Mathematical Modeling of a Porous Media Burner Based Methane Flame Fuel Cell

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A detailed two-dimensional axisymmetric computational model of a flame fuel cell (FFC) unit was developed and presented. The FFC unit is based on the integration of a fuel-rich methane flame in a porous media burner and a micro-tubular solid oxide fuel cell (SOFC). The model considered the coupling effects of the chemical reactions and electrochemical reactions and the heat-transport, mass-transport and charge-transport processes in the FFC. The simulated temperature distribution and electrochemical characteristics showed good agreement with experimental data. The coupling mechanism of the fuel-rich flame and the SOFC anode were clarified. The Ni catalyst in the anode and the electrochemical reactions promoted the conversion of CH4 in porous media fuel-rich combustion.

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Schematics of (a) experimental setup and (b) model domain.

Ionic charge balance at the anode:
\[
\frac{C_{\text{dl,an}} S_{\text{act,an}}}{\partial t} (V_{\text{ion,an}} - V_{\text{el,an}}) + \nabla \cdot (-\sigma_{\text{eff,an}} \nabla V_{\text{ion,an}}) = Q_{\text{ion,an}}
\]
\[
= - (i_{\text{an,H}_2} \frac{C_{\text{TPR}}}{C_{\text{H}_2}} + i_{\text{an,CO}} \frac{C_{\text{TPR}}}{C_{\text{CO}}})
S_{\text{act,an}} \left( \exp \left( \frac{an_c F(V_{\text{el,an}} - V_{\text{ion,an}} - V_{\text{ref,an}})}{RT} \right) \right.
- \exp \left( - (1 - \alpha)n_c F(V_{\text{el,an}} - V_{\text{ion,an}} - V_{\text{ref,an}}) \right) \right)
\] [1]

Electronic charge balance at the anode:
\[
\frac{C_{\text{dl,an}} S_{\text{act,an}}}{\partial t} (V_{\text{ion,an}} - V_{\text{el,an}}) + \nabla \cdot (-\sigma_{\text{eff,an}} \nabla V_{\text{el,an}}) = Q_{\text{el,an}} = -Q_{\text{ion,an}}
\] [2]

Ionic charge balance at the cathode:
\[
\frac{C_{\text{dl,ca}} S_{\text{act,ca}}}{\partial t} (V_{\text{ion,ca}} - V_{\text{el,ca}}) + \nabla \cdot (-\sigma_{\text{eff,ca}} \nabla V_{\text{ion,ca}}) = Q_{\text{ion,ca}}
\]
\[
= i_{\text{ca,CO}} \frac{C_{\text{TPR}}}{C_{\text{O}_2}} \left( \exp \left( \frac{an_c F(V_{\text{el,ca}} - V_{\text{ion,ca}} - V_{\text{ref,ca}})}{RT} \right) \right.
- \exp \left( - (1 - \alpha)n_c F(V_{\text{el,ca}} - V_{\text{ion,ca}} - V_{\text{ref,ca}}) \right) \right)
\] [3]

Electronic charge balance at the cathode:
\[
\frac{C_{\text{dl,ca}} S_{\text{act,ca}}}{\partial t} (V_{\text{el,ca}} - V_{\text{cit,ca}}) + \nabla \cdot (-\sigma_{\text{eff,ca}} \nabla V_{\text{el,ca}}) = Q_{\text{el,ca}} = -Q_{\text{ion,ca}}
\] [4]

Ionic charge balance at the electrolyte:
\[
\nabla \cdot (-\sigma_{\text{eff,elec}} \nabla V_{\text{ion,elec}}) = 0
\] [5]

In Eqs. 1–5, \( t \) is time, \( C_{\text{dl}} \) is the specific interface double-layer capacitance between electronic and ionic conductor phases, \( Q \) is the transfer current source, and \( V_{\text{el}} \) and \( V_{\text{ion}} \) are the electric potentials of the two conductor phases.

