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Authors
Hessami, S.
Tobias, C.W.

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S. Hessami* and C.W. Tobias
(Ph.D. Thesis)

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On the Role of Mass-Transport in Electrodeposition of Nickel-Iron Alloys

Sholeh Hessami

(Ph.D. Thesis)

Department of Chemical Engineering
University of California

and

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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Chapter 1: Thesis Introduction

Rapid technological advances require an ever increasing number of new materials with precisely controlled properties. Thin films of alloys have emerged as critical components in various applications. Many requirements for appearance, corrosion and wear resistance, hardness, strength, photovoltaic, and magnetic applications which may not be met by pure elements can be satisfied by their binary or higher alloys. The ability to codeposit elements with large differences in vapor pressure, and to obtain non-equilibrium phase structures with an accurate control of composition, morphology, and uniformity of alloy deposits have made electrodeposition a valuable technique. Low capital and operating costs, and a high rate of deposition are additional advantages of electrodeposition compared to many alternative methods.

An extensive survey in the field of alloy electrodeposition has been compiled by Brenner (1963). Srivastava and Mukerjee (1976) have provided a review of recent developments in electrodeposition of binary alloys. Christie (1981) and Romankiw (1985) have described the applications of electroplating in the electronic industry. Many examples of alloy systems and the requirements for magnetic recording technology have been reviewed by Romankiw (1975), Howard (1986), and Brusic and Horkans (1990).

Earlier in our laboratory, Verbrugge and Tobias (1986) investigated periodic electrodeposition of cadmium-telluride which is a wide band-gap II-VI compound with applications in photovoltaic devices. The effects of periodic plating on alloy morphology and composition were examined by experimental and theoretical methods. The present area of research is the electrodeposition of binary alloys of nickel and iron which are
extensively used in magnetic recording technology. Magnetic properties such as high permeability and magnetization, low coercivity, and magnetostriction are very sensitive to alloy composition and are optimal at 19 weight percent iron (permalloy). The ability to control the uniformity of alloy composition and thickness over the topography of recording heads is crucial to their performance (Powers and Romankiw, 1972).

Despite the extensive use of nickel-iron, the mechanism of codeposition is not well understood. The interactions occurring during codeposition are such that nickel deposition is inhibited in the presence of iron, and the resulting alloy deposit has a much higher iron to nickel ratio than the electrolyte. This type of interactive deposition is an example of what has been termed anomalous codeposition, which is also used in describing electrocodeposition of iron group elements (iron, cobalt, and nickel) with each other, or with zinc, tin, lead, and cadmium.

In chapter 2 of this thesis, a critical review of the literature is presented. Various interpretations and proposed mechanisms for the anomalous deposition of the iron-group alloys, particularly nickel-iron, is discussed. The major objectives of this review are to provide unambiguous definitions for various codeposition schemes, including the anomalous deposition itself, reflect on some of the more widely accepted hypothesis describing this phenomenon, and summarize the more recent results of other investigators in the field.

To elucidate the electrodeposition mechanism of magnetic alloys, a mathematical model is developed in chapter 3. The model is applied to a rotating disk electrode system, with well understood hydrodynamics, and incorporates homogeneous reactions of metal-
hydroxide complexes. The effects of current density, agitation and bulk pH on alloy composition and current efficiency are simulated and compared to experimental results. In chapter 4, the model is further used to investigate the effect of buffering agents which are commonly used in electroplating baths.

The importance of surface concentration of various ionic species at the electrode surface has been recognized in electrodeposition and other electrochemical processes. Our understanding of the mechanism of electrode processes depends on the accurate measurement of these concentrations. The interfacial value of pH is particularly important for electrodeposition of the iron-group alloys. In chapters 5 and 6, an in-situ, non-intrusive technique for surface pH measurement is investigated by theoretical and experimental methods. A rotating ring electrode, monitored at open-circuit potentiometrically, is used to assess the pH at the disk electrode. The two dimensional convective-diffusive transport of protons in the presence of metal-hydroxide complex ions and buffering agents is analyzed. The effects of supersaturation of dissolved hydrogen gas and the ohmic drop sensed by the ring electrode are described. This technique is then applied to the in-situ pH measurement at the disk during deposition of nickel, iron and nickel-iron, which all involve concurrent hydrogen evolution. The method is also shown to be a rapid, in-situ technique for current efficiency measurement of nickel deposition.

References


Chapter 2: Review of Previous Research on Anomalous Codeposition of Nickel-Iron

Introduction

Nickel-iron alloys can be easily electrodeposited from non-complexing chloride or sulfate salts since the standard reduction potentials of nickel and iron are less than two tenth of a volt apart (Vanysek, CRC 1986).

\[
\begin{align*}
\text{Fe}^{2+} + 2\text{e}^- &\rightarrow \text{Fe} & E^0 = -0.409 \text{ volts} \\
\text{Ni}^{2+} + 2\text{e}^- &\rightarrow \text{Ni} & E^0 = -0.23 \text{ volts}
\end{align*}
\]

Hydrogen reduction occurs simultaneously both during the deposition of pure nickel and iron, and their codeposition. Thermodynamically, the reduction of hydrogen ions is favored over both nickel and iron:

\[
\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 & E^0 = 0.00 \text{ volts}
\]

To achieve a reasonable current efficiency, typical plating baths are operated at a pH ranging from 2 to 4. The hydrogen reduction potential is further shifted to more negative values because of charge-transfer rate limitations. It is known that nickel-iron alloys form solid solutions (Gorbunova and Polukarov, 1967); the Gibbs free energy of alloy formation should shift the deposition potential of each component to slightly more positive values. Relative to deposition in the pure form, only slight changes have been reported in the iron overpotential during codeposition with nickel. In contrast, the presence of iron always increases the nickel polarization, in effect inhibiting the deposition of nickel. The iron to nickel ratio in the resulting alloy is much higher than that in the electrolyte, although iron is the less noble component \(^\dagger\).

\(\dagger\) Less noble means thermodynamically less favored for reduction.
Electrodeposition of nickel-iron is an example of what has been termed *anomalous codeposition* when iron group elements (iron, cobalt and nickel) are codeposited with each other, or with zinc, tin, lead, and cadmium (Brenner, Vol. I, p. 191).

**Interpretations and Proposed Mechanisms**

Attempts at identifying the mechanism of *anomalous codeposition* have been summarized by Brenner (1963), Dahms and Croll (1965), Hall (1983), and by Croll and Romankiw (1987). Widely known hypotheses include those of Glassstone and Symes (1927), Brenner (1963), Vagramyan and Fatueva (1963), Dahms and Croll (1965), Gorbunova and Polukarov (1967), Nicol and Philip (1976), and Romankiw (1987). The underlying cause for anomalous codeposition is usually attributed to an interfacial phenomenon, such as underpotential deposition, adsorption of addition agents, variations in double layer ionic activities, or film formation with blockage of the electrode surface. In the next section, we shall examine various interpretations of the phenomenon itself, and reflect on some of the hypotheses in detail.

**Previous Interpretations of Anomalous Codeposition**

Considering the volume of publications concerned with electrodeposited alloys of the iron group, it is surprising that no formal definition for *anomalous codeposition* has been proposed. This lack of a definition has caused some confusion because the term anomalous codeposition has been applied to a variety of different phenomena. For example, alloys of nickel, iron and nickel with each other, and with zinc, are considered anomalous. However, while the electrode kinetics for the single metal deposition of nickel, iron and cobalt are similar, that of zinc is considerably faster (e.g. Erdey-Gruz,
Tanaka and Tamamushi). In addition, it is known that the mutual alloys of nickel, iron, and cobalt form solid solutions, but their electrodeposited alloys with zinc have various phases (Gorbunova et al.). There is also some confusion over the meaning of the term anomalous codeposition. Some researchers have described it as "the preferential deposition of the less noble metal" (Brenner, Vol. I, p.77); the word "preferential" remaining undefined. While some workers have used preferential to imply a larger partial current (e.g. Brenner, Dahms and Croll), others have interpreted it as a shift of the reduction potential to more positive values beyond thermodynamic predictions (Nicol and Phillip, 1976). The other common description of anomalous codeposition has focused on the distribution of the alloy components between the solution and the solid phases. The ratio of the activities of the less noble component in the alloy to that in the bath has been defined as the distribution coefficient (Brenner, Vol. I, p. 110). Swathirajan and Mikhail (1989) in their studies of nickel-zinc-phosphorus alloys defined the same quantity as "anomalous ratio". Other researchers have also used the distribution coefficient of the less noble component as the criterion for anomalous codeposition (e.g. Higashi et al., Hall).

Definitions

To describe various codeposition schemes and to avoid any further ambiguities, we will define a few terms. In this review, preferential deposition will mean that the partial current of the less noble (LNC) is larger than that of the more noble component (MNC); the resulting alloy deposit will contain a higher percentage of the LNC than the MNC. We will call this the alloy composition criterion, $A_c$. The alternative criterion will be the distribution coefficient, $D_c$, where the activity of the LNC in the alloy is higher than in the solution. In the ensuing examples, we will examine these two commonly used criteria.
based on the thermodynamics, kinetics and mass-transport of the deposition process. It will be shown that neither of these criteria is sufficient to describe a truly anomalous codeposition process. The examples deal with alloy deposits which have the LNC as their major component; i.e. the \( A_c \) criterion is met. In all of the figures, the magnitude of the cathodic electrode potential is used.

**Non-Interactive Codeposition**

When the rate of deposition of each alloy component, or its partial current, as a function of the electrode potential is the same in both pure and alloyed states, no interactions are involved. Under these conditions, the less noble metal (LNC) can have a larger current which can be generated simply by a difference in the electrode kinetics. Figure 2.1 shows the relationship between the current density and electrode potential under Tafel kinetics. As seen in figure 2.1, different Tafel slopes can lead to a faster deposition rate of LNC above a threshold potential, \( V_T \). For simplicity, we have assumed that the two metal ions have comparable concentrations and cathodic rate-constants. Also above \( V_T \), the value of \( D_c \) exceeds unity because the content of LNC in the deposit is higher than in the electrolyte. This situation would be categorized as anomalous using either the alloy composition or distribution coefficients criteria. It is clear, however, that there is nothing anomalous about this example.

Another simple system which would be misinterpreted as anomalous, by applying the alloy composition criterion, is one in which the MNC is subject to mass-transport

---

\[ \text{Tafel kinetics refers to the following relationship between current density and the electrode potential:} \\
\log i = \log i_0 + (\alpha nF / RT) V \]
Non-Interactive Codeposition

(a) LNC (single, alloy) \[ [\text{LNC}] = [\text{MNC}] \text{ in solution} \]

(b) \[ D_c = \frac{[\text{LNC}]/[\text{MNC}] \text{ alloy}}{[\text{LNC}]/[\text{MNC}] \text{ solution}} \]

[Fig. 2.1: Differences in electrode kinetics.]
limitations. This is shown in figure 2.2a, where again preferential deposition occurs to the right of $V_T$. However, it is evident in figure 2.2b that $D_e$ for this system does not exceed one, and so the distribution coefficient will not categorize this as anomalous codeposition. Depending on the criterion used, workers may or may not consider this system as anomalous. Nevertheless, like the previous example, there is nothing anomalous about it.

**Interactive Deposition**

In the last two examples, the codeposition was assumed to be non-interactive; the alloy deposition current was a simple sum of single metal deposition currents, as observed in the alloys of nickel-copper, lead-tin, and nickel-cadmium among others. We have demonstrated that differences in the electrode kinetics or mass transport conditions can lead to preferential deposition (alloy composition criterion), and that the distribution coefficient criterion can be met by differences in the electrode kinetics. Clearly, such ideal systems should not be termed anomalous. In reality, many metals are found to strongly interact during codeposition. Interactions are manifest through a change in the polarization, i.e. the relationship between overpotential and current, of either or both elements. The alloy deposit could then contain more of the LNC than the case where no interactions were involved.

Non-idealities during codeposition are best identified by comparing changes in the partial current of a metal induced by the presence of the other alloy component. Swathirajan and Mikhail (1989) stated that the anomalous ratio, which is the same as $D_e$, is unity in the absence of interactions. Clearly, this is a conclusion that should be
Non-Interactive Codeposition

\[ \log(i) \]

LNC (single, alloy)

MNC (single, alloy)

\[ [\text{LNC}] = x \, [\text{MNC}] \text{ in solution} \]

\[ x > 1 \]

\[ V_T \]

(a)

XBL 9011-3594

Fig. 2.2: Effect of mass-transfer limitations.

\[ D_c = \frac{[\text{LNC}]/[\text{MNC}] \text{ alloy}}{[\text{LNC}]/[\text{MNC}] \text{ solution}} \]

\[ 1/x \]

\[ V_T \]

(b)
avoided. It is the enhancement or suppression of the partial currents in the presence of the other alloy component that should be considered. In this thesis, we call a codeposition process anomalous when kinetic interactions caused by the presence of the other component either hinder deposition of the more noble element and/or enhance that of the less noble component. The enhancement of the less noble component has to be beyond the positive thermodynamic shift of the potential caused by alloy or compound formation (Kroger, 1978).

The interactions lead to a variety of deposits as shown in figure 2.3. The alloy content of the LNC may be higher than 50% (i.e. preferential deposition or $A_c > 1$) and with distribution coefficients larger or smaller than one. It might be composed of mostly the MNC, but with a $D_c > 1$ which means the percentage of LNC in the deposit is higher than in the bath. It could also be richer in the MNC, as in the previous case, but have a $D_c < 1$. The main point is that while anomalous codeposition can lead to all of these scenarios, the reverse does not hold.

Types of Interactive Codeposition

To understand anomalous codeposition, i.e. the enhancement of the LNC or suppression of the MNC, the underlying interactions must be investigated. Interactions of the alloy components can affect the thermodynamics and kinetics of the discharge process, the solution phase chemistry, and various transport processes for each species. The combination of all of these effects can alter the current-potential relationship of the discharge process.
Interactive Codeposition

Non-Interactive Codeposition

Alloy Composition = \( A_c = \frac{[\text{LNC}]}{[\text{MNC}]} \) alloy

Distribution Coefficient = \( D_c = \frac{[\text{LNC}]}{[\text{MNC}]} \) alloy

\[ \frac{[\text{LNC}]}{[\text{MNC}]} \text{ solution} \]

Fig. 2.3: Binary alloys obtained by electrodeposition.
Underpotential Deposition (UPD) of the LNC

As a possible mechanism for anomalous codeposition, Nicol and Phillip (1976) proposed the underpotential deposition of the LNC. Figure 2.4 shows the underpotential deposition of a LNC onto a substrate of pure MNC. The thermodynamic reduction potential of the LNC is shifted to the more noble values (less negative). Nicol and Phillip suggested that since the work function of a LNC is lower than a MNC, the underpotential deposition (UPD) can continuously occur provided the alloy work function lies between those of the components.

The UPD phenomenon has been primarily observed in the zinc alloys, but not in the alloys of nickel, cobalt and iron with each other or with tin. Swathirajan (1987) reported a case of UPD in nickel-zinc alloys. In the small potential region where the UPD of zinc occurred, the zinc partial current was lower than that of nickel; preferential deposition did not occur. At higher currents, both nickel and zinc deposited with a significant overpotential and the partial current of zinc was larger than that of nickel. It is not clear, however, whether the partial current of nickel and zinc during codeposition are different than their pure case. In the context of our earlier discussion, we consider these zinc alloys anomalous if there are interactions during the codeposition which lead to an alloy containing a higher zinc (LNC) compared to what would be predicted from the pure component data. Mathias and Chapman (1987) in their studies of zinc-nickel have alluded to the intrinsically slower kinetics of nickel deposition compared to that of zinc. It is possible that the combination of different electrode kinetics and the UPD phenomenon cause the high zinc content in these alloy systems.
Interactive Deposition

Fig. 2.4: Under-potential deposition of LNC.
Change in the Apparent Polarization

Unlike zinc alloys, the components of the iron group alloys have very similar exchange current densities and Tafel slopes. In these systems, the polarization of one or both components are affected in the presence of the other component. A very qualitative and simplified schematic of these interactions are shown in figure 2.5. The overpotential for the reduction of LNC can become smaller in the presence of the MNC, as illustrated in figure 2.5a. This situation has been observed in codeposition of nickel-tin alloys (Brenner, Vol. II, p. 326). The other type of interaction, shown in figure 2.5b, involves a strong inhibition of the MNC which is mostly observed in the mutual alloys of nickel, cobalt and iron.

Anomalous Deposition of the Iron-Group Alloys and Suggested Mechanisms

As has been emphasized in the previous section, the appropriate criterion for anomalous codeposition is the interaction between the alloy components. Some of the confusion about the meaning of anomalous codeposition has been caused by comparing the magnitude of the partial currents of each alloy component. For example, Dahms and Croll (1965) electrodeposited nickel-iron from a solution containing equivalent amounts of nickel and iron salts. Their experimental results showed that the partial current of iron (LNC) was larger than that of nickel (MNC). More recently, Andricacos et al. (1988) electrodeposited nickel-iron from a bath with a much lower concentration of iron than nickel. They observed that the partial current of iron was below that of nickel and commented that "based on these data alone no anomaly is evident". Once again, it is the comparison between the partial currents in the pure and alloyed states that must be made,
Interactive Deposition

Fig. 2.5: (a) Enhancement of LNC in the presence of MNC.

(b) Suppression of MNC in the presence of LNC.
and not the alloy partial currents by themselves. During alloy deposition, the single metal deposition currents for nickel and iron do not just add up; the nickel discharge is inhibited in the presence of iron. The resulting nickel-iron alloys, in both studies, contained more iron than if there were no such interactions involved.

Dahms and Croll (1965) focused on the suppression of nickel during codeposition with iron. They hypothesized that a high surface pH caused by hydrogen evolution produces a ferrous hydroxide containing film which provides a barrier for the discharge of nickel, but does not hinder iron deposition. In a different study, Yunus et al. (1965) also proposed that a zinc hydroxide precipitate suppresses cobalt discharge during zinc-cobalt codeposition. Romankiw (1987) suggested that ferric ions present in nickel-iron baths form a ferric hydroxide precipitate and inhibit nickel deposition. Thermodynamically, however, ferric hydroxide can not exist at the electrode surface at the cathodic potential region of nickel-iron deposition (Pourbaix, 1974). None of the proposed films formed at the electrode surface have been directly observed. An indirect method to detect any film formation was devised by Higashi et al. (1981). While codepositing zinc-cobalt in an unstirred solution, they measured the resistance between a capillary probe and the electrode surface by a current interrupt technique. They concluded that at high currents where surface pH rise was large enough to form zinc hydroxide, the surface resistance increased, and the content of cobalt in the alloy became much smaller than in the solution. Whether or not such a rise in the surface pH is common to most plating conditions, and if it is the cause of anomalous codeposition will be addressed in chapters 2 and 3 of this work. At this point, it is important to note that the change in surface pH and the formation of a possible metal-hydroxide film is dependent on the applied current density, bulk pH, mass-transport conditions, and the presence of buffering
agents in the bath.

**Effects of Plating Parameters**

Many important properties such as hardness, appearance, corrosion resistance, electronic and magnetic characteristics, are strong functions of the alloy composition. Various plating parameters, in particular, applied current density, degree of agitation, concentration of metal ions, bulk pH, temperature, and anions affect the deposition process. As an example, the iron content of the nickel-iron deposit increases with the applied current or potential, reaches a maximum and decreases thereafter. There is additional complexity as a result of coupling among the plating variables. For instance, the effects of agitation and bulk pH on composition depend on the applied current density. While at low currents increasing agitation decreases the iron content of the alloy deposit, at higher currents agitation enhances the iron content.

The challenge and importance of controlling the alloy composition will become more apparent when deposition of nickel-iron for magnetic recording heads is considered. Magnetic properties of nickel-iron alloys are optimum at 19 weight percent iron. At this composition the alloy, also known as permalloy, will have high permeability and magnetization, low coercivity, and nearly zero magnetostriction (Romankiw and Thompson, 1975). These properties are very sensitive to the alloy composition. Over the entire complex topography of a recording head, and also throughout the plated film thickness, the iron content should remain within 18 to 20 weight percent. This small tolerance for composition variation is essential for the performance of the head (e.g. Powers and Romankiw, 1972).
In what follows, we shall examine recent investigations of the dependence of alloy composition and current efficiency on the solution chemistry and agitation. With the exception of a few classic papers, this brief review will consider only the literature from the late 1970's to present. The focus will be primarily on nickel-iron alloys, unless available investigations on other alloys are considered to be relevant. For a broader review, the reader should refer to the recent article by Srimathi et al. (1982) on the electrodeposition of binary magnetic alloys, complementing Brenner's monograph, which has an extensive reference list on various studies in the field.

**Effects of Metal Ions Concentration**

It is well known that the partial current of metal deposition increases with concentration of the metal ions in the bath. In interactive codeposition of two metals, increasing one metal ion concentration may affect other concurrent electrode reactions. In permalloy deposition, it is observed that the rate of nickel deposition is suppressed with addition of ferrous ions. As a result, the enrichment of the alloy with iron is much larger than the hypothetical case where nickel deposition is not affected by the ferrous concentration. Wong, Andricacos, and Romankiw (1989) quantified this phenomenon and observed that increasing the ferrous concentration increased the partial current of iron and, at low potentials that of hydrogen, but reduced the partial current of nickel significantly. In an all-chloride bath, the inhibition of nickel was large enough to compensate the increase in partial current of iron. The resulting current efficiency of alloy deposition decreased. Raman et al. (1985) also reported a decrease in the current efficiency with the addition of ferrous salt to their mixed sulfate-chloride bath. Grande and Talbot (1989) reported that in their all sulfate bath, and at a given fixed electrode potential, increasing
Chapter 2

$C_{Fe^{+2}}$ resulted in a decrease in the total current density. They attributed this decrease to a reduction of hydrogen partial current, but it is possible that the potential range at which the reduction was observed was in the metal deposition region. In the absence of current efficiency data, it is not clear whether the addition of ferrous ions in this potential range has an effect on nickel and/or iron deposition reactions. Deligianni and Romankiw (1989) measured the pH close to the cathode during deposition of permalloy. They did not report any partial currents, but noticed that the addition of ferrous ions reduced the pH rise at the electrode surface.

Effects of bulk pH

It has been postulated that electrodeposition of iron, nickel, cobalt and zinc involves the discharge of a metal-hydroxide ion complex. Bockris, Drazic and Despic (1961) investigated the kinetics of deposition and dissolution of iron. They considered various mechanisms for the electrode reaction, and took into account hydrogen evolution with the corresponding rise in pH at the electrode surface. The mechanism most consistent with their experimental results showed that the exchange current density was proportional to $OH^-$ concentration, and that the discharge took place via a $FeOH^{+}$ ion. Raub (1976) observed that zinc overvoltage decreased with increasing pH, and suggested that hydrolysis products of zinc such as $ZnOH^+$ and $Zn(OH)_2$ deposit more readily than $Zn^{+2}$. Similarly, nickel electrodeposition studies of Matulis and Slizys (1964) showed that $NiOH^+$ was involved in the mechanism of cathodic reaction.

Although the value of pH may be different in the bulk than in the vicinity of the electrode surface, it is useful to study the effect of bulk pH on current efficiency, and in
the case of alloy deposition, on deposit composition. Glassstone and Symes (1927) observed that at low current densities, the more alkaline solution yielded a deposit with a high iron content, while at higher current densities the nickel content of the alloy was enriched. Horkans (1981) deposited nickel-iron from pH=2 and pH=3 baths in both chloride and sulfate media. The partial current of each metal increased in the higher pH bath, while the hydrogen evolution current decreased. The resulting composition of the alloy deposits showed a similar dependence on pH to that in the experiments of Glassstone and Symes. At low current densities, alloys obtained from pH=3 baths, had a higher iron content. At higher current densities, the percentage of iron decreased rapidly and was less than in the deposits obtained from pH=2 solutions. Studies by Clauss and Tremmel (1973) and by Nakamura and Hayashi (1985) on the codeposition of nickel-iron from a mixed bath of sulfate-chloride also support this dependence of the alloy composition on pH; however, the reported increase in partial current of nickel and iron with pH was not as significant.

