Surface Characterization: A User's Sourcebook
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37 Electrochemical methods

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37.1 Introduction

Corrosion processes on metals in aqueous environments and fused salts occur mainly as a result of electrode reactions. The corrosion rate for a metal depends on the basic thermodynamic conditions and on the kinetics of the anodic and the cathodic reactions occurring on its surface. In laboratory experiments one can study clean metal surfaces but under service conditions, for instance in a plant, a metal surface is most often partially contaminated and, moreover, covered by oxide or by corrosion products adhering more or less to the metal surface; these circumstances influence the experimental situation.

Corrosion investigations can be undertaken for various purposes, for example:

- to study basic mechanisms of corrosion reactions,
- to monitor corrosion equipment in a plant,
- to test corrosion under laboratory conditions or service conditions in a plant,
- to make field tests of metals, in the atmosphere or in soil.

Some of the current experimental methods are electrochemical, but there are many other methods in use based on different chemical or physical effects. In this chapter mainly purely electrochemical methods used for corrosion monitoring and corrosion testing, applied under different conditions, will be discussed. In some cases these methods may be non-destructive, but more commonly they are destructive for the metal surface under examination. Also metal surfaces coated with other materials, inorganic or organic, are treated in this context. Electrochemical methods used for studying basic reaction mechanisms are discussed only briefly.

If a metal is coated with another material then, of course, the protective properties of this coating material can be decisive as regards the resulting corrosion risk for the underlying metal. In this context one should distinguish between the cases:

a) coating with another metal, electrochemically more noble than the foundation metal,
b) coating with another metal, electrochemically less noble than the foundation metal,
c) thick, oxide coatings (electrically non-conducting) formed by oxidation of the foundation metal itself,
d) inorganic coatings with inhibitive properties, *e.g.* phosphate films,
e) organic coatings, *e.g.* paints, rubber linings.

The thicknesses of those coatings may vary between the magnitudes 10^{-6} m (*e.g.* case a and d) to more than 10^{-3} m (*e.g.* case e). From a corrosion view point interest is mainly focused on the corrosion properties of the coating material, the adhesion between the foundation metal and the coating material and the occurrence of cracks and pores in the coating. When a coating material is electrically conducting or semiconducting, it is possible to use electrochemical methods based on direct current (DC) or alternating current (AC) techniques. If a surface coating is an insulator, methods based on AC techniques can still be used. To locate defects in a coating the use of microelectrodes is a successful method.

The use of electrochemical methods is also recommended for monitoring the protective efficiency of corrosion inhibitors, for instance those used as additions in cooling water in an industrial plant.

Measurements of the electrode potential give qualitative information of the situation on a metal surface. For example, this kind of information can reveal whether a metal surface is electrochemically passivated or not, and, furthermore, still more reliable information can be obtained by monitoring the variation of the electrode potential with time. Measurements of the corrosion current give direct information on the general dissolution rate of a metal, but in a case of localized corrosion the area undergoing solution usually changes with time and is therefore not precisely known at any given time. Thus, the local corrosion rate of a metal may still be unknown even if the total corrosion current is measured.

37.2 Electrochemical methods

There most common measurements used in practice are determination of:

- the corrosion potential (E_{corr}) and its time dependence,
- the corrosion current in galvanic couples,
- polarization curves (E-logi relationships) with various techniques,
- electrochemical impedance by adopting small-amplitude alternating potential signals at varying frequencies,
- electrochemical noise, i.e. fluctuations of the corrosion potential or current fluctuations at constant potential.

Some important features of each of these aspects are discussed in the following sections together with references for further reading.

37.2.1 Measurement of corrosion potential

The corrosion potential of a metal is by definition a non-equilibrium potential, but it may correspond to a steady state value for a metal surface in the case of general corrosion. As regards localized corrosion the electrode potential varies at different spots on the metal surface and one can not define a common corrosion potential. By attaching of a capillary to a reference electrode or by use of a micro reference electrode it is possible to determine these local electrode potentials.

In the case of general corrosion, the corrosion potential is a ‘mixed’ potential, a non-equilibrium potential between the potential for the cathodic and the anodic reaction. The measurable potential corresponds to the potential difference across the electric double layer at the metal interface. This potential cannot be determined as an absolute value but it is measured by means of another electrode, a reference electrode. The measurement is usually done by means of a voltmeter with a high input resistance, or at least 10^{10} Ω in laboratory experiments. Under field conditions one can accept lower input resistances. The principle of the measurement of the corrosion potential of a metal is visualized in Fig. 37-1.

