Facilitated Direct Liquid Fuel Cells with High Temperature Membrane Electrode Assemblies

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Project ID FC128

Overview - Program

Timeline

Project Start Date: Oct 1, 2015
Project End Date*: Dec 31, 2018
Revised End Date**: June 30, 2019

*no cost extension
** Phase II

Funded Partners

LANL (P. Zelenay, Xi Yin): catalyst synthesis and fuel cell testing during Phase I

Budget ($)

Total Funding:	1,250,000
Advent Cost Share (20%):	250,000
Federal Share (80%):	1,000,000
Total DOE funds spent*	767,000

**As of December 31, 2018

Barriers (FCTO-MYRDDP, 2014)

A. Durability: new membrane approach
B. Cost: elimination of reformer, lower PGM
C. Performance: highly active anode catalyst

Incubator program to explore new, high impact areas

Advent

Relevance

Objective: Demonstrate direct dimethyl ether (DME) oxidation at high temperature MEA significantly better than direct methanol fuel cells (DMFC)

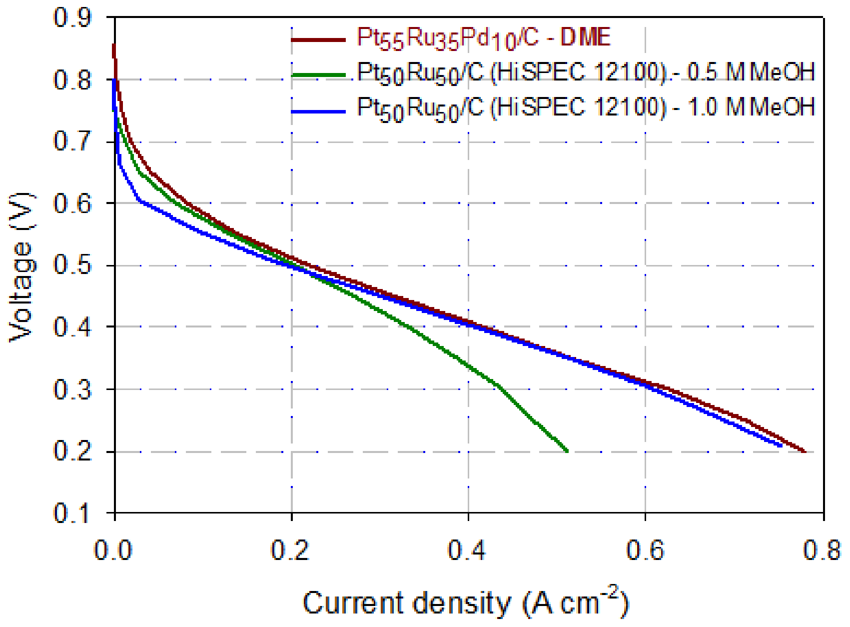
Program Targets

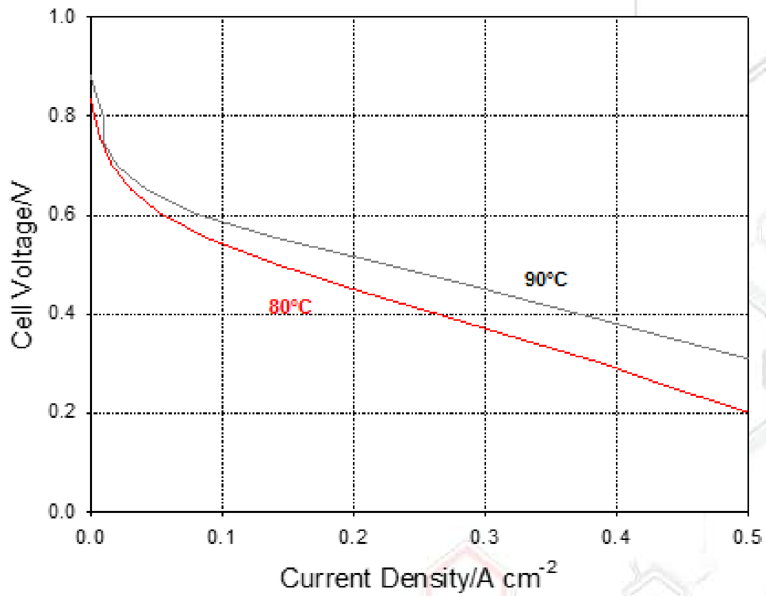
Key Performance Indicator	Current DMFC	Target Hi T Direct DME
Maximum power (>)	0.180 W/cm^2	0.270 W/cm^2
Total precious metal loading	5 mg$_{PGM}$/cm^2	3 mg$_{PGM}$/cm^2
Degradation rate	19 µV/h at a 0.2 A/cm^2	10 µV/h at a 0.2 A/cm^2
Loss in start/stop cycling	1.5 mV/cycle; cycle	0.75 mV/cycle; cycle
Anode mass-specific activity	50 A/g at 0.5 V	75 A/g at 0.5V

