Operation of SOFCs With Practical Hydrocarbon Fuels

Jiang Liu, Brian Madsen, Zhongliang Zhan, and Scott Barnett

Northwestern University

SECA Core Technology Program

Department of Energy: NETL & PNNL

R&D Objectives I

- Determine conditions where Ni-YSZ anodes operate reliably and coke-free with methane
  - Direct methane SOFC
  - Minimize pre-reforming requirements
    - Steam content
    - Volume of pre-reformer
  - Determine anode reactions with methane
- Test methods for removing coke
  - PO_2 range where C oxidizes and Ni remains metallic

R&D Objectives II

- Methods for improving redox and sulfur tolerance
  - Ni-YSZ: alter composition of electrolyte/anode interface
  - Ceramic-based anodes: alternate catalyst to Ni
- Reduce or eliminate anode Ni to allow operation with higher hydrocarbons
  - Ceramic-based anodes

Technical Approach

- Materials systems
  - Ni-YSZ with methane and natural gas
  - Ceramic-based anodes with propane, butane, etc.
- Experimental approach
  - Fuels ranging from pure to dilute hydrocarbons (simulating partially reformed fuel)
  - Techniques:
    - Impedance spectroscopy and single-cell testing
    - Anode product gas analysis
    - Open-circuit voltage measurements
    - Thermodynamic and kinetic modeling of anode reactions

Results to Date

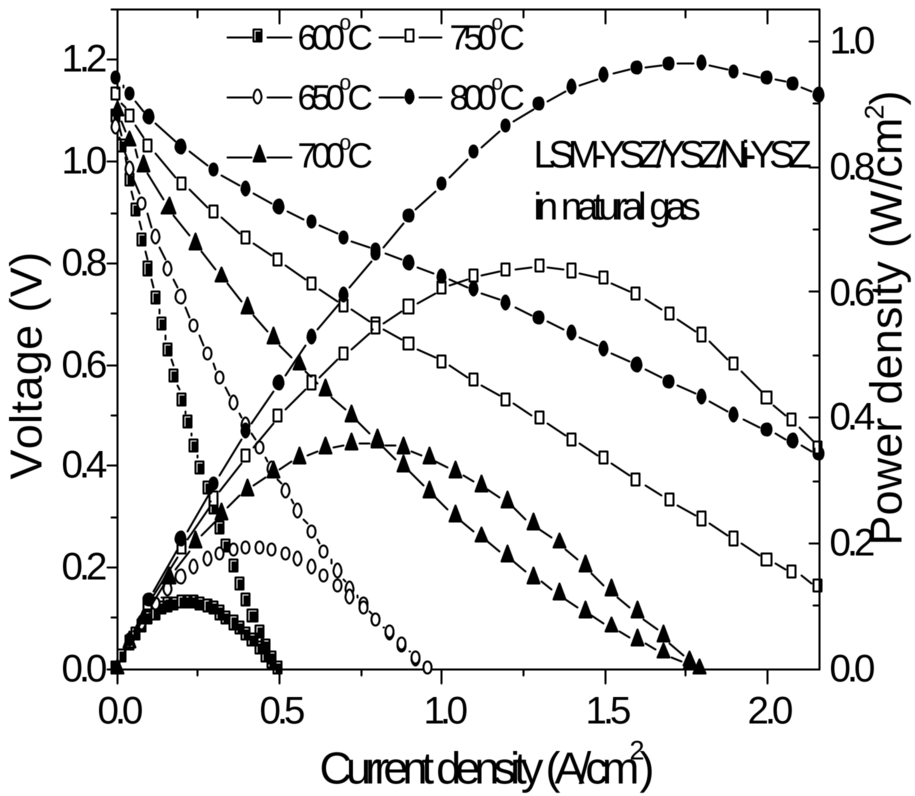
Ni-based anodes: methane and natural gas

- SOFC results
- Open circuit voltages
- Impedance spectroscopy
- Anode gas analysis
- Coking observations

- Ceramic-based anodes: propane and other fuels
  - SOFC results
  - Thermodynamic calculation: e.g. propane
  - Redox cycling

