OXIDATION OF DRY AND NEAR-DRY HYDROCARBONS AT HIGH-POWER-DENSITY ANODES

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Overall Objective and Approach

- High-power-density anode able to operate on as-received HC fuels
  - To reduce or eliminate need for fuel processing and contaminant removal upstream of the FC stack

- By fabricating anode bi-layer that has an active interlayer
  - Within the constraint of low melting point of Cu oxide
Interim Objective I

- Eliminate or reduce carbon deposition so that it does not compromise cell operation.
Dry CH$_4$ OCV at 800$^\circ$C with $\sim$600µm Anode, 13µm Electrolyte, $\sim$100µm Cathode
Dry CH₄ Performance at 800°C (~600μm Anode, 13μ Electrolyte, ~100μm Cathode)
Dry CH₄ Performance at 800°C and 0.5V (~600µm Anode, 13µ Electrolyte, ~100µm Cathode)
<table>
<thead>
<tr>
<th></th>
<th>GTI Results</th>
<th>Literature Results (U. Of Pennsylvania)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>OCV</strong></td>
<td>OCV declines from ~0.95 to ~0.7V after 200 hrs Some C</td>
<td>OCV initially ~0.93 Time dependence not available</td>
</tr>
<tr>
<td><strong>Constant Current</strong></td>
<td>V decline tracks OCV decline Load accelerates C Cell life &lt;250hrs</td>
<td>Not available</td>
</tr>
<tr>
<td><strong>Constant 0.5 V</strong></td>
<td>~32 mW/cm² to 75 mW/cm² in 5 hrs Then decline so that cell lasts for only 25 hrs Heavy C</td>
<td>Cell operates for &gt;1000 hrs Any C does not prevent operation</td>
</tr>
</tbody>
</table>

* On tape-cast, wet-impregnated Cu/Ceria/YSZ/LSM Cells. GTI cells are 2.85 cm² with 13µ electrolyte. Literature cells are <0.5 cm² with 60µ electrolyte.
Experimental Set-Up for 3 cm² Cells

- Outer Tube (Alumina)
- Inner Tube (Alumina)
- Ag Wire
- Air
- Ag Screen and Current Collector
- Fuel Cell
- Alumina Collar
- Cu Screen & Current Collector
- Cu Wire
- Soft Seals
- Cement
- Fuel
Dry CH₄ Polarization Curve
(~600µ Anode, 13µ Electrolyte, ~100µ Cathode)
SEM/EDAX of C Deposit at OCV (Dry CH₄, 800°C, 13µ Electrolyte, Top of Anode)
C Deposit at OCV (Dry CH$_4$, 800C, 13µ Electrolyte, Bottom of Anode)
## Post-Test Cell Resistance
(Thin Electrolyte)

<table>
<thead>
<tr>
<th>Description</th>
<th>Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOFC-03-04 Dry CH₄ (800,750,700°C)</td>
<td>978 Ω</td>
</tr>
<tr>
<td>SOFC-02-18 Dry CH₄ (800°C)</td>
<td>500 Ω</td>
</tr>
<tr>
<td>SOFC-02-07 H₂, 3%H₂O (700°C)</td>
<td>830,000-880,000 Ω</td>
</tr>
</tbody>
</table>
Candidate Reasons for OCV Decline

- Electrical short through seal and/or electrolyte due to C deposition
  - Stable OCV and long life with H₂
  - Thin electrolyte
  - No edge face seal
    - Observe C in seal area (as well as throughout the anode)
  - More stable OCV in humidified fuel
  - Low cell resistance at room temperature
- Gas-phase C deposition due to seal and/or electrolyte leak followed by changes in gas and/or electrolyte
- C deposition due to other test parameters followed by changes in gas and/or electrolyte
  - Could include anode microstructure, flow rate, flow/temperature distribution, supply line residence time, etc.
Plans For C Reduction

- Weight gain in dry HC flow
  - To rule out microstructure or fuel purity effects
- OCV stabilization
  - Thicker electrolyte
  - Thinner anode
  - Alternative sealing
  - Changing flow
  - Reduce temperature
  - Etc.
- Constant voltage experiments
  - After OCV is stabilized
Dry CH$_4$ Performance at 800$^\circ$C and 0.5V (194$\mu$m Anode, 83$\mu$m Electrolyte, ~46$\mu$m Cathode)

OCV is 980-983 mV
Interim Objective II

- Fabricate and scale-up cells with active inter-layer and sufficient mechanical strength
Status

- Fabricated cells up to 2.5”x4” area
  - By standard dual tape-casting, wet impregnation method
  - Cells do not yet contain active interlayer
  - Mechanical strength is less than desirable
Fabrication Approach I

- Tape-cast thick, porous, μ-particle size YSZ support
  Deposit μ-particle size active interlayer on anode support
  Deposit thin, μ-particle size YSZ electrolyte/co-sinter at 1400-1550°C
  Apply and sinter μ-particle size cathode
  Wet impregnation of Cu/ceria salts/calcine/reduce

