An Intensified Electro-Catalytic Process for Production of Formic Acid from Power Plant CO_2 Emissions

Project Number: DE-FE0031720

Performing Organization: University of Kentucky CAER

Principal Investigator: Jesse Thompson

caer.uky.edu/power-generation/

National Energy Technology Laboratory
Carbon Management and Natural Gas & Oil Research Project Review Meeting
Virtual Meetings, August 2 through August 31, 2021

Project Overview

- Develop and test a novel electro-catalytic method for the production of high-value formic acid from coal-derived CO_2 as a strategy to offset the cost of CO_2 capture.
- The project involves the development and testing of an engineered catalyst to selectively reduce CO_2 directly and exclusively to formic acid, along with process intensification aspects of the reactor design.

- **Project Period:** 1/1/2019 - 12/31/2021 (36 months)
- **Project Funding**: Federal - $800K; CS - $201K; Total - $1M
- **Project Team:** UK CAER and UNIST

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Project Objectives

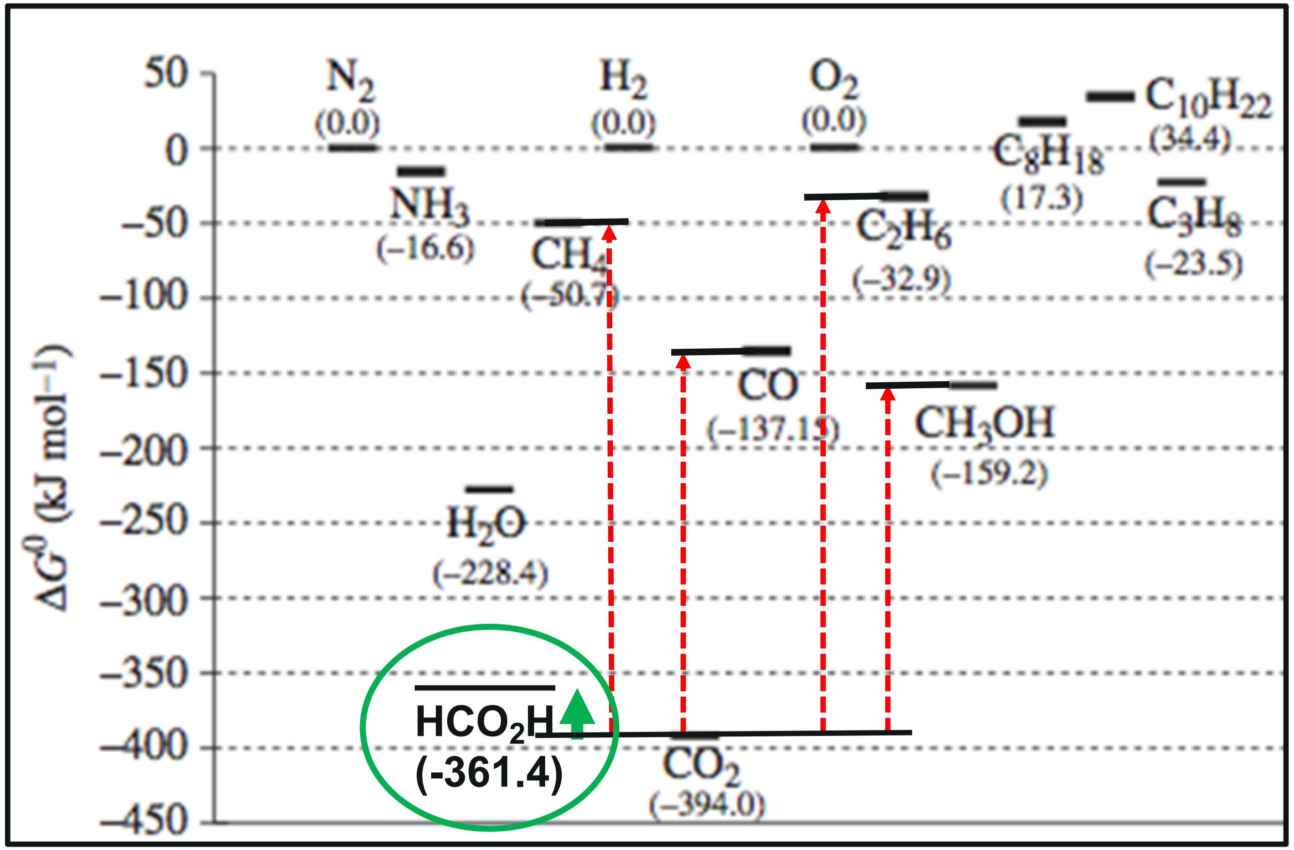
Develop CO_2 utilization technologies to reduce the cost of post-combustion CO_2 capture through:

1. Screening and production of engineered CO_2 reducing catalyst capable of exclusively producing formic acid;

2. Protection of the catalyst within a flow-through process to continually produce formic acid and increase catalyst lifetime;

3. Long-term stable operation with high selectivity towards formic acid

Motivation



Formic acid is the closest to CO_2 from an energy perspective, i.e. smaller hill to climb compared to other common CO_2 reduction products

