GINERELX
Giner ELX, Inc., 89 Rumford Ave, Newton, Ma. 02466

2020 DOE Hydrogen & Fuel Cells Program Review Presentation

ANODE - BOOSTED ELECTROLYSIS

PI: Monjid Hamdan
VP of Engineering

Giner ELX, Inc.
89 Rumford Ave.
Newton, Ma. 02466

Project ID: TA031

Overview

Timeline

- **Project Start:** Jan. 1, 2019
- **Project End:** Dec. 31, 2020
- **Percent Complete:** 45%

Budget

- **Total Project Budget: $2.20MM**
  - **Total Federal Share:** $1.74MM
  - **Total Recipient Share:** $0.46MM
  - **Total DOE Funds Spent*:** $0.8 MM

* As of 03/31/19

Technical Barriers (H2@Scale)

- Renewable H_2 transportation fuel pathway challenged by:
  - Capital costs, reliability, energy consumption, and footprint

Characteristics	Units	2018 Status	2022-25[1] Targets
H_2 Cost (product, delivery, comp.)	$/gge	13-16	7
Energy Consumption	kWh/kg	7	-
Station footprint	ft^2	18,000	10,800 (40% reduction)

[1] Target for the delivered cost of hydrogen generated from renewable feedstocks of $7/gge by 2025 and a 40% reduction in station footprint from the current baseline by 2022. DE-FOA-0001874 FY18 Hydrogen and Fuel Cell RD Funding Opportunity Announcement, Topic 2A, pg. 13

Partners

- **Pacific Northwest National Laboratory (National Lab)**
  Robert Weber, Ph.D., Jamie Holladay, Ph.D.
  – *Catalyst Synthesis, Characterization, Testing & Validation*
- **Oberon Fuels, Inc. (Industry)**
  Elliot Hicks, CEO Oberon Fuels, Inc.
  – *DME Pilot Plant, Technology Implementation & Validation*
- **Giner ELX, Inc. (Industry)**
  – *Electrolyzer Stack & System*

Relevance

Overall Project Objectives

- Electrolysis of Organic Anolytes
    - Hydrogen production for DME Fuel
    - Hydrogen fuel for use by FCEVs
- Wastewater Processing : Purification of non-potable water
- Improved Efficiency: Lower power requirements than water electrolysis
    - Energy to produce hydrogen via electrolysis is reduced by > 50% as compared to water electrolysis while simultaneously oxidizing the organic compounds in the waste stream

FY20 Objectives

- Develop catalysts/membrane for use in organic electrolysis to improve efficiency, cost, and durability in organic electrolysis
    - Demonstrate cell performance of ≤ 0.8V per cell at a current density of ≥300 mA/cm² (i.e., Operating at a cell potential that is 50% less than a conventional electrolysis cell)

Impact

- Successful deployment of an “Anode-Boosted” Electrolyzer would reduce the amount of energy required to produce hydrogen (via electrolysis) by 50% while simultaneously oxidizing the organic compounds from an adjacent waste stream (Wastewater Purification)

An Oberon DME Fuel Production and Distribution Facility

Synthetic fuel production from waste hydrocarbon feedstock while leveraging the existing infrastructure of the oil & gas industry

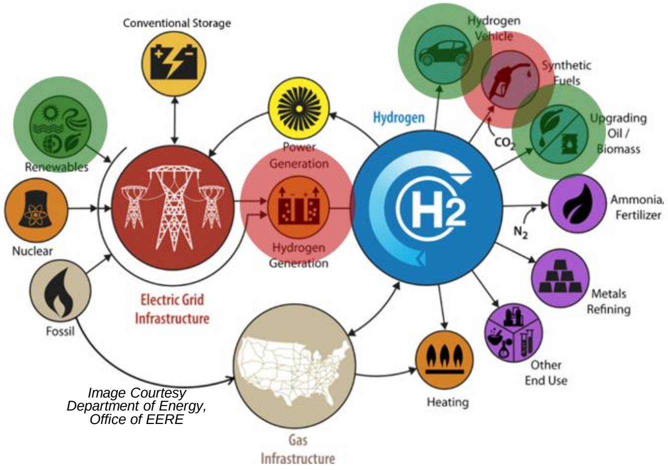
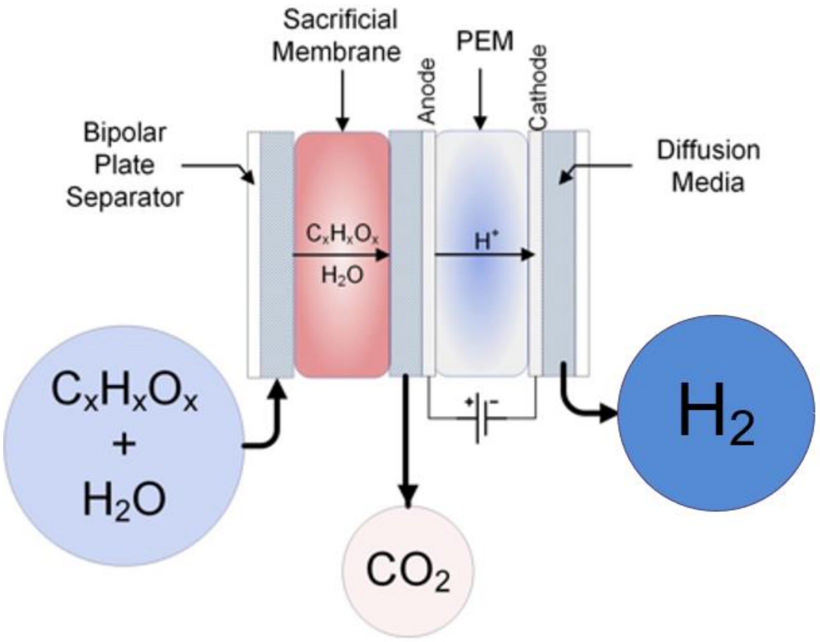


