Facilitated Direct Liquid Fuel Cells with High Temperature Membrane Electrode Assemblies

Emory S. De Castro
Advent Technologies, Inc.

June 6, 2017

Project ID FC128

Overview - Program

Timeline

Project Start Date: Oct 1, 2015
Project End Date: Sep 30, 2017

Funded Partners

LANL (P. Zelenay): 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*	663,000

*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)

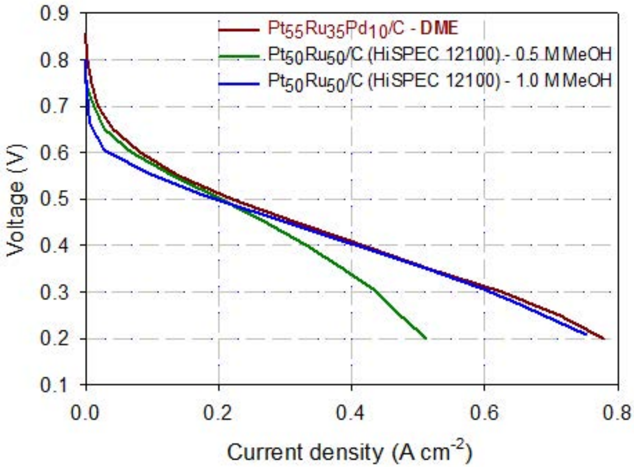
Program Targets

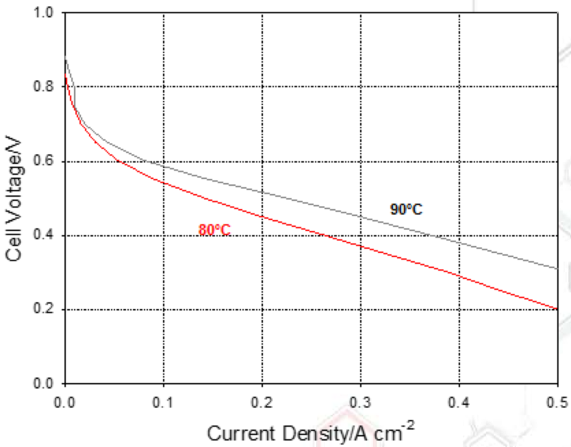
Key Performance Indicator	Current DMFC	Target Hi T Direct DME
Maximum power (>)	0.180 W/cm^2	0.270 W/cm^2
Total precious metal loading	5 mg_{PGM}/cm^2	3 mg_{PGM}/cm^2
Degradation rate	19 $\mu V/h$ at a 0.2 A/cm^2	10 $\mu V/h$ at a 0.2 A/cm^2
Loss in start/stop cycling	1.5 mV/cycle; cycle	0.75 mV/cycle; 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

2. GDE at 5 cm^2
6-12 mo.
Go/No Go

This period

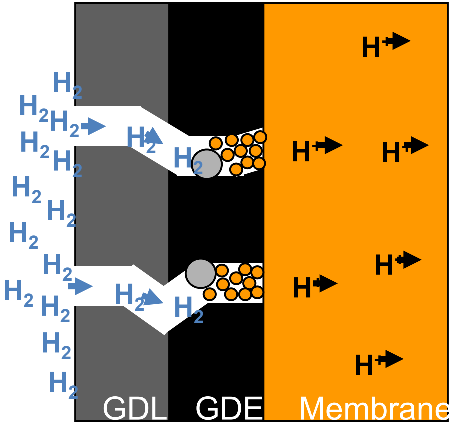
- Make gas diffusion electrode (GDE) with PtRu, run with DME
- Compare to LANL ternary anode catalyst
- Evaluate PBI and TPS DME cross-over and performance

3. Scale to 50 cm^2
12-24 mo.

- Optimize anode GDE for mass transport
- Refine cathode, if needed
- Adjust reaction conditions