Benefits:

1. Carbon-neutral auxiliary power for trucks and transport (HT PEM with reformed methanol already used as battery range extenders for BEV)
2. Slightly modified diesel engines (Volvo) run with DME today
3. DME as the energy carrier from CO_2 has a projected SUE (Source to Use) of 0.285 $/kWh, under the 0.3 $/kWh target

Approach: Pd to Cleave C-O Bond





DME *vs.* methanol fuel cell performance. **Anode:** 4.0 mg_{metal} cm^{-2} PtRuPd/C (HiSPEC® 12100); DME 40 sccm, bp 26 psig; 1.8 mL/min 0.5 M or 1.0 M MeOH. **Cathode:** 2.0 mg cm^{-2} Pt/C (HiSPEC® 9100); air 100 sccm, bp 20 psig. Membrane: Nafion® 212 (DME), Nafion® 115 (MeOH); cell: 80 °C.

Temperature dependence of DME fuel cell performance. **Anode:** 4.0 mg_{metal} cm^{-2} PtRu/C (HiSPEC® 12100); DME 40 sccm, bp 26 psig. **Cathode:** 4.0 mg cm^{-2} Pt black, air 500 sccm, bp 20 psig. Membrane: Nafion® 212; cell**:** 80 °C.

High DME activity with PtRuPd/C combined with temperature sensitivity

Approach - Overview

1. Benchmark

6 mo.

- Run high temperature MEAs at LANL
- Compare Pt anode w MeOH, DME (160 °C – 180 °C)
- Use both PBI and TPS HT MEAs

By March 31, 2018

2. GDE at 5 cm^2

6-12 mo.

Go/No Go

- Make gas diffusion electrode (GDE) with PtRu, run with DME
- Compare to LANL ternary anode catalyst
- Evaluate PBI and TPS DME crossover and performance at highest obtainable T

3. Optimize at 5 cm^2

12-24 mo.

Phase II (2019)

- Optimize GDE for mass transport
- Focus on optimum catalyst alloy
- Determine baseline durability

