Proton Conductor Based Solid Oxide Fuel Cells

S. Elangovan, J. Hartvigsen, F. Zhao,
D. Ramirez, B. Heck, and D. Larsen

10th Annual SECA Workshop

Pittsburgh, PA
14 July 2009
Supported by DOE SBIR Grant: DE-FG02-06ER84595

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Outline

- Thermodynamic Analysis Shows Higher Efficiency for Proton Cells compared to Oxygen Cells
- Stability addressed by the use of composite electrolyte
- Anode supported composite electrolyte cell shows good performance
- Stability in high CO_2 containing fuel demonstrated

Thermodynamic Analysis

- Cell Reversible Potential is

$$E = \frac{-\Delta G}{nF}$$

- Gibbs Energy For $H_2 + 1/2O_2 \rightarrow H_2O$

$$\Delta G = \Delta G^{\circ}(T) + RT\ln\left(\frac{a_{h2o}}{a_{h2}\sqrt{a_{o2}}}\right)$$

- Gibbs Energy For a Hydrogen Concentration Cell

$$\Delta G = RT\ln\left(\frac{a_{h2-cathode}}{a_{h2-anode}}\right)$$

- Cathode Hydrogen Activity

$$K_a = \left.\frac{a_{h2o}}{a_{h2}\sqrt{a_{o2}}}\right|_{cathode}$$

- Substitution Gives for a proton cell:

$$\Delta G = -RT\ln(K_a) + RT\ln\left(\frac{a_{h2o-cathode}}{a_{h2-anode}\sqrt{a_{o2-cathode}}}\right)$$

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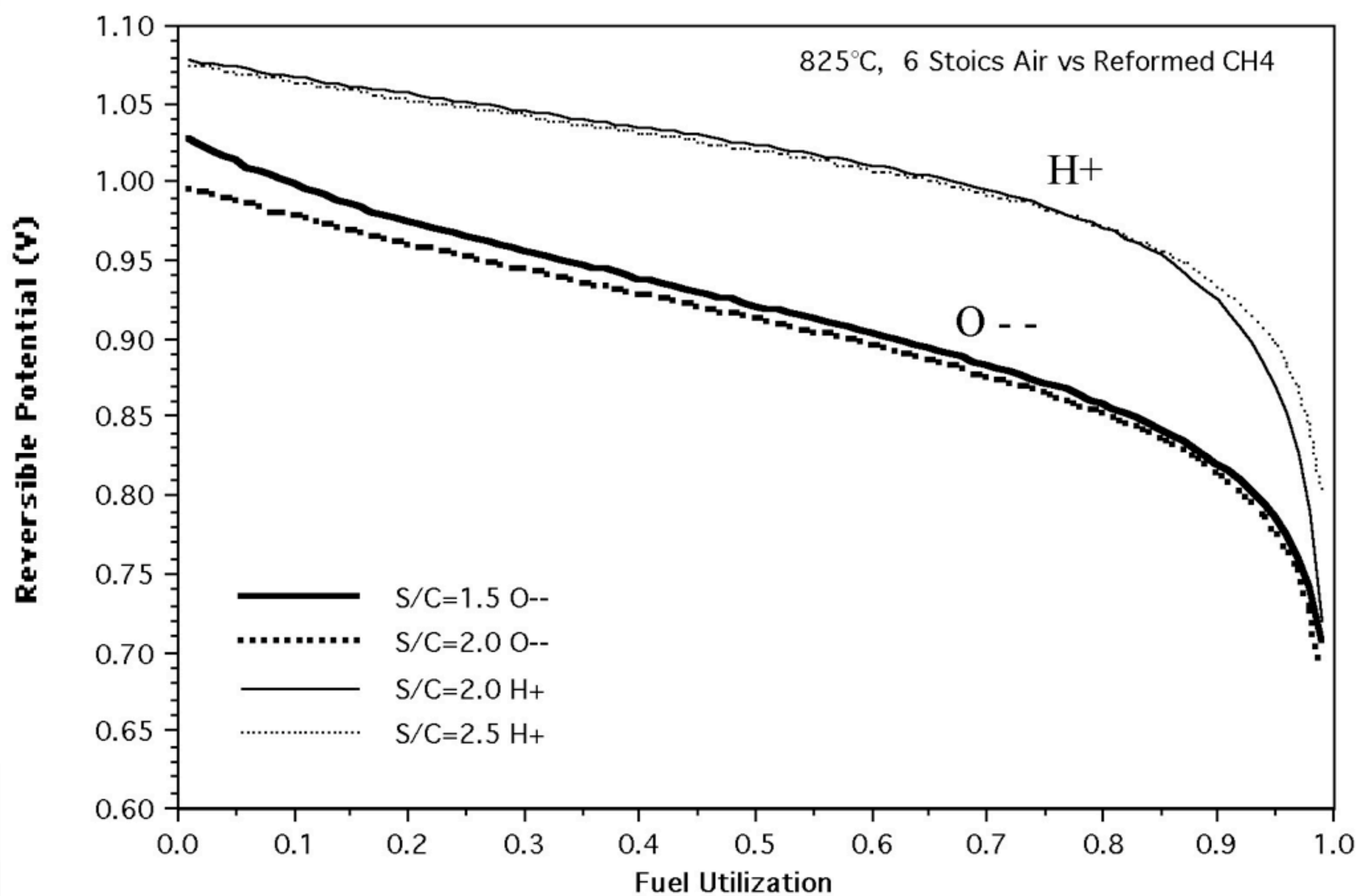
Driving Force Comparison



