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Process Intensification for Electrochemical Utilization of CO_2

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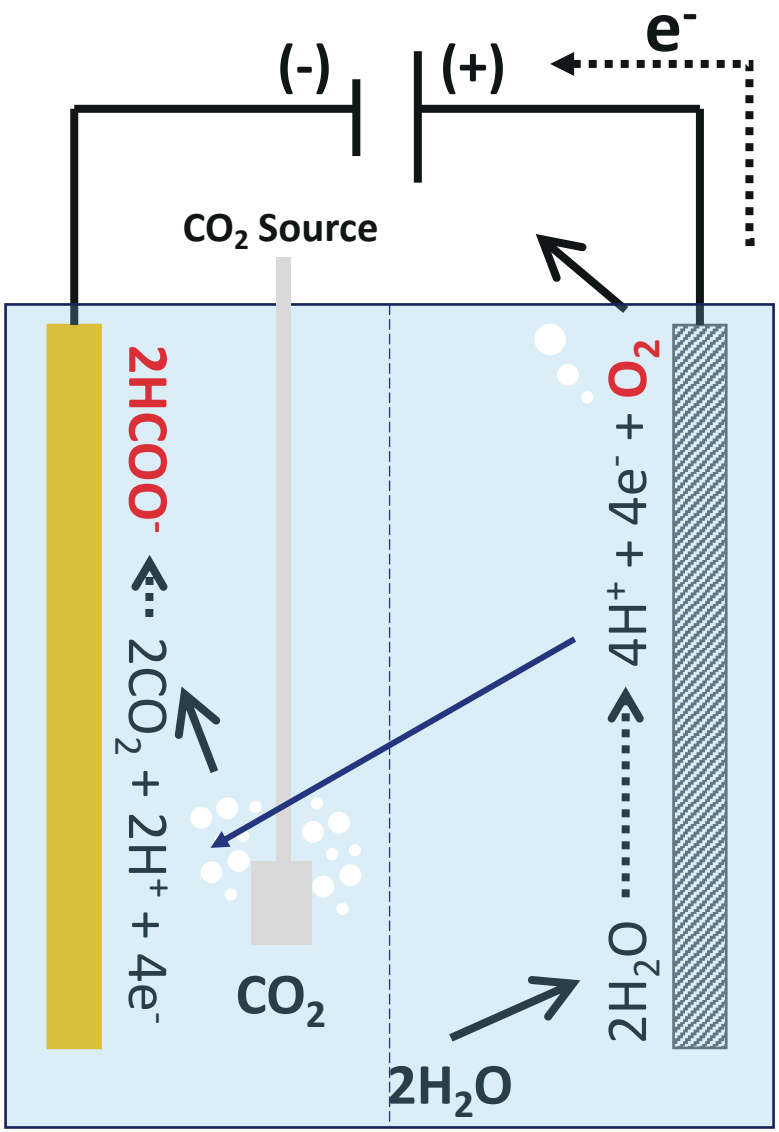
Electrochemical CO_2 Reduction



Anode Reaction:

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2$$

Cathode Reaction:

$$2CO_2 + 2H^+ + 4e^- \rightarrow 2HCOO^-$$

Net Reaction:

$$2H_2O + 2CO_2 \rightarrow 2HCOO^- + 2H^+$$

Water or hydrogen gas can be used to generate protons and electrons at the anode, but the reaction product at the cathode will depend on the electrode (catalyst) material.

Challenge: Many Products

*reported at pH=7

Ethylene:

$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$ E_0 = -0.33 V vs. RHE

Methane:

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ E_0 = -0.24 V vs. RHE

Methanol:

$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + 2H_2O$ E_0 = -0.38 V vs. RHE

Hydrogen:

$2H^+ + 2e^- \rightarrow H_2$ E_0 = -0.41 V vs. RHE

Formic Acid:

$CO_2 + H^+ + 2e^- \rightarrow HCOO^-$ E_0 = -0.49 V vs. RHE

Carbon Monoxide:

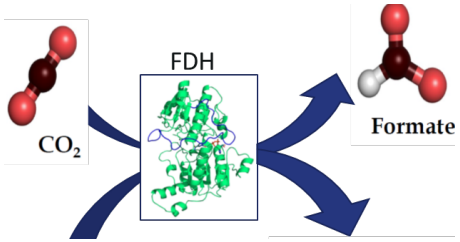
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ E_0 = -0.53 V vs. RHE

Indrakanti et al. EES 2009

CAER Approach to Address Limitations and Intensify Process and Enhance Formate production Efficiency

