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RPPR Final Report
as of 06-Apr-2021

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Proposal Number: 77276CHSB1 **Agreement Number: W911NF-20-P-0065**

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Final Report for Period Beginning 24-Aug-2020 and Ending 24-Feb-2021
Title: Generating Formate from CO2 on-site
Begin Performance Period: 24-Aug-2020 **End Performance Period:** 24-Feb-2021
Report Term: 0-Other

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STEM Degrees: 0 **STEM Participants:**

Major Goals: The main objective of this proposal was to build an electrochemical device that can convert waste carbon dioxide from point sources on outposts and bases into potassium formate (K-Formate). K-Formate is an environmentally friendly deicing agent with low corrosivity and suitable for roadway and runway deicing. It has already been formulated to meet the AMS 1435 standard for runways. BASF has tested its version of K-Formate with additives at airports, including Denver International Airport, while Eastman has tested a similar product in Europe.

Presently K-Formate is manufactured at chemical plants in Europe or Asia and is then shipped around the world for sale. Production and delivery costs could be substantially reduced by using inexpensive and/or waste materials (renewable electricity, carbon dioxide, sea salt) and synthesizing the chemical in reactors on-site. One of the Army’ s modernization priorities is to lower supply chain costs. By relieving pressures on the supply chain, the chemical stockpiles can also be reduced, reducing costs and potentially saving lives.

In the proposed work, we designed and developed a small unit to produce formic acid. We ran the device for 500 hours producing enough formic acid to yield of K-Formate using KOH neutralization, and delivered 5 lbs of the K-Formate solution to the ARO (Army).

3.2.1 Task 1: Design, construction, and testing of a 250 cm2 electrolyzer. (Completed).

This task was to scale-up the formic acid electrochemical technology from the laboratory 5 cm2 size to a 250 cm2 size utilizing one of our existing 250 cm2 CO2 electrolyzer designs. This included designing a new center flow compartment and examining alternate conductive ion exchange media forms to replace the loose ion exchange resin. Fabrication of anode and cathode GDE’s as well as membrane selection was also needed. Our target electrolyzer formic acid concentration was 10 wt%. We successfully scaled-up the formic acid electrolyzer design to 250 cm2, producing formic acid required for producing the K-Formate project deliverable

3.2.2 Task 2: Optimizing output and efficiency. (Completed).

This task was to measure and optimize the Faradaic efficiency of the formic acid electrolyzer as a function of CO2 and water flowrates, membrane and GDE catalyst compositions, and optimizing as needed. We had a target of at least a 60% Faradaic efficiency. We were able to operate the 250 cm2 for two runs, obtaining cell operation data at several current densities.

3.2.3 Task 3: Producing 5 lbs of K-Formate (50 wt% solution). (Completed).

This task was to produce sufficient formic acid from the 250 cm2 electrolyzer in order to produce our target of 5 lbs of K-Formate (50 wt%) for delivery to the ARO. The task involved looking at the neutralization of the formic acid with KOH and testing evaporation as a way to remove excess formic acid and achieve a 50 wt% K-Formate concentration. We successfully produced and delivered the 5 lbs of K-Formate solution.

3.2.4 Task 4: 500-hour test. (Completed).

This task was to operate the 250 cm^2 cell continuously for 500 hours and correcting any issues that arise during operation having an electrolyzer operating voltage target of less than 4.5 V. We achieved the operation of the 250 cm2 cell in two runs: 118 hours and 500 hours. The electrolyzer operating voltage was less than 4 volts and produced the formic acid required in producing the K-Formate product.

3.2.5 Task 5: Techno-economic model of scaled-up production costs. (Completed).

This task was to do preliminary techno-economic modeling to estimate the production costs for producing the K-Formate. This task will include spreadsheet-level calculations of the cost of producing the K-Formate. The task may also include ChemCad or Aspen Simulations of the separation section. We completed the techno-economic modeling for producing K-Formate at various cell Faradaic efficiencies, evaporation costs, and the source cost of KOH required. The OPEX costs for producing formic acid were still lower than commercial formic acid at electrolyzer Faradaic efficiencies as low as 30%. The cost of the sourced KOH is the major factor in the final cost of the K-Formate.

