A theoretical framework for multiphysics modeling of methane fueled solid oxide fuel cell and analysis of low steam methane reforming kinetics

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HIGHLIGHTS

- The first rigorous and comprehensive multi-physics model for CH_4 fueled SOFCs.
- Steam reforming kinetics for low steam methane is determined accurately.
- Experimental I–V relations are reproduced with no adjustable parameters.
- Common misconceptions about the OCV data are analyzed and corrected.
- Simulations yield detailed information about the CH_4 fueled SOFC operations.

GRAPHICAL ABSTRACT
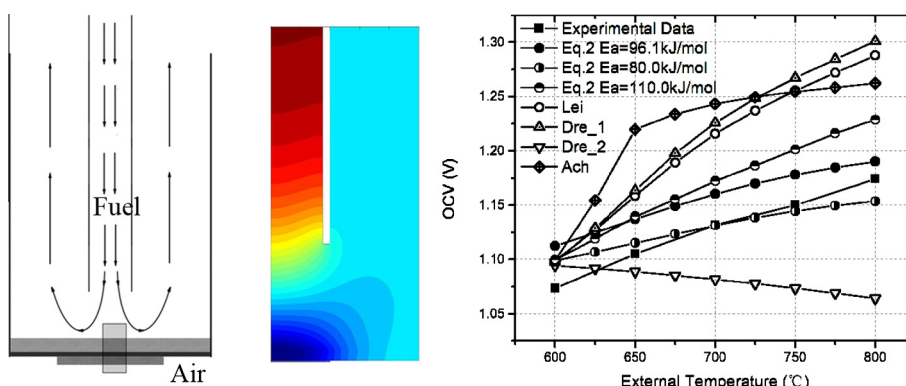
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ABSTRACT

Solid oxide fuel cell (SOFC) fueled by methane with low steam content is desirable from the energy efficiency and power density point of view. Improved understanding about the low steam methane fuel operation is required for advancing the technology. A rigorous and comprehensive multiphysics model for methane fueled SOFCs is described for the first time. The model considers explicitly the detailed balance of local electrical potentials for methane fueled SOFCs to ensure mathematical rigor. A commonly overlooked but important difference between the Nernst potential and the open circuit voltage (OCV) is critically analyzed. Numerical simulations with this multiphysics model show that OCV for low-steam methane fuel is sensitive to the methane steam reforming (MSR) kinetics. The steam reaction order and activation energy of MSR with low-steam methane are then determined accurately by a systematic comparison of the theoretical and experimental OCVs. Moreover, several literature MSR models are shown to be invalid for low steam methane. The multiphysics model and the deduced MSR kinetics are capable of producing the experimental I–V relations without any additional parameter adjustment, demonstrating the predictive power of the theoretical method.

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1. Introduction

The ability to use methane as fuel is an important attribute of solid oxide fuel cells (SOFCs) due to the abundance and low cost of natural gas and is vital for the broad adoption of SOFCs as a high

efficiency power generation technology. Carrying out the methane reforming reaction inside the fuel cell is favorable over the external reforming mode due to a number of considerations. The internal reforming (IR) operation eliminates the need of external reforming components and thus reduces system cost. IR also allows for the heat released by electrochemical reactions to be readily used by the endothermic reforming reaction, and thus improves the system efficiency. However, anode coking for the most widely used Ni-based anode is a serious issue for methane fuel. The anode coking may be prevented by adding a substantial amount of steam to the fuel stream so that the carbon deposition is thermodynamically unfavorable. Unfortunately, adding steam to the fuel is detrimental to the SOFC performance and should be avoided if possible. Interestingly, there have been a number of demonstrations that SOFCs with Ni-YSZ anode can operate stably without coking with low steam methane fuel when the cell current density is adequately high [1,2]. Moreover, adding a diffusion layer that is inactive for methane reforming may reduce the critical current density required for avoiding carbon formation [3]. The results are very appealing as the undesirable consequence of reduced Nernst potential and lowered current output with high steam content fuel may be circumvented. Furthermore, using low steam methane fuel is beneficial for simplifying the SOFC system as the low steam content can be realized by simply bubbling methane through water around room temperature. However, improved understandings about the scientific issues related to the use of low steam methane fuel are required so that informed choices of cell designs and operating parameters may be made to assure the technology's viability.

There are many interesting questions regarding methane fueled SOFCs with Ni-based anodes. This work aims to advance the understanding on two issues: (1) physical principle for the multi-physics numerical modeling of methane fueled SOFCs, (2) kinetic model for methane steam reforming (MSR) reaction with low steam content.

