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Investigation of the Mechanism for Acetic Acid Corrosion of Mild Steel

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ABSTRACT

Acetic acid is recognized as an important factor in mild steel corrosion. Like carbonic acid, acetic acid is a weak acid, which partially dissociates as a function of pH and the solution temperature. Stronger than carbonic acid (pKa 4.76 vs. 6.35 at $25^{o}C$), acetic acid is the main source of hydrogen ions when the concentration of each acid is the same. According to many studies, acetic acid enhances the corrosion rate of mild steel by accelerating the cathodic reaction. The mechanism of acetic acid reduction at the metal surface is still being debated. When the reduction of the adsorbed acetic acid molecule occurs at the metal surface, the mechanism is called "direct reduction". If the role of acetic acid is to dissociate near the metal surface to provide additional hydrogen ions and the only cathodic reduction is reduction of hydrogen ions, this mechanism is referred to as a "buffering effect". In the present study, electrochemical techniques such as potentiodynamic sweeps and electrochemical impedance spectroscopy were used in order to investigate the effect of acetic acid on the cathodic reaction. It was found that acetic acid affects only the limiting cathodic current, but had no effect on the charge transfer current. The charge transfer current is found to respond to a change of pH. It was concluded that the buffering effect was proven correct.

Key words: acetic acid, cathodic reactions, mild steel corrosion

INTRODUCTION

The presence of organic acids found in produced water was reported as a severe concern in mild steel pipeline corrosion for the oil and gas industry.[1, 2, 3, 4] In 1944, Menaul[3] reported 250 ppm of organic acids in the Katy field, Texas. Since then, the detrimental effects of organic acids on mild steel

corrosion were confirmed in the so-called bottom-of-the-line corrosion due to produced water as well as in top-of-the-line corrosion arising from water condensation. Typical concentrations of organic acid reported in the field are of the order of 100 ppm, while in some cases, up to 3000 ppm of organic acids was reported.[4] Among organic acids, acetic acid (CH_3COOH, or shortly HAc) is known as the dominant low molecular weight acid found in produced fluids (usually about 50-90% of the total).[5]

In the past few decades, a number of studies[4-9] have been dedicated to investigating the effect of acetic acid on mild steel corrosion in an aqueous CO_2 containing environment. Like the carbonic acid formed by hydration of dissolved CO_2, acetic acid is a weak acid, which partially dissociates (1) to an extent governed by pH and the solution temperature. Stronger than carbonic acid (pKa 4.76 vs. 6.35 at 25^oC), acetic acid is the main source of hydrogen ions when the concentration of each acid is the same.

$$HAc_{(aq)} \rightleftharpoons H^+_{(aq)} + Ac^-_{(aq)} \tag{1}$$
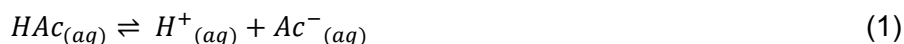
According to most mechanistic studies,[5-9] acetic acid enhances the corrosion rate of mild steel by accelerating the cathodic reaction. However, the exact mechanism remains controversial and it is not clear whether the adsorbed acetic acid molecule is reduced at the surface (in addition to any reduction of hydrogen ions); this mechanism is called "direct reduction". The alternative possibility is that the acetic acid dissociates and provides an additional source of hydrogen ions near the steel surface, while the only cathodic reaction is reduction of hydrogen ions, a mechanism referred to as "buffering effect". These two mechanisms are reviewed in detail below.

Direct Reduction

In the so-called "direct reduction" of acetic acid, it is reduced at the metal surface according to reaction (3), in addition to the reduction of hydrogen ions typical for all acids, reaction (2). This mechanism has been proposed by many authors[6, 7] in order to explain a high corrosion rate of mild steel in the presence of acetic acid.

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \tag{2}$$

$$2HAc + 2e^- \rightleftharpoons H_{2(g)} + 2Ac^-_{(aq)} \tag{3}$$

The anodic reaction that occurs at the same time at the metal surface, in order to balance the charge, is the dissolution of iron, reaction (4):

$$Fe_{(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2e^- \tag{4}$$

Garsany et al.[6] studied the role of acetate ion on the corrosion rate of carbon steel in a CO_2 environment using a rotating disk electrode. Their voltammograms showed two "waves," apparently resulting from the reduction of hydrogen ions and acetic acid. The authors also pointed out that due to the fast dissociation of acetic acid, it would be very difficult to experimentally distinguish between the reduction of acetic acid and that of hydrogen ions. Matos et al.[7] observed two different peaks using square wave voltammetry response on a platinum microdisk working electrode, suggesting the reduction of both hydrogen ions and the undissociated acetic acid.

Buffering Effect

On the other hand, another possible and simpler pathway is to consider acetic acid only as a source of hydrogen ions which are then reduced at the steel surface. In this scenario, the role of acetic acid is to act as a "buffer," which provides more hydrogen ions when the latter are consumed by the corrosion reaction at the surface, reaction (2). This mechanism is termed the "buffering effect." Therefore, in this

scenario, direct reduction of acetic acid, reaction (3), is not significant and can be omitted from the analysis so that only the reduction of hydrogen ions is taken into account.

