

# Simulation and Analysis of Electrochemical Systems

PhD Defense of  
**Michael S. Emanuel**  
in Applied Mathematics  
Monday April 28, 2025

## PhD Committee:

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[github.com/memmanuel/PhD-Thesis](https://github.com/memmanuel/PhD-Thesis)

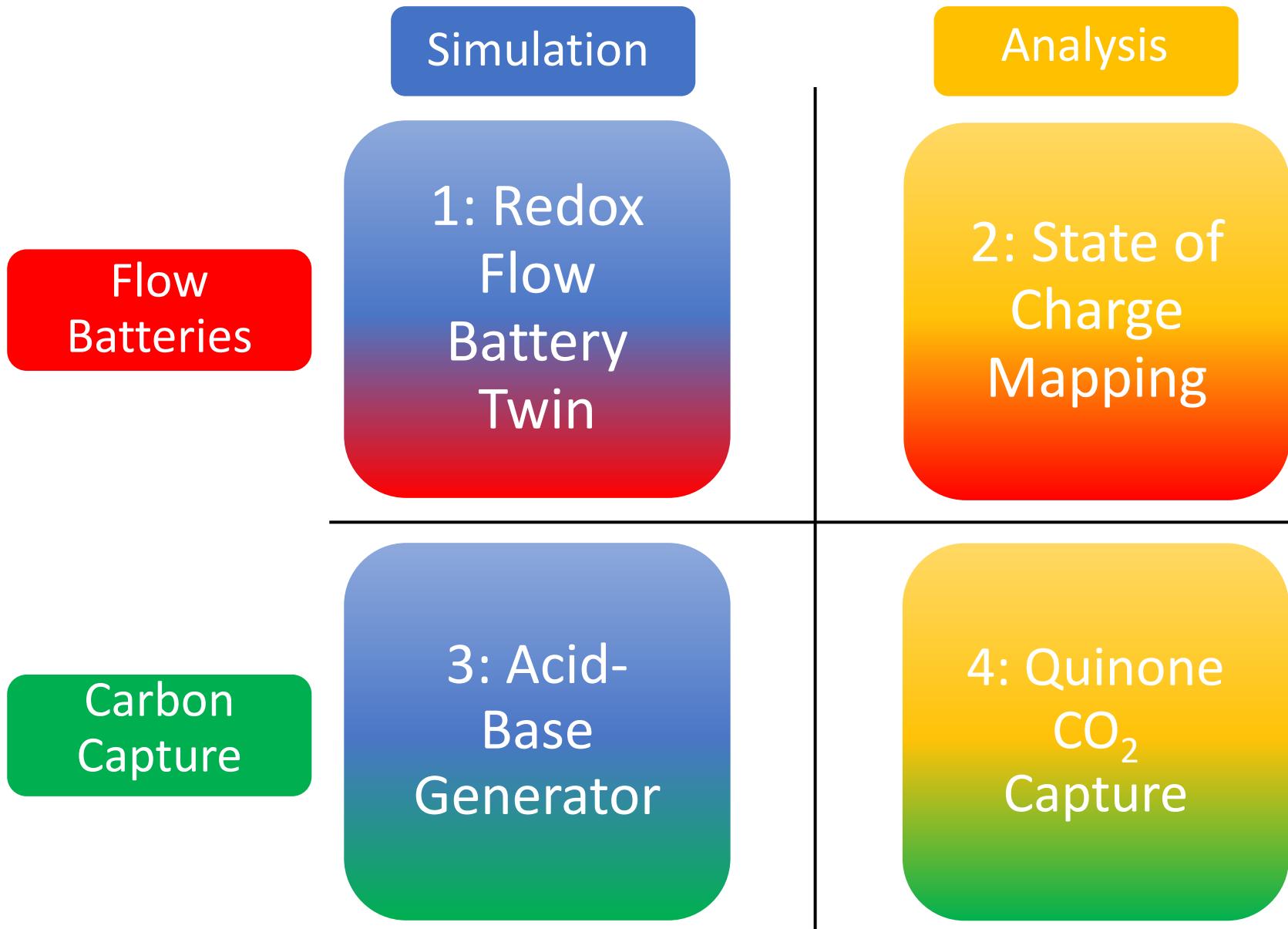
[linkedin.com/in/michael-emmanuel](https://www.linkedin.com/in/michael-emmanuel)



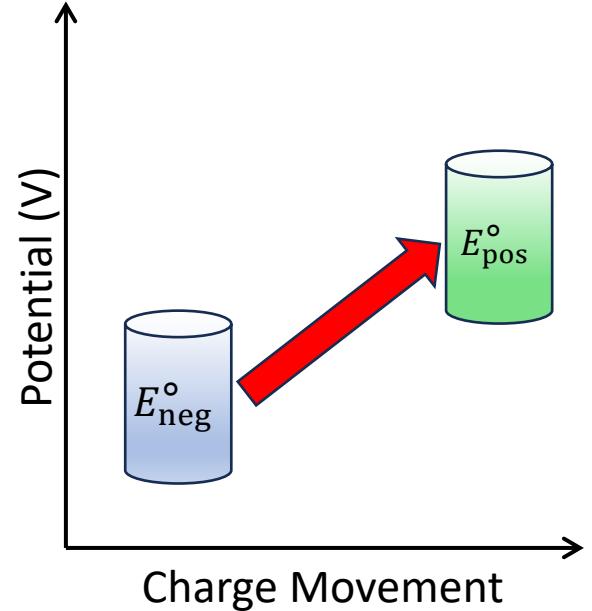
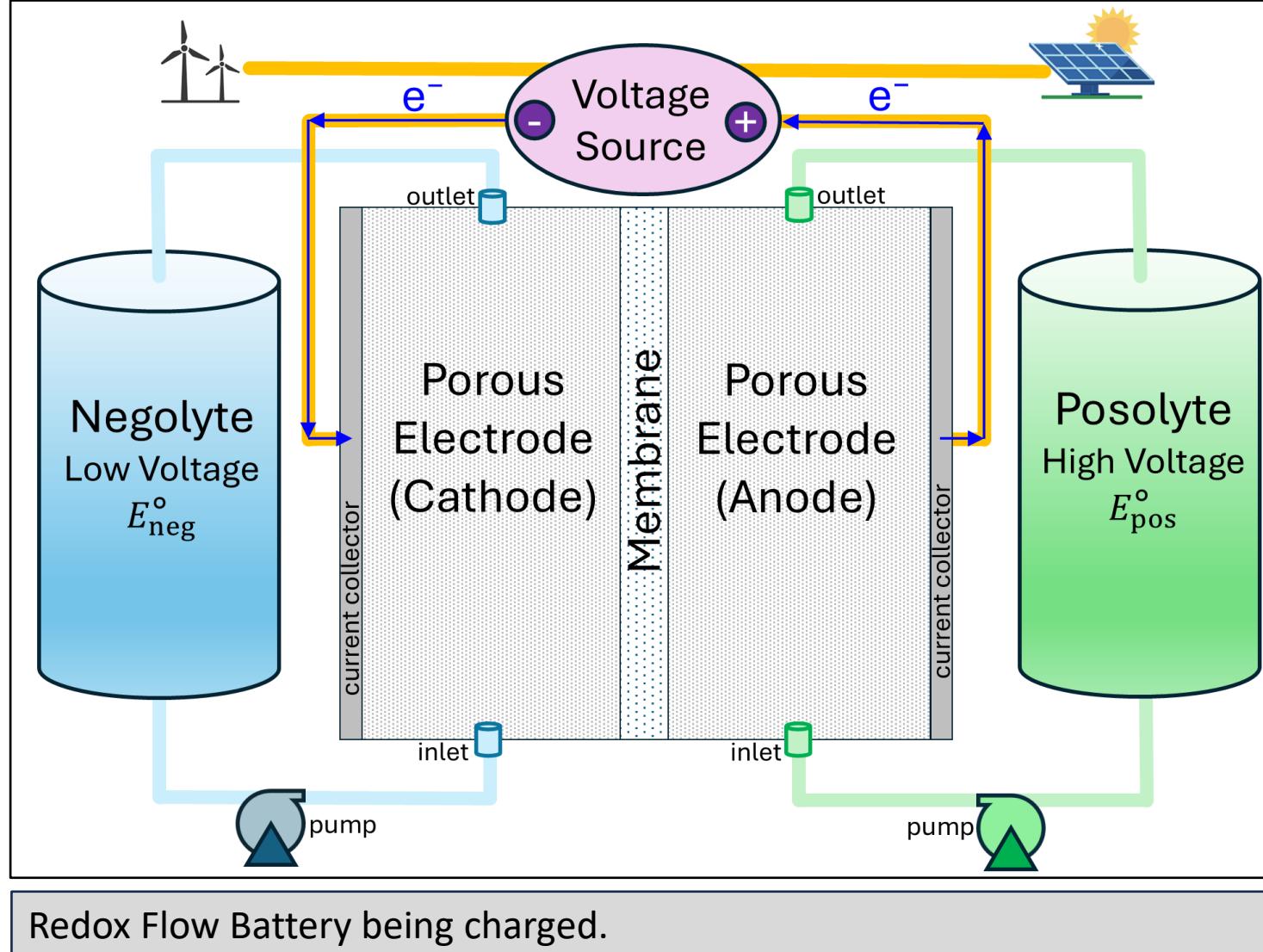
**Harvard John A. Paulson  
School of Engineering  
and Applied Sciences**

# Overview

# Four Scientific Works



# What is a Redox Flow Battery (RFB)?



Charge battery by moving charge “uphill” to higher potential.

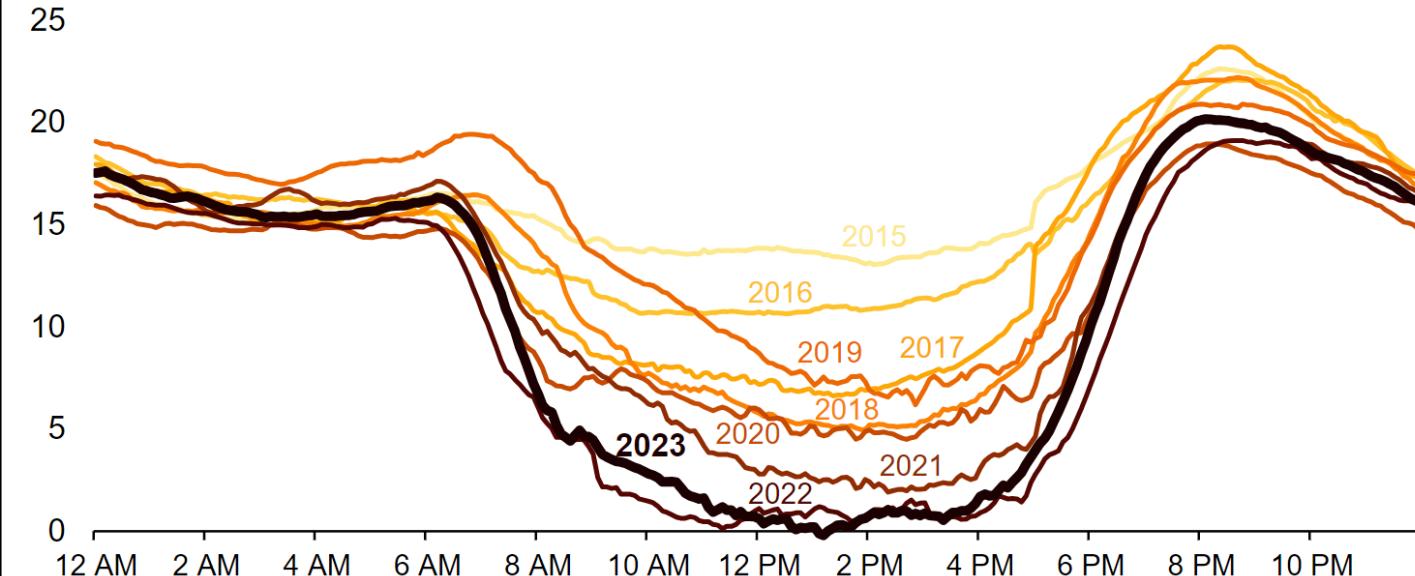
# Why Redox Flow Batteries?

1  
RFB  
Twin

2  
SOC  
Map

## California's duck curve is getting deeper

CAISO lowest net load day each spring (March–May, 2015–2023), gigawatts



Energy Information Administration.



Crimson Energy Storage in CA, 1400 MWh; largest BESS project to go live in the US in 2022 (Recurrent Energy)

- Solar and wind are the cheapest, cleanest electricity today...
- But they are intermittent: we need energy storage
- Redox Flow Batteries (RFBs) are a promising energy storage technology
- Decouples energy and power capacity; ideal for grid scale, long duration energy storage

# Why Carbon Capture & Storage (CCS)?

3  
ABG

4  
QCC



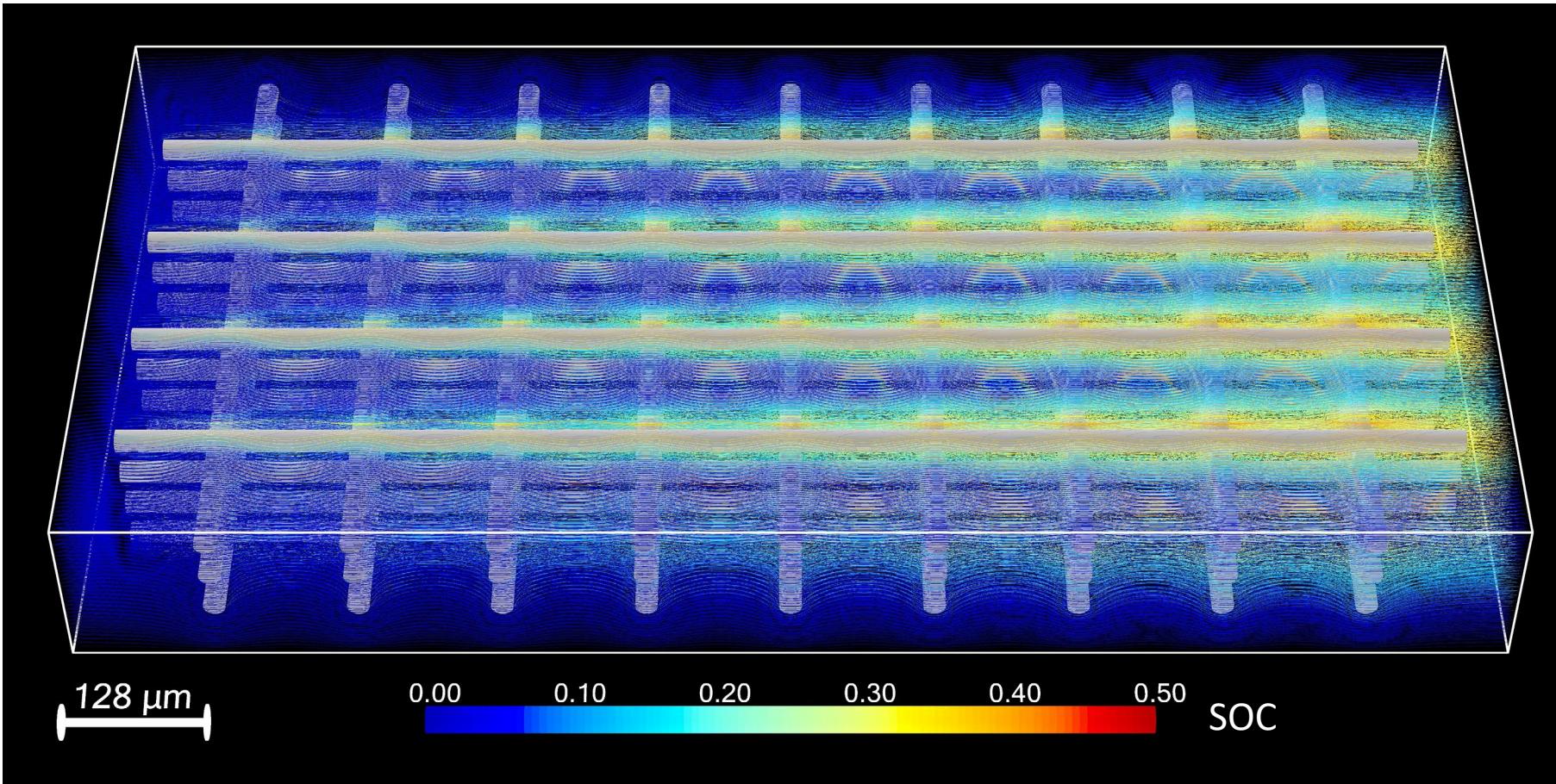
The Palisades Fire engulfs homes in the Pacific Palisades neighborhood of Los Angeles. (*Ethan Swope/AP*)



Petra Nova CCS facility at NRG WA Parish plant in TX. (*Recurrent Energy*)

- **Climate change** is real
- **Carbon Capture & Storage** (CCS) can be effective today for capturing **flue gas**...
- And might allow **future generations** to repair Earth's climate

