07 Oct 2016

Natural Convection and Forced Convection Model based on Electroneutrality and Migration in Redox MHD Systems

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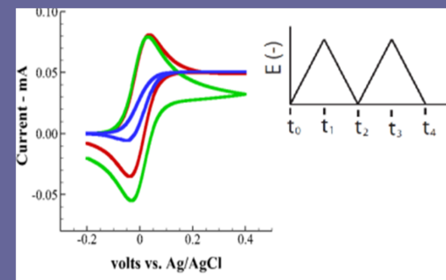
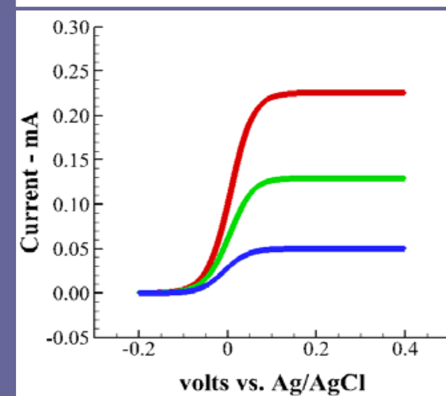
PRiME 2016/230th ECS Meeting, October 2-7, 2016
Honolulu

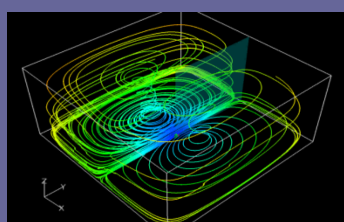
Acknowledgements

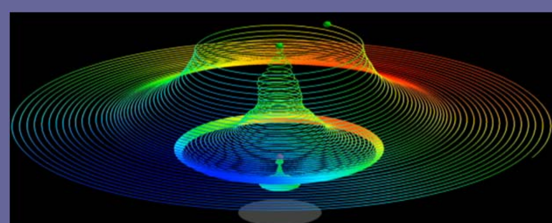
National Science Foundation Grants

Award number CBET-1336722
Award number CHE-0719097









Outline

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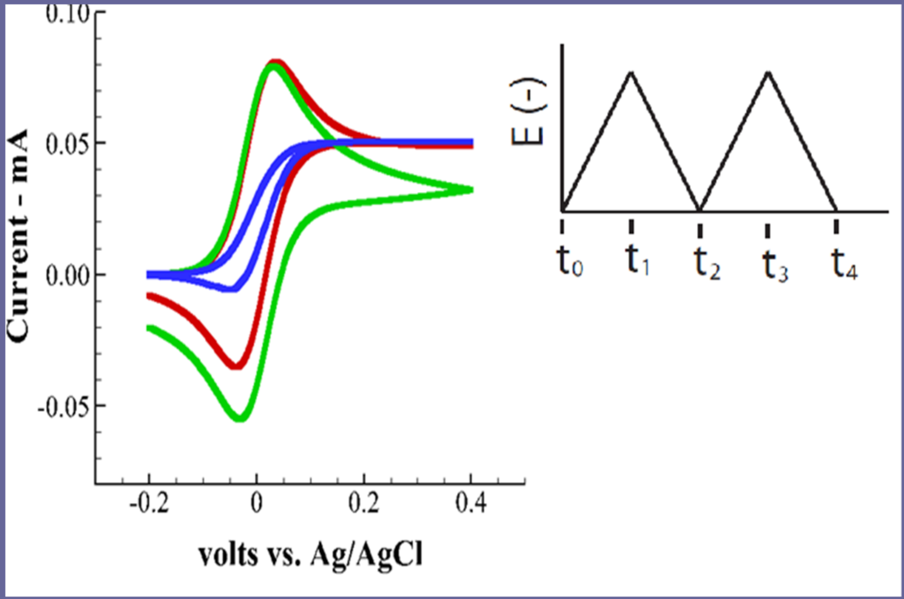


Motivation

- Potential impact on sensing: Natural convection has been studied in electrochemistry and Microfluidics due to its potential impact sensing.
- NC is less understood in redox systems: Natural convection is better understood and modeled in electrodeposition.
- Previous models do not have wide applicability.
- Experiments show influence observed phenomena.
- Selman and Newman* model:
- The authors modelled NC in redox electrochemistry by using an densification coefficient similar to the expansion coefficient in temperature-induced natural convection

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

Motivation (continued)

Selman and Newman model

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

α_i – densification coefficient

$C_i - C_{ib}$ is the change in concentration of species *i*.

