# 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

*no cost extension

**Funded Partners**

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

**Budget ($)**

Total Funding: 1,250,000

Advent Cost Share (20%): 250,000

Federal Share (80%): 1,000,000

Total DOE funds spent* 733,000

**As of 31 March, 2017

**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

# Relevance

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

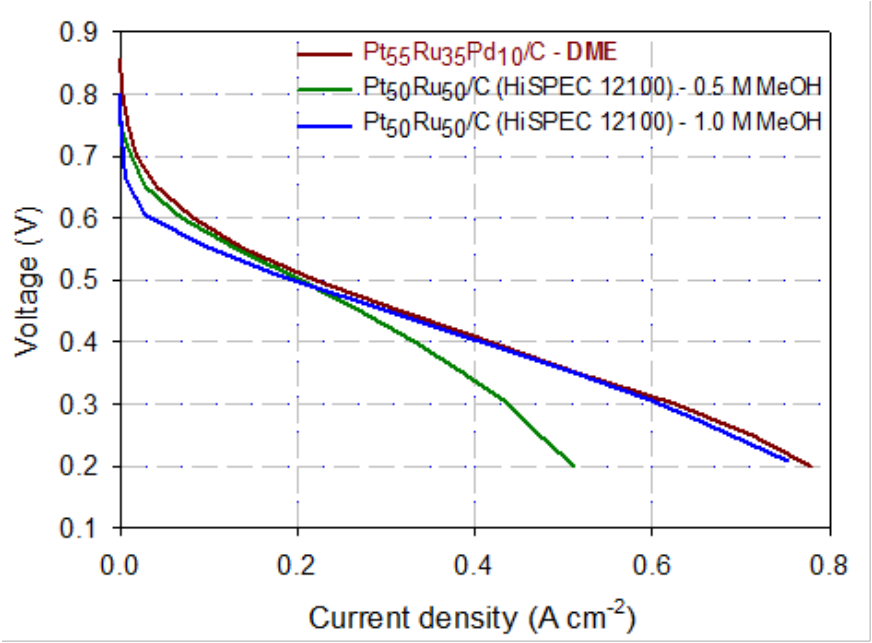
**Program Targets**

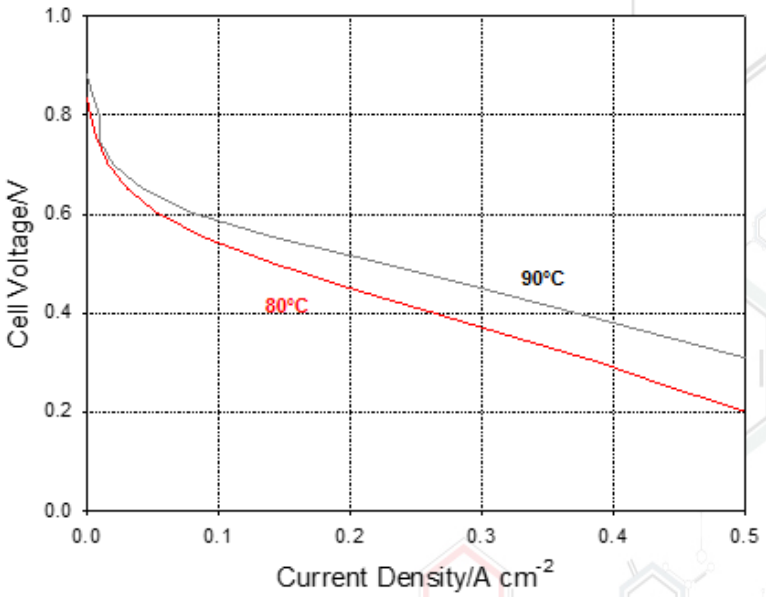
| Key Performance Indicator | Current DMFC | Target Hi T Direct DME |
|---|---|---|
| Maximum power (> ) | 0.180 W/cm$^2$ | 0.270 W/cm$^2$ |
| Total precious metal loading | 5 mg$_{PGM}$/cm$^2$ | 3 mg$_{PGM}$/cm$^2$ |
| Degradation rate | 19 μV/h at a 0.2 A/cm$^2$ | 10 μV/h at a 0.2 A/cm$^2$ |
| Loss 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



