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The Performance of Syngas-Fueled SOFCs Predicted by a Reduced Order Model (ROM): Temperature and Fuel Composition Effects

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Solid oxide fuel cells (SOFCs) offer high efficiency pathways to producing electricity from fuels.^{1–4} Systems are being developed for a variety of applications, operating on a range of fuels from hydrogen to natural gas to syngas.^{5–9} Computational models that can accurately describe the gas phase reactions, electrochemistry, and the heat and mass transfer within SOFC cells and modules are an invaluable tool for the design of efficient and cost-effective systems.^{10–17}

Models described in the open literature can be generally grouped into three categories - classical semi-empirical models, full-order models (FOM) and reduced-order models (ROM). The categories differ in how they manage the trade-off between accuracy and computational effort. Semi-empirical models estimate the cell voltage by subtracting the overpotentials resulting from activation, ohmic and concentration polarizations from the Nernst potential.¹⁸ Three major simplifications are typically used: 1) the Butler-Volmer equations are approximated by either linear or Tafel equations; 2) the concentration overpotential is correlated to gas diffusion using empirical or semi-empirical relationships; and 3) the model ignores cell geometry. These approximations simplify the analysis, but have several drawbacks: 1) coupling between the gas diffusion and activation/concentration losses is ignored, which is particularly problematic for systems using syngas fuel; 2) the exchange current density at the triple-phase-boundary (TPB) is more complicated for multi-step elementary reactions, also problematic for systems in which chemical reactions such as reforming or water-gas-shift are occurring; and 3) the limiting current density is obtained by an empirical relation, which means the effects of cell and stack design are not always captured accurately.

Full order models were first introduced in the 1990s.¹⁹ These approaches include all the relevant physical and chemical processes in the cell, including gas diffusion through the porous electrodes, mass and momentum conservation in the channels, charge transport within electrodes and the electrolyte as described by Ohm's law, and charge-transfer kinetics as described by the Butler-Volmer equation. Early versions described the H₂ electro-oxidation reaction using global reactions by a finite volume method.^{19,20} More recent FOMs have incorporated the microscale elementary reactions occurring near TPBs with cell performance.^{21–23} FOM approaches offer the highest resolution and accuracy (short of complete 3-D models), but are more computationally expensive than semi-empirical approaches, which could be an issue when applied to 3D SOFC stack simulations.

Reduced order models attempt to retain much of the accuracy of FOMs while reducing the computational burden. This is accomplished in several ways. A common approach is to simplify the physics, such as the gas diffusion or the electrochemical reactions. Specifically, the diffusion could be simplified to a single dimension, typically in the flow direction^{24–27} or anode-thickness direction.^{28–31} This captures some of the physics due to 1D gas diffusion and heterogeneous reactions at the solid/gas interfaces, while significantly reducing the computational effort required. Another more widely used approach to reducing the model order is by projection-based mathematical reduction, in which a set of data is mapped into sub-set with certain accuracy. One interesting ROM developed in this way by PNNL³² uses a sub-model to predict the performance and response of a SOFC stack. The sub-model was constructed using a simple empirical relationship generated from sampling a limited number of input parameters, ranking of input parameters, constructing relations between inputs and outputs, and studying sensitivity of inputs in different regions. Such an approach can be used to rapidly explore performance under specific scenarios to aid in the design process. Here, we use the first approach to developing ROMs, but instead of simplifying the diffusion procedure, we lowered the order of model by reducing the electronic/ionic charge transfer and the electrochemical reactions from the 3D electrode domains to the 2D electrode/electrolyte interface. Meanwhile, the electrolyte is treated as an interface between anode and cathode by a pure ionic resistor. Since the concentration of gas species varies significantly along the direction of gas flow and thickness, the 3D diffusion feature in the electrode domains is kept in this study for further development of stack model.

ROMs have been used successfully to explore the competition between different physical processes. Friedrich et al.^{33,34} developed a ROM that includes detailed H₂-oxidation elementary reactions for coupled charge-transfer and surface chemistry in the anode, and gas diffusion in the flow direction and cell thickness direction were decoupled and calculated separately. Another ROM developed by Campanari et al.³⁵ simulated the combined electrochemical oxidation of CO and H₂ (relevant to this work) with the assumption that exchange current density for CO oxidation is 0.4 times the H₂ oxidation without validation and the diffusion through the thickness was significantly simplified. Further progress can be made in several areas to increase the utility of ROMs, particularly for hydrocarbon or syngas fuels. First, additional experimental validation is needed to further demonstrate the usefulness of ROMs. Second, ROMs can be extended to explore the competition between direct electrochemical oxidation of

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Figure 1. Anode-Supported Planar Solid Oxide Fuel Cell simulated in this model: (a) Schematic illustration; (b) Computational domain ($z = 0$, cathode/anode interface).

fuel and indirect oxidation of fuels through chemical conversion to form hydrogen. This second issue is of particular interest in practical systems where the relative importance of internal reforming or water-gas-shift reactions can vary through the stack.

In this paper, we address these issues by developing a ROM for anode-supported SOFCs. We begin with a derivation of the ROM, and validate it using experimental data from the literature. We then explore the impact of syngas composition and temperature on the relative importance of direct and indirect oxidation modes. This paper is the first of a series of papers, aiming to lay the ground for systematically investigating the effects of pressure, temperature-field coupling and flow patterns on the performance of commercial-size planar SOFC stacks operated on syngas fuel.

Description of the Model

The SOFC modeled in this study is an anode-supported thin-film cell in a planar geometry. Figure 1 is a schematic illustration showing the cell, the computational domains, and some of the relevant electrochemical and chemical reactions. The materials of anode, electrolyte and cathode are YSZ/Ni, YSZ and LSCF, respectively. The fuel supplied to anode is a mixture of CO and H₂ with a certain composition (2:1, 1:1, 1:2) and temperature (700, 750, 800°C). There are three assumptions made in our ROM: 1) the electrolyte is a pure ionic resistor; 2) the role of the cathode/electrolyte buffer layer in electrochemical reaction is neglected; 3) all the electrochemical reactions occur at electrode/electrolyte interface, rather than a domain with a definitive thickness; and 4) temperature is uniform across the cell.

