

A Modified CPE Model to Fit EIS Data for Protective Coating Evaluation

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ABSTRACT

EIS (Electrochemical Impedance Spectroscopy) technique has been used in many areas such as biosensors, battery development, fuel cell development etc. Many efforts have also been made to apply this technique to paint/coating evaluations. The epoxy industrial coatings containing fillers or ceramic beads are commonly used in chemical processing, Mining/Mineral & Ore processing, Oil/gas, Power (fossil, hydroelectric, and nuclear), water/waste water, etc. These coatings provide excellent corrosion and erosion resistance for metal and concrete surfaces. EIS is a useful tool to investigate corrosion/erosion resistance of these protective coatings under various environment conditions.

EIS can measure impedance of coatings and phase angle of imposed AC voltage/current. The changes in impedance and phase angle can be used as indicators of coating structure changes caused by corrosion, erosion, water penetrations, etc. There are various ways to analyze EIS data to correlate the data with the performance of paint/coating products but these methods all have limitations when used to evaluate high performance protective coatings. In this presentation, we discussed the limitations of commonly used EIS data analysis methods. A modified CPE model is proposed to evaluate high performance protective coatings on water/chemical penetrations and/or surface deteriorations due to corrosion and/or erosion.

INTRODUCTION

EIS data fitting models are composed of resistors, capacitors, and other electronic components. These electronic elements can be used to simulate coating films, defects or damages of coating samples. In many models, a perfect coating film is considered as a capacitor.

Resistors and Capacitors in EIS Data Fitting Model

Resistors are electronic components which have constant electrical resistance. In both DC (direct current) and AC (alternating current) circuits, the impedance of a resistor can be calculated by $Z = \frac{U}{I}$. Resistors always have constant impedance which are independent of frequency of AC voltage in AC circuits.

Capacitors are different from resistors. In a DC circuit, current flow stops when a capacitor is fully charged, so the impedance is infinite. In an AC circuit, the impedance (also called reactance) of a capacitor can be calculated by equation: $Z_C = \frac{1}{2\pi fC} = \frac{1}{\omega C}$, where C is the capacitance of the capacitor, f is frequency, ω is angular frequency by radians. From this equation, the impedance of a capacitor is inversely proportional to the frequency of the AC power supply: $Z_C \propto \frac{1}{f}$ or $\frac{1}{\omega}$. At extreme high frequency, the impedance equals 0. At extreme low frequency (an AC circuit), the impedance is infinite, which means that there is no current flow through the capacitor.

Another big difference between a resistor and a capacitor is the phase angle difference between the voltage and current flowing through them. The two plots in Figure 1 illustrates the differences. For a resistor (left in Figure 1), the current flowing through it is always at the same phase as voltage. For an ideal capacitor (right in Figure 1), the current flowing through it always leads voltage by 90 degrees. For an imperfect capacitor, the phase angle difference of voltage and current is in the range of 0 ~ 90 degrees.

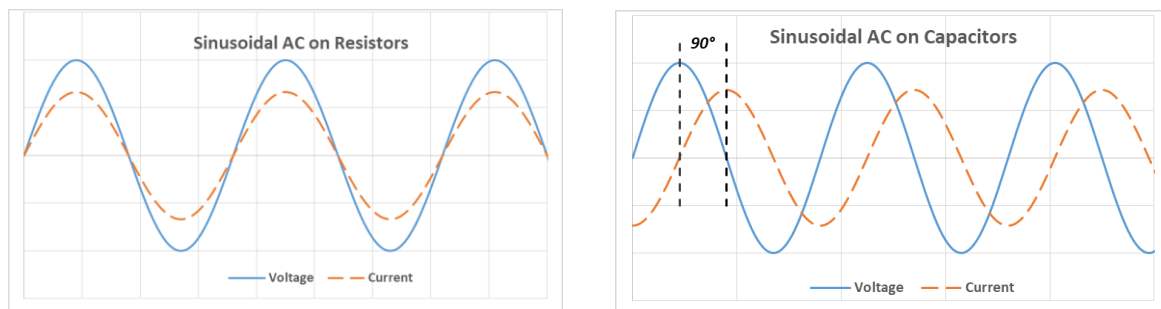


Figure 1. Phase angles of voltage and current for resistors and capacitors in Sinusoidal AC circuit

In EIS data analysis models for coating evaluation, ideal coating films are simulated by capacitors, and cracks/defects in coating films are described by resistors.