There are numerous multi-physics numerical simulations of methane fueled SOFCs [4–22]. The effect of internal methane reforming on fuel compositions and heat generation is normally taken into consideration. However, none of the theoretical formulations employed in the numerical simulations consider explicitly the effect of internal methane reforming on the open circuit voltage (OCV). Instead, the OCV is normally assumed to be equivalent to the Nernst potential computed according to the fuel and oxidant gases in both theoretical and experimental analyses [1–18,22–26]. As to be discussed below, this assumption may be acceptable for methane fuel with high steam content, but may overlook some important feature concerning low steam methane fuel. For example, the assumption ignores the fact that there are inherent electrochemical reactions in methane fueled SOFCs even at the OCV condition and the OCV result affects the I–V relation simulation. To properly understand the operations of SOFCs with low steam methane fuel, it is desirable to reexamine the relevant physical equations to eliminate the unnecessary assumption and its associated limitations.

The MSR kinetics has been studied extensively, but there are large discrepancies in the deduced kinetic models regarding the reaction order of steam [11,27]. An acceptable theory for the observed discrepancy is that the reaction kinetics is dependent on the steam-to-carbon (SC) ratio, while the experiments were performed with substantially different SC ratios [11,27]. This understanding points out the need to examine the steam reforming kinetics for low steam methane fuel as all the available kinetic data were obtained with relatively high steam content. However, the MSR kinetics with very low steam content is difficult to quantify experimentally and some novel analyzing approach is required to achieve the goal.

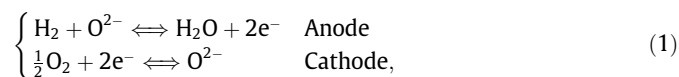This work addresses the issues discussed above by reformulating the electrochemical equations and performing numerical sim-ulations of some relevant experiments. A multi-physics mathematical model of a methane fueled SOFC is developed through a careful consideration of the detailed balance of local electrochemical potentials. Such a multiphysics model has recently been used to study the carbon deposition related issues [19], but the theoretical descriptions are presented here for the first time. Numerical simulations based on this multiphysics model are performed based on the geometric, material and operating parameters specified in the relevant experiments. A credible low steam MSR kinetic model is then deduced by comparing the experimental and theoretical OCV results. The multiphysics model is also validated by accurately reproducing I–V relations measured under different conditions [23,24].

2. Theoretical method

A series of experiments with very similar cell material designs and operating setups have been conducted to examine the performances of button cells fueled with low steam methane [1–3,23,24]. These experiments are highly valuable for testing the theoretical model and pursuing the goal of this study. Consequently, our multiphysics numerical models are constructed to correspond to the experimental specifications for the convenience of discussion and analysis. Fig. 1 illustrates a two-dimensional axisymmetric computational domain for an anode-supported button cell with a gas chamber at the anode side, as described in Ref. [24]. For numerical simulations, governing equations for the physical processes, material properties, boundary conditions, etc., are necessary and are described below.

2.1. Governing equations for electrochemical process and charge transport

The electrochemical oxidations of both H_2 and CO may take place in the anode three-phase boundary (TPB) [11,27–30]. The current output is a result of both H_2 and CO oxidations. Due to the rapidly proceeding WGS reaction that keeps the H_2 and CO compositions at the equilibrium, it is mathematically equivalent to consider only the H_2 oxidation with an adjusted effective oxidation rate, as has been widely adopted in literature [9,16,31]. Consequently, the electrochemical reactions are expressed as:

$$\begin{cases} H_2 + O^{2-} \Longleftrightarrow H_2O + 2e^- & \text{Anode} \\ \frac{1}{2}O_2 + 2e^- \Longleftrightarrow O^{2-} & \text{Cathode,} \end{cases} \quad (1)$$

The electrochemical process based on Eq. (1) appears to be identical to that with hydrogen fuel [32]. However, as will become clear later, there are important differences when it is coupled with the MSR reaction and it is worthy to repeat the basic electrochemical equations.

At the local equilibrium that there is no net electrochemical reaction, the balances of electrochemical potentials for Eq. (1) are:

$$\begin{cases} \mu_{H_2} + \mu_{O^{2-}} - 2F\varphi_{io}^{eq} = \mu_{H_2O} - 2F\varphi_{el}^{eq} & \text{Anode} \\ \frac{1}{2}\mu_{O_2} - 2F\varphi_{el}^{eq} = \mu_{O^{2-}} - 2F\varphi_{io}^{eq} & \text{Cathode,} \end{cases} \quad (2)$$

where φ_{io}^{eq} and φ_{el}^{eq} are the local equilibrium electrical potentials of the ionic-phase (e.g., YSZ) and electronic-phase (e.g., Ni for anode and LSM for cathode), respectively. μ_i is the chemical potential of species i. For reacting gas species, μ_i is related to the local partial pressure of i, as:

$$\mu_i = \mu_i^0 + \frac{RT}{n_iF} \ln \frac{p_i}{1 \text{ atm}}, \quad (3)$$

where μ_i^0 is the chemical potential of species i at p_i = 1 atm. n_i = 2, 4 and 2 for i = H_2, O_2 and H_2O, respectively.