DEVELOPMENT OF AN SOFC STACK PERFORMANCE MAP FOR NATURAL GAS OPERATION

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ABSTRACT

Successful commercial application of Solid Oxide Fuel Cell (SOFC) technologies will require selection of appropriate operating conditions. By varying operating conditions, a wide range of power and efficiency may be derived from an SOFC system. The operating parameters may be selected based on requirements for power, efficiency, or a function of both variables such as cost of electricity. The utility of a performance mapping, based on an isothermal closed form parametric performance model of a hydrogen fueled SOFC stack, has been demonstrated previously. The extension of this analysis methodology to include natural gas operation is shown. This model was applied to construct natural gas performance maps. The functional form of the model and the boundaries of the operating envelope provide useful insight into SOFC operating characteristics and a simple means of selecting conditions for natural gas operation.

INTRODUCTION

Ultimately, the power and efficiency delivered by a Solid Oxide Fuel Cell (SOFC) system is determined not solely by the stack characteristics, but together with the operating conditions. A wide range of power and efficiency figures can be generated from a particular SOFC device by the choices selected for stack temperature, fuel flow, and voltage. This fact poses the challenge to formulate SOFC power and efficiency relationships and to organize them in a meaningful form in terms of controllable operating parameters. Such relationships have been developed previously for stacks operated with hydrogen fuel.1 The additional analysis complexities introduced by natural gas operation are addressed.

It has been shown that the stack efficiency can be expressed simply in terms of operating voltage, fuel utilization, and thermoneutral voltage2.

\[ \eta_{\text{stack}} = \frac{V_{\text{op}} U}{E_m} \]  

(1)

Of these three factors, operating voltage is the only independent variable. Thermoneutral voltage is a property of the fuel defined as the heating value of the fuel divided by the number of Faradays of charge resulting from complete electrochemical oxidation of the fuel.
Utilization, defined as the ratio of delivered current to stoichiometric current, is an outcome that is dependent on stack resistance, operating voltage and fuel flow rate.

\[ U = \frac{I}{n n F} \]  

Given stack resistance and fuel composition, the only independent variables available to effect changes in power and efficiency are operating voltage and fuel flow rate. Stack resistance is of course a function of operating temperature. However, operating temperature is not considered as an independent variable here as it is assumed that to minimize resistance, the stack is operated at the highest temperature consistent with stack life and system balance of plant (BOP) constraints.

**SOFC PERFORMANCE MODEL**

Detailed stack models have been used to predict SOFC response to changes in operating conditions. Results from a number of cases may be assembled to construct performance maps. While these models provide detailed spatial resolution of processes and conditions in the stack, they are unnecessarily complex and cumbersome for operating point analysis and optimization. A more useful approach is to define relationships between fuel flow, area specific resistance, and operating voltage. These relationships can then be combined to create a closed form parametric model suitable for application in the construction of performance maps and operating point optimization and analysis. The functional form of the model and the boundaries of the operating envelope may provide useful insight into SOFC operating characteristics and an improved means of selecting operating conditions.

A useful metric is derived by casting fuel flow rate as an electrochemical term which represents the average current density required for 100% fuel utilization.

\[ j_f = \frac{n n F}{A} \]  

The driving voltage \( \Delta V_f \) which is the difference between the reversible potential \( E_n \) and operating voltage \( V_{op} \), required to sustain the full utilization current density can then be calculated using the stack area specific resistance (ASR, or \( R'' \)).

\[ \Delta V_f = j_f R'' \]  

At this point, the analysis is complicated somewhat by the fact that the reversible potential is not a constant value but a function of gas composition as given by the Nernst equation. The equation for \( E_n \) takes the familiar form.
In the case of an oxygen ion-conducting electrolyte such as an SOFC operating with hydrogen and oxygen, the oxygen concentration is that at the cathode, while hydrogen and water concentrations are those at the anode. In an operating fuel cell the concentration terms in [6] vary spatially. These concentrations also vary with gas flow rates and operating current. This expression is also valid for natural gas operation although it is complicated by reactions of hydrogen and water with methane, carbon monoxide and carbon dioxide. The reversible potential of a reformed natural gas stream could also be calculated based on the concentrations of carbon monoxide and carbon dioxide in the reformate stream.

\[
E_n = E' + \frac{RT}{2F} \ln \left( \frac{[H_2O]}{[H_2][O_2]^{1/2}} \right) \tag{6}
\]

These equations for the reversible potential yield identical results for gas mixtures in chemical equilibrium. This can be easily confirmed using the definition of the equilibrium constant and the fact that \( \Delta G \) is zero at equilibrium. Electrochemical oxidation of CO is possible, and likely occurs to some extent in SOFC operation using reformed hydrocarbon fuels. Fuel cells operated using mixtures of CO and CO\(_2\) have shown the electrochemical oxidation of CO to be an order of magnitude slower than that of hydrogen, as also reported by others.\(^5,6\) However, it is not necessary to distinguish whether the electrochemical oxidation step involves \( \text{H}_2 \) or CO in order to formulate a performance model as both equations 6 and 7 yield the same driving voltage from equilibrium gas compositions. Additionally, the electrochemical fuel value of CO is readily exchanged for hydrogen by the shift reaction as shown below.

