Model Development and Validation of Solid Oxide Fuel Cells (SOFCs) Using H_2-H_2O-CO-CO_2 Mixtures: From Button Cell Experiments to Tubular and Planar Cells

By
Rapeepong Suwanwarangkul

Supervisors : Professors E. Croiset, M. Fowler & P. Douglas
Collaborator : Dr. Evgueniy Entchev, CANMET

Department of Chemical Engineering
University of Waterloo

Outline

- Introduction
- General Approach of Mechanistic Modelling
- Experiments & Model:
  - Button Cell
- Simulation:
  - Cathode-Supported Tubular SOFCs (TSOFCs)
  - Anode-Supported Planar SOFCs (PSOFCs)
- Conclusions & Recommendations

Why SOFC?

- High system efficiency
- Low emissions
- Manufactured with Low Cost Materials
- Accommodate synthesis gas (H_2/CO)

- Little research involving synthesis gas
  - Past studies were essentially experimental research.
  - Very few modelling works have focused on synthesis gas.

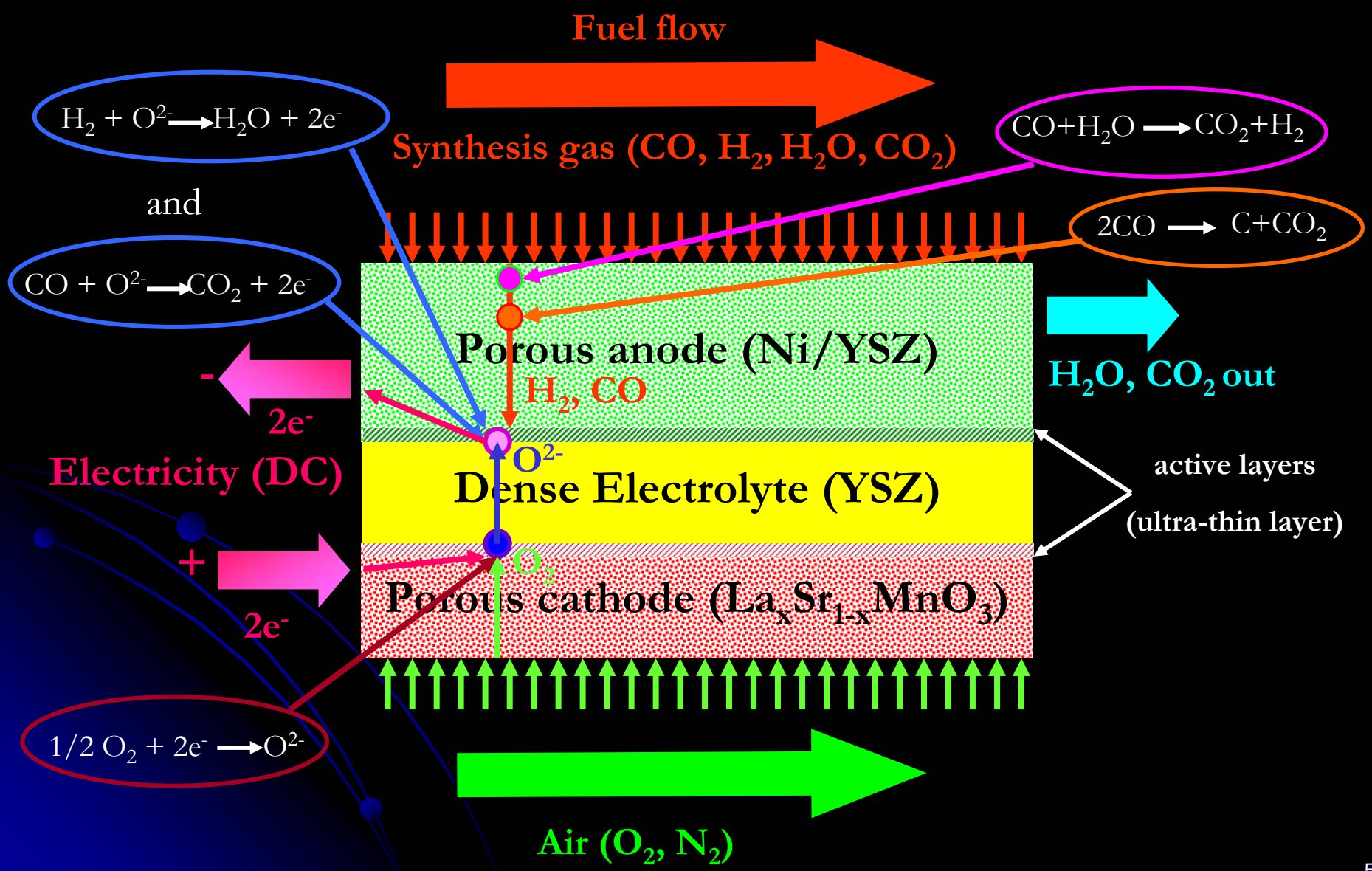
Objectives

- Develop and validate a steady-state mechanistic model for a single cell SOFC operating with mixtures of H_2, CO, CO_2, H_2O and N_2.

- Gain insight into the fundamental physics of momentum, heat, mass and charge transport in various SOFC designs.

- Investigate the impact of temperature, pressure, flow rate and mixture compositions on SOFC performance, fuel and air utilization factors, exit gas compositions and cell temperature.

SOFC Operation



General Approach of Mechanistic Modelling

Electrochemical reactions
H_2 & CO oxidation at anode
O_2 reduction at cathode

Energy transport
Heat conduction, convection & radiation
Heat consumption/generation by chemical & electrochemical reactions

Chemical reactions
Water-gas shift reaction
Carbon formation

Mechanistic Model

Mass transport
Mass diffusion and convection
Mass consumption/generation by chemical & electrochemical reactions

Momentum transport
Navier-Stokes equation

Charge transport
Ion transport
Electron transport

Current density distribution
Flow & pressure distribution
Cell performance
Species concentration distributions
Temperature distribution
Exit gas compositions

Button Cell Experiments & Model

- Performed at MTEC, Thailand.
- Electrolyte-supported cells (ESCs) from InDEC Co.

Cell specifications:

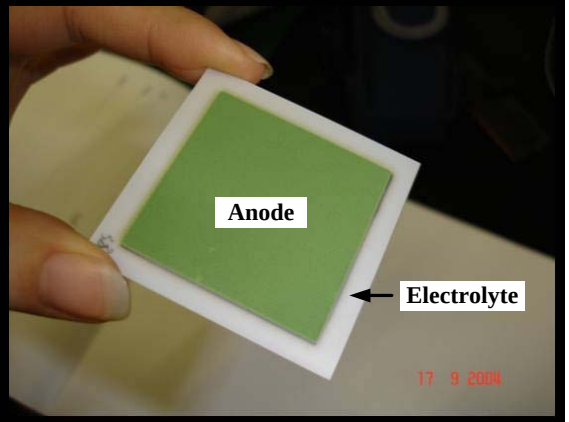
60 μm Ni-CeO_2-YSZ anode

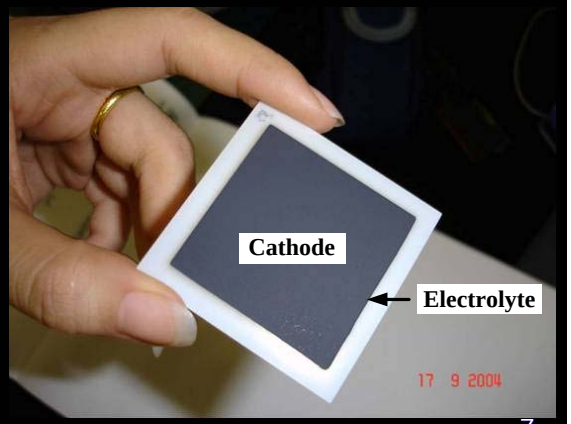
50 μm $La_{0.7}Sr_{0.2}MnO_{3-\delta}$ (LSM) anode

