



**Quinone electrochemistry in acidic and alkaline solutions  
& its application in large scale energy storage**

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Roy G. Gordon<sup>1,2</sup>, Michael J. Aziz<sup>1</sup>**

1) Harvard School of Engineering and Applied Sciences, Cambridge, MA 02138

2) Department of Chemistry and Chemical Biology, Harvard University, Cambridge MA 02138<sub>1</sub>

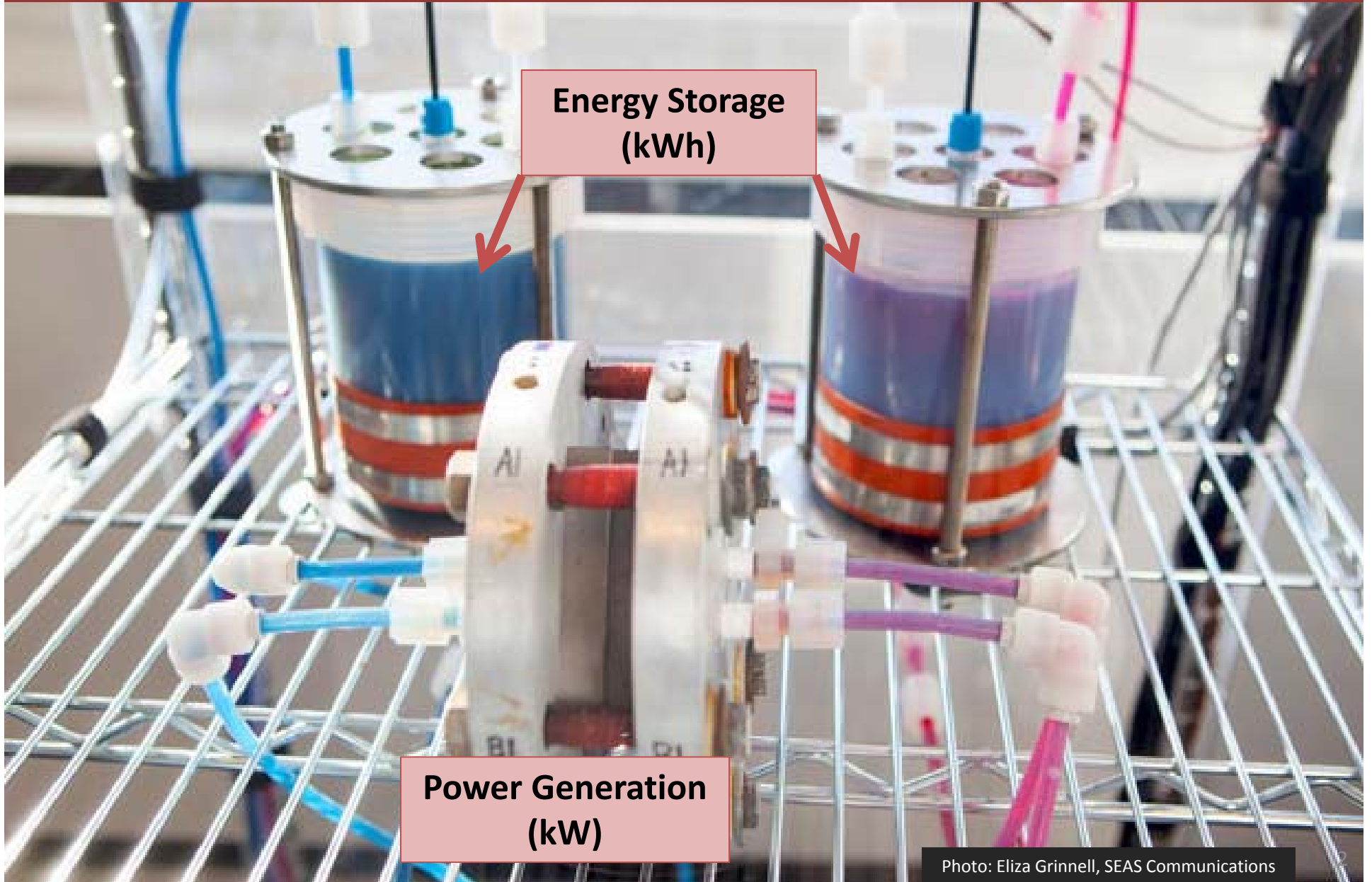
3) Department of Chemistry and Biochemistry, University of Colorado, Boulder CO 80309

# Flow Batteries Store Energy

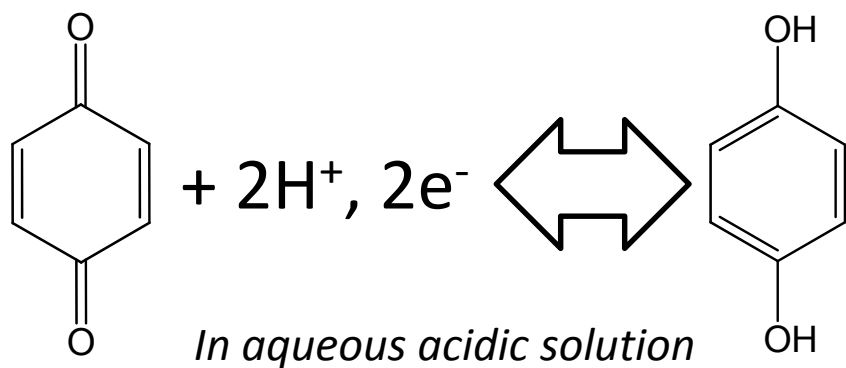
**Energy Storage  
(kWh)**

**Power Generation  
(kW)**

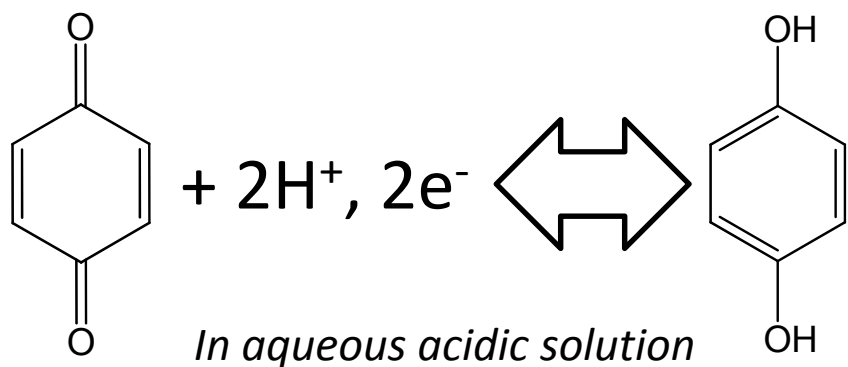
Photo: Eliza Grinnell, SEAS Communications



# Quinones are Cheap, Versatile, & Robust



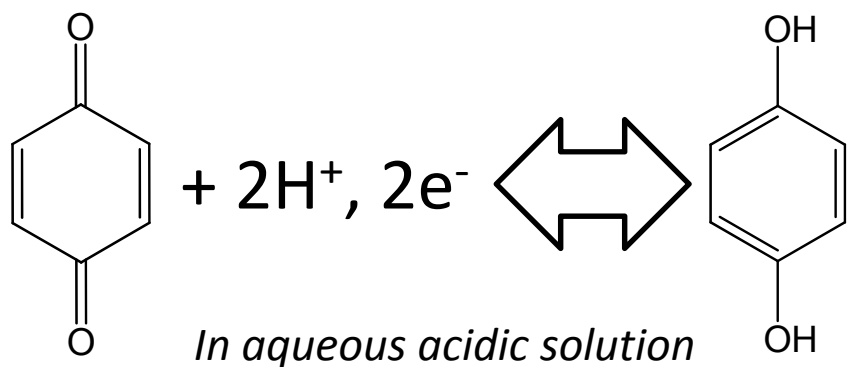
# Quinones are Cheap, Versatile, & Robust



Chemistry	Solution Cost (\$/kWh)
Quinone-Bromide	<\$27
Vanadium Redox	\$50 – \$180

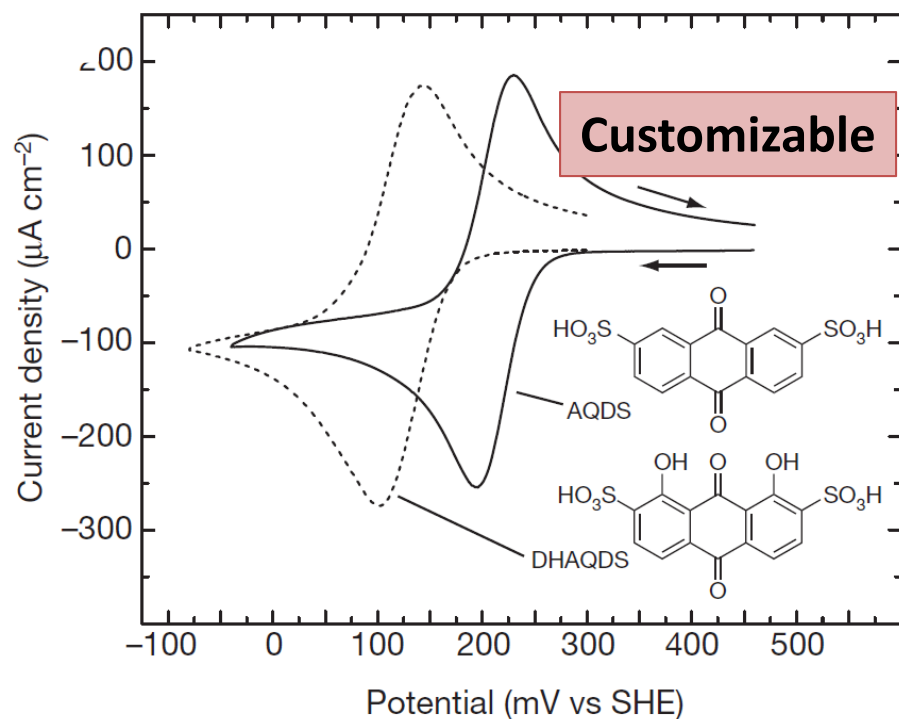
*"I wish I could get that price!"*

# Quinones are Cheap, Versatile, & Robust



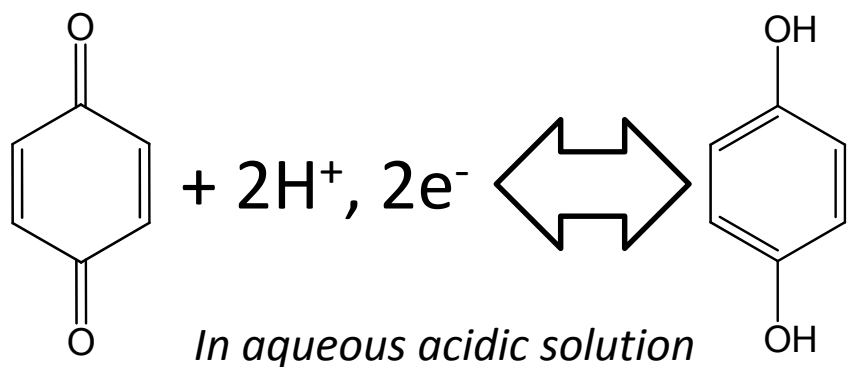
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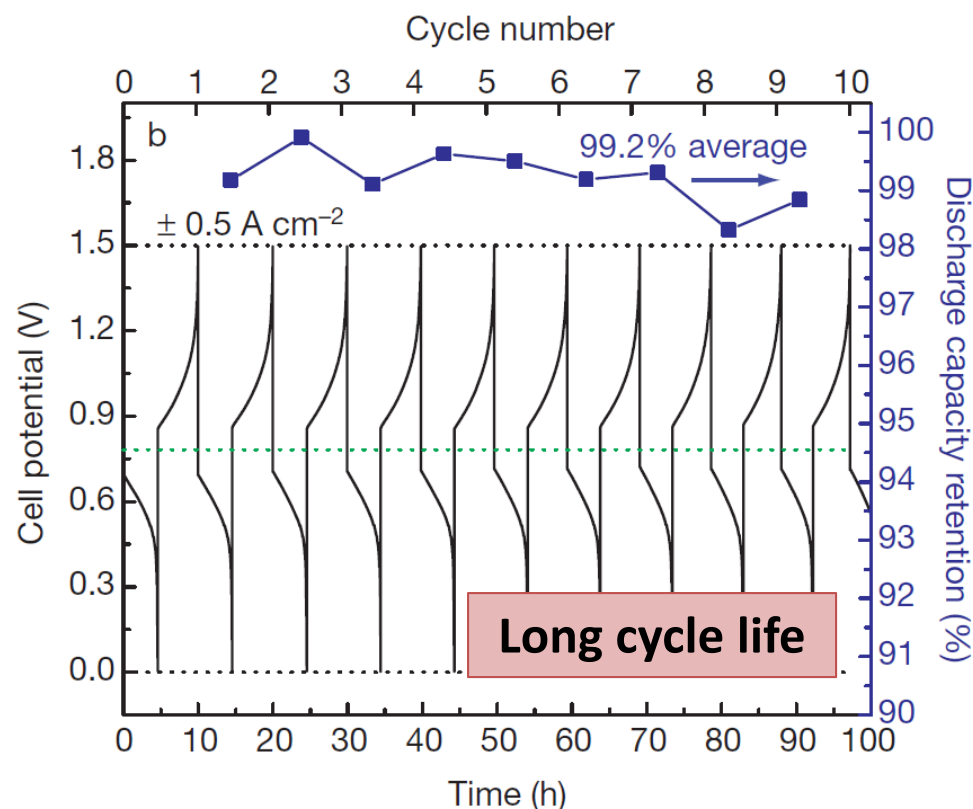
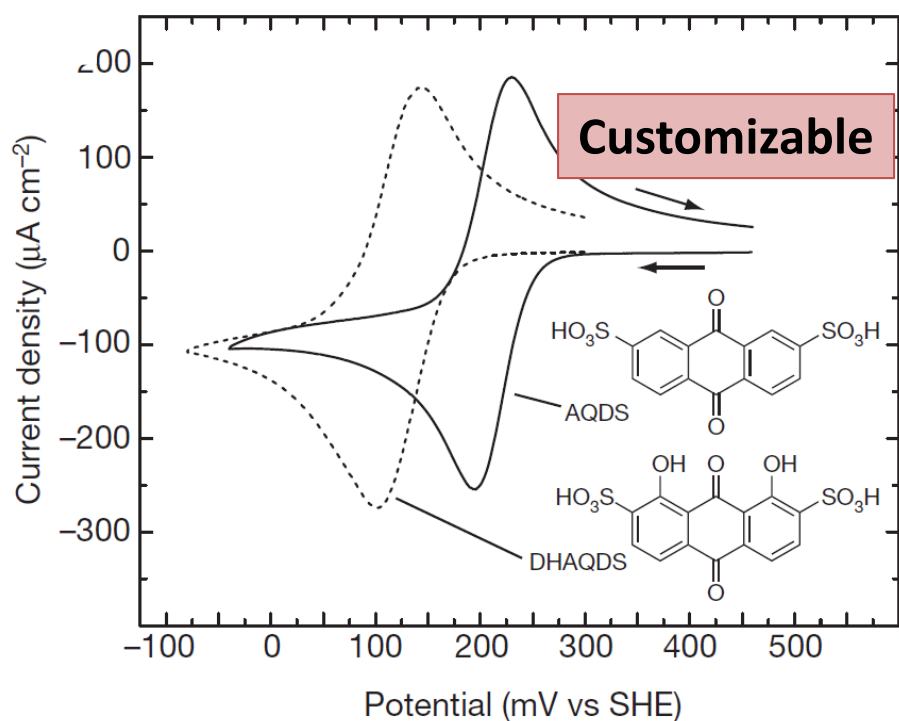
Huskinson, B., Marshak, M. P., Suh, C., Er, S., Gerhardt, M.R., Galvin, C.J., Chen, X., Aspuru-Guzik, A., Gordon, R.G., and Aziz, M.J. (2014). *Nature*, 505(7482), 195–198.

# Quinones are Cheap, Versatile, & Robust



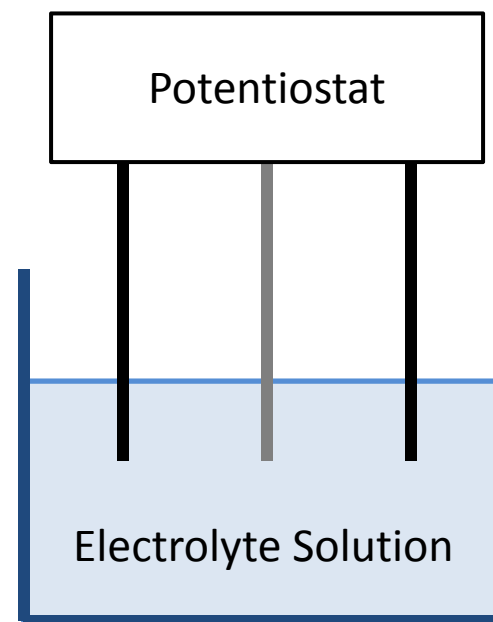
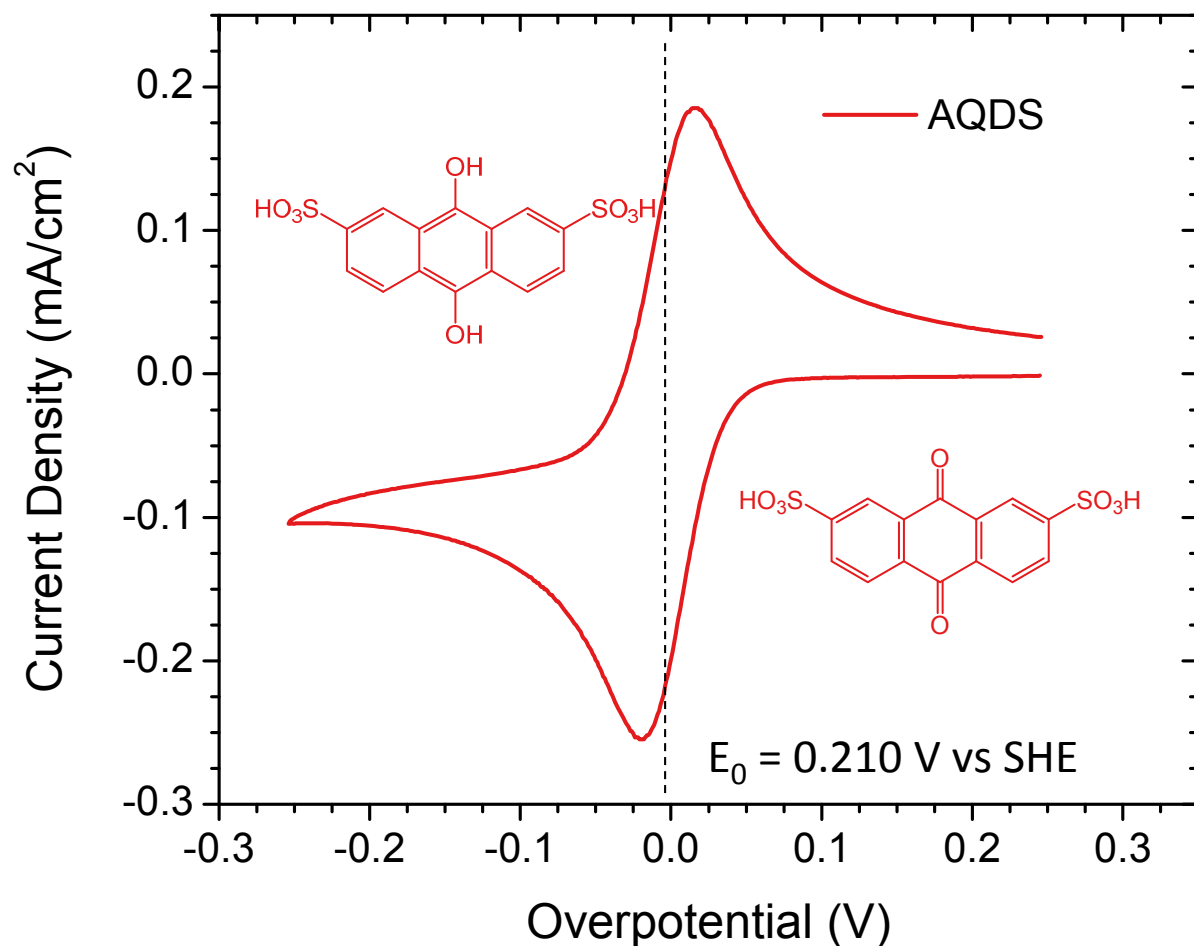
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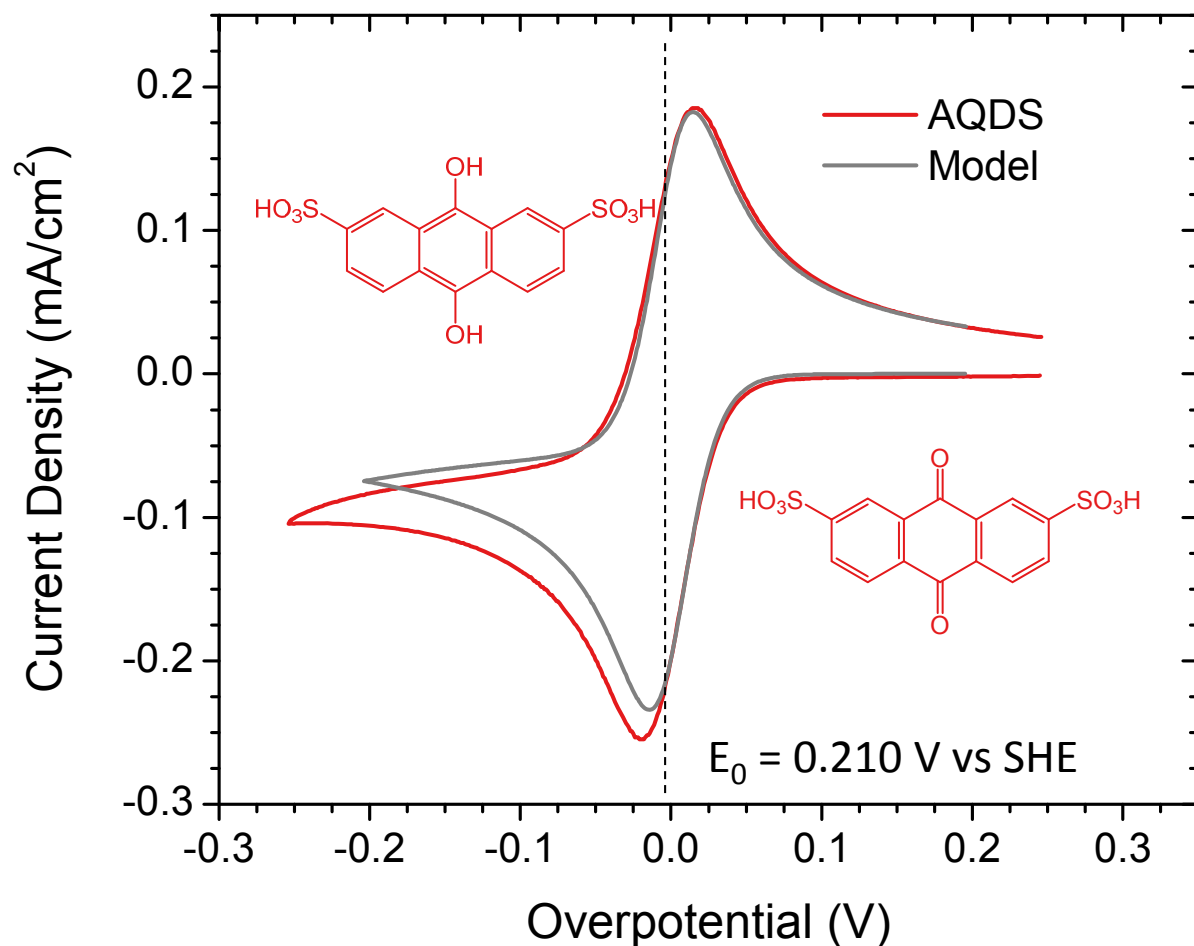
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# AQDS redox is reversible



- [1] K. B. Oldham, J. C. Myland, *Electrochim. Acta.* **56**, 10612–10625 (2011).  
[2] B. Huskinson *et al.*, *Nature.* **505**, 195–198 (2014).

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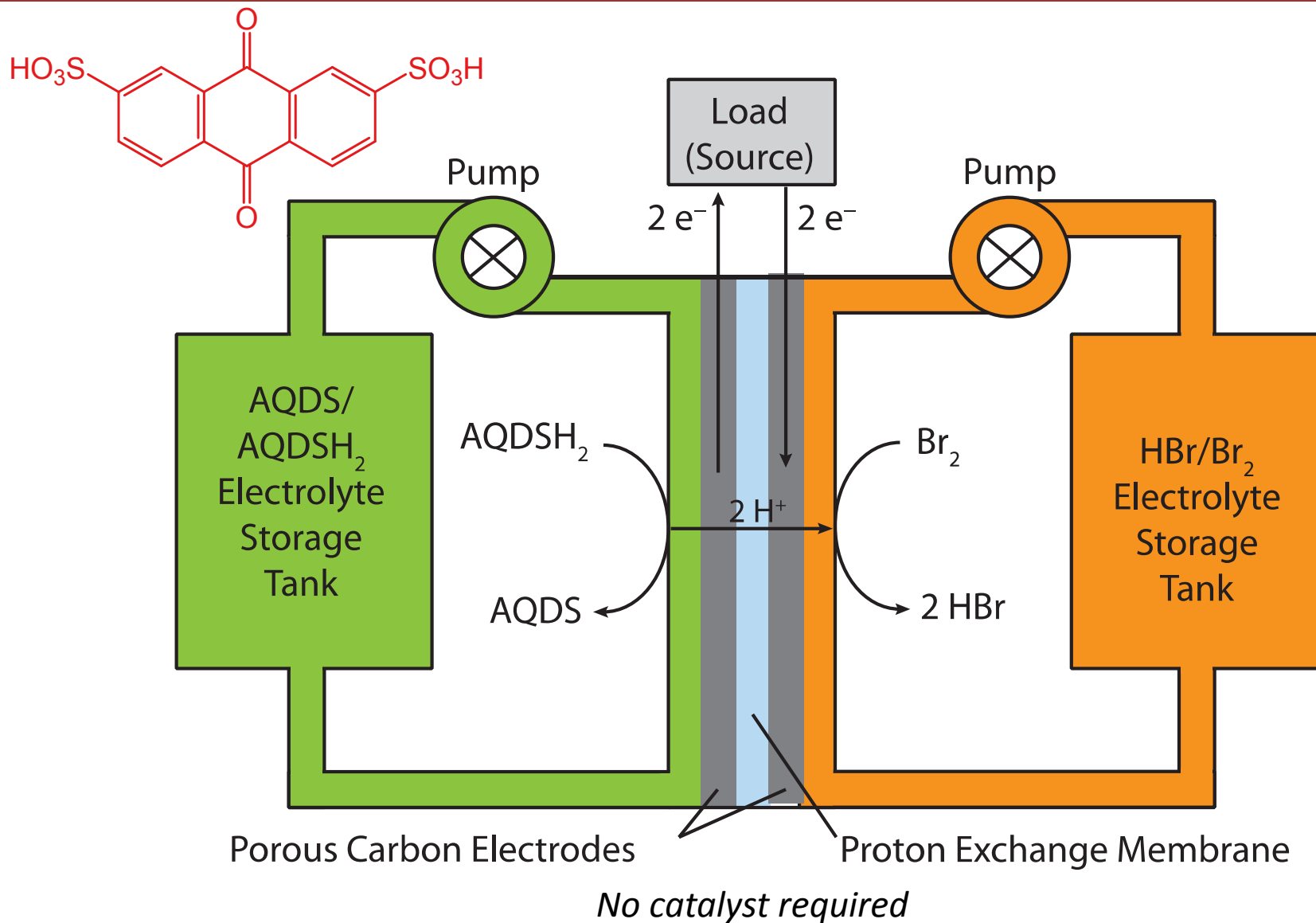
*Reversible* 2-electron model:  
assume AQDS concentration at  
electrode surface is dictated by  
Nernst equation [1]. Reaction  
rate is mass transport limited.

