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Corrosion of Mild Steel in an Aqueous CO_2 Environment – Basic Electrochemical Mechanisms Revisited

Thu Tran, Bruce Brown, Srdjan Nesic
Institute for Corrosion and Multiphase Technology,
Department of Chemical and Biomolecular Engineering, Ohio University
342 West State Street
Athens, OH 45701, USA

ABSTRACT

CO_2 corrosion has been recognized as a major problem in internal pipeline corrosion. In the presence of water, CO_2 forms carbonic acid, a weak acid which partially dissociates as a function of pH and the solution temperature. According to many studies, the presence of CO_2 and therefore, carbonic acid enhances the corrosion rate of mild steel by accelerating the cathodic reaction. The exact mechanism of carbonic acid reduction at the metal surface is still being debated. When the reduction of the adsorbed carbonic acid molecule occurs at the metal surface, the mechanism is called "direct reduction", originally proposed by deWaard and Milliams in 1975. An alternative explanation has carbonic acid providing additional hydrogen ions via its dissociation while the dominant cathodic reaction is reduction of hydrogen ions; this mechanism is referred to as a "buffering effect". In the present study, electrochemical techniques such as linear polarization resistance (LPR), potentiodynamic sweeps and electrochemical impedance spectroscopy (EIS) were used in order resolve this dilemma, i.e. to investigate the exact mechanism of the cathodic reaction in the presence of carbonic acid. It was found that carbonic acid affects only the limiting cathodic current, but has no effect on the charge transfer current. The charge transfer current is found to respond only to a change in pH, indicating hydrogen ion reduction as the main cathodic reaction. The buffering effect is therefore considered to be dominant; the direct reduction of carbonic acid appears to be insignificant compared to the reduction of hydrogen ions in the range of conditions covered by this study.

Key words: carbon dioxide, carbonic acid, cathodic reactions, mild steel corrosion

INTRODUCTION

Dissolved CO_2 gas is not a corrosive species. In the presence of water, however, CO_2 forms carbonic acid, which is corrosive for mild steel. While a detailed description of the current understanding of the CO_2 corrosion mechanisms is given elsewhere,[1,2] a brief outline is presented below.

The CO_2 gas dissolves in water:

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)} \tag{1}$$

A very small fraction of dissolved CO_2 hydrates to form carbonic acid:

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} \tag{2}$$

As a weak acid, carbonic acid partially dissociates into hydrogen ions and bicarbonate ions, which is followed by the dissociation of bicarbonate ions that form additional hydrogen ions and carbonate ions:

$$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO_3^-_{(aq)} \tag{3}$$
$$HCO_3^-_{(aq)} \rightleftharpoons H^+_{(aq)} + CO_3^{2-}_{(aq)} \tag{4}$$

Hydrogen ions are reduced at the steel surface to form hydrogen gas:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(aq)} \tag{5}$$

In addition to the reduction of hydrogen ions, it is often assumed that carbonic acid is directly reduced at the metal surface.[1,2,3]

$$2H_2CO_{3(aq)} + 2e^- \rightarrow H_{2(aq)} + 2HCO_3^-_{(aq)} \tag{6}$$
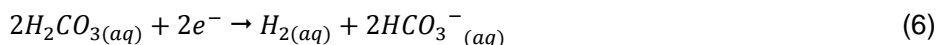
Surface iron atoms, give up electrons and dissolve into the aqueous solution to produce ferrous ions, resulting in steel corrosion:

$$Fe \rightarrow Fe^{2+}_{(aq)} + 2e^- \tag{7}$$

This mechanism, which was proposed originally by deWaard and Milliams and was subsequently widely accepted, is called "direct reduction" of carbonic acid.[3,4,5] There was always an alternative possibility: that carbonic acid dissociates and provides an additional source of hydrogen ions near the steel surface, while the only cathodic reaction is reduction of hydrogen ions (reaction 5), a mechanism referred to as the "buffering effect".[6,7] These two mechanisms are reviewed in detail below.

Buffering effect

In the buffering effect mechanism, carbonic acid, formed from the hydration of CO_2, partially dissociates to provide most of the $H^+_{(aq)}$ and $HCO_3^-_{(aq)}$ (reaction 3). Hydrogen ions from the bulk ($H^+_{(aq)}$) are then transported and adsorbed onto the surface and are subsequently reduced (reaction 5) to form hydrogen. The term "buffer" in this case means that carbonic acid acts as a "reservoir" of hydrogen ions, by replenishing them when they get depleted by the reduction reaction at the metal surface.

