New Anodes for Hydrocarbon SOFCs

Integrated Solid Oxide Fuel Cells

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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

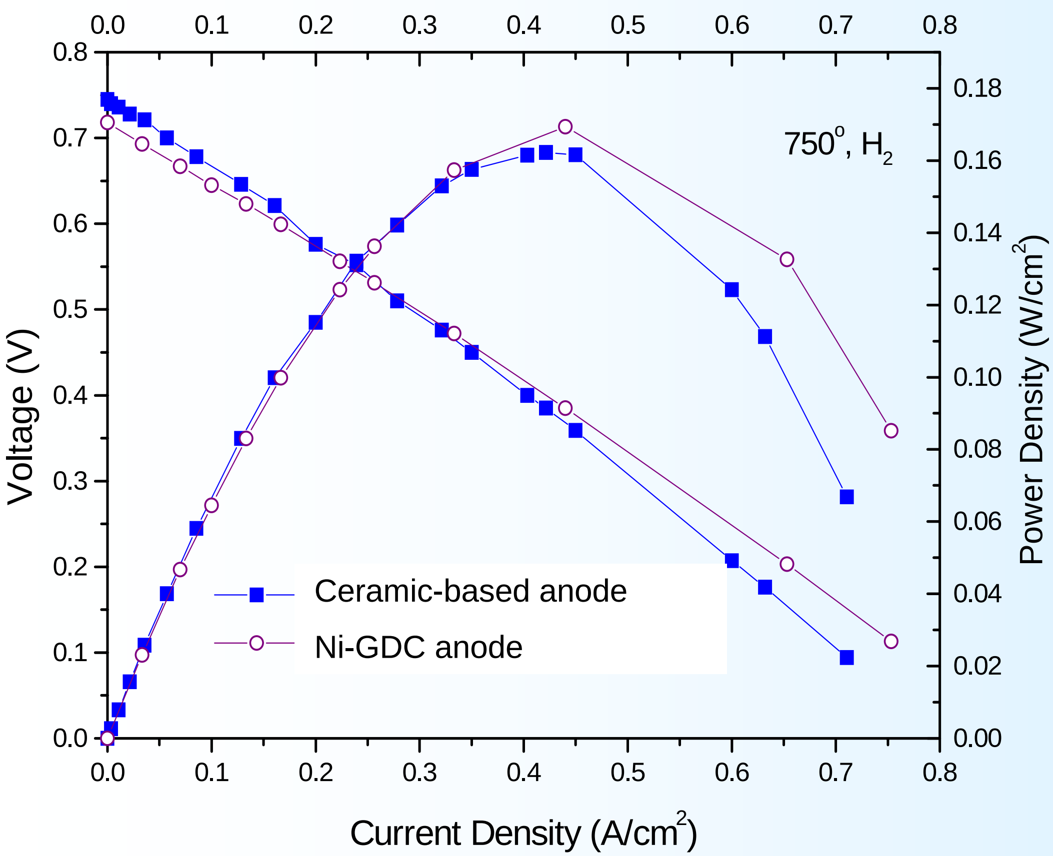
- Conventional Anode – Ni-based cermets
  - Works with H_2, methane, methanol

    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, $LaCrO_3$) [6,7,8]
  - No coking, but electrochemical performance worse than Ni-cermets

