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Electrochemical Analysis of an Anode-Supported Axially Symmetrical One Dimensional Tubular Solid Oxide Fuel Cell

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Abstract

Objectives: In this paper, modeling and simulation of an anode supported axially symmetric tubular SOFC was performed. The nodal and current density variation of properties of SOFC were analyzed. The tubular SOFC was fed with 89% H_2–11% water as fuel and high temperature air as the oxidant. The molar flow rates were adjusted so as to obtain the specified 85% fuel utilization & 25% O_2 utilization of air. The SOFC was operated at a reference of 1 std. atm. pressure and 1000ºC temperature. Also, electrochemical analysis and computational fluid dynamics study of various components was done. **Methods:** The model developed was in congruence with experimental data available for commercial prototypic 2.2 cm diameter Siemens Westinghouse tubular SOFC 1.5 m axial length located at Pittsburgh. **Findings:** The nodal variation graphs depicted a decreasing concentration of reactants and increasing one for the products along the length of the Tubular SOFC. The losses encountered due to polarizations are found to decrease along the SOFC. The Nernst potential and polarization losses as expected increase with an increasing current density. The graph for variation of Voltage with a change in current density showed a decrease in voltage developed with increasing current density and was found to very closely approach the plot developed for Siemens Westinghouse tubular SOFC experimental data. The results although closely matches the experimental results are also helpful in designing of a practical Tubular SOFC. **Applications:** The modeled tubular SOFC can be further improved by variation of properties along the radial direction; any angular variation in properties for homogenous system can still be ignored.

Keywords: Electrochemical Analysis, Nodal Variation, Polarization, Power Density, Voltage

1. Introduction

Combustion of fossil fuels forms the world's bulk energy requirements even till today. Combustion of fossil fuels causes environmental problems like air pollution, and the emission of greenhouse gases. New and alternate energy sources are required to meet the ever increasing demand for energy, and also keeping our environment clean from the effect of greenhouse gases and other air pollutants. The only solution to these environmental concerns is the increasing the use of advanced and efficient energy systems. Fuel cell systems are one such emerging source of combustion free clean energy production which can be harnessed without causing any harm to the environment. A fuel cell is a device that utilizes the chemical energy stored in fuels such as

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hydrogen (or source of hydrogen-rich fuel like CH4, C4H10or even diesel and gasoline) into electrical energy due to electron transfer from one electrode to the other when oxidation of hydrogen takes place.[1–3]

One single SOFC is a type of solid-state ionic based fuel cell devices with no moving parts and consists of an electrolyte between two comparatively thicker electrodes a porous negative one known as the anode and a porous positive one known as the cathode. The high temperature of operation of SOFCs typically 1000°C reform fuels internally, thereby enabling them to different fuels which gets reformed in-situ and no additional reformer is required in the system. Carbon monoxide (CO), which is a poison for other fuel cells, can even be used as fuel in a SOFC. They cause lesser pollution due to oxides of nitrogen and Sulphur which are associated with other power generation techniques. They quiet operation, allows them to be put in and around residential areas for supply of electrical power. Also, less maintenance is required due to absence of moving parts.[1]

1.1 Principles of Operation

The SOFC works on the principle of production of electricity due to electro-chemical reaction between fuel and an oxidant across an O^{2-}ions conducting electrolyte; as illustrated in Figure 1. The anode and the cathode are highly porous in nature and transport the fuel and the oxygen through them. The dense ionic conducting electrolyte is sandwiched between the electrodes. Fuel either Hydrogen or some hydrocarbon rich gas is fed to the anode where it oxidizes releasing electrons to the external circuit. The conventional current flows in opposite direction i.e. cathode to anode resulting in a DC electric current. Oxygen from the air fed to the cathode, receives electrons from the external circuit, and undergoes a reducing it leading to the formation of O^{2-} ions. The electrolyte allows oxide ions to permeate through it but restricts the movement of electrons through it. The O^{2-}reactwith H_2 from fuel at the Triple Phase Boundaries (TPB) and releasing more electrons.

