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MODELING AND SIMULATION
OF
ELECTROCHEMICAL MAGNETO HYDRO DYNAMICS

by

DEBAMOY SEN

A THESIS

Presented to the Faculty of the Graduate School of the
MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

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Approved by

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ABSTRACT

This thesis focuses on how the electrochemical magneto hydro dynamic problem is solved through numerical simulation for a two dimensional millielectrode electrochemical cell and a three dimensional microelectrode array cell. Electrochemical processes are enhanced by magnetic fields through the introduction of body forces such as Lorentz force. Through modeling and numerical simulations, experimental results can be integrated with theory. Such simulations will aid in the prediction of mass transfer limited currents and visualization of flow profiles in an electrochemical cell. The numerical solution of the equation system is made possible by the finite volume method used in the FLUENT Computational Fluid Dynamics (CFD) software code.

Potentiostatic mode of operation was employed for the modeling of both millielectrode and microelectrode systems. Through appropriate boundary conditions, simulations were conducted for the interplay of Lorentz forces, convection and concentration distribution under the Butler-Volmer electrode kinetics of a redox couple.

The simulation results described in this thesis show strong effect of magnetoconvection on the concentration contours. Also, gradual development of vortex structures is observed in the flow field.

These numerical simulation studies are of prime interest in the field of microfluidics, where automated control of small volumes of fluids is essential. These results will help determine possible direction of future research in developing redox magnetoconvection for microfluidic and lab-on-a-chip application.

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1. INTRODUCTION

1.1. ELECTROCHEMICAL SYSTEMS

Electrochemistry refers to the study of charge transfer across interfaces that bring about chemical changes like oxidation or reduction. In electrochemical systems, focus is primarily on the processes and factors that affect the transfer of charge across the interface. The study of such systems is concerned with the electrode/electrolyte interface and effects observed on the application of an electric potential and current passage.

1.1.1. Working Electrode. The working electrode in an electrochemical system is the electrode at which the reaction of interest is occurring. Depending on whether the type of reaction occurring is reduction or oxidation, it is referred to as either a cathode or anode. A good working electrode should behave as an ideal polarizable interface; allowing no current to pass, no matter what potential is applied. The potential at the working electrode is observed and controlled with respect to the reference electrode.

1.1.2. Reference Electrode. The reference electrode has a stable and well known electrode potential. Because of its constant makeup, its potential is fixed, no matter how large the current. It helps standardize the electrochemical cell. Thus, working electrode potential is measured with respect to the reference electrode. A good reference electrode should behave as an ideal non-polarizable interface.

1.1.3. Counter Electrode. The counter electrode is an electrode used in a three electrode electrochemical cell. The current and potential at the counter electrode are not measured. It is mainly used to ensure that current does not run through the reference electrode, thereby disturb the potential of the reference electrode. One important feature of the counter electrode is that in practice its surface area is much larger than that of the working electrode. This ensures that the reactions taking place at the working electrode are not surface area limited. In practice, counter electrodes are generally isolated from the working electrode. This prevents the test solution from being contaminated by any byproducts generated at the counter electrode.

1.1.4. The Three Electrodes Electrochemical Cell. In this electrochemical cell configuration, a working, a reference and a counter electrode are present. Here, the reference electrode is placed very close to the tip of the working electrode to minimize the solution resistance in the cell. In practice, along with this, a large concentration of the supporting electrolyte is used to minimize the solution resistance. A supporting electrolyte is an inert electrolyte, not participating in the electrode reactions, but increasing the conductivity and thereby decreasing the ohmic potential drop in the solution. Figure 1.1 illustrates a three electrode cell.

Figure 1.1. Three Electrode Electrochemical Cell

1.1.5. Faradaic Processes. These are processes that occur at the electrodes and categorized into faradaic and non-faradaic processes. Faradaic processes comprises the transfer of charge across the electrode/electrolyte interface, resulting in either oxidation or reduction reaction to occur. These reactions are governed by Faraday's law which states that the amount of chemical reaction due to the flow of current is proportional to the quantity of electricity passed. Hence, faradaic current is a measure of the redox reaction rate. Mathematically, this can be represented as

$$\frac{i}{nF} = \frac{dN}{dt} \quad (1)$$

where, i is the current at the working electrode, n is the number of participating electrons in the redox reaction, F is the Faraday constant, N is the number of moles electrolyzed.

1.1.6. Introduction to Mass Transfer. The redox reactions that take place at the electrode, and hence the current, are affected by the rates of electron transfer at the electrode, adsorption or desorption at the electrode surface, chemical reaction and mass transfer from the bulk solution to the electrode surface. For cases with rapid charge transfer and with no adsorption/desorption or chemical reaction before and after the electrode reaction, the electrode surface reaction rate and thereby the current are limited only by the rate of mass transfer of the electro-active species from the bulk solution to the electrode. There are three different modes of mass transfer, namely, migration, diffusion and convection. Mathematically, the mass transfer to an electrode can be represented by the Nernst-Planck equation

$$\bar{J}_i = -D_i \left(\frac{dC_i}{dx} + \frac{z_i F}{RT} C_i \frac{d\phi}{dx} + v C_i \right) \quad (2)$$

where, \bar{J}_i is the flux of electro-active species 'i', D_i is the diffusion coefficient of species 'i', C_i is the concentration of species 'i', $\frac{dC_i}{dx}$ represents the concentration gradient, $\frac{d\phi}{dx}$ is the potential gradient, z_i is the charge of species 'i', R is the Universal Gas Constant, T is the temperature, and v is the velocity of volume element in solution. The first, second and third terms in Equation (2) refers to the diffusion component, the migration component, and the convection component, respectively. For cases, as mentioned, where a large volume of supporting electrolyte is used, the migration component reduces to negligible values because of the negligible resistance of the solution.

1.2. INTERFACIAL CHARGE TRANSFER DYNAMICS

In electrochemical cells, heterogeneous electron-transfer refers to the movement of electrons between a chemical species and a solid-state electrode. In electrochemical systems, it is necessary to depart from equilibrium conditions for the heterogeneous

electron-transfer reactions to take place. Consider that the working electrode is present at a potential E_1 with respect to the reference electrode and no charge transfer takes place across the electrode/electrolyte interface. However, when the potential is changed to E_2 , current flow is observed, meaning that charge transfer takes place across the interface. Changing the electrode to this new potential reflects the non-equilibrium driving force necessary to make the heterogeneous electrode reactions take place at an appreciable rate. Hence, it is observed that the electrode reaction rate is a strong function of the potential.

Surface overpotential refers to the non-equilibrium driving force to drive the reaction at a certain rate, or the additional potential beyond the thermodynamic equilibrium requirement. It is measured as the potential of the working electrode relative to a reference electrode.

1.3. VOLTAMMETRY

It refers to a category of electro-analytical techniques involving the application of a potential to an electrode and monitoring the resultant current flow through the electrochemical cell. It helps to describe the faradaic current generated as a function of either the overpotential or time.

1.3.1. Potential Step Voltammetry. In this method, the applied potential is instantaneously changed from one value E_1 , where no faradaic processes take place, to another value E_2 , where the heterogeneous electron transfer reaction takes place. This method involves the measurement of the resulting faradaic current with respect to time. Figure 1.2 illustrates the required waveform for a potential step experiment.

Figure 1.2. Potential Step Waveform

1.3.2. Potential Sweep Voltammetry. Known as Linear Sweep Voltammetry, it involves the applied potential being changed as a linear function of time. This method measures the faradaic current as a function of overpotential. Figure 1.3 illustrates a linear sweep potential waveform.

Figure 1.3. Linear Potential Sweep Waveform

Cyclic Voltammetry is an extension of the linear sweep method, where the direction of the potential scan is reversed on reaching the switching potential. The corresponding current-overpotential curve obtained is known as Cyclic Voltammogram. Figure 1.4 illustrates a cyclic potential sweep waveform.

Figure 1.4. Cyclic Potential Sweep Waveform

1.4. MAGNETO HYDRO DYNAMICS (MHD)

It refers to the interaction between an applied magnetic field and a flowing, electrically-conductive fluid. The coupling of the fluid flow field and the magnetic field can be understood on the basis of a fundamental effect – Lorentz force, which results from the interaction of electric and magnetic fields.

