Spreadsheet Model of SOFC Electrochemical Performance

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Brief First Demo of Basic Model

Outline

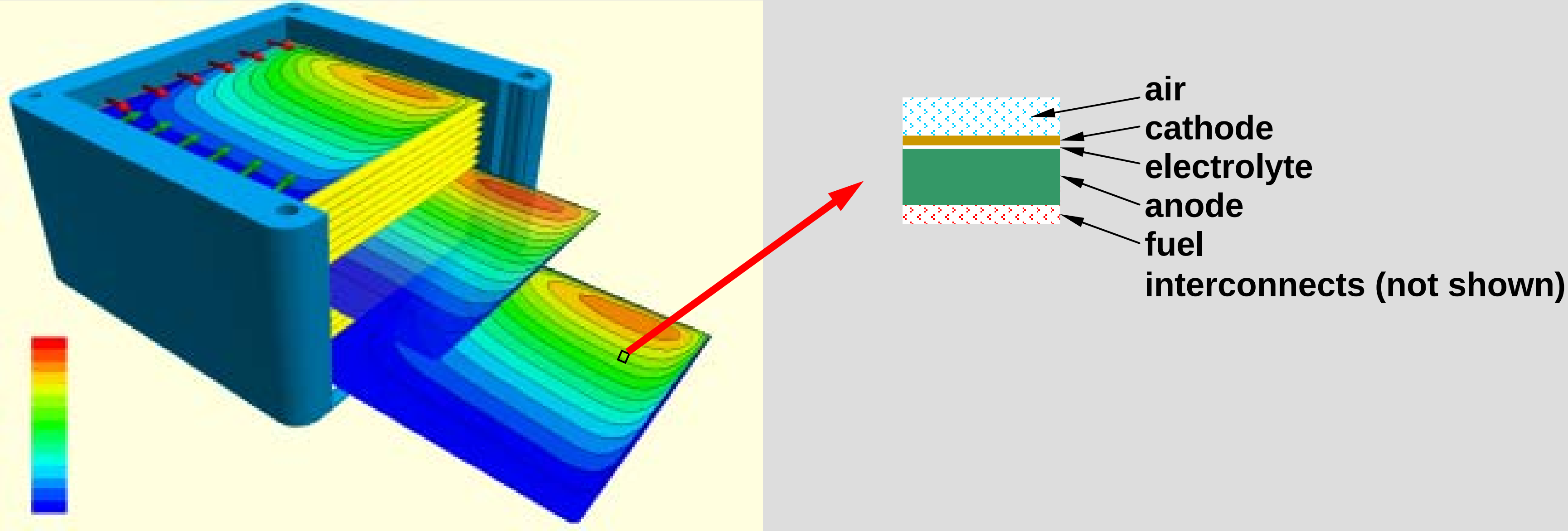
- Purpose of the spreadsheet model
- Strategy and assumptions
- Input parameters
- Calculation of IV response
  - Chemistry – water gas shift
  - Nernst potential
  - Ohmic loss
  - Effect of leaks
  - Cathode overpotential – Butler-Volmer
  - Anode overpotential – bulk and surface diffusion
- Calculation of heat generation
- Adjustable parameters – calibrating the model
- Future improvements

Purpose

- “One-dimensional” stack calculations
- Stack module for systems modeling
- Electrochemical algorithm to be embedded into CFD or FEA codes for “full-up” three-dimensional modeling of stacks
- Provide guidance for stack component development – How can we improve performance?

Strategy and Assumptions

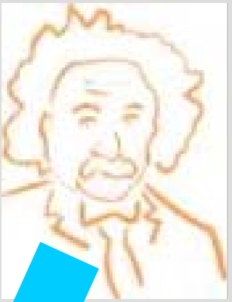
- Unit cell
  - homogeneous temperature
  - homogeneous gas compositions



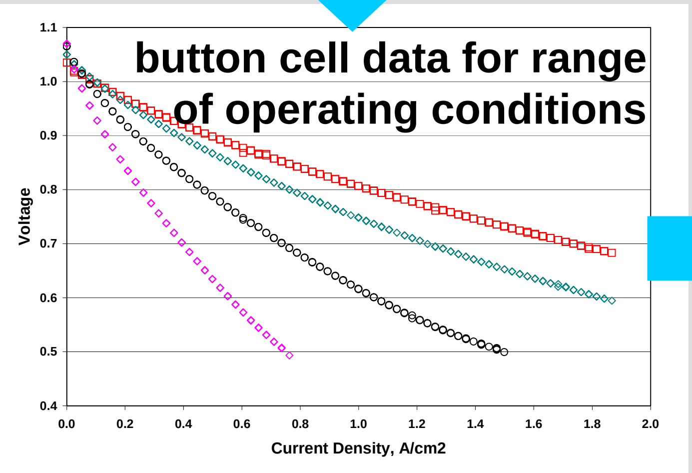
air
cathode
electrolyte
anode
fuel
interconnects (not shown)

Strategy and Assumptions, cont.

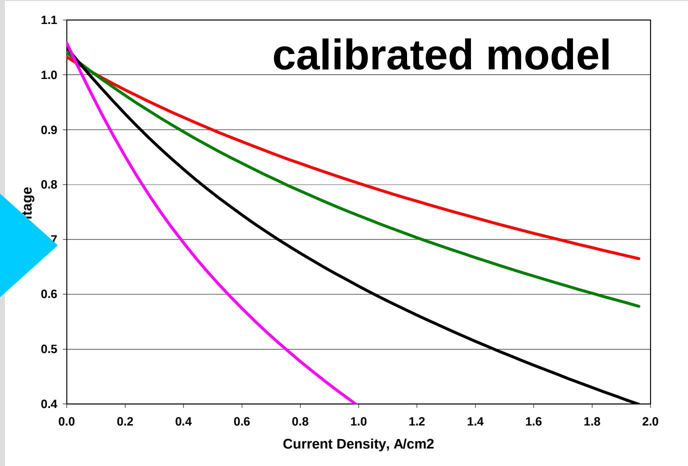
- Theoretically based
- Empirically calibrated



$$i_0 = \frac{4 \cdot F \cdot P \cdot D_{eff}}{R \cdot T \cdot l_{cath}} \cdot \ln\left(\frac{P}{P - P_{O_2}}\right)$$

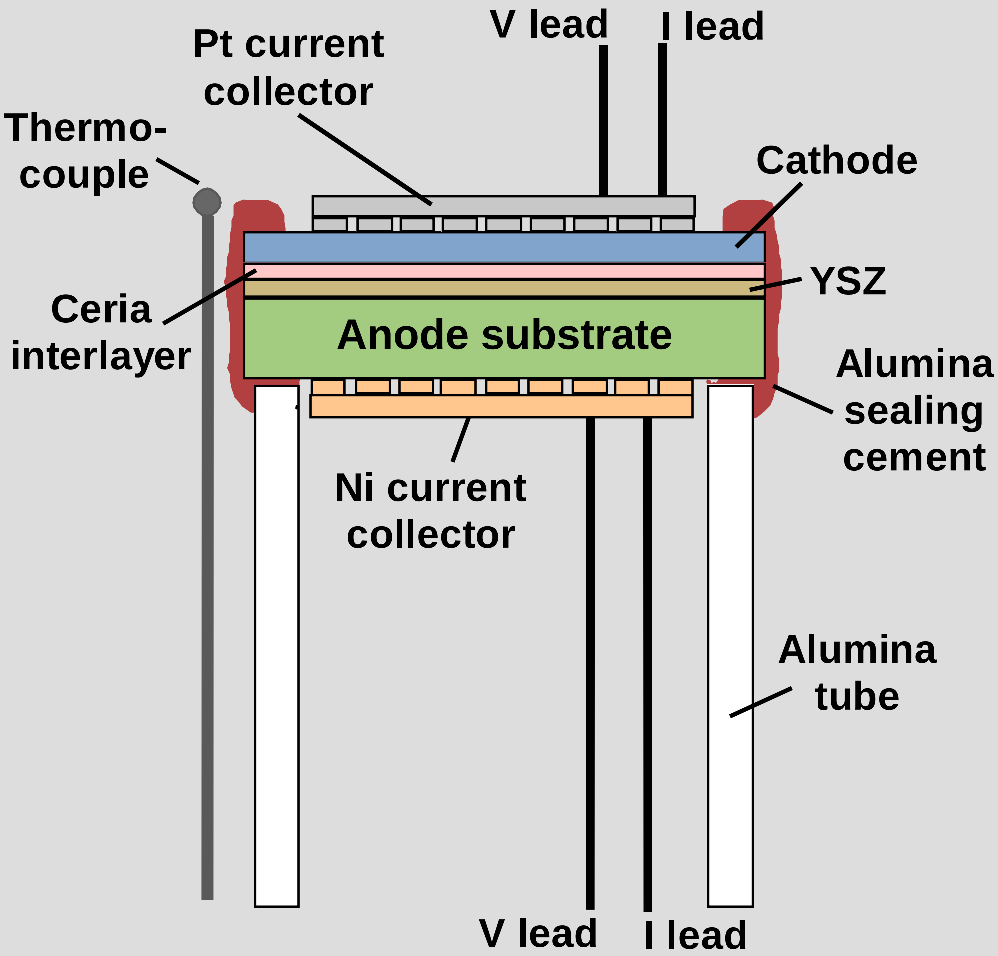


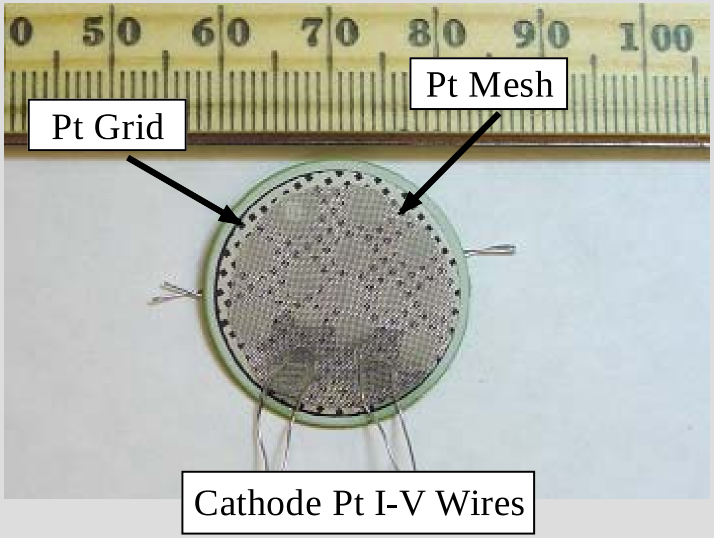
button cell data for range of operating conditions

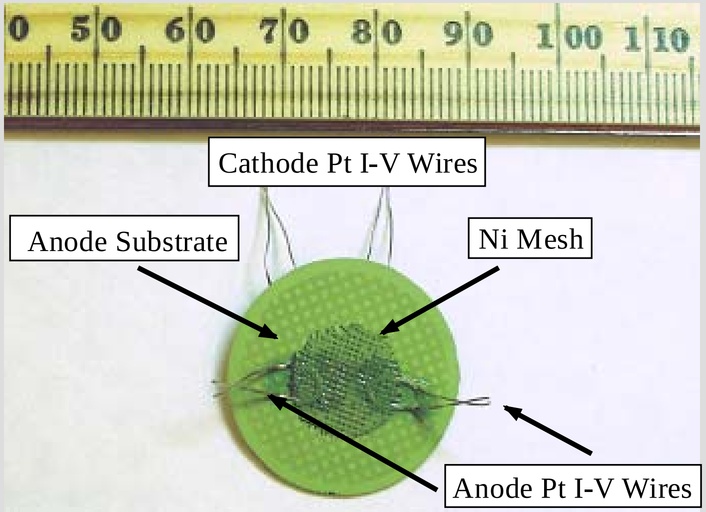


calibrated model

Button Cell Experimental Set-Up
~3cm^2 active area







Starting Points for SOFC Theory:

J.W. Kim, A.V. Virkar, K.Z. Fung, K. Mehta, .SC. Singhal, J. Electrochem. Soc. 146, 69 (1999).