The most appropriate anode is Nickel / Yttria – Stabilized Zirconia (Ni-YSZ) Cermet. The cathode is typically Lanthanum Strontium Magnetite LSM layer chemically expressed as $La_{1-x}Sr_xMnO_3$. To avoid thermal mismatch between components electrolyte is an Y_2O_3 doped ZrO_2 material called YSZ.[4,5]

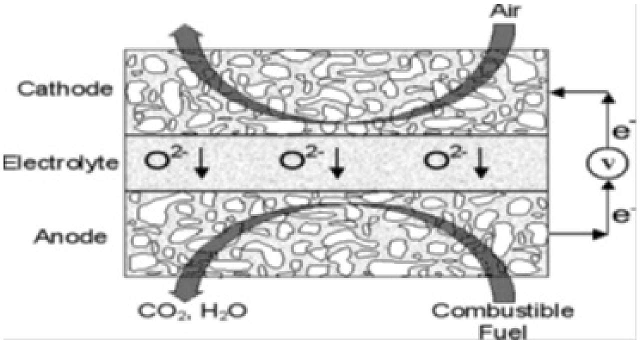


Figure 1. Principle of operation of a SOFC.[1]

The distinctive property of a good electrolyte of a SOFC is that it must be good O^{2-}ion-conductor formed by dissociation of oxygen at the cathode. The electrochemical cell reactions occur very close to the electrodes within a distance of less than 10–20 μm from the electrolyte surface.[6,7] The structure of the anode strongly affects the rate of chemical reaction between fuel & O_2 and therefore determines the performance of a SOFC. The co-existence of electrolyte, electron-conducting metal phase, and the gas phase is referred to as Three-Phase Boundary (TPB) which is responsible for the electrochemical reaction. For a typical Ni/YSZ anode and YSZ electrolyte, the TPB exists is shown in Figure 2.

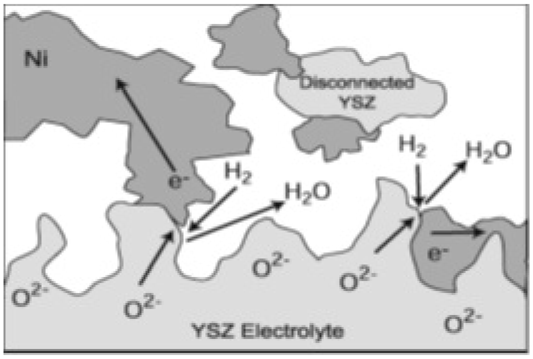


Figure 2. Schematic of Ni/YSZ anode three-phase boundary.[1]

The thickest of the three components of SOFC i.e. the cathode, anode, or electrolyte forms its structural support in an SOFC. The electrolyte supported SOFC require very high operating temperatures in order to increase the ionic conductivity of oxygen ions through them. Electrode- supported cell employ thin electrolytes giving a significant O^{2-} conductivity at lower temperatures. So, most of SOFC research is concentrated on employing either an Anode supported or a cathode supported one. In an anode-supported SOFC, anode is sufficiently thick to serve as substrate layer employing thin electrolyte thereby reducing the ohmic resistance.[8] Most of the research has been directed to the development of anode-supported cells and cathode supported SOFCs. Therefore, anode supported design has been employed in this research work. Another important factor in design is to maintain chemical compatibility of those parts that come in contact and to match the thermal expansion coefficients of the various components.

1.2 Electrochemical Reactions in SOFC

The Electrochemical cell reaction occurring in a SOFC involves the following individual reactions at the anode and cathode:[9]

(i) Oxidation of fuel/fuel rich gas at anode

$H_2 + O^{2-} \rightarrow H_2O + 2e^-$ ……..…[1]

(ii) Reduction of oxygen at cathode

$½\, O_2 + 2e- \rightarrow O^{2-}$ ……..….[2]

The oxygen ions migrate through the dense electrolyte and reach the TPB.

