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Effect of hydrogen peroxide on cobalt electrowinning

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ABSTRACT

The study is focused on the use of hydrogen peroxide on cobalt electrowinning and its advantages over conventional electrowinning cell practices. The current efficiency increased slightly to an optimum concentration of H_2O_2 , under fixed electrowinning conditions of current density-200Amp/ m^2 , pH-3, Co^{2+} -45g/L and separation of electrode by 50mm. Further increase of additive concentration resulted in decreasing values of current efficiency. SEM analysis, DSC analysis and X-ray diffraction pattern indicated improved microstructure with the hcp lattice of cobalt metal in presence of hydrogen peroxide. The improved microstructure resulted in improved microhardness. The addition of H_2O_2 also resulted in formation of less or no sludge and the mechanism for the same is proposed on basis of the cyclic voltametry. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Current efficiency;
Sludge;
Hydrogen peroxide;
Electrowinning.

INTRODUCTION

There is a growing interest in magnetic thin films, especially in cobalt films, due to their wide range of application as magnetic data storage devices^[1-5]. Electrodeposition is one of the easiest method to produce cobalt and has several advantages over dry processes^[6]. Electrodeposition does not require vacuum technology^[7,8] and consequently is less expensive. It can be easily scaled up for depositing uniform films on large sized complex surfaces without any shadowing effects. The experimental systems used are much simpler than evaporation or sputtering apparatus and electrodeposition can be a room-temperature technology. However, there are some drawbacks associated with the

process, such as the need for a conducting/ semi conducting substrate, the limited number of elements that can be deposited and the large number of variables that influence this process, like composition, pH, concentration, current density, temperature and agitation. Hexagonal close packing, hcp is the usual structure for electroplated cobalt. It is also known⁹ that face-centered cubic, fcc cobalt, which is stable at temperatures above 422°C, can sometimes be obtained from electrodeposition at ambient temperatures. Gelchinski *et al*¹⁰ have electroplated, cobalt-chromium alloys containing the cP8 structure type^[11,12] at room temperature, that is stable only at high temperatures, according to the equilibrium phase diagram. Several researchers^[9,13-22] have reported that the pH of the bath solution significantly af-

fects the structure of cobalt formed by electro deposition. A solution with a low pH (below 2.5) was reported to favor fcc cobalt, whereas a high pH (above 2.5), high temperature and agitation favored the formation of hcp cobalt in a sulfate or chloride bath^[17,18]. The high current densities in sulfamate solutions were found to favor the cubic structure^[19].

Lakshminarayanan et al.^[23] had patented the idea of use of vanadium pentoxide as additive to prevent the sludge formation and to get better morphology which is detrimental in mechanical properties of the metal. However for a commercial plant this idea is not practical as added vanadium pentoxide will remain in the spent electrolyte and enter the solvent extraction circuit which may build up in the system and oxidize the organic solvents.

Thus, there is a need of an additive which can improve the morphology without disturbing the cobalt metal production circuit. Hydrogen peroxide being a good reducing agent cheap, easily available and compatible with the electrolyte system can be considered as additive for the reduction of cobalt oxide sludge formation^[24-27,30]. Kongstein^[28] had reported that the quantity of cobalt oxide formed on the Ti/RuO₂-IrO₂-TiO₂ electrode dropped to less than half, on addition of 0.054 g/L H₂O₂ to the electrolyte prior to electrolysis. After electrolysis with higher H₂O₂ concentrations of 0.17 and 0.22 g/L, no deposit was seen on the anode surface. Furthermore, a small decrease was observed in the

TABLE 1 : Effect of H₂O₂ on current efficiency of the metal produced by electrowinning

Concentration of H ₂ O ₂ , in ppm	Current efficiency in %	Wt of CoOOH formed in g
0	68.1	0.30
30	70.2	0.20
60	71.4	0.10
150	74.4	0
200	72.8	0
300	69.7	0

TABLE 2 : Cyclic voltametric study on effect of hydrogen peroxide concentration on cobalt electrowinning.

