Application of Electrochemical Impedance Spectroscopy to evaluate cathodically protected coated steel in seawater

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HIGHLIGHTS

- Samples were coated with an intact and defected coating.
- Long term seawater expositions of samples kept at four different protection levels were performed.
- Electrochemical Impedance Spectroscopy spectra evaluation during the exposition.
- Corrosion rate investigation of cathodic protected samples.

ARTICLE INFO

ABSTRACT

Two types of organic coated carbon steel (S235JR2 grade) electrodes were exposed to artificial seawater environment. One prepared type was defect free while the other one had an intentionally introduced $\phi 0.5$ cm coating defect. Both kinds of samples were polarized during the exposure to four potentials corresponding to four different cathodic protection levels. Evolution of their EIS spectra is presented in this paper. Results obtained in the experiment indicate that protective organic coating condition could be estimated and monitored in time based on EIS investigations. If a sample is defected EIS allows recognition of overprotected and unprotected sample. Distinguishing a fully protected sample from partially protected sample based on EIS was troublesome.

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1. Introduction

Organic coatings are the most often and commonly used anti-corrosion technique [1,2]. Coatings provide passive barrier against the aggressive environment. However, coatings provide protection as long as they remain intact and active pigments are not replenished [3,4]. On the other hand, cathodic protection (CP) system is capable of reducing corrosion rate even if a coating fails. CP is an electrochemical technique thus it's not capable of stopping corrosion completely but it significantly reduces its rate [5,6]. Organic coatings and CP are jointly used to provide a holistic anti corrosion protection [7]. Without a coating current demand of CP system could be so great that it might be technically impossible to implement. A proper coating system may reduce current demand by over 99%. Even after years of operation coatings can reduce cathodic current demand by 70–80% or more [8]. However, it is impor-

tant to remember that certain coatings are not compatible with CP systems. Therefore it remains a factor and has to be taken into account when a complex corrosion protection system is designed [9]. A working CP system produces OH^- ions at the cathode increasing the alkalinity of the environment. There is always a risk that an ill-working CP system may cause coating deterioration and disbondment [10–12]. Especially if a critical potential is reached and water decomposition and hydrogen evolution occurs [13–15]. A cathodic protection system can rapidly increase coating deterioration without proper supervision.

Modern CP rectifiers are often controlled by microcomputers. Unlike old manually adjustable units functionality of the modern rectifiers can be easily extended. CP rectifiers could be equipped with automatic on/off switcher, GPS time stamp, data logger and transmission unit, a watchdog, electric resistance corrosion coupon probe electrode, array of reference electrodes for stray current detection or other devices [16–21]. Due to the rapid electronic device development even Electrochemical Impedance Spectroscopy (EIS) module could be fit [22]. EIS is a technique capable

of yielding information about impedance of the investigated system in the investigated frequency bandwidth. EIS data can be linked to the occurring electrochemical processes or physical properties of the investigated system [23–25].

In this paper an experiment involving EIS investigation of S235JR2 grade steel samples coated with organic coating under several cathodic protection conditions has been proposed. The coatings have been immersed in seawater for as long as 9 months. EIS data has been collected in order to verify its usefulness as a supplementary CP evaluation technique.

2. Materials and methods

A set of circular steel electrodes made of S235JR2 was manufactured. Composition of S235JR2 is presented in Table 1. Their radius equalled 6 cm and surface area 28, 25 cm^2. Steel substrates and cable connectors were embedded in epoxy resin and insulated from environment.

Specimens were sandblasted to the Sa3 NACE "white metal blast cleaning" surface roughness [26]. Substrates were covered with a commercially available epoxy coating. According to the product specification the coating was designed to be applied as a single or multi-layer system. The coating was also confirmed to be CP compatible. Average coating thickness equalled 350 μm and its standard deviation 13 μm. Two sets of samples were prepared. One type of specimen was defect-free, the other one had a ϕ0.5 cm holiday (Fig. 1).

Furthermore, weight loss coupons made of 100 cm^2 S235JR2 steel grade were manufactured and exposed under the same conditions as the test specimens. Their surface was prepared in the same manner as EIS specimens.

