

An Introduction to Electrochemical Impedance Measurement

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Introduction

The rapid and accurate measurement of electrochemical phenomena is of considerable importance for a range of studies, not only in research, but also in practical applications. Typical subjects include corrosion, effectiveness and life of surface coatings, battery testing and the investigation of biological and photoelectric effects. Of these, corrosion and surface treatments are probably the most important applications, although the basic mechanisms determining the characteristics of, for example, batteries are broadly similar.

It is possible to measure effects such as corrosion rate, or battery life, by direct analytical methods, for example weight loss measurements or solution analysis by spectroscopy; but, because the processes are slow, these methods are time consuming and inefficient. Additionally, they are restricted to systems in which the products formed by the process do not form adherent layers.

Because the processes under consideration are electrochemical, it is possible to analyse them using electrical methods, based on Faraday's law which relates the change in mass per unit area to the current flow. The advantages of this approach are a relatively short measuring time, high accuracy and the possibility of monitoring the process continuously. Naturally there are also disadvantages, the major of these being that the system under investigation has to be perturbed from its normal state by an external signal, which inevitably changes the properties of the system. The perturbation itself can be due to an ac or dc signal and it is primarily with ac methods that this paper is concerned.

The dc technique has been widely used for corrosion rate measurement, but the method generally requires a relatively large perturbation (or polarisation) signal and can, in fact, fail when the corrosion process is taking place in a low conductivity medium. Ac methods are finding increasing applications in electrochemical research, because only small perturbation signals (which do not disturb the electrode properties) need to be used and low conductivity media can be investigated.

Principles of Electrochemical Measurements

If a potential (voltage) is applied across an electrochemical cell (corroding material, battery etc.) a current is caused to flow through the cell, with a value determined by the mechanisms of the reaction taking place. The reaction is the formation of new chemical species as result of the movement of ions through the electrolyte. The ionic movements are caused by the applied potential difference, and constitute a flow of electric current.

If the applied potential is a sinusoid ($\Delta E \sin \omega t$) then the subsequent current will also be sinusoidal, with a value $\Delta i \sin(\omega t + \phi)$. Harmonics of this current ($2\omega, 3\omega \dots$ etc.) will also flow. The relationship between the applied potential and the current flow is known as the impedance, which is analogous to the resistance-current-potential relationship of a dc circuit. The impedance (Z) has a magnitude ($\Delta E/\Delta i$) and phase (ϕ) and is thus a vector quantity.

Now, if a sinusoidal potential is applied across a pure resistance of magnitude R , then the magnitude of the impedance $Z = R$ and the phase $\phi = 0$ for all frequencies. This is shown on a plot of the real (a) and imaginary (jb) components as a point on the real axis (Figure 1) overleaf.

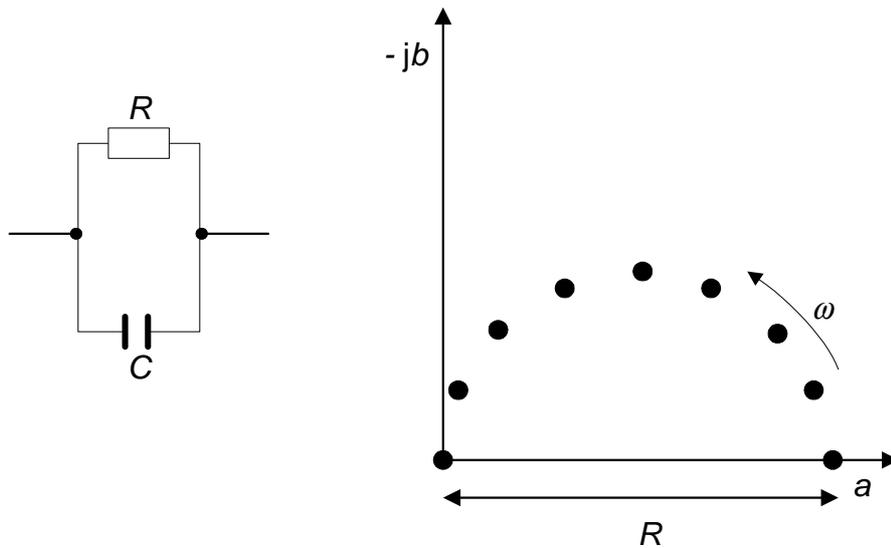


Figure 1 - Complex plane impedance spectrum - resistance

If the sinusoid is applied across a pure capacitance, the impedance is now dependent on the frequency, according to the relationship $Z = 1/\omega C$ and the phase angle is 90° . As the frequency increases the magnitude of the impedance decreases, as shown in the plot (Figure 2).