- High driving force even at high fuel utilization

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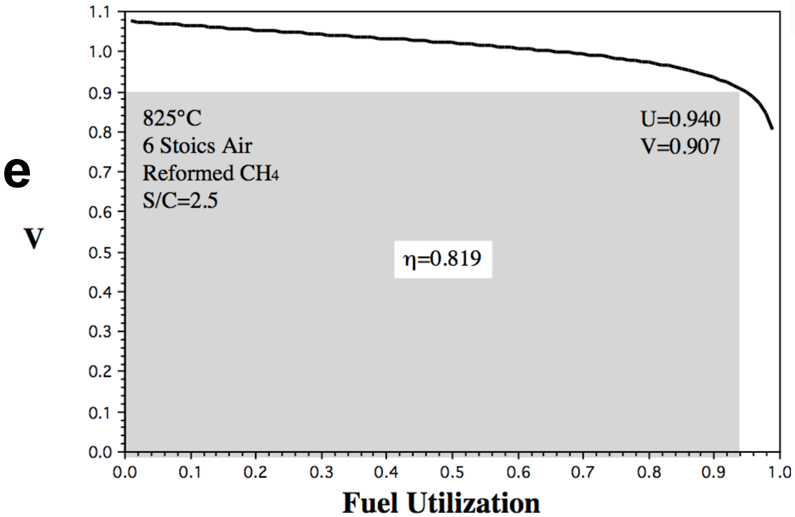
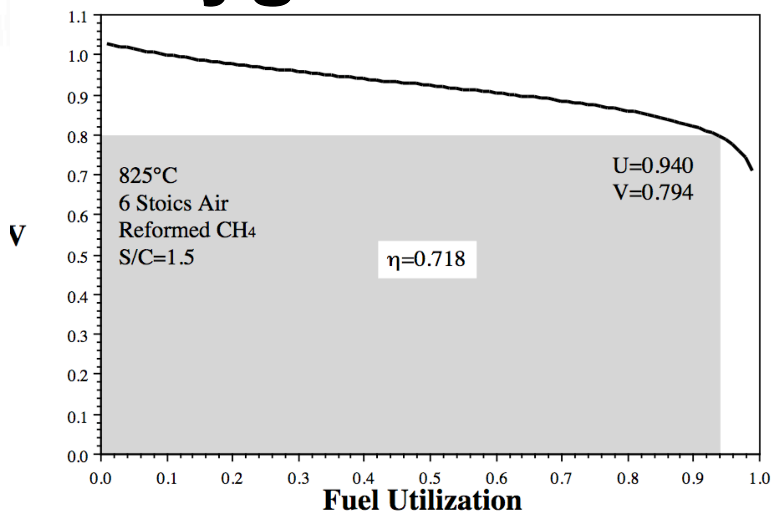
Max. Efficiency Comparison

