Simulation of Electrochemical Impedance Spectroscopy of a Solid Oxide Fuel Cell Anodes

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Abstract: The electrochemical impedance technique is the analysis of current response of a fuel cell to a small sinusoidal perturbation in voltage. The variation in frequency response makes it possible to separate processes and mechanisms in the electrochemical phenomena that are occurring at electrode surfaces. The purpose of the current study is to present modeling and simulation of the impedance of solid oxide fuel cell (SOFC) anodes. SOFCs are energy conversion devices that produce electricity and heat directly from fuel by electrochemical reaction. For evaluating the performance of SOFCs, efforts are devoted to developing numerical analysis tools capable of investigating the transport and electrochemical phenomena within the passages of fuel cells. Electrochemical impedance spectroscopy (EIS) is a non-destructive method, which is an effective approach for performance optimization, failure mode diagnosis, revealing dynamic properties and for obtaining information on individual losses in SOFCs. In this study the simulation is based on transient numerical simulations of the fuel cell system when a periodic variation of overpotential is imposed. This model fully couples electrochemical kinetics with gas phase diffusion. The electrochemistry at the anode is modeled using Butler-Volmer equation and gas diffusion model is based on the species equations of Maxwell-Stefan. A parametric simulation study was also carried out by changing parameters, such as temperature and the cell dimensions and the results are discussed. It is found that the Nyquist plot shows a capacitive semicircle which is identical to gas conversion impedance that has been documented in literatures. The diameter of the impedance semicircle changes with flow field properties, hence the gas phase transport limitation plays an important role in SOFC performance. This impedance feature is related to concentration polarization. The obtained results are in qualitative good agreement with experimental data published in literatures.

Key words: Solid oxide fuel cell (SOFC) · Transient simulation · Electrochemical impedance spectroscopy (EIS) · Impedance analysis

INTRODUCTION

Fuel cells appear as future energy conversion systems. Tremendous effort has been put into fuel cell researches over the last several decades. fuel cells have higher efficiency compared to conventional combustion engines due to the fact that their efficiency avoid the limitations of Carnot cycle, in addition the fuel cell itself has no moving parts making it quiet and reliable. Furthermore they have lower pollutant emissions, lower equipment maintenance and higher power density. Fuel cells generate electrical power by continuously converting chemical energy of a fuel into electrical energy through an electrochemical reaction [1]. These devices used in a variety of applications. SOFCs appear especially suitable for stationary electricity generation, both for power plant scales and for small residential applications (combined heat and power generation). An SOFC operates between 800 and $1100°C$ due to the low ionic conductivity of electrolytes such as yttria-stabilized zirconia (YSZ) at lower temperatures. In this type of fuel cell oxidation of hydrogen and reduction of oxygen produces the electricity, water and heat [2].

In order to improve the efficiency of the fuel cell, better understanding of the electrochemical reactions and mass transport in the fuel cell is essential. Therefore it is useful to numerically as well as analytically analyze the experimental results of the SOFC. Various studies with different levels of sophistication on transient modeling of the SOFCs have been published [3-7]. Achenbach [3,4]

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analyzed the dynamic operation of a planar solid oxide fuel cell. He examined the transient cell voltage performance due to temperature and current density changes with lumped assumption for the cell temperature distribution. Sedghisigarchi and Feliachi [5] combined heat transfer dynamics and species dynamics to form a new dynamic model. Also Xue, *et al*. [6], considered a one-dimensional transient model for heat and mass transfer simulation assuming an electrical circuit includes the ohmic resistances and capacitors for the energy storage mode of operation. Mollayi *et al*. [7] developed a transient model of a tubular SOFC using the control volume approach. In their study the local electrochemical parameters were calculated based on the local pressure, temperature and concentrations of the species. The model predicted the cell output voltage as well as the state variables during the start up. It also predicted the cell heat-up rate for hot input gases as well as the startup time of the SOFC.

On the other hand the electrochemical impedance spectroscopy (EIS) is a non-destructive method. EIS is an effective approach for performance optimization, failure mode diagnosis, revealing dynamic properties and for obtaining information on individual losses in the SOFCs [8]. Several researchers have developed SOFC impedance models. Initially EIS measurements were mainly used to determine the conductivity of the SOFC components such as electrolyte and electrode materials [9].

