Impedance Spectroscopy Study of a SDC-based SOFC with High Open Cell Voltage

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Abstract

A relatively high 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-δ} (BZCYYb)-NiO anode-supported thin SDC electrolyte, demonstrating a peak power density of 0.50 W/cm². 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 catalyst 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 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, maybe used to predict fuel cell performances and optimize the operating conditions.

Key words: SDC-based SOFC; Mixed ionic-electronic conductor; Impedance; Characteristic Frequency

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 $pO_2 (< 1 \times 10^{-19} \text{ atm})$, 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][29][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, Liu et al developed a novel 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,

demonstrating an OCV of 1.047 V and a peak power density of 0.50 W/cm² 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].

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 novel 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 catalyst activity at different operating temperatures; (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. Physical Circuit Modelling

2.1 Model Review

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][17][14][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 model shown in Fig.1.a^{[9][11][12][17]}, (b) both Nernst voltage E_N and DC load resistance R_{load} in Fig.1.b^[14], (c) ohmic contact resistance $R_{con,c}$ and $R_{con,a}$ at cathode and anode sides in Fig.1.c^{[19][20]}, and (d) finite diffusion resistance due to scale at anode/electrolyte in Fig.1.d^[27].

To date, diffusion barrier at anode/electrolyte interface of SOFCs with MIEC electrolytes has not been investigated quantitatively. A circuit model considering diffusion barrier will be presented subsequently.

2.2 Model Development

■ **Assumption and Conditions.** In this study, a circuit model is constructed to investigate both electrolyte electronic resistance and inter-diffusion layer at anode/electrolyte interface in addition to traditional charge reaction-transfer processes at anode and cathode sides. For the convenience of discussion, we name the physicochemical process originating from inter-diffusion layer as the third one and to name the traditional charge reaction-transfer

processes at anode and cathode sides as the first one and the second one, respectively. The present work aims at quantitatively examining the effect of the inter-diffusion layer at anode/electrolyte interface on ionic diffusion, electronic blocking, and catalyst activity, with emphasis on characteristic time constant, separation of polarization loss, and ionic transference number in terms of operating temperatures. Unless specified otherwise, the following assumptions are made in this analysis:

(i) Ohmic contact is assumed for both anode and cathode in addition to electrode/electrolyte interfacial polarization resistance;

(ii) Open circuit voltage and cell output voltage are considered under conditions of open circuit mode and external load modes, respectively;

(iii) Bulk properties (e.g., ionic transference numbers, ionic resistance, electronic resistance, and polarization resistance) correspond to the quantities averaged over the thickness of the electrolyte and for a given oxygen partial pressure range;

(iv) Three different physicochemical processes happening at SOFCs with MIEC electrolytes are considered and identified simultaneously;

(v) Local equilibrium prevails at all positions in the system and the whole system is in a steady-state.

(vi) There is no fuel crossover from the sealant and no pin-hole defection in the electrolyte.

■ **Circuit Model Extension.** As reported recently^[29], an inter-diffusion layer was observed at the interface of Ni-BZCYYb/SDC during co-firing at high temperature. The high OCV and good cell performance achieved in that work were attributed to the formulated interlayer.

However, quantitative investigation of the inter-diffusion layer on the performance is still lacking, in particular for its effect on electronic conduction, ionic diffusion, catalyst activity, and characteristic frequencies of sub-processes.

When scale exists at anode/electrolyte interface, oxygen ions have to diffuse through the inter-diffusion layer before they transfer from electrolyte to anode and then react with fuel in the anode side. Simultaneously, some electrons pass from anode side to electrolyte side through the inter-diffusion layer under the influence of the electric field. Electrons flow from anode side to cathode side could be suppressed further by the inter-diffusion layer due to the large excess resistance of electrons relative to oxygen ions through the inter-diffusion layer.

This suppression effect will be demonstrated by the subsequent impedance analysis.

Oxygen ions diffusion through inter-diffusion layer from electrolyte side to anode side originates from concentration gradient, while electron flow through both thinner scale and electrolyte from anode side to cathode side originates from electric field gradient.

Consequently, resistance ascribed to electron flow through scale and electrolyte is represented by electronic resistance R_e ; resistance ascribed to oxygen ion diffusion through a thinner inter-diffusion layer from electrolyte side to anode side is represented by finite diffusion Warburg impedance Z_w ^[35]. The finite diffusion Warburg impedance Z_w under transmissive boundary is expressed by Eq.(1),

$$Z_w = \frac{R_w}{\left(\frac{j\omega}{\tau}\right)^{0.5}} \tanh\left(\frac{j\omega}{\tau}\right)^{0.5} \quad (1-1)$$

$$\tau = \frac{D}{d^2} \quad (1-2)$$

where diffusion resistance at low frequencies (Warburg parameter) is denoted by R_w , diffusion time constant by τ , effective diffusion coefficient by D , and effective diffusion thickness by d for oxygen ion diffusion through scale layer.

