

Relaxation Voltammetry A technology for the evaluation of barrier coatings

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Introduction

Products made of steel have excellent mechanical properties. In addition, steel is an inexpensive material and therefore, iron in the form of steel is one of the most important technical raw materials of the daily life. Unfortunately, the chemical characteristics of steel are not so favourable. As a base metal, iron is sensitive to oxygen and humidity. As a consequence, unprotected steel corrodes very easily and the corrosion process not only affects the optical appearance but also influences the mechanical properties unfavourably.

One way to protect iron against corrosion is the application of organic coatings. The development of new coatings requires methods to optimise the formulation which have to be tested during their development by the coatings manufacturers. To obtain a ranking of the corrosion protective performance of new coating formulations, many different weathering tests are necessary. After the weathering, the degradation of the coating has to be evaluated using mainly mechanical tests or visual

examination. These tests are time consuming and the degree of degradation has to be estimated. The need of an objective and relatively fast evaluation method is obvious. Here, electrochemical impedance spectroscopy (EIS) is widely used for the characterization as well as for the detection of defects of the coating. Moreover, this method is also applied for the determination of the water uptake and the degree of blistering and delamination. EIS provides information about the mechanistic background of corrosion processes as well as detailed information about coating properties like capacity C_C or coating/pore resistance R_C .

For the interpretation of EIS-data, physical models like equivalent circuits are required. The basic models are given in figure 1. Model A describes a realistic perfect 'barrier coating' with the coating capacity C_C and the coating/pore resistance R_C . Model B represents the case of pores and defects in the coating with a second 'time-constant', which is correlated to the charge transfer, i. e. the charge transfer resistance R_{CT} and the double layer capacity C_{DL} . This model is widely used in many publications of EIS-results.

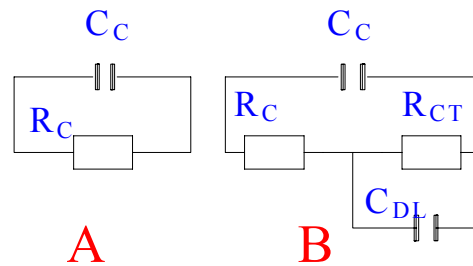


Fig. 1: Most popular basic equivalent circuits for the interpretation of EIS data

Unfortunately, the application of EIS in corrosion research shows some handicaps. For instance, commercially available 'barrier coatings' often show a low-frequency resistance around $10^{10} \Omega \cdot \text{cm}^{-2}$ or more. This requires a 'low frequency limit' of the measured spectrum in the mHz-region for the determination of R_C . Such measurements are rather time-consuming. They can easily exceed one hour.

Next, the measured system has to be in a steady state during the whole measuring time. Concerning water-uptake measurements for instance, it is safe to assume that the constancy of the coating parameters (i. e. C_C and R_C) is not given in the early state of immersion. At least, considering the ratio of the number of measured specimens and the time required for a single measurement, a single impedance measurement seems to be rather expensive.

In contrast to measurements of barrier coatings in the frequency domain, traditional methods in the time domain suffer from the special properties of this kind of systems. For instance, static DC-measurements enable the determination of R_C , but will not deliver any information of dynamic parameters, neither about the dielectric properties nor about 'dynamic' processes (like diffusion contributions) within the coating. Dynamic measurements in the time domain which are reported in the literature [1,2], i. e. current interrupt techniques, suffer from the high resistances of the coating materials too. On one hand, so-called electrometers have an excellent accuracy in measuring current. Unfortunately these electronic devices possess a poor resolution in time¹. Due to this fact, these instruments are not able to monitor (or to separate) fast processes. On the other side, the current interrupt technique reported in the literature [2], delivers a resolution in measuring current of only 120 pA/digit. As will be shown below, this resolution is by far too small.

A relatively new technology for the investigation of high-ohmic systems is the *Relaxation Voltammetry* (RV) [3-6]. This method is a current interrupt technique too, but was designed especially to overcome the problems noted above. The principle of this

¹ Usually, small currents are measured by integration a voltage drop at a shunt-resistor. But, the smaller the current the longer the time of integration for a given accuracy. As a consequence, the sampling rate of an electrometer is less than one point per second at the pA-level [1].

technique is depicted schematically in figure 2 and explained in the following.

