Dioxide Materials™

The CO_2 Recycling Company™

CO_2 and Renewable Electricity into Chemicals: Formic Acid Production From Coal Flue Gas DE-FE0031706

Hongzhou Yang

Dioxide Materials Inc.
Boca Raton FL 33431

U.S. Department of Energy
National Energy Technology Laboratory
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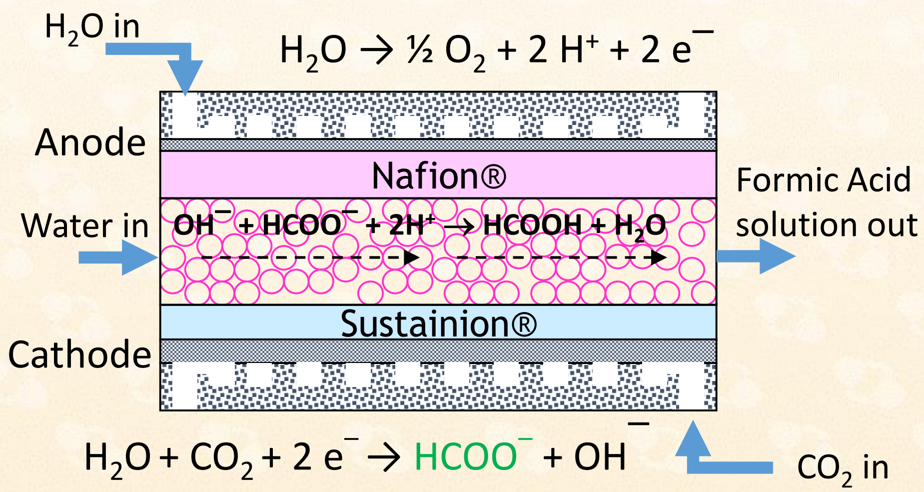
Project Overview

- **Project Overview**
  - Funding: $800,000 DOE, $200,000 Cost Share
  - Overall Project Performance Dates
    - 02/01/2019 to 01/31/2021
  - Project Participants:
    - Dioxide Materials: responsible for electrolyzer development
    - OCO: responsible for economic evaluation, testing at Talen Energy coal fired power plant
    - Talen Energy: Providing space/CO_2 for real tests
  - Overall Project Objectives
    - Understand how to run the electrolyzer for the conversion of CO_2 into formic acid using flue gas from a power plant as a source of CO_2.
    - Key questions
      - Can we run directly on the CO_2 produced by the power plant, or is separation needed?
      - What cleanup is needed?

Technology Background

3-Compartment Electrolyzer Cell Configuration and Reactions in the Cell



Technology Advantages

- Pure Formic acid production
- No need of the energy intensive extra step of formate conversion to formic acid
- Less energy required to produce pure formic acid that can be directly used

Gaps and Opportunities

- Formic acid as feed stock for bioprocessing industry
- Electrolyzer development (cell design, membranes, electrodes…)
- Understand the impurity effects on the performance and optimize operation conditions
- Formic acid production cost

Technology Background

- Technology development efforts prior to current project
  - Development of 3-compartment cell configuration
  - Demonstration of pure formic acid production using the 3-compartment cell configuration
  - Studies to understand the factors that affect cell performance.
- Technical challenges
  - Run the electrolyzer feeding with flue gas
  - How to mitigate the negative effect of flue gas on performance if any
  - Improve cell performance and long-term stability
- Technical and economic benefits
  - Development of conditions and methods to operate the electrolyzer and maintain the cell performance with flue gas
  - Knowledge for scale up
  - Low formic acid production cost for bioprocessing industry

Project Scope

Objectives

- Understand how to run the electrolyzer for the conversion of CO_2 into formic acid using flue gas from a power plant as a source of CO_2.
- Key questions
  - Can we run directly on the CO_2 produced by the power plant, or is separation needed?
  - What cleanup is needed?

Project schedule/Key Milestones

- Obtain 100 mA/cm^2 of current feeding a mixture containing 50% CO_2 (Oct 1, 2019)
- Modify the catalyst and operating conditions to obtain 200 mA/cm^2 current density feeding 50% CO_2. (March 1, 2020)
- Demonstrate 200 mA/cm^2 current for 1000 hours with 50% CO_2. (Sept 1, 2020)
- Modify the catalyst and operating conditions to obtain 200 mA/cm2 current density with a mixture containing 50% CO_2, 5% O_2. (Spet 1, 2020)
- 100 hours test with 100 ppm of SO_2 to determine whether there are any effects. (June 1, 2020)
- 100 hours test with 100 ppm of NOx to determine whether there are any effects. (July 1, 2020)
- Demonstrate 200 mA/cm^2 current density for 100 hours with 50% CO_2, 35ppb SO_2, and 5% O_2. (Feb 1, 2021)
- Test on flue gas. (Feb 15, 2021)

Project Scope

Project Success Criteria

- Demonstrate a formic acid electrolyzer running on 14% CO_2 with total faradaic efficiency (FE-HCOOH+FE-CO+FE-H_2) greater than 50%. (Mar 1, 2020, completed)
- Demonstrate a formic acid electrolyzer running for 1000 hours on 50% CO_2, with a cell voltage that never exceeds 4 V. (Nov 1, 2020, completed)
- Demonstrate a formic acid electrolyzer running on 50% CO_2 , 2% O_2 with total faradaic efficiency (FE-HCOOH+FE-CO+FE-H_2) greater than 50%. (July 1, 2020, completed)
- Production of a formic acid stream with at least 5% formic acid from CO_2 produced by a coal fired power plant. (Feb 14, 2021)

Significant Project risks and Mitigation Strategies

Significant Project Risks	Mitigation Strategies
Loss of key management personnel due to illness	DM is developing a business continuity plan to lower risks
FA cell technology	The basic FA technology have been demonstrated on bench scale and units have been delivered to customers. Confident of cell scale-up.
CO_2 and O_2 concentration effects	Higher CO_2 concentration requirements have an impact of costs. We have alternate technologies to use for concentrating CO_2 to requirements. There are numerous methods for adsorbing impurities
Stable FA cathode catalyst development	The current catalyst works. Experience for over 1000 hours with the current catalyst. There are a number of catalyst compositions that can make formate.

