

MODEL-BASED FRAMEWORK FOR TERNARY ALLOY ELECTRODEPOSITION PROCESSES: MODEL VALIDATIONS AND PARAMETER ESTIMATION

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Abstract: This paper deals with the use of a model-centric approach towards the definition of optimal electrodeposition schemes in the fabrication of nanometric multilayers materials with tailored properties. A model for such complex systems is used and validated against experimental data. These mathematical deposition models range from single depositions to alloys, and have the characteristic of having large number of parameters not available from literature or experiments. In this work the capabilities of modern modelling, simulation and optimization environments is exploited both for model development and parameter estimation and will be used in further optimization studies for fabrication improvement and control. *Copyright © 2007 IFAC*

Keywords: Complex Modelling, Parameter Estimation, Process Optimization, electrochemical Codeposition, Nanometric Multilayers.

1. INTRODUCTION

The electrodeposition of iron-group alloys has been widely studied due to their interest as materials used in computer magnetic data storage and sensing (Osaka, 1997; Osaka, *et al.*, 1998; Cooper *et al.*, 2005). Recently these materials have also received attention when they are layered with copper at the nanoscale. (Ross, 1994; Sun *et al.*, 2005) Nanometric multilayers exhibit giant magnetoresistance (GMR), a change in the materials resistance with an applied magnetic field. In order to improve the GMR property, it is imperative to tailor and control the composition and the compositional gradient within each layer to improve plating schemes for the multilayer deposits.

High-level equation-oriented declarative modelling languages have gained increased acceptance as the most appropriate tools to tackle the modelling process when full control over the scope and detail of the model is required (Foss *et al.*, 1998). Most contemporary modelling languages have evolved into multi-purpose process-engineering software

tools (*modelling, simulation and optimization environments* (MSOEs)). State-of-the-art MSOEs provide the modeller with a series of sophisticated tools and mechanisms that contribute enormously to an increase in the efficiency of the modelling process.

Thus, we have recently proposed a novel model-centric framework for integrated simulation, estimation/reconciliation and optimization of systems based on mechanistic process models (Rolandi and Romagnoli, 2005, 2006a, 2006b). By encapsulating the complex interactions at the interface level within a mechanistic model, describing the compositional gradients of each magnetic layer, the formulation of a model-centric strategy to support the experimental investigations will be considered in our approach. This unique integration establishes the foundation of the proposed strategy and will allow the tailoring and control of the composition within each layer.

In this paper, a mathematical model, following Zhuang and Podlaha (2003), is used to describe the composition within the magnetic alloy layer. In iron-

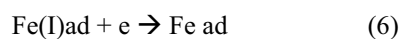
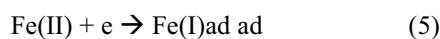
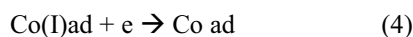
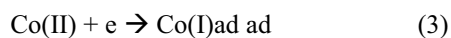
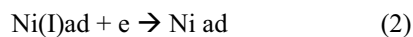
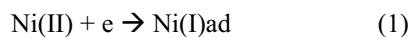
group alloy multilayers such as FeCoNi alloys separated by Cu layers, the anomalous kinetic deposition behaviour of the FeCoNi coupled mechanism and mass transport needs to be accounted for in order to simulate the deposit composition.

Anomalous codeposition refers to the unexpected preferential deposition of the less noble metal (i.e. Fe). (Brenner, 1963) The coupled reaction kinetics have been described by an adsorption approach. (Matlosz, 1993). The less noble metal preferentially adsorbs onto the electrode surface and blocks the codeposition of the other iron-group elements, Co and Ni. In certain cases the less noble metal can also be accelerated and has been modelled by treating the more noble species as a catalyst (Zech, *et al.*, 1998). Both features have been combined by Zhuang and Podlaha (2003) to predict a combined apparent inhibition and acceleration effect of the codeposition system. Since the reaction kinetics are dependent upon concentration, mass transport also plays a role when the driving force (i.e. applied potential or applied current) is large.

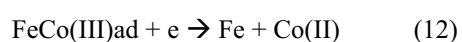
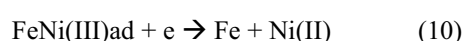
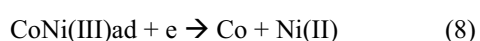
Process models are subject to parametric uncertainty and experimental data is corrupted by random errors, hindering the accuracy and usefulness of model-centric strategy. Consequently, in our approach, a validation step is undertaken in conjunction with the execution of parameter estimation studies. They rely on the maximum likelihood theory and require specifically generated set of experimental data. Laboratory data is analyzed to extract the coupled kinetic/diffusion information.

