

FUNDAMENTAL STUDY OF THE DEPOSITION OF COBALT FROM
ELECTROLYTES CONTAINING ZINC

by

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Abstract

The presence of cobalt in zinc electrowinning electrolytes acts to lower the current efficiency of zinc deposition. For this reason, industrially, cobalt is removed from zinc electrolytes by cementation with zinc dust.

The process of cementation of cobalt with zinc dust is an inefficient use of zinc. Up to 200 times the stoichiometric amount of zinc dust is needed to effectively remove cobalt to levels sufficient to electrowin zinc at a high current efficiency. To increase the rate of cobalt removal, zinc dust activators, such as antimony, arsenic, and copper are added to the electrolyte to increase the removal rate of cobalt.

The fundamental reasons for the inefficient reaction of zinc dust with cobalt were studied as they have not been determined previously. To study this system more effectively cobalt electrodeposition in the presence of zinc ions was studied. This method of deposition was shown to behave similarly to cementation where zinc metal rather than an electric current is used to reduce cobalt.

The deposition of cobalt in the presence of zinc was studied by cyclic voltammetry, potentiostatic deposition, AC impedance, and surface analysis. It was found that there were two regions of inhibition dependent of the overpotential of cobalt deposition. At low cobalt overpotentials it was proposed that zinc, in the form ZnOH^+ , adsorbs on the surface of the electrode blocking the deposition of cobalt. At higher cobalt overpotentials it was proposed that concurrent hydrogen generation increases the pH at the interface and Zn(OH)_2 precipitates. A chemical model of inhibition as a function of cobalt overpotential is presented.

Since the concentrations of the various species present in the cobalt-zinc-water system at the interface influences the concentration of ZnOH^+ and the precipitation of Zn(OH)_2 , the concentration of these species at the interface was calculated to test the proposed theories. This calculation showed that the onset of primary inhibition corresponds to a high concentration of ZnOH^+ , and secondary inhibition corresponds to conditions where the precipitation of Zn(OH)_2 is favored.

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List of Symbols**General notation:**

A	area: m^2, cm^2
C	concentration: $\text{mol}\cdot\text{L}^{-1}, \text{mol}\cdot\text{cm}^{-3}$
D	diffusion coefficient: $\text{cm}^2\cdot\text{s}^{-1}$
D_0	constant: $\text{cm}^2\cdot\text{s}^{-1}$
E	potential of an electrode vs. a reference: V
E°	standard potential of an electrode vs. a reference: V
E_{cell}	emf of a reaction: V
E_a	activation energy: $\text{J}\cdot\text{mol}^{-1}$
F	Faraday's constant, the charge on one mole of electrons: $\text{C}\cdot\text{equ}^{-1}$
ΔG	free energy: $\text{J}\cdot\text{mol}^{-1}$
i	current density: $\text{A}\cdot\text{m}^{-2}$
i_L	limiting current density: $\text{A}\cdot\text{m}^{-2}$
i_{ac}	activation controlled current density: $\text{A}\cdot\text{m}^{-2}$
I	current: A
k	rate constant: s^{-1}
K	equilibrium constant: depends
K	Langmuir constant: $\text{cm}^3\cdot\text{mol}^{-1}$
m	mass: g
M	molecular weight: $\text{g}\cdot\text{mol}^{-1}$
n	number of electrons transferred in an electrode reaction: $\text{equ}\cdot\text{mol}^{-1}$
Q	amount of charge passed in electrolysis: C
R	universal gas constant: $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
T	absolute temperature: K
t	time: s, h
V	volume: L, cm^3
z	charge on an ion in signed units of electronic charge: $\text{equ}\cdot\text{mol}^{-1}$

Greek symbols:

α	electron transfer coefficient: dimensionless
η	overpotential: V
μ	absolute viscosity: $\text{g}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}$
ν	kinematic viscosity: $\text{cm}^2\cdot\text{s}^{-1}$
θ	fractional coverage of an interface: dimensionless
ρ	density: $\text{g}\cdot\text{cm}^{-3}$
ω	rotation speed: s^{-1}

Subscripts:

a	anodic
c	cathodic
O	oxidized species in the reaction: $O + ne^- \rightleftharpoons R$
R	reduced species in the reaction: $O + ne^- \rightleftharpoons R$
T	total

Superscripts:

i	initial
f	final
b	bulk
s	surface

AC impedance notation:

a	radius of active surface area: cm
c	concentration: $\text{mol}\cdot\text{cm}^{-3}$
C	capacitance: F
C_{ad}	adatom capacity: F
C_{dl}	double layer capacity: F
f	frequency: s^{-1}
H	characteristic transfer functions: ohm

j	$\sqrt{-1}$
J	local flux density: $\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$
l	thickness: cm
N	number of active sites on a electrode surface: dimensionless
q	surface area of electrode: cm^2
R_ϕ, R_p	resistances: ohm
R	half distance between active and inactive surface area: cm
s	Laplace variable: $j\omega$
$S1$	active surface area: cm^2
$S2$	inactive surface area: cm^2
W	formal rate constant for lateral flux: s^{-1}
Z	impedance: ohm

Greek symbols:

α	$\sqrt{s/D} : \text{cm}$
β	$\sqrt{(s+W)/D} : \text{cm}$
ε	experimental parameter: dimensionless
γ	constant factor: dimensionless
ω	$2\pi f : \text{s}^{-1}$
σ	ratio of inactive to active surface area: dimensionless
θ	$\sigma / (1 + \sigma) : \text{dimensionless}$

Calculation of Surface Concentrations Notation:

N_i	Flux of species i : $\text{mol}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$
α_i	Levich transfer coefficient of species i : $\text{cm}\cdot\text{s}^{-1}$

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1. Introduction

Zinc can be produced by several different processing routes. These can be split into two categories: hydrometallurgical and pyrometallurgical. Although in the 1950's the percentage of the world's zinc produced by these two methods was equal, today, hydrometallurgical routes account for over 80% of the world's production.

The first hydrometallurgical production of zinc was pioneered by Anaconda, Electrolytic Zinc of Australasia, and Cominco in 1915, and this process has changed little since its inception. This process consists of three stages: roasting, leaching, and electrowinning. For this reason it is often referred to as the RLE process.

In the roasting stage, zinc sulfide concentrates are roasted to produce a zinc oxide-containing material called calcine. This product is leached in dilute sulfuric acid to produce a zinc sulfate electrolyte, which is purified, and then electrowon. The resulting zinc is melted and cast to form the final high purity product.

The other hydrometallurgical method of zinc production replaces the roasting and leaching stages of the traditional RLE process with a pressure oxidation process. In this process zinc sulfide concentrates are leached at elevated temperatures and pressures to generate a zinc sulfate electrolyte and sulfur is recovered in elemental form.

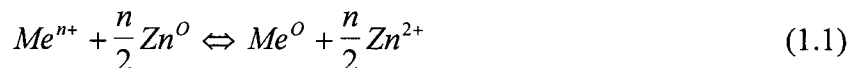
Although most descriptions of these processes give only passing mention to purification, successful electrowinning of zinc is dependent on a very pure zinc electrolyte. Impurities at concentrations as low as a few mg/L can decrease the efficiency of zinc deposition or produce an impure deposit. These impurities are removed by two separate purification processes: iron hydrolysis, and cementation.

During the hydrolysis of iron, the impure solution is oxidized by the injection of air, or by the addition of an oxidizing agent such as manganese dioxide, and the pH is raised by the addition of zinc calcine. Iron precipitates under these conditions as goethite, jarosite or hematite. Some arsenic, antimony, and germanium are also removed.

The second purification process, cementation, is a process where a less noble metal (more electronegative) is contacted with a solution containing a more noble metallic ion. Due to the

nobility of the metallic ion, the ion is reduced and “cements” on the less noble metal surface, and the less noble metal dissolves.

In the purification of zinc electrolyte, the less noble metal is zinc, and the reaction proceeds by the following simplified chemical reaction:



As this process is dependent on the surface area of the zinc/electrolyte interface, zinc is typically added as a dust formed by atomization of molten zinc, or by condensation of zinc vapors.

The presence of certain activators increases the removal rate of some impurities, in particular cobalt, from zinc electrolytes. Activators which are presently used for the removal of cobalt are arsenic or antimony, in combination with copper. Although these activators are present only in small concentrations, they can increase the removal rate of cobalt by a factor of 6 to 20 times[1]. While arsenic - copper activation increases the removal of cobalt the greatest, antimony - copper activation is more widely used as the arsenic - copper system is prone to toxic arsine (AsH_3) generation, and the higher concentration of arsenic required results in a hazardous waste which is difficult to treat.

Depending on the activators used, there are three schemes for zinc electrolyte purification using zinc dust. These are: arsenic - copper, antimony - copper, and reverse antimony - copper activated cementation.

In arsenic - copper activated cementation, arsenic and copper are added to the zinc electrolyte at an elevated temperature (75 - 100°C) to remove cobalt and nickel. This stage is commonly referred to as the “hot” stage. This stage is followed by a cementation stage in which copper and cadmium are removed without the addition of any activators. Due to the lower temperature of this operation (60°C) this stage is referred to as the “cold” stage.

Antimony - copper activated cementation is essentially the same as the arsenic - copper activated system, with the exception that, antimony and copper are used as activators. In reverse antimony - copper activated cementation, copper and cadmium are removed in the first stage, and cobalt and nickel in the second stage.

The “hot” stage of cementation to remove cobalt is a very critical step of zinc electrolyte purification. At levels as low as 0.5 mg/L, cobalt can be very detrimental to the deposition of zinc. As cobalt has a lower hydrogen overvoltage than zinc, the presence of small amounts of cobalt co-deposited with zinc increases hydrogen generation. This lowers the current efficiency for zinc deposition.

Cobalt cementation with zinc dust is an inefficient use of zinc dust. In cold stage cementation, to remove cadmium and copper, the amount of zinc dust required is very close to the calculated stoichiometric amount; however, for hot stage cementation of cobalt, an excess on the order of 100 to 200 times the stoichiometric amount of zinc dust is required to remove cobalt to levels required for electrowinning (typically below 0.3 mg/L). This poor efficiency is a result of hydrogen discharge which consumes zinc not used to reduce cobalt.

Thermodynamically, cobalt should be removed from zinc containing solutions with the addition of metallic zinc. However, in practice, studies of cobalt deposition from solutions of cobalt and zinc show that cobalt does not deposit, and that at suitably reducing potentials, zinc is deposited preferentially over cobalt. This phenomenon is known as anomalous deposition[2].

The inefficiency of cobalt removal using zinc dust for cementation has not been studied in depth. This knowledge is critical to obtaining higher removal rates of cobalt from zinc sulfate solutions. Thus, it is the aim of this thesis to determine why cobalt removal from zinc electrolytes is so inefficient.

2. Literature Review

2.1 Effects of Cobalt on Zinc Electrowinning

The effect of cobalt on zinc electrowinning appears to be complex. This complexity is illustrated in Table 2.1 where impurity concentrations of several zinc electrolytes are compared.

This table shows that the upper limit for cobalt ranges from 0.05 to 1.0 mg/L. The upper limit of cobalt varies between each zinc producer as the purity and current efficiency of zinc production are dependent on the overall purity of the electrolyte. Thus, higher cobalt levels can be tolerated if the level of other impurities is low.

Table 2.1: Upper limits of impurities in neutral solution[1].

Impurity (mg/L)	Mathewsons Zinc	Japan (Mean)	Hoboken- Overpelt	Cominco	National Zinc	Port Pirie
Cu	-	trace	0.2	-	<0.1	0.15
Cd	0.2	<0.1	1.0	0.3	2.3	0.35
Co	<1	<0.1	1.0	0.3	0.7	<0.05
Ni	0.1	<0.1	0.050	-	0.3	<0.05
Fe	-	1-6	20.00	<5	<0.1	8.0
As	<4	-	0.020	-	<0.01	0.01
Sb	<0.02	-	0.020	0.03	0.012	0.025
Ge	0.01	-	0.020	0.03	<0.010	0.003
Te	0.005	-	-	-	0.017	-
Tl	-	-	1.0	-	17	-
F	<2	-	-	<10	0.40	-
Cl	-	-	-	50-100	100.00	-

Cobalt can be considered the fourth worst impurity in zinc electrowinning as listed by Maja and Spinelli[3]. These authors rate the impurities in order of decreasing effect on current efficiency as: Ge, Sb, Ni, Co, Bi, Cu, As, Sn, and Fe. They conclude that the effect of the impurity on zinc deposition is not due to the deposition current of the impurity, but almost entirely to the low hydrogen overvoltage generated by its deposition.

Jaskic[4,5] groups cobalt with other impurities which are more electropositive than zinc, have a high melting point and a low hydrogen overvoltage: Ni, Co, Ag, and Cu. He also suggests that cobalt decreases current efficiency by causing increased hydrogen evolution, and further mentions that it can cause preferential redissolution of the zinc deposit. He suggests that

small amounts of cobalt (1 - 10 mg/L) co-deposit as zinc alloys, and not as separate metallic centers as found at higher cobalt concentrations. He based his conclusion on the absence of cobalt peaks during potential sweep and steady state polarization measurements, and thus his conclusion is not well founded.

Maja *et al*[6] studied the deposition of zinc on a cobalt substrate, using this system to model what they believed to be the effect of cobalt metallic "centers" that would deposit under normal plating conditions. They found that zinc deposits under underpotential deposition conditions, and then transfers to massive zinc deposition after a certain induction time. Furthermore, they found that this shift occurs only above a certain critical current density which was dependent on the acid concentration. They also found that the presence of cobalt in zinc plating baths affects the crystallographic orientation of the zinc deposit, but does not affect the overall morphology.

Akiyama *et al*[7] showed that cobalt raises the critical current density above which zinc deposits at a high current efficiency. They also showed that at low current densities (less than $100 \text{ A}\cdot\text{m}^{-2}$) cobalt is found in the zinc deposit at concentrations greater than in the electrolyte, whereas at higher current densities the concentration in the deposit is lower than in the electrolyte, indicating anomalous deposition.

The synergistic effect of cobalt and other impurities was first established by MacKinnon and his coworkers[8,9] who found that cobalt alone has no effect on the current efficiency of zinc deposition, but found that the presence of antimony and cobalt was very deleterious to zinc electrowinning. They suggested that antimony acts as a hydride former which facilitates the generation of hydrogen on electrodeposited impurities. This is supported by the fact that only a very small amount of antimony has been found in zinc deposits, and that only a small concentration of antimony is required to activate hydrogen evolution.

Bozhkov *et al*[10] also studied the synergistic effects of cobalt and other elements, in particular the effect of cobalt and nickel. They found that cobalt did not co-deposit with zinc; however, they established that the presence of cobalt increases the capacity of the electrode double layer by 60%, and suggested that this was due to the specific adsorption of cobalt complexes of the form: $\text{Co}(\text{SO}_4)_n^{(2n-2)-}$, particularly in strong sulfuric acid electrolytes. They

suggested that adsorption of these complexes facilitates the discharge of Ni^{2+} which accounts for the synergistic effect of Co^{2+} and Ni^{2+} .

2.2 Theory of Cementation

2.2.1 General Cementation Theory

Cementation, or metal displacement reactions as they are also known, are reactions in which a reducing agent in the form of a liquid or solid metal, is used to exert a sufficiently negative potential to a solution to reduce metallic ions. This method of reducing metallic ions has been used for the recovery of copper using iron, and in the purification of solutions.

Electrochemically, cementation can be considered as a short circuited electrochemical cell, the anodic reaction being the dissolution of the more electronegative metal, and the cathodic reaction being the reduction of the more noble metallic ion.

To gain a better understanding of the reactions involved it is beneficial to extrapolate the concept of the short circuited cell one step further, and devise Evan's diagrams to describe the relationship between the metals. The use of Evan's diagrams to describe the relationship between the metals in cementation has been given thorough treatment by Power and Ritchie[11], and Peters[12].

Evan's diagrams are beneficial in describing cementation reactions as they give the "current density" at which the short circuited cell is operating. This current density is related to the rate of the cementation reaction by the following equation:

$$r = \frac{i_c A_c}{zF} \quad (2.1)$$

where r is the rate of cementation in mol/s.

The work of Power and Ritchie[11] has led to the prediction of diffusion or activation control based on the differences in reduction potentials of the two species of interest. Figure 2.1 shows Evan's diagrams for cementation reactions under diffusion control, activation control, and the boundary between these two control types. The rate of the cementation reaction as given in Equation 2.1 can be calculated by taking the current where the anodic and cathodic reactions intersect as i_c . Under activation control, this intersection occurs in the Tafel regions for both reactions, while under diffusion control, the cathodic reaction is mass transfer limited. The

anodic reaction is not mass transfer limited under the typical concentrations of species used for cementation. This diagram shows that values of the limiting current density of the cathodic reaction (i_L), the exchange current densities ($i_{o,c}$, $i_{o,a}$), and the Tafel slopes of the two reactions are important in determining the control of the reaction and the reaction rate.

The limiting current density is related to the mass transfer conditions of the system, and can be considered the maximum rate that a reaction can occur under mass transfer limitations. The limiting current density of a reaction is linearly related to the concentration of the reactive species for consistent mass transfer conditions.

The exchange current densities are also related to the concentration of the reacting species by the following relationship:

$$i_0 = nFk^0 C_O^{s(1-\alpha)} C_R^{s\alpha} \quad (2.2)$$

It is important to note that Figure 2.1 provides only an illustration of cementation at a particular time. As the cementation reaction proceeds, the surface area for both the cathodic and anodic reactions and the concentration of the species will change. This will change the exchange current density and reversible potential of the reactions, and the current density of the intersection between the anodic and cathodic reactions will change.

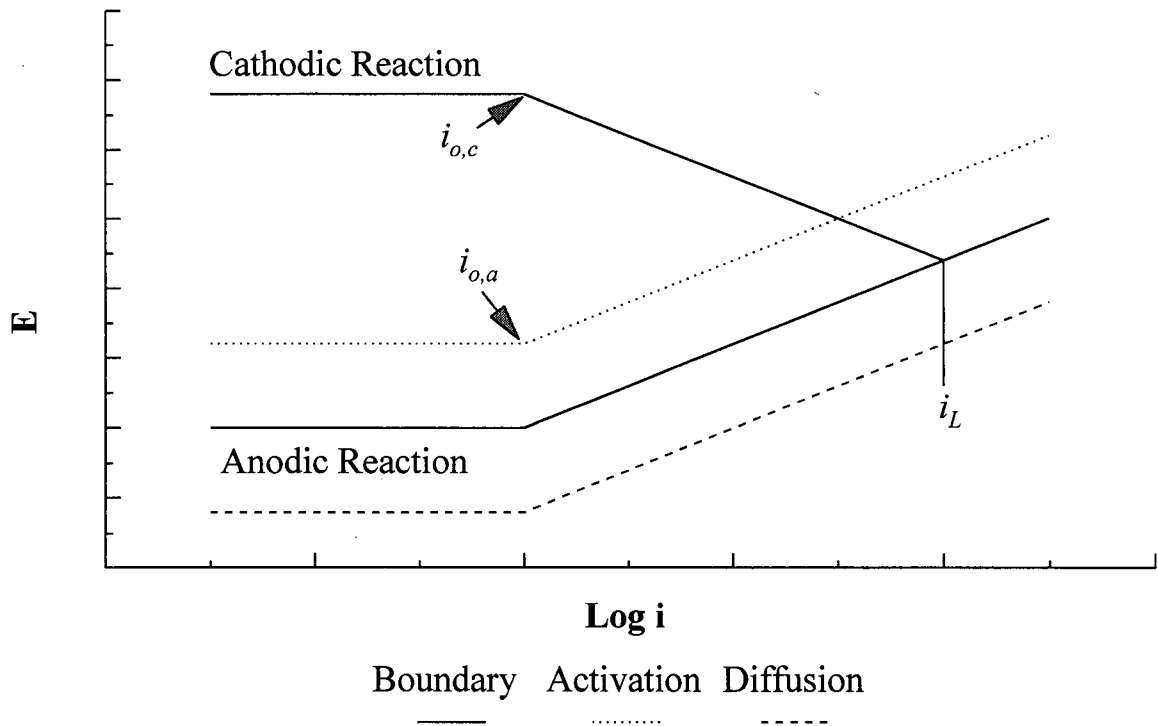


Figure 2.1 Evan's diagram portrayal of kinetic control mechanisms.

Using typical values for the exchange current densities, Tafel slopes, and limiting current densities of the reactants, Power and Ritchie found that for systems where the difference in reduction potential is greater than 0.36 V, the system should be under diffusion control, and for systems where the difference is less than 0.06 V, the system should be under activation control; however, they are quick to point out the limitations of this treatment.

As the surface areas of the species involved will change during the cementation process, rates predicted by the Evan's diagram will change. Furthermore, formation of alloys, and formation of oxide films will change the shape of the Evan's diagram, leading to different predictions.

When the surface during cementation is covered by an oxide film, or a precipitated product, the surface area available for deposition changes. This change usually decreases the surface area available for the depositing species, and the cementation rate decreases.

The electrodeposition of an alloy is often suggested as the effect of activators during cementation reactions. When a metal is deposited as an alloy, the electrode potential of the more noble element is shifted by the following relation, assuming that the activity can be approximated by mole fraction:[13]

$$\Delta E = -\frac{RT}{zF} \ln x \quad x = \text{mole fraction} \quad (2.3)$$

This treatment of the effects of alloying is simplistic, as the free energy associated with mixing is not included. Alloying will also affect the exchange current density of the deposited metal.

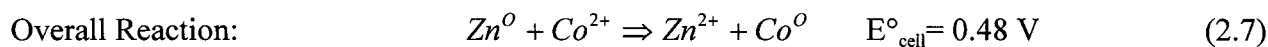
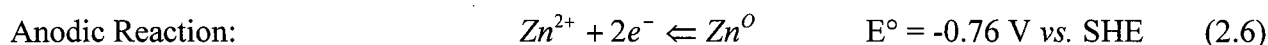
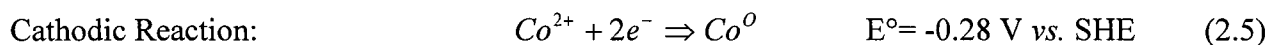
This differs from the formation of intermetallic compounds as the free energy of formation of the compound must be taken into account. Thus for the creation of an intermetallic compound, the standard potential is changed by:

$$\Delta E^{\ominus} = -\frac{\Delta G_f^{\ominus}}{mzF} \quad (2.4)$$

where ΔG_f° is the free energy of compound formation (always negative), and m is the stoichiometric coefficient of the metal in the equation of formation.

2.2.2 Theory Applied to Cobalt Removal

A simple examination of the thermodynamics of the cementation between cobalt and zinc shows that cementation should occur without difficulty. Equations 2.5-2.7 show the simplest case for cobalt reduction using zinc dust.



A more complete treatment of the reaction between cobalt ions and zinc dust takes into account the concentrations of the species involved, and the elevated temperature at which the reactions are occurring. This treatment has been accomplished by Lew[14], and adjusted to standard industrial conditions (150 g/L Zn, 20 mg/L Co, 73 °C), the actual potential difference between cobalt and zinc is 0.35 V. This difference should still be sufficient for cobalt removal; however, cobalt removal with only the addition of zinc dust is too slow, and the consumption of zinc dust is too high, to be considered economic. For this reason activators are added.

Zinc dust which is not used to reduce cobalt is corroded with a concurrent evolution of hydrogen. The generation of hydrogen on zinc is typically poor due to the high hydrogen overpotential of hydrogen on zinc; however, as mentioned in Section 2.1, the deposition of cobalt and other impurities, produces a surface which has a low hydrogen overvoltage, which increases the rate of hydrogen evolution.

The generation of hydrogen during cementation has two negative effects on cementation. First it consumes zinc which would otherwise be used for the deposition of cobalt. Second, it raises the pH in the vicinity of the zinc particle increasing the probability of zinc hydroxide or zinc oxide precipitation. As this precipitation occurs on the particle surface, further reaction is inhibited or depressed.

2.3 Removal of Cobalt using Cementation

2.3.1 Cobalt Purification Processes

There are three processes by which cobalt is removed industrially from zinc sulfate solutions: cementation with antimony - copper activation, cementation with arsenic - copper activation, or oxidation of Co^{2+} to Co^{3+} followed by precipitation by the addition of organic reagents such as α -nitroso- β -naphthol or xanthate. As the last method is in little use, it will not be included in this discussion.

It should be stressed that cobalt is not the only impurity removed during these processes, but for most zinc operations, it represents the major impurity removed. Other impurities removed are nickel and thallium. As these other impurities appear to be removed under similar conditions as cobalt, most experimental studies concern themselves only with cobalt removal.

In most zinc dust cementation schemes, zinc dust is added to the zinc electrolyte in the form of an atomized or condensed powder, either introduced as a slurry, or as a dry addition. Zinc dust size ranges from 10 - 200 μm . Activating agents may be added to the incoming electrolyte, or to the zinc dust slurry. The electrolyte typically contains: 150-160 g/L Zn and 1 - 20 mg/L Co. The pH of the electrolyte is 4-5.5 measured at 25°C.

Addition of arsenic and copper at an elevated temperature to remove cobalt from zinc sulfate electrolytes was patented in 1919[15]. Although this method of purification has a lower zinc dust usage than the similar antimony - copper system, this system is not practiced at all zinc plants due to the hazardous residues that are generated, and due to the possible production of arsine, a poisonous gas.

Typically arsenic - copper activated cobalt removal is operated at 50 - 200 mg/L As, 50 - 500 mg/L Cu, and at an elevated temperature (60-100°C)[16,17]. Arsenic is added either as its oxide, or as sodium arsenate. Copper is almost always added as copper sulfate. Zinc dust consumption for arsenic - copper activation can be as low as 1.3 g/L of electrolyte treated[10].

Antimony - copper activation benefits from the production of a less hazardous residue; however, the zinc dust consumption is high. Residues are less hazardous due to the low addition of antimony, typically 1 - 3 mg/L. Antimony is added either as an oxide or as potassium

antimony tartrate. Copper addition is 20 - 100 mg/L, and temperatures are high (60-90°C). Zinc dust usage under these circumstances is much higher, between 2 - 4 g/L.

2.3.2 Macro Effects of Zinc Dust Purification

2.3.2.1 Antimony-Activated Cementation

Antimony-activated cementation is affected by several different parameters including: the pH of the solution, the concentration of antimony and copper, the temperature, and the presence of other elements in solution. Lew *et al*[18] studied this system, and found the following initial conditions successful for cobalt removal from zinc sulfate electrolyte:

- a pH of 4.2 to 4.4 measured at 73°C
- an antimony concentration of 1.5 mg/L
- a copper concentration of 40 mg/L
- temperature greater than 70 °C

He found that a pH greater than 4.4 led to precipitation of basic zinc sulfate, and a pH lower than 4.2 increased hydrogen evolution which led to a loss of zinc dust. He also found that further additions of activating agents did not result in increased cobalt removal rates. Cobalt, copper, and antimony removal from solution followed first-order kinetics, with the concentration of antimony and copper decreasing substantially during the first part of cementation. Figure 2.2 shows the change in concentration for these three elements. The dependence of the removal rate on temperature showed an Arrhenius-type dependence and from the activation energy calculated, the system was considered to be under activation control.

Blaser and O'Keefe[19] studied the effect of similar variables on antimony-activated cementation of cobalt using zinc dust and incorporated statistical design. They found that temperature, followed by the mass of dust used, and the concentration of antimony were the most important factors in cobalt removal.

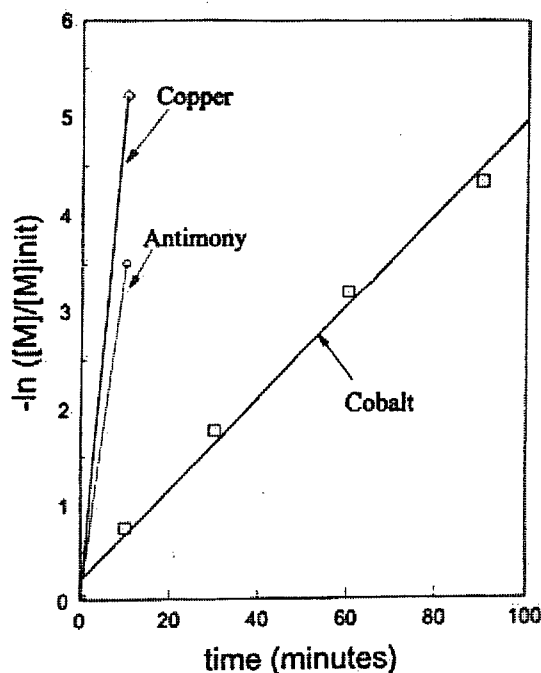


Figure 2.2 Removal of cobalt, copper and antimony during cementation. Conditions: pH = 3.6, 73°C, 10 g/L Zn dust, $C_{Co} = 27$ mg/L, $C_{Cu} = 36$ mg/L, $C_{Sb} = 1.5$ mg/L.

The effect of cadmium on antimony-activated cobalt removal was studied by Adams and Chapman[17]. They found that the concentration of cadmium was important in cobalt removal from de-copperized solutions. They found that the cobalt removal rate increased with increasing cadmium concentration up to 515 mg/L Cd, and suggested that cadmium may alloy with cobalt increasing the cobalt removal rate. The addition of small amounts of copper did not appear to be as beneficial as the addition of cadmium. They also found that using zinc dust containing 0.8% Pb led to a lower final cobalt concentration.

The beneficial effect on cobalt cementation of lead additions to zinc dust was also found by Bodson[20], who stated that lead added to zinc dust at levels near 1% reduced the tendency of cobalt to redissolve. He stated that lead added to solution in the form of lead sulfate or acetate increases the removal of thallium and antimony. Bodson's patent covers a process in which no copper is used in antimony activated zinc dust purification of cobalt. In this patent Bodson states that with a zinc dust condensed from vapor, copper is not necessary for cobalt removal.

Contrarily, Salin[21] noted that the removal of cobalt from solution only occurred when there was simultaneous cementation of copper; however, he noted that the presence of high

amounts of copper in solution may cause redissolution of cobalt as copper can displace cobalt by the following reaction.



With the co-cementation of copper during cobalt cementation, Lange[22] found that hydrogen generation is increased. He suggested that the mechanism of cobalt deposition is one of alloy formation between cobalt and copper, or cobalt and zinc.

Internal work performed by Cominco Ltd.[23] on antimony activated cobalt removal has shown that with increasing antimony content, the initial pH change increases. Although no conclusion is made in the paper, this result appears to suggest that antimony acts to increase hydrogen evolution. This is consistent with the mechanism suggested of antimony in zinc electrowinning; that is, as a hydride generator which increases hydrogen generation.

Houlachi *et al*[24] studied the effects of organics on antimony-activated cobalt cementation. They found that typical organics found in zinc electrolytes, such as flocculants, levellers, and foaming agents, had a deleterious effect on the removal of cobalt even at levels as low as 0.5 mg/L. They suggest that organics may inhibit cobalt removal by flocculating the zinc particles during the cementation process, or by chelating the cobalt rendering it unavailable for cementation.

2.3.2.2 Arsenic-Activated Cementation

The most thorough work on the arsenic activated cementation system has been accomplished by Fugleberg *et al*[16, 25]. Their optimal conditions for cobalt cementation mirror those obtained with antimony activation: the optimal pH is near 4.0, cobalt removal is under activation control, and the removal rate has an Arrhenius dependence with temperature.

Hamilton[26] studied the effect of different arsenic addition schemes on the removal of cobalt and zinc dust usage. He found that the addition of arsenic as As_2O_3 had the lowest zinc dust usage; however, the addition of dissolved zinc arsenate was very comparable. The addition of copper arsenate required a lower solution pH and thus led to higher zinc dust usage due to increased hydrogen evolution.

2.3.3 Mechanistic Studies of Zinc Dust Purification

2.3.3.1 Antimony System

Most mechanistic studies of the antimony-activated cementation system have postulated that antimony and/or copper, alloy with cobalt lowering the reduction potential for cobalt deposition.

Fischer-Bartelk *et al*[27] examined the electrochemical nature of several zinc - cobalt alloys that were produced by electrodeposition, and equilibrium thermal alloys. They found that electrodeposited alloys were different than thermally prepared alloys of the same cobalt - zinc ratio. Identifying phases in the electrodeposited alloy, they found that cobalt was present only as the γ phase of the Co-Zn alloy, in a matrix of pure zinc. They correlated the rest potentials of these alloys connected to a reference electrode of pure zinc to an equilibrium phase diagram for Co-Zn. Figure 2.3 shows that in the zinc-rich area of the diagram, the potential difference between zinc and the Co-Zn alloy is small. They suggested that poor cementation of cobalt by zinc is due to this small potential difference.

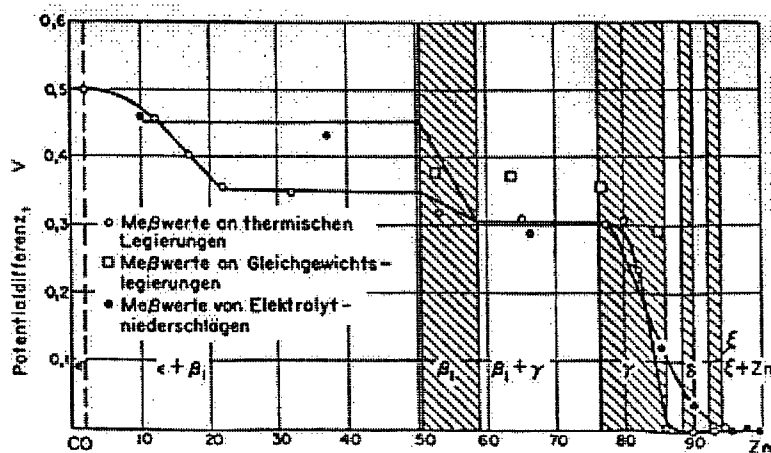


Figure 2.3 Potential difference between Co-Zn alloys and pure zinc (electrolyte: 0.01 mol/L Zn^{2+}) o - theoretical Potentials, ▨ - equilibrium alloy, • - electrodeposited alloy

The deposition of γ alloys from Zn-Co solutions was also observed by Alcalá *et al*[28]. Studying the chloride system, they found that cobalt and zinc deposit as a γ alloy when the zinc overpotential is low or the ratio of zinc to cobalt is greater than 1:9, and heterogeneously when the overpotential is high, or when the ratio of zinc to cobalt is less than 1:9.

de Blander and Winand[29] used anodic dissolution and radioactive tracers to investigate the method of cobalt deposition under antimony activated cementation conditions. Figure 2.4 shows the results of one of their tests. They found that cobalt and antimony electrodeposited from a zinc solution anodically dissolve at the same potential. They used this fact to postulate that cobalt and antimony form alloys which have a low cobalt activity. Copper was found to increase the cobalt removal rate more significantly than antimony and it was thus suggested that cobalt, antimony, and copper form triple alloys.

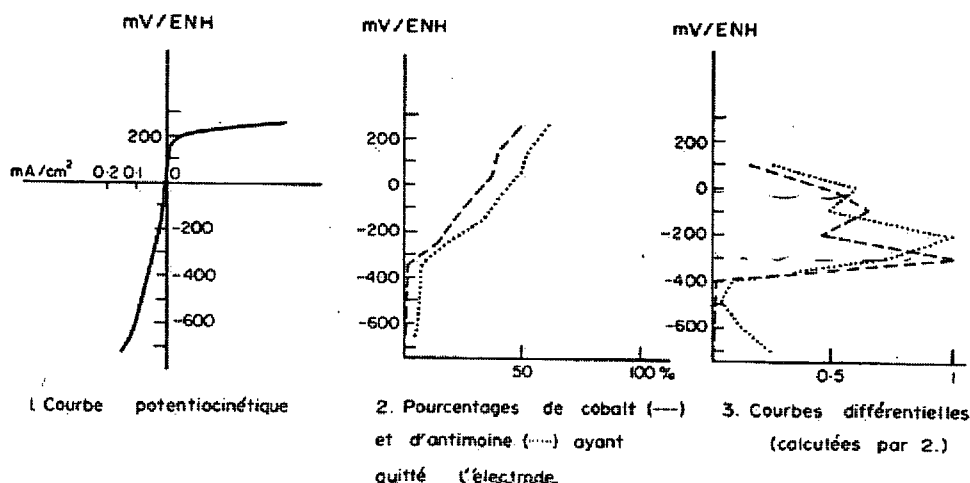


Figure 2.4 Anodic dissolution of a potentiostatic deposit. Dissolution conditions: saturated K_2SO_4 , $70^\circ C$, pH 6.5, sweep rate 12 mV/min, magnetic agitation. Deposition conditions: -730 mV vs. SHE, Pt electrode, 160 g/L Zn^{2+} , 10 mg/L Co^{2+} , 10 mg/L Sb_2O_3 , 4 mg/L H_2SO_4 , $70^\circ C$, 43 min, pH 4.

Kroleva[30] studied the removal of cobalt by zinc dust which had been pre-treated by contact with a solution of copper sulfate and antimony tartrate. She found that the pre-activated zinc dust was effective at removing cobalt and suggested that Cu_2Sb was formed. It was also suggested that this surface had a lower overvoltage for cobalt deposition, and a higher overvoltage for hydrogen evolution.

Aitkenhead[31] studied the removal of cobalt using zinc dust, activating the process with metallic antimony dust. He found that the presence of antimony dust increased the cobalt removal rate as compared to zinc dust alone and the presence of copper was inhibitory, not beneficial to cobalt removal under these conditions. He suggested that the activating role of antimony metal is not due to the formation of cobalt - antimony alloys, as this would require six

cobalt atoms to one antimony atom for the alloy he proposed, but that the effect of antimony metal is to depassivate the zinc surface improving cobalt deposition.

van der Pas[32] investigated the deposition of cobalt from zinc electrolytes to antimony and copper surfaces. She found that when cobalt deposits on an antimony surface, the morphology of the deposit is different than when cobalt deposits on copper. She concluded that the activating effect of antimony was to change the orientation of the cobalt deposit, leading to a cobalt deposit which has a lower nucleation overpotential for deposition.

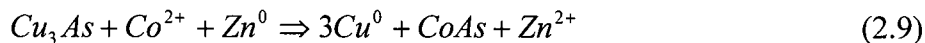
2.3.3.2 Arsenic System

Both the antimony- and arsenic- activation systems were studied by Tozawa *et al*[1]. They used a rotating zinc disk to study the effect of arsenic and antimony on the removal of cobalt. They found that arsenic was more effective than antimony at removing cobalt and proposed that the mechanism for cobalt removal was deposition of Co-As and Co-Sb alloys based on E-pH diagrams. Examination of the deposits on the rotating zinc disk showed that with arsenic activation, cobalt deposits on Cu-As centers, but with antimony activation, cobalt deposits on the edges of the Cu-Sb deposit.

Lawson and Nhan[33] used the rotating disk geometry to study arsenic-activated cobalt removal. They found that the presence of zinc in solution greatly inhibits the removal of cobalt. They found that arsenic-activated cobalt deposition changes from diffusion to chemical control with the addition of zinc to the solution. On studying the effects of pH, they found that the rate of deposition increased as the initial pH was lowered. They hypothesized that at higher pH values, the surface of the zinc disk would become coated with insoluble basic zinc sulfate. They found that at temperatures less than 80°C cobalt is precipitated as CoAs, and at temperatures greater than this as CoAs₂. They also found that dissolved oxygen had a detrimental effect on cobalt cementation.

Fugleberg *et al*[16] have studied the arsenic-activated system extensively. They found that copper was not critical to cobalt cementation as analysis of residues showed that copper is only found with arsenic as Cu₃As and cobalt was found as a separate phase. They hypothesized that this phase was CoAs or had a stoichiometry close to this. They further validated the non-critical nature of copper by using pre-activated residue with no copper present in solution. The results were comparable; however, small additions of copper to the solution were found to be

beneficial. Further research suggested that the presence of copper was beneficial[16]. Based on this work they postulated that due to the high activation energy of cobalt deposition, the most likely reaction mechanism was:



2.3.4 Other Cementation Studies

Internal work performed at Cominco Ltd.[34] showed that manganese powder is up to 3 times more effective than zinc powder under conditions similar to zinc dust cementation; however, the manganese tenor of the electrolyte becomes too high for successful electrowinning and the cemented cobalt has a tendency to redissolve.

MacKinnon[35,36] used Te^{4+} to activate cobalt removal with zinc dust. He found that the optimal ratio of Co:Te:Cu was 1:0.4:10 and that further copper additions led to redissolution of the cobalt deposit. He also found that cadmium present in the solution at concentrations greater than 200 mg/L lowered cobalt removal rates. In tests where an ammonium acetate-acetic acid buffer was used, he found that cementation rates were improved. He suggested that this increase was due to inhibition of a surface zinc hydroxide film by buffer addition.

2.4 Anomalous Deposition

Anomalous deposition is defined as electrodeposition of two metals where the less noble metal deposits preferentially over the more noble metal. Examples of anomalous deposition encountered in industry are the preferential deposition of iron over nickel and cobalt, and the preferential deposition of zinc over cobalt and nickel[2].

2.4.1 Anomalous Deposition Involving Zinc

Xiong and Ritchie[37] studied the anomalous deposition of cobalt and zinc with reference to cementation, by use of impedance spectroscopy, cyclic voltammetry, and x-ray diffraction. They suggested that inhibition of cobalt deposition from solutions containing zinc is a combined effect of the following types:

1. Inhibition due to the effect of adsorbed zinc ions on the double layer.
2. Inhibition due to adsorbed hydrogen. It becomes significantly greater when the solution pH is lower than 4.5.

3. Inhibition due to the blanketing of the surface with products such as zinc hydroxide or basic zinc sulfate.
4. Inhibition due to air which may cause passivation of the zinc surface or the deposited cobalt.
5. Inhibition due to the preferential adsorption of Zn^{2+} at active zinc sites which reduces the rate of cobalt nucleation.

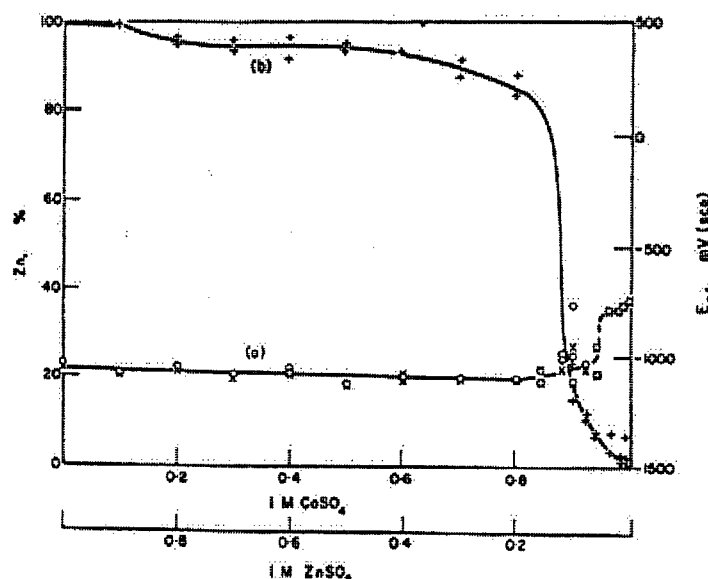


Figure 2.5 a. Influence of composition of the solution on cathodic polarization measured at $500 \text{ A}\cdot\text{m}^{-2}$. b. Influence of the composition of the solution on zinc content of deposits obtained at $500 \text{ A}\cdot\text{m}^{-2}$

Yunus *et al*[38] studied the inhibition of cobalt deposition by zinc in solution, and found that zinc ions have a very strong effect on the deposition of cobalt. They found that from solutions containing $0.94 \text{ mol/L CoSO}_4$ and $0.06 \text{ mol/L ZnSO}_4$, or higher zinc concentrations, cobalt and zinc deposit anomalously. The deposition potential and percentage zinc in deposits as a function of cobalt and zinc concentrations are depicted in Figure 2.5. Cobalt was found to deposit on the edges of hydrogen bubbles adsorbed on the surface. The inhibition of cobalt deposition was found to be the effect of two factors. First, as zinc was present in the deposit as heterogeneous inclusions, it was concluded that zinc adsorbs on the active centers, reducing cobalt deposition, and increasing the generation of hydrogen. Second, the generation of hydrogen would make the pH in the vicinity of the cathode basic and this would lead to the precipitation of colloidal zinc hydroxide on the surface of the electrode, further inhibiting deposition.

Kharlamov *et al*[39] also studied the morphology of deposition. On studying the anomalous deposition of Ni and Zn, they found that when the concentration of zinc is low, the distribution of zinc is homogeneous throughout the nickel matrix; however, at higher zinc concentrations, zinc deposits non-uniformly. They suggest that zinc acts as an “anti-leveling” agent towards nickel deposition, causing nickel to deposit only at specific sites.

Fukushima and Higashi[40] studied the deposition of cobalt and other iron-group metals with zinc. They found that above a certain current density, the deposition is anomalous. They further elucidated that anomalous deposition occurs as the pH in the vicinity of the cathode is higher at greater current densities, which leads to the precipitation of a zinc hydroxide film. The formation of this film leads to inhibition of iron-group metal deposition. The composition of the deposit and the current efficiency as a function of current density are shown in Figure 2.6. This figure clearly shows that a high current density leads to anomalous deposition.

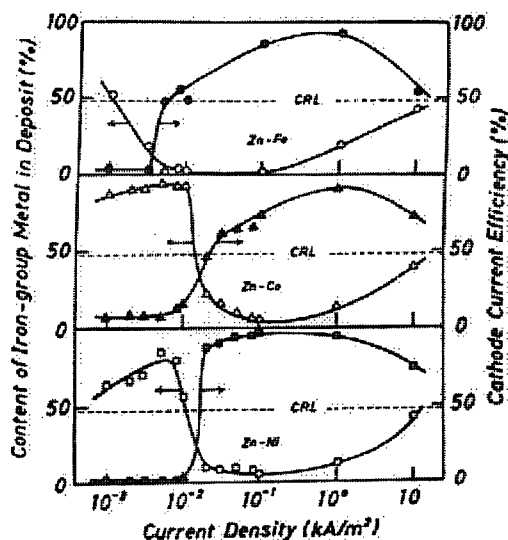


Figure 2.6 Effect of current density on deposit composition and current efficiency for zinc deposited with iron group metals.

Higashi *et al*[41] proposed that the anomalous deposition of zinc and cobalt is entirely due to the formation of a zinc hydroxide layer, and that zinc deposition takes place with this formation as a preceding step. They further explain that cobalt ions must discharge through the hydroxide film and this leads to the anomalous behavior. Using an antimony microelectrode, they were able to measure the pH in the vicinity of the cathode and found that anomalous deposition occurs when the pH is high enough to precipitate $\text{Zn}(\text{OH})_2$.

Testing the theory that hydroxide precipitation is responsible for the anomalous deposition of cobalt and zinc, Karwas and Hepel[42] tested the effect of boric acid, a known pH buffer, on the anomalous deposition of cobalt and zinc. Surprisingly, they found that the addition of boric acid increased the anomalous effect and attributed this to blocking of the electrode interface by adsorbed boric acid species.

The most thorough study of anomalous zinc-cobalt deposition was performed by Yan *et al*[43,44]. Their theory is also based on the hydroxide precipitation model. They observed that the potential during the deposition of cobalt and zinc oscillates and proposed the following model to explain this behavior:

1. Cobalt deposits on the substrate.
2. The deposition of cobalt lowers the hydrogen overpotential and hydrogen evolution increases leading to a higher pH at the interface.
3. The high pH at the interface leads to the precipitation of Zn(OH)_2 .
4. The precipitation of Zn(OH)_2 causes the surface of the electrode to be blocked and the potential to decrease.
5. When the potential decreases, Zn(OH)_2 is reduced to Zn, and the inhibitory layer is removed. The surface area increases and the potential increases.
6. Cobalt deposits on the substrate.

O'Keefe[45] studied the effects of antimony, germanium and arsenic on the anomalous deposition of cobalt and zinc. He found that of the three additives, antimony is the most effective at limiting the anomalous behavior. Furthermore, he found that agitation and low current densities increase the reversing effect of antimony, and that the addition of glue lowers the effect.

Studying the Zn-Ni system, Nicol and Philip[46] were the first to suggest the cause of anomalous deposition was due to the underpotential deposition of zinc. Using galvanostatic deposition and cyclic voltammetry, they found that zinc deposits at a potential ~100 mV higher than is predicted by thermodynamics.

The theory of underpotential deposition was further studied by Swathirajan[47], who also studied the Zn-Ni system. He found that deposition from a Ni-Zn solution to a Pt rotating disk

did not show underpotential deposition; however, if a thin layer of Ni was pre-deposited on the disk, zinc would deposit underpotentially.

2.4.2 Anomalous deposition of Nickel and Iron

The anomalous deposition of nickel and iron has been more thoroughly studied than other anomalous systems due to the importance of Ni-Fe alloys as magnetic materials. In the deposition of nickel and iron, iron is found to deposit preferentially over nickel.

The pioneering work in this area was performed by Dahms and Croll[48]. They developed a model to predict the surface pH during Ni-Fe deposition and suggested that anomalous deposition of nickel and iron is due to a ferrous hydroxide layer which precipitates as a result of a high surface pH due to excessive hydrogen evolution. They further proposed that ferrous hydroxide preferentially adsorbs on the surface, blocking the deposition of nickel, and that all anomalous deposition must be a result of this layer.

Gangasingh and Talbot[49] investigated this system using a rotating disk. They found that anomalous deposition occurs for all potentials and rotation speeds investigated. Using a model to predict the surface pH based on the model developed by Dahms and Croll[48], they found that a sudden rise in interfacial pH is not necessary for anomalous deposition to occur, which differs from the conclusions of Dahms and Croll. Investigating the effect of a boric acid buffer, they found that the presence of this buffer had no effect on anomalous deposition.

Matlosz[50] addressed the anomaly between the work of Dahms and Croll and Gangasingh and Talbot. His model does not take surface pH into consideration, but rather states that the cause of anomalous deposition of nickel and iron is competitive adsorption. He suggested that the concentration of iron adsorbed intermediates is higher than nickel intermediates and that this accounts for anomalous deposition. He recognized that pH does have an effect on anomalous deposition and suggested that it is not the simple metal cations that are reduced, but rather the mono-hydroxide species FeOH^+ and NiOH^+ . Since the dissociation constant of NiOH^+ is 1000 times greater than that of FeOH^+ , lower pH values will favor Fe discharge.

Hessami and Tobais[51] used the competitive adsorption system generated by Matlosz to generate a mathematical model to predict the anomalous deposition of nickel and iron with and without the presence of a buffer. Using their own and other researchers' experimental results,

they were able to predict accurately the partial current densities of nickel and iron considering competitive adsorption of NiOH^+ and FeOH^+ .

2.5 Summary and Focus of Present Study

Previous research on cementation of cobalt using zinc dust and on the deposition of cobalt from electrolytes containing zinc, clearly indicates that deposition of cobalt from zinc electrolytes is inhibited.

Most studies of cementation have addressed the behavior of activators. These studies of cementation have proposed the following effects of activators increase the removal of cobalt:

1. The activating elements alloy with cobalt increasing the potential difference between zinc and the depositing species.
2. The activating elements deposit creating a surface which is amenable to cobalt deposition and not amenable to hydrogen evolution.
3. The activators depassivate the electrode surface, increasing the deposition of cobalt.

Studies of anomalous deposition have attempted to address why the less noble component (in the case of zinc cementation) deposits preferentially over the more noble component (in this case cobalt). The following mechanisms have been suggested as responsible for inhibiting cobalt deposition in the presence of zinc:

1. adsorption of a zinc species
2. adsorption of hydrogen
3. precipitation of Zn(OH)_2 or basic zinc sulfate
4. underpotential deposition of zinc

As most of the anomalous deposition studies have not been concerned with cementation, none of the anomalous deposition studies have been carried out under conditions close to cementation. Typically the temperature of the solutions is ambient and the concentration of the species does not approach those used industrially for cementation. Similarly, studies of cementation appear to ignore the conclusions from studies of anomalous deposition. With the exception of depassivation of the surface, indicated as the activating effect by one researcher, none of the research into cementation has sought to explain the behavior of activators as somehow overcoming the inhibitory effects of zinc on cobalt deposition. This is likely due to the hesitation of many researches to identify the cementation of cobalt as an isolated electrochemical

deposition process. All of the research into cementation has used the oxidation of zinc as the reductive power for cobalt. While this more closely approximates real cementation conditions, it makes study of the deposition of cobalt from cementation solutions difficult.

