

CFD Approach to Investigating Electrochemical Hydrodynamics and Mass Transport in a Copper Electrodeposition Process Using a Rotating Disk Electrode

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Three-dimensional electrochemical mass transport and concentration gradient distributions on a rotating disk electrode (RDE) were simulated in a copper electrodeposition system. This approach is based on solving the electrochemical reaction kinetics under diffusion-controlled mass transport using the Computational Fluid Dynamics (CFD) coupling technique. Diffusive boundary layer thicknesses were locally derived in association with the concentration gradient under a galvanostatic electrolysis. The simulated average diffusion boundary layer thicknesses over the electrode surface were well matched with those from the Levich correlation.

Keywords: Rotating Disk Electrode, Copper Electrodeposition, Electrochemical Hydrodynamics, Mass Transport, CFD

1. INTRODUCTION

An electrochemical hydrodynamic technique using a rotating disk electrode (RDE), as an electroanalytical tool, has been widely used in experimental electrochemistry for the investigation of electrode reaction kinetics under controlled mass transport conditions [1-3]. The RDE in laboratory-scale reactors provides well-defined electrolyte hydrodynamics and supports various fundamental research on material electrodeposition characteristics.

The RDE system has found a wide variety of applications in investigating the designs of commercial-scaled systems. Mass transport at a rotating disk provides an experimental reproducibility to easily control the rate at which an electroactive species arrives at the electrode surface. In this cell configuration, the flux of the electrolyte solution towards the disk surface does not vary with the radial distance from the axis of rotation. This phenomenon enabled Levich [1] to use a relatively simple one-dimensional (1-D) correlation to describe the mass transport for the RDE.

Understanding the uniformity of the tertiary current distributed on the electrode is a key factor in the application of the RDE system. A three-dimensional (3-D) electrochemical study can reflect the effects of the cell structure and provide a more flexible means for a rigorous analysis of an electrochemical system. A few studies have presented the mass transport and concentration profiles on the working electrode of the RDE using CFD (Computational Fluid Dynamics) based 2 or 3-D tertiary current simulation [4-6]. The 3-D electrochemical hydrodynamics model led us to investigate a more realistic uniformity of the deposition rate over the working electrode surface.

In this study, a CFD modeling approach was used to investigate the electrochemical mass transport behaviors in an RDE system. Simulated thickness distributions of the concentration boundary layer on the rotating electrode were compared with a well-known diffusion-limited correlation [2] for the RDE in a copper electrodeposition system.

2. THEORY

2.1. Mass Transport Correlation

A RDE is a polished disc imbedded in a rod of insulating material. This structure is rotated about an axis perpendicular to the surface of the disc electrode. The electrode is attached to a motor and rotated at a certain frequency. This rotation movement leads to a well-defined solution of the flow pattern shown in Fig. 1.

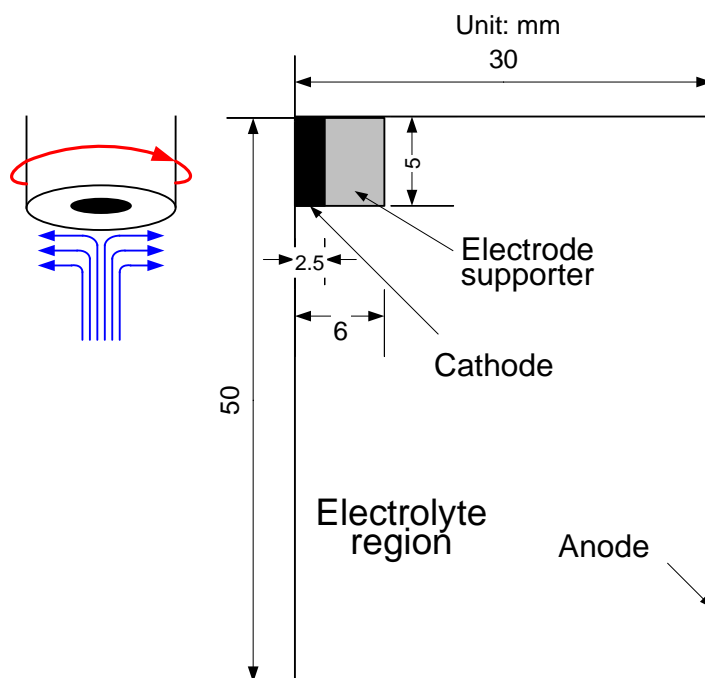


Figure 1. RDE and schematics of the solution flow towards its surface (left) and flow of the solution near its surface (right). Black area shows the conductive electrode material; grey area is insulation.