NQ Minh, T. Takahashi, Science and Technology of Ceramic Fuel Cells, Elsevier Publishers, Amsterdam (1995).

E.L. Cussler, Diffusion: Mass Transfer in Fluid Systems, 2nd Edition, Cambridge University Press, Cambridge, UK (1977) Chapter 3.

I. Reiss and J. Schoonman, in CRC Handbook of Solid State Electrochemistry, CRC Press, Boca Raton, 291 (1977).

Y. Jiang and A.V. Virkar, J. Electrochem. Soc. 150, 7 (2003).

Input Parameters

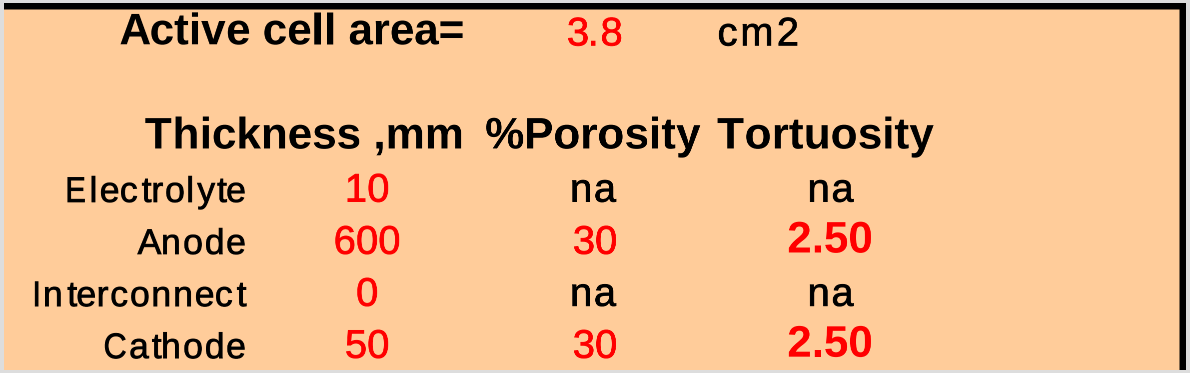
- Stack materials properties and dimensions
  - active area
  - component thickness
  - porosity

- Stack operating conditions
  - temperature
  - fuel composition

- Adjustable parameters, used in calibrating model to fit experimental data sets

Input Parameters, Cont

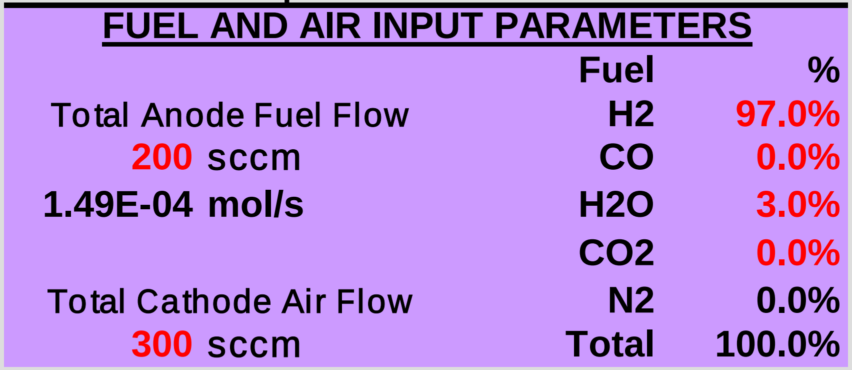
- Stack materials properties and dimensions
  - Basic model: red font cells in the range E10-H16



Active cell area=		3.8	cm2
	Thickness ,mm	**%Porosity**	**Tortuosity**
Electrolyte	10	na	na
Anode	600	30	**2.50**
Interconnect	0	na	na
Cathode	50	30	**2.50**

Input Parameters, Cont

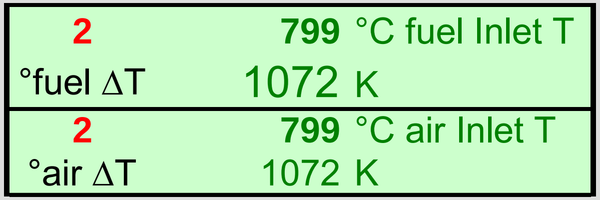
- Stack operating parameters
  - Fuel and air parameters: B1-G9



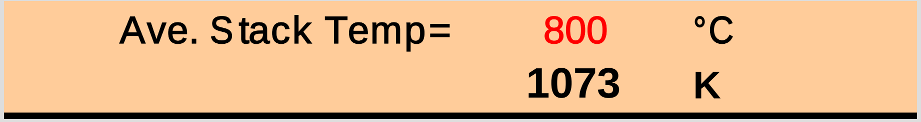
FUEL AND AIR INPUT PARAMETERS

	Fuel	%
Total Anode Fuel Flow	H2	97.0%
200 sccm	CO	0.0%
1.49E-04 mol/s	H2O	3.0%
	CO2	0.0%
Total Cathode Air Flow	N2	0.0%
300 sccm	Total	100.0%

  - Stack temperatures and ΔTs: B21, B23 and G18

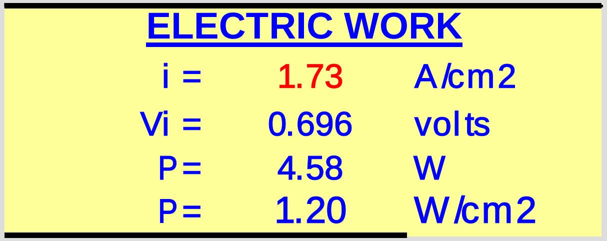


2	799	°C fuel Inlet T
°fuel ΔT	1072	K
2	799	°C air Inlet T
°air ΔT	1072	K



Ave. Stack Temp=	800	°C
	1073	K

  - Stack current density: I6



ELECTRIC WORK

i =	1.73	A/cm2
Vi =	0.696	volts
P=	4.58	W
P=	1.20	W/cm2

Input Parameters, Cont

- Adjustable parameters
  - Surface adsorption parameters: G21 and G22
  - Offset voltage due to leaks: H24
  - Contact resistance: H25
  - Butler-Volmer parameters: G28, G29 and G30

Anode TPB Surface Adsorption and Diffusion

$D_{surf,H2}$ (Θ=0) = 1.00E-01 cm^2/sec

$D_{surf,H2}$ (Θ=1) = 5.00E-04 cm^2/sec

Offset voltage due to leak = -0.07 volts

Contact Resistance= 0 Ohm-cm^2

Butler-Volmer Parameters

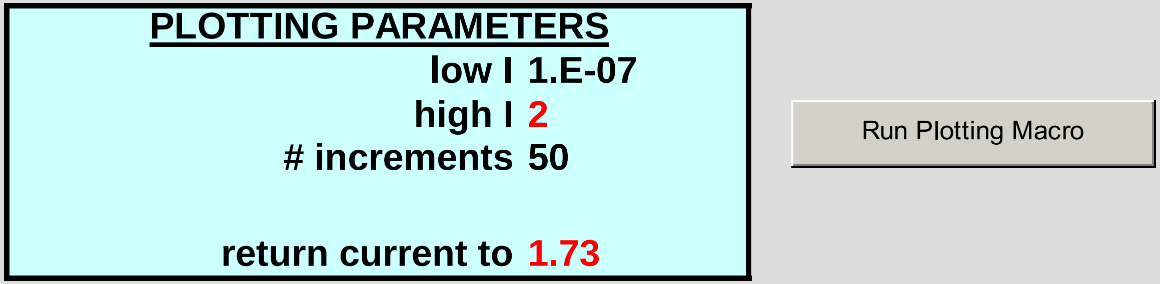
α= 5.50E-01 unitless

Pre-expon.= 3.50E+05 A/cm^2

E_{act}= 1.20E+05 J/mole

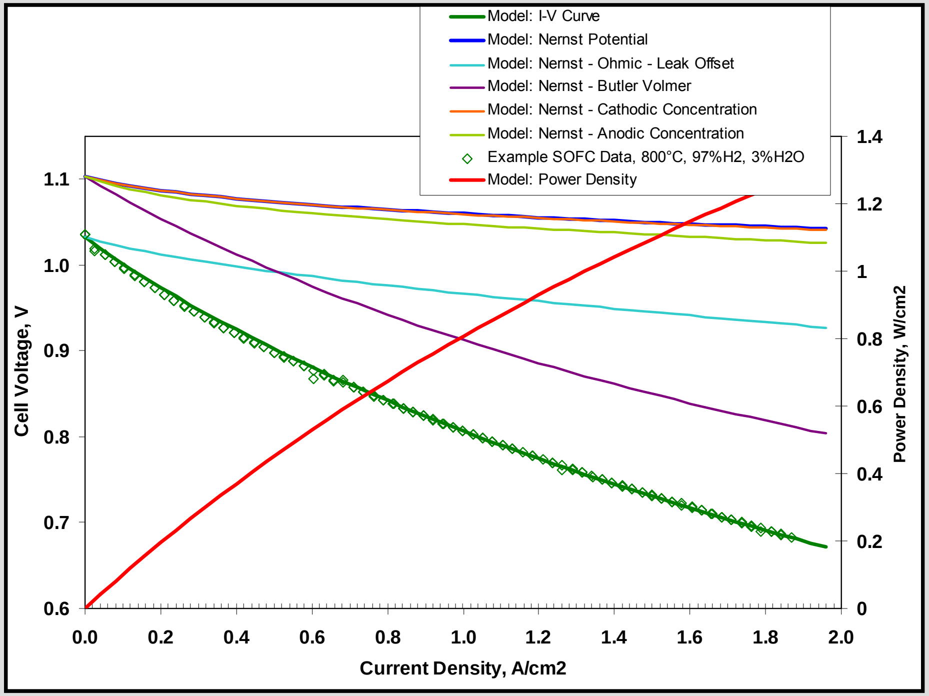
Input Parameters, Cont

- Plotting Parameters: O3 and O6



PLOTTING PARAMETERS

low I	1.E-07
high I	2
# increments	50
return current to	1.73



Note: plots can be dragged and dropped to uncover calculation cells.

