LINEAR ELECTROCHEMICAL TECHNIQUES - ARE THEY ALL THE SAME?

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ABSTRACT. This paper describes a computer simulation which has been used to explore the relationship between polarization resistance and ac impedance measurements. This has demonstrated that all measurement techniques which assume a linear electrode response can be related to one another (or, to quote MacDonald, are sampling the same impedance response). The process of simulating the system has required a detailed examination of the physical processes concerned in the very simple electrochemical system which has been investigated, and has revealed some unexpected results. For example, it has been shown that the polarization resistance for this system is not directly related to the rate of reaction (when the latter is defined as the impedance at zero frequency), although conventional polarization resistance measurement techniques may, somewhat fortuitously, give a result which is approximately equal to the charge transfer resistance, which does give a measure of rate of reaction.

1. Introduction

The work presented in this paper has been concerned with an examination of the premise that a range of electrochemical techniques which assume a linear response of a metal-solution interface are essentially equivalent, and can be interrelated through transformations between the time and frequency domains. While the link between the time and frequency domains is well known, this view of linear electrochemical methods has given useful insights into the significance of particular results.

The investigations presented here originated when considering the relationship between ac impedance measurements\(^1\), measurements of linear polarization resistance\(^2\) and transient measurements for steel in concrete\(^3\). These exhibit somewhat contradictory characteristics, in that polarization resistance measurements made with a sweep period of around 30 seconds appear to give good correlation with weight loss, whereas ac impedance measurements need to go down to very low frequencies, and measurement periods of the order of hours, in order to define the response. Similarly analysis of the transient response of the same electrochemical system has been used to determine time constants of the equivalent circuit comparable to those which can be obtained by ac impedance measurements, but in a somewhat shorter time. As any periodic waveform can be expressed as a sum of sine waves, through the Fourier transform, it seemed probable that this contradiction could usefully be explored through the transformation of the polarization resistance and transient information to the frequency domain, to confirm, as we supposed, that they were actually measuring an appropriate part of the impedance response.

In order to avoid complications due to non-ideal behaviour of real electrochemical systems, experiments performed to date have been concerned with a computer model of a 'simple' four
component electrochemical interface. This has described the potential-time behaviour of the interface in response to a controlled current waveform. This permits the simulation of linear polarization resistance measurements by using appropriate current waveforms. The resultant potential waveform, together with the driving current waveform, have been transformed to the frequency domain by a standard fast Fourier transform (FFT), and the impedance computed as the voltage spectrum divided by the current spectrum.

The results have demonstrated that the impedance can be measured from the results of waveforms such as those used for linear polarization resistance measurement, but they have also shown significant limitations of this method and requirements for measurement frequency and sensitivity which might not be obvious at first sight. Probably the most useful outcome of this work was the improvement in our understanding of the physical system. This insight is commonly obtained by the development of a detailed simulation, but is difficult to convey in a written paper.

2. Nomenclature

The measurement and analysis procedures use a number of similar variables, particularly with respect to time intervals, and for clarity these are defined here:

- Cycle period, $\tau$, the period of one full cycle of the current waveform.
- Sample period, $\delta t$, the time between individual samples used for Fourier transform analysis. If there are $n$ samples per cycle, then $\delta t \times n = \tau$.
- Subsidiary sample period, the period used between calculations of the model. This may be equal to the sample period if the latter is small, or it may be a fraction of the sample period.

3. The Model

![Figure 1. Model Electrochemical Interface](image)

The model used was a simple four component network (figure 1), consisting of a solution resistance, $R_{\text{sol}}$, a double-layer capacitance, $C_d$, a diffusion process between the bulk solution and the metal-solution interface, and an activation-controlled reaction at the metal-solution interface. While the charge transfer and diffusion processes are, in total, equivalent to a charge transfer resistance and a Warburg impedance, it may be noted that the point of separation is slightly
different in this model. The diffusion component is used only to determine the surface concentration of cathodic reactant, while the charge transfer component calculates the overpotential as a function of the surface concentration and the faradaic current.

In order to simplify the analysis a single cathodic reaction has been considered, with diffusion of the oxidised state of the cathodic reactant to the metal surface. A practical example of such a system would be the reduction of dissolved oxygen at a platinum electrode. In order to fix the steady-state potential of the interface the current waveform applied consists of an average current, $I_{dc}$, which is a fraction of the limiting current (typically 25 or 75%) on which a small fluctuation is superimposed (5% of the limiting current). While this example may seem rather remote from real corrosion systems, it should be appreciated that it can be thought of as a system with a fixed (e.g. mass transport limited) anodic current (equal to $I_{dc}$) and a cathodic current which is under mixed control. For a corroding system, such as iron in aerated water the system is analogous, except that the cathodic current (due to oxygen reduction) may be current limited, while the anodic reaction will be under mixed control. Thus the model used should give a realistic indication of the behaviour to be expected from a corroding interface, although some of the details are rather simpler (for example, for iron the response is complicated by the solution oxidation of ferrous to ferric, which will modify both the limiting current for the cathodic reaction and the diffusion component of the anodic reaction). It also avoids a problem inherent in systems giving a diffusional impedance due to anodic species diffusing away from the interface. In the latter case the diffusional impedance will only be observed if the rate of the anodic back reaction is significant, and this would therefore also have to be included in the analysis.

