the pH 1 to 4 solutions with NaNO₂ is greater than that in the corresponding pH solutions without NaNO₂, which is also due to the presence of NO₂⁻.²⁰

Figure 5 shows the EIS of X65 samples in pH 1 to 5 HNO₃ solutions without and with 0.01 mol L⁻¹ NaNO₂ at the stable OCP value. From Figure 5, the influence of 0.01 mol L⁻¹ NaNO₂ addition on the EIS characteristic of X65 carbon steel in pH 1 to 5 HNO₃ solutions is also remarkable.

In the pH 1 to 3 solutions without NaNO₂, the three Nyquist plots are composed of two capacitive semicircles at the high frequency zone and an inductive semicircle at the low frequency zone. However, in the pH 4 to 5 solutions without NaNO₂, the presence of two capacitive semicircles and the absence of inductive semicircle are observed on the two Nyquist plots. From the previous discussion, for the two capacitive semicircles, one is attributed to the deposition of corrosion product on the X65 surface and the other one is due to the process of charge transfer between double electron layer;²⁰ the presence of inductive semicircle is attributed to the adsorption relaxation process of H⁺;²⁰ and the disappearance of inductive semicircle further confirms the different cathodic reaction: H⁺ reduction (equation 2) in the pH 1 to 3 solutions without NaNO₂ and O₂ reduction (equation 4) in the pH 4 to 5 solutions without NaNO₂. From Figure 5a, the radius of capacitive semicircle enlarges significantly with the raise of pH value, indicating the decrease of corrosion rate. In the pH 1 to 5 solutions with NaNO₂, the five Nyquist plots are composed of two capacitive semicircles at the entire frequency zone, which is also due to the deposition of corrosion product and the charge transfer between double electron layer. From Figure 5b, the radius of capacitive semicircle also enlarges with the raise of pH value.

Further, the method of equivalent electrical circuit (EEC) interpretation is applied to fit the EIS results. For the EIS obtained in the pH 1 to 3 solutions without NaNO₂, two capacitive semicircles and an inductive semicircle are present, so the EEC model shown in Figure 6a is appropriate to fit the corresponding EIS. In Figure 6a, \( R_s \) represents the solution resistance, CPE\(_c\) and \( R_c \) represent the capacitance and resistance of corrosion product, respectively, CPE\(_{dl}\) and \( R_{ct} \) represent the double layer capacitance and the charge transfer resistance, respectively, \( R_L \) represents the inductive resistance, and \( L \) represents the inductance. At the same time, for the EIS obtained in the pH 4 to 5 solutions without NaNO₂ and in the pH 1 to 5 solutions with NaNO₂, only

![Figure 5. EIS of X65 samples in pH 1 to 5 HNO₃ solutions: (a) without 0.01 mol L⁻¹ NaNO₂ and (b) with 0.01 mol L⁻¹ NaNO₂.](image)

![Figure 6. EEC model to fit EIS shown in Figure 5. (a) EIS obtained in the pH 1 to 3 HNO₃ solutions without NaNO₂ and (b) EIS obtained in the pH 4 and 5 HNO₃ solutions without NaNO₂ and in the pH 1 to 5 HNO₃ solutions with NaNO₂.](image)
two capacitive semicircles are present, and the EEC model shown in Figure 6b is suitable to fit the corresponding EIS.

Further, the ZVIEW software was applied to analyze the results of EIS. Table 2 lists the calculated results of CPE\(_c\), R\(_c\), CPE\(_{dl}\) and R\(_{ct}\).

From Table 2, both in the pH 1 to 5 solutions without NaNO\(_2\) and with NaNO\(_2\), the values of R\(_c\) and R\(_{ct}\) increase with the raise of pH value, indicating the decreased corrosion rate.\(^{30}\) Besides, the values of CPE\(_c\) and CPE\(_{dl}\) decrease with the raise of pH value, suggesting the decrease of corrosion area on the WE surface.\(^{31}\) The above results further confirm that the corrosion rate of X65 carbon steel in the high pH solutions is less than that in the low pH solutions, which is in agreement with the results of potentiodynamic polarization curve.

Figure 7 shows the EIS of X65 samples in pH 1 to 5 HNO\(_3\) solutions with 0.01 mol L\(^{-1}\) NaNO\(_2\) at the applied potential of 1.0 V\(_{SCE}\): (a) Nyquist plot and (b) Bode plot. From Figure 7b, two points of intersection can be observed on each Bode plot, indicating two time constants. Therefore, the EEC model shown in Figure 8 is applied to fit the EIS shown in Figure 7, in which CPE\(_p\) and R\(_p\) represent the capacitance and resistance of passive film, respectively.