2. MATHEMATICAL MODEL AND IMPLEMENTATION

The reaction equations that occur for the NiCoFe ternary alloy are as follows



In addition to the above reactions, mixed metal intermediates are formed.



When the reactions are controlled by kinetics the rate, described in electrochemistry as the partial current densities, i , is dependent upon potential, E , rate constants, k , species concentrations in the electrolyte at the electrode surface C and adsorbed species θ . Table 1 show the partial current density kinetic rate expressions used for NiCoFe ternary alloy deposition, assuming a Tafel rate law.

Table 1 Partial current density kinetic rate expressions

$$\begin{aligned}
 i_{\text{Ni},1} &= -F k_{\text{Ni},1} \theta_e C_{\text{Ni(II)}} \exp(-b_{\text{Ni},1} E) \\
 i_{\text{Ni},2} &= -F k_{\text{Ni},2} \theta_{\text{Ni(I)ad}} \exp(-b_{\text{Ni},2} E) \\
 i_{\text{Co},1} &= -F k_{\text{Co},1} \theta_e C_{\text{Co(II)}} \exp(-b_{\text{Co},1} E) \\
 i_{\text{Co},2} &= -F k_{\text{Co},2} \theta_{\text{Co(I)ad}} \exp(-b_{\text{Co},2} E) \\
 i_{\text{Fe},1} &= -F k_{\text{Fe},1} \theta_e C_{\text{Fe(II)}} \exp(-b_{\text{Fe},1} E) \\
 i_{\text{Fe},2} &= -F k_{\text{Fe},2} \theta_{\text{Fe(I)ad}} \exp(-b_{\text{Fe},2} E) \\
 i_{\text{CoNi},1} &= -F k_{\text{CoNi},1} \theta_e^2 C_{\text{Co(II)}} C_{\text{Ni(II)}} \exp(-b_{\text{CoNi},1} E) \\
 i_{\text{CoNi},2} &= -F k_{\text{CoNi},2} \theta_{\text{CoNi(III)ad}} \exp(-b_{\text{CoNi},2} E) \\
 i_{\text{FeNi},1} &= -F k_{\text{FeNi},1} \theta_e^2 C_{\text{Fe(II)}} C_{\text{Ni(II)}} \exp(-b_{\text{FeNi},1} E) \\
 i_{\text{FeNi},2} &= -F k_{\text{FeNi},2} \theta_{\text{FeNi(III)ad}} \exp(-b_{\text{FeNi},2} E) \\
 i_{\text{FeCo},1} &= -F k_{\text{FeCo},1} \theta_e^2 C_{\text{Fe(II)}} C_{\text{Co(II)}} \exp(-b_{\text{FeCo},1} E) \\
 i_{\text{FeCo},2} &= -F k_{\text{FeCo},2} \theta_{\text{FeCo(III)ad}} \exp(-b_{\text{FeCo},2} E)
 \end{aligned}$$

The fraction of available surface sites (θ_e) is determined by taking into account the occupied surface coverage of metal ions.

$$\begin{aligned}
 \theta_e &= 1 - \theta_{\text{Ni(I)ad}} - \theta_{\text{Co(I)ad}} - \theta_{\text{Fe(I)ad}} - \theta_{\text{CoNi(III)ad}} \\
 &\quad - \theta_{\text{FeNi(III)ad}} - \theta_{\text{FeCo(III)ad}} \quad (13)
 \end{aligned}$$

A one dimensional model describes the change of the species concentration in the electrolyte and predicts their surface concentration. The surface concentration in turn dictates the rate of reaction and thus the deposit composition. The domain of the model is from the surface of the electrode to the edge of the mass transport boundary layer, δ .