Progress and Current Status of Project

Recent accomplishments

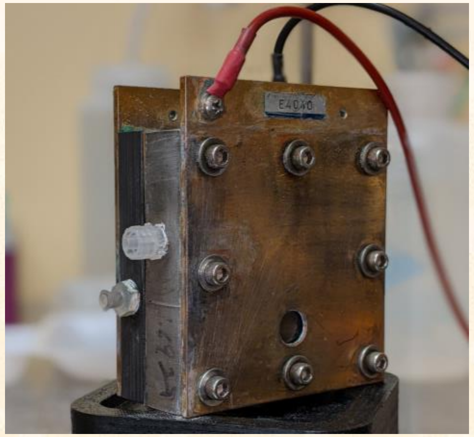
- Modification of cell configuration and components to improve the overall cell performance
- Demonstrated 1000 h runs at 200 mA/cm^2 current density feeding with 100% and 50% CO_2, respectively
- Demonstrated long-term run at 200 mA/cm^2 current density feeding with 14% CO_2
- Completed studies of O_2, SO_2 and NOx effects on cell performance; Developed methods and strategies to mitigate the effects

Challenges addressed

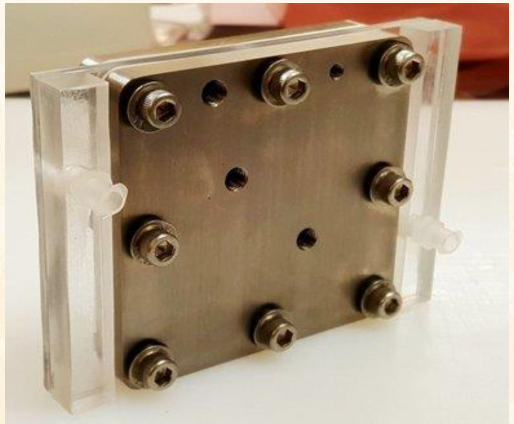
- How to improve the performance of the electrolyzer (cathode and anode, anion exchange membrane, operation conditions), especially with low CO_2 concentration and impurities in the flue gas
- Long-term stability

