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 CH₄ to CH₃OH 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.

<table>
<thead>
<tr>
<th>Metric</th>
<th>State of the Art</th>
<th>Proposed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton-conducting solid electrolyte fuel cell</td>
<td>Cell Voltage of 625 mV at 200 mA/cm² and 500°C</td>
<td>Cell Voltage of &gt;780 mV at 200 mA/cm² and 500°C</td>
</tr>
<tr>
<td>Methane coupling carbon efficiency</td>
<td>&lt;30%</td>
<td>50%</td>
</tr>
<tr>
<td>Fuel cell manufacturing cost</td>
<td>$4000/kW</td>
<td>$1500-2000/kW</td>
</tr>
</tbody>
</table>
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
    - $2\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O}$
    - $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_3\text{OH}$
      
      \textit{Issue: Products are more readily oxidized than CH}_4 \textit{leading to CO}_2
  - Non-oxidative Coupling of Methane (NOCM)
    - $2\text{CH}_4 \leftrightarrow \text{C}_2\text{H}_6 + \text{H}_2$
      
      \textit{Issue: Large positive }\Delta G\textit{, 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.

![Diagram showing the process of non-oxidative coupling of methane using a proton-conducting fuel cell.](image)

**Diagram Notes:**
- **Anode:** $2H_2 \rightarrow 4H^+ + 4e^-$
- **Cathode:** $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
- **Propane to Propylene:** $C_3H_8 \rightarrow C_3H_6 + H_2$
- **Methane to LPG:** $2CH_4 \rightarrow C_2H_6 + H_2; C_2H_6 + CH_4 \rightarrow C_3H_8 + H_2; \text{ etc.}$
- **Air** supplies oxygen for the cathode reaction.
- **Effect of H$_2$ removal on propylene yield** is shown for 700°C, 600°C, and 500°C.
KEY TECHNICAL CHALLENGES

- Proton-conducting ceramic-based fuel cell that generates >200 mW/cm² at 500°C operating on H₂
- 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/kWₑ
PROJECT TIMELINE AND MAJOR MILESTONES

- **October 1, 2014** – Project initiated.

- **September 30, 2015** – Demonstrate a 25 cm² single cell operating on H₂ at 500°C with a current density >100 mA/cm² for 50 h. (Completed using button cell)

- **December 31, 2015** - Demonstrate a 25 cm² single cell operating on propane at 500°C with a current density >50 mA/cm² for 24 h and a product yield ≥50% and selectivity >95% to propylene. (In progress using button cell)

- **June 30, 2016** - Demonstrate a 25 cm² single cell operating on H₂ at 500°C with current density >200 mA/cm² for 100 h. (Completed using button cell)

- **September 30, 2016** - Demonstrate a 25 cm² a single cell operating at 500°C on methane (simulated shale gas) with a current density >100 mA/cm² 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/SiO₂.

- 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.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dehydrogenation TOF (h⁻¹)</th>
<th>t = 0 h</th>
<th>t = 18 h</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe²⁺/SiO₂</td>
<td></td>
<td>4.3</td>
<td>5.5</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Fe⁰ NPs</td>
<td></td>
<td>45.5</td>
<td>-</td>
<td>32%</td>
</tr>
<tr>
<td>Bulk Fe₂O₃/SiO₂</td>
<td></td>
<td>Low activity and selectivity</td>
<td></td>
<td></td>
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PROPAENE 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?

![Reaction Diagram]

**Rate of Reaction**

```
<table>
<thead>
<tr>
<th>Time on Stream, h</th>
<th>Turnover Frequency (s⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>10</td>
<td>1.6</td>
</tr>
<tr>
<td>20</td>
<td>1.2</td>
</tr>
<tr>
<td>30</td>
<td>0.8</td>
</tr>
<tr>
<td>40</td>
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<tr>
<td>50</td>
<td>0.2</td>
</tr>
<tr>
<td>60</td>
<td>0.0</td>
</tr>
</tbody>
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```

**Selectivity to C-H activation**

```
<table>
<thead>
<tr>
<th>Time on Stream, h</th>
<th>Propylene, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>95</td>
</tr>
<tr>
<td>20</td>
<td>90</td>
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<td>30</td>
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<tr>
<td>40</td>
<td>80</td>
</tr>
<tr>
<td>50</td>
<td>75</td>
</tr>
<tr>
<td>60</td>
<td>70</td>
</tr>
</tbody>
</table>
```

CH₄ + ⎢ + H₂  →  CH₄  + H₂  
Dehydrogenation  C-H activation (desired)
Cracking  C-C activation (undesired)
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

**CHEMICAL EQUATIONS**

\[ 2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2 \]

\[ \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \]

\[ \text{CH}_4 + \text{C}_2\text{H}_6 \rightarrow \text{C}_3\text{H}_8 + \text{H}_2 \]

\[ \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2 \]

**CH₄ 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 PERFORMANCE TARGETS

- **Anode**
  - Composition stability in simulated shale gas.
  - ASR of $<1.5 \ \Omega \cdot \text{cm}^2$ in hydrogen.
  - ASR of $<3 \ \Omega \cdot \text{cm}^2$ in simulated shale gas.

- **Electrolyte**
  - Composition stability in simulated shale gas.
  - Proton conductivity of $>8 \ \text{mS/cm}$ and proton transference number $>0.90$ in hydrogen.
  - Proton conductivity $>8 \ \text{mS/cm}$ in simulated shale gas.

- **Cathode**
  - No targets defined.

- **Fuel Cell**
  - Current density $>200 \ \text{mA/cm}^2$ operating on $\text{H}_2$ at 500°C for 100 h
CONDUCTIVITY OF BZY ELECTROLYTE AS A FUNCTION OF TEMPERATURE IN AIR AND H₂

- Proton conductivity 8.8 mS/cm at 500°C in H₂ (AC impedance method).
- Proton transference number >0.95 at 500°C in H₂. (measured using concentration cell).
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.)
- 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

- Anode (substrate)
- Gold O-ring
- Cathode Gas
- To GC or hood
- Spring
- Al₂O₃Rod
- Al₂O₃Disk
- film (proton conducting ceramic)
- Cathode (porous Pt + mesh)
- Anode Gas
- pt or Ni mesh
- Al₂O₃Tubes
- Gold O-ring
- Pt leads/or gold leads
I-V AND POWER DENSITY PERFORMANCE OF A SINGLE BUTTON CELL OPERATING ON H₂

- Power density of 180 mW/cm² at 350 mA/cm² at 500°C
- Power density of 280 mW/cm² at 550 mA/cm² at 600°C
<10% LOSS IN PERFORMANCE OBSERVED OVER 100 H OPERATING ON H₂ AT 500°C

- Current density of 203 mA/cm² at t=0
- Current density of 187 mA/cm² 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/cm² at 600 mA/cm² at 500°C
- Power density of 480 mW/cm² at 900 mA/cm² 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/cm² to ~220 mW/cm² 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.
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
- $\text{H}_2$ 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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