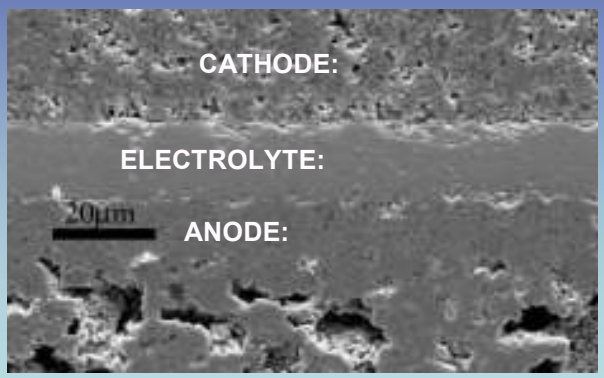
Introduction to Solid Oxide Fuel Cells

Basics
Electrochemistry
Microstructure Effects
Stacks

Solid Oxide Fuel Cell (SOFC)



$(La,Sr)(Mn)O_3$ (LSM)

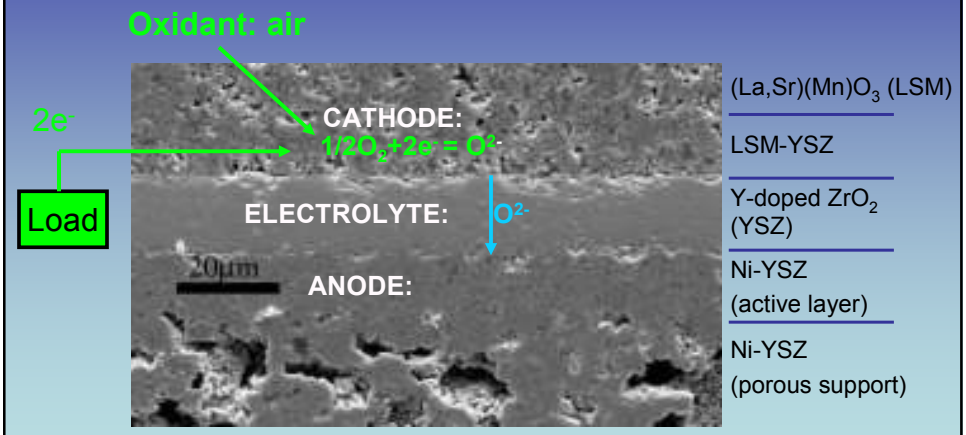
LSM-YSZ

Y-doped ZrO_2 (YSZ)

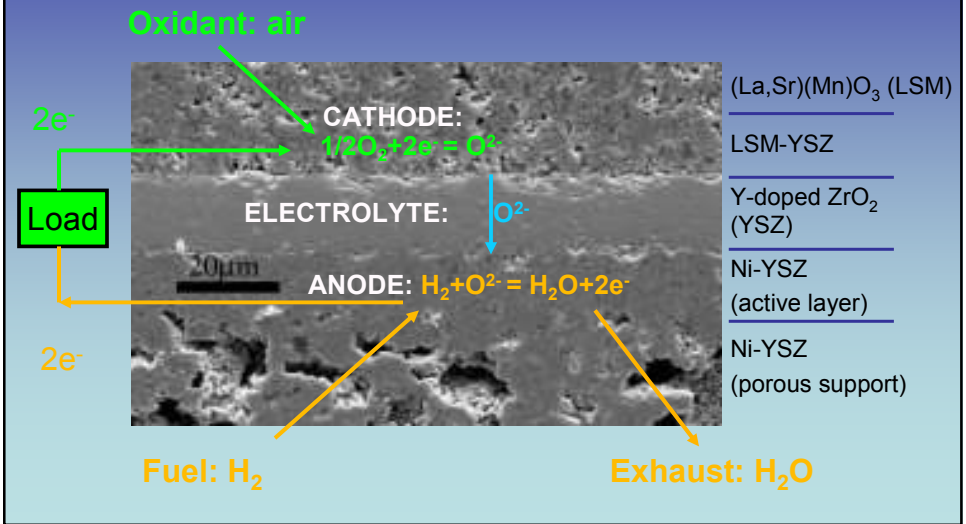
Ni-YSZ (active layer)