(iii) Overall Cell reaction

$H_2 + ½\, O_2 \rightarrow H_2O$ ………[3]

2. CFD Model of SOFC

2.1 Diffusive Transport in SOFC

In this paper, the overall diffusion of reactant gases occurs by a mechanism of involving both ordinary binary diffusion and Knudsen diffusion. The binary diffusion equation is represented as

$$D_{AB} = 1.858 \times 10^{-3} T^{\frac{3}{2}} \frac{\left[\frac{(M_A + M_B)^{\frac{1}{2}}}{M_A M_B}\right]}{P \sigma_{AB}^2 \Omega_D} \tag{1}$$

For a multi-component mixture, the diffusivity of hydrogen to the surface of reaction through the multi-component mixture was represented by equation:

$$D_{H2m} = \frac{1 - y_{H2}}{\Sigma_{k \neq i} \frac{y_k}{D_{H2k}}} \tag{2}$$

The Knudsen diffusion through the porous media was characterized by the equation:

$$D_{kH2} = \frac{2}{3}\left(\frac{8RT}{\pi M_{H2}}\right)^{\frac{1}{2}} r \tag{3}$$

The effective diffusivity of H_2, $D_{H2,eff}$ through the multi component fuel mixture and porous media was represented by the equation given below:[10]

$$D_{H2\ eff} = \frac{\varepsilon}{\upsilon}\left(\frac{1}{D_{H2,m}} + \frac{1}{D_{kH2}}\right)^{-1} \tag{4}$$

The overall diffusion expression of H_2 can also be applied for an analogous system involving diffusion of O_2 through the cathodic chamber resulting in the formation of O^{2-} ions which transport through the electrolyte to react with the fuel at the TPB.

2.2 Governing Electrochemical Equations

2.2.1 Rate of Cell Reaction

The rate of cell reaction for H_2 oxidation was represented based upon the assumed value of current density by an equation by given below:[11,12]

$$r_{cellreaction} = \frac{iA_{cell}}{2F} \tag{5}$$

Since, H_2 oxidation is the only reaction depicted in this research work, the total rates of reactions for the three components present in the anodic chamber of the SOFC i.e. H_2, H_2O and O_2 are given below as:

$$Sumr_{H_2} = -r_{cellreaction} \tag{6}$$

$$Sumr_{H_2O} = r_{cellreaction} \tag{7}$$

$$Sumr_{O_2} = [-0.5\ (r]_{cellreaction}) \tag{8}$$

2.2.2 Nernst Potential or Open Circuit Voltage

The Nernst Potential based upon thermodynamic analysis was found out based upon the $\Delta G_{cell\ reaction}$ and partial pressure of various components by an equation as given below:[1,3]

$$E_{nernst} = \left(\frac{-\Delta G_{cellreaction}}{2F}\right) + \left(\frac{RT_f}{2F}\right) ln \left(\frac{P_{H_2} P_{O_2}^{0.5}}{P_{H_2O}}\right) \tag{9}$$

2.2.3 *Voltage Developed*

Knowing the Nernst Potential & the various losses, the actual developed voltage was then given by:[3]

$$V = E_{nernst} - \eta_{act} - \eta_{ohm} - \eta_{conc} \quad (10)$$

2.2.4 *Power Density*

The Power density of our SOFC, was then calculated by just multiplying the developed voltage with current density i;[3]

$$P = V \times i \quad (11)$$

3. Mathematical Modeling of SOFC

Since for a axially symmetrical tubular geometry forms a system involving typical one dimensional flow has been chosen in this modeling system.[11,12] The finite element method with linear discretization along the axial direction of the tubular geometry was done to evaluate the variation of important thermodynamic parameters, such as concentration, current density, voltage and power density etc., along the cell.

