Short communication

Local thermal non-equilibrium effects in porous electrodes of the hydrogen-fueled SOFC

David L. Damm, Andrei G. Fedorov [*]

Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0405, USA

Abstract

The assumption of local thermal equilibrium (LTE) between the gas and solid matrix within porous electrodes of solid oxide fuel cells (SOFCs) is commonly used in predictive state-of-the-art thermal-fluidic models, yet its validity has never been properly established. In this paper, a two-equation, thermal non-equilibrium model of heat transfer between the gas and solid phase and its simple scaling analysis are used to estimate the magnitude of the temperature difference that would be expected between the gas and solid phase, and thus the significance of local thermal non-equilibrium (LTNE) effects. A simple criterion is developed for determining under what conditions LTNE effects may safely be neglected, and when they are likely to become significant.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Solid oxide fuel cell; Thermal modeling; Porous media

1. Introduction

Thermal modeling is a vital tool in the design and development of SOFCs due to the close coupling between temperature, reaction kinetics, ionic resistance of the electrolyte, current density, operating voltage, fuel utilization, and flow fields. Accurate prediction of the temperature fields within SOFCs is not only essential to predicting and optimizing overall cell performance, but is also a prerequisite to mitigating thermo-mechanical degradation and failure of the delicate anode–electrolyte–cathode structure. These concerns have resulted in the development of highly detailed CFD/FEM-based models whose ability to predict *global* quantities such as average current density, voltage, and temperature has been well established through experimental validation. However, lack of *detailed* experimental data such as local temperature fields or current density distribution has prohibited a more thorough validation of the numerical models. Thus, simplifying assumptions of the models can and should be challenged from a physical standpoint in order to maintain rigor and to provide the required careful justification (and limits of validity) of those assumptions.

One such assumption is that the temperatures of the gas phase and solid matrix within porous electrodes are locally the same, i.e. the gas and solid are in local thermal equilibrium (LTE). A survey of the relevant literature indicates that most (possibly all) of the current models make this assumption with little or no justification given. (Recently, however, Hwang [1] has addressed this issue in modeling low temperature proton exchange membrane fuel cells.) Three typical conditions found in the porous electrodes of SOFCs bring the assumption of local thermal equilibrium into question: (1) the presence of volumetric heat generation in the medium, (2) very low Reynolds number flow, and (3) large difference in thermal conductivities of the solid and gas phases. Under these conditions, the gas and solid temperatures can differ greatly and local thermal non-equilibrium (LTNE) modeling is often required [2]. To carefully address these issues, LTNE effects are investigated here through an order of magnitude analysis, which results in the development of a single LTNE parameter that can be used to assess the validity of the local thermal equilibrium assumption in SOFCs.

2. Model formulation

During steady state operation, all of the heat generated within the anode–electrolyte–cathode structure of a well-insulated cell

---

[*] Corresponding author. Tel.: +1 404 385 1356; fax: +1 404 894 8496.
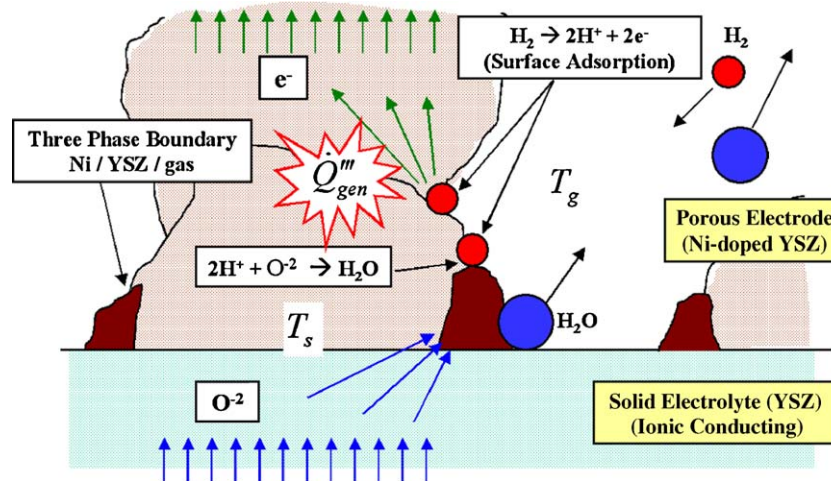*E-mail address:* andrei.fedorov@me.gatech.edu (A.G. Fedorov).