There were two objectives in this thesis, both of which have been realized. First, the identification and quantification of cementation as a separate electrode process was accomplished. This was achieved by isolation of the reduction process of cobalt from industrial zinc electrolytes and correlation of this isolated process with the industrial process. Second, as there are several theories as to how cobalt deposition is inhibited by zinc, identification of the process by which zinc inhibits cobalt deposition in conditions similar to cementation was accomplished by investigating the cobalt-zinc system using various electrochemical techniques.

3. Experimental Methods

The experiments performed can be divided into three sections:

1. Deposition of cobalt from industrial electrolytes to a planar electrode cell.
2. Determination of some of the fundamental properties of cobalt deposition using a rotating disk electrode.
3. Investigation of the inhibition of cobalt deposition by zinc using a rotating disk electrode.

3.1 Planar Electrode Cell

To investigate the deposition of cobalt from solutions similar to industrial cementation, the cathodic and anodic reactions were separated. A cell was designed with a copper cathode and a platinum anode which was separated from the solution by a glass frit. The cell used follows from the cell used by Yamashita *et al*[52] who used a diaphragm cell with a copper electrode as the cathode. Their cell incorporated a zinc plate as an anode and they added copper powder to the cathodic compartment of the cell to increase the cathodic surface area. The cell used in this study differed from theirs in that copper powder was not added to the catholyte compartment as this produces an unknown surface area and a variable potential for the cathode surface. The cell in this study also used a platinum anode rather than a zinc anode. Initial research showed that if oxygen evolved at the anode was prevented from coming into contact with the cathode surface, cobalt would be effectively removed.

The cell was designed so that the ratio of surface area to volume was at a maximum for the cell configuration used. This allowed the decrease in cobalt concentration to be followed as a function of time.

3.1.1 Apparatus

A depiction of the cell used appears in Figure 3.1. The cell consisted of a 500 mL beaker into which various devices were placed.

A counter electrode consisting of a 1 mm diameter platinum wire, with an exposed surface area of approximately 1 cm², was placed in a glass tube with a fritted glass disk at the bottom of the tube. The glass frit was 20 mm in diameter and was oriented parallel to the cathode. The purpose of the glass frit was to ensure that oxygen evolved at the counter electrode

would not come into contact with the working electrode, while allowing the exchange of ions with the bulk solution. A copper sheet, polished with 600 grit paper and having a surface area of 36 cm^2 was used as the working electrode. The back and sides of the copper sheet were masked by non-conductive paint to ensure that deposition occurred only on the front surface of the electrode.

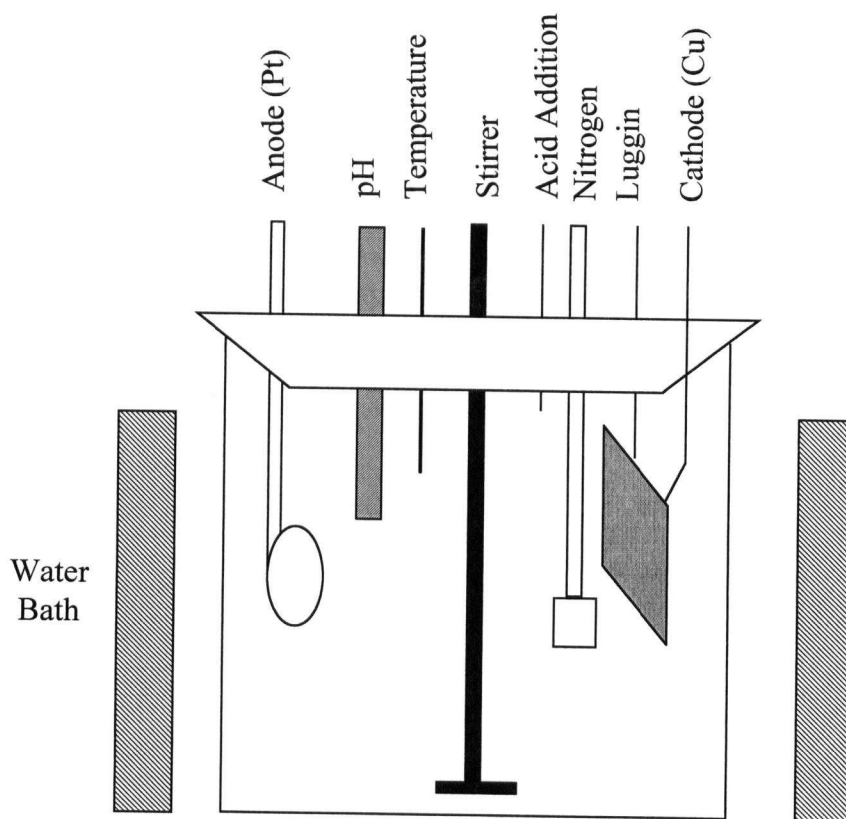


Figure 3.1 Experimental cell for cobalt deposition on a copper electrode.

To monitor and control the pH of the system, a pH controller, connected to a pH probe, metered dilute sulfuric acid to the cell by controlling a pump. Nitrogen was sparged continuously for 15 minutes before and during the experiment to purge the system of oxygen. The cell was continuously agitated by a marine-type impeller.

Temperature was controlled by a steam-heated constant temperature water bath to $\pm 1^\circ\text{C}$. Temperature was measured by a glass shrouded temperature probe placed in the beaker.

A Luggin capillary was placed in the cell so that the tip of the capillary came from behind through a small hole drilled in the working electrode. While this hole would lead to non-uniformity of the current density around the hole, due to the small size of the hole, this effect can be considered insignificant. The tip of the capillary was about 2 mm from the cathode surface.

A saturated calomel electrode, SCE, (Fisher) was contacted with the Luggin capillary and acted as the reference electrode. The reference electrode was held outside of the cell at 25°C.

Current was controlled using a constant current DC power supply (Xantrex 20-3). For experiments where potentiostatic control was needed, a Solartron 1286 potentiostat attached to a microcomputer was used.

3.1.2 Reagents

Zinc sulfate solution was obtained from Cominco, Ltd. This solution is the purified solution *after* cementation from Cominco's Trail operations. This solution is termed "clarifier overflow" internally by Cominco. An assay of the solution is listed in Table 3.1. The solution was treated with activated carbon to remove entrained organics.

Table 3.1 Assay of zinc sulfate solution obtained from Cominco, Ltd.

Species	Concentration	Units
Zn	157	g/L
Co	0.2	mg/L
Sb	0.025	mg/L
Fe	2	mg/L
Cd	0.1	mg/L
Cu	0.2	mg/L
Tl	0.1	mg/L
Ge	<0.01	mg/L
Ni	<0.05	mg/L
Mn	2.1	g/L
F	12	mg/L
Cl	190	mg/L
Mg	3	g/L
pH @ 75°C	3.6	

Cobalt, antimony, and copper concentrations of the zinc sulfate solution were adjusted by the addition of $\text{CoSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{KSbO} \cdot \text{C}_4\text{H}_4\text{O}_6$, and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ respectively. pH was adjusted with reagent grade sulfuric acid or zinc oxide depending on the pH required. For experiments in which arsenic was used as an activator, arsenic concentration was adjusted by the addition of As_2O_3 .

3.1.3 Procedure

For each experiment, the apparatus was set up as described in Section 3.1.1 and the solution described above was added to the cell. The electrolyte was allowed to reach the experimental temperature, and then current was applied to the cell. A list of the base set of experimental conditions is found in Table 3.2.

Table 3.2 Base experimental conditions for antimony activated experiments

Property	Value
Volume of solution	400 mL
Current density	50 A·m ⁻²
Time	6 h
Zinc concentration	150 g/L
Cobalt addition	20 mg/L
Antimony addition*	3 mg/L
Copper addition	0 mg/L
Temperature	75°C
pH (at 75°C)	3.6
Agitation speed	800 RPM

*For arsenic-activated experiments, the conditions above were used with no antimony present, and 75 mg/L As added.

For each test, the concentration of cobalt, the pH, the cell voltage, and the potential of the working electrode were continuously monitored. Cobalt was assayed using a colorimetric technique[53] (Appendix I). Initial and final cobalt assays were repeated by atomic absorption spectrophotometry performed by Cominco, Ltd. Initial and final antimony, copper, and arsenic assays were also performed by Cominco, Ltd. when required.

The morphology of some of the deposits was examined. This examination was performed by SEM and EDX by Cominco. Ltd.

3.2 Rotating Disk Electrode Experiments

3.2.1 Apparatus

The apparatus consisted of a rotating disk assembly (Pine) with a Pt rotating disk (area = 19.63 mm²) as the working electrode (EG&G). This rotating disk electrode is abbreviated in this thesis as 'RDE'. This electrode was encased in Teflon® and was surrounded by a ceramic sleeve to prevent solution from entering the sides of the electrode at high temperatures. A Pt coil

housed in a fritted glass sleeve served as the counter electrode. A saturated calomel electrode, SCE (Fisher), was used as the reference electrode. The reference electrode was contacted to the solution via a Luggin capillary. A 100 mL conical flask (EG&G, K0060) was used as the electrolysis cell. The reference electrode was held outside the electrolysis cell at a temperature of 25°C. The electrolysis cell was placed in a water bath. Electrolyte temperatures were adjusted to the set temperature $\pm 1^\circ\text{C}$.

Before each experiment, the Pt working electrode was polished with 0.05 μm alumina powder, cleaned with concentrated nitric acid for 2 min, and rinsed with deionized water for 1 min. Before each test the solution was sparged with nitrogen for a minimum of 15 min and a nitrogen blanket was maintained above the solution during the test.

The potential or current density, depending on the type of experiment performed, of the rotating disk was controlled using a Solartron 1286 potentiostat controlled with a personal computer. All potentiostatically controlled experiments were feedback compensated for ohmic drop. Experiments controlled galvanostatically were corrected for ohmic drop after the experiment was completed.

3.2.2 Reagents

To approximate the conditions of industrial cementation with Zn dust, the ionic strength of the solution was adjusted to match the ionic strength of the industrial process. This was achieved by the addition of 2.4 mol/L MgSO_4 . CoSO_4 and ZnSO_4 reagent grade salts were added to the electrolyte to achieve the target Co and Zn concentrations. The pH was adjusted with H_2SO_4 . All other chemicals used were reagent grade or higher.

3.2.3 Ohmic Drop Correction

Ohmic drop is an important consideration when operating an controlled potential experiment. A voltage drop occurs when the reference electrode is not positioned directly at the surface of the working electrode. When the reference electrode or the tip of the Luggin capillary is positioned away from the electrode surface, the resistance of the electrolyte between the surface and the electrode causes the applied potential to shift to a more negative potential. The difference between the *actual* applied potential, and the potential controlled by the potentiostat is

known as the ohmic drop. Since it is almost impossible to position a reference electrode at the surface, an ohmic drop always occurs.

The ohmic drop can be expressed by the following equation:

$$V_{\Omega} = iAR_{\Omega} \quad (3.1)$$

where R_{Ω} is the ohmic drop resistance, and V_{Ω} is the voltage of the ohmic drop.

Thus if the ohmic drop resistance is 5Ω , and the current density is $50 \text{ A} \cdot \text{m}^{-2}$, for a surface area equal to the area of the rotating disk electrode used, the ohmic drop is equal to $\sim 5 \text{ mV}$. Thus if the applied potential was -0.8 V vs. SCE , the actual potential would be -0.805 V vs. SCE .

If the current density is constant, as in a galvanostatic experiment, the potential of the electrode can be corrected after the experiment by subtracting the value of the ohmic drop. If the experiment is controlled potentiostatically, particularly when the potential is swept, and the current changes dramatically, post-experimental correction does not result in an accurate correction.

The potentiostat employed in this experimental program can correct for ohmic drop by a procedure known as "feedback compensation". In feedback compensation, if the ohmic drop resistance is known before the experiment is begun, this value can be entered in the potentiostat and applied potentials are continuously corrected for ohmic drop. A good introduction to the electronics of applying this correction and to the electronics of potentiostats in general can be found in the book by Gileadi *et al*[54].

The difficulty of correcting for ohmic drop is calculation of ohmic drop resistance. Ohmic drop resistance can be calculated by incorporating the conductivity of the electrolyte and the distance between the surface of the working and reference electrodes; however, often these values are not known with good accuracy. A better method is to measure the ohmic drop *in situ*.

To compensate for ohmic drop, the method outlined by Gileadi *et al*[54] was incorporated. In their method, a small triangular voltage wave is applied to the electrode in a region where no reaction takes place, and the resulting current response wave is observed on an oscilloscope. The ohmic drop is calculated by increasing the input value for the ohmic drop on the potentiostat until the current wave begins to oscillate. At this point the potentiostat is "over-compensated". The ohmic drop is calculated by choosing a value $\sim 85\%$ of the value that caused

the oscillation. While this method only calculates a rough approximation to the ohmic drop, it is usually good enough to lower contributions from solution resistance to less than 1 mV.

For calculation of the ohmic drop in this thesis, the electrode was subjected to a triangular potential wave of ± 50 mV at 50 Hz centered at 0 V vs. SCE. In this region there should not be any reaction occurring. The ohmic drop was then calculated using the above procedure.

3.2.4 True and Apparent Current Densities

The current density of a particular reaction occurring on the surface of an electrode cannot be measured directly. Rather, the current of the reaction is measured or calculated, and the current density is obtained by dividing the current by the area of the electrode:

$$i = I / A \quad (3.2)$$

The problem with this treatment is that the area of the electrode is often not known with sufficient accuracy, or the surface of the electrode is obscured by precipitates. As a first guess, the geometric surface area of the electrode is used for the area. If the surface area of the electrode is not smooth, the *true* surface area will be larger than the geometrical surface area and using the geometrical surface area to calculate the current density will result in an erroneously large current density. Similarly, if the surface of the electrode is obscured by precipitated products, the current density based on the geometric area will result in an erroneously small current density.

In this paper, reported current densities are calculated using the geometric surface area, and can be considered *apparent* current densities. Qualitative references made to the *true* current density consider how the current density will change when the surface of the electrode becomes obscured with precipitates, or more rough.

3.2.5 Calculation of Diffusion Coefficients

The diffusion coefficient is an important parameter in determining whether a reaction is activation or transport controlled. In this thesis, the diffusion coefficients of Co^{2+} and H^+ were determined as they were needed to calculate the concentration of species at the surface of the electrode.

When a reductive potential is applied to an electrode, the ion being reduced must be transported to the electrode surface, where it undergoes reaction. The rate of reduction can be

expressed by the current density of the reaction, is a function of potential, and can be expressed by the following reaction:

$$i_c = i_0 \left[\exp(\alpha_a F \eta / RT) - \exp(-\alpha_c F \eta / RT) \right] \quad (3.3)$$

This equation is known as the Butler-Volmer equation, and includes contributions from both cathodic and anodic currents. For a cathodic reaction, if the absolute value of the cathodic overvoltage is high, the anodic term can be ignored. This equation accurately describes the current density of the reaction as long as transport of the ion to the surface of the electrode does not limit the reaction.

When the reaction rate becomes limited by the transport of the ion to the surface of the electrode, the current is no longer related to overpotential and is related only to mass transport. The current then becomes:

$$i_L = nFD / \delta \quad (3.4)$$

where δ is the thickness of the Nernst diffusion layer. This phenomenon can be used to calculate the diffusion coefficient if an accurate measure of δ can be found.

An approximation of δ can be obtained by using a rotating disk electrode. To calculate the diffusion of a species to a rotating disk electrode, the method developed by Levich and represented by the Levich equation can be used. The Levich equation, which incorporates a value of δ , is as follows:

$$i_L = 0.62nFD^{2/3}v^{-1/6}\omega^{1/2}C^b \quad (3.5)$$

Using this equation, the diffusion coefficient can be calculated if the rotation speed, ω , and the kinematic viscosity, v , are known. In order to calculate the kinematic viscosity both the absolute viscosity, and the density of the solution must be known. It is by this method that the diffusion coefficients of cobalt ion and protons are calculated in this thesis.

3.2.5.1 Density Measurements

The density of 2.4 mol/L MgSO_4 electrolyte was obtained by the use of a pycnometer. A 25 cm^3 pycnometer bottle was filled with electrolyte, and the bottle was brought to temperature by a temperature controlled water bath. The bottle was then removed, and excess solution and water were removed from the bottle. The bottle was then weighed to 0.1 mg accuracy. To calibrate the pycnometer, deionized water was subjected to the same treatment as the electrolyte

at 25°C, and the pycnometer was calibrated assuming a density of water of 0.997 g/cm³. The density of the electrolyte is then given by the following equation:

$$\rho_{el} = \left(\frac{m_{el}}{m_{H_2O}} \right) \rho_{H_2O} \quad (3.6)$$

3.2.5.2 Viscosity Measurements

Viscosity was measured using a Brookfield LVIII rheometer, with a ULA type spindle at a rotation speed of 50 RPM. To calculate the absolute viscosity, 2.4 mol/L MgSO₄ was added to the holding chamber and brought to either 25, 50 or 75°C. The spindle was allowed to rotate for 2 minutes, until an steady value was achieved.

3.3 Determination of Tafel Slopes

Tafel slopes of the discharge of cobalt and of hydrogen were determined by the following methods:

For Co:

1. A solution containing 2.4 mol/L MgSO₄, 0.01 mol/L Co²⁺ at pH 5 and 75°C was used. The rotation speed of the RDE was set at 3600 RPM.
2. The potential of the electrode was swept from 0 to -0.85 V vs. SCE at a sweep rate of 1 mV/s to deposit a thin cobalt surface. This sweep rate was chosen as it is low enough to ignore transient effects from sweeping the potential.
3. The direction of the sweep was reversed and the potential - current response recorded. The potential was decreased until dissolution of cobalt was observed.
4. The resulting current - potential curve during the reverse sweep was fitted to a modified Butler - Volmer equation using the commercial software package Microcal Origin™.

For H₂:

1. A solution containing 2.4 mol/L MgSO₄, at pH 4 and 75°C was used. The rotation speed of the RDE was set at 3600 RPM.
2. The potential of the electrode was swept from 0 to -1 V vs. SCE at a sweep rate of 1 mV/s. The potential - current response was recorded.
3. The resulting current - potential curve from the forward sweep was fitted to a modified Butler - Volmer equation using the commercial software package Microcal Origin™.

3.4 Potential Sweep Methods

Potential sweep methods can be divided into two categories: linear potential sweep, and cyclic voltammetry. In linear potential sweep experiments, the potential is swept at a fixed rate between two fixed values. In cyclic voltammetry, the potential is swept forward and backward at a fixed rate between two fixed values. With cyclic voltammetry, the potential may be swept back and forth once or several times depending on the experiment.

Linear potential sweep and cyclic voltammetry are useful techniques to determine *qualitatively* the reactions occurring for a given system. While *quantitative* expressions have been derived for these methods, they are dependent on having a consistent surface during the experiment. Thus they are useful only when all of the oxidized and reduced species are soluble. For this reason, no quantitative calculations were attempted.

For qualitative determination of the reactions occurring, cyclic voltammetry is a very useful method. If the sweep rate is high, species oxidized or reduced at the surface of the electrode do not have time to diffuse to the bulk solution before the potential of the electrode is reversed and the oxidized or reduced species can be observed reducing or oxidizing respectively. Thus, cyclic voltammetry is useful in determining the reactions occurring for a given system; however, one must always remember the qualitative nature of cyclic voltammetry. In the words of Gileadi[55], on summarizing the usefulness of potential sweep methods: "*cyclic voltammetry should always be the first experiment performed in a new system, but never the last*".

3.4.1 Cyclic Voltammetry of Cobalt Solutions

Cyclic voltammetry was performed with only cobalt in solution. These experiments were performed to determine whether the deposition of cobalt involved any intermediates that were reduced at a different potential than the bulk reduction of cobalt.

To perform these experiments a solution containing 2.4 mol/L MgSO_4 and 0.01 mol/L Co^{2+} at pH 5 was cycled at 50 mV/s. The upper potential limit of the voltammogram was set by the dissolution of cobalt, and the lower potential limit was set by the diffusion limitation of cobalt deposition. The experiments were performed in stagnant solutions.

3.4.2 Linear Potential Sweep in Cobalt - Zinc Solutions

Linear potential sweep experiments of cobalt-zinc solutions were performed to determine if, when the potential was swept fast enough to limit processes to surface controlled processes, cobalt deposition would be inhibited.

To perform these experiments, the potential of the electrode was swept at 50 mV/s from -0.6 to -1 V vs. SCE in solutions containing 2.4 mol/L MgSO_4 , 0.01 mol/L Co^{2+} and various concentrations of zinc at pH 5 and 75°C.

3.4.3 Cyclic Voltammetry in Cobalt - Zinc Solutions

3.4.3.1 Sweep Rate 2 mV/s

A sweep rate of 2 mV/s was chosen to perform cyclic voltammetry as this sweep rate was found to give a good representation of the phenomena occurring. This sweep rate is low enough to not only show surface processes, yet high enough to not be considered as being under steady-state conditions.

To perform these experiments, the potential of the electrode was swept at 2 mV/s with an upper limit of -0.3, a lower limit of -0.925, and starting and ending at -0.5 V vs. SCE. The electrolyte used was 2.4 mol/L MgSO_4 , 0.01 mol/L Co^{2+} at 75°C with varying zinc concentration, pH's and rotation speeds.

3.4.3.2 Sweep Rate 0.1 mV/s

These tests were performed to approximate the steady-state deposition of cobalt from solutions containing zinc, as at this low sweep rate, the change of the potential with time can be considered low enough to assume steady-state at each potential. These potential of the electrode was swept under conditions identical to those at 2 mV/s, but with the different sweep rate.

3.5 Galvanodynamic Experiments

Galvanodynamic experiments are similar to potential sweep experiments or cyclic voltammetry with the exception that the current, not the potential, is being changed at a constant rate. In galvanodynamic experiments the rate of electron transfer is controlled. This differs from

potentially controlled experiments which can be thought of as controlling the free energy available for reaction.

For galvanodynamic experiments, the current density was swept from 0 to $-75 \text{ A}\cdot\text{m}^{-2}$ to $75 \text{ A}\cdot\text{m}^{-2}$. Electrolyte was 2.4 mol/L MgSO_4 , $0.01 \text{ mol/L Co}^{2+}$ at a pH of 4. The concentration of zinc, rotation speed, and sweep rate were varied.

3.6 Surface Analysis

3.6.1 SEM Investigation

The surface of the RDE was examined using scanning electron microscopy (SEM). To prepare the surface of the electrode for SEM, the electrode was removed from the electrolyte and rinsed under de-ionized water for 60 s. The electrode was allowed to air dry, and then was placed in the chamber of a Hitachi scanning electron microscope fitted with a Kevex energy dispersive x-ray spectrometer (EDX). Photomicrographs were taken using an accelerating voltage of 10 keV. EDX analysis was aided by Gaussian fitting.

3.6.2 STEM Investigation

Scanning transmission electron microscopy (STEM) analysis was performed by a Hitachi STEM. An accelerating voltage of 100 keV was used. The deposit on the surface was scraped off using a scalpel, and placed on a copper grid. Photomicrographs were taken as well as EDX analysis of the surface. Selected area electron diffraction (SAED) was performed on some areas.

3.7 Determination of Partial Current Densities

Partial current densities of cobalt and hydrogen were calculated to determine what fraction of the current density was due to hydrogen evolution and what fraction was due to deposition of cobalt. From cyclic voltammetry tests, one can only assume what percentage of the current is due to hydrogen discharge, but by performing partial current density experiments, the fraction can be determined accurately. Partial current density tests were performed to support cyclic voltammetry data and to generate values for the partial current densities so that the surface concentrations of various species could be determined.

Partial current densities were determined by the following method:

1. The electrode was held at the set potential for 30 minutes and the deposit was formed.
2. The electrode was removed from solution and rinsed in de-ionized water for 60 seconds.
3. The electrode was allowed to air dry.
4. 2-3 drops of concentrated nitric acid were placed on the deposit. The deposit dissolved in 20-30 seconds.
5. The dissolved deposit was rinsed into a 15 mL volumetric flask and the volume was made up with de-ionized water.
6. The solution was analyzed by atomic absorption spectrophotometry (Perkin-Elmer 306) for cobalt. Additional dilutions were made when necessary.

The assay of the solution was related to the partial current density at the set potential by the following equation:

$$i_{Co} = \frac{Q_T M}{n F C_{Co} V} i_T \quad (3.7)$$

where V is the volume of the assayed cobalt solution, C_{Co} is the cobalt assay from atomic absorption. All other variables have their usual meanings. The total amount of charge passed (Q_T) was determined by integrating the current with time. Since hydrogen evolution is the only other reaction which is thermodynamically feasible for the solutions employed over the potential region studied, the partial current density of hydrogen evolution was taken as the difference between the total current density and the partial current density due to cobalt deposition.

3.8 AC Impedance

3.8.1 Introduction

In the section on cyclic voltammetry (Section 3.4) the need for performing cyclic voltammetry at different sweep rates was discussed. By using different sweep rates, one can measure either the surface processes or the bulk processes and gather information on intermediates that may be formed. The use of AC impedance is very similar. In the case of AC impedance, different frequencies, rather than different times or rates, are used to gather information about a system. The power of AC impedance is that it is not confined to one frequency, and a large range of frequencies can be employed in a single test generating much information about the system.

The term impedance arises from the current response to an applied potential, and can be defined for a system as:

$$Z(t) = \frac{E(t)}{I(t)} \quad (3.8)$$

when this equation is transformed to the Laplace domain, it becomes:

$$\bar{Z}(s) = \frac{\bar{E}(s)}{\bar{I}(s)} \quad (3.9)$$

To transfer to the frequency domain, one only has to replace s by $j\omega$.

To understand how the impedance of a reaction is calculated, a simple case of charge transfer under semi-infinite diffusion conditions will be investigated based on the treatment of MacDonald[56].

Consider the case of a cathodic reactant, O, being reduced to R. The equation describing the reaction is:



The diffusion of these species near the surface of the electrode can be described using Fick's second law:

$$\begin{aligned} \frac{\partial C_O}{\partial t} &= D_O \frac{\partial^2 C_O}{\partial x^2} \\ \frac{\partial C_R}{\partial t} &= D_R \frac{\partial^2 C_R}{\partial x^2} \end{aligned} \quad (3.11)$$

subject to the following boundary conditions:

$$\begin{aligned} C_O &= C_O^b, C_R = C_R^b \text{ if } t = 0, x > 0 \\ C_O &\rightarrow C_O^b, C_R \rightarrow C_R^b \text{ if } t > 0, x \rightarrow \infty \\ \frac{I}{nFA} &= D_O \frac{\partial C_O}{\partial x} \text{ if } t > 0, x = 0 \end{aligned} \quad (3.12)$$

The Laplace transform solution of the diffusion equations using the above boundary conditions for the concentrations at the surface of the electrode are:

$$\begin{aligned}\bar{C}_O^s &= \frac{C_O^b}{s} - \frac{\bar{I}}{nFAD_O^{1/2}s^{1/2}} \\ \bar{C}_R^s &= \frac{C_R^b}{s} - \frac{\bar{I}}{nFAD_R^{1/2}s^{1/2}}\end{aligned}\quad (3.13)$$

Now, the current for reaction 3.10 can be expressed by a modified Butler-Volmer equation:

$$I = nFAk \left(C_O^s \exp[-b(E - E^0)] - C_R^s \exp[a(E - E^0)] \right) \quad (3.14)$$

where a and b are the inverse Tafel constants and k is the standard rate constant.

The applied potential with the small perturbation related to the impedance is given by:

$$E(t) = E_i + \Delta E(t) \quad (3.15)$$

Substituting Equation 3.15 into Equation 3.14 and linearizing the equation gives:

$$I = nFAk \left(C_O^s [1 - b\Delta E] \exp[-b(E_i - E^0)] - C_R^s [1 + a\Delta E] \exp[a(E_i - E^0)] \right) \quad (3.16)$$

Equation 3.16 shows that the current is a function of 3 time-dependent variables, the surface concentration of R and O, and the value of ΔE . Thus taking the full differential of the current and dividing by dE gives:

$$\frac{1}{Z_f} = \left(\frac{\partial I}{\partial E} \right)_{C_O, C_R} + \left(\frac{\partial I}{\partial C_O} \right)_{E, C_R} \frac{dC_O}{dE} + \left(\frac{\partial I}{\partial C_R} \right)_{E, C_O} \frac{dC_R}{dE} \quad (3.17)$$

The differentials of the Laplace transforms of surface concentrations can be evaluated from Equation 3.13, and when substituted in Equation 3.17, give the faradaic impedance as:

$$Z_f = \left[\left(\frac{\partial I}{\partial E} \right)_{C_O, C_R} \right]^{-1} + \frac{(\partial I / \partial C_O)_{E, C_R} / (\partial I / \partial E)_{C_O, C_R}}{nFAD_O^{1/2}s^{1/2}} - \frac{(\partial I / \partial C_R)_{E, C_O} / (\partial I / \partial E)_{C_O, C_R}}{nFAD_R^{1/2}s^{1/2}} \quad (3.18)$$

Substituting R_{ct} for the differential in the square brackets, β and γ for the numerator of the O and R diffusion terms respectively, noting that $s = j\omega$, and utilizing Demoivre's theorem: $j^{-1/2} = (1 - j) / 2^{1/2}$, the following expression can be written for the faradaic impedance:

$$Z_f = R_{ct} + \frac{\beta / D_O^{1/2} - \gamma / D_R^{1/2}}{nFA\sqrt{2}} (1 - j)\omega^{-1/2} \quad (3.19)$$

The first term in Equation 3.19 represents the charge transfer resistance and the second term, with the $-1/2$ dependence on the frequency is known as the Warburg impedance which is demonstrative of semi-infinite diffusion. Note that these two elements are in series with each

other. When the capacitance of the double layer and the solution resistance are also taken into account, the equivalent circuit in Figure 3.2 can be used to represent the interface.

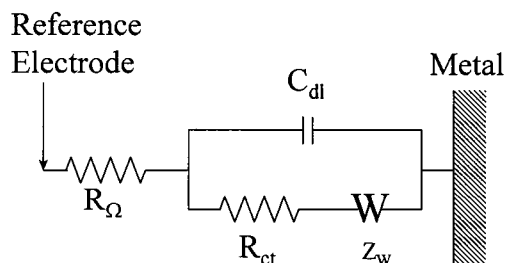


Figure 3.2 Equivalent circuit for a simple charge transfer process under semi infinite diffusion control.

In this figure Z_w represents the Warburg impedance, C_{dl} represents the double layer capacitance, and R_Ω represents the ohmic drop due to solution resistance.

While this is only a simple model of the interface and does not apply to the system studied in this thesis, it gives a good example of how the impedance of a given system is determined. Using an equivalent circuit model such as this to represent the

impedance of the surface, valuable parameters can be derived.

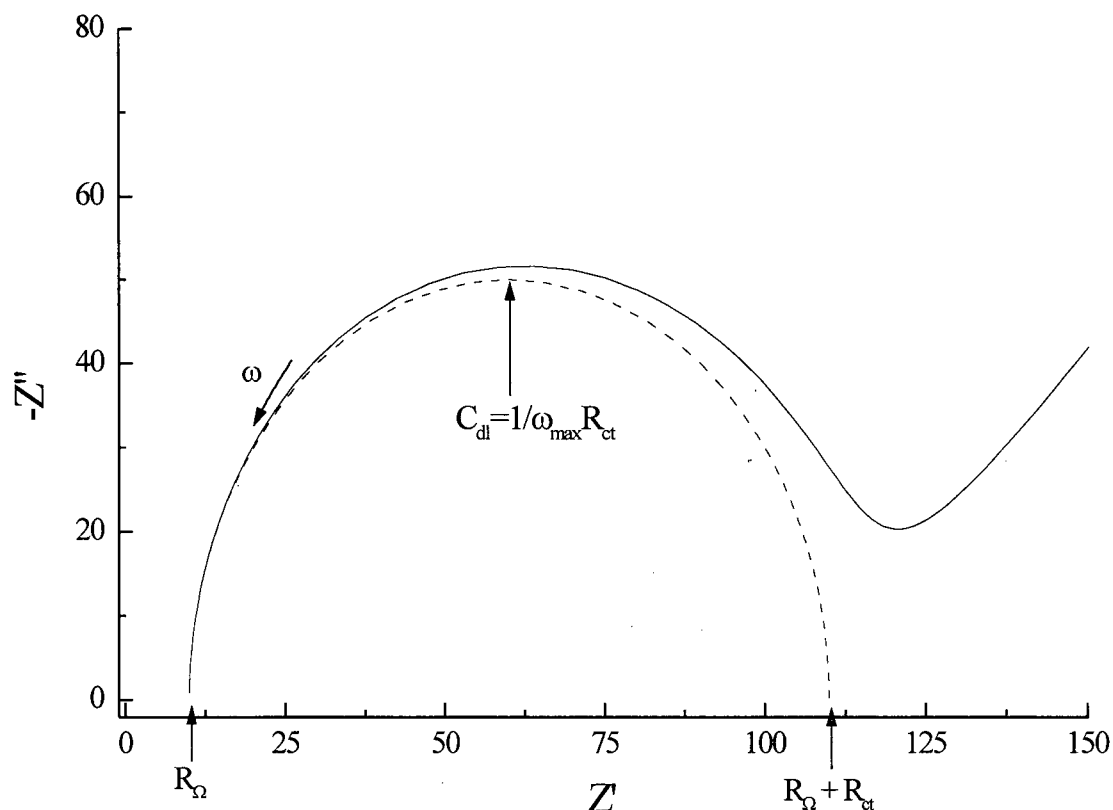


Figure 3.3 Complex plane impedance plot of the impedance represented by Figure 3.2.

The complex plane representation of the impedance for this semi-infinite diffusion condition is shown in Figure 3.3. The impedance for semi-infinite diffusion is characterized by a semi-circle that deviates to a straight line with a slope of 45° at low frequencies. From this

figure, several of the parameters indicated in the equivalent circuit can be determined. At the high frequency intercept of the real axis, the value of the ohmic drop (R_Ω) can be determined. Similarly the low frequency extrapolated intercept with the real axis (shown by the dotted line), is the sum of the ohmic drop and the charge transfer resistance ($R_\Omega + R_{ct}$). The double layer capacitance (C_{dl}) can be obtained by the relationship, $C_{dl} = 1/\omega_{max}R_{ct}$, where ω_{max} is the frequency at the highest point on the semi-circle.

One of the most important parameters in AC impedance is the charge transfer resistance. The value of the charge transfer resistance is defined from Equation 3.18 as the partial differential of current with respect to potential to the -1 power. If we evaluate this differential from Equation 3.14 and ignore the contribution due to the reverse reaction, this value becomes:

$$R_{ct} = \left(\frac{\partial I}{\partial E} \right)_{C_O, C_R}^{-1} = \frac{1}{-bI} = -\frac{RT}{\alpha FI} \quad (3.20)$$

Since the current is negative for a cathodic reaction, the value of the charge transfer resistance is positive.

3.8.2 Procedure

AC impedance was performed using a Solartron 1250 FRA and a Solartron 1286 potentiostat attached to a microcomputer. To achieve steady state, the electrode was held at the assigned potential for 15 minutes. The frequency range employed was between 65 kHz and 0.1 Hz, and a 3.5 mV_{rms} sinusoidal voltage wave was used to calculate the impedance. Impedance spectra were checked by using a 7 mV_{rms} wave and by obtaining the impedance spectra by either increasing or decreasing the frequency. The same spectra were obtained for both of these checks. Furthermore, Kramers-Kronig relations were employed to evaluate the consistency of the impedance data (see Appendix V). The spectra shown represent the frequency range where these relations agree with the experimental data.

4. Cobalt Removal Using a Planar Electrode

4.1 Introduction

Traditional studies of cobalt cementation have consisted of batch reactors into which metered amounts of zinc dust and activators are added to investigate the cementation reaction. This process is undesirable for studying the cementation reaction as the composition, size, and morphology of the zinc dust used are difficult to reproduce as are the agitation conditions. An improvement to this method of studying cobalt cementation is the use of a rotating zinc disk, which quantifies variations in mass transfer and eliminates the uncertainty in the available surface area of zinc. However, this method also has its shortcomings. Use of a rotating zinc disk limits the study of cobalt removal from zinc-containing solutions to one potential - the potential of zinc dissolution.

In the following section, cobalt deposition to a copper plate is investigated. Using this cell, a correlation between cobalt removal using a copper electrode and more traditional studies using zinc dust and zinc rotating disks was attempted.

4.2 Results and Discussion

4.2.1 Antimony Activation

Changes in the removal of cobalt with current density are shown in Figure 4.1. The logarithm of the concentration of cobalt decreases linearly with time. This result suggests that the removal of cobalt in this system follows first-order kinetics for a batch reactor. First-order kinetics are based upon the following mathematical equation:

$$\frac{dC}{dt} = -kC \quad (4.1)$$

Integration of this equation gives:

$$\log(C^f) - \log(C^i) = -k't \quad (4.2)$$

This equation adequately describes the cobalt concentration with time with one variation. For the first 0.5 hour, no cobalt is removed. The existence of this "induction period" was reconfirmed by tests where samples for cobalt analysis were taken every 10 min for the first 2

hours of the test. These tests confirmed that no cobalt is removed in the first 30 min, and after this time cobalt is removed based upon first-order kinetics.

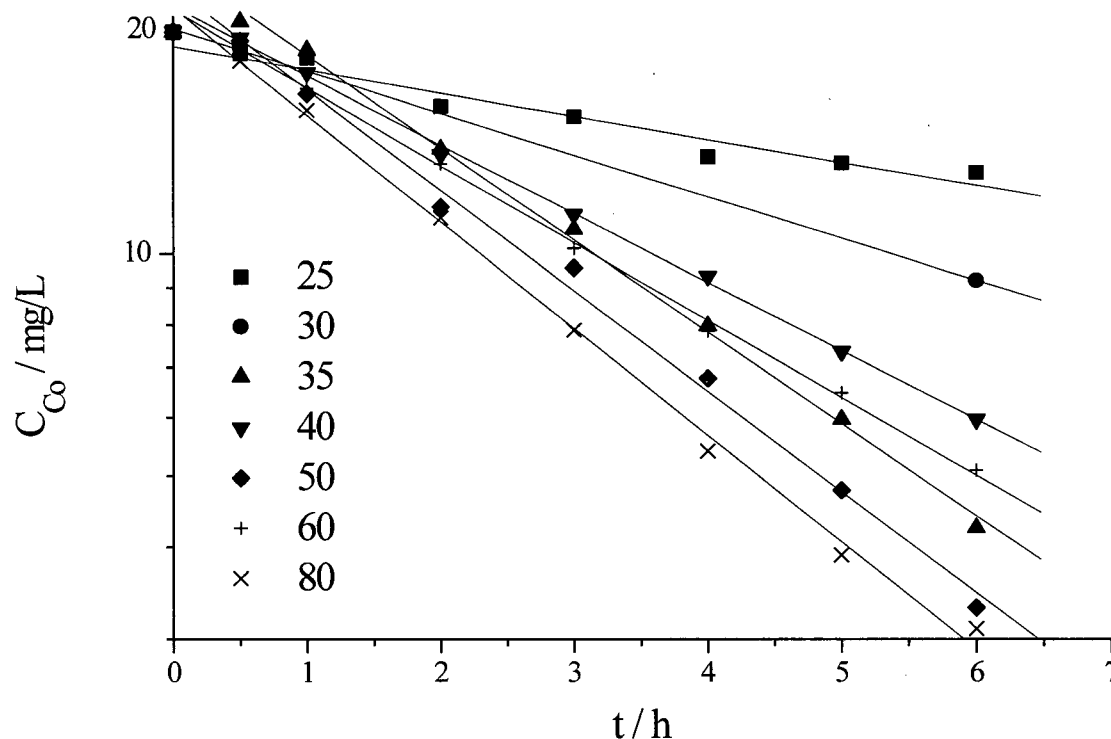


Figure 4.1 Variation of current density. Legend refers to current density in $\text{A}\cdot\text{m}^{-2}$. Conditions other than current density are listed in Table 3.2.

Increase of the cobalt removal rate with current density becomes scattered above $35 \text{ A}\cdot\text{m}^{-2}$. Figure 4.2 shows the change in removal rate with current density. The removal rate is linear up to $50 \text{ A}\cdot\text{m}^{-2}$, and above this value appears to plateau at $\sim 0.14 \text{ h}^{-1}$. It appears that deposition of cobalt peaks at this value and at current densities above $35 \text{ A}\cdot\text{m}^{-2}$, an increase in current density leads to an increase in secondary electrode reactions - either hydrogen evolution or zinc deposition.

To further support this theory, the appearance and deposition potential also indicate the presence of a secondary reaction. At current densities less than $35 \text{ A}\cdot\text{m}^{-2}$ the deposit was very thin and black in appearance. The pH rose quickly indicating high rates of hydrogen evolution at the cathode and the potential of the electrode was between -0.770 and -0.800 V vs. SCE . At current densities above $35 \text{ A}\cdot\text{m}^{-2}$, the deposits were thicker than at lower current densities and were gray in color indicating that zinc had deposited. The potential of the electrode at these current densities varied between -0.970 and -0.990 V vs. SCE , values near the reversible

potential of zinc in these solutions. Also, at current densities greater than $35 \text{ A}\cdot\text{m}^{-2}$, the pH decrease with time was greater than at current densities below this value. As the pH changes are due to the balance between the flux of acid from the anolyte chamber and the discharge of hydrogen at the cathode, this further suggests that zinc deposited, as there is a high overpotential for the hydrogen evolution reaction on zinc surfaces.

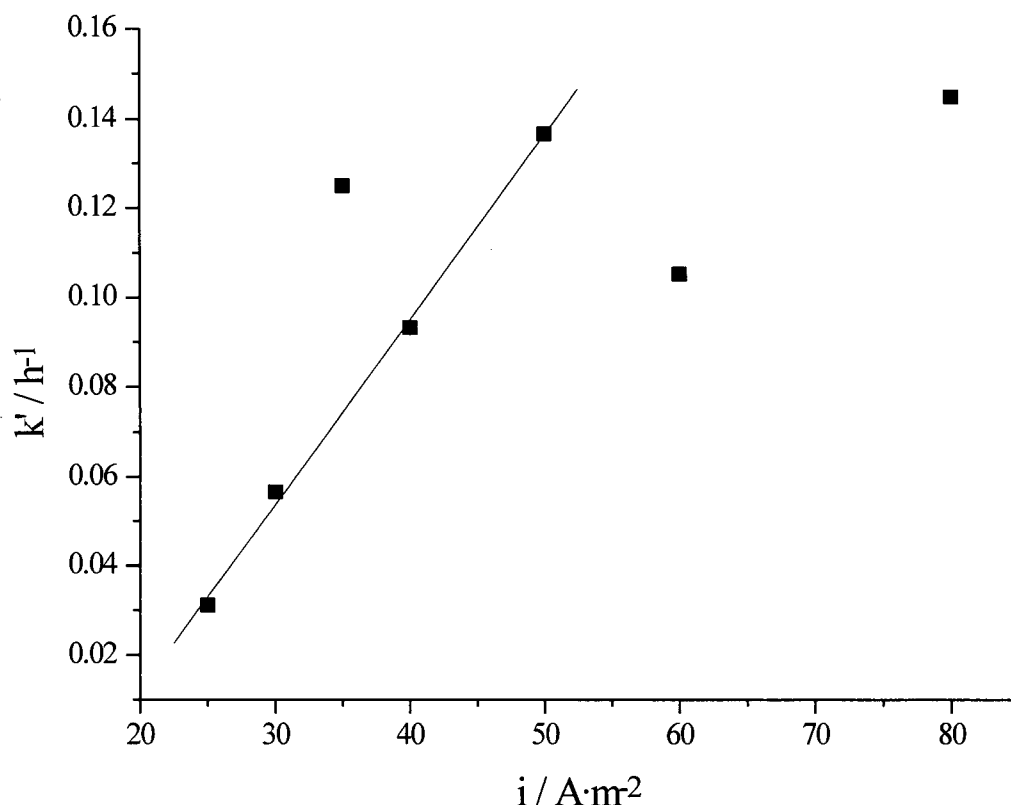


Figure 4.2 Variation of first-order rate constant with current density.

An extension of these tests to times greater than 6 hours was needed to ascertain whether cobalt can be electrolytically removed to levels necessary for the industrial electrowinning of zinc (typically near 0.3 mg/L). To determine this, tests were run for 15 hours. These tests showed that cobalt can be removed to 0.3 mg/L electrolytically. To remove cobalt to this level it was found that additional antimony had to be added to the solution. Tests in which only 3 mg/L of antimony was added at the beginning of the test showed cobalt redissolution at 12 hours. In a test where an additional 3 mg/L of antimony was added at 10 hours, redissolution did not occur, and cobalt removal followed first-order kinetics for the duration of the test.

During the test, antimony decreased from the starting concentration of 3.0 mg/L to less than 0.1 mg/L. EDX analysis of the electrode deposits confirmed the presence of antimony. Thus, it is assumed that antimony was deposited with cobalt.

Several tests under the base set of conditions were performed to calculate the variance of the cobalt removal rate constant. These tests indicate that the removal rate constant has a variance of 3.5%.

To investigate the effect of antimony on the removal of cobalt, various initial antimony concentrations were investigated. The conditions incorporated were those listed in Table 3.2, but with different initial antimony concentrations. Four initial antimony concentrations were investigated: 0, 1.5, 3, and 6 mg/L. With no antimony present in solution, cobalt was not removed. Deposits obtained without any antimony present in solution were bright gray in color indicating a deposit consisting of pure zinc. At 1.5 mg/L Sb, cobalt is still effectively removed, but to a lesser extent than at 3 mg/L. At initial antimony concentrations of 6 mg/L, no increase in cobalt removal was observed; hence, higher concentrations of antimony were not investigated.

Several different starting pH values were investigated. For starting pH values greater than 3.5, there is no appreciable difference in cobalt removal. At a pH of 3.0, the cobalt removal rate is ~23% of the removal rate at higher pH values. At this pH value, the deposit appeared similar to deposits obtained at current densities less than $35 \text{ A}\cdot\text{m}^{-2}$: the deposits were thin and the cathodic potential was $\sim -0.800 \text{ V vs. SCE}$.

It should be noted that the pH was only controlled from rising above the set value by the addition of sulfuric acid. For most tests, the pH was controlled at the set point for the first hour of the test and then the pH decreased uncontrolled due to flux of acid from the anolyte chamber. For example, a test using the base conditions outlined in Table 3.2, with a starting pH of 3.6, had a final pH of 3.0. To determine whether the low final pH had an effect on the cobalt removal rate, a test was performed where the pH was prohibited from becoming lower by the addition of zinc oxide. This test showed kinetics identical to those tests in which the pH was uncontrolled. Thus the dependence of cobalt removal on pH appears to be affected only by the initial pH.

The variation of the removal rate with temperature for a solution-phase reaction should follow an Arrhenius relationship[57]. Figure 4.3 shows the relationship between removal rate

and temperature plotted as an Arrhenius plot. This figure shows that temperature and cobalt removal rate do follow an Arrhenius relationship, governed by the following equation:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (4.3)$$

The activation energy (E_a) for the removal of cobalt in this system was found to be 24 kJ/mol.

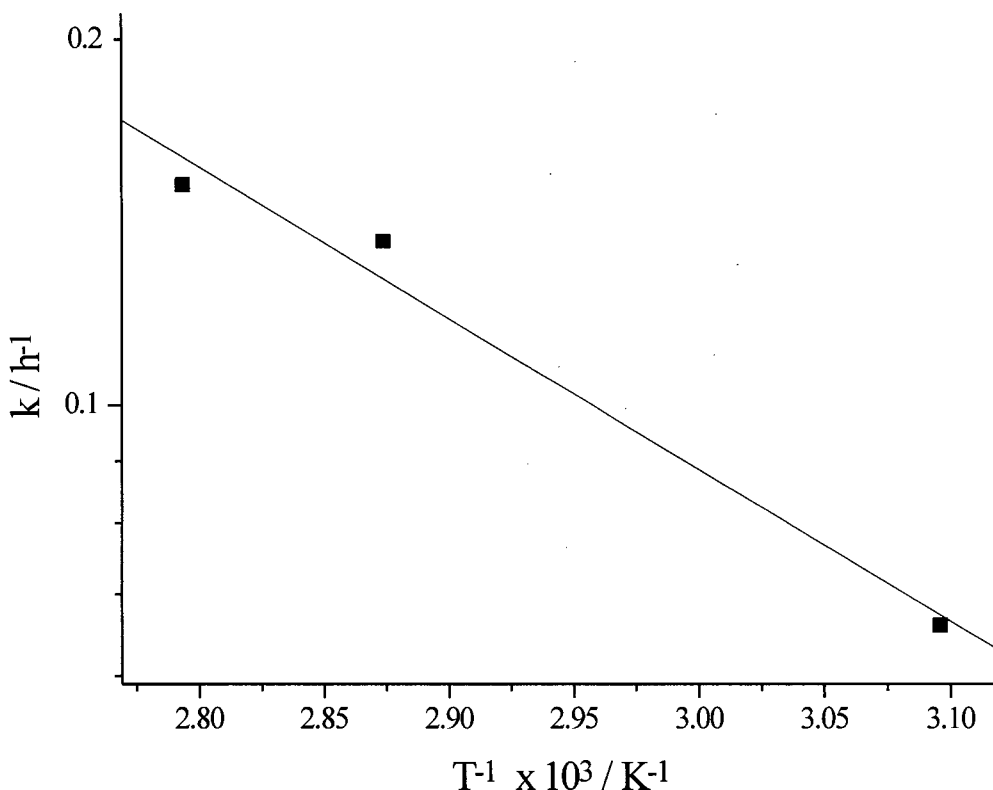


Figure 4.3 Arrhenius plot showing the dependence of cobalt removal on temperature. Conditions listed in Table 3.2.

Some of the other physicochemical parameters investigated are summarized below:

- Lowering the agitation rate from 800 RPM to 470 RPM had no effect on the removal of cobalt; however, in the absence of agitation, the removal rate dropped to ~55% of the rate with agitation. This suggests that within the range of agitation rates investigated, the removal of cobalt is activation controlled.
- The removal rate of cobalt did not change when N_2 sparging was omitted.
- With no glass frit present to prohibit oxygen evolved at the counter electrode from entering the catholyte, the removal rate of cobalt dropped to ~42% of the removal rate when the anode was in a separate compartment.

- When the electrolyte was not pretreated with activated carbon to remove entrained organics, the removal rate of cobalt dropped to ~78% of the value with activated carbon treatment.
- The cobalt removal rate using a stainless steel substrate (318) rather than a copper substrate did not change; however, when using an aluminum substrate, removal rates were ~33% of the rate obtained on copper.

Comparing the above results with results obtained from cementation studies shows similarities. Both the system investigated in this thesis and cementation studies show cobalt removal as following first-order kinetics.

In the system investigated in this thesis, variation of agitation rate showed no change in the cobalt removal rate. This indicates that the removal of cobalt is not under mass transfer control for the agitation rates investigated, but is under activation control. This compares with studies of cobalt cementation using zinc dust which were also found to be under activation control[33].

While the removal rate of cobalt was the same with and without N_2 sparging, removal of the glass frit, allowing oxygen to enter the catholyte was detrimental to the removal of cobalt. Again this compares to studies of cementation that have shown that oxygen lowers the cementation of cobalt, likely due to the oxidation of the cemented cobalt[33].

In studies of cementation, organics have been found to inhibit the deposition of cobalt by adsorbing on active centers where cobalt would preferentially deposit [24]. In this study, organics decreased the removal rate of cobalt.

While no cementation studies have been performed using stainless steel or aluminum, discussion with researchers of cobalt cementation indicates that when using stainless steel agitators in cementation vessels, a black cobalt-containing sponge is observed on the surface[58]. No research on aluminum-containing vessels was found.

A test in which the current was controlled by the Solartron potentiostat was performed to obtain better information on the behavior of the potential during galvanostatically controlled tests. Figure 4.4 shows the variation of potential with time for a galvanostatically controlled test using this device under the base set of conditions.