130 μm 3 mol% YSZ (TZ3Y) electrolyte

16 cm^2 active area

Electrochemical cell

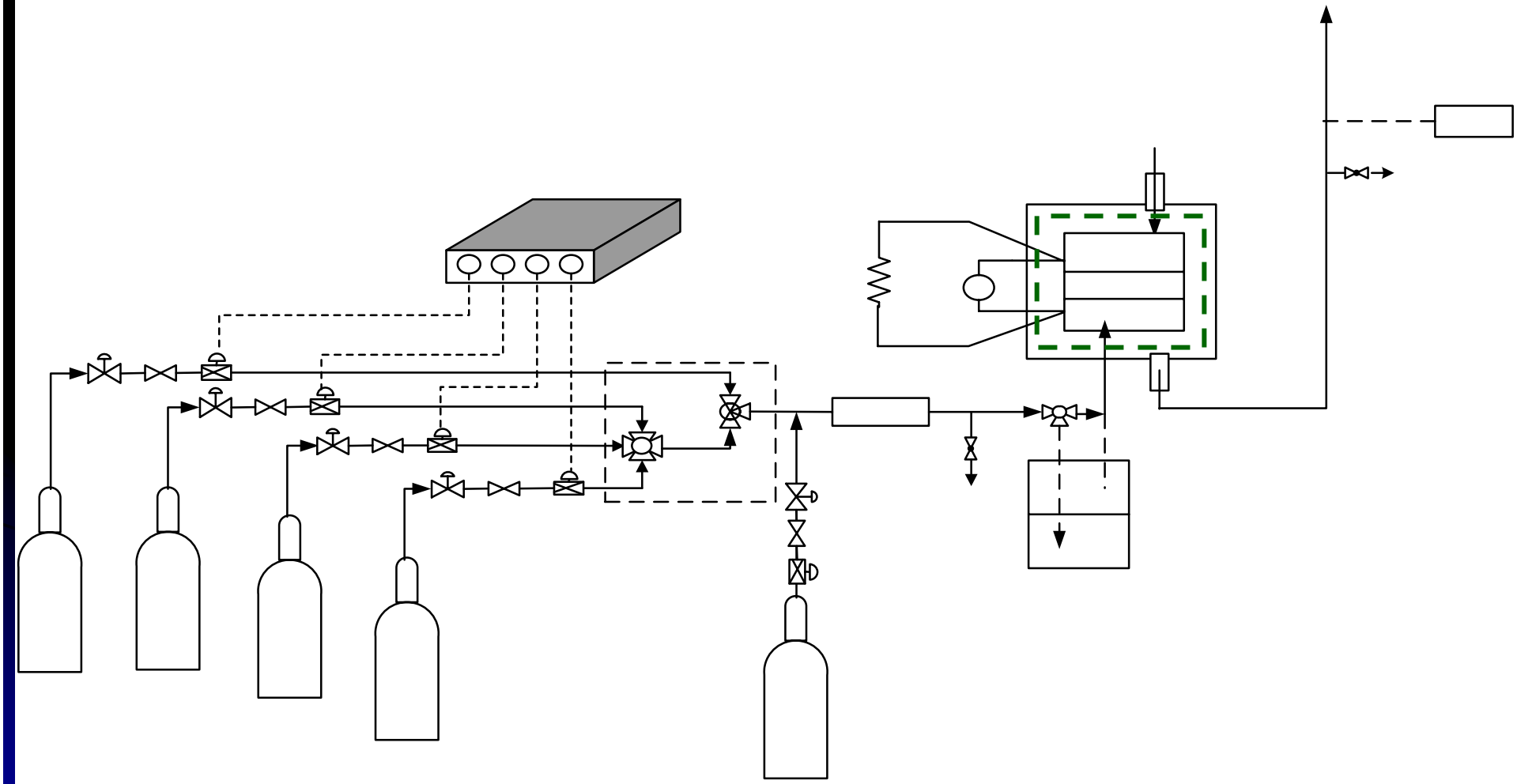




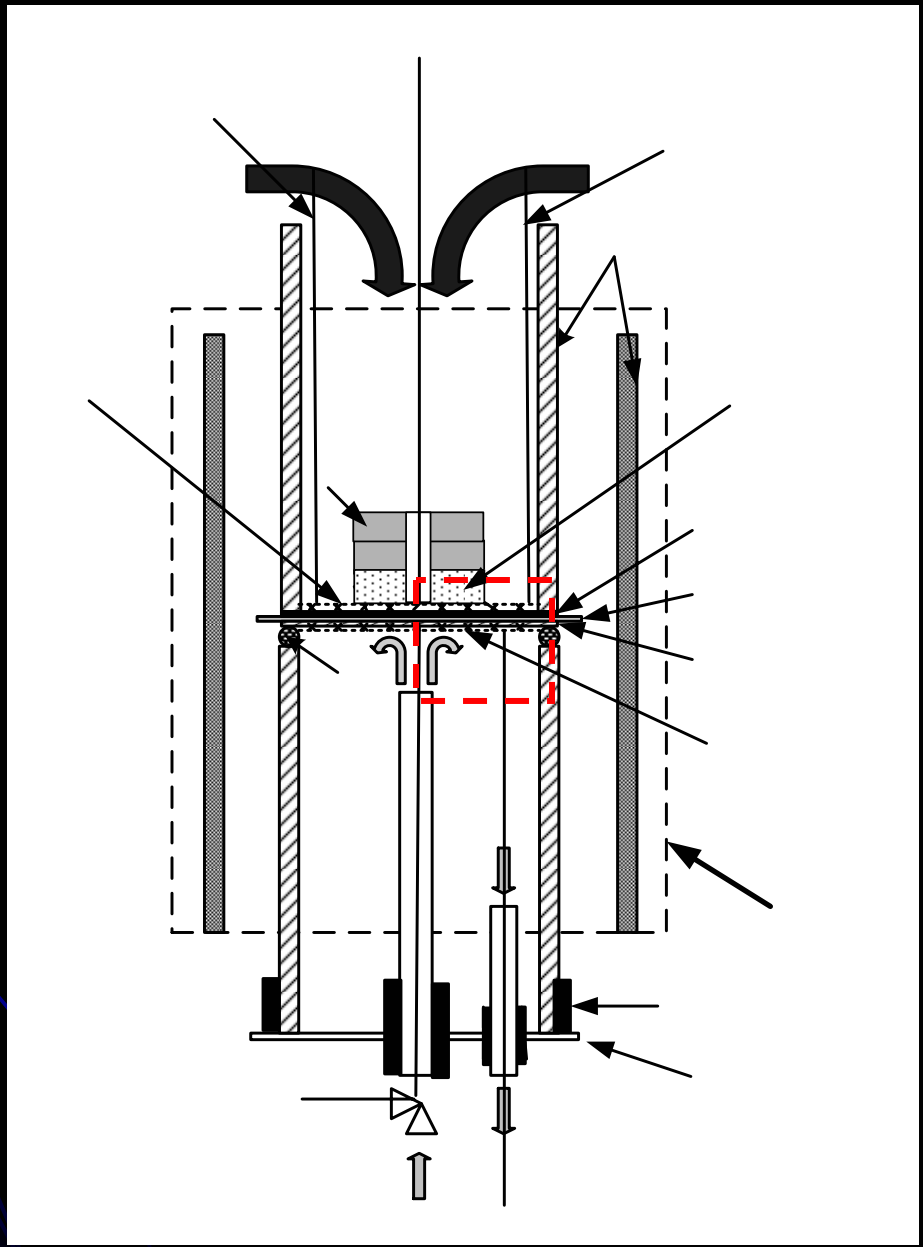
- Experimental objective: study the effects of
  - N_2 dilution
  - CO_2 dilution
  - H_2+CO mixtures
  - Simulated synthesis gases

On the cell performance at 800°C and 900 °C

Experimental Setup



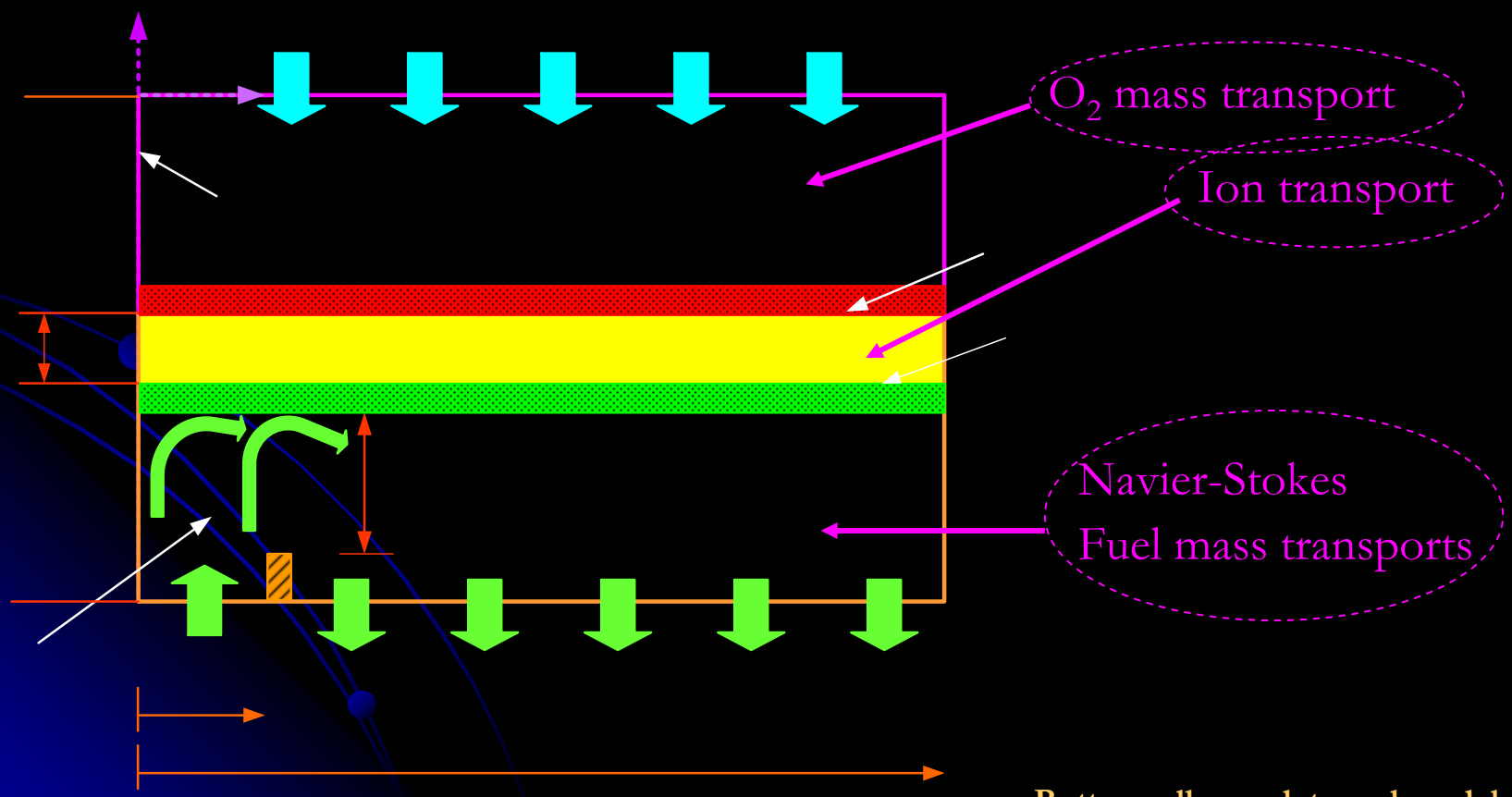
Cell Setup



Button Cell Mathematical Model

Assumptions

- Negligible mass-transport and ohmic resistances within the porous electrodes.
- Uniform temperature and gas density.
- Occurrence of electrochemical reactions and the WGSR at electrode/electrolyte interfaces.



Algorithm for Model Calibration

- Determination of contact resistances ($R_{Contact}$) between current collectors and electrodes that make the model fits the experimental values.