Conc. of H ₂ O ₂ in ppm	Nucleation Over potential in V	Cross over potential in V	anodic peak potential	Anodic peak current in mA
0	-0.63	-1.03	0.33	6.5
50	-0.66	-0.89	0.29	5.4
100	-0.66	-0.89	0.28	4.1
200	-0.65	No Cross over	0.13	4.4
300	-0.65	No Cross over	0.33	6.7

anode potential with H₂O₂ in the electrolyte. No changes were detected in the plated cobalt metal or cathodic current efficiency when cobalt was deposited from an electrolyte containing 0.22 g/L H₂O₂ with a soluble cobalt anode. From the experiments carried out by Kongstein^[28], it was not possible to conclude if H₂O₂ resulted in suppression of the cobalt oxide deposition reaction, or cobalt oxide was redissolved by H₂O₂.

In the present study an attempt has been made to study the effect of hydrogen peroxide as additive on the morphology and phase structure of cobalt metal electrodeposited from a sulfate bath under standard electrowinning conditions.

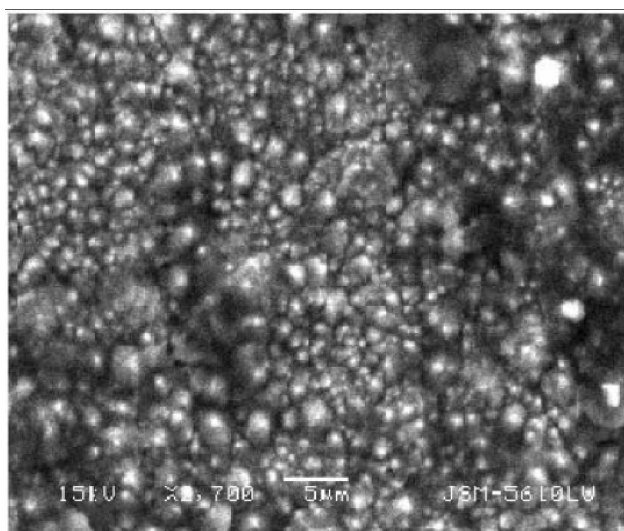
EXPERIMENTAL

Electrowinning

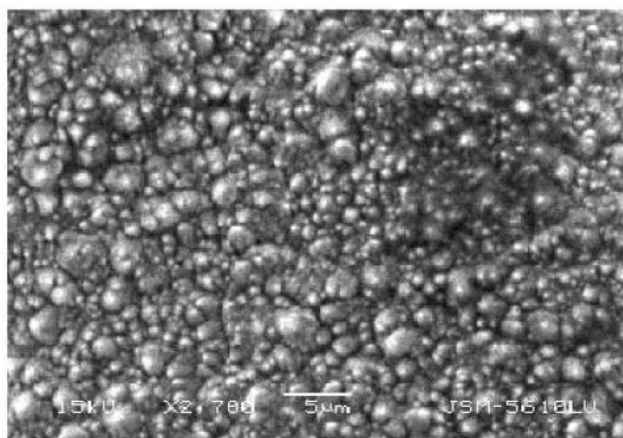
The electrowinning experiments were performed in an acrylic cell of 1.4 L, equipped with two lead-antimony alloy (50×100×8 mm) anodes separated by 50mm stainless steel cathode (60×100×2mm) using cobalt pregnant electrolyte containing 45 g/L of cobalt, prepared from cobalt sulphate hepta hydrate (Merck). Flow rate of the pregnant electrolyte was maintained at 5 mL/min using a peristaltic pump, throughout, for all the experiments. Hydrogen peroxide was used as received from National peroxide limited without further purification. H₂O₂ was added to the feed tank containing 1.8 L of pregnant electrolyte before electrowinning using a graduated pipette for the concentration between 50ppm to 300 ppm. Each experiment was carried out for 6 hours at current density of 200 A/m². Cathode and anodes were removed at the end of the experiment, washed with distilled water and dried in oven at 120°C for 30 min. Weight of the deposit and sludge were calculated by difference in weights of the cathode and anodes before and after the experiment.

