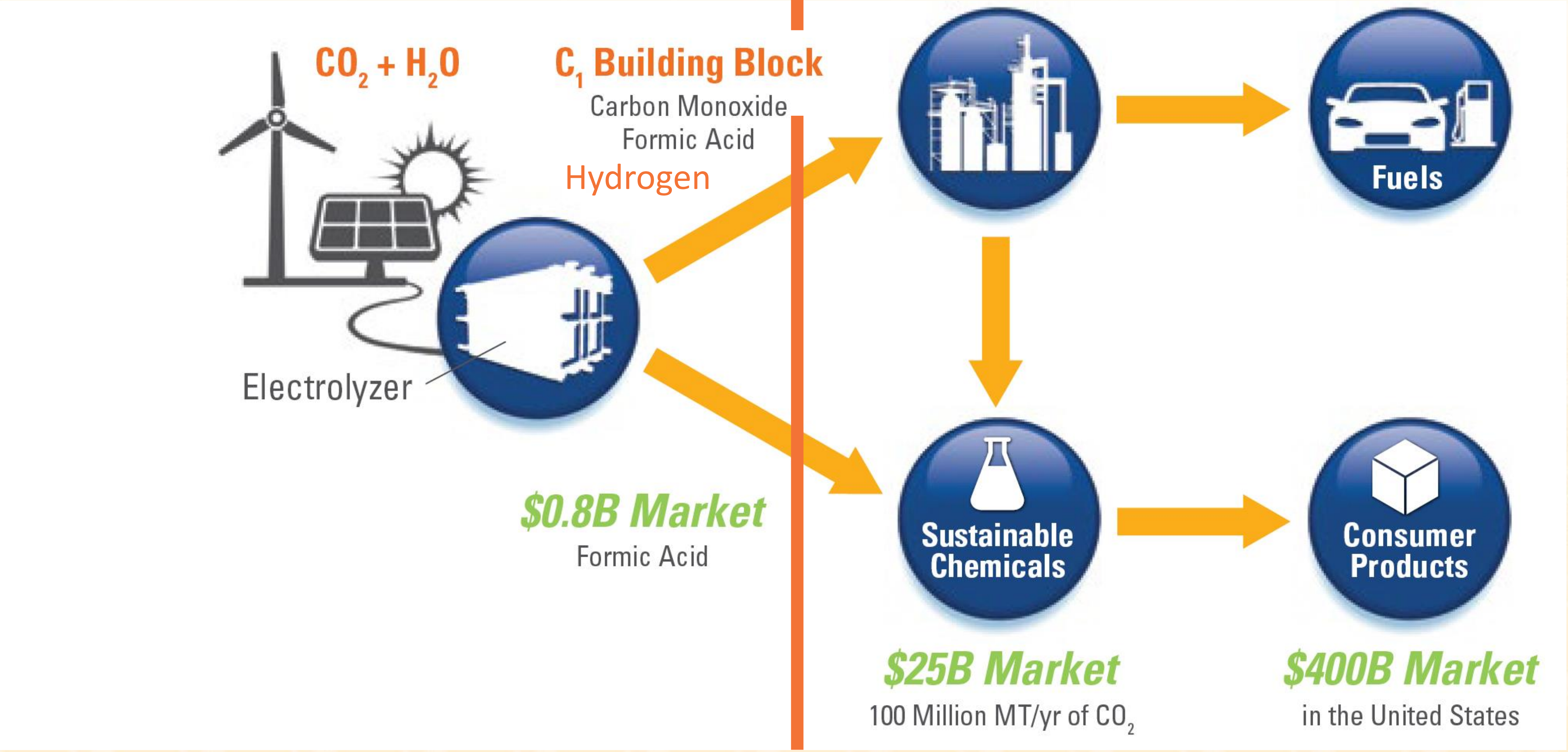
CO_2 Electrolyzer to Produce Formic Acid Using Flue Gas at Industry Relevant Current Density (F05-0812)

Hongzhou Yang

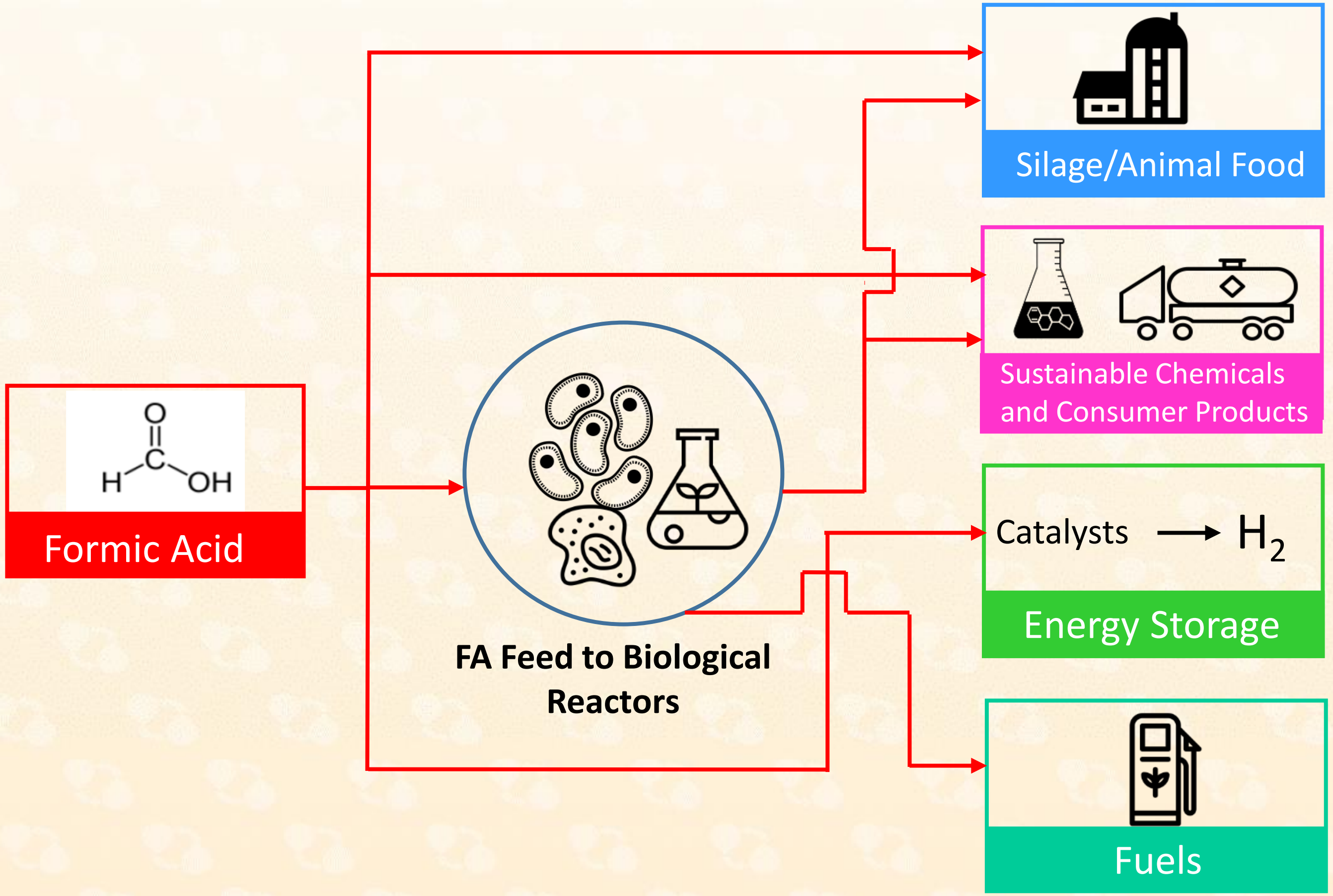
Dioxide Materials Inc.
Boca Raton FL 33431