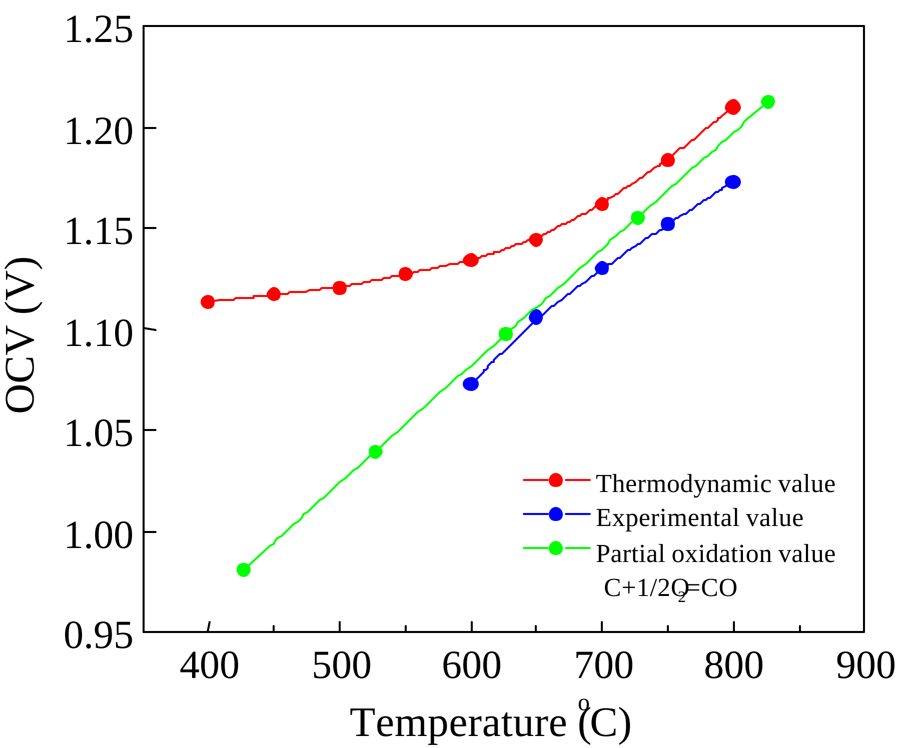
Single-Cell Test: Natural Gas

Ni-YSZ / YSZ / LSM-YSZ



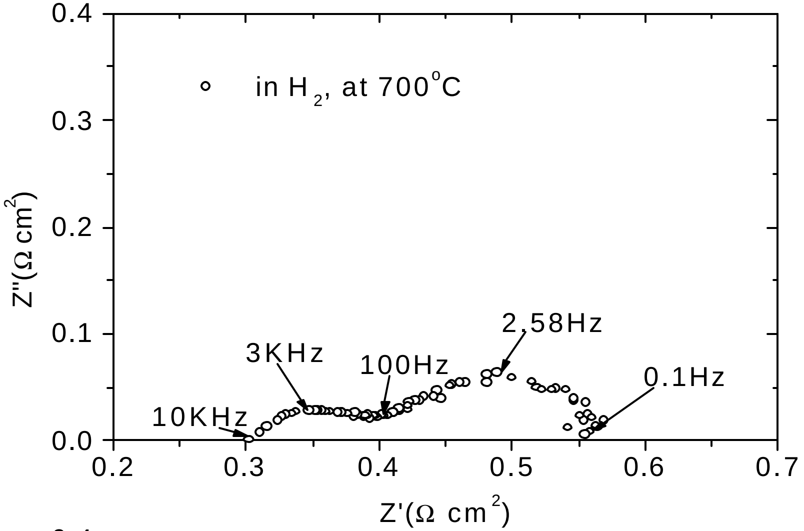
- Tested in air and humidifed sulfur-free natural gas
- ≈ 1 W/cm^2 at 800C
- Results similar for pure methane
- 80-90% of power densities with H_2
- OCV increases with increasing T

