Direct Operation of Anode Supported SOFCs on Methane

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Direct-Hydrocarbon SOFCs

Definition: Hydrocarbon fed directly to anode with little or no steam

Advantages:

- Simplified, lower-cost system
- Higher voltage and efficiency than reforming
- Liquid HCs: high volume energy density for portable and transportation applications

Problems:

- Carbon deposition promoted by Ni
- Poor electrochemical activity for Ni-free anodes

SOFCs using hydrocarbon fuels

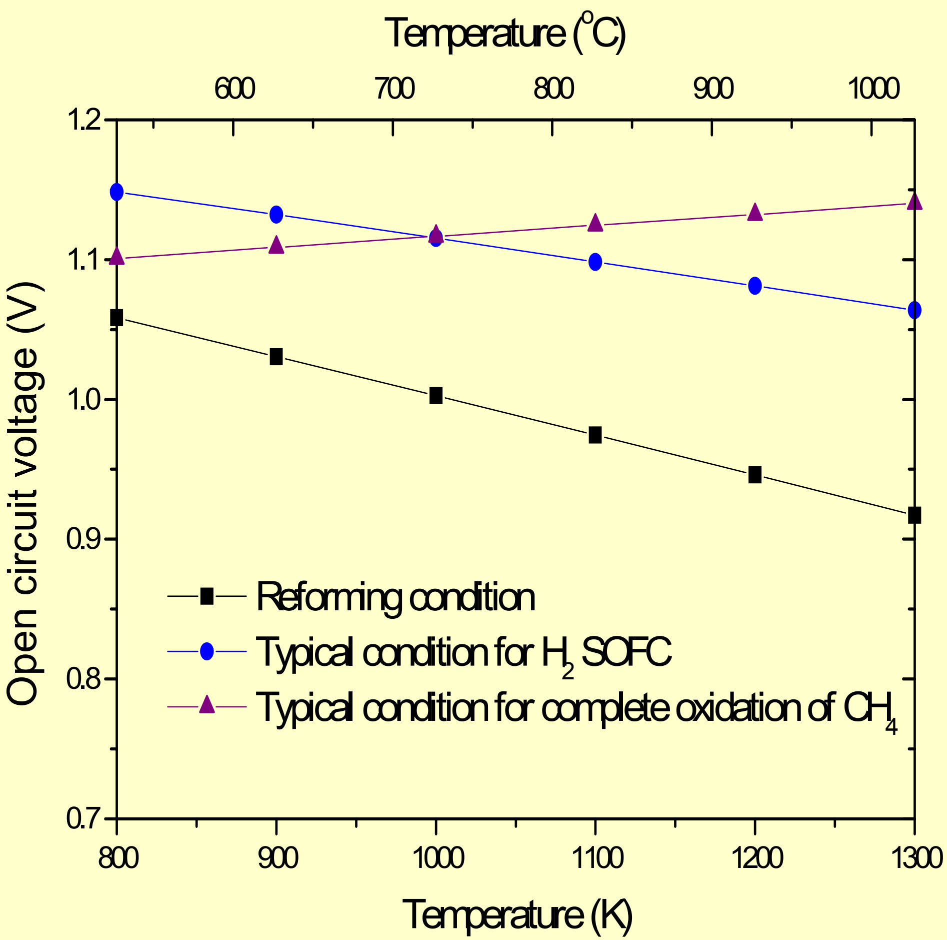
Internal reforming

- Strongly endothermic
- Significant steam is needed to prevent carbon deposition
  - System complication
  - Low OCV

Direct Hydrocarbon

- Exact reaction is unknown
  - Direct oxidation reactions are thermally neutral
  - OCV different for different reactions
- No added steam
  - Simpler system
  - Low steam content increases cell voltages

OCV for Methane Internal Reforming SOFCs



The OCV calculated from Nernst Equation

- Carbon:Steam=1:2(mol)
- At ambient pressure, high temperature, the favored reaction:

$(1\text{-}x)CH_4+(1\text{-}x)H_2O=xCO+3xH_2$

At equilibrium, P_{H2O}~0.23, P_{H2}~0.56

The cell reaction:

$H_2+(1/2)O_2=H_2O$

OCV Comparison

- High steam content in reformate gives >10% lower OCV
- The OCV for direct oxidation of methane increases with T

