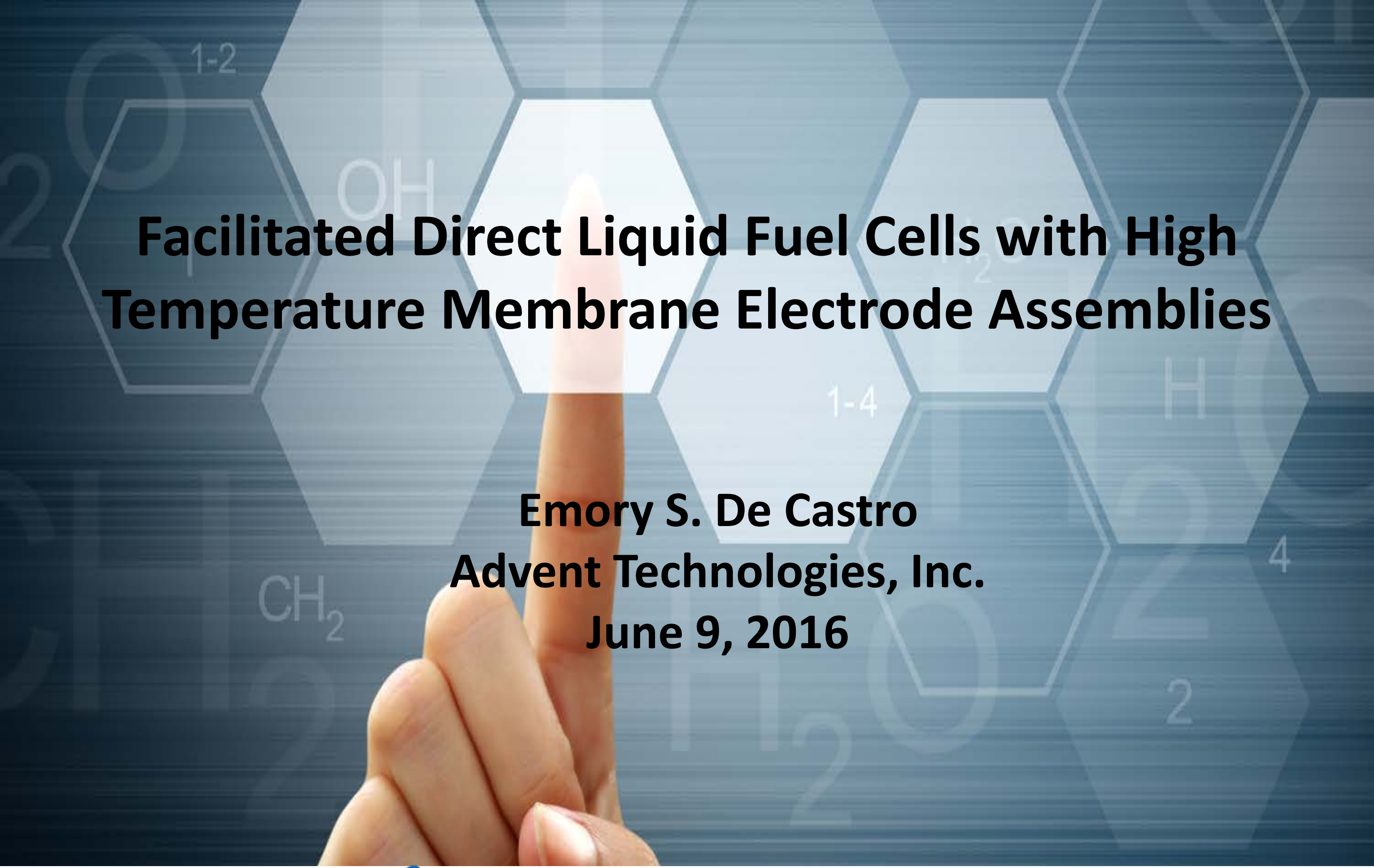

Facilitated Direct Liquid Fuel Cells with High Temperature Membrane Electrode Assemblies

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Advent Technologies, Inc.
June 9, 2016

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:	$1,251,000
Advent Cost Share:	$252,000 (20%)
DOE Funds Spent FY16*	$292,000

*(Includes $225,000 to LANL)

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

Benefit: carbon neutral auxiliary power for trucks and transport; extended run backup power

Approach - Overview

This period

1. Benchmark

6 mo.

