

ANODIC DISSOLUTION OF NICKEL IN SULPHURIC ACID SOLUTION

K V VENKATESWARAN, P RAMACHANDRAN, V NANDAKUMAR AND S VISVANATHAN

Central Electrochemical Research Institute, Karaikudi - 623 006, INDIA

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Anodic dissolution of nickel is a technique adopted for the electrolytic preparation of nickel salts. This electrochemical route is attractive from the points of view of product purity, ease of preparation and use of nickel scrap as the starting material.

Studies on the anodic dissolution of nickel in sulphuric acid solution are reported with respect to current efficiency and anode potential. The effects of current density, concentration of sulphuric acid and temperature have also been examined. Addition of chloride ion inhibits anode passivation and its role in aiding the dissolution process has been discussed.

Key words: Anodic dissolution, nickel, passivation, chloride addition

INTRODUCTION

Nickel anodes find extensive application in electroplating industries. Considerable amount of research has been done for a better understanding of nickel dissolution in order to produce an anode which will operate with maximum yield of metallic salt and will be immune to passivity over a wide range of plating conditions [1 and 2]. In this context, two types of anodes have been reported, namely, carbon or sulphur depolarised anodes. The function of an ideal soluble anode is to dissolve as completely as practicable and uniformly at low polarisation leaving behind minimum amount of residues which will otherwise contaminate the electrolyte.

Moreover, the anodic dissolution of nickel is significant in the context of electrolytic preparation of salts like nickel sulphate, nickel chloride etc [3 and 4]. In the alternate chemical method, nickel shot and powder are treated with concentrated sulphuric acid which creates problems related to high temperature handling, control of fumes and intake of impurities. Electrochemical method is attractive from the points of view of purity of the product, ease of operation and scrap reuse. In a recent work, nickel plating nodules have been investigated as a source for the electrochemical recovery of nickel in the form of nickel sulphate, which can be used for captive consumption.[5] Anodic behaviour of nickel is influenced by its tendency to become passive exhibiting high dissolution potential. This results in decreased anodic efficiency as low as 5%. In the present study, the anodic dissolution of nickel in sulphuric acid has been investigated. The effect of chloride ion, current density, sulphuric acid concentration and temperature on dissolution efficiency has been studied.

EXPERIMENTAL

The electrolytic cell consists of a one litre beaker with two cathodes of stainless steel of dimension 10 × 2 cm and a centrally located soluble S-nickel anode of the same dimensions. The electrolyte employed for the studies was sulphuric acid solution of concentration ranging from 0.1 to 1.0 M. Chloride addition was made as nickel chloride or sodium chloride and its content in the electrolyte was varied between 0-10 g.l⁻¹. A direct current ranging from 0.1 – 0.7 A was applied using a regulated power supply. Anode potentials were measured and expressed with respect to

saturated calomel electrode (SCE). Electrolysis was carried out for 4h and the dissolution efficiency was calculated from weight loss measurement. The electrolyte was analysed after each experiment for determining the nickel content using EDTA for confirming the weight loss data. In the case of anodic dissolution experiments at higher temperature a thermostatic bath was employed for maintenance of temperature within ±1 K.

RESULTS AND DISCUSSION

The influence of current density on current efficiency for nickel dissolution in 0.1M sulphuric acid solution is shown in Fig. 1. It is clear from the curve that with increase of anodic current density, current efficiency decreases rapidly. Appreciable dissolution rates are possible only at current densities lower than 50 A.m⁻². The decrease in current efficiency at higher current densities results in enhanced oxygen evolution, which promotes the formation of nickel oxide leading to passivation of the electrode [6]



Figure 2 depicts the effect of sulphuric acid concentration on current efficiency at 400 A.m⁻² and 303K. The current efficiency of dissolution which was as low as 15% till 0.5M concentration of sulphuric acid, increased steeply attaining a value of 70% at 1.0 M. concentration. The increase in acid concentration inhibits passivation as follows:



Similar behaviour could be noticed from anode potential measurements illustrated in Table I.