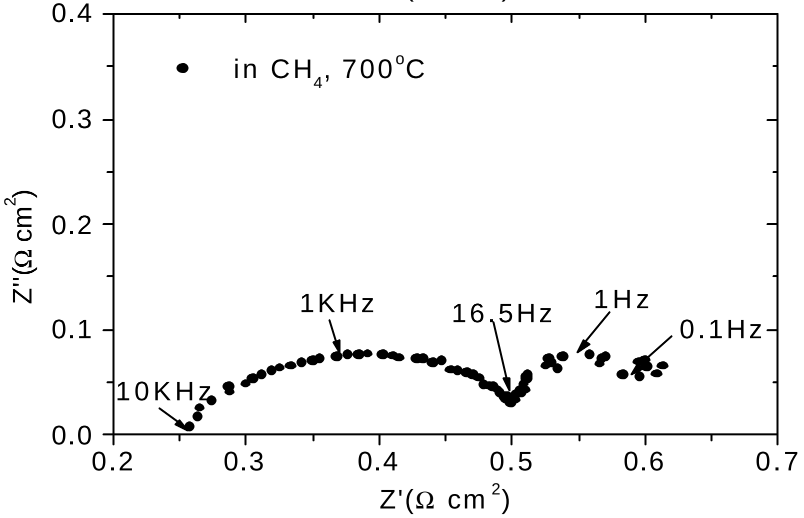
Methane OCV: Experimental vs Nernst Equation



- Inlet fuel:97%CH_4 + 3%H_2O
- ≥ 700C: Agrees with equilibrium calculation
  - 25 mV deviation same as for H_2 OCV
- <700C: deviation from equilibrium calculation
  - Non-equilibrium gas composition?
  - Agrees with C partial oxidation over full T range
- Does not agree with direct methane oxidation

