Design and Analysis of Distributed Feed Solid Oxide Fuel Cell Stacks

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Outline

- Motivation
- Hydrogen Fed Case
- Internal Reforming
- Multi-Dimensional Analysis
- Conclusions
Tubular Design SOFC

Anode

2H₂ + 2 O= → 2 H₂O + 4 e⁻

Cathode

O₂ + 4 e⁻ → 2 O=

Heat

Solid Electrolyte

2H₂ → 2H₂O

O₂

2 O= → 4 e⁻

4 e⁻
Flat-Plate Hydrogen Fed SOFC

Fuel Cell Stack

Anode Flow

Cathode Flow

2H₂ + 2 O= ↔ 2 H₂O + 4 e-

O₂ + 4 e⁻ → 2 O=— HEAT RELEASED

2H₂ 2H₂O

Anode

Solid Electrolyte

Cathode

2O= 4 e⁻

O₂

4 e⁻

HEAT RELEASED
Planar Design Characteristics

Advantages:
• Shorter current path => Lower ohmic loss
• Lower fabrication cost

Disadvantages
• Expensive seals
• Susceptible to thermal stresses

=> Shorter life-span
Review of SOFC Electrochemistry

Electrochemical Reaction: \( H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O \)

Heat Generation:

\[
\dot{Q} = \frac{j}{nF}(-\Delta H + \Delta G) + j^2 \left( \sum \sigma_i l_i \right)
\]
\( j = r_{H_2} h n F \)

Reaction Rate: \( r_{H_2} = \alpha(T) + \beta(T) \ln \left( \frac{C_{H_2}}{C_{H_2O}} \right) \)
Flow Configurations

- Air Channel
- Fuel Channel
- Interconnect
- Cathode
- Anode
- Electrolyte
- Fuel Flow
- Air Flow
Plug Flow Reactor Analogy

Conventional Design

Feed

Exhaust

Reaction Rate
Thermal Stresses in the Literature

Peters et al., state that

“Large temperature gradients in either direction can cause damage to one or of the components or interfaces due to thermal stresses”

Yakabe et al., state that

“... the internal stress would cause cracks or destruction of the electrolytes”

Figure taken from Selimovic Dissertation, Lund University, (2002).
Internal Reforming SOFC

Fuel Cell Stack

Fuel Channel

Air Channel

Interconnect

Cathode

Electrolyte

Anode

CH₄ → H₂O + CO₂ + H₂

Fuel Flow

O₂

Air Flow

O₂ + H₂ → H₂O
Internal Reforming

\[ H_2 + \frac{1}{2} O_2 \stackrel{r_{H_2}}{\leftrightarrow} H_2O \quad \text{Exothermic} \]

\[ CH_4 + H_2O \xrightarrow{k_{\text{ref}}} CO + 3H_2 \quad r_{CH_4} = -k_{\text{ref}} C_{CH_4} \]

\[ k_{\text{ref}} \text{ is very large} \quad \text{Endothermic} \]

\[ CO + H_2O \xleftarrow{k_{\text{shift,f}}} CO_2 + H_2 \quad r_{CO_2} = k_{\text{shift,f}} \left( C_{H_2O} C_{CO} - \frac{C_{H_2} C_{CO_2}}{K_{eq}} \right) \]

\[ k_{\text{shift,f}} \text{ is also large} \quad \text{Exothermic} \]
The Promise of Internal Reforming

Clarke et al, (1997) claim: “Internal reforming offers:

• Reduced System Cost (reforming unit eliminated).
• Less Steam Required (anode reaction makes steam).
• More Uniform Temperature Distribution.
• Higher Conversions (equilibrium limiting products consumed by the other reaction).”
Impact of Internal Reforming

Figure taken from Selimovic Dissertation, Lund University, (2002).
Plug Flow Reactor Analogy (Internal Reforming)
Effective Structure of IR SOFC

