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Synergistic corrosion inhibition on galvanically coupled metallic materials

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ABSTRACT

The present paper brings report on a newly observed effect of synergistic corrosion inhibition of galvanically coupled metals by the combination of inhibitors. 1,2,3-Benzotriazole and $Ce(NO_3)_3$ were investigated here as a synergistic inhibiting mixture for Zn + Fe model galvanic couple. Microelectrode array cell specifically designed for investigation of inhibition processes on multi-material galvanic couples was applied for the first time utilising scanning vibrating electrode technique (SVET) as method of galvanic current quantification. The obtained results demonstrate a strong potential of inhibitor combinations for high efficiency suppression of corrosion processes when different inhibition mechanisms are employed at the same time. This effect is observed especially in the cases when the same inhibitor combination does not show synergy on the uncoupled single Zn and Fe metals.

1. Introduction

Multi-material combinations are actively introduced nowadays to different applications especially in the transport industry where light weight structures are very attractive from standpoint of energy saving and reduction of carbon footprint. In the case of joining dissimilar conductive materials the galvanic corrosion can become a limiting factor. Since the current anti-corrosion approaches are mainly suitable for single-material structures, the need of development of the new strategies of active and passive corrosion protection for the multi-material applications is evident.

One of the promising approaches recently suggested is application of self-healing corrosion protection coatings based on the inhibitors encapsulated in "smart" nanocontainers [1]. However, the efficient inhibitors which can be used for galvanically coupled materials yet to be discovered. 1,2,3-Benzotriazole (BTA) is among the effective corrosion inhibitors for different metals especially for copper and its alloys as has been known for more than sixty years [2]. BTA acts as a mixed type inhibitor through adsorption and different Cu-BTA complex formation mechanisms providing its predominant effect on inhibition of anodic reaction [3]. Similarly, BTA forms a protective complex compound with Zn [4–6] and Fe [7]. BTA co-operates synergistically with some chemical species like benzylamine [8] and sodium dodecylsulphate (SDS) [9]. Also very known is the synergism with iodide anions [10] based on co-adsorption of I^- and BTA and more effective complex formation with Cu or Fe [7]. However, according to the literature, the synergistic effect amongst BTA and other compounds for corrosion prevention of galvanically coupled metals was never observed before, equally like for any other combinations of corrosion inhibitors.

The driving idea for the present work was to combine an anodic corrosion inhibitor with a cathodic one in scope of synergistic suppression of galvanic corrosion on Zn-Fe model couple. 1,2,3-Benzotriazole (BTA) was chosen as the anodic inhibitor taking into account the arguments presented above, while cerium (III) nitrate was selected as the cathodic one. Cerium cations are known cathodic inhibitors, forming blocking hydroxide precipitates due to local pH increase at cathodic sites [11–14]. However, the inhibition efficiency in this case depends on the intensity of cathodic reaction, since deposits with different barrier properties can be formed [15].

In this work additionally to conventional electrochemical impedance spectroscopy (EIS) method the scanning vibrating electrode technique (SVET) was used especially for monitoring of galvanic corrosion [16]. As a new development the recently proposed multi-electrode cell for SVET [17] was modified for standalone Zn and Fe electrodes and separate galvanic combination. The use of SVET allows to detect locally the anodic and cathodic activities and can thereby complement significantly the integral EIS results.

2. Experimental

2.1. Electrochemical measurements

In this work three inhibitor-containing solutions were tested: BTA and $Ce(NO_3)_3$ inhibitors with 0.005 M additions and the mixture of same inhibitors of 0.005 M gross inhibitor concentration (0.0025 M of each) in 0.05 M NaCl corrosive medium.

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EIS measurements were carried out using a three-electrode cell consisting of a saturated calomel reference electrode, a platinum wire counter electrode and the sample (pure Zn, Fe or Zn + Fe couple) as working electrode with exposed area of 0.785 cm^2 for each metal. The measurements were performed using an AutoLab PGSTAT 302N with FRA2 (Ecochemie). Selected frequency range was from 10^5 to 10^{-2} Hz, with a 10 mV RMS of sinusoidal perturbation. All the spectra were recorded at open circuit potential. ZView (Scribner Associates Inc.) software was used for fitting the impedance data.

SVET was applied to observe cathodic and anodic currents based on local ionic fluxes using Applicable Electronics Inc. (USA) instrumentation controlled with the ASET software from ScienceWares (USA). The vibrating microelectrode had a 10–20 μm spherical platinum black tip and vibrated with 20 μm amplitude at the distance of 100 μm above the sample surface.

The multi-electrode cell for SVET was made using pure metal Zn and Fe wires (MaTeck GmbH) with diameter of 250 μm embedded into inert epoxy resin (Epo-Kwick (Buehler GmbH)) mount [17]. The surface of multi-electrode array was renewed routinely before experiments with 2500 grit silicon carbide paper, rinsed with Millipore deionised water and dried with pure ethanol.

2.2. Calculation of corrosion parameters

The values of the inhibition efficiency (*IE*) were calculated using the following equation:

$$IE = \frac{CR_0 - CR_{inh}}{CR_0} \quad (1)$$

where CR_0 is the corrosion rate in the non-inhibited medium, estimated by the SVET current or the inverse of charge transfer resistance (R_{ct}) from EIS data in 0.05 M NaCl solution and CR_{inh} is the corrosion rate in the presence of inhibitor.

