



Electrochemical Impedance at a rotating
disk electrode

GAMRY
INSTRUMENTS

Perspective and goal

- Perspective:
 - Researcher interested in using EIS at RDEs
 - Basic echem understanding
 - Some EIS exposure
- Goal:
 - Provide an introduction and practical framework to run EIS at RDEs.

Topics

- Steady state mass transfer
- RDE basics and the Levich equation
- Nernst diffusion layer (NDL) and the porous bounded Warburg

Application

- Electroactive species in biofilms
- Impedance behavior of electrochemically active biofilms (EAB) at an RDE

Why use an RDE?

- Achieve the steady state mass transfer condition:
 - $i = nFA(D/\delta)(C_{\text{bulk}} - C_{\text{surface}})$
 - $i_L = nFA(D/\delta)(C_{\text{bulk}})$ where C_{surface} is zero
 - Current is limited by the mass transfer rate
 - Electrode potential is predicted by the Nernst equation
 - “steady state” = does not change with time

- Difficult to achieve in a stationary system:
 - $\delta(t) \sim (Dt)^{1/2}$
 - t is time elapsed after a large potential step
 - Derived from the Cottrell equation

Difficulty with stationary systems

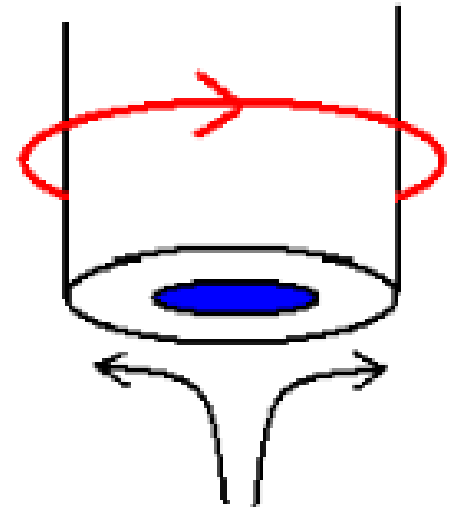
- Background convection impacts the current measurement
 - After $t > 20s$, becomes more pronounced
 - Thermal gradients, vibration, other external factors
- The transient current behavior and background convection influence conflicts with the EIS stability requirement, especially when wanting to run EIS at a non-zero DC current
- EIS generally limited to running at the open circuit potential for diffusion-limited stationary systems

Why use an RDE?

- Gives you a reproducible and well-defined way of introducing convection to control diffusion of electroactive species near the electrode surface

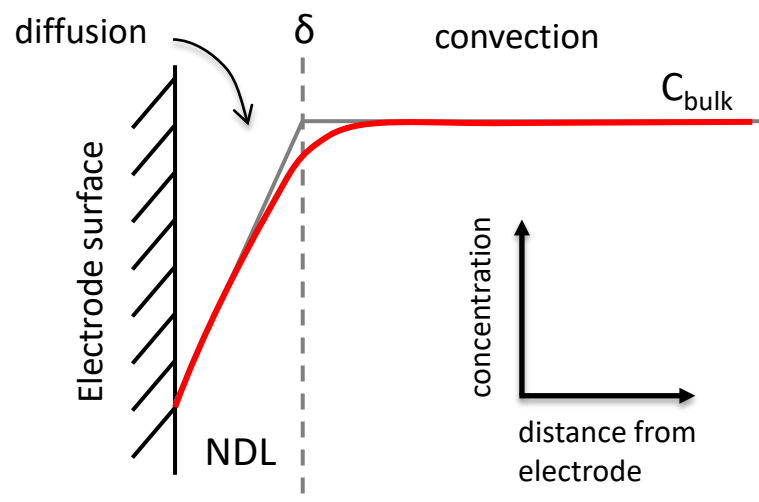
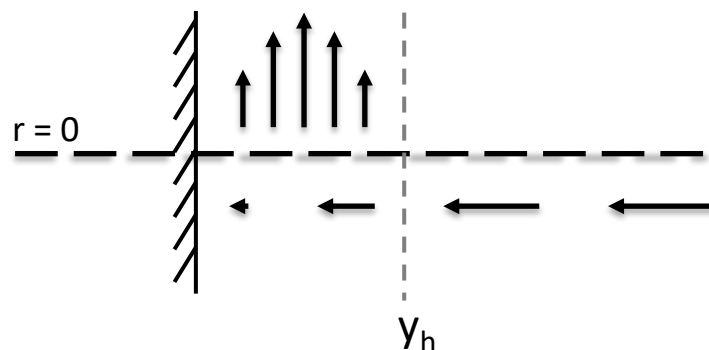
Rotated disk theory

- disk electrode (blue) is embedded in a larger, non-conducting shroud
- entire assembly is rotated (red arrow)
- Solution is drawn up along the axis of rotation and past the electrode (black arrows)
- There is laminar (i.e., smooth) flow past the electrode surface
- The electrode potential is set to the limiting current region



Rotated disk theory

- solution at the surface is dragged along by the rotating disk
 - Hydrodynamic layer, y_h
- there is a thin layer that is unstirred
 - Nernst diffusion layer, δ
- $y_h/\delta = 2(v/D)^{1/3}$
 - NDL is $\sim 5\%$ of hydrodynamic layer in water for an electroactive species such as ferricyanide

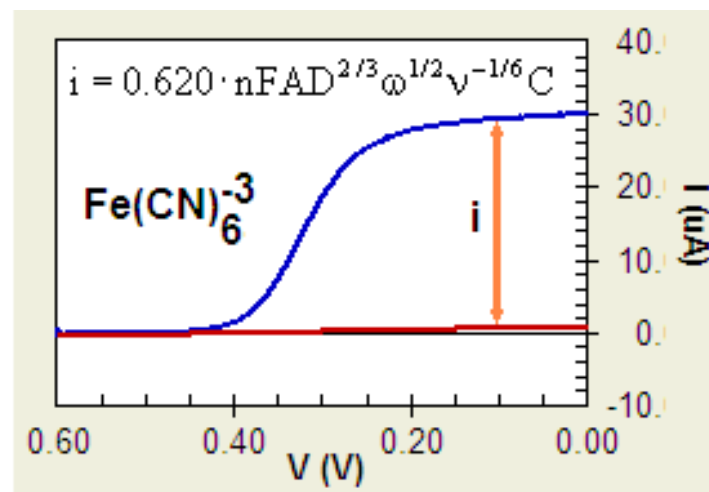


Rotated disk theory

- Limiting current, i_L , is given by the Levich equation
 - $i_L = 0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C_{\text{bulk}}$
 - Levich equation is the steady state solution to the convective-diffusion system
- Combining the Levich equation with our earlier equation* yields:

$$\delta = 1.61 \cdot D^{1/3} r^{-1/2} \nu^{1/6}$$

δ = Diffusion Layer Thickness
 D = Diffusion coefficient
 r = rotation rate (rad/s)
 ν = viscosity



*Slide 4: $i_L = nFA(D/\delta)(C_{\text{bulk}})$

Porous bounded Warburg

- The hydrodynamics described for RDEs fits the requisites for a 'Porous Bounded Warburg':
 - There is a thin layer of unstirred solution next to the electrode
 - Large, stirred, homogeneous source of material outside that layer
 - Between these regions there is a (virtual) membrane that is porous to the diffusing molecule.
- Sometimes referred to as the Nernst circuit element because it fits the model of the Nernst Diffusion Layer.