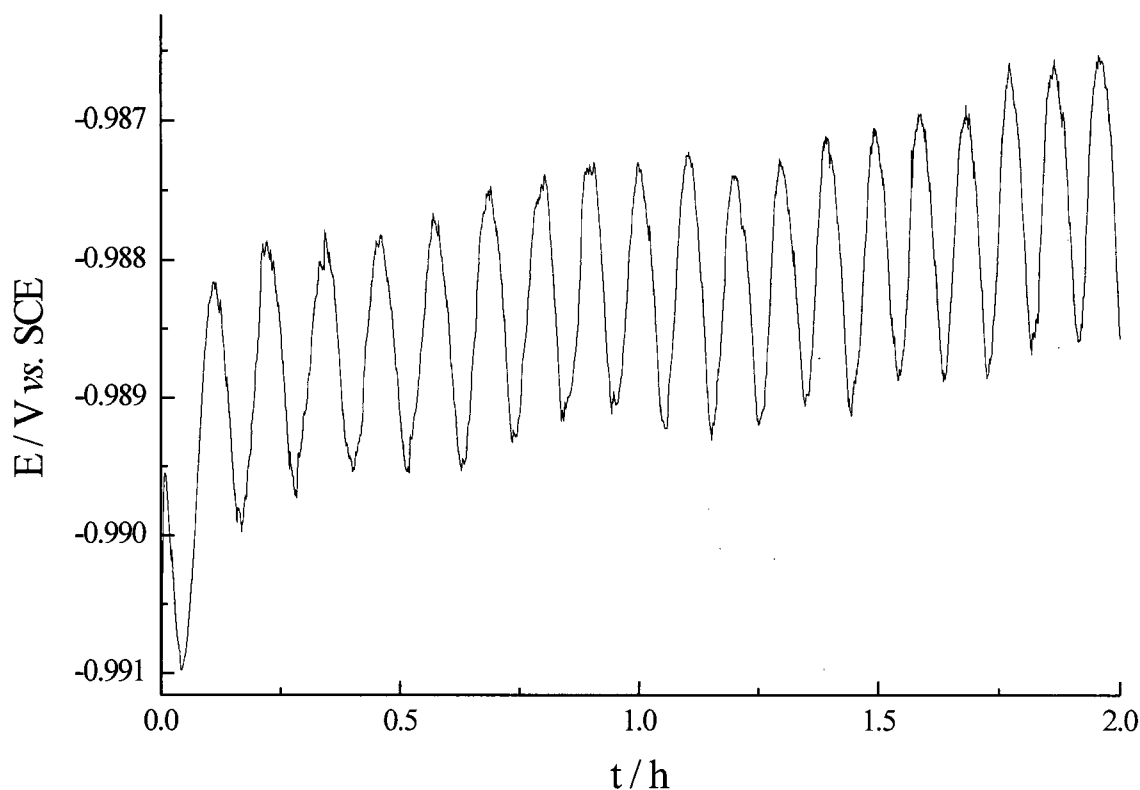
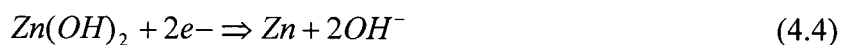


Figure 4.4 Potential response with time for a test under conditions listed in Table 3.2.

Figure 4.4 shows that the potential oscillates approximately 2 mV around an average potential of -0.989 V vs. SCE, and that the potential increases with time. This phenomenon has been documented previously by Yan *et al*[44]. Although their study incorporated different concentrations and temperatures, they found oscillations. They found when potentiostatically depositing Zn-Co alloys from a bath containing 620 g/L $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 125 g/L $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and 75 g/L Na_2SO_4 at a pH of 2 and a temperature of 25°C that the current oscillated between 0.8 and 1.1 $\text{mA} \cdot \text{cm}^{-2}$ at a potential of -1.060 V vs. SCE. Based on their theory, in the present work, the potential oscillations can be described by:

1. The precipitation of $\text{Zn}(\text{OH})_2$ due to concurrent hydrogen evolution causes the potential to decrease.
2. When the potential decreases to a suitable level, Zn deposition occurs due to breakdown of the $\text{Zn}(\text{OH})_2$ layer by the following reaction:



3. After the deposition of zinc, the potential increases and cobalt and hydrogen discharge on the zinc surface.
4. Due to hydrogen evolution, Zn(OH)_2 precipitates again and the process repeats itself.

4.2.2 Antimony Activation with Copper Present

Tests were performed with copper ions added to the solution to see if an improvement in the rate of cobalt removal could be obtained. Tests were performed galvanostatically, as for tests where no copper was added, and potentiostatically.

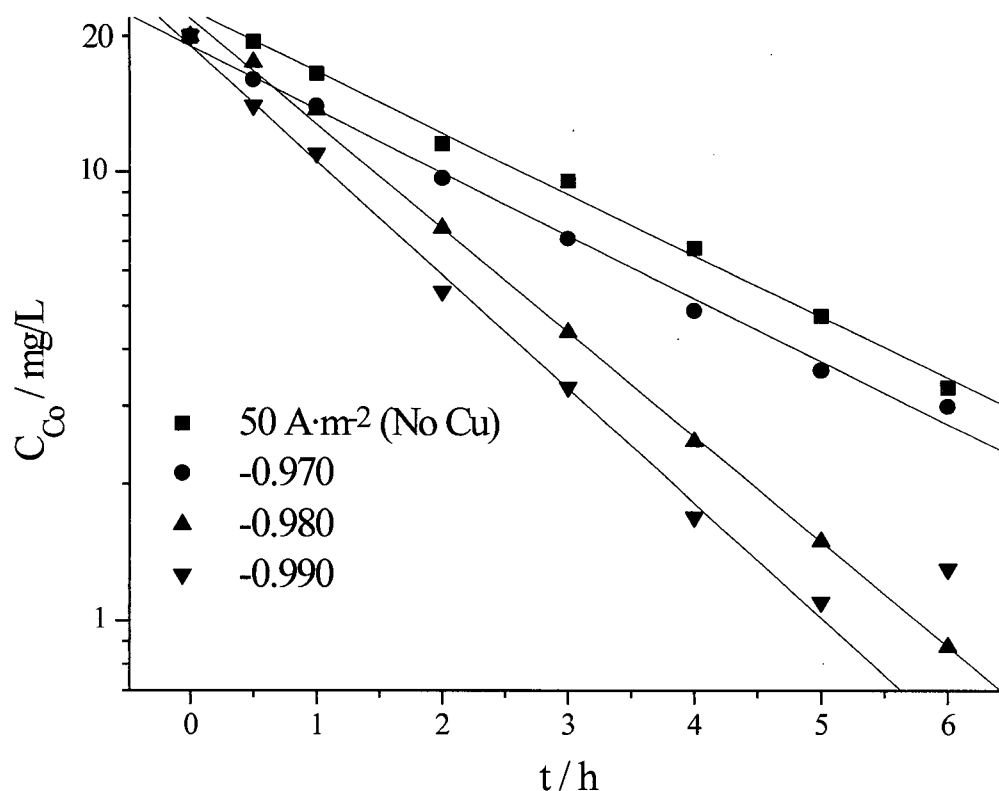


Figure 4.5 Cobalt concentration as a function of time for tests with copper additions. Base conditions listed in Table 3.2, $C_{\text{Cu}} = 30$ mg/L except where noted. Legend values refer to potential in V vs. SCE.

For tests operated galvanostatically with 30 mg/L Cu added to the base conditions listed in Table 3.2, the cobalt removal rate decreased to ~29% of the value obtained without copper added. The appearance of the deposits was similar to those obtained without copper additions at

current densities less than $35 \text{ A}\cdot\text{m}^{-2}$: they were black, indicating too low of a current density to co-deposit zinc. All of the copper was removed from the solution in 1 hour.

Studies of cementation have suggested that copper additions increase the surface area for deposition. If this is true, in these tests, the *apparent* current density (based on the geometrical area of the electrode) is higher than the *true* current density (based on the actual surface area of the electrode). Thus the cell cannot be controlled at a known current density without measurement of the true surface area of the electrode which is difficult to accomplish. To overcome this difficulty, further tests where copper was added to the solution were controlled potentiostatically.

Removal of cobalt as a function of potential with copper present is depicted in Figure 4.5. From this figure it is evident that as the potential of the electrode approaches the reversible potential of zinc ($E^\circ_{\text{Zn}} = -1.004 \text{ V vs. SCE}$), the removal rate of cobalt increases. At -0.990 V vs. SCE , the best removal rate obtained, the removal rate of cobalt is 1.9 times greater than the removal rate at $50 \text{ A}\cdot\text{m}^{-2}$ with no copper present; however, this increase can also be attributed to an increase in the surface area of the electrode.

Table 4.1 Average apparent current density for potentiostatic tests with copper present.

Potential (V vs. SCE)	Apparent Current Density ($\text{A}\cdot\text{m}^{-2}$)
-0.970	65
-0.980	80
-0.990	90

As Table 4.1 illustrates, the current density increases as the potential becomes more negative. At -0.990 V vs. SCE the current density is 1.8 times greater than at $50 \text{ A}\cdot\text{m}^{-2}$, but since the removal rate of cobalt is similar at 1.9 times greater, no improvement in the efficiency of cobalt removal has been obtained. If we assume that the *true* current density has remained constant, the increase in the *apparent* current density is due to an increase in the surface area. Thus, it can be assumed that in the presence of copper, improvement of cobalt removal is solely due to an increase in cathodic surface area.

Examining the removal of cobalt and copper during these experiments (Figure 4.6) showed that the removal rate of copper is higher than that of cobalt. This further supports the theory that cobalt removal is not under mass transfer control. As both copper and cobalt have

similar diffusion coefficients[61], if both of these ions were removed under mass transfer control, they should have similar removal rates. As the removal rate of cobalt is much lower than that of copper, it can be assumed that cobalt deposition is not under mass transfer control.

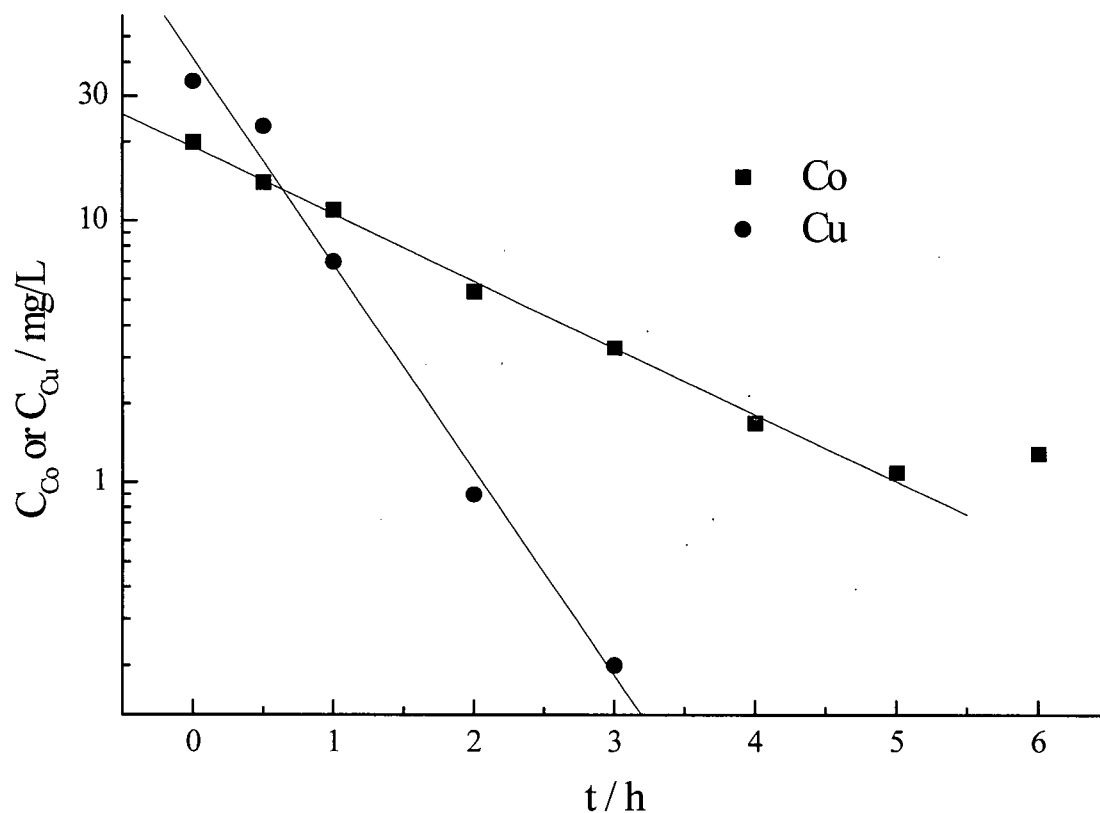


Figure 4.6 Cobalt and copper concentration as a function of time for tests with copper additions. Base conditions listed in Table 3.2. Potential = -0.990 V vs. SCE, $C_{Cu} = 30$ mg/L.

4.2.3 Arsenic Activation

For comparison purposes, the arsenic activation system was studied. In these tests, no attempt to optimize all of the parameters affecting deposition was attempted, only optimization of variations in current density and copper concentration.

In tests where arsenic but no copper was added to the solution, the cobalt removal rate was similar to the cobalt removal rate obtained with antimony activation. Figure 4.7 shows cobalt removal at two different current densities for arsenic activation.

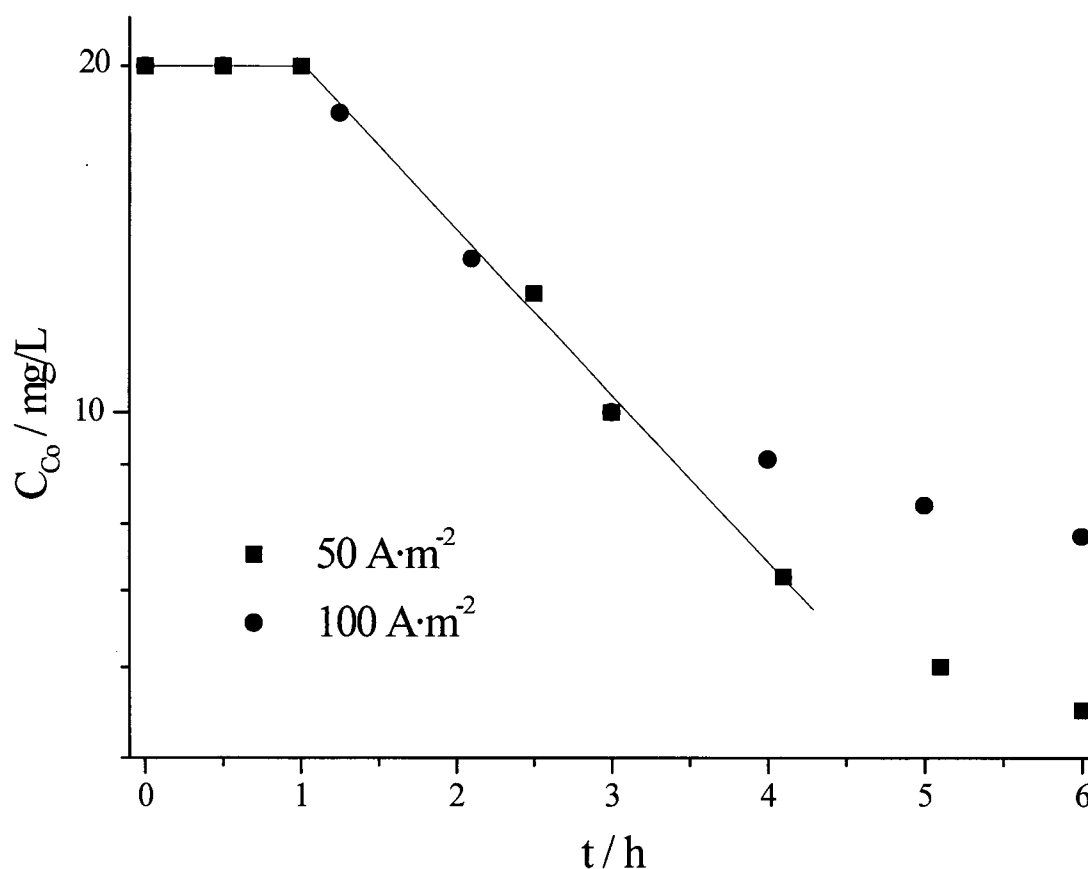


Figure 4.7 Cobalt removal as a function of time at 50 and 100 A·m⁻². Conditions are listed in Table 3.2, except $C_{Sb}=0$, $C_{As}=75$ mg/L.

The cobalt removal rate at both current densities is the same, and furthermore, the removal rate with arsenic is similar to that obtained with antimony at the same current density (50 A·m⁻²). The removal of cobalt also appears to decrease after 4 hours for the test performed at 50 A·m⁻² and at 2½ hours for the test performed at 100 A·m⁻². As was noted with antimony-activated cobalt removal, an induction time is present. For arsenic-activated removal this induction time has increased to 1 hour.

A probable reason for the lowering of the removal rate after 5 hours, and for the similar removal rates obtained at two different current densities is that the cathodic deposit is poorly adherent to the substrate. After only 10 minutes of the test, the solution turned brown due to particulate matter that had broken off of the substrate. It is expected that this particulate matter is the As-Co deposit, which will re-dissolve leading to low effective cobalt removal rates.

The potential of the electrode during electrolysis was between -0.850 and -0.800 V vs. SCE for tests with arsenic activation and the deposits were dark in color indicating that zinc did not deposit.

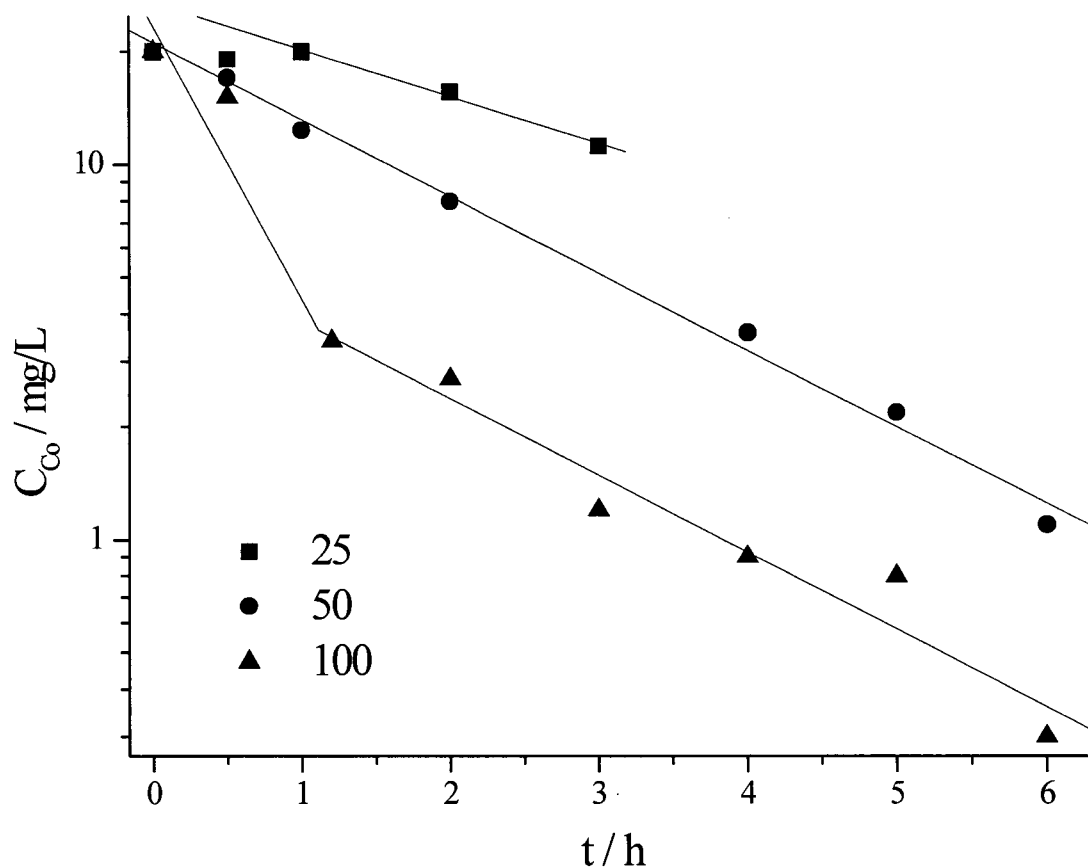


Figure 4.8 Cobalt removal as a function of time using arsenic - copper activation at various current densities. Legend refers to current density in $\text{A}\cdot\text{m}^{-2}$. Base conditions are listed in Table 3.2 except: $C_{\text{Sb}} = 0$, $C_{\text{As}} = 75$ mg/L, $C_{\text{Cu}} = 150$ mg/L.

The addition of 150 mg/L of copper to the solution improves cobalt removal rates dramatically. Figure 4.8 shows cobalt removal with copper and arsenic present at various current densities. The deposits for these tests were more adherent to the substrate than those obtained without copper in solution, although some particulate matter was observed in the solution.

When copper was added to the solution using arsenic activation, the potential of the electrode varied between -0.800 and -0.750 V vs. SCE. This potential is ~ 50 mV more negative than the -0.85 to -0.80 V vs. SCE observed without copper present.

At $25 \text{ A}\cdot\text{m}^{-2}$, there is an induction time of 1 hour before cobalt is removed. At $50 \text{ A}\cdot\text{m}^{-2}$, the induction time disappears and at $100 \text{ A}\cdot\text{m}^{-2}$, the induction time is replaced by an initial 1

hour period where cobalt removal is rapid. All of these regions are followed by cobalt removal at similar rates. An initial high cobalt removal rate followed by a lower secondary removal rate has also been observed by Tozawa *et al*[1] in the investigation of arsenic-copper activated cobalt removal using a zinc rotating disk.

Cobalt removal using copper in addition to arsenic is greater than removal using arsenic alone, or using antimony activation. Comparing the test at $100 \text{ A}\cdot\text{m}^{-2}$ with copper present to the tests without copper present, the initial removal rate is 4.6 times greater and the secondary removal rate is 1.4 times greater.

As addition of copper increases the removal of cobalt with arsenic activation, increasing levels of copper were added to solution. The results from the addition of various amounts of copper to the solution with arsenic activation appear in Figure 4.9.

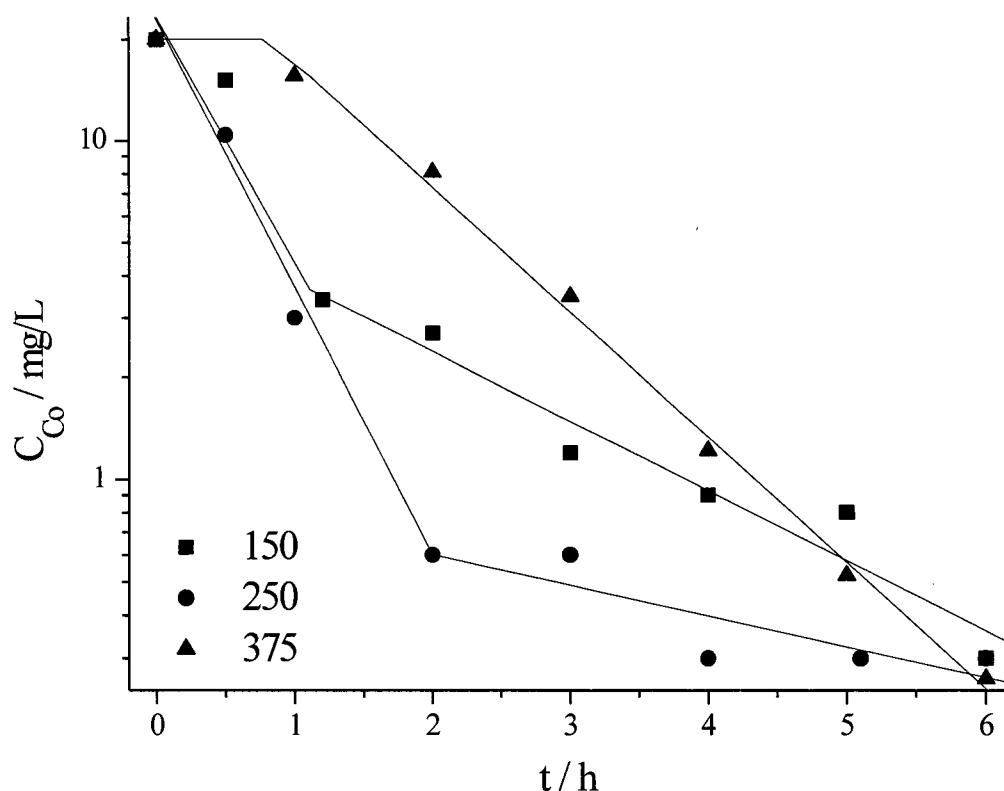


Figure 4.9 Cobalt removal as a function of time using arsenic - copper activation at various copper concentrations. Legend refers to copper concentration in mg/L. Base conditions are listed in Table 3.2 except: $C_{\text{Sb}} = 0$, $C_{\text{As}} = 75 \text{ mg/L}$, $i = 100 \text{ A}\cdot\text{m}^{-2}$.

With 250 mg/L Cu added to the solution, the initial enhanced cobalt removal region is increased; however, the cobalt removal rate during the second region is only 43% of the rate

obtained with 150 mg/L copper present in solution. With 375 mg/L Cu in solution a 1 hour inhibition region is observed. The removal rate of cobalt at this level of copper is 1.8 times greater than the secondary removal rate and 56% of the initial enhanced rate with 150 mg/L Cu present. Thus, the rate at this copper concentration is approximately the mean of the rates from the two kinetic regions with 150 mg/L Cu present. For all levels of copper, the final concentration of cobalt at 6 hours is approximately the same, viz, 0.3 mg/L.

Insight into the two rate regions of cobalt removal was obtained by investigating the removal of copper during these tests. Figure 4.10 shows copper and cobalt removal during a test with 150 mg/L copper present. This figure shows that the removal of copper closely mirrors the removal of cobalt.

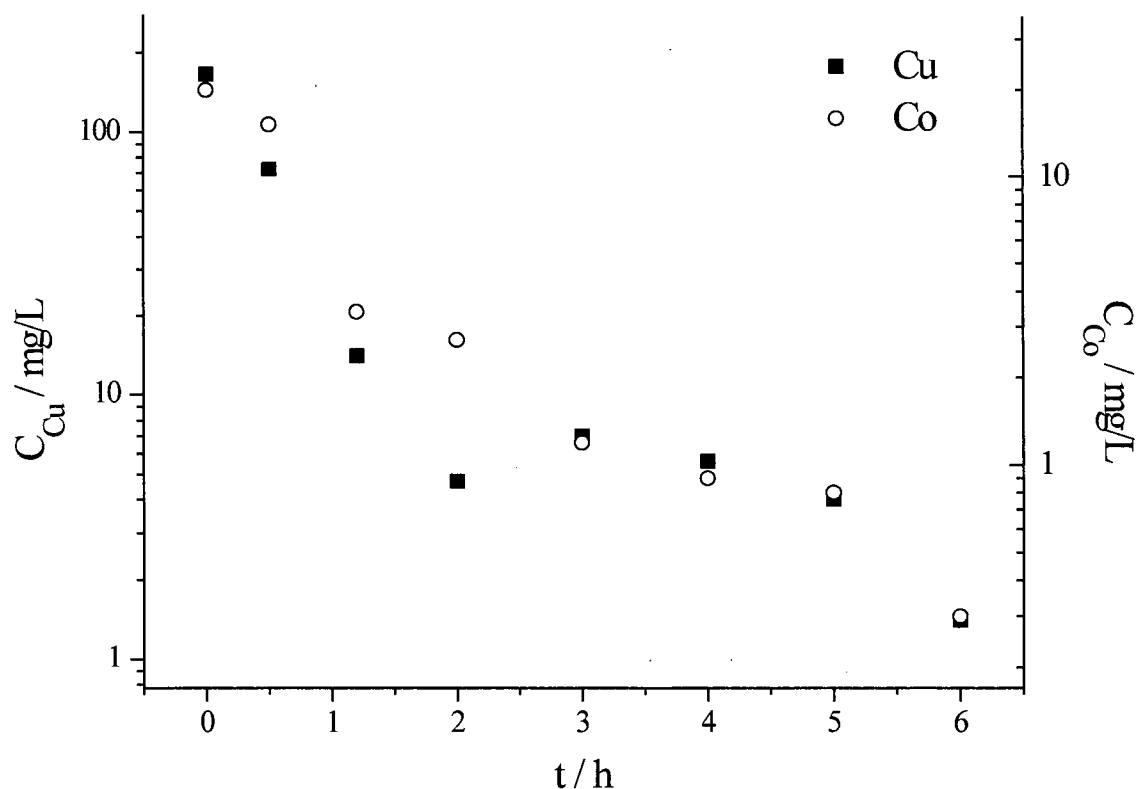


Figure 4.10 Cu and Co removal as a function of time during As-Cu activation. Data from 150 mg/L Cu addition test (see Figure 4.9).

During arsenic-copper activated cobalt removal, both cobalt and copper are being depleted from solution. Also during all tests (but much less with copper present), some of the deposit is breaking off the electrode surface, creating particulates mixed in with the catholyte. The deposit that breaks off the electrode surface will no longer be subjected to the reducing

potential of the cathode and will be subjected to a range of potentials in the catholyte chamber. As the particulate matter is subjected to more positive potentials, both cobalt and copper will dissolve. Thus there are two kinetic rates for cobalt and copper: the rate of the two species depositing on the cathode surface and the rate of the two species dissolving. The rate of deposition is a function of the concentration of the two species as outlined in Equation 4.1. The rate of dissolution is related to the concentration of particulate matter in solution, and is assumed constant. Thus in the first two hours of the test, where the first kinetic region is observed, the rate of dissolution is small in comparison to the rate of deposition, and the cobalt removal rate constant is high. In the second kinetic region, the rate of dissolution becomes more of a factor, and the cobalt removal rate constant decreases.

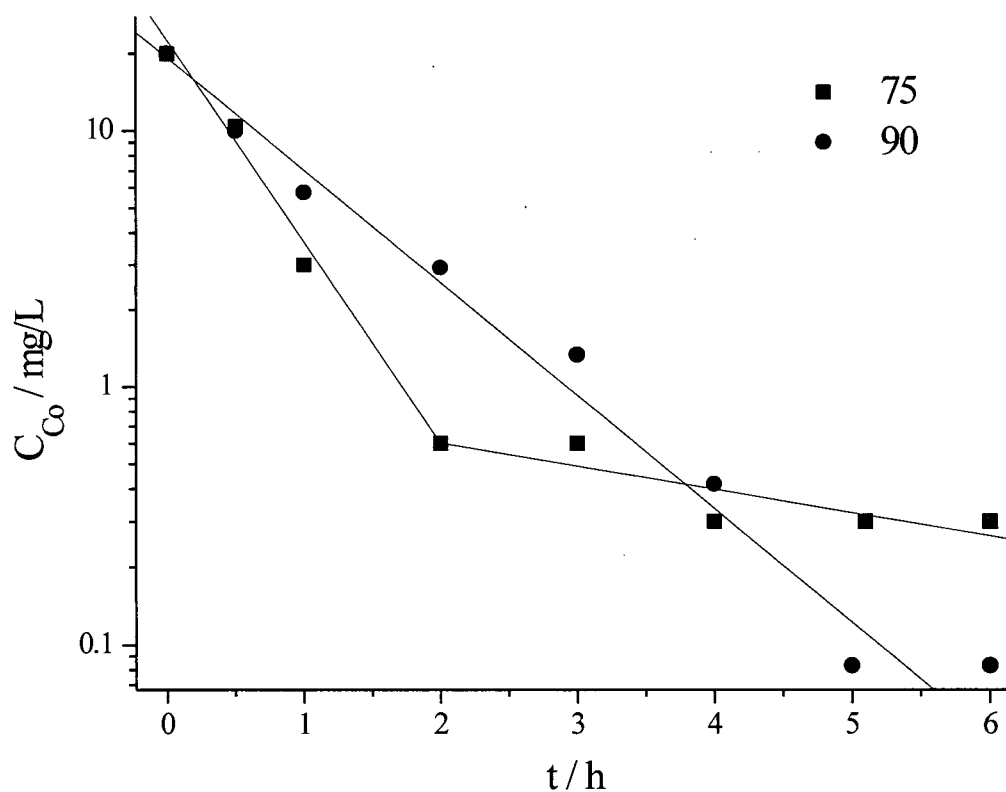


Figure 4.11 Cobalt removal as a function of time using arsenic - copper activation at two temperatures. Legend refers to temperature (°C). Base conditions are listed in Table 3.2 except: $C_{Sb} = 0$, $C_{As} = 75$ mg/L, $C_{Cu} = 250$ mg/L, $i = 100$ A·m⁻².

This phenomenon can also be used to explain the detrimental effect of high copper content. At higher copper contents, the deposit will become more dendritic, leading to a higher rate of particulate break-off and dissolution of copper, cobalt and arsenic. Thus the rate for 375

mg/L Cu present is reduced from that obtained at lower copper concentrations. This is supported by visual observation of a high amount of particulate matter present at this high copper concentration.

Arsenic - copper activated cobalt removal is typically performed at temperatures near 90°C. For this reason, experiments were performed at this temperature. Figure 4.11 compares cobalt removal over time at 75 and 90°C.

The effect of increasing temperature changes the shape of the removal curve from the two rate curve observed at 75°C to a curve which is depicted by one first-order removal rate. Although the curve at 90°C begins at a rate lower than that observed at 75°C, this rate is sustained for 5 hours. After 5 hours cobalt is no longer removed; however, at this point the final cobalt level is 0.1 mg/L. This cobalt concentration is the lowest level that was obtained in any of the tests performed.

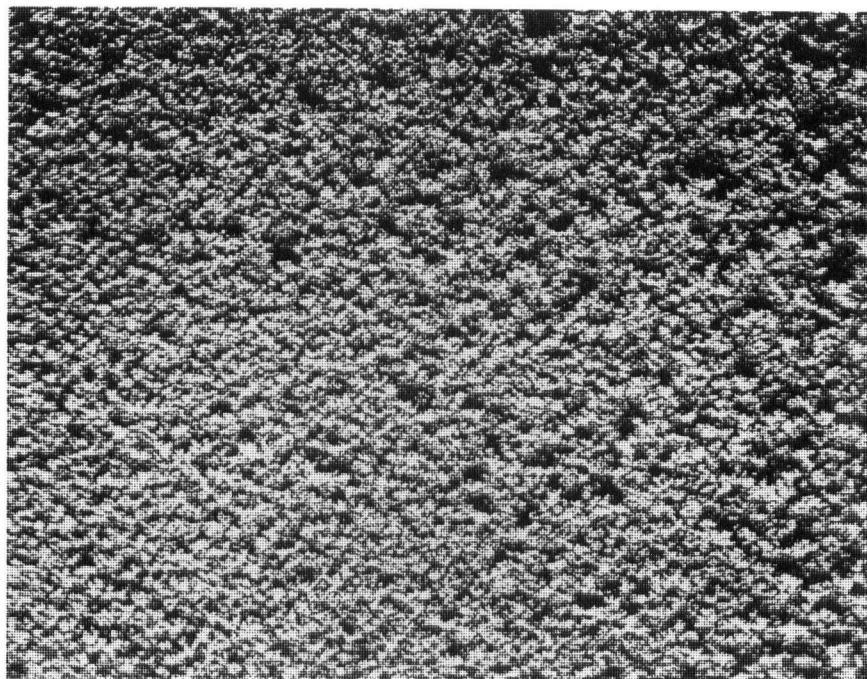
The potential of the working electrode at 90°C varied between -0.650 and -0.700 V vs. SCE which is ~100 mV higher than the potentials observed at 75°C.

4.2.4 Morphology

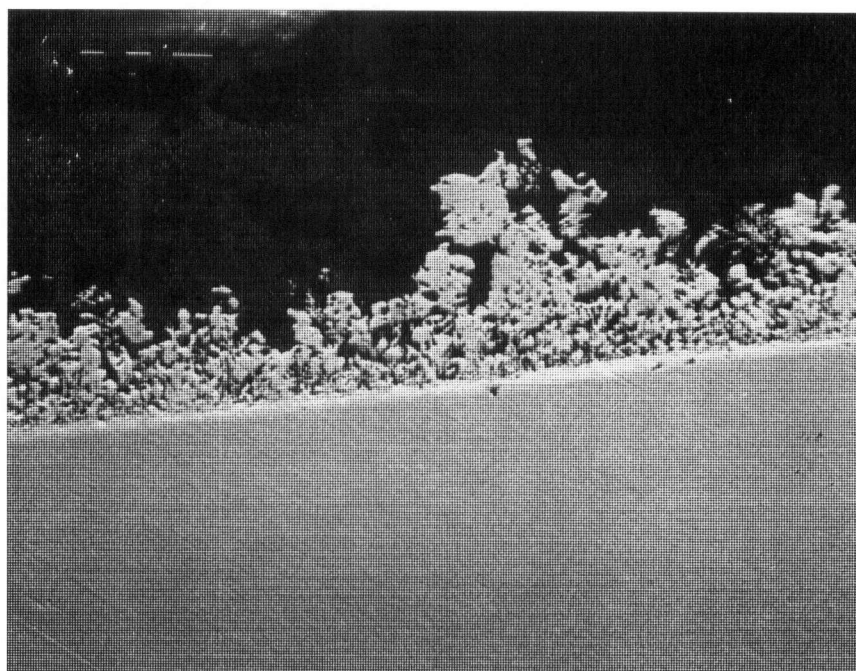
SEM analysis of the deposits was performed on the surface and cross-sections of the working electrode. These SEM photomicrographs appear in Figure 4.12. As no appreciable difference in morphology was seen between the deposits obtained with and without copper in solution, only SEM photomicrographs without copper in solution are presented.

The morphology of the surface of the electrode shows that the deposit is composed of unevenly dispersed nodular growth. Although the growth is not dendritic, by examining the cross-section of the electrode, the deposit appears to grow in randomly oriented clusters away from the electrode. The deposit also appears to be porous in nature. As the deposit consists primarily of zinc, this porosity could be attributed to redissolution of the zinc deposit.

To determine approximate concentrations of cobalt and zinc deposited, EDX analysis was performed. Figure 4.13 shows how cobalt, zinc and copper are distributed in the deposit for both antimony and antimony-copper activated tests.



(a)



(b)

Figure 4.12 SEM photomicrographs of (a) the surface of the electrode and (b) a cross section of the electrode. Conditions are listed in Table 3.2. Magnification (a) 25X, (b) 500X.

With no copper present in solution (a), cobalt appears to deposit only *directly* on the copper substrate. The uneven nodular growths above this layer are entirely zinc. No cobalt was found in these growths. This thin layer of cobalt or perhaps a cobalt-zinc alloy on the surface can

be observed in the cross-sectional SEM in Figure 4.12 as a thin white colored layer. Unfortunately, due to the size of the electron beam used, one can not be sure if the thin white layer is cobalt, or a cobalt-zinc alloy. EDX analysis indicated both elements; however, due to the large aperture of the beam, the zinc assay could have come from the nodular growths.

When copper is added to solution, the nodular zinc growths become covered with copper, and these growths then become amenable to cobalt deposition. This is depicted in (b) in Figure 4.13 which shows that cobalt is found throughout the deposit.

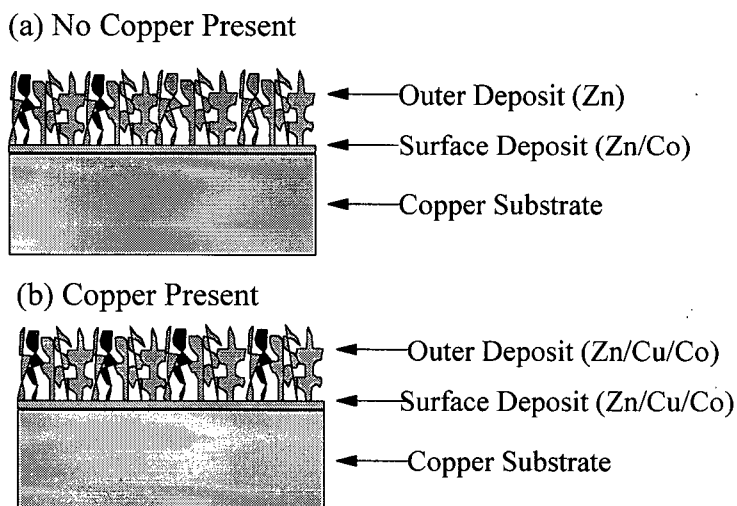


Figure 4.13 Figure showing correlation of EDX analysis with morphology of deposits obtained with antimony activation.

The distribution of cobalt throughout the deposit correlates with the removal rates of cobalt observed in Sections 4.2.1 and 4.2.2, where the increase in cobalt removal with copper present was attributed to an increase in surface area. By examining the morphology of the deposits, it can be observed that the surface area of the deposit does not change; however, the surface area of copper containing phases increases with the addition of copper. This in turn enables cobalt to deposit on a greater surface area as it appears that cobalt will only deposit on a substrate containing copper and not on pure zinc.

Compositional analysis of the deposit was obtained by EDX and by dissolving the deposit in a 1 mol/L H_2SO_4 with an anodic current density, followed by atomic absorption analysis. Using these two forms of analysis, the ratio of zinc to cobalt in the deposit was found to be 35:1.



Figure 4.14 SEM photomicrograph of arsenic-copper activated cobalt deposition. Conditions are listed in Table 3.2 except $C_{Sb} = 0$, $C_{As} = 75$ mg/L, $C_{Cu} = 250$ mg/L. Magnification 30X.

The morphology of the deposit obtained with arsenic-copper activation (Figure 4.14) shows a loosely packed, porous, nodular growth. The deposit was not adherent to the cathode, and broke off often during electrolysis and during subsequent handling. For this reason a cross-section of the deposit was not obtained.

EDX analysis of the deposit revealed that the deposit is composed almost entirely of copper, arsenic and cobalt. A small amount of zinc was detected which can be attributed to entrained solution.

4.2.5 Comparison to Cementation

To evaluate how this method of cobalt removal from zinc sulfate solutions compares to cobalt removal using cementation, the rates obtained in this thesis were compared to rates obtained by other researchers. This comparison appears in Figure 4.15. To ensure that the rate constants compared were of the same units, the rate constants obtained, typically in units of time^{-1} , were converted using the volume of the reactor and the surface area of reaction (either a rotating disk or zinc dust) to cobalt removal rate constants in cm/s. The method used for conversion of published rates can be found in Appendix II.

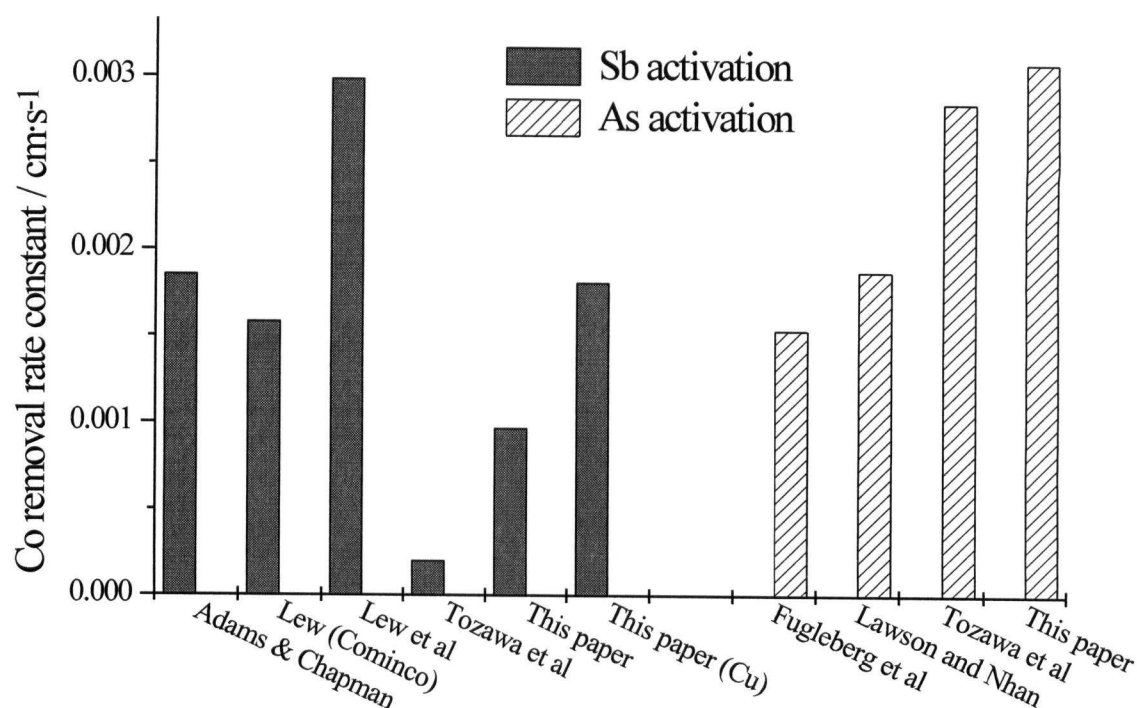


Figure 4.15 Comparison of obtained vs. published cementation rates. References: Adams and Chapman[17], Lew (Cominco)[59], Lew *et al*[18], Tozawa *et al*[1], Fugleberg *et al*[16], Lawson and Nhan[33].

Tozawa *et al*, Lawson and Nhan, and Adams and Chapman, used a rotating zinc disk for cobalt removal. All other researchers used a reactor with zinc dust.

Figure 4.15 shows that for antimony activation, the rates obtained by electrochemical removal are similar to the rates obtained by cementation, particularly when copper was present. As copper was present in all of the cementation tests performed by other researchers, this comparison is valid. The one anomalous rate, that of Lew *et al*, was obtained by using the mean zinc dust particle size to calculate the surface area, and when the full particle size distribution is used to calculate the cementation rate (Lew (Cominco)), the rate is similar to that obtained with electrochemical removal. It is interesting to note that the removal rate measured by one researcher who used a rotating zinc disk to remove cobalt with antimony activation (Tozawa *et al*) is substantially lower than the other rates. This suggests that the other rates may be artificially high due to an inaccurately low surface area being used based on an assumption of spherical particles.

The removal rate obtained for arsenic activation is also similar to the rates obtained by other researchers. As no optimization of the arsenic removal process was attempted, it can be

seen that electrochemical removal of cobalt using this type of activation is as good or better than removal using a zinc reductant.

Having established that the rates of cementation are similar using the antimony- and arsenic-activated systems, the question remains as to whether the zinc dust "usage" is the same. To compare electrochemical removal to zinc dust usage, the coulombs required to remove cobalt electrochemically were converted to grams of zinc dust assuming 1 mole of zinc dust contains $2F$ coulombs. For this calculation, the antimony-activated system was used.

As the rate of removal varies with concentration, an initial and final concentration must be selected for comparison. For electrochemical removal, a starting concentration of 20 mg/L and a final concentration of 0.5 mg/L was chosen.

From Figure 4.1 the concentration of cobalt can be described as a function of time starting from 20 mg/L, at $35 \text{ A}\cdot\text{m}^{-2}$ by the following reaction (t in hours, C_{Co} in mg/L):

$$\log C_{\text{Co}}^f = 1.40 - 0.125t \quad (4.5)$$

Thus to reach a final concentration of cobalt of 0.5 mg/L, the time required is: 13.6 h.

The number of coulombs required to perform this removal is given by the following equation:

$$Q = iAt \quad (4.6)$$

Using a time of 13.6 h, a current density of $35 \text{ A}\cdot\text{m}^{-2}$, and surface area of 36 cm^2 , the total number of coulombs needed are 6170 C. This corresponds to 2.1 g/L of zinc dust. This compares favorably to industrial cementation reactors which typically require greater than 4 g/L of zinc dust to remove cobalt to this level[60].

5. Fundamental Properties

5.1 Introduction

A full description of the fundamental chemical and electrochemical properties of cobalt and zinc under conditions similar to cementation is necessary before more complex experiments can be performed. In this section the following properties are measured or calculated:

1. Diffusion coefficients of cobalt ions and protons.
2. Tafel slopes of cobalt and hydrogen discharge.
3. The mechanism of cobalt deposition.
4. E-pH diagrams for cobalt, zinc and hydrogen.
5. The cyclic voltammetry behavior of cobalt.

5.2 Results and Discussion

5.2.1 Diffusion Coefficients

To determine the diffusion coefficients of Co^{2+} and H^+ in the background electrolyte, the kinematic viscosity is required. The absolute viscosity and density of the background 2.4 mol/L MgSO_4 solution were obtained by the methods described in Section 3.2.5. The kinematic viscosity was obtained by dividing the absolute viscosity by the density of the solution. The following values were obtained:

Table 5.1 Density, absolute viscosity, and kinematic viscosity of 2.4 mol/L MgSO_4 at various temperatures.

Temperature (T, °C)	Density (ρ , $\text{g}\cdot\text{cm}^{-3}$)	Absolute Viscosity (μ , $\text{g}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}$)	Kinematic Viscosity (ν , $\text{cm}^2\cdot\text{s}^{-1}$)
25	1.234	0.051	0.041
50	1.246	0.030	0.024
75	1.256	0.020	0.016

To calculate the diffusion coefficients of cobalt ions in this solution, the method of Levich was applied. An electrolyte consisting of 0.01 mol/L CoSO_4 and 2.4 mol/L MgSO_4 as the background electrolyte was used. The potential of the electrode was swept from -0.6 V vs. SCE to the potential just before breakdown of water leads to an increase in cathodic current, and back

at a sweep rate of 2 mV/s, at 5 different rotation speeds. The limiting current density was taken at the plateau of the current, where it reached its limiting value. Figure 5.1 shows these potential sweeps for a temperature of 25°C. Potential sweeps for other temperatures can be found in Appendix III.

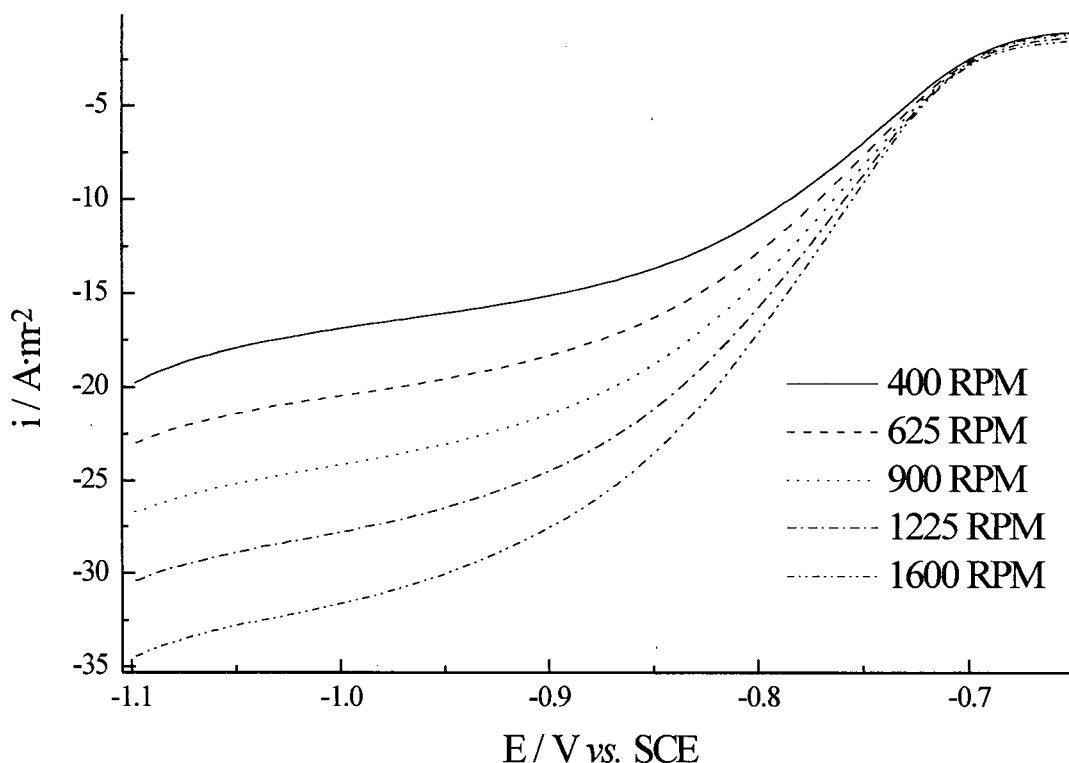


Figure 5.1 Cathodic potential sweeps of 0.01 mol/L Co in 2.4 mol/L MgSO₄ at various rotation speeds. Temperature: 25°C, pH 5.

Using the limiting current density for each rotation speed at each temperature, Levich plots can be obtained that show the limiting current density against the square root of the rotation speed. These plots appear in Figure 5.2.