Image Courtesy Department of Energy, Office of EERE

🔴 Anode-Boosted Project
🟢 Future Considerations

Anode-Boosted Electrolysis Background

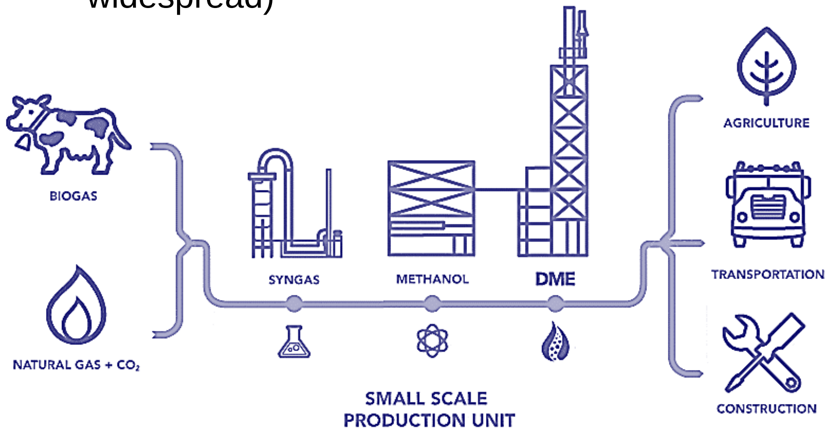


Anode-Boosted Electrolyzer (Repeating Cell unit)

- Organic anolyte transported across sacrificial membrane(s)
- Organic electrochemically decomposed to produce hydrogen
- CO_2 neutral process (closed carbon cycle)

Anode-Boosted Related Benefits in DME Processes

- Dimethyl Ether (DME), Oberon Process
  - Low-cost, low-carbon, zero-soot alternative to diesel
  - Reduces greenhouse gases by 68-101% over diesel
  - First biogas-based fuel approved under the US EPA's Renewable Fuels Standard
  - Liquid under moderate pressure, eliminates need for high-pressure containers
  - Can be used to upgrade gasoline or as a hydrogen carrier (when FCEVs are more widespread)



Current Oberon DME fuel production process

- Hydrogen generated is incorporation into hydrogen-rich fuels for internal combustion engines (DME)
- Syngas is deficient in hydrogen, requires renewable hydrogen sources

Approach: Program Overview

Hydrogen generated from renewable feedstocks of <$7/gge

Catalyst & Membrane Optimization

- Catalytic anodes: Complete synthesis and fabrication for use in Anode-Boosted electrolyzers
- Membranes: Develop membranes for use with organic containing anolytes. Demonstrate a minimum of 200 hours of operation without membrane fouling
- Performance: Demonstrate electrolysis of organic containing anolytes at a cell voltage of ≤ 0.8V (at ≥ 300 mA/cm²)

BP 1

Scale-up

- Scale-up select anode catalyst for use in Anode-Boosted electrolyzer. Develop batch catalyst process
- Scale-up select membrane. Fabricate minimum of 30 membranes with an active area of 300 cm²

Demo

- Integration in DME Process
  - ☐ Prototype Demonstrate Anode Boosted flow electrolyzer that produces 80 sLPM of H2 (10 kg/day)
  - ☐ Over target: system capable of following the dispatching of renewably sourced electricity for one week.

BP 2

Approach: BP1 Tasks & Milestone Progress

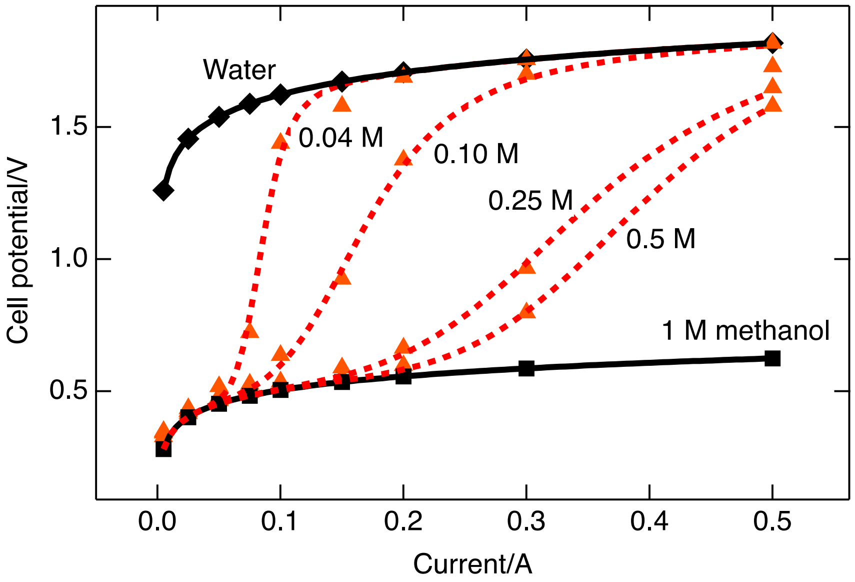
Task No.	Task Title	Mile-stone	Milestone Description (Go/No-Go Decision Criteria)	Progress Notes	Percent Complete
1	Site sampling and analysis	M1.1	Develop list of organic analytes and industrial processes that are applicable for use with anode-boosted electrolysis	Winter sampling completed. Summer sampling completed.	100%
2	Anode catalyst synthesis, characterization and testing	M1.2	Complete synthesis and fabrication of catalytic anodes. Synthesize anode catalyst and electrode structures for use in Anode-Boosted electrolyzers	Synthesizing of anode catalyst and electrode structures completed	100%
3	Membrane selection for PEM-based electrolyzer	M1.3	Develop membranes for use in organic containing analytes. Demonstrate a minimum of 200 hours of operation without membrane fouling	PFSA currently in use. Upcoming: sPEEK	100%
4	Preparation and Testing of Membrane Electrode Assemblies	M1.4	Demonstrate performance of Anode-Boosted electrolyzer to oxidize an organic containing analytes at a cell voltage of ≤ 0.8V	Test Stand: 100% complete Preliminary AB stack Design complete (Active area of 50 cm^2 for catalyst & membrane evaluations)	100%

Go/No-Go Decision Y1	**Demonstrate Anode-Boosted Electrolyzer cell performance of ≤ 0.8V per cell at a current density of ≥300 mA/cm^2** (Operating at a cell potential that is 50% less than a conventional electrolysis cells).	Demonstrated cell performance of **0.749V/cell at a Current Density of ~1A/cm^2**	✓

