MODELING OF LIMITING CURRENT AND GROWTH FRACTAL FOR ELECTRODEPOSITION UNDER MAGNETIC FIELD INFLUENCE

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MODELING OF LIMITING CURRENT AND GROWTH FRACTAL FOR ELECTRODEPOSITION UNDER MAGNETIC FIELD INFLUENCE

by

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LIST OF ABBREVIATIONS

CA	Chronoamperometry
DLA	Diffusion Limited Aggregation
LSV	Linear Sweep Voltammetry
MED	Magnetoelectrodeposition
MHD	Magnetohydrodynamic
MFE	Magnetic Field Effect
SEM	Scanning Electron Microscope

LIST OF SYMBOLS

		Unit
A	Electrode area	cm^2
B	Magnetic Field Strength	Tesla
C_{bulk}	Concentration of the electro active species	M
d	Diameter	mm
D	Diffusion coefficient of the electroactive species	cm^2/s
i_B	Limiting current under a magnetic field effect	mA
j	Current density	mA/cm^2
K	Constant	
m	Mass	g
M	Molarity	mol/L
n	The number of electrons involved in the redox process	-
R	Radius	mm
v	Kinematic viscosity of the electrolyte	stoke
V	Voltage	Volt

PEMODELAN ARUS MENGEHAD DAN FRAKTAL PERTUMBUHAN BAGI ELEKTROENAPAN BAWAH PENGARUH MEDAN MAGNET

Abstrak

Kekasaran adalah salah satu masalah utama dalam proses elektroenapan dan banyak kajian yang telah dilakukan untuk mengurangkan masalah itu. Salah satu kaedah untuk mengatasinya adalah magneto elektroenapan (MED). MED memainkan peranan penting dalam proses elektroenapan untuk mensintesis logam aloi, selaput nipis dan peranti mikroelektronik. Walau bagaimanapun, teknologi MED ini masih belum banyak diterokai secara meluas. Kajian ini bertujuan untuk mengkaji arus mengehad di bawah kesan medan magnet (MFE) bagi sistem elektroenapan kobalt, timah dan plumbum yang masing-masing mewakili spesies feromagnetik, paramagnetik dan diamagnetik. Dalam kajian ini, asid borik, glukonat dan sorbitol digunakan sebagai elektrolit tambahan bagi sistem MED kobalt, timah dan plumbum. Arus mengehad sangat penting kerana ia akan mempengaruhi pengangkutan jisim optimum yang diperoleh dalam proses elekroenapan. Dalam kajian ini, kesan medan magnet pada arus mengehad elektroenapan dikaji dari segi luas elektrod (A), kepekatan spesies elektro aktif (C_{Bulk}), pekali resapan spesies elektro aktif (D), kelikatan kinematik elektrolit (v), kekuatan magnet (B) dan jumlah elektron yang terlibat dalam proses redoks (n). Kesan MFE dengan ketumpatan fluks sehingga 0.3 T terhadap elektroenapan kobalt, timah dan plumbum dengan kehadiran elektrolit tambahan telah dikaji. Model semi-empirik untuk arus mengehad di bawah pengaruh magnet untuk kobalt, timah dan plumbum MED iaitu: $i_{B(Co)} = \mathrm{K}\ C_{Bulk}^{\ 1.297}\ A^{0.748}\ D\ v^{-0.664} B^{0.336} \mathrm{n}^{1.385}$, $i_{B(Sn)} = \mathrm{K}\ C_{Bulk}^{1.272} A^{0.746}\ Dv^{-0.67} B^{0.334} \mathrm{n}^{1.382}$ dan $i_{B(Pb)} = K\ n^{(f+1)} C_{Bulk}^{\ 1.271}\ A^{0.743}\ Dv^{-0.673} B^{0.33}$. Pada masa yang sama, kesan MFE pada fenomena pemindahan jisim dalam larutan cecair telah

dianalisis menggunakan voltametri sapu lelurus (LSV) dan *Chronoamperometry* (CA), manakala morfologi fraktal enapan elektro dianalisis menggunakan mikroskop elektron imbasan (SEM). Keadaan optimum bagi fraktal timah yang diperolehi dari kaedah pengoptimuman Taguchi ialah 0.01 M $SnSO_4$, 1 M H_2SO_4, 0.15 M glukonat dan 0.3 T kekuatan magnetic, keadaan ini digunakan untuk mendapatkan fraktal yang terbaik. Fraktal terbaik diperolehi dalam kajian ini mempunyai 216 mg massa, 10,80 mm jejari dan 2,26 dimensi. Akhirnya, model pertumbuhan fraktal timah yang terbaik telah dibangunkan menggunakan algoritma ubahsuaian pengagregratan resapan terhad (DLA) Witten - Sander. Model yang dibangunkan didapati berupaya menghasilkan fraktal yang mempunyai corak dan ciri yang sama sebagaimana yang dihasilkan melalui eksperimen.

