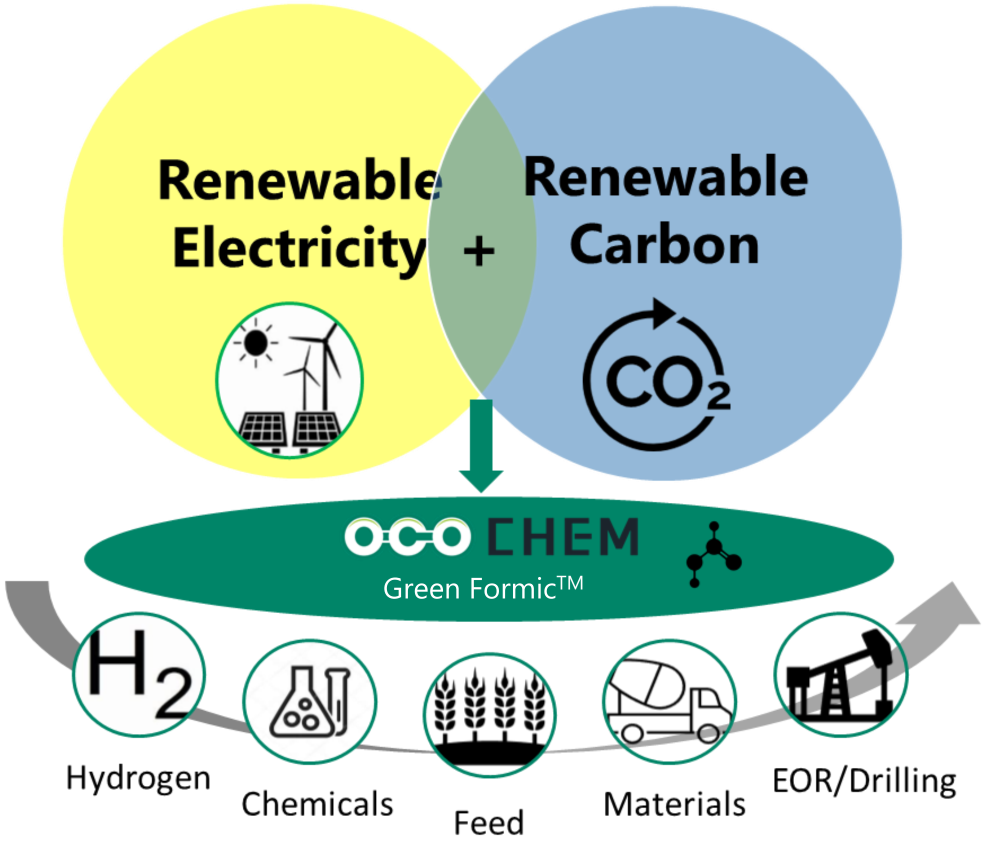
Formic Acid-based Hydrogen Energy Production and Distribution System

DE-FOA-0002792-1512

OCOchem: Arun Agarwal, Matt Phillips, Ying Wang, Brooke Lauderback, Jerry Kaczur, Todd Brix;

Pacific Northwest National Laboratory (PNNL): Tom Autrey, Mark Bowden, Uriah Kilgore, Mi Yeon Byun



AMR Project ID # ST245

OVERVIEW: End-to-End Demonstration of Formic Acid as Liquid Hydrogen Carrier

- **Primary goal** - develop and demonstrate at an industrially relevant size an end-to-end cost-effective high performance novel clean liquid hydrogen carrier (LHC) production, distribution and dispensing supply chain using formic acid as the liquid hydrogen carrier.
- OCOchem is developing an industrial-scale height (1.15m) CO_2 electrolyzer device that converts captured CO_2, water and clean electricity into a liquid hydrogen carrier, formic acid. It is the world's largest CO_2-Formate electrolyzer using cutting-edge falling film gas diffusion electrode technology operating at 80% Faradaic Efficiency and 95% formic selectivity with a reactor output concentration of 40 wt.%. PNNL has developed a formic reforming process that de-hydrogenates formic acid and separates H_2 from CO_2 to liberate fuel-cell grade hydrogen. Together the technologies provide a safer and lower cost to make, store, move and use clean hydrogen using an energy-dense carrier.

	Key Milestones & Deliverables
Year 1	• Scale-up Electrolyzer cell 10x to industrial-scale height and width (1.15m x 1.30m) • Scale-up Formic reformer 100x to 0.01 kg_H_2/hr. Achieve 99.7% H_2 Purity
Year 2	• Scale-out Electrolyzer 4x more to a 4-cell stack producing 150 kg/day. 40x scale-up+out total • Scale-up Formic reformer 100x more to 1.0 kg_H_2/hr. Achieve 99.997% H_2 Purity

Benchmarks

- **BP1/Year 1** - Achieve two of the performance targets precisely at stated target values (Hydrogen production rate of 0.01 kg/hr, formate electrolyzer faradaic efficiency of 80%) and the rest of the performance targets within a +/- 20% variance
- **BP2/Year 2** - Achieve the performance targets within a +/- 10% variance

Performance Targets by Budget Period

	Budget Period:	**Baseline**	**BP1-Pilot**		**BP2-Demo**	
	Criteria	Baseline	Target	20% Variance	Target	10% Variance
H2 Evolution	Au/C Catalyst Loading (g:g ratio)	0.250	0.025	0.031	0.025	0.028
	CO by-product generated, ppm	< 1	< 1	<1	< 1	<1
	Separated Hydrogen Purity, % wt.	N/A	98.7%	79.0%	99.997%	90.0%
	Hydrogen Production Rate, kg/hr.	0.0001	**0.01**	**0.01**	**1.00**	**1.00**
	Operation Duration, hrs	1	24	19	100	90
Formic Production	Elecrolyzer Scale Up	1 Tall Cell	1 Full Cell		4 Full Cells	
	Electrolyzer Scale, Active surface Area, m^2	0.162	1.62		6.48	
	Avg. Current Density, mA/cm^2	125	125	100	125	112.5
	Avg. Cell Voltage, V	4.5	4.5	5.4	4.5	5.0
	Avg. Faradaic Efficiency	80%	**80%**	**80%**	**80%**	**80%**
	Formic Acid Production Rate, kg/day	3.75	37.5	30	150	135
	Operation Duration, hrs	8	100	80	240	216

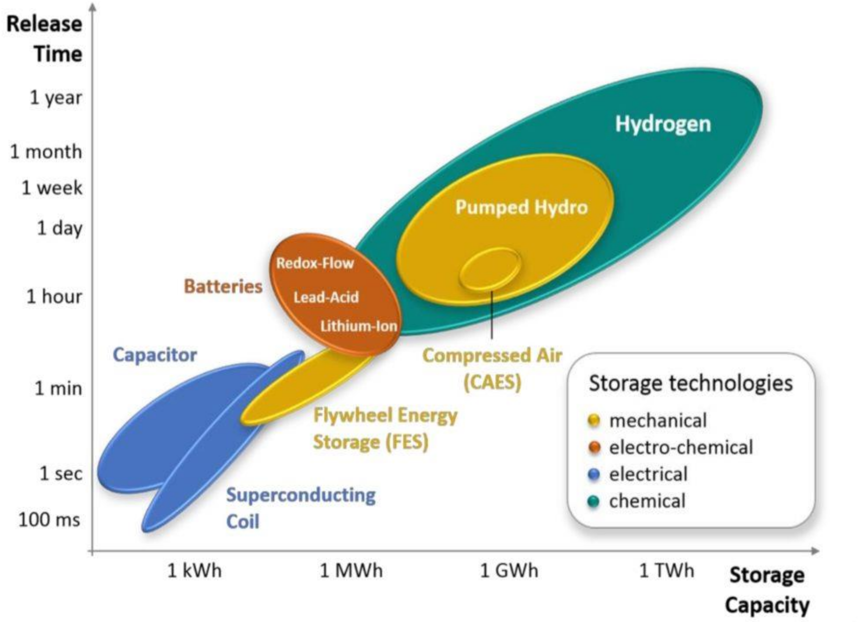
Note: **Bolded performance targets** are precise targets, with no variance allowance in BP1 or BP2.