240th ECS Meeting
October 10-14, 2021

Dioxide Materials' Focus: Produce Fuels and Chemicals From CO_2, Water and Renewable Energy

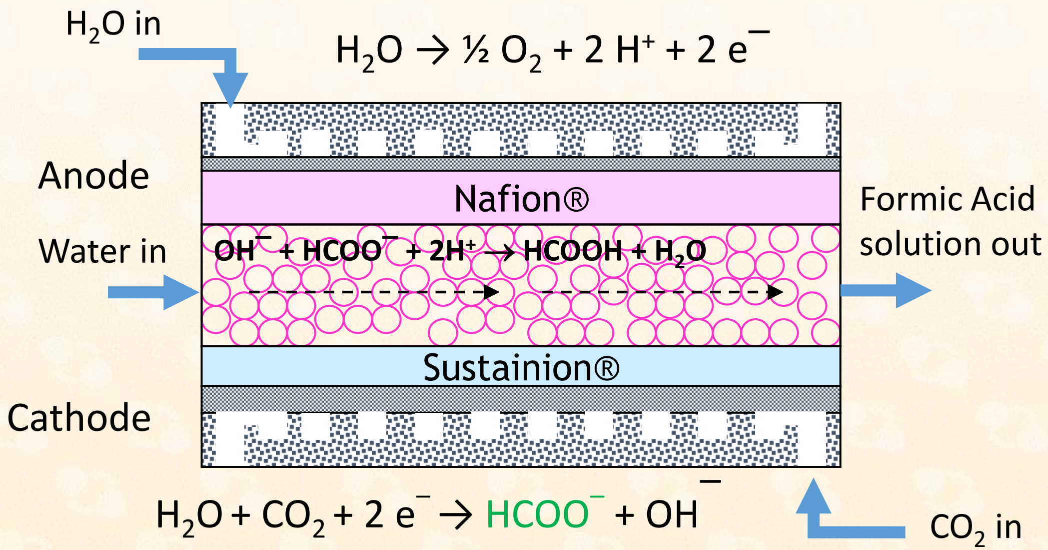


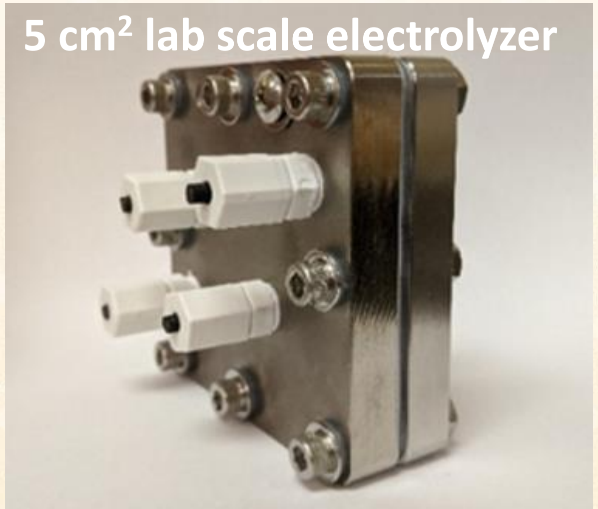
Potential Formic Acid Applications



Technology Background

3-Compartment Electrolyzer Cell Configuration and Reactions in the Cell





- Formic acid is formed directly
  - No need of energy intense conversion step (formate to formic acid)
  - No need to continuously supply KOH
- Industry relevant currents obtained at relatively low voltages

Technology Background

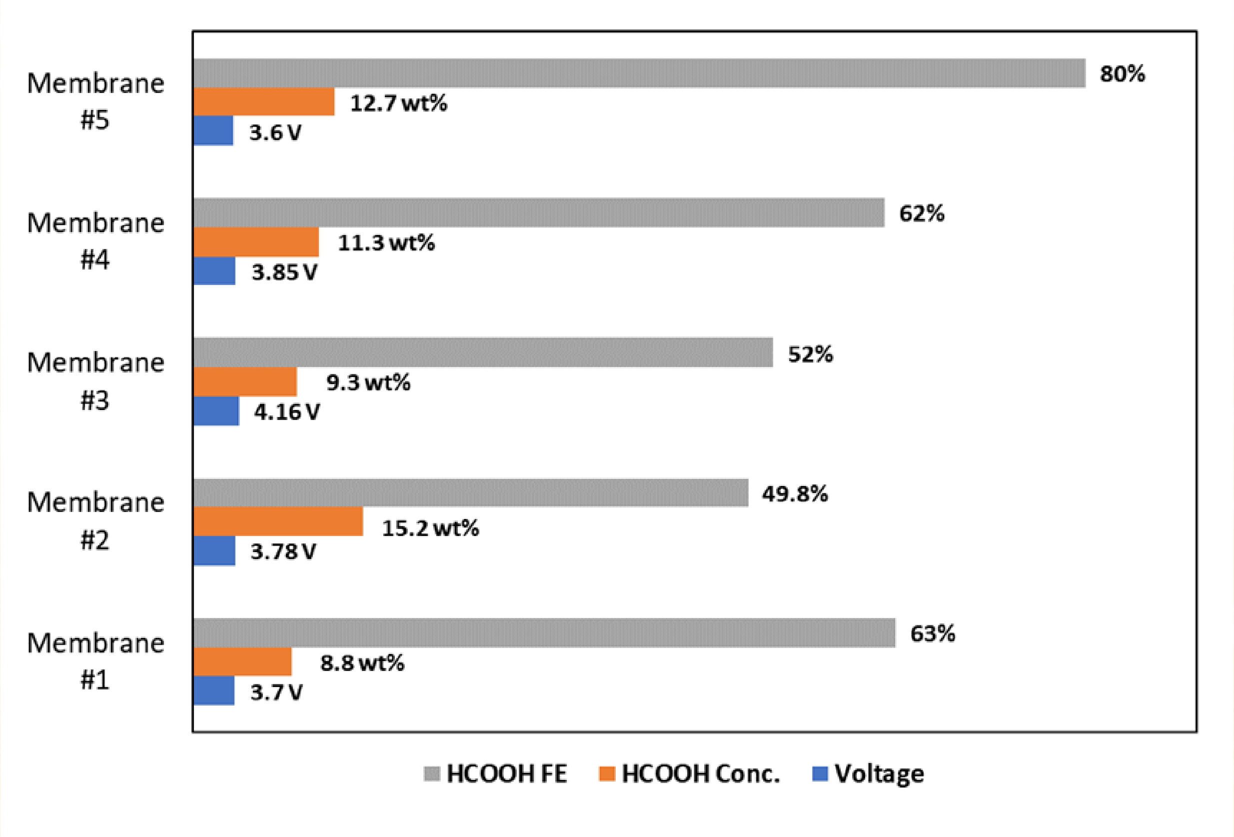
Flue gas as CO_2 source for CO_2 electrolysis