MODELING OF LIMITING CURRENT AND GROWTH FRACTAL FOR ELECTRODEPOSITION UNDER MAGNETIC FIELD INFLUENCE

Abstract

Roughening is one of the main problems in the electrodeposition process and numerous studies have been carried out to reduce it. One of the methods of tackling this problem is by using the magnetoelectrodeposition (MED). MED plays a vital role in the electrodeposition process to synthesize metal alloys, thin films, and microelectronics devices. However, this MED technology has not been widely investigated. This work is aimed to study the limiting current under magnetic field effects (MFE) on an electrodeposition system of cobalt, tin and lead which represents ferromagnetic, paramagnetic and diamagnetic species respectively. Boric acid, gluconate and sorbitol are used in this study as additives electrolyte of cobalt, tin and lead MED systems, respectively. The limiting current is very important because it will affect the optimum mass transport achieved in the electrodeposition process. Here, the MFE on limiting current electrodeposition are investigated in terms of variations in the electrode area (*A)*, the concentration of the electro active species (C_{Bulk}), the diffusion coefficient of the electroactive species (*D)*, the kinematic viscosity of the electrolyte (*v)*, magnetic strength *(B)* and the number of electrons involved in the redox process (*n)*. MFE with flux density of up to 0.3 T on cobalt, tin and lead electrodeposition in the presence of additive electrolyte were investigated. The semi-empirical models for the limiting current under magnetic field for cobalt tin and lead MED obtained are $i_{B(Co)} = \mathrm{K}\, C_{Bulk}^{1.297} A^{0.748} D\, v^{-0.664} B^{0.336} \mathrm{n}^{1.385}$, $i_{B(Sn)} = \mathrm{K}\, C_{Bulk}^{1.272} A^{0.746}\, Dv^{-0.67} B^{0.334} \mathrm{n}^{1.382}$ and $i_{B(Pb)} = K\, n^{(f+1)} C_{Bulk}^{1.271}\, A^{0.743}\, Dv^{-0.673} B^{0.33}$, respectively. At the same time, the MFE on limiting current and diffusion

coefficient were analyzed using Linear Sweep Voltammetry (LSV) and Chronoamperometry (CA) while the morphology of the fractal of the electrodeposits were analyzed using a Scanning Electron Microscope (SEM). The optimum conditions of the tin fractal obtained from the Taguchi optimization method were 0.01 M of $SnSO_4$, 1 M of H_2SO_4, 0.15 M of gluconate and 0.3 T of magnetic strength. Those optimum conditions were then used to obtain the best growth fractal which was 216 mg of mass, 10.80 mm of radius and 2.26 of dimension. Finally, the best of the tin growth fractal was modeled using a modified diffusion limited aggregation (DLA) of the Witten - Sander algorithm. It is found that the model developed can produce fractal which has same pattern and similar characteristic to the best growth fractal produced from the experiment.

CHAPTER I

INTRODUCTION

1.1 Research Background

1.1.1 Conventional Electrodeposition

Electrodeposition is a plating process that uses an electrical current to reduce cations of a desired material from a solution to coat a conductive object with a thin layer of the material such as a metal. Electrodeposition is used to improve contact resistance, to reflect material properties and to impart friction properties. It is also used to impart corrosion resistance or a particular desired physical or mechanical property on the metal surface (James, 1984). This process has many applications such as to produce electronic parts, hardware, automotive parts and microelectronics device.

In an electroplating or electrodeposition unit, there are several important terms involved; namely the electrode, the electrolyte and the limiting current. An electrode is two electronically conducting parts of an electrochemical cell that is used to make contact with an electrolyte. There are two kinds of electrodes in an electrodeposition cell: the anode and the cathode. The anode is defined as the electrode at which electrons leave the cell and oxidation occurs while the cathode is the electrode at which electrons enter the cell and reduction occurs. Therefore, an electrodeposition process is actually a combination of the oxidation and reduction processes. This process is also termed as a redox reaction as this is a situation where one material gives up electrons (being oxidized) and another material gains electrons (being reduced) (Mohler, 1969).

An electrolyte is any substance containing free ions that makes the substance electrically conductive. The electrolyte is further classified into three types: the electro

active species, the supporting electrolyte and the additive. The electro active species is a species or substance in a solution that can take part in an electrode reaction. The supporting electrolyte is an electrolyte added to the solution to increase solution conductivity and does not take part in any reactions (James, 1984). The additive electrolyte is the addition of some organic materials in the plating baths which can influence the properties of the plated metal films. Some additives are adsorbed at the working electrode or cathode during deposition and thus alter grain structure, ductility, hardness, and surface smoothness (Yong and Kim, 2003; Hong *et al*., 2004). Each additive in electrodeposition could have a specific function; for example, boric acid in cobalt electrodeposition can lead to a smoother surface (Santos *et al.,* 2007); gluconate in tin electrodeposition is useful as a complexing agent and as an inhibitor against corrosion (Torrent-Burgues *et. al.,* 2002) and sorbitol in lead electrodeposition acts as a stabilizer to avoid bath decomposition and acts as an effective grain refiner (Siqueira *et al.,* 2007).

In the electrodeposition process, the limiting current is referred as the maximum current that can be achieved for an electrode reaction at a given concentration of the reactant in the presence of a large excess of supporting electrolytes (Levich, 1962). The limiting current is very important because it will affect the optimum mass transport achieved in the elecrodeposition process. It can be measured by using linear sweep voltametry (LSV).

1.1.2 Magnetoelectrodeposition (MED)

The problem of obtaining a uniform, dense and compact deposition has plagued researchers ever since the discovery of the electrodeposition process in the early 1800s. Various methods have been devised to address this problem; from controlling the electrolyte bath temperature and its pH level as well as using sophisticated plating bath formulae to obtain better control over the working characteristics of the electrodeposition process. Among these methods, the option of introducing an external magnetic field to produce a uniform and compact deposit is found to hold a promising future. This method is known as magnetoelectrodeposition (MED) (Ackland and Tweedie, 2007).

Magnetoelectrodeposition (MED) is an electrodeposition process under a magnetic field effect (MFE). The connection between magnetic field effects and electrodeposition was established since 1881 when Remsen observed the effect of a magnetic field in copper electrodeposition. As a result, research on the correlation between electrodeposition and MFE has gained the interest of many researchers (Nikolai *et al*., 2004).