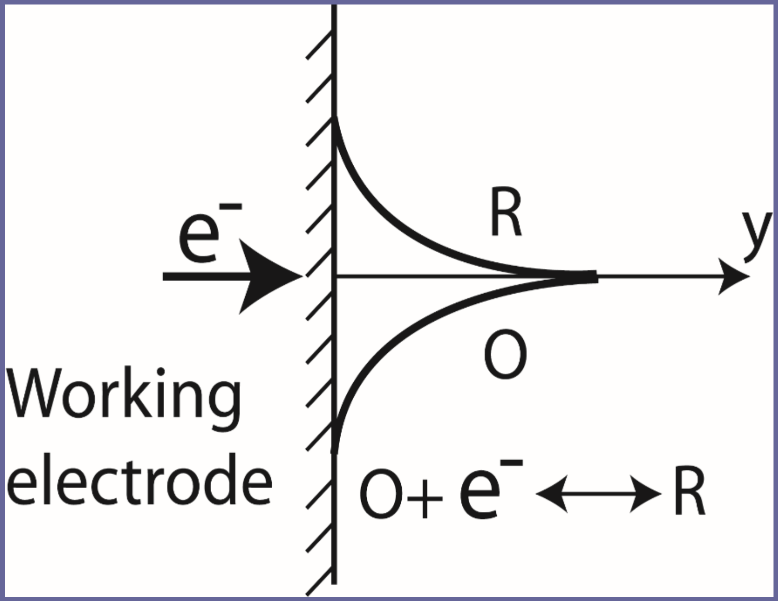
Background

- Migration to satisfy electroneutrality and solvation effect models
- The former is more widely accepted as the source of NC
- Balance sheet approach of Bard and Faulkner*
- Supporting electrolyte ions migrate toward the electrode to satisfy Electroneutrality
- The effect is dependent on 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

- 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 move 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

$$Ra_L = \frac{g(\rho_s - \rho_b)L^3}{\mu D}$$

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

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

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 length
δ – Diffusion layer thickness
d – Electrode dimension