<u>From the model :</u> specified cell potential (V_{cell}) to calculate the average current density

$$J_{\text{avg}} = 2r_b^{-2}\int_0^{rb} r\left(J_{H_2} + J_{CO}\right)\Big|_{z=z_{An}} dr$$

Actual cell potential delivered to the load ($V_{delivered}$) was estimated as:

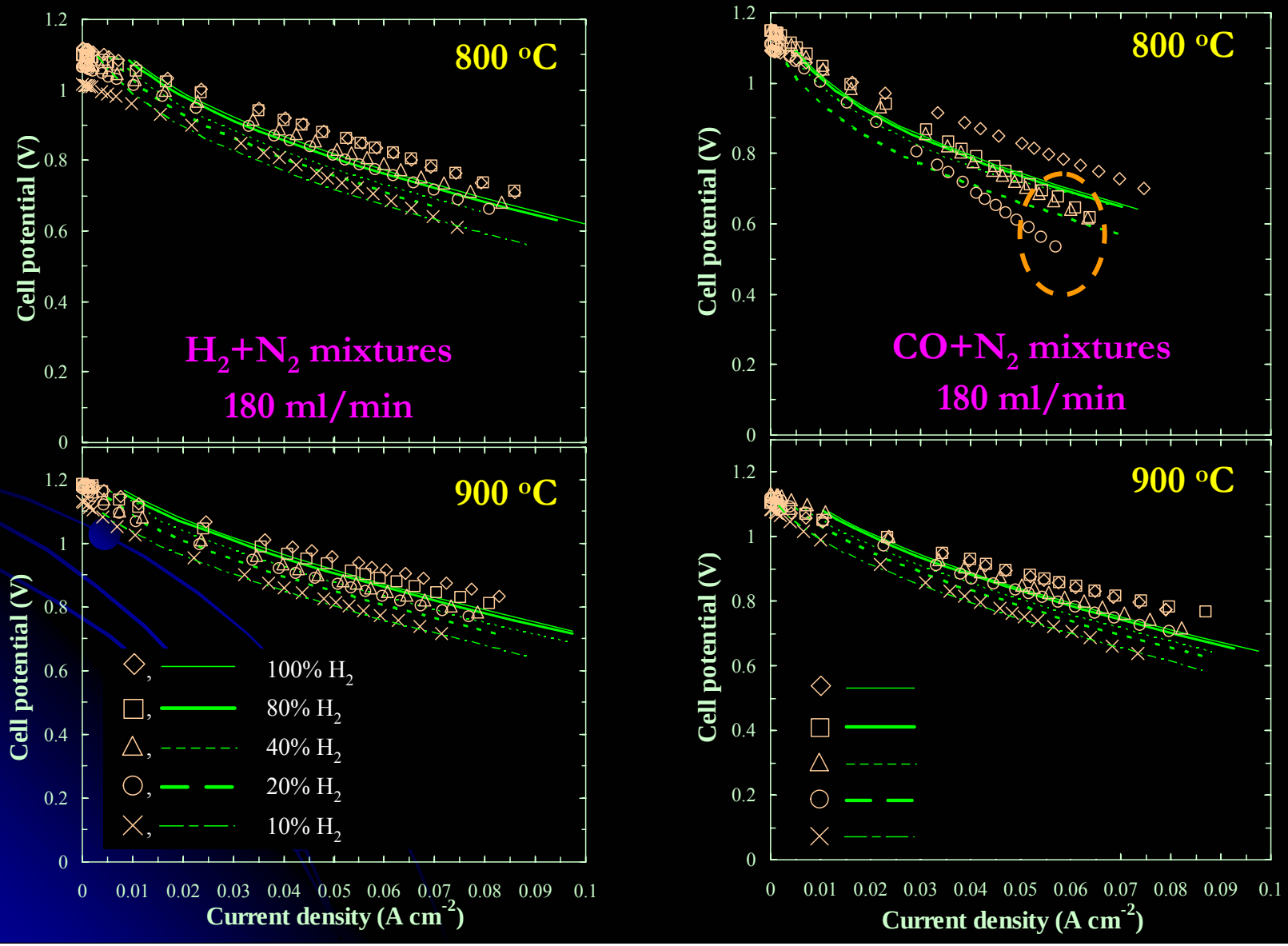
$$V_{delivered} = V_{cell} - J_{avg} \times R_{Contact}$$

- $R_{Contact}$ was determined by calibrating the model against experimental data using humidified H_2 as the fuel source for cell operating at 800°C and 900°C.

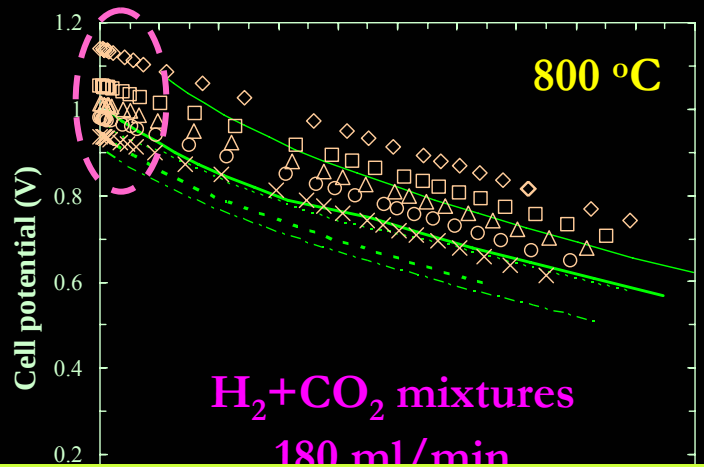
- Then, $R_{Contact}$ obtained from humidified H_2 was used for the entire experimental investigation of the effect of syngas compositions at each cell operating temperature.

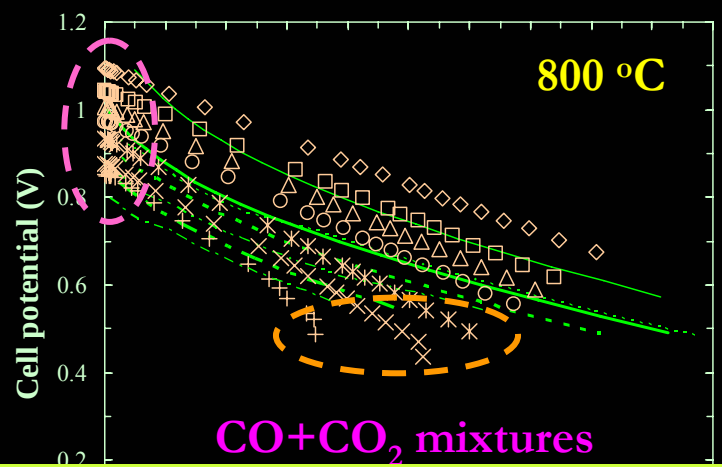
- $R_{Contact}$ at 800°C and 900°C were estimated to be 1.6 Ω cm^2 and 1.2 Ω cm^2, respectively.

Exp. & Model Results for N_2 Dilution

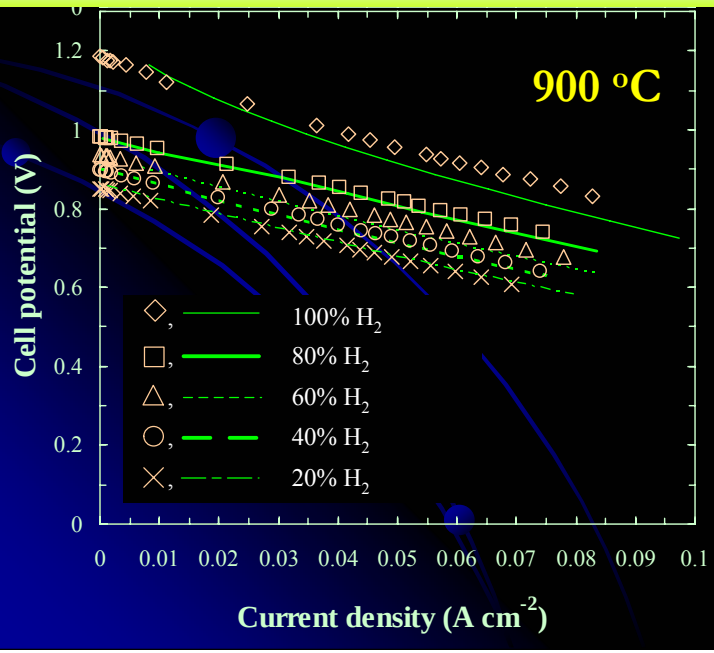


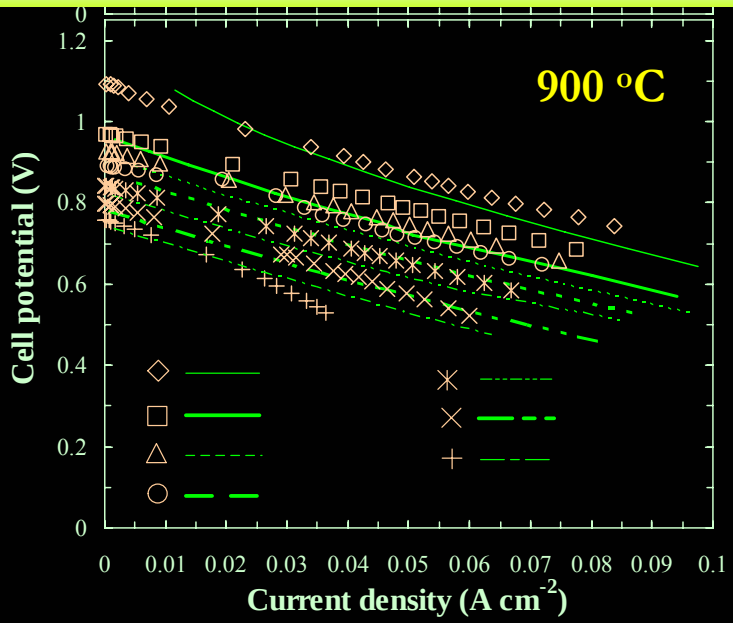
Exp. & Model Results for CO_2 Dilution





Effect of CO_2 dilution on the cell performance is more pronounced than that of N_2 dilution