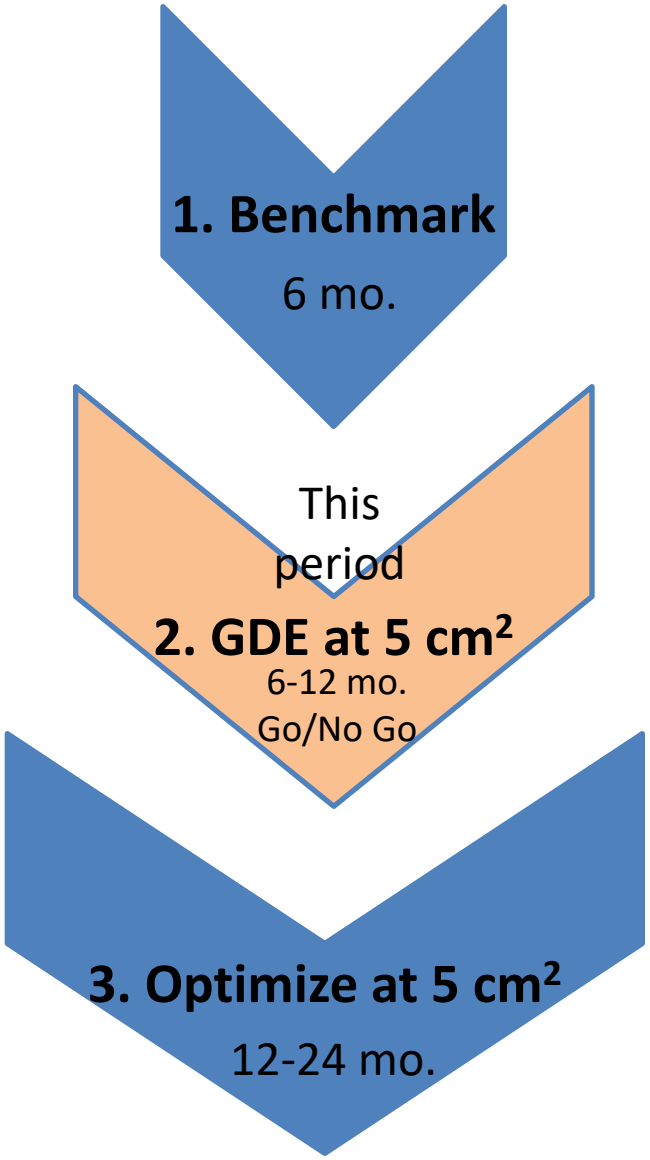




**DME *vs.* methanol fuel cell performance.**
**Anode:** 4.0 $mg_{metal}$ $cm^{-2}$ PtRuPd/C (HiSPEC® 12100); DME 40 sccm, bp 26 psig; 1.8 mL/min 0.5 M or 1.0 M MeOH.
**Cathode:** 2.0 mg $cm^{-2}$ Pt/C (HiSPEC® 9100); air 100 sccm, bp 20 psig. Membrane: Nafion® 212 (DME), Nafion® 115 (MeOH); cell: 80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



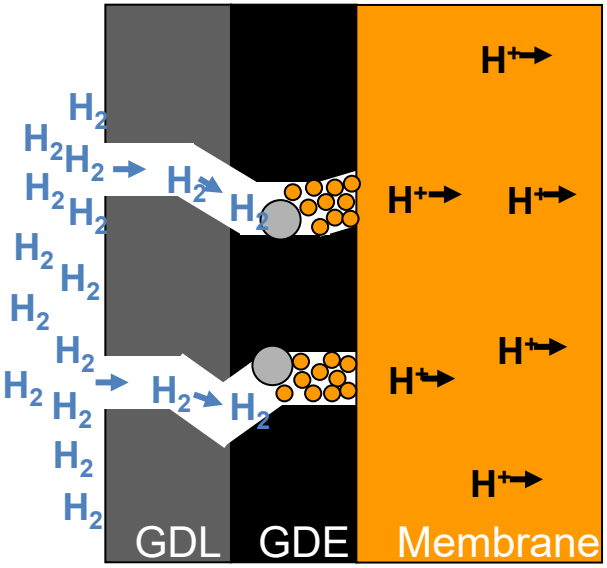

- Run high temperature MEAs at LANL
- Compare Pt anode w MeOH, DME (160 °C – 180 °C)
- Use both PBI and TPS HT MEAs

- 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

- Optimize anode GDE for mass transport
- Focus on optimum catalyst alloy
- Optimize electrode-membrane interface for TPS, higher T operation

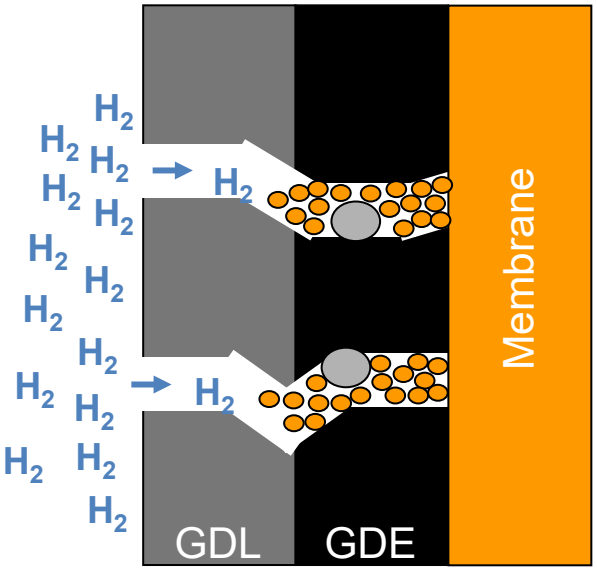
**Leverage enhanced kinetics at higher T**