Effects of Agitation

With the exception of a few well-characterized flow systems, the large body of electrodeposition literature lacks a clear description of the agitation scheme. Additionally, a considerable amount of work has been performed in stagnant solutions under free convection conditions. In the systems where only one electro-active species is present, it is clear that agitation enhances the rate of electrode reaction. When more than one electrode reaction occurs, the dependence on agitation may become more complicated. The nickel-iron plating system provides an interesting example where two metal deposition reactions and hydrogen evolution occur simultaneously. The typical
concentration of nickel in the bath is at least an order of magnitude larger than that of ferrous and of hydrogen ions. The rates of reactions of ferrous and hydrogen ions should be more sensitive to agitation than nickel if there were no interactions involved. Experimental observations of Glassstone and Symes (1927) showed, as expected, that increasing agitation enhanced the iron content of the plated alloys at high current densities. Surprisingly, at low current densities, the iron percentage decreased with faster rates of agitation.

The importance of agitation becomes more evident when the complex topography upon which the alloy films must be plated is considered. To achieve a uniform thickness and composition during fabrication of devices, commercial baths employ bubble stirring, an impinging jet (e.g. Croll, 1967), or a reciprocating paddle. The paddle cell, invented by Powers and Romankiw (1972), is commonly used for nickel-iron electrodeposition and provides a challenging tertiary current distribution problem. Schwartz et al. (1987) analyzed the simpler problem of copper deposition under mass-transfer limited conditions in a paddle cell, and developed correlations for mass-transfer coefficients. They showed that the mass-transfer rate of the discharging species is modulated depending on the paddle position and frequency.

To gain a more fundamental understanding of agitation effects on nickel-iron electrodeposition, Andricacos et al. (1989) used the uniform and well characterized flow to the surface of a rotating ring-disk electrode. The results confirmed that the alloy composition is quite sensitive to agitation. Interestingly, it was observed that the partial current of nickel decreased with increasing agitation, to the extent that at a constant electrode potential, the total current density decreased despite the increase in the iron
partial current. The combined decrease in the nickel deposition current and the increase in the hydrogen partial current led to a drop in the current efficiency. For a complex system such as nickel-iron, understanding these agitation effects are essential in obtaining a precisely-tailored alloy film for a given application.

Effects of Boric Acid and Buffering Agents

It has been observed that addition of certain compounds such as boric, citric and ascorbic acid can affect the appearance and properties of the electrodeposits. Boric acid has long been used in various plating baths: it is a component of the Watts bath for electroplating bright nickel, and is also extensively employed in permalloy plating baths. Many studies have focused on understanding the role of boric acid and the mechanism by which it affects the morphology and appearance of the electrodeposits. Cotton and Wilkinson (1972) use a pK value of 9 at low concentrations and 6.8 for higher concentrations of boric acid. It is not clear whether boric acid is a buffer and reduces the interfacial pH rise caused by hydrogen evolution, or if it adsorbs at the electrode surface causing a change in the mechanism or kinetics of the electrode reaction.

To examine the buffering alternative, Horkans (1979) studied hydrogen evolution in sulfate and chloride baths containing boric acid. Her experiments showed no significant changes in the limiting current of hydrogen in the presence of boric acid, but indicated a decrease in the overpotential for water discharge. Deligianni and Romankiw (1989) reported an increase in the buffering capacity of the solution upon addition of boric acid. Their conclusion was based on a reduction in the pH rise at the electrode surface during H₂ evolution. If boric acid is truly a buffer, at a given potential and for a given partial
current of hydrogen, the interfacial pH should be lower than in the unbuffered case. However, a lower interfacial pH could also result if hydrogen evolution is inhibited by boric acid. In the absence of polarization data, a decrease in the interfacial pH rise is not conclusive evidence for buffering.

During metal deposition, boric acid exhibits a complex behavior. Hoar (1986) investigated the effect of boric acid in a Watts bath. He concluded that boric acid masquerades as a buffer, and in fact inhibits hydrogen evolution. He suggested that boric acid may act as a catalyst for nickel discharge, possibly by complexation with nickel ions. Croll and May (1987) examined the effect of buffering agents on the magnetic properties of cobalt electrodeposits. No partial currents were reported in that study, but the narrow region of bulk pH in which the abrupt transition in crystallographic and magnetic properties of cobalt films occurred broadened with the addition of boric acid or ammonium ions. Since ammonium salt is a Lewis acid, the observation was thought to be due to a buffering effect.

The effects of boric acid during alloy deposition can be more complex. Horkans (1981) reported a decrease in the partial current of nickel from a chloride bath in the presence of boric acid during nickel-iron deposition. The results in sulfate media were pH dependent. Her earlier work (1979) showed a decrease in the total current density of nickel-iron with addition of boric acid. Whitney and Croll (1989) while reporting on the role of sodium hypophosphite on permalloy electrodeposition, also observed that boric acid inhibits nickel deposition when ferrous ions are present. No partial currents for hydrogen or iron were reported. Suppression of nickel discharge by boric acid in the presence of iron is the opposite of the catalytic role of boric acid for deposition of pure
nickel as hypothesized by Hoar. Grande and Talbot (1989) observed that boric acid in permalloy sulfate bath increased the partial current of hydrogen, and at higher potentials, where alloy deposition is dominant, decreased the total current density. Deligianni and Romankiw (1989) measured the pH behind a cathode screen, with a glass electrode, during deposition of nickel, iron and nickel-iron. In all cases, the addition of boric acid reduced the rise in pH. However, partial currents for discharge of various species were not reported in this work either. Understanding the role of boric acid via a buffering versus an adsorptive-inhibitive mechanism will require a complete set of partial current data.

The impact of boric acid on zinc alloys have also been investigated. Karwas and Hepel (1988) analyzed nickel-zinc and cobalt-zinc alloys plated at constant potential by stripping voltammetry. When pure metals were electroplated, boric acid suppressed the nickel deposition but enhanced that of zinc. It had the opposite effect during codeposition; it enhanced the nickel deposition while suppressing that of zinc. Partial currents were not reported, but the alloy current efficiency increased in the presence of boric acid. Karwas and Hepel (1989) did not find these trends in codeposition of cobalt-zinc; unlike nickel, cobalt deposition in both the pure state, and alloyed with zinc, was suppressed in the presence of boric acid while zinc deposition was enhanced. Based on the high overvoltage for hydrogen evolution on zinc, the current efficiency followed the zinc content of the alloy deposits.

Data for other commonly used buffering agents are scarce. Horkans (1979) observed that hydrogen evolution increased significantly when citric acid was present. Biallozor and Leider (1985) investigated the effects of boric acid, D-mannitol, ascorbic
acid and citric acid. For solutions without nickel and iron salts, all added organics increased the partial current of hydrogen and the buffering capacity. This increase was larger for the compound with the smaller pK value. During alloy deposition, the partial current of both nickel and iron decreased at a given potential in the presence of buffers while that of hydrogen increased. The combined effect on the alloy composition yielded a deposit with a lower iron content at low potentials, but significantly higher at larger overpotentials, compared to the alloy deposits obtained in the absence of a buffer.

In summary, for an added compound to serve as a buffer, it should provide additional protons to lower the interfacial pH rise caused by hydrogen reduction. The effects of these agents during deposition of alloys which involve simultaneous hydrogen reduction are more complex. It is not well-understood how the partial currents of hydrogen and alloy components are influenced by these compounds. Unfortunately, there are only a few available experimental data on the effects of buffering agents on alloy deposition. Additionally, most of the published research in the field lacks a complete set of measurements. Often, when the experimental results of metal deposition in the presence of a buffering agent are reported, only the total applied current is mentioned; no potential measurements and partial currents are presented. Our understanding of various electrode processes and the ability to discern among alternative mechanisms describing the role of various added compounds will depend on knowing the partial currents of hydrogen and metal deposition, in addition to the electrode potential.
Conclusions

The interactive electrodeposition of alloys, in particular nickel-iron, presents a challenging problem both from practical and fundamental points of view. The importance of these materials in applications such as magnetic recording technology and corrosion protection demand a sound understanding of the fundamental principles involved in the deposition process. Significant improvements in performance can be obtained when the effects of plating parameters on the deposit composition, uniformity, and morphology are well understood. We have tried to clarify the concept of anomalous codeposition, and suggested that it is the interactions between the alloy components during codeposition that should be analyzed. On a more fundamental level, there are a wide range of unanswered questions to be investigated. There is a definite need to understand the basic mechanism of discharge for each component when deposited separately. The next step is to understand the nature of interactions which occur during codeposition and lead to either suppression or enhancement of a component. Additional experimental work, under well-characterized agitation conditions, should address questions regarding the role of various plating parameters. Finally, a predictive model based on well-understood thermodynamic, kinetic, and mass-transport principles should be developed. Such a model can save costly empirical trial and error efforts in optimizing the plating conditions to tailor a specific alloy deposit.
References


Chapter 2


Chapter 3: A Mathematical Model for Anomalous Codeposition of Nickel-Iron on a Rotating Disk Electrode

Abstract

A mathematical model for anomalous alloy deposition onto a rotating disk electrode has been developed. The convective diffusion equations, coupled with the homogeneous dissociation reactions of water and metal-hydroxide ions, are numerically solved, and the calculated interfacial concentrations are used to describe the electrode processes. The role of metal-hydroxide ions in the deposition of single metals, reported by other researchers, is extended to codeposition. The kinetic parameters of the alloy deposition are assumed to be the same as those of the single metals involving the discharge of both metal and metal-hydroxide ions; however, during codeposition, the metal-hydroxide ions are allowed to discharge only at a fraction of surface sites proportional to their interfacial concentration.

The simulation was applied to the electrodeposition of nickel-iron. In agreement with the experimental observations reported in the literature, the percentage of iron in the deposit is much higher than in the electrolyte, and goes through a maximum as a function of applied potential. The estimated effect of agitation on alloy composition and current efficiency is in qualitative agreement with experiments. The model also predicts that while the polarization behavior of nickel is shifted to more cathodic values during codeposition, the iron behavior shows no significant change.
Introduction

It is well known that codeposition of certain metals, such as members of the iron group, zinc, lead, and tin, from acid baths of pH range 2 to 4 show a complex behavior. The discharge rate of the more noble component is inhibited, causing the appearance of the less noble component at a much higher ratio in the deposit than in the electrolyte. For example, a typical nickel-iron bath with 2% iron in the electrolyte can yield an alloy deposit with 20% iron content although the kinetics of deposition of nickel and iron as pure metal are similar. As discussed in chapter 2 of this work, a number of explanations and reviews for this phenomenon have been published. However, the mechanism of anomalous codeposition is not well understood yet.

Part of the complexity of these systems is a consequence of hydrolysis of the metal ions in the solution. Hydrogen evolution takes place simultaneously during metal deposition and causes an increase in the pH in the cathodic boundary layer, which in turn leads to a non-uniform degree of hydrolysis. It is important to distinguish the hydrolysis product ions (metal-hydroxide ion complexes) from metal-hydroxides (solid phase precipitates). Hydrolysis product ions such as FeOH$^+$ and NiOH$^+$ have long been studied (Sillen, 1959). They have much larger dissociation constants than their metal hydroxides, which allow them to be thermodynamically stable at several pH units lower than the hydroxides (e.g. $K_{Fe(OH)_2}^{P} = 4.84 \times 10^{-17}$ vs. $K_{FeOH}^{eq} = 5.78 \times 10^{-8}$, NBS Table of Thermochemical Data, 1982).

The importance of hydrolysis in the deposition of single metals has been described by some researchers. Bockris et al. (1961) in their studies of iron polarization did include
changes in the surface pH, and after analyzing various mechanisms, they concluded that both cathodic and anodic processes take place via a FeOH\(^+\) ion. Hydrolysis effects are also important for nickel electrodeposition. Based on experimental evidence, Matulis et al. (1964) suggested that the NiOH\(^+\) ion is involved in the mechanism of nickel deposition. They noted that nickel polarization initially increases with pH, then sharply decreases in the range 3.5-4.5, and continues to increase gradually thereafter. They concluded that when pH is larger than 4, nickel deposition occurs mainly through discharge of NiOH\(^+\) ions.

The formation of metal hydroxide precipitates requires a much higher pH than metal-hydroxide ions. Whether or not such a high pH is achieved at the surface depends on the solution chemistry (e.g. pH, buffering agents), mass-transfer conditions, current density, and degree of super-saturation. By solving the transport equations for a Nernstian boundary layer, Harris (1973) has calculated the change in surface pH during electrodeposition of a bivalent metal. His analysis showed that metal-hydroxide ions can act as a buffer and moderate the alkalinity of the cathodic boundary layer. Thus, even when the limiting current of hydrogen ion is exceeded, the pH at the surface may not be high enough to lead to metal-hydroxide precipitation. Romankiw (1978) measured the surface pH during the electrodeposition of nickel and iron both as single metals and as alloys over a range of conditions. The rise in the surface pH was eliminated when ultrasonic agitation was applied, while in the absence of agitation the surface pH increased by many units. Transmission electron microscopy (TEM) studies of electrodeposited nickel films (1970) have shown that nickel-hydroxide precipitate is included in the deposit only in the absence of agitation.
The interdependence of surface pH, current density, degree of agitation, and hydrolysis in the nickel-iron system was recognized by Dahms and Croll (1965). Their experimental results showed that anomalous deposition occurred when hydrogen limiting current was exceeded. They concluded that the resulting high surface pH should lead to the formation of ferrous hydroxide, Fe(OH)$_2$, and proposed that this adsorbed intermediate inhibits the nickel deposition by blocking the electrode surface, while iron deposition is not affected. However, recent experimental results of Horkans (1981), Mathias and Chapman (1981), and Andricacos et al. (1989) show anomalous behavior even at small fractions of the hydrogen ion limiting current. This implies that anomalous deposition can occur at a much lower surface pH than that required by the hypothesis of Dahms and Croll.

In the following, basic principles of mass-transfer and interfacial kinetics are applied to evaluate the surface concentration of metal ions, their metal-hydroxide ions and the surface pH during electrodeposition of nickel-iron and hydrogen. Our goal is to construct a model to predict the effect of plating parameters such as agitation, bulk pH, bath composition, and applied potential (or current) on alloy composition and current efficiency. We shall use the recent experimental results of Andricacos et al. (1989) for a test of our model.

Mathematical Model

Consider the alloy system of nickel-iron plated onto a rotating disk electrode (RDE) from a simple chloride plating bath. The ionic species of interest are:
H\(^{+}\), OH\(^{-}\), Fe\(^{2+}\), Ni\(^{2+}\), FeOH\(^{+}\), and NiOH\(^{+}\). The material balance equation for species i can be written as:

\[
\frac{\partial \tilde{C}_i}{\partial t} = - \nabla \cdot \vec{N}_i + R_i \tag{3.1}
\]

where \(R_i\) denotes the homogeneous reaction. For the nickel-iron system, the following homogeneous reactions are considered:

\[
\begin{align*}
H_2O &= H^{+} + OH^{-} \\
FeOH^{+} &= Fe^{2+} + OH^{-} \\
NiOH^{+} &= Ni^{2+} + OH^{-}
\end{align*}
\]

It is assumed that these reactions are infinitely fast such that equilibrium is reached:

\[
\begin{align*}
K_{H_2O} &= \tilde{C}_{OH} \tilde{C}_H^{\ast} \tag{3.2} \\
K_{FeOH^{+}} &= \frac{\tilde{C}_{OH} \tilde{C}_{Fe^{2+}}}{\tilde{C}_{FeOH^{+}}} \tag{3.3} \\
K_{NiOH^{+}} &= \frac{\tilde{C}_{OH} \tilde{C}_{Ni^{2+}}}{\tilde{C}_{NiOH^{+}}} \tag{3.4}
\end{align*}
\]

We will treat the system as a one-dimensional problem, and neglect the radial variations. For a small disk, in the presence of well-supported electrolyte and mass-transfer and kinetic overpotentials, this is a good approximation (Newman, 1973). The convective-diffusive flux can be written as follows:

\[
\vec{N}_i = - D_i \frac{\partial \tilde{C}_i}{\partial z} - a \omega \left( \frac{\omega}{v} \right)^{1/2} \tilde{z}^2 \tilde{C}_i \tag{3.5}
\]

The problem can be formulated in terms of dimensionless parameters:
\[ N_i = \frac{\tilde{R}_i}{i_{tot}} ; \quad C_i = \frac{\tilde{C}_i}{\tilde{C}_i^b} ; \quad x = \frac{z}{\delta} \]  

[3.6]

where \( \delta \) is the mass transfer boundary layer of the ion with the smallest diffusion coefficient.

\[ \delta = \left( \frac{3D_i}{a \nu} \right)^{1/2} \left( \frac{\nu}{\omega} \right)^{1/2} \]  

[3.7]

Substituting Eqs. [3.6] and [3.7] in [3.1-3.5] the dimensionless form of the equilibrium and flux equations reduce to:

\[ C_{H^+} \cdot C_{OH^-} = 1 \]  

[3.8]

\[ C_{Fe^{2+}} \cdot C_{OH^-} = C_{FeOH^+} \]  

[3.9]

\[ C_{Ni^{2+}} \cdot C_{OH^-} = C_{NiOH^+} \]  

[3.10]

\[ N_i = - \beta_2 D_i \tilde{C}_i^b \frac{dC_i}{dx} - \beta_1 \tilde{C}_i^b C_i x^2 \]  

[3.11]

\[ a \omega \left( \frac{\omega}{\nu} \right)^{1/2} \delta^2 F \]  

where \( \beta_1 = \frac{a \omega}{i_{tot}} \delta \) and \( \beta_2 = \frac{F}{i_{tot} \delta} \).

At steady state and taking into account the homogenous dissociation reactions of the metal hydroxide ions and water, the material balance equations reduce to:

\[ -\nabla \cdot N_{Fe^{2+}} - \nabla \cdot N_{FeOH^+} = 0 \]  

[3.12]

\[ -\nabla \cdot N_{Ni^{2+}} - \nabla \cdot N_{NiOH^+} = 0 \]  

[3.13]

\[ -\nabla \cdot N_{OH^-} + \nabla \cdot N_{H^+} + \nabla \cdot N_{Fe^{2+}} + \nabla \cdot N_{Ni^{2+}} = 0 \]  

[3.14]

Eqns. [3.8-3.10] and [3.12-3.14] are the six equations to solve for the six ionic species of
Chapter 3

interest.

*Boundary Conditions*

At the electrode surface, there are three overall reactions: hydrogen evolution, and two metal deposition reactions. The hydrogen reaction can occur both by hydrogen ion discharge and at higher potentials by discharge of water.

\[
H^+ + e^- = \frac{1}{2} H_2
\]

\[
H_2O + e^- = \frac{1}{2} H_2 + OH^-
\]

We assume that the hydrogen remains dissolved in the solution, and the flow field is not affected. The alloy components are allowed to deposit both from the metal and the metal-hydroxide ions:

\[
FeOH^+ + 2e^- = Fe + OH^{-}
\]

\[
Fe^{+2} + 2e^- = Fe
\]

\[
NiOH^+ + 2e^- = Ni + OH^{-}
\]

\[
Ni^{+2} + 2e^- = Ni
\]

The partial current densities are related to the fluxes at the electrode surface. Appendix 3.A shows that the boundary conditions at $x=0$ for various ions can be written as:

\[
N_{Fe^{+1}} + N_{FeOH^+} = \frac{i_{Fe}}{2i_{tot}}
\]  \[3.15\]

\[
N_{Ni^{+2}} + N_{NiOH^+} = \frac{i_{Ni}}{2i_{tot}}.
\]  \[3.16\]
\[-N_{OH^-} + N_{Fe^{2+}} + N_{Ni^{2+}} + N_{H^+} = \frac{2i_{H_2} + i_{Fe} + i_{Ni}}{2i_{tot}} = 1 - \frac{\eta}{2}\]  \[3.17\]

where \(\eta\) is the current efficiency, \(\eta = 1 - \frac{i_{H_2}}{i_{tot}}\).

In the bulk, the normalized concentration of all species is:

\[C_i = 1\]  \[3.18\]

**Kinetics of Electrode Reactions**

A modified Butler-Volmer type of kinetics is used for the electrode processes. We introduce two assumptions for the electrodeposition of the alloy components: 1) both metal and metal-hydroxide ions can be discharged, and 2) the metal-hydroxide ions compete for surface sites. In the Tafel region, the kinetic expression for various electrode reactions takes the following form:

\[\frac{i_{H_2}}{F} = k_{H^+}^c \tilde{C}_{H^+} e^{(\alpha_{Fe} FV/RT)} + k_w^c e^{(\alpha_{Fe} FV/RT)} \]  \[3.19\]

\[\frac{i_{Fe}}{2F} = k_{Fe^{2+}}^c \tilde{C}_{Fe^{2+}} e^{(\alpha_{Fe^{2+}} FV/RT)} + k_{FeOH^+}^c (1 - \theta) \tilde{C}_{FeOH^+} e^{(\alpha_{FeOH^+} FV/RT)} \]  \[3.20\]

\[\frac{i_{Ni}}{2F} = k_{Ni^{2+}}^c \tilde{C}_{Ni^{2+}} e^{(\alpha_{Ni^{2+}} FV/RT)} + k_{NiOH^+}^c (\theta) \tilde{C}_{NiOH^+} e^{(\alpha_{NiOH^+} FV/RT)} \]  \[3.21\]

where \(V\) is the absolute value of the cathodic potential with respect to N.H.E. corrected for ohmic drop, and \(\theta\) is the fraction of the surface available for the NiOH\(^+\) discharge.

\[\theta = \frac{\tilde{C}_{NiOH^+}^s}{\tilde{C}_{NiOH^+}^s + \tilde{C}_{FeOH^+}^s}\]  The expression for \(\theta\) as discussed in Appendix 3.B can be
derived from a Langmuir isotherm for two species with equal adsorption equilibrium constants at high coverage.

The set of coupled, non-linear differential equations [3.8-3.10] and [3.12-3.14] with the non-linear boundary conditions [3.15-3.18] are solved using the Galerkin Finite Element Method with linear basis functions in conjunction with the Newton-Raphson technique to linearize the non-linear set of algebraic equations. Lapidus and Pinder (1982) is a good reference for the FEM and other numerical methods. For a given applied cathodic potential and rotation speed, the concentration profiles and partial current densities (i.e. alloy composition and current efficiency) are calculated. The flux boundary conditions, equations [3.15-3.17], depend on the surface concentration of ions as seen in equations [3.19-3.21]; therefore, an iterative scheme is used which begins with an assumed concentration profile for the ions, calculates the boundary conditions, and after solving the set of differential equations compares the calculated concentrations with the assumed values until they converge.

Model Parameters

The kinetic parameters and dissociation constants are listed in Table 1. The bath composition and diffusion coefficients used in the calculations are listed in Table 2. Dissociation constants are calculated from the Gibbs free energy of formation data reported in the NBS Table of Chemical Thermodynamic Properties. The transfer coefficients of nickelous and ferrous ions listed in Table 1 correspond to Tafel slopes of approximately 140 and 120 mv/decade as reported by Andricacos et al. (1989), and Bockris et al. (1965). The other kinetic parameters are chosen to approximate the experimental results, but have not been optimized. Based on experimental evidence that
partial currents of both nickel and iron increase with pH (Bockris et al., Matulis et al., Biallozor et al., Bard), the rate constants and transfer coefficients for the electrode reactions of NiOH\(^+\) and FeOH\(^+\) were assigned to be larger than those of Ni\(^{+2}\) and Fe\(^{+2}\) ions.

