

Short communication

Bi-layer structures as solid oxide fuel cell interconnections

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Received 7 January 2005; accepted 18 February 2005

Available online 11 July 2005

Abstract

A new approach for lower operating temperature solid oxide fuel cells (SOFCs) interconnections (IC) consisting of a bi-layer structure is proposed and analyzed. The bi-layer structure consists of a p-type layer exposed to cathodic gas (air/oxygen) and an n-type layer exposed to anodic gas (fuel). It is theoretically shown that the interfacial oxygen partial pressure which is an important designing variable, is dependent primarily on the oxygen partial pressure gradient across the IC, the low level oxygen conductivities of the two layers and is largely independent of their electronic conductivities and the total current density through the IC material. By careful design of the composition and thicknesses of the two layers, one can, in principle, obtain an IC with a low cell-to-cell resistance.

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PACS: Fuel cell (84.6 D)

Keywords: SOFC; Interconnection; Bi-layer; p-Type; n-Type

1. Introduction

Current research on solid oxide fuel cells (SOFCs) is focused on reducing the operating temperature from a nominal temperature of 1000 °C to 600–800 °C. Reducing the operating temperature allows the use of low-cost stack and manifolding materials, shorter heat up time, and enabling use in small scale residential and transportation applications [1–3]. However, reducing the operating temperature also has the unintended negative consequences of higher electrode polarization, and higher area specific electrolyte and interconnection resistances [4,5]. In particular, doped LaCrO₃, a high temperature p-type semiconductor which is used as the interconnection material in state-of-the-art high temperature SOFCs is a very poor choice for an interconnection material in the 600–800 °C temperature regime for two different reasons [6–8]. First, the conduction mechanism in doped LaCrO₃ is small polaron hopping which is a thermally activated process. Thus, the p-type conductivity of this material decreases exponentially with decreasing temperature. Secondly, the inter-

connection material like the solid electrolyte in the SOFC, is exposed to highly oxidizing conditions on the cathodic side ($p_{O_2} = 0.21$ atm) and highly reducing conditions on the anode side of the where a highly reducing atmosphere (10^{-18} to 10^{-21} atm) exists. Thus, a gradient in the electronic conductivity exists across the interconnect with a high conductivity on the cathode and side and poor conductivity on the anode side leading to an overall low average electronic conductivity across the interconnect. Bi-layered electrolyte has been considered for use in SOFC or membranes with the objectives of blocking electronic current, improving open-circuit voltage and increasing interfacial oxygen partial pressure to enhance chemical stability of materials under reducing environment [9–19]. In this paper, we propose and analyze a novel concept for an improved SOFC interconnection structure with a high average conductivity across the entire thickness.

2. Bi-layer interconnection

The new interconnection concept, we propose is shown schematically in Fig. 1. The concept we propose consists of a bi-layer structure with one p-type layer and one n-type

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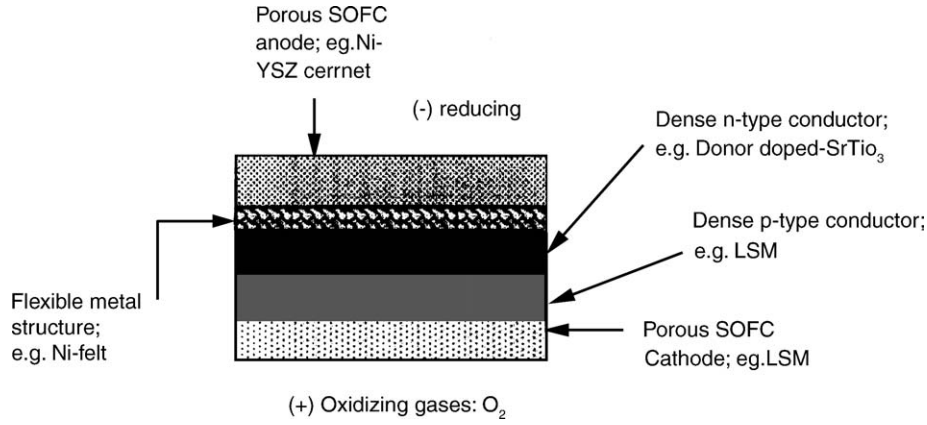