The boundary layer is determined from the empirical Eisenberg eqn. (1954) for rotating cylinder electrodes

$$\delta = 99.62 \cdot v^{-0.4} D^{0.344} S^{0.356} \quad (14)$$

Where, D is the diffusion coefficient, v the kinematic viscosity and S the rotation rate. The diffusion flux of each species at the cathode surface is related to the electrochemical reaction.

$$D_{\text{Ni(II)}} \frac{dC_{\text{Ni(II)}}}{dx} = -\frac{i_{\text{Ni},1}}{F} \quad (15)$$

$$D_{\text{Co(II)}} \frac{dC_{\text{Co(II)}}}{dx} = -\frac{i_{\text{Co},1}}{F} - \frac{i_{\text{CoNi},1}}{F} \quad (16)$$

$$D_{\text{Fe(II)}} \frac{dC_{\text{Fe(II)}}}{dx} = -\frac{i_{\text{Fe},1}}{F} - \frac{i_{\text{FeNi},1}}{F} - \frac{i_{\text{FeCo},1}}{F} \quad (17)$$

The material balance of each species in the electrolyte is assumed to be at steady state and is governed by the change of the diffusional flux. A

Nernst boundary layer approach is taken assuming that there is no convection or migration within the boundary layer.

$$D_{M(II)} \frac{d^2 C_{M(II)}}{dx^2} = 0 \quad (18)$$

At the end of the diffusion layer the concentration of metal ions equals its bulk concentration

$$C_{M(II)} = C_{M(II)}^b \quad (19)$$

The partial current densities are summed as follows:

$$i_{Ni} = i_{Ni,1} + i_{Ni,2} \quad (20)$$

$$i_{Co} = i_{Co,1} + i_{Co,2} + i_{CoNi,1} + i_{CoNi,2} \quad (21)$$

$$i_{Fe} = i_{Fe,1} + i_{Fe,2} + i_{FeNi,1} + i_{FeNi,2} + i_{FeCo,1} + i_{FeCo,2} \quad (22)$$

and the weight percent composition of the alloy is determined from the partial current densities and their molecular weight M_i .

$$Ni\% = \frac{M_{Ni} i_{Ni}}{M_{Ni} i_{Ni} + M_{Co} i_{Co} + M_{Fe} i_{Fe}} 100 \quad (23)$$

$$Co\% = \frac{M_{Co} i_{Co}}{M_{Ni} i_{Ni} + M_{Co} i_{Co} + M_{Fe} i_{Fe}} 100 \quad (24)$$

$$Fe\% = \frac{M_{Fe} i_{Fe}}{M_{Ni} i_{Ni} + M_{Co} i_{Co} + M_{Fe} i_{Fe}} 100 \quad (25)$$

In our parameter estimation studies, the side reaction was not modelled, since the surface coverage of hydrogen is expected to be negligible and did not affect the final composition of the deposit, thus did not affect parameter estimation problem.

The modelling work was carried out using gPROMS modelling language and embedded into our model-centric framework for integrated simulation, estimation/reconciliation and optimization of systems which provides a complete environment for modelling/analysis of complex systems.

The diffusion flux partial differential equations are solved using IPDAEs which is defined within gPROMS environment. A second order backward finite difference method is used as the numerical method for the distributed system with a number of finite elements of at least three hundred. Boundary layer thickness is used for the axial domain. The DASOLV used as a solver for the solution of mixed sets of differential equations in gPROMS is based on variable time step/variable order Backward Differentiation Formulae (BDF).

Mathematical simulations to describe NiCoFe ternary deposition can be executed using different concentrations of the metals. An example of the capabilities of the model is shown in Figure 1, using an alloy electrolyte concentration of 0.025 M Co(II), 0.2 M Ni(II) and 0.025 M Fe(II), and showing the

metal weight percent compositions that are simulated vs. potentials. Results for the surface coverage of metals and current densities can also be obtained.

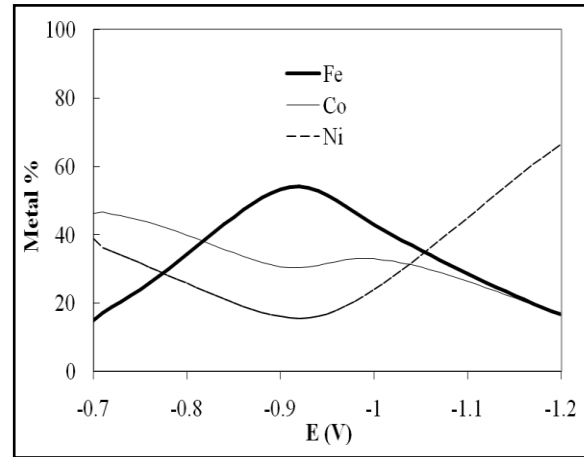


Fig. 1. Simulation of Fe, Co and Ni metal weight percent composition in the alloy deposited at constant potential.