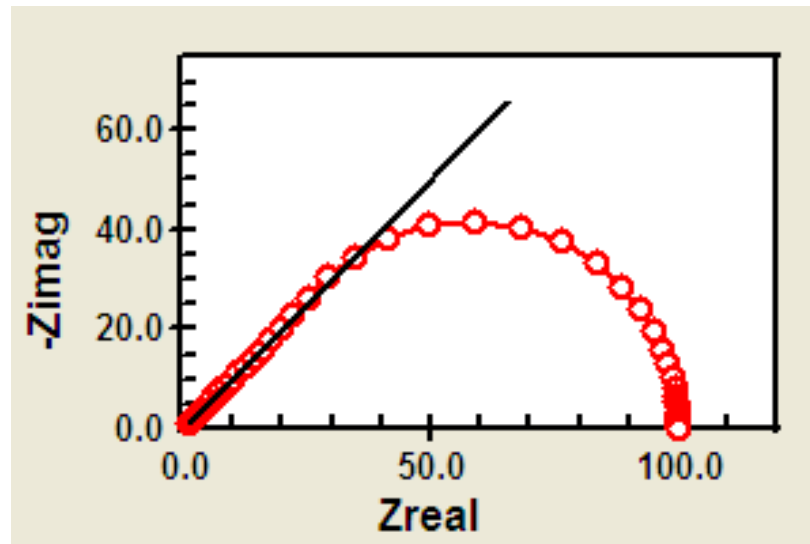
Porous bounded Warburg

Transient diffusion layer thickness

$$\Delta x \approx \sqrt{D \cdot \Delta t} = \sqrt{D / f}$$

Nernst diffusion layer thickness

$$\delta = 1.61 \cdot D^{1/3} \cdot \nu^{-1/2} \cdot \omega^{1/6}$$



the diffusion layer thickness is “bounded” by the steady state limit (NDL)

Porous bounded Warburg

- In our basics of EIS application note¹, this is described as:
 - “At high frequencies, the Warburg impedance is small since diffusing reactants don't have to move very far.”
 - “At low frequencies, the reactants have to diffuse farther, increasing the Warburg impedance.”

¹<https://www.gamry.com/application-notes/EIS/basics-of-electrochemical-impedance-spectroscopy/>

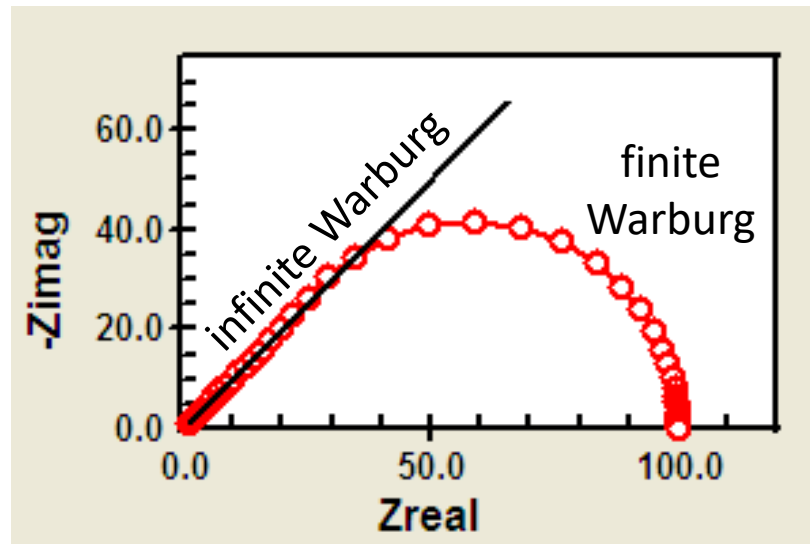
Porous bounded Warburg

Transient diffusion layer thickness

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Nernst diffusion layer thickness

$$\delta = 1.61 \cdot D^{1/3} \cdot r^{-1/2} \cdot \nu^{1/6}$$



the diffusion layer thickness is “bounded” by the steady state limit (NDL)

Porous bounded Warburg

- Characterized by two parameters, B and Y_0 .
- The equation for Z is shown here, along with the gruesome definitions of B and Y_0 .
- The parameter B (in $\text{sec}^{1/2}$) is a measure of the time it takes for the reactant to diffuse across the NDL.
- B depends upon the NDL thickness, which in turn, depends upon the rotation speed (r) of the electrode
- Y_0 is the magnitude of the admittance at a frequency of 0.16 Hz (or angular frequency of 1 rad/s), proportional to the Warburg coefficient¹, σ .

$$Z = \left[(1/Y_0) / \sqrt{(j \cdot \omega)} \right] \tanh \left\{ B \sqrt{(j \cdot \omega)} \right\}$$

$$B = \delta / \sqrt{D} = 1.61 \cdot r^{-1/2} \cdot (\nu / D)^{1/6}$$

$$Y_0 = \frac{n^2 F^2 A}{RT \left(\frac{1}{C_0 D_0^{1/2}} + \frac{1}{C_R D_R^{1/2}} \right)}$$

$$Y_0 = \frac{1}{\sigma \sqrt{2}}$$

EIS setup in the Gamry software

Acquisition: Framework

Potentiostatic EIS

Default Save Restore OK Cancel

Estat IFC1010-20135 JB

Test Identifier

Output File

Notes...

Initial Freq. (Hz)

Final Freq. (Hz)

Points/decade

AC Voltage (mV rms)

DC Voltage (V) vs Eref vs Eoc

Area (cm²)

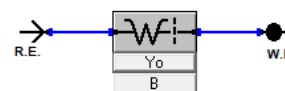
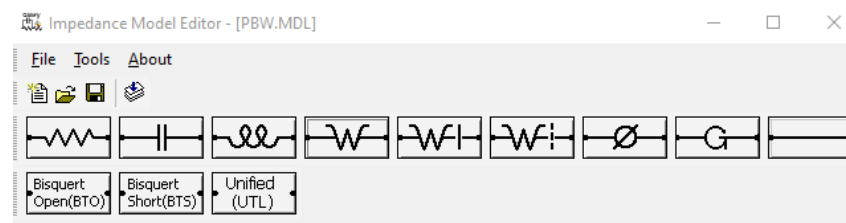
Conditioning Off Time (s) E (V)

Init. Delay On Time (s) Stab. (mV/s)

Estimated Z (ohms)

Optimize for: Fast Normal Low Noise

Analysis: Echem Analyst



Parameter

Parameter Name:

Initial Value: S*s^(1/2)

Lower Limit Test

Enable S*s^(1/2)

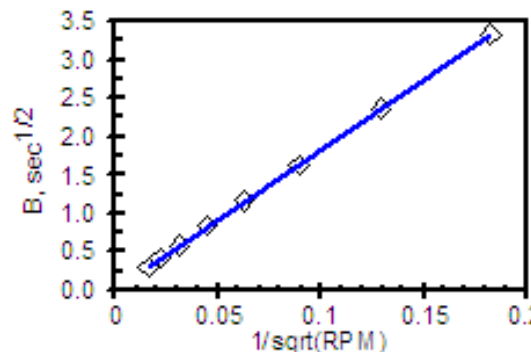
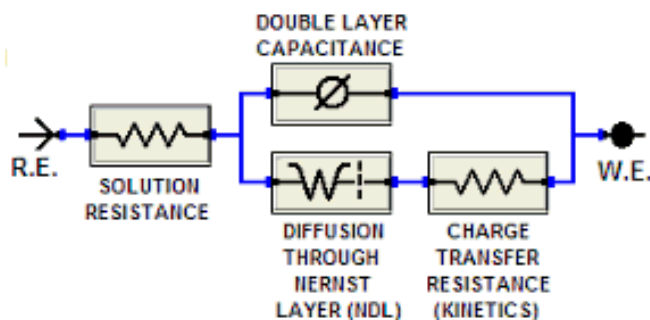
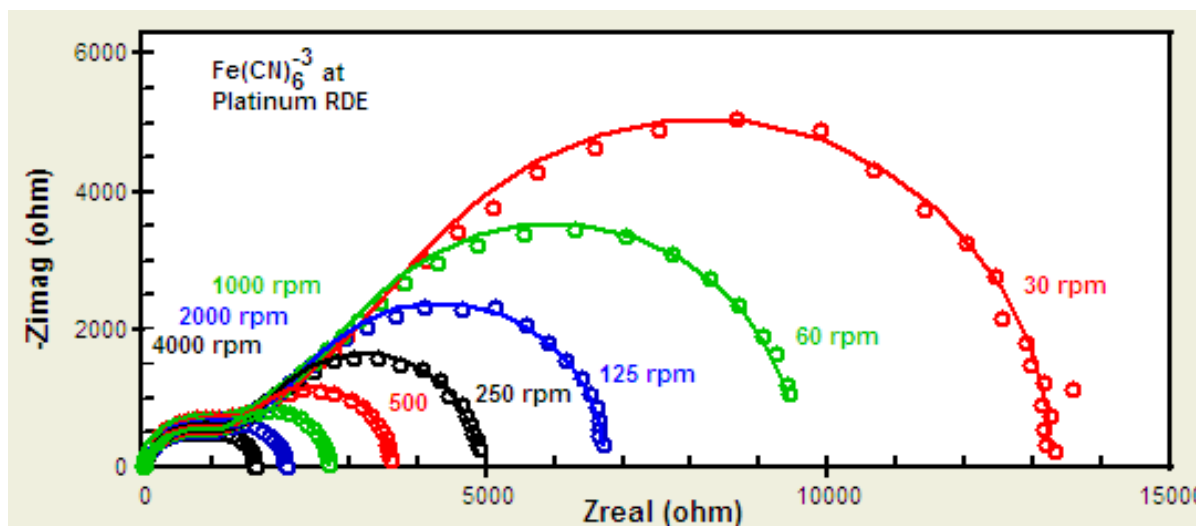
Upper Limit Test