Outline

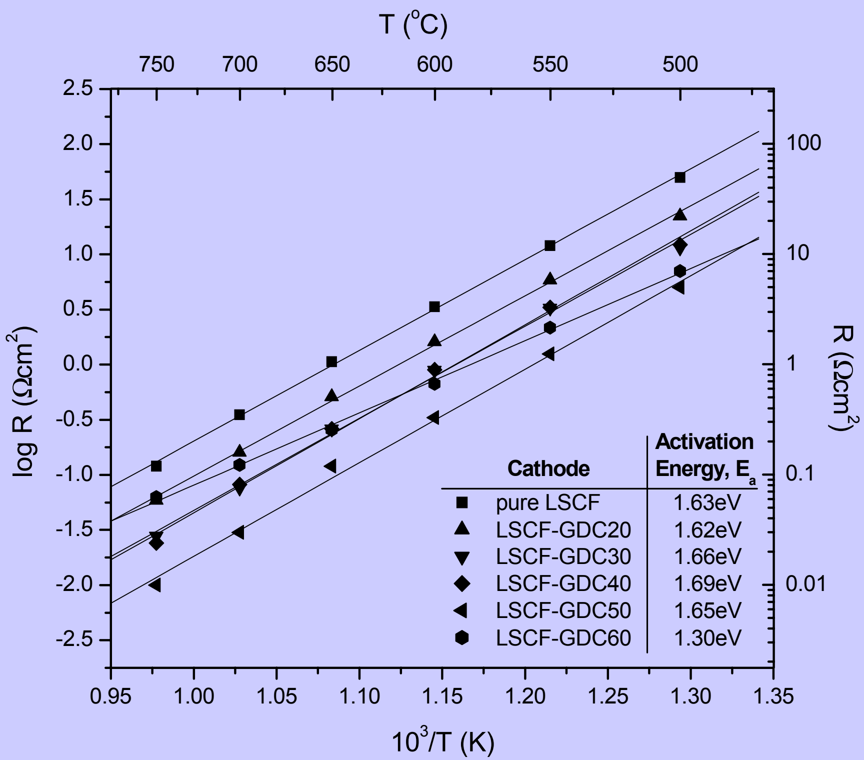
- Introduction
- SOFC fabrication
  - Anode supported SOFCs made by centrifugal casting technique
  - LSM-YSZ and LSCF-GDC cathodes
- SOFC results
  - Methane
  - Natural gas
- Comparison of OCVs with Nernst equation
- Conclusions

Cell Fabrication

- Conventional Ni-YSZ anode supports
- YSZ electrolyte
  - Centrifuge coating technique
  - 25 microns thick
- LSM-YSZ or LSCF-GDC cathodes

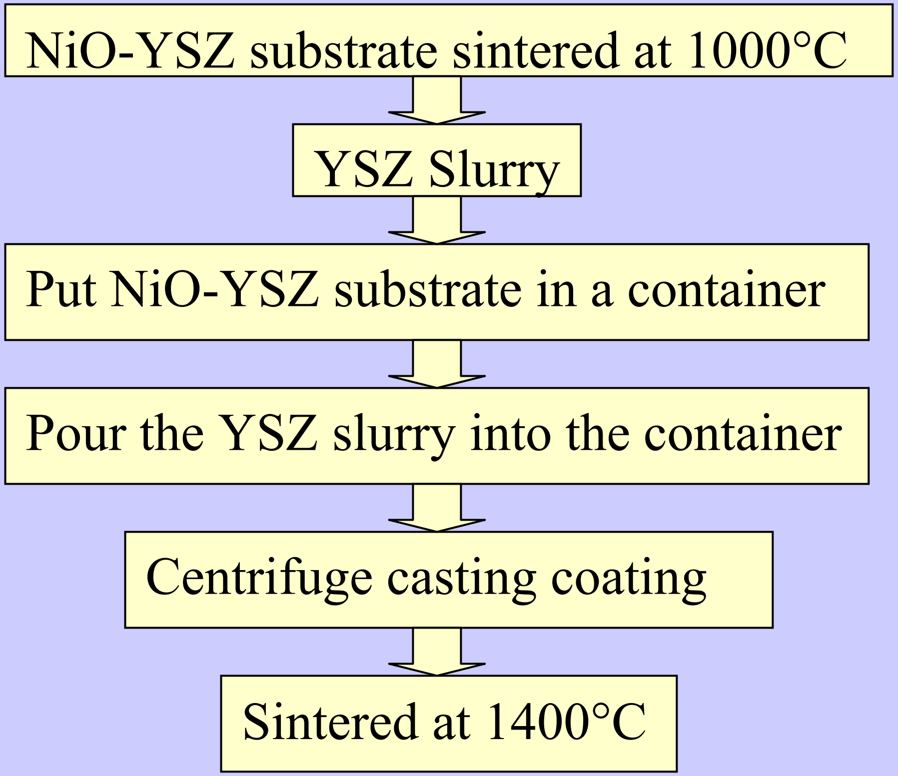
- LSCF-based cathodes can potentially provide low polarization at < 700°C