3.2.6 Task 6: Plan for Phase II. (Completed).

This task includes doing a preliminary design of a skid mounted device capable of producing 100 lbs/day of K-Formate. The task may also include skid design, identification of initial equipment list, creating an initial project schedule, developing a budget, and documenting the findings in the form of a Phase II proposal. We included preliminary CAPEX costs for producing 50 gal/day of K-Formate solution (565 lb/day) in our Techno-Economic modeling in Task 5. We have also submitted our Phase II proposal on March 29, 2021.

3.2.7 Task 7: Reporting (Completed).

This task will include reporting as required by the program. We have completed all reporting tasks. Our summary report submittal was late due to miscommunication of the report requirement.

Project Optional Period – Program Manager Approval

3.3.8 Task 8: Long term tests.

This task will includes running the 250 cm^2 cell until failure, identifying the failure mode, and correcting what we find. It may also include some additional modifications to improve the design.

3.3.9 Task 9: Optimizing output and efficiency.

This task includes measuring the Faradaic efficiency of the cell as a function of CO2 and water flowrate, membrane and catalyst composition, and optimizing as needed. Target: at least 70% average Faradaic efficiency.

Accomplishments: 3.2.1 Task 1: Design, construction, and testing of a 250 cm2 electrolyzer. (Completed).

We successfully scaled up our formic acid electrolyzer design from a bench scale 5 cm2 to a 250 cm2 size unit using a modified cell design used in our CO2 electrolyzer program work. We scaled-up the electrolyzer anode and cathode catalysts and designed several center flow compartments. The 250 cm2 electrolyzer was successfully operated, producing formic acid used in the preparation of the K-Formate project deliverable.

3.2.2 Task 2: Optimizing output and efficiency. (Completed).

We worked on the development of the cell center compartment ion exchange (IX) wafers over the past few months, preparing various IX wafers using commercial resin beads and powered ion exchange resin for testing in our smaller 5 cm2 laboratory cells to optimize voltage drop and formic acid efficiency. We have also identified and designed a new cathode cooling plate for the 250 cm2 electrolyzer design which will allow us to control the temperature of the cathode.

3.2.3 Task 3: Producing 5 lbs of K-Formate (50 wt% solution). (Completed).

The 5 lbs of K-formate were prepared from the formic acid produced from the 250 cm2 formic acid electrolyzer formic acid product 118 hr run. The formic acid solution product produced in our November, 2020 118 hour cell run was used in producing the 50 wt% K-Formate solution product. Approximately 16 liters having a formic acid concentration of about 8 wt%, containing about 1,286 gm (2.5 lb) of formic acid solution (100% basis) was collected during the run. The FA cell product solution was neutralized in 4 liter batches to a pH of 7.2 using a stirring bar, calibrated pH probe, and with slow addition of a 45% commercial KOH solution (City Chemical). Multiple 2 liter batches of the K-Formate solution were evaporated on stirred hot plates to obtain a concentration of about 50 wt%. The 5 lbs of K-Formate (50 wt% solution) were packaged for delivery to the ARO to meet the 5 lb milestone delivery. The product solution had a specific gravity of 1.339, K-formate content of 50.29 wt%, and pH of 10.80. 1H NMR showed a basically pure K-Formate solution product.

3.2.4 Task 4: 500-hour test. (Completed).

We successfully scaled-up and operated our laboratory 5 cm2 cell to a 250 cm2 electrolyzer unit. We conducted two operating runs, the first being a shakedown run to determine how well the cell operated at the current densities that we operated the 5 cm2 bench scale cell.
The Dioxide Materials 250 cm2 formic acid electrolyzer design was first successfully operated in a 118 hour shakedown run in November, 2020. The electrolyzer was operated at two current densities, 100 mA/cm2 and 200 mA/cm2. The cell voltage was 3.42 – 3.82 V at 200 mA/cm2, significantly less than our milestone target goal of 4.5 V. The formic acid product ranged from 5.3% to 9.19%, which was dependent on the flow we used in the center compartment and the operating current density.