The simulations using gPROMS of NiCoFe ternary alloy deposition and single metal depositions were performed successfully. Validation of the model is further achieved taking advantage of parameter estimation entity, within gPROMS, using experimental data.

3. PARAMETER ESTIMATION

3.1- Problem Definition

In terms of our specific application, a considerable number of parameters, such as diffusion coefficients and kinetic parameters are involved in the model of this complex system under study. Consequently, in our approach, a validation step will be undertaken in conjunction with the execution of parameter estimation studies. We will rely on the maximum likelihood theory and will require a specifically generated set of experimental data. In our formulation we propose the following general mathematical definition for the *estimation problem*:

$$\min_{\theta, \beta, \omega, \gamma} \phi(\tilde{z}(t), z(t), \sigma(t)) \quad (26)$$

$$F(\dot{x}(t), x(t), y(t), u(t), p, \theta, \beta) = 0, t \in [0, t_f] \quad (27)$$

$$I(\dot{x}(0), x(0), y(0), u(0), p, \theta, \beta) = 0 \quad (28)$$

$$\sigma(t) = \sigma(\tilde{z}(t), z(t), \omega, \gamma), t \in [0, t_f] \quad (29)$$

With

$$\theta^{\min} \leq \theta \leq \theta^{\max} \quad (30)$$

$$\beta^{\min} \leq \beta \leq \beta^{\max} \quad (31)$$

$$\omega^{\min} \leq \omega \leq \omega^{\max} \quad (32)$$

$$\gamma^{\min} \leq \gamma \leq \gamma^{\max} \quad (33)$$

where $\varphi(t)$, is a generic objective function. The symbol Z designates our experimental observations and will be considered explicitly in the objective function. The decision variables of the estimation problem are the vectors θ , ω and γ ; note that these parametric variables correspond to different features of the overall mathematical model, for example θ , are our kinetic and diffusion parameters which need to be estimated using the experimental data, ω and γ are associated with the statistical information about the experimental observations (see below). $F(\cdot)$ and $I(\cdot)$ denote, in general, the set of partial differential algebraic equations encompassing the fundamental process model and the set of initial conditions respectively. In these equations x and y denote the differential and algebraic variables respectively, in addition $u(t)$ are the set of input variables. Additionally, the variable $\sigma(t)$, which is *intrinsic* to the objective function, will be an explicit function of the model predictions $z(t)$, the experimental observations $\tilde{z}(t)$, and the parametric variables ω and γ . Depending on the nature of $\varphi(t)$, $\sigma(t)$ can either be the variance of the measurement errors or, simply, the weight of individual variables within this multivariable objective function.

The form of the objective function is determined by a series of implicit and explicit assumptions made while defining a given parameter estimation problem. For instance, maximum likelihood (ML) estimation makes use of the information on the statistical distribution of the observations to derive an expression of the objective function. Assuming, that the *random measurement errors are additive, independent and normally distributed, with zero mean and constant standard deviation, and the independent variables and unknown parameters are non-random*, then the following objective function gives a *maximum likelihood estimator*:

$$\varphi_{ML}(\tilde{z}, z(t), \sigma(t)) = \frac{1}{2} \cdot \left(N \ln(2\pi) + \sum_j \sum_k \left(\ln(\sigma_{j,k}^2) + \left(\frac{\tilde{z}_{j,k} - z_{j,k}}{\sigma_{j,k}} \right)^2 \right) \right) \quad (34)$$

Not only this Equation capture the idea of maximising the likelihood of predicting the experimental set of measurements with great flexibility (or minimising the error between the experimental measurements and predicted values instead), but it also accommodates rigorously for situations where the common assumption of constant standard deviation (homoscedasticity) is violated (this occurs when the observed error variance increases proportionally, for example with the amplitude of the signal from the measuring device). Consider the following variance model

$$\sigma^2 = \omega^2 (\tilde{z}^2 + \delta)^v \quad (35)$$

The convenience of this equation is given by the fact that most conventional statistical variance models can be derived from it: *homoscedastic (constant)*

variance, $\gamma = 0$; *constant relative* variance, $\gamma = 1$; and *heteroscedastic* variance $0 < \gamma < 1$. It is important, at this point, to mention that the estimators and statistical variance models presented above are currently supported by the model-centric framework for integrated simulation, estimation/reconciliation and optimization of systems (described before) and will be used extensively in our approach.

