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Photoelectrochemical Water-splitting Ancillary Components

Robert A. Allen
DePauw University

Todd G. Deutsch
DePauw University

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Overview

- Khasalev and Turner developed a high efficiency Photoelectrochemical (PEC) cell for water-splitting under zero bias (Figure 1). The Solar-to-Hydrogen efficiency was reported at 12.4%
- Use of surfactant is crucial to extend cell lifetime by removing H_2 bubbles swiftly from the photocathode
- However, yellowing of solution and cell performance loss over time are still observed.
- These issues are believed to be due to fouling of the counter-electrode from surfactant oxidation

Figure 1a: Khasalev and Turner PEC Device

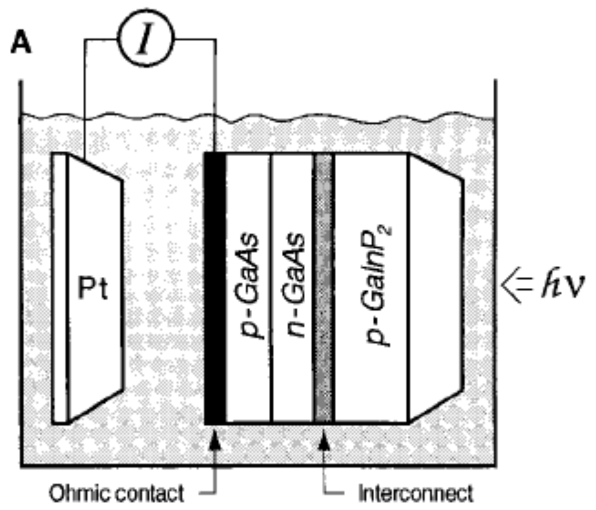
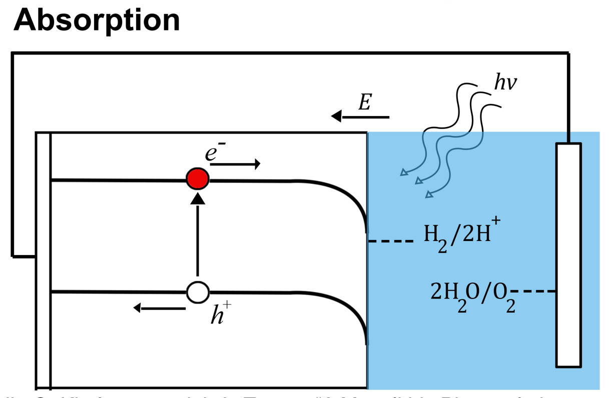


Figure 1b: Photoelectrode Light Absorption



Photocredit: O. Khalesev, and J. A. Turner, "A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting," Science. 280, 425-427 (1998).

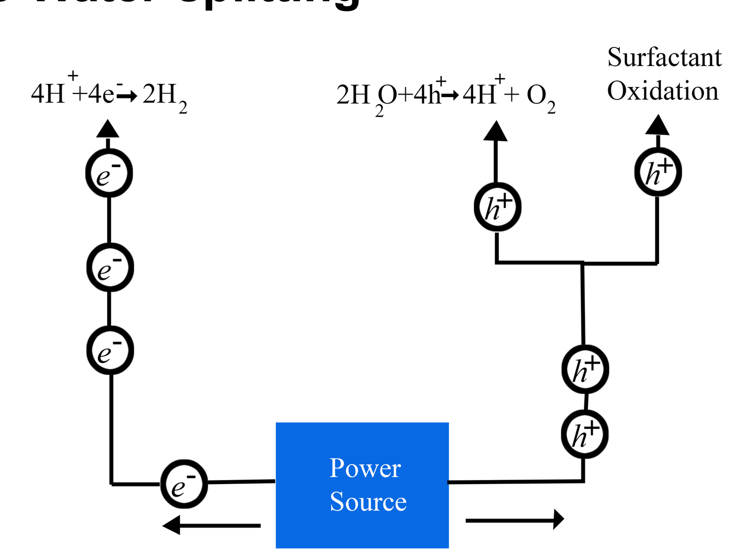
Redox Reactions for Water Electrolysis in Acid

	Potential vs. NHE at STP (V)
Reduction: $4H^+ + 4e^- \rightarrow 2H_2$	0.0
Oxidation: $2H_2O + 4h^+ \rightarrow 4H^+ + O_2$	1.23

