HIGHLY ACCURATE ELECTROCHEMICAL IMPEDANCE MEASUREMENT

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ABSTRACT

Electrochemical Impedance Spectroscopy (EIS) has found widespread applications in the field of materials characterization. It is routinely used in the characterization of coatings, batteries, fuel cells, and corrosion phenomena. EIS can indicate the presence and the rate of corrosion, and the moisture content of the coating prior to corrosion. For ease of impedance calculation, EIS is used either in a potentiostatic or galvanostatic mode. However, this approach yields in some cases unexplained phenomenon, which makes EIS data interpretation a difficult task. In this paper, a new approach to the computation of impedance is presented where the linear portion of the nonlinear I-V characteristic is represented by a convolutional model, and thus the impedance of the EIS system is computed using robust deconvolution algorithms [1]. Very promising results are obtained particularly when the noise statistics are not known a priori.

1.   INTRODUCTION

While there is no doubts that EIS has become a very powerful tool for the analysis of complex processes, (such as corrosion) that are influenced by many variables with regard to electrolyte, materials and interfacial geometry. It has also become evident that corrosion scientists and engineers sometimes find experimental data quite confusing [2]. Often it is stated that despite the fact that EIS has produced interesting results, its use has not been pursued further because of the complexity of the data analysis. These observations point out to the need of advanced algorithms that can be applied to analyze EIS data. In most cases, equivalent circuits (EC) are used to model the electrochemical process. Fitting techniques are used to compute the values of the EC components. However, for the optimizing technique to converge, initial guesses of the EC components have to be sometimes very close to the actual values.

We believe that the way impedance computation is performed is inherently error prone as the potential (or current) cannot be maintained constant over the whole frequency range and thus, we propose a new technique based on a robust deconvolution technique to extract the impedance in situations where neither potentiostatic nor galvanometric mode is used. But, first let's expose the basis behind EIS techniques.

2.   EIS BASIC PRINCIPLES

In an EIS measurement, an alternating voltage is applied to the corroding metal shown in Fig. 1, and the impedance, *Z*, is measured using both magnitude and phase data of the current and voltage signals.

Contrarily to the dc measurement, known as linear polarization technique, used for bare metal in many situations, EIS is most suited for coated metals with an electrically insulating material such as paint. Behavior of the electrochemical system is highly dependant on the signal frequency, and thus, the signal frequency is swept across a frequency range that span from a few mHz to 100 kHz and the system impedance is measured for each frequency.

To make use of the data collected and correlate it to the physical process taking place, the system under test is modeled by an electrical circuit connected in such a way to produce the same frequency response as the EIS system under test. For a bare metal, (Fig.1), ions that are absorbed at the metal-solution interface create what acts like a leaky capacitor. The bulk of the electrolyte is fairly conductive and acts as a resistor. To complete the analysis of the EIS data for use in corrosion evaluation, one or more of the model parameters must be associated with important aspects of the corrosion process.
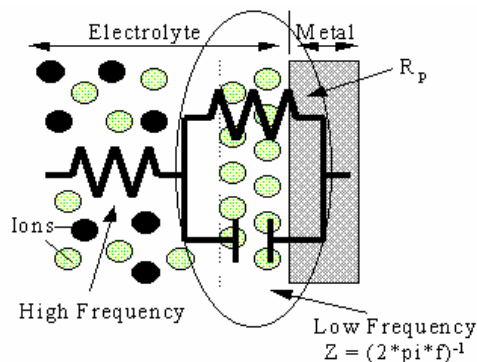

Figure 1: Circuit model for a corroding metal

2.1 EIS MEASUREMENT CELL

The electrochemical cell for an EIS experiment conventionally consists of three electrodes that are immersed in an electrolyte, Figure 2.