- Heat and steam produced not used by reforming.
- Pre-heating steam is expensive.
- Steam in the feed lowers hydrogen utilization (reaction rate is a function of hydrogen to steam ratio).

\[
CH_4 + H_2O \rightarrow 3H_2 + CO \\
CO + H_2O \leftrightarrow H_2 + CO_2
\]

\[
H_2 + O^= \rightarrow H_2O
\]
Additional Impacts of Non-Uniformity

- Electrolyte under-utilized at low temperatures
- Hot-spots force the use of more expensive high temperature tolerant materials
- Large temperature range restrict operational window
Distributed Feed Plug Flow Reactors

- Makes PFR act like a CSTR.
- Improves Yield and Selectivity.
- Improves Thermal Management.
Material Balance

Side Feed Variables
\( \hat{F}, \hat{T}, \hat{C}_{H_2}, \hat{C}_{H_2O} \)

Anode Channel
\( F_z, T_z, v_z, C_{H_2}(z), C_{H_2O}(z) \)

Control Volume
\( F_{z+d z}, T_{z+d z}, v_{z+d z} \)
\( C_{H_2}(z+d z), C_{H_2O}(z+d z) \)
Isothermal Model

General Model:

\[ \frac{dF}{dV} = f_s \]
\[ \frac{d(FC_{H_2})}{dV} = f_s \hat{C}_{H_2} - r_{H_2} \]
\[ \frac{d(FC_{H_2O})}{dV} = f_s \hat{C}_{H_2O} + r_{H_2} \]

Rate Equations:

\[ r_{H_2} = \alpha(T) + \beta(T) \ln \left( \frac{C_{H_2}}{C_{H_2O}} \right) \]
\[ j = r_{H_2} h n F \]
\[ \dot{Q} = \frac{j}{nF} (-\Delta H + \Delta G) + j^2 \left( \sum \sigma_i l_i \right) \]

\( f_s \): Distributed feed flow per reactor volume \((m^3 \text{ sec}^{-1} \text{ m}^{-3})\).
\( \hat{C}_i \): Concentration of species \(i\) in the distributed feed.
\( F \): Volumetric flow rate in the fuel cell channel.
Achieving Uniform Heat Generation

\[ \dot{Q} = \frac{j}{nF} (-\Delta H + \Delta G) + j^2 \left( \sum \sigma_l l_i \right) \]

\[ j = r_{H_2} h n F \]

\[ r_{H_2} = \alpha(T) + \beta(T) \ln \left( \frac{C_{H_2}}{C_{H_2O}} \right) \]

**HSR:** \( \frac{C_{H_2}}{C_{H_2O}} = \text{Constant} \Rightarrow \text{Constant } \dot{Q} \)
Isothermal Design of Distributed Feed Flow Rates

Define: \( \rho(z) = \frac{C_{H_2}(z)}{C_{H_2O}(z)} \) and \( \rho_{sp} = \) the desired HSR

Set \( \frac{d\rho}{dz} = 0 \quad \Rightarrow \quad r_{H_2} = \alpha + \beta \ln(\rho_{sp}) = \text{Constant} \)

This is achieved if

\[
f_s = f_s^* = \frac{(\rho_{sp} + 1)[\alpha + \beta \ln(\rho_{sp})]}{(\hat{C}_{H_2} - \hat{C}_{H_2O} \rho_{sp})}
\]

\( \rho(0) = \rho_{sp} \)
Energy Model

\[ 0 = w \dot{Q} - d_h h_c (T_s - T_c) - d_h h_a (T_s - T_a) \]

\[ F C_a C p_a \frac{dT_a}{dz} = d_h h_a w(T_s - T_a) + \hat{F} \hat{C}_a C p_a (\hat{T} - T_a) \]

\[ F_c C_c C p_c \frac{dT_c}{dz} = d_h h_c w(T_s - T_c) \]

