Performance of Selemion AMV in Solar Fuels Device

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Abstract:

In membrane electrode assemblies, the membrane plays an important role as it allows the transport of charge-carrier ions while inhibiting that of CO_2 reduction products in order to prevent re-oxidation reactions which compromise the device's overall efficiency. When running the device in a mildly alkaline environment with a highly negative working potential, the production of liquid fuel hydrocarbons increases while production of hydrogen decreases. However, as the working potential becomes increasingly negative, device instability can also increase. The goal of this study is to develop an experimental approach that implements a highly negative working potential while maintaining a high and stable current density. Chronoamperometry (CA) was used to monitor device stability over time and potentiostatic electrochemical impedance spectroscopy (PEIS) was used to gauge the extent of membrane degradation.

Introduction

- C-C coupling best promoted in a mildly alkaline environment
- Selemion AMV employed due to the following properties:
  - Anion exchange membrane
  - Ability to handle high current densities
  - Commercially (readily) available
  - Widely studied, providing wealth of reference materials

Team

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Outlook

By studying the capabilities of a commercial membrane to maintain a high and stable current density, as well as its resistance to decay, a foundation is laid for additional improvements for experimentation in the future and in turn, improvements to overall device operation.

Acknowledgments

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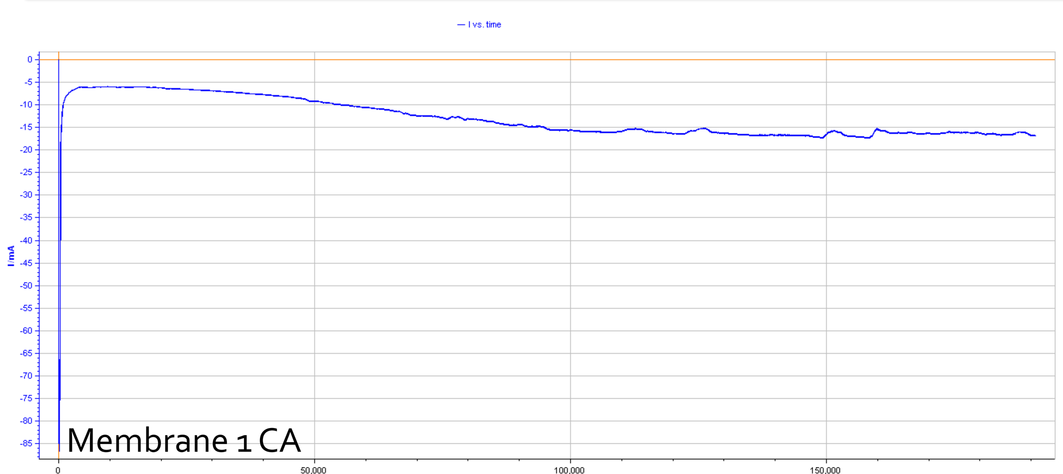
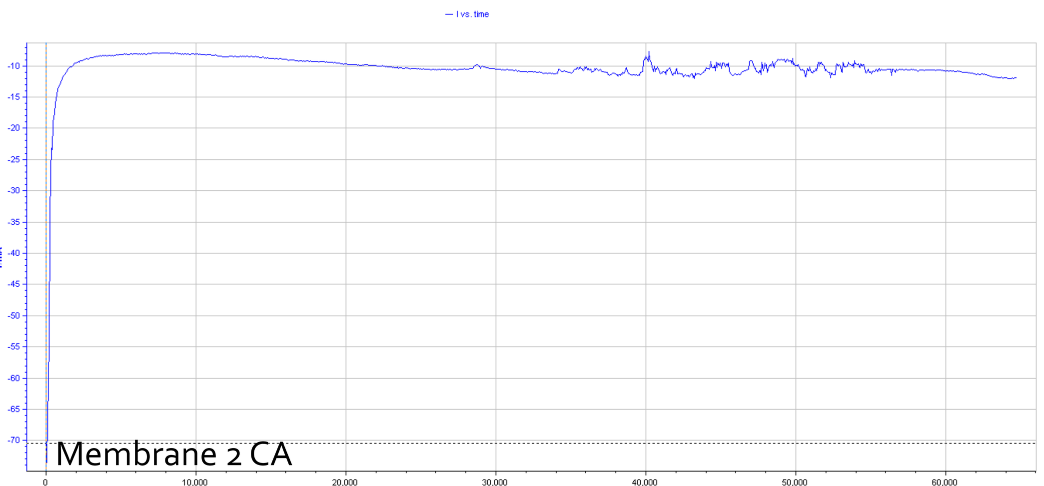
Results, Highlights, and Accomplishments