In the anode, H₂/H₂O/CO/CO₂ multi-species gas diffusion, water gas shift (WGS) reaction are coupled with the electrochemical oxidation of H₂ and CO at the anode/cathode interface. In the cathode, O₂/N₂/H₂O multi-species gas diffusion is correlated with the oxygen reduction reaction at the cathode/anode interface. The inlet gas species concentration is assumed to be uniform at the electrode/current collector interface. Such boundary conditions enable us to focus on the gaseous species profiles in the z -direction (thickness direction), even though the computational domain is still 3D. In the future work, channels will be added to study the profile along the gas flow direction. Since the cell is typically operated under 75% fuel utilization or higher in stacks, the concentrations of gas species vary in the thickness as well as flow channel directions, which will result in the cell performance variation in three-dimensional space.

Reduced order model for electrochemistry.—One purpose of this paper is to demonstrate the usefulness of a ROM for simulating electrochemical reactions so that it can be used to reduce the computational expense of future studies involving large SOFC stack modeling. The

ROM simulation was performed with a goal of studying the effects of fuel composition and temperature on cell performance in this study.

At a given current density, the operating cell voltage (V_{cell}) is the difference between the thermodynamic reversible cell potential (E_{rev}) and overpotentials (η):

$$V_{cell} = E_{rev} - \eta_a - \eta_c - \eta_{el} \quad [1]$$

where η_a , η_c , and η_{el} are the activation overpotentials at the anode and cathode, and ohmic overpotential in the electrolyte, respectively; E_{rev} is the thermodynamic reversible potential, or open circuit voltage of the cell, which can be expressed by

$$E_{rev} = E_0 + \frac{RT}{2F} \ln \left(\frac{p_{H_{2,a}}}{p_{H_{2,O_a}}} \right) + \frac{RT}{4F} \ln \left(\frac{p_{O_{2,c}}}{p_0} \right) \quad [2]$$

where, $p_{H_{2,a}}$, $p_{H_{2,O_a}}$, are the respective partial pressures of H₂ and H₂O. Note that the partial pressures of H₂ and H₂O are assumed to be in thermodynamic equilibrium with those of CO and CO₂ under the open circuit condition. It can, therefore, also be expressed by a similar equation, but with H₂ and H₂O being replaced by CO and CO₂, respectively. $p_{O_{2,c}}$ is partial pressure of oxygen at the interface; $p_0 = 1$ atm is the reference pressure in calculating standard reversible cell potential E_0 .

The anode activation overpotential η_a is related to the total currents produced by both H₂ and CO electro-oxidation, which are detailed in section Mechanisms of hydrogen electro-oxidation and Mechanisms of carbon monoxide electro-oxidation. The cathode activation overpotential η_c is a function of oxygen reduction reaction rate and is discussed further in section Mechanisms of oxygen reduction reaction. At a certain location, the total local current density i and partial currents associated with H₂ ($i_{H_{2,a}}$) and CO ($i_{CO,a}$) electro-oxidation in the anode and O₂ ($i_{O_{2,c}}$) electro-reduction in the cathode follows:

$$i = i_{H_{2,a}} + i_{CO,a} = i_{O_{2,c}} \quad [3]$$

Note that all the currents are treated as scalars in Eq. 3. However, in computation the positive current flows from the anode to the electrolyte, and then from the electrolyte to the cathode. The ohmic overpotential is related to the ionic conductivity and thickness of the electrolyte by:

$$\eta_{el} = i R_{el} = \frac{i L_{el}}{\sigma_0 \exp(-E_{el}/RT)/T} \quad [4]$$

where L_{el} is the electrolyte thickness, (m); σ_0 is the pre-factor in Arrhenius relationship of ionic conductivity (S · K/m); i is the total local current density, (A/m²); E_{el} is the activation energy of the ionic conductivity, (J/mol); T is temperature, (K). At a given voltage, the local overpotentials and current density can be solved by Eqs. 1 and 3 at the anode/cathode interface.

Figure 2. Heterogeneous elementary charge-transfer reaction steps including H_2 oxidation, CO oxidation and O_2 reduction, as well as WGS reaction in the gas phase of the anode.

Mechanisms of hydrogen electro-oxidation.—Electro-oxidation of syngas is expected to occur through the co-electro-oxidation of H_2 and CO. The H_2 electro-oxidation is modeled by five elementary hydrogen spillover steps,^{27,36,37} as shown in Fig. 2. The five elementary steps of H_2 electro-oxidation are:

Adsorption of H_2 on nickel:

Transfer of O^{2-} from bulk to surface YSZ sites:

Charge-transfer reactions at the TPB (YSZ/Ni/gas):

Desorption of H_2O from YSZ:

In the above five elementary steps, $\text{H}(\text{Ni})$ is an adsorbed hydrogen atom; (Ni) is an empty surface site on Ni-surface, $e^-(\text{Ni})$ represents electrons in the Ni phase. Within the YSZ phase in the anode, $\text{O}^{2-}(\text{YSZ})_b$ and $(\text{YSZ})_b$ represent lattice oxygen and YSZ site in the YSZ phase. On the YSZ surface, there are three species, $\text{O}^{2-}(\text{YSZ})_s$, $\text{OH}^-(\text{YSZ})_s$ and $\text{H}_2\text{O}(\text{YSZ})_s$ considered, along with empty YSZ-sites $(\text{YSZ})_s$.

It has been previously reported that the second charge-transfer step (H4) is rate-limiting at lower current densities, and the hydrogen adsorption step (H1) becomes rate-limiting at higher current densities. Therefore, at lower current densities, the Butler-Volmer equation governs Reaction H4, and can be given by:²⁷

$$i_{\text{H}_2, \text{H4}} = i_{\text{H4}}^0 \left[\exp\left(\frac{1.5F\eta_a}{RT}\right) - \exp\left(-\frac{0.5F\eta_a}{RT}\right) \right] \quad [5]$$

where, $i_{\text{H4}} = i_{\text{H4}}^0 \frac{(p_{\text{H}_2\text{O}}/p_0)^{3/4} \cdot (p_{\text{H}_2}/p_{\text{H}_2,0})^{1/4}}{1 + (p_{\text{H}_2}/p_{\text{H}_2,0})^{1/2}}$, $p_{\text{H}_2,0} = \frac{A_{\text{des}} \Gamma^2 \sqrt{2\pi RT M_{\text{H}_2}}}{\gamma_{\text{H}_2}} \times \exp\left(-\frac{E_{\text{des}}}{RT}\right)$, the meanings and values of these parameters are given in

Table IV. It is worthy to mention that the expression for i_{H4} derived by Zhu²⁷ has an error in defining the reference current density. We introduced $p_{\text{H}_2,0}/p_0$ term to make the whole fraction term dimensionless. $p_{\text{H}_2,0} = 1/K_{\text{H1}}$, K_{H1} is the equilibrium constant of the hydrogen atom adsorption Reaction H1. As the activation energy for desorption reaction E_{des} is positive (see Table IV), a higher temperature will lead to a lower K_{H1} and higher $p_{\text{H}_2,0}$.

