Mathematical Modeling of Electrodeposition

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INTRODUCTION

Mathematical modeling of electrodeposition is a process that yields information about the plating system of interest. The process consists of first determining the composition of the plating bath of interest by using thermodynamic information. The second step consists of specifying or determining the electrochemical reactions that occur on the electrodes and the chemical reactions that occur on the electrodes and in the bath. The third step consists of specifying the governing equations (material balance equations) for the concentrations of the species in the bath. Next, reaction rate expressions must be specified for the electrochemical reactions that occur at the electrodes. Finally, the geometry of the plating bath must be specified. Since the material balance equations for species in the bath depends on fluid flow, the flow conditions in the tank must be specified. In some cases the material balance equations for the concentration of species in the bath and the momentum balance equations for the fluid flow must be solved simultaneously because the electrodeposition process can give rise to density changes at the surface of the working electrode. These density changes cause the hydrodynamics in the bath to change. Sparging and stirring of the bath also effect the flow conditions at the work piece. The hydrodynamic effects are sometimes lumped together and described by a hydrodynamic boundary layer. Similarly, the mass transfer effects in plating baths are often lumped together and represented by a diffusion layer. These concepts of boundary layers and diffusion layers have been used to simplify the mathematical modeling of electrodeposition.

Our work[1] on the mathematical modeling of electrodeposition began with a study of electrodeposition of copper from an acid chloride bath containing iron. We used the

diffusion layer thickness on a rotating disc electrode to normalize the distance from the disk. We included ionic species complexed with chloride ions, multiple electrode reactions, and a homogeneous reaction between the complexed ferric and cuprous ions in the diffusion layer. This gave rise to a reaction plane in the diffusion layer. We also included in the model the effect of ionic migration in the solution, and a reaction rate expression for the electrochemical reactions that includes the relative activity of iron in the deposit but not copper, since it was assumed that solid copper would be the dominant species in the deposit. We were able to predict the conditions under which very little iron was deposited. This study was limited to the center of the disk only. To determine the effect of position on the disk, we[2] solved for the current density distribution across the disk surface for copper deposition from an acid bath on a rotating disk electrode.

Next, we extended[3] our work on mathematical modeling of alloy to remove the restriction that the deposit was mostly copper with a small amount of iron. We did this by expanding the dependence of the exchange current density and the open-circuit potential for each electrodeposition reaction to include the composition of each species in the alloy (see equation 27 of reference 3). This new electrochemical reaction rate expression (*i.e.*, extended Butler-Volmer equation) enabled us to predict the composition of the alloy as a function of the composition of the plating bath, system parameters, and potential driving force for the reaction.

The next step in the development of our framework for mathematical modeling of electrodeposition was to extend our modeling work to include galvanostatic pulse plating,[4] and the thickness of the deposit. The electrodeposition of a NiCr alloy by pulse plating was used to illustrate the utility of our simulation model. According to the

predictions of the model, a periodic steady state is established after about four pulse cycles. This simulation was used to show quantitatively that hydrogen evolution can be reduced by using pulse plating instead of direct current plating.

Our pulse plating modeling[4] also included the effect of ionic migration, which was shown to be important near the surface of the working electrode. The predicted concentration of Cr^{2+} at the electrode surface depends on whether or not the effect of ionic migration is included in the simulation. In many cases the concentration of Cr^{2+} is predicted to be lower at the surface when the effect of ionic migration is ignored. This is due to the unrealistically large predicted overpotential causing Cr^{2+} to be reduced to Cr.

Our work on pulse plating of alloys was preceded by work published by Verbrugge and Tobias.[5,6] Unfortunately, they did not include the effect of ionic migration in their transport equation, but they did include the effect of short-range, nearest neighbor interaction in their CdTe deposit. This solid state interaction is important and should be included in models for the electrodeposition of alloys that do not form ideal, solid state alloys such as CdTe. We have also published other articles[7-11] on mathematical modeling of electrodeposition that may be of interest to the readers.

