

STUDY ON ELECTROWINNING OF COBALT BY CYCLIC VOLTAMMETRY TECHNIQUE

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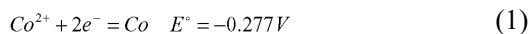
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Abstract: Nowadays cobalt is mostly produced through the electrowinning process of sulfate solutions. Regarding to the competition between the precipitation of cobalt ions and evolution of hydrogen gas on the cathode surface during the reduction process in a sulfate bath, investigation on the mechanism of metal precipitation is of great importance. In the present work, study on the kinetics of cobalt electrowinning and the mechanism of the involved reactions have been carried out. The obtained results, confirm the mechanism of cobalt precipitation by depletion of hydroxides. The effects of temperature and scan rate parameters were studied on electrowinning of cobalt by cyclic voltammetry technique. The diffusion coefficient and rate constant of the reactions were measured and calculated by performed experiments.

Keywords: Cobalt, Electrowinning, Mechanism, Kinetics and Cyclic voltammetry

1. INTRODUCTION

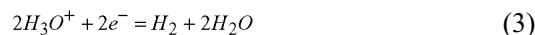
In electrowinning of cobalt, the main electrolyte is sulfate or chloride solution. For the electrowinning of cobalt from sulfate solution assistance of some additives such as acid boric seems to be necessary [1]. When a sulfate solution is used, cobalt is deposited on the cathode and at the same time oxygen gas is evolved from the anode. The cathodic reactions are as follows:



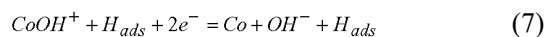
The standard potential of cobalt is rather negative in compare with hydrogen; therefore hydrogen gas can be produced on the cathode as well, which is not in favour of cobalt deposition. It reduces the current efficiency and should be maintained at its minimum amount.

During the electrowinning of cobalt from aqueous solutions, the hydrogen evolution reaction takes place more readily because of its position in the emf series. This may lead to formation of OH^- ions causing local pH increase in the diffusion layer [2]. Regarding to this fact that cobalt and nickel are in the same group with similar standard potential, it is expected to have a similar deposition mechanism. It is reported that

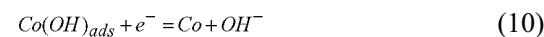
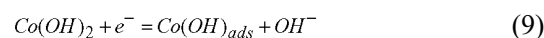
the electrochemical deposition of Ni is carried out by formation of NiOH^+ ions. Heuser [3], Scoyer and Winand [4] proposed a similar mechanism for cobalt deposition which is performed and developed by formation of CoOH^+ or CoOH^+ and Co(OH)_2 . Variation of pH in the vicinity of cathode and deposition of cobalt through hydroxide mechanism can be improved by following sequences:



At lower pH, the cathode surface is covered by Hydrogen and the reaction proceeds as follows:



Co^{2+} ions are hydrolyzed by reaction 5. At higher pH (4-4.5) the reactions proceeds as follows:



It seems that cobalt is deposited from its hydroxide compounds. Reactions 3-10 show that

OH⁻ ions are formed by different reactions and cause increase of pH in the surface [2].

As it was mentioned earlier, according to thermodynamics aspects, reduction of hydrogen is prior to cobalt deposition. In spite of spread research works on the electrowinning of cobalt [5-10], less attempts have been made to prove the actual mechanism. In the present work a simple study on electrowinning of cobalt from sulfate bath has been carried out by using cyclic voltammetry technique to confirm the above mechanism. Also some kinetics parameters were measured and calculated by applying appropriate and reliable techniques.

2. EXPERIMENTAL PROCEDURE

The equipments used for experiments were as follows:

1. A Potentiostat/Galvanostat model 273A EG&G Princeton Institute which is controlled by corrosion analyzing software model 352 ("Fig. 1").
2. Calomel reference electrode (SCE)

For preparation of electrolyte, a specific ratio of cobalt sulfate (60 g/l) and boric acid (30 g/l) with triply distilled water were used. All of the used chemicals were reagent grade. The pH of solution was measured by using an EDT pH-meter and adjusted to 4 with the addition of sufficient H₂SO₄.

Voltametric experiments performed with a conventional three-electrode cell ("Fig. 1"). The

working electrode (substrate) was made of a platinum wire with total exposed surface 0.17 cm² and the pure platinum plate anode was utilized with total surface about 10 times larger than cathode surface. All potentials were referred to a saturated calomel electrode (SCE) from Fisher. The electrode system joined with EG&G equipment set to voltametric tests on cobalt sulfate. The result recorded with Potentiostat / Galvanostat equipment. The current and voltage were regularly stored in a computer. All investigations were conducted at ambient temperature, except the ones that was carried out at 50°C for investigating the effect of temperature.

