ELSEVIER

Journal of Power Sources 58 (1996) 87-91

JOURNAL OF POWER SOURCES

Cool-down time of solid oxide fuel cells intended for transportation application

Yufei Chen, James W. Evans *

Energy and Environment Division, Lawrence Berkeley National Laboratory and Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720, USA

Received 8 August 1995; revised 1 December 1995; accepted 1 December 1995

Abstract

To provide answers to the concern as to how quickly the temperature of solid oxide fuel cells (SOFCs) for transportation application will drop, a thermal analysis of the cool-down time of an SOFC stack during vehicle idle or stand-by has been carried out. Because a large amount of thermal energy is stored in high-temperature SOFC stacks, it is important to select suitable thermal insulations to reduce heat loss. Three typical kinds of thermal insulating materials have been selected in the present calculations. The results indicate that a high-performance, vacuum-multifoil thermal insulation can be applied to significantly reduce heat loss and to maintain temperature uniformity across a cell stack. Consequently, the cool-down time from 1000 to 800 °C is extended from 2 h (with a 5 cm thick conventional material) to about 31 h (with a 1 cm thick high-performance material).

Keywords: Solid oxide fuel cells; Cool-down time; Transportation

1. Introduction

Solid oxide fuel cells (SOFCs) have many attractive features [1,2] (e.g. high energy efficiency, low emission, rapid refueling, etc.), and are thus under consideration as an alternative power source for transportation application [3]. Current SOFCs must be operated at temperatures around 1000 °C, in order to reduce the resistance of yttria stabilized zirconia (YSZ) electrolytes. Many efforts [4] have been focused on reducing SOFC operation temperature from 1000 °C to as low as 500 °C, by developing thinner YSZ layer fabrication technology [5] or by developing electrolytes with lower resistance [6]. However, even for the lower operating temperatures of about 500 °C, thermal management plays an important role in the successful operation of SOFCs.

In general, a thermal management system is responsible for raising the temperature of an SOFC stack to its operating temperature before system start-up, and for maintaining the operational temperature and temperature uniformity across a stack during cell operation (e.g. if excess heat is generated during cell operation, cooling is required, also, thermal insulation is needed during vehicle idling or stand-by). In typical SOFCs, the thicknesses of the cathode and the anode are of the magnitude of about 100 to 200 μm, the electrolyte thickness is of a few tens of micrometers, and fuel and air gases flow through the fuel and air channels in the interconnect layers. Therefore, the warm-up time may be kept short (because thermal energy can be brought into the cell by hot gases, and the heat-transfer path is short within each individual cell), if the all-ceramic structure of SOFCs can withstand large thermal stresses. The maintenance of operating temperature and temperature uniformity during cell operation will need judicious design of the cell stack including cell configuration (cross-flow, co-flow and counter-flow). For the transportation application of SOFCs, one important concern is how quickly the temperatures in a stack will drop below the operating temperature at open-circuit conditions, which is related to the requirements for thermal insulation. In this report, a simple thermal analysis (for a fuel cell stack) of cool-down time and suitable thermal insulation is presented. In addition to the fuel cell stack, a SOFC power source would also contain a fuel processor, an air preheater, and some other components. Therefore, more rigorous analyses will have to be done after a whole system has been engineered.

2. Planar SOFC configuration and the mathematical model

A tubular design of SOFCs is now at the most advanced stage of development among different designs. However, pla-

* Corresponding author.