MHD Lorentz forces involve three physical fields that are perpendicular to each other. The flow or velocity field is aligned perpendicular to both the electric and magnetic fields, which are also perpendicular to one another. Manipulation of any two of these fields results in the change of the third one.

Redox MHD involves electro-active species undergoing either oxidation or reduction process at the surface of the working electrode in an electrochemical cell, thereby generating an electric field, which interacts with an existing applied magnetic field to produce a body force, known as Lorentz force, on the electrolytic conductor, causing it to get displaced, setting up a convective motion. Through MHD, control of the flow rate is possible by varying the magnetic field intensity or changing the redox species concentration. MHD helps to change the direction of flow by simply alternating the electrode polarity or reversing the magnetic field.

MHD technology requires a relatively dense current to induce significant flow rate. At larger scales, it is not practical. However, on a small scale it is very effective. MHD provides an excellent mechanism for microfluidic propulsion. Moreover, it applies to both aqueous and organic solutions.

2. PREVIOUS WORK

2.1. ELECTROCHEMICAL MAGNETO HYDRO DYNAMICS

The application of magnetic fields in electrochemical systems has increased over the last couple of decades or so. The most well known effect of magnetic field on electrochemical systems is hydro dynamics convection, also known as stirring, of the electrolyte. This magnetic stirring occurs due to the Lorentz force, which is represented by the cross product of the current flux and the magnetic flux, in accordance with the direction given by the right hand rule. It is this Lorentz force acting on a differential volume element of the electrolyte that sets the electrolyte in motion, generating convection. Such MHD effect manifests itself in increased mass transport. Leventis et al. [1] conducted Cyclic Voltammetry across the first oxidation wave of N,N,N',N'-tetramethyl- p- phenylenediamine (TMPD) using gold disk electrode of 1.6mm diameter in CH₃CN/0.5M TBAP outside and inside a transverse magnetic field of intensity 1.75 Tesla. Figure 2.1 illustrates the Cyclic Voltammograms obtained in their experiments.

Figure 2.1. Cyclic Voltammograms Obtained Through Experiments [1]

Leventis et al. [2] also gave an expression for mass transfer limited current, which showed the non-linear dependence of the limiting current on the number of electrons involved in the redox process. It was possible to obtain mass transfer limited currents similar to those observed with rotating electrodes. Moreover, using permanent Nd-Fe-B magnet, evolution of flow profiles around a gold disk electrode of area 0.0412cm^2 under potential step was reported by Leventis et al. [3]. Figure 2.2 illustrates those results obtained.

Figure 2.2. Flow Profile Evolution Using Permanent Magnet Under Potential Step [3]

Such MHD effect is potentially very important, as it could be applied for stirring to augment mass transport where cell design does not allow mechanical stirring of the electrolyte. This suggests applying electrochemical MHD for flow control in

microfluidics. The use of MHD to pump, control and stir fluids in micro-devices has also been proposed [4, 5]. Moreover, controlling the individual branches of a fluidic network by MHD was given by Bau et al. [6]. Here, by treating the potential difference as the controlling parameter at various branches, it was possible to direct fluid flow in any desired way, thereby overcoming the need for any mechanical pumps or valves.

Some elegant fundamental studies involving redox MHD at microelectrodes have also been reported [7, 8]. Attempts have been made to use MHD in microfluidic applications without redox species [9, 10]. The systems showed problems of heating and bubble formation. It has been shown that redox MHD can be used with both aqueous and non-aqueous solutions in microfluidic systems and avoid bubble formation [11, 12]. The effects of redox MHD-induced convection at microband electrode arrays have been reported [13]. Here, however, only one size of the array was used. When operating with such small electrodes, imaging of the flow field is of primary concern. Scanning Electrochemical Microscopy (SECM) have been used [14]. On referring to the manifestation of MHD in increased mass transport, it has been found that other effects like concentration gradients, density gradients, magnetic field gradients and paramagnetic forces might also influence mass transport [15]. Three types of body forces have been found operating in electrolytic solutions that can be associated with magnetoconvection in electrochemical systems: Lorentz force or MHD force, force due to magnetic field gradient, and force due to paramagnetic concentration gradient [3]. Hence, an integration of experiments, modeling and numerical simulation is desired to delineate the various mechanisms.

2.2. SIMULATION OF ELECTROCHEMICAL PROCESSES

The MHD flow of an electrolyte solution between two parallel electrodes in the presence of abundant supporting electrolyte and fast electrochemical reactions was solved numerically by Boum and Alemany [16]. A finite element approach for numerical simulation of Linear Sweep Voltammetry at wall tube electrodes was done by Compton et al. [17]. Here, the Butler-Volmer model was used to specify the boundary conditions in

case of quasi-reversible conditions. Mandin et al. modeled and simulated the hydrodynamic processes associated with a rotating disk electrode in a confined electrochemical cell [18]. The finite difference method was used by Compton et al. to simulate the Cyclic Voltammetric response of electrodes with reactive blocks [19]. The strongly coupled species' mass transport and momentum equations for MHD flow of a redox electrolyte in a two-dimensional straight conduit and three-dimensional microfluidic channels have been recently solved numerically using the commercial finite element package FEMLAB [20, 21]. Streeter and Compton have numerically solved the potential step chronoamperometry case under low supporting electrolyte concentrations [22]. In this approach, the finite difference method was used with the Nernst-Planck-Poisson equation systems to model the mass transport phenomena. The approximations included were that of negligibly small electrical double layer and electroneutrality. Compton et al. used the finite difference model to perform two-dimensional numerical simulation of Chronoamperometry and Voltammetry at an annular microband electrode [23]. However, a computational fluid dynamics (CFD) simulation of the coupled conservation equations of mass, momentum and species in geometries of practical interest have not yet appeared in literature.

3. MODELING AND SIMULATION OF MILLIELECTRODE SYSTEMS

3.1. INTRODUCTION

As it is not possible to obtain rigorous analytical solutions of the electrochemical MHD equations, this study has been initiated to integrate electrochemical MHD experiments with modeling and numerical simulation using computational fluid dynamics (CFD) tools. Here, electrochemical MHD of redox electrolytic solutions has been considered. Redox electrolytic solutions undergo electrochemical reactions at the electrode surfaces, thereby eliminating many of the problems that accompany the MHD technology, namely bubble formation, electrode corrosion and depletion of electrolyte during operation. Factors affecting the operation and performance of redox-based MHD devices are concentration of the electroactive species and supporting electrolyte, type of the redox species, electrode configuration, applied potential or current and strength of magnetic field. This work presents a CFD simulation of the coupled conservation equations of mass, momentum and species in geometries of practical interest, involving millielectrode redox systems. Through these CFD simulations, it would be possible to gain insight into the processes taking place in an electrochemical cell operating in the presence of a magnetic field and predict important parameters such as mass transfer limiting current. It would also be possible to visualize many aspects of the processes such as the flow field variations, concentration contours in the whole domain and concentration profiles near the working electrode surface.

3.2. BUTLER-VOLMER MODEL OF ELECTRODE KINETICS

It has been established that the electrode reaction rate and hence the current is a strong function of the potential. Hence, potential dependent reaction rate constants are required to accurately describe the interfacial charge-transfer dynamics. The Butler-Volmer model relates the current density flowing through the electrode/electrolyte interface due to electrode reaction to the overpotential in terms of the two kinetic parameters and the charge transfer coefficient. This model gives the precise way in which

the forward and backward reaction rates depend on the overpotential. Thus, reactivity at the electrode surface can be controlled through the potential difference.