# Digital Twin for Porous Electrodes in RFBs

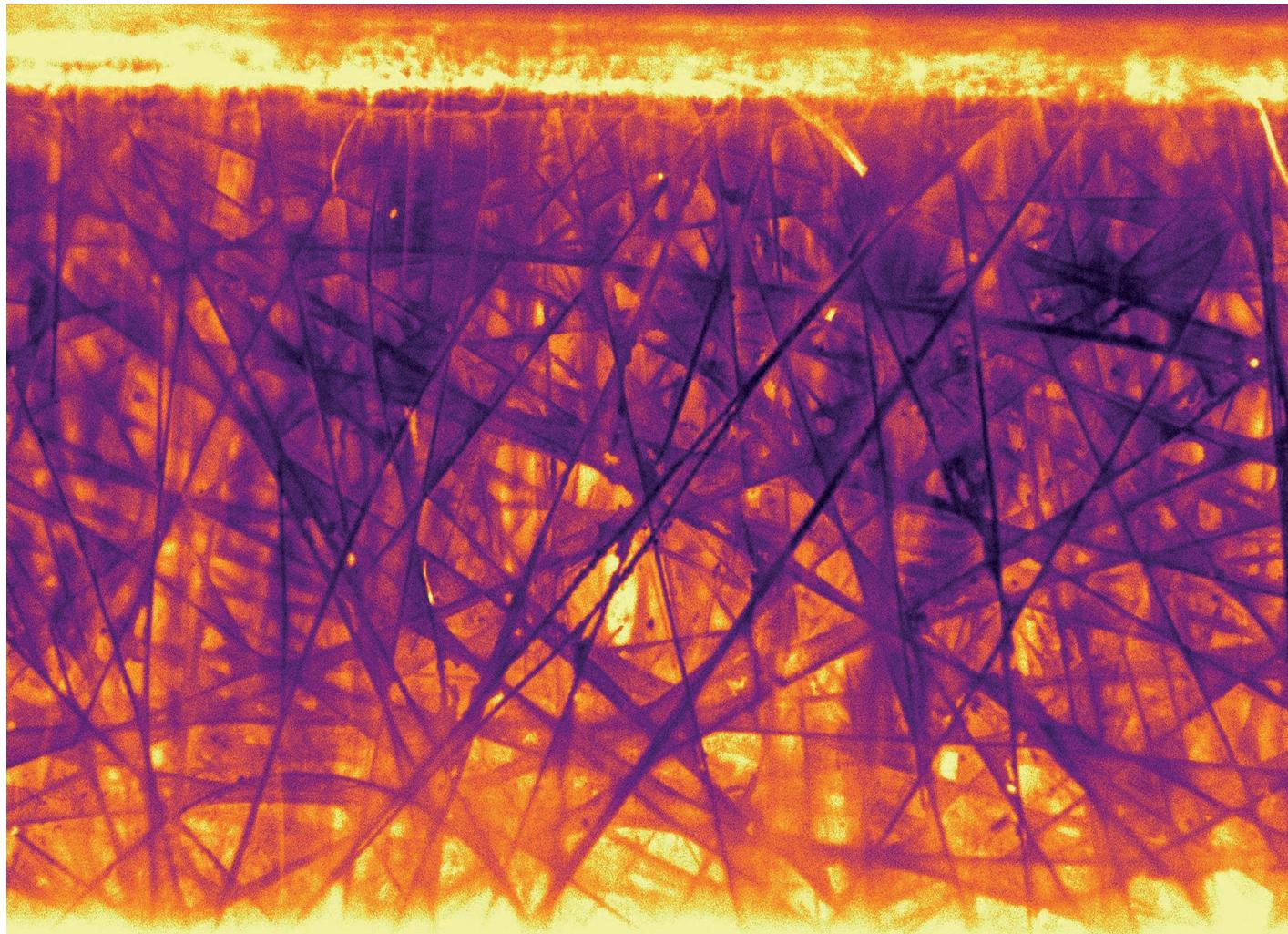


- Direct numerical solution of governing PDEs
- Phenomena—fluid **flow**, **mass transport**, electrochemical **reaction**
- **Unprecedented scale**—800M cells, 1.25  $\mu\text{m}$
- **SOC**—state of charge (fraction of available energy stored locally)

*Magnum Opus*

M. S. Emanuel, C. H. Rycroft, *Digital Twin for Porous Electrodes in Redox Flow Batteries*. arXiv (planned submission to Physics of Fluids). DOI 10.48550/arXiv.2502.08034.

# Calculating State of Charge from Image Data



100

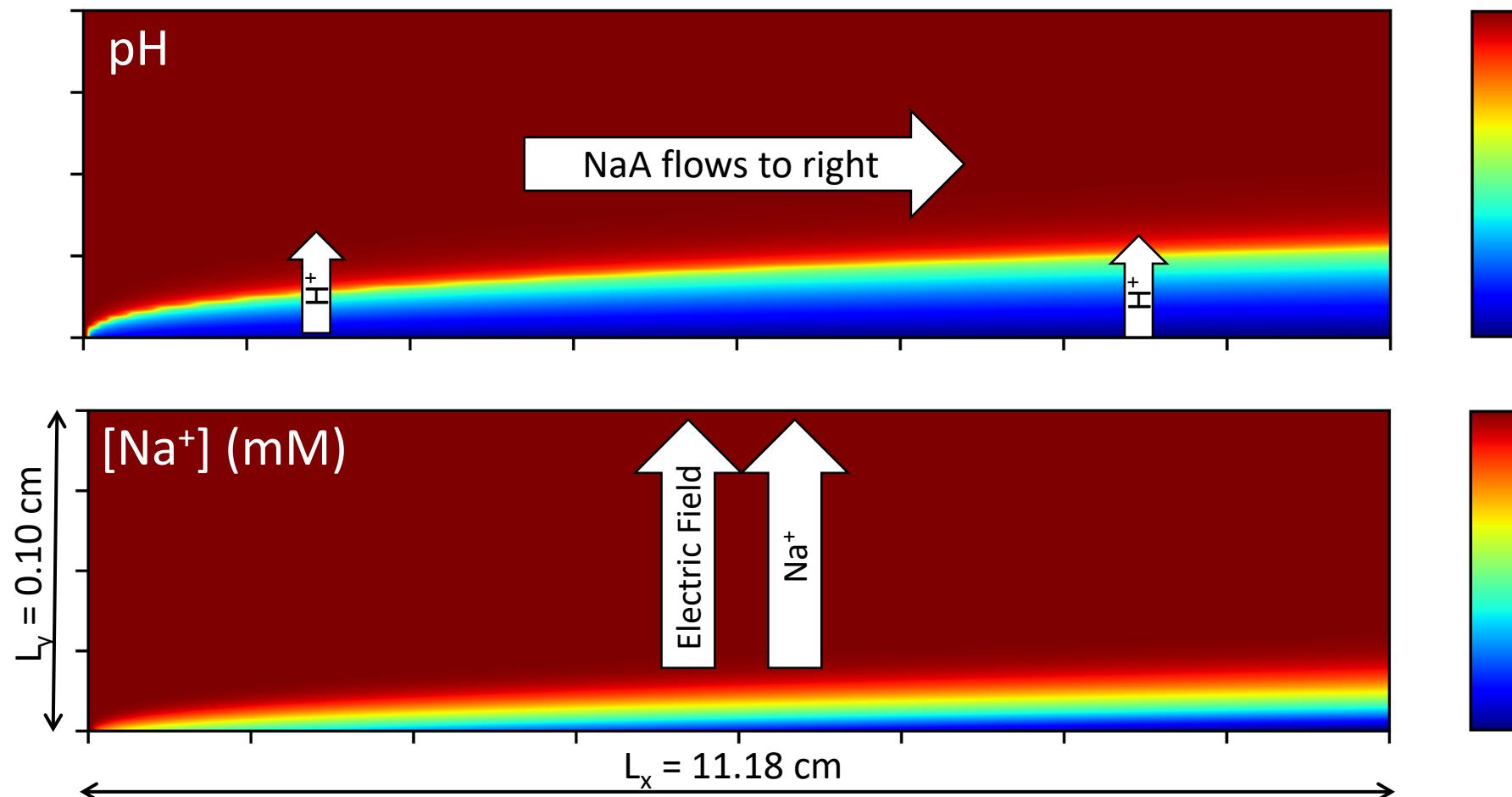
50

0

- Commercial porous electrode was imaged
- Reduced species is brighter than oxidized species
- But SOC calculations failed:  
shadows, nonlinear response, misalignment
- Model of light production and optical transfer

Salvaging a manuscript.

# Simulating an Acid-Base Generator

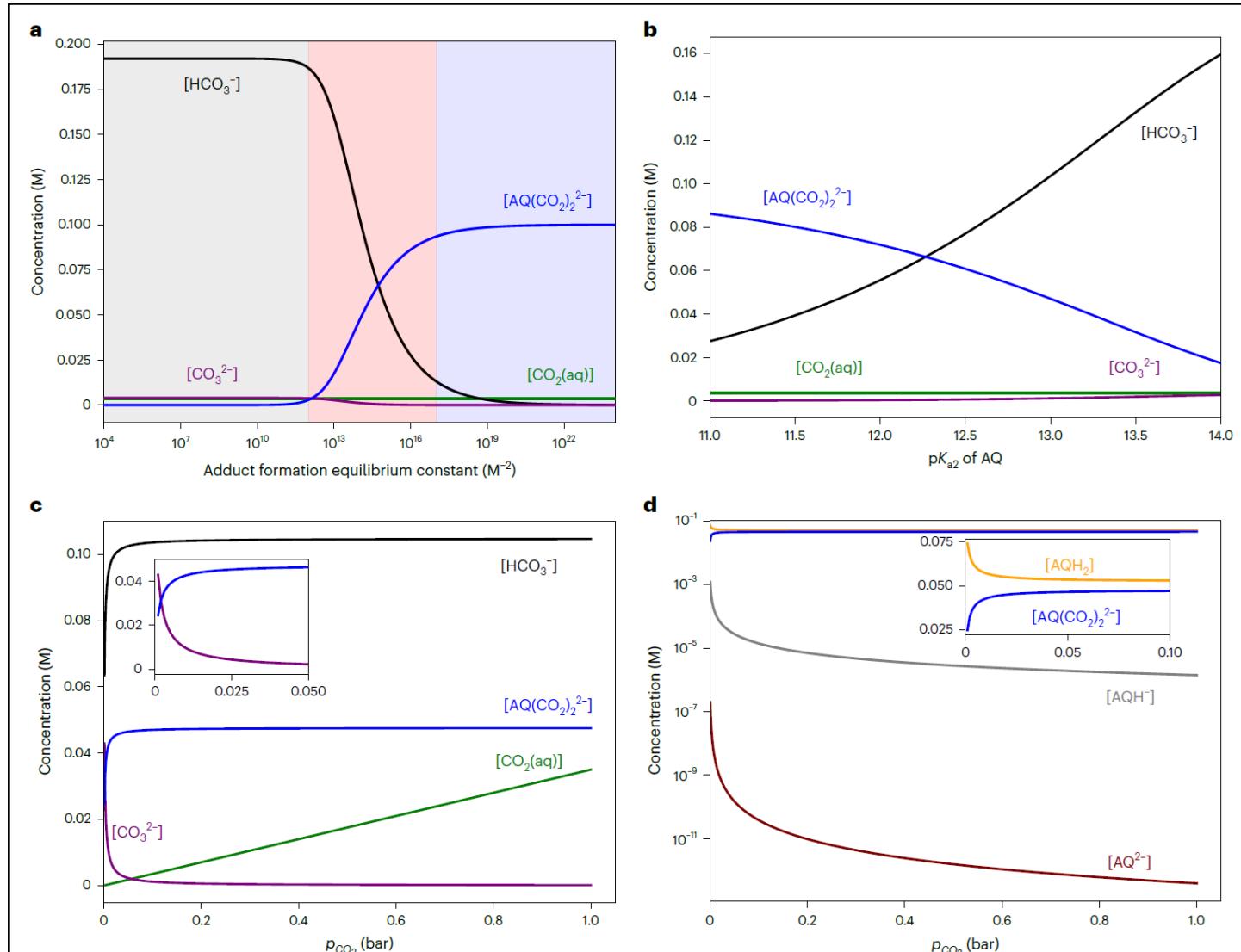


- Simulation of Acid-Base Generator (Dawei Xi)
- Mass transport in 2D
- Crossover—problem where species crosses into the “wrong” chamber
- Computational answer to an engineering question about crossover

“COMSOL doesn’t work!”

D. Xi, Y. Zheng, M. S. Emanuel, P. Zhao, M. J. Aziz, *Electrochemical Acid-Base Generators for Decoupled Carbon Management*. Energy & Environmental Science. DOI 10.1039/D4EE05109B.

# Thermodynamic Analysis of a Quinone CCS

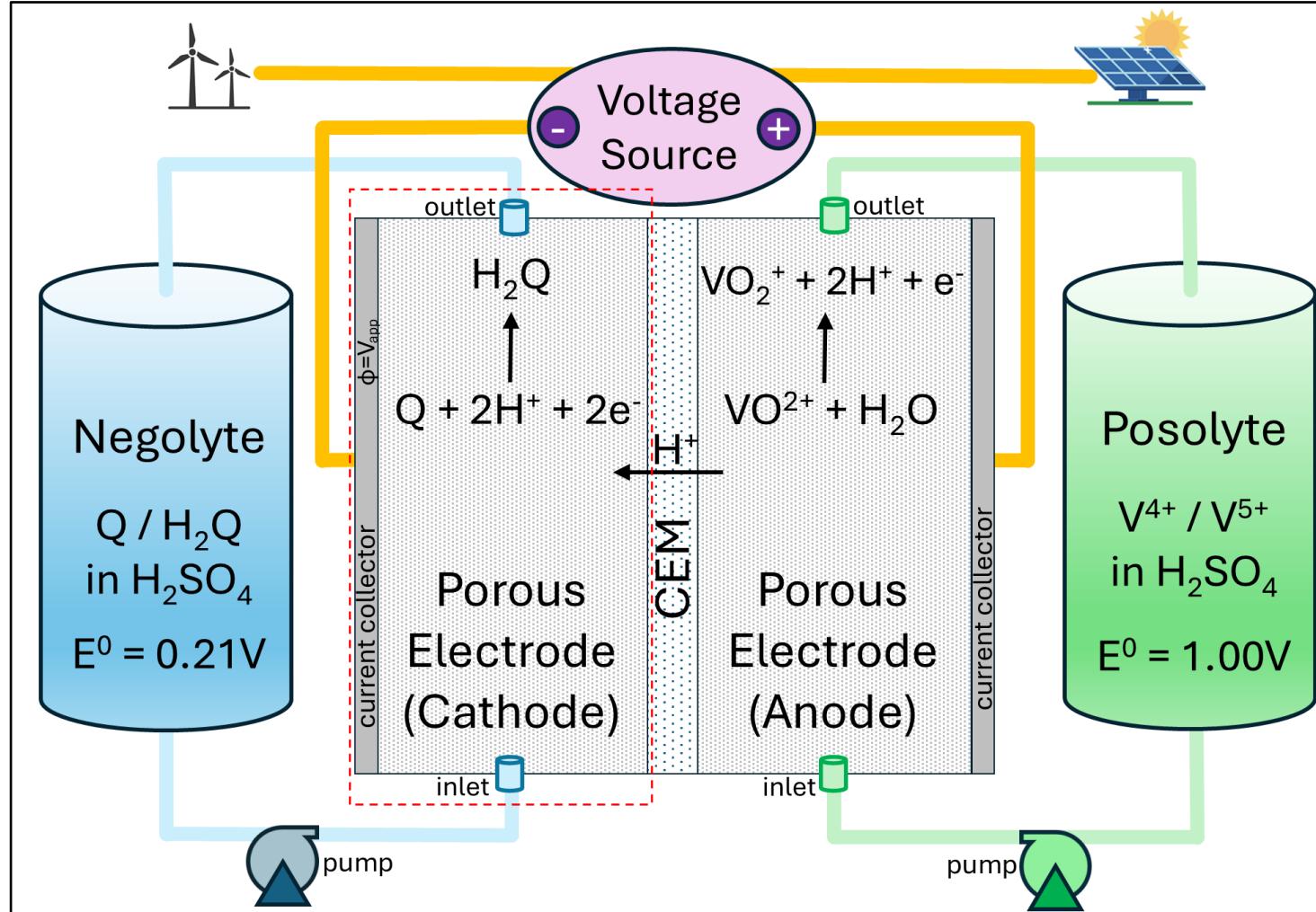


- **Quinone based CCS system** (Kiana Amini)
- Two capture mechanisms, **pH swing** and **nucleophilic swing**
- “Simple” **thermodynamic calculation** can explain their relative importance
- Solved equilibrium simple **numerical techniques**
- Conclusion: **three regimes** varying by dominant capture mechanisms

“I have a problem...”

# 1. Digital Twin for Porous Electrodes in Redox Flow Batteries

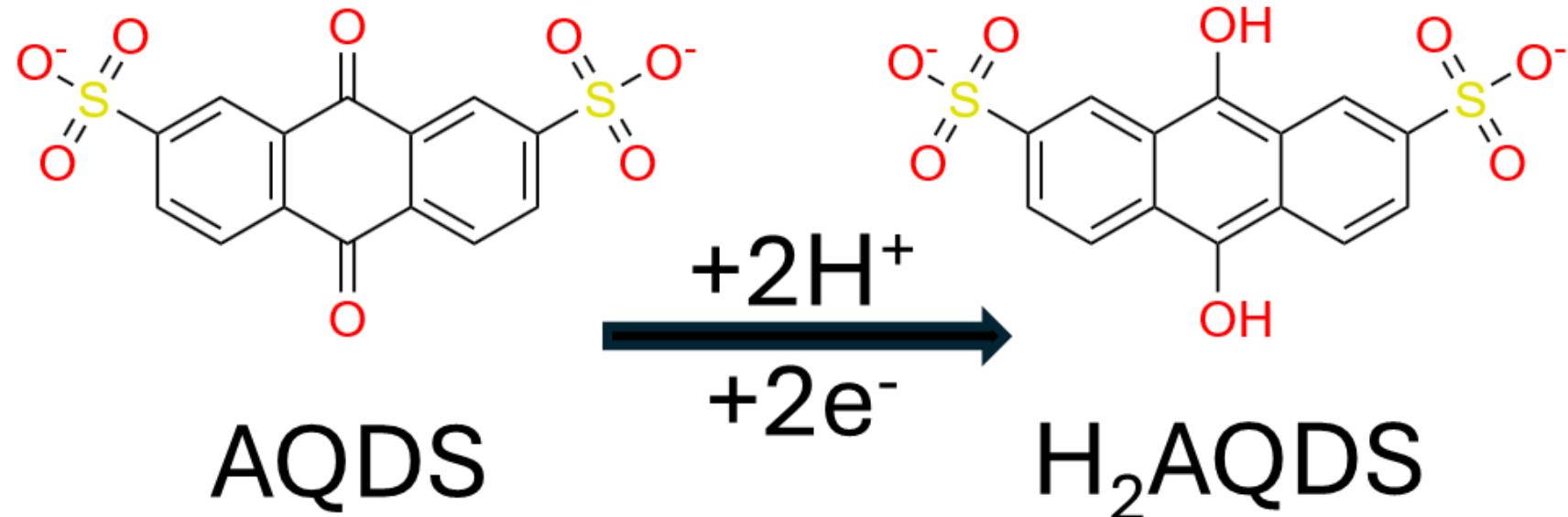
# Simulation Overview of Redox Flow Battery



- Simulated the **porous electrode** at the **cathode** (dashed **red rectangle**) while the battery is charged.
- **Membrane** is at a constant voltage
- Current collector held at a lower, **applied reducing voltage**,  $V_{ar}$
- Porous electrode also at  $V_{ar}$
- This drives **reduction** of Q to H<sub>2</sub>Q
- H<sup>+</sup> crosses CEM, balancing charge

Digital Twin for Porous Electrodes in Redox Flow Batteries.