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

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 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

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)

M3

- Demonstrate 1.5x (75 A/g at 0.5 V) improvement over DMFC anode activity

M4

- Select best PBI or TPS for scale-up

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

Approach – Milestones – Phase 2

3 months | 3 months | 3 months | 3 months

M5

- Scale to 50 cm^2
- Mass transport < DMFC using H_2 gain as reference

M6

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

M7

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

M8

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

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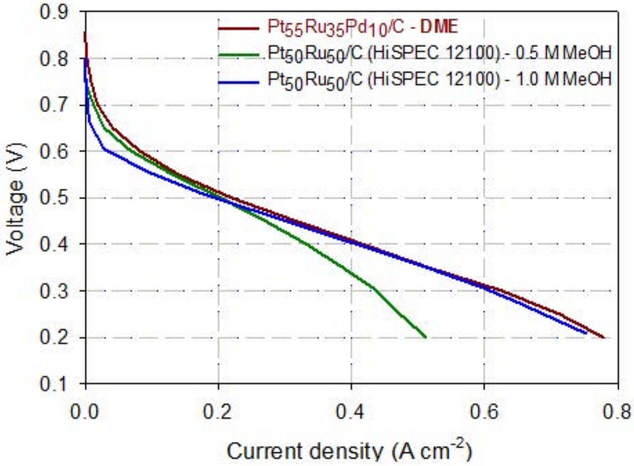
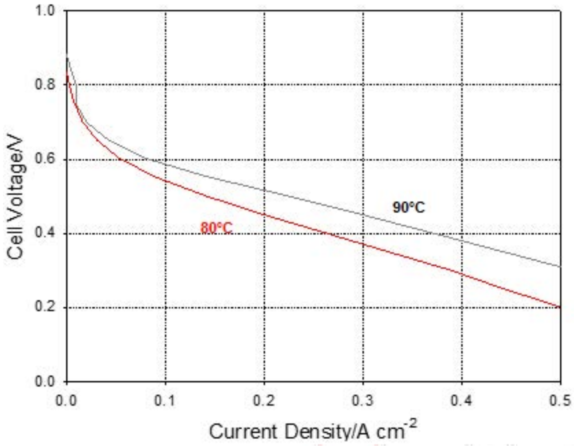
Pre-Program Idea Basis





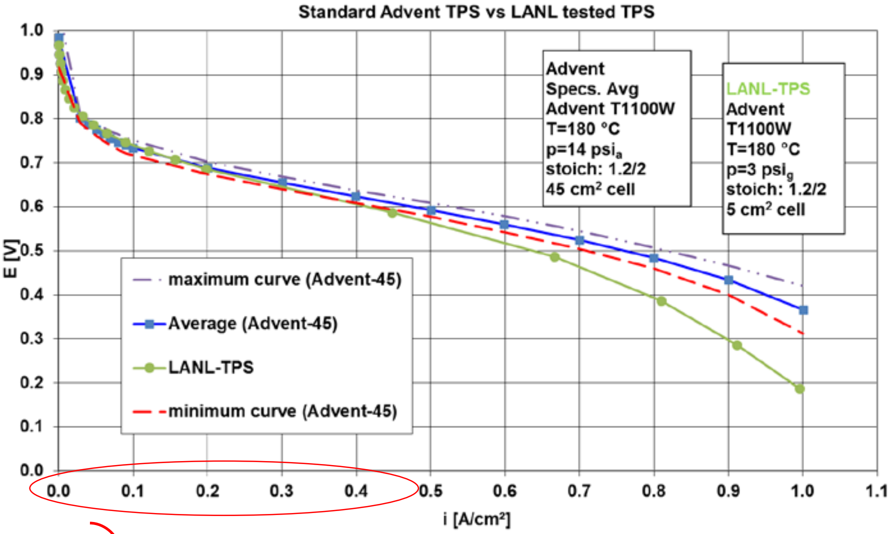
DME *vs.* methanol fuel cell performance.
Anode: 4.0 mg_{metal} cm^{-2} PtRuPd/C (HiSPEC® 12100); DME 40 sccm, bp 26 psig; 1.8 mL/min 0.5 M or 1.0 M MeOH.
Cathode: 2.0 mg cm^{-2} Pt/C (HiSPEC® 9100); air 100 sccm, bp 20 psig. Membrane: Nafion® 212 (DME), Nafion® 115 (MeOH); cell: 80 °C.

