



Time evolution of Electrochemical Impedance spectra of cathodically protected steel in artificial seawater



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HIGHLIGHTS

- Usability of EIS data for better cathodic protection control was investigated.
- Time evolution of Electrochemical Impedance spectra was evaluated.
- Quantity of physical and electrochemical processes was evaluated by usage of Chi2 function.
- EIS proved to be useful for hydrogen evolution detection.

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ABSTRACT

Usability of Electrochemical Impedance Spectroscopy data for better cathodic protection control was investigated. Carbon steel – S235JR2 grade specimen were exposed in artificial seawater environment. Samples were polarized and their potentials corresponded to four different cathodic protection degrees. Time evolution of Electrochemical Impedance spectra was investigated. Goodness of fit function (X^2) was analysed in terms of proper time-constant quantity determination. It was possible to observe and detect occurrence of new phenomena by X^2 evaluation. Weight-loss corrosion coupons were used to calculate corrosion rates. At initial stage of exposition impedance measurements complemented proper protection potential data. Quantity of physical and electrochemical processes was evaluated and linked to the state of specimen providing valuable supplementary data. EIS proved to be useful for hydrogen evolution detection which is a great risk which has to be recognised and prevented.

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1. Introduction

Organic coatings combined with cathodic protection (CP) are currently the most widely utilised means of corrosion protection for buried and immersed steel structures [1]. These corrosion protection technologies are complementary. Organic coatings form a physical barrier to isolate a construction from environment [2–4]. However, to achieve a full degree of long lasting corrosion protection a proper cathodic protection (CP) system has to be implemented as well. Cathodic calcareous sediments which may form on a CP protected surface also provide a coating-like effects. Oxygen diffusion to the protected surface is slowed down and effective electrode surface area is decreased. Thus sediments reduce protection current demand as well. Typical cathodic sediments mostly consist of CaCO_3 and $\text{Mg}(\text{OH})_2$ [5].

Protection current can be either supplied by sacrificial anodes or by an Impressed Current Cathodic Protection (ICCP) [6,7]. Sacrificial anodes are passive and do not require any additional equipment. However there are also methods for driving galvanic anodes [8,9]. Cathodic rectifiers (ICCP) are far more complex devices [10]. They are either manually or microcomputer controlled units. Thus CP rectifiers provide better control of cathodic polarization conditions than galvanic anodes. Microcomputer (uC) driven CP rectifiers might have additional features, such as an internal GPS module, synchronous on/off potential switch, data logger and data transmission device i.e. GSM, intranet, landline [11,12] enabling access to accurate and real time information. Furthermore, application of an uC gives an opportunity to introduce additional functionality to the CP rectifier, such as electrical resistance corrosion probes inspection or EIS probes [13,14].

Knowledge of surface condition is crucial to efficient corrosion protection. Electrochemical Impedance Spectroscopy (EIS) is a technique capable of providing valuable electrical data which can be associated with surface evolution and kinetics of electrochemi-

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cal processes. Application of this technology as a diagnostic tool for CP systems has been proposed. Proper data interpretation of collected EIS data could reduce costs of CP maintenance, especially when visual examination costs are considered. There are several controversies regarding cathodic protection criteria, especially with determination of instantaneous corrosion rates in cathodic protection conditions. Furthermore potential criteria and widely used potential measurements give no information about corrosion rates. Thus the ultimate goal is knowledge of momentary corrosion rates of a cathodically polarized sample.

In this paper an experiment involving EIS investigation of steel samples polarized to different cathodic protection levels has been proposed. Time evolution of EIS spectra and determined corrosion rates have been investigated. Every EIS data set was fit to three cell models consisting of one, two and three time constants. Goodness of fit function (X^2) was analysed in terms of proper time-constant quantity determination, which translates to number of currently occurring phenomena and system complexity. Chi squared is a measure describing discrepancies between measured values and a model under investigation. The lower X^2 value is the better the fit is (1).

$$X^2 = \sum \frac{(\text{measured} - \text{expected})^2}{\text{expected}} \quad (1)$$

2. Materials and methods

A set of circular S235JR2 steel samples has been prepared. Steel composition is presented in Table 1. Specimen radius equalled 6 cm and their surface area 28.25 cm². For preliminary EIS experiments additional round electrodes were prepared in the same manner but their area equalled 1 cm². Electrodes were mounted in epoxy resin and their surface was sandblasted to Sa3 NACE “white metal blast cleaning” [15].

Specimen were immersed in 30 l of artificial seawater in 50 × 20 × 30 cm tanks. The water was composed in agreement with ASTM D1141-98 standard and is presented in Table 2 [16]. Salts with lower content than KBr were not used in the experiment.

