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

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National Energy Technology Laboratory
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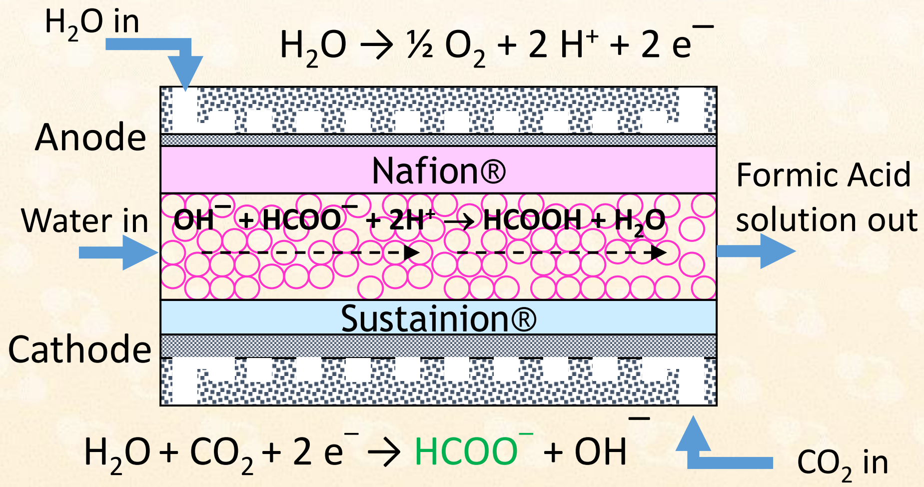
Project Overview

- **Project Overview**
  - Funding: $800,000 DOE, $200,000 Cost Share
  - Overall Project Performance Dates
    - 02/01/2019 to 09/30/2021
  - Project Participants:
    - Dioxide Materials: responsible for electrolyzer development and on-site test
    - OCO: responsible for economic evaluation, on-site test at Talen Energy coal fired power plant
    - Talen Energy: Providing space/CO_2/technical supports for on-site 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

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)
- 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,)
- 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)
- Production of a formic acid stream with 5% formic acid from CO_2 produced by a coal fired power plant. (Jul 29, 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

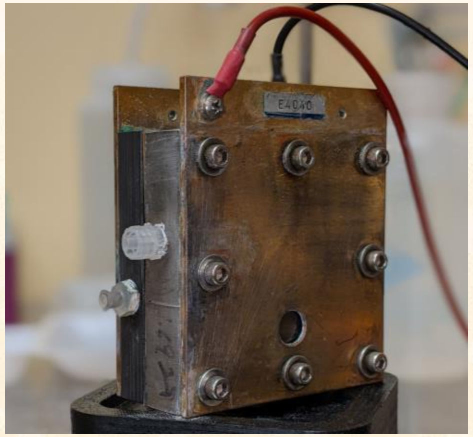
- Modification of cell configuration and components to improve the overall cell performance
- Demonstrated 1000 h runs at 200 mA/cm^2 current density feeding with 100% and 50% CO_2, respectively
- Demonstrated long-term run at 200 mA/cm^2 current density feeding with 14% CO_2
- Completed studies of O_2,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

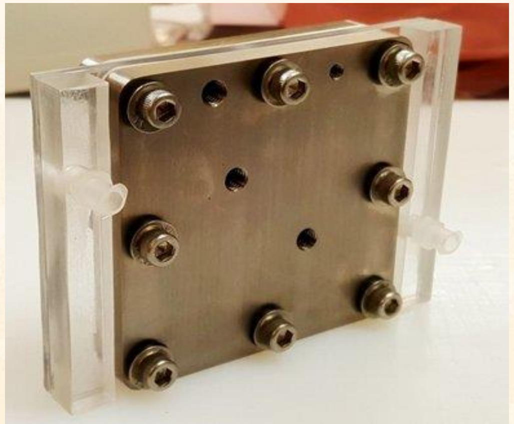
Challenges addressed

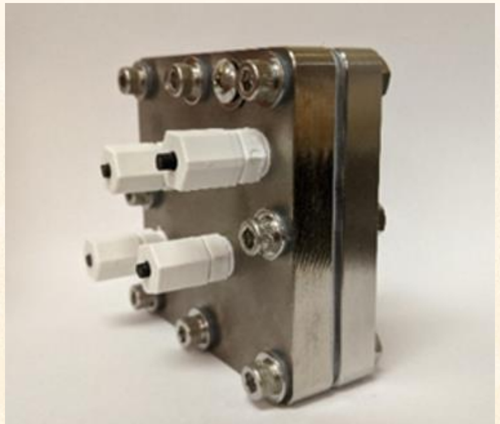
- How to improve the performance of the electrolyzer (cathode and anode, anion exchange membrane, operation conditions), especially with low CO_2 concentration and impurities in the flue gas
- Long-term stability