# What is AQDS (Anthraquinone Disulfonate)?

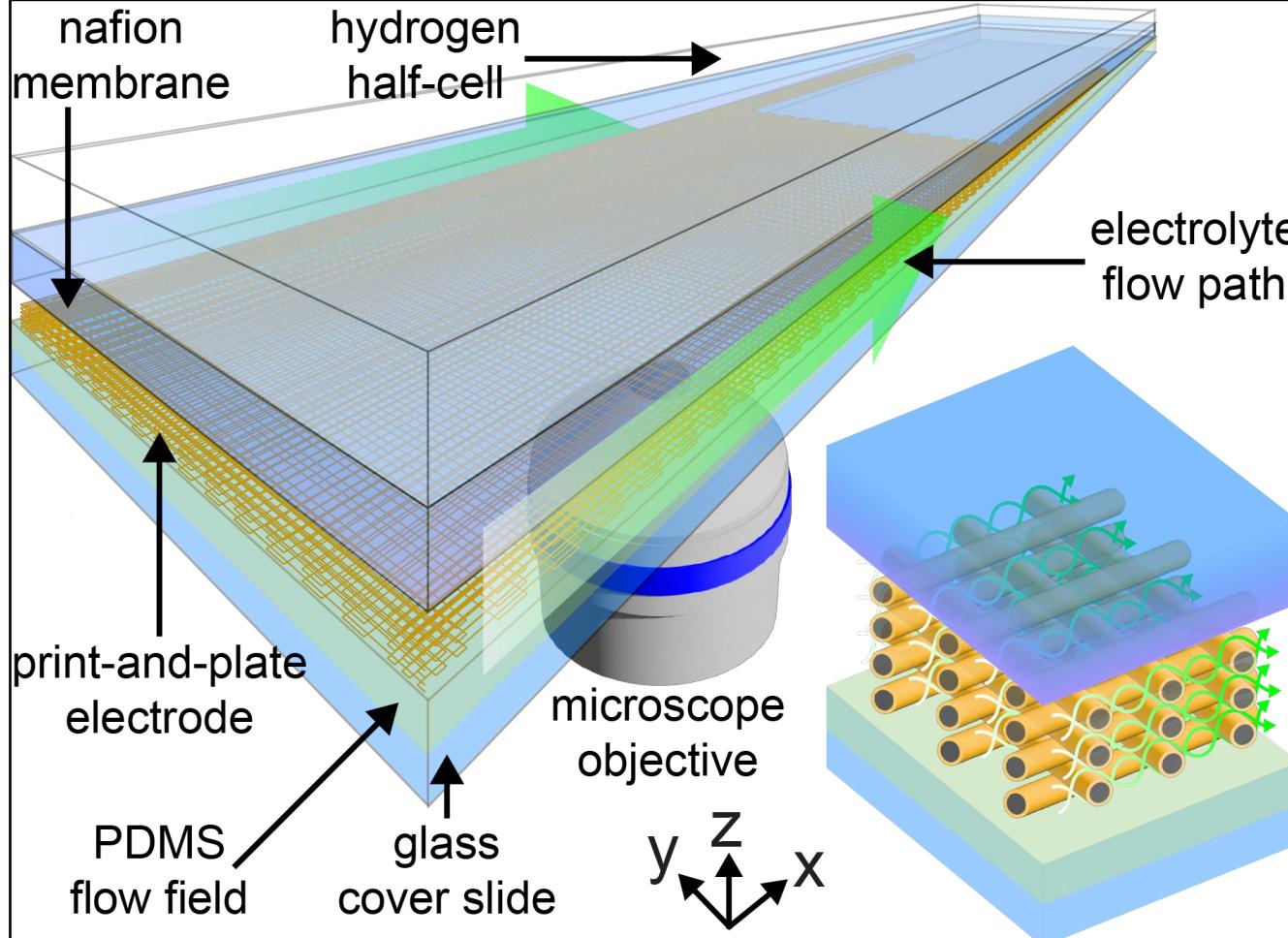


Digital Twin for Porous Electrodes in Redox Flow Batteries

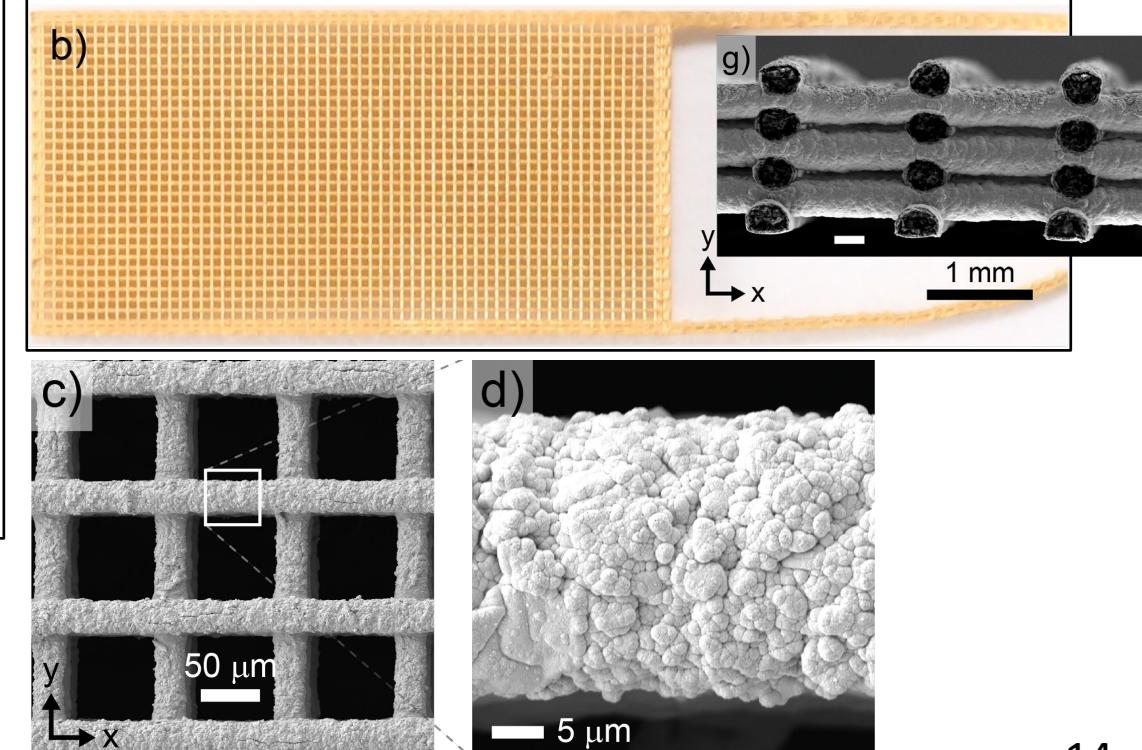
- **Aqueous organic:** dissolves in water, carbon based
- **Redox active:** undergoes a reversible electrochemical reaction...
- Desirable properties:
  - **Fast kinetics**
  - **High solubility** in water
  - **Long lifetime**
  - **Earth abundant elements**
- Discovered by [Aziz-Gordon](#) collaboration [2014]



# Experiment with a 3D Printed Electrode



- Architected electrodes were **3D printed** and **electroplated** (Ni, Au)
- Known, regular “**logpile**” geometry
- Commercial electrodes—**tangle** of fibers
- Imaged in 3D using **confocal microscopy**
- Gold wires at a **reducing voltage**  $V_{ar} < 0$
- Task: **simulate** in 3D at a **sub-fiber scale**



D. M. Barber, S. Edgar, M. S. Emanuel, M. D. Nelwood, B. Y. Ahn, B. Román-Manso, T. Cochard, J. Platero, K. Amini, C. H. Rycroft, S. Rubinstein, M. J. Aziz, J. Lewis, *Print-and-Plate Architected Electrodes for Electrochemical Transformations Under Flow*. Advanced Functional Materials. DOI 10.1002/adfm.202419748.

# Loosely Coupled Problems & Discretization



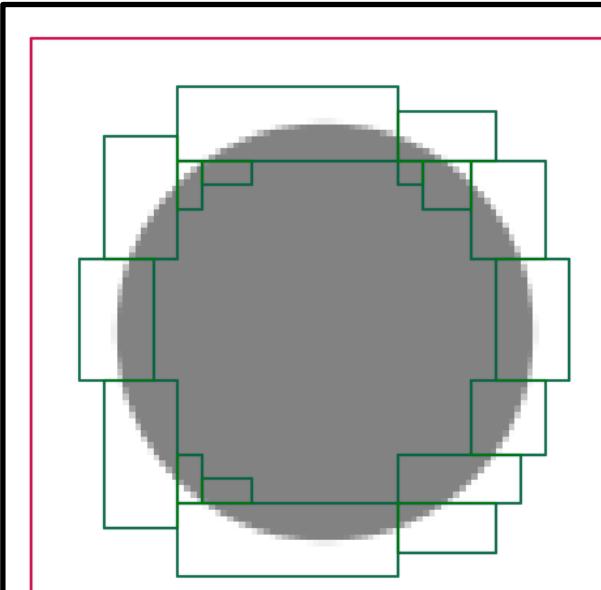
## Fluid Flow

- Navier-Stokes equation
- Incompressibility condition
- Chorin Projection Method

Decoupled

## Electrochemistry

- Nernst-Planck equation (transport)
- Butler-Volmer equation (kinetics)
- Fixed-Point Iteration



Example of **cut cells** and **mesh refinement** in 2D

## Numerical Methods

- AMReX Library
- Cut cells with implicit boundary
- Algebraic Multigrid solvers (HYPRE)
- Highly scalable MPI program

## Steady State

- Main concern for RFBs
- Faster to simulate than full dynamics



# Fluid Flow: Navier-Stokes Equation

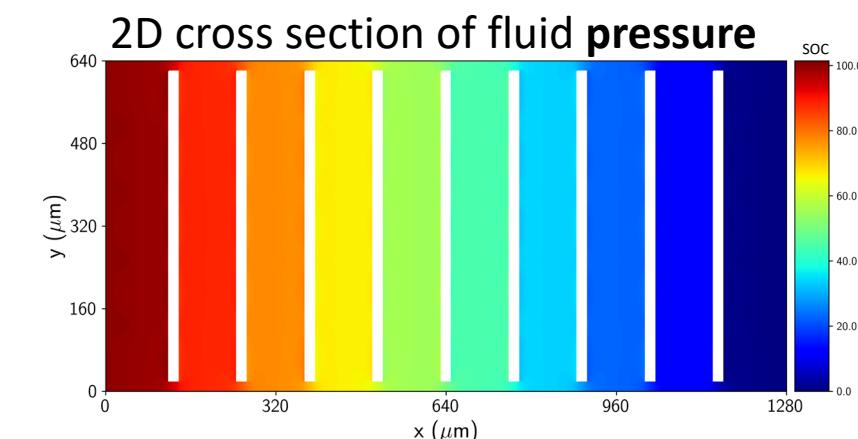
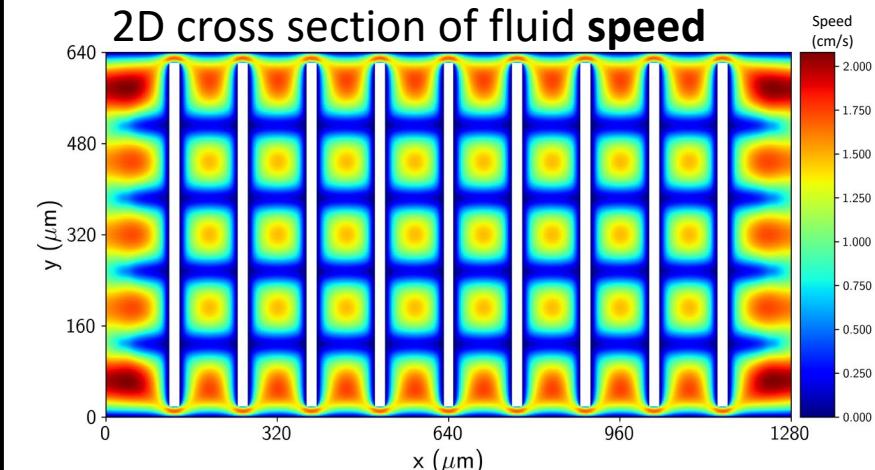
## Navier Stokes equation

$$\underbrace{\rho \frac{\partial \mathbf{u}}{\partial t}}_{\text{Momentum Change}} + \underbrace{\rho \mathbf{u} \cdot \nabla \mathbf{u}}_{\text{Momentum Transport}} = - \underbrace{\nabla p}_{\text{Pressure Gradient}} + \underbrace{\mu \nabla^2 \mathbf{u}}_{\text{Viscous Term}}$$

## Incompressibility condition

$$\nabla \cdot \mathbf{u} = 0$$

Term	Concept	Units
$\rho$	Fluid <b>density</b> (constant scalar)	$\text{kg} \cdot \text{m}^{-3}$
$\mu$	Dynamic <b>viscosity</b> (constant scalar)	$\text{Pa} \cdot \text{s}$
$\mathbf{u}$	Fluid <b>velocity</b> (vector field)	$\text{m} \cdot \text{s}^{-1}$
$p$	Fluid <b>pressure</b> (scalar field)	Pa

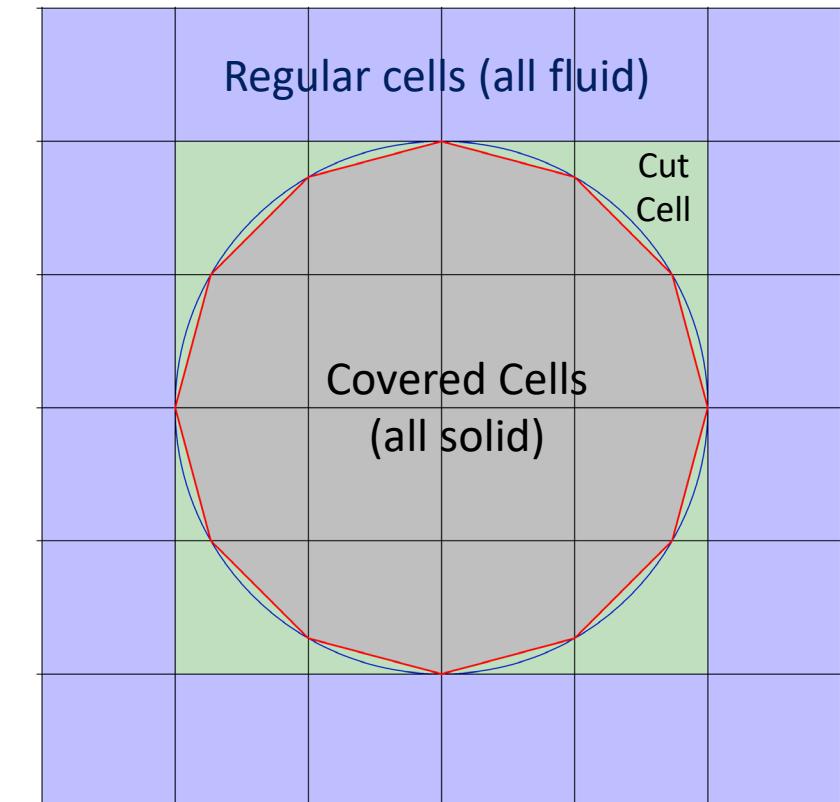


# Mass Transport: Nernst-Planck Equation

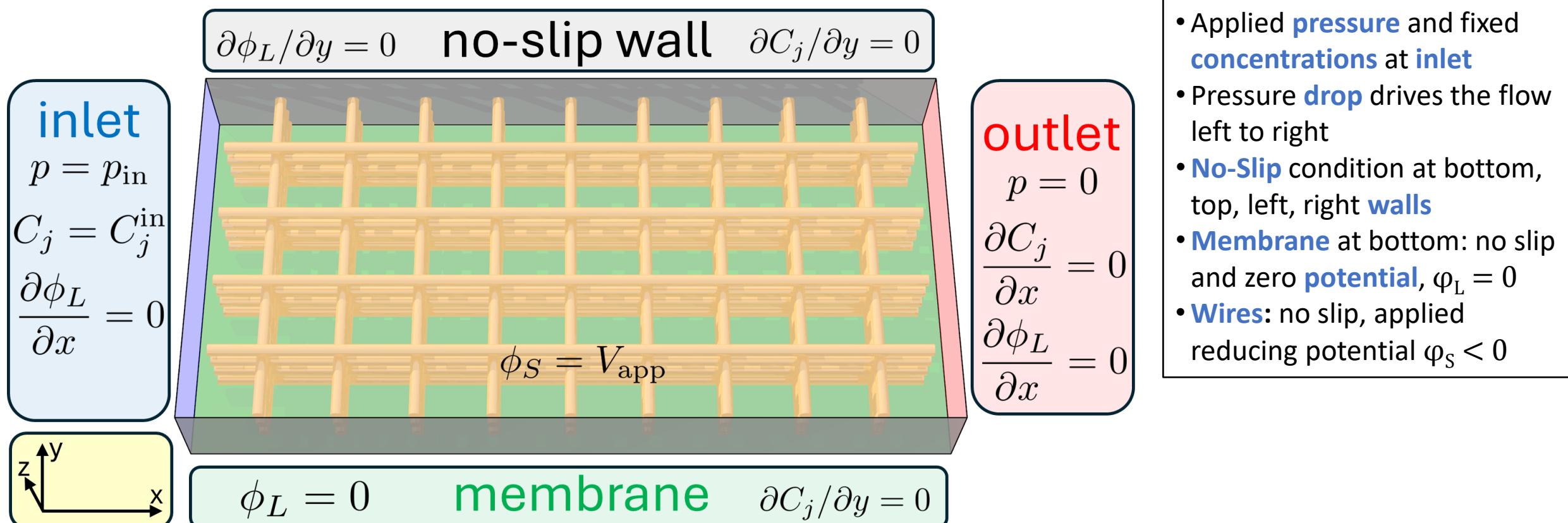


$$\frac{\partial C_j}{\partial t} = \underbrace{-\mathbf{u} \cdot \nabla C_j}_{\text{advection}} + \underbrace{D_j \nabla^2 C_j}_{\text{diffusion}} + \underbrace{\frac{z_j D_j F}{RT} \nabla \cdot (C_j \nabla \phi_L)}_{\text{electromigration}} + \underbrace{S_j}_{\text{source}}$$

Term	Concept	Units
$\mathbf{u}$	Steady state fluid <b>velocity</b>	$\text{m}\cdot\text{s}^{-1}$
$D_j$	<b>Diffusivity</b> of species j	$\text{m}^2\cdot\text{s}^{-1}$
$z_j$	<b>Charge number</b> of species j	1
$C_j$	<b>Concentration</b> of species j	$\text{mol}\cdot\text{m}^{-3} = \text{mM}$
$S_j$	Chemical <b>source</b> term of species j	$\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$
$\phi_L$	Electrical <b>potential</b> in liquid electrolyte	$\text{V} = \text{Joule}\cdot\text{Coul}^{-1}$
F	<b>Faraday's constant</b>	$\text{Coul}\cdot\text{mol}^{-1}$
R	<b>Ideal gas constant</b>	$\text{Joule}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
T	Absolute <b>temperature</b> (Kelvin)	K



# Boundary Conditions & Simulation Overview



Digital Twin for Porous Electrodes in Redox Flow Batteries.

