MODELLING OF ELECTRODE PROCESSES AND SURFACE CHEMISTRY IN CO₂ CORROSION

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Abstract

Corrosion processes and the rates of the individual electrode reactions in carbon dioxide containing solutions are well known to be affected by solution composition and hydrodynamics. There are many different mechanistic explanations for the observed cathodic current - potential - rotation speed (of rotating disc electrodes) relationships, most of which obtain the observed currents by the simple addition of two or more currents due to processes (e.g. chemical reactions and diffusion) which are considered to act independently. The validity of this approach is not clear since many of the species contributing interact in the boundary layer.

A model is described which derives current densities and surface solution chemistries for the rotating-disc electrode over the range of conditions of practical relevance. The model allows for the slow homogeneous chemical step of carbon dioxide hydration, diffusion, convection, charge transfer processes and the rapid acid-base equilibria. It is shown that the experimental data are adequately modelled without the need to consider a heterogeneous surface hydration of carbon dioxide, and that the electrochemical response under conditions not previously studied is predicted. Further, the increase in cathodic limiting current at pH > 6 is shown to be a consequence of the solution chemical equilibria and the direct reduction of bicarbonate is not necessary to explain the experimental data. None of the mechanisms previously proposed is valid over the entire pH range of interest. The concentration profiles in the near surface region throw light on the rate determining steps in the cathodic process and can be used to predict the possibility of surface film formation.
Introduction

There have been several studies of the kinetics and mechanism of the cathodic reaction in slightly acidic oxygen-free CO₂-containing solutions of the type encountered in oil and gas production\textsuperscript{1,5}, and several different reaction mechanisms have been proposed. The majority of these studies have been in the pH range 4-4.5, with the pH controlled by the partial pressure of carbon dioxide, and whilst there are still disagreements about the precise mechanism, the involvement of potentially complex preceding or subsequent chemical reactions is known to modify the electrochemical responses. The initial aim of the modelling described here was to calculate the local solution chemistry at the metal surface especially in terms of the possibility of carbonate film formation of interfacial pH. However, the model also calculates the cathodic current as a function of bulk pH and pCO₂, for a rotating disc electrode, and this also helps understand the mechanism of the cathodic process.

Mechanism of Cathodic Reaction in CO₂ Corrosion

There have been many studies of the cathodic reaction mechanism and several different processes and rate determining steps have been proposed. These include rate determining reduction of carbonic acid with subsequent reformation from the bicarbonate and protons\textsuperscript{1} and rate limiting diffusion of bicarbonate\textsuperscript{2}.

The first, whilst consistent with the experimental data at the time does not explain that obtained subsequently, and the second covered only a small pH range and does not explain the results obtained using rotating disc electrodes. It has been shown\textsuperscript{3,4,6} that there is a cathodic limiting current but this current is not purely a diffusion limited current. This limiting current depends on the rotation speed of the disc, $\omega$ (rad s\textsuperscript{-1}), according to equation 1.

\[
I_{lim} = I_R + \omega^{\frac{1}{2}}
\]  

(1)

This experimental observation has been widely confirmed but there are
different interpretations regarding its mechanistic interpretation.

The rotation speed dependent component has been associated with the diffusion of protons to the surface and the intercept to the reduction of carbonic acid the rate of production of which is controlled by the slow hydration reaction of dissolved carbon dioxide with water. The original observations of this were due to Schmitt and Rothmann\(^3\) and based partly on the non-linearity of a plot of \(i_r\) vs \(pCO_2\), and partly on the effect of metal composition on the intercept, they suggested that this hydration was of adsorbed carbon dioxide. However the intercept with platinum and iron is similar.

