THE ESTIMATION OF CORROSION RATE FROM AC IMPEDANCE MEASUREMENTS

R.A. Cottis and S. Turgoose
Corrosion and Protection Centre, UMIST, P.O. Box 88
Manchester, M60 1QD, UK

ABSTRACT
The interpretation of electrochemical impedance spectra has been re-examined from first principles using a numerical model of the metal-solution interface, together with conventional equivalent circuit models. This has shown that there is no single parameter that can be used for the estimation of corrosion rate from impedance spectra, and obtaining a reliable estimate requires a knowledge of the correct physical model of the interface.

INTRODUCTION
The electrochemical impedance technique is well-established as a method for the investigation of electrochemical reactions. However, the analysis of the resultant data remains difficult. The most common approach is that based on the equivalent circuit concept, exemplified by the model of Randles[1]. Unfortunately the use of this approach has tended to become divorced from a consideration of the specific electrochemical processes occurring. Various authors[2][3][4] have remedied this situation by a detailed comparison between the reaction mechanism and the resultant impedance spectrum. While this is undoubtedly the optimal approach to obtaining detailed mechanistic information, it is rather complex for application to the 'simple' problem of estimating the corrosion rate, especially in the rather ill-defined circumstances obtaining in the real world. This paper attempts to bring together these two approaches in order to provide guidance for the estimation of corrosion rate from ac impedance spectra. In previous work[5], the relationship between polarization resistance and ac impedance measurements has been investigated using a physical model of a very simple system. This revealed that, for the particular system investigated, the rate of reaction could be related to the charge transfer resistance, whereas it was not related to the polarization resistance (when the latter was defined as the zero frequency limit of the ac impedance, less any solution resistance). At the time this work was presented, the authors were unable to present a clear view of the general principles involved in extracting the corrosion rate from an ac impedance.
measurement, and the present paper addresses this question. Care has been taken to
derive impedance spectra on the basis of detailed physical models of the corrosion process,
although much of the work has used a conventional equivalent circuit approach to the
generation of impedance spectra, but with the values of the circuit components being
derived from the underlying physical constants, rather than being arbitrarily assigned. In
addition the numerical model described previously has been used to investigate the
significance of non-linearity in the estimation of corrosion rates of simple systems.

SUMMARY OF EXPECTED IMPEDANCE SPECTRA

The analysis of the electrochemical impedance of metal-solution interfaces has primarily
been developed on the basis of redox reactions of solution species, and in consequence
assumptions have been made that are not necessarily valid for corroding interfaces. In
particular, for corroding systems the anodic and cathodic reactions will not, in general, be
linked in any way, except in so far as the net current will be zero (in free corrosion
conditions). Thus the anodic reaction may be activation controlled while the cathodic
reaction is diffusion controlled (or vice versa). Consequently, when an equivalent circuit
approach is used to model or analyze electrochemical impedance spectra for corroding
systems, it is important to incorporate all possible reactions as parallel circuit elements. It
must also be recognized that the 'standard' derivation of the Warburg impedance is not
applicable to a corroding system, as it assumes a redox reaction with the forward and
reverse reactions in equilibrium (this will be discussed in more detail in [8]). The more
common processes are discussed below in terms of the appropriate equivalent circuit
representation.

(a) Anodic Metal Dissolution

The general reaction is

\[ M \rightarrow M^{n+} + n \, e^- \]

As written this reaction can only be activation controlled, since the only reactant (metal M)
is a solid, and will therefore always have an activity of 1. It is important to recognize that,
at least in dilute solutions, the rate of the forward reaction does not depend on the
concentration of \( M^{n+} \). In practice other forms of polarization will inevitably occur at
sufficiently high potentials, a common example being resistance polarization due to the
deposition of a salt film. However, in less extreme conditions this reaction can be expected
to give rise to a charge transfer resistance given by equation (1), with no diffusional
impedance (since the rate of reaction does not depend on the concentration of any
diffusible species). The charge transfer resistance will be inversely proportional to the rate
of dissolution.