# Nernst Equation and Overpotential



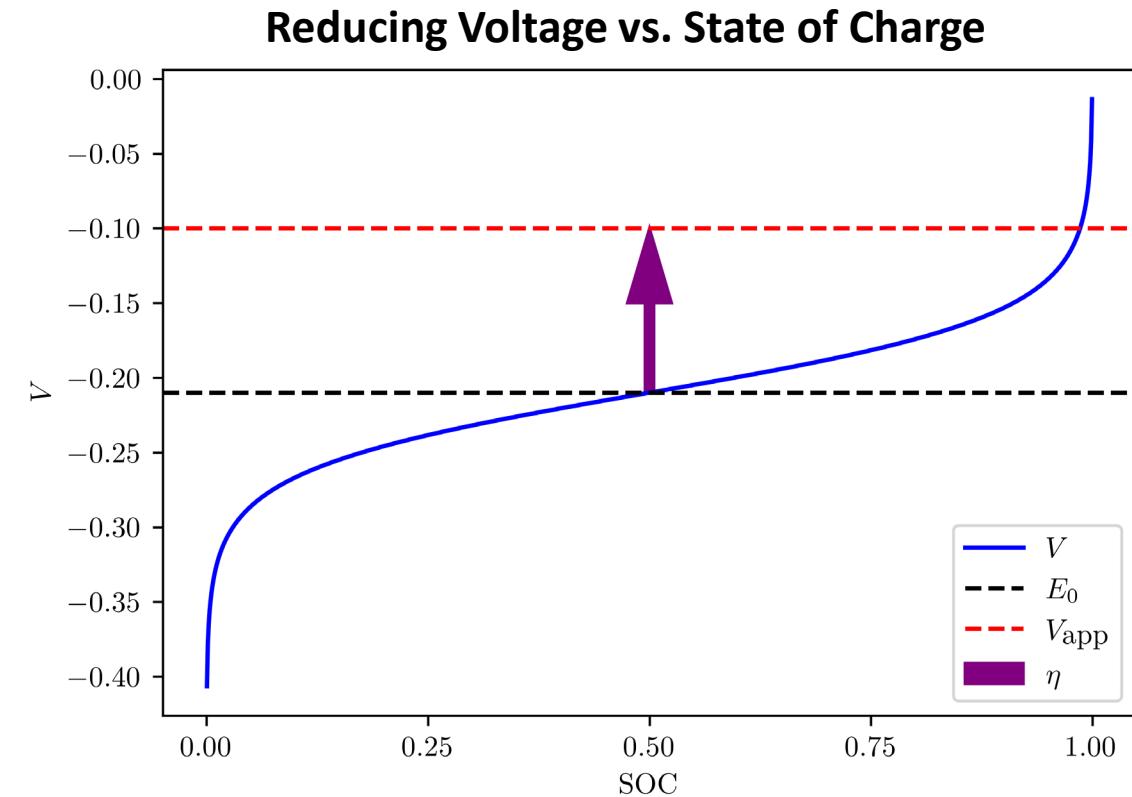
- The **Nernst equation** gives equilibrium potential  $E_{\text{eq}}$  vs. reference potential  $E^0$  as concentration varies

$$E_{\text{eq}} = E^0 + \frac{RT}{n_e F} \ln \left( \frac{C_O C_H^{n_p}}{C_R} \right)$$

- $\eta$  is called the **overpotential**

$$\eta = \phi_S - \phi_L - E_{\text{eq}}$$

- $O$ : oxidized species
- $R$ : reduced species



Sign convention:  $V_{\text{ar}}$  is “reducing voltage.”  
A larger reducing voltage drives reduction (charging)

# Reaction Kinetics: Butler-Volmer Equation

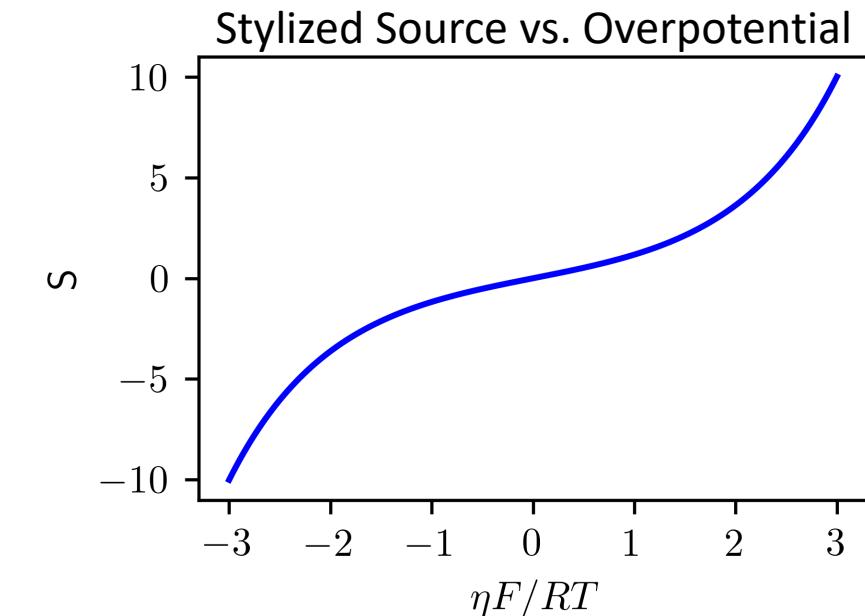


$$S = a k_0 C_O^{\alpha_O} C_R^{\alpha_R} \left[ \exp\left(\frac{n_e F \alpha_O}{RT} \eta\right) - \exp\left(-\frac{n_e F \alpha_R}{RT} \eta\right) \right]$$

Typically, we assume a perfectly reversible reaction, i.e.  $\alpha_O = \alpha_R = 0.5$ , so

$$S = 2 a k_0 \sqrt{C_O C_R} \sinh\left(n_e/2 \cdot F/RT \cdot \eta\right)$$

Term	Concept	Units
O	Generic <b>oxidized</b> species, e.g. quinone Q	—
R	Generic <b>reduced</b> species, e.g. hydroquinone H <sub>2</sub> Q	—
S	Chemical <b>source term</b> ; concentration change rate	mol·m <sup>-3</sup> ·s <sup>-1</sup>
a	<b>Specific area</b> of solid-liquid interface	m <sup>-1</sup> = m <sup>2</sup> /m <sup>3</sup>
k <sub>0</sub>	Reaction <b>rate constant</b>	m·s <sup>-1</sup>
$\alpha_j$	Charge transfer <b>coefficient</b> of species j	1
$\eta$	Activation <b>overpotential</b>	V



# Model Overview: Three Levels of Fidelity



## Butler-Volmer

- Solve for potential  $\phi_L$
- Source  $S$  from Butler-Volmer
- Advection  $\mathcal{A}$ , diffusion  $\mathcal{D}$ , electromigration  $\mathcal{E}$  (Nernst-Planck)
- Implicit time step:  $\mathcal{A}, \mathcal{D}, \mathcal{E}, S$
- Highest fidelity, slowest speed due to coupled nonlinear terms

## Simplified BV

- Assume  $\phi_L = 0$ , directly calculate  $\eta$
- Calculate  $S$  from Butler-Volmer
- Implicit time step:  $\mathcal{A}, \mathcal{D}, S$
- Disregard electromigration - good assumption with high conductivity supporting electrolyte
- Medium fidelity, medium speed

## Nernst

- Initialize overpotential  $\eta = 0$
- Directly calculate SOC on cut cells
- Implicit time step:  $\mathcal{A}, \mathcal{D}$
- Disregard electromigration
- Iteratively update  $\eta$  to offset  $\mathcal{D}$
- Steady state only
- Same fidelity as SBV but faster

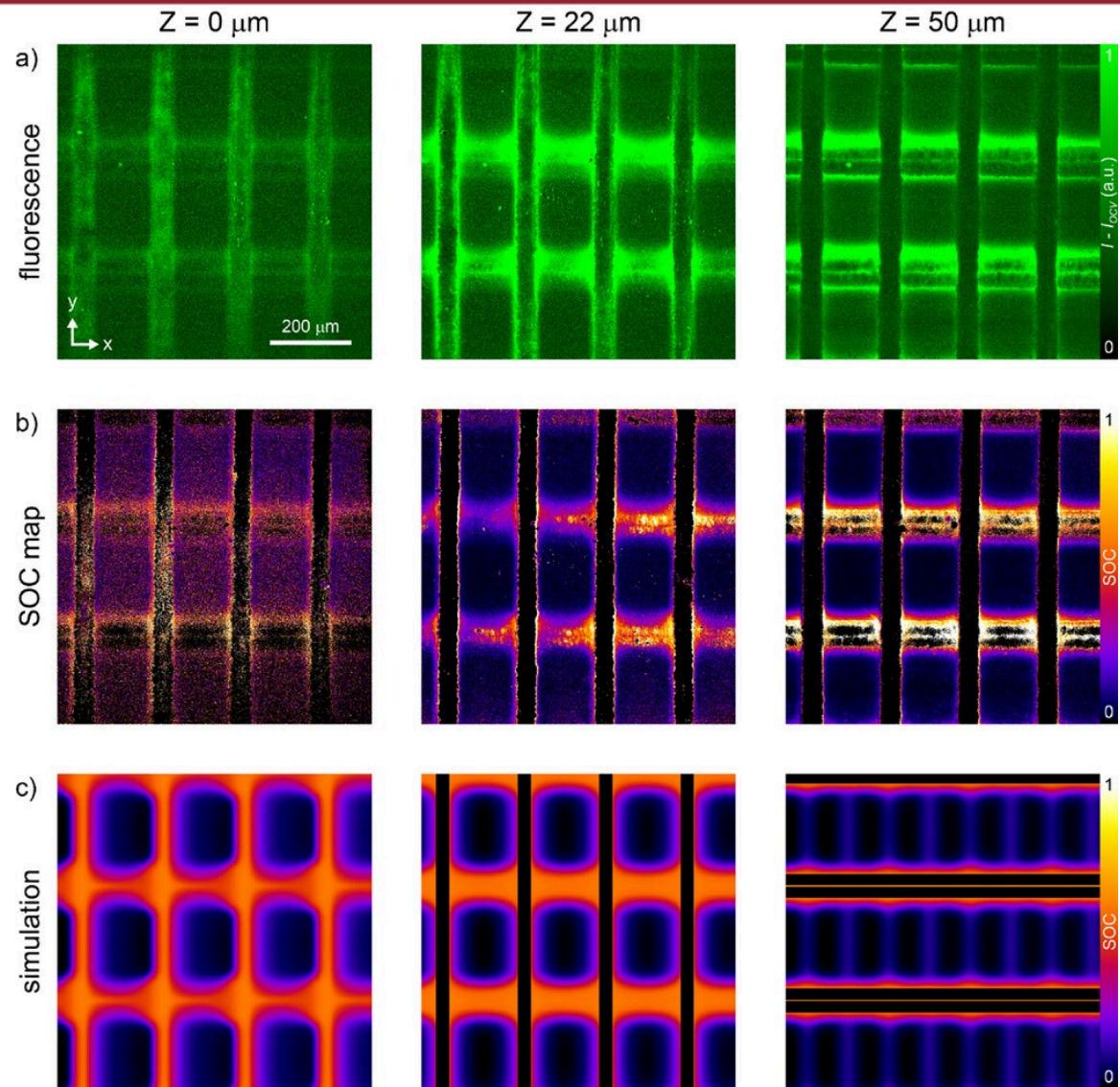
$$\kappa_L \nabla^2 \phi_L = \nabla \cdot \rho_c$$
$$\eta = \phi_S - \phi_L - E_{\text{eq}}$$
$$S \sim \sinh(\tilde{\eta}/2)$$

$$\eta = V_{\text{app}} - E_{\text{eq}}$$
$$S \sim \sinh(\tilde{\eta}/2)$$

$$s = [1 + e^{(\tilde{V} - \tilde{\eta})}]^{-1}$$
$$\eta^I \sim \sinh^{-1}(\mathcal{D}/ak_0)$$
$$\eta = \omega \eta^I + (1 - \omega) \eta$$

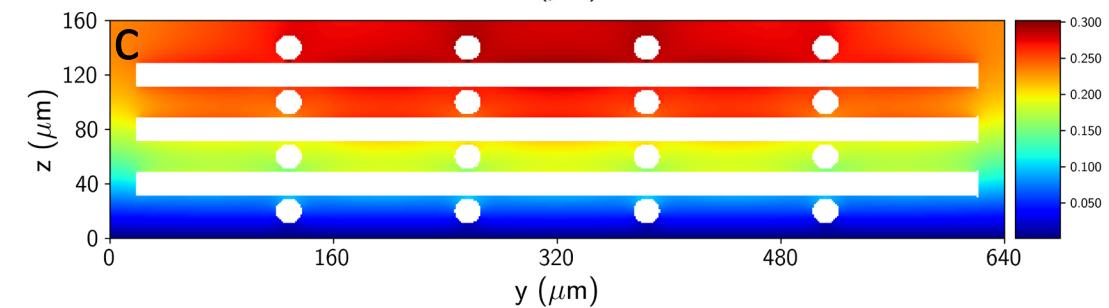
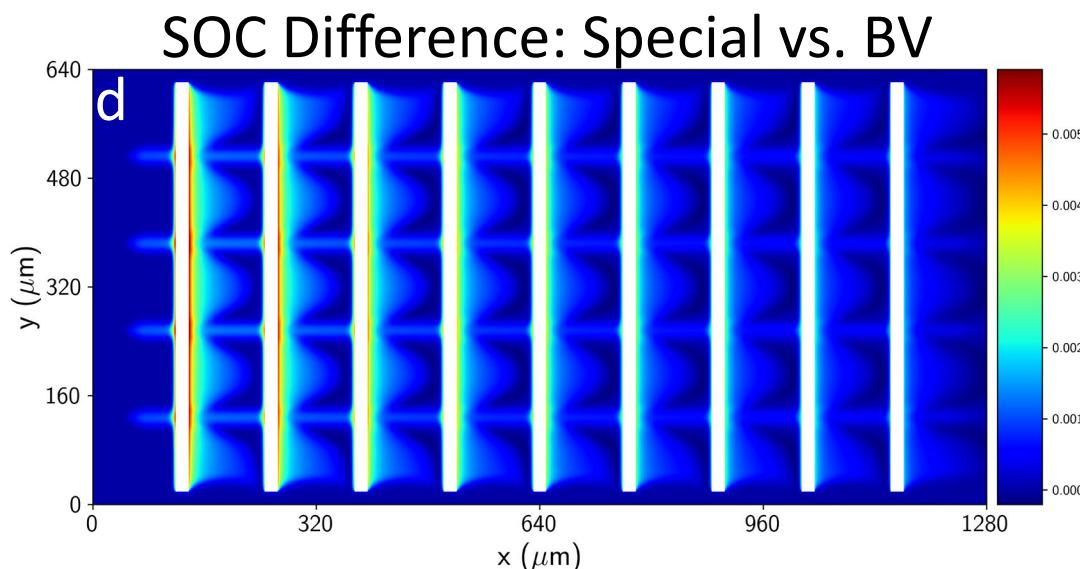
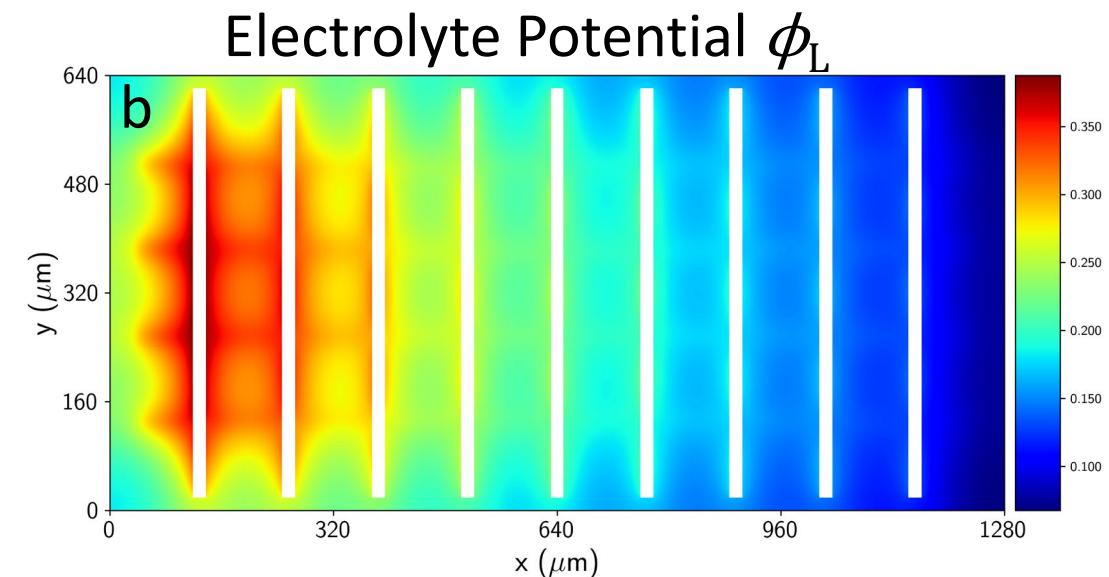
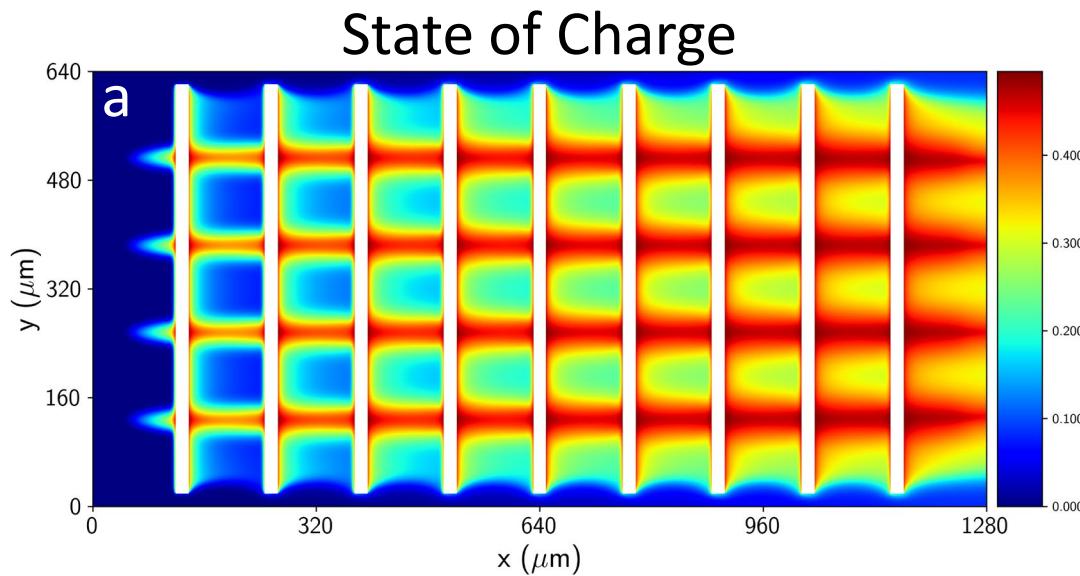