Progress and Current Status of Project

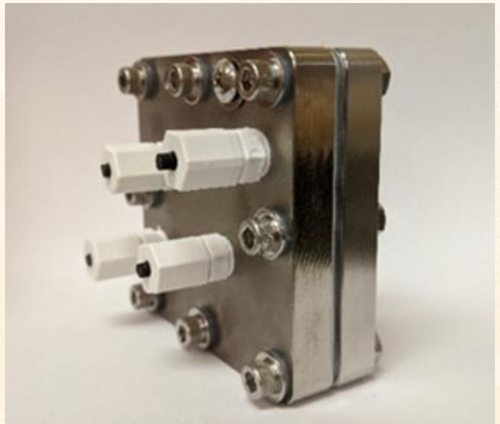
Development of the electrolyzer



Original Version



Second Version

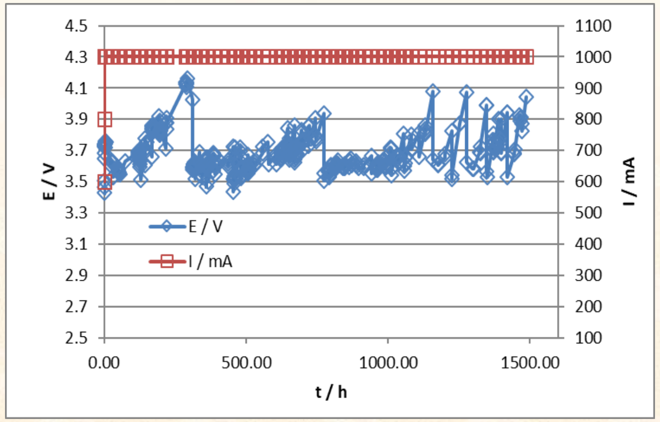


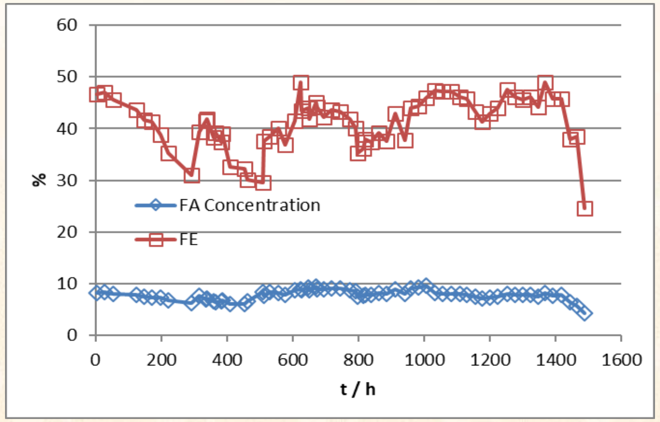
Current Version

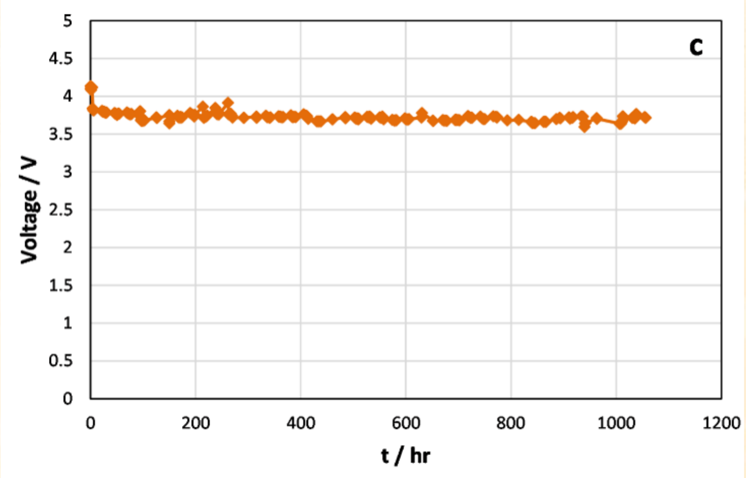
- Reduced size and weight and more robust
- Eliminated leaking and anode side corrosion in long-term operation
- Provided a good foundation for scale up

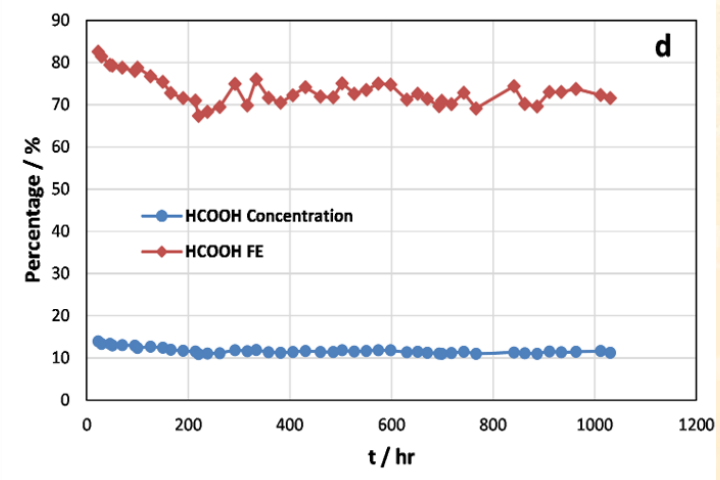
Progress and Current Status of Project

Improvement of 1000 h long-term stability at 200 mA/cm² with 100% CO_2









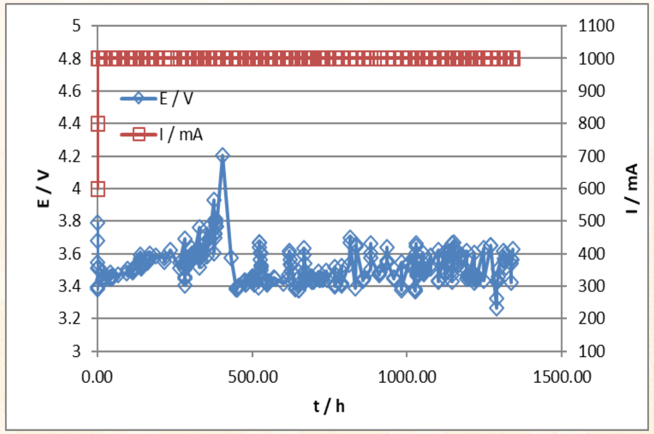
- 1000 h testing results obtained early this year
    - 30-50% formic acid FE
    - 6-9.5 wt% formic acid product
    - Unstable voltage, >4.0V

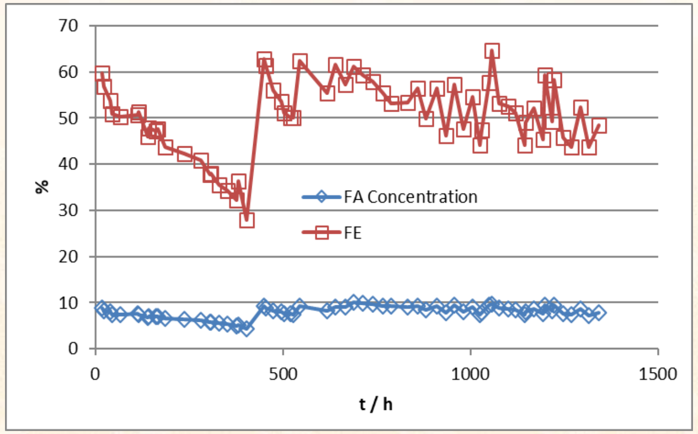
Modification: anion exchange membrane, cathode catalyst, operation conditions

- 1000 h testing results obtained recently
    - 71-83% formic acid FE
    - >10 wt% formic acid product
    - stable voltage, ~3.6V
    - Developed a method to maintain cell performance