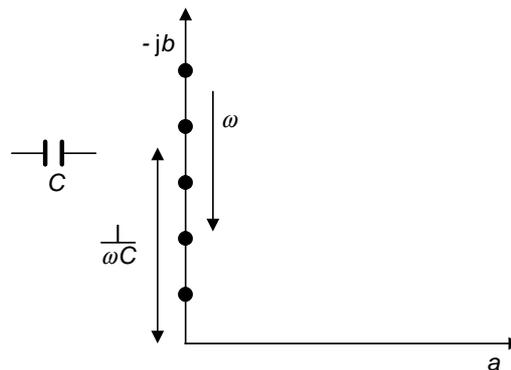


Figure 2 - Complex plane impedance spectrum - capacitance

The result of combining these two basic circuit components, in series or parallel, can be easily deduced, with two simple examples being shown in Figure 3, for a series resistance and capacitance and a parallel resistance and capacitance.

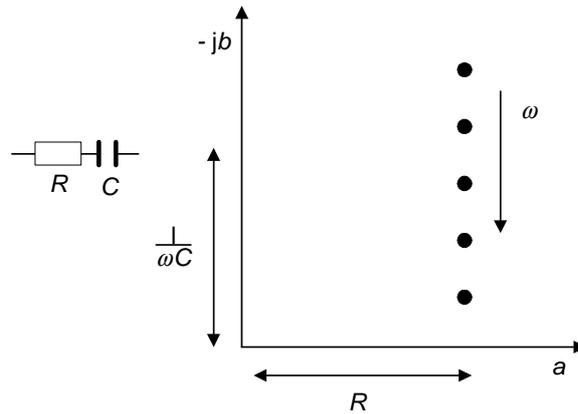


Figure 3a - Complex plane impedance spectrum - series resistance, capacitance

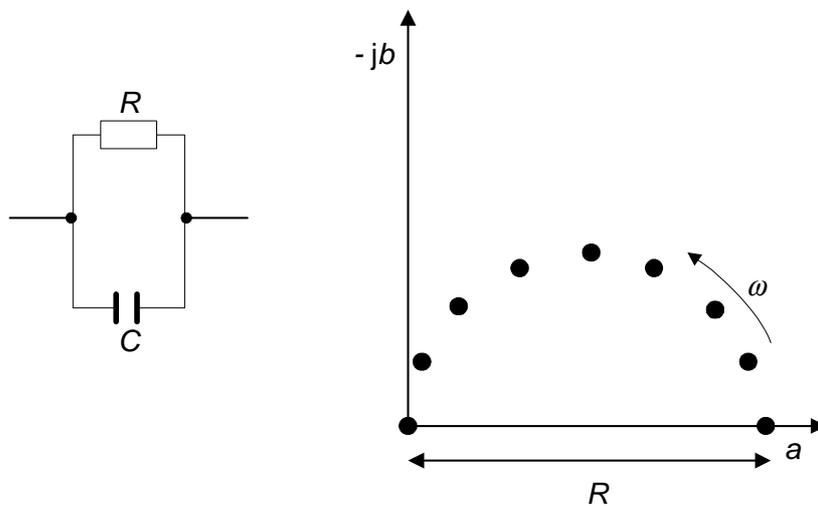


Figure 3b - Complex plane impedance spectrum - parallel resistance, capacitance

An electrochemical cell can be represented by a network of resistors and capacitors - known as an equivalent circuit. From an impedance spectrum, (plotted in the real/imaginary plane, or as gain and phase versus frequency) it is possible to deduce the equivalent circuit and determine the significance of the different components.

In order to understand the measurement instrumentation used to derive the impedance characteristics it is necessary to look at some basic aspects of the electrochemical cell.