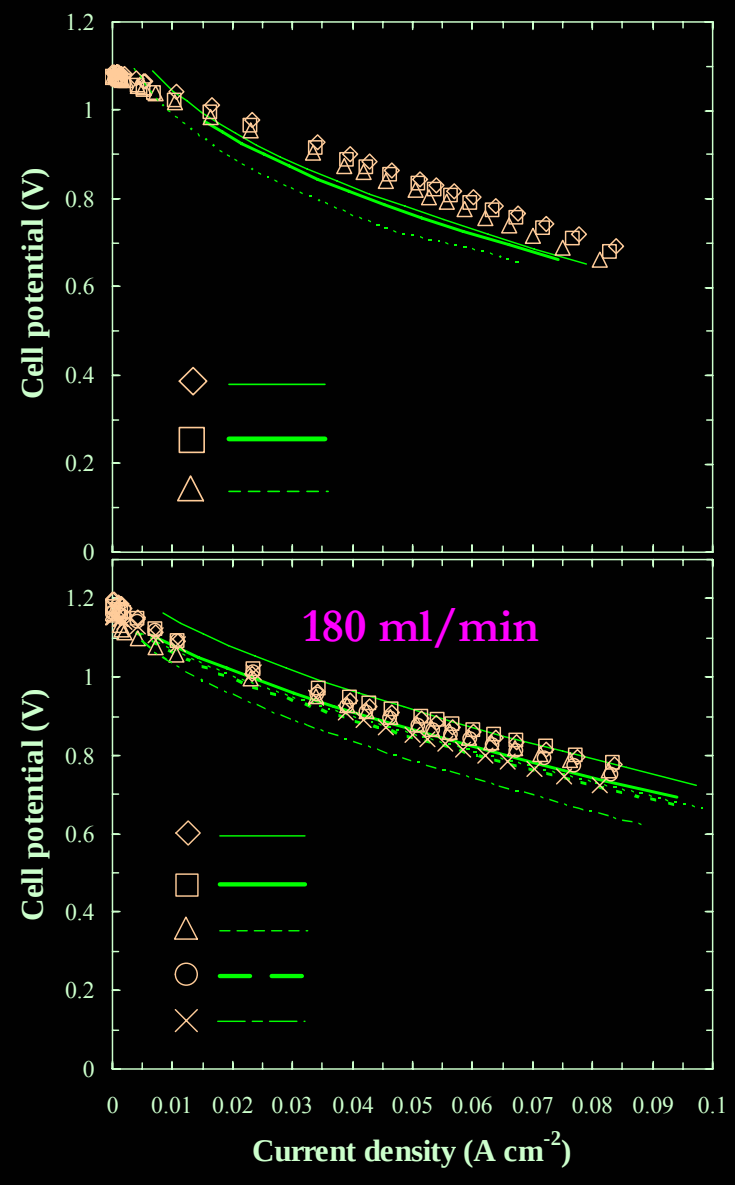




Exp. & Model Results for H_2+CO Mixtures

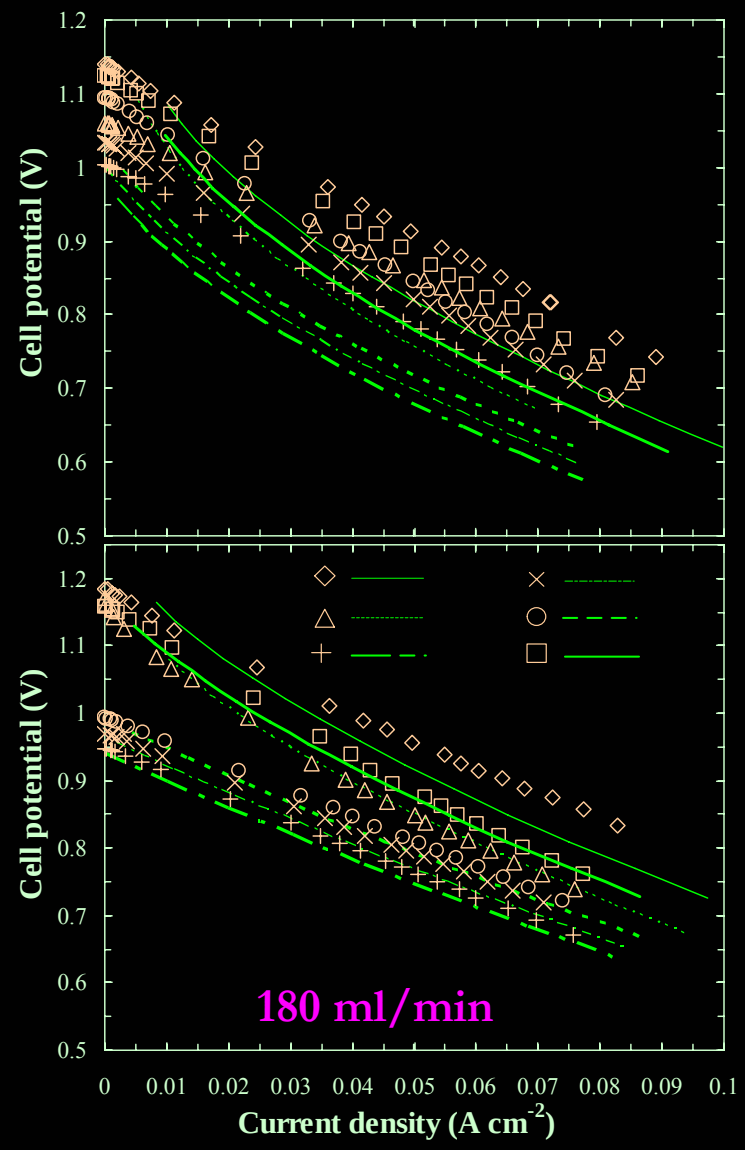
- CO is a useful fuel for SOFC.

- Reason : the contributions of the cathodic & ohmic overpotentials to the overall performance are higher than the anodic overpotential.



Exp. & Model Results for Simulated Synthesis Gases

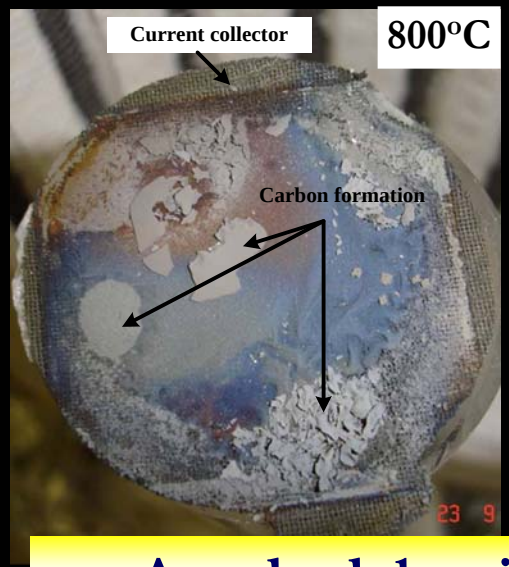
Fuel no.	Gas compositions (%)				
	H_2	H_2O	CO	CO_2	N_2
F1	97	3	-	-	-
F2	20	3	-	-	80
F3	20	3	-	14	66
F4	20	3	20	14	43
F5	32	3	45	15	3
F6	20	3	20	0	57

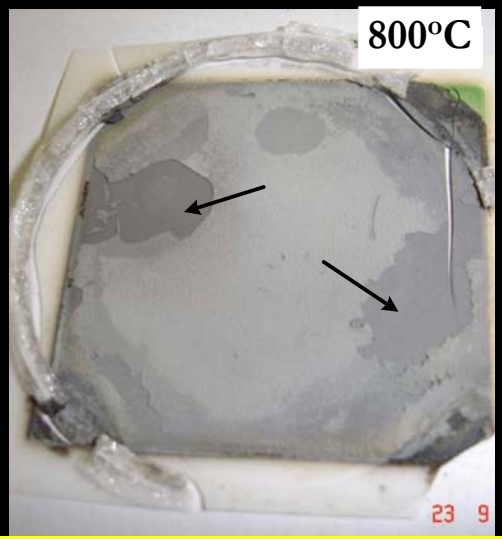


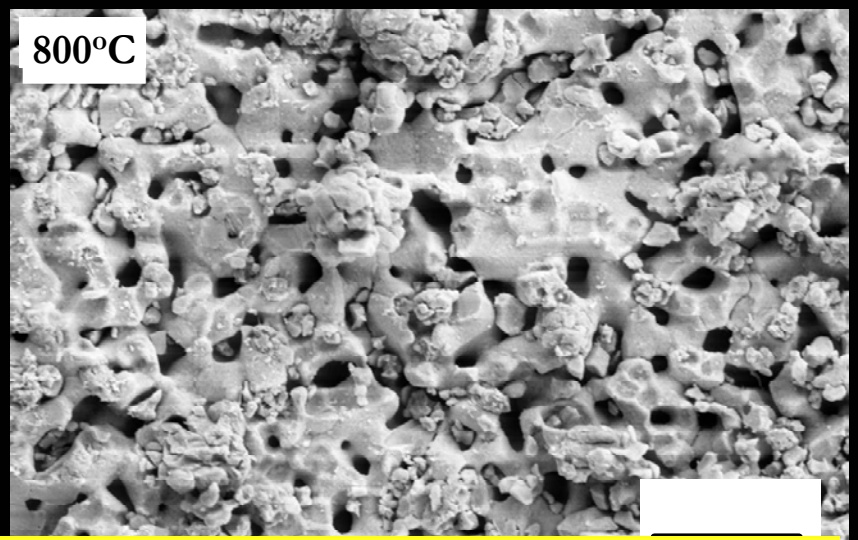
Cell performance comparison

F1 > F6 > F2 > F5 > F4 > F3

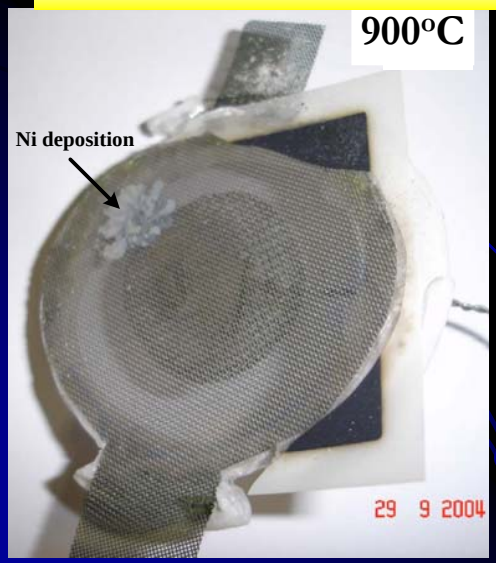
Cell Visualization After Operation

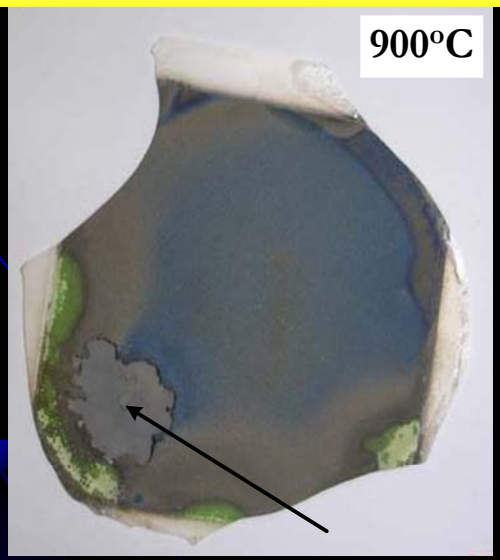


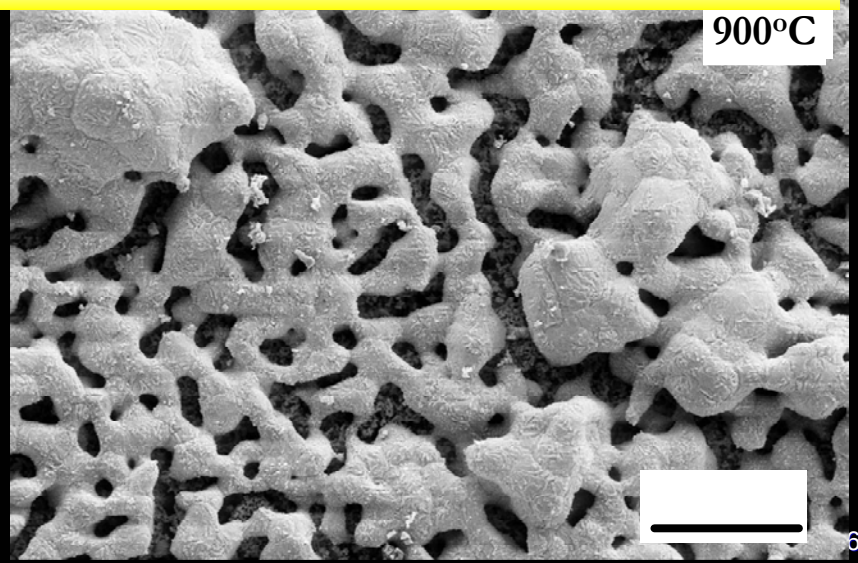




Anode delamination should be related to carbon formation.