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.

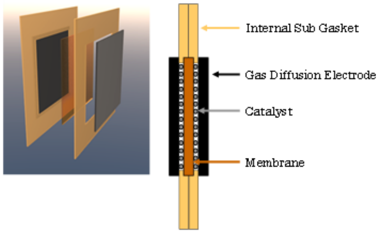
High DME activity with PtRuPd/C combined with temperature sensitivity

Accomplishments and Progress (1)

Milestone 1: “down-scaled” MEA at LANL within expected variation



Region of interest



Components of standard high temperature MEA including internal sub gasket, which was extended for testing 5 cm^2 MEAs in a 45 cm^2 test cell

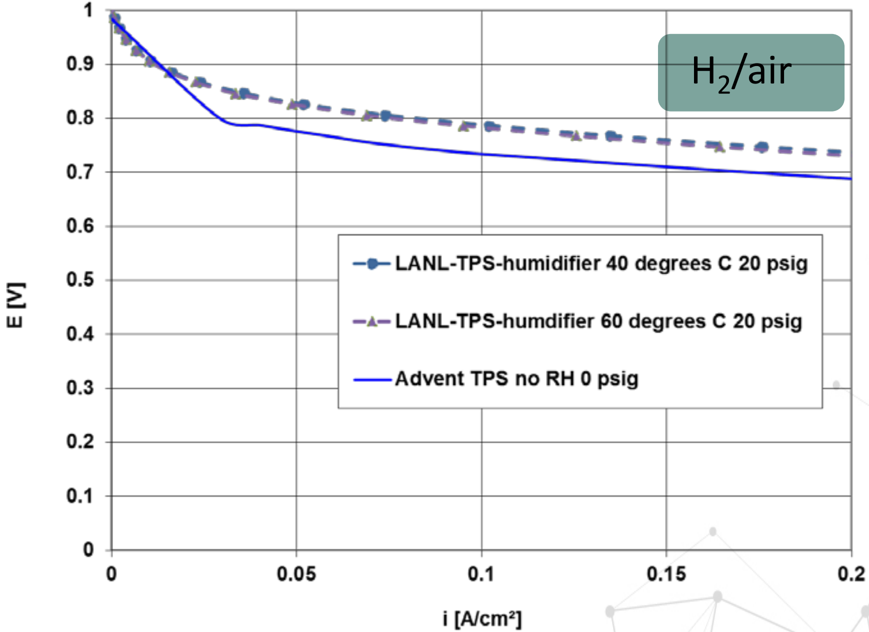
HT PEM Membranes

TPS = higher solids, lower acid, pyridine
PBI = lower solids, higher acid, imidazole

Good agreement between Advent (45 cm^2) and LANL (5 cm^2) testing

Accomplishments and Progress (2)

Milestone 2: Define reaction envelope (i.e., H_2O range)



TPS MEAs with different water content in hydrogen fuel at 180 ºC.
For the 40 ºC and 60 ºC humidifier case, anode backpressure 26 psig, cathode backpressure 20 psig. Air/H_2 stoich 2/1.2. MEAs at 5 cm^2

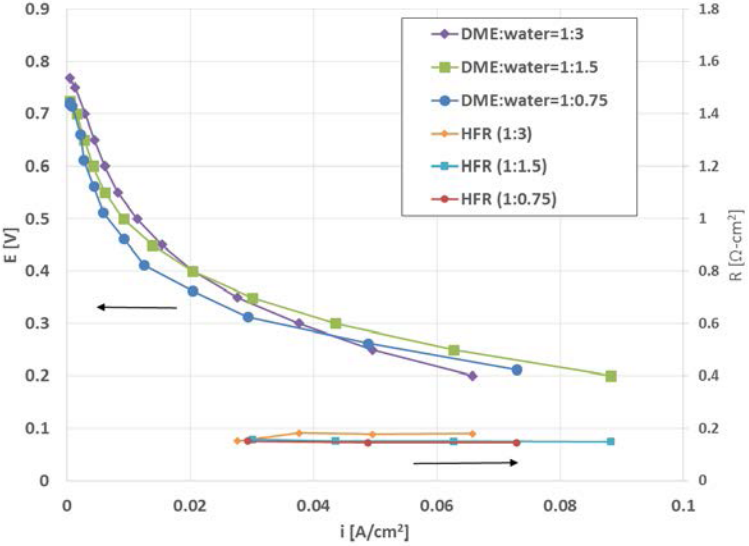
General Guideline
H_2O <20% anode feed
(reformate operation)