The working electrode is grounded, usually through an operational amplifier that is part of the current-to-voltage converter. The counter electrode is made from an inert metal. It is connected to a potential control device called potentiostat that applies a suitable voltage between the working and the reference electrode. The reference electrode is constructed so that its contact potential is negligible regardless of the environment in which it is placed.
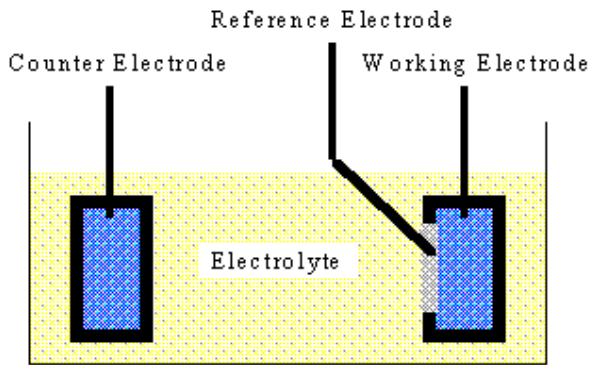

Fig. 2: Conventional EIS Cell for laboratory measurements

2.2. EIS INSTRUMENTATION

There are two options commonly found in EIS instrumentation. One option uses a swept sine wave system and the other uses a spectrum analyzer that has transfer function capability and a white noise source.

The swept wave system is more prevalent technique, because it is the basis for most commercially available EIS package systems. Nonetheless, the spectrum analyzer approach offers a significant advantage.

The white noise stimulus consists of the superposition of sine waves for each of the frequency that are been used. The system thus, is stimulated with all frequencies at ounce and a Fourier transformed is used to extract the system impedance at each frequency.

2.3. EIS DATA ANALYSIS

The modeling of any electrochemical system is complicated and coated metals are at the extreme of complexity. There are several models that occur during the life of a coating, and the most general one is shown in Figure 3. In this model, Rs is the resistance of the electrolyte, Rc and Cc are the resistance and capacitance of the coating, Rct is the polarization resistance, which is inversely proportional to the corrosion rate, Cdl is the double layer capacitance at the electrode-electrolyte interface.

During the life of a coating, the equivalent circuit model changes because of processes such as moisture penetration, onset of corrosion, and break up of the coating. When a coating is new and effective, Rct, Cdl, Rp are not present in the model. As moisture penetrates the coating, Rp comes into the picture.

When corrosion starts, Rct and Cdl become operable. If the coating breaks up, Cp and Rp, become inoperable and the system acts like a bare metal. The importance of EIS lies in the fact that these processes can be distinguished if their time constants differ sufficiently. This is not possible with conventional dc polarization techniques.

2.4   CORROSION SYSTEM MODELING

Obtaining the parameters of an equivalent circuit model that describes the coating system's impedance is only part of the challenge in devising a system that is useful for assessing the current condition of a coating and predicting its performance into the future. To accomplish this goal, one or more parameters of the equivalent circuit models must be related to the current and future condition of the coating. Rp and Cp have been shown to be related to the moisture content of water in organic coatings, but they have not been shown to be quantitative predictors of a coating's life.7 A problem with Rp is that it depends on the concentration of ionizable impurities. Rct should be insensitive to the content of moisture and ionizable impurities in the coating, and it should provide a quantitative measure of the existing corrosion rate. The deficiency with this parameter is that corrosion must be occurring before Rct can be measured.
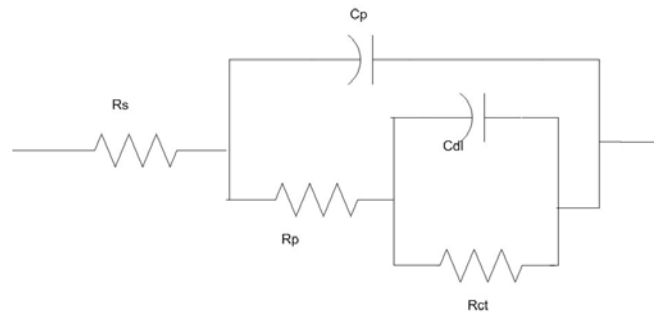

Figure 3: Equivalent circuit of pipeline coating.