LSCF-GDC Cathodes on YSZ

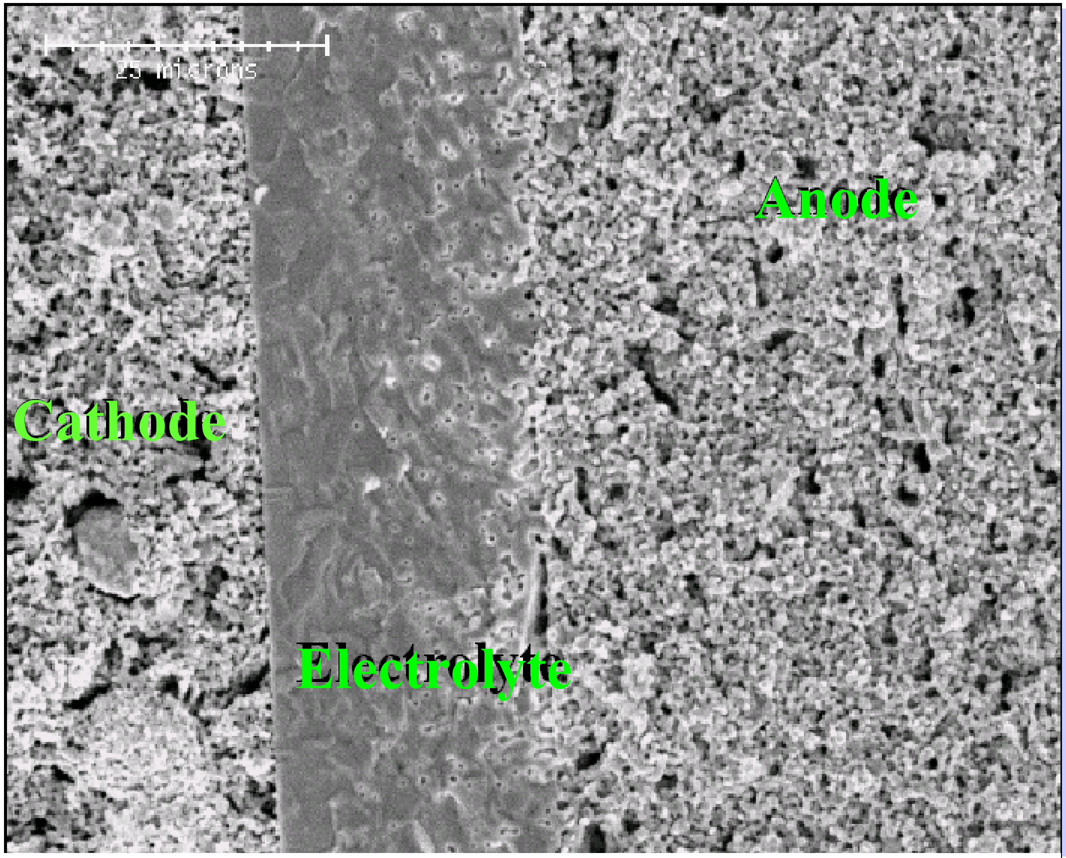


- LSCF = $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$
- 30 - 50 wt% GDC yields very low overpotential
  - 0.3 Ωcm^2 at 600C
  - 0.01 Ωcm^2 at 750C
- Results below show good stability
- Promising low-T cathode but needs more study