Table 3.1: Dissociation Constants and Kinetic Parameters

<table>
<thead>
<tr>
<th></th>
<th>Fe(^{+2})</th>
<th>FeOH(^+)</th>
<th>Ni(^{+2})</th>
<th>NiOH(^+)</th>
<th>H(^+)</th>
<th>H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_{\text{diss}}) (M)</td>
<td>-</td>
<td>(5.78 \times 10^{-8})</td>
<td>-</td>
<td>(4.5 \times 10^{-5})</td>
<td>-</td>
<td>(1.0 \times 10^{-14})</td>
</tr>
<tr>
<td>(k_{\text{f}}) (cm/sec)</td>
<td>(8.5 \times 10^{-10})</td>
<td>(1.6 \times 10^{-9})</td>
<td>(1.16 \times 10^{-9})</td>
<td>(5.9 \times 10^{-7})</td>
<td>(3 \times 10^{-3})</td>
<td>(2.3 \times 10^{-16})</td>
</tr>
<tr>
<td>(\alpha_i)</td>
<td>0.27</td>
<td>0.36</td>
<td>0.21</td>
<td>0.33</td>
<td>0.11</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 3.2: Bath Composition and Diffusion Coefficients

<table>
<thead>
<tr>
<th></th>
<th>Fe(^{+2})</th>
<th>FeOH(^+)</th>
<th>Ni(^{+2})</th>
<th>NiOH(^+)</th>
<th>H(^+)</th>
<th>OH(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\bar{C}_i) (mol/lit)</td>
<td>(4.99 \times 10^{-3})</td>
<td>(8.65 \times 10^{-7})</td>
<td>0.2</td>
<td>(4.4 \times 10^{-8})</td>
<td>(1.0 \times 10^{-3})</td>
<td>(1.0 \times 10^{-11})</td>
</tr>
<tr>
<td>(D_i \times 10^5) (cm(^2)/sec)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>
Results and Discussion

We will compare the results of the model with two sets of experimental data reported by Andricacos et al. (1989). The measured current efficiency and alloy composition as a function of the applied potential for 1600 and 3600 rpm and the corresponding simulation results are shown in figures 3.1 and 3.2. The normalized concentration profiles of the six ionic species of interest, at various potentials, for a pH_{bulk} = 4 and 3600 rpm are shown in figures 3.3 to 3.5. The depletion of Fe^{+2} and H^{+} ions increases and becomes significant with increasing cathodic potential. There is very little concentration polarization for nickel since only a small fraction of its limiting current is being passed. The concentration profiles of OH^{-} and Fe^{+2} are shown in figure 3.6. With increasing potential, the hydrogen evolution current increases, which in turn increases the pH at the surface. The FeOH^{+} ions initially build up at the surface as a result of higher pH; then, as the partial current density of iron increases and the surface begins to be depleted of ferrous ions, the surface concentration of FeOH^{+} starts to decrease leading to the maximum in the concentration profile, as shown in figure 3.7.

Effect of Agitation

The simulation results of figures 3.1 and 3.2 are in qualitative agreement with the experimental data. Increasing agitation results in enhanced mass-transfer of H^{+} and reduction of current efficiency. The effect of agitation on alloy composition is more complex. As seen in figure 3.2, increasing agitation at low potentials slightly decreases the percentage of iron, but at higher potentials it enriches the alloy with iron. Partial
Fig. 3-1: Current Efficiency as a function of absolute value of applied cathodic potential: pH and agitation effects. Experimental data taken from Andricacos et al. (15).
Fig. 3-2: Alloy composition as a function of absolute value of applied cathodic potential: pH and agitation effects. Experimental data taken from Andricacos et al. (15).
Fig. 3-3: Normalized concentration profiles at 3600 rpm and V=0.6 volts.
Fig. 3-4: Normalized concentration profiles at 3600 rpm and V=0.68 volts.
Fig. 3-5: Normalized concentration profiles at 3600 rpm, V=0.76 volts.
Fig. 3-6: Normalized Concentration Profiles of Fe$^{+2}$, and OH$^-$
Fig. 3-7: Normalized Concentration Profiles of FeOH⁺
Fig. 3-8: Calculated partial current density of iron, agitation and pH effects.
Fig. 3-9: Calculated partial current density of nickel, agitation and pH effects.
current densities of iron and nickel during codeposition are shown in figures 3.8 and 3.9. It can be seen that an increase in agitation increases iron partial current density, but decreases that of nickel.

The dual effect of agitation on the iron content of the alloy can be described with the aid of figure 3.10, which shows the normalized surface concentrations of OH⁻, Fe²⁺ and FeOH⁺. At low potentials there is very little depletion of Fe²⁺ ions, but hydrogen evolution is high enough to cause an accumulation of hydroxide ions at the surface. As a result, the interfacial concentration of FeOH⁺ is also higher than the bulk. As shown in figure 3.10, increasing agitation decreases the overpotential of hydrogen ions which means the amount of hydroxide at the surface decreases with agitation. Therefore, at low potentials, as a result of higher FeOH⁺ concentration at the interface, the iron current density is higher at lower agitation. As the polarization increases, the surface concentration of Fe²⁺ and later that of FeOH⁺ start to decrease. Higher rates of agitation slow down the decrease in the surface concentration of both Fe²⁺ and FeOH⁺ ions, thereby causing the higher iron content.

It has been experimentally observed that the partial current of iron is below its mass transport limited value when the iron content of the alloy is at its peak (Horkans, 1981 and Andricacos, 1989). Slow ionic diffusion through a Fe(OH)$_2$ film was considered as a possible cause for this phenomenon (Horkans, 1981). However, concentration profiles of figures 3.3-3.5 indicate that the partial current of iron is far from its limiting value. Thus, the model presented here is in agreement with experimental observations without the assumption of diffusion through a solid film.
Effect of bulk pH

The simulated effect of pH on the partial currents of nickel and iron is shown in figures 3.8 and 3.9. The partial currents of both nickel and iron increase with pH. The overall effect of bulk pH on alloy composition is shown in figure 3.2. In agreement with the experimental observations of Glassstone (1927) and Horkans (1981), with increasing pH, the iron content of the alloy is higher at low potentials, and sharply decreases at higher potentials.

The pH effect on the nickel-iron system can be better understood by examining the relationship between ionic species and pH. Varying pH while keeping the concentration of metal salts constant, changes the ratio of metal-hydroxide to metal ions. Higher pH increases the concentration of metal-hydroxide ions leading to a reduction in overpotential and an increase in metal partial current. From Eqs. [3.3-3.4], it can be seen that the concentration of metal-hydroxide ions depends on both pH and the dissociation constant; increasing pH by one unit, and reducing the dissociation constant by a factor of ten are equivalent. This implies that the calculated results of figure 3.2 can also be viewed as the case of pH=3 for two different sets of dissociation constants. The pK values for the dissociation constants listed in Table 1 correspond to 7.2 and 4.3 for FeOH\(^+\) and NiOH\(^+\), respectively; however, pK values ranging between 6 to 10 for FeOH\(^+\) and 3 to 7 for NiOH\(^+\) have been reported (Sillen, (1959), Bard et al.(1985)). Uncertainty in the value of dissociation constants is one of the causes leading to the lack of quantitative agreement between the model and experiments.
Fig. 3-10: Normalized surface concentration of Fe$^{+2}$, OH$^-$, and FeOH$^+$ at 1600 and 3600 rpm.
Fig. 3-11: Calculated Partial Currents of Nickel and Iron Single vs. Alloy (1600 rpm)
Inhibition of Nickel Deposition

One of the main characteristics of anomalous alloy deposition is the decrease in the discharge rate of the more noble metal in the presence of the less noble component. The simulated partial current densities of nickel and iron by themselves and during codeposition are compared in figure 3.11. The reduction of nickel partial current during alloy deposition can be explained by considering the relative concentrations of metal-hydroxide ions. The FeOH\(^+\) concentration is higher than NiOH\(^+\) because it has a much smaller dissociation constant. Presence of FeOH\(^+\) ions has two consequences: 1) FeOH\(^+\) ions compete with NiOH\(^+\) ions for surface sites, and 2) the pH rise at the surface is somewhat buffered causing a lower concentration of NiOH\(^+\) compared with the pure nickel deposition case. Subsequently, the nickel deposition is inhibited in the presence of iron.
Conclusions

Application of a mathematical model to the codeposition of nickel-iron in a RDE system was successful in predicting the following salient features of anomalous deposition: 1) the ratio of the less noble metal (iron) is much higher in the alloy than in the electrolyte; 2) the percentage of the less noble metal as a function of the applied potential goes through a maximum; 3) the presence of the less noble metal inhibits the discharge of the more noble metal (nickel), and 4) current efficiency of alloy deposition increases with applied potential. The effects of agitation and pH on the alloy system were simulated, and the results were in qualitative agreement with experimental observations.

Accurate measurement of partial current densities, (i.e. current efficiency and alloy composition) during both individual component and alloy deposition, are crucial in assessing the real kinetic parameters. A sensitivity analysis for the kinetic parameters and homogeneous dissociation constants, followed by an optimization procedure requires more experimental data, and should be the next step. The role of buffering agents which are commonly used in electroplating baths can be taken into account by an extension of this work. While the results reported here are for the nickel-iron system, the model is general and could have application to other anomalous alloy systems. Obviously, the complex nature of anomalous codeposition will not be fully understood unless extensive experimental studies, in particular in situ surface sensitive measurements, are carried out.
LIST OF SYMBOLS

\( a \)       rotating disk hydrodynamic constant (0.51023)
\( C_i \)     normalized concentration of species \( i \)
\( \bar{C}_i \) concen. of species \( i \) (mol/cm\(^3\))
\( D_i \)     diffusion coefficient of species \( i \) (cm\(^2\)/s)
\( F \)       Faraday's constant (96,487 C/eq)
\( i_{\text{tot}} \) total cathodic current density (amp/cm\(^2\))
\( K_i \)     dissociation constant of species \( i \)
\( k_i^c \)   cathodic rate constant for species \( i \)
\( N_i \)     dimensionless molar flux
\( \bar{N}_i \) molar flux (mol/cm\(^2\)-s)
\( R \)       universal gas constant, 8.3143 J/mol-K
\( R_i \)     homogeneous reaction rate (mol/cm\(^3\)-s)
\( t \)       time (s)
\( T \)       absolute temperature, K
\( V \)       absolute value of the cathodic potential (volts) with respect to NHE
\( x \)       dimensionless distance from electrode
\( z \)       distance from electrode (cm)

Greek Characters:
\( \alpha_i \) cathodic transfer coefficient
\( \beta_i \) coefficients defined after Eq. 3.11
\( \delta \)   mass-transfer boundary layer defined by Eq. 3.7
\( \eta \)     current efficiency of alloy deposition
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\( \theta \)  fraction of surface available for discharge of metal-hydroxide ions

\( \nu \)  kinematic viscosity (cm\(^2\)/s)

\( \omega \)  disk rotation speed (rad/s)

Superscripts

\( b \)  bulk

\( s \)  surface

\( c \)  cathodic

Subscripts

\( \text{ads} \)  adsorption

\( \text{des} \)  desorption
References


Appendix 3A: Flux Boundary Conditions

For metal deposition and hydrogen reduction, the electrode reactions are:

a. $M^{+2} + 2e^- \rightarrow M$

b. $\text{MOH}^+ + 2e^- \rightarrow M + \text{OH}^-$

c. $\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2$

d. $\text{H}_2\text{O} + e^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^-$

e. $\text{HA} + e^- \rightarrow \frac{1}{2}\text{H}_2 + A^-$

f. $M^{+2} + \text{H}_2\text{O} + e^- \rightarrow \frac{1}{2}\text{H}_2 + \text{MOH}^+$

The flux boundary condition for a species $i$, $\tilde{N}_i$, can be related to the electrochemical reaction $j$:

$$\tilde{N}_i + \sum S_{ij} \frac{n_j}{n_j F} = 0$$

where $S_{ij}$ is the stoichiometry of species $i$ in the electrochemical reaction $j$ and $n_j$ is the number of electrons transferred. At the electrode surface, the flux of each electroactive species is related to the above electrode reactions:

$$\tilde{N}_{\text{M}^{+2}} = \frac{i_M}{2F} + \frac{i_{\text{H}_2}}{F}$$

$$\tilde{N}_{\text{MOH}^+} = \frac{i_M}{2F} - \frac{i_{\text{H}_2}}{F}$$

$$\tilde{N}_{\text{H}^+} = \frac{i_{\text{H}_2}}{F}$$
Appendix 3A

Now, since the metal deposition current density is the sum of currents in electrode reactions a and b, and that of hydrogen is the sum of electrode reactions c through f, the following holds:

\[
\tilde{N}_{OH^-} = -\frac{i_{H_2}^d}{F} - \frac{i_M^b}{2F}
\]

\[
\tilde{N}_{HA} = \frac{i_{H_2}^e}{F}
\]

Since the metal deposition current density is the sum of currents in electrode reactions a and b, and that of hydrogen is the sum of electrode reactions c through f, the following holds:

\[
\frac{i_M}{2F} = \frac{i_M^a}{2F} + \frac{i_M^b}{2F}
\]

\[
\frac{i_{H_2}}{F} = \frac{i_{H_2}^c}{F} + \frac{i_{H_1}^d}{F} + \frac{i_{H_2}^e}{F} + \frac{i_{H_2}^f}{F}
\]

which is equivalent to

\[
\frac{i_M}{2F} = \tilde{N}_{M^{2+}} + \tilde{N}_{MOH^+}
\]

\[
\frac{i_{H_2}}{F} = \tilde{N}_{H^+} - \tilde{N}_{OH^-} + \tilde{N}_{HA} - \tilde{N}_{MOH^+}
\]
Appendix 3.B: Interfacial Adsorption Processes

An idealized description of adsorption processes, known as Langmuir isotherm, assuming energetically equivalent adsorption sites, negligible interactions among the adsorbed species, and a maximum monolayer coverage has found many applications in the area of heterogeneous catalysis and surface science (see e.g. Hill, 1977). Although Langmuir isotherm does not provide a completely realistic picture for adsorption of charged species onto a polarized electrode, we shall use it as a starting point for including adsorption processes in the discharge mechanism. In what follows a brief description of the Langmuir isotherm and its extension to the \( \text{NiOH}^+/\text{FeOH}^+ \) system will be presented.

For a single species adsorbed at a solid surface, the idealized rates of adsorption and desorption can be expressed in terms of the fraction of sites occupied by the adsorbed species, its concentration in the solution phase, and a rate constant:

\[
\begin{align*}
    r_{\text{ads}} &= kC (1 - \theta) \\
    r_{\text{des}} &= k' \theta
\end{align*}
\]

[3B.1]

At equilibrium

\[
r_{\text{ads}} = r_{\text{des}}
\]

[3B.2]

which is the Langmuir isotherm description of the fraction of active sites occupied by the adsorbed species:

\[
\theta = \frac{KC}{1 + KC}
\]

[3B.3]

where \( K' = \frac{k}{k'} \) is the equilibrium adsorption constant.

For multiple species adsorbed onto a solid surface following a Langmuir isotherm (e.g. Hill, 1977), [3B.3] can be extended:
If NiOH\(^+\) and FeOH\(^+\) are the major adsorbed species, then

\[ \theta_i = \frac{K_i C_i}{1 + \sum K_j C_j} \]  \hspace{1cm} \text{[3B.4]}

For equal adsorption equilibrium constants and high coverage \(K_i C_i \gg 1\)

\[ \theta_{\text{NiOH}^+} = \frac{K_{\text{NiOH}^+} C_{\text{NiOH}^+}}{1 + \sum K_j C_j} \]

\[ \theta_{\text{FeOH}^+} = \frac{K_{\text{FeOH}^+} C_{\text{FeOH}^+}}{1 + \sum K_j C_j} \]

which are the expressions used in Eqs. [3.20] and [3.21].
Chapter 4: Buffering Effects in Interactive Codeposition

Abstract

The effects of buffering agents on alloy composition and current efficiency were investigated by using the mathematical model presented in the previous chapter. The additional protons available in a buffer increase the partial current of hydrogen while the interfacial pH rise is reduced. The lowering of surface pH decreases the interfacial concentration of metal-hydroxide complexes and the partial current of metal deposition. In the presence of a buffer, the combined increase of the hydrogen current and decrease of the alloy deposition current lead to a drop in the current efficiency. Since the discharge kinetics of the alloy components are different, the alloy composition is also affected by the presence of a buffering agent. Contrary to the hypothesis prevailing in the literature, the results of this work indicate that a buffer can increase the content of iron (the less noble component) in the alloy deposit. The simulated results of this model are in qualitative agreement with the observed behavior for some buffering agents such as ascorbic acid, D-mannitol and citric acid.
**Introduction**

Simultaneous hydrogen evolution during electrodeposition of metals such as iron, nickel, cobalt and their alloys can increase the pH in the region very close to the electrode surface. The degree of alkalinity in the interfacial region depends on electroplating parameters, such as current density, agitation and bulk pH. Under certain conditions, the interfacial pH may be high enough to cause undesirable precipitation or inclusion of metal hydroxides in the deposit. It has been observed that addition of certain compounds such as boric, citric or ascorbic acid is an effective method of substantially inhibiting the hydroxide precipitation and improving the deposit appearance. It is also generally observed that the hydrogen evolution increases in correlation with the pK $\dagger$ of these acids: the lower the pK, the larger the hydrogen partial current at a given electrode potential. Therefore, it has been postulated that the primary mechanism by which these acids affect the deposition process is "buffering". As discussed in chapter 2, there has been a renewed interest in understanding the role of these materials from basic principles rather than relying solely on empirical observations. Some of the more recent investigations on boric acid have already shown that the buffering picture is simplistic (Hoar, 1986), and a more detailed knowledge of the interfacial kinetics is needed.

In the electrodeposition of alloys, the role of these agents are even less well-understood. Addition of these acids affects not only the current efficiency and the appearance of the electrodeposit, but also the alloy composition. Examples of the effects of boric acid on the codeposition of nickel-iron, nickel-zinc, and cobalt-zinc alloys were

$\dagger$ pK = $-\log K_{HX}$ where $K_{HX}$ is the dissociation constant of the acid.
given in chapter 2. Understanding the impact of these materials on alloy composition is dependent on our understanding of the alloy deposition mechanism. For example, as discussed in chapter 2, boric acid can increase the iron content of nickel-iron alloys. Horlans (1981) argued that boric acid can not be a buffer, based on the Dahms-Croll hypothesis: the high surface pH caused by hydrogen evolution leads to a ferrous hydroxide precipitate which inhibits nickel deposition while not affecting the discharge of iron. Horlans argued that a true buffer, by reducing the formation of ferrous hydroxide, should yield a deposit with a lower iron content. It was concluded that boric acid can not be a buffer because it enhances the iron percentage, hence increasing the anomalous nature of nickel-iron codeposition. These effects were then attributed to an adsorptive-inhibitive process involving boric acid.

There has been no other published theoretical work to investigate the effect of a buffering agent on anomalous alloy deposition. The focus of this chapter is to extend our basic model for the interactive alloy deposition, presented in chapter 3, to include the presence of a buffering agent. We will analyze the interactions which occur as a result of the surface pH modifications caused by a buffering agent. Unlike what was previously thought, it will be shown that a buffer can increase the content of the less noble component in the alloy deposit. While the model can be used for other alloy systems, we shall only consider the codeposition of nickel-iron alloys in the presence of a buffer.
Mathematical Model

Solution Chemistry and Material Balances

Similar to the procedure outlined in chapter 3, material balances are formulated. In addition to the six ionic species, $H^+$, $OH^-$, $Fe^{+2}$, $Ni^{+2}$, $FeOH^+$, and $NiOH^+$, we include the buffer, $HX$, and the conjugate base, $X^-$. The solution chemistry of the nickel-iron system in the presence of a buffering agent is shown in figure 4.1. To understand the behavior of this system accurately, the homogeneous reactions must be included in the transport model. As in the previous chapter, we assume that the following equilibrium relationships exist among the various species:

$$H_2O = H^+ + OH^- \quad K_{H_2O} = \frac{\bar{c}_{OH^-} \cdot \bar{c}_{H^+}}{\bar{c}_{H_2O}} \quad [4.1]$$

$$FeOH^+ = Fe^{+2} + OH^- \quad K_{FeOH^+} = \frac{\bar{c}_{OH^-} \cdot \bar{c}_{Fe^{+2}}}{\bar{c}_{FeOH^+}} \quad [4.2]$$

$$NiOH^+ = Ni^{+2} + OH^- \quad K_{NiOH^+} = \frac{\bar{c}_{OH^-} \cdot \bar{c}_{Ni^{+2}}}{\bar{c}_{NiOH^+}} \quad [4.3]$$

$$HX = H^+ + X^- \quad K_{HX} = \frac{\bar{c}_{H^+} \cdot \bar{c}_{X^-}}{\bar{c}_{HX}} \quad [4.4]$$

Using the dimensionless parameters introduced in equation 3.6, the material balances at steady-state can be written as:

$$-\nabla \cdot N_{Fe^{+2}} - \nabla \cdot N_{FeOH^+} = 0 \quad [4.5]$$

$$-\nabla \cdot N_{Ni^{+2}} - \nabla \cdot N_{NiOH^+} = 0 \quad [4.6]$$

$$-\nabla \cdot N_{OH^-} + \nabla \cdot N_{H^+} + \nabla \cdot N_{Fe^{+2}} + \nabla \cdot N_{Ni^{+2}} - \nabla \cdot N_{X^-} = 0 \quad [4.7]$$
Solution Chemistry of Nickel-Iron Deposition

Fig. 4-1: Homogeneous reactions and transport of ionic species involved in the electrodeposition of Ni-Fe.
Chapter 4

\[ -\nabla \cdot N_{\text{HX}} - \nabla \cdot N_{X^-} = 0 \] \[ [4.8] \]

Equations [4.1-4.8] are sufficient to solve for the concentration profiles of the eight species of interest.

**Boundary Conditions**

In the bulk, the normalized concentration of all species is unity.

\[ C_i = 1 \] \[ [4.9] \]

At the electrode surface, the flux boundary conditions for hydrogen evolution should be modified to include the presence of a buffer.

\[ N_{\text{Fe}^{2+}} + N_{\text{FeOH}^+} = \frac{i_{Fe}}{2i_{tot}} \] \[ [4.10] \]

\[ N_{\text{Ni}^{2+}} + N_{\text{NiOH}^+} = \frac{i_{Ni}}{2i_{tot}} \] \[ [4.11] \]

\[ -N_{\text{OH}^-} - N_{X^-} + N_{\text{Fe}^{2+}} + N_{\text{Ni}^{2+}} + N_{H^+} = \frac{2i_{H_2} + i_{Fe} + i_{Ni}}{2i_{tot}} = 1 - \frac{\eta}{2} \] \[ [4.12] \]

\[ -N_{X^-} - N_{\text{HX}} = 0 \] \[ [4.13] \]

where \( \eta \) is the current efficiency.

The kinetics of electrode reactions are described in equations [3.19-3.21]. The values for the kinetic parameters, dissociation constants and diffusion coefficients are taken from Tables 3.1 and 3.2. The diffusion coefficients of both HX and X\(^-\) are set to be \(10^{-5} \text{ cm}^2/\text{sec}\). An iterative scheme, also described in chapter 3, is employed to solve for the concentration profiles and partial currents at a given rotation speed and electrode.
potential, for various buffer pK values. The bath composition was taken to be the base case, i.e. 0.2M nickel, 0.005M ferrous ions, and 0.4M of total added HX with the bulk pH adjusted to 3. Unless otherwise stated, the agitation is set at 3600 rpm in the simulations.

Results and Discussion

The partial currents of hydrogen, iron and nickel for different values of the buffer pK are shown in Figs. 4.2-4.4. The smaller the buffer pK, or the larger the value of $K_{\text{HIX}}$, the easier it will dissociate. The simulation results for a very weak buffer with a pK of 9 was equivalent to the absence of a buffering agent. The hydrogen partial current is larger for buffers with a smaller pK value simply because there is a larger proton source available for reduction. Unlike that for hydrogen, the metal deposition partial current increases with an increase in the buffer pK. As illustrated in figure 4.5, the combined effects of the increase in hydrogen and the decrease in the metal deposition rates decrease the current efficiency. The dependence of the total current density on the potential is shown in Fig. 4.6. It is seen that at low potentials depolarization occurs; i.e. at a given electrode potential a higher current can pass. This is a consequence of the higher hydrogen evolution current while the metal deposition rate has not decreased much. At higher applied potentials, the metal deposition current is significantly reduced which leads to an increased polarization.