At this study, finite diffusion Warburg impedance is used to simulate the sub-process of oxygen ion diffusion, which is coupled with anode reaction-diffusion process in series, as shown in Fig.2.a. Based on the above discussion and assumption, an extended circuit model, as shown in Fig.2.b, is constructed, with an attempt to identify the effect of the inter-diffusion layer.

On one hand, the extended physical circuit model as shown in Fig.2 is suitable for both DC and AC cases, similar to our previous work^[27]; on the other hand, a circuit component of finite diffusion Warburg impedance is embedded in the present circuit model to take into consideration of the third physicochemical process associated with the diffusion barrier at the anode/electrolyte interface. In this study, DC analysis and AC fitting are combined to extract richer thermo-kinetic information under condition of both electronic resistance R_e and the diffusion barrier Z_w considered simultaneously. The equivalent circuit model and the corresponding analytical results are presented below.

2.3 Theory Analysis

For the overall reaction in an SOFC as described in Eq.(2)

the corresponding Gibbs free energy of the reaction can be expressed as follows:

$$\Delta G = \Delta G^\circ - RT \ln \left(\frac{a_{H_2} \cdot a_{O_2}^{1/2}}{a_{H_2O}} \right) \quad (3-1)$$

where ΔG^0 denotes the Gibbs free energy of the reaction at the fuel cell operating temperature and standard pressure, R the universal gas constant, T the operating temperature in Kelvin, a_{H_2} , a_{O_2} , a_{H_2O} the activities of H_2 , O_2 , and H_2O , respectively. Assuming an ideal gas, activities of a_{H_2} , a_{O_2} , a_{H_2O} can be approximated by the partial pressures: p_{H_2} , p_{O_2} , p_{H_2O} , respectively. Hence, Eq.(3-1) can be rewritten as:

$$\Delta G = \Delta G^0 - RT \ln \left(\frac{P_{H_2} \cdot P_{O_2}^{1/2}}{P_{H_2O}} \right) \quad (3-2)$$

Since

$$\Delta G = -nFE_N \quad (4-1)$$

$$\Delta G^0 = -nFE^0 \quad (4-2)$$

In view of Eq.(4) to Eq.(3-2), the Nernst potential of the fuel cell, E_N , can be expressed as:

$$E_N = E^0 + \frac{RT}{nF} \ln \left(\frac{P_{H_2} \cdot P_{O_2}^{1/2}}{P_{H_2O}} \right) \quad (5-1)$$

$$E^0 = -\frac{\Delta G^0}{nF} \quad (5-2)$$

where E^0 is the standard potential, F Faraday's constant, n the number of electrons released for every hydrogen molecule reacted. In this analysis, the fuel cell performance (I-V-P) data and the impedance data were taken from the fuel cells using air (21 vol% O_2) as oxidant and humidified hydrogen (3 vol% H_2) as fuel^[29]. Summarized in Table 1 are the calculated Nernst potential E_N , the measured open circuit voltage V_{OCV} , and the cited ion conductivity σ_i for SDC at temperatures of 500~750°C^[30] E_N , U_{OCV} , and σ_i combined with both AC data fitting and DC circuit analysis based on the extended circuit model, we will investigate the kinetic properties of ceria-based SOFC in the following section.

Under the condition of open circuit (i.e., $R_{load} = \infty$ and $I_{ext} = 0$), the equivalent circuit shown in Fig.2 is reduced to the one shown in Fig. 3.a. Accordingly, the EIS data collected under open circuit condition can be analyzed using this equivalent circuit, as to be discussed in the following section. Similarly, when the cell is discharged at a finite rate (i.e. $R_{load} \neq \infty$ and $I_{ext} \neq 0$) in a steady state, the equivalent circuit shown in Fig. 2 is reduced to the one shown in Fig. 3.b, since the capacitors can be regarded as open circuit and the finite diffusion Warburg impedance Z_W approaches a DC diffusion resistance R_W in the limit of $\omega \rightarrow 0$. This simplified equivalent circuit can be used to gain insight into the fuel cell steady-state performance (e.g., the I-V-P data) measured under the condition of a DC load. From simple circuit analysis, the impedance function of the equivalent circuit shown in Fig.3a, $Z(j\omega)$, can be expressed as:

$$Z(j\omega) \stackrel{\text{def}}{=} R_{con,a} + \frac{R_e \left\{ \frac{[R_{p,a} + Z_W] \frac{1}{j\omega C_1} + R_i + \frac{R_{p,c} \frac{1}{j\omega C_2}}{R_{p,c} + \frac{1}{j\omega C_2}} \right\}}{R_e + \frac{[R_{p,a} + Z_W] \frac{1}{j\omega C_1} + R_i + \frac{R_{p,c} \frac{1}{j\omega C_2}}{R_{p,c} + \frac{1}{j\omega C_2}}} + R_{con,c} \quad (6-1)$$

where Z_W defined in Eq.(1) can be written into Eq.(6-2) for convenience of fitting discussion.

