Dioxide Materials™

The CO_2 Recycling Company™

CO_2 Electrolyzer to Produce Formic Acid at Industry Relevant Current Density

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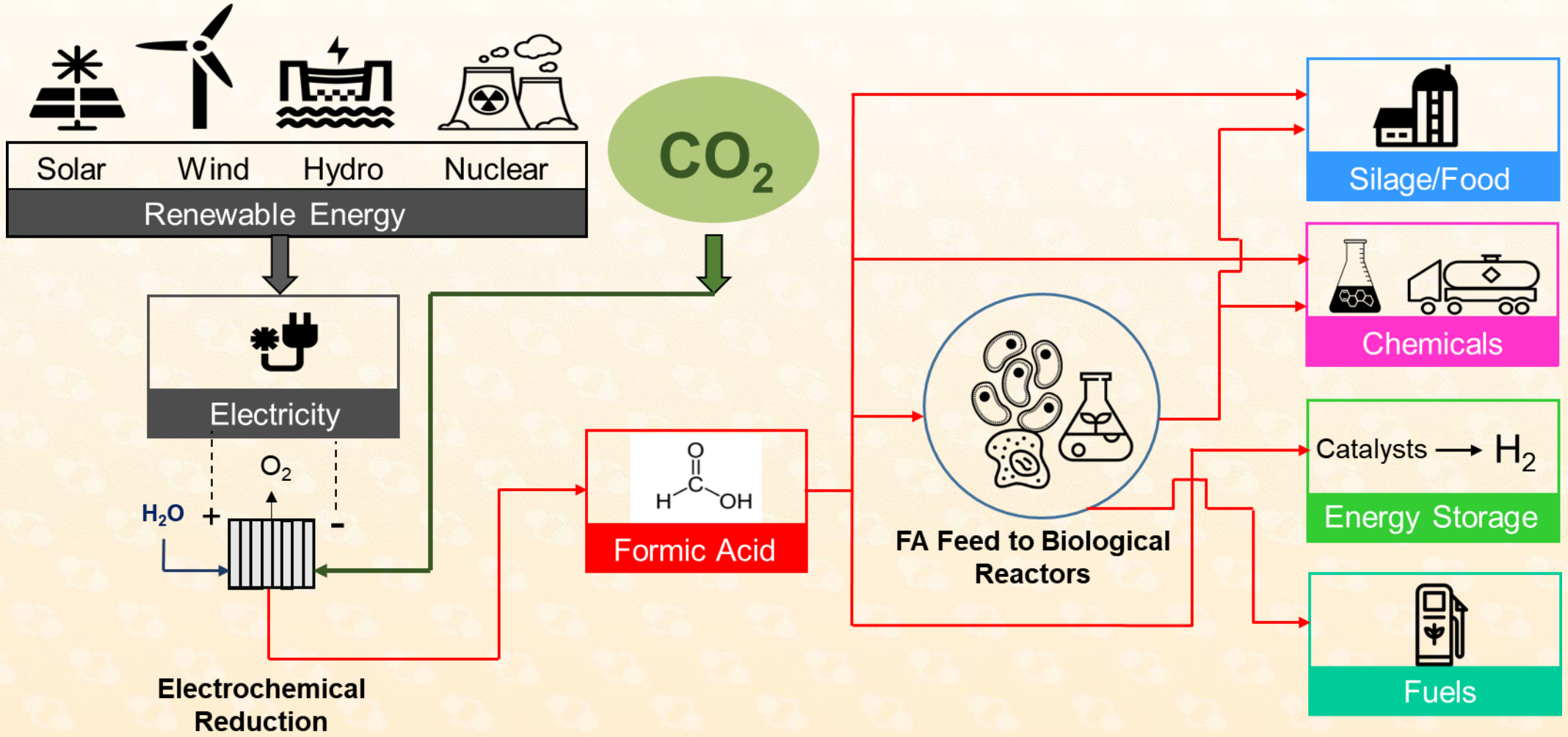
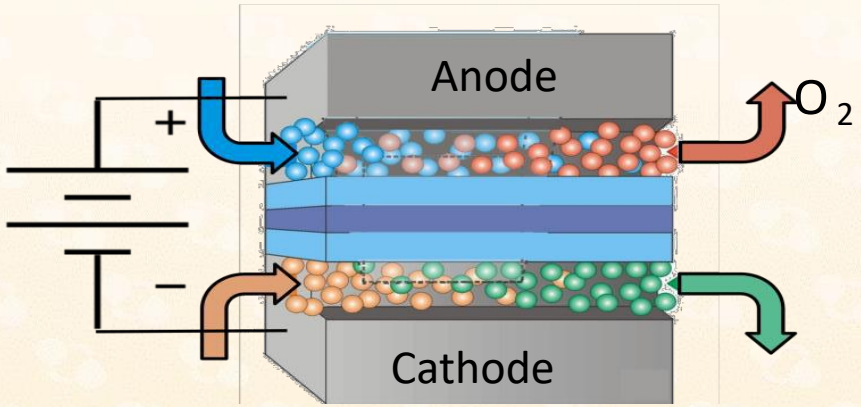
Dioxide Materials' CO_2 Conversion Route and Potential Formic Acid Applications