Characterisation

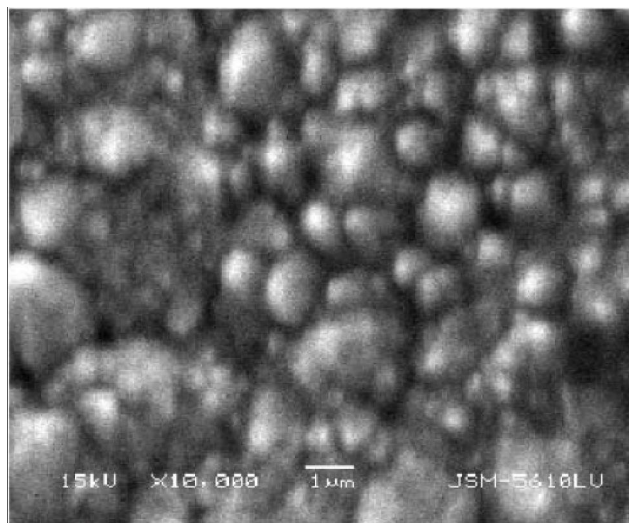
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a



b



c

Figure 1 : SEM image of cobalt metal deposited a) in absence H_2O_2 b) in presence of H_2O_2 c) in presence of H_2O_2 at higher magnification

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Cyclic voltammetric studies were carried out in a 25mL capacity cell equipped with a three electrode assembly of Ag/AgCl as reference electrode, Glassy carbon (BAS) as working electrode and platinum counter electrode using Potentiostat G750 (Gamry Instruments Ltd.).

Differential scanning calorimetric thermograms were recorded on Mettler Toledo, (DSC-30) using aluminum crucible in the temperature range of 35 to 590°C at 10° C/min under nitrogen atmosphere.

Scanning Electronmicroscope Analysis was done on JOEL- 300 model. Sample was sprayed on the stub, coated with gold ions and finally observed under scanning electron microscope.

Microhardness

Micro Hardness was measured by applying 50g load for 10 seconds on sample using the instrument Wilson Wolpert Micro Vickers, Model No- 401MVD (Hardness Vickers method –ASTM-384).

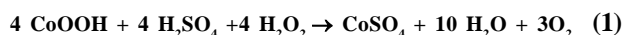
X-ray diffraction analysis

X-ray diffraction analysis was done on Panlytical diffractometer of XPERT PRO Model with Cu-k-alpha radiation.

RESULTS AND DISCUSSION

Electrowinning

Hydrogen peroxide acts as a reducing agent in presence of acid as per the equation (1).



In the electrowinning cell acid is generated along with oxidation of small amount of cobalt at the anode. Quantity of CoOOH formed with respect to concentration of hydrogen peroxide is presented in TABLE.1. Based on the data from TABLE. 1., it can be concluded that the addition of hydrogen peroxide reduces the sludge formation as per the equation (1). This observation is similar to the observation reported by Tejus akre^[26] and Kongstein *et al*^[28]. Kongstein *et al* have reported that addition of 55 ppm of H_2O_2 reduced CoOOH formation to half and in presence of 170 to 220 ppm of H_2O_2 there was no formation of CoOOH. In the present study we have found that at H_2O_2 concentration higher than 150 ppm no sludge was formed.