Potential Impact: The Hydrogen Economy is Arriving

Renewables are expected to provide >50% of global energy production by 2050. **Batteries will only provide 2% of energy storage** and is not adequate for most mobile, off-grid, high-duty, large volume and long-duration energy storage applications. Therefore, **the use of hydrogen and hydrogen carriers is inevitable.**

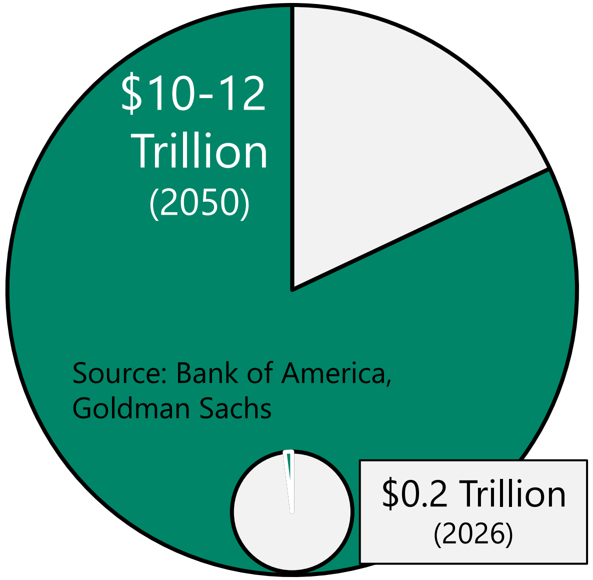
Energy Storage Technologies

Only Chemically Bonded Hydrogen and Hydrogen Carriers Can Store TWh-scale Energy World Needs



Hydrogen Market Size

80% of the $10-12 Trillion in Hydrogen market growth over the next 25 years will be delivered Hydrogen. Today, only 2% of Hydrogen is delivered.



Market Trends

Hydrogen is being adopted as a fuel for many systems.

Hydrogen Vehicles

$3/kg
Production Tax Credit (U.S.)

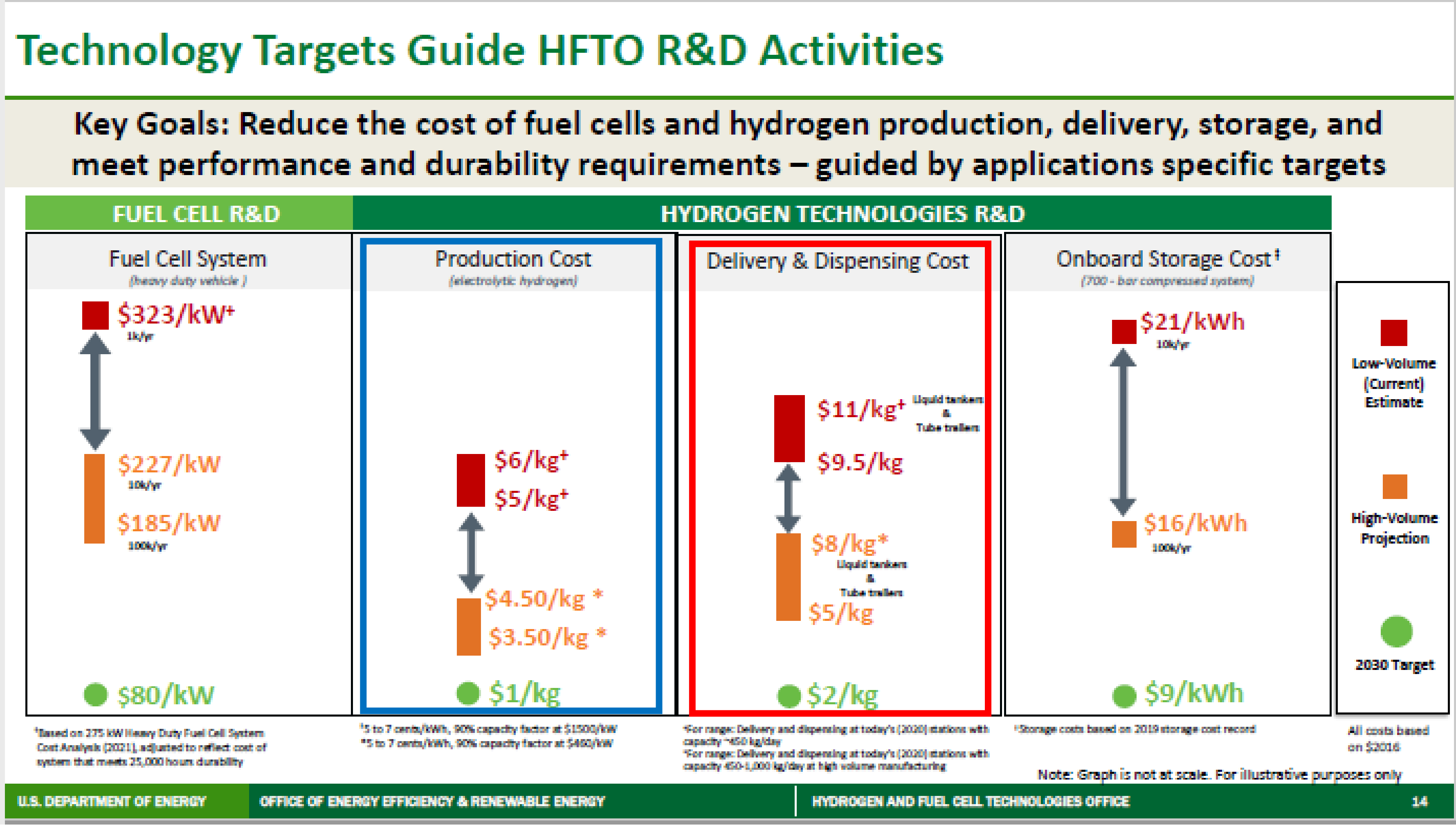
Potential Impact: For H2 to be delivered affordably, Distribution Cost is the Key

Production Cost

- Green Hydrogen ($6/kg)
- Gray Hydrogen ($1.50/kg)
- This cost is falling due to larger more efficient electrolyzers, lower electricity cost and production tax credits

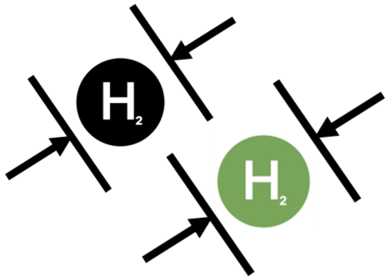
Distribution Cost

- Gray Hydrogen ($11/kg)
- Green Hydrogen ($11/kg)
- This cost has not fallen since 2015