Centrifugal Casting Technique

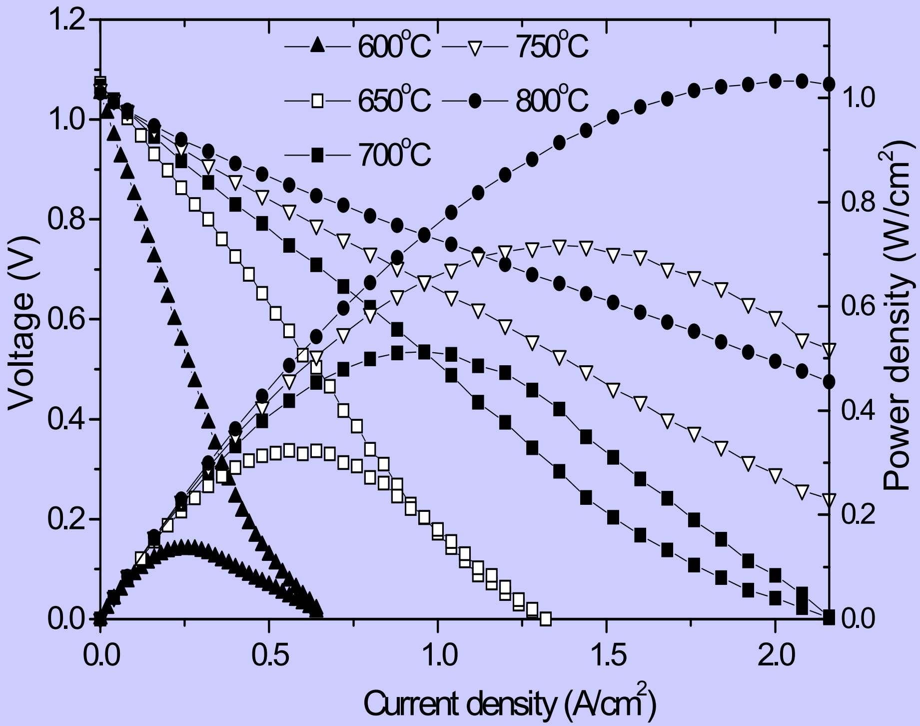


Cross-Section SEM Image



- Dense YSZ electrolyte
- Thickness of ~25μm
- Porous and uniform anode
- Porous cathode, microstructure not perfect

Single-Cell Test: Hydrogen

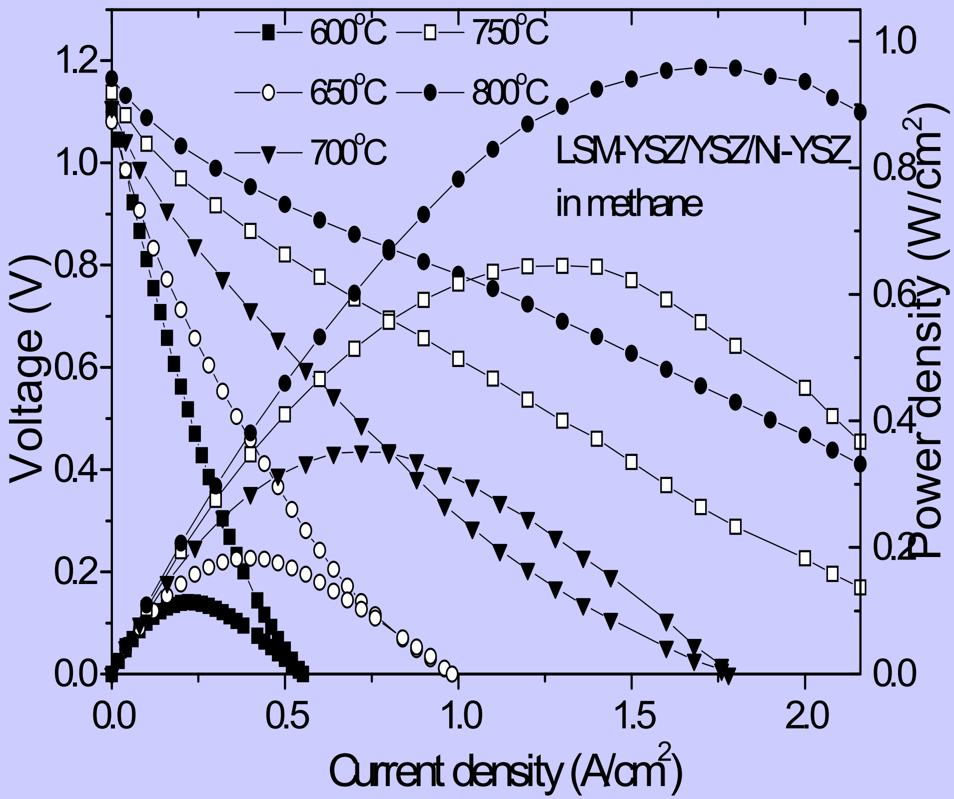


- LSM-YSZ/YSZ/Ni-YSZ
- Tested in air and humidifed H_2
- > 1 W/cm^2 at 800°C
- Cathode area = 0.5 cm^2