Progress and Current Status of Project

Development of the electrolyzer

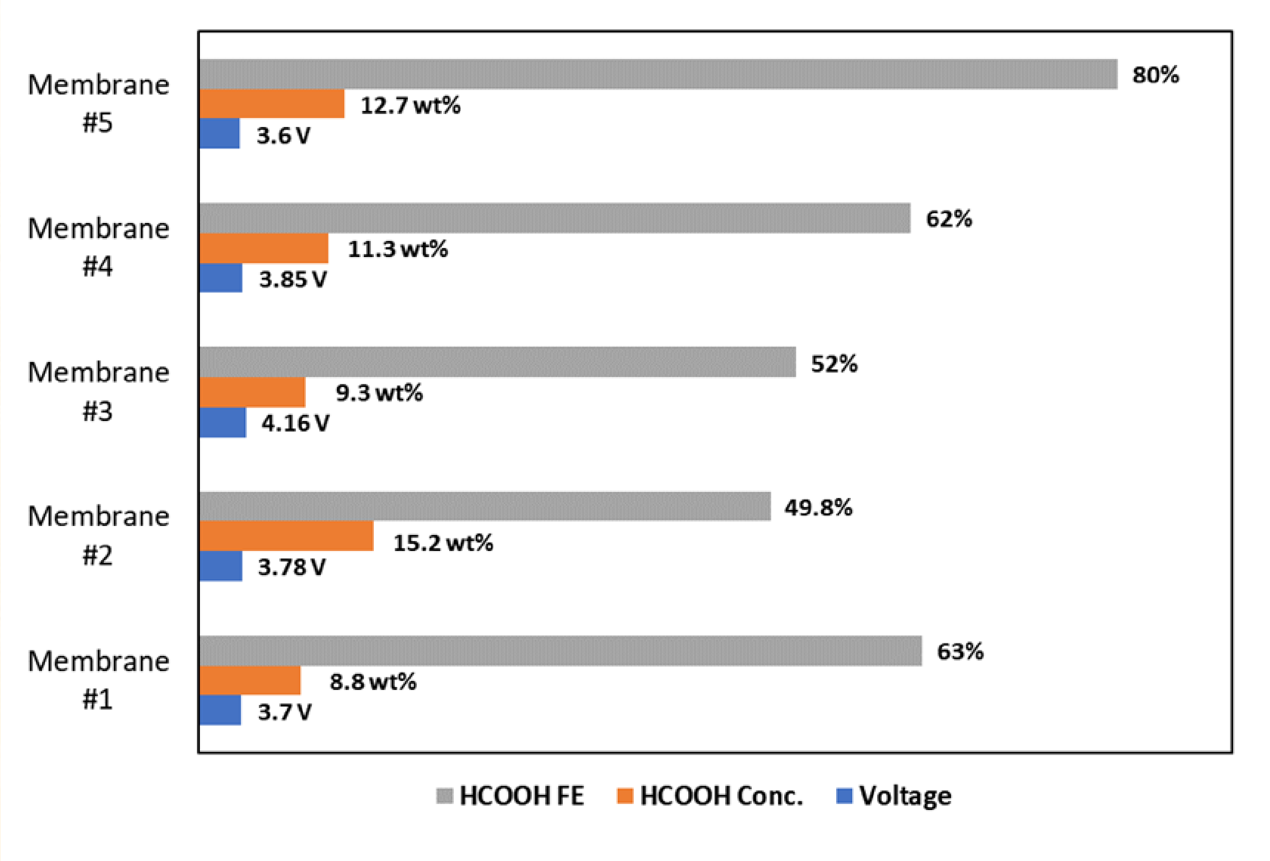

Original Version


Second Version


Current Version

- Reduced size and weight and more robust and dependable
- Eliminated leaking and anode side corrosion in long-term operation
- Provided a good foundation for scale up
- Dioxide Materials started selling the current version of the electrolyzer to our customers