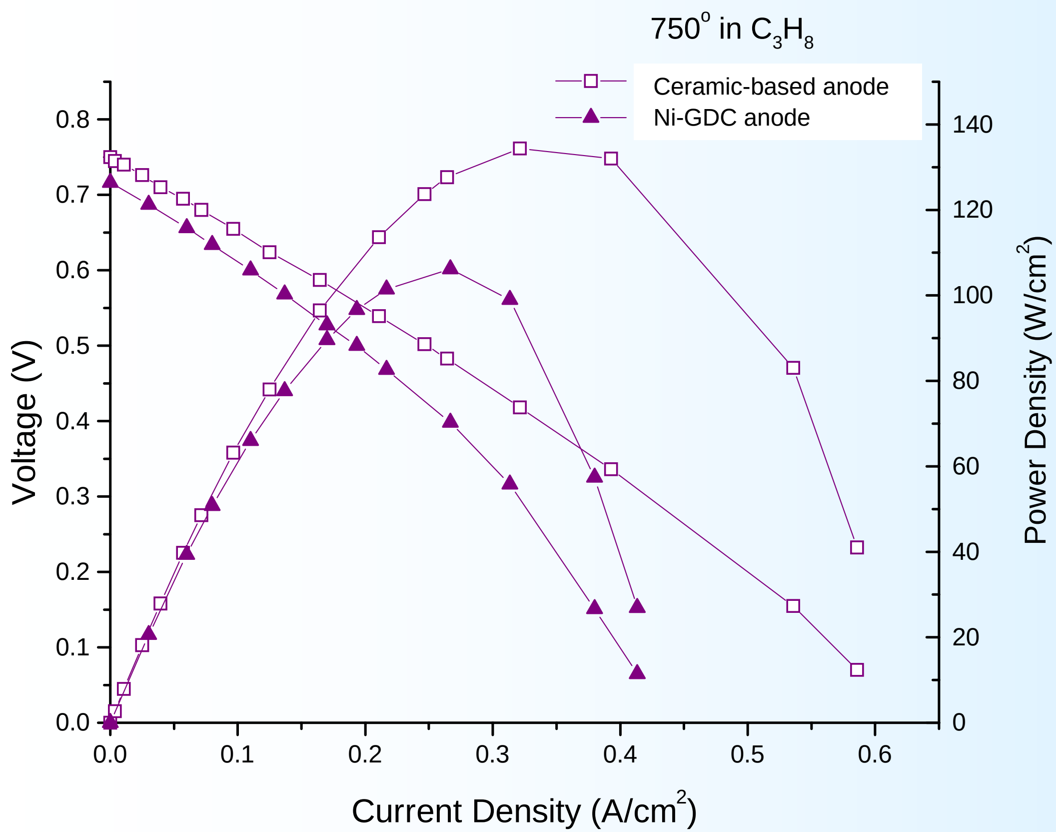
[1]E.P. Murray, Nature **400**, 649.
[2]E.P. Murray, SOFC VI, 1001.
[3]S. Park, Nature **404**, 265.
[4]S. Park, App. Cat. A **200**, 55.
[5]H. Kim, J. Electrochem. Soc. **148**, A693.
[6]C. Xia, Solid State Letters **4**, A52.
[7]T. Norby, 1st Euro. SOFC Forum Proc., 217.
[8]S. Primdahl, J. Electrochem. Soc. **148**, A74.

Cell Performance Comparison: Hydrogen



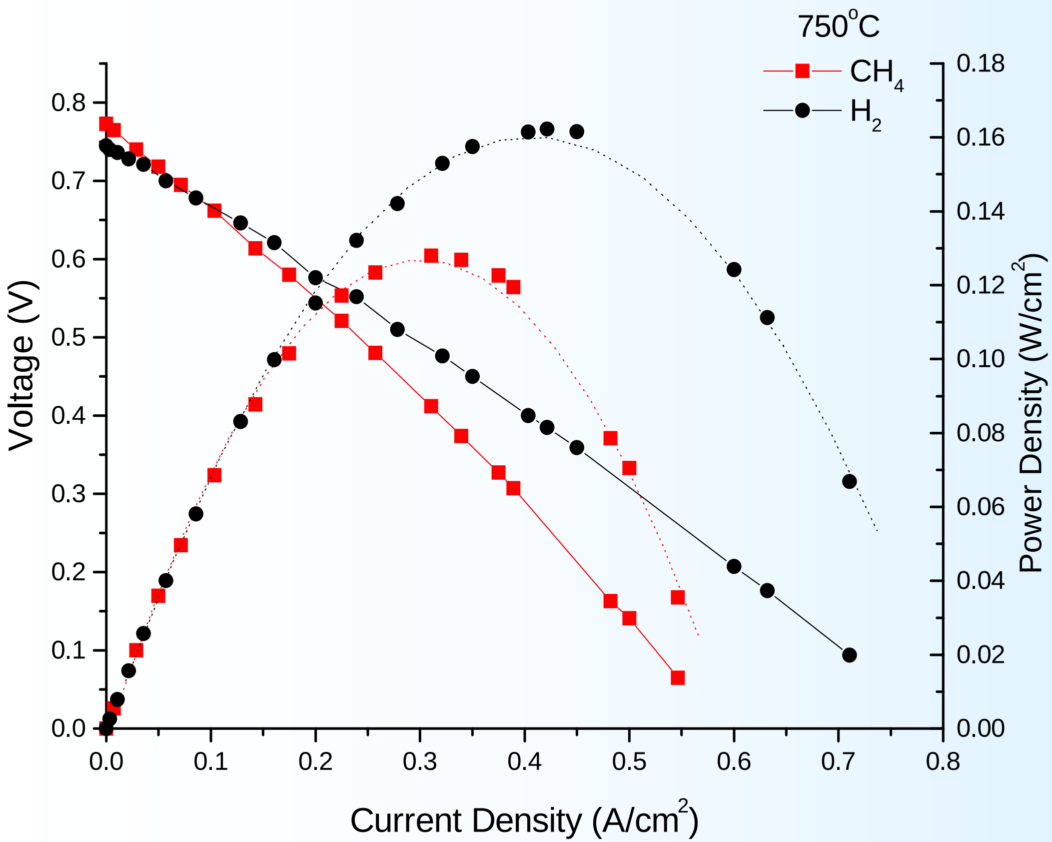
- Anode/bulk GDC/LSCF
  ATFI Ceramic Anode
  vs. Ni-GDC
- Comparable performance of ceramic and Ni-GDC anodes
- ~40% of cell resistance due to bulk GDC electrolyte
- Low OCV due to GDC

