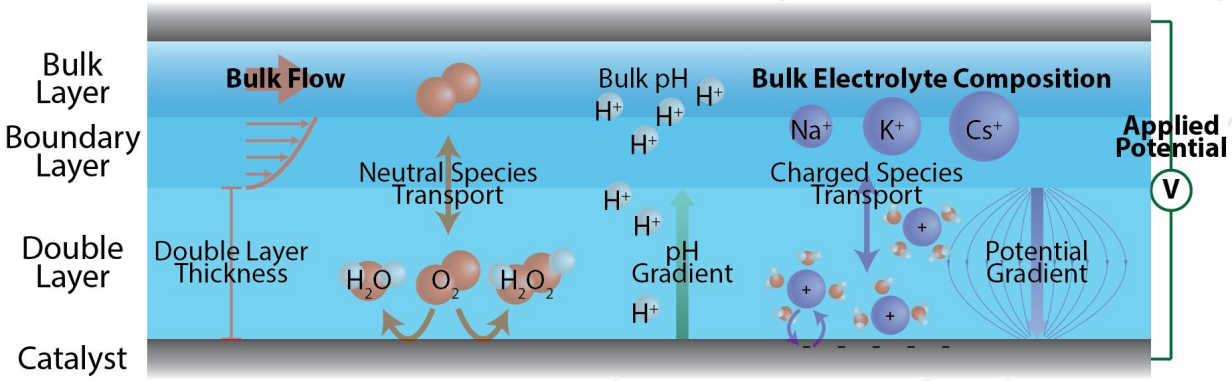
Mathematical investigation of Bulk and Local Effects in Electrocatalysis



Niall M. Mangan
Assistant Prof.
Eng. Sci. & Applied Math
Northwestern University

Northwestern
PAULA M. TRIENENS INSTITUTE FOR SUSTAINABILITY AND ENERGY

Yifan Zhang

Grace Hooper

Yash Deodhar

Dr. Alasdair Hastewell

NU Center for Sustainability and Engineering Resilience

SIMONS FOUNDATION

NU Center for Optimization and Statistical Learning

U.S. DEPARTMENT OF ENERGY | Office of Science

NIH National Institutes of Health — Turning Discovery Into Health

BILL & MELINDA GATES foundation

DEVCOM CHEMICAL BIOLOGICAL CENTER

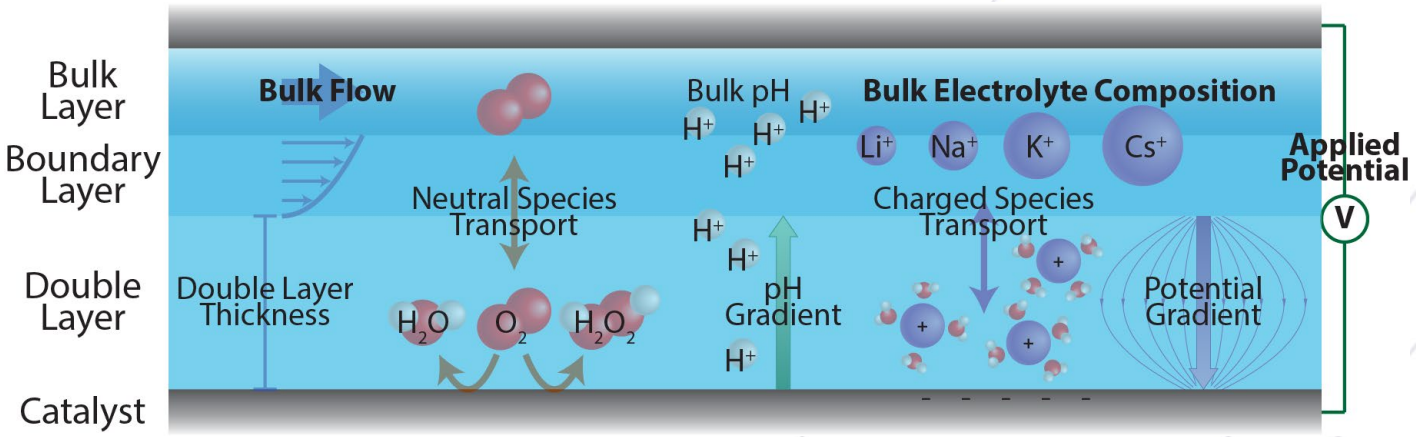
Northwestern
PAULA M. TRIENENS INSTITUTE FOR SUSTAINABILITY AND ENERGY

CITY OF CHICAGO — INCORPORATED 4th MARCH 1837

WALDER FOUNDATION

IDPH ILLINOIS DEPARTMENT OF PUBLIC HEALTH

Reaction Environment Tuning



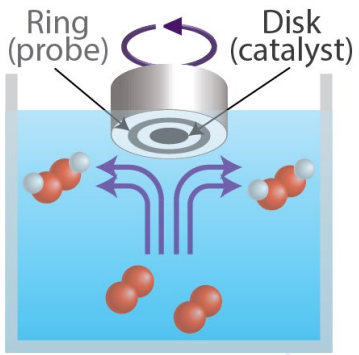
Prof. Linsey Seitz

Dr. Jithin George

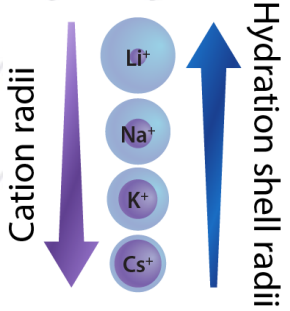
Dr. Brianna Ruggiero

Yash Deodhar

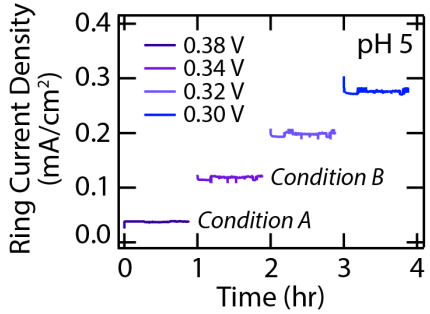
Mass Transport



Electrolyte Composition



Operating Potential / Current

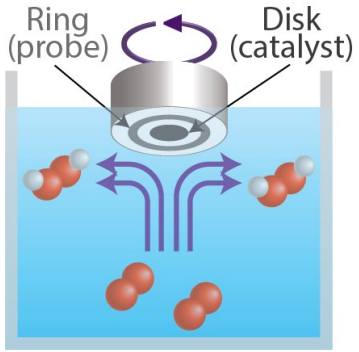


How do **macroscale** system properties…

…affect **microscale** environment at the catalyst surface…

…which impact **reactor performance** and **product selectivity**?

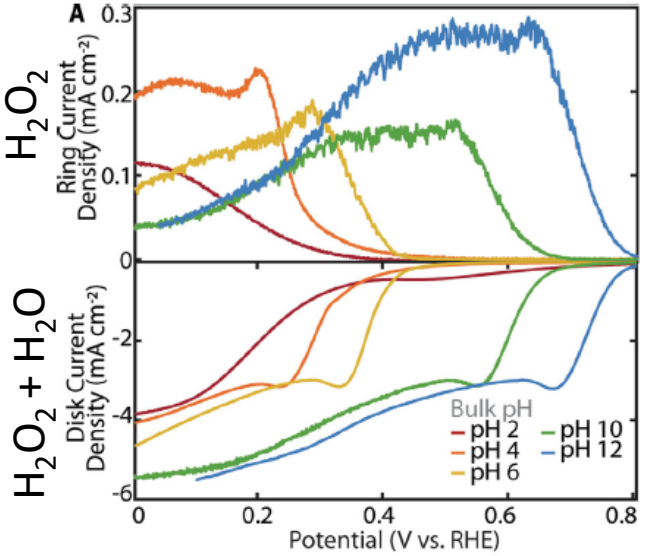
pH effects on reactor performance



Experimental Set up:

- Oxygen reduction reaction (ORR) for peroxide production
- Mesoporous carbon black CMK-3 catalyst
- Rotating Ring-Disk electrode
- Iridium oxide local pH sensing

Linear Sweep Voltammetry

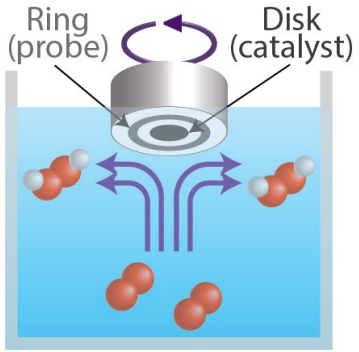


Prof. Linsey Seitz

Dr. Brianna Ruggiero

Ruggiero et al. *Journal of Catalysis* 414 (2022): 33-43.