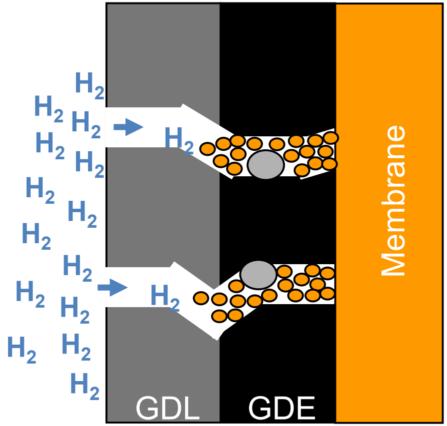
Leverage enhanced kinetics at higher T

Approach – Tuning Electrode Architecture

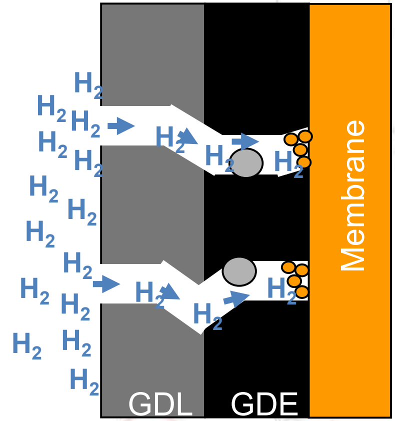


Pore size: 0.5-5 µm

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

3 months | 3 months | 3 months | 3 months

Complete

M1
- Benchmark lab performance

Complete

M2
- Power with Pt and DME
- Define reaction envelope (T, H_2O stoich, flow)

Partial

M3
- Demonstrate 1.5x (75 A/g at 0.5 V) improvement over DMFC anode activity
- Achieved 50 A/g at 0.5 V with PtRu

Complete

M4
- Select best PBI or TPS for scale-up
- PBI selected

Go/No-Go
- 5 cm^2 cell exceeds best DMFC
- Total PM <4.5 mg/cm^2
- Anode mass-specific activity 75 A/g @0.5V
- 5 cm^2 cell anode mass-specific activity for HT DDME FC > LT DDME FC
- Total PM 4.1 mg/cm^2
- DDMEFC Cross-over much better than DMFC at 80 °C

Demonstrated potential for DDMEFC better than DMFC

Approach – Milestones – Phase 2

3 months | 3 months | 3 months | 3 months

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 270 mV; better than DMFC's 320 mV (at 5 cm^2)

Pending

M6

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

Not relevant

M7

- If DME cross-over impacts cathode, select alternative cathode catalyst

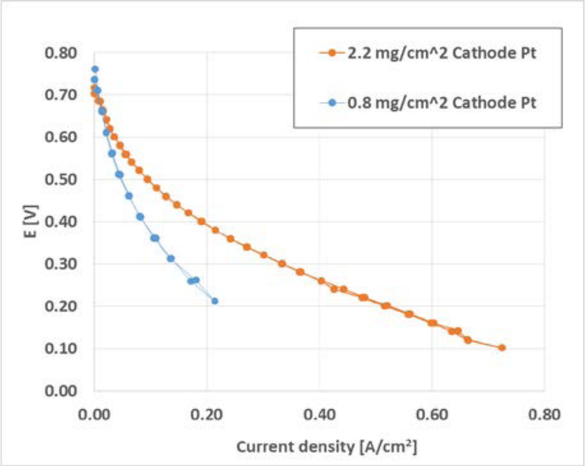
M8

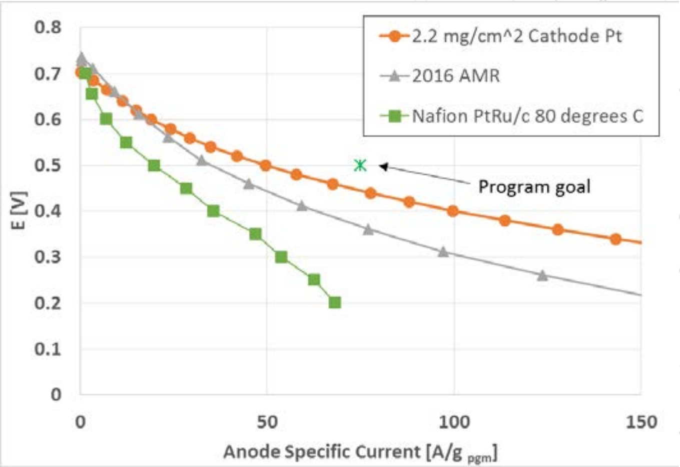
- DDMEFC Hi-T MEA > DMFC per Slide 3 targets

Focus on maximizing PtRuPd activity in electrode

Accomplishments and Progress (1)

