An alternative method to calculate the harmonic components from Electrochemical Frequency Modulation data using polynomial fitting

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Abstract. The Electrochemical Frequency Modulation (EFM) technique applies a potential signal consisting of two sinusoids of the same amplitude and different frequencies to a corroding system. The analysis of the nonlinear components at harmonic and intermodulation frequencies of the system’s response can give information about the corrosion behavior, such as Tafel slopes and corrosion current. These components are usually computed using the Fast Fourier Transform (FFT) algorithm on the current response. This work proposes an alternative method for computing the harmonic components from EFM data. The proposed method uses a polynomial fitting for modeling the current response of the electrochemical system in order to calculate the harmonic components analytically. The method was evaluated by processing theoretical data based on the Butler-Volmer equation. Results indicate that a polynomial fitting of fifth order can give a good approximation of the Tafel constants and corrosion current. Additionally, the method was tested on experimental data from a three-electrode system consisting of an AISI 316L working electrode, platinum counter electrode and Saturated Calomel Electrode (SCE) as the reference electrode in a 1 \textit{mol L}^{-1} \textit{NaCl} solution. Results suggest that using polynomial fit could reduce estimation error.

1. Introduction

Corrosion causes significant expenses in industry [1–3]. Therefore the development of methods for measuring corrosion has an important interest. The electrochemical techniques have become a useful tool for measuring corrosion rate [4–6]. Two techniques widely studied by various authors are the Linear Polarization Resistance (LPR) and Potentiodynamic Polarization (PDP), which have become of common use in industry [5,7–11].

After the work of Mészáros \textit{et al} [12,13] and Kendig \textit{et al} [14] on the harmonic technique, Bosch and Bogaerts introduced a technique based on intermodulation distortion [15]. This technique was named by the authors as Electrochemical Frequency Modulation (EFM) [16], it consists to apply a potential signal perturbation with two frequency components to a corroding system, then Tafel slopes and corrosion current can be calculated by measuring the current density response at intermodulation frequencies (sums, differences, and multiples of the two
base components), and using equations that are derived from a modified Butler-Volmer equation for activation-controlled, diffusion-controlled and passivating systems, as reported by Bosch et al. [15, 16]. Thus only the harmonic components are needed in order to compute the corrosion current and Tafel slopes.

The EFM technique has been studied and reviewed by various authors [5, 17–24] who reported a good agreement between the EFM technique and other electrochemical techniques, if the excitation frequencies are sufficiently low to avoid any capacitive effect [23, 24]. This condition limits the application of the technique in materials with high corrosion resistance or relative high capacitance.

Commonly, the Fast Fourier Transform (FFT) algorithm is used to compute the magnitude of harmonic components and intermodulation products [16]. On the other hand, the use of polynomial fitting for electrochemical tests was studied by Rocchinni [25, 26] for the analysis of LPR measurements. In this work, an alternative method is proposed to estimate the harmonic components of the EFM data using a polynomial fitting.

2. Materials and methods

2.1. Proposed method

The proposed method uses a polynomial fitting on EFM measurements, in order to model the total current density response of an electrochemical reaction as a function of the applied potential, as shown in equation (1).

$$i_{\text{reac}}(\eta) = \sum_{k=1}^{z} \theta_k \eta^k$$  

Where $i_{\text{reac}}$ is the estimated total current density response of the electrochemical reaction based on a polynomial model, $z$ the order of the polynomial, $\theta_k$ are the coefficients of the polynomial and $\eta$ is the applied overpotential. If the input signal is known to be a sum of cosines, the equation (1) can be expressed as a function of time and decomposed in harmonics and intermodulation products using trigonometric identities, from which the magnitude of each frequency component can be obtained.

In order to select the best polynomial order, a cost function was defined (see equation (2)) and evaluated over a thousand randomly generated data samples based on the Butler-Volmer equation, including a double-layer capacitance, to take into account the faradaic and charging current densities (see equation (3)). The ranges listed in Table 1 were used to generate the data samples. The cost function compares the mean squared error between a set of known generated current density responses and the estimated response of each set of assigned parameters of equation (3). The MSE resulting vector of equation (2) contains in ascending order the evaluated mean squared errors for each studied order.

$$\text{MSE} = \frac{1}{2N} \text{diag}((i_{\text{farad}} - i_{\text{farad}})^T(i_{\text{farad}} - i_{\text{farad}}))$$  

