Intermediate Temperature Hybrid Fuel Cell System For The Conversion Of Natural Gas To Electricity And Liquid Fuels

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Reliable Electricity Based on Electrochemical Systems (REBELS) - Category 3

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 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

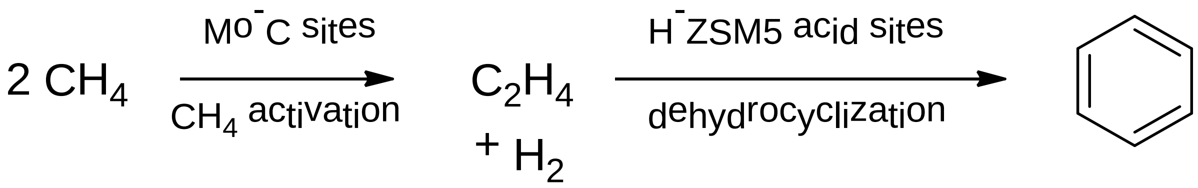
- Two pathways for the direct conversion of methane (non-syn gas route) to higher hydrocarbons – thermodynamic challenges for both pathways
  - Oxidative Coupling/Selective oxidation
    - $2CH_4 + ½O_2 \rightarrow C_2H_6 + H_2O$
    - $CH_4 + ½O_2 \rightarrow CH_3OH$

    Issue: Products are more readily oxidized than CH_4 leading to CO_2
  - Methane coupling
    - $2CH_4 \leftrightarrow C_2H_6 + H_2$

    Issue: Large positive ΔG, high temperature required for even low conversion
- 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

Some Literature Reported Methane Coupling Catalysts

Mo@H-ZSM5 is active for CH_4 dehydroaromatization



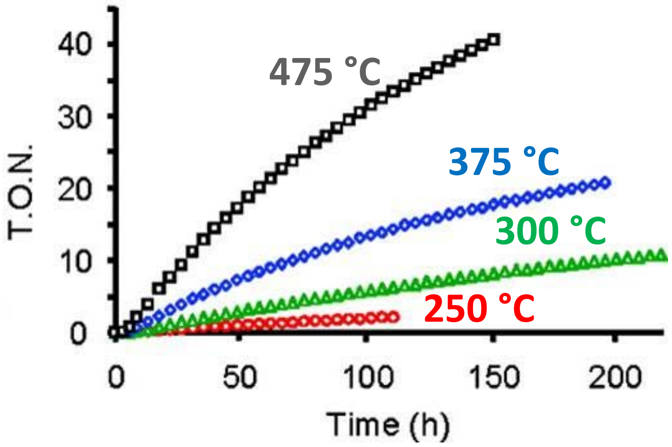
$$2\ CH_4 \xrightarrow[CH_4\ \text{activation}]{\text{Mo}^{-}\text{C sites}} C_2H_4 + H_2 \xrightarrow[\text{dehydrocyclization}]{\text{H}^{-}\text{ZSM5 acid sites}}$$