Hence, under heterogeneous surface reaction conditions, the Butler-Volmer equation can be employed to describe the kinetics of the electrode reactions [24, 25], where the forward and backward reaction rates are given by

$$k_f = k^0 \exp\left(-\alpha \frac{nF}{RT} \eta\right) \quad (3)$$

$$k_b = k^0 \exp\left((1-\alpha) \frac{nF}{RT} \eta\right) \quad (4)$$

For the redox system represented by the reaction



where O and R represent the oxidized and reduced species, respectively, e is the electronic charge and n is the number of electrons exchanged in the reaction, using this Butler–Volmer formulation, it is possible to calculate the flux from the surface reaction in Arrhenius form, given by

$$\mathbf{n} \cdot \mathbf{N}_R = -\mathbf{n} \cdot \mathbf{N}_O = C_{O|_{\text{electrode}}} k^0 \exp\left(-\alpha \frac{nF}{RT} \eta\right) - C_{R|_{\text{electrode}}} k^0 \exp\left((1-\alpha) \frac{nF}{RT} \eta\right) \quad (6)$$

where \mathbf{n} is the unit normal vector to electrode surface, N_j is flux of species j (here j represents species R and O), α is the charge transfer coefficient (ranging from 0.0 to 1.0), R is the universal gas constant, T is the temperature, η is the overpotential applied and k^0 is standard reaction rate constant. Isothermal conditions of operation is considered here and hence do not include the temperature dependence in the Arrhenius equation. It is to be noted that the first and second terms on the right hand side of Eq. (6) represent the forward and backward reaction rates, respectively. Thus, the reaction rates

depend on the concentrations of the electroactive species at the electrode surface and on the overpotential applied.

3.3. MATHEMATICAL MODEL

The two-dimensional model to be set up for the simulation of the MHD phenomena comprises the oxidation and reduction of an electroactive species at the working electrode and the convection induced by Lorentz force through interaction of faradaic current and external magnetic field. The redox couple can be represented by Eq. (5). For such systems, the faradaic current density is represented by the equation

$$j = nFD_O \left(\frac{\partial C_O}{\partial x} \right)_{x=0} \quad (7)$$

where j is the faradaic current density, A is the area of the electrode, D_O is the diffusion coefficient of species O . The current, i , can be calculated by integrating the current density over the electrode surface. If it is assumed that current density is a constant over the electrode area, the current is given by

$$i = nFAD_O \left(\frac{\partial C_O}{\partial x} \right)_{x=0} \quad (8)$$

The term in parenthesis in Eq. (8) is the concentration gradient of species O at the electrode surface. Thus, the faradaic current is related to the concentration gradient of the redox species. In order to obtain the concentration gradient, it is needed to solve the Diffusion – Convection equation, represented as

$$\frac{\partial C_O}{\partial t} + v \frac{\partial C_O}{\partial x} = D_O \frac{\partial^2 C_O}{\partial x^2} \quad (9)$$

where subscript i represents species O and R in the medium and C_i is the concentration of species i , under appropriate initial and boundary conditions [26]. It is to be noted that the evolution of the concentration profiles of the electro-active species i is given by Eq. (9) in the presence of an excess amount of supporting electrolyte. Corresponding to the redox system of Eq. (5), Eq. (9) represents two species conservation equations. If it is to be considered that initially both oxidized and reduced species exist, then the initial conditions become

$$C_O(t=0)=C_O^* \quad (10)$$

$$C_R(t=0)=C_R^* \quad (11)$$

and for the application the appropriate electrode surface boundary conditions, heterogeneous surface reactions are employed, under which the Butler-Volmer equation describes the kinetics of the electrode reactions. Also, for the redox reaction represented by Eq. (5), the following boundary condition also applies

$$D_O \frac{\partial C_O}{\partial \xi} + D_R \frac{\partial C_R}{\partial \xi} = 0 \quad (12)$$

where ξ is the normal direction to the electrode surface. The solution of the species conservation equations allow for the calculation of the faradaic current and from it the Lorentz force, \vec{F}_L which is obtained by taking the cross product of current density vector, \vec{j} , and magnetic flux vector, \vec{B} . The direction in which this Lorentz forces acts is given by the right hand rule. The current density, \vec{j} , is represented as $\vec{j} = j_x \vec{e}_x + j_y \vec{e}_y + j_z \vec{e}_z$, where \vec{e}_x , \vec{e}_y and \vec{e}_z are unit vectors in x , y and z directions, respectively, and j_x , j_y and j_z are current density components in the x , y and z directions, respectively. In the present case of the two-dimensional model \vec{e}_z drops out. Also, in the present case, it has

been assumed that the uniform magnetic flux is in the positive z direction. Hence, $\vec{B} = B \vec{e}_z$, where B is the magnitude of the applied uniform magnetic field. Hence, Lorentz force is given by $\vec{F}_L = \vec{j} \times \vec{B} = (j_x \vec{e}_x + j_y \vec{e}_y) \times B \vec{e}_z = -j_x B \vec{e}_y + j_y B \vec{e}_x$. This force acting on a unit volume element, ΔV of the electrolytic conductor, accelerates it and displaces in the direction of the force. A void is created, which gets replenished by fresh electrolyte rushing in from the bulk, setting up a convective motion. Mathematically, this Lorentz force appears as the body force term in the Navier–Stokes (N–S) momentum equations. Solution of the N–S equations gives the flow and thereby the velocity in the medium, which in turn influences how the concentration profiles of the species develop. This in turn affects the faradaic current generated in the system and ultimately affects the Lorentz force. Hence, it can be rightly concluded that the magneto-electrochemical processes are characterized by a complex interplay of Lorentz forces, flow and concentration distributions. Hence, witnessing the strong coupling between the momentum and mass transport equations, it is to be acknowledged that it is highly desirable to solve the flow and species conservation equations in a coupled manner. Figure 3.1 illustrates the simulation flow chart to solve the electrochemical and hydro dynamic problem in a coupled manner.

Figure 3.1. Simulation Flow Chart

The set of equations for mass and momentum conservation for incompressible flow are as follows

$$\nabla \cdot \bar{\mathbf{u}} = 0 \quad (13)$$

$$\rho \frac{D\bar{\mathbf{u}}}{Dt} = -\nabla p + \mu \nabla^2 \bar{\mathbf{u}} + \rho \bar{\mathbf{g}} \quad (14)$$

where, $\bar{\mathbf{u}} = u_x \mathbf{e}_x + u_y \mathbf{e}_y + u_z \mathbf{e}_z$ is the fluid velocity, with u_x , u_y and u_z being velocity components in the x , y and z directions, respectively, ρ is the density, p is the pressure, μ is the dynamic viscosity and \mathbf{g} is the gravity. For a two-dimensional problem the conservation equations will have two components in x and y directions.

3.4. NUMERICAL MODELING AND SIMULATION

Electrochemistry involves different modes and regimes of operation. Hence, appropriate models need to be developed before attempting numerical solution of the governing equations involving the Navier-Stokes equations. The N-S equations are based on the continuum assumption. The present simulations are for Newtonian fluid in incompressible, laminar flow. The mass, momentum and species equations are solved in a coupled manner.

3.4.1. Introduction to CFD. CFD is the technology used for the mathematical study of the dynamics of flow. CFD helps to bridge the gap between pure theory and pure experiment, and gives an alternative approach to solve fluid dynamics problems. It utilizes computational power to perform numerical calculations, aiding the interpretation of results without actually conducting experiments, thereby reducing cost and time.

CFD is based on numerical techniques by which the solution domain is discretized into nodes, and using discretization schemes the conservation equations are transformed into algebraic ones. Hence, at the core of any CFD calculation there is a

computational grid, dividing the solution domain into elements where the problem variables are computed. In the present case, for the numerical solution of the governing equations, the commercially available software package FLUENT [27] is used. FLUENT employs a finite volume method, by which the nodes are at the center of the finite volumes, and for these nodes the conservation equations are written and discretized in their integral form. In FLUENT, an unstructured grid topology can be used, by which the shape of the elements can be quadrilaterals and triangles for the two – dimensional simulations. For the present study, Gambit was chosen as the meshing tool, which is a preprocessor to FLUENT, to create these finite volume elements.

3.4.2. Introduction to User Defined Functions (UDFs). UDFs allow great deal of flexibility in solving a wide range of phenomena. UDFs are basically C/C++ routines programmed by the user and linked dynamically with the FLUENT flow solver to augment standard features of the code. These UDFs are compiled and linked during problem set up. Then they are invoked by the solver during the solution process. UDFs allow to access FLUENT solver data and perform tasks like specifying source terms and special boundary conditions.