Ni-YSZ (porous support)

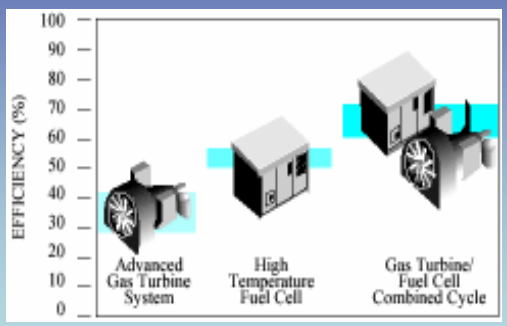
Solid Oxide Fuel Cell (SOFC)



Solid Oxide Fuel Cell (SOFC)



SOFC Motivations



- High efficiency
  - High T waste heat
  - Low CO_2 emission
- Low emissions of other pollutants
  - Sulfur removed
  - NO_x not formed
  - No CO
  - No particulates

Nernst Potential 1

- Work done to move an electron from a potential V_1 to V_2 is just $e(V_2 - V_1)$
  - If a fuel cell has an equilibrium potential E $(= V_2 - V_1)$ across it, moving an electron across it requires work eE
    - Note that $e = 1.6 \times 10^{-19}$ coul
  - In an electrochemical reaction, consuming one mole of reactants moves n moles of electrons across the potential, *e.g.*
    - $H_2 + O^{2-} = H_2O + 2e-$ ($n = 2$)
  - Electrical work W_{el} done by rxn of one mole of reactants is:
    - $W_{el} = -nN_{Av}\, eE$
      - $N_{av} = 6 \times 10^{23}$ molecules/mole
      - The product $N_{av}e = F$ = Faraday's constant = 96,487 coul/ mol e-
    - $W_{el} = -nFE$

Nernst Potential 2

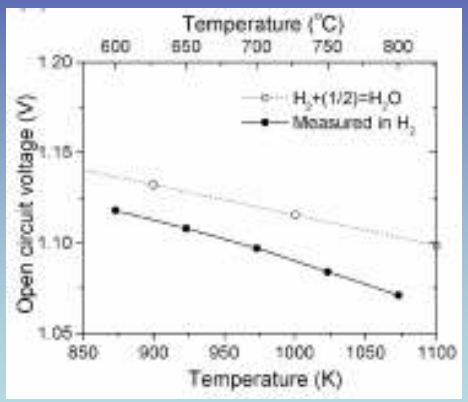
- Work done equals the Gibbs free energy ΔG change of the reaction that moves the electrons
  - Conservation of energy
  - $W_{el} = -nFE = \Delta G$
- $\Delta G = \Delta H - T\Delta S$
  - ΔH = enthalpy change of electrochemical reaction
  - T= temperature
  - ΔS = entropy change of electrochemical reaction

Nernst Potential 3

- General fuel cell reaction:
  - aA + bB = cC + dD
  - $\Delta G^0 = cG_C^o + dG_D^o - aG_A^o - bG_B^o$
    - Standard free energy change of reaction at P = 1 atm and constant T
  - Note that the pressure dependence of G_i^o is given by $G_i^o(P_i) = G_i^o(P_i=1atm) + RT \ln P_i$
  - Thus, for the overall reaction: $\Delta G = \Delta G^0 + RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b}$
    - R = gas constant
    - Based on our expression relating free energy and potential

      $E = E_0 - \frac{RT}{nF} \ln \frac{P_C^c P_D^d}{P_A^a P_B^b}$ $\quad E_0 = -\Delta G^0/nF$
    - Note that for a truly general reaction, the *ln* term has all products in the numerator and reactants in the denomimator

