

COMPREHENSIVE DEPICTION OF A SUCCESSFUL CFD MODELING FOR A REAL GEOMETRY SOLID OXIDE FUEL CELLS



P M V Subbarao

Associate Professor

Mechanical Engineering Department

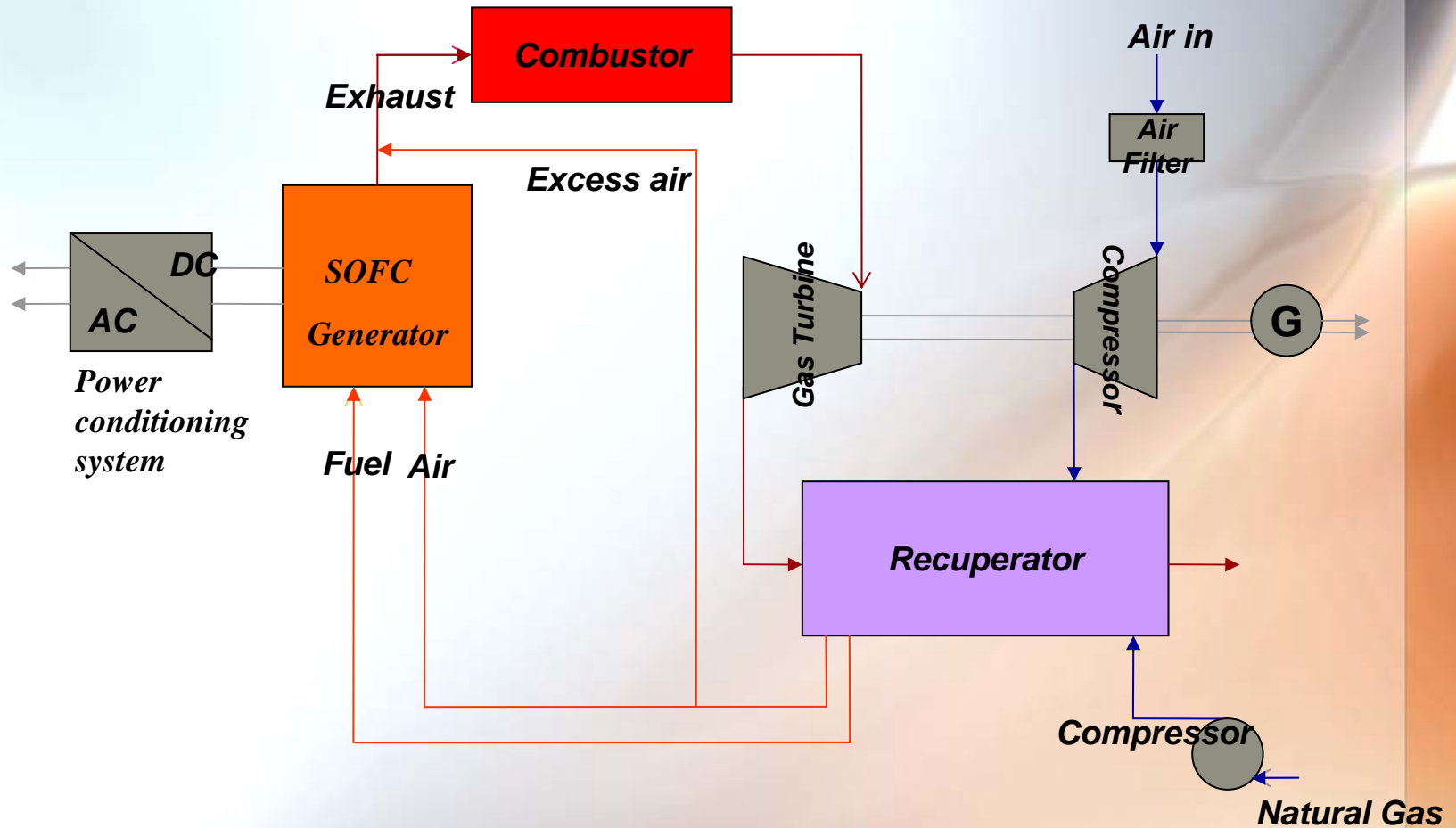
Indian Institute of Technology – New Delhi

More You Can See Through More Confidence...

Research Interests

- Use of high end experimental and computational fluid flow and heat transfer methods for solving Real Time Problems.
- CFD simulation of In-cylinder flow in I.C. Engine to predict mixture preparation in advanced engines.
- Experimental mapping of temperature and heat transfer coefficient in advanced fin and tube heat exchangers.
- Experimental and Computational analysis of fluid flow with shocks in Super Sonic Ejectors.
- CFD analysis of SOFC Stacks for Distributed Power Generation.

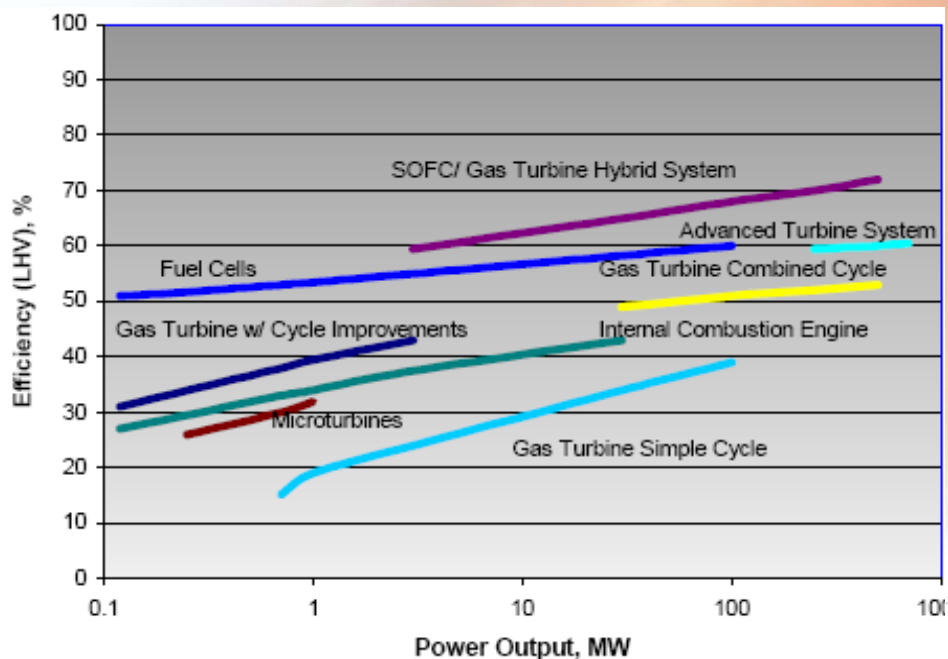
Reference SOFC-GT system – Regenerative Brayton cycle



Motivation for hybridization

- Due to the polarization losses, 100% utilization of hydrocarbon fuel is not possible in the fuel cell stack
- Hydrocarbon fuels used in SOFC that produce power also produce rejected heat. **(Reversible reaction, Process irreversibility)**.
- The heat must be rejected in order to maintain its temperature at a desired level.

US energy studies



CFD Modeling of SOFC Stacks

- Solid Electrolyte.
- High temperature and high pressure fluid flow with heat generation.
- Complex flow geometry: Flow through a system of micro channels.
- Stack of such geometries.
- Many fuel options.
- Huge scope for optimization and improvements.

Overall Research Objective

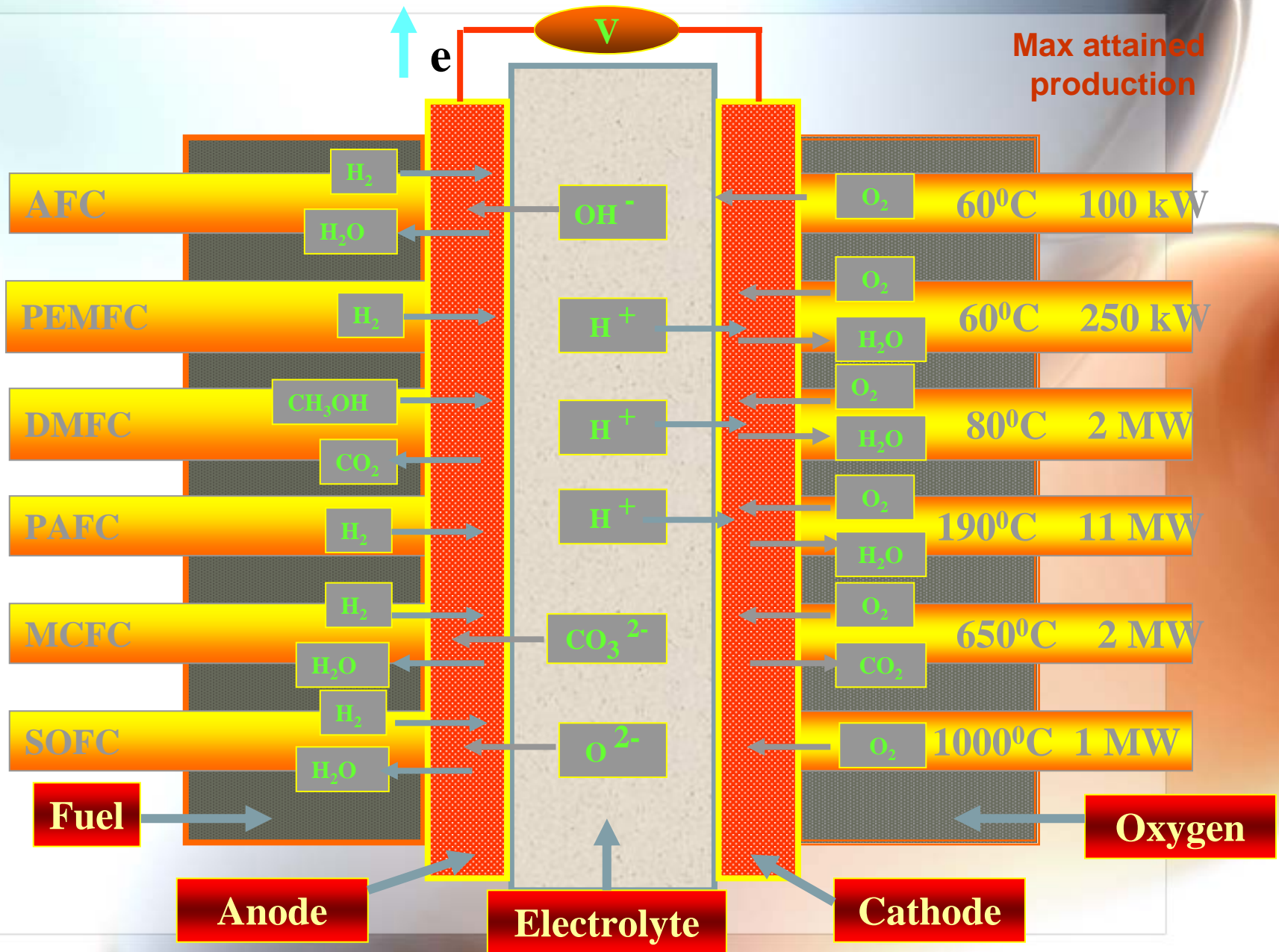
- To Investigate / develop SOFC based power generation processes

- Achieve high electricity generation efficiencies

- Key Issues to be Investigated:
 - fuel composition (Especially H₂ and CO mixtures),
 - utilization factor,
 - Temperature & pressure,
 - operating cell voltage or current density,
 - efficiency (stack and hybrid cycle) and
 - cost (if possible)

