HYBRID FUEL CELL TECHNOLOGY FOR PRODUCING CHEMICALS, FUELS, AND ELECTRICITY

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REBELS CHALLENGE AND TARGETS

- **Challenge:** Develop an intermediate temperature fuel cell technology that could enable the partial oxidation of CH_4 to CH_3OH or the formation of carbon-carbon bonds to make liquid fuels or higher value chemicals.
  - This use of an electrochemical cell likens it to a small-scale gas-to-liquids reactor (GTL).
  - Electrochemical GTL has the potential to outperform small-scale GTL systems in cost, throughput, and efficiency while keeping the footprint small.
- **Targets:** A competitive system would have a lower cost per capacity, high process intensity, high selectivity, and long lifetime.

Metric	State of the Art	Proposed
Proton-conducting solid electrolyte fuel cell	**Cell Voltage of 625 mV at 200 mA/cm² and 500°C**	**Cell Voltage of >780 mV at 200 mA/cm² and 500°C**
Methane coupling carbon efficiency	**<30%**	**50%**
Fuel cell manufacturing cost	**$4000/kW**	**$1500-2000/kW**

CHALLENGES FOR CONVERTING METHANE TO A LIQUID FUEL

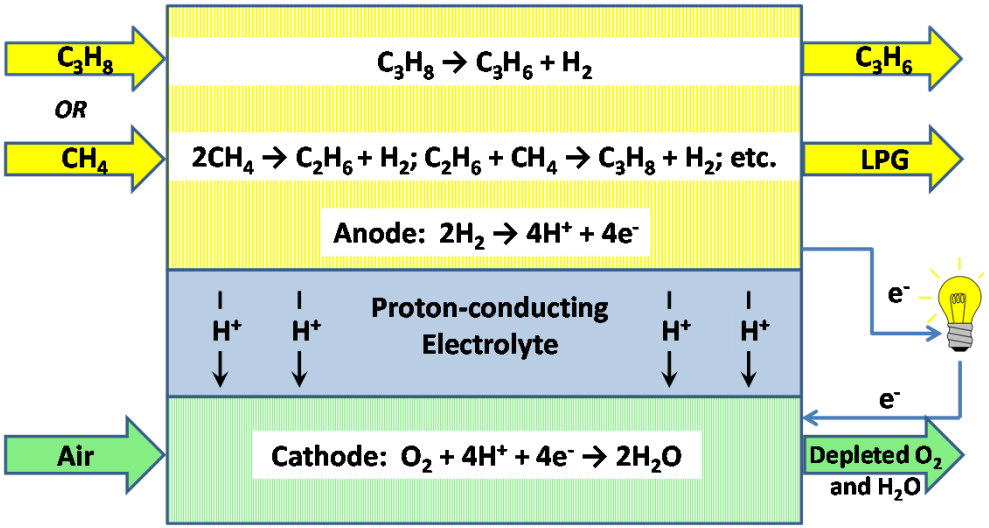
- Two pathways for the direct conversion of methane (non-syn gas route) to higher hydrocarbons – thermodynamic challenges for both pathways
  - Oxidative Coupling/Selective oxidation
    - $2CH_4 + ½O_2 \rightarrow C_2H_6 + H_2O$
    - $CH_4 + ½O_2 \rightarrow CH_3OH$

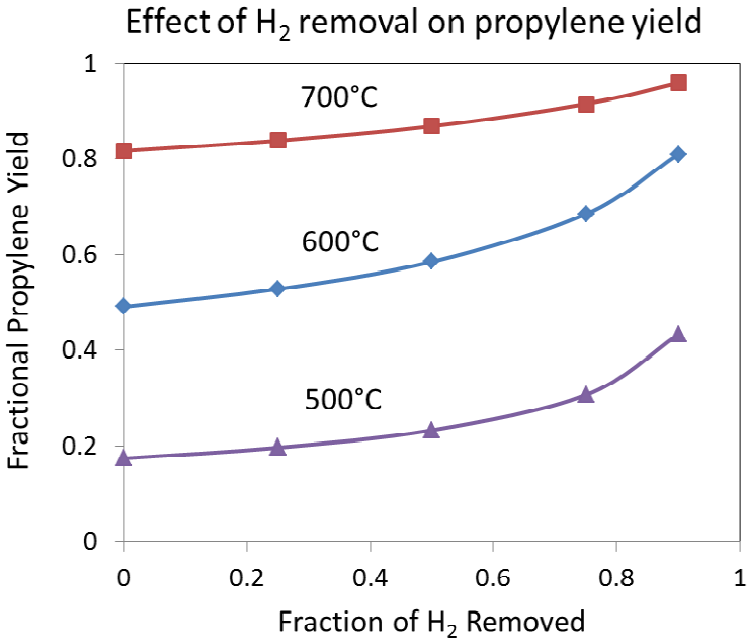
      Issue: Products are more readily oxidized than CH_4 leading to CO_2
  - Non-oxidative Coupling of Methane (NOCM)
    - $2CH_4 \leftrightarrow C_2H_6 + H_2$

      Issue: Large positive ΔG, high temperature required for even low conversion, high carbon deposition
  - Various approaches have been investigated for overcoming the thermodynamic challenges
    - Controlled delivery of oxygen to limit oxygen concentration including the use of ceramic membranes or solid oxide fuel cells
    - Removal of hydrogen using ceramic membranes for methane coupling to overcome thermodynamic limitation

OUR APPROACH – "NON-OXIDATIVE COUPLING OF METHANE" USING A PROTON-CONDUCTING FUEL CELL

- **Project Goal:** Develop an intermediate temperature fuel cell system that either dehydrogenates propane (natural gas liquids) to propylene or converts natural gas to liquefied petroleum gas (LPG) while co-generating electricity.
- **Unique Aspect:** Integrate propane dehydrogenation and/or methane coupling catalyst(s) into a proton-conducting solid oxide fuel cell to overcome the thermodynamic limitation of the propane dehydrogenation or methane coupling reactions.