Nernst Potential 4



- For a specific reaction,
  - $H_2 + (1/2)O_2 = H_2O_{(gas)}$

$$E = E_0 + \frac{RT}{2F}\ln\frac{P_{H_2}P_{O_2}^{1/2}}{P_{H_2O}}$$

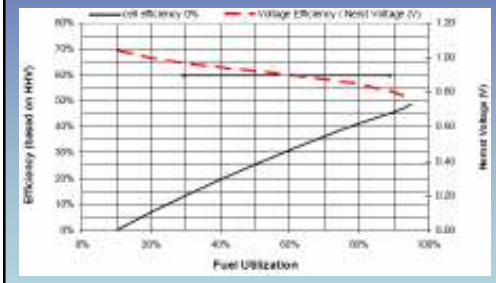
- Note: quantities going into $E_0 = -\Delta G^0/nF = (\Delta H - T\Delta S)/nF$ obtained from:
  - JANAF thermochemical tables
  - Also need heat capacities c_p
- Calculated OCV decr w/ incr T
  - $P_{H2} = 0.97$ atm; $P_{O2} = 0.02$ atm; $P_{H2O} = 0.03$ atm
  - Note: any rxn where the number of gas molecules decreases has $\Delta S < 0$
  - Oxidation is exothermic, $\Delta H < 0$
- Experimental OCV slightly lower

Fuel Efficiency

$$\eta = \frac{\Delta G}{\Delta H}\frac{V_{cell}}{E}\chi$$

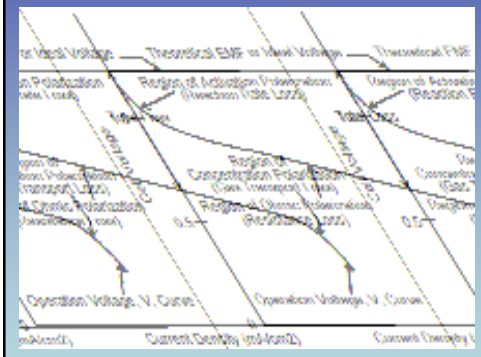
- Thermodynamic efficiency $W_{el}/\Delta H = \Delta G/\Delta H = (\Delta H - T\Delta S)/\Delta H$
  - For H_2 oxidation, this equals 0.83
  - For a cell reaction where $\Delta S < 0$ (entropy decreases, e.g. H_2 oxidation), η decreases with increasing T
    - Note that $\Delta H < 0$
  - Follows decrease in E noted above
- Voltage efficiency
  - When a current flows in the cell, the operating voltage drops below the Nernst potential
  - Energy produced equals the charge transferred times voltage
    - Charge depends only on the moles of fuel reacted
  - Thus, the voltage efficiency equals V_{cell}/E
- Fuel utilization χ
  - There is a maximum fraction χ of the fuel that can be utilized, typically ~ 80%
    - Higher utilization decreases cell performance
      - Cell voltage drops when H_2O/H_2 ratio increases

Efficiency Illustration



- Example: SOFC
- Red curve: OCV versus fuel utilization
  - Nernst voltage as low as 0.8V
- Black curve: overall efficiency
  - Maximum efficiency of ~ 50%

Fuel Cell Losses



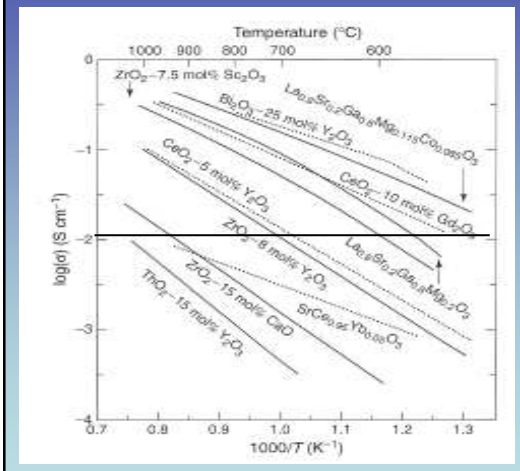
$V = E - iR_{\Omega} - \eta_a - \eta_c$

- E = equilibrium EMF
- R_{Ω} = Ohmic resistances
  - Often associated with electrolyte
  - But may also result from electronic resistance associated with an electrode, or a contact resistance
- η_a = anode polarization
- η_c = cathode polarization
- Each of the electrodes can have two main types of polarization
  - Activation polarization
  - Concentration polarization

State of the Art SOFC

- Air,LSM-YSZ/YSZ/Ni-YSZ,H_2
- T>700°C
  - Polarization losses: activation + concentration
  - Power > 1 W/cm^2
- T<700°C
  - Polarization losses: activation + ohmic
  - Low power density
    - *e.g.* 0.2 W/cm^2 at 600°C
- Losses increase with decreasing temperature!

