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Modelling of a cathode-supported tubular solid oxide fuel cell operating with biomass-derived synthesis gas

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Abstract

A mechanistic model for the operation of a tubular solid oxide fuel cell (SOFC) using synthesis gas as a fuel source has been successfully developed and validated against experimental data reported in the literature. The model considers momentum-, mass-, energy- and charge-transport equations coupled with electrochemical and water-gas shift reactions. This avoids the use of empirical correlations for estimating heat and mass transfer coefficients. The model is solved to predict SOFC performance and behavior by determining the distributions of current density, temperature and species concentrations throughout the cell. The developed model was used to predict the effect of the composition of biomass-derived synthesis gas fuels on cell performance and behavior.

Keywords: Mechanistic modelling; Tubular SOFC; Cathode-supported; Synthesis gas; Biomass fuel

1. Introduction

Heat engines that are widely employed to produce electricity and heat for homes and industries have relatively low energy efficiency and emit large amounts of greenhouse gases. Tubular solid oxide fuel cells (TSOFC) show great promise as potential candidates to replace conventional heat engines. TSOFCs have, indeed, higher energy efficiency and emit lower amounts of greenhouse gases. Furthermore, they are designed for mid- to large-scale applications up to 2 MW [1], similar to the capacity of heat engines. A major advantage of TSOFCs over other types of fuel cells is that a variety of hydrocarbon-based gases or their synthesis derivatives, such as natural gas, biomass and coal can potentially be used as fuel sources. CO present in the synthesis gas can be oxidized in TSOFCs to generate CO_2 and electrical energy.

Recently, the use of biomass-derived synthesis gas as a fuel has gained attention because it is abundant and renewable. Omosun et al. [2] performed a system analysis on a SOFC combined with biomass gasification. The biomass was gasified in air yielding a syngas composition of 17% H_2, 13% CO, 11% CO_2, 4% CH_4, 15% H_2O and 40% N_2. A simple SOFC model developed in gPROMS accounted only for the electrochemical oxidation of H_2 and the consumption of CO via the water-gas shift (WGS) reaction. In addition to presenting the overall model, the main objective of this paper was to compare cleanup of hot gas to that of cold gas. Panopoulos et al. [3] also carried out a system analysis of an SOFC integrated with a biomass steam gasification process. The resulting humidified syngas had the following composition: 26.2% H_2, 15.9% CO, 6.0% CO_2, 2.6% CH_4 and 49.1% H_2O. The SOFC model was a simple equilibrium model developed in AspenPlus. Cordiner et al. [4] simulated a biomass gasifier coupled with an SOFC. The gasification process was considered to be at equilibrium whereas they developed a 3D model for a single planar SOFC. The composition of the syngas leaving the gasifier and fed to the SOFC was 56% H_2, 39% CO and 6% CO_2. In their SOFC model, only the electrochemical

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oxidation of H_2 was considered and CO was consumed only via the WGS reaction. They determined that the whole system had an efficiency close to 46%. Aloui and Halouani [5] developed an isothermal 1D model for an SOFC fed by biomass syngas that considered the electrochemical oxidation of both CO and H_2. A somewhat surprising result of their analysis was that biomass syngas (26% H_2, 24% CO, balance mostly N_2) yielded better performance than diluted humidified hydrogen (49% H_2, 1.5% H_2O, 46% N_2, balance CO and CO_2). It is difficult to assess this result more deeply especially since it was unclear whether the water-gas shift reaction was taken into account.

Van Herle et al. [6–8] investigated a slightly different system from the previously described works in that the fuel fed to the SOFC was a biogas reformate instead of biomass-gasified syngas. The composition of this reformate was 35.8% H_2, 29.6% CO, 3.6% CO_2, 0.2% CH_4, 4.3% H_2O and 26.5% N_2. Van Herle et al. developed a flowsheet for the entire system, including the biogas reformer, where the SOFC was simulated using a simplified isothermal model. Vasileiadis and Ziaka-Vasileiadou [9] also considered reforming of biogas prior to an SOFC. They focused more on the reformer and very little detail was given regarding the SOFC. Very recently, a biogas reformer/SOFC system was also investigated by Athanasioua et al. [10]. The composition of the biogas reformate fed to the SOFC was 19% H_2, 11% CO, 5% CO_2, 1% CH_4, 23% H_2O and 43% N_2. Their model was equilibrium based with the assumption of 80% CO utilization.