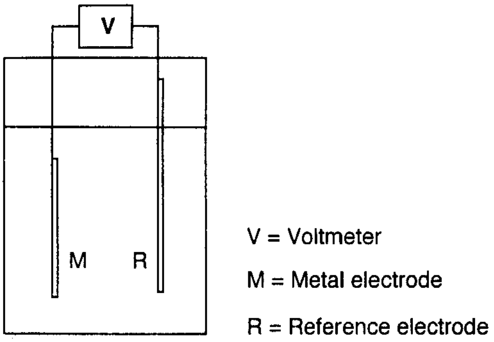


Fig. 37-1. Measurement of the corrosion potential of a metal in an aqueous solution.

Various types of reference electrode are used in practice and the most common are listed in handbooks and textbooks within this field (Shreir *et al.*, 1994). Many reference electrodes are based on the metals Hg or Ag, which thus act as electrodes of the second kind, i.e. $Me/MeX/X^-$-electrodes. For such an electrode two of the activities of the species involved in the equilibrium are fixed. For instance, if Me = Ag and X = Cl^-, then we have $a_{Ag}(s) = 1$ and $a_{AgCl}(s) = 1$. The ion X^- must be compatible with the system under observation and therefore the choice of reference electrode must be based on this and certain other considerations. One should be aware of the appropriate temperature interval for each of these electrodes. If a reference electrode is placed outside the system and is connected to it by a liquid junction, the associated liquid-junction potential must be considered. At high pressures special types of reference electrode must be used. In monitoring applications it is particularly important to have control of the long-term stability of the reference electrode.

Sometimes in field tests, for which commercial reference electrodes are too fragile, a polymer-coated metal wire, exposed only at the end, may be appropriate as a reference electrode. The reference potential is, in this case, the corrosion potential of the ‘reference’ metal wire. An example is a coated zinc wire used as a reference in sea water.

For potential measurements in soil often a robust Cu/$CuSO_4$ -electrode is used; this is reversible electrode of the first kind. For such an electrode one of the activities is fixed, in this case $a_{Cu}(s) = 1$.

The experimental potential values, obtained using different reference electrodes, can be transferred to a common potential scale, usually with reference to the standard hydrogen electrode (SHE).

It should be observed that all rest potentials are not equal to corrosion potentials. For instance, in deoxygenated aqueous solutions the rest potential for a metal may correspond to an electrode potential of the first kind, i.e. a Me/Me^{z+} electrode, where (Me^{z+}) has a very low value. Another example is platinum, that is passivated in many environments, and thereby acts as an electron-conducting substrate for redox reactions taking place on its surface. The measurable electrode potential then corresponds to the electrode potential for a redox couple with both species dissolved in the solution. Any equilibrium potential can be expressed by means of the Nernst equation (Koryta and Dvorak, 1987):

$$E = E^{O} + \frac{RT}{zF} \ln \frac{[ox]^{m}}{[red]^{n}} \tag{37-1}$$

For the purpose of corrosion monitoring the corrosion potential-time relationships are often of special interest. After exposure in a corrosive environment, passivating metals, *e.g.* stainless steels, show an increasing positive electrode potential due to an improved passive layer on the metal surface. In fact, depending on the aggressiveness of the environment, this increase can be accompanied by oscillating potential variations. Once a steady-state potential has been attained in a process solution, one can monitor the occurrence of local corrosion attacks by sudden decreases of the corrosion potential. If the passive film repeatedly repairs itself, the recoveries can be monitored as successive potential increases. However, a definite potential drop may indicate that the propagation of a local corrosion attack has occurred.

A descending potential value for a non-passivating metal after exposure to a solution can also be interpreted as a positive sign. For instance, it could be the result of the formation of a stable salt layer that gives mechanical passivity to the metal beneath it.

In some environments the control of the corrosion potential may be a method to avoid critical potential ranges, for instance in avoiding stress corrosion cracking of stainless steel in high purity water at high temperatures (Rosengren and Rosborg, 1984).

Measurement of corrosion potential can also be used as a tool for controlling the effect of corrosion inhibitors, *e.g.* in cooling water systems, especially in combination with another monitoring method.

By measurement of corrosion potentials of various metals and alloys under controlled laboratory conditions one may establish a galvanic series. A galvanic series gives qualitative indication of the probability of galvanic corrosion when coupling different metals together, but gives no direct information of the resulting corrosion rates.

In laboratory investigations of the effects of intermetallic phases, slag inclusions and other microscopic heterogeneities in metals on corrosion, one can measure the localized corrosion potentials of selected spots on the surface of the metal. For this purpose it is necessary to use a reference electrode with a capillary filled with electrolyte. However, the resolution in this kind of measurement is limited by the dimensions of the tip of the electrode capillary, commonly 0,5-1 mm. To obtain much finer resolution one has to use microelectrodes with capillary tips as small as 10-20 μm (Cleary, 1968).

The use of reference electrodes with a capillary is necessary in measurement of electrode potentials of metals acting as the anode or the cathode in an external electric circuit, but the techniques for the measurement of electrode potentials are otherwise the same as those used for the measurement of corrosion potentials.

