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PNNL-32595
TCF-20-21431

Hydrogen Storage and Delivery using Electrochemically Generated Formic Acid

CRADA 484

January 2022

Robert S. Weber

OCO, Inc.

U.S. DEPARTMENT OF
ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Abstract

We will marry existing, electrochemical technology for converting carbon dioxide into formic acid (FA), with separations, and with a new, compact reformer to produce H₂ at elevated pressure that can be fed to a fuel cell located at an electrical power plant to provide large scale and low-cost power buffering.

Introduction

This project, funded by a CRADA between OCO Chem, Inc. and Pacific Northwest National Laboratory, advanced the technology for recovering hydrogen from formic acid. The overall envisaged process uses noncarbogenic electricity to electrolytically generate formic acid from waste CO₂ and then decomposes the formic acid to recover the hydrogen that can be used to fuel a fuel cell (Figure 1).

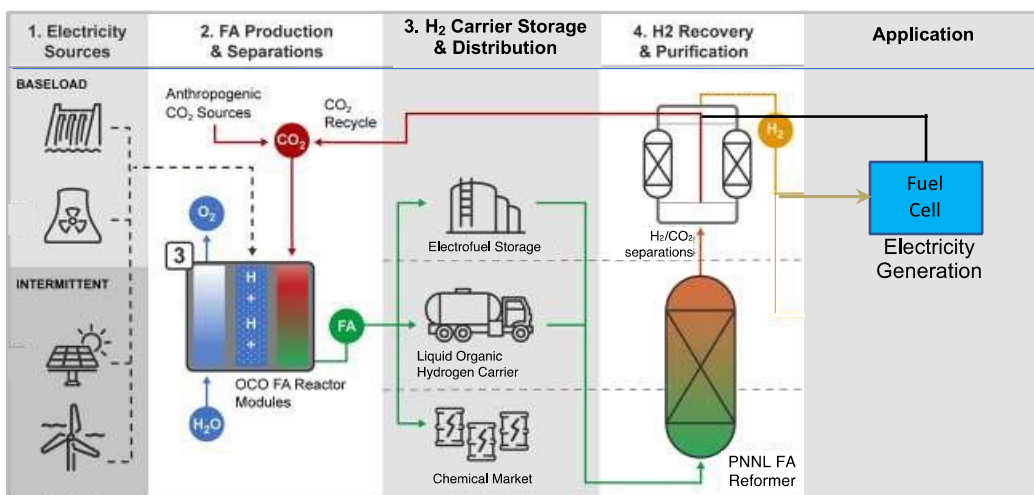


Figure 1. Overall process for storing and then recovering non-carbogenic electrical energy. The research described here is represented by panel 4.

The research consisted of two thrusts, 1) developing a compact reactor for the decomposition reactor and 2) developing a separation method for purifying the hydrogen. Preferably, the separation method would be passive (e.g., membrane, sorption) rather than active (e.g., pressure swing adsorption) to minimize the amount and cost of the equipment.

Formic acid, HCOOH, decomposes either to release gaseous H₂ and CO₂ (dehydrogenation, Reaction 1) or to release gaseous H₂O plus CO (dehydration, Reaction 2). Both reactions are exergonic and spontaneous (negative free energy change). The first reaction is exothermic and the second is endothermic starting from gas phase formic acid (both reactions are endothermic starting from liquid phase formic acid)¹.



The first reaction is catalyzed by platinum group metals; the second by acids (including formic acid itself).

Here we are interested in the first reaction because it releases the hydrogen. Combining the two reactions could produce a “green” synthesis gas in stoichiometric ratios (H₂:CO₂) that could

span the needs of many C_1 processes. Here, ideally, the second reaction would be suppressed completely to ensure that the product stream contained no carbon monoxide, which inhibits the cathode catalyst in a fuel cell.

Schematically, the system consists of two, unit operations: the decomposition reactor and the separator (Figure 2) in addition to the feed and safety provisions. The reactor itself both vaporizes the aqueous formic acid and decomposes the vapor into the component gases (Figure 3). By separating the catalyst from the liquid formic acid we have been able to enhance catalyst longevity (obviates the leaching we observed when we allowed the liquid formic acid to contact the catalyst) and to increase the catalyst activity (by maintaining it a temperature higher than the boiling point of the mixture). The reactor accommodates catalysts in the form of pellets, wafers and impregnated foams or felts. A reflux loop would permit high conversions of the formic acid (multiple passes). However, we found that we could attain conversions higher than 90% at high contact times.