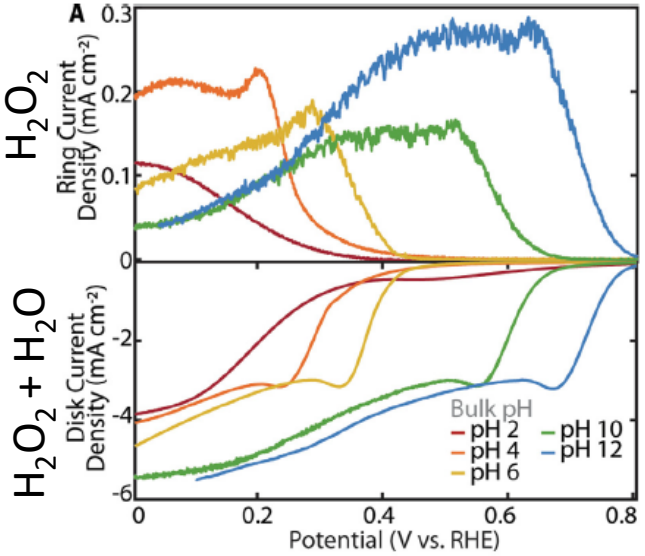
pH effects on reactor performance



Experimental Set up:

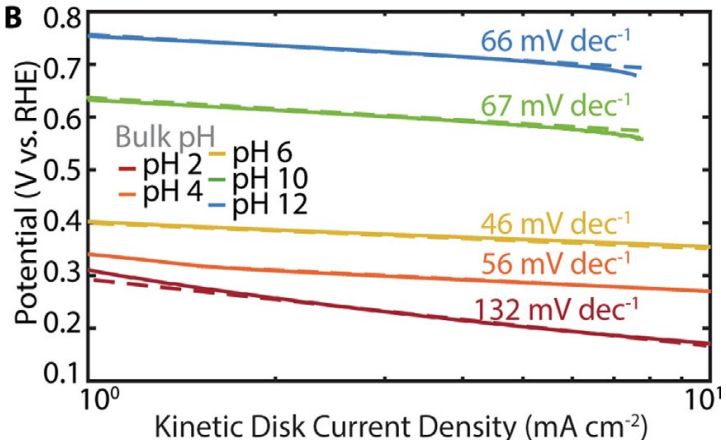
- Oxygen reduction reaction (ORR) for peroxide production
- Mesoporous carbon black CMK-3 catalyst
- Rotating Ring-Disk electrode
- Iridium oxide local pH sensing

Linear Sweep Voltammetry



Tafel slope approximation

$$\eta = a + b * \log(j_{disk,kin})$$

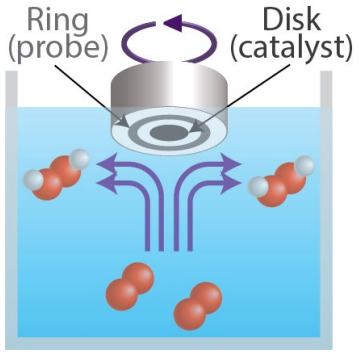


Prof. Linsey Seitz

Dr. Brianna Ruggiero

Ruggiero et al. *Journal of Catalysis* 414 (2022): 33-43.

pH effects on reactor performance



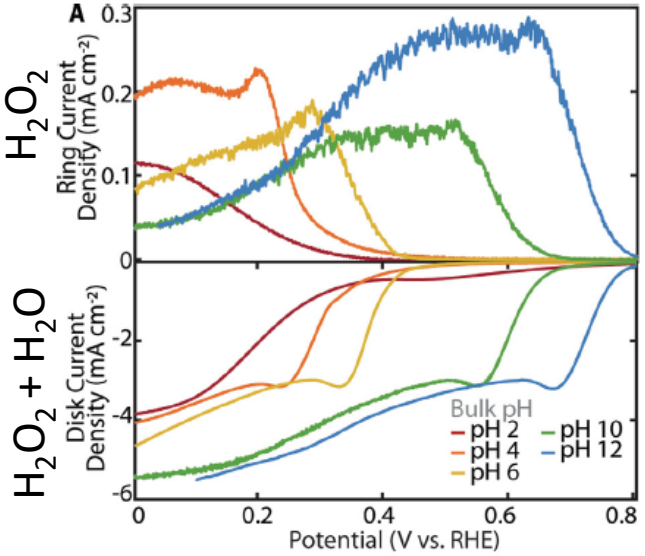
Experimental Set up:

- Oxygen reduction reaction (ORR) for peroxide production
- Mesoporous carbon black CMK-3 catalyst
- Rotating Ring-Disk electrode
- Iridium oxide local pH sensing

Prof. Linsey Seitz

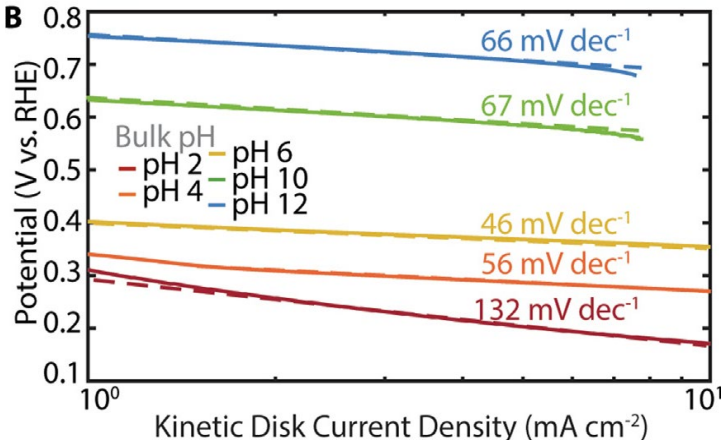
Dr. Brianna Ruggiero

Linear Sweep Voltammetry

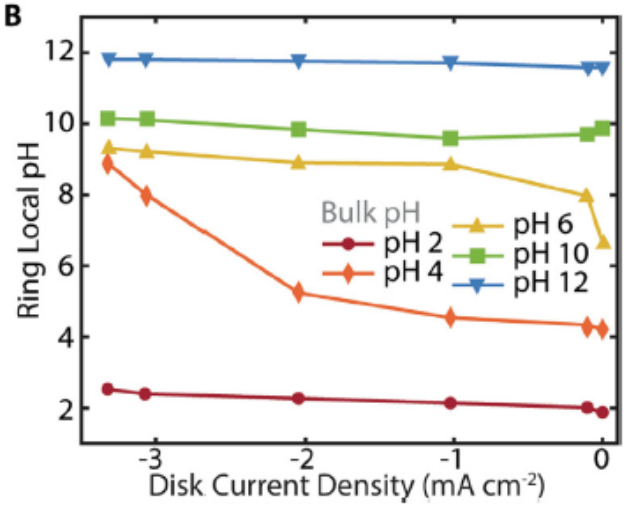


Tafel slope approximation

$$\eta = a + b * \log(j_{disk,kin})$$

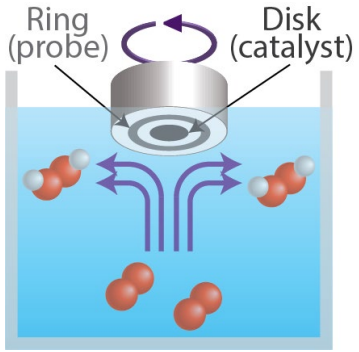


Local vs bulk pH



Ruggiero et al. *Journal of Catalysis* 414 (2022): 33-43.

pH effects on reactor performance



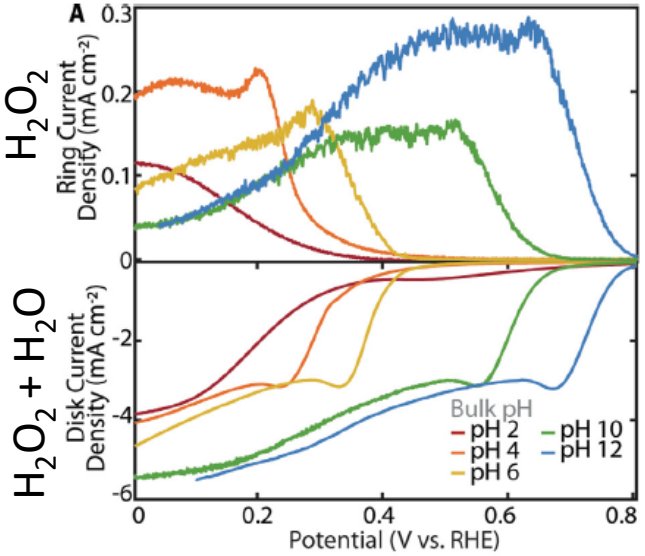
Experimental Set up:

- Oxygen reduction reaction (ORR) for peroxide production
- Mesoporous carbon black CMK-3 catalyst
- Rotating Ring-Disk electrode
- Iridium oxide local pH sensing