<table>
<thead>
<tr>
<th>Interconnect</th>
<th>Adiabatic Wall</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
<td>Ta(z)</td>
</tr>
<tr>
<td>Anode</td>
<td>h_a</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Q(z), Ts(z)</td>
</tr>
<tr>
<td>Cathode</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>hc</td>
</tr>
<tr>
<td></td>
<td>Te(z)</td>
</tr>
<tr>
<td></td>
<td>d z</td>
</tr>
</tbody>
</table>

z
Hydrogen to Steam Ratio
Conventional vs. Side Feed
Electrolyte Temperature
Conventional vs. Side Feed

![Graph showing electrolyte temperature comparison between conventional and side feed channels.](image)
Continuous vs. Discrete Fuel Injection

Feed

Exhaust

ΔL₁  ΔL₂  ΔL₃  ΔL₄

F₁  F₂  F₃  F₄  F₅

A

Exhaust
Hydrogen Fed Simulations

Hydrogen to Steam Ratio

- Conventional Channel
- Continuous Distributed Feed
- Discrete Distributed Feed

Length (m) vs. Hydrogen to Steam Ratio
Hydrogen Fed Simulations

Solid Temperature Profile

![Solid Temperature Profile Graph](image-url)
Hydrogen Fed Simulations

Fuel Temperature Profile

![Graph showing fuel temperature profile with different feed methods: Conventional Channel, Continuous Distributed Feed, Discrete Distributed Feed. The graph plots temperature (K) against length (m).]
Hydrogen Fed Simulations

Air Temperature Profile

![Graph showing Air Temperature Profile with different feed types: Conventional Channel, Continuous Distributed Feed, and Discrete Distributed Feed.](image-url)
Variations in Air Side Flow Rate

Case 1:
Fuel to Air Flow Rate Ratio = 1:5000

Case 2:
Fuel to Air Flow Rate Ratio = 1:50

Case 3:
Fuel to Air Flow Rate Ratio = 1:10
Impact of Reducing Air Flow Rate

Fuel to Air Ratio 1:5000

Fuel to Air Ratio 1:50

Solid Temperature
Further Reduction in Air Flow Rate

Fuel to Air Ratio 1:50

Fuel to Air Ratio 1:10

Solid Temperature
Impact of Reducing Air Flow Rate

Fuel to Air Ratio 1:5000

Fuel to Air Ratio 1:50

Air Gas Temperature
Impact of Injection Point Location

![Diagram showing the impact of injection point location with labeled feed points F1, F2, F3, F4, and F5 spaced along a line marked as Feed. The exhaust direction is indicated at the right end.]
Impact of Injection Point Location

Solid Temperature at Fuel to Air Ratio of 1:5000
Impact of Injection Point Location

Solid Temperature at Fuel to Air Ratio of 1:10
Full Energy Model

\[- k_s a \frac{d^2 T_s}{dz^2} = w \dot{Q} - d_h h_c (T_s - T_c) - d_h h_a (T_s - T_a) \]

\[FC_a C_p a \frac{dT_a}{dz} = d_h h_a w (T_s - T_a) + \hat{F}C_a C_p a (\hat{T} - T_a) \]

\[F_c C_c C_p c \frac{dT_c}{dz} = d_h h_c w (T_s - T_c) \]

Solid Temperature

Boundary Conditions:

Zero Heat Flux at \( z = 0 \) and \( z = L \)
Impact of Heat Conduction Term

Without Conduction

With Conduction

Solid Temperature at Fuel to Air Ratio of 1:5000
Impact of Heat Conduction Term

Solid Temperature at Fuel to Air Ratio of 1:10
Fuel Utilization in the Hydrogen Fed Case

\[ U = \frac{C_{H_2, in} - C_{H_2, out}}{C_{H_2, in}} \]

Changes in utilization achieved by variations in fuel feed flow rate
Summary of the Hydrogen Fed Case

- Continuous distributed feed will mitigated temperature non-uniformity.

- Discrete injection and air side convection will reduce uniformity.