37.2.2 Measurement of corrosion current

Direct measurement of the corrosion current is possible only in those cases where the anodic and cathodic reactions are completely separated. Such a situation may occur when two metals, with quite different electrode potentials, are connected in a galvanic couple. The principle underlying the measurement of the corrosion current in a galvanic cell is visualized in Fig. 37-2. The measurable corrosion current is then equal to the anodic current flowing through the surface of the less noble metal in the couple. The mass loss of the anode caused electrochemically is directly proportional to the current according to Faraday's law:

$$E = \frac{1}{m}\frac{M}{z}It \tag{37-2}$$

where m = amount of electrochemically dissolved metal (g), F = Faraday's constant (96485 As mol^{-1}), M = molar weight of the metal (g), z = valency change, I = current (A), t = time (s).

In a case where the anode is a homogeneous alloy that dissolves uniformly the ratio M/z (the equivalent weight) can be replaced by the mean equivalent weight (E_m) of the alloy. E_m can be obtained from the expression:

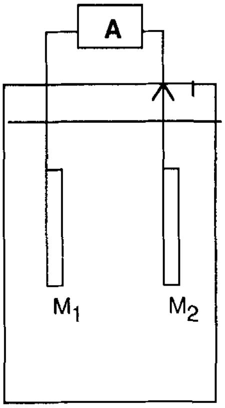
$$E = \frac{100}{\sum_{i=1}^{n} \frac{X_i}{E_i}} \tag{37-3}$$

where E_i = the equivalent weight of the ith component of the alloy and X_i= the weight percentage of the ith component of the alloy.

In heterogeneous alloys there may be various solution rates for the different phases. In those cases this expression can serve as an approximation.

The galvanic corrosion currents obtained experimentally in aqueous solutions with dissolved oxygen as the oxidant, will depend on various factors (Jones, 1992).

If the corrosion current density is not limited by the diffusion rate of oxygen the initial potential difference between the metals is of decisive importance for the resulting galvanic current. Measurement of galvanic currents of various metal couples can be used for many purposes in laboratory testing. An example is comparative studies of various dental alloys: *e.g.* what happens with common dental alloys when gold (Au) is replaced by titanium(Ti) in dentures? Au and Ti are assumed to act as cathode materials in these cases.



A = Ammeter
M_1 = Metal 1 (anode)
M_2 = Metal 2 (cathode)
I = Corrosion current

Fig. 37-2. Measurement of the corrosion current in a galvanic cell.

Another example is the measurement of the crevice current in laboratory testing of crevice corrosion of stainless steels. A specially prepared crevice is connected to an outer, free surface of the same metal via a zero-resistance ammeter. After the dissolved oxygen is consumed within the crevice, the resulting crevice current may be representative of both the initiation stage and the primary propagation stage of the corrosive attack. Later on, during the propagation stage, when the pH within the crevice has stabilized in the acidic range, there will be a contribution to the dissolution of the metal in the crevice by the reduction of the hydrogen ions formed locally.

The galvanic current can be measured by means of a special zero-resistance ammeter or a galvanometer that is built into a potentiostat (Jones, 1992). Sometimes it is sufficient to connect a resistance in series with the electrochemical cell and then measure the potential drop over this resistance. However, this additional resistance must be much smaller than the resistance of the electrolyte and the polarization resistances at both the electrodes. Guidance on galvanic corrosion testing is given in the standards ASTM G71:1981(R1986) and ASTM G82:1983.

37.2.3 Recording and evaluation of polarization curves

In a continuous corrosion process there is at least one anode and one cathode reaction involved. For corrosion in an active state the kinetics for both the processes can be described by means of the Butler-Volmer equation (if no mass transfer process is rate-determining):

$$i_a = i_{0,a}\left[\exp\left(\frac{\alpha_{a,a}F(E_{corr}-E_a)}{RT}\right)-\exp\left(-\frac{\alpha_{c,a}F(E_{corr}-E_a)}{RT}\right)\right] \qquad (37\text{-}4)$$

where i_a = the net anodic current density for the anode reaction (A m^{-2}), $i_{0,a}$ = the exchange current density for the anode reaction (A m^{-2}), $\alpha_{a,a}$ = transfer coefficient for the anodic direction of the anode reaction, $\alpha_{c,a}$ = transfer coefficient for the cathodic direction of the anode reaction, E_a = equilibrium potential for the anode reaction (V), E_{corr}= resulting corrosion potential of the metal (V), F = Faraday's constant, R = gas constant (8.314 Ws K^{-1}, mol), T = the absolute temperature (°C +273.15) in degrees Kelvin (K):

$$i_c = i_{0,c}\left[\exp\left(\frac{\alpha_{a,c}F(E_{corr}-E_c)}{RT}\right)-\exp\left(-\frac{\alpha_{c,c}F(E_{corr}-E_c)}{RT}\right)\right] \qquad (37\text{-}5)$$

where i_c = the net cathodic current density for the cathode reaction (A m^{-2}), $i_{0,c}$ = the exchange current density for the cathode reaction (A m-^{2}), $\alpha_{a,c}$ = transfer coefficient for the anodic direction of the cathode reaction, $\alpha_{c,c}$ = transfer coefficient for the cathodic direction of the cathode reaction, E_a = equilibrium potential for the cathode reaction (V) and other symbols are as for eq. 37-4 above.