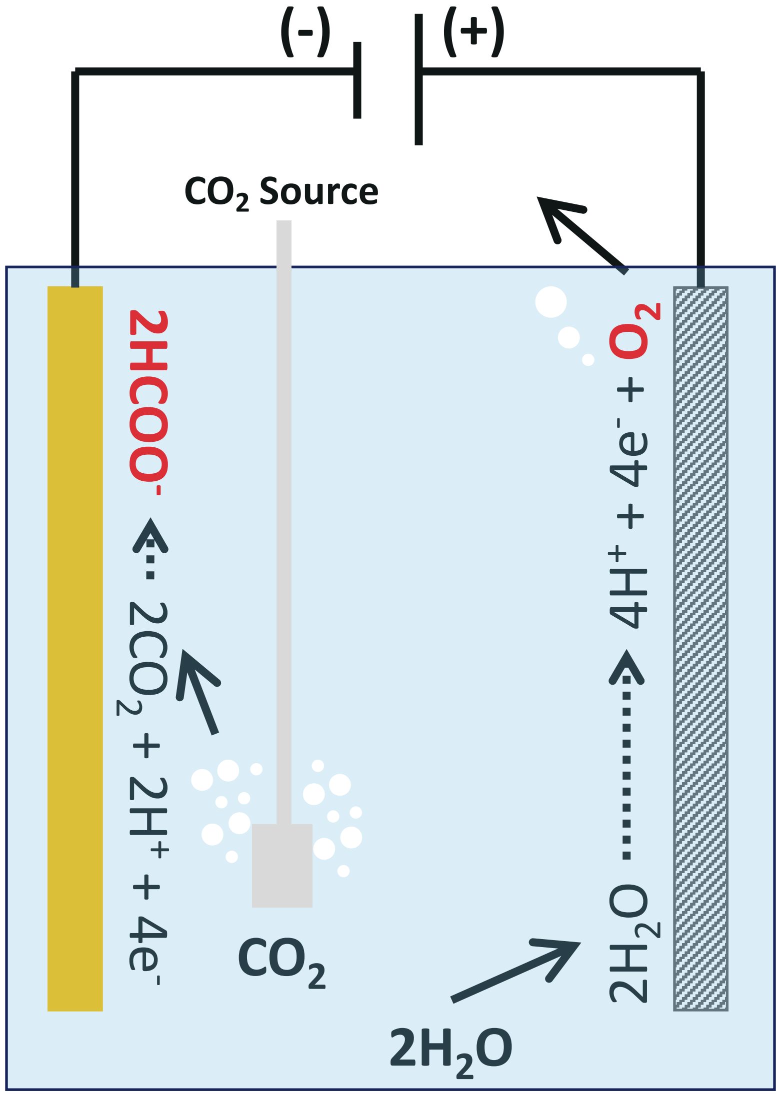
The current commercial market for formic acid is relatively small, mainly as a preservative in animal feed, at ~1M tonnes per year.

Two potential new markets with lower cost formic acid:

- Formic acid-based fuel cells
- Liquid H_2 storage medium

Phil. Trans. R. Soc. A **2010**, *368*, 3343; *ACS Catal.* **2017**, *7*, 5381; *J. Phys. Chem. Lett.* **2015**, *6*, 4073

Technology Background



Electrochemical CO_2 Reduction

Formic Acid produced with CO_2 and H_2O as inputs:

<u>Anode Reaction</u>:

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

<u>Cathode Reaction</u>:

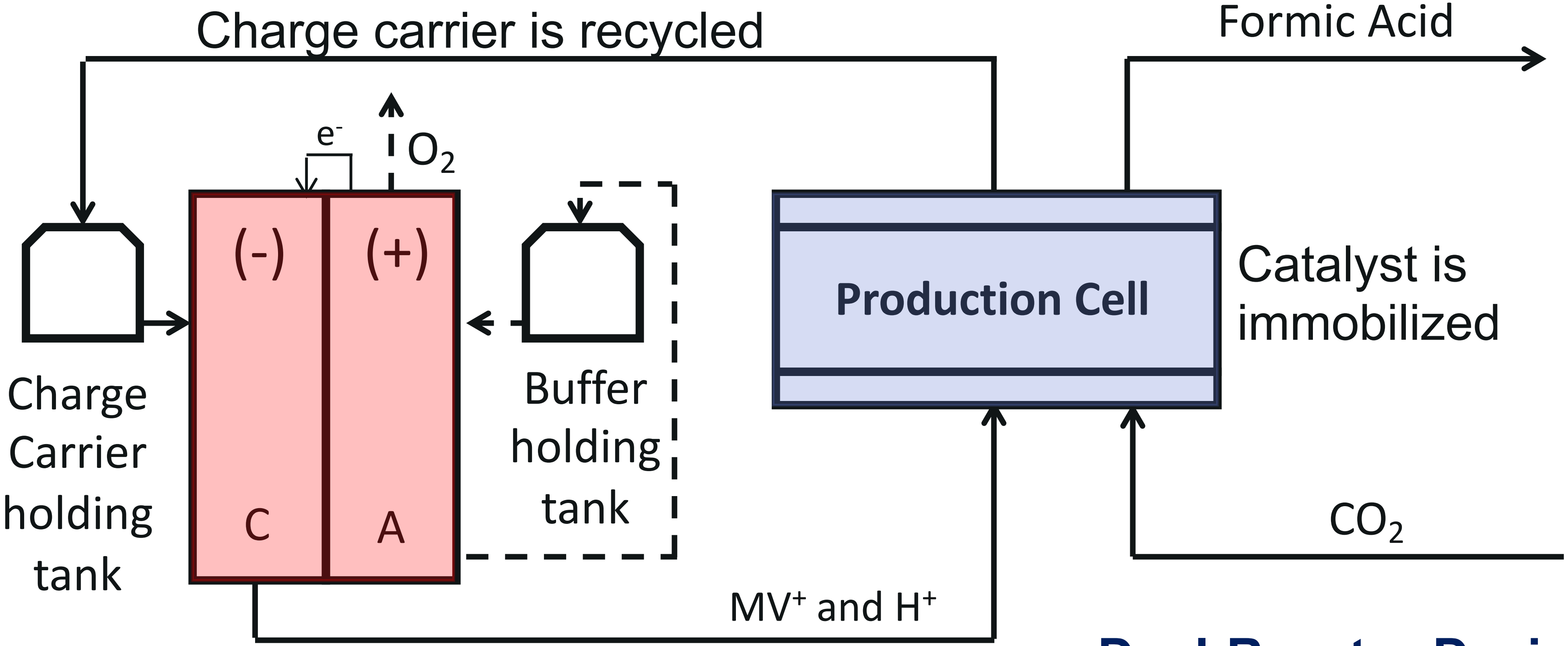
$$2CO_2 + 2H^+ + 4e^- \rightarrow 2HCOO^-$$

<u>Net Reaction</u>:

$$2H_2O + 2CO_2 \rightarrow 2HCOO^- + 2H^+ + O_2$$

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 <u>*electrode material and catalyst*</u>.