In Eq.(6-2), we fix P and set it to be 0.5, $Z_W(R) \stackrel{\text{def}}{=} R_W$, $Z_W(T) \stackrel{\text{def}}{=} T$, and $Z_W(P) \stackrel{\text{def}}{=} P$.

$$Z_W \stackrel{\text{def}}{=} \frac{R_W \tanh[(jT\omega)^P]}{(jT\omega)^P} \quad (6-2)$$

Based on the DC equivalent circuit shown in Fig3.b, some intermediate variables including total contact resistance R_{con} , bulk electrolyte resistance R_b , and total polarization resistance R_p , can be defined as follows for convenience of discussion:

$$R_{con} \stackrel{\text{def}}{=} R_{con,a} + R_{con,c} \quad (7-1)$$

$$R_b \stackrel{\text{def}}{=} \frac{R_e R_i}{R_e + R_i} \quad (7-2)$$

$$R_p \stackrel{\text{def}}{=} R_W + R_{p,a} + R_{p,c} \quad (7-3)$$

Moreover, we could calculate the values of $Z(j\omega)$ in the limit of both $\omega \rightarrow \infty$ and $\omega \rightarrow 0$ using Eq.(6),

$$R_{ohm} \stackrel{\text{def}}{=} \lim_{\omega \rightarrow \infty} Z(j\omega) = R_{con} + \frac{R_e R_i}{R_e + R_i} \quad (8-1)$$

$$R_t \stackrel{\text{def}}{=} \lim_{\omega \rightarrow 0} Z(j\omega) = R_{con} + \frac{R_e(R_p + R_i)}{R_e + R_p + R_i} \quad (8-2)$$

where R_{ohm} and R_t denote ohmic resistance and cell resistance, respectively.

If R_H and R_L are defined as the intercepts of the impedance loop with the real-axis at high frequencies and low frequencies, respectively, they can be approximated as follows:

$$R'_p \stackrel{\text{def}}{=} R_L - R_H \quad (9-1)$$

$$R_H \approx R_{con} + \frac{R_e R_i}{R_e + R_i} \quad (9-2)$$

$$R_L \approx R_{con} + \frac{R_e(R_p + R_i)}{R_e + R_p + R_i} \quad (9-3)$$

Based on the equivalent circuit shown in Fig3.b and the above assumption, the relationship between the measured open circuit voltage U_{ocv} and the calculated Nernst potential E_N can be expressed as^[36],

$$U_{ocv} = \frac{R_e}{R_e + R_p + R_i} E_N \quad (10)$$

Now let's turn to determination of analytical solutions for R_e , R_{con} , and R_p from Eq.(9) and Eq.(10). R_H and R_L can be determined from the measured impedance loop, the measured U_{ocv} and the calculated E_N are listed in table 1, and R_i could be calculated from $R_i = \frac{l}{\sigma_i}$, where l

is about 30 μm and σ_i is given in table 1. Accordingly, the values for $R_H, R_L, R'_p, U_{ocv}, E_N$, and R_i can be obtained at different operating temperatures. Combining Eq.(9) and Eq.(10), we can then express the analytical solutions for R_e , R_{con} , and R_p in terms of $R_H, R_L, R'_p, U_{ocv}, E_N$, and R_i as follows:

$$R_e = \frac{U_{ocv}R_i + E_N R'_p + \sqrt{(U_{ocv}R_i - E_N R'_p)^2 + 4(E_N)^2 R'_p R_i}}{2(E_N - U_{ocv})} \quad (11-1)$$

$$R_p = \frac{E_N R'_p - U_{ocv} R_i + \sqrt{(U_{ocv}R_i - E_N R'_p)^2 + 4(E_N)^2 R'_p R_i}}{2U_{ocv}} \quad (11-2)$$

$$R_{con} = R_H - \frac{R_i \left\{ U_{ocv} R_i + E_N R'_p + \sqrt{(U_{ocv}R_i - E_N R'_p)^2 + 4(E_N)^2 R'_p R_i} \right\}}{E_N R'_p - U_{ocv} R_i + 2E_N R_i + \sqrt{(U_{ocv}R_i - E_N R'_p)^2 + 4(E_N)^2 R'_p R_i}} \quad (11-3)$$

The ionic transference number of the bulk electrolyte t_i is defined as^[36]:

$$t_i \stackrel{\text{def}}{=} \frac{\sigma_i}{\sigma_t} = \frac{R_e}{R_e + R_i} \quad (12-1)$$

where σ_i and σ_t denote ionic and total conductivities of the bulk electrolyte, respectively.

When the interfacial polarization resistances are ignored, the ionic transference number of the bulk electrolyte can be approximated by^[37]:

$$t_i = \frac{U_{ocv}}{E_N} \quad (12-2)$$

When interfacial polarization resistances are considered, the ionic transference number of the bulk electrolyte can be estimated from^[14]:

$$t_i = \frac{U_{ocv}}{E_N} * \frac{R_e + R_i + R_p}{R_e + R_i} \quad (12-3)$$

In this formulation, it is noted that, $R_p = R_W + R_{p,a} + R_{p,c}$, which is quite different from a previous formula^[33] since a finite diffusion Warburg impedance element was added to the present equivalent circuit model.