Development of anion exchange membranes

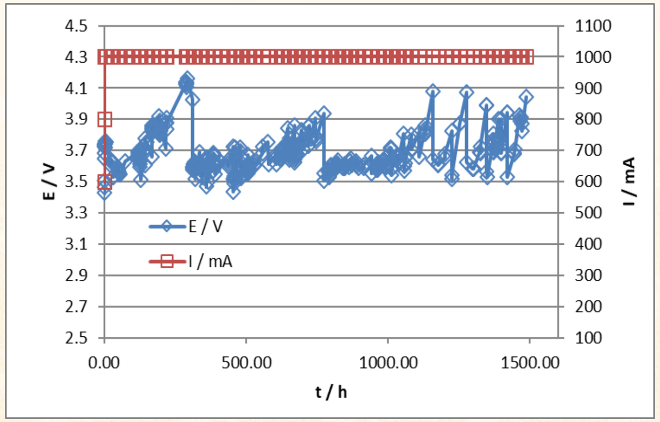


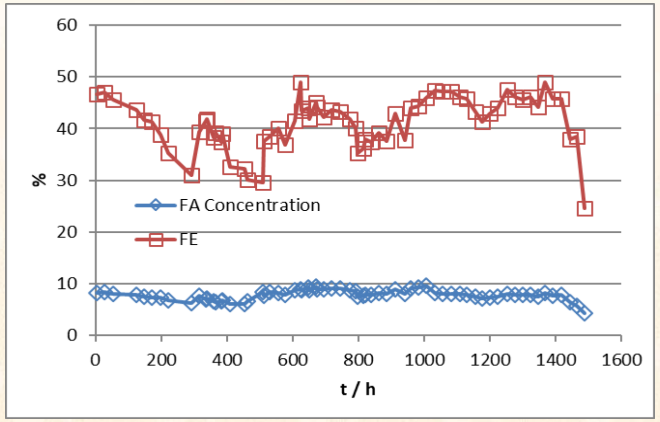
Comparison of the electrolyzer performance with different anion exchange membranes. (All the membranes were tested in the cell at 200 mA/cm^2 current density except membrane #1 at 160 mA/cm^2)

- Original Sustanion® membrane shows good FE with low current and short testing time
- Membrane modification includes the adjustment of mechanical stability, conductivity, water uptake et. al.
- New membrane results in good formic acid FE, formic acid concentration, voltage at 200 mA/cm^2 and long-term stability.
- Dioxide Materials started selling the membrane for interested customers.

Progress and Current Status of Project

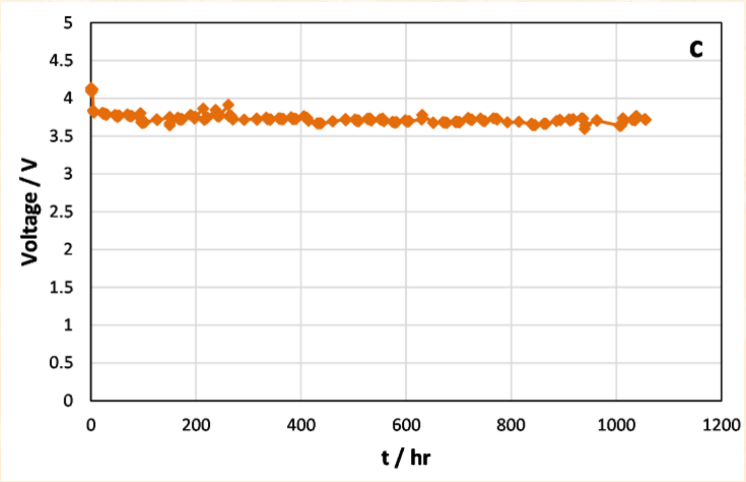
Improvement of 1000 h long-term stability at 200 mA/cm² with 100% CO_2

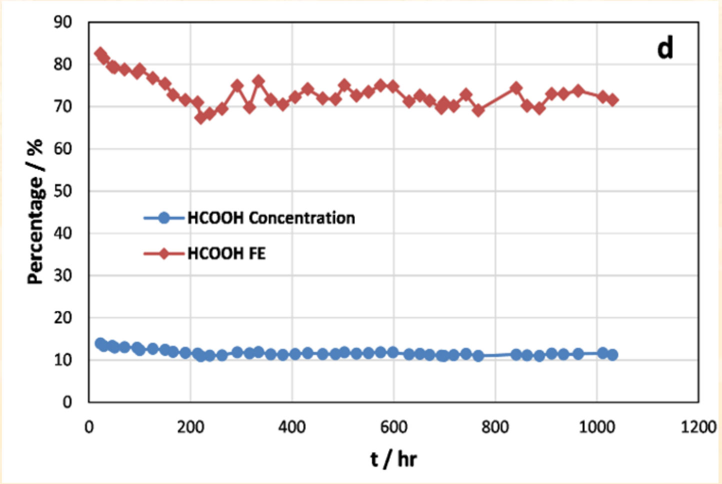




- 1000 h testing results obtained early this year
  - 30-50% formic acid FE
  - 6-9.5 wt% formic acid product
  - Unstable voltage, >4.0V

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 long-term stability at 200 mA/cm^2 with 50% CO_2