Objectives

- Perform electrolysis where the evolved gases can be collected and compared with a theoretical amount of gas that should have been created given the amount of coulombs passed through the cell. The ratio of the two values is known as the **Faradaic Efficiency**.
- Compare the Faradaic efficiencies calculated using different surfactants and combinations of electrodes. In order to understand if counter-electrode fouling is really happening

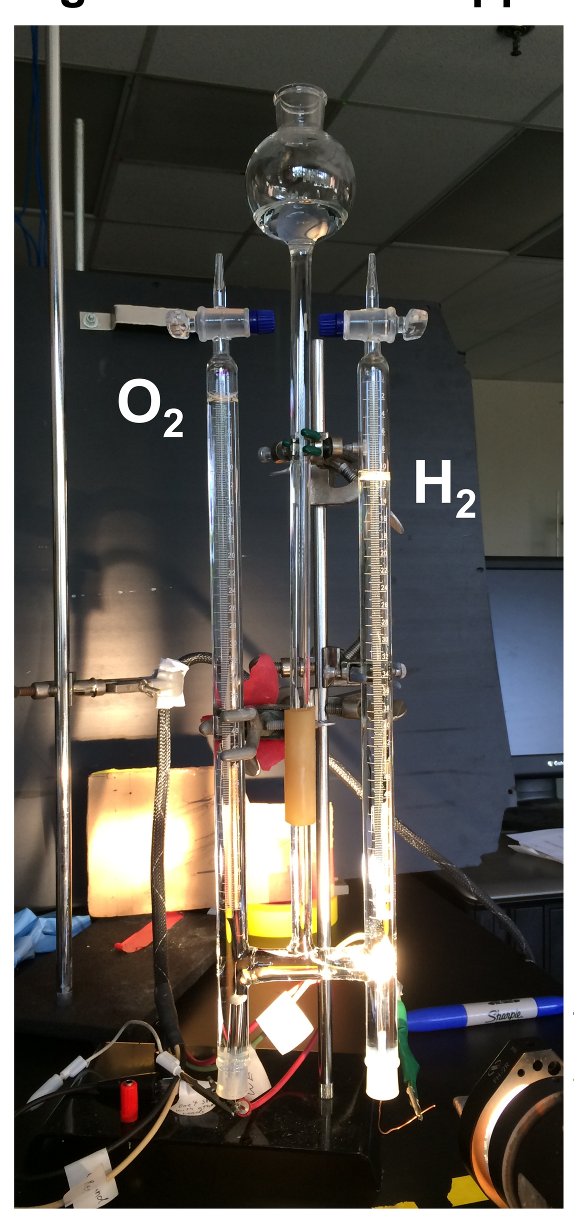
Figure 2: Possible Current Pathways for PEC Water-splitting



Electrolysis

- Electrolysis was performed in the presence of three different surfactants over a range of electrode combinations
- **Cathodes Used (Hydrogen Evolving Electrodes):** Pt and III-V photoelectrode ($GaInP_2$)
- **Anodes Used (Oxygen Evolving Electrodes):** Pt, Pt Black and RuO_2
- **Surfactants:** Triton X-100, Zonyl FSN-100, Capstone FS-3100
- **Electrolyte:** 3 M H_2SO_4 (Sulfuric Acid)

Figure 3: Hoffman Apparatus



Faradaic Efficiency Calculation:

$$Faradaic\ Efficiency\ (H_2) = \frac{\left(\frac{P_g V}{RT}\right)}{(Coulombs\ Passed) * \left(\frac{mol\ e^-}{96485\ C}\right) * \left(\frac{1\ mol\ H_2}{2\ mol\ e^-}\right)}$$

P_g= (Atmospheric pressure- Water Vapor Pressure + Electrolyte Pressure)

V = measured Volume

R= 0.08206 L*atm/mol*K

T= Temperature in Kelvin

An estimate for oxygen solubility in solution was also added to O_2 Fardaic effiencies, given 7.25 mg/L

Figure 4a and 4b: Electrodes

4a: Working-electrodes from left to Right: Pt, Pt w/ epoxy and back contact, $GaInP_2$ with back contact