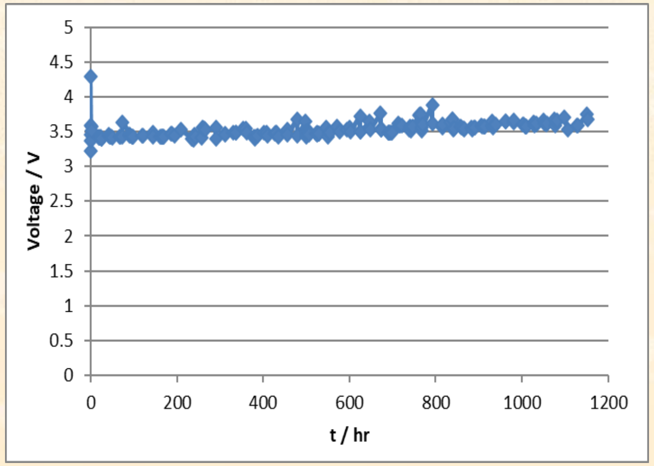
Progress and Current Status of Project

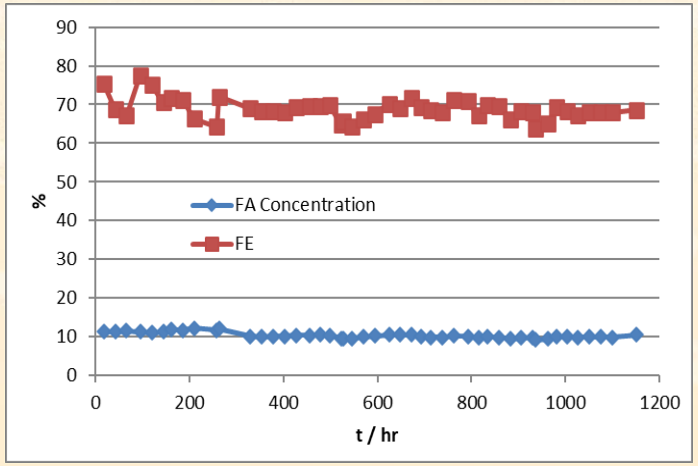
Improvement of 1000 h long-term stability at 200 mA/cm^2 with 50% CO_2





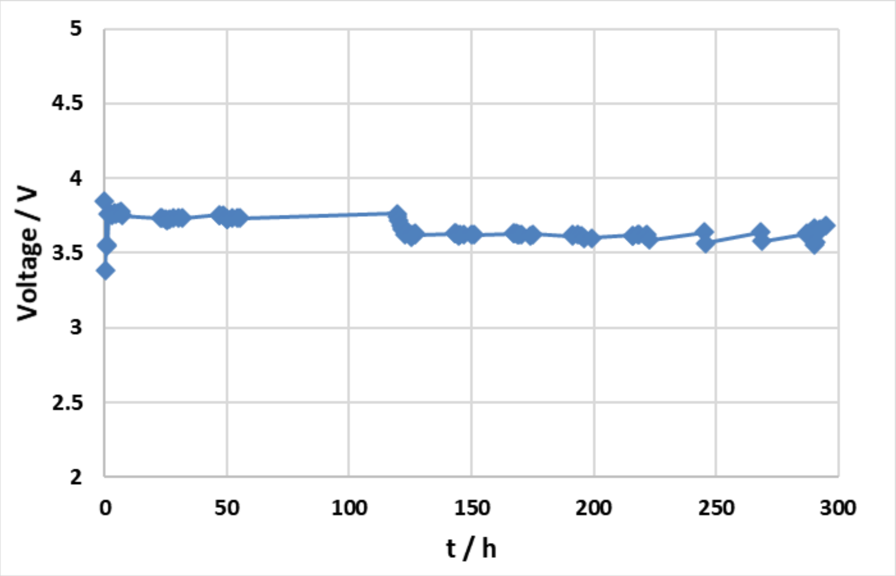
- 1000 h testing results obtained early this year
  - 40-60% formic acid FE
  - 5-9.5 wt% formic acid product
  - Unstable voltage, 3.3-4.2V

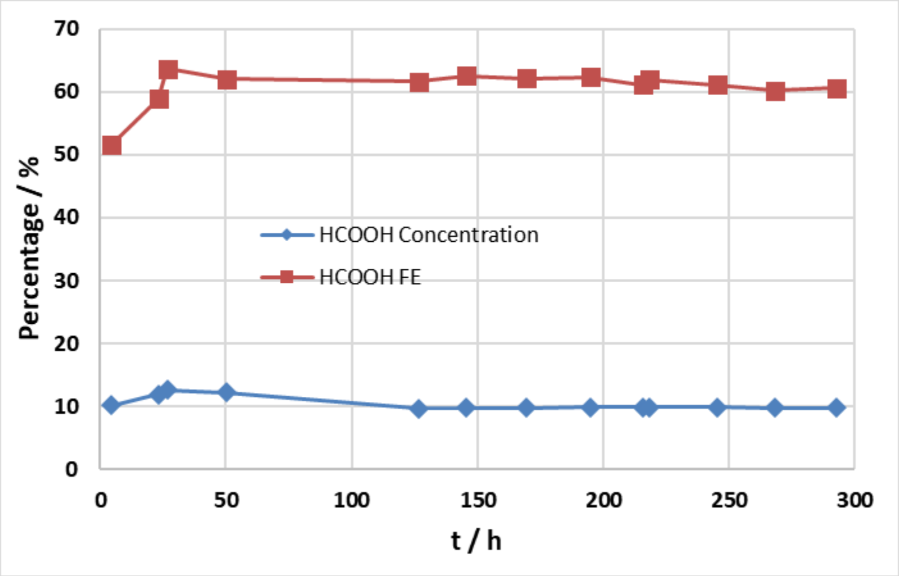




- 1000 h testing results obtained recently
  - 63-79% formic acid FE
  - ~10 wt% formic acid product
  - stable voltage, 3.4-3.8V