By conducting a series of potentiodynamic sweeps on a rotating cylinder electrode at pH 4, George[8] argued that if acetic acid was reduced at the surface, the corrosion current density would increase proportionally with increasing acetic acid concentrations, which was not observed by his experimental data. According to his study, only the cathodic limiting current is accelerated, while the anodic reaction is retarded in the presence of acetic acid. Therefore, the author suggested that the role of acetic acid is to be a "reservoir" providing hydrogen ions as needed for the cathodic reaction.

Similar results and conclusions were made by Amry.[9] In addition, the author proposed a mechanism where the dissociation of adsorbed acetic acid is followed by a Volmer-Heyrovsky step, reactions (5) and (6).

$$HAc_{ad} \rightleftharpoons H^+ + Ac^- \rightleftharpoons H_{ad} + Ac^- \qquad \text{Volmer step} \qquad (5)$$

$$H_{ad} + H^+ + e^- \rightleftharpoons H_2 \qquad \text{Heyrovsky step} \qquad (6)$$

It remains important to distinguish these two mechanisms, not least because the corrosion rate prediction depends strongly on this assumption. If direct reduction of acetic acid occurs at the surface, the corrosion rate will keep increasing with the increasing acetic acid concentration at the same pH, irrespective of the controlling step (charge or mass transfer control). However, if the only cathodic reaction that happens at the metal surface is the reduction of hydrogen ions (buffering effect), the corrosion rate will stop increasing beyond a certain acetic acid concentration, when the control shifts from mass transfer to charge transfer control.

As this brief review of critical literature shows, so far, the answer to this dilemma is not clear. Therefore, the goal of the present work is to provide additional empirical evidence which could help determine whether the direct reduction of acetic acid occurs or not. Furthermore, a study leading to an improved understanding of acetic acid corrosion mechanisms will provide a good starting point for a similar analytical approach to be applied to studying CO_2 corrosion mechanism. There it is similarly assumed that the weak carbonic acid either acts as a reservoir of hydrogen ions[14-16] (buffering effect) and/or can be reduced directly at the steel surface.[10-13]

EXPERIMENTAL PROCEDURE

Method

As discussed above, the enhanced rate of the cathodic hydrogen evolution is due to either direct reduction of adsorbed acetic acid or simply due to the ability of acetic acid to dissociate and act as a hydrogen ion "buffer." If the latter is true, the charge transfer rate due to reduction of hydrogen ions should remain the same at the same pH, irrespective of the presence of acetic acid. However, in the previous corrosion studies carried by George,[8] it has been difficult to observe this behavior as the charge transfer region for the reduction of hydrogen ions overlaps with the region where the dominant reaction is anodic dissolution of iron. This led to a choice of a different substrate in the current work for the study of acetic acid reduction mechanisms. After trying out several noble metals (platinum and gold), the best and most consistent results were obtained by using a passive metal - a stainless steel SS304 (UNS S30400) electrode. The charge transfer current arising from reduction of hydrogen ions on SS304 could be examined without interference from the anodic iron dissolution reaction seen on a mild steel electrode (e.g. made from X65 pipeline steel (UNS K03014). An additional benefit of using a passive stainless steel electrode over one made from noble metals was that the former could be considered to be more similar to a mild steel surface and any catalytic effects of hydrogen reduction seen on noble metals would be avoided. As Figure 1 shows, a good agreement was obtained between

the measured limiting currents of both steels (SS304 vs. X65) under the same environmental conditions. Based on this analysis, it was assumed that the nature of the cathodic reaction on mild steel can be revealed by examining the behavior of the same reaction on stainless steel at comparable conditions.
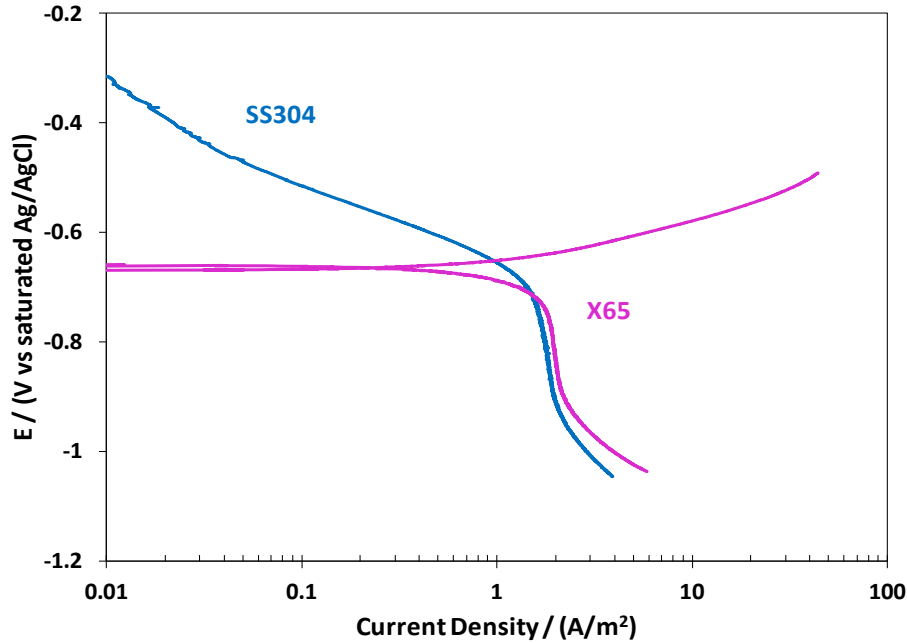