Previous Research on Electrochemical CO_2 Conversion to Formic Acid/Formate

$2OH^- \rightarrow H_2O + 2\,e^- + ½\,O_2$



$H_2O + CO_2 + 2\,e^- \rightarrow HCOO^- + OH^-$

$HCOO^- + KOH \rightarrow HCOOK + OH^-$

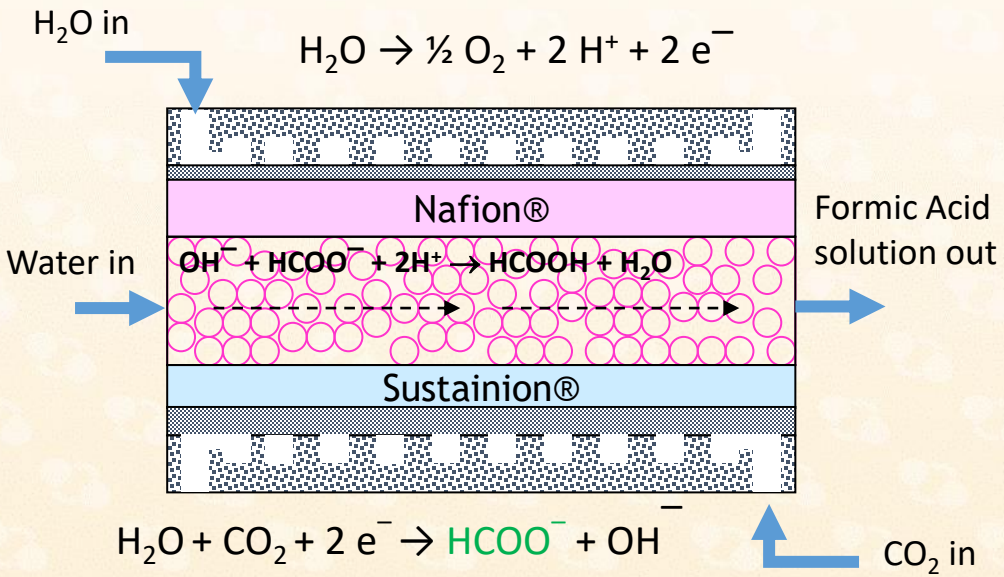
Technical Issues

- Low current density/high potential
- Catalyst life/Stability
- GDE flooding
- CO_2 solubility
- Low selectivity
- Short test runs
- Crossover/Membrane Availability
- Product separation cost

- Cell design that prevents cathode GDE flooding
- Development of a highly conductive, alkaline stable anion membrane
- Selection of cathode catalysts
- Cell design and components modification to improve conductivity
- Increased current density and longer time stability testing (>100 mA/cm^2, 1000h)

Dioxide Materials' Patented Formic Acid Technology

3-Compartment CO_2 electrolyzer



Technical advantages

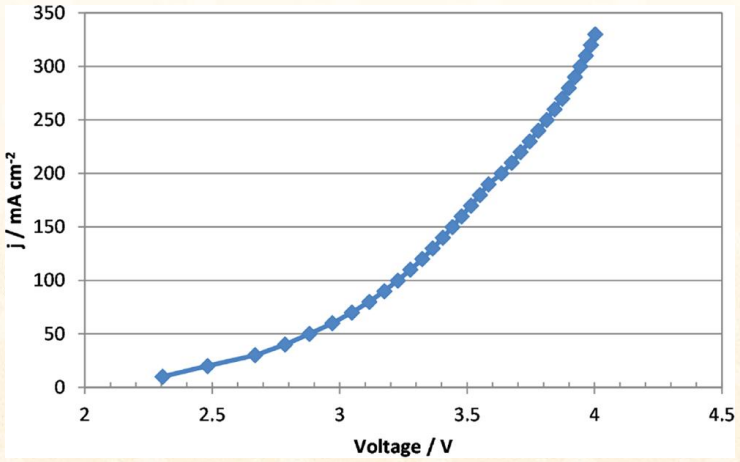
- Pure formic acid production, no need of costly formate to formic acid conversion step
- Improved CO_2 mass transport
- Improved GDE flooding issue
- Improved current density
- Reduced FA crossover
- DI water as electrolyte

