Effects of Oxygen on Scale Formation in CO2 Corrosion of Steel in Hot Brine: In Situ Synchrotron X-ray Diffraction Study of Anodic Products

Bridget Ingham,1 Monika Ko,2, a Patricia Shaw,1 Mobassar Hassan Sk,3,b Aboubakr M. Abdulla, a Nick Laycock,2 and David E. Williams 3,C

1 Callaghan Innovation, Lower Hutt, New Zealand
2 Quest Integrity Group, Lower Hutt 5045, New Zealand
3 Center for Advanced Materials (CAM), Qatar University, Doha, 2713, Qatar
4 Qatar Shell Research and Technology Centre, Doha 3747, Qatar
5 School of Chemical Sciences and MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Auckland, Auckland 1142, New Zealand

The effect of low concentrations of oxygen on the anodic dissolution of carbon steel in CO2-saturated aqueous NaCl at 80°C is simply to change the dissolution product from colloidal amorphous material assumed to be amorphous ferrous carbonate to a crystalline carbonate green rust, Fe,(OH)2CO3, which forms rapidly. This material is deposited from solution and does not inhibit the dissolution. Corrosion is limited by the nucleation onto the surface and growth of a crystalline scale of siderite (FeCO3), as in the absence of oxygen. The effects of oxygen and of solution flow can be understood in terms of effects on supersaturation for carbonate crystallization, and on the effect on the surface pH, caused by the precipitation of carbonate green rust. The formation of crystalline chukanovite (Fe2(OH)2CO3) is strongly affected in the presence of trace oxygen, both by flow and electrode potential, effects which are consistent with lower supersaturation and higher surface pH caused by green rust precipitation. In the presence of trace oxygen, FeOOH and Fe3O4 could be detected in small amounts, and are assumed to form as a consequence of the oxidation of chukanovite. The formation of magnetite comes into focus.

Low levels of oxygen can be introduced into production wells and pipelines through injection of production chemicals. Operators do not normally take any steps to remove this oxygen before injection because the dilution effect is assumed to reduce the concentration in the pipelines to negligible levels. Oxygen may also possibly be introduced as a result of upsets in water-injection systems for enhanced oil recovery. Hence the effects of trace oxygen on the corrosion of pipeline steel by hot, CO2-saturated brine have been little studied although there has been interest in the context of operation of older wells. Martin1 has stated that the acceleration of corrosion and the duration of such acceleration in closed vessels is greater than would be supported by the oxidising power of the oxygen present: that is, the corrosion rate in the presence of trace oxygen is not determined by oxygen reduction. He reported no effect of oxygen on the anodic polarization curve and proposed that there was a change in the surface corrosion products that accelerated the cathodic reaction. Others have reported that the effectiveness of corrosion inhibitors was diminished in the presence of oxygen. Earlier in-situ diffractometry studies have shown that, in the presence of trace oxygen in CO2-saturated brine, pH 6.8 at 80°C, carbonated green rust (Fe,(OH)2CO3) may be formed as the first phase appearing, followed by siderite (FeCO3) and chukanovite (Fe2(OH)2CO3) and then by FeO, Fe2O3 and FeOOH. Even in the presence of trace oxygen over the first few hours of immersion the corrosion rate dropped rapidly, an observation confirmed by Rosli et al2 who also noted that significant pitting corrosion was a result of the presence of oxygen: that the presence of oxygen did not completely impede the formation of siderite at 80°C and that Fe2O3, Fe3O4 and FeOOH (goethite) were also formed. Galvanic coupling of magnetite corrosion product to the steel is a likely explanation for the acceleration of corrosion, including localized corrosion; thus the mechanism of formation of magnetite comes into focus.

Using in-situ diffractometry, Burkle et al. reported that, in the absence of oxygen, siderite, FeCO3, is the only crystalline phase formed at open-circuit in CO2-saturated brine at 80°C over the pH range 6.3 to 7.8 and considered that the appearance of other phases was a consequence of trace oxygen. Other studies, covering a range of pH and temperature, nominally in the absence of oxygen, have indeed shown a number of different corrosion products, evolving differently over time. Alam et al. and Chan, at 45°C and pH 6 showed the formation first of chukanovite followed by magnetite. At 80°C, again nanocrystalline chukanovite was the primary product, followed by siderite and magnetite. In our earlier work, we showed the formation of siderite only, or of siderite and chukanovite with ratio dependent on the solution pH. The formation of chukanovite comes into focus because Azoulay et al. showed that the oxidation of chukanovite in solutions containing Fe(II) and CO2 led directly to FeOOH, without the intermediate formation of Fe(OH)2CO3: that compound was formed by the oxidation of Fe(OH)2. They also noted the formation of an oxidized chukanovite, Fe5+2xFe3+x(II)3(III)1−x(OH)2−xCO3 (x < 0.25) without alteration of the crystal structure. Siderite is only very slowly oxidized to iron oxides (timescale of years at 80°C).