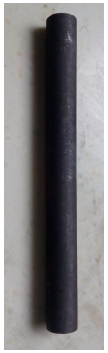
- Reaction rate
- Product selectivity

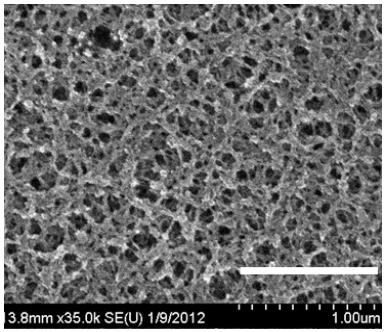
1 Catalyst Development



- Electrode degradation
- Electrode charge density

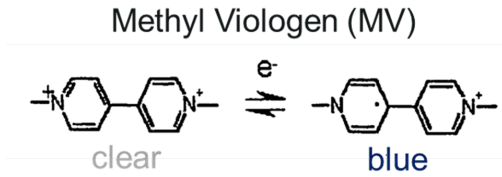
2 Low cost Electrodes



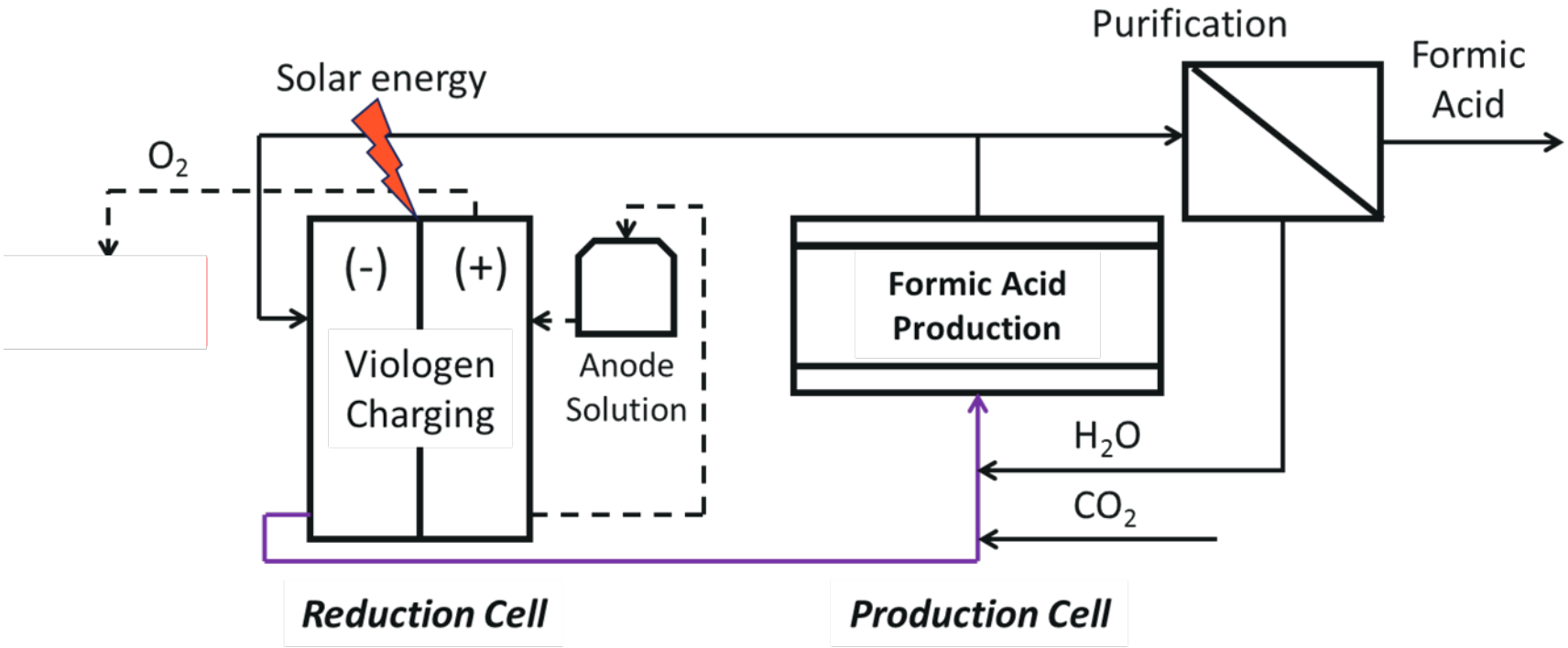


- Catalyst stability
- Process Intensification

3 Charge Carrier



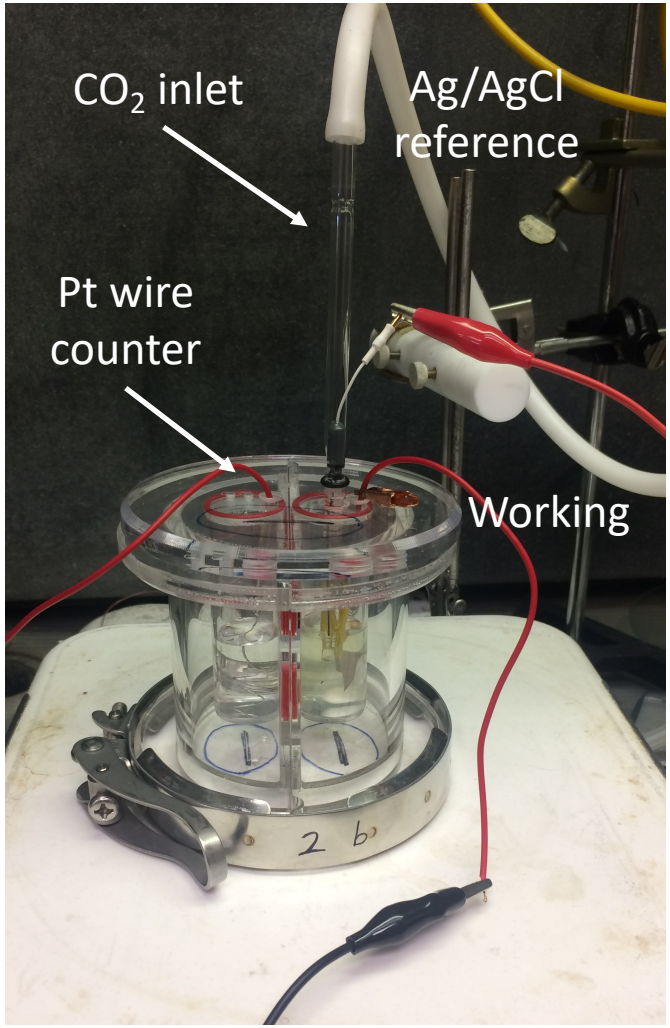
UKy-CAER Andora Integrated Process



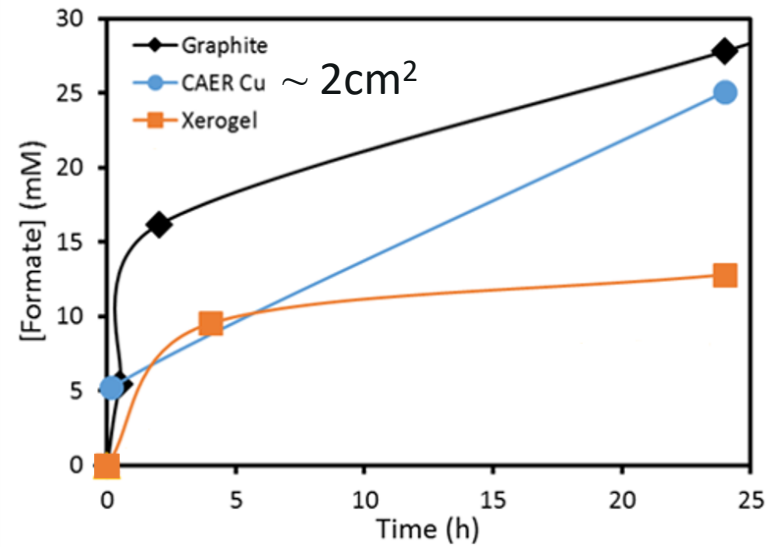
To provide a selective and robust process, the UKy-CAER Andora process focuses on:

1. Use of a charge transfer mediator to limit the cell voltage and degradation pathways of the electrochemical process
2. Separate charging and formic acid production reactors/cells to effectively encapsulate and preserve the catalyst to provide a steady stream of formic acid
3. Oxygen produced from reduction cell can be used for energy production
4. Formic acid purification via distillation or zeolite dewatering, but not current focus