For long exposures four potentials corresponding to different cathodic protection levels were chosen (Table 3). Mesh mixed metal oxide auxiliary electrodes (15 × 20 cm) and saturated Zn/ZnSO₄ reference electrodes were used. The auxiliary electrode – anode were placed approximately 40 cm away from the working electrodes to ensure uniform current distribution. Reference electrode was placed close to the specimen to diminish IR related potential drop. For every CP protection level a dedicated potentiostat was used.

Samples were exposed to artificial seawater for approximately 9 months. Throughout the entire course of the experiment EIS Electrochemical Impedance Spectroscopy measurements were performed. Prior to the long term exposure also preliminary EIS tests were carried out on smaller (1 cm²) electrodes. For both exposures same sample surface preparation method and EIS experiment conditions were chosen. Preliminary EIS experiments were conducted in order to investigate if there are any features in EIS spectra which could be linked to corrosion rates and potential cathodic protection criteria at various cathodic potentials.

Amplitude of the perturbation signal equalled 15 mV and frequencies ranged from 0.05 to 50 kHz. In the initiatory experiment the DC offset ranged from 0 mV to –450 mV against Open Circuit Potential (OCP), EIS spectra were measured every –25 mV. The OCP of the specimen corresponds to approximately –695 mV against Ag|AgCl|Seawater reference electrode.

During the long term exposure EIS experiments were performed at DC offset potentials corresponding to the chosen cathodic protection levels (Table 3). Gamry Interface 1000 potentiostat was used to drive the experiments.

In order to identify more rapid changes in the specimen at the beginning of the exposures, shorter time intervals between measurements were selected. They equalled from 2 to 7 days. As the exposures proceed the intervals were increased to approximately 30 days.

In order to determine corrosion rate of the samples weight loss coupons were manufactured. Coupons' surface was also sandblasted to the Sa3 – NACE “white metal blast cleaning” in order to achieve exactly the same degree of surface preparation as the electrodes [15].

3. Results and discussion

EIS spectra obtained during the preliminary experiment are presented in Figs. 1 and 2. Several states of the system can be distinguished from EIS spectra, their correspondence to different cathodic protection levels and electrode potentials. When a specimen was cathodically polarized the low-frequency impedance of the system increased. This occurred until potential of approximately –0.125 V vs OCP was reached (Fig. 1). The low frequency phase angle shifted towards lower frequencies indicating reduced reaction time constant. Between –0.125 V and –0.375 V it was hard to distinguish local phase angle minimum due to its flattening. Below –0.375 V vs OCP low frequency resistance decreased because of water decomposition and hydrogen evolution reaction. Equivalent R(QR(QR)) circuit model was proposed with two time constants. Electrolyte resistance and charge transfer resistance in function of potential are presented in Figs. 3 and 4 respectively. Calculated electrolyte resistance was potential independent and equalled approximately 5 Ω. Initial low charge transfer resistance could be explained by occurrence of two reactions – iron oxidation and hydrogen reduction. Charge transfer resistance reached its maximum of ~13,5 kΩ at –175 mV vs OCP (–870 mV vs Ag|AgCl|Seawater electrode) due to diffusion limitation of oxygen transport. When potential equalled –870 mV vs Ag|AgCl|Seawater DNV RP-B401 cathodic protection criterion for aerobic conditions was met [17]. At lower potentials charge transfer resistance dropped down due to oxides and hydroxides species reduction and ultimately water decomposition [18–20]. Goodness of fit was satisfactory and equalled less than 10^{–4}. This indicates that techniques such as EIS or DEIS (Dynamic Electrochemical Impedance Spectroscopy) with a probe electrode could be applied in real life situation. Complementary data to current/potential relationship could be beneficial for instance when hydrogen embrittlement risk is concerned.

Long term exposures of coated specimen were performed in order to investigate applicability of EIS to investigate changes of corrosion protected systems – coated and cathodically protected.

Exemplary EIS Nyquist and Bode plots for four protection levels are presented in Figs. 5–8. Firstly, it was noticed that spectra between analysed cathodic protection levels differ. The initial spectra were similar for all protection levels and consisted of one time constant. However they evolved in time – new time constants appeared due to surface alterations. The longer the exposure lasted the more complex the system was to analyse. Determination of a proper electrical equivalent model became formidable. Determining numerical relations linked to corrosion rate was even harder. Only a few representative spectra are presented in the graphs to make the data more accessible to the viewer. All of the plots illustrated below develop gradually.

A free-corroding sample can be considered as a reference. According to the impedance spectra the electrolyte resistance was consistent and equalled approximately 1–2 Ω. The low frequency impedance limit of the sample altered with time, ranging from 20 to 150 Ω. Initially the impedance modulus increased but over time it started to decline. The initial increase of sample's

Table 1
Composition and ultimate tensile strength of S235JR2 steel.

Element ultimate tensile strength	C [%]	Mn [%]	Si [%]	P [%]	S [%]	N [%]	UTS [N/mm ²]
S235JR steel	0,17–0,20	Max 1,3	–	0,045	0,045	0,009	360–490

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