Under DC condition, the correlation between I_i , I_e , and I_{ext} as shown in Fig.3.b can be expressed in terms of Kirchhoff's Current Law (KCL)^[27]:

$$I_i - I_e = I_{ext} \quad (13-1)$$

In the limit of $R_{load} \rightarrow \infty$ (i.e. open circuit), external current (or output current) I_{ext} approaches zero (i.e. $I_i = I_e$), as shown in Fig.3.b, and the internal shorting current I_{short} can be expressed as follows.

$$I_{short} \stackrel{\text{def}}{=} \frac{E_N}{R_e + R_p + R_i} \quad (13-2)$$

3. Analysis of Impedance Spectra

Following the above impedance simulation, we now turn to the analysis of the impedance data acquired for the novel cell structure of Ni-BZCYYb supported SDC electrolyte cell with an emphasis on understanding the effect of the inter-diffusion layer at the interface between anode and the electrolyte on cell performance.

3.1 Comparison of U_{ocv} , t_i , and I_{short}

To quantitatively evaluate the effect of the inter-diffusion layer at the Ni-BZCYYb/SDC interface on ionic diffusion, electronic blocking, and catalyst activity, we made an attempt to gain more insight from the impedance data using the equivalent circuits developed in previous sections. Once the values of R_H , R_L , R'_p , U_{ocv} , E_N , and R_i are determined as discussed earlier, R_e , R_{con} , and R_p can be obtained from Eq.(11-1)~Eq.(11-3).

Shown in table 2 are the results of electronic contact resistance R_e , polarization resistance R_p , contact resistance R_{con} derived from the analytical calculation using Eq. (11-1), Eq.(11-2) and Eq.(11-3), respectively, and the result of ionic resistance R_i calculated via $R_i = \frac{l}{\sigma_i}$. Moreover, t_i and I_{short} can be calculated from Eq.(12-2) and Eq.(13-2), respectively. Fig. 4 shows the variation in the observed U_{ocv} , the theoretical E_N , the calculated t_i , and the deduced I_{short} under the testing conditions at temperatures of 500~750°C.

At temperatures of 500~600°C, the relatively low open circuit voltages (U_{ocv2} varied from 0.905 to 0.825 V) for the cell base on a ceria electrolyte (cell #2)^[27] were consistent quantitatively with the low t_{i2} and high I_{short2} , as shown in Fig.4.

When an electron-blocked layer of ScSz was deposited onto the SDC electrolyte to form a cell based on a bi-layer electrolyte (cell #3)^[38], open circuit voltages U_{ocv3} above 1.0 V were achieved below 550°C. However, bi-electrolyte layer not only increases the fabrication cost but also introduces extra ohmic loss. The inter-diffusion layer formed at the interface between the Ni-BZCYYb and the SDC could effectively block the electronic conduction of ceria-based electrolytes for SOFCs^[29] leading to higher open circuit voltages (U_{ocv1} varied from 1.065 to 0.995 V) at 500 to 750°C due to higher t_{i1} and lower I_{short1} .

3.2 Breakdown of Polarization Losses

Table 2 gives a gloss view of breakdown results including R_e , R_p , R_{con} , and R_i for ceria-based cell #1 BZCYYb-NiO/SDC/LSCF^[29], in particular for electrolyte ionic resistance R_i and electrolyte electronic resistance R_e . In order to further split the polarization loss into

different sub-processes as defined above, we could conduct impedance analysis in depth resorting to a suitable equivalent circuit model developed or selected^[33].

Prior to data fitting, we conduct impedance simulation in order to give a brief profile of impedance spectra corresponding to the circuit model as constructed in Fig.3.a. Here we adopt the fitted parameters as shown in Fig.6.f for the purpose of impedance simulate mentioned above. The simulation results in Fig.5 show three visually recognizable arcs within the impedance spectra with the frequency range from 1 *mHz* to 10*kHz* under condition of R_e considered and not considered. f_a , f_c and f_W are defined as characteristic frequencies for the three sub-processes including $R_{p,a} // C_1$, $R_{p,c} // C_2$ and Z_W , respectively. The characteristic frequencies for $R // C$ and Z_W are defined in Eq.(14-1) and Eq.(14-2)^[32], respectively, hence we can calculate: $f_a = 100.8 \text{ Hz}$, $f_c = 17.7 \text{ Hz}$, and $f_W = 0.3 \text{ Hz}$.

$$f_{RC} \stackrel{\text{def}}{=} \frac{1}{2\pi RC} \quad (14-1)$$

$$f_W \stackrel{\text{def}}{=} \frac{2.53 \cdot \tau}{2\pi} \quad (14-2)$$

The results shown in Fig.5.b suggest that physical adjoints of sub-processes do not mean the corresponding impedance arcs necessarily adjoin each other because the relative positions of impedance spectra arcs not rely on the physic-electrochemistry occurrence-order in time domain but on the occurrence-order in frequency domain. This disagreement results in the ambiguity and complication on interpreting physicochemical processes in terms of impedance spectra. Compared to impedance spectra between shorting current considered and no shorting current as shown in Fig.5.a, impedance spectra are seriously depressed along real axis direction and its depression extension relies on the size of ionic transference number. One

point needs to be emphasized, electronic conductance of ceria-based electrolyte might result in a deceptive elusion phenomenon of very low polarization resistance.