Because the mass transport at a rotating disk is known to be uniform, this condition has enabled us to use a relatively simple 1-D mathematical correlation for the electrode reaction kinetics. Under a limiting current condition, Levich [2] deduced a 1-D expression relating the diffusion boundary layer thickness (δ_{diff} , cm) with experimental variables such as the diffusion coefficient (D_i , cm²/s), kinematic viscosity (ν , cm²/s) and the rotation speed of the electrode (ω , rad/s) as follows:

$$\delta_{diff} = 1.61 \times D_i^{1/3} \times \nu^{1/6} \times \omega^{-1/2} \quad (1)$$

In this correlated expression, limiting current increases linearly with the square root of the rotation rate.

The RDE is constructed from a disk of the electrode material imbedded in a rod of insulating material. Various dimensions and electrode materials of the RDE are commercially available. The RDE is used as a working electrode surrounded by an insulating sheath with a substantially larger diameter. The diameter ratio of the electrode to a supporting cylinder and cell configuration could also affect the electrochemical hydrodynamics.

2.2. CFD model

Charge transfer is driven by applying current to the cell, and then, the electrochemical reactant is consumed on the cathode. The mass transfer rate (j_w) per unit area from the bulk electrolyte to the rotating electrode surface is proportional to the concentration gradient and may be related with the mass transfer coefficient (k_i) and is described as follows:

$$j_w = -D_i \left. \frac{\partial C}{\partial r} \right|_w = -k_i (C_{bulk} - C_w) \quad (2)$$

, where C_{bulk} and C_w are the concentration of the electroactive species in the bulk electrolyte and at the electrode surface, respectively. The first term indicates that the concentration gradient ($\left. \frac{\partial C}{\partial r} \right|_w$) in the radial direction (normal to the electrode wall) can be evaluated at the electrode surface in the CFD platform.

3-D CFD simulation are used to solve the local concentration profiles near the electrode surface with the electrolyte turbulence model. The local diffusion boundary layer thickness (δ_x) can be obtained from the precedent mass flux equation as follows:

$$\delta_x = \frac{C_{bulk} - C_w}{\left. \frac{\partial C}{\partial r} \right|_w} \quad (3)$$

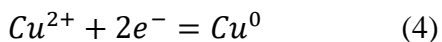
, where x is the space coordinate. This equation is used as an additional variable that spatially figures out the local thicknesses of the diffusion boundary layer on the cathode [7]. Those user-defined expression variables can be obtained by solving the species transport equation in the CFD software.

The cell geometries shown in Fig.1 use a dimension of the commercial RDE system [8]. A 3-D model uses a 90 degree segment of the cylindrical RDE cell system due to an assumed rotational symmetry within an electrolyte fluid domain using the Ansys-CFX software [9].

3. RESULTS AND DISCUSSION

This study for a CFD benchmark simulation used the same electrochemical properties of a copper electrodeposition system from an acid sulphate electrolyte containing 50 mM CuSO₄ and 0.5M Na₂SO₄

at 20°C in the RDE cell as described in detail in the literature [10]. In this system, the electrodeposition of copper involves the reduction of Cu^{2+} ions from the electrolyte at the cathode as follows:



When the electrode in a RDE system is rotated, it pumps fresh solution from the bulk of the electrolyte onto the cathodic disk surface. Fig. 2 shows the typical fluid flow pattern of the RDE system. The colored flow streamlines and velocity vectors were tracked according to the various rotation speeds. When the electrode is rotated, it pumps fresh solution from the bulk of the electrolyte onto the cathodic disk surface. Accordingly, there is a thin layer in which only diffusion takes place with no convection near the rotating cathode surface. The electrode reaction corresponds to the diffusion of the electroactive ion towards the electrode surface.