Enable S*s^(1/2)

OK Cancel



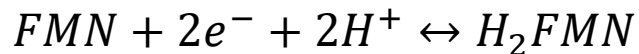
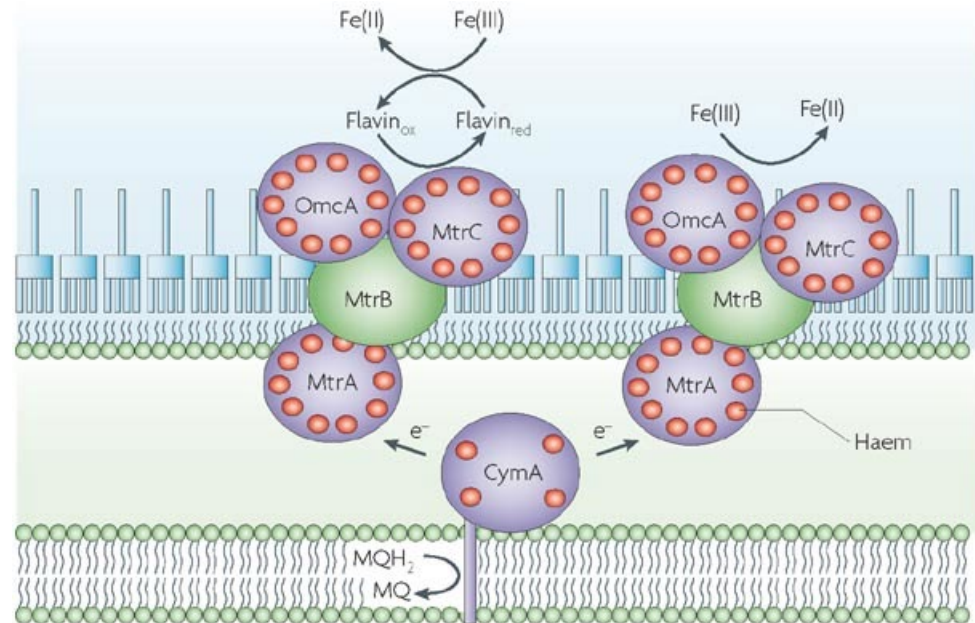
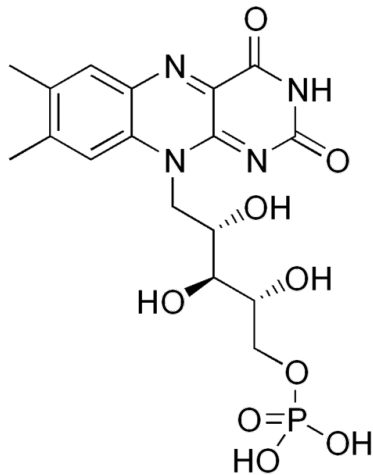
Sequence of EIS experiments at increasing rotation rates



$$B = \delta / \sqrt{D} = 1.61 \cdot r^{-1/2} \cdot (\nu / D)^{1/6}$$

Electroactive compounds in biofilms

FMN



$$E^{\circ} = -411 \text{ mV}_{\text{Ag/AgCl}}$$

Considerations before EIS-RDE experiments

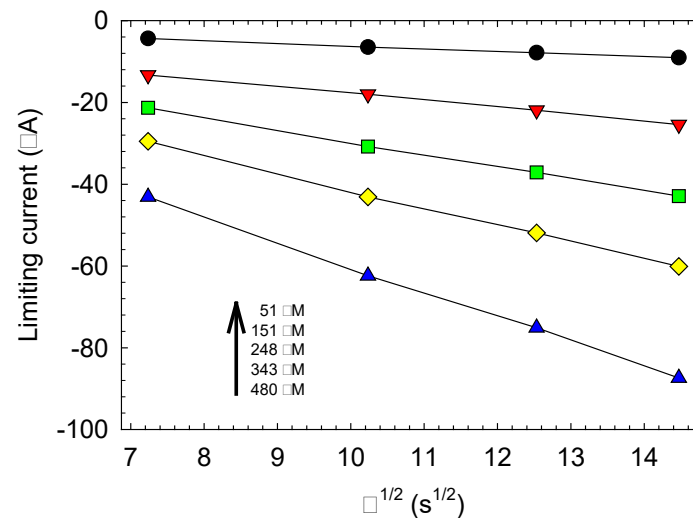
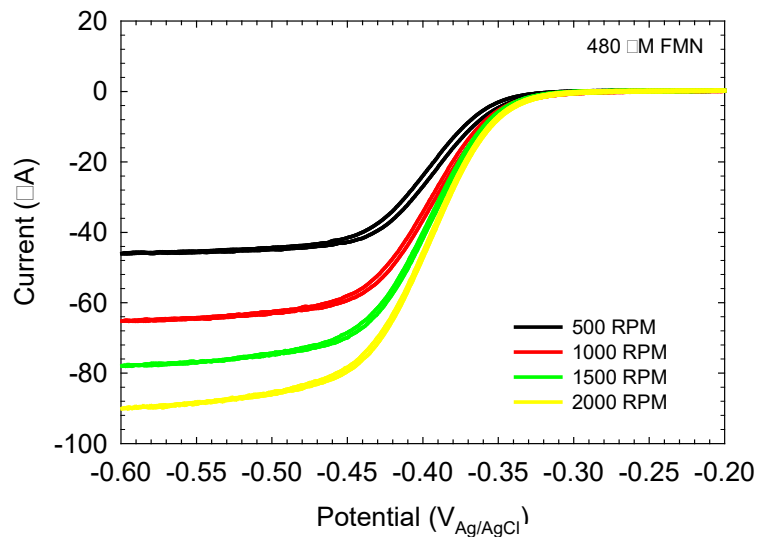
- Run CVs first at varying rotation rates and bulk concentrations
- Based off CVs, select a suitable DC voltage based such as:
 - The percentage of limiting current¹
 - $E_{1/2}$ where current is half the limiting current value
 - An operating voltage you'd like to mimic
 - Open circuit potential
- AC voltage should be small enough to maintain linearity at the chosen DC voltage
- 100 kHz to 100 mHz is generally a good starting frequency range

¹Impedance of a rotating disc electrode with a reversible reaction, M Boillot, S Didierjean, F Lapicque, J. Appl. Electrochem., 34 (2004) 1191-1197.

