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PHYSICALLY-BASED DECONVOLUTION OF IMPEDANCE SPECTRA: INTERPRETATION, FITTING AND VALIDATION OF A NUMERICAL MODEL FOR LANTHANUM STRONTIUM COBALT FERRITE-BASED SOLID OXIDE FUEL CELLS

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ABSTRACT

In this study, a physically-based model for the interpretation of the impedance spectra of an anode-supported LSCF/GDC/YSZ/Ni:YSZ solid oxide fuel cell is presented. The model locally describes transport and reaction phenomena within the cell components through mass conservation equations. The microstructural properties of the electrodes are predicted through numerical three-dimensional reconstruction of the microstructure, with input parameters obtained from the analysis of SEM pictures of each layer. Simulations show that the model reproduces impedance spectra obtained in different operating conditions with the same set of fitting parameters, comprising material-specific kinetic constants and electrochemical capacitances, which fairly agree with independent literature data and a previous analysis of the spectra through DRT. The model allows for the deconvolution and quantification of the characteristic resistance and frequency of the different physical processes that build up the impedance of the cell. In particular, 7 processes are identified: charge-transfer reactions between LSCF/GDC, GDC/YSZ and Ni/YSZ interfaces appear in the high-frequency range, the medium-frequency feature is due the oxygen reduction reaction and the gas diffusion in the anode, while the low-frequency arc is mainly due to the gas conversion in the anodic channel. An additional low frequency contribution (<1 Hz), not considered in the model, is observed and tentatively attributed to the adsorption of oxygen onto the LSCF surface. Simulation results suggest that more efforts must be dedicated to characterize and improve the oxygen transfer at the LSCF/GDC and GDC/YSZ interfaces. The study shows that a quantitative interpretation of impedance spectra is possible with a reduced number of fitting parameters when a physically-based approach is adopted, making the model an attractive tool for diagnostic purposes.

1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical systems aimed to produce electricity from the electrochemical conversion of the chemical energy of a fossil or renewable fuel at high temperature [1,2]. This technology offers several advantages, such as low emission of pollutants [3], fuel flexibility [4] and high efficiency [1,2]. During operation, the efficiency of energy conversion is reduced by the internal resistances arising within the cell components. In particular, the behavior of an SOFC is the result of the interplay of different physical and electrochemical phenomena, such as electrochemical reactions and transport of charged and gaseous species within the cell components, each one contributing with its own resistance and characteristic dynamics [5–7].

Recognizing and decoupling the contribution of each physical process that build up the cell resistance is a demanding task that

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Abbreviations: CSTR, continuously stirred tank reactor; DGM, Dusty Gas Model; DRT, distribution of relaxation times; EIS, electrochemical impedance spectroscopy; GDC, gadolinia-doped ceria; LSC, lanthanum strontium cobalt oxide; LSCF, lanthanum strontium cobalt ferrite; OCV, open-circuit voltage; SEM, scanning electron microscope; SOFC, solid oxide fuel cell; TPB, three-phase boundary; YSZ, yttria-stabilized zirconia.

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Nomenclature

A_{cell}	surface area of the cell (m^2)
B_0	electrode permeability (m^2)
C_k^a	capacitance of the k-th double layer per unit area (F m^{-2})
d_p	mean pore size (m)
D_{ij}	binary gas diffusivity of pair i-j (m^2 s^{-1})
D_i^k	Knudsen gas diffusivity of species i (m^2 s^{-1})
E_a	activation energy (J mol^{-1})
f	frequency (Hz)
F	Faraday constant (C mol^{-1})
$i^v_{dl,k}$	current density of the k-th double layer per unit volume (A m^{-3})
$i_j^{a/l}$	local current density per unit of interfacial area (a) or TPB length (l) of reaction j (A m^{-2} or A m^{-1})
i_j^0	exchange current density of reaction j (A m^{-2} or A m^{-1})
i_j^{00}	pre-exponential factor of exchange current density of reaction j (A m^{-2} or A m^{-1})
i_j^v	local current density per unit volume of reaction j (A m^{-3})
I	total current density (A m^{-2})
J	total molar flow in the channel (mol s^{-1})
k_i	effective conductivity factor of the phase for species i (−)
L_{cat}	cathode thickness (m)
n_i^e	charge of species i (−)
n_j	number of charges exchanged in reaction j (−)
N_i	molar flux of species i (mol m^{-2} s^{-1})
p	pressure (Pa)
p_i	partial pressure of species i (Pa)
r_v	ratio defined in Eq. (12) (−)
R	universal gas constant (J mol^{-1} K^{-1})
t	time (s)
T	absolute temperature (K)
V_{ch}	channel volume (m^3)
x	coordinate along cell thickness (m)
y_i	molar fraction of gas species i (−)
z_{ij}	stoichiometric coefficient of species i in reaction j (−)
Z	impedance (Ω m^{-2})