CURRENT DENISITY DISTRIBUTIONS

Prediction of current density distributions is useful in designing the electrode configurations for plating baths. Earlier[12-14] we presented methods for predicting secondary current density distributions. These methods are based on the finite element method. Unfortunately, the computation time for the finite element method has in the past been too long to be useful for rapid prototyping of electrode configurations.

However, a relatively new software package (FEMLAB[15]) based on the finite element technique and MATLAB[16] is now available for two dimensional (two spatial coordinates) problems and current density distributions for a variety of geometrical configurations, operating conditions, and kinetic parameters. For example, figure 1 presents the potential distribution for a Hull cell with the physical conditions and operating conditions given in Table 1. Figure 2 presents the potential distribution for a cylindrical anode in the center of the bearing for the same operating conditions.   Figure 3 presents the potential distribution with superimposed anodes for the current density distributions for the current density versus overpotential relationship that exists for a composite of electrochemical reactions which includes the current density due to a mass transfer limited reactant (see equation 20 of ref. 17).

FEMLAB software can also be used to predict the partial current density associated with a binary allow deposition process for hypothetical components A and B. For illustration purposes, assume that it is reasonable to describe the deposition of these two species (A and B) according to the following expressions.

$$i_A = i_{0,A}\left(\exp(0.5\eta) - \exp(-0.5\eta)\right) \tag{1}$$

and

$$i_B = i_{0,B}\left(\exp(0.5(\eta - 0.2)) - \exp(-0.5(\eta - 0.2))\right) \tag{2}$$

where

$$\eta = \phi_c - \phi \tag{3}$$

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Comparing equations 1 and 2 reveals that the potential difference between the open-circuit potentials of A and B is 0.2. The total current density is equal to the sum of the potential current densities (*i.e.*, i_A and i_B) and must equal the gradient of the potential in the solution at the electrode surface:

$$\frac{\partial \phi}{\partial x} n_x + \frac{\partial \phi}{\partial y} n_y = \frac{1}{\kappa} \left[i_A + i_B \right] \tag{4}$$

The current density distribution for this binary alloy deposition case for the Hull cell is shown in figure 4 and for the bearing case in figure 6. It should be noted that FEMLAB can be used easily for a nonlinear kinetic expressions such as the Butler-Volmer equation.

Recently,[18] Subramanian and White presented a semianalytical method for predicting current density distributions for two dimensional systems. Their method is very useful for rapid prototyping because the method utilizes a solution procedure that provides a general solution for a given geometric configuration. The solution obtained can be used to determine easily the current density distribution for different operating conditions of the bath (different set potentials of the electrode, e.g.), different boundary conditions (linear and nonlinear), different geometries in the y direction. This capability of the semianalytical method is also useful for doing rapid nonlinear parameter estimation for determining the kinetic parameters (exchange current density, e.g.) given the configuration of the electrodes, operating conditions, and current density distributions data. Recently, we extended the semianalytical method to provide a means of predicting the thickness of the deposit as a function of time for a given system. Figure 6 presents the growing metal deposit in a working electrode predicted using our semianalytical method facing an anode (working electrode is half the size of anode) embedded with insulators.[19]

SUMMARY

Our mathematical modeling of electrodeposition has been reviewed briefly. We began in 1977 (reference 1) by considering a steady-state one spatial coordinate problem for copper deposition in the presence of iron. We presented later a more complete method for predicting deposited alloy composition for both steady cases[3] and for galvanostatic pulse plating.[4] Next we reviewed the methods we have used in the past to predict current density distributions for single reactant cases and showed here how to extend current density predictions to include binary alloy deposition. We also mentioned our semianalytical technique[18] for determining current density distributions, which we have recently extended to include the capability of predicting the deposit thickness as a function of time. In conclusion, we hope that our contributions and those of others workers in the area of mathematical modeling of electrodeposition will be used to improve the processes of electroplating and surface finishing. It should be possible now to test many plating ideas on a computer (through mathematical modeling) before investing time in chemicals, electrodes and tanks.

