Solid Acid Fuel Cell Stack for APU Applications

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May 22, 2009

Project ID# fc_45_duong

Overview

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Timeline

- Start – July 2008
- Finish – July 2010
- 40% complete

Budget

- Total project funding
  - DOE - $492,000
  - SPI cost share - $123,000
- DOE funding received for FY'08
  - $492,000

Collaborator

- California Institute of Technology
- Richard Mistler, Inc.

Barriers

- Barriers
  - A. Durability
    - Tolerance to reformed fuel
    - Operating hours
  - B. Cost
    - MEA fabrication
    - Catalysts
  - C. Performance

- Technical Targets

	Stack	System*
Power (W)	300	3000
Durability (h)	2000	2000
Efficiency (%LHV)	55	25
CO tolerance (%)	10	N/A
H_2S tolerance (ppbv)	50	N/A
Specific power (W/kg)	55	TBD
Power density (W/L)	160	TBD
Cost ($/kW$_e$)	300	800

** System projections based on conceptual design*

Introduction to SAFC

Solid Acid Electrolytes
Fundamentals

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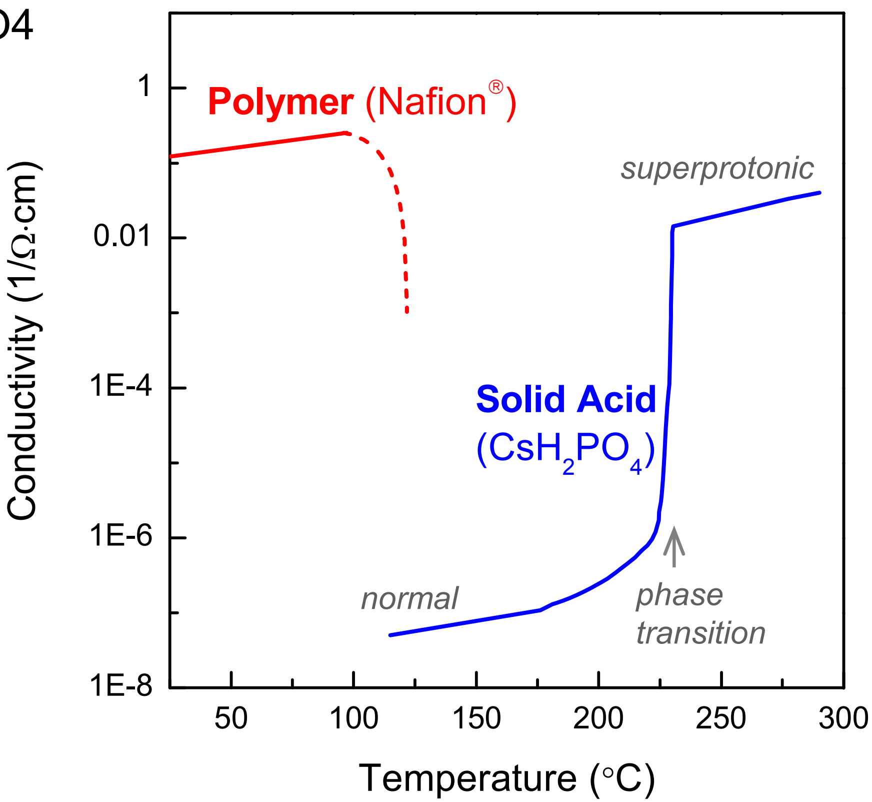
- Intermediate salts and acids
  - $1Cs_3PO_4 + 2H_3PO_4 \rightarrow 3CsH_2PO_4$
  - General Formula: $M_xH_y(XO_4)_z$
    - M = Cs, Rb, K, NH_4, Tl
    - X = S, Se, P, As
- Physically similar to salts
  - Brittle
  - Water soluble
- Properties
  - Solid state proton conductivity
  - Impermeable

Solid Acid Conductivity



Cesium Dihydrogen Phosphate
Electrical properties

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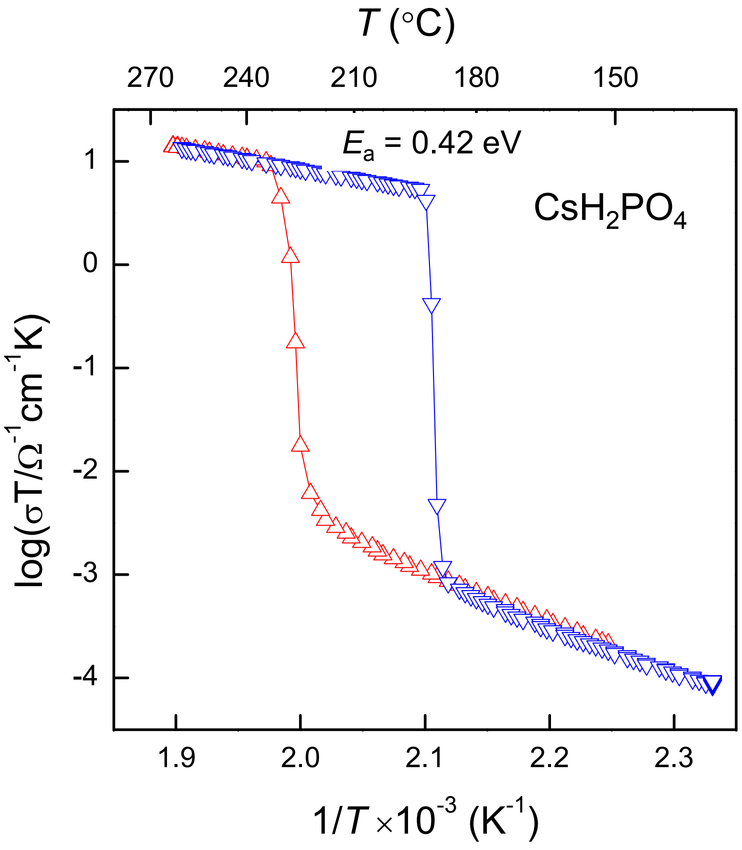
- Superprotonic phase transition
  - T_{SP} = 231°C
  - Proton conductivity jump
    - < 8.5 x 10^{-6} $\Omega^{-1}cm^{-1}$ at 223°C
    - > 1.8 x 10^{-2} $\Omega^{-1}cm^{-1}$ at 233°C
  - Hysteresis
    - Upon cooling 5-30 °C
- Superprotonic conductivity
  - Typical conductivity
    - ~ 2.5 x 10^{-2} $\Omega^{-1}cm^{-1}$ at 250°C
  - Temperature range
    - 232-280°C*