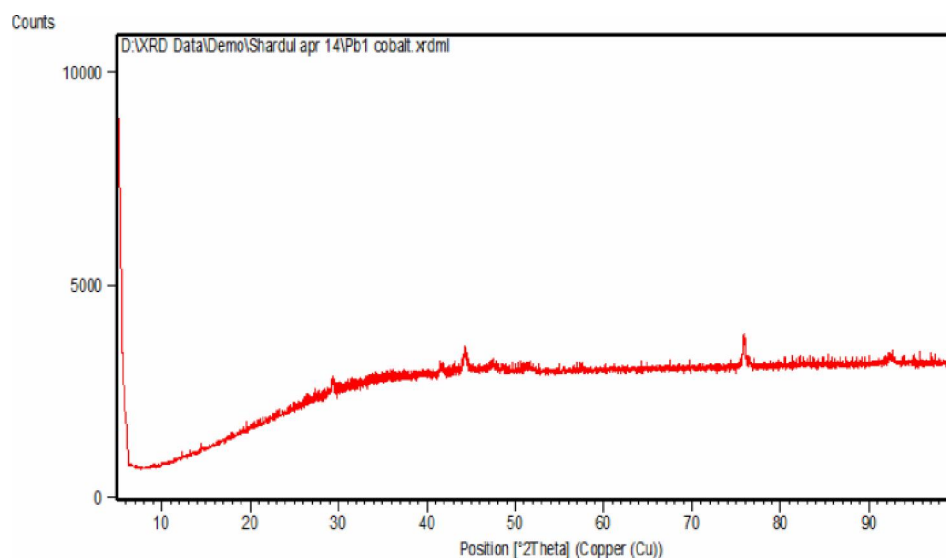


Figure 2a : XRD of cobalt metal produced without hydrogen peroxide

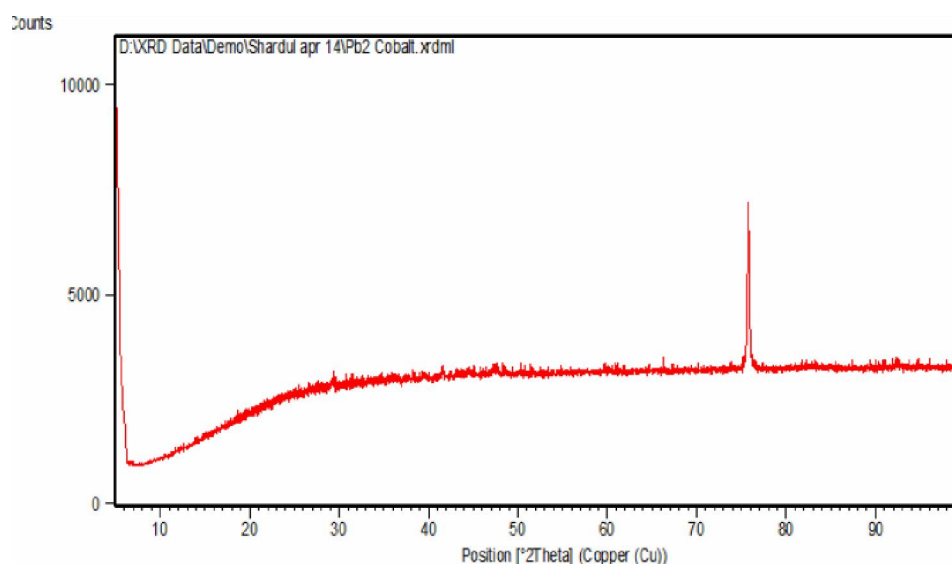


Figure 2b : XRD of cobalt metal produced in presence of hydrogen peroxide

A small increase in current efficiency was observed upto 150 ppm of H_2O_2 and further addition of the additive reduced the current efficiency (TABLE.1). The reason for reduced current efficiency could be redissolution of the metal in acidic media and can be expressed as equation 2.



The decreased current efficiency at higher concentrations of H_2O_2 is reported by Tejus akre^[26] as well. They have observed 5% decrease in current efficiency when 260 ppm of H_2O_2 was added. The controversy in the results of current efficiency obtained by Tejus akre and Kongstien might be due to range of concentrations of H_2O_2 selected. Kongstien used lower concentration

of H_2O_2 so he could not observe any appreciable change in the current efficiency, where as Tejus akre used higher concentration of H_2O_2 which lead to decreased current efficiency. In the present study as we worked with a wider range of H_2O_2 concentraions we found both observations to be true and 150 ppm of H_2O_2 is the optimum concentration.

In order to understand effect of H_2O_2 on sludge formation and Current efficiency cyclic voltametric studies were carried out.

Cyclic voltametry

Cyclic voltammograms of 45 g/L cobalt solution at $50mVs^{-1}$ on the glassy carbon electrode, without and

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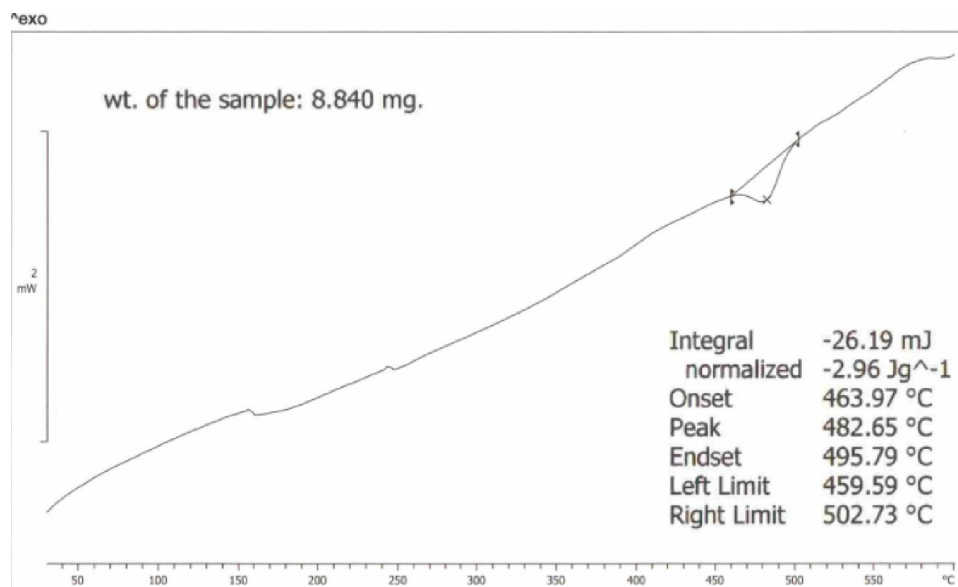