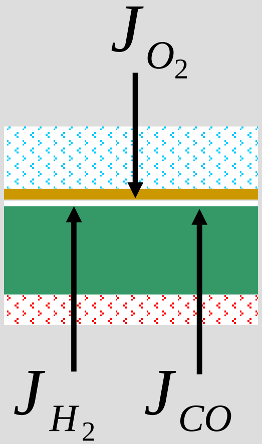
Chemical Calculations

- Calculations based on current density.

- Current density establishes rate of oxygen transport through electrolyte, which establishes rate of fuel consumption:

$$J_{O_2} = \frac{i}{4 \cdot F}$$

$$J_{H_2} + J_{CO} = 2 \cdot J_{O_2}$$



$$1\,(\mathrm{A/cm^2}) \Rightarrow 2.59\ \mathrm{x}\ 10^{-6}\ \mathrm{moles}\ \mathrm{O_2/sec/cm^2}$$

$J_{O_2} \equiv$ oxygen flux through electrolyte (moles/cm^2/sec)

$i \equiv$ current density (A/cm^2)

$F \equiv$ Faraday constant (coulomb/mole of electrons)

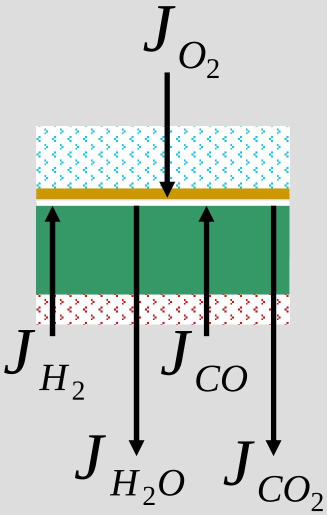
Chemical Calculations, cont.

- Product fluxes are opposite of reactant fluxes

$$J_{H_2O} = -J_{H_2}$$

$$J_{CO_2} = -J_{CO}$$

$$\frac{J_{H_2}}{J_{CO}} = ?$$



- Ratio of H2 oxidation to CO oxidation is unknown.

$$\frac{J_{H_2}}{J_{CO}} = ?$$

Chemical Calculations, cont.

- Assume fuel gas is always in equilibrium with regard to the water-gas shift reaction:

$$\mathrm{CO_2 + H_2 \Leftrightarrow CO + H_2O}$$

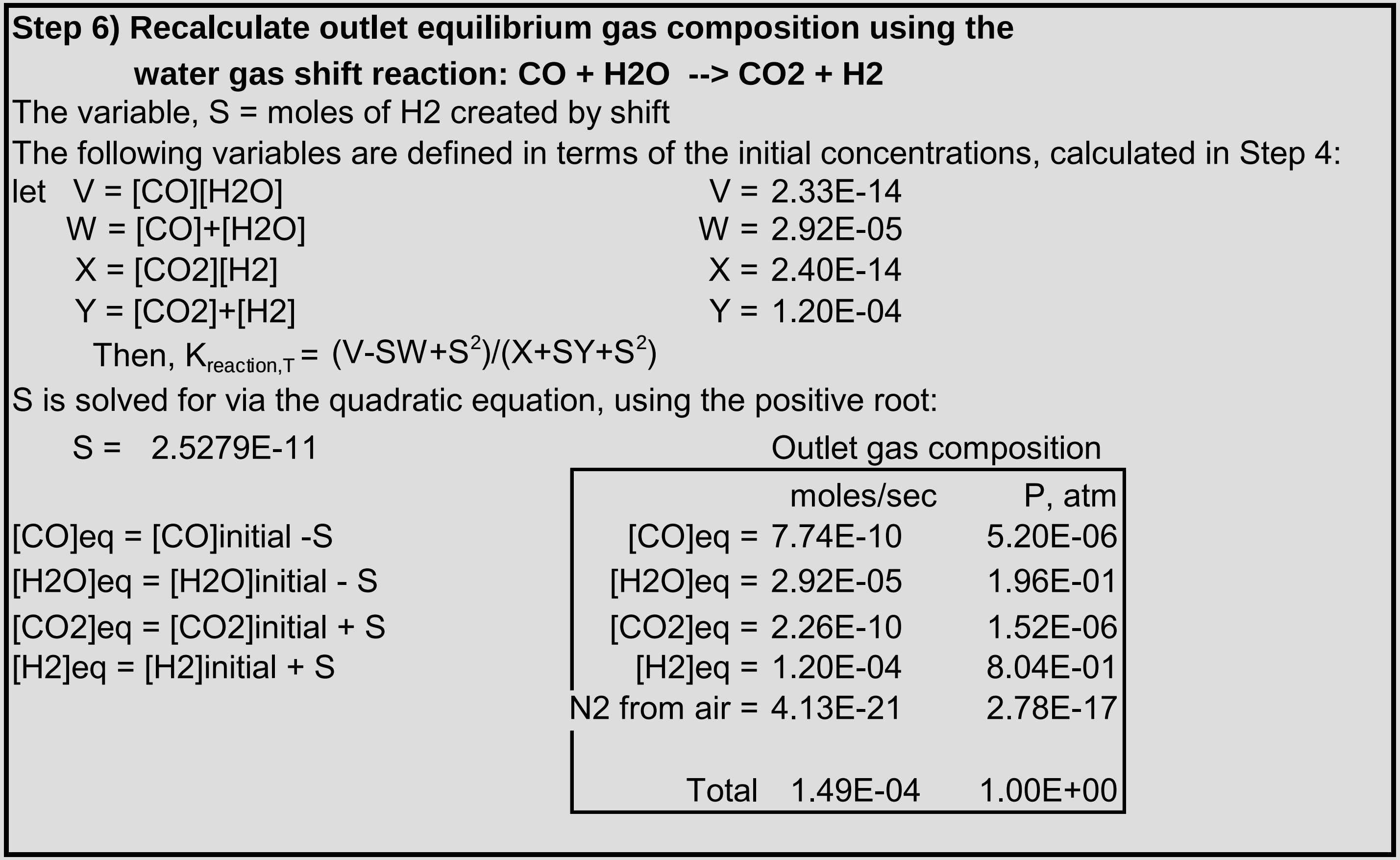
$$\mathrm{K_{eq}} = \frac{[\mathrm{CO}]\cdot[\mathrm{H_2O}]}{[\mathrm{CO_2}]\cdot[\mathrm{H_2}]} = \exp\left(\frac{-\Delta G_{form,CO} - \Delta G_{form,H_2O} + \Delta G_{form,CO_2}}{R \cdot T}\right)$$

$$\text{where } \Delta G_{form,j} = \Delta H_{0,j} + A_j \cdot T \cdot \log T + B_j \cdot T^2 + \frac{C_j}{T} + D_j \cdot T$$

where $A_j - D_j$ are fitted parameters from CRC Handbook of Chemistry and Physics, 50th Ed., page D-45. These agree closely with values from Janif Tables.

Chemical Calculations, cont.

- Fuel gasses are adjusted via shift eq. after input and prior to output
- Example: Basic Model, cells B89-H108



Step 6) Recalculate outlet equilibrium gas composition using the water gas shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$

The variable, S = moles of H_2 created by shift

The following variables are defined in terms of the initial concentrations, calculated in Step 4:

let $V = [CO][H_2O]$ — V = 2.33E-14

$W = [CO]+[H_2O]$ — W = 2.92E-05

$X = [CO_2][H_2]$ — X = 2.40E-14

$Y = [CO_2]+[H_2]$ — Y = 1.20E-04

Then, $K_{reaction,T} = (V-SW+S^2)/(X+SY+S^2)$

S is solved for via the quadratic equation, using the positive root:

S = 2.5279E-11

$[CO]eq = [CO]initial - S$

$[H_2O]eq = [H_2O]initial - S$

$[CO_2]eq = [CO_2]initial + S$

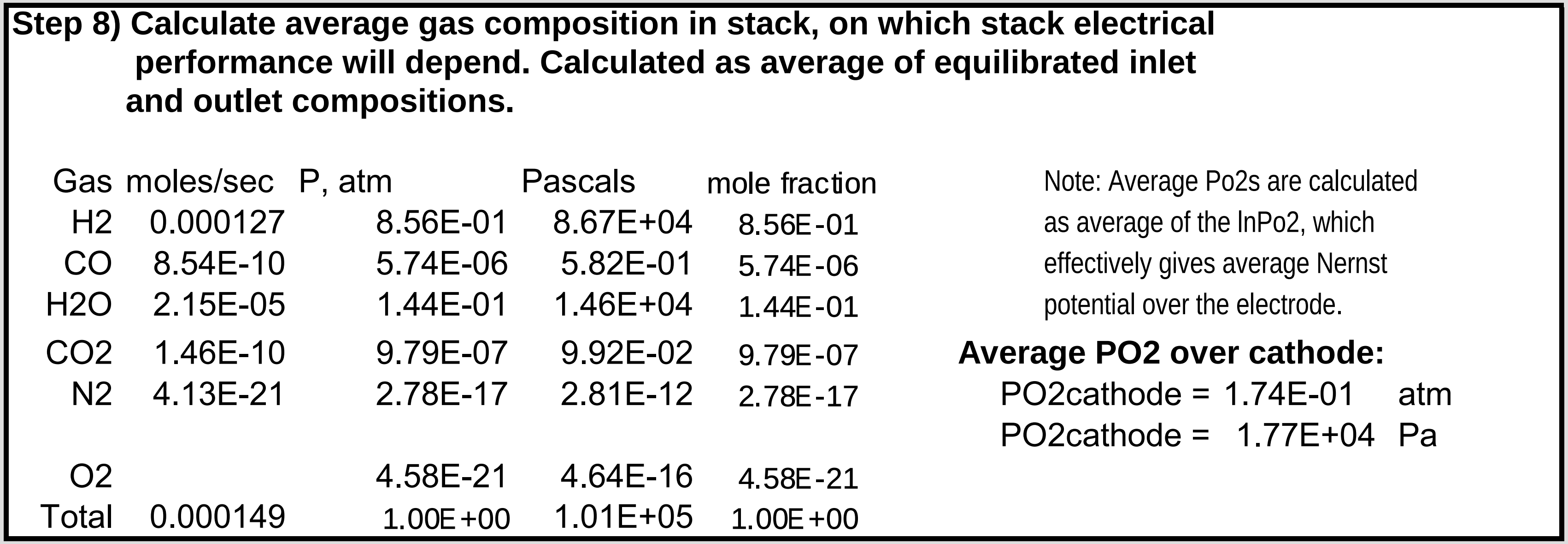
$[H_2]eq = [H_2]initial + S$

Outlet gas composition

	moles/sec	P, atm
[CO]eq =	7.74E-10	5.20E-06
[H2O]eq =	2.92E-05	1.96E-01
[CO2]eq =	2.26E-10	1.52E-06
[H2]eq =	1.20E-04	8.04E-01
N2 from air =	4.13E-21	2.78E-17
Total	1.49E-04	1.00E+00

Chemical Calculations, cont.

- Overpotentials are calculated based on the average of the shift-equilibrated inlet and output gas compositions.
- Example: Basic Model, cells B112-J124



Step 8) Calculate average gas composition in stack, on which stack electrical performance will depend. Calculated as average of equilibrated inlet and outlet compositions.