Arrhenius Plot of Conductivity



* Dependant on P_{H2O}

Haile et al, Faraday Discussions, 2007

SAFC Characteristics

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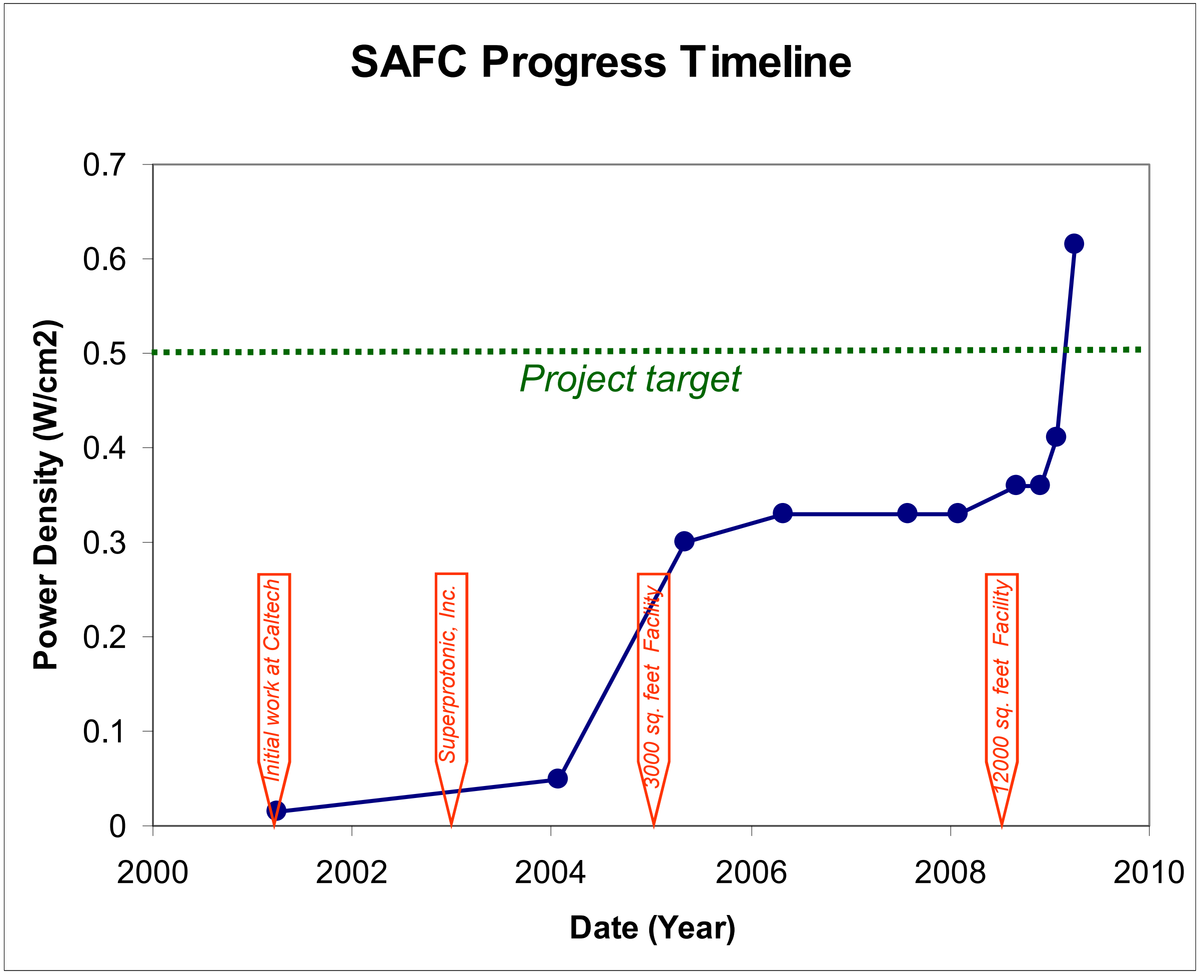
- Solid acid electrolytes
  - Solid state proton conducting membranes - CsH_2PO_4
  - Operate at favorable temperatures - 230-280°C
- Fuel flexibility
  - Hydrogen, methanol, ethanol, reformed fossil fuels
  - Optimal temperature for low T gas shift
  - High tolerance to CO (>10%), H_2S(100ppm), & NH_3 (100ppm),
- Low cost/high performance potential
  - Optimized microstructure for improved catalysis
  - Better catalysis/less platinum

SAFC History at Superprotonic



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Project Update

Objective - Relevance

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The main focus of the project is to develop a solid acid fuel cell stack

- that operates on diesel reformate
- with performance characteristics approaching or exceeding most of the DOE's 2010 technical targets for an APU.

Performance Measure	Units	SPI Stack	SPI System*	DOE 2010 APU System Target	Technical Barrier(s) Addressed**
Power	Watts	300	3000	N/A	N/A
Durability	Hours	2000	2000	20000	A,B,C
Efficiency	% LHV	55	25	35	B,C
CO tolerance	%	10	N/A	N/A	A,B
H_2S tolerance	ppbv	50	N/A	N/A	A,B
Specific power	W/kg	55	TBD	100	B,C
Power density	W/L	160	TBD	100	B,C
Cost♣	$/kW$_e$	300	800	400	B

**SPI System projections will be based on scaled up stack and conceptual system design*

***Barriers: A-Durability, B-Cost, C-Performance*

♣ Cost will be projected based on production of 100000 3 kW units/year

Approach

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- **Task 1: Development of SAFC MEA**
  - Fabricate and test 3 cm^2 and 20 cm^2 MEA
  - Optimize MEA performance
  - Develop proposal for scaling up MEA fabrication to 125 cm^2
- **Task 2: Fabrication of 125 cm^2 SAFC MEA**
  - Fabricate using method based on 3 cm^2 and 15 cm^2 MEA
  - Fabricate using scaled up method
- **Task 3: Characterization of SAFC MEA**
  - Evaluate SAFC performance on reformate with CO and H_2S
  - Evaluate 3 cm^2 and 15 cm^2 MEA performance
  - Evaluate 125 cm^2 performance (durability, efficiency, specific power, power density, etc.)
- **Task 4: Design & Modeling of SAFC stack**
  - Design 300W stack components
    - Bipolar plates
    - Cooling plates
    - Sealing
  - Model 300W stack
    - Flow field distribution
    - Pressure gradient
- **Task 5: Fabrication of 300W SAFC stack**
- **Task 6: Characterization of SAFC stack**
  - Durability
    - Long term stability
    - Thermal cycling
  - Efficiency
  - Specific power
  - Power density
  - Test on reformate
- **Task 7: Design 3kW SAFC stack**
  - Scale up 300W design
  - Modeling
  - High volume cost projection
- **Task 8: Design 3kW SAFC system**
  - Control and ancillary subsystems
  - Start-up and shutdown procedures and algorithm