Figure 1: Comparison of cathodic sweeps obtained on SS304 stainless steel and X65 mild steel at 25°C, pH 4.0, aqueous solution saturated with N_2 with 3 wt.% NaCl, 0 ppm HAc, RCE rotating speed 1000 rpm.

Procedure

Both a rotating disk electrode (RDE) and a rotating cylinder electrode (RCE) were used in this work. Experiments were conducted in a 150-milliliter glass cell for the RDE and a 2-liter glass cell for the RCE, using a standard 3-electrode setup (Figure 2). The glass cell was filled with 3 wt.% NaCl electrolyte. Before each experiment, the solution was purged with nitrogen for at least 2 hours to facilitate electrolyte deoxygenation.

The concentration of acetic acid added to the glass cell, $[HAc_{tot}]$, which is the total amount of acetate in the solution present as either undissociated acetic acid $[HAc]$ or acetate ion $[Ac^-]$), was calculated from the desired undissociated acetic acid concentration $[HAc]$, the equilibrium constant K_a, and the hydrogen ion concentration $[H^+]$:

$$HAc_{tot} = [HAc] \cdot \left(1 + \frac{K_a}{[H^+]}\right) \qquad (7)$$

where K_a is a function of temperature T_K (in Kelvin)[17]

$$K_a = 10^{-\left(6.66104 - 0.0134916 \times T_K + 2.37856 \times 10^{-5} \times T_K^2\right)} \qquad (8)$$

Whenever not specifically stated, the acetic acid concentration mentioned in this work refers to the undissociated acid $[HAc]$ concentration.

The pH was adjusted by adding deoxygenated hydrochloric acid or sodium hydroxide. Before immersion into the test solution, the stainless steel electrodes were polished using 150, 400 and 600 grit silicon carbide paper and then washed with isopropyl alcohol and air dried.

The electrochemical tests started when the measured corrosion (open circuit potential, OCP) potential stabilized within ± 1mV over at least 2 minutes. The open circuit potential was always found to be in the range between -250 mV and -450 mV with respect to the saturated Ag/AgCl electrode. For the cathodic sweeps, the working electrode was polarized from the open circuit potential in the negative direction using a scan rate of 0.2 mV/s. Once this was done and the OCP potential stabilized, the impedance measurements were conducted by applying an oscillating potential of ±10 mV around a given fixed potential using a frequency range from 10,000 Hz to 0.01 Hz.
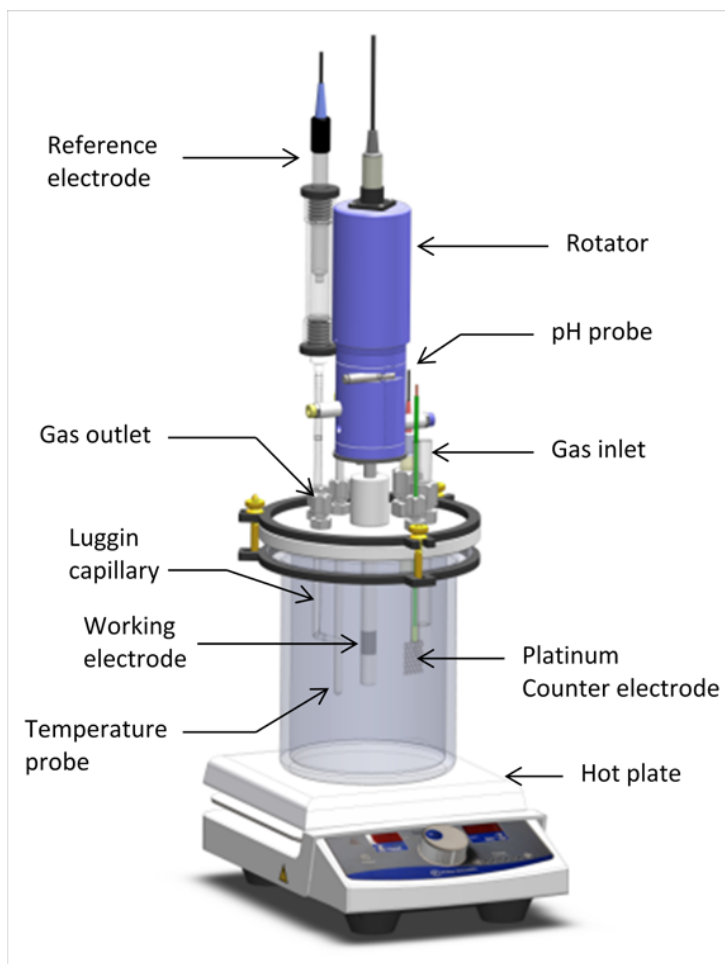
Figure 2: Schematic of the glass cell with the three-electrode electrochemical system.

