Simulation of Organic Coating Penetration on Metal Using Impedance Spectroscopy

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Abstract

This paper proposes an alternative model for simulating electrochemical impedance spectra of protective organic coatings on the metal substrate. It describes broadening of the semicircle in the complex plane (Nyquist plot) and Bode plots behavior using commercial software Software ZSimpWin 3.22 in the absence and with of corrosion reactions. Before this process, the appropriate modified electrical equivalent circuit had selected where constant phase element had used instead of a capacitor for reach to reality. The result helps to understand the system under study i.e. the change of impedance behavior with electrochemical processes.

Introduction

Organic coatings remain the most widely used way of protecting metal from corrosion. Organic coatings protect metals against corrosion)by various mechanisms, which can be summarized as follows: (a) suppression of the anodic and/or cathodic reaction, (b) the introduction of a high electrical resistance into the circuit of the corrosion cell, and (c) a barrier to aggressive species (oxygen, water, and ions)[1].

Coating systems commonly comprise a primer layer that contains corrosion inhibitor and top coat that provide aesthetic value. The top coat is often also intended to be a barrier to environmental moisture and any entrained, corrosive ions reaching the substrate. The protective ability of a coating system is very well monitored by electrochemical impedance spectroscopy, EIS, since it can measure change as the protective coating deteriorate, as they absorb water as they permit the substrate to corrode.[2] An effective means of reducing the corrosion rate of metals, is to protect the surface with coatings. Generally, due to aging of the protective systems, coatings are permeable to water and some ions, so the corrosion reactions proceed at the metal-coating interface. The rate of corrosion depends upon the transport of corrosive species through the film [3].

In order to characterize the protective characteristics of coated metals by electrochemical impedance spectroscopy (EIS), different electric equivalent circuits have been used for mechanistic analysis , where capacitive and admittance contributions have been incorporated as constant phase elements (CPE). Furthermore, separate models as a function of time are also proposed . Del Amo et al. interpret the coating response with three different circuits in accordance with defective coatings, high barrier effect coatings and non-defective coatings. EIS has proved to be efficient in measuring dielectric properties accurately [4].
The inputs for describing the coating are its resistive and capacitive properties. Based on simple continuum theory, the capacitance and resistance of a smooth coating are given as functions of the size of the material and intrinsic properties. The capacitance, *C*, for a parallel plate capacitor is given by:

$$C = \frac{\varepsilon_o \, \varepsilon_R \, A}{d} \qquad (1)$$

where ε_o is the permittivity of free space (8.8542×10^{-12} F/m), ε_R the coating dielectric constant, *A* the area of the parallel plate capacitor, and *d* is the coating thickness. The coating resistance per unit area is given by

$$R = \frac{\rho d}{A} \qquad (2)$$

where *R* is the resistance, ρ the electrical resistivity (a material constant), *d* the coating thickness, and *A* is the area. We will describe the model data based solely on models for *R* and *C* in which changes are only in the film thickness, film resistivity or film dielectric constant. These variables will not be treated as fitting parameters for general *R* and *C* circuit elements, but as coating variables, based on the knowledge developed by coating and polymer scientists for changes in coatings due to well-described processes such as film thickness loss due to UV degradation, film swelling, or due to aqueous diffusion. One can describe multi-layer coatings as Randles circuits in series to account for gradients in water and ion concentrations. The present model homogenizes the water and coating into a single material as the diffusion front advances[5].

Theory

Impedance spectroscopy data is commonly analyzed by fitting it to an equivalent electrical circuit model [6].The Randle cell is a simple yet useful combination of a capacitor and two resistors {Fig.(1)} this electrical circuit can be used to represent a coating or corroding metal, although the values and meaning of the components are different[7]. Randle cell can't recover all the physical and chemical processes occur during the corrosion process (electrochemical process). Therefore we need to use more complicated equivalent circuit gives appropriate fitting with experimental. A change of elements values and/or the shape of equivalent circuit during test process will be indicated to what happened in sample under study and evaluation the organic coating. In (Fig. 2) the equivalent circuit is overlaid on schematic of a coated metal substrate[8].