Milestone 3: Anode Mass-Specific Activity





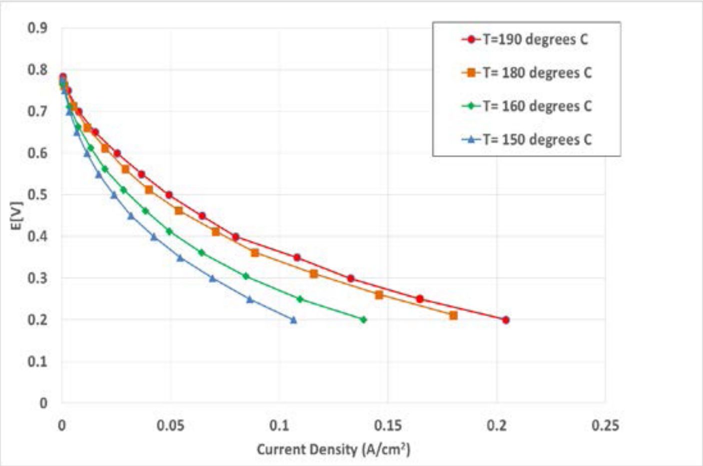
PBI-based MEA DME fuel cell performance at 180 °C.
Cathode: Pt-alloy/C as indicated; air 500 sccm, backpressure 3.5 psig.
Anode: HiSPEC® 12100 PtRu/C 1.9 mg/cm²; DME 125 sccm, humidified at backpressure 3.5 psig.

PBI-based MEA DME fuel cell performance at 180 °C.
Orange: replot data on left as anode specific current
Gray: 2016 AMR, HiSPEC® 12100 PtRu/C 1.9 mg PGM/cm², Pt/C 0.8 mg Pt/cm²
Green: LANL data from prior program, DME at PtRu, low temperature, total 8 mg/cm² PGM, **26 psig *vs.* 3.5 psig of this program**

Key learning that cathode loading limited MEA performance

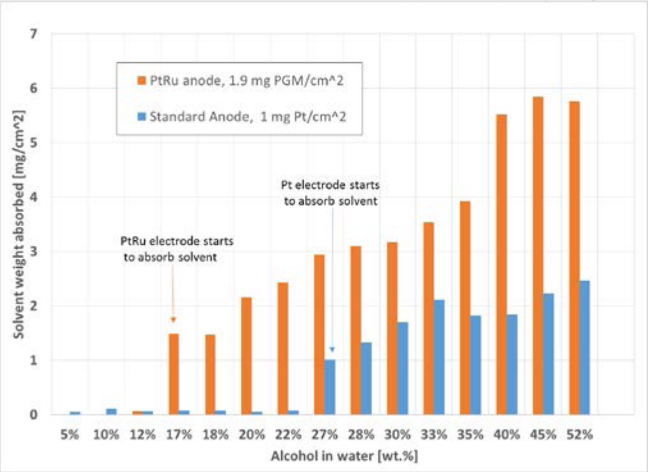
Accomplishments and Progress (2)

Temperature effect



Anode: PtRu 4.5 mg/cm^2; 3.5 psig DME/H_2O backpressure; DME 500 sccm; water 1.2 mL/min, DME:water = 1:3; **Cathode:** Pt alloy, 0.8 mg Pt/cm^2; 3.5 psig air backpressure; 500 sccm; **Membrane:** PBI; 150-180 °C Cell size: 5 cm^2 *(Performance limited by low loading cathode.)*

Electrode hydrophobicity

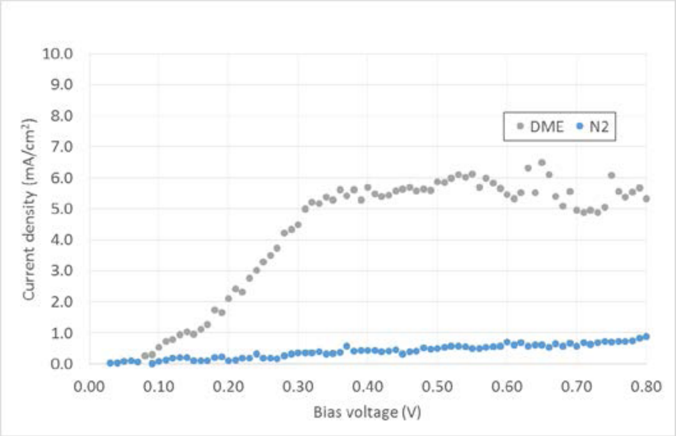


Cobb Titration: developed in earlier DOE program. Provides relative hydrophobicity of electrode structures. Indicates HiSPEC® 12100 PtRu/C is more hydrophilic than Pt on Vulcan XC72. Both have same level of hydrophobic binder. *Therefore possible acid flooding of PtRu electrode.*

High temperature improves performance. Important to modify electrode.