Lab scale electrolyzer with 5 cm^2 active area

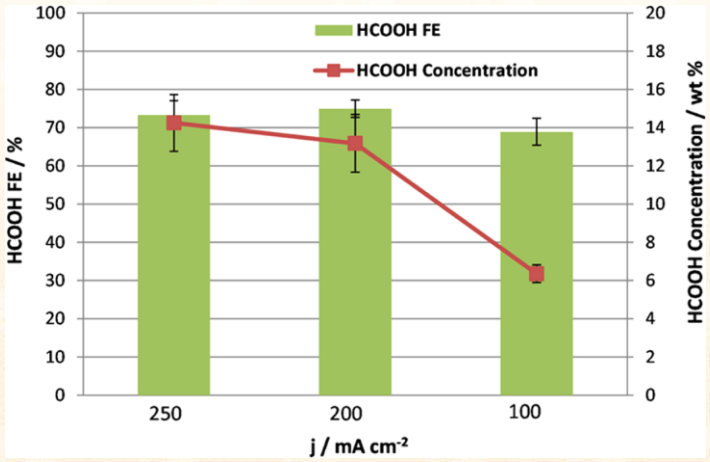
Can we feed flue gas as CO_2 source into the electrolyzer?

- **Flue gas from coal-fired power plant as CO_2 source**
  - CO_2 concentration effect on electrolyzer performance
    - 14% CO_2
  - Impurity effect on electrolyzer performance
    - SOx
    - NOx
    - O_2
  - How to mitigate the effect if any

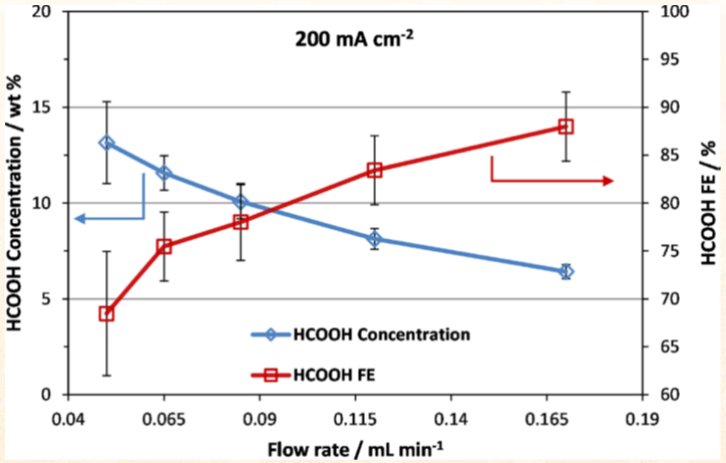
Determine Current Density and Central Compartment DI Water Flow Rate



The electrolyzer current density versus electrolyzer cell voltage The cell was operated in single-pass flow mode.