3.1 Model Assumptions

The simplifying assumptions while deriving the axially symmetrical steady state model of tubular SOFC were:

- fuel and oxidant are ideal gas mixtures;
- isotropic and homogeneous electrodes and
- No radial and angular variation of concentration and current density has been assumed. The diffusion of gases normal to the flow direction was not considered for studying the concentration distribution of components.
- SOFC was considered to be operating under steady-state conditions.
- The principal fuel for SOFC was 89%-H_2 and 11% H_2O as used in the operation of SeimensWestinghouse experimental SOFC.
- The electrolyte YSZ was considered to be sandwiched within Ni-YSZ anode and LSM cathode.
- The air & fuel flow over the surfaces of cathode & anode respectively.
- The various Polarization losses were studied along the axial direction and by changing the current density.

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 Figure 3.

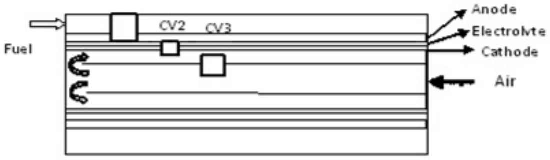


Figure 3. Discretization model of SOFC.

The typical tubular configuration of the SOFC, developed by Siemens consisted of the cell, i.e.an anode, a cathode and an electrolyte.11,12 The air as an oxidant was circulated through a central inner tube which gets preheated and reverses its path on reaching the other end. On reversal of direction of air, the air & fuel flow parallel to each other. The oxygen from the air channel upon gaining electrons reduces to O2- ions in the cathode. The O2- ions pass through the electrolyte to react with fuel in the TPB formed on the surface of anode. A finite-element axial-symmetric steady simulation of the SOFC tube was then performed. The overall control volume was discretized by means of vertical slices into 101 plans orthogonal to the axial direction of the cylinders. Thus, the system was divided into 100 equal sized nodes. The node 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 formulated both for SOFC tube in order to determine the variation of all the thermodynamic, chemical and electrical properties within those components.

The tubular SOFC tube was analyzed on the basis of the fixed parameters shown in Tables 1 and 2. The SOFC under investigation is fed by air, with the typical

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

Component	Total	H2	H2O	O2	N2
Molar flow rate (Air stream)	7.20476E-06	-	-	1.513E-06	5.69176E-06
Molar flow rate (Fuel stream)	5.0E-07	4.45*E*–07	5.5*E*–08	-	9.82*E*–09

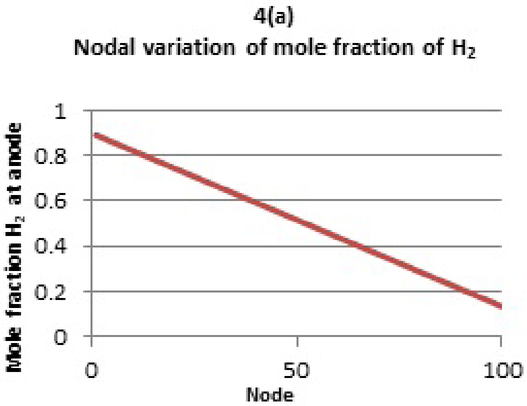
Table 2. Fixed parameters of the case study