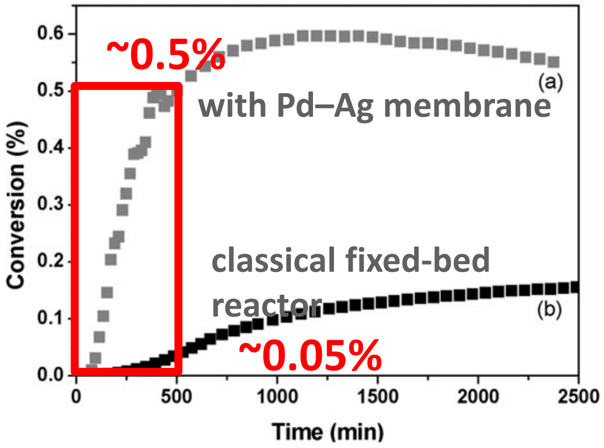
Chem. Commun., 2001, 1952

Ta@SiO_2 and W@Al_2O_3 are active for CH_4 coupling

$$2\ CH_4 \xrightarrow[T]{Ta@SiO_2} C_2H_6 + H_2$$

$$2\ CH_4 \xrightarrow[350\ ^oC]{W@Al_2O_3} C_2H_6 + H_2$$



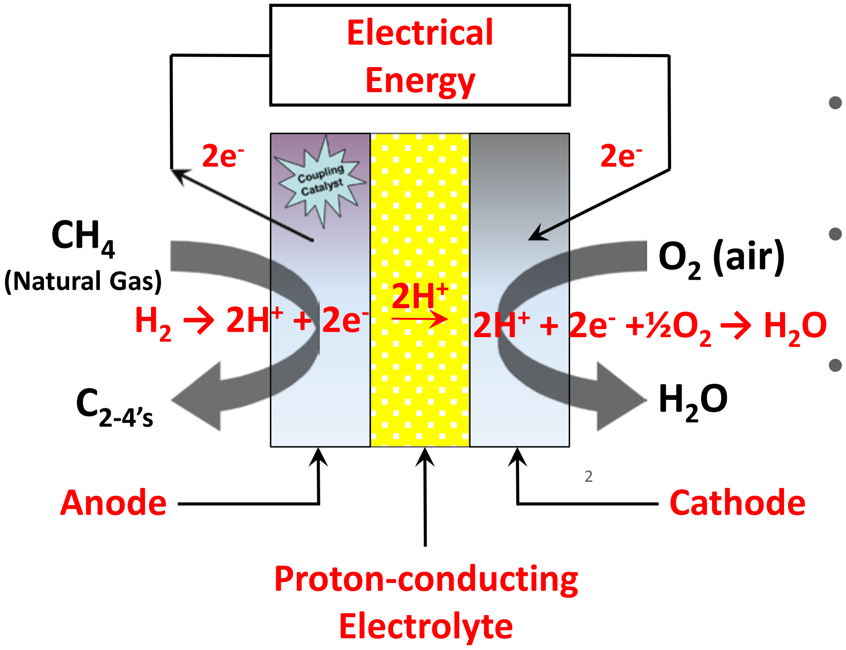


J. Am. Chem. Soc. 2008, 130, 5044

Chem. Commun. 2010, 46, 3985

Our Approach: A Proton-Conducting SOFC that Integrates a Methane Coupling Catalyst into the Anode

Hybrid Fuel Cell System



Fuel Production

Methane Coupling: $2CH_4 \rightarrow C_2H_6 + H_2$

Dehydrogenation: $C_2H_6 \rightarrow C_2H_4 + H_2$

Key Technical Challenges

- A proton-conducting ceramic-based fuel cell capable of generating >200 mW/cm^2 at 500°C.
- A methane coupling catalyst that is capable of achieving >50% methane conversion efficiency .
- A methodology for integrating the methane coupling catalyst into the anode of the fuel cell.
- A manufacturing cost of <$2000/kW.

Deliverable

- Demonstrate a 25 cm^2 single cell operating on methane (natural gas) with a product yield ≥50% generating a current density >100 mA/cm^2 for 100 h at 500^{o}C.

Project Timeline and Major Milestones

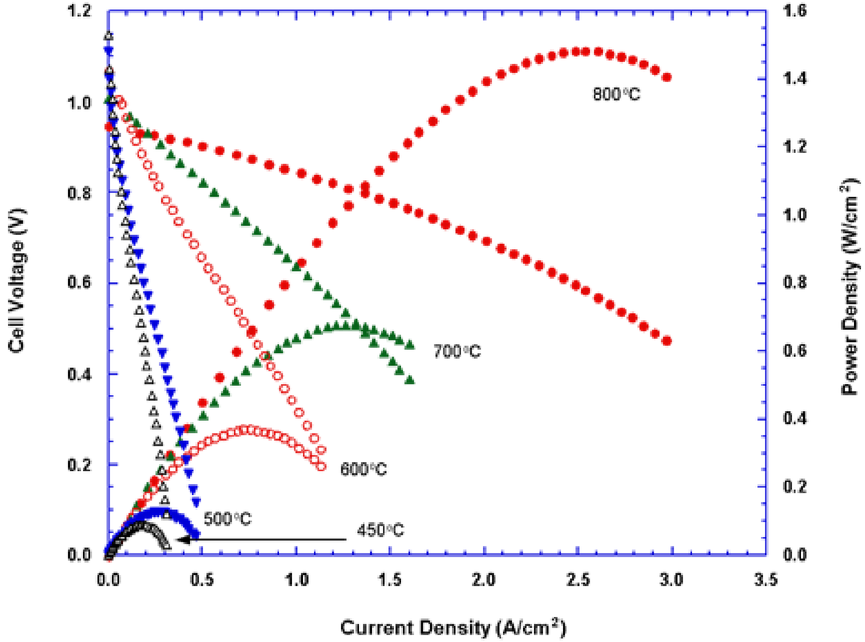
- **October 1 , 2014** – Project initiated. Funding $2.1 M for 2 years (5% cost share).
- **September 30, 2015** – Demonstrate a 25 cm^2 single cell operating on H_2 at 500°C with a current density >100 mA/cm^2 for 50 h.
- **December 31, 2015** - Demonstrate a 25 cm^2 single cell operating on propane at 500°C with a current density >50 mA/cm^2 for 24 h and a product yield ≥50% and selectivity >95% to propylene.
- **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.
- **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.

Work Structure Breakdown

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

Our Approach to Developing a Proton-Conducting Solid Oxide Fuel Cell

- 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.