At higher current densities, the hydrogen adsorption step (H1) becomes rate-limiting, resulting in the following Butler-Volmer expression:²⁸

$$i_{\text{H}_2, \text{H1}} = i_{\text{H1}} p_{\text{H}_2} \left[1 - \exp\left(-\frac{2F\eta_a}{RT}\right) \right] \quad [6]$$

where, $i_{\text{H1}} = \frac{a_{\text{TPB}}(2F)\gamma_{\text{H}_2}}{\sqrt{2\pi M_{\text{H}_2}} RT}$; the meanings and values of these parameters are given in Table IV.

In our model, the switch-over from elementary Reaction H4 to H1 as the rate-limiting step occurs when the current predicted by Eq. 6 becomes less than the current predicted by Eq. 5 using the following function:

$$i_{\text{H}_2}^0 = \min\{i_{\text{H}_2, \text{H1}}, i_{\text{H}_2, \text{H4}}\} \quad [7]$$

Finally, temperature can also contribute to the current density by affecting the exchange current density through the activation energy $E_{\text{act},a}$, which is a combined effect resulted from different reactions. The value of $E_{\text{act},a}$ is selected based on the experimental data reported in Ref. 38.

$$i_{\text{H}_2} = i_{\text{H}_2}^0 \exp\left(-\frac{E_{\text{act},a}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad [8]$$

where $T_0 = 800^\circ\text{C}$, and $i_{\text{H}_2}^0$ is the current density at T_0 .

Mechanisms of carbon monoxide electro-oxidation.—We expect two pathways for the electro-oxidation of CO. First, CO can be directly consumed at the anode. Here, we use the global reaction to simulate CO electro-oxidation, as shown in Fig. 2:

Table I. Gas diffusion equations and variables.⁴¹

Domain	Governing equation	Dependent variable
SOFC cathode pores	$\nabla \cdot \left(-\rho \omega_i \sum_{j=1}^3 D_{ij}^{eff} \left(\frac{M_j}{M_i} \left(\nabla \omega_j + \omega_j \frac{\nabla M}{M} \right) \right) \right) = R_i \quad \omega_3 = 1 - \sum_{i=1}^2 \omega_i \quad (i = 1, 2)$	$\omega_1, \omega_2, \omega_3$
SOFC anode pores	$\nabla \cdot \left(-\rho \omega_i \sum_{j=4}^6 D_{ij}^{eff} \left(\frac{M_j}{M_i} \left(\nabla \omega_j + \omega_j \frac{\nabla M}{M} \right) \right) \right) = R_i \quad \omega_7 = 1 - \sum_{i=4}^6 \omega_i \quad (i = 4, 5, 6)$	$\omega_4, \omega_5, \omega_6, \omega_7$

The Butler-Volmer equation governing CO electro-oxidation is given by:^{38,39}

$$i_{CO} = i_{CO}^0 \exp \left(-\frac{E_{act,a}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right) \cdot p_{CO}^{0.75} \cdot p_{CO_2}^{0.25} \times \left[\exp \left(\frac{0.5F\eta_a}{RT} \right) - \exp \left(-\frac{1.5F\eta_a}{RT} \right) \right] \quad [9]$$

Here, η_a is the same as that in Section Mechanisms of Hydrogen Electro-Oxidation because all the gas species are assumed to be in equilibrium under the open circuit condition, i_{CO}^0 is the exchange current density given in Table IV.

A second pathway for CO electro-oxidation involves conversion of $CO + H_2O$ to $H_2 + CO_2$ through the water gas shift reaction (WGS). Although both H_2 and CO electro-oxidation may occur simultaneously in the syngas-fueled SOFC, the faster kinetics of electro-oxidation for H_2 over CO is expected to deplete H_2 within the anode. This promotes the forward WGS reaction $CO_2 + H_2O = CO_2 + H_2$ to consume CO and produce H_2 , which can subsequently be electro-oxidized. The kinetics of the WGS reaction will be covered in a later section.

Mechanisms of oxygen reduction reaction.—The overall oxygen reduction and incorporation at the electrode-electrolyte interface can be represented by:^{27,36}

where, $O^{2-} (YSZ)$ denotes the oxygen ion in YSZ electrolyte, $e^- (LSCF)$ is the electron in the LSCF cathode. It is assumed that the oxygen reduction proceeds in two steps, as shown in Fig. 2:

1) Adsorption/dissociation:

2) Charge-transfer and incorporation at the TPB:

$O_{ad}(LSCF)$ and $(LSCF)$ are the adsorbed oxygen atom on the LSCF cathode surface and the unoccupied LSCF cathode surface site, respectively. The current density is rate-limited by the charge-transfer Reaction O2, and can be expressed by:^{27,40}

$$i_{O_2} = i_c^0 \exp \left(-\frac{E_{act,c}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right) \times \left[\exp \left(\frac{0.5F\eta_c}{RT} \right) - \exp \left(-\frac{0.5F\eta_c}{RT} \right) \right] \quad [10]$$

where, $i_c^0 = i_{O_2} \frac{(p_{O_2}/p_{O_2,0})^{1/4}}{1+(p_{O_2}/p_{O_2,0})^{1/2}}$, $p_{O_2,0} = A_{O_2} \exp \left(-\frac{E_{O_2}}{RT} \right)$; parameters are given in Table IV.

Chemical reactions in the porous anode.—In addition to the electrochemical reactions at the interface, the WGS reaction takes place in the pores of the anode simultaneously, as shown in Fig. 2:

Table II. Associated parameters used in the gas diffusion model.