Prediction of Carbon Formation

- Study the effect of CO portion and current density on the risk of carbon formation for various operating temperatures, pressures and H_2 & CO_2 compositions.

<u>Carbon formation reaction</u> ($2CO \rightarrow C + CO_2$)

- Mainly caused by the Boudouard reaction.
- No well established kinetic data.
- Carbon activity (α_C) is used to justify the occurrence of this reaction.

$$\alpha_C = \frac{K_{eq,B}\, p_{CO}^2}{p_{CO_2}}$$

Carbon formation is unfavoured if $\alpha_C < 1$

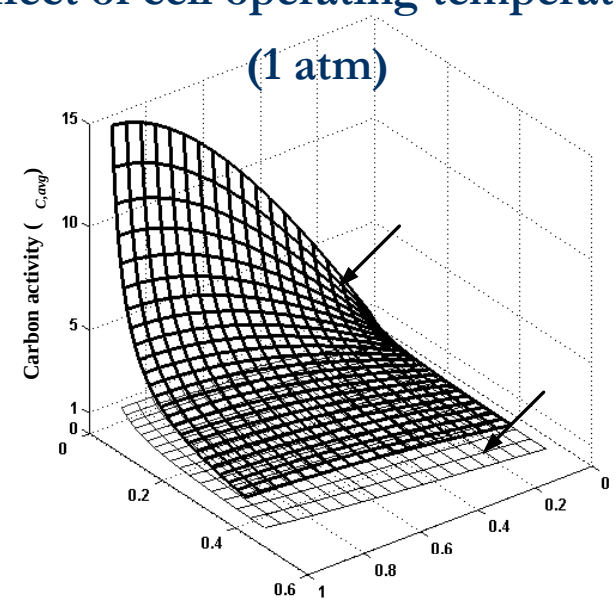
Prediction of Carbon Formation (Cont'd)

To reduce the risk of carbon formation :

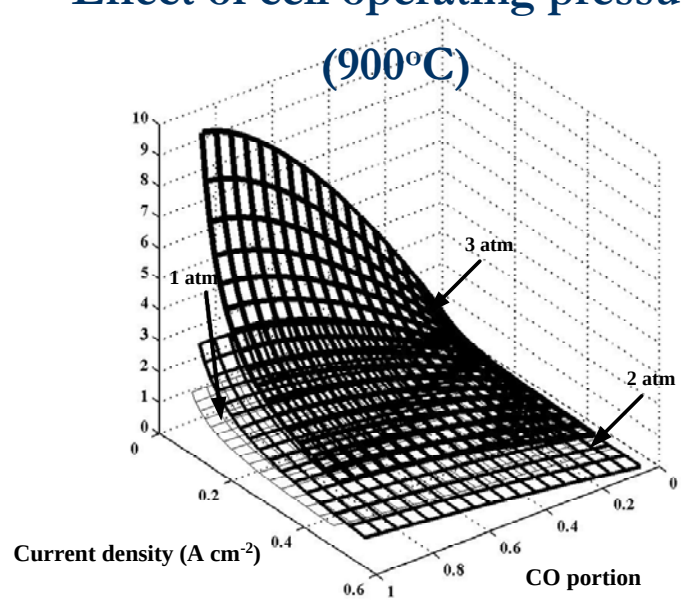
- Increase current density & reduce CO portion.
- Increase temperature & reduce pressure.

$$\alpha_{C,avg} = 2r_b^{-2}\int_0^{r_b} r\alpha_C(r)\Big|_{z=z_{An}} dr \qquad \text{CO portion} = \frac{\text{Mole fraction of CO}}{\text{Mole fraction of CO} + \text{Mole fraction of } H_2}$$

Effect of cell operating temperature (1 atm)



Effect of cell operating pressure (900°C)

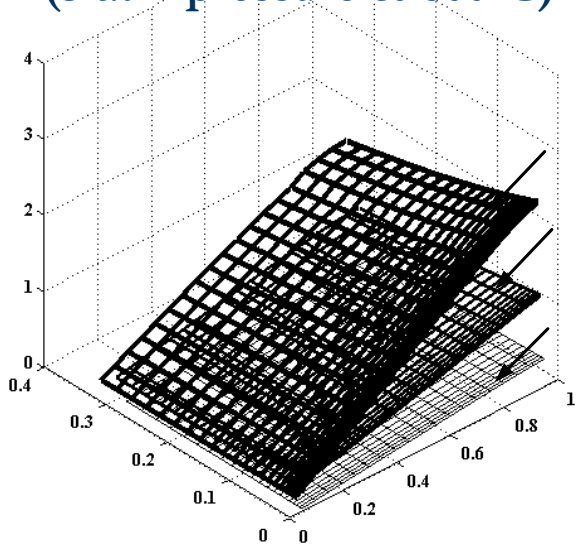


Prediction of Carbon Formation (Cont'd)

- Adding H_2O or CO_2 into fuel gas results in reducing the risk of carbon formation at the expense of cell performance.
- 20% of H_2O or CO_2 is good enough to avoid the risk of carbon formation.

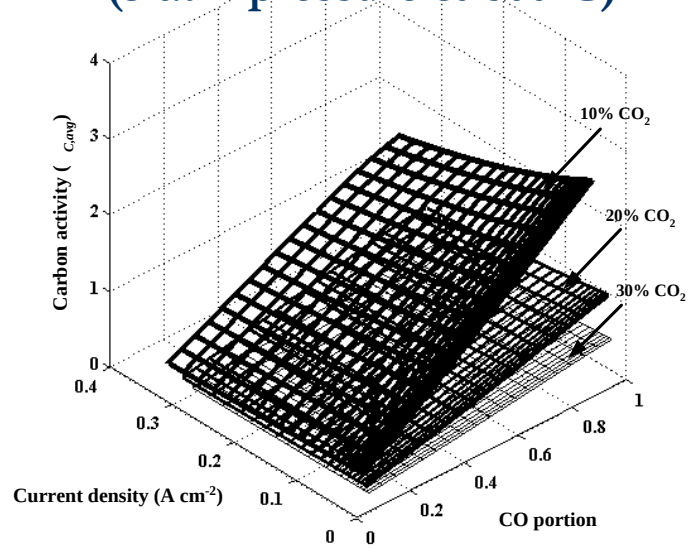
Effect of H_2O composition

(3 atm pressure & 800°C)



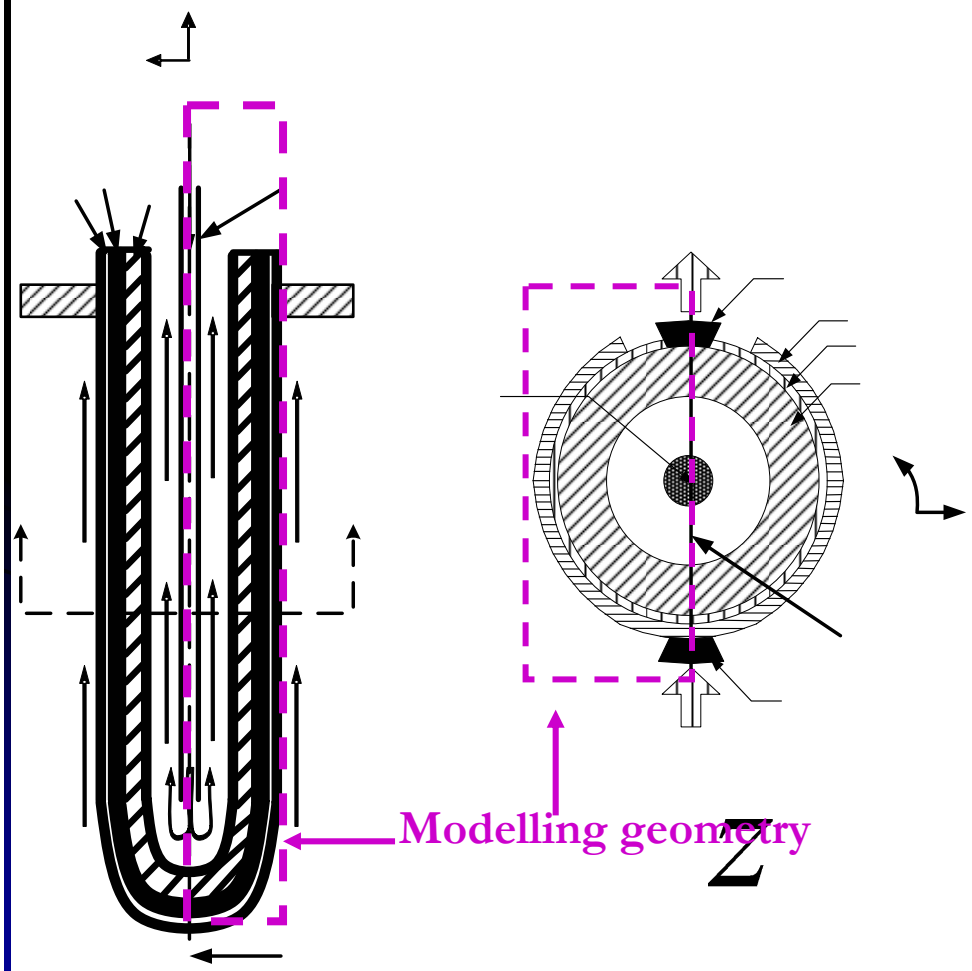
Effect of CO_2 composition

(3 atm pressure & 800°C)