# Good Agreement with Experiments



**a)** **Fluorescence** data of logpile electrode at three slices;  
background is subtracted  
**b)** Calibrated **experimental** SOC  
**c)** Corresponding **simulated** SOC  
  
Note **good qualitative agreement**  
with build-up of high SOC above  
vertical and horizontal wires, and in  
convective tails coming off them

# Electromigration is Negligible – Model Refinement



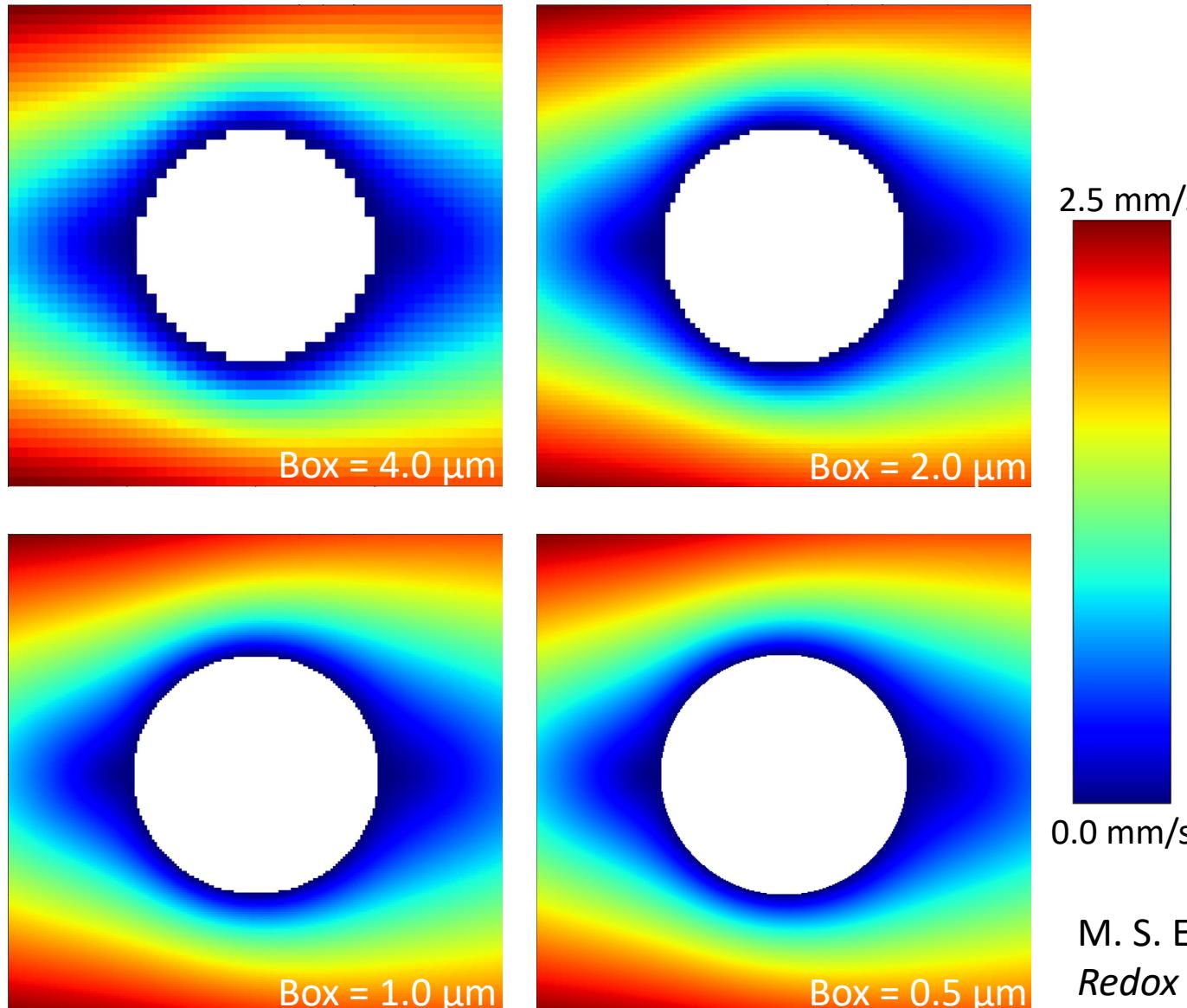
Simulation of a **logpile geometry**; cross section at mid-plane

**(a)** state of charge; reduced species builds up and spreads out due to diffusion as flow moves through electrode

**(b-c)** potential in electrolyte is **negligible**, max of 0.47 mV

**(d)** special model is **very close** to full BV, RMSE just 8.6E-4

# Iterative Upsampling: “Multigrid on Steroids”



- Fluid simulation of a 100  $\mu\text{m}$  diameter **single wire** in an open channel of 1.0 x 1.0 mm
- **Resolution doubles** at each step
- Each simulation is **initialized** with **results** of the **coarser** resolution
- **Convergence time** improved from 41 hours to under one hour

M. S. Emanuel, *Simulating Porous Electrodes in Redox Flow Batteries*. APS DFD talk, 21Nov2023.

# Steady State PDE in Terms of State of Charge $s$



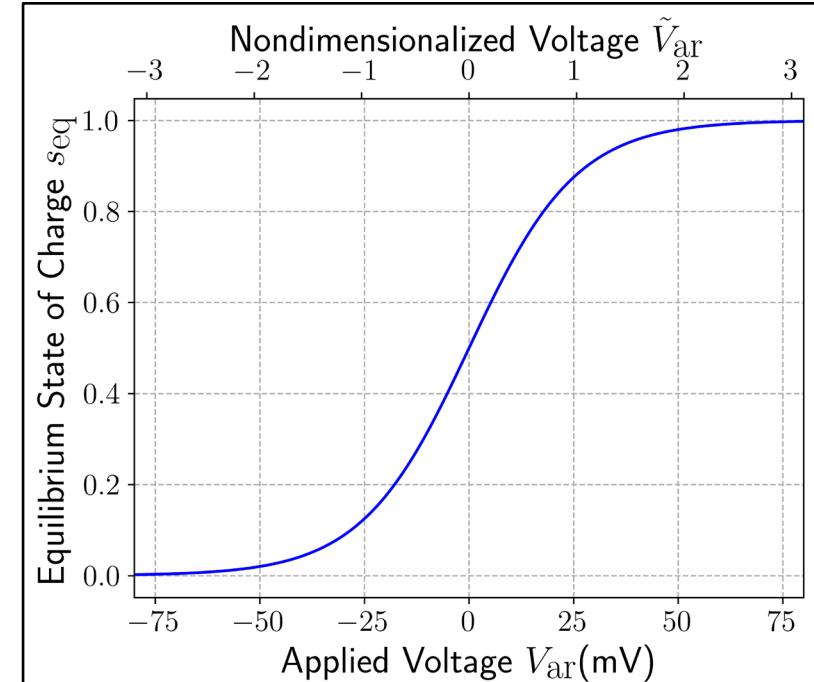
- Simplified Nernst-Planck at **steady state** in terms of  $s$

$$\mathbf{u} \cdot \nabla s = D \nabla^2 s \quad (\text{interior})$$

$$s = \sigma(\tilde{V}_{\text{ar}} - \tilde{\eta}) \quad (\text{surface})$$

$$\sinh(\tilde{\eta}/2) = - \left( \frac{D/2ak_0}{\sqrt{1(1-s)}} \right) \nabla^2 s \quad (\text{surface})$$

- In electrolyte **interior**, *advection balances diffusion*
- On electrode **surface**, the *reaction balances diffusion*
- $\sigma$  is the **sigmoid** function  $\sigma(x) = \frac{1}{1+e^{-x}}$



$\tilde{V}_{\text{ar}} = \frac{n_e V_{\text{ar}}}{V_T}$  and  $\tilde{\eta} = \frac{n_e \eta}{V_T}$  are **nondimensionalized** voltage & overpotential



# Nernst Model

- Given the SOC field, obtain new estimate of overpotential  $\tilde{\eta}_I$  to balance reaction vs. diffusion

$$\tilde{\eta}_I = 2 \sinh^{-1} \left( \frac{-D \nabla^2 s}{2ak_0 \sqrt{s(1-s)}} \right)$$

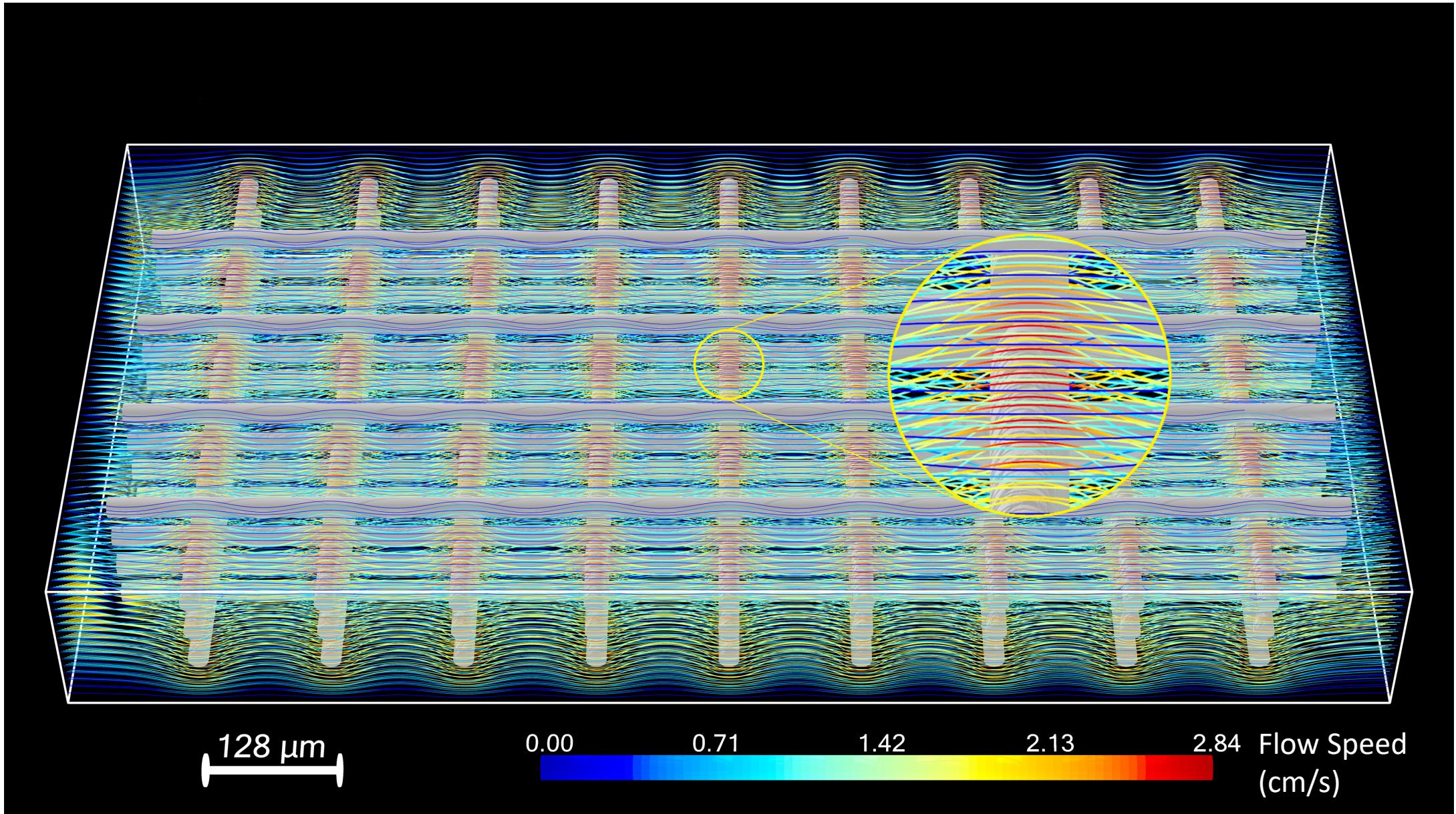
- Iteratively refine overpotential  $\eta$  and SOC  $s$  on electrode surface;  $\omega$  small relaxation parameter

$$\tilde{\eta}^{(n+1)} = (1 - \omega) \tilde{\eta}^{(n)} + \omega \tilde{\eta}_I(s^{(n)})$$

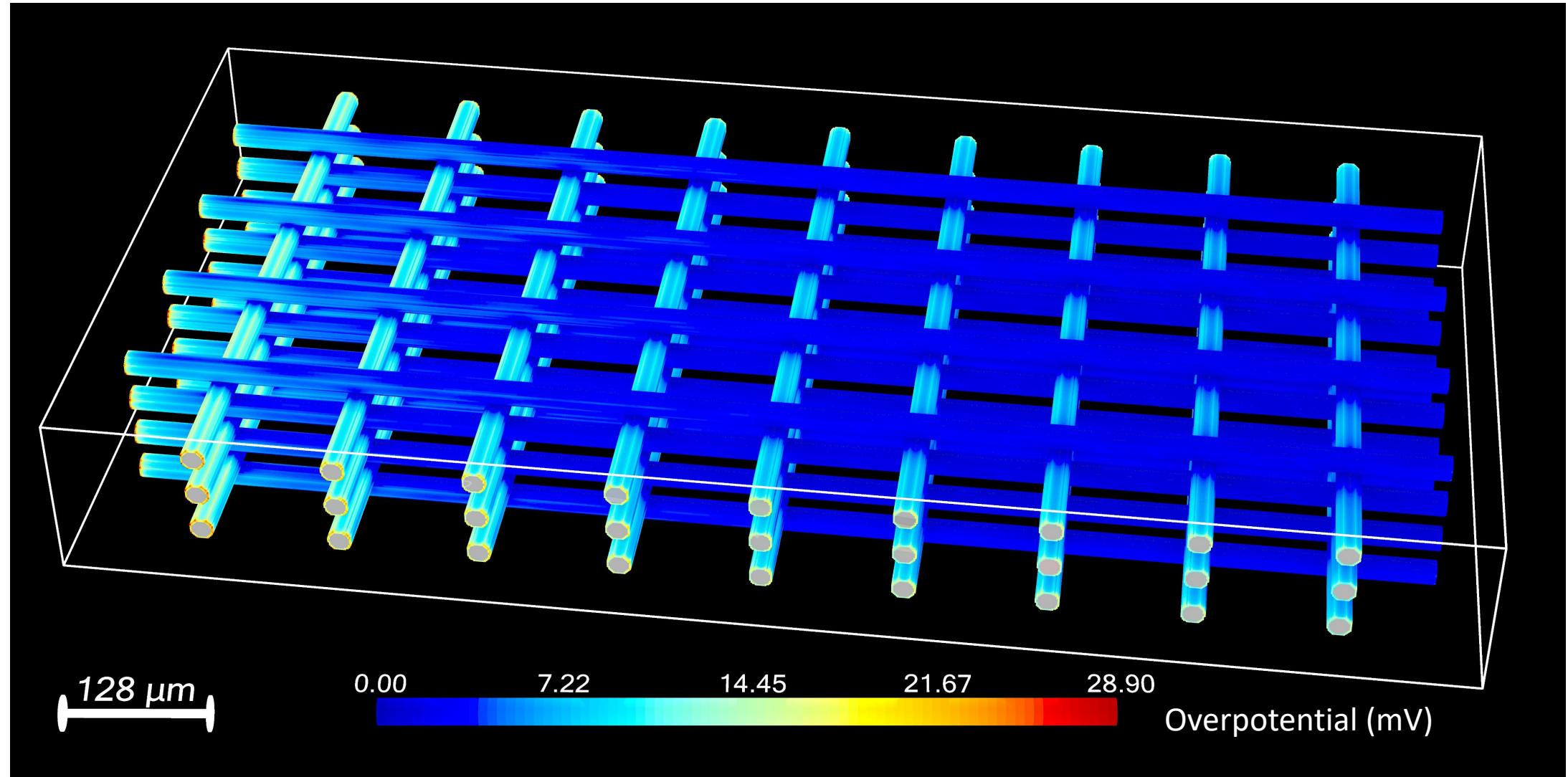
$$s^{(n+1)} = \sigma \left( \tilde{V}_{\text{ar}} - \tilde{\eta}^{(n+1)} \right)$$