Fig. 1. Schematic representation of the TPB region of the porous anode and solid electrolyte of a SOFC. Oxygen ions migrate from the cathode side, through the electrolyte, and react with hydrogen ions adsorbed on the surfaces of the anode to form water vapor. Heat generated due to electrochemical reaction and ohmic losses is dissipated by three mechanisms: convection to the gas phase, conduction through the solid, and intra- and inter-pore radiative exchange.

is transferred to the fuel and oxidizer flow streams, which carry it out of the cell. In the porous electrodes, most of the heat is generated near the electrode–electrolyte interface (see Fig. 1) and is dissipated by (i) conduction through the solid matrix, (ii) heat transfer from the solid to the gas phase by convection within the porous electrodes, and (iii) advection of the gas through the micro-pores of the electrode into the flow channel. These processes are accounted for in the following two-equation, thermal non-equilibrium model, derived from conservation of energy in the gas and solid phases, and applied to a two-phase representative elementary volume of the porous electrode [2]:

$$0 = \nabla \cdot (k_{s,\text{eff}} \nabla T_s) + h_{\text{sf}} a_s (T_f - T_s)$$
$$+ \sum \dot{Q}'''_{\text{gen}_i} \quad \text{(solid phase)},$$
$$\nabla \cdot (\rho \vec{V} c_p T_f) = \nabla \cdot (k_{f,\text{eff}} \nabla T_f) - h_{\text{sf}} a_s (T_f - T_s) \quad \text{(gas phase)}$$
(1)

where h_{sf} is the solid to gas phase convective heat transfer coefficient, a_s the specific (per unit volume) surface area within a representative volume of the media, ρ the density, c_p the specific heat, and $\vec{V}$ the velocity of the gas phase, and $\dot{Q}'''_{\text{gen}_i}$ represents sources of volumetric heat generation within the solid phase. The simplest models for isotropic effective thermal conductivity of the solid and gas phases are

$$k_{s,\text{eff}} = (1 - \varepsilon)k_s, \qquad k_{f,\text{eff}} = \varepsilon k_f \qquad (2)$$

respectively, where ε is porosity. This space-homogenized, volume-averaging model is most commonly used in modeling fuel cell porous electrodes, in contrast to the discrete-phase, microstructure-based models, in which two phases (gas and solid) are spatially separated and usually analyzed using computationally intensive Lattice–Boltzmann formalism.

The magnitude of the difference in local temperatures between the gas and solid phases, $\Delta T = T_s - T_f$, is an indicator of the validity of the assumption of local thermal equilibrium (LTE). Since heat generation is the driving force behind any

thermal non-equilibrium in SOFCs, an order of magnitude analysis of the energy conservation equation for the solid phase in Eqs. (1) yields a proper estimate of the magnitude of ΔT. As a first approximation, temperature gradients in the solid (first term on the right-hand side) can be assumed small compared to the other two terms in the equation and can be neglected. This requires that the remaining two terms balance each other, and the expected temperature difference is then scaled as

$$\Delta T \sim \frac{\dot{Q}'''_{\text{gen}}}{h_{\text{sf}} a_s} \qquad (3)$$

This temperature difference is the greatest possible (upper bound) that can be expected for the problem at hand, because it assumes that all the heat generated in the solid is dissipated by convection to the gas phase. For verification, examine the effects of the assumption that the heat conduction term is negligible. As solid conduction effects become significant, this provides an additional route for heat transfer, leading to a reduction in convective heat transfer, and thus, reducing the temperature difference between solid and gas. The radiative heat transfer is also neglected in this analysis. In similar manner to heat conduction, this additional heat transfer mechanism, if significant, would provide an additional route for heat removal via intra-pore radiative heat exchange within the solid matrix of the porous electrode, thus only diminishing the expected temperature difference between the gas and solid phases. Therefore, Eq. (3) is a conservative indicator of whether or not LTNE effects should be neglected. The remaining task is to estimate the magnitude of the heat generation term and the interstitial heat transfer coefficient, $h_v = h_{\text{sf}} a_s$, that would be expected in the SOFC.