3.4.3. Fluent Simulation Geometry. For the present simulations, a rectangular electrochemical cell model is used. The cell extends to +/- $\frac{L}{2}$ in the z direction, thus allowing a two – dimensional formulation. This means that the solution is identical in planes normal to the z axis, i.e. current is only in the xy plane and there is no velocity / flow in the z direction. The working electrode is a band electrode, placed at the center of the bottom surface. The entire top surface is the counter electrode. Figure 3.2 illustrates the two-dimensional domain used.

Figure 3.2. Two-Dimensional Computational Domain

The actual meshed two-dimensional computational domain has approximately 28,000 quadrilateral cells, distributed non - uniformly with higher grid density near the working electrode. Figure 3.3 illustrates the meshed domain.

Figure 3.3. Meshed Computational Domain

This is because the ionic flux drops off quickly away from the working electrode, and hence Lorentz force is significant only near the working electrode. So, to capture the

fine features of the processes taking place near the working electrode, the grid needs to be clustered densely there. The grid becomes coarser away from the working electrode. This non – uniform grid structure helps to optimize the computational time within practical limits, and at the same time acquire all the important features of the processes. Due to this non–uniform spacing and non–orthogonality, the mesh differs from that made up of rectangular volume elements. The solutions are obtained on a computational domain different from the physical domain, and the mapping between the two is established via the transformation metrics [28].

3.4.4. Simulation Setup. An unsteady formulation is used to simulate the time - varying phenomena. Figure 3.4 illustrates the flow diagram depicting the major steps in the simulation process.

Figure 3.4. Simulation Flow Diagram Depicting Major Steps

The coupled mass, momentum and species conservation equations are solved at each time level, till the user–specified convergence criteria are met. The solution then advances to the next time level. The conservation equations, Eq. (13) and (14), are different from the basic fluid flow equations because of the electrochemistry phenomena and the presence of the magnetic field. The Lorentz force terms present as body forces in

the momentum equations and the coupling of the species boundary condition with the applied voltage / potential is handled by code written by the user, known in FLUENT as User-Defined Functions (UDFs). In the present case, using UDFs it is possible to modify the governing equations to include source terms like Lorentz forces and define species boundary conditions in terms of the applied potential/current. Here, the DEFINE_SOURCE macro has been used to calculate the Lorentz force, which is a body force source term, from the current density and magnetic field intensity. While iterating through the solution sequence, DEFINE_ADJUST macro has been used to calculate the current density flux from the ionic flux at the working electrode surface. At the end of every time-step, DEFINE_EXECUTE_AT_END macro has been used to write the current density in a text file. Using UDFs it is also possible to make the user's model include solution-dependent properties like viscosity of non-Newtonian fluids. Equations such as Laplace's and Poisson's, that govern electric and magnetic fields, can also be solved using this framework in a coupled manner, and made part of the overall solution. Using this approach it has been possible to successfully solve a wide range of problems including adsorption, combustion [29], multiphase flow [30] and thermophoresis [31].

When the problem was setup in FLUENT, the two-dimensional, unsteady, laminar model was used. For the unsteady formulation, the second-order implicit algorithm was employed. Also, for better solution accuracy, the coupled solution algorithm was used. Two Text-User Interface (TUI) commands were used at certain stage of the problem setup to instruct the solver to store the mass-fraction gradients. This would assist in the calculation of the species concentration gradients, and thereby the Lorentz force.

As depicted by the flow diagram in Figure 3.4, the major steps in the solution procedure involve generating the mesh files in Gambit and reading it into FLUENT. After reading the meshed geometry, a grid check was performed to check for negative volumes, which indicate improper connectivity between the cells, and can affect the discretization process resulting in unphysical results. The checked grid was then scaled down to the required dimensions. This is followed by the case setup for the particular problem. This step involves appropriate selection of models and specification of the boundary conditions. Next, initialization of the problem is done by specifying the initial

molar concentrations of species O and R in the medium. Finally, the solution process is started by iterating the solver at a particular defined time step for certain duration of time. It is to be noted that for such unsteady problems, as in the present case, storage of the solutions at desired time intervals for post-processing and analysis is done.

3.5. SIMULATION RESULTS AND DISCUSSION

As discussed previously, a two-dimensional model is used for simulation of electrochemical magneto hydro dynamics for a millielectrode system. Figure 3.5 illustrates the actual geometrical dimensions of the computational domain used for the present simulations.

Figure 3.5. Dimensions of Computational Domain

Figure 3.5 is actually the cross-sectional view of Figure 3.2. The domain size is $2 \times 1 \text{ cm}^2$. A 2 mm wide band working electrode has been used, which is centrally placed at the bottom surface. The entire top surface acts as counter electrode. Since simulation of the electrochemical MHD of redox electrolytic solution is to be done, a redox species N,N,N',N'- tetramethyl- p- phenylenediamine (TMPD) is used. The supporting electrolyte used is tetrabutylammoniumperchlorate i.e. TBAP in acetonitrile. When setting up the problem in FLUENT, three species were defined, the oxidized and reduced

forms of TMPD and a bulk species for the supporting electrolyte. Molecular weight of TMPD used is 164.25 kg/kmol and that of TBAP is 341.92 kg/kmol. The dynamic viscosity used for the redox species is 0.0015 kg/m-s and that for supporting electrolyte is 0.0005179 kg/m-s. The density of the redox species and of supporting electrolyte used is 992 and 826.1 kg/m³, respectively. The diffusivities of species O and R used are $2.4 \times 10^{-9} \text{ m}^2/\text{s}$ and $2.3 \times 10^{-9} \text{ m}^2/\text{s}$, respectively. The initial concentration of reduced species used is 10.89 mM, which corresponds to a mass fraction of 0.00216 used in simulation set up, and that for supporting electrolyte is 0.5 M. The initial concentration of oxidized species is set to 0 mM, i.e. initially only the reduced species R is present. Having defined the redox electrolyte, the magnetic field is applied in the positive z direction, with a magnitude of 1.75 Tesla. Since the Butler-Volmer of electrode kinetics is employed, which is assumed to have an Arrhenius form, the standard reaction rate constant k^0 is taken as 0.55 cm/s [32]. For the potential step mode of operation, the applied overpotential is 0.7V, and for the potential sweep mode, the overpotential is swept from -0.25 to 0.4V. Referring to Eq. (6), it is to be noted that k^0 and η are the two controlling parameters that govern the working electrode surface flux boundary conditions. At high negative η , the forward reaction dominates and on moving towards a more positive η the backward reaction dominates. It is to be noted for the potential step case defined above, just as the solution starts, the backward reaction dominates as the stepped overpotential is positive. However, for the potential sweep case, though the overpotential is swept from a negative to a positive value, the forward reaction cannot dominate because the initial concentration of oxidized species is zero. While swept overpotential becomes more and more positive, the backward reaction dominates more and more. Hence, it can be concluded that as the solution proceeds, based on the applied overpotential and concentrations of the electroactive species, either the forward or the backward reaction dominates. It is to be noted that a zero flux boundary condition is used for the counter electrode. In all the computations, the temperature is maintained at $T = 298.15 \text{ K}$. An integration time step of 0.01s is used for all simulations. The results obtained from simulations were post-processed to get velocity vectors, velocity magnitude contours, and molar concentrations of redox species as it develops with time. Profile plots were

obtained of the concentration of species O and R near the working electrode surface, by creating a line surface from the middle of working electrode and perpendicular to it.

3.5.1. Potential Step Voltammetry. Here, the potential is stepped up, in both the absence and presence of a magnetic field, to 0.7V. In the absence of magnetic field, i.e. for the diffusion-only problem, the solution is allowed to proceed for a short time of 2–6s. The concentration profile plots obtained numerically are compared with those obtained from the approximate analytical solution of the diffusion problem, given in terms of the error function. The current density is also obtained over a long period of 150s, and compared with the current density given by the Cottrell equation [24]. With the magnetic field is on, concentration contours and velocity vectors are obtained for comparison to results in the absence of magnetic field.