- Then update  $s$  on interior with advection and diffusion terms
- Continue until convergence criteria met

# Results: Fluid Flow Streamlines

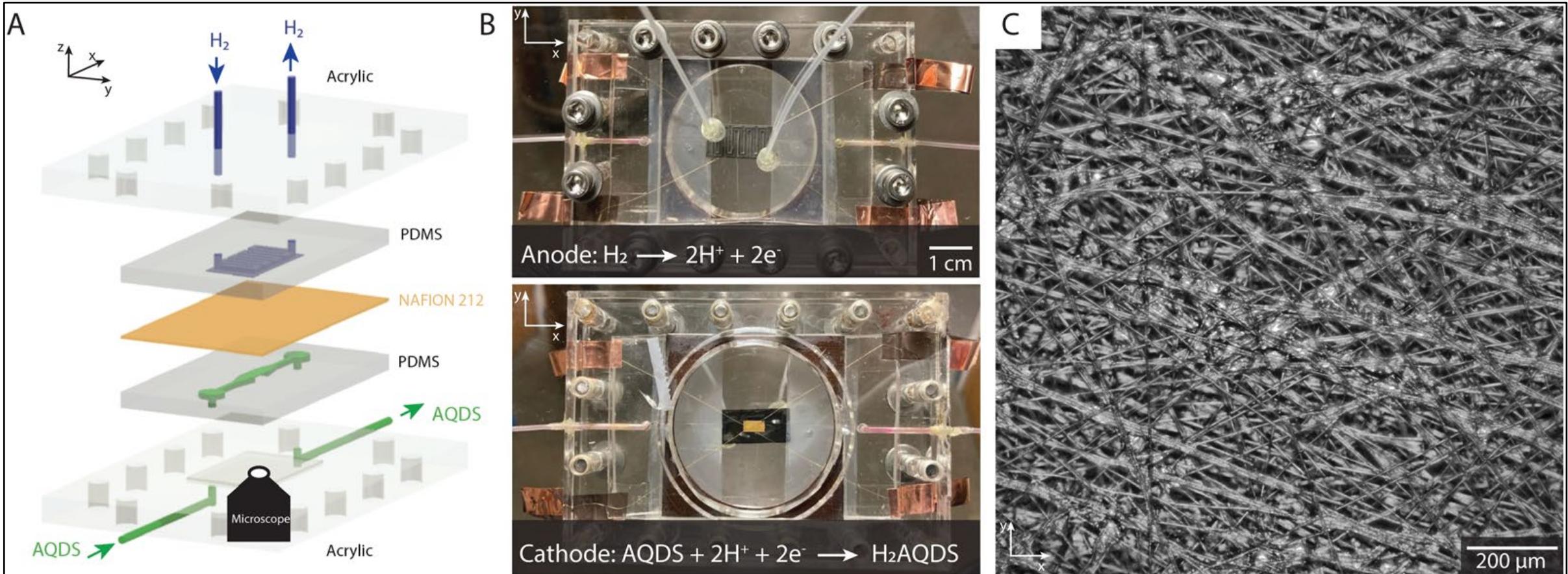


# Results: Overpotential on Electrode



## 2. Calculating SOC from Images of a Commercial Porous Electrode

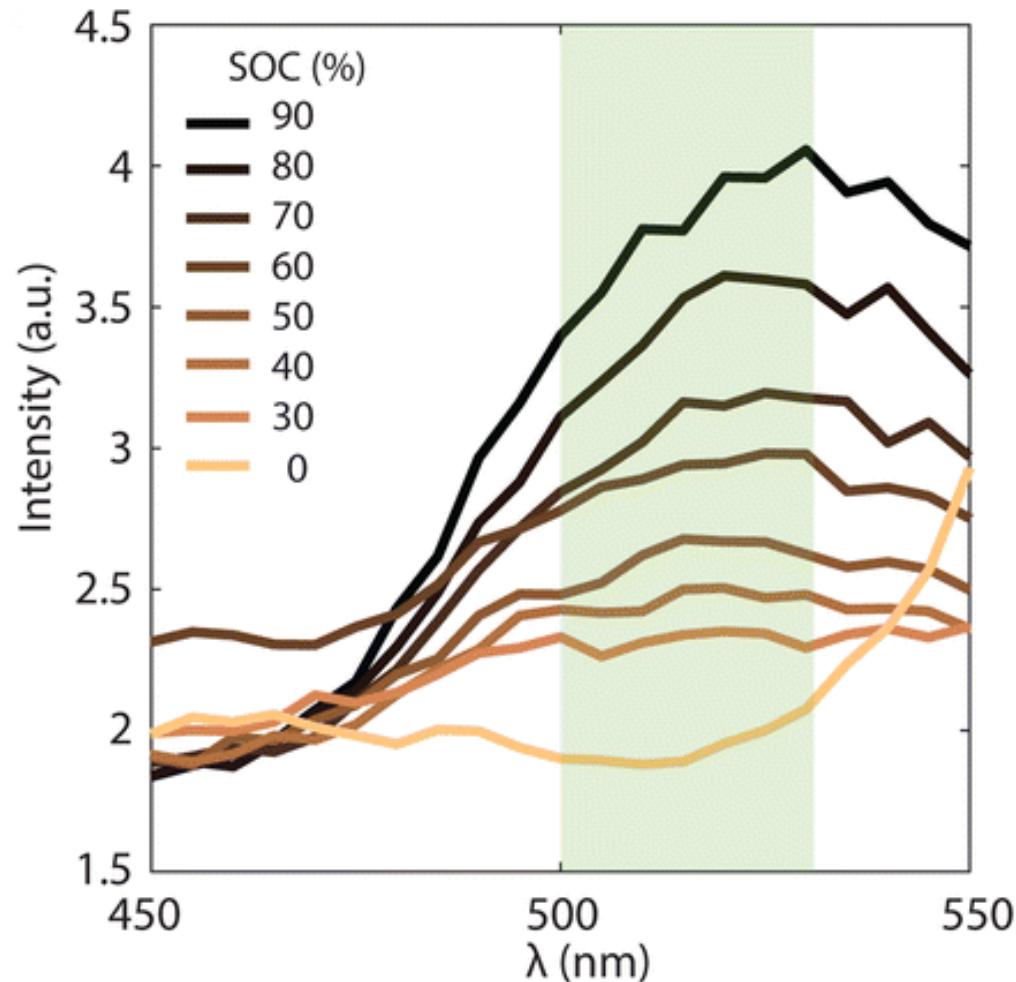
# QEFSM Experimental Setup



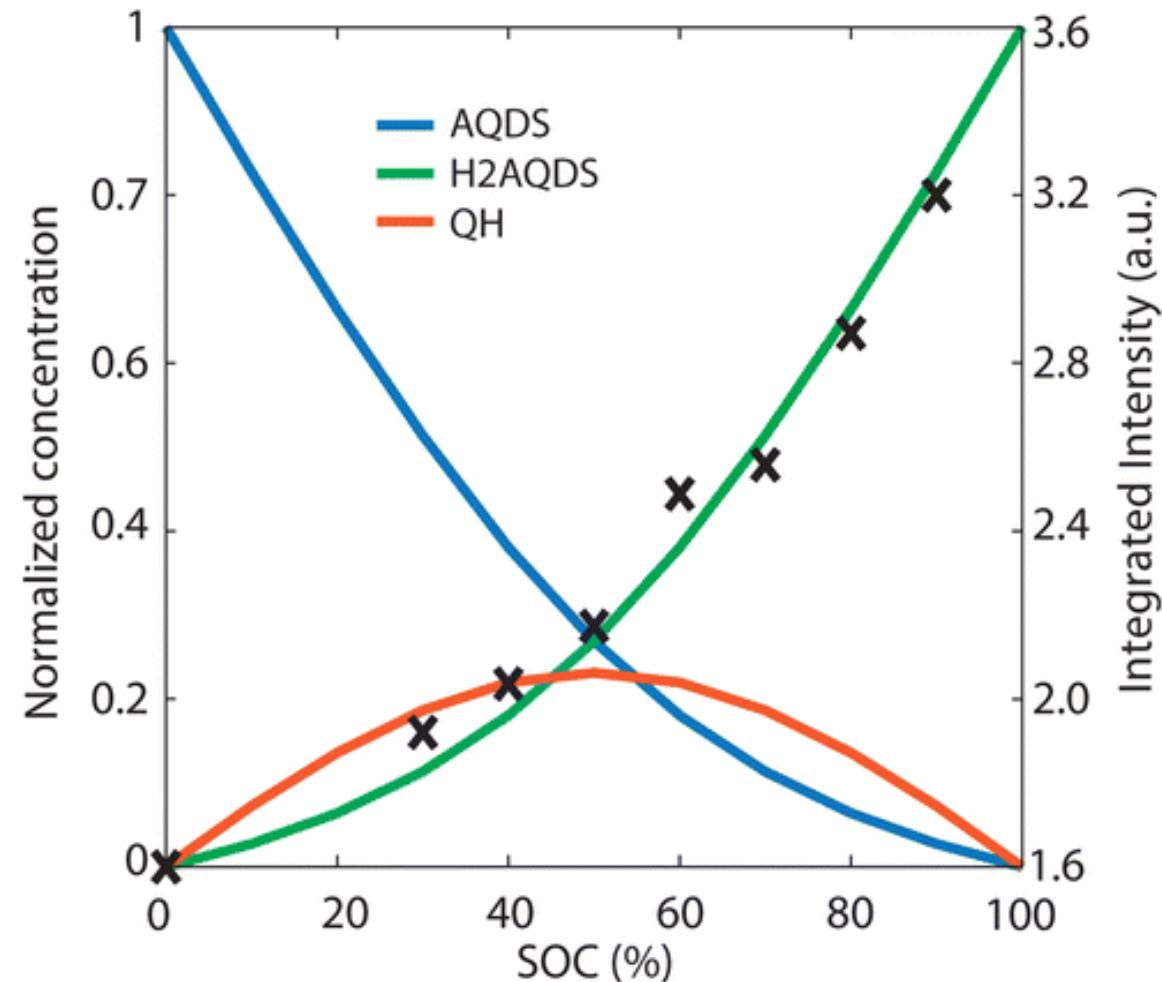
A. M. Graf, T. Cochard, K. Amini, M.S. Emanuel, S. M. Rubenstein, M. J. Aziz, *Quantitative Local State of Charge Mapping by Operando Electrochemical Fluorescence Microscopy in Porous Electrodes*. Energy Advances.

Microfluidic flow cell compatible with electrochemistry and confocal microscopy. **A)** Exploded view of the individual components with labeled coordinates. **B)** Images of assembled cell from above (top) and below (bottom). Working electrode visible in bottom image. **C)** Widefield optical microscopy image of commercial AvCarb MGL 190 electrode.

# Fluorescence Difference of AQDS Redox Pair



Emission spectra of 40 mM AQDS solutions vs. wavelength  $\lambda$  at different SOCs obtained from excitation wavelength  $\lambda_{ex} = 405$  nm. Shaded rectangle—accepted range of green band-pass filter.



Raw intensities integrated over shaded region of (B) vs. SOC. Solid lines: theoretical concentration fraction of each species from dimer model.

# Modeling Brightness vs. Concentrations

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- 28 **operating images** (4 concentrations x 7 voltages)
- One bright **calibration image** at high, uniform SOC
- Challenges: **shadows, misalignment, nonlinear** response
- **Light production** model

$$P_{ri} = \alpha[\text{AQ}]_{ri} + \beta[\text{H}_2\text{AQ}]_{ri} + \gamma[\text{QH}]_{ri} + \delta$$

- **Optical** model

$$I_{ri} = F_i \cdot Pr_i$$

- AQ, H<sub>2</sub>AQ and QH are oxidized, reduced and dimer
- Indices **r** for reaction condition, **i** for pixel

# Calculating SOC from Brightness



- **Optical factors:** from bright image,  $F_i = \frac{B_i}{\bar{B}}$

- **Brightness coefficients:**  $C = [\alpha; \beta; \gamma; \delta]$

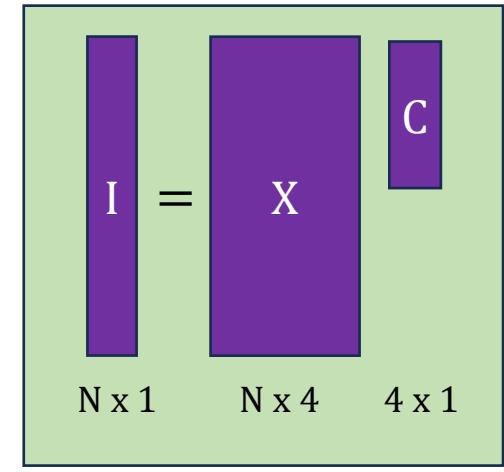
- **Weighted Concentration:**

$$X_{ri} = [AQ, H_2AQ, QH, 1]_{ri} \cdot Fi$$

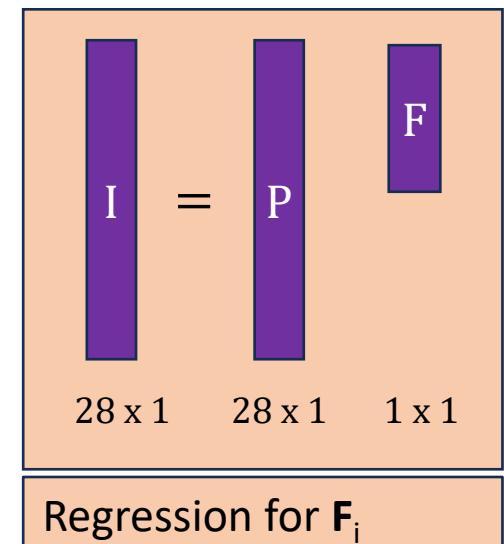
- **Regress**  $\bar{I} = \bar{X}C$  (by *mean* on 28 runs)

- **Iterate brightness:** regress  $I = XC$  (by *pixel*)

- **Iterate factors:** regress  $I_r = P_r F_i$  (by *run*)