Gas	moles/sec	P, atm	Pascals	mole fraction
H2	0.000127	8.56E-01	8.67E+04	8.56E-01
CO	8.54E-10	5.74E-06	5.82E-01	5.74E-06
H2O	2.15E-05	1.44E-01	1.46E+04	1.44E-01
CO2	1.46E-10	9.79E-07	9.92E-02	9.79E-07
N2	4.13E-21	2.78E-17	2.81E-12	2.78E-17
O2		4.58E-21	4.64E-16	4.58E-21
Total	0.000149	1.00E+00	1.01E+05	1.00E+00

Note: Average Po2s are calculated as average of the lnPo2, which effectively gives average Nernst potential over the electrode.

Average PO2 over cathode:

PO2cathode = 1.74E-01 atm

PO2cathode = 1.77E+04 Pa

Second Demo and Discussion of Basic Model

- Chemical calculations

Ohmic Losses

- Resistive loss of cell components
  - Area specific resistance (ASR):

$$ASR_j = \frac{l_j}{\sigma_j}, \text{ where } l_j \text{ is thickness and } \sigma_j \text{ is conductivity}$$

  - Voltage loss due to ohmic resistance:

$$V_{ohmic} = i \cdot ASR_j, \text{ where } i \text{ is the current density}$$

  - electrolyte (considerable resistance)

$$\sigma_{YSZ} = A \cdot T^3 + B \cdot T^2 + C \cdot T + D$$

where A - D are empirically derived coefficients

  - electrodes (relatively small resistance)

$$\sigma_{eff,electrode} = \sigma_{electrode} \cdot (1 - 0.018 \cdot V_{electrode}), \text{ where } V_{electrode} \text{ is the percent porosity of the electrode}$$

$$\sigma_{cath} = \frac{A}{T} \cdot \exp\left(\frac{-E_{act}}{k \cdot T}\right)$$

$$\sigma_{anode} = 1000\ \Omega - cm^{-1}, \text{ assumed independant of T}$$

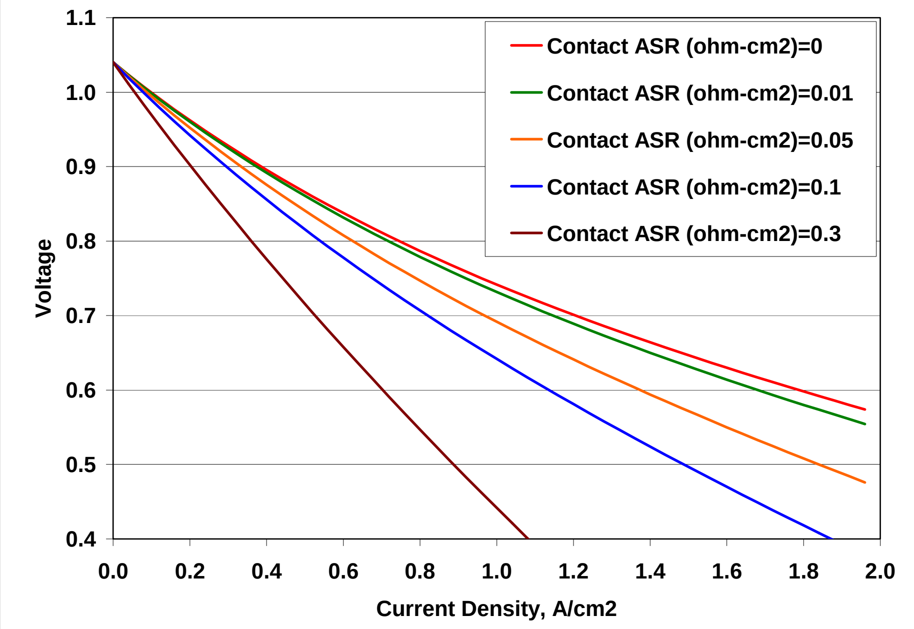
Ohmic Losses, cont.

- Resistive loss of interconnect components and interfaces
  - conductivity of stainless steel

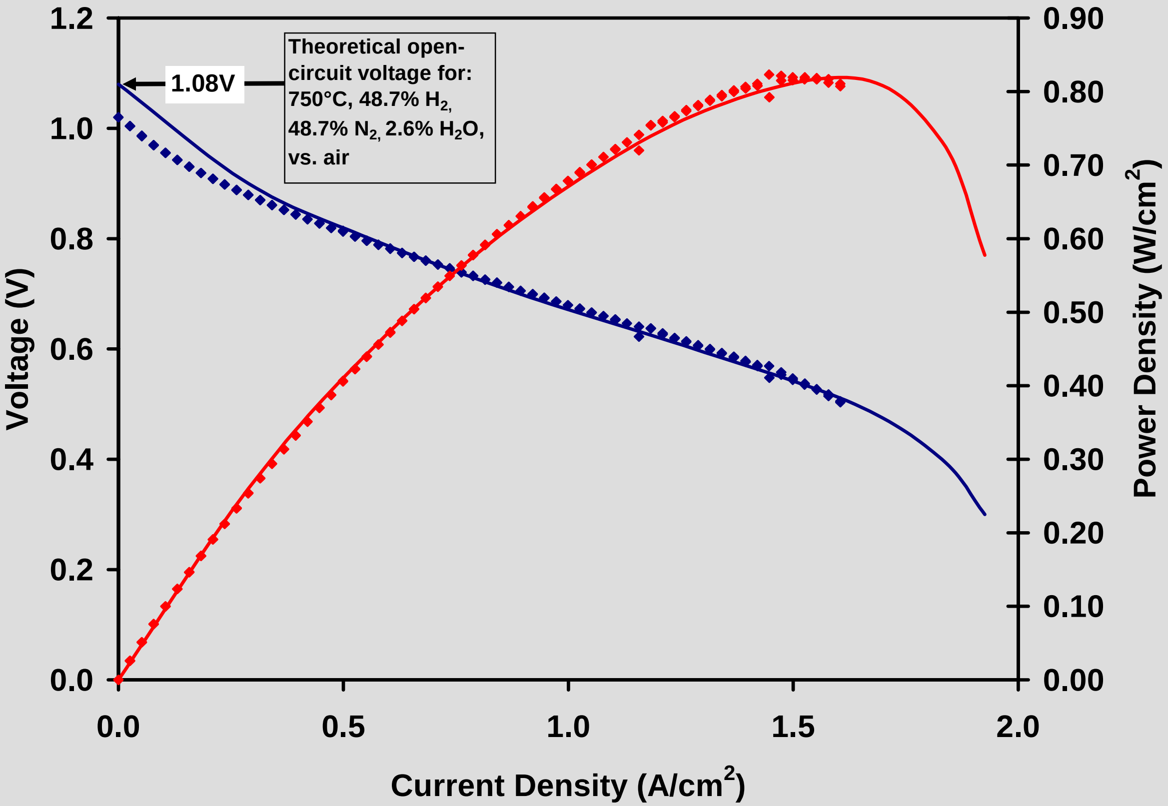
$$\sigma_{\text{ferritic SS}} = \frac{1}{A \cdot T + B}$$

  - additional ohmic resistance, such as contact resistance due to formation of oxide scale

$$ASR_{contact} = \text{adjustable parameter}$$

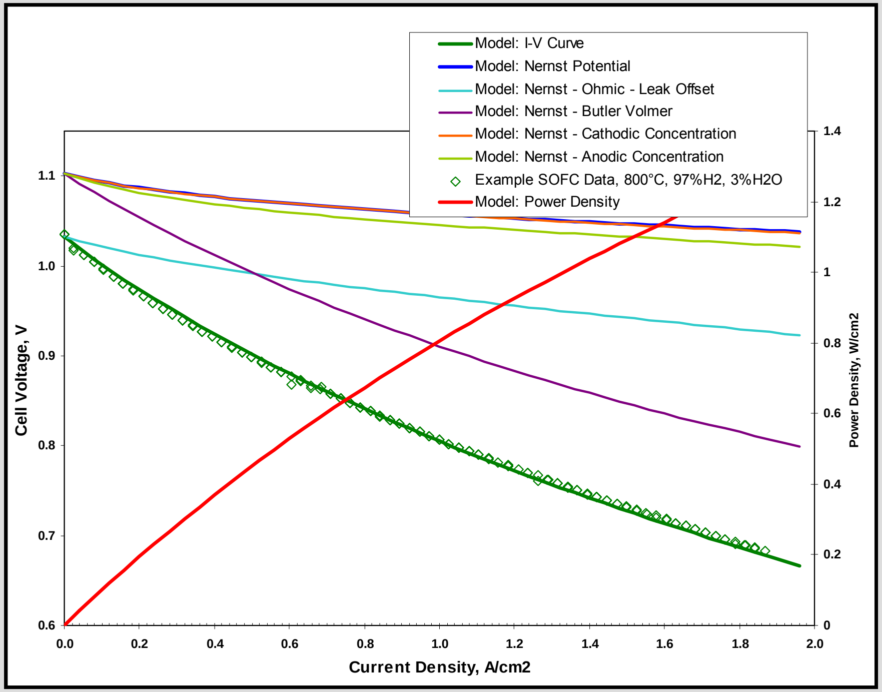


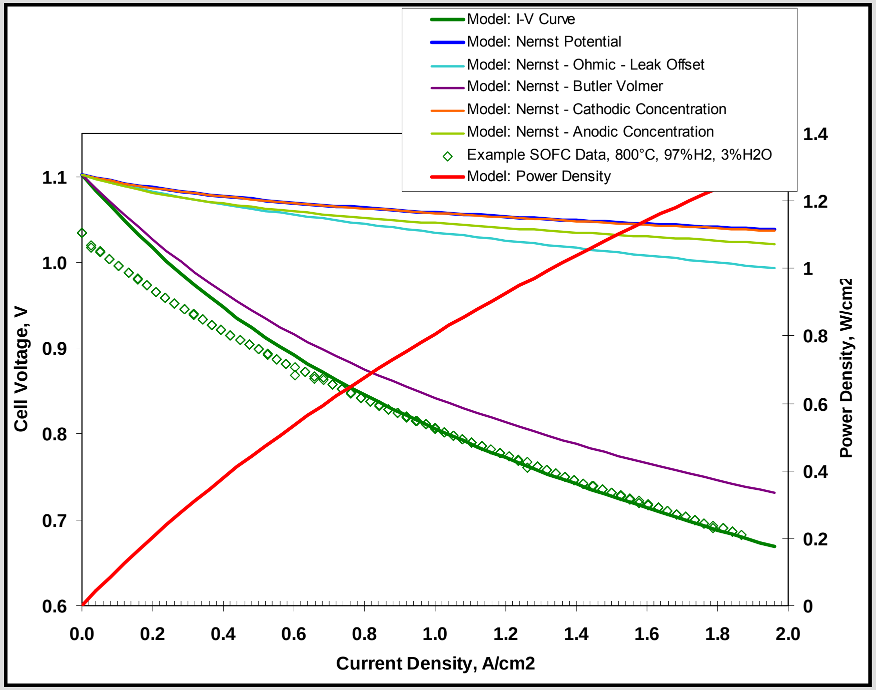
Effect of Leak on I-V Curve



- Two cells were tested, one a 2.5cm button cell, known to have a small leak from anode to cathode, through porous ceramic seal (filled diamonds).
- The other, a 7cm x 7cm cell with gas-tight glass seal (lines).
- Cells had identical materials, processing, and operating conditions.
- Comparison of I-V curves shows that the effect of the leak is “washed out” as the current increases.