Source terms/Parameters	Mathematical expressions
Binary diffusion	$D_{ij} = k \frac{T^{1.75}}{p(v_i^{1/3} + v_j^{1/3})^2} \left[\frac{1}{M_i} + \frac{1}{M_j} \right]^{1/2}$
Knudsen diffusion	$D_{Kn,i} = \frac{d_{pore}}{3} \sqrt{\frac{8RT}{\pi M_i}}, d_{pore} = \frac{2}{3} \frac{ed_p}{1-\epsilon}$
Average Bosanquet diffusion coefficient	$D_{ij}^{eff} = \frac{1}{2} \left(\frac{1}{\frac{1}{D_{ij}} + \frac{1}{D_{Kn,i}}} + \frac{1}{\frac{1}{D_{ij}} + \frac{1}{D_{Kn,j}}} \right)$
Source term at the electrode/electrolyte interface	$R_i = \frac{s_{ij} M_i}{nF}$
Source term in the electrode	$R_i = s_{ij} r_{bj} M_i$

Table III. Boundary conditions used in the model.

Boundary	Stefan-Maxwell diffusion
Dependent Variable	ω_j
Cathode/CC interface	$O_2:N_2:H_2O = 0.21:0.76:0.03$
Cathode/electrolyte interface	$-\underline{n} \cdot \underline{N}_i = 0$
electrolyte/Anode interface	$-\underline{n} \cdot \underline{N}_i = 0$
Anode/CC interface	$H_2:H_2O:CO:CO_2 = 0.5:0.02:0.5:0.02071$
Other surfaces	$-\underline{n} \cdot \underline{N}_i = 0$

Note: $\underline{N}_i = -\rho \omega_i \sum_j D_{ij}^{eff} \underline{d}_j + \rho \omega_i \underline{d}_j = \left(\frac{M_j}{M_i} (\nabla \omega_j + \omega_j \frac{\nabla M}{M}) \right)$;

CC represents current collector.

The WGS reaction catalyzed by Ni in the anode electrode can convert $H_2O + CO$ into $H_2 + CO_2$. This provides a second, indirect pathway for CO electro-oxidation. Its reaction rate is given by:²⁶

$$r_{b,wgsr} = k_{sf} \left(p_{H_2O} p_{CO} - \frac{p_{H_2} p_{CO_2}}{K_{ps}} \right) \quad [11]$$

where, $K_{ps} = \exp(-0.2935Z^3 + 0.6351Z^2 + 4.1788Z + 0.3169)$, $Z = \frac{1000}{T(K)} - 1$, $k_{sf} = 0.0171 \exp(\frac{-103191}{RT}) (mol \cdot m^{-3} \cdot Pa^{-2} \cdot s^{-1})$.

Gas diffusion in porous electrodes.—The well-known Stefan-Maxwell formula is used to calculate the diffusion of multiple gas species in the porous electrode media. In the model, we coupled the gas diffusion with the electrochemical reactions at the interface and chemical reactions within electrodes. The governing equations and dependent variables for each domain are given in Table I. The source terms and associated parameters are listed in Table II, whereas the boundary conditions are listed in Table III.

Computational method.—There are a total of 9 dependent variables in the model, including the overpotential η_a and η_c , mass fraction of the gas species, ω_j ($\omega_1, \omega_2, \omega_3$ in the cathode, $\omega_4, \omega_5, \omega_6$, and ω_7 in the anode). By combining Stefan-Maxwell diffusion equations in each electrode with the electrochemical Equations in Eqs. 1 and 3, as well as the chemical rate equations in Eq. 11, those variables are solved simultaneously.

The model was solved by Finite Element Method, which was performed with a commercial software package COMSOL Multiphysics 5.3 using a workstation equipped with an Intel Core i7-4700MQ

Figure 3. Validation of the model by experimental data.⁴²

processor @2.4GHz and 2.39GHz and 16GB of RAM. Transport of Concentrated Species module, and Boundary ODEs are utilized as the governing equations. The numeric solution was approximated by a set of quadratic basic functions. The computational domain was discretized by swept mesh, and refined until a converged solution was reached. The Direct Solver was applied to solve the stationary study of the problem. The relative tolerance is set to 0.001, and the maximum number of iterations is 150.

Validation.—We used SOFC testing results from a relevant study using syngas as the fuel to validate our model.⁴² Data from three gas compositions, i.e. $H_2/CO = 20:80$, $32:68$, $45:55$, was used. The results are shown in Fig. 3, where the model predictions are co-plotted with the experimental VI data at $H_2/CO = 20:80$, $32:68$ and $45:55$. The R-square values were 0.98, 0.99 and 0.94, respectively. It indicates that the model predictions show a better accuracy at higher H_2 composition. With higher CO composition, the CO direct oxidation starts to play a role in the total current. To reduce computational expense, we used the global CO direct oxidation kinetics, which could be the reason for the slightly lower R-square.

There are some early studies that have also used the same set of data to validate their models. For example, Ong et al. stated that the predictions of the combined H_2 and CO direct oxidation model agree well with experimental data over a wide range of H_2/CO mixture.³⁰ However, the authors did not give the accuracy of each predicted curve. The model seemed to produce comparable fitting results at $H_2/CO = 20:80$ to those presented in this study, but the deviation between the modeled and experimental results were higher at high H_2 ratio and low cell voltage, especially when H_2 concentration is more than 32% and cell voltage is lower than 0.5V. In contrast, our model gives a better prediction at higher H_2 in the entire range of voltage. It is believed that the difference is caused by the divergent CO direct oxidation mechanisms in the two studies.

Overall, a reasonably good agreement has been reached between experimental data and model predictions. Under these cases, H_2 electro-oxidation dominates the performance of the cell at low currents, and hydrogen adsorption reaction takes over at high currents. The parameters extracted from the validation are used in the model and listed in Table IV.

Results and Discussions

The validated model was used to investigate the effects of fuel composition and temperature on the cell performance. The current density was evaluated by the interface-integration-average method. Because of the anode-supported design, significant activation/concentration

overpotential in the thick anode layer can develop under some operating conditions. Therefore, only the profile of each gas species within the anode layer is plotted along the thickness. As shown in Fig. 1b, the electrochemical reaction interface is located at $z = 0$; $z = 1.1\text{mm}$ corresponds to the anode/current-collector interface. Also, since the Nernst potential of Eq. 2 depends on the local fuel and oxygen concentrations at the anode/cathode interface, the concentration overpotential is excluded from the Nernst potential. The details on this justification are given in Appendix A.