Performance Targets[1] for the Proton-Conducting Solid Oxide Fuel Cell

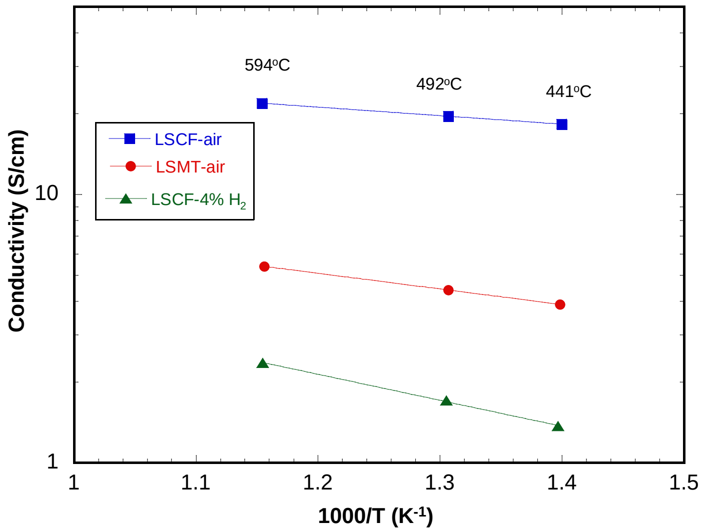
- Anode
  - Composition stability in simulated shale gas.
  - ASR of <1.5 Ω-cm^2 in hydrogen.
  - ASR of <3 Ω-cm^2 in simulated shale gas.
- Electrolyte
  - Composition stability in simulated shale gas.
  - Proton conductivity of >8 mS/cm and proton transference number of >0.90 in hydrogen.
  - Proton conductivity of >8 mS/cm in simulated shale gas.
- Cathode
  - No targets defined.

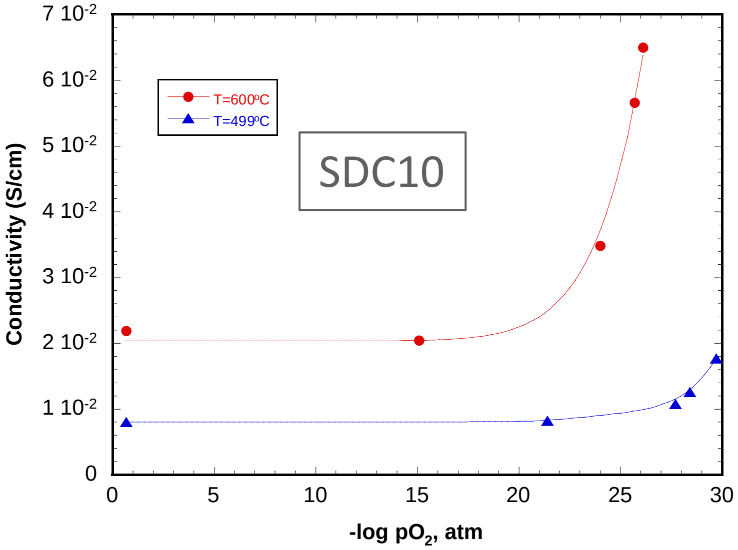
[1] All performance targets measured/evaluated at 500°C.

Anode Development

Three Anode Compositions Were Evaluated

- $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_3$ (LSCF)
- $(La_{0.25}Sr_{0.75})_{0.95}Mn_{0.5}Ti_{0.5}O_3$ (LSMT)
- $Ce_{0.9}Sm_{0.1}O_2$ (SDC10)