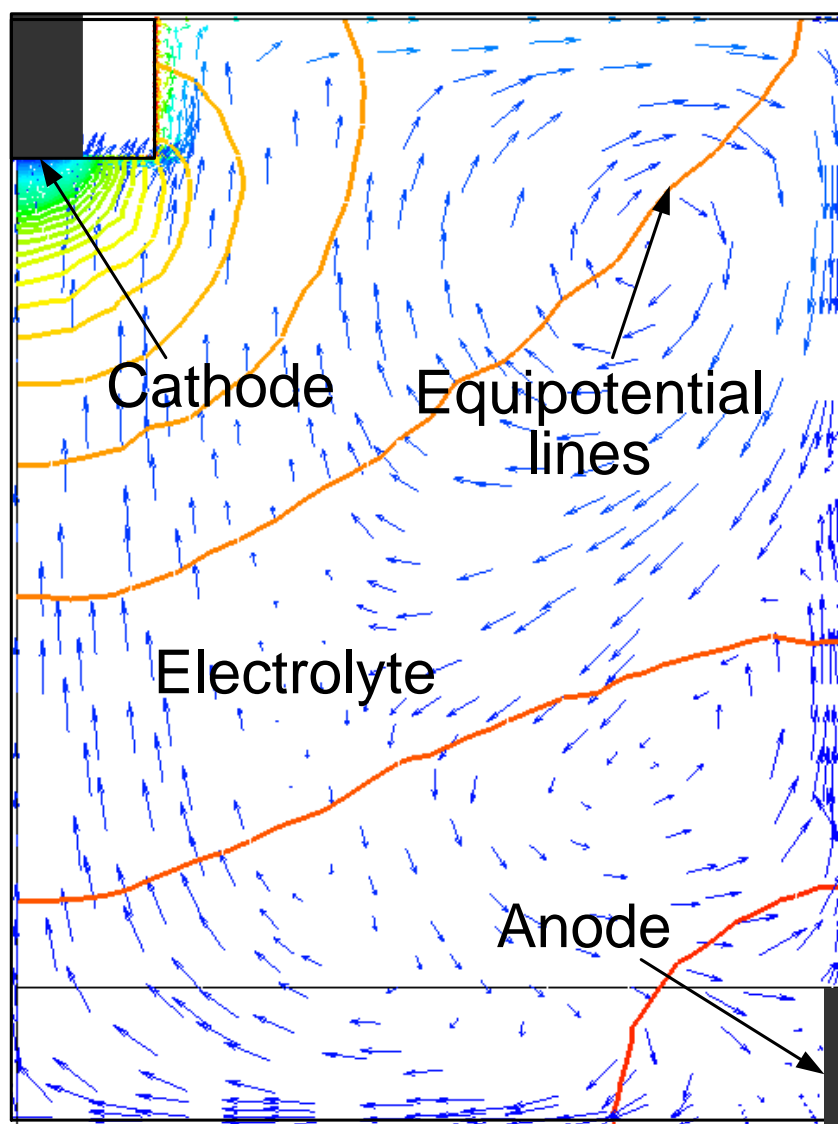


Figure 2. Equipotential lines and velocity vectors of the electrolyte flow towards the RDE surface in the copper electrodeposition system.

While Cu^{2+} ions are reduced and consumed in the cathode under the galvanostatic electrolysis condition, the ion concentration decreases as it nears the cathode surface. The concentration profiles near the electrode surface were obtained using an applied current density of 20 mA/cm^2 by varying the rotation speed of the RDE as seen in Fig.3. The concentration profiles are caused by depletion of reactant ions at the cathode surface from the bulk electrolyte. The 1-D local concentrations were obtained by taking an average value at the nodal distance away from the cathode surface as expressed in Eq.(5). The average concentration (c_{avg}) can be calculated by the integral constraint of the local values over the electrode surface area as follows:

$$c_{avg} = \frac{\int_A c_x ds}{A} \quad (5)$$

, where c_x is the local concentration, A is the electrode surface area (cm^2), and s is the surface element for a numerical integration. In the CFD platform, this estimation was taken using the locator-based function, which is expressed as the area-weighted average on the electrode surface.