Eriksud & Sontvedt\(^5\), stated that the calculated diffusion independent current for the CE process (an electrochemical step preceded by a chemical reaction) shown in equation 2, with the chemical process being the homogeneous CO\(_2\) hydration reaction, was close to that observed.

\[
\begin{align*}
    \text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3 \\
    \text{H}_2\text{CO}_3 + \text{e} & \rightarrow \text{H} + \text{HCO}_3^- 
\end{align*}
\]  

(2)

Wieckowski et al\(^4\) also did not consider it necessary to assume a heterogeneous reaction to explain the observed currents, and found little evidence of adsorbed CO\(_2\) from electrochemical and radio-tracer studies\(^7\). However, they concluded that the electrochemical response was consistent with a catalytic EC' mechanism where the reduction of carbonic acid or bicarbonate yields bicarbonate or carbonate, respectively, which subsequently reacts with water to regenerate the starting material plus hydroxide, equation 3.

\[
\begin{align*}
    \text{H}_2\text{CO}_3 + \text{e} & \rightarrow \text{HCO}_3^- + \text{H} \\
    \text{HCO}_3^- + \text{e} & \rightarrow \text{CO}_3^{2-} + \text{H} \\
    \text{HCO}_3^- + \text{H}_2\text{O} & \rightarrow \text{CO}_3^{2-} + \text{OH}^- \\
    \text{CO}_3^{2-} + \text{H}_2\text{O} & \rightarrow \text{HCO}_3^- + \text{OH}^- 
\end{align*}
\]  

(3)
The CO₂-Water System

Solution Chemistry

The chemistry of the CO₂-water system discussed below is from Kern⁸, unless otherwise stated. Carbon dioxide dissolves in water according to equation 4

\[
\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq}) \tag{4}
\]

with \( K_D = 10^{-1.5} \). The dissolved carbon dioxide reacts with water to give carbonic acid according to the slow equilibrium, equation 5,

\[
\frac{k_f}{k_b} \quad \frac{\text{CO}_2(\text{aq})}{\text{H}_2\text{CO}_3} \tag{5}
\]

with \( k_f = 0.0375 \) and \( k_b = 13.7 \), giving \( K = 0.0027 \). In alkaline solutions carbon dioxide hydration can also occur by equation 6,

\[
\text{CO}_2(\text{aq}) + \text{OH}^- \xrightleftharpoons[k_{f2}]{k_{b2}} \text{HCO}_3^- \tag{6}
\]

with \( k_{f2} = 8500 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \) and \( k_{b2} = 1.9 \times 10^4 \text{ s}^{-1} \).

Carbonic acid undergoes dissociation, first to bicarbonate, equation 7, then to carbonate, equation 8.

\[
\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^- ; \quad \text{pK}_{a1} = 3.77 \tag{7}
\]

\[
\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} ; \quad \text{pK}_{a2} = 10.3 \tag{8}
\]

As a result of these equilibria the concentration of each species in solution, at \( \text{pCO}_2 = 1 \), is as given in Figure 1. It is important that the actual \( \text{pK}_{a1} \) is much
Figure 1 Concentrations vs pH for bulk solutions, pCO₂ = 1 atm

lower than that normally reported (pKₐ₁ = 6.3) since this latter value is based on carbonic acid plus dissolved CO₂ and not just on carbonic acid. A result of this is that the solutions are less well buffered, over short time scales, than would otherwise be expected.

Analytical Solution for CE Mechanism

The chemical hydration controlled reaction scheme proposed by Schmitt and Rothmann and Eriksud and Sontvedt for the flow independent current can be described as being of the CE type, with a chemical reaction preceding the electrochemical process. The current expected can be calculated, assuming that the hydration is a homogeneous solution reaction, using the rate constants above.

The variation of current with angular velocity of a rotating disc, for the CE reaction scheme in equation 2 is given by equation 9,

\[ i = \frac{nFDC^*}{\delta_x} \frac{\mu}{\kappa} \]  (9)

with the terms defined by equation 10.
\[ C^* = [CO_2]_{bulk} + [H_2CO_3]_{bulk} \]
\[ \delta_n = 1.61 \ D^\frac{1}{2} \nu^\frac{1}{2} \omega^\frac{1}{2} \]
\[ \mu = (\frac{D}{R})^\frac{1}{2} \]
\[ k = k_r + k_b \]
\[ K = k_r/k_b \]  \hspace{1cm} (10)

Equation 9 is valid for the conditions given in equation 11.

\[ \omega < k \left( \frac{\nu}{D} \right)^\frac{1}{2} \]  \hspace{1cm} (11)

At higher rotation rates the current approaches the limiting diffusion current for carbonic acid reduction.