Electrolyte Ohmic Resistance

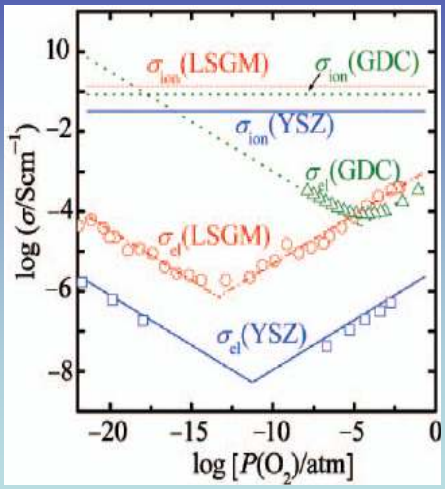


T. Ishihara, Handbook of Fuel Cells, p. 1109

- Conductivity decreases with decreasing temperature
- Common electrolytes
  - Y-stabilized ZrO_2 (most common)
  - Sc-stabilized ZrO_2 (SSZ)
  - Gd-doped CeO_2 (GDC)
  - (La,Sr)(Ga,Mg)O_3 (LSGM)
- Target area-specific resistance: 0.1 Ωcm^2
  - Consistent with 1 W/cm^2
  - Line calculated for a 10 μm thick electrolyte
- YSZ okay down to ~700°C
- Alternate materials needed below 700°C
  - GDC, LSGM good to ~550°C

Features of Key Electrolytes

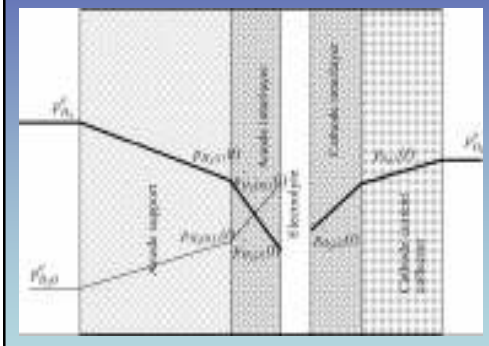
800°C



- Compares ionic and electronic conductivities
  - Good electrolyte has low electronic conductivity
  - High ratio $t_I = \sigma_I/\sigma_E$
- P_{O2} range encountered in fuel cell
  - Air - 0.2 atm; fuel - 10^{-20} atm
- YSZ and LSGM have wide P_{O2} range with high σ_I/σ_E
- GDC is a mixed conductor in reducing fuels
  - Leads to low open-circuit voltage

Yokokawa et al., MRS Bull., 30 (2005) 591

Concentration Polarization



- Current based on Fick's first law: $i = nFD(P_B - P_S)/d$
  - n = electrons involved in rxn
  - D = diffusion coefficient = $D_0\varepsilon/\tau$
  - $P_S - P_B$ = pressure difference between surface and bulk
  - d = electrode thickness
- Limiting current $i_L = nFDP_B/d$ for $P_S = 0$
- Nernst potential decreases

  from $E(i=0) = E^0 + \frac{RT}{nF}\ln P_B$

  to $E(i) = E^0 + \frac{RT}{nF}\ln P_S$

  as the current increases
  - The potential difference is:

$$\eta_{c,con} = -\frac{RT}{4F}\ln\left(\frac{p'_{O_2}(i)}{p^0_{O_2}}\right) \qquad \eta_{a,con} = -\frac{RT}{4F}\ln\left(\frac{p'_{H_2}(i)p^0_{H_2O}}{p^0_{H_2}p'_{H_2O}(i)}\right)$$

$$\Delta E = \eta_{conc} = \frac{RT}{nF}\ln\frac{P_S}{P_B} = \frac{RT}{nF}\ln\left(1 - \frac{i}{i_L}\right)$$

