Factors Affecting Redox Magnetohydrodynamics for Flow in Small Volumes

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FACTORS AFFECTING REDOX MAGNETOHYDRODYNAMICS FOR FLOW IN SMALL VOLUMES
FACTORS AFFECTING REDOX MAGNETOHYDRODYNAMICS FOR FLOW IN SMALL VOLUMES

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Microelectronics-Photonics

By

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Milwaukee School of Engineering
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August 2009
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Abstract

Lab-on-a-chip technologies offer the possibility of developing analytical devices that are low-cost, portable, disposable, fast, and operable by non-technical personnel. Such devices require automated methods to manipulate ultra-small volumes (picoliters) of samples and solution, including pumping, stirring, and positioning. Current methods for ultra-small volume microfluidics have limitations that restrict their use including high voltage requirements, disadvantageous flow profiles or rates, and relatively complicated fabrication due to mechanical parts. Redox magnetohydrodynamics (RMHD) that utilizes permanent magnets for portability shows promise as a micropump with ease of switching flow direction, no moving parts, compatibility with both aqueous and non-aqueous solutions, low voltages (10-100 mV), and ability to easily pump in a loop. But its fundamentals, including the forces involved and what factors affect the flow profile, must be better understood before its full potential can be realized.

Fluid flow in both cells and channels for RMHD systems utilizing high concentration of redox species in supporting electrolyte was investigated. The effects of the placement of walls of the cell and passive (unbiased) conductors relative to active electrodes on fluid flow using RMHD in cells provided evidence that the magnetic force resides primarily in the diffusion layer in these systems, not in the electrolyte between the counter and working electrodes. The effects of channel and working electrode geometry also supported this conclusion. The outcome has important ramifications in designing microfluidic devices that employ RMHD as the pumping method and in the simulation of RMHD.
This thesis is approved for
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Chapter 1: Background

1.1 Lab-on-a-Chip Technologies

Lab-on-a-chip technologies offer the possibility of developing analytical devices that are low-cost, portable, disposable, fast, and operable by non-technical personnel. Such devices require automated methods to manipulate ultra-small volumes (picoliters) of samples and solution, including pumping, stirring, and positioning. Current methods for ultra-small volume microfluidics have one or more limitations that restrict their use including high voltage requirements, disadvantageous flow profiles or rates, and relatively complicated fabrication due to mechanical parts. Redox magnetohydrodynamics (RMHD) that utilizes permanent magnets for portability shows promise as a micropump with ease of switching flow direction, no moving parts, compatibility with both aqueous and non-aqueous solutions, low voltages (10-100 mV), and ability to easily pump in a loop.\(^1\)\(^-\)\(^3\) But its fundamentals, including the forces involved and what factors affect the flow profile, must be better understood before its full potential can be realized.

1.2 Current Micropump Technologies

Micropumps can be separated into two categories: mechanical and non-mechanical. Mechanical pumps use a physical mechanism to transfer kinetic energy to the fluid. Some types of mechanical micropumps include electrostatic, piezoelectric,
thermo-pneumatic, bimetallic, shape memory alloy, ion conductive polymer film, electromagnetic, and phase change type micropumps. Mechanical micropumps are generally more complicated to fabricate because they have moving parts and are therefore less likely to be suitable for portable, disposable devices.

Non-mechanical micropumps convert various forms of stored energy into kinetic energy in the fluid. Some examples of non-mechanical micropumps include magnetohydrodynamic (MHD), electrohydrodynamic, electroosmotic, electrowetting, bubble type, flexural planar wave, electrochemical, and evaporation type micropumps. They are generally easier to manufacture because they do not have moving parts. However, some non-mechanical micropumps—certain subcategories of MHD, electrohydrodynamic, electroosmotic, and bubble type—have the limitation of high voltage requirements, and are therefore less suitable for portable devices. Also, some non-mechanical micropumps—including bubble type, electroosmotic, evaporation based, flexural planar wave, and electrochemical—have very low flow rates, which may limit their use for certain applications.

MHD micropumps can be further subcategorized into ac, dc, and redox micropumps. AC MHD micropumps use high voltages (which limits portability) and have electrode heating due to induced eddy currents (which limits what samples could be processed). DC MHD micropumps also use high voltages, which result in bubble formation due to electrolysis and short electrode lifetimes, limiting the scope of viable applications. Redox MHD (RMHD) micropumps have multiple advantages over the other MHD micropumps, which stem from the low voltage requirements (less than 1V) due to presence of redox species: no bubble issues (dc) or eddy current electrode heating
These advantages give RMHD high potential for use in microfluidic applications, though there are limitations to consider. The presence of redox species can interfere with detection for some analytical experiments. Reducing the necessary redox species concentration or separating the pumping fluid from the fluid of interest for testing could help eliminate this potential problem. Although RMHD can pump in a loop, pumping against pressure gradients has not been demonstrated. This becomes an issue in dealing with the backpressures established when using open-air reservoirs.

1.3 The Forces Involved in RMHD

The three main forces described in the literature for RMHD flow using permanent magnets are the magnetic force, magnetic gradient force, and paramagnetic concentration gradient force. Although each will be presented, the magnetic force is of primary concern for this study and will be the focus in the discussion of experimental results.

1.3.1 The Magnetic Force

The magnetic force, $F_B$—also referred to as the magnetohydrodynamic force in the literature—is the most studied of the three forces. It accounts for the interaction of an electrically conducting fluid with an externally applied magnetic field, and is derived from the Lorentz equation:

$$F_L = q (E + v \times B)$$

Equation 1
where $F_L$ (N) is the vector force acting on the ions, $q$ (C) is the ion charge, $E$ (V/m) is the electric field vector, $v$ is the ion velocity vector (m/s), and $B$ (T) is the magnetic field vector. When the second term, which is associated with the magnetic field, is volume normalized, the magnetic force results:

$$F_B = j \times B$$

Equation 2

where $F_B$ (N m$^{-3}$) is the vector force acting on the ions, $j$ (C sec$^{-1}$ cm$^{-2}$) is the vector flux of ions, and $B$ (T) is the externally applied magnetic field vector. The flux of ions can be initiated by oxidation or reduction at an electrode. Net ion movement results from diffusion that equilibrates concentration gradients, charge compensation (migration), and density gradients.\(^7\)

### 1.3.2 The Magnetic Gradient Force

The magnetic gradient force should be considered when the externally applied magnetic field is not uniform, as is typically the case when using permanent magnets. There is not a complete consensus within literature published on the magnetic gradient force as to the appropriate equation to describe it\(^8-19\)—the reader is cautioned to take special care as to the vector notation used in different publications to ensure the proper mathematical equation is used in the interpretation of results—but upon examination of its derivation, the following equation is proposed for the magnetic gradient force, $F_{\varphi B}$, given the parameters of the redox systems studied here:

$$F_{\varphi B} = 2 N_A C_D [(m^*)^2 / kT] (B \cdot \nabla)B$$

Equation 3
where \( N_A \) is Avogadro’s number, \( C_D \) is the concentration of the dipolar species with spin \( \frac{1}{2} \), \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( \mathbf{B} \) is the effective magnetic field in the electrolytic medium, \( m^* \) is \( g(\frac{1}{2})\mu_B \), \( g \) is the Lande’s g factor, and \( \mu_B \) is the Bohr magneton. The derivation for the magnetic gradient force is based on the gradient in magnetic energy per unit volume in the solution, which also gives rise to the paramagnetic concentration gradient force. A detailed derivation is included in Appendix F.

### 1.3.3 The Paramagnetic Concentration Gradient Force

The paramagnetic concentration gradient force, \( F_{\varphi C} \), is currently under debate. Leventis and Dass\(^{20}\) give a thorough history of the debate, starting from its first appearance in literature, as well as evidence of its effects in an electrochemical system. The equation for the paramagnetic concentration gradient force derived by Leventis and Dass is

\[
F_{\varphi C} = N_A [(m^*)^2 / kT] |\mathbf{B}|^2 \nabla C 
\]

A counter-argument is given by Coey \etal\(^{21}\).

### 1.4 Passive Conductor Effects

In a redox system, passive conductors can have an equilibration effect on the concentration of redox species immediately surrounding them by allowing electron transfer through the passive conductor. This principle has been especially studied in the
field of scanning electrochemical microscopy (SECM)\textsuperscript{22-25}. An illustration of this effect is shown in Figure 1.4.1. Passive conductors could be used to manipulate gradient-driven flux of ions because they redistribute the ratio of oxidized-to-reduced forms of the redox species, and thus where in solution the magnetic force is applied, as shown in Figure 1.4.2. For this reason, studying the effect of passive conductors in redox systems is of interest to the design of RMHD micropumps.