As demonstrated in figure 4.7, the pH rise at the electrode surface which is about 0.5 units in the absence of a buffering agent (pK=9) reduces to only 0.05 units for a buffer with pK=2. To understand the decrease in the partial current of both nickel and iron, the interfacial concentrations of the discharging ions should be considered. The surface
concentration of Fe$^{+2}$, FeOH$^+$ and NiOH$^+$ ions at various cathodic potentials are plotted in Figs. 4.8 to 4.10. It is seen that for both nickel and iron the interfacial concentration of metal-hydroxide ions increase with the buffer pK. Since the discharge kinetics of the metal-hydroxide ions were taken to be faster than their corresponding metal ions, the higher surface pH and metal-hydroxide ion concentration lead to the increase in the metal deposition current with the increase in the buffer pK. The percentage increase in the metal deposition current is potential dependent, and as seen in Figs. 4.2 to 4.3, the partial currents of iron and nickel are affected differently. To understand this behavior, we must consider the relationship between the metal deposition current and the interfacial concentration of metal and metal-hydroxide ions, as discussed in chapter 3 (see equations [3.20] and [3.21]. For a metal deposition reaction, the current can be written as

$$i = k_M^{c_1} C_{M^{+1}} f(V) + k_{MOH^+}^{c_2} C_{MOH^+} \theta_{MOH^+} f'(V)$$

[4.14]

where $\theta_{MOH^+}$ is the fraction of sites available for the MOH$^+$ discharge defined in chapter 3. As seen in figures 4.10 and 4.11 for nickel deposition, both the interfacial concentration of NiOH$^+$ ions and the fraction of sites for their discharge, $\theta$, increase with the buffer pK. The surface concentration of Ni$^{+2}$ hardly changes from its bulk value since only a small fraction of the nickel limiting current is passed. Therefore, the increase in the second term of equation [4.14] with the buffer pK, leads to the significant increase in the nickel current as seen in figure 4.3. The partial current of iron, in contrast to that
Fig. 4-2: Effect of buffer pK on hydrogen partial current for a bulk pH=3 and 0.4M HX present.
Fig. 4-3: Effect of buffer pK on iron partial current for a bulk pH=3 and 0.4M HX present.
Fig. 4-4: Effect of buffer pK on nickel partial current for a bulk pH=3 and 0.4M HX present.
Fig. 4-5: Effect of buffer pK on current efficiency.
Fig. 4-6: Effect of buffer pK on polarization.
Fig. 4-7: Effect of buffer pK on the surface pH, bulk pH = 3.
Fig. 4-8: Effect of buffer pK on surface concentration of Fe$^{+2}$
Fig. 4-9: Effect of buffer pK on surface concentration of FeOH⁺
Fig. 4-10: Effect of buffer pK on surface concentration of NiOH⁺
Fig. 4-11: Effect of buffer pK on θ
of nickel, does not increase very much with pK. This can also be understood with the aid of equation [4.14]. While the surface concentration of FeOH$^+$ increases, both the fraction of sites for the discharge of FeOH$^+$, i.e. $1 - \theta$, and the interfacial concentration of Fe$^{+2}$ decrease with pK. The resulting alloy composition is shown in figure 4.12. At lower values of the applied potential, the iron content of the alloy increases with an increase in the buffer pK. At higher potentials, the opposite holds; a low pK buffer enhances the amount of iron in the alloy at a given electrode potential.

The ratio of the surface sites for NiOH$^+$ discharge, i.e. $\theta$, at different pK values with respect to pK=9 (no buffer) is plotted in Fig. 4.13. The smaller the buffer pK, the smaller is the value of this ratio. The percentage of change of the normalized $\theta$ at different potentials is illustrated in Fig. 4.14. While in the presence of a buffer the normalized $\theta$ is always decreasing, there is a minimum between 0.7 and 0.72 volts. This potential range corresponds to the region in Fig. 4.12 where the transition in Fe% is observed. The sharp decrease in the iron content at potentials larger than 0.72 volts can be related to the increase in the partial current of nickel caused by the rapid increase of the value of $\theta$.

Comparison with experiments

We will compare the results of the simulation with the work of Lieder and Biallozor (1984) and Horkans (1981). The addition of boric acid, D-mannitol, ascorbic acid and citric acid to a chloride bath of Ni-Fe, with pK values of approximately 6 to 3 respectively, was studied by Lieder and Biallozor. They reported that at a given electrode
Fig. 4-12: Effect of buffer pK on alloy composition.
Fig. 4-13: Normalized $\Theta$ as a function of potential.
Fig. 4-14: Rate of increase in normalized $\Theta$
potential, the partial current of hydrogen decreased while those of both nickel and iron increased. The exception was the case of boric acid where all of the partial currents decreased. The percentage of iron in the alloy deposits did not show a uniform trend at low potentials; however, at higher polarizations, in the presence of the organic compounds the alloy was richer in iron, as predicted by our model.

Horkans (1981) focused on the effect of boric acid and bisulfate ions on the nickel-iron alloys. Since her experiments were conducted under controlled current conditions, with no electrode potentials reported, direct comparison with the model is not possible. Horkans observed that the current efficiency of nickel-iron deposition from sulfate was lower than from chloride baths, while the percentage of iron in the alloy deposits were generally higher. Both the current efficiency and alloy composition trends may be partially explained by the buffering effect of bisulfate ions. Horkans reported that boric acid did not change the current efficiency, but increased the iron content significantly. Once again, in the absence of potential values, it is not possible to fully understand the role of boric acid and bisulfate ions in the electrodeposition of nickel-iron alloys. Qualitatively, however, the presence of bisulfate ions which have a pK value of about 2 could be the reason for the low current efficiency of the sulfate baths. As seen from the simulations, the pK of boric acid which is somewhere between 6 to 9, is too low to affect the current efficiency. The simulated effects of a buffer with a pK similar to that of boric acid indicates that the percentage of iron can increase.
Conclusions

The simulation results show that in the presence of a buffer in nickel-iron plating baths, while the partial current of hydrogen increases, those of the metals decrease. The buffer provides a reservoir of protons which means that at a given hydrogen current density, the rise in surface pH becomes smaller. This lowering of the surface pH decreases the interfacial concentration of metal-hydroxide complexes. Since the discharge kinetics of these complexes are faster than their corresponding metal ions, the partial current of metal deposition decreases. The rate of decrease for deposition of each alloy component depends on the electrode potential. Consequently, the change in the alloy composition also varies with potential. One important aspect of the simulated results is that unlike what was previously thought, a buffer can increase the content of the less noble component (e.g. iron in the nickel-iron alloys). Thus, the main criterion for a component in the electrolyte to be a true buffer is its ability to increase the hydrogen current at a given electrode potential. The changes in alloy composition will then be a function of the deposition mechanism. Our simulated results of a buffering agent are qualitatively similar to the observed behavior for ascorbic acid, D-mannitol, and citric acid. Additional experimental results are needed for determining the role of boric acid. The differences between nickel-iron deposition from a chloride and a sulfate bath may be partially explained by a buffering mechanism involving bisulfate ions.
References


Appendix 4

Program Alloy

The current efficiency and composition of nickel–iron electrodeposition is calculated. The electrode geometry is a rotating disk system for which experimental data for the nickel–iron system is available. Further, the RDE has a uniform axial flow and a well understood hydrodynamic. In this program the partial currents for nickel, iron and hydrogen at a given agitation speed, and electrode potential are calculated. The convective diffusive equations to be solved for each ionic species has the following form:

dCi /dt = -del.Ni + sum (Rij)

where the Ni is the flux of species i, and Rij is the rate of homogeneous reaction j for species i.

For the electrodeposition of nickel–iron and simultaneous hydrogen evolution, the following species are considered:
Fe+2, Ni+2, H+, OH-, FeOH+, NiOH+, HX and X-, where MOH+ ions are the mono–hydroxide complex ion, HX is a buffering agent with its conjugate base x-.

The hydroxide ions (FeOH+, NiOH+) are assumed to be at equilibrium with the Fe+2, and Ni+2. Water dissociation constant is used to relate the equilibrium of H+ and OH-.
There are 8 species and 8 equations which reduce the problem to the following four equations (4 mat’l bal, 4 Equilib).

-(del.Nfe+del.Nfeoh)=0
-(del.Nni+del.Nnioh)=0
-(del.NOH-del.Nh-del.nFe-del.Nni)=0
-(del.Nx-del.NHX)=0

For a well–supported electrolyted (ignoring migration), the convective–diffusive flux for species i is

Ni = -D grad Ci + Ci v

The input variables are the agitation rate (omega), V (the electrode potential), temperature (T), and the bath composition. Additionally, the kinetic parameters for each electrochemical discharge reaction, and thermodynamic values such as dissociation constant for the metal–hydroxide complexes should be specified.
Boundary Conditions:

Far away from the electrode surface, the concentration of each species approaches its bulk value.

At the electrode, the flux of ionic species are related to the electrochemical reactions. For the Tafel kinetics, the partial current of iron can be related to the discharge of ferrous and ferrous-hydroxide ions as follows:

\[ i_{Fe} = k_{c1}c_{Fe} \cdot \exp[(1-b1)2FV/RT] + k_{c2}c_{FeOH} \cdot (1-theta) \cdot \exp[(1-b2)2FV/RT] \]

where theta is the fraction of available surface sites for nickel-hydroxide ions.

Partial currents depend on the surface concentration of each species. The surface concentrations are obtained by solving the mass-transport problem subject to the flux boundary conditions (i.e. electrode reactions) at the electrode surface. Therefore, an iterative scheme is used. Initial guess for the surface concentrations is used to calculate the partial currents and the boundary condition. The transport problem for the set of coupled, non-linear second order differential equations is then solved. The new calculated surface concentration is then compared with the previously used value. The procedure is continued until convergence is obtained.

Finite element formulation:

Unknowns: \( F_{ej}, N_{ij}, H_j, X_j \)

No of elements = ne

No of equations : nsize=4*(ne+1)

Current density is used to non-dimensionalize the fluxes.

The domain is non-dimensionalized with respect to the smallest diffusion coefficient of the ionic species.

\( kmat := \) the banded form of the Jacobian matrix (nsize,15)

\( res := \) the load vector

\( Bandwidth=15 \)

real*8  kmat(200,15),tkmat(15,200),s(200)
real*8  cfeij(60),chij(60),cohij(60),cniij(60)
real*8  cfejit(60),chjit(60),cnijit(60)
real*8  cfeohjt(60),cniohjt(60)
real*8  cfeohj(60),cniohj(60)
real*8  chxj(60),cxj(60)
real*8  chxjt(60),cxjt(60)
real*8  sk(200,200), res(200), phi(2), phix(2),y(60)
Fluxes

\[ \text{dx, w(3), gp(3), sum, tol, domain} \]
\[ \text{cfe, ch, coh, cni, cfeoh, cnioh, cx, chx} \]
\[ \text{dch, dce, dcni, dcoh, dceoh, dcnioh, dcx, dchx} \]
\[ \text{Dh, Dfe, Dni, Doh, Dfeoh, Dnioh, Dxj, Dhx} \]
\[ \text{cfe0, cni0, Chx0} \]
\[ \text{cfe2, cni2, Chx2} \]
\[ \text{dx, w(3), gp(3), sum, tol, domain} \]
\[ \text{cfe, ch, coh, cni, cfeoh, cnioh, cx, chx} \]
\[ \text{dch, dce, dcni, dcoh, dceoh, dcnioh, dcx, dchx} \]
\[ \text{Dh, Dfe, Dni, Doh, Dfeoh, Dnioh, Dxj, Dhx} \]
\[ \text{cfe0, cni0, Chx0} \]
\[ \text{cfe2, cni2, Chx2} \]

\[ \text{correct for the convective and diffusive fluxes of hydroxides} \]
\[ \text{Nh(200), Noh(200), Nfe(200), Nni(200)} \]
\[ \text{Nfeoh(200), Nnioh(200), Nx(200), Nh(200)} \]
\[ \text{RT, alpha} \]

\[ \text{comparison with the old values of unknowns} \]
\[ \text{cfejo(60), cnijo(60), chjo(60)} \]
\[ \text{cfeohjo(60), cniohjo(60), cxjo(60), chxjo(60)} \]
\[ \text{tolc, sumc} \]

\[ \text{b1 = 1 - beta1; b2 = 1 - beta2} \]
\[ \text{V potential with respect to she} \]
\[ \text{kc1, kc2 = cm / sec i nm = kc1} \]

\[ \text{kcni, kc2ni, kc1fe, kc2fe, kch, kcw} \]
\[ \text{b1ni, b2ni, b1fe, b2fe, bh, bw} \]
\[ \text{V(30), gain, vd} \]

\[ \text{Take into account some blocking effect:} \]
\[ \text{theta} \]

\[ \text{theta parameter is the fraction of surface area available} \]
\[ \text{for the deposition} \]

\[ \text{maxcount, counti, counto} \]
\[ \text{n, nlc, nuc, ia, m, ib, ijob, ier, i, j, k, ne} \]
\[ \text{mm, 11, m1, l, ndim, nsize, iL, LL, LM, np, datap} \]
\[ \text{parameter (ndim = 200, F=96500, a=0.51023)} \]
Equilibrium constants of water, NiOH, FeOH (mole2/cm6)

parameter (kw=1d-20)

c Gauss Quadrature Points and their corresponding weights

common / gauss / gp, w
data gp / 0.1127, 0.5, 0.8873 /
data w / 0.27778, 0.44444, 0.27778 /
common / basis / phi, phix

c Required for IMSL matrix inversion routines
common / worksp / rwksp
real rwksp(54306)
call iwkin(54306)

open (unit=1, file=‘polarv.in’, status=‘old’)

c Kinetic parameters
read (1,*) kc1ni, kc2ni, kc1fe, kc2fe, kch, kw
read (1,*) b1ni, b2ni, b1fe, b2fe, bh, bw

c Dissociation constants for NiOH+, FeOH+, and HX
read (1,*) ki, k2, kb

c Number of elements, tolerance values
read (1,*) ne, tol, tolc

cc c Diffusivities
read (1,*) dh, dfe, dni, dfeoh, dnioh, doh, dx, dxj

c Total concentration of nickel and iron salts, bulk pH, and
buffer concentration in mole/lit
read (1,*) Cfeo, Cni0, chb, chx0

c The potential is dimensionless \( v / (RT / F) \)
c np is the number of points (i.e. electrode potential points)
read (1,*) np, RT
do i=1, np
read (1,*) v(i)
end do
Agitation rate \( \omega \) in rpm, and kinematic viscosity \((\nu)\)

```fortran
read (1,*)omega,kinvis
```

Domain for the calculation (Normalized distance in the axial direction)

```fortran
read (1,*)domain
read (1,*)maxcount
read (1,*)gain
close (1)
```

Limiting current calculations

\( \Delta \) is actually \( L^* \) in my notes. \( \Delta \) is \( \gamma(4/3) \cdot \text{deltamasstrans} \)

of the ion with the smallest diffusion coefficient

changing \( \omega \) from rpm to rad/sec

limiting current calculations \((\text{amp/cm}^2)\)

```fortran
ilimfe=0.019376*cf\text{e}_0*2*(\omega^{5.5})*(\text{dfe}^{10*5})*((2.0 \times 3.0)\times 10^{-6})*
& (100*\text{kinvis})^{-1/6}.

ilimi=0.019376*\text{cni}_0*2*(\omega^{5.5})*(\text{dni}^{10*5})*((2.3)/6)*
& (100*\text{kinvis})^{-1/6}.

ilimh=0.019376*\text{chb}*(\omega^{5.5})*(\text{dh}^{10*6})*((2.3)/6)*
& (100*\text{kinvis})^{-1/6}.
```

Initialize concentration profiles of all species

```fortran
open (unit=4, file='initial.in', status='old')
read (4,*)ne

     do i=1, ne+1
         read(4,*)cfej(i),chj(i),cnij(i),cohj(i),cfeohj(i),cniohj(i),\n&cxj(i)
     end do

close(4)
```

```fortran
ns\text{ize}=4*(\text{ne}+1)
\text{dx}=\text{domain}/\text{float(\text{ne})}
```
The undissociated buffer concentration \( chx \):
\[
chxb = chx0 / (1 + kb / chb) \\
cxb = chx0 - chxb
\]

Output file for all of the polarization data:

electrode potential, total current density, percentage of iron in the alloy, partial currents of iron, nickel and hydrogen

\[
\text{open (unit=7, file='polarv.pol', status='new')} \\
\text{write(7,2111)} \\
\text{format(' "V, itot, e, fep, ife, ih2, ini"')} \\
\text{write(7,2111)}
\]

Change omega to rad/sec
\[
\text{omega} = \text{omega} * 3.14 / 30.0
\]

Delta is calculated to be the boundary layer thickness of the ion with the smallest diffusion coefficient
\[
\text{alpha} = a * \text{omega} * (\text{omega} / \text{kinvis})^{0.5} \\
\text{delta} = (3 * \text{dfe} / (a * \text{kinvis}))^{0.5} * (\text{kinvis} / \text{omega})^{0.5}
\]
write(2, 5) delta
format(' delta=', el2.5)
write(2, 6)
format(' mole (cm3): cfeb, cnib, chb, cohb, cfeohb, cniohb')
write(2,25) cfeb, cnib, chb, cohb, cfeohb, cniohb
write (2,7) alpha
format(' alpha=', el2.5)
write(2,71) kcl ni, kclfe, kcl2ni, kcl2fe, kch, kcw
format(6el2.5)
write(2, * ) bl ni, b2ni, blfe, b2fe, bh, bw

datap=0

This is to take a vector input of v

6000 datap=datap+1
if (datap .gt. np) goto 10000
write(2,* ) datap

The body of the simulation begins:
counto=0

The first loop only
do i=1, ne+1
  cfejo(i)=cfej(i)
cnij(i)=cnij(i)
chj(i)=chj(i)
cfeohjo(i)=cfeohj(i)
cniohjo(i)=cniohj(i)
cxj(i)=cxj(i)
end do
goto 3010
goto 3000

General

3000 do i=1, ne+1
  cfej(i)=cfej(i)+gain*(cfejt(i)−cfejo(i))
cnij(i)=cnij(i)+gain*(cnijt(i)−cnijo(i))
chj(i)=chj(i)+gain*(chjt(i)−chj(i))
cfeohj(i)=cfeohj(i)+gain*(cfeohjt(i)−cfeohjo(i))
cniohj(i)=cniohj(i)+gain*(cniohjt(i)−cniohjo(i))
  cxj(i)=cxj(i)+gain*(cxjt(i)−cxjo(i))
cfejo(i)=cfej(i)
cnij(i)=cnij(i)
chj(i)=chj(i)
cfeohjo(i)=cfeohj(i)
Calculating the flux at the electrode surface based on the kinetic parameters for the electrode reactions:

\[ v_d = V_{(\text{datap})}/0.0256 \]
\[ i_{fe1} = 2f^*k_{c1fe}^*c_{fej}(1)^*c_{feb}^*\text{dexp}(b_{1fe}^*2^*V_d) \]
\[ i_{fe2} = 2f^*k_{c2fe}^*c_{feohj}(1)^*c_{feohb}^*\text{dexp}(b_{2fe}^*2^*V_d) \]
\[ i_{ni1} = 2f^*k_{c1ni}^*c_{nij}(1)^*c_{nib}^*\text{dexp}(b_{1ni}^*2^*V_d) \]
\[ i_{ni2} = 2f^*k_{c2ni}^*c_{niohj}(1)^*c_{niohb}^*\text{dexp}(b_{2ni}^*2^*V_d) \]
\[ i_h = F^*k_{ch}^*c_{Hj}(1)^*c_{chb}^*\text{dexp}(b_{h}^*V_d) + f^*k_{cw}^*\text{dexp}(b_{w}^*V_d) \]

Calculation of theta, assuming the Langmuir adsorption constants are the same for FeOH+ and NiOH+:

\[ \theta = \frac{c_{niohj}(1)^*c_{niohb}}{c_{niohj}(1)^*c_{niohb} + c_{feohj}(1)^*c_{feohb}} \]

Damp the simulation by taking the avg. of the currents of two iterations

\[ i_{fe}(\text{counto}) = 0.5*(i_{fe}(\text{counto}-1)+i_{fe1}+(1-\theta)*i_{fe2}) \]
\[ i_{ni}(\text{counto}) = 0.5*(i_{ni}(\text{counto}-1)+i_{ni1}+\theta*i_{ni2}) \]
\[ i_{h2}(\text{counto}) = 0.5*(i_{h2}(\text{counto}-1)+i_{h}) \]

The partial currents are all in amp/cm2 since the simplex routine that calculates the kci and the betas reads the currents in amp/cm2.

if (ih2(counto) .gt. ilimh) then
  print*,' hydrogen limiting current exceeded'
endif

if (ife(counto) .gt. ilimfe) then
print*(" iron current set to .999 ilim")
ife(counto)=0.9*ife(counto)
goto 3021
endif

if (ini(counto) .gt. ilimni) then
   print*(" nickel limiting current exceeded")
endif

c Define efficiency and fe% based on the calculated partial current
c densities: negative sign to take care of the cathodic nature.
itot=-(ife(counto)+ini(counto)+ih2(counto))
e=-(ini(counto)+ife(counto))/itot
fep=ife(counto)/(ife(counto)+ini(counto))

c The current had to be in amp /cm2

c c betal and beta2 in my notes correspond to p1 and p2 in the code
pl=2*alpha*f*delta**2 /itot
p2=F/(delta*itot)
c
cccc

c Write (2, *counto
c write (2, 4) itot, e, fep
c4 format(’ itot=’f8.4 ’ efficiency=’f7.3, ’ %fe=’f8.4)
c write(2,41) ifel,ife2,inil,ini2
c41 format(’ ifel,ife2’,2e12.5, ’ inil,ini2=’e12.5)
c

cccc

c We start module alloy as before at this point

999 counti=0
1000 counti=counti+1
   if (counti .gt. maxcount) then
     write(2,1001)
c1001 format(’ count exceeded the limit’)
     goto 5000
   endif
   do i=1, nsize
     res(i)=0
     s(i)=0
     do k=1,nsize
       sk(i,k)=0
      end do
   end do
Calculation of concentrations and fluxes at each node

2000    do 100 i=1, ne
       y(i+1)=y(i)+dx
    do 99  j=1, 3

       call tfunct(gp(j),dx)

Linear basis functions

Cfe=cfej(i)*phi(1)+cfej(i+1)*phi(2)
Ch=chj(i)*phi(1)+chj(i+1)*phi(2)
Cni=cnij(i)*phi(1)+cnij(i+1)*phi(2)
Dcfe=cfej(i)*phix(1)+cfej(i+1)*phix(2)
Dch=chj(i)*phix(1)+chj(i+1)*phix(2)
Dcni=cnij(i)*phix(1)+cnij(i+1)*phix(2)
Coh=1./Ch
Cfeoh=cfe*coh
Cnioh=cni*coh

Concentration gradients:

Dcoh=-Dch/Ch**2
Dcfeoh=dcefe*coh+dcoh*cfe
Dcniho=dcni*coh+dcoh*cni

Concentration and concentration gradients of conjugate base
and the undissociated buffer.

