CORROSION BEHAVIOUR OF LOW CARBON STEEL IN ARTIFICIAL SEAWATER USING TP, LP, EIS, HARMONIC ANALYSIS (HA) AND NEW METHOD DYNAMIC ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (DEIS)

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Abstract

Electrochemical methods play an important role in corrosion researches so; there is a wide range of techniques for the monitoring of corrosion. The aim of this paper was to collect experimental data with different methods and to find correlation between them. The corrosion behaviour of low carbon steel (AISI 1026) has been studied in artificial seawater using tafel extrapolation (TP), linear polarisation (LP), electrochemical impedance spectroscopy (EIS), harmonic analysis and very a new method dynamic electrochemical impedance spectroscopy (DEİS). All results were determined and compared with each other.

Keywords Corrosion; Low carbon steel; Tafel extrapolation (TP); Linear polarisation (LP); Electrochemical impedance spectroscopy (EIS); Harmonic analysis (HA); Dynamic electrochemical impedance spectroscopy (DEİS);

1. Introduction

Low carbon steel is a very important alloy that finds wide applications in industry, metallurgy and construction fields. Also, carbon steels has been widely employed as a construction materials for pipe work in the oil and gas production such as down hole tubular, flow lines and transmission pipelines [1-2].

Instantaneous corrosion rate measurements are often obtained through the use of electrochemical measurements such as LP, ER and EIS. Electrochemical impedance spectroscopy has become a very powerful tool for the analysis of corrosion processes. It used as a method of general applicability for investigation of localized corrosion. But EIS has limitations. For good results the corrosion system must be stable [3]. Recently, Darowicki et al. [4-5] have presented a new mode (DEIS) of electrochemical impedance measurement. In this method the impedance spectra are determined for narrow periods of time. So, this method can be appropriate for impedance measurements of corrosion. Harmonic analysis response of a system to a sinusoidal voltage or current perturbation has been interest to electrochemists for a number of years [6-7]. The main advantage of harmonic analysis (HA) is that the measurement of corrosion rate does not employ presumed values for the Tafel slopes. Measurements can be undertaken in a fraction of the time of conventional methods (e.g., LP, ER and EIS) [8].

In the present investigation, it is proposed to compare the corrosion behaviour of low carbon steel in artificial seawater with five different electrochemical methods such as TP, LP, EIS, DEIS and harmonic analysis.

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2. Experimental Approach

2.1. Materials

Electrochemical measurements were all carried out in a three-electrode type cell with separate compartments for the reference electrode (Ag/AgCl) and the counter electrode was platinum (Pt) plate. Experiments were performed under nonflowing conditions. The working electrode was a low carbon steel (AISI 1026). The area of this electrode was 0.785 cm^2 and Surface of the working electrode was prepared by grinding abrasive paper of 400-1800 gradation. Next they were rinsed with distilled water and degreased with acetone. Before main experiments the working electrode was immersed in aerated artificial seawater and allowed to stabilize for 30 minutes [9]. The low carbon steel (AISI 1026) had the composition; (wt. %): 0.22-0.28 C, 0.90-1.10 Mn, 0.3 Ni, 0.3 Cr, 0.04 (max) P, 0.05 (max) S and the rest Fe. Chemical Composition of the artificial seawater is given in Table 1. [10]. pH of this water was 8.10 and Resistivity was (ρ) 25 Ω-cm. We measured resistivity with Nilsson electrical resistance Conductance meter model 400.

Table 1

Analyze of artificial seawater that we used

Component	Concentrations, g/l
NaCl	24,53
MgCl$_2$	5,20
Na$_2$SO$_4$	4,09
CaCl$_2$	1,16
NaHCO$_3$	0,201
KBr	0,101
H$_3$BO$_3$	0,027

2. Results and discussion

2.2.1 Corrosion current at open circuit potential

In order to estimate the corrosion current at the open circuit (corrosion) potential, the electrode potential must be perturbed according to any of the methods of Tafel extrapolation, linear polarisation or EIS. All these three methods were investigated and the results shall be compared below.