Leverage enhanced kinetics at higher T

Approach – Milestones – Phase 2

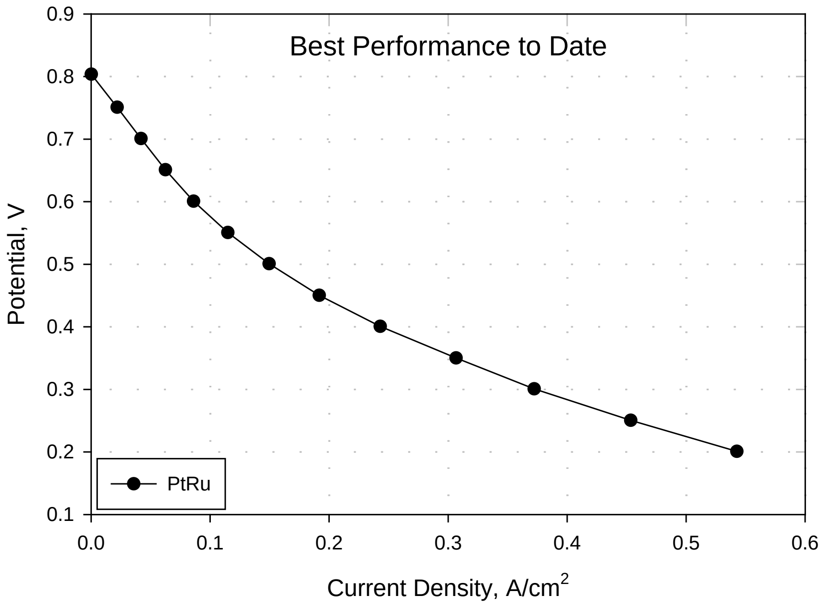
Milestones 2019

By March 31, 2019	By April 30, 2019	By June 30, 2019	Final Report
In Progress	In Progress	Pending	
M5 • Demonstrate in house test capability for 5cm² DDFC by reproducing LANL Phase I data (3x)	**M6** • Determine baseline decay at 80% max power or at 0.2A/cm² • Improve mass transport H_2 gain< 50% *vs.* DMFC	**M7** • Demonstrate <10µV/hr decay at best durability conditions and/or <1.5mV loss per off/on cycle • Demonstrate 0.270W/cm² maximum power with < 4.5 mg/cm² PGM	**Final Deliverable** • Summary report submitted

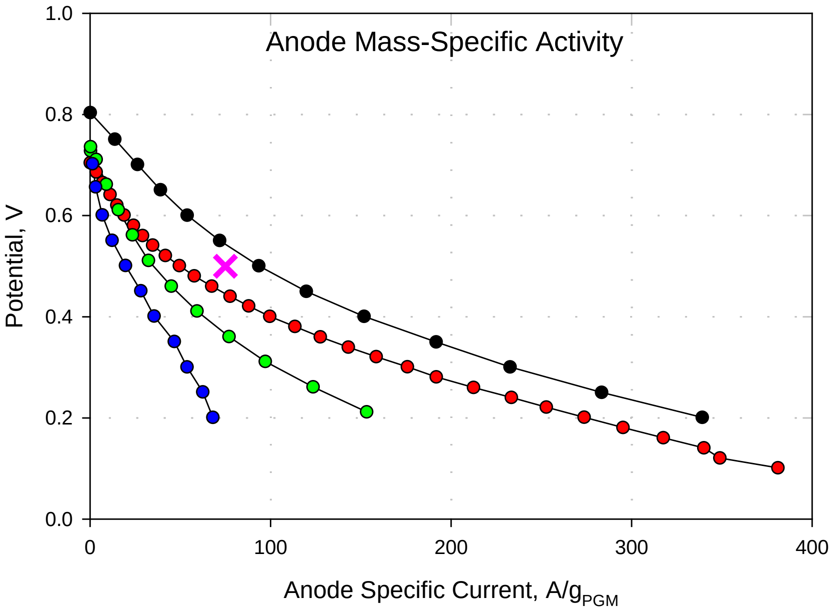
Focus on testing capability, durability, and maximum power

Accomplishments and Progress (Phase I)

Milestone 3: Anode Mass-Specific Activity



High T MEA DME fuel cell performance at 240 ºC.
Cathode: Pt-alloy/C 2.9mg/cm^2; air 500 sccm, backpressure 30 psig.
Anode: HiSPEC® 12100 PtRu/C 1.6 mg/cm^2; DME 125 sccm, DME:water = 1:3, humidified at backpressure 30 psig.
Membrane: PBI