Selecting initial CV parameters

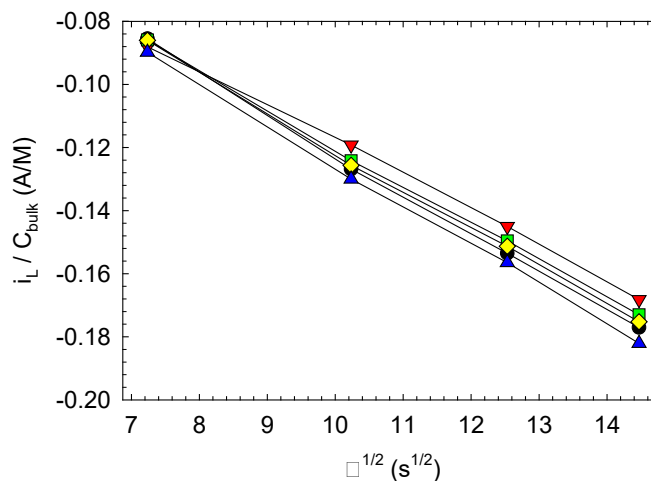
- Voltage window:
 - within a known working region
 - Starts in a region without faradaic current
 - Stops at the working region limit or when limiting current is observed
- Scan rate:
 - 100 mV/s initially, slower if hysteresis is visible
- Cycle #:
 - Usually two cycles to ensure stability
- Rotation rate:
 - Low to high, dictated by RPM rating of the RDE
 - Look for stubborn bubbles trapped on the electrode surface

Levich behavior in practice



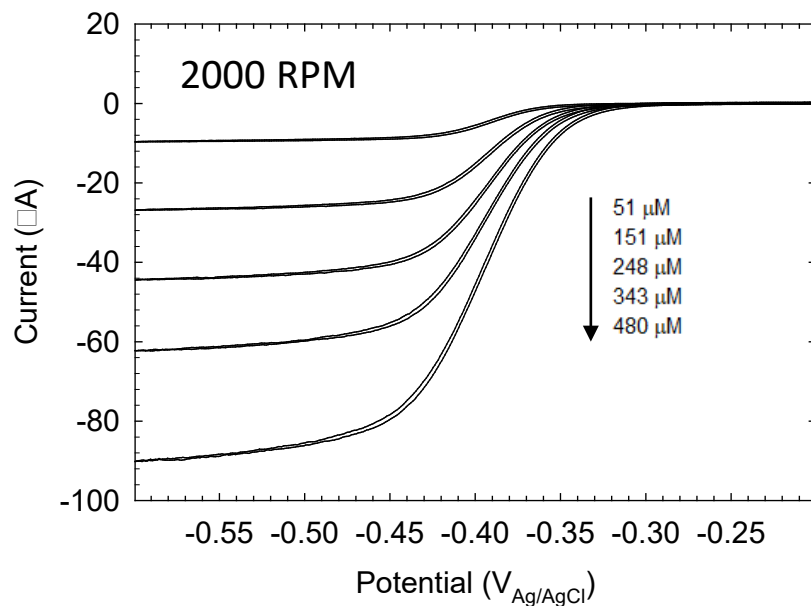
Levich equation

$$i = 0.620 \cdot n F A D^{2/3} \omega^{1/2} \nu^{-1/6} C$$

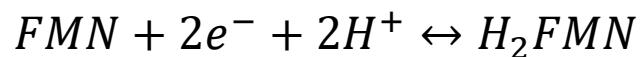
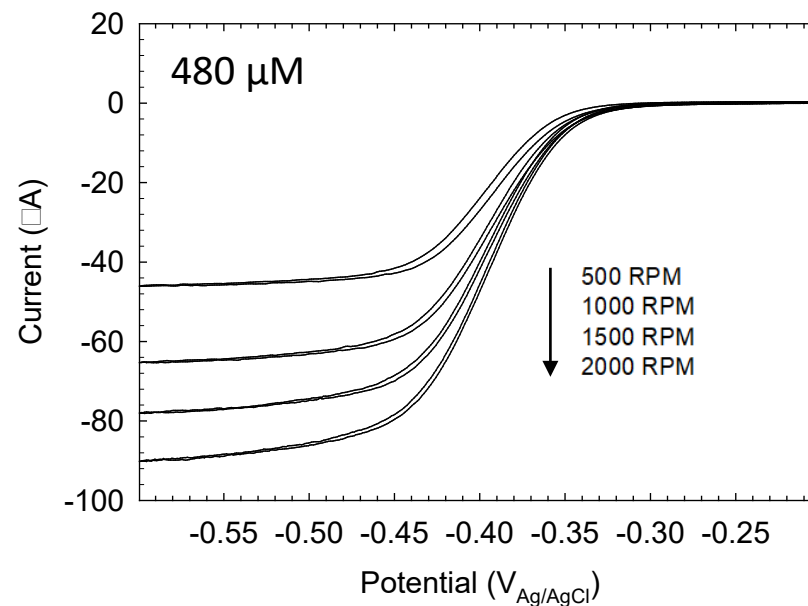


FMN reduction at a glassy carbon RDE

Increasing bulk concentration



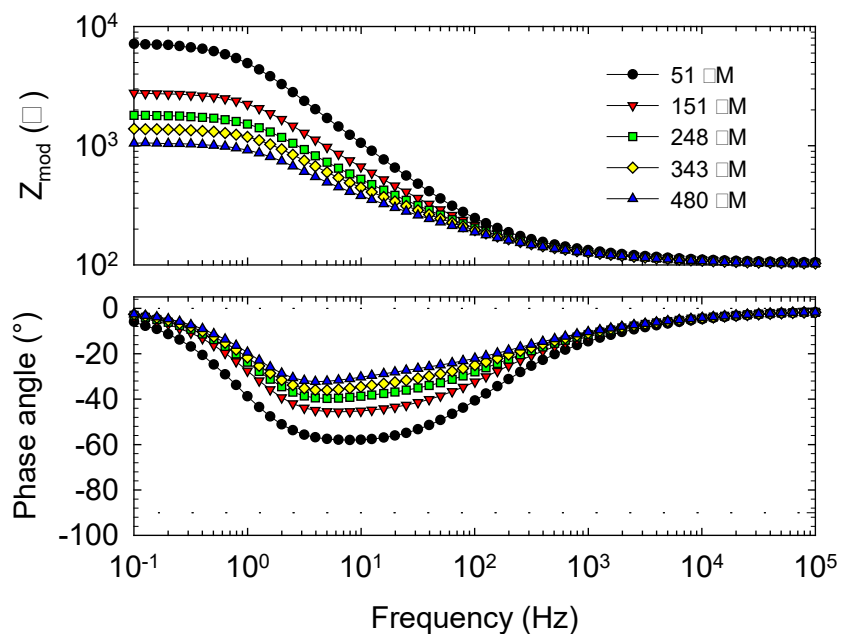
Increasing rotation rate



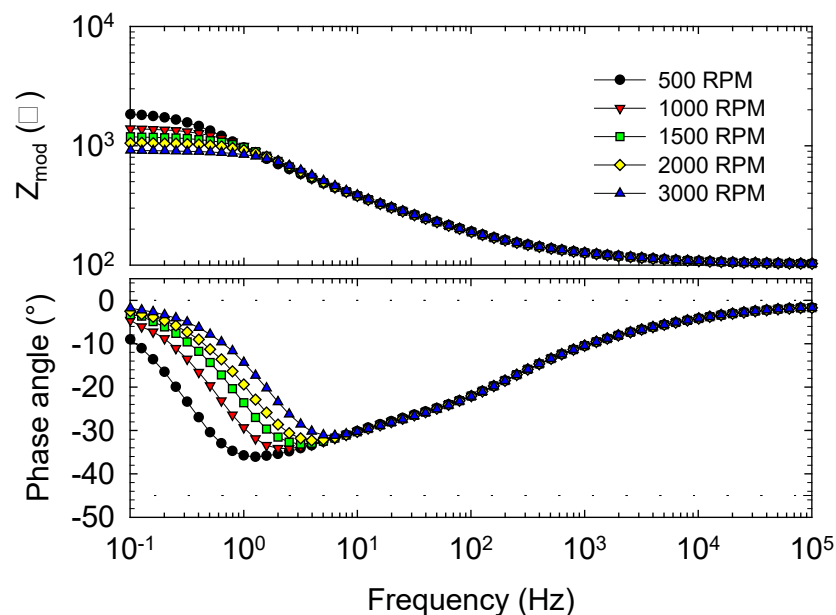
$$E^{\circ'} = -411 \text{ mV}_{\text{Ag/AgCl}}$$