For this study a constant variance is used for experimental data measurements where: $\sigma^2 = \omega^2$. Experimental measurement variances are found for current densities. Potential is used as adjusted control variable which in this case is time invariant since we consider steady state conditions.

3.2- Parameter Estimation Study for Single Metal and Alloy Deposition

Sensitivity analysis is performed prior to the parameter estimation in order to determine which parameters have greatest effect on the model predictions. Insensitive parameters can be disregarded from the parameter estimation problem, since a wide range of values can be used in their place. For the case of NiCoFe simulation, a parameter can be varied maintaining the rest constant, and monitoring the change of the weight percent composition of the metals and total current. The rate constants of nickel, cobalt and iron that participate in the single, elemental two-step mechanism ($M_i(II) + e \rightarrow M_{ads,i}(I)$; $M_{ads,i}(I) + e \rightarrow M(s)$) are the most sensitive parameters. The parameters of the mixed metal intermediate equations, ($M_i(II) + M_j(II) + e \rightarrow M_{ads,i,j}(III)$; $M_{ads,i,j}(III) + e \rightarrow M_i(s) + M_j(II)$) are the least sensitive.

Parameter estimations are performed using single metal deposition and alloy depositions. For single metal deposition estimations, two simulations are performed for concentration of cobalt of 0.025 M and 0.1 M and another two simulations for concentrations of iron of 0.025 M and 0.1 M. To achieve 100% weight composition of cobalt or iron, the other metal concentrations are set to zero. For the alloy an electrolyte concentration consisting of 0.025 M cobalt, 0.2 M nickel and 0.025 M iron is used. Experimental data consisting of current densities are used to fit the parameters. The parameters which are estimated for the single metal deposition are rate constant $k_{Co,1}$, $k_{Co,2}$, k_{Fe1} , k_{Fe2} and Tafel slopes b_{Co1} , b_{Co2} , b_{Fe1} , b_{Fe2} . For the NiCoFe alloy the parameters estimated are the rate constants $k_{Ni,1}$, $k_{Ni,2}$, $k_{CoNi,1}$, $k_{CoNi,2}$ and the Tafel slopes $b_{Ni,1}$, $b_{Ni,2}$, $b_{CoNi,1}$, $b_{CoNi,2}$. The same procedure is performed for single metal and alloy parameter estimations. Table 2 shows the final optimum estimates obtained for the four single metal depositions.

Table 2 NLP optimization optimal results for single metal deposition

Rate constants		Inverse Tafel Slopes	
0.025M			
k _{Co1}	9.61E-10 <i>cm s⁻¹</i>	b _{Co1}	13.58 V ⁻¹
k _{Co2}	6.76E-09 <i>mol cm⁻² s⁻¹</i>	b _{Co2}	13.58 V ⁻¹
k _{Fe1}	1.18E-25 <i>cm s⁻¹</i>	b _{Fe1}	45.28 V ⁻¹
k _{Fe2}	1.00E-25 <i>mol cm⁻² s⁻¹</i>	b _{Fe2}	45.28 V ⁻¹
0.01 M			
k _{Co1}	1.23E-12 <i>cm s⁻¹</i>	b _{Co1}	20.32 V ⁻¹
k _{Co2}	3.98E-09 <i>mol cm⁻² s⁻¹</i>	b _{Co2}	20.32 V ⁻¹
k _{Fe1}	2.64E-28 <i>cm s⁻¹</i>	b _{Fe1}	57.48 V ⁻¹
k _{Fe2}	1.28E-16 <i>mol cm⁻² s⁻¹</i>	b _{Fe2}	57.48 V ⁻¹

Using these optimum parameters, simulations were performed, and compared to experimental data. Figure 2 shows the partial current density of Co at two different electrolyte concentration data. Figure 3 reports the partial current density of Fe at two different electrolyte concentration data.

