

# Mathematical modelling of the transport phenomena and the chemical/electrochemical reactions in solid oxide fuel cells: a review

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## Abstract

The activity in the field of SOFC modelling activities has been increasing steadily over the last decade. A vast range of models exist today, varying in complexity and in the number of assumptions employed. These range from detailed models on individual components to entire stack models. One-, two-, and three- dimensional, as well as parametric models have been developed for several different geometries. Some of the models use empirical data like heat transfer coefficients while others use CFD to give a full- field solution. The goal of this paper is to highlight the major modelling accomplishments by presenting the state-of-the art in SOFC modelling. More importantly, the paper will identify the areas where further improvements are required.

In the past, the emphasis in a majority of the models has been either on the transport processes or on the electrochemical processes. This paper intends to show by properly incorporating both aspects, the physico-electro-chemical processes occurring in a SOFC can be described more accurately.

The areas where improvements can be made are numerous, but the most important developments must be based on an understanding of the detailed electrochemical reaction mechanism and by accounting for the complex transport processes occurring in the porous media at the micro-scale level.

## 1 Introduction and background

A detailed mathematical model of the transport and the electrochemical processes within a solid oxide fuel cell (SOFC) can be a powerful tool for the development of these fuel cells. Considerable progress in computational SOFC modelling over the last two decades has led to an improved understanding of relevant physical, electrical, and chemical phenomena. However, a complete understanding of these processes still eludes us.

A reliable and predictive well-designed SOFC model requires that the effective heat, mass, species, charge and momentum transport in the porous substrates as well as electrochemical and chemical reactions are accurately described. However, a majority of the models presented in the

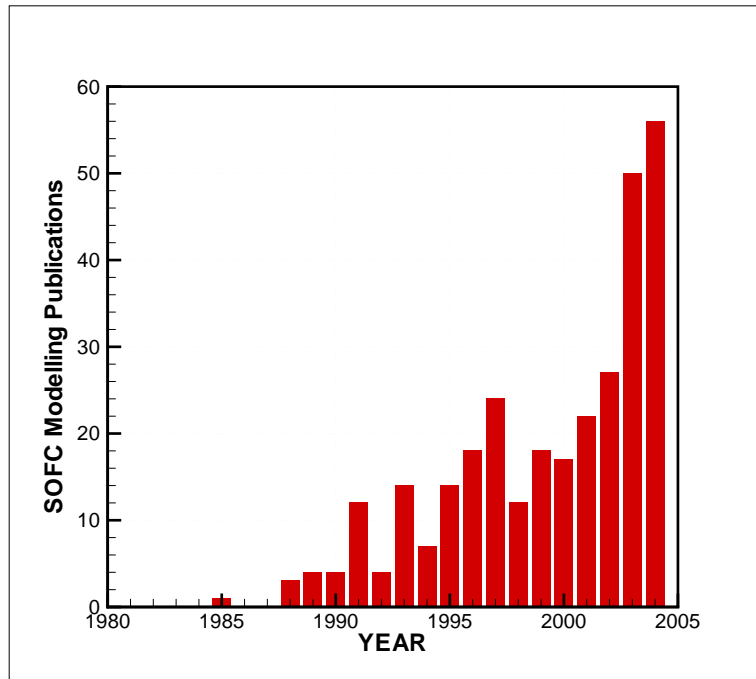


Figure 1: Increased solid oxide fuel cell modelling activity (2004 data is projected)

literature focus on either the transport processes while making simplifying assumption regarding the electrochemical processes or vice-versa. Such models may not be reliable in predicting the impact of design or operational changes.

This paper reviews the SOFC modelling accomplishments to date. Since the first models developed in the early 1980s [1], the quantity and complexity of the mathematical modelling has increased. The number of SOFC modeling papers has been increasing over the past few years as depicted in the Figure 1 shows an almost exponential growth in the number of modeling papers published with time.

Early papers [1, 2, 3, 4] used basic unit cell elements of a planar geometry and solved the transport equations incorporating the electrochemical reactions. Fluid flow was solved in one dimension and only the overall reaction was considered. Much of the physical processes were not accounted for including momentum transport and the variation of partial pressure in the electrodes.