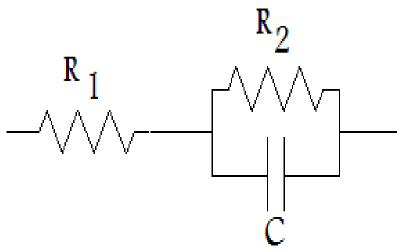

Fig.(1): Randle circuit.

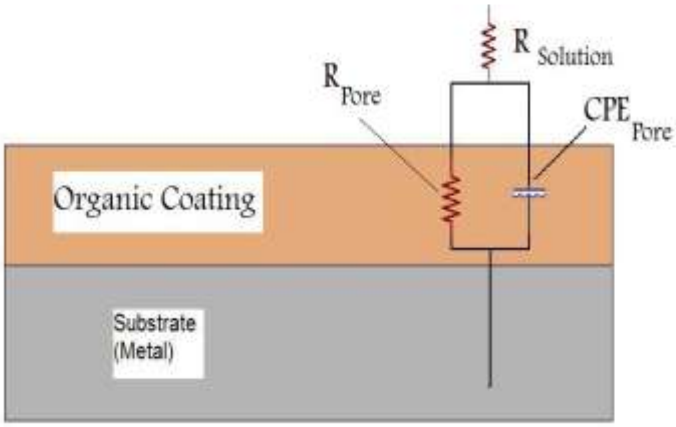

Fig.(2):Electric equivalent circuit of intact organic coating.

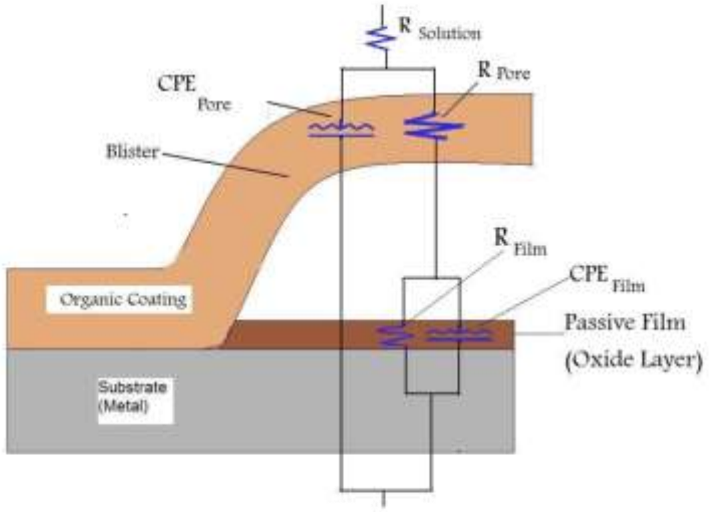

Fig.(3): Modified equivalent circuit for a painted metal substrate that has suffered major damage.

The impedance behavior of a purely capacitive coating was discussed above. Most coatings degrade with time, resulting in more complex behavior. After a certain amount of time, water penetrates into the coating and forms a new liquid/metal interface under the coating. Corrosion phenomena can occur at this new interface. The capacitance of the intact coating is represented by C_c. Its value is much smaller than a typical double layer capacitance. Its units are pF or nF, not mF. R_{po} (pore resistance) is the resistance of ion conducting paths that develop in the coating. These paths may not be physical pores filled with electrolyte. On the metal side of the pore, we assume that an area of the coating has delaminated and a pocket filled with an electrolyte solution has formed. This electrolyte solution can be very different from the bulk solution outside of the coating. The interface between this pocket of solution and the bare metal is modeled as a double layer capacity in parallel with a kinetically controlled charge transfer reaction. When EIS is used to test a coating, the data is fitted to this type of model. The fit estimates values for the model's parameters, such as the pore resistance or the double layer capacitance. These parameters are then used to evaluate the degree to which the coating has failed [6].