A. 500 Hour Run.

The electrolyzer from the 118 hour run had to be rebuilt because of an anion membrane pinhole leak. The electrolyzer was reassembled, and the decision was made to operate the reassembled electrolyzer for a full continuous 500 hour run to meet the milestone.
The starting cell voltage at 80 mA/cm2 was about 3.80 V at 22.5 hours and decreased to about 3.62 V at 70 hours, and then very slowly increased during the rest of the run ending at 3.71 V. During the run, the formic acid Faradaic efficiency varied in the range of 22.4 – 26.6%, showing a slow FE decline from about 244 h at 26.6% down to 23.6% at the end of the run. The cathode temperature slowly increased during the 500 hr run from about 57 to 60.5 °C.

B. 500 Hour Run Performance Results Discussion and Summary.

• The 500 hour test run demonstrated that the 250 cm2 electrolyzer scale-up design showed a stable operation performance, producing pure formic acid at concentrations of about 6.5 wt% and having a cell voltage in a range of about 3.62 - 3.71 V at a current density of 80 mA/cm2. The average formic acid FE% was in the range of about 22.4-26.6%. 3.62 – 3.71 V at 80 mA/cm2, FE: 22.4 – 26.6%
• The initial 118 hour run reported in December, 2020 was operated at higher current densities at voltages still well below 4.5 volts:
i) 3.59 V at 120 mA/cm2 FE: 38-44%, ii) 3.74 V at 200 mA/cm2 FE: 28-29%, iii) 3.40 V at 120 mA/cm2 FE: 24-26% (later in run)

C. Future Modification Items for the 250 cm2 Electrolyzer.

• The use of an IX wafer in the 250 cm2 cell will greatly improve the cell assembly.
• The anode and cathode operating temperatures are critically important in achieving high formic acid based Faradaic efficiencies, especially the cathode. We have two cathode cooling designs that we can fabricate and test in the electrolyzer.

3.2.5 Task 5: Techno-economic model of scaled-up production costs. (Completed).

The prepared a Techno-Economic model of the scaled-up production costs. We did the electrolyzer mass balance, and put together an economic model of the scaled-up production costs as required in the task.

A. Techno-Economic Model of Scaled-up Production Costs.

An economic model covering the scale-up production costs in producing 50% K-formate has to take into account both capital costs (CAPEX) and the operating (OPEX) costs.

B. Estimates on the K-Formate Scaled-Up Model Production Requirements.

The scale-up of the K-formate process requires the quantity of K-formate that will be required. In this scenario, we found out from the available literature on companies that sell deicers that approximately 1- 3 gal of K-formate is used per 1000 ft2 of runway (Information from Peters Chemical Company website). In the model, we used the 70% FA and 3.5 V electrolyzer performance , and calculated the daily amount of 50% K-Formate which would be required.

C. K-Formate System Scale-Up Production Model OPEX Estimate.

Our preliminary techno-economic model of scaled-up production costs showing
operating costs, OPEX, and capital costs, CAPEX, for a nominal production volume of 18,000 gal/yr of K-Formate. The OPEX electrochemical production costs of formic acid, even at 70% and 30% Faradic efficiencies, were calculated to be $147 and $342 per ton of FA respectively. Both OPEX production costs are still below the market cost of formic acid, $600 - $900/ton Internationally and $1200/ton in the USA. On final analysis, the cost of KOH is about 60 – 80% of the cost of manufacture. The KOH supply price ultimately determines the final production cost. Depending on the KOH source, the actual price of the K-Formate can range from $0.52 - $1.27 based on KOH ranging from $800 - $2500 per ton (100% basis).

D. K-Formate System Scale-Up Production Model CAPEX Estimate.

A preliminary scale-up production CAPEX estimate for a K-Formate system producing about 50 gal/day of 50 wt% potassium formate solution was done. Using ambitious estimates, the electrolyzer estimate for a 10 cell stack using 0.5 m2 size cells, is about $51,000. Electrolyzer system instrumentation and related equipment was about $11,500. Formic acid conversion to K-formate with storage is about $25,000. The total estimated cost was about $88,000. Cost estimates were made for non-identified equipment. These estimates did not include any installation and maintenance costs, assuming a building structure already available. Utilities such as city water and electricity would have to be provided.

3.2.6 Task 6: Plan for Phase II. (Completed).

We have submitted a proposal for Phase 2B submission on March 29, 2021. The information in the techno-model scale-up will supply the estimates for a 100 gal/day K-formate (1134 lb/day) production system for Phase II.

3.2.7 Task 7: Reporting. (Completed).

All technical monthly reports during the project have been submitted as required. The final project report has been submitted late due to a miscommunication.