FMN reduction at a glassy carbon RDE

Increasing bulk concentration

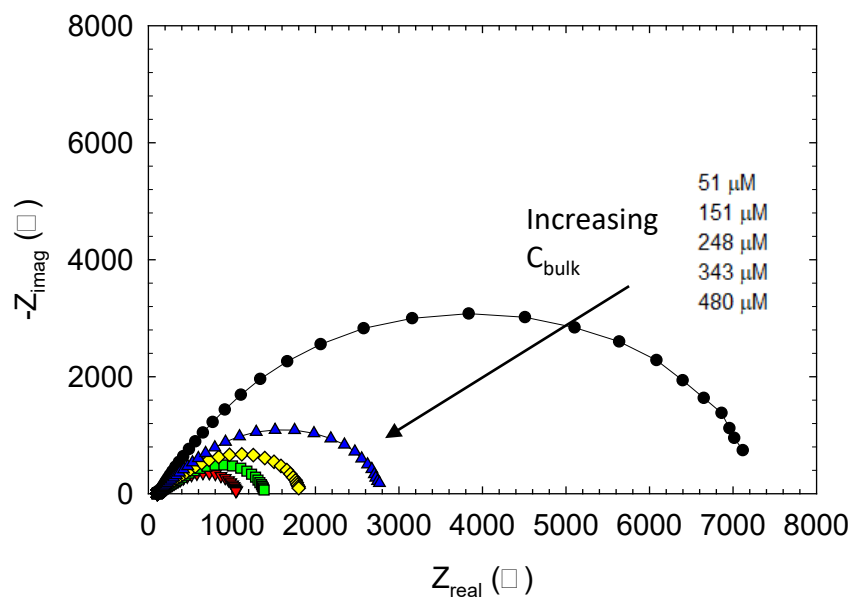


Increasing rotation rate

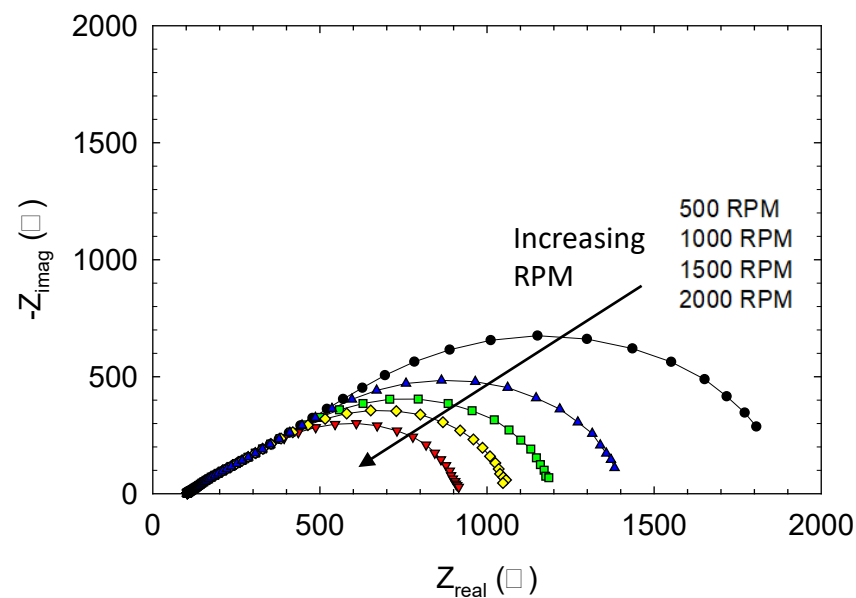


FMN reduction at a glassy carbon RDE

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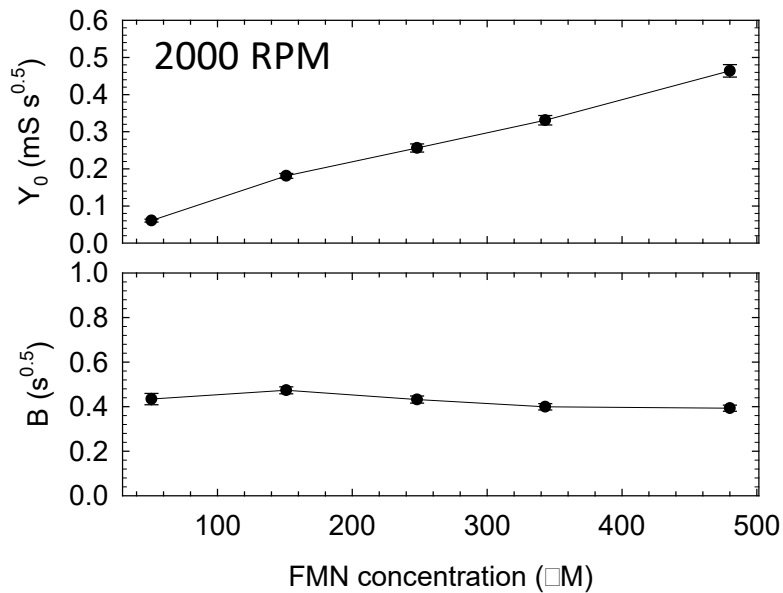


Increasing rotation rate

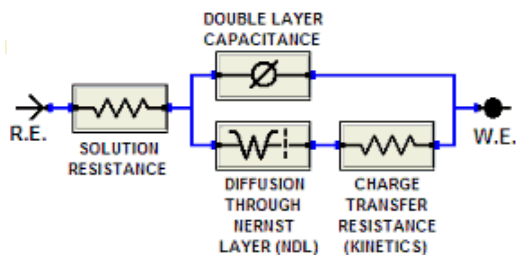
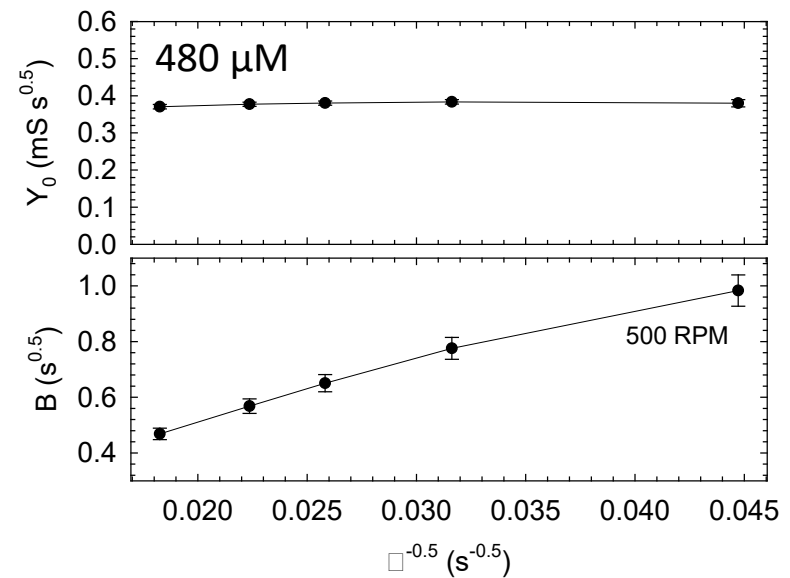