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KEY TECHNICAL CHALLENGES

- Proton-conducting ceramic-based fuel cell that generates >200 mW/cm^2 at 500°C operating on H_2
- Propane dehydrogenation catalyst for producing propylene with a selectivity of >95%
- Methane coupling catalyst for converting methane to LPG with a conversion efficiency of >50% and selectivity >95% to gaseous products (process level, not single pass)
- Method for integrating the propane dehydrogenation or methane coupling catalysts into the fuel cell
- A manufacturing cost of <$2000/$kW_e$

PROJECT TIMELINE AND MAJOR MILESTONES

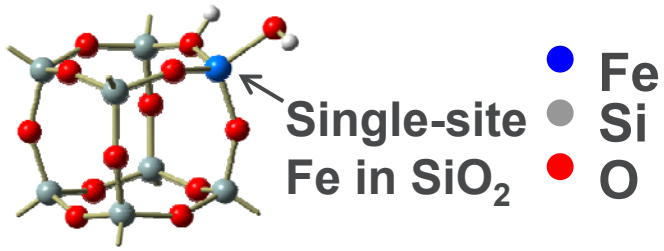
- **October 1 , 2014** – Project initiated.
- **September 30, 2015** – Demonstrate a 25 cm^2 single cell operating on H_2 at 500°C with a current density >100 mA/cm^2 for 50 h. (Completed using button cell)
- **December 31, 2015** - Demonstrate a 25 cm^2 single cell operating on propane at 500°C with a current density >50 mA/cm^2 for 24 h and a product yield ≥50% and selectivity >95% to propylene. (In progress using button cell)
- **June 30 , 2016** - Demonstrate a 25 cm^2 single cell operating on H_2 at 500°C with current density >200 mA/cm^2 for 100 h. (Completed using button cell)
- **September 30, 2016** - Demonstrate a 25 cm^2 a single cell operating at 500°C on methane (simulated shale gas) with a current density >100 mA/cm^2 for 100 h and a product yield ≥50% and selectivity >95% to gaseous carbon-containing species. (To be completed)

WORK STRUCTURE BREAKDOWN

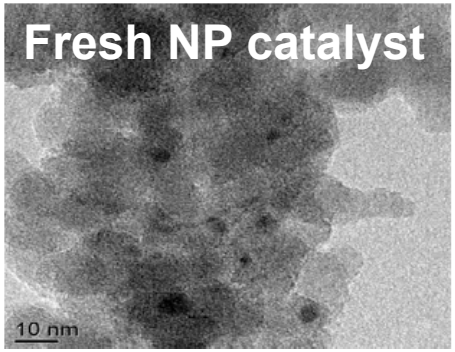
- Task 1 – PDH and NOCM Catalyst Development
- Task 2 – Proton-Conducting Electrolyte Development
- Task 3 - Anode Development
- Task 4 - Fuel Cell Development and Demonstration
- Task 5 – Tech-to-Market (T2M)

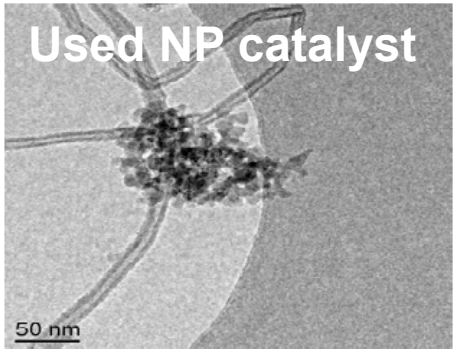
METHANE COUPLING AND ALKANE DEHYDROGENATION CATALYST DEVELOPMENT

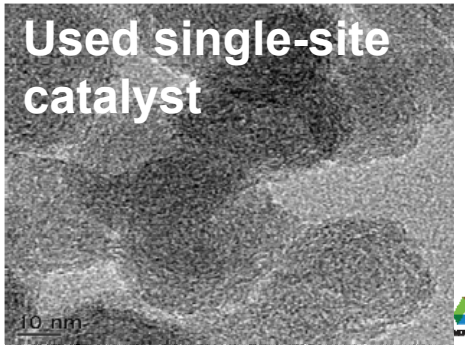
- Methane coupling and alkane dehydrogenation catalysts are based upon Argonne/IIT “single-site” metal catalyst technology being developed in our BES-funded catalysis program. An example of a single-site metal catalyst is Fe/SiO_2.
- Coking is a major cause of catalyst deactivation in methane coupling and alkane dehydrogenation processes. “Single-site” catalysts are less prone to coking than conventional supported metal nanoparticle catalysts.



Catalyst	Dehydrogenation TOF (h^{-1})		
	t = 0 h	t = 18 h	Selectivity
Fe^{II}/SiO_2	4.3	5.5	>99%
Fe^0 NPs	45.5	-	32%
Bulk Fe_2O_3/SiO_2	Low activity and selectivity		