Later models addressed some of these issues. For instance, Ferguson et al. [5] solved a three-dimensional model and determined the local distribution of the potential, species contribution, and temperature. This was done while considering the separate reactions occurring at each electrode. Melhus et al. [6] advanced the field by adding the conservation of momentum equation to their SOFC model. Models solving the tubular geometry were also introduced [7, 8, 9].

As models developed, it became clear that the electrochemical behaviour was not accurately accounted for. A number of very important models were developed that described the electro-

chemically active region of the catalyst layer in detail [10, 11]. Several researchers extended the modeling effort to include a description of porous electrode microstructure in terms of porosity and particle size. These models were aimed to improve the understanding of the electrochemical reactions associated losses [12, 13, 14, 15]. These models typically considered only a single electrode and did not consider an entire cell.

The current state-of-the-art in SOFC modelling is to use computational fluid dynamics (CFD) to solve the transport equations and couple the solution to an electrochemical model. Many researchers have used this approach [16, 17, 18, 19, 20], but the quality of the electrochemical model varies from one model to the other.

## 2 Goals for this paper

This paper aims to summarize the state-of-the-art in SOFC modeling while identifying the existing gaps. A comprehensive review paper is under preparation. Recognizing that the ultimate objective is to improve SOFC efficiency and aid the commercialization of this technology, this paper hopes to allow modellers to understand the state-of-the-art quickly so that contributions can be made efficiently and the main problems in SOFC modelling can be addressed. The goals of this paper are as follows:

- Highlight major modelling accomplishments
- Present the modeling approach for individual components of a SOFC and associated governing equations
- Emphasize the development of a predictive model that is based on accurate description of physico-electro-chemical processes and physical structure/microstructure

This paper presents the mathematical models that have been used to describe the fundamental processes occurring in the individual components of a fuel cell - the flow channels, the electrodes, the electrolyte and the interconnect.

## 3 The flow channels

The key function of flow channels is to allow the distribution of gases to be distributed throughout the fuel cell to the porous electrodes with as little losses as possible. The anode fuel channel brings supplies fuel-rich stream, which is usually a humidified hydrogen stream or a reformat gas mixture composed of primarily hydrogen. Fuel in excess of that required by the stoichiometry of the reaction is supplied to ensure that fuel is present at every reaction site and because gas stream exiting anode flow channel is usually recirculated to increase the system efficiency. The anode flow-channel also serves to remove the water produced during the electrochemical oxidation of hydrogen to be transported out of the cell. The cathode or air channel is similar to the anode channel except it typically only contains oxygen and nitrogen and does not need to allow for the removal of any gases. Plenty of excess air, up to 500% excess air, is used for cooling. Cathode gas is usually not recirculated.

### 3.1 Governing transport equations

The specifics of the gas and temperature flow in the channels is very dependent on the geometry. The anode gas in a tubular cell is not constrained in a typical channel, for example. Regardless of the geometry, however, the governing equations are the same.

The conservation of mass:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = S_m \quad (1)$$

where  $\vec{v} = (u, v, w)$  and  $S_m$  represents the additional mass sources.

The conservation of momentum or Navier-Stokes equation: Although sometimes neglected, the momentum balance equation is essential to correctly model the fluid velocity and species partial pressures.

$$\frac{\partial}{\partial t}(\rho \vec{v}) + \nabla \cdot (\rho \vec{v} \vec{v}) = -\nabla p + \rho \vec{g} + \nabla \cdot \bar{\tau} + \vec{S}_M \quad (2)$$

where  $\bar{\tau}$  is the stress tensor ( $\bar{\tau} = \mu[(\nabla \vec{v} + \nabla \vec{v}^T) - \frac{2}{3} \nabla \cdot \vec{v}]$ ) and  $S_M$  is the external body forces. In the literature, the flow in the channels is always assumed to be laminar. There is a good chance that the flow in an internal tubular cathode will be turbulent. In this case a turbulent model is necessary to determine  $\bar{\tau}$ .