Fuel composition effects.—In this section, we investigate the effect of different fuel compositions at 800°C . Specifically, we compute the current contribution from both H_2 and CO direct oxidation, as well as the equivalent current from the water gas shift reaction, along with the concentration distributions of gaseous species in the anode.

Effect on electrochemical performance.—From the ROM presented in section Reduced order model for electrochemistry, the Nernst potential of the cell, Eq. 2, and the local current density Eqs. 7, 9 and 10, the rates of chemical reactions of Eq. 11, and the gas diffusion rates shown in Table I, are all dependent of the H_2/CO partial pressures. Varying the fuel composition will impact the performance of a cell. Figure 4a shows the predicted V-I curves at 800°C under different $CO:H_2$ ratios, 2:1, 1:1, 1:2. The cell current density is seen to increase with H_2 concentration, especially at lower cell voltage. Taking $V_{\text{cell}} = 0.7\text{V}$ as the benchmark operating voltage for commercial cell, the projected current density increases from 13969A/m^2 at $CO:H_2 = 2:1$ to 16766A/m^2 at $CO:H_2 = 1:2$, a 20% improvement. Increasing the $CO:H_2$ ratio also significantly increased diffusion-controlled limiting current density, from 29892A/m^2 to 43076A/m^2 . A 44% enhancement was observed when the feed concentration of H_2 was increased from 33% to 67%.

Figure 4b shows the current contribution from the CO-oxidation vs total current. The CO contribution was less than 14% in maximum, for all voltages calculated. This confirms the dominance of the H_2 -oxidation kinetics in the overall current density. A minimum CO/total current ratio corresponding to an onset voltage was observed. This is related to the switch-over voltage for H_2 direct electro-oxidation, which follows different current-overpotential relationship according to Eqs. 5 and 6. Above this threshold voltage, the current density increases exponentially with overpotential (Eq. 5). Below the threshold, the current density response is flatter because of the adsorption mechanism (Eq. 6) and more CO direct oxidation due to the increased CO/H_2 ratio. It is also noticed that the switch-over voltage decreases with H_2 concentration. For example, at 0.7V and $CO:H_2 = 2:1$, the total current density is 13969A/m^2 , in which only 757A/m^2 or 5.4% is from CO-oxidation; at 0.3V and $CO:H_2 = 2:1$, the total current density is 29892A/m^2 , in which 4071A/m^2 or 14% is from CO-oxidation; at the same 0.3V but $CO:H_2 = 1:2$, the total current density is 43076A/m^2 , in which 1385A/m^2 or only 3.2% is from CO-oxidation. Since the operating voltage of a practical SOFC is usually controlled at 0.7V , the overall current density is mainly produced by the H_2 oxidation reaction; most of CO indirectly contributes to the current through WGS reaction.

These predictions are in agreement with the results of Campanari et al.,⁴⁵ in which CO oxidation contributed to 7% of the overall voltage at atmospheric pressure. Ghoniem³⁰ predicted 13% and 34% CO direct oxidation for $54\%H_2:46\%CO$ and $20\%H_2:80\%CO$ at a cell voltage of 0.4V and 0.6V , respectively. The higher ratio of CO direct oxidation involvement is resulted from two sources: 1) higher operating current density (meaning lower operating voltage); 2) higher content of CO in the fuel. Above 0.6V , the current contribution from CO direct oxidation is negligible, which is consistent with our predictions.

To further understand the fundamental reasons of the cell performance variation under different fuel compositions, the cell Nernst potential and overpotentials are plotted as a function of current density in Fig. 5. As indicated in Section reduced order model for electrochemistry, under the open circuit condition, all the gas species are assumed to be in equilibrium. Therefore, the

Table IV. Parameters used in the model.

Parameter	Value	Reference
Test conditions		
Temperature, T_0	800(°C)	-
Fuel composition	$H_2:H_2O:CO:CO_2 = 0.5:0.03:0.5:0.02071$	Initial Equilibrium
Cell features		
Thickness of Electrolyte, L_{el}	25(μm)	35,42
Thickness of Anode, L_a	1.1(mm)	35,42**
Thickness of Cathode, L_c	30(μm)	35,42
Cross section dimension, $H \times W$	70(mm) $\times$ 70(mm)	43
Tortuosity, Anode/Cathode	3.4/4.0	35
Porosity, Anode/Cathode	0.54/0.5	35,42**
Diameter of spherical particle, Anode/Cathode, d_p	1(μm)	35
Electrochemical reaction parameters		
Sticking Coefficient of H_2 on Ni, γ_{H_2}	0.01	27
Pre-exponential factor, A_{des}	$5.59 \times 10^{19} (s \cdot cm^2/mol)$	27
Surface site density, Γ	$2.6 \times 10^{-9} (mol/cm^2)$	27
Activation energy of hydrogen desorption rate, E_{des}	88.12(kJ/mol)	27
Exchange current density pre-factor, $i_{H_4}^0$	$8.69 \times 10^4 (A/m^2)$	*
Nominal TPB area, a_{TPB}	0.009	*
Pre-exponential factor, A_{O_2}	$4.9 \times 10^8 (atm)$	37
Activation energy of oxygen reduction reaction rate, E_{O_2}	200(kJ/mol)	37
Exchange current density pre-factor, i_{O_2}	$2.8 \times 10^4 (A/m^2)$	37
Reference exchange current density for CO electro-oxidation, $i_{0,CO}$	$0.5 \times 10^4 (A/m^2)$	*
Activation energy of anode, $E_{act,a}$	62[kJ/mol]	38
Activation energy of cathode, $E_{act,c}$	110[kJ/mol]	40
Pre-factor in Arrhenius relationship of ionic conductivity, σ_0	$3.6 \times 10^7 (S \cdot K/m)$	36
Activation energy of ionic conductivity E_{el}	$8 \times 10^4 (J/mol)$	36
Diffusion parameters		
Reference diffusivity, k	$3.16 \times 10^{-8} (m^2/s)$	44
Kinetic volume of O_2 , v_{O_2}	16.6×10^{-6}	44
Kinetic volume of N_2 , v_{N_2}	17.9×10^{-6}	44
Kinetic volume of H_2O , v_{H_2O}	12.7×10^{-6}	44
Kinetic volume of H_2 , v_{H_2}	6×10^{-6}	44
Kinetic volume of CO_2 , v_{CO_2}	26.9×10^{-6}	44
Kinetic volume of CO, v_{CO}	18.9×10^{-6}	44
Kinetic volume of CH_4 , v_{CH_4}	25.14×10^{-6}	44

*are parameters adjusted in the fitting procedure.