Cx=cxj(i)*phi(1)+cxj(i+1)*phi(2)
Dcx=cxj(i)*phix(1)+cxj(i+1)*phix(2)
Chx=Cx*Ch
DChx=dcx*ch+dch*cx

For transient problem need to keep track of the old values

Cfeo=cfejo(i)*phi(1)+cfejo(i+1)*phi(2)
Cho=chjo(i)*phi(1)+chjo(i+1)*phi(2)
Cnio=cnijo(i)*phi(1)+cnijo(i+1)*phi(2)
Coho=1./cho
Cfeoho=cfeo*coh
Cnioho=cnio*coh
Take care of remeshing
For now, without remeshing take x the Gauss-point
\[ mm = 3(i-1)+j \]
\[ x(mm) = y(i) + gp(j) \cdot dx \]

Calculation of the flux of various species at the node \( i \) including migration(m), diffusion(d) and convection(c)

\[
\begin{align*}
N_{fem}(mm) &= -2 * p1 * ufe * cfeb * cfe * dp \\
N_{fed}(mm) &= -p2 * dfe * cfeb * dcf \\
N_{fec}(mm) &= -.5 * p1 * cfeb * (x(mm)**2) * cfe \\
N_{fe}(mm) &= N_{fed}(mm) + N_{fec}(mm)
\end{align*}
\]

\[
\begin{align*}
N_{hm}(mm) &= -p1 * uhb * chb * chb * dp \\
N_{hd}(mm) &= -p2 * dh * chb * dch \\
N_{hc}(mm) &= -.5 * p1 * chb * x(mm)**2 * ch \\
N_{h}(mm) &= N_{hd}(mm) + N_{hc}(mm)
\end{align*}
\]

\[
\begin{align*}
N_{ohm}(mm) &= p1 * uoh * cohb * cohb * dp \\
N_{ohd}(mm) &= -p2 * doh * cohb * dcoh \\
N_{ohc}(mm) &= -.5 * p1 * cohb * x(mm)**2 * coh \\
N_{oh}(mm) &= N_{ohd}(mm) + N_{ohc}(mm)
\end{align*}
\]

\[
\begin{align*}
N_{nid}(mm) &= -p2 * dni * cnib * dci \\
N_{nic}(mm) &= -.5 * p1 * cnib * x(mm)**2 * cni \\
N_{ni}(mm) &= N_{nic}(mm) + N_{nid}(mm)
\end{align*}
\]

\[
\begin{align*}
N_{fiohd}(mm) &= -p2 * dfeoh * cfeohb * dcf \\
N_{fiohc}(mm) &= -.5 * p1 * Cfeohb * x(mm)**2 * cfeoh \\
N_{fioh}(mm) &= N_{fiohd}(mm) + N_{fiohc}(mm)
\end{align*}
\]

\[
\begin{align*}
N_{niohd}(mm) &= -p2 * dniob * cniohb * dcnioh \\
N_{niohc}(mm) &= -.5 * p1 * cniohb * x(mm)**2 * cnioh \\
N_{nioh}(mm) &= N_{niohd}(mm) + N_{niohc}(mm)
\end{align*}
\]

Effect of Buffers:
\[
\begin{align*}
N_{xd}(mm) &= -p2 * dxj * cxb * dcx \\
N_{xc}(mm) &= -.5 * p1 * cxb * x(mm)**2 * cx \\
N_{x}(mm) &= N_{xd}(mm) + N_{xc}(mm)
\end{align*}
\]

\[
\begin{align*}
N_{hx}(mm) &= -p2 * dhx * chxb * dchx \\
N_{hx}(mm) &= -.5 * p1 * chxb * x(mm)**2 * chx \\
N_{h}(mm) &= N_{hx}(mm) + N_{hx}(mm)
\end{align*}
\]
Element by element construction of the load vector (residual) vector, and stiffness matrix (SK)

Residual vector

Row Indexing; 4 unknowns in every element

\[ L_1 = 4i - 3 \]

\[
\text{do 98 } L=1,2 \\
\text{LL}=4(L-1)
\]

Residual for the cfe

\[
\text{res}(L1+LL)=\text{res}(L1+LL) - w(j)\times dx \times (Nfe(mm)+Nfeoh(mm)) \times \phi x(L) \\
+ w(j)\times dx \times p1 \times (cfe\times cfeb+cfeoh\times cfeohb) \times x(mm) \times \phi(L)
\]

Residual for the Cni

\[
\text{res}(L1+LL+1)=\text{res}(L1+LL+1) - w(j)\times dx \times \phi x(L) \times (Nni(mm) \\
+ Nnioh(mm)) + W(J) \times dx \times p1 \times (Cni\times cnib+cnioh\times cniohb) \times x(mm) \times \phi(L)
\]

Residual for the Ch

\[
\text{res}(L1+LL+2)=\text{res}(L1+LL+2) - w(j)\times dx \times \phi x(L) \times (NOH(mm) - Nh(mm) \\
- Nfe(mm) - Nni(mm) + Nx(mm)) + w(j)\times dx \times x(mm) \times \phi(L) \times p1 \times (coh\times cohb- \times ch\times chb \\
- cfe\times cfcb - cni\times cnib + cx\times cxb)
\]

Residual for the Cx

\[
\text{res}(L1+LL+3)=\text{res}(L1+LL+3) - w(j)\times dx \times \phi x(L) \times (Nx(mm) + Nh(mm)) \\
+ w(j)\times dx \times x(mm) \times \phi(L) \times p1 \times (cx\times cxb + ch\times chxb)
\]

Assembling the Jacobian

\[
\text{do 97 } M=1,2 \\
\text{LM}=4(M-1) \\
dpipj=w(j)\times dx \times \phi x(L) \times \phi(M) \\
dpidpj=w(j)\times dx \times \phi x(L) \times \phi x(M) \\
\text{pipj}=w(j)\times dx \times \phi(L) \times \phi(M)
\]
c First parent matrix: \( \frac{\delta R_{cfe}}{\delta c_{fej}} \)

\[
\text{sk}(L_1+L_1+L_1+L_1) = \text{sk}(L_1+L_1+L_1+L_1) - p_2*(dfe*cfeb+dfeoh* \\& Cfeohb*coh) - 0.5*p_1*dpijp*(cfeb+cfeohb*coh)*x(mm)**2 - p_1*pipj*cfeb \\
&+*(1+cohb*coh)*x(mm)
\]

c Second parent matrix: \( \frac{\delta R_{cfe}}{\delta R_{cnij}} = 0 \)

c Third parent matrix: \( \frac{\delta R_{cfe}}{\delta Chj} \)

\[
\text{sk}(L_1+L_1+L_1+L_1+L_1) = \text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1) - p_2*(dfeoh*cfeohb*dpijp*} \\
&(cfe /ch**2)+0.5*p_1*cfeohb*dpijp*cfe /ch**2)*x(mm)**2 + p_1*pipj*cfeohb* \\
&+cfe /ch**2)*x(mm)
\]

c Fourth = \( \frac{\delta R_{cfe}}{\delta cx} = 0 \)

c Fifth parent matrix: \( \frac{\delta R_{cnj}}{\delta c_{fej}} \)

\[
\text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1) = \text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1) - p_2*(dni*cnib \\
&+dnioh*cniohb*coh)*dpijp - 0.5*p_1*pipj*(cnib+cniohb*coh) \\
&+x(mm)**2 - p_1*cnib*(1+cohb*coh)*x(mm)*pipj
\]

c Sixth parent matrix: \( \frac{\delta R_{cnj}}{\delta c_{ni}} \)

\[
\text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1) = \text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1) - p_2*(dni*cnib \\
&+dnioh*cniohb*coh)*dpijp - 0.5*p_1*cnib*coh)*x(mm)**2 + p_1*cnib*coh)*x(mm)
\]

c Seventh parent matrix \( \frac{\delta R_{cnj}}{\delta ch} \)

\[
\text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1) = \text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1) - p_2*(dni*cnib*dpijp*} \\
&(cohb /ch**2)+0.5*p_1*cnib*coh)*x(mm)**2 + p_1*cnib*coh)*x(mm)
\]

c Eighth pm \( \frac{\delta R_{cnj}}{\delta cx} = 0 \)

c Ninth parent matrix: \( \frac{\delta R_{cch}}{\delta c_{fej}} \)

\[
\text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1) = \text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1) - p_2*(dni*cnib*dpijp*} \\
&+0.5*p_1*cfeb*x(mm)**2 + p_1*x(mm)*pipj*cfeb
\]

c Tenth parent matrix: \( \frac{\delta R_{cch}}{\delta c_{ni}} \)

\[
\text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1) = \text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1) - p_2*(dni*cnib*dpijp*} \\
&+0.5*p_1*cnib*x(mm)**2 + p_1*x(mm)*pipj*cnib
\]

c Eleventh parent matrix: \( \frac{\delta R_{cch}}{\delta ch} \)

\[
\text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1) = \text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1) - p_2*(dni*cnib*dpijp*} \\
&+0.5*p_1*cnib*x(mm)**2 + p_1*x(mm)*pipj*cnib
\]

c Twelfth: \( \frac{\delta R_{cch}}{\delta cx} \)

\[
\text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1) = \text{sk}(L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1+L_1) - p_2*(d_ni*cnib*dpijp*} \\
&+0.5*p_1*cfeb*x(mm)**2 + p_1*x(mm)*pipj*cfeb
\]

c Thirteenth and Fourteenth are \( \frac{\delta R_{cx}}{\delta c_{fej}} \) and \( \frac{\delta R_{cx}}{\delta c_{ni}} = 0 \)
c Fifteenth: \( \frac{\partial R_x}{\partial c_{x,j}} \)
\[
\text{sk}(L_l+L_l+3L_l+3L_l+2) - \text{dpipj} \times p_2 \times (dh_x \times c_{x,b} \times cx) - 0.5 \times p_1 \times \text{dpipj} \times c_{x,b} \times c_x \times (mm)^2 - p_1 \times \text{pipj} \times c_{x,b} \times c_x \times (mm)
\]

c Sixteenth: \( \frac{\partial R_x}{\partial c_{x,j}} \)
\[
\text{sk}(L_l+L_l+3L_l+3L_l+3) - \text{dpipj} \times p_2 \times (dx_j \times c_{x,b} + dh_x \times c_{x,b} \times c_{x,b}) - 0.5 \times p_1 \times \text{dpipj} \times (c_{x,b} \times c_{x,b} + c_{x,b} \times c_{x,b}) \times (mm)^2 - p_1 \times \text{pipj} \times (c_{x,b} + c_{x,b} \times (mm))
\]

ccccccccccccc FINALLY IT IS DONE!!!!!!!!!!!!!!!!ccccccccccccccc

97       continue
98       continue
99       continue
100      continue
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc

c Boundary condition on the last node

do    j= 1, nsize
    do   m=1, 4
         sk(nsize+1-m,j)=0
    end do
end do


c At \( x=1 \), \( C_i = C_{ibulk} \), potential=0

do   m=1, 4
    sk(nsize+1-m,nsize+1-m)=1
    res(nsize+1-m)=0
end do

cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc

c Boundary condition for the dimensional fluxes at the electrode surface:
c (for non-dimensional, must divide by \( \text{itot} /F \))
c \( X=0, \text{Nfe} + \text{Nfeoh} = \text{ife} /2F, \text{Nni} + \text{NnioH} = \text{ini} /2F \)
c \( \text{Nfe} = \text{ife} 1 /2F, \text{Nfeoh} = \text{ife} 2 /2F \)
c \( \text{Nni} = \text{ini} 1 /2F, \text{NnioH} = \text{ini} 2 /2F \)
c \( \text{Nh} = \text{ih} 1 /F, \text{Noh} = -\text{ih} 2 /F - \text{ife} 2 /2F - \text{ini} 2 /2F \)
c \( \text{Nh} + \text{Nh} = 0 \)
c \( \text{ife} = \text{fe}% \times \text{e} \times \text{itot}, \text{ini} = (1-\text{fe}%) \times \text{e} \times \text{itot} \)
c where \( e \) is the current efficiency \( = 1 - \text{ih} 2 /\text{itot} \)

res(1)=res(1) - e*fe% /2
res(2)=res(2) - e*(1-fe%) /2
res(3)=res(3)+(1-e /2)
changing the jacobian matrix to the banded form ukmat
using Surendra's Band subroutine

  call band(ndim,nsize,sk,nuc,nlc,kmat)

Checking the residual and jacobian

  if (counti .lt. 10 ) then
  write (2, 106)counti
  c106 format(' counti=',i5)
  write(2,107)
  c107 format(' Jacobian')
  if (counti .eq. 5) then
    do i=1, nsize
      write (2,*) (sk(i,j), j=1, nsize)
    end do
  endif
  write(2 ,108)
  c108 format(' residual vector')
  do i=1, nsize
    write(2,*)(res(i))
  end do
  endif

Matrix inversion IMSL routine : Transpose of the banded matrix is inverted

  do j=1, 15
    do i=1, ndim
      tkmat(j,i)=kmat(i,j)
    end do
  end do

  call DLSARB ( nsize,tkmat,ndim, nlc,nuc, res, ijob, s)

The IMSL routine for the general matrix:

  call DLSARG (nsize,sk,ndim,res,1,s)

  do mm=1, 3*ne, 3
    write(2,17),mm
  end do
format( ' Gauss point',i4)  
c  c  write(2,19)  
c19 format( ' Diffusion flux:')  
c  write(2,25)nfe(mm),nhd(mm),nnid(mm),nohd(mm),nfeohd(mm),nxd(mm)  
c  WRITE (2,22)  
c22 format( ' Total flux: x,nfe, nh, nni, noh, nfeoh nx')  
c  write (2,25)x(mm),nfe(mm),nh(mm),nni(mm),noh(mm),nfeoh(mm),nx(mm)  
c end do  
ccccccccccccccccccccccccccccccccccccccccccccccccccccccc

c Time for updating the values of all unknowns  
c  write(2,30)  
c30 format( ' S values for fe,ni,h,x')  
  do i=1, ne+1  
    if (s(4*i-3) .lt. -.999*cfej(i)) s(4*i-3)=-0.999*cfej(i)  
    if (s(4*i-2) .lt. -.999*cnij(i)) s(4*i-2)=-0.999*cnij(i)  
    if (s(4*i-1) .lt. -.999*chj(i)) s(4*i-1)=-0.999*chj(i)  
    cfej(i)=cfej(i)+s(4*i-3)  
    cnij(i)=cnij(i)+s(4*i-2)  
    chj(i)=chj(i)+s(4*i-1)  
    cxj(i)=cxj(i)+s(4*i)  
    chxj(i)=cxj(i)*chj(i)  
    cohj(i)=1./chj(i)  
    cfeohj(i)=cfej(i)*cohj(i)  
    cniohj(i)=cnij(i)*cohj(i)  
    write (2,*),s(4*i-3),s(4*i-2),s(4*i-1),s(4*i)  
  end do  
ccccccccccccccccccccccccccccccccccccccccccccccccccccccc

if (cfej(1) .lt. 0) then  
  print*,(' Negative Concent., Lower the current')  
endif  
sum = 0  
do 150 k=1, nsize  
  sum = sum+(res(k)**2)  
  sum = sqrt(sum)  
  print*,('counto='),counto  
  print* , ('iteration='),counti  
  print*,('sum of residuals= '), sum
c write (2,151) counti,sum
cl51 format(’ counti’,i4,’ sum’, e12.5)

c Compare the value of the cfej(1) with the bulk
c if ((cfej(1) .gt. cfej(ne+1)) .and. (e .gt. 0)) then
  write(6,152)
c format(’ wrong concent. grad!’)
c go to 5000
c endif

if (sum .gt. tol) goto 1000

c
Check to see if the surface concentrations are
the same as the value we started with.
The new surface concentrations are used with the
kinetic parameters to get new current densities.

sumc=0
sumc=(cfej(1)-cfejo(1))**2+(cnij(1)-cnijo(1))**2
sumc=sqrt((sumc+(chj(1)-chjo(1))**2))

If the surface concentrations do not give the currents
that the outer loop was using, then we go through the
outer loop again and use the new partial currents.
The surface concentrations are modified with a damping
factor called gain.

if (sumc .gt. tolc) then
  do i=1, ne+1
    cfejit(i)=cfej(i)
    cnijt(i)=cnij(i)
    chjt(i)=chj(i)
    cfeohjt(i)=cfeohj(i)
    cniohjt(i)=cniohj(i)
    cxjt(i)=cxj(i)
  end do
  goto 3000
end if

4000 continue

5000 open (unit=5, file=’polarv.con’, status=’new’)
format (6e10.3,1e12.5)
write(5,*),ne,domain
write(7,23)V(datap),itot,e,fep,ife(counto),ih2(counto),ini(counto)
write(7,25)cfej(1),chj(1),cnij(1),cohj(1),cfeohj(1),cniohj(1),
&cxj(1)
23
format(1f7.3,6e11.3)
do i=1, ne+1
write(5,50001)cfej(i),chj(i),cnij(i),cohj(i),cfeohj(i),
&cniohj(i), cxj(i)
end do
write(5,211)
211
format(" cfej, chj, cnij, cohj, cfeohj,
&cniohj, cxj")
omega=omega*30.0 /3.14
write(5,210)omega
210
format(" omega(rpm)=",f12.2)
omega=omega*3.14 /30.0
write(5,2101)counti,counto,maxcount
2101
format(" counti=",i5, ", counto=",i5, ", maxcount=",i5)
write(5,212)ilimfe,ilimh,ilimni
212
format(" ilim(a /cm2):fe=",e12.5, ", h=",e12.5, ", ni=",e12.5)
write(5,213)V(datap),-itot
213
format(" V=",f7.3, ", itot(a /cm2)=",f9.5)
write(5,215)e,fep
215
format(" efficiency="e12.5, ", fe%=",e12.5)
write(5,214)ife(counto),ih2(counto),ini(counto)
214
format(" ife, ih, ini=",3e12.5)
write(5,216)k1,k2,kb
216
format(" dissociation constants:feoh, nioh, hx=",3e12.5)
write(5,2161)
2161
format(" Cb(mol /cm3): Fe, Feoh, Ni, Nioh, H, Hx, HX0")
write(5,2162)cfeb,cfeohb,cnib,cniohb,chb,chxb,chx0
2162
format(7e12.5)
write(5,217)
217
format(" kc1fe, kc2fe, kc1ni, kc2ni, kch, kcw=")
write(5,2172)kc1fe,kc2fe,kc1ni,kc2ni,kch,kcw
2172
format(6e12.5)
write(5,218)b1fe,b2fe,b1ni,b2ni,bh,bw
218
format(" b1fe,b2fe,b1ni,b2ni,bh,bw",6f7.3)
write(5,219)tol,tolc
219
format(" tol,tolc="",2e12.5)
if (ife(counto) .eq. 0) goto 2201
write(5,220)ife2 /ife(counto)
220
format(" "ife2 /ife="",e12.5)
2201 if (ini(counto) .eq. 0) goto 11000
write(5,221)ini2 /ini(counto)
221
format(" "ini2 /ini="",e12.5)
write(5,222)theta
222
format(" "theta="",f7.5)
write(5,223)nfed(1),nfeohd(1),nfeoch(1)
format(" nfed, nfeohd, nfeoch",4e12.5)
write(5,224)ife1,ife2, ini1, ini2
224
format(" ife1, ife2, ini1, ini2",4e12.5)
write(5,225)nhd(1), nhc(1), nohd(1), nohc(1)
format(" nhd, nhc, nohd, nohc",4e12.5)
write(5,9000)
9000 format(" --------------------------------")
goto 6000
11000 write(5,222)theta
write(5,9000)
goto 6000
10000 close(5)
c close(2)
stop
end

c Subroutine tfunct calculates phil, phi2, phix1, phix2
c which are the local basis functions and their derivatives
c at any point within the local domain.

c Subroutine tfunct

define real*8 position,dx
real*8 phi(2), phix(2)
common /basis /phi, phix

c Remember to modify derivatives based on dx
phix(1) = -1./dx
phix(2) = 1./dx
phi(1) = 1-position
phi(2) = position
return
end
Chapter 5: Method for In-Situ Measurement of pH on the Surface of the Disk Using a Rotating Ring-Disk Electrode

Abstract

A rotating disk electrode with a pH sensitive ring, held at open-circuit, can be used for the in-situ measurement of pH at a disk. This mode of operating RRDE differs from the conventional amperometric usage which is based on a mass-transfer-limited consumption of the disk reaction-intermediate at the ring. The technique takes advantage of the well-characterized velocity field at the rotating disk electrode and has the added advantage that the pH probe, the ring electrode, is not interfering with the flow field and the current distribution on the disk. The ring establishes a potential corresponding to the average concentration of hydronium ions in the ring region. To determine the pH at the disk electrode by measuring the potential at the ring, the radial transport of hydronium ions across the insulating gap and on the ring taking into account the effect of homogeneous dissociation reactions of water, metal-hydroxide complexes, and buffering agents, is analyzed. For metal deposition reactions with concurrent hydrogen evolution, the additional shifts in the ring potential caused by hydrogen super-saturation and ohmic drop are investigated.
Chapter 5

Background

Electrochemical processes such as corrosion, electro-synthesis, and electrodeposition often result in pH changes at the electrode-solution interface. The interfacial pH may differ considerably from that in the bulk solution, and in turn may affect the charge transfer process occurring at the electrode surface. The importance of this phenomenon in electrochemical systems has been recognized for some time, and has led researchers to devise methods for measuring these effects. In a review article, Kuhn (1983) affirms the importance of pH measurement near the electrode surface, and discusses various techniques including colorimetric and optical, sampling, and electrometric methods. The last of these techniques involves placement of a pH sensitive electrode in the vicinity of the working electrode. For example, antimony microelectrodes (Matulis and Slizys, 1964), flat bottomed glass electrodes positioned behind thin, fine mesh cathodes (Romankiw, 1987), platinized platinum or bismuth embedded in the working electrodes (Gunther et al., 1979) have been used to measure pH at the electrode surface.

Bek and Borodikhina (1978) were first to propose that a rotating disk electrode with a pH sensitive ring could be used for in-situ measurement of pH at a disk, but offered neither theory nor experimental results. Albery and Calvo (1982) presented the first actual application of this system for surface pH measurement. The technique takes advantage of the well-characterized hydrodynamics of the rotating disk electrode and the pH probe, the ring electrode, does not interfere with the flow field and the current distribution on the disk (Fig. 5-1). This mode of operating the rotating ring-disk electrode, RRDE, is in contrast with the amperometric usage which is based on a mass-
Fig. 5-1: Rotating Ring-Disk Electrode (RRDE).

The ring electrode is monitored at open circuit potential.
transfer-limited consumption of the disk reaction-intermediate at the ring. The pH sensitive ring material establishes a potential corresponding to the average concentration of hydronium ions in the ring region. To determine the pH at the disk electrode by measuring the potential at the ring, the radial transport of hydronium ions across the gap and the ring regions must be understood.

In this work, the effect of hydrogen evolution at the disk electrode on the interfacial pH rise and the subsequent ring response will be investigated. Albery and Calvo (1983) followed by Albery and Mount (1989) have previously used a bismuth oxide ring electrode to investigate proton fluxes through a thionine-coated disk electrode. In our work, we have used a platinum-black ring in hydrogen atmosphere to investigate metal electrodeposition with concurrent hydrogen evolution. For this system, the interfacial pH measurement on the disk surface requires an analysis of the cathodic shift of the ring potential in the presence of metal-hydroxide complexes, buffering agents, hydrogen gas super-saturation and ohmic drop.

**Transport in the RRDE System**

Consider the convective diffusive transport of a single reacting species in the RRDE system. The thinness of the diffusion layer (high Sc number) and a large Peclet number in the radial direction simplify the material balance to the following form:

\[
\frac{\partial y \Omega (\frac{\Omega}{v})^{1/2}}{\partial y} \left( r \frac{\partial C}{\partial r} - y \frac{\partial C}{\partial y} \right) = D \frac{\partial^2 C}{\partial y^2} \quad [5.1]
\]

where migration is assumed negligible, and there are no homogeneous chemical reactions. Introducing a dimensionless axial distance from the electrode,
\[ \zeta = y \left( \frac{\Omega}{v} \right)^{1/4} \left( \frac{a v}{3D} \right)^{1/3} = y \alpha \]  

Eq. [5.1] can be written as:

\[ 3\zeta \left[ \frac{r}{\partial C}{\partial r} - \zeta \frac{\partial C}{\partial \zeta} \right] = \frac{\partial^2 C}{\partial \zeta^2} \]  

The disk electrode is taken to be uniformly accessible to the electro-active species, an assumption which strictly holds at limiting current. Far away from the electrode, the concentration approaches that of the bulk solution. The normalized concentration profile, \( \Theta \), in the disk zone can be expressed as:

\[ \Theta = \frac{C - C_d}{C^b - C_d} = \frac{1}{\Gamma (4/3)} \int_0^\zeta e^{-x^2} dx \]  

The current density at the disk is related to the flux at the electrode,

\[ \frac{i}{F} = -D \left. \frac{\partial C}{\partial y} \right|_{y=0} \]  

while the normal flux of the reacting species on the insulator is zero. The boundary condition at the ring electrode depends on the mode of operation of the RRDE. In the open-circuit, potentiometric application of the RRDE, the normal flux of the electro-active species is zero since no net charge-transfer reaction occurs.