The most basic form of a cell comprises two electrodes immersed in an electrolyte (Figure 4). Application of a potential across the electrodes causes a current to flow through the cell. The electrodes are known as the working electrode, at which the interface between electrolyte and electrode is investigated and the secondary (or counter) electrode, which allows the current to pass through the cell. This type of arrangement is used for the investigation of electrolyte properties, such as conductivity, when the dominant parameter is the electrolyte resistance.



Figure 4 - 2-terminal electrochemical cell

In other cases the reaction at the working electrode needs to be examined to determine the relationship between the current on the one hand and the voltage that is required to drive this reaction on the other. This requires a third electrode (the reference electrode). Measurement of the potential between the working and reference electrodes allows the change in potential of the working electrode needed to cause current to flow to be found. Normally the reference electrode is remote from the working electrode, in a separate compartment. The compartment is then connected with the working electrode by a narrow glass tube (known as the Luggin capillary) which contains the electrolyte. This permits separation of the bulk properties of the electrolyte from the interfacial properties (Figure 5). The arrangement does, however, impose a small (but, in some cases, significant) additional resistance due to the electrolyte between the tip of the Luggin capillary and the working electrode. This is minimised by placing the two as close as possible without disturbing the current flow to the working electrode.

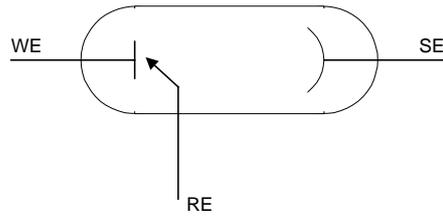


Figure 5 - 3-terminal electrochemical cell

Finally, a 4-terminal cell can be used to provide an analysis of processes occurring within the electrolyte, between two measuring electrodes separated, for example, by a membrane. In this case the purpose of the working and secondary electrodes is only to enable the current flow. This permits the study of ion transport through the membrane (Figure 6).

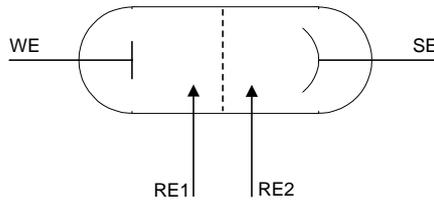


Figure 6 - 4-terminal electrochemical cell

The 1287 Electrochemical Interface

To make the measurements outlined above, a correlation frequency response analyser (FRA), such as the Solartron 1250, or 1255, can provide a sinusoidal excitation signal and measure the response to this as a ratio of one channel to the other. If the response signals represent, on one channel, the cell potential and on the other the cell current, then the impedance (or admittance) can be measured.

The analyser however, cannot always be connected directly to a cell and requires an interface with suitable input/output and control characteristics - these are provided by potentiostat such as the 1287 Electrochemical Interface.

The basic circuit of the 1287 is shown in Figure 7, from which it can be seen that the instrument may be considered in five basic parts:

1. Adding amplifier - providing the cell polarisation level.
2. Polarisation control
3. Electrode connection
4. Current measurement
5. Voltage measurement