In the present work, we study the effect of trace oxygen, inadvertently introduced as a consequence of diffusion through silicone rubber tubing, on the corrosion products and on the protective surface scale formed on steel during anodic dissolution in hot (80°C) CO2-saturated brine, under solution flow using in-situ synchrotron grazing-incidence X-ray diffraction. We show that the protective scale is siderite and that its formation is not affected by oxygen directly; that Fe2(OH)2CO3 forms from reaction of iron in solution; that chukanovite formation is not correlated with the formation of siderite but rather seems to be controlled by surface pH and supersaturation which are dependent on solution flow rate, electrode potential and Fe2(OH)2CO3 precipitation; and that FeOOH and Fe3O4 form later.

Experimental

The electrode material was an API J55 pipeline steel with ferritic-pearlitic microstructure, composition given in Table I. The synchrotron electrochemical cell described in previous work was modified to provide a rectangular flow channel, 2 x 2 mm: Figure 1. The sample (a 1.5 mm diameter rod, coated with a thin layer of high temperature epoxy) fitted tightly into a hole in the base of the channel, with the electrode surface recessed from the channel base.

C756 Journal of The Electrochemical Society, 165 (11) C756-C761 (2018)

Manuscript submitted July 2, 2018; revised manuscript received August 7, 2018. Published August 16, 2018.

ECS The Electrochemical Society Member.
× Electrochemical Society Member.
† Present address: BP Institute and Department of Chemistry, Cambridge University, Cambridge CB2 1EW, United Kingdom.
E-mail: David.williams@auckland.ac.nz

Manuscript submitted July 2, 2018; revised manuscript received August 7, 2018. Published August 16, 2018.

ECS The Electrochemical Society Member.
× Electrochemical Society Member.
† Present address: BP Institute and Department of Chemistry, Cambridge University, Cambridge CB2 1EW, United Kingdom.
E-mail: David.williams@auckland.ac.nz
The recess depth was determined in each experiment and ranged from 0.17 to 0.42 mm. If the sample is placed flush with the channel base then the concentration boundary layer thickness and hence the local supersaturation varies with position across the sample.\textsuperscript{16} For an electrode in a circular recess in the channel wall, the flow pattern is complex\textsuperscript{17,18} but the current density across the electrode face is essentially uniform.\textsuperscript{18,19} The cell, fabricated from Perspex, featured a reservoir with a tapered extension to a thin slot with a window that was covered with Kapton film, through which the X-rays passed. The reservoir fitted snugly into a heating block. The solution flow rate was covered with Kapton film, through which the X-rays passed. The experimental arrangement mounted on the synchrotron diffraction stage. The cell lid with reference and counter electrode, and the tubing delivering CO\textsubscript{2} and solution into the cell are not in place in this image. The schematic diagrams show cross-sections of the flow channel and the cell, fitted into the heating block.

![Figure 1](image)

**Figure 1.** Experimental arrangement mounted on the synchrotron diffraction stage. The cell lid with reference and counter electrode, and the tubing delivering CO\textsubscript{2} and solution into the cell are not in place in this image. The schematic diagrams show cross-sections of the flow channel and the cell, fitted into the heating block.