3.5.1.1 Absence of magnetic field. In these simulations, the overpotential was stepped to 0.7V, so that concentration near the working electrode approaches zero and it becomes possible to approach mass-transfer controlled region. Concentration profiles are noted for a short time of 2–6s, so that their development near the working electrode should be similar to that of the linear diffusion case. For overpotential step up to mass-transfer controlled regime, i.e. when current becomes diffusion-limited, using Laplace transform the concentration profile of species R can be represented in terms of an error function [24], given by

$$C_R(x,t) = C_R^* \operatorname{erf} \left[\frac{x}{\sqrt{4Dt}} \right] \quad (15)$$

where, x is the distance perpendicular to the working electrode, C_R^* is the bulk concentration of species R, t is the time elapsed. Figure 3.6 illustrates the profile plots obtained through simulation in comparison with the approximate analytical solution at a time of 2s from start.

Figure 3.6. Profile Plot Comparisons at Time 2s

Here, the numerical and approximate analytical solutions agree to a high extent to each other. It was noted that the agreement becomes better as time proceeds. For instance, at a time of 6s, the concentration profile plots show better agreement. Figure 3.7 illustrates the profile plot comparisons at time 6s.

Figure 3.7. Profile Plot Comparison at Time 6s

In this case, the concentration profile from numerical simulation approaches zero at the working electrode surface. This can be attributed to the fact that for the numerical solution, the initial concentration of species R at the working electrode surface was same as the bulk concentration. Hence, as the solution proceeds, it takes iterative few steps to get that concentration to approach zero.

The current-density at the working electrode surface was also calculated from the simulation. Comparison are made with the diffusion-limited current given by the Cottrell equation [24].

$$j(t)=j_d(t)=nFD_R^{1/2}C_R^*/\pi^{1/2} t^{1/2} \quad (16)$$

It is noted that the current density–time curve obtained from numerical simulation follows the same pattern as given by Eq. (16), and the values are also comparable. It is seen that the current–density obtained from simulation is slightly higher at large times. This can be attributed to the fact that for the numerical simulation, a two–dimensional model has been employed in comparison to the linear diffusion case approximated by the Cottrell equation. Figure 3.8 illustrates the current-density vs. time curves obtained from simulation in comparison to that predicted by the Cottrell equation.

Figure 3.8. Current-Density vs. Time Curves

These strong agreements of the numerically simulated results with the approximate analytical solutions, make the present modeling approach and set up trustworthy. Figures 3.9 illustrates the molar concentration contours of species R at time 6s.

Figure 3.9. Concentration Contours of Species 'R' at Time 6s in the Absence of Magnetic Field

3.5.1.2 Presence of magnetic field. A magnetic field of magnitude 1.75Tesla is applied parallel to the working electrode surface, in the positive z direction. Figure 3.10 illustrates the molar concentration contours at time 2s.

Figure 3.10. Concentration Contours Under Magnetic Field for Species 'R' at Time 2s from Start

On comparison of the concentration contours given by Figures 3.9 and 3.10, it can be noted that the concentration contours just start to deflect towards the right, and the effects of the magnetic field starts to influence the flow properties, but not to a very large extent. However, at a time of 6s, the strong influence of magnetoconvection becomes evident on the concentration contours. Figure 3.11 illustrates the molar concentration contours at time 6s under magnetic field.

Figure 3.11. Concentration Contours Under Magnetic Field for Species 'R' at Time 6s from Start

The concentration contours get deflected to a large extent towards the right, depicting the strong influence of Lorentz force. These trends are in accordance with published experimental results. Figure 3.12 illustrates more clearly the strong effect of MHD Lorentz force at a time of 15s from the start.

Figure 3.12. Concentration Contours Under Magnetic Field for Species 'R' at Time 15s from Start

It is noted that the diffusion layer keeps on becoming thin above the working electrode surface with time. This is because at the middle of the working electrode, the current is nearly normal to the electrode surface, and since the magnetic field is parallel to the electrode surface, the x -component of the Lorentz force predominates, resulting in a diffusion layer much thinner compared to that in the absence of the magnetic field. In all these cases, expansion of the contours to the right is understood from the fact that the Lorentz force influences the solution of the N-S equations, meaning it influences the convective flow in the medium, which in turn influences the development of the concentration profiles of the species. It is also observed that most of the fluid flow is confined to the working electrode region, because of the zero-flux boundary condition for the redox species at the counter electrode. As time proceeds, the flow field becomes stronger near the working electrode. It is to be noted that the magnitude of the concentrations is given in kmol/m^3 .

The development of the velocity vectors at specific times from the start is reported next. The magnitude of the velocities is given in m/s. Figure 3.13 illustrates the velocity vectors at time 2s from start.

Figure 3.13. Velocity Vectors Under Magnetic Field at Time 2s

The gradual formation of a counter-clockwise vortex near the working electrode is observed. This vortex develops with time, as the influence of the Lorentz force on the flow field increases. Figure 3.14 illustrates the velocity vectors at time 6s.

Figure 3.14. Velocity Vectors Under Magnetic Field at Time 6s

The region of the flow field affected has increased from a time of 2s to 6s. The formation of this vortex is due to the presence of the Lorentz force. As overpotential at the working electrode is positive, the y -component of current density points in the positive- y direction, i.e. away the electrode. Hence, based on the right hand rule, the x -component of Lorentz force points in the positive- x direction, and thereby causing the counter-clockwise convective motion. Also, the y -component of Lorentz force is in the negative- y at the left edge of the working electrode and in the positive- y direction at the right edge. This is because the x -component of current points in the positive- x and negative- x directions, respectively, at the left and right edge of the electrode. Thus, the rightward, upward and downward directions of the Lorentz force at the surface, right edge, and left edge, respectively, of the working electrode sets up the counter-clockwise motion as seen in the figure. It is noted that with further increase in time, the vortex strengthens. Figure 3.15 illustrates the velocity vectors at time 15s from start.

Figure 3.15. Velocity Vectors Under Magnetic Field at Time 15s

3.5.2. Cyclic Voltammetry. This is the most widely used technique for characterization of redox systems, providing qualitative information about electrochemical reactions. The power of Cyclic Voltammetry results from its ability to provide considerable information on the thermodynamics of redox processes and the kinetics of heterogeneous electron-transfer reactions. Cyclic Voltammetry consists of scanning linearly the overpotential of a working electrode using a triangular overpotential waveform. Figure 3.16 illustrates the potential sweep waveform.

Figure 3.16. Potential Sweep Waveform Employed in Simulations

Present simulations involve only one cycle of the waveform. The current density at the working electrode surface has been noted and plotted against the overpotential to generate the desired Cyclic Voltammogram (CV) at particular potential sweep rates.

3.5.2.1 Absence of magnetic field. Here, CVs are obtained from numerical simulations for potential sweep rates of 5, 10, 20, and 40 mV/s. Figure 3.17 illustrates current density responses against swept overpotential at various sweep rates.

Figure 3.17. Simulated CV at Various Potential Sweep Rates

When different sweep rates have been employed, it is observed that each curve has the same form, but the total current density increases with increasing sweep rate. This phenomena can be rationalized by the size of diffusion layer and the time taken to record the sweep. As current density is proportional to the flux at the electrode surface, it can be concluded that the flux at the electrode surface is considerably smaller at slow sweep rates that it is at faster sweep rates. These current density responses against varying sweep rates are in accordance to published experimental results [1]. Also, normalization of the Cyclic Voltammograms has been done by dividing the current density response by

the square root of the respective sweep rates. On normalization, Cyclic Voltammograms are supposed to collapse on top of each other, depicting potential sweep rate independence. In the present simulation case, normalization does not perfectly collapse the curves on each other, but the very near results obtained are quite encouraging, keeping in mind that the simulations were done on a two-dimensional domain compared to the practical three-dimensional experimental setup. Figure 3.18 illustrates the normalized curves in relation to Figure 3.17.