Milestones

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Month/Year	Milestones or Go/No-Go Decision
August 2008	Go/No-Go decision: Complete evaluation of MEA fabrication and assess scalability with existing manufacturing processes. Conduct feasibility of electrolyte layer deposition using a sprayer and electrolyte densification via roller compaction. (Status – met)
September 2008	Go/No-Go decision: Complete evaluation of SAFC stack functionality and stability on synthetic reformate with high CO (10%) and H_2S (100 ppm) content. (Status – met)
October 2008	Milestone: Complete 300W stack design completed based on existing 50W stack configuration. (Status – 75% complete)
November 2008	Milestone: Complete evaluation of 20 cm^2 SAFC stack functionality and stability on reformed methanol and liquid propane gas (Status – 100% complete)
January 2008	Milestone: Model flow field and pressure gradient on a 300W SAFC stack. (Status – 50% complete)
February 2008	Milestone: Fabricated 125 cm^2 SAFC MEA based on current 20 cm^2 MEA fabrication process (Status – 10% complete)
March 2008	Go/No-Go decision: Complete feasibility of SAFC stack functionality on reformed diesel fuel. (Status met)
October 2009	Milestone: Demonstrate micro-porous layer deposition using tape casting technique (Status – planned)
November 2009	Milestone: Demonstrate anode and cathode catalyst layer deposition using a sprayer (Status – planned)
December 2009	Go/No-Go: Fabricate 125 cm^2 SAFC MEA (10 minimum) using proposed fabrication process. (Status – planned)

Development of SAFC MEA fabrication

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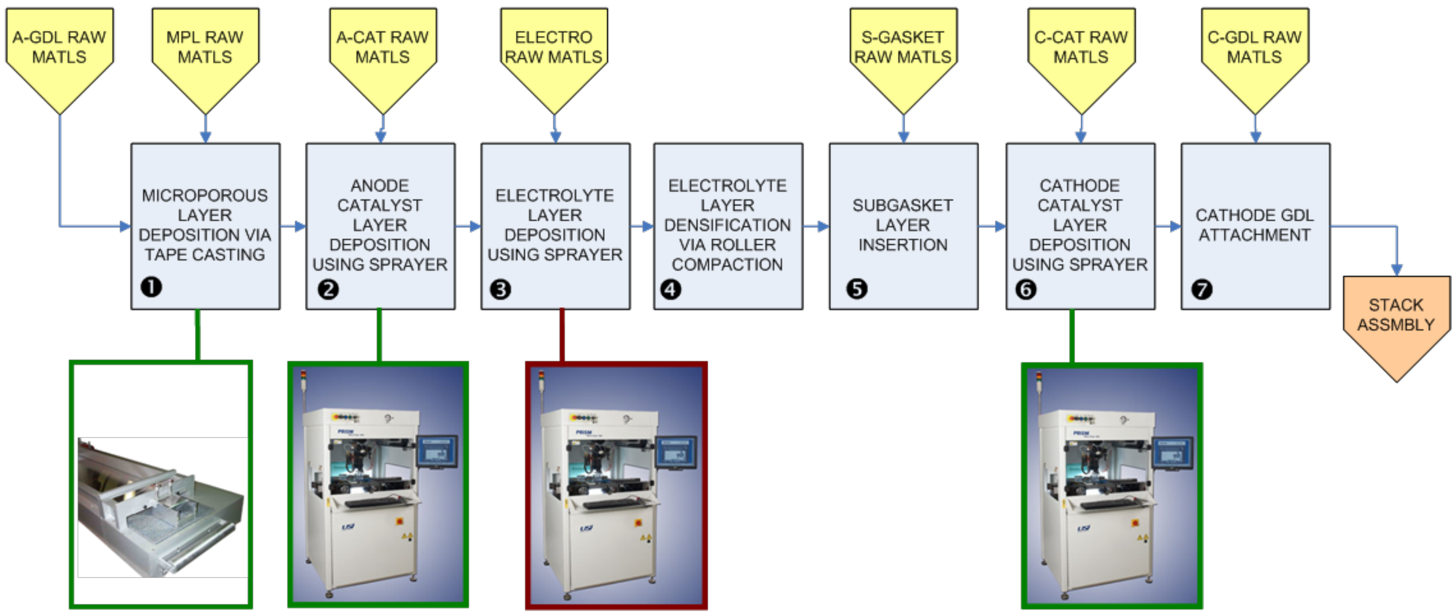


1. Micro-porous layer (MPL) deposition via the tape casting process;
2. Anode catalyst layer (ACL) deposition using a sprayer with positive displacement pumps;
3. Electrolyte layer deposition using a sprayer with positive displacement pumps;
4. Electrolyte layer densification via the roller compaction method;
5. Sub-gasket layer insertion;
6. Cathode catalyst layer deposition using a sprayer with positive displacement pumps;
7. Cathode gas diffusion layer (GDL) attachment.

SAFC Performance on Synthetic Reformate

- Minimal effect of reformate on twenty 20 cm^2 cell stack performance
  - Mostly H_2 dilution effect
  - Degradation was ~0.06%/hr on reformate
- Gas flow/compositions
  - Cathode: 7 SLPM air + 0.3 bar H_2O
  - Anode:

    Hydrogen: 2.0 SLPM H_2 + 0.3 bar H_2O

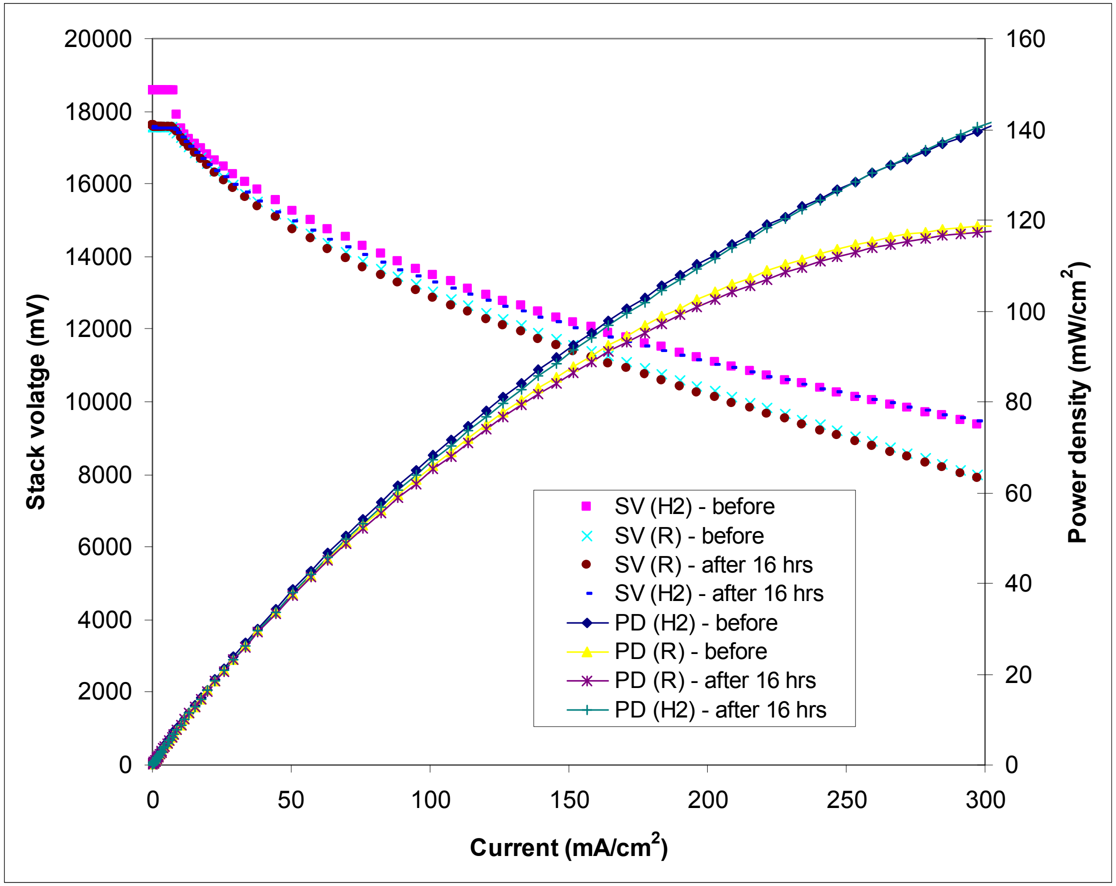
    Reformate: 4 SLPM synthetic reformate + 0.3 bar H_2O
  - **synthetic reformate:**

