



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 $\text{Ce}(\text{NO}_3)_3$ 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.

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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 $\text{Ce}(\text{NO}_3)_3$ 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 cm² for each metal. The measurements were performed using an AutoLab PGSTAT 302N with FRA2 (Ecochemie). Selected frequency range was from 10⁵ 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 · *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 Ce³⁺ cations are comparable to those for BTA-containing solutions and to the mixture of these inhibitors. In the case of Zn (Fig. 1b) the Ce³⁺ 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 Ce³⁺ 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.

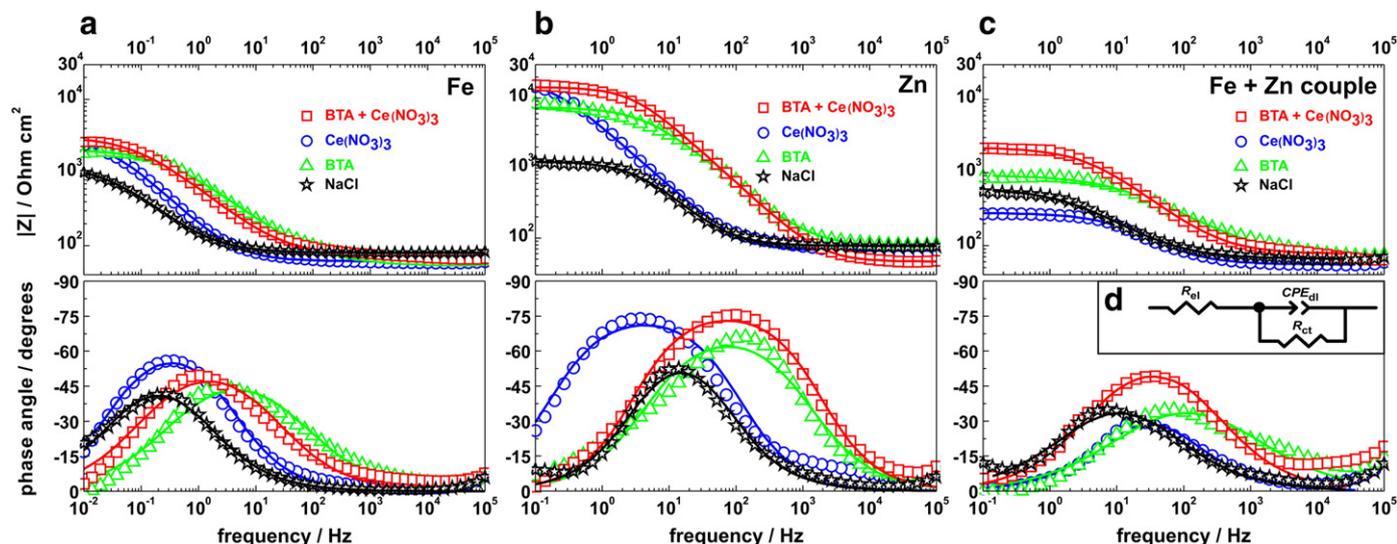


Fig. 1. Bode plots obtained after 2 h of immersion in 0.05 M NaCl with 0.005 M addition of Ce³⁺ and BTA inhibitor and mixture of inhibitors with 0.0025 M of Ce³⁺ + 0.0025 M of BTA for Fe (a), Zn (b) and Fe + Zn couple (c). Used equivalent circuit (d) with *R*_{el} (electrolyte resistance), *CPE*_{dl} (constant phase element for double layer capacitance) and *R*_{ct} (charge transfer resistance).

Table 1

Estimated charge transfer resistances (R_{ct}) and accumulated (cathodic + anodic) ionic (SVET) currents (I_{sum}) for all studied systems. Calculated inhibition efficiencies (IE) and synergistic parameter (S).