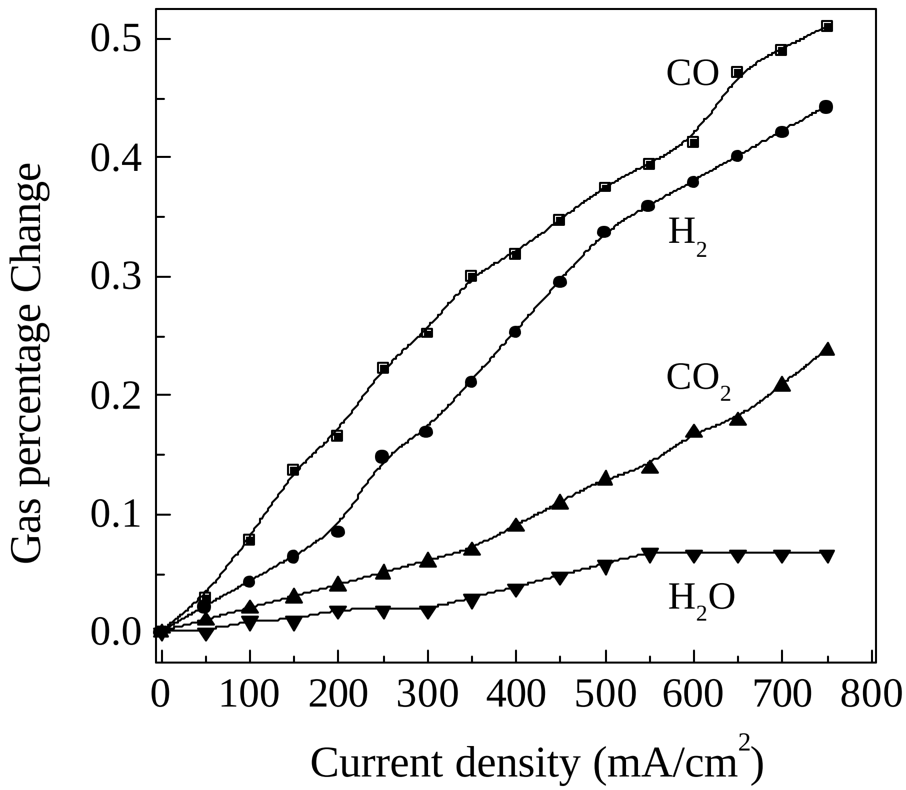
Impedance Spectra: H_2 vs CH_4





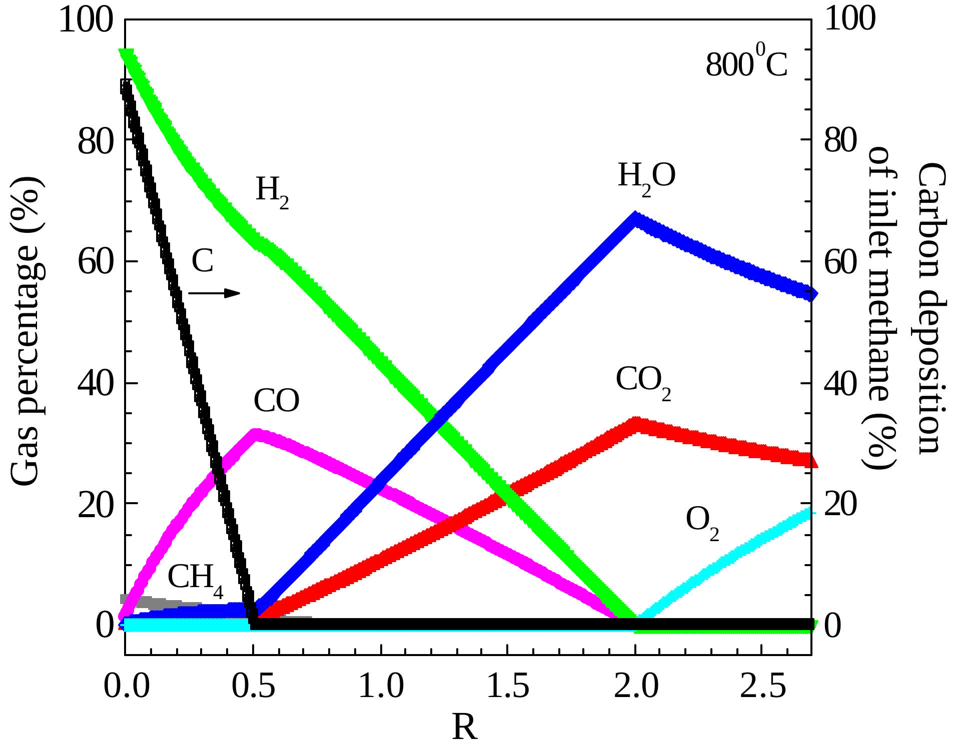
- Measured at open circuit
- Higher frequency arc:
  - Increased from ~0.1 Ωcm^2 (H_2) to ~0.3 Ωcm^2 (CH_4)
  - Frequencies agree with anode/electrolyte/anode samples
  - Conclusion: anode arc
- Low-frequency arc decreases slightly for CH_4
  - Probably cathode arc
  - Measurement interaction?

Product Gas Composition



- Test temperature: 800°C
- H_2 and CO are main products
  - Agrees with equilibrium calc
  - H_2 should be higher – mass spec sensitivity problem
  - Electrochemical partial oxidation
- Concentration changes are small due to small fuel utilization

Equilibrium Calculation: Methane-Oxygen Mixture



R = O_2-to-CH_4 ratio

- R < 0.5:
  - Carbon deposition
  - C, CO, and H_2 main products
- R > 0.5:
  - No carbon
  - H_2O and CO_2 increase
- Comparison with experiment
  - R < 0.05
  - CO high and increases: agrees
  - H_2 high: agrees (trend disagrees)
  - H_2O and CO_2 low: agrees
  - Very little coking: disagrees

Why is coking suppressed?

- Local equilibrium?
  - Overall O_2-to-CH_4 ratio $R \sim 0.05 \rightarrow$ coking
    - Based on total CH_4 flow
  - But consider region within anode:
    - Local R value actually >0.5 (non-coking) if <10% of methane actually enters anode
  - We are developing a kinetic calculation to consider this