Classification based on electrolyte used

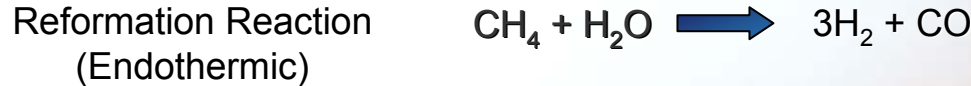
Max attained production



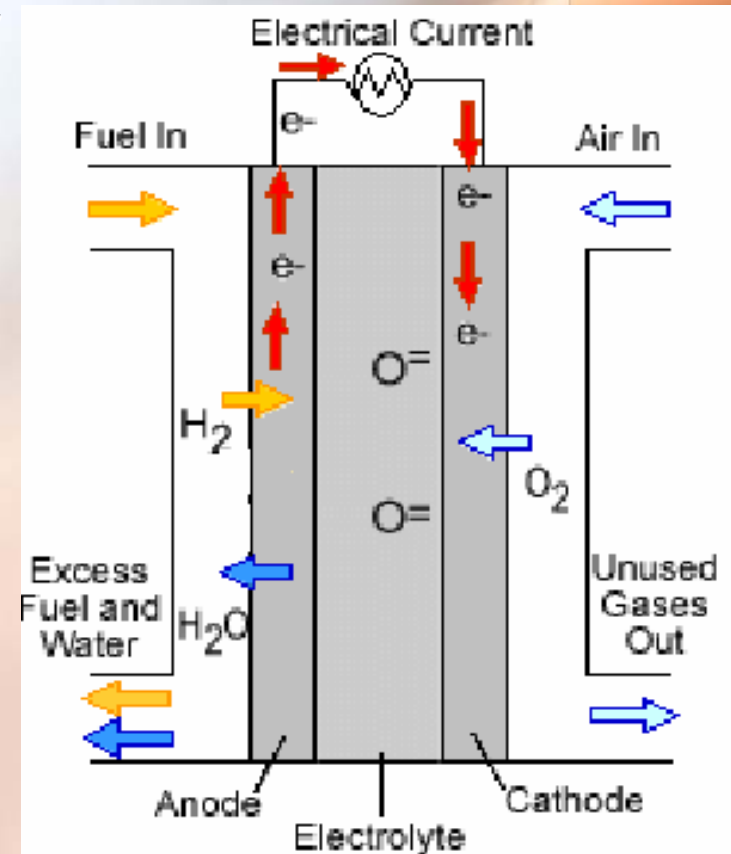
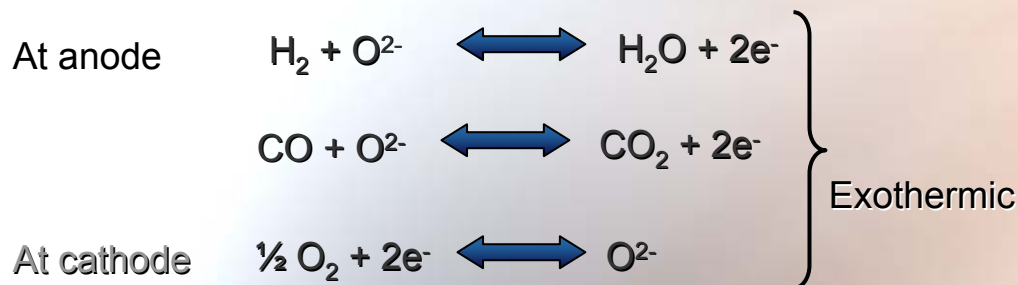
Solid Oxide Fuel Cells

- Electrolyte is solid and conducts oxygen ion at 650 °C
- High operating temperature and solid electrolyte permits flexibility in choosing the fuel
- Ideal fuel is hydrogen but any hydrocarbon fuel can be used after reformation
- Fuel reformation can be done internally or externally

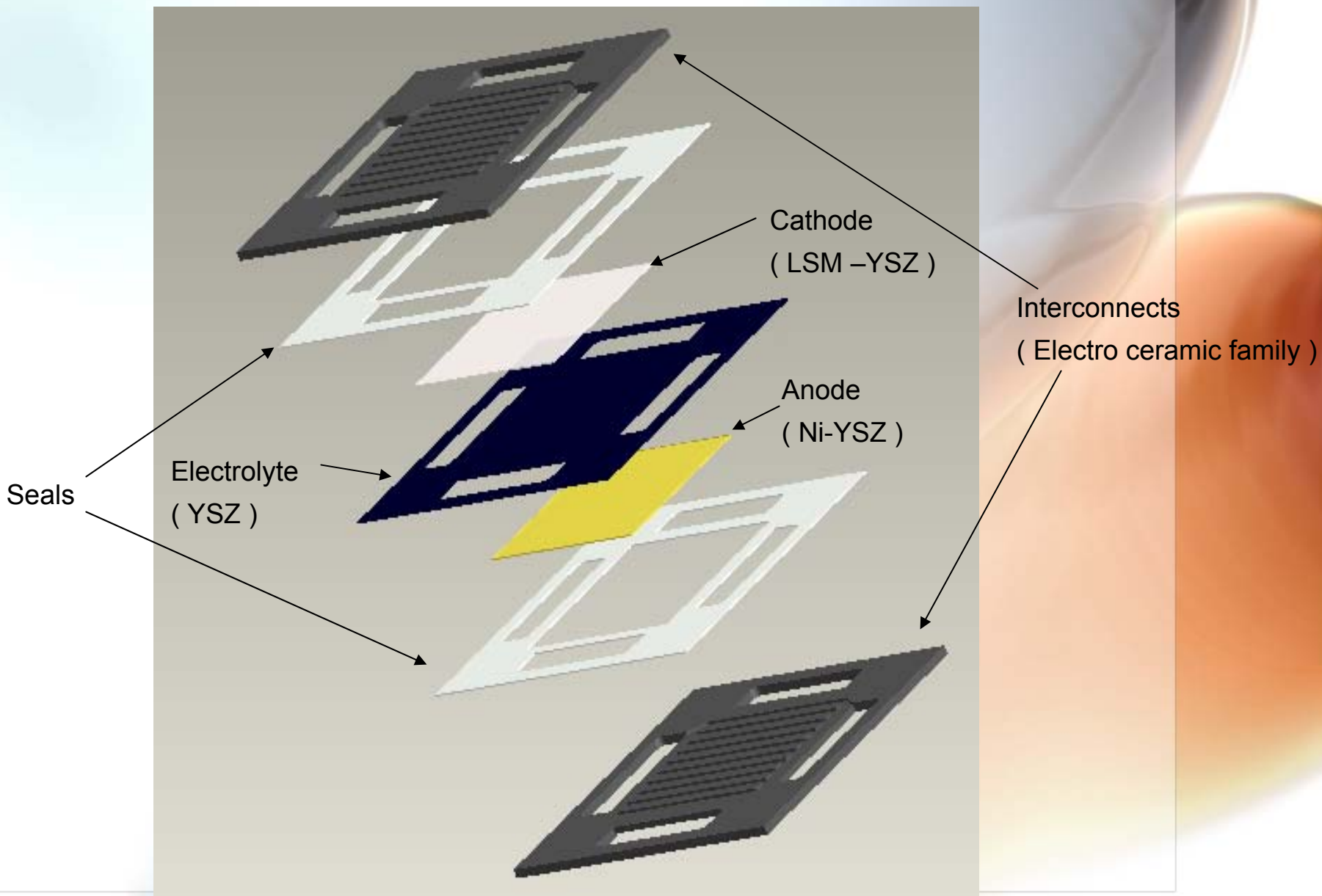
Chemical Reactions



Electrochemical Reactions

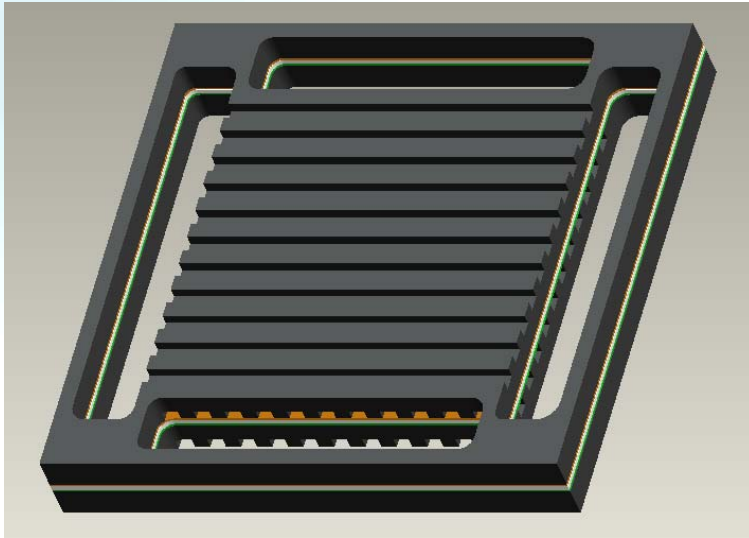


Single cell - dismantle view

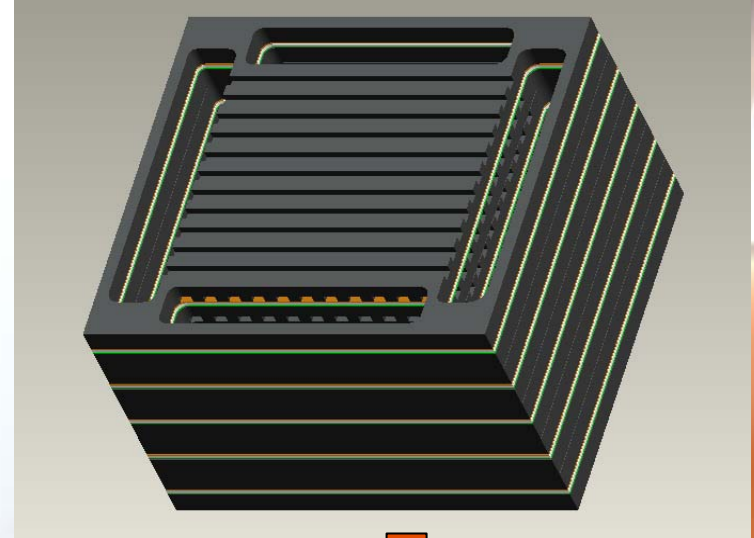
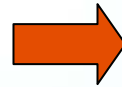


Stack assemble

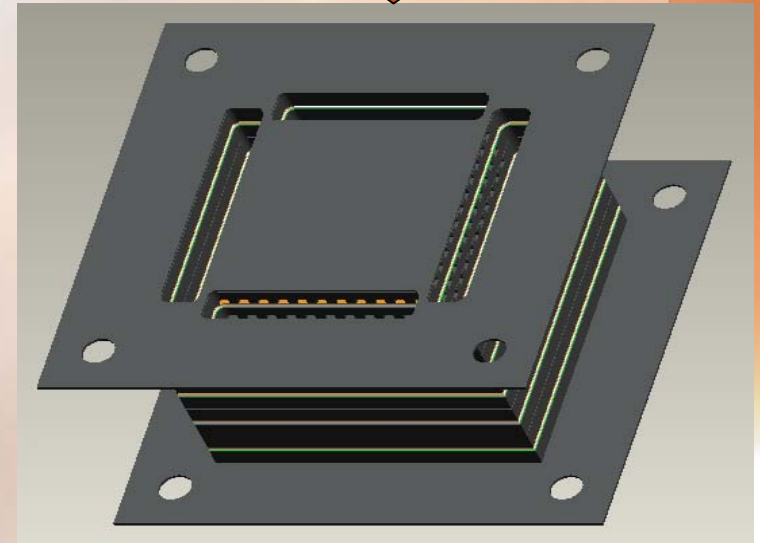
Individual fuel cells must be combined to produce appreciable voltage levels