The defining equations for the system described are thus:

3.1. CAPACITANCE

$$\frac{dV}{dt} = \frac{I_{cap}}{C_{dl}}$$

3.2. DIFFUSION PROCESS

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

or, when expressed in terms of the finite difference model used for this work,

$$C_{n,t+\Delta t} = C_{n,t} + \frac{D\Delta t}{\Delta x^2} (C_{n+1,t} + C_{n-1,t} - 2C_{n,t})$$

3.3. CHARGE TRANSFER

$$i = k C_s \exp \left(-\frac{E\alpha n F}{RT}\right)$$
3.4. SOLUTION RESISTANCE

\[ V = I R_{sol} \]

In order properly to test the applicability of the Fourier transform approach to the analysis of polarization resistance measurements, it is important that the computer model provides a precise response over all frequencies of significance. While analytical solutions for the response of an electrochemical interface to a current transient are available, they necessarily make assumptions that are not of general validity. Thus individual solutions are available for the response of the discharge of the double layer capacitance and the diffusion process, but these do not describe the behaviour in the intermediate regime where both the capacitance and the diffusion contribute to the response. In addition it is a fundamental assumption of the Fourier transform that the waveform being analysed is repetitive. If the period of the waveform is sufficiently long the system may attain near steady-state conditions during the cycle, but for shorter cycles this will not occur, and the steady-state starting conditions assumed by any analytical solution will not exist. Therefore the model is based on a numerical analysis, using a finite difference model of the diffusion process, and calculating the potential for each time step by iteratively balancing the potential across the double layer capacitance against the potential due to the faradaic current. In order to allow the system to attain stable conditions, the analysis is run for several cycles before recording the voltage response. Considerable care is necessary to avoid the introduction of spurious information at higher frequencies as a result of instability of the analysis. For example, when a triangular current waveform was analysed using the procedure which had been 'tuned' for use with the square current waveform, the resultant voltage-time trace appeared perfectly satisfactory to the unaided eye. However there were small steps in the results, due to an improper convergence test, and the resultant impedance spectrum showed marked peaks in amplitude.

The program used to create the model voltage-time response was written in Turbo Pascal, running on an IBM PC AT compatible. The period of the repetitive waveform and the number of samples taken over one cycle could be independently varied. For longer intervals between recorded samples, more frequent subsidiary samples were taken, such that the time between samples was significantly less than the \( R_p C_{dl} \) time constant and the time for the concentration of the elements in the diffusion process to change significantly. When this 'oversampling' process was used the sample values recorded were the average of all of the voltages determined during the period of one sample. In effect this corresponds to filtering the measured voltage signal to limit the high frequency response to the sampling frequency.

4. Data Analysis

Most of the data analysis has been performed using 1024 samples per cycle. These records have been analysed using a commercial program (Asystant) which provides very easy processing of waveform data. For longer time records (up to 65536 points per sample) a special-purpose program is being developed, running on an Opus PC7, which uses an 80386 processor and can therefore handle very large data arrays.

The stages of the analysis procedure are indicated in figure 2. A conventional discrete Fourier transform is used to convert the voltage-time and current-time records to complex frequency spectra. In both cases the complex component of the input time records are taken to be zero.
Run simulation to calculate potential and current for 1024 points through the cycle

Transform current and potential waveforms to the frequency domain with FFT

Remove zero values from transformed data

Divide potential transform by current transform to calculate real and imaginary components of impedance.

Display results as Bode or Nyquist plot

Figure 2. Data Analysis Procedures

throughout, and no windowing or trend removal is used prior to the Fourier transform. The result of the Fourier transform is an array of real and imaginary amplitudes at a range of frequencies 0, 1/τ, 2/τ, ..., (n-1)/τ, where τ is the period of one cycle, and n is the number of points in that cycle. For many regular current waveforms (such as the square and triangle waves used in this work) the amplitude at certain frequencies is zero, and these are removed prior to further calculation, to avoid division by zero errors. Then the voltage amplitude at each frequency is divided by the current amplitude at that frequency (using complex division) to give an impedance. This should then correspond directly to the impedance that would be measured by a transfer function analyser, and can be plotted as a Nyquist or Bode plot.