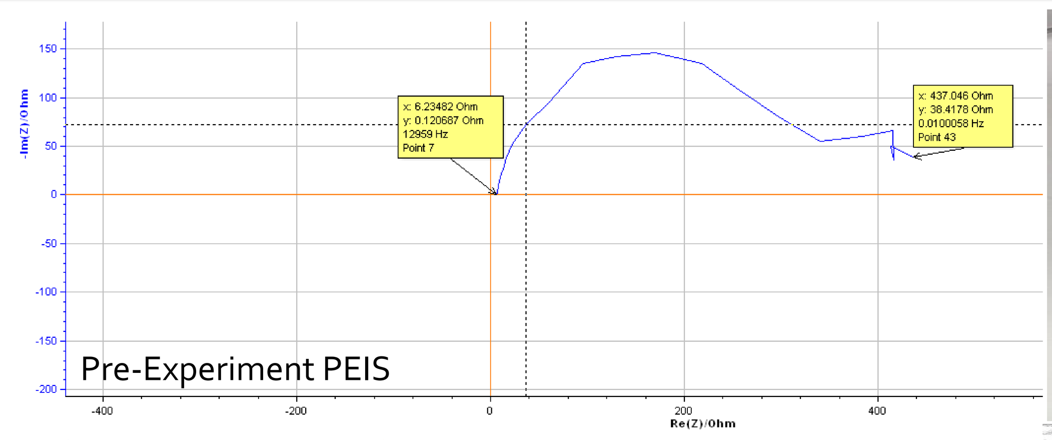


Membrane 1 CA

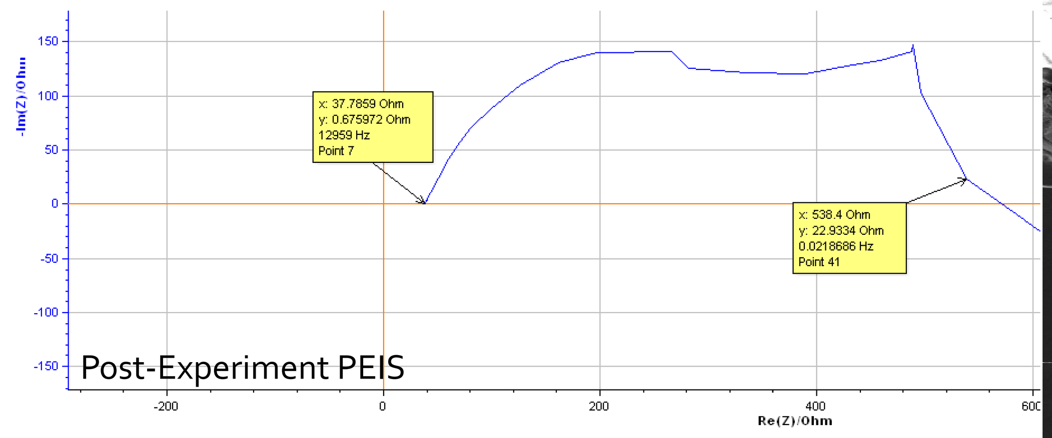


Membrane 2 CA

- Reproducible, stable current
- Current density plateaus from 1.25-2.75 h
- Average magnitude of plateau: 4-14 mA
- Gradual increase in current density
  - Suggests membrane degradation
- Fluctuations begin to occur between 11-15 h
  - Fluctuations approximately 1.5-3 mA in magnitude
  - Intervals last 1.5-2.5 h
  - Potentially explained by gas buildup/membrane drying out and subsequently re-equilibrating with liquid electrolyte