RESULTS

Potentiodynamic Sweeps

Potentiodynamic sweeps were performed at the same pH in order to investigate the effect of acetic acid on the charge transfer current. At pH 4, an increase of acetic acid concentration only affects the limiting current, arising from mass transfer, but has no influence on the charge transfer current (Figure 3 and Figure 4). The same result was obtained in a laminar and turbulent flow regime (using the RDE and RCE): the charge transfer current does not change with the acetic acid concentration. This indicates

that, besides the reduction of hydrogen ion, there are no additional electrochemical reactions at the metal surface, such as the hypothesized reduction of acetic acid. Similar results were observed at pH 3 (Figure 5). In other words, under all these conditions, acetic acid acts primarily as a source of hydrogen ions which only causes an increase in the mass transfer controlled limiting current for hydrogen evolution.
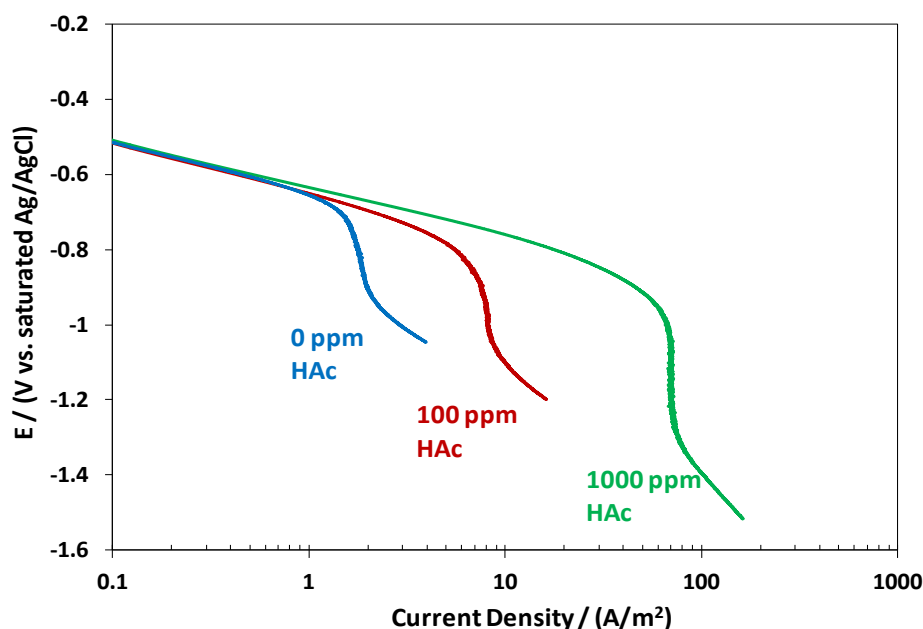