PII S0378-7753(96)02326-9

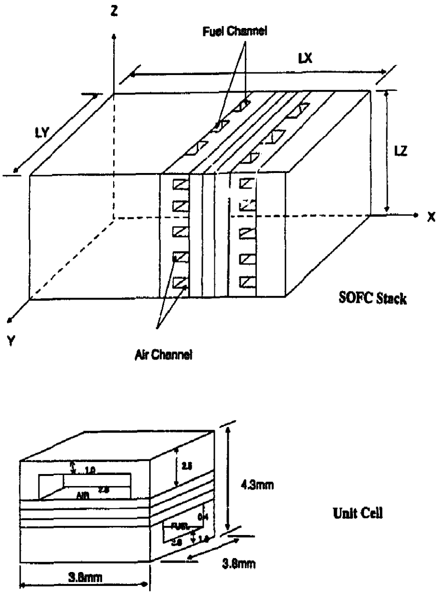

Fig. 1. Schematic setup of a planar SOFC stack and unit cell dimensions.

nar SOFCs are considered to be more compact and of higher power density in comparison with the tubular SOFCs. Therefore, a planar SOFC configuration is adopted in the present modelling. A planar SOFC stack [7] is shown in Fig. 1. A stack includes many cell layers and each layer consists of many unit cells. A cell is composed of three layers: $Ni_{0.35}(ZrO_2)_{0.65}$ cermet anode (fuel side electrode, porosity 0.4 to 0.6), $(ZrO_2)_{0.90}(Y_2O_3)_{0.10}$ electrolyte (porosity <0.06), and $La_{0.84}Sr_{0.16}MnO_3$ cathode (air side electrode, porosity 0.3 to 0.5). The ceramic interconnects, $La_{0.84}Sr_{0.16}CrO_3$ (porosity <0.05) act as bipolar current collectors (if a high-temperature alloy or a conducting oxide-coated metal is used as bipolar plate, the present thermal calculations should be conducted with a suitable adjustment of thermophysical parameters). Fig. 1 also shows the unit cell dimensions [8]. To obtain high power and to simplify the design for bringing air and fuel into SOFCs, stacks with large cross-sectional areas are preferable (provided that additional problems will not be caused by temperature and current distribution). However, only cell sizes of up to 400 cm^2 have been fabricated to date [9]. Therefore, in this calculation, the cross-sectional area of the stack is assumed to be 20 cm × 20 cm (i.e. $L_y = L_z = 20$ cm, see Fig. 1). With current SOFC technology, electrode power densities below 0.25 W/cm^2 have been achieved [10]. If a power output of 20 kW is designed for an SOFC system, a minimum total electrode area of 8 m^2 is required, that is, 200 cells with electrode area of 20 cm × 20 cm. Consequently, the thickness L_x of the stack is 86 cm (thermal insulation not included).

An SOFC stack has heterogeneous thermal properties. It is reported [11] that if this characteristic is taken into consideration, the time to compute temperature distributions will be too long for stacks of practical size, which is similar to our observation in thermal modelling of lithium/polymer batteries [12]. A way of circumventing this difficulty is to treat the stack as having effective, anisotropic thermal properties. This treatment is a good approximation for a stack consisting of many cell units and many cell layers. In this case, the transient heat-transfer equation for an SOFC stack at open-circuit conditions can be represented as:

$$\rho C_p \frac{\partial T}{\partial t} = k_x \frac{\partial^2 T}{\partial x^2} + k_y \frac{\partial^2 T}{\partial y^2} + k_z \frac{\partial^2 T}{\partial z^2} \quad (1)$$

where k_x, k_y, k_z are the effective thermal conductivities in different directions. ρ and C_p are the average stack density and specific heat, respectively.

Heat loss is caused by natural air flow and thermal radiation on the external surface of a stack. To significantly reduce heat loss to the surroundings, high-performance thermal insulation materials may be needed so that the temperature at the external surface of the insulation case is close to that of the ambient air. It is assumed that an SOFC stack is enclosed in an insulation case and that the temperature gradients within the insulation case will be at a quasi-steady state. Therefore, the boundary condition for thermal insulation established for lithium/polymer batteries [13] can be used, that is:

$$-k_n \frac{\partial T(n)}{\partial n}\Big|_{n=0,L_n} = (h_n + h_r)\left(1 + \frac{h_n L_{in}}{k_{in}}\right)^{-1}(T_n - T_\infty) \quad (2)$$

where $h_r = 4\,\epsilon\sigma T_\infty^3$ [14] is a radiation heat-transfer coefficient. h_n the coefficient of heat transfer by natural air flow in different directions, L_n ($n = x,y,z$) the dimension of the cell stack, L_{in} the thickness of thermal insulation case, k_{in} the thermal conductivity of the insulation case, and T_∞ the ambient temperature.