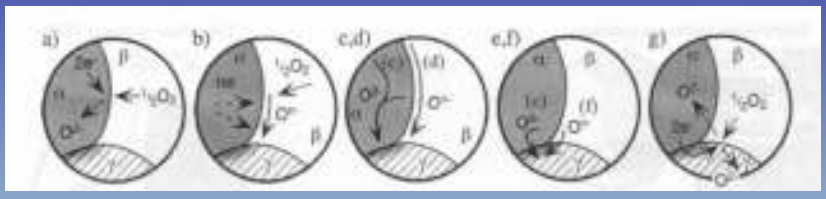
Activation Polarization

- The rate, and hence the current density, associated with a particular rate-limiting reaction is given by (Butler-Volmer):

$$i = i_0\left[\exp\left(\frac{\alpha n F \eta_{act}}{RT}\right) - \exp\left(-\frac{\alpha n F \eta_{act}}{RT}\right)\right]$$

  - i_0 = exchange current density
  - α = electron transfer coefficient relevant to reaction and electrode in question
  - Can be derived directly from elementary rate kinetics
- Solving for overpotential yields the Tafel equation: $\eta_{act} = a + b \ln i$
  - $a = (-RT/\alpha nF)\ln i_0$
  - $b = RT/\alpha nF$
- Similarity between chemical and electrochemical reactions:
  - Activation barrier must be overcome
  - Driven by electrical potential for electrochemical reactions

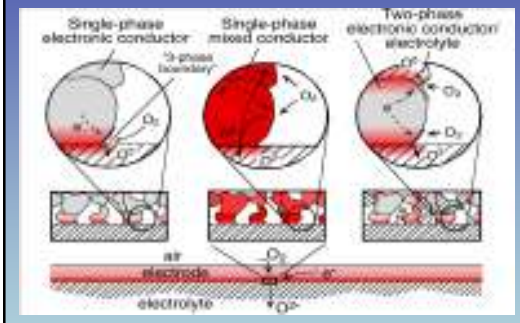
Activation Polarization: Possible Reaction Pathways



S.B. Adler, *Chem. Rev.*, **104** (2004) 4791-4843

- Multiple physical mechanisms may be involved
  - adsorption
  - full/partial reduction
  - bulk transport
  - surface transport
  - charge transfer across interface
- Above expressions approximate a case where one mechanism dominates (rate limiting step)

Effect of Electrode Microstructure



•Schematic views of three basic electrode types
•Red indicates interfaces where electrochemical reactions occur

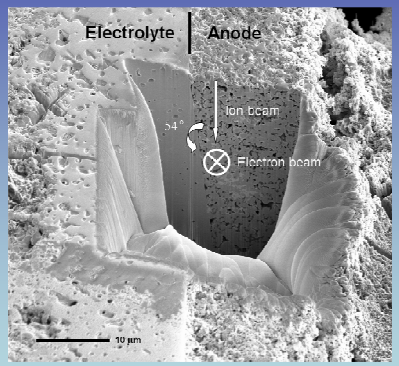
S.B. Adler, *Chem. Rev.*, **104** (2004) 4791-4843

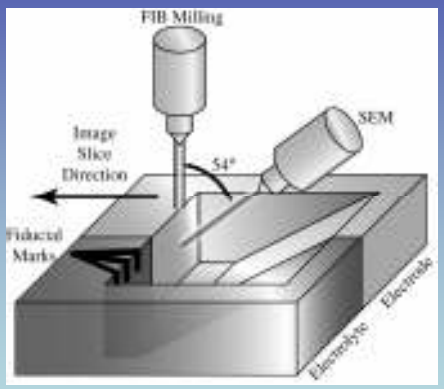
- Electrode types
  - Electronic conductor
    - $(La,Sr)MnO_3$ (LSM)
  - Mixed conductor
    - $(La,Sr)CoO_3$ (LSC)
  - Two-phase
    - LSM-YSZ, Ni-YSZ
- Key quantities
  - Triple-phase boundary length
  - Phase connectivity
  - Gas phase tortuosity
  - Surface areas

Example: Ni-YSZ Anodes

- First: describe 3D microstructure measurements
  - State of the art electrodes have complex interconnected three phase structure
    - Difficult to quantify structure with 2D images
  - New method for 3D characterization
    - Micro- and nano-structures
    - Focused ion beam - scanning electron microscopy (FIB-SEM)
- Then: examine Ni-YSZ anodes, including triple-phase boundaries