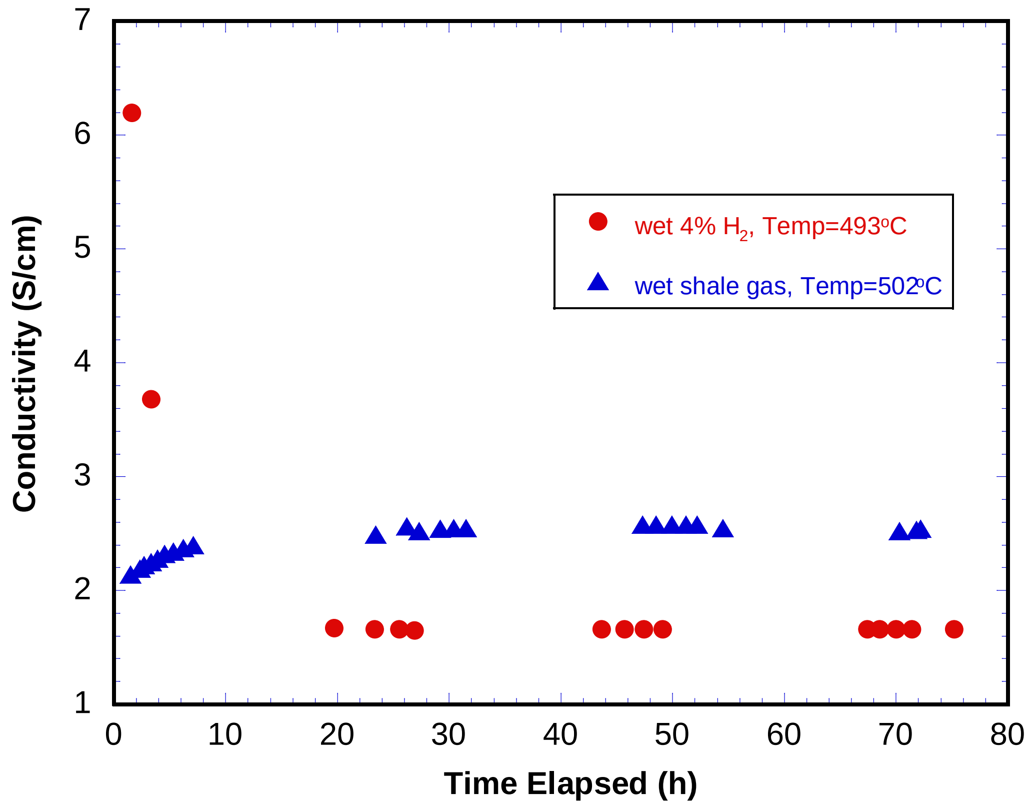




- **LSCF showed p-type electronic conductivity which exceeded the conductivity target in hydrogen.**
- **LSMT was unstable in the presence of hydrogen.**
- **SDC10 developed n-type electronic conductivity at low pO_2 but is not high enough to be used as an anode.**

Anode Development

LSCF Exhibited Stable Conductivity in Hydrogen or Simulated Shale Gas[1] in Durability Studies

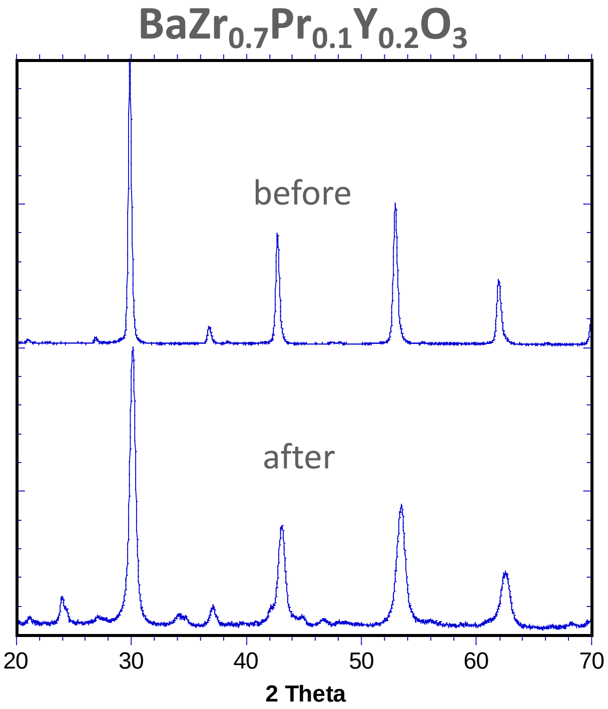


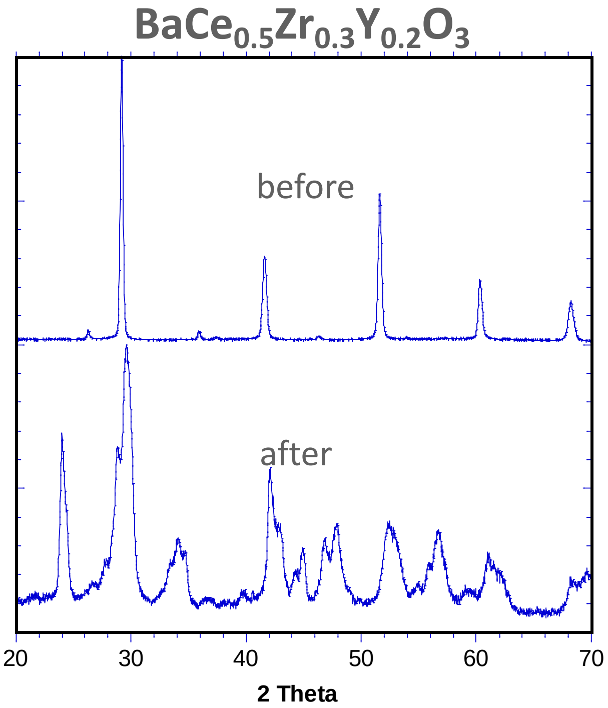
[1] simulated shale gas: 1% CO_2, 4% C_3H_8, 15% C_2H_6, 80% CH_4