Fig. 1. Bi-layer interconnection element.

layer adjacent to each other. In an actual device, the p-type layer of the bi-layer interconnection will be exposed to an oxidizing environment and the n-type layer exposed to reducing conditions. During operation of the cell, the layer exposed to the cathodic side will develop p-type conductivity and the layer exposed to the anodic side will develop n-type conductivity. If designed correctly, such a structure has the potential to serve as an excellent SOFC interconnection, maintaining a high electronic conductivity across its thickness. In what follows, we analyze species transport across the proposed bi-layer interconnection and derive equations that provide design criteria for such a structure.

3. Theoretical analysis

Fig. 2 shows a schematic of the bi-layer interconnection and associated transport directions of oxygen ions O^{2-} , holes h^+ and electrons e^- . The generalized current density of species ‘ k ’ is given by [20],

$$J_k = -\frac{\sigma_k}{z_k e} \nabla \eta_k \quad (1)$$

Applying Eq. (1) to transport of O^{2-} , h^+ and e^- , the species current densities can be written as,

$$J_i = \frac{\sigma_i}{2e} \nabla \eta_i \quad (2a)$$

$$J_p = -\frac{\sigma_p}{e} \nabla \eta_p \quad (2b)$$

$$J_n = \frac{\sigma_n}{e} \nabla \eta_n \quad (2c)$$

The sum of the species current densities can then be equated to the total current density through the bi-layer interconnection under SOFC operating conditions, i.e.

$$J = J_i + J_p + J_n \quad (3)$$

The next step in the analysis is the assumption that local thermodynamic equilibrium prevails between neutral oxygen gas, oxygen ions and electrons/holes, i.e. the following reactions are in thermodynamic equilibrium everywhere across the interconnection structure.

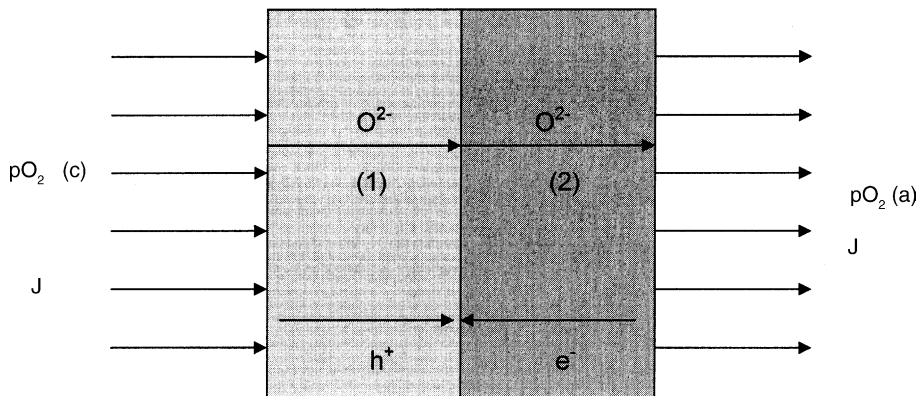


Fig. 2. Species transport direction in bi-layer interconnection.

Assumption of thermodynamic equilibrium of the above reactions gives,

$$\frac{1}{2} \nabla \mu_{O_2} + 2 \nabla \eta_n = \nabla \eta_i \quad (4)$$

$$\frac{1}{2} \nabla \mu_{O_2} = \nabla \eta_i + 2 \nabla \eta_p \quad (5)$$

$$\nabla \eta_n + \nabla \eta_p = 0 \quad (6)$$

Substituting Eqs. (2a)–(2c), (4)–(6) in (3), it can be shown that:

$$J_{el} = J_n + J_p = \frac{\sigma_n + \sigma_p}{\sigma_i + \sigma_n + \sigma_p} J - \frac{1}{2e} \frac{\sigma_i(\sigma_n + \sigma_p)}{\sigma_i + \sigma_n + \sigma_p} \nabla \mu_{O_2} \quad (7a)$$

$$J_i = \frac{1}{2e} \frac{\sigma_i(\sigma_n + \sigma_p)}{\sigma_i + \sigma_n + \sigma_p} \nabla \mu_{O_2} + \left(\frac{\sigma_i}{\sigma_i + \sigma_n + \sigma_p} \right) J \quad (7b)$$