Figure 1.4.1: Effect of passive conductor on concentration in redox system

Figure 1.4.2: Effect of passive conductor on magnetic force in redox system (not to scale)
1.5 Fabrication Materials and Methods

1.5.1 Chip Design

The chips designed for use in experiments in Chapter 2 and 3 were modifications on a design reported by Anderson for individually addressable microband electrodes in an array. Four copies each of three different chip designs were included on the first wafer, MATT1, whose autoCAD layout is shown in Figure 1.5.1.1. The autoCAD layout for the first chip design, DES1, is shown in Figure 1.5.1.2 with “g” indicating a gap dimension and “e” indicating an electrode dimension. In her investigation of RMHD flow using microelectrode arrays, Anderson reported on the effects of electrode size for a single pumping electrode and the effect of pumping electrode spacing for reinforcing and opposing flows. Though passive conductors were present within the diffusion length at times reported in her experiments, she did not report on any effects they may have on the magnetic force spatial distribution or flow profile for her experiments. DES1 allowed for testing the flow profile for reinforcing, opposing, and single pumping electrode flows using 50 µm wide pumping electrodes spaced 650 µm apart, with and without a passive conductor located within the diffusion length. This thesis did not report any experimental results using DES1.

The second design, DES2, is shown in Figure 1.5.1.3. This design also allowed for testing the flow profile of reinforcing and opposing flows with pumping electrodes spaced 650 µm apart, with and without passive conductors between the pumping electrodes. DES2 used 650 µm wide pumping electrodes so that the opposing magnetic forces on each side of the pumping electrode would be sufficiently separated to identify
Figure 1.5.1.1: MATT1 AutoCAD wafer design. Black lines represent dicing lines.
Figure 1.5.1.2: DES1 AutoCAD chip design
Figure 1.5.1.3: DES2 AutoCAD chip design
changes in the flow profile over the pumping electrodes. DES2 was used for experiments reported in Chapter 2 and 3.

The third design, DES3, is shown in Figure 1.5.1.4. This design allowed for comparing reinforcing flow using pumping electrodes with a width of 650 µm spaced 50 µm apart with the same electrodes spaced 650 µm apart from DES2. It also allowed for comparing flow using a single pumping electrode with a width of 650 µm and a passive conductor 50 µm away from its edge with the same setup but without a passive conductor (DES2). DES3 also allowed for testing reinforcing flow using 50 µm-wide pumping electrodes with an array of 50 µm passive conductors between. DES3 was used for experiments reported in Chapter 3.

The second wafer design, CGRAD1, contained six chip designs for the concentration gradient tracking experiments described in Chapter 5 and the RMHD channel flow experiments described in Chapter 4 and 5. Wafer CGRAD1 is shown in Figure 1.5.1.5. The first chip design, CG1_1, is shown in Figure 1.5.1.6. CG1_1 utilized a 650 µm pumping electrode which could be centered in a large cell. The 10 µm “probe” electrodes on top were spaced so that they occurred in 25 µm increments away from the edge of the pumping electrode for the first 100 µm; then they occurred in 50 µm increments until 300 µm from the edge of the pumping electrode. Below the pumping electrode, the probes were spaced at 100 µm and 300 µm from the edge of the pumping electrode to compare with the probes spaced the same distance above the electrode. By comparing the voltage of probes the same distance apart, the passive conductor effect of the probes above the electrode could be investigated to determine if the 10 µm width significantly affected the diffusion (voltage measurements within 10%). The probe had a
Figure 1.5.1.4: DES3 AutoCAD chip design
Figure 1.5.1.5: Wafer CGRAD1 AutoCAD chip design. Black lines indicate dicing lines.
Figure 1.5.1.6: CG1_1 AutoCAD chip design
10 µm width because this is the resolution limit for photoplots. A width of 2 µm could be used for future chip designs utilizing photomasks after the concept of tracking the concentration gradient in the manner described in Chapter 5 has been experimentally demonstrated.

The second chip design, CG1_2, is shown in Figure 1.5.1.7. This design was identical to CG1_1 with the exception that the first probe above the 650 µm electrode was replaced with a 5.5 mm wide passive conductor. The other dimensions remained the same. This design allowed testing of the effect of a passive conductor with a much larger area than that of the working electrode (almost by a factor of 10) on the flow profile and diffusion layer. The third chip design, CG1_3, is shown in Figure 1.5.1.8. This design allowed for square loop channel pumping, similar to the circular loop channel pumping reported in Chapter 4.

The fourth chip design, CG1_4, is shown in Figure 1.5.1.9. CG1_4 was used in the rectangular loop channel pumping experiments reported in Chapter 4. It allowed for a channel width up to 2 mm, tapered and non-tapered termination of pumping electrodes, variable pumping electrode widths up to 975 µm depending upon channel wall placement, gaps between pumping electrodes of 50 to 800 µm, and corner pumping electrodes where all of the pumping electrodes only spanned a short distance of the channel length. A description of channel width and placement to achieve different pumping electrode setups is included in Section 5.2. The fifth chip design, CG1_5, is shown in Figure 1.5.1.10. CG1_5 was designed with the same rectangular loop channel dimensions as CG1_4, but with pumping electrodes that spanned a little more than half the distance of the channel. Though this design has not yet been tested, it was not
Figure 1.5.1.7: CG1_2 AutoCAD chip design
Figure 1.5.1.8: CG1_3 AutoCAD chip design
Figure 1.5.1.9: CG1_4 AutoCAD chip design
expected to produce circulation across the height or width of the channel. The last chip design, CG1_6, is shown in Figure 1.5.1.11. This design was used for the circular loop channel experiments reported in Chapter 4. This chip was designed with only one pumping electrode that spanned the entire length of the channel. The counter and pseudo-reference electrodes were located in two separate cells connected by channels which stemmed off of the circular loop channel.

1.5.2 Chip Fabrication

The chip designs were photo plotted on transparency masks (Advance Reproductions Corporation, North Andover, MA) for use in fabrication using photolithography techniques. For the metal deposition of all wafers used in chip fabrication, a gold coin (Canadian Maple Leaf, 99.99%) and a chromium plated tungsten rod (Kurt J. Lesker...
Company, Clairton, PA) were used as source materials in an Edwards Auto306 Turbo Thermal Evaporator (West Sussex, England). Layers of 50 Å Cr and 500 Å Au were deposited on each 5” diameter p-doped (111) silicon wafer with 2µm pre-grown thermal SiO₂. The Cr was used to provide adhesion of the gold to the wafer.

For the photolithography process, an Eaton 6000 Spin Coater was used to apply 2.5 µm AZ4110 positive photoresist (Clariant), bake, and cool the gold-coated silicon wafer. A Karl Suss microtec MA150 350 W aligner was used in conjunction with the first dark field photoplot (metal layer) to pattern the photoresist. AZ400k developer (Clariant) was used in a 1:3 ratio of developer to water to develop the photoresist. After the metals were wet etched, the remaining photoresist was exposed for triple the previous exposure time and developed using the same photoresist developer. The wafers were then spin-coated using a MTI MultiFab cassette coater with 5 µm of benzocyclobutene (BCB) 4024-40 negative photoresist (Dow Chemical Co.) after applying a VM652 adhesion promoter (HD Microsystems Ltd.). After soft-baking at 80 °C for 90 s, the
BCB was patterned using the Karl Suss aligner and the second clear field photoplot (BCB layer). The BCB was developed using DS2100 developer. After developing, the wafers were hard baked in a Blue M oven with N₂ curing and peak temperatures of 250 °C for 4 hours. The BCB residue was removed using reactive ion etching (RIE) in a Plasma-Therm SLR720 at 250 mTorr and 200 W with oxygen (O₂) and sulphur hexafluoride (SF₆) gas flow (32 and 8 sccm, respectively) for 30 s. The BCB layer was used to passivate the gold on the chip that should not be exposed to the solution. After RIE, wafers were diced into individual chips using a MicroAutomation Model 1100 Dicing Saw. The number of chips per wafer depends upon the design.

1.5.3 Channel and Cell Wall Fabrication

Walls for the channels and cells were fabricated from poly-dimethyl siloxane (PDMS). The polymer was prepared from a 10:1 ratio by weight of pre-polymer to curing agent. This mixture was degassed using a Welch 2025 self-cleaning vacuum system (Thomas Industries Inc. Skokie, IL) until bubbles were no longer visible. The mixture was transferred to glass cover slides (VWR International) that were pre-cleaned with OS-30 and dried in a VWR oven (Sheldon Manufacturing, Cornelius, OR) at 65 °C for 30 minutes. The slides were spun for 40 s at about 220 rpm using a Model P6700 Spincoater from Specialty Coating Systems Inc (Indianapolis, IN). The PDMS-coated glass cover slides were cured at 100 °C overnight in the VWR oven. After curing, the PDMS was removed from the cover slides by pealing and cut to the correct geometry using a metal stencil and razor blade. PDMS thickness was calculated from a
measurement taken between two glass cover slides using a micrometer. The glass cover slides increase the contact area of the micrometer to the PDMS and thus minimize error from the elasticity of the PDMS.