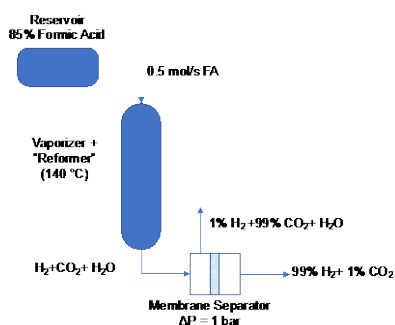


Figure 2. System schematic showing both the decomposition reactor and the separator units.

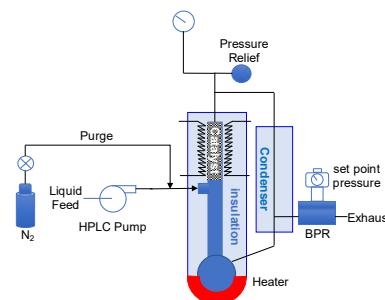


Figure 3. Schematic of the reactor, envisaged to comprise reactive distillation of the formic acid at elevated pressure.

Accomplishments this quarter

Decomposition of formic acid.

We tested the reactive distillation reactor in a stainless-steel assembly that can be pressurized (Figure 4). The reactor consists of a capillary preheat section and a catalyst-packed upflow section (left hand side), a condenser (upper right) and a reservoir to catch the condensate and eventually to allow it to be released (lower right). We have pressure tested this assembly to 1000 psig and we have operated it at low pressures and at low flow rates, 0.015 mL/min for 18 hours. The formic acid produces an equimolar mixture of H_2 and CO_2 , using a commercial catalyst, 20wt% Au/C (4 nm particles, Premetek, P60N200), that we had first tests in a glass reactor. Small amounts of CO that we had found previously seem to have come from a catalyst-contaminated pressure gauge. Once we replaced that gauge, the amount of produced CO dropped below detectable limits (GC). The catalyst maintained its activity and selectivity for more than 3 days of operation at 406 K and 5 bar pressure, producing flows of H_2 that exceeded 140 mol/mol_{Au}/h ($\approx 30\%$ conversion).

We also tried a range of other catalysts (Table 1) but found that the carbon-supported Au was the most active.

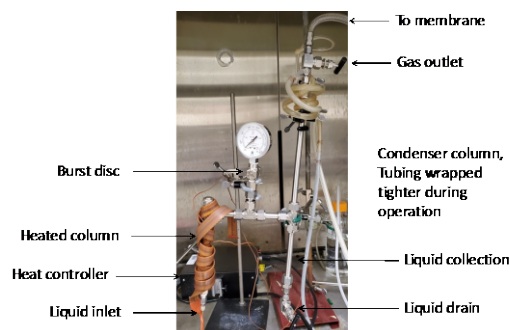


Figure 4. Bench scale, stainless steel reactive distillation unit

Table 1. Activities of tested catalysts at a feed rate of 0.1 mL 85% formic acid/min.

Catalyst	T/K	P/bar	Conversion	Rate/mol _{H₂} mol _{metal} ⁻¹ min ⁻¹
WC/C (supplied by Prof. Suljo Linic)	374	1		nil
MoC/C (supplied by Prof. Suljo Linic)	374	1		nil
Pd 4 wt%/carbon felt (Alfa Aesar)	374	1		nil
Ir@CTF 4 wt%/carbon felt ²	393	20	0.23	9.1
	403	20	0.43	17.6
	413	20	0.64	26.0
Pd 0.3 wt%/C (Aldrich)	398	1	0.07	0.011
	410	1	0.17	0.027
	416	1	0.19	0.029
	422	1	0.24	0.037
	428	1	0.29	0.044
Au 20%/C (Premetek)	433	1	0.34	0.054
	406	1	0.28	2.05
	416	1	0.35	2.51
	426	1	0.49	3.58
	436	1	0.60	4.40
	406	5	0.34	2.46
	406	10	0.45	3.28
<i>20% Au/C at 10 bar, extrapolated to 436 K</i>			<i>0.98</i>	<i>7.12</i>

Although the Ir-based catalyst was the most active, likely due to the high exposure of the metal, we preferred to test steady state operation at elevated pressure using the carbon-supported Au catalyst that the literature³ promised to be both active and selective. The catalyst did prove to be both: it decomposed the vaporized formic acid into the nearly 50:50 mixture of H₂ and CO₂ at rates comparable to those previously reported (*Figure 5*). Moreover, it would likely be less costly than the supported Ir, which uses both an expensive metal and an expensive ligand.