Effect of Leak on I-V Curve





Basic model subtracts constant voltage at all currents to compensate for leak effect.

Based on recent data, recommend assuming effect of leak is overcome as current increases.

Butler-Volmer Approximation

- Electrode charge-transfer overpotential
- Combined for both electrodes
- Three adjustable parameters for calibration

$$V_{B-V} = \left(\frac{R \cdot T}{\alpha \cdot F}\right) \cdot \sinh^{-1}\left(\frac{i}{2 \cdot i_0}\right)$$

$$i_0 = P_{\exp} \cdot \exp\left(\frac{-E_{act}}{R \cdot T}\right)$$

$\alpha \equiv$ adjustable parameter

$i \equiv$ average cell current density

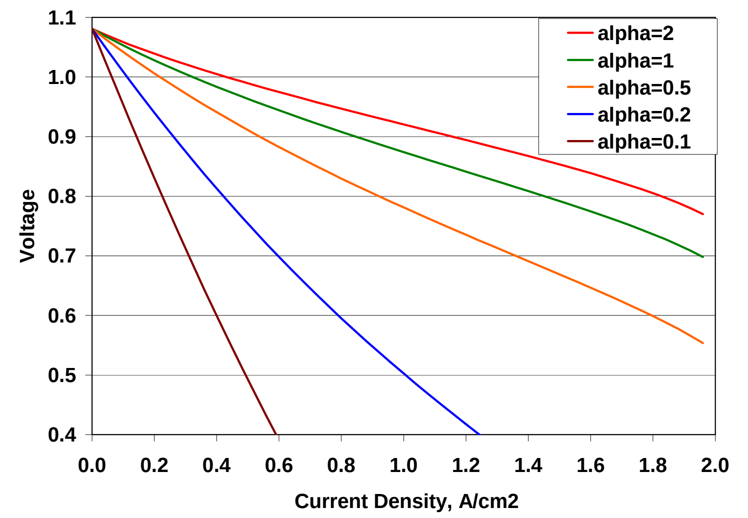
$i_0 \equiv$ exchange current density

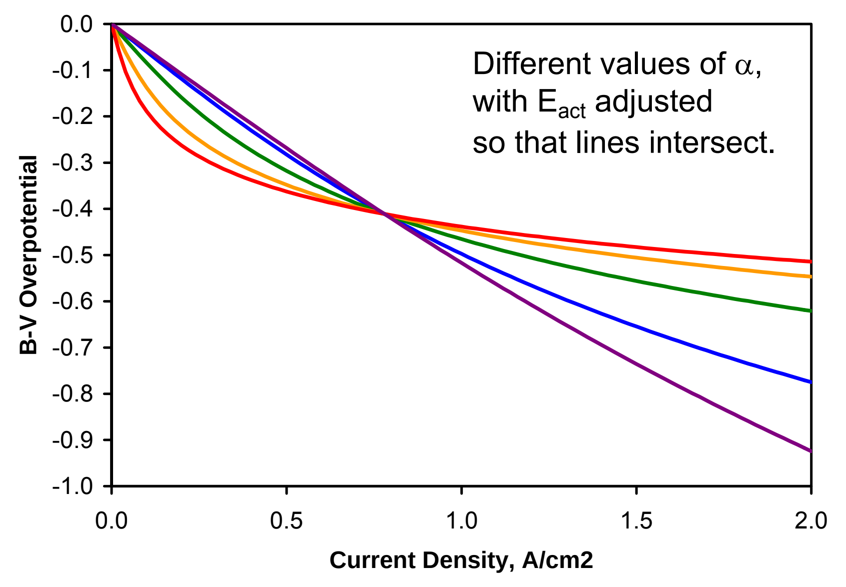
$P_{\exp} \equiv$ pre – exponential (adjustable)

$E_{act} \equiv$ activation energy (adjustable)

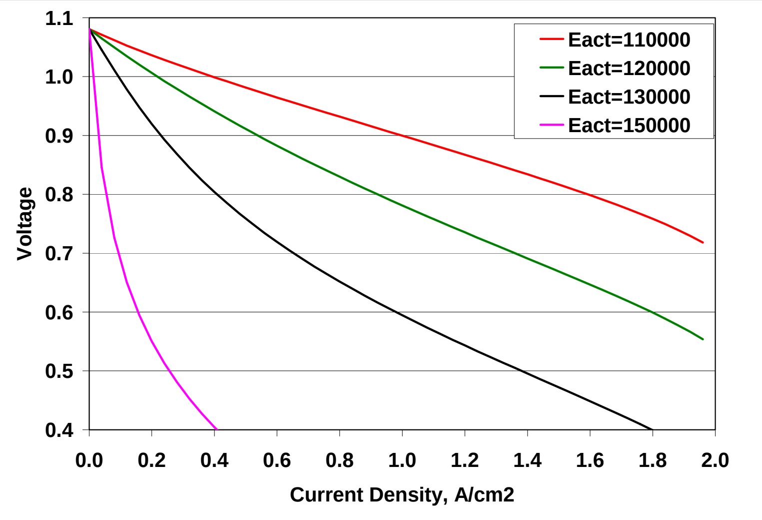
Effects of adjusting Butler-Volmer Parameters

- Slope, curvature and temperature dependence





Different values of α, with E_{act} adjusted so that lines intersect.



Cathode Diffusion Loss

- Loss due to depletion of O_2 at the cathode-electrolyte interface
- No adjustable parameters

$$V_{cath} = \left(\frac{R \cdot T}{4 \cdot F}\right) \cdot \ln\left(\frac{1 - i}{i_{cath}}\right)$$

$$i_{cath} = \left(\frac{4 \cdot F \cdot P \cdot D_{eff,cath}}{R \cdot T \cdot l_{cath}}\right) \cdot \ln\left(\frac{P}{P - P_{O_2}}\right)$$

$$D_{eff,cath} = D_{O_2 - N_2} \cdot \left(\frac{V_{cath}}{\tau_{cath}}\right)$$

$$D_{O_2 - N_2} = \left(\frac{T^{1.75}}{P}\right) \cdot \left(\frac{\sqrt{\dfrac{1}{M_{O_2}} + \dfrac{1}{M_{N_2}}}}{(r_{O_2} + r_{N_2})^2}\right)$$

$D_{eff,cath} \equiv$ effective diffusion coefficient

$l_{cath} \equiv$ cathode thickness

$P \equiv$ system pressure

$P_{O_2} \equiv$ average partial pressure of oxygen over cathode

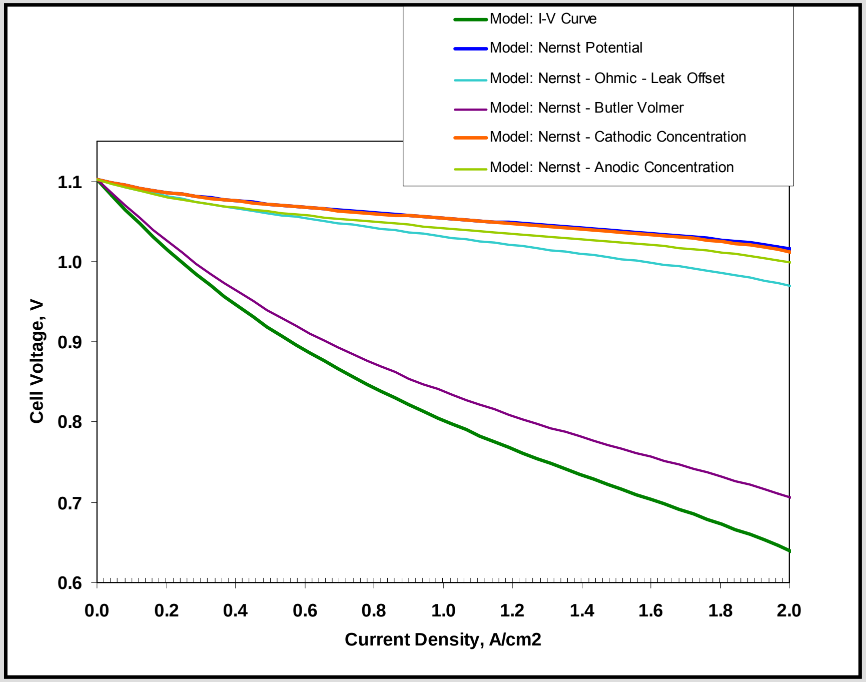
$D_{O_2 - N_2} \equiv$ binary diffusion coefficient

$M_{O_2} \equiv$ molecular weight

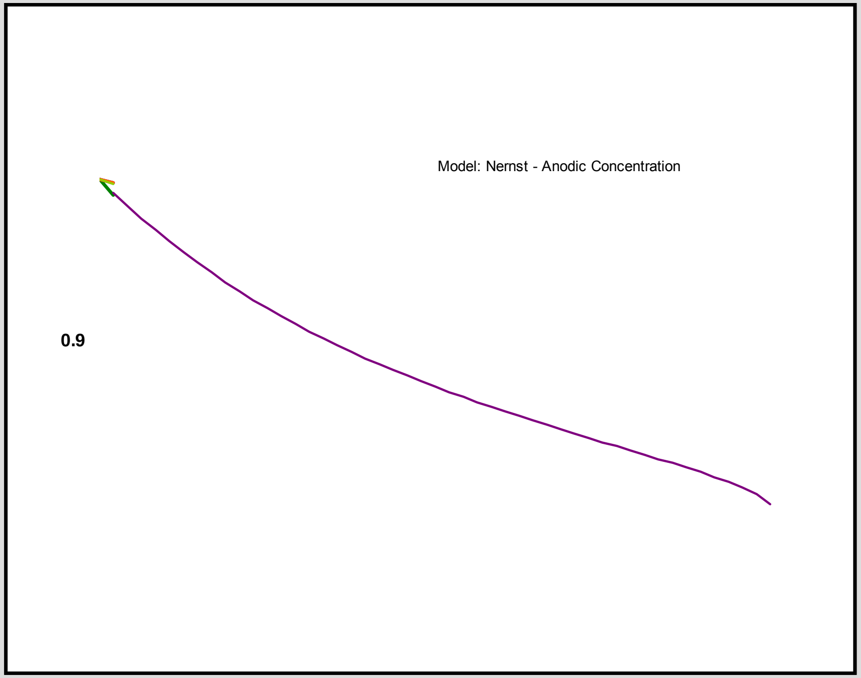
$r_{O_2} \equiv$ empirical molecular radius

Cathode Diffusion Loss, Cont.

- No significant overpotential until oxygen is almost completely gone.



- 90% O_2 utilized at 2 A/cm^2
- 50 μm cathode, 30% porosity, τ=2.5
- No discernible effect



- 100% O_2 utilized at 2 A/cm^2
- 50 μm cathode, 30% porosity, τ=15
- Significant effect at high currents.