Figure Captions

1. Predicted potential distribution in a Hull cell during alloy plating.

2. Potential distribution in a bearing cell during alloy deposition.

3. Potential distribution with superimposed anodes for composite electrochemical reactions.

4. Predicted partial current densities in a Hull cell.

5. Predicted partial current densities along the cylindrical bearing anode.

6. Growing metal deposit predicted by semianalytical method.

Nomenclature

i   current density (dimensionless)

i_0 exchange current density (dimensionless)

ϕ dimensionless potential

η overpotential (dimensionless)

κ conductivity (dimensionless)

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BOUNDARY CONDITIONS	
Insulators	$$\frac{\partial \phi}{\partial n} = 0$$
Anode	$$\phi = 1$$
Cathode	$$i = i_{0,A}\left(\exp(0.5\eta) - \exp(-0.5\eta)\right)$$ $$+ i_{0,B}\left(\exp(0.5(\eta - 0.2)) - \exp(-0.5(\eta - 0.2))\right)$$

Boundary Conditions
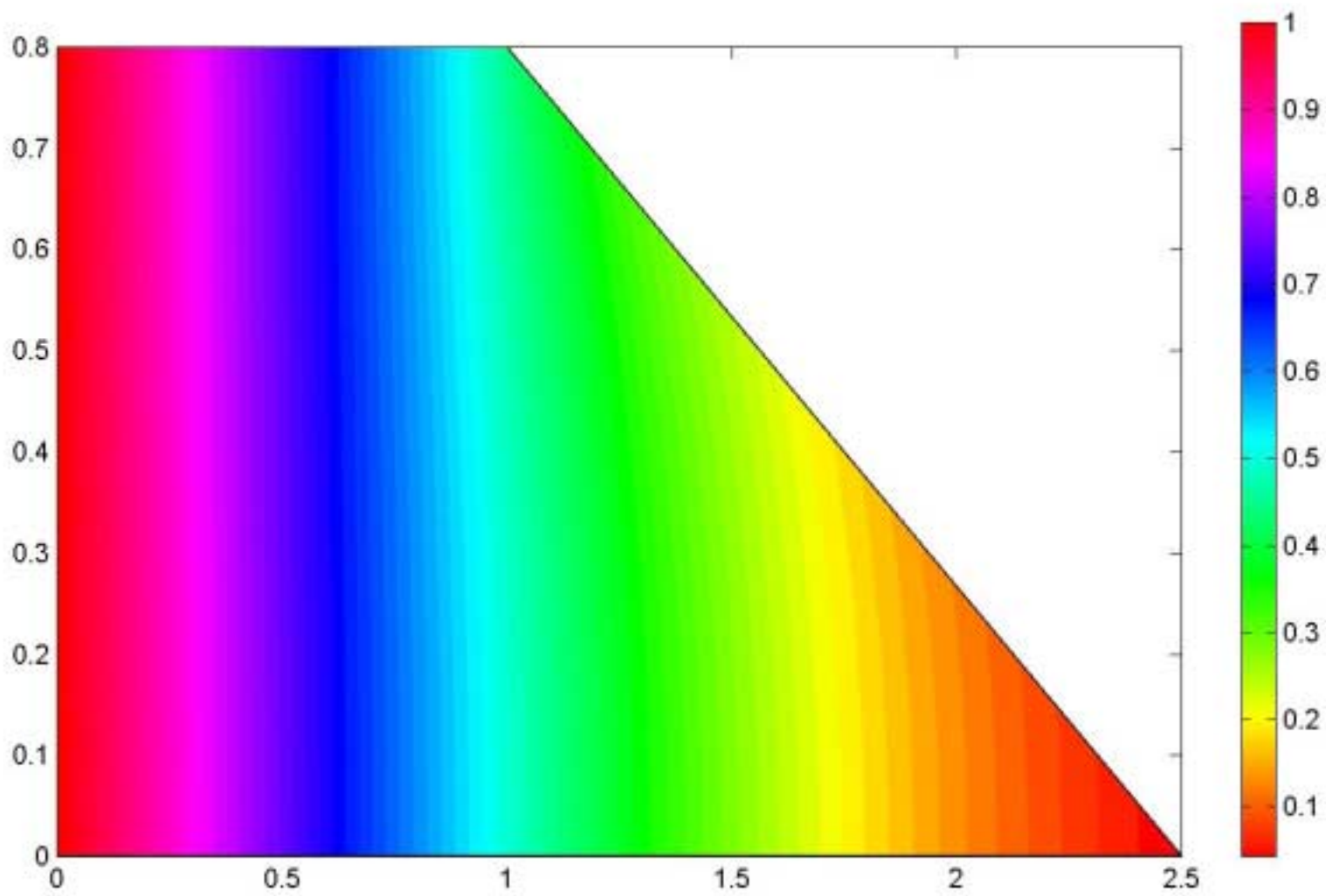
Figure 1: Predicted potential distribution in a Hull cell during alloy plating.
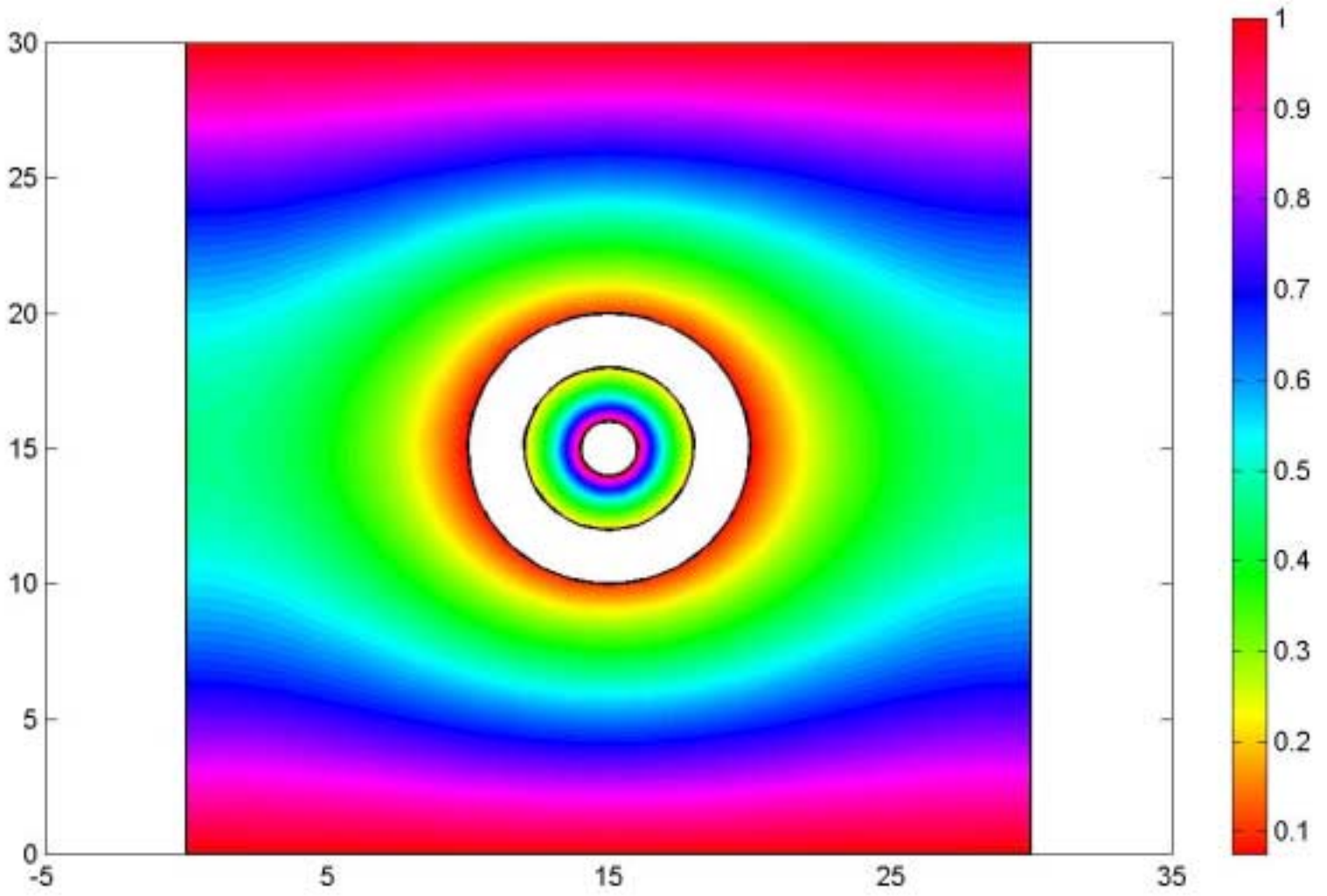
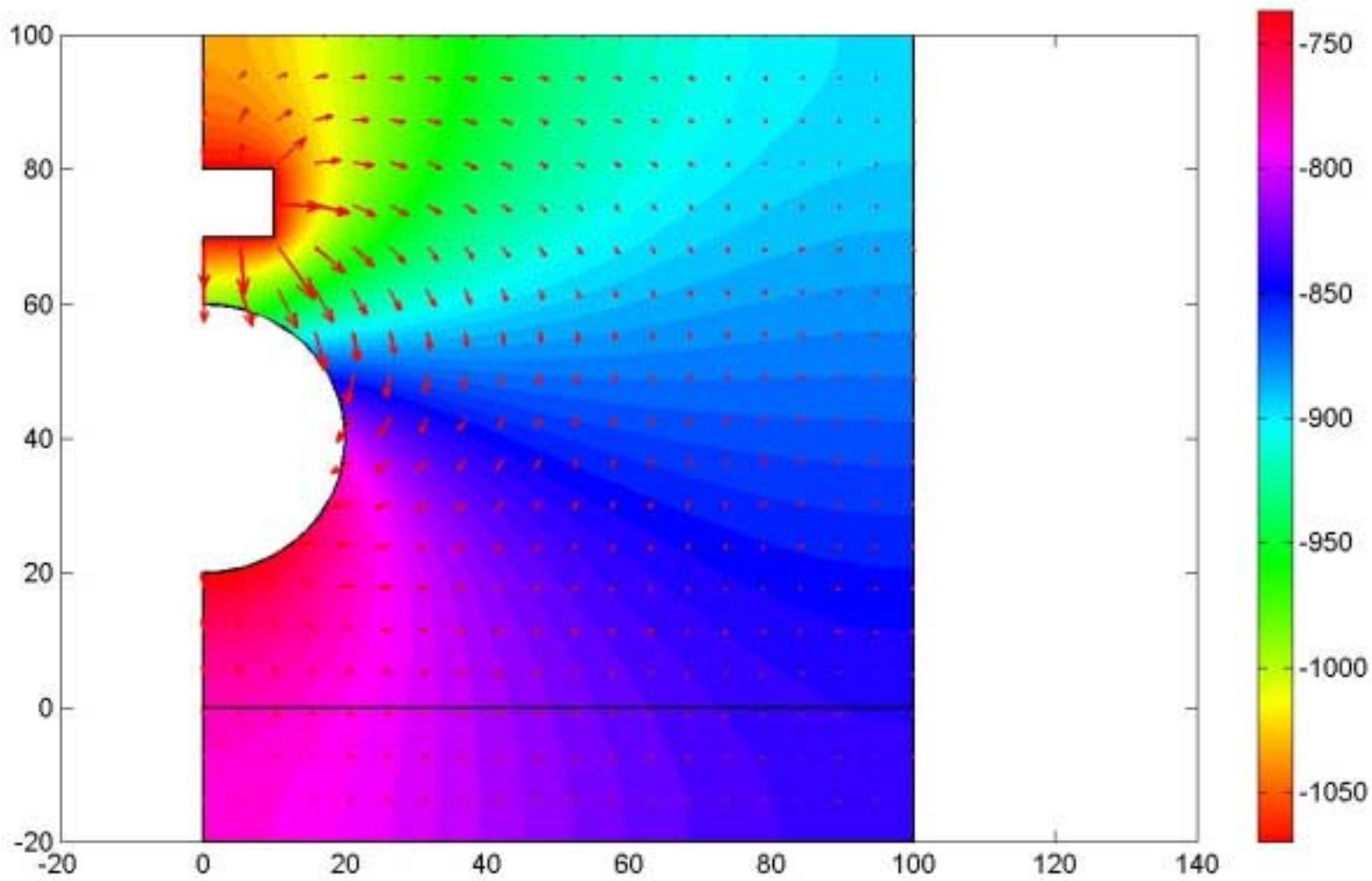Figure 2: Potential distribution in a bearing cell during alloy deposition