FIB-SEM Geometry

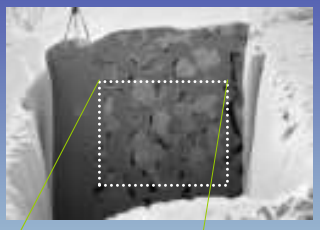




FIB-SEM: Zeiss 1540XB Crossbeam

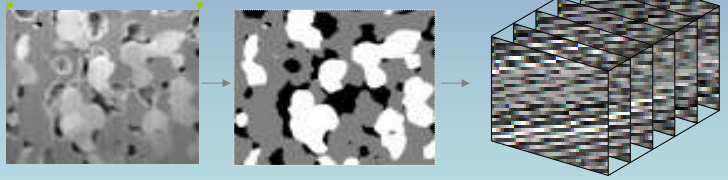
- Sample volume: 5 micron on a side
- 50nm between images

3D Electrode Reconstruction Using FIB-SEM



Example: Ni-YSZ anode

Wilson et al., Nature Materials 2006

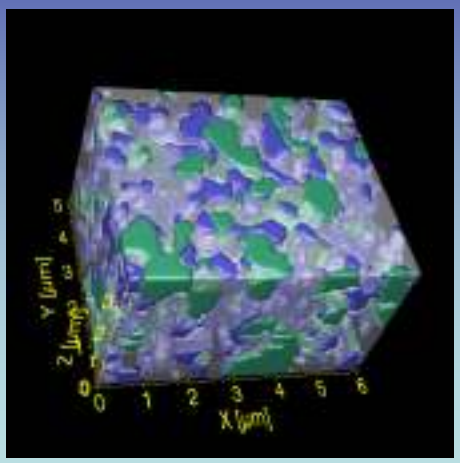


1) Align, crop, filter

2) 3-Color phase image

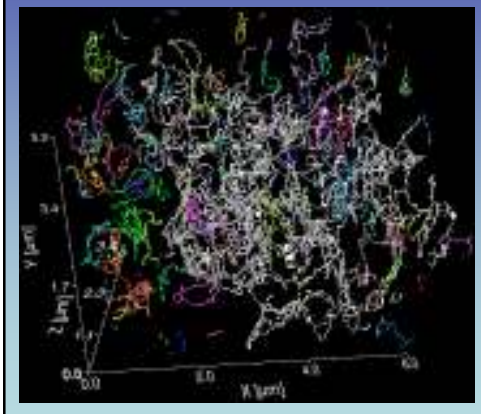
3) Reconstruct using IDL software

3D Anode Image



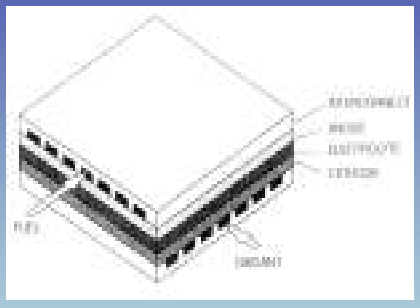
- Example: 3D image of Ni-YSZ anode
  - Green: Ni metal
  - Clear: Yttria-stabilized zirconia (YSZ)
  - Blue: open pores
- Calculated quantities
  - Ni and YSZ volumes
  - Interface areas
  - Three-phase boundaries
  - Tortuosity calculation
    - Gas phase tortuosity ~2

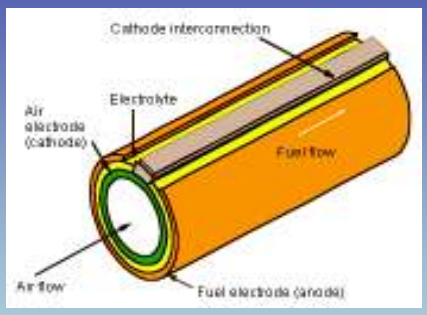
Three-Phase Boundaries



- Sites where reaction occurs:
  - $O^{2-}(YSZ)+H_2(pore) = e^-(Ni)+H_2O(pore)$
- Measured TPB density
  - ~ 4.28×10^8 cm/cm^3
- Estimated polarization resistance
  - Measured resistance per TPB length - patterned electrodes:
    - $1/R = 9*10^{-4} * L_{TPB}$ at 700°C
    - Bieberle *et al. J. Electrochem. Soc.* (2001)
  - Assume 10 μm thick anode active region
  - Result: 0.25 Ωcm^2 at 700°C
  - Reasonable compared with measured cell ASR: 0.7 Ωcm^2