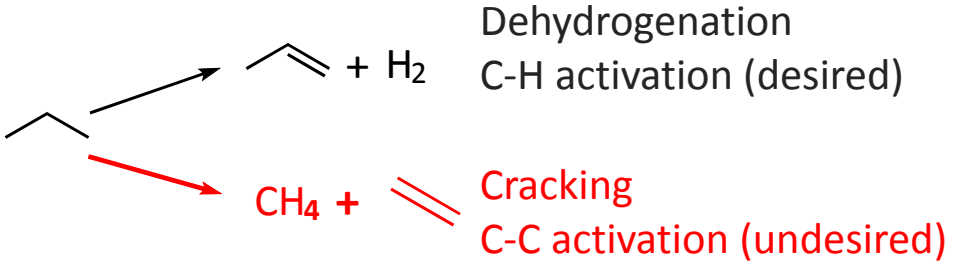


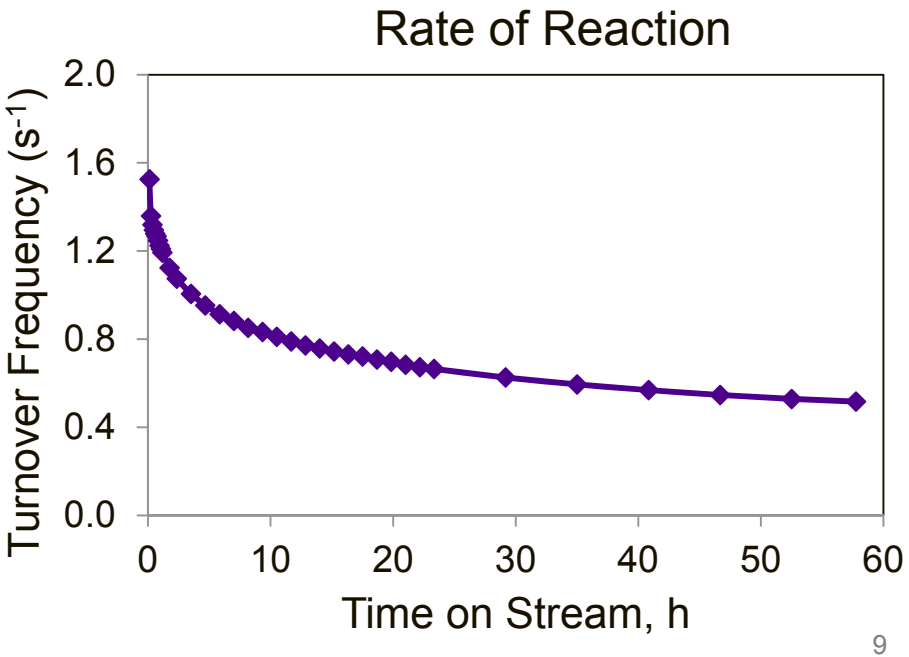


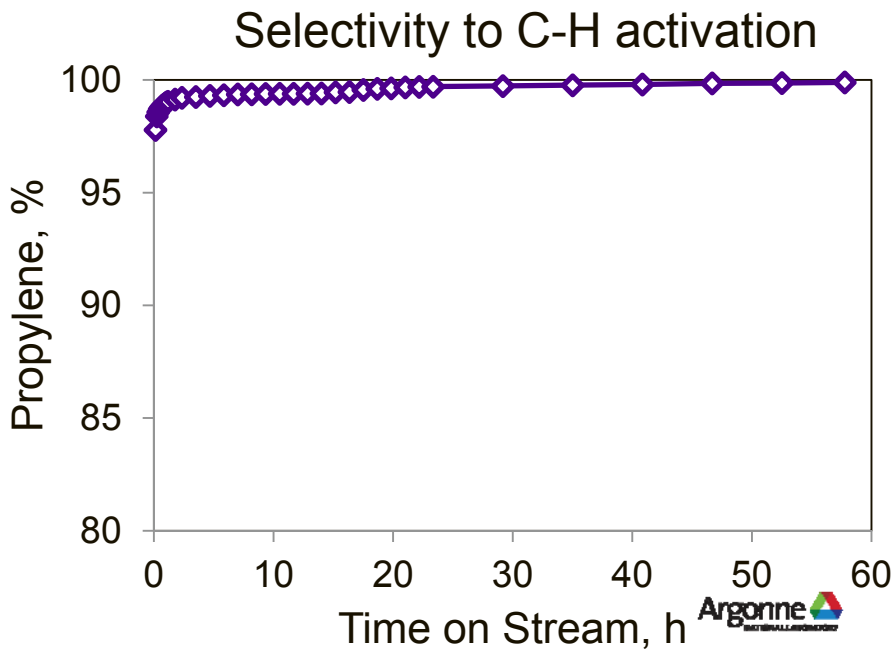


PROPANE DEHYDROGENATION CATALYST DEVELOPMENT

- Challenges
  - More active catalyst required
  - Maintain high selectivity to propylene while inhibiting cracking
  - Could anode be used as a support for a “single-site” catalyst?







METHANE COUPLING CATALYST DEVELOPMENT

- Challenges
  - No evidence that a “single-site” catalyst could promote C-C bond formation
  - Low temperature activity (500-700°C)
  - Inhibit coke formation