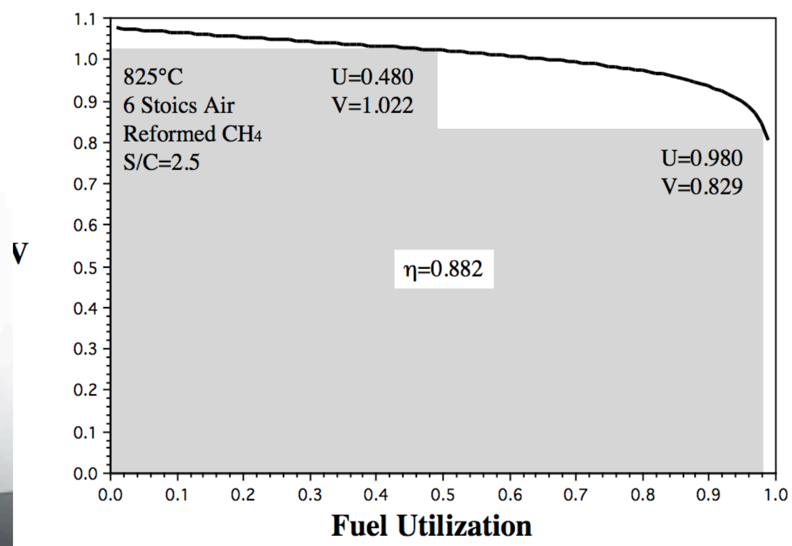
- **Proton Cell**
- **Oxygen Cell**

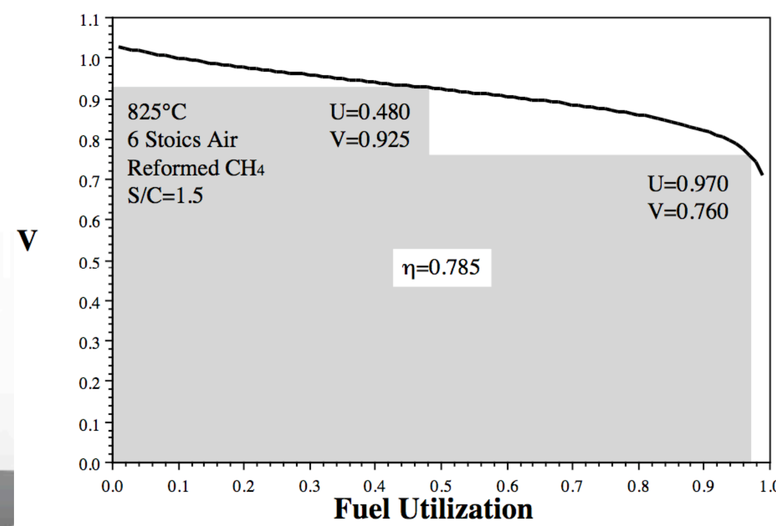
Single Stage





Two Stage





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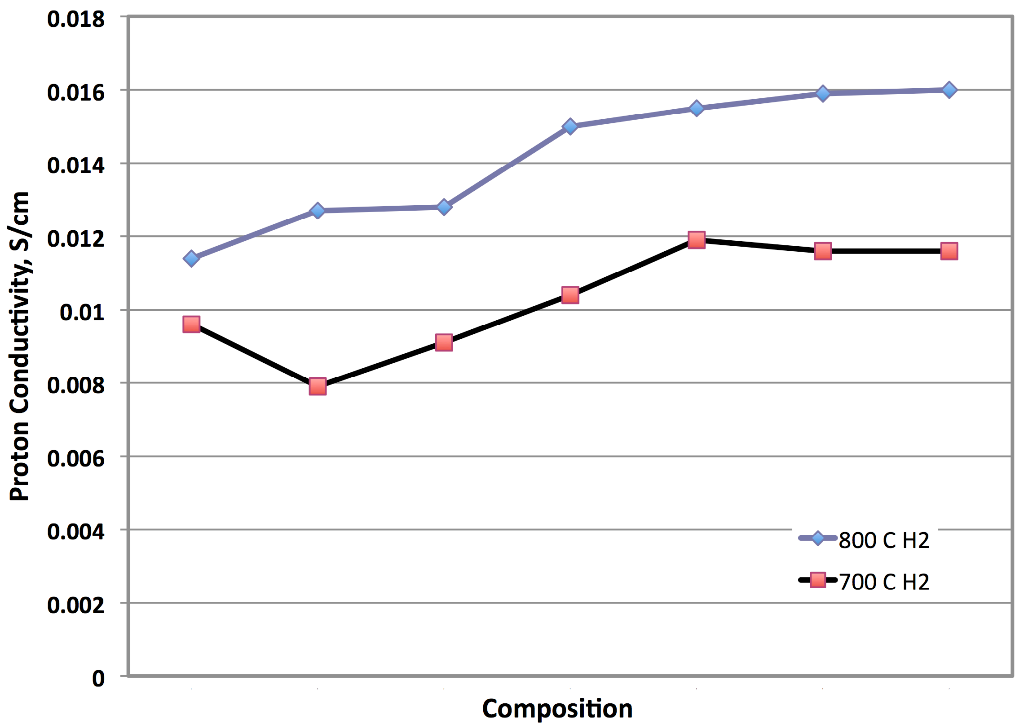
$BaCeO_3$ Proton Conductivity



- Highest conductivity range from 0.01 to 0.016 in 700° to 800°C range
- ~ half the oxygen ion conductivity of 8YSZ

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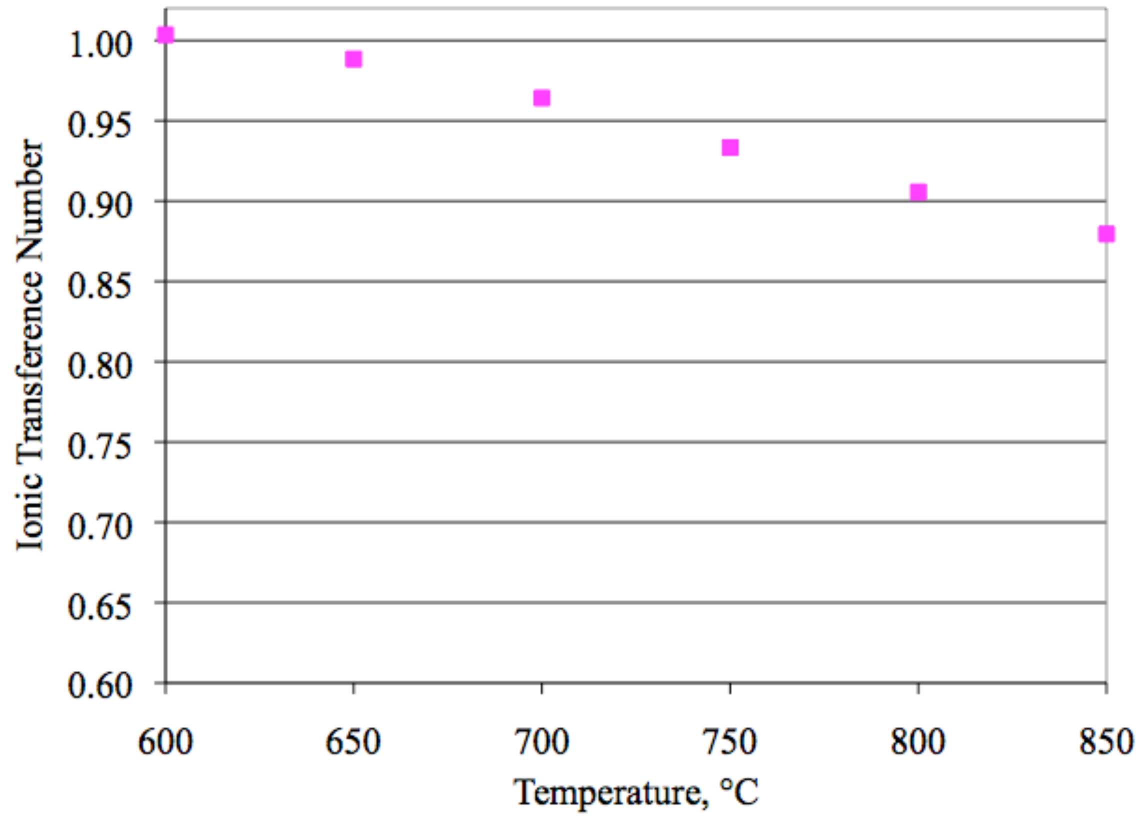
Ionic Transference Number