1.6 Thesis Layout

The remainder of this thesis is organized as follows:

Chapter 2 is a quantitative characterization study for the lateral and vertical flow profiles utilizing large (650 µm) pumping electrodes positioned for reinforcing flow in a cell. This study illustrates pumping in a cell with parabolic lateral and vertical flow profiles.

Chapter 3 is a qualitative study for RMHD in cells where the effect of wall and passive conductor placement with respect to the pumping electrode is investigated. This study provides evidence that the magnetic force is applied primarily within the diffusion layer.

Chapter 4 is a qualitative study for RMHD in channels investigating the effect of channel and pumping electrode geometries on whether circulation across the width or height of the channel occurs. Chapter 5 is a description of suggested future work.
Chapter 2: Lateral and Vertical Flow Characterization of Reinforcing Flow for Wide Microband Electrodes

2.1 Abstract

The steady-state lateral and vertical redox magnetohydrodynamic (RMHD) flow profiles were characterized for wide microband electrodes in a rectangular cell during diffusion-limited chronoamperometry experiments. Polystyrene microbeads were used to visualize the flow in a high concentration 50/50 mixture redox species with supporting electrolyte. Both the vertical and horizontal flow profiles maintained a parabolic nature. The vertical flow profile has a slight offset towards the cell ceiling, which was accounted for by the beads’ tendency to rise.

2.2 Experimental

2.2.1 Chemicals and Materials

Aqueous solutions were prepared from reagent grade deionized water obtained from Ricca Chemical Company (Arlington, TX). Potassium ferricyanide (K₃Fe(CN)₆) was obtained from EM Science (Gibbstown, NJ), potassium ferrocyanide trihydrate (K₄Fe(CN)₆ • 3H₂O) was obtained from JT Baker (Phillipsburg, NJ), and potassium chloride (KCl) was obtained from EMD (Darmstadt, Germany). All chemicals were used as received.
2.2.2 Redox-Magnetohydrodynamic Setup

The cell geometry used in this setup and the positioning of the electrodes within the cell are illustrated in Figure 2.2.2.1. Figure 2.2.2.1b shows the video view focused on the chip surface with the entire length and width of the electrodes not included in the video view. The xyz coordinate system shown was adopted for the remainder of this chapter with u designated as the velocity in the x direction. The silicon chip (DES2) patterned with the individually-addressable gold electrodes constituted the cell floor (see Section 1.5.1 for fabrication materials and methods). The 650 µm high cell walls were constructed from poly-dimethyl siloxane (PDMS), the fabrication process for which is described in section 1.5.2. A glass cover slide (VWR International) formed a transparent lid on the cell, which allowed for video microscopy. A 3.7 cm diameter and 1.2 cm thick Ni-Cu-Ni plated NdFeB permanent disc magnet (Amazing Magnets, Irvine, CA) was placed directly under the silicon chip and supplied a 0.31 T positive magnetic field directed up, perpendicular to the chip, as measured by a DC magnetometer (AlphaLab, USA) at the surface of the chip placed in contact with the magnet in its center. The magnet was positioned so that the working electrodes always resided approximately in the center of the magnet to minimize magnetic field gradients.

The experimental setup was based in part on reinforcing flow studies reported by Anderson. The relatively wide working microband electrode width of 650 µm was chosen to separate the counter-directional magnetic forces on each side of the working electrode. This allowed for an increase in the separation of counter-flow forces. A gap of 650 µm was chosen based on the study by Anderson that indicated this spacing maximized the velocity for reinforcing flow for 50 µm-wide working electrodes.
Figure 2.2.2.1: (a.) Cell geometry and positioning of electrodes. (b.) Video microscopy view focused at 150 µm above the chip surface. Position within cell of view indicated by red box.
2.2.3 Electrochemical Initiation of Ion Movement

A potential was applied to two 650 µm-wide working electrodes, using the chronoamperometry mode of a CH Instruments electrochemical workstation (CHI760B, Austin, TX). Constant potentials of 0.15 V and -0.15 V were applied at working electrodes 1 and 2, respectively, for 40 s. A 4-electrode setup was used, where the two conductors labeled as “reference” in the figures were shorted together to serve as a single pseudo-reference electrode and the two counters labeled as “counter” were shorted together to serve as a single counter electrode. A solution containing a 50:50 mole ratio of the reduced and oxidized forms of a well-behaved redox species in electrolyte was used for all experiments. It consisted of 0.3 M potassium ferrocyanide, 0.3 M potassium ferricyanide, and 0.1 M KCl electrolyte. This high concentration of redox species allowed for higher velocities, which was beneficial for determining the shape of the vertical and lateral profiles and was the same pumping solution used by Anderson in previous reinforcing flow studies. 1

2.2.4 Flow Visualization and Bead Velocity Evaluation

To visualize the flow, the method utilizing 10-µm diameter polystyrene latex microbeads (Alfa Aesar) described by Anderson was adopted.1 The microbeads were diluted in the redox solution in a ratio of 1:300 by volume. Video microscopy was performed using a Nikon Coolpix 990 digital camera at 15 frames/s and interfaced to a Nikon Eclipse ME600 microscope. Video processing for bead tracking was performed using World-In-Motion Physics Toolkit software (WIM, www.physicstoolkit.com).
To calculate the velocity of a bead, the position of the bead in 11 consecutive frames was determined using WIM software. The scale (pixel to distance ratio) was set in WIM for the video by the distance between the two working electrodes, measured by a Dektak 3030 profilometer (Veeco, Plainview, NY) as 656 μm. The velocity between consecutive frames was calculated using Microsoft Excel from the bead position data. The average velocity was calculated from the numerical average of the ten velocity points, over a time period of 0.67 s. A scale bar superimposed over the trajectory in Microsoft Paint determined the lateral (y) position of the bead with y=0 centered between the edges of the working electrodes.

Evaluation of bead trajectories at an initial height began at 10 s when the current was within 15% of its average steady state value. At approximately 25 seconds into the experiment, the height was raised to the next height for evaluation. The next experiment began at the height from the previous experiment’s end. In this way, the trajectories at each height were evaluated during two experiments and time periods: from 10 to 25 s during one experiment and from 25 to 40 s during a second experiment. This technique standardized the effects of variables between experiments.

2.3 Results and Discussion

Figures 2.3.1 shows the \( u \) bead velocity profiles versus the lateral (y) distance between electrodes at heights (z) of 150, 300, 450, and 600 μm above the chip surface, with each data point representing \( u \) for one bead. Figure 2.3.2 shows the vertical (z) profile for the average bead velocity, \( u \). The points at 0 and 650 μm represent the assumed no-slip
Figure 2.3.1: (TOP) Lateral (y) profile of bead velocities at different heights above the chip surface. (BOTTOM) Side view indicating heights for graph.
Figure 2.3.2: Vertical (z) profile for average bead velocity within 162 µm of center between working electrodes. Horizontal error bars indicate ±1 standard deviation (15 ≤ N ≤ 34). Vertical error bars based on focus and bead rise rate.

The four data points are a numerical average of velocities for beads traveling between y = ±162.5 µm. The vertical profile is parabolic with a slight offset toward the cell ceiling, which may be due to the beads’ tendency to rise. Both the positive and negative vertical error bars include 30 µm to take into account the bead position relative to the focal plane. The negative vertical error bars also include 40 µm to take into account the tendency of the beads to rise: beads coming into focus were more likely to be chosen for tracking than beads going out of focus because beads that begin below the focal plane remain in focus longer than those that begin above the cell floor and ceiling.
focal plane. The average velocity $u$ between the pumping electrodes was $7.40E-04 \pm 0.52E-04$ m/s ($N=27$) at a current of $130 \, \mu$A and a height of $300 \, \mu$m above the chip surface (approximately halfway between the chip and cover slide).