Simulation of Cathode-Supported Tubular SOFCs

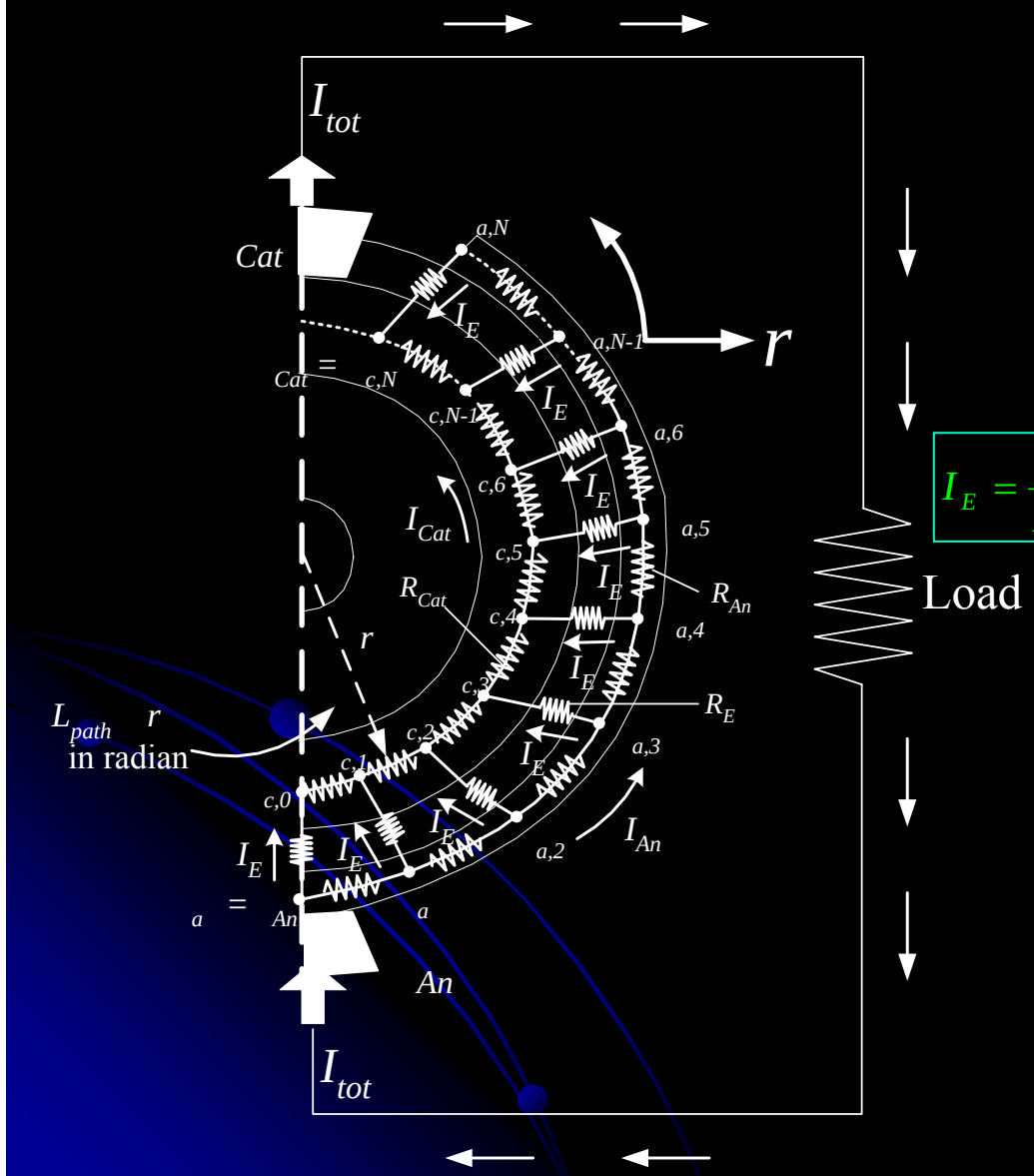
Basic features of the tubular cell



Model Assumptions

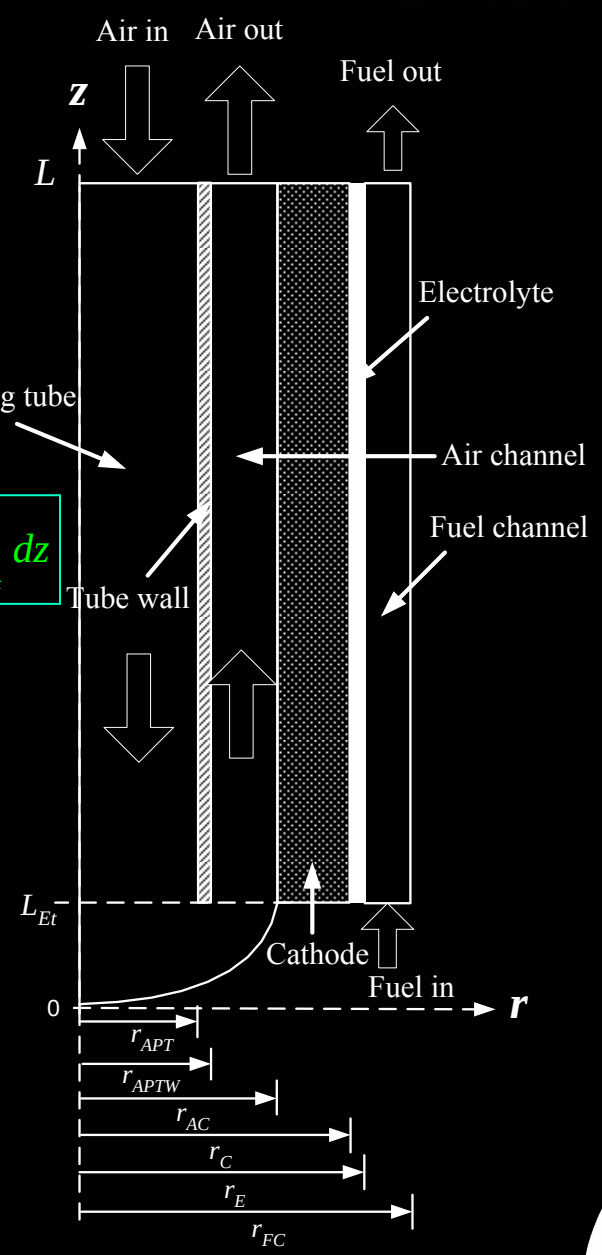
- Steady-state, non-isothermal operation using humidified H_2 and synthesis gas (H_2, CO, CO_2, H_2O, N_2).
- Laminar flows in the gas channels.
- In the case of synthesis gas fuel, constant velocity along the fuel channel.
- Only heat conduction within the porous cathode.
- Occurrence of heat radiation between the air-preheating tube and cell structure.
- Negligible electronic resistances through the electrode thicknesses.
- Negligible mass-transfer resistance through the porous anode.

Model Geometry



$$I_E = \frac{1}{L}\int_0^L J_{O_2}(z)\Big|_{r=r_{Cat}} dz$$

Load



Governing Equations & BCs

Air pre-heating tube (APT)

- Energy transport
- Momentum transport

Tube wall (TW)

- Energy transport

Air channel (AC)

- Energy transport
- Momentum transport
- O_2 mass transport

Cathode (Cat)

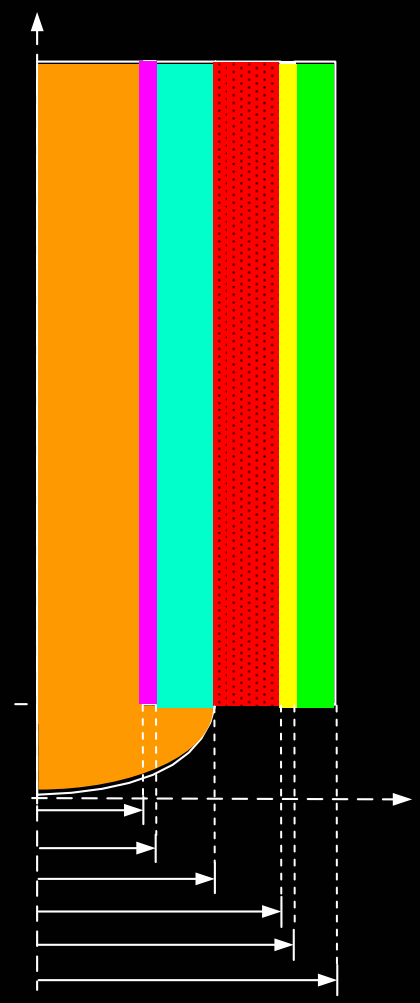
- Energy transport
- O_2 mass transport

Electrolyte (E)

- Energy transport
- Ion transport

Fuel channel (FC)

- Energy transport
- Momentum transport (humidified H_2)
- Fuel mass transports



BCs : General $\mathbf{n}\cdot\vec{\Phi}=0$

Air inlet ($0 < r < r_{APT}$, L) :

$T = T_{a,in}$, $y = y_{O2,in}$, $v = -v_{a,in}$

Fuel inlet ($r_E < r < r_{APT}$, L_{Et}) :

$T = T_{f,in}$, $y = y_{i,in}$, $v = v_{f,in}$

$r = r_E$: $\mathbf{n}\cdot\vec{N}_{H_2} = -J_{H_2}/2F + R_{WGSR}$

$\mathbf{n}\cdot\vec{N}_{CO} = -J_{CO}/2F - R_{WGSR}$

$\mathbf{n}\cdot\vec{N}_{H_2O} = J_{H_2}/2F - R_{WGSR}$

$\mathbf{n}\cdot\vec{N}_{CO_2} = J_{CO}/2F + R_{WGSR}$

$\mathbf{n}\cdot\vec{q}_{Cond} = Q_{electrochem} + Q_{Chem}$ $\quad \mathbf{n}\cdot\vec{i} = J_{H_2} + J_{CO}$

$r = r_C$: $\mathbf{n}\cdot\vec{m}_{O_2} = -M_{O_2}J_{O_2}/4F$

$\mathbf{n}\cdot\vec{q}_{Cond,E} = \mathbf{n}\cdot\vec{q}_{Cond,Cat}$ $\quad \mathbf{n}\cdot\vec{i} = -J_{O_2}$