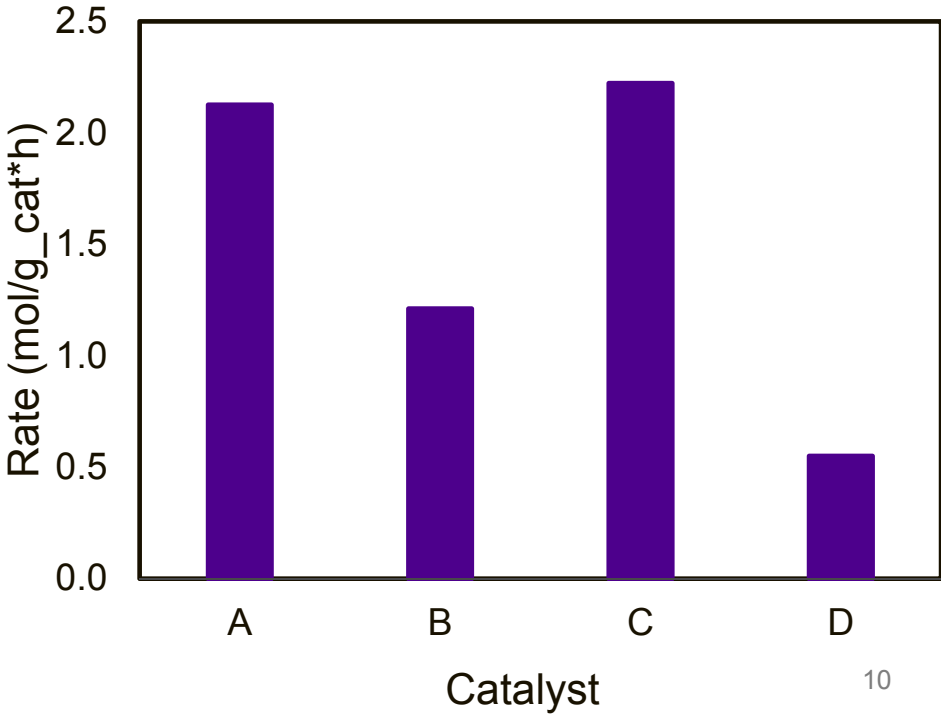
$$2CH_4 \rightarrow C_2H_6 + H_2$$

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

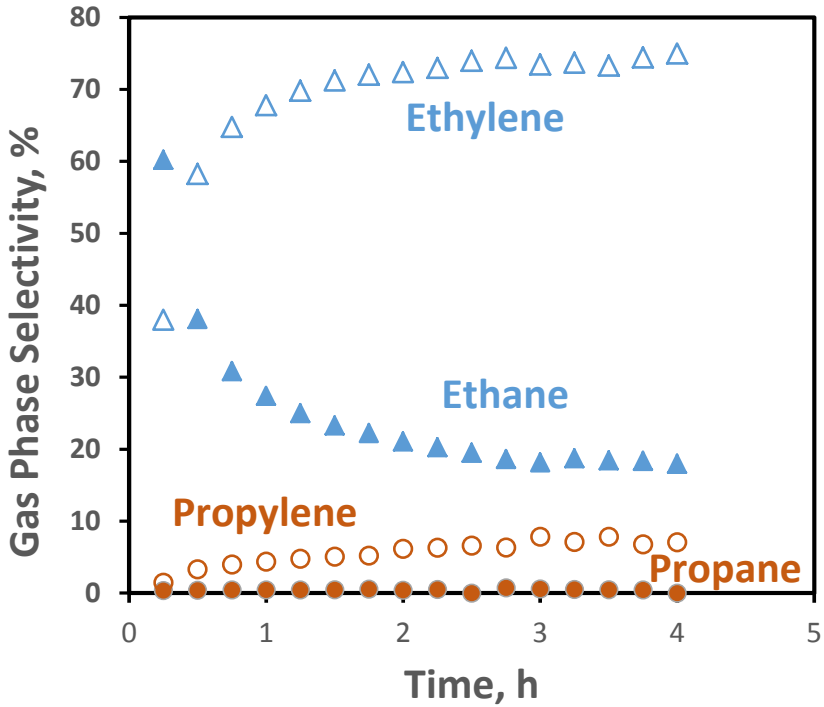
$$CH_4 + C_2H_6 \rightarrow C_3H_8 + H_2$$

$$C_3H_8 \rightarrow C_3H_6 + H_2$$

CH_4 Conversion @ 600°C

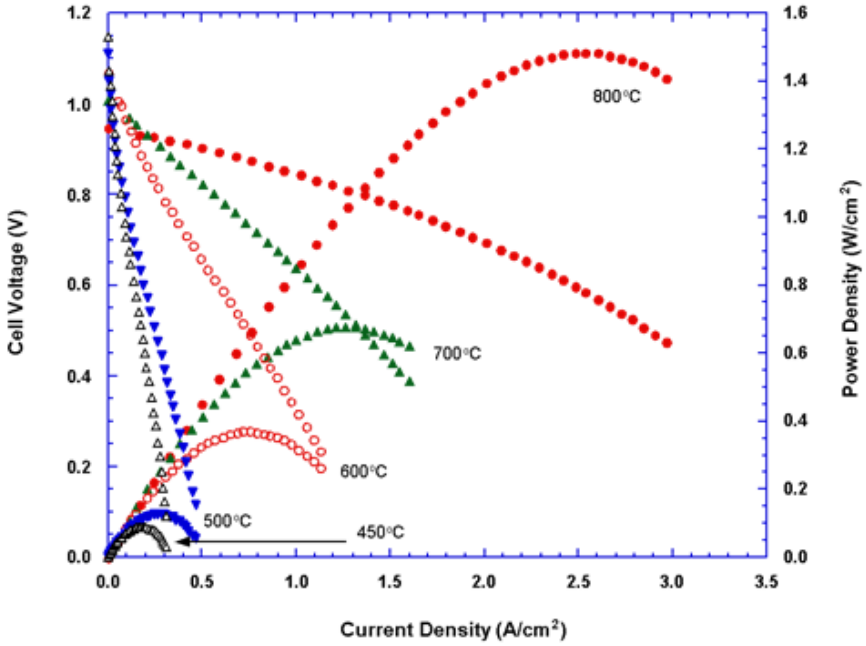


Selectivity @ 600°C



PROTON-CONDUCTING FUEL CELL DEVELOPMENT

- Our proton-conducting solid oxide fuel cell is based upon Argonne ceramic membrane technology developed for hydrogen separation.
- Materials developed for ceramic membranes, such as yttrium-doped barium cerate (BCY), exhibit high conductivity when operated in a proton-conducting fuel cell.

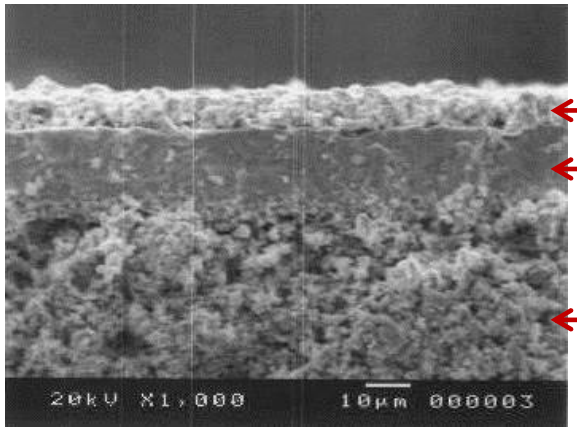


Polarization curves of a proton-conducting hydrogen/air fuel cell with a 10 μm yttrium-doped barium cerate electrolyte (BCY) supported on a Ni/BCY anode with a Pt paste/Pt mesh cathode.

FUEL CELL PERFOMANCE TARGETS

- Anode
  - Composition stability in simulated shale gas.
  - ASR of <1.5 Ω-cm^2 in hydrogen.
  - ASR of <3 Ω-cm^2 in simulated shale gas.
- Electrolyte
  - Composition stability in simulated shale gas.
  - Proton conductivity of >8 mS/cm and proton transference number >0.90 in hydrogen.
  - Proton conductivity >8 mS/cm in simulated shale gas.
- Cathode
  - No targets defined.
- Fuel Cell
  - Current density >200 mA/cm^2 operating on H_2 at 500°C for 100 h