The species balance equation: To solve for the full species field, the species balance equation must be solved.

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \cdot \vec{J}_i + S_{s,i} \quad (3)$$

where  $Y_i$  represents the mass fraction of species  $i$ ,  $\vec{J}_i$  is the diffusive flux of species, and  $S_{s,i}$  represents the additional species sources. The diffusive flux,  $\vec{J}_i$ , is given in units of  $kg/(m^2 \cdot s)$ . It is often more convenient to discuss a molar diffusive flux,  $\vec{N}_i$  since a molar flux can easily be converted to a current density. The molar diffusive flux,  $\vec{N}_i$  is simply related to the species flux,  $\vec{J}_i$  through the component's molar mass,  $\vec{N}_i = \vec{J}_i / \tilde{M}_i$ .

An equation of the form of Equation 3 will be solved for  $n - 1$  species where  $n$  is the total number of species present. The last species can be solved because the sum of the mass fractions equals one. The flow in the channels is mainly convective and often researchers ignore diffusion in the channels to simplify calculations.

Energy conservation equation: Material properties and reaction rates can be a strong function of temperature. Therefore, it is important to account for temperature variation within the cell by solving the conservation of energy.

$$\frac{\partial}{\partial t}(\rho e) - \frac{\partial P}{\partial t} + \nabla \cdot (\rho \vec{v} e) = \nabla \cdot \left[ k \nabla T - \sum_i h_i \vec{J}_i \right] + S_e \quad (4)$$

This equation balances energy storage and convected energy with conduction (heat diffusion), energy due to species diffusion and a source term,  $S_e$ .

Early SOFC models used correlations to determine parameters such as mass and heat transfer coefficients or pressure drop. These were based on the assumptions of fully developed, laminar, internal flow. However, present day computing resources allow the full set of governing equations to be solved relatively rapidly.

### 3.2 Reforming

One of challenges in modeling the flow channels is accounting for the numerous chemical reactions that may occur in the anode. For natural gas fueled SOFCs, usually the gas entering the flow-channel is pre-reformed and contains at least  $CH_4$ ,  $H_2$ ,  $CO$ ,  $H_2O$ , and  $CO_2$  are usually present. Although much of the reforming is expected to occur in the electrode, steam reforming (Reaction 5) does occur in the channels. Reforming inside the cell is known as Internal Direct Reforming.



The steam reforming reaction is often assumed to have fast kinetics and modeled via local equilibrium assumption. It has been reported that at 1173K, the steam reforming occurs 42 times faster than the electrochemical reaction of hydrogen [21].

If  $CO$  is present, the water-gas shift reaction becomes very important because it affects the concentration of hydrogen at the reaction sites



It is generally thought that for a gas mixture containing  $CO$  and  $H_2$ , electro-oxidation of  $H_2$  dominates over that of  $CO$ . In fact, it has been reported that approximately 98% of the current is a result of the electrochemical conversion of hydrogen [22]. The consumption of hydrogen forces the Reaction 6 to occur in the forward direction.

The formation of carbon is important because carbon can have a negative effect on the reactive area of the anode. The Boudouard Reaction is thought to be an important source of soot.



The chemical kinetics of the reactions occurring in the fuel channel and anode are not completely understood. Although, kinetic rate expressions have been used in the literature [4, 8, 19, 23, 24]. It is often assumed that the chemical reactions are at equilibrium.

Kinetics of chemical reactions are a strong function of temperature, it is important to model the temperature profile correctly. However, coupling the energy equation with the chemical kinetics is a challenge. For instance, steam reforming is an endothermic reaction while partial oxidation reforming and the water shift reaction is exothermic. These reactions should be incorporated into the model as species and energy sources and sinks. Aguiar et al. [25] preformed an SOFC model where the temperature in the fuel cell was coupled to the temperature in the endothermic reformer (Internal Indirect Reformer).

### 3.3 Radiation

The high operating temperature of the SOFC suggests that radiation heat transfer could be an important mode of energy transfer and must be included for an accurate model, and yet the majority of the existing models ignore it. Equation 4 does not include radiation and, thus, an additional radiation model must be added.