- $BaCe_{0.8}Y_{0.2}O_{3-\partial}$ measured using a concentration cell

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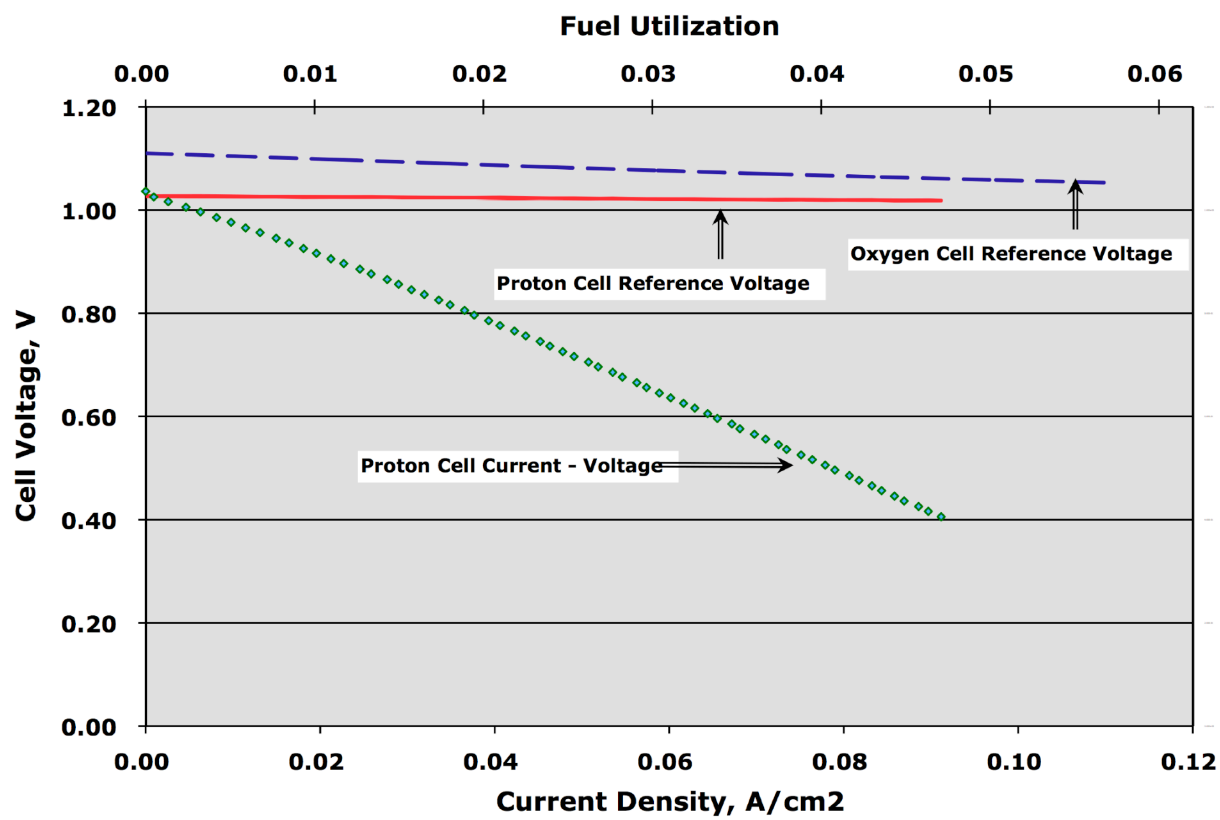
Comparison of Driving Force

0.5 mm thick pellet of BCY (800°C)



- Proton cell shows negligible change in driving potential compared to Oxygen cell

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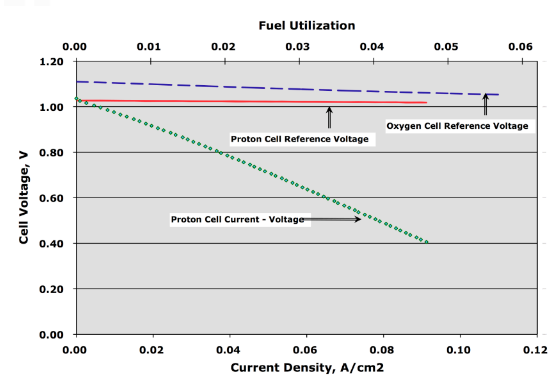
Observations

- OCV for P-SOFC is lower at 800°C, but approaches O-SOFC at lower temp.
- Even with lower OCV, the Nernst potential crosses over at utilization of >10%
- Absolute value of proton conductivity in $BaCeO_3$ is lower than the oxygen conductivity in YSZ
  - Generally electrode losses dominate cell performance



