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Direct reforming of biogas on Ni-based SOFC anodes: Modelling of heterogeneous reactions and validation with experiments

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HIGHLIGHTS

- Operational maps of a tubular SOFC cell running on direct reforming of biogas.
- Kinetic model of chemical and electrochemical conversion of biogas in solid oxide fuel cells (SOFC).
- Validation of the model through polarization and GC analysis of anode exhaust gas.
- Use of the model to predict and analyze the gas composition along the anode in different geometries and operating conditions.

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ABSTRACT

This work focuses on the heterogeneous reactions taking place in a tubular anode-supported solid oxide fuel cell (SOFC) when the designated fuel is biogas from anaerobic digestion directly feeding the fuel cell. Operational maps of the fuel cell running on direct reforming of biogas were first obtained. Hence a mathematical model incorporating the kinetics of reforming reactions on Ni catalyst was used to predict the gas composition profile along the fuel channel. The model was validated against experimental data based on polarization curves. Also, the anode off-gas composition was collected and analyzed through a gas chromatograph. Finally, the model has been used to predict and analyze the gas composition change along the anode channel to evaluate effectiveness of the direct steam reforming when varying cell temperature, inlet fuel composition and the type of reforming process. The simulations results confirmed that thermodynamic-equilibrium conditions are not fully achieved inside the anode channel. It also outlines that a direct biogas utilization in an anode-supported SOFC is able to provide good performance and to ensure a good conversion of the methane even though when the cell temperature is far from the nominal value.

1. Introduction

As suggested by recent advances in bio-chemical science and technology, biogas from anaerobic digestion is an alternative to conventional fuels for producing electricity in a distributed generation framework [1,2]. Biogas can be produced starting from several wastes that include the organic fraction of municipal solid waste (food waste, mostly), sewage, agricultural (or green) waste (e.g., straw and harvest residues) and animal manure. Industrial and municipal waste-water treatment (WWT) plants – often combined together – and landfills are generally the two largest biogas producers [3].

The typical gas composition includes mostly methane (50–70% vol.) and CO_2 (30–50% vol.), plus some nitrogen (~ 1% vol.); Several trace contaminants such as sulfur compounds (including COS and mercaptans), halogens, siloxanes, etc. are also found [3–5]. The high methane content (variable according to the biomass waste/feedstock used, and micro-biological treatments in the digester) of biogas makes it a good substitute of natural gas.

Usually, biogas is burnt in engines to produce mechanical power then converted into electricity; as an alternative, it could be used to feed a solid oxide fuel cells (SOFCs) to generate electricity via a high-efficiency electrochemical conversion process. The SOFC can be safely operated with direct biogas once contaminants are removed, or reduced at acceptable values, in a processing/cleaning

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section. Also, a certain oxygen-to-carbon (O/C) ratio (generally above 2) must be provided at the anode inlet to avoid carbon build-up in the Ni-based anode electrode; the oxygen carrier is either H_2O, CO_2, or even O_2, that can be available externally or through the recirculation of a fraction of the anode exhaust (H_2O and CO_2, only) [6–9].

Especially if a direct use of biogas in the SOFC is sought, it becomes important to understand and predict both the chemical processes (heterogeneous catalytic reactions) and electrochemical reactions occurring within the anode volume [10,11] as well as their coupling [12–15]. So far the elementary kinetic steps involved in the electro-oxidation of H_2 and CO in a Ni–YSZ anode have been only partially understood, especially for the CO compound.

In particular, it is interesting to understand for a multi-component fuel mixture containing CH_4, H_2 and CO (as for direct reforming of biogas) – plus an oxygen carrier in the form of CO_2 and steam – which species are actually reacting on the TPB region.

For instance, for H_2–CO mixtures with an high amount of H_2 (>55% was mentioned in the work of Jiang and Virkar [16]), the water gas-shift reaction is considered so fast in a NI–YSZ electrode to prevent the direct electro-oxidation of CO that is rather converted catalytically to H_2. This conversion pathway for CO within an SOFC seems likely also looking at the reported lower kinetics for CO electro-oxidation [16], even though CO electrochemical activity was experimentally verified in a Ni–YSZ SOFC [17,18].