Hurlen, was one of the first to describe the effect of dissolved CO_2 as a buffer source for the reduction of hydrogen ions.[8] Linter and Burstein agreed and concluded that the reduction of carbonic acid was not a contributing factor because it was thermodynamically unfavorable in comparison to the reduction of hydrogen ions, even if it is not entirely clear that thermodynamic arguments can be convincingly used to reach such a conclusion.[6]

In another more recent electrochemical study, Remita et al. conducted glass cell experiments using a rotating disk electrode.[7] The authors argued that the effect of carbonic acid was to create additional hydrogen ions, which corresponded to the buffering effect mechanism. They stated that the direct

reduction of carbonic acid would lead to an increase of the surface pH in the presence of CO_2 compared to a saturated N_2 solution, which was not observed in their measurements. The authors therefore concluded that the buffering effect of carbonic acid was sufficient to explain the CO_2 corrosion mechanism. However, their experiments were limited to atmospheric pressure.

Direct reduction

In the direct reduction mechanism, reactions 3-5 are assumed to be still occurring. However, it is assumed that carbonic acid is also adsorbed onto the metal surface and then directly reduced (reaction 6). The first CO_2 corrosion study putting forward this mechanism was that of deWaard and Milliams in 1975.[3] A higher corrosion rate was observed in the CO_2 saturated solution compared to a completely dissociated acid at the same concentration. This was attributed to the direct reduction of carbonic acid at the metal surface. However, only the effects of temperature and partial pressure of CO_2 were included in the original study, and the maximum tested pressure was no higher than atmospheric. Furthermore, the de Waard and Milliams model assumed that the corrosion reaction is always charge transfer controlled. The effect of mass transport and slow chemical reactions was neglected.

Many of the subsequent studies adopted the direct reduction of carbonic acid at the metal surface.[10,11] For example Nesic et al. argued that carbonic acid reduction must be accounted for in the corrosion process in order to explain his experimental results.[4,12] However, most of his experiments were conducted in a glass cell at atmospheric pressure, where the direct reduction carbonic acid could not be easily distinguished from reduction of hydrogen ions. A similar argument in favor of the direct reduction of carbonic acid was included in the mechanistic models proposed by Pots in order to predict CO_2 corrosion rates under multiphase flow conditions.[5]

Hypothesis and Objective

Although the direct reduction and buffering effect mechanisms are identical from a thermodynamic point of view (beginning and end state are the same), the distinction of the pathway is essential for modeling of the reaction kinetics. This is shown in Figure 1, where the potential is plotted versus the logarithm of current density. If the direct reduction of carbonic acid mechanism is accepted, the corrosion rate should increase steadily with partial pressure of CO_2, regardless of the controlling step (limiting current control or charge transfer control). On the other hand, if the dominant cathodic reaction is the reduction of hydrogen ions and the buffering mechanism is valid, increasing CO_2 partial pressure affects the corrosion rate only when the corrosion process is limiting current controlled. This implies that the corrosion rate at a constant pH the corrosion rate should stop increasing beyond a certain partial pressure of CO_2 (see Figure 1 and Figure 2). This logic can be used to distinguish the two corrosion mechanism if adequate experiments can be executed. The main practical difficulty is associated with the high CO_2 pressures required, making accurate electrochemical measurements more difficult.

The goal of the present work was to clarify the corrosion mechanisms of mild steel in the presence of CO_2 in order to determine whether the direct reduction of carbonic acid needs to be accounted for or whether the simple buffering effect mechanism is sufficient. Furthermore, this research was meant to provide a good reference point for studies of the corrosion mechanisms of mild steel in other weak-acid environments.[13-18] A similar approach was already applied to study the corrosion mechanism in the presence of acetic acid and there, the direct reduction of undissociated acetic acid was found to be insignificant.[13]
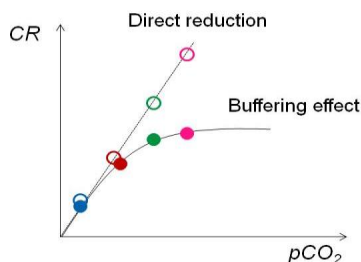
Figure 1: Illustration of corrosion rate change as a function of CO_2 partial pressure for direct reduction and buffering effect mechanism.
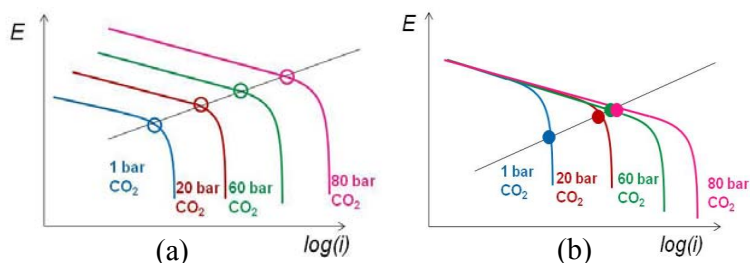

