Nanocomposite Electrodes for a Solid Acid Fuel Cell Stack Operating on Reformate

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Project Team and Objectives

ARPA-E REBELS Category 1 Project

Project Outline
100 W stack prototype

CsH₂PO₄ electrolyte

Reformed natural gas fuel

Major Objectives
Electrical Efficiency > 50%

Pt loading < 0.1 mg/cm²

Current > 225 mA/cm² at 0.78 V
Superprotonic Solid Acids

Hydrogen-bonded ionic solids
Polymorphic phase transitions at $T>100 \, ^\circ\text{C}$
$H^+$ conductivity increases $>1000x$ across phase transition
Water soluble

$\text{CsH}_2\text{PO}_4$ (CDP)

Proton Conducting Oxides
Crystal Symmetry Controls H$^+$ Conductivity

Paraelectric (RT)

- 4 Oxygen sites per unit cell
- 4 H-bonds (----) possible per tetrahedron

Superprotonic (>228 °C)

- 24 Oxygen sites per cell, each with 1/6 occupancy
- 6 H-bond (----) orientations possible per tetrahedron
Proton Transport in Superprotonic CDP

Bulk proton transport includes both oxyanion reorientation and hydrogen bond transfer.
Water solubility
- Must keep humidity below dew point of water
- $P_{H_2O} < P_{H_2O}(T_{dew})$

Superprotonic transition temperature
- No fuel cell operation until $T > 231^\circ C$
- Requires independent system for heating upon start-up

Dehydration temperature
- Both fuel and air streams must be hydrated
- Maximum operating temperature $T_{dehyd} \sim 280^\circ C$
Solid Acid Fuel Cells (SAFC)  
CsH₂PO₄ Electrolyte, Pt Catalysts

![Circular Shapes with Active Areas](image)

**Circular**
- 3/4" D = 1.5 cm² active area
- 2" D = 15 cm² active area
- 5" D = 110 cm² active area

**Rectangular**
- 7 x 9 = 50 cm² active area
- 10 x 15 = 125 cm² active area

![Graph](image)

**Graph Information**
- T = 250°C
- pH₂O = 0.3 atm
- H₂/Air = 1.2/2 @ max current

**Cell Voltage [mV]**
- 1100
- 1000
- 900
- 800
- 700
- 600
- 500
- 400

**Current Density [mA/cm²]**
- 500
- 400
- 300
- 200
- 100
- 0
SAFCell SAFC Products
10 W to 1,500 W stacks

Portable power

Premium & auxiliary power

10-100W 100-300W 500-1500W

Stack power

Aluminum and stainless steel hardware, polymer seals
Light-off T > 450 °C

O/C ratios control reforming process
  - low: steam reforming (endothermic)
    - low CH₄ conversions, H₂ yields
  - high: partial oxidation (exothermic)
    - high CH₄ conversions, H₂ yields
Reformer Efficiency Greater Than 80%

Optimal efficiency at O/C = 1
- 85% fuel energy converted to H₂ (LHV basis)
- 98% inlet fuel energy converted to H₂ if all CO shifted to H₂ over downstream WGS catalyst

WGS catalysts can be integrated into MEA
## System flows, Compositions, Temperatures

<table>
<thead>
<tr>
<th>Flow (slpm)</th>
<th>Gas</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.37</td>
<td>CH4</td>
<td>16%</td>
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<tr>
<td>0</td>
<td>CO</td>
<td>0%</td>
</tr>
<tr>
<td>1.1</td>
<td>H2O</td>
<td>47%</td>
</tr>
<tr>
<td>0.18</td>
<td>O2</td>
<td>8%</td>
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<td>0.69</td>
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<td>H2</td>
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<tr>
<td>0.14</td>
<td>CO</td>
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<tr>
<td>0.88</td>
<td>H2O</td>
<td>30%</td>
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<tr>
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<td>CO2</td>
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<tr>
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<tr>
<td>1.1</td>
<td>H2</td>
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<tr>
<td>0</td>
<td>CO</td>
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<td>0.74</td>
<td>H2O</td>
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<tr>
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**Diagram:**
- **Preheater/Vaporizer:** 25 °C, 200 °C, 230 °C
- **Heat Exchanger:** 230 °C
- **Reformer:** 500 °C, 550 °C
- **WGS Catalyst:** 25 °C, 230 °C
- **SAFC Stack:** 100 W electricity
- **100 W Electricity:** 230 °C
SAFC Anodes


CO, CO\textsubscript{2} and H\textsubscript{2}S Tolerance at the Stack Level

- Minimal effect of impurities on performance
  - Mostly H\textsubscript{2} dilution effect
  - 20 cell stack (2” MEA)

- Gas flow/compositions
  - Cathode:
    1.5 LPM air + 0.3 bar H\textsubscript{2}O
  - Anode
    0.6 LPM + 0.3 bar H\textsubscript{2}O

- Stack stability under high CO & H\textsubscript{2}S confirmed
  - 5.3% CO & 200ppm H\textsubscript{2}S

![Graph showing average cell voltage over elapsed time]

- 20 cell SAFC stack
- T = 240\degree C
- pH\textsubscript{2}O = 0.3 atm
- 100mA/cm\textsuperscript{2}
State-of-the-Art SAFC Cathode
Pt is the ORR catalyst and the sole electronic phase
Electrolyte Surface Area Has Large Effects on Cathode Performance

Baseline Cathodes at Lower Pt Content

Sub-critical Pt coating limits e\textsuperscript{-} pathways

"Mixed conductor" eliminates the problem of conductivity loss at low Pt content
Advanced Cathode Architecture
Very recent results suggest improvement to parity with SOTA electrode performance at 0.7 mg cm$^{-2}$.
Carbon Corrosion Must Be Confronted

Chemical stability of MWNTs is adequate...

...But electrochemical stability is the issue

\[ C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \]

1.0 V, 250 °C, 75 °C dew point, N₂

Graphitized MWNTs

TGA, air, 10 °C/min

~450 °C

~575 °C

250 °C
Pt Particles Coarsen During Operation

Lower Pt content in advanced electrodes may mitigate this effect

Graphite

\[ \text{Intensity [arb. units]} \]

\[ \text{2θ [degrees]} \]

4 nm \( \rightarrow \) 8 nm

- fresh 60%Pt/g10
- 60%Pt/g10 24 hrs FC @ 250 C
- 60%Pt/g10 500 C 1 hr heat treatment

250 C Fuel Cell Operation
Advanced Cathodes Over 100+ hrs

0.6 V, 250 °C,
75 °C dew point
H₂-air 30/75 sccm

Current Density [mA cm⁻²]

5%Pt@(7.5:1 CDPi:O+)
0.7 mg cm⁻²

Elapsed Time [h]
Summary

- ORNL, UTK, and SAFCell are developing a reformed NG fuel cell system based on the CsH₂PO₄ electrolyte.

- Anodes have low impedance and are impurity tolerant.

- Cathode activity is a key obstacle.

- Nanocomposite electrode architectures using MWCNTs suggest 75% reduction in Pt is possible.
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Hau Duong
Mandy Abbott
Fernando Campos
Project Summary

Timeline
Project start date: 10/1/14
Project end date: 9/30/17*
*project continuation determined annually by DOE
Percent complete: 20%

Budget
Total project funding: $3050k
  Federal share: $2750k
  Recipient share: $300k
FY15 amount: $1002k

Partners
University of Tennessee
SAFCell, Inc.

Barriers
Reduction of Pt loading
  Target: 0.1 mg/cm²
Cathode Activity
  Target: 225 mA/cm² at 0.78 V