Figure 3.18. Normalized Cyclic Voltammograms

Reported values of the standard reaction rate constant vary over several orders of magnitude. To provide some insight into the effect of the value of the rate constant on the results, Cyclic Voltammograms were obtained from numerical simulation by varying standard reaction rate constants, keeping all other parameters unchanged. The standard reaction rate constants were varied from values on the order of 10^{-2} m/s to 10^{-5} m/s. Varying the standard reaction rate constant in the present simulations, it has been possible to move the position of occurrence of the maximum current density. Using lower

standard reaction rate constant values, the peak-to-peak separation has been increased. Also, lesser magnitude of the maximum current density has been obtained by decreasing the standard reaction rate constant. Figure 3.19 illustrates the influence of standard reaction rate constants on the shape of the Cyclic Voltammograms.

Figure 3.19. CV Under Various Standard Reaction Rate Constants

Keeping other parameters unchanged, simulation cases have been run with different initial concentration values of species R and have witnessed that the maximum current density can be increased with increase in initial species R concentration.

3.5.2.2 Presence of magnetic field. CVs have been obtained in the presence of a magnetic field of intensity 1.75Tesla. The sweep rate used was 20mV/s and a standard reaction rate constant of $5.5 \times 10^{-11} \text{ m}^2/\text{s}$. Figure 3.20 illustrates the CV obtained from numerical simulation in the absence and presence of the magnetic field.

Figure 3.20. CV in the Absence and Presence of Magnetic Field

This Cyclic Voltammogram generated numerically is compared with that obtained experimentally by Leventis et al. [1]. Figure 3.21 illustrates the published experimental results.

Figure 3.21. Published Experimental Results from Leventis et al. (1998)

On comparison of the numerical and experimental Voltammograms in the absence of magnetic field, it is found that both have comparable peak current densities. The experimental anodic and cathodic peak currents are 38×10^{-6} and -23×10^{-6} A, respectively, when measured from the published diagrams. These measured currents correspond to current densities of 18.9 and -11.44 A/m^2 , respectively, since the area of the electrode used was 0.0201 cm^2 . The numerical peak current densities obtained from the present numerical simulations are 16.25 and -11.58 A/m^2 . Hence, it can be easily recognized the high degree of agreement between the values. The small differences in the current density values can be attributed to the fact that the experimental data corresponds to a three-dimensional domain with circular electrode, compared to the two-dimensional geometry with band electrodes that have been used for the present simulations. The current density response obtained in the presence of the magnetic field also shows a very high degree of agreement. It has been possible to reproduce through simulations, for the very first time, the current density behavior of redox magneto hydro dynamics phenomena. These simulations have been able to generate the steady-state mass-transport-limited current density behavior of Cyclic Voltammograms under magnetic field.

4. SIMULATION OF REDOX MHD IN MICROELECTRODE SYSTEMS

4.1. INTRODUCTION

Practical microelectrode systems comprises working electrodes which have their critical dimension as width w , in the range above $25\mu\text{m}$. The length can be much larger, even in the centimeters range. These bands of microelectrodes can be fabricated together to form micro-channels, and when placed in a small volume cell containing redox species, can be used to study electrochemical phenomena in micro-band electrode arrays. Redox MHD can be used to induce fluid convection around these inter-digitated microelectrode band array. Redox MHD is of importance in the field of microfluidics, where it is necessary to control the flow of small volumes of fluid in micro-channels.

The need for redox MHD in microelectrode systems is understood from the fact that, though several methods presently exist to control and move small volumes of fluids, namely, electro-kinetic, mechanical and centrifugal pumping, there are limitations.

The electro-kinetic method, though gives better control and ease of changing flow direction, its sensitivity to channel materials is a major disadvantage. Miniaturization is difficult with the mechanical method of pumping. Centrifugal method is incapable of reversing the flow direction. Redox MHD has features that can complement these methods – ability to operate under both aqueous and non-aqueous solutions, ease of switching the flow direction, no moving parts and no bubble formation and negligible joule heating.

4.2. EXPERIMENTAL SETUP AND RESULTS

Extensive experiments involving redox MHD around microelectrode arrays have been carried out by Fritsch et al. [33]. They fabricated and used a silicon chip having an array of individually addressable micro-band electrodes. Figure 4.1 illustrates the experimental setup used.

Figure 4.1. Experimental Setup Used by Fritsch et al. [33] for Redox MHD Around Microelectrode Arrays

Based on the biasing, any one or more of the microbands can be made to serve as the working electrode. Figure 4.2 illustrates the microband electrode array chip used.

Figure 4.2. Microband Electrode Array Chip Used by Fritsch et al. [33]

There were 16 microbands in the array region, each 2mm long. Width of the microbands were 25 μm , 50 μm and 100 μm - in different chips used in the experiments. The reference and counter electrodes were placed on the chip itself. The height of the

microcell was $350\mu\text{m}$. Figure 4.3 illustrates the exact dimensions of the array chip used for the $50\mu\text{m}$ width electrodes with $50\mu\text{m}$ gaps.

Figure 4.3. Dimensions of the 50 by 50 Microband Electrode Array (Fritsch et al. [33])

The flow induced due to MHD was monitored with the help of polystyrene beads of dimension $10\mu\text{m}$ and a digital video camera. The results show that when electrodes were oppositely biased, they produced Lorentz force in the same direction, leading to additive flow in between the microelectrodes. Figure 4.4 illustrates the nature of flow obtained from experiments on opposing bias of electrodes.

Figure 4.4. Nature of Flow and Direction of Lorentz Force Between Two Oppositely Biased Electrodes (Fritsch et al. [33])

Also, experiments were carried out with electrodes biased in the same way. It was observed that the generated Lorentz force in between the microelectrodes opposed each other. Figure 4.5 illustrates the nature of flow obtained on similarly biased electrodes.

Figure 4.5. Nature of Flow and Direction of Lorentz Force Between Two Similarly Biased Electrodes (Fritsch et al. [33])

The use of scanning electrochemical microscopy (SECM) to image the convection around the microband arrays needs to be supplemented with computer-based modeling and simulation to highlight more clearly not only the flow features, but also to delineate the various mechanisms at play. Such modeling and numerical simulation can be used to quickly and inexpensively develop the effects of various microelectrode dimensions and orientations on the nature of the flow. These simulations will aid in better control of the fluid flow through micro-channels induced by redox MHD.

4.3. MODELING AND SIMULATION SETUP

The mathematical model used to simulate redox MHD in an array of microelectrodes is exactly the same as used in the case of millielectrodes systems, as presented in Section 3.4. The same set of N-S equations needs to be solved involving the flow, momentum and species conservation equation. The flux will be calculated similarly

using the surface reaction in Arrhenius form, thereby implementing the electrode surface boundary conditions via the heterogeneous surface reactions. The only difference is that the three-dimensional form of these equations, which has an additional momentum equation in the z-direction, will be used, instead of the two-dimensional ones.

For the calculation of the Lorentz force, all three components of the current density vector will be used, which is $\vec{j} = j_x \mathbf{e}_x + j_y \mathbf{e}_y + j_z \mathbf{e}_z$. Hence, on taking the cross product with a uniform magnetic flux in the positive z direction, the Lorentz force would be given by $\vec{F}_L = \vec{j} \times \vec{B} = (j_x \mathbf{e}_x + j_y \mathbf{e}_y + j_z \mathbf{e}_z) \times B \mathbf{e}_z = -j_x B \mathbf{e}_y + j_y B \mathbf{e}_x$.

In this case, a three-dimensional solver model was chosen instead of a two-dimensional one. The unsteady formulation and solution algorithms chosen were the same as in the two-dimensional case. Here also, the solver was instructed to store the mass fraction gradients. However, due to the enormous number of cells generated from the customized meshing of the three-dimensional cell, insufficient memory allocation problems had to be bypassed by simplifying the geometry to a certain extent, but without influencing the main features of the solution.

