ROLE OF BORIC ACID IN NICKEL ELECTROWINNING - A CYCLICVOLTAMMETRY STUDY

P.Ramachandran, V.Nandakumar, K.V.Venkateswaran, S.Visvanathan

Central Electrochemical Reasearch Institute, Karaikudi-623 006, India

ABSTRACT

Role of boric acid in the electrowinning process of nickel has been investigated through cyclicvoltammetry. Addition of boric acid to the nickel electrolyte has been found to decrease the hydrogen evolution, a side reaction at the cathode, as indicated by the features of a voltammetric peak for the oxidation of hydrogen codeposited in nickel. Control in alkalisation at the cathode vicinity has been discussed on the basis of the tendency of boric acid to release H^+ ions through complex formation with nickel in the electrolyte. An attempt has also been made to fix up the amount of boric acid required on the basis of cyclicvoltammograms generated.

Key words: Nickel electrowinning, Boric acid, Cyclic voltammetry, Inhibition of hydrogen evolution

INTRODUCTION

In the extraction of nickel from the nickel bearing ore bodies, electrowinning is an important stage where the current efficiency and purity of metal deposited call for much attention. When the nickel is electrowon from the sulphate electrolyte, the free sulphuric acid content should be restricted to a lower level and its higher contents drastically reduce the current efficiency for the nickel deposition. Simultaneous evolution of hydrogen at the cathode is the obvious reason for this as the electrode

Portugaliæ Electrochimica Acta, 11 (1993) 289-296

potentials for nickel deposition and hydrogen evolution are closer. Hydrogen evolution occuring as a side reaction in the process of nickel deposition would raise the interfacial pH, facilitating the chemical precipitation of basic nickel salts. As a result, the yield and quality of the metal deposited are affected. Hence the pH of the electrolyte has to be controlled by the addition of suitable buffers and boric acid is one of them commonly employed for this purpose.

In the present work, evidence is presented through cyclicvoltammetry for the role of boric acid in inhibiting hydrogen evolution as well as alkalinity developed in the vicinity of the cathode during the process of nickel deposition.

An attempt is also made to fix up the concentration of boric acid required, on the basis of voltammetric data generated.

EXPERIMENTAL

Cyclicvoltammetric studies were carried out with platinum disc of 0.2 cm^2, embedded in a teflon rod, as working electrode using a Wenking potentioscan and an X-Y recorder. A platinum foil was used as the auxiliary electrode. An H-type glass cell of 200 cm^3 capacity was used. The electrolyte employed was 1M nickel sulphate solution containing 20 g dm^{-3} sodium sulphate. The concentration of boric acid added, was varied from 0 to 20 g dm^{-3}. The pH of the electrolyte was adjusted to 2.5 in all the experiments. Platinum working electrode was chosen because it is reltively inert and its electrochemistry is well known.

A scan rate of 10 mV s^{-1} was used in all the experiments. Cyclic voltammograms were recorded with 0.3V as the

initial potential and -1.0 V, -1.1V or -1.25V as the reversal potential. Voltammetric charge for the oxidation of codeposited hydrogen on nickel was determined by measuring the area under the peak.

A saturated calomel electrode (SCE) was used as the reference electrode. All potentials are quoted with respect to this reference unless otherwise stated.

RESULTS AND DISCUSSION

Fig.1 shows the cyclic-voltammogram for the platinum in nickel sulphate solution without any addition of boric acid. A cathodic peak seen at -0.50 V (indicated by A) is due to adsorption of hydrogen on platinum, a phenomenon which is well established [1]. On further polarisation in the cathodic direction, a current rise occurs at -0.90 V (indicated by B) for nickel deposition with simultaneous evolution of hydrogen. The current rise ends in a peak formation (indicated by C) as the increased evolution of