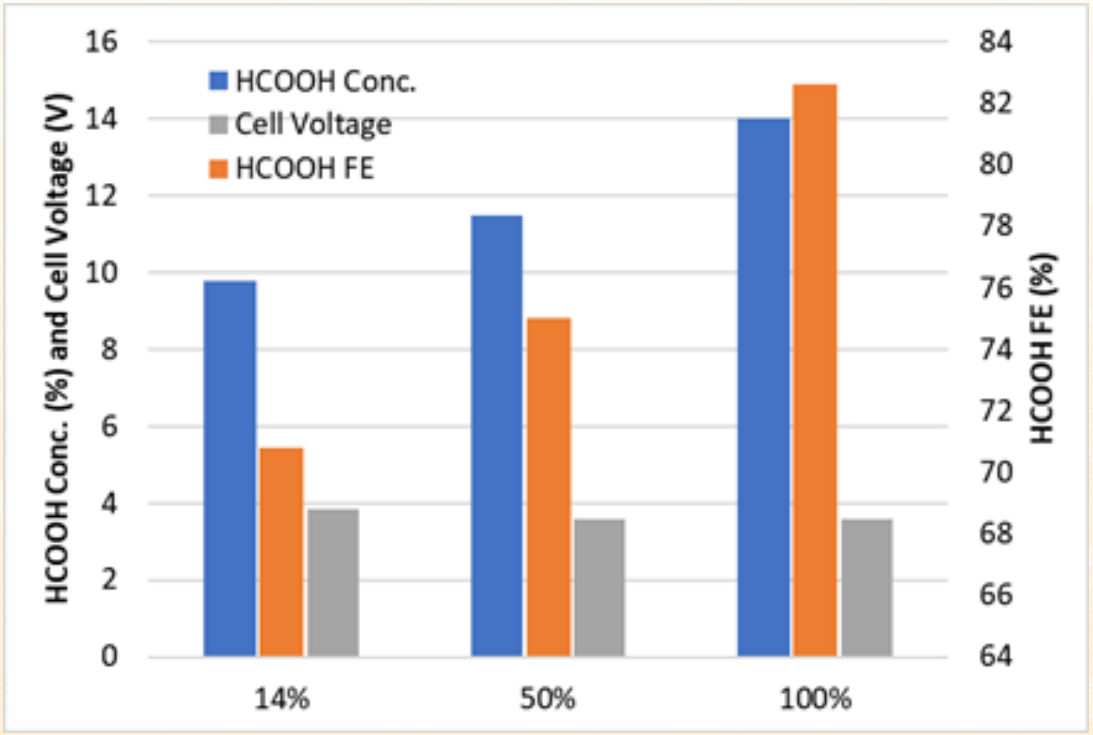
Formic acid FE and concentration at different current densities.



Formic acid concentration and Faradaic efficiency (FE) as a function of the center compartment DI water flow rate. Electrolyzer operating at 200 mA cm^{-2} current density.

- Electrolyzer can operate with current density >200 mA cm^{-2}, 200 mA cm^{-2} as operational current density gives good combined cell performance
- Central compartment water flow rate is crucial in achieving good cell performance and adjusting FA concentration and FE
- Electrolyzer run at room temperature and atmospheric pressure

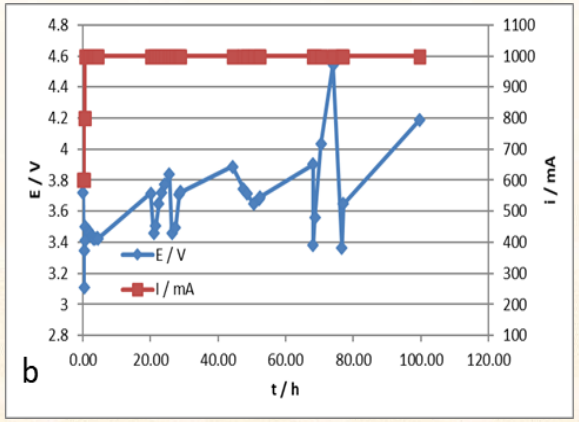
Electrolyzer performance at different CO_2 concentration

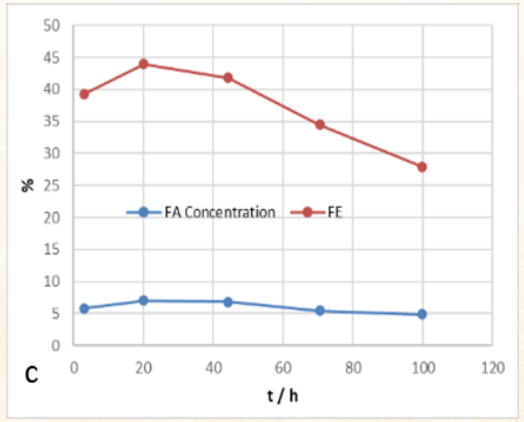


Comparison of electrolyzer performance with different CO_2 concentration

- 200 mA/cm^2
- 2 to 3 times of the flow rate of the stoichiometric CO_2
- Short-term performance decreased with CO_2 concentration
- Electrolyzer can still produced 9.8 wt% formic acid with over 70% formic acid FE
- Possible to feed flue gas as a source of CO_2