Use of humidifiers = low control of water introduction

Relatively robust performance to changing H_2O content

Accomplishments and Progress (2)

Milestone 2: baseline DME oxidation with Pt anode



Used HPLC pump to introduce H_2O
Sensitivity to DME:H_2O (1:3 chemical)
Feed dilution at DME:H_2O 1:3

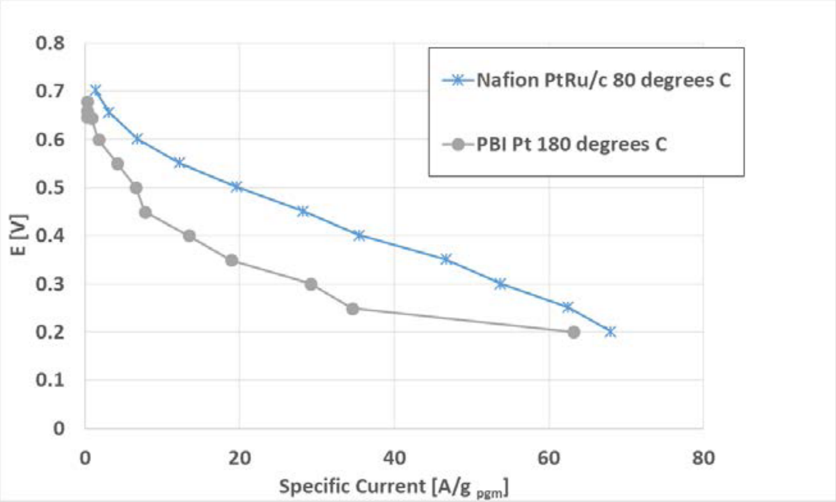
Activity with methanol insignificant (results not shown)

TPS MEAs with different DME:water stoichiometry at 180 °C.
Anode: Pt/C, 1 mg/cm^2; DME 500 sccm; backpressure 30 psig.
Cathode: Pt-alloy/C 1 mg/cm^2; air 500 sccm; backpressure 30 psig.
MEAs: 5 cm^2

Confirmed new set-up has precise H_2O control

Accomplishments and Progress (3)

Comparison baseline HT PEM DME oxidation with Nafion®



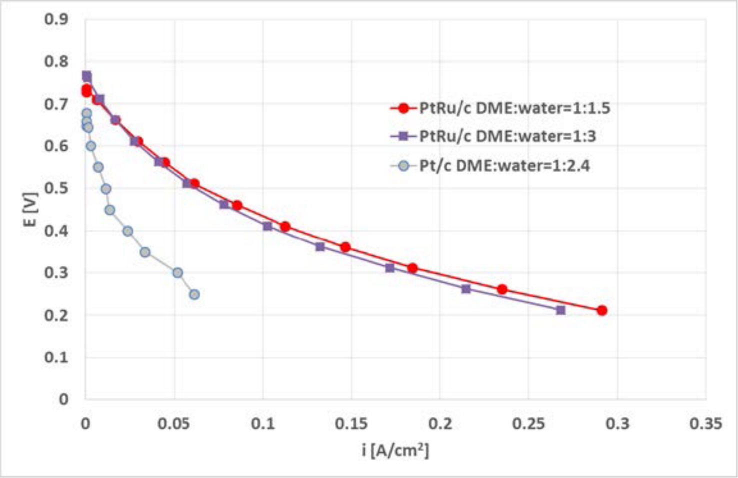
MEA	Specific Power@0.2V W/g PGM
Nafion	14
PBI	13