3. Interstitial heat transfer coefficient

The solid to gas phase heat transfer coefficient, h_{sf}, depends on the thermal conductivity of the fluid, the Reynolds number of the flow, and the geometric characteristics of the medium. The specific surface area, a_s, also depends on the structure of the

solid matrix. As a first approximation for this order of magnitude analysis, the structure of the porous electrode material can be assumed isotropic, consisting of roughly spherical particles of diameter, d_p. This is a conservative approximation—more so than considering a continuous solid phase, which would enhance conductive heat transfer, thereby reducing LTNE effects. The SOFC electrodes have pores or voids of diameter, d_v, which has been experimentally measured as 0.3–0.4 μm for anode materials [3]. (For simplicity, we assume that pore size in the cathode is of the same magnitude.) The relationship between specific surface area and void diameter given by Vafai [4] is $a_s = 4\varepsilon/d_v$. This yields a specific surface area of the order of $4 \times 10^6 \, \text{m}^{-1}$. Particle diameter can be estimated from the equation for the specific surface area for either spherical particles [5]:

$$a_s = \frac{6(1-\varepsilon)}{d_p} \tag{4}$$

or for sintered metal beads [6]:

$$a_s = \frac{20.346(1-\varepsilon)\varepsilon^2}{d_p} \tag{5}$$

yielding 0.9 and 1.1 μm, respectively. Although the exact value of these parameters is uncertain for the available porous electrode materials, it is clear that a_s is proportional to $1/d_p$, and particle and void diameters are the same order of magnitude.

Another area of uncertainty in determining interstitial heat transfer coefficient is the Reynolds number, $Re_d = \rho_f u d_p/\mu_f$, of the gas flow through the micro-pores of the electrodes. In general, it is reasonable to expect that the transport through the electrodes, especially near the electrode–electrolyte interface, is dominated by diffusion [3,7]. In this region, known as the triple phase boundary (TPB) region, the electrochemical reaction takes place at the junction of catalyst, electrolyte and gas phase. As a first estimate, the order of magnitude of the average velocity here can be found from conservation of mass and Faraday's law, which relates moles of reactants or products to electrical current. Specifically, for a given current density, the required mole flux of the relevant species (e.g. H_2) to the TPB is given by, $\dot{n} = i/2F$, where i is the current density of the cell (A m^{-2}), F is Faraday's constant (96,500 $\text{C mol}^{-1} \text{e}^{-1}$), and the 2 appears because 2 electrons are produced by the balanced electrochemical reaction. For a representative current density of $10^4 \, \text{A m}^{-2}$ the corresponding mass flux of H_2 to the TPB region is of the order $0.1 \, \text{g m}^{-2} \text{s}^{-1}$. Dividing by density and porosity yields a gas phase velocity on the order of $0.01 \, \text{m s}^{-1}$. Given such small velocity and using the previously estimated particle diameter and appropriate fluid properties, it becomes apparent that $Re_d \ll 1$ in the electrochemically active region of the porous electrode.

A very common correlation for h_{sf}, developed by Wakao and Kaguei [8] from an extensive collection of experimental data (for spherical particles) is

$$h_{sf} = \frac{k_f}{d_p} \left[2 + 1.1 \, Re_d^{0.6} Pr_f^{0.33} \right] \tag{6}$$

where k_f is the thermal conductivity of the fluid and Pr_f is the Prandtl number of the fluid. This correlation is valid over a large range of Re_d, although little data exists for very low Reynolds numbers. However, the correlation does asymptotically approach the correct theoretical value of h_{sf} in the limit of $Re_d \rightarrow 0$ (pure conduction through the gas phase). (Other frequently used correlations, such as that of Kar and Dybbs [9], do not appear to be valid at this limit [2].) Using the fact that $Re_d \ll 1$ as previously discussed, Eq. (6) is reduced to

$$h_{sf} \sim \frac{2k_f}{d_p} \tag{7}$$

This is the most conservative estimate of h_{sf} since it considers only heat transfer by conduction in the gas. Any increase in Re_d would only increase the heat transfer coefficient from this baseline value.