![Graph of Z_i vs f](image1)

![Graph of Z vs f](image2)

**Figure 7.** EIS of X65 samples in pH 1 to 5 HNO\(_3\) solutions with 0.01 mol L\(^{-1}\) NaNO\(_2\) at the applied potential of 1.0 V\(_{SCE}\): (a) Nyquist plot and (b) Bode plot.

**Figure 8.** EEC model to fit EIS shown in Figure 7.

Table 2. Calculated results of CPE\(_c\), R\(_c\), CPE\(_{dl}\) and R\(_{ct}\) from the ZVIEW software

<table>
<thead>
<tr>
<th>pH</th>
<th>CPE(_c) (F cm(^{-2}))</th>
<th>R(_c) (Ω cm(^2))</th>
<th>CPE(_{dl}) (F cm(^{-2}))</th>
<th>R(_{ct}) (Ω cm(^2))</th>
<th>CPE(_c) (F cm(^{-2}))</th>
<th>R(_c) (Ω cm(^2))</th>
<th>CPE(_{dl}) (F cm(^{-2}))</th>
<th>R(_{ct}) (Ω cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.32 × 10(^{-4})</td>
<td>12.71</td>
<td>4.94 × 10(^{-4})</td>
<td>18.33</td>
<td>8.76 × 10(^{-4})</td>
<td>0.78</td>
<td>1.59 × 10(^{-3})</td>
<td>1.09</td>
</tr>
<tr>
<td>2</td>
<td>1.28 × 10(^{-4})</td>
<td>16.92</td>
<td>2.13 × 10(^{-4})</td>
<td>22.72</td>
<td>7.70 × 10(^{-4})</td>
<td>1.48</td>
<td>1.52 × 10(^{-3})</td>
<td>2.39</td>
</tr>
<tr>
<td>3</td>
<td>7.54 × 10(^{-5})</td>
<td>132.87</td>
<td>1.87 × 10(^{-4})</td>
<td>267.70</td>
<td>5.92 × 10(^{-4})</td>
<td>23.01</td>
<td>1.49 × 10(^{-3})</td>
<td>22.51</td>
</tr>
<tr>
<td>4</td>
<td>2.74 × 10(^{-5})</td>
<td>172.41</td>
<td>8.74 × 10(^{-5})</td>
<td>963.91</td>
<td>5.80 × 10(^{-4})</td>
<td>21.27</td>
<td>1.17 × 10(^{-3})</td>
<td>96.47</td>
</tr>
<tr>
<td>5</td>
<td>1.18 × 10(^{-5})</td>
<td>317.50</td>
<td>7.81 × 10(^{-5})</td>
<td>1083.00</td>
<td>5.61 × 10(^{-4})</td>
<td>32.88</td>
<td>8.93 × 10(^{-4})</td>
<td>356.21</td>
</tr>
</tbody>
</table>

CPE\(_c\): corrosion product capacitance; R\(_c\): corrosion product resistance; CPE\(_{dl}\): double layer capacitance; R\(_{ct}\): charge transfer resistance.

Table 3 lists the calculated results of R\(_p\). From Table 3, the R\(_p\) value increases gradually with the raise of pH value, which is consistent with the results of E\(_{trans}\) and i\(_{crit}\) shown.
The Comparative Investigation of Corrosion and Passivation for X65 Carbon Steel


in Table 1. Therefore, it is concluded that for the X65 steel in the pH 1 to 5 solutions without NaNO₂, the passivation capability of X65 carbon steel in the high pH solutions is stronger than that in the low pH solutions.³³

**Conclusions**

In this work, the influence of 0.01 mol L⁻¹ NaNO₂ addition in pH 1 to 5 HNO₃ solutions on the corrosion and passivation of X65 carbon steel was investigated and compared. In the pH 1 to 5 solutions without NaNO₂, X65 carbon steel presented the electrochemical behavior of activation, and the corrosion rate decreased with the raise of pH value. With the addition of 0.01 mol L⁻¹ NaNO₂ in pH 1 to 5 HNO₃ solutions, the electrochemical behavior of X65 carbon steel transferred from the active dissolution to the anodic passivation. For the X65 steel in the pH 1 to 5 solutions with NaNO₂, with the raise of pH value, the corrosion rate decreased, and the passivation capability strengthened. The corrosion and passivation of X65 carbon steel in pH 1 to 5 HNO₃ solutions without and with 0.01 mol L⁻¹ NaNO₂ were associated with the cathodic reactions of H⁺ reduction, O₂ reduction and NO₂⁻/HNO₂ reduction.

**Acknowledgments**

This work is supported by the National Natural Science Foundation of China (contract 51601133).

**References**


Submitted: May 8, 2019
Published online: October 7, 2019

This is an open-access article distributed under the terms of the Creative Commons Attribution License.