- Flue gas from coal fired power plant
- Learn how to run the electrolyzer with flue gas as CO_2 source at industry relevant current density
  - 200 mA cm^{-2} current density
  - Low CO_2 concentration effect (~14%)
  - Impurity effect (O_2, SO_x, NO_x…)
  - Long-term stability (>1000 h)
- Produce formic acid that can be directly used in some of the bioprocesses

Development of Anion Exchange Membranes

General Requirement

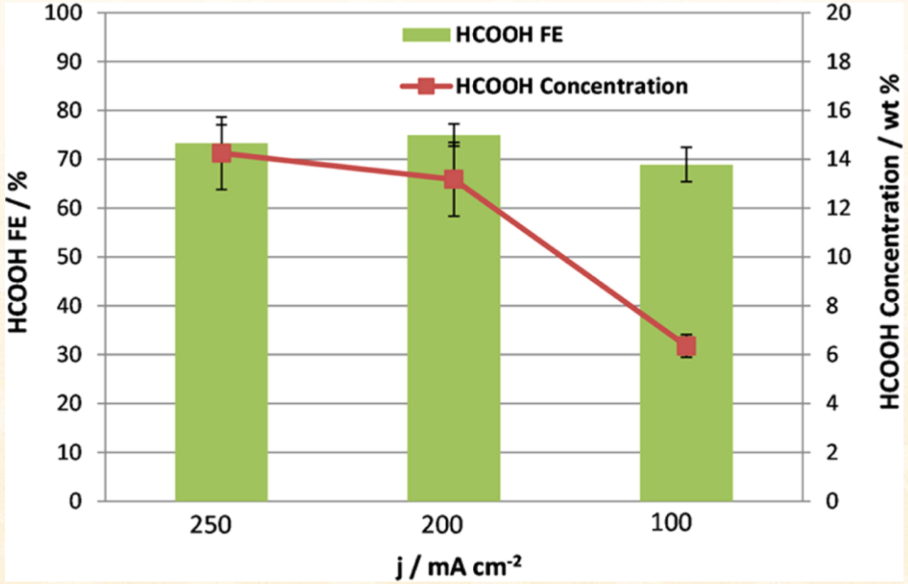
- high ion conductivity
- good mechanic stability
- minimized proton transfer to cathode side
- minimized formic acid crossover
- balanced water uptake



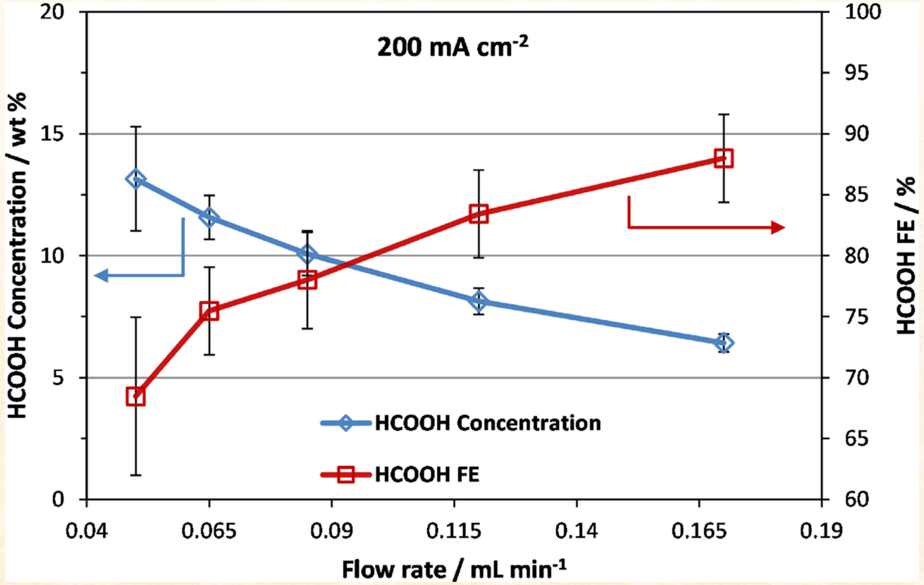
Comparison of the electrolyzer performance with different anion exchange membranes. (All the membranes were tested in the cell at 1 A current except membrane #1 at 0.8 A current)