**Mass conservation.**—The mass conservation equation of species \( i \) in the anode can be expressed as:
\[
\frac{\partial (\rho_{\text{fuel}} Y_i)}{\partial t} + \nabla \cdot (\rho_{\text{fuel}} u_i - \rho_{\text{fuel}} Y_i \sum_{j=1}^{N} D_{ij}(\nabla x_i)) = R_i
\] [6]

where \( \rho_{\text{fuel}} \) is the gas density at the anode, \( \varepsilon \) is the porosity, \( u \) is the velocity, \( R_i \) is the mass source of species \( i \). The mass sources from the chemical reactions and the electrochemical reactions in the anode were considered. The water-gas shift reaction (WGS) and the internal reforming reaction (DIR) are taken into consideration:

\[
\text{CO} + \text{H}_2 \text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2
\] [7]

\[
\text{CH}_4 + \text{H}_2 \text{O} \rightleftharpoons \text{CO} + 3\text{H}_2
\] [8]

The global expressions of the reaction rates are:

\[
R_{\text{WGS}} = k_{\text{WGS}} \left( p_{\text{H}_2} p_{\text{CO}} - p_{\text{H}_2} p_{\text{CO}_2} \right) \frac{k_{p,\text{WGS}}}{k_{p,\text{WGS}}}
\] [9]

\[
k_{\text{WGS}} = 0.0171 \exp \left( \frac{-103191}{RT} \right)
\] [10]

\[
K_{\text{WGS}} = \exp(-0.2935Z^3 + 0.6351Z^2 + 4.1788Z + 0.3169)
\] [11]

\[
Z = \frac{1000}{T} - 1
\] [12]

\[
R_{\text{DIR}} = k_{\text{DIR}} \left( p_{\text{CH}_4} p_{\text{H}_2} - p_{\text{H}_2}^3 p_{\text{CO}} \right) \frac{k_{p,\text{DIR}}}{k_{p,\text{DIR}}}
\] [13]

\[
k_{\text{DIR}} = 2395 \exp \left( \frac{-231266}{RT} \right)
\] [14]
The mass source term of species $i$ can be calculated as follows:

$$R_{i} = -\frac{-i_{\text{trans},an,H}_i S_{\text{act},an} W_{H_i}}{2} + R_{\text{WGS}} W_{H_i} + 3 R_{\text{DIB}} W_{H_i}$$

$$R_{CO} = -\frac{-i_{\text{trans},an,CO S_{\text{act},an} W_{CO}}}{2} - R_{\text{WGS}} W_{CO} + R_{\text{DIB}} W_{CO}$$

$$R_{H_{2}O} = -\frac{-i_{\text{trans},an,H}_i S_{\text{act},an} W_{H_{2}O}}{2} - R_{\text{WGS}} W_{H_{2}O} - R_{\text{DIB}} W_{H_{2}O}$$

$$R_{CO_2} = -\frac{-i_{\text{trans},an,CO S_{\text{act},an} W_{CO_2}}}{2} + R_{\text{WGS}} W_{CO_2}$$

$$R_{CH_4} = -R_{\text{DIB}} W_{CH_4}$$

**Model parameters.**—The parameters related to the combustion models were presented in the previous paper.10 The parameters related to the other regions are shown in Tables I and II.
Results and Discussion

Model validation.—The combustion model was validated by the measured temperature distribution and gas compositions reported in the previous paper.\textsuperscript{16} In this paper, the modeled temperature distribution of the entire FFC reactor was compared with the experimental results obtained at an equivalence ratio of 1.6 and a gas velocity of 0.15 m/s, as shown in Fig. 2. It can be seen that the simulated profile matched the experimental results well. Then, the experimental data of the electrochemical performance published by our group was used to further validate the model.\textsuperscript{16} Fig. 3 shows the modeling and experimental IV curves of the FFC unit at various equivalence ratios. The modeled curves agree well with the experimental data, which means that the model developed can be used to represent actual conditions.