Measured rate constant  
 $k_0 = 7.2 \times 10^{-3}$  cm/s [2]

[1] K. B. Oldham, J. C. Myland, *Electrochim. Acta.* **56**, 10612–10625 (2011).

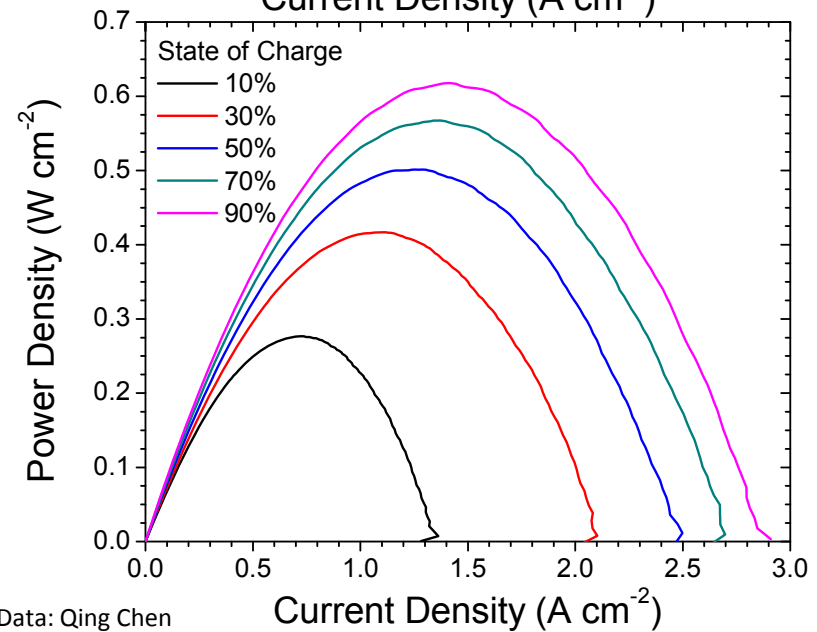
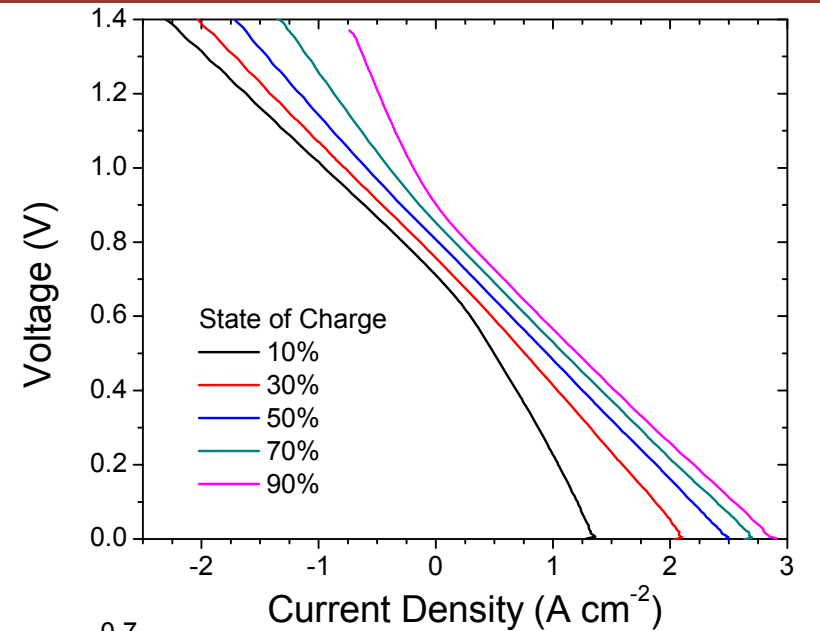
[2] B. Huskinson *et al.*, *Nature.* **505**, 195–198 (2014).

# The Quinone – Bromine Flow Battery



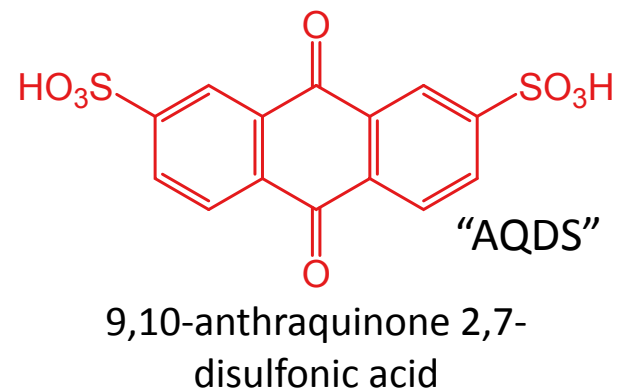
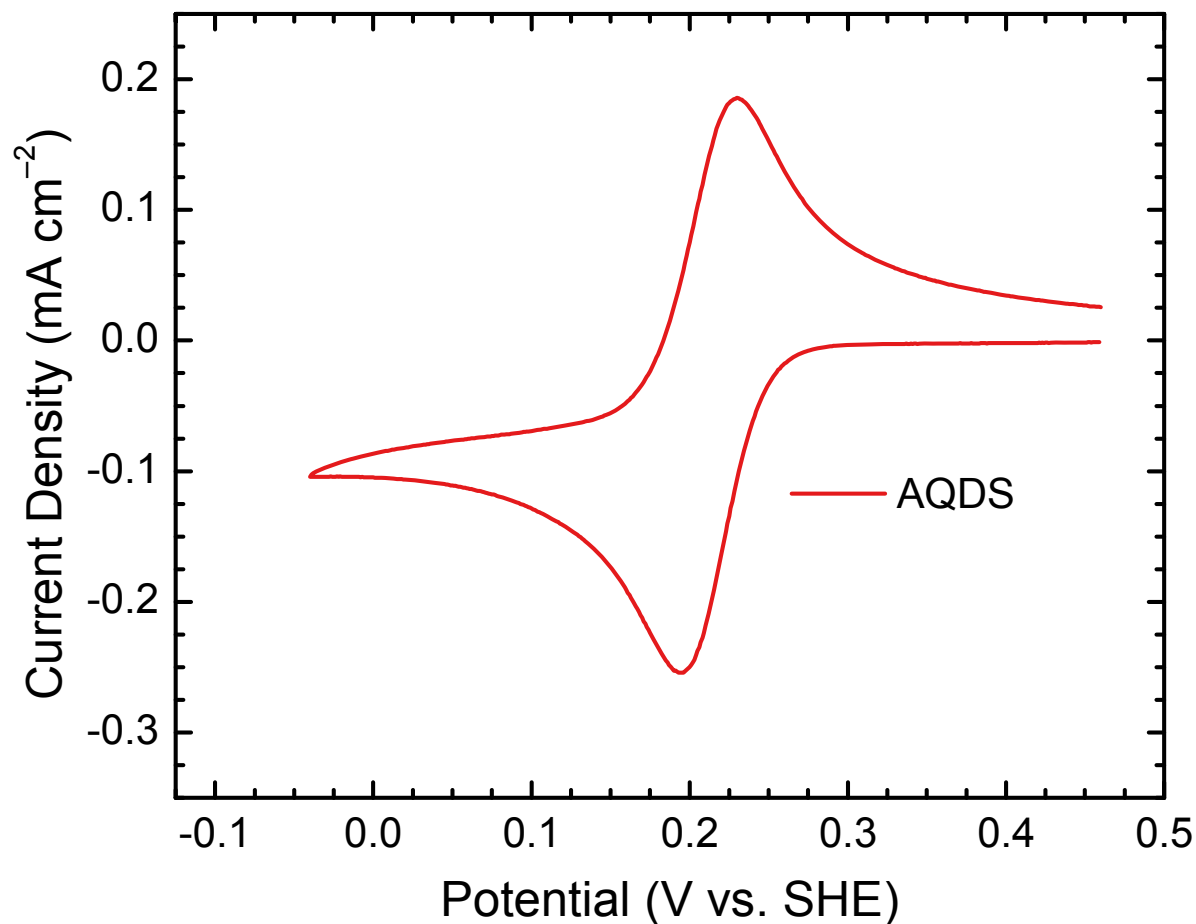
Huskinson, B., Marshak, M. P., et al. (2014). *Nature*, 505(7482), 195–198.

# High Power Operation with AQDS/HBr battery



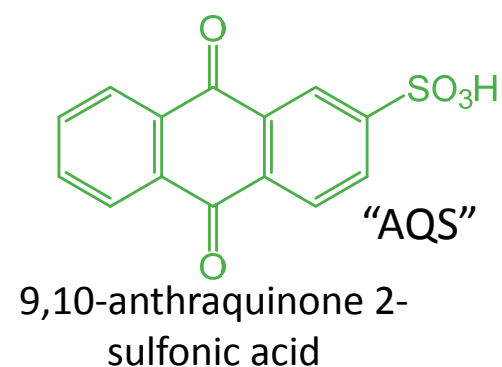
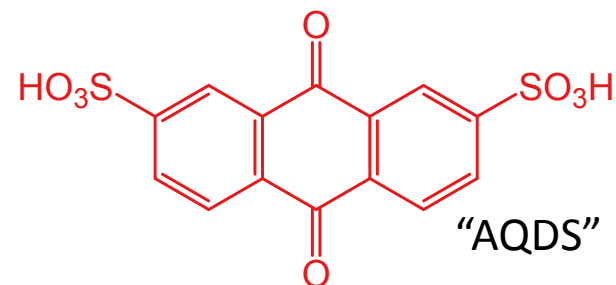
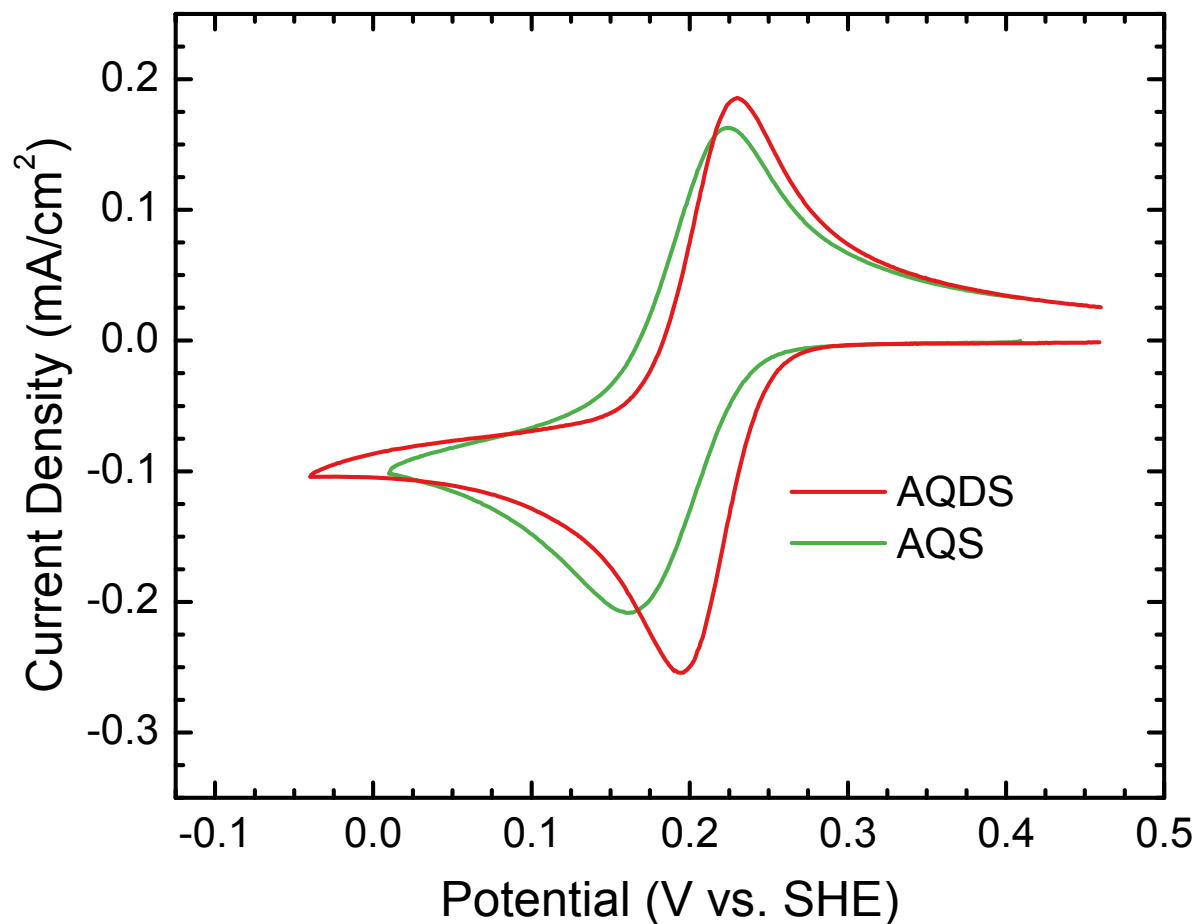
Data: Qing Chen

# Increase Cell Voltage by Tuning Quinone Redox



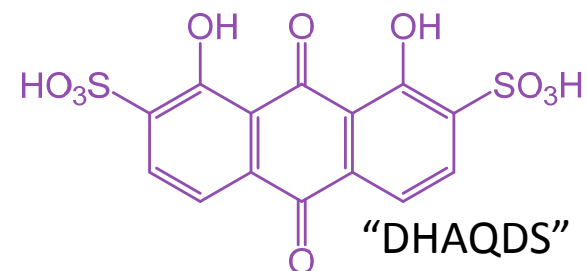
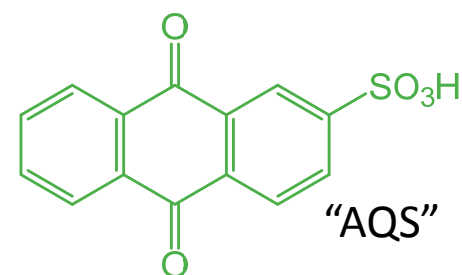
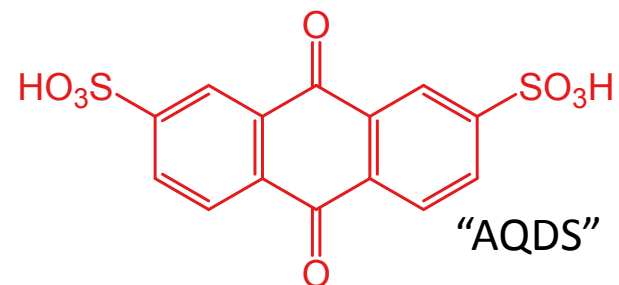
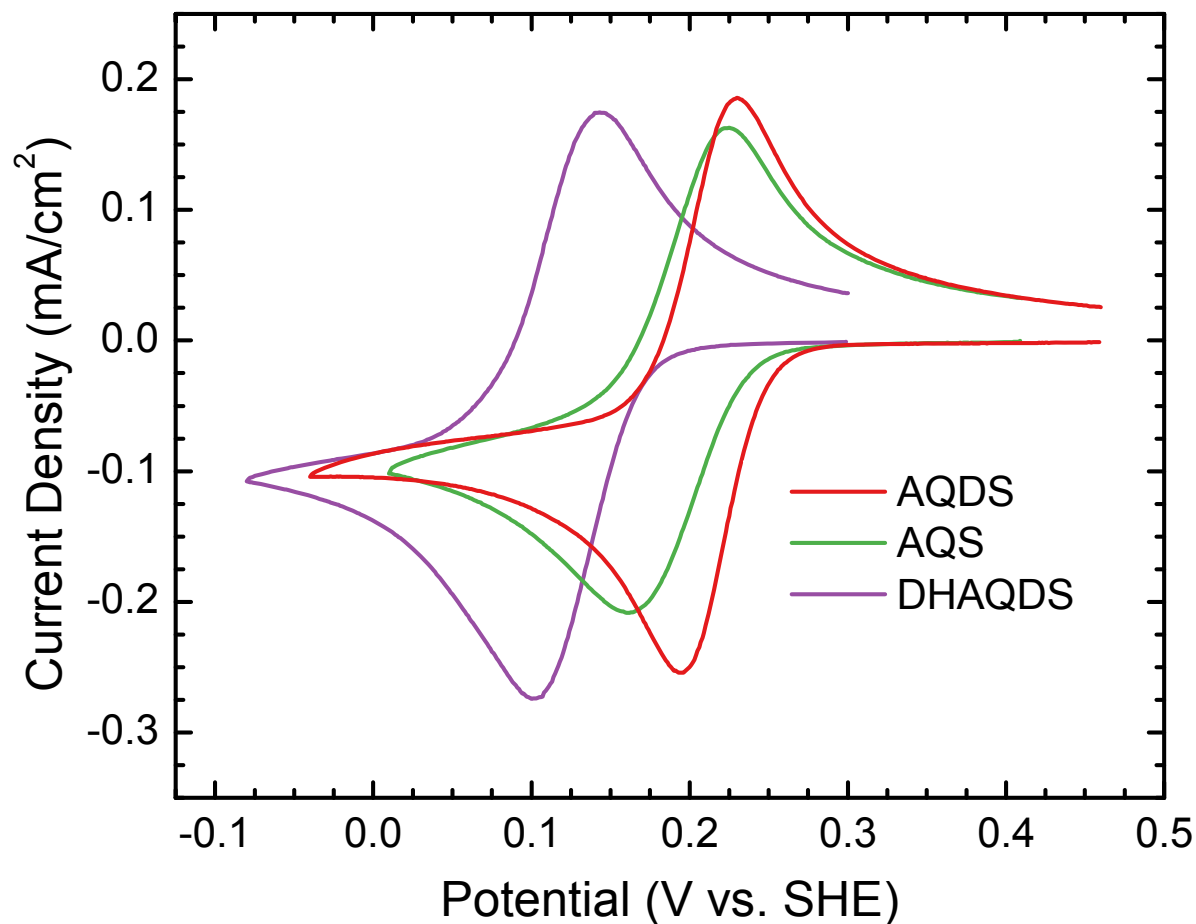
Glassy carbon electrode, 3 mm dia, 25 mV/s scan rate, 25 °C. Ag/AgCl reference.  
Pt coil counter electrode. Supporting electrolyte 1 M H<sub>2</sub>SO<sub>4</sub>  
Quinone concentration 1 mM

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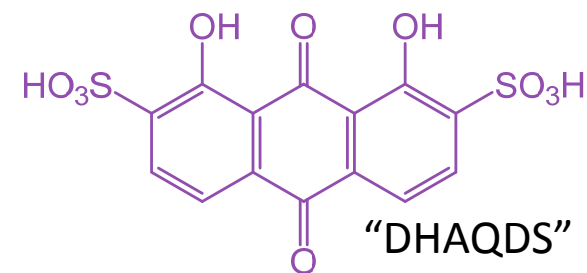
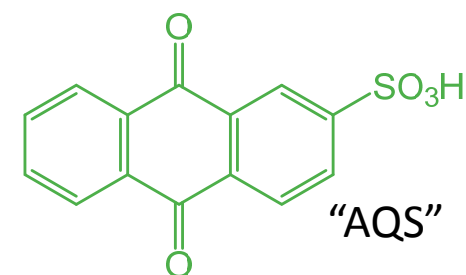
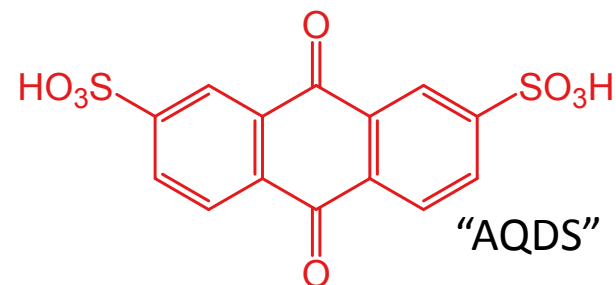
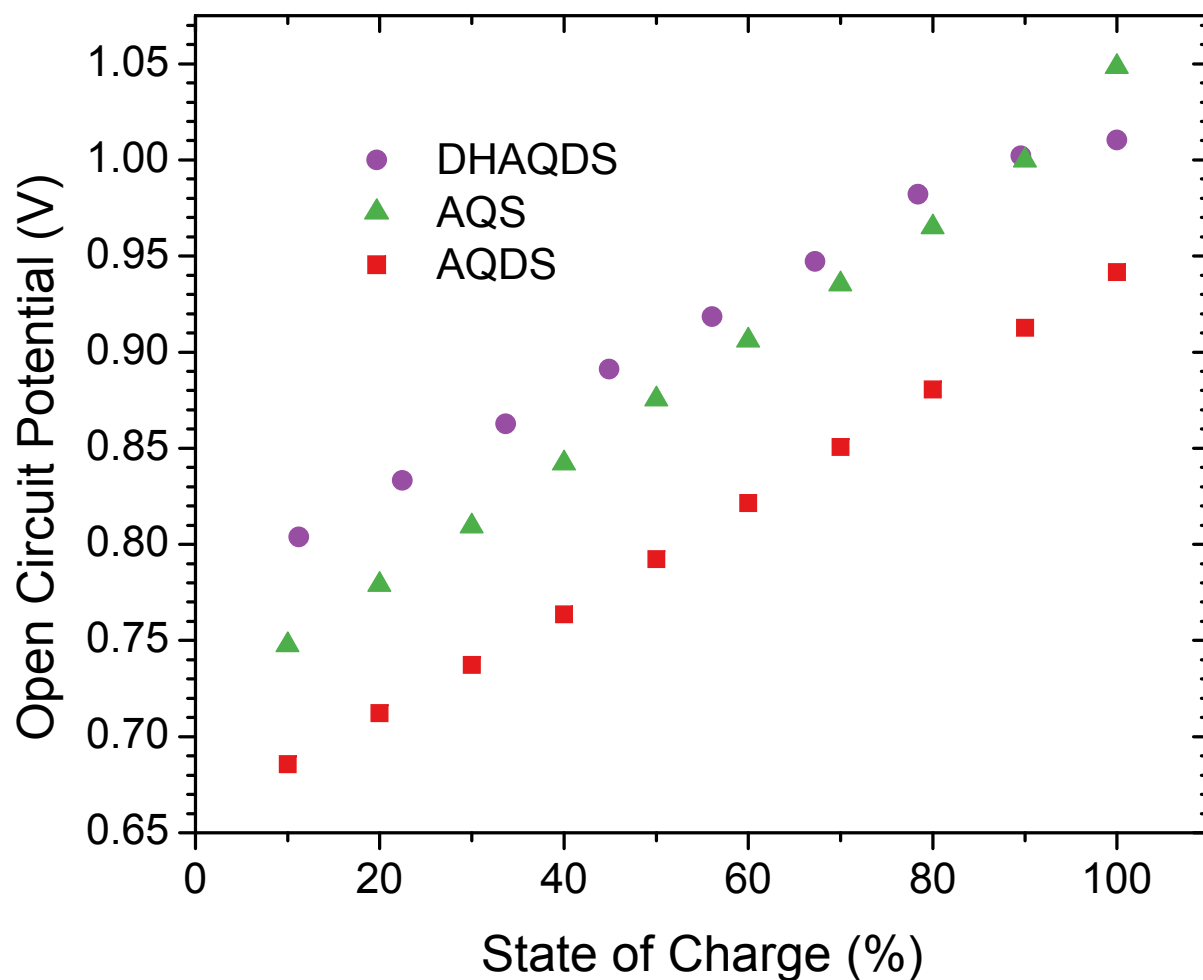
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Glassy carbon electrode, 3 mm dia, 25 mV/s scan rate, 25 °C. Ag/AgCl reference. Pt coil counter electrode. Supporting electrolyte 1 M H<sub>2</sub>SO<sub>4</sub>. Quinone concentration 1 mM

1,8-dihydroxy 9,10-anthraquinone  
2,7-disulfonic acid

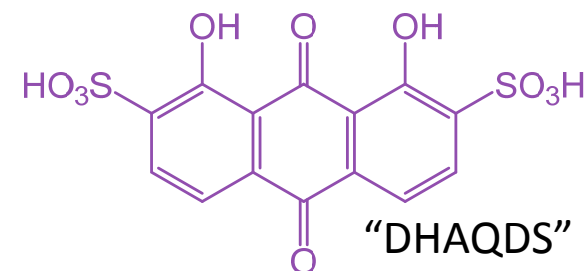
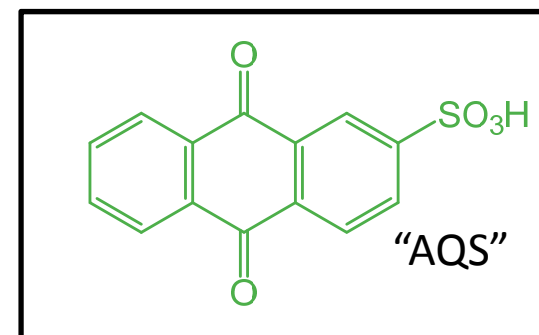
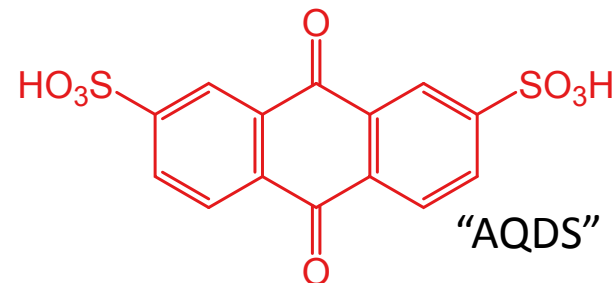
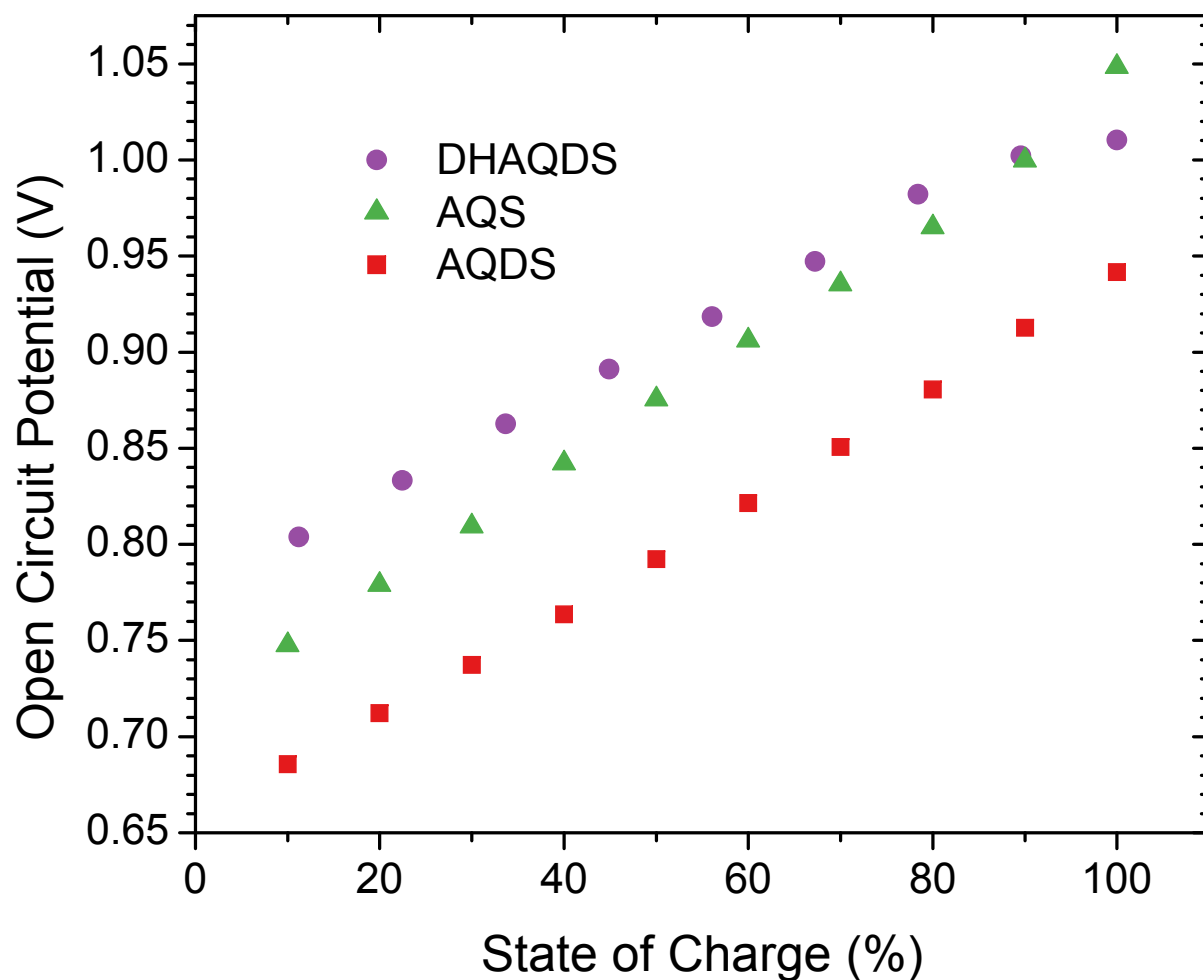
# Increase Cell Voltage by Modifying Molecules