Albery and Brukenstein (1966) have carried out the solution to this problem in the gap and ring regions by using Laplace transformation of the \( r \) variable. Smyrl and Newman (1972) applied Lighthill transformation and superposition integrals to solve the above problem. Both methods lead to the following description for the radial concentration profile on the plane of the RRDE:

\[ \frac{C^{(r)} - C_d}{C^b - C_d} = F(\rho) ; \quad \rho = \left( \frac{r}{r_0} \right)^3 - 1 \]
where \( F(p) = \frac{1}{4} + \frac{3}{2\pi} \tan^{-1}\left[ \frac{2p^{1/3} - 1}{\sqrt{3}} \right] + \frac{\sqrt{3}}{4\pi} \ln \left[ \frac{1 + p^{1/3}}{1 + p} \right] \).

Equation [5.6] relates the concentration at the disk surface, \( C^d \), to the concentration at other points on the plane of RRDE, and the insulating annulus, \( C_{(r)} \). This relationship depends only on the geometry: the disk radius, \( r_0 \), and the radial distance from the center of the disk. Since the ring is kept at open circuit, it can also be considered as part of the gap or insulator region.

To relate the radial concentration on the plane of the RRDE to the current density at the disk, we take advantage of the relationship between the current density and the disk surface concentration:

\[
1 - \frac{C^d}{C^b} = I = \frac{i}{i_{\text{lim}}} \tag{5.7}
\]

where \( I \) is the fraction of the mass-transfer limiting current. The dependence of \( C_{(r)} \) on the applied current density can now be obtained by rearranging Eq. [5.6] and using Eq. [5.7]:

\[
\frac{C_{(r)}}{C^b} = 1 - I \left[ 1 - F(p) \right] \tag{5.8}
\]

where the geometry dependent term \( 1 - F(p) \) is plotted in Fig. 5-2.

Depletion of the electro-active species, caused by the disk reaction, is felt downstream by the ring electrode. In Fig. 5-3 a map of normalized concentration away from the disk electrode, both in the axial direction, and radially on the plane of RRDE, is
Fig. 5-2: Geometry dependent term.
Fig. 5-3: Comparison of radial and axial variation of normalized concentration, 900 rpm, disk radius = 0.4 cm.
shown. It can be seen that for a rotation speed of 900 rpm, $D_i = 10^{-5} \text{cm}^2/\text{sec}$, $v = 0.01 \text{cm}^2/\text{sec}$, and $r_0 = 0.4 \text{cm}$, the axial variation in concentration occurs over distances comparable to the mass-transfer boundary layer thickness of 20 μm. In the radial direction, the variation in concentration takes place over much larger distances. As an example, for detecting $\Theta = 0.5$, the probe should be placed 7 μm away from the disk surface axially, or 300 μm away from the edge of the disk, on the plane of RRDE. In other words, while in the axial direction mass-transfer limitations are confined to a very small region, in the radial direction convection carries the depleted solution to much larger distances. This implies that the ring electrode as a probe is not only non-intrusive, but also has a very good sensitivity for detecting concentration changes.

**Interfacial pH Rise at the Disk**

Having established the inter-dependence of the disk surface concentration, current density, and the radial concentration profile, Eqs. [5.6-5.8], we now return to the measurement of the interfacial pH on the disk by potentiometric operation of the ring.

In aqueous media, the transport of protons is coupled with other species such as hydroxyl ions, metal-hydroxide complexes, and buffers. The presence of any other electro-active species, e.g. discharging metal ions during electroplating, requires modification of the analysis presented for a single reactive species. We limit our analysis to hydrogen evolution as the source of pH rise at the disk electrode.

- **Base Case**

We first analyze the base case where hydrogen is evolved from an acidic media in
the absence of buffers. The overall discharge reactions leading to hydrogen deposition are:

\[ H^+ + e^- \rightarrow \frac{1}{2} H_2 \]
\[ H_2O + e^- \rightarrow \frac{1}{2} H_2 + OH^- \]

The material balance equations for \( H^+ \) and \( OH^- \) ions are coupled through the water dissociation equilibrium maintained throughout the solution. If formation of bubbles and surface films such as metal-hydroxide precipitates can be neglected, the combined equation for the two species can be written:

\[ ay\Omega \left( \frac{\Omega}{v} \right)^{1/2} \left[ r \frac{\partial (C_{H^+} - C_{OH^-})}{\partial r} - y \frac{\partial (C_{H^+} - C_{OH^-})}{\partial y} \right] = \frac{\partial^2}{\partial y^2} \left[ C_{H^+} - \frac{D_{OH^-}}{D_{H^+}} C_{OH^-} \right] \quad [5.9] \]

As a result of both hydronium ion and water discharge, the boundary condition at the disk can be related to the hydrogen current:

\[ \frac{i}{F} = -D_{H^+} \frac{\partial}{\partial y} \left[ C_{H^+} - \frac{D_{OH^-}}{D_{H^+}} C_{OH^-} \right] \quad \text{at } y = 0 \quad [5.10] \]

The hydrogen and hydroxyl concentrations are correlated by the equilibrium dissociation of water:

\[ C_{H^+} \cdot C_{OH^-} = K_w \quad [5.11] \]

The exact solution to this full 2-D non-linear problem requires a numerical method. However, the analytical results obtained by superposition integrals can be used if the problem is linearized by the approximation of equal diffusivities. In Appendix 5 we apply a perturbation analysis to evaluate the error associated with this assumption. Qualitatively, since the radial transport is dominated by convection in the RRDE system, the effect of
different diffusivities of various species is not as pronounced as in the axial direction.

The equal-diffusivity approximation simplifies Eqs. [5.9-5.10] to the following form:

\[
\frac{\partial \Omega}{\partial y} \left( \frac{\Omega}{v} \right)^{1/2} \left( r \frac{\partial \bar{C}}{\partial r} - y \frac{\partial \bar{C}}{\partial y} \right) = D \frac{\partial^2 \bar{C}}{\partial y^2} \tag{5.12}
\]

\[
\frac{i}{F} = -D \frac{\partial \bar{C}}{\partial y} \bigg|_{y = 0} \tag{5.13}
\]

where

\[
\bar{C} = C_{\text{H}^+} - C_{\text{OH}^-} = C_{\text{H}^+} - \frac{K_w}{C_{\text{H}^+}} \tag{5.14}
\]

The solution to this linearized problem obeys Eq. [5.8],

\[
\frac{\bar{C}(r)}{\bar{C}^b} = 1 - I \left[ 1 - F(\rho) \right] \tag{5.15}
\]

For various fractions of the hydrogen-ion limiting current, the radial variation of $C_{\text{H}^+}$ normalized to $C_{\text{H}^+}^b$ is shown in Fig. 5-4. These profiles were obtained by solving equation 5.15 after substituting for $C_{\text{OH}^-}$. Unless otherwise stated, the bulk pH is taken to be equal to 3 in the calculations. At current densities exceeding the limiting current, the solution near the plane of the RRDE becomes alkaline. The transition from basic to acidic regions, extending to the gap and ring regions, is shown in Fig. 5-5. Depending on the size of the disk electrode, pH rise can occur over large radial distances. If the ring material responds to the activity of protons reversibly, i.e. following the Nernst equation, for every decade decrease in concentration a -59.1 mv shift in the ring potential will be observed,

\[
E = E^0 + \frac{RT}{F} \ln \frac{a_{\text{H}^+}}{P_{H_2}^{1/2}} = 0 + 59.1 \log \frac{a_{\text{H}^+}}{P_{H_2}^{1/2}} \tag{5.16}
\]
Chapter 5

The ring potential is a radial average because of its finite thickness. Using an Extended Trapezoidal Rule (e.g. Press et. al.), we have numerically calculated the radial average of proton concentration for two different RRDE geometries listed in Table 5.1. The resulting shift in the ring potential versus fraction of the hydrogen limiting current passed at the disk is shown in Fig. 5-6.

Table 5.1: Dimensions of the Ring-Disk Geometries

<table>
<thead>
<tr>
<th>Geometry</th>
<th>( r_0(cm) )</th>
<th>( r_1(cm) )</th>
<th>( r_2(cm) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.383</td>
<td>0.398</td>
<td>0.422</td>
</tr>
<tr>
<td>B</td>
<td>0.383</td>
<td>0.416</td>
<td>0.557</td>
</tr>
</tbody>
</table>
Fig. 5-4: Radial concentration of protons for different fractions of hydrogen limiting current, bulk pH=3.
Fig. 5-5: Acid-base transition on the plane of the RRDE, bulk pH=3.
Fig. 5-6: Ring response to pH rise at the disk.
Supersaturation of $H_2$

A reversible ring to hydrogen evolution reaction responds to the changes in both pH and hydrogen pressure. With hydrogen gas evolution at the disk electrode, there will be some supersaturation which is felt by the ring with a corresponding shift in the potential, described by Eq. [5.16]. The increase in the dissolved hydrogen concentration at the disk electrode, can be related to the current density as follows:

$$\frac{C_{H_2}^d}{C_{H_2}^b} = 1 + \frac{1}{2} \frac{C_{H^+}^b}{C_{H_2}^b} \frac{i}{i_{lim, H^+}}$$  \[5.17\]

where it was assumed that the diffusivities of dissolved hydrogen and protons are the same. This is not a bad assumption since available experimental data (e.g. Shibata, 1960, or Perry and Chilton, 1973) indicate a diffusion coefficient of $5 \times 10^{-5} \text{cm}^2/\text{s}$ for hydrogen in aqueous electrolytes.

The bulk concentration of $H_2$ can be approximated from Henry's Law constant. Prausnitz et al. (1986) report for the solubility of the $H_2$ in pure water

$$\log(L_X) = 4.86 = \log H_{H_2}$$  \[5.18\]

which means that for 1 atm hydrogen gas pressure, the mole fraction in water is $1.4 \times 10^{-5}$.

This translates to a hydrogen solubility of $7.6 \times 10^{-7} \text{mole/cm}^3$ at room temperature, corresponding to $17 \text{cm}^3$ of $H_2/\text{lit}$, in good agreement with values reported by other workers (see e.g. Ruetschi and Amile, 1966). The hydrogen solubility in electrolyte is lower than that in pure water. This "salting-out" effect is often expressed as:

$$\log \frac{S_i^0}{S_i} = k_s C_s$$  \[5.19\]

where $S_i$ is the solubility in electrolyte, $k_s$ is the salting-out parameter, and $C_s$ is the salt
concentration. Since \( k_s \) is a salt specific parameter, we use \( k_s = 0.11 M^{-1} \) corresponding to NaCl which is the supporting electrolyte in our solutions. In 1.5 M NaCl solution, the hydrogen solubility, or the concentration of the dissolved hydrogen, is \( 5 \times 10^{-4} M \). Using this value for \( C_{H_2}^b \), and calculating \( C_{H_2}^d \) from Eq. [5.17], we can estimate the radial profile of dissolved \( H_2 \) as shown in Fig. 5-7. The cathodic shift in the ring potential, plotted in Fig. 5-8, is associated with the hydrogen supersaturation.

The ring response to the changes in the dissolved hydrogen gas concentration is smaller than the shift of potential corresponding to hydrogen ions, as reflected by the difference between the scale of x axis in Fig. 5-6 and 5-8. This difference can be understood by the stoichiometry of \( H_2 \) and \( H^+ \) in the hydrogen evolution reaction and the smaller slope of \( H_2 \) in the Nernst equation (see Eq. 5.16).

*Effect of \( MOH^+ \) Ions*

Hydrogen evolution is the important side reaction when base metals such as iron, nickel, cobalt are electroplated. The metal-hydroxide complexes formed by hydrolysis can reduce the pH rise caused by hydrogen evolution:

\[
M^{2+} + H_2O \rightarrow MOH^+ + H^+
\]

Taking into account the homogeneous metal-hydroxide reaction, the material balance for hydrogen ions becomes:

\[
- \nabla \cdot N_{H^+} + \nabla \cdot N_{OH^-} + \nabla \cdot N_{MOH^+} = 0 \]

[5.20]
Fig. 5-7: Normalized concentration of dissolved hydrogen.
Fig. 5-8: Ring response to hydrogen super-saturation.
The equal-diffusivity approximation, simplifies the material balance and the boundary condition for the RRDE system to Eqs. [5.12,5.13]. For this case,

$$\bar{C} = C_{H^+} - C_{OH^-} - C_{MOH^+}.$$  

As discussed earlier, the concentration varies radially as described by:

$$\frac{\bar{C}(r) - \bar{C}^b}{\bar{C}^d - \bar{C}^b} = 1 - F(\rho)$$  

[5.21]

and $\bar{C}(r)$ can be related to the current density of hydrogen evolution at the disk electrode:

$$I = \frac{i}{i_{lim,H^+}} = \frac{\bar{C}^b - \bar{C}^d}{C^b_{H^+}}$$  

[5.22]

where $i_{lim,H^+}$ is the hydrogen-ion limiting current in the absence of MOH$^+$ ions.

Rearranging [5.21] and using Eq. [5.22] gives

$$\frac{\bar{C}(r)}{\bar{C}^b} = 1 - I \frac{C^b_{H^+}}{C^b_{H^+}} (1 - F).$$  

[5.23]

The surface concentration of hydrogen ions is related to the bulk by

$$\bar{C}^d = C^d_{H^+} - C^d_{OH^-} - C^d_{MOH^+} = \bar{C}^b - I C^b_{H^+}.$$  

[5.24]

If we assume that the homogeneous reactions are much faster than the transport processes, the concentration of MOH$^+$ ions can be related to those of protons and metal ions by an equilibrium relationship:

$$C_{MOH^+} = \frac{K_w C_{M}^{z-2}}{K_d C_{H^+}^{z}}$$  

[5.25]

where $K_d$ is the dissociation constant for MOH$^+$ ions.
The dissociation equilibrium of MOH\(^+\) ions cushions the build-up of hydroxide ions, resulting in a higher hydrogen ion concentration compared to the case where no metal-hydroxide ions are present. Thus, the pH rise caused by hydrogen evolution is reduced both at the electrode surface and throughout the solution. The reduction of the disk interfacial pH rise in the presence of metal-hydroxide ions is demonstrated in Fig. 5-9. Here the total concentration for metal ions is .2M, and it is assumed that this concentration remains constant throughout the solution. This is only an approximation because if a significant fraction of the limiting current for metal deposition passes on the disk electrode, depletion of the metal ions becomes important. Under this assumption, the relationship between the \(C_{\text{MOH}^+}\) and proton concentration can be expressed as:

\[
C_{\text{MOH}^+} = \frac{C_{TM}}{1 + \frac{K_d}{K_w}C_{H^+}}
\]  

Equation 5.26

The effect of MOH\(^+\) ions on the radial profile of hydrogen ions, evaluated using Eqs. [5.23-5.26], is shown in Figs. 5-10 and 5-11. With decreasing \(K_d\) values, the buffering effect of MOH\(^+\) becomes more pronounced. For a direct comparison, profiles obtained for various \(K_d\) at \(I = 1.5\) are shown in Fig. 5-11. Note that \(I = 1.5\) means that the current going into hydrogen evolution is 1.5 times the hydrogen limiting current in the absence of MOH\(^+\) ions.

The practical implication of these results is that a substantially higher hydrogen current can be passed at the disk electrode before the interfacial pH becomes 7.
Fig. 5-9: Calculated interfacial pH rise at the disk versus fraction of hydrogen limiting current, bulk pH = 3, 0.2M metal ions.
Fig. 5-10: Radial proton distribution in the presence of metal-hydroxide ions, $K_d = 1e-7$. 
Fig. 5-11: Effect of metal-hydroxide ions.
Consequently, formation of solid metal hydroxide precipitates, which require a high interfacial pH, is inhibited. Suppression of pH rise in the presence of metal-hydroxide ions is related to the hydrogen ion limiting current enhancement. Similar to Eq. [5.22], we can define an enhancement factor caused by metal-hydroxide ions, $I_{LM}$:

$$\frac{i_{\text{lim}}}{i_{H^+\text{lim}}} = 1 + I_{LM} = 1 + \frac{C_{\text{MOH}^+}^d - C_{\text{MOH}^+}^b}{C_H^b}$$  

[5.27]

Shown in Fig. 5-12, is the dependence of $I_{LM}$ on $K_d$ for various bulk pH values. The smaller the dissociation constant of metal-hydroxide ions, $K_d$, the larger the enhancement. The maximum obtainable enhancement depends on the bulk pH and MOH$^+$ concentration. For example, at pH=2 and .2M total metal ion concentration, the maximum $I_{LB}$ is 20.

The influence of metal-hydroxide complexes on the overall ring response, i.e. cathodic shift caused by both pH rise and hydrogen supersaturation, as a function of $I$ for the RRDE geometry B is shown in Fig. 5-13. The bulk pH is taken to be 3 and the dissolved hydrogen gas concentration is $5 \times 10^{-4}$ M, corresponding to a hydrogen atmosphere. The ring response begins to decrease when the dissociation constant of MOH$^+$ ions is smaller than $10^{-5}$ M.

The relationship between the ring response and the pH rise at the disk, including the effect of metal-hydroxide complexes, is shown in Fig. 5-14. It is interesting to see the pronounced reduction of interfacial pH rise caused by the buffering action of metal-hydroxide ions. In the absence of metal-hydroxide ions, or for large values of $K_d$, there is a threshold in the ring potential shift which corresponds to a titration at the disk when the
Fig. 5-12: Enhancement of hydrogen limiting current in the presence of 0.2M metal ions.
Fig. 5-13: Calculated ring response as a function of hydrogen ion limiting current.
Fig. 5-14 a: Ring response to the interfacial pH rise in the presence of MOH+ ions for geometry A.
Fig. 5-14 b: Ring response to the interfacial pH rise in the presence of MOH+ ions for geometry B.
hydrogen limiting current is exceeded. When metal-hydroxide ions are present, the generated hydroxyl ions are used up in the homogeneous reaction of MOH$^+$ formation which leads to the marked decrease in the disk interfacial pH rise. As seen in Fig. 5-14a and 5-14b, the threshold potential response for the ring is -22 mv for geometry A and -12 mv for geometry B. For cathodic shifts smaller than the threshold values, the interfacial pH rise is less than 2 units while for larger ring responses, the pH rise varies significantly depending on the dissociation constant of metal-hydroxide ions present. It is interesting to note that at a given ring response, the smaller pH rise brought about by metal-hydroxide complexes, does not mean that the same hydrogen current is passed at the disk electrode. In fact, as seen in Fig. 5-13, a -30 mv response corresponds to $I = 2.2$ while for $K_d = 2.5 \times 10^{-8}$, $I = 3$. In other words, in the presence of metal-hydroxide complexes not only is the interfacial pH rise lower than the base case, but for a given ring response a higher hydrogen current has passes at the disk.

- **Effect of a Buffering Agent**

Addition of a buffering agent to the electrolyte provides a reservoir for protons which can lead to a significant increase in the limiting current for hydrogen evolution.

$$\text{HX} \leftrightarrow \text{H}^+ + \text{X}^-$$

The enhancement of the hydrogen limiting current caused by the presence of the buffering agent, $I_{LB}$, can be described analogous to Eq. [5.27] as:

$$\frac{i_{\text{lim}}}{i_{\text{H}^+,\text{lim}}} = 1 + I_{LB} = 1 + \frac{C_{\text{HX}}^b - C_{\text{HX}}^d}{C_{\text{H}^+}^b} \quad [5.28]$$

The undissociated buffer concentration is related to the hydrogen ion concentration and the
total buffer concentration, $C_{TB}$, assuming equilibrium holds:

$$C_{HX} = \frac{C_{H^+ \cdot} C_{TB}}{C_{H^+ \cdot} + K_b}$$ \[5.29\]

where $K_b$ is the buffer dissociation constant. Using [5.29] for $C_{HX}$, it can be shown that

$$I_{LB} = \frac{C_{TB}}{C_{H^+ \cdot}} \left[ \frac{1}{1 + \frac{K_b}{C_{H^+ \cdot}^b}} - \frac{1}{1 + \frac{K_b}{C_{H^+ \cdot}^d}} \right] = u \frac{C_{TB}}{C_{H^+ \cdot}^b}$$ \[5.30\]

Parameter $u$, defined in Eq. 5.30, represents the difference between the concentration of the undissociated buffer in the bulk solution and that at the electrode surface with pH=7.

The solution to the convective-diffusive transport obeys Eq. 5.23 in the previous section. Here, the assumption of equal diffusivity leads to:

$$\bar{C} = C_{H^+ \cdot} - C_{OH^-} + C_{HX}$$ \[5.31\]
or

$$\bar{C} = C_{H^+ \cdot} - \frac{K_w}{C_{H^+ \cdot}} + \frac{C_{H^+ \cdot} C_{TB}}{K_b + C_{H^+ \cdot}}$$ \[5.32\]

Enhancement of the hydrogen limiting current in the presence of a buffering agent for various bulk pH is shown in Fig. 5-15. Note that the increase in the limiting current as a function of the buffer pK goes through a maximum. To understand this behavior, consider Fig. 5-16 showing $u$ as a function of $K_b$. Recall that the difference between the concentration of HX in the bulk and at the electrode surface is represented by $u$. The undissociated HX acts as a reservoir for protons. The difference between the interfacial concentration of HX and its bulk value contribute to $I_{LB}$. When pK of the buffer is large,
Fig. 5-15: Dependence of the limiting current on buffer $K_b$, 0.1 M HX.
Fig. 5-16: \( u \) dependence on buffer \( K_b \) for 0.1 M HX.
i.e. small $K_b$, the dissociation of HX is very small. On the contrary, for a small pK, hardly any undissociated HX is left. Intermediate values of $K_b$, therefore, yield the maximum in $u$.

It is also important to consider the effect of bulk pH on the performance of a given buffer. As shown in Fig. 5-17, with an increase in the bulk pH, the degree of buffer dissociation in the bulk also increases, while $u$ decreases. Since $I_{LB}$ is also inversely proportional to $C_{H^+}$, Eq. [5.30], the limiting current in the presence of a given buffer increases with bulk pH and eventually reaches a plateau as seen in Fig. 5-18.

In the presence of a buffering agent, the concentration of $H^+$ ions can be significantly higher than that in the absence of a buffer. The radial concentration profiles for various fractions of the hydrogen limiting current, obtained from Eqs. [5.23], [5.31] and [5.32], is shown in Fig. 5-19 for a solution which has .1M of a buffer with pK=2.5. Parallel to the analysis of the effect of metal-hydroxide ions, we are normalizing the current density with the limiting current of hydrogen ions in the absence of any $MOH^-$ ions or buffering agents. Note that the second term in Eq. [5.26], $C_{OH^-}$, is much smaller than the others, which means that $H^+$ concentration can be obtained by solving a quadratic equation instead of a cubic. In contrast to the profiles obtained in the absence of a buffer, shown in Fig. 5-4, the pH rise is less than one unit even when $I$=16. Accordingly, the ring response to the change in proton concentration will become much smaller, depending on the buffer pK, as seen in Fig. 5-20.
Fig. 5-17: $u$ dependence on bulk pH for 0.1M HX.
Fig. 5-18: Dependence of the limiting current on pH in the presence of 0.1M HX.
Fig. 5-19: Effect of 0.1 M buffer with pK=2.5 on the radial concentration profile of protons.
Fig. 5-20: Effect of buffer pK on the ring potential shift.
• Ohmic Component

Although no current is passed through the ring electrode, it registers an ohmic potential drop since passage of current through the electrolyte establishes an electric field. The potential distribution for our application of the RRDE is closer to the case of uniform current distribution on the disk, or that of mixed kinetics and mass-transfer control in the case of simultaneous hydrogen and metal deposition. However, the well-known primary current distribution provides an upper-bound for the potential distribution outside the disk region as qualitatively depicted in Fig. 5-21. It is also known that experimental techniques such as current interrupt, measure the ohmic resistance corresponding to the primary current distribution (Newman, 1970).