    50% H_2

    40% N_2

    10% CO

    100 ppm H_2S



SAFC Performance on Methanol Reformate

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- Minimal effect of reformate on twenty 20 cm² cell stack performance
  - Mostly H_2 dilution effect
- Gas flow/compositions
  - Cathode: 7 SLPM air + 0.3 bar H_2O
  - Anode:

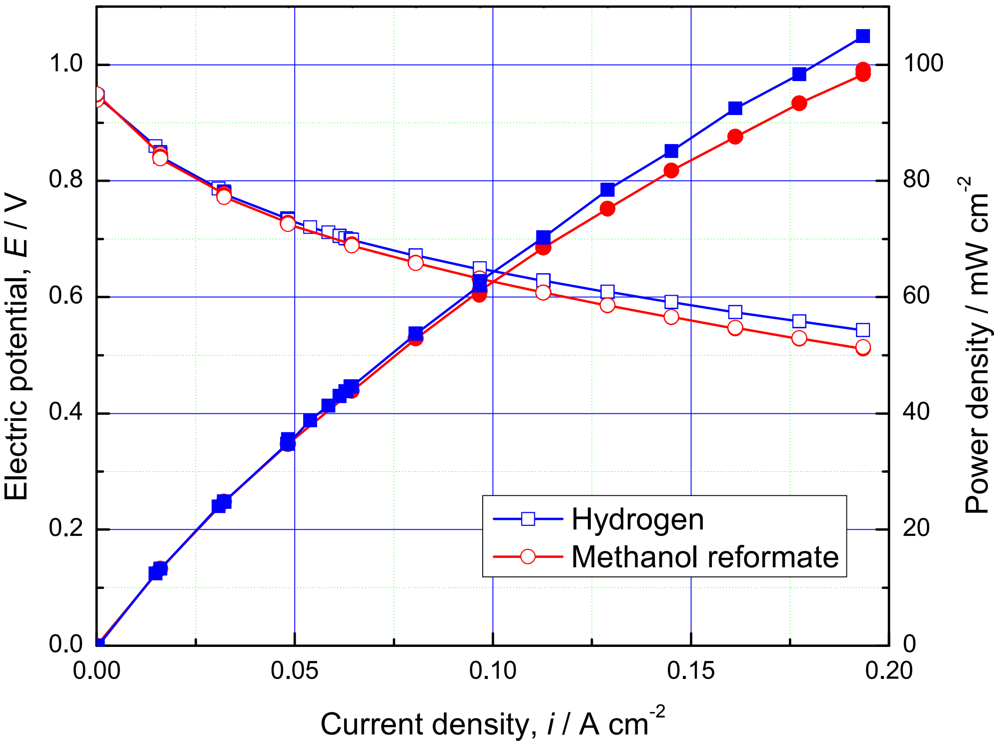
    Hydrogen: 1.0 SLPM H_2 + 0.3 bar H_2O

    Reformate: 2.8 SLPM methanol reformate + 0.3 bar H_2O
  - **methanol reformate:**

    74.2% H_2

    6.8% CO

    18.2% CO_2



SAFC Performance on Propane Reformate

- Minimal effect of reformate on twenty 20 cm^2 cell stack performance
  - Mostly H_2 dilution effect
- Gas flow/compositions
  - Cathode: 6.4 SLPM air + 0.3 bar H_2O
  - Anode:

    Hydrogen: 1.0 SLPM H_2 + 0.3 bar H_2O

    Reformate: 5.8 SLPM commercial propane reformate + 0.3 bar H_2O
  - **commercial propane reformate:**

    41.1% H_2

    34.6% N_2

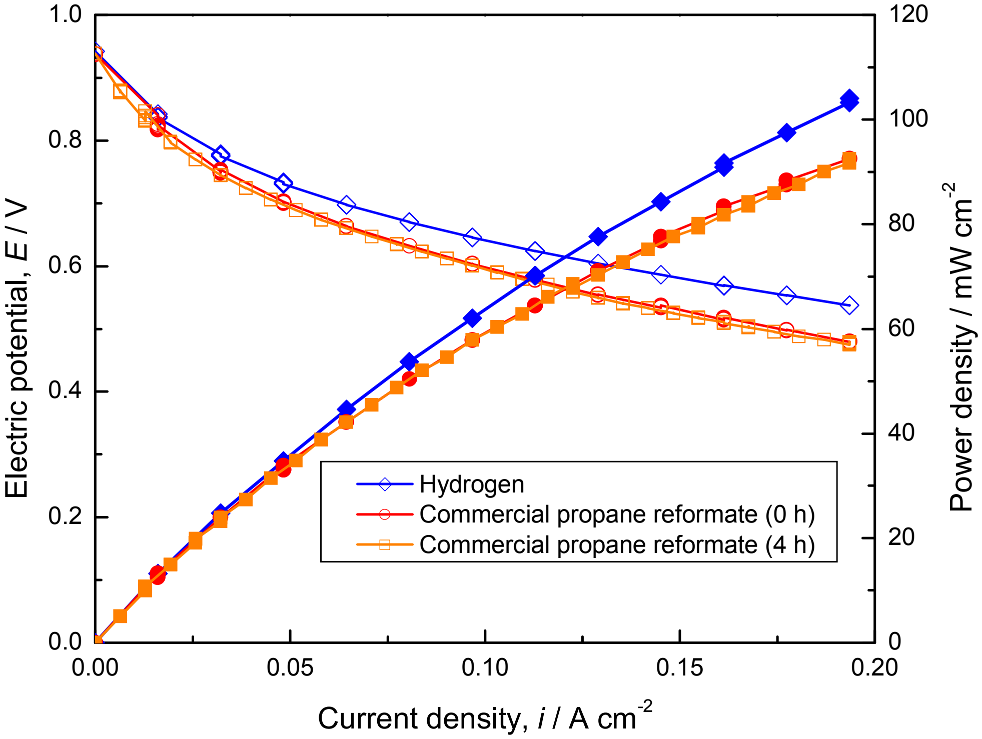
    10.6% CO

    9.84% CO_2

    0.24% CH_4

    0.005% C_3H_8

    0.5ppm H_2S



SAFC Performance on Diesel Reformate

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- Some effect of reformate on ten 20 cm^2 cell stack performance
  - Strong H_2 dilution effect
- Gas flow/compositions
  - Cathode