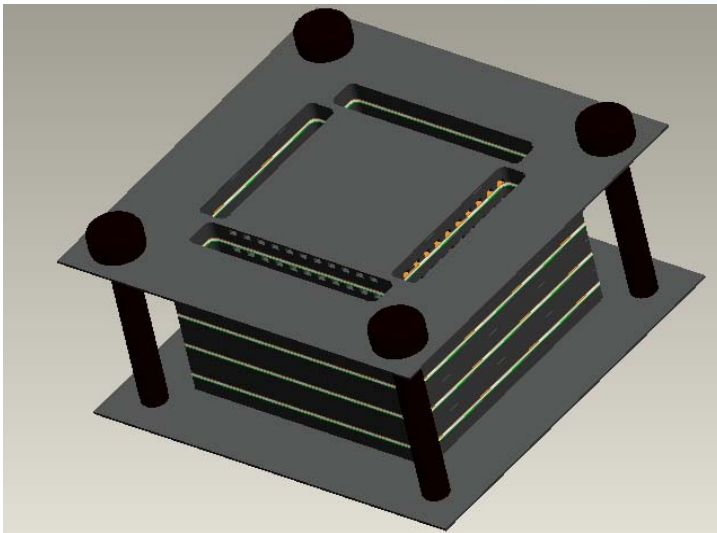
Single cell assemble



Array of cells



Array of cells with insulation plate



Stack assemble

Stack modeling

- Single cell geometry is analyzed for the given inlet fuel
- Stack effect is evaluated by multiplying the number of cells with single cell's result

- Stack Power $P = N_{\text{cell}} \sum IV$

- Effluent heat $Q = Q_{\text{elect}} + Q_s - Q_r - Q_{\text{surr}}$

Electrochemical process $Q_{\text{elect}} = i \sum \eta + T\Delta S$

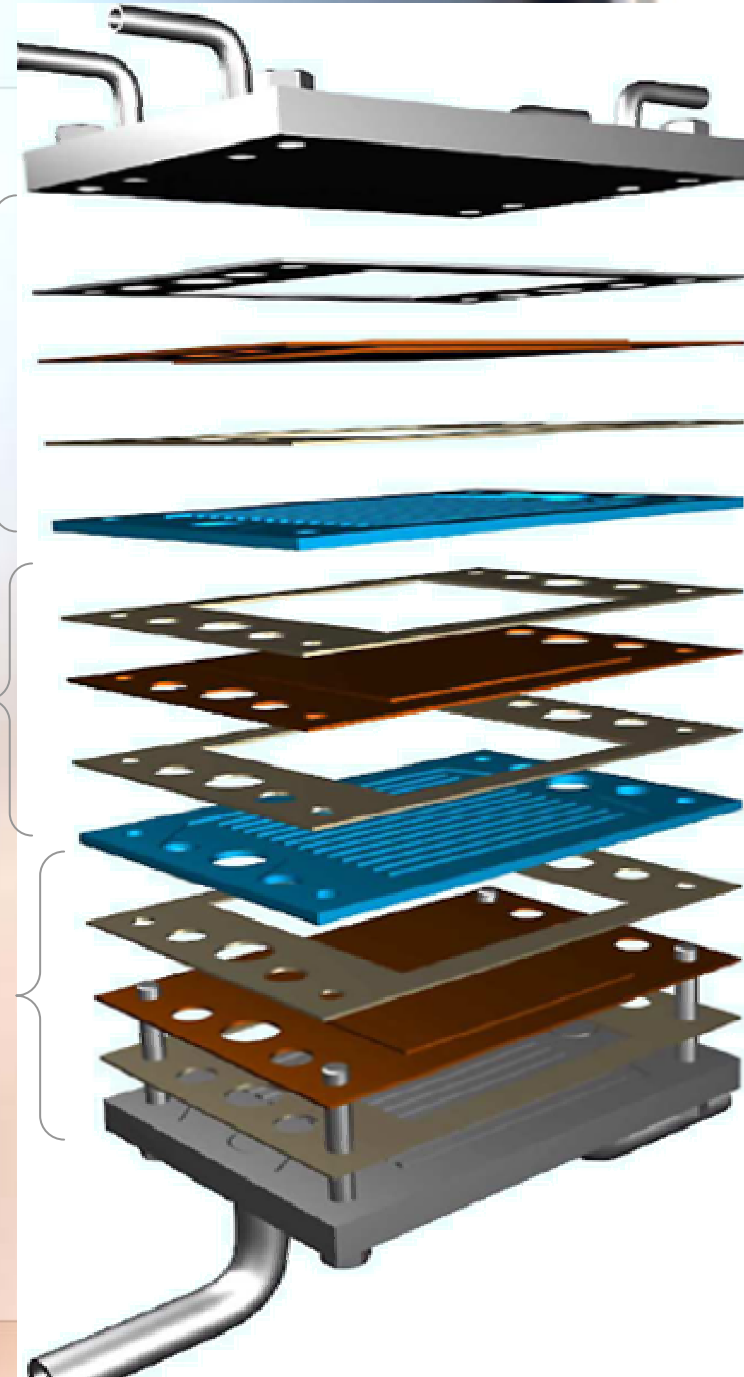
Heat consumed by reforming Q_r

Heat associated with shift gas reaction Q_s

Top most cell

Intermediate cell

Bottom cell



System Modeling - Macroscopic approach

- Thermodynamic modeling of a single cell and a stack
- Polarization modeling for a fuel cell
- Performance analysis of SOFC-GT hybrid power generation cycle

Cell Potential Calculation

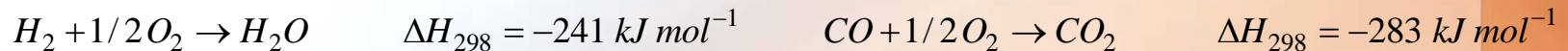
General form of *Nernst* Expression
$$\Delta G = \Delta G^0 + RT \ln \frac{[C]^c [D]^\delta}{[A]^\alpha [B]^\beta}$$

Ideal cell potential
$$E = E^0 + \frac{RT}{nF} \ln \frac{\prod [\text{reactant activity}]}{\prod [\text{product activity}]} \quad (\text{i.e.}) \quad \Delta G = -nFE$$



$$E = E^o + \frac{RT}{2F} \ln \left(\frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \right)$$

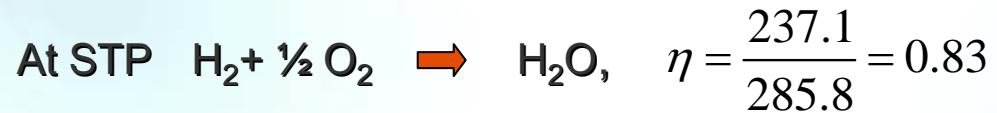
Solid oxide fuel cell



$$E_{H_2} = E^o + \frac{RT}{2F} \ln \left(\frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \right) \quad E_{CO_2} = E^o + \frac{RT}{2F} \ln \left(\frac{P_{CO} P_{O_2}^{1/2}}{P_{CO_2}} \right)$$

Actual cell potential (V_{actual}) = Ideal cell potential (E) – losses or polarization

Fuel Cell Efficiency



$$\eta_{ideal} = \frac{\text{useful energy}}{\Delta H}$$

$$= \frac{\text{useful power}}{\Delta G / 0.83}$$

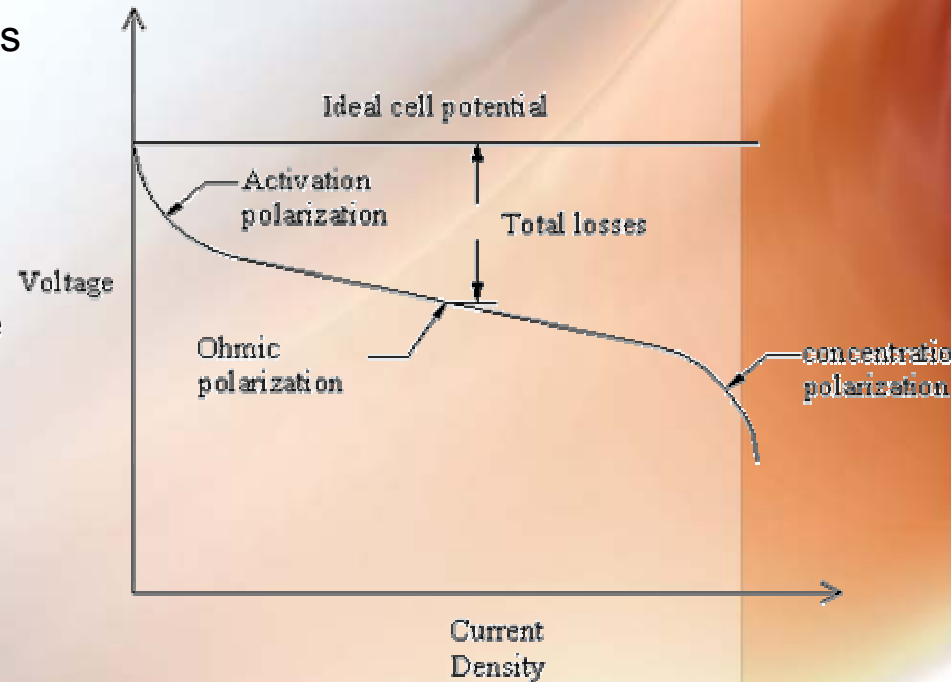
$$= \frac{(\text{volts})_{actual} \times \text{current}}{(\text{volts})_{ideal} \times \text{current} / 0.83} = \frac{0.83 V_{actual}}{V_{ideal}}$$

Polarization Distinctiveness

Actual potential of the cell is less than the equilibrium potential due to irreversible losses or *polarization*.

Losses or polarizations in Actual Performance

- **Activation over potential** (η_{act}) – Flow of ions should overcome the electronic barrier.
- **Ohmic over potential** (η_{ohm}) – Resistance offered by the total cell components to the flow.
- **Concentration over potential** (η_{con}) – Gas transport losses, dilution of fuel as the reactions progress.



V-I Characteristics of the Fuel cell

Summation of electrode polarization

Activation and concentration polarizations – both Anode and Cathode

$$\eta_{anode} = \eta_{act,a} + \eta_{con,a}$$

$$\eta_{cathode} = \eta_{act,c} + \eta_{con,c}$$

Polarizations increase Anode potential and decrease Cathode potential

$$V_{anode} = E_{anode} + |\eta_{anode}|$$

$$V_{cathode} = E_{cathode} - |\eta_{cathode}|$$

Cell potential

$$V_{actual} = V_{cathode} - V_{anode} - iR$$

$$V_{actual} = (E_{cathode} - |\eta_{cathode}|) - (E_{anode} + |\eta_{anode}|) - iR$$

Fuel flow rate calculation

- For every molecule of hydrogen (H₂), two electrons are Liberated

$$m_{H_2} = (1/2) * (1/96487) * (2.0158) = 1.04445 * 10^{-5} \text{ kg H}_2 / \text{s} - \text{kA}$$

- For every molecule of methane (CH₄), eight electrons are liberated

$$m_{CH_4} = (1/8) * (1/96487) * (16) = 2.0728 * 10^{-5} \text{ kg CH}_4 / \text{s} - \text{kA}$$

For 1 MW plant $I = \text{Power} / \text{Voltage} = 1000000 / 0.7 = 1429 \text{ kA}$

$$m_{CH_4} = 1429 * 2.0728 * 10^{-5} \quad (\text{or}) \quad m_{H_2} = 1429 * 1.04445 * 10^{-5}$$