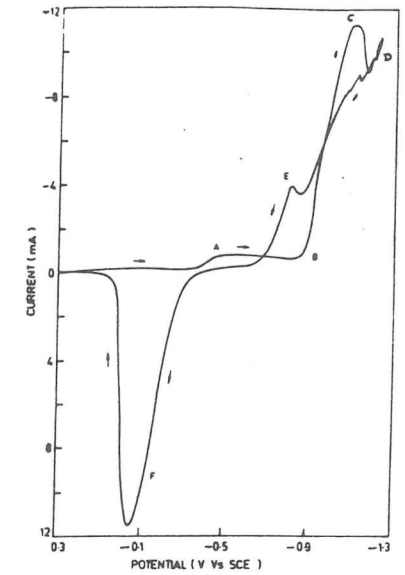

Fig.1 Cyclicvoltammogram of Pt in 1M $NiSO_4$ at 10 mV s^{-1} with reversal potential of -1.25V

hydrogen depletes nickel concentration in the cathode vicinity. Further polarisation results in another current rise (indicated by D) which is due to evolution of hydrogen. Current oscillations seen here are obviously due to resistance arising out of hydrogen gas bubble formation.

When the potential scan is reversed in the anodic direction, at the reversal potential of -1.25 V, there is a cathodic peak at -0.82 V (indicated by E). This cathodic peak may be due to reduction of nickel hydroxide formed chemically. When the electrode is scanned to a high negative potential of -1.25 V, hydrogen evolution is promoted. As a result, alkalinity develops at metal-solution interface, resulting in the chemical formation of nickel hydroxide which,inturn,gets reduced,giving rise to a voltammetric peak in the reverse scan. On further scanning in the anodic direction, a large, well defined peak (indicated by F) is seen at -0.18 V for the oxidation of codeposited hydrogen on nickel, which has been already reported by Hoare in the context of nickel plating from the Watts bath [2]. It is well known that hydrogen can dissolve in nickel to form Ni -H alloy [3]. The height as well as charge of this hydrogen - oxidation peak depends on the extent of cathodic scan, as indicated by the cyclic voltammograms in Fig.2, where the curves 1 and 2 correspond to the reversal potential of -1.10 V and -1.0 V respectively. As the reversal potential is made less negative, the tendency for the hydrogen evolution becomes less, as indicated by the reduced peak height as well as charge for the oxidation of hydrogen on nickel.

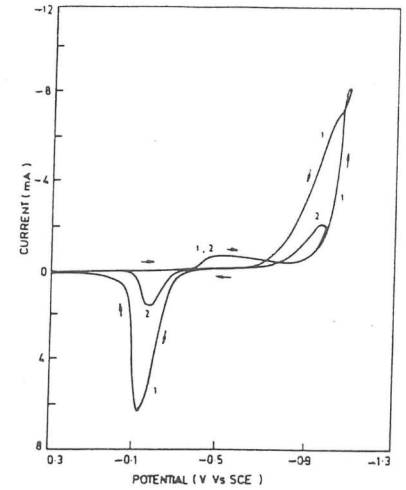

Fig.2 Cyclicvoltammograms of Pt in 1M $NiSO_4$ at 10 mV s^{-1} with reversal potential of 1, -1.1V and 2, -1.0V

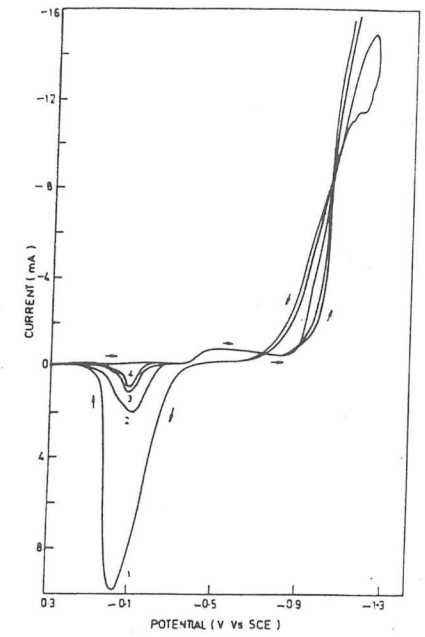

Fig.3 Cyclicvoltammograms of Pt in 1M $NiSO_4$ at 10 mV s^{-1} with reversal potential of -1.25V containing 1, 1 g dm^{-3}; 2, 5 g dm^{-3}; 3, 10^{-3} g dm^{-3} and 4, 20 g dm^{-3} of boric acid

