Collaborative Research: Actively Controllable Microfluidics with Film-Confined Redox-Magnetohydrodynamics -- Video and Data

01 Jun 2017

Natural Convection in Redox Electrochemistry: Model, Simulation and Experiments

Fangping Yuan

Kakkattukuzhy M. Isaac
Missouri University of Science and Technology, isaac@mst.edu

Natural Convection in Redox Electrochemistry: Model, Simulation and Experiments

Fangping Yuan
K. M. Isaac

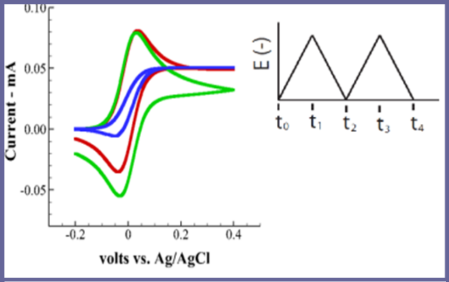
Missouri University of Science & Technology
Aerospace Engineering

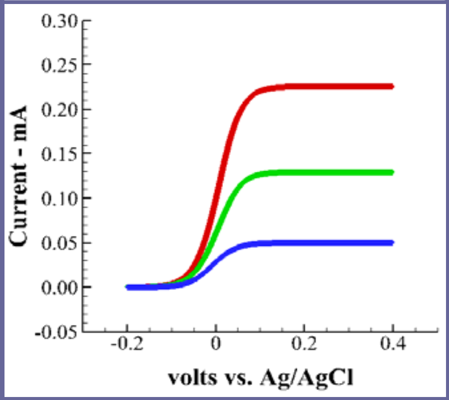
231st ECS Meeting, May 28-June 1, 2017
New Orleans

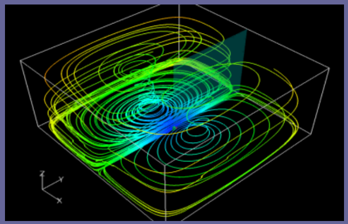
Acknowledgements

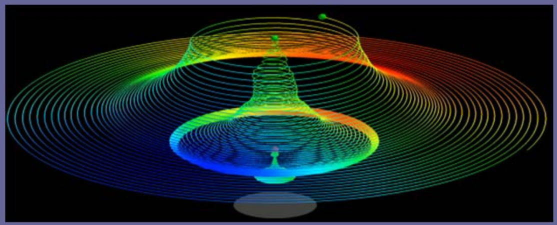
National Science Foundation Grants

Award number CBET-1336722
Award number CHE-0719097



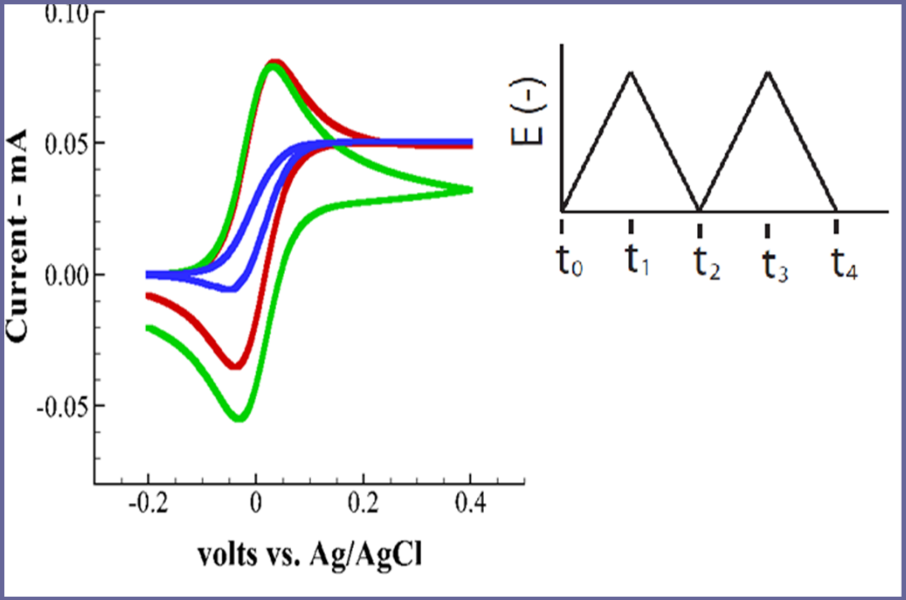






Outline

- Motivation
- Problem Description
- Simulation Highlights
- Results: Simulations
- Results: Experiments
- Discussion
- Conclusions
- Ongoing and Future Work



Motivation

- Potential impact on sensing: Natural convection has been studied in electrochemistry and Microfluidics due to its potential impact on sensing.
- Electrochemistry-driven Natural convection is less understood in redox systems: NC is better understood and modeled in electrodeposition.
- Previous models are limited due to their empirical nature.
- Experiments show NC influences observed behavior.
- Selman and Newman* model:

  The authors modeled NC in redox electrochemistry by using a **densification coefficient** similar to the expansion coefficient in temperature-induced natural convection.

**JR Selman and J Newman, J. Electrochem. Soc., 118, 7, 1971*

Selman and Newman model*

$$\frac{\rho - \rho_b}{\rho_b} = \sum_i \alpha_i \left(C_i - C_{ib}\right)$$

α_ι– densification coefficient
$(C_i - C_{ib})$ is the change in concentration of species *i*.

**JR Selman and J Newman, J. Electrochem. Soc., 118, 7, 1971*

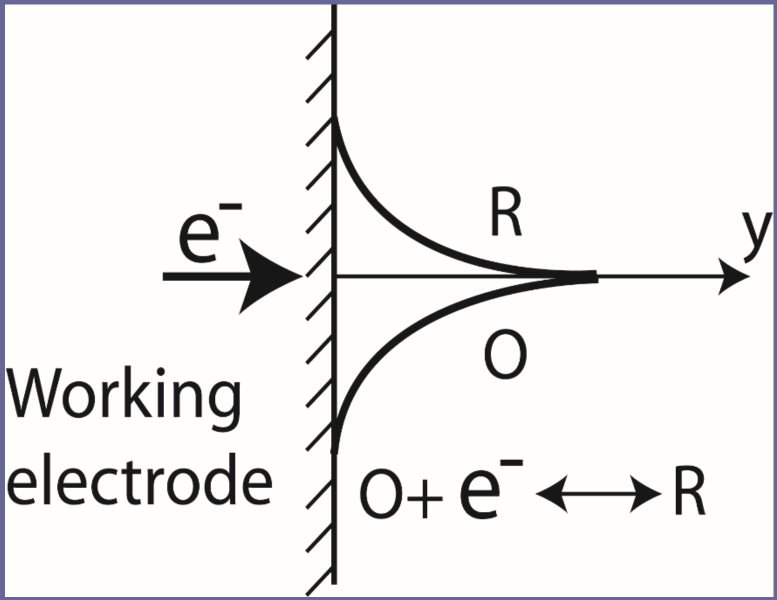
Background

- Satisfying electro-neutrality has been proposed by other investigators as the underlying reason for NC.
- Balance sheet approach of Bard and Faulkner* can be used to quantify NC.
- Key concept: Supporting electrolyte ions migrate in/out of the diffusion layer to satisfy Electroneutrality.
- The strength of NC is dependent on the difference in the molecular weights of the positive and negative ions of the supporting electrolyte.