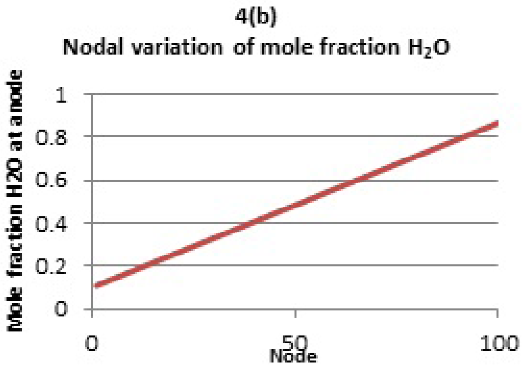
Parameter	Value	Parameter	Value
Current density i	3000 A/m^2	Cathode tortuosity factor, υc	5.90
Anode thickness la	180 µ m	Anode conductivity, ó$_a$	10^5 W/m K
Cathode thickness lc	50 µ m	Cathode conductivity, ó$_c$	10^7 W/m K
Electrolyte thickness le	50 µ m	Electrolyte conductivity, ó$_e$	1.00 W/m K
Cell length, l	1.50 m	Anode porosity, å$_a$	50%
Number of slices, N	100	Anode tortuosity, υa	5.90
Fuel inlet pressure, P_f	1 atm	Anode pore diameter, d_a	0.5 µm
Air inlet pressure bar, P_a	1 atm	Cathode pore diameter, d_c	µm
Fuel inlet temperature, T_f	1000°C	Conductivity anode (W/m K)	10^5
Air inlet temperature, T_a	1000°C	Conductivity electrolyte (W/m K)	1
Anode porosity, å$_a$	50%	Conductivity cathode (W/m K)	10^6
Anode tortuosity factor,	5.90	Effective Diffusivity anode (m^2/s)	2.96535E-06
Cathode porosity, $_å$c	50%	Effective Diffusivity cathode (m^2/s)	7.39816E-07

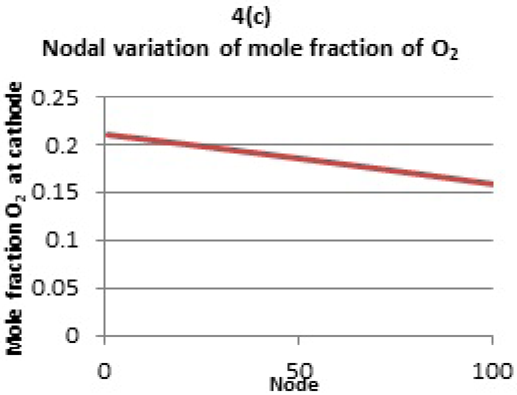
atmospheric air composition, and by the fuel as per the composition given in table 1.

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 fuel consisting of 89%-H_2 and rest H_2O and air as oxidant having the usual molar composition of 21%-O_2 and 79%-N_2.The nodal variations of mole fractions of different gaseous reactants &products have been represented in Figure 4.







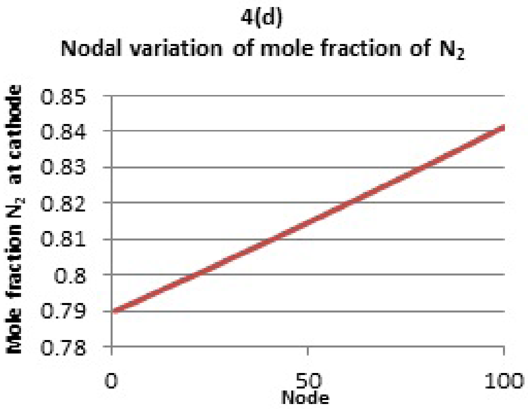
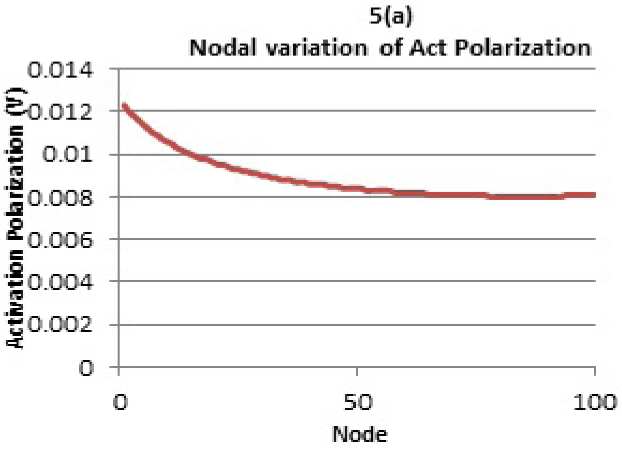
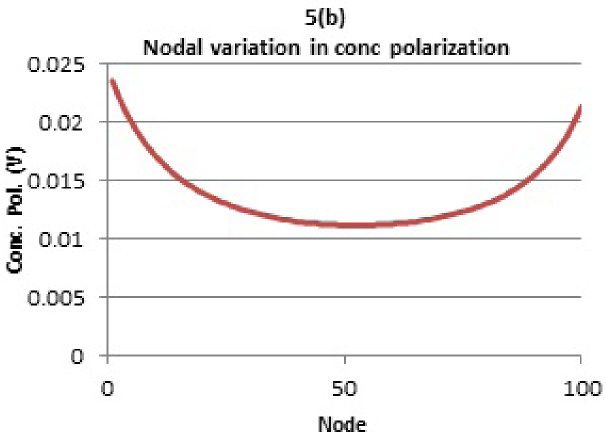
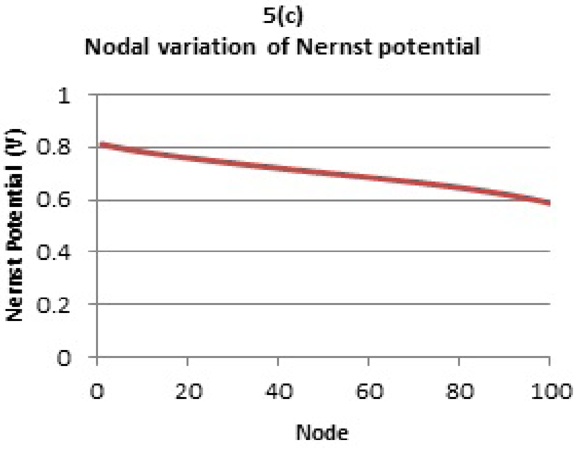