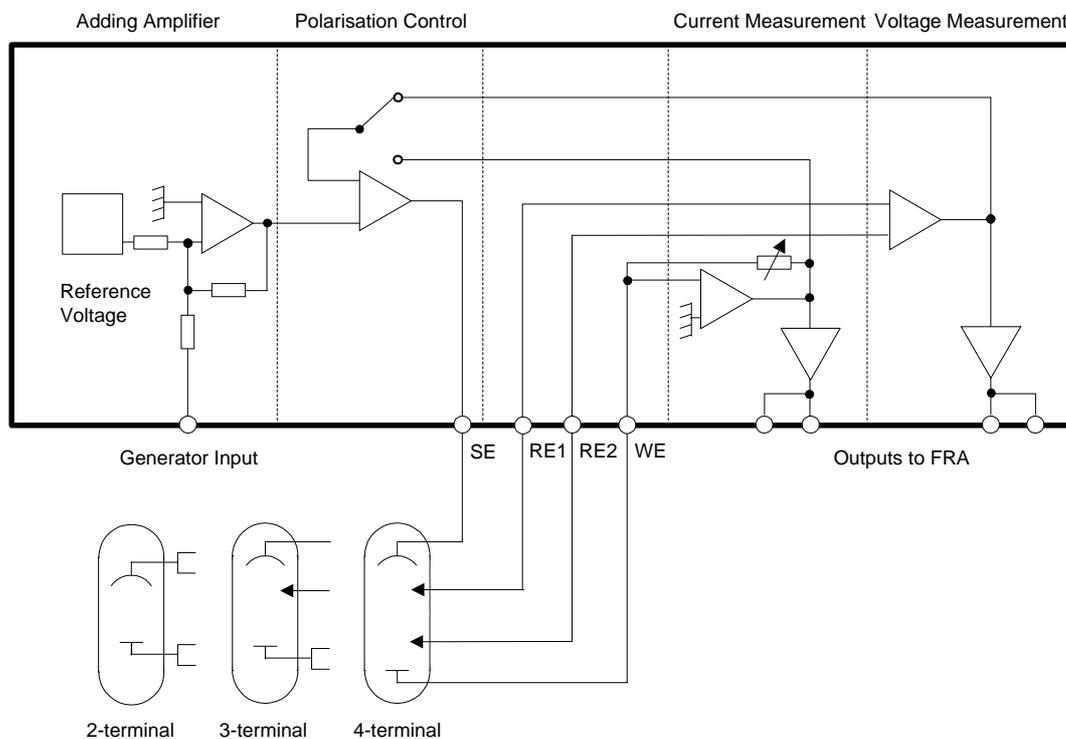


Figure 7 - Schematic of 1287 Electrochemical Interface

Each of these sections will be described briefly:

1. Polarisation Level

Two polarisation signals are available, dc and ac, these being summed in the adding amplifier. The dc signal can be used on its own to measure the dc characteristics of a cell (such as current-potential curves) or in conjunction with the ac signal. The ac signal is derived from the FRA generator, generally as a high amplitude signal which is then divided by 100 at the 1287 input to provide a good quality, low amplitude signal to perturb the cell.

2. Polarisation Control

To avoid problems of cell stability when applying the polarisation signal, and to enable multi steady state systems to be investigated, it is necessary to regulate the applied signal. This is achieved by applying negative feedback to ensure that the polarisation of the electrochemical interface follows a reference quantity set by the experimenter. The regulated quantity may be the interface potential (for potential measurements), or the interface current (for galvanostatic measurements) and is compared with the reference quantity using a differential amplifier. A difference in the two quantities causes the regulated quantity to be adjusted by a change in the amplifier output to make this difference zero.

The regulated polarisation level is then output to the secondary electrode of the cell, SE, via a cut-out switch, which isolates the cell if the current becomes saturated. This avoids damage to the cell if the system goes unstable.

3. Electrode Connections

The two reference electrodes (RE1 and RE2) are used to measure the required characteristics and the working electrode (WE) provides the electrode/electrolyte interface at which the reaction occurs.

For 2-terminal cells RE1 is connected to SE and RE2 to WE, at the cell. For 3-terminal cells RE1 is used to measure the interface characteristics (via, for example, a Luggin capillary) while RE2 remains connected to WE. In the 4-terminal mode the electrodes are connected independently.

4. Current Measurement

Current measurement is based on Kirchoff's laws, using a virtual earth technique. The current to the virtual earth is the same as that flowing through the Standard Resistor in the feedback loop, where the Standard Resistor is selected to match the impedance of the cell as closely as possible. This technique avoids loading the circuit, as happens with the series resistor method.

The voltage due to the cell current is output to the FRA input appropriate to the characteristic (impedance or admittance) being measured.

5. Voltage Measurement

The voltage, or potential, is measured using a high impedance differential amplifier across the reference electrodes and, again, output to the FRA.

In both current and voltage measurement any dc content in the signal may be backed-off at the 1287 output, so that the FRA receives only the ac content.

Two other features are provided: Real Part Correction and Positive Feedback Polarisation Control (IR Compensation).

Real part correction allows an amount to be subtracted from the in-phase (real) component, equivalent to the electrolyte resistance due to the distance between the reference electrode capillary (Luggin tip) and the working electrode. It will be remembered that a pure resistance provides a response to a sinusoid which has a zero phase shift for all frequencies.