On the insulator plane, following Newman (1966), the potential obtained by solving Laplace’s equation can be expressed as:

\[
\frac{\Phi}{\Phi_0} = 1 - \frac{2}{\pi} \tan^{-1} \chi; \quad \chi = \sqrt{\left(\frac{r}{r_0}\right)^2 - 1}
\]

where \(\Phi_0\) is the potential in the solution at the disk electrode and the counter-electrode potential, located at infinity, is taken to be zero. The potential difference between the disk electrode and the counter-electrode is related to the total current, i.e. both hydrogen current and other concurrent electrode reactions such as metal deposition current, disk radius, and solution conductivity.

\[
\Phi_0 = \frac{I_{tot}}{4\pi r_0}
\]

The finite thickness of the ring requires calculating the average potential value. Miksis
Fig. 5-21: Potential variation on the RRDE plane.
and Newman (1976) have calculated primary resistances for various ring-disk geometries by superposition. The ohmic resistance between the ring and the disk, $R_{rd}$ was expressed as:

$$\frac{\Phi}{\Phi_0} = \kappa \frac{r_2}{r_1} R_{rd} \frac{4r_0}{r_2}$$

[5.35]

where $\kappa$ $r_2$ $R_{rd}$ values were tabulated by these authors. As an example, $r_0 / r_1 = 0.9$ and $r_1 / r_2 = 0.8$, yields a $\Phi/\Phi_0 = 0.588$. The average potential obtained from Eq. [5.34], for this geometry, $r_1 / r_0 = 1.1$ and $r_2 / r_0 = 1.46$, is also close to 0.588.

Unlike the other components of the ring potential which respond to the hydrogen gas evolution current, the ohmic drop is dependent on the total current at the disk electrode. This is particularly important for metal deposition where high currents are passed. Note that $I_{tot}$ in Eq. 5.33 refers to the total current at the disk which is a product of the disk area and the total current density. The ohmic effects can be reduced by increasing the conductivity of the electrolyte, and by using a smaller disk electrode. The insulator thickness is also a key parameter in determining the ohmic drop felt by the ring. Although the sensitivity of the ring to the changes in pH at the disk surface increases, placing the ring very close to the disk has the disadvantage of being in a region where variations in $\Phi_0$ are very abrupt as seen in Fig. 5-22. The uncertainty in the ohmic component of the ring response can be detrimental to the accuracy of the RRDE method for in-situ pH measurement.
Fig. 5-22: Potential variation on the plane of RRDE calculated from primary current distribution.
Conclusions

Potentiometric application of a pH sensitive ring electrode for \textit{in-situ} determination of pH at a rotating disk electrode has been analyzed. The two-dimensional transport of protons in the RRDE system, including homogeneous reactions of MOH\(^+\) ions and buffering agents was investigated. Equal-diffusivities were assumed to allow linearization of the transport equations leading to analytical solutions. It is shown that at a given hydrogen current, the ring response depends on the RRDE geometry, bulk pH, fraction of the hydrogen limiting current, concentration of metal ions and dissociation constant of metal-hydroxide complexes, concentration and dissociation constant of buffering agents, degree of supersaturation of dissolved hydrogen, and solution conductivity. It is hoped that by understanding these effects in the RRDE system, both the design of experiments for interfacial pH measurement and the interpretation of results are enhanced. Although we have limited our discussion to the pH measurement, this method can be applied to the measurement of the concentration of other ionic species such as metal ions, provided the ring is reversible and selective to the ionic species of interest.
**List of Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>rotating disk hydrodynamic constant, 0.51023</td>
</tr>
<tr>
<td>C</td>
<td>concentration, mol/cm³</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient, cm²/s</td>
</tr>
<tr>
<td>f</td>
<td>fugacity, atm</td>
</tr>
<tr>
<td>F</td>
<td>Faraday's constant 96,487 C/eq</td>
</tr>
<tr>
<td>H</td>
<td>Henry's Law constant</td>
</tr>
<tr>
<td>i</td>
<td>current density, A/cm²</td>
</tr>
<tr>
<td>$i_{H^+, lim}$</td>
<td>hydrogen ion limiting current in the absence of buffering agents and MOH⁺ ions</td>
</tr>
<tr>
<td>I</td>
<td>current, A</td>
</tr>
<tr>
<td>I</td>
<td>fraction of the limiting current</td>
</tr>
<tr>
<td>$I_{LB}$</td>
<td>enhancement of the limiting current by buffer</td>
</tr>
<tr>
<td>$I_{LM}$</td>
<td>enhancement of the limiting current by metal-hydroxide</td>
</tr>
<tr>
<td>$k_s$</td>
<td>salting-out parameter, $M^{-1}$</td>
</tr>
<tr>
<td>$K_b$</td>
<td>dissociation constant of buffer</td>
</tr>
<tr>
<td>$K_d$</td>
<td>dissociation constant of MOH⁺ ions</td>
</tr>
<tr>
<td>$K_w$</td>
<td>water dissociation constant</td>
</tr>
<tr>
<td>r</td>
<td>radial distance, cm</td>
</tr>
<tr>
<td>R</td>
<td>universal gas constant, 8.3143 J/mol-deg</td>
</tr>
<tr>
<td>S</td>
<td>solubility, M</td>
</tr>
<tr>
<td>T</td>
<td>absolute temperature, K</td>
</tr>
<tr>
<td>u</td>
<td>dimensionless concentration difference of buffer, defined by Eq. 5.30</td>
</tr>
<tr>
<td>x</td>
<td>mole fraction</td>
</tr>
</tbody>
</table>
Chapter 5

y axial distance, cm

Greek Characters:

α normalizing distance in the axial direction, \( cm^{-1} \), defined in Eq. [5.2]

Φ electric potential, volt

κ conductivity, mho/cm

χ dimensionless radial distance on the plane of the RRDE defined in [5.33]

Ω disk rotation speed, radian/sec

ν kinematic viscosity \( cm^2/s \)

Θ dimensionless concentration, \( \Theta = \frac{C - C^d}{C^b - C^d} \)

ξ similarity variable defined after [5A-17]

ζ dimensionless axial distance, defined in [5.2]

Superscripts

b bulk
d disk surface

Subscripts

0 pure water

lim mass-transfer limiting
tot total
References


Appendix 5: Effect of Different H\(^+\) and OH\(^-\) Diffusivities

In the analysis presented in Chapter 5, the material balance equations and their boundary conditions were linearized by assuming equal diffusivities for all reacting species. To take into account the difference between diffusivities of the hydrogen and hydroxide ions, we apply a regular perturbation technique (Nayfeh, 1973) with the parameter \(\varepsilon\) defined as:

\[
\frac{D_{OH^-}}{D_{H^+}} = 1 - \varepsilon
\]  \[5A-1\]

The corresponding expansion for hydrogen and hydroxyl ions can be written:

\[
C_{H^+} = \sum_{n=0}^{\infty} \varepsilon^n C_{H^+}^{(n)} ; \quad C_{OH^-} = \sum_{n=0}^{\infty} \varepsilon^n C_{OH^-}^{(n)}
\]  \[5A-2\]

where \(C_{i}^{(n)}\) is the nth order term of the expansion.

Introducing a dimensionless axial distance from the electrode,

\[
\zeta = y \left( \frac{\Omega}{v} \right)^{1/2} \left( \frac{a v}{3 D_{H^+}} \right)^{1/3} = y \alpha
\]  \[5A-3\]

along with substitution of Eqs. [5A-1], [5A-2] in [5.6-5.8] yield the following sets of material balances:

Zeroth Order Term:

\[
3\zeta \left[ r \frac{\partial C_{H^+}^{(0)}}{\partial r} - \zeta \frac{\partial C_{H^+}^{(0)}}{\partial \zeta} \right] = \frac{\partial^2 C_{H^+}^{(0)}}{\partial \zeta^2}
\]  \[5A-4\]

where \(C_{H^+}^{(0)} = C_{H^+}^{(0)} - C_{OH^-}^{(0)}\). From water equilibrium and Eq. [5A-2],

\[
C_{OH^-}^{(0)} = \frac{K_w}{C_{H^+}^{(0)}}
\]  \[5A-5\]
Higher Order Terms:

\[ 3 \zeta \left[ r \frac{\partial C^{(n)}}{\partial r} - \zeta \frac{\partial C^{(n)}}{\partial \zeta} \right] = \frac{\partial^2 [C^{(n)} + C^{(n-1)}]}{\partial \zeta^2} \]  

[5A-6]

where \( C^{(n)} = C^{(n)}_H - C^{(n)}_{OH^-} \). Once again, the water equilibrium and perturbation expansion provide the relationship between \( C^{(n)}_{OH^-} \) and \( C^{(n)}_H \):

\[ C^{(n)}_{OH^-} = - \sum_{j=1}^{n} \frac{C^{(j)}_H C^{(n-j)}_{OH^-}}{C^{(0)}_H} \]  

[5A-7]

In the following, we limit the analysis to the effect of first order terms of \( \varepsilon \).

• Disk Region

For a uniformly accessible disk, the convective-diffusive material balances become one-dimensional and only a function of axial distance. The boundary conditions at the disk electrode are:

\[ \frac{i}{F} = - \alpha D_H \frac{dC^{(0)}}{d\zeta} \]  

[5A-8]

\[ 0 = \frac{d(C^{(1)} + C^{(0)}_{OH^-})}{d\zeta} \]  

[5A-9]

and for \( \zeta \to \infty \):

\[ C^{(0)}_i \to C_{i,b} \quad ; \quad C^{(1)}_i \to 0 \]  

[5A-10]

where \( i = H^+ \) and \( OH^- \) ions.

For the zeroth order system, the concentration profile of \( C^{(0)} = C^{(0)}_H - C^{(0)}_{OH^-} \) obeys
the following analytical solution:

\[
\frac{C^{(0)} - C_d^{(0)}}{C_d^{(0)} - C_d^{(0)}} = \frac{1}{\Gamma(4/3)} \int_0^\xi e^{-\xi^2} d\xi \quad [5A-11]
\]

Calculation of the concentration profiles for the first order system requires additional steps. Both the boundary conditions [5A-8, 5A-9], and the first order system are coupled to the zero-order problem as seen in the material balance equation:

\[
\frac{d^2(C^{(1)} + C_{OH^-}^{(0)})}{d\zeta^2} + 3\zeta^2 \frac{dC^{(1)}}{d\zeta} = 0 \quad [5A-12]
\]

The profile of \( C_{OH^-}^{(0)} \) in the disk region is evaluated using Eqs. [5A-5] and [5A-11]. To obtain profiles of \( C^{(1)} = C_{H^+}^{(1)} - C_{OH^-}^{(1)} \), Eq. [5A-12] with boundary conditions [5A-9] and [5A-10] is numerically solved.

- **Gap and Ring Region**

Since the ring is kept at open circuit, it can be treated as part of the gap or insulator region. The concentration of protons on the plane of RRDE, outside the disk electrode, will gradually increase and approach the bulk value. The normal component of the flux is zero at the plane of the electrode surface:

\[
0 = \left. \frac{\partial C^{(0)}}{\partial y} \right|_{y = 0} \quad [5A-13]
\]

\[
0 = \left. \frac{\partial(C^{(1)} + C_{OH^-}^{(0)})}{\partial y} \right|_{y = 0} \quad [5A-14]
\]

To calculate the radial variation in concentration of \( C^{(0)} \) and \( C^{(1)} \), we take advantage of the linearity of equations [5A-4] to [5A-10] and of the boundary conditions, and apply
Duhamel's superposition integral technique (see e.g. Hildebrand) to the radial direction of the RRDE system.

The full 2-D material balances for the zeroth and first order systems (Eqs. [5A-4, 5A-5]) can be written as:

\[
\frac{d^2 C^{(0)}}{d\xi^2} + 3\xi^2 \frac{dC^{(0)}}{d\xi} = 0
\]

\[
\frac{d^2 [C^{(1)} + C_{\text{OH}^-}^{(0)}]}{d\xi^2} + 3\xi^2 \frac{d[C^{(1)} + C_{\text{OH}^-}^{(0)}]}{d\xi} - 3\xi^2 \frac{dC_{\text{OH}^-}^{(0)}}{d\xi} = 0
\]

where \(\xi\) is a similarity variable.

\[
\xi = y \frac{r}{(r^3 - r'^3)^{1/3}} \left( \frac{a v}{3D} \right)^{1/3} \left( \frac{\omega}{v} \right)^{1/2} = \frac{y r \alpha}{(r^3 - r'^3)^{1/3}}
\]

A more general formulation for Eqs. [5A-15, 5A-16] can be written as:

\[
\frac{d^2 C}{d\xi^2} + 3\xi^2 \frac{dC}{d\xi} + H = 0
\]

where \(H\) is a known function of \(\xi\) which vanishes for the zeroth order system.

The dimensionless concentration

\[
\Theta = \frac{C_{(r)} - C_d}{C_b - C_d}
\]

is evaluated by using superposition as follows:

\[
\Theta_{(y, r)} = \Theta_{(0)}^{(y, r)} + \int_0^r \Theta_{(y, r-r')}^* \frac{d\Theta_{(0)}}{dr} |_{r = r', dr'} dr'
\]

where \(\Theta^0 = \Theta_{(y = 0)}\) and \(\Theta^*\) is the solution to the unit step problem shown schematically in Fig. 5A-1. Taking the derivative of Eq. 5A-18 with respect to \(y\) and evaluating it at \(r'\) results:
\[
\frac{\partial \Theta}{\partial y}\bigg|_{0, r'} = \alpha \frac{d \Theta^0}{d \xi} \bigg|_{\xi = 0} \int_0^{r'} \frac{dx}{(r'^3 - x^3)^{\frac{1}{3}}} \frac{d \Theta^0}{dr} \Big|_{x}
\]

We can obtain an explicit expression for the \(\Theta^0\), variation of concentration on the plane of RRDE, following the procedure in Appendix II of Newman and Smyrl (1972).

\[
\Theta^0_{(r')} = \frac{3}{\Gamma(1/3) \Gamma(2/3)} \frac{1}{\alpha \frac{d \Theta^*}{d \xi} \bigg|_{\xi = 0}} \int_0^{r'} \frac{dr'}{(r'^3 - r'^{3})^{\frac{2}{3}}} \frac{\partial \Theta}{\partial y} \bigg|_{0, r'}
\]

Since in the regions outside the disk electrode no current is being passed, the normal component of the flux is zero.

\[
\frac{\partial \Theta}{\partial y} \bigg|_{y=0, r>r_0} = 0
\]

Therefore, the integral in [5A-20] needs to be only evaluated in the disk region. Using

\[
\frac{1}{\alpha} \frac{\partial \Theta}{\partial y} \bigg|_{0, r\ll r_0} = \frac{d \Theta^*}{d \xi} \bigg|_{\xi = 0}
\]

[5A-20] is simplified:

\[
\Theta^0_{(r')} = \frac{1}{\Gamma(2/3) \Gamma(4/3)} \int_0^{r_0} \frac{dr'}{(r'^3 - r'^{3})^{\frac{2}{3}}} = F(\rho)
\]

where \(\rho = (\frac{r}{r_0})^3 - 1\) and \(F(\rho)\) is given after Eq. [5.3].

This is an important result since the differential equation [5A-17] has the additional term, \(H(\xi)\). The implication of [5A-22] for the perturbation problem at hand is that for both the zeroth and first order systems the radial profiles depend on the concentration at the disk, in the bulk, and the radial distance away from the center of the disk. The zeroth...
order concentration profile on the plane of RRDE can be expressed as:

$$\frac{C_{(r)}^{(0)} - C_{d}^{(0)}}{C_{b}^{(0)} - C_{d}^{(0)}} = F$$  \[5A-23\]

Similarly for the first order concentration

$$\frac{[C_{(r)}^{(1)} + C_{(OH^-,r)}^{(0)}] - [C_{d}^{(1)} + C_{(OH^-,d)}^{(0)}]}{[C_{b}^{(1)} + C_{(OH^-,b)}^{(0)}] - [C_{d}^{(1)} + C_{(OH^-,d)}^{(0)}]} = F$$  \[5A-24\]

where $C_{d}^{(0)}$ and $C_{d}^{(1)}$ are the zeroth and first order concentrations at the disk, determined by the hydrogen current density and calculated from Eqs. [5A-8] to [5A-12]. From equilibrium relationships, the zeroth order and first order proton concentrations are related to $C_{(0)}$ and $C_{(1)}$ as follows:

$$C_{H^+}^{(0)} = \frac{C^{(0)} + [C^{(0)}^2 + 4K_w]^{1/2}}{2}$$  \[5A-25\]

and

$$C_{H^+}^{(1)} = \frac{C^{(1)}}{1 + \frac{C_{OH^-}^{(0)}}{C_{H^+}^{(0)}}}$$  \[5A-26\]

The zeroth order concentration, i.e. equal diffusivity approximation, profiles for protons were shown in Fig. 5-3. The radial profile for $C_{H^+}^{(1)}$ is seen in Fig. 5A-2 which shows a maximum corresponding to the transition from alkaline to acidic regions. It is interesting that the correction to the equal diffusivity assumption, $C_{H^+}^{(1)}$, has a negative sign. In other words, taking into account the smaller diffusion coefficient of OH$^- $ions leads to a smaller hydrogen ion concentration. The negative value of $C_{H^+}^{(1)}$ can be better understood with the aid of boundary conditions; at the disk electrode, the flux of $C^{(1)}$ is negative that of the OH$^- $ flux. Since the hydroxyl ions accumulate at the electrode
surface, $C^{(1)}$ and $C_{H^+}^{(1)}$ must be smaller at the electrode surface than in the bulk. The bulk values for all perturbation terms are zero which means that $C_{H^+}^{(1)}$ values must be negative.

To compare the perturbation results with the equal diffusivity approximation, a value for $\varepsilon$ should be chosen. Since the diffusion coefficient of OH$^-$ ions is roughly half of that of hydrogen ions (e.g. Newman, 1973), we use $\varepsilon = 0.5$. The radial pH values as calculated from the total concentration $C_{H^+} = C_{H^+}^{(0)} + \varepsilon C_{H^+}^{(1)}$ and the equal diffusivity approximation, $C_{H^+} = C_{H^+}^{(0)}$, are compared in Figs. 5A-3 and 5A-4. The correction for the difference in the diffusivity of H$^+$ and OH$^-$ ions is appreciable only when hydrogen current exceeds its mass-transfer limiting value since, at limiting current, flux of OH$^-$ ions increases very abruptly and significantly.

Assigning a large value to the diffusion coefficient of OH$^-$ by equating it with that of H$^+$ ions means that the hydroxyl concentration gradient is underestimated. In reality, the smaller diffusion coefficient of OH$^-$ ions leads to a higher OH$^-$ concentration at the disk electrode, for a given current density, compared to that evaluated by the zeroth order approximation. Since mass transfer close to the electrode surface in the radial direction is dominated by convection, an increase in the disk-solution interfacial concentration is felt by the ring: radial convection outward to the gap and ring regions carries a larger concentration of OH$^-$ ions compared to the equal diffusivity approximation. Consequently, neglecting the smaller diffusivity of hydroxide ions, yields the lowest possible estimate of OH$^-$ concentration, i.e. the lowest estimate for pH, in the ring region.

Although we have not performed a full numerical treatment of the material balance equations [5.6-5.8], the perturbation method gives a qualitative understanding for the error
associated with the equal diffusivity approximation. As seen in the perturbation results, even with $\epsilon$ as large as .5, the error in assigning $D_{OH} = D_{H^+}$ is only appreciable at high currents and is limited to a small radial region. For example, when hydrogen current is 1.5 times the proton limiting current, the error becomes negligible when the ring is placed 1.03$r_0$ away from the edge of the disk electrode. The implication is that by choosing the dimensions of an RRDE appropriately, experimental results can be easily analyzed based on the equal diffusivity approximation, without introducing any significant errors.
Fig. 5A-1: Duhamel's Superposition Integral.
Fig. 5A-2: First Order Term.
Fig. 5A-3: Variation in pH, equal diffusivity vs. perturbation.
Fig. 5A-4: Variation in pH, equal diffusivity vs. perturbation.
Chapter 6: In-Situ Measurement of Interfacial pH and Current Efficiency Using a Rotating Ring-Disk Electrode

Abstract

A non-intrusive technique for the in-situ measurement of interfacial pH and current efficiency has been developed. A ring electrode, operated potentiometrically at open-circuit, is used as a probe for the pH change at a rotating disk electrode. A stable and reproducible hydrogen ion sensor with a Nernstian response to the changes in the bulk pH is obtained using a platinized ring electrode in a hydrogen-saturated electrolyte. The ring was calibrated for the interfacial pH rise by evolving hydrogen at the disk electrode, from a dilute acid solution, in the absence of other electrochemical reactions. This technique was then applied to the determination of the current efficiency of nickel deposition with concurrent hydrogen evolution. The method was found to be a powerful tool for the rapid, in-situ measurement of current efficiency without the need for passing a large amount of coulombs. The interfacial pH rise during electrodeposition of nickel, iron, and nickel-iron from electrolytes with a bulk pH of 3 was also evaluated in-situ. The maximum interfacial pH for nickel electrodeposition was less than 5, under the process conditions investigated in this work. For the nickel-iron alloy deposition, the pH rise at various agitation speeds was less than 1 unit for current densities below 8 mA/cm². At higher current densities, the pH rise is estimated to be less than 3 units, depending on the dissociation constant of the metal-hydroxide ions. These results indicate that the interfacial pH is not high enough for the precipitation of a metal-hydroxide film which was hypothesized, by other workers, to be the cause for the "anomalous codeposition" of the iron-group alloys.
Introduction

The importance of interfacial hydrogen ion concentration in electrochemical systems, along with various techniques for the *in-situ* determination of pH were discussed in the previous chapter. Theory for two dimensional transport was developed to allow application of a rotating ring electrode, monitored at open-circuit, as an *in-situ* sensor of the pH at the disk. The analysis included the effect of metal-hydroxide complexes, buffering agents, and dissolved hydrogen super-saturation on the potential shift of the ring electrode. These factors were taken into account so that this mode of operation of the rotating ring-disk electrode (RRDE) can be applicable to the electrodeposition of base metals, such as nickel, which involve simultaneous hydrogen evolution. Since metal deposition currents are high compared to the hydrogen evolution, except in the case of chromium deposition, care must be taken to subtract the ohmic component of the ring response which can significantly affect the accuracy of the measurement. The magnitude of the ring potential shift caused by the ohmic drop was analyzed based on the primary current distribution calculations, and was related to the RRDE geometry and solution conductivity. In this chapter, experimental results will be presented on a platinum black ring in a hydrogen-saturated electrolyte during nickel electrodeposition. Before going into the details of our work, it is appropriate to consider previous application of the RRDE for pH measurement in more detail.

Albery and Calvo (1983) used a bismuth-oxide ring electrode as a potentiometric sensor in 0.1 mol dm\(^{-3}\) NaClO\(_4\) solution with a bulk pH of 7. Generation of H\(^+\) and OH\(^-\) on gold, nickel and thionine-modified electrodes with agitation speeds ranging from 2 to 25 Hz (120 to 1500 rpm) were investigated. No measure of the ohmic drop as
sensed by the ring was reported; however, the currents passed at the disk were lower than 100 µA which implies that the ohmic component could have been insignificant. The transient time on the nickel disk electrodes were 5 seconds when current was turned on, but significantly higher, on the order of 100 seconds, when the current was switched off. The authors attributed this slow response to the irreversibilities associated with the release of the OH\(^-\) ions from the nickel surface, and not to the bismuth electrode. The technique was sensitive to fluxes of H\(^+\) or OH\(^-\) ions as low as \(10^{-12}\, mol/cm^2s\).