Figure 2: Illustration of cathodic behavior, with points indicating the intersection between the anodic line and the cathodic line: (a) if direct reduction of carbonic acid were dominant at the surface; (b) if buffering effect mechanism is dominant.

EXPERIMENTAL PROCEDURE

Equipment

Experiments were conducted in a 2 L glass cell at atmospheric pressure and a 7.5 L autoclave at high pressure (Figure 3).

A rotating cylinder electrode (RCE) was used as the working electrode in the glass cell. A stationary electrode was used as the working electrode in the autoclave, where the solution was stirred by an impeller, since the original RCE setup did not enable stable and reproducible electrochemical measurements at high pressure. Saturated Ag/AgCl reference electrodes and platinum counter-electrodes were used in both setups. The pH was monitored and the temperature was controlled during the experiments.
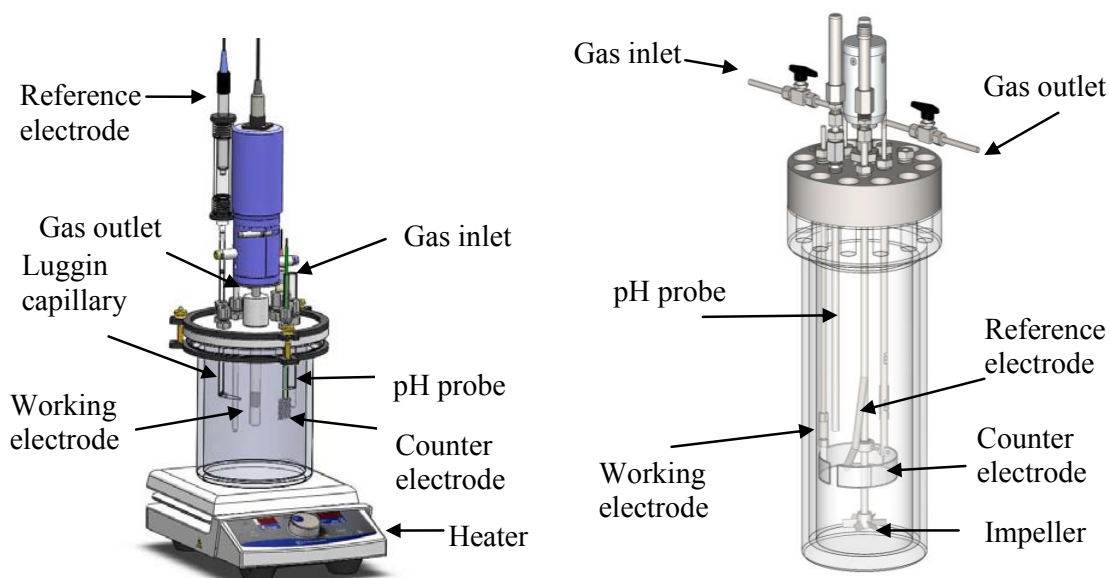
**Figure 3: (a) Schematic of a 2 L glass cell.
(b) Schematic of a 7.5 L autoclave. (Images courtesy of Cody Shafer, Institute for Corrosion and Multiphase Technology)**