The initial condition is:

$$T = T_0 \text{ at } t = 0, \text{ any } x, \text{ any } y, \text{ and any } z \quad (3)$$

where T_0 is the operational temperature of an SOFC stack. The above equations have been solved by the modified implicit alternating direction technique [15] on a DEC 5900 RISC computer.

3. Thermo-physical parameters

It appears that the thermo-physical properties for the component materials of SOFCs are not available in the open literature. In the present work, the thermo-physical properties of anode ($Ni_{0.35}(ZrO_2)_{0.65}$), cathode ($La_{0.84}Sr_{0.16}MnO_3$), electrolyte ($(ZrO_2)_{0.90}(Y_2O_3)_{0.10}$), and interconnect ($La_{0.84}Sr_{0.16}CrO_3$) are estimated in terms of the properties for Ni, ZrO_2, La_2O_3, Sr_2O_3, Mn_2O_3, Mn_2O_3, Y_2O_3, Cr_2O_3, and the compositions of the cell components (composition data in volume percentage is used for ρ and k, while weight % for C_p). The properties for some of the oxides are unknown

Table 1
Thermo-physical properties of nickel, some oxides, air and fuel [a]

Parameter	Ni	ZrO_2	La_2O_3	Sr_2O_3	Mn_2O_3	Y_2O_3	Cr_2O_3	Air	H_2
$\rho(g/cm^3)$	8.90	5.60	6.51	4.63 [b] z	4.50	5.01	5.21	0.353×10^{-3}	0.0244×10^{-3}
$C_p(J/(g\,K))$	0.5178	0.6149	0.4061	0.5366	0.8694	0.5621	0.8318	1.10	14.71
$k(W/(cm\,K))$	0.718	0.00197	0.03 [c]	0.0215 [d]	0.034	0.0374	0.016 [e]	0.672×10^{-3}	4.28×10^{-3}

[a] Collected from Refs. [16–20]. Those values are considered as the average values within the temperature range of interest.
[b] Averaged value of SrO (density 4.70 g/cm^3) and SrO_2 (density 4.56 g/cm^3).
[c] Arbitrarily chosen from the value range for ceramics.
[d] Value for $SrO+TiO_2+Li_2O-ZrO_2-SiO_2$.
[e] Value for $Cr_2O_3+MgO+Fe_2O_3$.

Table 2
Thermo-physical properties of anode, cathode, electrolyte, interconnect and an SOFC stack

Material	$\rho(g/cm^3)$	$C_p(J/(g\,K))$	$k(W/(cm\,K))$
$Ni_{0.35}(ZrO_2)_{0.65}$ (porosity 0.50)	3.03	0.5951	0.0584
$La_{0.84}Sr_{0.16}MnO_3$ (porosity 0.40)	3.31	0.5726	0.0186
$(ZrO_2)_{0.90}(Y_2O_3)_{0.10}$ (porosity 0.06)	5.16	0.6058	0.0216
$La_{0.84}Sr_{0.16}CrO_3$ (porosity 0.05)	5.55	0.5562	0.0228
SOFC stack	$\rho(g/cm^3)$	$C_p(J/g\,K)$	$k_n(W/cm\,K)$
	3.54	0.5582	$k_x=0.01132$
			$k_y=0.01606$
			$k_z=0.01444$

too, and are chosen within a reasonable value range for ceramics as indicated in Table 1. Table 2 lists the estimated values for the thermo-physical properties of cell components and the average density, specific heat, and the effective thermal conductivities of a cell stack. The latter are determined in a similar way to calculating the equivalent electric resistances in an electric circuit (series/parallel models).