**The anode thickness and porosity are selected based on button-cell experimental data from Reference 42 and 35, where the key model parameters are extracted. The tortuosity is taken as the inverse of porosity square. These values may be different from others used in commercial anode-supported planar SOFCs. However, the established model is not limited to this thickness and porosity. It can be readily applied to any other anode-supported planar cells with any thickness and porosity.

Figure 4. (a) Cell voltage as a function of current density; (b) Ratio of CO current vs total current (%) as a function of cell voltage under different fuel compositions at 800°C.

Figure 5. (a) Nernst potential; (b) Overpotential as a function of total current density under different fuel compositions at 800°C.

cell Nernst potential can be represented by H₂ oxidation reaction, Eq. 2. Figure 5a shows that the Nernst potential is increased by roughly 10 mV between any two fuel compositions, which is close to the value calculated by $\left(\frac{RT}{4F} \ln \text{Big}\left(\frac{p_{\text{H}_2,2}/p_{\text{H}_2,1}}{p_{\text{H}_2,0.2}/p_{\text{H}_2,0.1}}\right)\right)$ under a given current density. In addition, the range of operational current density under CO:H₂ = 1:2 is significantly broadened, which is consistent with the V-I curves shown in Fig. 4.

The reduced anode overpotentials at higher H₂ concentration are also an important source of performance improvement. This can be seen in Fig. 5b. As the partial pressure of H₂ increases, the anode overpotential is reduced significantly. For example, at CO:H₂ = 2:1, the highest anode overpotential is 0.24V at the highest current density, but that of the electrolyte and cathode at the same current density is similar, around 0.17V. At CO:H₂ = 1:2, the highest anode overpotential decreases dramatically to 0.137V at the highest current density, while that of the electrolyte and cathode is 0.25V and 0.23V at the same current density, respectively, becoming the major source of voltage losses. Another observation of the overpotential is that cathode and electrolyte overpotentials (Fig. 5b) show a more linear variation with current density for different fuel compositions, which is very different from the curved profiles of anode overpotential shown in Fig. 5b. The large deviations of anode overpotential at higher current density for different fuel compositions is resulted from the CO-oxidation reaction. Higher H₂ in the fuel leads to more significant contributions from the H₂-oxidation, and, therefore, better performance.

Effect on spatial distributions of gaseous species.—Since the concentration of gaseous species determines the electrochemical performance of a SOFC, we further explore how the fuel composition affects the concentration distribution of each active gaseous species in the anode, and eventually its influence on the V-I curves shown in Fig. 4.

Figure 6 shows the respective isothermal distributions of H₂, H₂O, CO and CO₂ molar fractions along the thickness of anode under different operating voltages for three fuel compositions: CO:H₂ = 2:1, 1:1, 1:2. For H₂-profile in the anode, there are two competing sources: electrochemical consumption at the interface and simultaneous production by WGS reaction. For the case of CO:H₂ = 1:2, Figure 6a shows that the large anode overpotential variation in Figure 5b arises from the decreased interfacial H₂ concentration (from 0.59 to 0.37) as the cell voltage is lowered from 0.9 to 0.3 V. For CO:H₂ = 2:1, the interfacial H₂ concentration and its variation (0.37@0.9 V, 0.27@0.3 V) are significantly lowered compared to that with CO:H₂ = 1:2. These trends are similar to those observed in Fig. 6c for the CO profiles. Specifically, the interfacial CO concentration

varies more significantly with CO:H₂ = 2:1. This is also consistent with faster H₂ consumption relative to CO. The corresponding H₂O and CO₂ concentration profiles shown in Figs. 6b and 6d confirm that at the same fuel composition, more H₂O and CO₂ are produced under a lower cell voltage 0.3V. The interfacial CO₂ and H₂O at 0.3V are 0.25 and 0.2, respectively. Note that we only observe 14% current contribution from CO-oxidation in Fig. 4. Such a high concentration of CO₂ and H₂O suggests a strong likelihood for the occurrence of WGS reaction. For all cases studied, the concentration profiles of all gaseous species for CO:H₂ = 1:1 reasonably lie in between those of CO:H₂ = 2:1 and 1:2.

Discussion.—To further confirm the importance of the WGS reaction, we calculated the WGS reaction rate. Figure 7a shows the WGS reaction rate across the anode thickness, as calculated from Eq. 11. The initial fuel composition is at equilibrium, which corresponds to no WGS reaction at the inlet. Under 0.9V, the high CO composition such as CO:H₂ = 2:1 results in a higher WGS reaction rate, 19 mol/m³/s, compared to 12 mol/m³/s with CO:H₂ = 1:2. Under 0.7V, it increases to 66 mol/m³/s for CO:H₂ = 2:1 and 36 mol/m³/s for CO:H₂ = 1:2, respectively. Under 0.3V, the highest WGS reaction rates were predicted. Surprisingly, the highest rates corresponded to the CO:H₂ = 1:1 composition, rather than CO:H₂ = 2:1, due to the competition between the WGS reaction and CO electro-oxidation reaction. The magnitude of the WGS reaction rate at ambient pressure was comparable to that reported by Campanari et al.⁴⁵

In Fig. 7b, the equivalent current density calculated by integrating the rate of WGS reaction, R_{WGS} , throughout the anode and then dividing by the cross-section area ($I_{\text{WGS}} = \frac{2F}{A} \int \int_{\text{Anode}} R_{\text{WGS}}$). In all cases, the equivalent WGS current was much higher than the CO direct oxidation current. As CO composition increases, with CO:H₂ = 2:1 at 0.3V for example, there is an inflection at high current density in V-I curve for the equivalent WGS current, suggesting the consumption of CO through WGS reaction becomes limited by the increased CO direct oxidation.

