Use Of High Temperature Electrochemical Cells For Co-Generation Of Chemicals And Electricity

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Approach

- Direct-Methane Solid Oxide Fuel Cells (SOFCs) for:
  - Electricity generation and
  - Production of syngas (H_2+CO) or other chemicals

Motivation

- Increase value of SOFC stacks via sale of both electricity and chemical products
  - Improve prospects for commercialization
  - Achieve highly efficient utilization of natural gas
- Reduce cost of syngas produced from natural gas
  - Cost of hydrogen (from syngas) too high compared with DoE targets ($2.50/kg, equivalent to 1 gallon gasoline)
  - Reduce cost of liquid fuels derived from syngas (methanol, synthetic diesel)

Other Advantages

- No dilution of syngas by nitrogen, as in air partial oxidation
- Avoids explosive methane-air mixtures as in partial oxidation reformers
- More appropriate H_2/CO ratio (≈2) for Fischer-Tropsch synthesis than steam reforming

Electrochemical Partial Oxidation (EPOx)

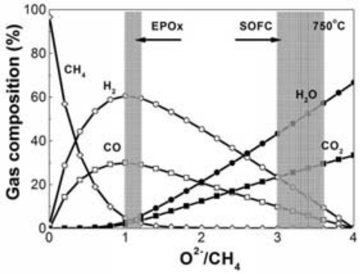
- Desired reaction is partial oxidation:

$$CH_4 + O^{2-} = CO + H + 2e^- (-22KJ@750^o)$$

  - Adjust CH_4 flow rate such that $O^{2-}/CH_4 \sim 1$
  - 3-4 times that in a direct-methane SOFC, where the aim is to produce electricity by completely oxidizing methane:

$$\frac{1}{4}CH_4 + O^{2-} = \frac{1}{4}CO_2 + \frac{1}{2}H_2O + 2e^- (-200KJ@750^o)$$

- Predicted equilibrium products versus O^{2-}/CH_4



Problems with EPOx

- Issues in prior EPOx work:
  - Anode coking during direct methane SOFC operation
  - SOFC power densities and syngas production rates were relatively low
  - Expensive non-standard SOFC anode materials, *e.g.* Pt, used to avoid coking
- Thermal self-sustainability of EPOx reactor
  - Minimum requirement: **-ΔH= E_{FC}**

    -ΔH=22kJ mol^{-1} CH_4 at 750°C (reaction enthalpy change)

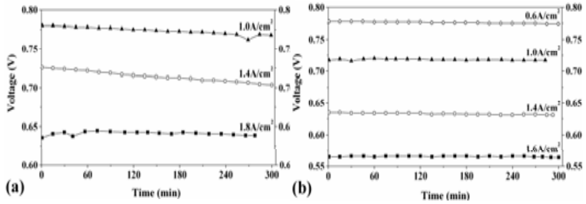
    E_{FC}=nFV=135kJ / mol CH_4 (V=0.7V, n=2 electrons/ CH_4) (electrical energy extracted)

Project Objectives

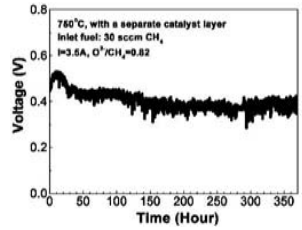
- Demonstrate EPOx in high-performance SOFCs
- Evaluate conditions and geometries that yield stable direct methane operation
- Demonstrate stable direct-methane operation
- Evaluate conditions for thermally self-sustained operation
- Extend from methane to natural gas

Solutions to Stable SOFC Operation

- Stable, coke-free, high power density operation realized with barrier/catalyst layer
  - Cell voltage versus time at constant current *J* for SOFCs operated in humidified methane at 800oC without (a) and with (b) barrier layer.

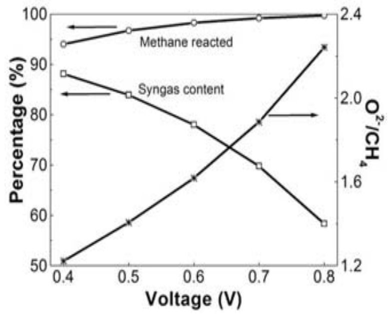


- Voltage versus time for the SOFC with a catalyst layer, Ru-CeO_2|PSZ|Ru-CeO_2, and 3.5 A (O^{2-}/CH_4 =0.82).

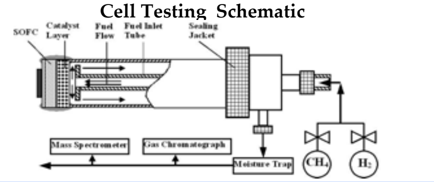


Tactics for Thermal Self-Sustainability

- Thermo-neutral operation can be achieved by:
  - Lower operating voltage, less electrical energy extracted per mole of methane
    - But high enough to maintain high power output
  - Increase O^{2-}/CH_4 above 1, yielding more heat by increased complete oxidization

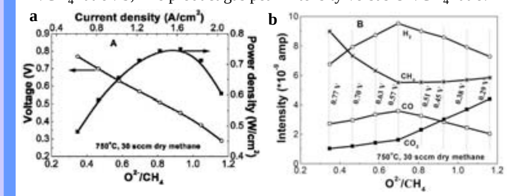


Cell Testing Schematic

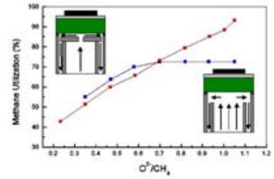


Experimental Results

- Results for the SOFC NiO-YSZ|YSZ|YSZ-LSM, LSM, tested in 30 sccm dry methane in the anode and ambient air in the cathode at 750 °C. **a**, Voltage and power density versus current density or O^{2-}/CH_4 ratio . **b**, The product gas peak intensity versus O^{2-}/CH_4 ratio.



- Methane utilization versus O^{2-}/CH_4 ratio for SOFCs operated on 30 sccm dry methane at 750°C. Results are compared for identical SOFCs with the standard (▪) and modified (•) gas-flow geometries indicated schematically in the insets (the arrows illustrate the fuel flow path).



Conclusions

- Methane-fueled SOFCs operated under appropriate conditions produce both syngas and electricity
- Coking can be suppressed by using barrier layers
- SOFCs operated at T≈750 °C, V≈0.4V, and O^{2-}/CH_4 ≈1.2:
  - High electrical power output (~0.7 W cm^{-2})
  - High syngas production rates (~20 sccm cm^{-2})
  - Thermally self-sustaining conditions
- Can produce syngas/hydrogen at lower cost than other methods
  - Due to the value of the electricity produced
- Sale of both electricity and syngas increases the value of the fuel cell
  - Important because fuel cell cost is a key barrier to commercialization

Acknowledgments

The authors gratefully acknowledge the financial support of the DOE HiTec programs during the course of this work.