Figure 3a : DSC thermogram of cobalt metal produced in the absence of hydrogen peroxide

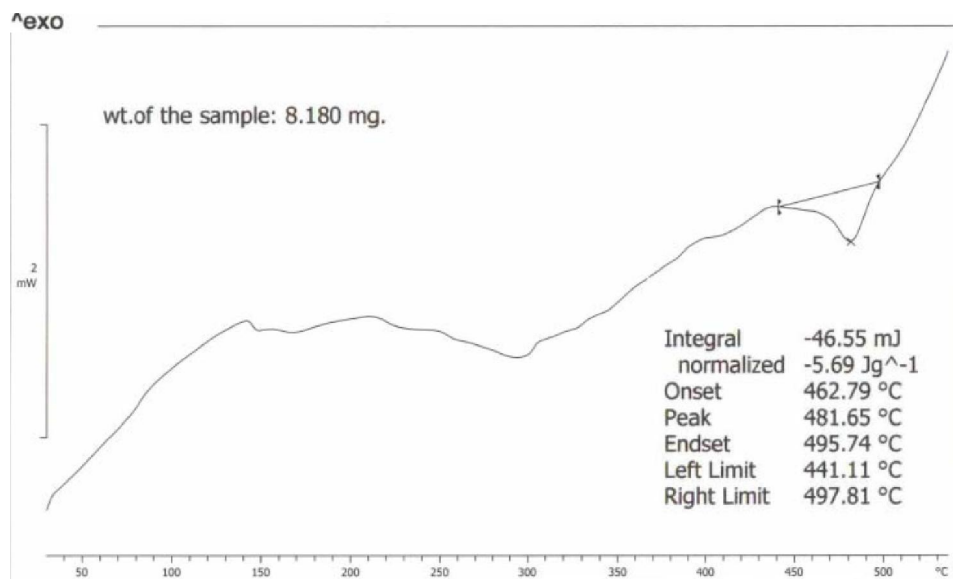