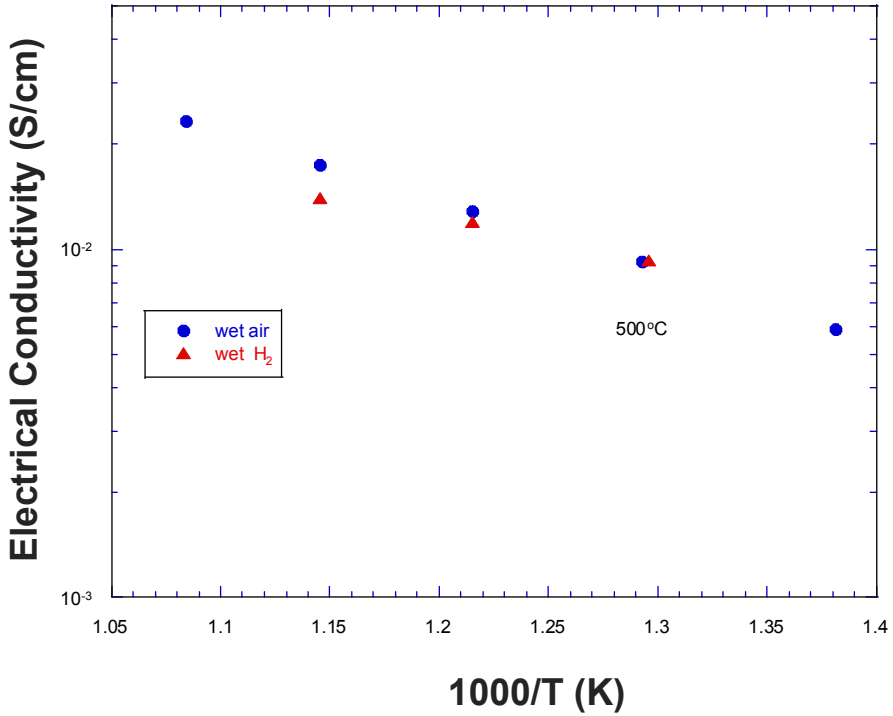
CONDUCTIVITY OF BZY ELECTROLYTE AS A FUNCTION OF TEMPERATURE IN AIR AND H_2



Cathode

Composite BZY electrolyte

Ni-BZY composite anode



- Proton conductivity 8.8 mS/cm at 500°C in H_2 (AC impedance method).
- Proton transference number >0.95 at 500°C in H_2. (measured using concentration cell).

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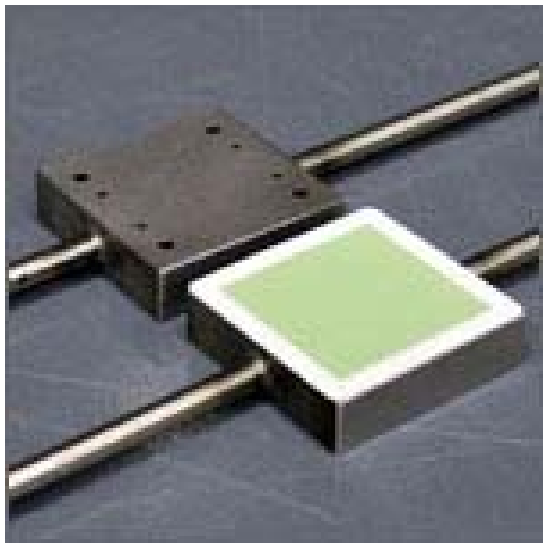
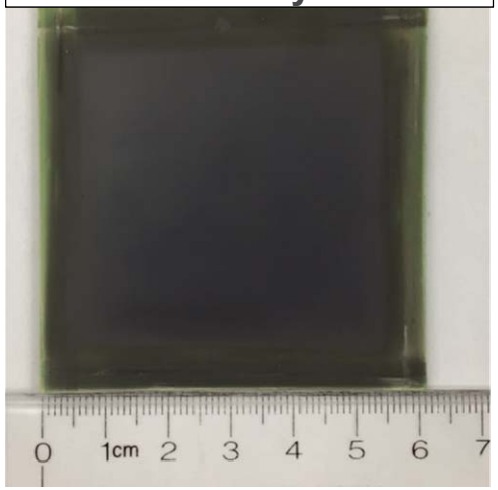
5 CM X 5 CM CELLS HAVE BEEN PRODUCED BUT QUALITY CONTROL HAS BEEN A MAJOR ISSUE



- 5 cm x 5 cm Test Fixture Kit for anode or electrolyte-supported solid oxide fuel cells purchased from Fuel Cell Materials.com (division of NexTech Materials, Ltd.)