UK CAER Andora Process



Dual-Reactor Design

Cathode Reaction (-): Reduction of Methyl Viologen (MV)

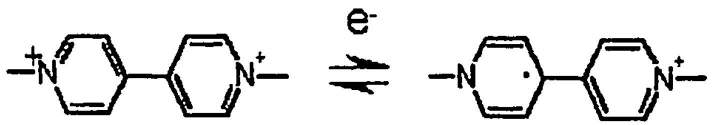
$4MV^{2+} + 4e^{-} \leftrightarrow 4MV^{+}$ E = -0.67 vs. Ag/AgCl

Anode Reaction (+): Water Oxidation

$2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-}$ E = 0.617 vs. Ag/AgCl, pH=7

Charge Carrier

Methyl Viologen (MV)

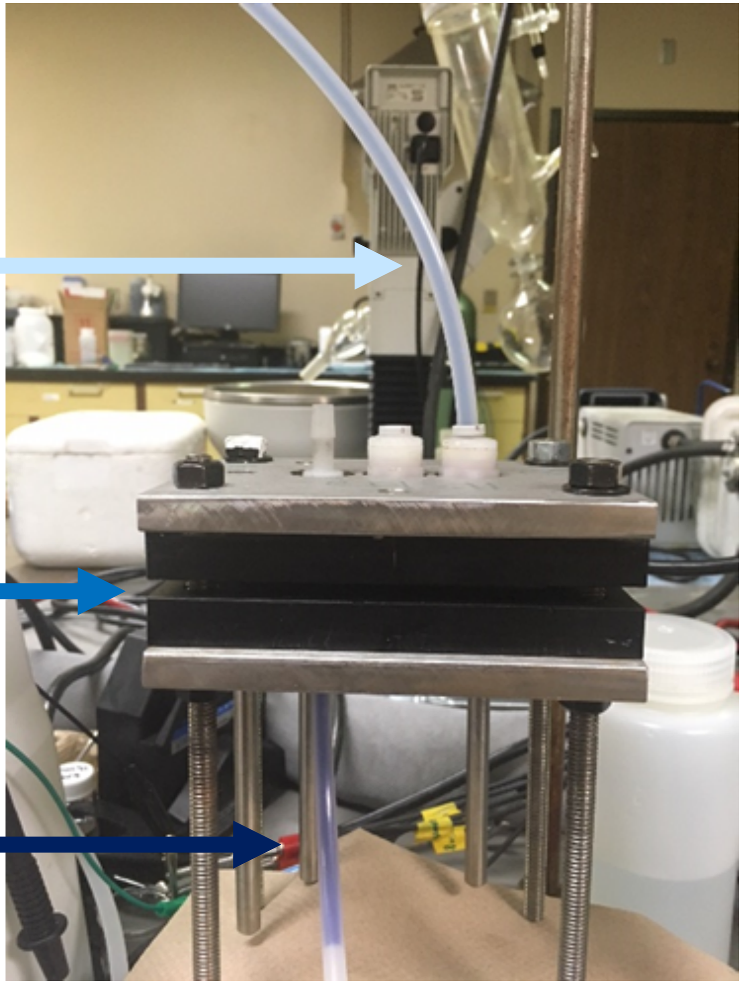


clear　　　　　**blue**

Oxidized Methyl Viologen loses its blue color after e^- transfer

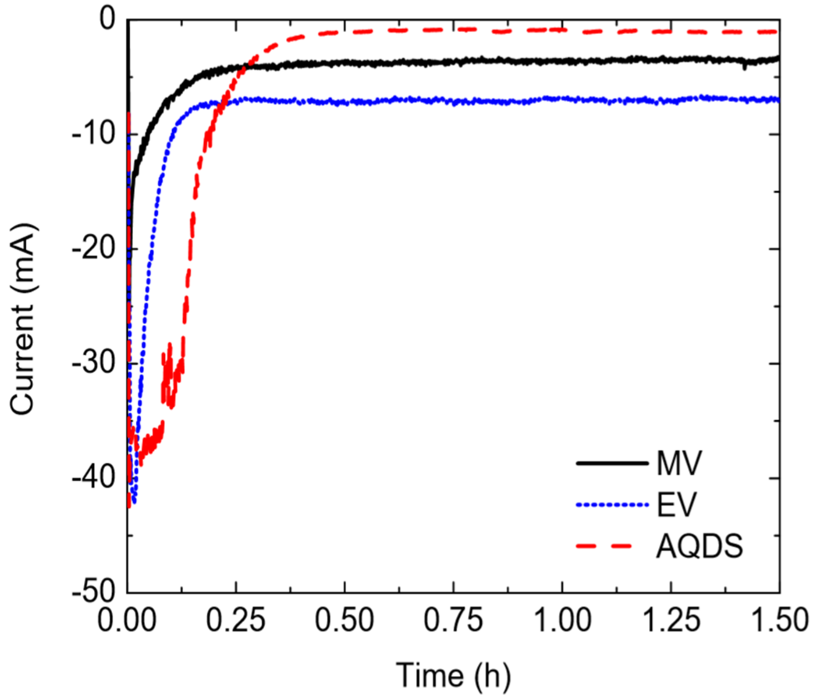
Formic acid production cell where methyl viologen transfer e^- to the catalyst

