MONTE CARLO SIMULATION OF ELECTROCHEMICAL NOISE RESISTANCE MEASUREMENTS

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

ABSTRACT

A Monte-Carlo model of electrochemical noise generation by an anodic pulse emission process has been developed. This has produced simulated electrochemical potential and current noise time records which have been analysed by conventional spectral analysis procedures. At low frequencies the results have been consistent with previous mathematical models of the process, but the high frequency behaviour does not correlate well with these models.

INTRODUCTION

Several workers have demonstrated that electrochemical noise resistance measurements provide a good indication of corrosion rate (see, for example, the papers at the ASTM Symposium on Electrochemical Noise, held at Montreal in 1994). The measured noise resistance has generally been assumed to be equivalent to the linear polarization resistance, although only limited theoretical analyses have been undertaken. These analyses have typically used equivalent circuit approaches to analyse the response, but it is not clear that this is appropriate for all of the components of the metal-solution interface. In particular it appears questionable to treat the charge transfer process as a linear circuit element when that process is giving rise to the electrochemical noise by virtue of its non-uniform behaviour.

The objective of the work described here has been to simulate the electrochemical noise generation process in order to test the validity of equivalent circuit models of the noise resistance measurement.
ASSUMPTIONS AND SIMULATION PROCEDURES

As in previous work\(^2\)\(^3\), it has been assumed that the anodic process occurs as discrete bursts of charge. Individual pulses are assumed to be independent of other pulses, and the charge in each pulse is constant. The anodic process is assumed to be under activation control, and a simple consideration of 'average' behaviour, exemplified by Tafel's Law, shows that the characteristic inter-pulse interval will have an exponential relationship with the metal-solution potential.

Oxygen reduction is assumed for the cathodic process. In principle this should probably be treated as a four electron Poisson process, but it is computationally infeasible to use this approach for realistic ratios of anodic to cathodic charge. Consequently the cathodic process is treated as a constant current density, independent of potential (since oxygen reduction is assumed to be occurring at the limiting current density). This assumption also ignores the possibility of mass transport fluctuations leading to noise in the cathodic reaction.

The electrochemical potential of the specimen will vary with time as a result of charging and discharging of the double layer capacitance (assumed for the purposes of this analysis to be a perfect capacitor). Thus, the dc equilibrium potential will be that potential at which the average rate of charge generation due to the anodic process will be equal and opposite to the limiting current due to the cathodic process.

In order to model the electrochemical noise resistance measurement technique, two electrodes are modelled as described above. Then the measured noise current will result from the different numbers of anodic pulses on the two electrodes (since the cathodic currents are necessarily equal). To simulate the effect of a solution resistance between the two working electrodes the two electrodes are treated independently. Then the current flowing between the two electrodes will result from (and tend to reduce) the difference in potential.

In order to allow for low solution resistances, such that the potential between the two electrodes changes significantly in the period between consecutive pulses, a full analytical solution for the potential and current behaviour has been used. If we note that the change in potential due to the cathodic current will be an identical linear ramp for both electrodes (figure 1), we can see that we may ignore this in analysing the current flow between the electrodes. This then becomes a simple problem of the discharge of a capacitor through a resistor, leading to an exponential decay in the potential difference. Then the potential difference (in the absence of pulses of charge) is described by:

\[
\Delta E = \Delta E_0 \cdot e^{-\frac{2t}{R_{sol}C_d}}
\]

(the factor 2 arises because the double layer capacitances on the two electrodes are both discharging simultaneously). Integration of \(\Delta E/R_{sol}\) (the current flowing between the two electrodes) gives the charge flowing in the interval \(\Delta t\):

\[
Q = \int_{0}^{\Delta t} \Delta E_0 \cdot R_{sol} \cdot e^{-\frac{2t}{R_{sol}C_d}} dt
\]

We may note that if we consider the average potential of the two electrodes, this is unaffected by the current flowing between the electrodes (since this causes equal and opposite changes in the potential of the two electrodes). Hence the average potential over a period \(\Delta t\) is simply:
\[ E_{mean} = \frac{1}{\Delta t} \int_0^{\Delta t} \left( \frac{E_1 + E_2}{2} \right) dt = \left( \frac{E_1 + E_2}{2} \right) - \frac{1}{2} i_{\text{lim}} \Delta t \]

It may be noted that this analysis is similar to that for the treatment of exponential pulses in the absence of solution resistance effects.