A number of researchers have reported that some unique phenomena appear when magnetic fields are superimposed on the electrodeposition process. They are the increase of the limiting current and a drastic change of the growth pattern which leads to more uniform growth, compact and smoother surface of deposition (O'brien and Santhanam, 1997; Waskaas and Kharkats, 2001; Chopart *et al.*, 2002; Motoyama *et al.*, 2005; Matsushima *et al.*, 2006; Fernandez and Coey, 2009 ; Levesque *et al.*, 2009; Tschulik *et al.*, 2009; Koza *et al.*, 2010). This effect, known as the magneto-

hydrodynamic effect (MHD), is generally explained by the appearance of the Lorentz force. A magneto-hydrodynamic (MHD) effect is actually generated by the magnetic field effect (MFE). The MFE leads to a convective movement of the species to the surface of the electrode; for the electrochemical systems limited by the mass transfer, it induces an increase of the limiting currents (Legeai *et al.*, 2004).

MED technology has several noticeable advantages when compared to the conventional process. They are (Fernanda and Paulo, 2005) as follows:

i. Electrodeposition does not require vacuum technology and consequently is less expensive;
ii. It can be easily scaled up for use in large size areas;
iii. The experimental systems are simple; and
iv. It can be a room temperature technology.

With those benefits, MED technology plays a vital role in the electrodeposition process to synthesize metal alloys, thin films, multilayers, nanowires, multilayer nanowires, dot arrays and nanocontacts, which are the technology of the future to build the next generation of microelectronics devices.

1.2 Problem Statement

The concept of MED is not new; in fact, the first observations of magnetic field effects on electrochemical systems dates more than a century ago and have been credited to M. Faraday. Nevertheless, the last decades have witnessed an unprecedented activity in the area owing to the possibility of introducing an additional degree of freedom in controlling important electrochemical parameters. However, the possibilities

for the control of the morphology of the deposits and the limiting current are still unclear (Leventis, 1998).

Many researchers have reported that the limiting current of electrodeposition drastically increases when a magnetic field is introduced to the electrodeposition process (Fricoteaux *et al.*, 2003; Leventis *et al.*, 1998; Legeai *et al.*, 2004, and Rabah *et al.*, 2004, Fernandez and Coey, 2009 ; Levesque *et al.*, 2009; Tschulik *et al.*, 2009; Koza *et al.*, 2010). The limiting current is very important in both conventional electrodeposition and MED because optimum mass transport occurs at this limiting current. However, predicting and calculating the limiting current under a magnetic field is difficult in the MED process. Presently, there are two models that are used to predict the limiting current under magnetic field i.e. rigorous analytical model and semi-empirical model.

The rigorous analytical model is developed by using basic hydrodynamics models. Even though the basic hydrodynamic models governing mass transport under a magnetic force are well understood, rigorous analytical models of i_B are not available because of the nonlinear characteristic of those models. Moreover, neither the velocity nor the concentration profile near the electrode can be well defined. Consequently, the relationships relating the mass-transport-limited current, i_B, with the various system parameters are based partly on experimental data and partly on approximations (Leventis *et al.*, 1998). As a result, semi-empirical models are preferred in order to establish expressions governing the mass transport phenomena under the magnetic field influence (Fricoteaux *et al.*, 2003; Leventis *et al.*, 1998; Legeai *et al.*, 2004, and Rabah *et al.*, 2004).

However, the problem in this semi-empirical model is the different form of this model for each different material system hence; many material systems of MED have yet to be established. In our hypothesis, the different forms of those semi-empirical models are caused by the different characteristic of those materials towards a magnetic field. Based on the effects of the magnetic field on those materials, they can be divided into three types of materials known as ferromagnetic, paramagnetic and diamagnetic materials. At the same time, the presence of some additives in the MED system normally gives different forms of the semi-empirical model. Therefore, a study on the combination effect between MFE and additives on the limiting current of MED needs to be carried out.

In electrodeposition, it is important to control the growth pattern, mass and size of fractal properties. Therefore, the simulation that shows the mechanism and probability of the growth fractal pattern with its size and mass is very important in order to obtain a better understanding of the MFE on growth fractal electrodeposits. However, the growth fractal of each material system of MED has different characterictics and patterns. Hence, the MFE on the growth fractal of many material systems of MED are still unclear. Many reseachers have simulated the growth fractal on MED but the growth fractal of tin MED in the presence of additives is still unclear (Mansur Filho *et al.*, 2004; Mhiochain *et al.*, 2004; Mogi *et al.* 2004 and Nikolai *et al.*, 2004). Therefore, the effect of a magnetic field on growth fractal in the presence of additives needs to be studied and simulated. Furthermore, it is also important to identify the optimum conditions to produce the best growth fractal.

1.3 Research Objectives

The objectives of the study are :

1) to develop semi-empirical models of the limiting current under magnetic field effect, i_B, for cobalt, tin, and lead magnetoelectrodeposition.
2) to study the effect of electrode area (*A)*, concentration of the electro active species (C_{Bulk}*)*, diffusion coefficient of the electroactive species (*D)*, kinematic viscosity of the electrolyte (*v),* magnetic strength *(B)* and number of electrons involved in the redox process (*n)* on cobalt, tin, and lead magnetoelectrodeposition in the presence of an additive electrolyte.
3) to determine the optimum conditions of tin magnetoelectrodeposition in the presence of additives.
4) to develop a model for the best sample of growth fractal for tin magnetoelectrodeposition in the presence of additives.