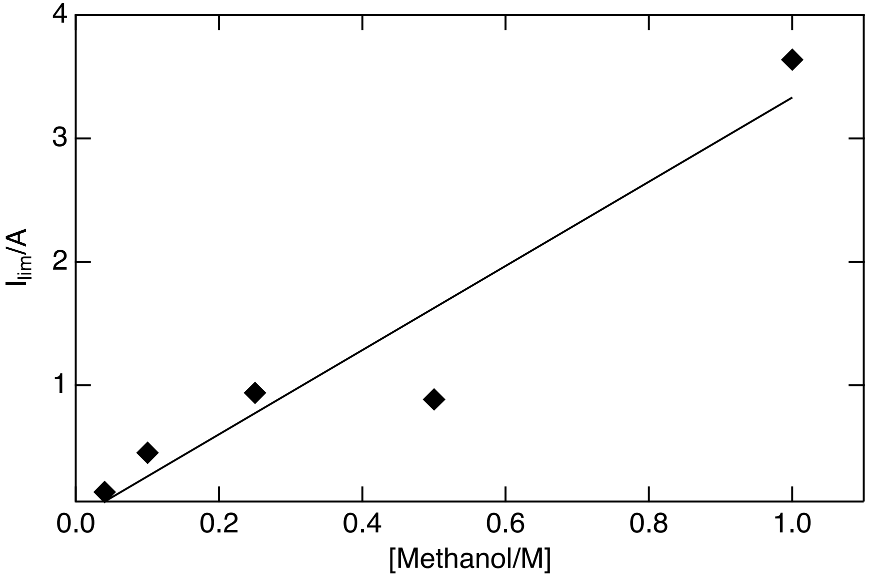
Progress- Site Sampling and Analysis (PNNL)

- Representative anolyte samples evaluated in anode-boosted cell
  - Methanol concentration level: 0.04 to 1.0M (0.16 to 4.1 % by volume)
  - Minimum chemical oxygen demand (COD) of waster water near Oberon DME plant measured at 1900 mg/L (0.16% Methanol)
  - Methanol electrolysis is current limited at lower concentrations

Anode boosting electrolysis of various Methanol concentrations



Limiting current density for the electrolysis of the dilute solutions of methanol



Progress – Catalyst Synthesis, Characterization, and Evaluation (PNNL)

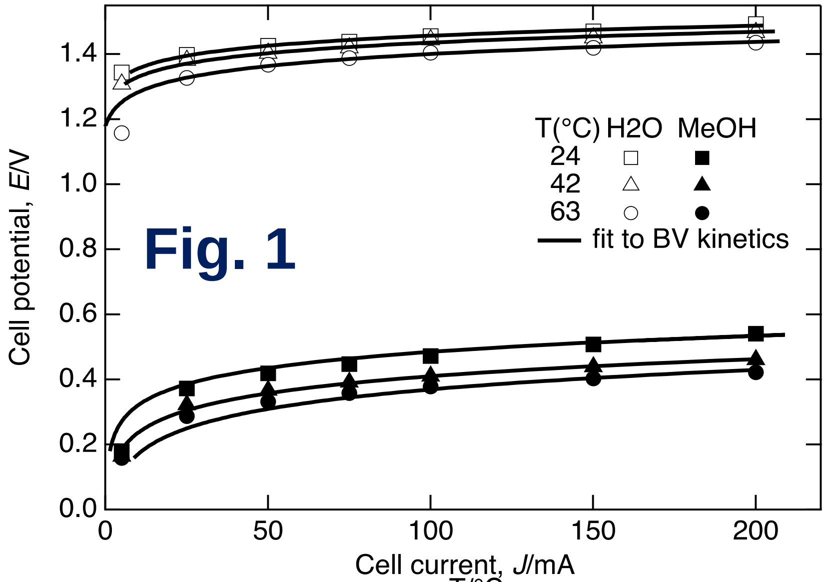


Fig. 1

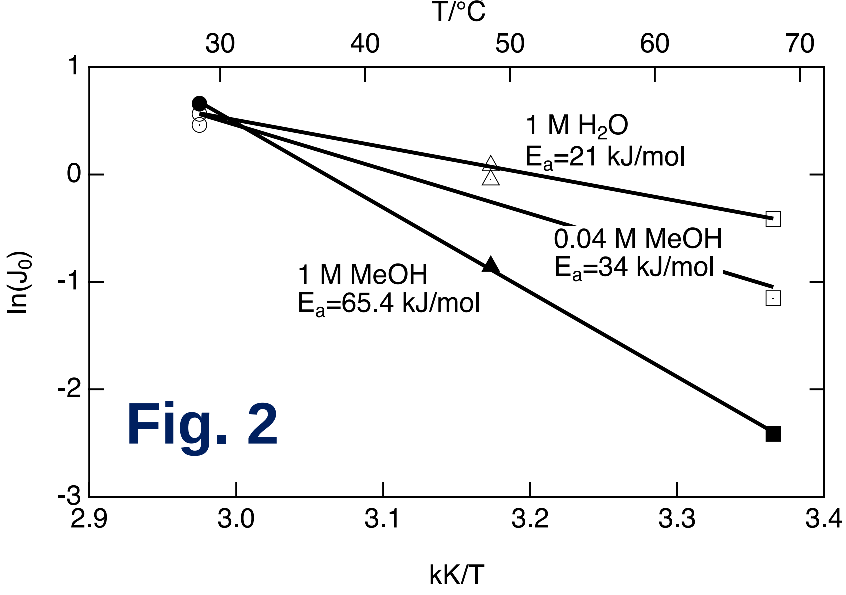


Fig. 2

Demonstrated improved performance at elevated temperature, increased methanol concentration, and enhanced catalyst architectures (& supports)

- **Fig. 1** - Effect of temperature on the electrolysis of pure water and 1 M methanol anolytes at three temperatures
- **Fig. 2** - Arrhenius graph comparing the effect of temperature on activation energy (E_a) and Current (J_o) for water with that of dilute methanol (0.04 M and 1.0 M)
- **Fig 3** - Comparison of a commercial anode with one made by supporting the catalyst on a carbon felt for the electrolysis of 1.0 M methanol