Posolyte: 0.5 M  $\text{Br}_2$ , 3 M HBr

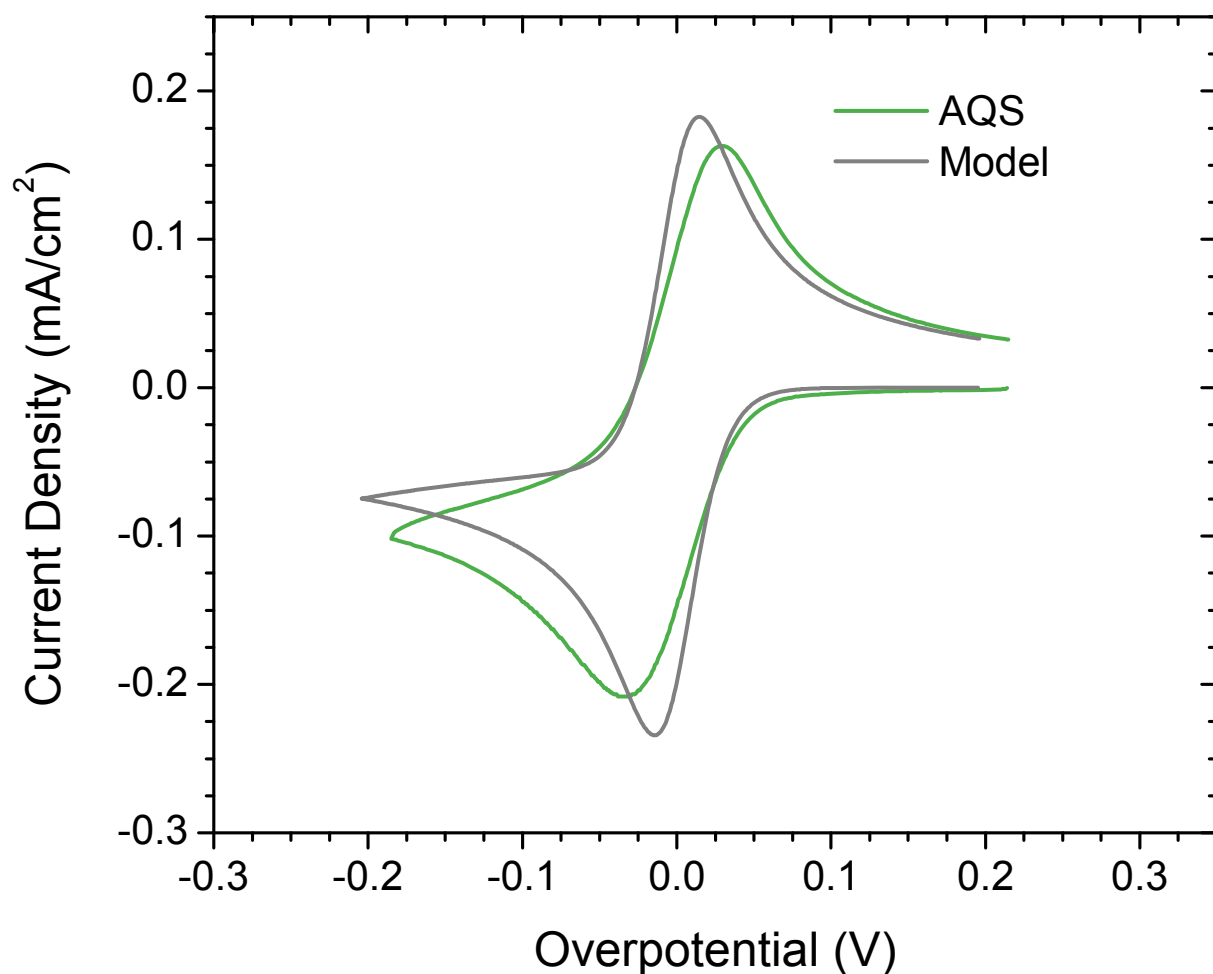
Negolyte: 1 M quinone, 1 to 2 M  $\text{H}_2\text{SO}_4$  (3 M total proton concentration)

# Increase Cell Voltage by Modifying Molecules



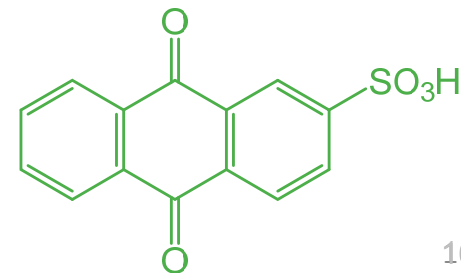
Posolyte: 0.5 M  $\text{Br}_2$ , 3 M HBr  
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# AQS redox is not quite reversible

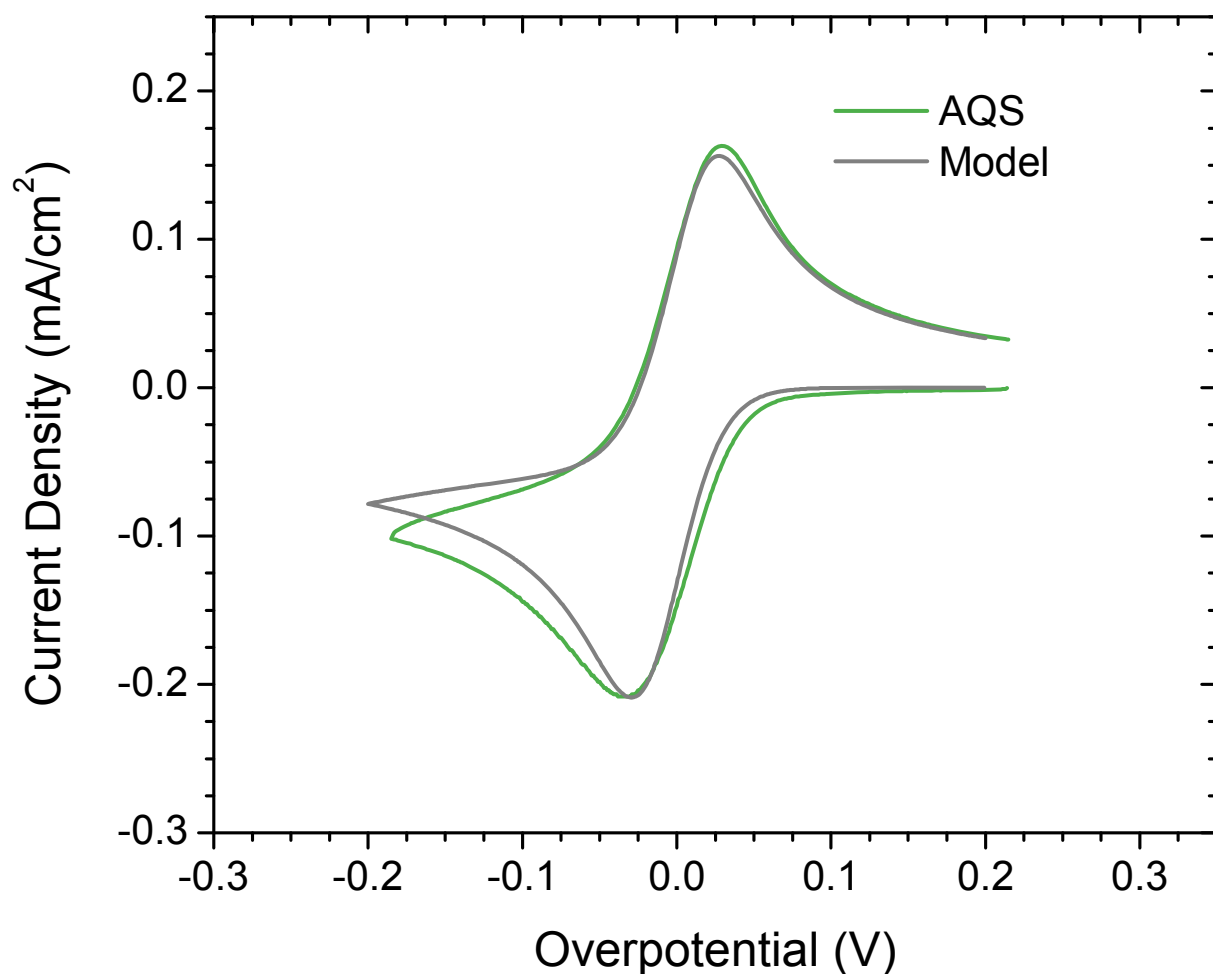


*Reversible 2-electron model:*  
assume AQS concentration at electrode surface is dictated by Nernst equation [1].  
Reaction rate is mass transport limited.

Glassy carbon electrode, 3 mm dia, 25 mV/s scan rate, 25 °C. Ag/AgCl reference.  
Pt coil counter electrode. Supporting electrolyte 1 M H<sub>2</sub>SO<sub>4</sub>. Quinone concentration 1 mM  
[1] K. B. Oldham, J. C. Myland, *Electrochim. Acta.* **56**, 10612–10625 (2011).

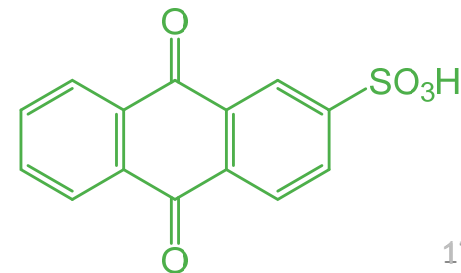


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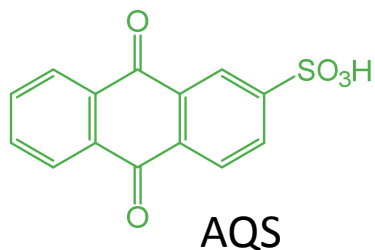
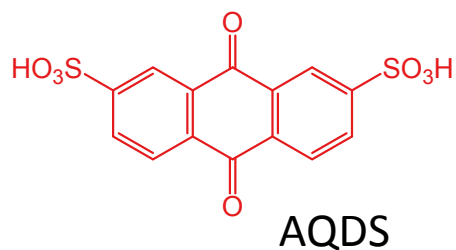
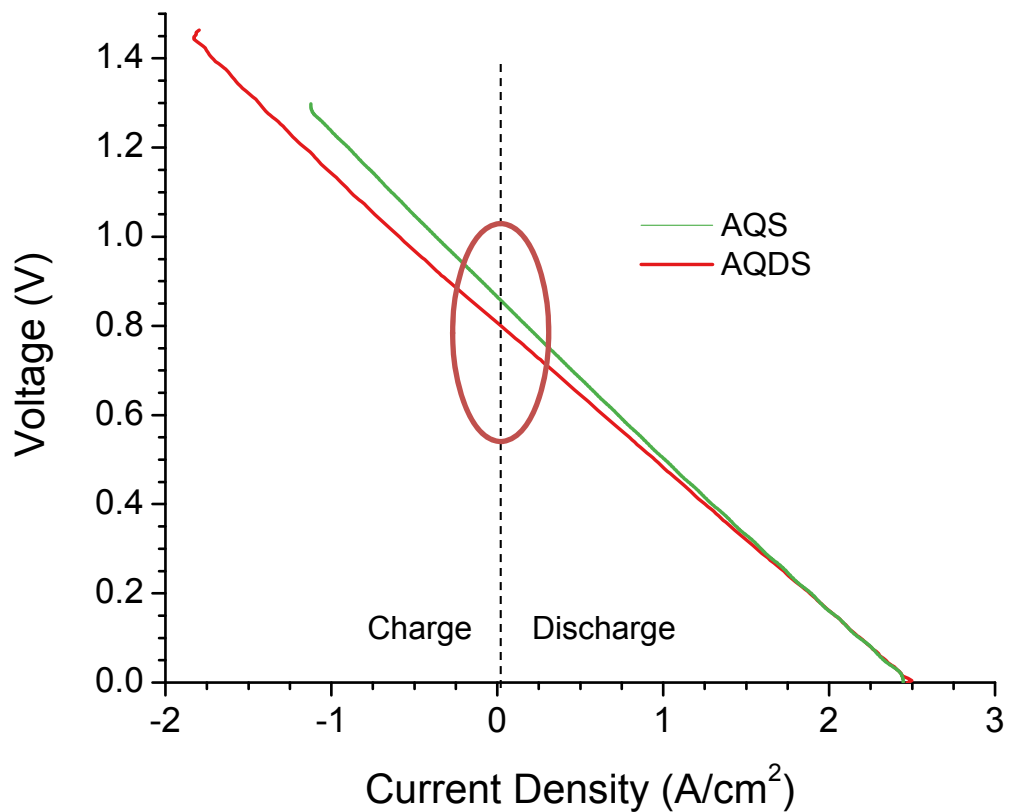


*Quasireversible model:* Assume Butler-Volmer kinetics with a rate constant  $k_0 = 2 \times 10^{-3}$  cm/s [1].

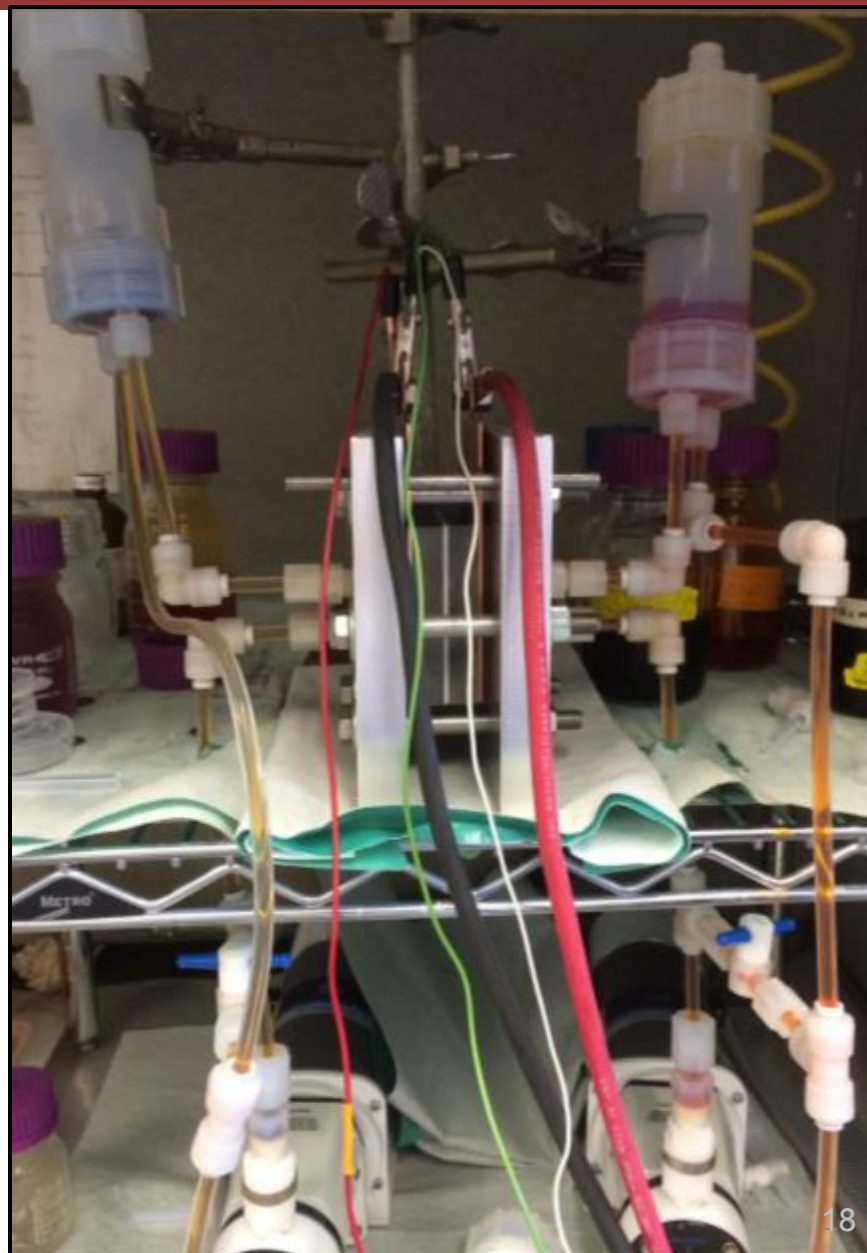
Glassy carbon electrode, 3 mm dia, 25 mV/s scan rate, 25 °C. Ag/AgCl reference.  
Pt coil counter electrode. Supporting electrolyte 1 M H<sub>2</sub>SO<sub>4</sub>. Quinone concentration 1 mM  
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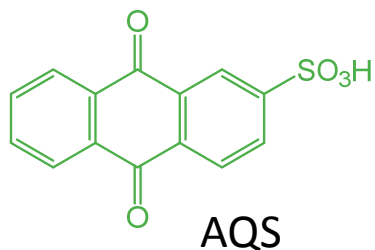
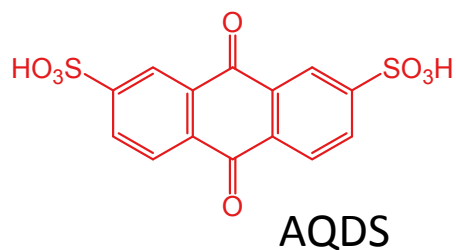
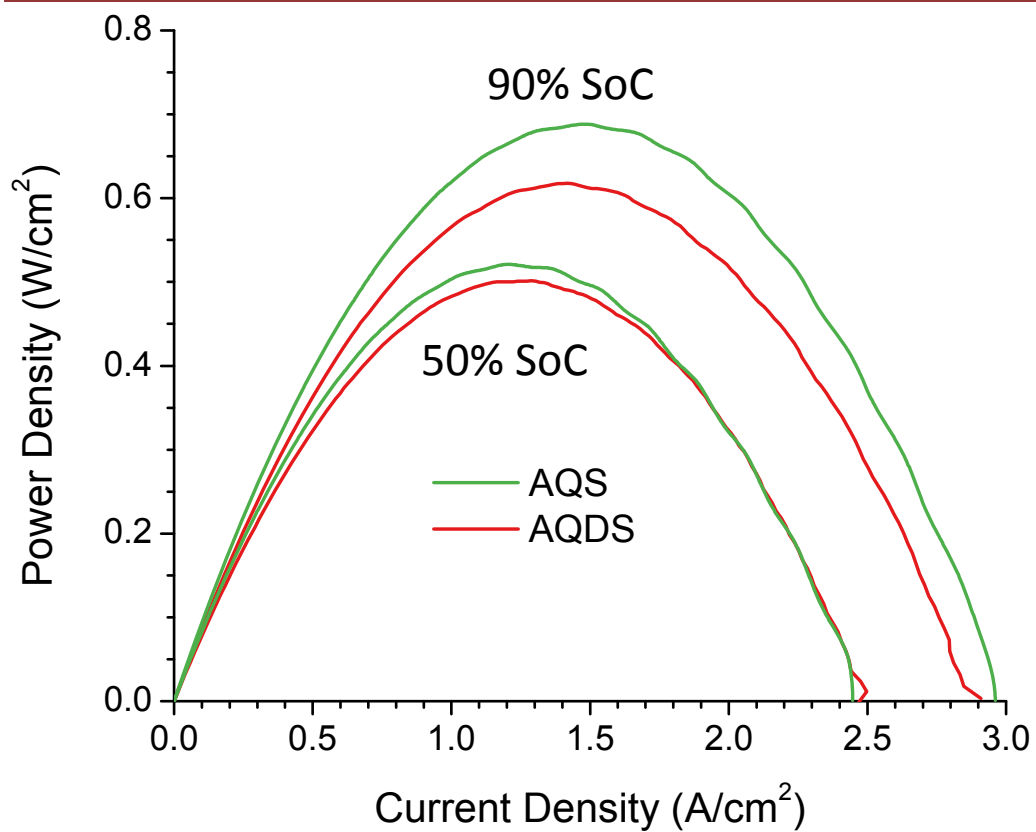
# Switching Molecules Leads to Higher Power



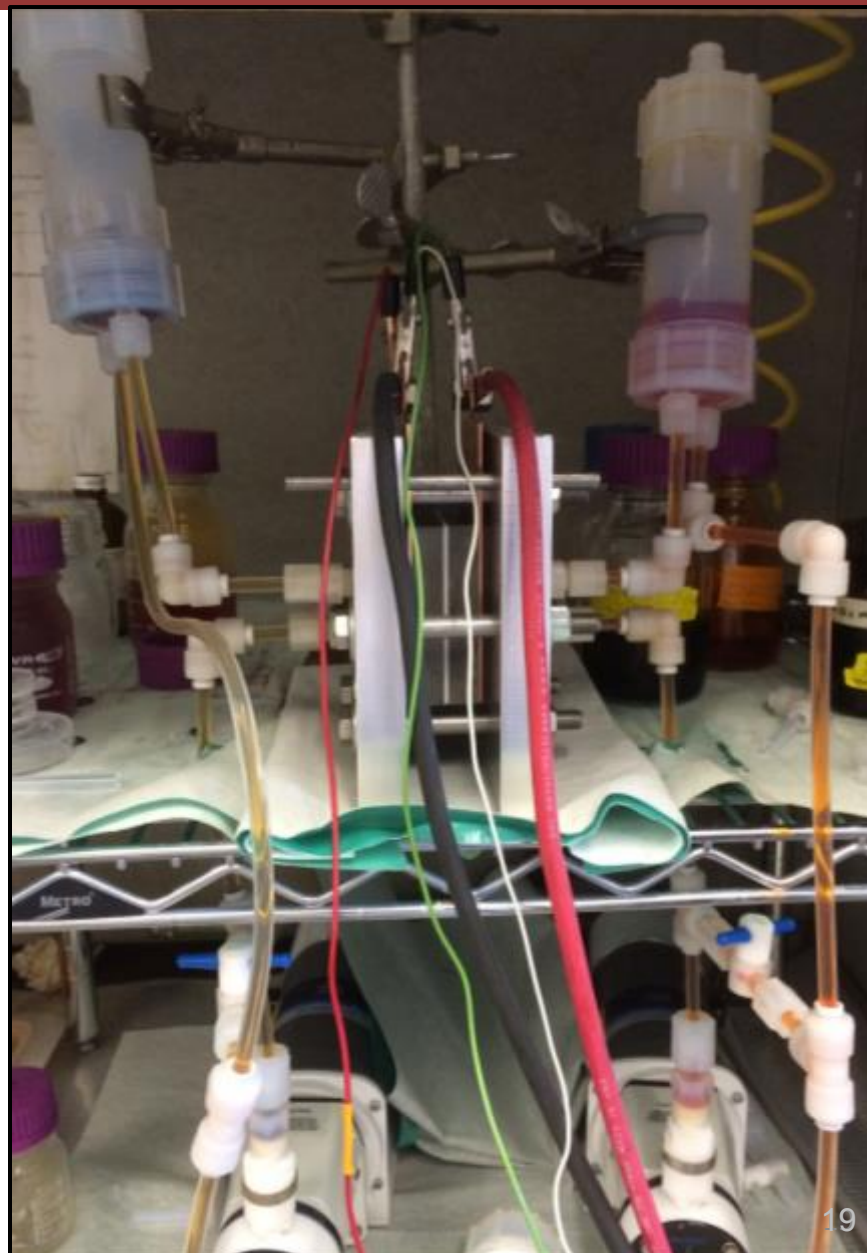
Posolyte: 0.5 M Br<sub>2</sub>, 3 M HBr



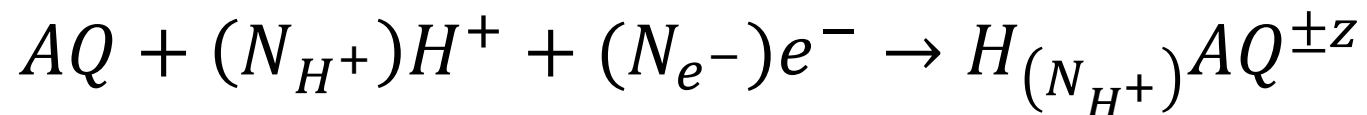
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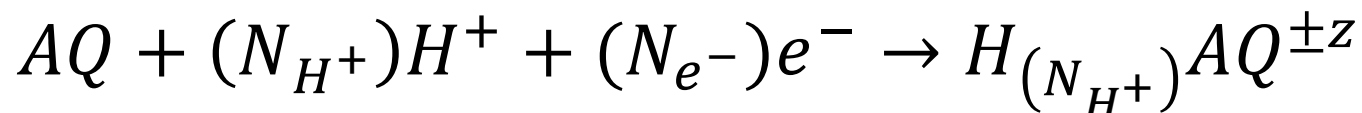
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# pH affects AQDS electrochemistry

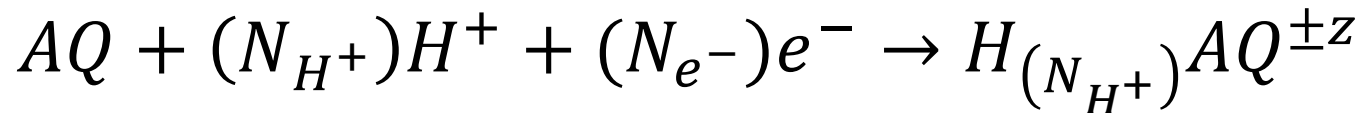


# pH affects AQDS electrochemistry



$$E = E^{0'} + \frac{RT}{(N_{e^-})F} \ln \left( \frac{[AQ][H^+]^{N_{H^+}}}{[H_m AQ^{\pm z}]} \right)$$