1.4 Scope of Study

The aim of this study is to investigate the effect of magnetic strength and additive electrolyte on cobalt, tin, and lead electrodeposition which represent ferromagnetic, paramagnetic and diamagnetic species. The research project is divided into three main parts. The first part deals with the experiments to develop a semi-empirical model of i_B for cobalt, tin and lead MED. The second part focuses on the study of the growth fractal and the morphology of the electrodeposits of tin MED in the presence of additive electrolytes and optimization using the Taguchi methods. The last part involves the modeling of the best growth fractal for tin MED using DLA Witten – Sander algorithm.

Several parameters affect the limiting current of i_B such as the working electrode area (A), the bulk concentration of the electroactive species (C_{Bulk}), the diffusion coefficient of the electroactive species (D), the kinematic viscosity of the electrolyte (v), magnetic strength (B) and the number of electrons involved in the redox process (*n).* However, the effect of the diffusion coefficient of the electroactive species (D) and the kinematic viscosity of the electrolyte (v) are studied by varying the concentrations of the supporting and additive electrolyte.

The effect of the concentration of the electroactive species (C_{Bulk}) towards the limiting current (i_B) on cobalt, tin and lead MED is studied by varying the concentrations of $CoSO_4$, $SnSO_4$ and $Pb(NO_3)_2$, respectively. The influence of the working electrode area (A) on the limiting current (i_B) in all the MED systems are studied by using four platinum working electrodes of different areas.

The effects of the diffusion coefficient of the electroactive species (D) and the kinematic viscosity of the electrolyte (v) are observed by varying the supporting and additive electrolytes. The supporting electrolytes used in cobalt and tin MED are H_2SO_4 and Na_2SO_4, while NaOH and KOH are used as supporting electrolytes in lead MED. Boric acid, gluconate and sorbitol are used as additive electrolytes for cobalt, tin and lead MED, respectively.

Several important parameters that affect the performance of tin MED such as the concentration of tin sulphate, sulphuric acid, gluconate additive and the magnetic strength were used as parameters in the Taguchi statistical methods to find the optimum operation conditions of tin MED. For the performance of the tin MED, three important

indicators were examined; mass, radius and dimension of the fractal. Finally, a modified DLA Witten - Sander algorithm is used to simulate of the best growth fractal of tin electrodeposits.

1.5 Organization of the Thesis

This thesis is divided into five chapters. Chapter One gives the general overview of magnetoelectrodeposition, the semi-empirical model of the limiting current (i_B) and the modeling of the growth fractal. The problem statement, objectives and the scope of study of this research are also stated in this chapter.

Chapter Two provides the overall literature review of MED, the mass transport phenomena in MED, the semi-empirical model of the limiting current under a magnetic field (i_B), cobalt, tin and lead MED, the optimization of the growth fractal and the model of the growth fractal. Some background information about electroanalytical chemistry which is related to this is also presented.

Chapter Three focuses on the details of the materials and the methods implemented in this research. The first part of this chapter presents the raw materials and the equipment used, followed by the description of the experimental set up for the development of semi-empirical model i_B. Then, the experimental procedures for investigating the MFE on the growth fractal and the modeling of the growth fractal algorithm are explained.

Chapter Four presents the results and discussion of the findings in this research. It is divided into three parts. The first part of this chapter contains the study of the effect

of the working electrode area (A), the bulk concentration of the electroactive species (C_{Bulk}), the diffusion coefficient of the electroactive species (D), the kinematic viscosity of the electrolyte (v), magnetic strength (B) and the number of electrons involved in the redox process (*n)* towards the limiting current of cobalt, tin and lead MED. Then, the development of the semi-empirical models of the limiting current (i_B) is discussed. The final part of this chapter consists of the study on the effect of the magnetic field on tin growth fractal. This part includes the optimum conditions of tin MED, the effect of MED on the surface morphology and the modeling of the best growth fractal.

Finally, Chapter Five summarizes the conclusions of the research and recommendations for future study based on the overall results obtained. Some recommendations that are required or deemed appropriate are stated in this chapter as a guideline to improve the results for future research work.

CHAPTER TWO

LITERATURE REVIEW

2.1 Magnetoelectrodeposition (MED)

Electrodeposition or electroplating is the process of depositing solid materials on an electrode surface using electrolysis. It is also defined as a process that produces a thin, metallic coating on the surface of another metal (or any other conductor). The metal substrate to be coated is used as the cathode in an electrolytic cell which contains the cations. When current is applied, the electrode reaction occurring on the cathode is reduced from metal ions to metal. The anode material can either be the metal to be deposited or nonreactive materials (James, 1984).

The effect of a magnetic field on the electrode potential (EP) was observed by Gross in 1885 and it was confirmed by the experiments of other researchers. They found that the magnetized electrode became more negative in the magnetic field. In 1887, Janet and Duhem found that paramagnetic and ferromagnetic materials became more positive while diamagnetic materials became more negative in comparison with the non-magnetized ones. However, these qualitative expressions gave no numerical values but only the signs of the effect (Nikolai *et al.*, 2004). No proper explanation for the effects of a magnetic field on electrodeposition was suggested since the 19^{th} century even though electrodeposition was discovered during that period. Today, electrodeposition has many applications such as to produce microelectronics devices thus MED has become more important and interesting to study.