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Instability of Perovskite

- Stability of $BaCeO_3$ in hydrocarbon based fuel is a major known issue

$$BaCeO_3 + CO_2 = BaCO_3 + CeO_2$$

$$BaCeO_3 + H_2O = Ba(OH)_2 + CeO_2$$

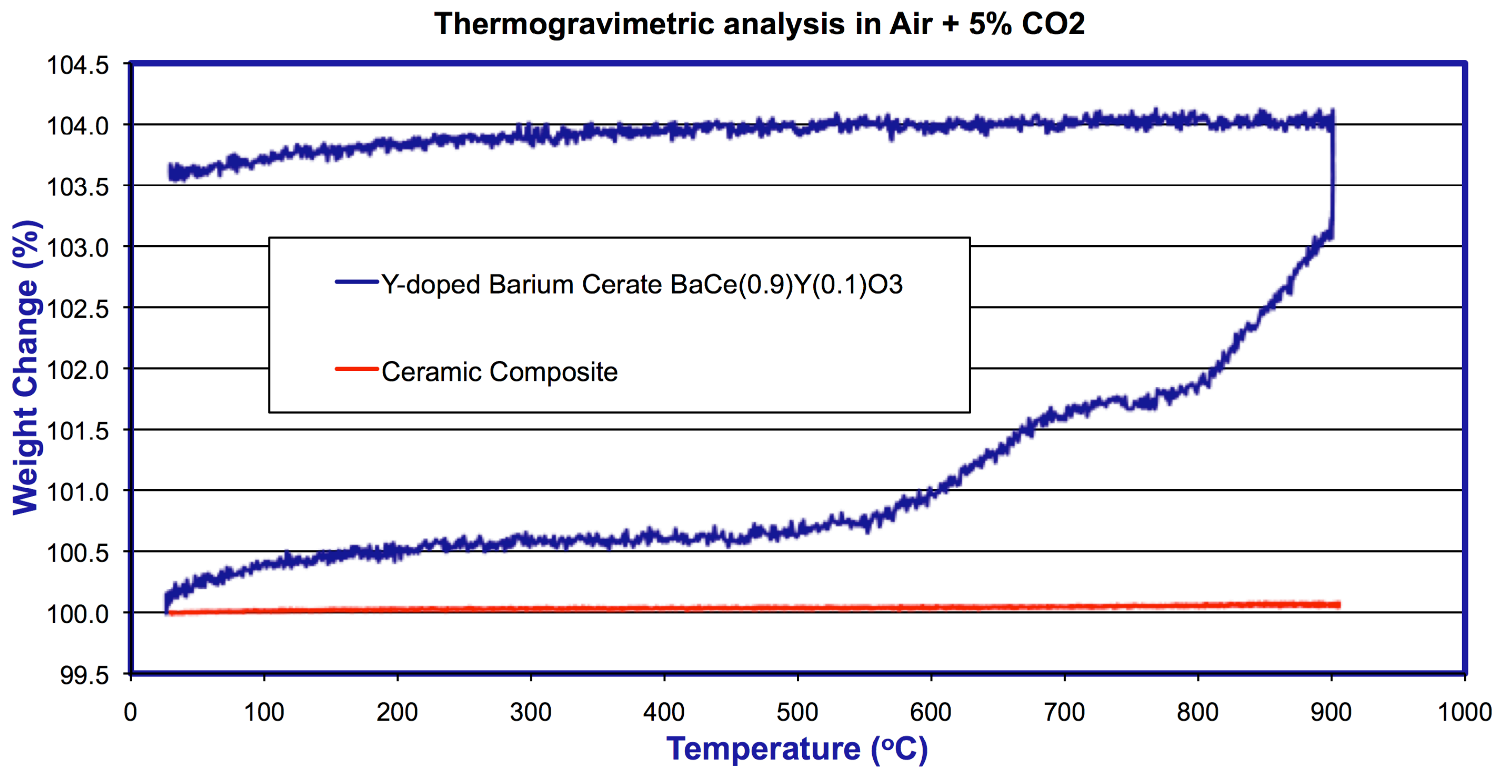
Reaction Product: CeO_2

- Traditional use for its high oxygen ion conductivity
- Challenging as solid oxide fuel cell electrolyte due to mixed conduction in fuel atmosphere

Composite of BCY + YDC ??

Enhanced Thermochemical Stability

Ceramic Composite over BCY



- **Stability in CO_2+Air mixture (TGA)**
  - **BCY + YDC (crushed sintered disk)**

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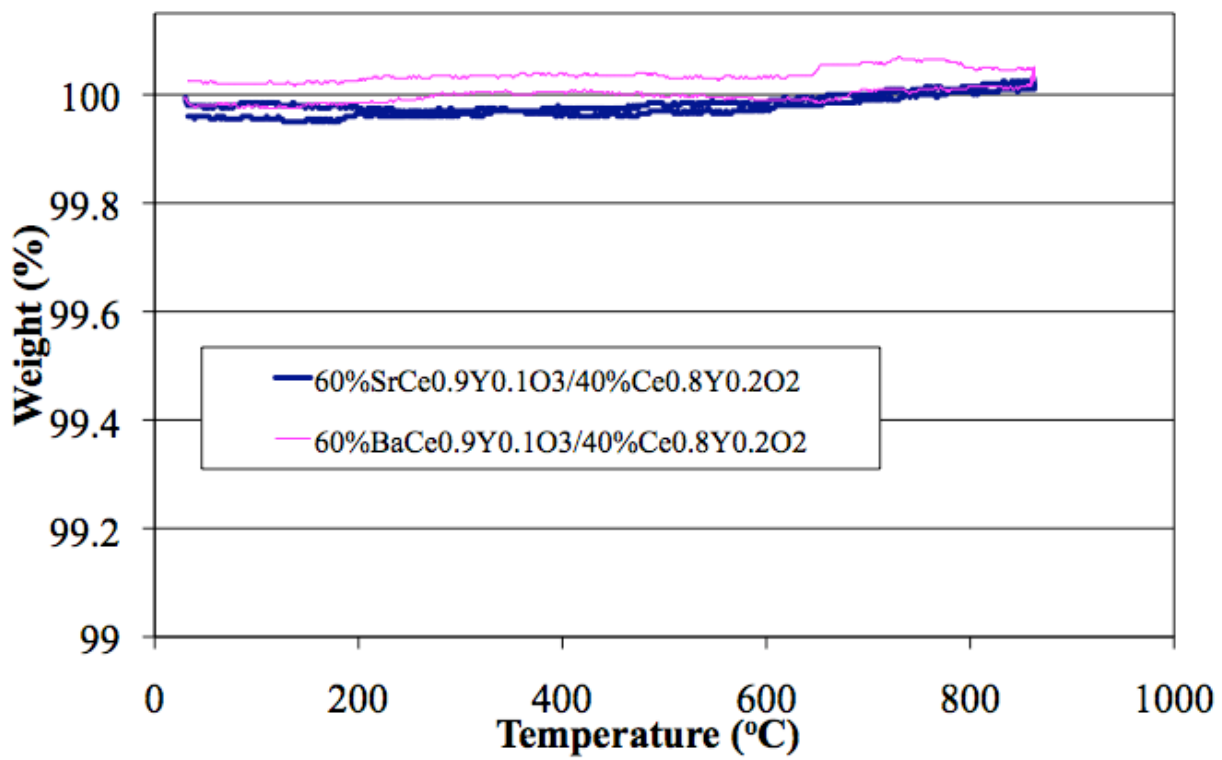
Composite Stability in Syngas