At 500 to 750°C for cell #1, the detailed fitting plots were shown in Fig.6. Clearly, the simulated impedance data fit well to the measured impedance data at different operating temperatures and this agreement is the precondition for the forthcoming kinetic investigation based on the constructed circuit model. One point need to be noted, the fittings deviate more from the actual data at very high frequencies due to the artificial induction effect of lead wires, which becomes significant at very high frequencies.

In terms of these fitted results as shown in Fig.6, we are able to further split polarization process into three sub-processes, including $R_{p,a} // C_1$, $R_{p,c} // C_2$, and Z_W as defined above, at operating temperatures ranging from 500 to 750°C. Table 3 lists the fitted results in detail for cell #1 as shown in Fig.6 at different operating temperature. It was noted that both electronic resistance R_e and ionic resistance R_i adopt the fixed values from analytical solution when we fit the measured impedance data to the presented circuit model as shown in Fig.3.a. The fitted parameters as shown in table 3 demonstrate a reasonable evolution trend for parameter set totally, except one value $Z_W(T)$ at 500°C is not in agreement with all other values. We don't fully understand why this point is away from its trend; it might be caused by activation energy change of the SDC electrolyte /inter-diffusion layer at that operating condition or some contamination of the raw impedance data during electrochemical testing. More experiments will be conducted in the future work to further verify this equivalent

circuits model and which in turn can be used to predict fuel cell performances and optimize the operating conditions, as to be discussed in a subsequent communication^[39].

Subsequently, these fitted results will be given further analysis and interpreting. If we name contact resistance R_{con} and polarization resistance R_p derived from analytical calculation using Eq. (11-2) and Eq.(11-3), respectively, as $R_{con,cal}$ and $R_{p,cal}$ separately. Similarly, we name R_{con} and R_p from AC impedance fitting results as $R_{con,fit}$ and $R_{p,fit}$. Shown in Fig. 7 are the comparisons of $R_{con,cal}$ v.s. $R_{con,fit}$ and $R_{p,cal}$ v.s. $R_{p,fit}$ with respect to operating temperatures of 500~750 °C. It can be found that $R_{p,dc}$ and $R_{con,dc}$ almost overlap with $R_{p,ac}$ and $R_{con,ac}$, respectively. This good agreement between analytical calculation and AC impedance fitting partially suggests our diagnosis results is valid.

Shown in Fig.8 are the breakdown results for different polarization losses at different operating temperatures according to AC impedance fitting results as shown in Fig.6. As shown in Fig.8.a, with the increase in operating temperatures, the ohmic contact resistance R_{con} for ceria-based cell #1 decreased slightly; while both bulk resistance of electrolyte R_b and polarization resistance R_p experienced a more dramatic decrease. This is anticipated since ionic conductivity and catalyst activity is more sensitive to operating temperature than phase contact resistance does. Below 600 °C, polarization resistance and bulk resistance of electrolyte are the key factors that limit cell performance. Above 700 °C, however, the cell performance was more impeded by the contact resistance than polarization resistance.

Fig.8.b shows a further breakdown of R_p into anode active polarization resistance $R_{p,a}$, cathode active polarization resistance $R_{p,c}$ and inter-diffusion layer resistance R_W .

Breakdown results of R_p by AC impedance fitting indicate: (i) active polarization loss at the

anode side is much smaller than that at the cathode side below 700°C, which is in agreement with the conclusion via reference electrode combined with half-cell by Liu et al^[40]; (ii) when operating temperatures above 750°C, $R_{p,c}$ is comparable to $R_{p,a}$ and R_W becomes dominated in polarization loss firstly; (iii) with the increase of temperature, the rate of decrease in $R_{p,c}$ remained approximately the same over the whole operating temperature range, while the decrease rate for $R_{p,a}$ and R_W undergo a notable change; (iv) the inter-diffusion layer was effective in depressing electronic conduction for ceria-based cell #1 as shown in Fig.4, and it simultaneously lowers down catalyst activity of anode side and introduce considerable polarization loss, in particular at operating temperatures below 600°C. It was reported that the inter-diffusion at the interface of Ni-BZCYYb and SDC formed a new phase of doped barium cerate, Ba(Ce, Sm, Zr, Y, Yb)O₃ which might prevent the reduction of SDC electrolyte and result in high OCV^[29]. Doped barium cerate is a mixed proton, oxygen ion, and electron conductor. The ionic and electronic transfer number was influenced significantly by the operating conditions. Over temperature range of 500~750°C as shown in Fig.8.b, it is found that polarization resistance R_W due to oxygen ion diffusion through the inter-diffusion layer firstly becomes less than $R_{p,c}$ and $R_{p,a}$ at 650°C.