MFE has a significant influence on electrodeposition. The most striking effects of MED are the impressive increase in the limiting current and a dramatic change in the morphology of the fractal electrodeposit (Mhiochain *et al.*, 2004; Matsushima *et al.*, 2006). Both phenomena could happen because the magnetic field could increase the rate of the transport of electroactive species to or from the electrode. The possible force which could be responsible for the enhancement of the mass transfer is known as the Lorenz force (Bund *et al.*, 2003; Matsushima *et al.*, 2006).

2.2 Mass Transport in MED

Mass transport is the phenomenon of movement (transportation) of mass (e.g. chemical compounds, ions) from one part of the system to another (James, 1984). Magnetohydrodynamic (MHD) is the transport mechanism in the MED process which originates through the interaction of magnetic fields with electrolyte flows leading to the induction of electrical potentials and currents (Waskaas and Kharkats, 1999; Legeai *et al.*, 2004). This MHD effect is caused by the Lorenz force which acts on the migration of charged ions inside the electrolyte and induces a convective flow of electrolytes close to the electrode surface (Coey *et al.*, 2001).

When the MHD effect is present, the convective flow will create mixing in the diffusion area and reduce the thickness of its Nernst diffusion layer in front of the electrode effectively. As the Nernst diffusion layer decreases, the limiting current density will increase thus increasing the deposition rate (Fahidy, 2001). Limiting current density is the maximum current density that can be achieved for an electrode reaction at a given concentration of the reactant in the presence of a large excess of supporting electrolytes. The mass transport occurs exclusively through diffusion in the diffusion

layer, driven by the concentration difference of the reactant between the edge of the diffusion layer and the electrode surface (James, 1984).

This mass transport phenomenon also has an effect on the growth of fractal electrodeposits. The pattern formation in these deposits is very sensitive to the growth conditions which can be manipulated by the MFE. This makes the metal grains grow uniformly and have smoother and more compact surfaces (Fahidy, 2001, Mogi and Kamiko, 1996; Takahashi *et al.*, 1999). The mass and size of the fractal electrodeposits will increase with a higher amount of electrolyte concentration and voltage. Their form also changes from diffusion-limited aggregation (DLA) to compact dendrite (Mogi and Kamiko, 1996; Mhiochain *et al.*, 2004).

2.3 Semi-empirical Model of Limiting Current under Magnetic Field, i_B

The basic hydrodynamic equations of the mass transport limiting current under the magnetic force, i_B, or fundamental MHD is well understood. This model can express the hydrodynamic problem; it is coupled via the concentration of the electroactive species with a fundamental electrochemical model which can solve the electrochemical problem via its boundary conditions. However, this model is not available for some cases because of the nonlinear characteristic of the equations and the hydrodynamic problem that needs velocity profiles under a magnetic field or in a complicated electrochemical problem that cannot be solved by the Levich equations (Leventis *et al.*, 1998). Consequently, the parameters on the equations relating to the mass-transport-limiting current, i_B, are based partly on experimental data and partly on approximations. Aogaki *et al.* (1976) reported that for the electrodeposition of copper in open-ended cells of two closely spaced (1 to 2 mm apart) parallel electrodes in magnetic fields of 0.1-0.6 T, the

limiting current is proportional to $(C_{bulk})^{3/2}B,^{1/2}$ where C_{bulk} is the bulk concentration of the redoxactive species and B is the magnetic field strength. Using copper magnetoelectrolysis and a rotating disk electrode in magnetic fields of 0-1.2 T, Chopart *et al.* (1991) showed that the limiting current is proportional to $(C_{bulk})\alpha^{1/3}$ where α is the magnetohydrodynamic velocity gradient. By using the ferri-ferrocyanide couple and an impedance technique where B was varied sinusoidally, Aaboubi *et al.* (1990) showed that α is proportional to $(C_{bulk})B$ while the limiting current is proportional to $(C_{bulk})^{4/3}B^{1/3}$.

Many researchers have used the rigorous hydrodynamic equations as a guide to the system parameters that could control the mass transport limiting current. They vary all those parameters systematically using a range of compounds and solvents. This model is known as the semi-empirical treatment of the steady-state mass-transport-limiting current, i_B. Leventis *et al.* (1998) presented this model as follows:

$$i_B = nFAmC_{Bulk} \tag{2.1}$$

where F is Faraday constant and m is the parameters that control the mass transport coefficient which has a major role in this equation. In this context, m depends on the parameters that influence the velocity, v, and the volume element of the electrolyte, V. According to the fundamental hydrodynamic equation, these parameters should include the concentration of the electroactive species, C_{bulk}; the electrode area, A, the diffusion coefficient of the electroactive species, D, the kinematic viscosity of the electrolyte, v, the magnetic field strength, B, and the number of electrons of the redox process, n. Then, the mass transport coefficient becomes:

$$m = K\, C_{Bulk}{}^{a} A^{b} D^{c} \nu^{d} B^{e} n^{f} \qquad (2.2)$$

where *k is* the constant. The limiting current in the magnetic field given by Leventis *et al.*, 1998; Fricoteaux *et al.*, 2003; Legeai *et al.*, 2004, and Rabah *et al.*, 2004 is :

$$i_B = K\, n^{(f+1)}\, C_{Bulk}{}^{a+1} A^{b+1} D^{c} \nu^{d} B^{e} \qquad (2.3)$$

where *K* is a constant and the Faraday constant (F) is included in *K*. The exponents *a* to *f* can be determined by varying systematically all the parameters in Equation 2.3.

Leventis *et al.* (1998) developed a semi-empirical treatment using a redox-active compound electrodeposition system. The redox-active compounds that were studied were *N*,*N*,*N*,*N*-tetramethyl-*p*-phenylenediamine (TMPD), *N*-methylphenothiazine (MePTZ), *N*,*N*-dimethylphenazine (DMePAZ), ferrocene (Fc), and *N*,*N*-di-*n*heptylviologen dichloride ($DHVCl_2$). The angular flow profile near the electrode surface was also mapped using an electrochemical generation/collection method.