Fig.3 shows the cyclicvoltammograms recorded for the nickel deposition involving boric acid. The peak for the reduction of nickel hydroxide, as seen in Fig.1, is absent here indicating that alkalinity is controlled by the inhibition of hydrogen evolution brought about by boric acid. The size of the hydrogen - oxidation peak progressively gets reduced with increasing amounts of boric acid added. The charge, as determined by measuring the area under the peak, can be taken as a measure

of codeposited hydrogen. It can be inferred that lesser this charge, lower will be the rate of hydrogen evolution and higher the rate of nickel deposition.

Fig 4 shows the plot of voltammetric charge for the oxidation of codeposited hydrogen against concentration of boric acid added. The charge progressively decreases with concentration of boric acid and the minimum of charge corresponds to 10 g dm^{-3} which is fixed up as the required concentration of boric acid.

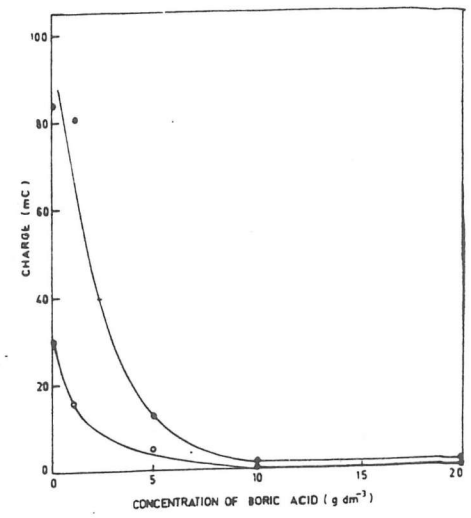

Fig. 4 Plot of charge against concentration of boric acid for the oxidation of codeposited hydrogen in the cyclic-voltammetry of Pt in 1M $NiSO_4$ with reversal potential of (●) -1.25V and (o) -1.10V

In the electrodeposition of nickel alkalization arises as a result of hydrogen evolution [4].

$$2H_2O + 2e \text{ -----> } 2OH^- + H_2 \quad (1)$$

The hydroxyl ions produced at the cathode react with Ni^{2+} ions to form soluble $NiOH^+$ species.

$$Ni^{2+} + OH^- \text{ -----> } NiOH^+ \quad (2)$$

Nickel deposition proceeds mainly from $NiOH^+$ [5]

$$NiOH^+ + e \text{ -----> } NiOH_{ads} \quad (3)$$

$$NiOH_{ads} + NiOH^+ + 3e \text{ -----> } 2Ni + 2OH^- \quad (4)$$

When the rise in alkalinity is abrupt or is not controlled as in the case of unbuffered solutions, nickel hydroxide is precipitated.

$$Ni^{2+} + 2OH^- \text{ -----> } Ni(OH)_2 \quad (5)$$

Boric acid, by virtue of its buffering action, decreases the alkalization. The buffer capacity is greater due to the complexation of Ni^{2+} with boric acid [6].

$$H_3BO_3 \text{ <-----> } H^+ + H_2BO_3^- \quad (6)$$

$$Ni^{2+} + 2H_2BO_3^- \text{ -----> } Ni(H_2BO_3)_2 \quad (7)$$

Addition of boric acid also results in lesser polarisation for nickel deposition as shown in Fig.5. Current rise for nickel deposition occurs relatively at lower cathodic potential in presence of boric acid. Nickel deposition takes place more easily from the complex formed between nickel ions and boric acid. This is also obvious from the nature of the hysteresis seen between the cathodic and anodic going sweeps in the potential region of nickel deposition. Hysteresis is larger due to