# Approach – Tuning Electrode Architecture

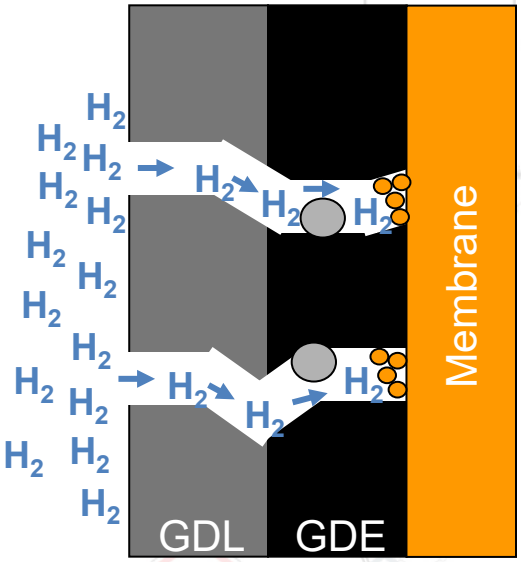



Pore size: 0.5-5 µm

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



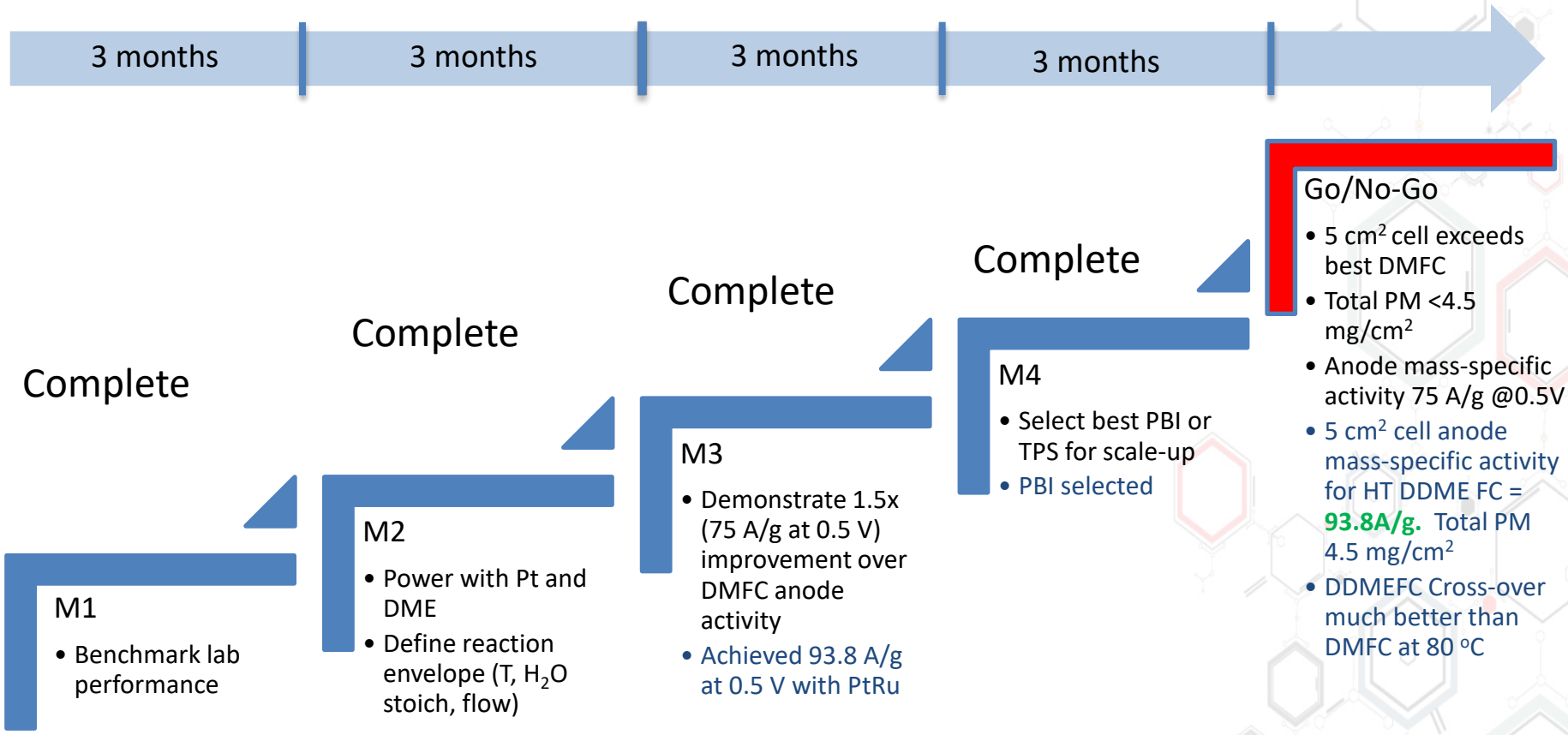

**Acid flooding**: The fuel ($H_2$/DME) cannot get in contact with the catalyst.




**Acid starvation**: Insufficient electrolyte limits the proton transport.

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

# Approach – Milestones – Phase 1




**Go/No Go achieved**
**Demonstrated potential for DDMEFC better than DMFC**

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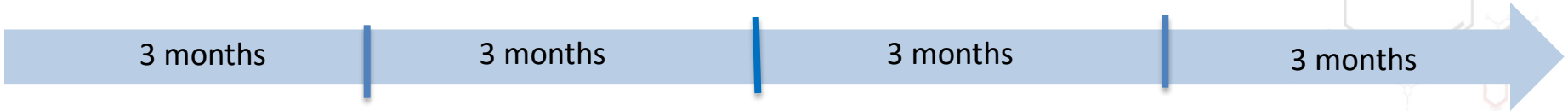