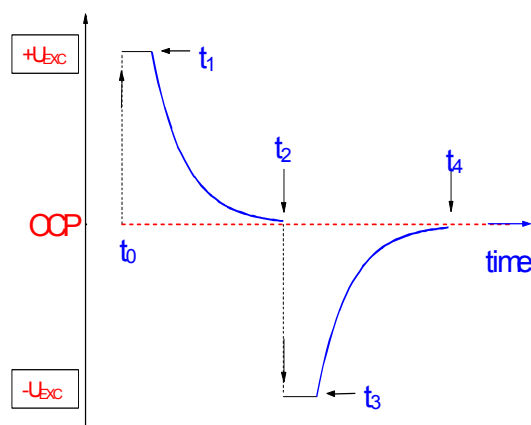


Fig. 2: The principle of RV

The potential $+U_{EXC}$ is superimposed to the open circuit potential (OCP) and causes a transient current (I_{EXC}) which tends to be constant after a certain time ($t_1 - t_0 = t_{EXC}$). After the current reaches this stationary state, it is switched off and the following decay of the potential $U(t)$ is recorded as a function of time (t_1 to t_2). The initial stage of this relaxation process is monitored using a sampling rate of 600 points per second (about 40 to 100 values) and then the sampling rate is lowered. After the potential reaches approximately the value of the OCP (at t_2 in figure 2), the procedure is repeated using the same potential but with the opposite sign ($-U_{EXC}$).

Concerning the following considerations, the experimental procedure of RV differs essentially from 'traditional interrupt techniques':

1. In general, each electrochemical experiment is characterized by two parameters, potential and current. In potentiostatic mode of operation for instance, a potential is applied whereas the corresponding quantity (the current) is measured as a function of the actual potential. In contrast, in RV, a constant potential is applied and after interrupting the current, again the potential is recorded as a function of the relaxation time. This kind of operation offers mainly two advantages. First of all, a potential in the range of 10^{-3} to 10^{-6} V can be measured more precisely than a current in the range of 10^{-12} to 10^{-15} A in principle. Secondly, the current (\pm) I_{EXC} is measured at its highest level, integrating over a small interval (about five seconds) before the interrupt which improves the accuracy additionally.

2. Anodic and cathodic excitation are performed and both transients are measured. For the evaluation of the transient response $U(t)$, the values of both half-cycles are averaged, resulting in a 'symmetrical square-wave perturbation' around the OCP - similar to EIS.

3. This 'symmetrical' operation is important, considering the experimental fact obtained from measurements of barrier coatings that the transients will not return exactly to the value of the OCP before

the excitation. In a continuous mode of operation, t_{EXC} and/or U_{EXC} can be varied in subsequent cycles. Performing only anodic or cathodic excitation - like in 'traditional interrupt techniques' - would result in a shift² of the OCP. This would lead to erroneous results due to a superimposed (rest-) relaxation caused by the offset between the 'end-potential' (at t_2/t_4 in figure 2) and the OCP. To overcome this problem, in RV the OCP is 'updated' after each half-cycle from the values of the 'end-potential' of the actual and the latter half-cycle (for instance: $OCP = \frac{1}{2} (U_{t_4} + U_{t_2})$).

The applicability and performance of RV can be best represented by an example and in comparison to a measurement using EIS. In figure 3, the result of an RV measurement of a barrier coating is plotted as a function of the square root of 'the relaxation time (upper diagram) whereas an impedance spectrum of the same specimen is shown at the bottom of figure 3.

The DC accuracy of RV is best reflected regarding the small value of I_{EXC} ($1.33 \pm 0.01 \cdot 10^{-12}$ A), resulting from the total DC-resistance of the coating ($1.5 \cdot 10^{10} \Omega$ or $6.75 \cdot 10^{10} \Omega \cdot \text{cm}^{-2}$)³. The small diagram on the right side of the upper part of figure 3 shows the initial voltage decay of the relaxation as a function of time. As indicated in the figure, the early state of the relaxation was measured with the higher sampling rate. The evaluation of this part of a RV-transient delivers information about the dielectric properties of the system under investigation and therefore gives an estimate of the dynamical performance of RV. This part will be discussed below in detail.