Training Opportunities: Nothing to Report

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

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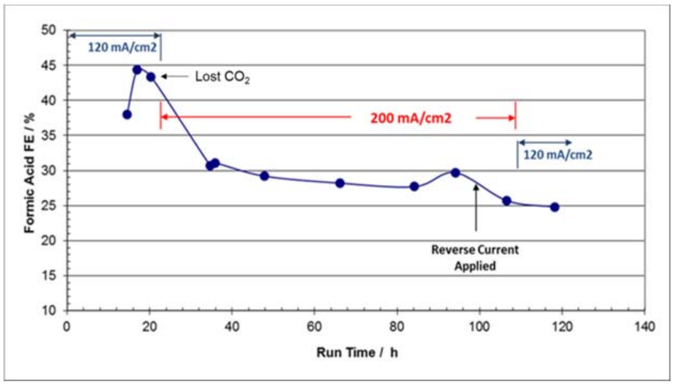
Person Months Worked: 4.00
Funding Support:
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Other Professional
Participant: Daniel Carillo
Person Months Worked: 1.00
Funding Support:
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

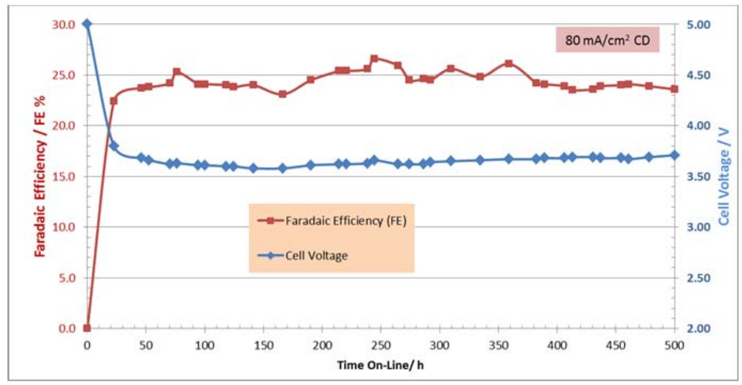
1. Formic Acid Electrolyzer Performance Summary

The performance of the Dioxide Materials DXM formic acid cell is summarized in Figure 1 for the two runs conducted with the 250 cm2 electrolyzer. Figure 2 shows the experimental formic acid electrolyzer operating system.

Figure 1. Performance of the two 250 cm^2 formic acid electrolyzer runs.