Current and flow rate for operating electrolyzer

Electrolyzer performance at different current densities



Central compartment flow rate effect

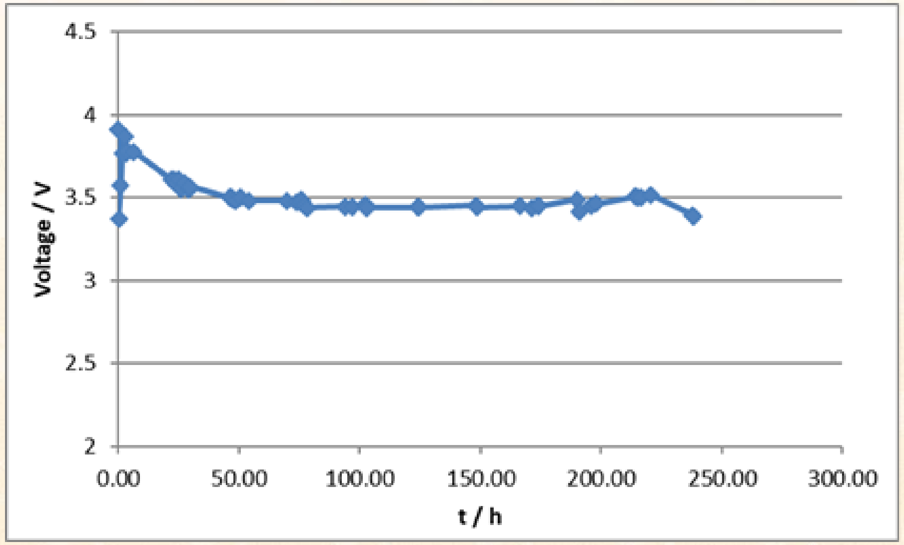


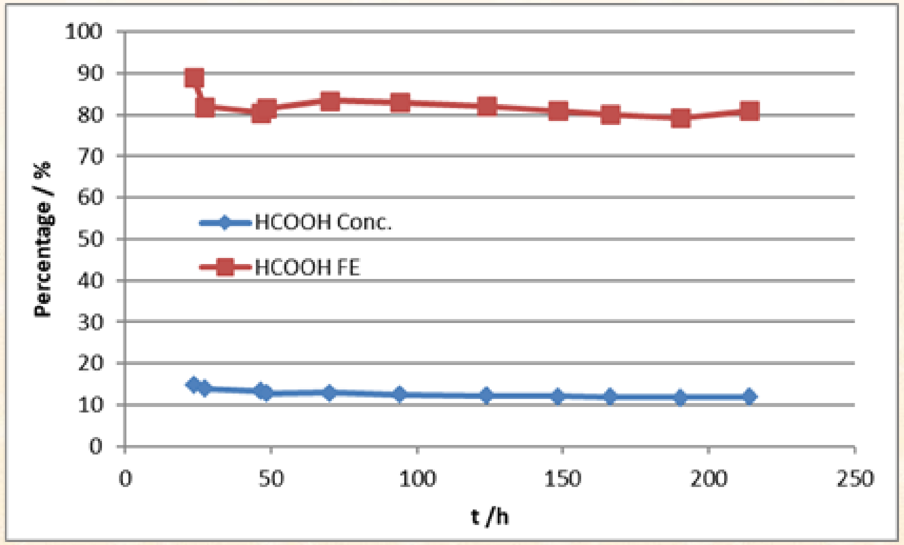
H. Yang et al. Journal of CO_2 Utilization 42 (2020) 101349

- 200 mA cm^{-2} current density for the testing
- Central compartment flow rate to adjust FA concentration and FE

Development of cathode catalyst

Sn, In, Bi based metals, oxides, or alloys cathode catalysts

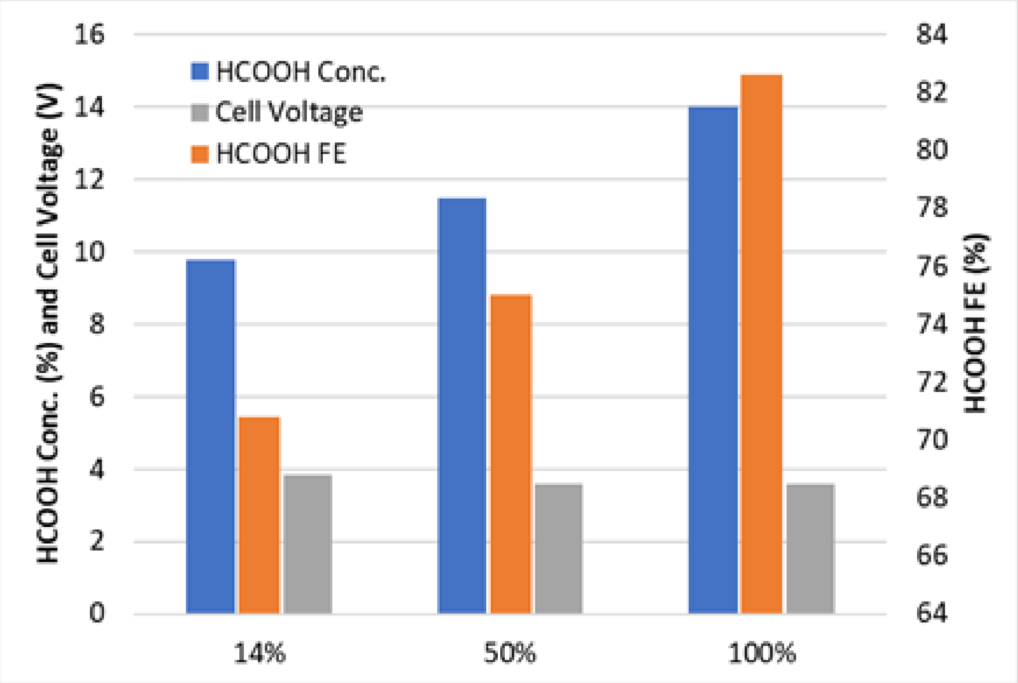




The electrolyzer performance at 200 mA/cm^2 current density with the chosen cathode catalyst

CO_2 concentration effect on electrolyzer performance

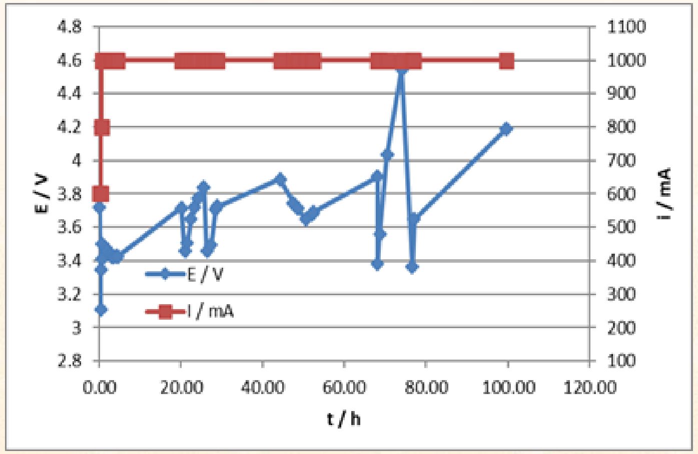
- 14, 50, 100% CO_2 concentration (balanced with N_2)
- 5 cm^2 active area electrolyzer
- 200 mA cm^{-2} current density
- Short term testing results

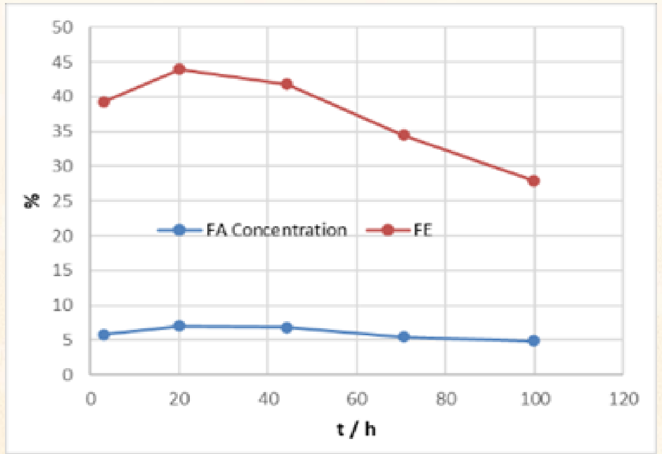


- Electrolyzer performance decreases with CO_2 concentration
- The electrolyzer could perform with 14% CO_2
- Possible to directly use flue gas as CO_2 source