It would not be surprising if a calculated electrochemical response were to give a near-perfect impedance measurement, especially with all calculations being undertaken with double precision arithmetic. In real systems, even if the electrochemical system obeys the appropriate equations exactly, the measurement will introduce errors. These have been simulated in this work in one of two ways. Errors due to noise in the voltage measurement have been simulated by adding normally-distributed random noise to each measurement point. Errors due to limited resolution of
the measurement have been simulated by quantising the voltage values to a suitable proportion of the full-scale voltage.

5. Results and discussion

5.1. POWER SPECTRUM OF EXCITATION SIGNAL

![Power Spectral Density](image)

Figure 3. Power spectrum of square wave

An important aspect of the use of polarization resistance types of measurement for the determination of impedance characteristics is the amount of power present in the input signal as a function of frequency. In the square wave used for most of this work (figure 3) the maximum power is present in the fundamental frequency \((1/\tau)\), and the high frequency power is low relative to the fundamental. One might therefore expect to get a better impedance spectrum using signals such as random or pseudo-random noise, which have a more balanced frequency content\(^4\). However, this is not the primary purpose of this paper, and has not been pursued here.

5.2. IMPEDANCE SPECTRA - THE EFFECT OF CYCLE PERIOD AND SAMPLING INTERVAL.

There are fundamental limits to the information which can be obtained from a sampled waveform. It is impossible to obtain information about frequencies below that corresponding to the cycle period. One way in which this can be expressed is that the bandwidth of the analysis is given by 1/cycle period. This limits the low frequency information which can be obtained, particularly from measurements with shorter cycle periods. In order to obtain reasonable resolution of the full Warburg impedance, the cycle period should be at least twice the time required for the diffusion process to reach near-steady-state. At high frequencies the Nyquist frequency \((n/2\tau)\) provides an upper bound to the measurement. A further problem at high frequencies is that of aliasing, in which frequency components above the Nyquist frequency are effectively measured as being the corresponding frequency interval below the Nyquist frequency. The perfect triangle and square
waves used in this work have infinitely high frequency components present, and this results in the slight 'flattening' observed at the high frequency end of the power spectrum shown in figure 3. This has significant implications for the measurement procedures examined in this work. It might be hoped that the result of a measurement with a relatively low Nyquist frequency, when expressed as an impedance spectrum, would be a section of the spectrum which is correct over the valid frequency range of the analysis. The results of a series of experiments performed with a range of cycle periods are given in figure 4. In general it can be seen that the points in the low frequency end of the impedance spectrum are correct (if sparse), but serious errors can occur at high frequencies (typically frequencies above about half the Nyquist frequency). For the reasonably typical interface characteristics used in this work it should be noted that the measurement sample period must be of the order of 1 ms or less if the high frequency part of the impedance spectrum is to be determined with reasonable accuracy. These difficulties at high frequencies are thought to be due primarily to aliasing effects, particularly in respect of the current waveform, together with a mismatch between the effective filtering applied to the current and potential waveforms. The former problems can be reduced (though never entirely overcome) by filtering the current waveform to remove frequencies above the Nyquist frequency, prior to application of the current waveform to the cell. Alternatively the current waveform can be calculated as the sum of the appropriate series of sine waves, which should eliminate aliasing problems. The latter approach is extremely computer-intensive, owing to the need to calculate many sine terms for each measurement time, and a simpler alternative is for the measurements to be taken with a range of cycle periods and the higher frequency components of each analysis discarded (reasonable accuracy appears to be achieved for frequencies up to half the Nyquist
frequency). These errors also indicate that the frequency response of measurement systems must be well above the highest time constant to be measured. This constraint applies to transient measurements as well as measurements aimed at the determination of impedance spectra by the approach described here.

5.3. IMPEDANCE SPECTRA - THE EFFECT OF MEASUREMENT NOISE.

![Figure 5. The effect of noise on the impedance spectrum](image)

The effect of measurement noise on the calculated spectrum can be seen in figure 5. With a standard deviation of measurement of 1 μV (compared to a maximum overpotential of around 6 mV) there is a significant, but probably tolerable scatter in the calculated impedance spectrum. With 10 μV of noise the errors become far more significant, although the general form of the curve can still be distinguished. It should be noted that the results of figure 5 correspond to white noise (i.e. the power spectral density is the same for all frequencies). Other noise sources, such as mains frequency interference, may have markedly different effects.