Accomplishments and Progress (3)

DME cross-over at PBI PtRu/C MEA



H_2 gain as relative transport indicator
Milestone 5

Current density (A/cm^2)	H_2 gain (mV)	
	DMFC	DDMEFC
0.1	320	270
0.2	330	330
0.3	340	410

Anode: PtRu 2.52 mg/cm^2; N_2 3.5 psig backpressure 100 sccm; **Cathode**: Pt alloy; 3.5 psig DME/H_2O backpressure, DME : water = 1 : 3; DME 125 sccm; water 0.3 ml/min; **Membrane**: PBI; 180 °C
Cell size: 5 cm^2

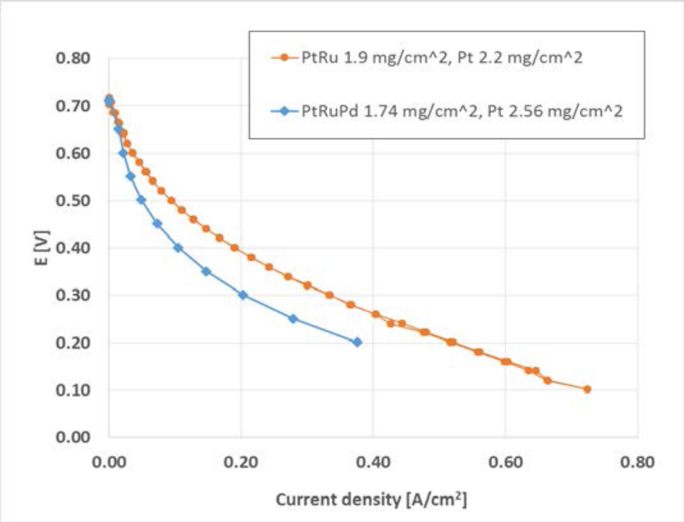
DDMEFC: PBI; 180 °C, from slide 4
DMFC: Nafion® 115 Membrane, 80 °C, cell size 5 cm^2. HiSPEC® 12100 PtRu 4 mg/cm^2, Pt 4mg/cm^2, H_2-Air, 20 psig backpressure, 1.0 M MeOH
Preliminary structures show relatively improved mass transport DDMEFC vs DMFC

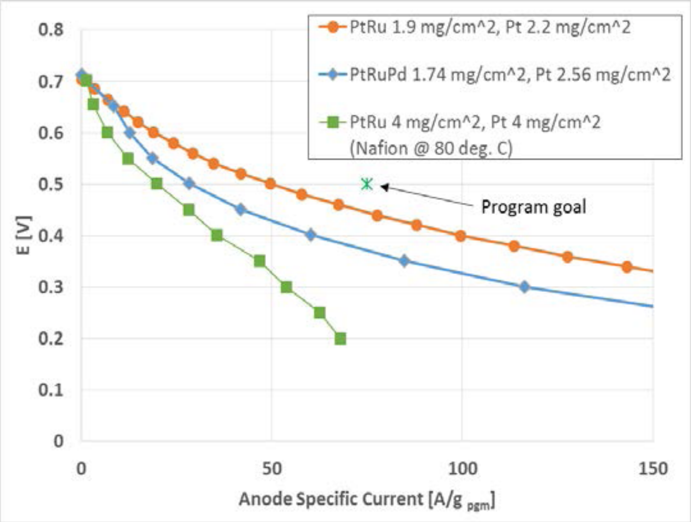
HT PEM DDMEFC crossover current 10-20× lower than DMFC

Advent

Accomplishments and Progress (4)

Preliminary PtRuPd





PBI-based MEA DME fuel cell performance at 180 °C.
Cathode: Pt-alloy/C; air 500 sccm, backpressure 3.5 psig.
Anode: HiSPEC® 12100 PtRu/C, DME 125 sccm, humidified at 90 °C, or LANL PtRuPd/C; DME 125 sccm, humidified at 90 C, backpressure 3.5 psig. **Green line**: previous data of Nafion MEA at *26 psig*.
Catalyst loading are specified in the plots.

PtRuPd/C substantially different than PtRu/C: electrode design to be improved

Response to Previous Year's Review

1. *Performance of these systems and possibilities for commercial relevance are project weaknesses*
   - 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 already equivalent to DMFC specific anode activity, and an order of magnitude lower in cross-over current.
2. *The project does not align with the transportation focus of EERE*
   - Volvo has demonstrated a fleet of diesel trucks running on DME, also known as "environmental diesel" for an aggregate >1,000,000 km. The ability to also directly convert DME to electricity as auxiliary power would greatly enhance this transportation segment, which is part of EERE's focus.