**AJ Bard and LR Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd Ed., Wiley, 2001*

Problem Description

- Figure shows oxidized and reduced species concentration profiles at the working electrode due to electron transfer.
- Results in a charge imbalance causing deviation from Electroneutrality.
- Supporting electrolyte ions migrate in and out of the electrode region to re-establish electroneutrality.



Reduction reaction at the electrode

Problem Description (continued)

Non-dimensional parameters

Rayleigh number for pure natural convection

$$Ra_L = \frac{g|\rho - \rho_{\mathbf{0}}|_{\boldsymbol{max}}\, L^3}{\mu D}$$

BF number, the ratio of MHD force to buoyancy force for mixed convection.

$$BF = \frac{j_{ele} B}{g|\rho - \rho_0|_{\mathrm{max}}}$$

BF number does not account for volume effects.

Problem Description (continued)

We introduce a *TN* number to account for the volume effect.

$$TN = BF * \text{Volume ratio} = \underbrace{\frac{j_{ele}B}{g\left|\rho - \rho_0\right|_{\max}}}_{BF} \underbrace{\frac{L^3}{\delta d^2}}_{\text{volume ratio}}$$

L – Cell characteristic dimension
δ – Diffusion layer thickness
d – Electrode characteristic dimension

Diffusion length for semi-infinite diffusion

$$\delta \approx \sqrt{Dt}$$

Problem Description (continued)

Charge concentrations in the diffusion layer

Reduced species ionic charge concentration

$$I_R = (C_R - C_R^*)z_R$$

Oxidized species ionic charge concentration

$$I_O = (C_O - C_O^*)z_O$$

Sum of I_R and I_O gives the charge imbalance.

Supporting electrolyte ions migrate into the diffusion layer to neutralize the charge imbalance.

Problem Description (continued)

Density change is calculated from the change in concentrations of the supporting electrolyte ions, given by the following equation.

$$\Delta\rho = \Delta C_{S^-} M_{S^-} + \Delta C_{S^+} M_{S^+}$$

Migration ratio:
Determined by their respective transference numbers (ion transport numbers).

Density is calculated as

$$\rho = \rho^* + \Delta\rho$$

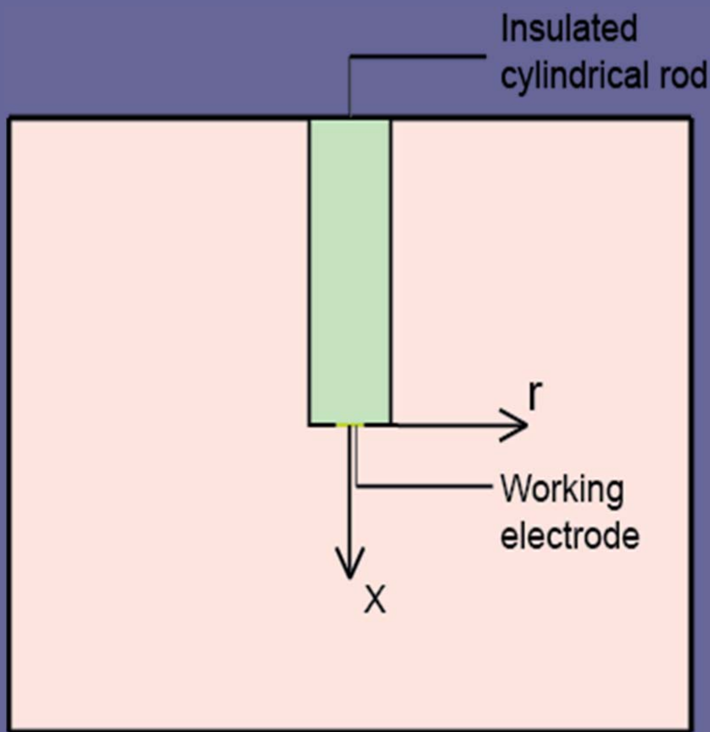
Body force term is calculated as

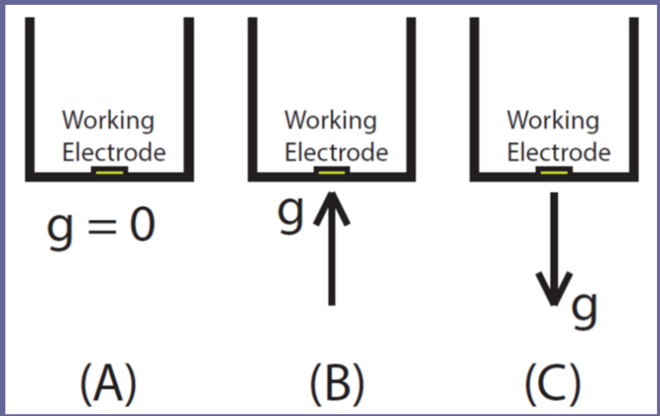
$$f_\rho = -\Delta\rho g$$

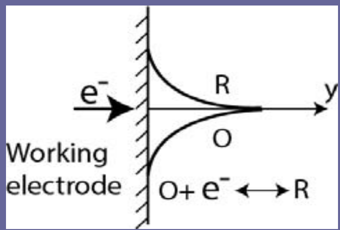
Solution Highlights

- Software package: ANSYS FLUENT
- Write a user-defined function (UDF) for NC, and add the UDF module to the solver module
- Natural convection will appear as a body force term in the modified momentum equation
- 3D domain with a disk working electrode was used.
- Continuity, momentum and species equations are solved in a coupled manner
- Time-accurate solution is obtained up to ~300s elapsed time
- Solved on Intel 8-core workstation
- CPU time up to several days

Case Summary







Material Properties

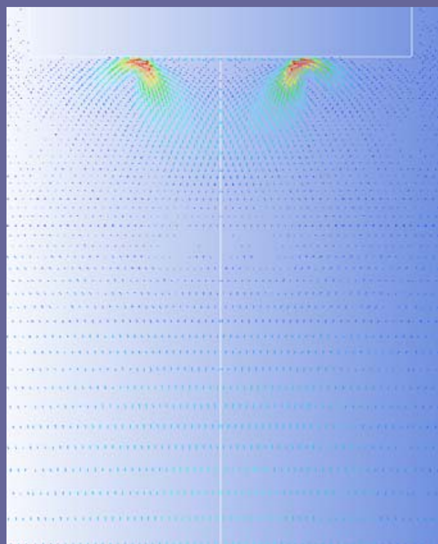
- Redox species: TMPD
- supporting electrolyte: CH3CN/0.5M TBAP
- Initial concentrations: $C_{TMPD-} = 10.3$ mM, $C_{TMPD+} = 0$
- Temperature: Uniform at T = 298K. Joule heating is neglected
- Operating mode: Potential step, high enough for operation in the diffusion-limited regime
- Electrical conductivity of the bulk solution $\chi = 0.625$ S/m
- Density: Calculated using the present model

Next slide………..