Leventis and Gao (1999) studied steady-state voltammetry with stationary disk millielectrodes in magnetic fields in order to obtain a nonlinear dependence of the mass-transfer limiting current on the electron balance of the faradaic process. They reported that the intensity of the hydrodynamic convection generated by the conventional disk millielectrodes in the magnetic fields was intimately related to the nature of the faradaic process and that the mass-transfer limiting current, i_B, was proportional to $n^{3/2}$ where *n* is the number of electrons involved in the heterogeneous electron transfer.

Fricoteaux *et al.* (2003) investigated the mass transport of copper electrodeposition from a sulfuric acid solution under a magnetic field influence and proposed modifications for the MHD equation of the limiting diffusion current versus the magnetic field amplitude proposed by Aaboubi *et al.* (1990). They established a new relationship of the limiting current that took into account the electron number involved and the kinematic viscosity. Despite using different theoretical approaches, Leventis' relationship and their limiting current equation have very small differences.

Legai *et al.* (2004) studied the mass transport phenomena of the oxidation reactions of hexacyanoferrate (II) and hydroquinone in KCl media on disk platinum electrodes using chronoamperometry under a strong magnetic field (1.74 T). They developed a semi-empirical equation of the steady-state mass transport limiting current in the magnetic fields by the semi-empirical treatment. They observed that there was a drastic influence of the electrolyte dielectric constant (ε) on the limiting current under a magnetic field. They also used the electrolyte dielectric constant as a parameter in the semi-empirical limiting current equation.

Rabah *et al.* (2004) analyzed the magnetic force effect on Cu (II). They found that a magnetic field perpendicular to the surface of a plane electrode created convective effects. These effects were enhanced when the species involved was paramagnetic. Their study showed that the limiting currents under these conditions were proportional to $B^{2/3}C^{4/3}$. The use of the MHD transfer function made it possible to check this dependence. However, this relation seemed valid only for a small range of

concentrations and magnetic fields. It is thus necessary to extend their studies to widen the range of the magnetic field.

The major features of the semi-empirical model of i_B that have been investigated by previous researchers are listed in Table 2.1. The work is tabulated in ascending order of publication, from 1974 – 2004. The table shows that different species lead to different formulas of the semi-empirical equations. The different forms of those semi-empirical equations are caused by the different magnetic properties of the materials. Moreover, the presence of some additives in the MED system automatically affects the form of the semi-empirical equation. From the literature, studies on the effect of the combination between MFE and additives on the limiting current of MED have yet to be established. Therefore, this research is focused on three materials i.e. cobalt, tin and lead, which represent the ferromagnetic, paramagnetic and diamagnetic species, respectively. All the materials have been used together with suitable additives: boric acid, gluconate and sorbitol (Torrent-Burgues et.al, 2002; Santos *et al.*, 2007 and Siqueira *et al.*, 2007).

Table 2.1: Summary of literature reviews of the semi-empirical model of the limiting current in magnetic fields (i_B)

No.	Limiting Current Equation	ED System	Magnetic strength	Additive	Magnetic properties	Reference
1.	$i_B = 0.678nFD^{2/3} C_{Bulk}^{*} d^{5/3} \alpha^{1/3}$ where $\alpha = kBC_{Bulk}^{*}$	Ferri - ferrocyanide	0 – 1 T	-	Ferromagnetic	Mollet *et al.* (1974)
2.	$(C_{bulk})^{3/2}B^{1/2}$	Redox active species	0 -13 T	-	Diamagnetic	Aogaki *et al.* (1976)
3.	$i_B \propto (C_{bulk})\alpha^{1/3}$	Ferri-ferrocyanide couple	0 – 2 T	-	Ferromagnetic	Chopart *et al.* (1991)
4.	$i_B \propto B^{1/3} \times C_{Bulk}^{4/3}$	Nitrobenzene and Acetophenone in CH_3CN	0 - 1.65 T	-	Diamagnetic	Aaboubi *et al.* (1990)
5.	$i_B = 4.31x\ 10^3\ n^{F+1} FA^{3/4} B^{1/3}\ Dv^{-1/4} A^{0.746}\ C_{Bulk}^{4/3}$	TMPD, $DHVCl_2$, DMePAZ, Fc, MePTZ	0.85 - 1.75 T	-	Diamagnetic	Leventis *et al.* (1998)
6.	$i_B = 4.31x\ 10^3\ n^{3/2} FA^{3/4} B^{1/3}\ Dv^{-1/4} A^{0.746}\ C_{Bulk}^{4/3}$	$DHVCl_2$, TCNQ, TMPD, TTF, and DMePAZ	0.85 - 1.75 T	-	Diamagnetic	Leventis and Gao (1999)
7.	$i_B \propto B^{1/3} \times C_{Bulk}^{4/3}$	$K_3Fe(CN)_6$, $K_4Fe(CN)_6$ and KCl	0 - 1.65 T	-	Paramagnetic	Aaboubi *et al.* (2002)
8.	$i_B = 5x\ 10^3\ n^{4/3} FA^{5/6} B^{1/3}\ D^{2/3} v^{-2/3}\ C_{Bulk}^{4/3}$	Copper (Cu) in H_2SO_4	0 – 1 T	Glycerol	Paramagnetic	Fricoteaux *et al.* (2003)
9.	$i_B = K\ nd^{5/3} B^{1/} Dv^{-2/3}\ C_{Bulk}^{4/3} \varepsilon^{-7/4}$ $K = (1.2 \pm 0.1)\ x\ 10^9\ A\ mol^{-4/3}\ m^{1/3}\ scS^{2/3}\ T^{-1/3}$	Hexacyanoferrate(II) and Hydroquinone in KCl	0 - 1.74 T	Ethanol	Ferromagnetic	Legai *et al.* (2004)
10.	$i_B = k\ nFd^{7/4} B^{2/3}\ D^{2/3} v^{-2/3}\ C_{Bulk}^{4/3}$ where d = a circular electrode of diameter	Cu (II) in H_2SO_4	0 - 1.6 T	-	Paramagnetic	Rabah *et al.* (2004)