Cell Performance Comparison: Propane



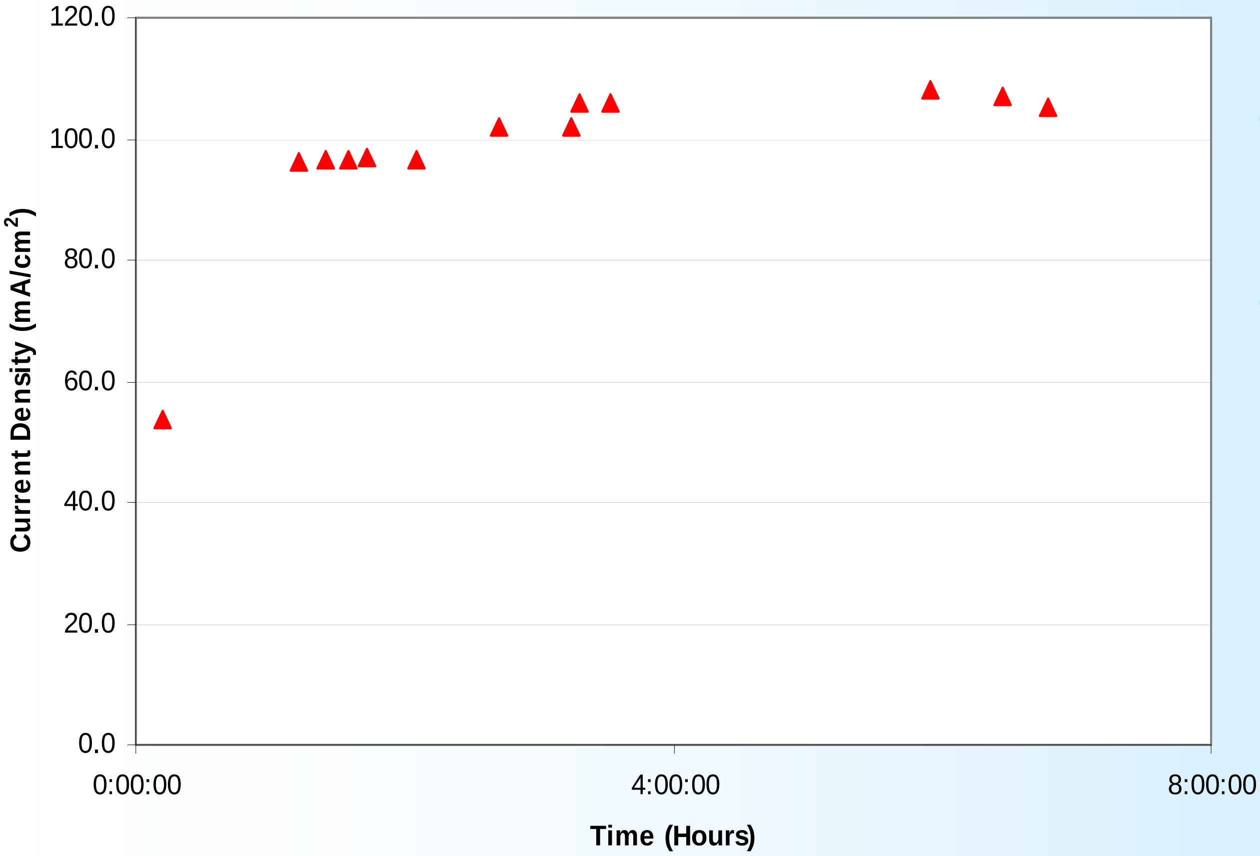
- ATFI Ceramic Anode vs. Ni-GDC
- ATFI Ceramic Anode outperforms Ni cermet anode in C_3H_8
- No coking on ceramic anode
- Ni cermet failed due to coking