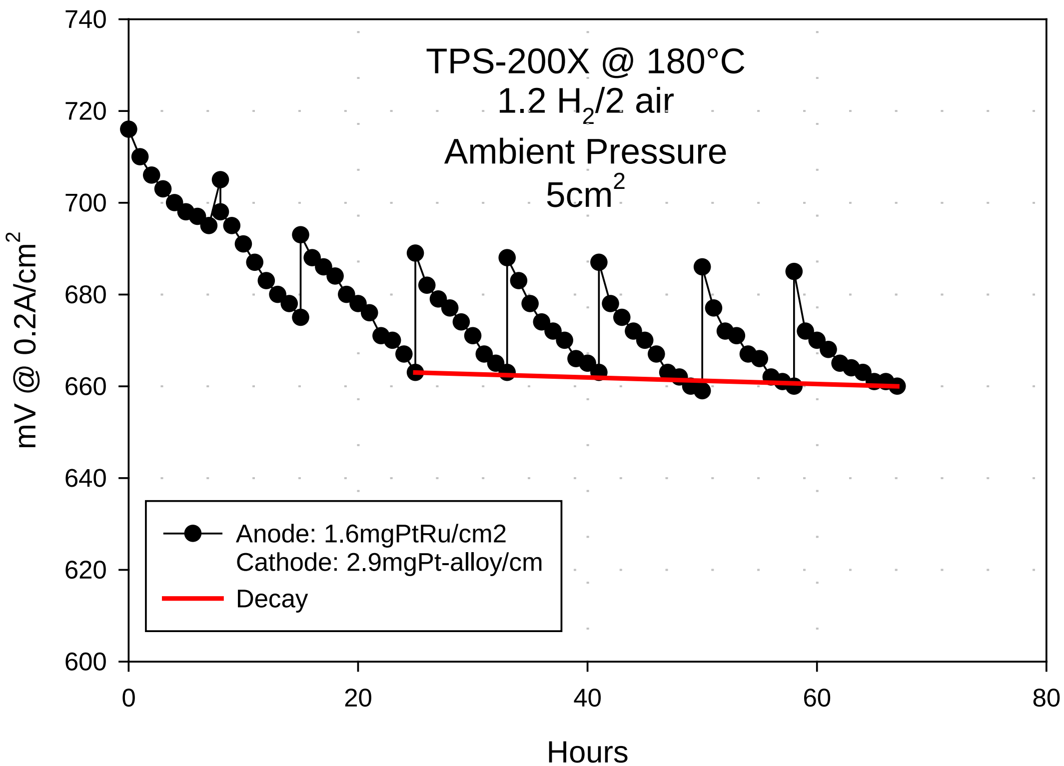
PBI-based MEA DME fuel cell performance.
Black: replot data on left as anode specific current
Red: 2017 AMR, Anode HiSPEC® 12100 PtRu/C 1.9 mg/cm^2 Cathode Pt-alloy 2.2 mg/cm^2, 3.5psig, 180°C
Green: 2016 AMR, Anode HiSPEC® 12100 PtRu/C 1.9 mg/cm^2 Cathode Pt-alloy 0.8 mg/cm^2, 3.5psig, 180°C
Blue: LANL data from prior program, DME at PtRu 80 °C, total 8 mg/cm^2 PGM; 26psig
Pink X: Program target, 75A/g @ 0.5V

Achieved go/no go

Cathode loading & temperature limited MEA performance

Accomplishments and Progress (Phase II)

Combined start/stop and durability test
Preliminary PtRu durability - test still in progress



- Off/on cycle loss 0.6mV/cycle
- With 25hr conditioning, 1 cycle = 8-9hrs @0.2A/cm^2 + 1 shutdown / startup)
- "Pseudo" degradation rate, at end of each day, 30µV/hr (slope of red line)
- Performance losses during testing are nearly 100% recoverable
  - Indicates not catalyst degradation, but need for improved phosphoric acid management in thick catalyst layers