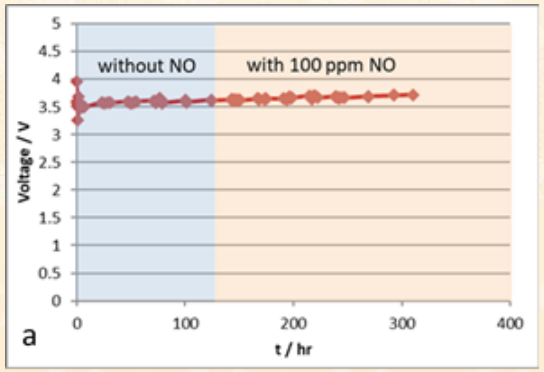
Impurity effect on electrolyzer performance

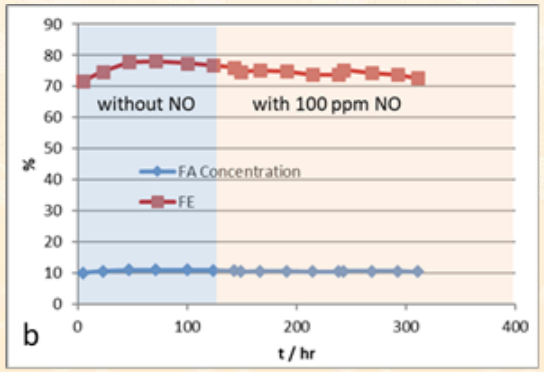




5% O_2

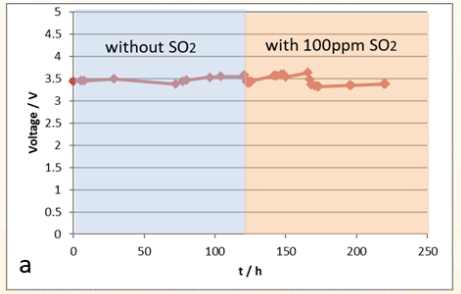
- Detrimental effect of O_2 on cell performance