Stack Configurations



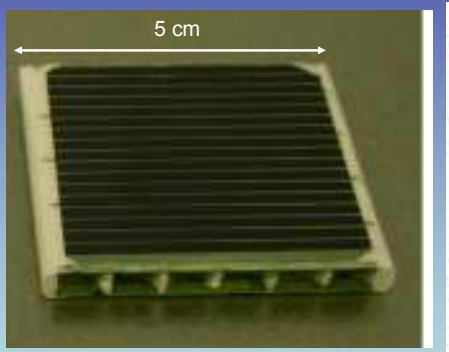


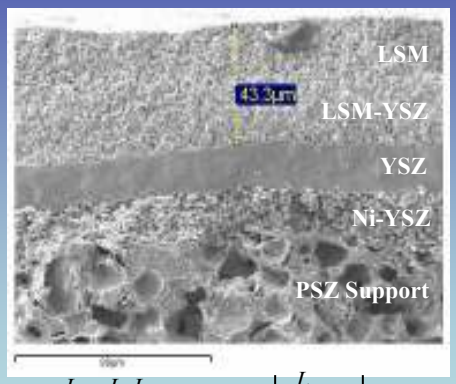
- Separate interconnect
- Large-area gas seals
- High volume power density
  - Short electrode current paths

- Thin, integral interconnect
- Only tube-end gas seals
- Low volume power density
  - Long electrode current paths

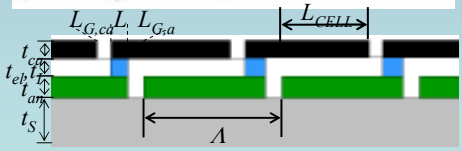
N.Q. Minh, *J. Am. Ceram. Soc.*, **76** [3] 563-88 (1993)

Segmented-In-Series SOFCs



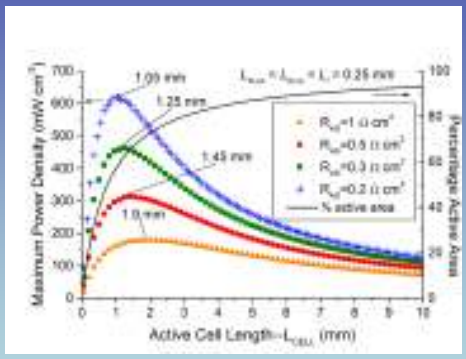


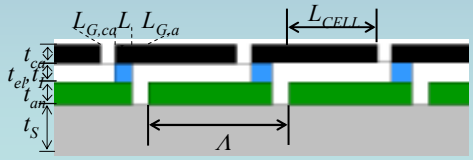
- Flattened tube with fuel-flow channels
- 16 2.4-mm cells on each side
- Prior work: >10-mm cells
  - Power limited by long current path



Calculation: Cathode Resistance Effect

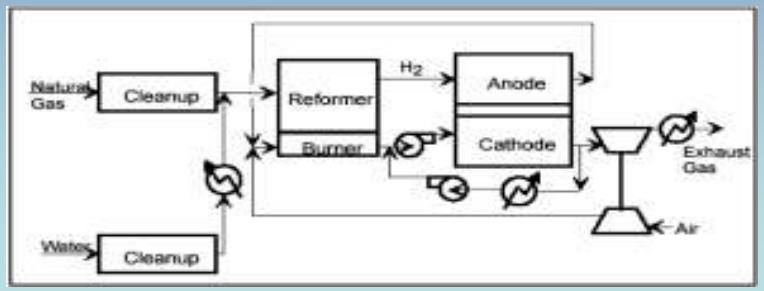
- Maximum power (including cell and interconnect area)
  - Fix inactive area based on processing limitations: $L_{G,an}$ = $L_{G,ca}$ = L_I = 0.25 mm
  - t_I = 20 μm, ρ_I = 1 Ω cm
  - 20 μm thick electrodes
- Optimal length L_{CELL}=1-2 mm
  - Power drops at low L_{CELL} due to low fraction active area
  - Power drops at high L_{CELL} due to cathode resistance