2.2.1.1. Tafel extrapolation (TP)

This technique uses data obtained from cathodic and anodic polarization measurements. Cathodic data are preferred, since these are easier to measure experimentally. The total anodic and cathodic polarization curves corresponding to hydrogen evolution and metal dissolution are superimposed as dotted lines. To determine the corrosion rate from such polarization measurements, the Tafel region is extrapolated to the corrosion potential, as shown in Fig. 1.
The polarisation resistance (Rp) was calculated using the Stern–Geary Equation. [12]:

$$i_{corr} = \frac{\beta_a \beta_c}{2,303(\beta_a + \beta_c)} \frac{1}{R_p} \qquad (1)$$

$$i_{corr} = \frac{B}{R_p} \qquad (2)$$

β_a, β_c and $\dot{\text{I}}$corr values obtained from fig.1. Results were listed in table 2. The experiment curves were recorded in anodic and cathodic direction at the scan rate of 1 mVs^{-1}.
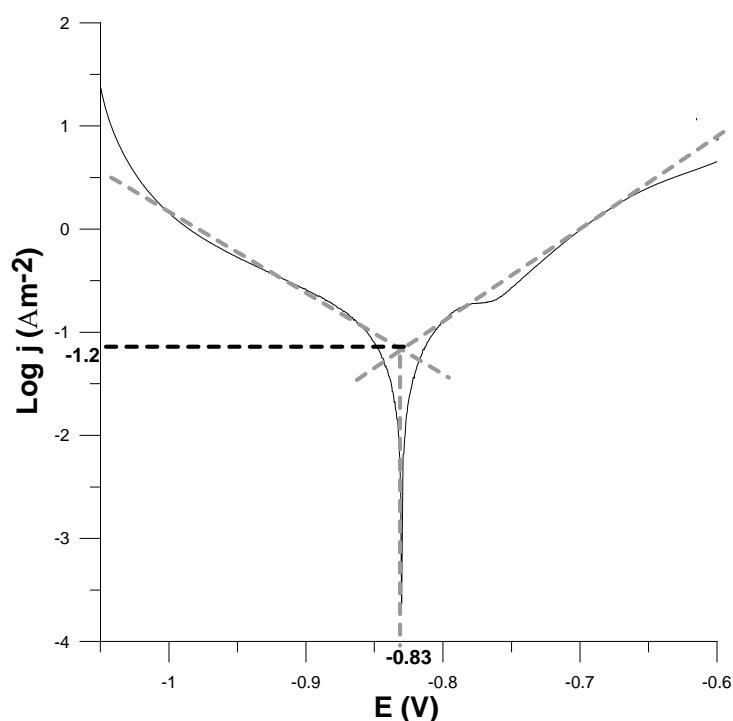

Fig.1. Tafel extrapolation curve of low carbon steel in artificial seawater

2.1.1.2. Linear polarisation resistance (LP)

The linear polarisation resistance method is an alternative to determining the corrosion rate at the open circuit potential. The perturbation potential was +/- 20 mV. Our scan rate was 0.166 mVs^{-1}. We obtained R_p value from fig. 2. If we compared E_{corr} and R_p results with Tafel extrapolation method (table 2.), there were some differences between them. Those differences were reported in a previous research study [13-14-15-16]. We thought that such differences could depend on scan rate and frequency. Because, we obtained similar results from comparison of linear polarisation and electrochemical impedance spectroscopy methods.