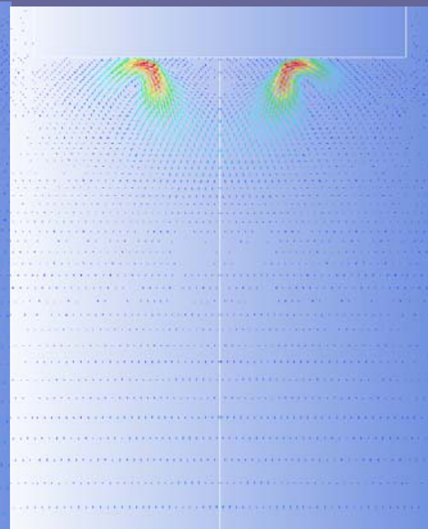
Case B velocity vector plots

Frame	t(s)	v_{max}
(a)	4.62	46.6 μm/s
(b)	6.62	82.4 μm/s
(c)	8.62	187 μm/s
(d)	10.62	481 μm/s
(e)	12.62	782 μm/s
(f)	14.62	1.46 mm/s
(g)	16.62	1.80 mm/s
(h)	18.82	1.50 mm/s

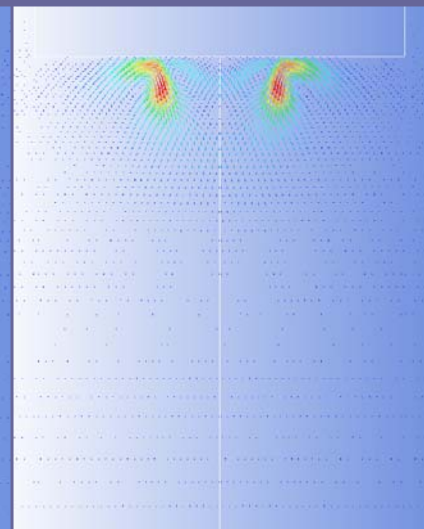
Case B



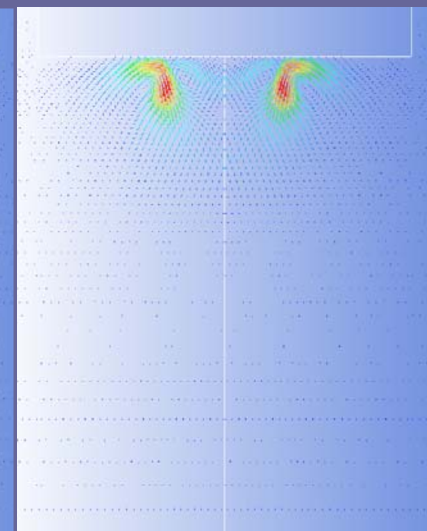
a (4.64s)



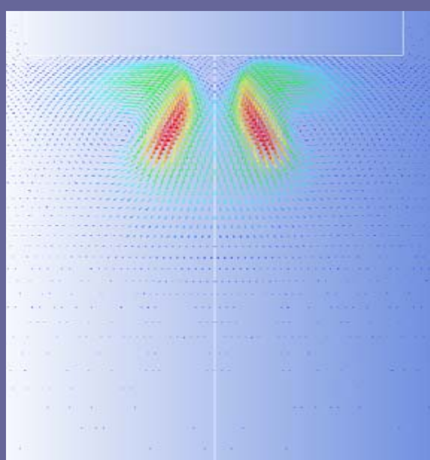
b 6.64s)



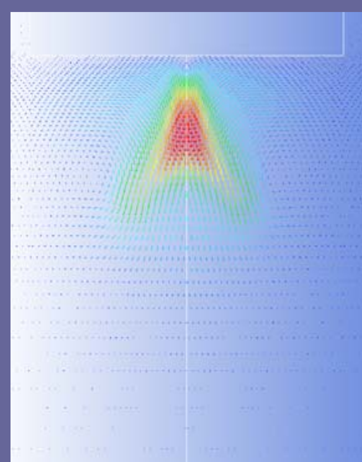
c (8.64s)



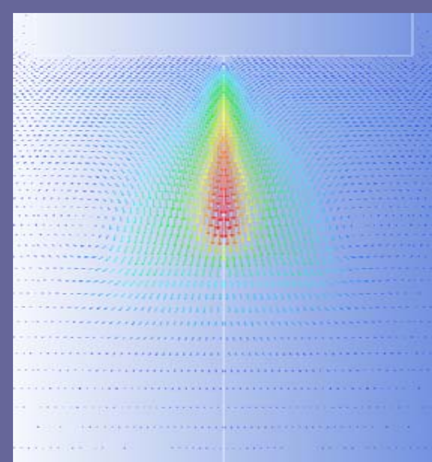
d (10.64s)



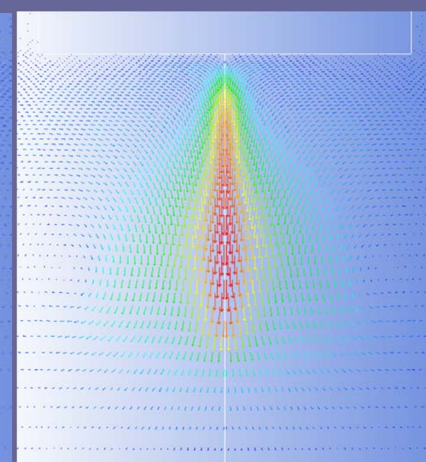
e (12.64s)



f (14.64s)

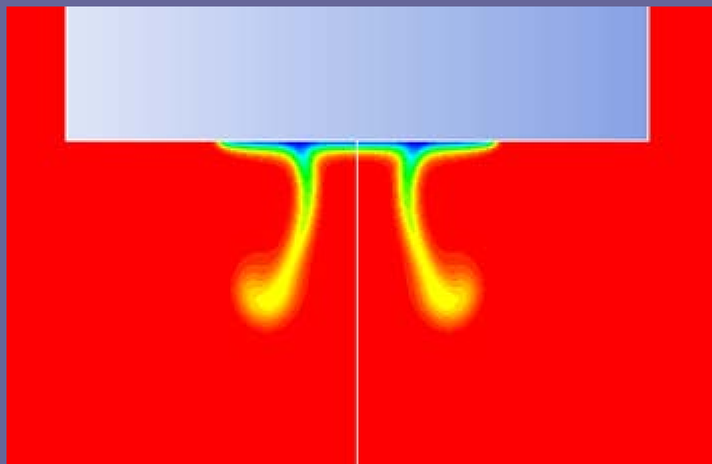


g (16.64s)