Number of cells in a stack

Therefore, for 1 MW,

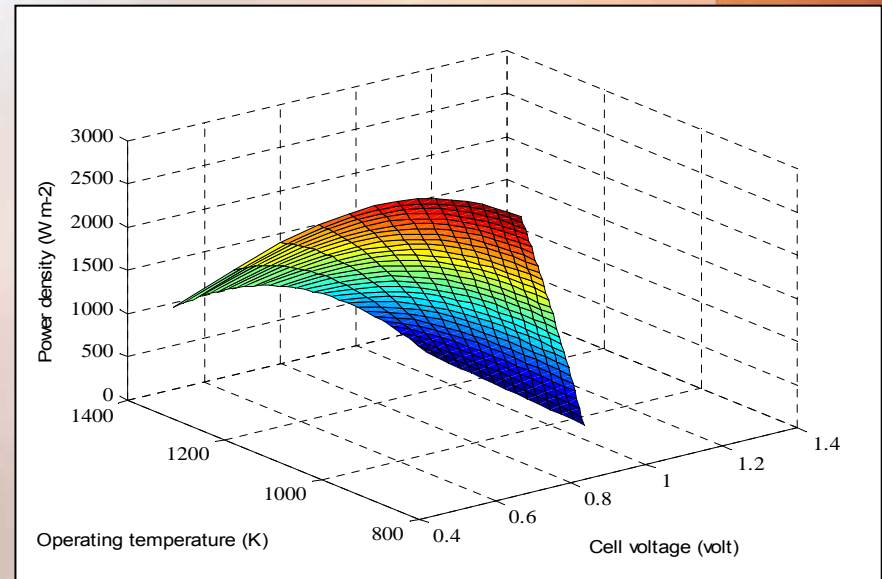
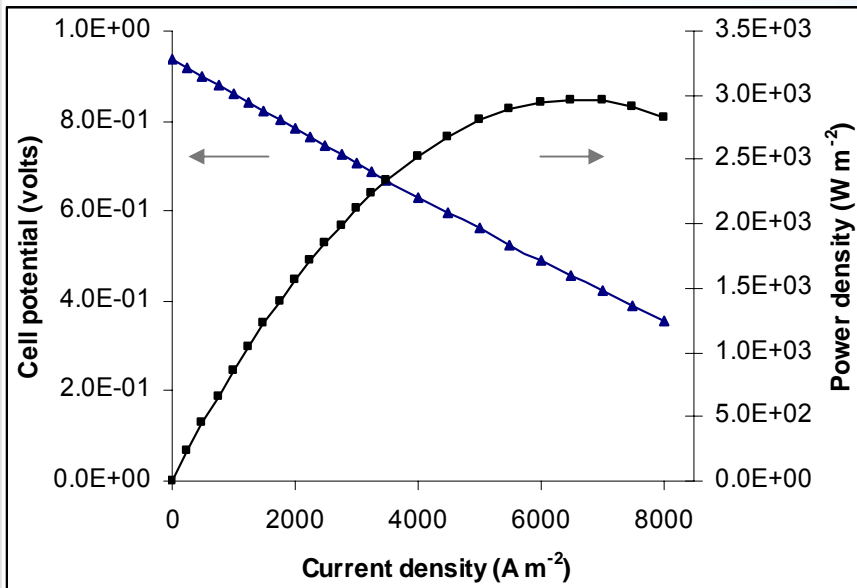
Total current = $1000000 / 0.7 = 1429000$ amps

Required area of the cell = Total current / Current density

No. of cells = required area / area of the individual cell

Performance characteristics of a single Cell

- Maximum power density is obtained at lower cell voltage which results in lower cell efficiency.
- To operate on the left side of the power density peak at a point that yields a compromise between low operating cost (high cell efficiency that occurs at high voltage and low current density) and low capital cost (less cell area that occurs at low cell voltage and high current density)
- Also, compromise should be made between cell voltage and current density.



Downside of the system modeling

- Macroscopic approach is used to understand and study the system's performance but examining/development of the system is not possible.
- Only mass and energy balancing of all the components are considered.
- The individual component's characteristics depends on internal behavior of the process which is totally neglected in system modeling.
- Small losses and variation in the single cell is neglected which will give significant amount when it comes to stack.
- Local variation of operating parameters are neglected which influences the chemical reactions, electrochemical reactions, material morphology and intensity of losses.
- All the reactions are considered as a single stage reactions.

Mechanistic Model – Microscopic approach

- Computational fluid dynamic modeling to predict steady-state cell performance and gas compositions.
- Investigate the influence of cell design, microstructure and operating variables on steady-state cell performance.
- Develop the cell performance map based on operation of H₂ and CO mixtures.

Modeling Tool Requirements

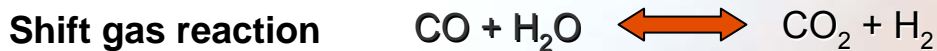
Versatile multi-physics analysis methods

- I. Fuel flows with or without steam
- II. Diffusion through the porous medium
- III. Ionic transport
- IV. Diffusion of oxygen molecule
- V. Air flow

Chemical Reactions



Endothermic

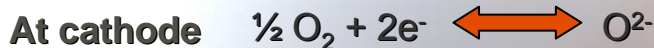


Exothermic or Endothermic

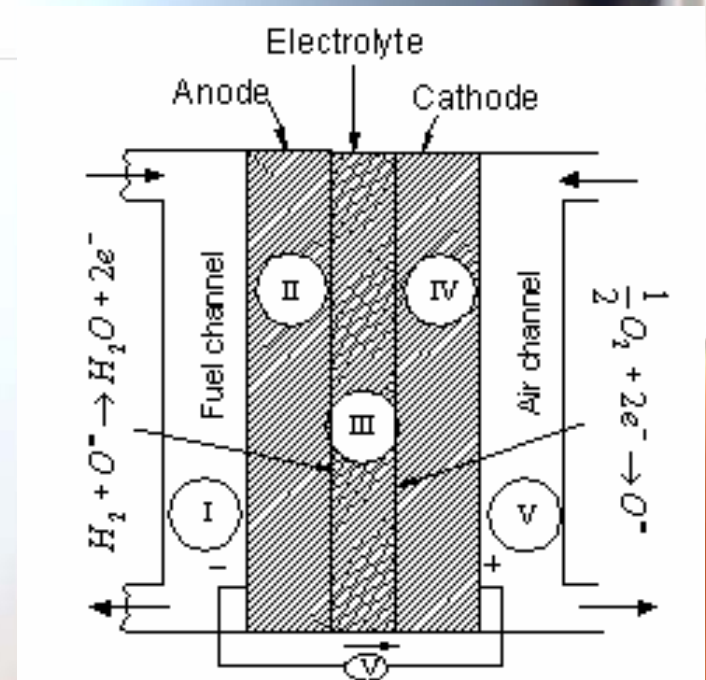
Electrochemical Reactions



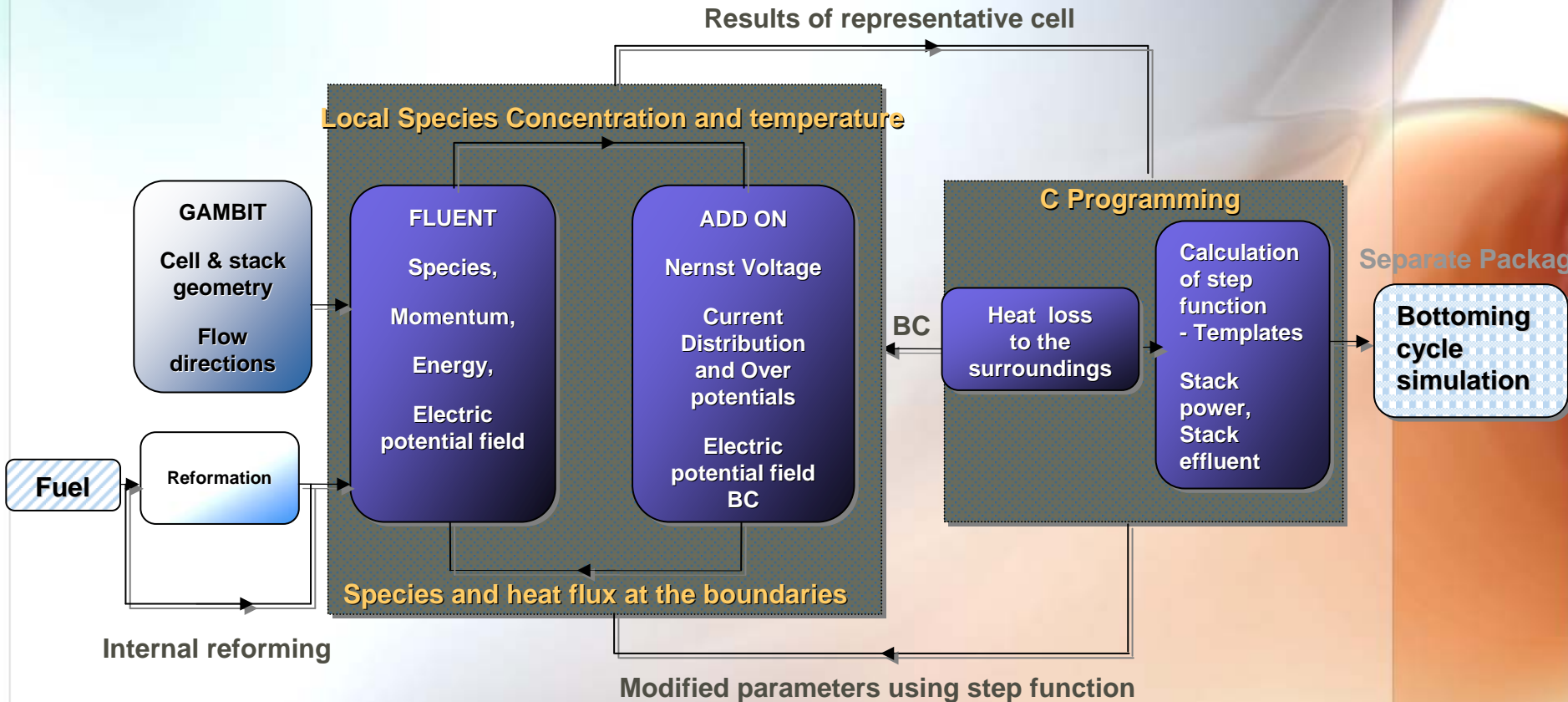
Exothermic



Cell potential should be calculated from these reactions



PROPOSED METHODOLOGY



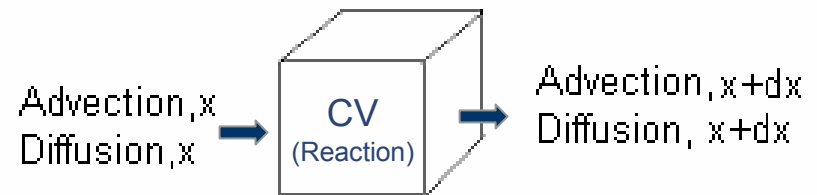
Governing Equations

- Specifics of the gas and temperature flow are very much dependent on geometry
- Regardless of the geometry, governing equations are same

Species Balance Equation

Full species field is obtained by solving species balance equation

$$\frac{\partial(\rho Y_i)}{\partial t} + \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \cdot \vec{j}_i + r_i$$



Chemical reactions

$$r_i = A_i T^{\beta_i} e^{-E_i / RT}$$

(Arrhenius expression)

Electrochemical reactions

$$|r_{H_2}| = 2|r_{O_2}| = \frac{i_{H_2}}{2F}$$

$$|r_{CO}| = 2|r_{O_2}| = \frac{i_{CO}}{2F}$$

(Faraday's Law)

Conversation of Momentum

Essential to model the fluid velocity and species partial pressure

- Gravitational body force is neglected (gases, forced convection, small dimension)
- Net work includes additional sink along with pressure and stress tensors

Newton's Second law

$$\left\{ \begin{array}{l} \text{Net rate of momentum flow =} \\ \text{(viscous, Pressure and Body forces)} \end{array} \right\} \frac{\partial}{\partial t} (\rho \vec{v}) + \nabla (\rho \vec{v} \vec{v}) = -\nabla p + \nabla(\bar{\tau}) + \vec{F}$$

Momentum sink term – Darcy's law

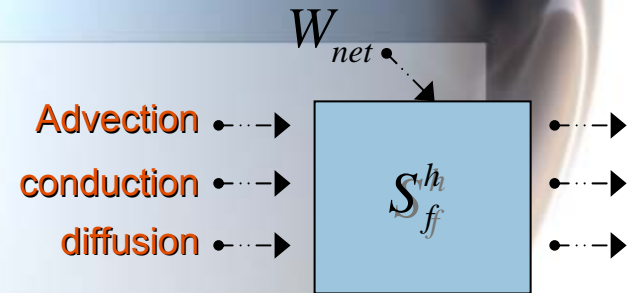
$$F_i = - \left[\sum_{j=1}^3 D_{ij} \mu v_j + \sum_{j=1}^3 C_{2ij} \frac{1}{2} \rho v_{mag} v_j \right] \quad \longrightarrow \quad \text{For Laminar flows} \quad F_i = \frac{\mu}{\alpha_{ij}} v_j$$