\[ R_{CT} = \frac{\beta_s}{I_{corr}} \]  \hspace{1cm} (1)

In reality, the rate-determining step of an anodic dissolution reaction may involve other
species in addition to the metal. For example, the rate-determining step for the dissolution
of iron is reported[6] to involve hydroxyl ions:

\[ \text{Fe} + \text{OH}^- \rightarrow \text{FeOH} + e^- \]
In this case a diffusional impedance may be observed for hydroxyl ion or proton diffusion (although this will presumably only be observed if the hydroxyl ions remain bound to the iron, and are not released in a later step in the reaction sequence).

(b) Cathodic Reduction of Solution Species

The most common cathodic reaction is probably the reduction of dissolved oxygen, but similar principles apply to the reduction of other solution species such as H\(^+\), Fe\(^{3+}\) or Cu\(^{2+}\). These will be subject to activation polarization, giving a charge transfer resistance which is inversely proportional to the rate of the reduction reaction, but in addition concentration polarization will occur at higher current densities. This gives rise to a diffusional impedance in series with the charge transfer resistance. For the case of diffusion through a limited boundary layer thickness (this is necessarily the case if valid impedance spectra are obtained, since an infinite diffusion layer thickness implies that the system will never be stationary) the low frequency limit of the diffusional impedance will be given by equation (2).

\[
R_p = R_{CT} + R_{diff} = \frac{\beta_c}{i_{corr}} + \frac{\beta_c}{(i_{lim} - i_{corr})}
\]

\[
= \frac{\beta_c i_{lim}}{i_{corr} (i_{lim} - i_{corr})}
\]

It will be appreciated that \(i_{corr}\) in equation 2 strictly refers to the rate of the reduction reaction, which will only be the corrosion current density if no other cathodic reactions are occurring.

(c) Cathodic Reduction of Water

In neutral solutions hydrogen evolution will occur predominantly through the reduction of water rather than hydrogen ions:

\[
2 \text{H}_2\text{O} + 2 e^- \rightarrow \text{H}_2 + 2 \text{OH}^-
\]

For reasonably dilute solutions the activity of water will be held constant at around one, and this reaction should only give rise to a charge transfer resistance, in accordance with equation (1).

(d) The Reverse, Metal Deposition, Reaction

If the anodic metal dissolution reaction is close to equilibrium, the reverse (metal deposition) reaction may start to occur at a significant rate due to the accumulation of metal ions at the metal-solution interface. While the metal ion concentration will not affect the kinetics of the forward (metal dissolution) reaction, it will influence the reverse reaction. This will give rise to a charge transfer resistance in series with a diffusional impedance. Note, however, that the concentration of metal ions is a function of the forward as well as the reverse reaction, consequently the range of behaviour that can be obtained is limited.
particularly when the bulk concentration of metal ions is zero. This can be described by a modification to the normal derivation of the diffusional impedance. In this case the diffusional component of the combined impedance of the forward and reverse reactions is related to the rate of dissolution (since it is a function of the surface concentration of metal ions), while the charge transfer resistance is not related to corrosion rate (since it is a function of a 'rate of reaction' which includes the exchange reaction, rather than the net dissolution rate).

MODELLING PROCEDURES

The above discussion is based on a 'conventional' equivalent circuit approach to the interpretation of ac impedance spectra. This is a very effective method, and permits rapid estimation of circuit parameters. However, it is subject to some limitations. The range of phenomena that can be handled is limited; it is necessary to assume that all circuit components are linear, and, less tangibly but perhaps equally important, the link between the physical processes occurring and the model is rather indirect. For this reason, this project has been based on a numerical model of the corroding metal-solution interface. For each reaction being considered the model has three components:

(a) Diffusion

Diffusion through a finite boundary layer thickness is handled by a one-dimensional finite difference model. In essence this involves describing the boundary layer as a series of 'boxes' of constant thickness. Then the concentration of the species being considered is given by the difference equation (3).

\[
C_{n,t+\Delta t} = C_{n,t} + \frac{D\Delta t}{\Delta x^2} \left( C_{n+1,t} + C_{n-1,t} - 2C_{n,t} \right)
\]

(3)

where \( C_{n,t} \) = concentration in box \( n \) at time \( t \)
\( D \) = diffusion coefficient
\( \Delta x \) = thickness of each box
\( \Delta t \) = time step for calculation

In the current work it is assumed that there is no convection, but it is possible to model controlled mass transport conditions (such as those experienced in the rotating disc electrode) by allowing material to move towards the metal surface on each time step. This has been reported for a steady-state analysis of the cathodic reaction in carbon dioxide containing systems[7].

(b) Double Layer Capacitance

The double layer capacitance is assumed to be linear, and is modelled with the difference equation:
\[ E_{t+\Delta t} = E_t + \frac{i_{\text{cap},t} \Delta t}{C_{\text{dl}}} \]  

where \( E_t \) = potential at time \( t \)  
\( i_{\text{cap},t} \) = capacitive current density  
\( C_{\text{dl}} \) = double layer capacitance

(c) **Charge Transfer**

The charge transfer process is modelled by the normal kinetic equation (5).

\[ i_t = k C_{0,t} \exp \left( -\frac{E_{\text{an}}F}{RT} \right) \]  

where \( i_t \) = current density at time \( t \)  
\( k \) = rate constant  
\( C_{0,t} \) = surface concentration of reactant  
\( E_t \) = applied potential at time \( t \)  
\( \alpha \) = transfer coefficient  
\( n \) = number of electrons  
\( F \) = Faraday's constant  
\( R \) = gas constant  
\( T \) = temperature

As a result of the flow of current, \( i_t \), the surface concentration, \( C_{0,t} \), will be modified by the amount of the relevant species consumed in the reaction. This produces the interaction between charge transfer and the diffusion process that is described in equivalent circuit models by the Warburg impedance.

**SYSTEMS INVESTIGATED**

1. **Cathodic oxygen reduction under mixed control, anodic metal dissolution at limiting current density.**

This system is essentially that studied previously[5]. Oxygen reduction occurs at a predefined proportion of the limiting current density, the cathodic current being balanced by a fixed anodic current. This can be thought of in terms of a passive system with a fairly high passive current density (or a low oxygen concentration). The fixed anodic current density implies an infinite impedance for this process, and this is therefore not detected in the impedance measurement, as it is in parallel with the finite cathodic impedance (Figure 1).

This gives a simple diffusion process with an uncharged species (\( O_2 \)) giving rise to the diffusional impedance. Furthermore it is a very simple process to investigate experimentally, using an applied current on an inert electrode in place of the current limited anodic reaction.
At low current densities, the cathodic reaction is predominantly charge-transfer controlled, and the impedance spectrum (Figures 2 and 3) reflects this, with the charge transfer resistance falling as the mean current density increases. In contrast, the diffusional impedance is small at low current densities, and tends to infinity as the current density approaches the limiting current density.

For this system, it is very clear that the corrosion rate ($i_{\text{corr}}$) is related to the charge transfer resistance, in accordance with equation (6), but is related only indirectly to the diffusional impedance (or $R_p$), in accordance with equation (2). This will generally be true for diffusional impedances involving diffusion of solution species to the interface, as the diffusional impedance is inversely proportional to the surface concentration of reactant.

$$i_{\text{corr}} = \frac{\beta \rho}{R_{\text{CT}}} \quad (6)$$

2. Cathodic oxygen reduction under mixed control, anodic metal dissolution under activation control.

The nearest example of this system would perhaps be the corrosion of copper in an aerated...
non-oxidizing acid, with a low copper content in solution (such that the reverse reaction \( \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \) does not occur to a significant extent). However, copper ions would accumulate at the metal-solution interface, and the impedance of the reverse anodic reaction could not safely be ignored. Conversely, for a more active metal, such as iron, the impedance of the hydrogen evolution reaction would also need to be considered.