The diffusion coefficient can now be calculated using a modified version of the Levich equation which for rotation speed given in RPM, is:

$$i_L = 0.20nFD^{2/3}\nu^{-1/6}(RPM)^{1/2}C^b \quad (5.1)$$

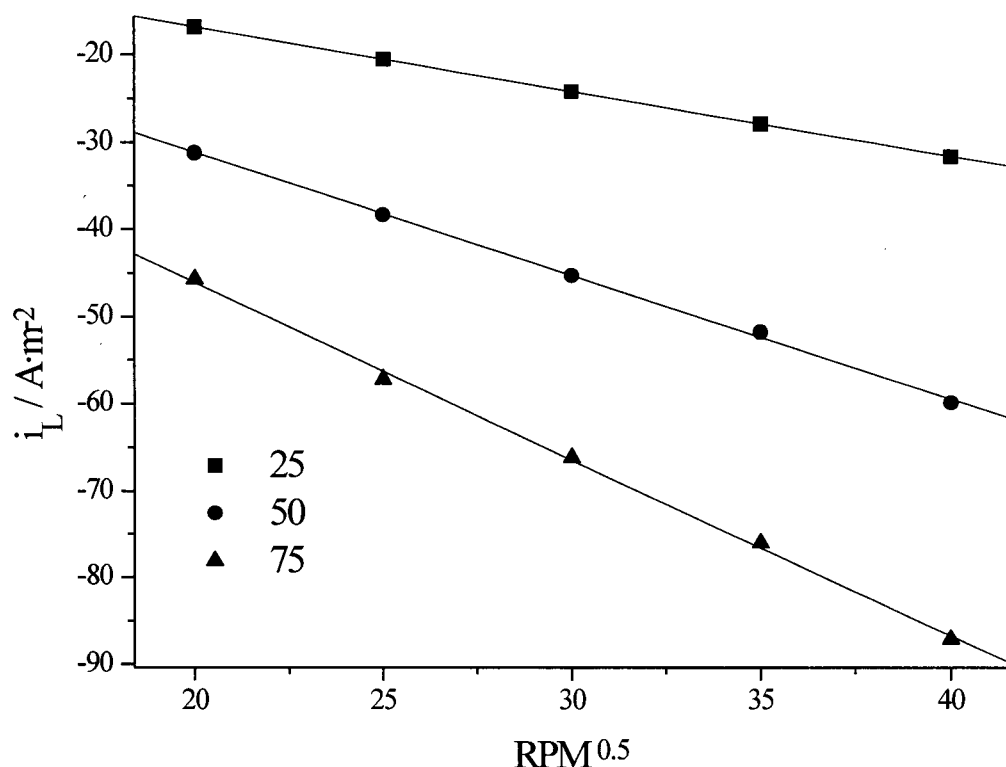


Figure 5.2 Levich plots for cobalt at various temperatures. Legend refers to temperature in °C. 0.01 mol/L Co²⁺ and 2.4 mol/L MgSO₄.

The following values were used to calculate the diffusion coefficients:

Table 5.2 Properties used to calculate diffusion coefficients.

Property	Value	Units
$i_L / \text{RPM}^{1/2}$	Figure 5.2 slopes/ 10^4	$\text{C} \cdot \text{s}^{-1} \cdot \text{cm}^{-2} \cdot \text{min}^{-0.5}$
n	2	equ/mol
F	96500	C/equ
D	Calculated from Equ. 4.2	cm^2/s
ν	From Table 5.1	cm^2/s
C^b	$0.01/10^3$	mol/cm^3

Using these properties the following values were obtained for the diffusion coefficient of cobalt ions in these solutions:

Table 5.3 Diffusion coefficients of Co²⁺ in 2.4 mol/L MgSO₄ at various temperatures.

Temperature (T , °C)	Diffusion coefficient ($D \times 10^5$, cm^2/s)
25	0.117
50	0.274
75	0.425

A similar treatment was applied to obtain the diffusion coefficients of protons in the same solution. Levich plots for proton discharge can be found in Appendix III. For calculation of the diffusion coefficients of H^+ , a pH 4 solution of 2.4 mol/L $MgSO_4$ was used. The diffusion coefficients for the same three temperatures were calculated. The values obtained were:

Table 5.4 Diffusion coefficients of H^+ in 2.4 mol/L $MgSO_4$ at various temperatures.

Temperature (T , °C)	Diffusion coefficient ($D \times 10^5$, cm^2/s)
25	5.23
50	22.3
75	25.5

To calculate the activation energy of the diffusion coefficients, the diffusion coefficients for cobalt ions and protons were plotted as Arrhenius plots (Figure 5.3).

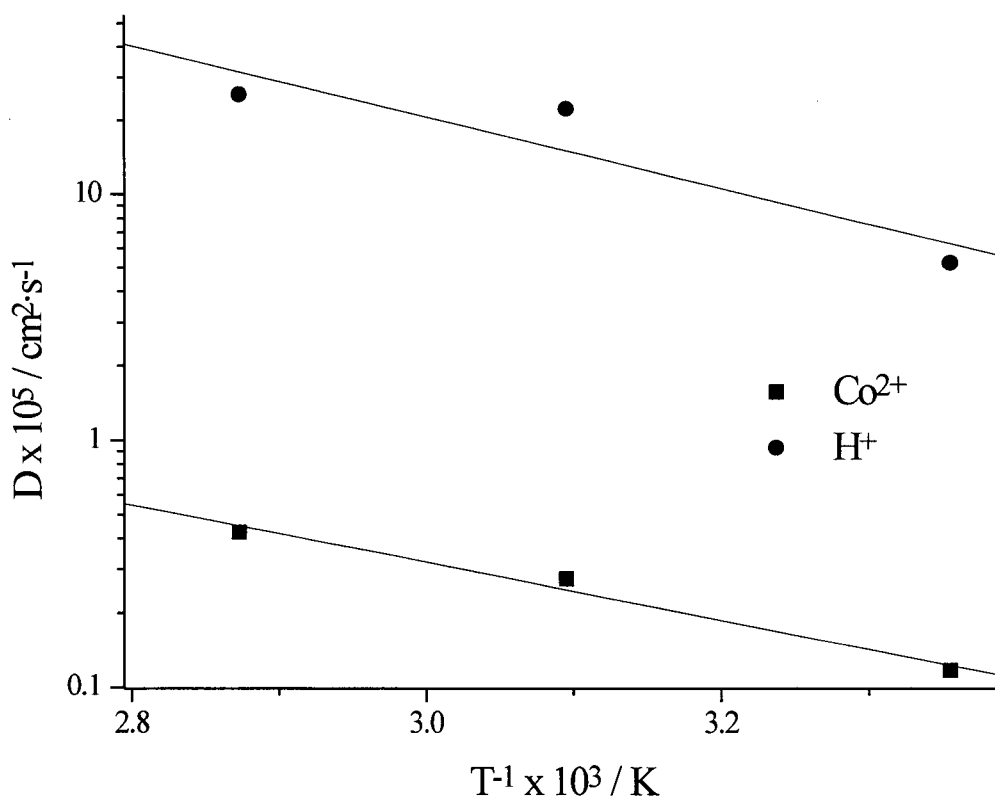


Figure 5.3 Arrhenius plots showing the variation of the diffusion coefficients of Co^{2+} and H^+ with temperature.

The resulting Arrhenius equations for the diffusion of cobalt ions and protons are based on the following equation, where D_0 is a constant:

$$D = D_0 \exp\left(\frac{E_a}{RT}\right) \quad (5.2)$$

From Figure 5.3 the values for D_0 and E_a are:

Table 5.5 Values for the Arrhenius equation for the diffusion of cobalt ions and protons.

Species	D_0 (cm ² /s)	E_a (kJ/mol)
Co ²⁺	0.0103	22.4
H ⁺	4.79	27.9

It is interesting to note that the two diffusion coefficients have similar values for the activation energy, as should be expected for ions in the same solution. Note that the diffusion coefficients of H⁺ are close to 50 times larger than the diffusion coefficients of Co²⁺. To explain this difference and to check the obtained values, further discussion is necessary.

Diffusion coefficients are related to the absolute viscosity and temperature of a solution by the Nernst - Einstein equation[61]:

$$\frac{D_i \mu}{T} = \text{const.} \quad (5.3)$$

Assuming that the diffusion coefficient of cobalt ions is 0.7×10^{-5} cm²/s at infinite dilution and 25°C[61], using the absolute viscosities from Table 5.1, values for the diffusion coefficients of cobalt ions can be calculated using Equation 5.3:

Table 5.6 Diffusion coefficients of Co²⁺ as calculated by the Nernst-Einstein equation.

Temperature(T , °C)	$D(\text{Co}^{2+}) \times 10^5$ (cm ² /s)
25	0.14
50	0.25
75	0.41

Comparing the values in Table 5.6 with the measured values (Table 5.3) it is observed that the diffusion coefficients of cobalt ions agree closely. Unfortunately, this method cannot be used to predict the diffusion coefficient of the proton. Protons diffuse by a "proton jump" mechanism, where the excess proton transfers between water molecules by rearrangement of the

hydrogen bonds[62]. Thus the diffusion coefficient of protons cannot be obtained by the Nernst-Einstein equation.

5.2.2 Tafel Behavior

The Tafel slopes for both cobalt deposition and hydrogen evolution were calculated by performing a potential sweep at 1 mV/s. For the Tafel behavior of hydrogen evolution, the platinum rotating disk was pre-plated with cobalt before the behavior of the hydrogen evolution reaction was determined. Tafel behavior was determined at 75°C as this is the approximate temperature of the industrial cementation of cobalt.

Figure 5.4 shows potential sweeps for both hydrogen and cobalt. It is important to note that the potential sweep for cobalt was performed in a pH 5 solution to limit the contribution of hydrogen evolution to the total current, while the sweep for hydrogen was performed in a pH 4 solution so that current densities due to hydrogen evolution would be higher.

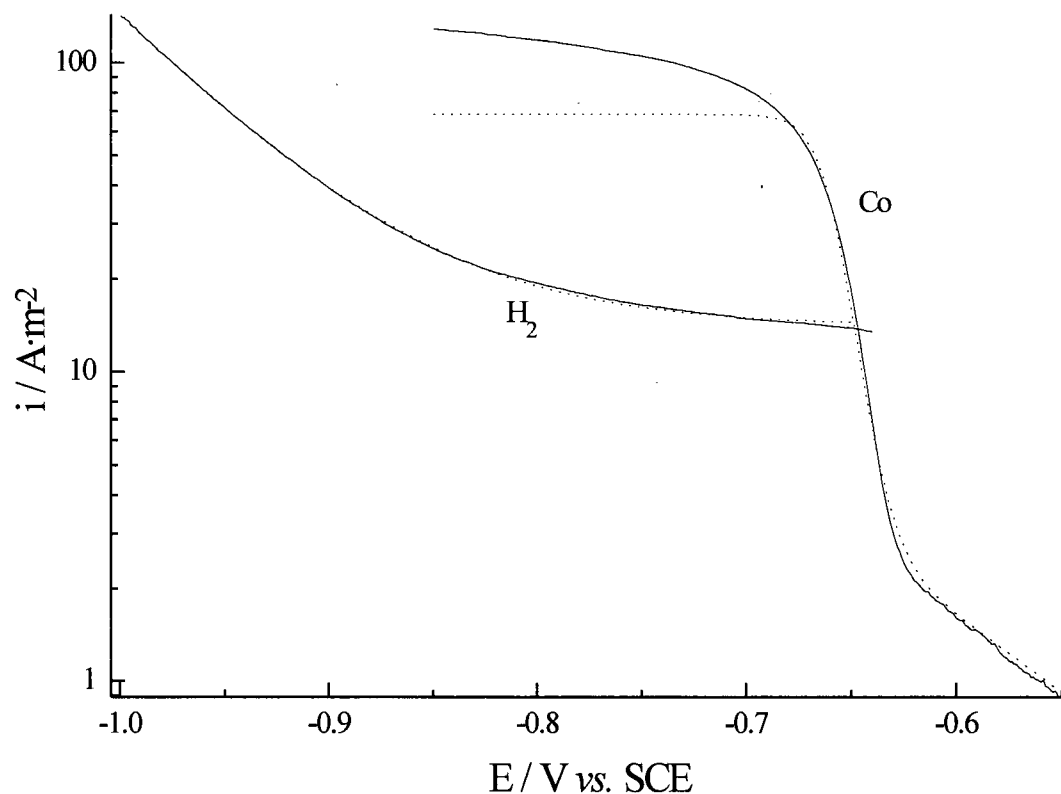


Figure 5.4 Potential sweeps showing the Tafel behavior of Co and H_2 . Dotted lines indicate fitted curves. Conditions: (Co) 0.01 mol/L Co^{2+} , 2.4 mol/L MgSO_4 , pH 5, 75°C, 3600 RPM; (H_2) 2.4 mol/L MgSO_4 , pH 4, 75°C, 3600 RPM.

The current-potential behavior of cobalt deposition can be described by two kinetic regions in series, followed by a mass transfer limited region in parallel (limiting current density), and can be described by the following equation:

$$\frac{1}{i} = \frac{1}{i_{ac1} + i_{ac2}} + \frac{1}{i_L} \quad (5.4)$$

Fitting this equation to the curve shown in Figure 5.4 for cobalt deposition using a software curve fitting routine, the following values are obtained:

$$i_{ac1} = 1.52 \times 10^{-3} \exp\left(\frac{-0.35FE}{RT}\right) \quad (5.5)$$

$$i_{ac2} = 4.75 \times 10^{-38} \exp\left(\frac{-4.1FE}{RT}\right) \quad (5.6)$$

$$i_L = 75 \quad (5.7)$$

where all current densities are in units of $A \cdot m^{-2}$.

The equations for i_{ac} are a form of the Tafel equation relating to potential rather than to overpotential. In the equation for i_{ac1} , 0.35 is the value of α . This value corresponds to a Tafel slope of 177 mV at 25°C. For i_{ac2} , the value of α is 4.1 which corresponds to a Tafel slope of 15 mV. Note that the equation for cobalt does not accurately describe the current-potential behavior of cobalt in these solutions for currents near to and above the limiting current density, as the value of the current in this region is affected by concurrent hydrogen evolution.

The current-potential behavior of hydrogen is the sum of two reactions. At potentials above -0.8 V vs. SCE, the following reaction occurs at its limiting current density:



At potentials below this value the following reaction takes place:



As this reaction is not diffusion limited (i.e. the concentration of water is too high), this reaction follows activation control. The total current is related to the current of these two reactions in the following manner:

$$i = i_{H^+} + i_{H_2O} \quad (5.10)$$

These two currents have the following relationships with potential:

$$i_{H^+} = 14 \quad (5.11)$$

$$i_{H_2O} = 1.02 \times 10^{-5} \exp\left(\frac{-0.5FE}{RT}\right) \quad (5.12)$$

where all current densities are in units of $A \cdot m^{-2}$.

Note that the deviation of the hydrogen current from these equations at more positive potentials is due to the dissolution of the cobalt substrate. The value of α for hydrogen evolution due to the breakdown of water is 0.5 which corresponds to a Tafel slope of 120 mV at 25°C.

5.2.3 The Mechanism of Cobalt Deposition

The deposition of cobalt is characterized by two kinetic regions that occur concurrently. Insight into these two regions can be found by investigating the reaction mechanism for cobalt.

5.2.3.1 Epelboin and Wiart's Model

For polyvalent metals (Me^{z+}), electrodeposition occurs in several steps. For cobalt the reaction mechanism has been investigated most thoroughly by Epelboin and Wiart[63], who propose the following reaction mechanism for cobalt deposition.

Cobalt is deposited through an intermediate ion, $CoOH_{ads}$ which is formed first by the creation of the mono-hydroxide ion:



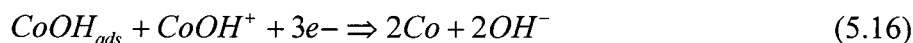
This ion adsorbs according to the following transfer reaction:



After this initial adsorption step, there are different theories as to how electrocrystallization occurs. Heusler and Gaiser[64] proposed that, for iron group metals, the adsorbed species acts as a catalyst and deposition of cobalt occurs as follows:



The other theory which was supported by Epelboin and Wiart for nickel reduction (unfortunately their studies on cobalt were hampered by the pH dependence of cobalt reduction) suggests that the adsorbed species acts as an intermediate and the reaction proceeds as follows:



This reaction, as it includes a three-electron transfer, takes place over several steps.

From this description of the reduction of cobalt, it can be seen that cobalt reduction is sensitive to the ability of the formed CoOH^+ to adsorb on the surface of the electrode and create an adsorbed intermediate. Furthermore, the concentration of CoOH^+ is a critical factor in determining the rate of the reduction reaction, and all reaction must take place through this intermediate.

5.2.3.2 Proposed Model

Epelboin and Wiart proposed that cobalt reduction takes place through a CoOH_{ads} intermediate which is formed by the partial reduction of CoOH^+ . Formation of CoOH^+ is dependent on the concentration of OH^- at the electrode interface. It is proposed that the concentration of OH^- at the surface of the electrode becomes high enough for deposition through this intermediate only when H_2 is discharged by the breakdown of H_2O . Based on this assumption, the following mechanisms are proposed to explain the two kinetic regions observed for cobalt discharge.

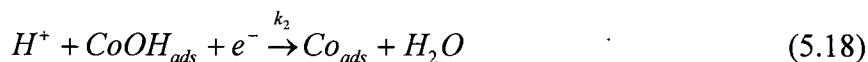
- In the potential region below the reversible potential of cobalt, but above the potential where H_2 generation from H_2O occurs, the concentration of OH^- at the interface is too low to form CoOH^+ and cobalt discharge occurs with a high Tafel slope without the formation of the CoOH^+ intermediate, presumably through direct reduction of Co^{2+} .
- In the potential region below the potential where H_2 generation from H_2O occurs, cobalt discharges by the mechanism described in Section 5.2.3.1, through the formation of CoOH^+ , with a low Tafel slope.

A value of 4.1 appears to be large for the value of α during the deposition of cobalt, but depending on the charge transfer mechanism, the value of α can have a wide variety of values. A charge transfer mechanism which produces a value of 4 for α is outlined below, based on the mechanism proposed by Epelboin and Wiart:

The first electron transfer reaction proposed by Epelboin and Wiart is:



Breaking the next reaction in the series (Equation 5.16) into a series of single electron transfers with the same overall equation, the following reactions can be proposed:



If we assume that the third reaction is rate limiting (Equation 5.19), that the other two reactions are at equilibrium, and that surface coverage follows a Langmuir isotherm, the following equations describe the current and coverage of the species:

$$\frac{\theta_{CoOH}}{1 - \theta_{CoOH} - \theta_{Co}} = K_1 C_{CoOH^+} \exp\left(-\frac{FE}{RT}\right) \quad (5.20)$$

$$\frac{\theta_{Co}}{\theta_{CoOH}} = K_2 C_{H^+} \exp\left(-\frac{FE}{RT}\right) \quad (5.21)$$

$$i = nFk_3\theta_{Co}^2 \quad (5.22)$$

If we assume that the fractional surface coverage of the two adsorbed species is low and the value $(1 - \theta_{CoOH} - \theta_{Co}) \approx 1$, the current can be written as:

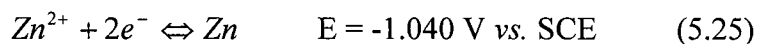
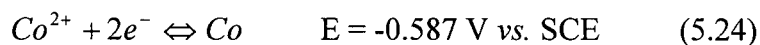
$$i = nFk_3 K_1^2 K_2^2 C_{CoOH^+}^2 C_{H^+}^2 \exp\left(\frac{4FE}{RT}\right) \quad (5.23)$$

It should be cautioned that this is only a proposed reaction mechanism, and no experimental evidence has been obtained to support this reaction sequence. This reaction mechanism only shows a possible reaction sequence that produces a value of α of 4.

5.2.4 Thermodynamic Properties and E-pH diagrams

The reversible potentials of cobalt and zinc in solution are needed to determine the potentials at which further testing should be performed. As the solutions used are at a different temperature and concentration than solutions under standard conditions, the reversible potentials must be adjusted.

The reversible potentials of Co^{2+}/Co and Zn^{2+}/Zn , after adjusting for a temperature of 75°C by the method of Criss and Cobble[65] and concentration of 0.01 mol/L, are:



E-pH diagrams were constructed for both the zinc-water, and the cobalt-water system at 75°C. Although there is a large concentration of sulfate in solution, in the potential-pH range investigated, it has been assumed that no solid sulfate species are formed.

It should be noted that the choice of $\text{Zn}(\text{OH})_2$ as the precipitating species at neutral pH values and the assumption of no solid sulfate species are based upon thermodynamic analysis of the possible precipitation products. Species from the Zn - SO_4 - H_2O system which could precipitate in the pH range tested are listed in Table 5.7 along with the pH of their precipitation.

Table 5.7 Precipitating species from the Zn - SO_4 - H_2O system. Conditions: $C_{\text{Zn}} = 0.01 \text{ mol/L}$, $C_{\text{SO}_4} = 2.4 \text{ mol/L}$, 75°C.

Species	pH of precipitation
$\text{Zn}(\text{OH})_2$	5.9
ZnO	6.6
$\text{ZnO} \cdot 2\text{ZnSO}_4$	4.7

As no precipitates were observed in solutions made using the conditions listed in Table 5.7 at a pH of 5, $\text{ZnO} \cdot 2\text{ZnSO}_4$ must have a high activation energy of precipitation and solutions at this pH can be considered super saturated with respect this compound.

$\text{ZnO} \cdot 2\text{ZnSO}_4$ is often claimed to be a form of an industrial precipitate "basic zinc sulfate". Many papers in regard to cementation report the formation of this species[14,18]; however, the chemical structure of this species has not been determined accurately. In fact there is a report that this species lacks a diffraction pattern and can be considered amorphous[66]. For these reasons and due to the low precipitation pH of this compound, it has not been included in this thermodynamic analysis.

Figure 5.5 shows the E-pH diagrams for cobalt, zinc, and water superimposed over each other. The potential scale used was V vs. SCE, and a value of -0.2412 V vs. SHE was taken as the value of the saturated calomel electrode[67]. Thermodynamic data for the species involved[67,68] were adjusted by the method of Criss and Cobble[65] (See Appendix IV) to 75°C. All metal species are at 0.01 mol/L and an activity coefficient of unity is assumed.

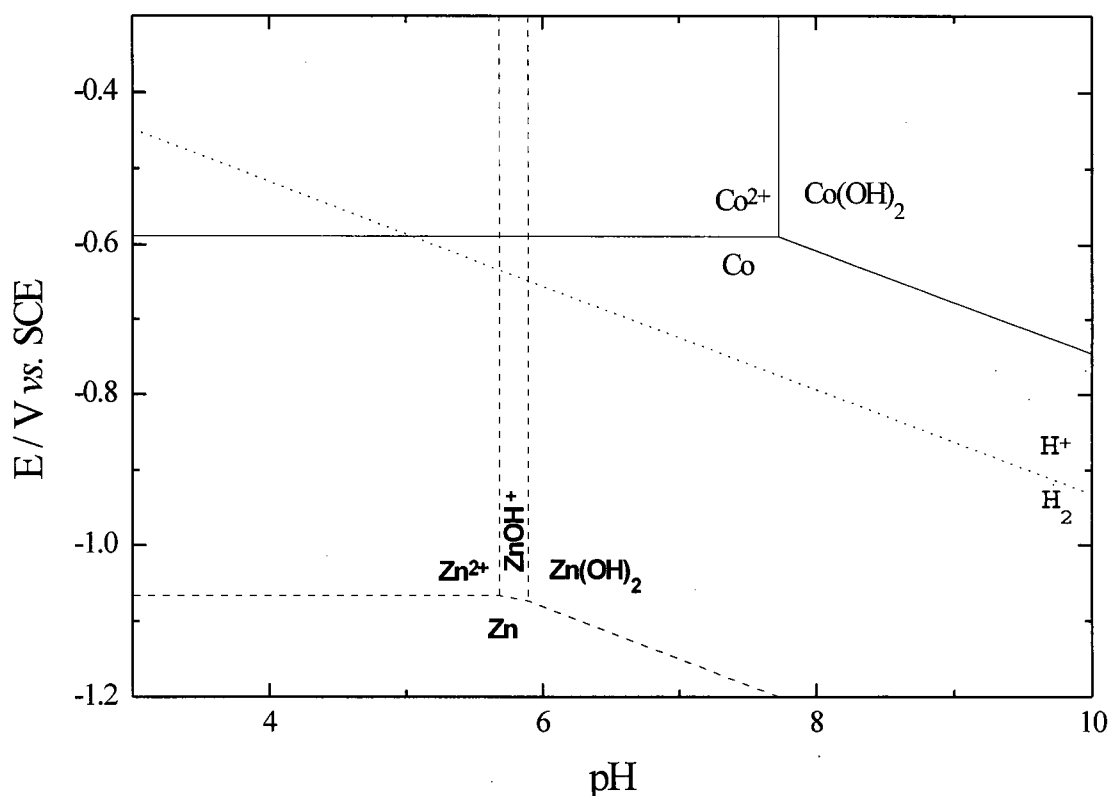


Figure 5.5 E-pH diagram showing the predominance of cobalt, zinc, and hydrogen species. Concentration of metal ions: 0.01 mol/L. Temperature: 75°C. Boundaries of : (—) cobalt, (-----) zinc, (·····) hydrogen.

This E-pH diagram shows that at the pH values associated with cementation (pH 4-5), the stable aqueous species are Co^{2+} and Zn^{2+} ; however, if the pH is raised above ~ 5.6 , the predominant aqueous zinc species is ZnOH^+ and at a pH above 5.8, Zn(OH)_2 will precipitate. These values are important as it is suggested[40,41] that the pH at the interface can be greater than 2 pH units above the bulk pH when depositing iron group metals with zinc. This would lead to blockage of the electrode by Zn(OH)_2 precipitation.

5.2.5 Cyclic Voltammetry

Cyclic voltammetry was performed on a stationary platinum disk electrode in an electrolyte containing 0.01 mol/L Co^{2+} with a background electrolyte of 2.4 mol/L MgSO_4 . The voltammograms at various temperatures and sweep rates appear in Figure 5.6. The voltammograms presented are “steady-state voltammograms”. This signifies that the potential of the electrode is swept between the positive and negative potential boundaries until the shape of

the voltammogram does not change. This figure clearly shows that cobalt deposition on platinum is straight forward, without any observable intermediates.

With increasing temperature, particularly at 75°C, the nucleation overpotential of cobalt on the platinum disk decreases and deposition occurs more rapidly. The sharp cathodic peaks observed at higher temperatures support this.

The difference between the peak potentials of the anodic and cathodic peaks is smaller at higher temperatures and the effect of increasing sweep rate is not as pronounced at higher temperatures. These two facts suggest that the discharge of cobalt becomes more reversible. For a reaction to be reversible, the concentrations of the reactants and the products at the interface must be equal at all times to their equilibrium values. Completely reversible reactions show no dependence on sweep rate, whereas irreversible reactions show a linear dependence on the log of the sweep rate.

The peak current density increases with increasing temperature and with increasing sweep rate. The peak current density is expressed by the following relation for an irreversible electrode process at a flat disk[57]:

$$i_p = 5.1 \times 10^6 n \alpha^{1/2} D^{1/2} C^b \nu^{1/2} T^{-1/2} \quad (5.26)$$

where ν is the sweep rate in V/s. This expression clearly shows that the peak current density increases with increasing sweep rate; however, the dependence on temperature is not so clear. While the peak current density is a function of $T^{-1/2}$, which would indicate that as temperature is increased, the peak current density would decrease, it is also a function of $D^{1/2}$. Examination of the ratio of D to T shows that the diffusion coefficient increases faster for a given temperature than the temperature. Thus the increase in the peak current density can be explained by the increase in D .

Unfortunately, as the true surface area of the electrode is not known at the time that the peak current is reached, Equation 5.26 cannot be used to re-calculate the value of α .

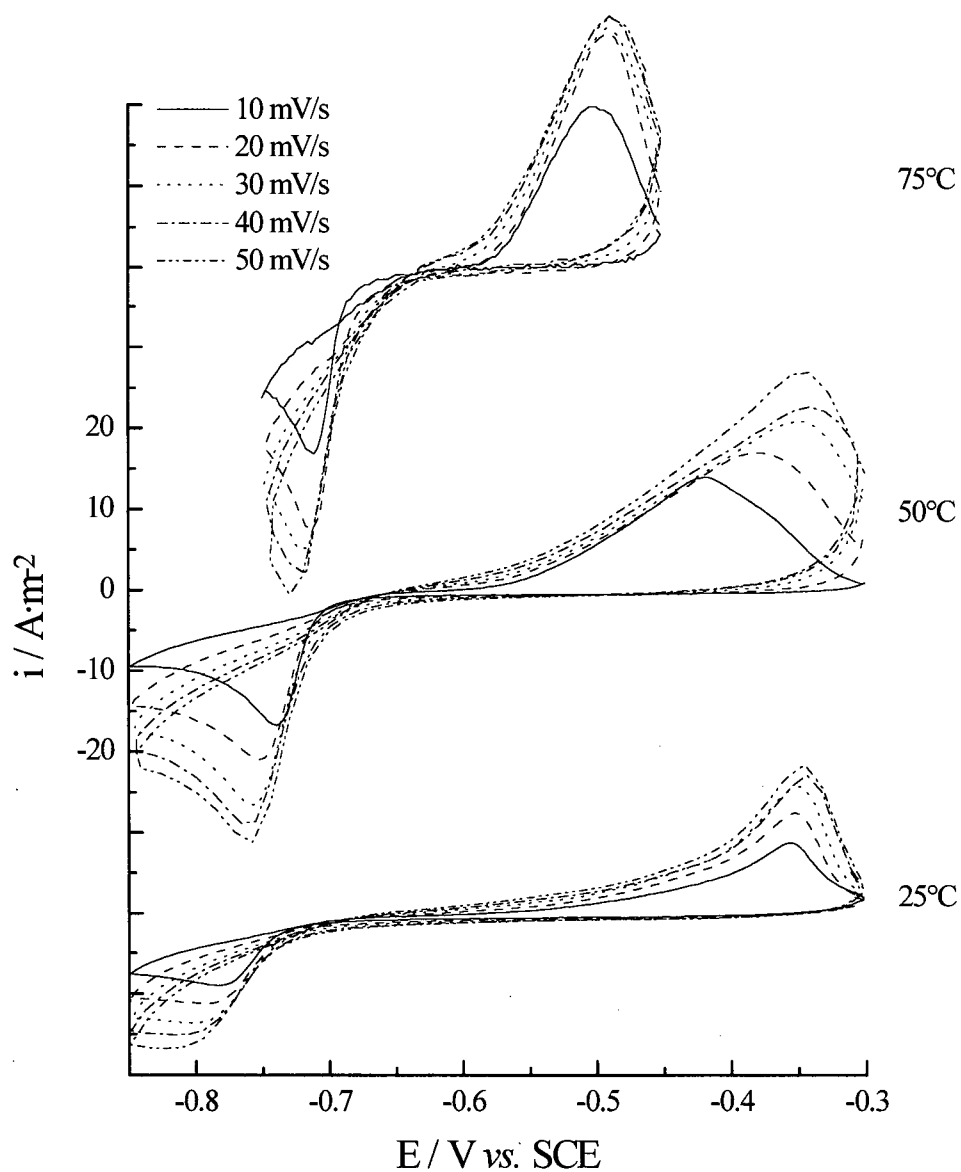


Figure 5.6 Cyclic voltammetry at a stationary platinum electrode. Conditions: 0.01 mol/L Co^{2+} , 2.4 mol/L MgSO_4 , various temperatures and sweep rates.

5.2.6 Morphology

Figure 5.7 shows a SEM photomicrograph of a deposit obtained from a cobalt-containing solution at 75°C where the electrode was held at limiting current conditions for 60 s. This photomicrograph shows that the cobalt deposit is a tightly packed nodular deposit, indicative of an unorientated dispersion type deposit[69] which would be obtained under limiting current conditions.

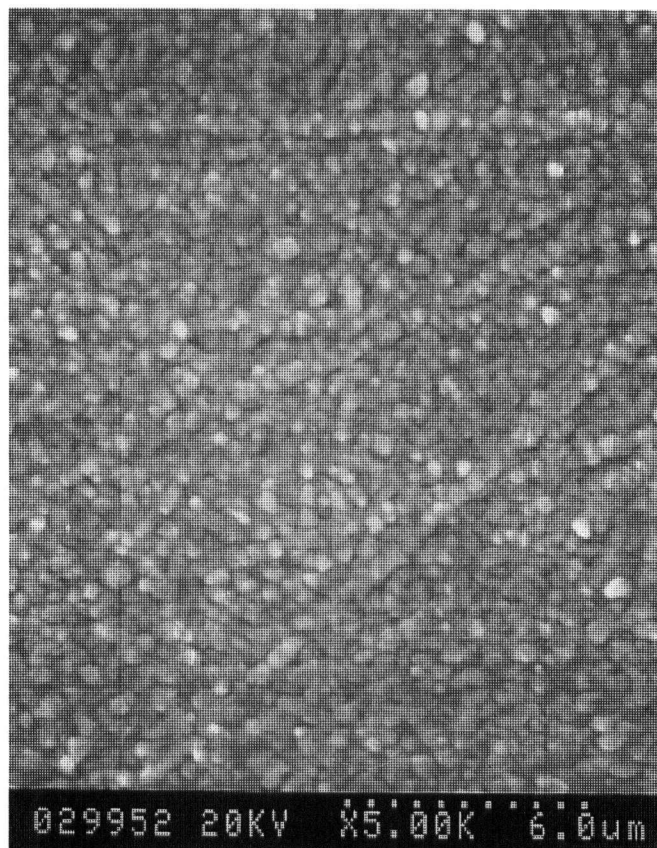


Figure 5.7 SEM photomicrograph taken of a sample obtained at -1 V vs. SCE. Conditions 75°C, 0.01 mol/L Co^{2+} , 2.4 mol/L MgSO_4 .

6. Deposition of Cobalt from Electrolytes Containing Zinc

6.1 Introduction

As discussed in the literature review, there are many different theories as to why zinc, present in solution, inhibits the deposition of cobalt. In this section, the inhibiting effect of zinc on the deposition of cobalt will be characterized and the method of inhibition will be determined. Since the aim of this thesis is to discover why cobalt cementation by zinc dust from electrolytes containing zinc sulfate is inefficient, studying this reaction by incorporating “true” industrial solutions and a zinc surface for deposition would be a logical choice. Unfortunately these conditions do not give suitable information on the inhibition of cobalt deposition by zinc for the following reasons:

1. Using a zinc surface for deposition limits study of the deposition of cobalt to potentials below the dissolution potential of zinc. As cobalt deposition begins several hundred millivolts above the dissolution of zinc, this does not provide a very large potential region of study.
2. In solutions containing industrial levels of zinc (150 g/L) and cobalt (20 mg/L), the current associated with the deposition of cobalt is of the same order of magnitude as the background electrochemical noise and cannot be readily observed.
3. Industrial zinc solutions contain impurities, such as Mn and Cl, the effects of which on cobalt deposition are not known and thus these species should be eliminated from solution to isolate the effects of zinc.

For these reasons and for comparison purposes to the preceding section, this study will be carried out using a platinum rotating disk with solutions that have a lower concentration of zinc and a higher concentration of cobalt.

6.2 Results and Discussion

6.2.1 Linear Sweep Voltammetry

Figure 6.1 shows linear sweeps from -0.6 to -1.0 V vs. SCE at 50 mV/s for cobalt solutions containing various amounts of zinc. This figure shows that as the concentration of zinc is increased, the deposition of cobalt is inhibited.

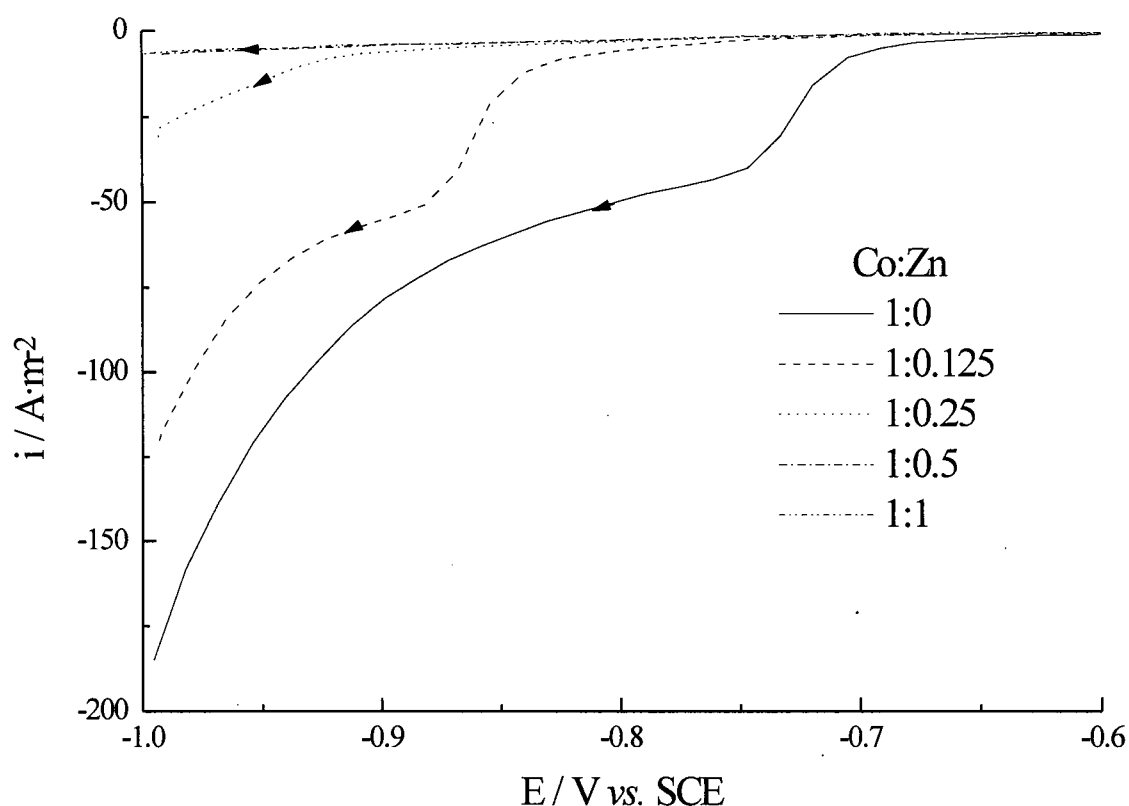


Figure 6.1 Linear sweep voltammetry at 50 mV/s. Conditions: 0.01 mol/L CoSO_4 , 2.4 mol/L MgSO_4 , pH 5, 400 RPM, 75°C. Ratio refers to molar ratio of cobalt to zinc in solution.

With no zinc present in solution, the magnitude of the reductive current increases with decreasing potential to the limiting current density for cobalt deposition at a value of $-50 \text{ A}\cdot\text{m}^{-2}$ at -0.740 V vs. SCE . At potentials below this value, the reductive current increases because of the evolution of hydrogen caused by the reduction of water. At a cobalt to zinc molar ratio of 1:0.125, the potential where cobalt begins to deposit shifts left to more negative potentials. As the concentration of zinc is further increased, the onset of deposition shifts further. At a cobalt to zinc molar ratio of 1:1, cobalt does not deposit in the potential range investigated.

Increase of the nucleation overpotential of cobalt deposition by the presence of zinc in solution suggests that zinc ions adsorb on the electrode surface, preventing cobalt deposition. This phenomenon has been documented by Yunus *et al*[38] who studied the deposition of cobalt-zinc alloys in sulfate solutions. They postulated that the inhibition in the plating of Co was caused by specific adsorption of zinc on the active centers of the substrate.

6.2.2 Cyclic Voltammetry

6.2.2.1 2 mV/s Tests

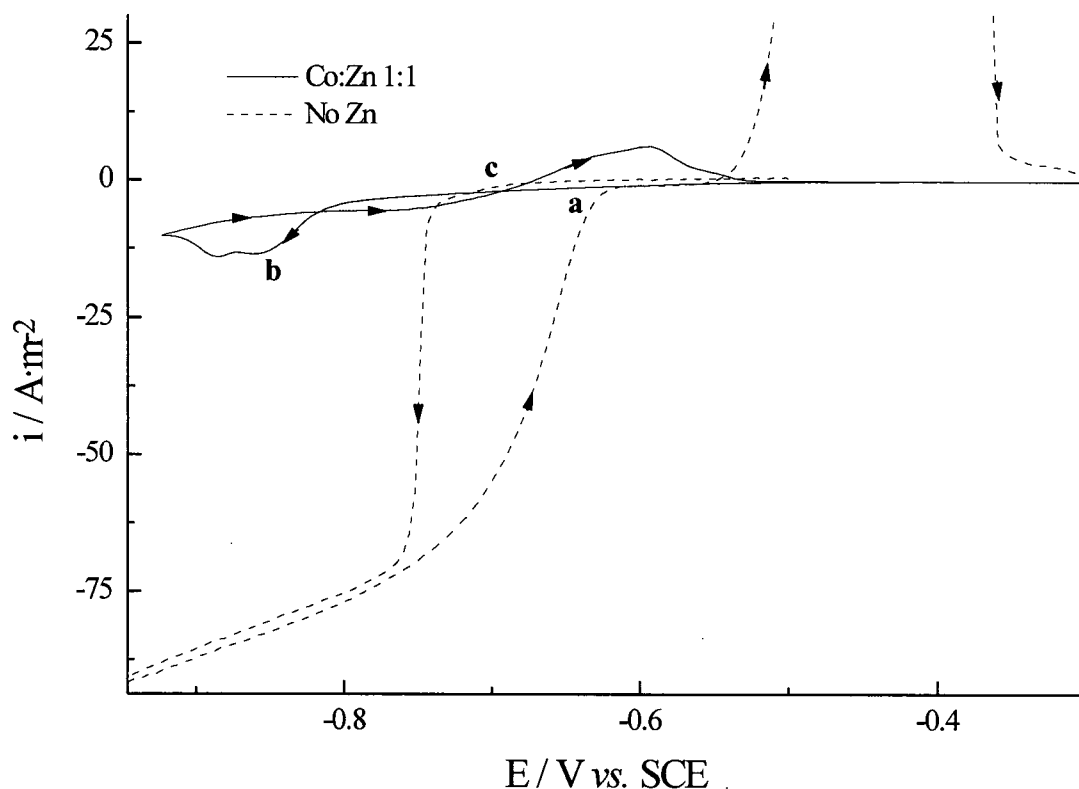


Figure 6.2 Cyclic voltammetry at 2 mV/s. Conditions: 0.01 mol/L CoSO_4 , 2.4 mol/L MgSO_4 , pH 5, 1600 RPM, 75°C. Ratio refers to molar ratio of cobalt to zinc in solution.

When the sweep rate is lowered to 2 mV/s, there are very significant differences between the voltammograms obtained in the presence and absence of Zn (Figure 6.2). Without Zn, the forward sweep shows that Co deposition begins at ~ -0.730 V vs. SCE and reaches its limiting current at -0.760 V vs. SCE. Co deposition is characterized by an initial steep Tafel region which is followed by a limiting current region at a potential of -0.760 V vs. SCE. This plateau has a small slope because of concurrent hydrogen evolution. On the reverse sweep the deposit dissolves at potentials more positive than -0.550 V vs. SCE, which is close to the reversible potential for Co^{2+}/Co . At -0.300 V vs. SCE, Co has been completely dissolved.

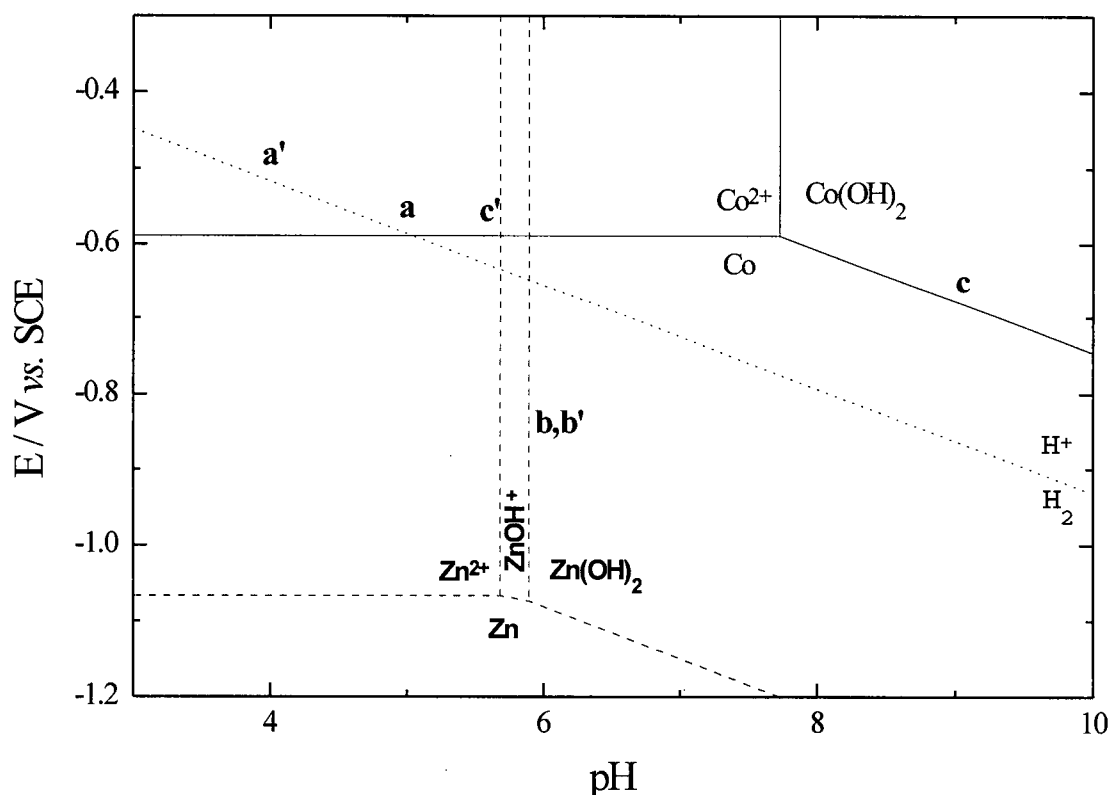


Figure 6.3 E-pH diagram showing the predominance of cobalt, zinc, and hydrogen species. Concentration of metal ions: 0.01 mol/L. Temperature: 75°C. Boundaries of : (—) cobalt, (-----) zinc, (.....) hydrogen (from Figure 5.5).

The voltammogram changes significantly upon the addition of 0.01 mol/L Zn. Deposition does not begin until -0.800 V vs. SCE as compared to -0.730 V vs. SCE for the solution without zinc. With Zn the maximum reductive current density for deposition is $15 \text{ A}\cdot\text{m}^{-2}$ as compared to $90 \text{ A}\cdot\text{m}^{-2}$ for the Zn free solution. Furthermore, deposition is inhibited at potentials more negative than -0.850 V vs. SCE, and the reductive current density decreases at potentials lower than -0.890 V vs. SCE. During the reverse sweep, a reductive current density is observed but it is lower than obtained during the forward sweep showing that Co deposition is still inhibited. This continues until -0.700 V vs. SCE where the deposit dissolves. Thus, in the presence of Zn, the deposit starts to dissolve at a potential 0.150 V lower than without Zn. This shows that the deposit obtained with Zn is not as noble as that obtained without it.

The E-pH diagram shown in Figure 6.3 can be used to quantitatively understand the voltammogram obtained in the presence of Zn (Figure 6.2), and show how the potential and pH

at the interface of the working electrode change when the potential is swept. Letters on the cyclic voltammogram correspond to letters on the E-pH diagram.

- a. Hydrogen evolution begins. The hydrogen evolution rate increases as the potential decreases and increases the pH at the electrode/electrolyte interface.
- b. Deposition of Co begins at -0.800 V vs. SCE and is inhibited by the precipitation of Zn(OH)_2 . Hydrogen continues to evolve at lower potentials and during the beginning of the reverse sweep; however, cobalt deposition is still inhibited by the Zn(OH)_2 deposit.
- c. Cobalt dissolves; however, as the pH at the interface is high, the dissolution reaction occurs at a potential of -0.700 V vs. SCE, 0.150 V lower than the reversible potential of Co, by reaction 6.1.

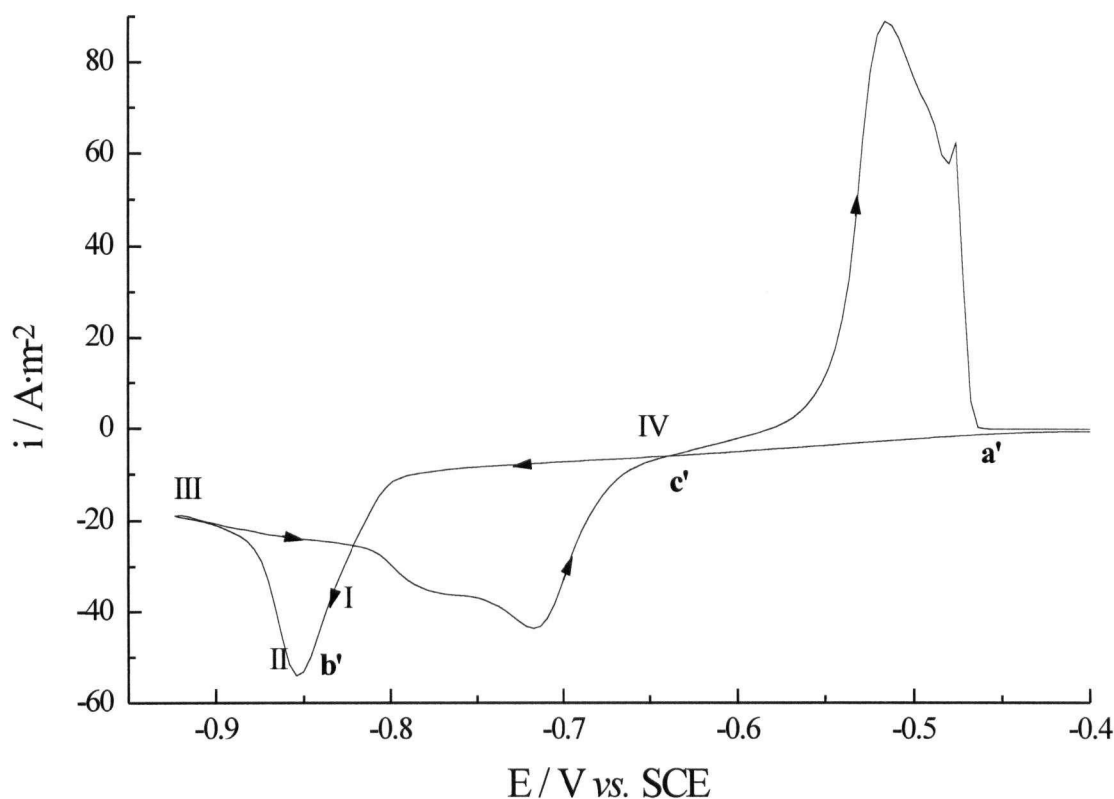
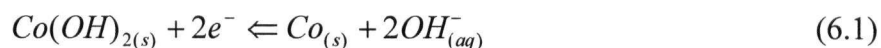


Figure 6.4 Cyclic voltammetry at 2 mV/s. Conditions: 0.01 mol/L CoSO_4 , 0.01 mol/L ZnSO_4 , 2.4 mol/L MgSO_4 , pH 4, 1600 RPM, 75°C.

For this reaction to occur at -0.700 V vs. SCE, the pH at the interface must be higher than 8. This high interfacial pH value can only be reached if the Zn(OH)_2 precipitate blocks the ionic

diffusion of H^+ . Thus while the pH in the bulk electrolyte is 5, the interfacial pH can be much higher.

Because interfacial pH increases may be responsible for changes in the mechanism of Co deposition, voltammograms were obtained under the conditions shown in Figure 6.2 but at different bulk pH values. Figure 6.4 shows a voltammogram obtained with Zn and Co in the electrolyte and at a bulk pH of 4. The reactions taking place during this sweep can also be described with the aid of the E-pH diagram shown in Figure 6.3.

- a'**. Hydrogen evolution begins. This results in a reductive current which increases with decreasing potential.
- b'**. At -0.800 V vs. SCE, Co deposition starts and the rate of deposition increases as the voltage decreases until it is inhibited by the precipitation of $Zn(OH)_2$ after reaching a maximum reductive current density of $55\text{ A}\cdot\text{m}^{-2}$ at point **b'**. Inhibition of Co deposition continues for the remainder of the forward sweep. During the beginning of the reverse sweep, the reductive current *increases*. This can be explained as follows: as H_2 evolution decreases from -0.925 to -0.700 V vs. SCE, the coverage of $Zn(OH)_2$ decreases. This increases the deposition of cobalt as more surface area is available for deposition. Deposition of cobalt decreases as the potential approaches the reversible potential of cobalt.
- c'**. Cobalt dissolves to form Co^{2+} .

