Dioxide Materials™

The CO_2 Recycling Company™

Electrochemical Conversion of CO_2 to Formic Acid: Effects of Operation Conditions on Electrolyzer Performance

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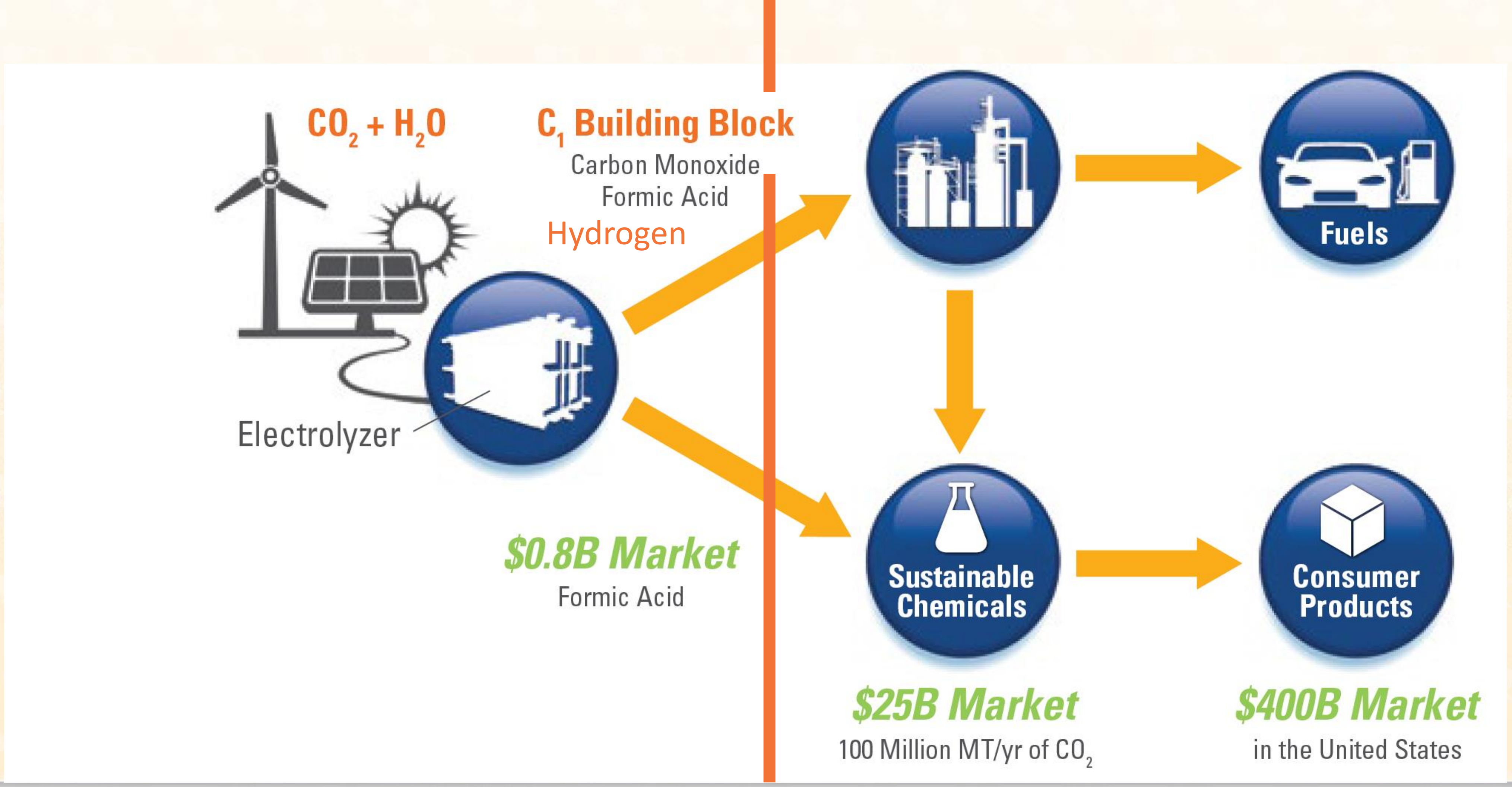
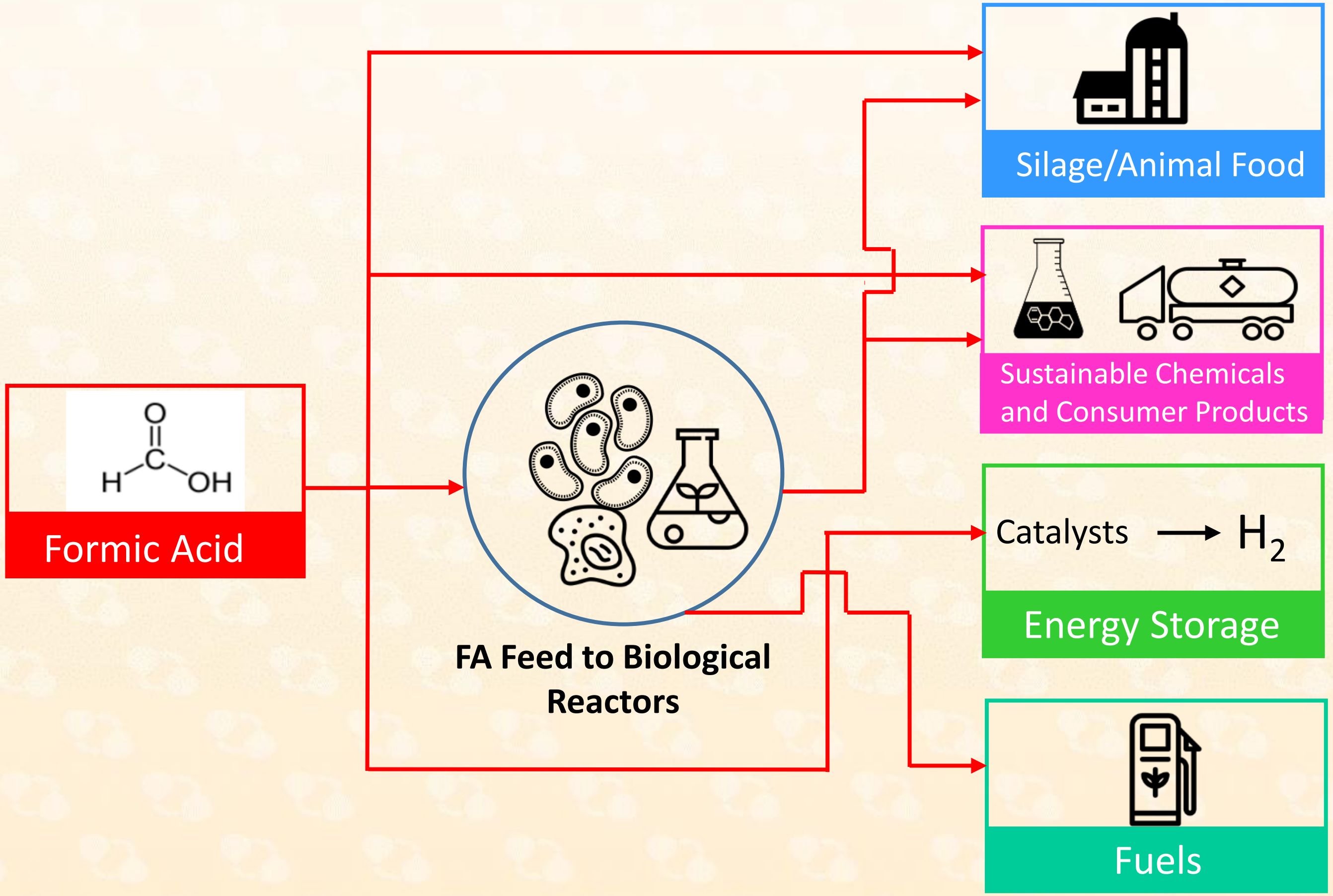
Dioxide Materials' Focus: Produce Fuels and Chemicals From CO_2, Water and Renewable Energy