# Approach – Milestones – Phase 2




**Partial**

**M5**

- Scale to 50 $cm^2$
- Mass transport < DMFC using $H_2$ gain as reference
- $H_2$ gain @0.1 A/$cm^2$ for DDMEFC 240 mV; better than DMFC's 320 mV (at 5 $cm^2$)

**Pending**

**M6**

- Improve mass transport
- < 50% *vs.* DMFC

**Pending**

**M7**

- Demonstrate 0.270W/$cm^2$ maximum power with < 4.5 mg/$cm^2$ PGM

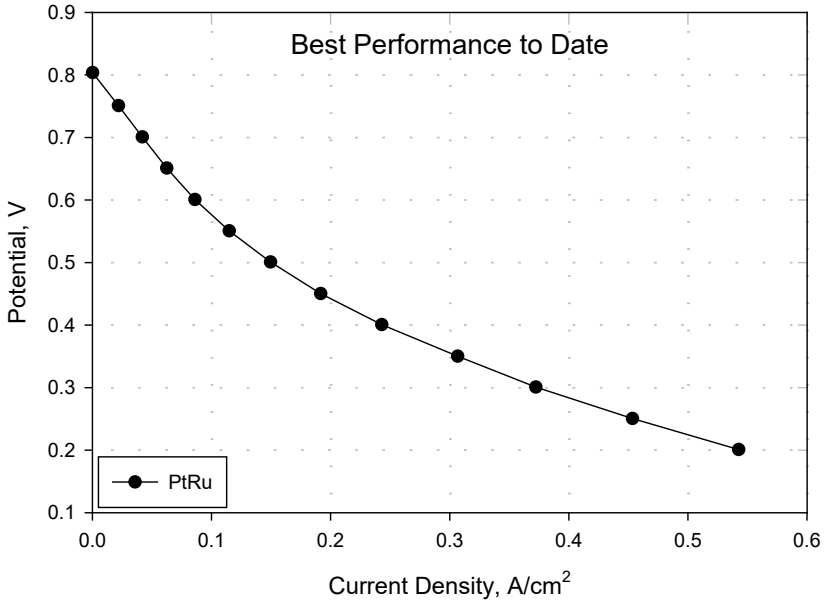
**M8**

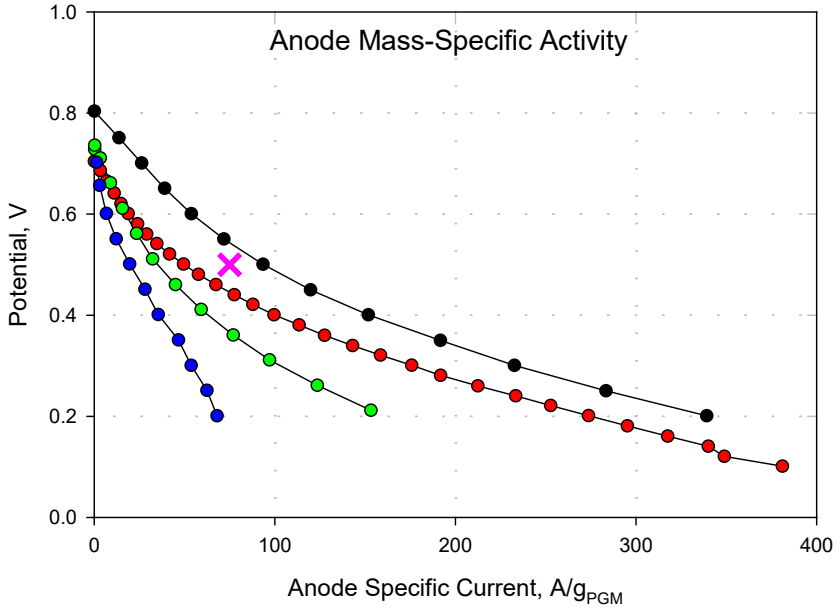
- DDMEFC Hi-T MEA > DMFC per Slide 3 targets