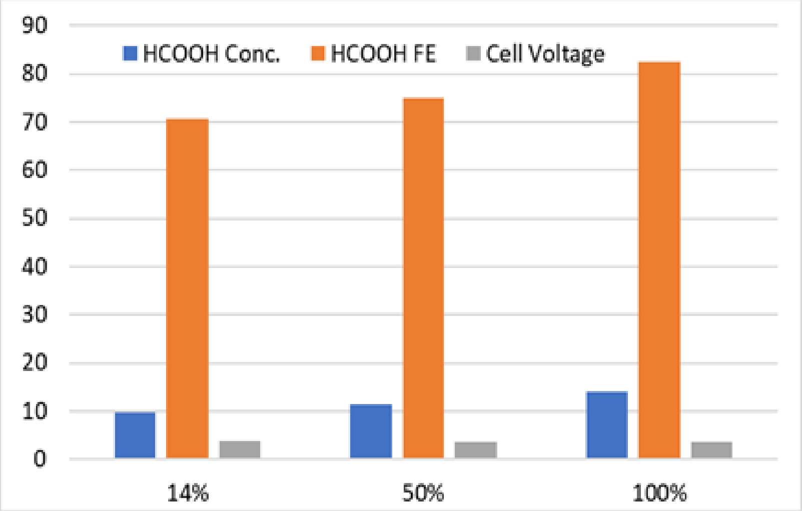
Table 1. Performance of electrolyzers operated with 50% CO_2 before and after cell component modification

	Before Modification	After Modification
Cell Current Density (mA/cm^2)	200	200
Cell Voltage (V)	3.5	3.5
HCOOH Concentration (wt%)	9-10	11
HCOOH FE (%)	~55	~70
Operation Time (h)	100	>1000

Improvement of long-term stability at 200 mA/cm^2 with 14% CO_2

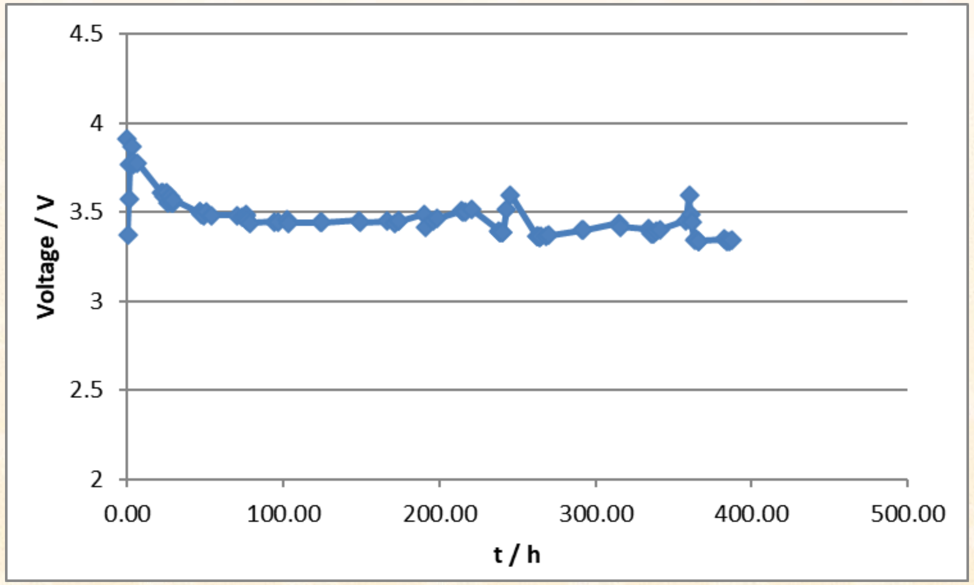
Table 2. Performance of electrolyzers operated with 14% CO_2 before and after cell component modification

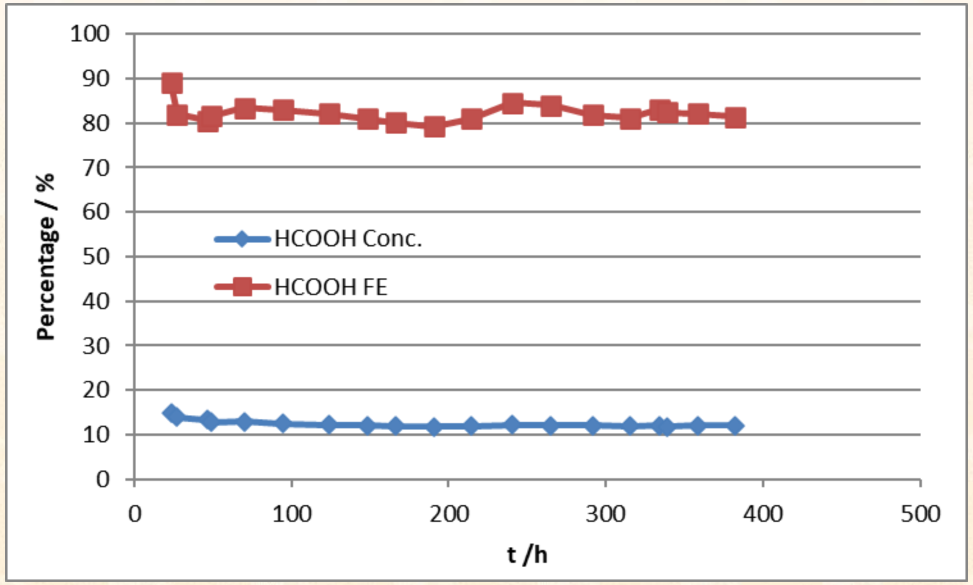
	Before Modification	After Modification
Cell Current Density (mA/cm^2)	100	200
Cell Voltage (V)	3.6-3.7	3.6-3.7
HCOOH Concentration (wt%)	6-7	9-10
HCOOH FE (%)	~35	~60
Operation Time (h)	100	300