FMN reduction at a glassy carbon RDE

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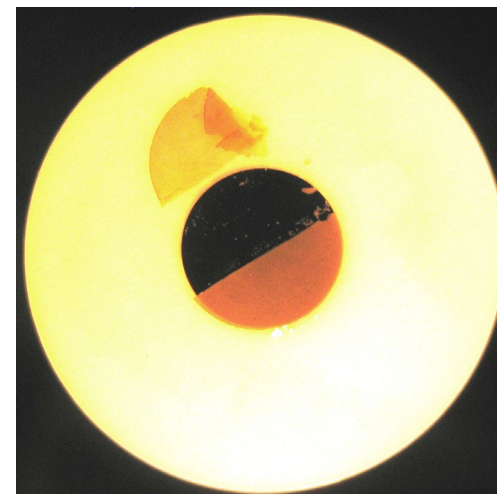
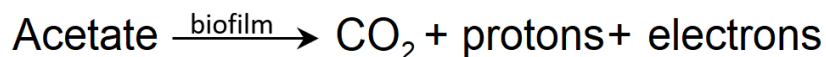
$$Z = \left[(1/Y_0) / \sqrt{j\omega} \right] \tanh \left\{ B \sqrt{j\omega} \right\}$$

$$B = \delta / \sqrt{D} = 1.61 \cdot r^{-1/2} \cdot (\nu / D)^{1/6}$$

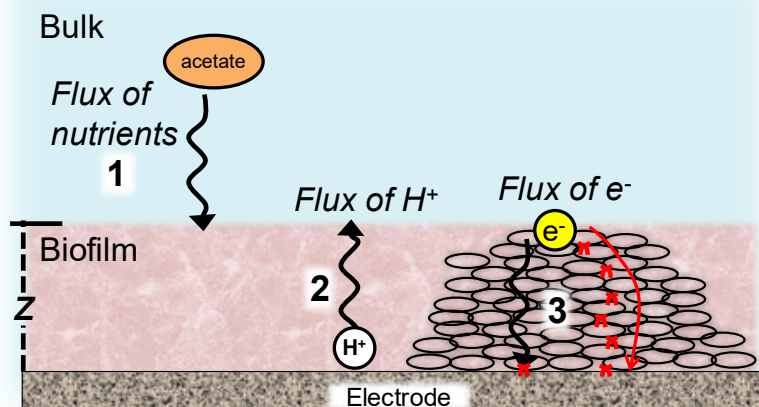
$$Y_0 = \frac{n^2 F^2 A}{RT \left(\frac{1}{C_0 D_0^{1/2}} + \frac{1}{C_R D_R^{1/2}} \right)}$$

Geobacter sulfurreducens biofilm on electrodes

- *G. sulfurreducens*, an oxygen-intolerant species of bacteria able to grow as biofilms on electrodes¹.
- Biofilm metabolizes acetate (a source of organic carbon).



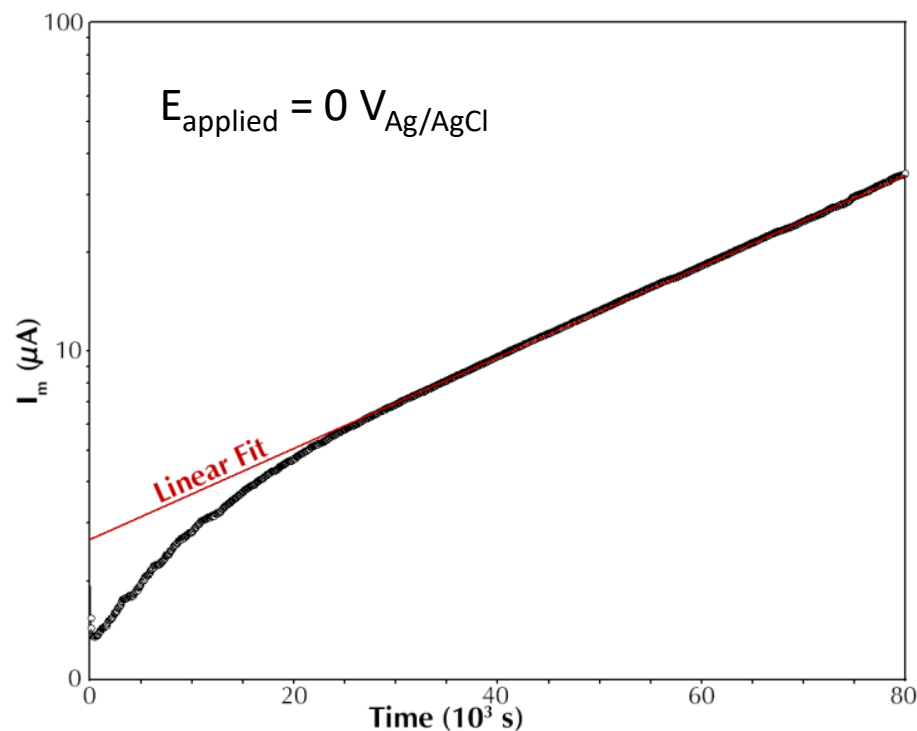
Photograph of biofilm grown on a glassy carbon rotating disk electrode



¹Bond, D.R. and Lovley, D.R., *Appl. Environ. Microb.* 2003, **69**(3), 1548–1555.

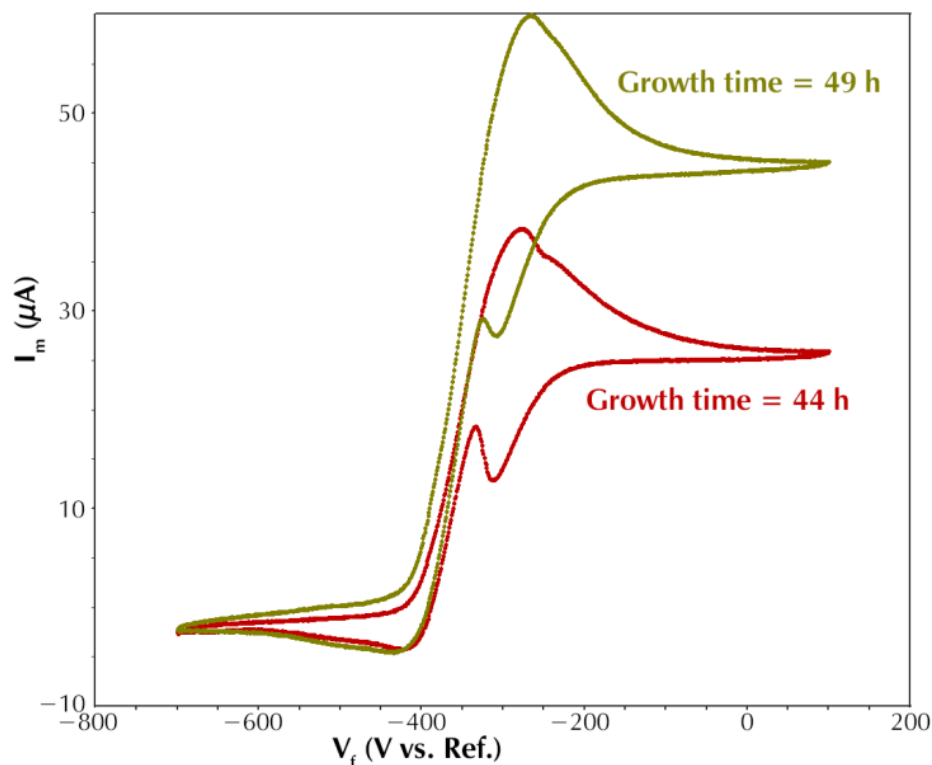
Current is a proxy for biofilm respiration rate

- For *G. sulfurreducens* biofilm, the acetate half-reaction is activated above $-0.4 V_{\text{Ag/AgCl}}$.
- The electrode potential needs to be polarized above this to allow biofilm growth.
- *G. sulfurreducens* cells are added.
- Cells that attach to the electrode form the initial biofilm.
- The initial biofilm metabolizes acetate and produces electrons at an increasing rate.