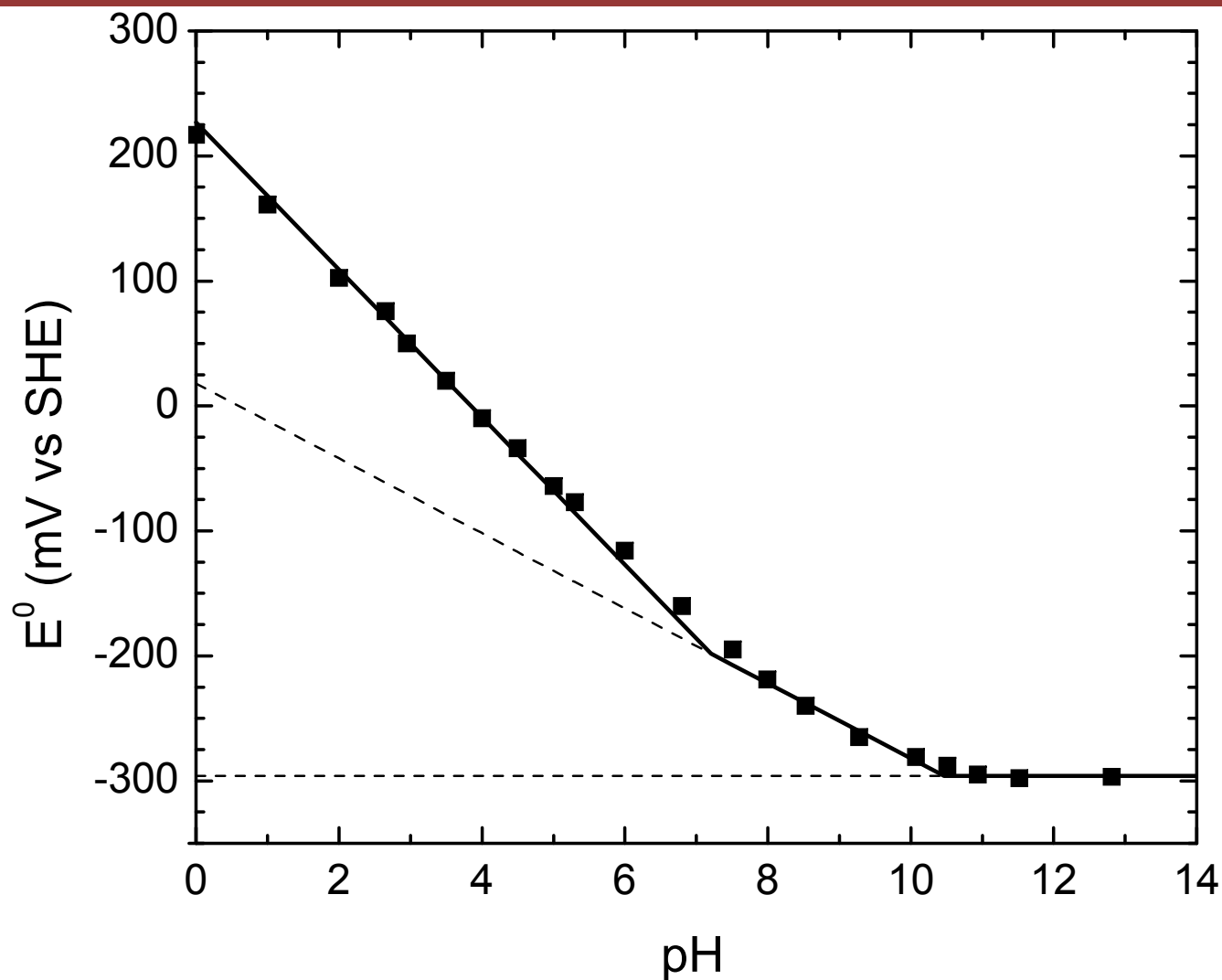
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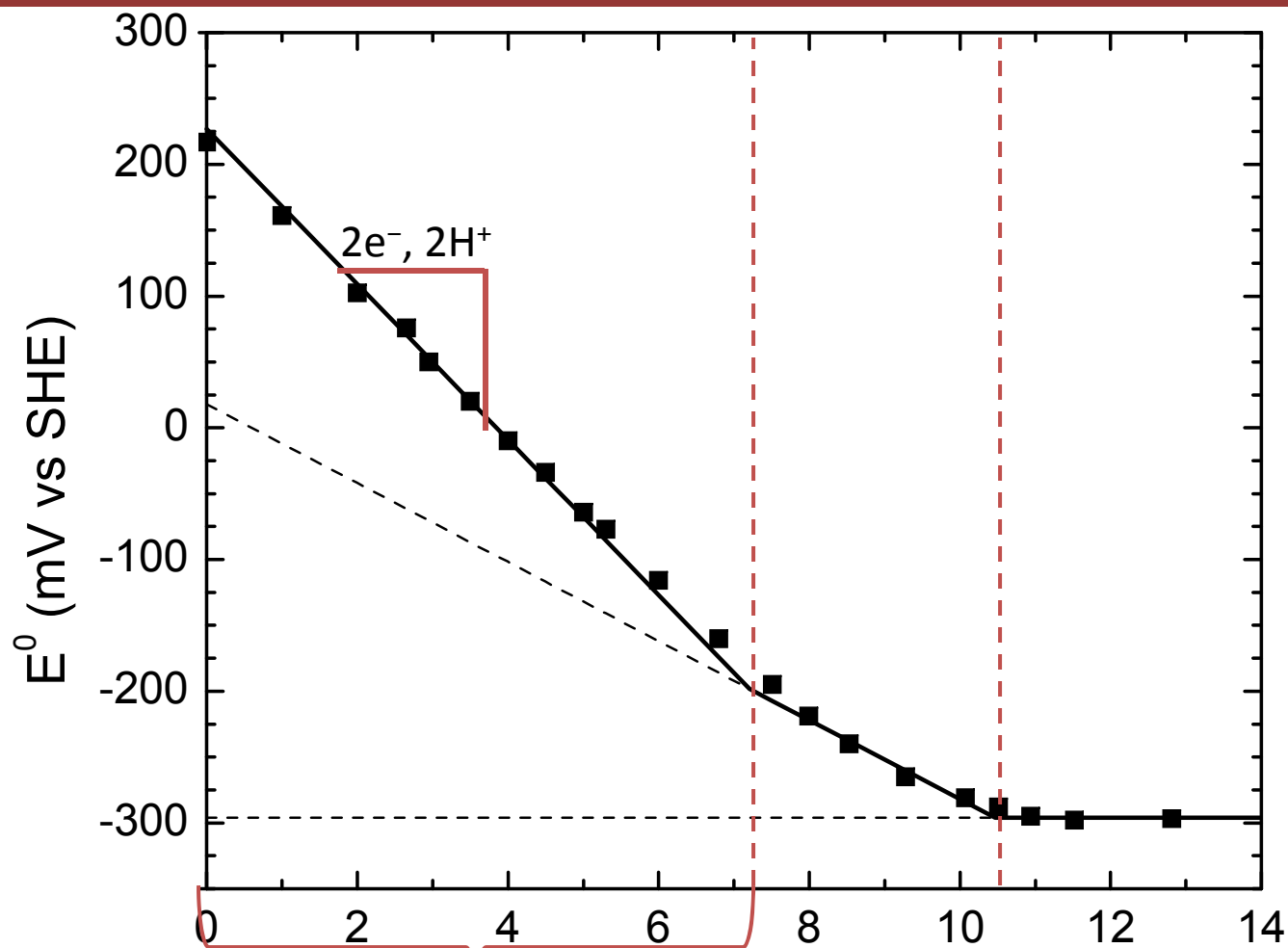
$$E = E^{0'} - \frac{RT}{F} \left( \frac{N_{H^+}}{N_{e^-}} \right) (\text{pH}) + C$$

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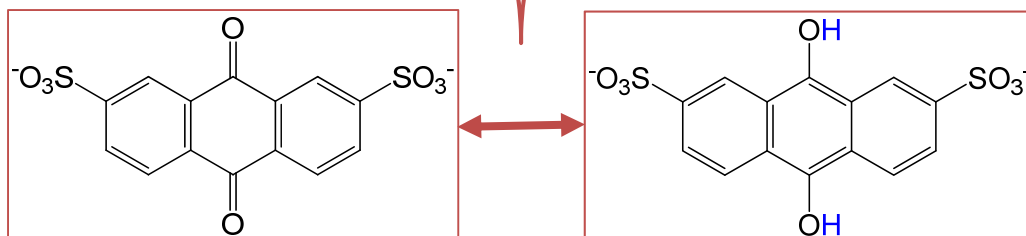


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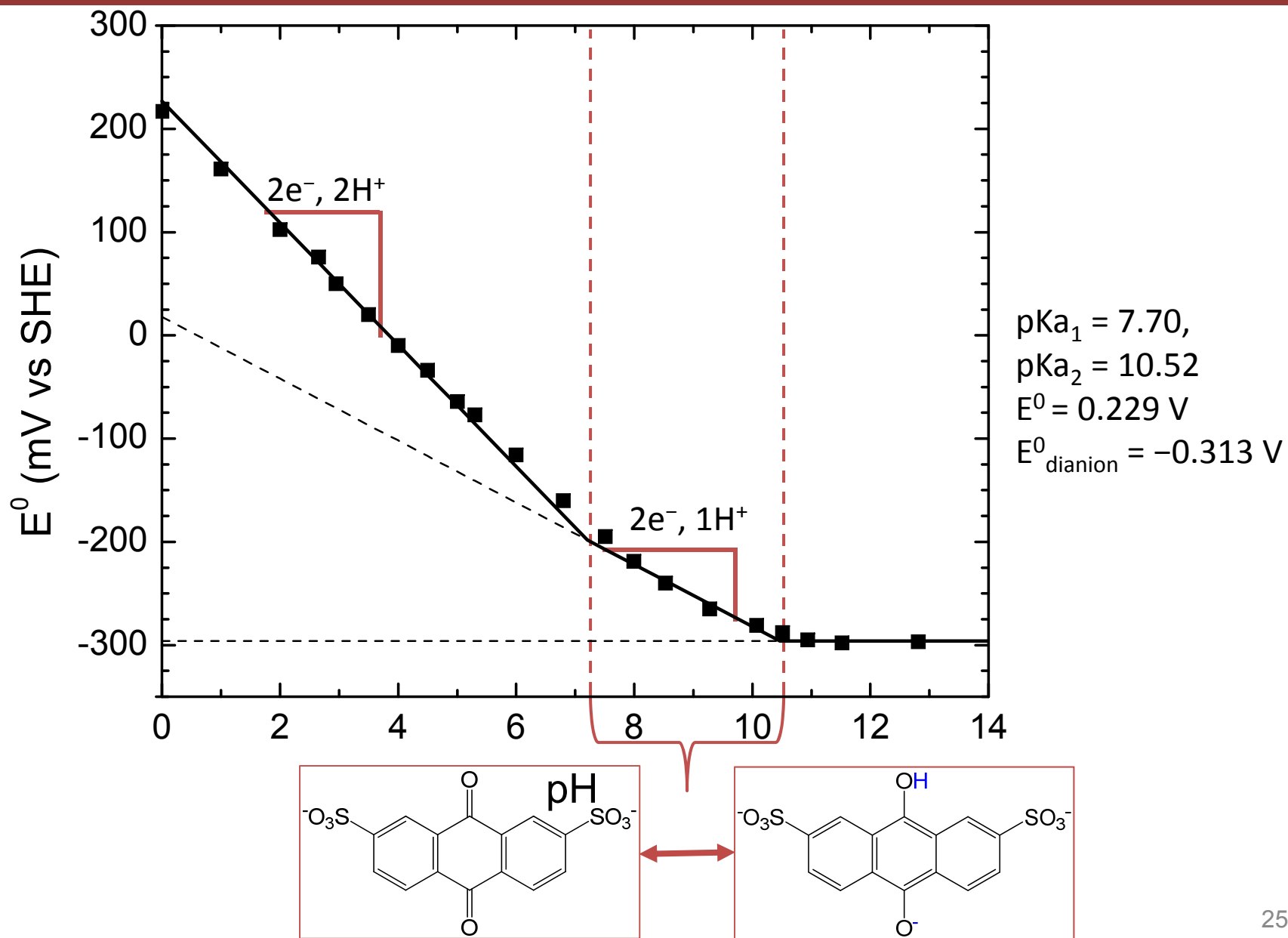
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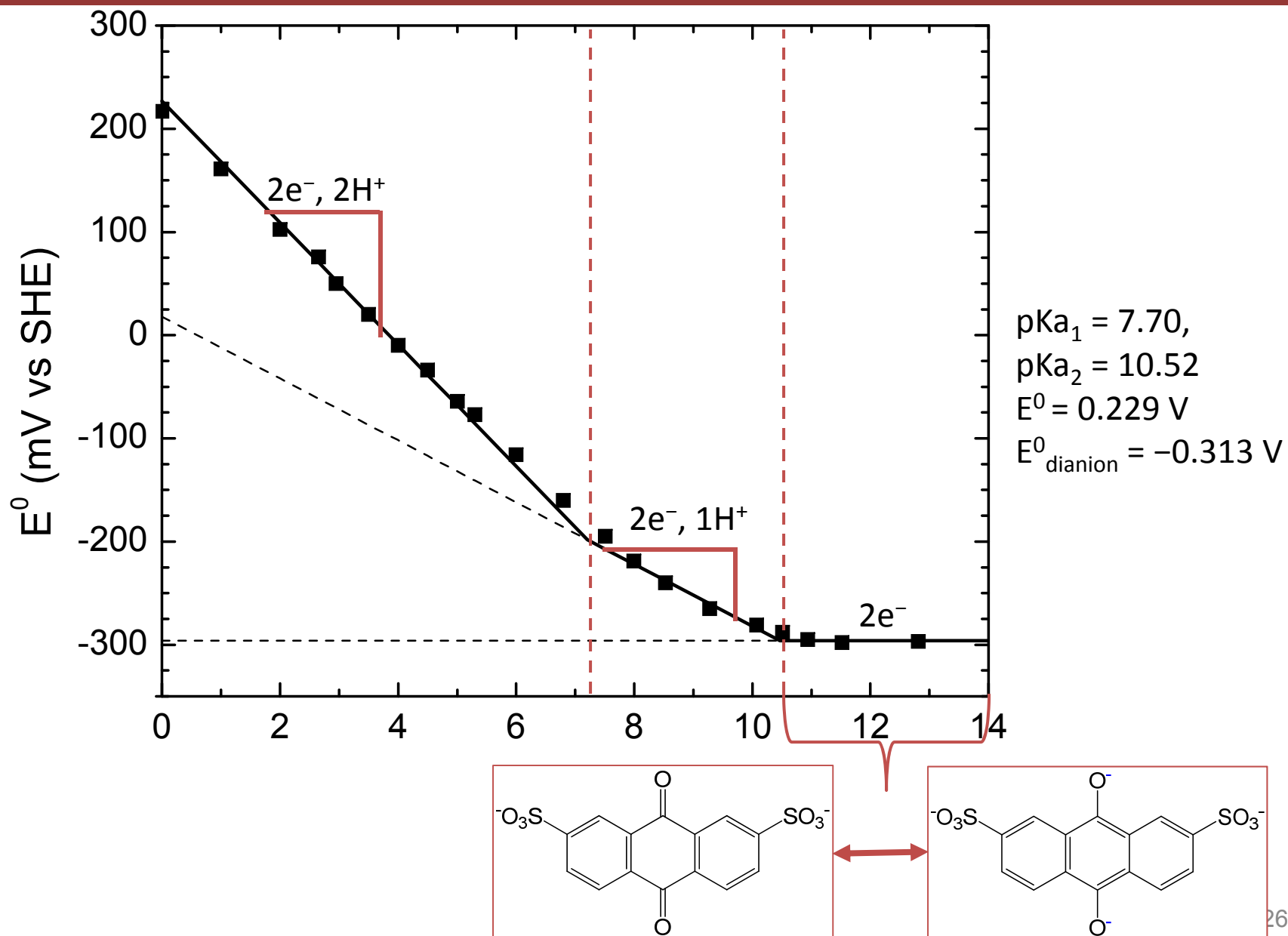
$pK_{a1} = 7.70$ ,  
 $pK_{a2} = 10.52$   
 $E^0 = 0.229 \text{ V}$   
 $E^0_{\text{dianion}} = -0.313 \text{ V}$



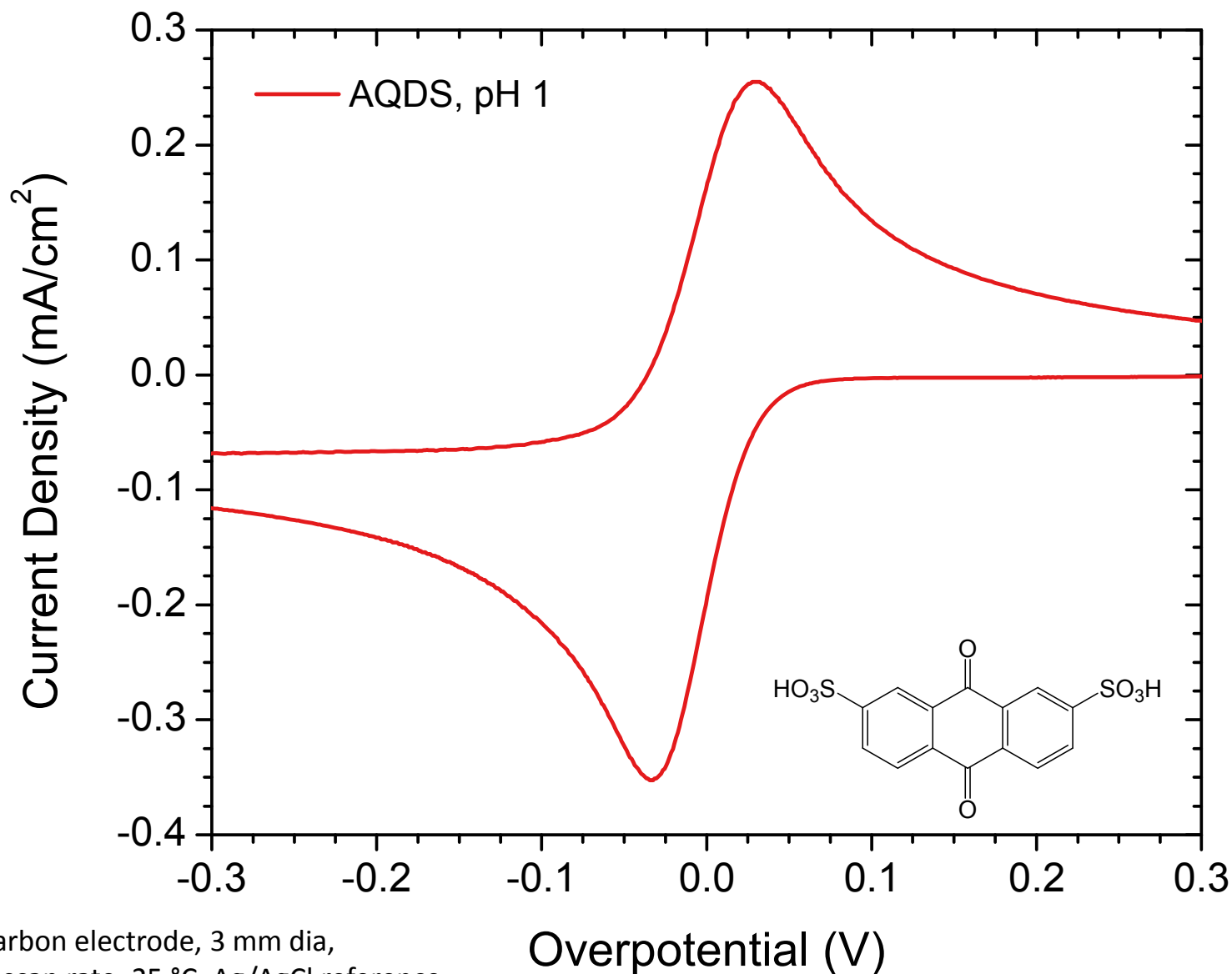
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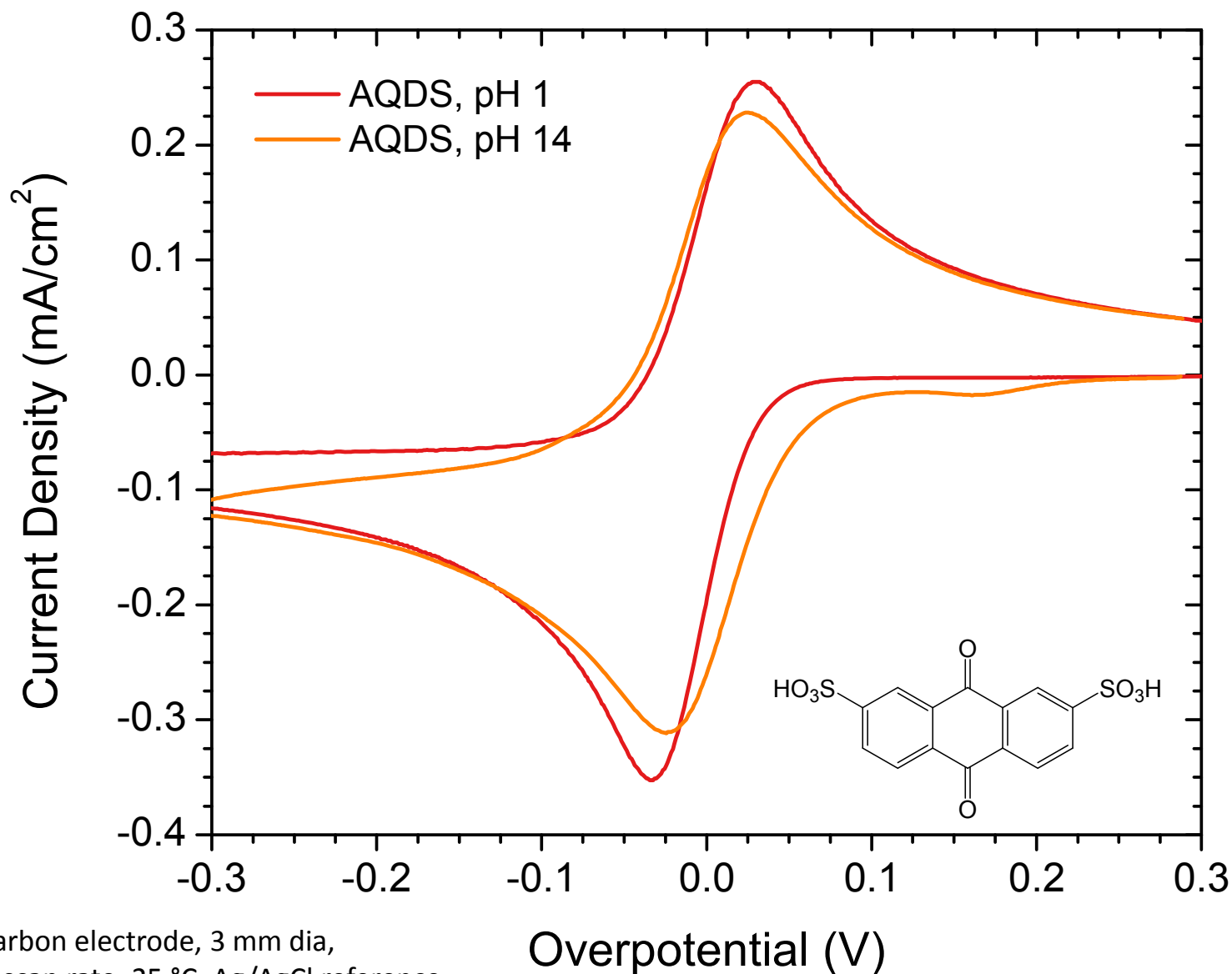
# AQDS reduction kinetics as function of pH



Glassy carbon electrode, 3 mm dia,  
50 mV/s scan rate, 25 °C. Ag/AgCl reference.

Pt coil counter electrode. Supporting electrolyte H<sub>2</sub>SO<sub>4</sub> or KOH. Quinone concentration 1 mM

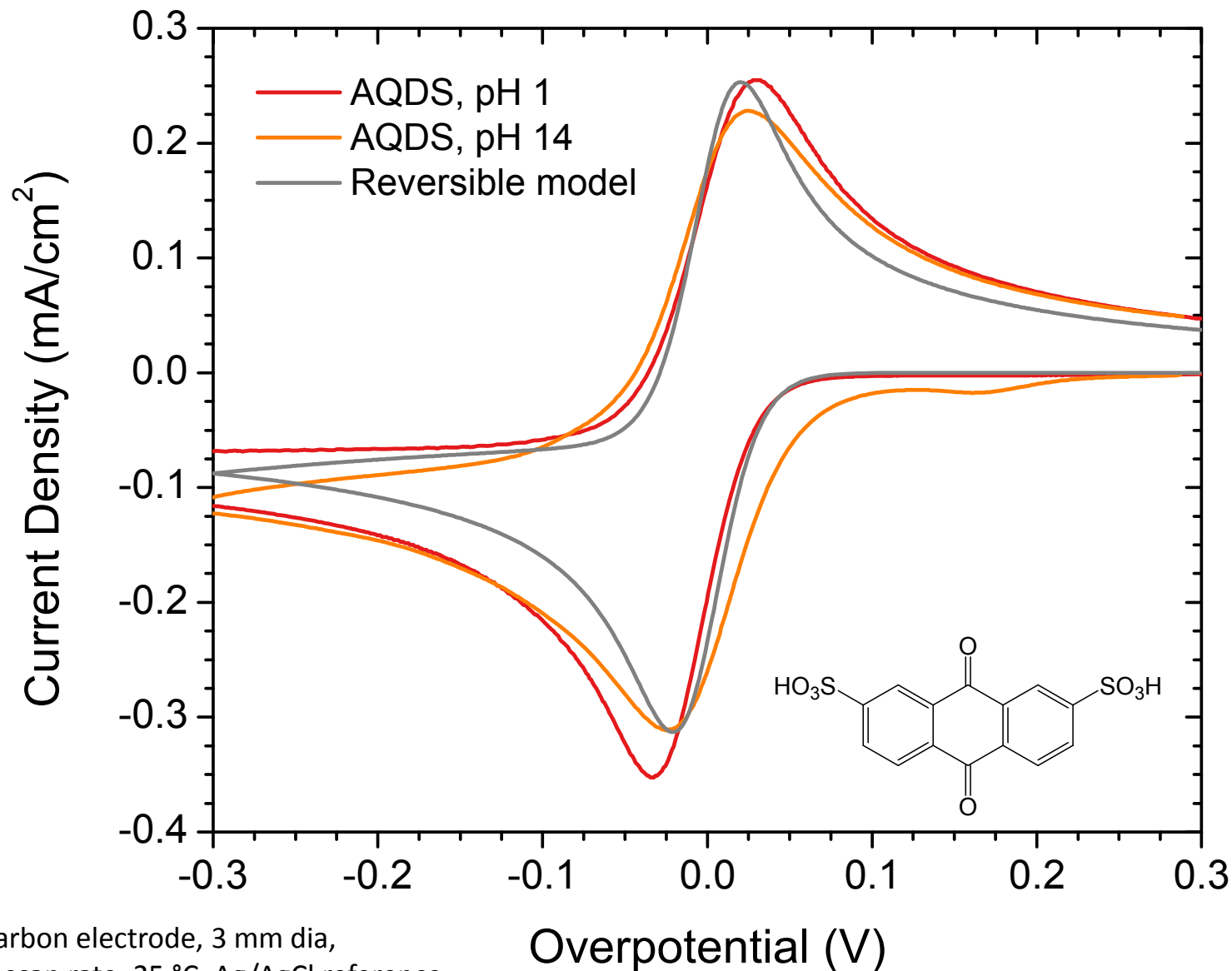
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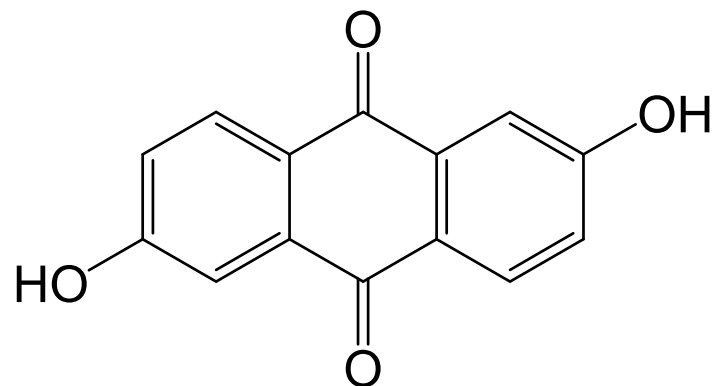
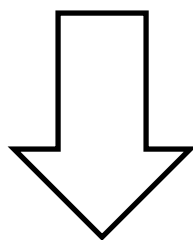
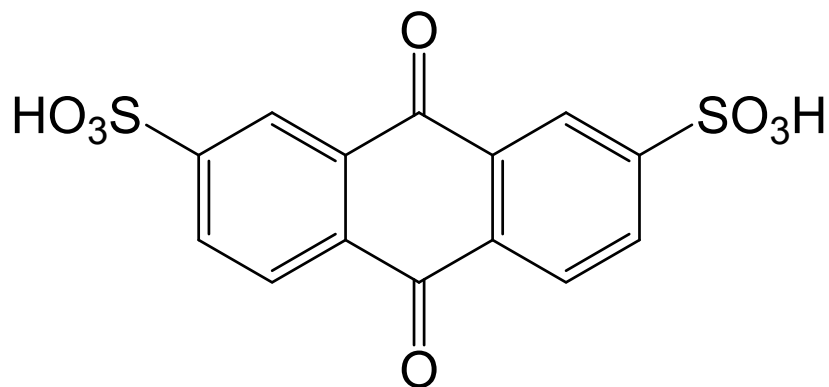
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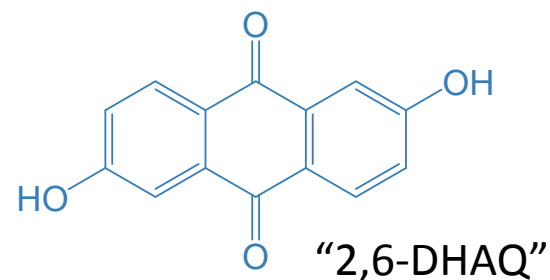
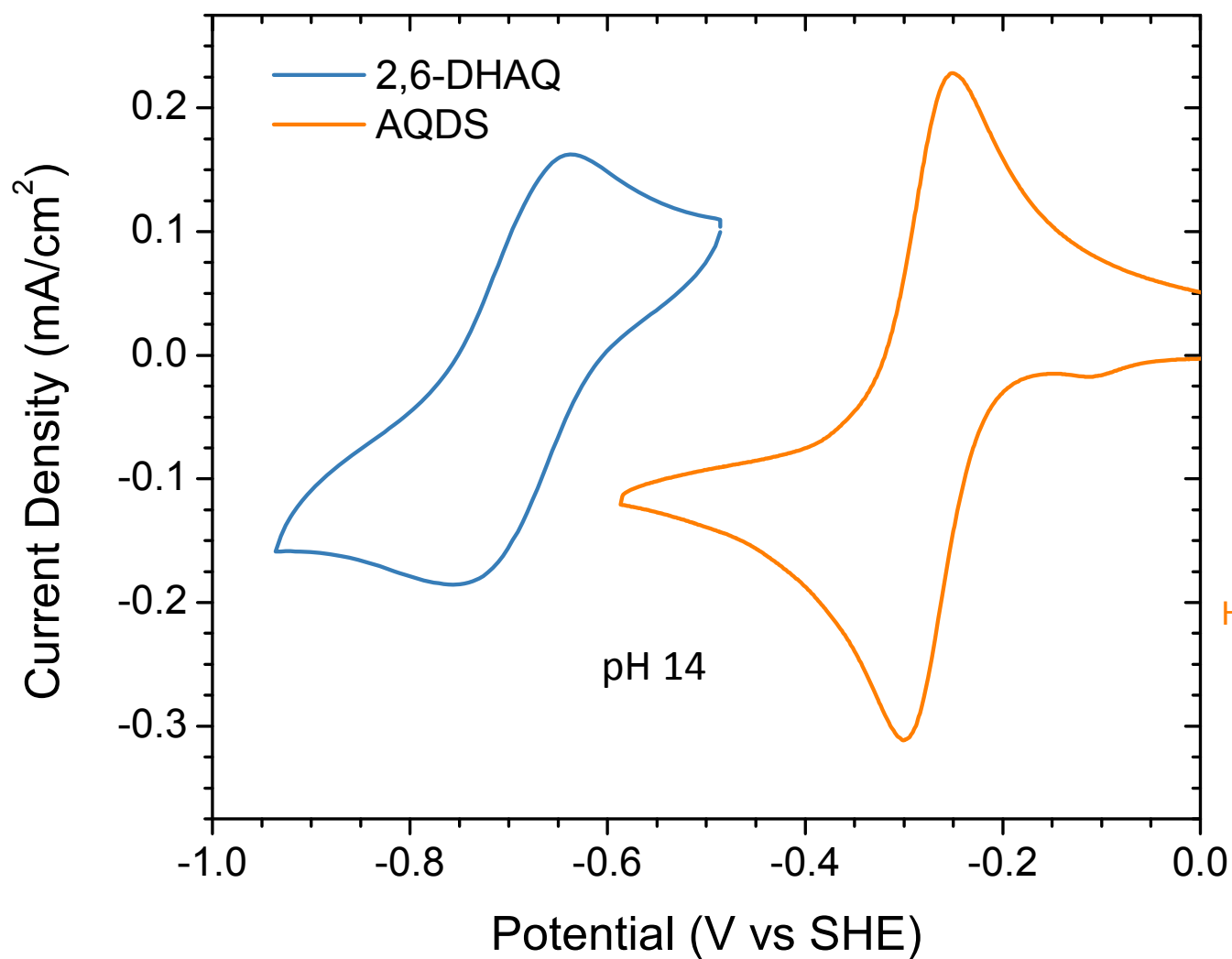
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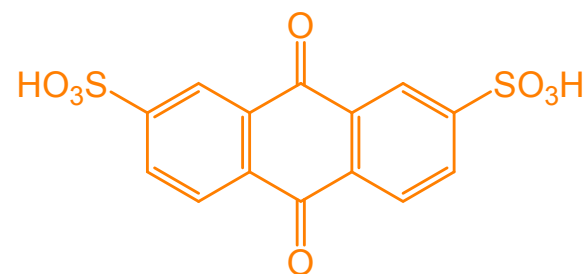
# Optimizing molecule for basic solutions