4b: Counter-electrodes from left to right: Pt, Pt (Black), RuO_2

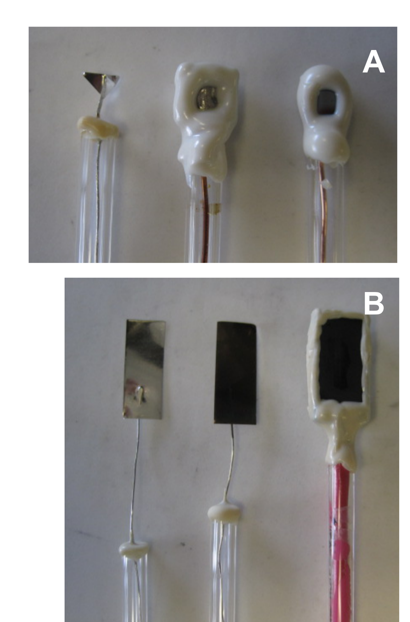


Figure 5a: Triton X-100

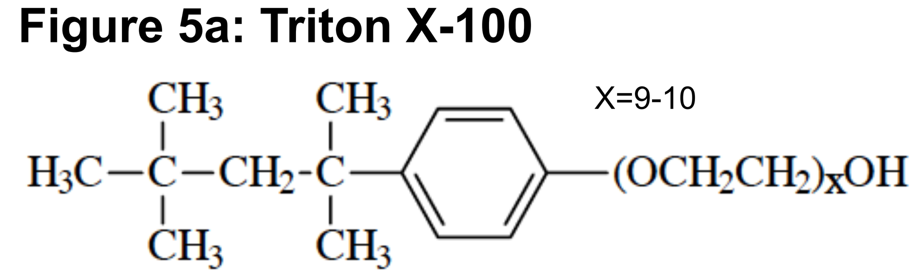
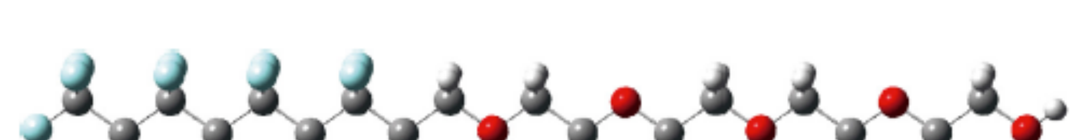


Figure 5b: Zonyl FSN-100



Hydrophobic part (fluorocarbon chain) — **Hydrophilic part** (polyoxyethylene chain)

Zonyl FSO-100 : $F(CF_2CF_2)_{1-7}CH_2CH_2O(CH_2CH_2O)_{0-15}H$

Zonyl FSN-100 : $F(CF_2CF_2)_{1-9}CH_2CH_2O(CH_2CH_2O)_{0-25}H$

Photocredits: Figure 4a. SIGMA, "Triton X-100," Product Information, sigma-aldrich.com (17July 2014). Figure 4b. W. Lingyun, L. Zhang, and C. Lu, "Applications in Analytical Chemistry using the Attractive Properties of Non-ionic Flurosurfactants," TrAC, **54**, 45-55 (2014)

Faradaic Efficiency

Figure 6a: H_2 Faradaic Efficiencies (~80 mA/cm² Working Electrode)