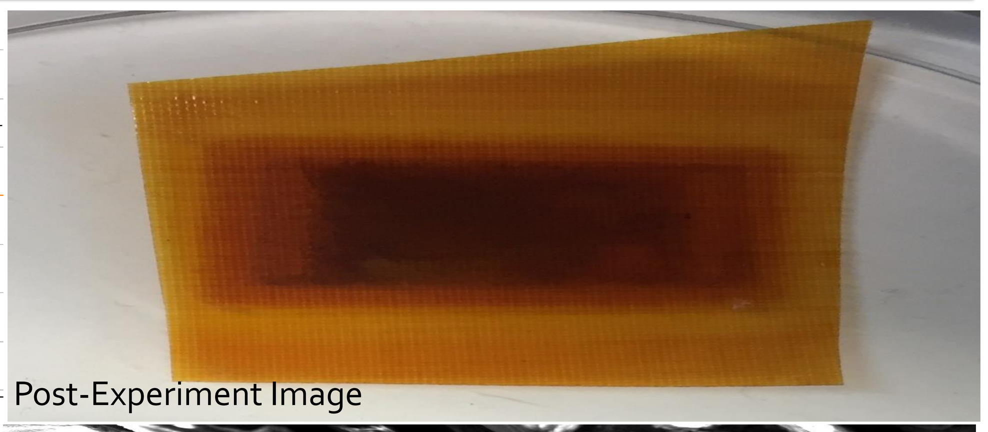


Pre-Experiment PEIS

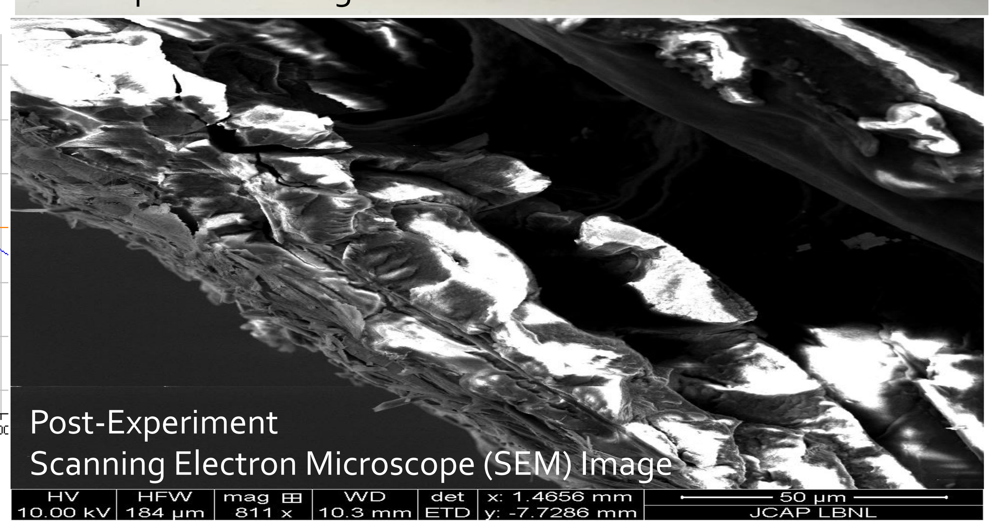


Post-Experiment PEIS

- Average increase of intercept 1: 30-40 Ω (increased membrane resistance)
- Average increase of intercept 2: 100 Ω (implies corrosion of electrodes)
- Increase of current density typically associated with a drop in resistance
- Potential explanations for anomaly:
  - Membrane degradation could allow greater ionic transport, leading to an increase in current density
  - Buildup of catalyst/precipitate on membrane surface causing inflation of resistance
  - Side reaction with membrane to provide another source of ions/current