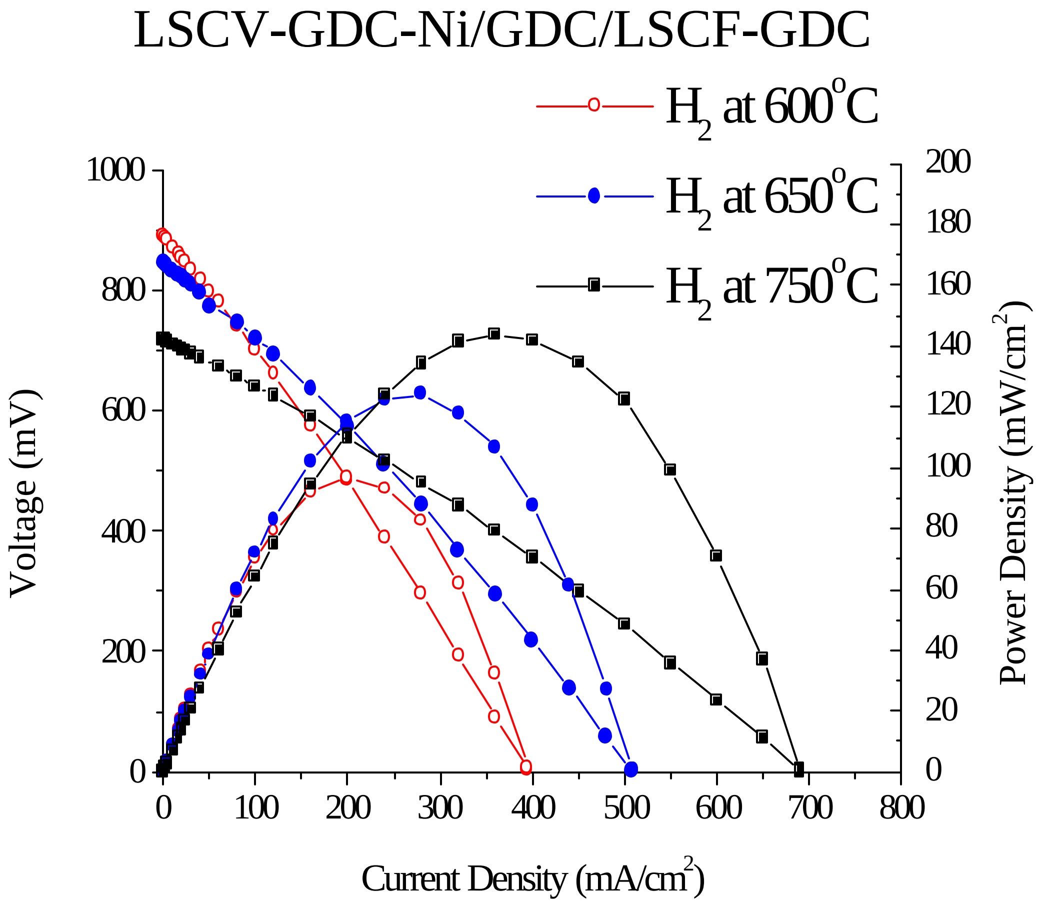
Results to Date

- Ni-based anodes: methane and natural gas
  - SOFC results
  - Open circuit voltages
  - Impedance spectroscopy
  - Anode gas analysis
  - Coking observations
- **Ceramic-based anodes: propane and other fuels**
  - SOFC results
  - Thermodynamic calculation: e.g. propane
  - Redox cycling

SOFC Implementation

- Anode
  - Electronic conductor (~ 48 %):
    - $La_{0.8}Sr_{0.2}Cr_{0.8}Mn_{0.2}O_3$ (LSCM)
    - $La_{0.80}Sr_{0.20}Cr_{0.98}V_{0.02}O_3$ (LSCV)
    - $Sr_{0.86}Y_{0.08}TiO_{3-\delta}$ (SYT)
  - Ionic conductor (~ 48 % $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC))
  - Electrochemical catalyst (4% Ni)
- Electrolyte (GDC, ~0.5 mm thick)
- Cathode (LSCF-GDC)