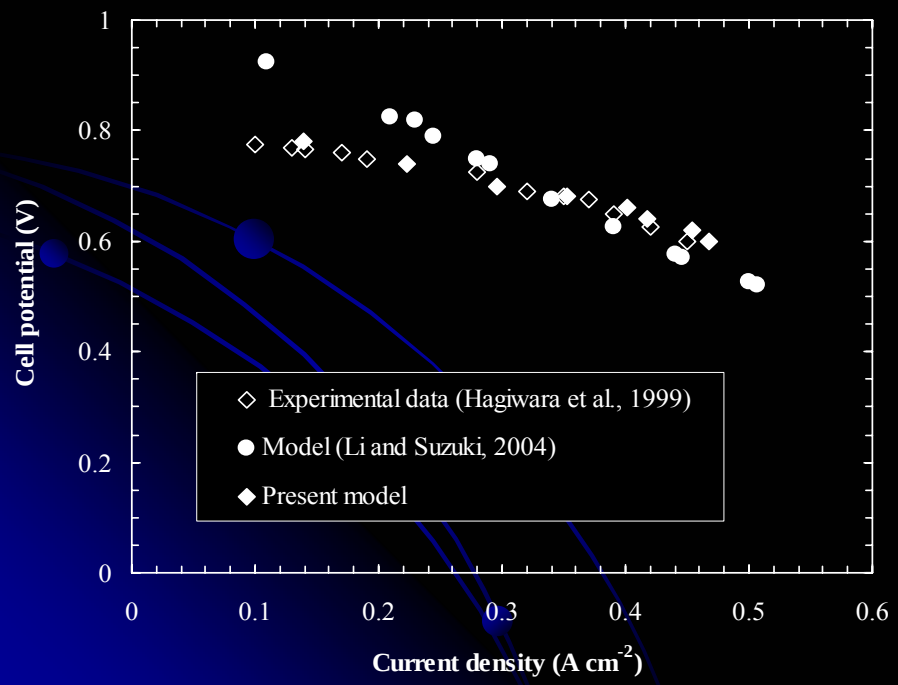
$r = r_{APTW}$: $\mathbf{n}\cdot\vec{q}_{Cond} = q_{Rad,Cat-APTW}$

$r = r_{AC}$: $\mathbf{n}\cdot\vec{q}_{Cond} = -q_{Rad,Cat-APTW}$

Model Validation

Hagiwara *et al.* (1999)

- Fuel: 98.6% H_2, 1.4% H_2O
- Fuel utilization: 85%
- O_2 utilization: 16.7%
- Inlet fuel temperature: 870 °C
- Inlet air temperature: 600 °C
- Inlet pressure: 1 atm



Model comparison

Hirano *et al.* (1992)

- Fuel: 55.7% H_2, 27.7% H_2O, 10.8% CO and 5.8% CO_2
- Fuel utilization: 80%
- O_2 utilization: 25%
- Inlet fuel temperature: 800 °C
- Inlet air temperature: 600 °C
- Inlet pressure: 1 atm
- Current loading: 0.185 A/cm^2

Parameter	Results	
	Exp.	Model
Cell potential (V)	0.715	0.69
Max. cell temp. (°C) (location, mm)	~1000 (140)	1021 (120)
Gas outlet temp. (°C)	~860	840
Fuel flow rate (kg/h)	-	0.0091
Air flow rate (kg/hr)	-	0.081

Cell Performances for Various Syngas Compositions

Model Inputs

- Cell geometry = Based on Hagiwara *et al.* (1999)
- Fuel utilization = 85%
- O_2 utilization = 16.7%
- Inlet fuel temperature = 870 °C
- Inlet air temperature = 600 °C
- Operating pressure = 1 atm
- Cell potential = 0.7 V
- Fuel inlet composition (%)

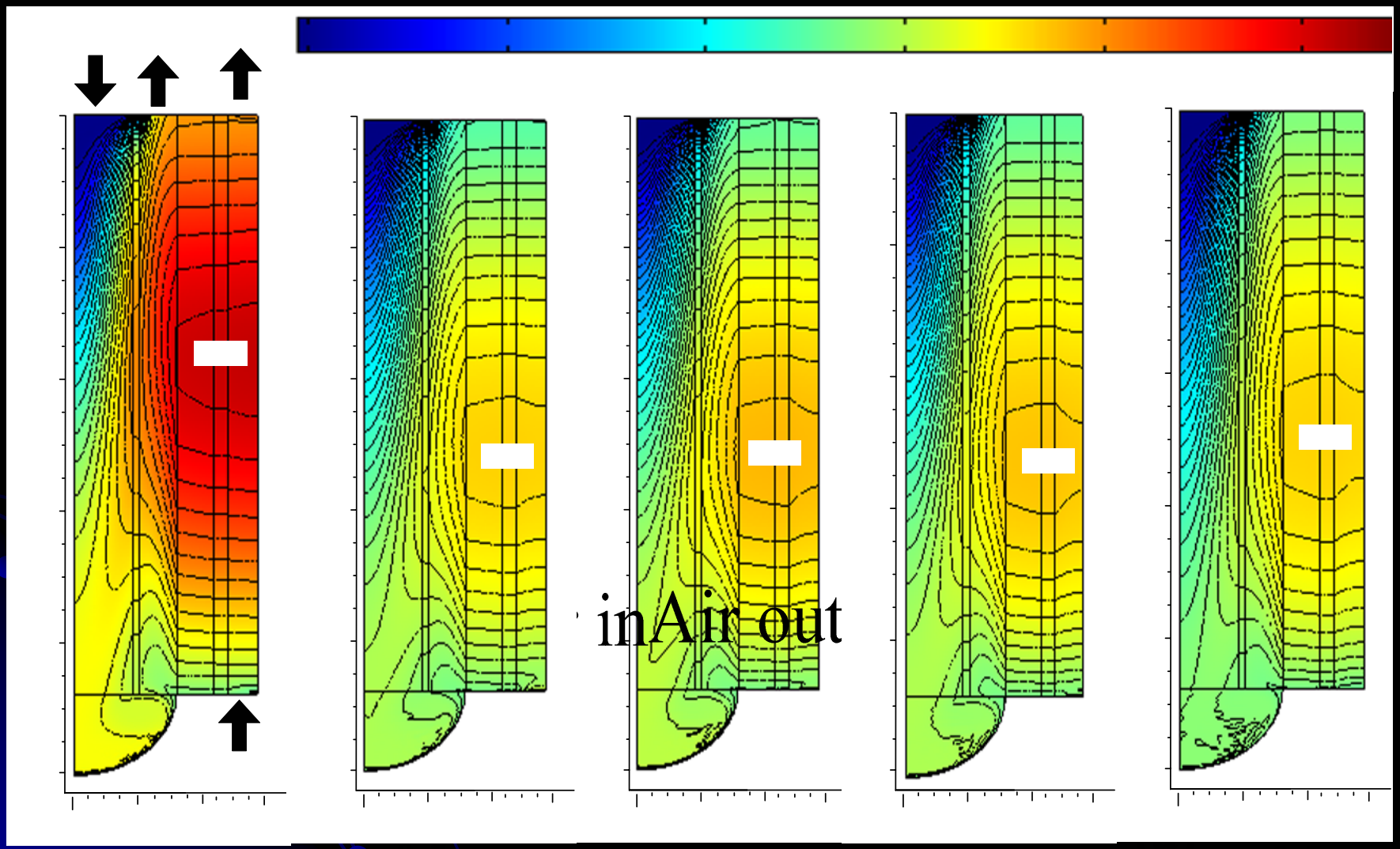
F1 = 97 H_2/ 3 H_2O/ 0 CO/ 0 CO_2/ 0 N_2
F2 = 20 H_2/ 3 H_2O/ 0 CO/ 14 CO_2/ 43 N_2
F3 = 20 H_2/ 3 H_2O/ 20 CO/ 14 CO_2/ 43 N_2
F4 = 32 H_2/ 3 H_2O/ 45 CO/ 15 CO_2/ 3 N_2
F5 = 20 H_2/ 3 H_2O/ 20 CO/ 0 CO_2/ 57 N_2

Effect of syngas compositions on the cell performance

Fuel	Power density (W/cm^2)	Thermal efficiency (%)	Average cell temperature (°C)
F1	0.24	53.80	1040
F2	0.11	48.20	929
F3	0.12	41.56	940
F4	0.13	40.50	935
F5	0.15	38.20	933

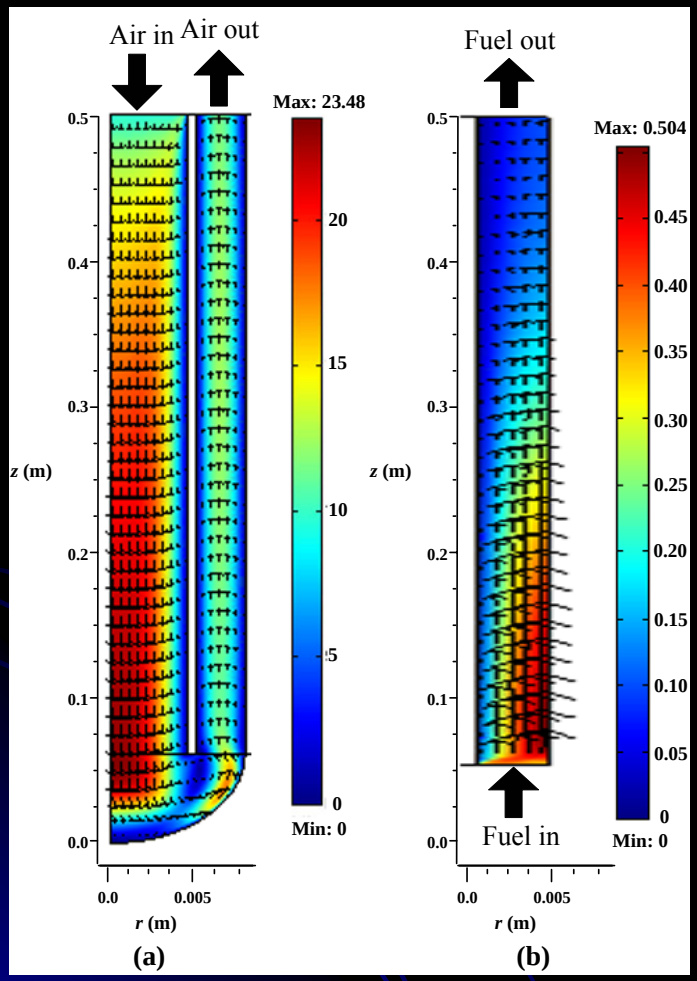
- Cell performance obtained from humidified H_2 is greater than the cell performances obtained synthesis gases.
- Power density is increased at reduced efficiency.