For a tube with air on one side (pressure, \(P\)) and water on the other side (permeability, \(P_e\)) the permeability of the tube to oxygen. If the volumetric flow rate through the tube is \(Q\) then the concentration, \(c\), at the exit of the tube is

\[
c = (1/Q) (dn/dt).
\]

The oxygen permeability depends on the glass transition temperature of the rubber and the filler.\textsuperscript{20,21} Stern et al.\textsuperscript{20} give \(P_e/s \approx (198 \times 10^{-15}) \exp(-1111/T) = 8.5 \times 10^{-13}\) at 353 K (80°C). Hence, \(P_e/mol s^{-1} m^{-1} Pa^{-1} \approx 8.5 \times 10^{-15} \times 1000/32 = 2.7 \times 10^{-13}\). Hence, from Eq. 1, \((dn/dt) \approx 1.6 \times 10^{-8} mol. s^{-1}\). The estimated oxygen concentrations for the flow rates employed in these experiments, from Eq. 2, and the average flow velocity, \(v\), in the channel over the electrode are given in Table II. For comparison, the concentration of oxygen in water at 80°C in equilibrium with air is \(1.6 \times 10^{-4}\) mol. dm\(^{-3}\)\textsuperscript{22}

X-rays strike the polished surface of the sample rod at grazing incidence (< 1°; the exact angle of incidence could not be determined due to the small size of the electrode and the geometry of the cell). In the region of the sample rod the solution thickness is 2 mm. The X-ray beam energy was 15 keV (i.e. \(\lambda = 0.82653\) Å) and the beam size was \(0.2 \times 0.7\) mm\(^2\) (vertical \times horizontal). Diffraction images were recorded using a MarCCD detector (pixel size 79 \(\mu\)m, resolution 2048 \(\times\) 2048) located 209 mm from the sample. Due to the significant scattering intensity from the solution, the scans recorded prior to the potential being applied were averaged and this average was subtracted from each scan recorded with the potential applied. This enables the diffraction peaks from the film to be resolved more easily. After each experiment, the solution was removed and a long scan recorded. This scan was inspected to determine the crystalline phases that were present. The solution-subtracted scans were then analyzed by fitting the most intense peak for each phase. In some cases, peak overlap could be significant. This was treated by constraining parameters such

| Steel composition, wt% of alloying elements (balance is Fe). |
|------------------|---|---|---|---|---|---|---|---|
| C    | Si    | Mn | Cr | Mo | S | P | Ni | Cu | V |
| J55  | 0.29  | 0.33 | 1.3 | 0.06 | 0.04 | 0.001 | 0.009 | 0.02 | 0.02 | 0.001 |

---

Table I. Steel composition, wt% of alloying elements (balance is Fe).

| Table II. Estimated oxygen concentration, \(c\), as a consequence of the hot solution flow through silicone rubber tubing (volumetric flow rate, \(Q\); average solution velocity in the rectangular channel above the electrode, \(v\)). |
|---------------------|-----|-----|-----|
| \(Q\) / cm\(^3\) s\(^{-1}\) | 0.33 | 0.72 | 2.03 |
| \(v\) / cm s\(^{-1}\) | 8.3 | 18 | 51 |
| \(10^5\) \(c\) / mol. dm\(^{-3}\) | 5 | 2 | 0.8 |

---

Downloaded on 2019-04-27 to IP 207.241.231.82 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
as peak width and position, particularly when the peak intensity was low. To convert relative peak areas to relative amounts of each phase, scans were fitted using both the peak intensity method and full-pattern fitting; then the results for each phase were divided by the intensity of the (110) diffraction peak for iron, measured immediately before the potential step from the open-circuit potential, $E_{OC}$, at the start of the experiment. This gives a measure of the relative volume of each phase, compared from one experiment to another. The reference electrode was a micro Ag/AgCl, KCl (3 mol. kg$^{-1}$) electrode, and the counter electrode was a Pt wire, both inserted directly into the electrolyte in the cell. In previous work, reference electrode drift caused by the temperature dependence of solubility of silver chloride was assessed by measurement against an identical reference electrode in the same solution at room temperature, connected via an electrolyte bridge of identical composition. The initial potential difference of the reference electrodes was 1.2 mV and the potential drift was less than 4 mV in 1.5 hour giving a total potential difference of around 5.2 mV.

The electrolyte was 0.5 mol kg$^{-1}$ aqueous NaCl with 20 g / kg of 2 mol. kg$^{-1}$ aqueous NaOH added, to give calculated pH = 6.8 at 80°C for the CO$_2$ – saturated solution (pH 6.3 at room temperature). Solutions were prepared volumetrically at room temperature and are expressed gravimetrically to account for the change of density with temperature. The empty cell was mounted on the diffractometer. Preheated, CO$_2$-saturated electrolyte was injected into the empty cell and the beam aligned to strike the electrode whilst the temperature re-stabilized at 80°C, with the solution flowing. Total time at the $E_{OC}$ before the potential step was approximately 15 min, with at least 5 min at 80°C. We saw no evidence that cathodic polarization evolving hydrogen prior to starting the experiment had any effect on the results, so we did not do this, to avoid issues of hydrogen bubbles trapped in the space above the electrode.