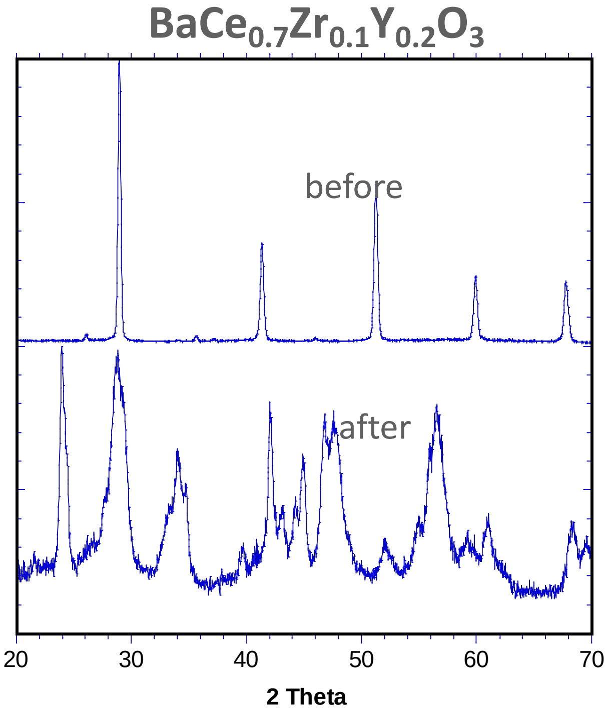
- **LSCF is stable in hydrogen and simulated shale gas at ≈500°C.**
- **Electrical conductivity of >1 S/cm was observed in shale gas.**