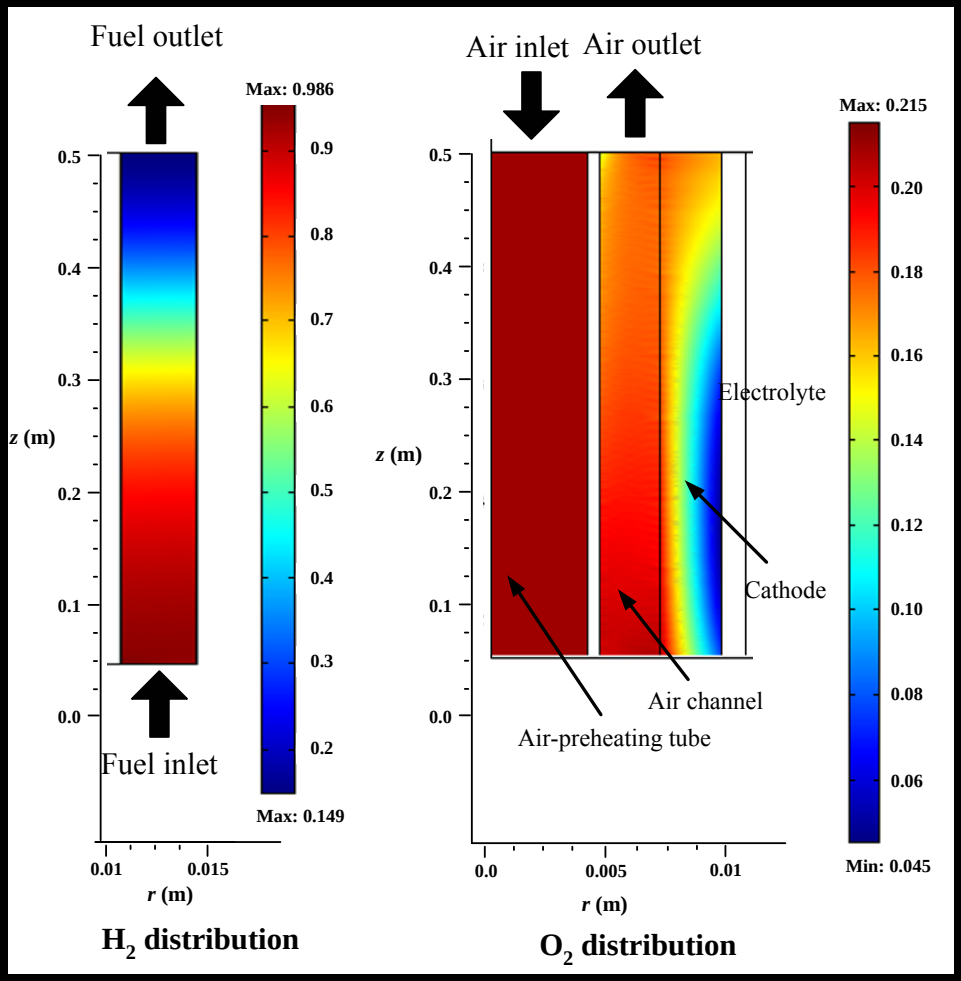
Temperature Distributions



F1 F2 F3 F4 F5

Flow Behaviour & Gas Conc. using Humidified H_2 as Fuel

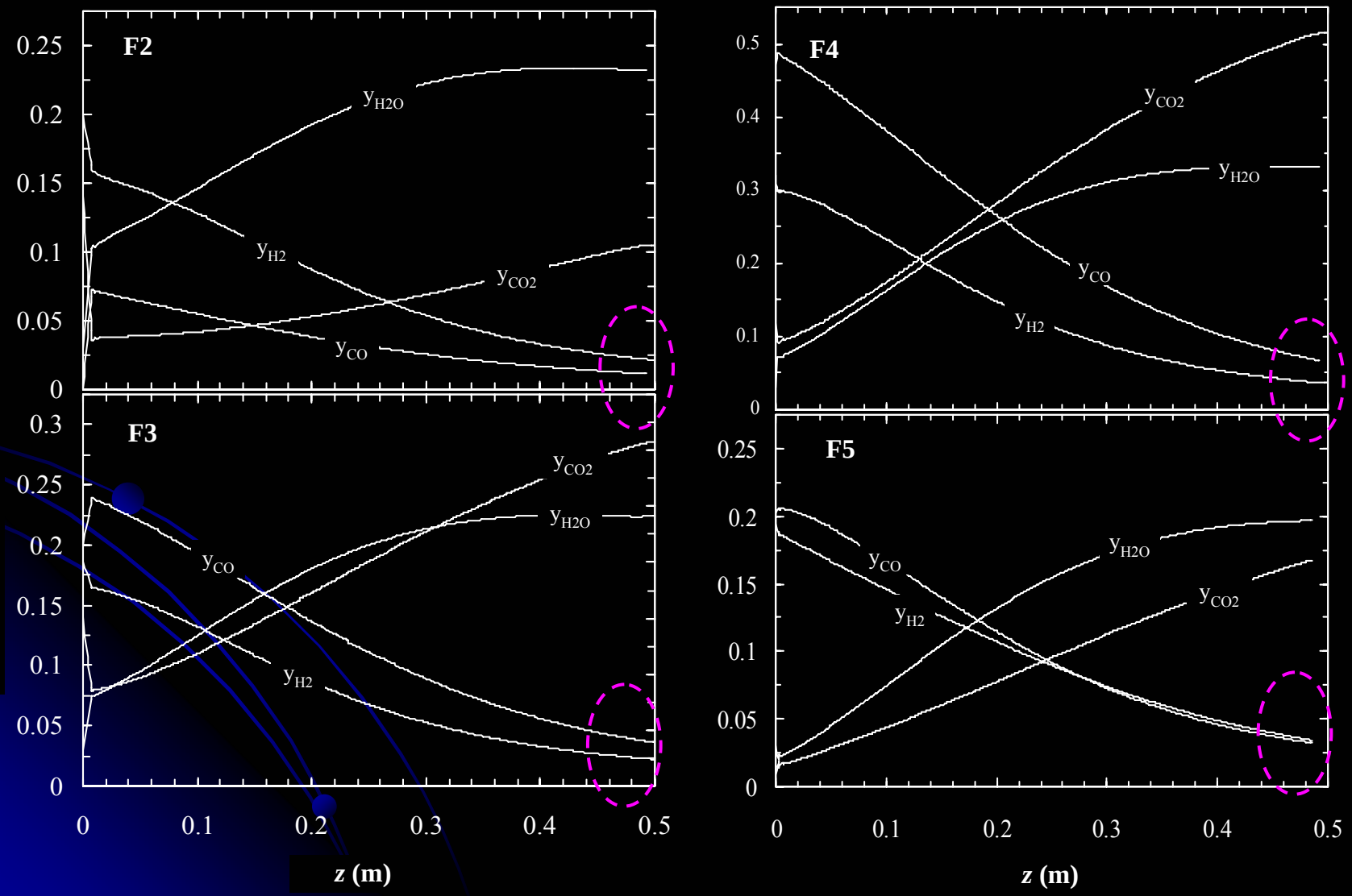




Flow behaviour

Gas concentration distributions (mole fraction)

Gas Concentration Distributions using Synthesis Gases as Fuel



Variation of Cell Operating Parameters

- Base on F3 fuel: 20% H_2, 20% CO, 14% CO_2, 3% H_2O & 53% N_2
- In order to perform the parametric study, only one parameter is changed from the base case conditions at a time.

Cell parameter	Cell performance indices				
	Cell power	Cell efficiency	Fuel utilization	Average cell temperature	Outlet CO_2 concentration
Inlet fuel flow rate ↑	Increase ↑	Increase ↑	Decrease ↓	Increase ↑	Decrease ↓
Inlet air flow rate ↑	Decrease ↑	Decrease ↑	Decrease ↑	Decrease ↑	Decrease ↓
Inlet fuel temperature ↑	Increase ↑	Increase ↑	Increase ↑	Increase ↑	Increase ↑
Inlet air temperature ↑	Increase ↑	Increase ↑	Increase ↑	Increase ↑	Increase ↑
Operating pressure ↑	Increase ↑	Decrease ↓	Decrease ↓	Increase ↑	Decrease ↓
Cell potential ↓	Decrease Increase	Decrease Increase	Increase ↑	Increase ↑	Increase ↑

Conclusions

Button Cell Experiment and Model Validation

- CO is a useful fuel for SOFCs.
- Carbon formation has a significant impact on the cell performance.
- The effect of CO_2 dilution is more pronounced than that of N_2 dilution.
- The validated mechanistic model of the button-cell SOFC was developed.
- The risk of carbon formation increases when the SOFC is operated at intermediate temperature (800°C or below) and high pressure (greater than 1 atm).
- Adding H_2O or CO_2 into synthesis gases containing high CO portion help reduce the risk of carbon formation.

Conclusions (Cont'd)

Simulation of Cathode-Supported Tubular SOFCs

- The validated mechanistic model of the cathode-supported tubular SOFCs was successfully developed.
- Cell performance achieved from tubular SOFCs operating with humidified H_2 is greater than that obtained from synthesis gas.
- Syngas composition has a significant impact on the cell performance.
- From sensitivity analysis, the operating cell potential plays the most important role in changing cell performance.

Recommendations

- Construct a new test rig that allows air and fuel utilization factors.
- Study the reliability of cell performance for cell operating with synthesis gas.
- Develop the dynamic model.
- Develop mechanistic models for other geometries such as flat-plate tubular cell and cross-flow planar cell.
- Develop a model for indirect-internal-reforming SOFCs.

Acknowledgements

- Financial support by the Canadian Program for Energy Research and Development (PERD) and the CANMET CO_2 consortium.
- Financial support by the National Metals and Materials Technology Centre (MTEC), Thailand.
- Profs. P. Douglas, E. Croiset & M. Fowler from UW.
- Dr. Evgueniy Entchev from CETC.
- Prof. Paritud Bhandhubanyong & Dr. Sumittra Charojrochkul from MTEC.
- Researchers from MTEC SOFC research group.