### 2.4 Summary

The vertical and lateral flow profiles for steady-state reinforced RMHD flow were shown to maintain a parabolic nature. The vertical flow profile exhibited a slight offset towards the cell ceiling, though this may be on account of the tendency of the polystyrene microbeads to rise in the high-concentration ferri / ferro cyanide redox solution. The bead velocity between the pumping electrodes was $7.40E-04 \pm 0.52E-04$ m/s ($N=27$) at a current of $130 \, \mu$A and a height of $300 \, \mu$m above the chip surface (approximately halfway between the chip and cover slide).
3.1 Abstract

In redox magnetohydrodynamics (RMHD) the flow around a microband electrode and the center of circulation was changed significantly by the placement of the working (biased) electrode with respect to the walls. The center of circulation was shifted even outside of the space directly over the working electrode area. In addition, passive (unbiased) conductors shifted the center of circulation because of a shift in the magnetic force due to changes in local ion concentrations resulting from equilibration of redox species in the adjacent solution. The results provided evidence that the magnetic force resided primarily in the diffusion layer in these systems, not in the electrolyte between the counter and working electrodes.

3.2 Experimental

3.2.1 Chemicals and Materials

Aqueous solutions were prepared from reagent grade deionized water obtained from Ricca Chemical Company (Arlington, TX). Potassium ferricyanide (K₃Fe(CN)₆) was obtained from EM Science (Gibbstown, NJ), potassium ferrocyanide trihydrate (K₄Fe(CN)₆ • 3H₂O) was obtained from JT Baker (Phillipsburg, NJ), and potassium
chloride (KCl) was obtained from EMD (Darmstadt, Germany). All chemicals were used as received.

### 3.2.2 Redox-Magnetohydrodynamic Setup

Two cell geometries were used to investigate the effects of passive conductors and working electrode placement. The narrow cell illustrated in Figure 3.2.2.1.a used DES2 and positioned the working electrode at the center of the rectangular cell. It allowed the flow pattern across the entire width of the cell to be observed at once. The xyz coordinate system shown was adopted for the remainder of this chapter with \(u\) designated as the velocity in the x direction. The larger rectangular cell shown in Figure 3.2.2.2.a enlarged the cell and offset the working electrode to one side in one of two configurations: adjacent to the wall (with cell wall overlap of the working electrode) and approximately 350 µm away from the cell wall (without cell wall overlap of the working electrode). The large cell allowed for considerable offset of the working electrode to one side, which allowed for a measurable effect on the center of circulation. The large cell was also tested with (DES3) and without (DES2) a passive conductor 50 µm away from the edge of the working electrode. The xyz coordinate system shown was adopted for the remainder of this chapter with \(u\) designated as the velocity in the x direction. The silicon chip (DES2 or DES3) constituted the cell floor (see Section 1.5.1 for fabrication materials and methods). The cell walls were 830 µm high and constructed from polydimethyl siloxane (PDMS). A glass cover slide (VWR International) formed a transparent lid on the cell, which allowed for video microscopy. Figure 3.2.2.2.b shows
Figure 3.2.2.1: (a.) Experimental setup for narrow cell with working electrode centered and (b.) cross-sectional view of narrow cell. The red box indicates where the videos are captured in the cell.
Figure 3.2.2.2: (a.) Experimental setup for larger rectangular cell with working electrode offset to one side and (b.) video view focused on chip surface.

the size of the field of view for videos relative to the size of the cell, where the camera was focused on the chip surface. A 3.7 cm diameter and 1.2 cm thick Ni-Cu-Ni plated NdFeB permanent disc magnet (Amazing Magnets, Irvine, CA) placed directly under the silicon chip, supplied a 0.31 T positive magnetic field directed up, perpendicular to the
chip, as measured by a DC magnetometer (AlphaLab, USA) at the surface of the chip placed in contact with the magnet in its center. The magnet was positioned so that the working electrode always resided approximately in the center of the magnet to minimize magnetic field gradients.

3.2.3 Electrochemical Initiation of Ion Movement

Current was applied to the working electrode, using the chronopotentiometry mode of a CH Instruments electrochemical workstation (CHI760B, Austin, TX). Greater control of the magnetic forces was possible by applying the current (below the mass transfer limit) instead of applying a potential. In an applied potential experiment, the current, and therefore the resulting magnetic forces, will change during the experiment because of variations in ion flux caused by RMHD convection and increases caused by redox cycling with neighboring passive electrodes. To determine what current should be applied during the chronopotentiometry experiments, the diffusion limited current for all experimental setups (including PDMS coverage of working electrode) was determined using chronoamperometry and a value below the lowest diffusion limited current was chosen. Figure 3.2.3.1 shows an example of the diffusion limited current with PDMS coverage of the working electrode, given the experimental setup shown in Figure 3.2.3.2. A constant anodic current of 50 µA (about half the diffusion limited current for the experiment with a smaller working electrode area) was applied for 40 s. A 3-electrode setup was used, where the two conductors labeled as “reference” in the figures were shorted together to serve as a single pseudoreference electrode and the two counters
Figure 3.2.3.1: Example chronoamperometry experiment to determine diffusion limited current.

Figure 3.2.3.2: Experimental setup for example chronoamperometry current versus time graph.
labeled as “counter” were shorted together to serve as a single counter electrode. A solution containing a 50:50 mole ratio of the reduced and oxidized forms of a well-behaved redox species in electrolyte was used for all experiments. It consisted of 0.3 M potassium ferrocyanide, 0.3 M potassium ferricyanide, and 0.1 M KCl electrolyte.

3.2.4 Flow Visualization

To visualize the flow, 10-µm diameter polystyrene latex microbeads (Alfa Aesar) were diluted in the redox solution in a ratio of 1:50 by volume. Video microscopy was performed using a Nikon Coolpix 990 digital camera at 15 frames/s and interfaced to a Nikon Eclipse ME600 microscope. Video processing for bead tracking was performed using World-In-Motion Physics Toolkit software (WIM, www.physicstoolkit.com) with all trajectories captured at 3 frames/s. Evaluation of bead trajectories took place over a 10 s period, and began at least 30 s after the current was applied to allow for the development of long diffusion lengths and more stable velocity profiles.

3.3 Results and Discussion

The velocity profile based on the bead trajectories measured in the narrow cell can be best explained by a primary magnetic force located within the diffusion layer. Figure 3.3.1 shows trajectories at z = 450 µm (450 µm above the chip surface, which is approximately half-way between the substrate and lid of the cell) for the narrow cell without a passive conductor. The magnetic forces are applied in the diffusion layer
surrounding the working electrode where the net ionic flux is perpendicular to the magnetic field, as shown in Figure 3.3.2. If the average diffusion coefficient for ferricyanide and ferrocyanide is approximated as $0.8 \times 10^{-9} \text{ m}^2/\text{s}$, the diffusion length was between 220 and 250 µm when the videos were processed (after applying current for between 30 and 40 seconds). The diffusion length could also be decreased slightly in the presence of the magnetic-field induced convection, as reported by Lioubashevski et al. The diffusion length was shorter than the distance between the electrode edge and PDMS wall. A circulation flow developed with its center located in the middle of the working electrode because the magnetic forces were symmetric around the working electrode, and the electrode was located half-way between the walls. It is of note that circulation flow
was also established near the counter electrodes, though with a lower velocity because the lateral flux of ions was proportionally smaller given the much larger area of the counter electrode. The counter electrode flow was not of primary concern in these experiments.

Offsetting one wall (left) so that it was much farther away from the working electrode than the other wall (right) caused the center of fluid circulation to shift away from the center of the working electrode and toward the more distant (left) wall by approximately 325 µm. The center of circulation thus shifted to the left edge of the working electrode, as shown in Figure 3.3.3.a, where the magnetic force applied in the opposite direction began, as illustrated in Figure 3.3.4.a. The magnetic forces on both sides of the working electrode were the same in both the narrow and wide cells because the current was the same. The higher velocities on the right side of the center of
Figure 3.3.3 Shift of center of circulation as a result of placement of passive conductor. Trajectories for left wall offset from the working electrode. (a.) Passive conductor not within the diffusion layer; (b.) Passive conductor within the diffusion layer.
Figure 3.3.4: Net ion movement, resultant force, and observed flow for left wall offset from the working electrode. (a.) Passive conductor not within the diffusion layer; (b.) Passive conductor within the diffusion layer.
circulation than the left were explained by the concept in fluid dynamics of conservation of mass for an incompressible flow. Essentially, to conserve mass on both sides of the electrode, the greater cross-sectional area to the left of the electrode produced a slower velocity (µm/s) but over a greater distance from the electrode than the velocity in the smaller cross-sectional area to the right of the electrode. An assumed no-slip condition for the cell walls accounted for the shift in the center of circulation. When the left wall was offset away from the working electrode, the zero-velocity no slip condition moved with it.