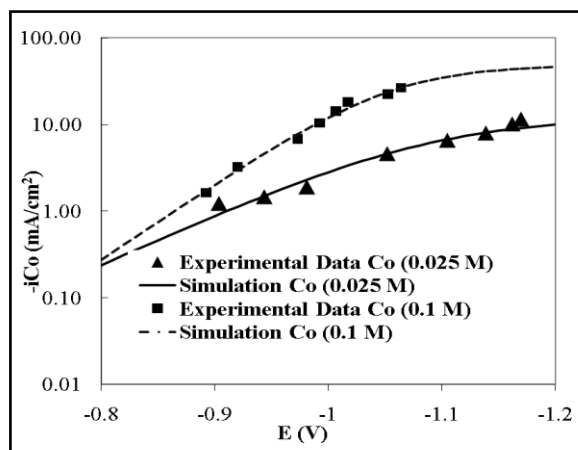


Fig. 2. Partial Co current density simulation and experimental results comparison; bulk Co(II) concentration is 0.025M and 0.1M

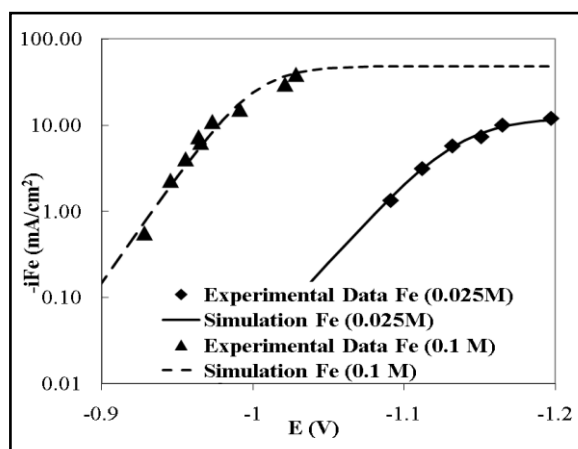


Fig. 3. Partial Fe current density simulation and experimental results comparison; bulk Fe(II) concentration is 0.025M and 0.1M

Table 3, shows the final optimum estimates obtained for the alloy.

Table 3 NLP optimization optimal results for alloy Ni(0.2M)Co(0.025M)Fe(0.025M).

Rate constants		Inverse Tafel Slopes	
k_{Ni1}	$2.07E-11 \text{ cm s}^{-1}$	b_{Ni1}	18.2 V^{-1}
k_{Ni2}	$5.03E-12 \text{ mol cm}^{-2} \text{ s}^{-1}$	b_{Ni2}	8.8 V^{-1}
$k_{CoNi,1}$	$6.17E-13 \text{ cm}^4 \text{ mol}^{-1} \text{ s}^{-1}$	$b_{CoNi,1}$	18.7 V^{-1}
$k_{CoNi,2}$	$8.85E-13 \text{ mol cm}^{-2} \text{ s}^{-1}$	$b_{CoNi,2}$	18.7 V^{-1}

Figure 4 shows the simulation results of estimated parameters for nickel current density of the Alloy electrolyte containing 0.025 M Co(II), 0.2 M Ni(II) and 0.025 M Fe(II).

The graphical representations indicate an excellent prediction of the model, when compared to experimental data, for both single cobalt and iron deposition and nickel deposition during NiCoFe alloy fabrication.

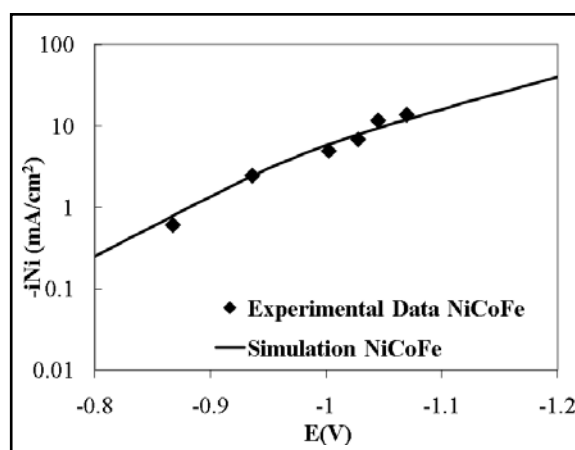


Fig. 4. Partial Ni current density simulation and experimental results comparison of the alloy.

Further statistical analysis performed during the parameter estimation studies shows that the residuals are within the statistical limits (Chi-squared values) proving the goodness of the fit.