    3 SLPM air + 0.3 barH_2O
  - Anode:

    Hydrogen: 1.0 SLPM H_2 + 0.3 bar H_2O

    Reformate: 3.0 SLPM ultra low sulfide diesel reformate + 0.3 bar H_2O

    Ultra Low Sulfide Diesel :

    35% H_2

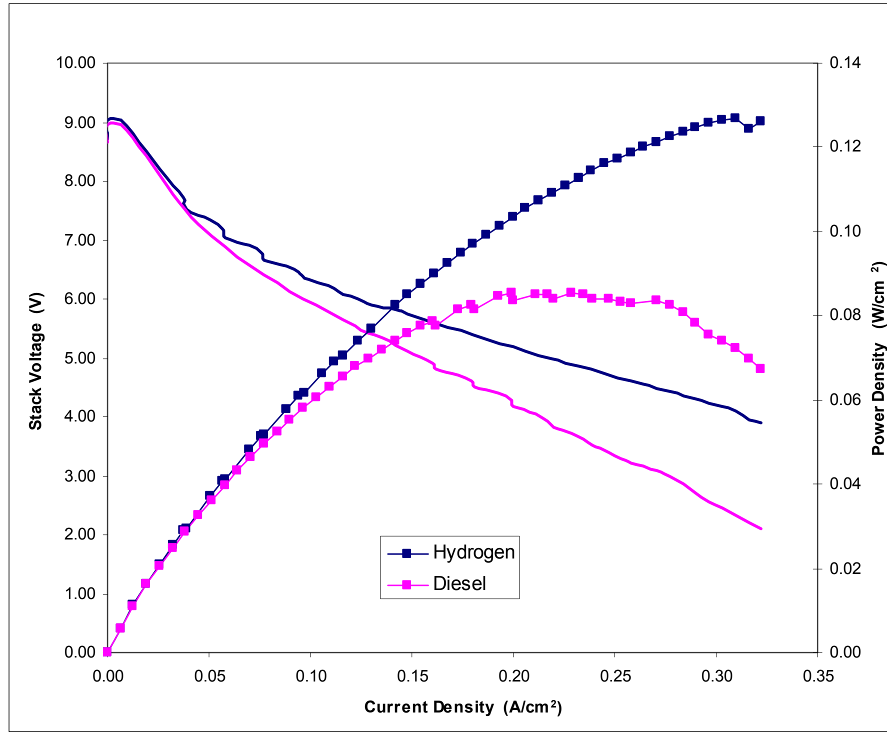
    41% N_2

    14% CO

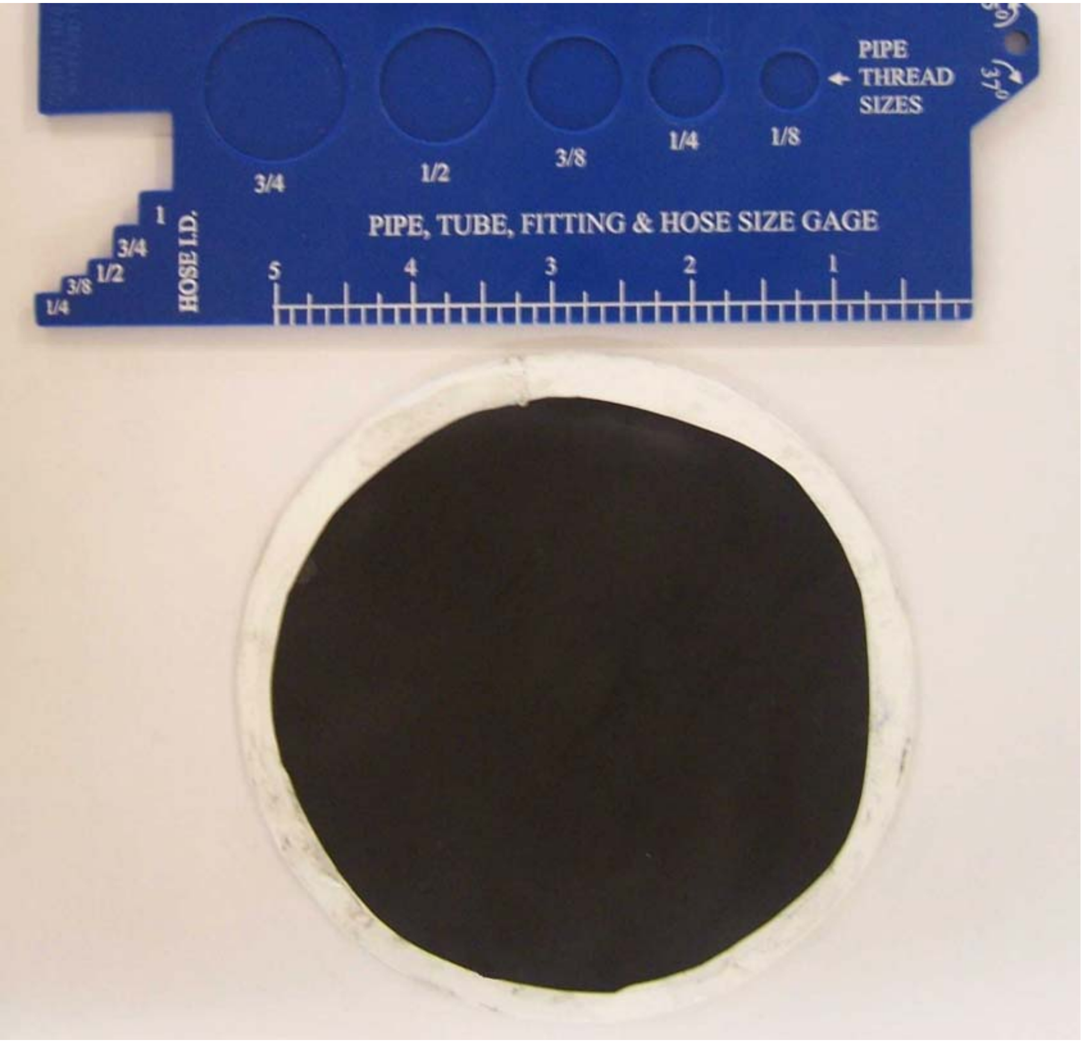
    10% CO_2

    0.3% CH_4

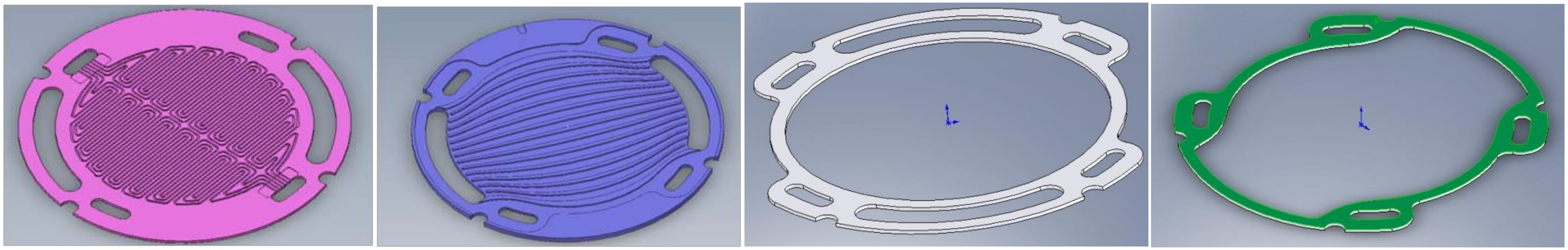
    1ppm H_2S (by Volume)

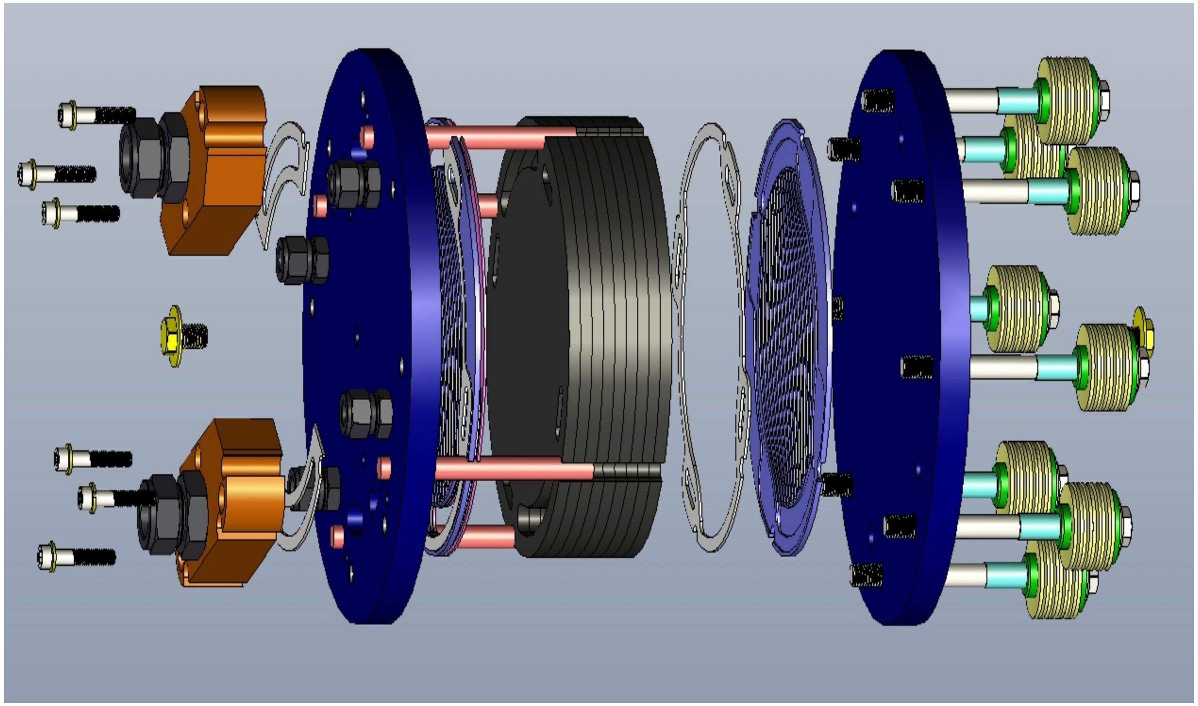


Fabrication of 125 cm^2 SAFC MEA



300 W Stack Design