Each of the above Eqs. (7a) which represents the total electronic current density (electron and hole current density) and (7b) which represents the total ionic current density has two terms. One associated with J the total external current density and the other $\nabla \mu_{O_2}$ the gradient in the neutral oxygen chemical potential gradient. The transport coefficient multiplying $\nabla \mu_{O_2}$, namely $\frac{\sigma_i(\sigma_n + \sigma_p)}{\sigma_i + \sigma_n + \sigma_p}$ is easily recognized as the ambipolar conductivity of the individual layers. In general, the conductivities σ_i , σ_n and σ_p will be functions of temperature and composition. Since the composition is both a function of the local electrostatic potential and the oxygen partial pressure, the conductivities are expected to vary as a function of position. In what follows, we make relevant simplifying assumptions to derive analytical expressions that can guide design of the bi-layer interconnection.

Firstly, we assume that the ionic conductivity in the two layers is invariant with p_{O_2} . Secondly, we assume that the ionic conductivity is much smaller in magnitude than the sum of the electron and hole conductivities, i.e. $\sigma_i \ll (\sigma_n + \sigma_p)$. The first assumption is true of most p-type and n-type oxide electronic conductors. In these materials, the oxygen ionic conductivity is determined extrinsically, i.e. it is a stronger function of the aliovalent dopant level rather than p_{O_2} . The second assumption is a necessary condition to be satisfied of any candidate interconnection material. With the second of these assumptions, Eqs. (7a) and (7b) can be simplified to,

$$J_{el} = J - \frac{1}{2e} \sigma_i \nabla \mu_{O_2} \quad (8a)$$

$$J_i = \frac{1}{2e} \sigma_i \nabla \mu_{O_2} \quad (8b)$$

These assumptions imply that at steady state, the current passing through the bi-layer interconnection is substantially electronic in nature. Further, the rather small oxygen ionic current through the bi-layer given by Eq. (8b) does not depend on the total current through the interconnection but only on

the cathodic and anodic side p_{O_2} 's. Assuming that the chemical and electrostatic potential gradients are one-dimensional and integrating Eq. (8b) over both layers it can be shown that:

$$J_{i1} = \frac{k_B T \sigma_{i1}}{2e \delta_1} \ln \left[\frac{p_{O_2}(c)}{p_{O_2}(i)} \right] \quad (9a)$$

$$J_{i2} = \frac{k_B T \sigma_{i2}}{2e \delta_2} \ln \left[\frac{p_{O_2}(i)}{p_{O_2}(a)} \right] \quad (9b)$$

The interfacial oxygen partial pressure $p_{O_2}(i)$ which is an important design parameter as will be seen shortly can be derived by equating the ionic current densities through the two layers at steady state, i.e. $J_{i1} = J_{i2}$, i.e.

$$p_{O_2}(i) = \left[\{ p_{O_2}(c) \}^{(\sigma_{i1}/\delta_1)} \{ p_{O_2}(a) \}^{(\sigma_{i2}/\delta_2)} \right]^{1/((\sigma_{i1}/\delta_1) + (\sigma_{i2}/\delta_2))} \quad (10)$$

Eq. (10) gives the interfacial oxygen partial pressure as a function of the oxygen partial pressure on the cathodic and anodic sides, the oxygen ionic conductivities in the two regions and the thickness of the two layers.