Comparing the results of EIS and RV in figure 3, the complementary nature of both techniques becomes aware. Considering the time (frequency) scale of both methods, one has to conclude that EIS handles the high frequency part (say above 1 Hz) accurately and without consuming too much time for the measurement. But at lower frequencies, the measuring time increases drastically which restricts the number of measured points (i. e. only 5 points below 1 Hz in the above example) in practical measurements in a coating manufacturer's laboratory which may result either in a loss of accuracy or of information.

On the other side, RV handles the middle and large relaxation range (above 1 second) which corresponds to the 'middle and low-frequency part' of an impedance spectrum very well. This fact is simply expressed by the number of measured points ($n > 2500$ above 1 second). A sufficient 'overlap' between the time scale of both methods arises from the initial sampling rate of RV which is shown in the following.

² A similar effect which is commonly observed in water-uptake measurements results from the drift of the OCP caused by the measured system itself.

³ Measuring area : 4.5 cm^2

The ‘dynamic’ performance of RV

As noted above, the total DC-resistance R_T can be calculated immediately from the applied potential ($\pm U_{EXC}$) and the current ($\pm I_{EXC}$) before the interruption. In addition, RV delivers the coating capacity C_C without the need of a detailed interpretation of the

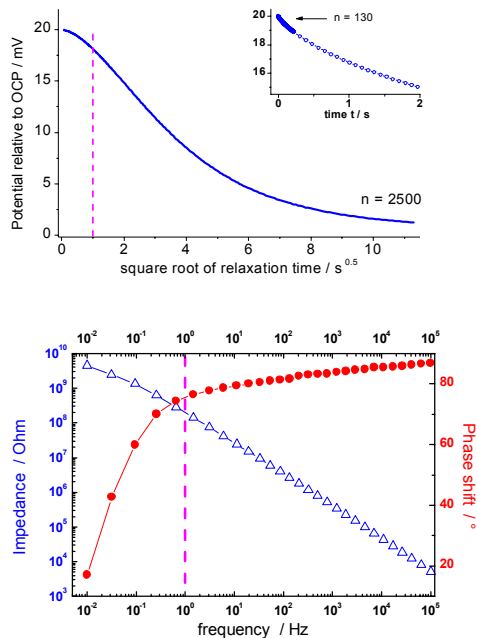


Fig. 3 : RV and EIS as complementary techniques (see text)

overall relaxation process. Adopting the models for the interpretation of EIS-data (figure 1), this parameter is accessible from the initial slope (ISL) of the potential decay and I_{EXC} (scheme 1). From a theoretical point of view, the determination of C_C founded on the ISL is exact for model A and an excellent approximation in the case of model B⁴. If necessary, the applicability of the ISL approach can be extended mathematically, involving the quadratic term of the underlying power series (ISL_{EXC}).

$$U(t) = I_{EXC} R_T \cdot e^{-\frac{t}{R_T C_C}} = I_{EXC} R_T - \frac{I_{EXC}}{C_C} t + \frac{I_{EXC}}{2 \cdot R_T \cdot C_C^2} t^2 \pm \dots$$

$$ISL = \lim_{t \rightarrow 0} \frac{dU}{dt} = -\frac{I_{EXC}}{C_C}$$

$$ISL_{EXC} = \lim_{t \rightarrow 0} \frac{dU}{dt} = -\frac{I_{EXC}}{C_C} + \frac{I_{EXC}}{2 \cdot C_C^2 \cdot R_T}$$

Scheme 1 : The initial slope approximation (ISL)

From a practical point of view, the scope and accuracy of the ISL approximation was first verified by measurements at the equivalent circuits. From the results of these measurements [3-6] the accuracy

⁴ The physical background of this approximation is that the current through the capacitor C_{DL} can be neglected at the initial stage of the relaxation and therefore, model B in figure 1 reduces to model A.

of the determination of C_C is about 10% or less for typical values which are observed when measuring coating materials, i. e. capacities in the range of ≥ 100 pF and total DC-resistances of ≥ 50 M Ω respectively. Two examples for the determination of C_C using the ISL approximation are depicted in figure 4.