At E_{corr} we can neglect the cathodic term for the anode reaction and the anodic term for the cathode reaction. i_{corr} is equal to i_a (= - i_c). An applied anodic current can be expressed as $(i_a + i_c) = i_{appl}$ or:

$$i_{appl} = i_{corr}\left[\exp\left(\frac{\alpha_{a,a}F\eta}{RT}\right)-\exp\left(-\frac{\alpha_{c,c}F\eta}{RT}\right)\right] \qquad (37\text{-}6)$$

where the polarization $\eta = E - E_{corr}$.

By linearization of this expression close to E_{corr} we obtain:

$$\eta = \frac{i_{appl}RT}{i_{corr}(\alpha_{a,a}+\alpha_{c,c})F} \qquad (37\text{-}7)$$

By inserting in eq. 37-7 the Tafel slopes (i.e. the linear slopes of polarisation curves in E-logi plots) for the anodic reaction (b_a) and the cathodic reaction (b_c), respectively, we get the following expression:

$$\eta = \frac{i_{appl}b_a|b_c|}{i_{corr}(b_a+|b_c|)\ln 10} \qquad (37\text{-}8)$$

where the Tafel slopes correspond to the definitions:

$$b_a = \frac{RT\ln 10}{F\alpha_{a,a}} \text{and} b_c = -\frac{RT\ln 10}{F\alpha_{c,c}}$$

More detailed analysis of electrode kinetics is given in textbooks on electrochemistry (Koryta and Dvorak, 1987). The slope of the polarization curve (E *vs* logi) given in eq. 37-8 corresponds to the polarization resistance (R_p) close to the potential E_{corr}, i.e.:

$$\frac{d\eta}{di_{appl}} = \frac{b_a|b_c|}{i_{corr}(b_a + |b_c|)\ln 10} = R_p \qquad (37\text{-}9)$$

If the applied current is cathodic one gets a minus sign in eq. 37-8 and the slope will also be negative while the polarization resistance still has a positive value.

This means that measurement of the polarization resistance gives values of i_{corr}, since i_{corr} is inversely proportional to R_p. Moreover, one must have knowledge of the values of the Tafel slopes or determine the factor including these slopes as system constant for the corroding metal by using another experimental method. The determination of the polarization resistance has been a popular method for corrosion monitoring in plants, and in many textbooks within this field one can find details of this method (Jones, 1992).

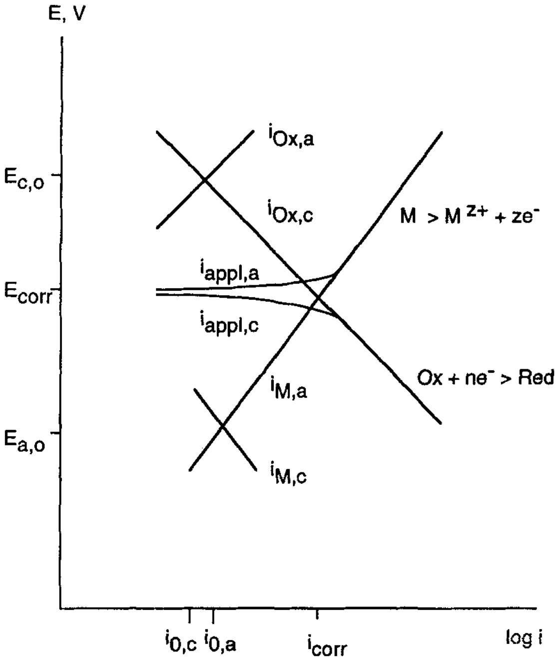


Fig. 37-3. Principle polarisation curves of an oxidant (Ox), cathodic reaction, and a corroding metal (M), anodic reaction. $E_{a,o}$=equilibrium potential of the anodic reaction, $E_{c,o}$=equilibrium potential of the cathodic reaction, $i_{0,a}$=exchange current density of the anodic reaction, $i_{0,c}$=exchange current density of the cathodic reaction, E_{corr} = corrosion potential, i_{corr} = corrosion current density.