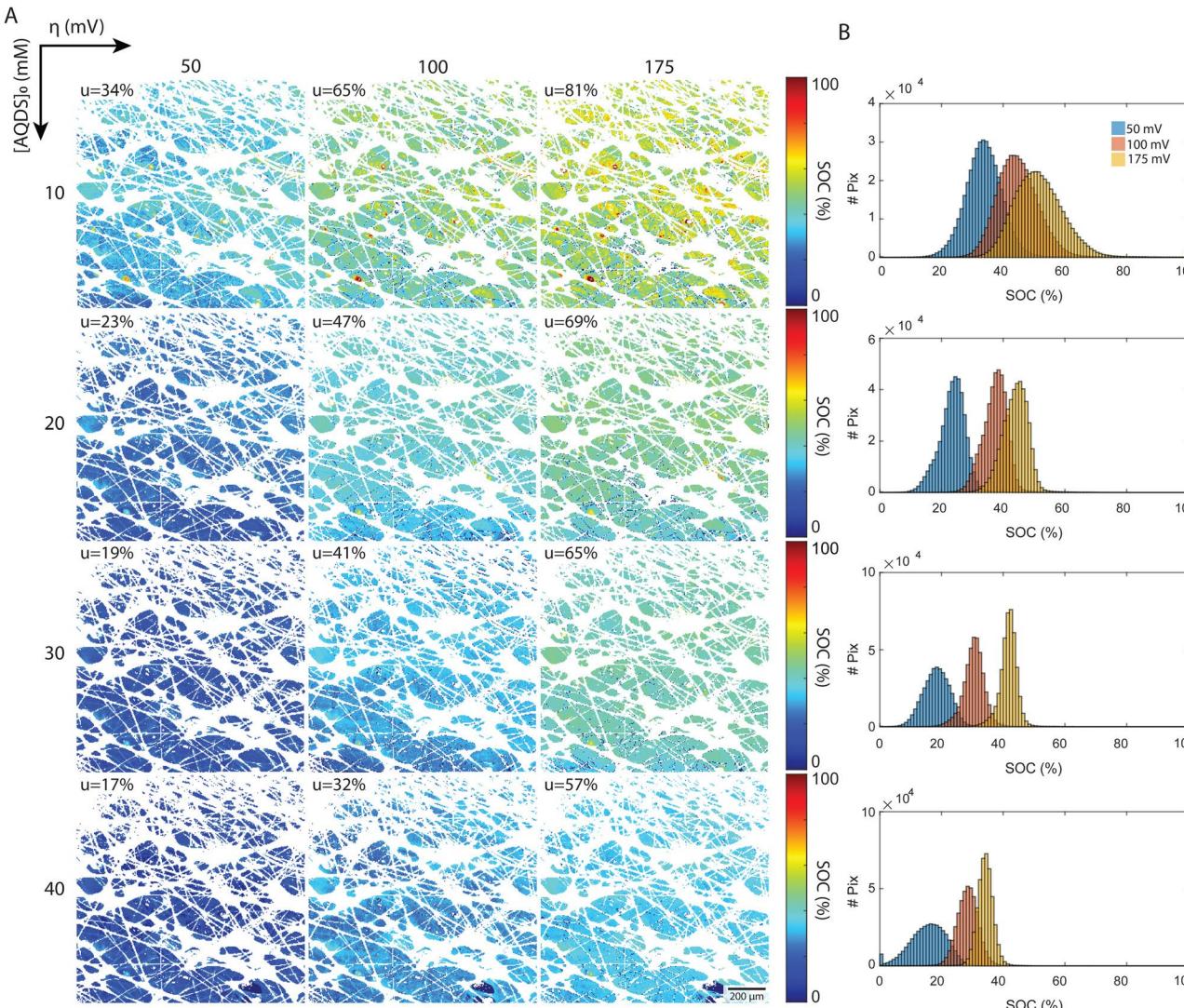


Regression for  $C$



Regression for  $F_i$

# QEFSM Results—Minimal Visual Artifacts



**Local SOC from image data**

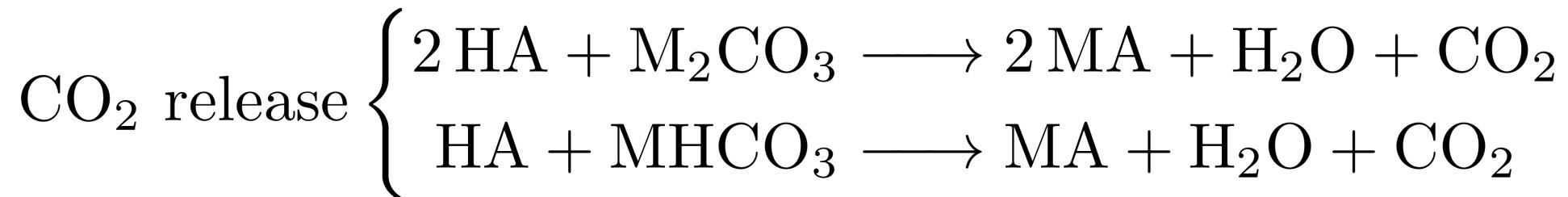
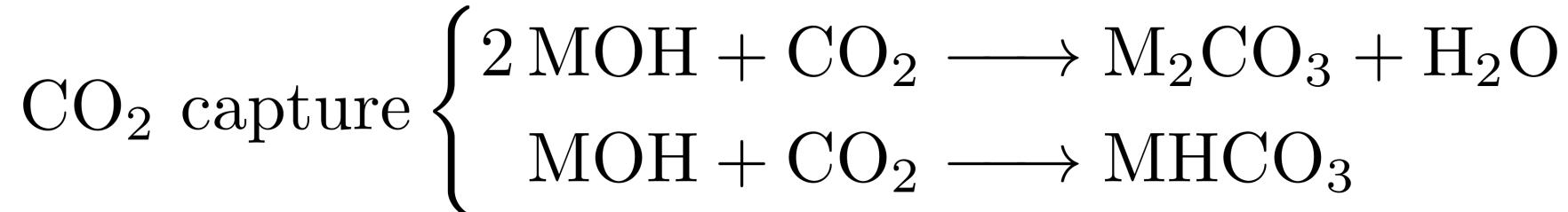
**A)** Steady state **SOC maps** under varying conditions.

**B)** **Histograms** of SOC distribution over valid pixels for each image.

Note significant departures from linear gradient predicted by mean-field theory.

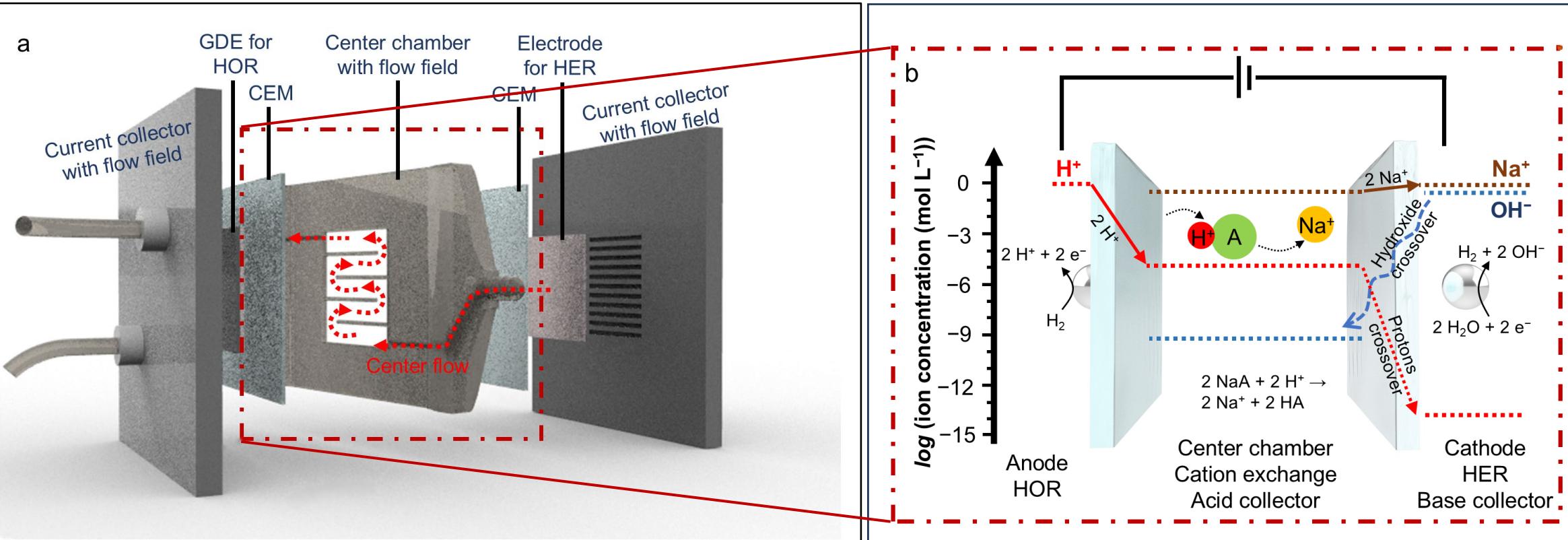
# 3. Simulating an Acid-Base Generator

# pH Swing Mechanism for Carbon Capture



- **M** – generic **metal** ion with +1 charge, e.g. **sodium**
- **A** – conjugate base a generic **acid** with -1 charge, e.g. **acetate** ( $\text{CH}_3\text{COO}^-$ )
- **Basic** solution **absorbs** carbon dioxide to form **carbonate** and **bicarbonate**
- Carbon dioxide is **released** when this solution is later **acidified**

# Acid-Base Generator Cell Structure



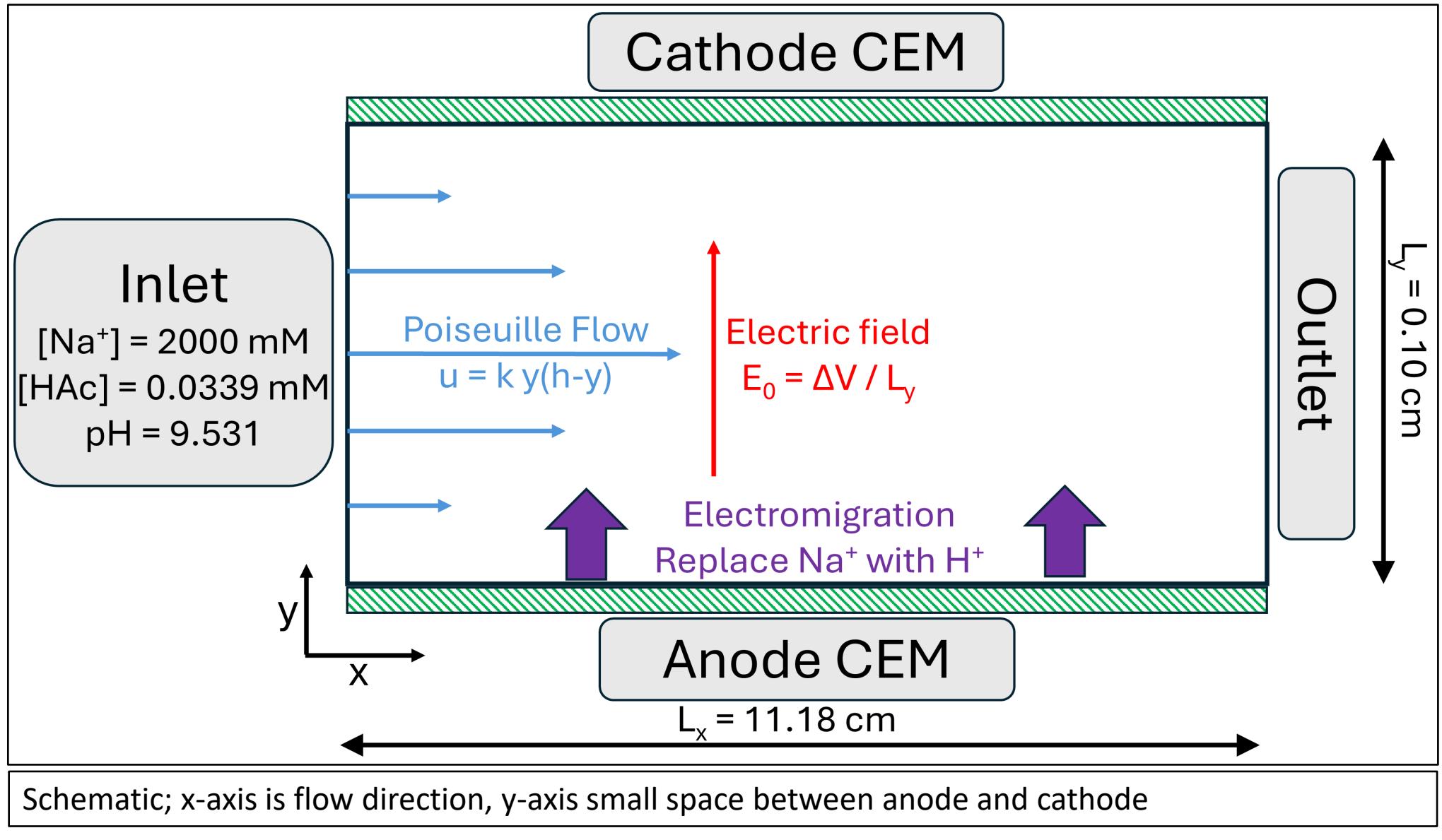
D. Xi, Y. Zheng, M. S. Emanuel, Z. Panlin, M. J. Aziz, *Electrochemical Acid-Base Generators for Decoupled Carbon Management*. Energy & Environmental Science.

# ABG Schematic & Simulation Approach



Flow Field

Unfurling serpentine  
flow path to x-axis



# Explicit Time Steps for ABG Simulation

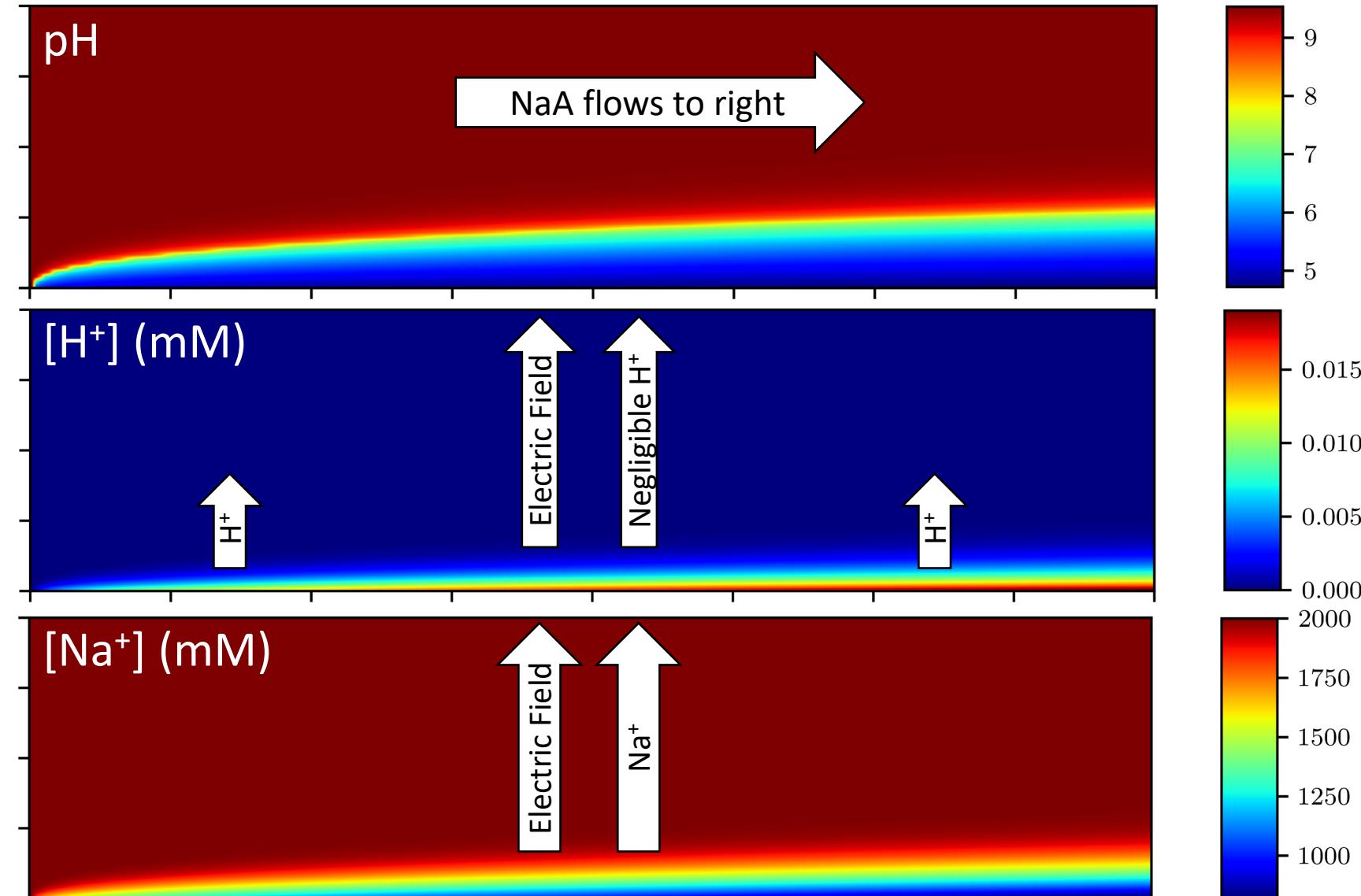


$$\frac{\partial C_i}{\partial t} = - \underbrace{\mathbf{u} \cdot \nabla C_i}_{\text{advection}} + \underbrace{D_i \nabla^2 C_i}_{\text{diffusion}} + \underbrace{\frac{z_i D_i F}{RT} \nabla \cdot (C_i \nabla \phi_L)}_{\text{electromigration}}$$

- **Plane Poiseuille flow** (analytical solution)
- **Nernst-Planck** equation for mass transport
- **Membrane** boundary condition: electromigration replaces  $\text{H}^+$  with  $\text{Na}^+$
- Uniform **electric field** from anode to cathode,  $E_0 = V_{\text{app}} / L_y$
- **Explicit** step—advection, diffusion, electromigration operators
- **Electroneutrality** imposed;  $r = \rho^+ / \rho^-$ ,  $f = \sqrt{r}$ , concentrations adjusted by  $r$
- **Chemical equilibria** solved—water and acetic acid dissociation



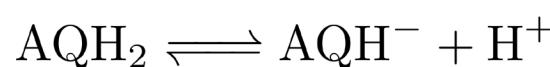
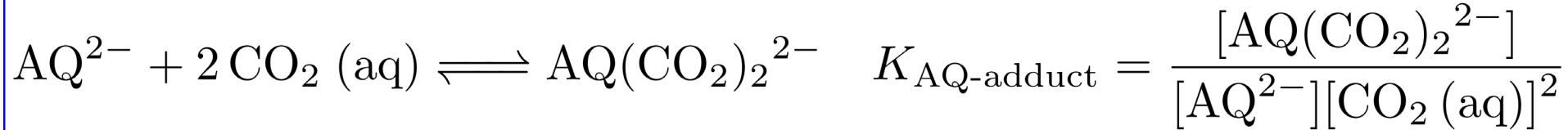
# Acid-Base Generator Simulation Results



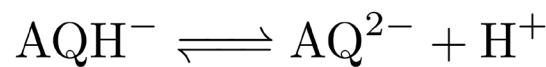
- Simulation **validates** Dawei's engineering design
- **High H<sup>+</sup> concentration** at top would indicate crossover...
- There is **negligible crossover** attributable to mass transport as described by Nernst-Planck
- Experimental findings of low crossover; hypothesis – due to **membrane effects**
- Tractable with appropriate **modeling assumptions**
- Difficult to get this level of **intuition** from experiments

# 4. Thermodynamic Analysis of a Quinone Carbon Capture System

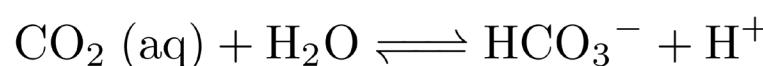
# Thermodynamic System of Equations (9)



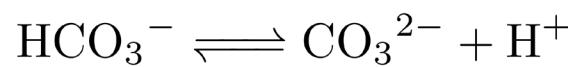
$$K_{a1} = \frac{[\text{AQH}^-][\text{H}^+]}{[\text{AQH}_2]}$$