O_2 effect on electrolyzer performance

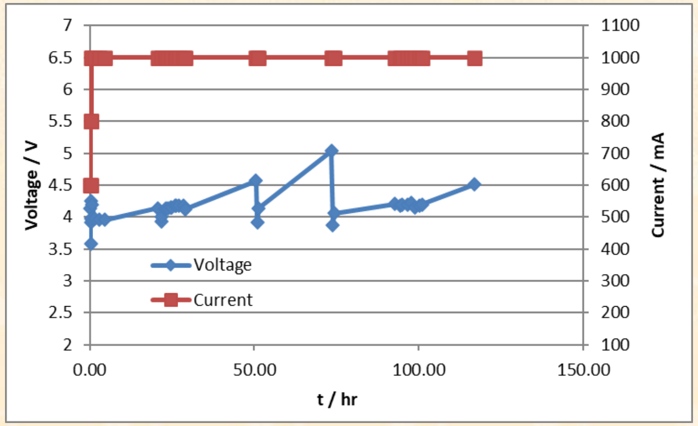
O_2 Effect on cell performance with 5% O_2 in CO_2

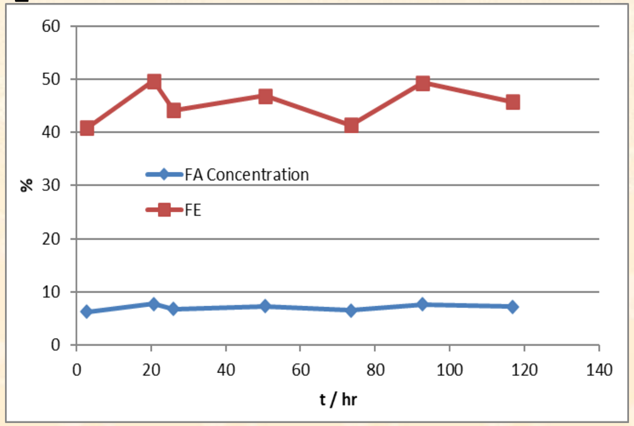




- Rapid decline of electrolyzer performance (unstable voltage, low FA concentration, low and declined FA FE)
- Mitigate the O_2 effect
  - Block or slow down O_2 transport to cathode catalyst surface
  - Remove O_2 from the CO_2 gas stream

Cathode modification to mitigate the O_2 effect on cell performance



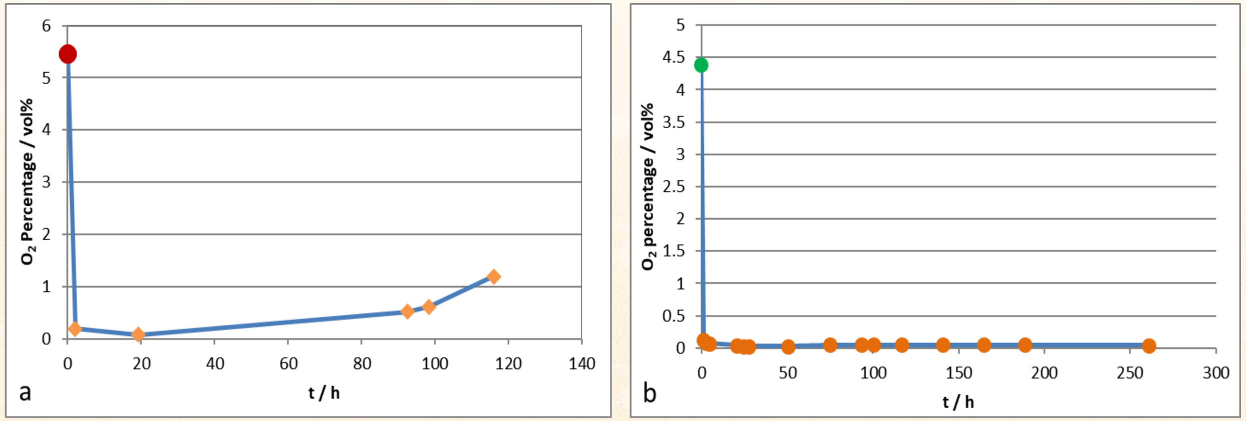


The electrolyzer performance with cathode modification to slow O_2 transport to cathode

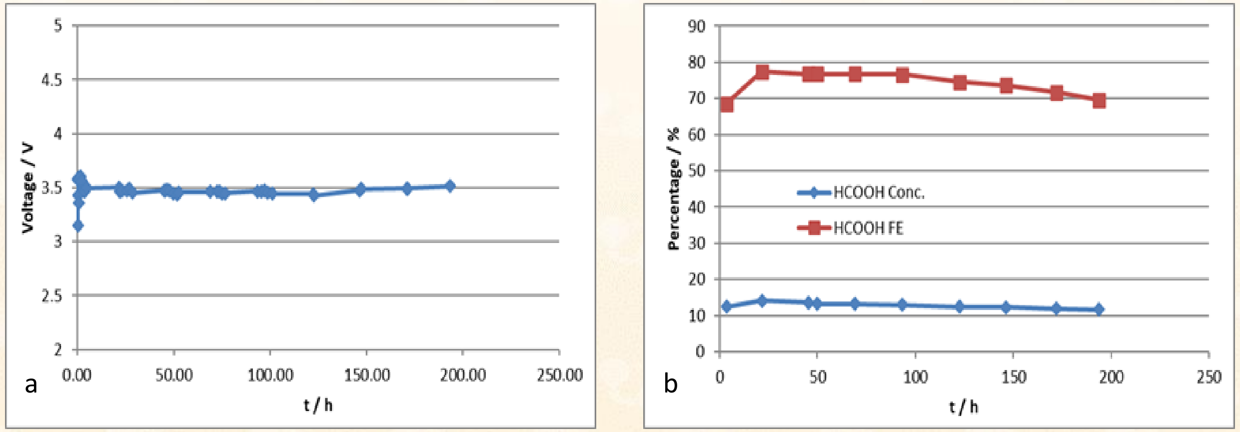
- Improved performance stability (FE, voltage)
- High voltage, low concentration and FE