Potential Impact: Molecular H_2 has Several Challenges

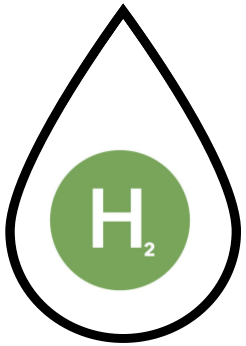
The adoption of the **hydrogen economy** is inhibited by current hydrogen storage, distribution and compression problems. These **problems can be overcome** via the use of the liquid hydrogen carrier, formic acid, produced by **OCOchem's patented electrolyzer technology.**



Compressed Hydrogen (250 Bar)

Conventional (Green or Gray)

- × Gas
- × Less Energy Dense (17.6 g _H_2/L)
- × High Pressure (250 bar)
- × Explosive
- × Difficult to See, Smell or Detect
- × Specialized New H_2 Infrastructure
- × Expensive to Distribute (>$10/kg)



Formic Acid

OCOCHEM

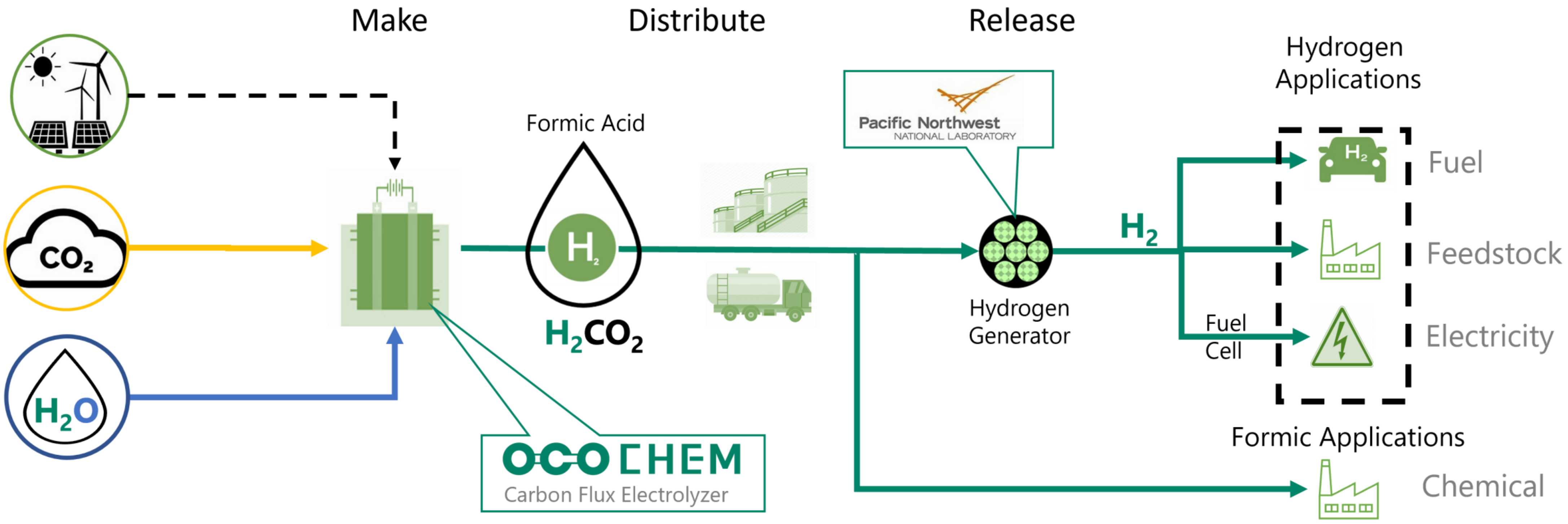
Formic Acid

- ✓ Liquid
- ✓ Energy Dense (53.4 g_H_2/L)
- ✓ Standard Pressure and Temperature
- ✓ Low Flammability
- ✓ Easy to See, Smell and Detect
- ✓ Generic Existing Liquid Infrastructure
- ✓ Affordable to Distribute (<$0.50/kg)

By making and storing green hydrogen **directly** into a liquid hydrogen carrier form, one can avoid the many cost and safety issues of molecular hydrogen

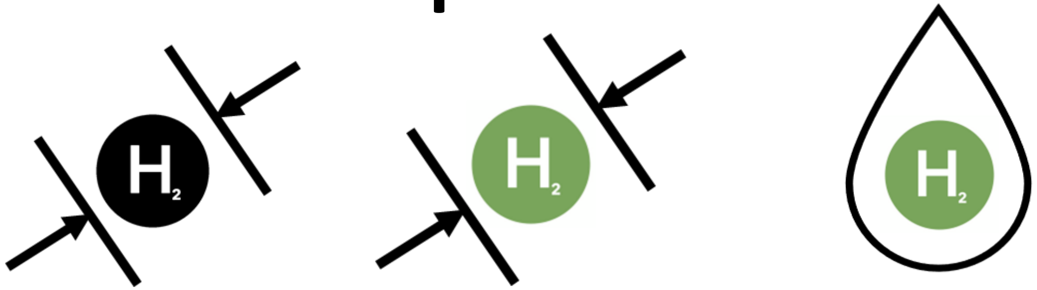
Potential Impact: Using CO_2 to Carry H_2 in a Liquid Form

OCOchem's process directly converts CO_2, water and clean electricity into a liquid hydrogen carrier, which can be stored and moved like a conventional liquid, and then reformed to generate H_2 on-demand



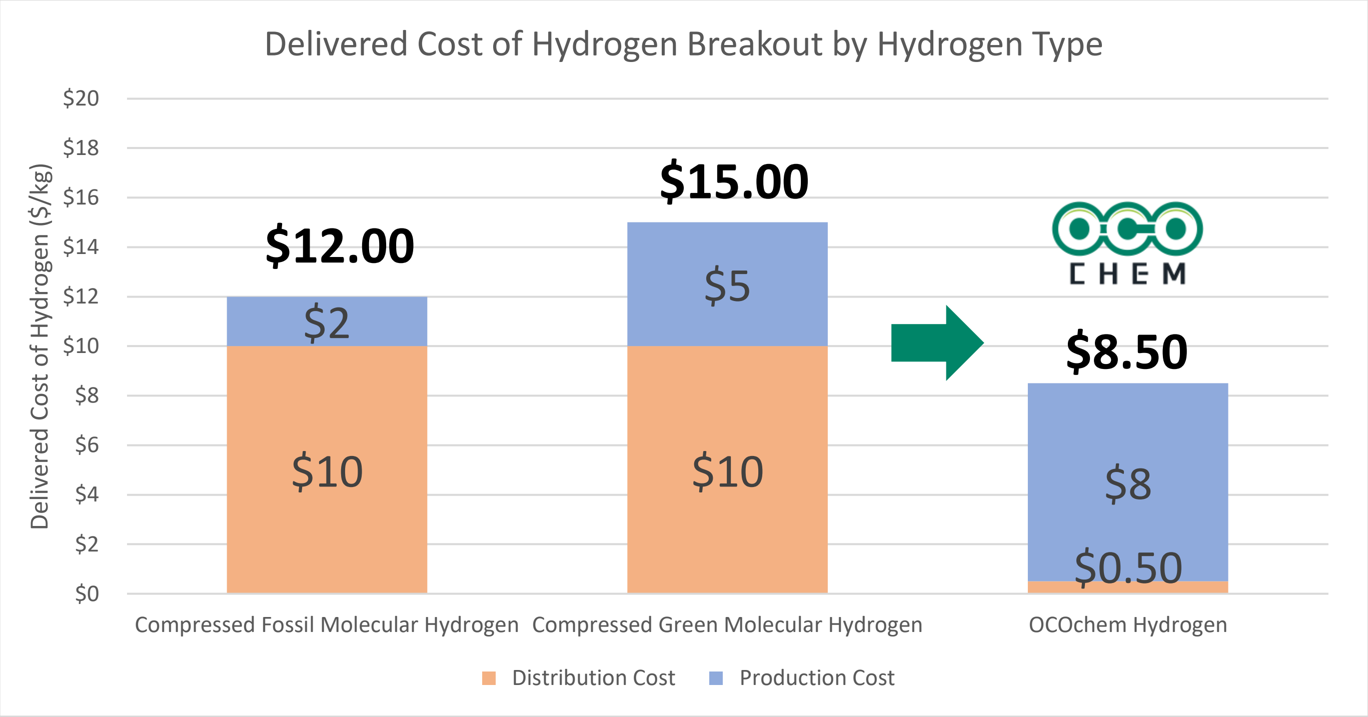
Potential Impact: Hydrogen Basis Cost Comparison

OCOchem plans to deliver Hydrogen at a **30-45% lower cost** than green or gray Molecular Hydrogen (H_2) because liquids are 20x less expensive to store and move than compressed gases.