Table 2

A comparison of R_p and E_{corr} results from linear polarisation and Tafel extrapolation methods

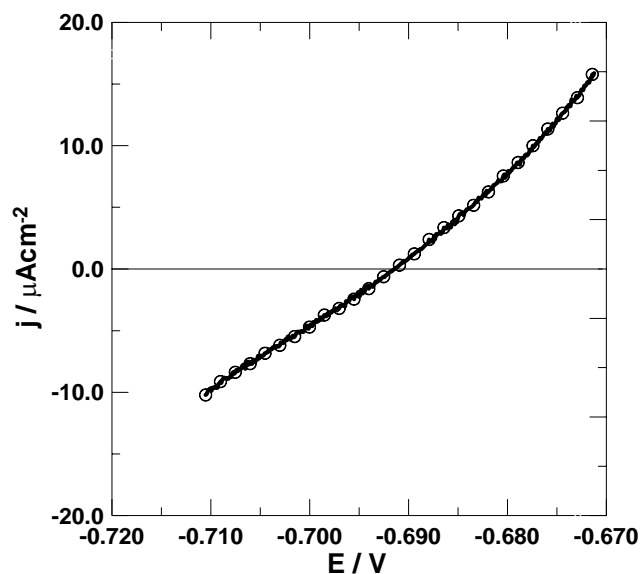| Analyze	R_p (Ωcm^{-2})	E_{corr} (V)
Linear polarisation	2630	-0.667
Tafel extrapolation	3150	-0.823

Fig. 2. Linear polarisation curve of low carbon steel in artificial seawater

2.1.1.3. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range 1 MHz to 0.01 Hz with a signal amplitude perturbation of 10 mV.with PARSTAT 2263 electrochemical Analyze equipment. We obtained fig. 3. and fig.4. from EIS measurement. For such curves we used the Zsimpwin 3.20 software to evaluate the polarisation resistance and the results are given in table 3.
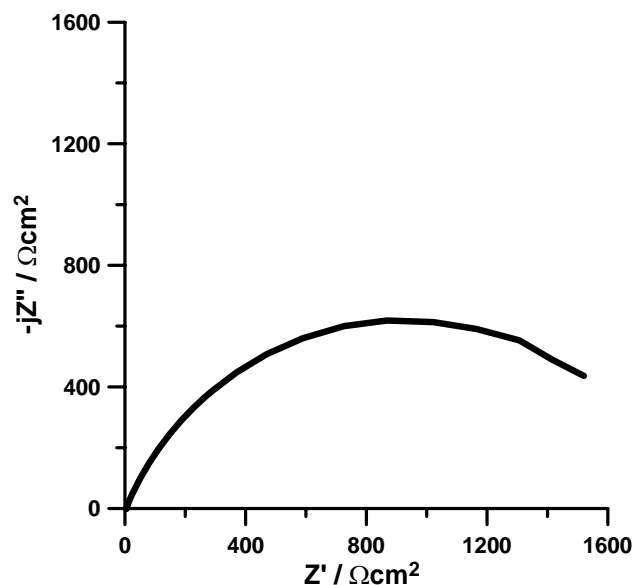
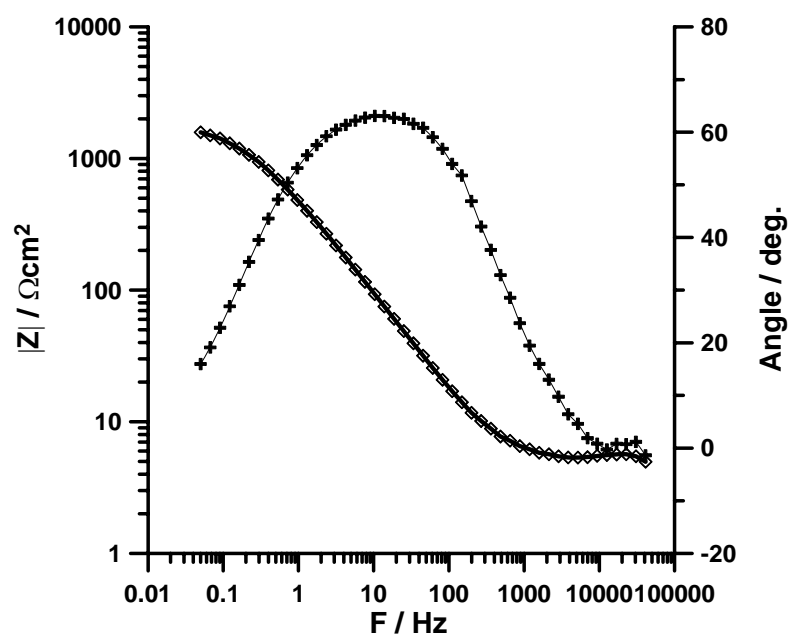Fig. 3. Nyquist plot for the low carbon steel in artificial seawater solution.