O_2 effect on electrolyzer performance

O_2 removal strategy to mitigate the O_2 effect on cell performance



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

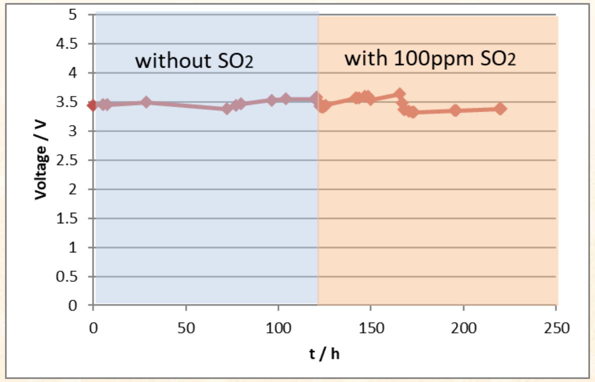


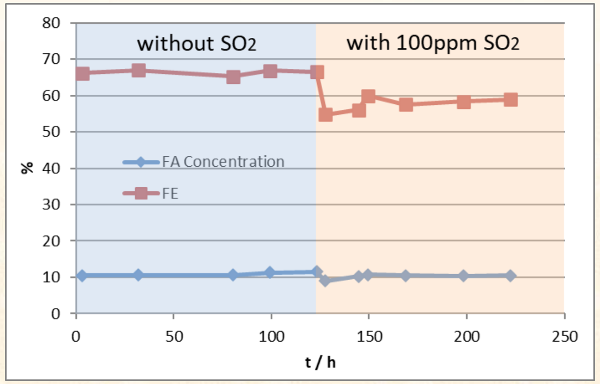
Electrolyzer performance with 5% O_2 in CO_2 feed using a modified O_2 removal device.

- O_2 removal device can efficiently reduce O_2 concentration in CO_2 gas to less than 0.2%
- Electrolyzer performance was greatly improved with O_2 removal device

SO_x effect on electrolyzer performance

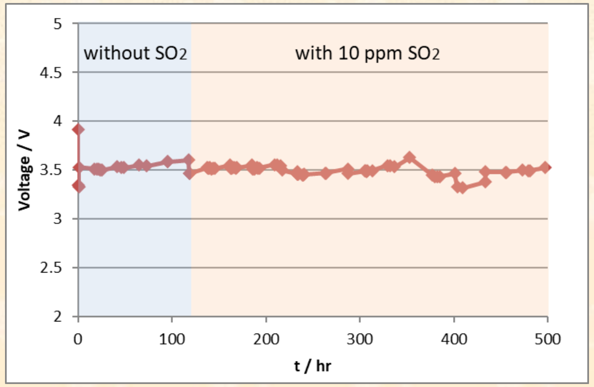
SO_2 effect on cell performance (100 hours test with 100 ppm and 10 ppm SO_2)

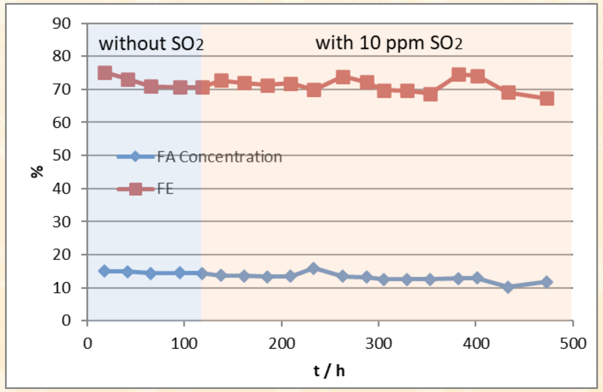




100 h cell test with 100 ppm SO_2 in CO_2

- 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





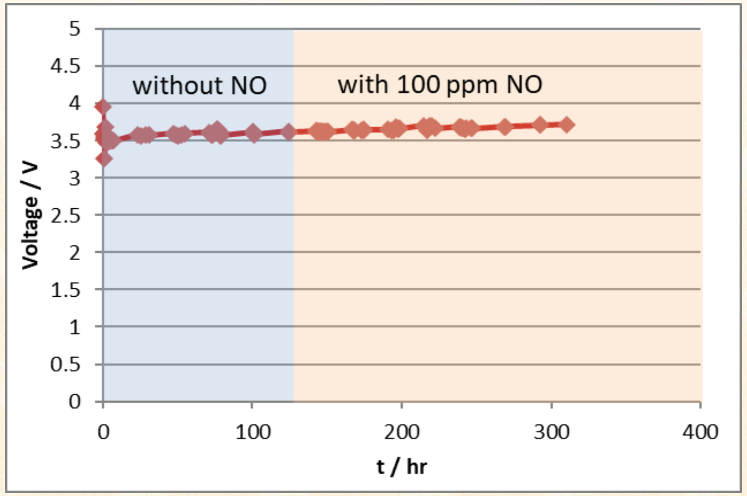
300 h cell test with 10 ppm SO_2 in CO_2

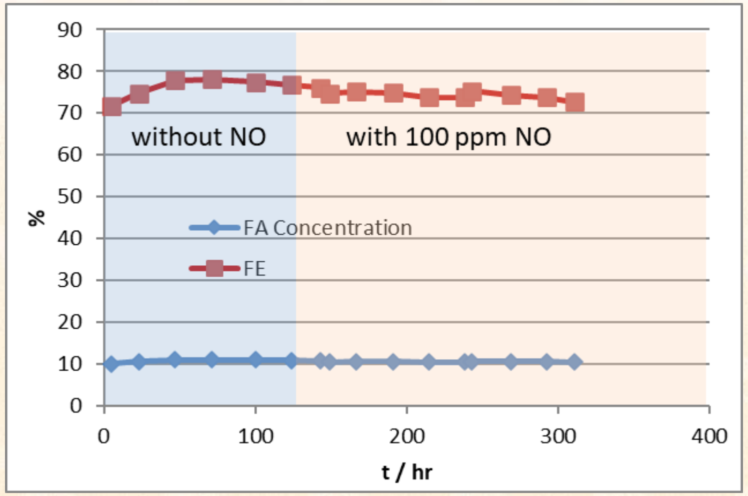
- No apparent effect of 10 ppm SO_2 on cell performance
- Stable performance in 300 h run with 10 ppm SO_2

NO_x effect on electrolyzer performance

NO effect on cell performance (200 hours test with 100 ppm NO)

