MATHEMATICAL MODEL FOR THE ASSESSMENT OF CARBON DEPOSITION RISK IN THE SOFC ANODE

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Abstract

Internal reforming in the solid oxide fuel cell is desirable for increasing system efficiency and decreasing cost. However, the conditions for stable and sustained internal reforming are not clear yet. Carbon deposition may occur in the solid oxide fuel cell when a low steam/carbon ratio fuel is used. In this work, a first analysis of the tendency toward carbon deposition is carried out, using a model which includes methane cracking and the Boudouard reaction.

Introduction

Direct use of hydrocarbons as a fuel in the solid oxide fuel cell (SOFC) has inherent advantages which are high efficiency and elimination of the cost of an external reformer. However, the oxidation of hydrocarbon at the fuel electrode appears to have rather slow kinetics[1], and may be accompanied by reactions leading to carbon deposition on the pore walls of the fuel electrode. Nickel in the porous fuel electrode is both electronic conductor and catalyst. Once carbon deposits on the surface of the nickel particles, it will inhibit the reforming reaction. Therefore, hydrocarbons must be converted to hydrogen and carbon monoxide by steam reforming before there is a chance that carbon deposition occurs. The steam/carbon (S/C) ratio of the fuel feed has a direct relationship with carbon deposition. Although the mechanism of carbon deposition in the porous fuel electrode is probably complicated, thermodynamic equilibrium calculations offer a simple way to investigate the tendency toward carbon deposition under various conditions.

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A S/C ratio of 3 or more is usually considered safe. The critical S/C ratios for carbon deposition calculated from thermodynamic data for various temperatures and pressures typically used for the SOFC have been published in the literature[2,3]. A comprehensive model to assess the tendency toward carbon deposition in the porous fuel electrode is desirable in order to optimize its design and prolong cell life. In this work we attempt to develop and demonstrate a first approach to such a model.

Theory and Mathematical Model

The mathematical model of the SOFC anode selected for this work is based on the macro-homogeneous porous-electrode concept[4]. The anode is considered to be a homogeneous mixture of electronic conductor, ionic conductor and gas-filled pores(void fraction). The details of this model can be found in Reference [5].

A SOFC with direct internal reforming capability uses natural gas(mostly methane) as a fuel. Carbon deposition may take place either by methane cracking in the case of insufficient steam supply or by the Boudouard reaction in case of excess carbon monoxide.

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{C} + 2\text{H}_2 \\
2\text{CO} & \rightarrow \text{C} + \text{CO}_2
\end{align*}
\]

Under 1 atm total pressure, methane is thermodynamically unstable above 600°C[2]; on the other hand, carbon monoxide is unstable thermodynamically below 600°C, but above 600°C carbon dioxide in contact with carbon tends to form carbon monoxide. When carbon deposition takes place, reactions (1) and (2) will occur simultaneously. To evaluate the tendency toward carbon deposition at low S/C ratio, it is convenient to determine the activity of carbon in the anode by combining (1) and (2) together.

\[
\text{CH}_4 + 2\text{CO} \rightarrow 2\text{C} + \text{CO}_2 + 2\text{H}_2
\]
Consequently, the carbon activity is

\[ f_c = \sqrt{\frac{C_{CH_4}^2}{K_{CH_4}C_{CO}^2}} \times \left( \frac{C_{CO_2}^2}{K_{CO_2}C_{H_2}^2} \right) \]  

According to thermodynamic principles, if \( f_c \) is less than unity, reaction (3) is to the left, i.e., carbon deposition does not take place. On the contrary, if \( f_c \) exceeds unity, carbon deposition takes place until the gas composition in the anode has changed sufficiently to make \( f_c = 1 \).

Parameters such as temperature, pressure, and S/C ratio determine the thermodynamic tendency toward carbon deposition. Of course, in a SOFC porous electrode, these parameters have locally different values due to finite-rate reaction kinetics, temperature distribution, and transport (flow and diffusion). Therefore the critical local S/C values and the tendency toward carbon deposition vary.

A simple planar-geometry SOFC is used as a model in these calculations. A sketch of the mathematical domain is shown in Figure 1. To eliminate the microscopic complexity of the porous electrode, which is due to the geometric variations of particles and pore sizes, a macrohomogeneous model is used. In addition, in-plane variations are neglected and one-dimensional transport is assumed inside the fuel electrode (in the x direction only) and in the fuel gas channel (in the y direction only).