Commonly used EIS data analysis methods for coatings

EIS has been proven to be an effective tool to evaluate coatings ^{[1] [2] [3] [4] [5]}. An ideal coating film is considered as a capacitor in many studies ^{[1] [2] [3] [4]}. The Bode chart obtained from a Gamry EIS is shown in Figure 2 below:

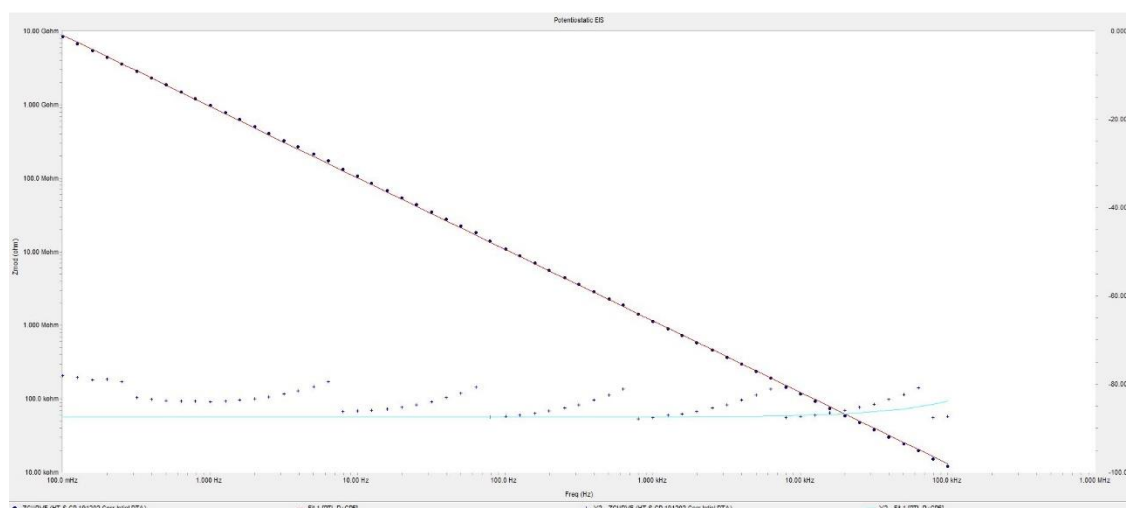


Figure 2. A typical bode chart from EIS measurement

The impedance (left Y axis) decreases as frequency increases. The phase angle of the current (Right Y axis) is shown on the bottom of the chart. For an ideal capacitor, the phase angle of the current should be -90 degrees (lead voltage 90 degrees). But in our studies, the phase angle always deviates from -90 degrees slightly indicates that coating films are not perfect capacitors.

In practice, the EIS data can be analyzed in several ways to evaluate and compare coating performances. But they all show limitations when used to evaluate high performance protective coatings.

- (1) Measured Impedance value. Impedance value at a certain frequency measured by EIS can be used to compare performance of different coatings. Log value of impedance is used in many situations. But this method has limitation.

As mentioned in previous sections, a perfect coating film can be considered as a parallel plate capacitor. The impedance value is inversely proportional to capacitance of the capacitor (coating film). The capacitance C is determined by dimensions (coating thickness etc.) and the properties of the material (dielectric constant) between the two plates of the capacitor (coating film). The

measured impedance values vary with coating thickness. For high performance protective coatings, the measured impedance changes caused by corrosion or other test conditions were small, and they were easily interfered by the variations caused by coating thickness.

(2) REAP (Rapid Electrochemical Assessment of Paint) and REAP2CPE models [1].