The RRDE potentiometric sensor was also applied to the studies of charge-transport mechanism. Albery and Mount (1989) used the bismuth-oxide ring electrode to measure the flux of protons and hydroxyl ions in and out of a thionine-coated electrode in solutions with the bulk pH ranging from 4 to 9. The authors concluded that, unlike what was previously thought, electron transfer and not the counter-ion diffusion is the rate limiting-step in the charge transfer process.

In what follows, experiments involving the RRDE method to assess the interfacial pH rise at the disk caused by hydrogen evolution will be described. The focus of the technique will be on the electrodeposition of nickel, and nickel-iron alloys which involve concurrent hydrogen evolution. The bulk pH for these systems is kept above 2 to obtain a reasonable current efficiency, and below 4 to avoid hydroxide precipitation. The current densities for electrodeposition in the present study range from 1-20 mA/cm\(^2\), considerably higher than the current densities in the systems studied by Albery et al.
Experimental Apparatus

Glass cells of 300 and 600 ml capacity, with separate compartments for counter, reference and glass pH electrodes, are used (Fig. 6-1). A platinum-platinum ring-disk electrodes made by Pine Instrument Company is employed for all of the RRDE measurements. The dimensions of the RRDE are $2r_0 = .765\text{ cm}$, $2r_1 = .833\text{ cm}$, and $2r_2 = 1.113\text{ cm}$ corresponding to Geometry B in Chapter 5. When a different substrate such as nickel is employed for the disk electrochemical reaction, a thin layer of the desired material is electroplated on top of the Pt disk. The potentiometric ring operation as a pH sensor requires a material which is reversible to hydrogen ions. Platinum black is an excellent material for hydrogen electrode (Hills and Ives, 1961), and can be easily prepared.

For measuring the current efficiency of electrodeposition, replaceable copper disk electrodes with a diameter of 1.25 cm are used (Fig. 6-2). A Mettler Instrument Corp. analytical balance with a sensitivity of 0.1 mg is used to weigh the electrodes before and after electrodeposition. The replaceable electrodes with the shaft, adaptor, and teflon sleeve are shown in Fig. 6-3.

A Pine Instrument rotator, model ASRP2, with a speed controller is used to vary the speed of agitation. The counter electrode is a strip of platinum which is housed in one of the glass sections separated from the main cell by a fritted glass. For the measurement of bulk pH a Cole Parmer DigipHase pH meter and a combination glass pH electrode with a
Figure 6-1: Electrochemical cell with separate compartments for the working, counter, reference, and glass pH electrodes.
Figure 6-2: Replaceable copper electrodes and rotating ring-disk electrode.
Figure 6-3: Replaceable electrodes shown disassembled.
calomel reference electrode are employed. Buffer solutions of pH 1.68 and 4.00 (Radiometer Copenhagen) are used for calibration of the pH electrode. A hydrogen atmosphere is maintained before and during experiments by bubbling hydrogen through the solution.

The electrochemical reactions on the disk electrode are controlled by a Potentiostat / Galvanostat Model 273, EG&G Princeton Applied Research. All potential measurements are made against a calomel reference electrode kept in a separate compartment. The current and potential values measured at the disk are displayed on a digital Nicolet 4094 oscilloscope and later transferred to an IBM Personal Systems/2 for data analysis and storage. The potential of the ring electrode is monitored at open circuit against the same reference electrode as that of the disk. Since the input impedance of the oscilloscope is not high enough, the output of a reference electrode buffer amplifier model BA-1 is used to display the ring potential on the scope. We found that it was necessary to power the buffer amplifier with batteries to avoid ground loops. This instrumentation (Fig. 6-4) allows simultaneous recording of both the ring and the disk potential in addition to the disk current.

The electrolyte conductance is measured by a Wayne Kerr Universal bridge B224 conductivity bridge and a YSI 3401 cell. The cell constant was measured with a 71.1 g/kg solution of KCl at 18 °C and found to be 1.22 cm⁻¹.
Figure 6-4: Instrumentation for controlling the disk current and potential, and monitoring the ring potential at open-circuit.
Experimental Procedure

The electrodes are polished following the standard metallographic techniques to a surface finish of 1 μm in roughness. A Hellige Certified 1% platinic chloride with 0.012% lead acetate solution is used to deposit platinum black on the ring electrode. High quality deposits with good adherence and electrode coverage are obtained when plated at 2-4 mA/cm² with 500 mC of charge passed over the 0.427 cm² area of the ring.

All solutions are made with distilled, deionized water. To minimize ohmic effects, i.e. to have a better current distribution on the disk and a small ohmic component in the ring potential shift, 1.0-1.4M NaCl (certified A.C.S. Fisher Scientific) is used as supporting electrolyte. The bulk pH of electrolyte is adjusted by addition of HCl or NaOH, as needed. The solutions are sparged with H₂ for 10 minutes prior to experiments. Before entering the cell, hydrogen gas (Liquid Carbonic) passes through a sparging column to saturate the gas with electrolyte. The electrodes are dipped in a dilute nitric acid solution and thoroughly rinsed with water before each experiment. The ring potential obtains its equilibrium value very rapidly if the disk is spun to enhance transport of the dissolved hydrogen from the vicinity of the sparger to the bulk.

To insure that the platinized ring electrode in hydrogen atmosphere is working properly, tests were made at various bulk pH values. The ring response to the change in bulk pH is shown in Fig. 6-5 which indicates a slope of 56.6 mv/decade. This is in good agreement with a theoretical response of 58.1 mv/decade at 20 °C (see Eq. 5.27). The intercept of the experimental results is -250.4 mv, also in good agreement with the saturated calomel reference electrode potential on the hydrogen scale: -247.7 mv.
Fig. 6-5: Ring response to the bulk pH
Hydrogen Evolution Experiments

As the first step for in-situ pH measurement at the disk using the RRDE method, hydrogen evolution in the absence of any competing electrochemical reactions was studied. These experiments were considered to be the calibration test of the ring response to the interfacial pH change at the disk. All hydrogen evolution experiments were conducted from dilute acid solutions with 1.4 M NaCl as supporting electrolyte. Steady-state measurements were made by stepping the current at the disk and monitoring the ring potential as shown in Fig. 6-6.

Dynamic experiments were performed by ramping the potential at the disk electrode with simultaneous recording of the disk current and the ring potential. A typical set of results at four different rotation speeds is shown in Fig. 6-7. Very large cathodic shifts in the ring potential are observed. At current densities higher than the proton limiting current, hydrogen bubbles grow which cause some complexities; in addition to altering the current density by covering portions of the disk electrode, radial transport of protons to the ring is hindered by bubbles adhering presumably at the edge of the disk and the inner edge of the ring. The ring response to hydrogen evolution normalized to the proton limiting current, I, as measured by both the steady-state and potential sweep methods is shown in Fig. 6-8. The theoretical cathodic shift in the ring potential is also drawn for comparison. It can be seen that a slow sweep rate of 5 mv/sec gives the evolved hydrogen enough time to form bubbles and suppress the ring response. At high currents, the steady-state results also begin to show a reduced response as compared to the theory, but the 25 mv/sec sweep rate does not show this tendency.
Fig. 6-6a: Current Step Experiments, H2 on Pt
pH=2.95, 900 rpm
Fig. 6-6b: Ring response to hydrogen evolution on Pt
pH=2.95, 900 rpm
Fig. 6-7a: Hydrogen evolution on Pt disk at 1800, 1200, 900 and 600 rpm.
Fig. 6-7b: Ring response to hydrogen evolution on Pt disk at 1800, 1200, 900 and 600 rpm.
Fig. 6-8: Ring response to hydrogen evolution,
900 rpm, pH=2.9
Substrate Effect

Since we are applying the RRDE technique to measure the interfacial pH changes during electrodeposition of nickel, it is essential to investigate hydrogen evolution on a nickel substrate and the corresponding cathodic potential shift in the ring. The hydrogen evolution current-potential relationship on platinum and nickel disks are compared in Fig. 6-9a. As expected, hydrogen evolution on platinum has faster kinetics than on nickel, but the limiting current which is only a function of bulk pH and agitation is the same. The shift in the ring potential as a function of the current passed at the disk is shown in Fig. 6-9b.

The transport analysis presented in the preceding chapter shows that the ring response depends on the fraction of the hydrogen limiting current passed at the disk. When the kinetics of the electrochemical reaction are rapid, the assumption of uniform current distribution which was used in obtaining an analytical solution for hydrogen ion concentration profile on the plane of the RRDE becomes less valid. Hydrogen evolution on nickel has a more uniform current distribution than on platinum because of a higher kinetic resistance. However, it is interesting that for this RRDE geometry and the range of currents studied, the difference in current distribution uniformity does not seem to be affecting the ring response significantly.
Fig. 6-9a: Substrate effect on hydrogen evolution
900 rpm, pH=2.95
Fig. 6-9b: Ring response to hydrogen evolution on different substrates, 900 rpm, pH=2.95
Effect of boric and citric acid

Boric acid is commonly added to metal plating baths for improving the deposit appearance. To understand the role of boric acid, i.e. whether it is a buffer or a surface-active agent, hydrogen evolution from a solution containing 0.4 M boric acid (Fisher Scientific, certified ACS) was investigated. Supporting electrolyte was 1.4M NaCl and the pH was adjusted by adding HCl. Figure 6-10 compares the hydrogen evolution current on a nickel electrode with and without boric acid as a function of the electrode potential. Addition of boric acid did not change the limiting current, but increased the rate of discharge as evidenced by a higher current at a given disk potential. This observation is in agreement with previous work by Horkans (1979). Interestingly, the ring response was not affected by boric acid as seen in Fig. 6-11. The pK of boric acid ranges from 6 to 9 depending on its concentration. In the preceding chapter, the increase in the limiting current caused by the presence of a buffering agent was discussed. For a solution with a bulk pH of 3 and 0.4M concentration of a buffering agent, the enhancement of the limiting current is approximately 5 for a pK of 9, and more than 350 for a pK of 6. Although in the presence of boric acid we did not observe any enhancement of the hydrogen limiting current, the potential at which the current started to sharply increase was about -0.9 volts versus the calomel reference electrode. This potential is 0.2 volts more anodic than the thermodynamic potential of hydrogen evolution from water. This is significant since the rise in hydrogen current after the limiting current is reached has been attributed to the discharge of water (Horkans, 1979). Surprisingly, Horkans's data (1979, Fig. 5) also indicate a threshold potential of -0.7 volts with respect to NHE in the presence of boric acid. Since water discharge at these potentials is not possible, it is
reasonable to assume that boric acid, perhaps with a slow dissociation kinetics, provides
the protons needed for the current rise.

To find out how the ring would respond to the presence of a "real" buffering agent, hydrogen evolution was studied in the presence of citric acid, which is known to be a good buffer with a pK of 3 (CRC). A 0.1 M solution of citric acid (Baker Analyzed Reagent, Monohydrate Granular) was used with 1.4 M NaCl supporting electrolyte, and pH adjusted by addition of NaOH. The current-potential relationship of hydrogen evolution on a nickel disk electrode from this solution is shown in Fig. 6-12. The hydrogen current at -1.0 volt is almost 10 times the limiting current in the absence of citric acid. In Fig. 6-11, the ring response to hydrogen evolution from citric acid is compared to the base case. For a given hydrogen current, the cathodic shift in the ring potential was much smaller in the presence of citric acid. This is in qualitative agreement with our theoretical predictions (e.g. see Fig. 5-16).
Fig. 6-10: Effect of boric acid on hydrogen evolution on Ni
pH=2.9, 900 rpm, 25mv/sec
Fig. 6-11: Hydrogen evolution on Ni substrate: Boric and Citric Effect

$pH=2.9$, $900$ rpm, $25$mv/sec
Fig. 6-12: Hydrogen evolution from 0.1M citric acid solution
900 rpm, 10mv/sec
Measurement of the Ohmic Drop

The current interrupt technique was used to measure the ohmic potential drop registered by the ring. Although the ring is kept at open circuit, it senses the electric field in the solution when current passes through the disk electrode. Fig. 6-13 shows a typical response of the ring potential upon interruption of the current at the disk. There is a 3-5 μsec transient for the complete current turn off, but the potential at the ring undergoes oscillations, caused by active circuit elements of the buffer amplifier, lasting 20 μsec. Although the ring does not find a steady value in less than 5 μsec as the current does, the ringing occurs around its steady value. Since typical double-layer relaxation times are longer than 100 μsec (e.g. Newman 1966, Nisancioglu and Newman, 1973), the shift in the ring potential must be attributed to the ohmic drop. To obtain the ohmic resistance between the ring and the reference electrode, the slope of the potential drop as a function of current should be measured. Fig. 6-14 is an example of such measurement for a nickel plating solution containing 0.2M NiCl₂, and 1 M NaCl. The slope representing the ohmic resistance between the ring and the reference electrode is 2.5 ohms. The conductivity of this electrolyte is 0.12 Ω⁻¹cm⁻¹ which yields a calculated ohmic resistance of 2.8 ohms, for this RRDE geometry, based on primary current distribution ‡. It is not surprising that the measured resistance is smaller than the calculated value because primary current distribution provides the upper limit for ohmic drop. The kinetic overpotential for both nickel deposition and hydrogen evolution, in addition to the mass-transport limitations at high hydrogen currents, result in a much more uniform current distribution for our system compared to the primary.

‡ Primary current distribution assumes that the potential obeys Laplace's equation everywhere and there is no resistance to charge transfer at the electrode surface. This is the most non-uniform current distribution and only depends on the system geometry.
Fig. 6-13a: A typical current-interrupt experiment
Fig. 6-13b: Ring response to current interrupt at the disk
Fig. 6-14: Ohmic drop measurement by current-interrupt:
slope=2.5 ohms, primary current distribution calculation=2.8 ohms.
Nickel Electrodeposition

Steady-State Experiments

Nickel was electroplated from a 0.2 M solution of NiCl₂ certified Fisher Scientific with 1M NaCl as supporting electrolyte. The ring responds to the simultaneous hydrogen evolution at the disk electrode. An example of such measurements is shown in Fig. 6-15a,b which is obtained by stepping the current on the initially bare platinum disk to 6 mA/cm². It should be remembered that platinum is a better catalyst for hydrogen discharge than is nickel. Initially, the partial current of hydrogen is high on the bare platinum, leading to a large cathodic shift in the ring potential. As the disk becomes covered with nickel, the hydrogen partial current is reduced as reflected in the ring potential moving in the positive direction (i.e. smaller pH rise at the disk surface). The steady-state ring response a series of different current steps on a nickel disk electrode is shown in Fig. 6-16.

The change in the ring potential as a function of the total disk current is compared for hydrogen evolution by itself and during co-discharge with nickel in Fig. 6-17a. If the cathodic shift of the ring potential, in its entirety, is caused by hydrogen evolution, the partial current of hydrogen during nickel deposition can be easily evaluated from the hydrogen evolution data obtained in the absence of nickel ions. As discussed in Chapter 5, the ring response to hydrogen evolution is related to the fraction of mass-transfer limited current. Since the ionic strength of the nickel plating solution was made to be close to the hydrogen evolution calibration baths, the difference in diffusivities and viscosities should be insignificant; this leads to the same limiting hydrogen current for a
Fig. 6-15a: Nickel deposition onto a Pt disk electrode, 900 rpm, pH=2.95
Fig. 6-15b: Ring response to nickel deposition onto a Pt disk, 900 rpm, pH=2.95
Fig. 6-16a: Ni deposition, \( i = 2, 4, 6, 8 \) mA/cm\(^2\) at 900 rpm.
Fig. 6-16b: Ring response to Ni deposition, $i=2, 4, 0, 6, 8 \text{ ma/cm}^2$ at 900 rpm.
given bulk pH and agitation speed.

The current efficiency, $\eta = 1 - \frac{(i_{H_2})}{(i_{tot})}$, as estimated by using this method is shown in Fig. 6-17b. Independent current efficiency results obtained by using the replaceable disk electrodes are also shown in Fig. 6-17b. The total charge passed during nickel deposition is monitored, and the charge going into nickel plating is inferred from the added weight of the electrode and Faraday's law. The values obtained by the RRDE method are less than the coulometry/weighing results. This can be attributed to the ohmic component of the ring potential which must be corrected. As discussed previously, the ohmic component is proportional to the total current which can be significant at high currents associated with the metal deposition. The ring response without the ohmic component is shown in Fig. 6-17a for hydrogen evolution by itself and concurrent with nickel electrodeposition. Using the corrected values of the ring response, the current efficiency obtained from the RRDE measurements increases, shown in Fig. 6-17b, and the agreement between the RRDE and the coulometry/weighing methods improves.

**Dynamic Measurements**

We have investigated the dynamic response of the RRDE method in nickel electrodeposition experiments by sweeping the potential at the disk. Fig. 6-18 is an example of the cathodic wave form applied to the disk potential and the corresponding current at the disk and potential shift of the ring. The response time is less than 0.1 second, much smaller than what was reported for the RRDE system used by Albery and Calvo (1983). The dynamic measurements show a hysteresis in the ring response as a function of the total disk current. As shown in Figs. 6-19 and 6-20, within the ranges of
Fig. 6-17a: Ring response to hydrogen evolution by itself, and to nickel deposition with simultaneous hydrogen evolution, bulk pH=3, 0.2M NiCl2, 900 rpm.
Fig. 6-17b: Current efficiency of nickel deposition as measured with the RRDE and coulometry/weight methods, bulk pH=3, 0.2M NiCl2, 900 rpm.
Fig. 6-18: Linear sweep voltammetry of nickel electrodeposition at 600 rpm, 5mv/s.
Fig. 6-19: Effect of sweep rate on the ring response during Ni plating, 900 rpm
Fig. 6-20: Effect of agitation on the ring response during Ni plating
Fig. 6-21: Effect of Boric Acid on Nickel Plating

\[ \text{pH}=2.9, \text{ 900 rpm, 5mv/sec} \]
agitation and sweep rates studied, the presence of the hysteresis is not affected. Addition of 0.4M boric acid, shown in Fig. 6-21, shifts the ring response to more positive values and eliminates the hysteresis.

Interfacial pH Rise at the Disk During Electrodeposition

In Chapter 5 the relationship between the pH rise at the disk and the ring response was investigated. For the RRDE used in these experiments, geometry B, cathodic shifts larger than 12 mv are needed for a surface pH rise larger than 2 units (see Fig. 5-14). In the presence of species such as MOH$^+$ ions or a proton-donor buffering agents, the transition to large pH rise occurs at even larger cathodic shifts.

Nickel Electrodeposition

The ring response to the electrodeposition of nickel with concurrent hydrogen evolution, corrected for the ohmic drop, can be used to assess the interfacial pH at the disk. A typical set of such results is shown in Fig. 6-22 where a potential sweep is applied to the disk electrode. Comparison of the ring response to Fig. 5-14 indicates that the pH has risen less than 2 units in the baths without any boric acid, and less than 1 when boric acid is present. The flattening of the ring potential-shift as a function of the total disk current means that the hydrogen current is not increasing with potential. In other words, with current density or applied potential the nickel current increases which leads to the improvement of the current efficiency.

Iron Electrodeposition

Application of the RRDE method for deposition of iron from ferrous containing solution was investigated. Fig. 6-23a shows the disk current as a function of a
potentiostatic cathodic sweep for a solution of 0.04M FeSO₄, 1M NaCl with a bulk pH of 3. The current on the initially bare platinum disk electrode increases in each sweep cycle. The ring response when corrected for the ohmic drop, Fig. 6-23b, shows a periodic behavior indicating the partial current of hydrogen is not changing from cycle to cycle. The implication is that the increase in the disk current is because of the rise in the partial current of iron deposition. The maximum ring potential shift is -10 mV which is less than 1 pH unit rise on the disk surface.

Nickel-Iron Electrodeposition

Nickel-iron was electrodeposited from a solution of 0.2M NiCl₂, 0.005M FeSO₄, 1M NaCl and 0.4M boric acid. The concentration of the metal ions and the range of current densities and agitation rates were the same as in the electrolytes used by Andricacos et al. (1989). The experiments were performed on a platinum disk electrode, coated with a thin layer of electroplated nickel-iron (2 coulombs of total charge passed) at 20 mA/cm² with the agitation speed set to 900 rpm.

The steady-state ring response to current-steps is shown in Fig. 6-24 for agitation speeds of 400, 900 and 1600 rpm. The shift in the ring potential is more cathodic at lower agitation rates indicating a higher pH rise at the disk. The ring potential shift translates to different values of the pH rise depending on the value of the dissociation constant for NiOH⁺ and FeOH⁺. With the aid of the analysis presented in Chapter 5 (e.g. Fig. 5-14b), the interfacial pH rise as a function of current density is shown in Fig. 6-25. At current densities below 8 mA/cm², the interfacial pH rise for all agitation speeds, and different $K_d$ values, is less than 1 unit. At higher current densities, the pH rise is about 3 units for a large dissociation constant of $K_d = 10^{-5}$ and only 1 unit for $K_d = 2.5 \times 10^{-8}$.
The composition of Ni-Fe alloys electrodeposited under similar conditions (Andricacos et al., 1989) show that the percentage of iron in the alloy increases rapidly with current density, and passes its maximum of 40 weight percent before 10 mA/cm². At higher current densities, the percentage of iron in the alloy deposit begins to decrease. The minimum pH for precipitation of a solid metal-hydroxide with the concentration of metal ions in this electrolyte, is 6.6 for nickel, and 7.8 for ferrous-hydroxide (Pourbaix, 1974). In the current density range where iron percentage is at its maximum and the nickel deposition is strongly inhibited, our measurements indicate that the pH at the interface is only about 4. Even at higher currents, the interfacial pH is at most 6 which is not high enough for a metal hydroxide film to precipitate. This is strong evidence that the inhibition of nickel deposition leading to the high percentage of iron in the alloy deposit (refer to the literature reviews in Chapters 2 and 3) is not caused by a hydroxide precipitate. In refuting the film precipitate hypothesis, our simulation of nickel-iron alloys based on a mechanism involving NiOH⁺ and FeOH⁺ ions predicts a pH rise of less than 1 unit at the disk surface (Chapter 4), in qualitative agreement with the RRDE measurements.
Fig. 6-22: Ring response to nickel plating corrected for ohmic drop. 0.2M NiCl$_2$, pH=2.9, 900 rpm, 5mv/sec.
Fig. 6-23a: Iron deposition onto an initially bare Pt disk
at 900 rpm, 25mv/s and 10mv/s
Fig. 6-23b: Iron deposition onto an initially bare Pt disk at 900 rpm, 25mv/s and 10mv/s
Fig. 6-24: Ring response to Ni-Fe deposition at various rotation speeds, 0.2 M nickelous, 0.005 M ferrous, 0.4M boric acid, 1 M NaCl, pH=3.1.
Fig. 6-25: Interfacial pH rise at the disk during Ni-Fe electrodeposition corresponding to the data in Fig. 6-24.
Conclusions

A platinized ring electrode in a hydrogen-saturated electrolyte, monitored at open-circuit potentiometrically, has been shown to be a stable and reproducible sensor for the pH at the rotating disk. This method was applied to the electrodeposition of nickel, iron and nickel-iron alloys which involve simultaneous hydrogen evolution. The interfacial pH rise during deposition of nickel from a bulk pH of 3 was less than 2 units for the process parameters studied in this work. The electrodeposition of nickel-iron also showed a pH rise of less than 1 unit for current densities below 8 mA/cm². Depending on the dissociation constant of the metal-hydroxide ions, at higher currents the pH rise ranges from 1 to 3 units. These results are strong indications that a film of metal-hydroxide precipitate, requiring an environment with a pH higher than 6.5, is not formed and can not be the cause for the "anomalous codeposition" of nickel-iron alloys.

This mode of operating the RRDE can also be applied to measure current efficiency in a fast, non-intrusive and in-situ manner. Alternate methods such as weighing are laborious and require long deposition times to obtain sufficient amounts of deposit. Roughening of the surface, hence changing the true current density, and even a loss of deposit by peel-off are possible errors with these methods. The RRDE method is immune to these problems and can be advantageously used in developing plating baths and optimizing process parameters.
References