In Fig. 37-3 schematic polarization curves for an oxidant and a corroding metal are shown, to explain some of the concepts used in eqs. 37-4 to 37-9. This kind of polarization curve is obtained by quasi-stationary techniques. Recordings are made with slow sweep rates by means of a potentiostat or a galvanostat. An electrochemical cell with three electrodes is used, the metal to be investigated is the working electrode (WE), the counter electrode (CE) is needed to form a closed electric circuit and the reference electrode (RE) gives the desired potential value and serves as the control electrode in connection with a potentiostat. Modern potentiostats include a power source, amplifiers, instruments for the measurement of current and potential and enable the recording of both potentiodynamic and galvanodynamic polarization curves. The connection to the reference electrode must be made via a capillary filled with electrolyte to give potential values close to the surface of the working electrode and thus minimise the error arising from IR-drops in the electrolyte between the WE and the capillary tip of the RE. Another means of correcting for this error is to use a built-in function for IR-compensation. In practice, the counter electrode can be made of platinum but sometimes it is preferable to use a CE of the same material as the WE, for instance, in the case when no foreign substances are allowed in the system.

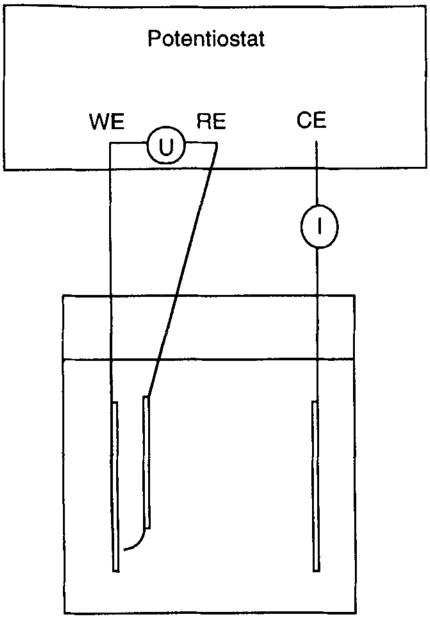


Fig. 37-4. Electrochemical cell with potentiostat for recording polarization curves.

A sketch showing the use of a potentiostat for recording polarization curves is shown in Fig. 37-4. This type of instrument provides the possibility of determining corrosion rates, as described previously, both in industrial monitoring and in laboratory corrosion testing.

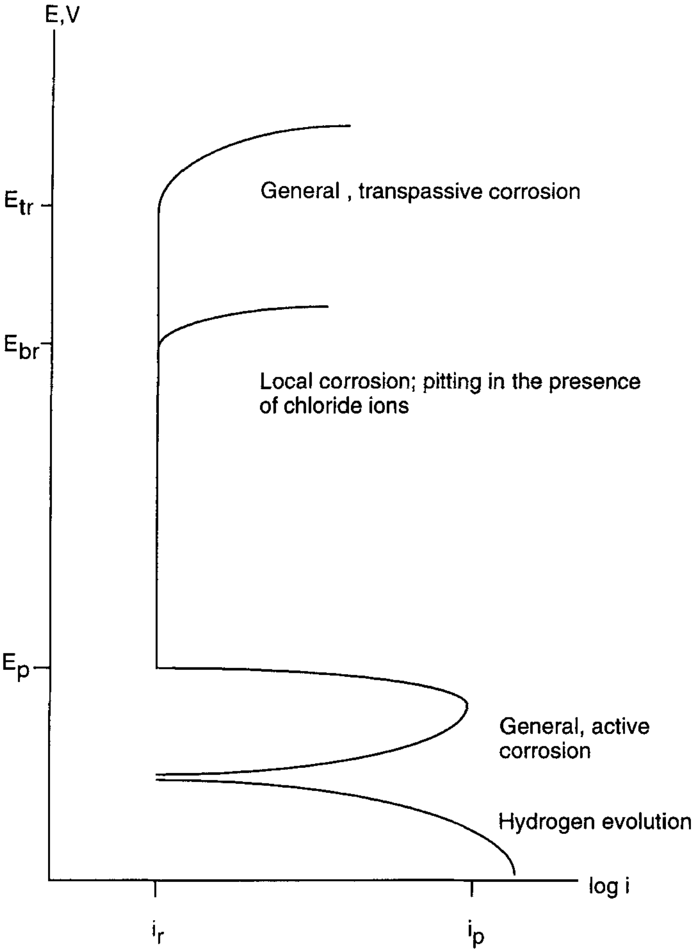


Fig. 37-5. Schematic polarization curves for a stainless steel recorded in a deoxygenated, acidic solution. E_p=passivation potential, i_p=passivation current density, E_{br}=break-through potential, i_r=residual current density in passive region, E_{tr}=transpassive potential.