Prof. Linsey Seitz

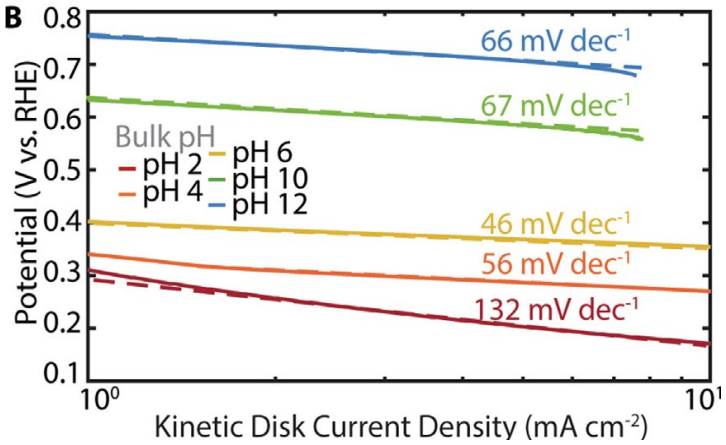
Dr. Brianna Ruggiero

Linear Sweep Voltammetry

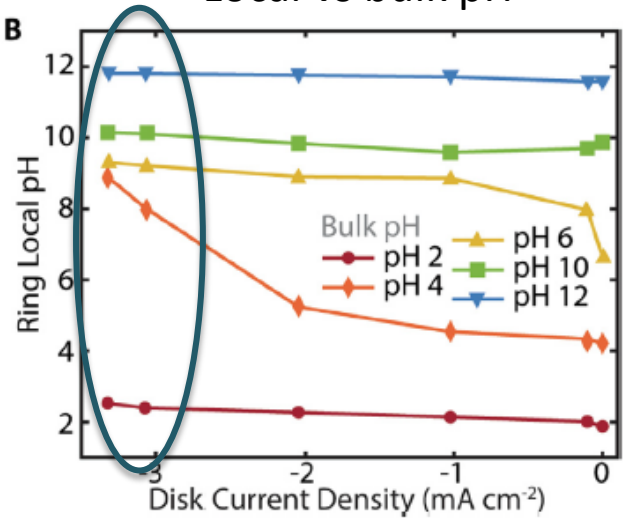


Tafel slope approximation

$$\eta = a + b * \log(j_{disk,kin})$$

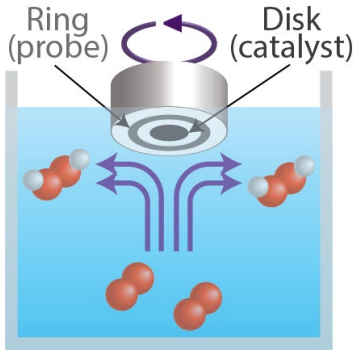


Local vs bulk pH



Ruggiero et al. *Journal of Catalysis* 414 (2022): 33-43.

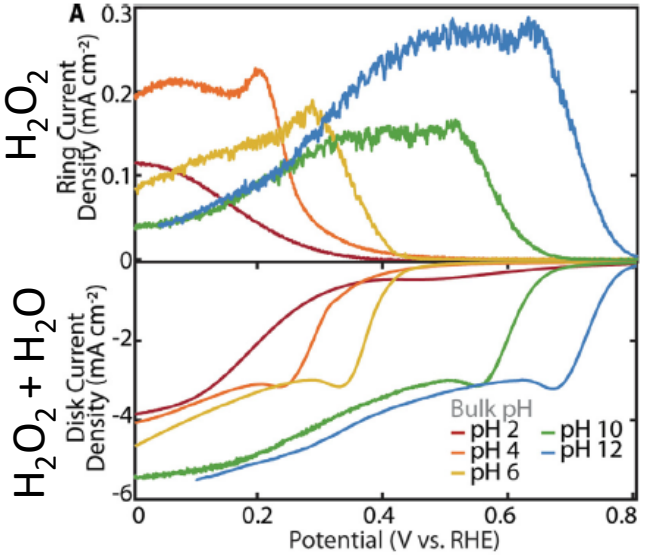
pH effects on reactor performance



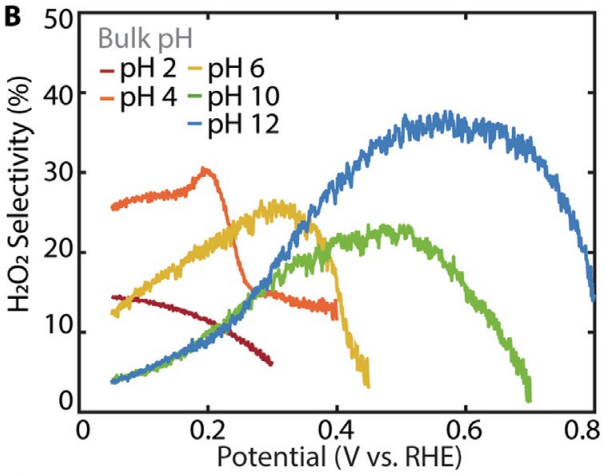
Experimental Set up:

- Oxygen reduction reaction (ORR) for peroxide production
- Mesoporous carbon black CMK-3 catalyst
- Rotating Ring-Disk electrode
- Iridium oxide local pH sensing

Linear Sweep Voltammetry



Selectivity

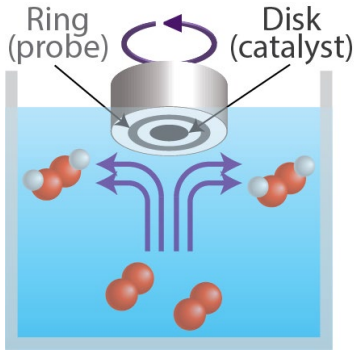


Prof. Linsey Seitz

Dr. Brianna Ruggiero

Ruggiero et al. *Journal of Catalysis* 414 (2022): 33-43.

pH effects on reactor performance



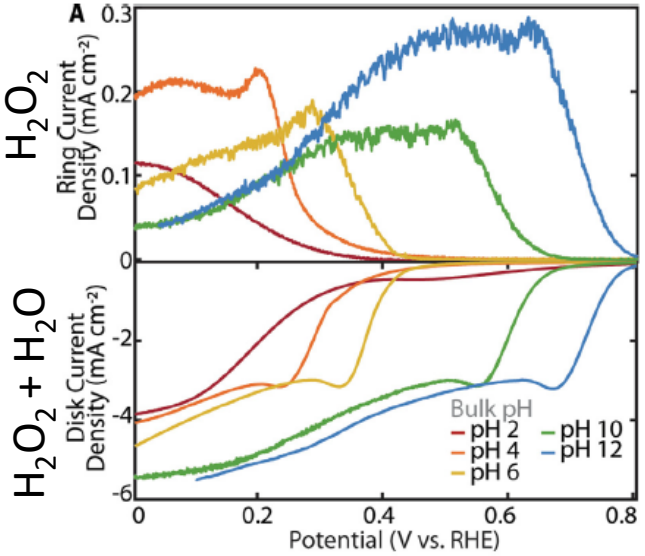
Experimental Set up:

- Oxygen reduction reaction (ORR) for peroxide production
- Mesoporous carbon black CMK-3 catalyst
- Rotating Ring-Disk electrode
- Iridium oxide local pH sensing