Figure 3: Potential distribution with superimposed anodes for composite electrochemical reactions.
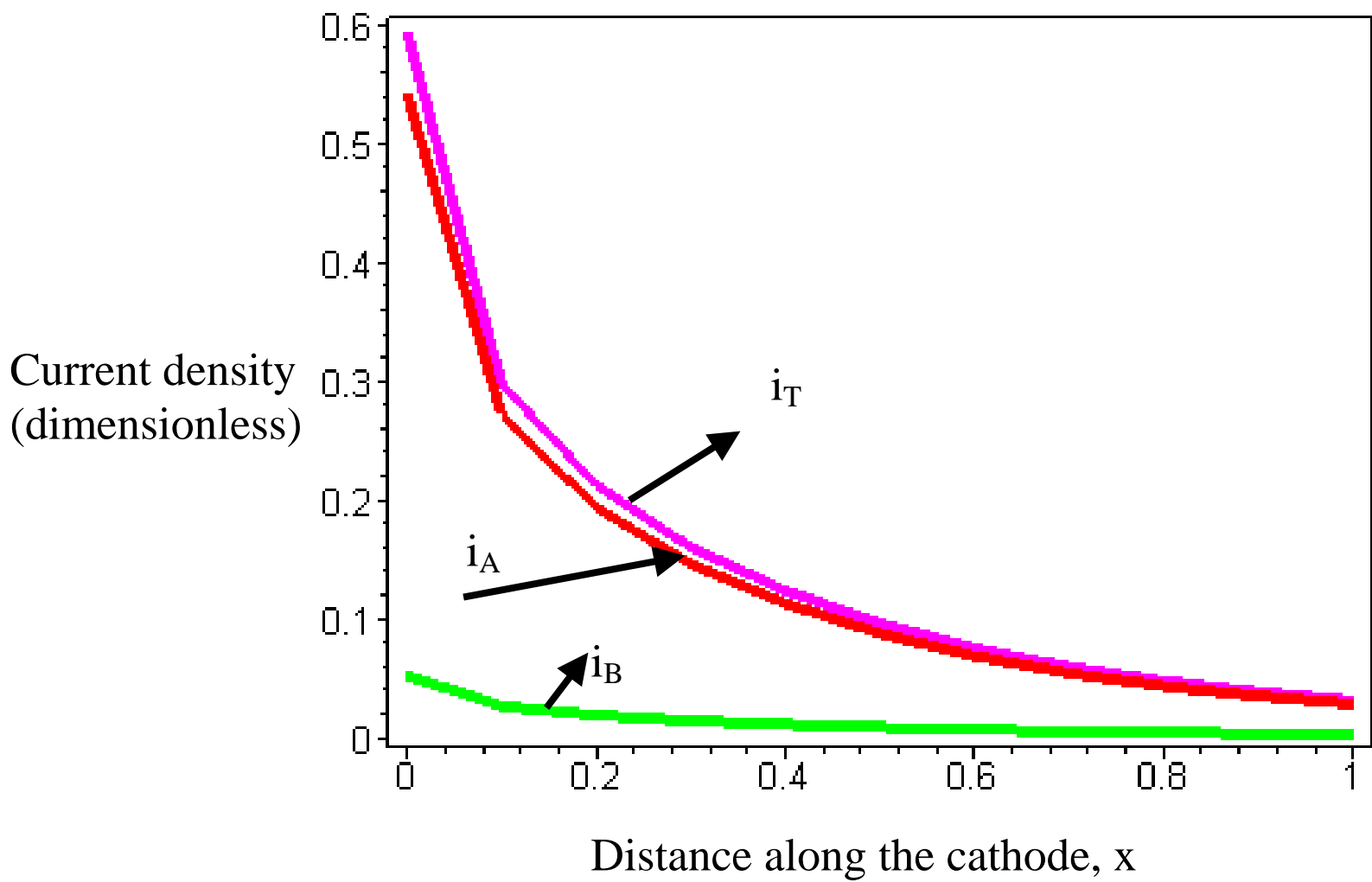