Method

As discussed above, the main difference between the buffering effect and direct reduction mechanisms is the pathway of the cathodic reaction. In the former case, the reduction of hydrogen ions is solely considered. In the latter, both reduction of hydrogen ions and direct reduction of carbonic acid are taken into account. In that case an increase of charge transfer current should be observed when CO_2 partial pressure increases. However, in previous corrosion studies carried out by Nesic[4] and others, it has been difficult to resolve this issue as the charge transfer region for the hydrogen ion reduction overlaps with the region where the dominant reaction is anodic dissolution of iron, and cannot be properly characterized. This led to a choice of different metal electrodes (substrates) in the current work for studying carbonic acid reduction mechanisms. After testing a noble metal such as platinum, the best and most consistent results were achieved using a passive metal - a stainless steel UNS S30400 electrode. The charge transfer current produced by the reduction of hydrogen ions on UNS S30400 could be examined without interference from the anodic iron dissolution reaction seen on a mild steel electrode (made from example from a X65 pipeline steel (API 5L X65)). An additional benefit of using a stainless steel electrode is its relative "similarity" to mild steel, at least when compared to noble metals; thereby, the strong catalytic effects of hydrogen reduction seen on noble metals were avoided. As Figure 4 shows, the rates of the cathodic reactions measured on the two steels (UNS S30400 and X65) under the same environmental conditions were similar (in the potential range where they overlapped). Because of this similarity, it was assumed that the mechanisms of cathodic reactions on mild steel could be uncovered by examining the behavior of the same reaction on stainless steel at comparable conditions.

Electrochemical techniques such as polarization sweeps and electrochemical impedance spectroscopy (EIS) were used to measure the cathodic current and the solution resistance, respectively. All sweeps were then corrected using the measured solution resistance.
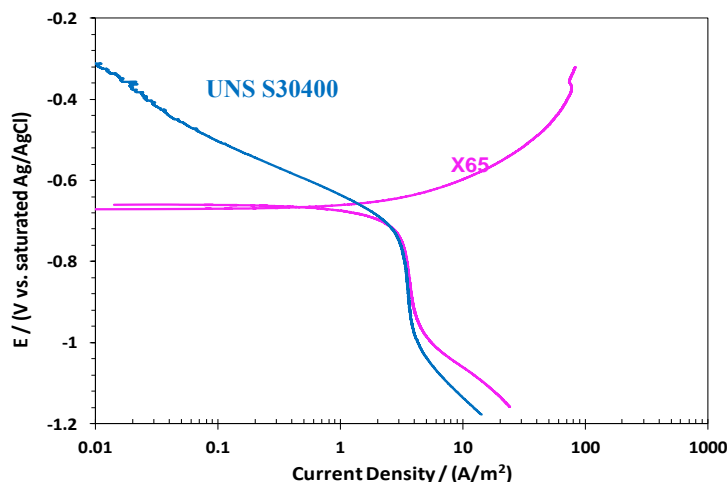
Figure 4: Comparison of polarization sweeps of UNS S30400 and X65, at 25°C, pH 4.0, 1 bar pCO_2, 3 wt.% NaCl, 1000 rpm.

Procedure

Glass cell experiments

The glass cell was filled with 2 L of deionized water and 3 wt.% NaCl. The solution was purged with N_2 or CO_2 gas for at least one hour to facilitate deoxygenation and saturation with N_2 or CO_2. In the case of CO_2, the pH was measured and verified at 3.9 ± 0.1 (the autogenous pH for a saturated CO_2 solution at atmospheric pressure). Hydrochloric acid (HCl) or sodium bicarbonate ($NaHCO_3$) was added to the solution to achieve the desired pH. Before immersion into the test solution, the X65 specimen was polished with 150, 400, and 600 grit silicon carbide paper using isopropyl alcohol, and then cleaned with isopropyl alcohol in an ultrasonic bath for five minutes. The UNS S30400 specimen was polished with 400 and 600 grit silicon carbide paper using water, and was also cleaned with isopropyl alcohol in an ultrasonic bath for five minutes. Following immersion, electrochemical tests were initiated after the measured corrosion potential (OCP) stabilized within ±1 mV over at least two minutes. The EIS measurements were conducted by applying an oscillating potential of ±10 mV around the OCP using a frequency range from 10,000 Hz to 0.01 Hz, mainly to determine the solution resistance. For the X65 specimens, LPR was then measured by polarizing the specimen from -5 mV vs. OCP to +5 mV vs. OCP. Cathodic sweeps were performed from the OCP in the negative direction with a scan rate of 0.2 mV/s. After waiting for the OCP to stabilize at its original value, an anodic sweep was conducted from the OCP in the positive direction with the same scan rate. For the UNS S30400 specimens, after measuring the solution resistance by EIS, only the cathodic sweep was performed.