- *Stack parameters**
  - *Diameter: 18 cm*
  - *Height: 11 cm*
  - *Weight: ~10 kg*

** Based on power density of 0.2W/cm²*

Flow field and pressure gradient modeling

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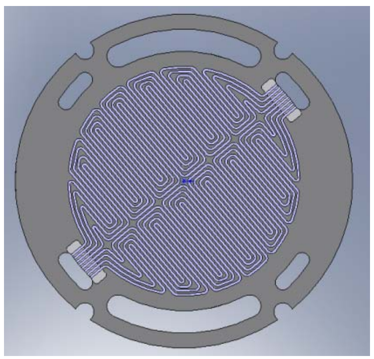
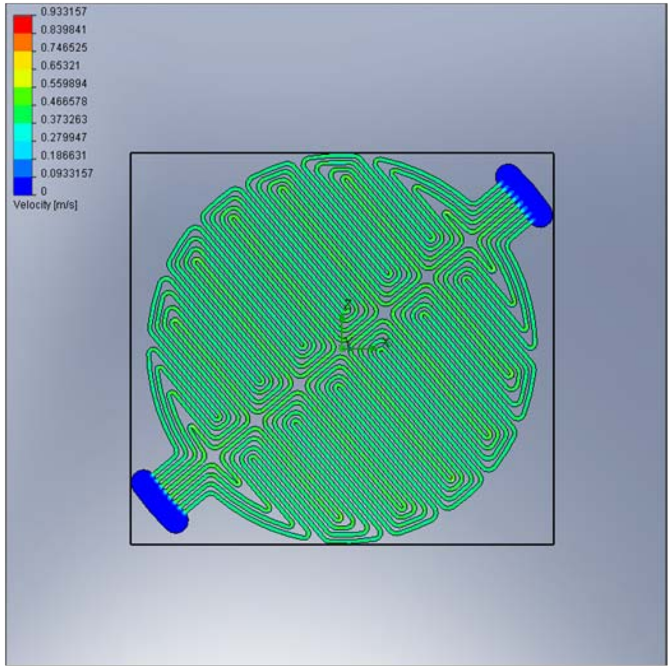
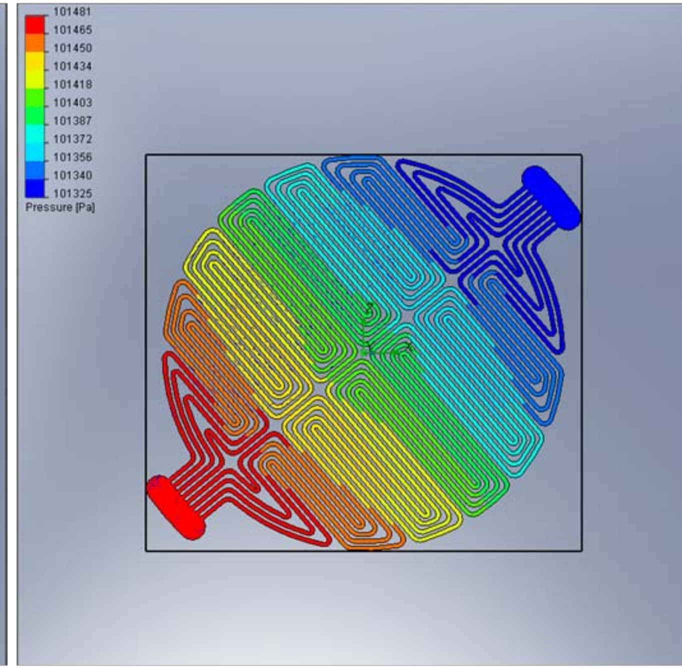
- ***Active area ~ 125 cm^2***
- ***Flow field***
  Channel depth: 0.9 mm
  Channel width: 1.1 mm
  Channel length: 68~76 cm
- ***Manifold Area: 2 cm^2***







