Determination of Local Corrosion Current from Individual Harmonic Components

Lukasz Burczyk and Kazimierz Darowicki

Department of Electrochemistry, Corrosion and Materials Engineering, Faculty of Chemistry, Gdansk University of Technology, 80-233 Gdansk, Poland

Harmonic analysis has been used in corrosion measurements for several decades. During this period the method has been refined and developed. Nevertheless, the technique has not been applied to properties determination in local scale yet. This paper is focused on local corrosion current measurements based on harmonic analysis. For this purpose, a non-linear nature of electrode processes is used and measured in local scale applying Harmonic Analysis Microscope (HAM).

DOI: 10.1149/2.1001713jes

The basis of harmonic analysis (HA) is perturbation of the system under investigation with alternating current signal and successive analysis of its feedback in the frequency function. As electrochemical and corrosion processes are non-linear, a polyharmonic signal responds to perturbation. Given the polyharmonic signal, particular harmonic components can be extracted and the values of required kinetic parameters can be calculated thanks to an applicable mathematical approach.

Dévay and Mészáros assumed that the processes of non-faradaic current flow are linear, so they do not generate higher harmonic response than the first component.1 In respect to non-linear nature of electrode processes, the current signal occurs due to electrode perturbation together with a sinusoidal signal. The current signal consists of a total number of harmonic components displaying the dispersion of frequency.

The main advantage of HA is that corrosion current and both Tafel coefficients can be obtained by single measurement. Subsequently, the measurement of corrosion rate does not employ presumed values for the Tafel slopes. The advantage of this method, comparing to impedance measurements, is the application of a single frequency. In addition, perturbation signal usually has low amplitude (below 30 mV) which helps to maintain steady state condition. However, under certain circumstances, low amplitude could become a disadvantage. Generated and effective voltage perturbation are not equal. It is caused by the ohmic drop due to solution resistance. The difference between both voltages decreases, when solution resistance is low compared with the polarization resistance. Another important aspect of HA is perturbation frequency. The values below 0.1 Hz are applied in most cases. This condition is dictated by the influence of capacitance current related to charging and discharging of the double layer in higher frequencies. Nevertheless, as it was reported earlier, the upper limit of frequency depends on particular properties of investigated system and assumed relative error.2

The majority of measurements in the field of corrosion science, with application of HA, has been performed on iron in acidic and neutral environments.3,4 Among the first applications was the determination of the corrosion rate at the metal/paint interface.5 As the authors suggest, the use of HA shall allow recognition of the role of binder for corrosion. Gill et al. examined mild steel in NaCl solution.6 The results of HA were comparable to those obtained with well-known electrochemical techniques and gravimetric analysis. Mild steel was also examined in various environments for susceptibility to carbon dioxide corrosion. More complex systems were investigated by Vedalakshmi et al.7 The work concerned rebar embedded in concrete in various environments with different chloride content. Similar approach was also adapted to real-time corrosion monitoring. For two years and half, the monitoring of copper corrosion rate in bentonite block has been examined.9 There have also been reports on studies of iron in acidic media in presence of corrosion inhibitors.10 At the beginning HA was limited to processes where both reactions were activation controlled or one of the reaction was under full-diffusion control. In that case, the harmonic analysis results are not questionable. However, the attempts of HA application to the systems with different controlling factors were made. Bosh et al. examined mild steel in 0.5 M Na2SO4, presenting mathematical model which applies to the reaction where anodic process is under activation control, but cathodic reaction is under mixed control.11 The obtained results were confirmed by Tafel extrapolation. For corrosion current calculation two extra parameters were required: diffusion coefficient and concentration profile of the oxidant. Jankowski also attempted to analyze more complex systems.12 Nonetheless, it is worth to notice that all of these results are global harmonic response of total investigated object. Rarely is a sample homogenous, thus conventional electrochemical measurements present response over the entire electrode/electrolyte interface. No information on localized electrochemical reactions is provided in the process of response analysis, which causes data misinterpretation. Investigating the material in local scale, it is possible to detect active and passive sites and measure their impact on material global properties.

The local approach to corrosion measurements was presented in the work of Galica et al.13 The studies were performed on magnesium alloy to investigate contribution of particular phase into overall corrosion rate. Thanks to Local Electrochemical Impedance Spectroscopy, it was possible to determine differences in corrosion rate of particular phases. Nevertheless, the impedance measurements implement a set of frequencies. Thus, the application of HA to local measurements should decrease time required for parameters mapping due to single frequency perturbation.

This paper is focused on determination of local corrosion current based on harmonic analysis. For this purpose, a non-linear nature of electrode processes is used and measured in local scale applying Harmonic Analysis Microscope (HAM). The advantage of utilized approach based on receiving simultaneous information on corrosion current and both Tafel coefficients, during a single measurement. Therefore, HAM allows determination of local changes of corrosion process kinetics, particularly important when evaluating the role played by microstructure of an alloy.