Recent work [26] has shown that radiation in the flow channels decreases both the operating temperature and temperature gradients and must be considered in order to develop an accurate and reliable model. This work also considers the radiative properties of  $H_2O$  and  $CO_2$ . Future work is needed to understand the role of participating gases, especially in tubular SOFCs.

## 4 The electrodes

The porous electrodes of fuel cells are where the electrochemical reaction takes place. These electrodes must serve several functions:

- must transport ions from the reaction site in the cathode to the electrolyte and from the electrolyte to the reaction site in the anode.
- must transport electrons from the anode sites and to the cathode sites
- must allow for gas transport/diffusion through the pores to the active sites
- must provide a site for the electrochemical reactions to occur

Each of the electrodes in an SOFC are porous structures that may be described as a combination of two distinct layers - a functional layer for the critical electrochemical reactions to occur and a porous diffusion layer that must conduct current (ions and electrons) through the ceramic matrix and allow for the diffusion of the chemical species. The performance of individual electrodes is influenced by the properties and composition of the constituent material as well as the microstructural parameters such as the particle size, the porosity and pore size, and the thickness. Mathematical modelling of both the anode and the cathode is important in optimizing these parameters and understanding their behaviour.

The electrochemical reactions occurring in the functional layer of the electrode involve oxide ions, electrons, and chemical species (see Equations 8 and 9). Thus, the electrode must allow access for all three components at an active site. These active locations are also known as the triple phase boundaries (TPB).

The cathode reaction:



The anode reaction for the hydrogen electrochemical reaction:



### 4.1 Mass transport

The first challenge in modelling the electrodes is in determining the rate at which the species diffuse and gases convect through the electrode. Several different empirical equations are used in the literature to determine the mass flux and concentration losses. The real challenge in determining

the transport related losses, however, is not in knowing which empirical relationship to use, but in knowing how to best solve the concentration gradients and species distributions in the domain. This requires knowledge of multicomponent diffusion in porous media and is not a trivial task.

Once the species distribution is solved, the concentration losses are incorporated into an SOFC model as the reversible potential decreases due to a decrease in the reactant's partial pressure.

In order to solve the species balance equation (Equation 3), the mass flux,  $\vec{J}$ , must be determined. Often the molar flux  $\vec{N}$  is determined and converted to mass flux. In the literature there are three basic approaches for determining  $\vec{N}$ .

1. Fick's Law is the simplest diffusion model and is typically used in dilute or binary systems, and is indicated in Equation 10. A multicomponent extension of Fick's Law is sometimes used (see [5] for example) and is given in Equation 11. Both of these forms of Fick's Law are used in the literature.

$$\vec{N}_i = -cD_{i,j}\nabla X_i \quad (10)$$

$$\vec{N}_i = -cD_{i,m}\nabla X_i + X_i \sum_{j=1}^n N_j \quad (11)$$

In Equations 10 and 11,  $c$  is the total molar concentration.

2. The Stefan-Maxwell model is more rigorous, more commonly used in multicomponent systems, and is used quite extensively in the literature.

$$-\nabla X_i = \sum_{j=1, j \neq i}^n \frac{X_j N_i - X_i N_j}{cD_{i,j}} \quad (12)$$

The biggest draw back of the Stefan-Maxwell model is that it is more laborious to solve. The  $D_{i,j}$  here are the binary diffusivities, and for an  $n$  component system,  $\frac{1}{2}n(n-1)$  binary diffusivities are required.

3. The Dusty Gas model, sometimes alternatively called the extended Stefan-Maxwell equation is also commonly used. It includes the Stefan-Maxwell formulation, but also takes Knudsen diffusion into account. Knudsen diffusion is wall-collision dominated diffusion and occurs when the particle's mean-free-path is similar or larger in size than the average pore diameter.

$$-\nabla X_i = \frac{N_i}{D_{i,k}} + \sum_{j=1, j \neq i}^n \frac{X_j N_i - X_i N_j}{cD_{i,j}} \quad (13)$$

In Equation 13,  $D_{i,k}$  is the Knudsen diffusion coefficient for species  $i$ .