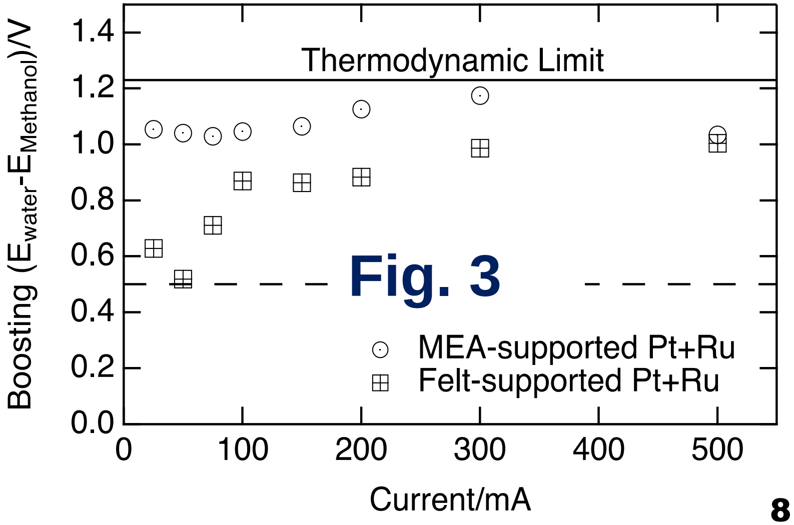


Fig. 3

Progress – Anode-Boosted Stack Evaluation

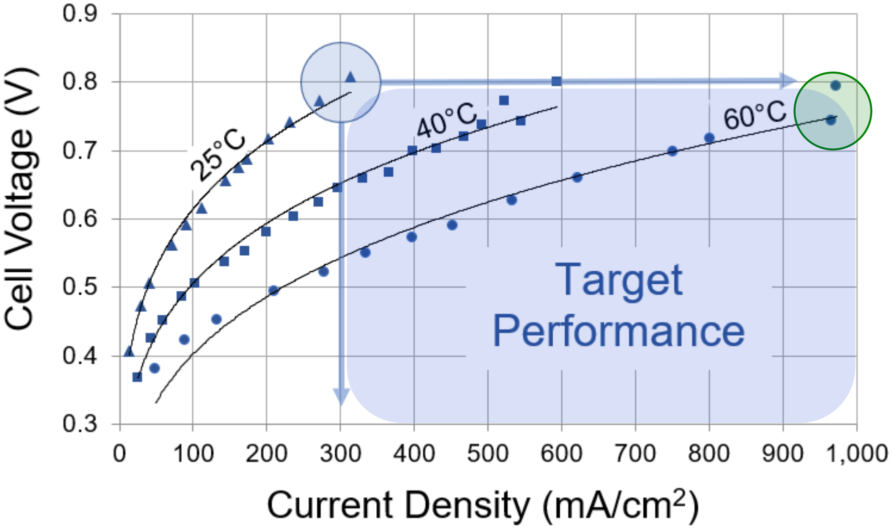


Fig. 1 Polarization Scan at various temperatures, 10% Methanol

Milestone Target Achieved

- Target: Demonstrate Anode-Boosted Electrolyzer cell performance of ≤ 0.8V/cell at a current density of ≥ 300 mA/cm^2) ○
  - Performance Achieved:

    0.749 V/cell at 950 mA/cm^2 ○
  - **Fig. 1** - Improved activity at higher temperature and concentration
  - **Fig. 2** - Ideal conditions: 4-10% methanol at 40-60^{o}C
  - **Fig.3** – Reduction in current density as organic anolyte is depleted