**Focus on maximizing PtRuPd activity**

# Accomplishments and Progress (1)

## Milestone 3: Anode Mass-Specific Activity



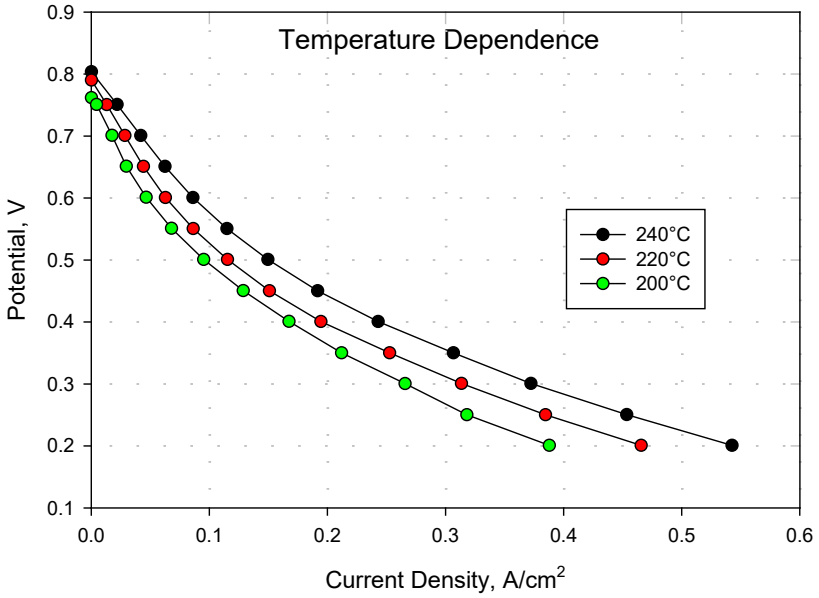

**High T MEA DME fuel cell performance at 240 °C.**
**Cathode**: Pt-alloy/C 2.9mg/cm$^2$; air 500 sccm, backpressure 30 psig.
**Anode:** HiSPEC® 12100 PtRu/C 1.6 mg/cm$^2$; DME 125 sccm, DME:water = 1:3, humidified at backpressure 30 psig.
**Membrane:** PBI

**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

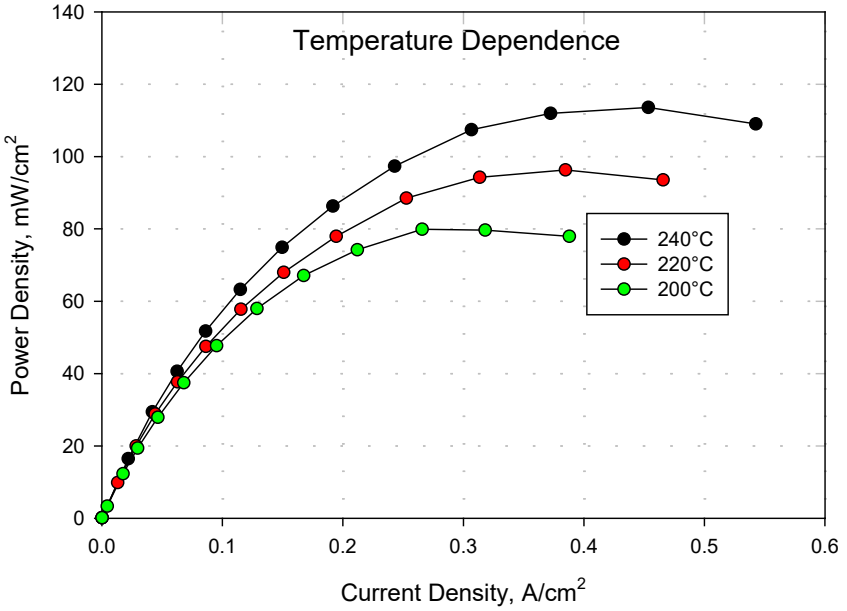
Achieved go/no go
Cathode loading & temperature limited MEA performance