![Figure 4](image)  **Figure 4**  Bode plot for system 2

![Figure 5](image)  **Figure 5**  Nyquist plot for system 2

![Figure 6](image)  **Figure 6**  Equivalent circuit for system 2

In this situation, the diffusional impedance associated with the cathodic reaction will be in parallel with the anodic charge transfer resistance, and will necessarily have a limited effect on the impedance spectrum (Figures 4 and 5). In practice, diffusional components may also be observed due to diffusion of species involved in the anodic process, the most probable species being the hydroxyl ion, or by the diffusion of corrosion product away from the interface. In the latter case, the diffusion process will affect the rate of the reverse reaction, and the correct equivalent circuit will be that shown in Figure 6. It should be noted, however, that the diffusional impedance associated with the reverse anodic reaction is dependent on the forward anodic reaction, since this modifies the surface concentration of metal ions. Mathematically this results in the impedance of the forward and reverse anodic reactions being represented by a single charge transfer resistance in series with a diffusional impedance[8]. However the relationship between the charge transfer resistance and the diffusional impedance differs from that for the standard derivation for a redox reaction, and to emphasize this point these impedances are shown as separate branches in Figure 6 and subsequent figures.
3. Anodic and cathodic reactions both under activation control.

\[ R_{\text{ct}} \text{ Anode} \quad R_{\text{ct}} \text{ Cathode (H}_2\text{)} \quad \text{Solution Resistance} \]

Double Layer Capacitance

**Figure 7** Equivalent circuit for system 3

An example of this type of process would be the dissolution of a metal such as zinc in a deaerated acid. In this case, the equivalent circuit will be as shown in Figure 7, and a pure charge transfer response will be observed, with the polarization resistance being given by the Stern-Geary equation.

4. Cathodic reaction limited by oxygen transport through a surface film, anodic reaction limited by accumulation of cations.

\[ R_{\text{ct}} \text{ Anode} \quad R_{\text{ct}} \text{ Rev. Anode} \quad \text{Warburg Impedance (Rev. Anode)} \quad \text{Solution Resistance} \]

\[ R_{\text{ct}} \text{ Cathode (O}_2\text{)} \quad R_{\text{ct}} \text{ Cathode (H}_2\text{)} \]

Double Layer Capacitance

**Figure 8** Equivalent circuit for system 4

This situation is essentially that expected for iron under a coating which reduces the diffusion rate. Owing to the limited access of oxygen the reduction of water may become significant. This can result in a high ferrous iron concentration at the metal-solution interface, and the appropriate equivalent circuit is shown in 8.

Figure 9 shows the Nyquist plot for different film thicknesses, but the same corrosion rate (i.e. \( D/\delta \) constant, in this case with a value of \( 10^{-3} \text{ cm s}^{-1} \)). In all cases the spectrum consists of a charge transfer resistance together with a diffusional impedance, but as the film thickness is reduced the characteristic frequency of the diffusion process becomes higher, and the two components of the spectrum become indistinguishable for the thinnest films.
As the oxygen reduction reaction is assumed to be operating at essentially its limiting current density, it has a very high diffusional impedance and is not detected. The hydrogen evolution reaction plays an important role in increasing the rate of the metal dissolution reaction relative to the oxygen reduction reaction, thereby allowing the rate of the reverse metal deposition reaction to become significant and giving rise to the observed diffusional impedance. The charge transfer resistance measured in this case is predominantly an indication of the exchange current density for the anodic reaction, and will considerably over-estimate the rate of corrosion. On the other hand, the low frequency limit of the diffusional impedance in the reverse reaction path will indicate the rate of transport of ferrous ions through the coating, although a detailed analysis of the spectrum is necessary to extract an accurate corrosion rate (this will be discussed further elsewhere[8]).