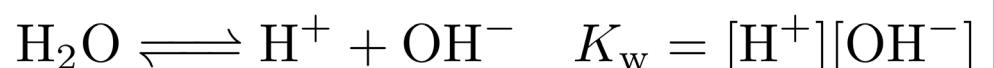
$$K_{a2} = \frac{[\text{AQ}^{2-}][\text{H}^+]}{[\text{AQH}^-]}$$



$$K_4 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2 \text{ (aq)}]}$$



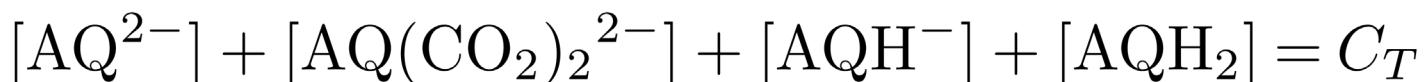
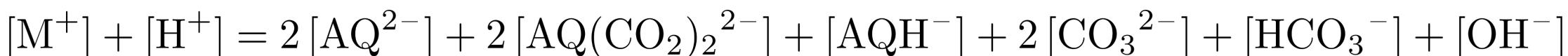
$$K_5 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}$$



## Kiana's Problem:

- Chemical **equilibria** (7)
- **Electroneutrality**
- Quinone **conservation**
- **Problem:** optimization in scipy doesn't work!

$$[\text{CO}_2 \text{ (aq)}] = C_{\text{Henry}} \cdot p_{\text{CO}_2}$$



# Strategy for Optimization Problems

---



- **Eliminate** variables
- **Nondimensionalize** physical quantities
- **Rescale** variables to mean near zero, variance near one
- Map **constrained** variables to the real line:
  - E.g. if  $x > 0$ , use  $\ln(x)$
  - E.g. if  $x$  in  $(0, 1)$ , use  $\text{logit}(x) = \ln\left(\frac{x}{1-x}\right)$
- Use **2-norm** composite error function, e.g.  $\varepsilon = \sqrt{\varepsilon_1^2 + \varepsilon_2^2}$
- Use a neutral initial **guess**

# Eliminating Variables



- **Operating** conditions:  $C_T$ ,  $p_{CO_2}$
- **Inorganic** concentrations:  $M^+$ ,  $H^+$ ,  $OH^-$ ,  $CO_2$  (aq),  $HCO_3^-$ ,  $CO_3^{2-}$
- **Organic** concentrations:  $AQH_2$ ,  $AQH^-$ ,  $AQH^{2-}$ ,  $AQH(CO_2)_2$
- **Solve** inorganic concentrations in terms of  $[H^+]$ :

$$[OH^-] = K_w / [H^+]$$

$$CO_2 \text{ (aq)} = C_{\text{Henry}} p_{CO_2}$$

$$[HCO_3^-] = K_4 \cdot [CO_2 \text{ (aq)}] / [H^+]$$

$$[CO_3^{2-}] = K_5 \cdot [HCO_3^-] / [H^+]$$

- **Solve** organic concentrations in terms of  $[AQH_2]$ :

$$[AQH^-] = K_{a1} \cdot [AQH_2] / [H^+]$$

$$[AQ^{2-}] = K_{a2} \cdot [AQH^-] / [H^+]$$

$$[AQ(CO_2)_2^{2-}] = K_{AQ\text{-adduct}} \cdot [AQ^{2-}] \cdot [CO_2 \text{ (aq)}]^2$$

- Left with **two variables**,  $[H^+]$  and  $[AQH_2]$

- Manipulate state variables to minimize **composite error**



# Transforming Variables & Calling Optimizer

- Two **state variables**,  $[H^+]$  and  $[AQH_2]$
- Apply **transformations** to state variables

$$[H^+] = e^x$$

$$x = \ln([H^+])$$

$$[AQH_2] = \frac{C_T}{1 + e^{-y}}$$

$$y = \ln\left(\frac{[AQH_2]}{C_T - [AQH_2]}\right)$$

- Define **errors**—**electroneutrality**, quinone **conservation**, and **composite**

$$\varepsilon_c = 2 \cdot \frac{(\rho^+ - \rho^-)}{(\rho^+ + \rho^-)}$$

$$\varepsilon_Q = \frac{Q_T - C_T}{C_T}$$

$$\varepsilon = \sqrt{\varepsilon_c^2 + \varepsilon_Q^2}$$

$$\rho^+ = [M^+] + [H^+]$$

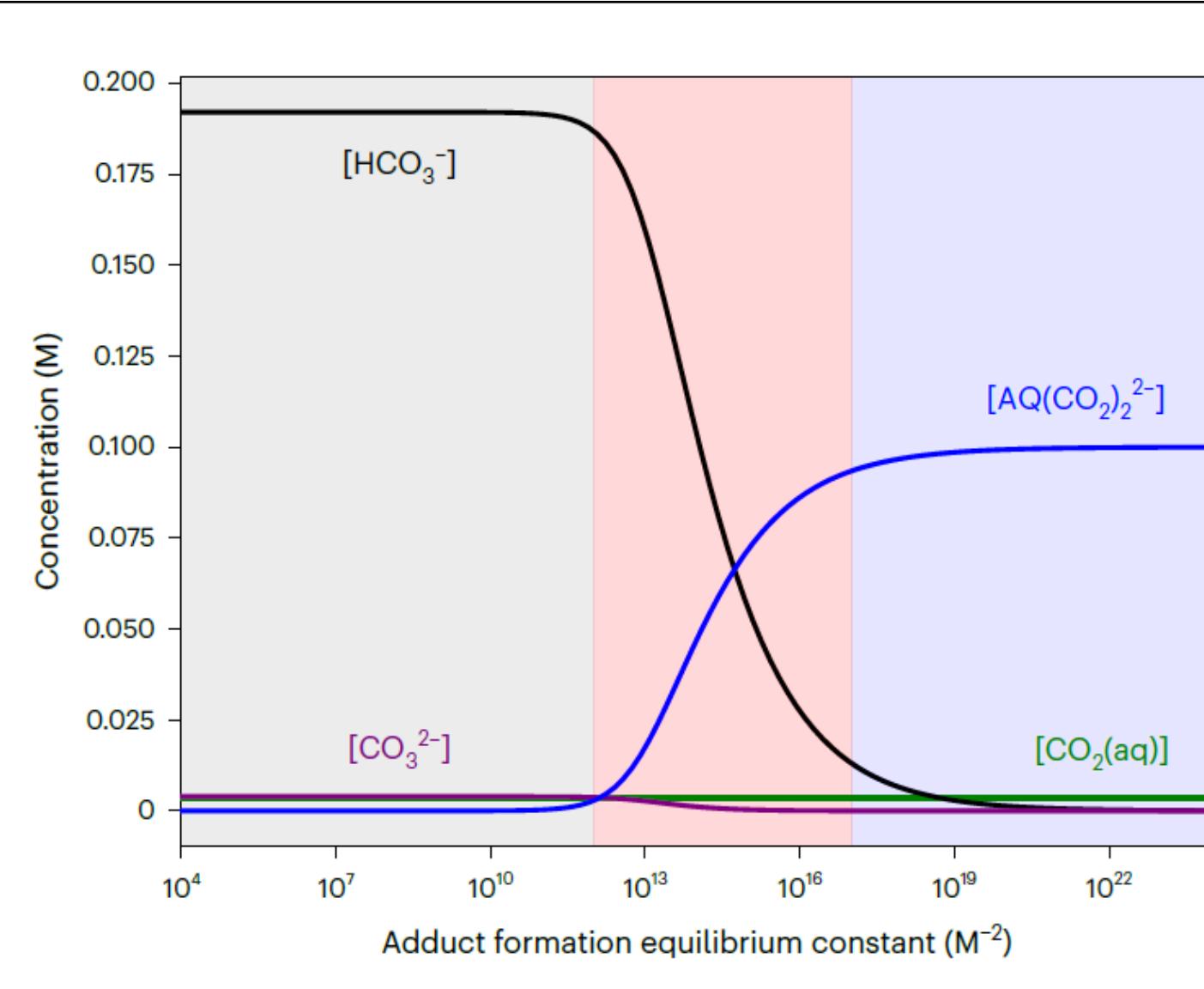
$$\rho^- = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [AQH^-] + 2[AQ^{2-}] + 2[AQ(CO_2)_2^{2-}]$$

$$Q_T = [AQH_2] + [AQH^-] + [AQ^{2-}] + [AQ(CO_2)_2^{2-}]$$

- Optimizer: **minimize** composite error by adjusting x and y



# Results: Three Behavioral Regimes



Concentrations of  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $CO_2(aq)$  and  $AQ(CO_2)_2^{2-}$  at different  $K_{AQ\text{-adduct}}$  values.

Gray region: pH swing dominates.

Blue region: nucleophilicity swing dominates.

Red region: both mechanisms in play.

Understanding dominant behavior leads to better molecular engineering strategies.

# Conclusions & Future Research Directions

# Scientific Conclusions

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- Modeling **steady state** easier than integrating dynamics
- Any **mass transport** system can be modeled at steady state by switching from **flux** to **boundary value** condition
- Useful to have a series of related models on same back-end with **increasing** levels of **fidelity**
- Porous electrodes in flow batteries are typically run in the **Stokes flow** regime with **negligible electromigration**
- A porous electrode geometry can be evaluated with a **single flow simulation** plus a **handful** of **reaction simulations**
- We can do **computational design** of electrodes!

# Comments on Scientific Computing

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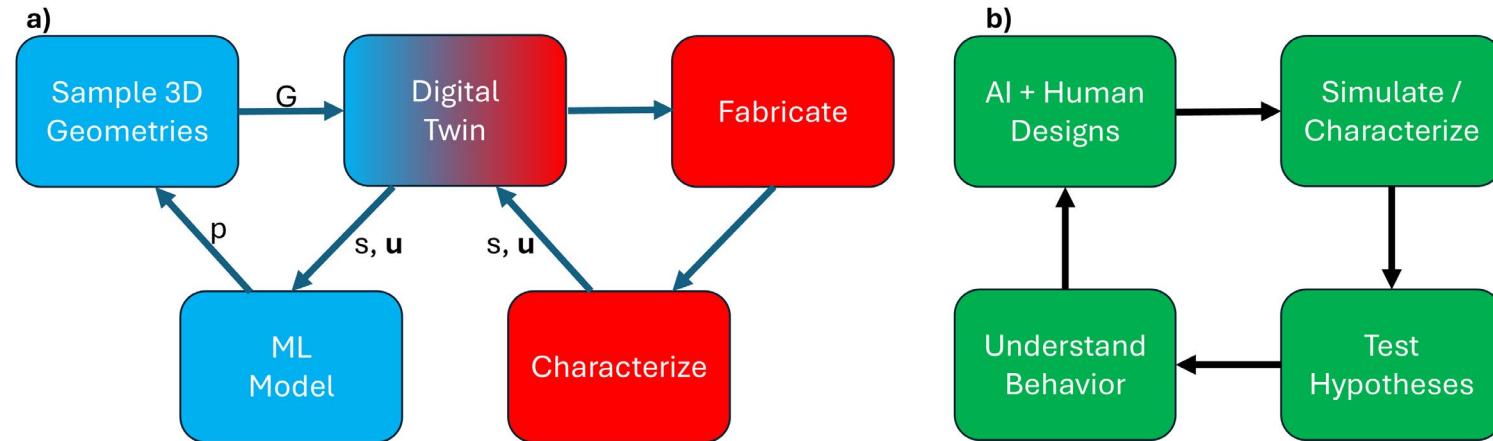


- We should **broaden** our **ambitions** in the **exascale age** of massive scientific supercomputers
- **Direct numerical** simulations of **PDEs** are now within reach
- **Explicit methods** are often underappreciated
- Applied mathematicians should **collaborate across disciplines** more...
- But **institutional support** and **incentives** are lacking
- **Data analysis** is now a specialty and should be treated as such

# Future Research Directions



- **Digital twin** for active learning and surrogate ML models



- **Darcy mosaic** model: 3D grid of box-shaped tiles
  - Coupled hydraulically by **Darcy flow**
  - Coupled electrochemically by SOC values on shared faces
- **Mass transfer coefficient**  $k_m$  as emergent vs. phenomenological

# Acknowledgments

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**Advisor:**  
Chris H. Rycroft



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**Co-Advisor:**  
Michael J. Aziz

# Rycroft Group



# Aziz Group



# Convexity Colleagues



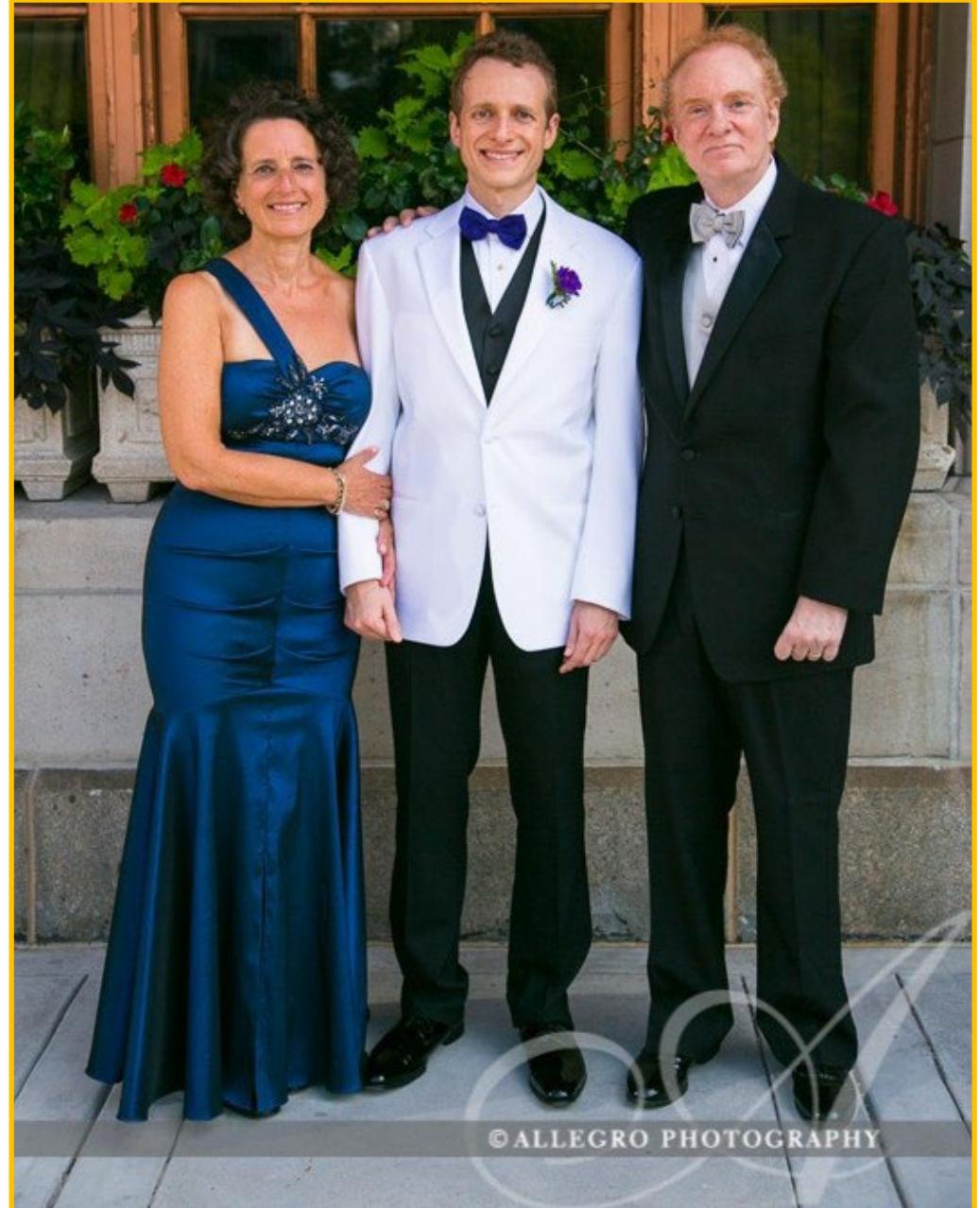
# Old Friends



# Gibson Family



# Emanuel Family (OG)



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# My Family



# Afterword: Responding to a Time of Crisis in America

# Defending Harvard Against Tyranny

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- Harvard is **under attack** by our own government
- Trump wants to control who we **hire**, what we **teach**, and even what we **think**
- As a **Jewish American** student, I know **antisemitism** *is* a real problem, but I say to Trump and his thought police:  
***You do not speak for me*** when you attack Harvard.  
*We are confronting our problems **together**, as a **community** of scholars, students and researchers. ***Stay out of it.****
- To the rest of you I say:  
***Please stand with me*** to ***defend Harvard*** against this ***unjustified*** and ***un-American attack!***

# Sustaining Science at Harvard and Beyond

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- Harvard may **ultimately prevail** in litigation, but not for years
- Even the Harvard **endowment cannot fund** our research
- We won't be able to **flip a switch** and “turn science back on”
- A handful of **influential philanthropists** could sustain science at Harvard until we emerge from this crisis
- I have one foot in each of the worlds of **finance** and **science**
- Even a **modest gift** could have a **transformational impact**
- If you or someone you know can help, **please contact me!**  
[michael.s.emmanuel@gmail.com](mailto:michael.s.emmanuel@gmail.com)

# Appendix

# Teasers to Read Dissertation

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- **Dedication** and acknowledgments
- **Epigraphs**—textual, musical (!) and youthful
- **Details**—conceptual, numerical and experimental
- **Foreword**—personalized overview of my research
- **Introduction**—larger scientific context of my work
- **Afterword**—addressing the crisis in American science

# Image URLs

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- <https://www.eia.gov/todayinenergy/detail.php?id=56880>
- <https://www.energy-storage.news/us-installed-grid-scale-battery-storage-capacity-reached-9gw-25gwh-in-record-breaking-2022/>
- <https://www.npr.org/sections/the-picture-show/2025/01/13/g-s1-42407/see-california-wildfire-devastation-pictures-altadena-eaton-palisades>
- <https://www.catf.us/resource/carbon-capture-storage-what-can-learn-from-project-track-record/>
- <https://en.wikipedia.org/wiki/Quinone>