Fig. 4. Bode plots for low carbon steel in artificial seawater solution.

Table 3
A comparison of *Rp* and *İcorr* results that obtained by all techniques

Analyze	$R_P(\Omega cm^{-2})$	$\dot{I}_{corr}\ (\mu Acm^{-2})$
Tafel extrapolation	3150	6.302
Linear polarisation	2630	7.548
EIS	2900	6.845
Harmonic Analysis	2683	6.80
DEIS	2174	9.13

2.2. Harmonic analysis (HA)

Harmonic analysis (HA) measurements were performed by means of voltage sine perturbation signal (amplitude 100 mV, frequency 7 Hz), generated by National Instruments DAQ-PCI 6052 A/D card. Parstat 2263 potentiostat was used a current-voltage converter.

2.2.1 Introduction of HA

In this technique the frequency of the measuring voltage must be selected carefully. Selection of the perturbation amplitude U_0, must be compromised between achieving steady-state conditions and the achievement of satisfactory accuracy in the measurement of the second and third harmonic components. It has been suggested that values of U_0 between $\beta/2$ and β (where β equals ba = 2.303 or bc = 2.303, whichever is smaller) are suitable [17] with errors in the vicinity of 10% when $U_0/\beta = 1$ and becoming negligible as U_0/β approaches 0.5. The capabilities of the instrumentation must also be considered when selecting U_0.

For the stern model of electrical double layer, an electrode polarized near the corrosion potential by a sinusoidal voltage of angular frequency ω and voltage amplitude U_0, over a period t, will yield a faradaic current density, current obtained by [18];

$$i = i_{corr}(exp(2.3U_0 sin\ \omega t/b_a) - exp(2.3U_0 sin\ \omega t/b_c)) \tag{3}$$

Where b_a and b_c were the anodic and cathodic Tafel slopes, and i_{corr} was the corrosion current density. The amplitudes of the harmonic components can be obtained by Fourier series expansion of the expantial terms in eq. (3) above,

$$i_f = i_0 + i_1 sin\omega t - i_2 cos2\omega t - i_3 sin3\omega t+..... \tag{4}$$

The first term of the series in eq.(4), i_0 is the DC component of the current caused by faradaic rectification, while the coefficients of the other components (i_1, i_2, $i_{3\ .....}$) were the amplitudes of the harmonic components. The magnitudes of the first three harmonic components were given by eqs. 5-6 and 7;

$$i_1 = i_{corr}\left(\frac{1}{\beta_a} + \frac{1}{\beta_c}\right)U_0 \tag{5}$$

$$i_1 = -i_{corr}\left(\frac{1}{\beta_a^2} + \frac{1}{\beta_c^2}\right)\frac{U_0^2}{4} \tag{6}$$

$$i_1 = -i_{corr}\left(\frac{1}{\beta_a^3} + \frac{1}{\beta_c^3}\right)\frac{U_0^3}{24} \tag{7}$$

Eqs. (5)–(6) can be employed with both small and large amplitude alternating voltages, with the value of U0 being limited by the potential range validity of Eq. (3). Devay and Maszaros [18] also proposed the following equations for the determination of corrosion currents and Tafel slopes;

$$i_{corr} = \frac{i_1^2}{\sqrt{48}\sqrt{2i_1 i_3 - i_2^2}} \tag{8}$$

$$\frac{1}{b_{a,c}} = \frac{1}{4.6U_0}\left(\frac{i_1}{i_{corr}} \pm 4\frac{i_2}{i_1}\right) \tag{9}$$