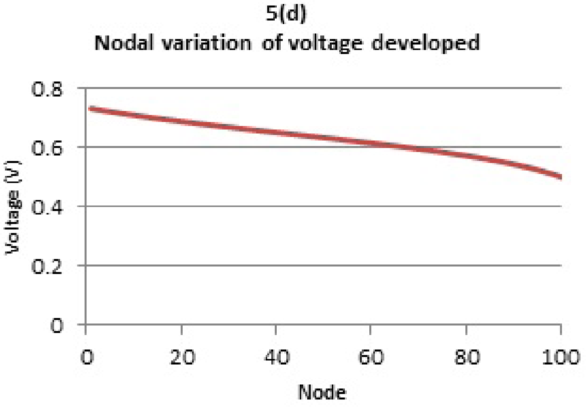
Figure 4. Nodal variation of mole fraction of (a) H_2 at anode (b) H_2O at anode (c) O_2 at cathode (d) N_2 at cathode.

- Figure 4 clearly depicts that the mole fraction of hydrogen, y_{H2} falls linearly from one node to another whereas a linear increase in mole fraction of water (steam) y_{H2O}, was observed due to its formation from the electrochemical cell reaction.
- The mole fraction of O_2, y_{O2} decreases from node to node in the cathode owing to its diffusion through the electrolyte as O^{2-} ions which then combine with H_2 forming H_2O. The mole fraction of N_2 which remains un-reacted in the system increases linearly owing to the decrease in concentration of O_2.