THE INFLUENCE OF NON-LINEARITY ON THE MEASURED SPECTRUM.

Figure 9 Nyquist plot for filmed steel with varying film thickness, but constant D/δ (and hence corrosion rate)

Figure 10 Effect of Amplitude of Perturbation, Current Control

Figure 11 Effect of Amplitude of Perturbation, Voltage Control

Figure 10 shows the effects of the amplitude of perturbation under current-controlled conditions, while figure 11 shows the corresponding response under potential-controlled conditions. The errors are not very marked when plotted as a Bode plot, owing to the 'compressing' effect of the log scale, consequently only the Nyquist plots are shown. With
current control the amplitude of the perturbing potential becomes small at higher frequencies due to the low impedance of the double-layer capacitance, consequently the effects of non-linearity are seen predominantly at low frequencies, with the major errors being in the amplitude response. When potential control is used, somewhat greater effects are seen at higher frequencies. These are associated with non-linearity in the charge transfer process. For the systems studied in this work there is generally a negligibly small effect of non-linearity for perturbing potentials of 10 mV, an error of less than 10 % for 30 mV, and quite large errors for 100 mV.

DISCUSSION AND CONCLUSIONS

The objective of this work has been to re-examine the interpretation of impedance data from first principles, in order to gain a clear understanding of the methods which should be used to estimate corrosion rates from impedance spectra. Unfortunately our conclusion is that even for simple model systems it is not possible to deduce the corrosion rate without knowledge of the corrosion processes giving rise to the impedance spectrum. Thus classical charge-transfer/limited diffusion spectra such as those shown in Figure 3 may be derived from at least three of the four systems we have considered. In one case, the charge transfer resistance may be used to estimate the corrosion rate, while the diffusional impedance (and hence $R_D$) may not. In another case, the charge transfer resistance is not related to corrosion rate, which may be estimated from the diffusional impedance. $R_D$ may also give reasonable results in the latter case as the charge transfer resistance will necessarily be rather small. In view of the difficulties experienced in the analysis of these simplified model systems, it might be expected that ‘real’ systems would pose greater problems.

As a general principle, we consider it most important that the interpretation of impedance spectra is based on a detailed physical model of the corroding system of interest. In much of this work we have enforced this link by deriving the impedance spectra directly from the physical model, but this is not necessary, and for linear systems an equivalent circuit approach can give essentially the same results much more quickly. However, if an equivalent circuit approach is used it is important to relate the individual circuit elements to physical processes occurring at the metal-solution interface, and to check that the values obtained are feasible. It is also important to recognize that a corrosion process consists of at least three parallel circuit elements; a double layer or film capacitance, the anodic reaction and the cathodic reaction. In many cases one or other of these elements (often the cathodic reaction) is undetectable because the reaction is mass transport limited (and hence has a very high impedance), but this should be explicitly stated, rather than being implicitly assumed. Similarly, care should be taken to link diffusional impedances to the diffusion of specific solution species, and to ensure that the diffusion of that species would indeed give rise to a diffusional impedance. This is particularly important because the diffusional impedance depends on the relative magnitudes of the relevant forward and reverse reactions (see [8] for further details).

A common real system would be rusty iron in a neutral aqueous solution. This provides a very complex problem. Transport of oxygen to the metal surface is largely diffusion controlled, but there may be a significant element of activation polarization. Chemical reactions occurring in the rust layers (such as the oxidation by dissolved oxygen of ferrous ions to ferric and hydrolysis reactions) may modify the concentration of solution species. Furthermore the diffusion coefficients may vary in both space and time as a result of rust...
deposition. The numerical model used for this work is capable of accommodating many of these effects, and proposed future developments are concerned with the extension of the model to cover phenomena such as these.

REFERENCES