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

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

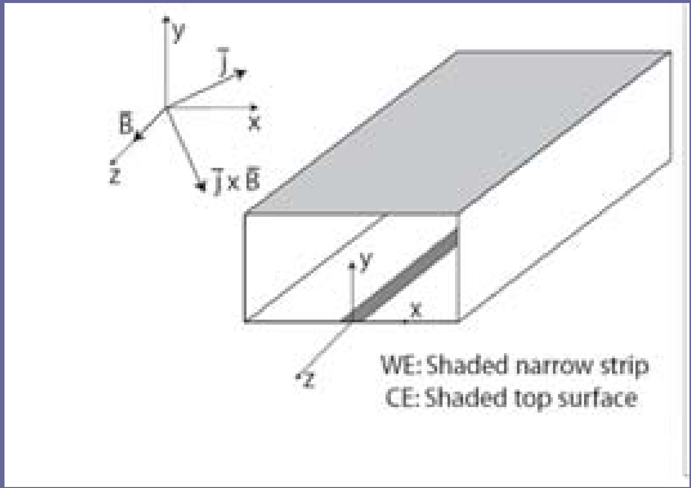
Solution Highlights

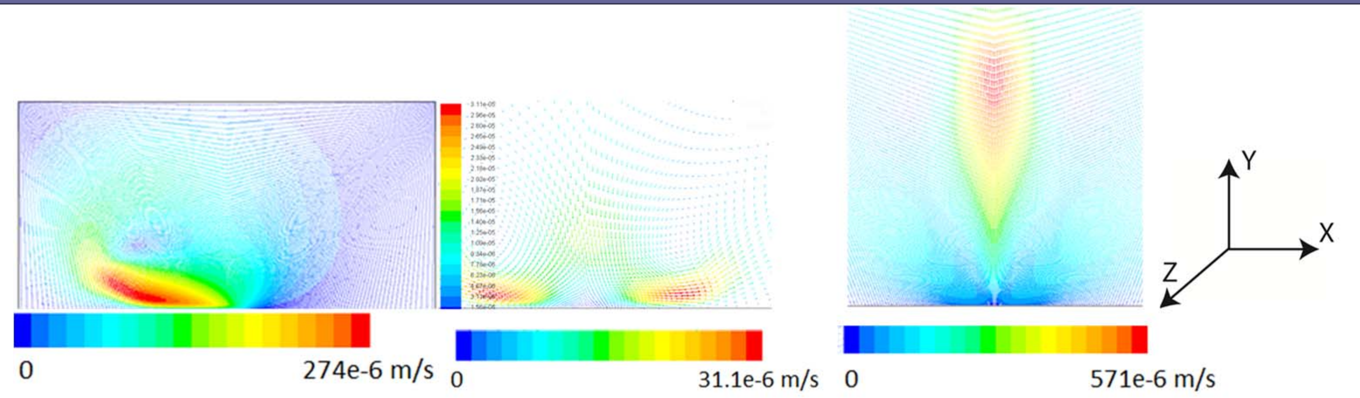
- Software package: ANSYS FLUENT
- Write a user-defined function (UDF) for natural convection
  Add the UDF module to the solver module
- Natural convection will show as a body force term in the modified momentum equation
- A 2D domain with a band working electrode was used
- Continuity, momentum and species equations are solved in a coupled manner
- Mesh size: ~42,000 quad cells
- Time-accurate solution is obtained up to 40s elapsed time
- Solved on Intel 8-core workstation
- CPU time up to several days

Results (B = 0)

Cell size: 20 mm x 10 mm
Working electrode width = 2 mm

(a) $g_x = -9.81\ m/s^2$(to the left), t = 35s
(b) $g_y = -9.81\ m/s^2$(toward the electrode), t = 39s
(c) $g_y = +9.81\ m/s^2$ (away from the electrode), t = 39s





(a) (b) (c)

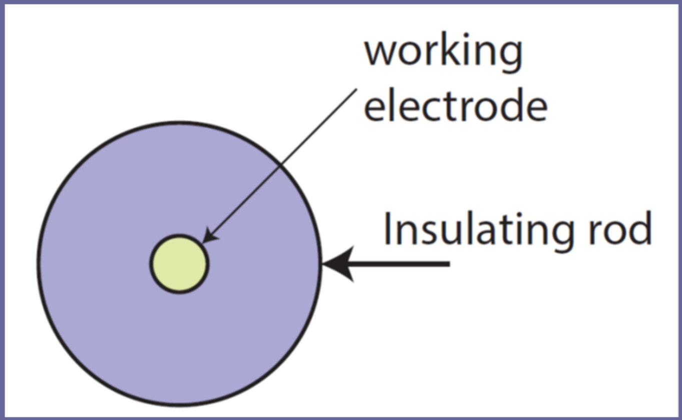
Simulation Results (B = 0)

- Maximum velocity = 0.571 mm/s at 39 s from the start of the potential step.
- Clockwise vortex is formed Frame (a) with gravity parallel to the electrode surface.
- Velocity magnitudes are an order of magnitude lower when the flow is toward the surface (Frames (b) and (c)).
- Maximum velocity location depends on the flow direction (toward or away from the surface, Frames (b) and (c))
- The flow features can be explained considering acceleration of the fluid elements along the streamlines due to the body forces.