Autoclave experiments

Specific start-up procedures were used for each experiment. The 7.5 L UNS S31600 stainless steel autoclave was filled with 5 L of deionized water and 3 wt. percent NaCl. The solution was bubbled with CO_2 gas for at least two hours to facilitate deoxygenation and saturation with CO_2 at atmospheric pressure. The pH was measured and verified to be 3.9 ± 0.1 (the autogenous pH for a saturated CO_2 solution at atmospheric pressure). Sodium bicarbonate was added to the solution to achieve the pH desired at high pressure. The X65 specimens were polished sequentially with 150, 400, and 600 grit silicon carbide paper using isopropyl alcohol, and cleaned with isopropyl alcohol in an ultrasonic bath for five minutes. The UNS S30400 specimens were polished sequentially with 400 and 600 grit silicon carbide paper using water, and cleaned with isopropyl alcohol in an ultrasonic bath for five minutes. After being dried with cold air, the specimen was mounted on the shaft of an autoclave lid. The

autoclave lid was then installed and the electrode immersed in the solution, with continuous CO_2 purging of the electrolyte at atmospheric pressure. The partial pressure of CO_2 was then increased to the desired conditions. After several hours, the solution was deemed to be CO_2 saturated for a given pressure, confirmed by measuring the pH.

A specific set of electrochemical measurements was conducted during each experiment. For the UNS S30400 specimens, the electrochemical tests started when the OCP stabilized within ±1 mV over at least two minutes. The EIS measurements were conducted by applying an oscillating potential of ±10 mV around the OCP using a frequency range from 10,000 Hz to 0.01 Hz to get the solution resistance. The cathodic sweeps were performed from the OCP in the negative direction with a scan rate of 0.2 mV/s. For the X65 specimens, the electrochemical tests started when the measured OCP stabilized within ±1 mV over at least two minutes. The EIS measurements were conducted by applying an oscillating potential of ±10 mV around the OCP using a frequency range from 10,000 Hz to 0.01 Hz to obtain the solution resistance. After two hours, LPR was measured every 30 minutes for three hours to ensure the corrosion rate was constant before performing the cathodic sweeps from the OCP in the negative direction with a scan rate of 0.2 mV/s. After the cathodic sweeps and another 30 minutes, the OCP stabilized to the initial value, and the anodic sweeps were performed from the OCP in the positive direction with the same scan rate. All sweeps were corrected using the measured solution resistance extracted from EIS results.

It is important to note that the flow in the autoclave was produced by an impeller while a rotating cylinder electrode (RCE) was used in the glass cell. With this setup and careful positioning of the electrodes, it was experimentally proven that at 800 rpm stirring speed in the autoclave using the impeller, similar mass transfer conditions were achieved as compared to a glass cell RCE at 1000 rpm[14]. Therefore, the 800 rpm stirring speed was chosen for all experiments conducted in the autoclave. All experiments were repeated at least once to establish reproducibility.

RESULTS AND DISCUSSION

Effect of pH and partial pressure of CO_2 on the cathodic reaction.

The goal of the initial experiments was to confirm the known effect of pH on the cathodic reaction at a fixed partial pressure of CO_2. Then experiments were done at a fixed pH by changing carbonic acid concentration, to determine whether direct reduction of carbonic acid at the metal surface needs to be accounted for as an additional reaction. The carbonic acid concentration was changed by adjusting the partial pressure of CO_2.

