



# Observation of L-cysteine enhanced zinc dissolution during cathodic polarization and its consequences for corrosion rate measurements



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## ABSTRACT

The corrosion inhibiting and accelerating effect of L-cysteine on Zn were correlated with the formation of Zn oxides by means of a novel coupling of impedance spectroscopy (EIS) with atomic emission spectroelectrochemistry (AESEC). A plateau of anodic Zn dissolution was discovered in the cathodic branch of the polarization curve, hidden by the large cathodic current. The effect of L-cysteine at all pH values and all concentrations was to increase the plateau current. The effect was most pronounced at high pH suggesting a synergy between hydroxide and L-cysteine. Due to the presence of Zn plateau current, Tafel extrapolation resulted in a wrong estimation of corrosion currents. The contribution of the anodic Zn oxidation in the plateau region to the total current was inversely proportional to the frequency of the AC perturbation.

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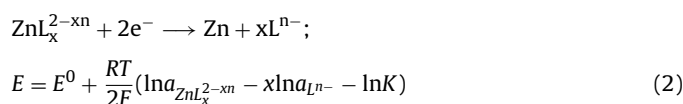
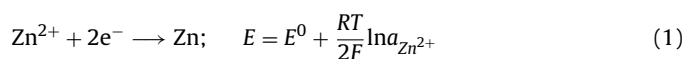
## 1. Introduction

The corrosion resistance of metal substrates is usually related to the structure and composition of the oxide layer on the metal surface [1–9]. The oxide layer on Zn in contact with aqueous electrolytes consists of an outer oxide/hydroxide film (known as Type I Zn oxide) and an inner compact layer (known as Type II Zn oxide) [8,9,10–15,16,17]. The inner layer has been postulated to form by the direct oxidation of Zn to ZnO driven by the cathodic reaction such as oxygen reduction on the surface of the ZnO semiconductor [8,12,13–15,18–20]. Zn<sup>2+</sup> ions may be ejected through the ZnO film and precipitate to Type I Zn porous oxides [4,6,8,9,13,16,21]. One can change the outer precipitated layer by varying the composition of the environment and enhance the barrier properties of Type I oxides. The barrier properties are related to the thickness, compactness, porosity, electrical conductivity and surface charge of these oxides. [1,2,4–6,9,22].

Organic ligands are often added to the environment to serve as corrosion inhibitors [22–24]. Inhibition may occur when the organic molecule seals the outer porous Zn oxides by adsorption on their surface enhancing the barrier between the metal and the

environment [22,25,26]. However, organic ligands may also destabilize the oxide film by increasing the solubility of the metal cations, resulting in an activation of the surface, evidenced by an enhanced dissolution rate [23,27,28]. In the recent work [29], we demonstrated that for Zn, L-cysteine showed both a slight inhibiting effect at low concentrations (probably due to L-cysteine adsorption on Zn oxides/hydroxides) and an accelerating effect at higher concentrations, associated with L-cysteine complexation with Zn<sup>2+</sup>. Although this may render dubious the use of L-cysteine as a practical inhibitor for Zn, it represents an excellent system for a closer look at the mechanisms of inhibition and acceleration by organic molecules.

The presence of complexing ligands (L) such as hydroxide or L-cysteine can result in a complete dissolution of Zn oxides on Zn surface with a cathodic shift of the equilibrium potential for Zn dissolution as given by (see Table 1 for the notation) [25,26]



The ligand induced Zn dissolution mechanism differs from the dissolution-precipitation mechanism by the absence of Zn(II) precipitates on the metal surface due to the complexation of Zn<sup>2+</sup> in the solution bulk. In the presence of small concentrations of the ligand

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**Table 1**  
Notation.

$Zn^{2+}$	free Zn cation in solution
$Zn(II)$	Zn containing species with Zn valence of two
RSH	L-cysteine
RSSR	L-cystine
$E$	electrical potential
$E^0$	standard $E$
$j_e$	total current measured by potentiostat
$j_e^*$	convoluted $j_e$
$j_{Zn}$	Zn current corresponded to formation of soluble Zn cations measured by AESEC
$j_{Zn}^{ins}$	Zn current corresponded to formation of insoluble Zn oxides
$j_{Zn}^{**}$	deconvoluted $j_{Zn}$
$j_c^*$	cathodic current calculated as $j_e^* - j_{Zn}$
$j_c^{**}$	cathodic current calculated as $j_e^{**} - j_{Zn}^{**}$
$j_{partial}^E$	$j_{Zn}$ or $j_c$
$j_{corr}^E$	corrosion current estimated by the direct measurement of $j_{Zn}^{**}$ from polarization curves at $E(j_e = 0)$
$j_{corr}^{AESEC}$	corrosion current estimated by Tafel extrapolation of $j_e$ to $E(j_e = 0)$
$j_{corr}^{SG}$	corrosion current estimated from Stern Geary relation
$b_a$	anodic Tafel slope
$b_c$	cathodic Tafel slope
$n$	number of electrons in electrochemical reactions
$Q_{ins}$	quantity of insoluble Zn corrosion products
$F$	Faradays constant
$v_{ZnO}$	rate of chemical dissolution of Zn oxides
$t$	time
$t_c$	time constant
$w$	frequency of AC perturbation
$f$	flow rate of electrolyte
$A$	surface area
$T$	temperature
$R$	gas constant
$R_p$	polarization resistance
$R_\Omega$	resistance of electrolyte
$R_x$	resistance of $x$ element
$Q_x$	constant phase element of $x$
$\alpha_x$	exponent of $Q_x$
$C_x$	concentration of $x$ species
$a_x$	activity of $x$ species
$i$	input discrete signal
$i^*$	output discrete signal
$i^{**}$	deconvoluted $i^*$ signal
$h$	transfer function
$\beta$ and $\tau$	parameters of $h$
$K$	stability constant of complex formation