Hydrocarbon Single Cell Test Conditions

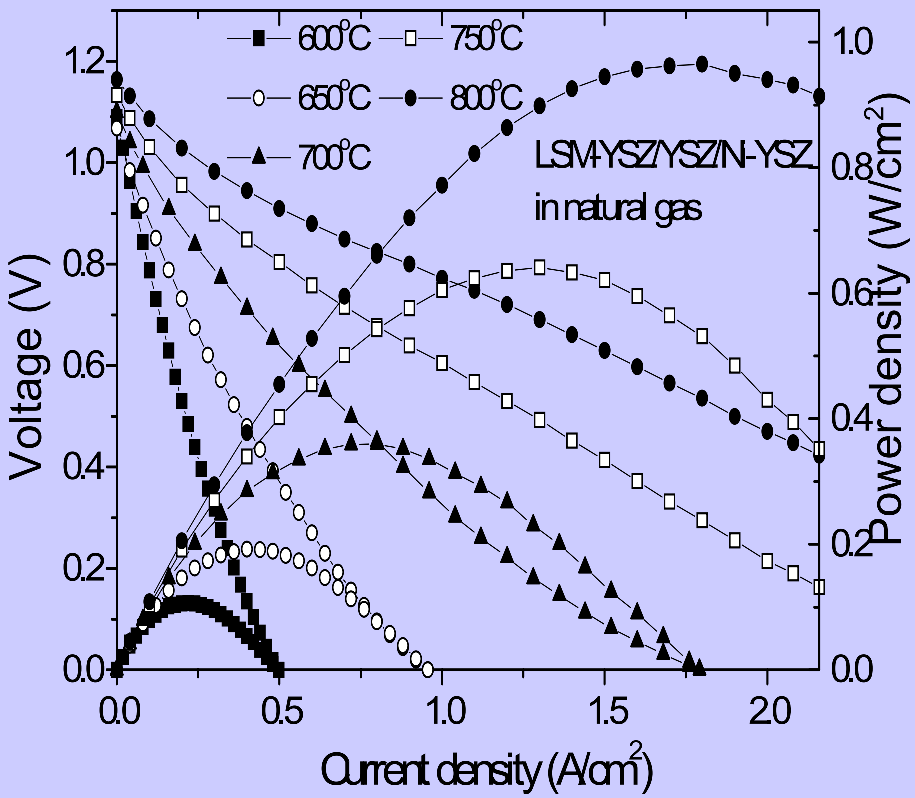
- Low methane fuel utilization
  - 1% assuming complete oxidation
  - 4% assuming partial oxidation
- Similar to conditions near fuel inlet of direct-methane stack
  - Coking most likely
  - Reaction products (i.e. H_2O and CO_2) make coking less likely elsewhere in stack