While the molecular diffusivity coefficient depends only on the temperature, pressure, and concentrations, the effective diffusivity in porous media also depends on the micro-structural parameters such as porosity, pore size, particle size, and tortuosity. The molecular gas diffusivity must be corrected for the porous media. A large portion of the corrections are made using the ratio of porosity to tortuosity ( $\varepsilon/\tau$ ), although in some cases, the Bruggeman correction ( $\varepsilon^{1.5}$ ) was used. Equation 14 shows these two corrections.

$$D_{i,j}^{eff} = \left(\frac{\varepsilon}{\tau}\right) D_{i,j}; \quad D_{i,j}^{eff} = (\varepsilon^{1.5})D_{i,j} \quad (14)$$

If the Knudsen number,  $Kn = \lambda/D_{pore}$ , is near 1 or higher than 1, Knudsen diffusion is important. The Dusty Gas diffusion model requires a Knudsen diffusivity in order to be solved while the other two models require a little more work to incorporate Knudsen diffusion. The Knudsen diffusion coefficient for gas species  $i$  can be calculated using Equation 15

$$D_{i,k} = \frac{2\bar{r}}{3} \sqrt{\frac{8RT}{\pi\tilde{M}_i}} \quad (15)$$

where  $\tilde{M}_i$  is the molecular mass of species  $i$ ,  $\lambda$  is the mean free path of the gas and  $\bar{r}$  is the average pore radius.

## 4.2 Electrochemical behaviour

The origin of potential and electrical currents may be attributed to the electrochemical reactions that occur in the two electrodes. The Nernst equation (Equation 16) is used to determine the electrical potential of the reaction. Equation 16 shows the potential for hydrogen electrochemically reacting with oxygen.

$$E_{ideal,H_2} = \frac{1}{2F} \left[ \Delta G(T) + (RT) \ln \frac{P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \right] \quad (16)$$

The Nernst equation should be used in a fuel cell model to find the local potential at the active locations given the half reactions (eg. Equation 8 and 9) and the species concentrations at the TPB.

Electrochemical kinetics is used to determine activation overpotential and the rate of species consumption and generation, which are coupled through the current density,  $i$ , and are solved together. The activation losses and the current density can be solved, given the proper boundary conditions and an understanding of the losses. The reaction rate depends on this current density and in turn local sink and source terms to the mass and species can be implemented into a model since the mass flux is related to the electric current by Faraday's law. For example,

$$S_{H_2} = -\frac{\tilde{M}_{H_2}}{2F} i \quad (17)$$

The two commonly employed approaches to modeling the functional layer of the electrode are the thin-film model and the micro-model. A thin film model assumes that the electrochemically active

region is a single plane and that electrochemical activity does not vary with the thickness of the electrode. Micro-models consider the functional or electrochemical active layer of the electrode to be a discrete volume comprising a randomly packed electrocatalyst (electron conducting) and electrolyte (ion conducting) materials. Sunde [12] and Fleig [14] discuss these models in more detail.

The Butler-Volmer Equation (Equation 18) describes the relationship between the current density and the activation losses.

$$i = i_0(T, P_i) \left[ \exp \left( \alpha_a \frac{nF\eta_{act}}{RT} \right) - \exp \left( -\alpha_c \frac{nF\eta_{act}}{RT} \right) \right] \quad (18)$$

where  $\eta_{act}$  is the electrode losses,  $i_0$  is the exchange current density,  $\alpha_{a/c}$  is the anodic and cathodic charge transfer coefficient and  $n$  is the number of electrons participating in the electrochemical reaction.

The Butler-Volmer equation applies to electrochemical systems where the entire electrocatalyst-electrolyte interface is active. This form of the Butler-Volmer equation assumes a single rate determining step, however, most SOFCs operate at intermediate current densities where both a charge-transfer process and a mass transport process can be rate limiting [15] and therefore, the controlling kinetics of the electrode play a large part in predicting accurately the activation losses.

