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Impedance Spectroscopy Study of an SDC-based SOFC with High Open Circuit Voltage

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ABSTRACT

A relatively high open circuit voltage (OCV) of 1.047 V at 600 °C was reported recently for a cell based on a $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$(BZCYYb)-NiO anode-supported thin SDC electrolyte, demonstrating a peak power density of 0.50 W/cm^2. In this study, an equivalent circuit model was developed for interpreting the behavior of this SDC-based SOFC. The mechanism behind the high OCV and the corresponding high peak power density were elucidated via separating the polarization processes and the corresponding characteristic frequencies, especially those for oxygen ion diffusion through the interlayer at the anode/electrolyte interface. Theoretical analysis and data fitting based on the presented circuit model indicate that the inter-diffusion layer between Ni-BZCYYb and SDC effectively suppresses electronic conduction while maintaining the catalytic activity and ionic conductivity. More importantly, careful analysis of the characteristic frequencies offers a powerful approach to assigning a specific part of the impedance data (e.g., an impedance arc or loop) to the corresponding physicochemical process. Further, any sharp change in the characteristic frequency for a physicochemical process also reflects a change in the inherent nature of that process under the testing conditions. Once validated by more experimental results under a broader range of testing conditions, the presented equivalent circuit model, in turn, may be used to predict fuel cell performances and optimize the operating conditions.

1. Introduction

The development of solid oxide fuel cells (SOFCs) is driven by the potential of their high energy efficiency and excellent fuel flexibility [1]. However, the commercialization of SOFC technology is hindered by the high operating temperature (800∼1000 °C) of SOFCs [2]. To reduce the operating temperature down to the intermediate temperature (IT) range (500∼700 °C) [3], thinner electrolytes with higher ionic conductivity at reduced temperatures are required [4]. Current fabrication techniques can easily produce electrolyte membranes of a few microns thick, approaching the limit thickness of electrolyte for practical applications [5].

Doped ceria is a promising electrolyte for IT-SOFC due to its excellent ionic conductivity in the intermediate temperature range. However, it is a mixed ionic-electronic conductor (MIEC) with considerable electronic conductivity under low p_{O_2} ($<1\times10^{-19}$atm), especially at temperatures higher than 600 °C due to the partial reduction of Ce^{4+} to Ce^{3+}. The electronic conductivity of doped ceria reduces the open circuit voltage and hence decreases fuel cell efficiency [6]. In order to improve the energy efficiency of the doped ceria- based SOFCs, many efforts have been made, both theoretical analysis [7–21] and experimental investigation [22–27], to suppress electronic conduction under fuel cell operating conditions. Several approaches were developed for effective blocking electronic conduction through an MIEC electrolyte of IT-SOFCs [28–30].

The use of a composite electrolyte or an interlayer at electrode/electrolyte interface is a promising method to suppress electronic conductivity while maintaining chemical stability for SOFC with MIEC electrolytes. For example, a cell structure composed of $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$(BZCYYb)-NiO anode supported SDC electrolyte was recently reported to demonstrate an OCV of 1.047 V and a peak power density of 0.50 W/cm^2 at 600 °C. However, the mechanism of blocking electronic conduction is yet to be determined. Detailed mechanistic understanding of the novel cell structure by separation of the polarization losses will help us to further optimize the cell structure and improve the performance [31].