Assumptions:

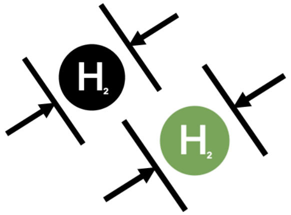
1. Assumes $40/MWh green electricity cost, $30/ton CO2 cost (Source: DOE, OCOchem extrapolated performance results)
2. Distribution cost includes compression, storage, transport and dispensing costs typical of one-way transport distance of 100km (Source: DOE)



Potential Impact: Hydrogen Transport Comparison

5.8x as much Hydrogen can be moved per truckload using formic as liquid hydrogen carrier than 250bar compressed molecular Hydrogen gas

Formic Acid



Compressed Hydrogen (250 Bar)

Conventional Liquid Tanker Truck

Pressure:	1 Bar (unpressurized)
Storage Capacity:	60,000L
Hydrogen Stored:	2,200 kg of H2
Explosion Hazard:	No
Cost of Tank Trailer (New):	$19,900-34,500

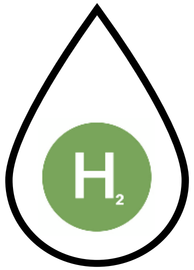
Steel Tube Trailer Truck

Pressure:	250 Bar*
Storage Capacity:	18,600L
Hydrogen Stored:	380 kg of H2
Explosion Hazard:	Yes
Cost of Tube Trailer (New):	$75,000-$90,000

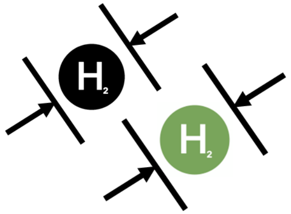
* Tube trailers are currently limited to pressures of 250 bar by U.S. Department of Transportation (DOT) regulations, but exemptions have been granted to enable operation at higher pressures (e.g., 500 bar or higher). Source: Department of Energy

Hydrogen Storage Comparison

The cost of storing 10,000kg of Hydrogen is 50x more expensive with compressed molecular H2 than using formic acid



Formic Acid



Compressed Hydrogen (400 Bar)

Above-ground Liquid Fuel Tank

Pressure:	1 Bar*
Storage Capacity:	1200 Barrels (185m^3)
Dimensions:	10m diameter x 2.5m height
Hydrogen Stored:	**10,000 kg of H2**
Explosion Hazard:	No
Cost of Tank Installed	$150,000-$200,000
Safety Perimeter needed `	0’
Total Land footprint Needed	1600 SQFT (12m x12m)

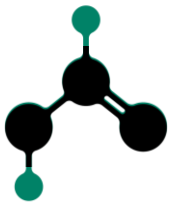
ASME Compressed Hydrogen Storage Spheres

Pressure:	400 Bar*
Storage Capacity:	1900 Barrels
Diameter:	18m
Hydrogen Stored:	**10,000 kg of H2**
Explosion Hazard:	Yes
Cost of Tank Installed:	$5,000,000 ($500/kg)
Safety Perimeter needed `	165’ (50m)
Total Land footprint needed	40,000 SQFT (60x60m)

*400 Bar enables refueling of high duty hydrogen FCEVs at 350 bar (est.

Energy Density Comparison

Equivalent Energy Storage Content (1.8 MWh) Total System Weight



H_2CO_2

1000L Formic Acid
1.2 tons

128 Compressed (200bar) H2 Cylinders 7 tons

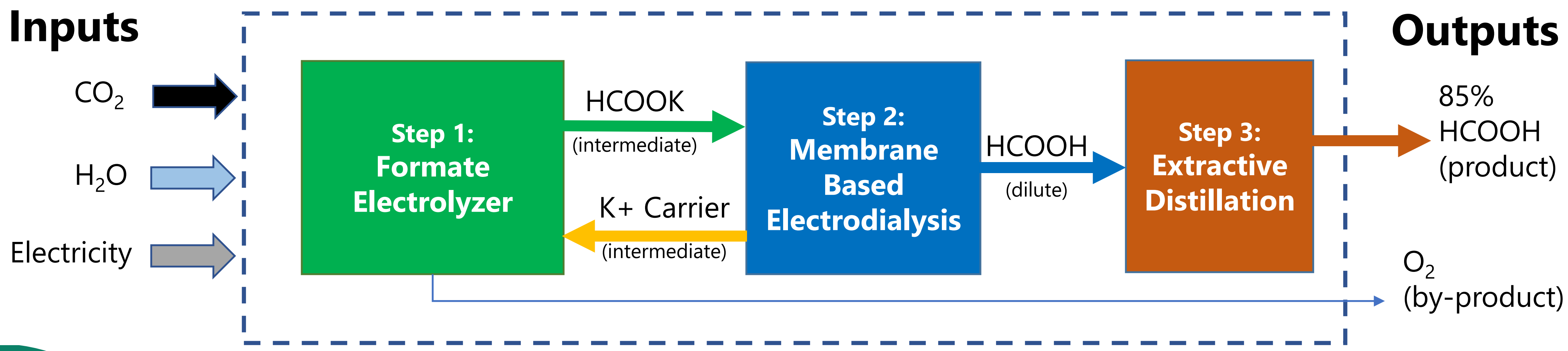
1 Li-Ion Battery
45 tons

Approach: Safety Planning.

- As part of the Q4 2023 report deliverables to the DOE, PNNL has provided the DOE with its hydrogen safety plan and is currently working with the DOE on making modifications as requested by the DOE.
- OCOchem and PNNL conform with lab safety measures for all operations of this project. The personnel involved are adequately trained to handle the experimental requirements.