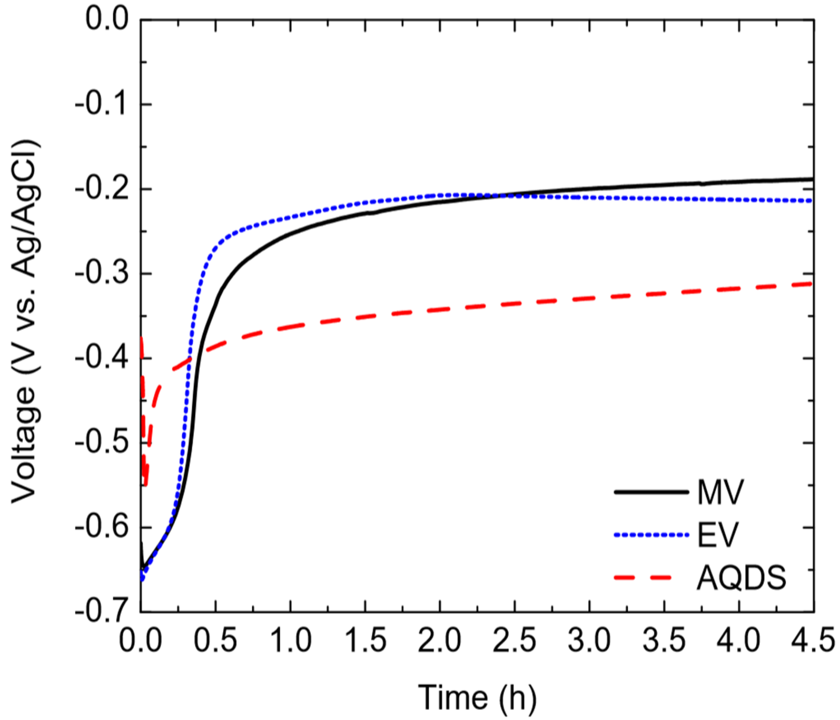
Reduced methyl viologen (blue) entering formic acid production cell



- MV^{2+} has been demonstrated to be a stable electron mediator
- The active catalyst can accept an electron not from working electrode directly, but from reduced $MV^{\bullet+}$.
- This type of electron transfer *minimizes overpotentials and catalyst degradation*

Charge Carrier

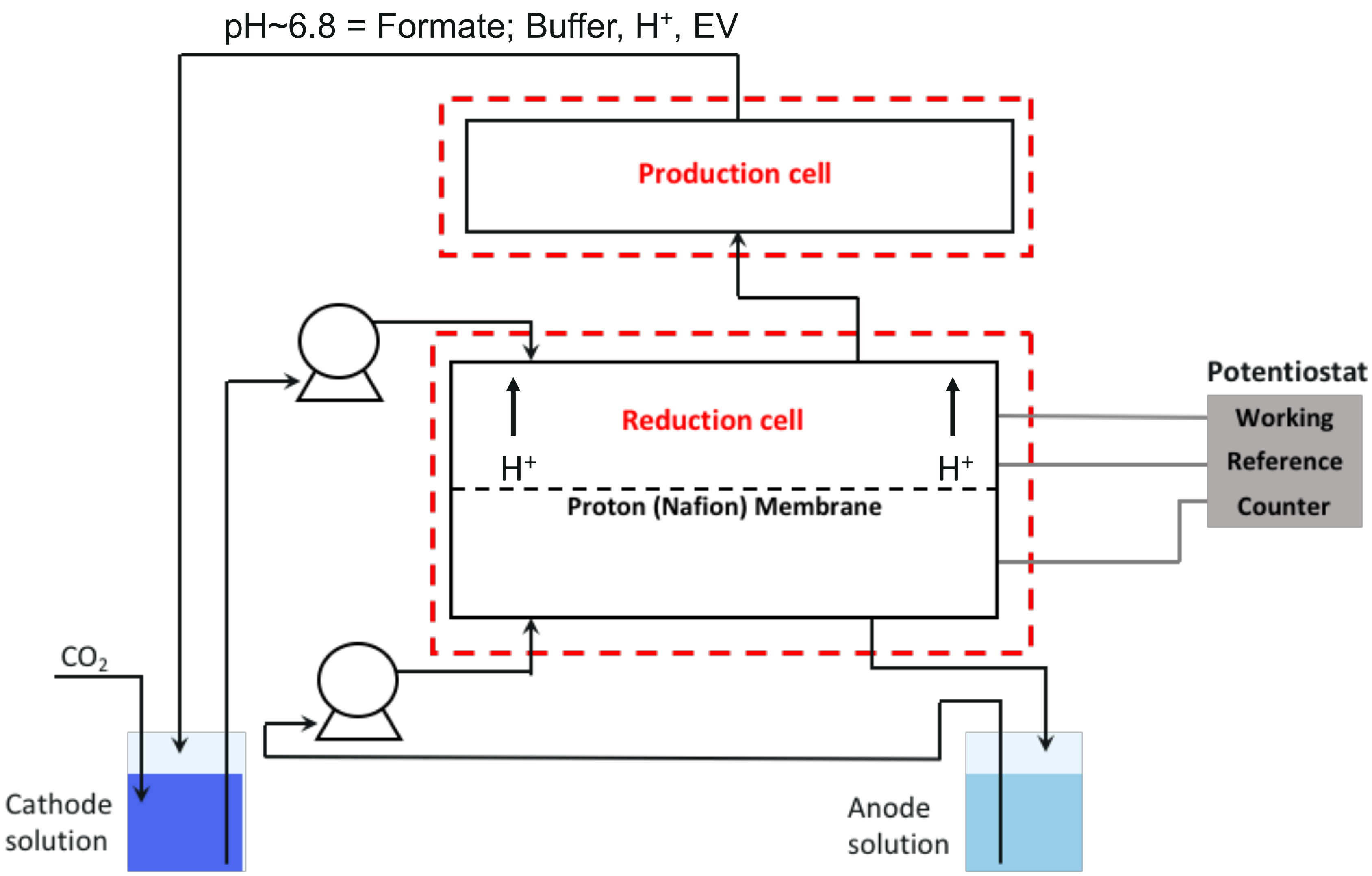




- Methyl Viologen (MV), Ethyl Viologen (EV) and Anthraquinonone Disulfonate (AQDS) charge mediators have low reduction voltages (-0.6 to -0.8 V vs. Ag/AgCl)
- Carbon felt electrode in H-cell, charged at -0.75 V vs. Ag/AgCl for 1.5 h (left), discharge (OCV run) for 4.5 h (right)