Combining Eq. (7) with Eq. (4) or (5) yields a lower bound estimate of the interstitial heat transfer coefficient, h_v. A typical value of this parameter for air, assuming electrodes with 1 μm particles and porosity of 30% is on the order of $10^{11} \, \text{W m}^{-3} \, \text{K}^{-1}$. This very high volumetric heat transfer coefficient is due to efficient heat transfer within the microscale porous structure of the electrodes because of the very large specific surface area. Since the calculations are sensitive to particle diameter and porosity, results will be presented for a range of these parameters.

4. Estimate of volumetric heat generation

An upper limit for the magnitude of the volumetric heat generation term, $\dot{Q}'''_{gen}$ in Eq. (3) is found from an examination of the thermodynamic effects associated with electrochemical reactions in the fuel cell and the ohmic heating effects in the ionic conducting electrolyte material. Although the processes by which heat is generated are complex and coupled, the overall energy balance of the cell effectively provides an estimate of the upper limit of heat generated without requiring an in-depth analysis of these processes. The total heat generation for a single cell can be calculated based on a given current density, and that entire quantity of heat is then applied to the TPB region (assumed to be a 10 μm thick layer next to the electrolyte [3]) on only one side of the electrolyte in order to estimate the upper bound of volumetric heat generation.

The reversible electrochemical reaction for the hydrogen-fueled cell [10] is

$$H_2 + \tfrac{1}{2}O_2 + 2e^- \rightleftharpoons H_2O + 2e^- \tag{8}$$
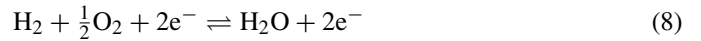
The limit of the energy available for electrical work is the Gibbs free energy, given at standard temperature (298 K) and pressure (1 atm) as

$$\Delta G^\circ = \Delta H^\circ - T^\circ \Delta S^\circ = -nFE^\circ \tag{9}$$

where n is the number of electrons (2) per mole of reactant, F is Faraday's constant and the $^\circ$ indicates standard values. For operating conditions other than standard, the Gibbs free energy is given by

$$\Delta G = \Delta H - T\Delta S = -nFE_{ideal} \tag{10}$$

where E_{ideal} is the ideal (reversible) operating voltage of the cell at operating temperature and pressure. Adding Eqs. (9) and (10) and solving for $T\Delta S$ yields the total *reversible* heat generated (kJ mol^{-1}) by the reaction:

$$Q_{rev} = -T\Delta S$$
$$= -T^{\circ}\Delta S^{\circ} + nF(E^{\circ} - E_{ideal}) + (\Delta H^{\circ} - \Delta H) \quad (11)$$

Faraday's law gives the *rate* of heat generation, and this is written on a volumetric basis as

$$\dot{Q}_{rev}''' = \frac{i}{L(1-\varepsilon)}$$
$$\times \left[-\frac{T^{\circ}\Delta S^{\circ} + (\Delta H^{\circ} - \Delta H)}{nF} + (E^{\circ} - E_{ideal}) \right] \quad (12)$$

where i is the current density, L the length scale (thickness) of the heat generating region, and ε is the porosity.

Because the cell does not operate ideally (reversibly), the operating voltage is lower than the ideal voltage. This voltage drop is primarily due to the ionic resistance of the electrolyte, activation overpotential, and concentration overpotential, resulting in additional (irreversible) heat generation which can be calculated as

$$\dot{Q}_{irrev}''' = \frac{i}{L(1-\varepsilon)}(E_{ideal} - E_{oper}) \quad (13)$$

Thus, by adding Eqs. (12) and (13), the total volumetric heat generation is expressed as

$$\dot{Q}_{total}''' = \frac{i}{L(1-\varepsilon)}$$
$$\times \left[-\frac{T^{\circ}\Delta S^{\circ} + (\Delta H^{\circ} - \Delta H)}{nF} + (E^{\circ} - E_{oper}) \right] \quad (14)$$