(ignoring convective acceleration and diffusion)

$$\text{Stress tensor} \quad \bar{\tau} = \mu \left[\nabla \vec{v} + \nabla \vec{v}^T \right] - \frac{2}{3} \nabla \cdot \vec{v} I$$

Energy Equation

Porosity weighted composite of solid and fluid phase



$$\frac{\partial}{\partial t} (\varepsilon \rho_f E_f + (1 - \varepsilon) \rho_s E_s) + \nabla \cdot (\bar{v} (\rho_f E_f + P)) = \nabla \cdot \left(k_{eff} \Delta T - \left(\sum_j h_j \bar{J}_j \right) \right) + S_f^h$$

➤ Conduction flux uses effective conductivity $k_{eff} = \varepsilon k_f + (1 - \varepsilon) k_s$

➤ Transient term includes the thermal inertia of the solid region

➤ Inclusion of species transport in energy equation $\nabla \cdot \left[\sum_j^n h_j \bar{J}_j \right]$

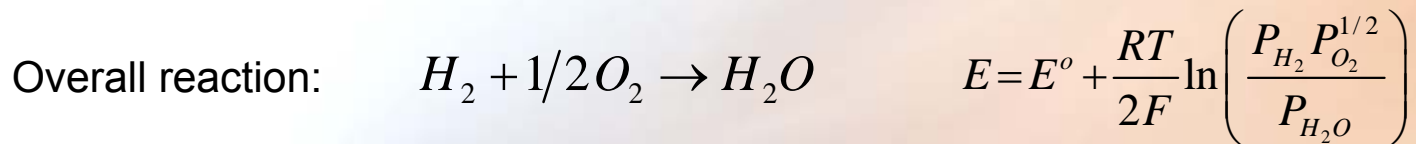
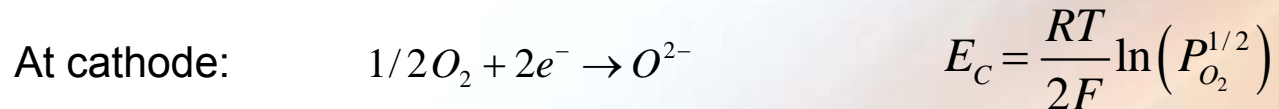
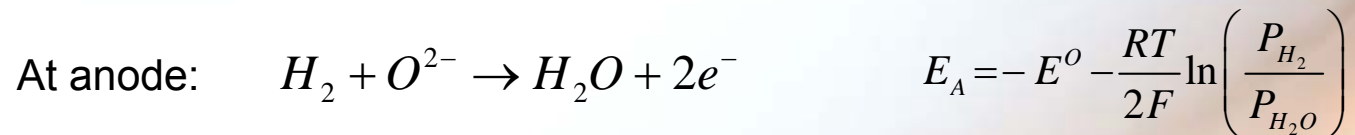
(enthalpy due to species diffusion, not neglected in case of Lewis Number $\ll 1$)

➤ Source term contributions (S_f^h) - Heat of chemical reactions and other volumetric sources

Modeling of Electrochemistry

Conventional approach

- Gibbs free energy that results from the overall reaction is arbitrarily assigned to the E/A interface only
- The oxide ion concentration at either of the interfaces is not accounted



Actual cell voltage: $E_{actual} = \left(E_C - |\eta_{cathode}| \right) - \left(E_A + |\eta_{anode}| \right) - iR$

Multistage Mechanism

- Split the Gibbs free energy into two parts one for the overall reaction occurring at the C/E interface, and one for those occurring at the E/A interface.
- Ionic concentration also measured experimentally using electronics impedance spectroscopy
- Losses are accounted locally i.e. post subtraction is avoided

Beberle reaction kinetics

$$\Delta G_{C/E}^o = -RT \ln(K)$$

$$\text{Where } K = \left(\frac{k_f}{k_b} \right)$$

$$-\Delta G^o = nFE^o$$

$$E_{A/E}^o = E^o - E_{C/E}^o$$

Reaction rate constants estimated from surface science literature data for $T=973$ K

Reaction	k_f	k_f [s^{-1}]	Parameters
$H_2(g) + 2ad \leftrightarrow 2H_{ad}$	k_1	10^7	$s_0(H_2) = 0.2$
	k_{-1}	2×10^8	$v = 2.5 \times 10^{13} s^{-1};$ $E = 96 \text{ kJ/mol}$
$H_2O(g) + ad \leftrightarrow H_2O_{ad}$	k_2	6×10^6	$s_0(H_2O) = 1$
	k_{-2}	2×10^{13}	$v = 10^{16} s^{-1}; E = 52 \text{ kJ/mol}$
		8×10^{10}	$v = 10^{13} s^{-1}; E = 39 \text{ kJ/mol}$
		2.5×10^9	$v = 10^{13} s^{-1}; E = 67 \text{ kJ/mol}$
		10^{11}	$v = 10^{13} s^{-1}; E = 38 \text{ kJ/mol}$
$O_{ad} + H_{ad} \leftrightarrow OH_{ad} + ad$	k_3	2×10^{11}	$v = 10^{13} s^{-1}; E = 33.7 \text{ kJ/mol}$
	k_{-3}	4×10^2	$v = 10^{13} s^{-1}; E = 193 \text{ kJ/mol}$
		4×10^1	$v = 10^{13} s^{-1}; E = 212 \text{ kJ/mol}$
$H_2O_{ad} + O_{ad} + ad \leftrightarrow 2OH_{ad}$	k_4	10^{12}	$v = 10^{13} s^{-1}; E = 17 \text{ kJ/mol}$
		4.5×10^6	$v = 10^{13} s^{-1}; E = 118 \text{ kJ/mol}$
	k_{-4}	2×10^2	$v = 10^{13} s^{-1}; E = 201 \text{ kJ/mol}$
		3×10^{10}	$v = 10^{13} s^{-1}; E = 48 \text{ kJ/mol}$
$H_2O_{ad} + ad \leftrightarrow OH_{ad} + H_{ad}$	k_5	6×10^5	$v = 10^{13} s^{-1}; E = 134 \text{ kJ/mol}$
		3×10^7	$v = 10^{13} s^{-1}; E = 102 \text{ kJ/mol}$
	k_{-5}	1.5	$v = 10^{13} s^{-1}; E = 239 \text{ kJ/mol}$
		10^{12}	$v = 10^{13} s^{-1}; E = 17 \text{ kJ/mol}$
$O_x^o + ad \leftrightarrow O_{ad} + V_O^o + 2e^-$	k_6	5×10^2	$i_0 = 0.042 \text{ A/cm}^2; R_t = 1 \Omega$
		8×10^{-6}	—
	k_{-6}	3×10^4	$i_0 = 0.042 \text{ A/cm}^2; R_t = 1 \Omega$
		3×10^{-4}	—

Local Cell Potential

Cathode - Electrolyte interface $1/2 O_2 + 2e^- \rightarrow O^-$

$$\Delta E_{PT,C/E} = E_{C/E}^o + \frac{RT}{2F} \ln \left(\frac{P_{O_2}^{1/2}}{P_{O^-}} \right) - \eta_C - IR_C$$

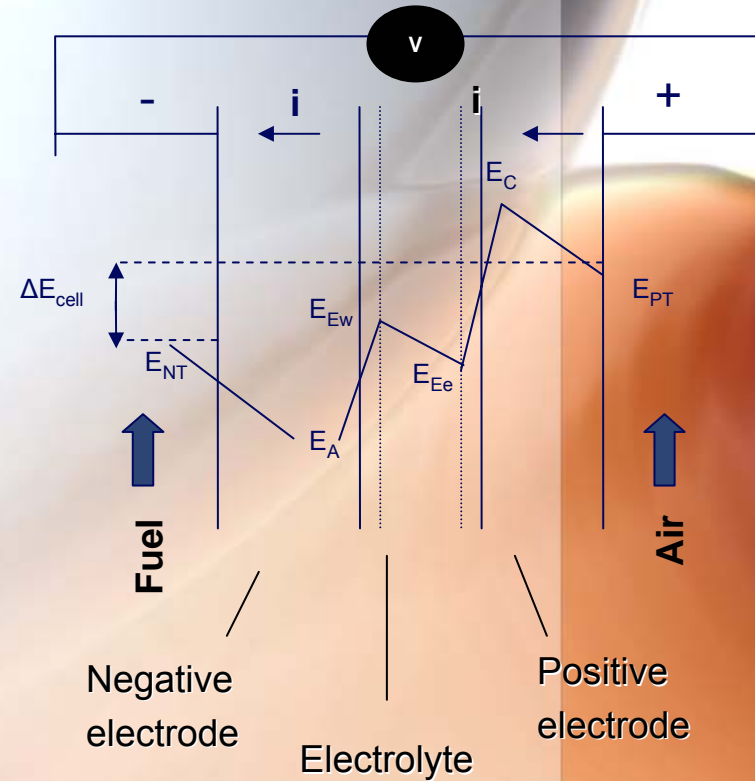
Anode - Electrolyte interface $H_2 + O^- \rightarrow H_2O + 2e^-$

$$\Delta E_{NT,A/E} = E_{A/E}^o + \frac{RT}{2F} \ln \left(\frac{P_{H_2} P_{O^-}}{P_{H_2O}} \right) - \eta_A - IR_A$$

Cell potential across PEN

$$\Delta E_{cell} = \left(E_{C/E}^o + \frac{RT}{2F} \ln \left(\frac{P_{O_2}^{1/2}}{P_{O^-}} \right) - \eta_C - IR_C \right) + \left(E_{A/E}^o + \frac{RT}{2F} \ln \left(\frac{P_{H_2} P_{O^-}}{P_{H_2O}} \right) - \eta_A - IR_A \right) - IR_{ele}$$

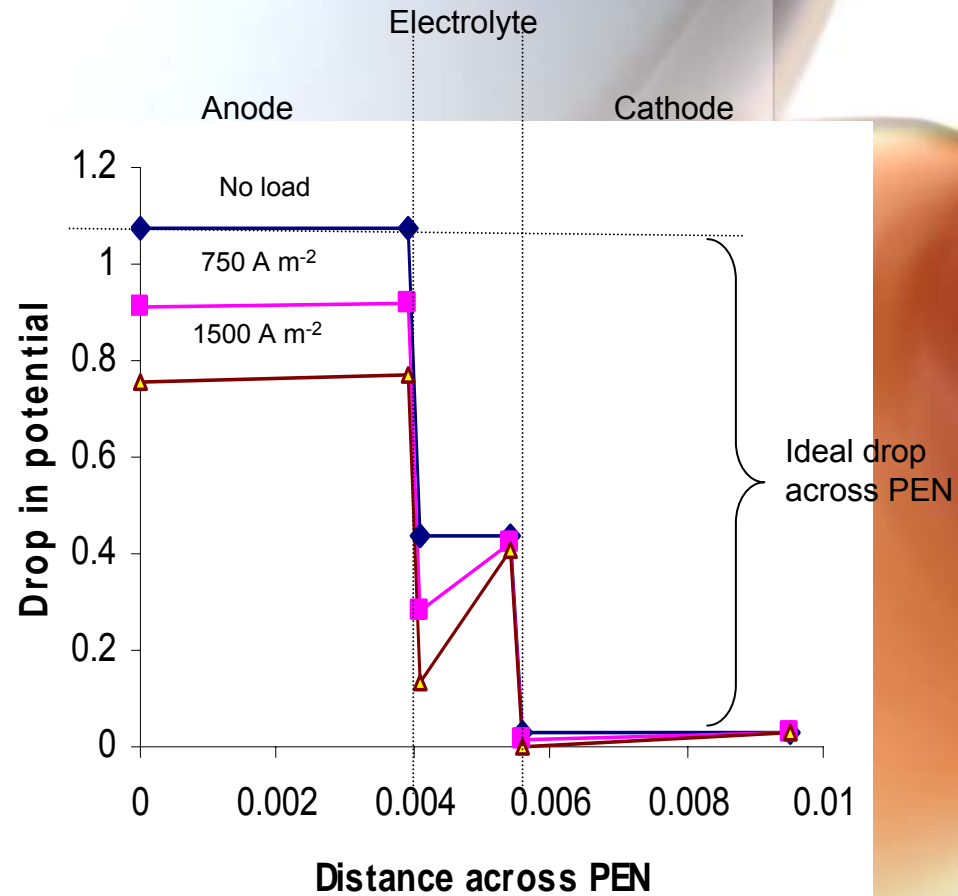
Variation of electric Potential across PEN