Metal	Solution	EIS		
		R_{ct} (k Ω cm 2)	IE	S
Zn	NaCl	1.163	0	
	Ce(NO $_3$) $_3$	19.162	0.939	
	BTA	7.336	0.841	
	Ce(NO $_3$) $_3$ + BTA	14.328	0.919	0.119
Fe	NaCl	1.164	0	
	Ce(NO $_3$) $_3$	2.878	0.596	
	BTA	2.036	0.428	
	Ce(NO $_3$) $_3$ + BTA	3.072	0.621	0.610
Fe + Zn	NaCl	0.539	0	
	Ce(NO $_3$) $_3$	0.226	-1.394	
	BTA	0.862	0.374	
	Ce(NO $_3$) $_3$ + BTA	2.194	0.754	6.091
Metal	Solution	SVET		
		I_{sum} (μ A cm $^{-2}$)	IE	S
Fe + Zn	NaCl	140.7	0	
	Ce(NO $_3$) $_3$	400.4	-1.845	
	BTA	118.1	0.161	
	Ce(NO $_3$) $_3$ + BTA	9.2	0.935	36.54

It was recently demonstrated that this approach has a high potential for screening the inhibiting properties of various compounds for different metals [17].

In Fig. 2a the schematic diagram of used multi-electrode/SVET cell is presented. The photograph in Fig. 2b shows the locations of embedded Zn and Fe electrodes in the test cell. In SVET maps (Fig. 2c–f) the anodic and cathodic activities are well defined on Zn and Fe electrodes, respectively, when these metals are galvanically coupled. Anticipatively no remarkable corrosion activity is observed by SVET on the uncoupled Zn and Fe electrodes because of significantly lower currents and their high

localisation with cross screening effect [17]. Thus the suggested multi-electrode approach with SVET detection fits better for the testing of galvanic couples than single-metal microelectrodes.

To characterise the activity of the Zn + Fe galvanic system the sum of both measured cathodic and anodic ionic currents was calculated by: $I_{sum} = |I_{AN}| + |I_{CAT}|$. As it can be seen from Fig. 2 and Table 1 the single Ce(NO $_3$) $_3$ and BTA inhibitors do not show a strong corrosion inhibition. In the case of Ce $^{3+}$ there is even an opposite effect which leads to an increase of the anodic and cathodic ionic currents (Fig. 2d). The observed effect also correlates well to the EIS data in Fig. 1c. The mixture of Ce $^{3+}$ and BTA decreases significantly the corrosion activity. Both anodic and cathodic currents are suppressed and almost invisible on the SVET map (Fig. 2f). The synergy factor calculated from measured ionic currents in this case is significantly above 1 ($S = 36.5$) demonstrating a high synergy between BTA and Ce $^{3+}$ cations. Since the SVET considers both the anodic and cathodic activities, the higher S is observed in comparison with EIS, where mainly the site with lower resistance responses. The result seems even more remarkable when taking into account the two times lower concentration (0.0025 M) of each particular inhibitor in comparison with 0.005 M single inhibitor solutions. Interestingly the synergistic effect between these inhibitors is observed only in the case of galvanic couple when for single Zn and Fe metals the synergism was not observed. This effect can be explained by the fact that the single metals have localised anodic and cathodic zones continuously moving and evenly distributed along the surface. It does not allow establishment of well defined cathodes and anodes especially at the initial period. In contrast the clear separation of anodic (Zn) and cathodic (Fe) zones occurs in the case of galvanic coupling. This separation leads to local acidification on Zn and a local alkalisation on the Fe surface. Thus the optimal conditions on Zn for BTA and on Fe for Ce $^{3+}$ are created. At the cathodic areas (Fe electrode), due to the local pH increase, the deposition of cerium hydroxide occurs [11–14]:

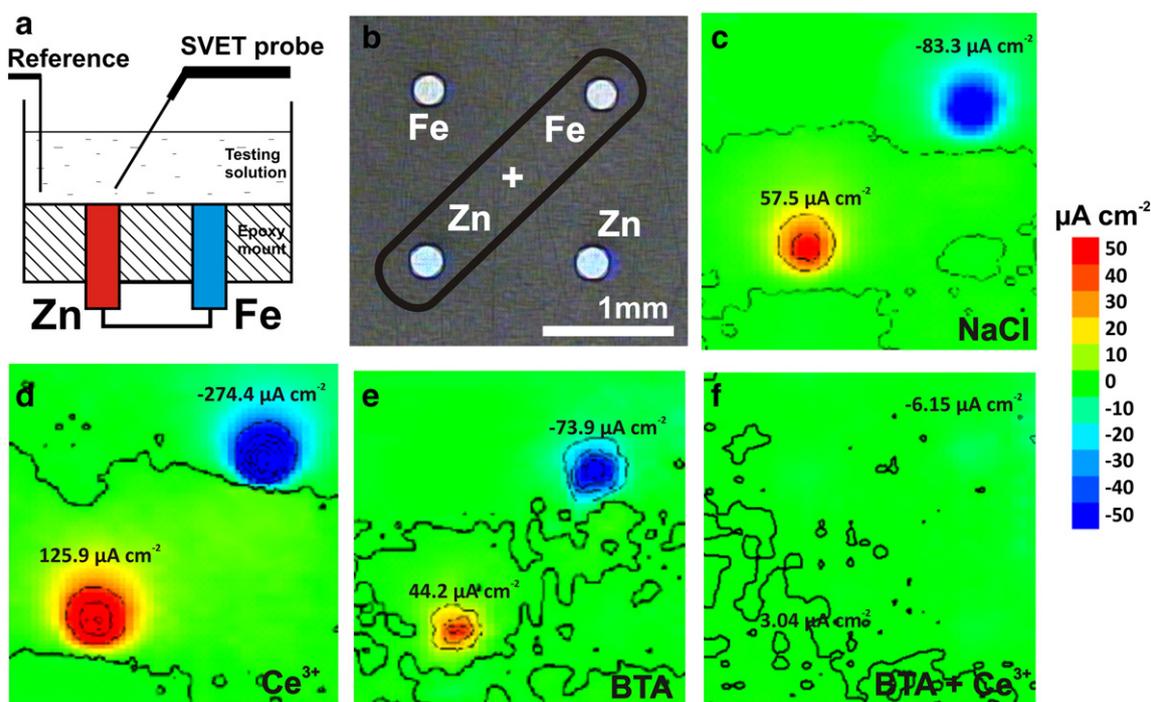


Fig. 2. Diagram of SVET microelectrode cell concept for Zn + Fe galvanic system (a), microphotograph of the galvanic cell configuration (b) and obtained SVET maps taken after 2 h of immersion in different inhibitor solutions with Fe and Zn electrodes electrically coupled in 0.05 M NaCl (c) and addition of inhibitor 0.005 M Ce(NO $_3$) $_3$ (d), 0.005 M BTA (e) and 0.0025 M Ce(NO $_3$) $_3$ + 0.0025 M BTA (f).

Concurrently in anodic areas, especially at lower pH values the BTA is acting as an adsorption based inhibitor [2–7,19] which results with a very high synergistic inhibiting action for Zn + Fe galvanic couple.

4. Conclusions

A novel combination of the adsorption based anodic inhibitor 1,2,3-benzotriazole (BTA) and the cathodic inhibitor ($\text{Ce}(\text{NO}_3)_3$) demonstrates a superior synergistic inhibition effect for the electrically connected Zn + Fe galvanic couple, in spite of the fact that the same combination does not show synergy on the uncoupled single Fe and Zn metals. Specific synergy only for naturally active galvanic Zn + Fe system can be explained with very effective separated specific localised inhibition mechanisms for cathodic ($\text{Ce}(\text{NO}_3)_3$) and anodic sites (BTA). The presented approach can be used to design highly effective active corrosion protection systems for multi-material assemblies used in different industries, particularly in the case of galvanised steel.

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