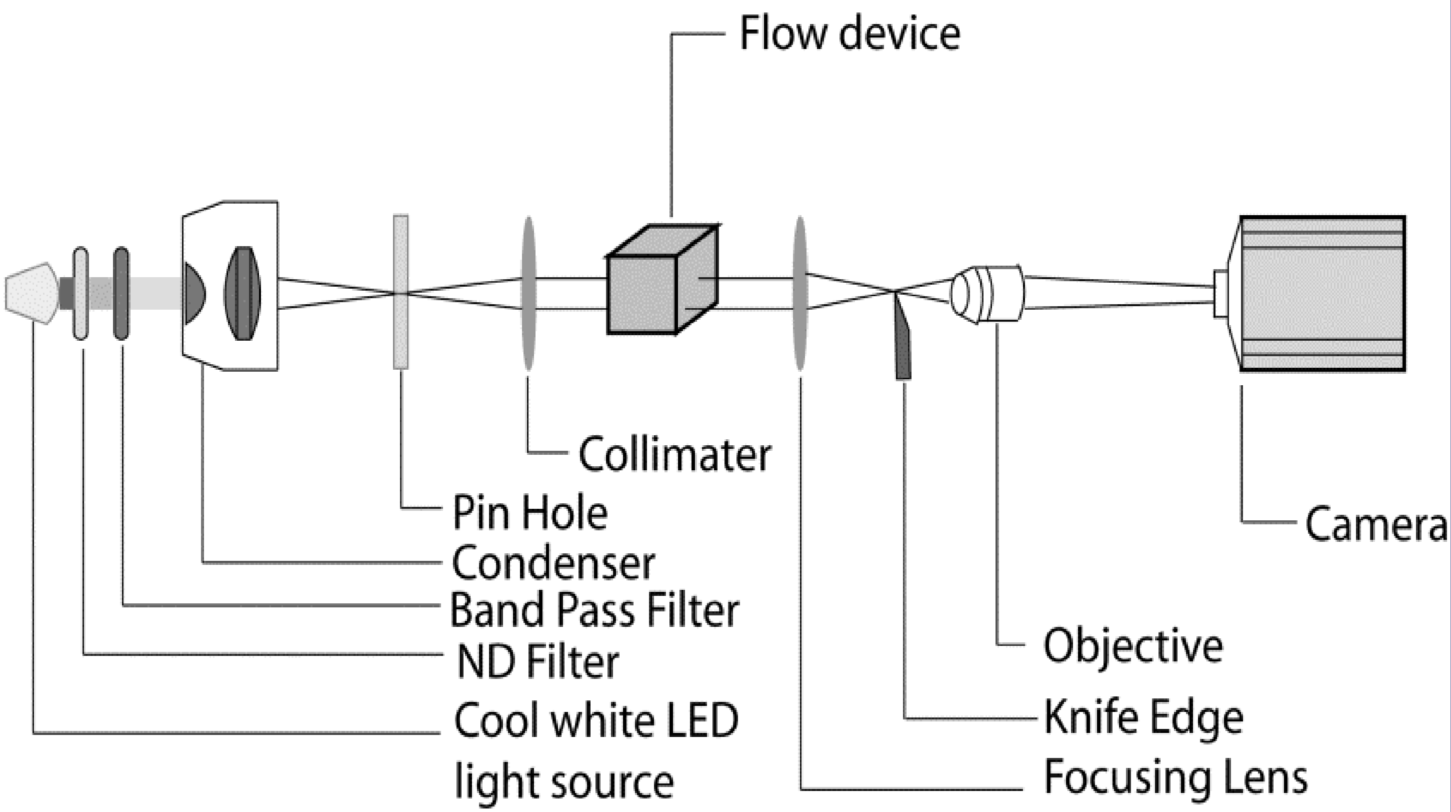
Experiments based on Schlieren Imaging

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

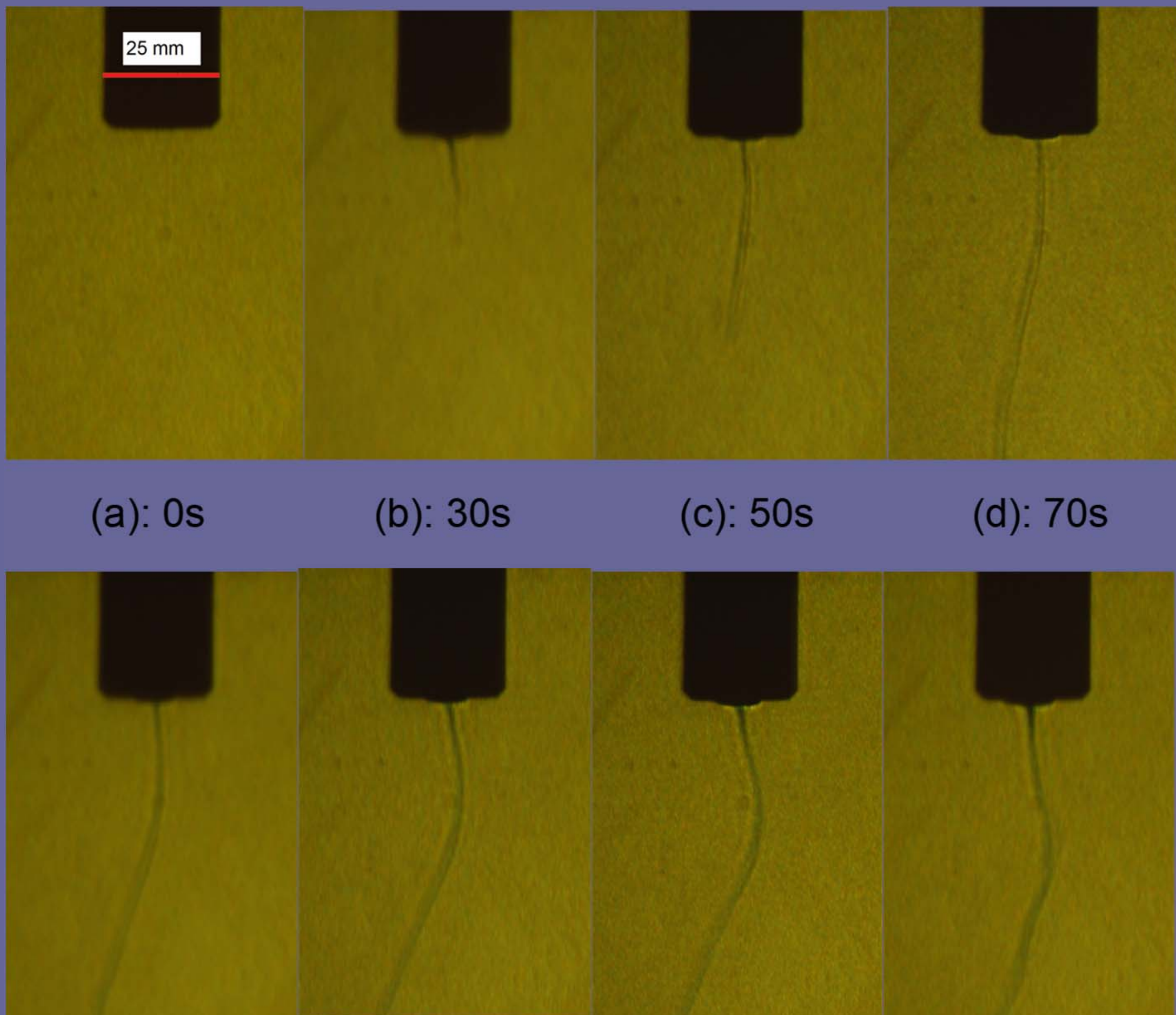
- Pt disk working electrode
- Pt wire counter electrode
- Ag/AgCl reference electrode
- 50 mm x 50 mm x 50 mm electrochemical cell with flat transparent walls for optical diagnostics



Micro Schlieren



Results



(a): 0s (b): 30s (c): 50s (d): 70s

(e): 110s (f): 170s (g): 230s (h): 290s

g

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.
- 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)

- A secondary wave of shorter wavelength is seen at t = 290s (Frame (h)).
- A slow diffusion broadening of the slender column can be seen the sequence (a) - (h).

Results: Schlieren Imaging (continued)

Behavior when potential is switched

- Initially, a blob forms on the electrode surface.
-
- Beyond the working electrode region, the concentration gradients are too weak to observe by schlieren.
- The maximum visible size of the blob is slightly larger than the electrode diameter.
- The current vs. time plot (not presented) is not as smooth as in the first case.
- At higher potentials, bubbles form at the electrodes.

Conclusions

- A model for mixed convection is proposed.
- 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 3D axisymmetric geometry 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.
- Obtain estimates of diffusion layer thickness for mixed convection model.
- Implement background-oriented schlieren (BOS) for quantitative measurement of the density field.