Initial Proof of Concept of Experiment



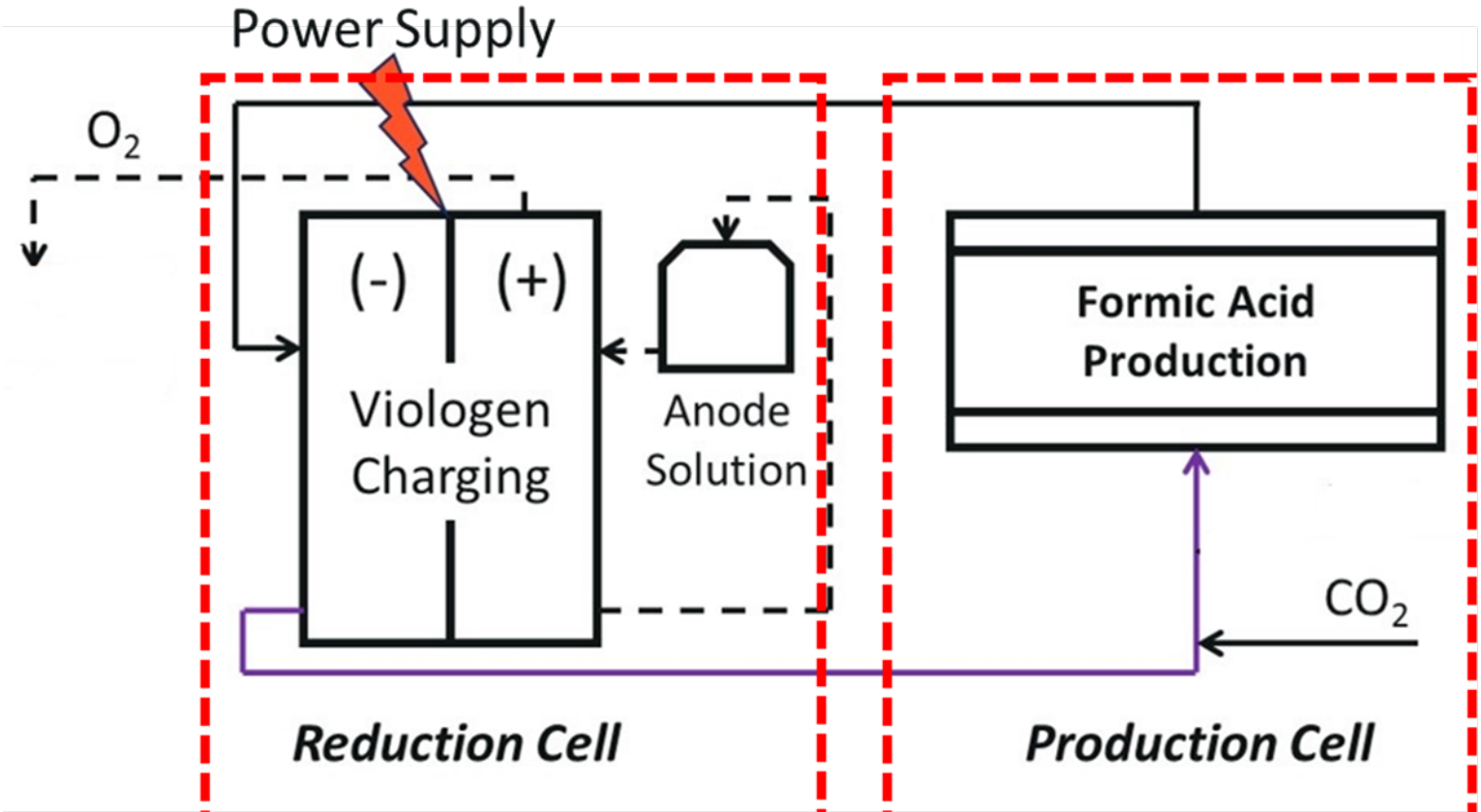
10 mM methyl viologen
200 mM Potassium Phosphate Buffer
1 mM sulfuric acid anolyte
Pt wire anode/counter electrode
-0.75 V vs Ag/AgCl cathode



Formic acid production of >25 mM achieved using a cell reactor with the engineered catalyst and methyl viologen charge carrier