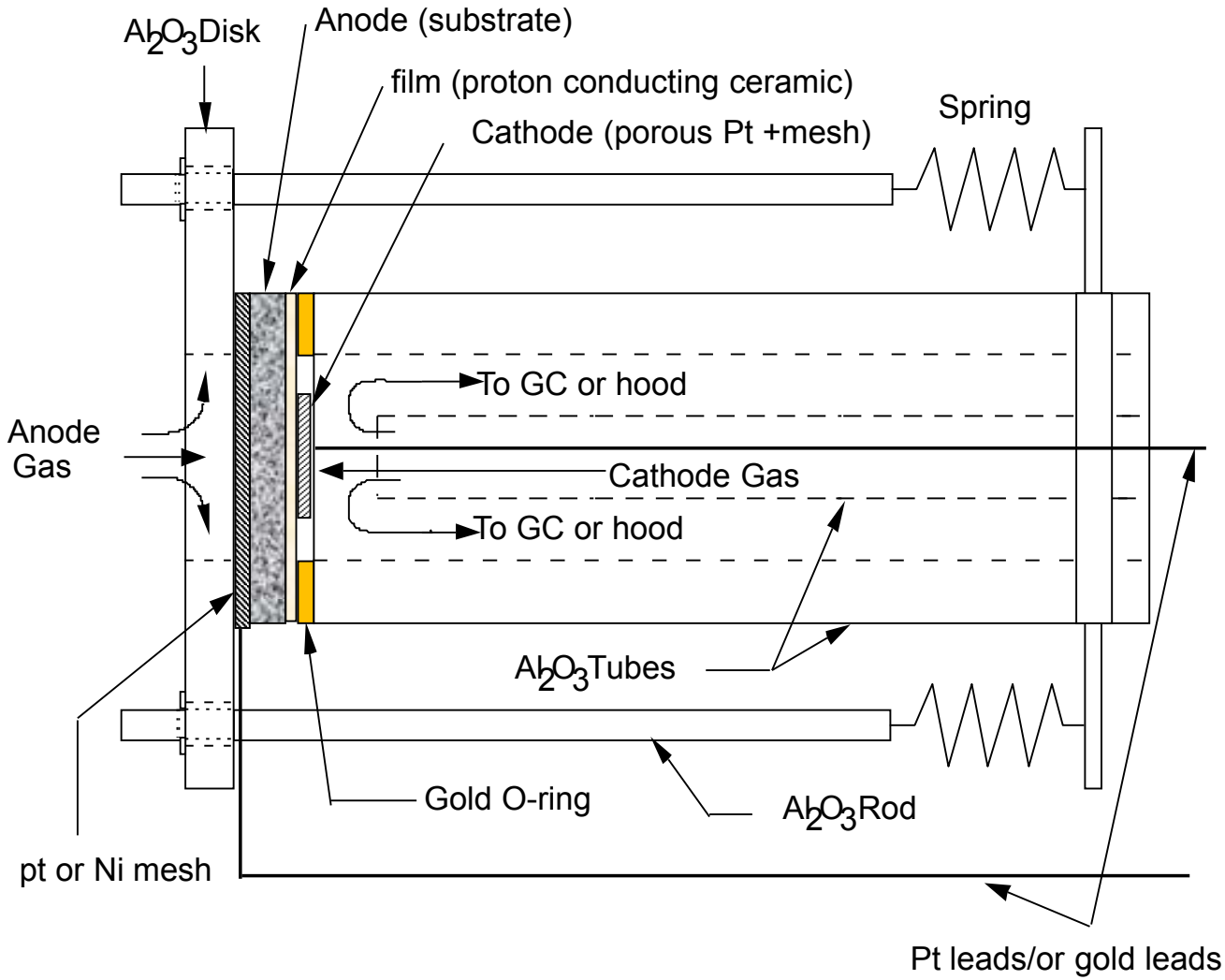
Electrolyte



Anode

- Example of a 5 cm x 5 cm cell. Cracking and delamination have been problematic.
- Exploring having a commercial vendor produce the cells.

SCHEMATIC OF BUTTON CELL TEST SYSTEM



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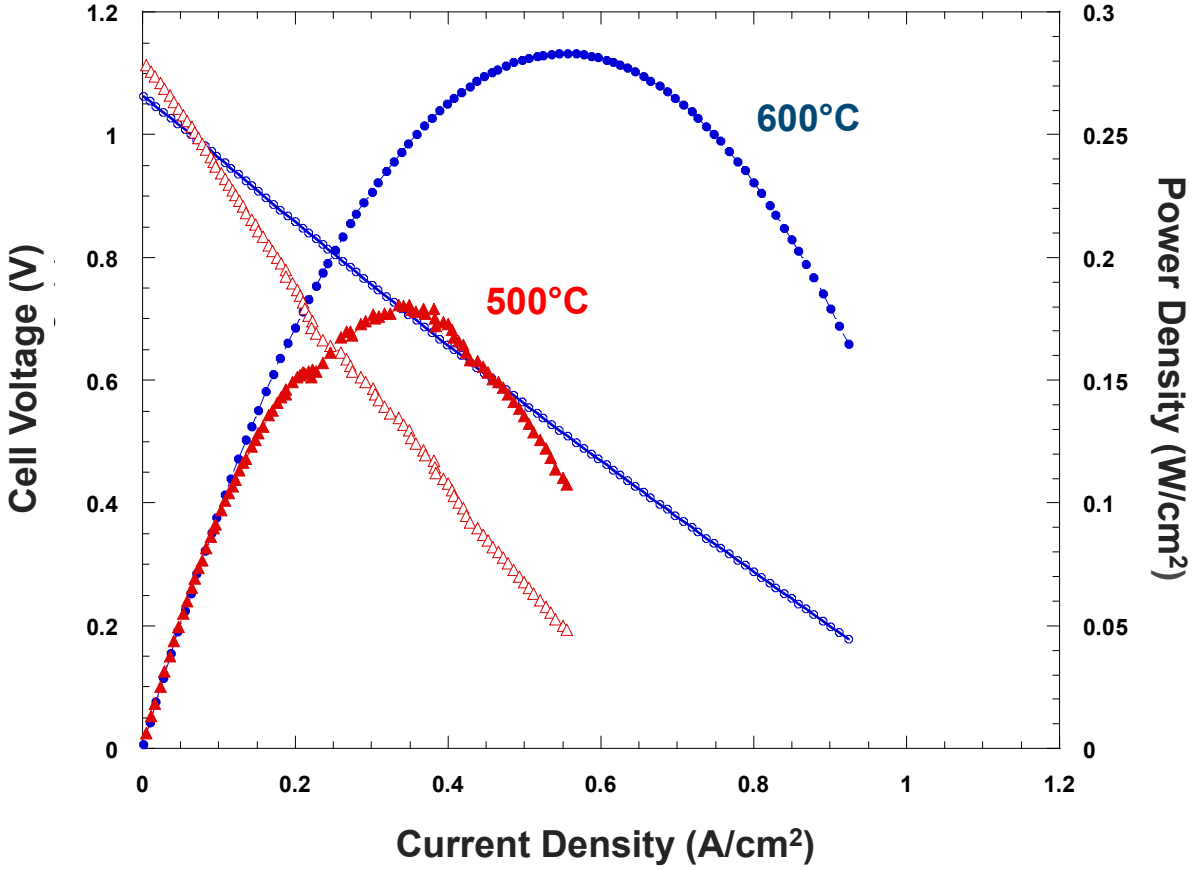
I-V AND POWER DENSITY PERFORMANCE OF A SINGLE BUTTON CELL OPERATING ON H_2



- Power density of 180 mW/cm^2 at 350 m A/cm^2 at 500°C
- Power density of 280 mW/cm^2 at 550 mA/cm^2 at 600°C