3.   PROBLEM FORMULATION

The complex interactive mechanisms within an electrochemical system (ECS) make its I-V characteristic highly non linear. In addition, the environmental noise present within the ECS system further complicates the extraction of the system impedance. For this, small signal analysis is used to extract the EIS impedance from a linear segment within the I-V curve. The accuracy of the impedance calculation depends on the method used.

 In this paper, the ECS is modeled as in Fig. 4, where the input signal represented by the current generates a noisy

output that is represented by the voltage. The mathematical representation of this model is in general defined below as:

$$v(t) = i(t) \otimes Z(t) + n(t) \qquad (1)$$

where $Z(t)$ is the inverse Fourier transform of the impedance $Z(\omega)$ and $n(t)$ is the noise.

To our knowledge, no one has used the convolutional model before. Either, $i(t)$ is made constant (galvanostatic mode) or $v(t)$ is made constant (potentiostatic mode) in which case, equation (1) simplifies considerably, and extraction of $Z(\omega)$ is usually straight forward, though, it is practically very costly to work in potentiostatic/galvanostatic mode.
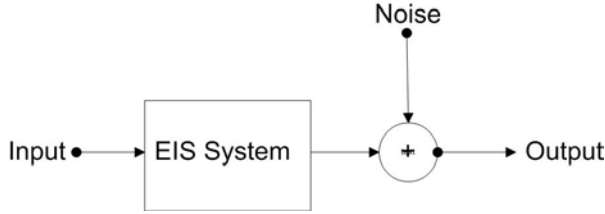

Figure 4: ECS Convolutional Model.

Typical electrochemical impedance experimental set-up consists of an electrochemical cell, a potentiostat/galvanostat, and a frequency response analyzer (FRA). The FRA applies the sine wave and analyses the response of the system to determine the impedance in the frequency range $0.001 \le f \le 100,000$ Hz. An equivalent electric circuit is chosen (figure 3), whose frequency response is the same as the measured EIS. Curve fitting techniques are used to estimate the system parameters based on a minimization of a cost function .

To test the proposed method, a painted conductor modeled by Fig. 3 is chosen, where the frequency of the signal $i(t)$ is swept from 0.01 Hz to 100 Khz, to compute $v(t)$ using Equ. (1). A deconvolution method is used to compute $Z(t)$ from the input-output signal pair $((i(t),v(t))$ using higher Order statistics [1] followed by an FFT to get $Z(w)$. The equivalent impedance $Z_e(w)$ is computed using initial values. A Bode plot of $Z(w)$ and $Z_e(w)$ is shown in Fig.6. To estimate the system parameters, a minimization of the cost function J using non linear regression routine

$$J = \sum_k \frac{(Z_{r,k} - \hat{Z}_{r,k})^2}{W^2_{r,k}} + \sum_k \frac{(Z_{j,k} - \hat{Z}_{j,k})^2}{W^2_{j,k}}$$

where $Z_{r,k}$ $Z_{j,k}$ are the real and imaginary part of the EIS data, and $\hat{Z}_{r,k}$ $\hat{Z}_{j,k}$ are the real and imaginary parts of the estimated impedance $Z_e(w)$, and $W_{r,k}$, $W_{j,k}$ are the real and imaginary weights. Fig.5 shows the plot J (square error) as a function of iteration.

4. TEST

A Physical Vapor Deposition (VPD) coated steel model was taken, whose EC is given in Fig. 3. First, the impedance $Z(w)$ is used in equ.(1) to compute the resulting voltage for a given sinusoidal current $i(t)$ (galvanostatic mode) and noise signal $n(t)$. This represents in practice the data acquisition part. Second, given the $i(t)$, $v(t)$ signals pair, we estimate the $Z_e(w)$ with and without filtering.

A Matlab program was written to perform such test, and it was found that the fitted model converges after 856 iterations, giving a highly accurate estimate of the model parameters. It was also found that for signal to noise ratio (SNR) greater than 10 dB no filtering is needed.