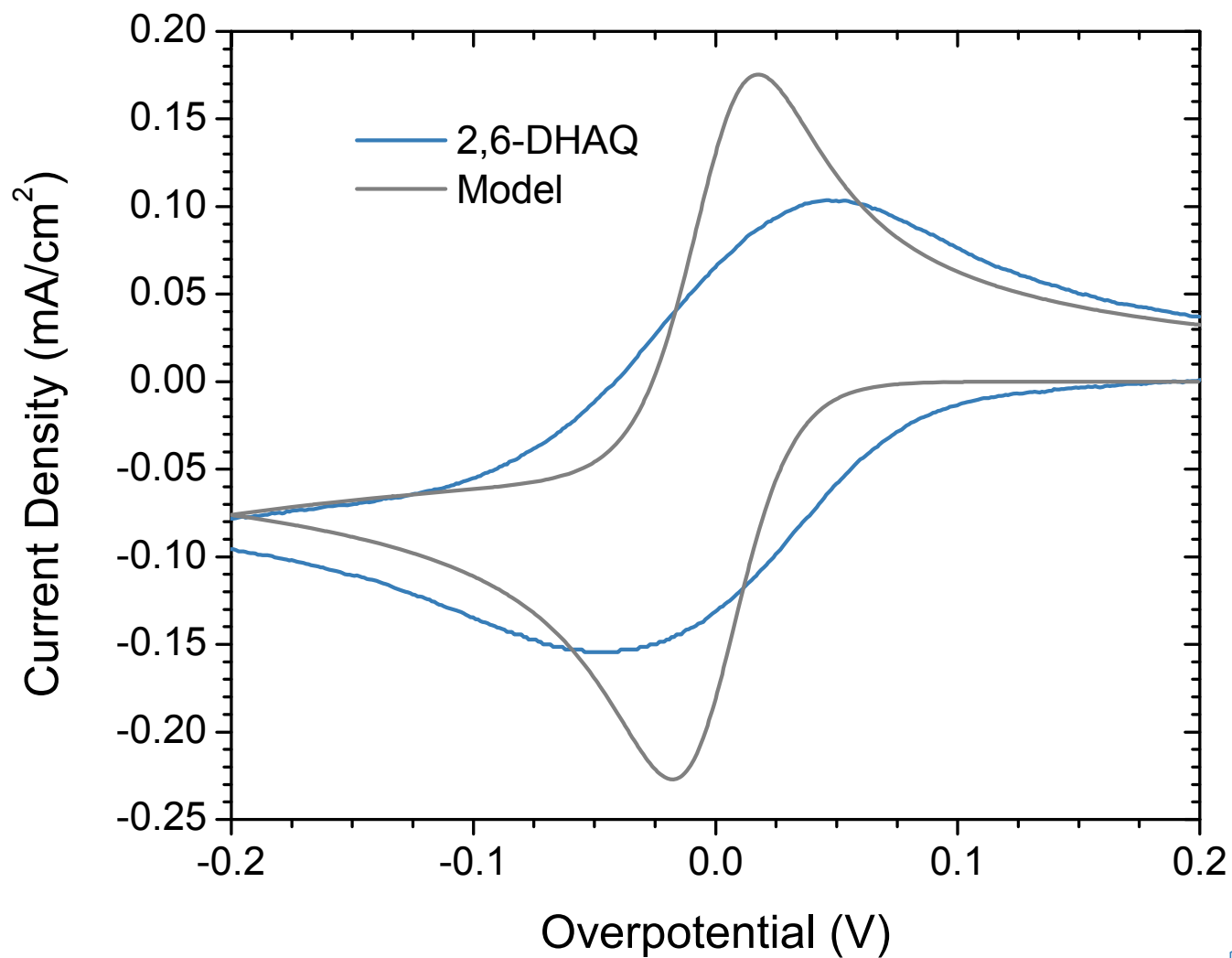
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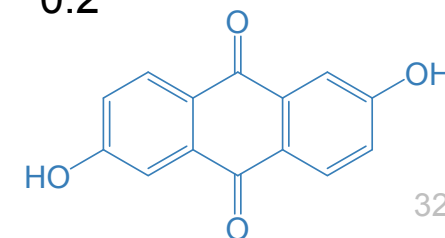
2,6-dihydroxy 9,10-anthraquinone



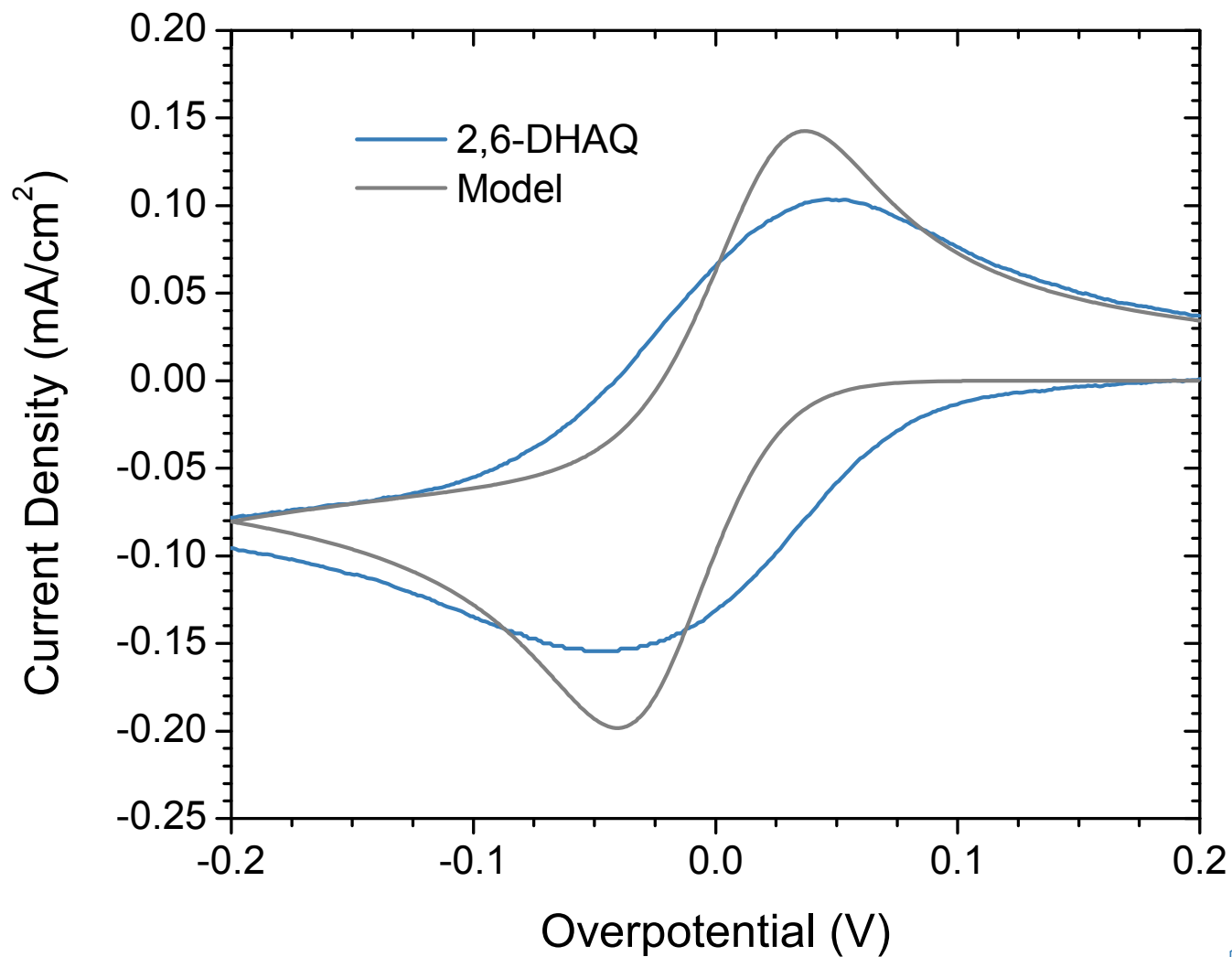
# Two-electron transfer model can't explain CV



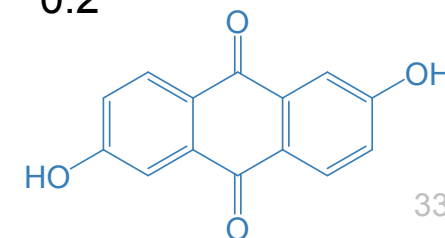
$$k_0 = 1 \times 10^{-2} \text{ cm/s}$$



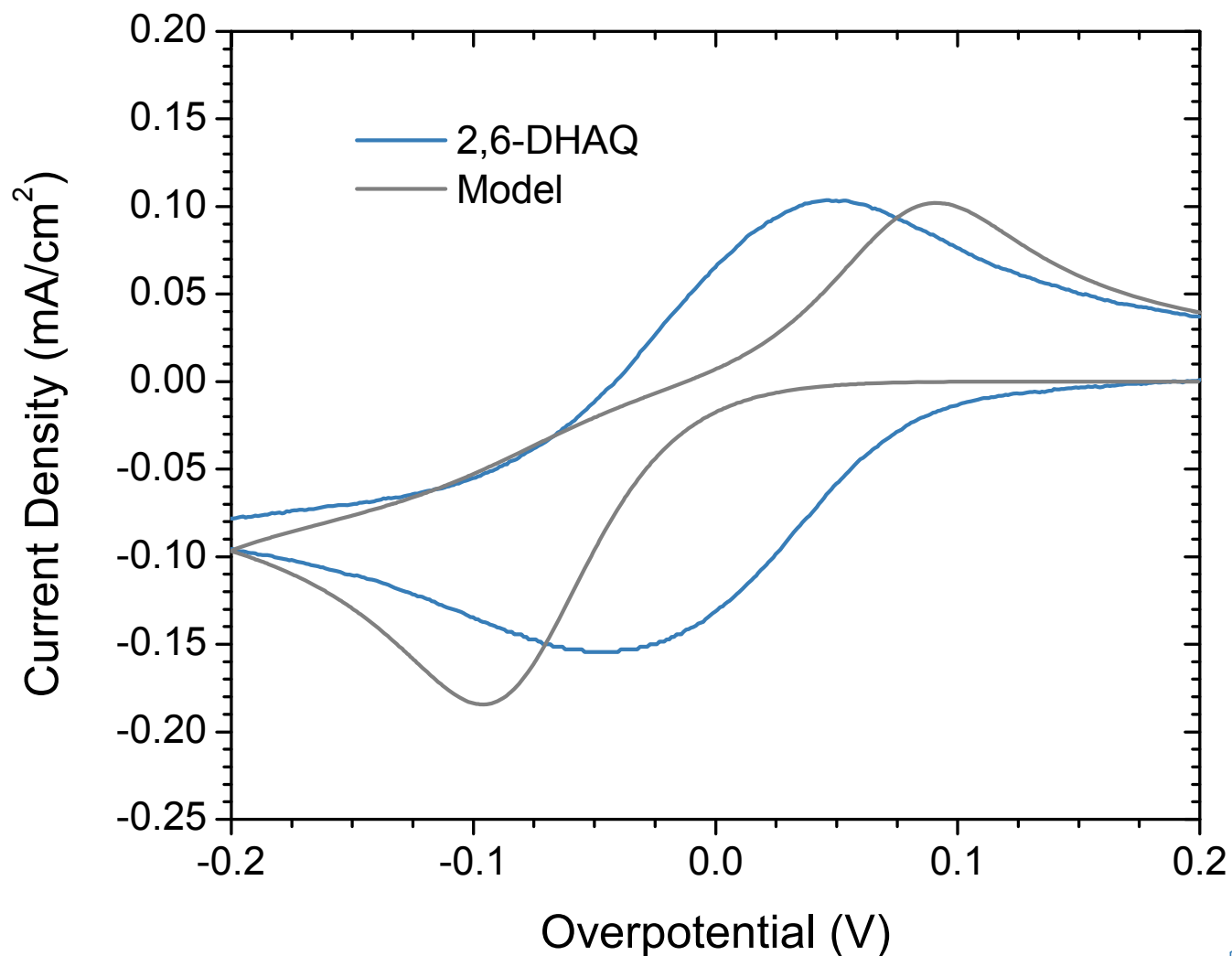
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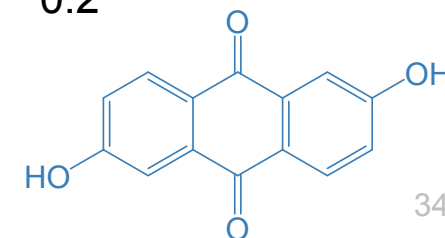
$$k_0 = 1 \times 10^{-3} \text{ cm/s}$$



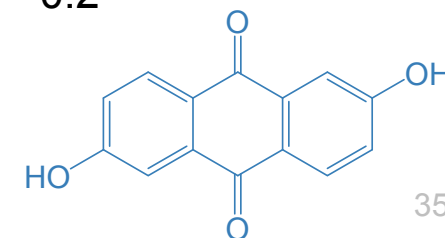
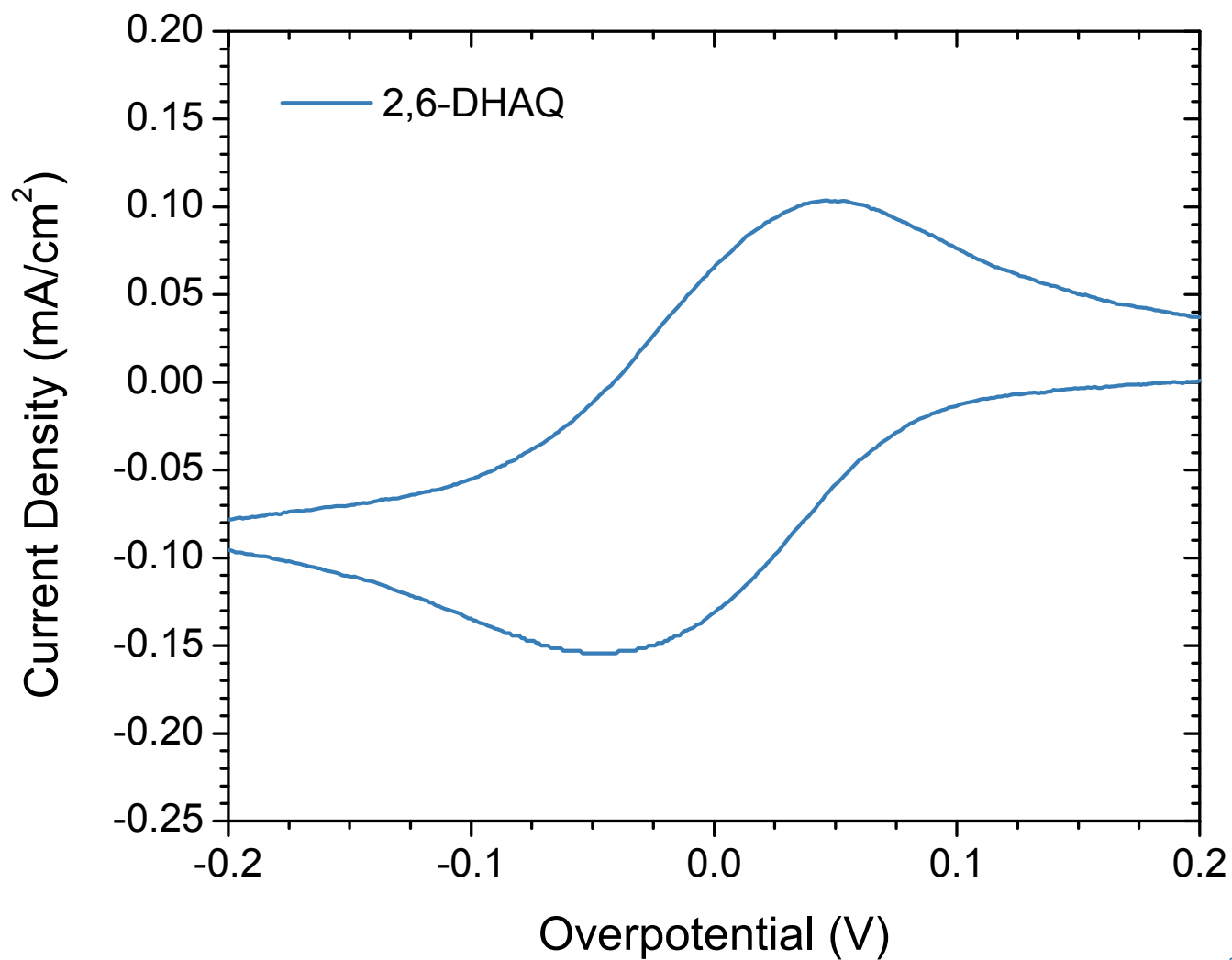
# Two-electron transfer model can't explain CV



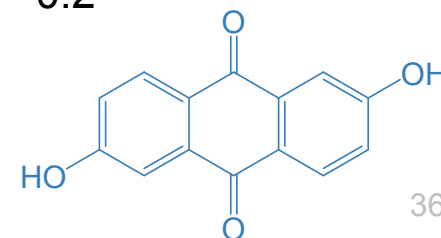
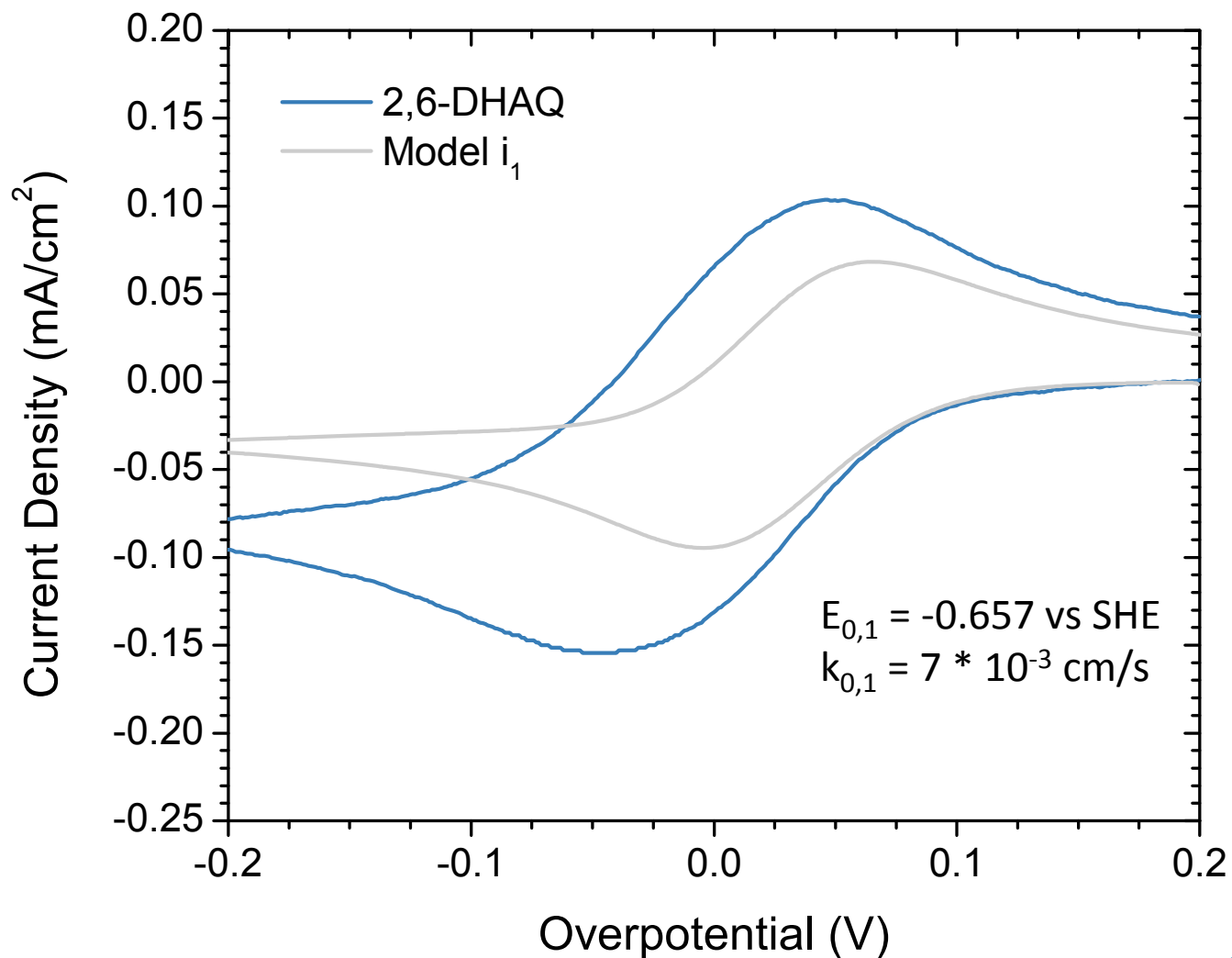
$$k_0 = 1 \times 10^{-4} \text{ cm/s}$$