When a passive conductor of the same width as the active electrode was moved within the 220 to 250 µm diffusion layer to a position 57 µm away from the active electrode’s edge in this cell setup with the left wall offset, the center of fluid circulation at \( z = 450 \) µm shifted toward the passive conductor (in the -y direction) by 70 µm. Figure 3.3.3.b shows the bead trajectories. This shift was due to the fact that some of the magnetic force was then applied on the other side of the passive conductor due to its equilibration effect, as illustrated in Figure 3.3.4.b. The results indicated that the magnetic force resided primarily in the diffusion layer in these systems, not in the electrolyte between the counter and working electrodes.

Two interesting effects occurred when the right wall of the wide rectangular cell covered part of the working electrode so that the working electrode was adjacent to it (in the absence of a passive electrode within the diffusion layer). First, the center of circulation at \( z = 450 \) µm shifted away from the right wall in the y direction to a distance of 950 µm from it so that the center of circulation was not positioned over the working electrode at all. Second, the clockwise direction of circulation was preserved (at first
glance, it was expected that the resultant magnetic force from the flux of ions would produce fluid flow in the opposite direction from that observed.) Figure 3.3.5.a shows the bead trajectories. Figure 3.3.6 illustrates where the magnetic force was applied and how the center of circulation shifted outside the area above the working electrode. Although the current was not changed, the electroactive area of the working electrode was smaller. This required the radial ion flux (perpendicular to the magnetic field) to increase proportionally to the ion flux parallel to the magnetic field. An approximate doubling of the measured potential at the working electrode when its area was approximately halved by the PDMS overlap proved this (0.048 V for overlap and 0.026 V without overlap). The increase in radial ion flux meant an increase in the magnetic force applied. The magnetic force was greatest close to the surface of the chip near the edges of the working electrode where the redox species flux had the largest component perpendicular to the magnetic field. Trajectories were recorded for 150 and 300 µm above the chip surface (not shown) and the centers of circulation at each height were determined (see Figure 3.3.6.b). At 150 µm above the chip surface, the center of circulation was near the edge of the working electrode. As the height increases, the center of circulation shifted away from the closest wall. It is of note that the velocities on the left of the center of circulation in Figure 3.3.5.a were lower compared to the velocities in Figure 3.3.3 and Figure 3.3.5.b despite the increase in magnetic force. This was a result of the higher level of dissipative effects due to the no-slip condition of the right wall because the magnetic force was applied much closer to that wall. The closer proximity of the right wall than the cell ceiling to the magnetic force caused a shift in the center of circulation to the left (-y direction) as z increased. This accounted for the shift
Figure 3.3.5 Shift of center of circulation as a result of placement of passive conductor. Trajectories for left wall offset from the working electrode and working electrode moved adjacent to wall with PDMS coverage. (a.) Passive conductor not within the diffusion layer; (b.) Passive conductor within the diffusion layer.
Figure 3.3.6: Net ion movement, resultant force, and observed flow for left wall offset from the working electrode and right wall placed over half of the working electrode (passive conductor not within the diffusion layer). (a.) top-down view with center of circulation indicated at $z = 450 \, \mu m$ (b.) cross-sectional view with center of circulations indicated at multiple $z$ values
in the center of circulation seen at \( z = 450 \) µm. Given the limitations of the experimental setup, it was unclear whether there was a component of the circulation in the x-z plane. These results strongly indicated that the magnetic force resided primarily in the diffusion layer in these systems, not in the electrolyte between the counter and working electrodes. When the 650 µm passive conductor was moved to a position within the diffusion layer, 57 µm away in the y direction from the edge of the working electrode that was half-covered with the right wall, the center of circulation shifted approximately 150 µm toward the working electrode and toward the nearest wall to a y distance of 800 µm, as shown in Figure 3.3.5.b. The velocities on the far left also increased approximately to a factor of two while the velocities to the right of the center of circulation remained approximately the same. The direction of circulation remained clockwise. The passive conductor changed where the magnetic force was applied in solution due to the equilibration effect, as depicted in Figure 3.3.7. Some of the magnetic force was then applied on the other side of the passive conductor which was farther away from the right wall and its no-slip condition. This allowed for an increase in velocity in the solution to the left of the passive conductor. The change in where the magnetic force was applied also accounted for the shift in the center of circulation. Although some of the magnetic force was still applied between the working electrode and passive conductor so that it was closer to the right wall than the cell ceiling, the magnetic force at the edges of the passive conductor allowed the center of circulation at higher z values to shift back toward the right wall in the y direction. Although these results indicated that the center of circulation can change with height (z position), data at different heights were not collected for the first experiments reported in this chapter. Given the current
Figure 3.3.7: Net ion movement, resultant force, and observed flow for left wall offset from the working electrode, working electrode moved adjacent to wall with PDMS coverage, and passive conductor within the diffusion layer. (a.) Top-down view with center of circulation indicated at $z = 450 \, \mu m$ (b.) cross-sectional view
understanding, height was not anticipated to have as pronounced of an effect on the center of circulation for those experiments because the no slip condition of the cell ceiling was closer to the application of force than the no slip condition of the PDMS walls. Further experiments could be used to confirm this hypothesis, but were not done within this thesis. Additional work could also focus on quantitative characterization of the flow including spatial velocity profiles (trajectories are included here, but quantitative results have not been calculated), vorticity, and circulation (herein the term “circulation” has been used to describe the flow pattern without verifying mathematically that the fluid dynamic computation for circulation is non-zero).

These results are important for simulation of RMHD systems with high supporting electrolyte concentration and the design of RMHD micropumps. With respect to micropump design, passive conductors can be used to change where the magnetic force is applied in solution to obtain desirable flow patterns. With respect to simulation, Qian\textsuperscript{26}, Bau\textsuperscript{28}, Alemany\textsuperscript{29} and respective co-workers have simulated RMHD channel flow assuming the magnetic force is applied throughout the entire solution according to current lines drawn between the working and counter electrodes. This method of calculating current is not valid for an electrolytic system (a more detailed description is included in Section 4.4). As a result of this error in calculating current, the simulations show RMHD channel flow to have a parabolic velocity profile (non-circulating) across the width and height of the channel. However, if the magnetic force is applied primarily only within the diffusion layer, circulation flow could result in cases where the previously applied theory does not predict it, depending upon electrode and wall geometry. White and coworkers also make the argument that the magnetic force
applied primarily within the diffusion layer when interpreting changes in current for voltammetry experiments at microdisk electrodes in the presence of a magnetic field.\textsuperscript{30, 31} Comparing simulation results with experimental results for different passive conductor setups could give further insight into whether or not the magnetic force is applied only within the diffusion layer when a high supporting electrolyte concentration is used.

3.4 Conclusions

A shift in the center of circulation for RMHD flow due to wall placement with respect to the working electrode and the use of passive conductors was demonstrated, and gave evidence that the magnetic force resided primarily in the diffusion layer in these systems, not in the electrolyte between the counter and working electrodes. The use of passive conductors to manipulate the flow profile was demonstrated and could help in future design of lab-on-a-chip devices which utilize RMHD for pumping.
Chapter 4: Redox Magnetohydrodynamic Channel Flow

4.1 Abstract

A qualitative study was conducted to determine whether RMHD channel flow is circulation based across the width or height of the channel when using pumping electrodes located on the channel floor. This electrode setup was easier to fabricate than side-wall electrodes and thus was preferred with regards to fabrication for use in disposable, portable analytical devices. RMHD flow in channels with sidewall pumping electrodes was simulated and shown to result in a parabolic velocity profile across the channel width and height, but flow for channel floor pumping electrodes was not simulated. Experimental results herein showed circulation across the width or height of the channel, depending upon the aspect ratio, when the pumping electrodes did not span the entire length of the channel and thus had edges that were not parallel to the channel walls. A parabolic velocity profile across both the height and width was observed in the case where the pumping electrode spanned the entire length of the channel.

4.2 Previous Work

To the knowledge of the author, there have been no experimental studies reported in literature to date with regards to velocity profiles for RMHD channel flow. Previous experimental work involving RMHD pumping was reported by Aogaki and coworkers, but the study focused on current measurements, not flow visualization. Previous
experimental work involving RMHD pumping was also reported by Aguilar et al.\textsuperscript{2} and Arumugam et al.,\textsuperscript{3} but the studies focused on current measurement and the visual identification of dye movement out of channels without visualization within the channel.

Other experimental work was reported on MHD channel flow without redox species. Bau and co-workers have reported on dc MHD pumps using electrolyte\textsuperscript{33} and a subsequent microfluidic network utilizing floor pumping electrodes,\textsuperscript{34} though problems of bubble generation and electrode dissolution were noted. Homsy et al.\textsuperscript{35} reported on a high current density DC MHD micropump using weakly conducting electrolytic solution that isolates the bubble formation. Experimental work by Lemoff et al.\textsuperscript{36} visualized ac MHD flow for sidewall electrodes by tracking 5 µm beads in solution.