### Results

Figure 2 shows a current – time transient and relative amounts of crystalline phases formed following potential step from $E_{OC}$ to $E = -500$ mV Ag/AgCl. Flow velocity 18 cm s$^{-1}$. Recess depth 0.42 mm. Electrode area 0.018 cm$^2$.

The current transient were as previously described: an increase of current and a shortening of the timescale to the current peak, with the development of the siderite signal well-correlated with the timescale to the current peak.

Figure 4 shows the effect of changing the solution flow rate at different electrode potentials. The formation of Fe(III) species was dependent on the solution flow rate only, and thus on the dissolved oxygen concentration, not on the electrode potential in the range investigated. At the lowest flow rate, where the dissolved oxygen concentration would be the greatest, the rate of formation of carbonated green rust was significantly higher than for the other conditions. However, the current – time transient was not sensibly affected (compare curves 3 and 4 in Figure 4a). The slight fall in amount of the phases determined at longer time (relative to the intensity of the Fe diffraction peak at time zero) could be because of the absorption of the diffracted X-rays by the increasing amount of material deposited on the electrode. The total amount of carbonated green rust, measured as the X-ray diffraction intensity, increased steadily with time, that is: in proportion to the total charge passed.

In previous work, the current peak was interpreted as due to the electrolycrystallization of siderite. The evolution of phase volume of siderite can be interpreted following the theory of Avrami adapted for random nucleation on a surface. Where $V_v$ denotes the limiting maximum coverage and the rate constant for phase formation is $k_{Avrami} = V/n$, $t_0$ being the characteristic timescale for the phase formation. The fit of experimental data to Equation 3 is shown in Figure 5. Values of the fitted parameters are given in Table III. The maximum rate of change of $V$ is at $t_{inflexAvrami} = t_0 \sqrt{(1-(1/n))}$. Figure 6a shows the linear correlation of $t_{inflexAvrami}$ with the time at the current peak in the electrochemical measurement. The value of $V_v$ decreased with increasing solution flow rate although the assumptions made in deriving these values should be borne in mind in making this comparison, particularly that the absorption of diffracted X-rays is constant through the experiment and that the comparison with the diffraction intensity of iron at $t = 0$ correctly accounts for all the set-up variation from run to run. The variation of rate constant with electrode potential was consistent with a Tafel-type equation (Figure 6b). At higher solution flow rate or lower electrode potential, the value of $n$ was lower.

The growth kinetics of chukanovite were significantly variable, both in the amount formed and in the time of formation relative to that of siderite: Figure 7. To make the comparison for the different experimental conditions, here the time scale has been expressed relative to the characteristic time for siderite growth, obtained by the fit...
Figure 4. Effect of flow rate on (a) current (legend shows electrode potential and flow velocity) and on (b) the formation of Fe(III)-containing phases at different electrode potentials: total phase amount, determined relative to the Fe (110) diffraction peak intensity at the start of the experiment, of Fe₆(OH₁₂CO₃), FeOOH and Fe₃O₄. The dominant phase was Fe₆(OH₁₂CO₃). Inset of (b) is an expanded scale; curve labels (volumetric flow rate, flow velocity and electrode potential) are: 1: 0.33 cm³ s⁻¹, 1.8 cm s⁻¹, −550 mV; 2: 0.72 cm³ s⁻¹, 1.8 cm s⁻¹, −500 mV; 3: 0.72 cm³ s⁻¹, 1.8 cm s⁻¹, −600 mV; 4: 2.03 cm³ s⁻¹, 1.8 cm s⁻¹, −500 mV.

to Equation 3. The amount of chukanovite was significantly increased at lower flow rate. The rate of formation was significantly accelerated at lower electrode potential: with decreasing electrode potential at a given flow rate, the formation of chukanovite shifted from following that of siderite to preceding it; that is, the rate constant for chukanovite formation accelerated significantly with respect to that for siderite with decreasing electrode potential. At fixed electrode potential, increase of flow rate accelerated the formation of chukanovite with respect to siderite.