Electrodes may exacerbate parasitic reactions that reduce efficiency

Improving Performance of Integrated Process

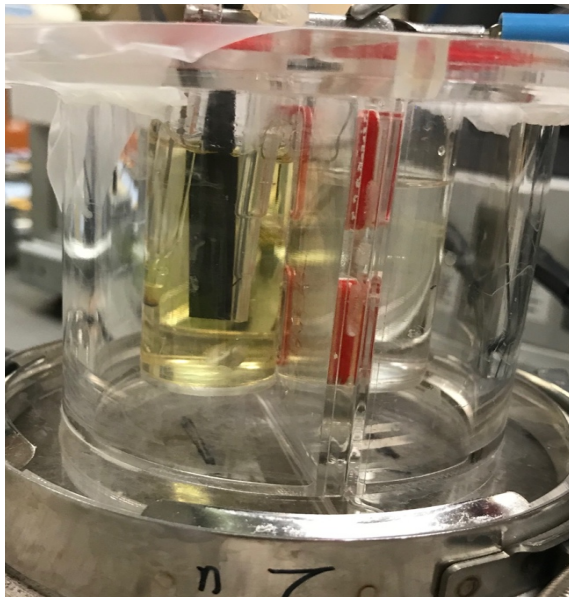


1. Charge Mediator Kinetics
2. Charge Mediator De-activation
3. Overall Cell Performance

1. Catalyst design and activity **(Ulsan)**
2. Catalyst immobilization

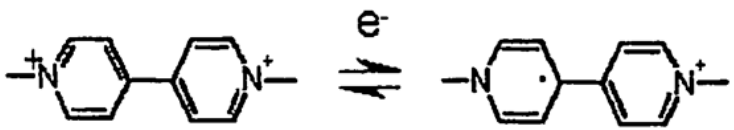
Charge Mediator Re-oxidation

Oxidized Methyl Viologen



Reduced Methyl Viologen

Methyl Viologen (MV)



clear blue

Viologen Reduction and OCV in Flow Mode

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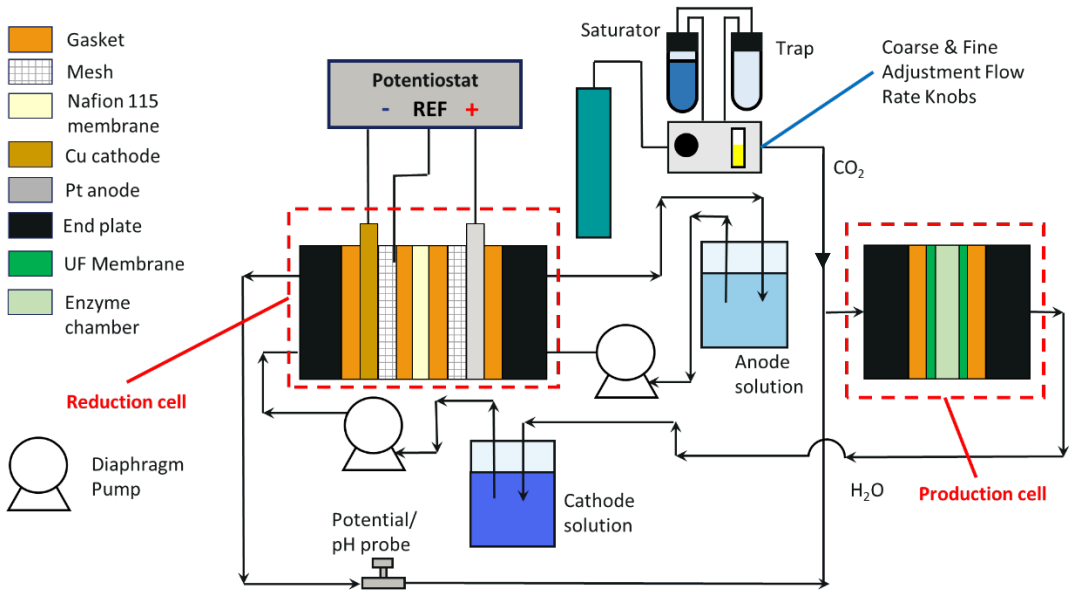
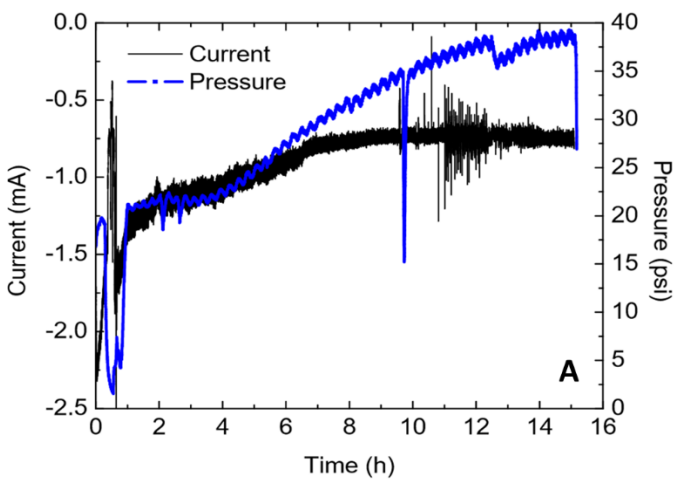