The reaction rate, r , was nearly zero order in formic acid pressure, P , ($r \propto P^{0.21}$) over a much wider pressure regime ($1 \text{ bar} < P < 10 \text{ bar}$) than had been measured to date.

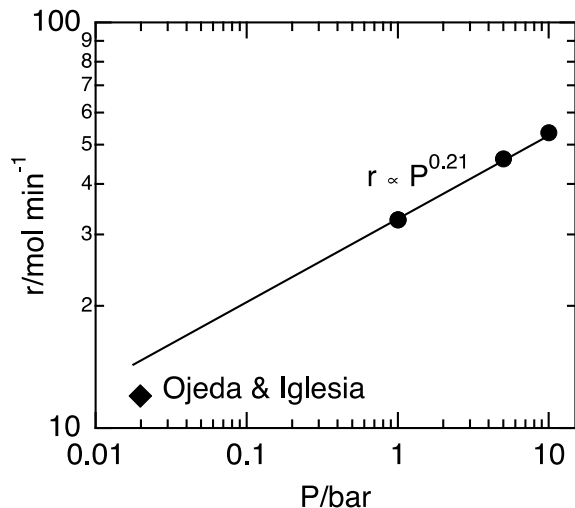


Figure 5. Kinetics of formic acid dehydrogenation. Filled circles: rates measured here using 375 mg of carbon-supported Au (Premetek, 20 wt%, 4 nm particles) at 406 K and the indicated pressure; Filled diamond: data from Ojeda and Iglesia, for the dehydrogenation catalyzed by 4 nm Au/Al₂O₃ and extrapolated to 406 K.

As would be anticipated from nearly zero-order kinetics, conversion increased approximately linearly with contact time (Figure 6).

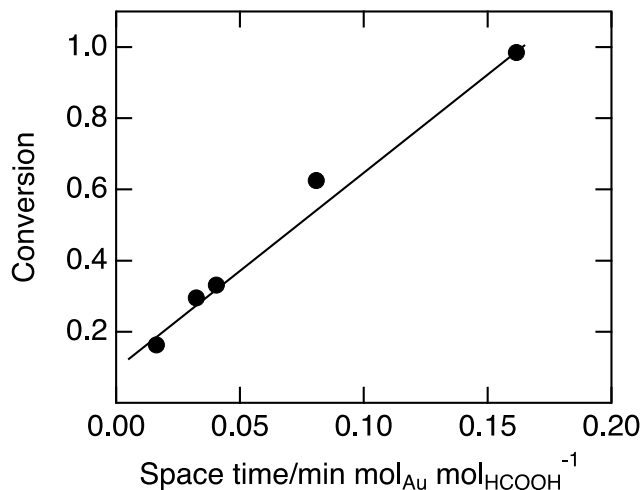


Figure 6. Conversion of the formic acid increases approximately linearly with contact time because the reaction is nearly zero-order reaction.

The apparent activation barrier, E_a , was 39 kJ/mol (Figure 7), also comparable to literature values, although near the low end of the range previously reported.⁴

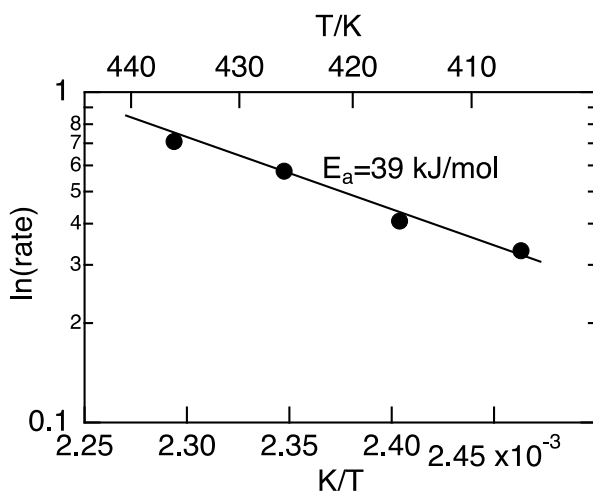


Figure 7. Arrhenius graph for the dehydrogenation of formic acid catalyzed by the carbon-supported Au (Premetek, 20 wt%, 4 nm particles) at 1 bar pressure.