Table III. Fitting parameters for siderite growth according to Equation 3 for the different experimental conditions.

| E/mV Ag/AgCl | Q/cm³ s⁻¹* | V₀ (relative) | n | t₀/μs |
|--------------|-------------|---------------|---|------|
| −550         | 0.33        | 31.1          | 3.5 | 900  |
| −500         | 0.72        | 24.6          | 3.0 | 520  |
| −550         | 0.72        | 17.3          | 3.0 | 1030 |
| −600         | 0.72        | 17.9          | 2.2 | 2130 |
| −500         | 2.03        | 15.3          | 1.6 | 1640 |

*average flow velocity, v, for each Q is given in Table II.

Figure 5. Growth kinetics of siderite phase, fitted to Avrami model.

Figure 6. Correlations of Avrami parameters for siderite growth. (a) Time to the peak current, tₚk, correlated with the time to maximum slope (the inflexion point), t_inf,Avrami, for the Avrami model fit to siderite growth. (b) Dependence of rate constant, K Avivam, on electrode potential, E; flow velocity 18 cm s⁻¹ (Q = 0.72 cm³ s⁻¹).

Discussion

The formation of carbonated green rust, Fe₆(OH₁₂CO₃), immediately following the potential step and increasing steadily with time, is a clear signature of the presence of oxygen. The rate of formation increased with the estimated oxygen concentration; that is, higher at lower flow rate through the system. The time evolution did not have the characteristic form of an electrocrystallization process and did
not correlate with the appearance of the current peak. We conclude that this material is formed from the oxidation of Fe(II) in solution, itself a consequence of the anodic dissolution reaction, and that its effect on the dissolution reaction and on the formation of the other phases is indirect. The current peak, and fall of current to low levels, correlated directly with the formation of siderite. This is illustrated by the correlation of the time to the current peak with the characteristic time for siderite formation. The siderite formation had the characteristics of a surface electrocrystallization reaction, with rate constant having a Tafel-like dependence on electrode potential. The formation of siderite had little or no dependence on the oxygen concentration. At higher flow rate or lower electrode potential, the Avrami exponent, $n$, was decreased. The value of $n$ reflects the way the crystals grow on the surface and the variation of crystal nucleation rate with time. For example, with the assumption that the linear growth rate in each dimension is equal and time-independent, a value $n = 3$ would indicate 3-D growth of crystals with instantaneous nucleation at $t = 0$ and insignificant further nucleation after that, or a nucleation rate that is uniform in time (progressive nucleation) of crystals that spread at constant height (2-D growth). Higher values indicate a 3-D growth with instantaneous nucleation at $t = 0$ and further progressive nucleation and lower ones a 2-D growth at lower supersaturation. Competition between the formation of siderite and chukanovite would result as a consequence of the oxidation of chukanovite. Galvanic coupling of magnetite corrosion product to the steel is a likely explanation for the acceleration of corrosion in the presence of trace oxygen.

Figure 7. Growth kinetics of chukanovite phase: chukanovite volume, $V_n$, relative to limiting siderite volume, $V_m$, siderite against time, $t$, relative to characteristic time for siderite growth, $t_{3, siderite}$, $V_{m, siderite}$ and $t_{3, siderite}$ obtained from fit of siderite growth to Avrami model.

Conclusions

In the corrosion of steel in CO$_2$-saturated hot brine, the key effect of the introduction of traces of oxygen is the alteration of the balance between chukanovite and siderite formation. This balance is altered as a consequence of the facile precipitation of carbonated green rust, Fe$_6$(OH)$_{12}$CO$_3$, altering the surface supersaturation and pH. Magnetite and goethite would result as a consequence of the oxidation of chukanovite. The formation of siderite had little or no dependence on the oxygen concentration. At higher flow rate or lower electrode potential, the Avrami exponent, $n$, was decreased. The value of $n$ reflects the way the crystals grow on the surface and the variation of crystal nucleation rate with time. For example, with the assumption that the linear growth rate in each dimension is equal and time-independent, a value $n = 3$ would indicate 3-D growth of crystals with instantaneous nucleation at $t = 0$ and insignificant further nucleation after that, or a nucleation rate that is uniform in time (progressive nucleation) of crystals that spread at constant height (2-D growth). Higher values indicate a 3-D growth with instantaneous nucleation at $t = 0$ and further progressive nucleation and lower ones a 2-D growth at lower supersaturation. Competition between the formation of siderite and chukanovite would result.

