

Modeling of a one dimensional Anode supported high temperature tubular SOFC

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Abstract : SOFCs are under research mainly for their use in stationary power generation application and other standby applications. A tubular one dimensional model has been developed in this research work. In the anode-supported SOFC, electrolyte and cathode are very thin (for an example, 50 μ m) but the anode thickness is generally thicker than 100 μ m, thinner electrolyte provides lesser resistance for the movement of O²⁻ through leading to higher value of developed voltage & power density. The SOFC tube has been discretized along its longitudinal axis with nodal variation of concentration of components, temperature, current and voltage along the axis of the tube. The numerical modelling considers internal reforming through the methane reforming and water gas shift reactions taking place along with the electrochemical reactions on the surface Ni-YSZ anode. Besides the reaction kinetics, the mass-transfer processes have also been included in this one dimensional model. In this paper, a novel approach for the axial symmetric simulation of the SOFC tube is presented by applying finite element method, taking into account the variation of the properties with their nodal variation due to change in concentration and temperature and their effect on the voltage and power density developed.

Keywords: Solid oxide fuel cell (SOFC), Ni-YSZ anode. Current density, Voltage, Power density.

1. Introduction

1.1 Background

The current energy supply systems commercially used till now are mainly based on the combustion of fossil fuels. It causes many environmental problems like air pollution, acid gas emissions, and the emission of greenhouse gases. Fuel cell technology has recently been investigated as an emerging technology for energy production in clean manner as it does not involve the typical combustion of fossil fuels. Instead, they use an electrochemical battery-like process to convert the chemical energy of fuel and generate electricity^{1,3}. SOFC is one type of solid-state ionic based fuel cell devices which have all the components i.e. the anode, the electrolyte and the cathode in solid state. One distinct advantage of SOFCs is that are fuel flexible; they are able to be run on various hydrocarbons based fuels like methane, with on board reforming making them a promising power generation technology for many applications. They are suitable to be installed in a variety of locations where combustion systems would not be appropriate. Without any moving parts, they are capable of being built almost anywhere without the threat of noise pollution and minimum maintenance. Being completely quiet, they can be put in and around residential areas for high efficient power generation techniques^{1,8}.

1.2 Principle of operation:

A Solid oxide fuel cell consists of three main parts: two porous electrodes and an electrolyte that separates them. In a SOFC system, the electrolyte material should be a good ionic conductor but it exhibits almost no electronic conductivity. The electrolyte should also be very dense, so that no fuel or air can pass through. The electrolyte in a SOFC should be as thin as possible to reduce ohmic losses and, thus maximize performance^{3,9}. The cell, however, must be mechanically strong enough to not crack or fail under electrochemical and mechanical load and, yet operate at high temperatures. While single cells can be anode, cathode or electrolyte supported, with much work done in the past on anode-supported cells, the research presented in this paper focuses on the electrolyte-supported cell design. This electrical current is in opposite direction to the movement of electrons. Fig1. shows the principle of operation of SOFC.

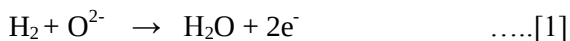
In a SOFC, Air (oxidant) enters the cell at the cathode where oxygen is undergoes reduction process to form negative O^{2-} ions. The O^{2-} ions pass through the electrolyte and react with Hydrogen (fuel) at the anode to form water and generate electrons. These electrons move through the external circuit from the anode to cathode to cause reduction of more oxygen at the cathode forming more O^{2-} ions. A single cell under operation produces an open circuit voltage of the order of 1 volt. This open circuit voltage is referred as the Nerst Potential $E_{\text{nerst}}^{1,3}$. To produce working commercial voltage, a number of SOFCs are normally connected in series by means of interconnecting plates.

2. Kinetics and Thermodynamics

2.1 Chemical Reactions in a SOFC

The Electrochemical cell reaction occurring in a SOFC involves the following individual reactions^{1,2} at the anode and cathode:

Oxidation of fuel at anode

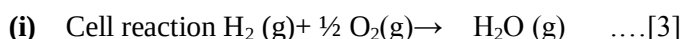


Reduction of oxidant at cathode



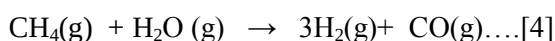
The O^{2-} ions migrate through the electrolyte and reach the anode.