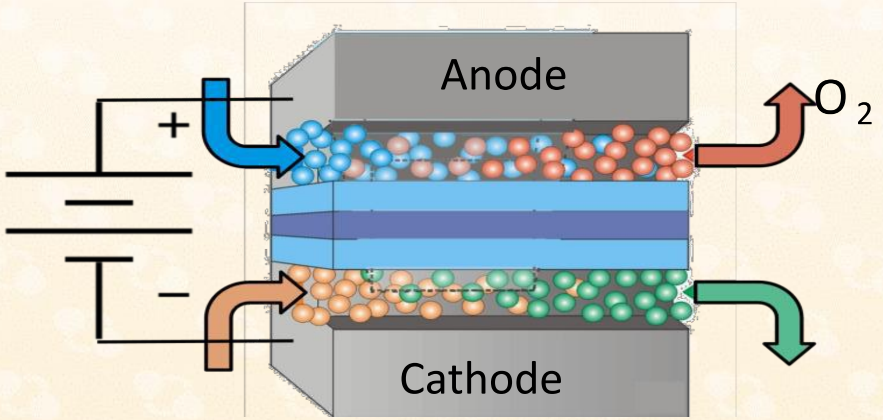


Potential Formic Acid Applications



Previous Research on Electrochemical Conversion of CO_2 to Formic Acid

$2OH^- \rightarrow H_2O + 2e^- + \frac{1}{2} O_2$



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

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

Technical Issues:

- Low Current Density
- High Voltage
- Catalyst Life/Stability (Short Test Runs)
- Formic Acid Separation (High Cost Step)
- Low Selectivity
- CO_2 Solubility
- Membrane Availability

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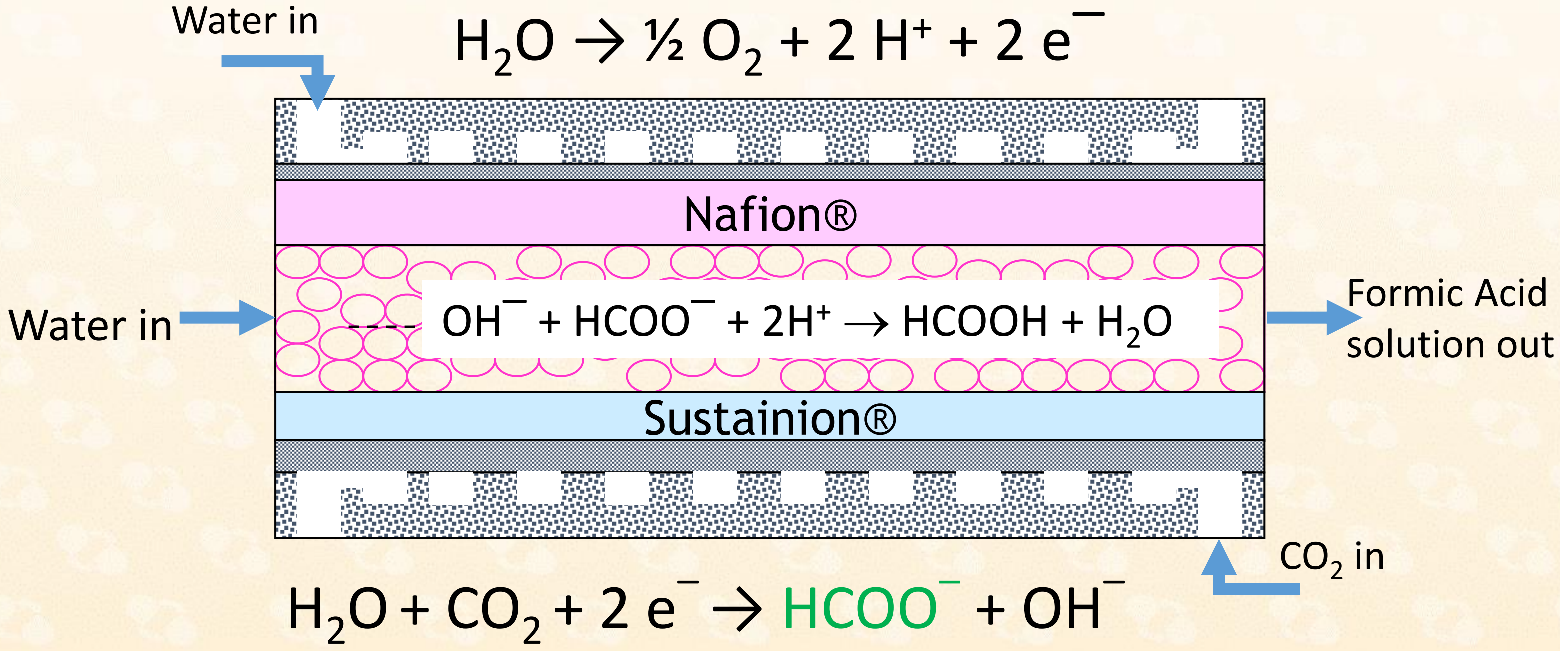
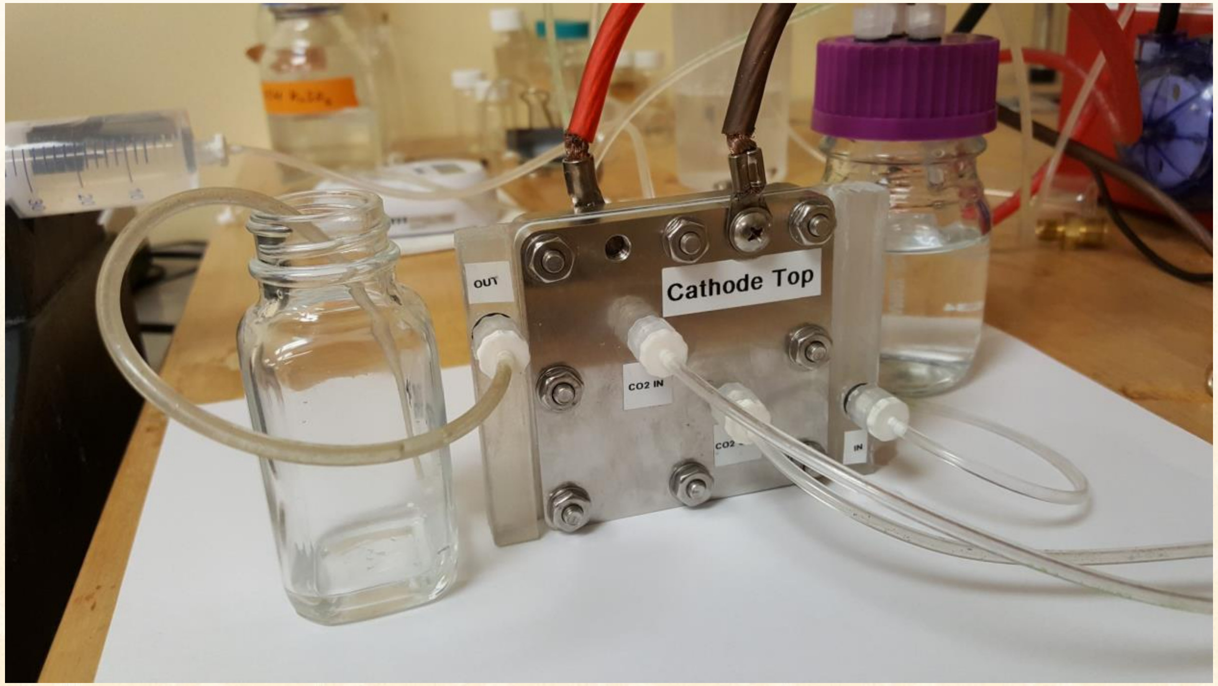
Dioxide Materials' Patented Formic Acid Technology