Authors often chose to analyze their measured EIS data in terms of a classical equivalent electrical circuit (Fig. 3). A capacitor C_c corresponds to the coating capacity, since most of the coating is non-conductive to ions. A resistor R_{po} represents the conductive paths through the coating pores and R_s represents the solution's resistance. This RC element corresponds to classical ion conduction in solution due to the electrical potential difference across the coating. A simple corrosion reaction is represented by the capacitor that stands for activation polarization and by the resistor presenting the concentration polarization of the corrosion cell in series, with an ionic conduction element. A non-defective protective coating does not have conductive paths (pores). Conduction through pores develops due to degradation of the coating. At the initial stage the polymer film can be described as a plain plate capacitor. After some time, pores fill with electrolyte solution and the protective coating can be described, in addition to coating capacitance, with the pore resistance [4]. In our case, the use of CPE in place of capacitors does not have proper background in electrochemical reality.

Constant Phase Element (CPE)

The impedance results for a solid electrode/electrolyte interface often reveal a frequency dispersion that cannot be described by simple elements such as resistances, capacitances, inductances or convective diffusion (e.g., Warburg) impedance. The frequency dispersion is generally attributed to a “capacitance dispersion” expressed in terms of a constant-phase element (CPE). Since the first paper devoted to the CPE, the time constant dispersion was attributed to a dispersion of the capacity or to a change of the capacity with frequency. Cole and Cole studied dispersion and absorption in dielectrics, and, obviously, the capacitance was the parameter under investigation. The major part of subsequent theoretical work devoted to this phenomenon considers the CPE to be associated with a distribution of the capacitance, and, in consequence, the model electrode for the corresponding experimental analysis was an ideally polarizable electrode. In the literature different equations were proposed. In the following equations, j is the imaginary number ($\sqrt{-1}$) and ω is the angular frequency ($\omega = 2\pi f$, f being the frequency). Lasia gives the impedance of the CPE as:

$$Z_{CPE} = \frac{1}{T(j\omega)^{\phi}} \qquad (2)$$

where T is a constant in F cm^{-2} $s^{(\phi-1)}$ and is related to the angle of rotation of a purely capacitive line on the complex plane plots. Brug et al. proposed:

$$Z_{CPE} = \frac{Q}{(j\omega)^{1-\alpha}} \qquad (3)$$

where Q is a constant (with dimensions F cm^2 $s^{-(1-\alpha))}$ and $1 - \alpha$ has the same meaning as in Eq. (2)[9].

A model is proposed and presented in Fig.(3), which helps to understand the system under study. First, the uncompensated electrolyte resistance between the working and reference electrodes is given by Rs. Next, the current passes through the paint film, which is described by the resistance of the blister (pore) as R_{po} in parallel with the capacitance of the coating, C_c. Next, the current must pass through the protective layer already formed; the film resistance is described by R_{film} in parallel with its capacitance C_{film}. Finally, the current passes through the metal-electrolyte interface where the corrosion reaction takes place. The charge transfer resistance, RT, in series with a finite diffusional contribution, represent the overall impedance of the corroding metal given by Z, is in parallel with the double layer capacitance of the metal. The above electric equivalent circuit {Fig.(3)} was employed in the fitting using a commercial software [4].

Software ZSimpWin

ZSimpWin is an Electrochemical Impedance Spectroscopy (EIS) Data Analysis Software utilizing the fast computation speed of recent computers. Innovative concepts have been implemented to achieve the following performance:

1. MInimal user input: The user specifies a job by selecting a model for an impedance data set, and simply requests execution to ZSimpWin.
2. Automatic analysis: Parameters associated with the selected model are determined automatically. ZSimpWin assigns an initial guess of these parameters (default = Auto Setup option), starts computation using the initial guess, finds results, improves these results a number of times until desired results are obtained, and then saves the final results.

3. Processing multiple jobs: Setup a batch by including multiple jobs, and process in sequence. Analysis results are saved in a designated folder.
4. Output results in various forms: Results consist of plots, estimated parameters, and historical records of computation process. Each or several combinations can be printed or copied to Windows clipboard. The most convenient form is printing estimated parameters and displayed plot on a single page.
5. Requires only mouse button clicks: The whole process requires no entry of numbers or character strings. Only mouse button clicks are required.