A method of quantifying changes in reactant gas composition with electrochemical activity in the fuel cell is required in order to calculate a driving voltage using equation 6. Four reversible reactions are considered in this system, though only three are independent when used to define chemical equilibrium. They are the steam reforming,

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \tag{7}
\]

water gas shift,

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \tag{8}
\]

Boudouard,

\[
2\text{CO} \rightarrow \text{C} + \text{CO}_2 \tag{9}
\]
and cracking reactions.

\[ \text{CH}_4 + 2H_2 \]

The system of non-linear equations formed by setting the equilibrium constant equal to the equilibrium product stated in terms of initial concentrations, extent of reactions 7, 8 and 9, and electrochemically added oxygen (fuel utilization) was solved simultaneously with an iterative method for the equilibrium extent of reaction values. An example of the calculated equilibrium composition as a function of fuel utilization is shown in Figure 1. The coupling of CO and H\(_2\) concentrations by the shift reaction, which is fast in the presence of anode materials at SOFC operating temperatures, effectively enables the CO content of the fuel to be utilized in the fuel cell.

![Reformate Equilibrium](image)

**Figure 1.** Reformate equilibrium composition as a function of fuel utilization

Fortuitously, the equilibrium concentration dependence on fuel utilization appears to be linear. Rather than finding independent regression fits of both hydrogen and steam equilibrium concentrations as functions of fuel utilization, an effective utilization \( U^* \) was defined.

\[ U^* = \frac{[H_2O]}{[H_2O] + [H_2]} \]
The calculated equilibrium concentrations are closely approximated by a linear fit of the effective utilization to the actual utilization. The reversible potential can then be formulated as a function of the effective utilization.

\[
E_N = E^0 + \frac{RT}{2F} \ln \left( \frac{[U^*]}{[1-U^*[O_2]]^{1/2}} \right) \tag{12}
\]

An average reversible potential \( \bar{E}_N \), which accounts for fuel composition variation from inlet to exit, is needed in order to calculate an average current density.

\[
\bar{E}_N(U) = \frac{\int_0^U E_N(U) dU}{U} \tag{13}
\]

Integration of equation [12], substituting the linear fit for \( U^* \), yields a closed form expression for \( \bar{E}_N \). While the integral in [13] is easily evaluated to obtain \( \bar{E}_N(U) \), it is not possible to obtain the inverse function and explicitly solve for \( U \) given \( \bar{E}_N \). The need to solve explicitly for exit utilization \( U \) may be eliminated by creating a parametric representation in \( U \) and \( \Delta V_f \) rather than working directly with the true physical independent variables \( V_{op} \) and fuel flow \( \Delta V_f \). Recalling the meaning of the full utilization driving voltage defined in equation [5], the utilization can be given as

\[
U = \frac{\bar{E}_N(U) - V_{op}}{\Delta V_f} \tag{14}
\]

which may be solved to obtain an expression for \( V_{op} \) in terms of the parameters \( U \) and \( \Delta V_f \).

\[
V_{op} = \bar{E}_N(U) - \Delta V_f U \tag{15}
\]

Average current density is simply stated as

\[
j_i = \frac{\bar{E}_N(U) - V_{op}}{R''} \tag{16}
\]

It follows that the product of operating voltage [15] and current density [16] gives average power density. The expression for efficiency given in equation [1] is compatible with this parameterization, while none is needed for utilization. From these relations, a complete set of performance maps can be created showing efficiency, current density,
power density and utilization in the independent variable space \((V_{op}, \Delta V_f)\) representing operating voltage, ASR, fuel flow and composition.

**PERFORMANCE MAPS**

A map of SOFC performance measures was created in \((V_{op}, \Delta V_f)\) space using the approach described previously. These results are valid for any plug flow SOFC configuration (e.g. cross flow or counter flow) under isothermal conditions at 800°C. Inlet fuel composition was equilibrium for a steam to methane ratio of 2. The utilization parameter was varied from 0.3 to 0.98, while the \(\Delta V_f\) parameter (representative of fuel flow) varied from 0.1 to 0.7 volts. This map of efficiency, power density, current density and utilization in the \(V_{op}, \Delta V_f\) plane is shown in Figure 2.

The domain is bounded to the right (high operating voltage) by utilization falling below 30% and to the left (low operating voltage) by utilization exceeding 98%. Several interesting observations can be made by a thorough examination of this mapping. There are two operating regimes demarked by the kink in the high utilization boundary. At values

![SOFC Performance Map, H2O/CH4 = 2.0, 0.5 ohm-cm2](image)

**Figure 2. SOFC Performance Map, 800°C**
of $\Delta V_f$ less than about 0.2 volts, power is limited by fuel flow, while above 0.2 volts $\Delta V_f$, power becomes limited by resistance. The location of the transition is a function of ASR. Power drops approximately in half, from the point of maximum power to the point of maximum efficiency. Efficiency drops by a similar ratio between the high efficiency and high power points. At a constant fuel flow (lines of constant $\Delta V_f$), the operating voltage for maximum efficiency and maximum power coincide. Along a line of constant efficiency, maximum power is achieved at the greatest fuel flow ($\Delta V_f$) or lowest operating voltage ($V_{op}$) possible.

**CONCLUSIONS**

A judiciously selected operating point is essential to extracting the most value from an SOFC installation. The closed form parametric model presented in this paper can be used to create performance maps to aid the process of operating point selection. The form of the model and the boundaries of the performance maps also provide insight valuable in the selection process. A commonly stated goal of high operating voltage (e.g. 0.7-0.8V) is not expected to be the highest efficiency point except at relatively low fuel flows. Similarly, commonly quoted numbers for high efficiencies, and power densities are not likely to be achieved simultaneously.

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