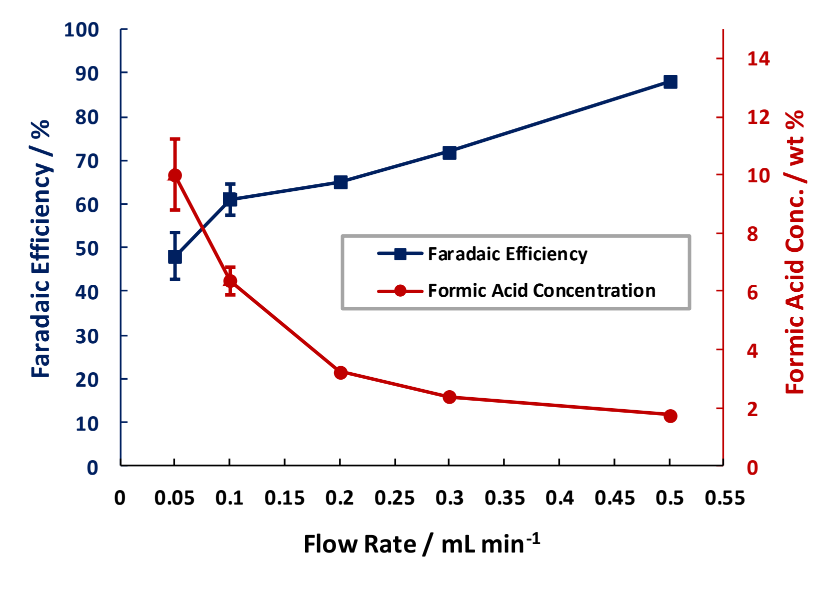
- **Formic acid is formed directly**
  - **No need of conversion step (formate to formic acid)**
  - **No need to continuously supply KOH**
- **Industrially relevant currents obtained at reasonable voltages**