Comparison of electrolyzer performance with different CO_2 concentration

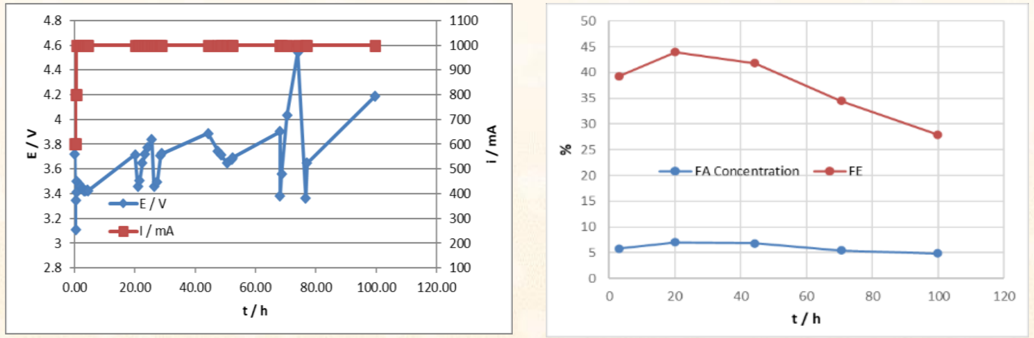
New cathode catalyst further improves the electrolyzer performance



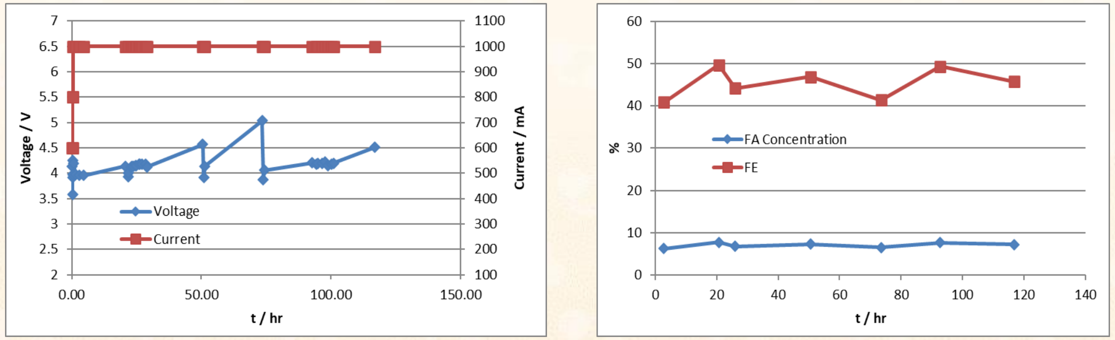


- Electrolyzer tested with 100% CO_2
- 12-15wt% FA 81-89% formic acid FE, <3.5V

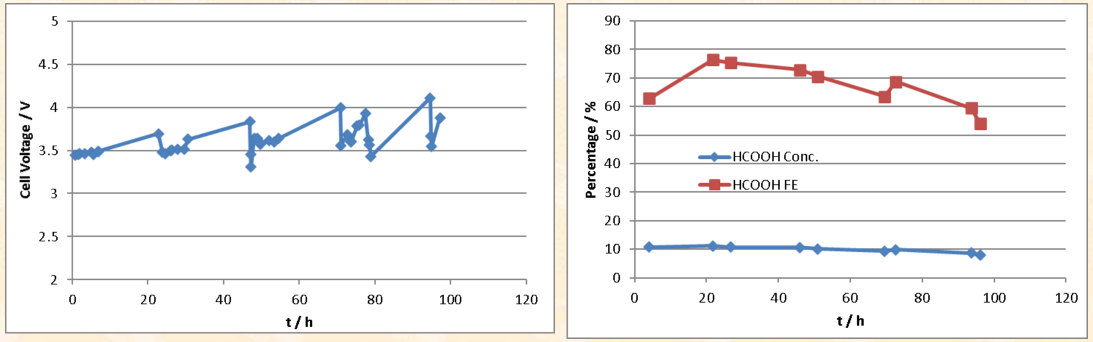
Mitigate O_2 effect on the electrolyzer performance