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Nomenclature

SOFC solid oxide fuel cell
EIS electrochemical impedance spectroscopy
CF characteristic frequency (Hz)
MIEC mixed ionic-electronic conductor
E_N Nernst potential (V)
OCV open circuit voltage (V)
U_{ocv} the measured open circuit voltage (V)
E^0 the standard potential (V)
F Faraday's constant $F = 9.6485 \times 10^4 (C/mol)$
n the number of electrons released for every hydrogen molecule reacted
ΔG^0 Gibbs free energy at operating temperature and standard pressure (J/mol)
R universal gas constant ($8.314 J/K/mol$)
T the operating temperature in Kelvin (K)
α_{H_2} the activity of H_2
α_{O_2} the activity of O_2
α_{H_2O} the activity of H_2O
p_{H_2O} the partial pressure of H_2 (atm)
p_{O_2} the partial pressure of O_2 (atm)
p_{H_2O} the partial pressure of H_2O (atm)
I_i ionic current through electrolyte (A/cm^2)
I_e electronic current through electrolyte (A/cm^2)
I_{ext} external current through DC load (A/cm^2)
I_{short} the internal shorting current under open circuit condition (A/cm^2)
$Z(j\omega)$ cell AC impedance under open circuit condition (Ωcm^2)
$Z_w(j\omega)$ finite diffusion Warburg impedance under transmissive boundary (Ωcm^2)
R_w diffusion resistance at low frequencies for Z_w ($j\omega$) (Ωcm^2)
τ diffusion time constant for Z_w ($j\omega$) (s)
D effective diffusion coefficient for Zw ($j\omega$) (cm^2/s)
d effective diffusion thickness for Zw ($j\omega$) (cm)
R_{load} load resistance (Ωcm^2)
R_i ionic resistance of the bulk electrolyte (Ωcm^2)
σ_i oxygen ionic conductivity of bulk electrolyte (S/cm or $\Omega^{-1} cm^{-1}$)
σ_t total conductivities of the bulk electrolyte (S/cm)
t_i ionic transference number of the bulk electrolyte
R_e electronic resistance of the bulk electrolyte (Ωcm^2)
$R_{p,a}$ anodic polarization resistance (Ωcm^2)
$R_{p,c}$ cathodic polarization resistance (Ωcm^2)
R_p total polarization resistance of the cell, $R_p \underline{\underline{def}} R_w + R_{p,a} + R_{p,c}$ (Ωcm^2)
$R_{con,a}$ ohmic contact resistance at the anode side (Ωcm^2)
$R_{con,c}$ ohmic contact resistance at the anode side (Ωcm^2)
R_{con} total ohmic contact resistance of the cell, $R_{con} \underline{\underline{def}} R_{con,a} + R_{con,c}$ (Ωcm^2)
R_{bulk} bulk electrolyte resistance, $R_b \underline{\underline{def}} \frac{R_e R_i}{Re + Ri}$ (Ωcm^2)
R_{ohm} ohmic resistance, $R_{ohm} \underline{\underline{def}} R_{con} + \frac{R_e R_i}{R_e + R_i}$ (Ωcm^2)
R_t total cell resistance, $R_t \underline{\underline{def}} R_{con} + \frac{R_e(R_p + R_i)}{R_e + R_p + R_i}$ (Ωcm^2)
R_H the intercepts of the impedance loop with the real-axis at high frequencies, $R_H \approx R_{con} + \frac{R_e R_i}{R_e + R_i}$ (Ωcm^2)
R_L the intercepts of the impedance loop with the real-axis at low frequencies, $R_L \approx R_{con} + \frac{R_e(R_p + R_i)}{R_e + R_p + R_i}$ (Ωcm^2)
R_p' ***apparent*** polarization resistance, $R_p' \stackrel{def}{=} R_L - R_H$ (Ωcm^2)
$R_{p,fit}$ total polarization resistance derived from impedance data (Ωcm^2)
$R_{con,fit}$ total ohmic contact resistance derived from impedance data (Ωcm^2)
$R_{p,cal}$ total polarization resistance derived from analytical calculation (Ωcm^2)
$R_{con,cal}$ total ohmic contact resistance derived from analytical calculation (Ωcm^2)
C_1 double layer capacitances at the anode side (Fcm^{-2})
C_2 double layer capacitances at the cathode side (Fcm^{-2})
l electrolyte thickness (cm)
f_{RC} the characteristic frequencies for $R//C$, $f_{RC} \underline{\underline{def}} \frac{1}{2\pi RC}$ (Hz)
f_w the characteristic frequencies for Z_w ($j\omega$), $f_W \underline{\underline{def}} \frac{2.53 * \tau}{2\pi}$ (Hz)
f_a the characteristic frequencies for $R_{p,a}//C_1$ (Hz)
f_c the characteristic frequencies for $R_{p,c}//C_2$ (Hz)
$log_{10}^{f_{a-c}}$ decade of difference frequency in logarithm between f_a and f_c defined as $\log_{10}^{f_{a-c}} \underline{\underline{def}} \log_{10}^{f_a} - \log_{10}^{f_c}$ (Hz)
$\log_{10}^{f_{c-w}}$ decade of difference frequency in logarithm between f_c and f_w, defined as $\log_{10}^{f_{c-w}} \underline{\underline{def}} \log_{10}^{f_c} - \log_{10}^{f_w}$ (Hz))

Electrochemical impedance spectroscopy (EIS) is a powerful tool to separate electrode polarization from ohmic loss, to identify electrode reaction mechanisms, and to discern interfacial processes under *in situ* conditions [32], once suitable models are developed that link the measured impedance data to the key parameters for the physicochemical processes [33]. In order to simplify the analysis, however, some important parameters related to physic- electrochemical processes, such as polarization resistance [9,11,12,17], DC load [14], contact resistance [19,20], and mass transfer resistance [27] were intentionally ignored in some analyses for ceria-based SOFCs. In this study, an equivalent circuit model considering all above parameters is developed to understand the structure of Ni-BZCYYb supported SDC electrolyte for SOFC with the following purposes: (a) to identify the effect of the inter-diffusion layer on electronic conduction, ion diffusion, and catalytic activity at different operating temperatures; and (b) to discern the effect of the inter-diffusion layer on the characteristic frequency of different physicochemical processes and on the ionic transference number.

2. Equivalent Circuit Modelling

2.1. Review of Exisiting Models

For impedance-based diagnosis, equivalent circuit models are often used in the interpretation of experimental data [32,33], in spite of their ambiguity and uncertainty to some extent [34]. During the past four decades, equivalent circuit models for solid-state cells based on MIEC electrolytes have also advanced much with the development of mechanistic understanding and decoding techniques. Shown in Fig. 1 are some equivalent circuit models for solid-state cells based on MIEC electrolytes [9,11,12,14,17,19,20,27]. While both R_i and R_e are considered in all circuit models, several important processes were ignored in these circuits: (a) polarization resistance at electrode/electrolyte interface in the circuit