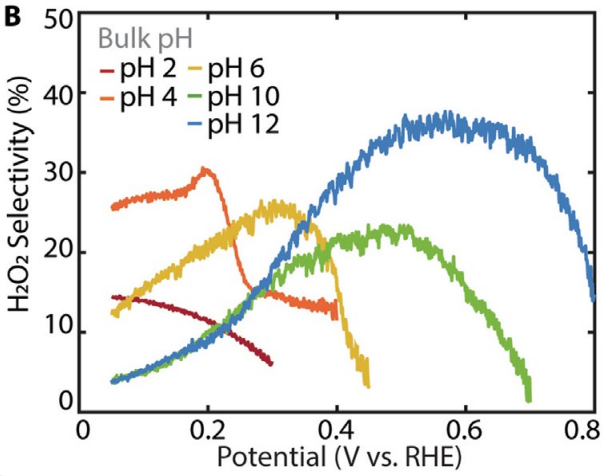
Prof. Linsey Seitz

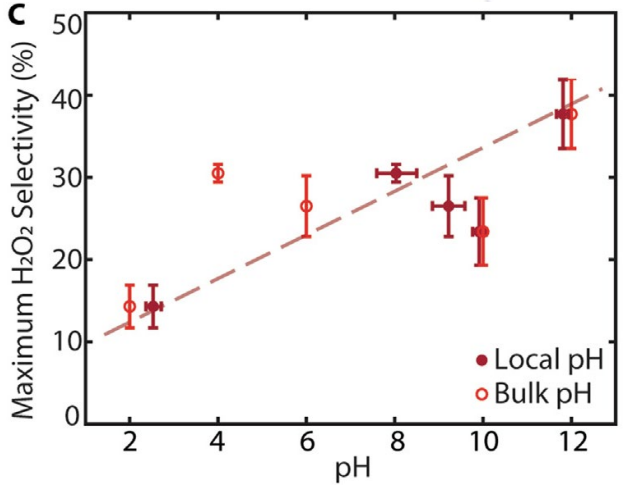
Dr. Brianna Ruggiero

Linear Sweep Voltammetry



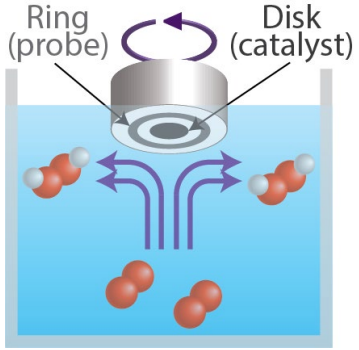
Selectivity

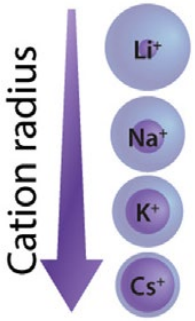


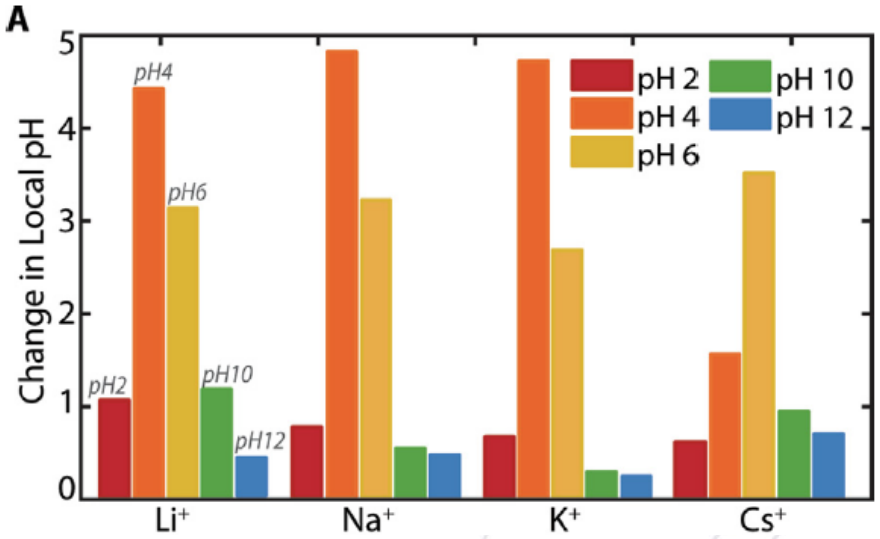


Ruggiero et al. *Journal of Catalysis* 414 (2022): 33-43.

Cation effects on reactor performance







Prof. Linsey Seitz

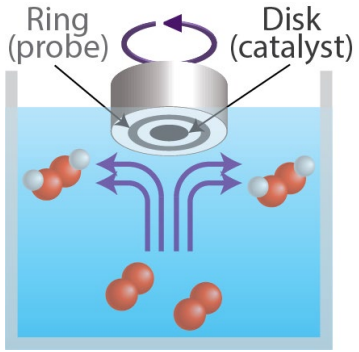
Dr. Brianna Ruggiero

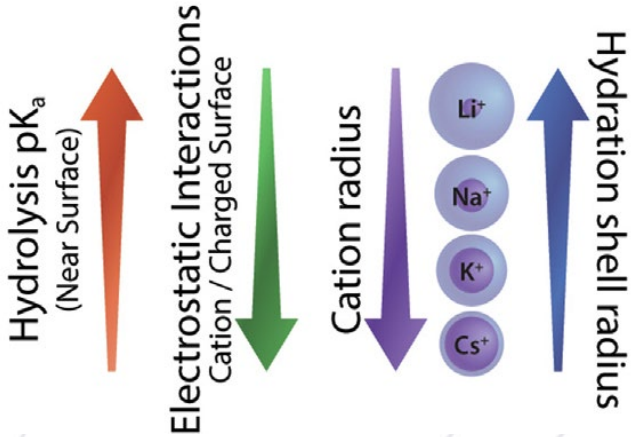
Ruggiero et al. *Journal of Catalysis* 414 (2022): 33-43.

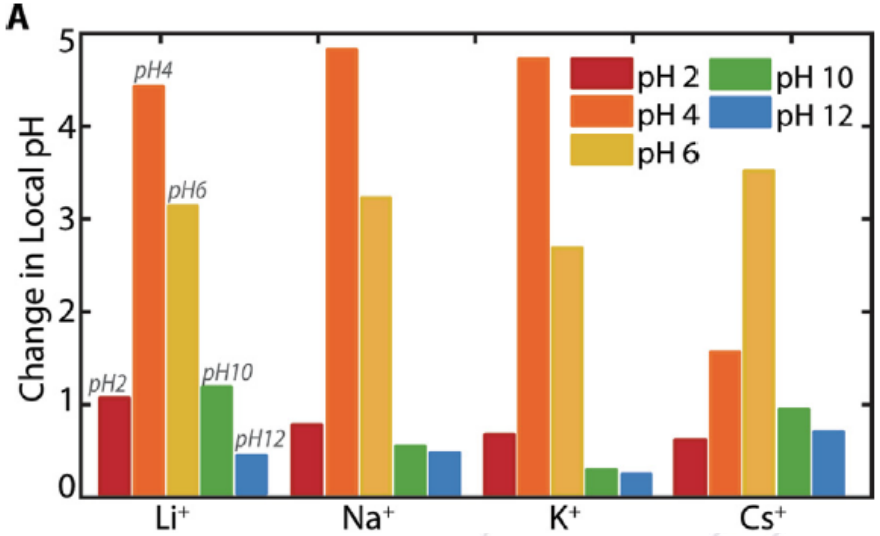
Cation effects on reactor performance

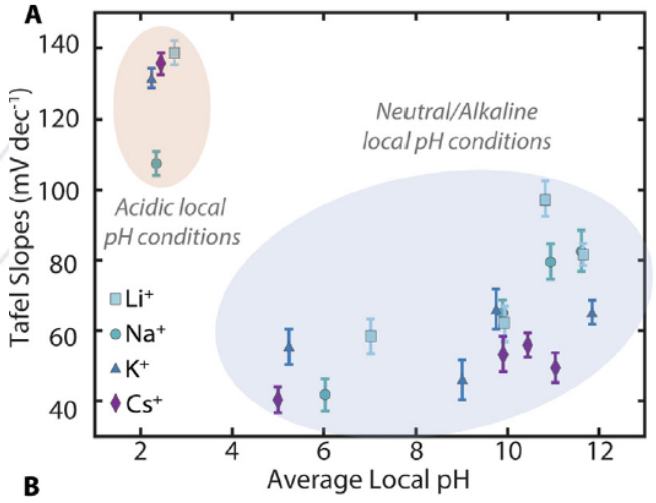
Prof. Linsey Seitz

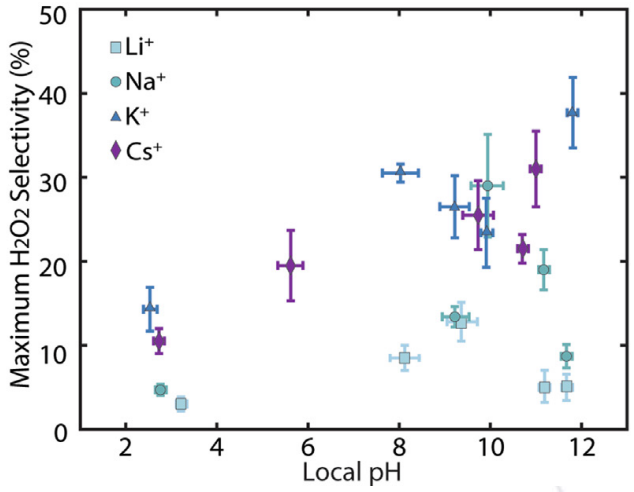
Dr. Brianna Ruggiero









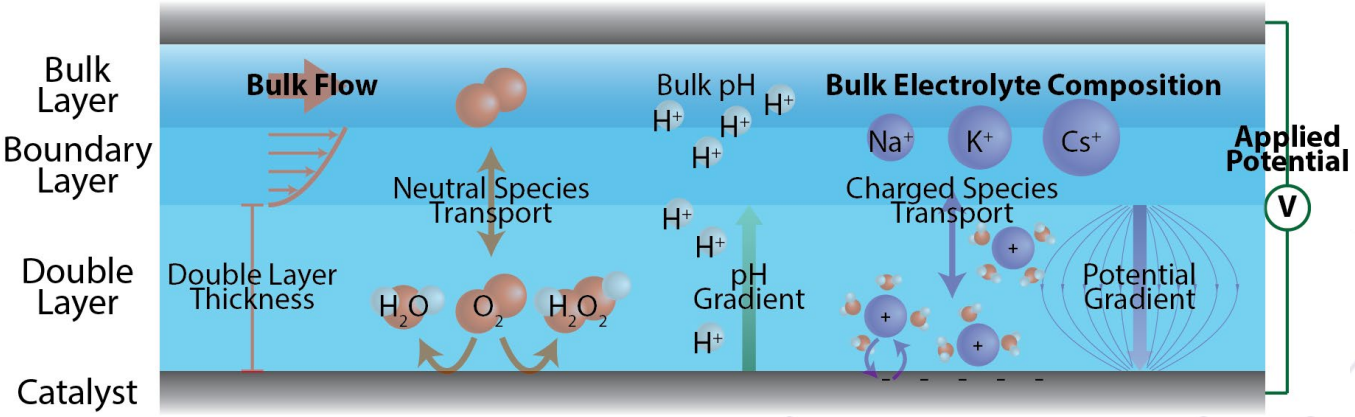


Ruggiero et al. *Journal of Catalysis* 414 (2022): 33-43.