Temperature effects.—The effects of temperature on cell performance were studied at a fixing fuel composition of CO:H₂ = 1:1. Three temperatures are selected: 700, 750 and 800°C. The current contributions from different sources to the electrochemical performance of the cell at different temperatures are presented and discussed.

Effect on electrochemical performance.—Figure 8 shows the total current density and CO direct oxidation current density vs cell operating voltage under different temperatures. As the temperature increased from 700 to 800°C, both the total current density and

Figure 6. Distribution of molar fraction along the thickness of anode under different operating voltages and fuel compositions. (a) H₂; (b) H₂O; (c) CO; (d) CO₂

CO-oxidation current density increased. This was most pronounced at low operating voltage. For example, at 0.3V and 700°C, the total and CO-oxidation current densities are 18444 A/m² and 421 A/m², respectively; at 0.3 V and 800°C, they increased to 37395 A/m² (103% increase) and 1922 A/m² (356% increase), respectively. Therefore, higher operating temperature leads to an increased current contribution from CO-oxidation to the total current under low voltage, as shown in Fig. 8b.

However, a higher operating temperature has a negative impact on the cell Nernst potential as is seen in Fig. 9a. The cell performance improvement at higher temperatures results primarily from the reductions in activation overpotentials and ohmic overpotential. This can be seen in Figs. 9b, 9c and 9d. From Eq. 5, one can see that higher temperature will also negatively impact on current density by increasing the reference hydrogen partial pressure $p_{H_2,0}$. On the other hand, from Eq. 8, higher temperature will enhance the exchange current density by the Arrhenius activation term. Figure 9b shows that the Arrhenius term in Eq. 8 virtually dominates the anode overpotential variation with temperature. Under the same current density, 15000 A/m², the anode overpotential decreases from 0.075V @700°C to 0.05V @800°C. Similarly, the cathode O₂-reduction current density shown in Eq. 10 also experiences competing effects from the reference

O₂ partial pressure $p_{O_2,0}$ and the Arrhenius activation. Since the activation energy of cathode (110 kJ/mol) is much higher than that of the anode (62 kJ/mol), the dominance of the Arrhenius term is even more obvious. As shown in Fig. 9c, under 15000 A/m², the cathode overpotential decreases from 0.28V at 700°C to 0.1V at 800°C. The ohmic overpotential is correlated to temperature in Eq. 4. Its variation under 15000 A/m² is from 0.21V at 700°C to 0.09 V at 800°C, indicating a temperature dependence similar to that for cathode overpotential. The corresponding profiles of gaseous species concentration are given in Appendix B.

Figure 10a shows the WGS reaction rate through the thickness of anode under different temperatures with a fixed CO:H₂ = 1:1, where both high operating temperature and low operating voltage are shown to be beneficial for high WGS reaction rate. According to Eq. 11, increasing temperature from 700 to 800°C, the equilibrium constant K_{ps} will be decreased from 1.54 to 1.04. This will tend to drive the backward reaction. However, k_{sf} is promoted by temperature simultaneously from 508 mol/m³/s to 1660 mol/m³/s. Therefore, increasing temperature still enhances the WGS reaction rate. The equivalent current from WGS reaction is shown in Fig. 10b, which is significantly increased by temperature. For example, at 0.3V, the WGS-current increases from 3232 A/m² @700°C to 9778 A/m² @800°C, which

Figure 7. WGS reaction rate (a) along the thickness of anode; (b) WGS-reaction-equivalent current density $I_{wgs} = \frac{2F \int \int_{Anode} R_{wgs}}{A}$, under different fuel compositions @800°C.

Figure 8. (a) Cell voltage as a function of current density (b) Ratio of CO current vs total current (%) as a function of cell voltage under different temperatures with CO:H₂ = 1:1.

is a 202% increase. Therefore, temperature enhances both the direct oxidation of H₂ and CO, and the WGS reaction.

Discussion of composition and temperature combined effect.—

In the previous two sections, it was shown that higher CO ratio in the fuel and higher operating temperature both promote the direct CO oxidation, thus increasing the ratio of CO-current vs total current. In Fig. 4, the maximum ratio of 14% has been predicted at CO:H₂ = 2:1 and 800°C. If we further increase the CO composition in the fuel to 75% (CO:H₂ = 3:1), the WGS reaction equivalent current and CO direct oxidation current will be 8369 A/m² and 6023 A/m², respectively, as shown in in Fig. 11a, which suggests that the CO direct oxidation has been enhanced to 23% of the total current. Meanwhile, the WGS-reaction-equivalent current inflection under low cell voltage becomes more pronounced. This phenomenon is mainly resulted from the concentration-related term in the WGS reaction rate equation (Eq. 11) as shown in Fig. B2 of Appendix B. In other words, the WGS-reaction-

equivalent current-density inflection occurs when CO consumed by direct oxidation becomes comparable to that by the WGS reaction. In addition, it is worthy to point out that WGS-reaction-equivalent current-density does not necessarily represent the actual H₂ oxidation current, in which H₂ has been converted from CO. The purpose for this equivalent current-density is mainly for evaluating how additional CO oxidation pathway contributes to the total current as shown in Fig. 2.

In Fig. 11b, the total current and CO partial current at CO:H₂ = 3:1 and two different temperatures are further shown. The CO partial current contribution increases to 13% (700°C) and 23% (800°C) of the total current, respectively. Overall, it is safe to say that the higher the CO in the syngas, the more contribution of CO to the direct oxidation. At 0.7V (nominal operating voltage of SOFC), H₂ dominates the cell performance with an inlet H₂ composition at as low as 25%. Under the same fuel composition, temperature appears to have less influence on the CO partial oxidation current.

Figure 9. (a) Nernst potential; (b) Anode overpotential; (c) Cathode overpotential; (d) ohmic overpotential as a function of total current density under different temperatures with CO:H₂ = 1:1.

Figure 10. WGS reaction rate (a) along the thickness of anode; (b) WGS-equivalent current density $I_{wgs} = \frac{2F \int \int \int_{Anode} R_{wgs}}{A}$, under different temperatures at CO:H₂ = 1:1.

Figure 11. Total and CO partial current density with respect to cell voltage, (a) 800°C at different composition; (b) CO:H₂ = 3:1 at different temperatures.