200 h cell test with 100 ppm NO in CO_2

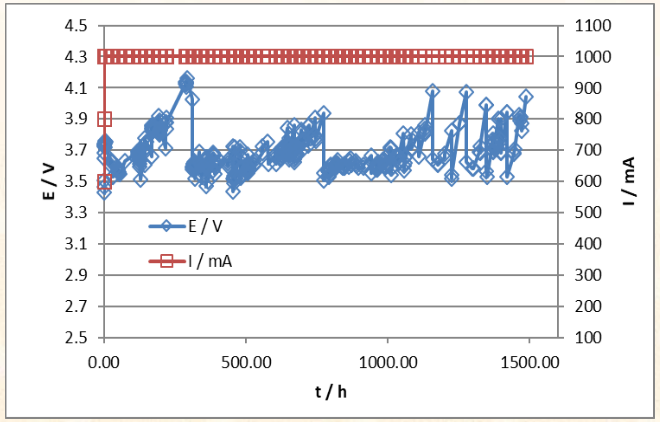


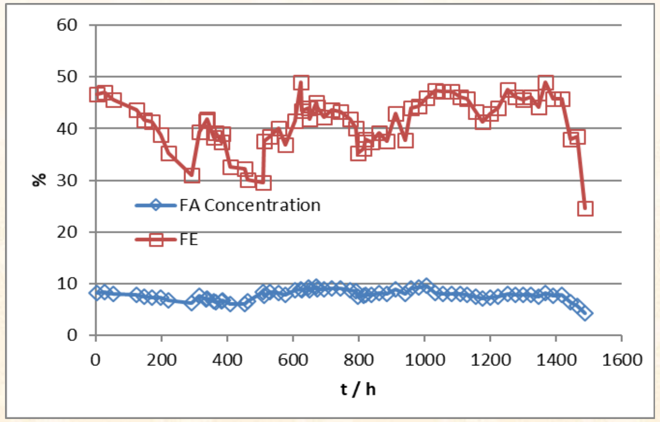


- No apparent detrimental effect of 100 ppm NO on cell performance
- Stable performance in 200 h run

Long-term testing at 200 mA cm^{-2} current density

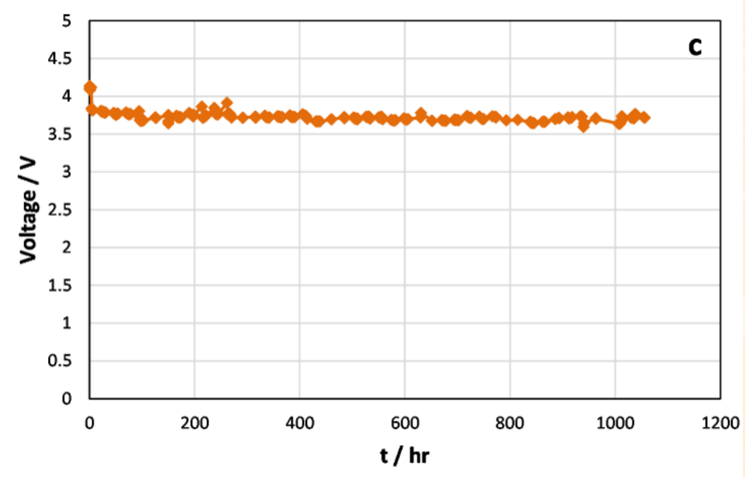
1000 h long-term performance at 200 mA/cm² with 100% CO_2

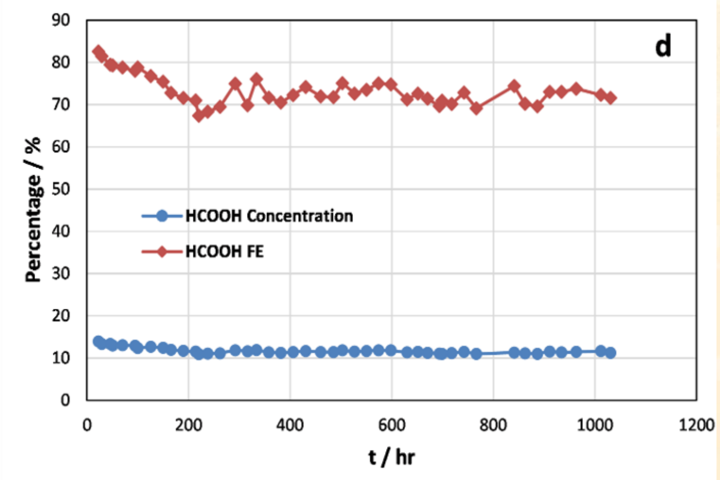




- Initial 1000 h testing results
  - 30-50% formic acid FE
  - 6-9.5 wt% formic acid product
  - Unstable voltage, >4.0V