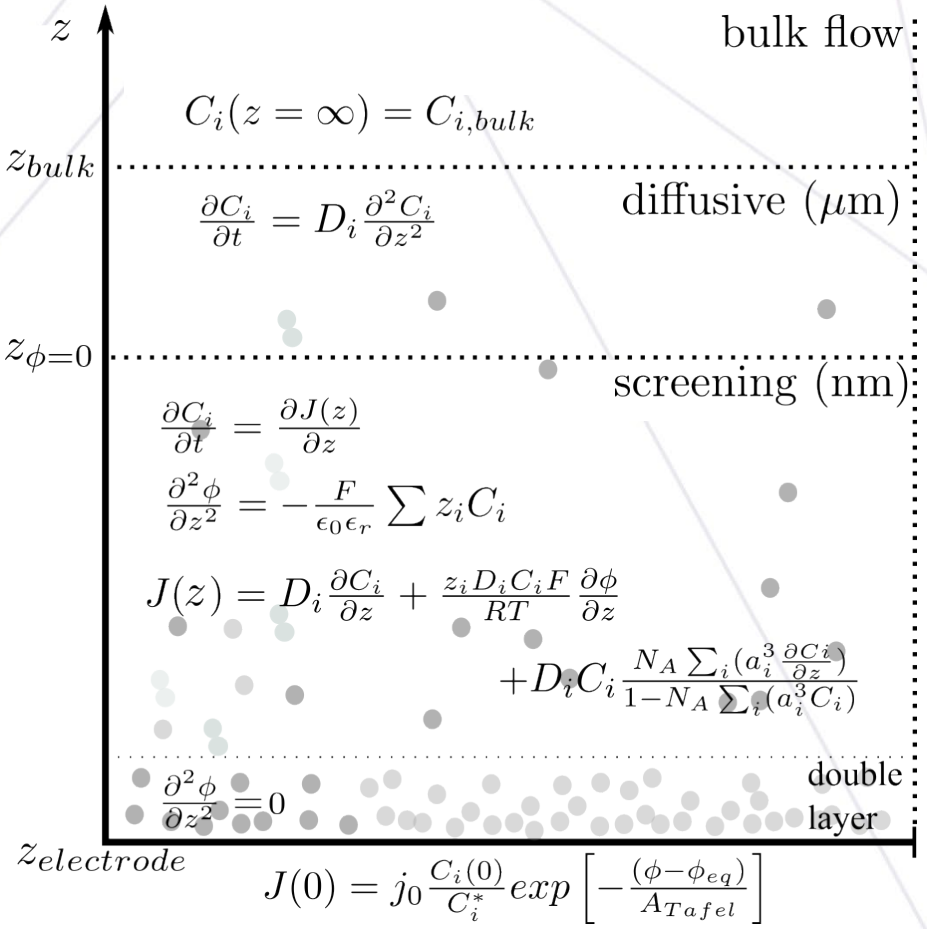
Electrocatalytic reactor modeling

Dr. Jithin George

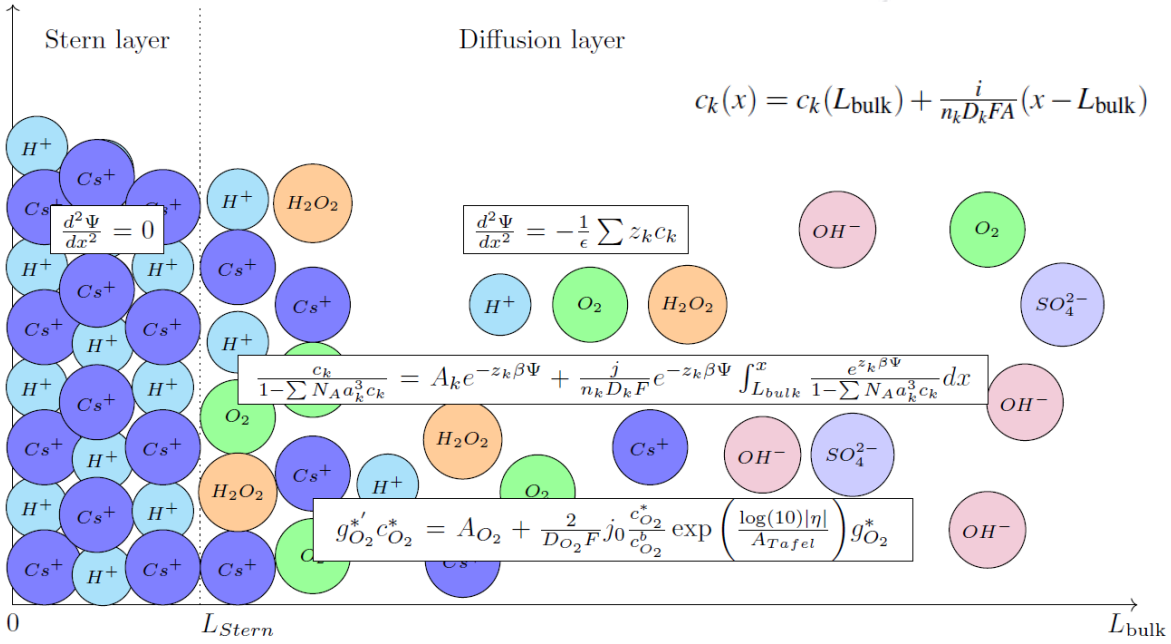
Yash Deodhar



- Solve at steady state $\frac{\partial C}{dt} \approx 0$
- Modified Poisson-Boltzmann equation
- Butler-Volmer boundary