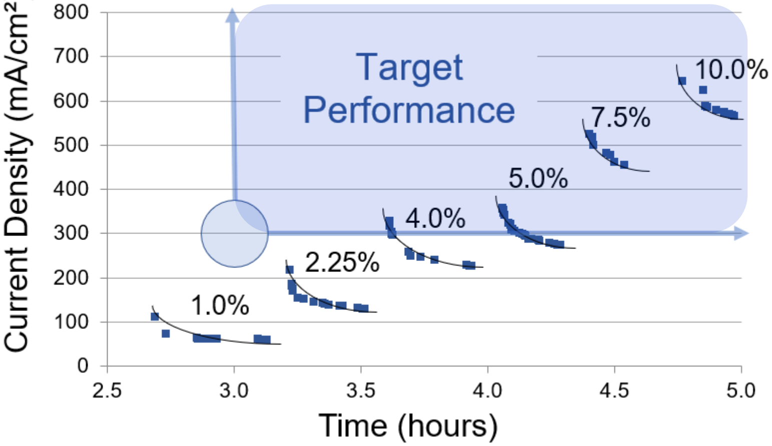


Fig. 2 Constant voltage operation (0.8V/cell), 1-10% Methanol, 45^{o}C

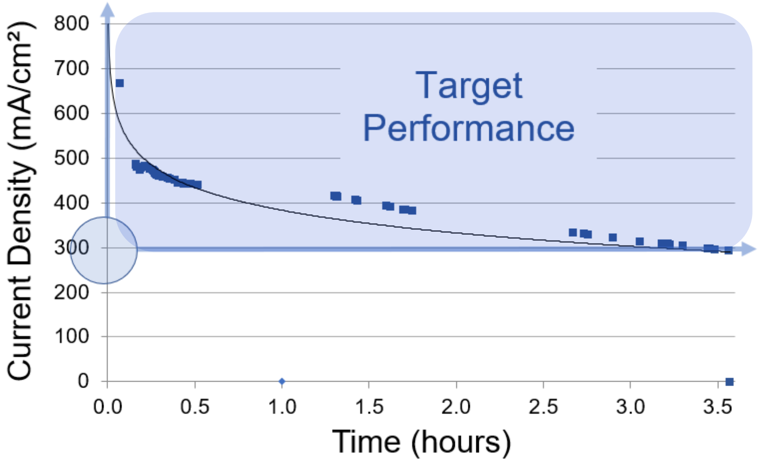
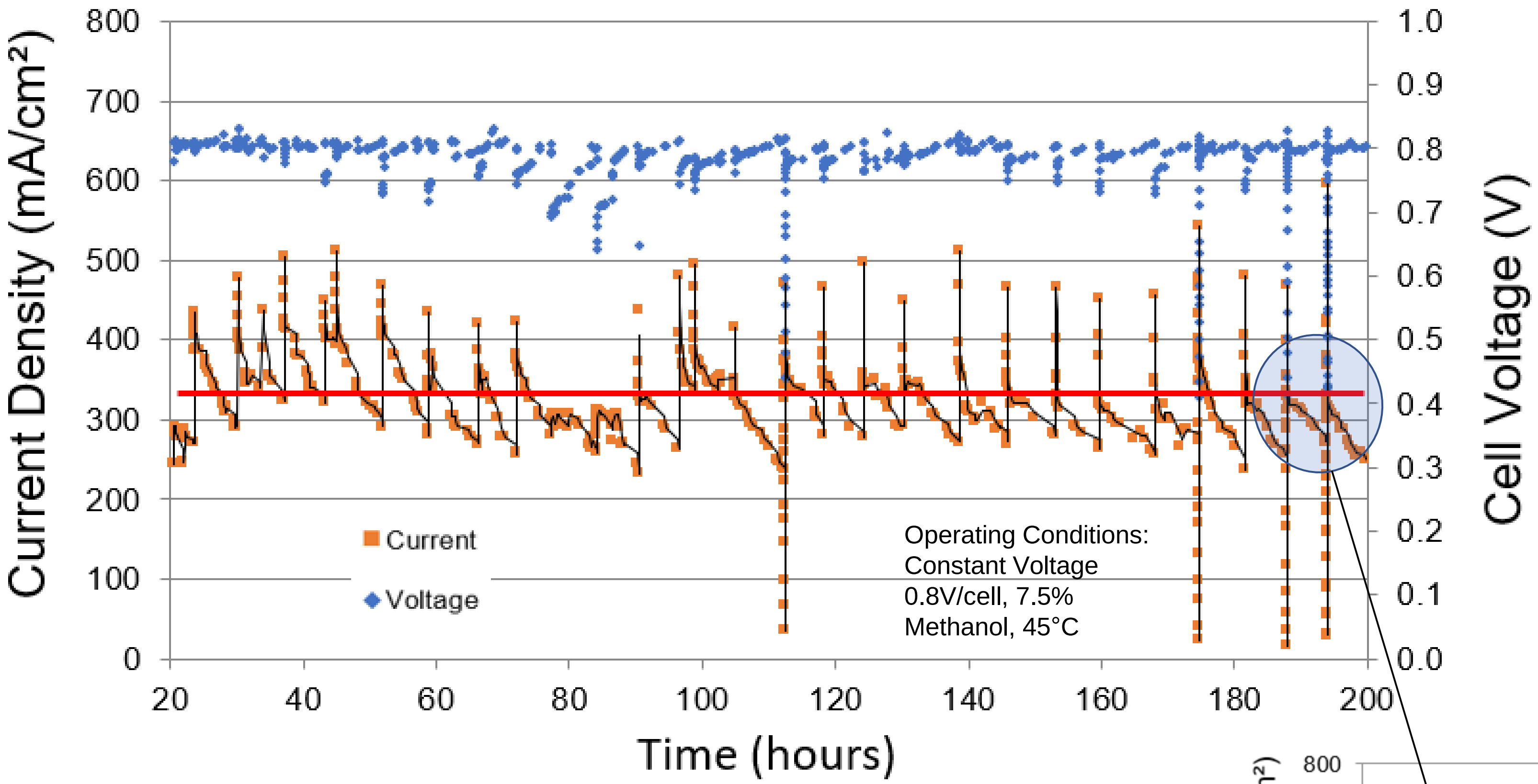
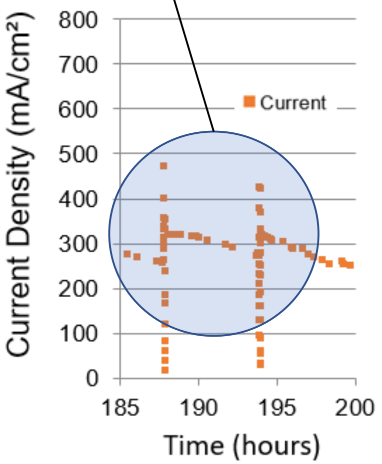


Fig. 3 Constant Voltage Operation (0.8V/cell), 10% Methanol, 40^{o}C

Progress – Membrane Lifetime/Membrane Fouling



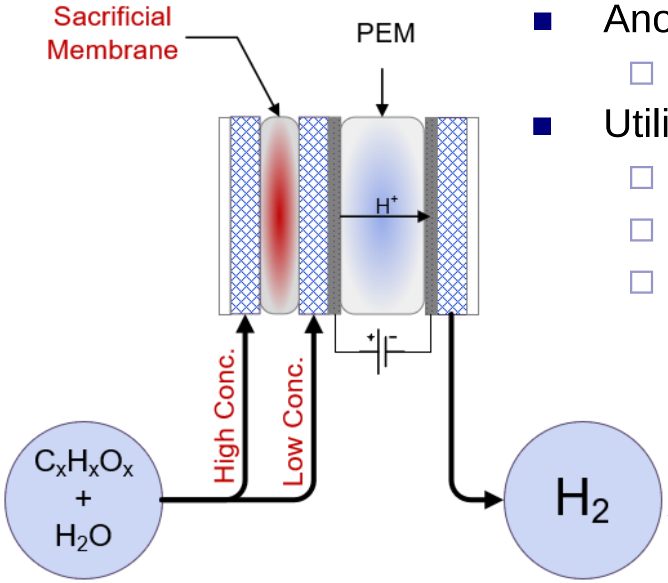
Operating Conditions:
Constant Voltage
0.8V/cell, 7.5%
Methanol, 45°C