the anodic dissolution of Zn may be limited by the concentration of the ligand. For a corroding system, it may prove difficult to discern the effect of a ligand on the anodic reaction as much of the anodic activity may be masked by the cathodic current. This makes the use of conventional electrochemical methods (polarization curves and/or electrochemical impedance spectroscopy (EIS)) difficult to interpret since a significant anodic current may be “hidden” underneath the cathodic branch.

In this work we use the AESEC (atomic emission spectroelectrochemistry) methodology [30] to measure the Zn dissolution rate as a function of potential during polarization experiments. In this way, the hidden anodic dissolution of Zn, masked by a large cathodic current is revealed, and the influence of L-cysteine on the anodic dissolution of Zn may be brought to light. The experiments were performed with and without  $10^{-2}$  M and  $10^{-3}$  M L-cysteine additions to show either an inhibiting or an accelerating effect of the L-cysteine respectively. Moreover, neutral and alkaline solutions were used to observe possible mutual effects of  $OH^-$  and L-cysteine on Zn dissolution. As the reaction also involves the formation of a slightly soluble oxide film, EIS/AESEC experiments were also conducted for the systems. The novel combination of conventional EIS with AESEC permits a direct monitoring of the effect of AC perturbations on the elemental dissolution rate [31,32].

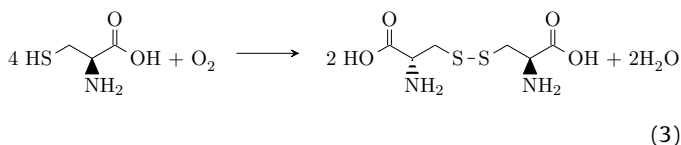
## 2. Experimental

### 2.1. Materials

A commercial hot dip galvanized steel (HDG) bonder plates (type: HDG/5) were supplied by “Chemetal”, Germany. The average thickness of the galvanization layer (approximately 0.1 % wt Al added to the Zn) amounts 20  $\mu$ m. The sample was cut into 2 cm  $\times$  4 cm coupons, cleaned with tetrahydrofuran, acetone and ethanol in ultrasonic bath for 10 min, dried under flowing nitrogen, then immersed in 1 M NaOH solution at 50 °C for 30 s, further rinsed with water and finally dried under flowing nitrogen again. The NaOH treatment was used to simulate the oxidizing effect of a conventional alkaline degreasing and to remove the residual oxides [33]. The experiments were performed in 0.5 M NaCl (analytical grade, VWR Prolabo, France) containing solutions in purified water (Millipore™ system, USA, 18 M $\Omega$  cm) with additions of  $10^{-2}$  M and  $10^{-3}$  M L-cysteine (analytical grade, Sigma Aldrich, Germany) at pH values of 6 and 12. The pH of solutions was adjusted by the addition of 1 M NaOH.

### 2.2. Aeration of L-cysteine solutions

Prior to the pH adjustment, the solutions containing L-cysteine were aerated for 20 min by an air pump in order to partially oxidize L-cysteine to its dimer L-cystine [29]:



In our previous publication [29] we showed that after 20 min of aeration 5 % of L-cysteine at pH 6 and 30 % of L-cysteine at pH 12 is converted to L-cystine independent of the L-cysteine concentration over the range of  $10^{-5}$  -  $10^{-3}$  M and the time of aeration.

### 2.3. AESEC technique

#### 2.3.1. Measurement principle

The on-line measurement of the Zn current during electrochemical impedance spectroscopy (EIS) and polarization experiments was performed by atomic emission spectroelectrochemistry (AESEC), described in detail elsewhere [30]. Briefly, it consists of an electrochemical flow cell coupled with an inductively coupled plasma atomic emission spectrometer (ICP-AES). In the flow cell, a reaction between the sample (hot dip galvanized steel) and an aggressive electrolyte occurs, leading to the production of dissolved ions and/or insoluble oxides. Then, the electrolyte is transported downstream to the ICP-AES, where its composition is continuously analyzed. The ICP-AES analysis shows only the soluble part of the released Zn(II) independent of its chemical form ( $Zn^{2+}$ ,  $Zn(RS)_2^{2-}$ , ...) etc, while the insoluble oxides or adsorbed Zn(II) species are not directly detected. This soluble part of the released Zn(II) was expressed as an equivalent Zn current ( $j_{Zn}$ ) and was calculated from the instantaneous Zn concentration ( $C_{Zn}$ ) using Faraday's law:

$$j_{Zn} = nFC_{Zn}f/A \quad (4)$$

where  $n = 2$  is the assumed oxidation state of Zn,  $F$  is the Faraday's constant,  $f$  is the flow rate and  $A$  is the geometric surface area. All symbols are presented in Table 1. The normalization of  $j_{Zn}$  by the geometric surface area was done only for convenience and does not imply that electrochemical reactions were uniformly distributed on the surface.

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