The overall cell reaction is



The other reactions which occur leading to in-situ reforming of methane at the anode and water gas shift reactions are as follows:

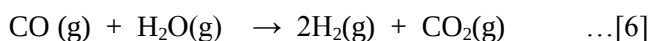
(ii) Partial Methane steam reforming



(iii) Complete Methane steam reforming



(iv) Water gas shift reaction



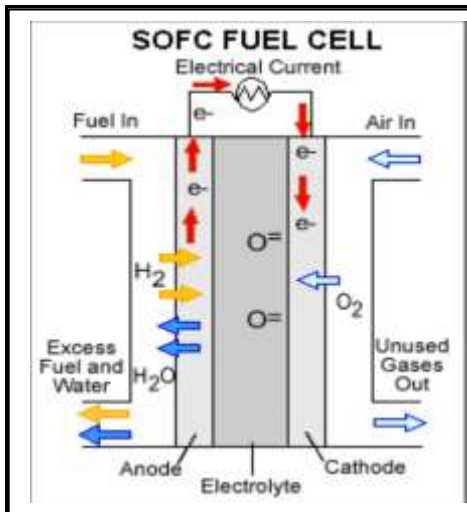


Fig1. Principle of operation of a SOFC²

2.2 Ideal Reversible voltage:

For a reversible system, the potential developed [1,2] is given by

$$E^0 = -\frac{\Delta G_r}{nF} \quad \dots(1)$$

Where ΔG_r refers to Gibb's energy change for electrochemical cell reaction. This potential E is also known as the Open Circuit Voltage (OCV), the condition where no current is drawn from the fuel cell. It also represents the maximum voltage encountered in fuel cell operation^{1,3}.

The Nernst equation gives the dependence of molar Gibb's free energy on reactant pressure, concentration and temperature.

$$E_{\text{nerst}} = E^0 + \frac{RT}{nF} \ln \frac{P_{\text{reactant activity}}}{P_{\text{product activity}}} \quad \dots(2)$$

Considering the electrodes to be equilibrium surfaces [r] the Nernst voltage is defined by

$$E_{\text{Nernst}} = E^0_{T,P} + \frac{RT}{nF} \ln \frac{P_{H_2} \times P_{O_2}}{P_{H_2O}} \quad \dots(3)$$

Certain irreversibilities in the SOFC operation which lead to a reduction in actual efficiency of a SOFC and thus a drop in open circuit voltage^{1,2}. The irreversibilities are (a) Activation polarization η_{Act} (b) Ohmic polarization η_{ohm} (c) Concentration polarization η_{Conc} .

The net voltage output for each cell

$$V = E_{\text{nerst}} - \eta_{\text{act}} - \eta_{\text{conc}} - \eta_{\text{ohm}} \quad \dots(4)$$

3. Modeling & Simulation of anode supported tubular SOFC

Since, the SOFC tubular configuration is still regarded as the most efficient, reliable, and stable one, has therefore been considered for modelling & Simulation. In the last few years, many researchers were involved in the investigation of tubular SOFC systems, analysing them with a multi-scale approach. SOFCs have been analysed with a number of different techniques and with different levels of accuracy. Many papers are available in the literature, dealing with parametric, 1-D, 2D and 3D CFD simulation of the SOFC tube or of some of its components anode, cathode, or electrolyte, in either transient or steady conditions. A reliable and

predictive well-designed SOFC model required the effective heat, mass, species, charge and momentum transport coupled with chemical reactions in the porous substrate⁷.