Using the kinetics reported above, 4.36 kg of catalyst (0.86 kg of Au), costing around \$50,000, would be required at a reactor temperature of 436 K, 10 bar pressure to produce sufficient hydrogen to fuel a 60 kW fuel cell (Table 2):

Table 2. Reactor design

Quantity	Value	Units
Design power	60	kW
Assumed cell voltage (50% efficiency)	0.6	V
Required current	100	kA
Required H ₂ flow rate	0.518	mol/s
Reaction rate (~98% conversion, 436 K)	7.12	mol _{H₂} /mol _{Au} /min
Required catalyst (20 wt% Au)	4.36	mol _{Au} (0.86 kg _{Au})
Cost of catalyst (@58,513 \$/kg _{Au})	50,315	USD
Catalyst density (estimated)	2	kg/L
Catalyst volume	2.15	L
Reactor inside diameter	0.0508	m (2 in)
Reactor length	1.06	m
Assumed run time	8	h
Volume of feed tank (85% formic acid)	10554	L

The catalyst cost would be decreased significantly if we could use a non-noble metal (possibly in a larger reactor) or if we could deploy the gold more frugally (e.g., fractional exposure higher than 25% or a shell@core architecture using a non-noble metal for the core). The calculation illustrated in Table 2 assumes a conversion 98% at 436 K, extrapolated using the apparent

activation energy from data measured at 406 K and 10 bar pressure. Operation at higher temperature should be possible to increase the conversion but we have not yet probed that sort of operational tuning.

Gas separations.

Because the molecular weights of H₂ and CO₂ are so different we first tried a separations method based on their different rates of Knudsen diffusion through a nanoporous material. The literature shows that separation factors as high as 80 can be achieved by differential diffusion through nanoporous ceramics.⁵ However the ceramics are susceptible to degradation when exposed to moisture and, likely, residual formic acid. Therefore, we resorted to a cylindrical metal filter (Figure 8). The manufacturer (Graver) promised 20 nm pores through a membrane that could withstand a pressure difference of 150 bar. The filter was connected to a source of test gas and a back pressure regulator that permitted varying the pressure upstream of the filter. Because of the long lead time needed to source the device and obtain approval for its operation in our laboratory at the end of the last reporting period we had only acquired one preliminary measurement, which showed a separation factor (of only 1.0).

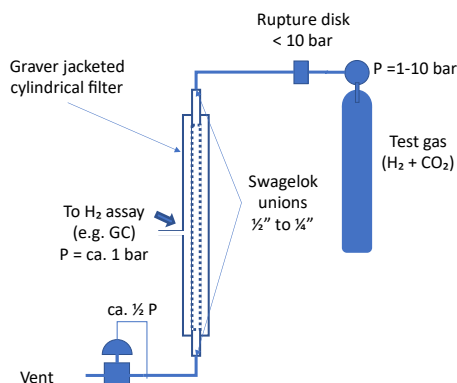


Figure 8. Schematic of metal membrane Knudsen separator. Arrow points at the join between the shell and the outlet



Figure 9. Photograph of separator as constructed. Arrow points at the join between the shell and the outlet.

As anticipated from the literature,⁵ our initial tests with a dry, equimolar mixture of H₂+CO₂ showed no separation (Separation factor = $[P_{H_2out}/P_{CO_2out}]/[P_{H_2in}/P_{CO_2in}] = 1$). The same literature report indicates that a much larger separation factor, S_f, can be attained with a moist mixture of the gases. Our very preliminary results directionally agree (Table 2) but when we outfitted the filter with a water saturator and heating tape to humidify the test stream, and keep the moisture from condensing, we found no improvement in the separation factor.

Table 3. Preliminary separation factors obtained with the ceramic-coated filter

Feed	S _f
Dry H ₂ + CO ₂	1.0
Slightly humidified H ₂ + CO ₂	1.04
Well humidified H ₂ + CO ₂	1.04

Our industrial partner, OCOChem, had arranged for us to receive a polymeric membrane separator manufactured by Sumitomo Chemical (Figure 10), which promised a much higher separation factor. By the end of the project, we had tested that device, using a 50:50 test

mixture of H₂ and CO₂, but could not measure any flow of hydrogen through the system at the tested pressure difference (5 bar).

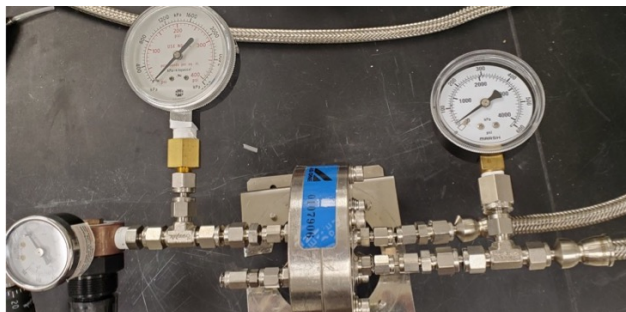


Figure 10. Sumitomo membrane test assembly

Overall process

We used ChemCad to estimate heat and mass flows through process representing all the operations of the lab scale reactor (Figure 10).