Anode Overpotential

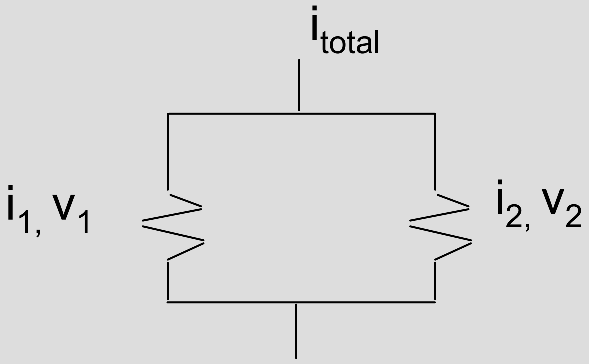
Outline

- Parallel reactions (H_2 & CO), solve by electrical circuit analogy

- Limiting currents for concentration polarization
  - Products - classical pore diffusion model
  - Reactants - surface adsorption/diffusion model

Anode Overpotential

- Two simultaneous reactions
  - $H_2+1/2O_2 \rightarrow H_2O$ and $CO+1/2O_2 \rightarrow CO_2$
- Solve by electrical circuit analogy



$$V_{H_2} = \frac{RT}{2F}\left[\ell n\left(1-\frac{i_1}{i_{H_2}}\right) - \ell n\left(1-\frac{i_1}{i_{H_2O}}\right)\right]$$

$$V_{CO} = \frac{RT}{2F}\left[\ell n\left(1-\frac{i_2}{i_{CO}}\right) - \ell n\left(1-\frac{i_2}{i_{CO_2}}\right)\right]$$

Kirchoff's Laws: $i_1+i_2=i_{total}$, $v_1=v_2$

(Cells M106-U131)

Anode Overpotential

- Solve by electrical circuit analogy
- Kirchoff's Laws: $i_1+i_2=i_{total}$, $v_1=v_2$
- The familiar quadratic solution

$$V_{anode} = \frac{RT}{2F} \ell n \left[\frac{-B + \sqrt{B^2 - 4AC}}{2A} \right]$$

$$A = \frac{i}{i_{H_2O} i_{CO_2}} + \frac{1}{i_{H_2O}} + \frac{1}{i_{CO_2}}$$

$$B = \frac{i}{i_{H_2O} i_{CO}} + \frac{i}{i_{H_2} i_{CO_2}} + \frac{1}{i_{H_2}} + \frac{1}{i_{CO}} - \frac{1}{i_{H_2O}} - \frac{1}{i_{CO_2}}$$

$$C = \frac{i}{i_{H_2} i_{CO}} - \frac{1}{i_{H_2}} - \frac{1}{i_{CO}}$$

(Cells M106-U131)

Anode Overpotential

- Each branch of circuit treats reactants (H_2,CO) and products (H_2O,CO_2), eg,

$$V_{H_2} = \frac{RT}{2F}\left[\ell n\left(1-\frac{i_1}{i_{H_2}}\right)-\ell n\left(1-\frac{i_1}{i_{H_2O}}\right)\right]$$

- Each term contains a ‘limiting current’ (i_{H2}, i_{H2O})
  - Defined by partial pressure (P_{H2}), effective diffusivity (D^{eff}), anode thickness (L_a)

$$i_{H_2} = \frac{2FP_{H_2}D^{eff}_{H_2}}{RTL_a} \qquad i_{H_2O} = \frac{2FP_{H_2O}D^{eff}_{H_2O}}{RTL_a}$$

(Cells M106-U131)

Anode Overpotential

- The limiting currents are derived for open circuit conditions, and assume that the reactant concentrations approach zero in the gas immediately above the reactive sites.

- This may not be true, but serves as a working approximation to investigate the importance of other mechanisms in the context of previous models, thus maintaining a connection (benchmark) to prior models.

Anode Overpotential

- Limiting current differs for reactants and products
- H_2 controlled by adsorption & surface diffusion to TPB, H_2O by bulk diffusion through pores
- The difference is how you treat the effective diffusivity

Reactant

$$i_{H_2} = \frac{2FP_{H_2}D_{H_2}^{eff}}{RTL_a}$$

Product

$$i_{H_2O} = \frac{2FP_{H_2O}D_{H_2O}^{eff}}{RTL_a}$$

(Cells M106-U131)

Anode Overpotential

- **<u>Product</u> (H_2O) limiting current controlled by bulk diffusion through pores (a classical model)**
- **ϕ=porosity, τ=tortuosity, x=mole fraction, P=total pressure, M=molec. wt., r=molec. radius**

$$i_{H_2O} = \frac{2FP_{H_2O}D^{eff}_{H_2O}}{RTL_a}$$

$$D^{eff}_{H_2O} = \frac{\phi D^{unary}_{H_2O}}{\tau}$$

$$D^{unary}_{H_2O} = \frac{1 - x_{H_2O}}{\sum\limits_{i \neq j} \frac{x_i}{D^{binary}_{ij}}}$$

$$D^{binary}_{ij} = \frac{0.001T^{1.75}\sqrt{\frac{1}{M_i} + \frac{1}{Mj}}}{P\left(r_i + r_j\right)^2}$$

(Cells W63-AD88)

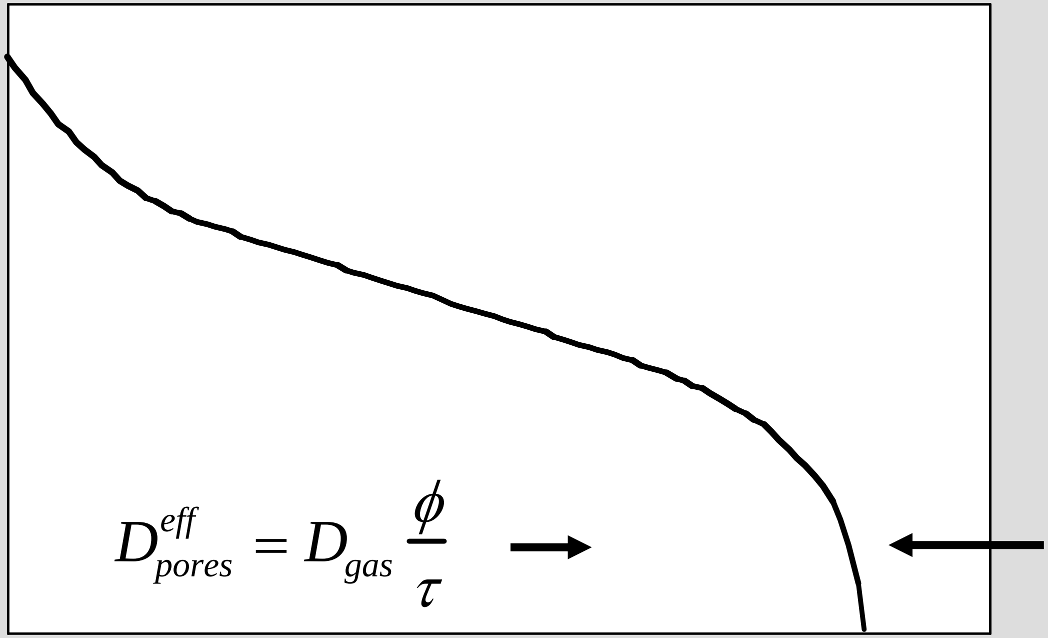
Anode Overpotential

- Concentration polarization due to limited reactant (H_2) supply rates may be caused by surface adsorption and diffusion mechanisms very near the TPBs, rather than by bulk diffusion mechanisms through the porous ceramic.

- The following is a proposed model currently under development.

Question

Is concentration polarization really caused by high *bulk* diffusion resistance (tortuosity)?



$$D_{pores}^{eff} = D_{gas}\frac{\phi}{\tau} \rightarrow$$

Modeling problems

Tortuosity is...

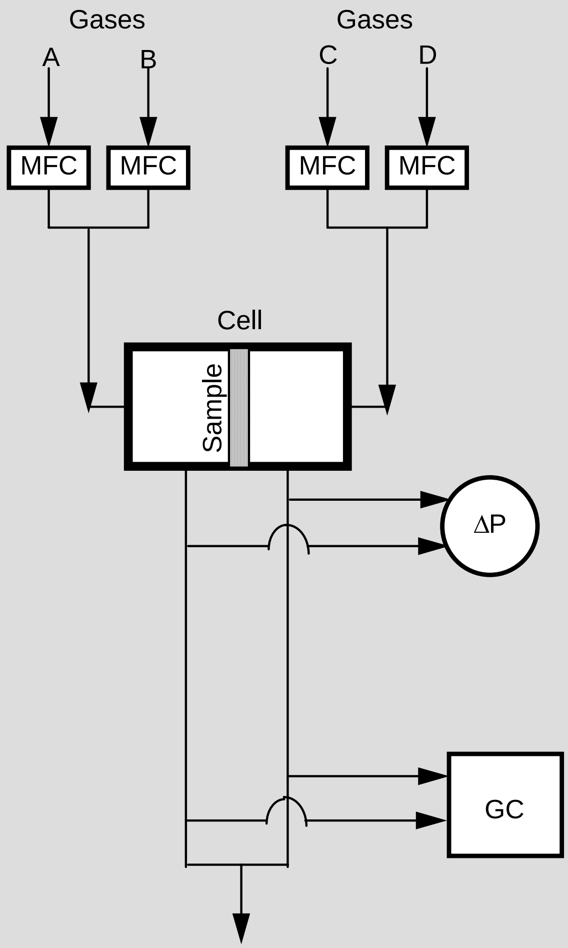
- Apparent diffusion path length / anode thickness.
- A measure of bulk diffusion resistance.
- An empiricism describing all we don’t know about the microstructure of the pore network.

This is Important Because...

- The maximum current (or power envelope) is not adequately predicted by SOFC models, unless…
- Anode tortuosity τ is assumed to be 10 - 17, which disagrees with historical data (τ = 2 - 6), and...
- Is misleading…smaller thickness or higher porosity compromises structural integrity.
- Does a high bulk diffusion resistance really exist?

