New Anodes for Hydrocarbon SOFCs

Integrated Solid Oxide Fuel Cells

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DOE SBIR

DOE, Calif. Energy Commission
New Ceramic Anodes for Direct Hydrocarbon SOFCs
Desired Improvements on Anode

- Ability to use hydrocarbon fuels (e.g. natural gas, propane, gasoline, diesel) without coking
  - Reduce balance of plant cost and volume
  - Make small-scale power plants viable

- Reduction-oxidation stability
  - Needed for small power plants with frequent on/off cycling
  - Useful for large power plants

- Sulfur tolerance
Anode Materials

- **Conventional Anode – Ni-based cermets**
  - Works with H₂, methane, methanol
    - At low T for methane and methanol \(^1,^2\)
  - Coking with higher hydrocarbons
  - Volume change, performance decrease upon reduction/oxidation

- **Alternate compositions needed for higher hydrocarbons**
  - Cu-Ceria-YSZ \(^3,^4,^5\)
  - Ceramic based (Ceria, LaCrO₃) \(^6,^7,^8\)
  - No coking, but electrochemical performance worse than Ni-cermets

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\(^1\)E.P. Murray, Nature **400**, 649.  \(^2\)E.P. Murray, SOFC VI, 1001.
\(^3\)S. Park, Nature **404**, 265.  \(^4\)S. Park, App. Cat. A **200**, 55.
Cell Performance Comparison: Hydrogen

- Anode/bulk GDC/LSCF
  - ATFJ Ceramic Anode vs. Ni-GDC
- Comparable performance of ceramic and Ni-GDC anodes
- ~40% of cell resistance due to bulk GDC electrolyte
- Low OCV due to GDC
Cell Performance Comparison: Propane

- ATFI Ceramic Anode vs. Ni-GDC
- ATFI Ceramic Anode outperforms Ni cermet anode in C₃H₈
- No coking on ceramic anode
- Ni cermet failed due to coking
Hydrocarbon Performance: Methane

- ATFI Ceramic Anode
- Power density drops ~ 20% for CH₄ compared to H₂
- Ceramic anode performance comparable to Ni-GDC
Lifetime Data with Hydrocarbon

- In $\text{C}_3\text{H}_8$ at 450 mV
- Stable operation over 7 hours
Hydrogen-Air Cycling

- Initial attempt at long-term cycling test:
  - Current decreases over first 24 hrs
  - Seal degradation after 85 hrs

- Little effect of seven redox cycles
Cell Test Results

- Direct operation with methane, propane, and butane without carbon deposition
- Cells exhibit stable behavior during operation
- Good stability during redox cycling in initial tests
- Performance similar to other direct hydrocarbon cells despite thick electrolyte:

<table>
<thead>
<tr>
<th>Anode</th>
<th>Hydrogen</th>
<th>Methane</th>
<th>Propane</th>
<th>Butane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Ceria-YSZ^4</td>
<td>0.30</td>
<td>0.115</td>
<td>-</td>
<td>0.105</td>
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<tr>
<td>ATFI Ceramic Anode</td>
<td>0.16</td>
<td>0.128</td>
<td>0.130</td>
<td>0.085</td>
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</tbody>
</table>

Conclusions

- Ceramic-based anode is promising for hydrogen or hydrocarbon-fueled SOFCs

- Considerable fuel-flexibility with improved performance expected upon varying:
  - Properties and amounts of electronic and ionic conductors
  - Metal catalyst composition and content

- Ceramic-based anode can potentially be prepared as support for thin-electrolyte SOFCs
  - Co-sintering with YSZ should be feasible
Integrated Solid Oxide Fuel Cells
(ISOFCs)
ISOFC Concept

Fuel

Anode (porous)  Interconnect (dense)  Electrolyte (dense)  Cathode (porous)  Substrate (porous)
Stacking ISOFC Elements

- Individual elements consist of many cells
  - High voltage, low current
  - Current collection at ends
- No separate interconnects
- Flattened tubes:
  - high power-to-volume ratio
  - minimal sealing problems
  - Number of flow fields reduced by 2 relative to planar SOFC
Other Advantages

- Thermo-mechanical properties
  - Support material is not an active cell component: can be chosen for thermo-mechanical properties.

- Manufacturing
  - Eliminates need of pressure contacts between SOFC and IC plates: reduced flatness requirements
  - Small-area cell design more tolerant of thin electrolyte defects
  - Flat tube geometry conducive to screen printing

- Stack Electrical Performance
  - Short electrode current paths – low ohmic loss
  - Minimizes effect of pressure contact resistances
Related Work: Banded Tubular Cells

- Cells and ICs deposited in bands around calcia-stabilized zirconia (CSZ) support tubes
  - Rolls-Royce

- Problems:
  - Difficulty of patterning deposits around full width of tube: e.g. slurry coating and EVD
  - Large cell widths
  - Current shunting due to conductivity of CSZ support at high T
Current Shunting by Support

- Conductivity measured for PSZ support (3 mm thick, ~30 vol% porosity)
- Assumptions for calculation:
  - 10 cm x 10 cm ISOFC
  - 0.5 W/cm² at 0.7 V (1.4 A, 31.5 V)

<table>
<thead>
<tr>
<th>T</th>
<th>600°C</th>
<th>700°C</th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (S/cm)</td>
<td>6.25 x 10⁻⁴</td>
<td>2.03 x 10⁻³</td>
<td>5.32 x 10⁻³</td>
</tr>
<tr>
<td>Leakage current</td>
<td>0.006 A (0.42%)</td>
<td>0.02 A (1.4%)</td>
<td>0.05 A (3.6%)</td>
</tr>
</tbody>
</table>

Substantially reduced loss for low-T SOFCs
Cross-Sectional SEM Image

- LSM-YSZ
- YSZ
- Ni-YSZ
- PSZ substrate

Mag = 1800 X
Conclusions

- Integrated SOFC potentially offers unique performance/processing/stacking advantages

- Initial demonstration of integrated SOFC structure
  - First round porous substrate development
  - Approximate substrate-layer shrinkage match
  - Screen printing of patterned components

- Substantial processing development required to demonstrate good stack performance