Single-Cell Test: Methane



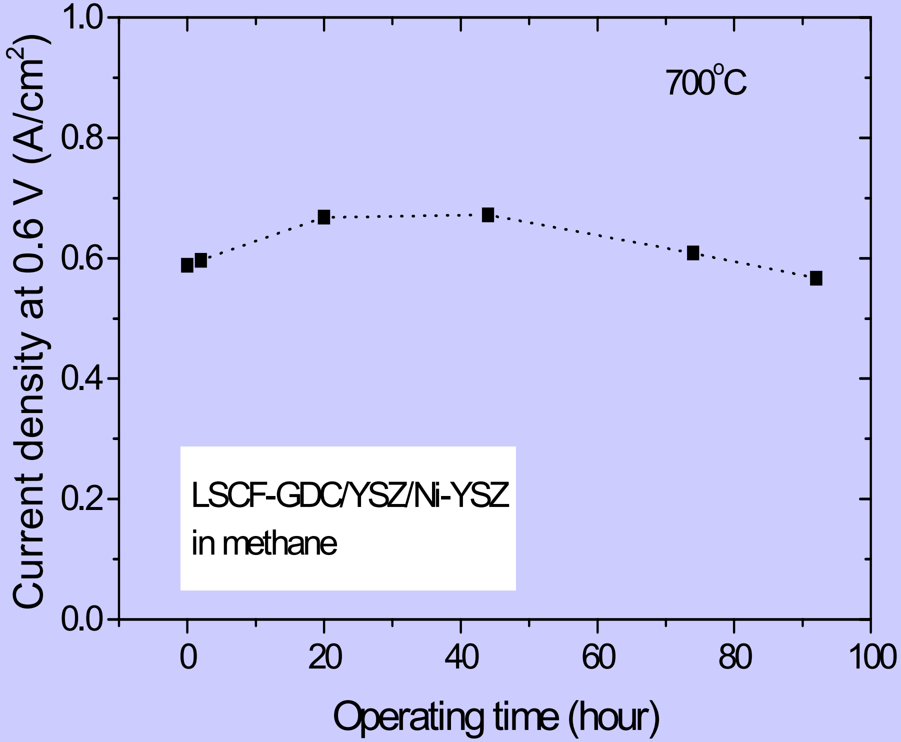
- LSM-YSZ/YSZ/Ni-YSZ
- Tested in air and humidified CH_4
- ≈ 1 W/cm^2 at 800°C
- 10-20% of power densities with H_2
- OCV increases with increasing T

Single-Cell Test: Natural Gas



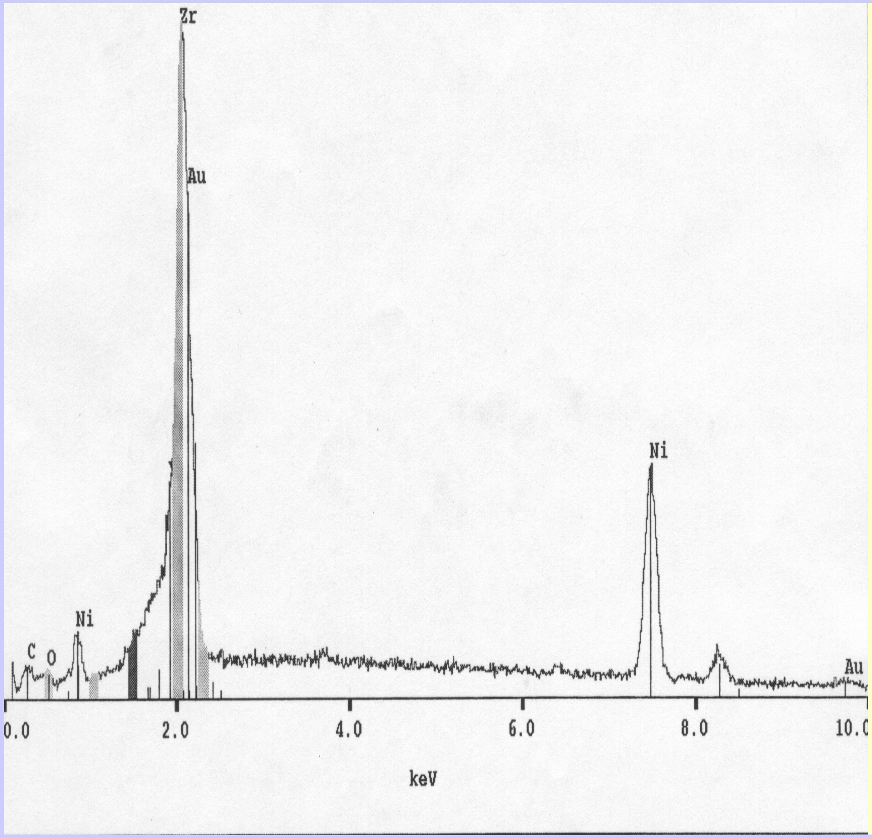
- LSM-YSZ/YSZ/Ni-YSZ
- Tested in air and humidifed sulfur-free natural gas
- ≈ 1 W/cm^2 at 800°C
- Results similar to pure methane

Life Test: Methane



- Reasonably stable performance
- Anode exposed to air for ≈ 10 min at 40 hrs
- No carbon deposition visible
- LSCF-GDC cathode provided stable performance

SEM-EDX Measurement



- After 90 h test at 700°C
- Near anode surface
- Small C peak detected
  - Coking mostly suppressed when current flowing