With the dependence of results on prior conditions that is implied by the combined influence of solution resistance and double-layer capacitance, it becomes questionable to use arbitrary initial conditions, and to avoid artefacts from this source, the simulation is run for 1000 anodic pulses plus a period of \(3 R_{\text{so}} C_{\text{dl}}\) (with the first 1000 pulses also being used to estimate the expected run time). The simulation is then run for a further 1001 simulation seconds, with the current and potential being recorded at \(1000/2^{16}\) intervals. This allows the power spectrum of the noise records to be calculated over the range of \(10^{-3}\) to \(32\) Hz. Note that both the current and potential values are obtained by integration over the sample period, and this will reduce the extent of aliasing at the high frequency end of the spectrum.

**ANALYSIS**

The theoretical analysis of an electrochemical process such as that described here has been presented in earlier papers\(^1,2\). These have suggested that the low frequency limit of the potential and current power spectrum may be used to determine the noise resistance and the charge in the current pulses that are responsible for the noise.

As a consequence of these predictions, the analysis of the results of the simulation have been based on the estimation of the power spectrum for the individual current and potential time records. While it is possible to process a 64K sample time record, this is computationally slow and difficult (at least on the IBM PC compatible computer used for this work), and the analysis has been performed on 1024 sample records. As well as being faster to compute, this also allows for averaging and hence smoothing of the spectrum.

The low frequency analysis has been performed by starting at the first sample and then constructing a new time record by averaging successive groups of 64 samples. This is effectively an integration process, and therefore reduces the effect of aliasing in the calculated power spectrum. The resultant time record is then transformed to the frequency domain using a conventional fast Fourier transform (FFT).

A similar procedure has been used for the estimation of the high frequency part of the spectrum, except that the time records have been taken as sequential groups of 1024 samples. This allows 64 power spectra to be calculated and averaged, thereby reducing the noise in the spectrum by a factor of 8. Where the high and low frequency spectra overlap the high frequency spectrum has been used.

**RESULTS**

**Power Spectra**

The time taken for the simulation is approximately proportional to the number of pulses within the simulation period, and hence to \(I_d/q_a\). This places a lower limit on the value of \(q_a\). An upper limit also exists, as very large but infrequent pulses cause very large changes in potential, and hence it becomes invalid to use an exponential distribution to estimate the time to the next pulse. Running on a 90 MHZ Pentium-based PC, the simulation with \(I_d=10^{-6}\)A and \(q_a=10^{-12}\)C takes around 12 hours, or around 2000 pulses.
per second. For this reason relatively few simulations have been performed. For the purposes of this work a small electrode (area 1 mm²) has been assumed, with a double-layer capacitance of 50 μF/cm² and a cathodic current density of 100 μA/cm². Figure 1 shows a section of a typical time record, obtained with \( I_o = 10^{-6} \text{A} \) and \( q_o = 10^{12} \text{C} \). Figures 2 to 4 show the potential and current power spectra for simulations performed at a variety of conditions. Note that the low frequency end of the spectra exhibit more noise as a result of the lack of averaging of the spectra. For comparison the predicted power spectra, based on the theoretical analysis presented in reference 1, are also plotted. It is clear that the comparison is generally good at the lower frequencies.

**Noise Impedance Calculation**

Various authors have suggested that the impedance of a corroding system can be calculated from the potential and current noise spectra. However, there are indications that noise produced according to the assumptions of this model will not give an impedance that is consistent with that estimated from a conventional equivalent circuit model. This is shown in Figures 2 to 4, where the predicted potential noise spectrum has been derived as the product of the predicted current noise and the equivalent circuit derived from a conventional polarization resistance analysis. This observation requires further study.

**CONCLUSIONS**

The development of a Monte Carlo simulation has helped to test the assumptions used in modelling and analysing electrochemical noise measurements. The low frequency limit of both the current and the potential noise (and hence the noise resistance) appear to be adequately described by models based on a shot noise analysis. However, the behaviour at higher frequencies is not in accordance with a simple model based on the current noise applied to a conventional metal-solution impedance.

**REFERENCES**


Figure 1 Time records for $I_a=10^{-6}$, $q_a=10^{-12}$.

Figure 2 Power spectra for $I_a=10^{-6}$, $q_a=10^{-8}$. 
Figure 3  Power spectra for $I_a = 10^6$, $q_a = 10^{-10}$.

Figure 4  Power spectra for $I_a = 10^4$, $q_a = 10^{-12}$. 