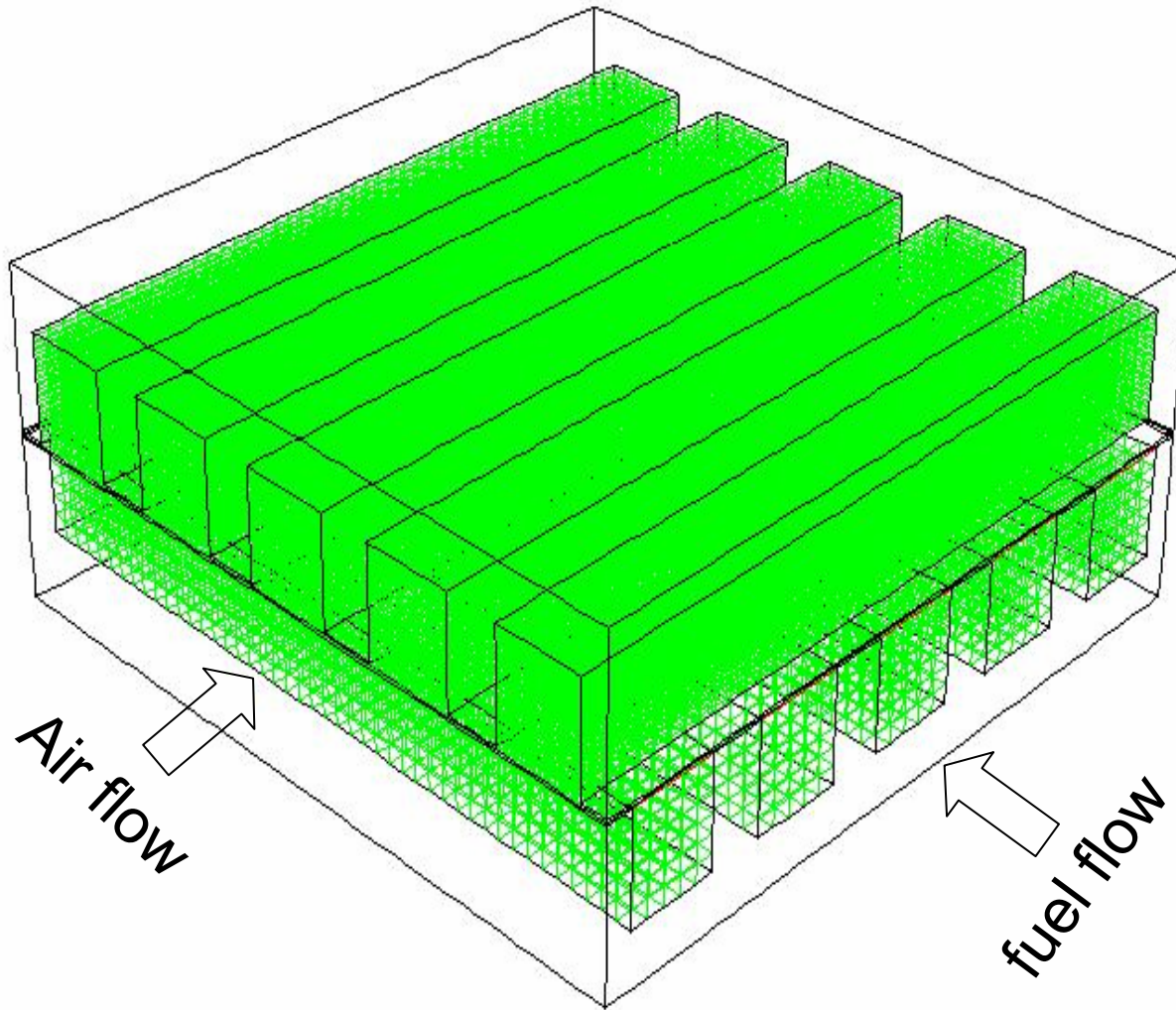
Potential Across PEN Structure

Conservation of charge: $\nabla(\sigma \nabla E) = s$

- 1D result for local potential across PEN structure
- Reaction rates are adapted from surface science literature
- Distance in 10^{-1} meters and potential in volts
- Potential difference is plotted for no load, 750 A m^{-2} and 1500 A m^{-2}
- Losses are accounted locally



16 mm SOFC with 5 air and 5 fuel channels of 2 mm X 2 mm cross section



Cell material (LSM-YSZ / YSZ / Ni-YSZ)

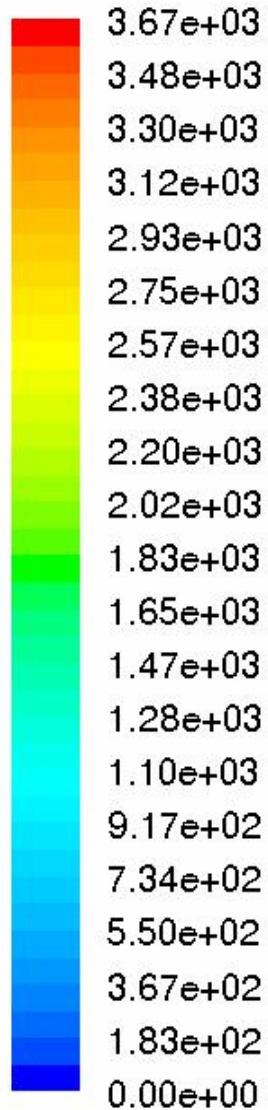
- Cross flow configuration,
- Electrolyte supported cell,
- Externally reformed fuel (H₂O, CO & H₂)
- Operated at 1273 K, 1 atm
- 0.512 amps cell load for examination

Current Density at wall electrolyte - cathode side

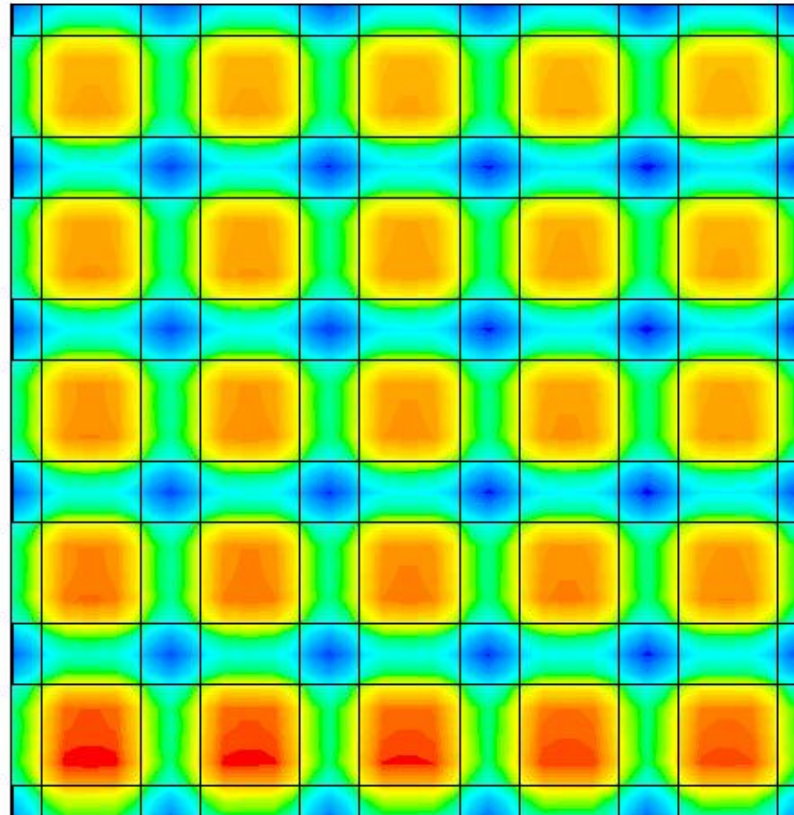
(Neglecting CO electrochemical reaction as in the literatures)

Anode side – 2.4358×10^{-6} kg/s, 0.51/0.31/0.17 ($H_2/H_2O/CO$)

cathode side – 2.653207×10^{-5} kg/s, 0.78/0.22 (O_2/H_2O)



Air flow →



Y
Z—X

↑
fuel flow

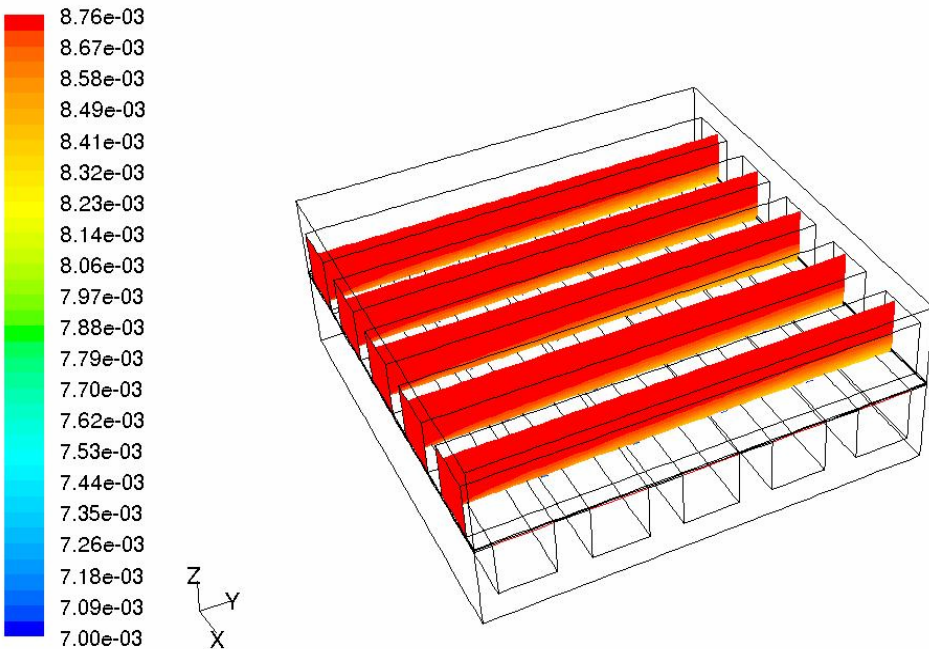
Porous media :