3.3. Confidence Intervals and Regions

Confidence intervals provide an indication of how far the estimate is expected from its true value (Beck and Arnold, 1977). Additionally, when two or more parameters are estimated in conjunction, confidence regions can be used to evaluate the correlation between parameters and their variation. This analysis and characterization steps are essential, especially when parameter uncertainty does exist and for model validation.

While confidence intervals are specified for individual parameters as an upper and lower limit, confidence regions are given as hyper-ellipsoids when errors are assumed additive, zero mean and, normal. In addition, the covariance matrix should be known.

$$(\mathbf{b} - \boldsymbol{\beta})^T \mathbf{P}^{-1} (\mathbf{b} - \boldsymbol{\beta}) = r^2 \quad (36)$$

Where $\mathbf{P} = \sigma^2(\mathbf{X}^T \mathbf{V}^{-1} \mathbf{X})^{-1}$ and r^2 gives an idea of the confidence on the intervals. The hyper-ellipsoid defined as before is centred on the estimated values of the parameters.

Figures 5 and 6 shows the resulting 95% confidence ellipsoids and confidence intervals given by gPROMS for rate constants and inverse Tafel slopes. Figure 5 results are from the estimated parameters for single metal deposition of Co(0.1 M) where the high inclination of the ellipsoid indicates that, in fact, there is a strong correlation between the rate constants and the inverse Tafel slope. Figure 6 shows the confidence ellipsoid for the alloy results, where as expected there is less correlation and small uncertainty between the two inverse Tafel slopes.

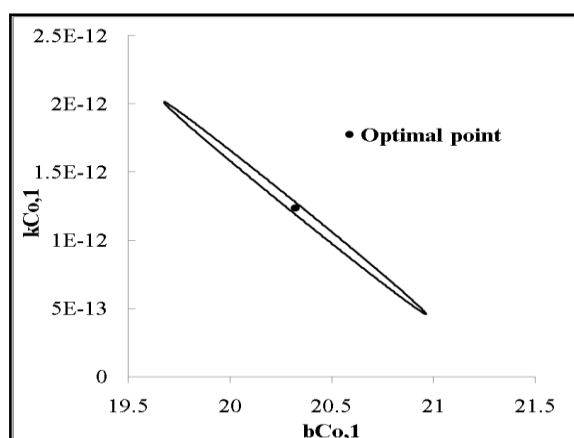


Fig. 5. Confidence intervals and ellipsoid for rate constant $k_{Co,1}$ and Tafel slope $b_{Co,1}$

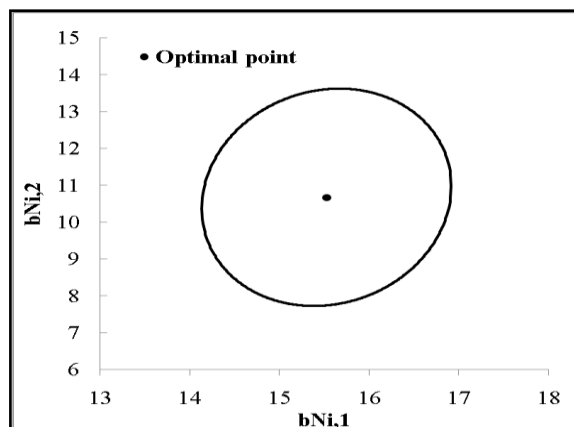


Fig. 6. Confidence intervals and ellipsoid for Tafel slopes $b_{Ni,2}$ and $b_{Ni,1}$.

4. CONCLUSION

Taking advantage of the functionalities of the capabilities of modern modelling, simulation and optimization environments, this paper describes the initial steps towards the development of a model based framework for ternary alloy deposition processes.

Since the model includes a considerable number of unknown parameters, such as rate constants, Tafel slopes and diffusion coefficients, parameter

estimation techniques using the maximum likelihood theory were tested and found to be successful for our studies. Statistical analysis techniques are also found useful for error analysis and uncertainty characterization.

Once final validated models are obtained they can be used for further manufacturing of interesting deposition schemes. Not only is this procedure available for Zhuang and Podlaha's (2003) model but it can be used for other electrodeposition systems.

Although, the results presented here are for steady-state conditions, they pave the way for further expansions of the model to include non-steady state behaviour. The model then could be used to predict concentration gradients, particularly important for the nanometric size multilayers. The use of experimental design techniques to further reduce the confidence regions are also planned and current work is underway in this direction.

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