3.1 Model Assumptions

The simplifying assumptions while deriving the axially symmetrical steady state model of tubular SOFC were: (a) fuel & oxidant are ideal gas mixtures; (b) isotropic and homogeneous electrodes and (c) negligible ohmic drop in electronically conductive solid matrix of porous electrodes as well as the current collectors (d) No radial and angular variation of concentration, temperature and current density has been assumed. (e) The diffusion of gases normal to the flow direction was not considered for studying the concentration distribution of components. (f) SOFC was considered to be operating under steady-state conditions. (g) The principal fuel for SOFC was methane. H₂ was produced by high temperature internal reforming of methane at the surface of anode.

$$D_{H_2 \text{ eff}} = \frac{\varepsilon}{\nu} \left(\frac{1}{D_{H_2, m}} + \frac{1}{D_{kH_2}} \right)^{-1} \quad \dots(5)$$

The total continuity equation for one dimension for an electrochemical steady state model is given by

$$\frac{\partial u}{\partial x} = 0 \quad \dots(6)$$

Where u refers to x-directed velocity along the axial direction of the tubular SOFC.

The component continuity for an ith component, therefore becomes

$$\frac{\partial C_i}{\partial t} + u \frac{\partial C_i}{\partial x} = \left(\frac{1}{V} \right) \sum r_{a, i} \quad \dots(7)$$

Where C_i refers to molar concentration of species i, $\sum r_{a, i}$ is the sum of rate of reaction of speciesi.

Applying Finite element method, the above equation be used to predict the concentration of (i+1)th node from the known concentration of ith node for all the components in the anodic fuel channel i.e. H₂, CH₄, CO, H₂O and CO₂.

$$\frac{C_{i+1} - C_i}{\Delta x} = \frac{1}{u} \sum r_{\text{reacted}} \quad \dots(8)$$

The rates of reforming and water gas shift reactions are surface reactions being catalysed by Ni are characterized by the following equations^{4,5}:

$$r_{MR1} = \frac{1}{DEN^2} \frac{k_1}{P_{H_2}^2 \cdot 5 \left[P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_{eqMR1}} \right]} \quad \dots(9)$$

$$r_{WGS} = \frac{1}{DEN^2} \frac{k_2}{P_{H_2} \left[P_{CO} P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_{eqWGS}} \right]} \quad \dots(10)$$

$$r_{MR2} = \frac{1}{DEN^2} \frac{k_3}{P_{H_2}^3 \cdot 5 \left[P_{CH_4} P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_{eqMR2}} \right]} \quad \dots(11)$$

$$DEN = 1 + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{CH_4} P_{CH_4} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}} \quad \dots(18)$$

Since, the current density has been assumed to be fixed in this simulation, the rate of cell reaction becomes a constant for a particular value of current density and is given by:

$$r_{CR} = \frac{i_{Acell}}{2F} \quad \dots\dots(12)$$

The rate of oxygen consumed at the cathode is half that of cell reaction and is therefore given by the expression:

$$r_{O_2} = \frac{i_{Acell}}{4F} \quad \dots\dots(13)$$

3.2 SOFC discretization:

In order to evaluate the profile of the most important parameters the SOFC tube, was discretized along their axes, as shown in Fig2. The typical tubular configuration of the SOFC, developed by Siemens which consists of the cell, i.e. anode, cathode and electrolyte, the inner channel for supply of oxygen to the cathode. In this paper, a finite-volume axial-symmetric steady simulation of the SOFC tube was implemented. There are two control volumes, CV1 extends from the surface of anode to the annular fuel channel. CV2 consists of the Electrolyte, the cathode and one half of cylindrical air channel.