Three viable charge carriers evaluated; EV selected for continued development based on activity, stability and lowest environmental concern

Flow-through Reactor Design



Operating variables:

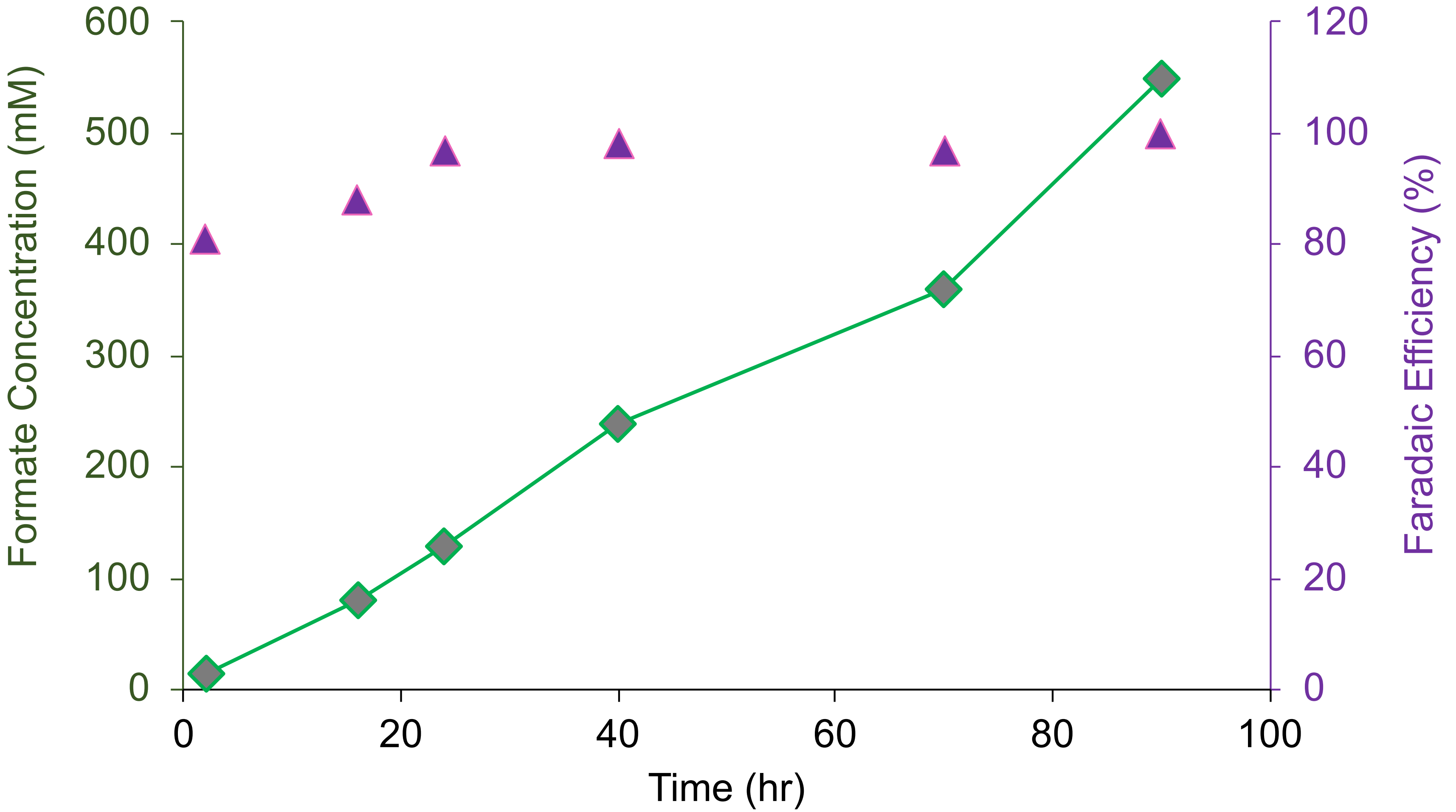
- Anode materials (Pt and Pt-Ir)

- Cathode solution flow rates from 1-9 mL/min

- Catalyst immobilization with low pressure drop membranes

- Sulfuric acid used as anode solution (proton source) at lab-scale, but can be replaced with H_2 or OER in next iteration

Flow-through Reactor Operation



Cathode: 200 mM phosphate buffer + 10 mM EV charge carrier; Carbon felt electrode operated at -0.74V vs Ag/AgCl