3. RESULTS AND DISCUSSION

The deposition of cobalt was initially studied using cyclic voltammetry. A representative plot of the cyclic voltammograms, CVs, for the SCE in 60 g/l cobalt solutions at 20, 50, 100 and 200 mVs⁻¹ at ambient temperature is shown in "Fig. 2". During the scan in the negative direction, the current increases sharply once cobalt nucleation begins. These curves indicate that cobalt reduction on the SCE starts at -750 mV and -800 mV at 20 mV s⁻¹ and 200 mVs⁻¹, respectively. Due to hydrogen evolution, an increase in the current density is observed at more cathodic potential and no clear limiting current density is observed.

Also some tests were conducted at 50°C, but the results were similar to the results of ambient temperature. Increasing the electrolyte temperature appears to enhance the deposition reaction. However, it was found that the hydrogen evolution reaction occurs more readily

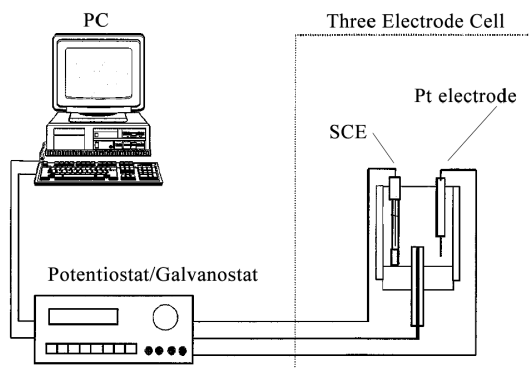


Fig. 1. The Potentiostat/Galvanostat equipment EG&G

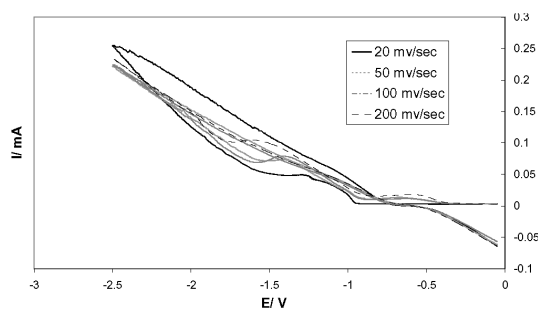


Fig. 2. Cyclic voltammogram for cobalt deposition on the platinum surface from sulfate-borate solution, $\nu=20, 50, 100$ and 200 mVs^{-1} (ambient temperature).

at higher temperature. To determine if this effect outweighs the gain in the cobalt deposition reaction, the current efficiency should be calculated at different temperatures.

It is assumed that both cobalt and hydrogen are plated cathodically first and then only cobalt is dissolved anodically. Upon reversing the scan direction, the current decreases and reaches zero. Then the current becomes anodic corresponding to the dissolution of the deposited cobalt. During the reversing sweep at the scan rates 50, 100 and 200 mVs⁻¹, two anodic peaks are observed whereas one anodic peak occurs in the case of 20 mV s⁻¹. Some researchers [8] reported that the two anodic peaks are associated with the dissolution of cobalt from the SCE surface to the solution from two different cobalt metal phases (CoOH⁺ and Co(OH)₂). Similar multiple peaks were also observed by Elsherief. [8].

The main cathodic reactions occurring in cobalt electrowinning are presented in "Eq. 1" and "Eq. 2". The production of hydrogen gas occurs because cobalt is less noble than the hydrogen electrode, as can be seen from the standard reduction potential of cobalt. The hydrogen evolution reaction is obviously not desirable because it represents a loss of useful current, and, therefore, it must be kept to a minimum by maintaining the pH at 4.

As shown in "Fig.2", the voltage is scanned at 20 mVs⁻¹ between 0 to -2.5 V vs. SCE. The cathodic current in the forward cycle (0 to -2.5 V) represents deposition of Co⁺² on Pt.

Also, it can be observed in "Fig.2" that an increase in the scan rate displaces cobalt reduction peaks to more negative potentials and higher current contributions. This behavior can be attributed to the irreversible reduction of cobalt from sulfate-borate solution.