3.3 Analysis of the Characteristic Frequency

EIS technique is sensitive to testing conditions, fitting process, and interpretation method^[33]. However, for a given test cell (once fabricated) imposed to a variety of external conditions such as operating temperature, gas flow, and load size, the characteristic frequency (CF) of each sub-process will keep relatively constant if no shift happens on the nature of the

investigated system^[41]. Accordingly, CFs offer one possibility to discern different sub-processes for stable system. In addition, if a notable change occurs on CFs, it might indicate that some internal properties of the system under investigation undergo an observable shift. Consequently, CFs of the sub-processes might act as a stability's indicator for the nature of electrochemical system under investigation.

Based on AC impedance fitting results for ceria-based cell #1, we could estimate its characteristic frequency f_a , f_c , and f_w for sub-processes $R_{p,a} // C_1$, $R_{p,c} // C_2$, and Z_W in light of Eq.(14-1) and Eq.(14-2), respectively. For the convenience of discussion, we define decade of difference frequency between f_a , f_c , and f_w as $\log_{10}^{f_a-c} \stackrel{\text{def}}{=} \log_{10}^{f_a} - \log_{10}^{f_c}$, and $\log_{10}^{f_c-w} \stackrel{\text{def}}{=} \log_{10}^{f_c} - \log_{10}^{f_w}$. Fig.9 shows how CFs for the three sub-processes defined-above evolve with respect to operating temperatures from 500 to 750°C. The detailed trends for CFs are as follows: (i) f_c remained relatively stable over the whole operating temperature range from 500 to 750°C. The relative stability of f_c hints that no observed shift on the internal properties happens at cathode side; (ii) both f_a and f_w undergo a notable change at temperature range from 600 to 650°C and remained relatively stable at temperature range below 600°C or above 650°C. The evolution trends for f_a , f_c , and f_w are in good agreement with that for $R_{p,a}$, $R_{p,c}$, and R_W as discussed above; (iii) at case of below 600°C, $\log_{10}^{f_a-c}$ is more than 1.41 decades of frequency and $\log_{10}^{f_c-w}$ less than 0.85 decade of frequency; at temperatures above 650°C, $\log_{10}^{f_a-c}$ is less than 0.68 decade of frequency and $\log_{10}^{f_c-w}$ more than 1.45 decades of frequency. Usually, 1.5 decades of difference in characteristic frequency between two neighboring sub-processes means their impedance spectra may be separated from each other via fitting to circuit model in precision.

The decade of difference in characteristic frequency calculated above agrees well with the overlapping and separation of impedance spectra plots as shown in Fig.6.

CF offers a new view to monitor the internal property stability for the investigated electrochemical system. In addition, CFs also offer a supplementary means to discern sub-processes and help the breakdown of polarization losses.

To validate the applicability of this equivalent circuit model to a broader range of testing conditions, more experiments are required, including a wider range of operating temperatures, electrical polarization (V or I), and partial pressures of fuels and oxidant. For instance, oxygen adsorption/desorption, dissociation, and surface diffusion on cathode surfaces can be investigated at lower partial pressures of oxygen or larger cathodic polarization in the low frequency range (close to 0.01Hz). Details of these studies will be reported in subsequent communications.

4. Conclusions

An improved equivalent circuit model, with the consideration of an inter-diffusion layer, was developed for the interpretation of the electrochemical behavior of a fuel cell based on a $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb)-NiO anode supported SDC electrolyte membrane. The mechanism behind the high OCV and the corresponding high peak power density of the cell was elucidated via separation of the polarization processes and the corresponding characteristic frequencies. In particular, impedance analysis suggests that the inter-diffusion layer effectively suppresses the electronic conduction of the SDC electrolyte, but does not adversely affect the catalyst activity and ionic conductivity. More importantly,

identification of the characteristic frequencies associated with different physicochemical process has greatly facilitated the separation of the processes with overlap in impedance data, offering more confidence in assigning a specific part of the impedance data (e.g., an impedance arc or loop) to a given physicochemical process. Also, it is noted that any change in the characteristic frequency for a physicochemical process implies a change in the inherent nature of that process. Once validated by more experimental results under a broader range of testing conditions, the presented equivalent circuit model, in turn, can be used to predict fuel cell performances and optimize the operating conditions.