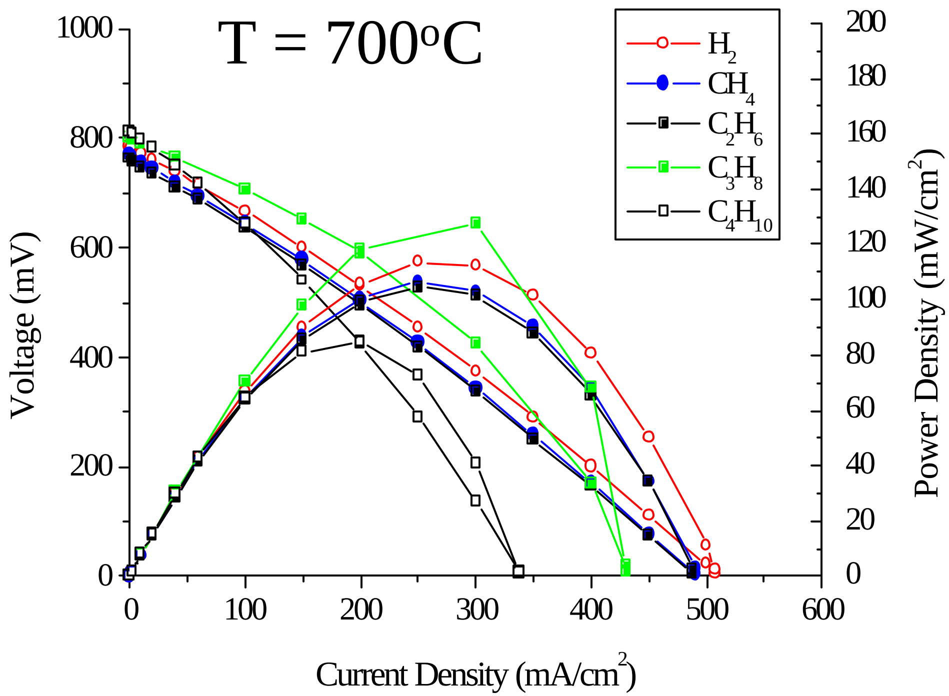
SOFC Performance vs T: H_2



- With increasing T:
  - OCV, resistance decreases
    - 1.05 V at 500°C
  - power increases
    - ~0.10 W/cm^2 at 600°C
    - ~0.15 W/cm^2 at 750°C
- Impedance spectra: 60-75% of resistance from bulk GDC