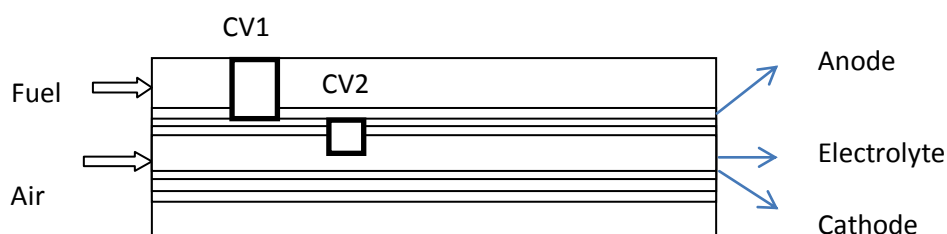


Fig2. Discretization of tubular SOFC

The overall control volume was discretized by means of slices obtained with 101 plans orthogonal to the axis of the cylinders. Thus, the system was divided into 100 slice. The slice can be considered as the elementary volume of the discretization, and is reported on the x-axis of the following figures. Appropriate algorithms, written in MATLAB, were developed both for SOFC tube in order to determine the profiles of all the thermodynamic, chemical and electrical properties within those components. These algorithms were based on the above discussed chemical, electrochemical and pressure drops models coupled with the energy balance equations.

The tubular SOFC tube was analyzed on the basis of the fixed parameters^{4,5,6} shown in Tables 1 and 2. The SOFC under investigation is fed by air, with the typical atmospheric air composition, and by the fuel as per the composition given in table1. Thus, the fuel stream consists of methane and nitrogen included in the system inlet fuel, which is typically the natural gas and also of CO, CO₂, H₂, and H₂O produced by the Steam Methane Reforming reactions.

Table 1 Molar flow rates of the inlet streams(kmol/s)

Component	CH ₄	CO	H ₂	H ₂ O	O ₂	CO ₂	N ₂
Air stream	-	-	-	-	9.24E-06	-	3.48E-05
Fuel stream	1.48E-07	1.68E-07	5.04E-07	4.05E-07	-	2.77E-07	9.82E-09

Table 2 Fixed parameters of the case study

Parameter	Value	Parameter	Value
Current density i	3000 A/m ²	Anode tortuosity factor,	5.90
Anode thickness l_a	180 μ m	Cathode porosity, ϵ_c	50%
Cathode thickness l_c	50 μ m	Cathode tortuosity factor, τ_c	5.90
Electrolyte thickness l_e	50 μ m	Anode conductivity, σ_a	10 ⁵ W/m K
Cell length, l	1.50 m	Cathode conductivity, σ_c	10 ⁷ W/m K
Number of slices, N	100	Electrolyte conductivity, σ_e	1.00 W/m K
Fuel inlet pressure, P_f	3 bar	Anode porosity, ϵ_a	50%
Air inlet pressure bar, P_a	3 bar	Anode tortuosity, τ_a	5.90
Fuel inlet temperature, T_f	921°C	Anode pore diameter, d_a	0.5 μ m
Air inlet temperature, T_a	860°C	Cathode pore diameter, d_c	0.5 μ m
Anode porosity, ϵ_a	50%		

4. Results and Discussions:

As an example of application of the simulation model of a tubular one-dimensional was described above, and a case study was performed. The tubular SOFC was considered to be operating with a full internal reforming, which balances the heat being generated by the exothermic electrochemical cell reaction and water gas shift reaction. The temperature varied throughout the SOFC leading to a variation of ΔG values for methane reforming and water gas shift reactions.

- CO concentration increased along the length of the tubular reactor. CO was produced by partial methane reforming but consumed during water gas shift reaction which rather showed a negative rate at the temperature, the concentration of CO increased exponentially along the length.
- CO₂ was only involved in the complete methane reforming leading to its small increase in concentration in the first portion of the graph. Water gas shift reaction, which showed a negative rate in the forward direction led to the small decrease in concentration in the CO₂ along later length of reactor.
- H₂O is a reactant for partial methane reforming & complete reforming leading to a decrease in its concentration initially, but as the concentration of H₂ builds up, its formation by electrochemical cell reaction, substantially overcomes its loss due to methane reforming flattening its decrease by the end of the SOFC.
- The concentration of H₂ increases along the length of the reactor due its production by methane reforming & water gas shift reactions. Its rise in concentration subsequently drops due its consumption in the electrochemical cell reaction which leads to the production of electric current.
- CH₄ which as a reactant for both partial & complete steam reforming decreases in concentration along the length of the SOFC. The rates of both of these reactions are substantial leading to a rapid decrease in its concentration.
- O₂ converts into O²⁻ ions on the cathode, which diffuses through the electrolyte and reacts with hydrogen formed by methane reforming and water gas shift reactions. The concentration of O₂ therefore progressively drops through the SOFC as shown in the figure below.