Although preliminary and without DME, encouraging life

Response to 2018 AMR Comments

1. *Durability*
   - Several viewers noted a lack of durability data. We placed 100% focus on achieving the go/no go. Now that we exceeded that milestone and the Advent test stations will be modified to run DME vapor-feed cells, testing capacity should increase, and we should be able to evaluate preliminary durability performance. Durability is expected to be evaluated as we work on remaining milestones (H_2 gain, power density).
2. *High PGM Loading*
   - Comparing DDFC PGM loadings to PEM PGM loadings is not an apt comparison. Comparisons should rather be made to other liquid systems (DMFC). In that case, the loadings here are in line with SOA DMFC systems developed at LANL. That said, lowering the PGM loading is absolutely a target in Phase II of this project.
3. *Alternative Membrane Options (Yu Seung Kim, LANL)*
   - While this work will continue to focus primarily on TPS® and PBI-based membrane technologies, if neither of these will be sufficient to achieve the stated Phase II targets, then additional membrane materials could be evaluated. We have started discussions with Kim and sent our standard electrodes. However, while the new Kim membranes have great potential, it may not be feasible to evaluate these membranes under the shortened Phase II of this project.

Collaborations

Commercial Catalyst Company #1

- Started small scale PtRuPd catalyst
- Also cathode alloys
- Extensive know-how on catalyst alloys
- Supplier to FC industry

Commercial Catalyst Company #2

- Started small scale PtRuPd catalyst
- Several other binary catalysts designed for DME
- Extensive know-how on specialty catalyst alloys and supports
- Supplier to FC industry

University of Cincinnati

- Professor Angelopoulos (PtBi alloy for DME)

University of Padova

- Professor Vito Di Noto (PtRu and derivatives)

Significant increase in collaborations to leverage catalyst discovery

Remaining Challenges and Barriers

1. Can the activity of DME oxidation alloys be realized at temperatures conducive to membrane stability?
   - Initiated catalyst collaborations with commercial and academic specialists to leverage expertise
2. PBI has limited stability at > 200 °C
   - TPS and cross-linked TPS can operate > 200 °C. Will evaluate in phase 2

Proposed Future Work

Milestone	Target	Path
M5 (March 31 2019)	- Replicate LANL Data (3x)	- Test station modification underway
M6 (April 30 2019)	- Determine baseline decay at 80% max power or at $0.2 A/cm^2$ - Improve mass transport H_2 gain< 50% *vs.* DMFC	- Baseline H2/air durability data underway - Optimize Phosphoric Acid distribution within electrode
M7 (June 30 2019)	- Demonstrate <10µV/hr decay at best durability conditions and/or <1.5mV loss per off/on cycle - Demonstrate $0.270 W/cm^2$ maximum power with < 4.5 mg/cm^2 PGM	- Currently demonstrating <1.5mV loss per off/on cycle in preliminary data - Pending, best data to date is $0.135 W/cm^2$

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

Advent

Technology-to-Market

Advent has approached Hi T MEA customers that currently build systems based on reformed methanol

Advantage will be reduction in system cost (no reformer) and simplicity

UltraCell LLC can use 45 cm^2 scale in their current systems

- o Expressed interest and joined Advent on hardware proposals

SerEnergy (Denmark) has interest in auxiliary power for marine systems that use low emission, carbon-neutral fuels

- o Advent will need to scale to at least 165 cm^2
- o DME is “environmental diesel” and runs in slightly modified diesel engines – well aligned with marine industry

Advent has been contacted by an Israeli drone company

- o Their simulations show DME best airborne fuel for electric drones

Summary

Key Performance Indicator this period	Current DMFC	Status DDFC	Target DDFC
Total precious metal loading	5 mg_{PGM}/cm^2	4.5 mg_{PGM}/cm^2	3 mg_{PGM}/cm^2
Anode mass-specific activity	50 A/g measured at 0.5 V [(1)]	93.8 A/g measured at 0.5 V (PtRu) [(5)]	75 A/g measured at 0.5 V
Maximum Power	160 mW/cm^2	135 mW/cm^2 [(3)]	270 mW/cm^2
Crossover	60-120 mA/cm^2 [(2)]	6 mA/cm^2	< DMFC
Off/On cycling loss	1.5mV/cycle	0.6mV/cycle [(4,5)]	0.75mV/cycle
Degradation Rate	<19µV/hr	30µV/hr [(4,5)]	<10µV/hr