Hydrocarbon Performance: Methane



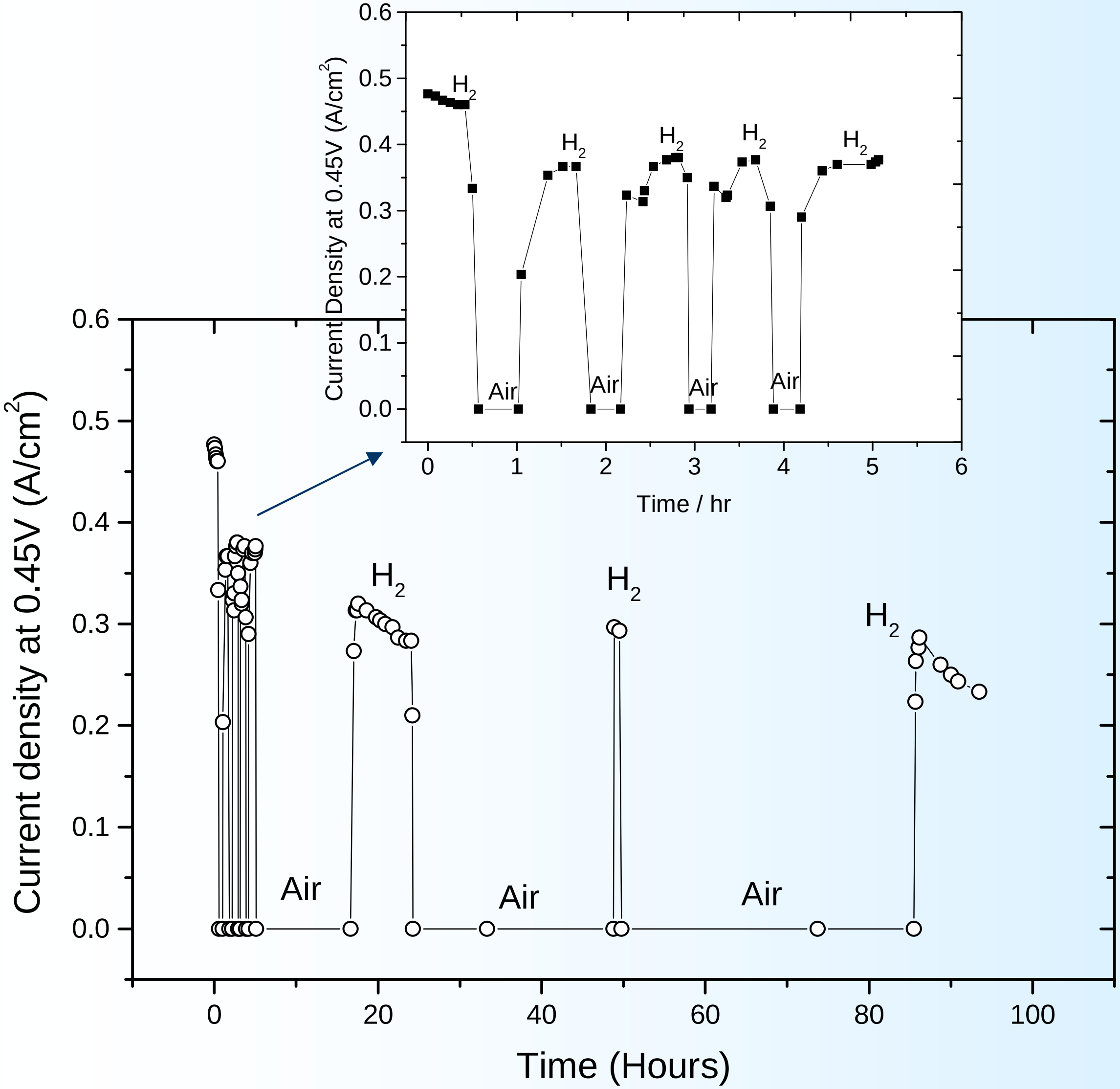
- ATFI Ceramic Anode
- Power density drops ~ 20% for CH_4 compared to H_2
- Ceramic anode performance comparable to Ni-GDC