Approach: OCOchem Formic Synthesis Process

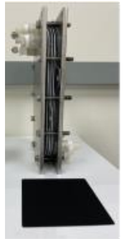
- Step 1: CO_2, water, K+ and electricity is converted into potassium formate (HCOOK)
- Step 2: HCOOK is acidified via electrodialysis to dilute formic acid (HCOOH) , and K+ (with proprietary anion) is recycled to Step 1 to "carry" formate
- Step 3: dilute formic acid is concentrated via extractive distillation to product purity (85%)



Approach: Scale-Up Process

OCOchem is iteratively scaling from small to full, industry sized, multi-cell systems

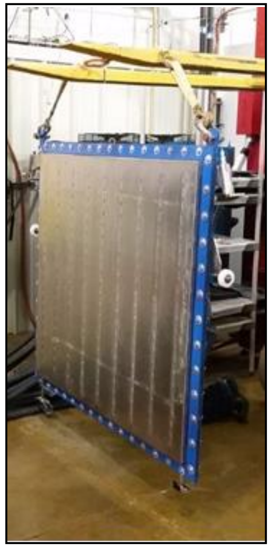
Tiny Cell
$10cm^2$
2010 -2018



Small Cell
$100cm^2$
Jan. 2021

Mid Cell
$150cm^2$
July 2022

Tall Cell
1600 cm^2
~5 kg/day
Dec 2022

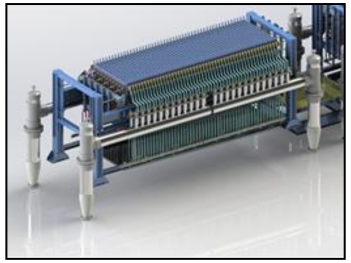


Full Cell (current)
16,000 cm^2
~35 kg/day
June 2024

Multi-Cell Pilot Plant
4 Cells/Stack
Design work in Progress
~150 kg/day
June 2025

Industrial-Scale Formic Production Module

(achieves project finance bankability)



50-Cell Production Module
50x Cells/Modules
2,500 kg day
2026

1st Industrial-Scale Formic Production Plant

60 Module Production Plant
60x Modules/Plant
150,000 kg/day
2027-8

We Started Here! (2023) → Ongoing (2023-4) Funded → Industrial Scale 50 Cell Production Module → 50,000 tpy Plant (60 Modules)

Approach: OCOchem Scale-up Strategy

1) Adapting to existing large scale electrochemical industry for leveraging hardware & expertise
   a) Chlor Alkali (C/A) industry uses ~ 3% of the worlds electricity for Cl2 & Caustic Soda, bulk chemicals with widespread uses
   b) C/A has progressed over the last 50-70 years, has multiple (>5) reactor cell manufacturers worldwide
   c) Rather than devising new cells, which will lead to significant supply chain, tooling/design issues, OCOchem focuses on adapting Chlor Alkali (C/A) cells to its technology, requiring only 15-20% modification of cell parts for its 1st generation cells
   d) OCOchem is modifying and using cells built for C/A industry, adapting it for the key differences in process chemistry (more benign), operating conditions (lower T/P), reactor configuration and products (O2 and formate vs. Cl2 and caustic).
   e) C/A cells, including ion exchange membranes typically demonstrate for 5-7 years of lifetime
   f) 100s – 1000s of cells can be sourced from one of the large-scale producers

2) OCOchem is currently modifying a chlor alkali full industry sized cell (15,000cm2 size), testing to commence soon

3) Optimization of the full cell, based on testing and learning from tall cell to be carried out through 2024

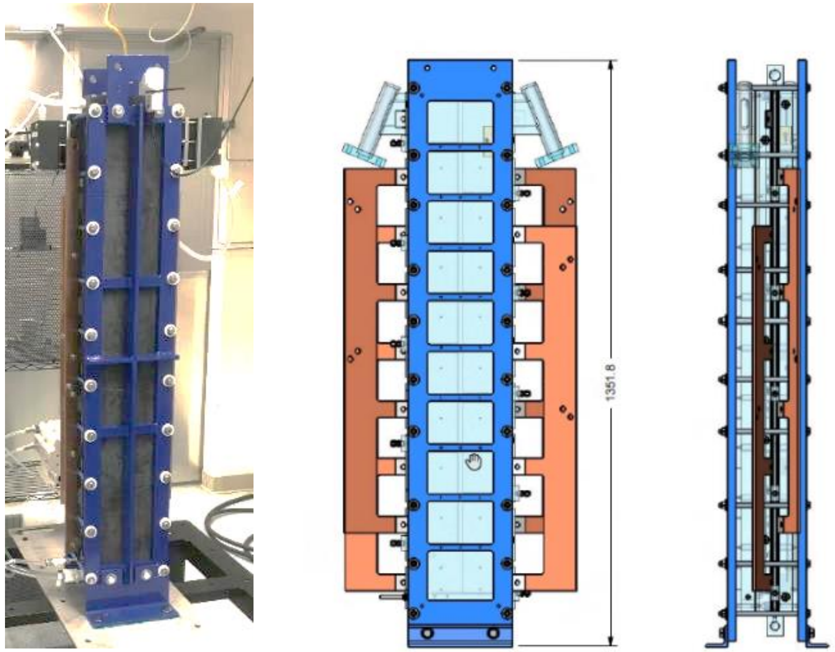
4) A 4-cell pilot plant, with 4 modified C/A full industry sized cells, along with electrodialysis and distillation systems for 100-200 kg/day in-house formic acid production will be completed at OCOchem facility by Q1 2025, and optimized for target performance through Q3 2025.

Accomplishments: Scale-Up Progress

Tiny Cell
10cm2
2020

Small Cell
100cm2
Jan, 2021

NS-01
(Mid-Cell)
150cm2
Advanced
July, 2022



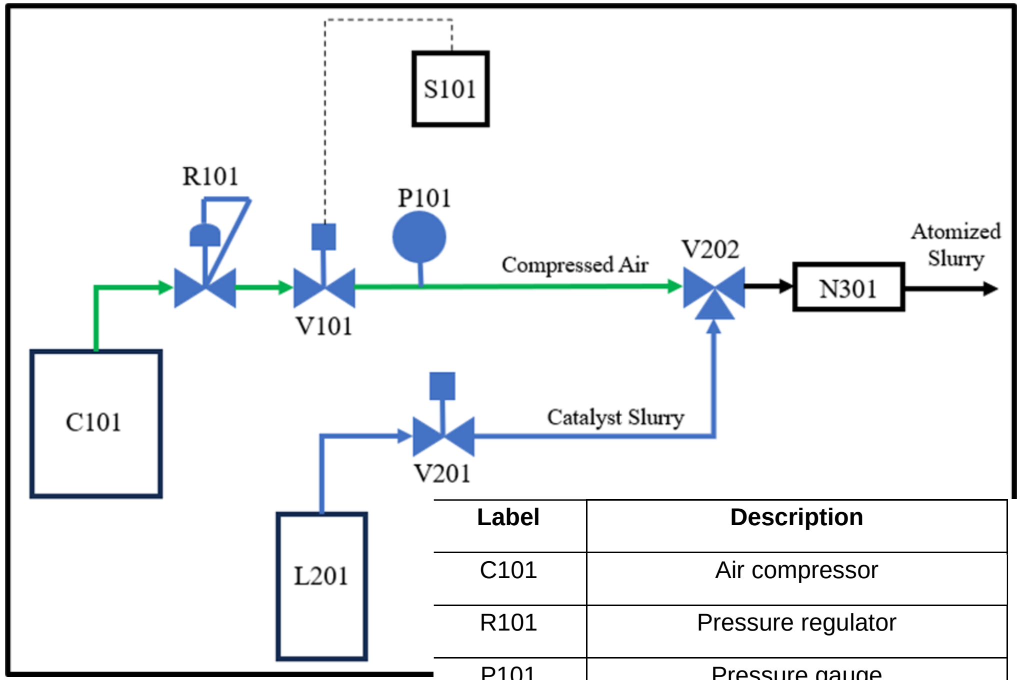
Tall Cell (actual and design)
1600 cm2
Advanced
Dec. 2022 – Aug 2023

- OCOchem has methodically scaled the formate technology 3 times by a total of 160x in 2.5 years including
  - Catalyst and electrode (GDE)
  - Ion exchange membranes
  - Process chemistry
  - Hydrodynamics impact
- Optimization to meet target performance achieved within 10%
- Currently scaling up to industrial sized full cells