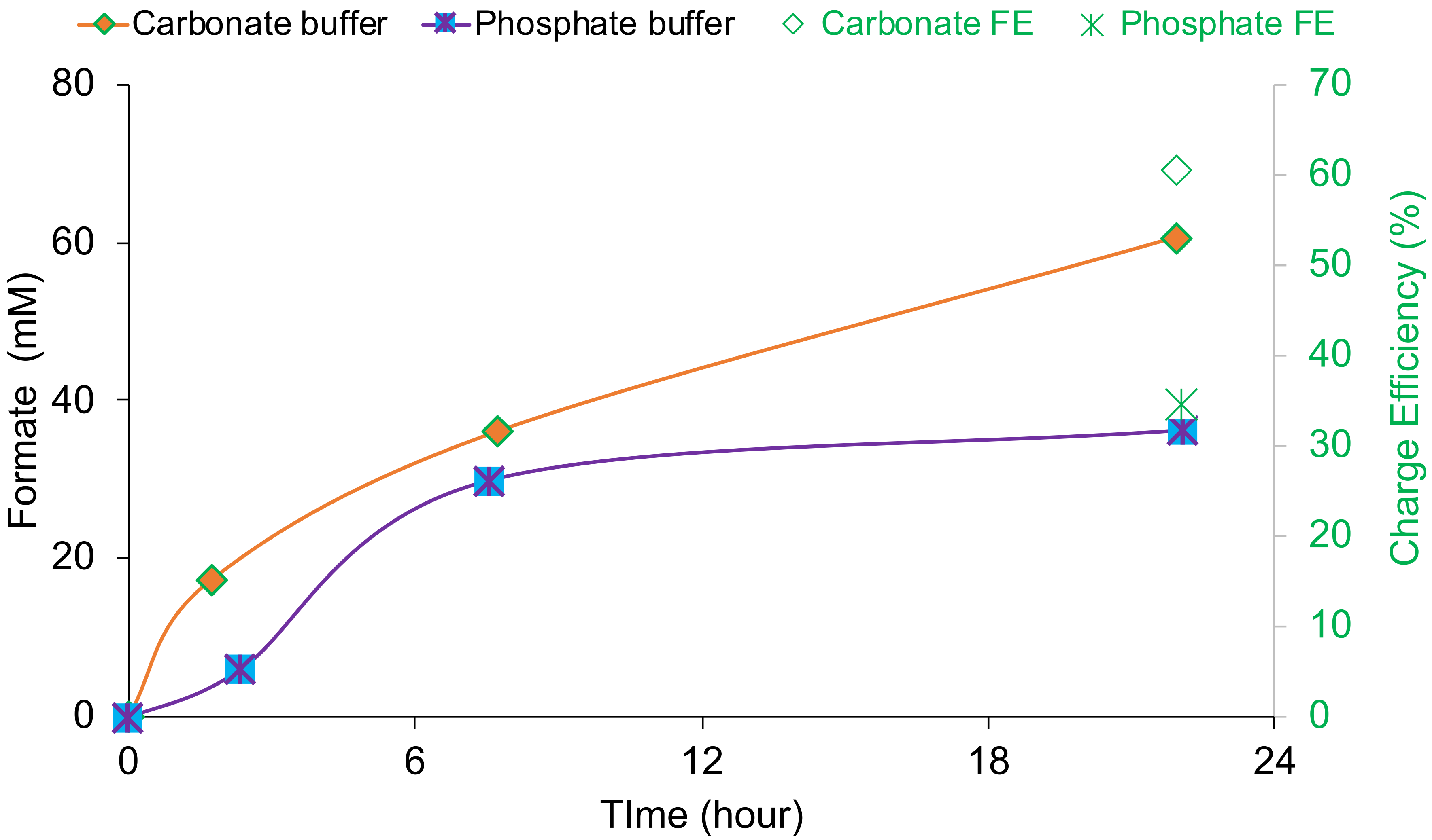
Anode: 100 mM Sulfuric acid proton source with platinum electrode and Nafion membrnae

Pure CO_2 gas purge

2 mL/min cathode flow rate

Achievement: > 500 mM *Formate* production with > 80% Faradaic efficiency (FE) and > 90% selectivity

Operating Options



- Pt wire anode
- Phosphate and carbonate buffer solutions
- CO_2 purging (15 mL/min)

Operating voltage -0.75V vs. Ag/AgCl

Formate production achieved using both a phosphate and carbonate buffer system

Formate/Formic Acid Separation

- Water + Formic Acid Azeotrope Distillation
- Membrane pervaporation pre-concentrating before distillation
- Liquid-liquid extraction
- Ion exchange (IEX)
    - Commercially available IEX with capacities up to 450 mg formate / g IEX from our process solution (viologen and buffer recycled)

Kaczur et. al., J Carbon Res., 2020, 6, 42 : Laitinen et. al., Ind. Eng. Chem. Res., 2021, 60, 5588-5599 : Zeidan and Marti, J. Chem. Eng. Data, 2019, 64, 2718-2727

Remaining Work

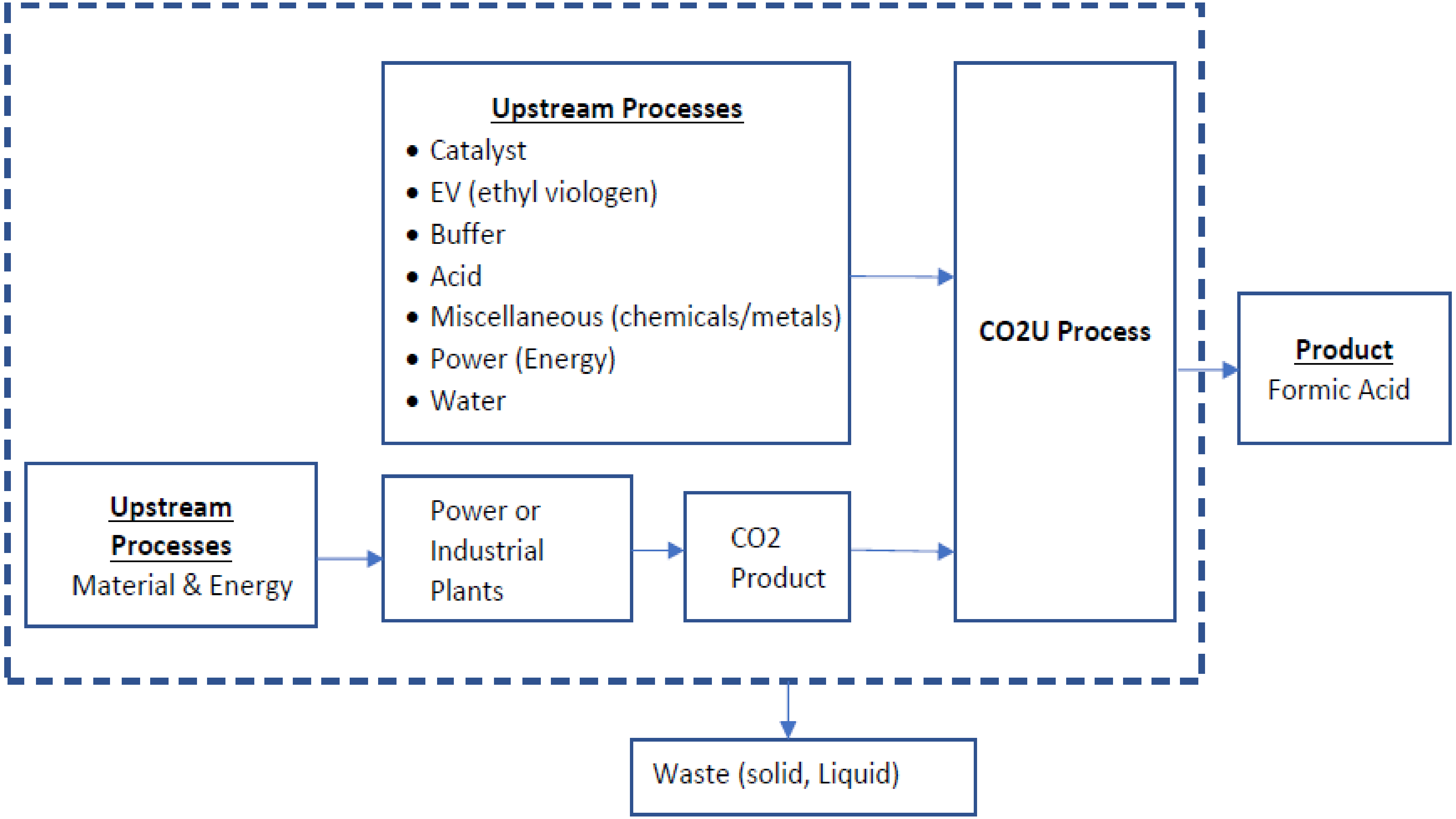
- Update Technology Maturation Plan (TMP)
  - Performance attributes and requirements will be re-evaluated. Post project maturation plans will be updated along with an assessment of the technology's current TRL level.