The two key electrochemical kinetic parameters are the charge-transfer coefficients and the exchange current density. In a number of modeling studies, the charge transfer coefficients typically take values between 0.0 and 1.0 and are constrained by  $\alpha_a + \alpha_c = 1$ . For a multi-step electrochemical reactions, these values can exceed one.

The exchange current density, as indicated in Equation 18, depends on the local partial pressure of reactants and the local temperature. The dependence of the exchange current density on the partial pressure at the reaction sites is an interesting fundamental concept. As the partial pressure of the reactants decreases, the exchange current density will also decrease, resulting in a decrease in performance. This clearly shows the coupling of activation and diffusion limitations and why the mass flux must be solved so precisely.

The exchange current density is found using a reference exchange current density and the following equations. One major problem is that the exchange current density is expressed in terms of geometric area, however, the actual reaction occurs at the active sites, which are a strong function of the microstructural parameters. These microstructural parameters are difficult to control and can vary dramatically depending on the processing techniques and conditions. Thus, for the same geometric area, two electrodes may have vastly different number of active sites and

$$i_{0,c} = i_{0,c}^0 \left( \frac{P_{O_2}}{P_{O_2}^0} \right)^\gamma \exp \left[ \frac{-E_{A,c}}{R} \left( \frac{1}{T} - \frac{1}{T^0} \right) \right] \quad (19)$$

$$i_{0,a} = i_{0,a}^0 \left( \frac{P_{H_2}}{P_{H_2}^0} \right)^{\gamma_1} \left( \frac{P_{H_2O}}{P_{H_2O}^0} \right)^{\gamma_2} \exp \left[ \frac{-E_{A,a}}{R} \left( \frac{1}{T} - \frac{1}{T^0} \right) \right] \quad (20)$$

where  $i_{0,c}^0$  and  $i_{0,a}^0$  are the reference exchange current density,  $\gamma_1 + \gamma_2$  is the reaction order, and  $E_A$  is the activation energy.

One of the key challenges in modelling the electrochemical behaviour is to finding reliable parameters. The reference exchange current density, the transfer coefficients, and the reaction order are all dependent on the rate determining step(s) of the complex electrochemical reaction as well as and the electrode microstructure. It is possible to determine electrochemical parameters that may be independent of the microstructure by normalizing with respect to the triple phase boundary length (tpbl). However, the estimation of tpbl is very difficult.

For a hydrogen-fueled SOFC with state-of-the-art electrodes (LSM cathode and Ni/YSZ anode), it is known that the activation polarization is much larger at the cathode than at the anode [13].

Several different approaches have been attempted to model the simultaneous oxidation of various gases such as  $CH_4$ ,  $CO$ , and  $H_2$ . The reaction order when using reformat has not been extensively studied and experimental kinetic data for the anode is still very scarce. Achenbach [4] assumed equal reaction orders for both  $H_2$  and  $CO$  fuel. Yakabe et al. [16] assumed that the oxidation of  $H_2$  is twice as fast as the oxidation of  $CO$ . There is a need on establish exactly how different fuels are simultaneously oxidized.

### 4.3 Ion/electron transport

Another key component of an SOFC electrode model is the modelling of the ion and electron transport. It is sometimes assumed that the electrolyte is the sole contributor to ohmic losses and therefore, the charge transport in the electrodes is sometimes neglected. Nevertheless, electronic and ionic transport is a fundamental process of fuel cell operation since both electrons and ions must be present at the reaction site.