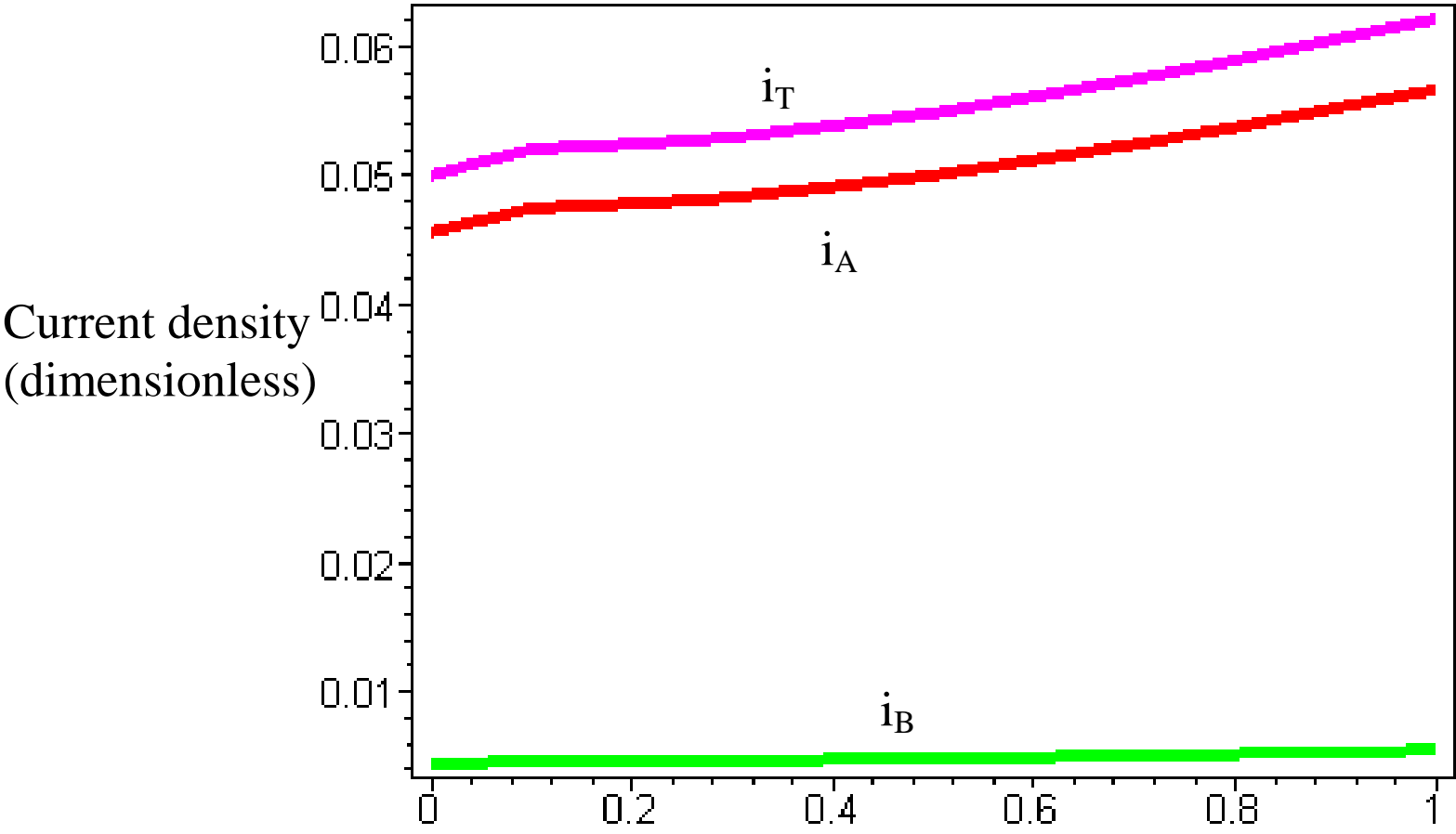
Figure 4: Predicted partial current densities in a Hull cell.