IR compensation uses positive feedback to compensate for the effect of the electrolyte resistance, but is subject to instability.

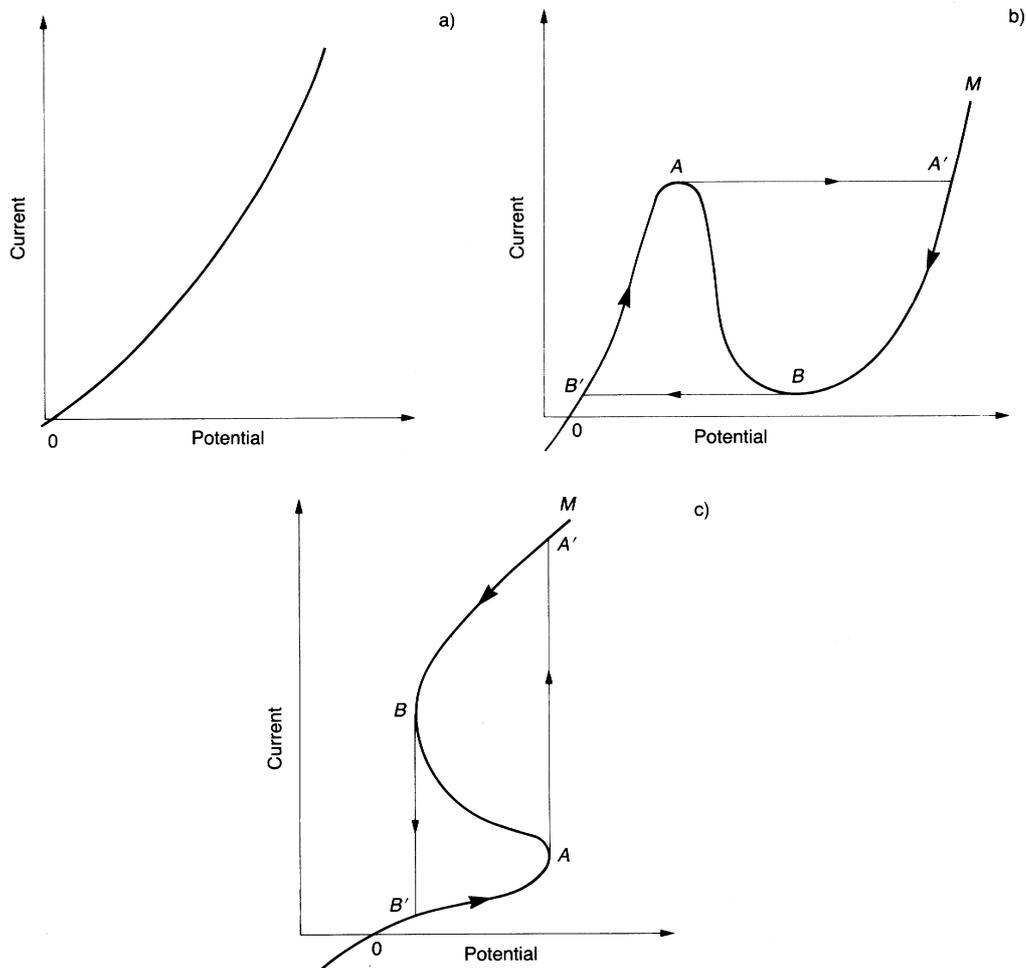


Figure 8 - Examples of non-linear current-potential curves

- (a) Exponential-shaped curve: potential or current-controlled interface.
- (b) N-shaped curve: potential-controlled interface.
- (c) S-shaped curve: current-controlled interface.

Choice of potentiostatic (constant voltage) or galvanostatic (constant current) control of the cell under test is governed by its dc current-potential characteristics. Figure 8 shows examples of typical non-linear current-potential curves.

Figure 8a can be derived by use of either a potential- or a current-controlled interface, as each point on the curve has a unique identity on both current and potential axes. For a response such as that shown in Figure 8b, the cell characteristic can only be obtained by potentiostatic operation. Were galvanostatic control to be used, an increasing current would cause the characteristic to follow the path OB'AA'M, whereas a decreasing current would produce the path MA'BB'O. Voltage control would allow the full characteristic OB'ABA'M to be determined unambiguously. Similarly, galvanostatic control is required to obtain the cell response shown in Figure 8c.