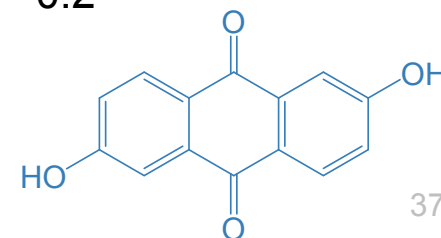
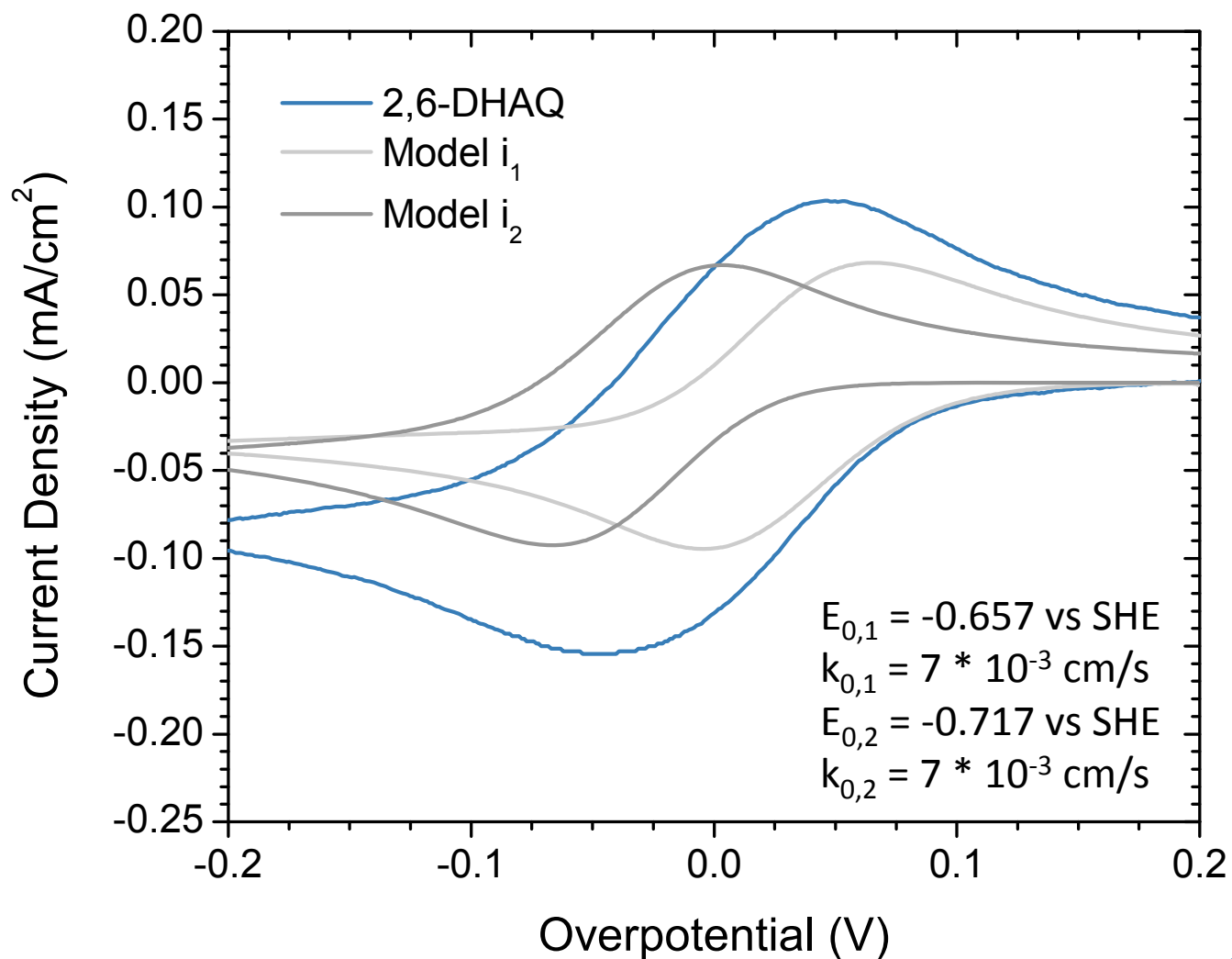
# Sequential 1 e<sup>-</sup> transfers could explain CV



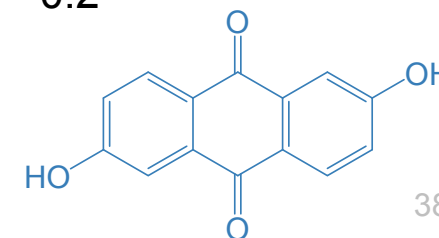
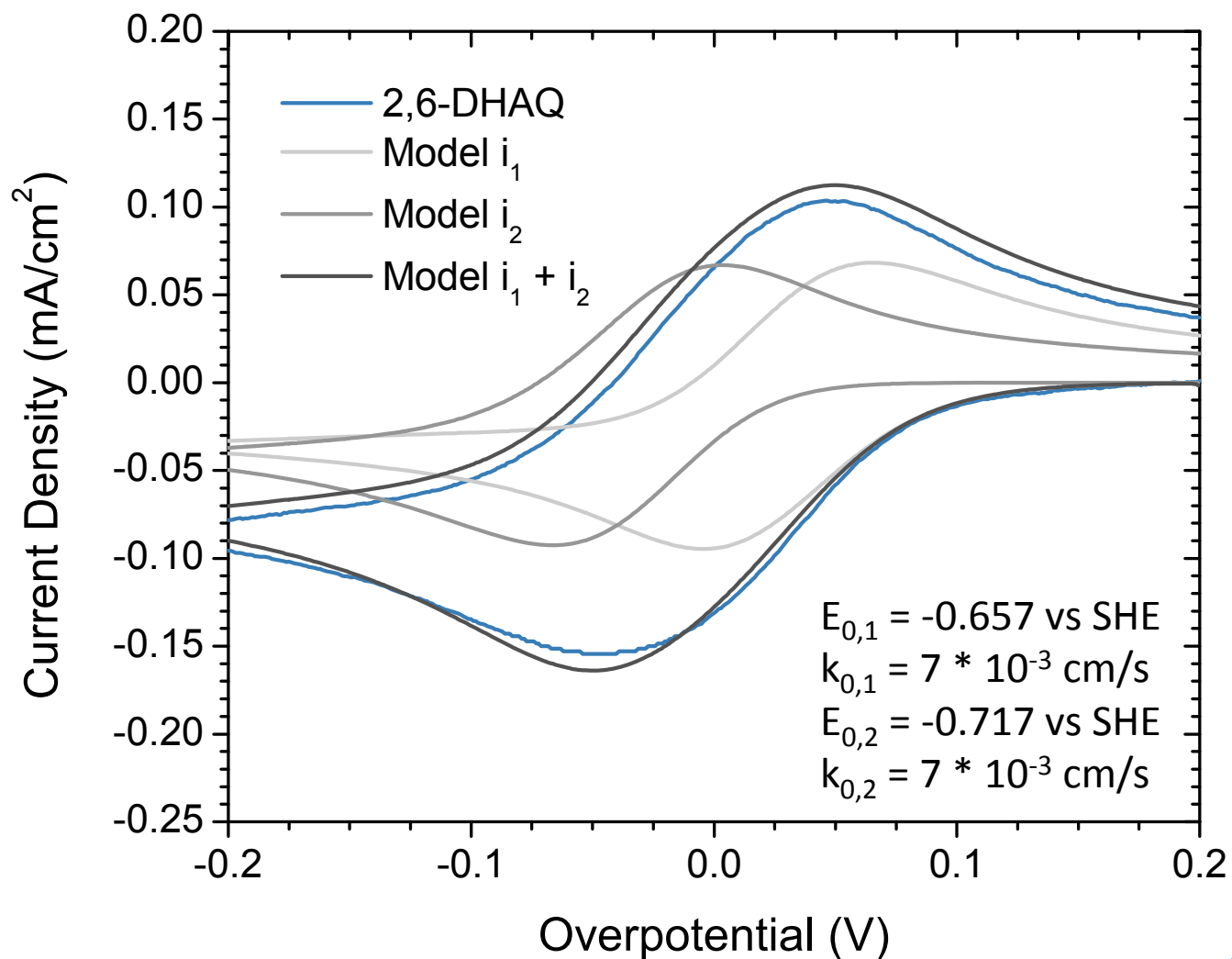
# Sequential 1 e<sup>-</sup> transfers could explain CV



# Sequential 1 e<sup>-</sup> transfers could explain CV



# Sequential 1 e<sup>-</sup> transfers could explain CV



# Quinone – Ferrocyanide Flow Battery

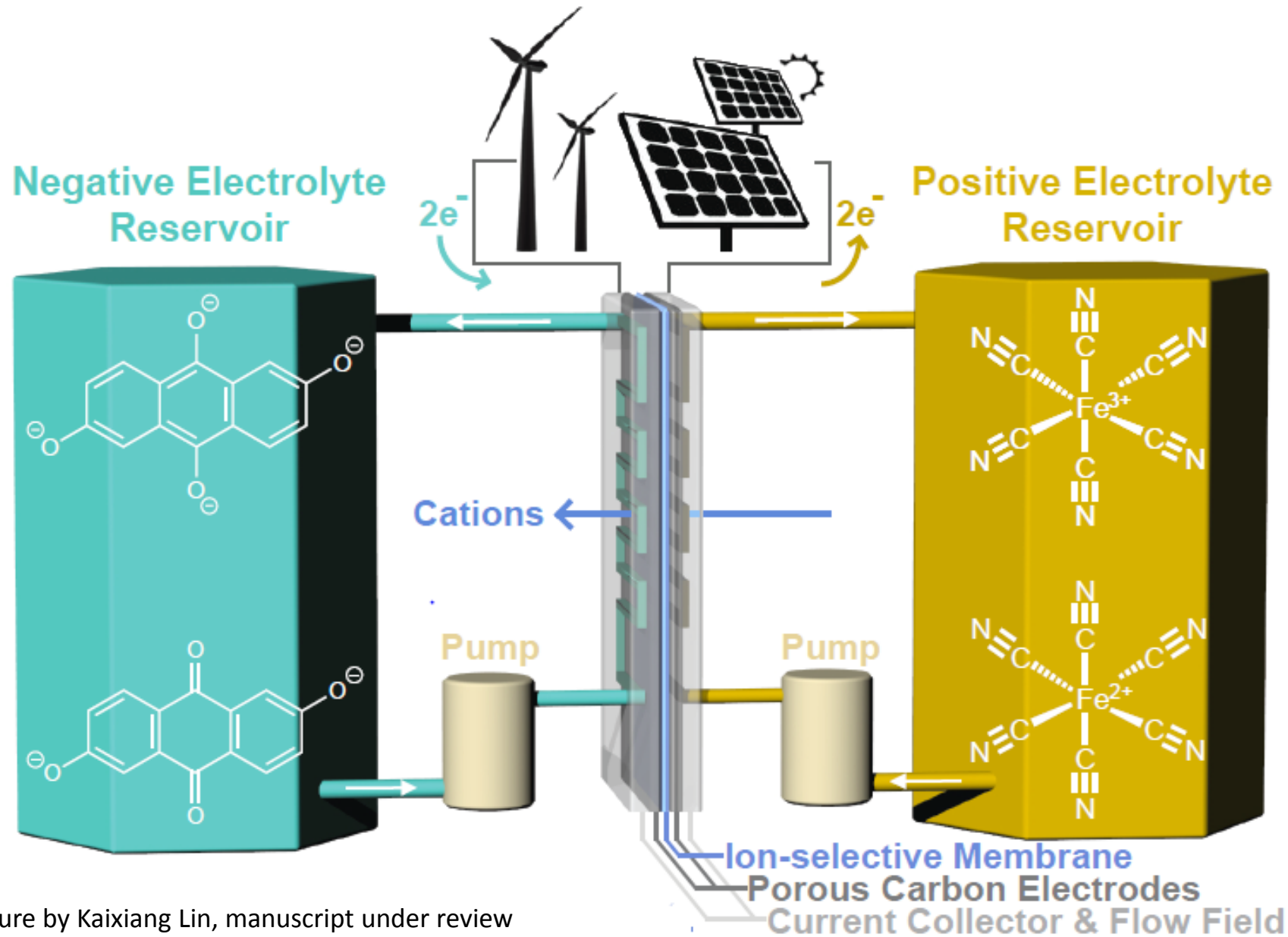
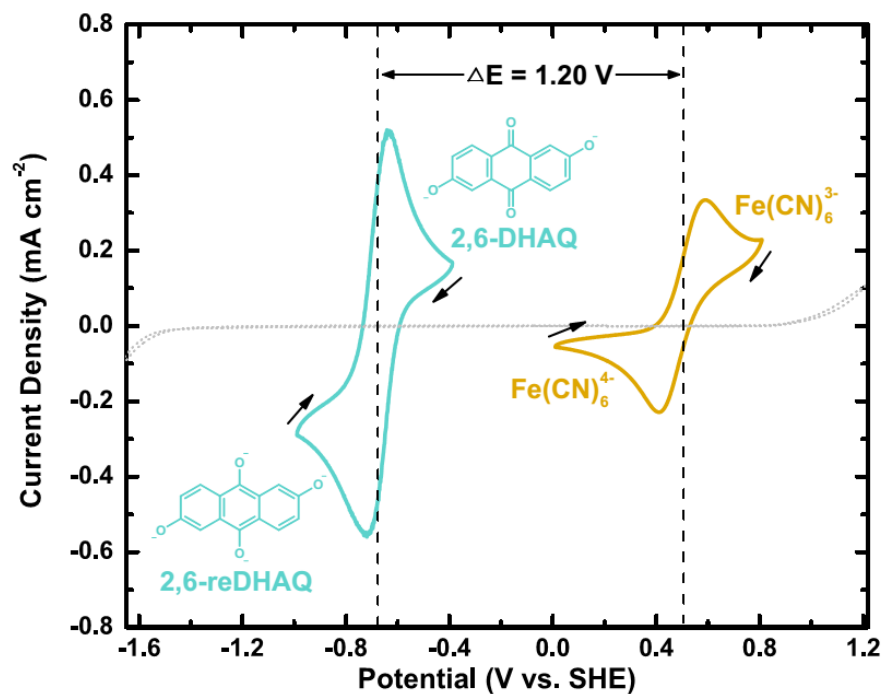
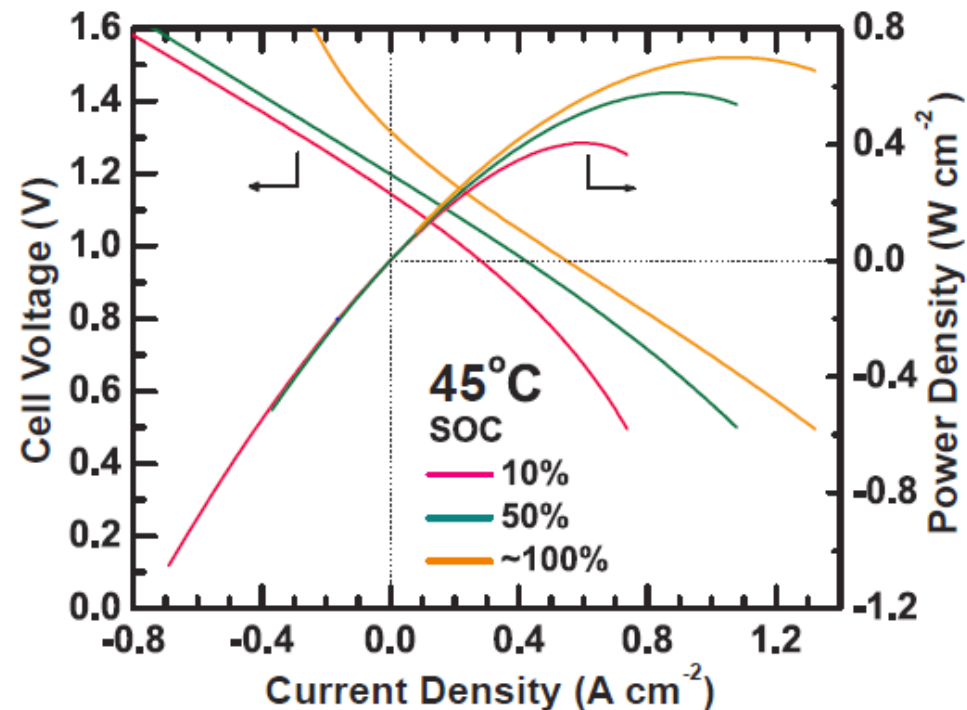


Figure by Kaixiang Lin, manuscript under review

# Quinone – Ferrocyanide Flow Battery

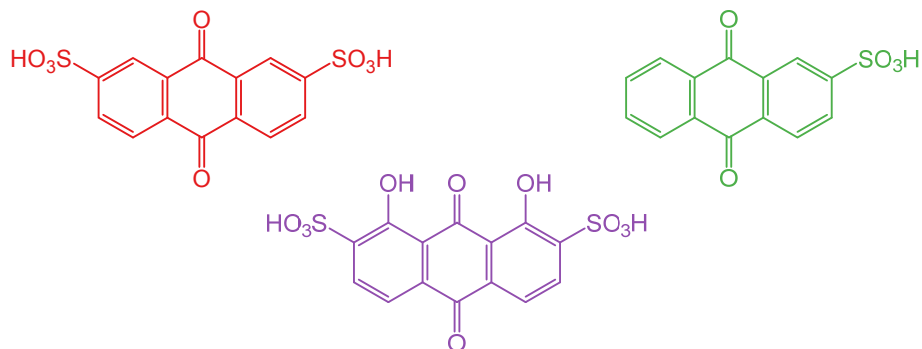
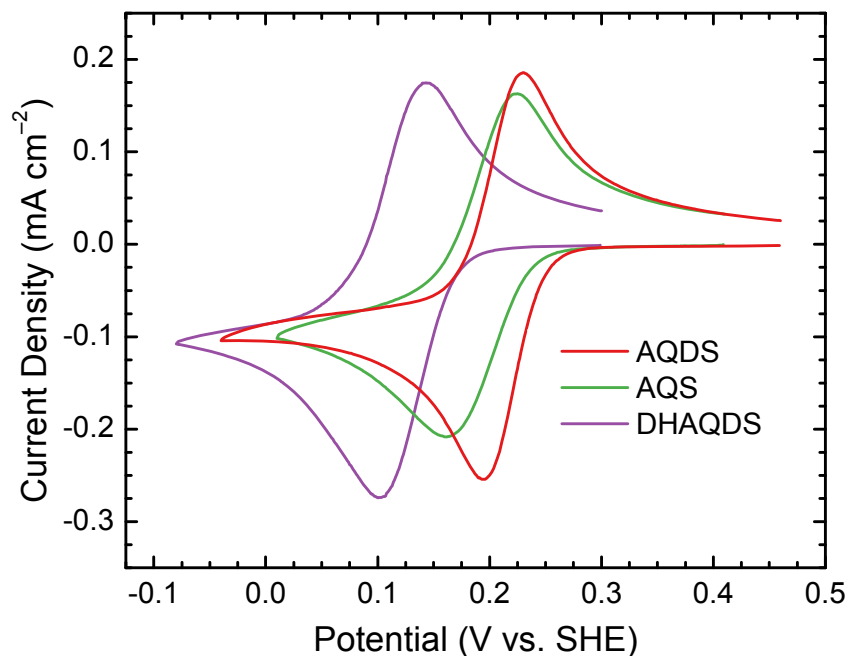


Cyclic voltammogram of 4 mM 2,6-DHAQ (dark cyan curve) and ferrocyanide (gold curve) scanned at 100 mV/s



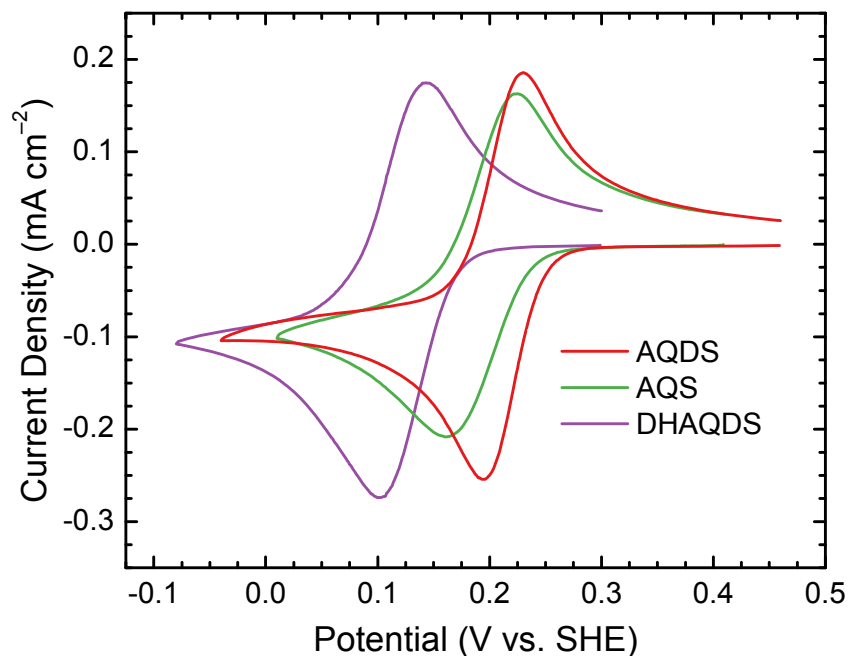
# Strategies for Increasing Cell Voltage

Use functional groups to create more reducing quinones

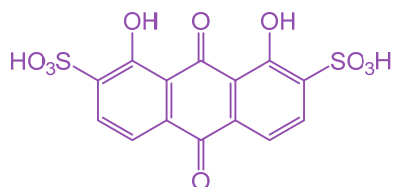
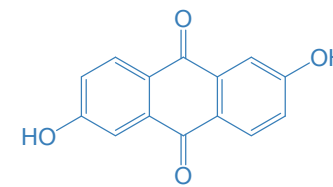
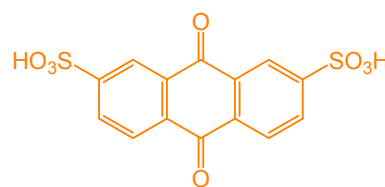
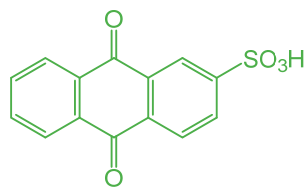
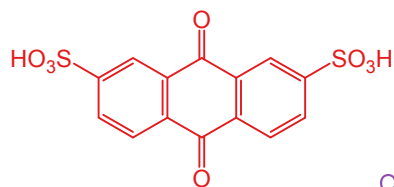
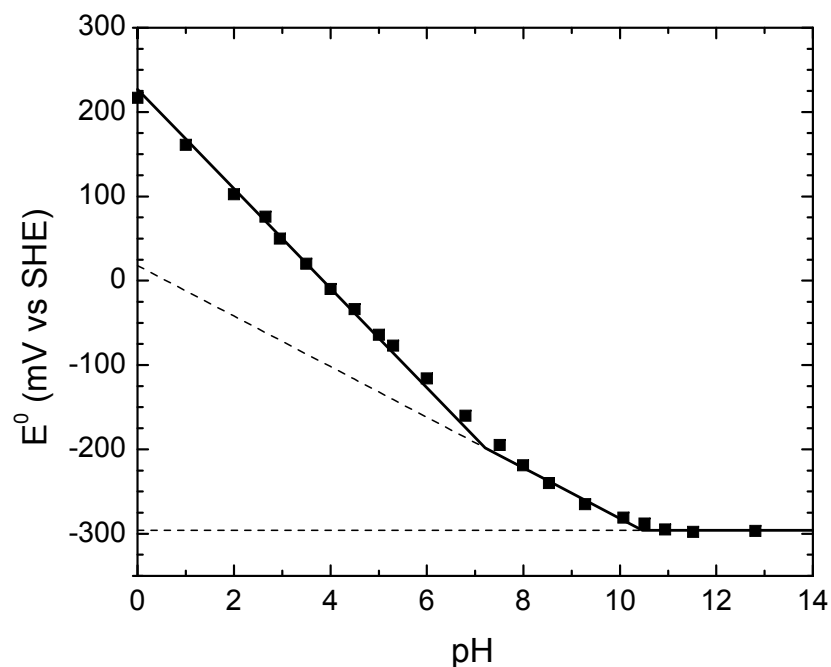


# Strategies for Increasing Cell Voltage

Use functional groups to create more reducing quinones

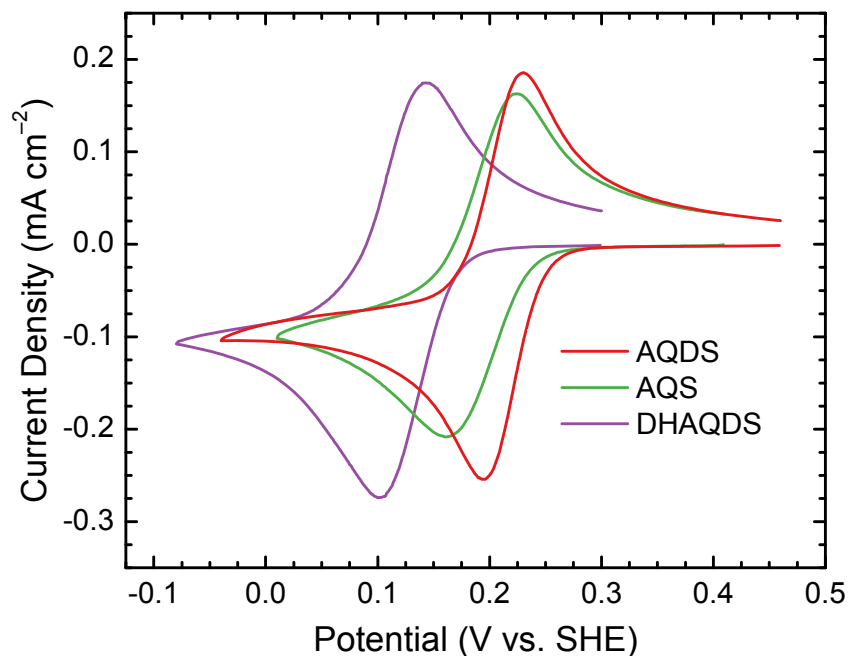


Use quinones in alkaline environment

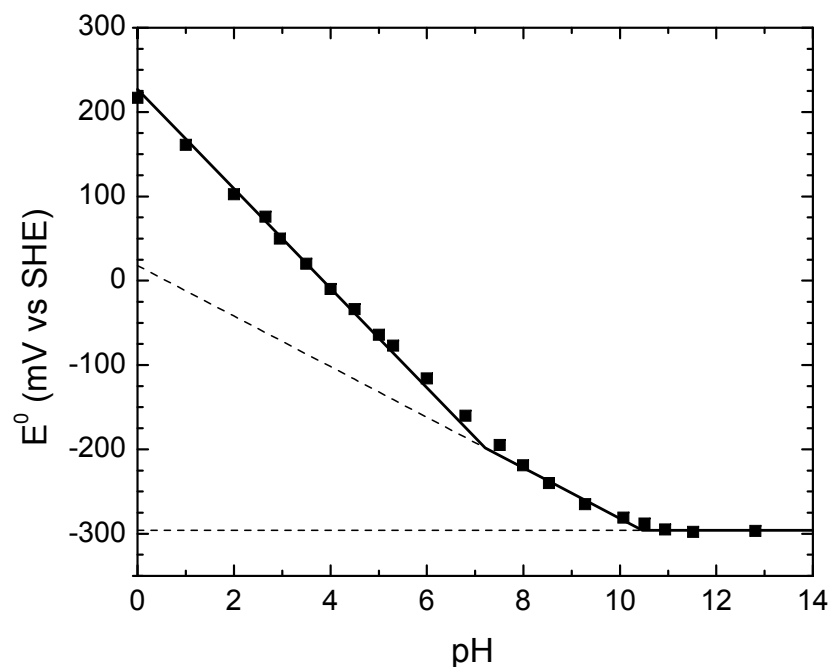


# Strategies for Increasing Cell Voltage

Use functional groups to create more reducing quinones

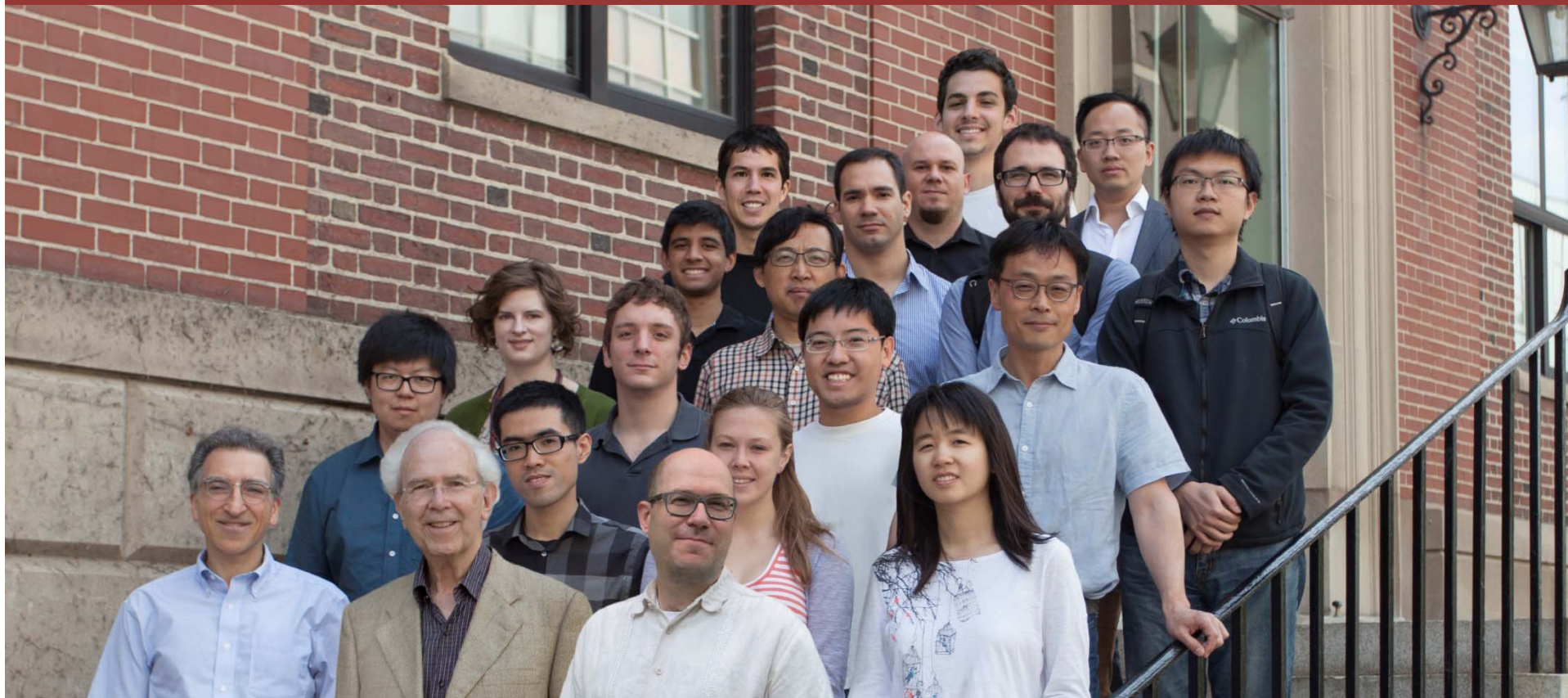


Use quinones in alkaline environment



**ENFL 403: Organic Aqueous Redox Flow Batteries**  
Prof. Michael J. Aziz  
Thursday, August 20, 1:35 pm Room 258B

# Thank You



**This work was partially funded through the US Department of Energy ARPA-E Award DE-AR0000348 and partially funded through the Harvard School of Engineering and Applied Sciences.**

*Top to bottom, left to right:*

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Lauren Hartle, Dr. Sungjin “James” Kim, Dr. Changwon Suh,  
Kaixiang Lin, Michael Gerhardt, Dr. Eugene Beh  
Dr. Qing Chen, Louise Eisenach, Jennifer Wei  
Prof. Michael Aziz, Prof. Roy Gordon, Prof. Alán Aspuru-Guzik

PLEASE DO NOT LOCK  
DOORS TO RAILINGS



# Assumptions for reversible case

- Linear, planar diffusion

$$- \frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2}$$

- Initial conditions:

$$- C_O(x, t = 0) = C_O^*, \quad C_R(x, t = 0) = 0$$

- Boundary conditions:

$$- C_O(x \rightarrow \infty, t) = C_O^*$$

- All current is diffusion controlled

$$- i(t) = nFAD_O \left( \frac{\partial C_O(x,t)}{\partial x} \right)_{x=0}$$

- Reversible reaction. Nernst equation applies:

$$- \frac{C_O(x=0,t)}{C_R(x=0,t)} = e^{(E_i - vt - E^0)nF/RT}$$

Notation follows Bard and Faulkner for the reaction  $O + ne \rightarrow R$ .