Modification: anion exchange membrane, cathode catalyst, operation conditions

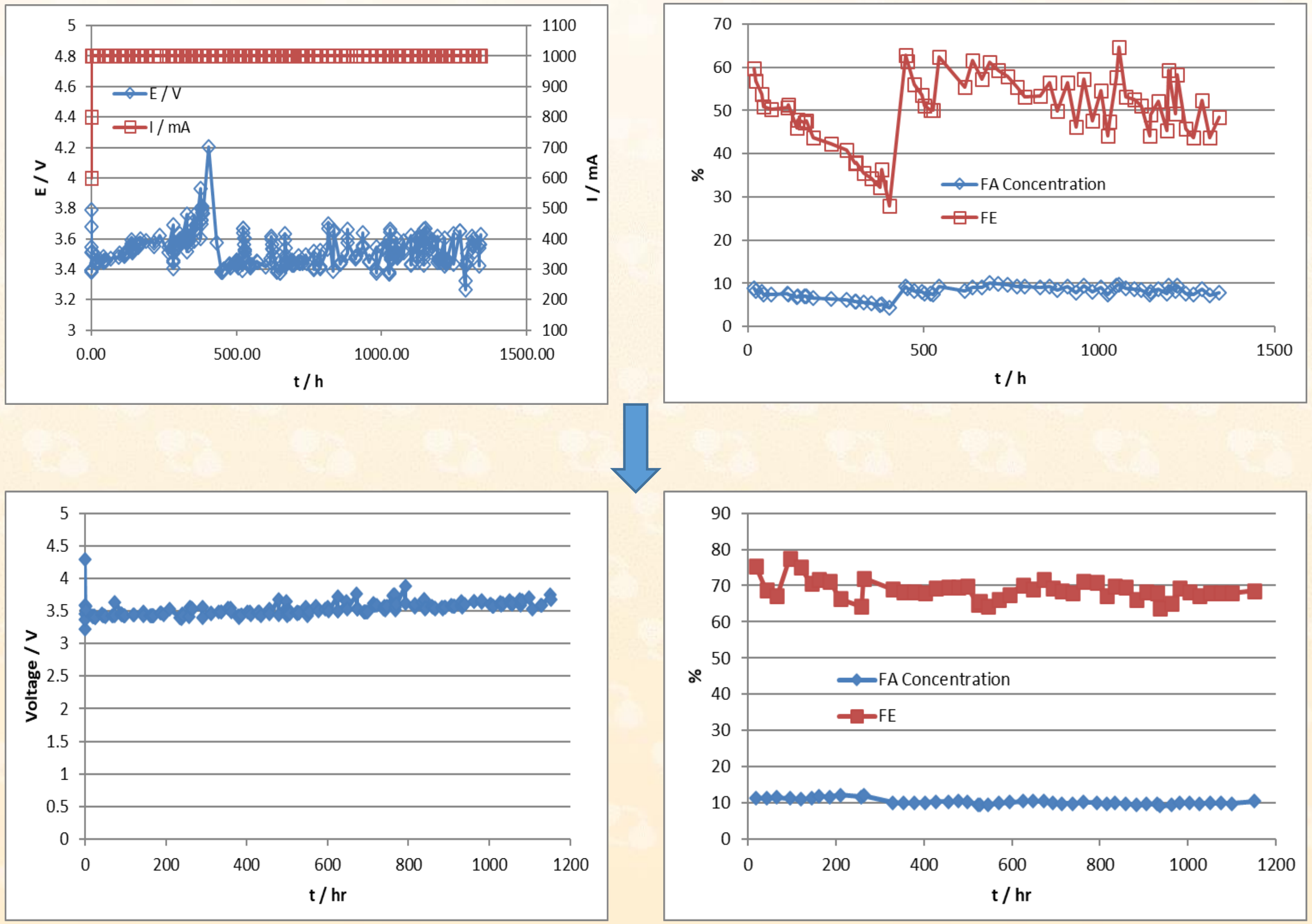




- 1000 h testing results obtained after modification
  - 71-83% formic acid FE
  - >10 wt% formic acid product
  - stable voltage, ~3.6V
  - Developed a method to maintain cell performance

Long-term testing at 200 mA cm^{-2} current density

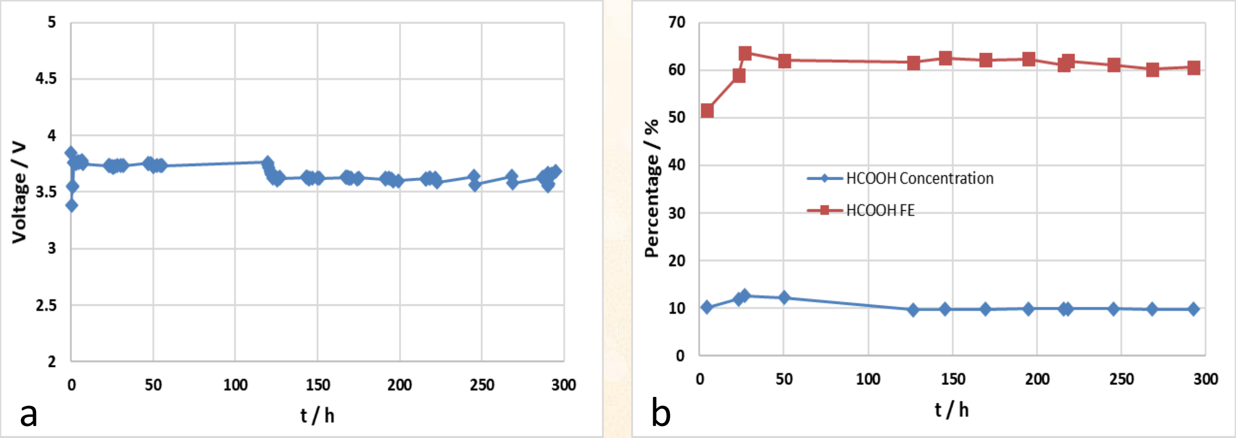
1000 h long-term performance at 200 mA/cm^2 with 50% CO_2



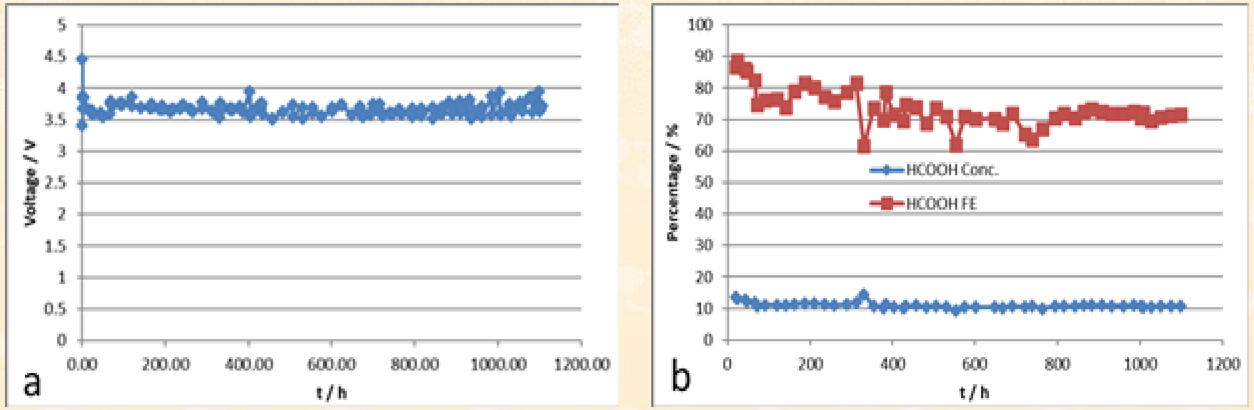
- Initial 1000 h testing results
  - 40-60% formic acid FE
  - 5-9.5 wt% formic acid product
  - Unstable voltage, 3.3-4.2V
- 1000 h testing results obtained after modification
  - 63-79% formic acid FE
  - ~10 wt% formic acid product
  - stable voltage, 3.4-3.8V

Long-term testing at 200 mA cm^{-2} current density

Long-term performance at 200 mA/cm^2 with 14% CO_2



Long-term performance at 200 mA/cm^2 with 50% CO_2 + 5% O_2 + 100 ppb SO_2



- high possibility of using flue gas from the coal fired power plant as the CO_2 source to produce formic acid
- More long-term tests are needed with 14% CO_2 with impurities

Summary

- DM developed a 3-compartment electrolyzer that can directly convert CO_2 to formic acid with good performance (10wt% FA, 80% FE) at 200 mA cm^{-2} current density.
- The electrolyzer works with low CO_2 concentration (~14%) as seen in typical flue gas from coal fired power plant.
- O_2 in the flue gas shows a detrimental effect on electrolyzer performance therefore it is critical to remove O_2 from the flue gas to achieve stable electrolyzer performance.
- Long-term (>1000 h) stability of the electrolyzer performance was demonstrated with different CO_2 concentration and in the presence of the impurities.
- Next: scale up and on-site testing at coal fired power plant

Acknowledgement and Disclaimer

Acknowledgement

This presentation is based upon work supported by the Department of Energy (DOE) of the United States under Award Number DE-FE0031706.

Disclaimer