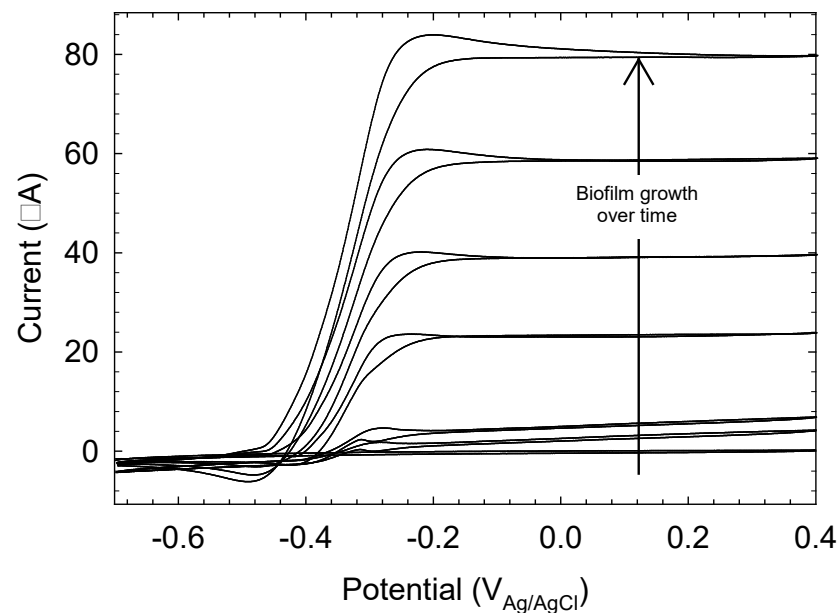
Biofilm CV

- During biofilm growth, the chronoamperometry script can be stopped without damaging the biofilm.
- Run cyclic voltammetry script (scan rate of 30 mV/s)
- A sharp increase in current is observed with several redox peaks superimposed
- Formal potential for acetate oxidation is $-483 \text{ mV}_{\text{Ag/AgCl}}$



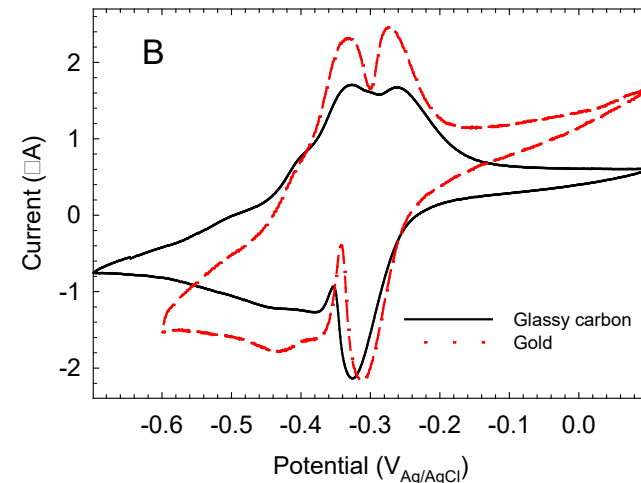
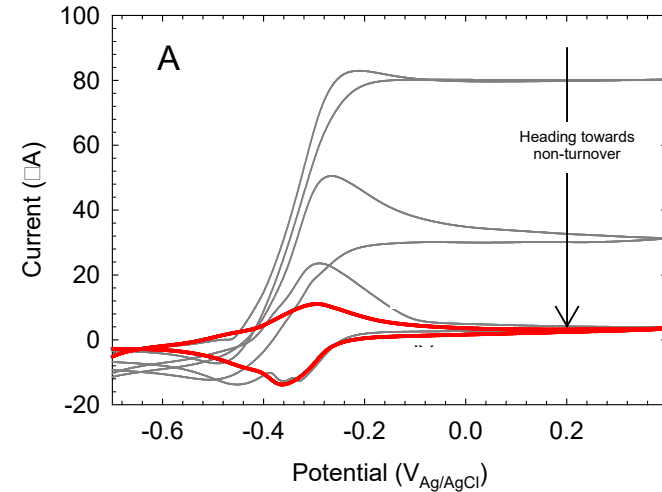
Turnover CV

- ‘Turnover’ refers to microbial turnover of the electron donor (acetate) during CV
- ‘Catalytic current’ refers to measured current caused by renewal of the reduced mediator by microbial turnover
- Turnover CVs have a characteristic sigmoidal voltammogram.



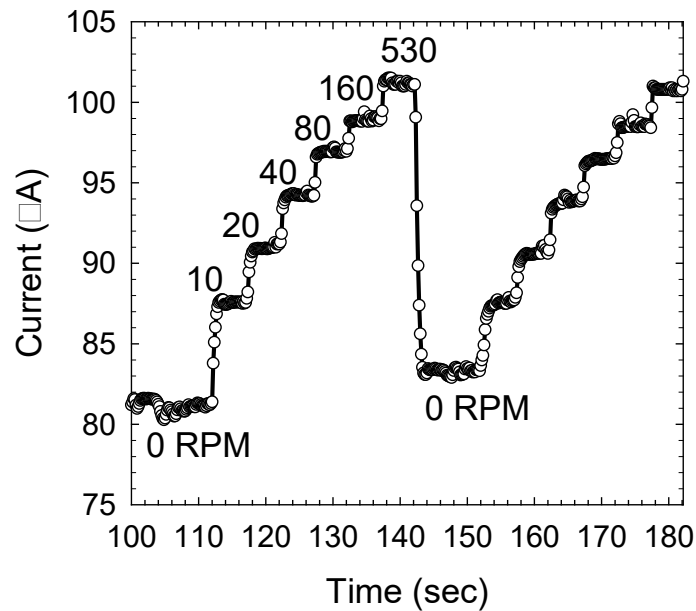
Non-turnover CV

- ‘Non-turnover’ refers to the absence of microbial turnover.
- Usually achieved by removing the electron donor (acetate)
- Also referred to as CV under ‘starving conditions’
- Voltammograms lose the sigmoidal shape
- Redox current peaks appear