In the low \( \omega \) region the current is proportional to \( \omega^{1/2} \), due to control by \( CO_2 \) diffusion, with this applying at \( \omega < 1 \text{ rad s}^{-1} \) and not being experimentally determinable. The transition from the chemically controlled current to carbonic acid diffusion control occurs around 140 rad s\(^{-1}\). The flow independent current calculated according to the data given previously, is 101 \( \mu A \text{ cm}^{-2} \) close to the diffusion independent current observed as pointed out by Eriksud and Sontvedt\(^6\).

Thus the flow-independent current found by Schmitt and Rothmann (and many others) can be explained as being due to this reaction sequence with the hydration reaction occurring in solution, and for this reason the model here only allows for the homogeneous reaction. The overall current could then be described as being given by addition of a diffusion controlled proton reduction.

However, it is not clear that this approach is valid under all conditions for the \( CO_2 \)-water system since the solution chemistry is more complicated than suggested by equation 2, or by equation 3. In particular the carbonic acid is in equilibrium with bicarbonate and protons and it is not obvious that the chemical process and proton diffusion can be considered separately and simply added.
Finite Difference Model

The basic approach to the development of this model follows, where appropriate, that given by Bard and Faulkner. The approach in this work is essentially to calculate the current decay, on a rotating disc electrode, for the cathodic process on application of a potential step from a potential where no reaction occurs to one in the limiting current region, although it is the steady-state current that is of interest. The model yields both the steady state currents and the concentration profiles of all species in the near surface region. The model considers the electron transfer reactions, diffusion, convection, the slow chemical hydration reactions and the rapid solution equilibria and an outline is given in Figure 2. The model has been described more fully elsewhere.

Figure 2 Finite difference model

An important consideration is that the model here makes no assumptions about the mechanism of any effect of solution chemical reactions on the cathodic current. The model, as described here, simply assumes that the current is generated by reduction of protons and carbonic acid. The component parts of the model are described briefly below.
Initial conditions
The concentrations of all species are set according to the equilibria in equations 4, 5, 7, and 8. The pH was either entered into the model or could be calculated as being controlled by the CO₂ pressure, reflecting the two possibilities in the system. The latter case reflects much of the published work whereas the former is probably more relevant in practice.

Box size and time interval
By experience it was found that division of the Nernst diffusion layer, δₙ, as defined in equation 10, into 30 boxes was sufficient, and the calculation was carried out over 60 boxes (2 * δₙ from the surface). The time interval was calculated by using equation 13 with the largest diffusion coefficient in the model (that for H⁺)

$$\frac{D \delta t}{\delta x^2} = 0.45$$  \hspace{1cm} (12)

The total time for each calculation was about twice the time, given by equation 14, required to reach within 1 percent of the steady state current, and involved about 5000 time steps.

$$t = \frac{2}{\omega} \left( \frac{v}{D} \right)^{\frac{1}{3}}$$  \hspace{1cm} (13)

Current calculation
The results reported here make the assumption that the current in each time interval is due to the consumption of protons and carbonic acid in the innermost box are consumed according to the reactions in equation 14, with the added constraint that the maximum amount of a species consumed must not be greater than that initially present. The concentrations of protons, carbonic acid and bicarbonate adjusted accordingly. Other calculations were run allowing for

$$H₂CO₃ + e → H + HCO₃^-$$  \hspace{1cm} (14)

$$H^+ + e → H$$
the reduction of bicarbonate but these are omitted here since this was not found necessary to explain measured currents or trends in behaviour. A current-potential curve is shown in Figure 3, assuming equal exchange current densities for proton and carbonic acid reduction. All other data presented relates to the limiting current region in Figure 3, where all protons and carbonic acid in the innermost box are consumed in each time interval.