Results and Discussions

The operating conditions and physical parameters are listed in Table 1[6]. Figure 2 shows the activity of carbon in the fuel channel. The utilization of the fuel for various S/C ratios is listed in Table 2. The maximum value of carbon activity occurs approximately one fourth of the length downstream the fuel channel. The maximum value exceeds 1.0 when the S/C ratio in the fuel channel is between 0.9 and 1.0. The critical S/C value agrees with the value calculated from thermodynamic data alone, assuming uniform gas composition. However, the location where the maximum value of carbon activity is reached, is not the entrance of the fuel channel.

Figure 3 shows the change in gas composition in the fuel channel on a ternary C/H/O diagram for a fuel of S/C ratio unity. Operation below the critical carbon boundary is usually considered safe. On the ternary C/H/O diagram it shows that the initial
composition corresponds to (a), the most critical condition to (b), and exit gas composition to (c). Note that due to the oxide ions, the gas composition goes toward oxygen-riched regime (oxygen corner). This shift in the location of the critical condition (Figure 3) is apparently due to multicomponent transport and the cooling effect of the endothermic reforming reaction. It implies that thermodynamic equilibrium calculations are not enough to predict the tendency toward carbon deposition. The effect of reaction distribution due to transport in the porous fuel electrode must be included. Figure 4 shows the profile of carbon activity at an S/C ratio of 2, for various temperatures of the air supply. A co-flow pattern is used and the air temperature is assumed to be uniform throughout the air channel. The heat flux from the cathode side enhances the reforming reaction.

Figure 5 shows the profile of carbon activity for various operating pressures. High pressure causes a high peak value of carbon activity; however, the activity decreases rapidly downstream.

Conclusions

The above calculations show that, at 1200 K and atmospheric pressure, an internally reforming SOFC operation at S/C ratio 1.0 is theoretically possible without any carbon deposition. The simulation reveals that the most critical point is not necessarily located at the entrance of the fuel channel. The range where carbon deposition can thermodynamically take place is shifted downstream by approximately one fourth of the length of the fuel channel. The shift depends on the temperature of both fuel and air, as well as the partial pressure of CH₄ in the fuel gas. Local variations of temperature and concentration, both in the gas phase and in the solid phase of the anode, may increase the tendency toward carbon deposition in the pores. Therefore, one generally uses gas mixtures of S/C ratio exceeding 3.

For an accurate simulation of actual carbon deposition, reliable expressions for the kinetics of carbon deposition are necessary.

References

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### Table 1. Standard SOFC parameters and standard gas composition

| Parameter                  | Value       |
|----------------------------|-------------|
| Gas composition:           |             |
| $X_{\text{CH}_4}$         | 0.33        |
| $X_{\text{H}_2O}$         | 0.66        |
| $X_{\text{H}_2}$          | 0.005       |
| $X_{\text{CO}}$           | 0.005       |
| $X_{\text{CO}_2}$         | 0.005       |

| Parameter                  | Value       |
|----------------------------|-------------|
| Fuel temperature $T_f$     | 1200 K      |
| Air temperature $T_a$      | 1200 K      |
| Fuel velocity $v_f$        | 0.25 m/s    |
| Air velocity $v_a$         | 1.0 m/s     |
| Fuel pressure $p_f$        | 1.0 bar     |
| Anode thickness            | 100 $\mu$m  |
| Cell surface area          | 10x10 cm$^2$|
| Thickness of fuel channel  | 5x10$^{-3}$m|
| Fuel utilization           | 90.8 %      |
| Air utilization            | 15 %        |

### Table 2. Relationship between S/C ratio and fuel utilization.

| S/C ratio | Fuel utilization(%) |
|-----------|---------------------|
| 0.9       | 68.9 %              |
| 1.0       | 71.5 %              |
| 1.5       | 85.4 %              |
| 2.0       | 90.8 %              |
Figure 1. Sketch of the mathematical domains of a SOFC

Figure 2. Profile of carbon activity along the fuel channel, S/C ratio as a parameter.
Figure 3. Operational curve of a gas with S/C ratio of unity in the ternary C/H/O diagram; utilization of the fuel is 71.5%.

Figure 4. Profile of carbon activity along the fuel channel for various air temperatures.
Figure 5. Profile of carbon activity along the fuel channel for various fuel pressures.