Conditions

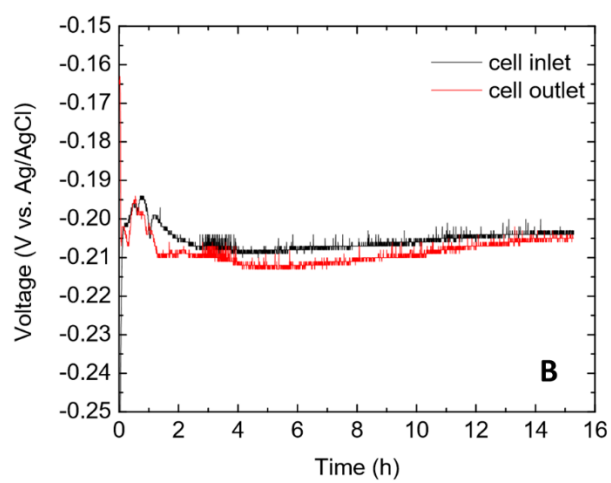
Catholyte and anolyte circulated at 10 mL/min

Trisep UF10 Membrane

No catalyst added



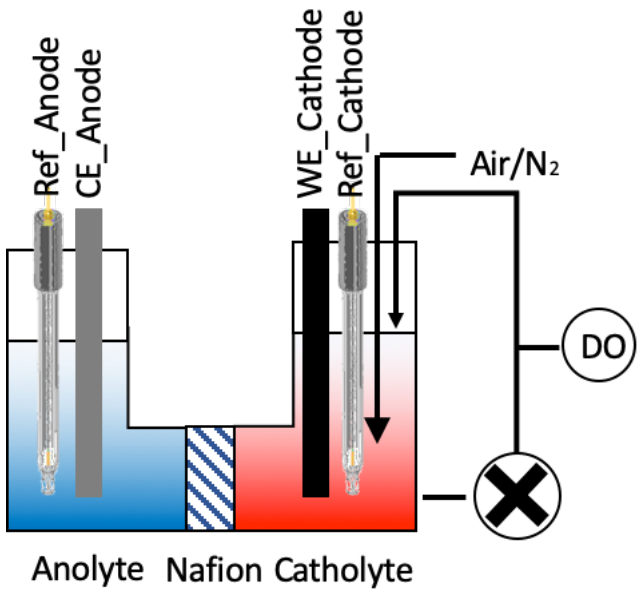
-0.75 V vs. Ag/AgCl

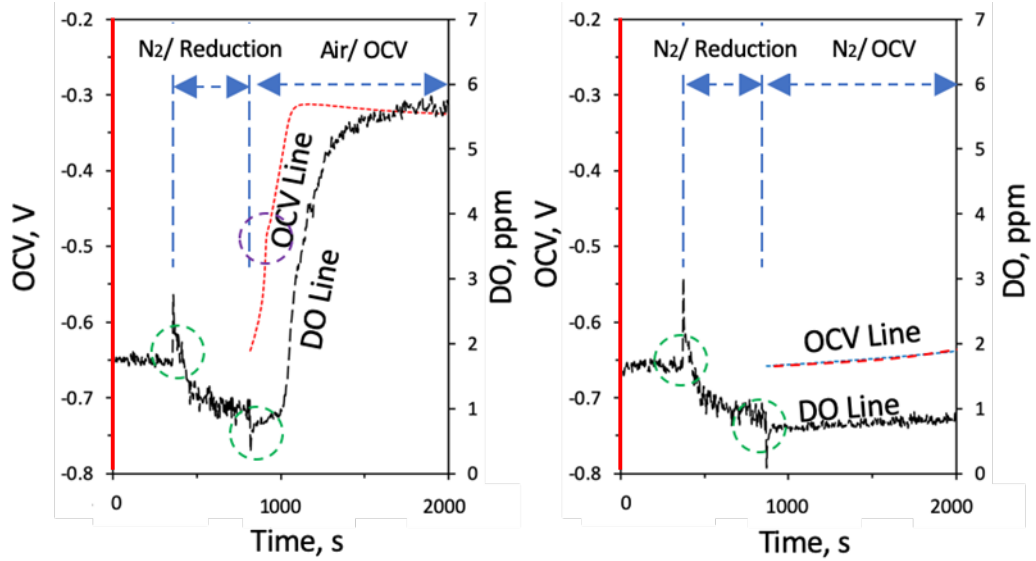


OCV Data

Loss of ~0.5 V to charge mediator re-oxidation

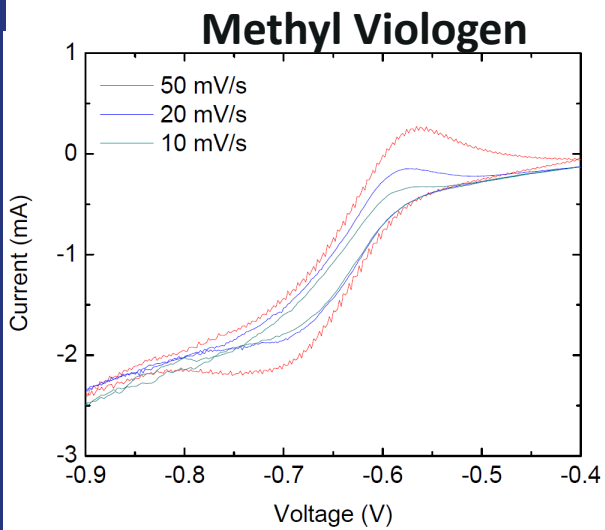
Stability of Methyl Viologen in Electrochemical Cell