- **Stability in CO-CO_2-H_2-H_2O mixture**

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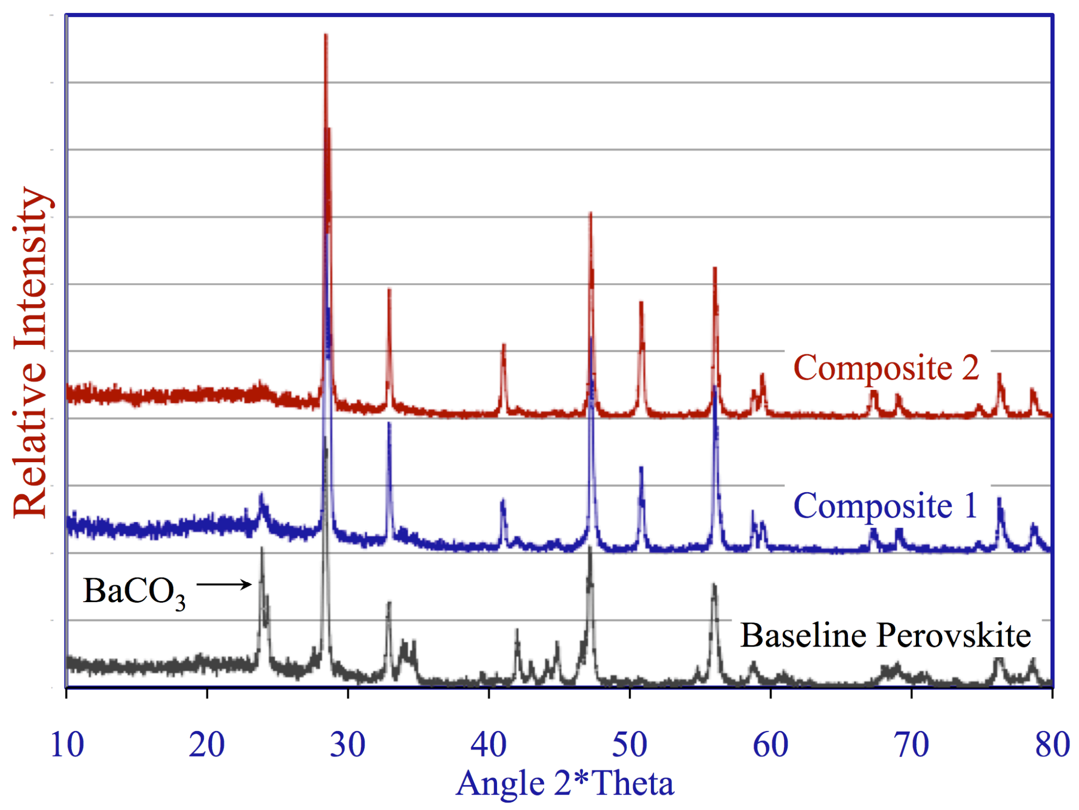
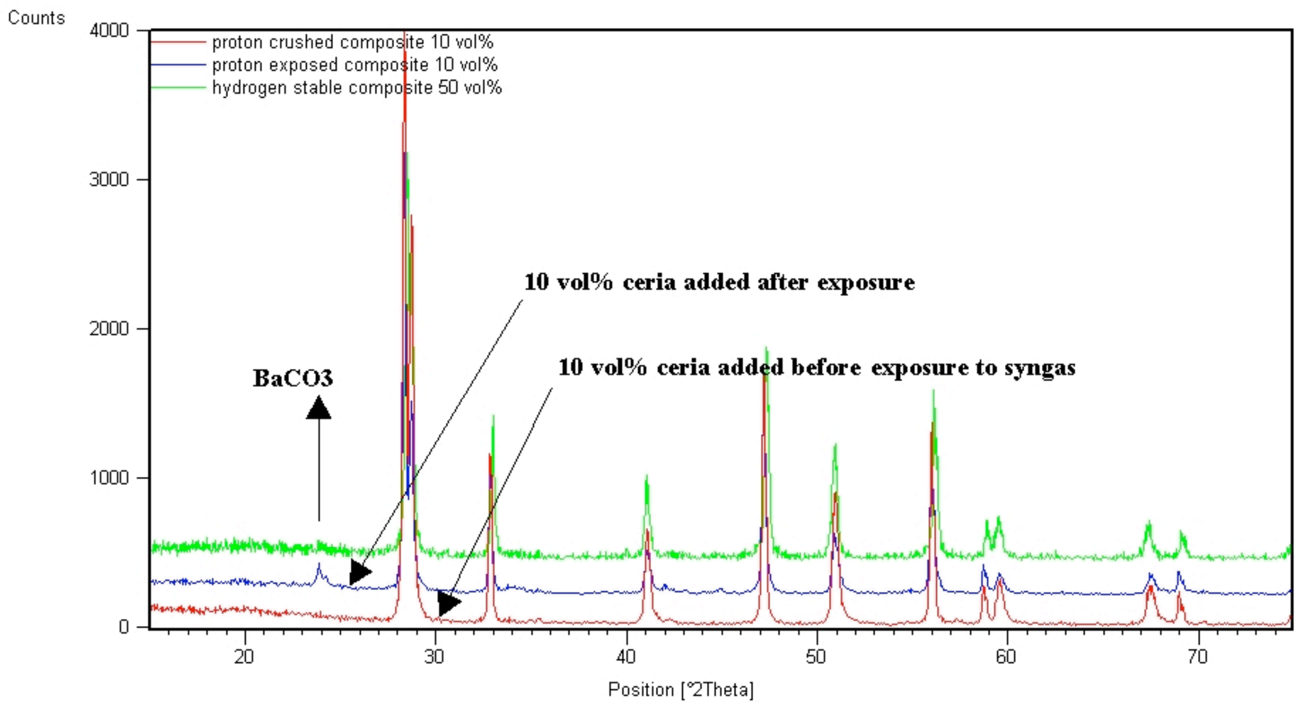
$BaCeO_3$ vs Composite Stability



- Exposure to syngas at 900°C

Exposure to Syngas at 700°C



- As low as 10 vol% Ceria shows improvement in stability

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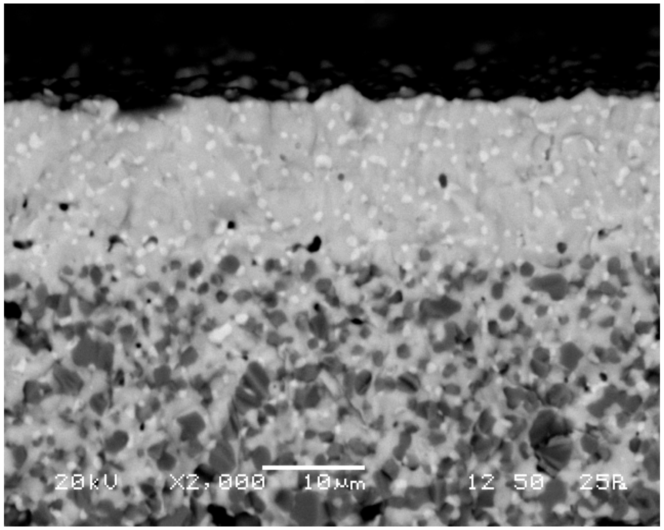
Anode supported thin film cell