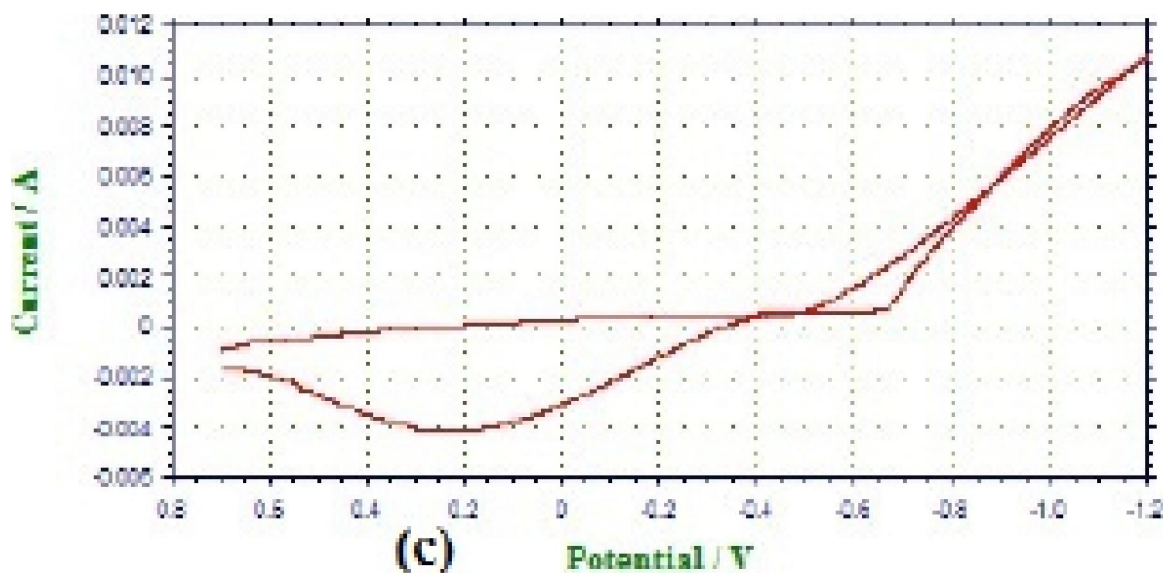
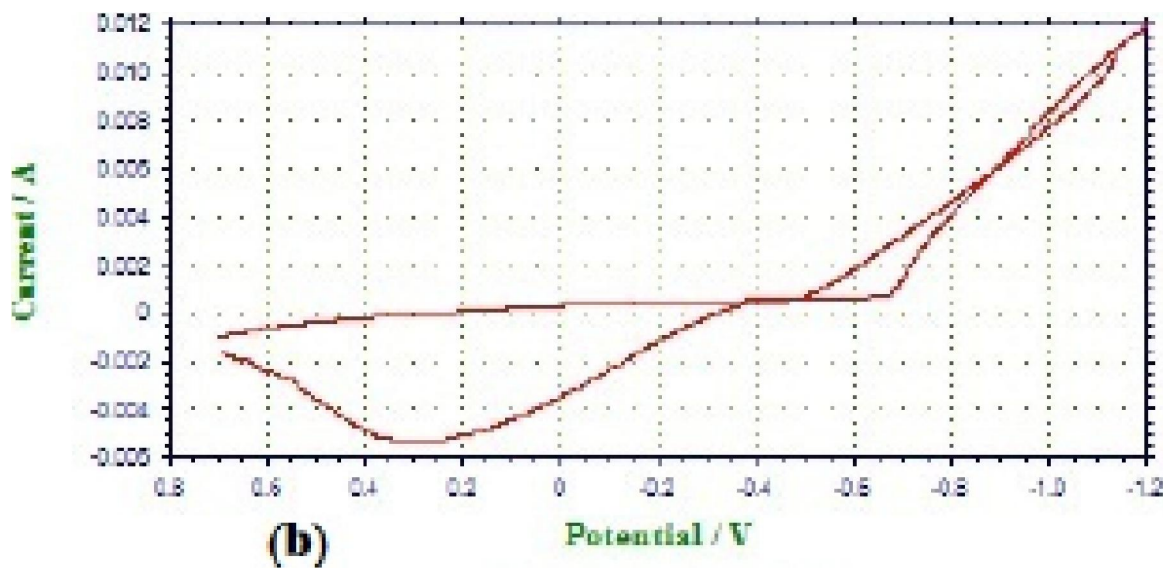
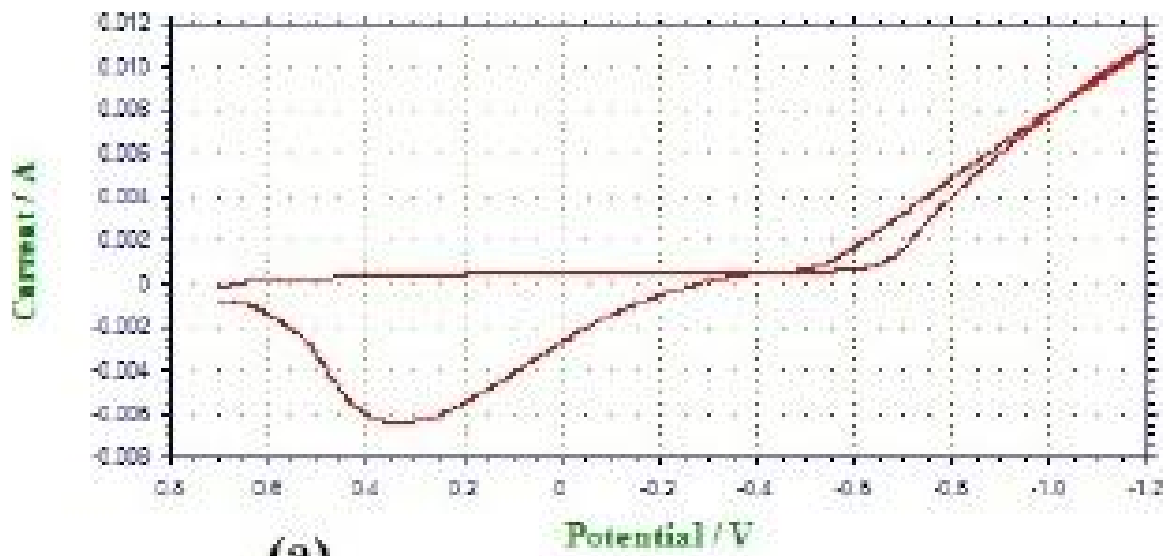