Experimental

The electrochemical measurements were performed by means of Autolab PGSTAT30 potentiostat/galvanostat (Ecochemie, The Netherlands). The system was expanded with NI PXI-4461 and NI PXI-4462 (National Instruments, USA) measurement cards for AC signal generation and acquisition, respectively. The aforementioned cards were operating in NI PXI-1031 chassis and controlled by NI PXIe-8105 embedded controller.

The measurements were carried out in five-electrode system. The conventional part consists of platinum counter electrode (CE), silver/silver chloride reference electrode (RE) and the investigated metal acting as a working electrode (WE). Two additional electrodes act
The SEM analysis was carried out by means of S-3400N microscope (Hitachi, Japan) with a tungsten source. The microscope is coupled with energy dispersive spectroscopy (EDS) analyzer UltraDry (ThermoFisher Scientific, USA).

The measurements were performed on M58 duplex brass. With regards to EDS measurements, metal consists of 58.9% zinc and 41.1% copper (wt%). Prior to measurements, the investigated sample was grinded with abrasive paper with increasing grit sized up to 2000. After mechanical preparation, brass sample was subjected to etching solution to reveal the structure. The treatment last for 60 second in etching solution composed of 100 cm³ H₂O, 30 cm³ HCl and 5 cm³ FeCl₃. The efficiency of etching was determined by Scanning Electron Microscope.

The sample area submitted to electrochemical investigations was 2 cm². A solution of 0.1 M KCl was used as an electrolyte. The conductivity of solution was 12.3 mS cm⁻¹. The solution was aerated prior to each experiment. During the experiment, the sample was held at open circle potential (E_{OCP} = −0.19 V vs Ag/AgCl).

### Results and Discussion

For the purpose of this work, the local corrosion rate was calculated on the basis of particular harmonic component. The measured drop of the voltage caused by perturbation signal between UME was subjected to Short-Time Fourier Transformation. The obtained spectrum was analyzed in order to describe values of the fundamental, the second and the third harmonic component. The amplitudes of particular harmonic were determined from the spectrum automatically by the authors’ original program. The amplitudes of harmonic potential were calculated to local current according to Equation 1 with respect to Ohm’s law:

\[
i(\omega)_{loc} = \frac{\Delta V(\omega)_{probe} \cdot \kappa}{d}
\]

where \(i(\omega)_{loc}\) is a value of local current, \(\Delta V(\omega)_{probe}\) is a drop of voltage measured between UME, \(\kappa\) is conductivity of the solution and \(d\) is distance between UMEs. As a result, the set of parameters was obtained, including fundamental, second and third harmonic current values with specific coordinates.

As the anodic and cathodic charge transfer reaction is non-linear, the form of faradaic current is a distorted sinusoid. Consequently, the faradaic current consists of fundamental harmonic component with frequency of \(\omega\) and higher harmonics with frequencies of \(k\omega\) (\(k = 2, 3, \ldots\)). Using the Fourier series, it is possible to describe faradaic current as follows:

\[
i_F = i_{corr} \left\{ I_0 \left( \frac{U_0}{\beta_0} \right) + 2 \sum_{k=0}^{\infty} (-1)^k I_{2k+1} \left( \frac{U_0}{\beta_0} \right) \sin (2k + 1) \omega t \right. \\
+ 2 \sum_{k=1}^{\infty} (-1)^k I_{2k} \left( \frac{U_0}{\beta_0} \right) \cos 2k \omega t \right\} e^{\frac{-\omega^2}{\kappa^2}} \\
- \left[ I_0 \left( \frac{U_0}{\beta_0} \right) - 2 \sum_{k=0}^{\infty} (-1)^k I_{2k+1} \left( \frac{U_0}{\beta_0} \right) \sin (2k + 1) \omega t \right. \\
+ 2 \sum_{k=1}^{\infty} (-1)^k I_{2k} \left( \frac{U_0}{\beta_0} \right) \cos 2k \omega t \right\} e^{\frac{-\omega^2}{\kappa^2}}
\]

where \(I_n\) (\(n = 0, 1, 2, \ldots\) ) are modified Bessel functions of the first kind.

The equation presented above allows to determine the value of current for each of the first three harmonic components. For the purpose of mathematical model simplification, the assumption that amplitude \(U_0\) is limited to the extent that the Bessel function could be approximated with Taylor polynomials is applied. In such case, the equations describing particular harmonic components could be presented as
The obtained maps of the particular harmonic are presented on Fig. 2. Each successive signal is characterized by a lower magnitude, in accordance with the theory. Furthermore, the high level of correlation can be distinguished between the second and the third harmonic map, as expected. Simultaneously, fundamental harmonic response is quite the opposite.