Cell before testing

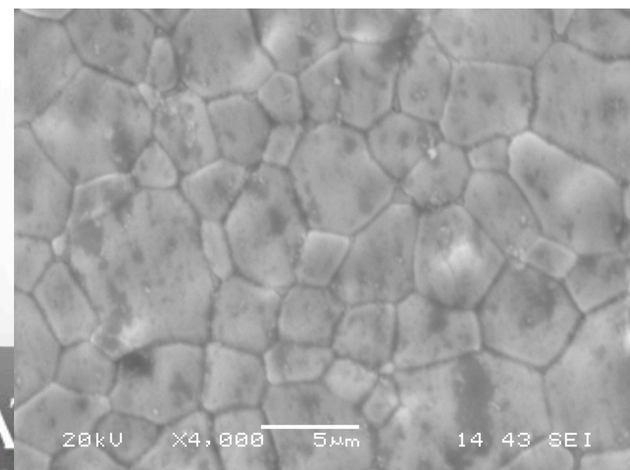


Dense thin film (~15 μm) BCY+YDC composite electrolyte

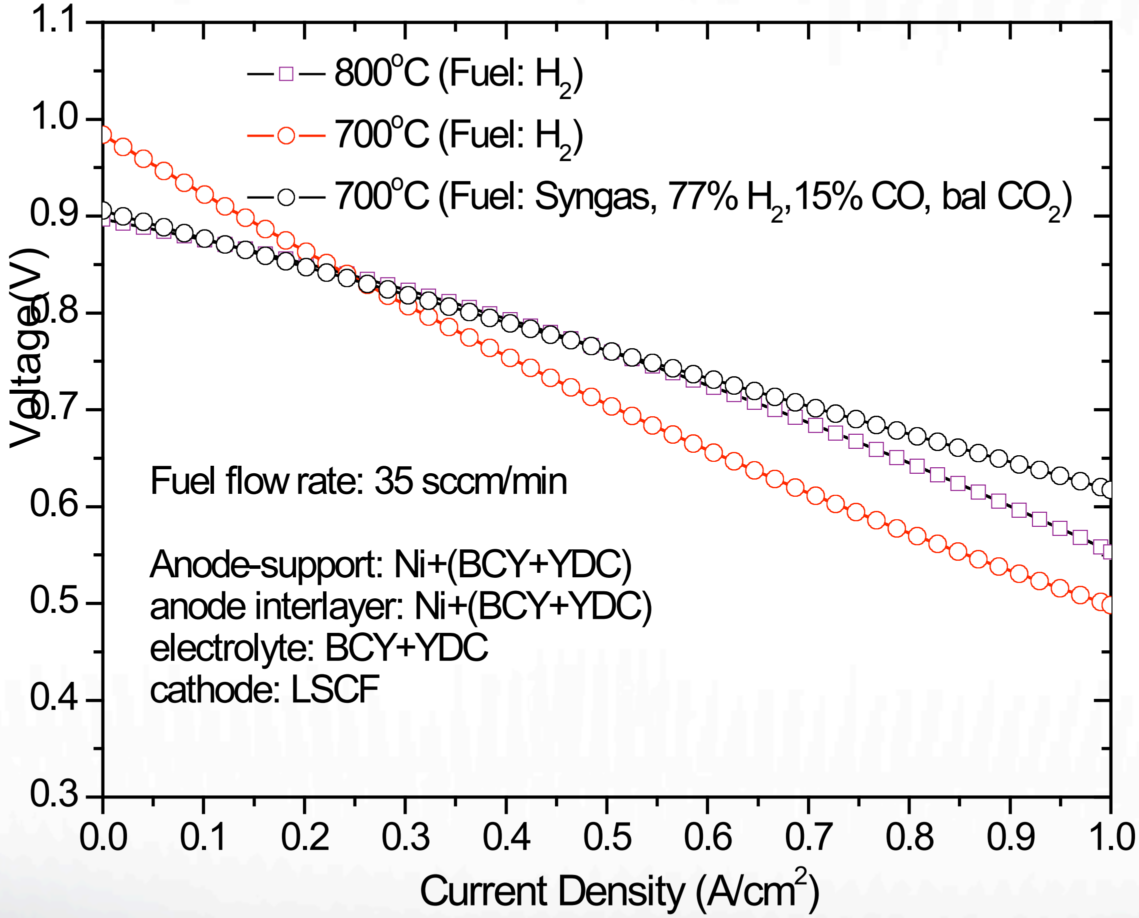
Anode: 50 wt% NiO and 50 wt% (BCY+YDC)