Testing System and Effect of Central Compartment Flow Mode



Testing system with a 5 cm^2 (active area) formic acid electrolyzer

Formic acid FE and wt.% vs. single pass flow rate

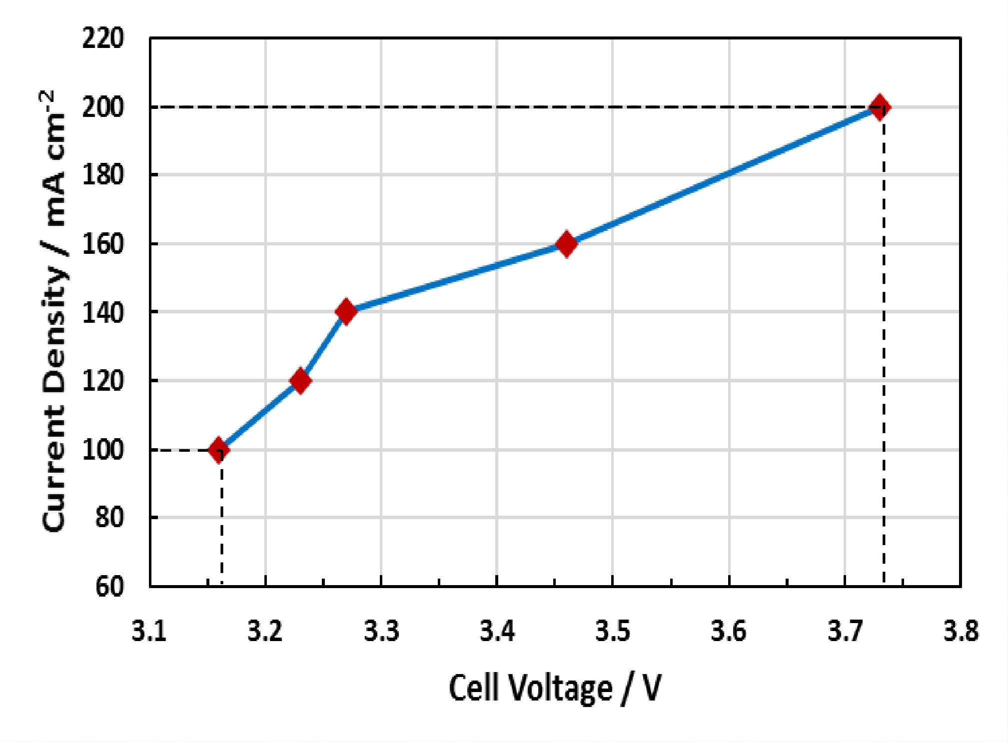


Formic acid FE and wt.% vs. recirculated flow mode, 2h operation

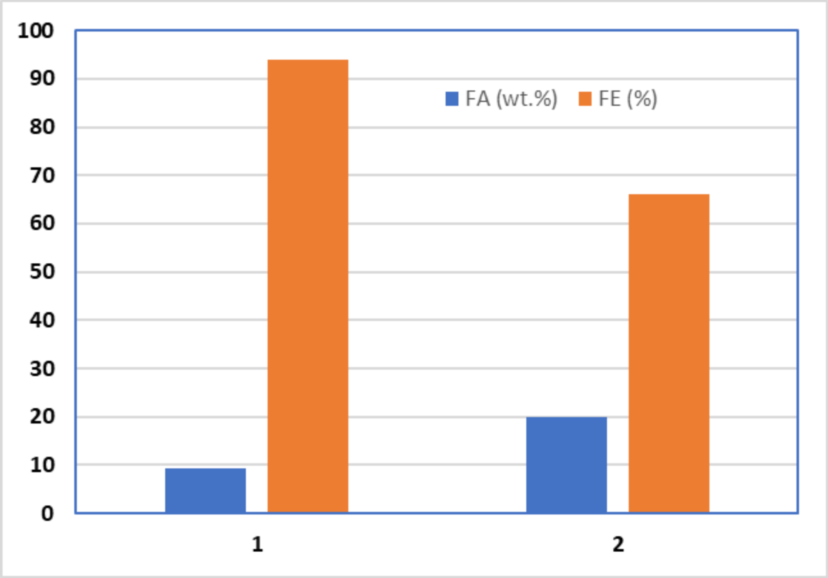
Starting formic acid concentration (wt%)	0	9.9	19.5
Final formic acid concentration (wt%)	2.3	11.2	20.4
Faradaic efficiency (%)	85	47	32