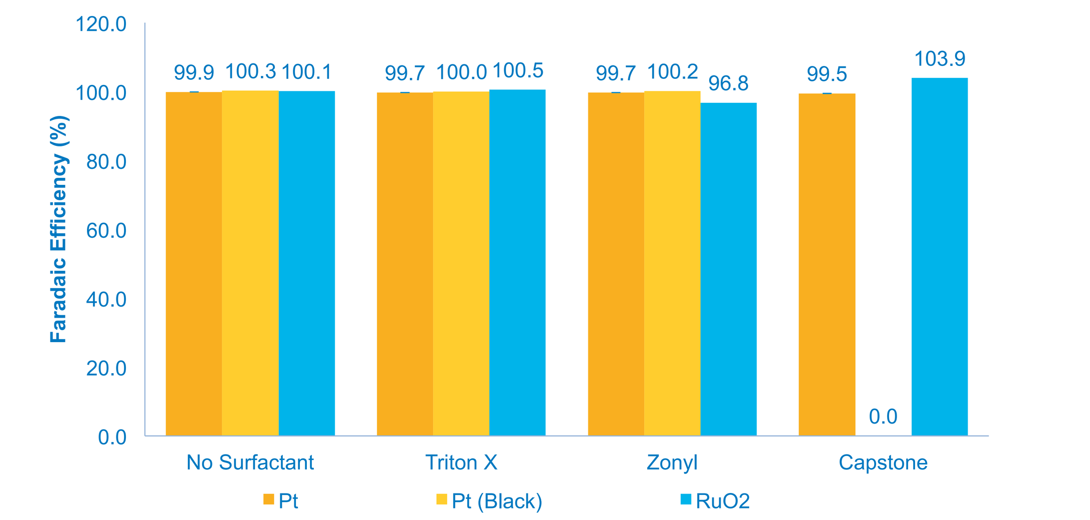
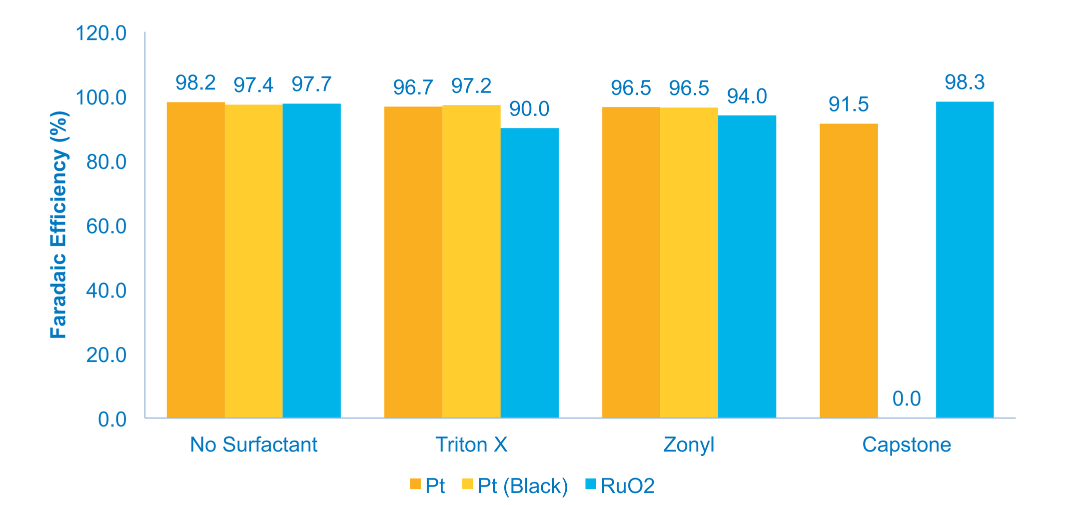


Figure 6b: O_2 Faradaic Efficiencies (~6 mA/cm² Counter Electrode)



- Efficiency results show little H_2 or O_2 loss regardless of surfactant (with Pt, Pt (Black) and RuO_2 electrodes). Assuming an uncertainty in measurement of roughly 3-4% based on the variability between multiple trials, the uncertainty in the dissolved oxygen, and the changing density of solution with different added surfactants.
- These results suggest surfactant does not oxidize in the presence of metal/metal oxide electrode under these conditions.