![Current density vs. potential](image)

**Figure 3** Current-potential relationship, pH4, \( \omega = 100 \), \( pCO_2 = 1 \) atm

**Diffusion**
This is allowed for using Fick's law, equation 15.

\[ \text{flux} = -D \frac{dC}{dx} \]  \hspace{1cm} (15)

**Convection**
The transport of solution by convection is dealt with according to equation 16, which defines the new \( x \)-coordinate (distance from electrode surface), \( x_2 \), after time \( \delta t \), for an element originally at \( x_1 \).

\[ \frac{1}{x_2} - \frac{1}{x_1} = 0.51 \omega^{\frac{3}{2}} v^{-\frac{1}{2}} \delta t \]  \hspace{1cm} (16)
In practice, especially in oilfield formation waters, the pH is not solely controlled by the CO₂, and the pH is often higher than those relevant to the above calculations. Figure 6 shows the variation of current with rotation speed for various bulk pH, at pCO₂ = 1 atm. The variation of slope and intercept with pH are shown in Figure 7, although the non-linearity that is apparent from Figure 6 introduces considerable uncertainty, especially in the latter. In the higher pH solutions the results of the model are slightly dependent on the time interval for the iteration. However, the effect of decreasing the time interval is to increase the calculated current and so the trends seen here are considered correct although the absolute numbers may need modification. It seems possible that the origin of this time interval dependence, which is not seen at pH 4-5 where most of the testing of the model was carried out, is in the much greater influence of the equilibration stage on the solution compositions at the higher pH.

![Figure 6](image_url)  
**Figure 6** Current vs rotation speed for various bulk pH, pCO₂ = 1 atm

In general the slope of the curves decreases as the pH is raised from 4 to 5 but increases again above pH 6. The curves in Figure 6 also show increasing currents at low rotation speeds. The suggestion that the slope of these curves represents the contribution of proton diffusion should, from the Levich equation, result in a linear relationship between slope and [H⁺], or a constant
value of slope/[H⁺]. This is true in the pH range 4-5, but not at higher pH. In
the region 5.5-6.5 the value of slope *[H⁺] is approximately constant. This
implies a diffusing species whose concentration is inversely proportional to the
proton concentration.

Concentration Profiles
The origin of some of the effects above can be deduced for the concentration
profiles in the boundary layers. Figures 8-11 show these for varying pH, with ω
= 100 rad s⁻¹ and pCO₂ = 1 atm. The profiles are plotted as differences between
Figure 9 Concentration profiles for pH 5, $\omega = 100$, $pCO_2=1$ atm

Figure 10 Concentration profiles for pH 6, $\omega = 100$, $pCO_2=1$ atm

the local concentrations and the bulk concentrations (given in Figure 1) to enable the different species to be shown on the same plot without using logarithmic axes. The horizontal axis in all the plots is the dimensionless distance $x/\delta_N$, where the Nernst diffusion layer thickness is that for protons. Figure 8 shows expected behaviour. The concentrations of both carbonic acid and protons decrease approaching the surface and the depleted layer is thicker for protons reflecting the higher diffusion coefficient. There is some depletion
Figure 11 Concentration profiles for pH 6.5, \( \omega = 100 \), \( pCO_2 = 1 \) atm of carbon dioxide at the surface, although this is only a small change from the bulk concentration, and bicarbonate concentration increases towards the surface. The changes in the concentrations of hydroxide and carbonate are small, as are the actual concentrations.

Figure 11 shows equivalent data for a bulk pH of 6.5. The most noticeable feature of this is the unusual bicarbonate concentration profile with the concentration increasing in the boundary layer and the decreasing again as the metal surface is approached. In this case significant increases in carbonate and hydroxide occur near the metal surface.

