A comprehensive simulation of gas concentration impedance for solid oxide fuel cell anodes

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ABSTRACT

This paper presents electrochemical impedance simulation of a solid oxide fuel cell anode. The model takes in to account the gas-phase transport processes both in the gas channel and within the porous electrode and couples the gas transport processes with the electrochemical kinetics. The gas phase mass transport is modeled using the transient conservation equations (mass, momentum and species equations) and Butler–Volmer equation is used for the anode electrochemistry. In order to solve the system of non linear equations, an in-house code based on the finite volume method is developed and utilized. Results show a depressed semicircle in the Nyquist plot, which originates from gas transport processes in the gas channel, in addition to a Warburg diffusion impedance originates from gas transport in the thick porous anode. The simulation results are in good agreement with published experimental data.

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1. Introduction

Today, existence of abundant manufactures and automobiles leads to environmental pollution and global warming. Therefore, tremendous effort has been put into environmentally friendly power sources such as fuel cells over the last several decades. Solid oxide fuel cells (SOFCs) are the safest type of high temperature fuel cells that generate electricity. Tubular, planar, and monolithic structures are primary SOFC structures. The solid electrolyte of SOFCs is made of a ceramic material, such as yttria-stabilized zirconia (YSZ), which requires the operating temperature range of 600–1100 °C. The high operating temperature allows for use of a wide range of fuels. Therefore, in the SOFC, not only hydrogen but also several hydrocarbons can be used as fuels. SOFCs can also be used in a wide range of applications. They can be used in hybrid power generating systems. They can be coupled with a gas turbine or a biomass gasifier, and as such can be integrated with other renewable technologies. The high operating temperature of the SOFC also provides excellent possibilities for combined heat and power generation [1].

Electrochemical impedance spectroscopy (EIS) appears to play an important role in fundamental and applied electrochemistry and materials science in the coming years. In EIS experiments, usually a harmonic excitation is imposed to the electrochemical

system and the amplitude and phase shift of the resulting response are measured. Measurements can be conducted over a wide range of frequencies until an impedance spectrum is obtained [2]. This non-destructive technique provides useful information on transport properties, materials characterization, and contributions from each type of losses in SOFC operation [3]. EIS measurements of SOFC anodes show that gas transport in the gas channel and within the porous electrode has a significant effect on the impedance spectra and results in low-frequency arc in the impedance spectra [4–6]. This feature is often referred to as gas diffusion and conversion impedance [4,5] or, more generally, gas concentration impedance [7,8].

The common approach for analyzing the experimental data of EIS is fitting the impedance spectra to an equivalent electrical circuit [6]. This approach is good enough for overall performance comparison, but a valid physical interpretation of the values obtained from this type of fitting is often not possible, especially due to the usually overlapping arcs of the spectrum. Recently, electrochemical impedance simulation using physical models appears as a useful tool for both analyzing the experimental results of EIS and study the fuel cells performance [9–16].

The effect of mass transport on the impedance spectra has been modeled by several authors [4,5,7–9,8,12,15,16]. Most of the mentioned researches on concentration impedance simulation of SOFC anodes mainly emphasize the mass transport in the porous electrode only [9] or in the gas channels only [7,8,12,15], where the electrode itself is treated as reactive channel wall without thickness on its own, thereby neglecting additional gas transport

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Nomenclature

a	empirical exponent of the exchange current density		R_{act}	activation resistance (ohm m^2)
b	empirical exponent of the exchange current density		R_g	gas transport resistance (ohm m^2)
C	total molar concentration (mole m^{-3})		r_p	average pore radius
$D_{i,j}$	binary diffusion coefficient between species i and j (m^2 s^{-1})		t	time (s)
			T	temperature (K)
$D_{i,j}^{eff}$	effective diffusion coefficients (m^2 s^{-1})		U_{in}	inlet velocity (m/s)
D_i^B	Bosanquet diffusion coefficient (m^2 s^{-1})		W	unit cell width (m)
D_i^k	Knudsen diffusion coefficient (m^2 s^{-1})		W_{ch}	channel width (m)
			W_{rib}	rib width (m)
E_{act}	activation energy of the exchange current density (kJ mol^{-1})		X_i	species mole fraction
			Y	complex admittance (ohm^{-1})
F	Faraday's constant (96,484.56 C mol^{-1})		Z	complex impedance (ohm)
f	frequency (Hz)			
H_{ch}	channel height (m)		*Greek symbols*	
i	current density (A m^{-2})		ρ	gas density (kg m^3)
i^0	exchange current density (A m^{-2})		η_{conc}	concentration overvoltage (V)
L	cell length (m)		η_{act}	activation overvoltage (V)
L_a	anode thickness (m)		η_{anode}	anode overvoltage (V)
M_i	species molar mass (kg kmol^{-1})		η_{steady}	steady-state overvoltage (V)
p_i^{in}	inlet partial pressure of species (Pa)		$\eta_{excitation}$	excitation amplitude (V)
p_i^{ra}	partial pressure of reactants and products at the reaction sites (Pa)		τ	anode tortuosity
			θ	time period (s)
p_{ref}	absolute atmospheric pressure (Pa)		γ	pre-exponential factor of the exchange current density (A m^{-2})
p_{out}	outlet pressure (Pa)			
R	universal gas constant (8.314 kJ kmol^{-1} K^{-1})		ε	anode porosity