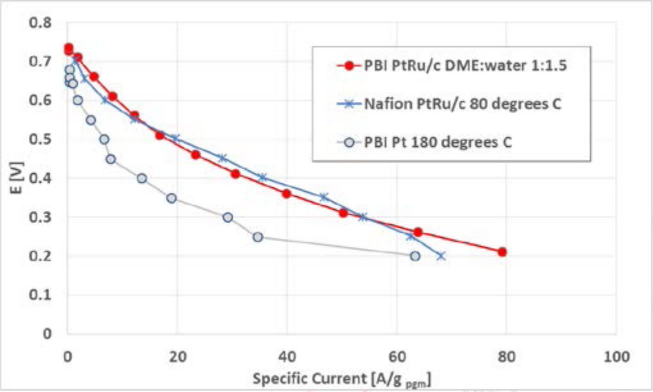
Comparison of PBI and Nafion-based MEA in DME fuel cells.
PBI MEA at 180 ºC: Anode: Pt/C, 1 mg/cm^2; DME 500 sccm, backpressure 30 psig; DME:H_2O = 1:2.4. Cathode: Pt-alloy/C 1 mg/cm^2; air 500 sccm, bp 30 psig.
Nafion 212 MEA at 80 ºC: Anode: PtRu black 4 mg/cm^2, DME 40 sccm (saturated with H_2O), bp 26 psig. Cathode: Pt black 4 mg/cm^2 ; air 500 sccm, backpressure 20 psig.

Higher T operation confirms increase in fuel cell performance

Accomplishments and Progress(4)

Initial PtRu HT PEM DME oxidation





MEA	Specific Power@0.2V W/g $_{PGM}$
Nafion PtRu	14
PBI Pt	13
PBI PtRu	17

PtRu *vs.* Pt: PBI-based MEA DME fuel cell performance at 180 ^{o}C. **Pt/C:** Anode: Pt/C, 1 mg/cm^2; DME 500 sccm, backpressure 30 psig. Cathode: Pt-alloy/C 1 mg/cm^2; air 500 sccm, backpressure 30 psig. **PtRu/C**: Anode: HiSPEC® 12100 PtRu/C 1.9 mg/cm^2; DME 500 sccm, backpressure 20 psig. Cathode: Pt-alloy/C 1 mg/cm^2; air 300 sccm, backpressure 20 psig.

PtRu/C increases fuel cell performance substantially

Response to Previous Year Reviewers

Project not reviewed last year

Advent

Collaborations

Next generation PBI membranes (later in project)

- University of South Carolina (B. Benicewicz)
- Independent of DOE H&FC Program
- Supplier of materials

Impact of high water in anode feed

- EHT-Zurich/PSI Switzerland (T. Schmidt)
- Independent of DOE H&FC Program
- Theoretical perspective on acid and water migration in HT PEM

Remaining Challenges and Barriers

- Is the optimum DME:H_2O ratio compatible with the membrane phosphoric acid
- Does the phosphoric acid promote unwanted chemical reactions with DME?

- Identifying upper H_2O limit in DME/H_2O fed to the fuel cell anode
- MEAs with PtRu/C as anode catalyst
- MEAs with PtRuPd/C as anode catalyst
- Scale-up from 5 cm^2 to 45 cm^2

Proposed Future Work

Milestone	Target	Path
3	Demonstrate 1.5x (75 A/g at 0.5 V) improvement over DMFC anode activity	Incorporate PtRu and PtRuPd anode catalysts, vary electrode structure
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	Select best of TPS or PBI MEAs; optimize reaction conditions and catalyst layer
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 on GDL
7	If DME crossover impacts cathode, select alternative cathode catalyst	Consider the new PGM-free cathode catalysts

Technology-to-Market

Advent will approach 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

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

Summary

Objective: Demonstrate direct DME oxidation with high temperature MEA and LANL catalyst significantly outperforming state-of-the-art DMFC

Relevance: DME is a carbon-neutral hydrogen carrier that can be used both for internal combustion and as cost-effective fuel for auxiliary fuel cell power systems in automotive transportation

Approach: Incorporate new ternary anode catalyst in gas diffusion electrodes designed for high temperature MEAs. Evaluate with two different high temperature membranes (PBI and TPS). Optimize structures and reaction conditions

Accomplishments: 1) Developed system for precise control of DME to water ratios, 2) demonstrated baseline operation with platinum MEAs, 3) higher temperature operation facilitates performance, and 4) Initial PtRu performance at higher temperature confirms approach