Milestone Target Achieved

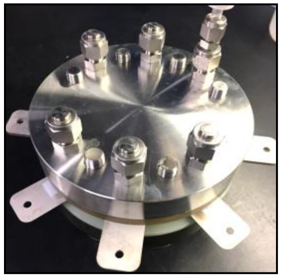
- Target: Develop MEAs for use in organic containing analytes Demonstrate a minimum of 200 hours of operation without membrane fouling
  - ☐ Membrane operated for > 200 hours
    - Daily on/off cycle, methanol solution replenished daily
    - 0.8V/cell, 7.5% Methanol, 45°C
  - ☐ Stable Performance: ≥ 300 mA/cm² at start-up, Current drops as methanol is depleted

Stack &Test Stand /Feasibility Studies



Anode-Boosted Stack

- Anode-boosted 6-Port stack design completed/assembled
  - ☐ Active area of 50 cm². Future design will be scaled-up to 300 cm²
- Utilizes dual-membrane cell architecture
  - ☐ Stack can accommodate low to high organic concentrations:
  - ☐ Organic anolyte concentrations ≤ 1.0 M, single membrane required
  - ☐ Organic anolyte concentrations > 1.0 M, dual membrane required
    - Secondary membrane imbibed with additive to mitigate swelling

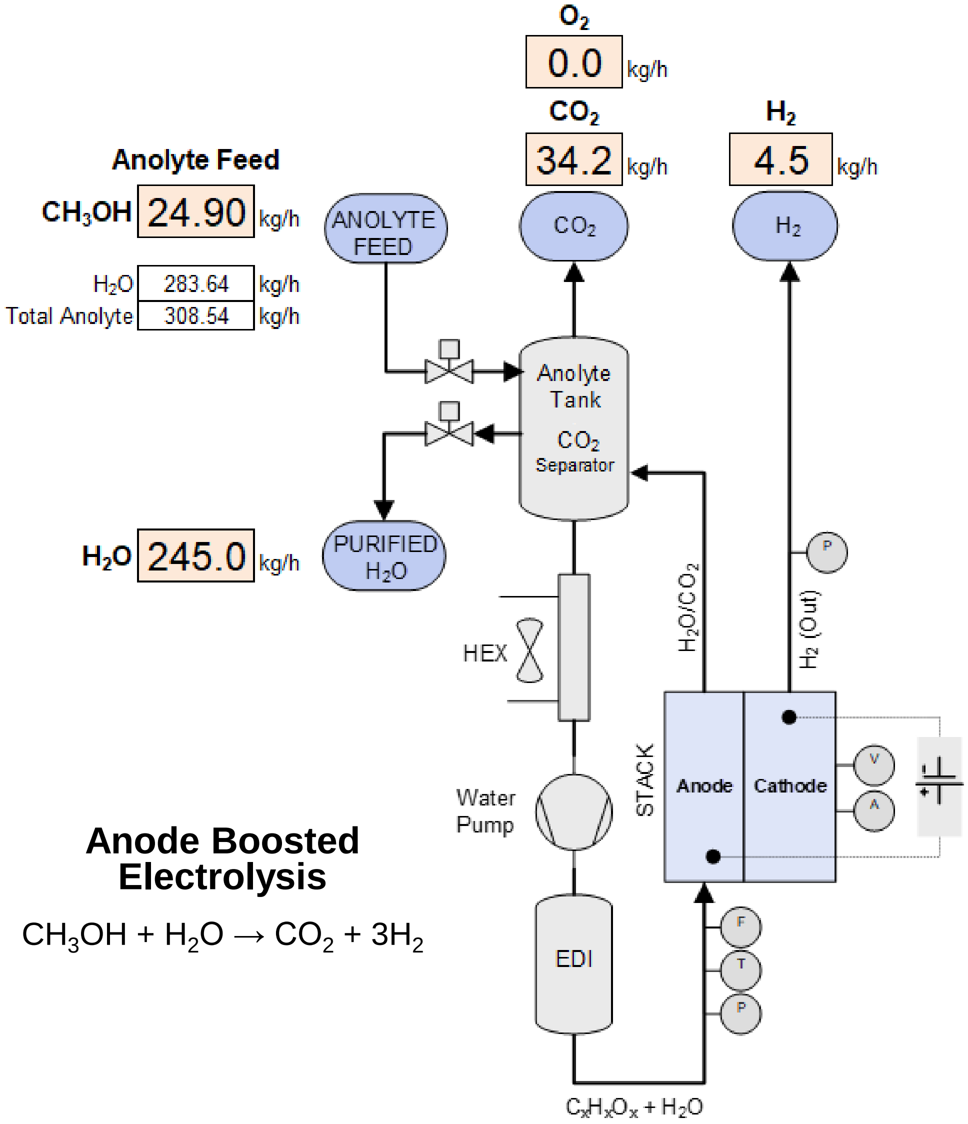


Anode-Boosted Test Stand

- Anode-Boosted electrolyzer test stand completed/operational
- Designed to operate prototype and full- and pilot-scale Anode-Boosted electrolyzer stacks
- System Feasibility Studies:
  - ☐ Electrolysis reaction kinetics
  - ☐ Destruction of the organic impurities
  - ☐ Durability of the catalyst/membrane
    - Membrane analysis: detect leaching, fouling, oxidative degradation

Process Flow –

Anode Boosted Electrolysis



Anode Boosted Electrolysis

$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$

- Electrical consumption: **21 kWh$_e$/kg-H$_2$**
  - > 56% electrical energy saving as compared to water electrolysis: 21 vs. 48 kWh$_e$/kg-H$_2$
- Faradaic losses (CH_3OH crossover)
  - Increases with temperature and concentration
  - Diminishes at higher operating current densities
  - Crossover current density, ~50-100 mA/cm²
    - Membrane dependent
- Ideal operating conditions: 50-60°C, 2M CH_3OH, 0.5 to 0.95 A/cm²
- PFD based on 100 kW stack