SOFC Systems

- Balance of plant: up to 75% of system cost
  - External fuel reformer uses heat from SOFC and spent fuel
  - Water tank or high-temperature fuel recycle pump
  - Air blower (stack cooling)
  - Fuel cleanup
  - Heat exchangers



Supplying H_2 To The SOFC

- Steam or dry reforming (methane)
  - $CH_4 + H_2O \rightarrow CO + 3H_2$ $\Delta H_{1000K} = 206$ kJ
  - $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ $\Delta H_{1000K} = 247$ kJ
  - Four syngas molecules per CH_4
  - Endothermic - requires external heat
- Partial oxidation reforming
  - $CH_4 + (1/2)O_2 \rightarrow CO + 2H_2$ $\Delta H_{1000K} = -37$ kJ
  - Three syngas molecules per CH_4
  - Exothermic - no external heat needed
  - Nitrogen dilution when air is used
- Autothermal - mixed reactions

Applications: Stationary Power Plants

- ~MW scale
- External steam reforming typically employed
  - Yields good fuel efficiency
- Internal reforming advantages
  - SOFC excess heat directly available for endothermic reforming reaction
    - Reduction of SOFC air cooling requirements
  - System simplification and cost reduction
    - Elimination of external reformer

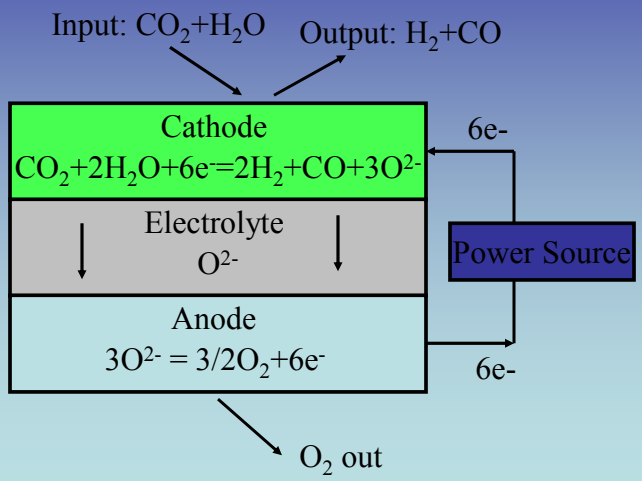
Applications: Small Generators

- < 100 W SOFCs - portable electronics
  - Device size and weight critical
    - Liquid hydrocarbon energy density higher than methanol
- SOFC strategy
  - Internal partial oxidation reforming
    - Supplies excess heat needed for small system
    - Compact system with no external reformer
  - Low temperature Ceria-electrolyte cells
- Small (~1W) thermally self-sustaining SOFC
  - Propane-fuelled single-chamber SOFC, 550^{o}C
  - *Shao, et al. Nature 435, 795 (2005)*

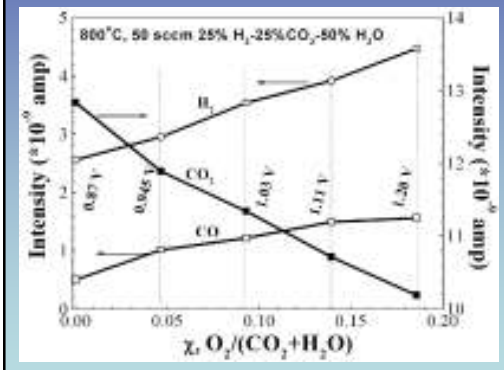
Applications: Transportation APUs

- Gasoline-fueled SOFC (5kW)
  - Partial oxidation used because reformer is compact
    - Limited fuel efficiency
    - Nitrogen dilution of reformate
    - *Mukerjee, et al. SOFC VIII, p.88*
- Exhaust gas recycle can improve fuel efficiency
  - Utilize SOFC waste heat for endothermic reforming rxns
    - *Botti et al. SOFC VIII, p 16*
  - Reduces air cooling requirements
  - Problem - Steam/dry reforming requires larger reformer
    - *Motivates use of internal reforming*

Application: Electrolysis



Solid Oxide Electrolysis



- Ni-YSZ||YSZ||LSM cell
- Mass spectrometer measurement
- CO_2-H_2O electrolysis
- Enabling technology for synthetic liquid fuel economy