The governing equations for the charge transport are Ohm's Law (Equation 21), a charge balance (Equation 22) on the electrons and ions, and the conservation of charge (Equation 23). Solving these equations gives the local currents and the local losses. Equation 22 describes the consumption of electronic charge and the formation of ionic charge. The following equations apply for a steady state analysis:

$$i_{el} = -\sigma_{el}^{eff} \nabla \phi_{el}; \quad i_{io} = -\sigma_{io}^{eff} \nabla \phi_{io} \quad (21)$$

$$\nabla \cdot i_{io} = -\nabla \cdot i_{el} \quad (22)$$

$$\nabla \cdot (\sigma_{el}^{eff} \nabla \phi_{el}) = S_{el}; \quad \nabla \cdot (\sigma_{io}^{eff} \nabla \phi_{io}) = S_{io} \quad (23)$$

where  $i_{el}$  and  $i_{io}$  are the local electronic ( $el$ ) and ionic ( $io$ ) current densities,  $\phi$  is the potential and  $\sigma^{eff}$  is the conductivity of the purely electronic or ionic conducting material. The ion and electron source terms are a result of the reaction.

The most common methods of solving the governing equations for the charge transport processes are:

1. Equivalent circuit approach
2. Charge balance approach

The equivalent circuit approach generally treats the reaction layer as a thin film or a boundary condition at the electrode/electrolyte interface and solves for the voltage drop due to electron transport through the electrodes using Ohm's Law. The equivalent circuit method is commonly used on composite electrodes as well, although the charge balance approach must be used for a more accurate solution since it accounts for local currents and local losses throughout the electrode.

The electrical conductivity of the pure material must be adjusted to an effective property in order to account for micro-structural effects, such as porosity. The effective conductivity is always lower than that of a pure material and effective conductivity models are available in the literature.

#### 4.4 Heat transport in the porous electrodes

Determining the temperature and temperature distribution is crucial in order to correctly predict temperature dependent parameters as well as rates of reaction and species transport. Solving for the heat transfer in the porous electrodes is a challenging task because all three modes of heat transfer are present. Although the heat transfer in electrodes is similar to that in the flow channels, there are a number of key differences.

1. Whereas the heat transfer in the flow channels is dominated by convection and radiation, conduction can play a dominant role in the porous electrodes.
2. The porous nature of the electrode complicates the issues as the relative role of convection, conduction, and radiation is unknown. It is very difficult to model the heat transfer from the gas phase to the solid phase at such a small scale.
3. The heat source in the electrodes is more complicated than the heat source in the flow channels. Determining the magnitude and the location of the energy sources and sinks is a key to correctly predicting the temperature distribution, but is not trivial.

The governing equation for the conservation of energy in the porous media is given in Equation 24.

$$(\rho c_p)^{eff} \frac{\partial T}{\partial t} + (\rho c_p)_f \vec{v} \cdot \nabla T = k^{eff} \nabla^2 T + S_e \quad (24)$$

It must be noted that certain parameters in the preceding equation are effective transport coefficients associated with the solid region and the fluid region (superscript of *eff*) while other parameters are that for fluid phase only (subscript of *f*).

The overall or effective thermal conductivity of a porous medium depends in a complex fashion on the geometry of the medium and the characteristics of the flow. Typically, a weighted arithmetic mean is used as indicated in Equation 25 assuming that the heat transfer through the solid phase and through the liquid phase occurs in parallel. This equation needs to be confirmed.

$$k^{eff} = \varepsilon k_f + (1 - \varepsilon) k_s \quad (25)$$

Heat is generated in the electrodes by several different methods.

- There is ohmic heat generation due to the irreversible resistance to current flow.
- There is heat generation due to the lost potential because of the non-ohmic losses (activation and transport). The available energy ( $\Delta G$ ) according to the Nernst equation (Equation 16) that is not transformed into current ends up as heat and this heat is released in the electrodes ( $Q_{loss} = \eta i$ ).
- There is heat generation that is associated with the change in entropy as a result of the electrochemical reaction. The energy of  $T\Delta S$  can not be utilized as electrical energy and result in heat generation ( $Q_{ent} = \frac{T\Delta S}{nF} i$ ). Entropic heat effects can be endothermic or exothermic and are generated at the two electrodes in unequal amounts.
- Internal reforming can be exothermic or endothermic and does occur in the anodes. Steam reforming, for example, must be modelled as a heat sink. The water shift reaction (Equation 6) and the other chemical reactions can also result in release or absorption of energy,  $Q_{chem}$ .

