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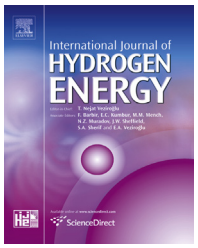

Theoretical analysis of the characteristics of the solid oxide fuel cells with a bi-layer electrolyte

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ABSTRACT

From the analytical model derived earlier [17], analytical expressions for the relative thickness ratio r_s of a bi-layer electrolyte and the maximum power density of a fuel cell are developed. Using these expressions, together with the other relationships from the analytical model, the characteristics of solid oxide fuel cells (SOFCs) with a bi-layer electrolyte are analyzed and theoretical analysis of the effect of the configuration of a bi-layer electrolyte on the SOFC performance is performed. The results show that the effectiveness of the bi-layer electrolyte depends strongly on its configuration. In the analyses, the variations of open circuit voltage and the maximum power density with the thickness ratio at different total electrolyte thicknesses and different operating temperatures are obtained. Furthermore, by taking into considerations of the oxygen partial pressure at the interface between the two layers of electrolytes, an analytical expression for the critical relative thickness ratio, above which, the electrolyte is stable, is obtained.

1. Introduction

Solid oxide fuel cells (SOFCs) have been widely studied as a promising electricity generating device. The traditional SOFC using yttria-stabilized zirconia (YSZ) as electrolyte typically works in the range of 800–1000 °C [1]. Acceptor-doped ceria (ADC) is a promising candidate material for SOFC electrolyte, because it lowers the operating temperature to intermediate temperatures (600–800 °C) [2] due to its considerably higher ionic conductivity. However ADC usually shows visible electronic conduction at low oxygen partial pressure [3], resulting in a significant reduction in the open circuit potential. Stabilized bismuth oxide (SBO) is another promising electrolyte material with very high ionic conductivity at the intermediate temperatures. However the instability of the SBO material under moderate reducing atmosphere, e.g. $10^{-13.1}$ atm at 600 °C [4], seriously limits its application in SOFCs [5]. A SOFC with a bi-layer electrolyte can reduce the electronic leakage current and protect the instable electrolytes, thus such a bi-layer electrolyte has the potential to offer both high ionic conductivity and chemical stability without significantly sacrificing the open circuit potential at intermediate operating temperatures [6].

Yahiro et al. [7] found that a thin YSZ layer sandwiched between the anode and an YDC (Yttria Doped Ceria) electrolyte can protect the YDC from reduction and increase the open circuit voltage. Then many researchers [8–11] fabricated bi-layer electrolytes with various methods and

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experimentally studied the effect of the bi-layer electrolyte on blocking the electronic current and protecting the inner electrolyte. Wachsman et al. [12,13] fabricated a ceria¦bismuth oxide bi-layer electrolyte and found that this bi-layer electrolyte shows slightly higher conductivity than SDC (Samaria Doped Ceria) and a significant increase in the open circuit voltage.

Virkar [14] studied the stability of a bi-layer electrolyte formed by an YSZ layer and a ceria or bismuth oxide layer and concluded that the stability of the electrolyte depends on the transport characteristics of the bi-layer, in particular the electrolyte near anode side. Marques and Navarro [15,16] studied the performance of a SOFC with a bi-layer electrolyte by an electrochemical permeability model taking p-type and n-type conductivity of the electrolytes into consideration and the effects of the YSZ layer on oxygen permeation and open circuit voltage are analyzed by the model. Shen et al. [17] developed an analytical model for a SOFC with a bi-layer electrolyte based on the transport equation and verified the model by experiment and model data in the literature. However the theoretical studies of the bi-layer electrolyte mentioned above were mainly based on the bi-layer electrolyte configuration of Anode|YSZ¦ADC|Cathode that the YSZ layer is sandwiched between the ADC electrolyte and anode. Very limited studies on bi-layer electrolyte with a configuration of Anode|ADC¦YSZ|Cathode have been reported and no theoretical analysis on the characteristics of the ceria¦bismuth oxide bi-layer electrolyte has been reported in the literature.