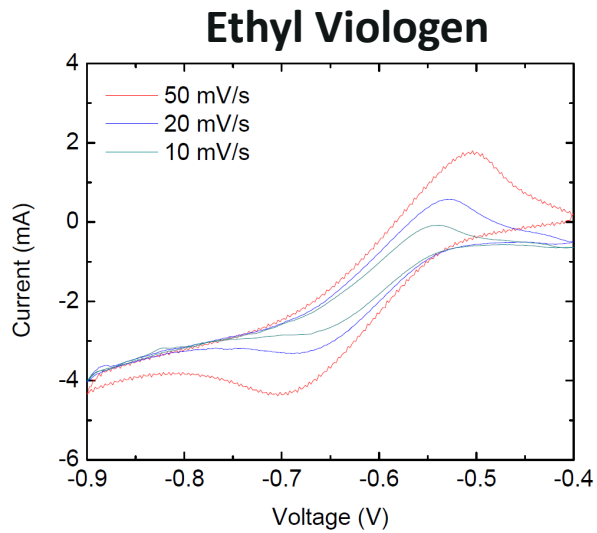


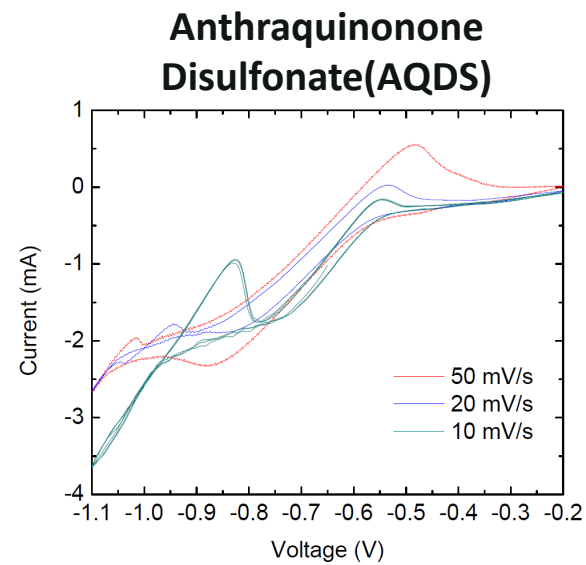


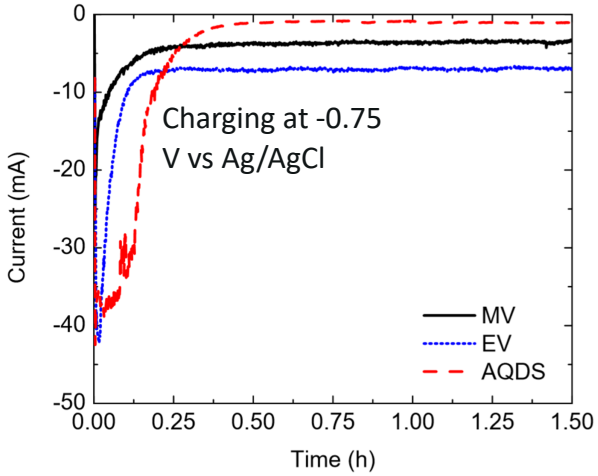
- DO monitored during experiment (black line)
- Reduction phase at -1V vs SCE cathode under N_2, followed by OCV (red line) in air (left) and N_2 (right)
- Air input exacerbates OCV decline
- **Cathodic oxygen reduction reaction evident from DO profile**
- Spikes evident during reduction and OCV onset