Conclusions

In summary, we have demonstrated an electrochemical ROM coupled with bulk chemical reactions in anode and Stefan-Maxwell diffusion equations in each electrode to simulate the performance of syngas-fueled SOFC operated under various fuel compositions and temperatures. The model was validated using experimental V-I data obtained with syngas fuel. The model predicted an 8.7% current density contribution from CO-oxidation at 0.7V and CO:H₂ = 2:1. We further confirm that H₂ electro-oxidation dominates the overall cell performance while CO contributes to it mainly via WGS-equivalent current at H₂ inlet composition > 25%. By varying temperature from 700 to 800°C, the cell performance can be improved by 139% at CO:H₂ = 1:1. The major source for such an enhancement is from Arrhenius activation term in the exchange current density. From WGS reaction rate distribution along the anode thickness, it is also found that higher temperature and lower voltage can enhance WGS reaction to meet the high demand for the accelerated electrochemical oxidation of H₂.

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Appendix A: Concentration Overpotential

For a redox reaction:

Where O is the oxidized species and R is the reduced species. The current is proportional to the rate of Reaction A1. The reactions in the cathodic and anodic directions occur simultaneously, each with its own dependence on the surface overpotential and reactant concentrations.

Therefore, the current could be expressed as:

$$r = \frac{i_n}{nF} = k_a c_R \exp \left[\frac{(1-\alpha)nF}{RT} V \right] - k_c c_O \exp \left[\frac{-\alpha nF}{RT} V \right] \quad [A2]$$

where k_a and k_c are rate constants for the anodic and cathodic reactions, respectively, and c_R and c_O are the concentration of the anodic and cathodic reactants, respectively. This implies that the cathodic and anodic reactions are first order in the reactants. α is the symmetry factor, which represents the fraction of the applied potential V that promotes the cathodic reaction.

At some value of potential, the rate the forward reaction equals the rate of the backward reaction, and the net rate of reaction is zero, therefore Eq. A2 becomes,

$$k_a c_R \exp \left[\frac{(1-\alpha)nF}{RT} U \right] = k_c c_O \exp \left[\frac{-\alpha nF}{RT} U \right] \quad [A3]$$

Solving U from Eq. A3,

$$U = \frac{RT}{nF} \ln \frac{k_c c_O}{k_a c_R} \quad [A4]$$

The potential at which the net rate of reaction is zero is known as the equilibrium potential, and the surface overpotential η is defined as the difference between the actual potential and the equilibrium potential:

$$\eta = V - U \quad [A5]$$

Substituting Eqs. A4 and A5 into A3 yield,

$$\frac{i_n}{nF} = k_a c_R \exp \left[\frac{(1-\alpha)nF}{RT} \eta + (1-\alpha) \ln \frac{k_c c_O}{k_a c_R} \right] - k_c c_O \exp \left[\frac{-\alpha nF}{RT} \eta - \alpha \ln \frac{k_c c_O}{k_a c_R} \right] \quad [A6]$$

With the definition of η and the exchange current density i_0 defined as:

$$i_0 = nF k_a^\alpha k_c^{1-\alpha} c_R^\alpha c_O^{1-\alpha} \quad [A7]$$

Eq. A6 can be written as:

$$i_n = i_0 \left[\exp \left[\frac{(1-\alpha)nF}{RT} \eta \right] - \exp \left[\frac{-\alpha nF}{RT} \eta \right] \right] \quad [A8]$$

Eq. A8 is the Butler-Volmer equation when the equilibrium potential is defined based on the local reactants concentration. If one defines an equilibrium potential corresponded to a certain fuel composition, U_0 , as follows:

$$k_a c_R^0 \exp \left[\frac{(1-\alpha)nF}{RT} U_0 \right] = k_c c_O^0 \exp \left[\frac{-\alpha nF}{RT} U_0 \right] \quad [A9]$$

$$U_0 = \frac{RT}{nF} \ln \frac{k_c c_O^0}{k_a c_R^0} \quad [A10]$$

Then, the overpotential is defined as:

$$\eta_0 = V - U_0 \quad [A11]$$

Eqs. Substituting A10 and A11 into A3 yield,

$$i_n = nF k_a^\alpha k_c^{1-\alpha} (c_O^0)^{(1-\alpha)} (c_R^0)^\alpha \left\{ \left(\frac{c_R}{c_R^0} \right) \exp \left[\frac{(1-\alpha)nF}{RT} \eta \right] - \left(\frac{c_O}{c_O^0} \right) \exp \left[\frac{-\alpha nF}{RT} \eta \right] \right\} \quad [A12]$$

Defining a different exchange current density as:

$$i_{00} = n F k_a^{\alpha} k_c^{(1-\alpha)} (c_O^0)^{(1-\alpha)} (c_R^0)^{\alpha} \quad [\text{A13}]$$

Eq. A12 can be written as:

$$i_n = i_{00} \left[\left(\frac{c_R}{c_O^0} \right) \exp \left[\frac{(1-\alpha)nF}{RT} \eta_0 \right] - \left(\frac{c_O}{c_O^0} \right) \exp \left[\frac{-\alpha nF}{RT} \eta_0 \right] \right] \quad [\text{A14}]$$

The two overpotential defined in Eq. A5 and A11 are related by:

$$\eta_0 - \eta = \frac{RT}{nF} \ln \frac{c_O/c_O^0}{c_R/c_R^0} \quad [\text{A15}]$$

Therefore, the difference between those two overpotential is the concentration overpotential reference to the equilibrium potential defined in Eqs. A9 and A10. In other words, if we define the equilibrium potential as Eqs. A3 and A4, the current density expression becomes much simpler, as shown Eq. A8. Also, the concentration overpotential is 0 under such condition. Since we considered complex heterogeneous elementary reaction in this model, using the latter equilibrium potential could simplify the current density expressions.

Appendix B: Additional Figures

Figure B2. $(p_{H_2O} p_{CO} - \frac{p_{H_2} p_{CO_2}}{K_{ps}})$ of Eq. 11 along the thickness of anode under different voltage @CO:H₂ = 3:1 and 800°C.

Figure B1. Distribution of molar fraction along the thickness of anode under different operating voltages and temperatures with CO:H₂ = 1:1. (a) H₂; (b) H₂O; (c) CO; (d) CO₂.

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