Another application of a potentiostat is in the mapping of the corrosion behaviour of a material over a broad potential range. This is especially interesting for passivating metals, frequently those used in many industrial applications, for example stainless steels and titanium and its alloys. Fig. 37-5 shows a schematic anodic polarisation curve for an austenitic stainless steel (18% Cr, 8% Ni, balance Fe) recorded in a deoxygenated acidic solution. If this solution also contains activating anions, *e.g.* chlorides, one may observe a break-through potential within the ordinary passive range. A steady-state value of the residual current density within the passive region will not be reached until several days of continuous exposure in the solution, and its value depends somewhat on the potential level applied. Under conditions of undisturbed passivity the current density may be as low as ca. 1 nA cm^{-2}. In laboratory testing, potentiostats are used among other things for general characterization of metals and alloys, measurement of corrosion rates, and, more specifically, the determination of critical potentials, such as pitting potentials, crevice corrosion potentials and reactivation potentials.

In laboratory experiments the working electrode is most often adapted in certain types of electrochemical cell to establish reproducible convection conditions and to control the potential and current distribution in the cell. For these purposes one uses rotating electrodes such as discs, cylinders or ring-discs. In the last case it may also be of interest to use a bipotentiostat. With this device it is possible to have different electrode potentials on the disc and the ring. This technique is important in the study of the detailed mechanisms of corrosion reactions.

Several standard electrochemical methods based on potentiostatic, potentiodynamic, galvanostatic or galvanodynamic techniques are used in laboratory testing of the sensitivity of metals and alloys to various forms of localized corrosion such as pitting, crevice corrosion and intergranular corrosion. Detailed information on these methods is given in appropriate handbooks in this field (Shreir *et al.*, 1994; ASM Metals Handbook, 1987).

37.2.4 Electrochemical transient methods

In using steady state methods, current-potential relations are evaluated in either a constant potential (potentiostatic control) or a constant current mode (galvanostatic control). Any selected, experimental value is kept constant for a sufficiently long time so that the other parameter may also approach an essentially constant value. To explain the complete mechanism of a corrosion reaction or to study fast reactions in general, the behaviour of the system variables with time must be determined; electrochemical transient methods are suitable for these purposes.

Transient methods involve the perturbation of a system from steady state (or equilibrium) conditions and the monitoring of the response of the system as a function of time using any accessible property of the interface, such as current, potential, charge or impedance. In using transient methods one has to consider the charging of the electric double layer at the metal-solution interface. Reviews of the transient methods available and exhaustive analyses of the theoretical and experimental aspects of these techniques can be found in the literature (Sarangapani and Yeager, 1984; Epelboin *et al.*, 1984; Macdonald, 1981). A few comments will be made here on the methods most commonly used in studies of corrosion processes.

Cyclic voltammetry has been used in the study of passivation processes on metals in aqueous solutions. One needs a fast potentiostat, a voltage generator giving the desired pulse form and a transient recorder. This method gives information on adsorption kinetics, the electroactive intermediates, and the presence of multiple steps in a corrosion reaction may be discerned. The perturbation shows the potential $E = f(t)$, while the response will be the resulting current $I=f(t \text{ or } E)$. In many cases the adsorption pseudocapacitance for processes that involve electrochemically adsorbed intermediates is much greater than the capacitance of the electric double layer. Therefore, the double layer charging current can be neglected in those cases without serious error. Otherwise, without adsorbed intermediates, the double layer capacitance (C_{dl}) must be known.

C_{dl} can be determined by means of a galvanostatic pulse method. For this measurement one needs a fast galvanostat and a transient recorder. The perturbation shows the current I = f(t), while the response will be the potential E = f(t). C_{dl} is then obtained from the experiment according to the expression:

$$C_{dl} = \frac{i}{\left(\frac{d\eta}{dt}\right)_{t\to 0}} \qquad (37\text{-}10)$$

The choice among the transient methods depends on whether one is trying to establish a complete reaction mechanism or whether one is determining kinetic parameters of a known mechanism. When complex heterogeneous reactions interact with the mass-transfer of the involved species, the interpretation of the results obtained can be very difficult.

37.2.5 AC impedance measurements

In the simplest model of an equivalent electrical circuit corresponding to a metal-solution interface we have an impedance ($Z_{M/S}$) consisting of a double layer capacitance (C) in parallel with a Faradaic resistance (R). The Faradaic resistance for an electrochemical, multistep reaction that occurs at an interface, is an average value obtained by a summation of the individual reaction resistivities divided by their number. In the measuring situation there will also be an Ohmic resistance (R_S) in series with the electrode impedance. In using this technique, a small-amplitude, sinusoidal potential is applied to the working electrode. This perturbation is repeated at a great number of discrete frequencies. At each frequency there is a current response that is phase-displaced in relation to the applied voltage signal. The electrochemical impedance will then be a frequency-dependent parameter (transfer function) showing the relationship between the applied AC voltage signal and the corresponding current response. In practice, the experimentally obtained frequency-dependent impedances may correspond to much more complex equivalent electrical circuits than that mentioned above. However, the impedance for the assumed case is Z and can be expressed as $Z = R_S + Z_{M/S}$ where:

$$\frac{1}{Z_{M/S}} = \frac{1}{R} + j\omega C \qquad (37\text{-}11)$$

$\omega = 2\pi f$, f = the frequency, $j = \sqrt{-1}$.