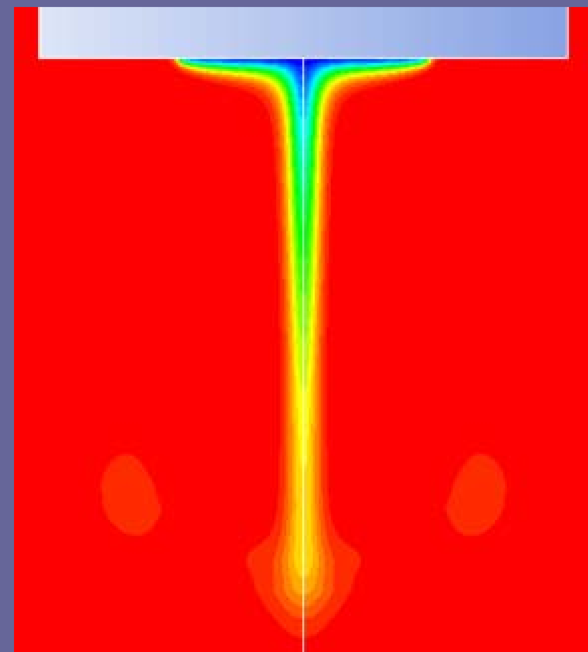


h (18.64s)