Figure 3: Comparison of potentiodynamic sweeps obtained using a SS304 for different undissociated acetic acid concentrations at 25°C, pH 4.0, aqueous solution saturated with N_2, 3 wt.% NaCl, RCE rotating speed 1000 rpm.
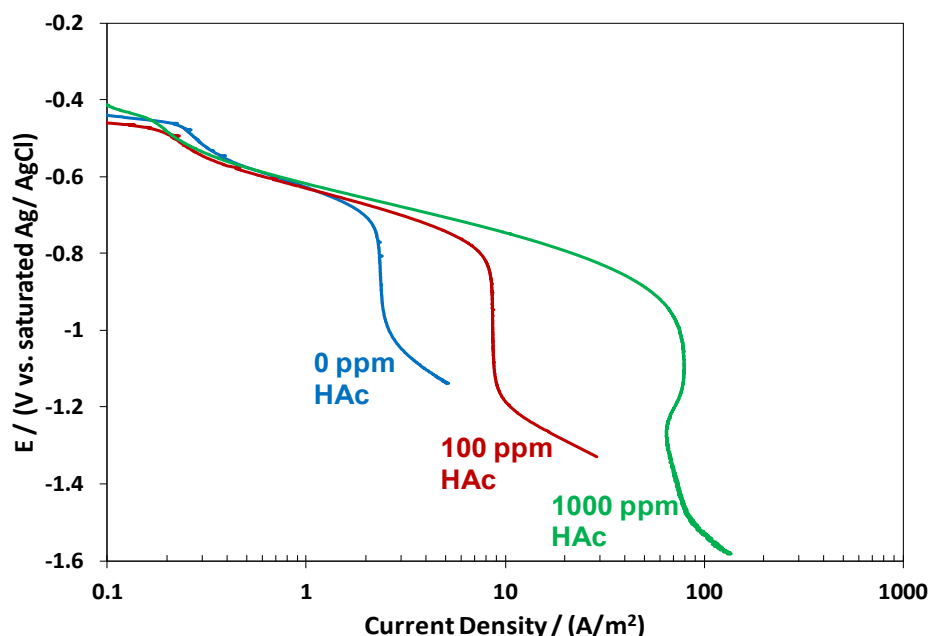
Figure 4: Comparison of potentiodynamic sweeps obtained using a SS304 for different undissociated acetic acid concentrations at 25°C, pH 4.0, aqueous solution saturated with N_2, 3 wt.% NaCl, RDE rotating speed 1000 rpm.
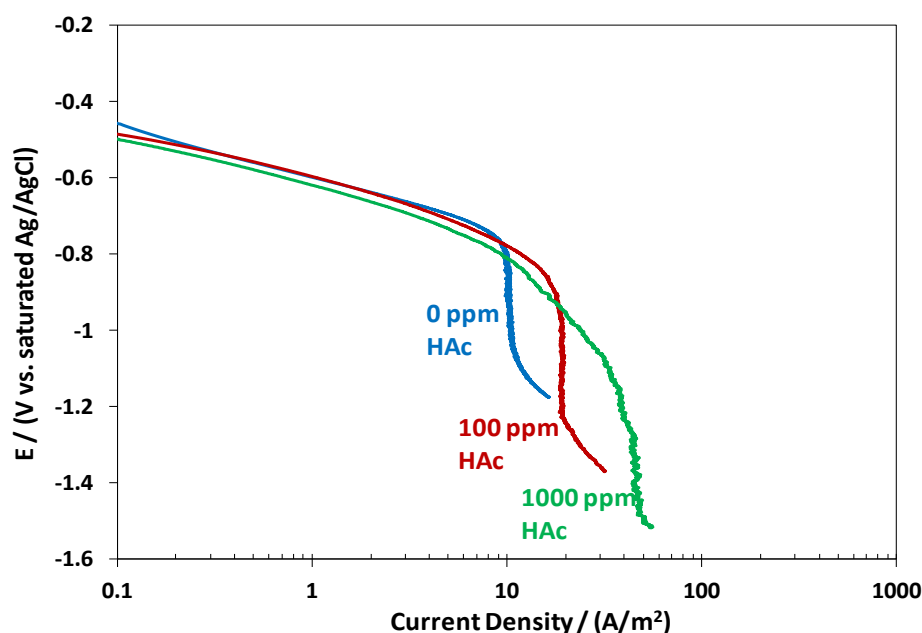
Figure 5: Comparison of potentiodynamic sweeps obtained using a SS304 for
different undissociated acetic acid concentrations at 25°C, pH 3.0,
aqueous solution saturated with N_2, 3 wt.% NaCl, RCE rotating speed 1000 rpm