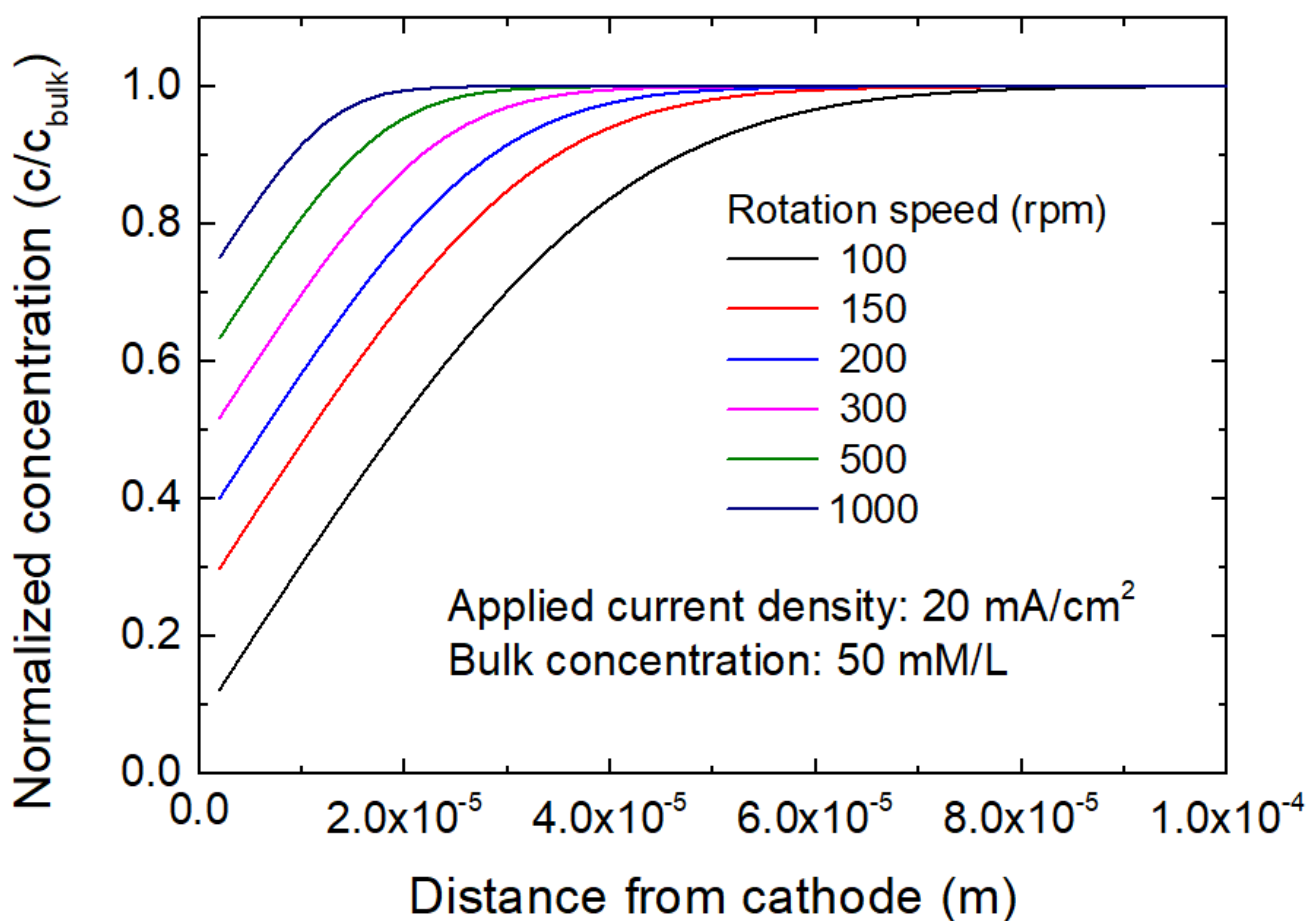


Figure 3. Concentration profiles at the distance away from the RDE surface in the copper electrodeposition system.