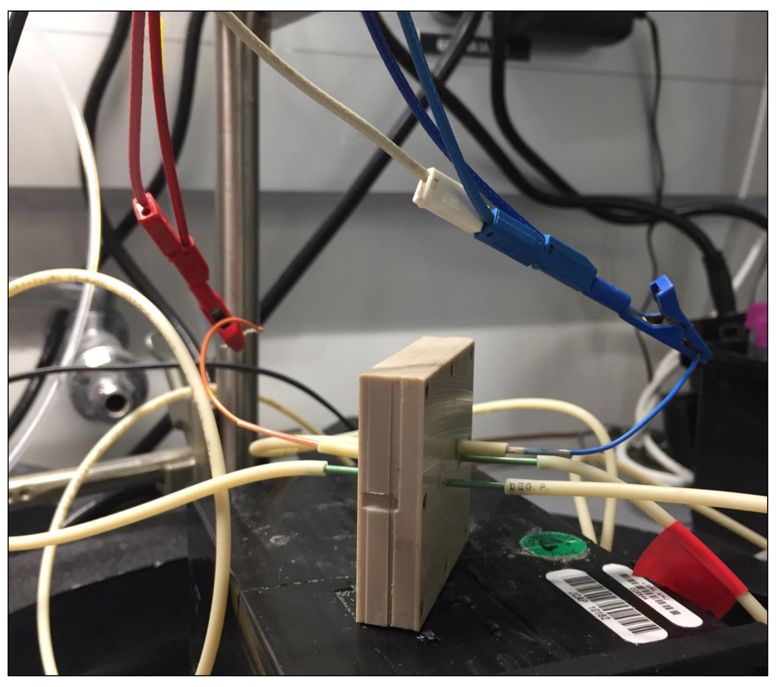
Post-Experiment Image



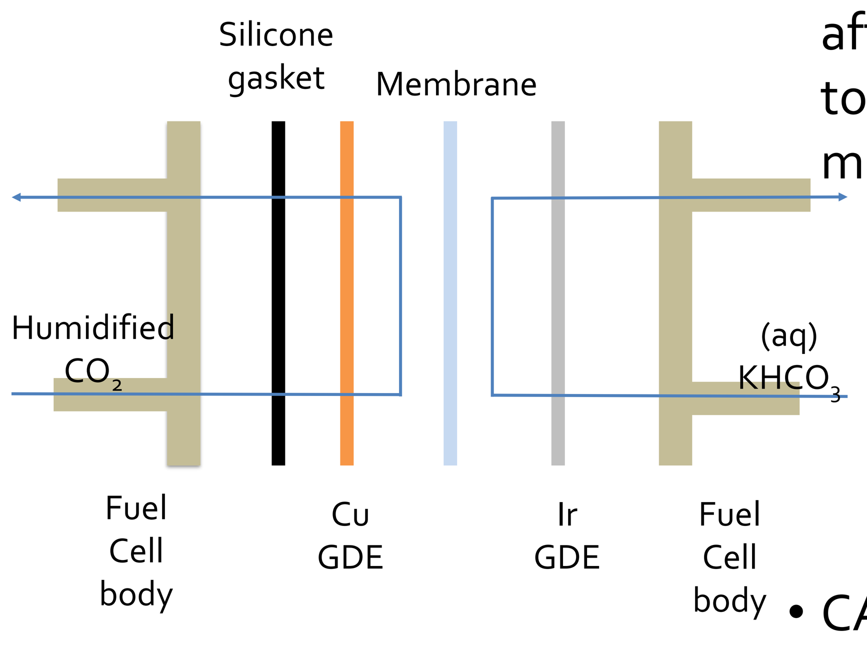
Post-Experiment Scanning Electron Microscope (SEM) Image

- Color change suggests chemical reaction (degradation) of polymer membrane
- Residual Cu and Ir observed on membrane surface
- SEM imaging does not reveal obvious degradation
  - Chain scission (on scale smaller than visible by SEM) likely due to presence of working voltage and oxygen

Experimental Setup/Conditions



- Copper catalyst (cathode)
- Iridium catalyst (anode)
- 0.1 M $KHCO_3$ anolyte
- Membrane equilibrated in 0.1 M $KHCO_3$ for 24 h
- 20-25 SCCM flowrate of humidified CO_2
- Open current voltage analyzed to ensure full equilibration of membrane
- PEIS performed before and after running CO_2 reduction to assess changes to membrane resistance
  - Sinusoidal AC excitations
  - Potential range: -10 V, +10 V
  - Frequency range: 200 kHz-10 mHz
- CA performed to measure current density and device stability
  - 24 h trials
  - -3.5 V working potential



Gas Diffusion Electrode Membrane Electrode Assembly

Improvements for Future Testing

- Rinse membrane prior to testing with ultrapure water to wash away excess salts/keep analyte out of cathode compartment
- Regularly replace aqueous $KHCO_3$ throughout equilibration process
- Reduce flow rate to prevent membrane from drying throughout experiment
- Addition of a reference electrode
- Wash and reuse same test strip to assess long-term effects of CO_2 reduction on membrane efficiency and structure
- Perform product analysis to confirm presence of side reactions with membrane or jeopardization of liquid fuels product via re-oxidation

References:

Krödel, M., Carter, B. M., Rall, D., Lohaus, J., Wessling, M., & Miller, D. J. (2020). Rational Design of Ion Exchange Membrane Material Properties Limits the Crossover of CO2 Reduction Products in Artificial Photosynthesis Devices. *ACS Applied Materials & Interfaces*, *12*(10), 12030-12042. doi:10.1021/acsami.9b21415