# Accomplishments and Progress (2)

## Temperature effect
(this period)




## Power



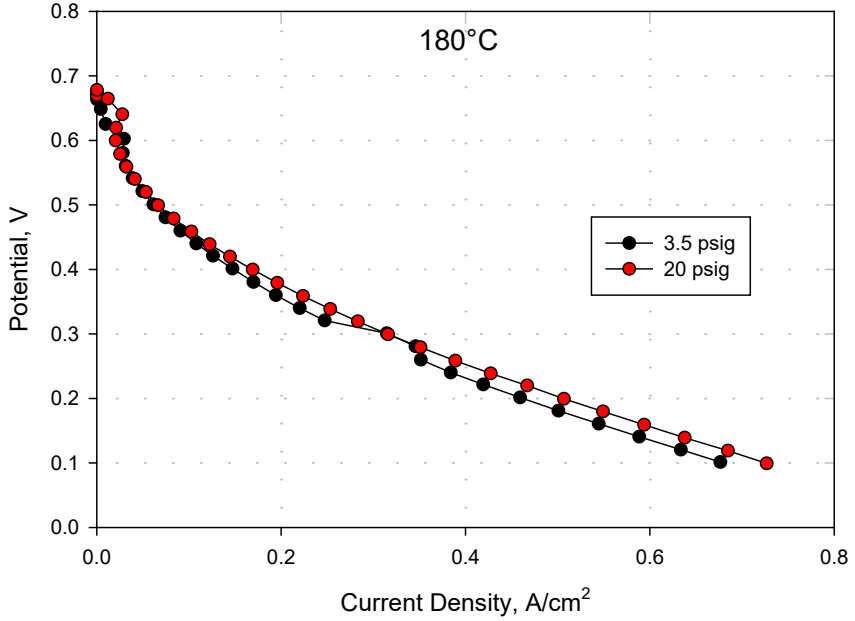

**Anode**: PtRu 1.6 mg/cm$^2$; 30 psig DME/$H_2O$ backpressure; DME 125 sccm, DME:water = 1:3
**Cathode:** Pt alloy, 2.9 mg Pt/cm$^2$; 30 psig air backpressure; 500 sccm
**Membrane:** PBI; 200-240 °C Cell size: 5 cm$^2$

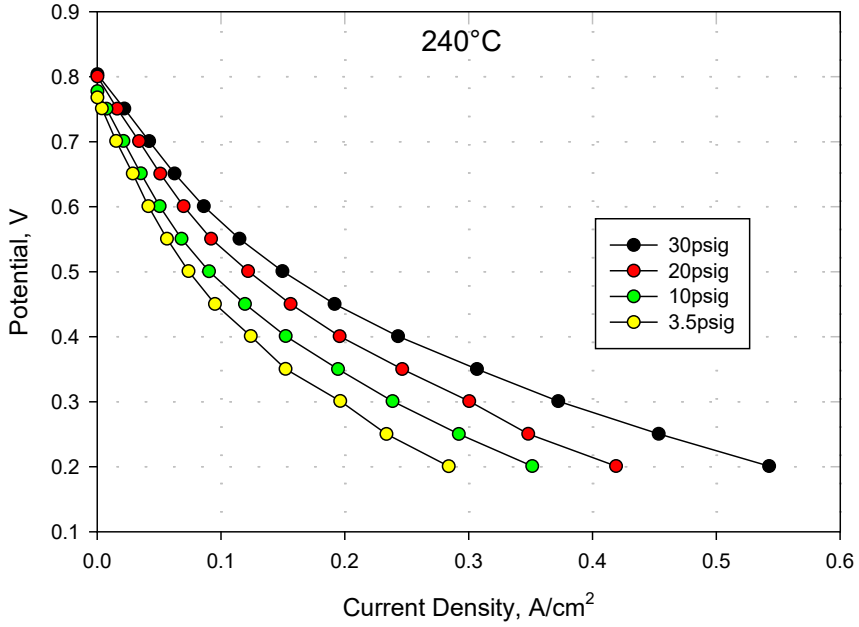
Same specifications as left-hand plot, demonstrating power density correlation to temperature

Highest temperature improves performance.

# Accomplishments and Progress (3)

## Pressure effects at various temperatures




**Anode:** 12100 HiSPEC® PtRu/C 2.23mg/cm$^2$; 125 sccm DME, DME:water = 1:3
**Cathode:** Pt-alloy 2.3 mg/cm$^2$; 500 sccm air
**Membrane:** PBI; 180 °C, 5cm$^2$ cell

**Anode:** 12100 HiSPEC® PtRu/C 1.6 mg/cm$^2$; 125 sccm DME, DME:water = 1:3
**Cathode:** Pt-alloy 2.9mg/cm$^2$; 500 sccm air
**Membrane:** PBI; 240 °C, 5cm$^2$ cell

Transition from 0$^{th}$ order to 1$^{st}$ order dependence on pressure at higher temperatures.

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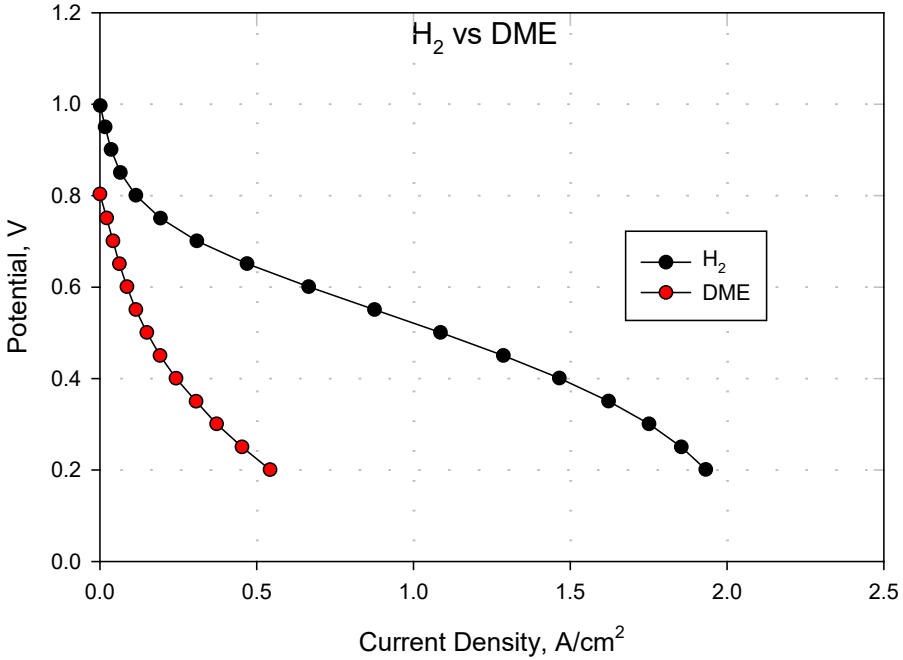
# Accomplishments and Progress (4)