4.4. SIMULATION GEOMETRY

While a two-dimensional computational domain was used to simulate the millielectrode system, here a three-dimensional computational domain will be employed to replicate the exact experimental setup. The experimental setup used by Fritsch et al. [33] for the redox MHD study had 16 microband working electrodes. In the present simulations, only 4 such microbands will be used. This simplification will capture the main features of the experimentally observed flow field, but will help reduce the computational time and overcome any hardware constraints, like insufficient memory, involved with such complex numerical simulation approaches. More powerful hardware will help remove this limitation. Figure 4.6 illustrates the bottom surface of the computational domain used for the present simulations involving 100 by 100 microelectrode array systems.

Figure 4.6. Dimensions of the Bottom Surface of the Three-Dimensional Computational Domain Hosting the 4 Microband Electrode Arrays

The height of the three-dimensional domain is 0.35mm. Figure 4.7 illustrates the actual meshed geometry of the three-dimensional domain.

Figure 4.7. Meshed Three-Dimensional Computational Domain

The three-dimensional meshed geometry had approximately 1.03 million cells. It can be noted that similar to the two-dimensional meshing, the finite difference grid is clustered near the working microband electrodes, so as to capture the fine features of the processes taking place in the region. This clustering extends through the computational volume in the z-direction, in the region close to the microband electrodes.

4.5. SIMULATION RESULTS AND DISCUSSION

For the present case, the same redox species and supporting electrolyte are used. All parameters involving the redox species and supporting electrolyte are kept the same. The only difference being that both the oxidized and reduced species are present initially with a concentration of 10.89mM, which corresponds to 0.002156 mass fraction of each species. The potential step method is used, with the overpotential applied being 0.7V. The magnetic field intensity is 1.75 Tesla, applied in the positive z direction.

4.5.1. 100 by100 Microelectrode Array Systems. Here, the width of the micro-band electrodes is 100 μ m or 0.1mm, and the separation between consecutive electrodes is also 100 μ m .

4.5.1.1 Alternate electrodes with opposite bias. Velocity vectors and contours of redox species concentrations are noted. Figure 4.8 illustrates the velocity vectors at time 10s from start on a plane parallel to the xy-plane and parallel to the bottom surface.

Figure 4.8. Velocity Vectors at Time 10s on a Plane Parallel to the XY-Plane, at 7.7×10^{-19} m from bottom plane

The strong effect of MHD Lorentz force on the flow field can be clearly seen. It is seen that because of opposite biasing of the alternate microelectrodes, velocity of flow in between them is very strong, with the flow taking place in the same direction. This verifies the experimental results which state that flow in such cases is additive [34]. It is also noted that small vortices begin to form at the ends between two oppositely biased electrodes. The current was calculated and was found to be $1.351 \mu\text{A}$ at a time 10s from start. Figure 4.9 illustrates the velocity vectors at time of 10s, on a plane parallel to the xy-plane, but midway in the domain.

Figure 4.9. Velocity Vectors at Time 10s on a Plane Parallel to the XY-Plane, Midway in the Domain

Here it is seen how the flow extends into the whole three-dimensional domain. It is seen that strong vortices are formed in the region of the microelectrode arrays, extending into the whole volume. Alternate clockwise and counter-clockwise vortices are observed. Figure 4.10 illustrates the concentration contours of species O, as it has developed at 10s from start, on a plane parallel to the xy-plane, and parallel to the bottom surface.

Figure 4.10. Concentration Contours of Species 'O' at Time 10s on a Plane Parallel to the XY-Plane, at 7.7×10^{-19} m from bottom plane

The concentration contours clearly reflect the influence of the MHD Lorentz force on the medium, with thin diffusion layers along the length of the band electrodes, in between oppositely biased electrodes. The reason for this is the additive nature of the Lorentz force.

4.5.1.2 Extreme electrodes with same bias. Here, the first (topmost) and the fourth (bottom) electrodes are given the same bias. The electrodes in between them, i.e. the second and third electrodes are without any potential bias. Figure 4.11 illustrates the velocity vectors at time 10s, on a plane parallel to the xy-plane, but parallel to the bottom surface of the domain.

Figure 4.11. Velocity Vectors at Time 10s on a Plane Parallel to the XY-Plane, at 7.7×10^{-19} m from bottom plane

The vectors show clearly that the flow in between the two extreme band electrodes have opposing Lorentz force effects, due to which, a counter-clockwise vortex of considerable size, all along the length of the electrode, is formed in between the extreme electrodes. This vortex influences the flow at the ends of adjacent electrodes, resulting in the gradual formation of vortices. These results agree with the experimental results available, from which it is expected that in such cases the flow between the extreme electrodes will have opposing Lorentz force effects. This opposing nature of flow is obtained through the present simulations. Figure 4.12 illustrates the velocity vectors at time 10s, on a plane parallel to the xy-plane, but midway in the domain.

Figure 4.12. Velocity Vectors at Time 10s on a Plane Parallel to the XY-Plane, Midway in the Domain

The flow obtained here is quite complicated. It can be seen that on the xy-plane midway in the z-direction, a number of clockwise and counter-clockwise vortices are formed in the electrode array region. Two large counter-clockwise vortices are formed at the ends of the first and fourth electrodes along their length. These two vortices interact with the large counter-clockwise vortex along the length in between the first and fourth electrodes, resulting in the formation of two clockwise vortices on the left and right side of the array region. It needs to be also noted that the large counter-clockwise vortex in between the first and fourth electrodes slowly start to disintegrate into two separate counter-clockwise vortices. Figure 4.13 illustrates the concentration contours of species O, as it has developed at 10s from start, on a plane parallel to the xy-plane, and parallel to the bottom surface.

Figure 4.13. Concentration Contours of Species 'O' at Time 10s on a Plane Parallel to the XY-Plane, at 7.7×10^{-19} m from bottom plane

4.5.1.3 Extreme electrodes with opposite bias. Here, the extreme, i.e. the first and the fourth electrodes have opposite bias, while the in between ones have no biasing. Figure 4.14 illustrates the velocity vectors at time 10s along a plane parallel to the xy-plane, and parallel to the bottom surface.

Figure 4.14. Velocity Vectors at Time 10s on a Plane Parallel to the XY-Plane, at 7.7×10^{-19} m from bottom plane

It can be clearly seen that the whole region in between the two oppositely biased electrodes have velocities in the same direction. This can be attributed to the additive nature of Lorentz force in between oppositely biased electrodes. This again conforms with the experimental findings. The current was calculated and was found to be $0.741 \mu\text{A}$. Figure 4.15 illustrates the velocity vectors at time 10s, on a plane parallel to the xy-plane, but midway in the domain.

Figure 4.15. Velocity Vectors at Time 10s on a Plane Parallel to the XY-Plane, Midway in the Domain

Here it is seen that vortices again start to form surrounding the electrode array region. A thin, elongated clockwise vortex forms in between the first and second electrode region. In between the third and fourth electrode region a similar vortex forms, but in the counter-clockwise direction. Figure 4.16 illustrates the concentration contours of species O, as it has developed at 10s from start, on a plane parallel to the xy-plane, and parallel to the bottom surface.

Figure 4.16. Concentration Contours of Species 'O' at Time 10s on a Plane Parallel to the XY-Plane, at 7.7×10^{-19} m from bottom plane

4.5.1.4 Adjacent electrode pairs having opposite bias. In this configuration, microband electrodes one and two have the same bias, while electrodes three and four have biasing opposite to that what the first and second have. Figure 4.17 illustrates the velocity vectors at time 10s along a plane parallel to the xy-plane, and parallel to the bottom surface.

Figure 4.17. Velocity Vectors at Time 10s on a Plane Parallel to the XY-Plane, at 7.7×10^{-19} m from bottom plane

The region in between the second and third electrode has oppositely biased electrodes on its two sides, and hence reflects an additive nature of flow in this region as expected. Electrodes one and two have same biasing and reflect the opposing nature of flow. The same opposing nature of flow is observed between the third and fourth electrodes. Current was calculated, and came out to be $0.91 \mu\text{A}$. Figure 4.18 illustrates the velocity vectors at time 10s, on a plane parallel to the xy-plane, but midway in the domain.