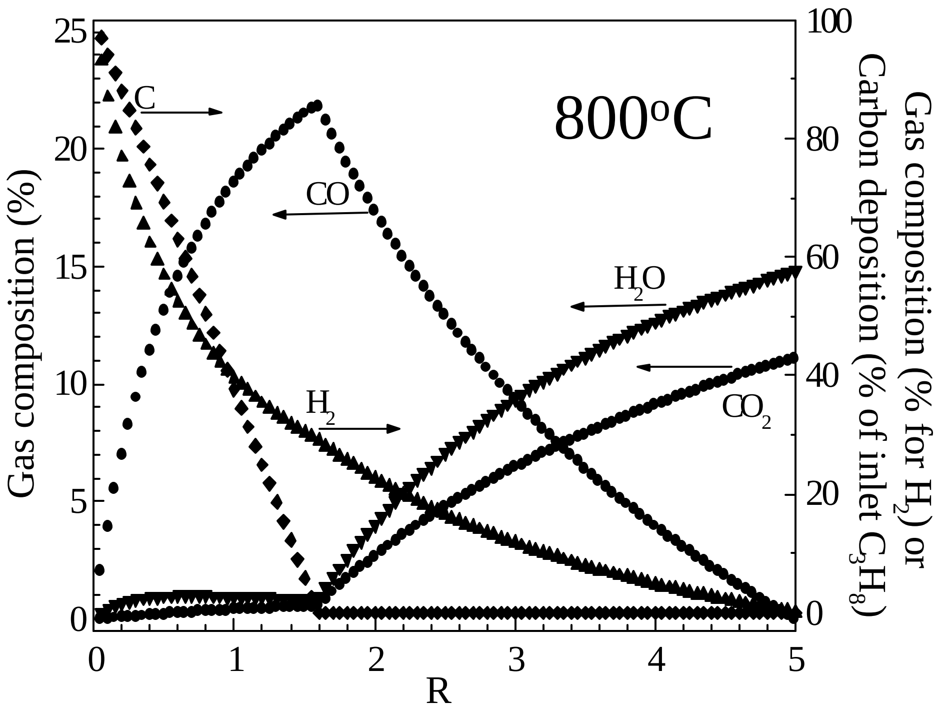
Performance With Various Fuels

LSCV-GDC-Ni/GDC/LSCF-GDC



- Similar performance with H_2, CH_4, C_2H_6, C_3H_8, C_4H_{10}
- Cell performance degraded slightly over several days
  - Fuel performance variations partly due to timing
  - Propane tested earlier
  - Butane tested later
- Limiting current for heavier molecules: gas diffusion?

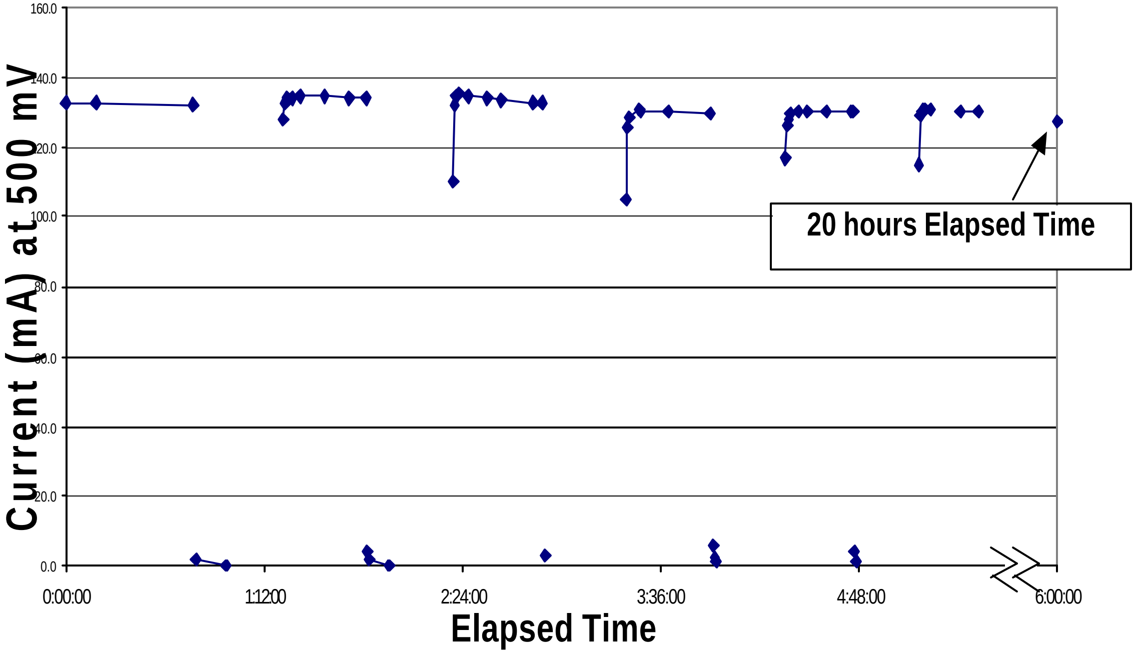
Equilibrium Reaction Products: Propane-Air



R = O_2-to-C_3H_8 ratio

- R < 1.5:
  - Carbon deposition
  - CO and H_2 main gaseous products
- R > 1.5:
  - No carbon
  - H_2O and CO_2 dominate
- Comparison with experiment
  - R < 0.05 in experiments
  - Well within coking range

