CORROSION EVALUATION USING A NEW ELECTROCHEMICAL IMPEDANCE MEASUREMENT TECHNIQUE

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ABSTRACT

In this paper, a new approach to the computation of electrochemical impedance spectroscopy (EIS) is presented where the EIS system is represented by a convolutional model, and thus the impedance of the EIS system is computed using robust deconvolution algorithms. Very promising results are obtained .

1. INTRODUCTION

It has become evident that corrosion scientists and engineers sometimes find experimental data quite confusing [1]. 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 [2] 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 propose a new technique based on a robust deconvolution technique to extract the impedance in situations where neither potentiostatic nor galvanometric mode is used.

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.
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.

2.1. 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 2. 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.

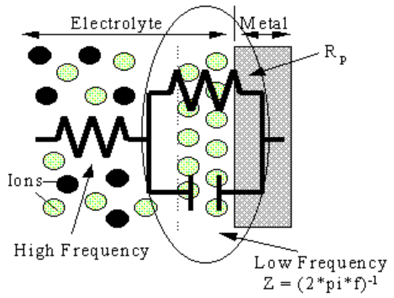

Figure 1: Circuit model for a corroding metal

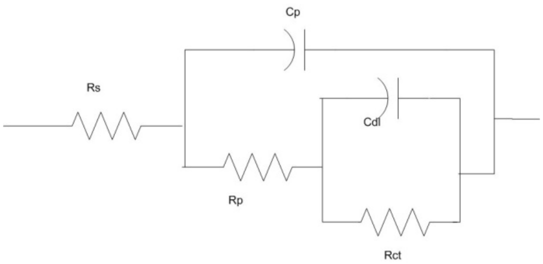

Figure 2: Equivalent circuit of pipeline coating.

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.

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. 3, 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.

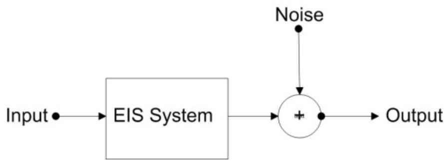

Figure 3: ECS Convolutional Model.

Curve fitting techniques are used to estimate the system parameters based on a minimization of a cost function given by:

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

where $Z_{r,k}$ $Z_{j,k}$ are the real and imaginary part of the EIS data, and $\widehat{Z}_{r,k}$ $\widehat{Z}_{j,k}$ 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.

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 [2] 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.5 where $Z_e(w)$ is computed at the initial values.

4. TEST

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.

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

	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.

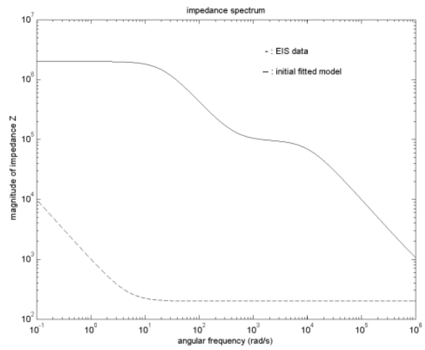

Figure 5: Bode plot of EIS and initial fitting model.

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.

ACKNOWLEDGEMENT

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REFERENCES

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[2] Yamani, A., Bettayeb, M., "High Order statistics-based deconvolution of NDT Ultrasonic data," SABIC Final Report (EE/SABIC/96-8), November 3, 1998.