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

University of Connecticut (Outside DOE, Prof. Radenka Maric)

- Discussion on the use of additives in phosphoric acid fuel cell anodes to increase O_2 solubility
- Employed additives at the anode to facilitate DME solubility in phosphoric acid

Los Alamos National Laboratory (Outside DOE, Rod Borup, Kathryn Berchtold and Raj Singh)

- Potential membranes that could separate DME from product CO_2 gas (for system operation)

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
    - Have only used PtRu electrode architectures as of this report: expect a significant boost from improved electrode design with PtRuPd
2. Will the low solubility of DME in phosphoric acid, responsible for such low cross over currents, be the ultimate limit for this approach?
    - Are investigating additives for anode
2. Scale-up from 5 cm^2 to 45 cm^2
    - Electrodes for this program are at the 60 cm^2 scale and cut smaller for initial testing

Proposed Future Work

Milestone	Target	Path
4	5 cm^2 cell exceeds best DMFC Total PGM < 4.5 mg/cm^2 Anode mass-specific activity 75 A/g @ 0.5 V with PtRuPd catalyst	Via Cobb titration, measure PtRuPd anode hydrophobicity, vary electrode structure / hydrophobicity Evaluate MEA fabrication variables
5 & 6	Scale to 50 cm^2 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
8	Demonstrate DDMEFC outperforming DMFC	Combine catalyst utilization with improvements in mass transfer: initiate life testing

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

- 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	4.1 mg_{PGM}/cm^2	3 mg_{PGM}/cm^2
Anode mass-specific activity	50 A/g measured at 0.5 V(**)	50 A/g measured at 0.5 V (PtRu)	75 A/g measured at 0.5 V
Crossover	60-120 mA/cm^2 (*)	6 mA/cm^2	< DMFC

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

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

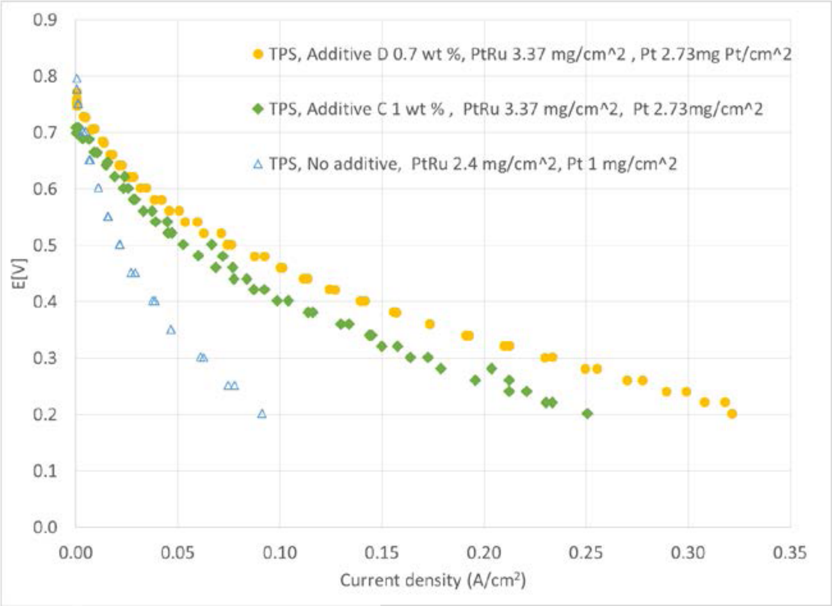
Technical Back-Up Slides

Contacts: EmoryDeCastro@Advent-Energy.com
Zelenay@LANL.gov

Advent

Los Alamos NATIONAL LABORATORY EST. 1943

Preliminary Results with Additives



- Additives added to only anode catalyst layer
- Dosage range critical
- Additive C employed additional hydrophobic binder to compensate for acid flooding
- Performance here not exceeding PBI/PtRu with out additives

Single cell testing (5 cm^2) of TPS MEAs, 180 ^oC, 3.5 psig DME/H_2O backpressure, 3.5 psig air backpressure; 500 sccm; Anode HiSPEC® 12100 PtRu/C, PGM loading as indicated; Cathode Pt-alloy/C, Pt loading as indicated. Additives “D” and “C” as indicated.

Additives offer potential to improve DME solubility in phosphoric acid

Separation of CO_2 from DME

When considering a system, how will the product CO_2 be separated from DME?

- High fuel utilization would minimize fuel loss to atmosphere
- Use a catalytic burner for the DME – this subsystem would also be used for heating system upon start up
- Use membrane separation (from Raj Singh, LANL)

  Size selective membranes:

  (a) polyamide, polyimide

  (b) inorganic membranes such as zeolites (SOD, has CO_2/DME selectivity 7 to 26 at 125 ^oC to 200 ^oC

Advent