Formic Acid Electrolyzer Perfomance

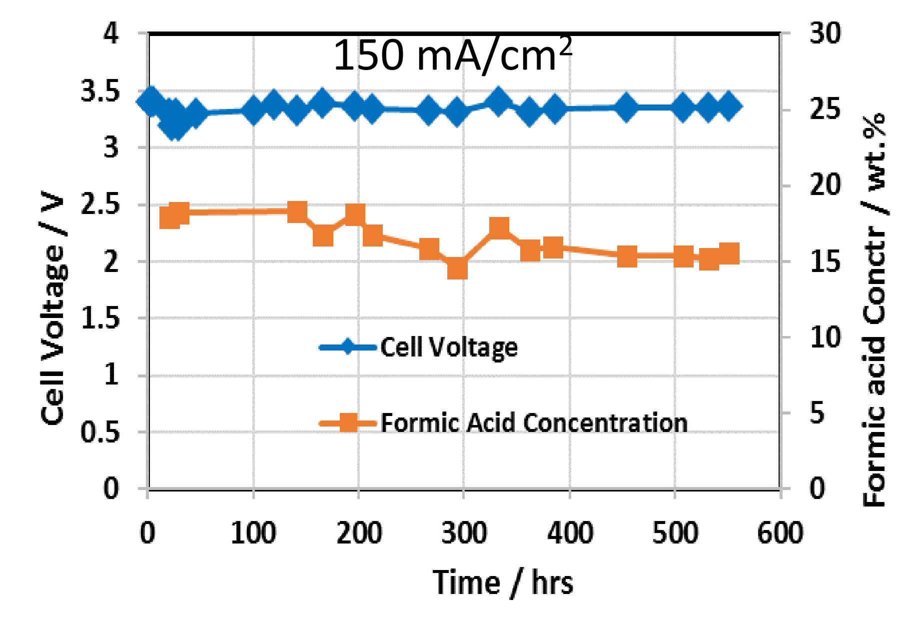
Voltage vs. Current Density in a 5 cm^2 electrolyzer



High formic acid concentration and Faradaic efficiency



Anode Flow Field Materials on Electrolyzer Performance



- Graphite anode flow field after 550 hours run
- Ti anode flow field (no corrosion problem for thousand hours testing)

Membranes on Electrolyzer Performance

Cation exchange membrane to reduce formic acid crossover and oxidation on anode

Membrane	Membrane thickness (μm)	Formic acid concentration (wt%)	A_{CO_2}/A_{O_2}
DuPont Nafion® 212	50.8	15	2.3
DuPont Nafion® 115	127	5	0.29
		8.7	0.31
		15.6	0.56
		16.8	0.70
DuPont Nafion® 324	150	8.5	0.03

GC peak area ratio of CO_2 and O_2 from anode side used to determine how much formate being oxidized on anode.