Result and Discussion

When using ZSimpWin3.22 to simulation electrochemical process , we must choose appropriate equivalent circuit and then input the elements values of this circuit for each case or each model as shown in figure(2,3). The models for coating behavior applied in this paper are based on the Randles circuit, a representation most often used for a nominally intact coating [10]. In this paper, the Randle circuit modified by replacement of the capacitor to the constant phase element (CPE) for overcome all the defects of the model simulation the reality.

Two models are investigated. The first model is associated with a intact organic coating on the metal as shown in Fig.(2) with its equivalent circuit (improvement Randle circuit) , and the second model is the changes occur in organic coating by swelling or ablation, then creation oxide layer (passive film) on the metal, which described by resistor and (CPE) too. More details in Fig(3). Presentation of impedance data is often done by use of three different graphs the Nyquist shown in Fig.(,plots the real(Z') and imaginary component (Z") of the impedance on x and y axis respectively . For Nyquist plot, shown corrosion data it can be assumed that the frequency decrease from left to right but the graph doesn't display the frequency for data collected , hence the same data is often also displayed using Bode plot show the relation between the frequency (f) with phase angle(θ) and the equivalent impedance (Z) as shown in Fig.(4) and Fig.(6). The initial effect of water absorption is to change the “value” of the capacitor, so the shape of the Nyquist plot does not change. The Nyquist plot is and will remain uninteresting until we begin to see resistive elements develop in the coating. The coating may also swell during this stage, which would have the effect of decreasing the capacitance. Because of the high dielectric constant of water, the effect of water absorption usually overwhelms the effect of swelling and the capacitance increases. The initial effect of water absorption is to change the “value” of the capacitor, so the shape of the Nyquist plot does not change. The Nyquist plot is and will remain uninteresting until we begin to see resistive elements develop in the coating. Nyquist plots for two cases in Fig.(4) and Fig.(6) we observed that new semicircle appeared in second case because created passive layer which have capacitive behavior for this reason passive layer inhabited the continued corrosion process in most cases. The Bode plots in Fig.(5) and Fig.(6) are the first and second cases respectively. the relation between the equivalent impedance for the all circuit element with frequency when the impedance decreases from first case to second case that refers to the sample suffers corrosion.

The relation between the phase angle and frequency clears the equivalent circuit behavior as resistive (Ohmic) or capacitive behavior. The resistive behavior when the phase angle closed to 0^{o} and the capacitive behavior when the phase angle closed to 90^{o}.the capacitive behavior is better than the Ohmic behavior as corrosion protection since the capacitor make polarized between two different charges layers which prevents charges translate.