It was found that a decrease of pH, i.e., an increase of hydrogen ion concentration, leads to an increase of charge transfer current whether CO_2 is present or not. Figure 5 shows that in the absence of CO_2 the charge transfer current increases when pH decreases from pH 5 to pH 4. A similar trend was observed in the presence of CO_2 (at both 1 bar and 10 bars) (Figure 6). These results confirm that hydrogen ions were always reduced at the metal surface.
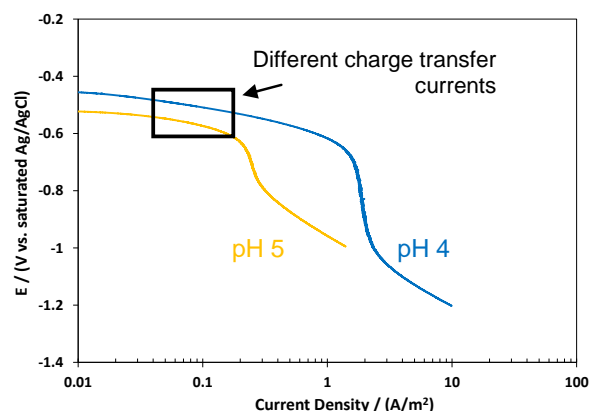
Figure 5: Comparison of charge transfer current on UNS S30400 at different pH, without CO₂, 25°C, 3 wt.% NaCl, RCE rotating speed 1000 rpm.
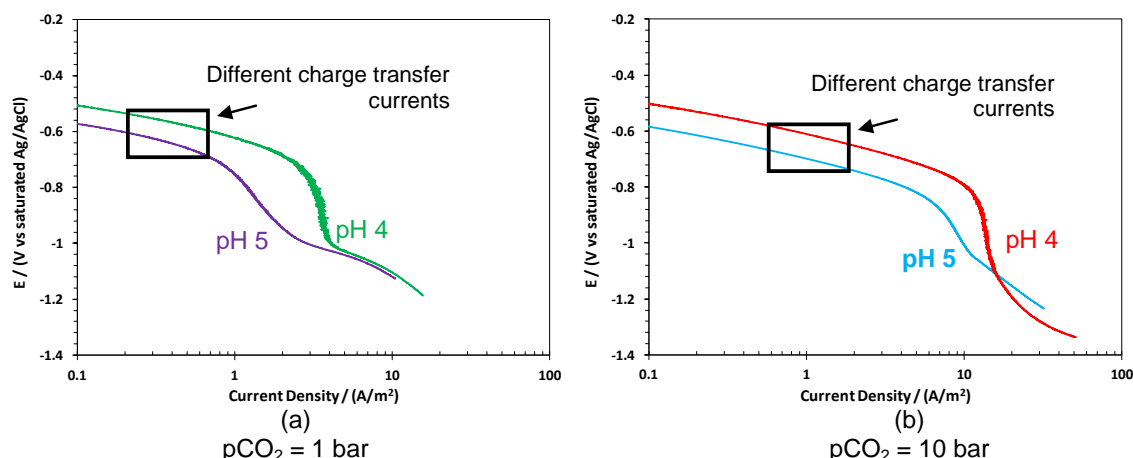

(a)
pCO₂ = 1 bar

(b)
pCO₂ = 10 bar

Figure 6: Comparison of charge transfer current on UNS S30400 at different pH, 25°C, 3 wt.% NaCl, impeller stirring speed 800 rpm: (a) 1 bar pCO₂; (b) 10 bar pCO₂

Conversely, Figure 7 shows that at a fixed pH, increasing the partial pressure of CO_2 does not affect the charge transfer current. In both cases (at pH4 and pH5), the carbonic acid was the dominant species (H_2CO_3 concentration at 10 bar pCO₂ is equal to 7×10^{-4} M). Nevertheless and additional cathodic reaction - direct reduction of carbonic acid cannot be detected. While the charge transfer currents remain the same, the limiting currents increase when CO_2 partial pressure increases due to the ability of carbonic acid to provide additional hydrogen ions as they are consumed by the corrosion reaction at the metal surface.
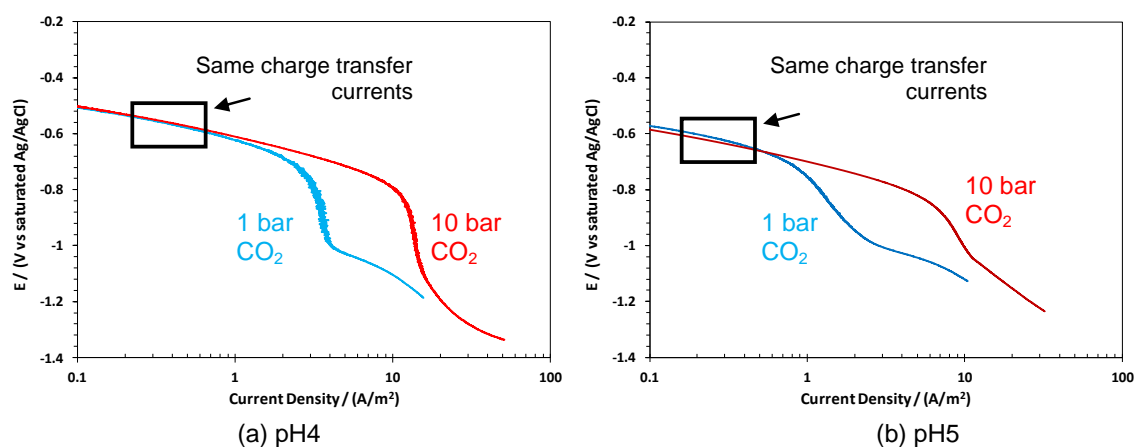
(a) pH4   (b) pH5