- Life-Cycle Analysis (LCA)
  - Demonstrate the proposed process to be a substantive CO_2 mitigation option and verify the life cycle GHG reduction potential of the products(s) and technology (on a percent reduction basis) relative to current state-of-the-art pathways.

- Initial Technical and Economic Feasibility Study (TEA)
  - A high-level return-on-investment (ROI) analysis will be conducted to assess the viability of the proposed process to reduce GHG emissions from power plants based on the collected lab-scale data.

LCA

System Boundaries



Generated using openLCA 1.10.3

LCA

Contribution of Different Sections in Global Warming Potential (GWP)

(TRACI 2.1 method)

Using sulfuric acid as proton source at lab-scale

Contribution	Process	Amount	Unit
100.00%	P CO2U -Base - Prop.	5.20394	kg CO2e
76.15%	P Sulfuric acid, at plant - RNA	3.96300	kg CO2e
15.60%	P Generic Power Grid Mixer	0.81159	kg CO2e
06.20%	P CO2 Source Mixer - Prop	0.32285	kg CO2e
02.05%	P Sodium_Thiosulfate	0.10650	kg CO2e
00.00%	P Dummy_Water for industrial use	1.97232E-16	kg CO2e
-00.00%	P Catalyst for CO2U - US-KY	-1.31831E-16	kg CO2e

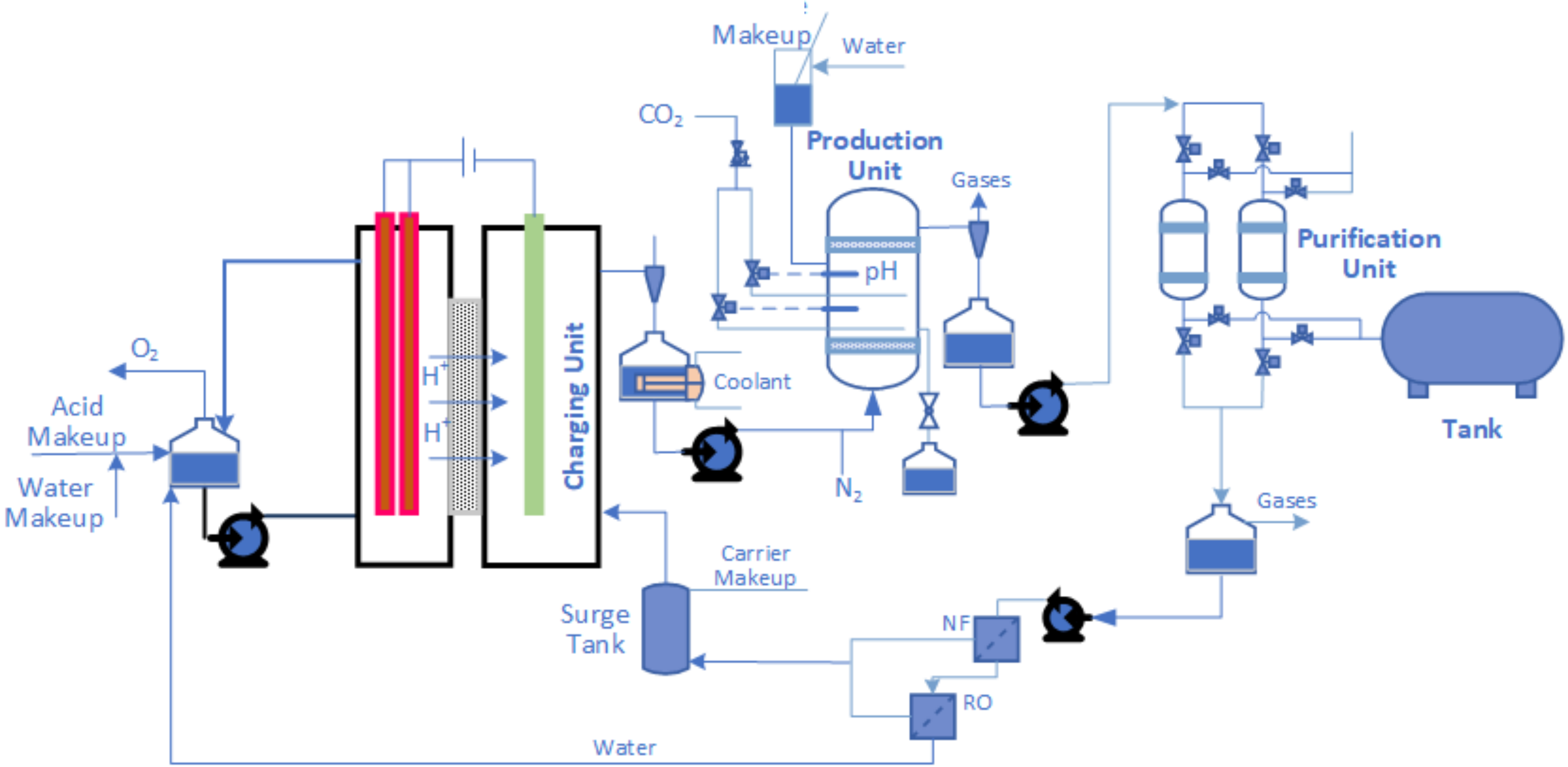
Switch to H_2 as proton source for scale-up