In response to the use of Eqs. (8) and (9), other authors [19] expressed concerns that a term was omitted from Eq. (5), which is equal to three times the absolute value of the third harmonic, and it should not be neglected, i.e., Eq. (5) becomes;

$$i_1 = i_{corr}\left[\left(\frac{1}{\beta_a} + \frac{1}{\beta_c}\right)U_0 + \frac{1}{8}\left(\frac{1}{\beta_a^3} + \frac{1}{\beta_c^3}\right)U_0^3\right] \tag{10}$$

and alters Eqs. (8) and (9) to;

$$i_{corr} = \frac{(i_1 + 3i_3)^2}{\left[4\sqrt{3}\left|2(i_1 + 3i_3)i_3 + i_2^2\right|^{1/2}\right]} \tag{11}$$

$$\frac{1}{b_{a,c}} = \frac{1}{4.6U_0}\left(\frac{i_1 + 3i_3}{i_{corr}} \pm 4\frac{i_2}{i_1 + 3i_3}\right) \tag{12}$$

2.2.2. Results of HA

An amplitude of 100 mV and frequency of 7 Hz were utilized in all HA measurements. The HA measurements were compared in table 3. The first, second and third harmonic currents were determined and the data were processed manually by using Eqs. (10)–(12). All measurement results are similar with each other. The reason of

differences was stated in *2.1.1.2.* part. But those differences were very small value. In table 4, we compared Tafel results and harmonic analysis results. There was good correlation between them. HA, spectrum was shown at fig. 5.

Table 4

A comparison of β_a, β_b and $\dot{I}corr$ results obtained by Tafel extrapolation and Harmonic analysis

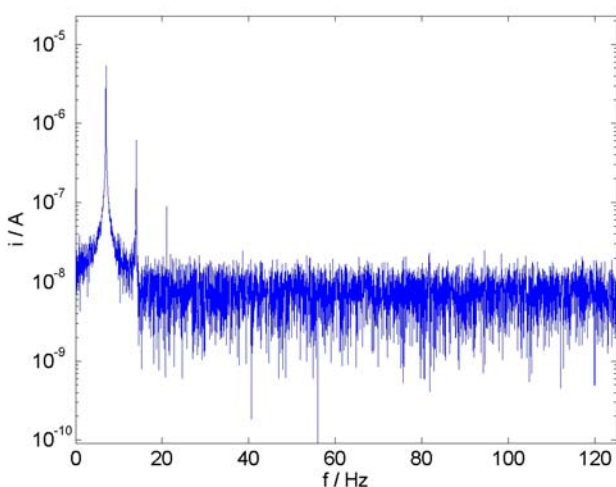| Analyze	$\beta_a(mV)$	$\beta_b\ (mV)$	$\dot{I}_{corr}\ (\mu Acm^{-2})$
Tafel extrapolation	58	216	6.3
Harmonic analysis	57.147	158.83	6.8

Fig 5. Harmonic analysis spectrum of low carbon steel in artificial seawater solution.

2.3 Dynamic electrochemical impedance spectroscopy (DEIS)

   Dynamic electrochemical impedance spectroscopy (DEIS) measurements were performed on a setup assembled in the Gdansk University of Technology by Department of Electrochemistry Corrosion and Materials Engineering [11]. Generation of the AC signal was performed with a National Instruments Ltd. PCI-6120 digital-analog card. The same card was used for measurement of the current and voltage signals. A KGLstat v. 2.1 potentiostat was used as a current-voltage converter. The perturbation signal was a package composed of voltage sinusoids of the frequency range 4.5 kHz to 700 mHz. The low limit of measurement frequency depended on the length of analyzing window (10s). In the other words the low frequency limit depended on the time scale of the analysis performed. The sampling frequency was 12.5 kHz. The amplitudes of all sinusoids were equal to 5mV.