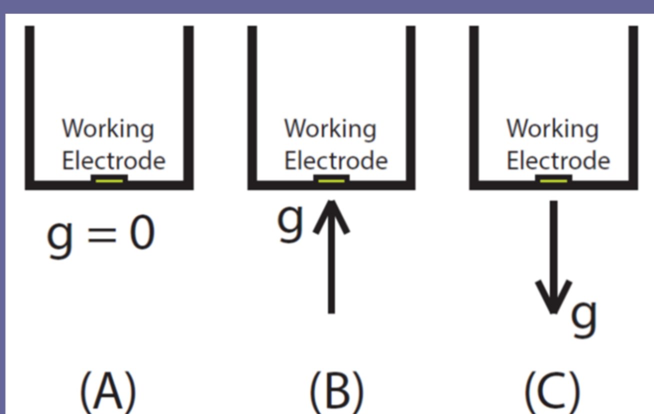
Case B Density Contours



a: t = 12.64s

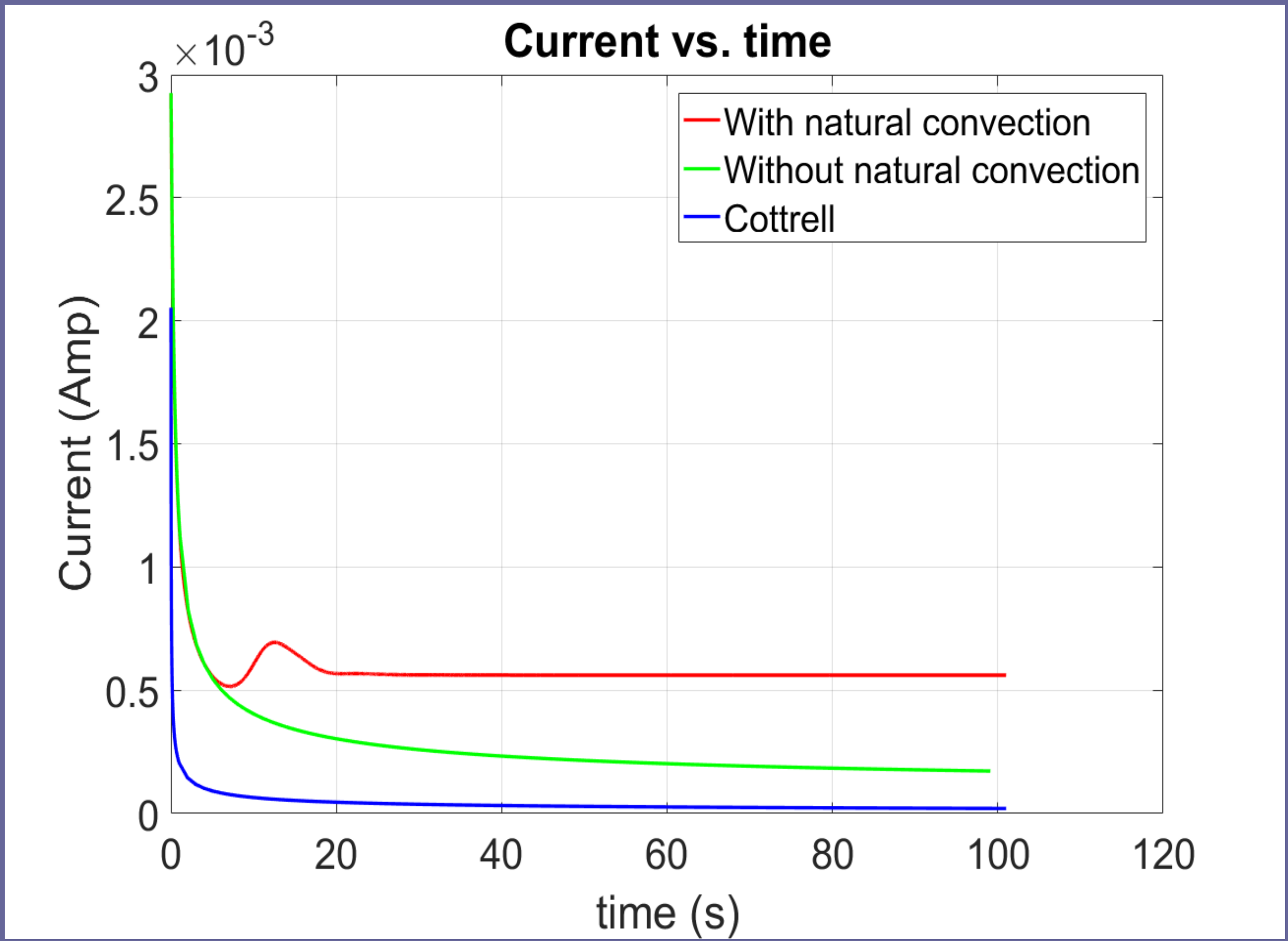


b: t = 19.64 s

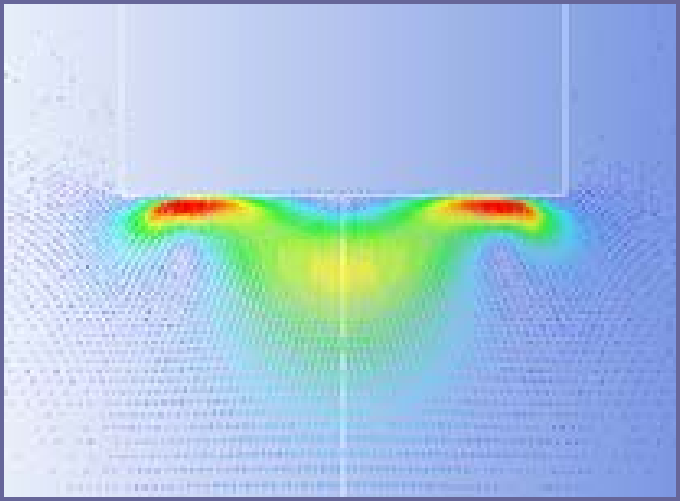


Color key:
red: 785 kg/m^3
blue: 783 kg/m^3

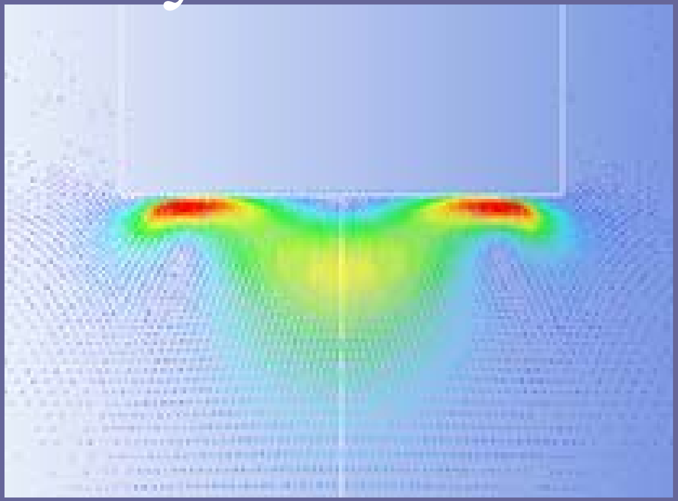
Case B


Current vs. time
×10^-3
3
2.5
2
1.5
1
0.5
0
Current (Amp)
0
20
40
60
80
100
120
time (s)
With natural convection
Without natural convection
Cottrell

