

Understanding the Roles of Additives in Metal Electrodeposition: An Experiment for Undergraduate Physical Chemistry Students

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Abstract. The goal of the present laboratory experiment is to deepen the understanding of the roles of additives in metal electrodeposition and some other concepts that are essential in electrochemistry. In this practical laboratory session, students first learn the blocking effect of additives on the deposition of metal by the potentials of the $E-t$ curve. Second, the utilization of the Tafel curves to analyse the electrochemical activity of deposits is described. Finally, it is shown how and why the electrochemical activities of the deposits change with the Watts solution with and without additives. The experiment is completed in a 4-h laboratory period for pairs of students in physical chemistry lab class. This material is also suitable for an analytical chemistry lab class.

Introduction

Electrodeposition, as a simple method, was introduced in the preparation of metal coating[1-3]. Electrodeposition process is normally associated with nucleation and crystal growth. The higher the nucleation rate, the finer the crystal grains grow. The mechanism of nucleation and growth determines the surface morphology and microstructure of the deposits as well as its properties[4]. In this method, additives such as thiourea and saccharin are commonly added to the deposition electrolytes, which are easy to be incorporated in metal deposits owing to its strong adsorbability and its consequent influence on the interfacial characteristics[5, 6]. Various types of organic and inorganic additives have been studied extensively to obtain enduring, uniform, and compact metal coatings for prevent corrosion. These additives tend to suppress electrodeposition currents at a fixed potential or, alternatively, increase the potential required for a given current. Therefore, it is important to show students that the roles of additives and that some experimental precautions must be taken into account in metal electrodeposition.

The aim of this laboratory experiment is to help the students to understand (i) the blocking effect of additives, (ii) the utilization of the Tafel curves and (iii) the changes of electrochemical activities of the deposits with additives.

Experimental

This is a 4-h experiment (one lab session) performed with 24 students working in couples. Students have to prepare, outside of the lab, a lab report of the experiment which should include a detailed response to the questions. The electrodeposition of nickel, for example, is shown in this laboratory experiment. Compositions of the deposition bath used are Watts basic solution: 250 g/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ + 45 g/L $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ + 40 g/L H_3BO_3 (pH = 4.2, adjusted by adding diluted NaOH or H_2SO_4 solution) and Watts bright solution: the basic solution + 20 ml/dm³ additives. The additive is a mixture that contains 10 g/L sodium benzene sulfonate, 100 g/L saccharine, 150 ml/L XNF and 10 g/L sodium dodecane sulfonate. Electrochemical measurements were performed in a three-electrode

cell consisting of a glassy carbon disc (4 mm diameter) as working electrode, a platinum foil of 1.5 cm² as counter electrode and a saturated calomel electrode as reference electrode. Use an appropriate current density such as 1 A/dm² and galvanostatically deposit nickel for 2 min, to obtain the GC/Ni electrodes and $E-t$ curves.

Tafel curve experiments was conducted in 3.5% NaCl with the GC/Ni obtained in the Watts solutions with and without additives as working electrodes, SCE as reference electrode and Ni sheet as counter electrode. Record the potential as a function of time. From the open circuit potential scan the potential ± 250 mV from cathodic to anodic potentials using a scan rate of 0.5 mV/s, to obtain the Tafel curves, then analyse the Tafel plots to identify the corrosion potential E_{corr} , corrosion current density i_{corr} and corrosion rate R_p and using the Tafel equation determine the kinetic coefficients α and i^0 .

Results and Discussion

Fig. 1 shows a series of galvanostatic curves ($E-t$) using the set of solutions with and without additives. Here, we can see the strong impact of the additives in the deposition solutions. The deposition potential in Watts bright solution is more negative than that in the basic solution. These additives tend to increase the potential required for the given current. The adsorption of surfactants aggregates onto electrodes can have large effects on the kinetics of the electron transfer and consequently on the electrodeposition process. The effect on the electron transfer rates includes blocking of the active sites by the surfactants, and electrostatic interactions between electroactive species and adsorbed surfactants[7]. Due to those effects it is possible to modify the crystals growth mode and tailor the morphology and structure of the electrodeposits. Thus, this simple experiment will help students to understand that the roles of additives is in fact related to the adsorption.

Thickness of nickel deposit is $0.41 \mu\text{m}$ ($j = 1 \text{ A/dm}^2$).

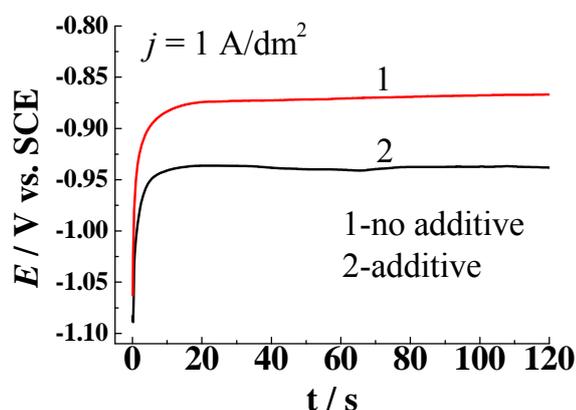


Fig. 1. The $E-t$ curves from the Watts basic solution (1) and the Watts bright solution (2).

$j = 1.0 \text{ A dm}^{-2}$. GC disc $d = 4 \text{ mm}$.