The total impedance of the system will then be:

$$Z = R_S + \frac{R}{\left(1+\omega^2R^2C^2\right)} - \frac{j\omega CR^2}{\left(1+\omega^2R^2C^2\right)} \qquad (37\text{-}12)$$

As is shown in eq. 37-12 both the resulting resistance and the capacitance contributions to the impedance will depend on the frequency. If this frequency analysis is performed with a corroding metal at the potential E_{corr}, the resistance R corresponds to the polarization resistance R_p. This equivalent electrical circuit with a corresponding Nyquist plot is shown in Fig. 37-6. As one can see by the Nyquist plot the impedance $Z \approx R_s$ at very high frequencies and $Z \approx R_s + R_p$ at very low frequencies. This type of analysis provides the possibility to separate the Ohmic resistance in the solution from the total resistance. To obtain a value of i_{corr} one still needs values of the Tafel slopes for both the anodic and the cathodic reactions, see eq. 37-9.

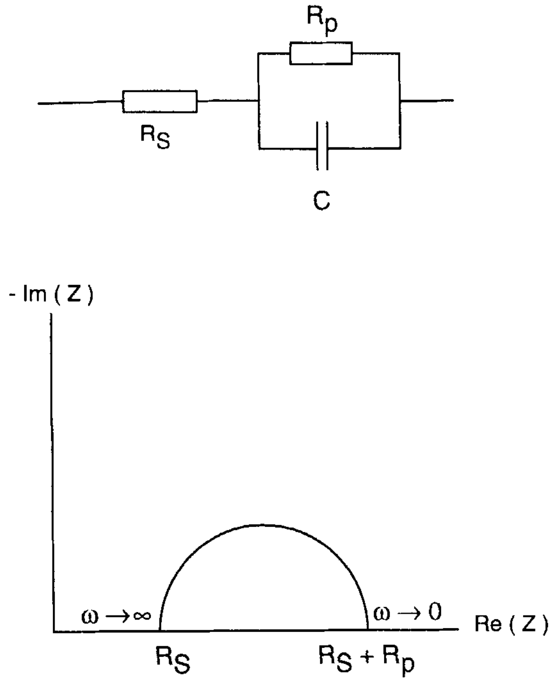


Fig. 37-6. Equivalent electrical circuit for a corroding metal/solution interface with the corresponding schematic impedance diagram according to a Nyquist plot.

There is a growing interest in the use of AC impedance techniques for corrosion monitoring. Special advantages can be found in systems with high resistivities.

In the simplest applications one uses two frequencies, *e.g.* 10^4 Hz and 10^{-1} Hz, to determine the values of R_S and $(R_S + R_p)$. Unfortunately, in practice many factors can disturb this simple model. The simultaneous presence of other electrochemical systems, such as non-steady state, local corrosion processes, mass transfer limitations and corrosion products partially covering the metal surface, can make it difficult to evaluate the experimental data obtained in a simple way. There are more complex models to be used in these situations but reliable interpretations require specialists in electrochemistry. Within the field of AC impedance techniques and Electrochemical Impedance Spectroscopy (EIS) appropriate literature is available (Macdonald, 1987; Sluyters-Rehbach and Sluyters, 1984).

Recent developments have made it possible to measure ionic currents associated with corrosion microcells on a metal surface. By scanning with a vibrating microelectrode (SVET) over the surface one can measure the current distribution in the solution. The vibrating probe is a thin platinum wire insulated except at the tip, which should be as small as 2-4 µm. For areas on the metal surface where there is a net uniform anodic or cathodic current the DC potential in solution will be proportional to the distance from the surface. By oscillating the Pt probe in this potential gradient an induced AC voltage will result. This AC signal can be measured accurately with a lock-in amplifier with reference to the oscillation frequency of the probe. DC current distribution in the solution above the metal surface has been mapped with the vibrating probe by scanning it at a distance of less than 50 µm above the metal surface. (Isaacs, 1987). By this technique one can measure currents in the solution with spatial and current density resolutions of the order of 15-20 µm and 5 nA cm^{-2} (Crowe and Kasper, 1986).

This technique can be used, for instance, for studies of initiation and propagation of local corrosive attack on passivated metal surfaces and of the porosity of organic and inorganic coatings on metals.

Further, recent developments have established techniques combining scanning technology with impedance methods to generate local AC impedance data for discrete areas on a metal surface; this is called local electrochemical impedance spectroscopy (LEIS) (Lillard *et al.*, 1992).