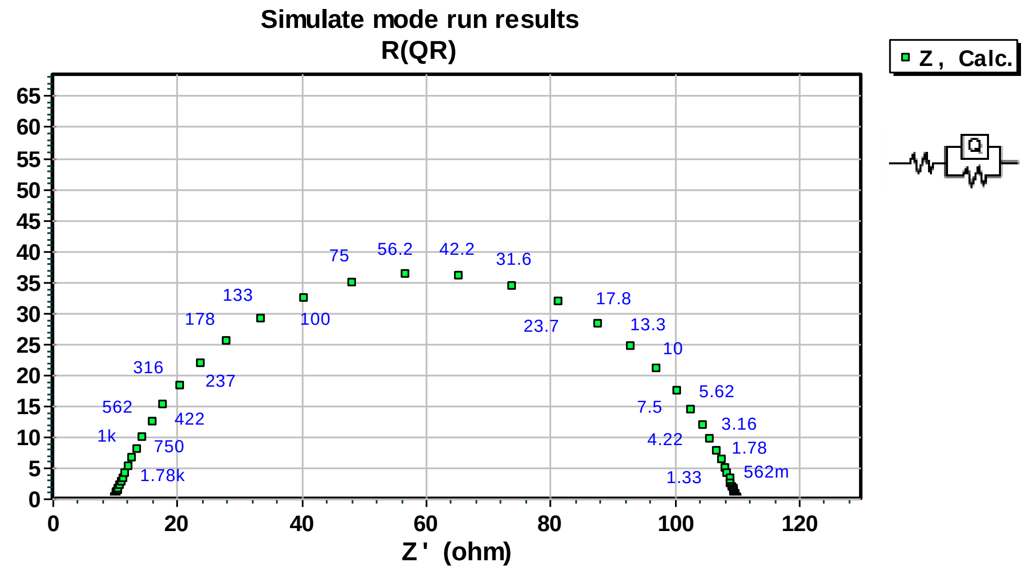

Fig.(4): Nyquist plot for intact organic coating

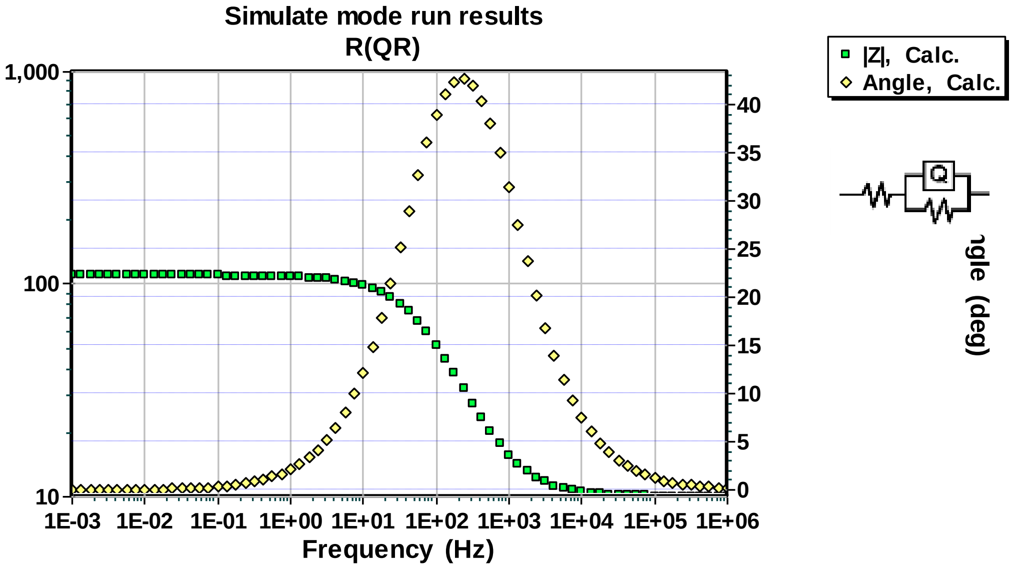

Fig.(5): Bode plot for intact organic coating.