O_2 Effect on cell performance with 5% O_2 in CO_2



The electrolyzer performance with cathode modification

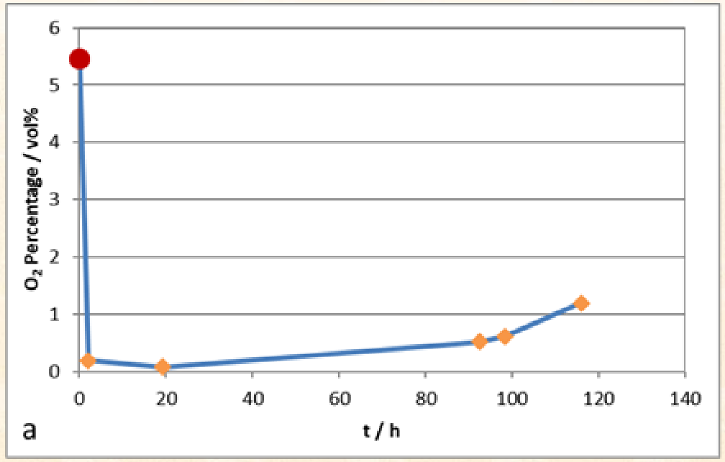


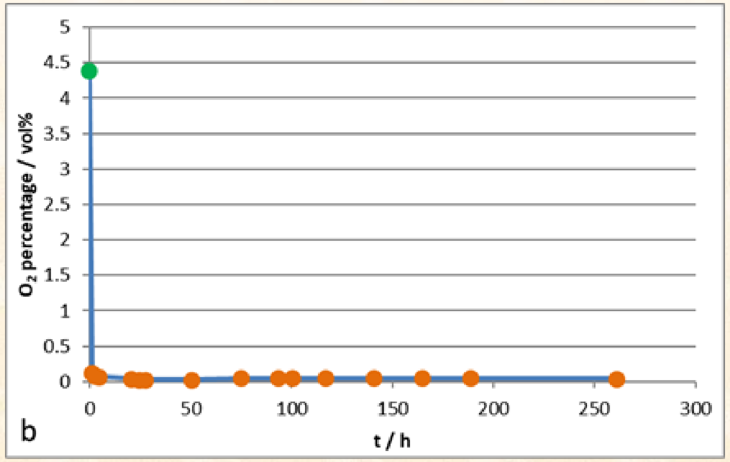
The electrolyzer performance with O_2 removal method

- 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

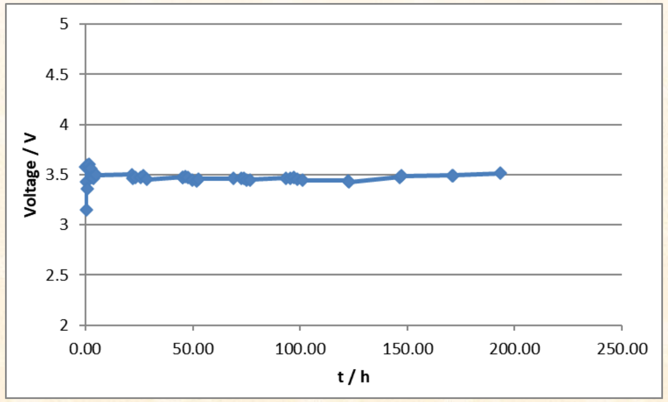
Mitigate O_2 effect on the electrolyzer performance

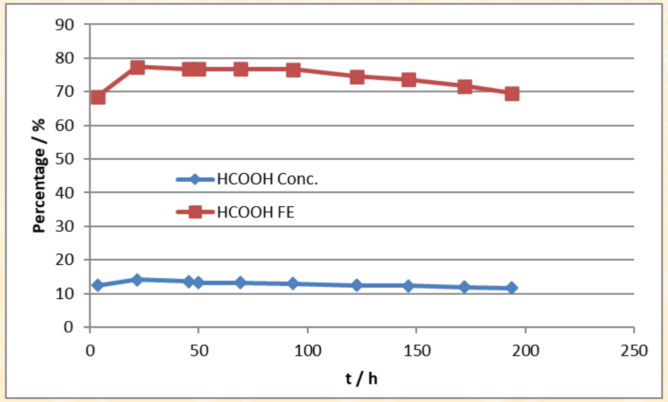
O_2 removal device performance comparison. a) original O_2 removal device, b) modified O_2 removal device.