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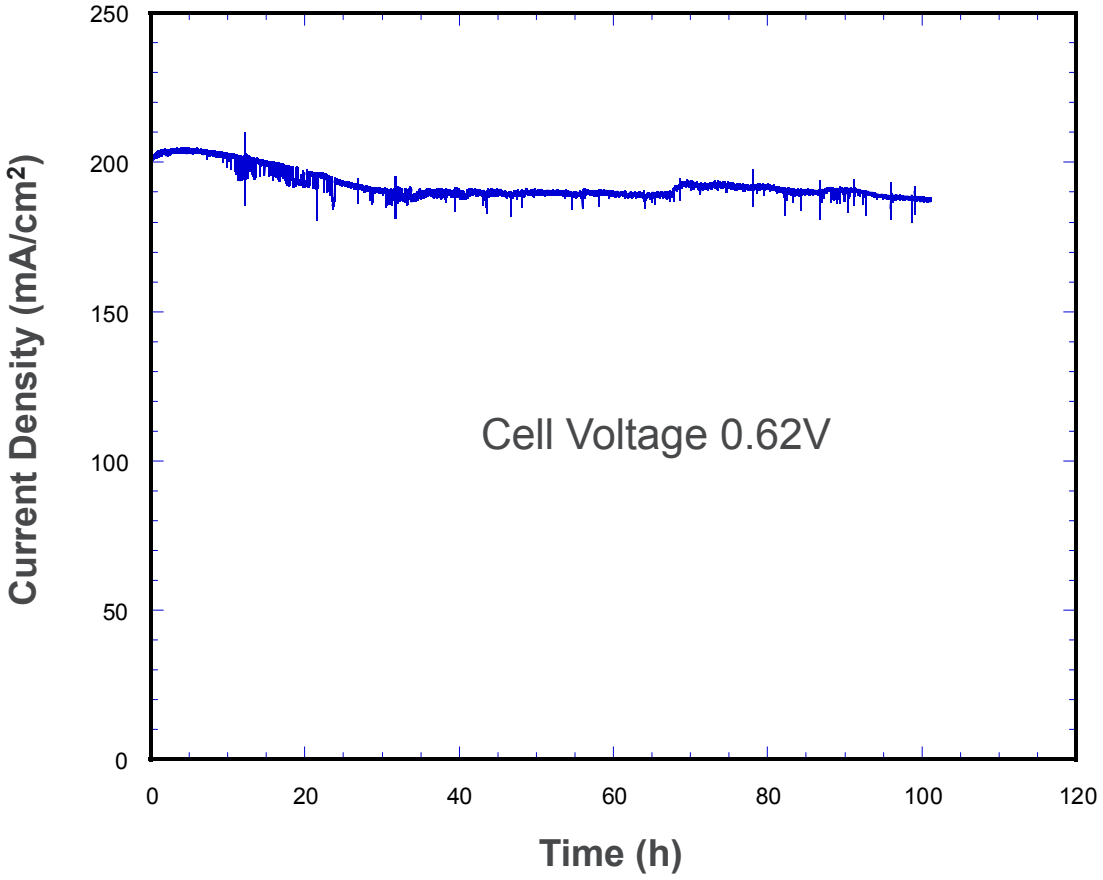
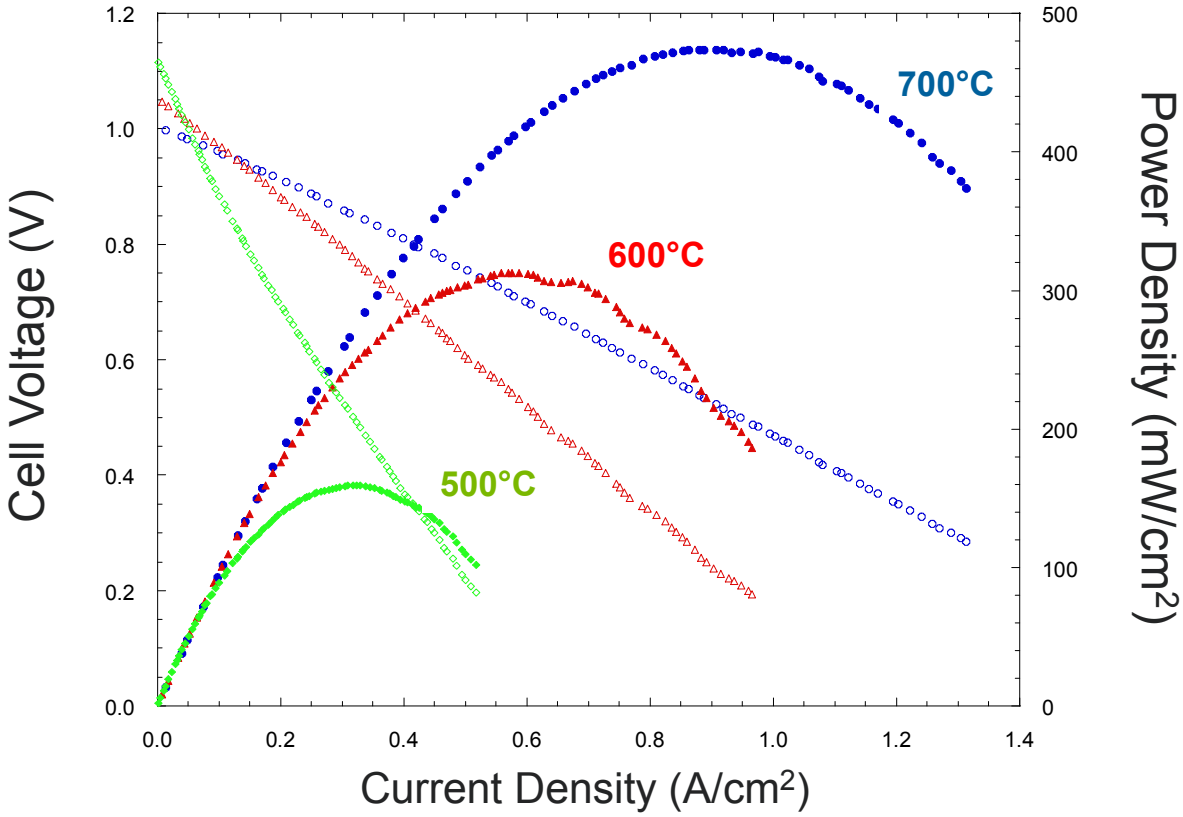
<10% LOSS IN PERFORMANCE OBSERVED OVER 100 H OPERATING ON H_2 AT 500°C



- Current density of 203 mA/cm^2 at t=0
- Current density of 187 mA/cm^2 at t=101 h