Electrolyte Development

Three Electrolyte Compositions Were Evaluated


$BaZr_{0.7}Pr_{0.1}Y_{0.2}O_3$


$BaCe_{0.5}Zr_{0.3}Y_{0.2}O_3$

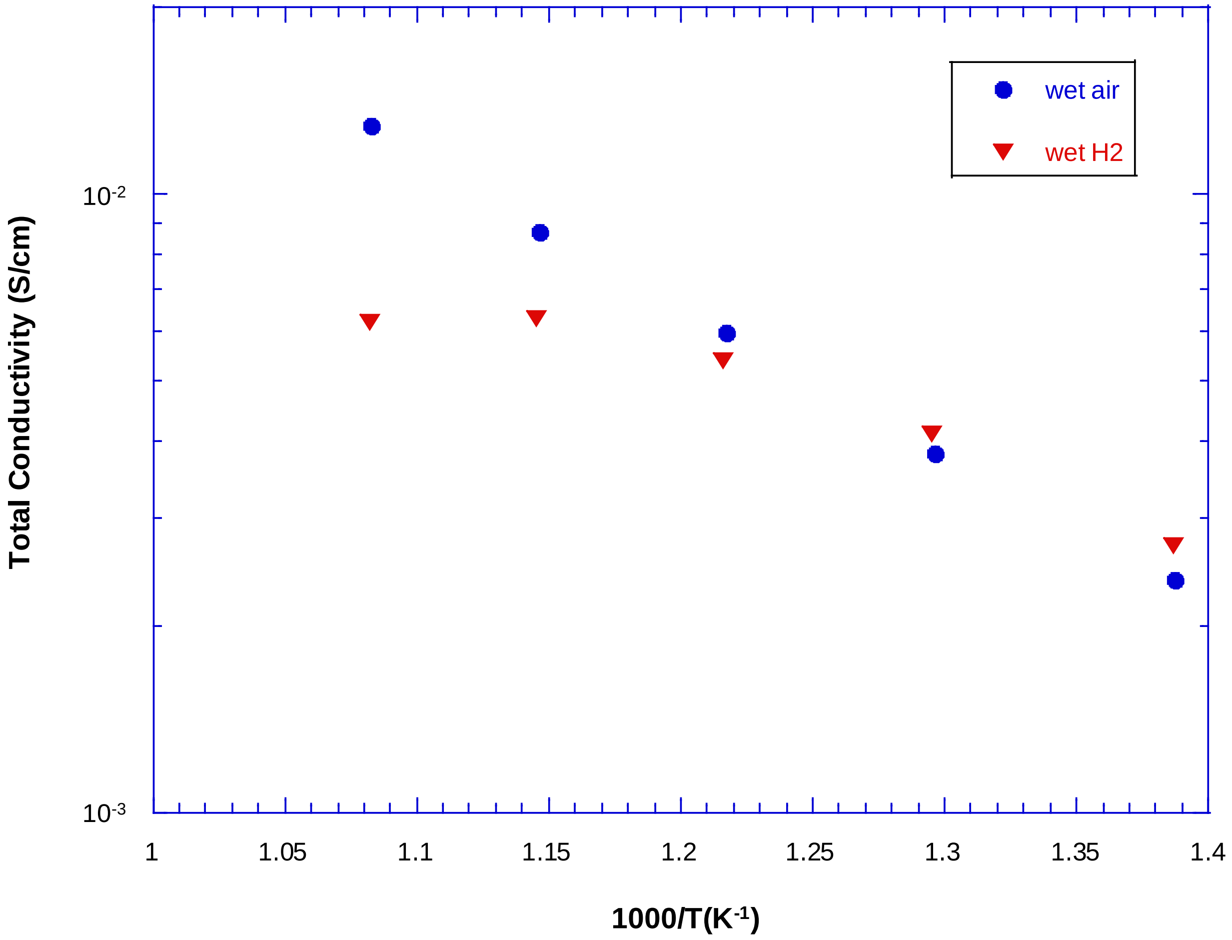

$BaCe_{0.7}Zr_{0.1}Y_{0.2}O_3$

Powders were heated for 100 h at 500°C in flowing simulated moist shale gas*

*simulated shale gas: 1% CO_2, 4% C_3H_8, 15% C_2H_6, 80% CH_4

- **$BaZr_{0.7}Pr_{0.1}Y_{0.2}O_3$ phase is stable in simulated moist shale gas.**
- **$BaCe_{0.5}Zr_{0.1}Y_{0.2}O_3$ and $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_3$ decomposed forming carbonates.**

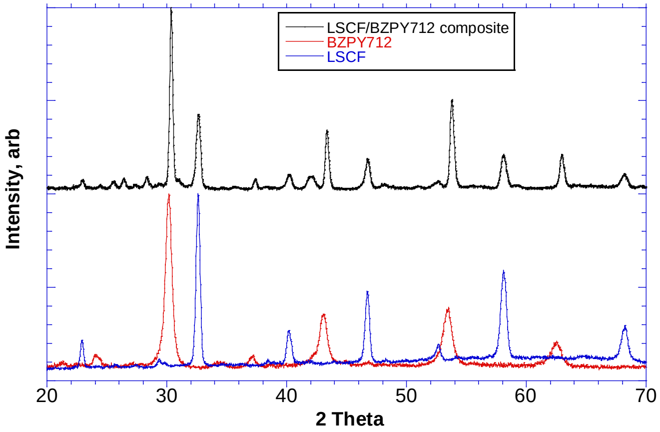
Conductivity of BZPY in Moist Air and Hydrogen

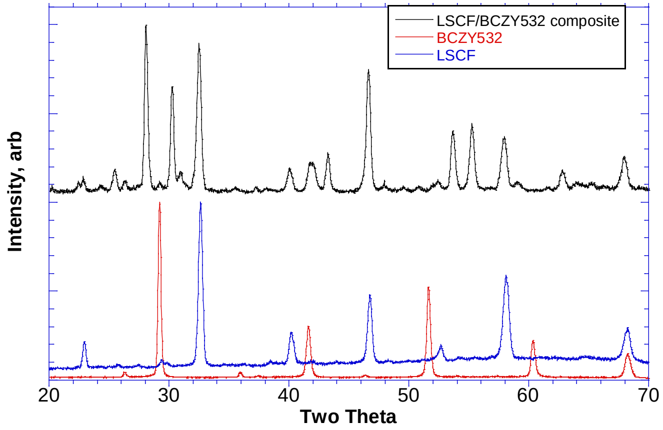


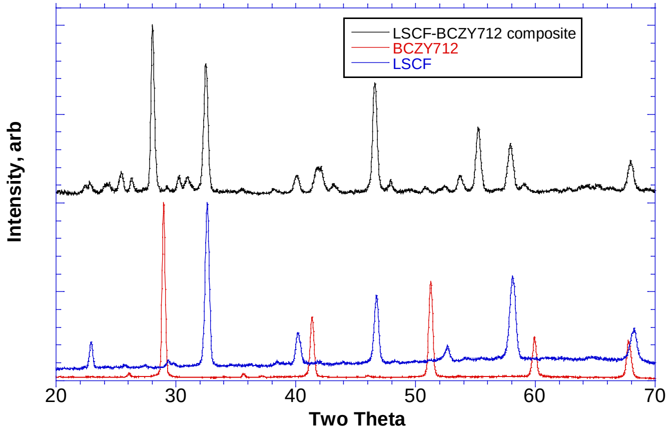
- **Conductivity of $BaZr_{0.7}Pr_{0.1}Y_{0.2}O_3$ (BZPY) electrolyte is 4.1x 10^{-3} S/cm at 500°C in hydrogen. (Target is 4 x 10^{-3} S/cm at 500°C)**