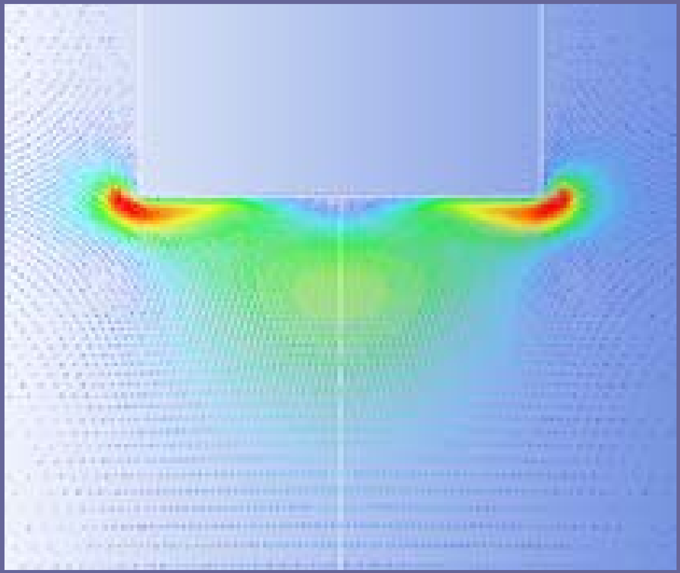
Case C Velocity Vectors



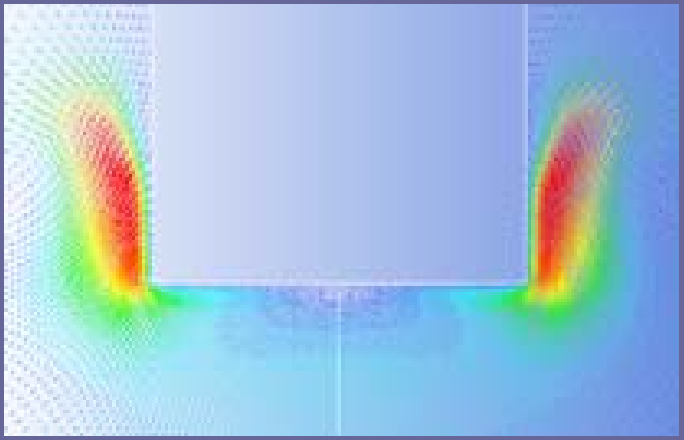
(a): t = 4.73s, V_{max} = 31.5e-2 μm/s



(b): t = 19.73s, V_{max} = 54.9 μm/s

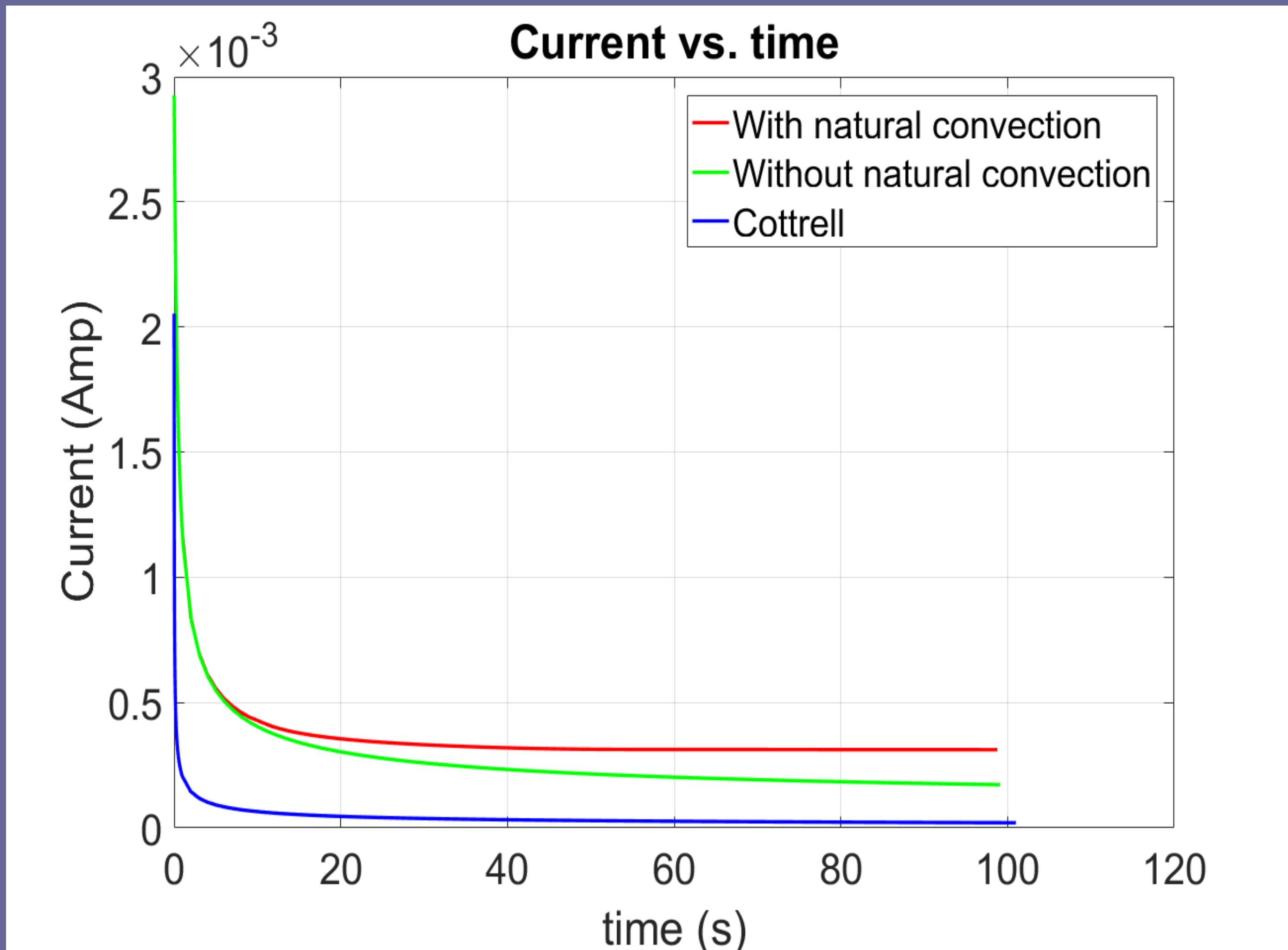


(c): t = 39.73s, V_{max} = 70.2 μm/s



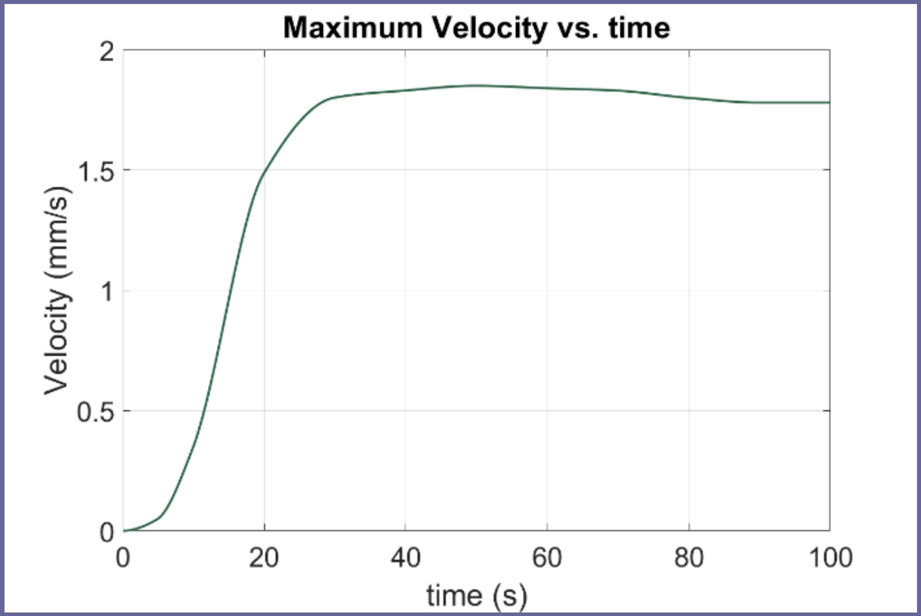
(d): t = 69.73s, V_{max} = 184 μm/s

Case C Current vs. time

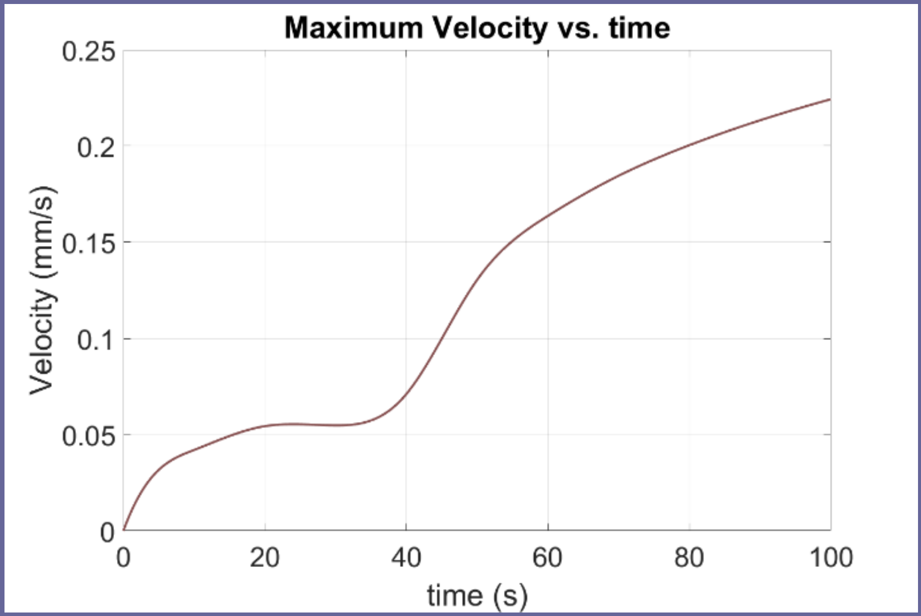


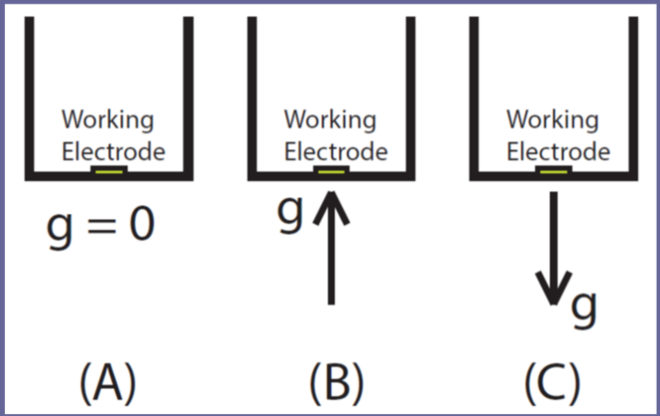
Maximum velocity vs. time

Case B

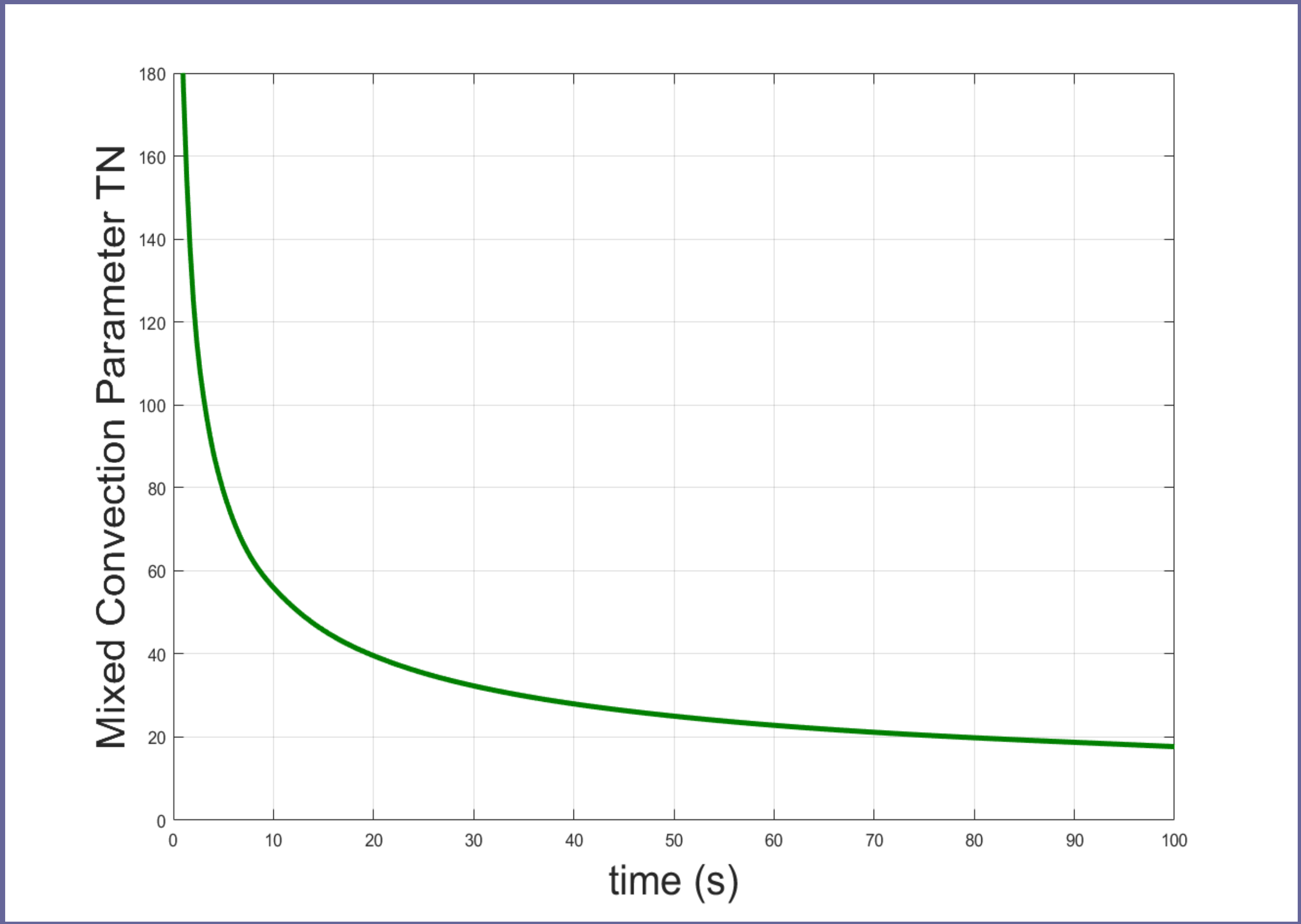


Case C





Mixed Convection Parameter TN vs. time



Results Highlights