Where $i_{\text{farad}}$ is an $N$ column vector of the known response for each sample set, $i_{\text{farad}}$ is a $N \times z$ matrix of estimated responses of $N$ samples, each one evaluated for orders up to $z$.

$$i_{\text{reac}}(\eta) = i_{\text{corr}} + C_{dl} \frac{d\eta}{dt}$$  

Where $i_{\text{reac}}$ is the total current density response of the reaction, $i_{\text{corr}}$ is the corrosion current, $n$ the number of electrons involved in the reaction, $T$ the temperature, $\eta$ the overpotential, $R$ the universal gas constant, $F$ the Faraday constant and $C_{dl}$ a double layer capacitance.
Table 1. Ranges of the parameters used in equation (3) to generate theoretical data samples.

| Variable | Range | Units         |
|----------|-------|---------------|
| $n$      | 1     | 3     | $e^{-}/mol$ |
| $T$      | 295   | 298   | $K$         |
| $\alpha$ | 0     | 1     | -            |
| $i_{corr}$ | 0.001 | 1000  | $\mu A$     |
| $E_{corr}$ | −1000 | −1    | $mV$        |
| $C_{dl}$ | 10    | 100   | $\mu F$     |

2.2. Experimental setup

EFM test was carried out in order to compare the estimation of corrosion current and Tafel slopes from harmonic components computed using FFT and the polynomial fit, in a condition were the EFM technique is expected to estimate a higher corrosion current than the determined by Tafel extrapolation technique, assuming that this high current estimations are due to errors associated with the capacitive effect or excitation overpotential. A potential sum of two cosines with frequencies of $0.2 \text{Hz}$ and $0.5 \text{Hz}$ with an amplitudes of $30 \text{mV}$ each and $15 \text{mV}$ each, were applied during 12 cycles of the resultant signals. The test was carried out at the corrosion potential exposing the electrode surface to salt water for one hour. Additionally, polarization curves were obtained to determine corrosion current and Tafel slopes from the Tafel extrapolation method. The scan rate was $0.1667 \text{mV/s}$ from an initial potential of $-250 \text{mV}$ and final potential of $+250 \text{mV}$ versus open circuit potential (OCP). Experiments were conducted on an electrochemical cell consisting of 1) a stainless steel AISI 316L probe as working electrode, 2) a platinum counter electrode, 3) a saturated calomel electrode (SCE) used as the reference electrode, and 4) a $1 \text{molL}^{-1} \text{NaCl}$ aqueous electrolyte. The electrochemical measurements were achieved by exposing $1 \text{cm}^2$ of the surface’s sample into the electrolyte.

3. Results

3.1. Order of the polynomial and estimation errors

Figure 1 shows the normalized $MSE$ as a function of polynomial order from a thousand randomly generated data samples with ranges listed in Table 1. From Figure 1 can be observed that a polynomial of fifth order gives the minimum $MSE$ value for the generated samples. Figure 2 shows one data sample based on equation (3) and the estimated EFM responses using FFT and fifth order polynomial fit. The following values were used to generate the current density response showed in Figure 2: $i_{corr} = 0.06 \mu A$, $E_{corr} = -139.2 \text{mV}$, $C_{dl} = 5 \mu F$, $\alpha = 0.5559$, $n = 2e^{-}/mol$, $T = 296.15K$, $\eta = a \cdot (\cos 0.4\pi t + \cos \pi t)$ and $a = 30 \text{mV}$. From Figure 2 can be observed that $i_{farad}$ shows a smooth line which corresponds to the faradaic current density response only, while $i_{reac}$ shows ellipsoids centered at $i_{farad}$, due to the phase shift generated by the capacitance. The estimation using polynomials is close to the faradaic response despite the charging current density added by the capacitance, while the estimation using the FFT algorithm looks amplified in comparison to the theoretical faradaic response. This is because the least squares regression matches the central line of the ellipsoids, avoiding two important sources of error which are the capacitive effect and the nonlinear behavior due to the applied overpotential. If the capacitance is known, the capacitive current can be subtracted lowering the error of estimation when using FFT [15]. Figure 3 shows the error behavior (computed as the
residual sum of squares over the total sum of squares) as increasing $C_{dl}$, it can be observed that using polynomial fit greatly reduces the error associated with the capacitance. Figure 4 shows the error behavior as increasing the amplitude of the excitation signal, it can be observed that using polynomial fit almost eliminate this source of error in a wide range of potentials, which is an advantage in noisy environments.