Although not involving model simulation, a noteworthy study on the use of biomass syngas in SOFC was the work of Xie et al. [11] who experimentally investigated the performance of a Ni–Cu alloy-based anode for low temperature SOFCs. The fuel used was a syngas produced from rice husk gasification (23.5% CO, 14.3% CO_2, 15.7% H_2, 6.2% CH_4 and 40.3% N_2). Their main conclusion was that the Ni–Cu alloy system was more stable than the Ni one because of significant reduction in carbon deposition due to the replacement of Ni by Cu. Baron et al. [12] also studied experimentally the effect of various simulated biomass gas compositions on the cell performance at an intermediate temperature of 650 °C. They found that the performance of the cell decreased at a CH_4 content of 10%. They also observed that replacing H_2 by CO had a negative impact on the cell performance, which they attributed mostly to differences in mass-transport properties between CO and H_2. This latter conclusion was also reached by Suwanwarangkul et al. [13] for higher temperature cells. Aravind et al. [14] also conducted experiments on the cell performance using Ni/GDC and SDC anodes for different types of biosyngas (air-blown, oxygen-blown and steam gasification) at operating temperatures between 750 and 1000 °C. For the syngas compositions they considered, they observed no significant carbon deposition, as expected from C–H–O ternary diagrams. Interestingly, they also performed experiments where 9 ppm H_2S was added to the simulated biogas (but only with the Ni/GDC anode) and observed no deleterious effects. One should note, however, that 9 ppm H_2S is below the level that would be expected in biosyngas (50–200 ppm [14]). Several studies on the direct use of biogas in SOFC have also been reported [15,16].

As just described, only a limited amount of research has been done to study the use of biomass-derived synthesis gas as a fuel source. Furthermore, the studies to date have focused mostly on system analysis and anode material development. No work has been found on the application of a mechanistic model to an actual tubular cell operating with a biomass-derived syngas. Since the composition of synthesis gas can vary widely depending on the biomass type and gasification process [17], there is an important need to develop mathematical models to predict the effect of fuel composition and other operating conditions on cell performance indicators such as power output, efficiency and outlet gas temperature and composition. In addition, such models can be used to study the complex interactions between physical phenomena and reaction processes (chemical/electrochemical) that take place in a TSOFC and are critical to optimize the cell performance and to help in designing the cell.

TSOFC models that have been recently developed have been reviewed by Suwanwarangkul [18]. The TSOFC models have so far focused almost exclusively on the use of H_2 [19,20], methane [21,22], and natural gas and pre-reformed natural gas [23–26]. One exception is a study on pre-reformed jet fuel in TSOFC [27]. In all the above models for TSOFC, the equilibrium of the WGS reaction was assumed. Also, with the exception of the work of Aguiar et al. [22], consumption of CO via the WGS reaction was considered, but not its electrochemical oxidation. On the other hand, Li and Chyu [25] showed that the Nernst potentials for CO and H_2 electrochemical oxidation are the same as long as the WGS equilibrium is assumed. They concluded that it is sufficient to consider H_2 oxidation to be the only anodic reaction if it is coupled to the consumption of CO via the WGS reaction at pseudo-equilibrium. Although it is generally accepted that the WGS reaction is fast and quickly reaches equilibrium at the temperatures encountered in an SOFC, this has not been firmly demonstrated and it is not clear yet whether this assumption would still be valid when a syngas containing a high concentration of CO is fed to the cell. One of the objectives of the present study is to test this assumption. Consequently, we make no assumption regarding the equilibrium of the WGS reaction in the model to be considered and so also explicitly include the electrochemical oxidation of CO. The main difference between our model and the TSOFC models described above is that the WGS reaction is not assumed to be at equilibrium *a priori* and therefore the inclusion of CO electrochemical oxidation is necessary in our model. Since biogas is composed essentially of CO_2 and CH_4, dry and steam reforming of methane would also become major reactions occurring in the SOFC. However, we do not consider methane reforming in the model to be presented and thus the results will be most relevant to the use of biomass-derived syngas.

In the present work, a comprehensive mathematical model of a TSOFC presented in detail in earlier publications [13,19] was used to simulate a TSOFC operating with biomass-derived syngas. The model aims at predicting such quantities as the current density and temperature distributions throughout the cell for different compositions of the fuel gas. Fuel gases considered in the model are humidified hydrogen and synthesis gas (mixtures of H_2, H_2O, CO, CO_2 and N_2) while the oxidant