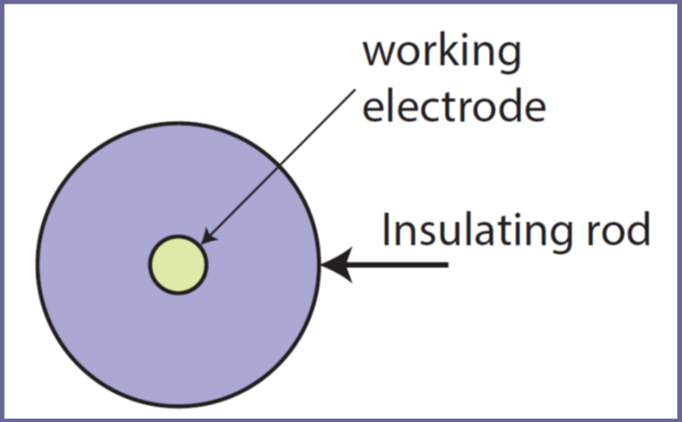
- Velocity magnitudes are an order of magnitude lower when the flow is toward the surface.
- Maximum velocity location depends on the flow direction (toward or away from the surface).
- The flow features can be explained considering acceleration of the fluid elements along the streamlines due to the body forces.

Experiments

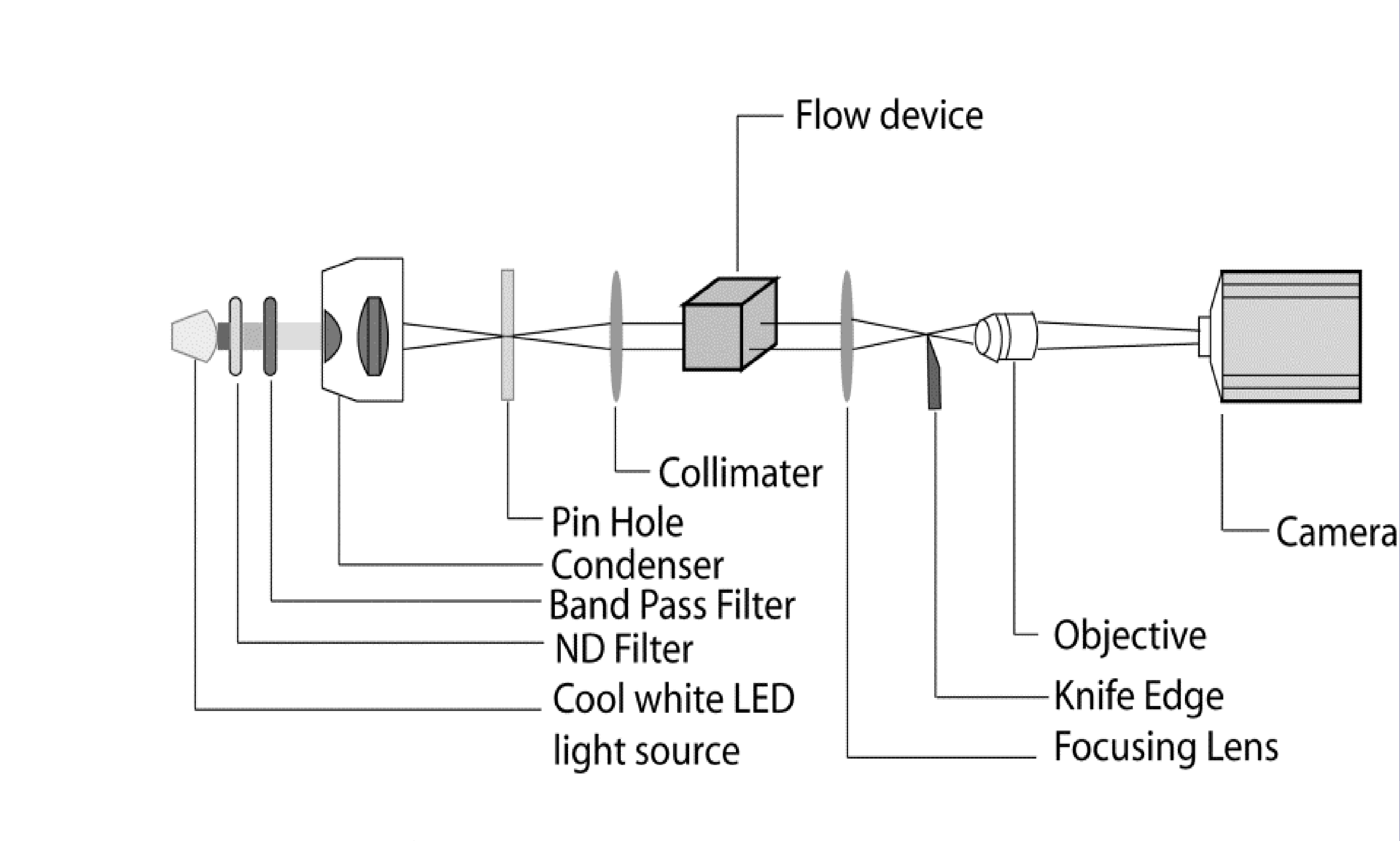
Experiments based on Schlieren Imaging

- Experiments were conducted on Ferri/Ferro with the KCl in aqueous solution as supporting electrolyte.
- Chronoamperometry was performed under potential step to plot *i* vs. *t*.