processes inside the porous structure. Moreover, most of the mentioned researches neglect the coupling of diffusive and convective transport occurring in any practical flow configuration, thereby considering a purely diffusive mass transport [4,5,9,12,16].

This paper improves previously published models by the authors for SOFC gas concentration impedance [15,16]. In order to simulate the gas transport-related impedance, a quasi-2D model was developed by the authors in Ref. [16], where only the diffusive transport was considered. In the present study, the model is extended to a more comprehensive 2-D model in order to include convective flow in gas channel. Moreover, the previous reported model [15] is improved in order to take in to account the effect of gas transport within the porous electrode. In addition, the non-linear kinetic is used to simulate the electrochemical kinetics. This is the first time to our knowledge a comprehensive 2D model for gas concentration impedance of SOFC anodes is reported which includes both the gas transport in the fuel channel and within the porous electrode considering the full coupling of diffusion and convection.

In this study, a planar SOFC is modeled and the steady state behavior and electrochemical spectra of the anode are obtained. The developed model couples the electrochemical kinetics with mass transport. The Butler–Volmer equation is used for the anode electrochemistry, and the transient conservation equations (momentum and species equations) are used for mass transport. In order to solve the system of the nonlinear equations, an in-house code based on finite-volume method is developed and utilized. Furthermore, a parametric study is carried out and the influence of electrode thickness, electrode porosity, inlet fuel velocity, inlet fuel composition and temperature on the impedance spectra is also investigated.

2. Modeling and simulation approach

Fig. 1 depicts the schematic view of a planar anode-supported SOFC and the computational domain.

In this study the electrolyte and cathode overvoltages are ignored while the SOFC anode overvoltage (η_{anode}) is analyzed. In addition, the anode ohmic overvoltage is neglected due to the high anode electronic conductivity [17–19]. Tables 1 and 2 show the cell geometry, as well as the assumed SOFC operational conditions.

2.1. Electrochemical model

The Nernst equation, which is used to determine the electromotive force of an electrochemical reaction, for SOFC is as follows [1]:

$$V_{Nernst} = -\frac{\Delta g_f^0}{2F} + \frac{RT}{2F} \ln \left(\frac{P_{H_2}^* P_{O_2}^{*1/2}}{P_{H_2O}^*} \right) \tag{1}$$
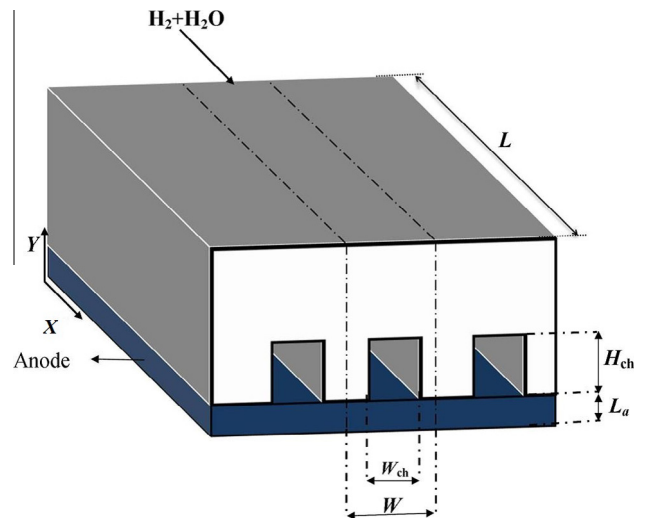

Fig. 1. Schematic diagram of a planar SOFC and computational domain [16].