Lifetime Data with Hydrocarbon



- In C_3H_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:

Anode	Hydrogen	Methane	Propane	Butane
Cu-Ceria-YSZ[4]	0.30	0.115	-	0.105
ATFI Ceramic Anode	0.16	0.128	0.130	0.085

[4] Park, Gorte, et.al. Applied Catalysis A: General (2000) 55-61

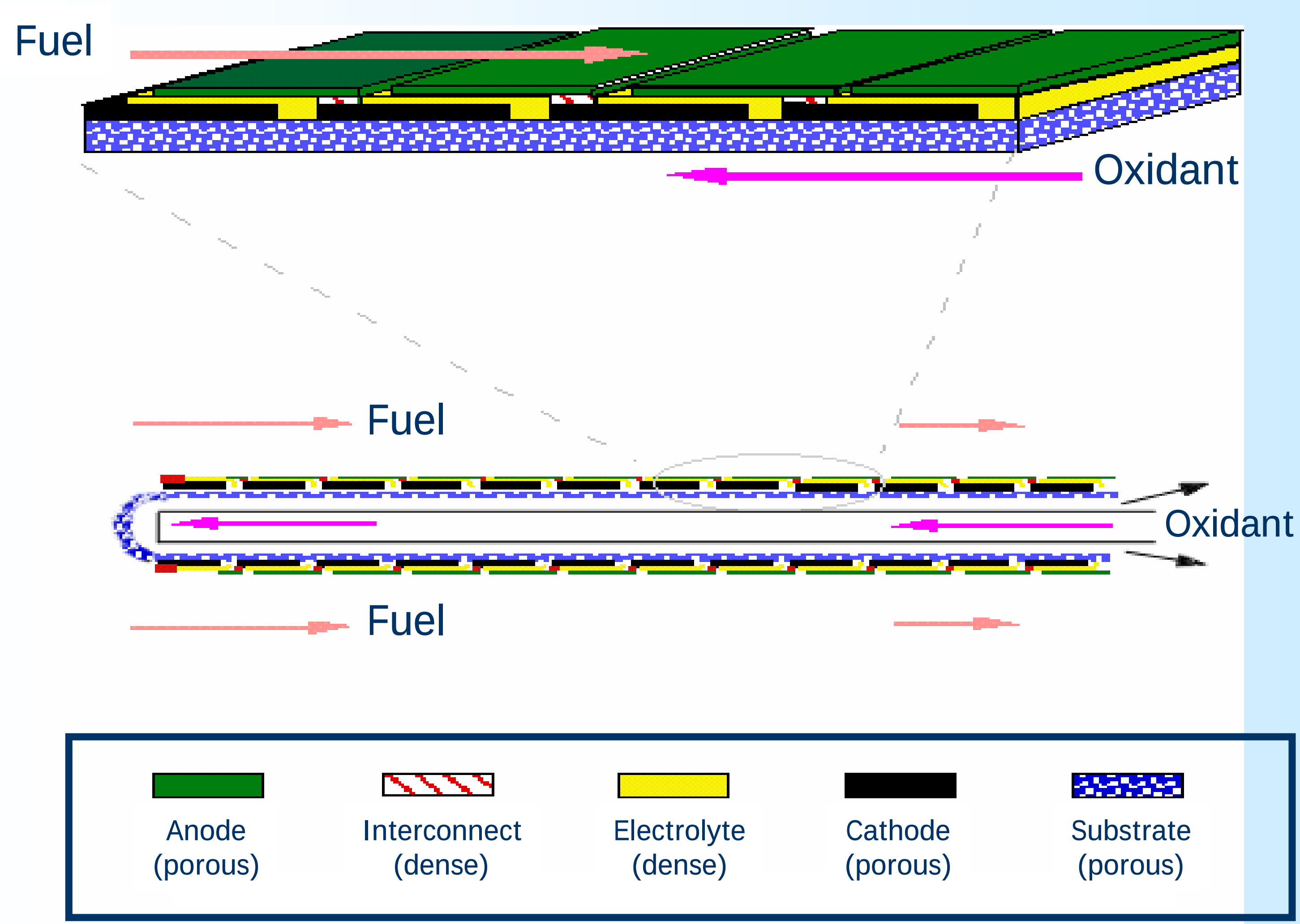
Conclusions

- 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