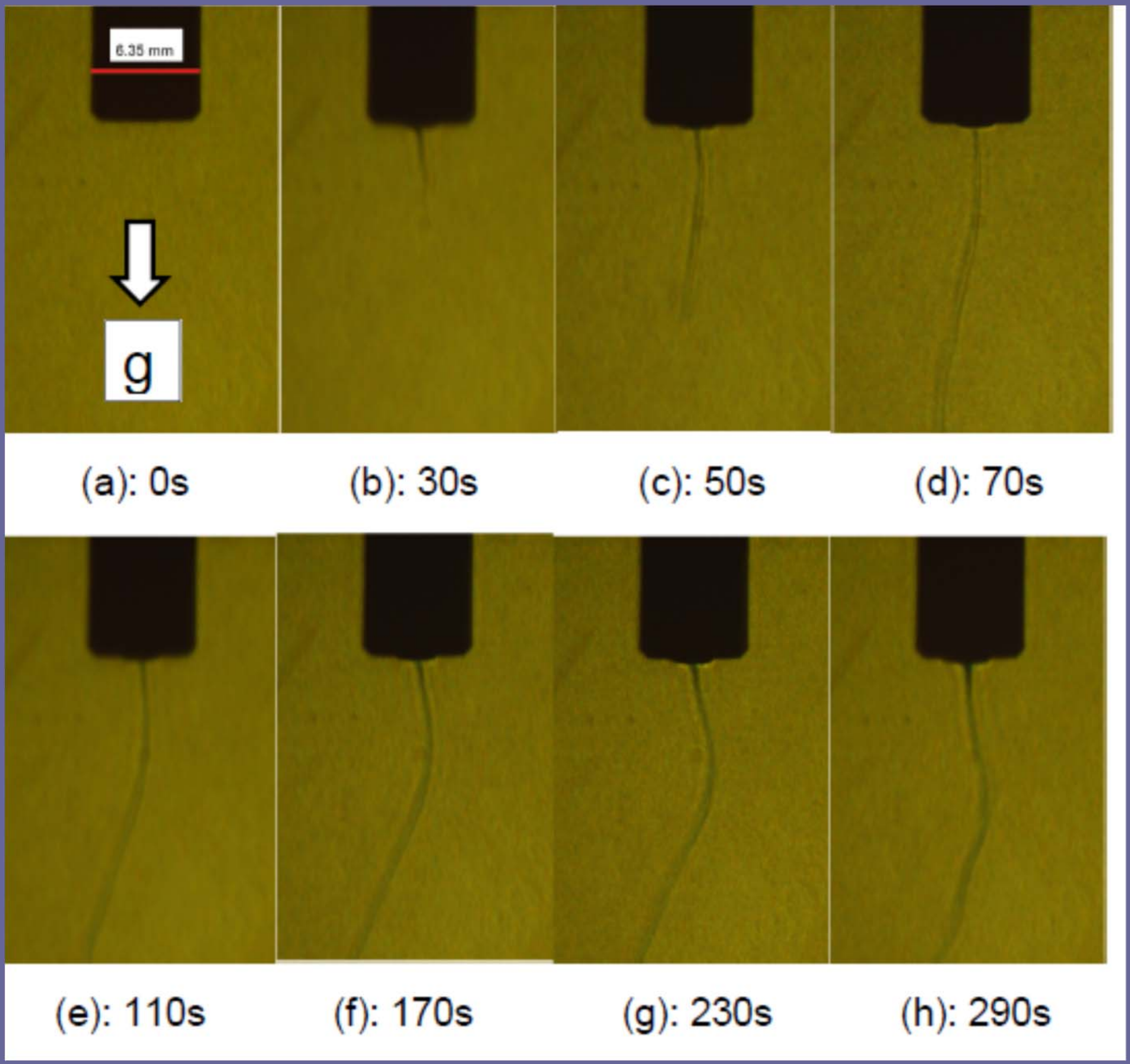
- Pt disk working electrode
- Pt wire counter electrode
- Ag/AgCl reference electrode
- 50 mm x 50 mm x 50 mm electrochemical cell with flat transparent walls for optical diagnostics



Schlieren/shadowgraph



Results



Shadowgraph images of 3 mm dia Pt electrode inlaid in 6.35 mm dia PEEK rod.
Ferri/ferro (0.1M/0.1M) in aqueous KCl (0.1M) solution
Chronoamperometry.
Potential step: 1V

Results: Schlieren Imaging

- Velocity estimates by measuring visible heights of the slender column

  u_y ~ 0.5 mm/s using frames (a) and (b)

  u_y ~ 1.4 mm/s using frames (b) and (c)

- Velocity magnitudes are in order of magnitude agreement with previous experiments of White’s group and Bau’s group.

- Initially, the velocity increases.

- A blob is formed on the circular flat face confined to the circular electrode region.

Results: Schlieren Imaging (continued)

- A slow diffusion broadening of the slender column can be seen in the sequence (a) - (h).
- A larger diameter convection column at larger times (Frames (f), (g) and (h) at t = 170s, 230s and 290 s, respectively) is formed with a height ~30 mm in Frame (h).
- The slender column has an instability indicated by the waviness. However, no oscillations were observed during the duration of the experiments.

Results: Schlieren Imaging (continued)

Behavior when potential is switched (images not included)

- Beyond the working electrode region, the concentration gradients are too weak to observe by schlieren.

- The current vs. time plot (not presented) is not as smooth as in the first case.

Conclusions

- A scaling parameter (TN) for mixed convection is proposed.
- A model for natural convection is developed.
- Simulations based on the model show reasonably good agreement with experiment.
- Experiments show natural convection in the form of a column that grows downward.
- When the reaction direction is reversed, a blob forms in the vicinity of the electrode.
- Schlieren doesn't appear to be sensitive enough to pick up the upward convection around the insulating rod.
- Simulations and the experiments show higher velocity magnitudes when natural convection direction is away from the electrode surface.

Future Work

- Conduct additional simulation case studies for different redox pairs, solution concentrations, and B-field strengths.
- Perform simulations of the Ferri/Ferro/KCL mixture of the experiments.
- Perform simulations and experiments for electrode sizes varying from 1mm to 25 μm to understand geometry dependence.
- Perform simulations of representative microfluidic cell.
- Implement background-oriented schlieren (BOS) for quantitative measurement of the density field.