	Rs (Ω)	Rp (KΩ)	Cp (nF)	Rct (MΩ)	Cdl (nF)
Actual	402	100	1	20	22
Estimated (30 dB noise)	402	100	1	19.99	22.1
Estimated (5 dB noise)	395	102	0.992	19.21	22.5
InitialValues	100	1	20	1	1

Table 1: actual, initial and estimated Model parameters.

In practice, each component represents physical phenomena and the values of which indicates the presence or absence of corrosion and its rate over time.
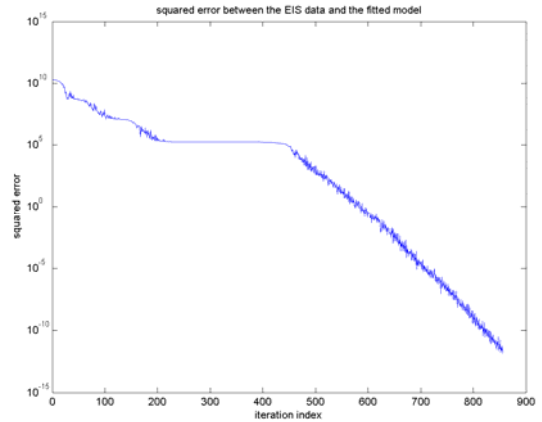

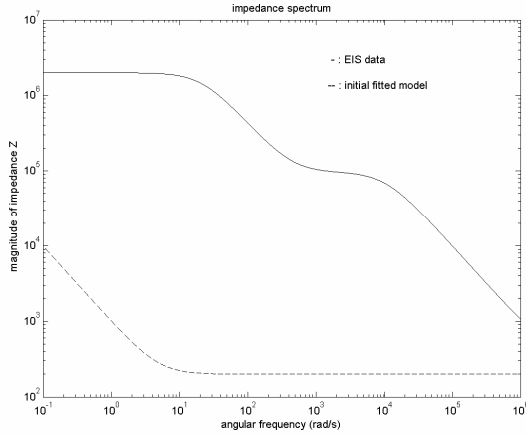Figure 5: Square error (J) versus iteration

Figure 6: Bode plot of EIS and initial fitting model.

Figure 6 shows Bode plot of $Z(w)$ with initial values compared to the actual impedance. This model converges rapidly giving the estimated parameters values as indicated in Table 1. While Fig. 7 represents the "measured" impedance in a noisy environment (5dB) as compared to the actual impedance.
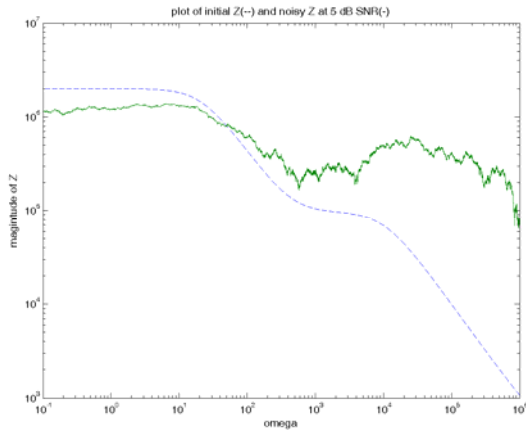

Fig. 7: Bode plot of noisy filtered EIS data

5. CONCLUSION

In this paper, we have compared the results of EIS data measured conventionally in industry with a filtered version of it. It has been found that for an SNR up to 10 dB, no filtering otherwise, misleading data will result. Though, industrial EIS uses some types of filtering, the assumption of constant current (or voltage) does lead to a presence of a phenomenon on the |Z| plot that is not understood by the corrosion engineers community.

Further work, will concentrate on the effect of other noise distribution on the computed Z. Here advanced deconvolution algorithms will be used which we expect to yield accurate results.

6. REFERENCES

[1] Yamani, A., Bettayeb, M., "High Order statistics-based deconvolution of NDT Ultrasonic data," SABIC Final Report (EE/SABIC/96-8), November 3, 1998.
[2] Silverman, Scully, and Kendig (Editors), "Electrochemical Impedance: Analysis and Interpretation", ASTM, 1993.