Comparing these findings with those obtained in Figure 6.2, it can be seen that:

1. Neither the potential at which Co plating begins (-0.800 V vs. SCE) nor the potential at which its plating is inhibited (-0.850 V vs. SCE) is affected by a change in bulk pH.
2. At a pH of 4, during the reverse sweep, the reductive current density *increases* whereas at pH 5 it *decreases*. Thus a change in bulk pH resulted in a change in interfacial pH that shifted it from values higher than 9 to values near 5.5 (point **c'**), presumably by breakdown of the inhibitory layer.
3. At a pH of 4, the voltage for Co dissolution is close to that measured without Zn (see Equation 5.24). This shows that at pH 4, $Zn(OH)_2$ did not precipitate to the same extent as at pH 5: at pH 4, the bulk pH is low enough to break down the $Zn(OH)_2$ barrier.

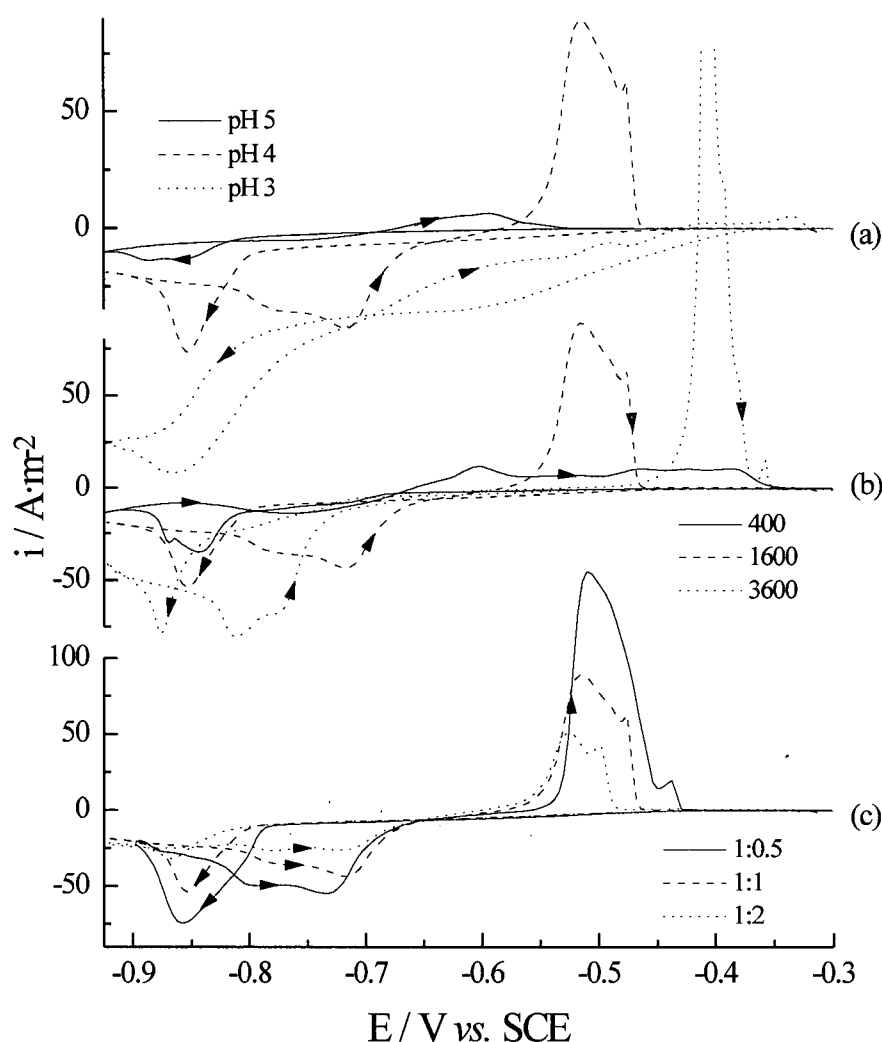


Figure 6.5 Cyclic voltammograms showing the effects of pH, zinc concentration and rotation speed. Base conditions: 0.01 mol/L CoSO_4 , 0.01 mol/L ZnSO_4 , 2.4 mol/L MgSO_4 , pH 4, 1600 RPM, 75°C . Variations from these conditions noted on graph: (a) variations in pH, (b) variations in RPM, (c) variations in Co:Zn molar ratio.

Voltammograms obtained under several experimental conditions are presented in Figure 6.5. In Figure 6.5a, it can be seen that by lowering the pH to 3, H_2 evolution begins at potential values as high as -0.300 V vs. SCE and continues until -0.800 V vs. SCE according to the following reaction:



The current density plateau at -0.800 V vs. SCE represents the limiting current of this reaction. At -0.800 V vs. SCE , water decomposition begins according to the following reaction:



This reaction continues for the remainder of the forward sweep and the beginning of the reverse sweep. The magnitude of the current density increases during the reverse sweep and the only indication of cobalt deposition is a small peak at -0.500 V vs. SCE which indicates cobalt dissolution. As the magnitude of this peak is small in relation to the dissolution peak at pH 4, it can be assumed that very little cobalt deposited.

Thus the effect of pH on the deposition of Co can be summarized as follows:

1. At pH 5, interfacial pH can reach values higher than 8, which leads to massive precipitation of Zn(OH)_2 .
2. At pH 3, H_2 is the dominant reaction; Co deposition is insignificant.
3. At pH 4, the interfacial pH is low enough to overcome the precipitation of Zn(OH)_2 , but is not low enough to promote H_2 evolution over Co deposition. At pH 4, Co deposition reaches a maximum.

Figure 6.5b shows how changes in mass transfer (change in RPM) affect the deposition of cobalt. Voltammograms for each rotation speed follow a similar pattern. The higher the RPM, the higher the reductive current. Co deposition starts near -0.800 V vs. SCE and is inhibited near -0.850 V vs. SCE. At 1600 and 3600 RPM, on the reverse sweep, deposition is inhibited until -0.800 V vs. SCE, at which point inhibition is reduced while cobalt deposition is increased. At 400 RPM, inhibition is present for all potentials during the reverse sweep. Dissolution peaks occur at more noble potentials as rotation speed is increased.

The voltammogram at pH 4 and a rotation speed of 400 RPM is similar to the voltammogram at pH 5 and 1600 RPM. Both show inhibition of Co deposition for all potentials during the reverse sweep and dissolution of cobalt beginning at -0.700 V vs. SCE. At pH 4 and 400 RPM, dissolution takes place between -0.700 and -0.350 V vs. SCE. For cobalt dissolution to begin at -0.700 V vs. SCE, the pH at the interface has to be higher than 8 (see Figure 6.3). Thus it appears that oxidation of Co to Co(OH)_2 occurs at 400 RPM.

As seen in Figure 6.5b, at 3600 RPM, inhibition of Co deposition occurs at a lower voltage than at 1600 or 400 RPM. Also the highest reductive current density was obtained at 3600 RPM. Thus it can be assumed that as the RPM is increased, the interfacial pH decreases, Zn(OH)_2 precipitation occurs at more negative potentials and Co deposition is enhanced.

Although it appears that at 3600 RPM cobalt dissolves at a more noble potential than at 1600 RPM, the potential where cobalt begins to dissolve is the same for both rotation speeds.

Voltammogram changes as a function of Co:Zn molar ratios are shown in Figure 6.5c. The potential at which Co starts to deposit decreases as the Zn concentration increases. Correspondingly, as the concentration of Zn increases, the maximum current density of Co deposition decreases. This shows that the concentration of Zn has a dominant effect on the plating of Co. Because the potential of the onset of inhibition and of the reversal of inhibition does not change, it can be concluded that the change in Zn concentration does not greatly affect the inhibition of Co by the precipitation of Zn(OH)_2 . The increase in inhibition with increased Zn concentration is likely caused by the increase in coverage of adsorbed zinc on the electrode. As the concentration of zinc only changes by a factor of 2, the onset of the precipitation of Zn(OH)_2 should not change dramatically.

Table 6.1 Ratio of anodic to cathodic charge for voltammograms in Figure 6.5.

Condition	Q_d/Q_c (%)
No zinc present	90
pH 5	13
pH 4	37
pH 3	0.5
Co:Zn = 1:0.5	52
Co:Zn = 1:2	18
400 RPM	34
3600 RPM	47

To calculate the percentage of anodic charge to cathodic charge, the voltammograms in Figure 6.5 were integrated with time for negative and positive current. These values are tabulated in Table 6.1. These values give the percentage of reduced species that are at the surface of the electrode for oxidation. Since, in the potential range studied, the only species which will be present at the electrode surface which can be oxidized is cobalt metal, these ratios represent the percentage of charge reporting to cobalt deposition. The balance of the charge is assumed to be hydrogen evolution.

Investigating Table 6.1, it can be seen that the results correlate with what has previously been discussed. With no zinc present, cobalt deposition accounts for 90% of the charge passed, when 0.01 mol/L of zinc is added to the solution, this ratio changes to less than 50%. The effect

of pH is clearly observed, with the charge associated with the deposition of cobalt reaching a low of 0.5 % at pH 3. Gains in the percentage of charge going to cobalt deposition can be obtained by increasing the rotation speed or lowering the concentration of zinc. The best charge efficiency (52%) was obtained at the lowest zinc level (Co:Zn = 1:0.5).

6.2.2.2 0.1 mV/s Cyclic Voltammograms

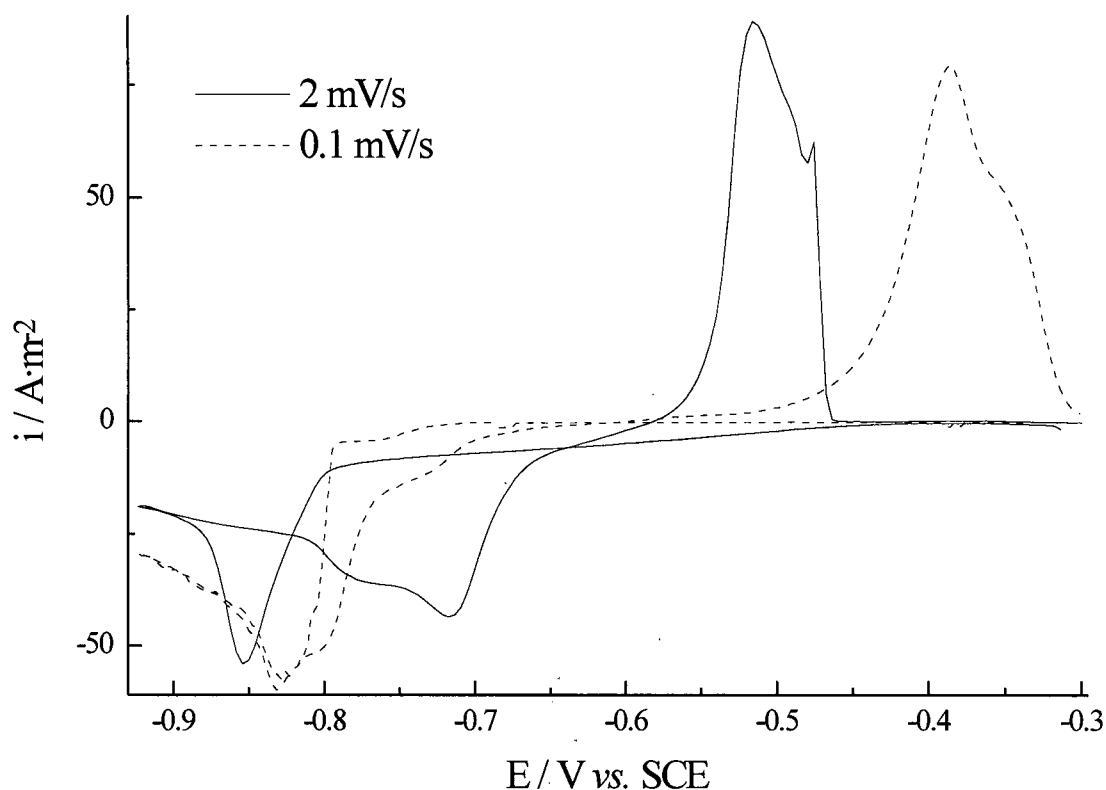


Figure 6.6 Voltammograms at different sweep rates. Conditions: 0.01 mol/L Co, 0.01 mol/L Zn, 2.4 mol/L MgSO_4 , 75°C, 1600 RPM.

As the cyclic voltammograms obtained in the previous section were not at steady-state at all potentials during the tests, cyclic voltammograms were obtained at a lower sweep rate to approximate steady-state behavior. The voltammogram obtained at pH 4 and 1600 RPM in the previous section is compared to a voltammogram under the same conditions as for the previous section, but at a sweep rate of 0.1 mV/s in Figure 6.6.

The voltammogram at a sweep rate of 0.1 mV/s shows that at a sufficiently low sweep rate, near steady-state behavior can be obtained. This voltammogram shows a sharper nucleation overpotential than at 2 mV/s as would be expected at a lower sweep rate. Also, inhibition occurs

~20 mV more positively at the lower sweep rate. Again this is a function of the lower sweep rate. At a higher sweep rate, the precipitation process of Zn(OH)_2 lags behind the potential as the potential is decreasing faster than the precipitation process is proceeding. The reverse sweep at 0.1 mV/s mirrors the forward sweep, with the exception that the nucleation overpotential is obviously not present. The redissolution of the Zn(OH)_2 precipitate that is observed at 2 mV/s is not present; however, there does appear to be a small peak at -0.720 V vs. SCE during the reverse sweep at 0.1 mV/s which would indicate breakdown of the inhibitory layer.

The peak of dissolution occurs at a more positive potential at 0.1 mV/s than for 2 mV/s, again due to the more steady-state nature of the slower sweep. Note that the potentials where cobalt *begins* dissolving, the "cross-over" potential, is the same for both sweep rates at -0.640 V vs. SCE.

6.2.2.3 Deposition on a Pre-Plated Cathode

To ascertain that a platinum substrate has no effect on the deposition of cobalt from solutions containing zinc sulfate, tests were performed where cobalt was pre-plated on the platinum surface and the cyclic voltammogram was reproduced. Figure 6.7 compares voltammograms on a platinum and a pre-plated cobalt substrate for the same conditions.

This voltammogram shows that, while there are some differences between the voltammogram obtained on the two different surfaces, the general phenomenon observed are the same. During the forward sweep, cobalt deposition follows the same current-potential line for both substrates and inhibition occurs close to the same potential. At the end of the forward sweep, the current for the pre-plated substrate is slightly higher than for the pre-plated substrate. On the reverse sweep, the current decreases due to the breakdown of the inhibitory layer for both substrates; however, the breakdown occurs at more negative potentials for the pre-plated substrate. Dissolution occurs at the same potential.

Based on this figure, it can be concluded that the deposition-inhibition mechanism is not greatly affected by the use of a platinum rather than a cobalt substrate. The differences that are observed can be attributed to the different surface area between the platinum substrate and the substrate pre-plated with cobalt. Also no nucleation potential¹ is observed with the pre-plated cathode.

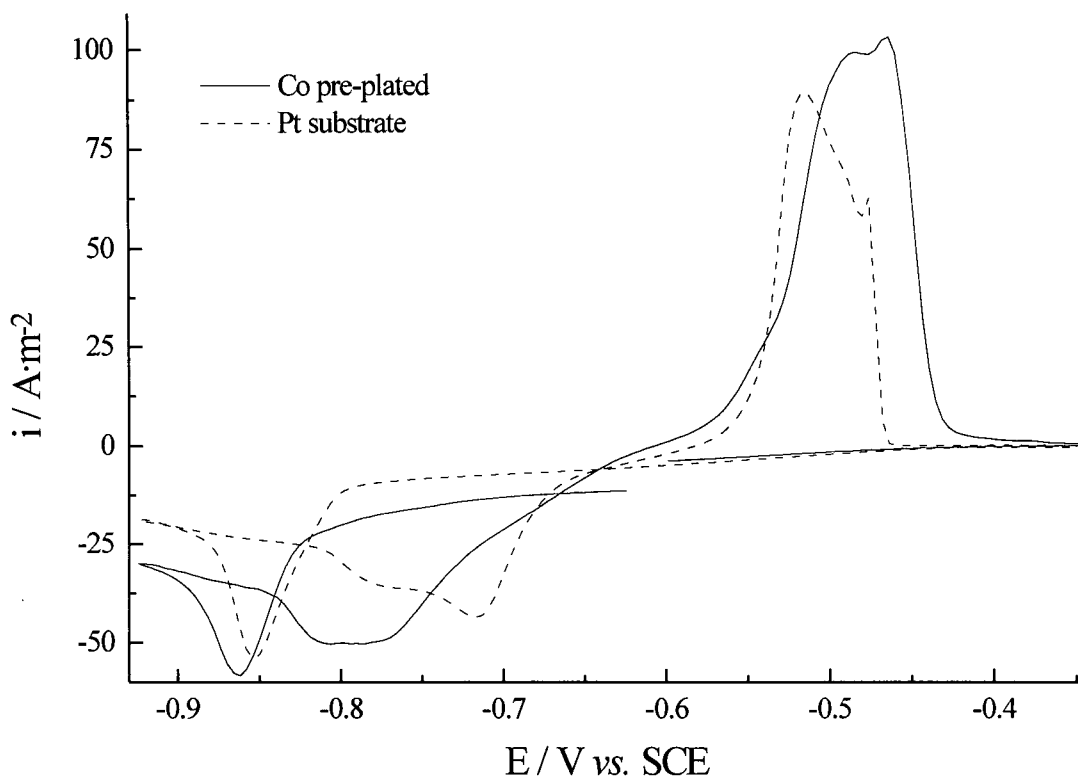


Figure 6.7 Cyclic voltammograms showing the effect of pre-plating cobalt. Conditions: 0.01 mol/L Co, 0.01 mol/L Zn, 2.4 mol/L MgSO_4 , 75°C, 1600 RPM.

6.2.2.4 Deposition from Perchlorate Solutions

To ascertain that the sulfate ion is not responsible for the inhibition of cobalt by zinc, tests were performed in a perchlorate medium. Figure 6.8 shows cyclic voltammograms for solutions with and without zinc present in a perchlorate medium.

The voltammogram for the solution without zinc present is not entirely visible in the figure due to scale limitations. The deposition of cobalt without zinc reached a maximum cathodic current density of $200 \text{ A}\cdot\text{m}^{-2}$ and a maximum anodic current density of $140 \text{ A}\cdot\text{m}^{-2}$. Upon the addition of only 0.05 mol/L $\text{Zn}(\text{ClO}_4)_2$, the voltammogram changes dramatically.

The nucleation overpotential of cobalt is increased by approximately 60 mV by the addition of zinc, deposition begins, but is almost immediately inhibited, reaching a maximum reductive current density of $5.5 \text{ A}\cdot\text{m}^{-2}$ at -0.770 V vs. SCE . At potentials below this value and during the reverse sweep, deposition of cobalt is inhibited. Note that there is no dissolution peak

for cobalt. Cobalt dissolves at potentials greater than -0.5 V vs. SCE over a wide potential region.

This figure shows that the inhibition of cobalt by zinc is greater in perchlorate solutions than in sulfate solutions. The increase in inhibition in these solutions is likely due to the increased activity of zinc in perchlorate solutions, thus even at a lower concentration of zinc, the activity will be higher in these solutions than in sulfate solutions.

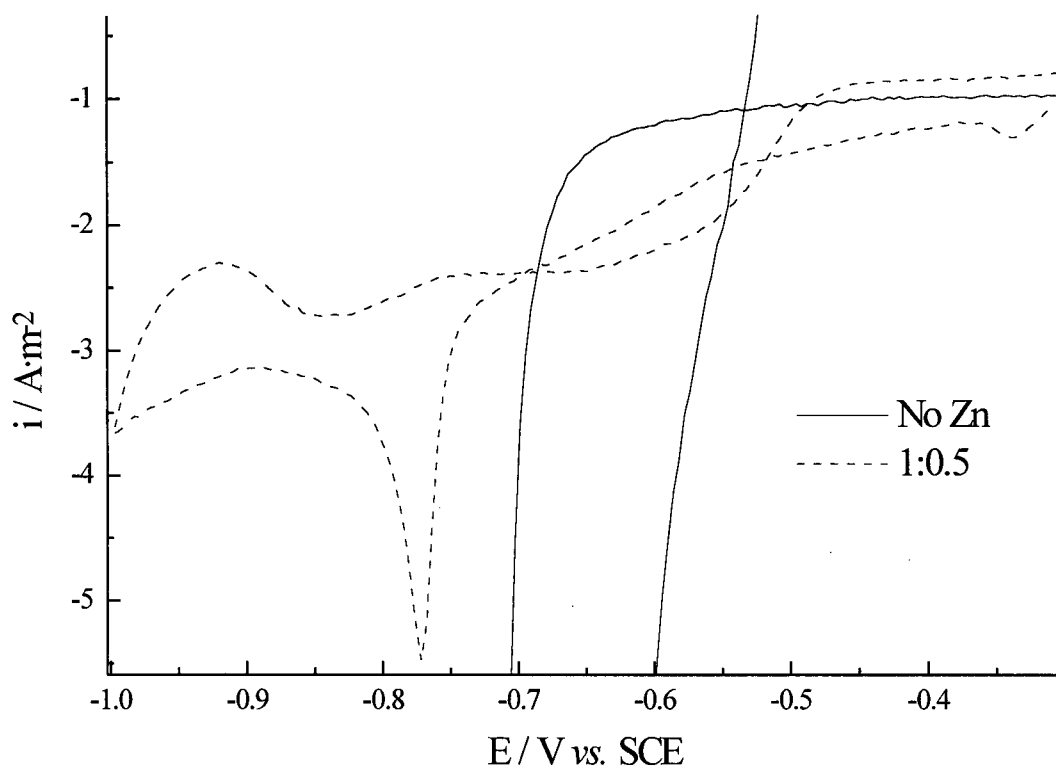


Figure 6.8 Cyclic voltammograms in perchlorate solutions. Conditions: 0.01 mol/L $\text{Co}(\text{ClO}_4)_2$, 0.5 mol/L NaClO_4 , 75°C , 2 mV/s, 1600 RPM, ratio refers to moles cobalt to zinc (zinc added as $\text{Zn}(\text{ClO}_4)_2$).

6.2.3 Galvanodynamic Tests

Galvanodynamic tests were performed for comparison purposes with the results obtained in the previous section using potentiodynamic tests. Experiments in which the current density is controlled can give different information from experiments in which the potential is controlled. For example, if there are different processes that occur at the same potential, but at different current densities, only galvanically controlled experiments will show both processes. Equivocally, if there are processes that occur at different potentials, but at the same current

density, as observed in the previous section, potentially controlled experiments are necessary. Only by performing both types of experiments can characterization of the system be completed.

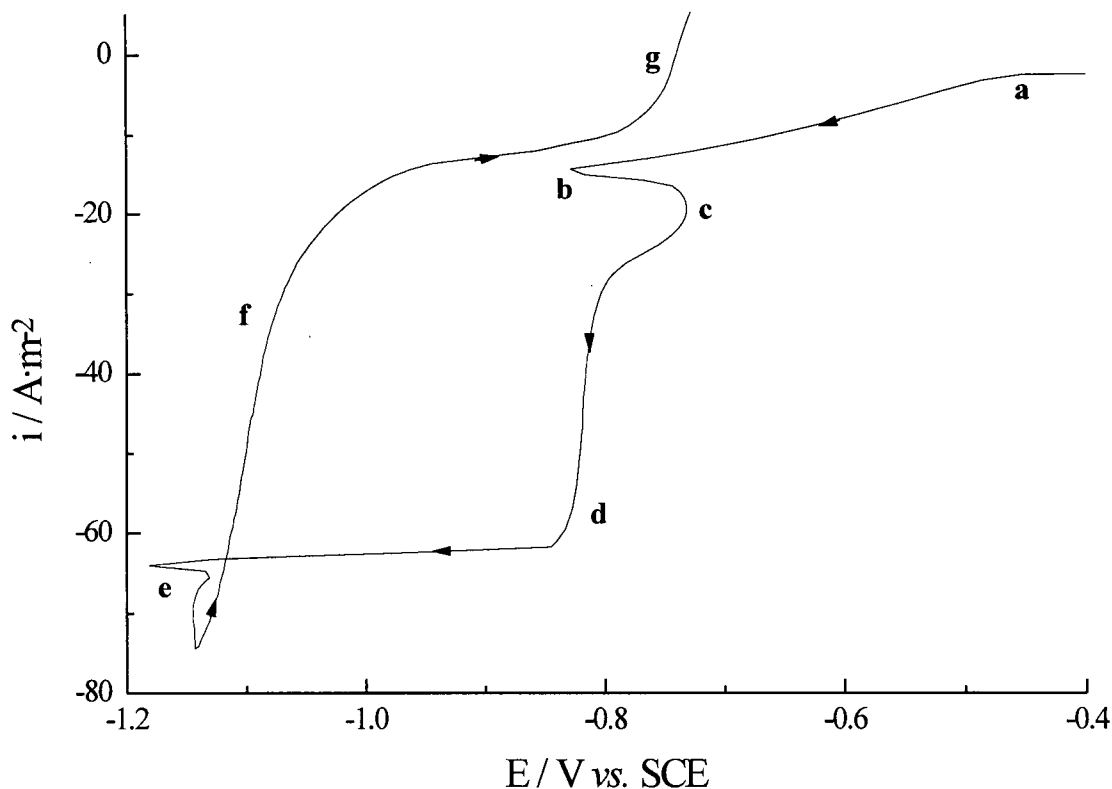


Figure 6.9 Galvanodynamic sweep from 0 to -75 to $75 \text{ A}\cdot\text{m}^{-2}$. Sweep rate $0.2 \text{ A}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$. Conditions: $0.01 \text{ mol/L CoSO}_4$, $0.01 \text{ mol/L ZnSO}_4$, 2.4 mol/L MgSO_4 , pH 4, 1600 RPM, 75°C .

Figure 6.9 shows a galvanodynamic sweep at $0.2 \text{ A}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ for a solution of the same composition as used for the voltammogram in Figure 6.4. The galvanodynamic sweep can be described by the letters on the figure:

- a.** The potential begins at positive values vs. SCE at a current of $0 \text{ A}\cdot\text{m}^{-2}$. At approximately $3 \text{ A}\cdot\text{m}^{-2}$ the potential moves to -0.370 V vs. SCE and hydrogen evolution begins.
- b.** Cobalt deposition begins. Due to the extra energy needed to overcome the nucleation overpotential, the potential lowers to -0.830 V vs. SCE and then increases as cobalt nuclei are established.
- c.** The first mono layer of cobalt is established and then the potential lowers to -0.820 V vs. SCE where steady-state cobalt deposition continues from $-35 \text{ A}\cdot\text{m}^{-2}$ to $-60 \text{ A}\cdot\text{m}^{-2}$.
- d.** This above region is better called an “unstable steady-state” as at $-60 \text{ A}\cdot\text{m}^{-2}$ the potential jumps to -1.17 V vs. SCE .

- e. Hydrogen evolution due to the breakdown of water predominates. This reaction predominates for the remainder of the forward sweep.
- f. Hydrogen evolution predominates during the reverse sweep.
- g. The deposited cobalt begins to dissolve.

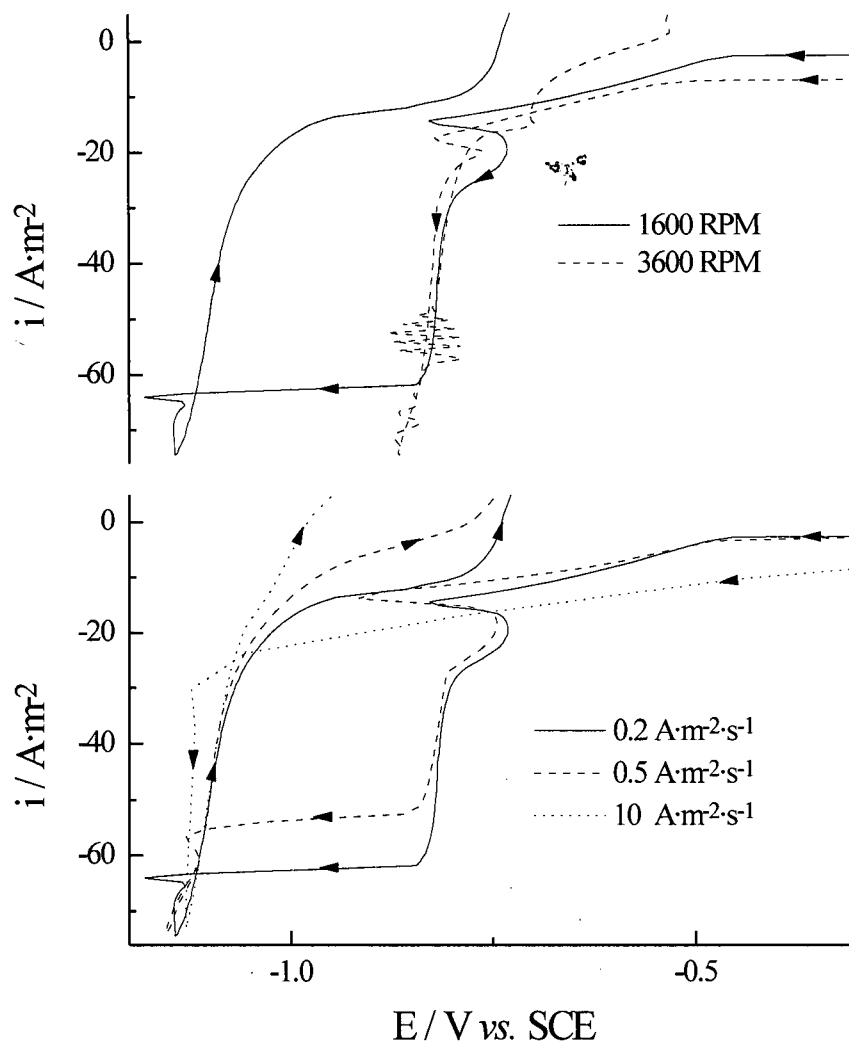


Figure 6.10 Galvanodynamic sweep from 0 to -75 to 75 $\text{A}\cdot\text{m}^{-2}$. Base conditions: Sweep rate 0.2 $\text{A}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, 0.01 mol/L CoSO_4 , 0.01 mol/L ZnSO_4 , 2.4 mol/L MgSO_4 , pH 4, 1600 RPM, 75°C . Variations to these conditions are noted on figure.

Figure 6.10 shows the effects of changing the sweep rate and the rotation speed. This figure shows that when the sweep rate is increased from 0.2 $\text{A}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ to 0.5 $\text{A}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, the nucleation overpotential is larger, and the “unstable steady-state” region is smaller. At 10 $\text{A}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, there is no nucleation of cobalt and the only reaction observed is breakdown of water which predominates starting at -25 $\text{A}\cdot\text{m}^{-2}$ during the forward sweep and continues throughout the

reverse sweep. No cobalt deposition is apparent at this high sweep rate as the sweep rate is too high for the “unstable steady-state” region to be established. These curves demonstrate the unstable nature of the steady state at -0.820 V vs. SCE. Due to the unstable nature of this steady-state, when experiments were performed galvanostatically, where one could assume that the current increases instantaneously to the set value, reductive currents greater than $20 \text{ A}\cdot\text{m}^{-2}$ lead to conditions where hydrogen evolution predominates.

Increasing the rotation speed to 3600 RPM causes the “unstable steady-state” region to increase, incorporating the full current density range tested. The curve at 3600 RPM is similar to the curve at 1600 RPM for the forward sweep; however, on the reverse sweep, the unstable nature of the steady-state is evident. At $-60 \text{ A}\cdot\text{m}^{-2}$, the potential oscillates around the steady-state value observed during the forward sweep, and does not stabilize until $-45 \text{ A}\cdot\text{m}^{-2}$.

The potential region at which the “unstable steady-state” occurs with galvanodynamic control appears to be an important potential region for cobalt deposition in the presence of zinc. This potential, between -0.800 and -0.850 V vs. SCE, is also the potential region where the maximum current density for cobalt deposition was observed during cyclic voltammetry in Section 6.2.2, and during arsenic activated electrochemical removal of cobalt in Section 4.2.3.

6.2.4 Surface Morphology

6.2.4.1 SEM Analysis

SEM photomicrographs taken at various points on the cyclic voltammogram shown in Figure 6.4 can be found in Figure 6.11. Both primary beam SEM photomicrographs and back scattered electron (BSE) images are shown at most of the potentials listed. Where BSE images are not provided, they do not provide any extra information about the surface.

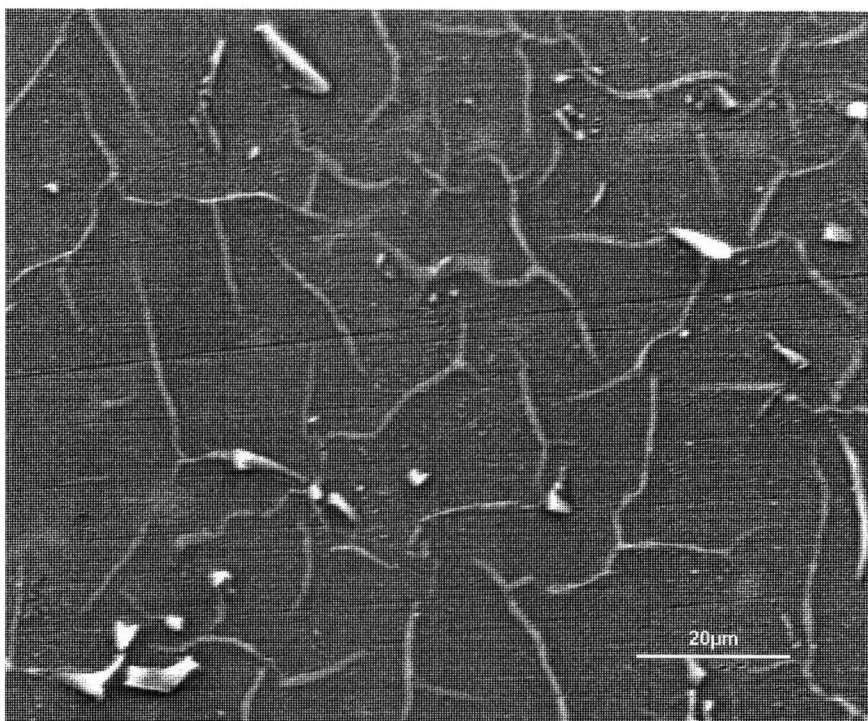
At point I on the voltammogram, the SEM image shows that the cobalt deposit is a thin surface coating on the electrode surface interrupted by white abrasions. There is no crystalline growth evident. An EDX assay of this surface showed that it is almost entirely cobalt, as the concentration of zinc was below the detection limit of the instrument.

Due to the lack of observed crystalline growth, it is assumed that cobalt grows as a thin film on the surface of the electrode, most of the growth occurring in the lateral direction rather than normal to the electrode surface. The white abrasions observed are likely the boundaries

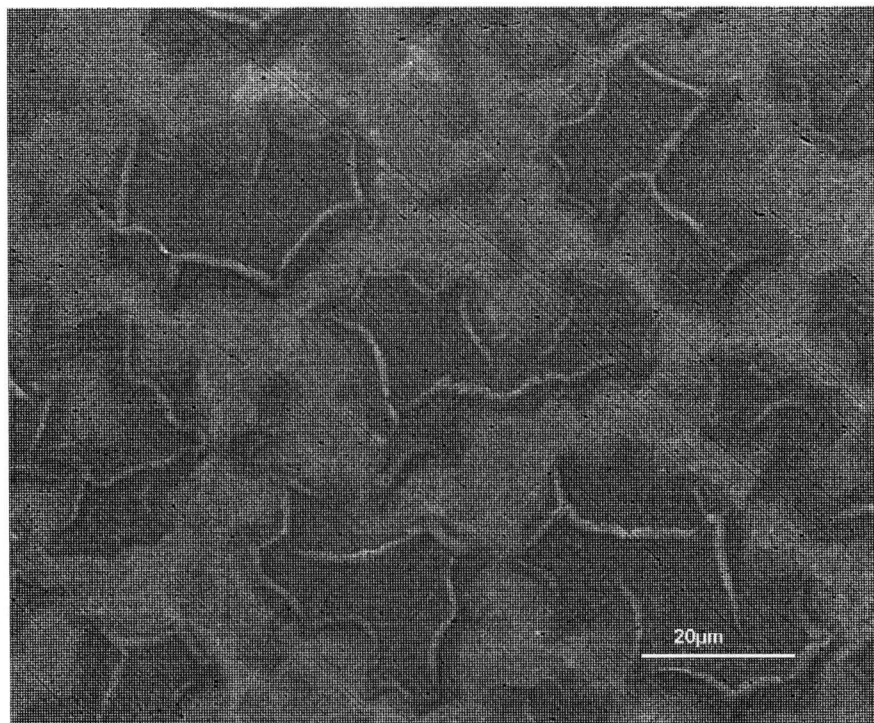
between regions of lateral growth and represent the area where growth fronts from two different regions impinge on each other.

Point II on the voltammogram occurs at the onset of inhibition, just before the deposition of cobalt decreases. The SEM photomicrograph in this case shows that the white abrasions on the surface evident at point I surround islands of a dark surface, which are surrounded by a light area. The deposit is thicker than at point I, as one would expect, as the scratches evident at point I have become less apparent. EDX analysis showed that the light areas are entirely cobalt and the dark areas are a mix of cobalt and zinc. Again no crystalline growth is evident.

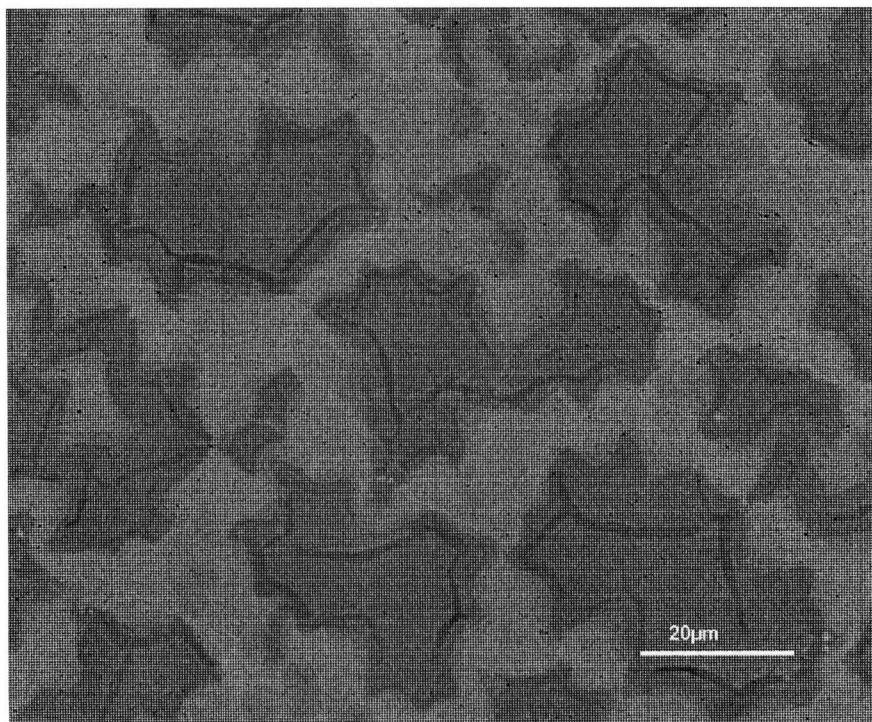
The most useful information about the surface at point II comes from the BSE image. With BSE images, the shade is related to the average atomic number of the atoms present. As the average atomic number of the atoms present decreases, the area becomes darker. Investigating the BSE image at point II it was observed that the light areas in the SEM have a high average atomic number, the dark areas have a lower average atomic number, and the white marks on the SEM have the lowest average atomic number.



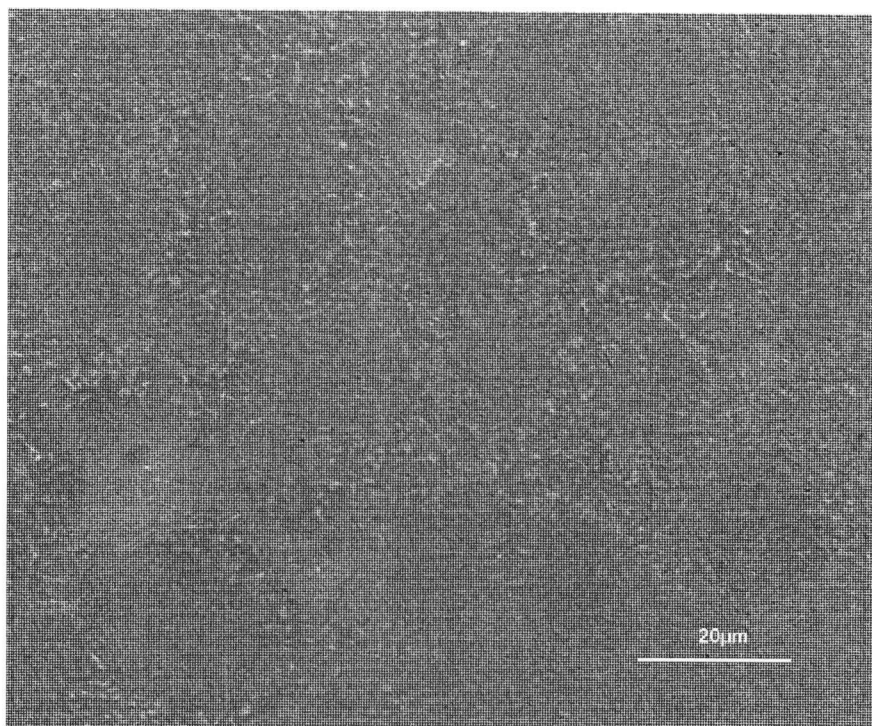
I (SEM)



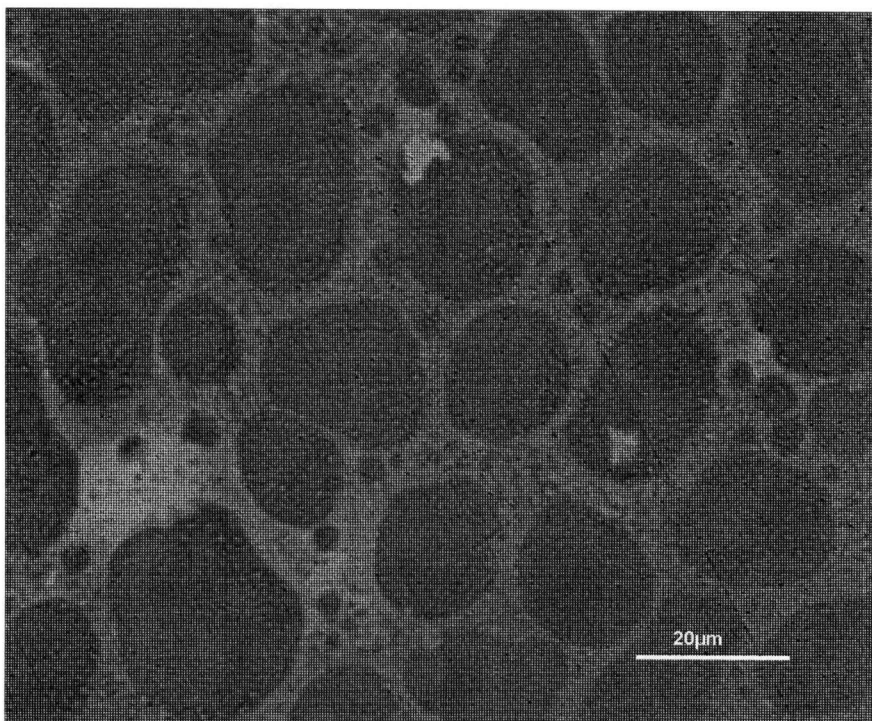
II (SEM)



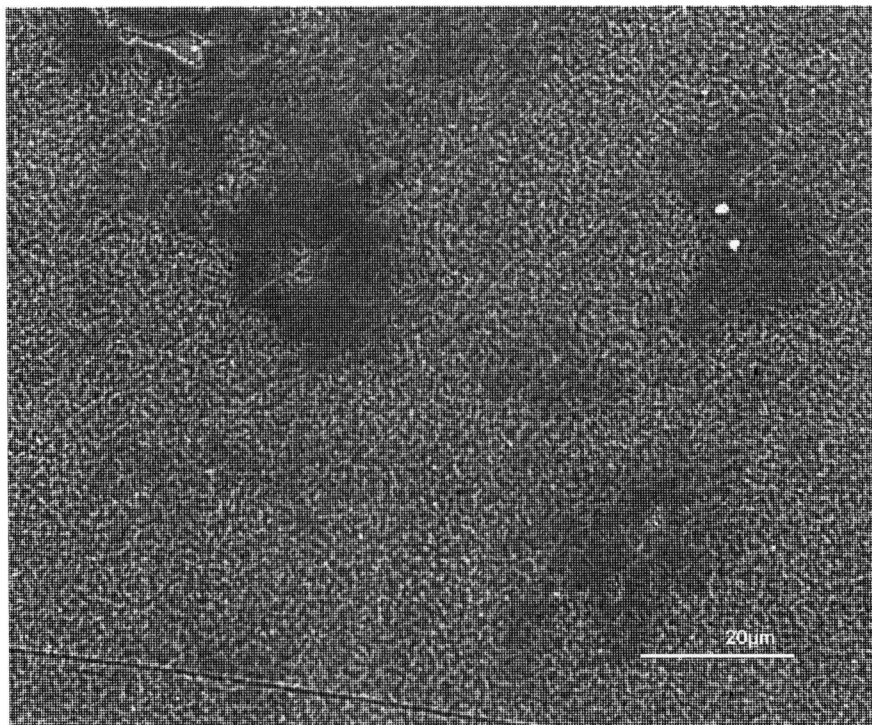
II (BSE)



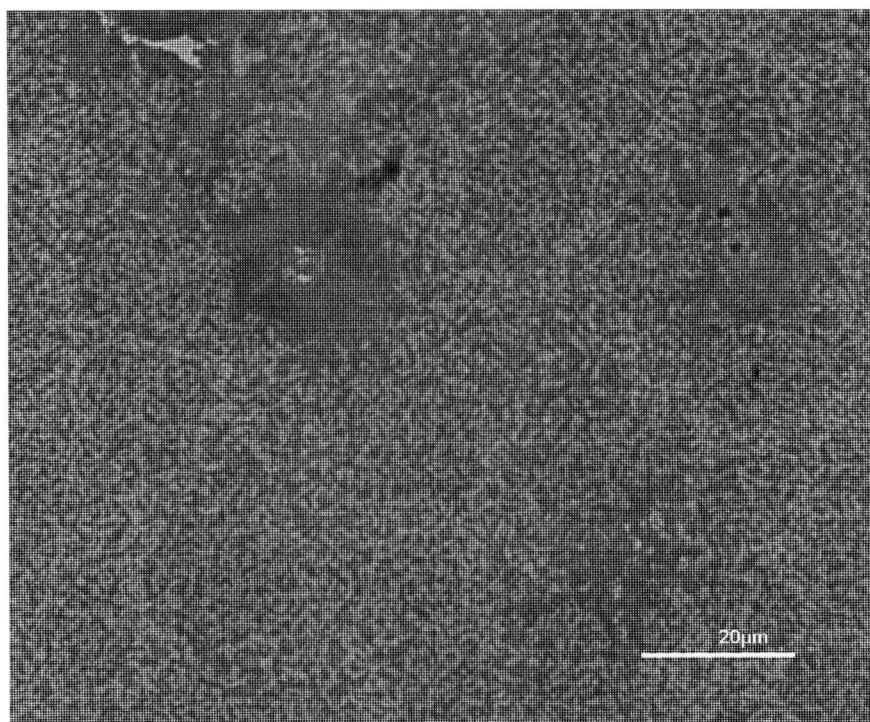
III (SEM)



III (BSE)



IV (SEM)



IV (BSE)

Figure 6.11 SEM and BSE photomicrographs taken at various potentials from Figure 6.4.

Complicating the analysis of the BSE image is that the platinum electrode, which will have the highest average atomic number of all the species present, is the predominant species present. Thus as the thickness of the deposit increases, the average atomic number will decrease. Hence the white marks on the SEM photomicrograph that appear dark on the BSE image are likely due to the thickness of these regions.

Nonetheless it appears as if zinc is precipitating, likely as Zn(OH)_2 in the dark islands, and cobalt growth, while present in the dark regions, is only uninhibited from growth in the light regions. Precipitation of zinc in and around the white marks on the SEM, would be expected as generation of hydrogen will likely occur on defects on the surface – the white marks. This is supported by the BSE as the dark islands and the abrasions on the SEM are dark on the BSE indicating that this region has a lower average atomic number (the average of Zn, Co, O, H, and Pt) than the light regions (the average of Co and Pt).

The SEM at point III on the voltammogram represents the minimum potential investigated and the potential of maximum inhibition. Investigation of the SEM photomicrograph shows a reasonably homogeneous surface. The BSE photomicrograph shows an entirely different situation. The BSE photomicrograph shows dark islands randomly situated in a white matrix. It would appear that the dark islands that were present at point II have grown into distinct circular regions.

Due to the homogeneity of the surface, differences in thickness cannot be considered accountable for the differences observed in the BSE photomicrograph. These differences must be solely the product of differences in average atomic number. As the potential at which this photomicrograph was taken at (-0.925 V vs. SCE) represents maximum inhibition of cobalt deposition, the surface is likely to be entirely covered by the Zn(OH)_2 precipitate. The dark regions that appear on the BSE photomicrograph are where precipitation began. Cobalt deposition was limited to the white regions until precipitation covered the entire electrode surface.

The SEM photomicrograph at point IV was taken at the potential where the current on the reverse sweep reaches the current on the forward sweep. At potentials below this value during the reverse sweep, the reduction of cobalt has increased due to the decrease of inhibition of Zn(OH)_2 . Thus at this potential, inhibition of cobalt should be at a minimum.

The SEM shows that the surface is a homogeneous layer of a porous white layer with a few dark regions randomly distributed throughout. These dark layers are also dark on the BSE photomicrograph and can be considered small patches of Zn(OH)_2 . The area covered by the dark regions has considerably shrunk at this potential as compared to the dark area coverage at points II and III, which is consistent with the reduction in inhibition seen in the voltammogram.

Table 6.2 EDX analysis of SEM photomicrographs in Figure 6.11.

Point	Potential (V vs. SCE)	%Co	%Zn
I	-0.825	100	-
II (light areas)	-0.850	100	-
II (dark areas)	-0.850	75	25
III	-0.925	75	25
IV	-0.650 (on reverse)	80	20

EDX analysis of the photomicrographs appears in Table 6.2. This table clearly shows that the inhibition caused by the precipitation of Zn(OH)_2 begins near -0.850 V vs. SCE and is characterized as the dark areas on the SEM. The weight ratio of 75% Co to 25% Zn appears to be the concentration representing full inhibition as at point III (where the cobalt deposition is fully inhibited) and in the dark areas at point II, this is the assay. At point IV, inhibition of cobalt deposition has decreased thus the percentage of cobalt has increased. It is interesting to note that the percentage of zinc is still significant suggesting that some Zn(OH)_2 has been “trapped” in the surface deposit.

6.2.4.2 TEM Analysis of Deposits

To determine the nature of the cobalt deposit, scanning transmission electron microscopy (STEM) and selected area electron diffraction (SAED) were performed on a cobalt deposit. The deposit was obtained by cycling a 1:1 molar ratio Co:Zn solution from 0.5 to -0.9 V vs. SCE at 1 mV/s. A sweep rate of 1 mV/s was chosen to produce a thicker deposit. To prepare this deposit for the STEM, the deposit was scraped off using a scalpel and placed on a copper grid for analysis.

Figure 6.12 shows the STEM and SAED photomicrographs of the deposit. The STEM image of the deposit is primarily platinum (confirmed by EDX), with small amounts of cobalt

and zinc. SAED analysis of the deposit was performed on the edge of the deposit as indicated in the photomicrograph. This was the only SAED pattern found on the surface of the deposit.