Permeability – 5.6818×10^{-10}

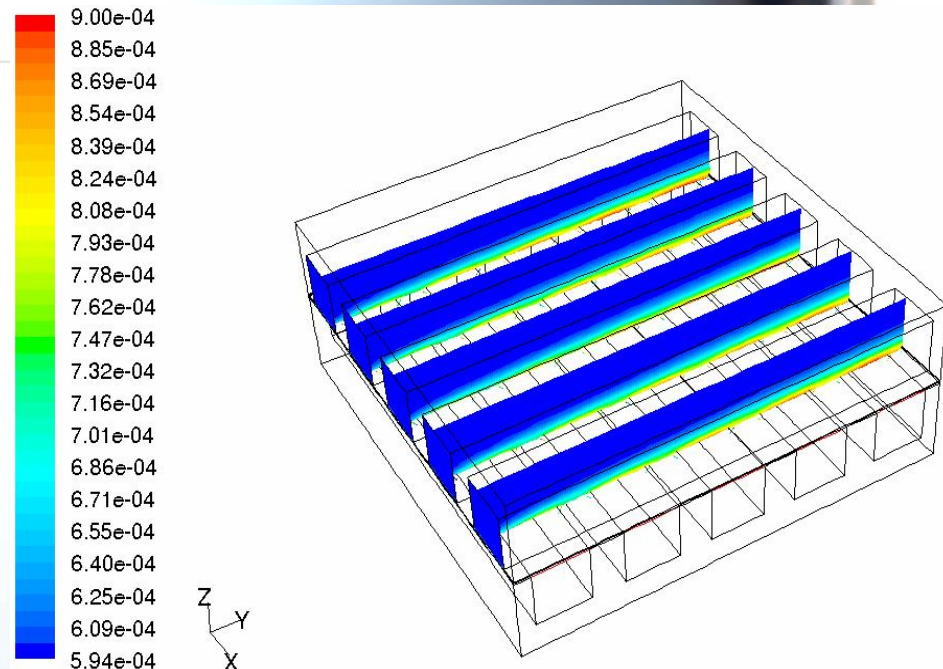
Porosity – 0.5

fuel flow

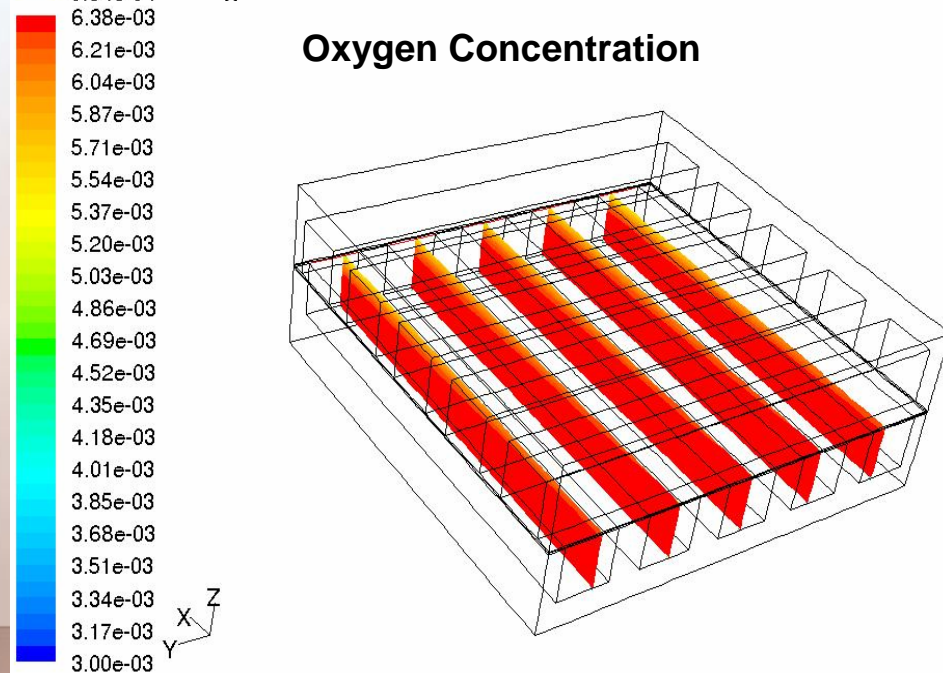
Hydrogen Concentration



Steam Concentration



Oxygen Concentration



**Species
Concentrations
along the channels**

Actual Cell Potential

$$\text{Actual cell potential } (V_{\text{actual}}) = \text{Ideal cell potential } (E) - \{ \text{Activation polarization} + \text{Ohmic polarization} + \text{Concentration polarization} \}$$

Ideal cell potential - (*Nernst* Expression)

Activation over potential – Flow of ions should overcome the electronic barrier.

Ohmic over potential – Resistance offered by the total cell components to the flow.

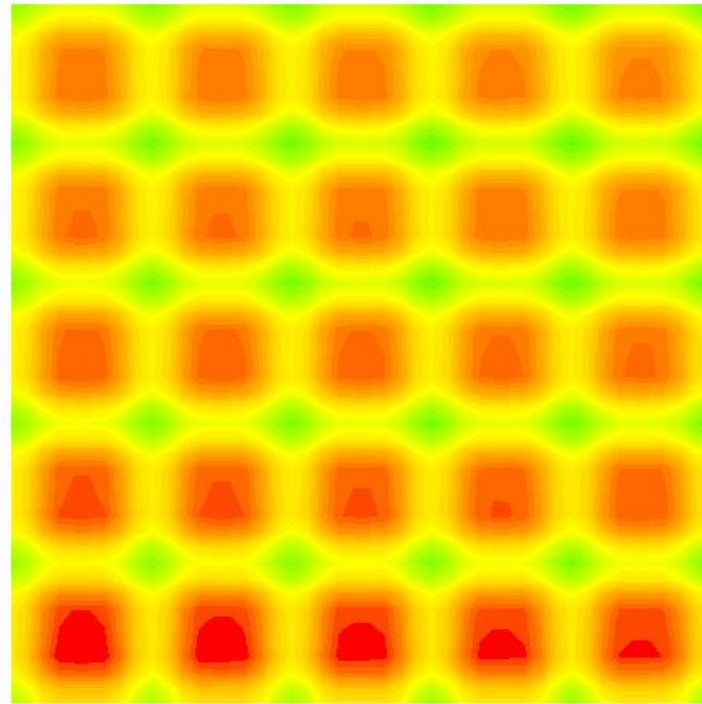
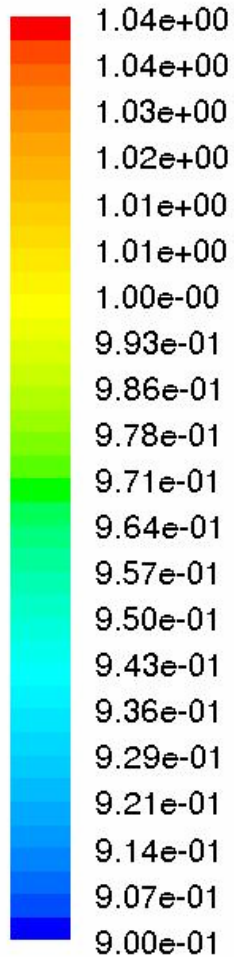
Concentration over potential - Gas transport losses, dilution of fuel as the reactions progress.

Ideal cell potential

Ideal cell voltage at wall electrolyte anode – 0.512 amps load

$$E = E^0 + \frac{RT}{nF} \ln \frac{\prod [\text{reactant activity}]}{\prod [\text{product activity}]}$$

(Neglecting CO electrochemical reaction)

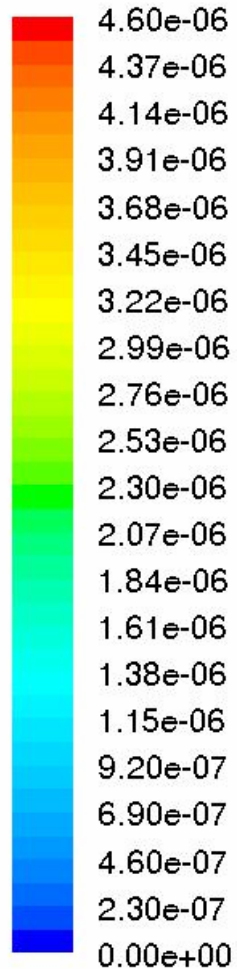


fuel flow

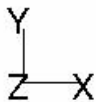
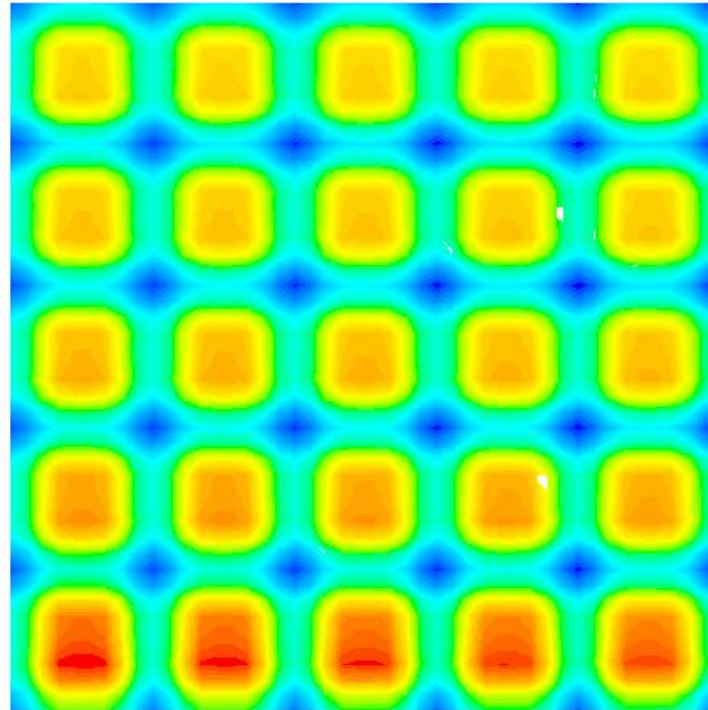
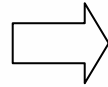
Activation over potential

Buttlet Volmer Equation

$$i = i_0 \left\{ e^{(1-\beta)nF\eta_{act}/RT} - e^{-\beta nF\eta_{act}/RT} \right\}$$



Air flow



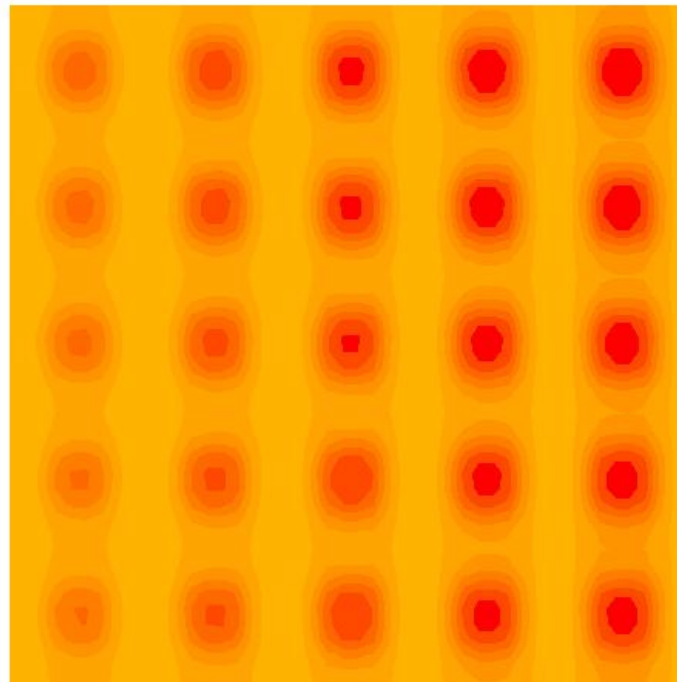
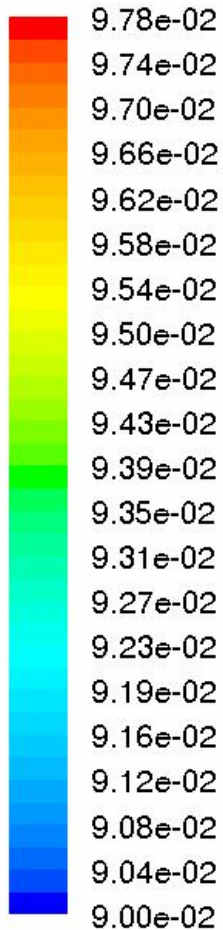
fuel flow

Ohmic over potential

Resistance to the flow of ions in the electrolyte material

$$\eta_{Ohmic} = iR^{eff}$$

R^{eff} - effective ionic resistance



Electrolyte resistivity in (ohm-m)

- Fig. shows that the resistivity of electrolyte only.
- As the temperature increases resistivity of the electrolyte decreases hence hot spots are visible with less resistivity and relatively cold spots are little more.
- Effective resistance for calculating ohmic polarization will be the summation of all material resistances