37.2.6 Electrochemical noise measurements

In measurements of electrochemical noise one studies the low-frequency and low-amplitude fluctuations of the rest potential or the resulting current that may occur between two electrodes of the same material in a corroding system. It is necessary to check that no significant contributions to the fluctuations arise from the electronic device used for the measurements. The real corrosion events may be a sudden rupture of the passive layer on a metal surface, release of a hydrogen bubble from a metal surface, etc. It is also possible to hold a constant current and record the potential fluctuations or hold a constant potential to register the variations in the current.

The simplest way to use data obtained from this kind of measurements, is to evaluate the standard deviation of the variations about a mean value. A more accurate analysis of the noise may be obtained by converting the measured time distribution into a power spectrum by means of Fourier transformation.

Some researchers have reported the possibility to recognizing different forms of local corrosive attack by using noise-power spectra (Uruchurtu and Dawson, 1987;

Hladky and Dawson, 1981). Others have correlated electrochemical noise data with corrosion rates (Searson and Dawson, 1988). In industrial corrosion monitoring this method has been used, for example, in cooling water systems and power-generation plants (Shreir *et al.*, 1994). However, these methods are under gradual development and the applications so far have been based on computerized fitting between empirical data and some corrosion parameters and not on a deeper understanding of the underlying surface phenomena.

37.2.7 Electrochemical methods for testing coatings on metals

Standard electrochemical procedures have been specially defined for the purpose of testing the corrosion-protective properties of various coatings on metals.

There is a standardized electrochemical test for the determination of the impedance of anodized coatings on aluminium and its alloys (ISO-standard 2931; ASTM B 457).

This test is non-destructive and intended to give a response to the sealing quality of the anodised layer by means of an AC signal between the anodised metal and an auxiliary electrode of platinum or stainless steel. The electrolyte is prescribed to be 3.5% NaCl. The thickness of the coating must also be determined. Bare Al has impedance values of about 1 kΩ while a well-sealed anodized coating will give values of about 100 kΩ. In some other tests the anodized coating is polarized with a cathodic current. The alkaline solution formed at the weak points in the coating will give a response on the quality of the sealing (ASTM B 538).

The EC (Electrolytic Corrosion)-test is used to control the pitting behaviour of decorative Ni/Cr plating on non-noble metals such as steel and zinc. In this test the metal is potentiostatically cycled between an anodic polarization level and an unpolarized potential. An indicator solution then reveals the presence of penetrating pits in the plated coating. The details of this test procedure are given in an ASTM standard (ASTM B 627).

The adhesion between a paint and a metal surface can be tested by the PASS-test. A scratch is made in the paint coating and the exposed metal surface is cathodically polarized. The auxiliary electrode is a platinum wire. The alkaline solution formed on the bare metal surface enhances the delamination process in this surface area. The degree of the destructive effect on the paint coating is determined by means of an adhesive tape; this test is called the Scotch tape test.

To measure corrosion potentials of metals covered by a thin layer of electrolyte, corresponding to the situation in atmospheric corrosion, M. Stratmann and co-workers have successfully adapted an established method for measurement of the surface potential. By using a Kelvin probe they avoided touching the corroding metal surface. An audio-frequency current drives a vibrator, and the vibrations are transmitted mechanically to a small disc mounted parallel with the metal surface and about 10 to 100 μm above it. The vibration of the probe causes a corresponding variation in the capacitance across the air gap, so that an alternating current is set up in the circuit. Its magnitude depends on the potential difference between the metal surface and the probe. This potential value has been correlated with the real corrosion potential of the exposed metal, both by means of other experimental methods and by theoretical calculations (Stratmann *et al.*, 1991). This experimental method may also be used for recording polarisation curves of metal surfaces covered with thin electrolyte layers and detection of defects in organic or inorganic coatings. AC impedance techniques have been developed to evaluate the performance of organic coatings (paint films) on metals. The method is non-destructive and very sensitive to changes in the resistive-capacitive nature of coatings. An advantage of these methods, is that it is possible to distinguish the high DC resistance of the organic coating from the total resistance, which is not possible with direct current methods. If the capacitance (C) of the coating is determined and the relative permittivity is known, then the thickness of the coating can be estimated for a given exposed area by use of the expression:

$$C = \frac{\varepsilon \varepsilon_0 A}{d} \tag{37-13}$$

where ε = the relative permittivity of the coating, ε_o = the permittivity of vacuum, A = the surface area, d = thickness of the coating. The quantity of water adsorbed in the polymer coating changes its relative permittivity and hence the capacity and can be measured by AC impedance measurements. The coating resistance can also be monitored as a function of the exposure time. Large decreases indicate permeation of ionic species through the coating or the presence of defects in the coating. It may also reveal delamination of the coating, the corroded metal area below the coating and its corrosion rate (Walter, 1991).

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