# Quasireversible Charge Transfer

- New boundary condition:

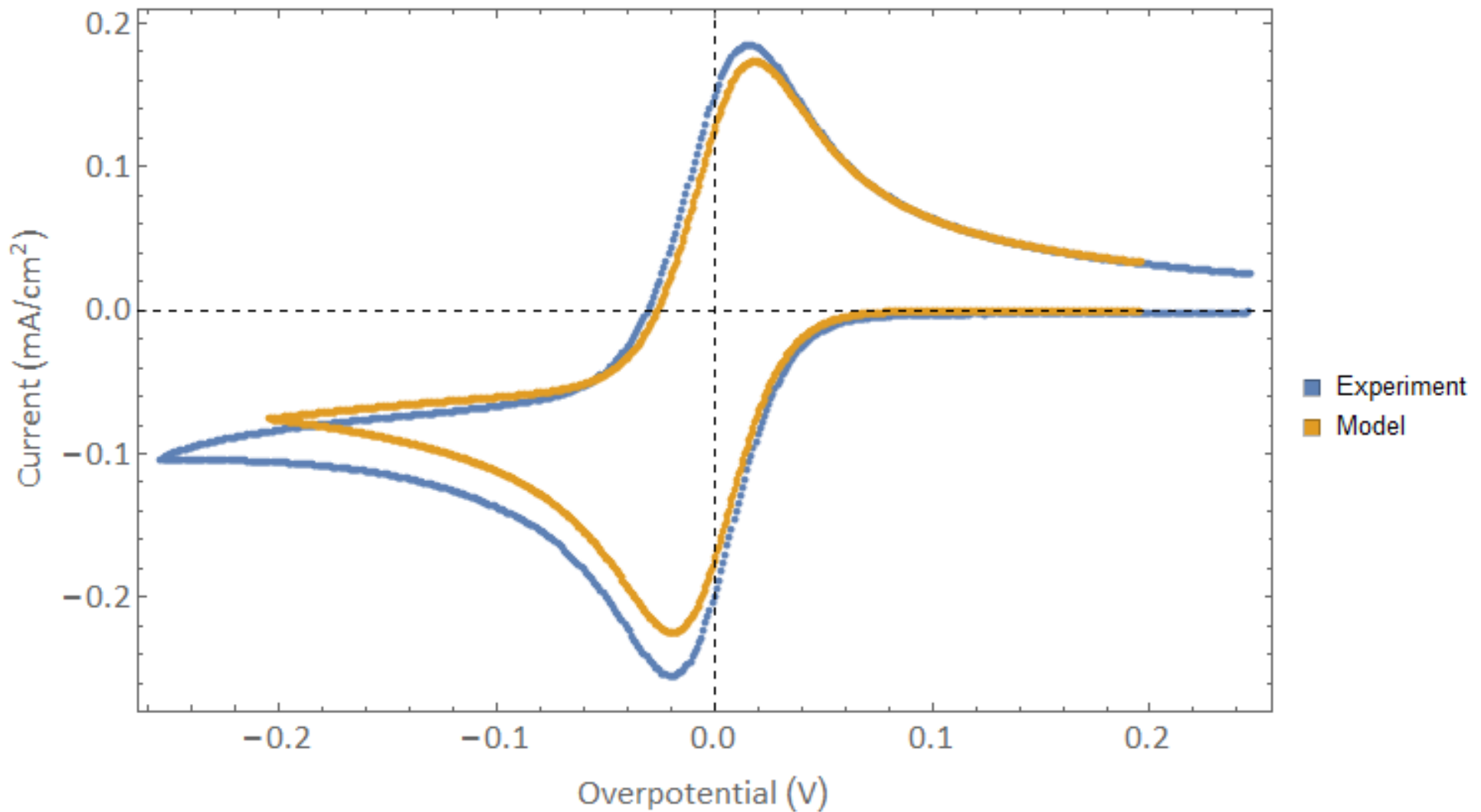
$$\frac{i(t)}{nFA} = D_O \left( \frac{\partial C_O(x, t)}{\partial x} \right)_{x=0} = k_f C_O(0, t) - k_b C_R(0, t)$$

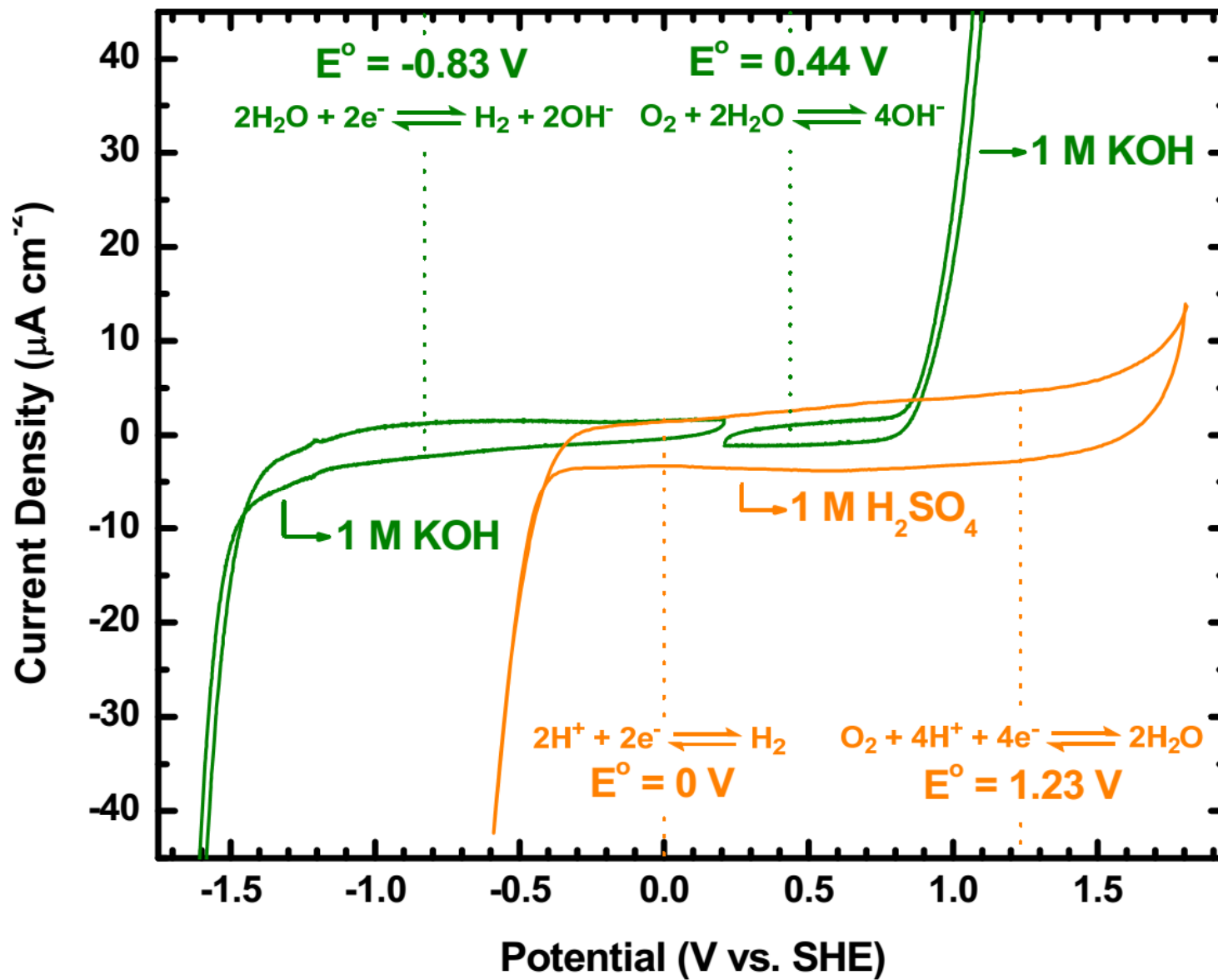
$$k_f = k_0 e^{\frac{-\alpha nF}{RT}(E-E^0)}, \quad k_b = k_0 e^{\frac{(1-\alpha)nF}{RT}(E-E^0)}$$

- Define a new variable:  $\psi = \frac{\gamma^\alpha k_0}{\sqrt{\pi a D_O}}$   $\psi \rightarrow \infty$ : Reversible  
 $\psi \rightarrow 0$ : Irreversible

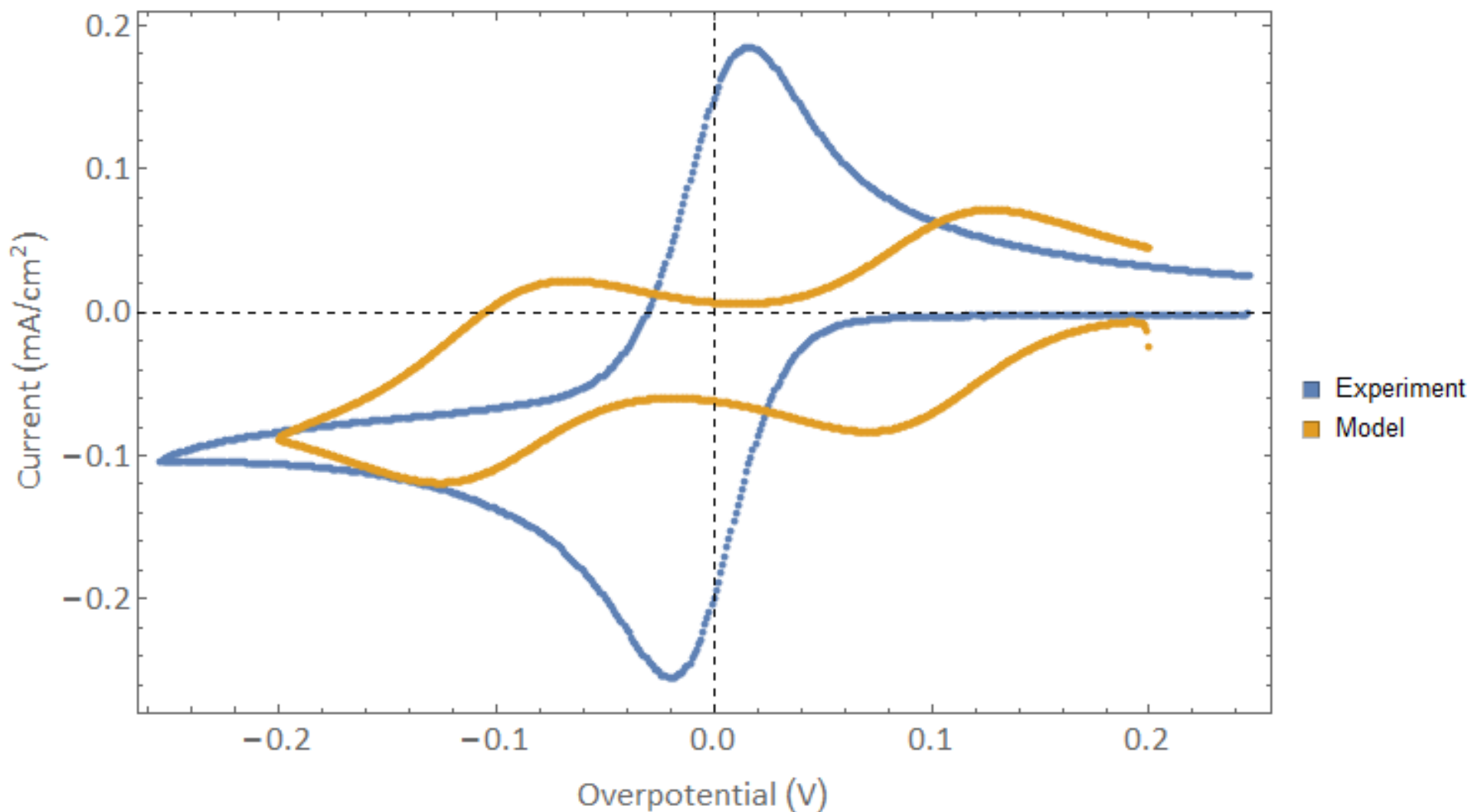
$$\frac{\chi(at) [\gamma(C_O^*/C_R^*) S(at)]^\alpha}{\psi} = 1 - S(at) - \int_0^{at} \frac{\chi(z) dz}{\sqrt{at-z}} - \gamma(C_O^*/C_R^*) S(at) \int_0^{at} \frac{\chi(z) dz}{\sqrt{at-z}}$$

# AQDS redox assuming $k_0 = 7.2 \times 10^{-3}$

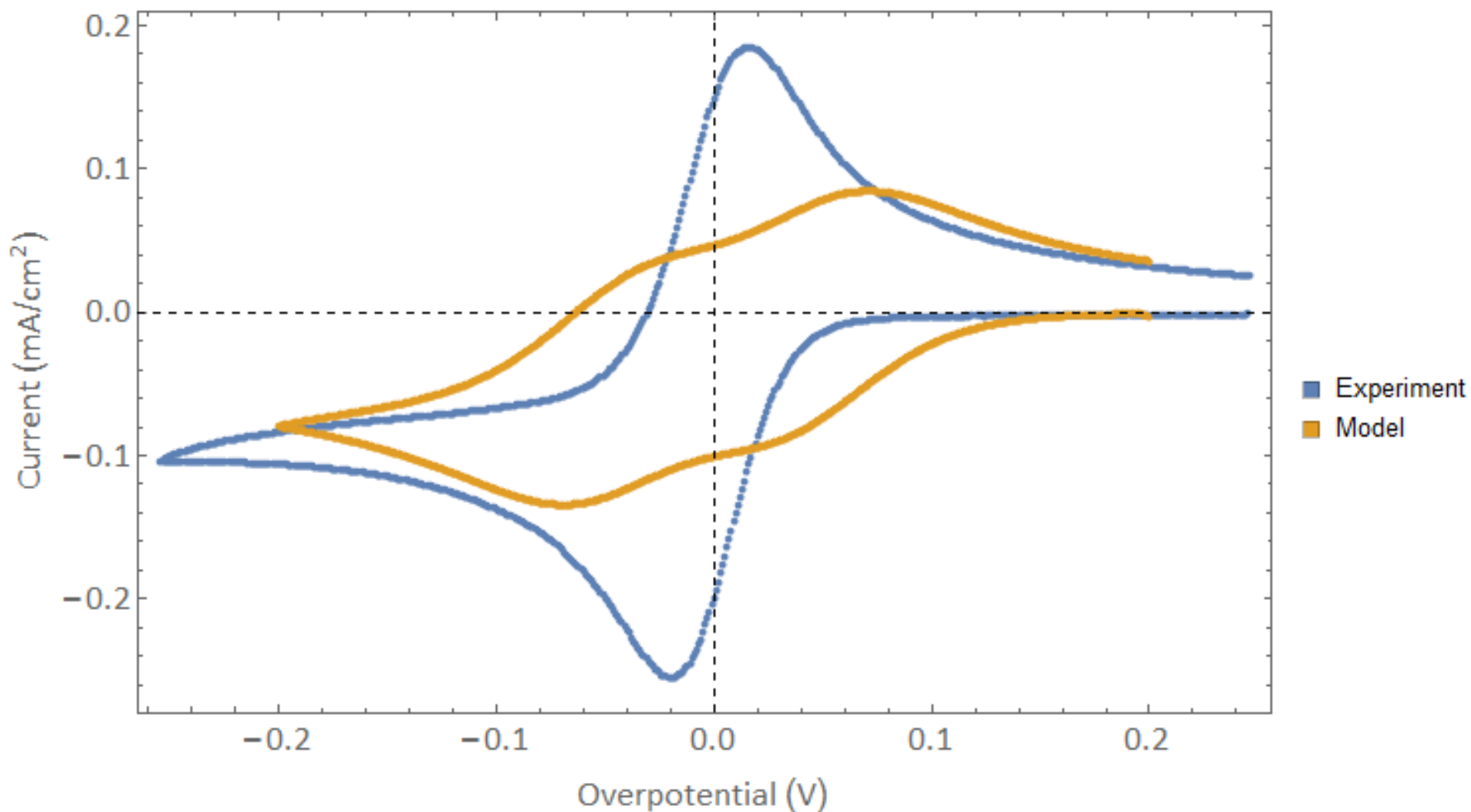




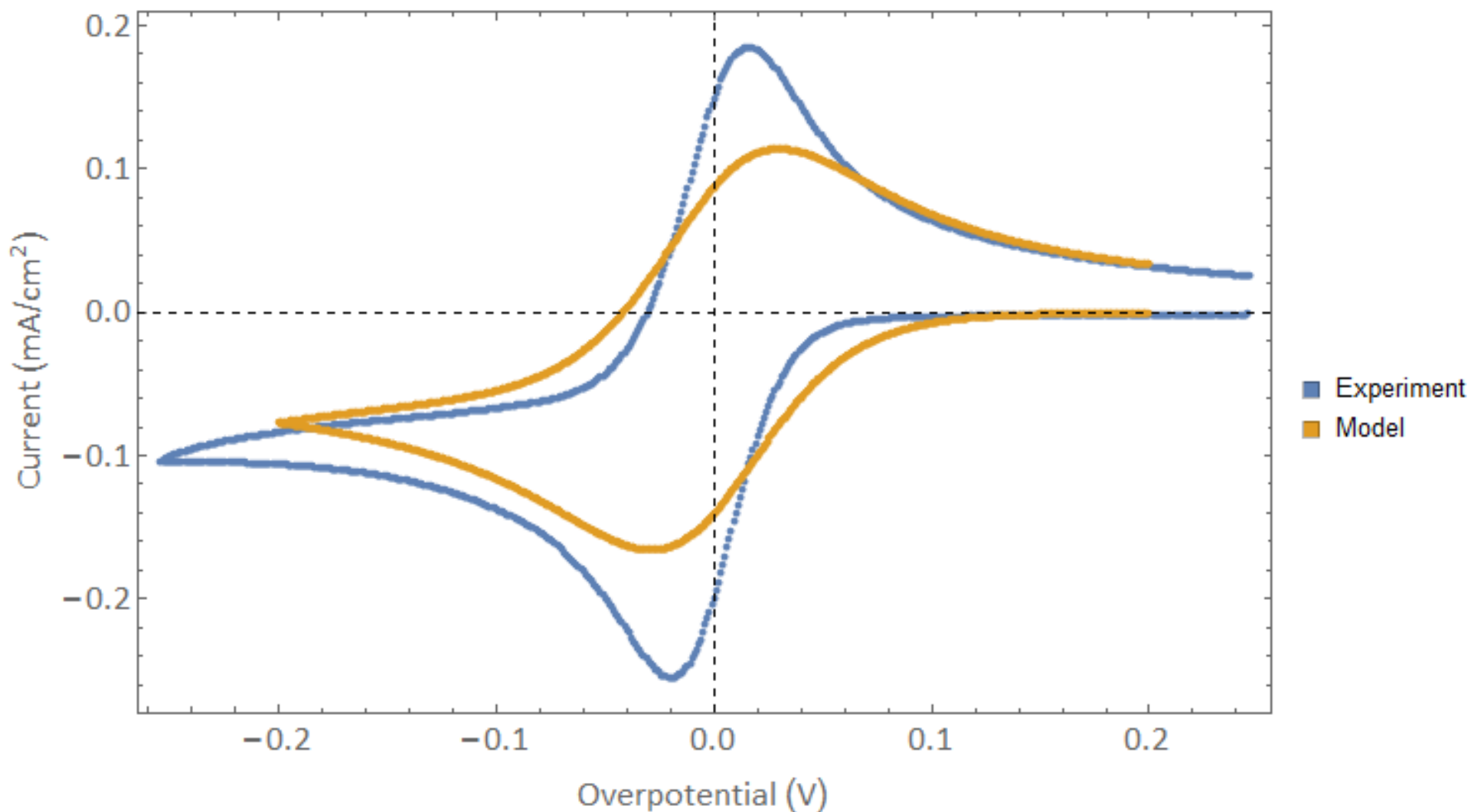
# The 1+1 model fails to explain AQDS redox



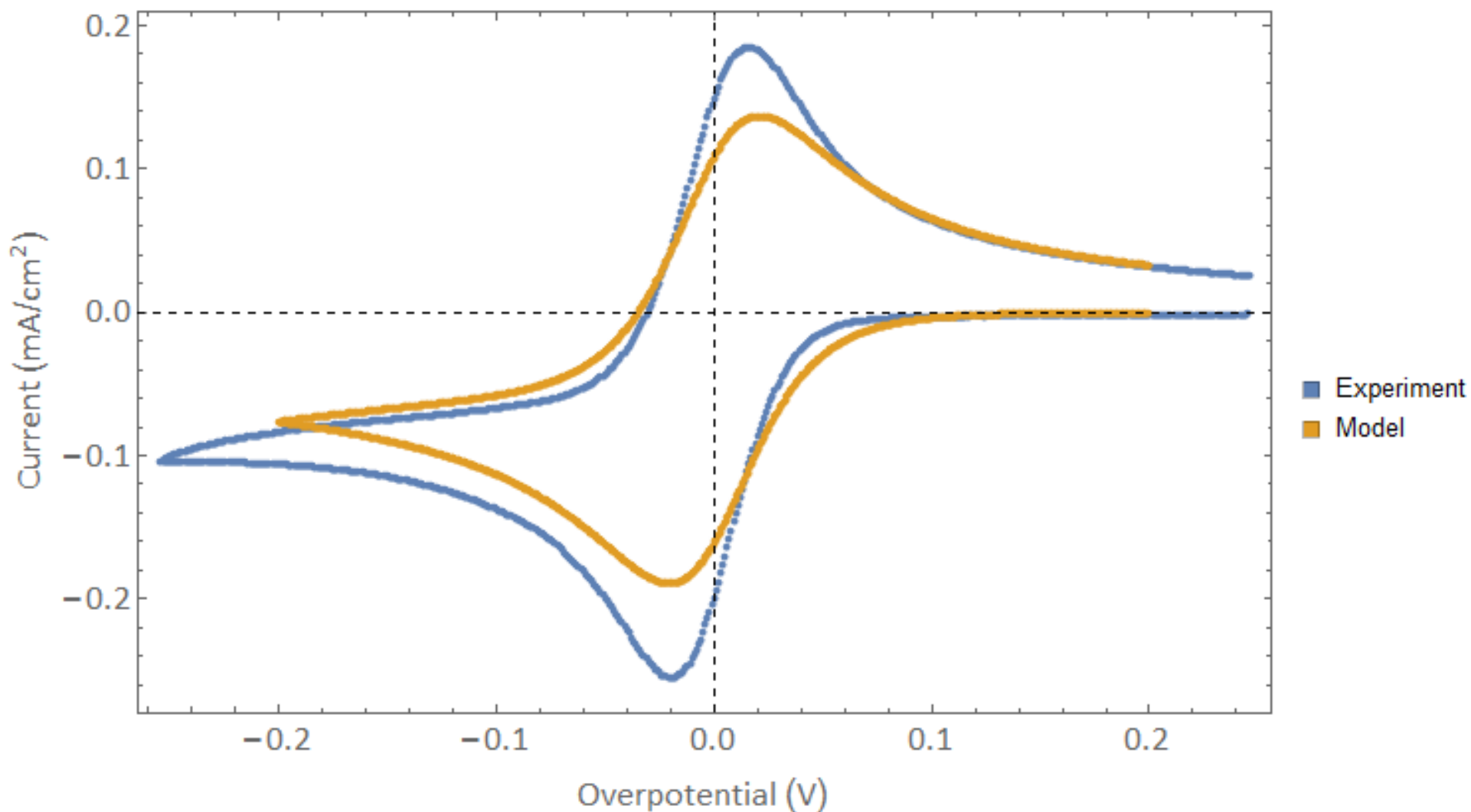
# The 1+1 model fails to explain AQDS redox



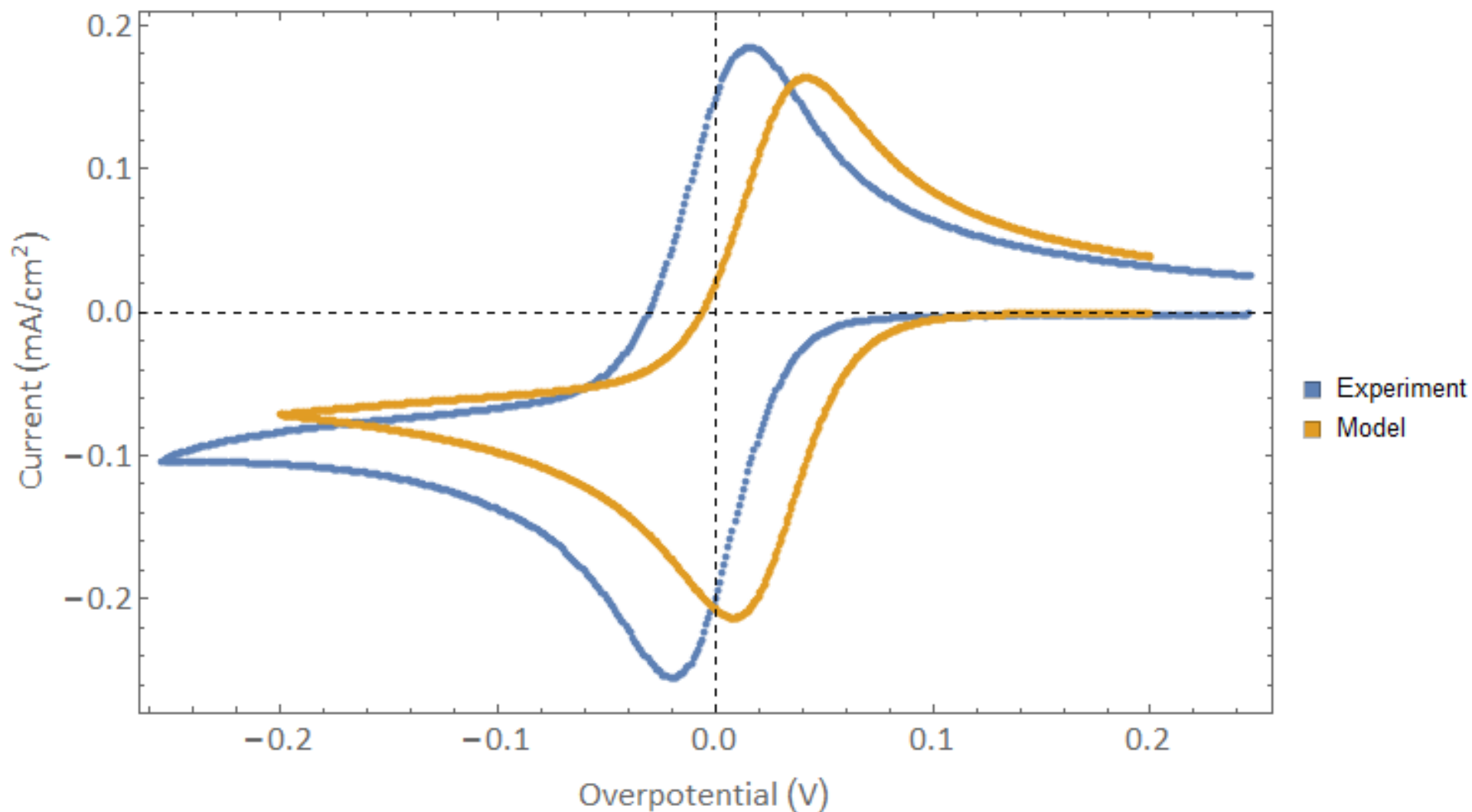
# The 1+1 model fails to explain AQDS redox



# The 1+1 model fails to explain AQDS redox



# The 1+1 model fails to explain AQDS redox



# Abstract text

Aqueous quinone/hydroquinone couples exhibit rapid redox kinetics, require no electrocatalyst, and are inexpensive, making them attractive candidates for large-scale energy storage devices such as flow batteries<sup>1–3</sup>. In acidic solutions, quinones undergo a rapid two-proton, two-electron reduction; however, in alkaline aqueous solutions, the picture is less clear<sup>4</sup>. Under the right conditions, a two-electron reduction can occur as successive one-electron steps separated by a small difference in the reduction potential of each step. The underlying mechanism for the reduction of various quinones is explored as a function of pH and reduction potential. Using substituted anthraquinones and the bromine/hydrobromic acid couple, a flow battery exhibiting an open circuit voltage above 1.0 V and a peak galvanic power density above 0.7 W cm<sup>-2</sup> is demonstrated. Furthermore, by employing soluble metal coordination complexes, a flow battery with an open circuit voltage exceeding 1.3 V is demonstrated. Mechanisms of capacity loss during cell cycling are discussed.