References

1. R. L. Martin, Corrosion consequences of oxygen entry into oilfield brines, in CORROSION 2002, p. 02270, NACE International (2002).
2. N. R. Rosli, The Effect of Oxygen in Sweet Corrosion of Carbon Steel for Enhanced Oil Recovery Applications, in, PhD thesis, Ohio University (2015).
3. E. Guibrelanden, J. Kvaereval, and H. Miland, Corrosion, 61, 1086 (2005).
4. G. R. Joshi, K. Cooper, J. Lapinski, D. L. Engelberg, O. Bikondoa, M. G. Dowsett, and R. Lindsay, In situ Grazing Incidence X-ray Diffraction of Sweet Corrosion Scaling on Carbon Steel, in CORROSION 2015, p. 5674, NACE International (2015).
5. D. Burkle, R. De Mott, W. Taleb, A. Kleppe, T. Comyn, S. M. Vargas, A. Neville, and R. Barker, Electrochimica Acta, 255, 127 (2017).
7. M. T. Alam, E. W. L. Chan, R. De Marco, Y. Huang, and S. Bailey, *Electroanalysis*, 28, 2166 (2016).
8. E. W. L. Chan, *Magnetite and its galvanic effect on the corrosion of carbon steel under carbon dioxide environments*, in PhD Thesis, Curtin University (2011).
9. A. M. Tansel, C. E. W. Lyn, D. M. Roland, H. Yanliang, and B. Stuart, *Electroanalysis*, 28, 2910 (2016).
10. B. Ingham, M. Ko, G. Kear, P. Kappen, N. Laycock, J. A. Kimpton, and D. E. Williams, *Corrosion Science*, 52, 3052 (2010).
11. B. Ingham, M. Ko, N. Laycock, J. Burnell, P. Kappen, J. A. Kimpton, and D. E. Williams, *Corrosion Science*, 56, 96 (2012).
12. M. H. Sk, A. M. Abdullah, M. Ko, B. Ingham, N. Laycock, R. Arul, and D. E. Williams, *Corrosion Science*, 126, 26 (2017).
13. I. Azoulay, C. Remazeilles, and P. Refait, *Corrosion Science*, 85, 101 (2014).
14. I. Azoulay, C. Remazeilles, and P. Refait, *Corrosion Science*, 98, 634 (2015).
15. M. Seguin, *American Journal of Science*, 264, 562 (1966).
16. D. E. Williams and J. V. Macpherson, in *Comprehensive Chemical Kinetics, Volume 37: Applications of Kinetic Modelling*, R. G. Compton and G. Hancock, Editors, p. 369, Elsevier, Amsterdam (1999).
17. J. J. Higdon, *Journal of Fluid Mechanics*, 159, 195 (1985).
18. S. M. Griffiths, R. H. Nilson, R. Bradshaw, A. Ting, W. D. Bonivert, J. T. Hachman, and J. M. Hruby, in *Micromachining and Microfabrication Process Technology IV*, p. 364 (1998).
19. S. Roy, Y. Gupta, and T. Green, *Chemical Engineering Science*, 56, 5025 (2001).
20. S. Stern, F. Onorato, and C. Libove, *AIChE Journal*, 23, 567 (1977).
21. K. Haraya and S.-T. Hwang, *Journal of Membrane Science*, 71, 13 (1992).
22. D. Tromans, *Hydrometallurgy*, 48, 327 (1998).
23. M. Ko, B. Ingham, N. Laycock, and D. E. Williams, *Corrosion Science*, 90, 192 (2015).
24. B. Ingham, M. Ko, N. Laycock, N. M. Kirby, and D. E. Williams, *Faraday Discussions*, 180, 171 (2015).
25. M. Fleischmann and H. R. Thirsk, in *Advances in Electrochemistry and Electrochemical Engineering*, Vol 3, P. Delahay and C. W. Tobias, Editors, p. 123, Wiley-Interscience, New York (1963).
26. M. Fleischmann, J. A. Harrison, and H. R. Thirsk, *Transactions of the Faraday Society*, 61, 2742 (1965).
27. M. Avrami, *The Journal of Chemical Physics*, 8, 212 (1940).
28. V. Pandarinathan, K. Lepkova, and W. van Bronswijk, *Corrosion Science*, 85, 26 (2014).