Coking Observations

- Open circuit or low current
  - Rapid coking at 800°C
  - Rate of coking low below 700 ° C
  - Agrees with prior measurements showing coking is slow on Ni-YSZ below 700°C

    (Finnerty, *et al.*, Catalysis Today 46 (1998) 137.)
- High cell current (~0.5A/cm^2 or above)
  - No visible coking from 600-800°C
  - Agrees with prior measurements at 1000°C

    (Ukai *et al.*, in Solid Oxide Fuel Cells VII, 2001, p. 375.)
  - Suppression of coking by oxygen ion flux and/or resulting products

Open Circuit Voltage

- Experiment: OCV increases with increasing T for methane and natural gas
- Explanation: Nernst equation
  - Assume that one anode reaction dominates
  - Various anode reactions considered
  - Product partial pressures assumed to be 0.03 atm

Reaction Pathways

Path I: Direct Electrochemical Reactions

$CH_4+2O_2=CO_2+2H_2O$
$CH_4+O_2=CO_2+2H_2$
$CH_4+(1/2)O_2=CO+2H_2$
$CH_4+O_2=C+2H_2O$

↓

$H_2+(1/2)O_2=H_2O$
$CO+H_2O=CO_2+H_2$
$CO+(1/2)O_2=CO_2$
$C+(1/2)O_2=CO$
$C+O_2=CO_2$

Path II: Cracking

$CH_4=C+2H_2$

↓

$H_2+(1/2)O_2=H_2O$
$CO+(1/2)O_2=CO_2$
$C+(1/2)O_2=CO$
$C+O_2=CO_2$

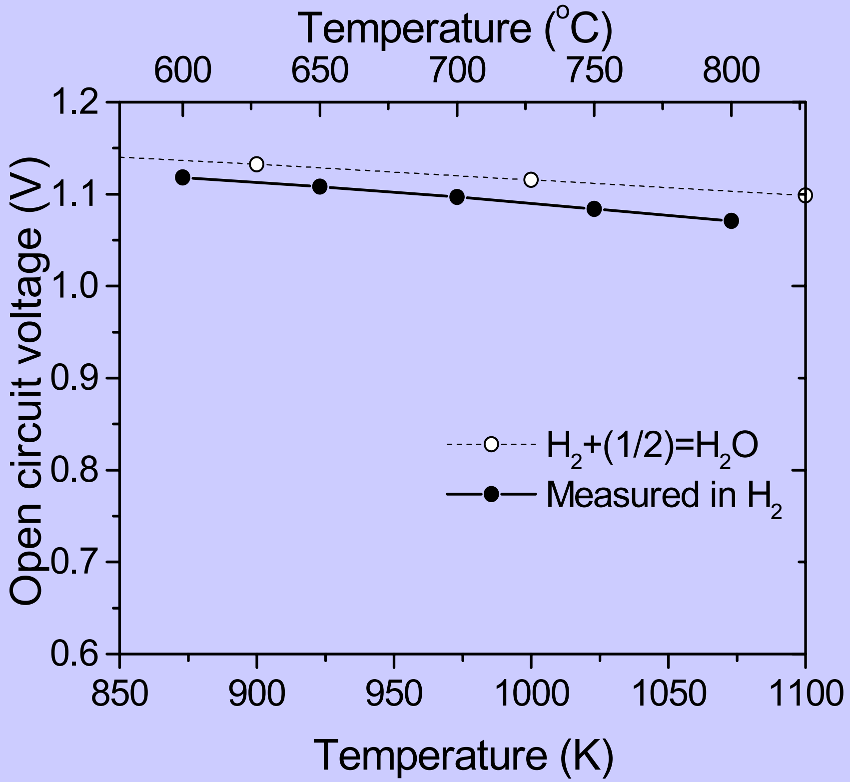
Path III: Reforming

$CH_4+H_2O=CO+3H_2$
$CO+H_2O=CO_2+H_2$

↓

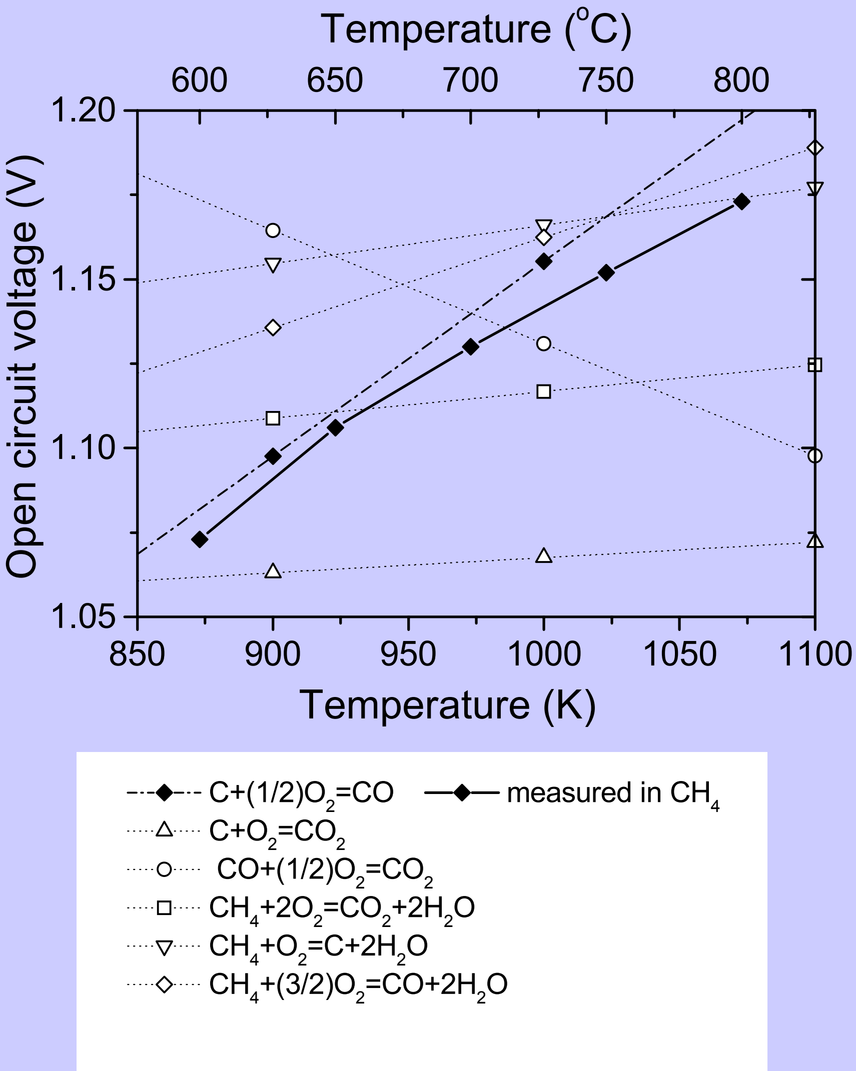
$H_2+(1/2)O_2=H_2O$
$CO+(1/2)O_2=CO_2$

OCV With Hydrogen



- Measured OCV agrees with Nernst equation
- ≈ 30 mV (~2.7%) lower than prediction
  - Explained by imperfect seals or electrolyte