Technical Back-Up Slides

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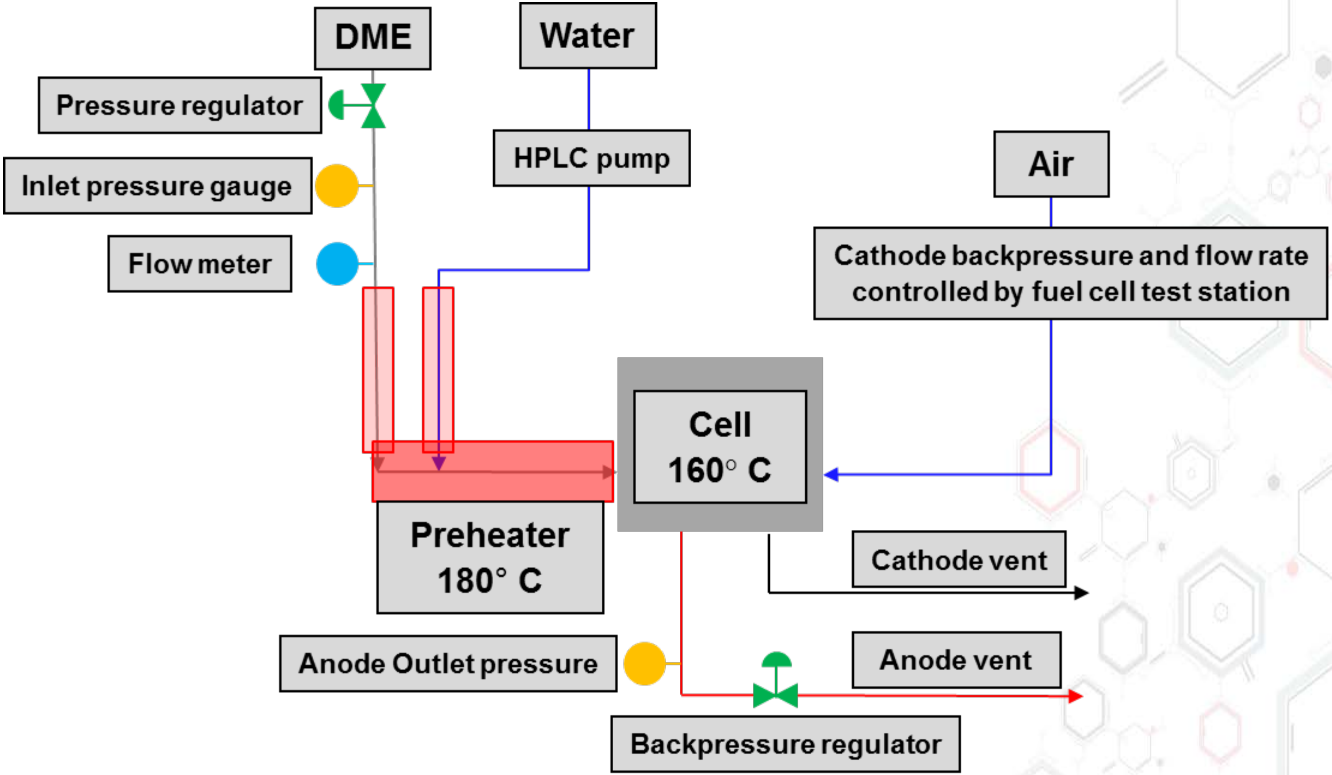
DME Feed with Controlled DME-to-H_2O



HPLC pumps precise H_2O into DME stream

Critical Assumptions and Issues

1. Assumption: Activation barrier to DME oxidation is from CO poisoning of catalyst, which is shifted with higher temperature.

Approach: Although preliminary results support this hypothesis, we have latitude in being able to adjust the make-up of the ternary catalyst to optimize high T performance.

2. Assumption: DME crossover limited by its solubility in phosphoric acid.

Approach: The TPS membrane has higher solids/lower acid content than PBI, so if our assumption is false, this platform should show an advantage. Furthermore, next-generation PBI membranes have higher solids.

3. Assumption: PtRu or PtRuPd will be stable at the higher T.

Consideration: Thermodynamics predicts segregation of Ru from Pt; however, target markets have 5,000 hour life expectations, which should still be within the stability window of these catalysts.

Publications and Presentations

Presentation: "A Disruptive Fuel in the System: Electricity from a Carbon-Neutral Fuel," Emory S. De Castro, Piotr Zelenay and Vasilis Gregoriou, Fuel Cell Seminar and Energy Exposition, Los Angeles, California, USA, November 16-19, 2015; Abstract 104.