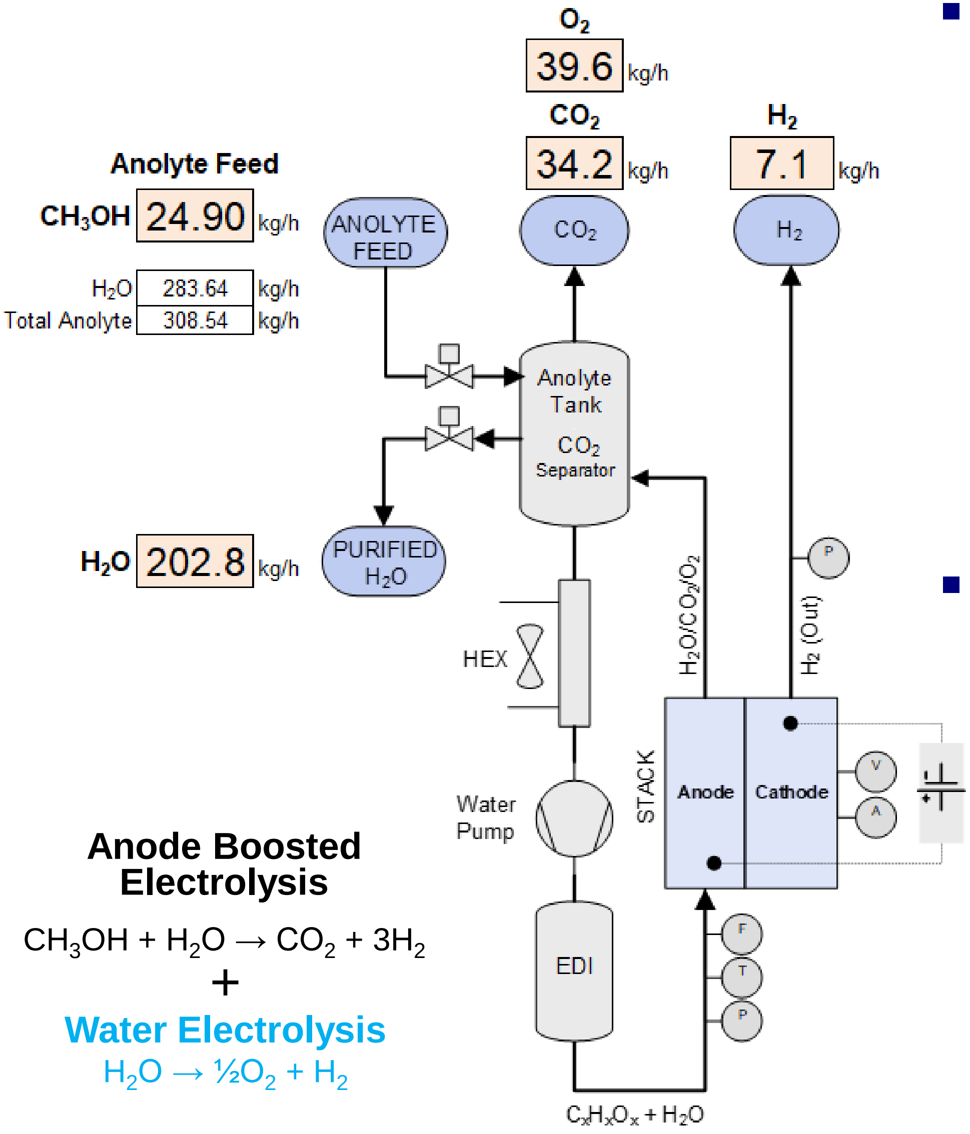
Energy Consumption

Energy	21.0	kWh/kg-H$_2$
Power	94	kW
Cell Voltage	0.75	Volts/cell
No. of Cells	100	Cells
Active Area	1250	cm²
Current Density	1.0	A/cm²
Current	1250	Amps
xover CD	0.052	A/cm²

Current Density	Cell Voltage	CH$_3$OH x-Over	Electrical Energy
A/cm²	V	mA/cm²	kWh$_e$/kg-H$_2$
0.00	0.00	195	-
0.25	0.51	98	22.3
0.50	0.62	80	19.6
0.75	0.70	72	20.5
1.00	0.75	52	21.0
>1.0	1.48+	-	-

Process Flow –

Anode Boosted Electrolysis + Water Electrolysis



Anode Boosted Electrolysis

$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$

+

Water Electrolysis

$H_2O \rightarrow ½O_2 + H_2$

- Anode-Boosted Electrolysis can be operated in water electrolysis mode if/when additional hydrogen production is required for the DME process:
  - Electrolysis of CH_3OH and water at potentials >1.5V/cell
  - Electrical energy estimate for 'Mixed Electrolysis': 46.5 $kWh_e/kg\text{-}H_2$ due to higher cell voltage for water electrolysis
  - Efficiency improvement to 28.0 $kWh_e/kg\text{-}H_2$ with 'mixed electrolysis' via pulsing stack or use of two separate stacks
- O_2 Production: 39.6 kg/h as compared to 55.7 kg/h with straight water electrolysis

Energy Consumption

Energy 46.5 $kWh/kg\text{-}H_2$

Power	328	kW
Cell Voltage	1.75	Volts/cell
No. of Cells	100	Cells
Active Area	1250	cm²
Current Density	1.5	A/cm²
Current	1875	Amps
xover CD	0.03	A/cm²

Technoeconomic Analysis

Total Cost of H_2

H_2 Cost Contribution	Current Status ($/kg)	
	DME Fuel	H_2 Fuel
Capital Costs[1]	1.95	1.30
Feedstock Costs[2]	0.81	1.96
Fixed O&M	0.70	0.70
Variable Costs	0.02	0.02
Total Hydrogen Production Cost	3.48	3.98
Delivery (CSD)[3]	0.00	2.24
Total H_2 Cost	3.48	6.22

Total Cost of H_2 in DME Fuel

Total Hydrogen Production Cost	3.48	3.98
Delivery (CSD)	Not required for DME	
Total H_2 Cost per kg of DME	0.45	0.52

[1] 20 year lifetime and design Capacity: 100 kg-H_2/hr, assumes large scale production (500 units/yr). Larger stacks (higher cell count) required for anode-boosted stacks operating at 1 A/cm² vs. 1.5A/cm²+ for water electrolysis stack. [2] Anode-Boosted operation at 21 KWh/kg-H2, and water electrolysis operation at 50.5 kWh/kg, electrical cost of $0.039/kWh. [3] Compression cost based on 40 bar output. DME process does not require high-pressure H_2, FCEV; 900 bar