FEA modeling suggests

- *Uniform flow distribution across electrode surfaces*
- *Uniform pressure drop between flow field channels*

300 W Stack Modeling

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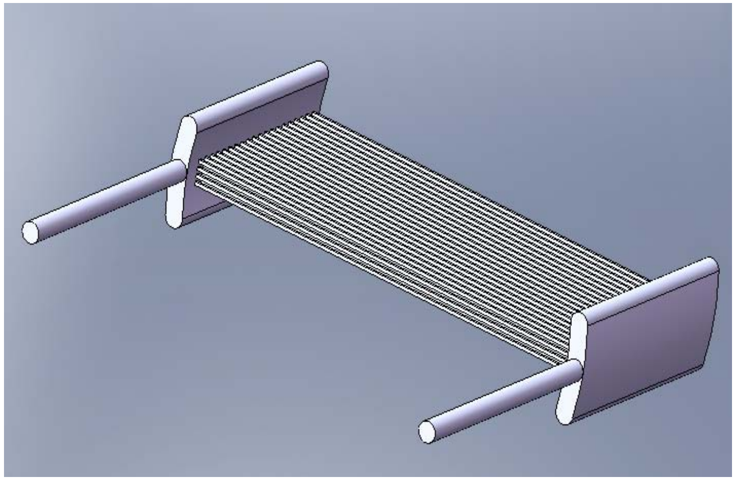

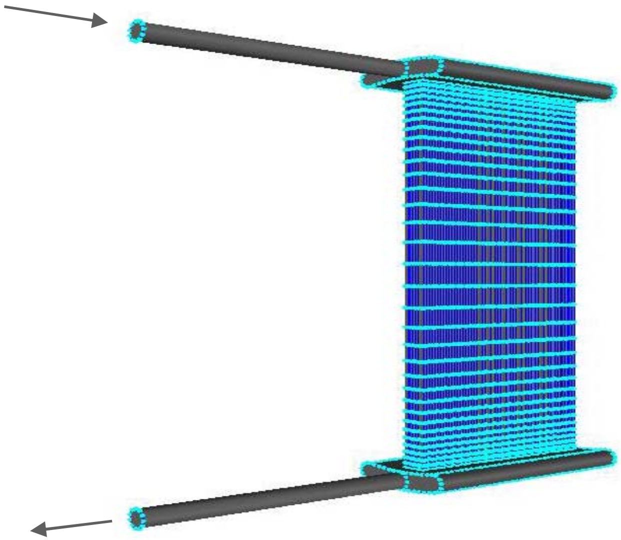

Full modeling requires too much memory, it was necessary to simplify the model

1. Straight channels replaced serpentine channels
2. Shorter channels replaced full-length channels to save memory
3. 20-cell stack was considered and each cell has four straight channels
4. Calculated velocity distribution between cells
5. Modeling geometry
    - Channel depth: 0.9 mm
    - Channel width: 1.1 mm
    - Channel length: 14~15 cm
    - Tube length: 7.6 cm
    - Manifold Area: 2 cm^2

Flow Distribution Modeling

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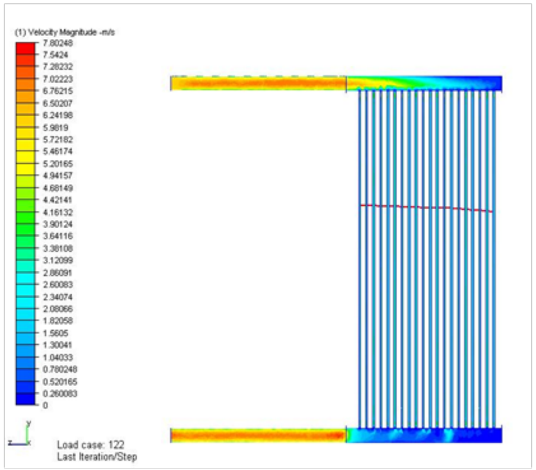
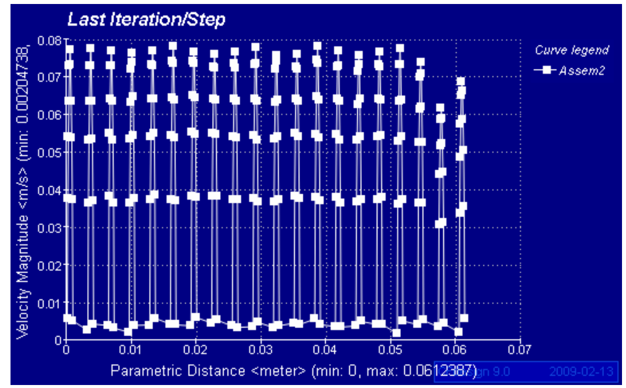
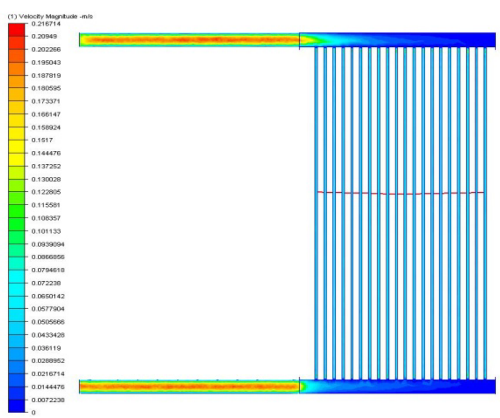
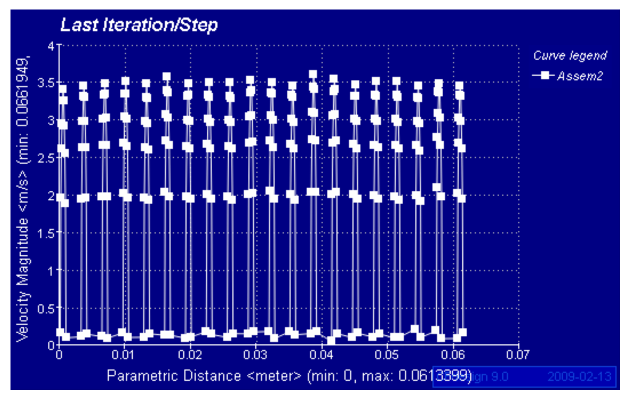
4 l/min





10 l/min





Collaborations

- **Academic**
  - Collaboration with the California Institute of Technology
    - Resource for analytical instrumentation;
    - Synthesis of CsH_2PO_4 electrolyte nanoparticles to increase the power density.
- **Industry**
  - Richard E. Mistler, Inc.
    - Determine whether the current formulation used at Superprotonics to produce micro porous layer can be scaled to production on a full length tape casting machine;
    - Develop a technique for the production with one step casting operation.