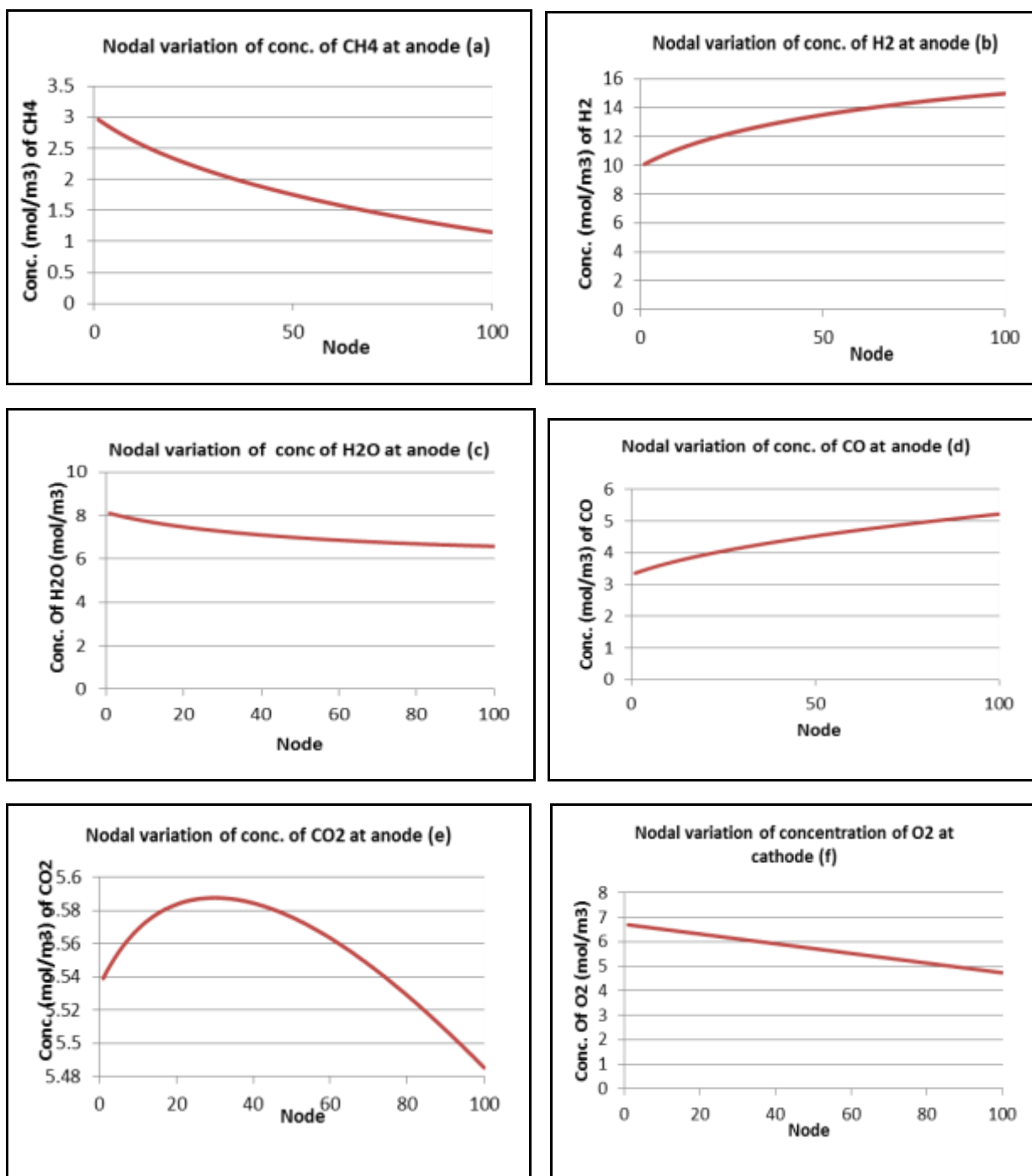


Fig3. Nodal variation of concentration of components (a) Methane (b) Hydrogen (c) Water (steam)(d) Carbon Monoxide (e) Carbon dioxide (f) Oxygen