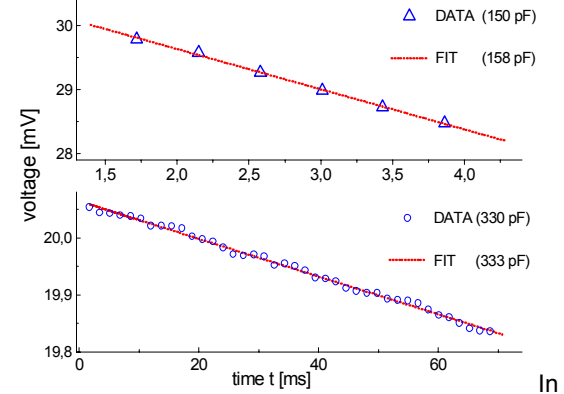


Fig. 4 : ISL of two dummy cells (model B)

In the upper part of the diagram an equivalent circuit (model B) with a total resistance R_T of 305 M Ω and a ‘coating capacity’ of 150 pF is shown. From the voltage decay (≈ 2 mV) in the first 4 milliseconds, an initial slope of -630 mV/s can be evaluated. Considering the current I_{EXC} (98.4 pA) yields a coating capacity of 158 pF. In the second example an equivalent circuit (model B) with a total resistance R_T of 18.7 G Ω and a coating capacity of 330 pF was used. The potential decay (≈ 200 μ V) in the first 60 milliseconds gives an initial slope of -3.3 mV/s. With the current I_{EXC} (1.1 pA) a coating capacity of 333 pF was calculated. The latter example demonstrates additionally that noise effects play no role at all at this early state of the relaxation. In both cases an excellent agreement between theoretical and experimental data results.

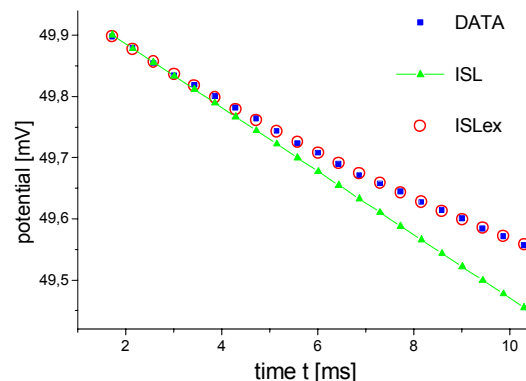


Fig. 5 : Typical ISL of a coating

Figure 5 shows a typical example for the evaluation of C_C of coatings using the ISL method. The voltage drop (squares) in the first 10 milliseconds is about 500 μ V. Comparing the starting potential decay with the values obtained from dummy measure-

ments it becomes evident that the linear range turns out to be much shorter than predicted from the models given in figure 1. The deviation from linearity (triangles = ISL) occurs already below 4 milliseconds. To evaluate the coating capacity the extended ISL_{EX} (circles) was used, therefore. The analysis of the linear part gives an initial potential decay of -53 mV/s, yielding a coating capacity of 250 pF. Further applications of RV in corrosion research of coated metals are reported in more detail in the literature [4, 7-9].

In a comprehensive analysis of a huge number of different coating materials over a wide range of relaxation times it was found that the dielectric relaxation in barrier coatings can be explained by a hopping (i. e. a random walk) process [10]. It is noteworthy that this so-called 'two-step continuous time random walk' (CTRW-2) exhibits a square root of time dependency of the corresponding time-law which seemed to contradict the results of EIS (see also [11,12]). However, in two recent publications [13,14] it was proven that there is no contradiction at all between the interpretation of the results of both techniques in principle, concerning the evaluated dielectric parameters.

Summary

It was shown that RV is a suitable tool for the investigation of high ohmic systems. Although other applications can be seen, RV was especially designed to meet the demands for the investigation of coated metals.

In contrast to 'traditional interrupt techniques', RV combines electrometer-type accuracy with an adequate resolution in time so that DC- as well as dielectric parameters of these systems are accessible. Both quantities are of great importance for the coatings manufacturer to improve their products. In comparison to EIS it is to state that both techniques should supplement each other ideally. Undoubtedly, the big advantage of EIS for the evaluation of high ohmic systems is the rapid determination of the dielectric properties whereas the strong points of RV are in the 'middle and low frequency range'. At least, the RV equipment is less expensive so that several measurements can be performed in parallel which reduces the time consumption in the manufacturer's laboratory additionally.

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