Qian and Bau also experimentally visualized stirring using side-wall electrodes and electrolytic solution without redox species both in the presence of net channel flow and without it.\textsuperscript{37} The net channel flow was provided not by pumping MHD electrodes, but by computer-controlled syringe pumps to minimize bubble formation during the experiment. Because this work was done without redox species and at high enough voltages, problems of bubble formation and electrode dissolution occurred.

Theoretical work has been reported for dc MHD with and without redox species and supporting electrolyte, though it concentrates on sidewall electrodes. Qian and Bau have done theoretical work for RMHD pumping in a rectangular cross-section channel with side-wall electrodes in the presence and absence of supporting electrolyte.\textsuperscript{28} They predict a parabolic velocity profile across the width of the channel. However, their work assumed the magnetic force was applied throughout the entire solution according to current lines drawn between the working and counter electrodes rather than only within
the diffusion layer where there is a net flux of charge-carrying redox species. There has also been work reported by Qian,\textsuperscript{26, 38} Alemany,\textsuperscript{29} and Wang\textsuperscript{39} in simulating dc MHD channel flow with sidewall electrodes but only without the presence of a redox species.

This experimental study is unique in that it focused on visualization of the velocity profile within the channel for RMHD channel flow. Based on the theory presented in Chapter 3 (the magnetic force is applied primarily within the diffusion layer in these systems and not throughout the entire solution) circulation across the width or height of a channel may be possible for certain channel and pumping electrode geometries. This chapter reports the results of a qualitative study on circulation within channels for RMHD channel flow.

4.3 Experimental

4.3.1 Chemicals and Materials

Aqueous solutions were prepared from reagent grade deionized water obtained from Ricca Chemical Company (Arlington, TX). Potassium ferricyanide (K\textsubscript{3}Fe(CN)\textsubscript{6}) was obtained from EM Science (Gibbstown, NJ), potassium ferrocyanide trihydrate (K\textsubscript{4}Fe(CN)\textsubscript{6} \cdot 3H\textsubscript{2}O) was obtained from JT Baker (Phillipsburg, NJ), and potassium chloride (KCl) was obtained from EMD (Darmstadt, Germany). All chemicals were used as received.
4.3.2 Redox-Magnetohydrodynamic Setup

Two channel geometries were used with chips CG1_4 and CG1_6 to investigate RMHD channel flow. The rectangular loop cell illustrated in Figure 4.3.2.1 utilized both the counter and working electrodes for pumping. The pumping electrodes were 2 mm long, spaced 50 µm apart, and did not span the entire length of the channel (thus having edges that were not parallel to the channel wall). Two termination configurations were used for the pumping electrodes: perpendicular to the channel wall and tapered. The tapered electrodes tested in this study were spaced 200 µm apart and located in the bottom right corner of the rectangular loop in Figure 4.3.2.1. The circular loop cell illustrated in Figure 4.3.2.2 utilized only the working electrode for pumping. The setup separated the pseudo-reference and counter electrodes from the circular loop channel. The working electrode spanned the entire length of the channel so all its edges were parallel to the channel walls.

The silicon chip (CG1_4 and CG1_6) constituted the channel floor (see section 1.5.1 for fabrication materials and methods). Two poly-dimethyl siloxane (PDMS) thicknesses used for the channel walls allowed for two channel heights: 2300 and 700 µm. A glass cover slide (VWR International) formed a transparent lid on the cell, which allowed for video microscopy. A 3.7 cm diameter and 1.2 cm thick Ni-Cu-Ni plated NdFeB permanent disc magnet (Amazing Magnets, Irvine, CA) placed directly under the silicon chip supplied a 0.31 T positive magnetic field directed up, perpendicular to the chip, as measured by a DC magnetometer (AlphaLab, USA) at the surface of the chip placed in contact with the magnet in its center. The magnet was positioned so that the pumping electrode(s) always resided approximately in the center of the magnet to
Figure 4.3.3.1: Rectangular loop channel geometry with electrodes.

minimize magnetic field gradients.

4.3.4 Electrochemical Initiation of Ion Movement

Current was applied to the working electrode using the chronopotentiometry mode of a CH Instruments electrochemical workstation (CHI760B, Austin, TX). A constant, anodic current of 100 µA was applied for 40 s with chronoamperometry being used to verify this current was below the diffusion limited current. A 3-electrode setup
was used, where the two conductors labeled as “reference” in the figures were shorted together to serve as a single pseudo-reference electrode and the two counters labeled as “counter” were shorted together to serve as a single counter electrode. A solution containing a 50:50 mole ratio of the reduced and oxidized forms of a well-behaved redox species in electrolyte was used for all experiments. It consisted of 0.3 M potassium ferrocyanide, 0.3 M potassium ferricyanide, and 0.1 M KCl.
4.3.5 Flow Visualization

To visualize the flow, 10-µm diameter polystyrene latex microbeads (Alfa Aesar) were diluted in the redox solution in a ratio of 1:50 by volume. Video microscopy was performed using a Nikon Coolpix 990 digital camera at 15 frames/s and interfaced to a Nikon Eclipse ME600 microscope. Video processing for bead trajectories was performed using World-In-Motion Physics Toolkit software (WIM, www.physicstoolkit.com). Multiple bead trajectories were added to a single video frame using Microsoft Paint.

4.4 Results and Discussion

The rectangular loop channel was tested using 2300 µm PDMS channel height and non-tapered electrodes. At 300 µm above the chip surface, the flow across the channel (x = constant) was to the right (positive x-direction)—there were no velocity sign transitions due to circulation flow. However, as z increased the bead velocities decreased at greater heights above the electrode, and there was a transition of beads moving to the left only (in the negative x-direction). Furthermore, beyond the end of the pumping electrodes, the beads disappeared quickly rising out of the focal plane. These results indicated there was vertical (x-z plane) circulation instead of lateral (x-y plane) circulation.

Bau reported on a microfluidic network with pumping electrodes located on the floor of the device to move electrolytic solution without redox species in a channel.34 The channel width was 1.1 mm and the channel height was 1.7 mm. In an appendix, they addressed the difference between sidewall and channel floor pumping electrodes in the
velocity profile. They noted that there was no flow under a threshold voltage, 2.0 V and afterward the flow velocity increased linearly with current. They noted bubble generation when pumping, which was evidence of electrolysis. Their method of simulating the magnetic force was based on current calculations from constant potential contours, shown in Figure 4.4.1. If a similar method of calculating the magnetic force based on current calculations from constant potential contours was used for the redox system described here, one would expect there to be forces across the entire height of the channel, thus resulting in a uni-directional flow. This method of calculating current is not valid for an electrolytic system because the supporting electrolyte creates a double layer, which acts like a capacitor. All of the potential drop due to a voltage applied between two electrodes occurs within the diffuse layer (less than ~100 Å) if no redox species is present and the concentration of the electrolyte is at least $10^{-2}$ M. If redox species is present, the potential difference between the reference electrode in bulk solution and another given point in solution is only non-zero in the diffusion layer. If the magnetic force is applied only within the diffusion layer, as the theory presented in this thesis purports, then x-z plane circulation flow could result based on the aspect ratio of width to height. The magnetic force is applied only near the surface of the chip between the working and counter electrodes (see Figure 4.4.2) and therefore the no-slip boundary condition of the PDMS channel walls are closer than the no-slip boundary condition of the glass cover-slide channel ceiling. Thus, it could be hypothesized that thinner PDMS will eliminate vertical circulation if the glass cover-slide ceiling is closer to the magnetic force than the PDMS walls.
Figure 4.4.1: Theoretical work for channel floor pumping electrodes: contours of constant potential (lines) and subsequent current (arrows).
Figure 4.4.2: Net ion movement and resultant magnetic force for 2300 µm height channel. (a.) Top-down view of channel (b.) Cross-sectional view of channel.
The same electrode setup was tested, but with a 700 µm PDMS height rectangular loop channel. Two sections of the same 40 s video with different positions along the length of the channel were evaluated to obtain the bead trajectories (identifying marks in the PDMS were used to determine the spatial overlap of the two sections of video). The bead trajectories at 3 frames/s located at $z = 300$ µm above the chip surface are shown in Figure 4.4.3, where green indicates movement to the right (positive x direction) and red indicates movement to the left (negative x direction). There was clearly circulation across the width of the channel in the x-y plane. The results of this experiment were consistent with application of the magnetic force within the diffusion layer only. The application of force for this setup is illustrated in Figure 4.4.4. The counter flow in the circulation was established offset in the +y direction because the force was applied offset in the –y direction from the middle of the channel: the channel was positioned so that the counter electrode on top had a larger area (1.5 mm$^2$) than the working electrode on the bottom (1.2 mm$^2$), as shown in Figure 4.4.3. A smaller circulation may have been present at the end of the working (bottom) electrode, but there were not sufficient beads in focus to map the flow in this area. This would result from the magnetic force caused by radial diffusion at the end of the working electrode. It is also of note that there was a net fluid flow around the channel of $0.99 \pm 0.21$ µL/min.