- Variations planned to address issues of deposition on porous substrate, thin-layer integrity, mechanical strength, Cu agglomeration
Fabrication Approach II

- Dry powder press porous, nm-particle size, Cu/ceria/YSZ anode
  Deposit nm-particle size, active interlayer on anode support
  Deposit nm-particle size, YSZ electrolyte
  Apply nm-particle size cathode
  Sinter structure below Cu oxide melting point

- Fabricated cermet anode support
- Variations planned to address issues of deposition on porous substrate, thin-layer integrity, mechanical strength, Cu agglomeration
Other Approaches Under Evaluation

- Tape-cast $\mu$-particle size cermet powder
  Follow steps in method 1 except for impregnation
- Tape-cast $\mu$-particle size Cu/ceria/YSZ cermet
  Deposition of nm-particle size interlayer and electrolyte
- Metallic-supported structures
Interim Objective III

- Develop a quantitative model for electrochemical performance in systems that are thermodynamically capable of depositing C
Status

- Thermodynamic modeling performed to compare mechanisms below for two fuel composition cases:

  1. Direct oxidation of methane

     \[
     \begin{align*}
     \text{CH}_4 + 4\text{O}^- & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{e} \quad \text{(anode)} \\
     2\text{O}_2 + 8\text{e} & \rightarrow 4\text{O}^- \quad \text{(cathode)}
     \end{align*}
     \]

     \[
     \text{CH}_4 + 2 \text{ O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}
     \]

  2. Methane reforming with water-shift reaction followed by oxidation of hydrogen

     \[
     \begin{align*}
     \text{CH}_4 + 2\text{H}_2\text{O} & \rightarrow \text{CO}_2 + 4\text{H}_2 \quad \text{(anode)} \\
     4\text{H}_2 + 4\text{O}^- & \rightarrow 4 \text{ H}_2\text{O} + 8\text{e} \quad \text{(anode)} \\
     2\text{O}_2 + 8\text{e} & \rightarrow 4\text{O}^- \quad \text{(cathode)}
     \end{align*}
     \]

     \[
     \text{CH}_4 + 2 \text{ O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}
     \]
Theoretical OCV for 40%CH₄/40%H₂O/20%CO₂ at 700C and Low CH₄ Conversion

Exp OCV is 833 mV. Theoretical OCV for oxidation of H₂ is ~836 mV at 1.25% CH₄ conversion.
Theoretical OCV for 19.61% CH₄/80.39% H₂O at 800°C and Low CH₄ Conversion

Exp OCV is 703 mV. Theoretical OCV for oxidation of H₂ is ~700 mV at 0.6% CH₄ conversion.
OCV at Lower $\text{H}_2\text{O}/\text{CO}_2$ Concentrations

Exp OCV is 980-983 mV. Theoretical OCV is 980 mV at 0.75% $\text{CH}_4$ conversion.

Graph showing the relationship between cell voltage and methane conversion for different reactions:
- $\text{H}_2 + 0.5\text{O}_2 = \text{H}_2\text{O} : 3\%\text{H}_2\text{O}, 3\%\text{CO}_2, \text{bal CH}_4$
- $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O} : 3\%\text{H}_2\text{O}, 3\%\text{CO}_2, \text{bal CH}_4$
- $\text{H}_2 + 0.5\text{O}_2 = \text{H}_2\text{O} : 1\%\text{H}_2\text{O}, 1\%\text{CO}_2, \text{bal CH}_4$
- $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O} : 1\%\text{H}_2\text{O}, 1\%\text{CO}_2, \text{bal CH}_4$
Plans

- Kinetic and thermodynamic modeling of dry and near-dry HC oxidation to develop mechanisms for:
  - Electrochemical performance
    - Changes in long-term, dry HC performance
    - Variations in C formation and cell performance under different operating conditions and cell geometries
  - OCV properties
    - OCV decline with time in thin-electrolyte cells
    - OCV variations with butane
    - Low dry CH₄ OCV on catalytic and non-catalytic anodes
Conclusions

- Dry or near-dry HC oxidation is worth investigating
  - No fuel processing, no steam, no recycle of steam or fuel, simpler piping and manifolding, simpler heat management, faster response time, simpler controls
  - Research has shown that laboratory cells operating on certain HC fuels are not compromised by C deposition after >1000 hours
  - Relatively simple periodic “cleaning” of the anode may be possible
Conclusions

- Cell life depends upon minimizing C formation
  - Higher electrolyte integrity or more tailored anode microstructure may be required for a dry HC cell as compared with a H₂-fueled cell
  - Recent results suggest that conditions for long-term operation can be achieved in 2.85cm² cells
- A range of approaches are available for fabrication of Cu-based cells containing an active interlayer
- Preliminary thermodynamic OCV modeling is consistent with a mechanism based on CH₄ reforming followed by H₂ oxidation