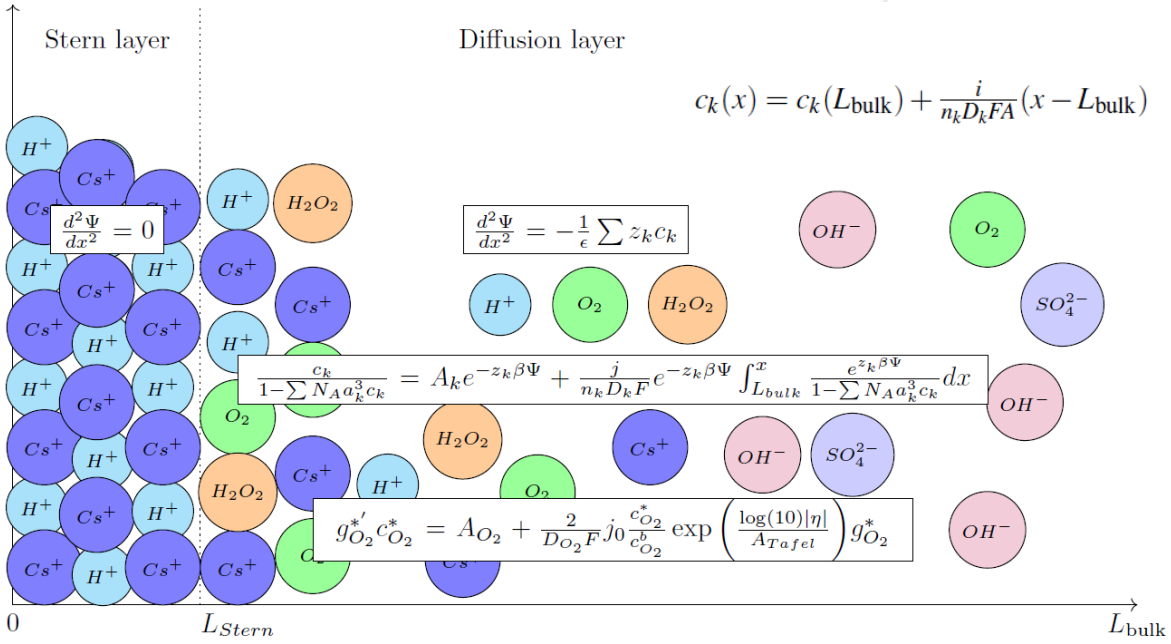


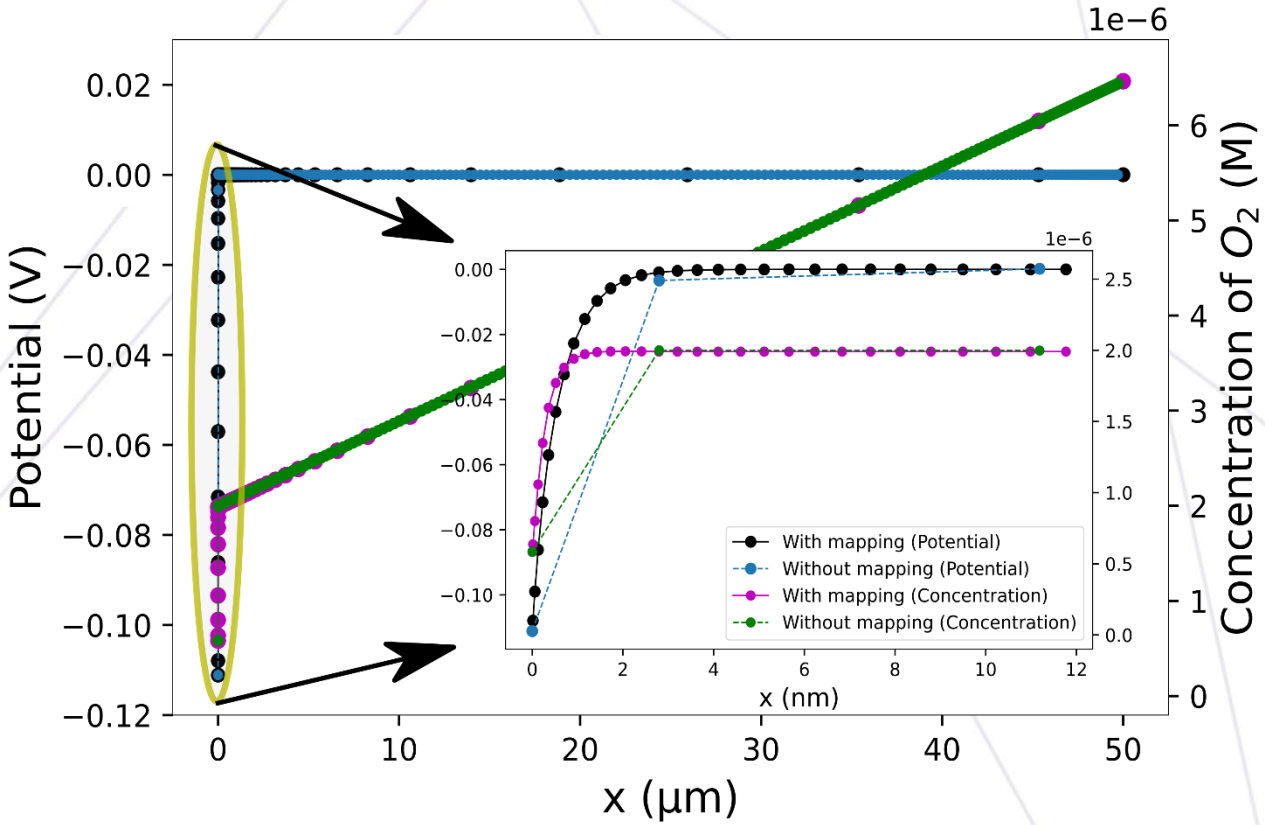
Mathematical/Computational analysis



- Solve outer diffusive regime explicitly
- Integrate inward from bulk switch from PDE-> ODE

Mathematical/Computational analysis

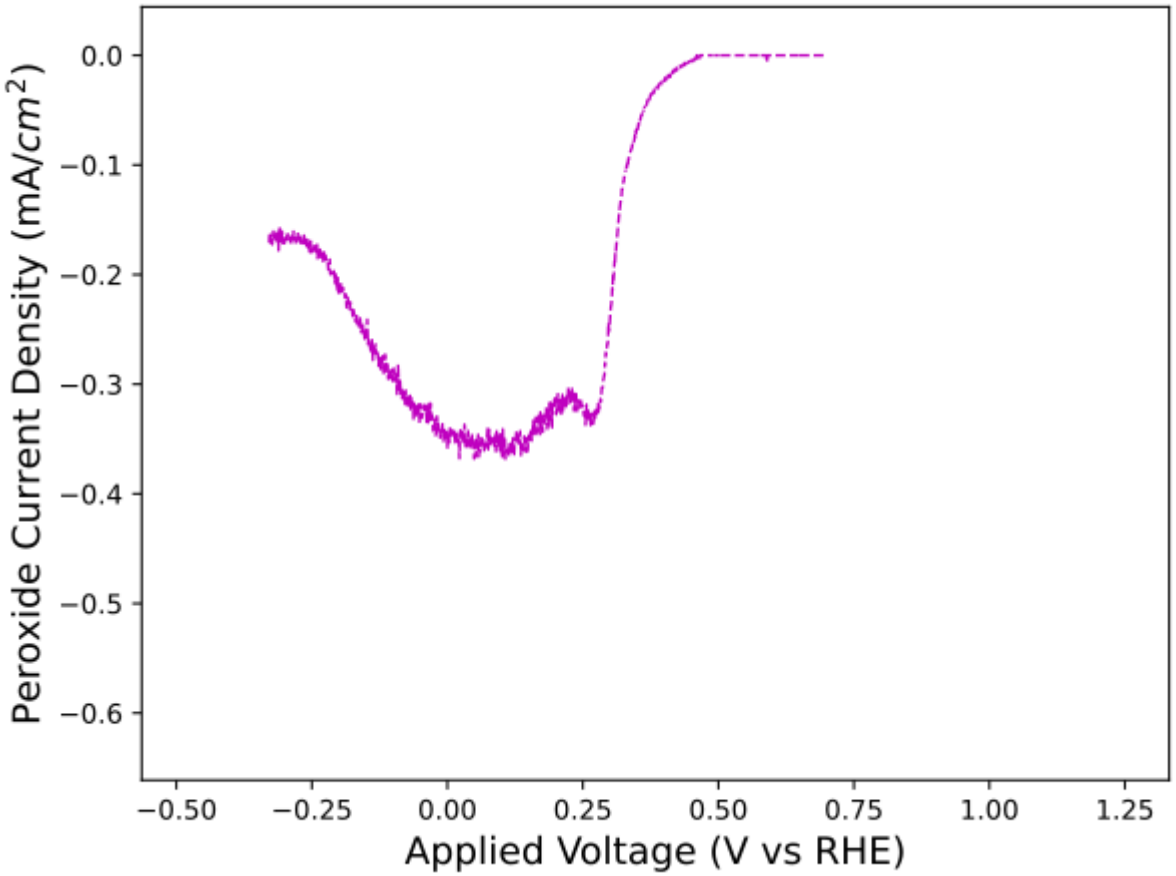




- Solve outer diffusive regime explicitly
- Integrate inward from bulk switch from PDE-> ODE

- Nonlinear mapping of space to resolve ~nm
- Spectral methods for spatial resolution