To determine if the tapered electrodes would eliminate the circulation, the same rectangular loop channel with a 700 µm height was used with tapered corner electrodes. The bead trajectories, shown in Figure 4.4.5, were plotted at $z = 300$ µm above the chip surface. Here again, there was circulation flow across the width of the channel. The tapered corner electrodes did not eliminate the circulation.
Figure 4.4.3: Top-down view of bead trajectories for rectangular loop channel with 700 µm thick PDMS taken at 300 µm above chip surface. Electrodes were not tapered. Trajectories were for 3 frames/s.
Figure 4.4.4: Net ion movement and resultant magnetic force for 700 µm height channel. (a.) Top-down view of channel (b.) Cross-sectional view of channel.
Figure 4.4.5: Bead trajectories (right) for rectangular loop channel (left) with 700µm thick PDMS taken at 300µm above chip surface. Electrodes were tapered. Trajectories were for 3frames/s.

The circular loop channel pumps fluid using only the working electrode, which spanned the entire length of the channel. The channel height was 2300µm. Bead trajectories were evaluated at 600 µm above the floor at three positions in the channel and are shown in Figure 4.4.6. (note that the lead in Figure 4.4.6.c is covered with BCB and so is not exposed to the solution). The flow was clockwise around the channel across the entire width of the channel. A video scanning the height of the channel verified that there was no vertical circulation. The elimination of circulation across the height or width of the channel was due to the pumping electrode spanning the entire length of the channel. This configuration eliminated the radial diffusion parallel to the channel walls, which would otherwise produce forces perpendicular to the channel walls. The net flow rate was increased approximately two orders of magnitude when compared to the rectangular loop channel with rotation across the width of the channel to 93 ± 41 µL/min.
4.5 Conclusions

For cases where the pumping electrodes did not span the entire length of the channel, thus producing non-parallel pumping electrode edges, circulation was induced across the height or width of the channel. When the pumping electrode did span the entire length of the channel, circulation across the width or height was not observed and a flow rate of $93 \pm 41 \, \mu$L/min was obtained. These results gave further evidence that the magnetic force was applied primarily within the diffusion layer, not throughout the entire solution.
Chapter 5: Future Work

Future work is suggested with the aim of coming to a better understanding of the forces involved in redox magnetoconvection and how they are applied throughout the solution. Work believed by the author to be beneficial toward this end includes tracking the concentration gradient, additional channel flow experiments, and simulation comparison with experimental results.

5.1 Tracking the Concentration Gradient

Further study is warranted to determine what factors (supporting electrolyte concentration, redox species concentration, etc) might change where in solution the magnetic force is applied from primarily within the diffusion layer to throughout the solution. One tool to aid in this study is the simultaneous tracking of the velocity profile and the redox species concentration gradient. The concentration of the redox species will be calculated from the measured potential at microband probe electrodes located adjacent to a generating (pumping) electrode, using the Nernst equation:

$$E = E^\circ + \frac{R T}{n F} \ln \left[ \frac{C_{o}(0,t)}{C_{R}(0,t)} \right]$$

Equation 1

A similar technique has been used to track concentration gradients in polymer films. An example setup for determining concentration profiles during RMHD is shown in Figure 5.1.1. To study how much redox species diffusion contributes towards $I_B$, the evolution of the concentration profile can be compared to the evolution of the velocity profile using different passive conductor geometries to change the redox concentration.
gradient by the equilibration effect. This will help identify where in solution the redox species ion flux occurs and to what extent it affects the local bead velocity.

5.2 Additional Channel Flow Experiments

Additional RMHD channel flow experiments with floor pumping electrodes ought to be conducted to better understand what factors affect the transition between circulation flow within the channel and pumping flow. Channel geometry, pumping electrode placement and geometry, and solution composition could by systematically varied to determine their effects on the flow type. Smaller channels with better defined features could be achieved using photo-lithography patterned SU-8 masters for PDMS templating. Some additional channel flow experiments that can be performed with the current rectangular loop chip design are illustrated in Figure 5.2.1.

A microfluidic network could be tested for stirring and pumping. An example network is shown in Figure 5.2.2. This chip design uses a pumping solution whose redox species does not interfere with the electrochemistry of the analyte to be detected. The height of the PDMS should be less than the width of the Inlet 1 channel. The outlet and
inlets can be connected to reservoirs with larger volumes of fluid that have intermediate channels so fluid can be pumped in an overall loop. In the center of the network is a square loop channel with a pumping electrode spanning the entire length of the interior wall and one detecting electrode at each corner of the square loop. At the beginning of the experiment, the channels are filled with the pumping solution. The pumping solution
with analyte is brought into the square loop by activating the Inlet 1 pumping electrodes and Outlet pumping electrodes until the analyte is detected by the top right detecting electrode. The Inlet 1 and Outlet pumping electrodes can be switched off and the square loop pumping electrode switched on. The plug of analyte can be pumped around the square loop and detected at each detecting electrode. Then the system can be flushed with the pumping solution only using Inlet 4 by activating the pumping electrodes at Inlet 4, the square loop, and Outlet. The pumping electrodes for Inlet 1 can be reversed so that only pumping solution remains in Inlet 1. To conduct an experiment with two analytes that must be mixed, Inlet 2 and 3 can be used. The wider channel from Inlet 2 and 3 to the square loop has offset pumping electrodes to establish circulation flow across the width of the channel while maintaining a small net pumping. This should help mix the solutions from Inlet 2 and 3 on the way to the square loop.
5.3 Simulation Comparison with Experimental Results

Multi-physics software packages can also be utilized to compare simulation and experimental results. A program that allows the input of a user-defined force could help determine if the simulated results for applying a force only within the diffusion layer are a close match to the experiment results obtained thus far. The COMSOL Multiphysics package with Reaction Engineering Lab (simulates reaction systems where the solution composition varies with time, taking into account kinetics), Chemical Engineering Module (designed to couple chemical reaction kinetics to computational fluid dynamics), and AC/DC Module (which allows for magnetostatics simulation), may prove useful to this ends.
References


40. Fritsch-Faules, I.; Faulkner, L. R. Analytical Chemistry 1992, 64, (10), 1118-1127.
Appendix A: Description of Research for Popular Publication
A medical team braves the hike to reach a mountainous village in Honduras where an outbreak of disease has halved the population to a few thousand. The village is not connected by any road to the rest of civilization so the team can only transport what supplies they can carry on their backs. Armed with battery-powered portable analytical devices, the team identifies not only the disease, but its source by performing tests on body fluid and community water samples that would otherwise require trained laboratory specialists and a facility with expensive bench-top scientific equipment. These devices bring the power of modern medicine to even the remotest areas of the world through the use of lab-on-a-chip (LOC) technologies, which perform complicated analytical tests in an automated fashion. One key to LOC technology is the ability to move pico-liters of fluid through channels with dimensions on the scale of the thickness of a human hair. The manipulation of fluid on the micrometer scale is one hurdle that must be overcome to make such devices a reality. Redox magnetohydrodynamics (RMHD), which utilizes magnetic and electric fields to move fluids, could be the solution that propels modern technology over this hurdle. The development of RMHD for small-volume fluid manipulation is one of the areas of research conducted by the Fritsch Research Group at the University of Arkansas.

The Fritsch Group has made some exciting progress in their recent research which could change the way scientists view RMHD. One graduate student connected with the recent progress, Matthew Gerner, commented on the situation. “Much of the prior work done in RMHD assumes the force is applied throughout the entire solution… but our work gives evidence to the contrary. This completely changes the way you model RMHD systems.” The recent work involves manipulating where the force is applied in solution using passive (unbiased) conductors and observing the changes in the flow profile. Time will tell whether this new perspective on RMHD will propel its development for LOC technology into the prototyping stage to make such portable analytical devices a reality.
Appendix B: Executive Summary of Newly Created Intellectual Property

The following list of new intellectual property items were created in the course of this research project and should be considered from both a patent and commercialization perspective.

1. A method for processing videos of bead movement in solution using World-in-Motion software, Microsoft Office Excel, and Microsoft Paint was developed to calculate the average velocity of beads in solution and depict the trajectory pictorially.