Cell after testing

Electrolyte surface



Anode supported P-SOFC



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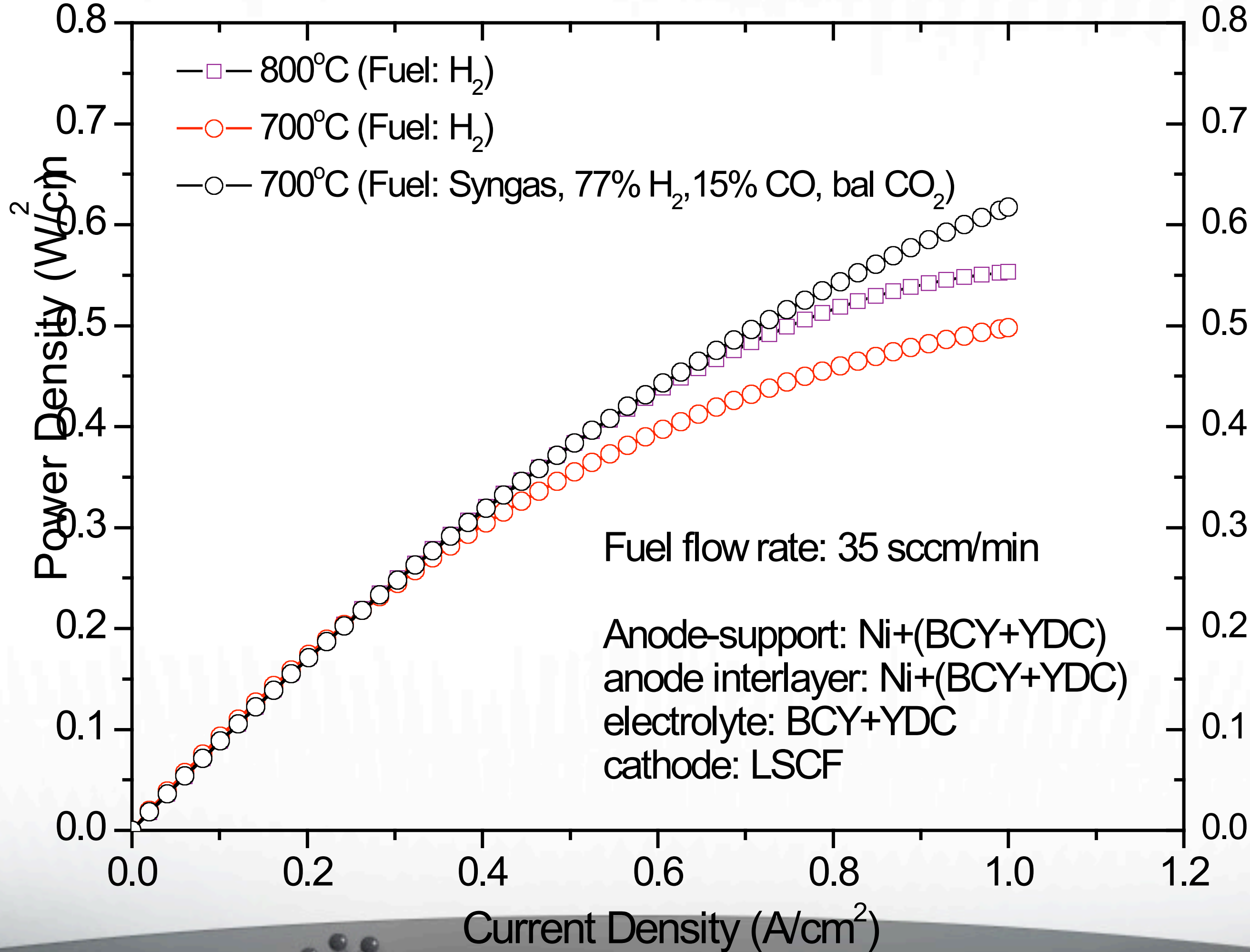
Anode supported P-SOFC



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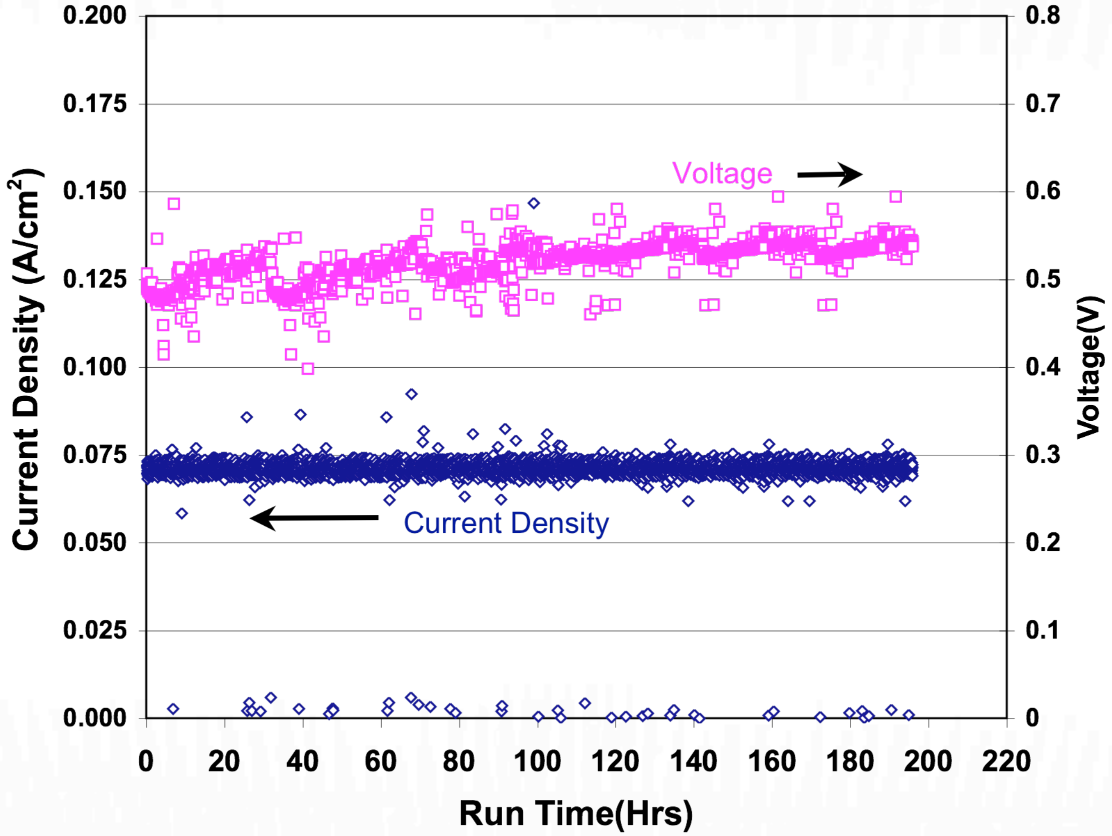
Stability in Syngas



- Fuel: Simulated high utilization (90% CO_2 - balance humidified H_2)

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Conclusions

- Proton SOFC shows high efficiency possibility
- Practical compositions requires operating temperatures of 700°C or below to realize high t_H
- Relatively lower proton conductivity requires thin, supported electrolyte cells
- Proton Cells Can Effectively Use CO Via the Water Gas Shift Reaction
- Chemical stability in syngas can be improved by the composite approach

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Work Supported by

DOE SBIR Grant: DE-FG02-06ER84595

<u>DOE PM</u>

Dr. Mani Manivannan

Dr. Joseph Stoffa