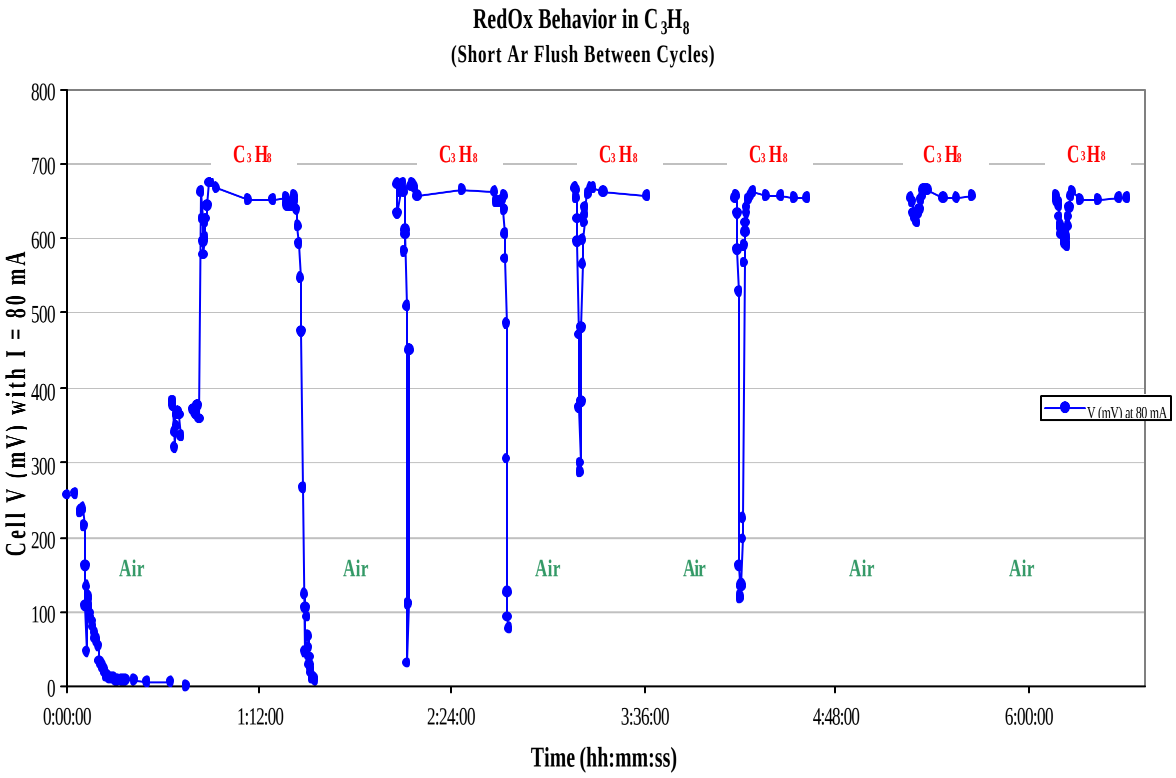
Hydrogen-Air Cycling



- Cell current at constant voltage
- 700^{o}C, humidified 5% H_2 (in Ar) or air
- Good stability through six redox cycles

Propane-Air Cycling

(Reduction-Oxidation at 700°C)



- Cell voltage at constant current (200 mA/cm^2)
- 1 hour period
- Gas lines purged with Ar – may explain transients
- No degradation of performance after many cycles

Conclusions: Ceramic Anodes

- Work well with $C_1 – C_4$ alkanes tested thus far
- >500h stable operation in cell test with many different fuels, redox cycles, etc.
- No degradation during many redox cycles
- Power densities low - limited by thick GDC electrolyte
  - Anode polarization resistance is acceptable
  - Ceramic anode supported cells should provide high power densities

Applicability to SOFC Commercialization

- Understanding of methane reactions on Ni-YSZ
  - Basic information for partial pre-reforming where substantial hydrocarbons are present at anode
  - Potential future direct-methane SOFCs
  - Methods for removing coke from stacks
- Ceramic-based anodes
  - Understanding of anode reactions
  - Coking resistance in higher hydrocarbons useful for some applications, e.g transportation, portable
  - Redox cycling tolerance can simplify stack design, improve reliability

Future Activities

- Further studies of reactions with Ni-YSZ
  - Full mapping of coking versus current, gas composition
  - Identify methane oxidation mechanism
  - Verify coke cleanup procedures
  - Sulfur tolerance observations
  - Redox cycling studies
- Improve understanding of ceramic anodes
  - Effect of catalyst metal composition, amount
  - Effect of ionic conductor
  - Possible titanate/chromite reactions with YSZ
- Verify potential of ceramic anodes to achieve high power density
  - Fabricate ceramic anode supported cells