Accomplishments & Progress

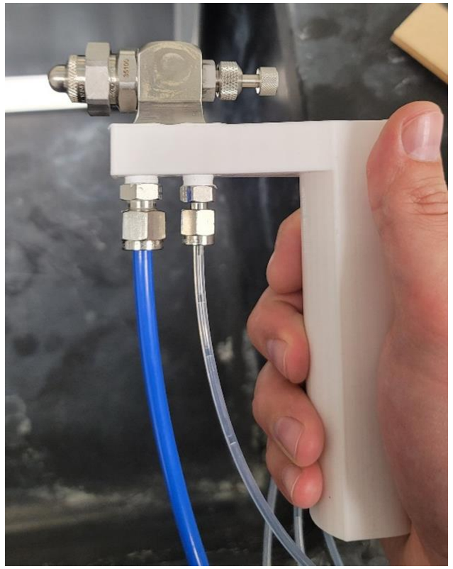
- As OCOchem started working on this project in October 2023, we have no improvements based on last year's comments. We look forward to your feedback this year.

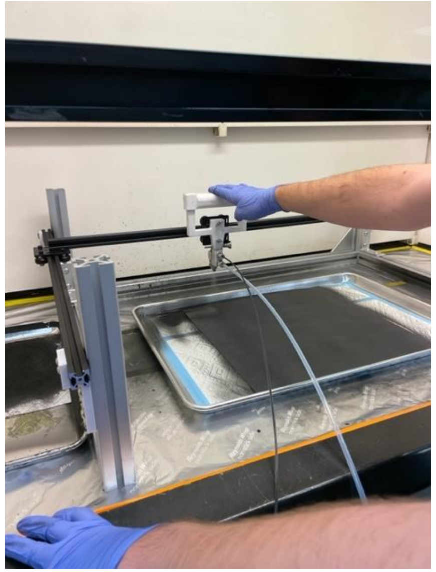
Accomplishments: In-house GDE semi-automated spray system



Label	Description
C101	Air compressor
R101	Pressure regulator
P101	Pressure gauge
V101	Gas solenoid valve
S101	Foot pedal power switch
L201	Slurry feed vessel
V201	Slurry flow regulator needle valve
V202	Nozzle shutoff valve
N301	Nozzle

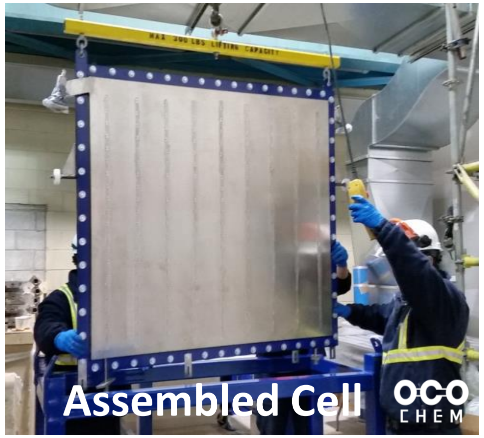
Multiple 40cm x 40cm panels spray capacity





Accomplishments: Single Full size cell Pilot Plant Progress

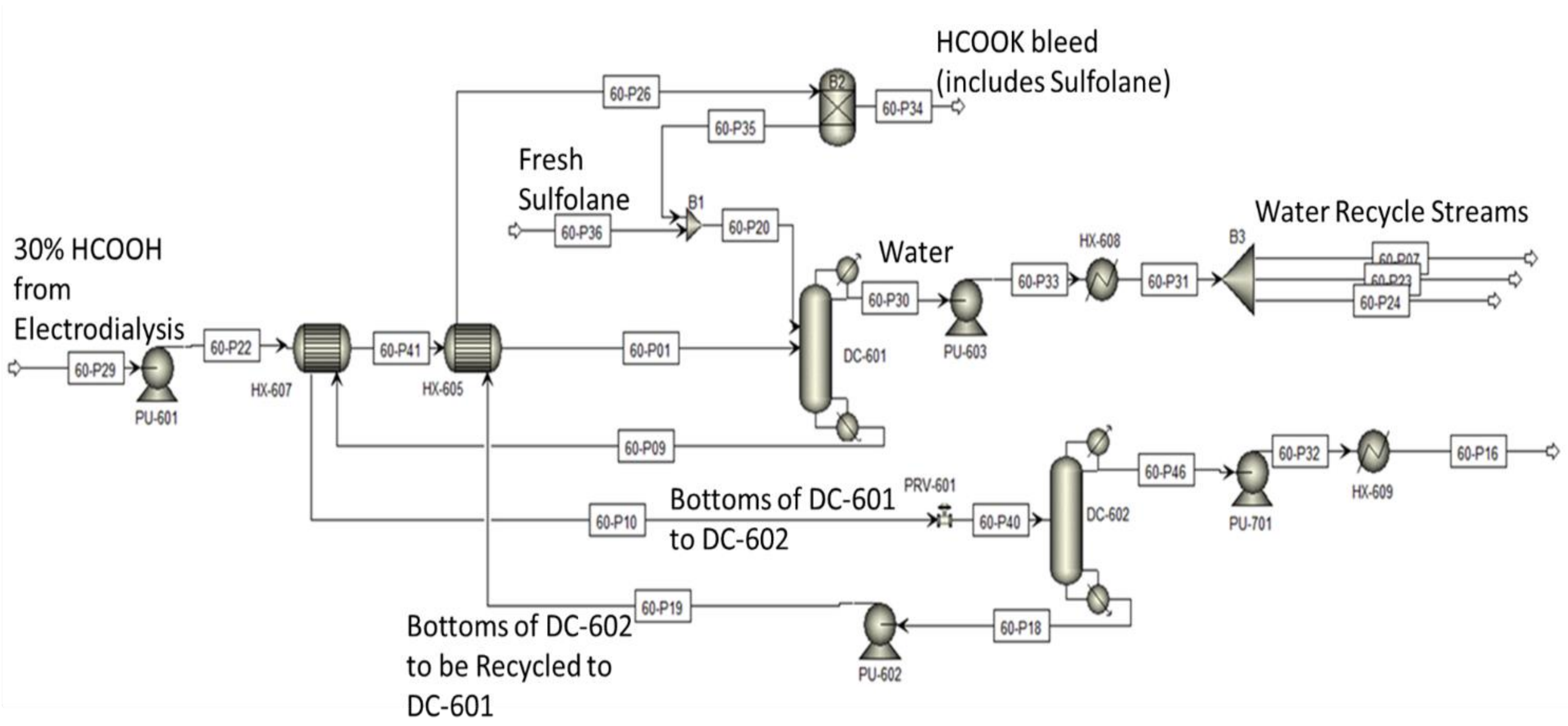
1.15m x 1.30m Electrolyzer Cell Housing Plates



Cell Mounting Carriage

- OCOchem has iteratively designed and constructed proprietary custom parts (GDE cathode, GDE holder, center compartment, mesh structure) to be assembled into the full cell.
- The remainder cell components, including the carriage have been procured.
- Currently modifying high-bay facilities at OCOchem's Richland WA labs for housing and operating the single full cell pilot system