OCV With Methane



- Measured OCV agrees with: C + 1/2O_2 = CO
- Higher than predicted for hydrogen over ~650°C
- ≈ 10 mV (~0.9%) lower than prediction
- But CO product partial pressure not defined
  - Absolute values not reliable
  - Slope more important

Interpretation

- High OCV agrees with prior result: 1.2V at 1000°C

  (Ukai *et al.,* in Solid Oxide Fuel Cells VII, 2001, p. 375.)
- Suggests carbon partial oxidation as anode reaction
  - Carbon presumably deposited by methane cracking
  - Agrees with observation of C on anode, suppression of coking by cell current
  - What happens to hydrogen produced by cracking?
- More data needed for definite conclusion

Direct Hydrocarbon Stack Issues

- Practical hydrocarbon stack **is possible** when working current is high enough

- Problem with break in cell operation
- Stack may be destroyed if current stops for a few minutes at 800°C
- Less problem if operating temperature ≤ 700°C

  ≥10 minutes for stack T to drop to a safe level (<600°C)

Conclusions

- Anode supported single SOFCs can operate directly on methane and natural gas
  - Relies on cell current to help suppress coking
  - Coking not a problem, except at high T and low current
  - Nernst analysis suggests partial oxidation of C as the anode reaction
- Single cell tests are believed to provide the most stringent test of coke-free operation—Direct methane SOFC stack is possible.
- LSCF-GDC is a potential solution for low-T low polarization cathode