In accordance to European Standard EN 12,473 "General principles of cathodic protection in sea water" four potentials corresponding to four different cathodic protection levels were chosen (Table 2). For every protection level a separate set of samples (no holiday/ϕ0.5 cm holiday) was prepared. During the entire exposure for every cathodic protection level there were dedicated water tanks and potentiostats to control electrochemical potential of specimens assigned. Specimens were immersed in 50 × 20 × 30 cm glass tanks filled with 30° l of artificial seawater. Artificial sea water composition was prepared in agreement with ASTM D1141-98 standard. Details are presented in Table 3 [27]. Salts with lower content than KBr were not used.

Anodes – auxiliary electrodes made of 20 × 15 cm mixed metal oxide covered titanium mesh were utilized. Saturated Zn|ZnSO$_4$ reference electrodes were chosen and placed as close as possible to the specimen in order to reduce IR drop. In order to ensure a good cathodic current distribution anodes were located as far away from the working electrodes as possible. During the exposure weight loss coupons and samples were electrically shortened. For EIS experiments Ag|AgCl|Seawater reference electrode was used. Every sample was then electrically disconnected and evaluated separately.

Electrochemical Impedance Spectroscopy experiments were performed at variable intervals. At the beginning of the exposure intervals between experiments were short: ranging from 2 to 7 days. Once specimens condition stabilized measurements were taken less often – and intervals increased gradually from 7 to 30 days. Perturbation amplitude equalled 15 mV and frequency band-
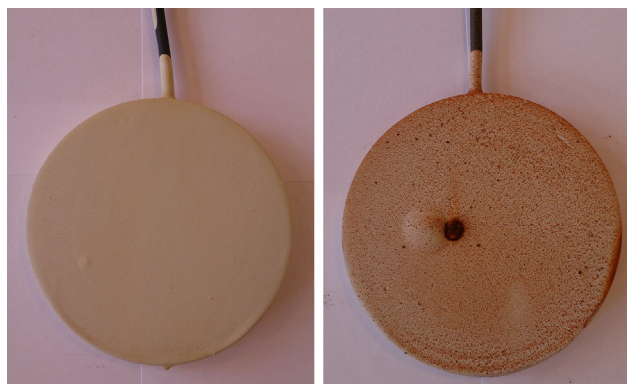

Fig. 1. Samples after exposure. A defect-free sample (left) and a sample with ϕ0.5 cm holiday (right).

Table 2
Cathodic protection levels and potentials of specimen.

Cathodic protection level	Potential vs Zn/ZnSO$_4$ (saturated) [mV]	Potential vs Ag|AgCl| Seawater [mV]
No protection	Free corrosion potential On average +363	Free corrosion potential On average −675
Under protection	+288 mV	−750
Full protection	+88 mV	−950
Overprotection	−162 mV	−1200

width ranged from 0.05 Hz to 10 kHz. All tests were carried out using Gamry 1000 potentiostat.

3. Results and discussion

Long term exposure of coated specimens was performed in order to review applicability of EIS for investigation of changes of cathodically protected systems in time. Specimens without a holiday were treated as reference samples. Differences between samples without coating disruptions and intentionally defected ones and their time evolution under four CP protection levels regimes were anticipated to be observed.

Defect free specimen without any degree of CP during the experiment exhibited a straight-like line in their Bode spectrum (Fig. 2). Phase angle was very close to 90° in the entire frequency range. A slight shift towards lower phase angles was observed in the low frequency range only, approaching a DC limit. A capacitive nature of the response suggests that the coating remains intact during entire exposure. Positive phase angle shift at the lowest frequencies indicates slow coating deterioration. Its character became more resistive. At low frequencies impedance moduli remained higher than 10^9 Ω. If a surface area of the specimen is taken into account it translates to approximately 2.8·10^{10} Ωcm^2. The impedance moduli and phase angles measured were characteristic for an unbroken, intact and fully protective coating (2).

Unlike the case of the unprotected sample, the other specimens show indications of coating deterioration. It is more than likely that cathodic protection accelerates coating deterioration. Characteristic spectra evolution of fully coated specimens was observed for all samples with any degree of cathodic protection (Figs. 3–5).

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