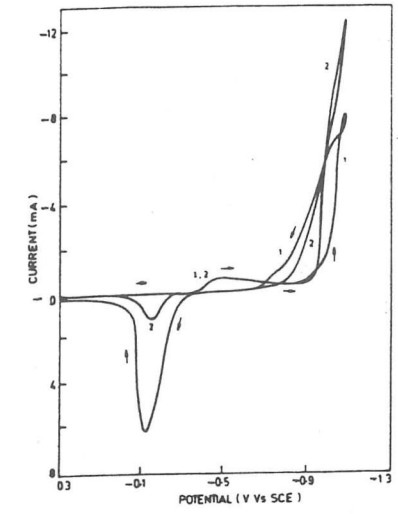

Fig. 5 Cyclicvoltammograms of Pt in 1M $NiSO_4$ at 10 mV s^{-1} with reversal potential of -1.1V containing 1, 0 g dm^{-3} and 2, 10 g dm^{-3} of boric acid.

simultaneous hydrogen evolution. Addition of boric acid makes it smaller as the hydrogen evolution associated with nickel deposition is largely avoided.

CONCLUSIONS

An anodic peak obtained for the oxidation of codeposited hydrogen, makes it possible to asses the extent of hydrogen evolution occuring in the process of nickel deposition. Progressive diminution in its size, brought about by the additions of boric acid, indicates that boric acid inhibits hydrogen evolution.

Cyclic voltammetry, in recent years, has led to the development of a rapid and novel method, in the monitoring of electrolytes. The present study provides similar scopes for nickel electrolytes employed in the plating as well as electrowinning processes. It would be possible to estimate the impurities and other constituents present in the electrolyte by generating cyclic voltammograms and analysing their features.

REFERENCES

1. J.P.Hoare, Electrochim. Acta 27, 1751 (1982)
2. J.P.Hoare, J. Electrochem. Soc. 133, 2491 (1986)
3. J.P.Fast Interaction of Metals and Gases, P.92. Barnes and Noble Inc., New York (1972)
4. L.B.Harris, J. Electrochem. Soc. 120, 1034 (1973)
5. I.Epelboin and R.Wiart, J. Electrochem. Soc. 118, 1577 (1971)
6. B.V Tilak, A.S.Gendron and M.A.Mosoiu, J. Appl. Electrochem. 7, 495 (1977)

(Received,29 Juni 1993
Revised form,2 November 1993)

THE ELECTROPHORETIC EFFECT IN ELECTROLYTE SOLUTIONS

Victor M.M. Lobo and Ana C.F. Ribeiro
Department of Chemistry, University of Coimbra
3000 Coimbra - Portugal

Abstract

The concept of the electrophoretic effect in electrolyte solutions and the way it has been presented in the literature is critically discussed.

Key words: solutions, electrolytes, electrophoretic effect

The interpretation of thermodynamic and transport properties of electrolyte solutions leads to models concerning the structure of those solutions and concepts about the hydrodynamic behaviour of ions moving through their media. One of those concepts is called *electrophoretic effect*. However, it has been presented in the literature in a variety of different ways, sometimes not equally clear.

The term electrophoretic effect firstly appears in the literature in 1932 [1] as follows:

"There are two different effects to be considered, namely the direct transfer of electric forces between the ions and a hydrodynamic effect, the so-called electrophoresis. The later effect was recognized by Debye and Huckel, while the former had been expected for a long time by those familiar with the properties of electrolytes.

...

The *electrophoresis* is most simply described and estimated for the case of electrical conduction where, for an electric field E,

$$k_0 = 0;\ k_i = e_i E \quad (i = I, .. s)$$