Accomplishments: Electrodialysis & Distillation Process Development

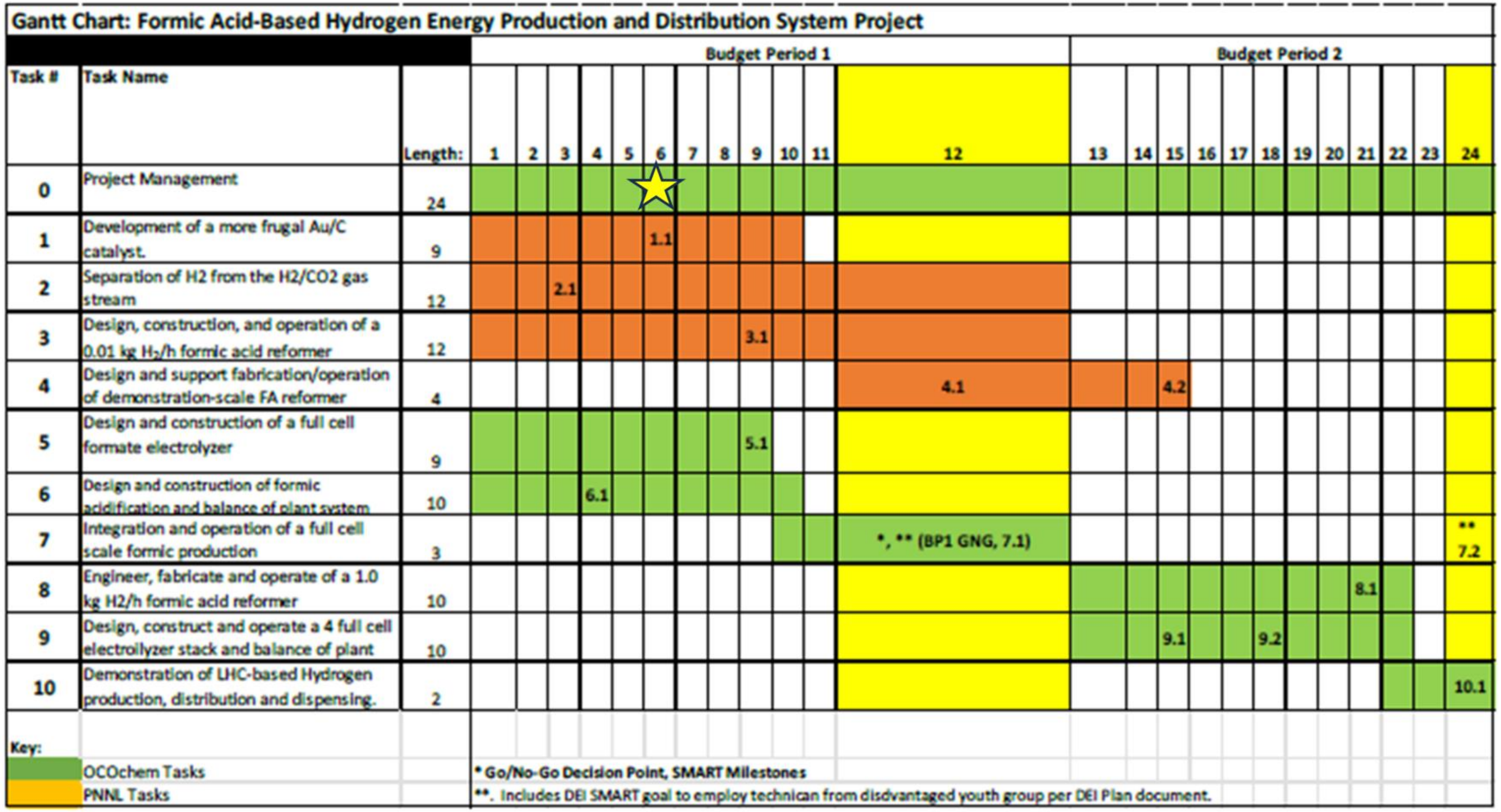


- Formate produced in the electrolyzer (Step 1), is converted in OCOchem's proprietary electrodialysis process to ~30 wt% formic acid
- Sulfolane based extractive distillation, selected and optimized for product grade formic acid (85wt%) as the distillate of the recovery column with negligible sulfolane impurity.
- Water in the distillate of the extraction column is pure and reused/recycled

Proposed Future Work

☆ We are here

- Before this project finishes, we anticipate:
  - Completing the design and construction of and operating a single full-cell scale formic acid demonstration plant
  - Completing the design and construction of and operating a 4 full-cell scale formic acid plant.



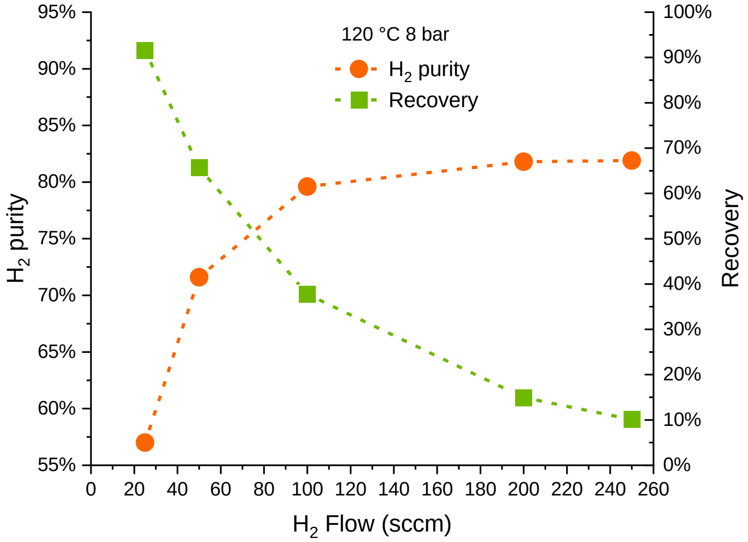
Collaboration & Coordination

- OCOchem and PNNL are collaborating on this project
- Regular Monthly meetings to review and communicate progress and discuss next steps
- Quarterly reports are written in collaboration with team members providing appropriate input based on their involvement in the tasks.

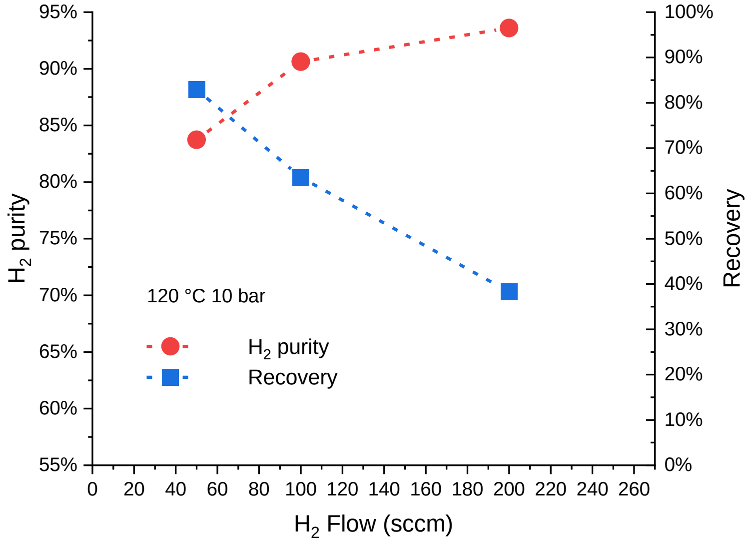
Accomplishment: Purification to > 90% H_2

- Purification of H_2 is accomplished with a commercial membrane that permeates H_2 faster than CO_2
- Performance is characterized by *purity* (the H_2 composition exiting the membrane) and *recovery* (how much of the H_2 fed to the separator ends up in the higher purity exit)