Similar works are present in literature, but usually performed over button cell design. Most of them are focused on detailed 1D studies through the anodic electrodes using simplified electrochemical models [19] or more complex ones [20]. Other works take into account the in-plane flow distribution of bulk species concentrations but only considering hydrogen as a fuel [21].

In this work, a detailed numerical model has been developed, which includes the model developed by Deutschmann et al. [13,14]. The aim of the proposed model is to evaluate the catalytic and electro-catalytic conversion of the fuel (i.e., biogas) in the fuel cell and to predict the anodic gas composition along the fuel channel. In particular, a real tubular commercial available cell was considered (with a higher level of significance compared to a button cell): in fact, the size of the cell implies that bulk species distribution can be taken into account. The model is validated against experimental data obtained for an anode-supported tubular SOFC: in particular, through the monitoring of the anode off-gas composition using a gas chromatograph. In fact, the model focusses to well reproduce the gas conversion due to heterogeneous reactions: the validation considering the outlet species concentration has been preferred compared to the polarization one, which usually is obtained simply by tuning some electrochemical macro-parameters. Also, operational maps of the SOFC were obtained, studying the impact of relevant operational variables (*FU*, fuel composition, steam addition) on cell performance.

2. The SOFC mathematical model

The numerical model was implemented using an in-house code based on Cantera tool [22]. The reforming process occurring inside the anode channel of a tubular anode-supported SOFC (a modified version of our kinetic model for planar cells is also available) was evaluated considering a detailed kinetic mechanics for heterogeneous reactions. Both thermodynamic and electrochemical phenomena are taken into account. The reaction volume (i.e., the anode channel) was discretized both in radial and axial directions. A grid independence analysis was performed by varying the number of nodes in both directions independently. Finally, the grid size was adequately reduced to minimize the computational time while preserving a fast convergence to stable solution.

2.1. Main model assumptions

Considering the peculiar flow characteristics established in a tubular fuel cell, the present model consists of a series of 1D problems along the axial direction. Species conservation is applied between adjacent elements. The whole approach represents an acceptable approximation since the fuel channel typically has a characteristic diameter less than a centimeter and mean velocities less than 1 m s^{-1} that imply the Reynolds number is in the order of hundreds. Very low Mach number and nearly constant pressure guarantee that also boundary conditions satisfy this approach. Hence the flow equations reduce to a set of ordinary differential equations in the radial coordinate.

The species-conservation equations can be written as:

$$\rho\frac{dY_k}{dt} = -\rho u\frac{dY_k}{dr} - \frac{dJ_k}{dr} + W_k\dot{\omega}_k \tag{1}$$

The convective terms were computed using an upwind differencing method, while a central differencing method was employed to compute the diffusive terms. Boundary conditions for species mass flows are set at the inlet (Dirichlet) and at anode/channel interface (Neumann). The fluxes J_k was computed using the mixture-averaged transport model, with the diffusion velocity being composed of three parts:

$$V_k = v_k + w_k + V_c \tag{2}$$

where v_k is the ordinary diffusion velocity and is given in the Curtiss–Hirschfelder [23] approximation by:

$$v_k = D_{km}\frac{1}{X_k}\frac{dX_k}{dx} \tag{3}$$

the mixture-averaged diffusion coefficient D_{km} is given explicitly in terms of the binary diffusion coefficients D_{kj}:

$$D_{km} = \frac{1 - Y_k}{\sum_{j\neq k}^{K}\frac{X_j}{D_{kj}}} \tag{4}$$

A zero thermal diffusion velocity w_k was considered in this preliminary isothermal simulation. The correction velocity V_c was included to insure that the mass fractions sum to unity. The formulation of the correction velocity is the one recommended by Coffee and Heimerl [24] in their extensive investigation of approximate transport models.

The electrochemical oxidation at the anode is attributed to hydrogen only. Once the current density i is set, it is possible to evaluate the molar flux of the gas species involved in the electrochemical reactions as:

$$J_{H_2,a} = -\frac{i}{2F} \tag{5}$$

$$J_{H_2O,a} = \frac{i}{2F} \tag{6}$$

A positive flux at the anode means a net species production.

The molar production rates $\dot{\omega}_k$ are evaluated using a heterogeneous reaction mechanism described in Table 1. The mechanism was taken from reference [25] and manually translated from