(1) Huskinson, B.; Marshak, M. P.; Suh, C.; Er, S.; Gerhardt, M. R.; Galvin, C. J.; Chen, X.; Aspuru-Guzik, A.; Gordon, R. G.; Aziz, M. J. *Nature* **2014**, 505 (7482), 195.

(2) Huskinson, B.; Marshak, M.; Gerhardt, M.; Aziz, M. *ECS Trans.* **2014**, 61 (37), 27.

(3) Yang, B.; Hooper-Burkhardt, L.; Wang, F.; Surya Prakash, G. K.; Narayanan, S. R. *J. Electrochem. Soc.* **2014**, 161 (9), A1371.

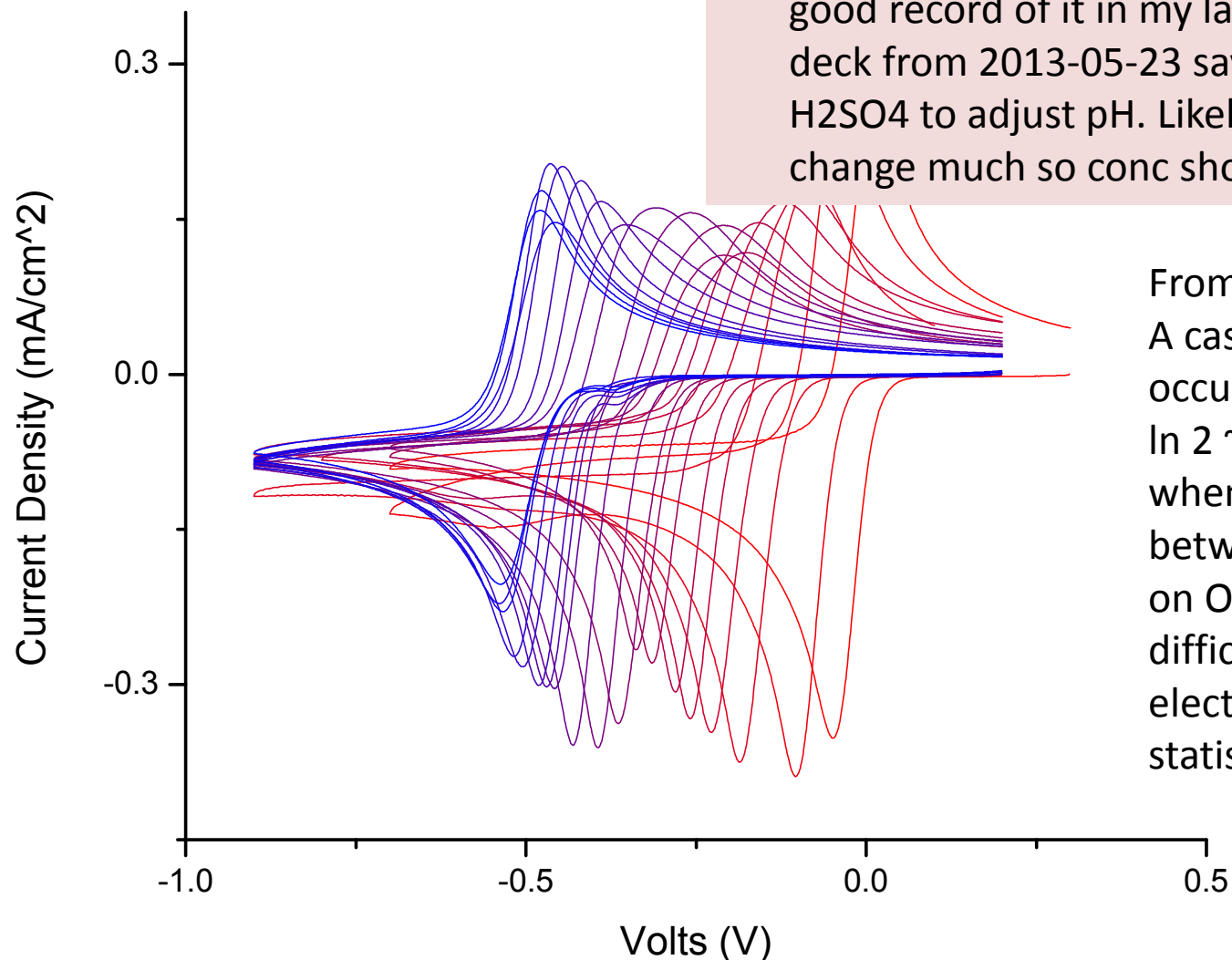
(4) Quan, M.; Sanchez, D.; Wasylikiw, M. F.; Smith, D. K. *J. Am. Chem. Soc.* **2007**, 129 (42), 12847.

Check out 2013-04-xx thru 2013-06-xx  
In Half Cell Electrochemistry

Also the Pourbaix diagram origin file

1. Is concentration constant?

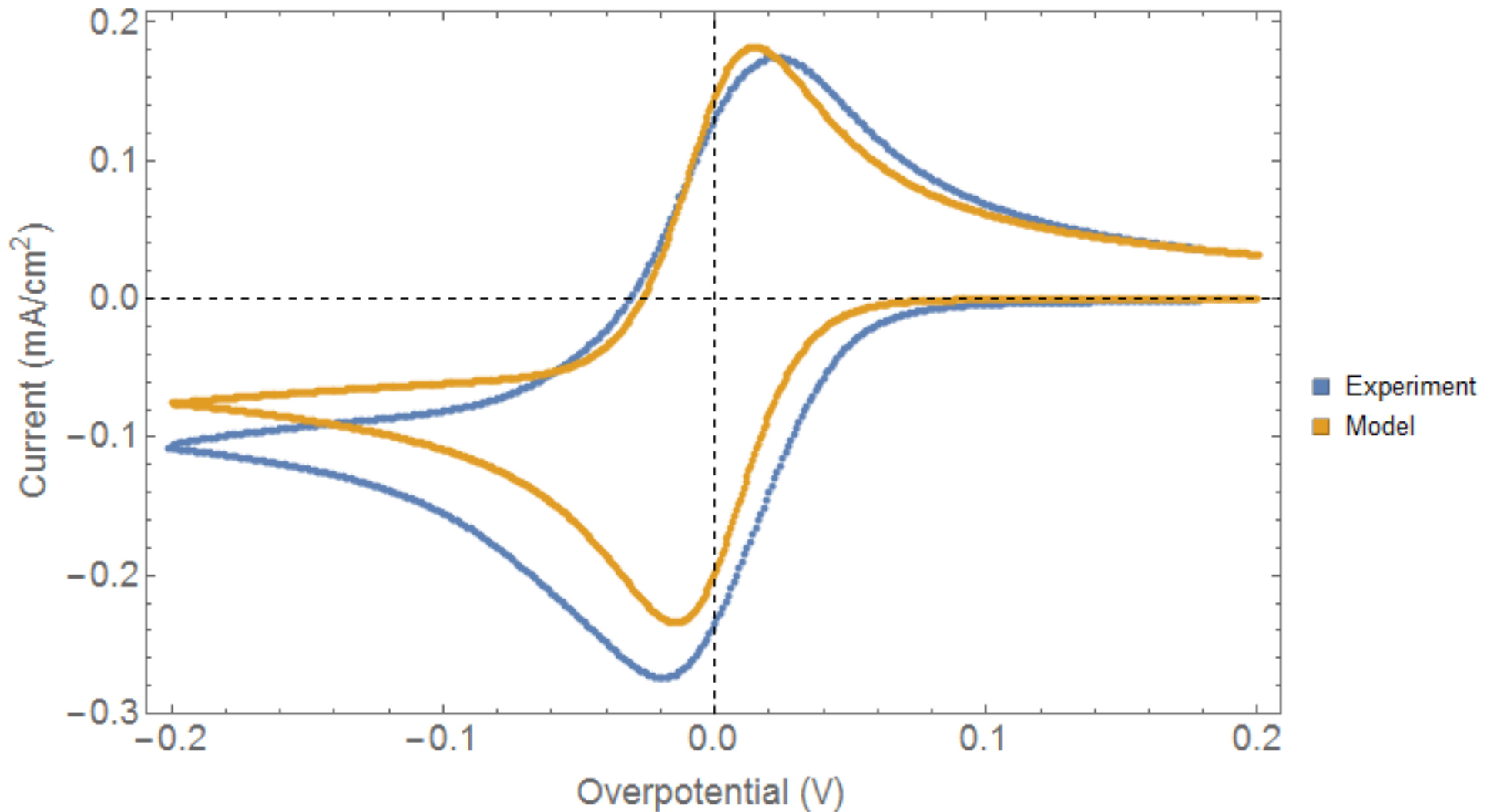
I think it's a fair assumption to make. I don't explicitly say it is anywhere and I don't have a good record of it in my lab notebook. But my slide deck from 2013-05-23 says I was adding KOH and H<sub>2</sub>SO<sub>4</sub> to adjust pH. Likely the volume didn't change much so conc shouldn't change much.



From Bard:

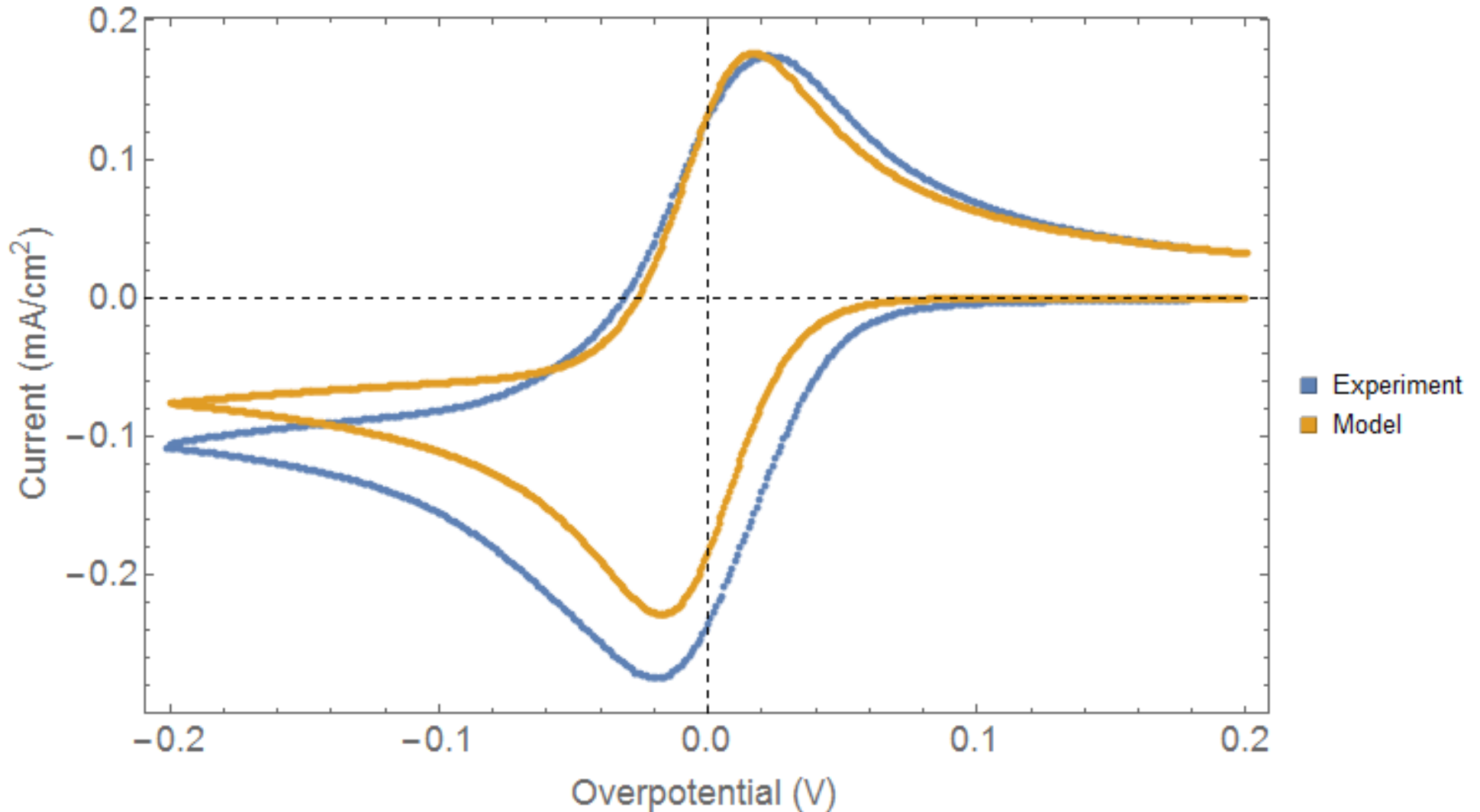
A case of particular interest occurs when  $\Delta E_0 = -2RT/F \ln 2 \sim -35.6$  mV. This occurs when there is no interaction between the reducible groups on O, and the additional difficulty adding the extra electron arises purely from statistical (entropic) factors.

# DHAQDS redox is less clear



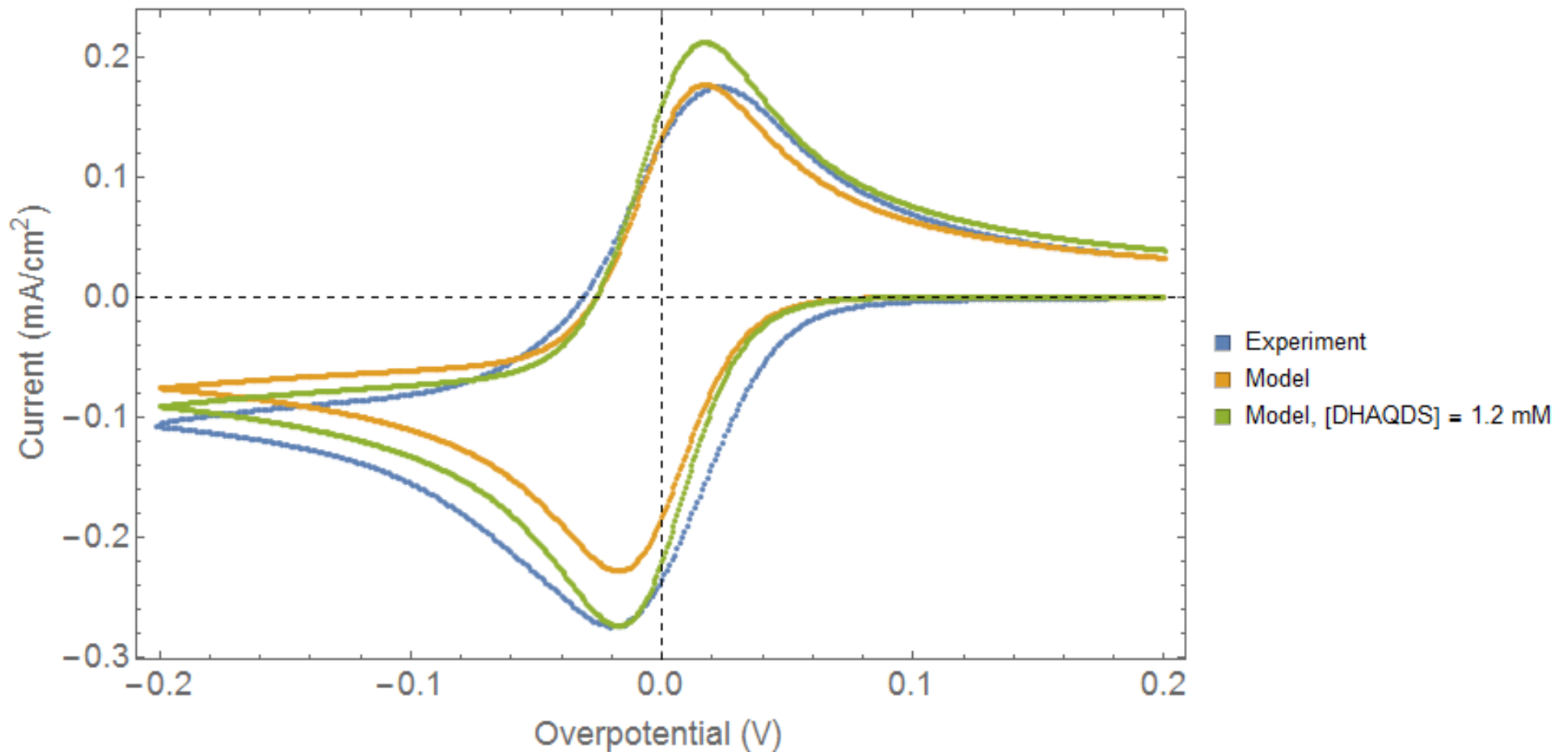
Reversible model doesn't quite fit

# DHAQDS redox is less clear



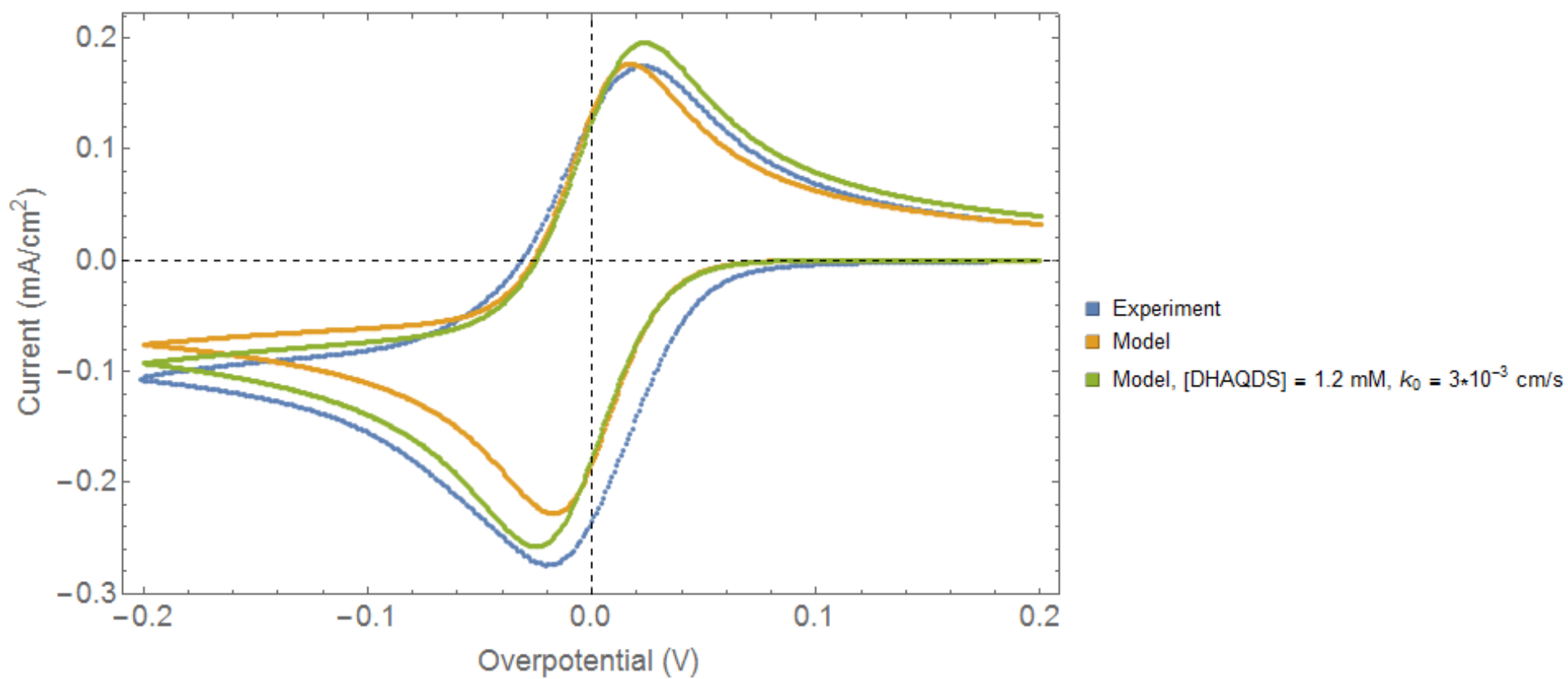
Plugging in measured  $k_0$  value helps a little

# DHAQDS redox is less clear



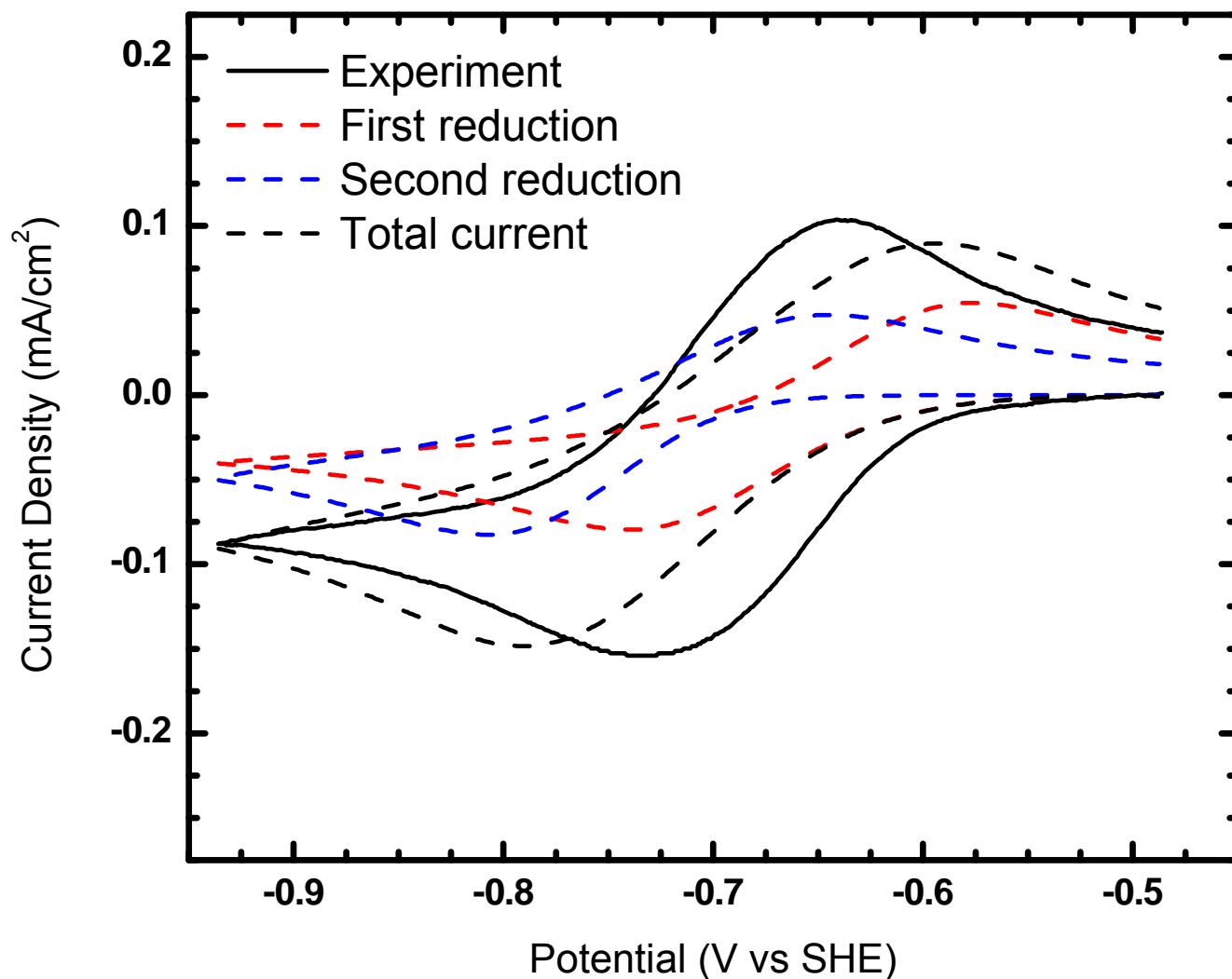
Assuming a higher bulk DHAQDS concentration explains the height of the reduction peak 59

# DHAQDS redox is less clear



Assuming more sluggish kinetics on top of concentration error doesn't explain it

# Setting a lower bound on $k_0$ for 2,6-DHAQ



$E_{0,1} = -0.657$  vs SHE  
 $k_{0,1} = 7 * 10^{-4}$  cm/s  
 $E_{0,2} = -0.717$  vs SHE  
 $k_{0,2} = 7 * 10^{-4}$  cm/s

# Sequential 1 e<sup>-</sup> transfers could explain CV