Analysis of the deposit by SAED shows that the dot pattern is a platinum single crystal diffraction pattern that is consistent with a (011) projection of a cubic crystal[70]. Measurement between the {111} poles on the SAED pattern gives a value of 2.3 Å and measurement between the {200} poles gives a value of 2.0 Å. These values are consistent with the FCC orientation of platinum which has values of 2.265 Å and 1.9616 Å for these two distances respectively[71].

Further analysis of the SAED pattern shows that there are two broad rings in the diffraction pattern. The first occurs around the first “ring” of diffraction spots and the second around the second “ring” of diffraction spots. The lack of defined spots in these rings suggests that they are the product of an amorphous deposit. These rings correspond to lattice spacings of 2.0-2.5 Å and 1.1-1.3 Å, which are two regions where cobalt has a strong diffraction pattern[72]. This fact coupled with the flat non-crystalline deposits observed in the previous section suggests that the deposit is micro-crystalline or amorphous.

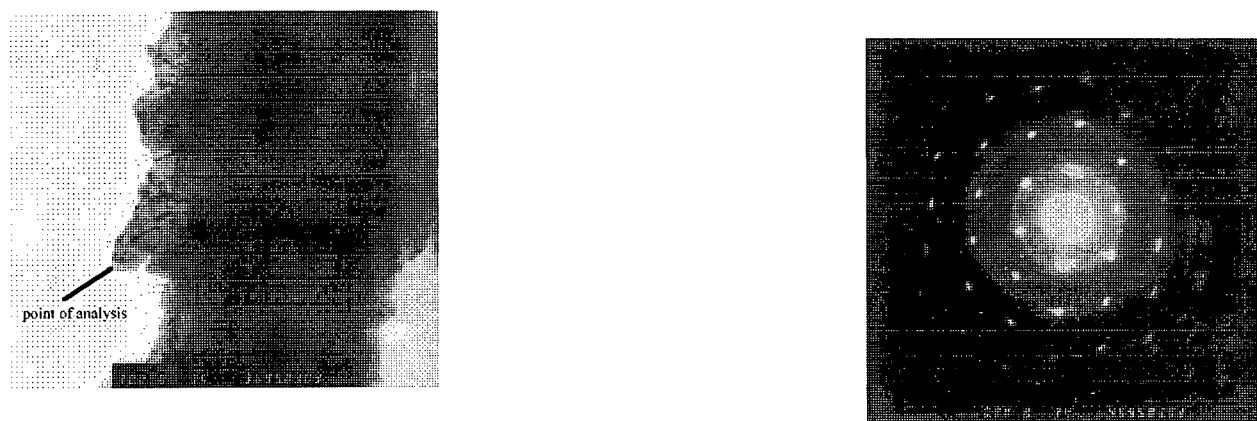


Figure 6.12 STEM and SAED images of deposit taken at -0.9 V vs. SCE. Conditions: 0.01 mol/L Co, 0.01 mol/L Zn 2.4 mol/L MgSO₄, 1600 RPM. Electrode swept from -0.5 V vs. SCE at 1 mV/s..

Micro-crystalline or amorphous deposits arise from conditions where the rate of nucleation is much greater than the rate of growth. For cobalt deposited in the presence of zinc, it is likely that once cobalt has nucleated, further cobalt deposition is inhibited by adsorption of Zn ions or precipitation of Zn(OH)₂. These two factors will limit the growth rate, leading to conditions favorable for micro-crystalline or amorphous deposits.

6.2.5 Partial Current Density

Potentiostatic experiments were performed to determine what percentage of the current density at a particular potential was cobalt deposition and what percentage was hydrogen evolution. Using these values, a chemical model of the interface was developed.

6.2.5.1 Results and Discussion

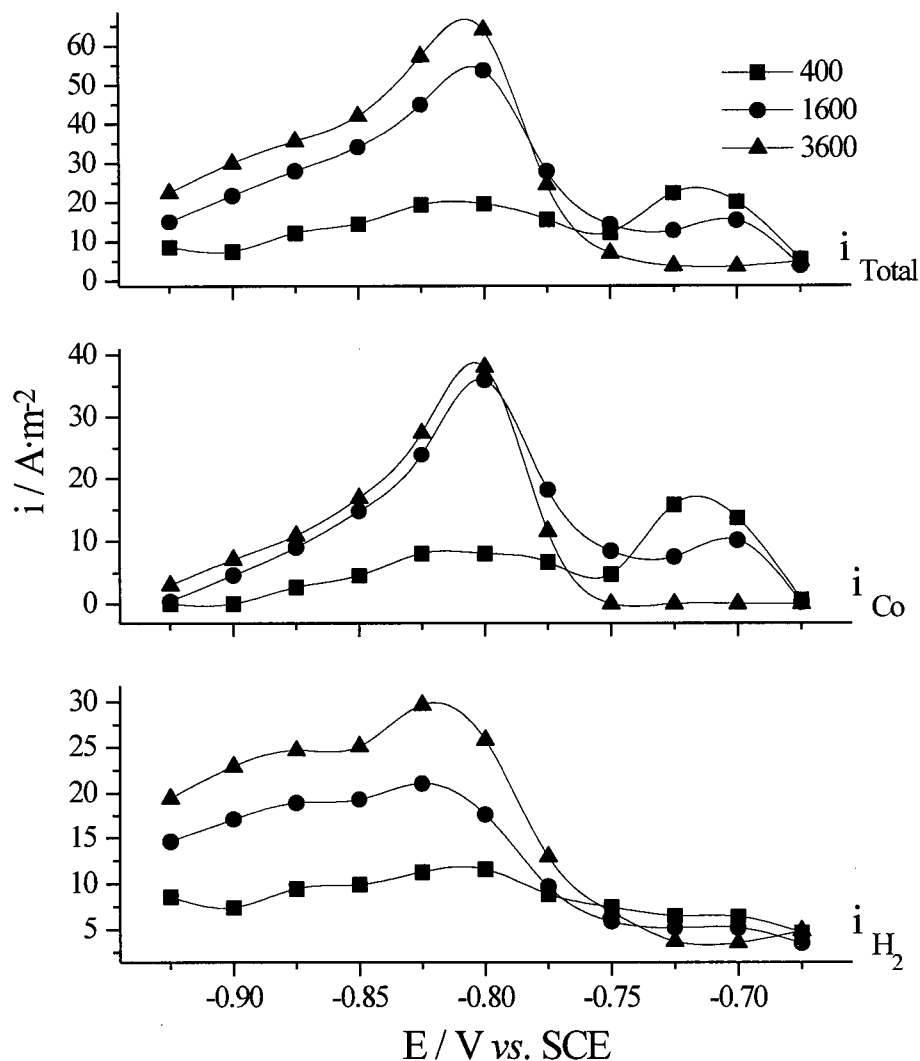


Figure 6.13 Partial current density breakdown after potentiostatic deposition. Conditions: 0.01 mol/L CoSO_4 , 0.01 mol/L ZnSO_4 , 2.4 mol/L MgSO_4 , pH 4, 75°C. Rotation speed as indicated on graph.

Figure 6.13 shows the current density breakdown for potentiostatic deposition at various potentials and at various rotation speeds. The top graph shows the average total current for each potential measured. This graph is characterized by a current peak at -0.710 V vs. SCE, followed

by a larger current peak at -0.800 V vs. SCE. Investigating the cobalt partial current density in the middle graph, it can be seen that both of these peaks are a result of cobalt deposition. The bottom graph, which plots the hydrogen partial current, shows an exponential growth of current with decreasing potential before reaching a limiting current density at -0.825 V vs. SCE. The limiting current density appears to be linearly related to the square root of the rotation speed as is predicted by Levich's equation (see Section 3.2.5).

The maximum current of the first cobalt deposition peak at -0.710 V vs. SCE, is inversely related to the rotation speed of the disk. This peak is terminated at a potential of -0.750 V vs. SCE, which corresponds to the beginning of hydrogen discharge.

The second cobalt deposition peak at -0.800 V vs. SCE is also related to rotation speed. At 400 RPM, the maximum current is low, and at 1600 and 3600 RPM the maximum current for cobalt deposition is approximately the same. This peak is characterized by a steep slope in current indicating increasing cobalt deposition, followed by inhibition at -0.800 V vs. SCE. The inhibition appears to begin near the limiting current for hydrogen discharge as indicated in the bottom graph. Inhibition below -0.8 V vs. SCE is likely caused by the precipitation of zinc hydroxide.

Note that the -0.800 V vs. SCE, the potential where cobalt deposition is at a maximum for potentiostatic deposition, is the same potential that was observed in Section 6.2.3 for the "unstable steady-state". As it appears that is the maximum potential before precipitation of $\text{Zn}(\text{OH})_2$, the precipitation of this species may be responsible for disruption of the steady-state.

Although the partial current density for hydrogen discharge plateaus at potentials below -0.800 V vs. SCE, the evolution of hydrogen has not reached its limiting current density. Examination of the current-potential plot for hydrogen generation (Figure 5.4) shows that at potentials below -0.800 V vs. SCE the discharge of hydrogen will increase due to the breakdown of water. The reason for the hydrogen evolution reaction not increasing and remaining stable is that the surface area available for discharge is continuously decreasing due to the precipitation of zinc hydroxide.

Figure 6.14 shows the apparent partial current density (taken as the 1600 RPM condition from Figure 6.13), the "true" current density related to the surface area available for reaction, and the surface area available for reaction. As the surface area available for reaction is decreasing

due to Zn(OH)_2 precipitation, the ratio of available surface area to the surface area of the Pt disk (A/A°) decreases after -0.800 V vs. SCE, where Zn(OH)_2 begins to deposit. By multiplying the true current density by this area ratio, the observed partial current density of cobalt can be obtained.

Examination of the cobalt partial current density at potentials below -0.800 V vs. SCE under the same conditions also shows this phenomenon. At these potentials, the deposition is increasingly inhibited by Zn(OH)_2 precipitation, leading to a partial current density for cobalt deposition near 0 at -0.925 V vs. SCE.

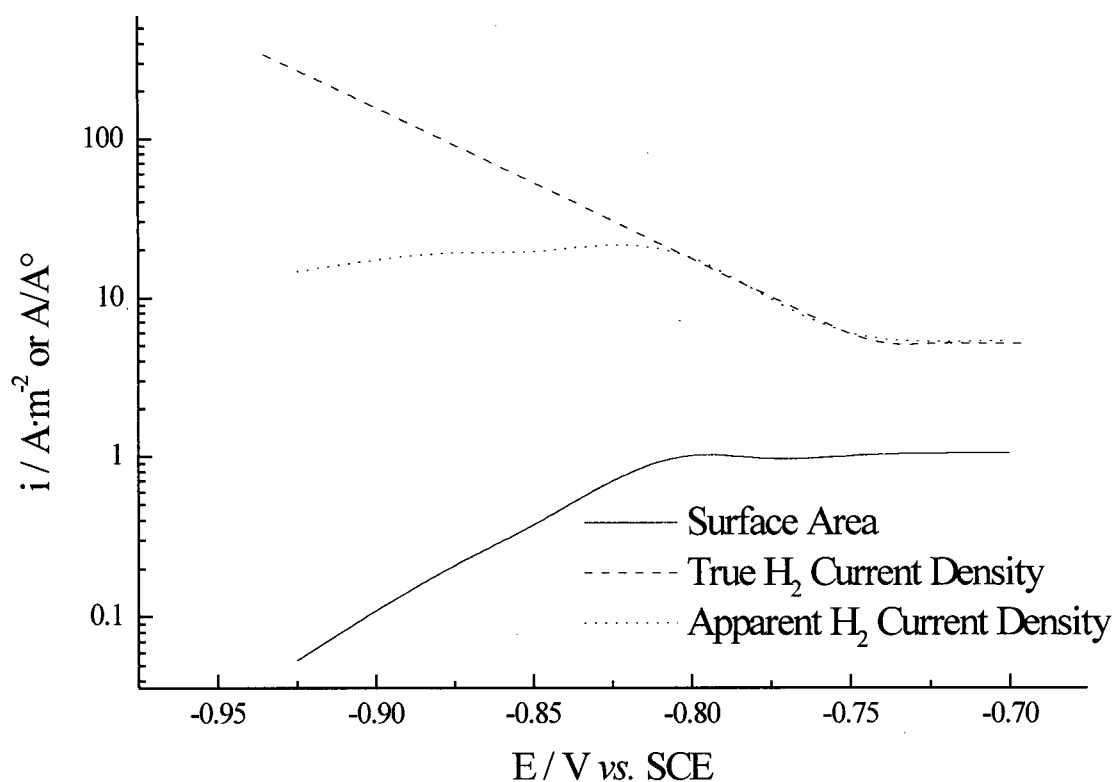


Figure 6.14 Plot showing how the apparent current density for cobalt is related to the true current density and the actual surface area.

Figure 6.15 shows the partial current density breakdown at different potentials and different pH values. This figure shows that at pH 4, the maximum current density for cobalt deposition is much greater than at pH 5. Cobalt deposition at both pH values peaks near -0.800 V vs. SCE and a second peak at potentials above this value is present. At pH 3, the maximum current density for cobalt deposition is approximately the same as it is for pH 4; however, the maximum current density peaks at -0.900 V vs. SCE at this pH. A small current peak is evident

near -0.800 V vs. SCE. It is important to remember that the limiting current density for cobalt deposition under these conditions without zinc present is ~ 85 $\text{A}\cdot\text{m}^{-2}$ (from Figure 5.2), and the maximum current density reached under these conditions with zinc present is less than half of that.

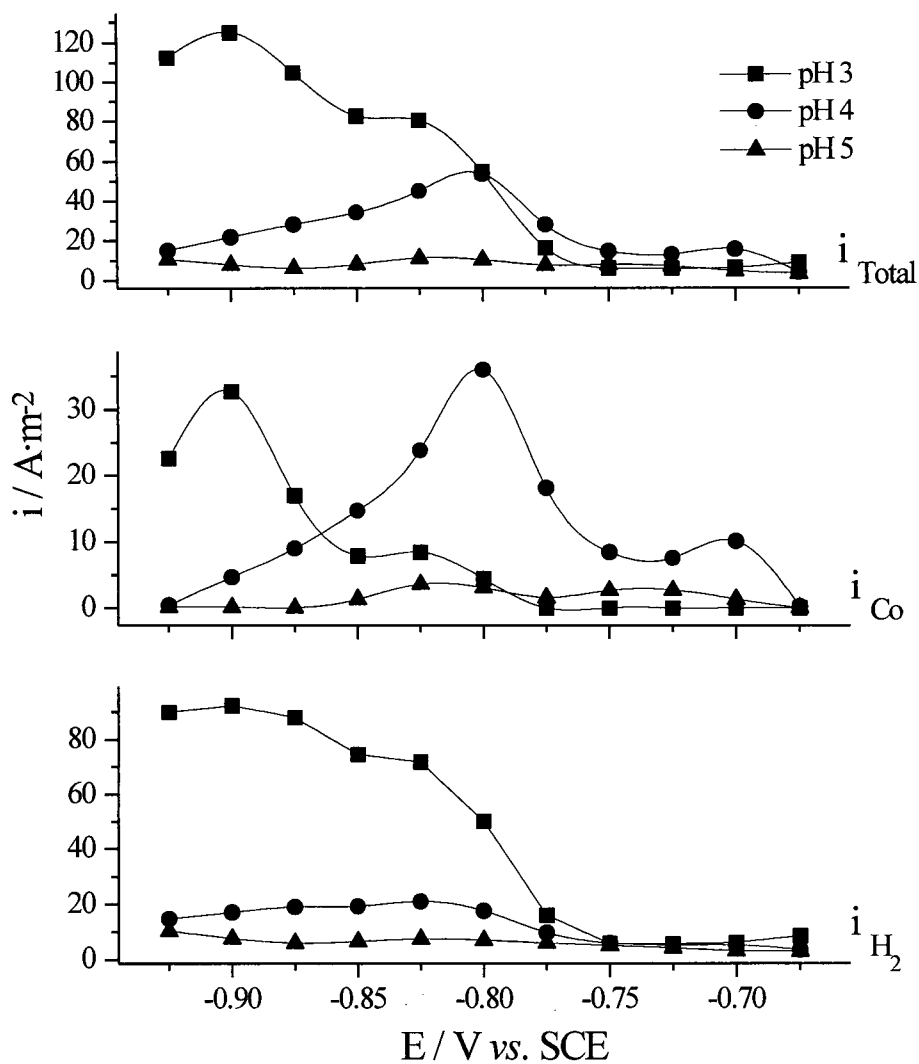


Figure 6.15 Partial current density breakdown after potentiostatic deposition. Conditions: 0.01 mol/L CoSO_4 , 0.01 mol/L ZnSO_4 , 2.4 mol/L MgSO_4 , 1600 RPM, 75°C . pH indicated on graph.

Hydrogen evolution increases with decreasing pH as is expected. For all pH levels, hydrogen evolution appears to begin at -0.750 V vs. SCE.

Figure 6.16 shows how the deposition of cobalt is affected by various concentrations of zinc. Concentrating first on the partial current density due to hydrogen evolution, the inhibition of hydrogen evolution by the precipitation of $\text{Zn}(\text{OH})_2$ can be clearly seen: the maximum partial

current density of hydrogen evolution increases with decreasing zinc concentration. This phenomenon is clearly seen comparing the hydrogen partial current density curves for cobalt to zinc molar ratios of 1:1 and 1:2, and is slightly apparent between cobalt to zinc molar ratios of 1:0.5 and 1:1. This can be explained as follows: The lower the zinc concentration in the bulk, the higher the pH at the interface needs to be to precipitate Zn(OH)_2 and thus a higher rate of hydrogen evolution can occur before the precipitate forms. Hence at a cobalt to zinc molar ratio of 1:0.5, the partial current density of hydrogen generation reaches a maximum of $30 \text{ A}\cdot\text{m}^{-2}$ at -0.850 V vs. SCE . At potentials lower than this value, the surface area is decreased by Zn(OH)_2 precipitation and the apparent partial current density of hydrogen evolution decreases.

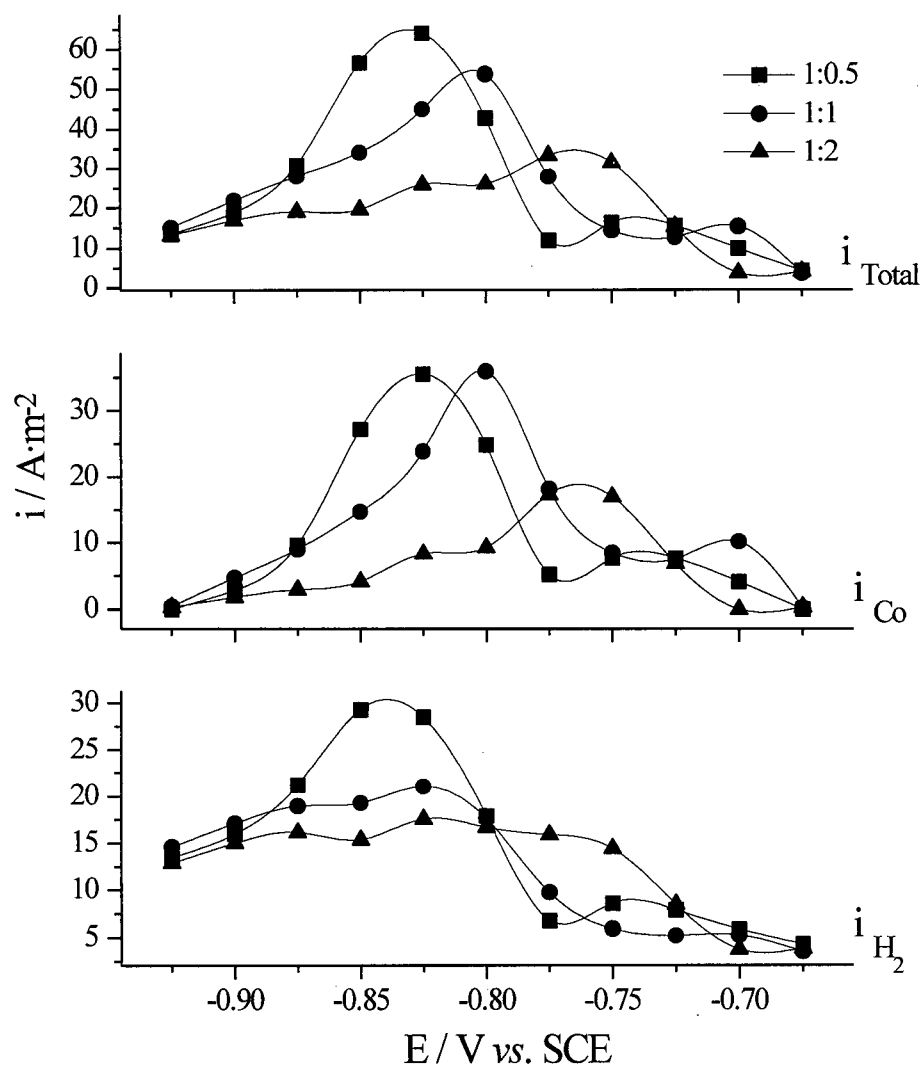


Figure 6.16 Partial current density breakdown after potentiostatic deposition. Conditions: $0.01 \text{ mol/L CoSO}_4$, 2.4 mol/L MgSO_4 , 1600 RPM , $\text{pH } 4$, 75°C . Co:Zn molar ratio indicated on graph.

Investigating the cobalt partial current density curves, it is observed that cobalt deposition occurs at successively lower potentials as the concentration of zinc is decreased. Comparing the partial current density curves for cobalt to zinc molar ratios of 1:1 and 1:0.5, it can be seen that the maximum cobalt partial current density for both levels of zinc is $35 \text{ A}\cdot\text{m}^{-2}$. The current density peak at a cobalt to zinc ratio of 1:0.5 is broader than at a cobalt to zinc ratio of 1:1 as inhibition by precipitation of $\text{Zn}(\text{OH})_2$ will be lower at the lower zinc concentration.

At a cobalt to zinc molar ratio of 1:2 the concentration of zinc is high enough that inhibition occurs $\sim 50 \text{ mV}$ higher and the maximum cobalt partial current density is lower than at other ratios.

It should be remembered that these experiments were operated potentiostatically and the partial current densities shown on the plots represent average values. Figure 6.17 shows how the current density changes with time for the first 5 minutes of deposition for four potentials. For the potentials of -0.675 and -0.775 V vs. SCE , the current density increases for approximately the first minute of deposition. Then the current density decreases until it reaches a steady state value at 5 minutes.

Vargas and Varma[73] in documenting this phenomenon proposed that it is a result of the balance of nucleation and diffusion. After an initial current maxima due to double-layer charging (not shown on graph), the current rises due to the formation of distinct nuclei. After nucleation covers the electrode, nucleation stops, and the current decays due to the formation of a diffusion layer.

At -0.800 V vs. SCE , a decline in current is not observed. At this potential it is likely that precipitation of $\text{Zn}(\text{OH})_2$ holds the electrode from fully nucleating the surface with cobalt, and the steady-state value of the current is a balance between the growth of cobalt and inhibition by $\text{Zn}(\text{OH})_2$.

At -0.925 V vs. SCE , the current density increases in the first minute, but is abruptly halted and then declines to a current density below that for -0.800 V vs. SCE . This is likely due to the precipitation of $\text{Zn}(\text{OH})_2$ halting the nucleation and most of the growth of cobalt. This inhibition is supported by the partial current density for cobalt at this potential, which has a value close to 0.

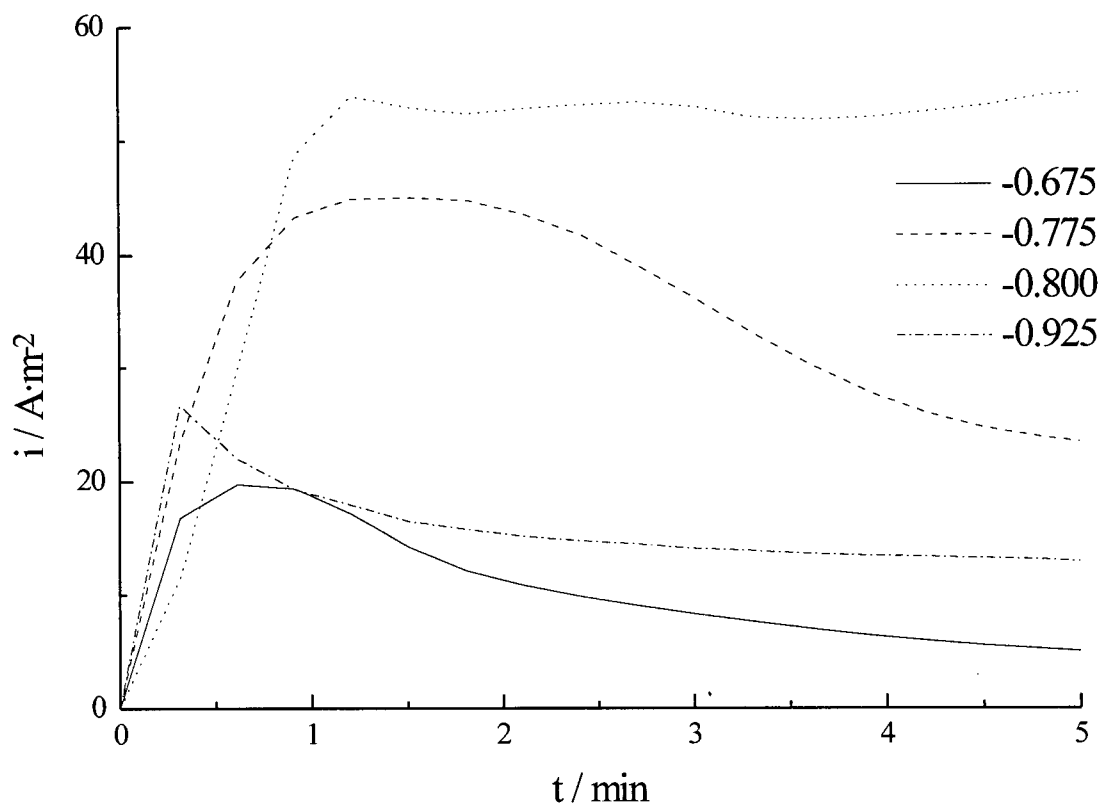


Figure 6.17 Current density as a function of time for potentiostatic deposition at four potentials. Conditions: 0.01 mol/L CoSO_4 , 0.01 mol/L ZnSO_4 , 2.4 mol/L MgSO_4 , pH 4, 75°C, 1600 RPM. Legend refers to potential in V vs. SCE.

6.2.5.2 Model of Inhibition Based on Partial Current Density Curves

Based on the partial current density breakdown from potentiostatic deposition, two current peaks of cobalt deposition are observed. The following factors govern the magnitude of these peaks and the generation of hydrogen:

For the cobalt deposition peak at -0.710 V vs. SCE.

1. The peak is inversely proportional to rotation speed and disappears at a rotation speed of 3600 RPM.
2. Shifts to -0.825 with a change from pH 4 to 3 and becomes lower in magnitude with a change of pH from 4 to 3.
3. Is broader and has a lower magnitude when the concentration of zinc is reduced by $\frac{1}{2}$.
4. Is associated in a region where hydrogen evolution is low.
5. Is terminated when hydrogen evolution increases.

For the cobalt deposition peak at -0.800 V vs. SCE.

1. Does not change upon increasing the rotation speed from 1600 to 3600 RPM and is decreased substantially upon lowering the rotation speed to 400 RPM.
2. Shifts to more negative potentials (-0.900 V vs. SCE) when the pH is changed from 4 to 3.
3. Shifts to more negative potentials as the concentration of zinc is lowered by $\frac{1}{2}$.
4. Is associated with increasing hydrogen evolution and peaks when the current for hydrogen evolution reaches a maximum.

For hydrogen evolution:

1. Hydrogen evolution is characterized by constant current above -0.750 V vs. SCE, followed by exponential increase at potentials below this value. Hydrogen evolution plateaus or decreases below -0.800 V vs. SCE.
2. As the square root of rotation speed increases, the plateau current at -0.800 V vs. SCE increases proportionately.
3. The plateau increases as pH is decreased.
4. At a Co:Zn ratio of 1:2 exponential increase of the current occurs 50 mV higher, at a Co:Zn molar ratio of 1:0.5; hydrogen evolution reaches a peak at -0.830 V vs. SCE before decreasing at potentials below this value.

Based upon the above observations, coupled with phenomena observed during cyclic voltammetry and linear sweep voltammetry, the following model is proposed to explain the results obtained from the partial current density tests.

Deposition of cobalt in the presence of zinc is inhibited by two phenomena. Where hydrogen evolution is low, cobalt is inhibited by an adsorbed zinc species, likely ZnOH^+ . At more negative potentials, as hydrogen evolution increases, the pH at the interface of the electrode increases, leading to precipitation of Zn(OH)_2 . A model of the interface is presented below which illustrates what processes are occurring at the interface and how these processes change as pH, rotation speed, and zinc concentration change.

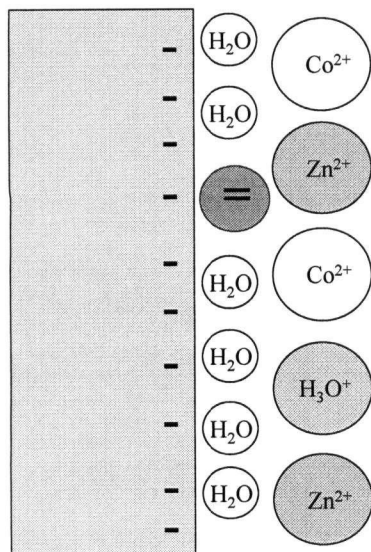


Figure 6.18 Interface at 0 V vs. SCE. (1)

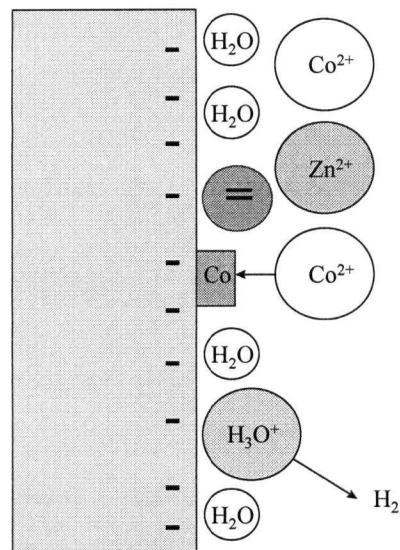
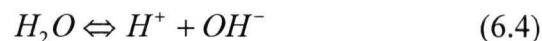


Figure 6.19 Interface at -0.7 V vs. SCE. (2)

1. At potentials greater than the reduction potential of cobalt or hydrogen, the interface is characterized by an adsorbed layer of oriented water molecules (the inner Helmholtz plane), some of which have been replaced by specifically adsorbed anions. Next to this layer is a layer of cations (larger due to associated hydration) made up of Co^{2+} , Zn^{2+} , and H_3O^+ ions (the outer Helmholtz plane).
2. Once the potential of the electrode is below the reduction potential of cobalt and hydrogen, cobalt discharges by reduction of Co^{2+} to Co and hydrogen discharges by the reduction of H^+ (or H_3O^+). In this region cobalt reduction is activation controlled and hydrogen reduction is mass transfer controlled as supported by the partial currents in this region. The concentration of OH^- at the surface of the electrode is controlled by the equilibrium:



This reaction leads to a small concentration of ZnOH^+ and CoOH^+ which will adsorb on the interface; however, this concentration is small. As the rotation speed decreases, or the bulk pH increases, this reaction shifts to the right. This shift as well as an increase in the concentration of zinc will increase adsorption of the mono-hydroxide ions, and reduce the current associated with the reduction of Co^{2+} (as seen in Figure 6.13, 6.14, and 6.15).

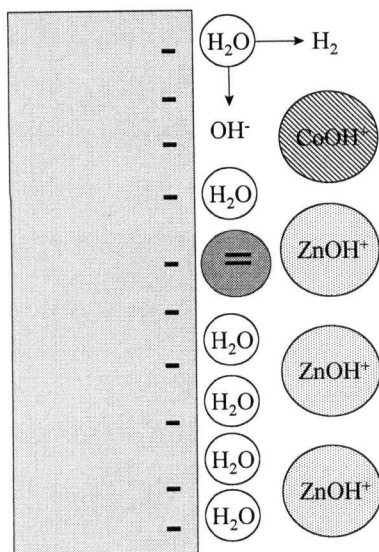


Figure 6.20 Interface at -0.75 V vs. SCE. (3)

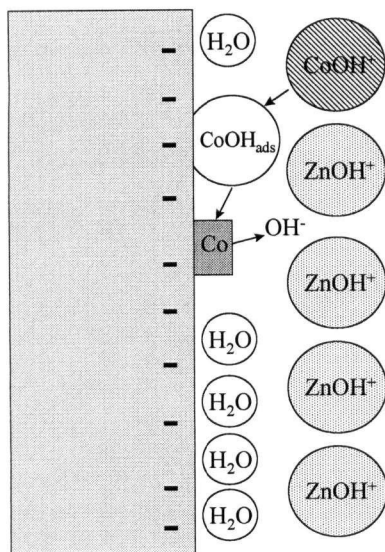


Figure 6.21 Interface at -0.8 V vs. SCE (4).

3. Near -0.750 V vs. SCE (at pH 4), hydrogen begins to discharge through the breakdown of water. This reaction results in an increase in the concentration of OH^- . Thus the concentrations of CoOH^+ and ZnOH^+ increase substantially. These two ions adsorb on the surface of the electrode and hamper any further reduction of cobalt by direct reduction of Co^{2+} . Again this reaction is controlled by increases in the concentration of zinc and pH, as these will shift the following reaction to the right, resulting in this reaction occurring at more positive potentials:



4. Between -0.750 and -0.800 V vs. SCE, cobalt discharges through the CoOH^+ ion. Because the surface of the electrode is covered by ZnOH^+ and CoOH^+ , this reaction occurs at a reduced rate dependent on the coverage of CoOH^+ by the following reaction:

$$i_{co} = k\theta \exp\left(\frac{-\alpha FE}{RT}\right) \quad (6.6)$$

Where θ is the coverage of CoOH^+ . The reduction of Co through the intermediate CoOH^+ is a function of pH. Thus at lower pH values, reduction is shifted to more negative potentials.

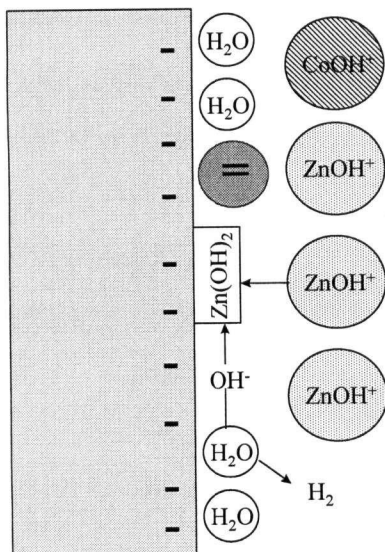


Figure 6.22 Interface at -0.85 V vs. SCE (5).

5. At potentials more negative than -0.800 V vs. SCE (under the base set of conditions), hydrogen evolution increases to the point that the pH at the interface of the electrode is high enough for Zn(OH)_2 to precipitate. The precipitation of this salt on the surface of the electrode inhibits further discharge of cobalt or hydrogen on the sites that it covers. The partial current density of cobalt decreases and the partial current density of hydrogen either decreases, or stays the same - the Tafel-controlled increase in the reduction of water offsetting the decrease in surface area. As neither the reduction of H_2O nor the concentration of Zn^{2+} at these potentials is controlled by mass transfer, changes in mass

transfer do not change the onset or magnitude of this phenomenon (see Figure 6.13). At higher concentrations of zinc, this reaction occurs at more positive potentials (lower concentrations of OH^-). At lower concentrations of zinc, this reaction will occur at more negative potentials and inhibition will not occur as rapidly (as observed in the broadened peak at high zinc concentration in Figure 6.16).

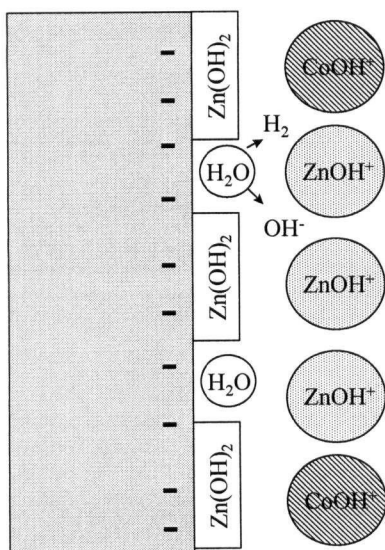


Figure 6.23 Interface at -0.925 V vs. SCE (6).

6. At -0.925 V vs. SCE, the coverage of Zn(OH)_2 is almost complete to the point that reduction of cobalt has been almost eliminated. Hydrogen evolution occurs at a rate just great enough to sustain the creation of Zn(OH)_2 . No further cobalt reduction is expected at potentials below this value until the Zn(OH)_2 layer is reduced to Zn if the potential was decreased.

6.2.6 AC Impedance

AC impedance spectra were obtained for 0.01 mol/L cobalt solutions with and without 0.01 mol/L zinc present. The spectra were obtained over a potential range of -0.75 to -0.925 V vs. SCE, at a rotation speed of 1600 RPM and at a pH of 4. Unfortunately the potentiostat used cannot use feedback ohmic drop compensation when AC impedance tests are being run. Thus, the stated potential represents the potential of the electrode without ohmic drop taken into consideration. Since the ohmic drop can be read off the complex plane impedance diagrams by taking the high frequency intercept of the real axis, the true potential of the electrode can be obtained using this value and the magnitude of the current (see Section 3.2.3).

6.2.6.1 Impedance with Only Cobalt Present

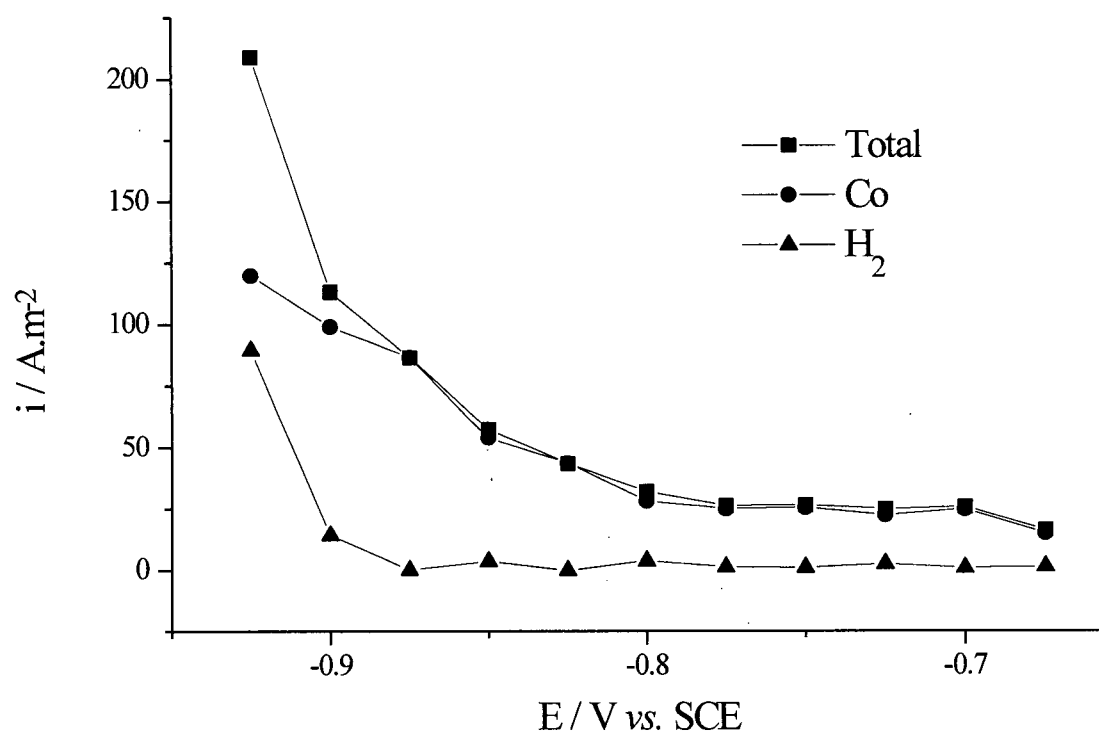


Figure 6.24 Partial current density breakdown after potentiostatic deposition. Conditions: 0.01 mol/L CoSO₄, 2.4 mol/L MgSO₄, 1600 RPM, pH 4, 75°C.

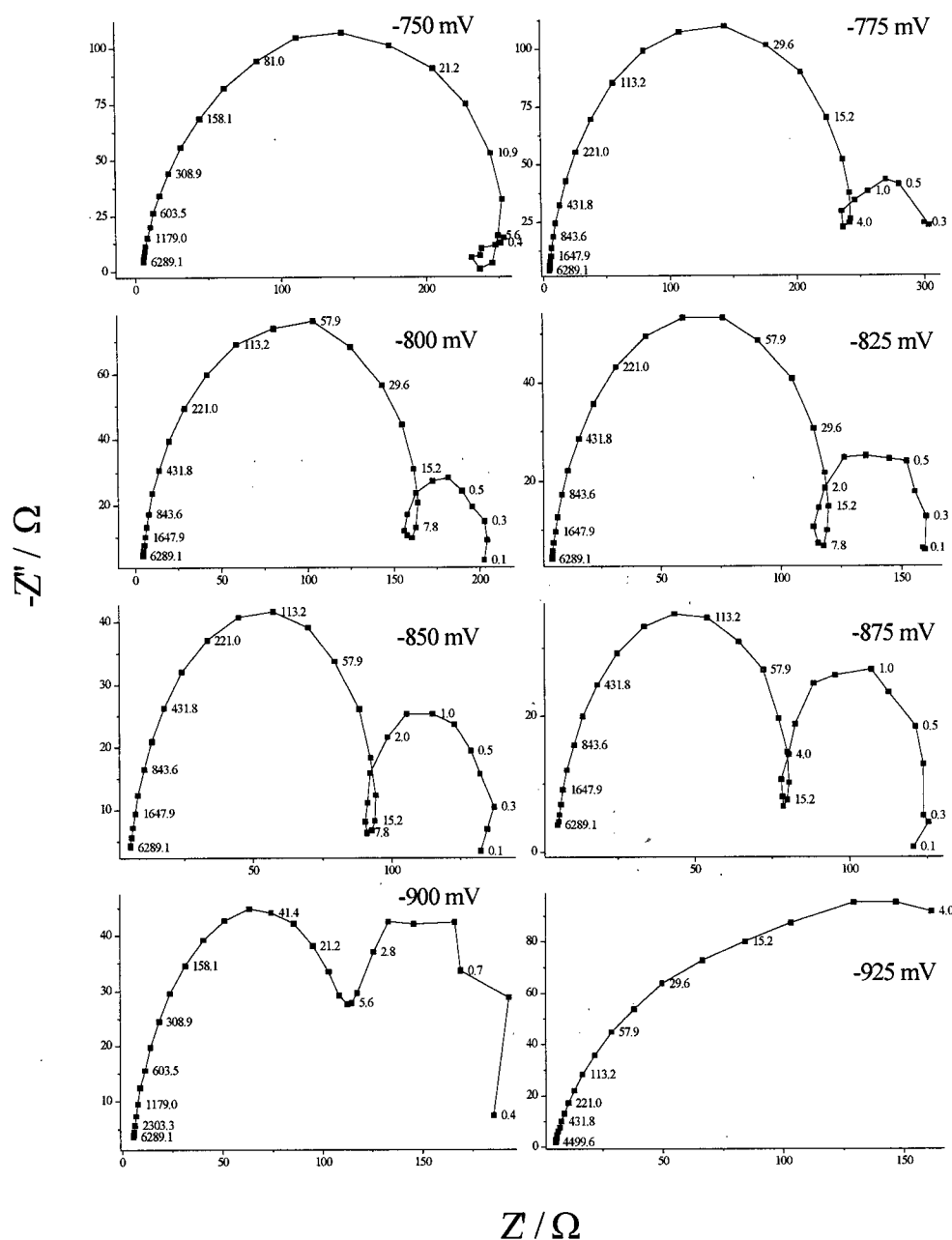


Figure 6.25 Complex plane impedance plots. Conditions: 0.01 mol/L Co, 2.4 mol/L MgSO_4 , 75°C, 1600 RPM. Potential refers to mV vs. SCE.

Figure 6.24 shows the steady state partial current density breakdown for a solution containing cobalt. This curve was obtained by incorporating the same partial current density method used in Section 6.2.5. Note that the partial current density of hydrogen is negligible for potentials greater than -0.85 V vs. SCE, and thus any AC impedance spectra obtained at these potentials can be considered a measurement of the cobalt reduction reaction.

While the partial current density breakdown was held at the set potential for 30 min, and the impedance was obtained by holding the potential at the assigned potential for only 15 minutes, impedance spectra obtained after 30 minutes confirmed that there was no change in the spectra.

Figure 6.25 shows complex plane impedance plots corresponding to various potentials on Figure 6.24. The impedance plots are characterized by two capacitive loops, a low frequency (LF) capacitive loop that does not appear to change in magnitude with potential, and a high frequency (HF) capacitive loop that decreases in magnitude as the potential is increased. Temporarily ignoring the LF capacitive loop, one can compare the impedance spectra with the steady-state curve. As the potential decreases and cobalt deposition increases, the charge transfer resistance (R_{ct}) decreases. This is observed as a decrease in magnitude of the HF capacitive loop. At -0.9 V vs. SCE, hydrogen evolution begins. This is observed as the breakdown of the two loop impedance spectra at potentials at and below -0.9 V vs. SCE.

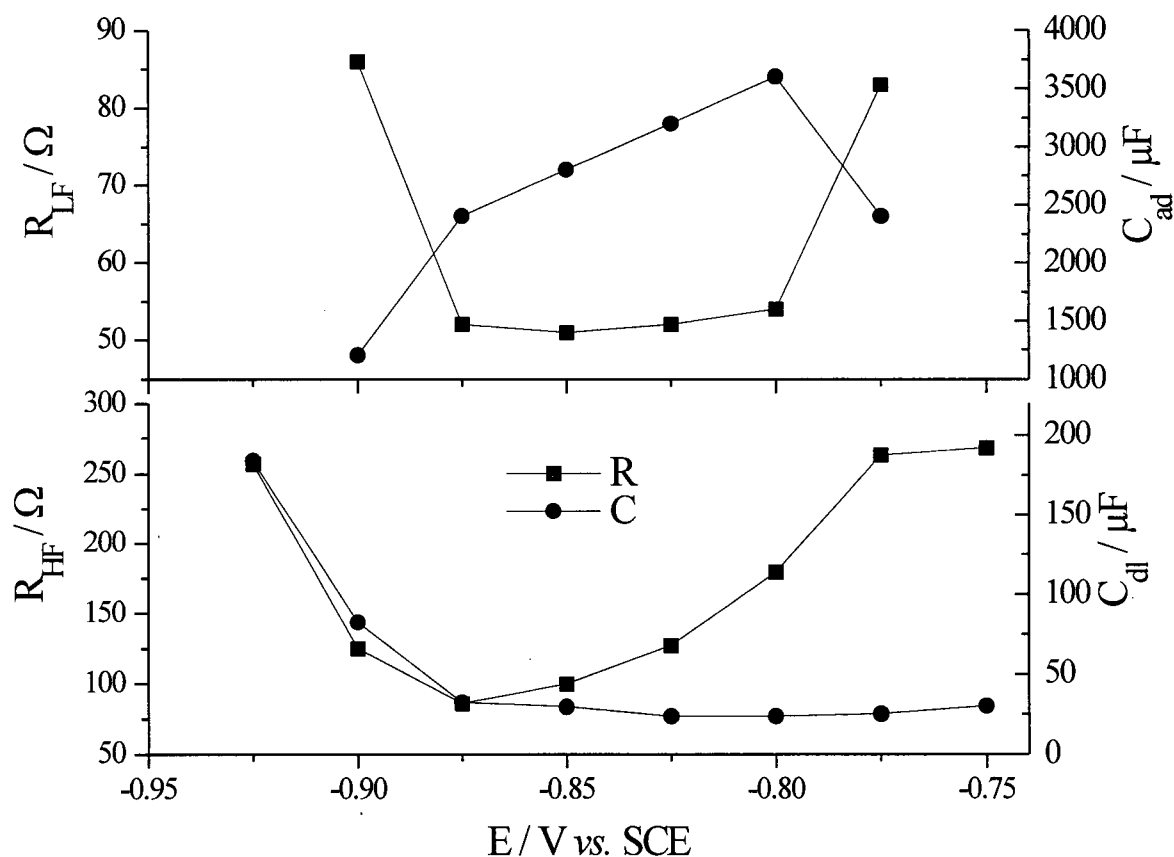


Figure 6.26 Charge transfer resistance and capacitance for high frequency (HF) and low frequency (LF) capacitive loops from Figure 6.25.

Figure 6.26 shows how the charge transfer resistance and the capacitance of the two loops change with potential. The charge transfer resistance of the LF loop remains somewhat consistent at $\sim 50 \Omega$. The capacitance of the LF loop also remains somewhat consistent at $\sim 3000 \mu\text{F}$. This high capacitance value is indicative of an adsorption pseudo-capacitance.

The HF charge transfer resistance decreases until -0.9 V vs. SCE and the capacitance remains constant below this potential at $30 \mu\text{F}$. This value is consistent with values for the capacitance of the double layer. At -0.9 V vs. SCE when hydrogen evolution begins, the capacitance and the charge transfer resistance of the HF loop increase. This increase in capacitance indicates increased adsorption.

The appearance of two capacitance loops is in agreement with the reaction mechanism outlined in Section 5.2.3 viz, the reduction of cobalt takes place through two charge transfer processes[55]. It is thought that the LF capacitive loop, as it does not change much as the potential is decreased, represents the reduction of cobalt due to the direct reduction of Co^{2+} , and the HF capacitive loop, as it has a strong dependence on potential, represents the reduction of cobalt through the CoOH^+ intermediate. Unfortunately, as there are two loops representing charge transfer, the simple expression relating charge transfer resistance to the current and Tafel parameters outlined in Section 3.8.1 cannot be used.

6.2.6.2 Partially Blocked Electrode Model

As outlined in Section 6.2.5.2, inhibition of cobalt deposition from electrolytes containing zinc is caused by two factors: adsorption of ZnOH^+ at moderate overpotentials and precipitation of Zn(OH)_2 , when hydrogen evolution due to the breakdown of water causes the pH at the interface of the electrode to rise to values where this species will precipitate. Both of these phenomena inhibit cobalt deposition by partially blocking the electrode surface.

Partially blocked electrode surfaces have been studied extensively by Gueshi, Tokuda and Matsuda[74,75,76], who proposed the following model of a partially blocked electrode surface.

They stated that electrode surfaces are often inhomogeneous due to physical phenomena such as varying crystal faces, or chemical phenomena, or partial coverage of oxides or electroinactive molecules and ions. They proposed a model based on a surface where a number of circular active sites are distributed uniformly in a rigid hexagonal array. This is depicted in Figure 6.27.

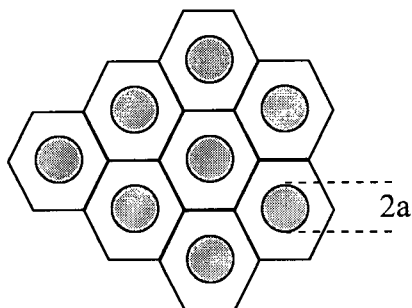


Figure 6.27 Diagram of electrode surface.

This figure shows the active area of the electrode (represented by the shaded regions), as circles of radius a , centered in a hexagonal array. Notice how similar this depiction of the electrode surface is to the observed surface during cyclic voltammetry in Section 5.2.6.

To simplify the solution of this problem, Guishi *et al.* considered a semi - infinite cylinder where the area of the end is equal to that of the hexagon and to regard one of these cylinders as a unit cell of the diffusion space. If the radius of the total unit cell is R , and the radius of the active region is a , the following equations can be written for the areas of the active and inactive surface areas:

$$\text{Surface area of active sites:} \quad q(1 - \theta) = \pi a^2 N \quad (6.7)$$

$$\text{Surface area of inactive sites} \quad q\theta = \pi (R^2 - a^2) N \quad (6.8)$$

Using this model of the electrode surface, Hitzig *et al.*[77] calculated the impedance for the deposition of silver to a partially active rotating disk electrode. The model is unique as it employs both transverse and lateral diffusion of the reactant. A schematic of the electrode surface appears in Figure 6.28.