First-generation membrane



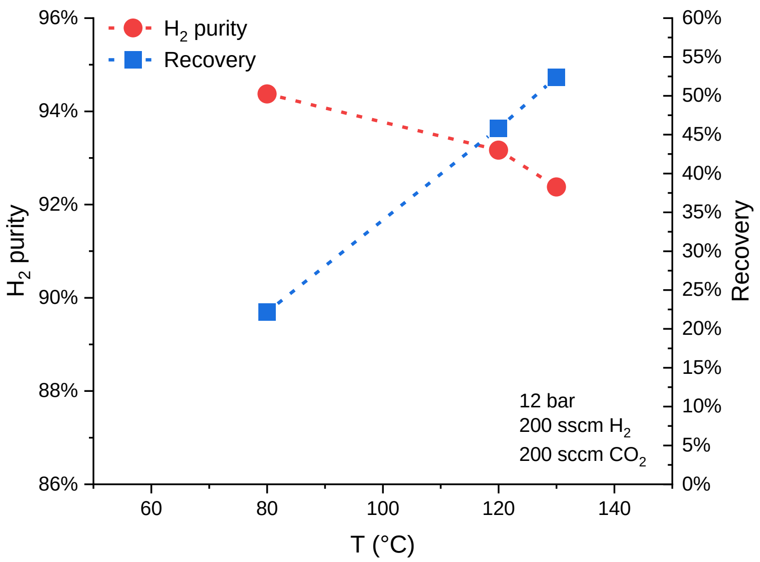
Second-generation membrane



Improvements to the membrane have provided a significant boost in recovery and purity. Increased recovery at high purity is a remaining challenge.

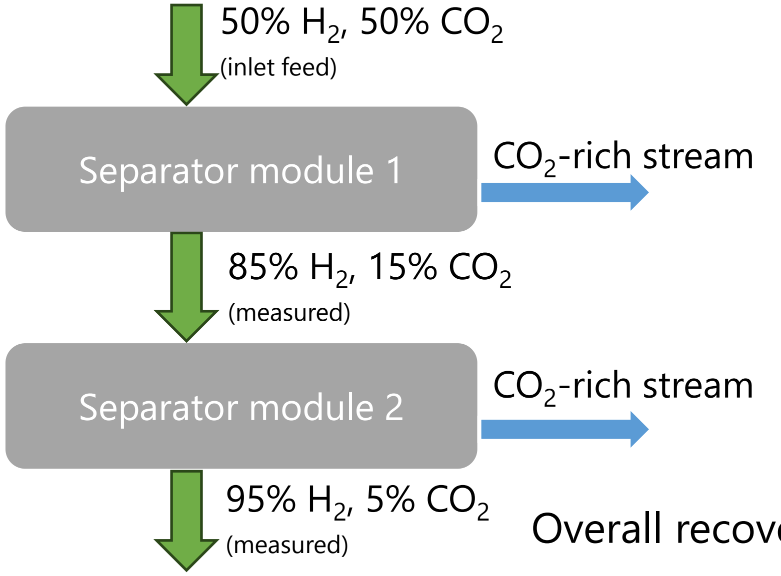
Accomplishment: 2-stage separator to increase recovery

Single-stage



Recovery improves at higher temperatures, without a significant compromise in purity

Two-stage



Overall recovery = 63%

Enrichment to 95% purity has been demonstrated. Improved temperature management will increase this to >99% H_2.

95% H_2 purity has been achieved by measurement of sequential separation stages
Pre-heating the gas will increase recovery since it has a strong temperature dependence.

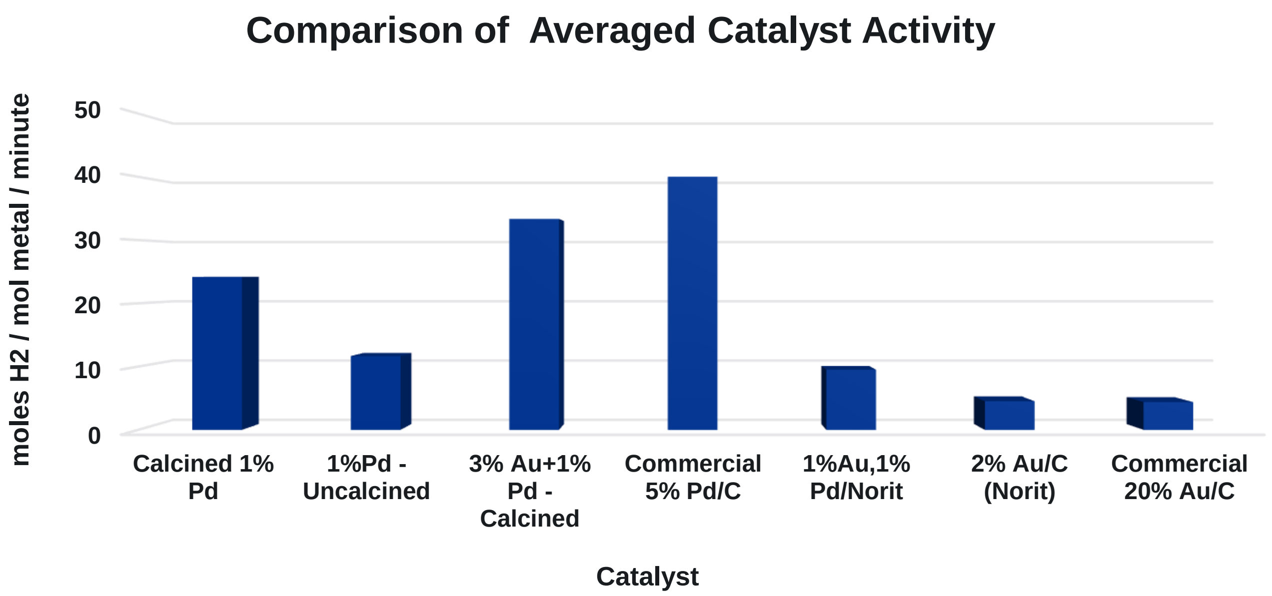
Accomplishment: Hydrogen release from formic acid

Formic acid dehydrogenation has been studied using carbon-supported metal catalysts at 160 °C

Dehydrogenation: $HCOOH \rightarrow H_2 + CO_2$

Dehydration: $HCOOH \rightarrow H_2O + CO$

- Pd on carbon and Au+Pd on carbon show highest turnover frequency
  - Exceeds project target of 10 mol H_2 (mol metal)$^{-1}$min^{-1}
  - Pd/C commercially available
  - 9 times higher than baseline study of 4.4 mol H_2 (mol metal)$^{-1}$min^{-1}
- Pd/C produces ~1% CO side product
- No CO observed with Au+Pd/C catalyst



A more cost-effective use of Pd/C catalysts for dehydrogenation of formic acid has been demonstrated compared to baseline performance. Small quantities of Au are effective at suppressing CO from the dehydration reaction.

Summary

- OCOchem is generating formic acid as a liquid hydrogen carrier (LHC) for an end-to-end, safe and cost-effective means for production, distribution and dispensing of hydrogen
- As part of this DOE project, OCOchem will be developing and demonstrating electrochemical formic acid production via CO_2 and water at pilot scales (with a 1.5 m^2 sized cell in year 1 and with a 4-cell sized pilot plant targeting 150 kg/day production in year 2)
- PNNL in collaboration with OCOchem, is developing the reformation technology to demonstrate effective conversion of formic acid to a H_2, CO_2 gas mixture, and then separation of pure H_2 from the mixture, thus completing the value chain