Anion exchange membrane to reduce water content on cathode surface to reduce side-reaction on cathode

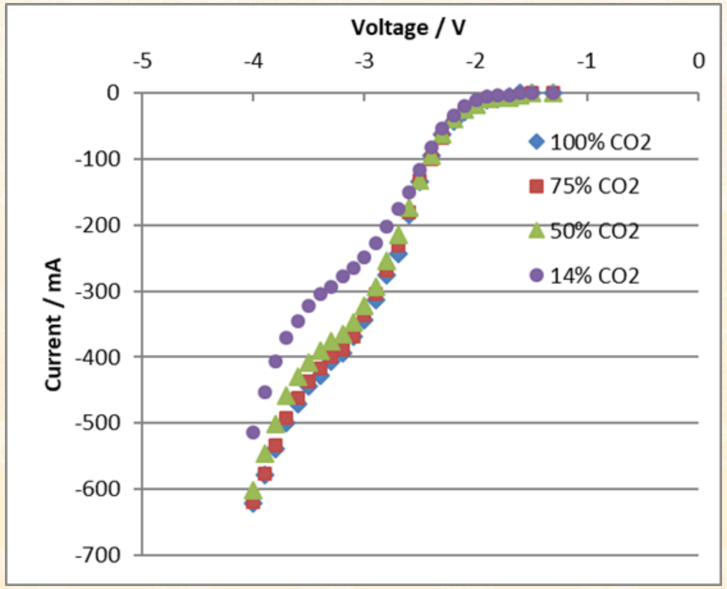
$$CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^-$$

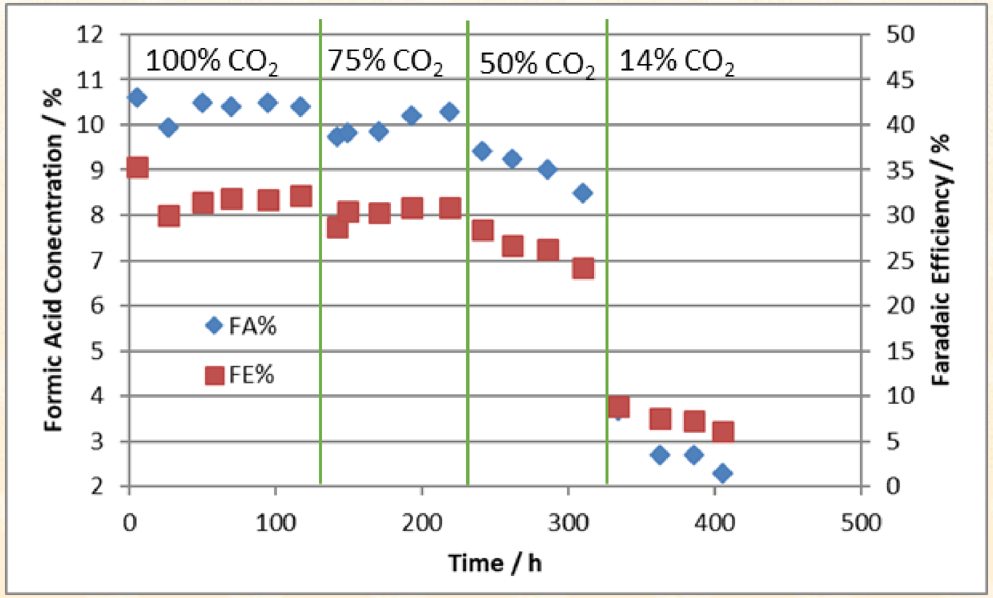
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

Sustainion® membrane	Water Content	FA (wt.%)	FE (%)	H_2% (GC Data)	CO% (GC Data)
#1	high	5.65	21	29.8	0.97
#2	low	17.8	43	18.8	3.28

CO_2 Concentration on Electrolyzer Performance

- 5 cm^2 (active surface area) formic acid electrolyzer
- Sn cathode
- I-V and constant current density (120 mA/cm^2)
- 14%, 50%, 75%, and 100% CO_2 (N_2 balanced)