Figure 4.18. Velocity Vectors at Time 10s on a Plane Parallel to the XY-Plane, Midway in the Domain

Again, it can be noted, on moving into the volume of the cell, formation of vortices and their interactions can be observed. The region surrounding electrodes one and two shows the formation of an elongated clockwise vortex. On the other hand, region comprising electrodes three and four depicts the formation of a counter-clockwise vortex. Figure 4.19 illustrates the concentration contours of species O, as it has developed at 10s from start, on a plane parallel to the xy-plane, and parallel to the bottom surface.

Figure 4.19. Concentration Contours of Species 'O' at Time 10s on a Plane Parallel to the XY-Plane, at 7.7×10^{-19} m from bottom plane

4.5.1.5 All electrodes having same bias. In this configuration, all the four microband electrodes have the same bias. Figure 4.20 illustrates the velocity vectors at time 10s along a plane parallel to the xy-plane, and parallel to the bottom surface.

Figure 4.20. Velocity Vectors at Time 10s on a Plane Parallel to the XY-Plane, at 7.7×10^{-19} m from bottom plane

Here, a gradual formation of localized vortices can be observed. Because all the electrodes have the same bias, the flow in between them gets opposed, resulting in negligible flow in the array region. Figure 4.21 illustrates the velocity vectors at time 10s, on a plane parallel to the xy-plane, but midway in the domain.

Figure 4.21. Velocity Vectors at Time 10s on a Plane Parallel to the XY-Plane, Midway in the Domain

A very large elongated clockwise vortex has formed in the region between the first and third electrodes. Also, two smaller clockwise vortices have formed at the ends of the elongated vortex. Two large counter-clockwise vortices can also be observed on the outside region of the first and fourth electrodes. Figure 4.22 illustrates the concentration contours of species O, as it has developed at 10s from start, on a plane parallel to the xy-plane, and parallel to the bottom surface.

Figure 4.22. Concentration Contours of Species 'O' at Time 10s on a Plane Parallel to the XY-Plane, at 7.7×10^{-19} m from bottom plane

4.5.2. 50 by 50 Microelectrode Array Systems. Here, the width of the microband electrodes is $50\mu\text{m}$ or 0.05mm , and the separation between consecutive electrodes being also $50\mu\text{m}$. For 50 by 50 microelectrode array systems, only the results for alternately biased electrodes and extreme biased electrodes are presented.

4.5.2.1 Alternate electrodes with opposite bias. Here, the velocity vectors and the concentration contours are noted. Figure 4.23 illustrates the velocity vectors at time 10s along a plane parallel to the xy-plane, and parallel to the bottom surface.

Figure 4.23. Velocity Vectors at Time 10s on a Plane Parallel to the XY-Plane, at 7.7×10^{-19} m from bottom plane

The nature of the flow obtained is identical to that obtained under same circumstances for the 100 by 100 electrode system. The current was calculated and found to be $0.95 \mu\text{A}$. For the same configuration and parameters, the 100 by 100 electrode system gave a current of $1.351 \mu\text{A}$. This is expected, because with decrease in electrode surface area and separation distance, lower current was observed through experiments by Fritsch et al. [33]. Figure 4.24 illustrates the velocity vectors at time 10s, on a plane parallel to the xy-plane, but midway in the domain.

Figure 4.24. Velocity Vectors at Time 10s on a Plane Parallel to the XY-Plane, Midway in the Domain

When the velocity vectors here are compared with the ones obtained under same circumstances for the 100 by 100 electrode arrays, it is noted that the alternating clockwise and counter-clockwise vortices have given way, and flow in one particular direction is obtained in the region containing the second and third electrodes. Also, it is noted that the magnitude of the velocities obtained is also less by a factor of ~ 0.1 .

4.5.2.2 Extreme electrodes with same bias. Here, only the velocity vectors are noted. Figure 4.25 illustrates the velocity vectors at time 10s along a plane parallel to the xy-plane, and parallel to the bottom surface.

Figure 4.25. Velocity Vectors at Time 10s on a Plane Parallel to the XY-Plane, at 7.7×10^{-19} m from bottom plane

The nature of the flow obtained here is identical to the one obtained for the simulations with the 100 by 100 electrode system. Here too, it is found that an elongated counter-clockwise vortex is formed in the region between the first and the fourth electrodes. Also, the magnitudes of the velocities obtained are in the same order.

5. CONCLUSION

This thesis summarizes the realization of the modeling and numerical simulation of MHD convection in a redox electrochemical cell. The mathematical model associated with the present simulation approach to solve the electrochemical MHD phenomena has been presented. Mathematical resolution of the desired equation system has been made possible by the finite volume method of programming in the FLUENT code.

This approach not only aids our understanding of the electrochemical MHD phenomena, but also gives us a picture of the flow field and concentration field as it develops with time. Lorentz force is found to exert great influence on the process. Results show how voltage biasing and magnetic field application can be used as controlling parameters for fluidic control. The good agreement of numerical solution with the approximate analytical solution and experimental results from published literature validates the results obtained here. With customized meshing of the two-dimensional domain for the millielectrode system and three-dimensional domain for the microelectrode system, it has been possible to obtain highly accurate numerical solutions. In the two-dimensional setup, the small size of the working electrode used is more similar to experimental geometries. Also, through the present three-dimensional simulation for redox MHD in microelectrode systems, it has been possible to show, for the first time, how the velocity and flow field develops in such microchannels under Lorentz force. These findings will prove to be a decisive step in controlling fluid flow through microchannels, and influence the design and orientation of electrodes used for such purposes. These simulations can be used to quickly and inexpensively develop lab-on-a-chip for microfluidic purposes. The vortices formed in the medium, contours of concentration of redox species, and most importantly the development of velocity vectors reported through these simulations will aid in better understanding of the electrochemical MHD phenomena. The numerical modeling framework developed here will help to explore the flow features under different geometries and different experimental parameters.

APPENDIX

CALCULATION OF REDOX SPECIES MASS FRACTION

In order to study the MHD effect, the electrolyte used was $\text{CH}_3\text{CN}/0.5\text{M TBAP}$. CH_3CN has a molecular weight of 41.05 kg/kmol and a density of 776.49 kg/m³. The molecular weight of TBAP is 341.92 kg/kmol. The redox species used was TMPD with a molecular weight of 164.25 kg/kmol and its concentration was 10.89 mM. If initially only the reduced form of the redox species, i.e. R, is present, then it is required to find the mass fraction of this species R, corresponding to its concentration 10.89 mM, so that the problem can be setup in FLUENT.

Calculation of resultant molecular weight of electrolyte is as follows:

Density of acetonitrile $\rho_{\text{AN}} = 776.49 \text{ kg/m}^3 = 0.77649 \text{ g/cm}^3 = 776.49 \text{ g/L}$

Hence, 1L acetonitrile has 776.49 g of acetonitrile

This implies 1L acetonitrile contains $776.49/41.05 = 18.916$ moles of acetonitrile

Concentration of TBAP is i.e. 0.5 M = 0.5 moles/L

Hence, total moles in 1L solution = $18.916 + 0.5 = 19.416$ moles

Mole fraction of acetonitrile = $X_{\text{AN}} = 18.916/19.416 = 0.97425$

Mole fraction of TBAP = $X_{\text{TBAP}} = 0.5/19.416 = 0.02575$

Hence, resultant molecular weight of electrolyte

$$= M_{\text{AN}} \cdot X_{\text{AN}} + M_{\text{TBAP}} \cdot X_{\text{TBAP}}$$

$$= 41.05 \times 0.97425 + 341.92 \times 0.02575 = 48.797 \text{ kg/kmol}$$

The initial mass fraction of the reduced species can now be calculated as follows:

1L solution has 10.89×10^{-3} moles of TMPD = $10.89 \times 10^{-3} \times 164.25 = 1.7887$ g of TMPD

$$\text{Total mass of 1L solution} = \underbrace{1.7887}_{\text{TMPD}} + \underbrace{826.1}_{\text{CH}_3\text{CN}/0.5\text{M TBAP}} = 827.8887 \text{ g}$$

Mass Fraction of TMPD i.e. species 'O' = $1.7887/827.8887 = 0.00216 = 2.16 \times 10^{-3}$

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