- Utilization also impacted.
Internal Reforming SOFC

- Heat and steam produced not used by reforming.
- Pre-heating steam is expensive.
- Steam in the feed lowers hydrogen utilization (reaction rate is a function of hydrogen to steam ratio).

\[ CH_4 + H_2O \rightarrow 3H_2 + CO \]
\[ CO + H_2O \leftrightarrow H_2 + CO_2 \]
Methane Fed Design Equations

General Model:

\[
\frac{dF}{dV} = f_s + \left(\frac{2}{C}\right)r_{CH_4}
\]

\[
\frac{d(FC_{CH_4})}{dV} = f_s \hat{C}_{CH_4} + r_{CH_4}
\]

\[
\frac{d(FC_{H_2})}{dV} = f_s \hat{C}_{H_2} - 3r_{CH_4} + r_{CO_2} - r_{H_2}
\]

\[
\frac{d(FC_{H_2O})}{dV} = f_s \hat{C}_{H_2O} + r_{CH_4} - r_{CO_2} + r_{H_2}
\]

\[
\frac{d(FC_{CO})}{dV} = f_s \hat{C}_{CO} - r_{CH_4} - r_{CO_2}
\]

\[
\frac{d(FC_{CO_2})}{dV} = f_s \hat{C}_{CO_2} + r_{CO_2}
\]

Rate Equations:

\[
r_{H_2} = \alpha(T) + \beta(T) \ln \left( \frac{C_{H_2}}{C_{H_2O}} \right)
\]

\[
r_{CH_4} = -k_{ref} C_{CH_4}
\]

\[
r_{CO_2} = k_{shift,f} (C_{H_2O}C_{CO} - \frac{C_{H_2}C_{CO_2}}{K_{eq}})
\]

\[
j = r_{H_2} h n F
\]

\[
\dot{Q} = -\sum \Delta H_i r_i + T\Delta S \ r_{H_2} + j^2 (\sum \sigma_i l_i)
\]
Carbon Deposition

\[ CH_4 \leftrightarrow C + 2H_2 \]
\[ 2CO \leftrightarrow C + CO_2 \]
\[ CO + H_2 \leftrightarrow C + H_2O \]
\[ CO_2 + 2H_2 \leftrightarrow C + 2H_2O \]

CMMSR is a suggested measure for the risk of carbon deposition under SOFC operating conditions.

\[ CMMSR = \frac{C_{CO} + C_{CH_4}}{C_{H_2O}} \]

If CMMSR > 1: Carbon deposition risk
CMMSR < 1: No risk of carbon deposition
Methane Fed Design Scheme

Again define: \( \rho(z) = \frac{C_{H_2}(z)}{C_{H_2O}(z)} \) and \( \rho_{sp} = \) the desired HSR

And set
\[
\frac{d\rho}{dz} = 0 \implies r_{H_2} = \alpha + \beta \ln(\rho_{sp}) = \text{Constant}
\]

This is achieved if
\[
f_s^* = \frac{(\rho_{sp} + K_{eq})(\rho_{sp} + 1)[\alpha + \beta \ln(\rho_{sp})] - (\rho_{sp}^2 + 2\rho_{sp} K_{eq} + 3\rho_{sp} + 4K_{eq})r_{CH_4}^*}{(\rho_{sp} + K_{eq})(\hat{C}_{H_2} - \hat{C}_{H_2O} \rho_{sp}) + (\rho_{sp} - 1)(K_{eq} \hat{C}_{CO} - \hat{C}_{CO_2} \rho_{sp})}
\]
\[
\rho(0) = \rho_{sp}
\]
Internal Reforming
Simulation Scenarios

Fuel to air flow rate ratio = 1:100

Inlet steam to carbon ratio (SCR) = $C_{H_2O,in} : C_{CH_4,in}$

Case 1: Conventional stack, inlet SCR = 2:1
Case 2: Conventional stack, inlet SCR = 1:1
Case 3: Distributed feed design, inlet SCR = 1:2
Case 4: Discrete injection, inlet SCR = 1:2
Non-Isothermal Simulation of the Internal Reforming Case
Non-Isothermal Simulation of the Internal Reforming Case
Impact of Fuel Flow Rate