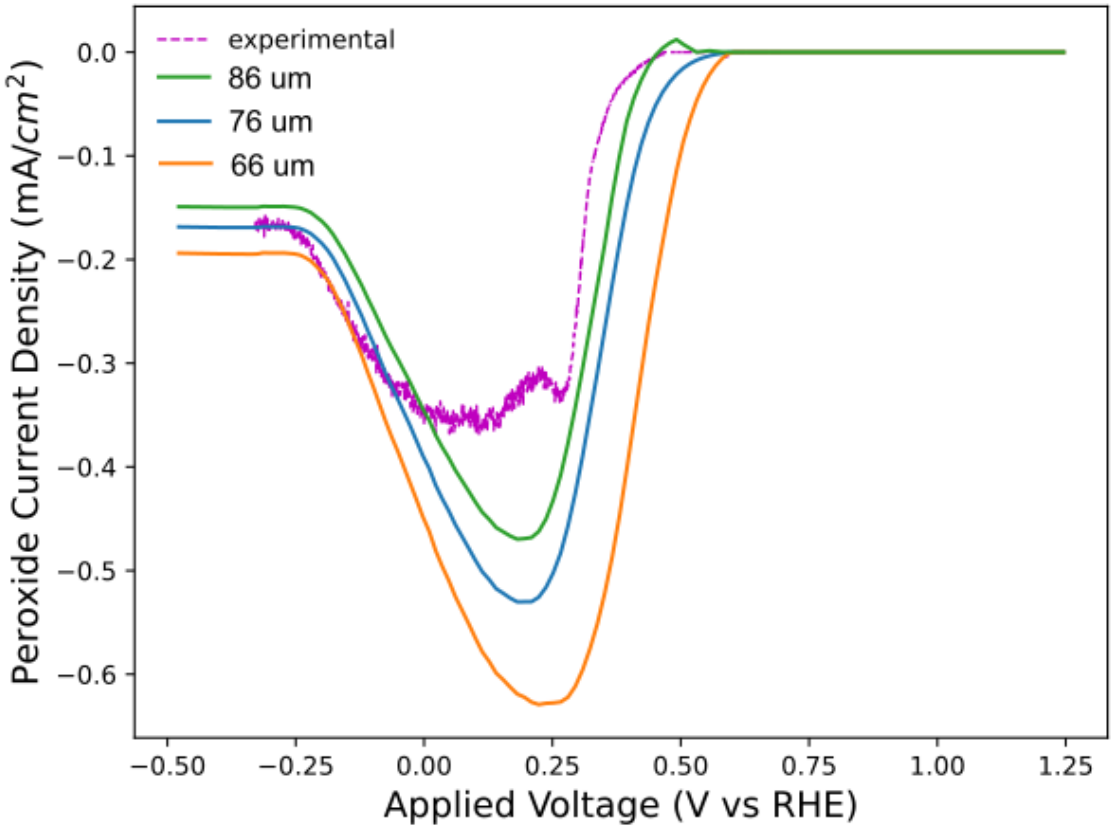
Current density of H_2O_2 production

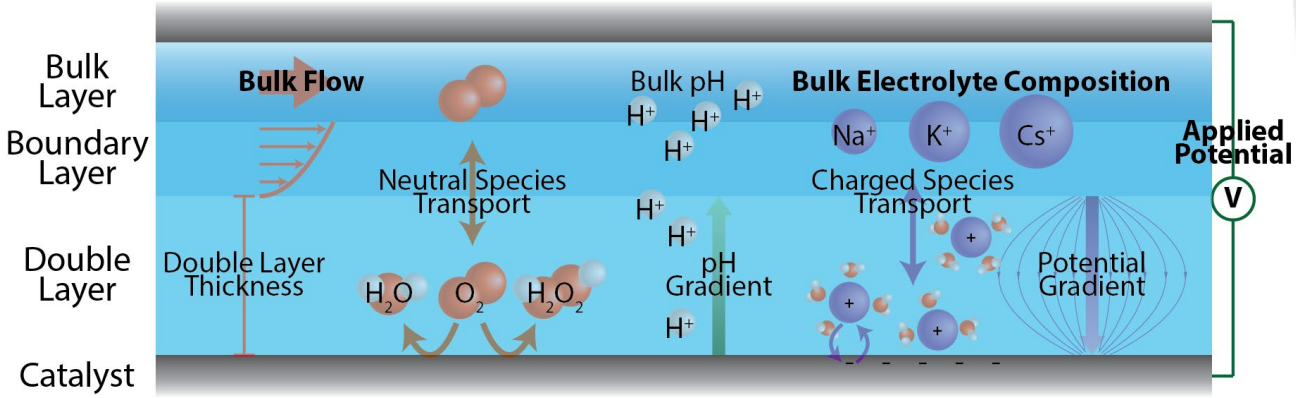


- pH 4
- Cs+ ions

- Goals:
  - Match behavior in experiment
  - Disambiguate steric interactions, transport, and reaction kinetic effects

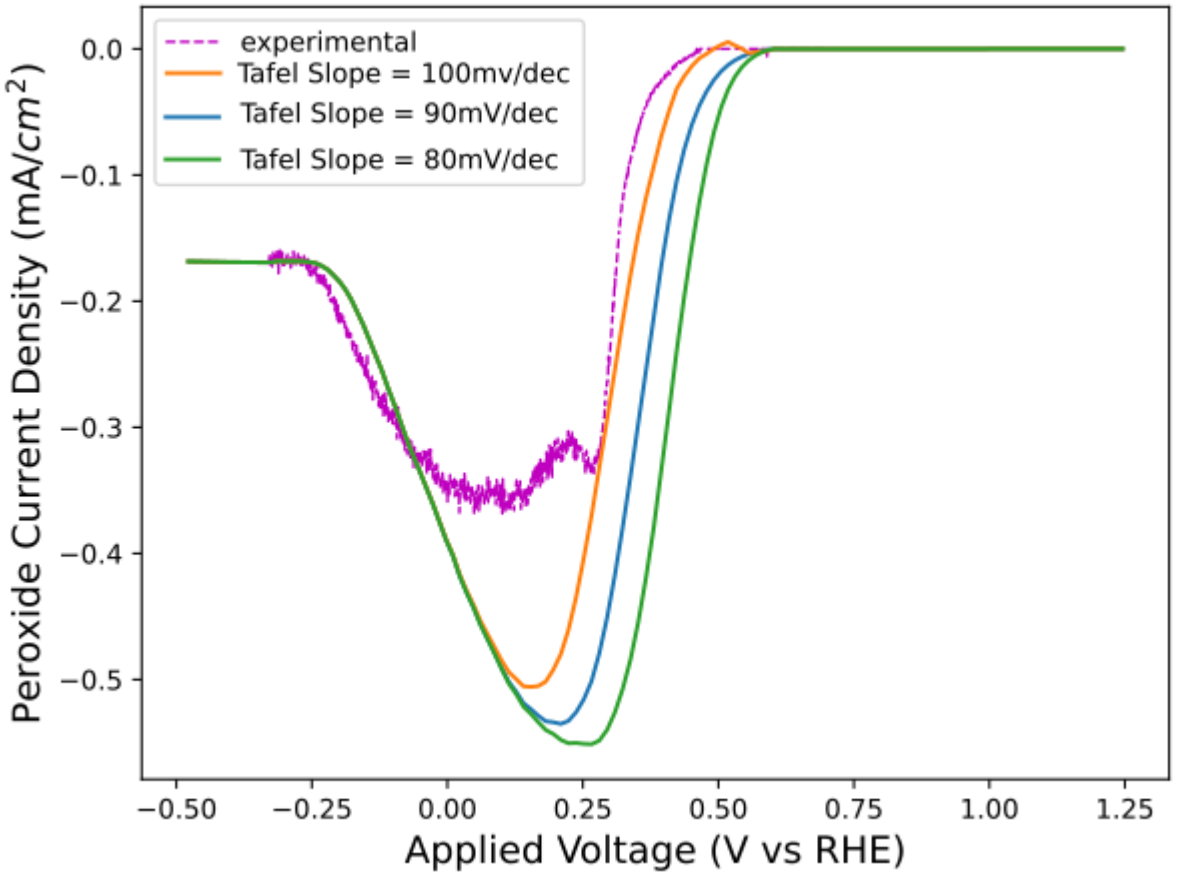
Varying length of diffusive region





- Sets transport (diffusion) limited current density
- decrease in current at higher voltage

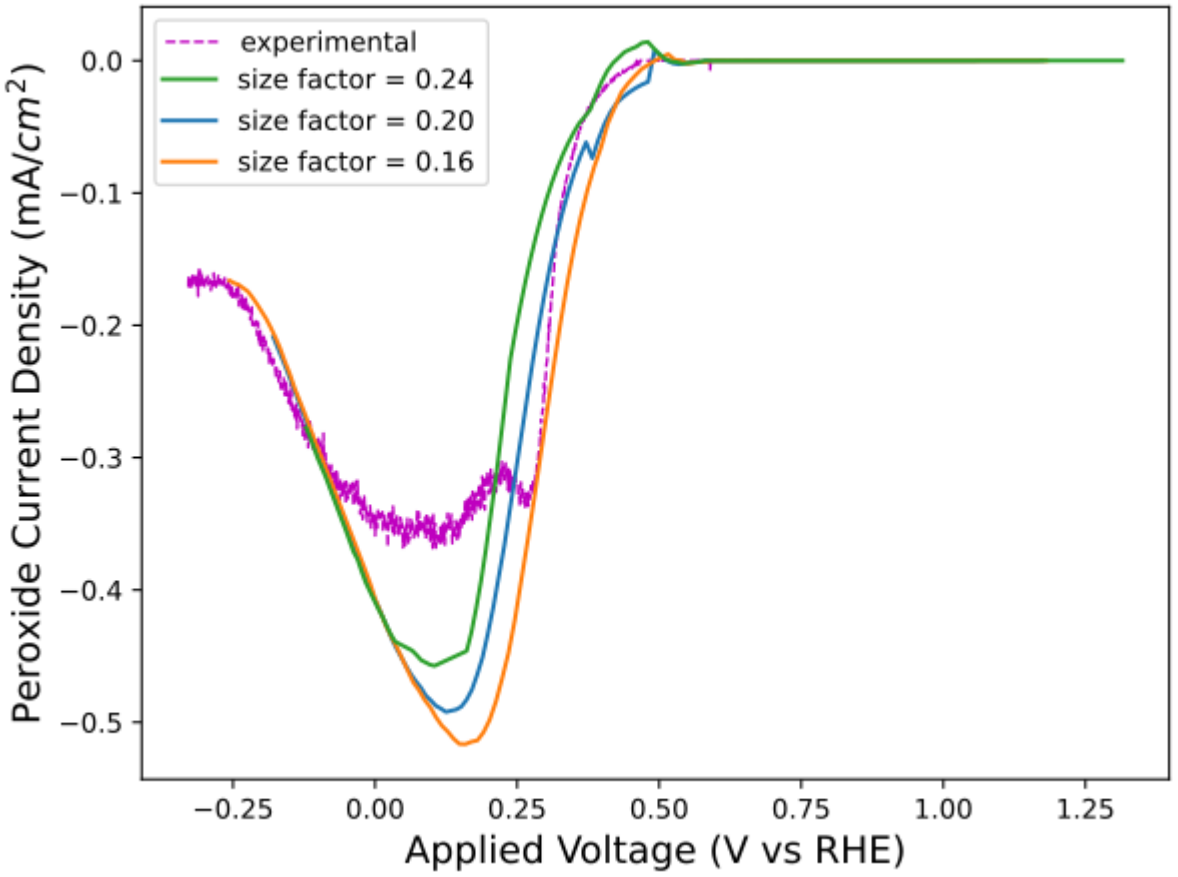
Varying kinetic reaction rate as Tafel slope



$$J(0) = j_0 \frac{C_i(0)}{C_i^*} exp\left[-\frac{(\phi - \phi_{eq})}{A_{Tafel}}\right]$$