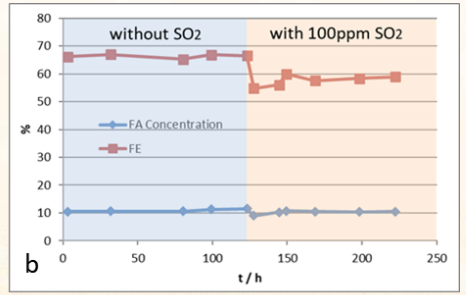


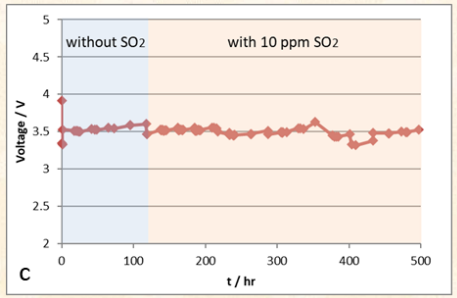


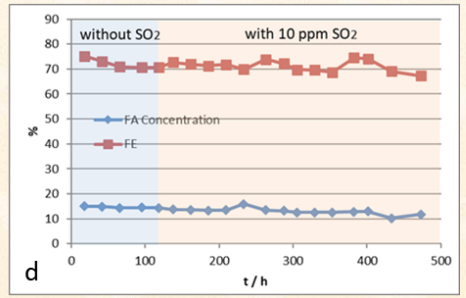
100 ppm NO

- No apparent effect









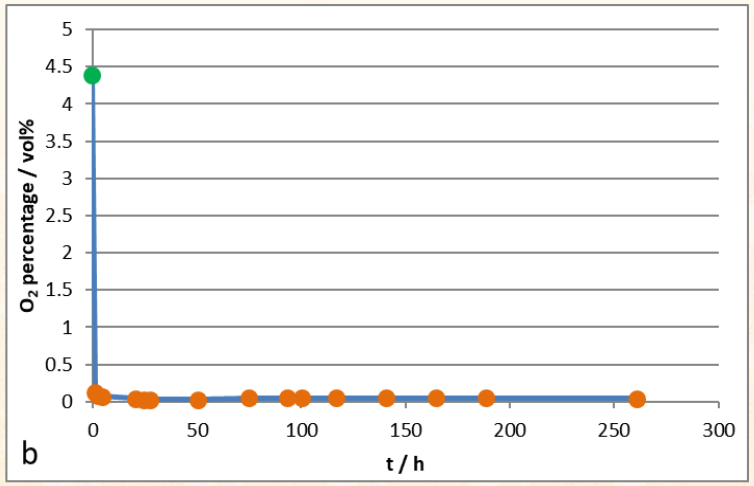
100 ppm SO_2

- Lower formic acid FE but stable during testing

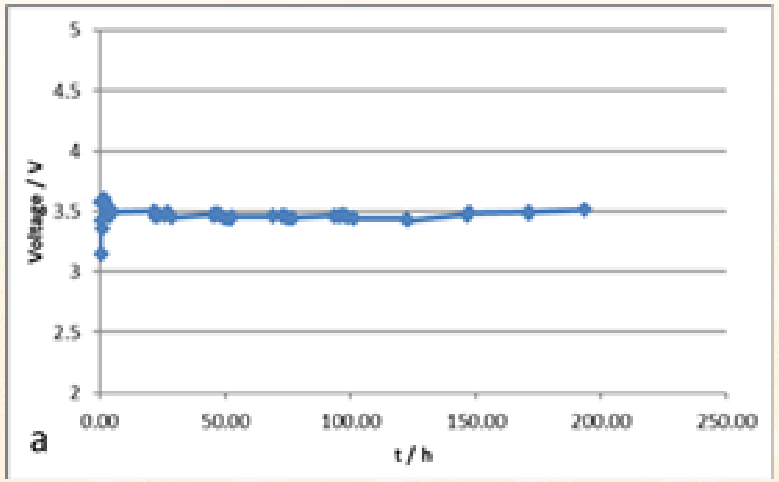
10 ppm SO_2

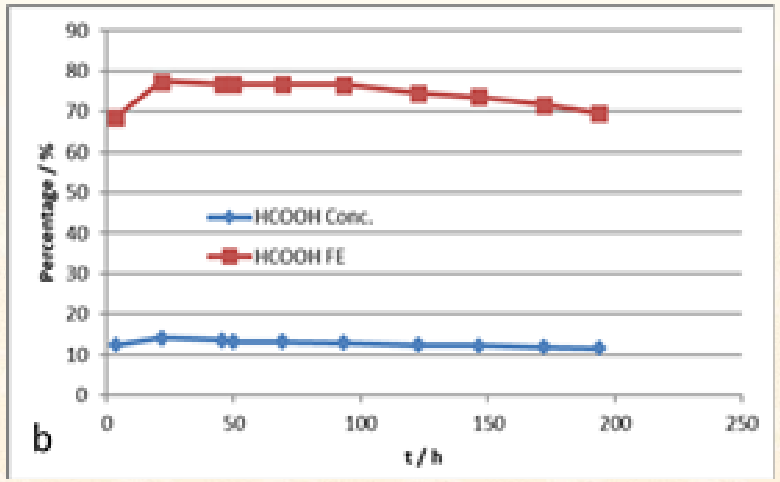
- No apparent change in formic acid FE and concentration
- Stable cell performance for >350 h

Mitigate O_2 effect



O_2 removal device performance. (O_2 Concentration in CO_2 gas, based on GC results)