It is also possible, while setting up or running a test, to monitor the potential at a relevant terminal, or measure the current, using either the 1287's own display, or an external dvm connected to the sockets on the rear panel.

Interpretation of AC Impedance Measurements

It has been shown that an FRA, used in conjunction with a potentiostat such as the 1287 Electrochemical Interface, allows a cell to be stimulated with an ac signal and the response, in terms of the cell potential and current, measured. Using the transfer function facility of the FRA the impedance (or admittance) can be determined directly. It will be recalled from the earlier discussion that a plot of the impedance, either as the real and imaginary parts against frequency, or the magnitude and phase against frequency, allows the characteristics of the system to be established.

As an example, a simple corrosion system can be represented by a parallel capacitance and resistance (which represent the corroding interface) in series with a second resistance, as shown in Figure 9. The response of this equivalent circuit is shown as an Argand diagram, from which the values of the circuit elements can be determined.

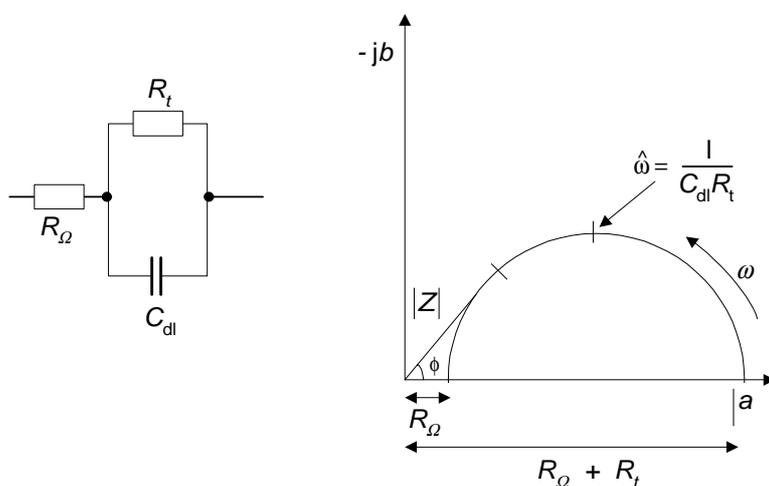


Figure 9 - Complex plane impedance spectrum - simple equivalent circuit

The series resistor, R_{Ω} , represents the resistance of the electrolyte, surface films and the leads used to connect the cell to the measuring system etc. The parallel resistance, R_t , is known as the charge transfer resistance and determines the rate of the corrosion reaction. The capacitance, C_{dl} , is known as the double layer capacitance, which occurs at the electrode/electrolyte interface. The electrode surface has a charge, due to an excess or depletion of electrons, which resides with the atoms in the first layer of the surface and is balanced by an equal number of oppositely charged particles in the electrolyte. The distribution of this charge determines the field strength of the interface, which, in turn, defines the speed of ion transfer.

To summarise the behaviour of this simple circuit; at high frequencies the capacitance (C_{dl}) conducts easily (effectively shorting out the charge transfer resistance R_t) leaving only the effect of the conduction series resistance (R_{Ω}). As the frequency decreases the conduction of the capacitance becomes less and less and the response due to R_t increases. As the frequency approaches zero the capacitor ceases to conduct and the cell impedance is a function only of R_t and R_{Ω} .

For most practical systems this simple approach is insufficient to define the reaction process and more complex models, or equivalent circuits, need to be derived. These include the effects of diffusion of charged species (e.g. ions) and the presence of inductive loops (with a positive imaginary component), the significance of which is not, at present, clearly understood.