Fuel LHV Rate 3.28 J/sec

Fuel LHV Rate 4.1 J/sec

Solid Temperature at Fuel to Air Ratio of 1:100
Impact of Fuel Flow Rate

Fuel LHV Rate 3.28 J/sec

CMMSR at Fuel to Air Ratio of 1:100

Fuel LHV Rate 4.1 J/sec
Impact of Air Flow Rate
Utilization in the Internal Reforming Case

\[ U = 1 - \frac{4F_{out}C_{CH_4}^{out} + F_{out}C_{H_2}^{out}}{4F_{out}C_{CH_4}^{in} + F_{out}C_{H_2}^{in}} \]
Measures of Efficiency

(a) Stack
Fuel Feed
1195° K
Power

(b) Stack
Fuel Feed
298° K
Steam Feed
ΔH_{pre}
1195° K
Power

(c) Stack
Fuel Feed
298° K
Steam Feed
ΔH_{net}
373° K
Power

Burner

373° K
Fuel Exhaust
Conventional Efficiency

\[ U = 1 - \frac{4F_{out}C_{CH_4}^{out} + F_{out}C_{H_2}^{out}}{4F_{out}C_{CH_4}^{in} + F_{out}C_{H_2}^{in}} \]

\[ \eta_1 = \frac{P_e}{LHV} \]
Modified Stack Efficiency

\[ \eta_1 = \frac{P_e}{LHV} \]

\[ \eta_2 = \frac{P_e}{LHV + \Delta H_{pre}} \]
System Efficiency

\[ \eta_2 = \frac{P_e}{LHV + \Delta H_{pre}} \]

\[ \eta_3 = \frac{P_e + 0.45(\Delta H_{post} - \Delta H_{pre})}{LHV} \]
Summary of Internal Reforming Case

- Greater uniformity in temperature is achieved.
- Less steam is required for CO protection.
- Utilization and efficiency improved.
Two Dimensional Analysis
2-D Distributed Feed Design
2-D Distributed Feed Design

Section of a stack layer
Sizing of the By-Pass Streams

Hagen-Poiseuille Equation:

\[
\hat{F}_i = f_s^* A \Delta L_i
\]

\[
\Delta P_{i,n} = \frac{8 \mu \Delta z_i F_{i,n} p_{i,n}^2}{A_{i,n}^3}
\]
Isothermal Velocity Profile for Hydrogen Fed DFSOFC Stack
Isothermal Concentration Profile
Hydrogen Fed DFSOFC
Mixing Issues

Surface: Concentration Arrow: \([x \text{ velocity (u), y velocity (v)}]\)

Length (m)
Width (m)

Max: 9
Min: 5
Alternative Design
Isothermal Velocity Profile for Hydrogen Fed DFSOFC Stack
Isothermal Concentration Profile for Hydrogen Fed DFSOFC Stack
Mixing Issues

Concentration peaks at injection points could cause high stress or carbon deposition regions.
Summary

• Distributed feed design successfully mitigated temperature non-uniformity.

• Utilization and efficiency was greatly improved in the internal reforming case.

• 2-D simulations indicate that static mixers are required to distribute fuel radially.
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• Process System Engineering Laboratory
Power Load Transition Dynamics

How does the stack get from one operating point to another?
Sensitivity Analysis

![Graph showing the reaction rate (mol/cm²) as a function of temperature (K) for different HSR values (0.1, 1, 10). The graph includes three lines, each representing a different HSR value. The y-axis represents the reaction rate in mol/cm², ranging from 0.00E+00 to 4.00E-06. The x-axis represents temperature in K, ranging from 800 to 1200. The lines are color-coded: green for HSR = 0.1, blue for HSR = 1, and red for HSR = 10.](image-url)