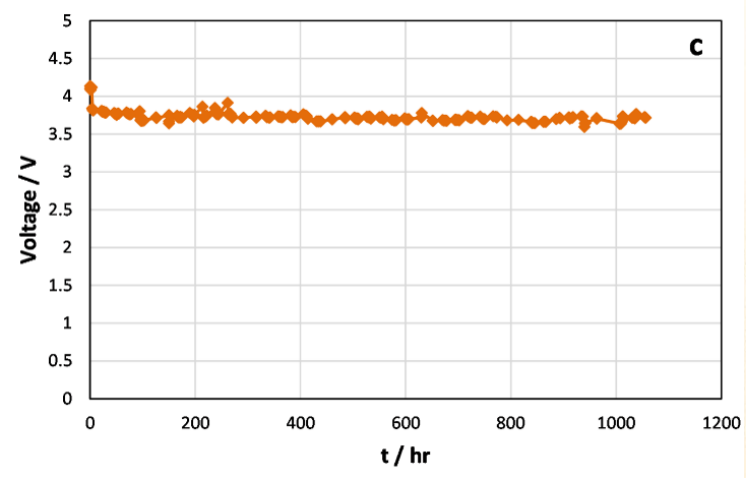


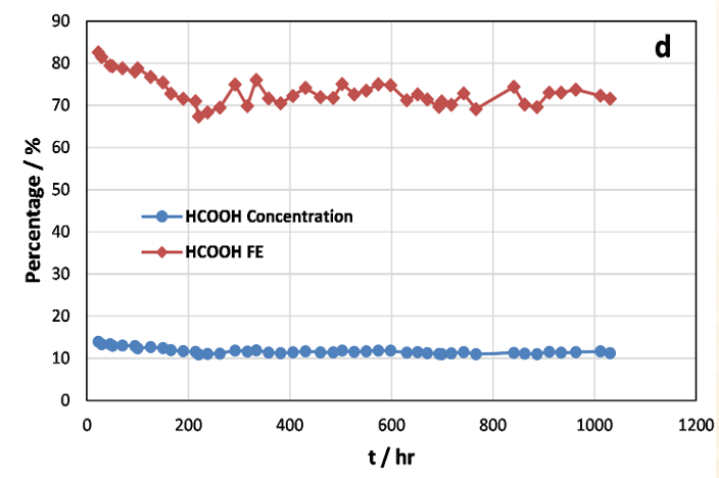
Electrolyzer performance with 5% O_2 in CO_2 feed using a modified O_2 removal device. a) Voltage during the testing at 200 mA cm^{-2}, b) Formic acid concentration and FE during the testing

- O_2 concentration in CO_2 less than 0.1% and stable in 250 hours test

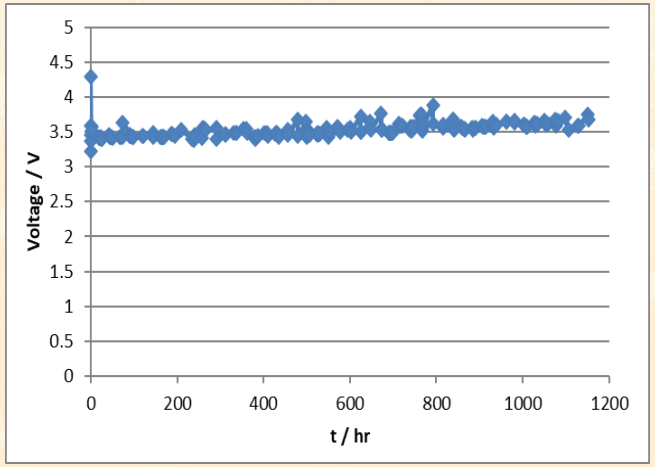
- Stable cell voltage (~3.5 V) in 200 hours testing
- Improved and stable formic acid concentration and FE
- It is critical to remove O_2 from the CO_2 feed gas to ensure good electrolyzer performance.

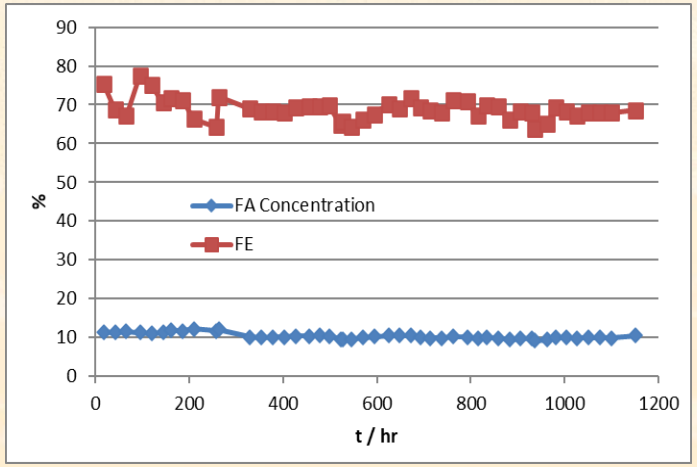
1000 h long-term performance with 100% and 50% CO_2





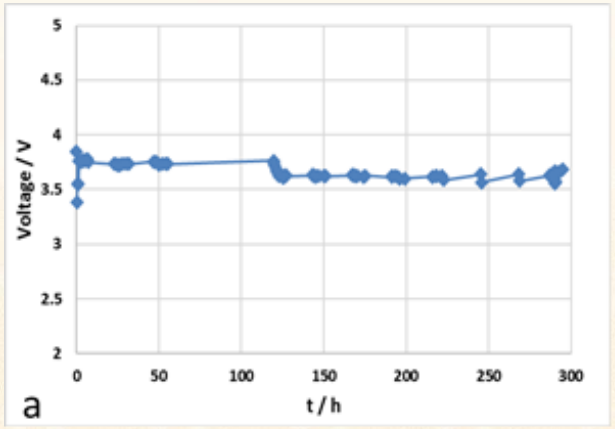
100% CO_2 at 200 mA/cm^2
- 71-83% formic acid FE
- >10 wt% formic acid product
- stable voltage, ~3.6V