Equations 6–8 describe relationship between individual harmonic components from specific parameters of system. Corrosion current may be calculated on the basis of the first three harmonic components separated from the signal, which require solving Eqs. 3–5.

$$i_{corr} = \frac{i_1}{4\sqrt{3} \frac{i_1}{i_3} - i_2^2}$$ \[6\]

If $\beta_c > \beta_a$

$$\frac{1}{\beta_a} = \frac{1}{2U_0} \left( i_{corr} + 4\frac{|i_2|}{i_1} \right)$$ \[7\]

$$\frac{1}{\beta_c} = \frac{1}{2U_0} \left( i_{corr} - 4\frac{|i_2|}{i_1} \right)$$ \[8\]

It was possible to calculate local corrosion rate by implementing equation 6 with respect to data presented on Fig. 2. Diard et al. discussed modification of Eq. 6 taking into account correlation between first and third harmonic. However, it is justified to neglect this modification for as long as Fourier transformation is used to extract particular component of harmonics and all components are measured simultaneously. Furthermore, the third harmonic component gives contribution of approx. 0.1% of the entire signal. The assumption made in Equations 3–5 causes error of about 10%, so neglecting the contribution of third harmonic in the first one is acceptable and does not generate higher error in the final result.

It should be noted that the above mathematical formulas and the approach overall is restricted to processes where both anodic and cathodic process are activation controlled. If the brass is exposed to corrosive environment, different phases size can be distinguished between the second and the third harmonic map. However, similar pattern could be distinguished between both figures. Higher corrosion current represents areas of β-phase, while lower values should be associated with α-phase.
Figure 3. Scanning electron image of brass surface prior to measurements (a). Map of calculated local current over brass (b).

According to Equations 7–8, calculation of both $\beta$ coefficients is possible based on HA measurements. The spatial distribution of particular parameters is presented on Figs. 4a and 4b. Both coefficients are higher in areas where corrosion current increases according to Fig. 3b. Nonetheless, it is worth to notice that $\beta_a$ is locally characterized by high values. Such behavior would imply that the dynamics of the cathodic reaction (oxygen depolarization, in neutral pH) is locally diversified. There are few possible reasons for such behavior, such as difference in local oxygen demand or locally altered adsorption of oxygen to the active sites. Moreover, the changes in $\beta_a$ Tafel slope lead to different corrosion currents. When the slope is rising, the current increases as well.

It should be noted that according to Equations 7–8 calculated Tafel coefficients depend on perturbation amplitude $U_0$, as was also discussed by Gabrielli et al. It was concluded that high correlation between obtained results was visible for perturbation amplitudes no greater than 30 mV. Higher values of $U_0$ should not be considered due to limitation resulting from application of Besell function.

In order to determine the type of control, series of Tafel plot were made. Polarization curves, as shown in Fig. 4c, are characterized by activation control of cathodic and anodic process. Average values of $i_{corr}$ and both $\beta$ coefficients resulting from Tafel’s plot with their standard deviation have been presented on Fig. 4d. Furthermore, the average values of the same parameters based on harmonic measurements were added for comparison. The results of both experiments are correspondent.

In order to compare changes of corrosion current with material structure, an additional measurement was made. The main objective of the measurement was one to one correlation of SEM image and corrosion current changes. For the purpose of measurement, sample surface was significantly limited through coverage by insulator. Series of line scans were performed in the limited area. Subsequently, the relevant areas were photographed with SEM in order to compare the results. The obtained corrosion current dependency from the distance was presented on Fig. 5b. Presumably, the corrosion current increased when the probe was located above $\beta$-phase, while decreasing over $\alpha$-phase. For comparison, Fig. 5a presents a white line to mark the place
of measurement. What is worth to mention is that with respect to dif-
fusion field, the line scan may have been performed a few micrometers
below or above the marked line.

Conclusions

The application of harmonic response in local scale was presented.
Using appropriate measuring setup and mathematical approach, it is
possible to calculate corrosion current and both Tafel coefficients
in microscale. In case of harmonic response analysis in scanning
mode choice of appropriate frequency is crucial for reasonable time
of experiment, and therefore, reliable results.

It is crucial to emphasize that presented values with HAM tech-
nique were obtained by equation which consists of certain approx-
imation described in this work. Nevertheless, applying of harmonic
analysis in local scale allowed to reveal differences in corrosion cur-
rent of particular phases.

Acknowledgment

The authors gratefully acknowledge the financial support from
the Polish National Science Centre (NCN) under grant no.
2015/19/N/ST5/02659. The authors thank prof. Artur Zielinski for
fruitful discussion and help with solving technical problems.

References