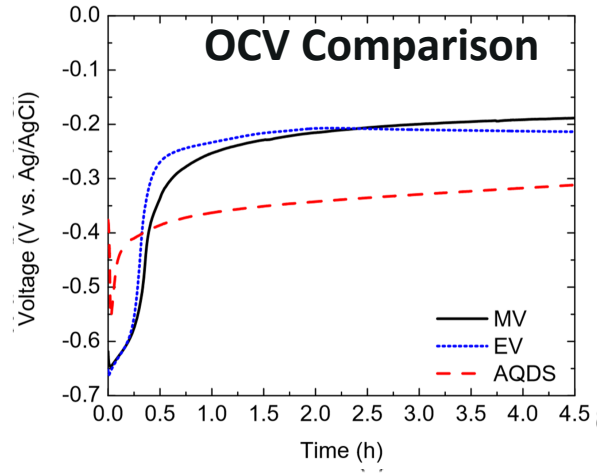
Screening of Alternative Charge Mediators to Mitigate Self Discharge





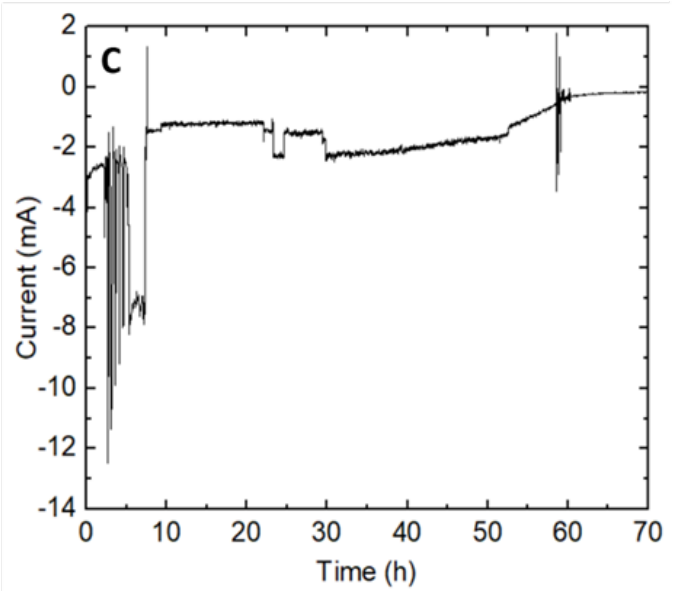


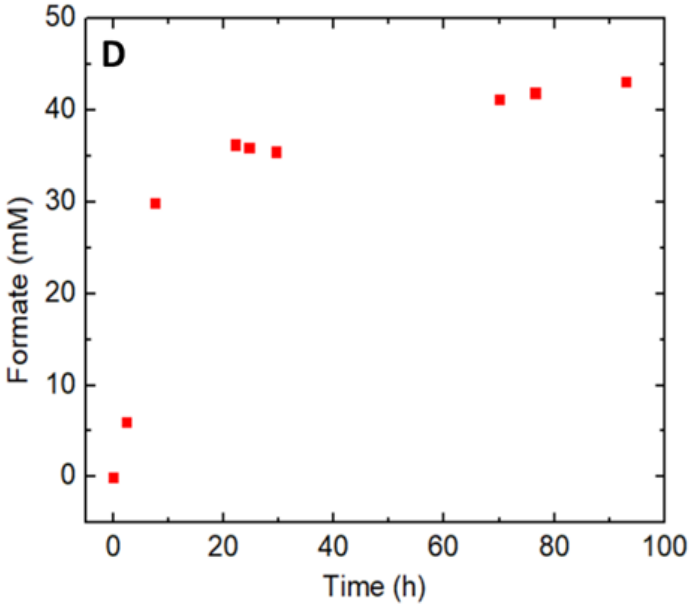




- All charge mediators have low reduction voltages (-0.6 to -0.8 V vs. Ag/AgCl)
- AQDS displays smallest current response and also better OCV degradation profile over time

Formate Production and Charge Efficiency with Enhanced Catalyst





- Generation II Catalyst – Supported Formate Dehydrogenase Catalyst
- Graphite Cathode and Pt Anode
- -0.75 V vs. Ag/AgCl
- Formate production boosted to 40 mM
- Charge efficiency at ~ 40%

Catalyst properties	
Specific activity:	47.86 µmole/mg-min
Content:	0.411 mg enzyme/mL resin (dilute)
Amount used per experiment	Approximately 2.5 mL

Final Remarks

- Engineered supported catalyst exhibits excellent capability for formic acid production and can be made more efficient
- Improvement/alternatives are needed for charge mediator re-oxidation
- Next steps will continue to focus on catalyst immobilization as well flow cell performance while increasing charge efficiency

Acknowledgements

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Thank You!