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Appendix A. Nomenclature

SOFC	solid oxide fuel cell.
EIS	electrochemical impedance spectroscopy.
CF	characteristic frequency (Hz).
MIEC	mixed ionic-electronic conductor.
E_N	Nernst voltage (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($8.314J/K/mol$).
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_2}	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 $Z_W(j\omega)$ (cm^2/s).
d	effective diffusion thickness for $Z_W(j\omega)$ (cm).
R_{load}	DC load resistance ($\Omega \text{ cm}^2$).
R_i	ionic resistance of the bulk electrolyte ($\Omega \text{ cm}^2$).
σ_i	oxygen ionic conductivity of bulk electrolyte (s/cm).
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 ($\Omega \text{ cm}^2$).
$R_{p,a}$	polarization resistance at anode side ($\Omega \text{ cm}^2$).
$R_{p,c}$	polarization resistance at cathode side ($\Omega \text{ cm}^2$).
R_p	total polarization resistance, defined as $R_p \stackrel{\text{def}}{=} R_W + R_{p,a} + R_{p,c}$ ($\Omega \text{ cm}^2$).
$R_{con,a}$	ohmic contact resistance at anode side ($\Omega \text{ cm}^2$).
$R_{con,c}$	ohmic contact resistance at anode side ($\Omega \text{ cm}^2$).
R_{con}	total ohmic contact resistance, defined as $R_{con} \stackrel{\text{def}}{=} R_{con,a} + R_{con,c}$ ($\Omega \text{ cm}^2$).
R_{bulk}	bulk electrolyte resistance, defined as $R_b \stackrel{\text{def}}{=} \frac{R_e R_i}{R_e + R_i}$ ($\Omega \text{ cm}^2$).
R_{ohm}	ohmic resistance, defined as $R_{ohm} \stackrel{\text{def}}{=} R_{con} + \frac{R_e R_i}{R_e + R_i}$ ($\Omega \text{ cm}^2$).
R_t	cell resistance, defined as $R_t \stackrel{\text{def}}{=} R_{con} + \frac{R_e(R_p + R_i)}{R_e + R_p + R_i}$ ($\Omega \text{ cm}^2$).
R_H	the intercepts of the impedance loop with the real-axis at high frequencies, approximated as $R_H \approx R_{con} + \frac{R_e R_i}{R_e + R_i}$ ($\Omega \text{ cm}^2$).
R_L	the intercepts of the impedance loop with the real-axis at low frequencies, approximated as $R_L \approx R_{con} + \frac{R_e(R_p + R_i)}{R_e + R_p + R_i}$ ($\Omega \text{ cm}^2$).
R'_p	an intermediate variable, defined as $R'_p \stackrel{\text{def}}{=} R_L - R_H$ ($\Omega \text{ cm}^2$).

$R_{p,fit}$	total polarization resistance derived from AC impedance fitting ($\Omega \text{ cm}^2$).
$R_{con,fit}$	total ohmic contact resistance derived from AC impedance fitting ($\Omega \text{ cm}^2$).
$R_{p,cal}$	total polarization resistance derived from analytical calculation ($\Omega \text{ cm}^2$).
$R_{con,cal}$	total ohmic contact resistance derived from analytical calculation ($\Omega \text{ cm}^2$).
C_1	double layer capacitances at anode side ($F \text{ cm}^{-2}$).
C_2	double layer capacitances at cathode side ($F \text{ cm}^{-2}$).
l	electrolyte thickness (cm).
f_{RC}	the characteristic frequencies for $R // C$, defined as $f_{RC} \stackrel{\text{def}}{=} \frac{1}{2\pi RC} (Hz)$.
f_W	the characteristic frequencies for $Z_W(j\omega)$, defined as $f_W \stackrel{\text{def}}{=} \frac{2.53*\tau}{2\pi} (Hz)$.
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
$\log_{10}^{f_a-c} \stackrel{\text{def}}{=} \log_{10}^{f_a} - \log_{10}^{f_c} (Hz)$.	
$\log_{10}^{f_c-w}$	decade of difference frequency in logarithm between f_c and f_w , defined as
$\log_{10}^{f_c-w} \stackrel{\text{def}}{=} \log_{10}^{f_c} - \log_{10}^{f_w} (Hz)$.	

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Capations of figures

Fig.1 Four typical circuit models to simulate solid-state cells based on MIEC electrolytes from simple to complex are shown as in (a)~(d), where Nernst voltage is denoted by E_N , ionic resistance and electronic resistance of the electrolyte bulk by R_i and R_e respectively, DC load resistance by R_{load} , polarization resistances and the corresponding double layer capacitances at cathode and anode sides by $R_{p,c} // C_1$ and $R_{p,a} // C_2$ respectively, ohmic contact resistance at cathode and anode sides by $R_{con,c}$ and $R_{con,a}$ respectively.

Fig.2 An extended circuit model for SOFC with MIEC electrolyte and inter-diffusion layer passivating layer at interface of anode/electrolyte. External current is denoted by I_{ext} , ionic current by I_i , electronic current by I_e , finite diffusion Warburg impedance by Z_W as defined above, and other parameters were defined in Fig. 1.

Fig.3 Circuit analysis for ceria-based SOFC and inter-diffusion layer passivating layer at interface of anode/electrolyte: (a) at AC case under open circuit condition, (b) at DC case under DC load condition.

Fig.4 Comparison of theoretical Nernst Potential E_N , the measured open voltage U_{ocv} , the calculated t_i , and the deduced I_{short} for Ceria-based SOFC at temperatures of 500~750°C, (a) Nernst Potential E_N , U_{ocv1} of cell #1 BZCYYb-NiO/SDC/LSCF^[29], U_{ocv2} of cell #2 HastelloyX/NiO-SDC/SDC/SSCo-SDC^[27], and U_{ocv3} of cell #3 SS430/NiO-SDC/ScSz/SDC/SSCo-SDC^[38]; (b) t_{i1} , I_{short1} , and t_{i2} , and I_{short2} for cell #1 and cell #2, respectively.