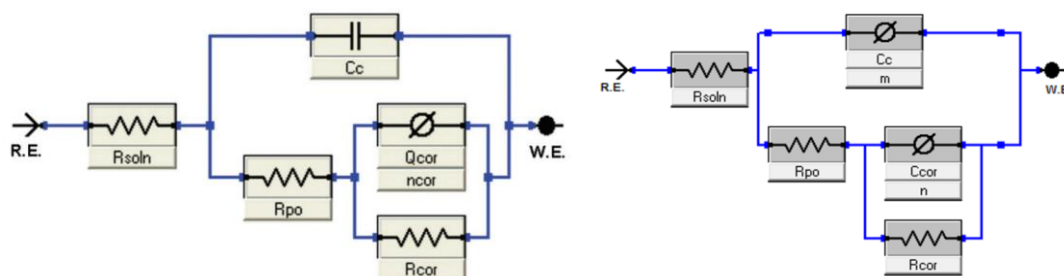


Figure 3. REAP (left) and REAP2CPE (right) Models

A REAP model (left of Figure 3) contains a capacitor $\text{---}\text{||}\text{---}$ (with a capacitance of C_c) simulating a perfect coating film, a resistor (with a resistance of R_{soln} $\text{---}\text{W}\text{---}$) simulating the electrolyte solutions used in EIS measurement. Two resistors with resistance of R_{po} and R_{cor} simulate defects caused by corrosion or other factors. In a REAP2CPE model (right of Figure 3), the capacitor is replaced by a CPE (Constant Phase Element $\text{---}\text{O}\text{---}$) which is a leaky capacitor simulating a non-perfect coating film. The parameters related to the capacitor, resistors and CPEs can be obtained by fitting EIS data with the models. These parameters can be used to analyze corrosion/erosion resistance of coating films.

In our study, the fitting of the two models with the EIS data of high performance epoxy coating samples are very poor. The parameters extracted from the models showed significant variations which were much bigger than calculated values. The reason of poor fitness of these two models is that these high performance coatings did not generate cracks and other defects which can be simulated by resistors in corrosion or erosion tests.

A simple CPE model to evaluate high performance protective coatings.

Epoxy protective coatings that we evaluated had very little changes even in a long period of time under harsh testing conditions. They do not generate significant defects, such cracks, pin holes etc., which can be simulated by resistors. We proposed a simple CPE (constant phase element) model (Figure 4) more suitable to evaluate incremental changes (deteriorations) of coatings under various conditions.

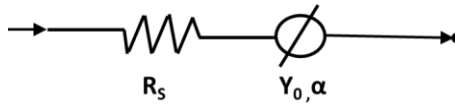


Figure 4. Simple CPE Model for Coating Evaluations

This model contains two electrical elements: a resistor with resistance R_s and a constant phase element (CPE). The resistor simulates electrolyte solution used in EIS measurement. The CPE simulates a coating film on a metal substrate. For a CPE, the impedance can be calculated by equation:

$Z_{CPE} = \frac{1}{(j\omega)^\alpha Y_0}$, while Y_0 is admittance which is a parameter describing how easy current flows through the CPE. It is an inverse parameter of impedance; ω is angular frequency (rad.S^{-1}); j is a virtual number, $j^2 = -1$; α is a number between 0 and 1. When:

- $\alpha = 1$, the CPE is a capacitor and Y_0 equals capacitance C .
- $\alpha = 0$, the CPE is a resistor, the resistance $R = 1/Y_0$.
- When $1 > \alpha > 0$, the CPE is a leaky capacitor and behaves between a resistor and a capacitor. If α value is close to 1, the CPE is close to a capacitor. If α value is close to 0, the CPE is close to a resistor. The α value is only related to coating structure/composition. It is not affected by thickness of coating films. It provides a consistent way to monitor coating's structure changes caused by corrosion or erosion.

By fitting the EIS experiment data with this model, three parameters can be obtained: R_s , Y_0 , α :

Parameter	Value	± Error	Units
R_s	4.070e-3	206.0	ohm
Y_0	413.3e-12	2.427e-12	$\text{S}^*\text{s}^\alpha\text{a}$
Alpha	887.9e-3	703.9e-6	
Goodness of Fit	77.99e-3		
HT-S EU 0% Humid blister.DTA			

Figure 5. Typical EIS Data Fitting Results

In Figure 5, the fitting of R_s value is poor - the error is higher than its value. This is because that the resistance of the electrolyte solution can only be calculated accurately with the data at extreme high frequency. At extreme high frequency, the impedance of the CPE (coating film) is close to 0 (Figure 6), then the resistance value of the electrolyte solution can be read accurately. In real situation, the frequency of the EIS instrument cannot reach high enough that the resistance of CPE reaches 0, thus it is impossible to get an accurate reading of R_s value. Although accurate R_s value can't be achieved by the data fitting, the values of Y_0 and α obtained are acceptable and reliable since Y_0/α are calculated independently of R_s in the model. The α value is only related to coating structure/composition and provides a consistent way to monitor structure changes of coating films.