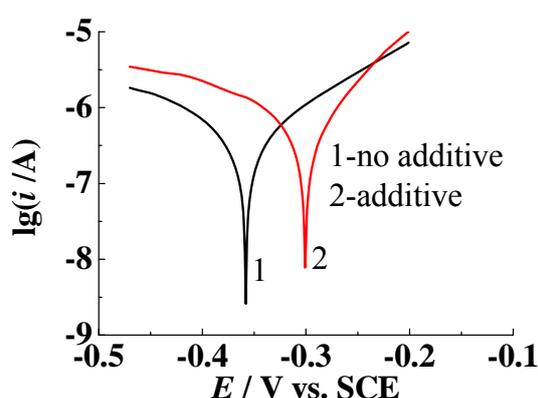


Fig. 2. Tafel curves from GC/Ni electrodes.

1: obtained in Watts basic solution, 2:

obtained in Watts bright solution.

The corrosion performance of the Ni coating on GC electrode (GC/Ni electrode) was studied by potentiodynamic polarization (Tafel curves). For comparison, the potentiodynamic polarisation curves of Ni coating obtained in Watts basic solution and the coating obtained in Watts bright solution were tested as well. The representative curves are shown in Fig. 2. We note that the Tafel slopes are necessarily robust for the extrapolated determination of corrosion current density (i_{corr}), the estimates of i_{corr} are supported by the extrapolation of the cathodic/anodic polarization data and its intersection with the true E_{corr} . The intersection point coordinate of the extended lines for the

straight line part of the anodic and cathodic polarization curves just corresponds to corrosion potential E_{corr} and corrosion current $\lg i_{\text{corr}}$, corrosion rate can be determined by i_{corr}/S , where S is surface area of electrode[8].

The corrosion current density of the Ni-coating sample obtained in Watts bright solution was lower than that of Ni-coating sample obtained in Watts basic solution (Fig. 2), indicating that corrosion resistance of the Ni coating is dramatically improved by the use of additives. It is noted that the additives are able to increase the corrosion of Ni coating considerably. These additives have showed a positive shift of E_{corr} values with respect to the Watts basic solution value indicating the cathodic control of the corrosion reaction.

When $\eta > 100/n$ mV, the reverse reaction rate is negligible compared to the forward reaction rate, the Tafel equation is tenable. The fit results of Tafel curves are shown in Fig. 3.

Calculation methods of the kinetic parameters (exchange current density i^0 , and transfer coefficient $n\alpha$.) by Tafel equation are given here[9]:

$$\eta = a + b \lg i \quad (1)$$

Where $a = -\frac{2.3RT}{\alpha nF} \lg i^0$, $b = \frac{2.3RT}{\alpha nF}$, $\lg i^0 = -\frac{a}{b}$, $i^0 = 10^{-a/b}$, At 323 K (50°C),

$$n\alpha = \frac{2.3RT}{bF} = \frac{0.0640}{b} (T = 323K).$$

(1) no additive (Watts basic solution)

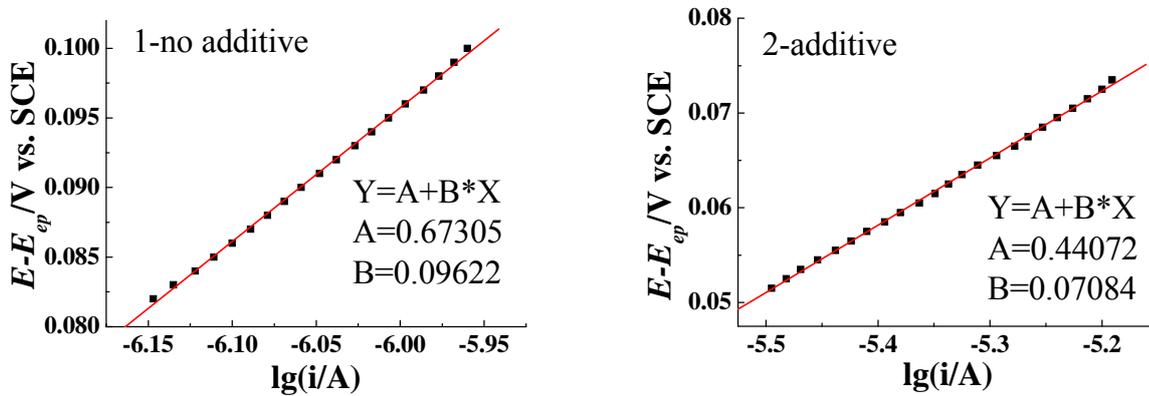


Fig. 3. The fitting results of Tafel slopes (data from Fig. 2)

$$n\alpha = \frac{2.3RT}{bF} = \frac{0.0640}{b} (T = 323K)$$

$$n\alpha = \frac{0.0640}{0.09622} = 0.6651$$

$$i^0 = 10^{-a/b} = 10^{-6.9949} = 1.01 \times 10^{-7} \text{ (A)}$$

(2) Additive (Watts bright solution)

$$n\alpha = \frac{2.3RT}{bF} = \frac{0.0640}{b} (T = 323K)$$

$$n\alpha = \frac{0.0640}{0.07084} = 0.9034$$

$$i^0 = 10^{-a/b} = 10^{-6.2213} = 6.01 \times 10^{-7} \text{ (A)}$$

Thus, the electrochemical activity of the nickel deposited from the Watts bright solution is lower than that from the Watts basic solution.

Summary

These results will help students to realize that the adsorption of surfactants aggregates onto electrodes can have large effects on the kinetics of the electron transfer and consequently on the electrodeposition process. Due to those effects it is possible to modify the crystals growth mode and tailor the morphology and structure of the electrodeposits and increase corrosion prevention. The experiment is completed in a 4-h laboratory period for pairs of students.

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