The concentrations at the cathode surface were less decreased when a higher rotation speed was applied. The rate of mass transfer is proportional to the concentration gradient at the electrode surface as shown in Eq.(2). Although the electrochemical conditions were different, the 1-D concentration

profiles with electrode rotation speed showed a similar behaviour to that of Tong' study [4]. The diffusion boundary layer thickness is locally estimated from the concentration gradient as expressed in Eq.(3). The diffusion boundary layer thicknesses at the electrode surface were computationally approximated from the local concentration gradients based on the 3-D CFD simulation. The local thicknesses of the diffusion boundary layer were spatially solved using an additional variable technique supported by the CFX-solver. This variable has meaning only on the electrode area in the space coordinate. This spatial coordinate approach is more realistic than a 1-D extrapolation method [11].

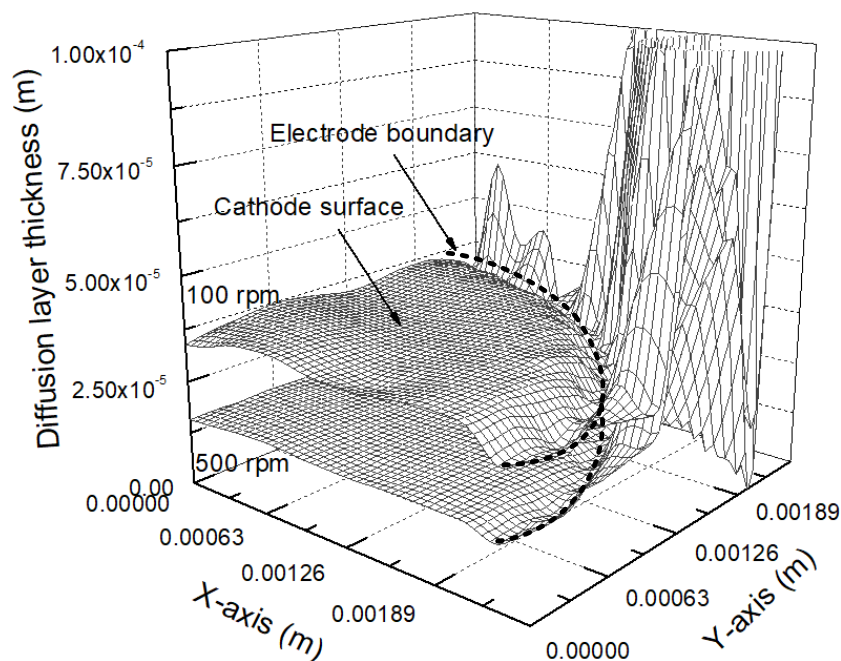


Figure 4. 3-D distributions of diffusion boundary layer thickness on the cathode surface at the different rotation speeds of the RDE in the copper electrodeposition system.

The 3-D distributions of the diffusion boundary layer thickness were figured out over the cathode surface for the two cases of the RDE rotation speed shown in Fig. 4. The simulated distributions of the diffusion layer thickness showed comparatively a uniform pattern within the cathode area boundary. The simulation result shows that a higher rotation condition leads to a more uniform and lower thickness distribution of the diffusion boundary layer. When a current is applied during the galvanostatic electrolysis, the electrode reaction coupled electrochemical hydrodynamics is governed by mass transport to the electrode surface. The diffusion-controlled tertiary current distributions are directly related with the boundary layer thicknesses and affected by the RDE rotation speed. A high rotation rate condition leads to a well-defined electrolyte flow pattern. From this result, it was found that high rotation rate conditions are required to derive the electrochemical kinetics constants for the application of a RDE system.

To see how the boundary layer thickness changes as the rotation speed of the RDE increases, transient calculations were used starting from a rotation speed of 50 to 600 rpm that varied over time. A transient simulation using a time step depending the variable electrode rotation speed was carried out to figure

out the change in the average diffusion layer thickness in accordance with the increasing rotation pace as a linear function of time.