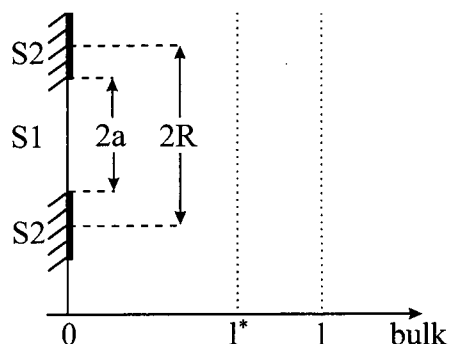


Figure 6.28 Representation of a partially active electrode.

In this diagram, S1 refers to the active area of the electrode, and S2 to the inactive area. At distances less than l^* from the electrode surface both lateral and transverse diffusion occur, between l^* and l , uniform transverse diffusion occurs. The value of l can be calculated by the Levich equation. Using this model of the electrode, Hitzig *et al.* arrived at the following equations to describe the impedance of the electrode (full calculation in Appendix VII). An equivalent circuit representation of the

impedance is depicted in Figure 6.29.

$$Z_s^{-1} = \left(Z_{N(s)} + \sigma Z_{\sigma(s)} \right)^{-1} + \left(\frac{1}{sC_{dl}} + \frac{Z_N}{s\sigma Z_{\sigma} C_{ad}} \right)^{-1} + sC_{dl} \quad (6.9)$$

$$Z_{N(s)} = \frac{RT}{z^2 F^2 c_{ss}^0} H_{1(s)} \quad (6.10)$$

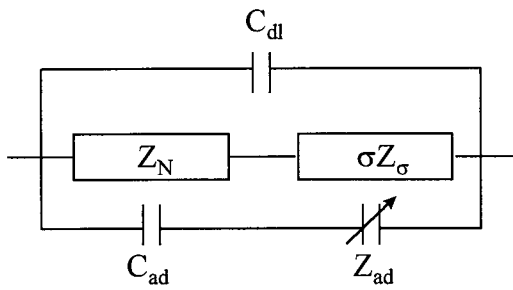
$$Z_{\sigma(s)} = \frac{RT}{z^2 F^2 c_{ss}^0} H_{2(s)} \quad (6.11)$$

$$H_{1(s)} = (Ds)^{-1/2} \tanh[l\sqrt{s/D}] \quad (6.12)$$

$$H_{2(s)} = D^{-1/2} (s+W)^{-1/2} \tanh[l^* \sqrt{(s+W)/D}] \quad (6.13)$$

$$W = 2D(1+\sigma)^2 R^{-2} \sigma^{-1} / \ln[1 + 0.25\sqrt{1+\sigma}] \quad (6.14)$$

$$\sigma = R^2/a^2 - 1 \approx |S1|/|S2| \quad (6.15)$$



Analysis of these equations shows that there are

the following adjustable parameters:

σ - the ratio of inactive to active surface area (if $\sigma = 0$ the electrode is fully active)

R - half distance between active and inactive regions.

l^* - the thickness of the non-uniform diffusion layer

Figure 6.29 Equivalent circuit of Z_s (note that $l^* \rightarrow l$ if $l < 2R$). according to (5.10). $Z_{ad} = Z_N/\sigma Z_{\sigma} C_{ad}$.

Simulation of the impedance represented by

Equation 5.10 was performed by computer, the code for which is found in Appendix VII. The following values were used for simulation:

Table 6.3 Base parameters for impedance simulation:

Property	Value	Units
D	4.25×10^{-6}	cm^2/s
l^*	1.19×10^{-3}	cm
l	1.19×10^{-3}	cm
σ	1	
R	5×10^{-3}	cm
c_{ss}^0	10^{-6}	mol/cm^3
C_{dl}	30	μF
C_{ad}	0	μF

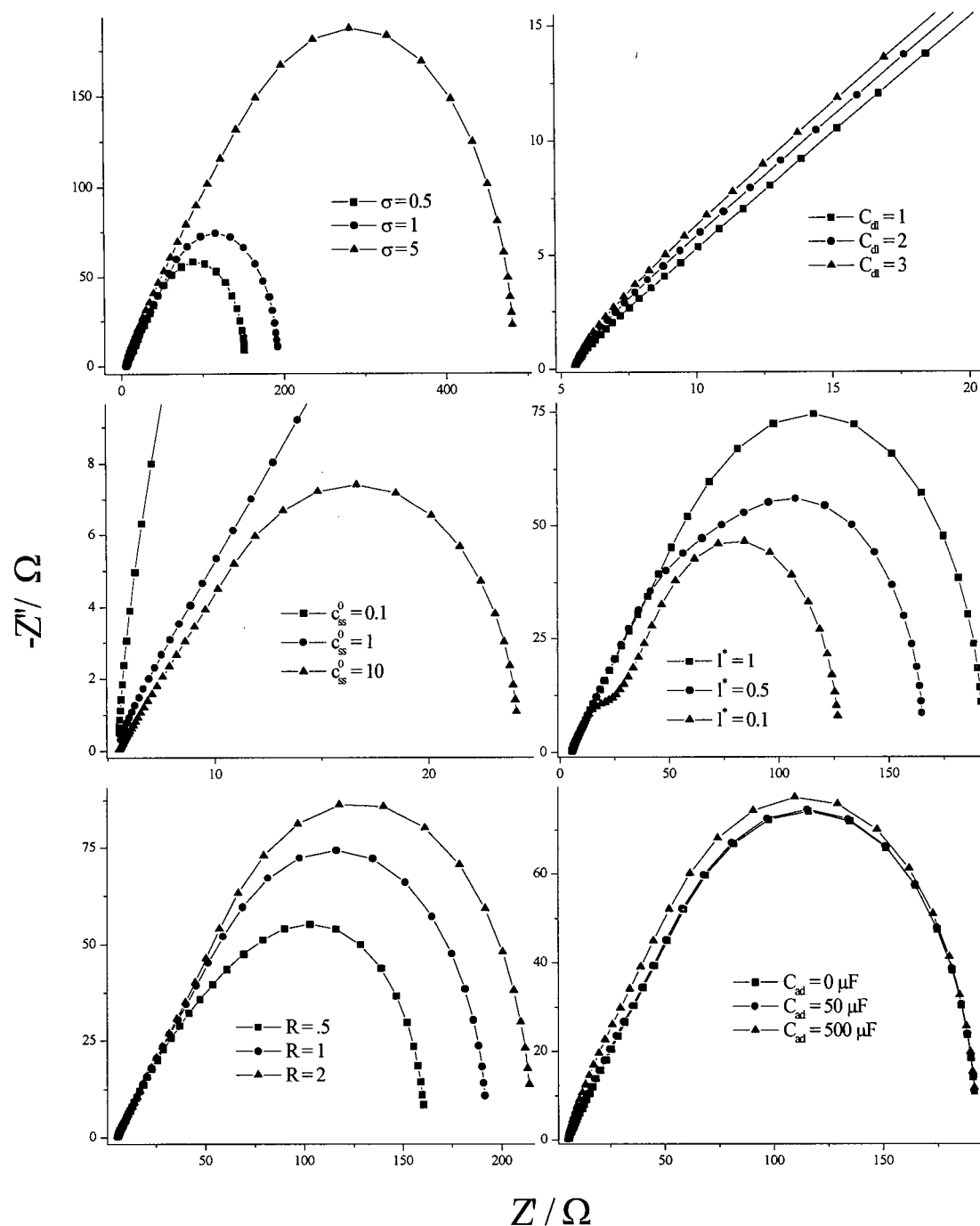


Figure 6.30 Simulation of impedance. Impedance based on Equation 5.10, conditions listed in Table 6.3, legend refers to fraction of parameter value.

These values are based upon the experimental conditions used. Note that σ , R , and l^* are adjustable parameters that are determined by the amount of adsorption. The value of c_{ss}^0 the concentration of cobalt at the interface is also not known and can be considered an adjustable parameter, with the upper limit set by the bulk solution concentration. The value of C_{dl} is taken

from the impedance measurements in Section 6.2.6.1, and the value of C_{ad} has been taken as equal to zero. The value of l has been taken by determining the diffusion layer thickness based on the Levich equation:

$$l = 1.61D^{1/3}v^{1/6}\omega^{-1/2} \quad (6.16)$$

The value of l^* for comparison purposes has been taken to equal l , and R has been assigned a value similar to that used by Hitzig[77].

Figure 6.30 shows the simulation of this impedance with respect to the parameters listed above. The curves are characterized by an initial linear region which has a 45° slope, which is followed by a capacitive loop. The effect of various parameters are summarized below:

- as σ is increased, both the linear region and the capacitive loop increase
- as C_{dl} is increased, a very HF region, with a slope greater than 45° is increased
- as c_{ss}^0 is increased, the initial slope increases and the LF capacitive loop increases
- as l^* is decreased a linear region with a slope less than 45° is observed between the HF linear region and the LF capacitive loop
- as R is increased, the slope of the linear region between the LF and HF regions increases
- as C_{ad} is increased, a very HF region with a slope greater than 45° appears

6.2.6.3 Impedance with Cobalt and Zinc Present

Comparison of the impedance spectra obtained with and without cobalt present was accomplished. Identical impedance spectra were obtained as those found in Section 6.2.6.1 but with 0.01 mol/L zinc present in solution. Figure 6.31 shows the partial current density breakdown for this solution (taken from Figure 6.13, Section 6.2.5). Figure 6.32 shows the impedance spectra at several potentials.

Investigating the impedance spectra, a marked difference is observed upon comparison with the impedance spectra without zinc present (Figure 6.25). Between -0.75 and -0.8 V vs. SCE the impedance with zinc present shows one capacitance loop which has a much larger charge transfer resistance than that observed without zinc present (see Table 6.4).

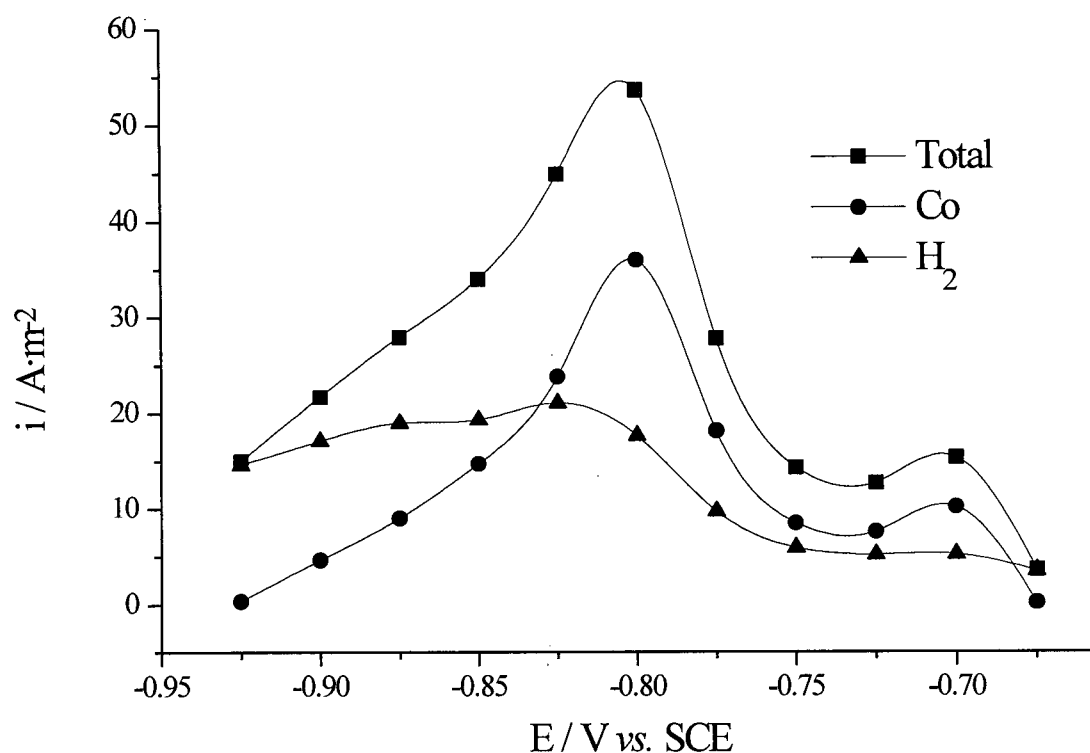


Figure 6.31 Partial current density plot. Conditions: 0.01 mol/L Co, 0.01 mol/L Zn, 2.4 mol/L MgSO_4 , 75°C, 1600 RPM.

Table 6.4 Values of resistance and capacitance for impedance obtained with and without zinc present.

Potential (V vs. SCE)	with zinc R_{ct} (Ω)	no zinc R_{ct} (Ω)	with zinc C_{dl} (μF)	no zinc C_{dl} (μF)
-0.750	3740	268	4	30
-0.775	1560	263	6	25
-0.800	661	179	30	23.5

This table shows that the charge transfer resistance with zinc present is 5-10 times larger with zinc present than that without. Investigating the partial current density plot under these circumstances shows that the current density is much smaller with zinc present than that without, as would be expected with the observed change in charge transfer resistance. The value of the double layer capacitance is smaller when zinc is present at -0.75 and -0.775 V vs. SCE; however, at -0.8 V vs. SCE, it approaches the value observed without zinc present.

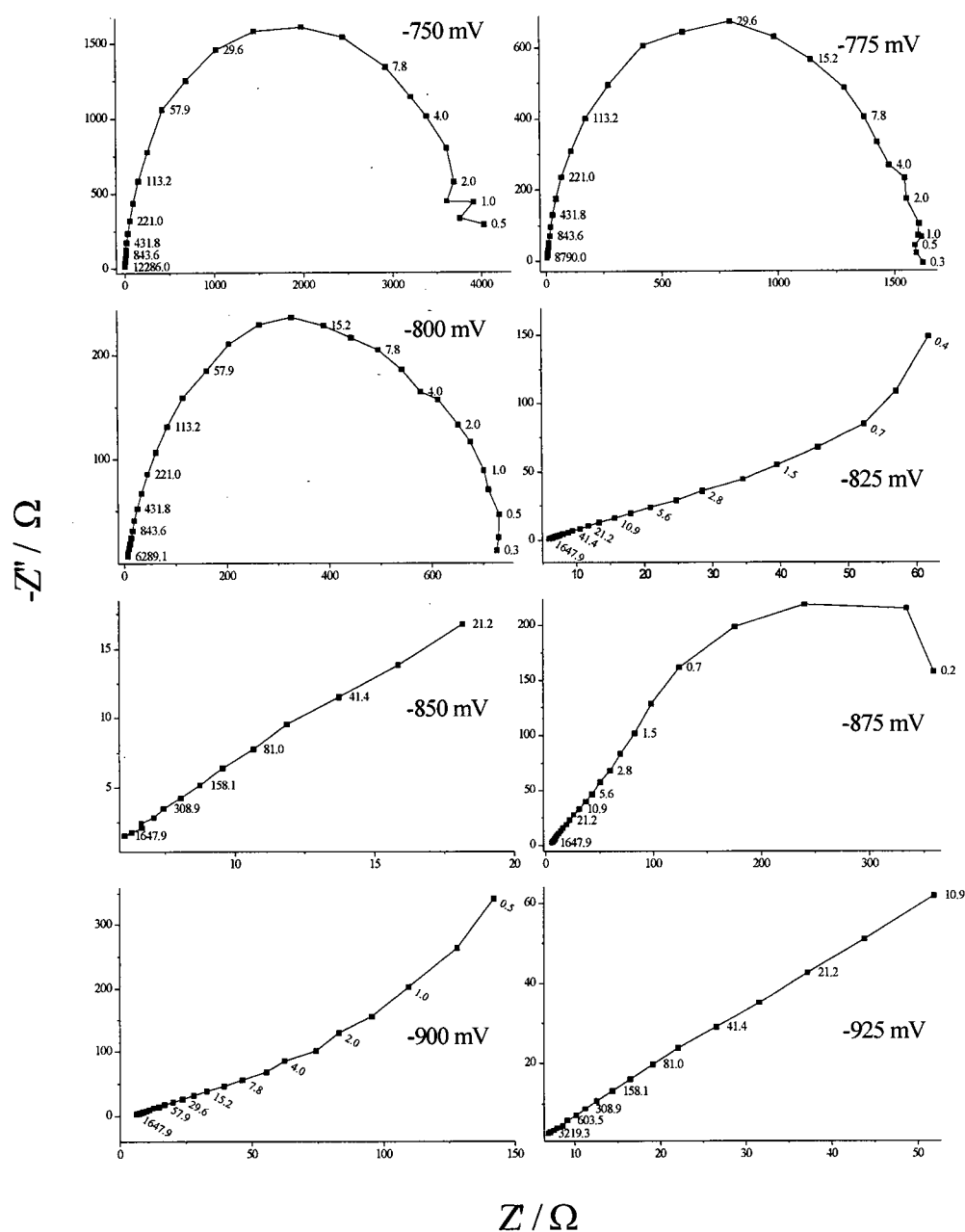


Figure 6.32 Complex plane impedance plots. Conditions: 0.01 mol/L Co, 0.01 mol/L Zn, 2.4 mol/L MgSO_4 , 75°C, 1600 RPM. Potential refers to mV vs. SCE.

At -0.825 V vs. SCE the impedance spectra change dramatically. The impedance is characterized by a linear HF region that has a slope near 45°, followed by an increased slope region at lower frequencies. The one deviation from this is at -0.875 V vs. SCE where the LF region is characterized by a capacitive loop.

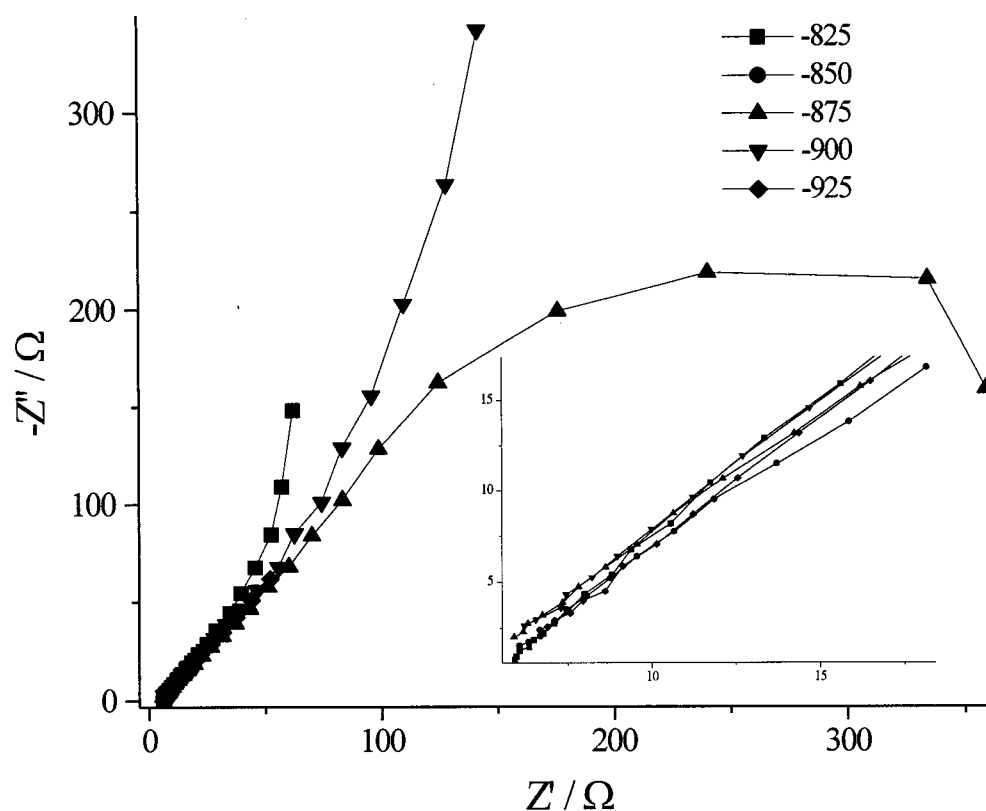


Figure 6.33 Impedance spectra of cobalt zinc solutions (from Figure 6.32). Inset shows HF region.

Re-plotting the impedance in this region in one graph (Figure 6.33) shows how similar these spectra are, particularly at high frequencies.

The shape of these curves, particularly the curve at -0.875 V vs. SCE, is very similar to the simulated curves in Section 6.2.6.2. Comparing the simulated curves to the experimental curves, the following similarities can be seen:

- Due to the lack of any linear region with a slope greater than 45° at very HF's the value of C_{ad} can be considered insignificant (~ 0) and the value of C_{dl} can be considered small (~ 30 μF).
- The initial linear region is followed by a linear region which has a slope $> 45^\circ$, suggesting that l^* is not less than l and that R is large.
- The shape of the curve at -0.875 V vs. SCE is almost identical to the simulated curves.

The shapes of the experimental curves differ from those of the simulated curves in the following ways:

- The initial slope of the experimental curves is slightly greater than 45° .
- A LF capacitive loop is only observed at -0.875 V vs. SCE

These differences notwithstanding, there is a general agreement between the simulated and experimental curves. This agreement suggests that the electrode becomes partially blocked above -0.800 V vs. SCE, which corresponds to the chemical mode outlined in Section 6.2.5.2.

Figure 6.34 shows a Bode plot of the impedance at -0.875 V vs. SCE and the base modeled case. A Bode plot plots the impedance as the absolute value of the impedance vs. the frequency, and the phase angle between the real and imaginary vectors vs. the frequency. This plot clearly shows the similarity between the model for the impedance and the experimentally obtained impedance.

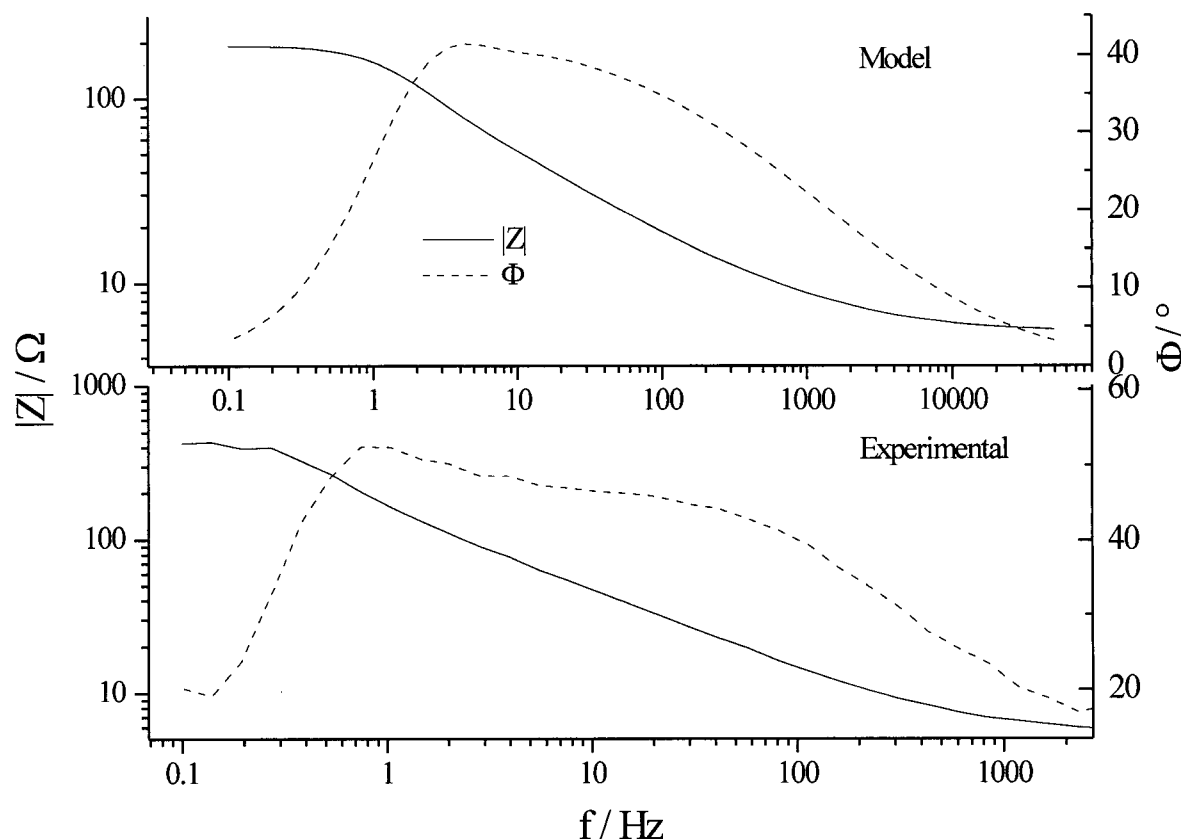


Figure 6.34 Bode plot showing the impedance for the experimental case -0.875 V vs. SCE and the modeled case outlined in Table 6.3.

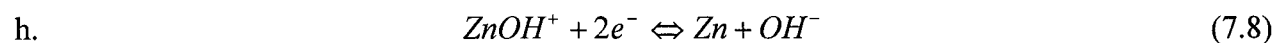
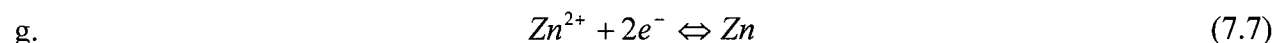
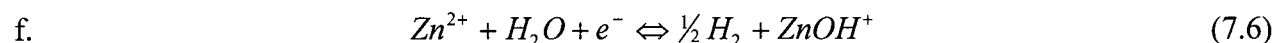
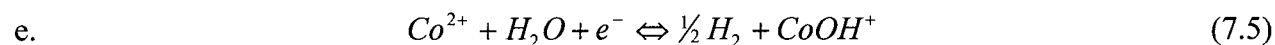
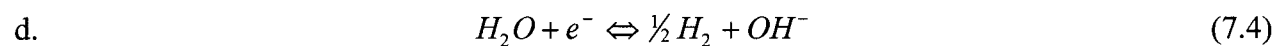
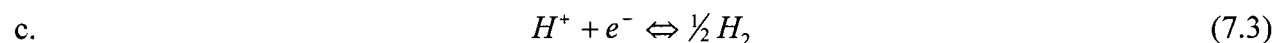
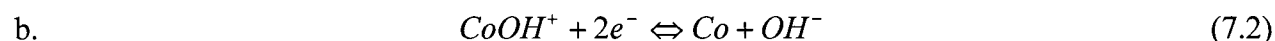
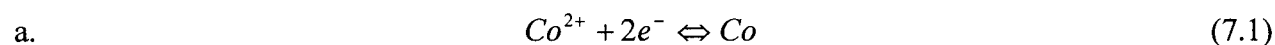
7. Calculation of Surface Concentrations

7.1 Derivation

A series of equations has been developed that calculate the surface concentrations of the species involved during the discharge of cobalt and hydrogen with zinc present. The following assumptions have been made in the derivation:

1. Only Co and H₂ discharge.
2. H₂ discharge does not affect the flow field.
3. The system can be considered one-dimensional in the direction perpendicular to the electrode surface (assigned the z - direction).
4. Mass transfer to the disk can be described by the Levich equation.
5. Electrodeposition has reached steady-state. (i.e. $i = \text{const.}$, and $E = \text{const.}$).
6. Migration is negligible due to the high ionic strength of the solution.

The following species are considered as being in equilibrium: Species (6) viz, Co²⁺, CoOH⁺, Zn²⁺, ZnOH⁺, H⁺, OH⁻. These species undergo the following electron transfer reactions:



The fluxes of the individual species are related to the currents of reactions a-h by the following relationships:

$$N_{Co^{2+}} = \frac{i_{Co}^a}{2F} + \frac{i_{H_2}^e}{F} \quad (7.9)$$

$$N_{CoOH^+} = \frac{i_{Co}^b}{2F} - \frac{i_{H_2}^e}{F} \quad (7.10)$$

$$N_{H^+} = \frac{i_{H_2}^c}{F} \quad (7.11)$$

$$N_{OH^-} = -\frac{i_{Co}^b}{2F} - \frac{i_{H_2}^d}{F} - \frac{i_{Zn}^h}{2F} \quad (7.12)$$

$$N_{Zn^{2+}} = \frac{i_{H_2}^f}{F} + \frac{i_{Zn}^g}{2F} \quad (7.13)$$

$$N_{ZnOH^+} = \frac{i_{Zn}^h}{2F} - \frac{i_{H_2}^f}{F} \quad (7.14)$$

However:

$$i_{Co} = \sum_n i_{Co}^n \quad (7.15)$$

$$i_{H_2} = \sum_n i_{H_2}^n \quad (7.16)$$

$$i_{Zn} = \sum_n i_{Zn}^n \quad (7.17)$$

Therefore:

$$\frac{i_{Co}}{2F} = N_{Co^{2+}} + N_{CoOH^+} \quad (7.18)$$

$$\frac{i_{H_2}}{F} = N_{H^+} - N_{OH^-} - N_{CoOH^+} - N_{ZnOH^+} \quad (7.19)$$

$$\frac{i_{Zn}}{2F} = N_{Zn^{2+}} + N_{ZnOH^+} \quad (7.20)$$

The current density at a rotating disk is related to the concentration change from the bulk to the surface by the following relationship[57]:

$$i_i = 0.620nFD_i^{2/3}\omega^{1/2}\nu^{-1/6}(C_i^b - C_i^s) \quad (7.21)$$

The flux of a species is related to the current density due to discharge of this species by the following relationship:

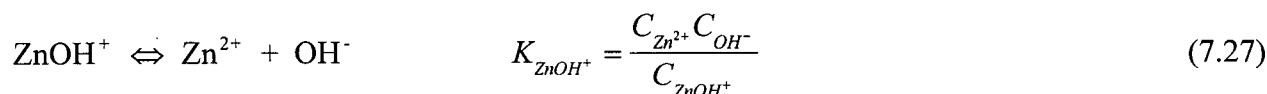
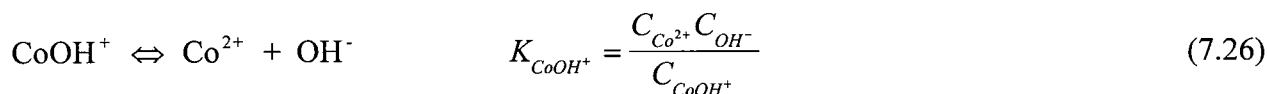
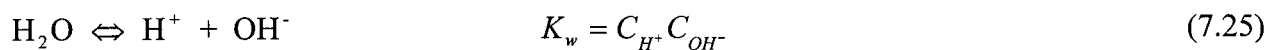
$$N_i = \frac{i_i}{nF} \quad (7.22)$$

The following equation can be written to relate the flux of the species to the concentration change of the species:

$$N_i = \alpha_i (C_i^b - C_i^s) \quad (7.23)$$

where:
$$\alpha_i = 0.620 D_i^{2/3} \omega^{1/2} \nu^{-1/6} \quad (7.24)$$

The following equilibrium equations also hold true both at the surface of the electrode and in the bulk:



Equations 7.18-7.20, Equation 7.23 (taken for each of the 6 species) and Equations 7.25 to 7.27 are 12 non-linear equations in 12 unknowns. The unknowns are the surface concentration and flux of each of the six species. These equations can be solved numerically using Brent's root finding method[78] after suitable algebraic manipulation of the equations. Appendix VIII contains a full derivation of the system and the computer code that was used to find the solution.

It should be noted that this problem has been previously solved by Hessami[79] for the nickel-iron system. This system is very similar to the zinc-cobalt system as the same 6 species (with Ni and Fe substituted for Co and Ni respectively) must be considered. Hessami modeled this deposition using a finite element approach to solve equations similar to those listed above; however, his solution is in error. To obtain his solution, he used a constant boundary layer thickness derived from the Levich equation:

$$\delta = 1.61 D^{1/3} \omega^{-1/2} \nu^{1/6} \quad (7.28)$$

This equation is directly related to the diffusion coefficient; however, since there are 6 different species, with 6 distinct diffusion coefficients, there are 6 distinct boundary layer thicknesses. Hessami used the smallest diffusion coefficient to calculate the thickness, but this will result in a large inaccuracy in the calculation of the surface concentration of hydrogen, an ion that typically

has a diffusion coefficient 10-50 times larger than that of metallic cations. Since the boundary layer thickness, under laminar flow conditions such as a rotating disk, is a constructed convenience and not a physical phenomenon, it cannot be used when more than one species is considered.

The following base parameters were used in the model:

Table 7.1 Base model parameters.

Parameter	Value	Units
K_w	1.3×10^{-19}	$(\text{mol}/\text{cm}^3)^2$
K_{CoOH^+}	5.6×10^{-8}	mol/cm^3
K_{ZnOH^+}	8.0×10^{-11}	mol/cm^3
$D_{\text{Co}^{2+}}$	0.425×10^{-5}	cm^2/s
D_{CoOH^+}	0.425×10^{-5}	cm^2/s
$D_{\text{Zn}^{2+}}$	0.425×10^{-5}	cm^2/s
D_{ZnOH^+}	0.425×10^{-5}	cm^2/s
D_{H^+}	3.25×10^{-4}	cm^2/s
D_{OH^-}	1.63×10^{-4}	cm^2/s
ν	0.0158	cm^2/s
ω	$\text{RPM} \cdot \pi/30$	s^{-1}
R	8.314	$\text{J}/\text{mol} \cdot \text{K}$
T	348	K

The values of the equilibrium constants have been adjusted to 75°C by the method of Criss and Cobble (see Appendix IV). The values of the diffusion coefficients of Co^{2+} and H^+ are those measured in Section 5.2.1 as is the value for the kinematic viscosity. The values for the diffusion coefficients of the other metallic ions have been set to be equal to that of Co^{2+} . The diffusion coefficient of OH^- has been set equal to $\frac{1}{2}$ of that of the hydrogen ion, as this is the ratio of their diffusion coefficients in dilute solution[61].

Using these values, the values for the bulk concentration of the species, and the partial current densities obtained by potentiostatic deposition from Section 6.2.5.1 (note that the current density of zinc deposition is 0), the surface concentration of the 6 species can be determined.

7.2 Results

Setting the partial current density of cobalt reduction to 0 in the program, the surface concentration of protons can be calculated as a function of current density. Figure 7.1 shows this relationship. This figure shows that as the hydrogen partial current density increases, the surface

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 concentration of H^+ decreases. Near the limiting current density of hydrogen (represented by the
 ELECTROLYTES CONTAINING ZINC
 dotted line extrapolation) the current density of hydrogen increases rapidly as the concentration
 of H^+ at the interface decreases. This is a result of the equilibrium between the species dictating
 the concentration rather than the diffusion of the species. Note that the extrapolated limiting
 current density of hydrogen is very close to the value obtained in Section 5.2.1.

PAUL GEORGE WEST-SELLS

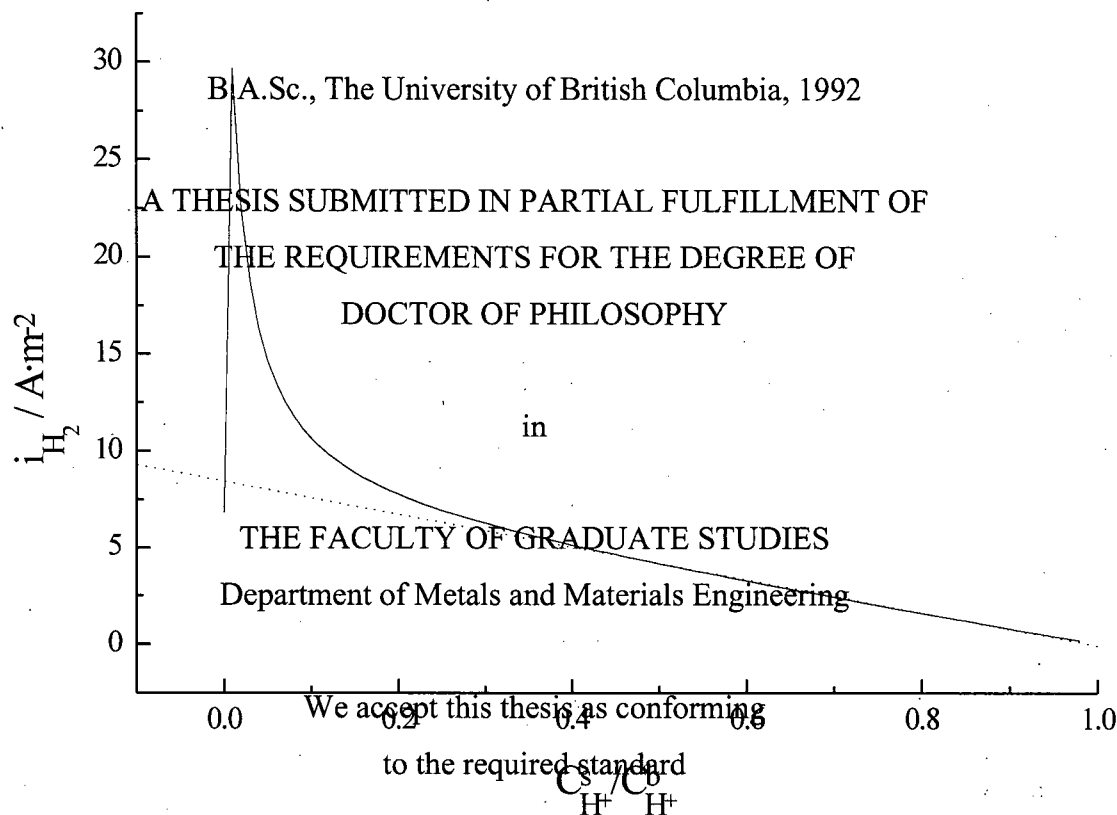


Figure 7.1 Hydrogen current density vs. hydrogen surface concentration. Conditions: 0.01 mol/L $CoSO_4$, 0.01 mol/L $ZnSO_4$, 2.4 mol/L $MgSO_4$, pH 4, 75°C, 1600 RPM. $i_{Co} = 0$.

Figure 7.2 shows the surface concentration for the 6 ionic species as a function of potential. The partial current densities for hydrogen and cobalt have been taken from the plot of partial current density vs. potential (taken from Figure 6.13). The following observations can be made from this plot:

1. The concentration of Co^{2+} does not change dramatically. As the current density of cobalt is far from its limiting current, this concentration is not expected to change much.
2. The concentrations of $CoOH^+$, $ZnOH^+$, and OH^+ all change with potential in an almost identical manner and the concentration of H^+ changes in an inverse relationship.

3. The concentration of H^+ appears to stabilize at a concentration of 4×10^{-6} mol/L after the deposition of cobalt begins to show inhibition at -0.800 V vs. SCE.
4. The concentration change of all species except for Co^{2+} and Zn^{2+} is directly related to the change in the partial current density of hydrogen.

Plots of surface concentration vs. potential for cobalt deposition under different conditions appear in Figure 7.3, Figure 7.4, and Figure 7.5. These figures are also associated with partial current density plots. These figures show much of the same phenomena as observed in Figure 7.2. In particular, the hydrogen ion concentration at which inhibition of cobalt deposition begins is close to 4×10^{-6} mol/L for all of the conditions tested, except when the concentration of zinc is doubled. In this case it is close to twice this value at 9×10^{-6} mol/L. This suggests that the precipitation of an inhibitory species occurs at this concentration of hydrogen ions.

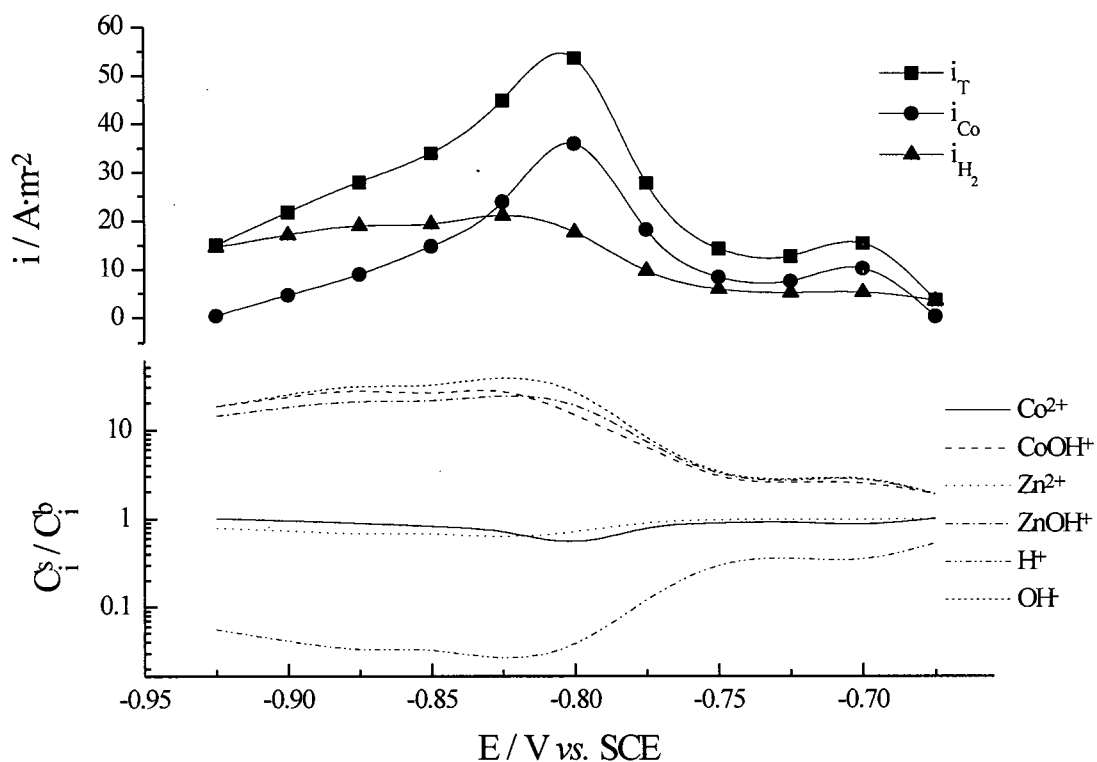


Figure 7.2 Plot showing the surface concentration of the species and partial current density breakdown as a function of potential. Conditions: 0.01 mol/L CoSO_4 , 0.01 mol/L ZnSO_4 , 2.4 mol/L MgSO_4 , pH 4, 75°C, 1600 RPM.

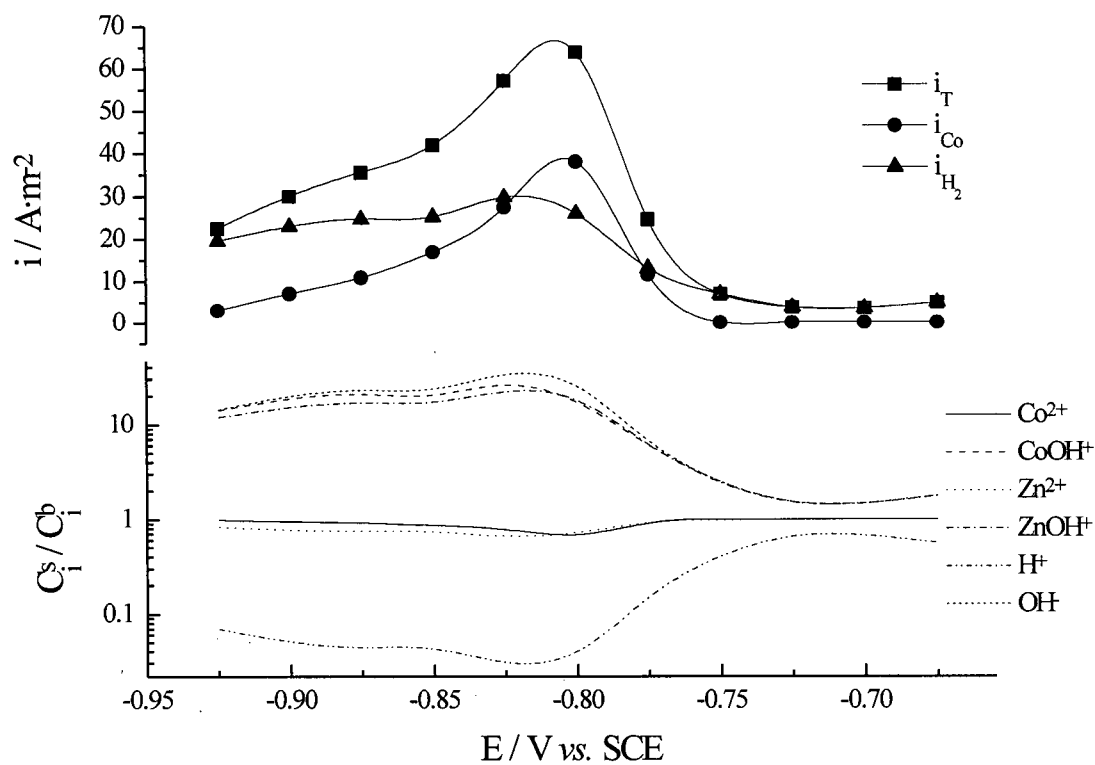


Figure 7.3 Plot under identical conditions as Figure 7.2 except 3600 RPM.

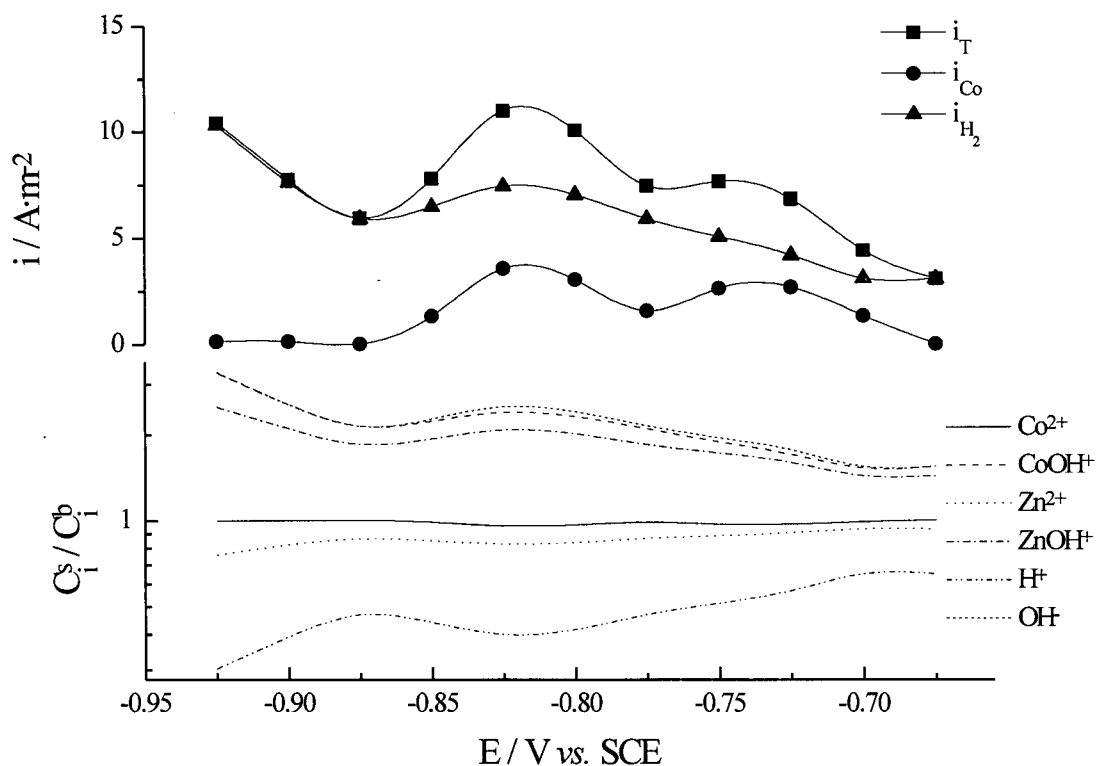


Figure 7.4 Plot under identical conditions as Figure 7.2 except pH 5.

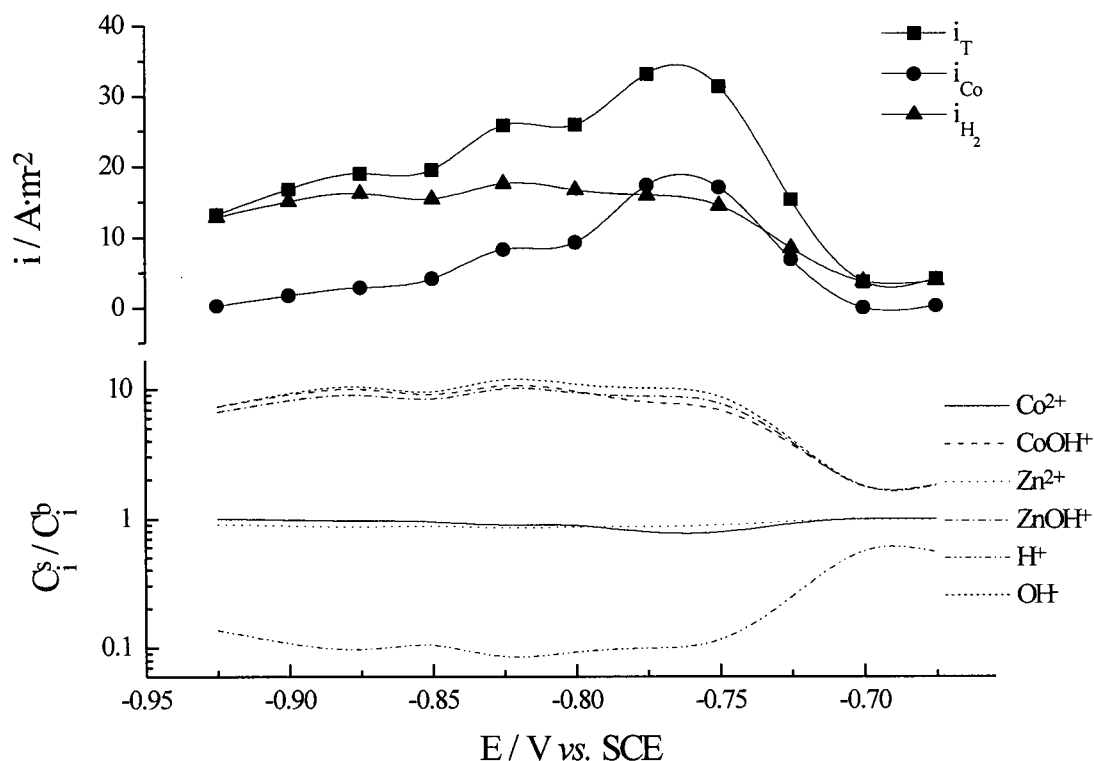


Figure 7.5 Plot under identical conditions as Figure 7.2 except $C_{\text{Zn}} = 0.02$ mol/L.

For the base conditions, this concentration of hydrogen corresponds to a pH of 5.4. This value is very close to the pH calculated for the precipitation of $\text{Zn}(\text{OH})_2$ of 5.89.

It appears as if the pH at the interface of the electrode is kept in equilibrium with the precipitate. As hydrogen generation increases, the pH at the interface rises and precipitation of $\text{Zn}(\text{OH})_2$ increases. Once $\text{Zn}(\text{OH})_2$ has precipitated, hydrogen generation decreases as the surface area available for discharge decreases. This lowers the pH at the interface of the electrode, causing the precipitate to dissolve.

The interfacial concentration of ZnOH^+ equilibrates at a value of 3×10^{-3} mol/L for solutions containing 0.01 mol/L Zn at potentials below -0.800 V vs. SCE. This concentration is much larger than that of CoOH^+ for this same potential range, which equilibrates at 6×10^{-6} mol/L, due to a smaller equilibrium constant for the formation of CoOH^+ than for ZnOH^+ . Hessami[79] successfully modeled the influence of competitive adsorption of NiOH^+ and FeOH^+ to account for anomalous nickel deposition by considering these two species to adsorb with equal adsorption constants at high coverage. Adapting the equation he used for adsorption for these

two species for use with ZnOH^+ and CoOH^+ , the following equation for the coverage of CoOH^+ can be derived:

$$\theta = \frac{C_{\text{CoOH}^+}^s}{C_{\text{CoOH}^+}^s + C_{\text{ZnOH}^+}^s} \quad (7.29)$$

Dividing the partial current density of cobalt by this equation, the following equation can be fitted between -0.750 and -0.800 V vs. SCE with very good accuracy ($R = 0.9999$):

$$i_{\text{Co}} = 2.4 \times 10^{-7} \theta \exp\left(\frac{FE}{RT}\right) \quad (7.30)$$

Note that in this equation, the value of α , the transfer coefficient, is 1. This value differs from the value obtained when zinc was not present of 4 (see Section 5.2.2). This proves that the mechanism of cobalt deposition has changed with the addition of zinc. Since the surface concentration of ZnOH^+ is much larger than that of CoOH^+ , it is unlikely that cobalt deposition occurs through a recombination of two Co_{ads} atoms as is suggested in Section 5.2.2. The TEM studies of the deposits in Section 6.2.4.2 suggest that the deposit is nearly amorphous suggesting a high nucleation to growth rate. If cobalt is deposited without an atom-atom recombination step as is suggested in the procedure outlined for cobalt deposition without zinc present, the deposit may not be amenable to growth. This will result in enhanced nucleation leading to an amorphous deposit.