Figures 9 and 10, for intermediate pH, show behaviour between the two above cases. The calculated surface pH is significantly higher than the bulk in all cases, ranging from about 6 for bulk pH 4 to above 8 for bulk pH 6.5.

Discussion

The results of the model at pH 4-4.5 agree well with published data. At pH 6.5 the current rotation speed plot is similar to that obtained by Al-Sayed\(^6\), who also showed that in static conditions the cathodic limiting current decreased slightly in the range pH 4-6 and increased greatly at higher pH. Again the
model predicts this effect of pH. Further experimental work is required to test the model at intermediate pH.

The data at the lower pHs can be explained in terms of the CE mechanism, which is due to the fact that chemical equilibration reactions following the electrochemical step have little influence on the local concentrations. At the higher pHs this approach does not predict the currents since under these circumstances the following reactions dominate the local concentrations. The concentration profiles in Figure 11 show that the proton flux near the surface is largely carried by bicarbonate and it is interesting that the depletion of bicarbonate can occur without any direct electrochemical reduction of bicarbonate. In physical terms it is not clear that this process should be considered a catalytic one but rather a process where the high bicarbonate concentration enables production of carbonic acid via a disproportionation reaction, equation 18

\[ 2\text{HCO}_3^- = \text{H}_2\text{CO}_3 + \text{CO}_3^{2-} \quad (18) \]

Chemically this is equivalent to the second stage of the EC' mechanism, equation 3, but with further reaction of the hydroxide with more bicarbonate. The conceptual difference is that here the source of the bicarbonate is not considered to be the initial electrochemical step, but to be, predominantly, the large bulk solution concentration. The concentration profiles on Figure 11 may also explain the pH dependence of the slope of the current-rotation speed plots, since the bicarbonate concentration, in the bulk at least, is inversely proportional to the bulk hydrogen ion concentration.

A further feature of interest is the higher than expected currents in the low rotation speed range. It is possible that this is an artefact of the model, since it has not been exhaustively tested under these conditions, but such behaviour has been reported in practice\(^4\), where the currents in static conditions were greater than expected from extrapolation of equation 1.

On the assumption that the corrosion rate is equal to the limiting cathodic
current the possible, ignoring the effect of any precipitation reactions, surface ferrous ion concentration can also be calculated in the model. When this is combined with consideration of the surface carbonate concentration the possibility of exceeding the solubility product of ferrous carbonate can be calculated. (The possibility of formation of a ferrous carbonate film also depends on the potential being high enough for it to be stable with respect to iron metal). When this was done it was found that pH 4 solutions with pCO₂ = 1 atm. gave surface conditions just saturated with ferrous carbonate (with a surface pH around 6), and therefore at bulk pH > 4 the formation of iron carbonate is possible.

Conclusions

The model describes the current-rotation speed behaviour for the cathodic process in CO₂ containing solutions and demonstrates that the various proposed mechanisms are simply special cases of the effects of the complex solution chemistry, with the nature of the important chemical steps dependent on the bulk solution chemistry. Consideration of both the calculated currents and the concentration profiles indicates that the CE mechanism is a good approximation in the pH range 4-5, but that above pH 6 the rate is controlled by the production of carbonic acid from the high concentration of bicarbonate.

Other features demonstrated by the model include:
1. the assumption of a heterogeneous hydration process for carbon dioxide is not necessary to explain present experimental data,
2. the increase in current at pH > 6 is explicable without needing to consider bicarbonate reduction, and
3. the surface pH is significantly higher than the bulk, reflecting the poor, in kinetic terms, buffering ability of the system, which means that surface carbonate film formation is possible even if the bulk chemistry is unfavourable.

At this stage the model considers film-free surfaces but extension to calculation
of conditions and electrode kinetics under films is comparatively simple, as is incorporation of other pH buffers into the model. With complex systems such as these numerical modelling would appear to be the only approach capable of calculating expected cathodic currents and surface chemistry.

References