For example, consider a cell operating at $E_{oper} = 0.5$ V and a current density of $i = 10^4$ A m^{-2}. For the reaction given in Eq. (8), the standard potential, E°, is 1.22 V, $T^{\circ}\Delta S^{\circ}$ is -13.2 kJ mol^{-1} (for water vapor as a product), ΔH° is -241.8 kJ mol^{-1}, and ΔH (evaluated at 1000 K) is -247.9 kJ mol^{-1} [11]. If all the generated heat is confined to the 10 μm thick TPB region and assuming a porosity of 0.3, the volumetric heat source term is of the order 10^9 W m^{-3}. Combining this result with the estimate for interstitial heat transfer coefficient found in Section 3, Eq. (3), gives an estimate of the local temperature difference between gas and solid phases to be of the order 10^{-2} K, i.e., negligible.

5. Estimate of LTNE effects

Having developed expressions for heat generation and interstitial heat transfer coefficient, the LTNE criteria given in Eq. (3) can now be used to estimate the maximum temperature non-uniformity between the solid and gas phases. However, to use Eq. (14) to calculate heat generation, the operating temperature, voltage and current must be known. If these are not known, an approximate upper bound is found by setting the operating voltage in Eq. (14) to zero (i.e., cell is short-circuited and drawing maximum current), and neglecting the first term in the brackets.
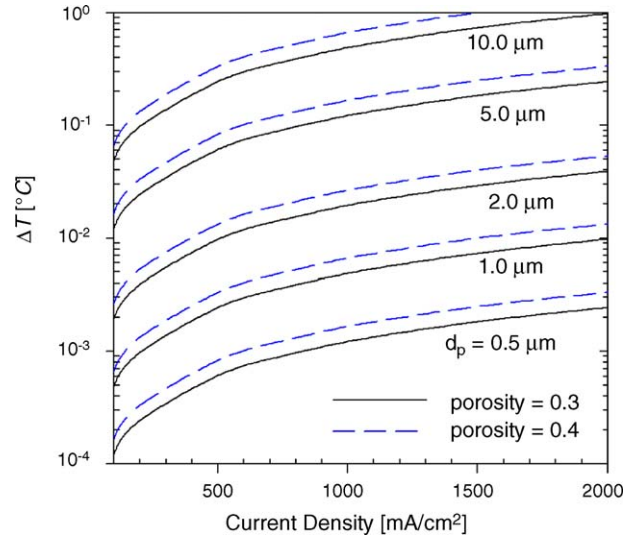

Fig. 2. The maximum expected temperature difference between the solid and gas phases of the porous electrode as a function of current density for various porosity and particle diameter of the porous medium (computed using representative $L = 10$ μm and thermal conductivity of air, $k_f = 0.5$ W m^{-1} K^{-1}).

This, along with Eqs. (4) and (7) are substituted into Eq. (3), yielding the upper bound of gas-to-solid temperature difference that can be expected in SOFC electrodes:

$$\Delta T_{max} \sim 0.1 \times \frac{id_p^2}{k_f L(1-\varepsilon)^2} \quad (15)$$

This parameter allows the user to determine if LTNE effects can safely be ignored, or if detailed non-equilibrium thermal modeling is required. Fig. 2 shows a plot of ΔT_{max} versus electrode particle diameter for various values of current density and porosity. Although our assumptions have erred on the side of maximizing the expected temperature difference, it should be
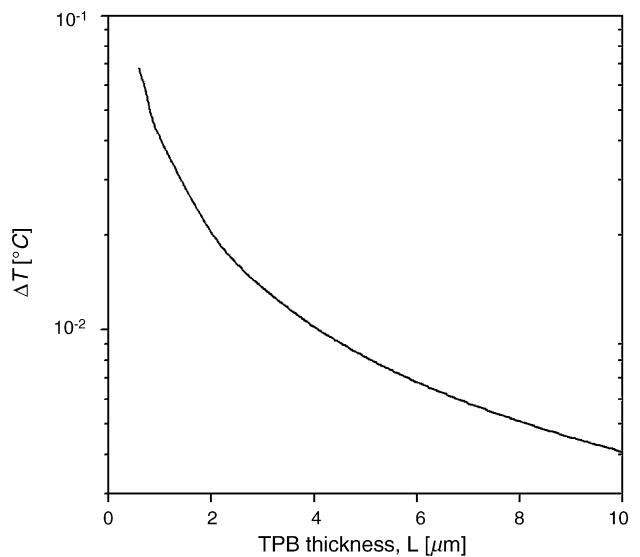