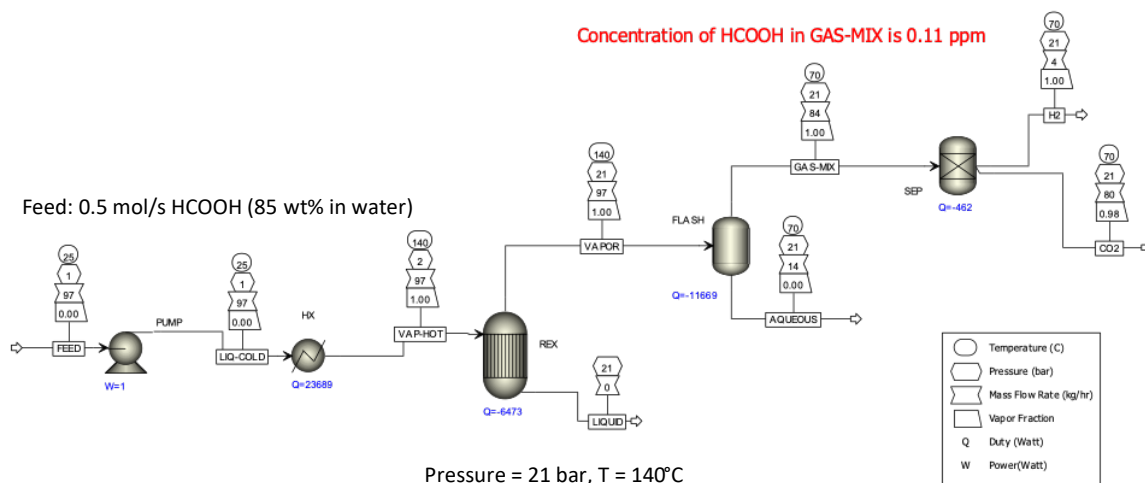


Figure 11. Process flow diagram for dehydrogenating formic acid at elevated pressure

Opportunities for process intensification by combining unit operations are evident from the diagram. For example, recuperating the heat of the reaction (-6.5 kW for feed rate of 0.5 mol HCOOH/s) and the heat of condensation (-11.7 kW) could supply a significant fraction of the heat of vaporization (+23.7 kW) but would require an efficient heat exchanger. At startup, the heat of vaporization would need to be supplied by an auxiliary power supply or heater. At steady state, the unrecovered difference between the exothermic and endothermic processes (>5.5 kW) would have to come either from a utility or from a parasitic load on the electricity produced by the fuel cell. For reference, at 50% efficiency, electrochemical combustion of 0.5 mol/s of H₂ would produce 58 kW of power ($=0.5 \text{ mol}_{\text{H}_2}/\text{s} \times 2 \text{ mol } e^- / \text{mol}_{\text{H}_2} \times 96486 \text{ Coul/mol} \times 50\% \times 1.23 \text{ V}$), so the parasitic load would amount to at least 10% of the produced power.

Summary

The project did advance readiness level of the formic acid decomposition reactor to produce a high-pressure mixture of hydrogen and carbon dioxide, containing negligible carbon monoxide. However, that gas could not be tested in a fuel cell because we could not identify a way to passively remove the carbon dioxide to the very low levels that would preclude generating CO at the anode (platinum group metals are good catalysts for the hydrogenation of carbon dioxide, i.e., reverse water gas shift reaction).

Plans for future work

Our industrial partner, OCOChem has initiated discussions with an engineering design, procurement and construction company to scale up the bench reactor described above to operation sufficient to feed a 10 kW fuel cell. OCOChem has also initiated discussions with a fuel cell supplier in anticipation of receiving follow-on funding to continue this work to demonstration scale.

We will continue to participate in business development conversations arranged by OCOChem to telescope the anticipated success of this technology. Proposals related to this project have been submitted to State of Washington Clean Energy Fund and to the State of Washington Department of Commerce through the Maritime Blue consortium. As part of that business development, we described this project in an invited, virtual presentation at the upcoming Canadian Chemical Engineering Conference (24-27 October, Montreal). That presentation has now been published.²

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