Since hydrogen ions appear to be the only cathodic reactants, the change of hydrogen ion concentration should affect the charge transfer current. Indeed, Figure 6 and Figure 7 show a change of charge transfer current when pH changes, in the absence and with the presence of acetic acid, respectively. In both cases, a higher charge transfer current is expected when pH decreases (i.e. the hydrogen ion concentration increases). This result confirms that hydrogen ions are the main cathodic reactant in the systems studied in this work.
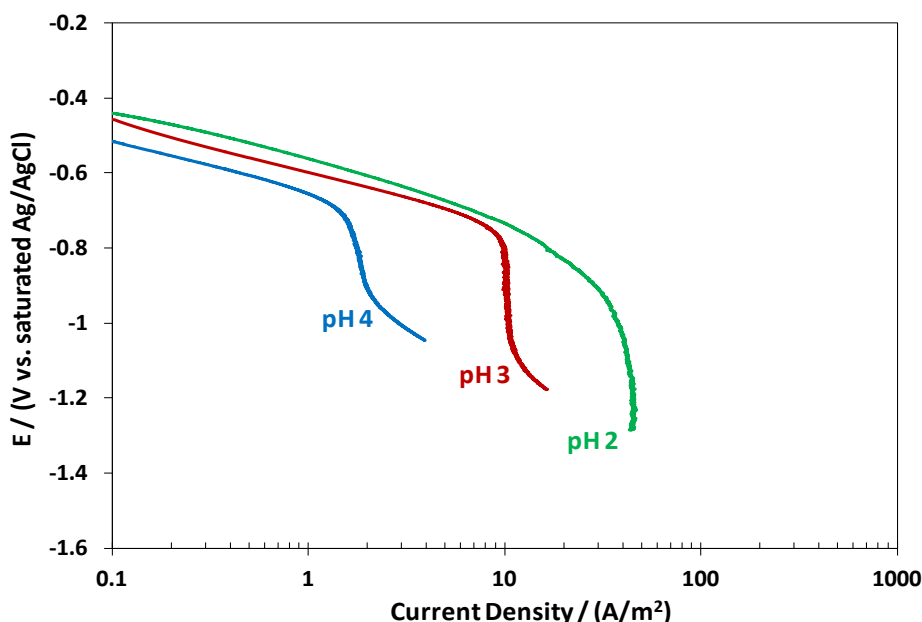
Figure 6: Comparison of potentiodynamic sweeps obtained using a SS304 for
different pH at 25°C, aqueous solution saturated with N_2,
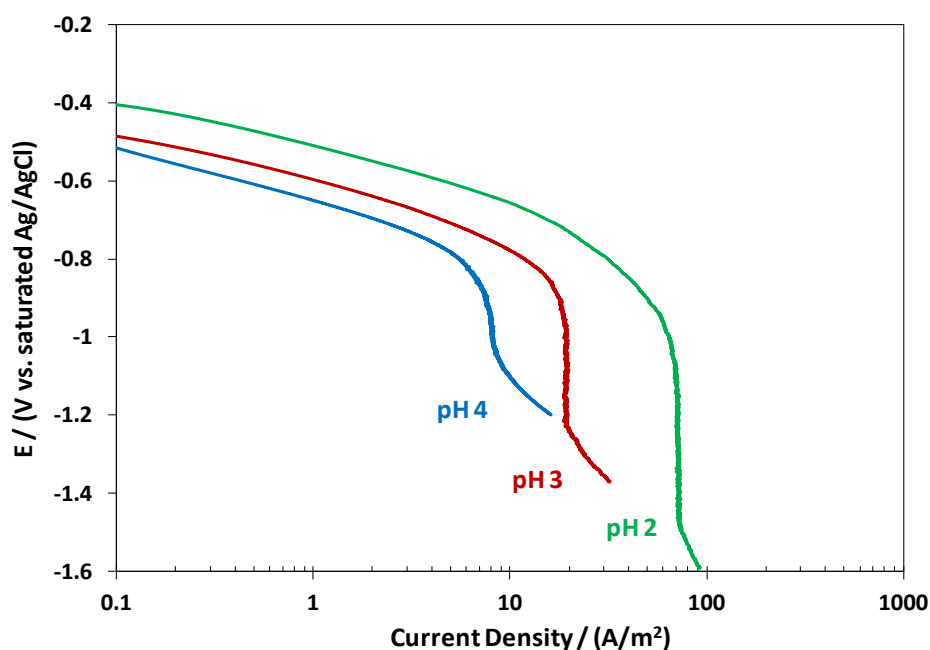0 ppm HAc with 3 wt.% NaCl, RCE rotating speed 1000 rpm.

Figure 7: Comparison of potentiodynamic sweeps obtained using a SS304 for different pH at 25°C, aqueous solution saturated with N_2, 100 ppm HAc with 3 wt.% NaCl, RCE rotating speed 1000 rpm.

Electrochemical Impedence Spectroscopy (EIS) Results

From the potentiodynamic sweeps, it appears that the charge transfer rates remain the same with an increase of acetic acid concentration at the same pH. Hence, the charge transfer resistance as measured by EIS should be the same as well. EIS measurements were conducted around the fixed potential of -0.6 V vs. a saturated Ag/AgCl electrode, which is according to the potentiodynamic sweeps in the middle of the charge transfer controlled region for the hydrogen reduction reaction. Figure 8 and Figure 9 show the Nyquist plots for 0, 100 and 1000 ppm of acetic acid at pH 4 and pH 3, respectively. The charge transfer resistance is roughly the same when the concentration of acetic acid changes at a fixed pH. The repeated tests at pH 4 (Figure 10) show that the charge transfer resistance is about 2000 $\pm$ 500 $\Omega.cm^2$ for different concentrations of acetic acid. The repeated tests at pH 3 (Figure 11) show that the charge transfer resistance is about 800 $\pm$ 400 $\Omega.cm^2$. If acetic acid were reduced at the surface, the charge transfer resistance would be expected to change proportionally to the change of acetic acid concentration at a fixed pH, which is not supported by these results.

In addition, since the hydrogen ions are the only species reduced at the surface, a decrease of pH leads to an increase of the charge transfer current and hence a decrease of the charge transfer resistance (compare Figure 12 and Figure 13).