Effects of Ni catalyst.—In the FFC unit, the anode and the porous media burner are directly integrated. The temperatures and gas compositions were calculated with and without the chemical reactions at the anode to analyze the effects of the Ni catalyst on the fuel-rich reformation. Although not shown here, the modeled temperature distribution varied little after considering the chemical reactions at the Ni catalyst. Simulation results with and without the chemical reactions at the Ni catalyst for the equivalence ratio of 1.6 and the gas velocity of 0.15 m/s are compared in Fig. 4. It should be noted that the species mole fraction shown in Fig. 4 is the calculated average mole fraction for each species within the anode. It can be seen that the mole fractions of H$_2$ and CO$_2$ increased, while the mole fractions of CO and CH$_4$ decreased due to the water-gas shift reaction and the direct internal reformation reaction that occurred at Ni surface. Fig. 5 further shows the composition distribution in the anode and anode channel. When the fuel-rich combustion exhausts entered the SOFC region, the mole fractions of H$_2$ and CO$_2$ increased, and a concentration gradient from the anode to the anode channel emerged. In constrast, CO and CH$_4$ were consumed at the anode. A concentration gradient from the anode channel to the anode emerged, which led to the decrease of CO and CH$_4$ in the anode channel. Consequently, the Ni catalyst in the SOFC anode promoted the conversion of CO and CH$_4$ to H$_2$, which has a catalytic enhancement effect on the fuel-rich combustion of methane in the porous media burner.

Effects of electrochemical reactions.—Since the fuel utilization efficiency of the FFC unit is only 1%\textsuperscript{16}, the average temperature of the SOFC only increased by 5–6 K after considering the heat effects of the electrochemical reactions. Meanwhile, the relatively low fuel utilization efficiency makes it difficult to investigate the effects of the electrochemical reactions on the composition distributions. However, the integration of a micro-tubular SOFC stack with the burner is necessary for the practical application of the FFC. Consequently, in this section, the effects of the electrochemical reactions on the fuel-rich combustion were analyzed given a fuel utilization efficiency of 36%.

Fig. 6 shows the calculated temperature distribution in the SOFC region with/without electrochemical reactions (at a voltage of 0.6 V). It can be seen that the heat release of electrochemical reactions led to a temperature increase at the anode/electrolyte interface $\partial/\Omega_{\text{an}}$. The temperature gradient from the anode/electrolyte surface to the anode/anode channel interface $\partial/\Omega_{\text{an}}$ further led to the temperature increase of the anode and the anode channel. The average temperature of the anode increased by 20–30 K after introduction of the electrochemical reactions. Since there exists a large gradient from the upstream to the downstream of the SOFC, the current density decreased rapidly along the axial direction of the SOFC, as shown in Fig. 7. Consequently, the heat released by the electrochemical reactions decreased rapidly. Upstream of the SOFC region, where the temperature is high, the temperature increased by 50 K due to the heat release of the electrochemical reactions.

The composition distributions along the anode-channel interface $\partial/\Omega_{\text{an}}$ are shown in Fig. 8. The mole fraction of H$_2$ showed a trend from decrease to increase along the axial direction. H$_2$ was consumed by the electrochemical reactions at the high-temperature region of the SOFC. However, the consumption rate of H$_2$ decreased due to the

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**Table II. Electrochemical Parameters.**\textsuperscript{21}

| Material          | Ionic Conductivity $\sigma_{\text{ion}}$ (s/m) | Electronic Conductivity $\sigma_{\text{elec}}$ (s/m) |
|-------------------|-----------------------------------------------|--------------------------------------------------|
| Anode Ni-YSZ      | $3.34 \times 10^4 \exp(-10300/T)$            | $3.27 \times 10^6 - 1063.5T$                      |
| Electrolyte ScSZ  | $0.002T + 1.4483$                             | -                                                |
| Cathode LSM-ScSZ  | $6.92 \times 10^4 \exp(-9681/T)$             | $4.2 \times 10^7 T \exp(-1150/T)$                |

Figure 2. Temperature distribution in the FFC unit.
Figure 3. Modeling and experimental IV curves of the FFC unit at various equivalence ratios.

decrease in the current density. At the low-temperature region of the SOFC, the production rate of H₂ by the chemical reactions exceeded the consumption rate of H₂ by the electrochemical reactions, which led to an increase in H₂. The mole fraction of CH₄ changed little while the mole fractions of CO and H₂O decreased at the low-temperature region, which indicates that the production of H₂ was mainly due to the water-gas shift reaction. In addition, the direct internal reformation of CH₄ reached equilibrium with/without electrochemical reactions since the mole fraction of CH₄ changed little at the low-temperature region.

Figure 4. Mole fractions of major species in SOFC anode with and without chemical reactions.