2.3.1 Cobalt MED

Cobalt is an element with excellent ferromagnetic properties. In addition, it is relatively stable against corrosion and easy to handle, which makes it even more useful for technical applications such as used to increase the appearance of metal in electrodeposition process and used to produce giant magneto resistant (Krause *et al.*, 2005). This property as well as others, such as hardness and the thermal stability of cobalt electrodeposits, has motivated further investigations on cobalt electrodeposition. Cobalt can be used to make electronic or microelectronic devices. These products must have thin layers and smooth surfaces. There are many methods to improve the quality of cobalt electrodeposition such as magneto electrodepostion and the introduction of additive electrolytes such as boric acid. However, the combination of the effect of a magnetic field and additives in cobalt electrodeposition is still unclear.

Matsushima *et al.* (2006) studied the electrodeposition of cobalt from sulfate solutions at different pH values using the electrochemical quartz crystal microbalance (EQCM) technique coupled with cyclic voltammetry. It was found that cobalt hydroxide was formed simultaneously with cobalt deposition during the early stages of reduction due to pH variation near the electrode surface.

Krause *et al.* (2005) investigated the influence of the magnetic field on the morphology of electrodeposited cobalt. They used $CoSO_4$ as an electrolyte with the addition of 0.1M Na_2SO_4 as a supporting electrolyte. It was found that the roughness of cobalt layers was influenced by magnetic fields as well as by the electrical potential. Moreover, holes in the cobalt deposits caused by hydrogen bubble formation during electrodeposition were avoided when a magnetic field was applied.

Santos *et al.* (2007) studied the effect of temperature on cobalt electrodeposition in the presence of boric acid. They reported that boric acid was added to the electrolyte as a buffer to avoid the local pH rise caused by a parallel hydrogen evolution reaction (HER). The results showed that the buffer contribution of boric acid was effective in cobalt electrodeposition at 25 °C. However, they did not study the effect of combination of boric acid and MFE on cobalt electrodeposition.

2.3.2 Tin MED

Tin has been used in industries as a coating on a large number of metals, particularly steel (tin plate), to impart corrosion resistance, increase appearance or improve solderability. Pure electroplated tin is used in microelectronics as an alternative for tin/lead finishes (Torrent-Burgues *et al.*, 2002). Tin has also been commercially electrodeposited from several acid and alkaline baths. Recently studies on tin and tin-alloy electrodeposition focused mainly on the influence of additives, bath compositions and plating variables to obtain coatings for commercial applications (Danilyuk, *et al.*, 1990; Torrent-Burgues *et al.*, 2002). However, the semi-empirical equation of the limiting current (i_B) and the modeling of its growth fractal under MFE have yet to be established.

Danilyuk *et al.*, (1990) studied the effect of a weak magnetic field (0.05-0.19 T) on the electrodeposition of films of tin in sulfate baths. The results showed that MFE has a significant effect on the tin electrodeposition process and improved the kinetics of electrodeposition. However, the MFE on the mass transport phenomena and the growth fractal of tin electrodeposition have not been addressed.

Using sulfate/gluconate as an additive in tin electrodeposition is a newly practiced system. Some reports show that the use of sulfate/gluconate baths is a promising alternative. Gluconate is reported to be useful as a complexing agent and as an inhibitor against corrosion (Torrent-Burgues *et al.*, 2002). MFE is also reported to be useful to increase compactness, and deposit uniformity and growth orientation on metal electrodeposition (Fahidy, 2001).

2.3.3 Lead MED

Lead is a diamagnetic material which has potential applications such as the production of a high purity active material for acid battery and semiconductors and the fabrication of electrochromic devices (Carlos *et al.*, 2003). Lead can also be used to produce micro electronic devices which have thin metal layers. These products are mostly in a nanoscale thickness range. There are many processes to produce thin layers such as electrodeposition, thermal evaporation, CVD (chemical vapor deposition), spray pyrolysis, sputtering, PLD (pulsed laser deposition), sol-gel process and atomic layer deposition (ALD). However, electrodeposition promises the best alternative since it is more productive, cheap and easy to control (Carlos *et al.* 2003).

Lead electrodeposition has been accomplished from various acid solutions such as nitrate, fluoroborate, fluorosilicate, perchlorate, pyrophosphate and acetate. As most acid electrolytes are toxic, alkaline electrolytes are more appropriate from an environmental point of view. Moreover, new alkaline solutions have been developed to carry out lead plating and lead scrap recycling. Alkaline electrolytes are also less corrosive compared to acid electrolytes. A plumbite solution ($Pb(NO_3)_2$), sorbitol and

NaOH are a new electrolytic solution for the electrodeposition of lead on a copper substrate. Sorbitol acts as an effective grain refiner in both acid and alkaline plating which will cause the electrodeposits to grow more compact with a higher purity of electrodeposits. At the same time, sorbitol acts as a stabilizer to avoid bath decomposition (Siquera and Carlos, 2007a).