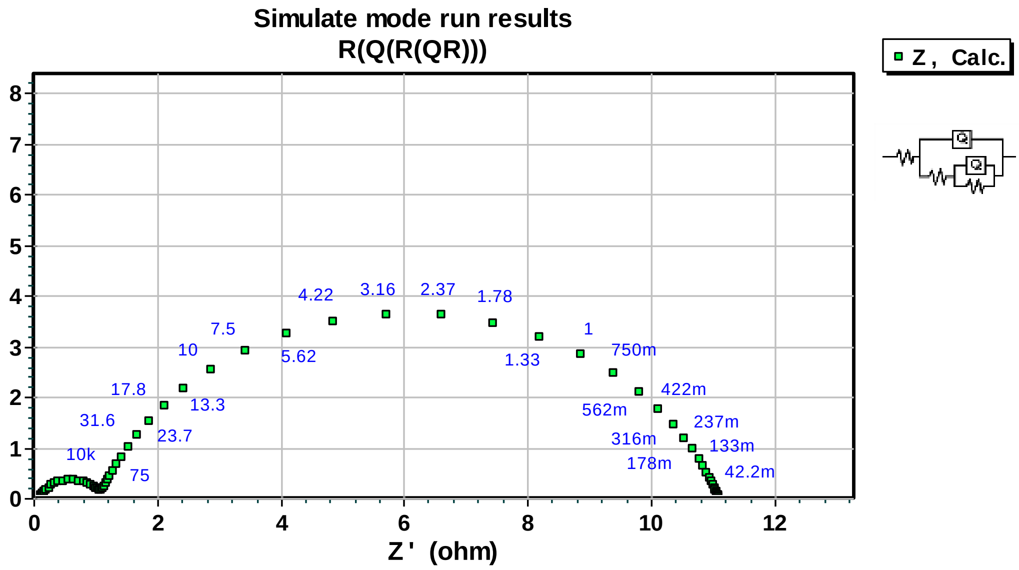

Fig.(7): Nyquist plot for the damage coating and created passive layer (oxide layer) on the metal.

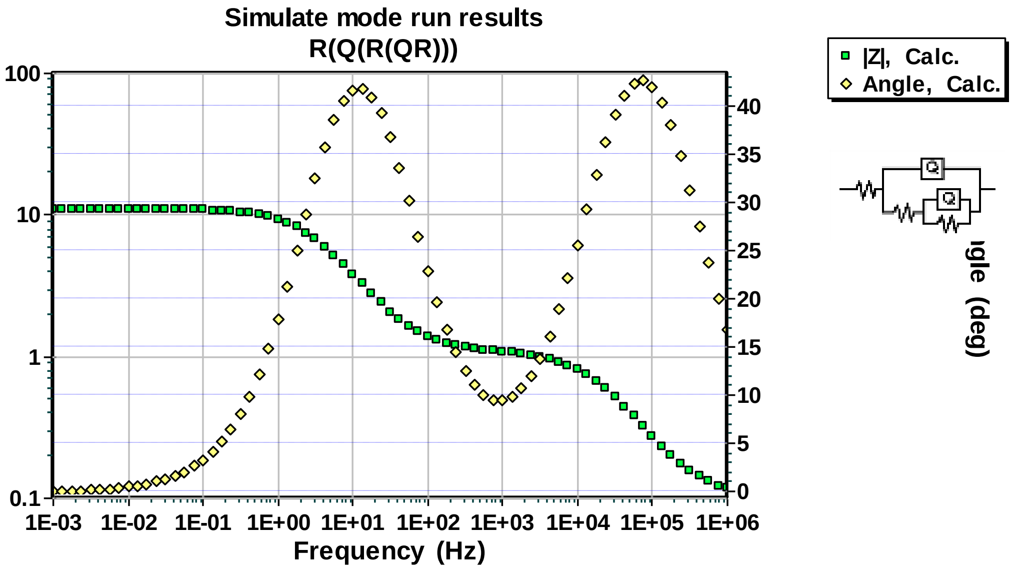

Fig.(8): Bode plot for the damage coating and created passive layer (oxide layer) on the metal.

Conclusion

When we look the result we understand how the change in the sample with corrosion reaction where using the CPE instead of the capacitor is benefit to reach to the reality. The appearing of new semicircle when the corrosion process occur refer to create passive film (oxide layer) on the metal substrate.

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تمثيل عملية تلف الغلاف العضوي الذي يحمي المعدن من التاكل باستخدام مطياف الممانعة الكهربائية

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الخلاصة

في هذا البحث تم تمثيل عملية تلف الغلاف العضوي الذي يحمي المعدن باستخدام برنامج ZSimpWin 3.22وايجاد طيف الممانعة بعد وضع نموذج معدل للدائرة الكهربائية المكافئة ولكل حالة من وجود وعدم وجود عملية التاكل ,وقد تم استبدال المتسعة ب CPE لغرض الوصول الى الحالة الواقعية.النتيجة التي حصلنا عليها تساعد في فهم عملية التاكل للمعدن بعد تلف الغطاء العضوي الواقي وذلك عن طريق ملاحظة التي تطرىء على سلوك المنحنيات الخاصة بمنحنيات النكوست والبودي وتغير الممانعة وزاوية فرق الطور مع التردد قبل وبعد عملية التاكل.