Synergistic parameter (*S*) was calculated using equation suggested by Aramaki and Hackerman [18]

$$S = \frac{1 - IE_{1+2}}{1 - IE_{12}} \quad (2)$$

where $IE_{1+2} = (IE_1 + IE_2) - (IE_1 \cdot IE_2)$. The parameters IE_1, IE_2 and IE_{12} are calculated inhibition efficiencies for inhibitors 1, 2 and the mixture of 1 and 2, respectively. The values $S > 1$ indicate the synergistic behaviour of selected inhibitor combination.

3. Results and discussion

Typical impedance spectra for bare Fe and Zn electrodes and galvanic combination of these metals (Zn + Fe) show only one well defined time constant which is related to the electrochemical corrosion process on the metal surface. The data presented in Bode plots (Fig. 1) clearly demonstrates the higher resistance at low frequencies in the case of inhibitor-containing electrolytes, while the pure 0.05 M NaCl solution causes remarkably higher corrosion after 2 h of immersion for bare Zn and Fe metals (Fig. 1a and b). At low frequencies the impedance values obtained on Fe (Fig. 1a) in the electrolyte with Ce^{3+} cations are comparable to those for BTA-containing solutions and to the mixture of these inhibitors. In the case of Zn (Fig. 1b) the Ce^{3+} and the mixture solution show slightly higher impedance values than BTA-containing electrolyte. The EIS spectra for Zn + Fe galvanic combination demonstrate clearly the superior performance of solution with mixture of inhibitors above cases with single inhibitors. Moreover, the addition of Ce^{3+} only promotes the corrosion activity on galvanically coupled metals (Fig. 1c).

To estimate the charge transfer resistance (R_{ct}) and consequently the corrosion current density the impedance data was fitted using simple equivalent circuit with one time constant. All the fitting results are also presented as solid lines together with experimental Bode plots in Fig. 1. The fitted R_{ct} values, inhibition efficiency factors (calculated using Eq. (1)) and the values of synergistic parameters *S* (estimated by Eq. (2)) are presented in Table 1. The selected inhibitors show a clear inhibition for Zn and Fe. However, the mixture of inhibitors demonstrates synergistic effect only for Zn + Fe galvanic couple, where the factor $S = 6.09$ clearly exceeds the unity.

The EIS technique is well suited for characterization of the corroding single metals. However, in the case of galvanic couples the situation is more complicated. When two or more metals are electrically coupled the EIS response is normally dominated by the more active electrode and do not characterise the whole galvanic system. Therefore application of EIS for characterization of inhibition efficiency on galvanic couples is not so straightforward although gives some first general indications.

Since the synergistic corrosion inhibition of Zn + Fe galvanic couple was the main goal of this study, the SVET method was additionally employed to estimate the localised corrosion activity on Zn + Fe couple.

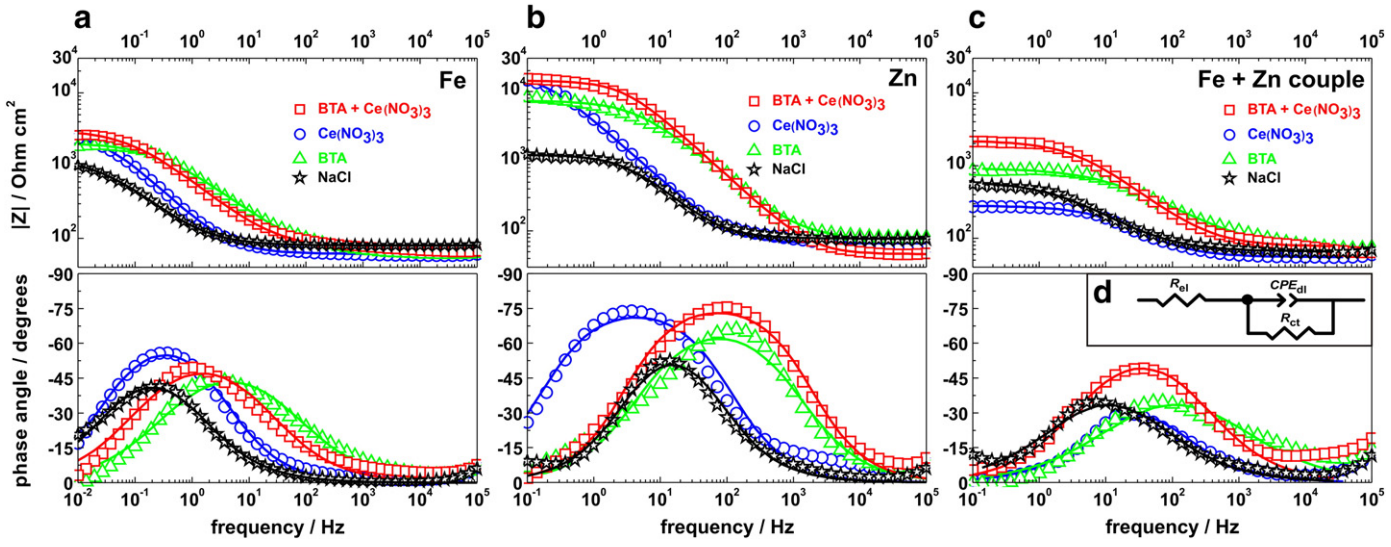

Fig. 1. Bode plots obtained after 2 h of immersion in 0.05 M NaCl with 0.005 M addition of Ce^{3+} and BTA inhibitor and mixture of inhibitors with 0.0025 M of Ce^{3+} + 0.0025 M of BTA for Fe (a), Zn (b) and Fe + Zn couple (c). Used equivalent circuit (d) with R_{el} (electrolyte resistance), CPE_{dl} (constant phase element for double layer capacitance) and R_{ct} (charge transfer resistance).