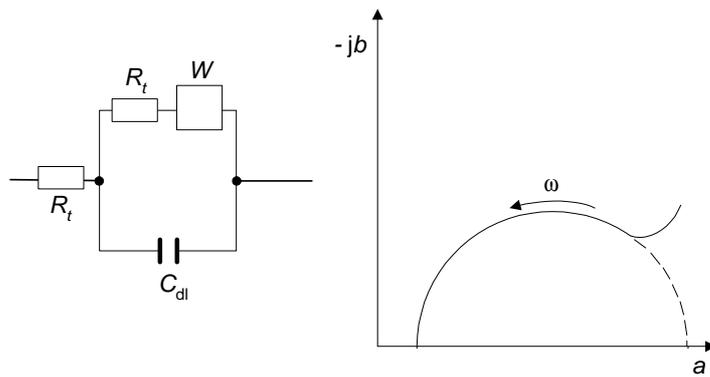


Figure 10 - Complex plane impedance spectrum - equivalent circuit with Warburg impedance

A typical equivalent circuit, to include mass transfer diffusion effects, is shown in Figure 10. The additional element, known as the Warburg impedance, is a complex quantity having real and imaginary parts which are equal. This impedance is proportional to the reciprocal of the square root of the frequency ($1/\sqrt{\omega}$). At high frequencies, therefore, this term is small and the diffusion process is only observed at low frequencies. Here the semicircle is distorted by the Warburg impedance (represented by a straight line at 45° to the axis). This simple analysis predicts that the Warburg impedance diverges from the real axis, but in practice the dc resistance of the cell is finite. Diffusion layer effects then cause the low frequency end of the impedance to bend over the real axis, giving rise to a double semicircle (Figure 11). Other effects, such as time constant dispersion, due to inhomogeneities in the electrode surface (which depresses the semicircle) and adsorption (which results in a second, low frequency semicircle) also further complicate the analysis.

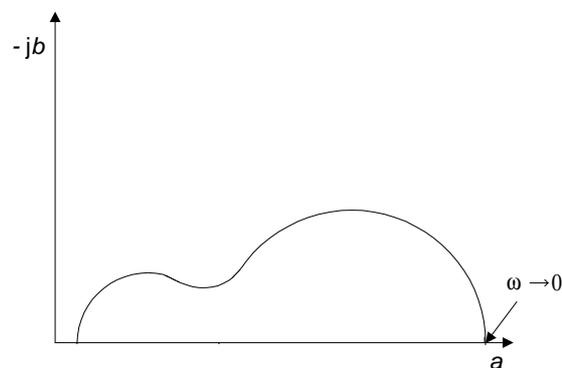


Figure 11 - Complex plane impedance spectrum - Warburg impedance as approaches 0

It can be seen from the diagrams (Figures 8, 9, 10, and 11) that the basic parameters - electrolyte resistance, double layer capacitance, the corrosion reaction and diffusion effects, can be determined from empirical impedance data provided that a sufficient frequency range is investigated. This range may extend from a low limit of $10\mu\text{Hz}$ to an upper frequency in the order of 1MHz , depending on the process being studied.

The low frequency region can provide information concerning charge transfer and diffusion phenomena and the high frequency part defines the solution resistance. As a practical example, it has been shown that the corrosion behaviour of coated metals can be described by corrosion reactions at the metal/coating interface, defined by low frequency measurements and, at high frequencies, the capacitive behaviour of the intact coating layer. An additional effect, due to penetration of the electrolyte, gives rise to a resistive component, which may be determined from intermediate and low frequency data.

Conclusions

Measurement of ac impedance data is a powerful tool for the analysis of corroding systems, particularly where these are highly resistive. The technique may be applied to investigate a wide range of electrochemical phenomena, including corrosion and surface treatments, battery testing, biological and photoelectric effects. Correlation frequency response analysis, using single sine stimulation of the system and measurement of the resultant current and voltage, via a potentiostat, enables accurate and repeatable determination of the response, in spite of low signal levels, high noise levels and the presence of non-linear reactions. It should be noted, however, that while the FRA is most commonly used for this type of investigation, researchers are studying broad-band stimulation and spectral analysis. Although the results are not as accurate and signal-to-noise ratios are not generally good, there can be a time saving using this method and it cannot, therefore, be ignored.

This note is intended only to be a basic introduction to electrochemical impedance measurement.

Further (more detailed) technical reports are available.

Bibliography

Other Technical Reports on Impedance Analysis and Electrochemistry available from Solartron:

Identification of Electrochemical Processes by Frequency Response Analysis

(C Gabrielli, Technical Report No. 4)

Frequency Response Analysis

(P E Wellstead, N D Cogger, R V Webb, Technical Report No. 10)

The Measurement of Signals from Electrochemical Phenomena

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