The electrowinning parameters of cobalt system in "Table.1" were determined by using the theory of cyclic voltammetry with respect to irreversible electrowinning developed by Nicholson and Shain [11], as below:

$$|E_p - E_{p/2}| = \frac{48}{\alpha_c n_a} \text{ mV at } 25^\circ\text{C} \quad (11)$$

$$i_p = -(2.99 \times 10^5) n (\alpha_c n_a)^{1/2} C_0^\infty D_0^{1/2} \nu^{1/2} \quad (12)$$

$$E_p^c = K - \frac{2.3RT}{2\alpha_c n_a F} \log \nu \quad (13)$$

$$K = E_e^\theta - \frac{RT}{\alpha_c n_a F} \left(0.78 - \frac{2.3}{2} \log \left(\frac{\alpha_c n_a F D}{k^\theta RT} \right) \right) \quad (14)$$

Where E_p is the peak potential, $E_{p/2}$ potential where $i = i_{p/2}$ in LSV, i_p peak current, α_c transfer coefficient, n_a numbers of electrons involved in the reaction determining step, C_0^∞ bulk concentration, ν scan rate, D diffusion coefficient and k^θ standard heterogeneous rate constant.

As shown in "Fig.3", at low potential sweep rates a reversible cyclic voltammogram is recorded. So, the rate of electron transfer is greater than that of mass transfer. As the sweep rate is increased, whilst, the rate of mass transport increases and becomes comparable to the rate of electron transfer and an irreversible cyclic voltammogram is recorded.

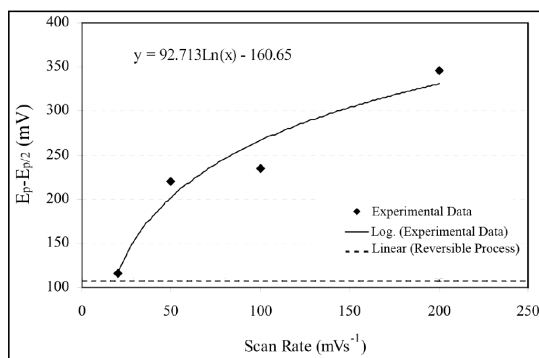


Fig. 3. $E_p - E_{p/2}$ versus ν curve for cobalt deposition from sulfate-borate solution at different scan rates from 20 to 200 mVs⁻¹

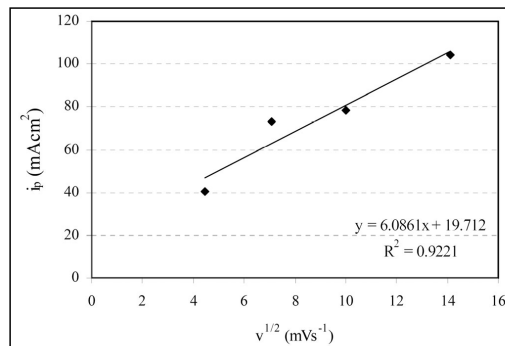


Fig. 4. i_p versus $\nu^{1/2}$, curves for cobalt deposition from sulfate-borate solution at different scan rates from 20 to 200 mVs⁻¹

With respect to "Fig.2" and by use of "Eq.11", αn_c for irreversible reduction of cobalt cations from sulfate-borate solution calculated. And so, by plotting i_p vs. $(\Psi)^{1/2}$ (in Fig. 4), the kinetic parameters of electrowinning are calculated according to "Eq.12" to "Eq.14". Eventually, calculated amounts of standard heterogeneous reaction rate and diffusion coefficient of cobalt cations during electrowinning are arrested in "Table 1".

Table 1. Kinetic parameters determined of cobalt reduction peak in sulfate-borate solution

Kinetic parameters	
αn_c	0.15
Diffusion coefficient, $D(\text{cm}^2/\text{s})$	6.7×10^{-6}
Rate constant, $k_s(\text{cm/s})$	9.05×10^{-3}

Based on these results, we conclude that at low enough scan rates or low enough overpotentials electrowinning of cobalt occurred under electron transfer control process. But, at high enough scan rates or high enough overpotentials electrowinning of cobalt occurred under diffusion-controlled process. However, chronoamperometry analysis is needed to study the exact mechanism of electrocrystallisation of cobalt from sulfate-borate solution.

4. CONCLUSION

Cobalt electrowinning experiments from sulphate solutions were carried out. It can be concluded that at low enough scan rates or low enough overpotentials, electrowinning of cobalt occurred under electron transfer control process. But, at high enough scan rates or high enough overpotentials electrowinning of cobalt occurred under diffusion-controlled process. Also, calculated amounts of standard heterogeneous reaction rate and diffusion coefficient of cobalt cations during electrowinning are $9.05 \times 10^{-3} \text{ cm/s}$ and $6.7 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively, by using cyclic voltammetry technique.

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