Superscripts

*	open-circuit conditions
ch	channel
eff	effective
in	inlet
out	outlet

Greek letters

α	transfer coefficient: anodic α_a, cathodic α_c (−)
ΔV_k	potential difference across the k-the double layer (V)
η_j	local activation overpotential of reaction j (V)
μ	dynamic viscosity of gas mixture (kg m^{-1} s^{-1})
$\tilde{\mu}_i$	electrochemical potential of species i (J mol^{-1})
σ_i	bulk conductivity of the material for species i (S m^{-1})
τ	tortuosity factor (−)
ϕ	porosity (−)
ω	angular frequency (Hz)

offers several benefits. First of all, identifying the phenomena that limit the performance allows for a specific system optimization tailored to reduce the bottlenecks. In addition, should a degradation mechanism start during operation, a specific intervention on the affected physical process can be undertaken to prevent the failure of the system.

The DC response of the system (e.g., the polarization behavior) is not sufficient to decouple the different contributions to cell resistance. On the contrary, electrochemical impedance spectroscopy (EIS), through sinusoidal perturbation of the system, allows for the identification of each contribution based on its own characteristic relaxation frequency [8–11].

Typically, the interpretation of impedance spectra is performed by adopting equivalent circuits, built *a posteriori* on the number and shape of the impedance features [12,13]. Another approach relies on the analysis of the data through the distribution of relaxation times technique (DRT) [9,14,15], which deconvolutes the spectra through an infinite chain of R//C elements, thus identifying the number, resistance and characteristic frequency of the processes. However, both these approaches do not normally allow for a direct and unambiguous link of the impedance response to the physical processes occurring within the cell, due to the simplifications introduced by the circuit elements (either connected in series or in parallel, without taking into account more complex interplays), the use of non-physical elements (such as the constant phase element) and the arbitrary and non-unique choice of the circuit elements [16,17].

An alternative approach relies on the physically-based modeling of the processes occurring within the cell through conservation equations and the numerical simulation of the system dynamics [16–23]. In this approach, the meaningful physical processes considered in the model are chosen *a priori*. Provided that model assumptions are correct, this approach reduces the ambiguity in the assignment of a feature to a specific phenomenon. In addition, the complex interplay among different processes is taken into account, such as the coupling between gas transport and distributed electrochemical reaction, which is hardly described with simple series and parallel connections [16,24]. Finally, model parameters have a clear physical meaning and can be directly linked to physical, chemical or microstructural properties of the system. These advantages allow for a deep and even predictive diagnosis of the cell dynamics, reducing the level of uncertainty in the impedance interpretation [16,17].

This study presents the development and use of a physically-based model for the deconvolution of impedance spectra of an anode-supported LSCF/GDC/YSZ/Ni:YSZ SOFC. The analysis, which comprises the reconstruction of the electrode microstructure, leads to the identification of the physical processes that contribute to cell resistance. The attribution of the impedance features to each specific physical process is discussed and compared with the indications provided by a previous DRT analysis on the same data [25]. In addition, material-specific parameters, useful for the modeling of similar SOFC configurations and for diagnostic studies regarding the degradation of the cell components, are extracted and compared with independent literature data.

The paper is organized as follows. In Section 2, the model and the numerical procedure to simulate impedance are presented. Section 3 reports the results of the simulation, that is, the fitting and validation of the model in different operating conditions, along with the discussion of model outcomes. The final conclusions of the study are reported in Section 4.

2. Modeling

A schematic representation of the cell considered in this study is reported in Fig. 1a. The cell consists of a LSCF-based cathode, a GDC interlayer, a YSZ electrolyte and a composite Ni:YSZ anode, which provides the mechanical support of the cell [25,26]. In particular, a segmented cell configuration is used in the experiments because this setup allows for the local control of the