The EIS results are therefore consistent with the potentiodynamic sweep data. One can draw the conclusion that there is no direct reduction of acetic acid at the steel surface. The only cathodic reaction is the reduction of hydrogen ions.
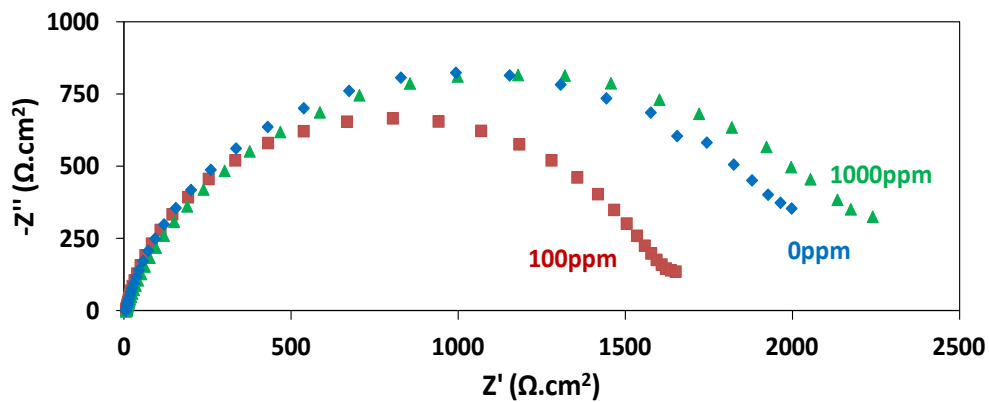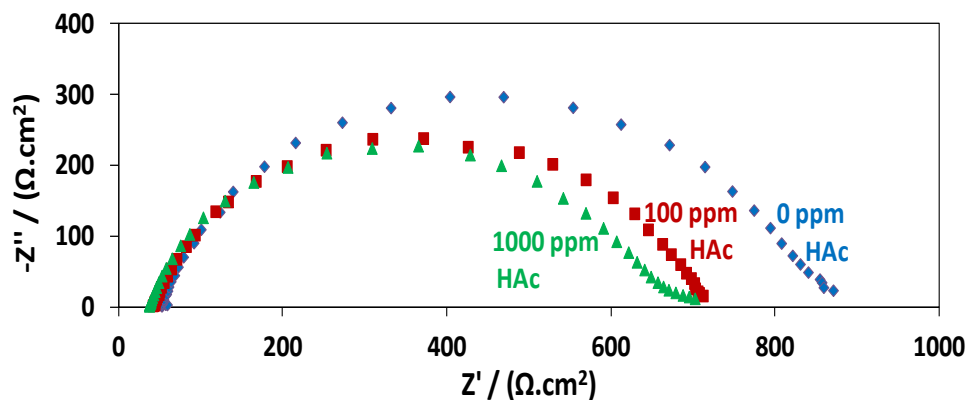
Figure 8: Nyquist plot at -0.6 V vs. a saturated Ag/AgCl electrode obtained by using an SS304 RDE electrode for different undissociated acetic acid concentrations at 25°C, pH 4.0, aqueous solution saturated with N_2, 3 wt.% NaCl, RDE rotating speed 1000 rpm.

Figure 9: Nyquist plot at -0.6 V vs. a saturated Ag/AgCl electrode obtained by using an SS304 RCE electrode for different undissociated acetic acid concentrations at 25°C, pH 3.0, aqueous solution saturated with N_2, 3 wt.% NaCl, RCE rotating speed 1000 rpm.
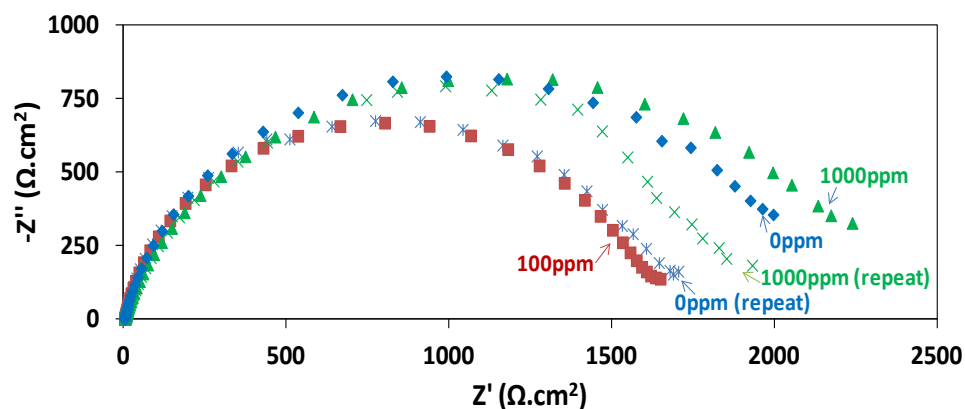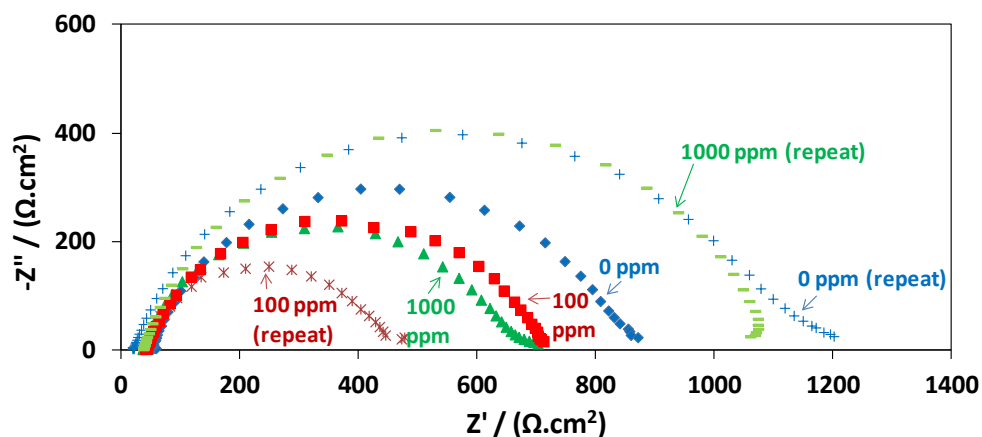

Figure 10: Repeated tests
Nyquist plot at -0.6 V vs. a saturated Ag/AgCl electrode obtained by using an SS304 RDE electrode for different undissociated acetic acid concentrations at 25°C, pH 4.0, aqueous solution saturated with N_2, 3 wt.% NaCl, RDE rotating speed 1000 rpm.