4. Results and discussions

In terms of the heat capacity ($\rho C_p=1.976$ J/(cm^3 K)) and the size ($L_x=86$ cm, $L_y=L_z=$ 20 cm) of the 20 kW SOFC stack, the thermal energy stored in the 1000 °C stack is estimated to be 18.4 kWh (with respect to 25 °C), which is of the same magnitude as the electric energy output of the 20 kW stack during 1 h operation. In other words, every 100 °C decrease of the stack temperature will correspond to 1.89 kWh thermal energy loss. Therefore, it is important to use suitable thermal insulation to reduce heat loss (a significant amount of heat is dissipated to the surroundings in the form of thermal radiation, in addition to the heat loss through the natural air flow on the stack surface).

The operating temperature of conventional SOFCs is about 1000 °C. However, cell operation may be started up at 800 °C, and it is possible to raise the stack temperature from 800 to 1000 °C by means of the heat generated during cell operation. Therefore, in the present calculations, the cool-down time is defined as the time period during which the temperature at the center of a stack drops from 1000 to 800 °C. Also, the cool-down time of a stack from 1000 to 500 °C is calculated, because many activities are under way aimed at developing thin film SOFCs with lower operating temperatures of around 500 °C.

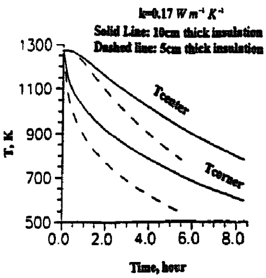

Fig. 2. Temperature variation as a function of time; SOFC stack: $L_x=86$ m, $L_y=L_z=20$ cm, $T_0=1273$ K; thermal insulation material: $k=0.17$ W/(m K).

Cool-down time is dependent upon the thermal insulation materials. Conventional thermal insulations are of thermal conductivities ranging from 0.17 to 0.03 W/(m K). Fig. 2 shows the variation of the temperatures at the center and at one of the eight corners of a stack (inside the insulated case) as a function of time when a vehicle is at stand-by. Calculations for two different thicknesses (5 and 10 cm) of the material ($k=0.17$ W/(m K)) are conducted. The cool-down time for 5 cm thick insulation is about 2 h (to 800 °C) and 5 h (to 500 °C), respectively, while for 10 cm thick insulation, the cool-down time is 3 h (to 800 °C) and 8 h (to 500 °C), respectively. The temperatures in the end cells are much lower than those of the cells in the stack center. Therefore, better thermal insulation is needed.

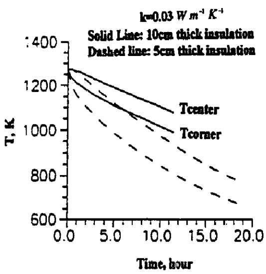

Fig. 3. Temperature vs. time; SOFC stack: $L_x = 86$ cm, $L_y = L_z = 20$ cm, $T_0 = 1273$ K; thermal insulation material: $k = 0.03$ W/(m K).

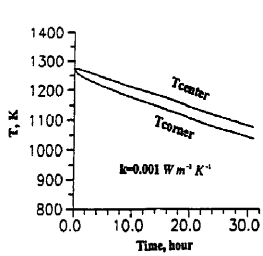

Fig. 4. Temperature vs. time; SOFC stack: $L_x = 86$ cm, $L_y = L_z = 20$ cm, $T_0 = 1273$ K; thermal insulation material: 1 cm thick, $k = 0.001$ W/(m K).

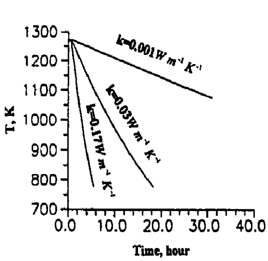

Fig. 5. Comparison of temperature variation at stack center vs. time for three different kinds of thermal insulation material; SOFC stack: $L_x = 86$cm, $L_y = L_z = 20$ cm, $T_0 = 1273$ K.