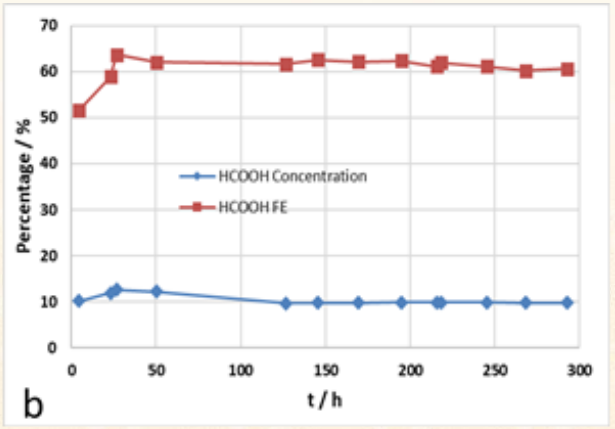


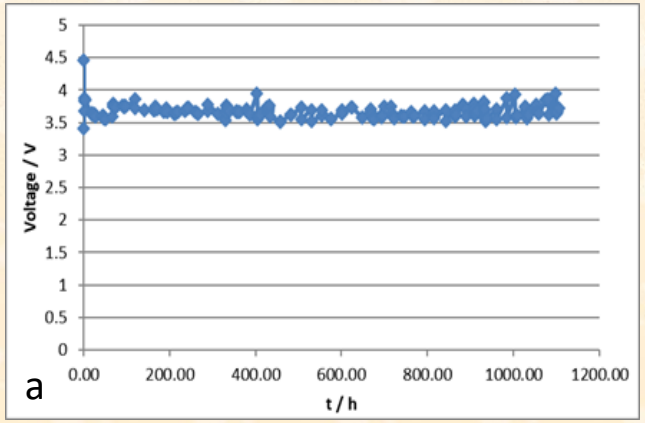


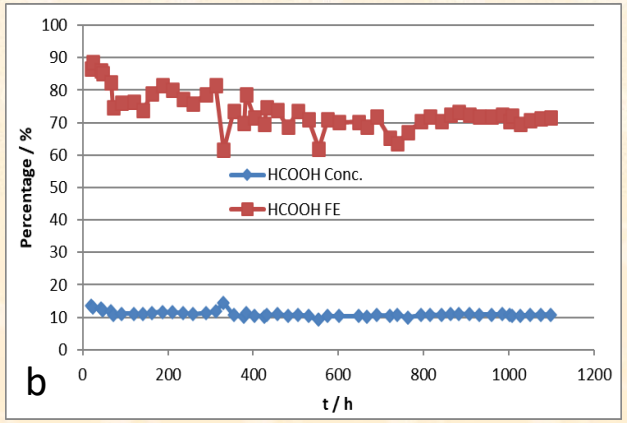
50% CO_2 at 200 mA/cm^2
- 63-79% formic acid FE
- ~10 wt% formic acid product
- stable voltage, 3.4-3.8V

Long-term performance with 14% CO_2 and impurities









14% CO_2 at 200 mA/cm^2
- 10 wt% FA with >60% FE
- Possible to use flue gas as CO_2 source

50% CO_2+5% O_2 + 100 ppb SO_2 at 200 mA/cm^2
- 10 wt% FA with 70% FE
- O_2 removal method works for long-term testing

Conclusions/Future work

- Dioxide Materials' 3-compartment electrolyzer technology produces pure formic acid that can be directly used in biological reactors.
- The electrolyzer demonstrated industrial relevant current density (200 mA/cm^2) and long-term stability (1000 h)
- The electrolyzer demonstrated potential of directly using flue gas as CO_2 source for electrochemical CO_2 conversion
- Key factors that impact the electrolyzer performance were identified

Future work

- Stability needs improvement: 1000 hr → 24000 hr
- Need to suppress hydrogen formation at higher HCOOH concentrations
- Need alternatives to IrO_2 for anode catalysts in 3 compartment cells
- Oxygen removal
- Need to run at higher KOH conversion in 2 compartment cell

Acknowledgements

- **This work was supported by the Department of Energy under contract DE-FE0031706**