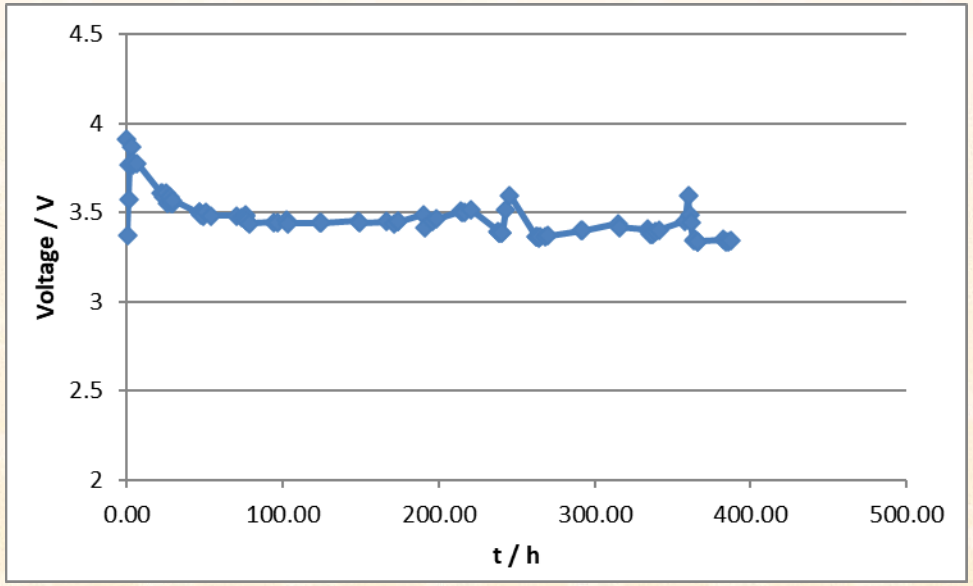
Electrolyzers can also run at 200 mA/cm^2 current density with 14% CO_2

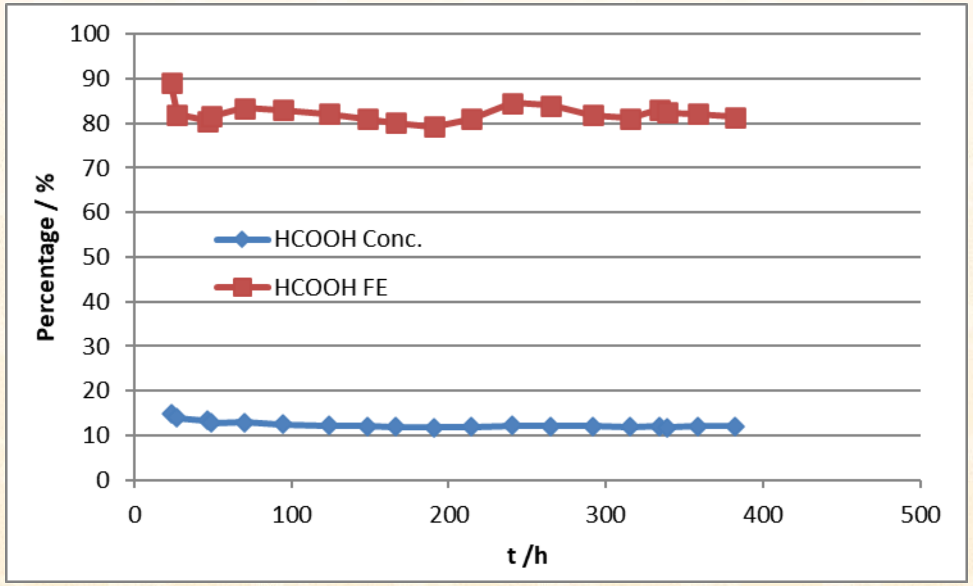




- ~9.9 wt% formic acid with >60% formic acid FE during 300 h testing
- Modification of the cell and the operational conditions may improve the cell performance

New cathode catalyst further improves the electrolyzer performance





- Electrolyzer tested with 100% CO_2
- 12-15wt% FA 81-89% formic acid FE, <3.5V

Progress and Current Status of Project

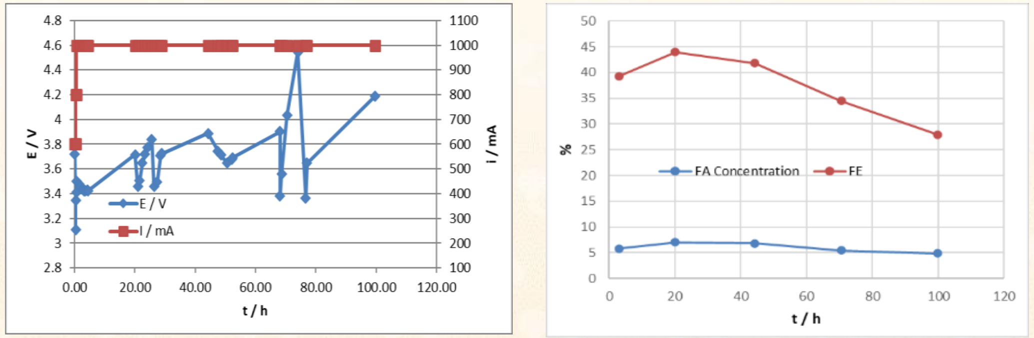
Only a few papers reported the cell performance on CO_2 reduction to formic acid