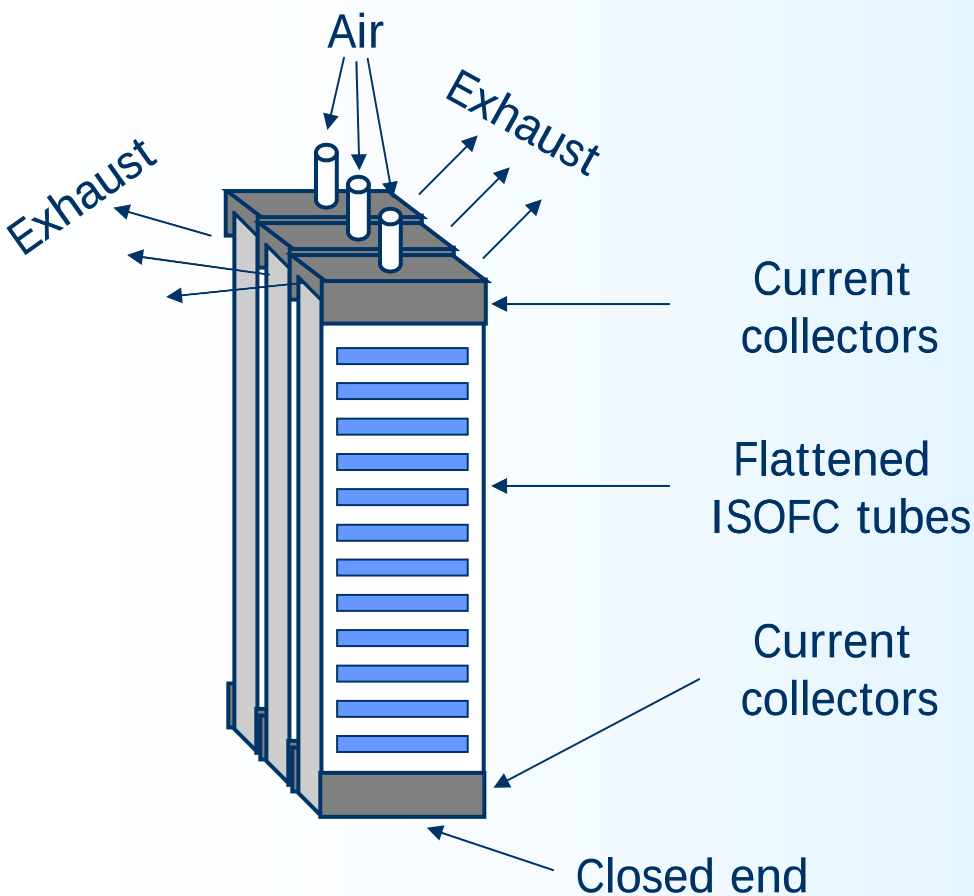
Integrated Solid Oxide Fuel Cells

(ISOFCs)

ISOFC Concept



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
  - *A. O. Isenberg, SSI, 3/4, 431 (1981)*
  - *N. Hisatome, N. Nagata, T. Saishoji, and S. Kakigami, SOFCIV(1995), p 216*
  - *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