The effect of chloride ion concentration on anodic current efficiency of nickel dissolution at 400 A.m⁻² in 0.1M H₂SO₄ at 303K is shown in Fig. 3. Current efficiency increased steeply from 15% to 95% as chloride concentration increased from 0 to 1.0 g.l⁻¹. Further addition of chloride had little effect on current efficiency. This is due to the adsorption of chloride ions on the anode which facilitates reactivation by aiding the break-down of the anodic oxide film in the following manner:



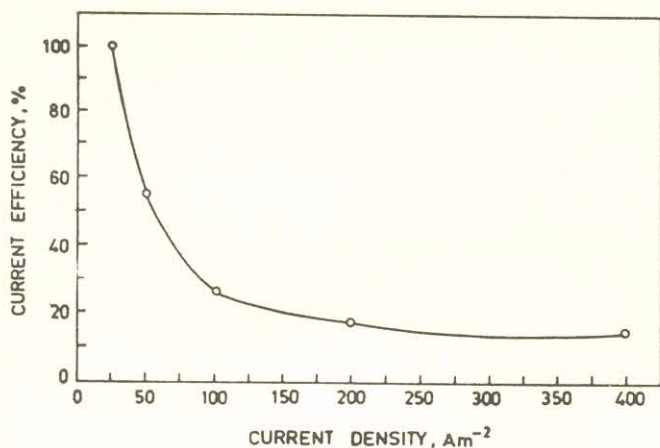


Fig. 1: Effect of current density on current efficiency for anodic dissolution of nickel in 0.1 M H₂SO₄ solution.

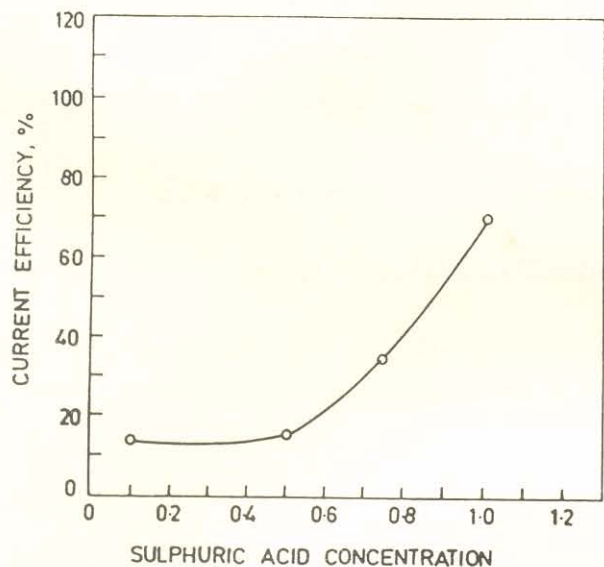


Fig. 2: Effect of H₂SO₄ concentration on current efficiency at 400 A.m⁻² for anodic dissolution of nickel.

TABLE-I: Effect of sulphuric acid concentration on anode potential at 400 A.m⁻² and 303K

| Sulphuric acid concentration (M) | Anode potential (Vs SCE) (V) |
|----------------------------------|------------------------------|
| 0.1 | 1.92 |
| 0.2 | 1.75 |
| 0.4 | 1.62 |
| 0.7 | 1.59 |
| 1.0 | 0.25 |

It could be inferred that the nature of cation, namely, nickel or sodium does not influence the dissolution appreciably. Effect of chloride addition on anode potential is given in Table II. The anode potential which was 1.53 V in a chloride - free solution, decreased drastically to 0.12 V and 0.27 V in the case of nickel chloride and sodium chloride, respectively, indicating the extent of depolarisation.