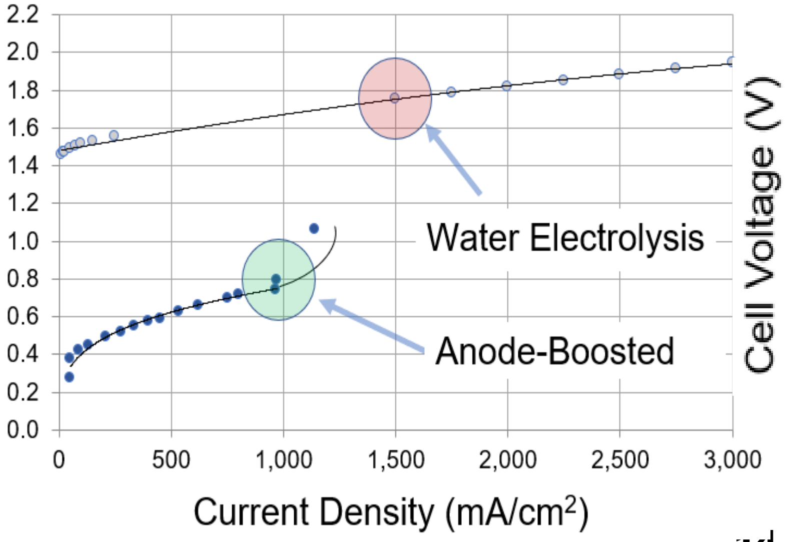
Demonstration path to achieve
< $7/kg-$H_2$ with renewable feedstock

CapEx[4]

	Anode Boost	Water Electrolysis
H_2 prod (kg/h)	100	100
# of Cells*	2100	1400
CD (A/cm²)	<1.0	≥1.5
Energy (kWh_e/kg)	21	≤50.5
H_2 prod (kg/h)	100	100
Catalyst	Pt/Ru	Pt/Ir

[4] Costs are based on large active area stacks (1250 cm²)

OpEx



Collaborations/Acknowledgements

Giner ELX, Inc. -Monjid Hamdan -Prime	Industry	Electrolyzer stack/system engineering, prototype development and deployment
Oberon Fuels -Elliot Hicks, CEO Oberon Fuels, Inc -Subcontractor	Industry	Hydrogen generation for incorporation into hydrogen-rich fuels for internal combustion engines (DME)
Pacific Northwest National Laboratory (PNNL) -Robert Weber, Ph.D., -Jamie Holladay, Ph.D. -Subcontractor	National Lab	■ Catalyst Development for Anode-Boosted Electrolysis □ Analyze/Characterize samples using standard methods (COD, elemental analysis, pH) ■ Synthesize/Procure catalyst powders (PNNL) □ Prepare anode catalyst powders consisting of mixed metal oxides □ Procure catalyst: mixed metal oxides & boron-doped diamond, boron-doped nanotubes, and nitrogen-doped nanotubes ■ Fabricate electrode structures (GINER/PNNL)

Department of Energy- DOE Fuel Cell Technologies Office (FCTO)

-Michael Hahn, DOE Technology Manager
-Dr. Sunita Satyapal

Summary

- **BP1 Milestone Achieved & Exceeded**:
  - Objective: Achieve cell performance of ≤ 0.8V per cell at a current density of ≥300 mA/cm²
    - Achieved 3x current density: **0.8V** at **950 mA/cm²**
- **Membrane/Catalyst**
  - Successfully engineered membranes that reduce fouling (and swelling) when used with organic-anolytes
  - PNNL completed synthesis of anode catalyst on supported structures for use with organic anolytes
    - Demonstrated 20% improvement in cell voltage over conventional catalyst structures
- **Stack**
  - Anode-Boosted stack design complete
    - Active area of 50 cm², to be scaled to 300 cm² for Oberon process
    - Stack design enables electrolysis of organic anolytes with wide concentration ranges, that can accommodate current-limiting conditions of anode-boosted electrochemical reactions
- **System**
  - Test Stand: 100% complete and operational
    - Completed catalyst & membrane evaluations, reaction kinetics
    - Detailed process flow diagrams
      - Used to model prototype system at Oberon site
- **Techno-economic Feasibility Studies**
  - Estimated cost of H_2 (levelized) from renewable feedstocks at \$6.22/kg-H_2 (Target: \$7/gge by 2025)
    - Demonstrated path to further reduce with improved efficiency of PNNL catalyst

Future Plans & Challenges (FY2020-21)

Future Plans*

- **Membrane/Catalyst:**
  - Implement use of PNNL’s supported (carbon felt) catalyst structure to further improve cell performance
  - Complete development and demonstration of alternative membranes to reduce permeation, improve efficiency
  - Scale-up select anode catalyst, membrane, and stack hardware (to 300 cm^2) for use in 80 sLPM-H_2 (10 kg/day) Anode-Boosted electrolyzer
- **System**:
  - Demonstrate pilot-scale Anode-Boosted electrolyzer with cell potential <50% than conventional electrolysis
  - Demonstrate system capability of following the dispatching of renewably sourced electricity for one week
- **Complete Techno-economic Feasibility Studies**
  - Demonstration path to achieve < \$5/kg-H_2 (levelized cost)

Future Challenges

- Cost of Ru has increased significantly (in small quantities).
  - Replace with carbon-felt supported Ru developed at PNNL (equitable cost). This will require additional validation studies

*Any proposed future work is subject to change based on funding levels

Responses to Previous Year Reviewers' Comments

This project was not reviewed last year

Publications and Presentations

Publications/presentations include:

- *Andrews, E. M.; Egbert, J. D.; Sanyal, U.; Holladay, J. D.; Weber, R. S. Energy & Fuels, Anode-Boosted Electrolysis in Electrochemical Upgrading of Bio-oils and in the Production of* H_2*, 2020, 34, 1162-1165, 10.1021/acs.energyfuels.9b02524.*

- *Advancements in PEM Electrolyzers and Uses in the Renewable Energy Economy*, AIChE Meeting, Orlando Fl. Nov. 11th, 2019

- *Electrolyzers as Utility Assets- Demonstration of Integrated Hydrogen Production and Consumption for Improved Utility Operations*, 2019 FCTO Program Review at Giner, Newton, MA. Sep. 25th, 2019