Anode Development

Composite Anode Development and Stability Testing



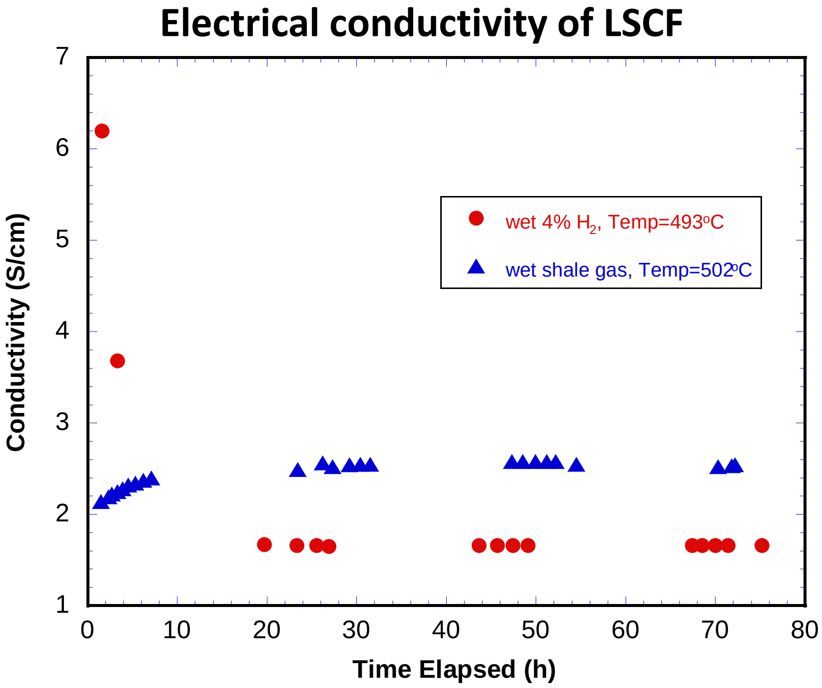


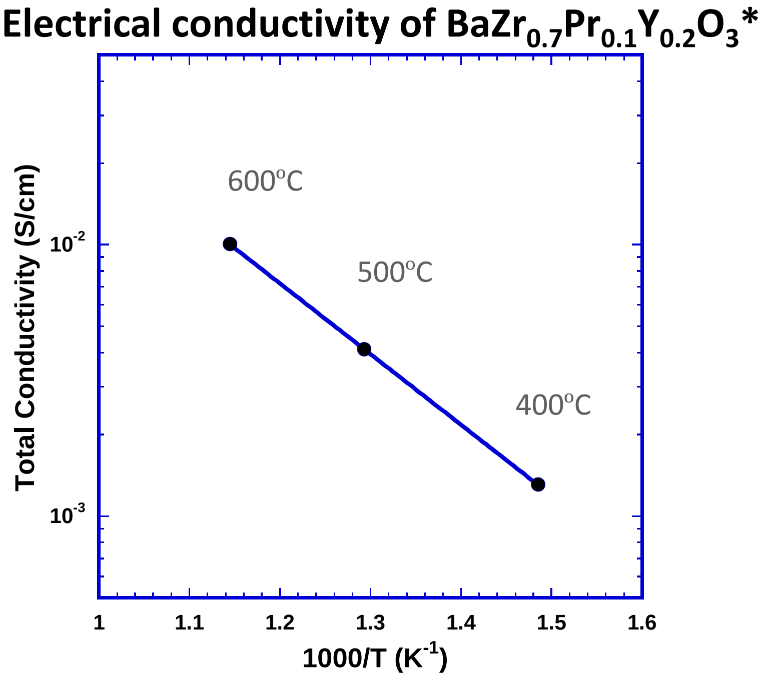


- Three composite anode materials were prepared and the phase stability was tested by sintering in air at 1300°C.
- LSCF reacted the least with the $BaZr_{0.7}Pr_{0.1}Y_{0.2}O_3$ (BZPY712).
- LSCF reacted heavily with other two electrolytes (BZCY532 and BZCY.712)

Anode Development

Area Specific Resistance (ASR) of LSCF Anode





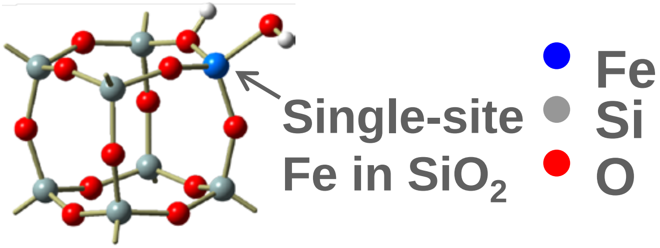
*Reference: Adv. Functional Mater., 21, 158 (2011)

- **ASR ≈8.6×10^{-2} Ω-cm^2 is expected for 1 mm thick LSCF anode (30% porosity) in hydrogen at 500°C.**
- **ASR ≈1.7×10^{-1} Ω-cm^2 is expected for 1 mm thick LSCF/BZPY (50:50 vol %) composite anode having 30% porosity in hydrogen at 500°C.**