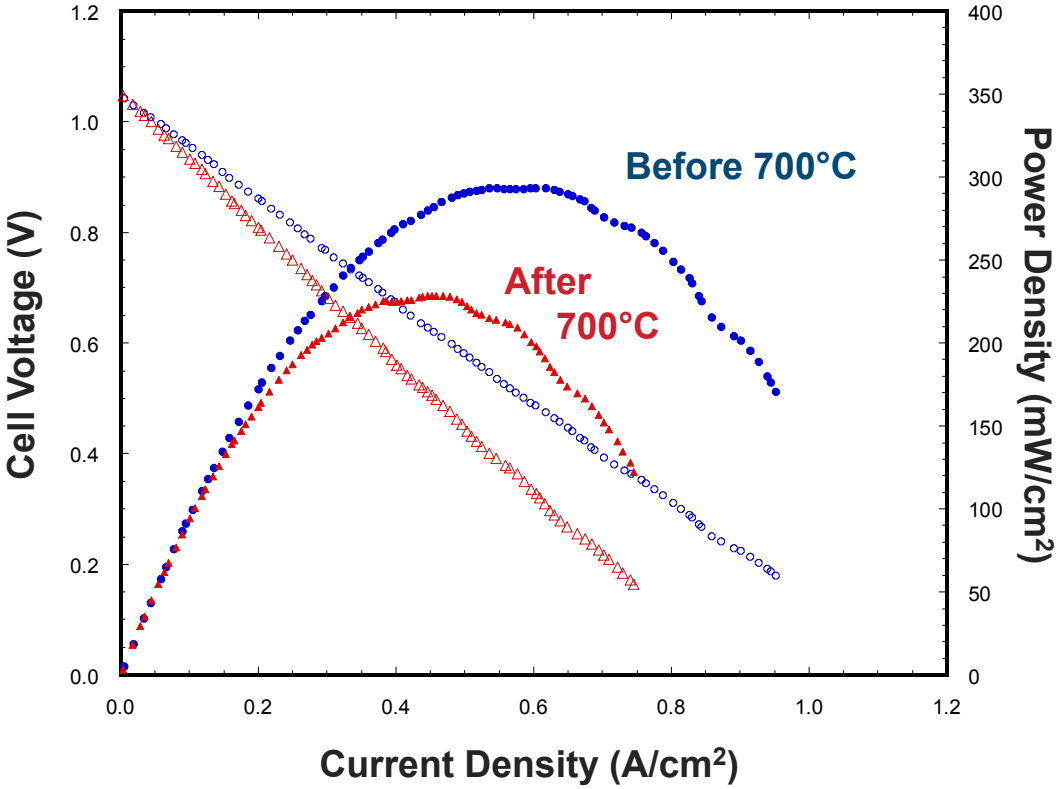
I-V AND POWER DENSITY PERFORMANCE AT 600 AND 700°C AFTER 100 H DURABILITY TEST

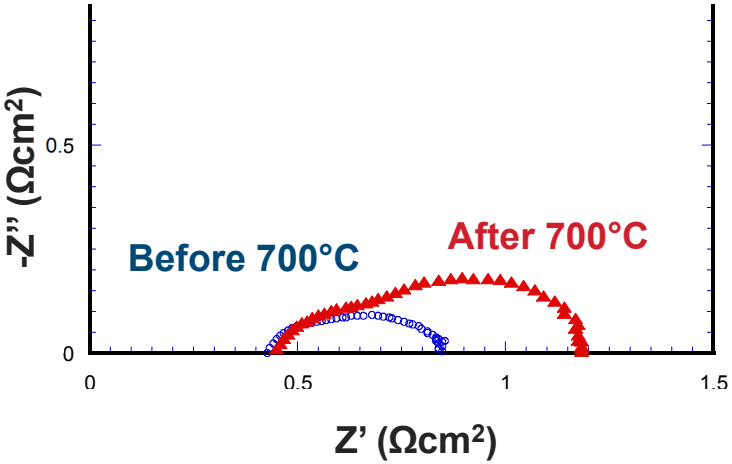
- I-V measured at 500°C before long-term durability test
- I-V measured at 600 and 700°C after long-term durability test



- Power density of 300 mW/cm^2 at 600 mA/cm^2 at 500°C
- Power density of 480 mW/cm^2 at 900 mA/cm^2 at 600°C

OPERATING AT 700°C RESULTED IN LOSS IN CELL PERFORMANCE AT 600°C





- Power density measured at 600°C decreased from ~300 mW/cm^2 to ~220 mW/cm^2 after operating at 700°C.
- Impedance measurement at 600°C before and after operating at 700°C shows that the electrode polarization increased operating at 700°C .Cause of electrode polarization is not known at this time.

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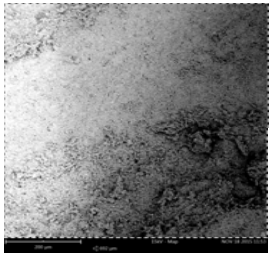
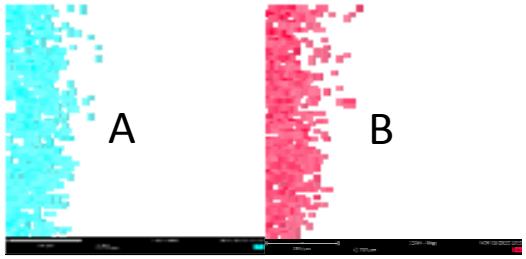
METHOD DEVELOPMENT FOR INTRODUCING PROPANE DEHYDROGENATION (PDH) CATALYST INTO FUEL CELL

Incipient Wetness Technique

- Method typically employed industrially for preparing heterogeneous catalysts
- Good dispersion of components A and B observed

SEM of anode after introducing the catalyst



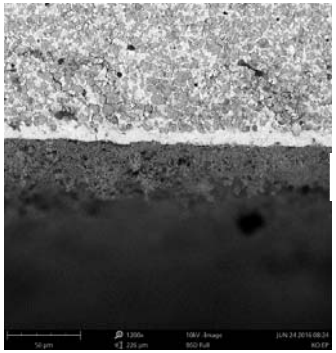


EDX suggests components A and B are well-dispersed

- Cells cracked when brought to operating temperature

Slurry Coating Method

- Slurry consisting of PDH catalyst, LSCF, and BZY coated on to BZY composite electrolyte and sintered
- SEM suggested good adhesion to the electrolyte



PDH/LSCF/BZY layer

- PDH catalyst was inactive
- H_2 treatment process regenerated PDH activity

IN SUMMARY

- Catalyst development
  - Propane dehydrogenation catalyst technology capable of achieving >95% selectivity to propylene has been developed.
  - Non-oxidative methane coupling catalyst with activity at 600°C has been identified.
- Intermediate temperature proton-conducting fuel cell
  - Anode and electrolyte materials developed that have met all project performance targets.
  - Method for introducing PDH catalyst into fuel cell has been developed.
- Testing on propane in progress.

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