8. Conclusions

The following conclusions can be made regarding the deposition of cobalt from zinc containing solutions under cementation-like conditions:

1. Effective removal of cobalt by reduction from solution was possible using a copper electrode, with a counter-electrode separated from solution by a glass frit. Cobalt was removed using antimony, antimony-copper, arsenic, and arsenic-copper as activators present in solution.
2. The rate of cobalt removal using antimony activation increased with increasing current density to a maximum at $35 \text{ A}\cdot\text{m}^{-2}$, at current densities above this value, the removal rate did not increase substantially. Variation of physicochemical parameters indicated that electrochemical removal behaved similarly to cementation with regard to parameters such as pH, temperature, oxygen concentration, and the presence of organics.
3. The presence of copper in antimony-activated cobalt removal was shown to increase the surface area available for cobalt deposition by depositing on nodules of zinc present in the deposit rendering them amenable to cobalt deposition.
4. Arsenic-copper activation gave higher removal rates than antimony activation or arsenic activation alone. A temperature of 90°C with arsenic-copper activation was necessary to remove cobalt to levels below 0.3 mg/L by electrodeposition.
5. The rates obtained by removing cobalt using antimony or arsenic activation were shown to be similar to those obtained by traditional studies of cementation. Furthermore, the equivalent mass of zinc dust required using electrochemical removal with antimony activation was shown to be half that typically required in industrial cementation.
6. The diffusion coefficients for cobalt and hydrogen in a solution approximating the ionic strength of industrial zinc sulfate electrolyte were determined. The Tafel behavior of cobalt in this solution was characterized, E-pH diagrams of zinc, cobalt and hydrogen were generated at elevated temperature, and the cyclic voltammetry behavior was also determined.
7. By analysis of fast linear sweep measurements, SEM and TEM data, partial current density experiments, and calculation of the surface concentrations of various chemical species in the Co-Zn- H_2O system, inhibition of cobalt deposition by zinc was found to be a result of adsorption of ZnOH^+ at the interface of the electrode. This adsorption caused the nucleation

potential to shift to more negative potentials, and the mechanism of cobalt deposition to change.

8. By analysis of cyclic voltammetry, SEM and TEM data, partial current density experiments and calculation of surface concentrations, further inhibition of cobalt deposition was found to be caused by the precipitation of Zn(OH)_2 . The precipitation of this species was found to occur at more negative potentials than inhibition by ZnOH^+ .
9. By SEM and TEM analysis, the morphology of the cobalt deposit was found not to be crystalline in nature and can be assumed to be amorphous when cobalt is deposited in the presence of zinc. The amorphous nature of the deposit may be due to inhibition of cobalt atom-atom recombination by adsorption of ZnOH^+ .
10. A potential of -0.800 V vs. SCE for a solution containing 0.01 mol/L Co and 0.01 mol/L Zn at a pH of 4 was found to produce the highest partial current density for cobalt deposition. This potential represents the minimum potential of the electrode before Zn(OH)_2 precipitates due to excessive hydrogen evolution. Galvanodynamic experiments showed that this potential represents a quasi-steady-state and planar cell electrode studies suggest that with As-Cu activation, this is the potential of the electrode.

These conclusions establish what this thesis originally sought to determine: how cobalt deposition is inhibited in the presence of zinc. Now that this information has been determined, further research into cementation can address overcoming the inhibition.

9. Recommendations for Further Work

This study has determined how zinc inhibits cobalt deposition in electrolytes similar to industrial zinc electrolyte. The concentrations of zinc and cobalt used in this study were very different than those used industrially to better understand the mechanism at work. Confirmation of the mechanism of inhibition proposed in this study in the case of industrial cementation solutions should be accomplished if possible.

The presence of ZnOH^+ as an adsorbed species which inhibits cobalt deposition has been proposed. Determination of the presence of this ion at the interface during cobalt deposition from solutions containing zinc would be beneficial in confirming this theory.

While SEM studies of the interface of the electrode showed that zinc was present as a precipitated product, the exact form of this precipitate has not been determined, although calculation of the surface pH of the electrode suggests that the precipitate is Zn(OH)_2 . The form of this precipitate should be determined.

While the behavior of arsenic and antimony has been examined in the introductory study on deposition to a planar electrode, how antimony and arsenic decrease the inhibition by zinc has not been addressed. Now that the inhibitory effects of zinc have been identified, how antimony and arsenic reverse this inhibition should be determined.

Using the information on how zinc inhibits cobalt deposition, other "activators" or processes that limit inhibition should be investigated. In particular, since both the formation of ZnOH^+ and Zn(OH)_2 are a function of hydrogen evolution, processes that limit the evolution of hydrogen should be examined.

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11. Appendices

11.1 1 - Colorimetric Assay of Cobalt in Zinc Solutions

The concentration of cobalt in a zinc sulfate solution was determined by a colorimetric technique developed by Cominco Ltd.[53]. In this procedure, a soluble colored complex between cobalt and Nitroso-R salt is developed. The color intensity is then measured using a colorimeter. The procedure is as follows:

1. A 2 mL sample of the solution to be analyzed and 18 mL of de-ionized water were added to a clean, dry 100 mL Erlenmeyer flask. No rinsing was performed.
2. 5 mL of freshly prepared 5 g/L α -Nitroso-R salt was added to the flask.
3. The flask was covered by a watch glass, placed on a hot-plate, and then allowed to come to a boil.
4. Upon the commencement of boiling, 1 mL of 30 g/L potassium bromate was added to the boiling solution.
5. The solution was allowed to boil for 1 min.
6. The flask was removed from the hot-plate, and 1 mL of concentrated nitric acid was added to the flask.
7. After the solution had cooled to room temperature, the solution was transferred to a clean, dry 30 mL vial.
8. The color intensity was measured using a Brinkmann P.C. 900 colorimeter at a wavelength of 520 nm. The intensity was compared to cobalt standards made using the above procedure from solutions with a known cobalt concentration.

The range of concentrations that this method can determine is approximately 1 - 20 mg/L.

11.2 II - Standardization of Cementation Data

Cementation studies are performed either using a rotating zinc disk or a batch reactor with zinc dust added. In both cases, the removal of cobalt usually follows a first-order reaction. A first-order reaction requires that the following equation be true:

$$\frac{dC}{dt} = k'C \quad (11.1)$$

The cobalt removal rate k' is related to the surface area of reaction, the volume of the reactor, and the kinetic removal constant by the following relationship:

$$k' = \frac{kA}{V} \quad (11.2)$$

Integrating Equation 11.1 and incorporating Equation 11.2, the final equation relating removal to the surface area, volume and mass transfer rate is:

$$\ln\left(\frac{C^i}{C^f}\right) = \frac{kA}{V} \quad (11.3)$$

The value of A/V is referred to as the specific surface area. As seen in Equation 11.3, it greatly effects the removal of cobalt. It is for this reason that zinc dust is used in industrial processes since it will maximize this value.

To calculate the specific surface area for a mass of zinc dust added to a reactor, the following equations can be derived:

Assuming that x g/cm³ of zinc dust is added to the reactor, the radius of the zinc particles is r cm, the density of zinc is ρ , and the particles can be approximated by spheres:

$$\text{Number of particles/Liter:} \quad N_p = \frac{x}{\frac{4}{3}\pi r^3 \rho} \quad (11.4)$$

$$\text{Surface area of each particle} \quad A = 4\pi r^2 \quad (11.5)$$

$$\text{Specific surface area (cm}^{-1}\text{):} \quad \sigma = \frac{3x}{r\rho} \quad (11.6)$$

As most removal rates reported in the literature are given in units of time⁻¹, one only has to divide this constant by the value from Equation 11.6 to achieve the kinetic removal constant (after conversion for time units) in cm/s.

Table 11.1 Summary of cementation rates obtained by other researchers.

Author	Activation	Dust load (g/L)	Mean D (μm)	Disk D (cm)	S.S.A. (cm^{-1})	Rate (min^{-1})	Rate ($\text{cm/s}) \cdot 10^3$	Source
Adams	Sb/Cd	2	66		0.255	0.029	1.9	Table 8, c
Lew*	Sb/Cu	4					1.6	
Lew	Sb/Cu	4	127.5		0.264	0.047	3.0	Table 1
Tozawa	Sb/Cu			4	0.126	0.0089	0.12	Figure 5
Thesis	Sb				0.090	0.0048	0.90	Figure 4.1
Thesis-Cu	Sb/Cu				0.090	0.0098	1.8	Figure 4.5
Fugleburg	As	0.5			0.750	0.069	1.5	Figure 8
Lawsen	As			5	0.196	0.016	1.4	Figure 6
Tozawa	As/Cu			4	0.126	0.018	2.4	Figure 11
Thesis	As/Cu				0.090	0.030	5.6	Figure 4.9

Table 11.1 gives a summary of the rates of cementation obtained by other researchers along with other parameters. These rates were used to generate Figure 4.15.

* In this paper, the total surface area was calculated. For this reason, no information is given for the zinc dust particles.

11.3 III - Levich Plot Data

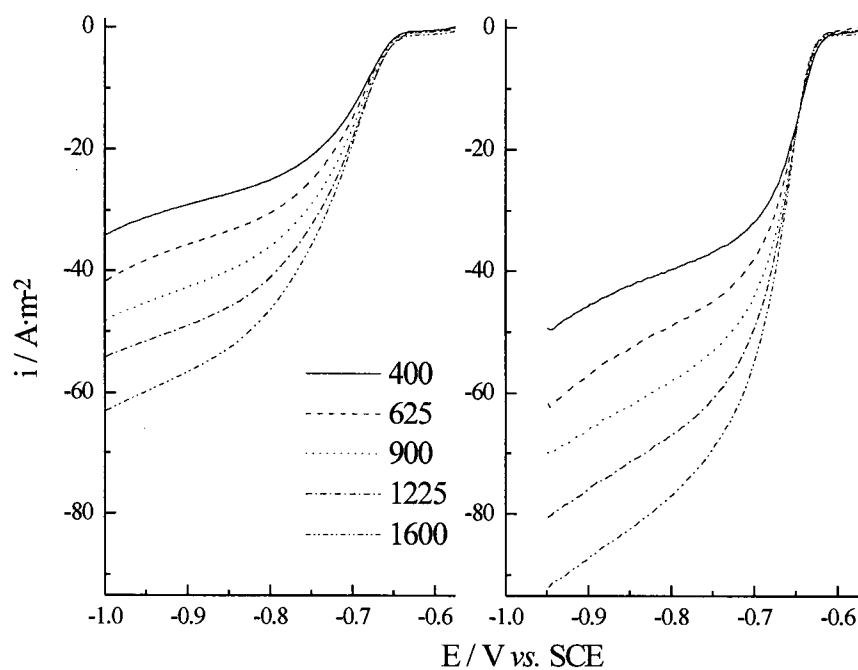


Figure 11.1 Cathodic potential sweeps of 0.01 mol/L Co in 2.4 mol/L MgSO₄ at various rotation speeds. Left: 50°C, Right: 75°C.

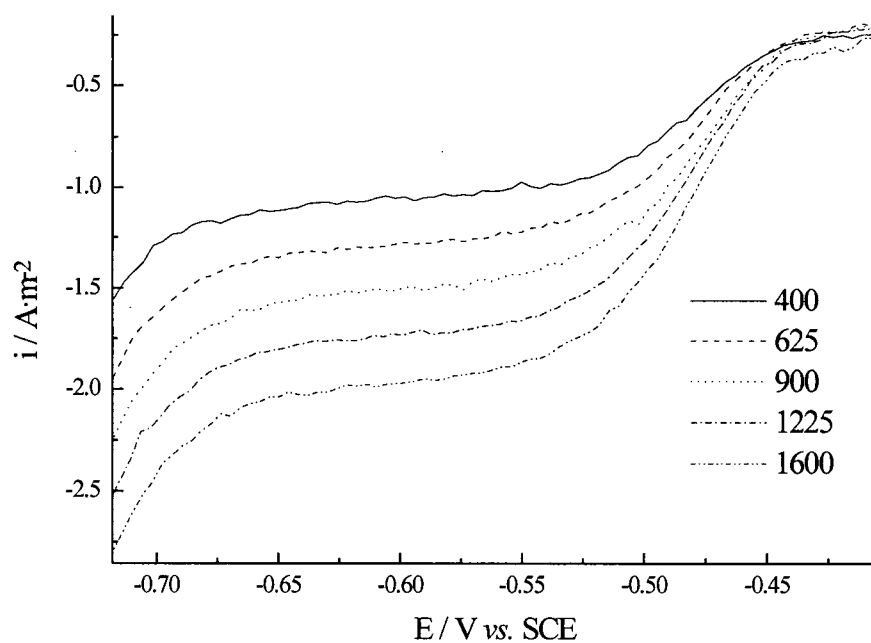


Figure 11.2 Cathodic potential sweeps of 2.4 mol/L MgSO₄, pH 4 showing hydrogen evolution at various rotation speeds. Temperature 25°C.

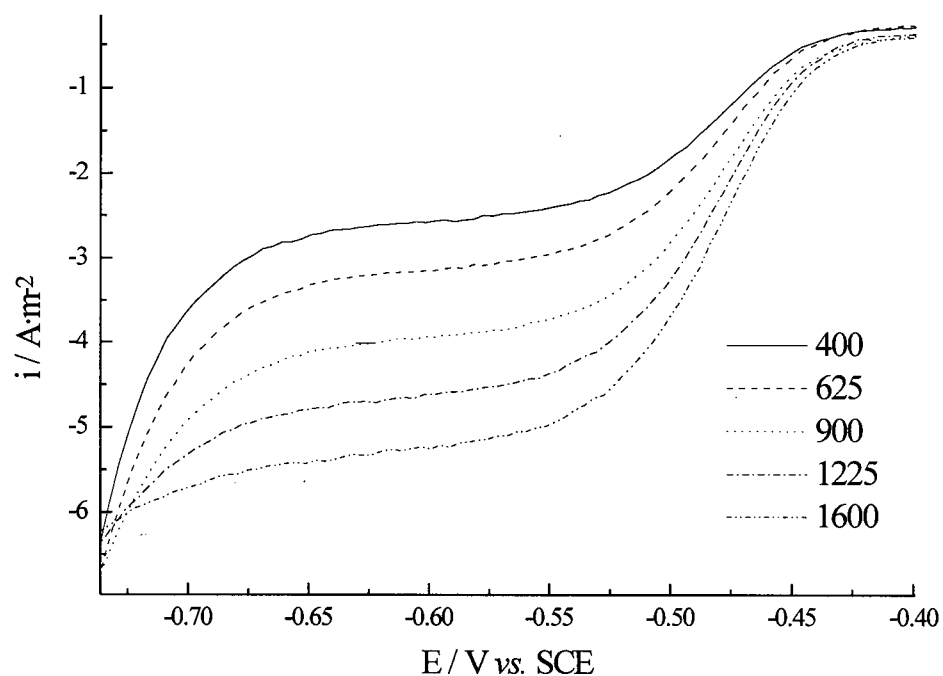


Figure 11.3 Cathodic potential sweeps of 2.4 mol/L MgSO_4 , pH 4 showing hydrogen evolution at various rotation speeds. Temperature 50°C .

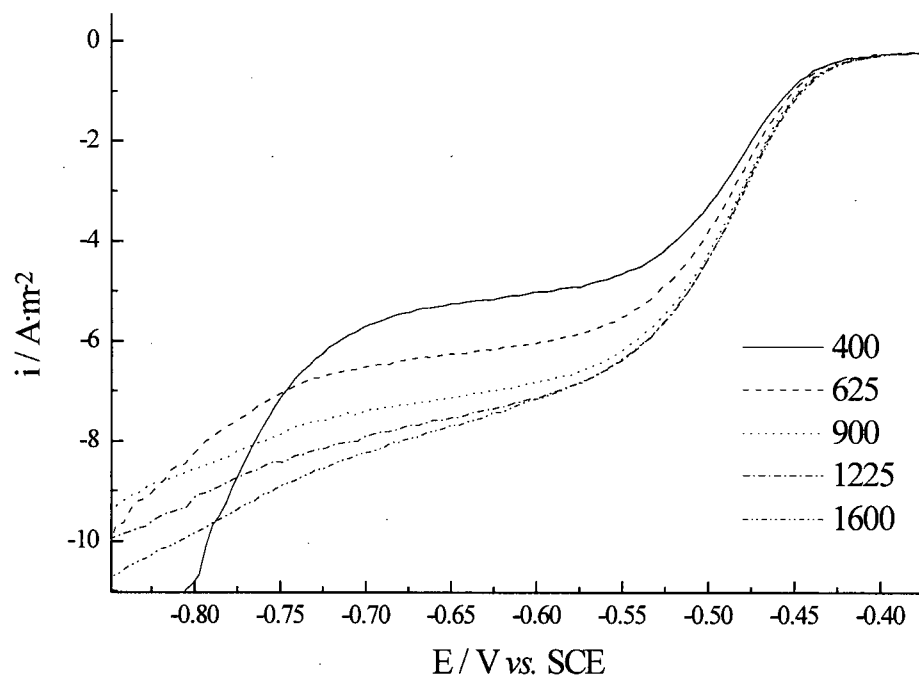


Figure 11.4 Cathodic potential sweeps of 2.4 mol/L MgSO_4 , pH 4 showing hydrogen evolution at various rotation speeds. Temperature 75°C .

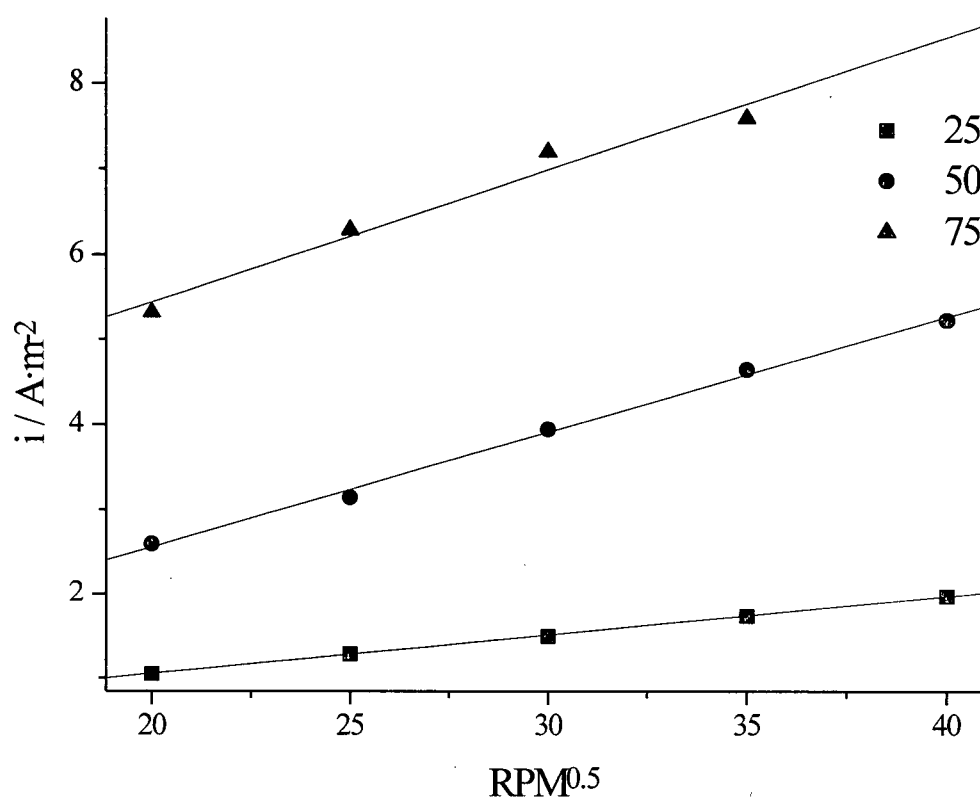


Figure 11.5 Levich Plot showing the variation of limiting current density with rotation speed and temperature.

11.4 IV - Adjustment of Thermodynamic Data to Elevated Temperatures

Criss and Cobble were the first to recognize the entropy change of ions with temperature. They noted that the entropy of an ion is a function of mass, charge and ionic size. Based on this model of entropy, they postulated that it is not necessary to know the complete functional dependencies and that the average entropy of an ion at elevated temperatures can be expressed as:

$$\bar{S}_{T_2}^0 = a_{T_2} + b_{T_2} \bar{S}_{T_1}^0 \quad (11.7)$$

where a bar denotes an average value.

Criss and Cobble defined the entropy needed to use this equation as the “absolute” ionic entropy and defined this as a function of the conventional entropy as follows:

$$\bar{S}_{abs}^0 = \bar{S}_{con}^0 - 5z \quad (11.8)$$

They found that ions could be grouped into four categories and that for each of these categories, the values of a and b were similar. The values of these constants for the ions of interest are tabulated in Table 11.2.

Table 11.2 a and b parameters for Criss and Cobble’s entropy equation

T °C	simple cations		simple anions		oxy anions		acid oxy anions	
	a_T	b_T	a_T	b_T	a_T	b_T	a_T	b_T
25	0	1.000	0	1.000	0	1.000	0	1.000
60	3.9	0.955	-5.1	0.969	-14.0	1.217	-13.5	1.380
100	10.3	0.876	-13.0	1.000	-31.0	1.476	-30.3	1.894
150	16.2	0.792	-21.3	0.989	-46.4	1.687	(-50.0)	(2.381)
200	(23.3)	(0.711)	(-30.2)	(0.981)	(167.0)	(2.020)	(-70.0)	(2.960)

Note that values in parentheses were estimated by extrapolation from lower temperatures

To calculate the change in free energy they used the following equation:

$$\Delta G_{T_2}^0 = \Delta G_{T_1}^0 + \Delta C_p^0 \int_{T_1}^{T_2} \Delta T - \Delta S_{T_1}^0 \Delta T - T_2 \Delta C_p^0 \int_{T_1}^{T_2} \ln \frac{T_2}{T_1} \quad (11.9)$$

To calculate the value of $\Delta C_p^0 \int_{T_1}^{T_2}$ the average value of C_p^0 between T_1 and T_2 for the ion in question is needed. This value is easily obtained from the entropy by the following equation:

$$\overline{C_p^0} \int_{298}^{T_2} = \frac{\overline{S}_{T_2}^0 - \overline{S}_{298}^0}{\ln(T_2/298)} \quad (11.10)$$

Combination of Equations 11.7 and 11.10 give the average value of the heat capacity based upon the coefficients given by Criss and Cobble.

It is important to remember that the values required for the calculation of the free energy at elevated temperature given in Equation 11.8 are the change of the individual thermodynamic quantities. Thus to calculate the free energy of OH^- at an elevated temperature, using the following chemical equation:



the value of the free energy and entropy at 298 K and the average value of the heat capacity from 298 K to T_2 are needed for H_2 , O_2 , and H^+ . For elements, these values are readily obtained from tables; however, for H^+ the values of the heat capacity and entropy are not tabulated. Criss and Cobble give the entropy of H^+ at various temperatures as tabulated values and using Equation 11.10, the value of the heat capacity for H^+ can be calculated. It is important to note that the free energy of H^+ is defined as 0 at all temperatures.

Using the above equations and interpolating between 60° and 100° C to obtain values of a and b at 75° C, the free energy of the species of interest at 75° C were obtained.

11.5 V - The use of Kramers-Kronig Relationships to Validate Impedance Data

Kramers-Kronig transforms have been used by several researchers to test the validity of impedance data. The derivation of the Kramers-Kronig transforms is based upon the fulfillment of four general conditions as stated by MacDonald[56]:

1. *Causality*. The response of the system is due only to the perturbation applied and does not contain significant components from spurious sources.
2. *Linearity*. The perturbation/response of the system is described by a set of linear differential equations. Practically, this condition requires that the impedance be independent of the magnitude of the perturbation.
3. *Stability*. The system must be stable in the sense that it returns to its original state after the perturbation is removed.
4. The impedance must be finite valued at $0 < \omega < \infty$.

If the above conditions are true, the following equations are also true and make up the content of the Kramers-Kronig transforms:

$$Z'(\omega) - Z'(\infty) = \frac{2}{\pi} \int_0^{\infty} \frac{xZ''(x) - \omega Z''(\omega)}{x^2 - \omega^2} dx \quad (11.12)$$

$$Z'(\omega) - Z'(0) = \frac{2\omega}{\pi} \int_0^{\infty} \left[\frac{\omega}{x} Z''(x) - Z''(\omega) \right] \frac{1}{x^2 - \omega^2} dx \quad (11.13)$$

$$Z''(\omega) = -\frac{2\omega}{\pi} \int_0^{\infty} \frac{Z'(x) - Z'(\omega)}{x^2 - \omega^2} dx \quad (11.14)$$

$$\phi(\omega) = \frac{2\omega}{\pi} \int_0^{\infty} \frac{\ln|Z(x)|}{x^2 - \omega^2} dx \quad (11.15)$$

In these equations, Z' refers to the real part, Z'' to the imaginary part, and ϕ to the phase angle of the impedance.

These equations allow calculation of the imaginary part of the impedance using only the real part of the impedance and the calculation of the real part of the impedance using only the imaginary part. Using these relationships, one can compare the real part of the impedance with the real part calculated by the Kramers-Kronig transforms and the imaginary part with the calculated imaginary part.

Figure 11.6 shows the real and imaginary data with associated transforms for a solution containing only cobalt at -0.8 V vs. SCE. For both the real and imaginary parts, the transformed data closely mirror the experimental data, which proves the validity of the data. The deviation observed for the real part transform from the experimental real data comes from inaccuracies in determining $Z'(\infty)$ or $Z'(0)$ needed to calculate the transform as indicated in Equations 11.12 and 11.13.

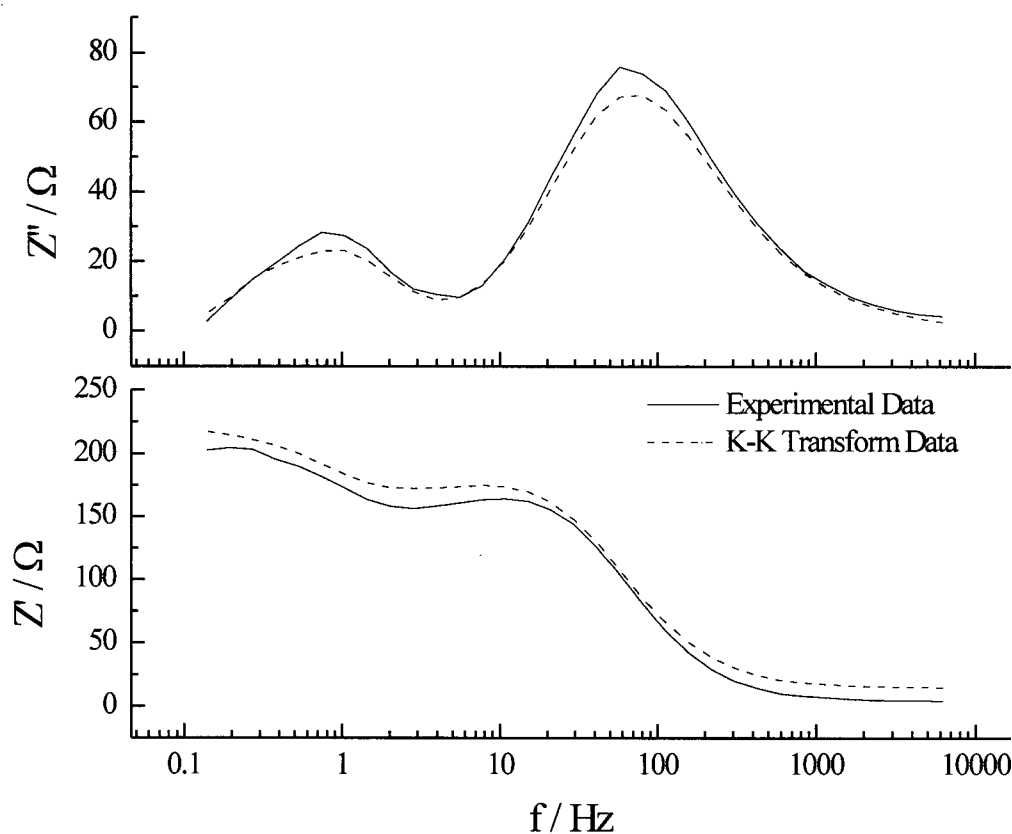


Figure 11.6 Kramers-Kronig transform of impedance data. Conditions: 0.01 mol/L Co, 2.4 mol/L MgSO_4 , 75°C, 1600 RPM, -0.8 V vs. SCE.

11.6 VII - Derivation of Partially Blocked Electrode Impedance

11.6.1 Derivation

At the surface of the electrode, the flux is related to the region of the electrode by the following equation:

$$-D \frac{\partial c}{\partial x} = J = \begin{cases} J_1 & \text{if } x = 0, (y, z) \in S_1 \\ J_2 & \text{if } x = 0, (y, z) \in S_2 \end{cases} \quad (11.16)$$

where S1 and S2 represent the active and inactive areas of the electrode as represented in Figure 6.28. From this figure, the following equations represent diffusion:

From ($l^* \leq x \leq l; 0 \leq r \leq R$)

$$\begin{aligned} \frac{\partial c}{\partial t} &= D \frac{\partial^2 c}{\partial x^2} \\ c &= c^b \text{ if } t = 0, \text{ or } x = l \\ c &= c^* \text{ if } x = l^* \end{aligned} \quad (11.17)$$

and from ($0 \leq x \leq l^*; 0 \leq r \leq R$)

$$\begin{aligned} \frac{\partial c}{\partial t} &= D \left[\frac{\partial^2 c}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) \right] \\ c &= c^b \text{ if } t = 0 \\ \frac{\partial c}{\partial r} &= 0 \text{ if } r = 0, \text{ or } r = R \\ c &= c^* \text{ if } x = l^* \end{aligned} \quad (11.18)$$

Equating the average flux in the x direction at $x = l^*$ gives the following equation:

$$DR^{-2} \int_0^R 2r \left(\frac{\partial c}{\partial x} \right)_{l^*} dr = D \left(\frac{\partial c}{\partial x} \right)_{l^*} = j^* \quad (11.19)$$

Now, transforming Equation 11.17 to the Laplace plane, solving for $c = c^*$ and differentiating with respect to x at $x = l^*$ gives:

$$\begin{aligned} \bar{j}^* &= (\bar{c}^* - c^b / s) D \alpha \coth[\alpha(l - l^*)] \\ &\text{with } \alpha = \sqrt{s/D} \end{aligned} \quad (11.20)$$

Solution of Equation 11.18 is more difficult. To determine the solution, first the concentration and fluxes must be converted to their average values. i.e.:

$$\begin{aligned}
 \langle J_1 \rangle &= a^{-2} \int_0^a 2rJ_1 dr \\
 \langle J_2 \rangle &= (R^2 - a^2)^{-1} \int_a^R 2rJ_2 dr \\
 \langle c_1^0 \rangle &= a^{-2} \int_0^a 2rc_{x=0} dr \\
 \langle c_2^0 \rangle &= (R^2 - a^2)^{-1} \int_a^R 2rc_{x=0} dr
 \end{aligned}
 \tag{11.21}$$

Transforming Equation 11.18 using the average values obtained in Equation 11.21 and integrating the resulting equations from 0 to a and from a to R , the following system of differential equations is produced:

$$\begin{aligned}
 \frac{\partial \langle c_1 \rangle}{\partial t} &= \frac{2aD}{R^2} \left(\frac{\partial c}{\partial r} \right)_{r=a} + D \frac{\partial^2 \langle c_1 \rangle}{\partial x^2} \\
 \frac{\partial \langle c_2 \rangle}{\partial t} &= -\frac{2aD}{R^2} \left(\frac{\partial c}{\partial r} \right)_{r=a} + D \frac{\partial^2 \langle c_2 \rangle}{\partial x^2}
 \end{aligned}
 \tag{11.22}$$

with the following boundary and initial conditions:

$$\left. \begin{aligned} \langle c_1 \rangle &= (1-\theta)c^b \\ \langle c_2 \rangle &= \theta c^b \end{aligned} \right\} t = 0
 \tag{11.23}$$

$$\left. \begin{aligned} \langle c_1 \rangle &= (1-\theta)c^* \\ \langle c_2 \rangle &= \theta c^* \end{aligned} \right\} t > 0, x = l^*
 \tag{11.24}$$

$$\left. \begin{aligned} -D \frac{\partial \langle c_1 \rangle}{\partial x} &= \langle J_1 \rangle \\ -D \frac{\partial \langle c_2 \rangle}{\partial x} &= \langle J_2 \rangle \end{aligned} \right\} t > 0, x = 0
 \tag{11.25}$$

where

$$\theta = \frac{\sigma}{1+\sigma}
 \tag{11.26}$$

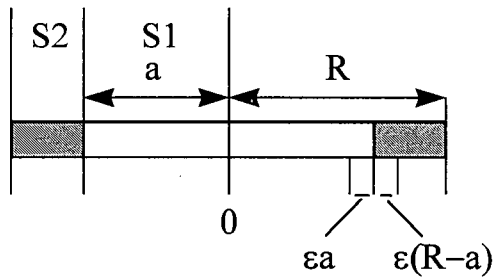


Figure 11.7 Schematic diagram of the electrode surface.

As shown in Figure 11.7, the electrode surface can be considered as divided into two regions: region S1, the active area of the electrode and region S2 the inactive area of the electrode. The value $\langle c_1 \rangle / (1-\theta)$ represents the mean concentration in a plane parallel to and separated by the distance x from the electrode surface in region S1 and $\langle c_2 \rangle / \theta$ represents the

concentration in the region S2. In Equation 11.22, the term $D(\partial c / \partial r)_{r=a}$ represents the flux from region S2 to region S1. To approximate this flux, Gueshi's approach was used[74].

The flux between region S1 and region S2 in the x - plane can be considered proportional to the difference between the mean concentrations in region S1 and S2. Thus, this problem can be treated as a steady-state radial diffusion in a cylinder. The mean concentrations are found at points inside and outside of the cylindrical plane at $r = a$: for region S1 at εa and for region S2 at $\varepsilon(R-a)$, with the parameter ε determined from experiments. This is depicted in Figure 11.7. Therefore:

$$D \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) \right] = 0 \quad (11.27)$$

with

$$\begin{aligned} r &= a + \varepsilon(r - a), c = \langle c_2 \rangle / \theta \\ r &= a - \varepsilon a, c = \langle c_1 \rangle / (1 - \theta) \end{aligned} \quad (11.28)$$

Equation 11.27 can be solved using the boundary conditions listed in 11.28 to give:

$$D \frac{\partial c}{\partial r} = \frac{D}{a \theta \ln(1 + \gamma / \sqrt{1 - \theta})} (\langle c_2 \rangle - \sigma \langle c_1 \rangle) \quad (11.29)$$

where

$$\gamma = \varepsilon / (1 - \varepsilon) \quad (11.30)$$

Substituting Equation 11.29 in Equation 11.22, the following equations result:

$$\begin{aligned} \frac{\partial \langle c_1 \rangle}{\partial t} &= D \frac{\partial^2 \langle c_1 \rangle}{\partial x^2} + W \frac{(\langle c_2 \rangle - \sigma \langle c_1 \rangle)}{1 + \sigma} \\ \frac{\partial \langle c_2 \rangle}{\partial t} &= D \frac{\partial^2 \langle c_2 \rangle}{\partial x^2} - W \frac{(\langle c_2 \rangle - \sigma \langle c_1 \rangle)}{1 + \sigma} \end{aligned} \quad (11.31)$$

where

$$W = 2D(1 + \sigma)^2 R^{-2} \sigma^{-1} / \ln[1 + \gamma \sqrt{1 + \sigma}] \quad (11.32)$$

Solving the set of differential equations in Equation 11.31 with the boundary conditions listed in Equations 11.23 to 11.26, the following expressions for the flux at $x = l^*$ and the concentration at $x = 0$ are found in the Laplace plane:

$$\bar{j}^* = (\bar{c}^* - c^b / s) D \alpha \tanh(\alpha l^*) + (1 + \sigma)^{-1} [\langle \bar{J}_1 \rangle + \sigma \langle \bar{J}_2 \rangle] / \coth(\alpha l^*) \quad (11.33)$$

$$\begin{aligned} \langle \bar{c}_1 \rangle - c^b / s &= \frac{\bar{c}^* - c^b / s}{\coth(\alpha l^*)} + \frac{\left[(\langle \bar{J}_1 \rangle + \sigma \langle \bar{J}_2 \rangle) \frac{\tanh(\alpha l^*)}{\alpha D} + \sigma (\langle \bar{J}_1 \rangle - \langle \bar{J}_2 \rangle) \frac{\tanh(\beta l^*)}{\beta D} \right]}{(1 + \sigma)} \end{aligned} \quad (11.34)$$

$$\langle \bar{c}_2^0 \rangle = \langle \bar{c}_1^0 \rangle + (\langle \bar{J}_2 \rangle - \langle \bar{J}_1 \rangle) \frac{\tanh(\beta l^*)}{\beta D} \quad (11.35)$$

where

$$\beta = \sqrt{(s + w) / D} \quad (11.36)$$

Eliminating c^* and j^* from Equations 10.33, 10.34 and Equation 10.20 gives:

$$\langle \bar{c}_1^0 \rangle - c^b / s = [\langle \bar{J}_1 \rangle (\bar{H}_1 + \sigma \bar{H}_2) + \sigma \langle \bar{J}_2 \rangle (\bar{H}_1 - \bar{H}_2)] (1 + \sigma)^{-1} \quad (11.37)$$

where H_1 and H_2 are given in Section 6.2.6.2.

To calculate the impedance, the following assumptions must be made.

1. Faradaic processes only occur in the region S1, thus:

$$J_F \Big|_{S1} \neq 0 \text{ in } S1 \\ J_F \Big|_{S2} = 0 \text{ in } S2 \quad (11.38)$$

2. In addition to faradaic processes, the current includes contributions from double layer charging and adatom capacity, thus:

$$I = zFJ + C_{dl} d\eta / dt \quad (11.39)$$

$$J = \begin{cases} J_F + J_{ad} = J_1 & \text{in } S1 \\ J_{ad} = J_2 & \text{in } S2 \end{cases} \quad (11.40)$$

with

$$zFJ_{ad} = C_{ad} d\eta / dt \quad (11.41)$$

The average admittance density of the total surface is defined by:

$$\bar{Z}^{-1} = R^{-2} \int_0^R 2r (\partial \bar{I} / \partial \bar{\eta}) dr \quad (11.42)$$

Assuming that C_{dl} and C_{ad} do not vary over the surface of the electrode and substituting local concentrations for average concentrations in S1, Equation 10.42 can be written as:

$$\bar{Z}^{-1} = zF(1 + \sigma)^{-1} [\partial \langle \bar{J}_1 \rangle + \sigma \partial \langle \bar{J}_2 \rangle] / \partial \bar{\eta} + sC_{dl} \quad (11.43)$$

Taking,

$$\frac{\partial \bar{c}_1^0}{\partial \bar{\eta}} = \frac{zF\bar{c}_{ss}^0}{RT} \quad (11.44)$$

from Nearst equilibrium, combination of Equations 10.35 to 10.44 gives the equations listed in Section 6.2.6.2.

11.6.2 Code for Simulation of Impedance

The following code calculates the impedance spectrum for a partially blocked electrode as outlined in Section 6.2.6.2. This program is written in C++ as this language employs operator overloading and thus can be used for complex arithmetic.

imped.cpp

```
#include <stdlib.h>
#include <stdio.h>
#include <math.h>
#include <complex.h>

double      R=8.314,           //the universal gas constant
            T=348,             //the temperature
            z=2,               //the number of electrons transferred
            F=96500,           //Faraday's number

            D=4.25e-6,         //the diffusion coefficient
            l=1.19e-3,         //distance of linear diffusion
            W,                 //a variable indicative of lateral diffusion
            Ra=20e-3,          //radius of the deposition zone
            lstar=1.19e-3,     //distance of mixed diffusion
            c0ss=5e-7,         //concentration of cobalt at the surface
            sig=1,             //ratio of active to inactive surface area
            Cad=0,             //adsorption pseudo-capacitance
            Cdl=3e-6,          //double layer capacitance
            a=0.1963;          //surface area of the electrode

complex Zfunc(double freq)     //function which calculated the impedance
{
    complex H1, H2, ZN, Zsig, s, Z_1;
    double rt;

    s=complex(0,2*M_PI*freq);

    H1= 1/sqrt(D*s)*tanh(l*sqrt(s/D));
    H2= 1/sqrt(D*(s+W))*tanh(lstar*sqrt((s+W)/D));
    rt= R*T/(z*z*F*F*c0ss);
    ZN= rt*H1;
    Zsig= rt*H2;
    Z_1=1/(ZN+sig*Zsig)+1/(1/(s*Cad)+ZN/(s*sig*Zsig*Cad))+s*Cdl;

    return 1/Z_1;
}

void main(void)               //main program which calls the impedance function
                              //and stores impedance spectra in a file
```

```
{
    FILE *fp;
    int i;
    complex Z;
    double freq, fmax=65000, fmin=0.1, step;

    //calculation of W

    W=2*D*pow((1+sig)/Ra,2)/(sig*log(1+.25*sqrt(1+sig)));

    fp=fopen("c:\\thesis\\c\\imp_dat.dat","w");
    step=(log(fmax)-log(fmin))/50.0;
    for(i=1;i<=50;i++)
    {
        freq=exp(log(fmax)-i*step);
        Z=Zfunc(freq);
        fprintf(fp,"%lf    %lf    %lf\n",freq, 4.5+real(Z)/a, -imag(Z)/a);
    }
    fclose(fp);
    printf("\n");
}
```

11.7 VIII - Calculation of Surface Concentrations

11.7.1 Derivation

Using the set of equations outlined in Section 7.1, the surface concentrations of the species of interest can be calculated as a function of the surface concentration of protons. Furthermore, the surface concentration of protons can be shown to be the root of the proton flux equation.

The following equations show how all fluxes and surface concentrations are a function of the surface concentration of protons.

Calculate the surface concentration of the hydroxyl ion using the equilibrium equation,

$$C_{OH^-}^s = \frac{K_w}{C_{H^+}^s} \quad (11.45)$$

and then rearrange Equations 6.18-6.27 to give the surface concentration of cobalt,

$$C_{Co^{2+}}^s = - \frac{\frac{i_{Co}}{2F} - \alpha_{Co^{2+}} C_{Co^{2+}}^b - \alpha_{CoOH^+} C_{Co^{2+}}^b \frac{K_w}{C_{H^+}^b K_{CoOH^+}}}{\alpha_{Co^{2+}} + \alpha_{CoOH^+} \frac{K_w}{C_{H^+}^s K_{CoOH^+}}} \quad (11.46)$$

and the surface concentration of zinc:

$$C_{Zn^{2+}}^s = - \frac{\frac{i_{Zn}}{2F} - \alpha_{Zn^{2+}} C_{Zn^{2+}}^b - \alpha_{ZnOH^+} C_{Zn^{2+}}^b \frac{K_w}{C_{H^+}^b K_{ZnOH^+}}}{\alpha_{Zn^{2+}} + \alpha_{ZnOH^+} \frac{K_w}{C_{H^+}^s K_{ZnOH^+}}} \quad (11.47)$$

Using the equilibrium equations, the concentrations of the mono-hydroxide species can be determined as:

$$C_{CoOH^+}^s = \frac{C_{Co^{2+}}^s C_{OH^-}^s}{K_{CoOH^+}} \quad (11.48)$$

$$C_{ZnOH^+}^s = \frac{C_{Zn^{2+}}^s C_{OH^-}^s}{K_{ZnOH^+}} \quad (11.49)$$

Calculate the fluxes for the mono-hydroxide species and for the hydroxide ion:

$$N_{CoOH^+} = \alpha_{CoOH^+} (C_{CoOH^+}^b - C_{CoOH^+}^s) \quad (11.50)$$

$$N_{ZnOH^+} = \alpha_{ZnOH^+} (C_{ZnOH^+}^b - C_{ZnOH^+}^s) \quad (11.51)$$

$$N_{OH^-} = \alpha_{OH^-} (C_{OH^-}^b - C_{OH^-}^s) \quad (11.52)$$

$$N_{H^+} = \alpha_{H^+} (C_{H^+}^b - C_{H^+}^s) \quad (11.53)$$

Substituting the fluxes into the hydrogen flux equation gives:

$$-\frac{i_{H_2}}{F} + N_{H^+} - N_{OH^-} - N_{CoOH^+} - N_{ZnOH^+} = 0 \quad (11.54)$$

The only surface concentration that Equation 11.54 is a function of is the surface concentration of H^+ . Thus this equation can be solved numerically for this concentration and the concentration of the other species of interest can be calculated from this concentration by the above equations.

11.7.2 Computer Code

The computer code for calculating the interfacial concentrations of the species is broken into two programs, the first program "conct.c" contains the calculation, and calls an external function "zbrent". The second program is "zbrent.c" and contains the code for finding the root of a non-linear equation by Brent's method as outlined in the book "Numerical Recipes in C"[78].

Conct.c

```
#include <math.h>
#include <stdio.h>
#include "nrutil.h"

#define NUMEL 6 //the number of elements
#define R 8.314 //the universal gas constant
#define F 96500 //Faraday's number

enum{co=1, cooh, zn, znoh, h, oh};

extern double zbrent(double (*func)(double), double x1, double x2, double tol);

double
    *Cb,          //bulk concentration of species in mol/cm3
    *Cs,          //surface concentration of species in mol/cm3
    *D,           //diffusion coefficients in cm2/s
    *a,           //Levich constant
```

```

Kcooh =5.6e-8,      //equilibrium constant  $\text{CoOH}^+=\text{Co}^{2+}+\text{OH}^-$ 
Kznoh =8.0e-11,    //equilibrium constant  $\text{ZnOH}^+=\text{Zn}^{2+}+\text{OH}^-$ 
Kw     =1.3e-19,    //equilibrium constant  $\text{H}_2\text{O}=\text{H}^++\text{OH}^-$ 

omega =1600*M_PI/30.0,      //rotation speed in rad/s
nu     =0.0158,             //kinimatic viscosity in cm2/s

ico,           //cobalt current density
ih,            //hydrogen current density
izn=0,         //zinc current density

T      =348;      //temperature in K

//The following function takes the surface concentration of hydrogen
//as it's input, and returns 0 when this concentration corresponds
//to the correct current density

double FC(double C)
{
    double      Ncooh, Nznoh, Nh, Noh, //Fluxes of species
               y;

    Cs[h] = C;      //set the input parameter equal to the H conc.
    Cs[oh] = Kw/Cs[h]; //and calculate COH

    //expressions for CCo and CZn at the surface

    Cs[co]=-(ico/(2.0*F)-a[co]*Cb[co]-a[cooh]*Cb[co]*Kw/(Cb[h]*Kcooh))/
            (a[co]+a[cooh]*Kw/(Cs[h]*Kcooh));
    Cs[zn]=-(izn/(2.0*F)-a[zn]*Cb[zn]-a[znoh]*Cb[zn]*Kw/(Cb[h]*Kznoh))/
            (a[zn]+a[znoh]*Kw/(Cs[h]*Kznoh));

    Cs[cooh]=Cs[co]*Cs[oh]/Kcooh; //equilibrium equations
    Cs[znoh]=Cs[zn]*Cs[oh]/Kznoh;

    Ncooh=a[cooh]*(Cb[cooh]-Cs[cooh]); //calculate fluxes
    Nznoh=a[znoh]*(Cb[znoh]-Cs[znoh]);
    Noh=a[oh]*(Cb[oh]-Cs[oh]);
    Nh=a[h]*(Cb[h]-Cs[h]);

    y=-ih/F+Nh-Noh-Ncooh-Nznoh; //hydrogen flux equation

    return y;
}

void main(void)
{
    int i,yn=0;
    double cx,dx,xmax,xmin,tol;
    FILE *fp;

```

```

Cb=dvector(1,NUMEL);
Cs=dvector(1,NUMEL);
D=dvector(1,NUMEL);
a=dvector(1,NUMEL);

Cb[co]=1e-5;          //set bulk concentrations
Cb[zn]=1e-5;
Cb[h]=1e-7;
Cb[oh]=Kw/Cb[h];
Cb[cooh]=Cb[oh]*Cb[co]/Kcooh;
Cb[znoh]=Cb[oh]*Cb[zn]/Kznoh;

D[co]=.425e-5;        //set diffusion coefficients
D[cooh]=.425e-5;
D[zn]=.425e-5;
D[znoh]=.425e-5;
D[h]=2.55e-4;
D[oh]=1.63e-4;

xmax=1e-7;            //set interval containing root
xmin=1e-11;
tol=1e-30;

                        //calculate Levich constants
for(i=1;i<=NUMEL;i++)
    a[i]=0.62*pow(D[i],2.0/3.0)*pow(nu,-1.0/6.0)*sqrt(omega);

do{
    printf("\nCobalt Current: ");
    scanf("%lf",&ico);
    printf("\nHydrogen Current: ");
    scanf("%lf",&ih);
    printf("\nGenerate plot data (1=yes): ");
    scanf("%i",&yn);

    ico=ico/10000.0;    //convert A/m2 -> A/cm2
    ih=ih/10000.0;

    if(yn)              //generate XY data for FC
    {
        fp=fopen("moddat.dat","w");
        dx=(xmax-xmin)/100.0;
        cx=xmin;
        for(i=1;i<=100;i++)
        {
            fprintf(fp,"\n%le    %le",cx,FC(cx));
            cx=cx+dx;
        }
        fclose(fp);
    }

    cx=zbrent(FC,xmax,xmin,tol); //calculate root

```

```
        printf("\n%le\n\n",cx);
        FC(cx);

        for(i=1;i<=NUMEL;i++) //print concentrations
            printf("\n%le",Cs[i]/Cb[i]); //covert to mol/L

        printf("\n");
    }while (ico>=0);

    free_dvector(Cb,1,NUMEL);
    free_dvector(Cs,1,NUMEL);
    free_dvector(D,1,NUMEL);
    free_dvector(a,1,NUMEL);
}
```

zbrent.c

```
#include <math.h>
#include <stdio.h>
#define ITMAX 100
#define EPS 3.0e-8

/*This subroutine has been taken from Numerical Recipes in C,
  2nd edition, page 361 */

double zbrent(double (*func)(double), double x1, double x2, double tol)
{
    int iter;
    double a=x1,b=x2,c=x2,d,e,min1,min2;
    double fa=(*func)(a), fb=(*func)(b),fc,p,q,r,s,tol1,xm;

    if((fa>0.0&&fb>0.0)|| (fa<0.0&&fb<0.0))
        printf("Root must be bracketed in zbrent");
    fc=fb;
    for(iter=1;iter<=ITMAX;iter++)
    {
        if((fb>0.0&&fc>0.0)|| (fb<0.0&&fc<0.0))
        {
            c=a;
            fc=fa;
            e=d=b-a;
        }
        if(fabs(fc)<fabs(fb))
        {
            a=b;
            b=c;
            c=a;
            fa=fb;
            fb=fc;
            fc=fa;
        }
        tol1=2.0*EPS*fabs(b)+0.5*tol;
        xm=0.5*(c-b);
        if(fabs(xm)<=tol1||fb==0.0) return b;
        if(fabs(e)>=tol1&&fabs(fa)>fabs(fb))
        {
            s=fb/fa;
            if(a==c)
            {
                p=2.0*xm*s;
                q=1.0-s;
            } else
            {
                q=fa/fc;
                r=fb/fc;
                p=s*(2.0*xm*q*(q-r)-(b-a)*(r-1.0));
                q=(q-1.0)*(r-1.0)*(s-1.0);
            }
        }
    }
}
```

```
        if(p>0.0) q= -q;
        p=fabs(p);
        min1=3.0*xm*q-fabs(tol1*q);
        min2=fabs(e*q);
        if(2.0*p<(min1<min2?min1:min2))
        {
            e=d;
            d=p/q;
        }else
        {
            d=xm;
            e=d;
        }
    } else
    {
        d=xm;
        e=d;
    }
    a=b;
    fa=fb;
    if(fabs(d)>tol1)
        b+=d;
    else
        b+=(xm>0.0?fabs(tol1):-fabs(tol1));
    fb=(*func)(b);
}
printf("Maximum number of iterations exceeded in zbrent");
return 0.0;
}
```