Fig. 3. The maximum expected temperature difference between the solid and gas phases of the porous electrode as a function of triple phase boundary (TPB) thickness. The computations are performed for representative parameters of $i = 1000$ mA cm^{-2}, $d_p = 1$ μm, $\varepsilon = 0.3$, and $k_f = 0.5$ W m^{-1} K^{-1}.

noted that local current density could be significantly higher than the average value used in Eq. (15) leading to local "hot spots" with increased LTNE effects. In addition, the thickness of the TPB region, L, may be much smaller than $10\,\mu m$ used in computing results presented in Fig. 2, resulting in an increased ΔT_{max}. To illustrate the magnitude of effect, Fig. 3 is a plot of ΔT_{max} versus L for typical conditions of $i = 1000\,\text{mA cm}^{-2}$, $d_p = 1\,\mu m$ and $\varepsilon = 0.3$. Although ΔT_{max} does indeed increase with a decrease in L, the temperature difference is still insignificant (less than one degree). This result should be used with care and only as a qualitative trend indicator, since the basic validity of volume-averaging model formulation becomes questionable as the TPB region size L becomes comparable or smaller than the elementary representative volume used for deriving Eq. (15). It is left to the discretion of the user to properly interpret the results of Eq. (15) and use relevant local values of i, k_f, L, and ε in assessing the validity of the LTE assumption for specific cases.

6. Concluding remarks

An order-of-magnitude analysis of the energy conservation equation for the solid phase of the SOFC porous electrodes is used to estimate the expected temperature difference between the gas and solid phases. This requires an estimate of the volumetric heat transfer coefficient between the two phases, and an estimate of the volumetric heat generation within the solid phase. Based on this analysis, a simple relationship is developed for estimating the maximum possible temperature difference that exists between gas and solid in SOFC porous electrodes. If the expected temperature difference (or error) is small enough to be tolerated, then the assumption of LTE is justified. However, caution should be exercised, as this analysis is specific to consideration of the idealized, isotropic, porous electrodes of hydrogen-fueled SOFCs and numerous simplifying assumptions have been made in estimating local cell parameters and structural characteristics.

References

[1] J.J. Hwang, Proceedings of the ASME Summer Heat Transfer Conference, San Francisco, CA, 2005.
[2] M. Kaviany, Principles of Heat Transfer in Porous Media, 2nd ed., Springer-Verlag New York Inc., 1995.
[3] R.E. Williford, L.A. Chick, S.P. Simner, G.D. Maupin, J.W. Stevenson, J. Electrochem. Soc. 150 (8) (2003) A1067–A1072.
[4] K. Vafai, Handbook of Porous Media, Marcel Dekker, 2000.
[5] F.A.L. Dullien, Porous Media Fluid Transport and Pore Structure, Academic Press, New York, 1979.
[6] G.J. Hwang, C.H. Chao, ASME J. Heat Transf. 116 (1994) 456–464.
[7] J. Yuan, M. Rokni, B. Sunden, Int. J. Heat Mass Transf. 46 (2003) 809–821.
[8] N. Wakao, S. Kaguei, Heat and Mass Transfer in Packed Beds, Gordon & Breach, New York, 1982.
[9] K.K. Kar, A. Dybbs, Proceedings of the ASME Winter Annual Meeting, Phoenix, AZ, 1982, pp. 81–91.
[10] Fuel Cell Handbook, 5th ed., EG&G Services, National Technical Information Service, U.S. Dept. of Comm., 2000.
[11] M.J. Moran, H.N. Shapiro, Fundamentals of Engineering Thermodynamics, 4th ed., Wiley & Sons, Inc, New York, 2000.