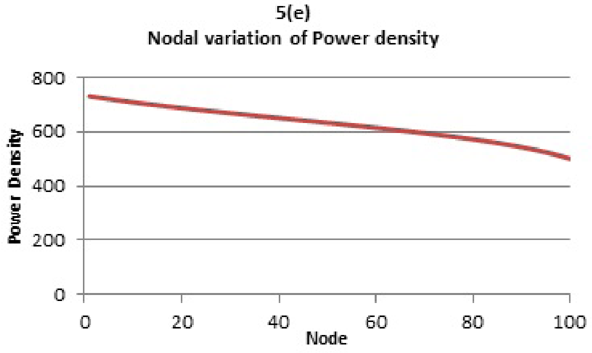
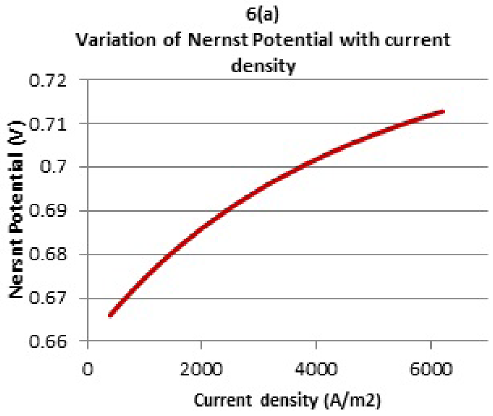
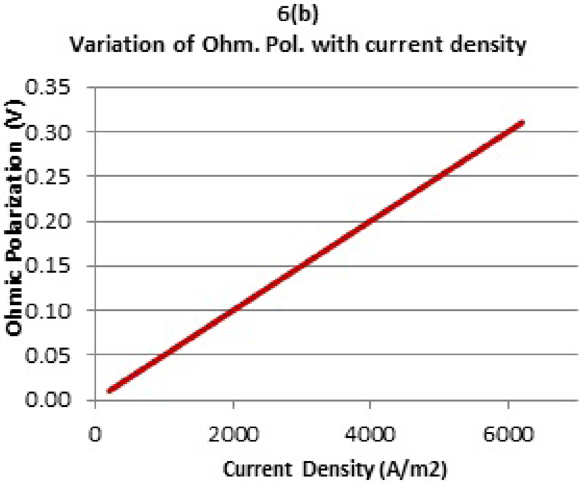
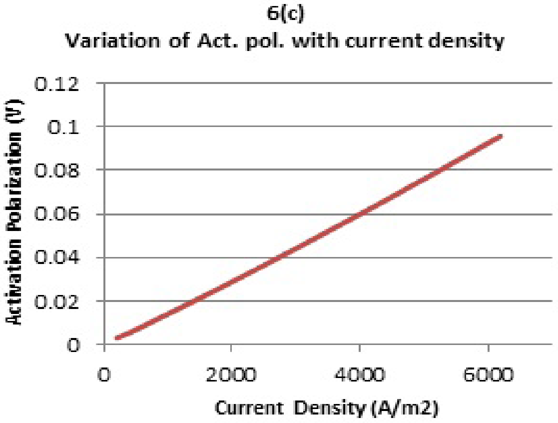


Figure 5. Nodal variation at fixed current density of 3000 A/m^2 (a) Activation Polarization (b) Concentration Polarization (c) Nernst Potential (d) Voltage developed (e) Power density.

- Figure 5(a) clearly shows that there is a decrease in Activation polarization loss in voltage at a particular current density due to an increase in total activation limiting current density in the axial direction.
- The Concentration polarization loss η_{conc} is a complex function of many factors. Figure caption 5(b) clearly depicts that the initial decrease its value is due to the decrease in i_{Oa} and i_{OC} along the axial direction. An increase in later part of the curve might be due to effect of variation of partial pressures of H_2, O_2 and H_2O.
- Figure 5(c) showed the nodal variation of Nernst Potential, the Open circuit voltage OCV which decreases along the axis owing to a decrease in partial pressure of H_2.
- The voltage developed shown in Figure 5(d) shows a similar trend, due to decrease in OCV.
- The power density figure also follows the similar pattern as shown in Figure caption 5(e) as mathematically it represents the voltage multiplied by a constant current density.







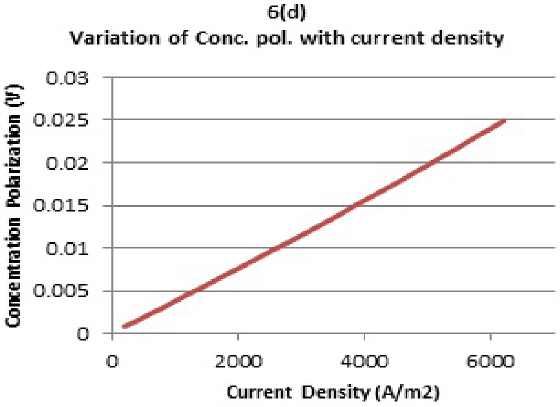


Figure 6. Effect of Variation of Current density on Nernst Potential & Polarizations.