The location where heat is released in the electrode is a critical question to answer since large temperature gradients can lead to unwanted effects. It is accepted that the majority of heat is released at cathode, however, for accurate modeling the specific entropy change of the half reaction must be included. Since the reforming reaction of methane is endothermic, the heat generated on the cathode must be transported to the fuel reforming area near the anode. Heat transfer through the electrodes is essential and modelling is very important in understanding how to enhance this heat transfer.

Most researchers ignore radiative transfer through the electrodes, but Murthy and Federov [27] showed that both Ni-YSZ anode and LSM cathode absorb, emit and transmit radiation. Enhancing this radiative transfer would help transferring the heat from the cathode to the anode.

## 5 The electrolyte and interconnect

While the electrolyte and the interconnect play a very different role in the fuel cell, there are several similarities in regards to modelling them. Most importantly, the transport of both charge and energy must be applied. Equation 21 and 23 must be solved in the electrolyte for the ion transport and in the interconnect for the electron transport.

Neither the electrolyte nor the interconnect are very porous, and thus the complications of finding an effective conductivity are avoided in both interconnect and electrolyte. Murthy and Federov [27], however, showed that the electrolyte is optically thin and does transmit, emit, and absorb heat radiation.

Contact resistance between electrode and electrolyte and electrode and interconnect can be significant and should be incorporated into the model. However, estimation of contact resistance based on the interfacial microstructure is not trivial. Internal currents can also be an issue for thin electrolytes and ceria based electrolytes.

## 6 Validation

Validation of a computational model, although essential, is one of the extremely challenging. High-temperatures coupled with small size make it difficult to probe and measure parameters of interest even in single cell test stations. Individual cells in a stack give a different performance than a single cell would give, and it is extremely difficult to instrument a stack.

Many researchers validate models with a single electrochemical performance data, usually the polarization (current versus voltage) curves. This is a good practice, but must be done with care if other parameters can not be validated. The problem with this approach is that several combinations of parameters can yield similar results. Models often have some significant simplifications and it is possible that different effects cancel each other out. More importantly, caution must be taken when a model is validated with a polarization curve because it is very easy to adjust parameters within the model so that the model matches the data.

It is well known that several researchers adjust the exchange current density and the charge transfer coefficients in the Butler-Volmer equation to fit their model to experimental work. This practice can be helpful to create a model to run parametric studies, but will not result in a validated model! This fitting of data should be done with extreme caution as it can result in very unphysical parameters.

## 7 Conclusion

Much progress has been made in SOFC modelling as shown in this paper, but there is much work that is still needed. For continued progress in this field, models must be based on accurate description of the fundamental principles underlying the various processes occurring at the micro-scale level. Constant improvements in SOFC modelling will allow models to be very useful for making design decisions and performance predictions and will help commercialize SOFCs.

Ten important questions or issues that future models must properly address are given below:

1. What is the role of Knudsen diffusion and is it always necessary to include it under all of the operating conditions?
2. The reference exchange current density, charge transfer coefficients, and reaction orders must be determined accurately for temperature, partial pressures, and different micro-structures.
3. Effective transport properties must be accurately determined for ion, electron, and heat transfer.
4. Where is the heat released in the electrode and electrolyte?
5. What are the half cell potentials and the change in entropy for the half-cell reactions?
6. What is the role of radiation heat transfer in the electrodes and in the electrolyte? Is radiation scatter important? What is the role of radiation with participating media?

7. Where exactly are the reactions occurring in the porous structure and what is the rate determining step? Does the rate determining step depend on the operating temperature?
8. Is the flow turbulent or transitional for the internal flow in tubular cells?
9. What is the best way of dealing with the simultaneous oxidation of the different fuels at the anode? How are the oxidation rates related?
10. Is there a way to validate an SOFC model?

## Acknowledgments

The authors are grateful for the help from colleagues at the Fuel Cell Research Centre, Fuel Cell Technologies, Inc., Queen's University, and the Royal Military College. Funding for this work has been provided by CAMM and NSERC. Special thanks must go to Chris Harris for compiling the database of SOFC model parameters.

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