	Cell performance from literature*	Cell performance from this project
Maximum Current Density	~220 mA/cm^2 from H-cell results	> 300 mA/cm^2
Current Density in long-term testing	30 mA/cm^2	200 mA/cm^2
Electrolyzer voltage	~3.0 V	~3.6V
Long-term testing time	100 h	1000 h
Formic acid Concentration	0.51 wt% (~0.11M)	11.2-14.0 wt% (2.5 – 3.1M)
Formic acid FE	~80%	72-83%

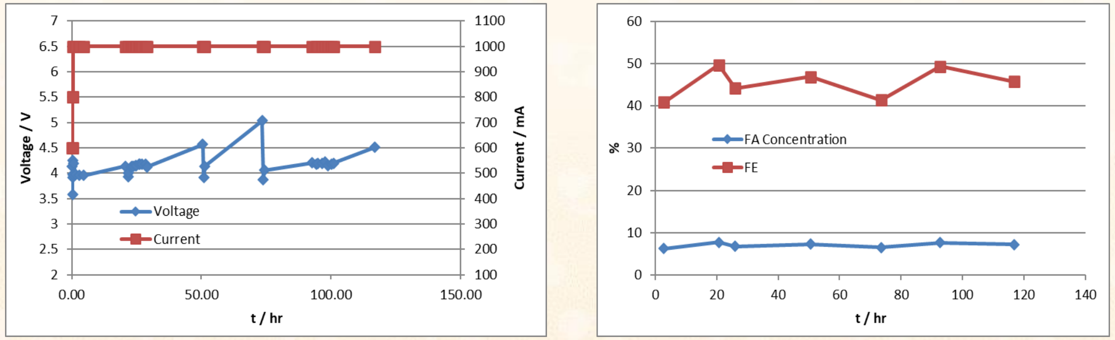
*C. Xia, P. Zhu, Q. Jiang, Y. Pan, W. Liang, E. Stavitsk, H.N. Alshareef, H. Wang, Nat. Energy. 4 (2019) 776–785. https://doi.org/10.1038/s41560-019-0451-x.

Progress and Current Status of Project

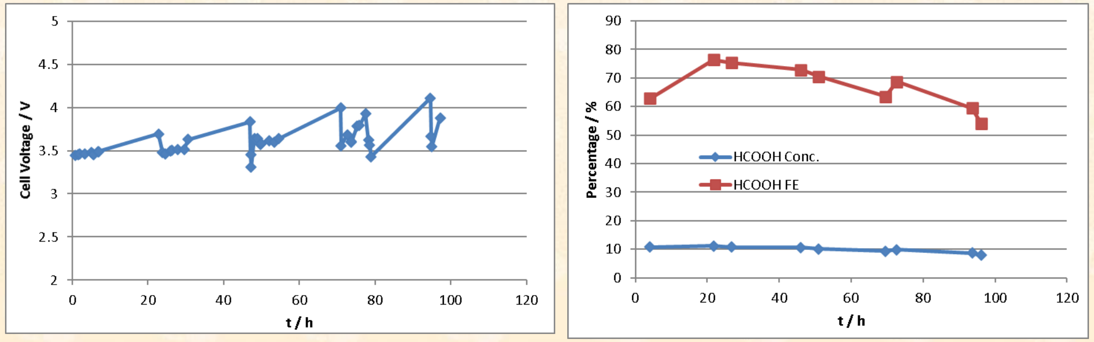
Mitigate O_2 effect on the electrolyzer performance



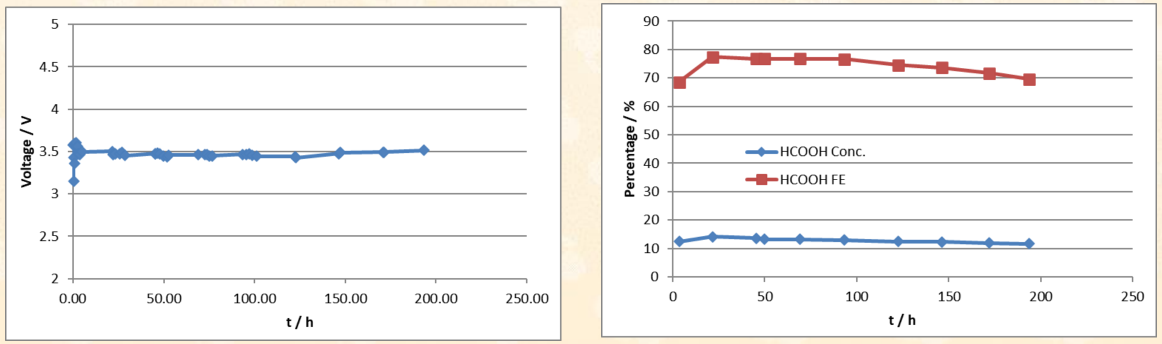
O_2 Effect on cell performance with 5% O_2 in CO_2