Figure 7a: H_2 Faradaic Efficiencies w/ Epoxy Covered Electrodes

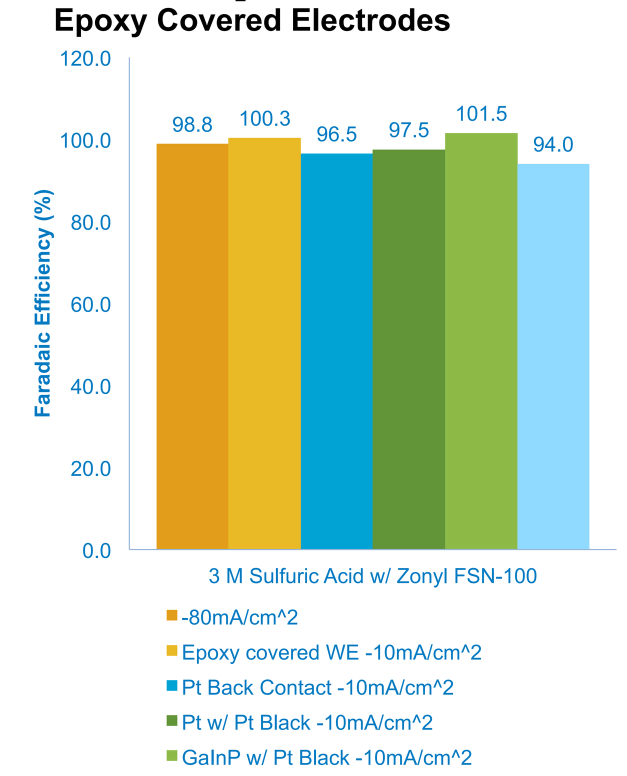
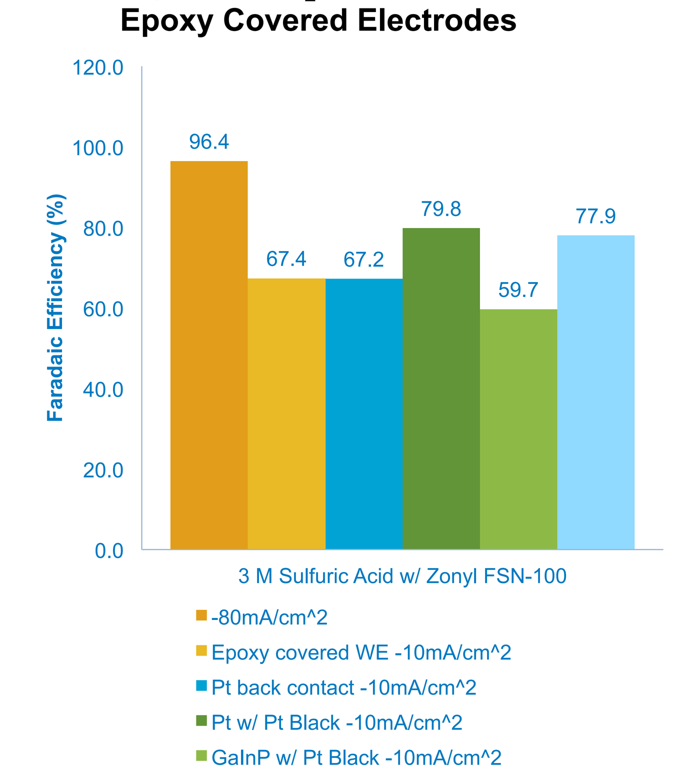


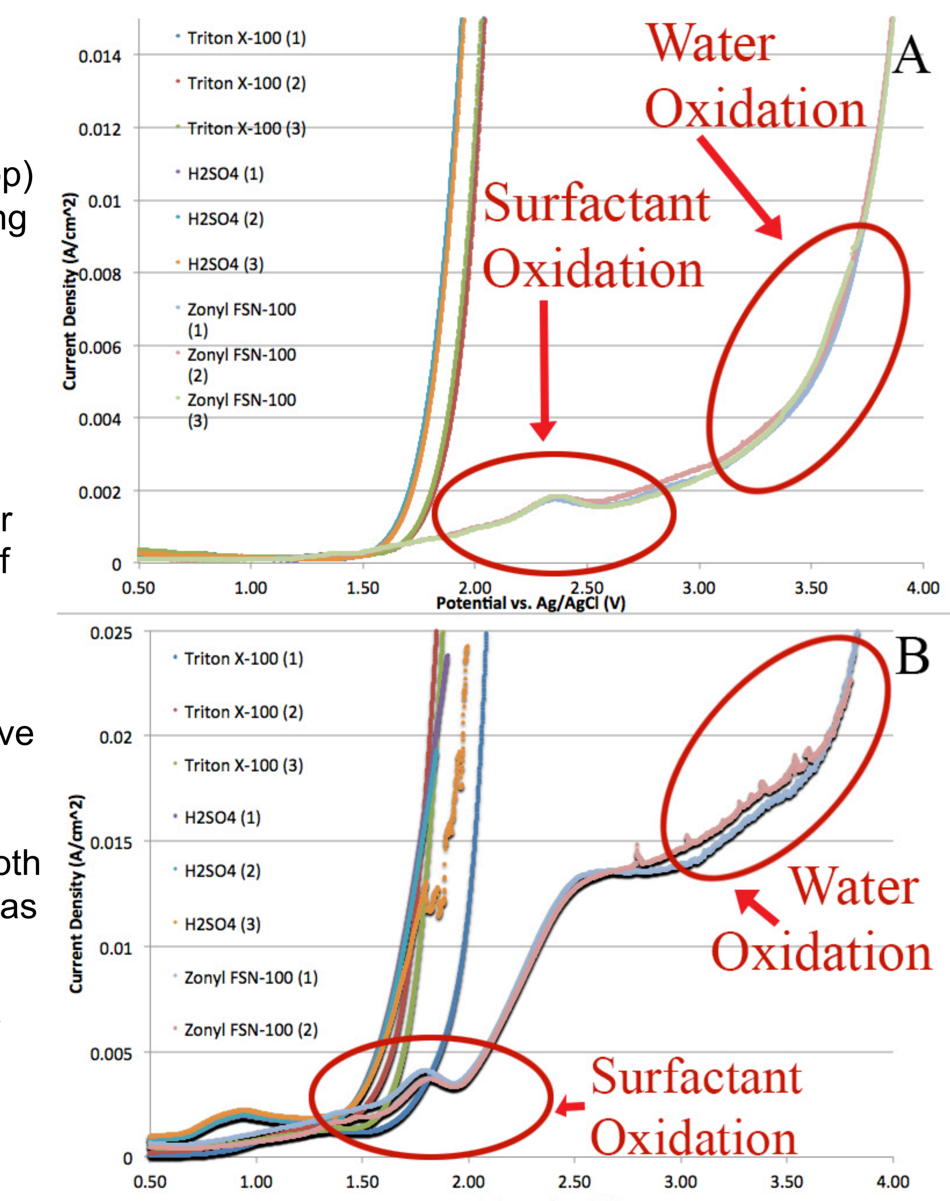
Figure 7b: O_2 Faradaic Efficiencies w/ Epoxy Covered Electrodes