Anode Tortuosity Experiments

Wicke-Kallenbach experiments



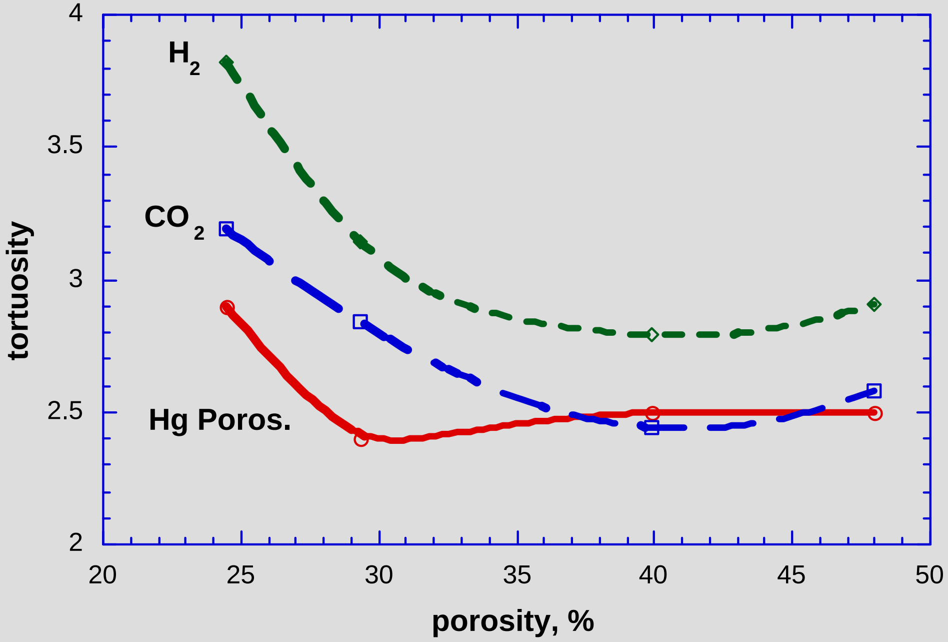
Maxwell-Stefan problem for counter-diffusing gases:

$$\frac{dy_i}{dz} = -\frac{N_i}{\beta_i D_{Ki}} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{y_i N_j - y_j N_i}{\frac{\phi}{\tau} D_{ij}}$$

Anode Tortuosity

τ = 2.5-3.5 for modern porous ceramic anodes

Anode diffusion resistance is not in the bulk material.



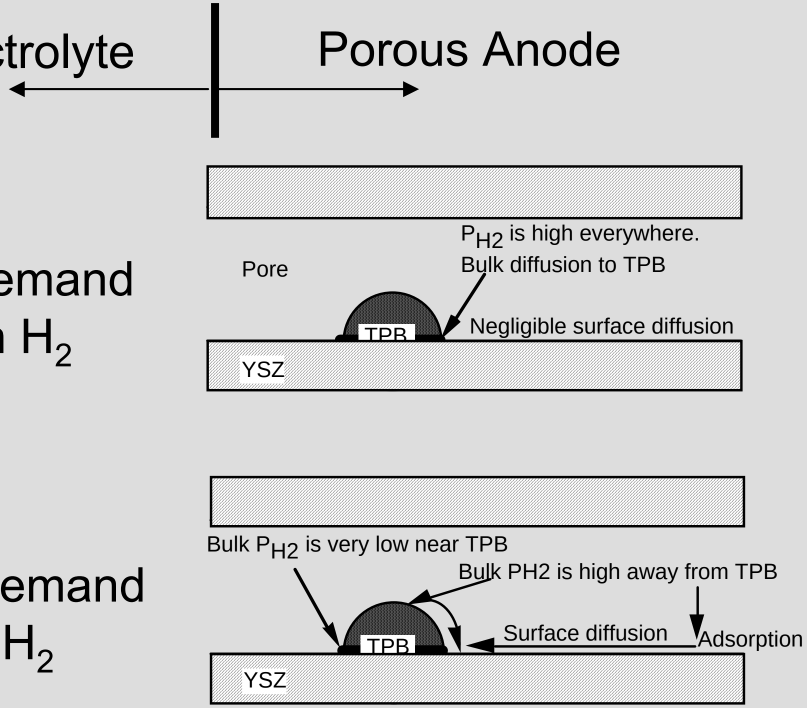
Possible Explanations

- Non-ideal gas behavior?
  - Minimal counter-diffusion effect in τ vs ϕ plot.
  - Two analysis methods showed negligible effect.

- Knudsen effects at anode/electrolyte interface?
  - Microscopy shows no change in pore structure.

- Competitive adsorption and surface diffusion?
  - A possible explanation.

Competitive Adsorption & Surface Diffusion at TPBs



P_{H2} is high everywhere.
Bulk diffusion to TPB

Negligible surface diffusion

Low demand
or high H_2

Bulk P_{H2} is very low near TPB

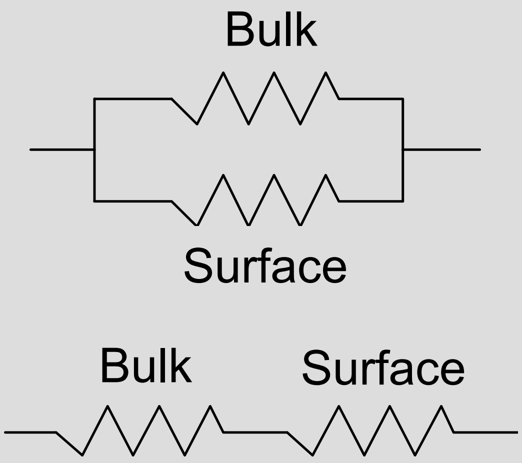
Bulk PH2 is high away from TPB

Surface diffusion

Adsorption

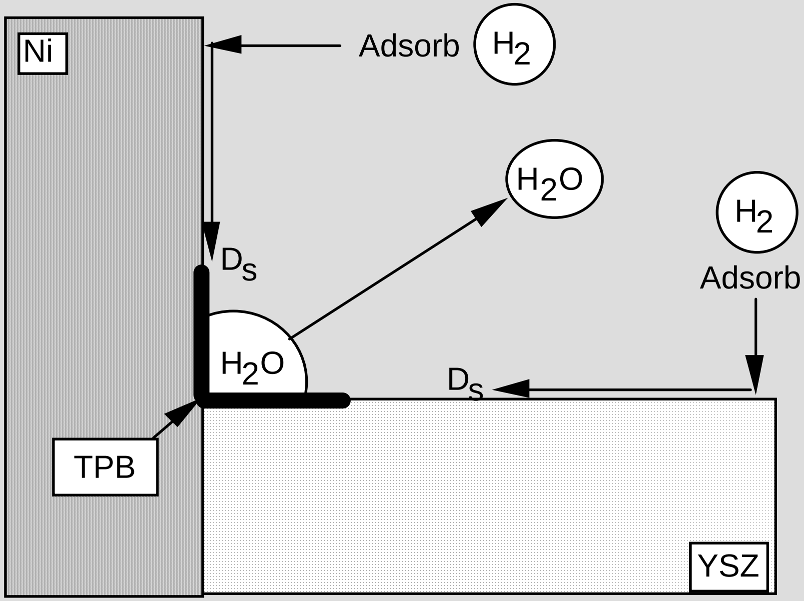
High demand
or low H_2

Diffusion Circuit



Proposed H_2 Mechanism

- **TPB active sites are occupied by H_2O at high T.**
- **Hydrogen adsorbs on regions *adjacent* to TPBs,**
- **diffuses along the surface *to* the TPBs,**
- **reacts at TPBs to form new H_2O, old H_2O desorbs.**



Competitive Adsorption near TPBs

$$\theta_i = \frac{b_i P_i}{1 + \sum_j b_j P_j}$$

Langmuir multi-gas isotherm

$$b_i = \frac{N_A A_i \tau_0}{\sqrt{2\pi R T M_i}} e^{\frac{Q_i}{RT}}$$

Q_i = Adsorption activation energy

θ_i=surface coverage ($0<\theta<1$)
b_i=Langmuir parameter for species i
P_i=partial pressure
N_A=Avogadro's number
A_i=area of molecule on surface
τ_0=vibrational period (10^{-13}/sec)
M_i=molecular weight

(Cells W90-AH104)

Surface Diffusion to TPB Active Sites

Transition from bulk to surface diffusion (Vignes, 1966)

$$\mathbf{D_{eff} = (D_{bulk})^{\Theta} (D_{surf})^{1-\Theta}}$$

A linear correlation between the diffusion *exponents*

$$10^{z} = \left(10^{x}\right)^{\Theta}\left(10^{y}\right)^{(1-\Theta)}$$

$$z = \Theta x + \left(1 - \Theta\right) y$$

(Cells W90-AH104)

Surface Diffusivity

Depends on coverage (θ_ι)

$$D_{s,i} = \frac{D_{s,i,0}^{1-\theta_i} D_{s,i,1}^{\theta_i}}{1-\theta_i}$$

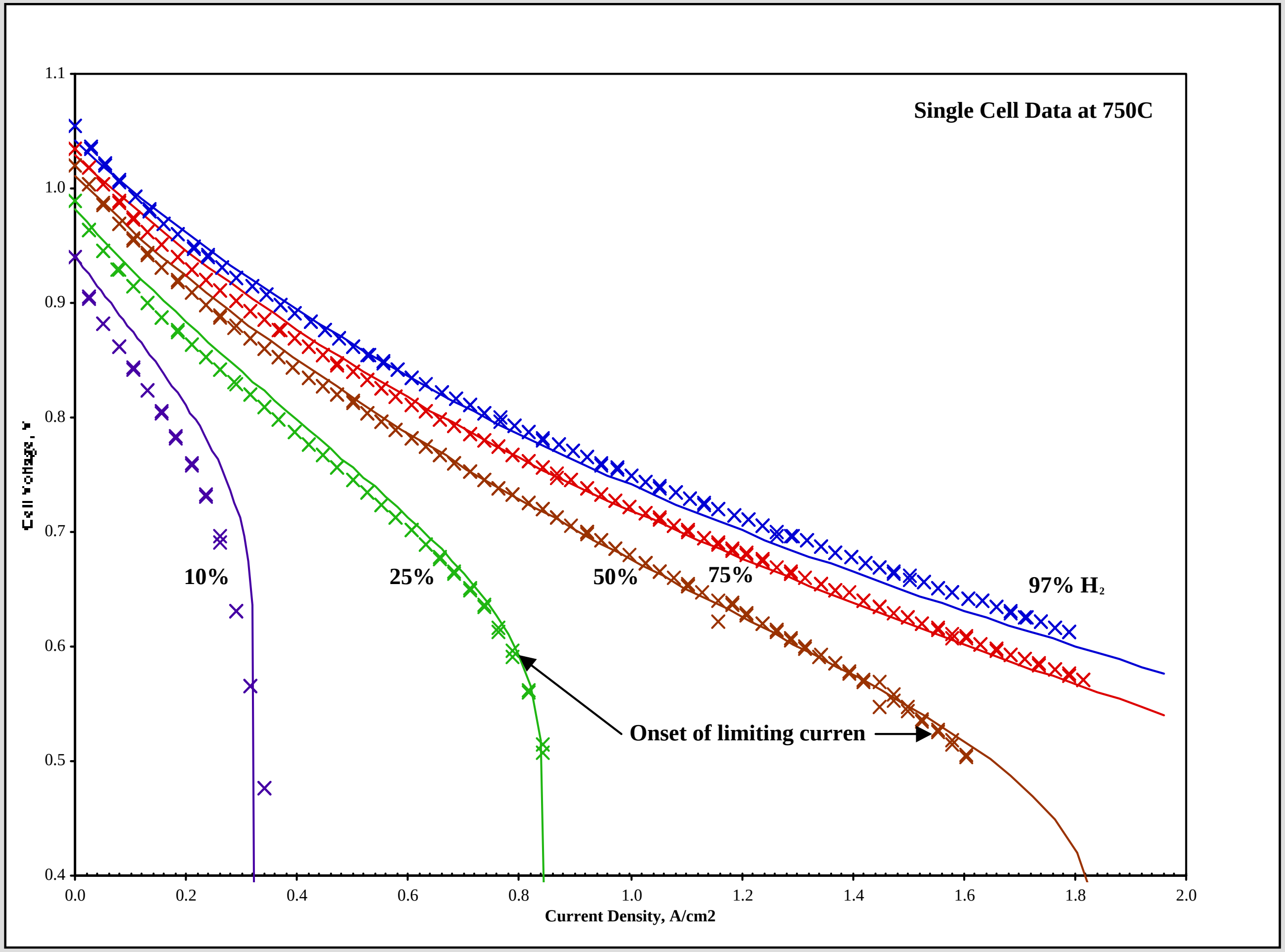
- For hydrogen on Ni at ~1023K

$D_{s,H,0}$~0.1 cm^2/sec at zero coverage
$D_{s,H,1}$~5x10^{-4} cm^2/sec at full coverage
1/(1-θ_H)= thermodynamic factor

(Cells W90-AH104)

Fit Q & D_s to Experimental Data

Results for H_2, PNNL SOFC Spread Sheet Model, 2002



Fitted parameters agree with independent data for H_2 on Ni @ 750C

Parameter	Fit	Data
Q_{H2} eV/molecule	0.425	0.2 - 0.4
$D_{s,H2}$ cm^2/sec	$5.6x10^{-4}$	$4.8\text{-}6.8x10^{-4}$

Anode Overpotential Summary

- Anode diffusion resistance
  originates at the anode/electrolyte interface,
  not in the bulk material.