Siquera and Carlos (2007b) also studied the effect of sorbitol on the morphological characteristics of lead–tin films electrodeposited from an alkaline bath. They found that the lead alkaline plating solution was successfully stabilized by the addition of sorbitol. No bath decomposition was observed during deposition. The smooth lead film on the copper substrate was adherent and thus could probably be used as a support in battery plates.

Carlos *et al.* (2003) studied the potentiodynamic electrodeposition of lead on a 1010 steel substrate. A new electrolytic solution was used to study the sensibility of the sorbitol additive in the production of lead film which is used in lead batteries. A 1010 steel disk (0.5 cm^2), a platinum (Pt) plate and a Hg/HgO/1 M NaOH electrode with an appropriate Luggin capillary were used as the working, auxiliary and reference electrodes, respectively. Each electrochemical experiment was performed in a bath containing 0.1 M $Pb(NO_3)_2$ and NaOH at various concentrations (0.40, 0.60, 0.8, 1.0, 2.0 and 3.0 M) in the presence and absence of 0.2 M sorbitol. From the scanning electron microscopy (SEM) photographs, it can be inferred that sorbitol has a beneficial effect on lead deposition since it reduced the propagation of dendritic growth more than glycerol.

Wong and Abrantes (2005) studied lead electrodeposition from a strong alkaline media using cyclic voltammetry and chronoamperometry. Electrodeposition was performed in a conventional three-electrode electrochemical cell with a saturated calomel electrode (SCE) as reference and a Pt foil counter electrode and the SS316 as working electrodes. They reported that the hydrogen evolution reaction (HER) on the lead electrodeposition process was prevented by the increase of lead content and the decrease of NaOH concentration.

In this present work, the effect of cobalt, tin and lead electrodeposition with additives and the magnetic field influence were studied. Boric acid, gelatin and sorbitol are considered as an additive of cobalt, tin and lead systems, respectively. The hypothesis is that an additive would avoid roughening and the magnetic field effect would increase the rate mass transfer and would also improve the morphology of cobalt electrodeposits.

2.4 Optimizations of MED Using Taguchi Method

The higher value of the fractal dimension indicates a better quality of electrodeposits produced by MED. This fractal dimension is affected by many influential factors such as the strength of the magnetic field, the concentration of the electroactive species and the supporting and additive electrolytes. The result of this fractal dimension can be used as a basis in the optimization analysis. To optimize the design of the MED process, it is necessary to identify the optimum conditions that have significant influence on the process. One of the designs of experiment (DOE) methods that can define the optimum conditions for the process is the Taguchi method.

DOE using the Taguchi approach is an engineering design optimization methodology developed by Genichi Taguchi to improve the quality of existing products and processes and simultaneously reduce their costs very rapidly with minimum engineering resources and development man-hours (Atkinson *et al*., 2007). Nowadays this method is also applied in engineering, biotechnology, marketing and advertising. The Taguchi experiment design involves reducing the variation in a process through the robust design of experiments. The Taguchi experiment design technique makes the product or process robust and therefore it is also called a robust design (Ranjit, 1990).

The Taguchi method is developed for designing experiments to investigate how dissimilar parameters affect the mean and variance of a typical process performance that defines how fit the process is functioning. The experimental design proposed by Taguchi involves using orthogonal arrays to arrange the parameters affecting the process and the levels at which they should be varied. Instead of having to test all possible combinations such as the factorial design, the Taguchi method tests pairs of combinations. This allows for the collection of the necessary data to determine which factors most affect product quality with a minimum amount of experiments thus saving time and resources. The Taguchi method is best used when there are an intermediate number of variables (3 to 50), few interactions between the variables, and when only a few variables contribute significantly (Ranjit, 1990). The Taguchi arrays can be derived or looked up. Small arrays can be drawn out manually; large arrays can be derived from deterministic algorithms. Generally, arrays can be found online and are selected by the number of parameters (variables) and the number of levels (states).

In the Taguchi method, optimization means the determination of the best levels of control factors. In turn, the best levels of control factors are those that maximize the

signal-to-noise ratios. The signal-to-noise (S/N) ratios are the *log* functions of the desired output characteristics. The experiments that are conducted to determine the best levels are based on orthogonal arrays; they are balanced with respect to all control factors and yet are minimum in number. This in turn implies that the resources (materials and time) required for the experiments are also the minimum (Ranjit, 1990).

The Taguchi method divides all problems into two categories: static or dynamic. Dynamic problems have a signal factor while static problems do not have any signal factors (Atkinson *et al*., 2007). In dynamic problems, optimization is achieved by using two kinds of S/N ratios; S/N of Slope and S/N of Linearity. In static problems, a process to be optimized has several control factors which directly decide the target or the desired value of the output. The optimization then involves determine the best control factor levels so that the output is at the target value. The optimization of static problems is achieved by using three kinds of S/N ratios (Ranjit, 1990). The three kinds of S/N ratio for static problems are:

a. Smaller-the-better :

$$\frac{S}{N_{(smaller)}} = -10\log\left(\frac{\sum y_i^2}{n}\right) \tag{2.4}$$

where y_i is a measured data. Taguchi's SN-Ratio of the smaller-the-better method is usually used for experiments in which the quality characteristic is an undesired output.

b. Larger-the-better :

$$\frac{S}{N_{(bigger)}} = -10\log\left(\frac{\sum\left(1/y_i^2\right)}{n}\right) \tag{2.5}$$