Future Work

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- FY2009
  - Continue to optimize SAFC MEA performance to levels of commercial viability
  - Build and characterize a 300W SAFC stack operating on hydrogen fuel
    - Employ micro-porous layer deposition using tape casting
    - Employ anode and cathode catalyst layer deposition using sprayer
    - Employ CDP electrolyte densification using compaction
    - Fabricate 125 cm^2 SAFC MEA using above processes
- FY2010
  - Build and characterize a 300W SAFC stack operating on diesel reformate
  - Complete conceptual design of 3 kW SAFC stack
  - Complete conceptual design of 3 kW SAFC system

Project Summary

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- **Relevance:** Demonstrate the feasibility of SAFC for energy efficient APU applications.
- **Approach:** Build and characterize 300 W SAFC stack on hydrogen and reformed diesel fuels; design 3 kW SAFC stack and system.
- **Technical Accomplishment and Progress:** Demonstrated SAFC functionality and stability on methanol, propane, and diesel fuels.
- **Technology Transfer/Collaborations:** Active partnership with the California Institute of Technology and Mistler, Inc..
- **Proposed Future Work:** Scale up SAFC MEA size and quantity; build 300 W SAFC stack; design 3 kW SAFC system.

Acknowledgements

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Superprotonic, Inc. gratefully acknowledge the support of the DOE under Cooperative Agreement Number DE-FG36-08GO88099.

This support does not constitute an endorsement by DOE of the material expressed in this presentation.

Further Information

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Supplemental Slides

Cesium Dihydrogen Phosphate
Thermal properties

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$$CsH_2PO_4 \leftrightarrow CsPO_3 + H_2O$$

- Long debated in literature
- Stability proven under water partial pressure (*P*H2O)
- How much *P*H2O to stabilize superprotonic CsH2PO4?

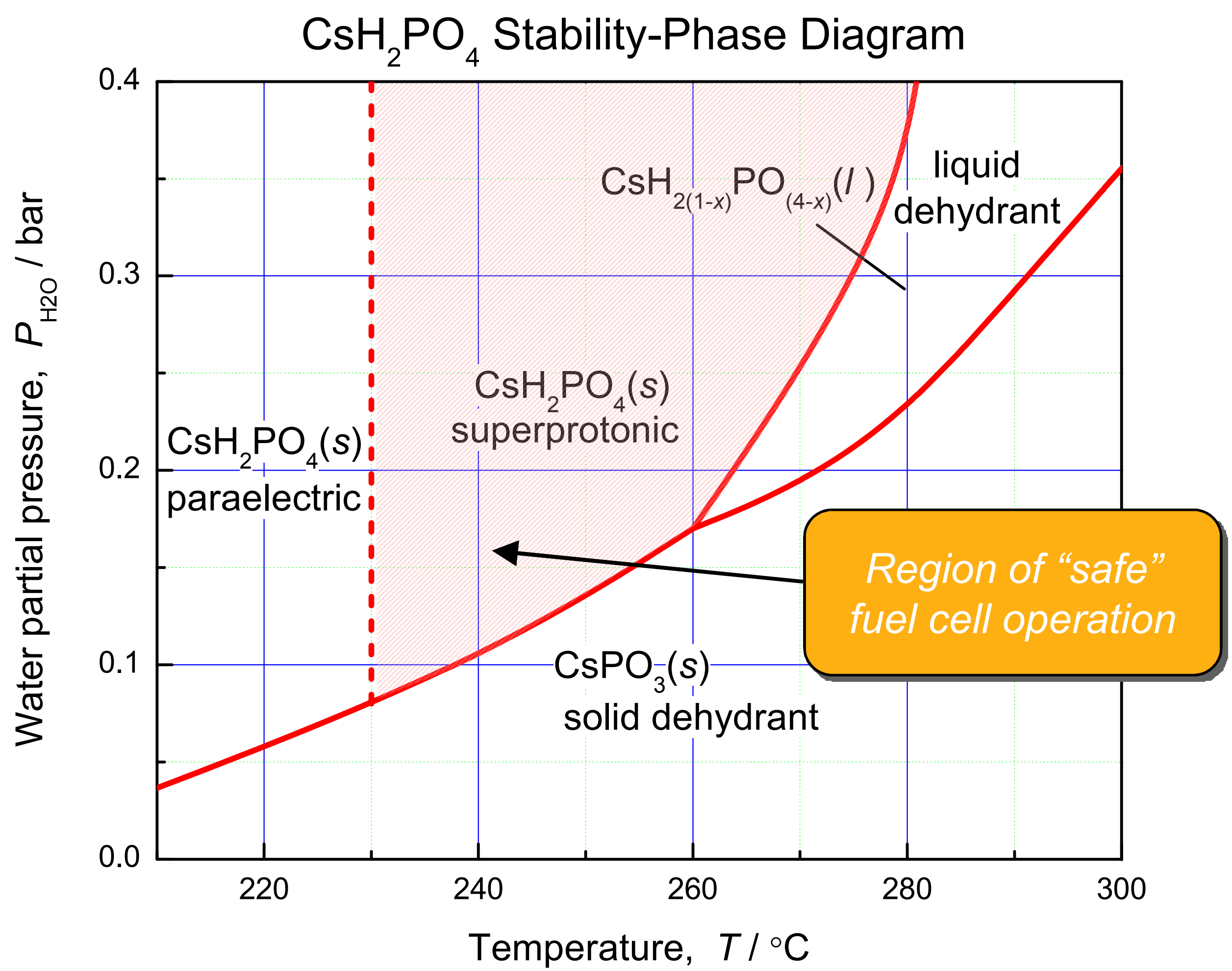
Dehydration temperature (T_d) is almost commensurate with superprotonic phase transition temperature (T_{SP}) at ambient humidity levels

$$T_d \approx T_{SP} \quad (P_{H2O} < 0.1\ bar)$$

Cesium Dihydrogen Phosphate

Humidity-temperature stability-phase diagram

Can easily avoid electrolyte dehydration with slight humidification (T_{dew} > 65 °C)



*Taninouchi, *J. Mater. Chem.*, 2007; Taninouchi, *Solid State Ionics*, 2007

Solid Acid Fuel Cells

Ammonia tolerance (100 ppm NH_3)

SAFC stable under 100 ppm NH_3