Taking into consideration, their well-matched thermal expansion coefficients (TEC) and high electrical conductivity, $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) and A site donor doped $SrTiO_3$ (AST) were chosen as the p-type and n-type layers, respectively [21,22]. Partial ionic conductivity literature data on both LSM and AST are limited. For the purposes of the present calculation, it is assumed that $\sigma_{i,LSM} = 10^{-7} \text{ S cm}^{-1}$, $\sigma_{i,AST} = 10^{-5} \text{ S cm}^{-1}$ at 900°C [23–25]. Assuming the cathode side oxygen partial pressure $p_{O_2}(c) = 0.21 \text{ atm}$ and anode side oxygen partial pressure, $p_{O_2}(a) = 10^{-18} \text{ atm}$, Eq. (10) can be employed to calculate the interfacial oxygen partial pressure as a function of the thickness of the two layers, which is displayed in Fig. 3. Fig. 4 shows the variation of $\log(p_{O_2})$ versus thickness of bi-layer LSM-AST interconnection at 900°C , $p_{O_2}(c) = 0.21 \text{ atm}$, $p_{O_2}(a) = 10^{-18} \text{ atm}$. The interconnection design criterion is $p_{O_2}(i) > p_{O_2}^*$, where $p_{O_2}^*$ is the decomposition p_{O_2} for the p-type materials. It is clear from Figs. 3 and 4 that higher the AST layer thickness, the more gradual is the decrease in interfacial p_{O_2} with increas-

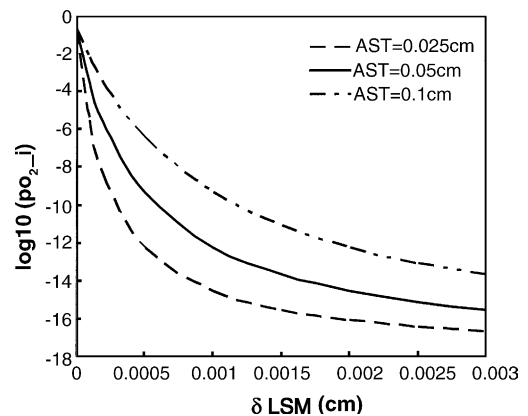


Fig. 3. Variation of interfacial oxygen partial pressure vs. thickness of LSM layer with the change of the thickness of AST layer.

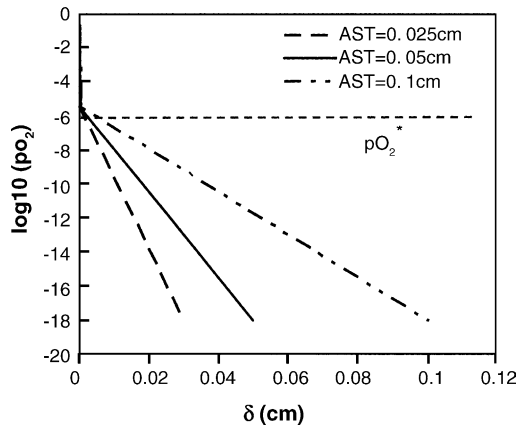


Fig. 4. Variation of $\log(p_{O_2})$ vs. thickness of bi-layer LSM-AST interconnection.

ing LSM layer thickness. Thus, it is more preferable to have a much thicker AST layer and a thinner LSM layer. A more precise determination of appropriate thicknesses will have to await measurements of variation of ionic partial conductivities as a function of temperature and p_{O_2} . This work is presently ongoing in our labs. This analysis shows that for a given pair of p-type (LSM) and n-type (AST) materials, by carefully choosing the thickness of the two layers, one can in principle ensure that the interfacial oxygen partial pressure remains higher than the decomposition partial pressure for the p-type layer.

4. Conclusions

The requirements for the bi-layer IC is high conductivity and excellent stability in a high oxygen partial pressure gradient. Analysis of bi-layer interconnection structure shows that when $\sigma_i \ll (\sigma_n + \sigma_p)$, interfacial p_{O_2} is independent of σ_n and σ_p . Region with higher σ_i will have a shallower p_{O_2} distribution. By carefully choosing the thicknesses of the two layers, one can, in principle, ensure that the interfacial oxygen partial pressure remains higher than the decomposition partial pressure for the p-type layer. More detailed measurements of σ_i as a function of p_{O_2} required for robust design of bi-layer interconnections.

Acknowledgment

Financial support from US-DOE through an Innovative Concepts-Phase I grant is gratefully acknowledged.

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