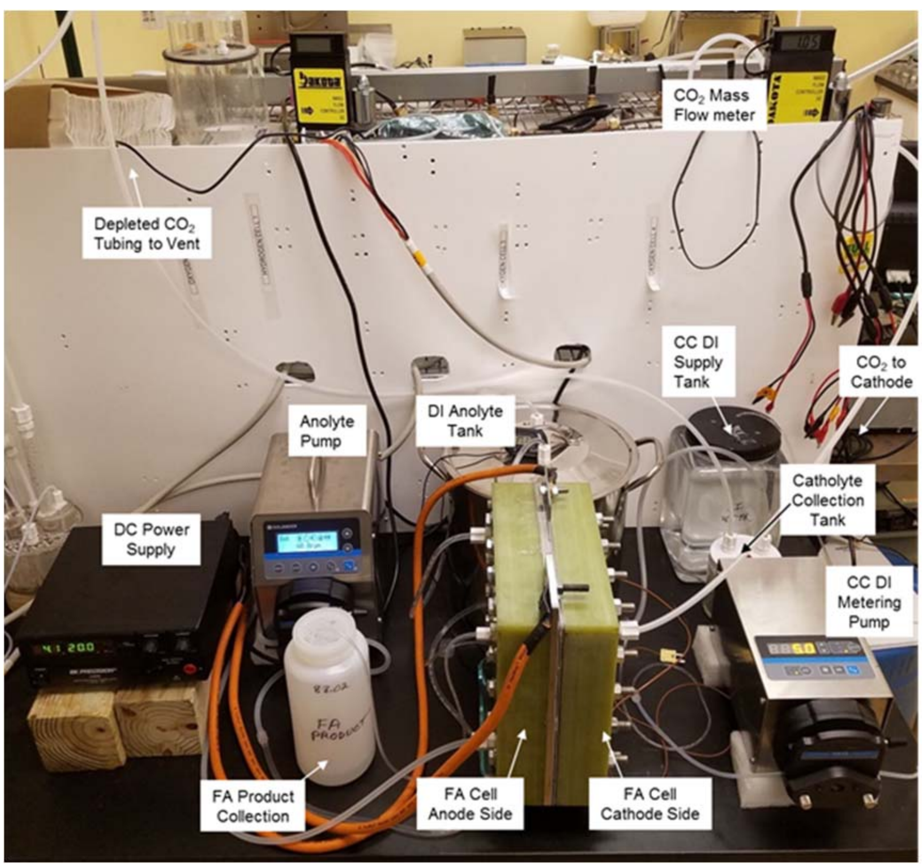


118 Hour Run



500 Hour Run

Figure 2. DXM Formic acid electrolyzer experimental operating system.



2. The Techno-Economic scale-up production model on generating K-Formate

A Techno-Economic model was generated covering the operating costs, OPEX, and the capital costs, CAPEX, in generating K-Formate using the DXM formic acid electrolyzer and KOH. The OPEX electrochemical production costs of formic acid, even at 70% and 30% Faradic efficiencies, were calculated to be $147 and $342 per ton of FA respectively. Both OPEX production costs are still below the market cost of formic acid, $600 - $900/ton Internationally and $1200/ton in the USA. On final analysis, the cost of KOH is about 60 – 80% of the cost of manufacture. The KOH supply price ultimately determines the final production cost. Depending on the KOH source, the actual price of the K-Formate can range from $0.52 - $1.27 based on KOH ranging from $1000 - $2500 per ton (100% basis). Table 1 shows the OPEX at a $1000/ton KOH pricing and Table 2 for a $2500/ton pricing.

Table 1. Techno-Economic scale-up production costs. OPEX Spreadsheet for two source pricing of KOH, $800/ton and $2500/ton, showing the impact on final K-Formate price.

1A

K-Formate Process Operating Unit Chemical and Energy Consumptions - per lb of K-Formate (100% Basis)				
70% FA Faradaic Efficiency				
	Unit	Units/lb Prod	$ Price/Unit	$/ lb Prod
Raw Materials and Utilities				
CO2 Consumption (3X Stoichimetry)	lb	4.56	0.0177	$0.081
CO2 Recovery Credit (1X)	lb	1.52	0.0177	$0.027
DI Water	lb	13.74	0.0024	$0.033
KOH Flake	lb	1.938	0.363	$0.704
Electrolyzer AC kWh Power (90% AC to DC)	kWh	2.935	0.05	$0.147
Electrical kWH For Evaporation	kWh	0.695	0.05	$0.035
Auxiliary Power kWh (Pumps)	kWh	0.200	0.05	$0.010
Co-Products				
Oxygen (vented - no credit)	lb	0.77	---	---
CO (vented - no credit)	lb	0.07	---	---
H2 (vented - no credit)	lb	0.02	---	---
			Total	$1.036
			Price Calculated as 50% K-Formate	**$0.52**

KOH Pricing: $800/ US ton ($0.363/lb)

1B

K-Formate Process Operating Unit Chemical and Energy Consumptions - per lb of K-Formate (100% Basis)				
70% FA Faradaic Efficiency				
	Unit	Units/lb Prod	$ Price/Unit	$/ lb Prod
Raw Materials and Utilities				
CO2 Consumption (3X Stoichimetry)	lb	4.56	0.0177	$0.081
CO2 Recovery Credit (1X)	lb	1.52	0.0177	$0.027
DI Water	lb	13.74	0.0024	$0.033
KOH Flake	lb	1.938	1.134	$2.198
Electrolyzer AC kWh Power (90% AC to DC)	kWh	2.935	0.05	$0.147
Electrical kWH For Evaporation	kWh	0.695	0.05	$0.035
Auxiliary Power kWh (Pumps)	kWh	0.200	0.05	$0.010
Co-Products				
Oxygen (vented - no credit)	lb	0.77	---	---
CO (vented - no credit)	lb	0.07	---	---
H2 (vented - no credit)	lb	0.02	---	---
			Total	$2.530
			Price Calculated as 50% K-Formate	**$1.27**

KOH Pricing: $2500/ US ton ($1.134/lb)