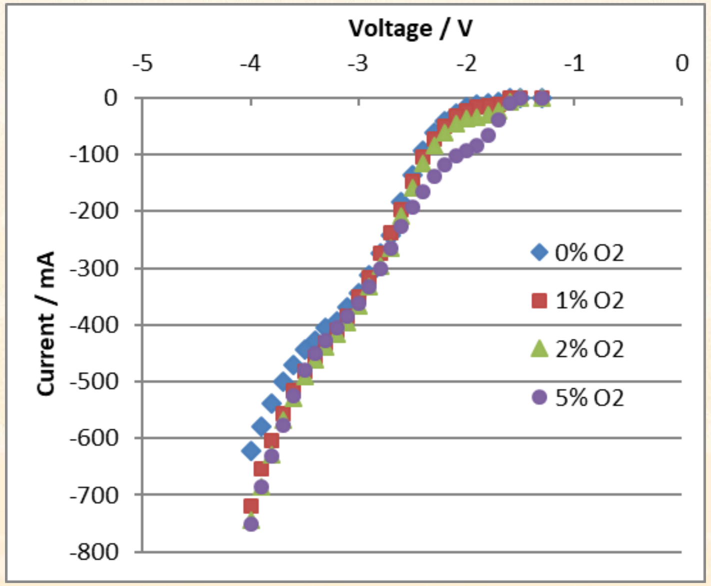


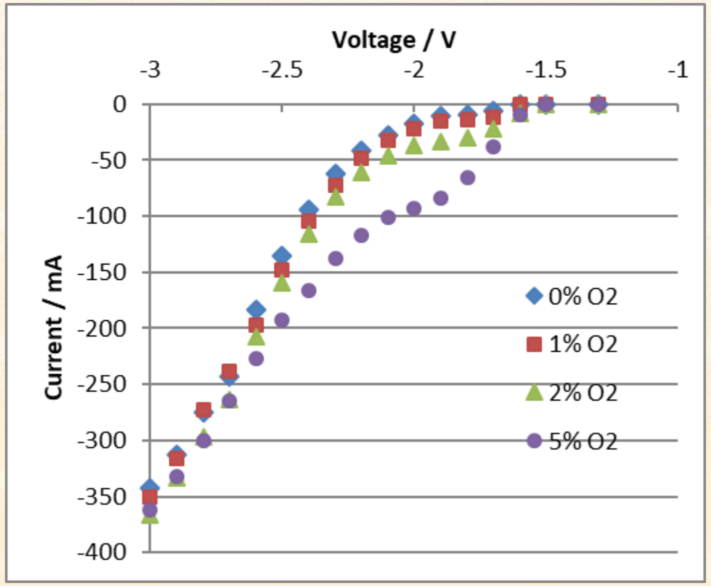


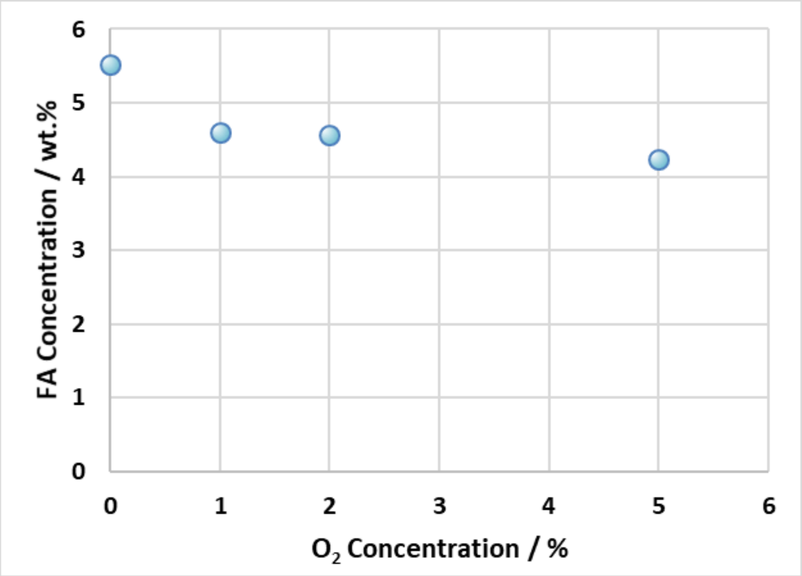
Catalysts with good performance at low CO_2 concentration

O_2 Concentration on Electrolyzer Performance

- 5 cm^2 (active surface area) formic acid electrolyzer
- Sn cathode
- I-V and constant current density (120 mA/cm^2)
- 1%, 2%, 5% O_2 mixed with CO_2







Catalysts with good performance in the presence of O_2

Dioxide Materials™
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Proprietary

Summary

- **Dioxide Materials developed a three-compartment formic acid electrolyzer which directly produces formic acid at an industrial relevant current.**

- **Important factors that affect the performance of formic acid electrolyzer were discussed (flow field materials, membranes, flow rate…).**

- **Formic acid electrolyzer performance decreased with low CO_2 concentration or in the presence of O_2, new catalysts and other improvements are needed for better electrolyzer performance under such critical operation conditions.**

Acknowledgements

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