- Figure caption 6(a) depicts the behaviour of Nernst Potential with an increase in current density. It clearly shows that the Nernst Potential increases slightly with a large increase in current density. Further, Figure caption 6(b), (c) and (d) depict the behavior of Polarizations with an increase in current density. For all types of polarizations, there is a linear increase in voltage loss with an increase in current density. Since, the ohmic polarization depends on current density & thickness of electrolyte, the ohmic voltage loss could be decreased to some extent by choosing a thinner electrolyte for cells operating at high current densities.

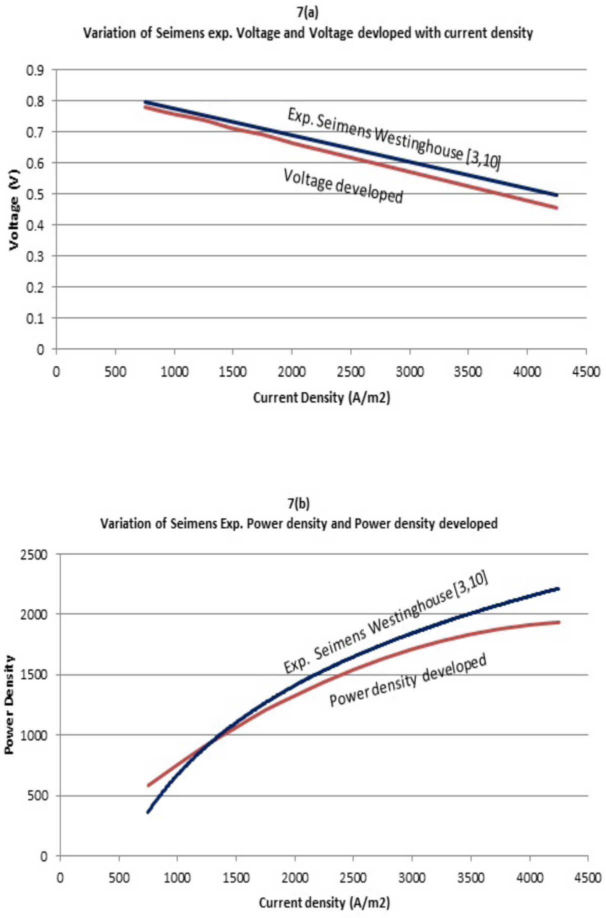


Figure 7. Variation of Voltage and Power density with current density.

- Figure caption 7(a) and (b) depicts the variation of Voltage and power density with current density. Clearly, there is a linear decrease in voltage developed with an increase in current density. The Voltage decreases owing to a rapid increase in Polarization losses with an increase in current density. Further, the Figure 7(a) also shows that the results are concordance with those predicted by Seimens Westinghouse data.
- Figure 7(b) shows the variation of Power density with an increase in current density. There is an exponential increase in power density with an increase in current density but the plot flattens out at higher values of current density. Ideally, the power density plot should reach a maxima & then fall with further increase in current density, but for this range of current density, the plot closely resembles the experimental plot to a large extent.

The fuel molar flow rates along the SOFC axis were analyzed putting in evidence the trend of the chemical and electrochemical phenomena occurring in the SOFC tube. The simulated 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. Variation of model parameters provide a better prediction of the realistic performance characteristics of the one-dimensional tubular SOFC. The simulation model presented allowed accurate calculation of the main physical, chemical, electrical and electrochemical properties in the system, such as chemical composition, polarizations, current, voltage and power density etc. Although some of the simplifying assumptions usually adopted in SOFC simulations are not rigorously acceptable, but still the model and the simulated results were in close concordance with that predicted from experimental data given by Seimens Westinghouse. 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 so as to more closely approach a more realistic model.

6. Acknowledgments

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