Figure 4 depicts the effect of temperature of the electrolyte on

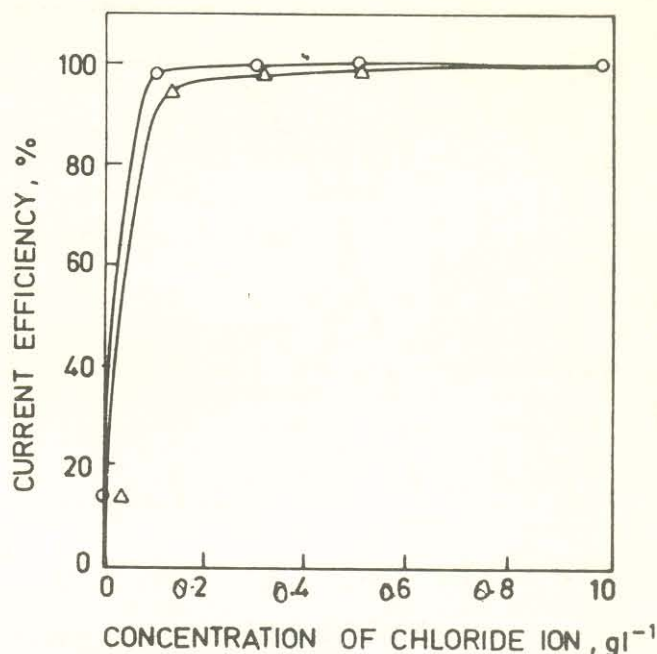


Fig. 3: Effect of chloride ion concentration on current efficiency for dissolution of nickel at 400 A.m⁻² in 0.1 M H₂SO₄ solution. (o-o) Sodium chloride; (Δ-Δ) - Nickel chloride.

TABLE-II: Effect of chloride ion concentration on anode potential in 0.1 M sulphuric acid at 400 A.m⁻² and 303K

| Chloride ion concentration g.l ⁻¹ | Anode potential, (Vs. SCE) (V) | |
|--|--------------------------------|------|
| | NiCl ₂ | NaCl |
| 0 | 1.53 | 1.53 |
| 1.0 | 0.52 | 0.62 |
| 3.0 | 0.45 | 0.49 |
| 5.0 | 0.23 | 0.35 |
| 10.0 | 0.12 | 0.27 |

current efficiency at 400 A.m⁻² for nickel dissolution which was as low as 15% at 303K, increasing to 100% above 333K. It may be due to complete breakdown of the passive film.

CONCLUSION

This study indicated that anodic dissolution of nickel is influenced by current density and sulphuric acid concentration of the electrolyte. Chloride ion plays a significant role in overcoming the problem of passivity. Higher temperature of the electrolyte improves the anodic dissolution of nickel. In weakly acidic solutions, the passivity may be related to anodic oxide formation. In this context, the effect of chloride ions could be linked to their ability in breaking the oxide film.

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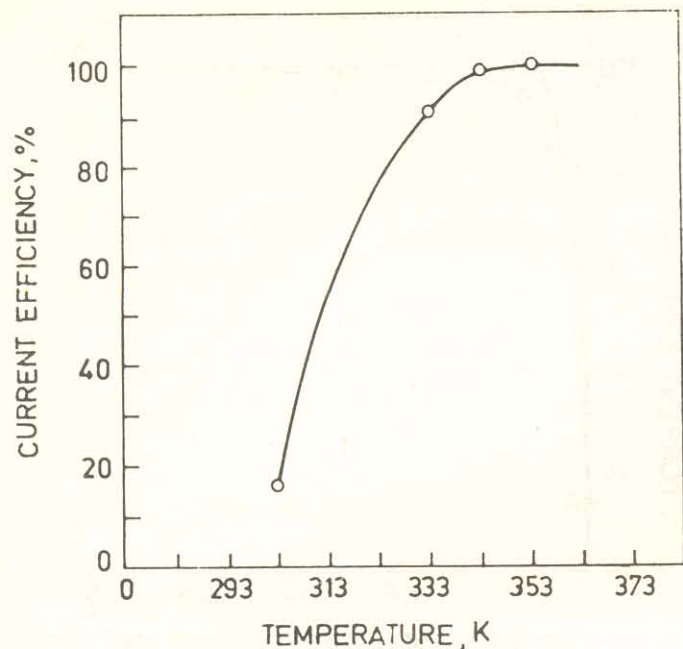


Fig. 4: Effect of temperature on current efficiency for nickel dissolution at 400 A.m^{-2} in $0.1 \text{ M H}_2\text{SO}_4$ solution.

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