The fuel molar flow rates along the SOFC axis, was analyzed putting in evidence the trend of the chemical and electrochemical phenomena occurring in the SOFC tube. In fact, in the first part of the tubular SOFC the internal steam reforming process is pre-dominant over the electrochemical reaction, inducing an increase of the hydrogen partial pressure. Conversely, in the same section the steam partial pressure decreases, because the amount of water used by the internal reforming process is much higher than the one released by the electrochemical process. Then, the steam reforming reactions quickly approach the equilibrium conditions, and then subsequently begin to increase.

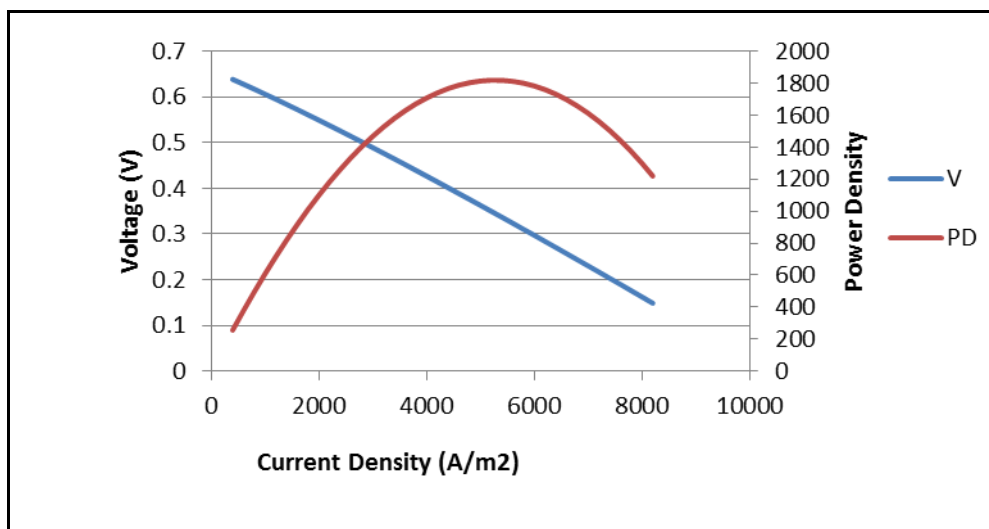


Fig4. Current density i Vs Voltage developed V (primary axis) Vs Power density P (secondary axis)

The fig4 clearly showed that the Voltage developed V decreased as the current density i increases as predicted by earlier researchers. The Power density increased exponentially with an increase in current density reached a maxima and then begins to decreases. This behaviour is in congruence with the fact that it is an anode supported SOFC & therefore possesses low ohmic losses at high current densities. Further, The predicted polarization curve is in good qualitative agreement with published experimental data. In addition to the current-voltage characteristics, the model was able to provide much more details on the transport and electrochemical processes occurring in SOFC.

5. Conclusion

The paper presented an original approach for the finite-volume axial-symmetric one dimensional modelling of a tubular SOFC based on the electrochemical and thermal phenomena. It was then successfully developed and simulated using MATLAB software. A better prediction of the realistic performance characteristics of a tubular SOFC stack can be achieved by adjusting the model parameters. The simulation model presented allowed accurate calculation of the main physical, chemical, electrical and electrochemical properties in the system, such as pressure, chemical composition, overvoltages, current, etc. The results showed that some of the simplifying assumptions usually adopted in SOFC simulations are not rigorously acceptable, but still the model and the simulated results were in concordance with that predicted from experimental techniques. The one-dimensional modelling can further be extended to multi-dimensional by taking variation of properties along the radial direction, although the variation along the angular direction θ still can be safely ignored.

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