Fig.5 AC impedance simulation and its characteristic frequency with $R_{con} = 0.115 \Omega \text{ cm}^2$, $R_{p,a} = 0.023 \Omega \text{ cm}^2$, $C_1 = 0.070 \text{ F cm}^{-2}$, $R_{p,c} = 0.024 \Omega \text{ cm}^2$, $C_2 = 0.373 \text{ F cm}^{-2}$, $Z_W(R) = 0.043 \Omega \text{ cm}^2$, $Z_W(T) = 1.263 \text{ s}$, $Z_W(P) = 0.5$, and $R_i = 0.047 \Omega \text{ cm}^2$, these parameters from the fitting results in Fig.6.f at 750°C. (a) impedance simulation for $R_e = 1.196 \Omega \text{ cm}^2$ and $R_e = \infty$; (b) impedance spectra and its corresponding arcs under condition of $R_e = \infty$.

Fig.6 AC impedance fitting results for cell #1^[29] based on AC equivalent circuit model as shown in Fig.3.a, (a) at 500°C; (b) at 550°C; (c) at 600°C; (d) at 650°C; (e) at 700°C; (f) at 750°C. f_a , f_c and f_w are characteristic frequencies defined in Eq.(14) for processes $R_{p,a} // C_1$, $R_{p,c} // C_2$, and Z_W , respectively.

Fig.7 Comparison of polarization resistance R_p and contact resistance R_{con} derived from two different methods. Here $R_{p,fit}$ and $R_{con,fit}$ derived from AC impedance fitting, while $R_{p,cal}$ and $R_{con,cal}$ derived from analytical calculation in terms of Eq.(11).

Fig.8 Analysis of polarization loss for ceria-based cell #1 is based on the fitting results in Fig.6. (a) Contact resistance R_{con} , bulk resistance of the electrolyte R_b , and total polarization resistance R_p ; (b) anode active polarization resistances $R_{p,a}$, cathode active polarization resistance $R_{p,c}$ and interlayer diffusion resistance $R_W = Z_W(T)$.

Fig.9 Characteristic frequencies evolve with respect to operating temperatures ranging from 500 to 750°C. (a) Characteristic frequencies f_a , f_c and f_w for sub-processes $R_{p,a} // C_1, R_{p,c} // C_2$, and Z_W , respectively; (b) difference frequency $\log_{10}^{f_a-c}$ and $\log_{10}^{f_c-w}$ for f_a , f_c and f_w in logarithm.

Capations of tables

Table 1. E_N , U_{OCV} and σ_i under given testing conditions

Table 2. R_e , R_p , R_{con} , and R_i derived from analytical calculation

Table 3. R_{con} , $R_{p,a}$, C_1 , $R_{p,c}$, C_2 , and $Z_W(R, T, P)$ derived from AC fitting

Figure 1

(a)

(b)

(c)

(d)

Figure 2

(a)

(b)

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1

Parameters \ T(°C)	500	550	600	650	700	750
E_N (V)	1.152	1.144	1.136	1.128	1.119	1.111
U_{ocv} (V) ^[29]	1.065	1.055	1.047	1.029	1.004	0.995
σ_i (s · cm ⁻¹) ^[30]	0.0066	0.0120	0.0210	0.0310	0.0460	0.0640

Table 2

<i>Resistance</i> \ <i>T(°C)</i>	500	550	600	650	700	750
$R_e (\Omega \text{ cm}^2)$	40.110	15.258	6.955	3.334	1.846	1.196
$R_p (\Omega \text{ cm}^2)$	2.822	1.040	0.447	0.224	0.146	0.092
$R_{con} (\Omega \text{ cm}^2)$	0.165	0.162	0.152	0.141	0.122	0.113
$R_i (\Omega \text{ cm}^2)$	0.455	0.248	0.144	0.097	0.065	0.047

Table 3

Parameter \ T(°C)	500	550	600	650	700	750
$R_{con} (\Omega \text{ cm}^2)$	0.193	0.172	0.161	0.147	0.126	0.115
$R_{p,a} (\Omega \text{ cm}^2)$	0.177	0.088	0.052	0.050	0.034	0.023
$C_1 (F \text{ cm}^{-2})$	0.001	0.002	0.006	0.031	0.045	0.070
$R_{p,c} (\Omega \text{ cm}^2)$	0.841	0.319	0.200	0.117	0.060	0.024
$C_2 (F \text{ cm}^{-2})$	0.022	0.029	0.038	0.096	0.173	0.373
$Z_W(R) (\Omega \text{ cm}^2)$	1.730	0.616	0.176	0.047	0.045	0.043
$Z_W(T) (s)$	0.227	0.093	0.092	0.870	1.218	1.263
$Z_W(P)$	0.5 (fixed)					