$H_2$ gain as relative transport indicator

Milestone 5




**Cathode**: Pt-alloy/C 2.9mg/cm$^2$; air 500 sccm, backpressure 30 psig.

**Anode:** HiSPEC® 12100 PtRu/C 1.6 mg/cm$^2$; humidified at backpressure 30 psig.

- **Black:** DME 125 sccm, DME:water = 1:3,
- **Red:** $H_2$ 200sccm

**Membrane:** PBI

| Current density (A/cm$^2$) | $H_2$ gain (mV) | |
|---|---|---|
| | DMFC | DDMEFC |
| 0.1 | 320 | 240 |
| 0.2 | 330 | 315 |
| 0.3 | 340 | 375 |

**DDMEFC**: PBI; 240 °C, from left-hand figure

**DMFC**: Nafion® 115 Membrane, 80 °C, cell size 5 cm$^2$. HiSPEC® 12100 PtRu 4 mg/cm$^2$, Pt 4 mg/cm$^2$, $H_2$-Air, 20 psig backpressure, 1.0 M MeOH

*Preliminary studies show relatively improved mass transport DDMEFC vs. DMFC*

HT PEM DDMEFC crossover current 10-20× lower than DMFC

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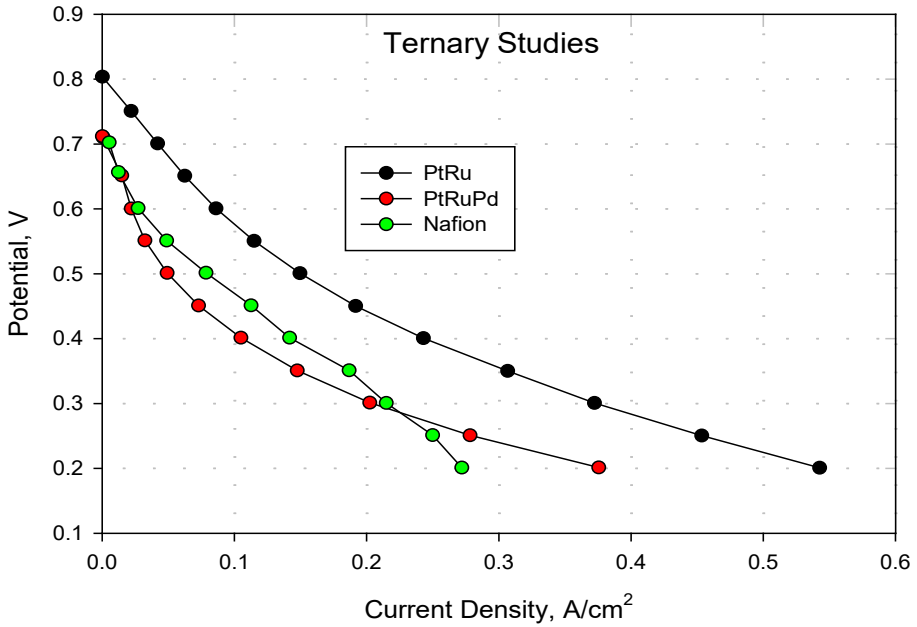
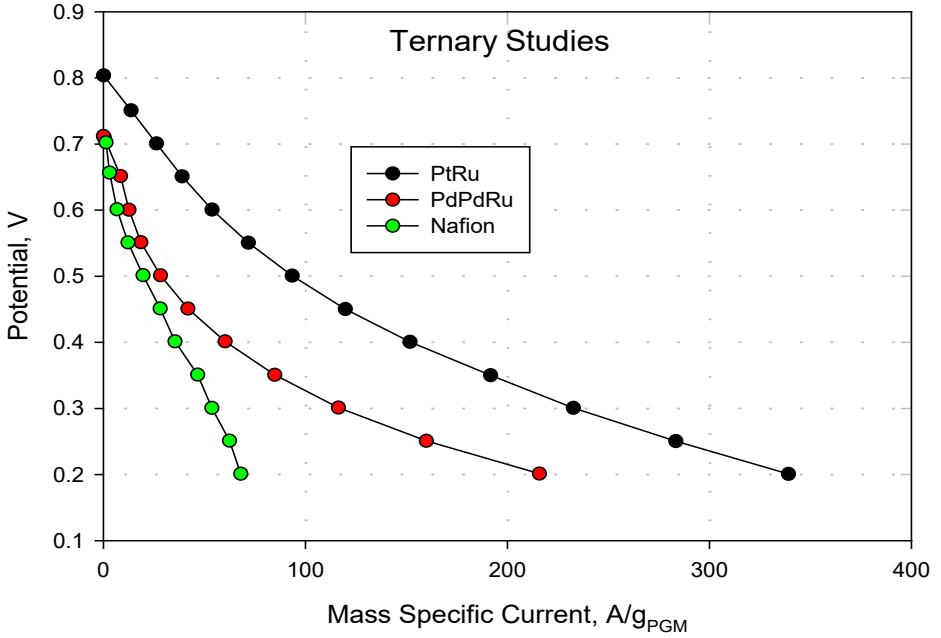
# Accomplishments and Progress (5)