Concentration over potential

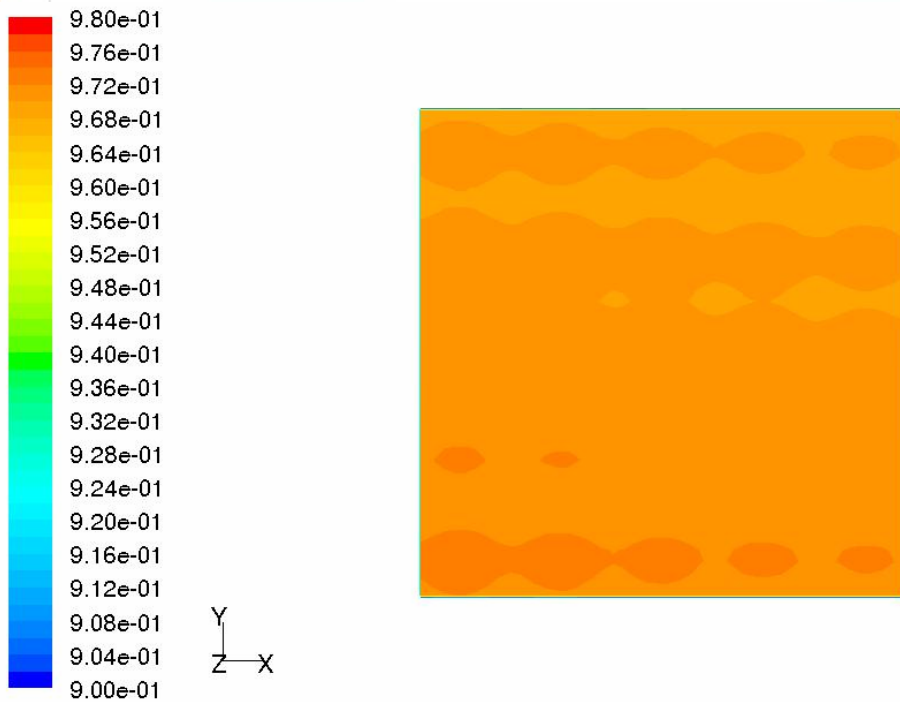
Gas transport losses, dilution of fuel as the reactions progress.

- Not considered separately
- It is accounted by considering local species concentration while calculating Nernst potential instead of considering species concentration at the inlet

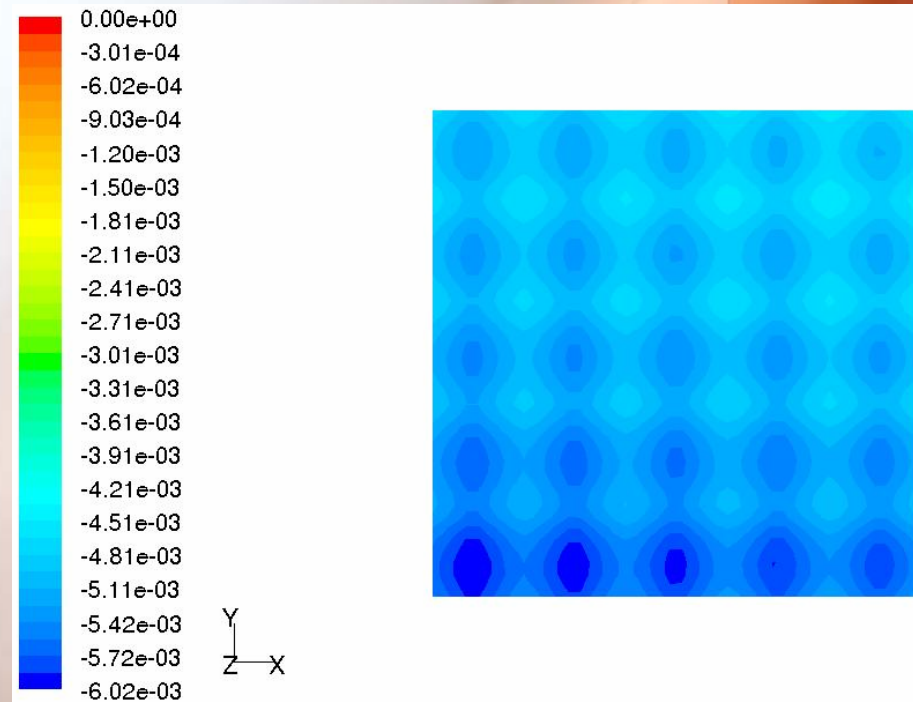
Actual cell potential

$$V_{cell} = E_{cathode} - |\eta_{cathode}| - [E_{anode} + |\eta_{anode}|] - \eta_{Ohmic}$$

Actual cell potential at anode



Actual cell potential at cathode



Few outcomes from the model

Findings

Cell is examined with two different permeability

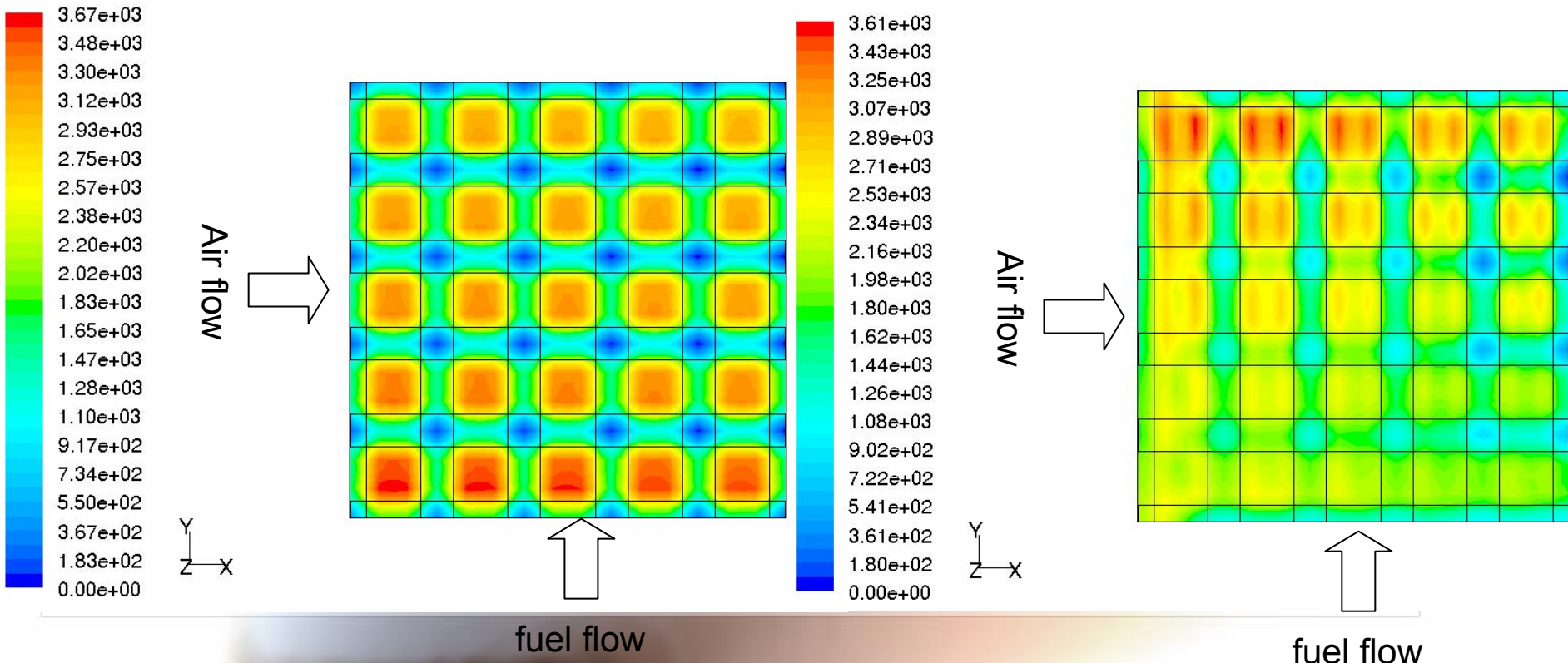
a) $5.68184e+10$ (Viscous resistance) from the literatures: b) $1e+13$ (Viscous resistivity) material manufacturers

Inference

- a) cell operation is not limited by mass transfer at any location of the cell. However, at lower cell voltages, it is seen that the current density is decreasing in the flow direction.
- b) Cell operation is limited by the low diffusivity of species at the inlet conditions

Result:

Interestingly both the cases will give the same over all output



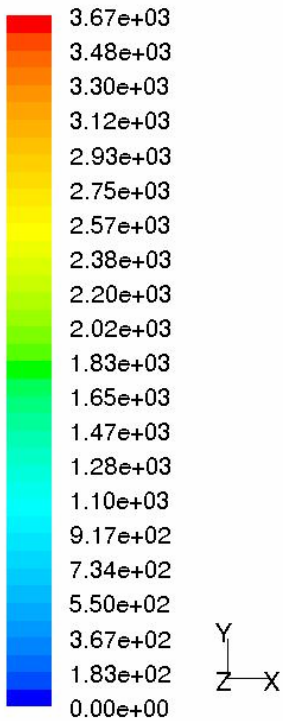
Findings...

1. Overall reaction: $H_2 + 1/2 O_2 \rightarrow H_2O$

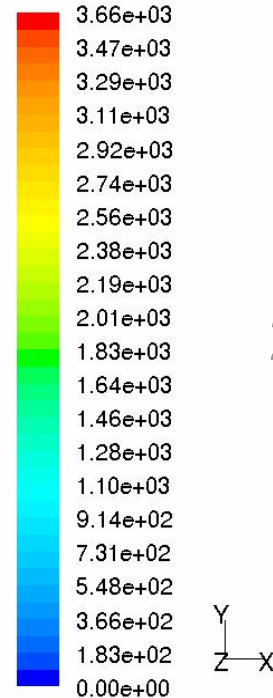
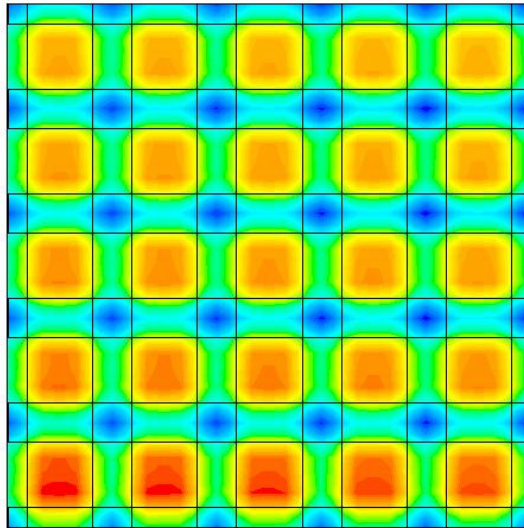
$$E = E^o + \frac{RT}{2F} \ln \left(\frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \right)$$

Neglecting CO electrochemical reaction

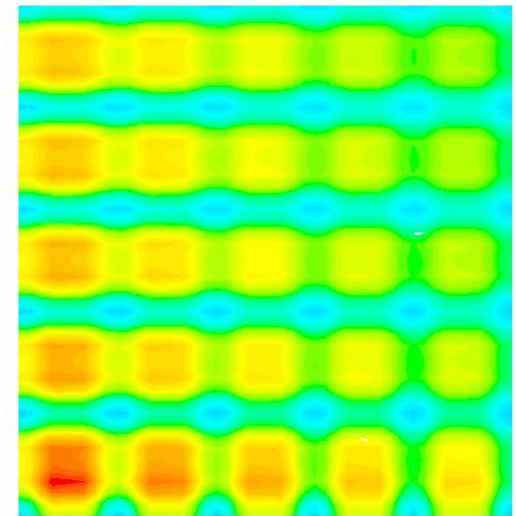
2. Both electrochemical Reactions are considered



1



2



Findings

- Hydrogen diffuses more faster than oxygen in the porous electrodes, so the rate limiting issue for the whole processes will be the diffusivity of oxygen in the porous cathode.
- If the porosity of the cathode is much higher than the anode then the process is governed by the ionic conductivity of the electrolyte.
- High current density increases ohmic losses leading to higher thermal gradients. This may In turn lead to mismatching of the assembly because of various coefficients of thermal expansion

"A painless tomorrow's energy"



Thankyou

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