The electrolyzer performance with modified O_2 removal method (CO_2+5% O_2)



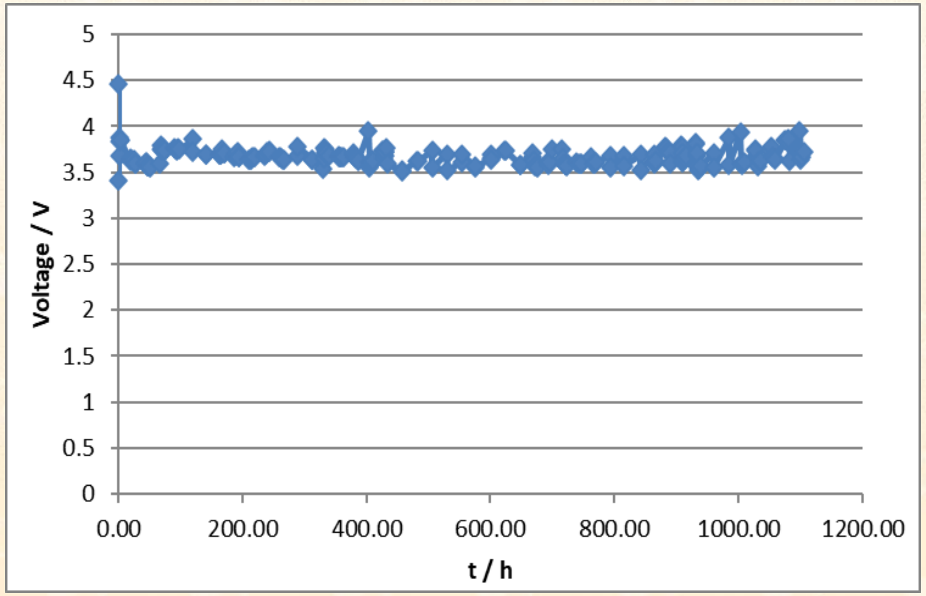


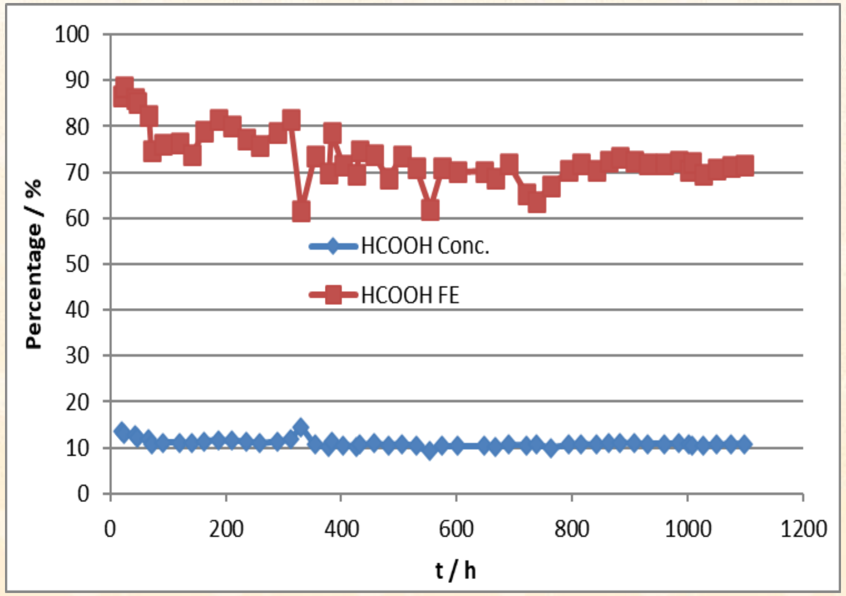
- Less than 0.1% O_2 with modified O_2 removal method
- Stable for at least 250 hours
- Significantly improved electrolyzer performance with modified O2 removal method.

Progress and Current Status of Project

1000 Hours testing with 50% CO_2 + 5% O_2 + 100 ppb SO_2 at 200 mA/cm^2

- Previous work on the effect of SO_2 and NO indicated no detrimental effect on the electrolyzer performance when feeding with CO_2 containing SO_2 (10 ppm, 100 ppm) and NO (100 ppm).
- O_2 removal device was applied to mitigate the detrimental effect of O_2 on the electrolyzer performance.





- Formic acid concentration mostly above 10 wt%
- Formic acid FE mostly around 70%
- O_2 removal device works for long-term testing

Progress and Current Status of Project

On-site testing at the coal power plant

- How the electrolyzer system performs in the real world feeding with the flue gas from a coal-powered plant

On-site testing demo device

- The demo device includes a lab scale CO_2 to formic acid electrolyzer, an impurity removal system, and a flue gas feeding system

On-site testing

- The demo device can produce formic acid by directly feeding flue gas from a coal power plant with CO_2 concentration less than 14% and O_2 concentration higher than 5%.
- Adjustment and modification are needed from both the power plant and the electrolyzer system for direct flue gas feeding for future development.