- ~22% and ~40% carrier-selectivity loss for O_2 seen with the use of the $GaInP_2$ photocathode depending on surfactant
- All trials with large oxygen losses were run at low current densities. Experiments, as a result, lasted for 8+ hours, depending on the trial. One possible explanation is that amines from the epoxy are being oxidized after diffusing from the cathode to the anode. This would reasonably require large timescales to see any effect.
- Similar loss **ALSO** seen with **epoxy covered Pt cathode**.
- Carrier-selectivity loss may be dependent on the use of Loctite ® 9462 Hysol ® epoxy, for electrode construction, more than any other variable
- The presence of surfactant, though, still seems necessary for the efficiency loss and **superior charge-carrier selectivity for O_2 is observed in Triton X-100** compared to Zonyl FSN-100

Surfactant Oxidation

Figure 8a and 8b: Three electrode J-V Curves for Surfactant Oxidation



- Three electrode *J-V* data taken with a Pt working electrode (top) and Pt (Black) working electrode (bottom) in H_2SO_4, H_2SO_4 with Triton X-100 and H_2SO_4 with Zonyl FSN-100
- Triton X-100 behavior quite similar to that of pure H_2SO_4
  - Similar water oxidation onset potentials and curve behavior
- Zonyl FSN-100 for both types of electrodes has a much higher onset potential and a **local maximum** at ~2.25V (top) and ~1.75V (bottom).

- Local maximum feature suggests surfactant oxidation in Zonyl FSN-100, **more readily than Triton X-100**
- **Exponential increase in current upon water oxidation onset potential. Suggests O_2 losses are dependent on operating at lower potentials where the two reactions are competitive with one another**
- **If operating potential is too high, the ratio of surfactant oxidation to water oxidation will be negligible.**

Conclusions

- The fluorosurfactant Zonyl FSN-100 was originally believed to offer greater resistance to oxidation than the hydrocarbon surfactant Triton X-100. Faradaic efficiencies with metal/metal oxide electrodes show no greater resistance to oxidation by running with Zonyl FSN-100
- Moreover, J-V measurements show that higher operating potentials are required with Zonyl surfactant as opposed to Triton X-100 making it beneficial to return back to the surfactant Triton X-100
- Significant O_2 gas losses are attributed to amine groups in the epoxy which diffuse and oxidize at the counter-electrode.
- **Future work:** (1) exploring Faradaic efficiency with the use of compression cells to eliminate presence of epoxy. (2) Whether the epoxy only needs to be present in solution to cause the effect, and not necessarily connected to the working electrode. (3) Electrolysis with Nafion® membrane separating electrodes

Acknowledgements

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