The electrolyzer performance with cathode modification



The electrolyzer performance with first O_2 removal method

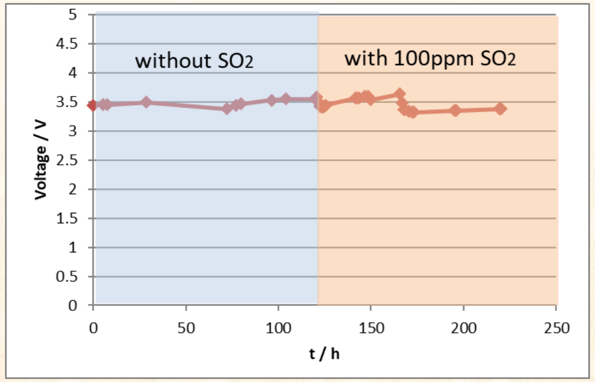


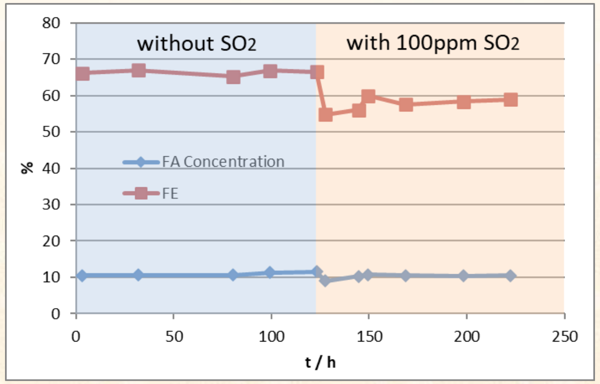
The electrolyzer performance with second O_2 removal method

- Significant negative effect on cell performance with O_2 in CO_2 (1-5% O_2 tested)
- O_2 removal method could greatly improve the cell performance

Progress and Current Status of Project

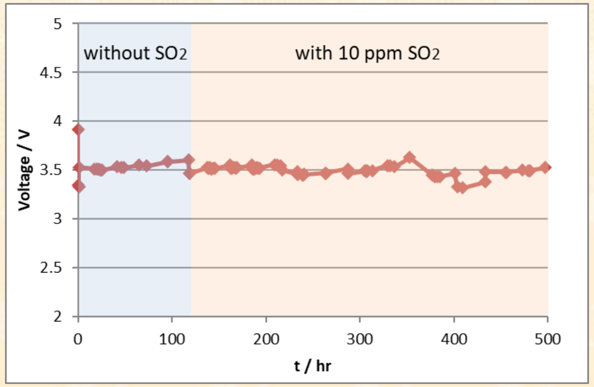
SO_2 effect on cell performance (100 hours test with 100 ppm and 10 ppm SO_2)

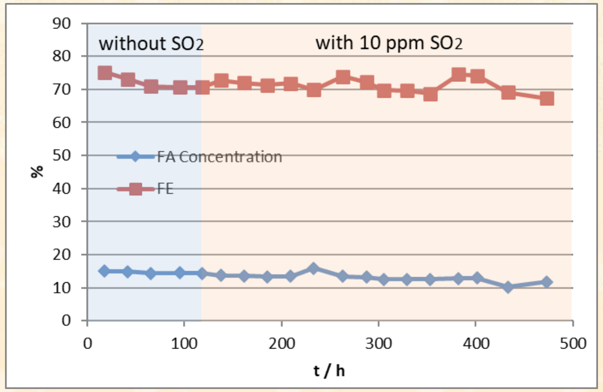




100 h cell test with 100 ppm SO_2 in CO_2

- Negative effect of 100 ppm SO_2 on cell performance compared with the one without SO_2
- Stable performance in 100 h run with 100 ppm SO_2



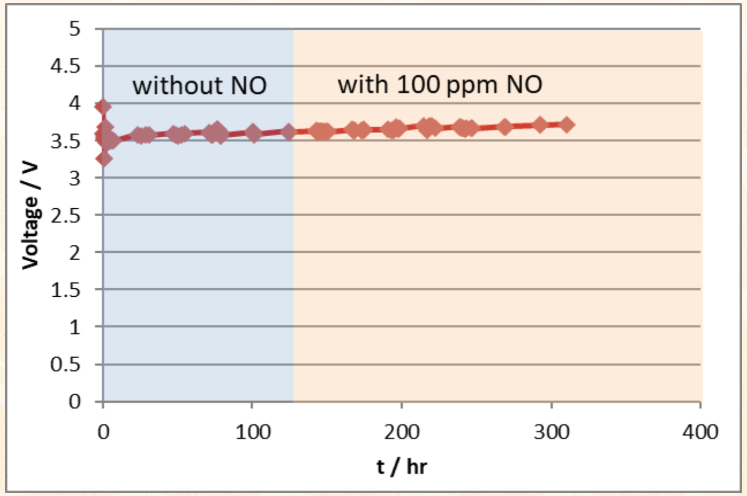


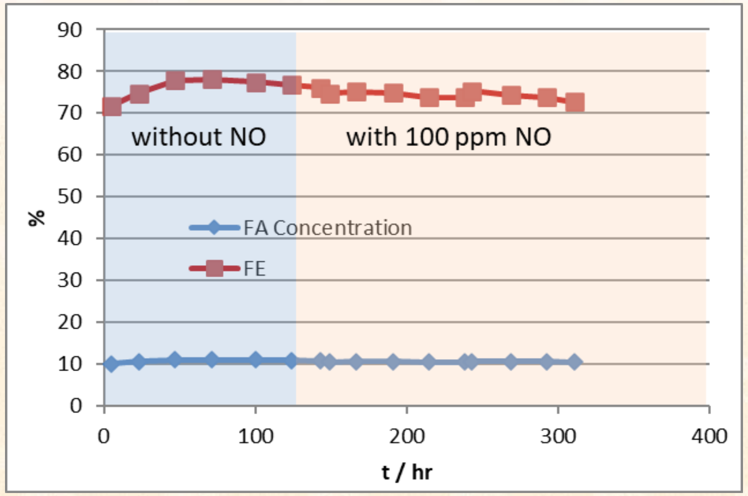
300 h cell test with 10 ppm SO_2 in CO_2