Figure 3b : DSC thermogram of cobalt metal produced in presence of hydrogen peroxide (150ppm)

with H_2O_2 solution are given in Figure 4a, Figure 4b-e and the peak potentials values for corresponding process are tabulated in TABLE 2. From figure 4.a., it can be seen that during negative direction of the scan, the current increases sharply once the cobalt nucleation begins. These curves indicate reduction of cobalt on the GCE at -0.63V. Due to evolution of hydrogen gas, an increase in the current density with no clear limiting value is observed at further cathodic potentials. It is assumed that both cobalt and hydrogen are reduced cathodically and upon reversing the scan direction, only cobalt is dissolved anodically.

As exhibited in the Figure 4b, in presence of 150 ppm H_2O_2 in nucleation over potential remained same however the cross over potential decreased to -0.89V. This may be due to the increase in deposition rate of cobalt metal in presence of H_2O_2 . The shifting of peak potential during anodic sweep might be due to the mixed effects of cobalt dissolution and oxidation of hydrogen peroxide. As the standard reduction potential for $H_2O_2/2H^+$ is -0.68V as which is much lesser than that for Co^{3+}/Co^{2+} causes reduction of cobalt oxide sludge.

To understand the mechanism, cyclic voltametric studies were carried out with H_2O_2 concentration in the



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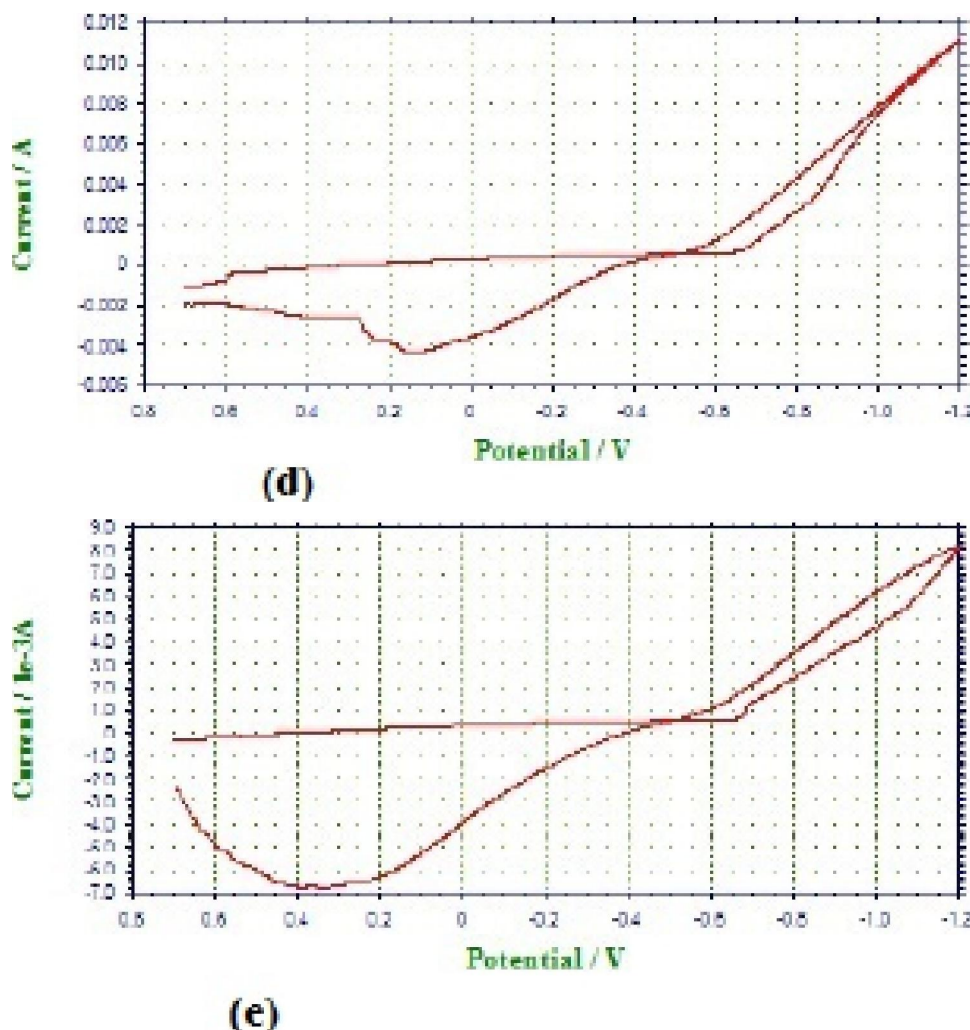