2. In Chapter 5 on suggested future work, a novel method for tracking the redox species concentration gradient based on the potential at probe electrodes was described, which will allow for simultaneous video microscopy. This method, though not yet tested, could be an alternative in limited applications to scanning electrochemical microscopy (SECM) if it proves effective.

3. In Chapter 3, a method was discussed for using passive conductors to change where in solution the magnetic force is applied for flow using RMHD. This concept has applications to designing micropumps using RMHD and could have future application in lab-on-a-chip technology.
Appendix C: Potential Patent and Commercialization Aspects of listed Intellectual Property Items

C.1 Patentability of Intellectual Property (Could Each Item be Patented)

The three items listed were considered first from the perspective of whether or not the item could be patented.

1. The method of processing videos using this collection of software cannot be patented because the World-in-Motion software is designed for tracking moving objects. Although the particular application of this software for use in video microscopy processing is not known to have been previously demonstrated, it could be considered obvious to one skilled in the art and familiar with this software. Additionally, the World-in-Motion software is freeware.

2. The novel method for tracking the redox species concentration gradient could be patented if properly developed, proven to work effectively, and shown to diverge sufficiently from previous work by Fritsch and coworkers in tracking the concentration of redox species in polymer films.

3. The method of using passive conductors to change where in solution the magnetic force is applied could be patented.

C.2 Commercialization Prospects (Should Each Item Be Patented)

The three items listed were then considered from the perspective of whether or not the item should be patented.

1. This method of processing videos cannot be patented.
2. At the present time, the novel method should not be patented—it must first be fully developed and proven effective. If it is shown as an advantageous alternative to SECM in particular applications, especially towards monitoring RMHD flow in LOC devices, it could prove commercially advantageous to patent the method at a later time.

3. This method should be patented if shown useful in obtaining an advantageous flow profile for pumping using RMHD that could otherwise not be obtained.

C.3 Possible Prior Disclosure of IP

The following items were discussed in a public forum or have published information that could impact the patentability of the listed IP.

1. This method of processing videos was discussed in a 6th grade classroom at McNair Middle School during a presentation on graduate level research in fall 2007.

2. The method described was discussed in a research document for a National Science Foundation Graduate Research Fellowship application submitted November 2008. This is not considered a public forum, nor were the full details of the method disclosed.

3. The method described for changing the spatial redox concentration gradient using passive conductors was described in the proposal to the National Science Foundation, Grant No. CHE-0719097.
Appendix D: Broader Impact of Research

D.1 Applicability of Research Methods to Other Problems

The method of tracking beads with World-in-Motion software could also be used to track movement in video microscopy for other applications.

D.2 Impact of Research Results on U.S. and Global Society

There are no foreseeable direct effects on the US and global societies from this research. However, this research could eventually be applied toward the development of a portable analytical device for water-sample testing or medical testing. Devices for testing water samples could determine whether a water supply is potable, and thus reduce contaminated-water related illnesses and deaths. This could impact the global society significantly, as potable water is becoming an increasingly important natural resource. Portable medical analytical devices could impact the effectiveness of hospitals in identifying illness in communities which lack developed medical facilities for lab testing.

D.3 Impact of Research Results on the Environment

There are no foreseeable direct effects on the environment from this research. However, this research could eventually be applied toward the development of a portable analytical device for water-sample testing. Such a device could help identify contaminants in water supplies and increase the efficiency and accuracy of water testing.
Appendix E: Microsoft Project for MS MicroEP Degree Plan
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Appendix F: Derivation of Magnetic Gradient and Paramagnetic Concentration Gradient Forces

This derivation modifies the derivation by Leventis\textsuperscript{8} for the magnetic gradient, $\vec{F}_{VB}$, and paramagnetic concentration gradient, $\vec{F}_{VC}$, forces. The derivation by Leventis is built upon the concept of “magnetic energy” from The Feynman Lectures on Physics\textsuperscript{41} and computes the two forces by finding the gradient of the average magnetic energy per unit volume. The derivation by Leventis focuses on a redox system utilizing milli- and microelectrodes whose dilute solutions contain permanent magnetic dipoles (paramagnetic species) having a spin of $\frac{1}{2}$. This derivation diverges from that of Leventis in the simplification described in footnote (14) after equation (11) on page 3985. The first part of the derivation will not be repeated here as it is found in its complete form elsewhere.\textsuperscript{8}

This derivation picks up at equation (11),

$$\vec{F}_V = -\nabla U_M|_{\text{per unit volume}} = \vec{F}_{VB} + \vec{F}_{VC}$$  \hspace{1cm} \text{Equation 1}$$

where $\vec{F}_{VB}$ and $\vec{F}_{VC}$ before the simplification of footnote 14 are as follows,

$$\vec{F}_{VC} = N_A \sum_{j=1}^{N_m} \left[ \left( \overline{m}_j \right) \cdot \vec{B} \right] \nabla C_j$$  \hspace{1cm} \text{Equation 2}$$

$$\vec{F}_{VB} = N_A \sum_{j=1}^{N_m} \left[ C_j \nabla \left( \overline{m}_j \right) \cdot \vec{B} \right]$$  \hspace{1cm} \text{Equation 3}$$

The simplification in footnote (14)

- expands $\nabla \left( \overline{m}_j \right) \cdot \vec{B}$
- assumes $\nabla \times \vec{B} = 0$
- eliminates two terms with $\vec{B} \times (\nabla \times \vec{B})$
- substitutes $\frac{(m^*)^2}{kT} \vec{B}$ for $\left( \overline{m}_j \right)$ according to equation (8)

and later assumes $\left( \vec{B} \cdot \nabla \vec{B} \right) = \vec{B} \cdot \left( \nabla \vec{B} \right)$ on page 3988, which is not mathematically valid.
Thus, \( \overrightarrow{F_{vb}} \) should be written

\[
\overrightarrow{F_{vb}} = 2N_A \sum_{j=1}^{j_{\text{max}}} \left[ C_j \left( \frac{m^*}{kT} \right)^2 \left( \overrightarrow{B} \cdot \nabla \right) \overrightarrow{B} \right]
\]

Equation 5

instead of the equation Leventis arrives at, which is

\[
\overrightarrow{F_{vb}} = N_A \sum_{j=1}^{j_{\text{max}}} \left[ C_j \frac{(m^*)^2}{kT} \left( \overrightarrow{B} \cdot \left( \nabla \overrightarrow{B} \right) \right) \right]
\]

Equation 6

In a similar manner, if you replace \( \langle \vec{m} \rangle_j \) with \( \frac{(m^*)^2}{kT} \overrightarrow{B} \), \( \overrightarrow{F_{vc}} \) can be simplified to yield the same equation that Leventis arrives at, which is

\[
\overrightarrow{F_{vc}} = N_A \sum_{j=1}^{j_{\text{max}}} \left[ \frac{(m^*)^2}{kT} \left( \overrightarrow{B} \right)^2 \nabla C_j \right]
\]

Equation 7
Appendix G: Identification of All Software Used in Research and Thesis Generation

Computer #1:
  Model Number: Dell Vostro 400
  Serial Number: 46B6MF1
  Location: CHBC 103
  Owner: Dr. Ingrid Fritsch
Software #1:
  Name: Microsoft Office 2003
  Purchased by: Dr. Ingrid Fritsch
Software #2:
  Name: AutoCAD LT 2004
  Purchased by: Dr. Ingrid Fritsch
Software #3:
  Name: AMPERES magnetic field simulation software
  Purchased by: Dr. Ingrid Fritsch
Software #4:
  Name: Microsoft Office Project Professional 2007
  Purchased by: Matthew Gerner
Software #5:
  Name: Endnote
  Purchased by: Dr. Ingrid Fritsch
Software #6:
  Name: Media Converter SA Edition
  Purchased by: Freeware
Software #7:
  Name: World-In-Motion Physics Toolkit Software
  Purchased by: Freeware
Software #8:
  Name: CHI760B Electrochemical Workstation
  Purchased by: Dr. Ingrid Fritsch

Computer #2:
  Model Number: Dell Optiplex 755
  Serial Number:
  Location: 131 S Hill Avenue
  Owner: Matthew Gerner
Software #1:
  Name: Microsoft Office 2007
  Purchased by: Matthew Gerner
Software #2:
Name: Media Converter SA Edition  
Purchased by: Freeware

Software #3:  
Name: World-In-Motion Physics Toolkit Software  
Purchased by: Freeware

Software #4:  
Name: Microsoft Office Project Professional 2007  
Purchased by: Matthew Gerner

___________________________   ___________________________
Matthew D. Gerner     Dr. Ingrid Fritsch