Figure 5. Mole fraction distribution of major compositions in the anode and anode channel.
region. The temperature increase caused by the electrochemical reactions promoted the forward movement of chemical equilibrium of the direct internal reformation reaction of CH$_4$, which promoted the conversion of CH$_4$ to H$_2$ and CO, and led to a decrease of the mole fraction of CH$_4$. The mole fraction of H$_2$O increased at the high-temperature region due to the electrochemical reaction of H$_2$. The production of H$_2$O provided reactant for the DIR and WGS reactions and promoted the conversion of CO and CH$_4$ to H$_2$.

Conclusions

A comprehensive 2D axisymmetric model of a flame fuel cell unit was developed in this paper. The model considers the coupling effects of chemical and electrochemical reactions, momentum transfer, heat transport, and mass transport in both the SOFC and the porous media burner. Numerical predictions of the temperature distribution and IV curves showed good agreement with experimental results for various equivalence ratios. The effects of the Ni catalyst and the electrochemical reactions on methane fuel-rich combustion were analyzed. Ni catalyst in the SOFC anode promoted the water-gas shift reaction and the direct internal reformation of methane in the fuel-rich reforming region. The heat released and the H$_2$O produced by the electrochemical reactions promoted the conversion of CH$_4$ and CO to H$_2$, which has a catalytic enhancement effect on the fuel-rich combustion of methane in porous media.

Acknowledgments

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Figure 8. Composition distributions along the anode-channel interface $\partial_\Omega_{\text{an}}$.  

List of Symbols

| Symbol | Definition |
|--------|------------|
| $C$    | concentration (mol m$^{-3}$) |
| $C_{dl}$ | specific interface double-layer capacitance (F m$^{-2}$) |
| $C_p$  | specific heat capacity (J kg$^{-1}$ K$^{-1}$) |
| $D_{\text{eff}}^{i,j}$ | effective diffusion coefficient (m$^2$ s$^{-1}$) |
| $F$    | Faraday constant (96,485 C mol$^{-1}$) |
| $I$    | current density (A m$^{-2}$) |
| $i_0$  | exchange current density (A m$^{-2}$) |
| $k$    | reaction rate constant (in terms of m, mol and s) |
| $K$    | equilibrium constant |
| $n_e$  | number of electrons participating in the reaction |
| $P$    | pressure (Pa) |
| $Q$    | transfer current source (A m$^{-3}$) or heat source (W m$^{-3}$) |
| $R$    | gas constant (8.314 J mol$^{-1}$ K$^{-1}$) or reaction rate (mole m$^{-3}$ s$^{-1}$ or mole m$^{-2}$ s$^{-1}$) |
| $R_i$  | mass source of species $i$ (kg m$^{-3}$ s$^{-1}$) |
| $S$    | molar entropy (J K$^{-1}$ mol$^{-1}$) |
| $S_{\text{act}}$ | active area per unit volume (m$^2$ m$^{-3}$) |
| $t$    | time (s) |
| $T$    | temperature (K) |
| $\bar{u}$ | velocity (m s$^{-1}$) |
| $V$    | electric potential (V) |
| $W$    | molar mass (kg mol$^{-1}$) |
| $x_i$  | mole fraction of species $i$ |
| $Y_i$  | mass fraction of species $i$ |

Greek

| Symbol | Definition |
|--------|------------|
| $\alpha$ | transfer coefficient or permeability (m$^2$) |
| $\varepsilon$ | porosity |
| $\eta$ | polarization voltage (V) |
| $\sigma$ | conductivity (S m$^{-1}$) |
| $\lambda_{\text{eff}}$ | thermal conductivity (W m$^{-1}$ K$^{-1}$) |
| $\mu_s$ | dynamic viscosity (Pa s) |
| $\xi$ | emissivity |
| $\rho$ | density (kg m$^{-3}$) |

Subscripts and Superscripts

| Symbol | Definition |
|--------|------------|
| an     | anode |
| DIR    | direct internal reforming |
| eff    | effective |
| el     | electronic |
| ion    | ionic |
| irr    | irreversible |
| ref    | referenced |
| rev    | reversible |
| s      | solid |
| trans  | transfer |
| TPB    | triple phase boundary |
| WGS    | water gas shift |
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