Figure 7: Comparison of charge transfer current on UNS S30400 at different pCO_2, 25°C, 3 wt.% NaCl, impeller stirring speed 800 rpm: (a) pH 4.0; (b) pH 5.0

Experiments were also performed at pH 6 to further minimize the effect of hydrogen ions and uncover any possible effect of carbonic acid. At 25°C and pH 6, the concentration of carbonic acid at 10 bar pCO_2 is about 7×10^{-4} M in the solution: 700 times more than the hydrogen ion concentration (10^{-6} M) and 10 times more than at 1 bar pCO_2. Yet this increase in the partial pressure of CO_2 does not influence the charge transfer current (see Figure 8a). Any direct reduction of carbonic acid is shown to be insignificant at 25°C, pH 6.

Since an increase in temperature accelerates all reactions, and more so the slower ones, it was thought that the direct reduction of carbonic acid may be revealed at higher temperatures. Therefore, the temperature was raised to 80°C with the aim of accelerating the direct reduction of carbonic acid so that it could be observed. As expected, the hydrogen ion reduction was also accelerated at 80°C. Figure 8b shows that even at 80°C, the charge transfer current only increases slightly (within the error of measurement), when the CO_2 partial pressure increased by a factor of 10. This suggests that any contribution from the direct reduction of carbonic acid was negligible at this condition as well.
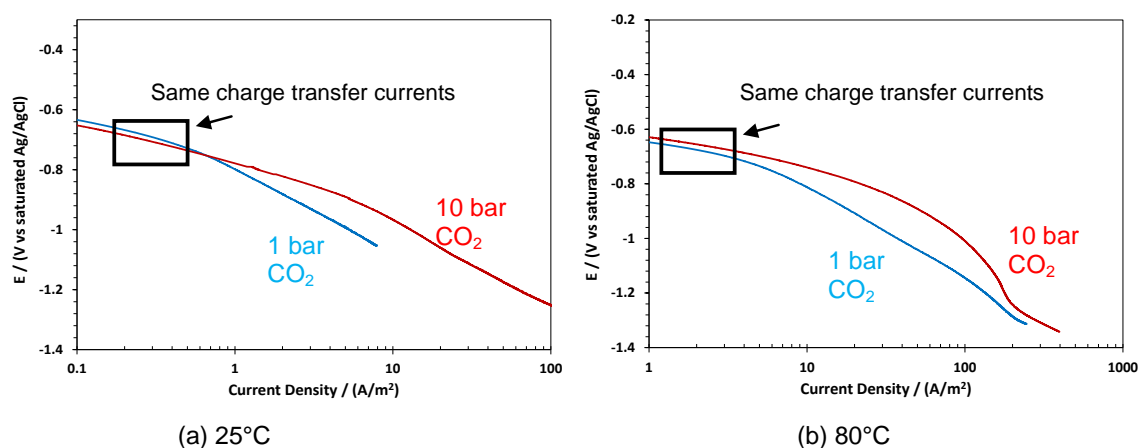

(a) 25°C   (b) 80°C

Figure 8: Comparison of charge transfer current on UNS S30400 at different pCO_2, pH 6.0, 25°C, 3 wt.% NaCl, impeller stirring speed 800 rpm: (a) 25°C; (b) 80°C

CONCLUSIONS

For the conditions covered in this study, it was found that:

- The dominant cathodic reaction mechanism related to reduction of carbonic acid on steel is the so called "buffering effect", i.e. then main cathodic reaction is reduction of hydrogen ions, and not the direct reduction of carbonic acid.
- The presence of carbonic acid only affects the cathodic limiting current due to the ability of carbonic acid to provide hydrogen ions by dissociation, when the latter are rapidly consumed by reduction at the metal surface.
- Carbonic acid concentration has a negligible effect on the charge transfer cathodic current since the direct reduction of carbonic acid is insignificant. Hydrogen ions are the dominant cathodic reactants reduced at the metal surface, irrespective of whether carbonic acid is present.

ACKNOWLEDGEMENTS

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