Figure 11: Repeated tests
Nyquist plot at -0.6 V vs. a saturated Ag/AgCl electrode obtained by using an SS304 RCE electrode for different undissociated acetic acid concentrations at 25°C, pH 3.0, aqueous solution saturated with N_2, 3 wt.% NaCl, RCE rotating speed 1000 rpm.
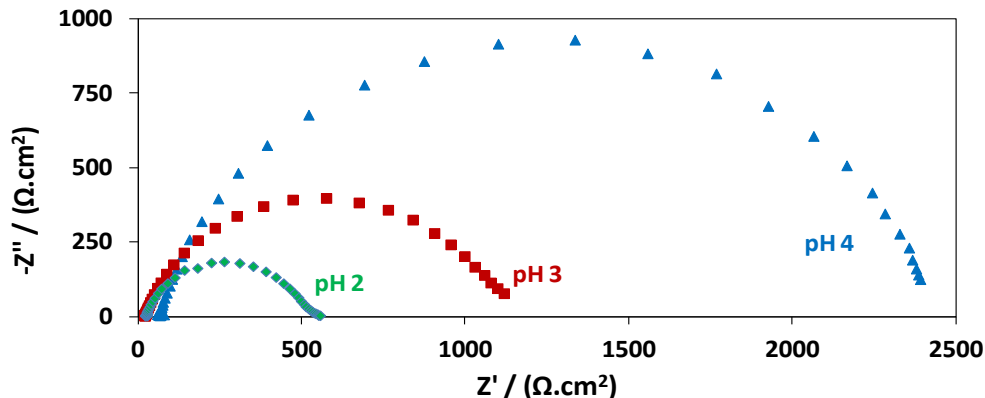

Figure 12: Nyquist plot at -0.6 V vs. a saturated Ag/AgCl electrode obtained by using an SS304 RCE electrode for different pH at 25°C, aqueous solution saturated with N_2, 0 ppm HAc, 3 wt.% NaCl, RCE rotating speed 1000 rpm.
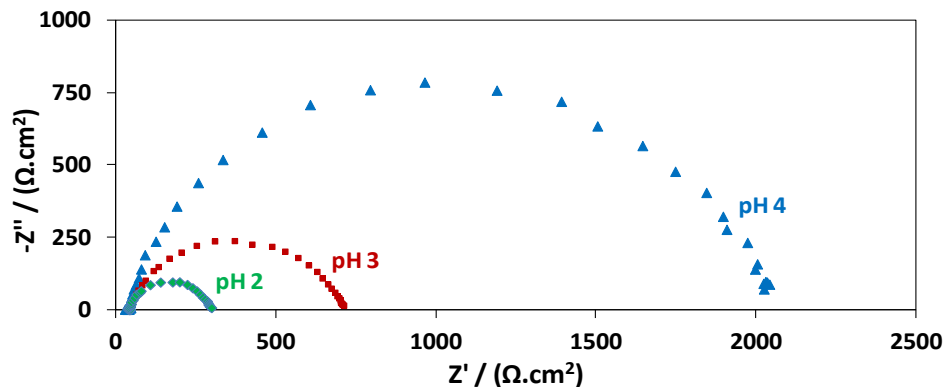

Figure 13: Nyquist plot at -0.6 V vs. a saturated Ag/AgCl electrode obtained by using an SS304 RCE electrode for different pH at 25°C, aqueous solution saturated with N_2, 100 ppm HAc, 3 wt.% NaCl, RCE rotating speed 1000 rpm.

CONCLUSIONS

- The dominant cathodic reaction mechanism related to reduction of acetic acid on steel is the so called "buffering effect."
- The presence of acetic acid only affects the cathodic limiting current due to the ability of acetic acid to provide the hydrogen ions by dissociation, when the latter are consumed at the metal surface.
- Acetic acid has no influence on the charge transfer cathodic current since no direct reduction of acetic acid can be detected. Hydrogen ions are the only cathodic reactants reduced at the metal surface. A change of pH leads to a change of the cathodic charge transfer current, as expected.
- A good agreement for the corrosion mechanisms was achieved from analyzing the results of both potentiodynamic sweeps and EIS measurements, what confirms the buffering effect hypothesis. Both methods indicate that there is no direct reduction of acetic acid at the metal surface.

ACKNOWLEDGEMENTS

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