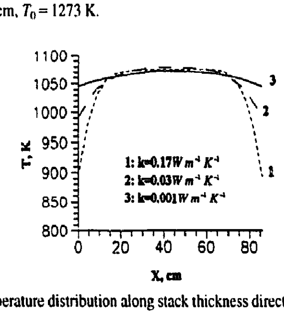

Fig. 6. Temperature distribution along stack thickness direction after 200 K decrease in temperature at the stack center: $y = L_y/2$, $z = L_z/2$; SOFC stack: $L_x = 86$ cm, $L_y = L_z = 20$ cm, $T_0 = 1273$ K.

Fig. 3 shows the temperatures at the center and at a corner of a stack as a function of time for a 5 cm thick insulation material with a lower thermal conductivity (0.03 W/(m K), the lower limit of the thermal conductivities of conventional insulations). The cool-down time from 1000 to 800 °C and to 500 °C is 6 h and 18 h, respectively. If 10 cm thick insulation of this type is used, the cool-down time from 1000 to 800 °C is 11 h.

The above results indicate that there are two problems with the conventional insulation materials, that is, very thick thermal insulation is required and over 100 °C temperature difference exists across a cell stack. Therefore, high-performance thermal insulation materials may be preferable from the temperature control point of view. If a 1.0 cm thick vacuum multifoil material with a thermal conductivity of about 0.001 W/(m K), developed for lithium/iron sulfide batteries [21], is applied, heat loss can be significantly reduced, and the cool-down time from 1000 to 800 °C is about 31 h (as is indicated in Fig. 4). Fig. 5 presents a comparision of the temperature variation in the center of a stack with three different kinds of insulation material. Fig. 6 shows the comparison of the temperature profiles across the stack center ($y = L_y/2$, $z = L_z/2$) when the temperature at the center drops to about 800 °C. It can be seen that with the high-performance insulation material, temperature uniformity across a stack can also be maintained.

5. Conclusions

To provide answers to the concern as to how quickly SOFCs for transportation application will cool down, a mathematical analysis has been conducted. The cool-down time is dependent upon thermal insulation materials. Three typical kinds of insulation material have been selected in the present calculations. The results indicate that:

1. If a 5 cm thick conventional insulation with a thermal conductivity of 0.17 W/(m K) is used, the cool-down times from 1000 to 800 or to 500 °C are about 2 and 5 h, respectively.
2. If a 5 cm thick insulation with a thermal conductivity of 0.03 W/(m K) (the lower limit of thermal conductivities of conventional insulation materials) is applied, the cool-down times from 1000 to 800 or to 500 °C are 6 and 18 h, respectively.
3. If a 1 cm thick high-performance insulation with a thermal conductivity of 0.001 W/(m K) (e.g. the vacuum, multifoil materials developed for lithium/iron sulfide batteries) is applied, the cool-down time from 1000 to 800 °C is about 31 h. With high-performance thermal insulation, heat loss can be significantly reduced, and temperature uniformity across a stack can also be maintained.

Acknowledgements

The authors are grateful to Dr A.Landgrebe, US Department of Energy for suggesting this study as important in the development of SOFCs. This work was supported by the Assistant Secretary for Energy Efficiency and Renewable

Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division of the US Department of Energy under Contract No. DE-AC03-76SF00098.

References

[1] K.A. Murugesamoorthi, S. Srinivasan and A.J. Appleby, in L.J.M.J. Blomen and M.N. Mugerwa (eds.), *Fuel Cell Systems*, Plenum, New York, 1993, p. 465.

[2] N.Q. Minh and T. Takahashi, *Science and Technology of Ceramic Fuel Cells*, Elsevier Science, Amsterdam, 1995, p. 11.