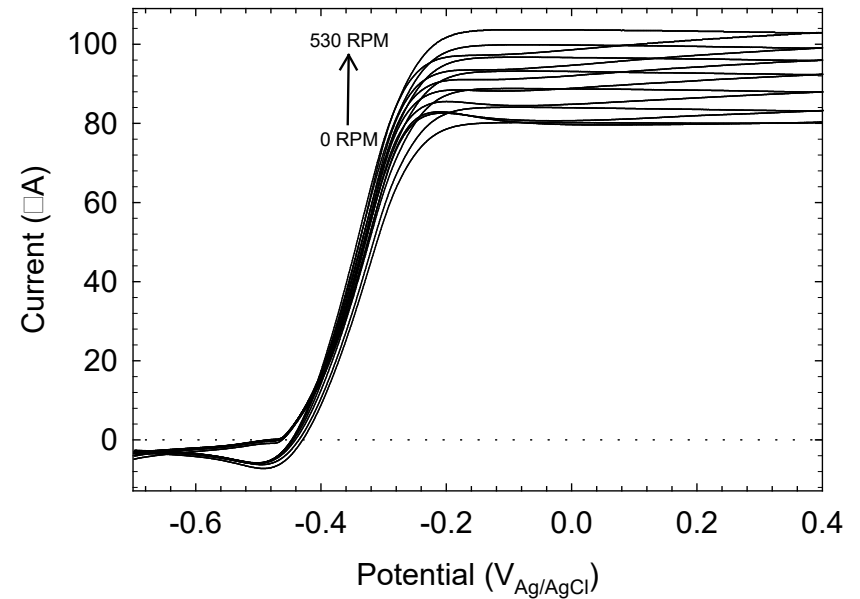


Acetate oxidation by biofilm

Current response to rotation

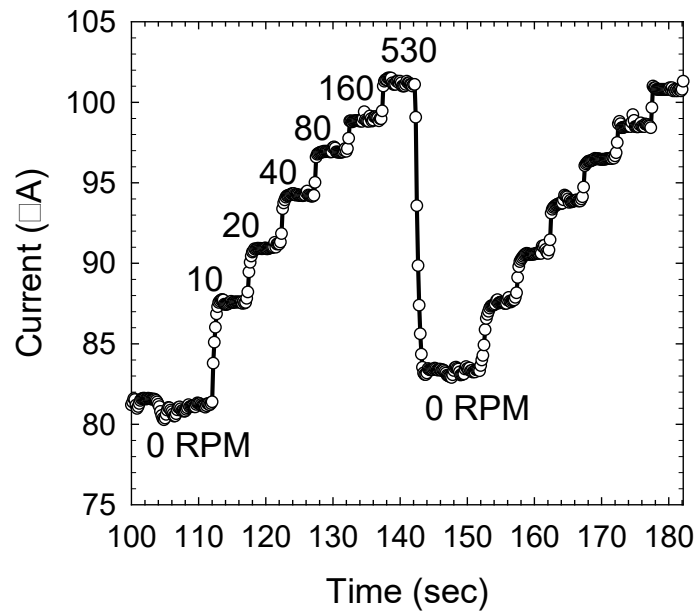


CV response to rotation

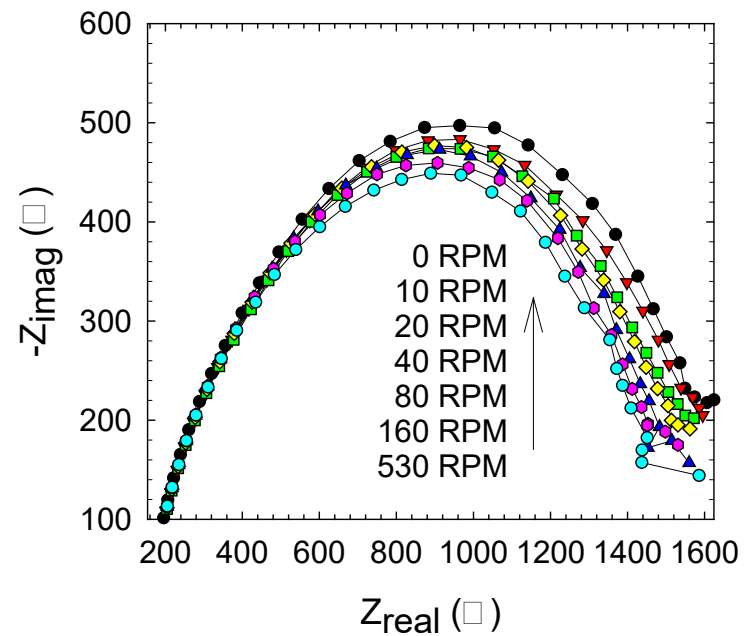


Acetate oxidation by biofilm

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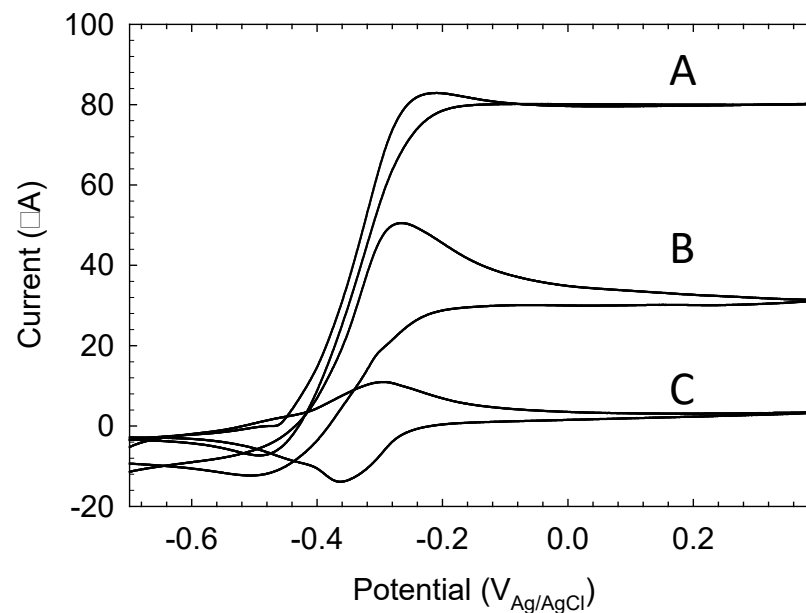


CV response to rotation

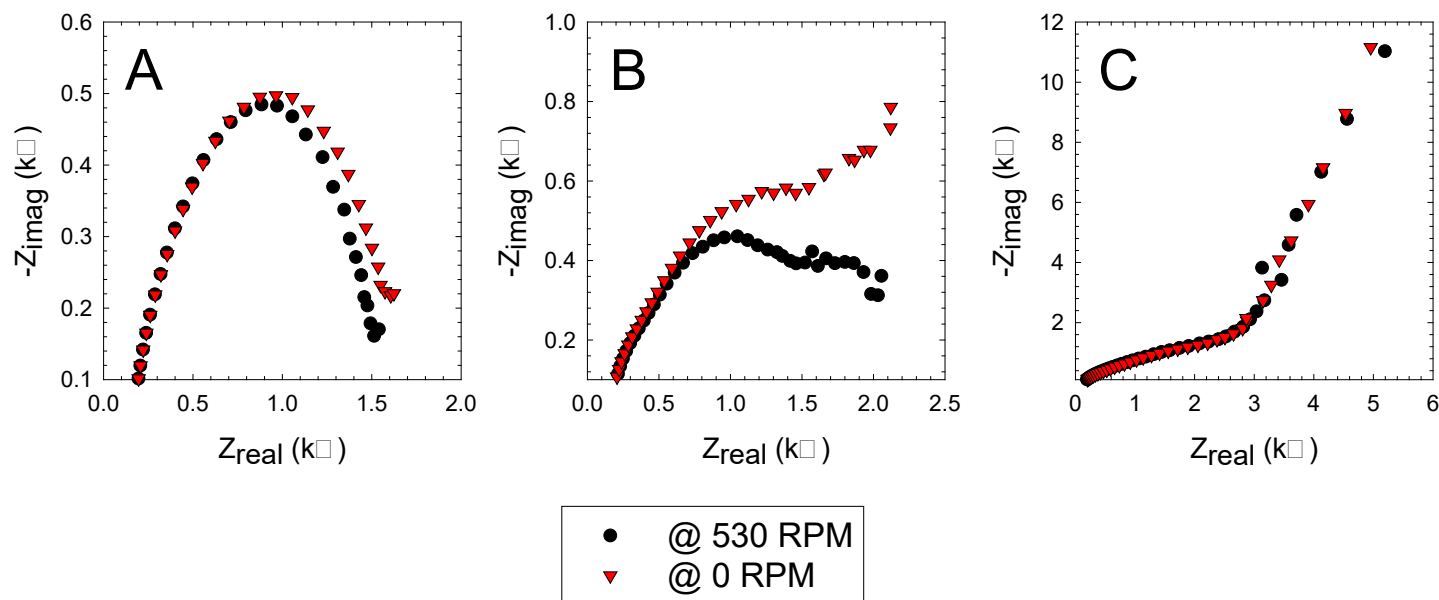


Lower acetate bulk concentration

- Track the biofilm impedance during a transition from turnover to non-turnover conditions
 - A: fully turnover
 - B: partially non-turnover
 - C: completely non-turnover



Rotation independent impedance response



By modulating both rotation rate and bulk acetate concentration, we identified a pseudo-capacitance tied to bound mediators in the biofilm

Summary

- The rotated disk electrode is one more tool in your electrochemical toolbox.
- It is well founded in theory, and can be used for simple voltammetric or potentiodynamic scans, as well as for impedance studies.
- When diffusion is modeled in an EIS experiment, the Porous Bounded Warburg or Nernst circuit element is the proper one to use.
- For simple systems, excellent fits can be obtained over a wide range of rotation rates.
- For complex systems, rotation-(in)dependent behavior can help point you in the right direction.
- Varying the rotation rate can be one way to test the validity of your model!

QUESTIONS?