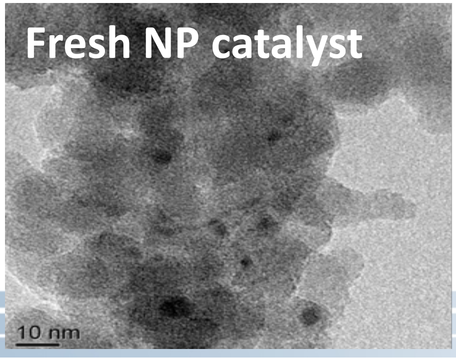
Our Approach to Methane Coupling and Alkane Dehydrogenation Catalysts

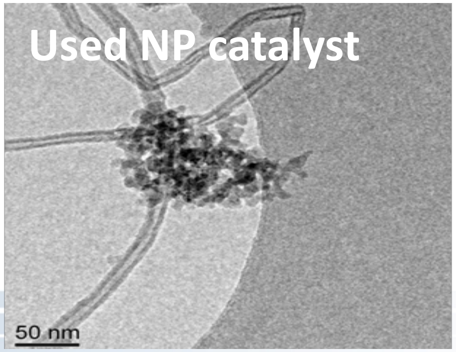
- Methane coupling and alkane dehydrogenation catalysts are based upon Argonne/IIT “single-site” metal catalyst technology being developed in our BES-funded catalysis program. An example of a single-site metal catalyst is Fe/SiO_2.

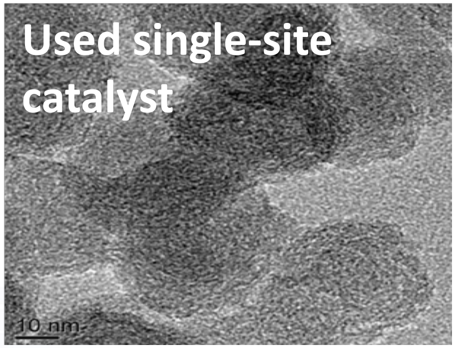
- Coking is a major cause of catalyst deactivation in methane coupling and alkane dehydrogenation processes. “Single-site” catalysts are less prone to coking than conventional supported metal nanoparticle catalysts.



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		







Performance Targets for Methane Coupling and Alkane Dehydrogenation Catalysts

- Integrate catalyst into the anode without compromising electrical and proton conductivity.
- Highly active at 500°C.
- Methane carbon conversion efficiency >50%.
- Does not promote carbon deposition, >95% carbon in gaseous carbon-containing products.
- Stable with <10% decrease in activity over 100 h.

Single Metal Single-Site Catalysts for Propane Dehydrogenation – High Selectivity but Low Rates

Catalyst	Initial Rate (mmol·h^{-1}·g^{-1}cat)	Carbon balance (%)	C_3H_6 selectivity (%)	CH_4 selectivity (%)	C_2H_4 selectivity (%)	C_2H_6 selectivity (%)	Temperature (°C)
LSCF	0.090	103	23.0	42.0	35.0	< 0.5	550
	0.031	99.8	88.5	2.4	6.3	2.8	500[1]
A-LSCF	0.043	99.9	96.3	1.0	0.8	1.8	500[1]
B-LSCF	0.060	100.5	60.0	16.0	16.0	8.0	550
C-LSCF	0.092	99.8	95.8	1.3	1.1	1.7	500[1]

[1] Reduced in 4% H_2 in He at 650°C prior to the introduction of propane.

Dual Metal Catalysts – Adding a Second Metal as a Promoter Leads to Higher Activity

Catalyst	Initial Rate (mmol·h^{-1}·g^{-1}cat)	Carbon balance (%)	C_3H_6 selectivity (%)	CH_4 selectivity (%)	C_2H_4 selectivity (%)	C_2H_6 selectivity (%)
M1/A-LSCF	0.427	97.5	79.7	17.4	2.6	0.4
M1/B-LSCF	0.427	96.1	85.6	13.5	3.2	0.1
M1/C-LSCF	0.419	97.2	74.4	22.5	2.9	0.2
M1-LSCF	0.107	98.2	94.6	1.0	2.2	2.1

- 0.1wt% M1 loading for all catalysts
- All catalysts reduced in 4% H_2 in He at 650°C prior to the introduction of propane.

Summary/Future Work

- Catalyst Development
  - Dual metal catalysts exhibit higher activity for propane dehydrogenation than single-site metal atom catalysts.
  - Four compositions have been down selected for optimization.
  - Screening of methane coupling catalyst formulations in progress.
- Anode Development
  - $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_3$ (LSCF) was selected for the anode. It has been shown to be stable with an observed electrical conductivity of >1 S/cm in simulated shale gas at 500°C.
- Electrolyte Development
  - $BaZr_{0.7}Pr_{0.1}Y_{0.2}O_3$ (BZPY712) was selected for the electrolyte. It has been shown to be stable in simulated shale gas at 500°C and a measured conductivity of 4.1x 10^{-3} S/cm at 500°C in hydrogen.
- Fuel Cell Development
  - Integration of propane dehydrogenation catalyst into anode is in progress.

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