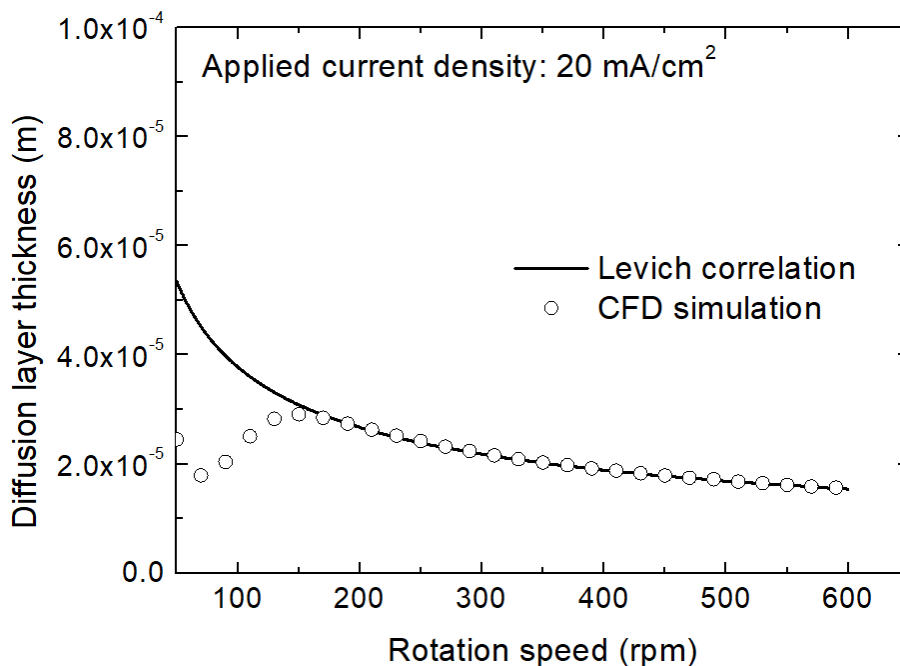


Figure 5. Comparison between the CFD simulation of the average diffusion layer thickness on the RDE and the Levich correlated equation as a function of the rotation speed in the copper electrodeposition system.

Fig. 5 shows a comparison between the present simulated average boundary layer thicknesses and the Levich correlated equation with increasing rotation speed. From the distribution of the local boundary layer thickness (δ_x), the average diffusion boundary layer thickness can be obtained with an integrated function based on the CFX expression. Simulation results were different from those of the Levich correlation at the initial steps of the low rotation speed, which were the steps towards the computational convergence in the transient runs but were well matched at rotation speeds greater than 160 rpm. A uniform current distributed under a high rotation rate condition could be characteristically consistent with the 1-D Levich correlation. The simulated diffusion boundary layer thicknesses based on CFD approach agree well with those from the Levich equation.

Flow patterns in the vicinity of the RDE are dependent on the geometry combination of the electrode and supporter (or without supporter), and electrode configuration and alignment [12-14]. An electrochemical reaction is limited by mass transport when using the conventional electrochemical cell with a RDE [15]. When improving a cell design to replace the classical RDE for a specific application, it is important to find an optimum electrode-supporter arrangement within the cell system. It could be thus proposed to design the optimal combination of the RDE rotating parts using this kind of CFD approach to improve the accuracy of practical applications.

4. CONCLUSION

This study demonstrated a 3-D modeling based on the full coupling of electrochemical reactions with the mass transport of ionic species in a copper electrodeposition system using a rotating disk electrode and a commercially available CFD platform. This approach enabled us to figure out the electrochemical hydrodynamics patterns occurring within the cell under galvanostatic electrolysis.

Average concentration profiles of an electroactive species consumed on the cathode were simulated under a mass transport limited condition using a CFD technique. The 3-D distributions of the boundary layer thicknesses were approximated from the local concentration gradients and agreed well with those of the Levich correlated equation in the practical range of the RDE rotation speed. The modelling approach implemented here can be useful to improve the accuracy of measurement in the design of a RDE cell system.

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