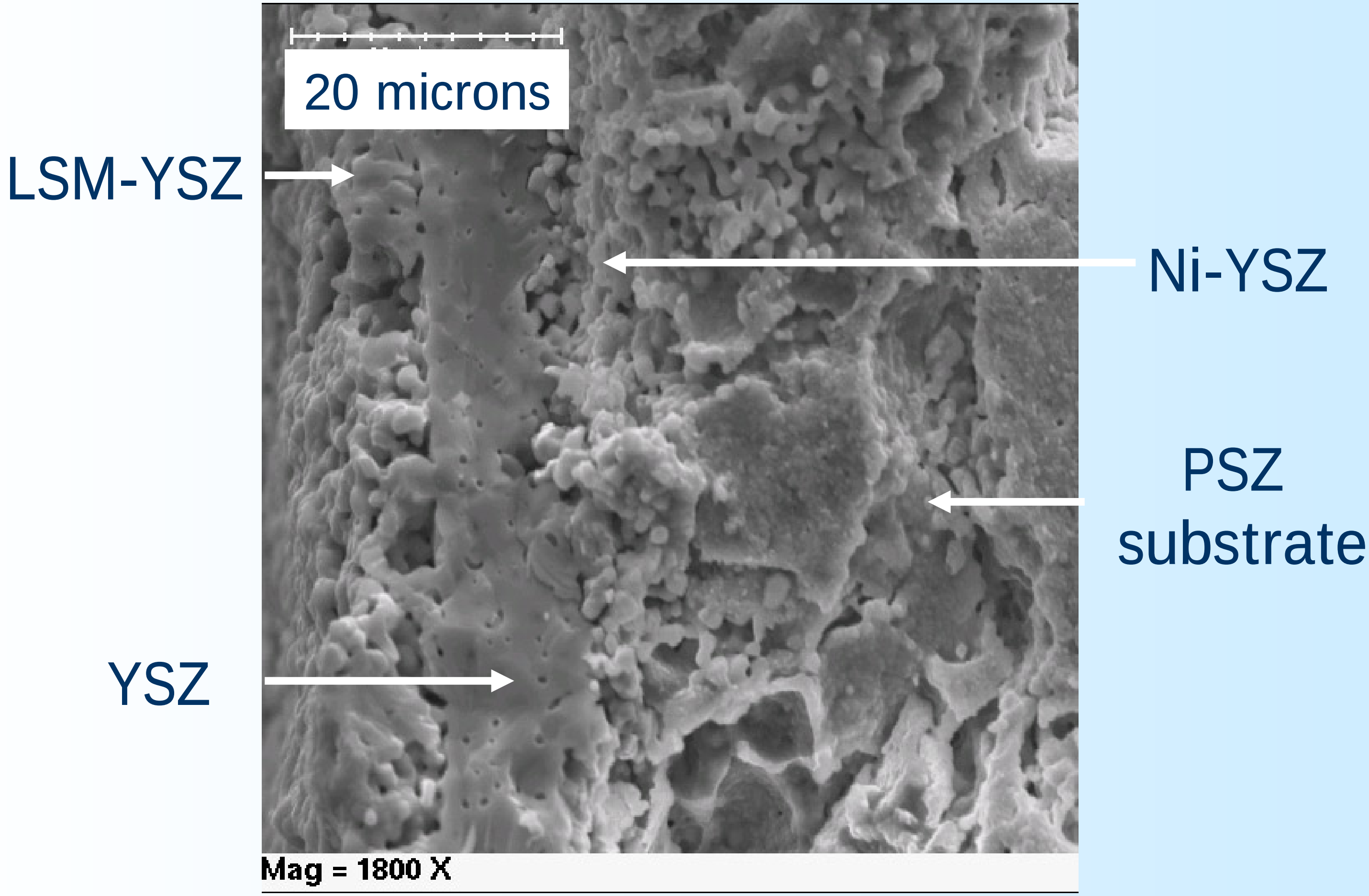
Current Shunting by Support

- Conductivity measured for PSZ support (3 mm thick, ~30 vol% porosity)
- Assumptions for calculation:
  - 10 cm x 10 cm ISOFC
  - 0.5 W/cm^2 at 0.7 V (1.4 A, 31.5 V)

T	600ºC	700ºC	800ºC
Conductivity (S/cm)	6.25×10^{-4}	2.03×10^{-3}	5.32×10^{-3}
Leakage current	0.006 A (0.42%)	0.02 A (1.4%)	0.05 A (3.6%)

Substantially reduced loss for low-T SOFCs

Cross-Sectional SEM Image



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