Figure 1. Normalized mean square error as a function of the polynomial order for a thousand theoretical samples.

Figure 2. Theoretical response of one data sample generated from equation (3) compared with the estimated responses using FFT and Polynomial fit.

Figure 3. Error as a function of the double layer capacitance for $i_{corr} = 0.06 \mu A$, $E_{corr} = -139.2 mV$, $\alpha = 0.5559$, $n = 2e^-/mol$, $T = 296.15 K$, $\eta = a \cdot (\cos 0.4 \pi t + \cos \pi t)$, $a = 30 mV$ and $C_{dl} = 0$ to $100 \mu F$.

Figure 4. Error as a function of the applied overpotential for $i_{corr} = 0.06 \mu A$, $E_{corr} = -139.2 mV$, $C_{dl} = 5 \mu F$, $\alpha = 0.5559$, $n = 2e^-/mol$, $T = 296.15 K$, $\eta = a \cdot (\cos 0.4 \pi t + \cos \pi t)$ and $a = 10$ to $45 mV$. 

3.2. Corrosion current and Tafel slopes

Table 2 compares the corrosion current and Tafel slopes computed from theoretical samples and experimental measurements. The estimated values of theoretical samples are compared with the true values of the simulation. The averaged results of experimental measurements are compared, with the values determined by Tafel extrapolation from potentiodynamic curves. Note that $\beta_{a,c} = b_{a,c}/(\ln 10)$. From Table 2 can be observed that for theoretical data the corrosion currents and Tafel slopes determined with EFM using polynomials are closer to the true values than the ones computed using the FFT algorithm. On the other hand, for experimental data the corrosion currents determined with EFM are higher than the obtained by Tafel extrapolation, this agrees with the reported by Kus et al. [23], this difference is usually attributed to the capacitive contribution since the selected base frequency is in the capacitive region of impedance of the AISI 316L [16,23]. However, the use of polynomial fitting apparently reduces this source of error, resulting in an estimated $i_{corr}$ smaller than the one computed with the use of FFT.

| Technique - Method          | $CR$  | $i_{corr}$ | $b_a$      | $b_c$      |
|----------------------------|-------|------------|------------|------------|
|                            | $[\mu m/year]$ | $[\mu A]$ | $[mV/dec]$ | $[mV/dec]$ |
| Theoretical                |       |            |            |            |
| EFM - FFT (30mV)           | 2.83  | 0.2663     | 78.4867    | 96.6263    |
| EFM - Poly (30mV)          | 0.80  | 0.0752     | 58.1080    | 70.1868    |
| True Values                | 0.64  | 0.0060     | 52.6750    | 65.9357    |
| Experimental               |       |            |            |            |
| EFM - FFT (30mV)           | 22.48 | 2.1169     | 141.7416   | 216.6875   |
| EFM - Poly (30mV)          | 13.95 | 1.3136     | 145.1159   | 230.2816   |
| PDP - Tafel                | 1.320 | 0.1240     | 126.0333   | 156.1333   |
| EFM - FFT (15mV)           | 6.29  | 0.5919     | 112.5437   | 125.5100   |
| EFM - Poly (15mV)          | 2.94  | 0.2772     | 77.98480   | 96.59360   |
| PDP - Tafel                | 1.31  | 0.1230     | 153.4000   | 186.3000   |

4. Discussion

Kus and Mansfeld concluded that the EFM technique is expected to estimate higher corrosion currents in systems with low corrosion rates [23]. They tested a SS 316 in 0.5M NaCl after 3 hours of exposure and used an excitation signal with an amplitude of 20mV and frequencies of 0.2Hz and 0.5Hz. Taken into account the differences in the experimental setup with respect to present work, similar results were found, the estimated corrosion rate using the FFT algorithm are higher than the determined by other techniques. Lowering the excitation amplitude can reduce this difference, but the signal to noise ratio decrease as well, affecting the estimation of the Tafel slopes. The polynomial approach can improve the estimation of the corrosion current but still higher values are obtained.

5. Conclusions

The use of polynomial fitting for computing the harmonic components could avoid estimation errors from the capacitance effect and non-linear behavior due to the amplitude of the excitation signal in a range of potentials. For theoretical data, the use of polynomial fit can give a better estimation of the faradaic current response than the use of the FFT algorithm, despite
charging currents from the double layer capacitance. For experimental data the estimated \( i_{corr} \) using polynomial fit was always lower than the one using FFT algorithm, which suggests that estimation error were reduced.

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