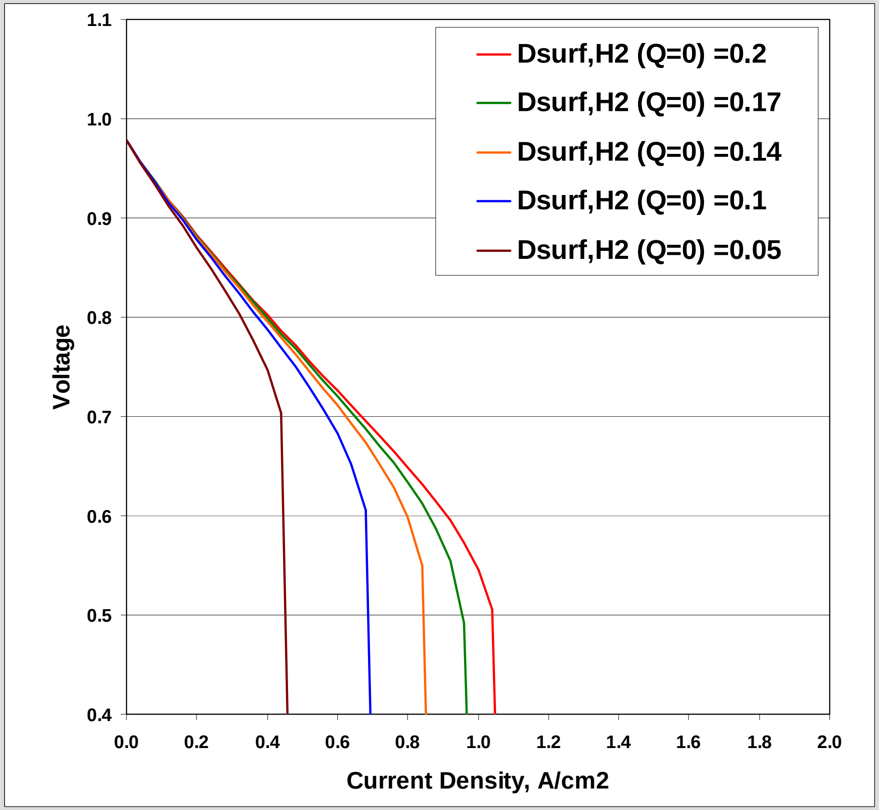
- Anodic concentration polarization may be caused by
  competitive adsorption and
  surface diffusion near TPBs.

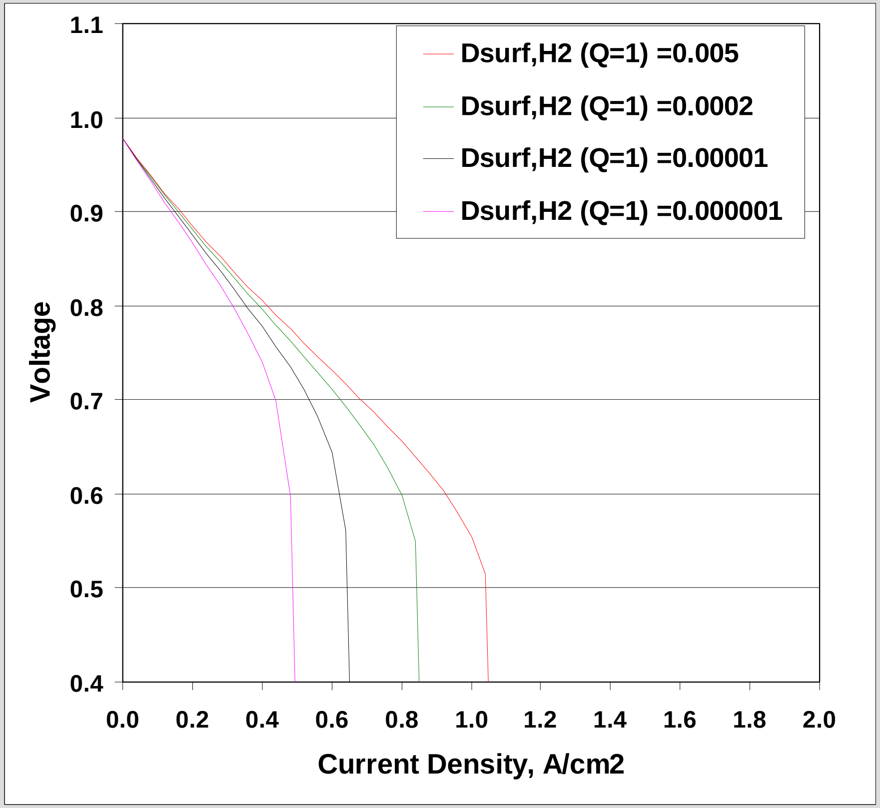
- Fitted Q_{H2} and D_s for H_2 agree with literature, so the model's physical foundations appear credible.

- Work is in progress to refine and extend the model.

Effect of adjusting Surface Diffusion Parameters

- Position of limiting current “tail”.





Enthalpy Calculations – Oxidation of Fuel

- Enthalpy changes related to fuel oxidation are calculated using standard "textbook" thermodynamics, taking advantage of the fact that enthalpy is a state function. Fuel gas is “virtually” cooled to RT, oxidized at RT, then heated to outlet temperature. (Cells C137-P195)
- The starting point for the calculations is the fuel gas composition as equilibrated at the inlet temperature expressed in flow rate for each species (Cells C13-C17).
- Step 1) The anode inlet gas mixture is cooled down to room temperature.
  - e.g: H_2 (T_{inlet}) ⟶ H_2 (298 K)

$$\Delta H_{H_2} = -\int_{T_{rt}=298}^{T_{inlet}} C_P = -A\cdot(T_{inlet}-298) - B\cdot(T_{inlet}^2 - 298^2) - C\cdot(\frac{1}{T_{inlet}} - \frac{1}{298})$$

  - Similar calculations for other species (CO, H_2O, CO_2, N_2)
  - $\Delta H_{cooling} = \sum \Delta H_i \qquad i = H_2, CO, H_2O, CO_2, N_2$

Enthalpy Calculations – Oxidation of Fuel

- **Step 2)** The appropriate amounts of H_2 and CO (based on inlet and outlet fuel concentrations) are oxidized at room temperature using room temperature enthalpies of formation for products and reactants.

$$CO + 1/2\ O_2 \longrightarrow CO_2 \qquad \Delta H_1 = \Delta H_f\ (CO_2) - \Delta H_f\ (CO)$$

$$H_2 + 1/2\ O_2 \longrightarrow H_2O \qquad \Delta H_2 = \Delta H_f\ (H_2O)$$

$$\Delta H_{ox} = \Delta H_1 + \Delta H_2$$

Enthalpy Calculations – Oxidation of Fuel

- Step 3) The anode outlet gas mixture is heated to the outlet temperature.
  - e.g: H_2 (298 K) ⟶ H_2 (T_{outlet})

$$\Delta H_{H_2} = \int_{T_{rt}=298}^{T_{outlet}} C_P = A\cdot(T_{outlet}-298)+B\cdot(T_{outlet}^2-298^2)+C\cdot(\frac{1}{T_{outlet}}-\frac{1}{298})$$

  - Similar calculations for other species (CO, H_2O, CO_2, N_2)
  - $\Delta H_{heating} = \sum \Delta H_i$ $i = H_2, CO, H_2O, CO_2, N_2$
- Step 4) The net enthalpy for fuel oxidation is obtained by summing the enthalpies from Steps 1-3:
  - $\Delta H_{net} = \Delta H_{cooling} + \Delta H_{ox} + \Delta H_{heating}$

Enthalpy Calculations – Oxidation of Fuel

- Step 5) The electrical power produced by the stack (as calculated by the model, see Cell I8) is then subtracted from the calculated enthalpy (Cell G175) to yield the net sensible heat produced by the cell/stack:

  $Q_{oxid} = \Delta H_{net} - Work_{elect}$

Enthalpy Calculations – Cathode Air

- Changes in enthalpy associated with the removal of heat by cathode air as it passes through the stack are calculated using the same methodology as for fuel oxidation.
- Starting point for calculation is inlet cathode air flow rate and temperature; oxygen removed via electrolyte membrane is subtracted from oxygen calculation:

$$N_2\ (T_{inlet}) \rightarrow N_2\ (T_{outlet})$$

$$\Delta H_{N_2} = \int_{T_{inlet}}^{T_{outlet}} C_P = A \cdot (T_{outlet} - T_{inlet}) + B \cdot (T_{outlet}^2 - T_{inlet}^2)$$

Similar calculation for oxygen

$$Q_{cath} = \Delta H_{cath} = \Delta H_{N2} + \Delta H_{O2}$$

Enthalpy Calculations – Final Answer

- The net sensible heat generated by the cell/stack is obtained by adding together the enthalpy of fuel oxidation and the enthalpy of cathode air heating.
- $Q_{net} = Q_{oxid} + Q_{cath}$
- Result is shown in Cell K6 (with incorrect units in Jan 03 release– should be W instead of W/cm^2)
- Remember that heat *losses due to radiation/convection form stack walls* are not included!!!

- Note: The thermodynamic values for the various reactants and products in the preceding calculations were taken from Appendix C of *Stoichiometry and Thermodynamics of Metallurgical Processes* by Y.K.Rao, Cambridge, 1985

Third Demo and Discussion of Basic Model

- Overpotential plotter.
- Eliminate leak correction.
- Adjust B-V parameters.
- Heat generation features.

Features of Advanced Model

- Enhanced plotting macro for calibration
- Temperature-dependent Butler-Volmer parameters

Demo and Discussion of Advanced Model

- Enhanced plotting macro
- General Seeker macro

Future Improvements

- Leaks ignored.
- Additional inert gasses: He, Ar as well as N2.
- Improved treatment of electrode diffusion.
- Temperature dependent contact resistance.
- Sheet resistance of cathode.