- Effects both slope after onset potential
- and decrease in current at higher voltage

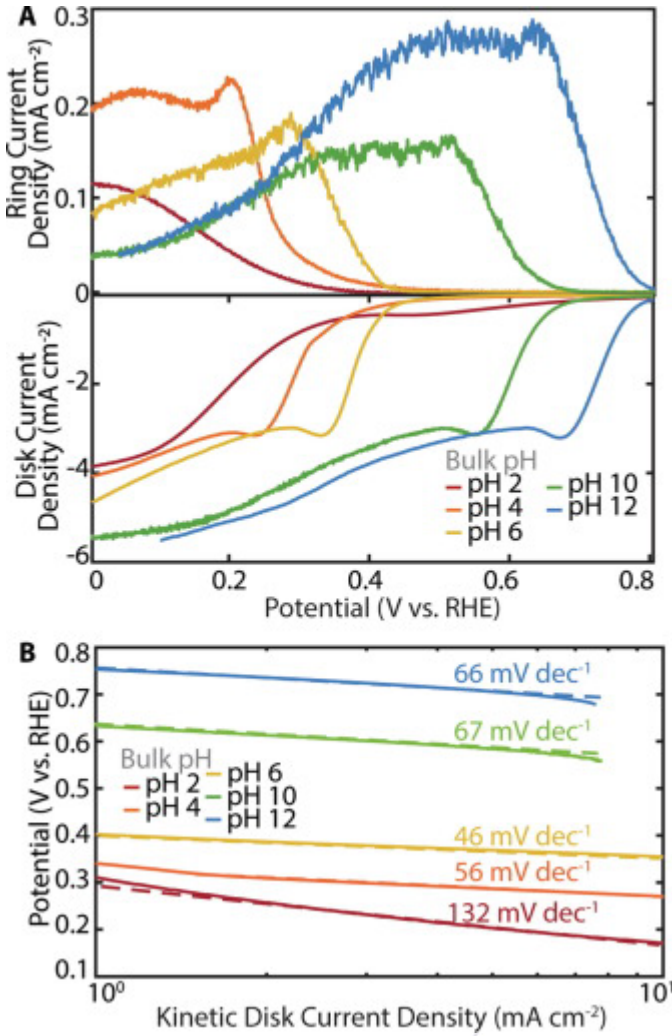
Varying effective radius of ions

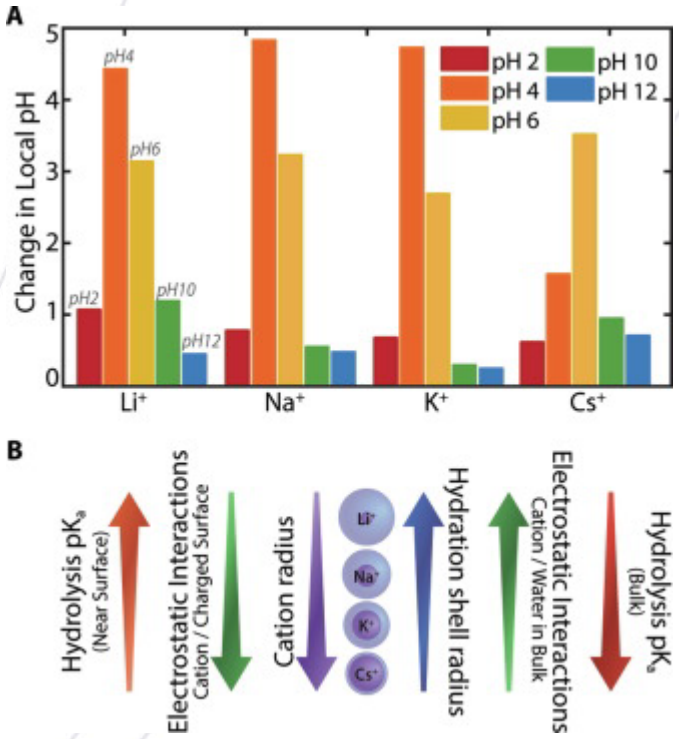


$$J(x) = D_i \frac{\partial C_i}{\partial z} + \frac{z_i D_i C_i F}{RT} \frac{\partial \phi}{\partial z} + D_i C_i \frac{N_A \sum_i (a_i^3 \frac{\partial Ci}{\partial z})}{1 - N_A \sum_i (a_i^3 C_i)}$$

- Larger ions block current due to steric exclusion
- Onset further left.

Next steps over more conditions:

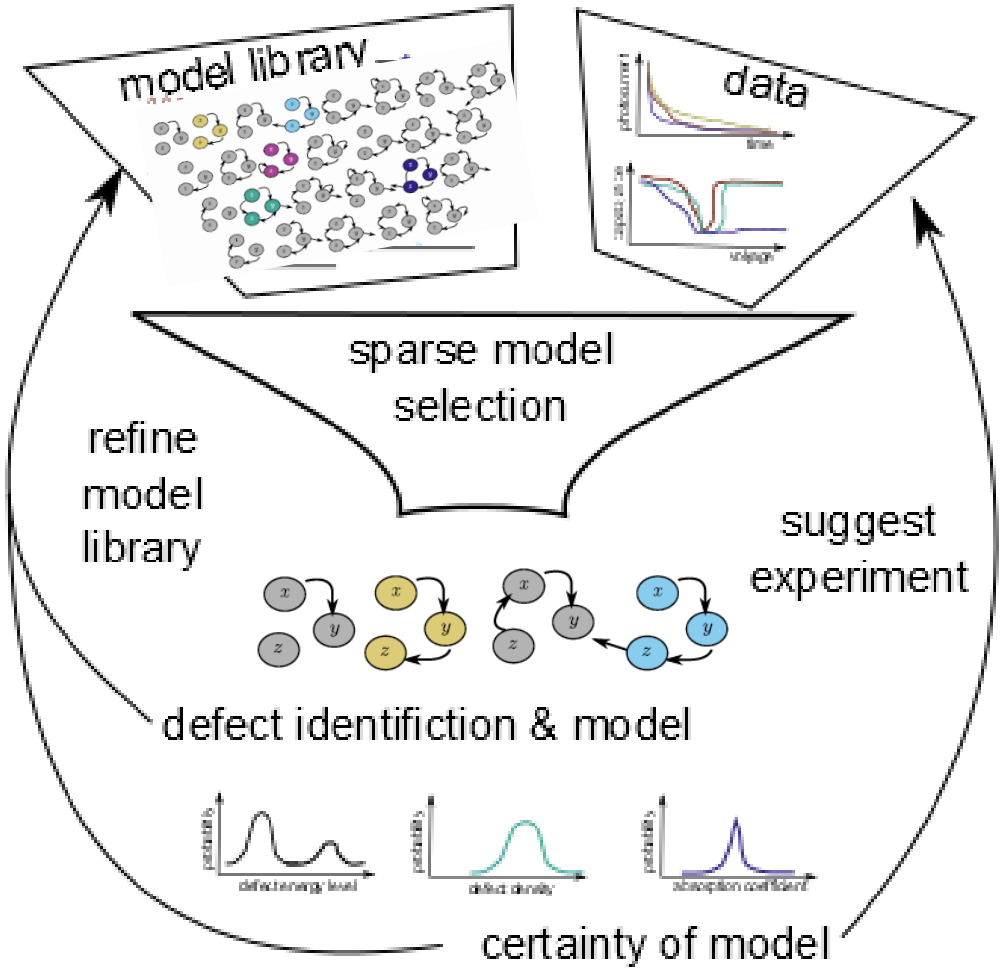




- Fit data to curves to determine most likely parameter set(s)
- Study across different ions and pH

Ruggiero, Brianna N., et al *Journal of Catalysis* 414 (2022): 33-43.

Mathematical methods for ChemBio



- Spatial modeling of electrochemical catalysis
- **Data-driven discovery of dynamical systems**

Yifan Zhang

Grace Hooper

Yash Deodhar

Dr. Alasdair Hastewell

SIMONS FOUNDATION

NSF

NU Center for Optimization and Statistical Learning

U.S. DEPARTMENT OF ENERGY | Office of Science

NIH National Institutes of Health
Turning Discovery Into Health

BILL & MELINDA GATES foundation

DEVCOM CHEMICAL BIOLOGICAL CENTER

Northwestern
PAULA M. TRIENENS INSTITUTE FOR SUSTAINABILITY AND ENERGY

CITY OF CHICAGO INCORPORATED 4th MARCH 1837

WALDER FOUNDATION

IDPH ILLINOIS DEPARTMENT OF PUBLIC HEALTH