In this work an analytical model of the SOFC with a bi-layer electrolyte developed in an earlier work [17] was briefly introduced. Based on this model, the variations of the open circuit voltage, maximum power density and interfacial oxygen partial pressure at open circuit with the relative thickness ratio are obtained. Using these expressions, together with the other relationships from the analytical model, the characteristics of solid oxide fuel cells (SOFCs) with a bi-layer electrolyte are analyzed and theoretical analysis of the effect of the configuration of a bi-layer electrolyte on the SOFC performance is performed.

2. Theoretical model

2.1. *Introduction of the theoretical model*

An analytical model of the SOFC with a bi-layer electrolyte was established in an earlier work [17] and this model will be used in this work to study the characteristics of SOFC's with bi-layer electrolyte. Thus, for completeness and for facilitating the understanding of the analyses, the fundamental theory, key assumptions and equations of the model are briefly introduced below.

The model is based on the charge transport equations with the assumption of constant ionic conductivity, and the mobile charges only contain oxygen ions and electrons, while the holes transport are neglected since major electrolytes used in SOFCs are n-type [15]. The simplified transport equations for oxygen ions and electrons are given as,

$$j_{O^{2-}} = \frac{\sigma_{O^{2-}}}{4q}\frac{\partial \mu_{O_2}}{\partial x} - \sigma_{O^{2-}}\frac{\partial \eta}{\partial x} \quad j_e = -\sigma_e\frac{\partial \eta}{\partial x} \tag{1}$$

The transports of oxygen ions and electrons are depicted in Fig. 1. The two kinds of electrolytes are respectively denoted by E1 and E2, and their thicknesses are denoted by s_1 and s_2, respectively.

The ionic conductivity of the electrolyte is constant and the electronic conductivity depends on the $-1/n$ power of oxygen partial pressure p_{O_2}. In this model n is specified to 4, thus

$$\sigma_e = \sigma_e^0 {p_{O_2}}^{-1/4} \tag{2}$$

where σ_e^0 is a temperature-dependent coefficient that is independent of oxygen partial pressure.

Both the anode and cathode electrodes are assumed to be reversible (neglecting activation overpotential) for simplicity. Under open circuit, the error caused by this assumption can be neglected except for situations with very serious leakage current. It is noted that when the fuel cell has an output electrical current this assumption can overestimate the cell performance; however will not change the characteristics of the fuel cell and it will not affect the results in comparative studies. The continuity of charges transport results in,

$$j_L = j_{O^{2-}} + j_e \tag{3}$$

When the SOFC is operated at a fixed voltage V, the ionic and electronic current densities can be obtained respectively as [17]:

$$j_{O^{2-}} = \sigma_{O^{2-}}^{eq}\frac{(V_{th} - V)}{L} \tag{4}$$

$$j_e = \sigma_{O^{2-}}^{eq}\frac{V_{th} - V}{L}\frac{M_1\left(p_{O_2}^{I}\right)^{-1/4} - \frac{1}{M_2}\left(p_{O_2}^{II}\right)^{-1/4}}{(M_1 - 1)\frac{\sigma_{O^{2-}}^{1}}{\sigma_e^{1,0}} + \left(1 - \frac{1}{M_2}\right)\frac{\sigma_{O^{2-}}^{2}}{\sigma_e^{2,0}}} \tag{5}$$

where the equivalent ionic conductivity is defined as:

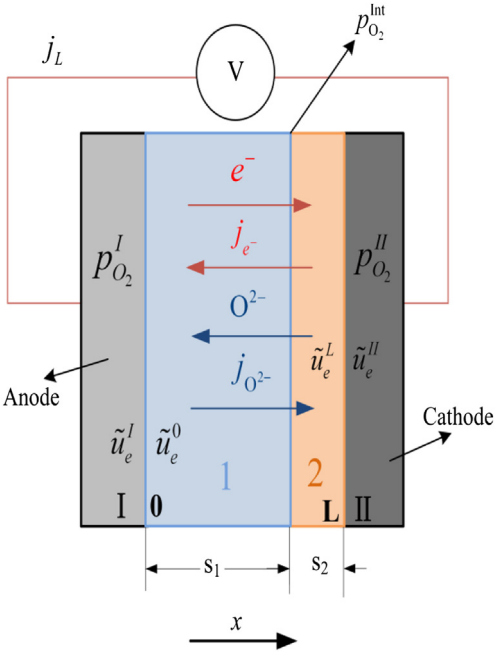

Fig. 1 – The schematic of the charge transport in SOFCs with a bi-layer electrolyte.