- No apparent effect of 10 ppm SO_2 on cell performance
- Stable performance in 300 h run with 10 ppm SO_2

NOx effect on cell performance (100 hours test with 100 ppm NO)

200 h cell test with 100 ppm NO in CO_2





- No apparent detrimental effect of 100 ppm NO on cell performance
- Stable performance in 200 h run

Summary

Key Findings

- The electrolyzer can be operated at 200 mA/cm^2 current density with CO_2 concentration down to 14%
- >10 wt% formic acid solution can be produced with formic acid FE > 80% at 200 mA/cm^2 current density
- The electrolyzer shows good long-term stability based on several 1000 h cell testing
- The presence of O_2 in CO_2 gas significantly affects the electrolyzer performance. It is critical to remove O_2 from CO_2 gas in order to get stable cell performance.
- 100 ppm SO_2 in CO_2 gas affects formic acid FE and concentration but no stability issue was observed in 100 h testing. 10 ppm SO_2 has no negative effect on cell performance
- 100 ppm NO has no negative effect on cell performance

Future Plans

- Modification of anion exchange membrane, cathode and anode, cell configuration to further improve performance and long-term stability
- >1000h cell testing
- Electrolyzer scale-up

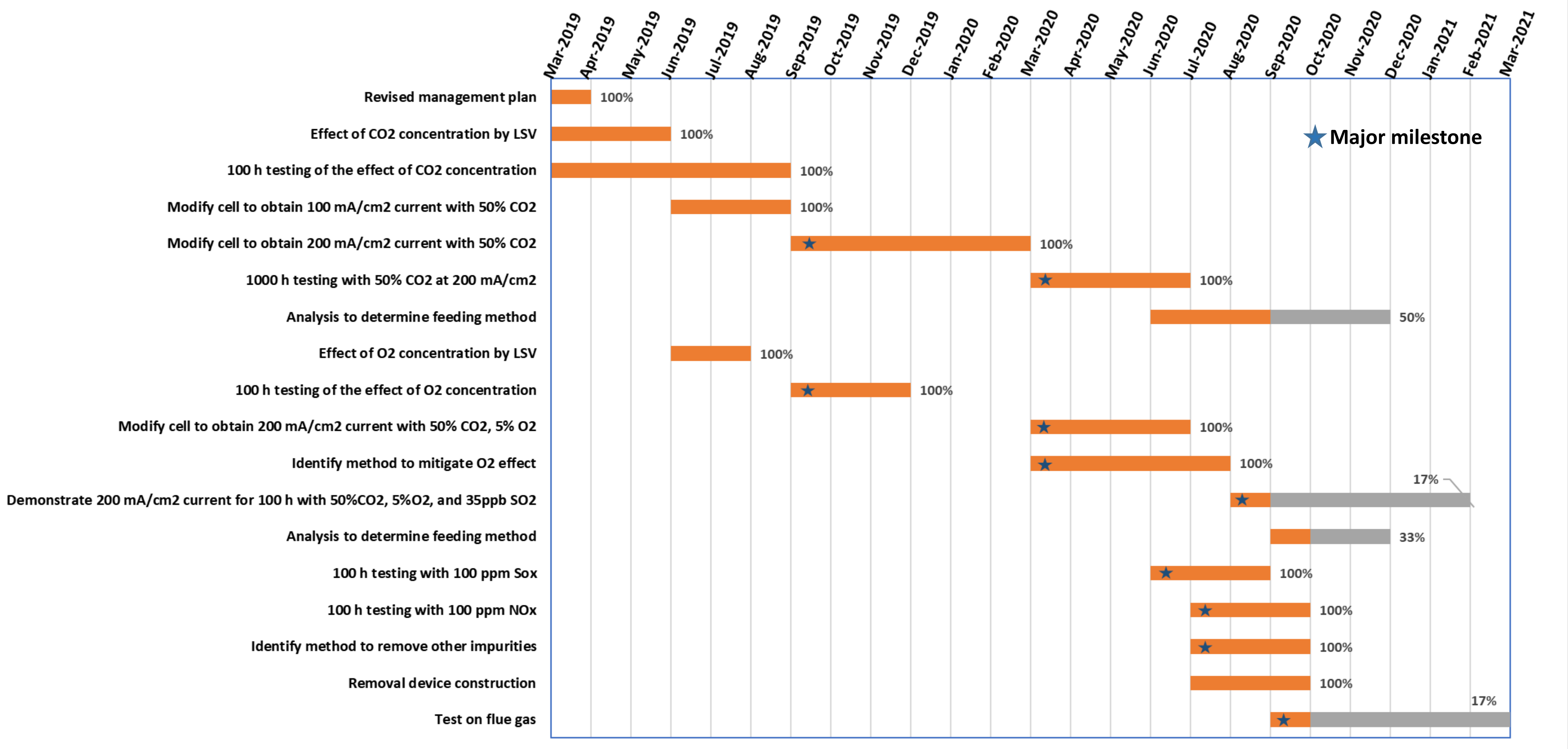
Takeaway Messages

- The technology developed in the project shows very promising application potential using the flue gas to produce formic acid. The critical factors that affect the cell performance were identified and methods to mitigate those effect were developed. The progress made in the current project would help to build a strong foundation for future development and scale up.

Appendix (Organization Chart)

- **Project Participants**
  - **Dioxide Materials**
    - Electrolyzer development
    - Lab scale testing
  - **OCO**
    - Economic evaluation
    - On-site testing
  - **Talen Energy**
    - Providing space/CO_2 for on-site testing

Appendix (Gantt Chart)



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