## Preliminary PtRuPd ternary studies




**Black:** PtRu/C 1.6 mg/cm$^2$; Pt-alloy 2.9 mg/cm$^2$; 30 psig; PBI, 240 °C
**Red:** PtRuPd/C 1.74 mg/cm$^2$; Pt-alloy 2.56 mg/cm$^2$; 30 psig; PBI, 180°C
**Green:** PtRu 4 mg/cm$^2$; Pt 4 mg/cm$^2$; 26 psig; Nafion, 80 °C

Same conditions as left-hand figure

PtRuPd/C substantially different than PtRu/C:

1. Electrode-catalyst design to be improved
2. Ternary to be run at higher T

# Response to Previous Year's Review

1. *Risk mitigation strategy for PtRuPd/C catalysts is necessary*
   - After 2017 AMR review, two companies have approached Advent with potential ternary catalysts, and the evaluation of those materials will be integral to Phase II, allowing for more comprehensive correlation of catalyst characteristics to DDMEFC cell performance. With proper characterization and correlation to cell performance, PtRuPd/C is still a viable alternative to PtRu/C.
2. *Concerns regarding size of market*
   - Two companies with commercial systems based on HT PEM (UltraCell, SerEnergy) have expressed interest in developing commercial systems based on DDMEFCs.
   - This year's work has demonstrated that by just utilizing commercial PtRu/C catalyst, the performance on direct DME oxidation is much better than DMFC specific anode activity, and an order of magnitude lower in crossover current.

# Collaborations

Los Alamos National Laboratory (subcontractor)

- Developer of the PtRuPd catalyst
- Extensive know-how on setting up and running direct DME FC systems
- First National Laboratory to qualify HT PEM testing and operation

Commercial Catalyst Company #1

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

Commercial Catalyst Company #2

- Started small scale PtRuPd catalyst
- Extensive know-how on specialty catalyst alloys and supports
- Supplier to FC industry

# Remaining Challenges and Barriers

1. Can the expected boost from using PtRuPd be realized?
- Innate hydrophobicity of this catalyst different than the Johnson Matthey PtRu on high surface area carbon
- Will initiate catalyst collaboration with commercial suppliers to explore impact of PtRuPd support and alloying on activity
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 |
|---|---|---|
| 5 & 6 | Scale to 50 $cm^2$<br>Mass transport < DMFC using $H_2$ gain as reference; then improve mass transport 50% | Optimize GDL and electrode layer; modify electrode layer hydrophobicity to accommodate additives that increase DME solubility in phosphoric acid |
| 7 | Demonstrate 0.270 $W/cm^2$ maximum power with < 4.5 $mg/cm^2$ PGM | Work with commercial catalyst suppliers to optimize ternary alloy and support. Increase utilization through electrode structures. |

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

# 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

- 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

- Advent will need to scale to at least 165 $cm^2$
- SerEnergy has previously demonstrated battery range extenders for electric vehicles using reformed MeOH
- DME is "environmental diesel" and runs in slightly modified diesel engines – well aligned with marine industry

# Summary

| Key Performance Indicator this period | Current DMFC | Status DDMEFC | Target DDMEFC |
|---|---|---|---|
| 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(*) | 93.8 A/g measured at 0.5 V (PtRu) | 75 A/g measured at 0.5 V |
| Maximum Power | 160 $mW/cm^2$ | 135 $mW/cm^2$ (***) | 270 $mW/cm^2$ |
| Crossover | 60-120 $mA/cm^2$ (**) | 6 $mA/cm^2$ | < DMFC |

(*) By comparison, LT direct DME FC obtained 25 A/g measured at 0.5 V with PtRu.
(**) 60 $mA/cm^2$ with 0.5 M MeOH, 80 $^oC$, Nafion® 117; 120 $mA/cm^2$ with 1.0M MeOH.
(***) 2.23$mg/cm^2$ PtRu anode, 2.3$mg/cm^2$ Pt-alloy cathode

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

# Technical Back-Up Slides

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