5.4. IMPEDANCE SPECTRA - THE EFFECT OF VOLTAGE QUANTISATION.

Typical data acquisition systems using moderately-priced analog-to-digital converters (ADCs) will measure to a resolution of 8 to 16 bits (i.e. 1 part in 256 to 1 part in 65536). Figure 6 shows the effect of quantisation of the voltage measurement corresponding to the use of 8 and 12 bit ADCs and assuming a full scale range of 10 mV. Providing the range of measurement of the ADC is closely matched to the range of the signal to be measured, a 12 bit ADC can give adequate performance. An 8 bit conversion will almost inevitably give a rather noisy spectrum, although the general features of the spectrum can be detected.

5.5. THE APPLICATION OF NUMERICAL MODELS TO IMPEDANCE STUDIES.

This work has been performed with a view to the validation of a particular interpretation of linear polarization resistance measurements. If it is required to compute the response of a system which is assumed to be linear, it is probably more efficient to use the Laplace transform method for the analysis (as discussed by MacDonald in this volume), or, for repetitive waveforms, to transform from the known solution in the frequency domain. However, these methods do not
readily accommodate non-linear responses, and for more complex systems, such as systems in which the diffusion wave is modified by reactions in solution, analysis of transients by means of a generalized numerical model may provide a useful method of deriving the impedance spectrum. This approach is currently being examined for a number of systems.

5.6. THE INTERPRETATION OF POLARIZATION RESISTANCE MEASUREMENTS.

Before considering the way in which polarization resistance measurements can be related to the impedance spectrum, it is useful to examine the component of the impedance spectrum which should be taken to determine the corrosion rate. For the simple system examined in this work, the response will include the charge transfer impedance, which is seen at higher frequencies, and the Warburg impedance, which dominates the response at low frequencies. The polarization resistance, \( R_p \), may be defined as the slope of the curve of potential versus current measured with a sufficiently slow sweep rate that the system remains in essentially steady-state conditions, or, in impedance terms, the impedance at zero frequency. Thus \( R_p \) includes both the charge transfer impedance and the Warburg impedance, together with any solution resistance. However, for the model considered in this work the Warburg impedance increases as \( I_{dc} \) increases, and \( R_p \) is not linearly related to \( I_{dc} \). On the other hand \( R_{ct} \) is related to \( I_{dc} \) through the relationship:

\[
R_{ct} = \frac{2 R T}{n F I_{dc}}
\]

Thus \( R_{ct} \) should, at least for this system, be used to determine \( I_{dc} \) (or, effectively, the corrosion rate). For systems in which the impedance response consists of a charge transfer resistance together with a Warburg impedance due to the diffusion of an anodic product away from the surface, the Warburg impedance is related to the rate of reaction (since it is related to the flux of the product away from the interface), and \( R_p \) will be approximately inversely proportional to the rate of reaction. However, as indicated above, the existence of such a Warburg impedance implies that the anodic back reaction is significant, and the calculated rate of reaction will not be an accurate measure of the corrosion rate.
While the polarization resistance is nominally measured under steady-state conditions, in practice the measurement will usually be made at a low enough frequency that the behaviour appears to have attained steady-state by examination of the potential-time or current-time record. Whether or not this will include any Warburg impedance will depend on the time required for the diffusion process to approach steady-state. For the case of steel in concrete, where the diffusion path is very long, there is no possibility of attaining equilibrium. Thus the measured 'polarization resistance' will depend on the period selected for the measurement. At first sight this appears to be a rather arbitrary decision, but careful consideration of the relationship between impedance and frequency suggests that there is a tendency to select a measurement period which will give a measured polarization resistance which relates reasonably well to the charge transfer resistance. Roughly-speaking the impedance measured with a polarization resistance technique will be equal to the amplitude of the impedance at a frequency corresponding to the cyclic frequency of measurement. The Bode diagrams of figures 4 to 6 tend to mask the variation in the impedance that will be measured as a function of time, since the log-log scales give a misleading impression of the relative time intervals. On linear scales (figure 7) it becomes clearer that there is a large range of cycle periods where $R_p$ will be determined as approximately $R_{ct}$ (ignoring solution resistance effects). This can also be seen in the hysteresis diagrams of figure 8, in which the potential for a triangular current waveform is plotted as a function of current for a range of cycle periods. While the diagram for a 10 second period shows a continuous curvature, and would probably not be taken as indicative of having attained steady-state, the curve for a 1 second period does show a reasonably linear region in the second half of each segment, and could easily be interpreted as the system having reached steady-state. The slope of the straight region of this curve gives a 'polarization resistance' of about 500 ohm, compared with a value of 347 ohm for $R_{ct}$, and about 1400 ohm for $R_p$. Careful examination reveals that even the 'true' steady-state curve obtained with a 1000 second period shows a significant curvature, due to the inherent non-linearity of the electrochemical system.
Figure 8. E/I hysteresis diagrams

6. References