(1) By comparison, LT direct DME FC obtained 25 A/g measured at 0.5 V with PtRu.
(2) 60 mA/cm^2 with 0.5 M MeOH, 80 °C, Nafion® 117; 120 mA/cm^2 with 1.0M MeOH.
(3) 2.23mg/cm^2 PtRu anode, 2.3mg/cm^2 Pt-alloy cathode
(4) Preliminary, measured via off/on cycling decay end of day voltages, H_2/air
(5) 1.6mg/cm^2 PtRu anode, 2.9mg/cm^2 Pt-alloy cathode

HT PEM and DDFC offers potential to outperform DMFC at lower cost

Technical Back-Up Slides

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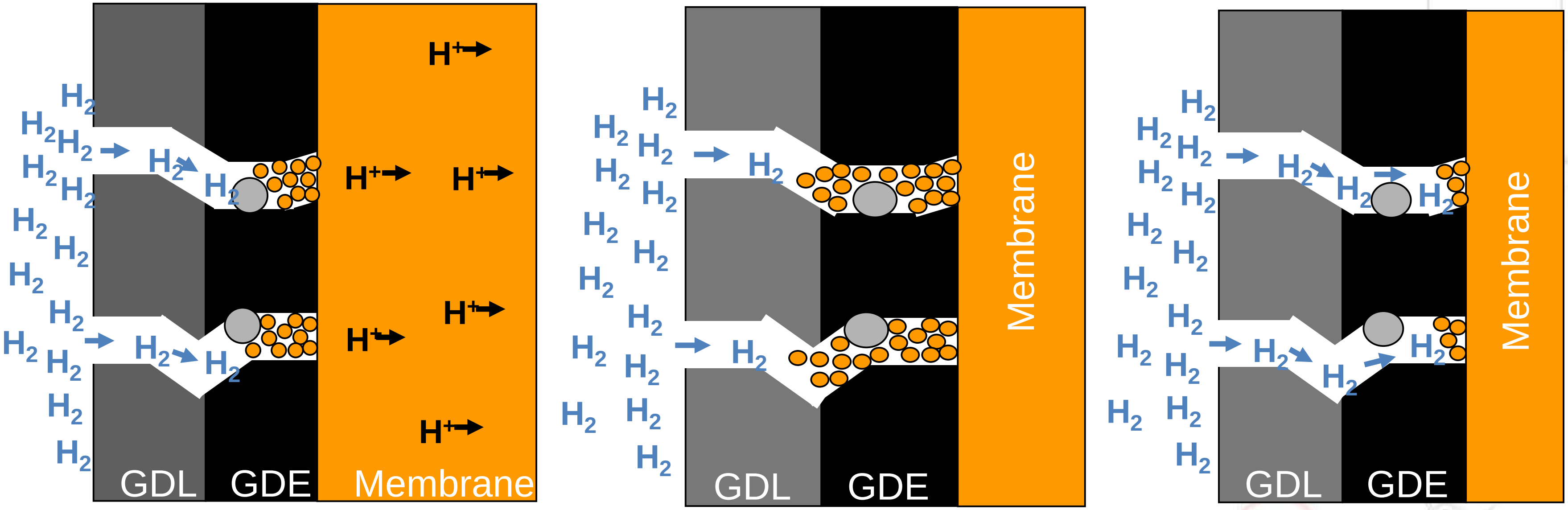
Approach – Tuning Electrode Architecture



Pore size: 0.5-5 µm

Balanced hydrophilic and hydrophobic properties for perfect wetting of the catalyst with phosphoric acid and optimal function of the MEA.

Acid flooding: The fuel (H_2/DME) cannot get in contact with the catalyst.

Acid starvation: Insufficient electrolyte limits the proton transport.

Key levers: type of carbon (catalyst), binder content, MEA build compression