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.
- SO_2 and NO (100 ppm) don't show negative impact on the cell performance.
- The electrolyzer system can produce formic acid directly using the flue gas from a coal power plant

Future Plans

- Modification of anion exchange membrane, cathode and anode, cell configuration to further improve performance and long-term stability; adjustment and modification of the flue gas feeding system
- Electrolyzer scale-up

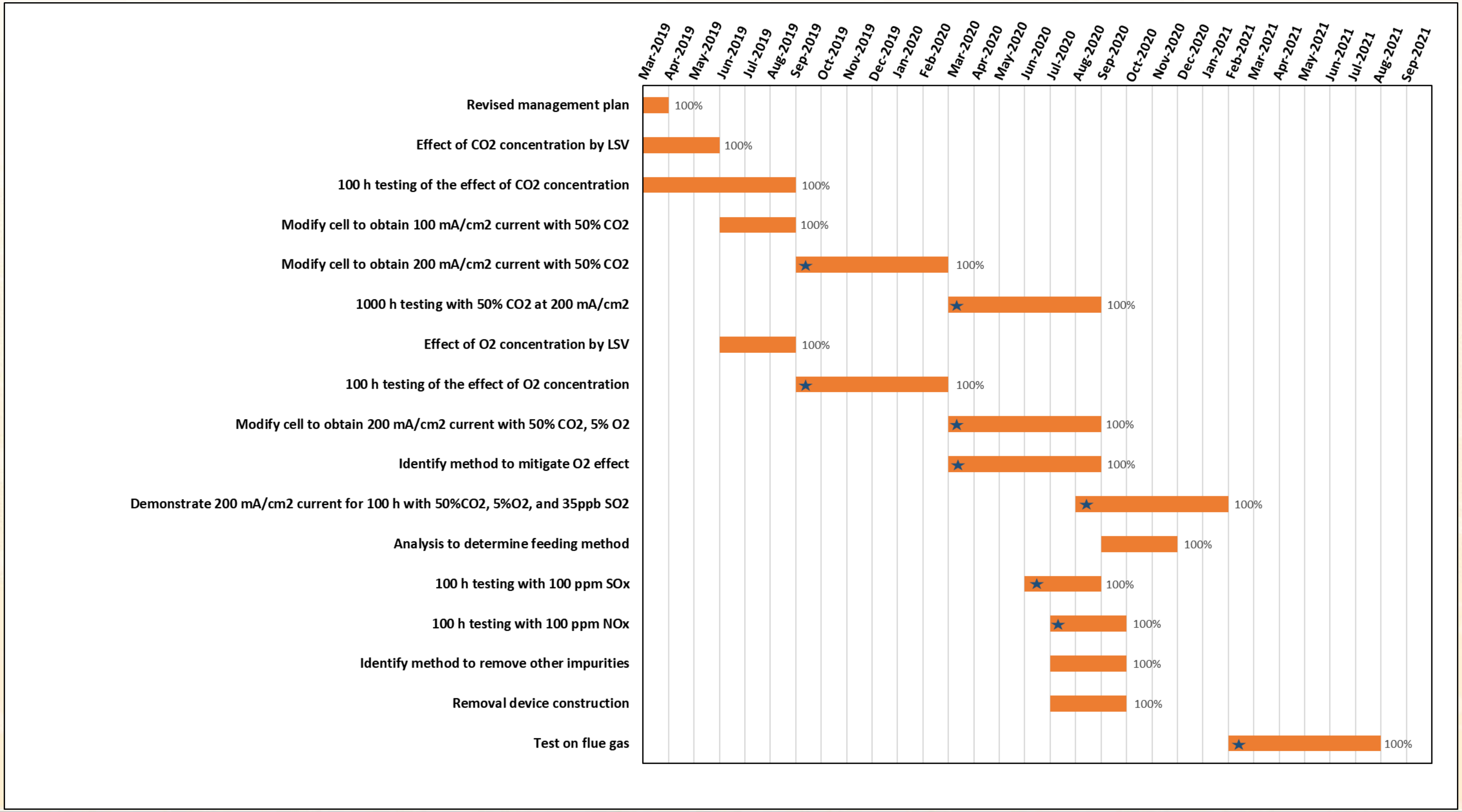
Takeaway Messages

- 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/flue gas for on-site testing

Appendix (Gantt Chart)



★ **Major milestone**

Dioxide Materials™

Acknowledgement and Disclaimer

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