Contribution	Process	Amount	Unit
100.00%	P CO2U (V2)- H2 inst H2SO4	2.27558	kg CO2e
49.28%	P CO2 Source Mixer - Comp	1.12143	kg CO2e
35.67%	P Generic Power Grid Mixer	0.81159	kg CO2e
10.37%	P Hydrogen Production - Steam Methane Reforming	0.23607	kg CO2e
04.68%	P Sodium_Thiosulfate	0.10650	kg CO2e
00.00%	P Dummy_Water for industrial use	0.00000	kg CO2e

By switching from sulfuric acid to H_2 the GWP was significantly reduced

TEA

- Detailed process design created for TEA



Knowledge Gained/Challenges

- Moving from a batch cell to a flow-through configuration can be challenging due to larger volumes, residence times, and matching reaction rates between both reactors/cells.
- Formate production achieved using both a phosphate and carbonate buffer system
- Proton (H^+) source in CO_2 reduction is an important factor in LCA

Milestones

Budget Period	Task Number	Title	Planned Completion Date	Actual Completion Date	Verification Method
1	1	Updated Project Management Plan	1/31/2019	1/31/19 (A) 3/14/2019 (B) 2/28/20 (C)	Revised PMP Revision A Revised PMP Revision B Revised PMP Revision C
1	1	Kickoff Meeting	3/31/2019	3/25/2019	Presentation file
1	1	Subcontracts Established	3/31/2019	10/16/2019	Written Verification
1	2	Issue Technology Maturation Plan	6/30/2019	6/30/2019	Appended to Quarterly Report
1	3	Quarterly production and delivery of improved catalyst with verified formic acid production capabilities	12/31/2020	12/31/2020	Quarterly Report
1	4	Production cell capable of 25 mM formic acid during continuous production at 2 ml/min with Faradaic efficiency of at least 50%	9/30/2021		Quarterly Report
1	5	Long-term formic acid production for >100 hours with produced concentrations of 25 mM	6/30/2020	7/6/2020	Quarterly Report
1	5	High-performance cell capable of >100 mM of continuous formic acid production	9/30/2021		Quarterly Report
1	6	Issue report on Life Cycle Analysis	12/31/2021		Appended to Quarterly Report
1	7	Issue Report on Technical and Economic Feasibility Study	12/31/2021		Appended to Quarterly Report

Success Criteria

Success Criteria (Task #)	Status
(#4) Electrochemical cell carrier charge efficiency of greater than 60%	Average 60% efficiency achieved ✔
(#4) Fabrication of the flow-through apparatus: Production cell capable of supporting flow rate of **2 mL/min** during continuous operation	Achieved - operating between 2-9 mL/min ✔
(#3) Catalyst production: Two grams of catalyst produced and supplied to UK CAER with stability (less than 25% deactivation) of greater than 100hr	Catalyst being provided in batches as needed ✔
(#4) Immobilization of catalyst: **90%** of catalyst retained in production cell during continuous operation as verification by analysis	Above **95%** retention ✔
(#5) Production of formic acid from CO_2: Continuous operation of reduction and production cells with a formic acid production of **25 mM** and a selectivity of greater than 80%	**25 mM** formic acid production with high (>90%) selectivity for >100 hours ✔

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Project Schedule

Task Number and Name	Start	End	FY2019				FY2020				FY2021			FY2022
			Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1
1. Project Management and Planning	1/1/19	12/31/21												
1.1 Task management and execution	1/1/19	12/31/21												
1.2 Update PMP	1/1/19	12/31/21												
1.3 Briefings and Reports	1/1/19	12/31/21												
2. Technology Maturation Plan	1/1/19	6/30/19												
Issue TMP		*6/30/19*		☆										
3. Development of Electro-Catalysts	1/1/19	12/31/20												
3.1 Screening of electro-catalysts	1/1/19	9/30/19												
3.2 Stability testing of electro-catalysts	7/1/19	3/31/20												
3.3 Scale-up production of catalysts	1/1/20	12/31/20												
Catalyst production		*12/31/20*								☆				
4. Electro-catalyst flow-through reactor design, fabrication and commissioning	1/1/19	12/31/20												
4.1 Immobilization of electro-catalyst	1/1/19	9/30/19												
4.2 System pressure and flowrate testing	10/1/19	6/30/20												
4.3 Charge carrier and production testing	10/1/19	12/31/20												
5. Lab-scale reactor testing	1/1/19	9/30/21												
5.1 Reactor operation and optimization	1/1/19	3/31/20												
5.2 Stability testing of flow-through reactor	10/1/19	9/30/21												
5.3 Evaluation of formic acid purification process	7/1/20	9/30/21												
25 mM formic acid producitons with 50% efficiency		*9/30/21*											☆	
Long-term FA 100 hr at 25 mM		*6/30/20*						☆						
100 mM Formic acid production		*9/30/21*											☆	
6. Life cycle analysis	1/1/21	12/31/21												
7. Initial technical and economic feasibility study	1/1/21	12/31/21												

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