[3] R. Kumar, M. Krumpelt and K.M. Myles, in S.C. Singhal and H. Iwahara (eds.), *Solid Oxide Fuel Cells*, Proc. Vol. 93-4, The Electrochemical Society, Pennington, NJ, USA, 1993, p. 948.

[4] K. Krist and J.D. Wright, in S.C. Singhal and H. Iwahara (eds.), *Solid Oxide Fuel Cells*, Proc. Vol. 93-4, The Electrochemical Society, Pennington, NJ, USA, 1993, p. 782.

[5] T.W. Kueper, S.J. Visco and L.C. De Jonghe, *Solid State Ionics, 251* (1992) 52.

[6] K. Mehta, A.V. Virkar, *Ext. Abstr., 181th Meet. The Electrochemical Society, St. Louis, CA, USA, 17–22 May 1992*, Abstr. No. 305.

[7] E.A. Barringer, D.P. Heitzenrater and M.R. Tharp, in S.C. Singhal and H. Iwahara (eds.), *Solid Oxide Fuel Cells*, Proc. Vol. 93-4, The Electrochemical Society, Pennington, NJ, USA, 1993, p. 711.

[8] H. Karoliussen and K. Nisancioglu, in S.C. Singhal and H. Iwahara (eds.), *Solid Oxide Fuel Cells*, Proc. Vol. 93-4, The Electrochemical Society, Pennington, NJ, 1993, p. 868.

[9] T. Hikita, M. Hishinuma, T. Kawashima, I. Yasuda, T. Koyama and Y. Matsuzaki, in *Solid Oxide Fuel Cells*, S.C. Singhal and H. Iwahara (eds.), Proc. Vol. 93-4, The Electrochemical Society, Pennington, NJ, USA, 1993, p. 714

[10] H. Tagawa, in S.C. Singhal and H. Iwahara, (eds.), *Solid Oxide Fuel Cells*, Proc. Vol. 93-4, The Electrochemical Society, Pennington, NJ, USA, 1993, p. 6.

[11] T. Sira and M. Ostenstad, in S.C. Singhal and H. Iwahara (eds.), *Solid Oxide Fuel Cells*, Proc. Vol. 93-4, The Electrochemical Society, Pennington, NJ, 1993, p. 851.

[12] Y. Chen and J.W. Evans, *J. Electrochem.Soc., 140* (1993) 1833.

[13] Y. Chen and J.W. Evans, *J. Electrochem. Soc., 141* (1994) 2947.

[14] M.N. Ozisik, *Heat Conduction*, Wiley, New York, 1993, p. 16.

[15] B. Carnahan, H.A. Luther and J.O. Wilkes, *Applied Numerical Methods*, Wiley, New York, 1969, p. 452.

[16] R.C. Weast (eds.), *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 61st edn., 1980–1981.

[17] Y.S. Touloukian and E.H. Buyco (eds.), *Thermophysical Properties of Matter, Vol. 5, Specific Heat: Nonmetallic Solids*, Plenum, New York, 1970.

[18] Y.S. Touloukian, R.W. Powell, C.Y. Ho and P.G. Klemens (eds.), *Thermophysical Properties of Matter, Vol. 2, Thermal Conductivity: Nonmetallic Solids*, Plenum, New York, 1970.

[19] Y.S. Touloukian and T. Makita (eds.), *Thermophysical Properties of Matter, Vol. 6, Specific Heat: Nonmetallic Liquids and Gases*, Plenum, New York, 1970.

[20] Y.S. Touloukian, P.E. Liley and S.C. Saxena (eds.), *Thermophysical Properties of Matter, Vol. 3, Thermal Conductivity: Nonmetallic Liquids and Gases*, Plenum, New York, 1970.

[21] Lithium/Iron Sulfide Batteries for Electric-Vehicle Propulsion and Other Applications, *Argonne National Laboratory Rep. ANL-80-128*, 1980, p. 174.