Distance along the cathode, 0 - 1 corresponds to 0 to 90°.

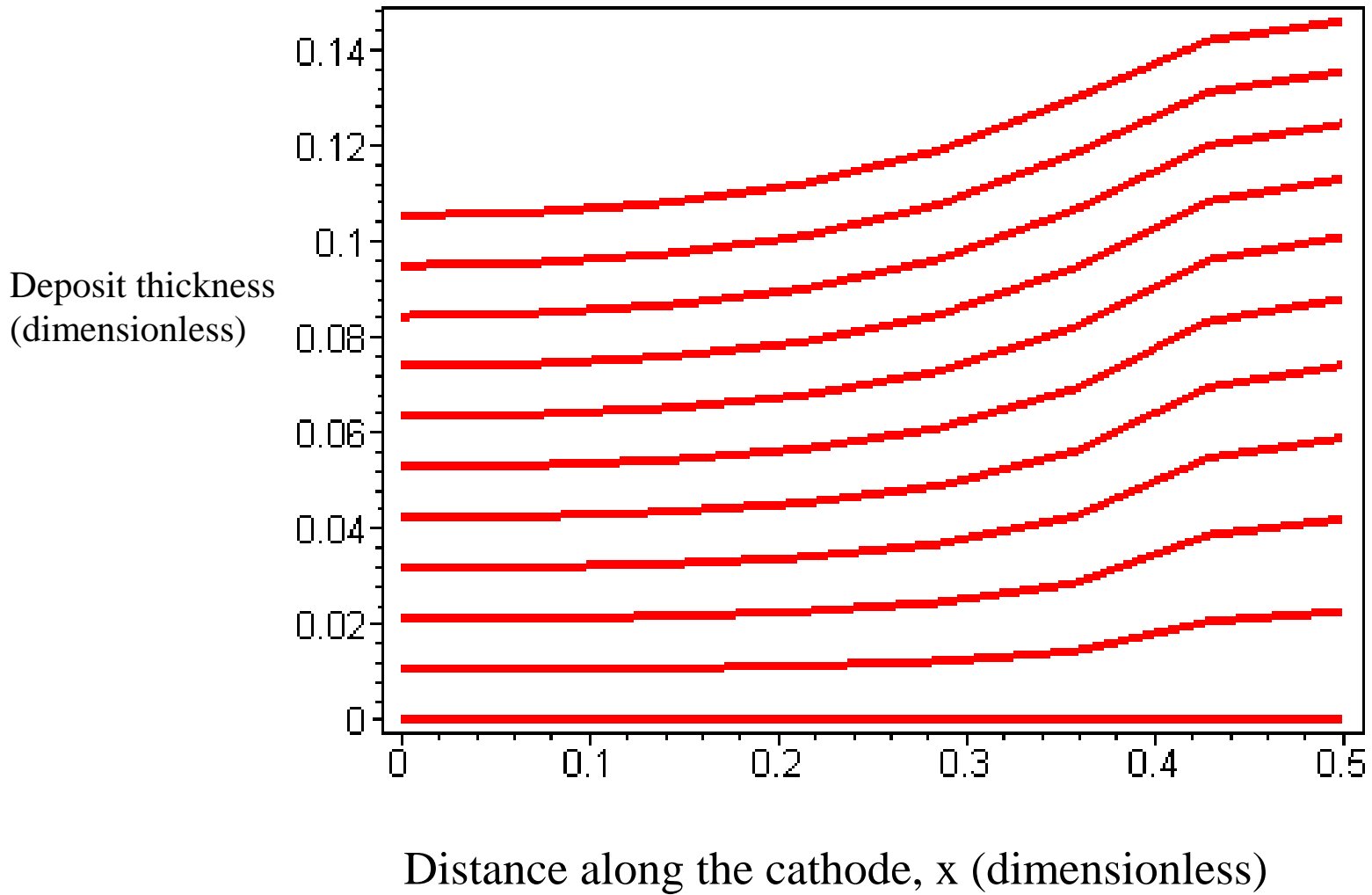Figure 5: Predicted partial current densities along the cylindrical bearing anode

Figure 6: Growing metal deposit predicted by semianalytical method