Figure 4 : Cyclic voltammogram of cobalt sulphate solution on Glassy carbon electrode in presence of different concentration of H_2O_2 : at 50 mV/s Vs Ag/AgCl (a) 0 ppm (b) 50 ppm (c) 100 ppm (d) 200 ppm (e) 300 ppm

range 50 ppm to 300 ppm. The cyclic voltammograms of H_2O_2 concentration from 0 to 300 ppm are given in Figure 4a to 4e. There is appreciable decrease in the peak current of H_2O_2 for 50 ppm to 200 ppm. But when the concentration was increased to 300ppm, anodic peak current increased more than that of electrolyte without H_2O_2 . This indicates that H_2O_2 redissolves the cobalt metal when it is added above 200ppm. This observation supports the report of Tejus akre as he used 270 ppm of H_2O_2 for $CoOOH$ reduction and end up with decreased current efficiency. Moreover upto 200ppm of H_2O_2 peak potential for oxidation of cobalt decreased, further addition of H_2O_2 increased the peak potential of oxidation of cobalt this indicates that upto 200ppm of H_2O_2 suppressed formation of $CoOOH$.

Morphological studies

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SEM

Figure 1a represents SEM image of the cobalt produced by conventional electrowinning and Figure 1b, is that of cobalt metal produced in the presence of H_2O_2 . Comparison of the two SEM images indicate that metal deposition in presence of small amount of hydrogen peroxide as additive leads to a well organized nodular growth of deposits with the homogeneous distribution of grains. The deposition without hydrogen peroxide leads to a random distribution with uneven growth of metal particles.

Differential scanning calorimetry

The DSC thermogram of cobalt metal produced by conventional electrowinning practice is given in Figure 3a. The standard heat of transformation for hcp to fcc is 8.03 J/g.^[30]. As it can be seen from the Figure 3a

that energy released for the phase transition is 2.96 J/g. It indicates that the metal consists of mixture of hcp and fcc microstructure. The Figure 3b is the DSC thermogram of cobalt produced in the presence of H_2O_2 (150 ppm). The phase transition energy is 5.69J/g, which is more than that for the metal produced by conventional electro-winning practice. This indicates relatively more of hcp microstructure in the metal when produced using H_2O_2 as an additive.

Micro hardness

Micro hardness of the cobalt metal deposited in absence of additive was found to be 424 HV and that of the metal deposited in presence of 150ppm of hydrogen peroxide was found to be 444 HV. The small increase in the mean values of the micro hardness of the Cobalt metal obtained with the addition of hydrogen peroxide might be attributed to the grain refinement and more of hcp lattice.

X-ray diffraction analysis

The X-ray diffraction pattern of cobalt metal produced by electro-winning from cobalt sulphate solution in presence of optimum concentration of hydrogen peroxide is given in Figure 2b. XRD data analysis indicates hcp structure with (100), (110) planes. X-ray diffraction pattern of cobalt metal produced by electro-winning in absence of hydrogen peroxide is given in the Figure 2a. which indicates a mixture of hcp & fcc with (111), (110) planes^[31].

CONCLUSIONS

From the study following conclusions were obtained.

- Addition of hydrogen peroxide in the cell reduces not only the sludge formation but also increases the current efficiency. Optimum concentration of H_2O_2 was found to be 150 ppm.
- On basis of DSC thermogram hcp lattice formation found.
- Improved morphology of metal was observed from SEM pictures
- Slight Increase in the Micro hardness of the metal at optimum concentration of H_2O_2 .
- Mechanism was proposed based on the Cyclic voltametric study.
- X-ray diffraction pattern indicated the mixture of

hcp and fcc phase structure with out hydrogen peroxide and addition of hydrogen peroxide lead to hcp phase structure.

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