   We took two measurements by using this method. First was 10 minutes after prepared our solution for experiment (fig. 6). From this figure we obtained that our system was non-stationary. So this method should be also use before every experiment for to take knowledge about system. At second measurement it was clear that our system was stationary. Impedance values were changing very slowly (fig. 7). Results that obtained from this method were listed at table 3.
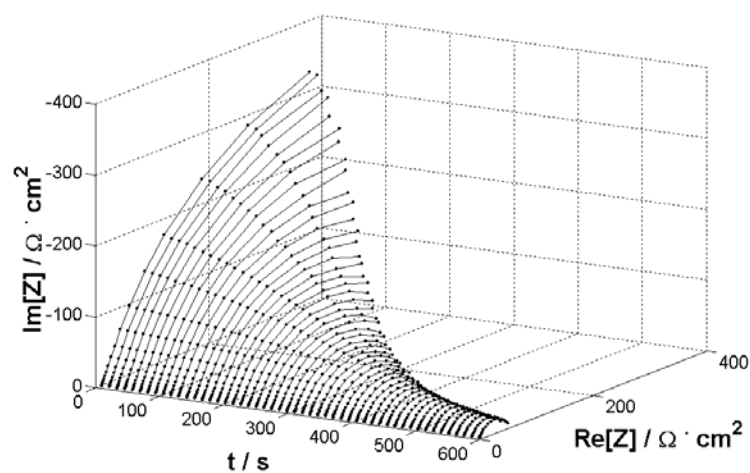
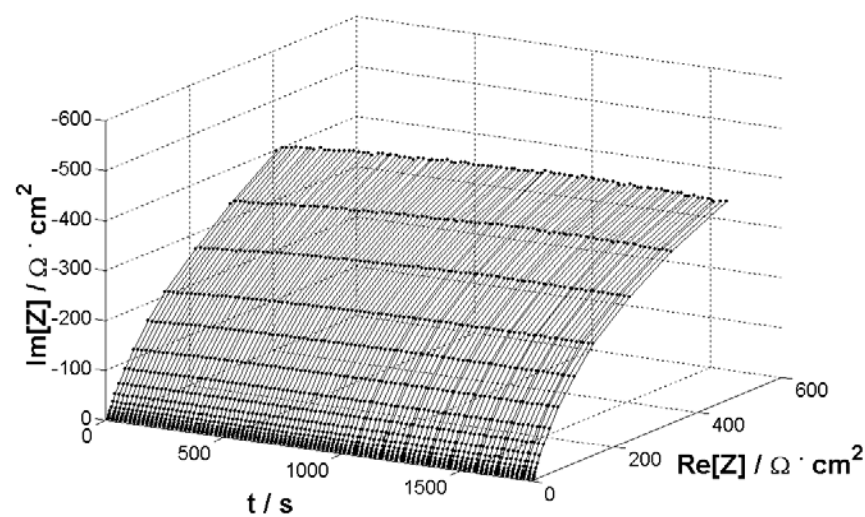Fig.6. First measurement of DEIS (after 10 minutes)

Fig.7. Second measurement of DEIS (after 30 minutes)

3. Conclusions

- Low carbon steel has been studied using Tafel extrapolation, Linear polarisation, EIS, Harmonic analysis and DEIS. All results were having small differences between each other. But those differences depend on measurement technique of methods.
- The results of this study demonstrate that HA is a relatively rapid measurement technique, which will vary depending on the frequency, chosen for the analysis.
- There are a few practical problems with HA technique. The levels of the harmonics can be quite low compared to the fundamental and can be hard to measure, especially in the presence of any noise.
- DEIS method should be use before every experiment for to take knowledge about system. It gives perfect results about system.

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