The purpose of the current study is to numerically investigate the electrochemical impedance of a SOFC anode. As known the performance of SOFC is strongly influenced by gas phase transport of reactants and products. These phenomena affected the electrochemical impedance spectra and resulted in a capacitive semicircle in Nyquest plot. The present study investigates the performance of SOFC anode by analyzing these features.

Model Description: The one-dimensional schematic of the planar SOFC anode is depicted by Figure 1. The cell size is given in [20]. As shown by the Fig 1. hydrogen as the fuel passed through anode channel. For simplification the polarization losses from electrolyte and cathode are neglected. In addition concentration polarization of the species within the porous anode is ignored and the transport processes of porous anode are included in the global electrode kinetic behavior. Furthermore gases are assumed to behave as ideal gases. In EIS measurements the individual behavior of each electrode is investigated using symmetrical single cells operated with identical hydrogen or oxygen supply in both compartments. In this
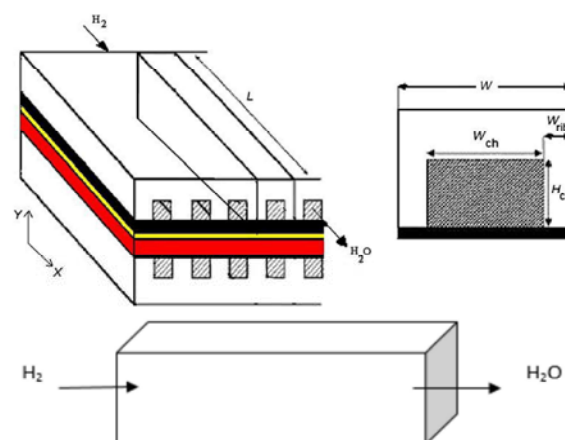

Fig. 1: Schematic of the planar SOFC anode

type typically there is only diffusive transport along electrode channel and there is no convection. Therefore the observed impedance feature is due to anodic gas-phase concentration variations only.

Electrochemical Model: For hydrogen fuel the electrochemical oxidation reactions of the SOFC at the anode channel wall is:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \tag{1}$$

The actual SOFC voltage is decreased from its open circuit voltage due to the irreversibility called polarization or over potential (η). In the present study the anode polarization (η_{anode}) of an SOFC is analyzed while the electrolyte and cathode are assumed to be ideal and polarization losses is ignored. The anode polarization is made up of concentration polarization (η_{conc}) and activation polarization (η_{act}):

$$\eta_{anode} = \eta_{conc} + \eta_{act} \tag{2}$$

The concentration over potential due to channel gas transport is calculated from the Nernst equation [9]:

$$\eta_{conc} = \frac{R\ T}{n_e F} \ln\left(\frac{y_{H_2}^{in} y_{H_2O}}{y_{H_2} y_{H_2O}^{in}}\right) \tag{3}$$

The activation polarization is determined from the Butler-Volmer equation that relates the surface over potential to the rate of reaction. The Butler-Volmer equation in implicit form for a symmetric two-electron transfer is as follows [2].

$$i = i^o \left\{ \exp\left(\frac{F}{RT}\eta_{act}\right) - \exp\left(-\frac{F}{RT}\eta_{act}\right) \right\} \quad (4)$$

Combining equations 2, 3 and 4 yields:

$$i = i^o \left\{ \left(\frac{y_{H_2}^{in} y_{H_2O}}{y_{H_2} y_{H_2O}^{in}}\right)^{-.05} \exp\left(\frac{F}{RT}\eta_{anode}\right) - \left(\frac{y_{H_2}^{in} y_{H_2O}}{y_{H_2} y_{H_2O}^{in}}\right)^{.05} \exp\left(-\frac{F}{RT}\eta_{anode}\right) \right\} \quad (5)$$

Mass Transfer Model: The one-dimensional gas-phase diffusion along the gas channel using the species conservation equation is as follow:

$$\frac{\partial(\rho y_i)}{\partial t} = -\frac{\partial J_i}{\partial x} + W_i \quad (6)$$

Where J_i is the diffusive mass flux and W_i is volume-specific mass production rates of species i. The diffusive mass flux of species i is given by Fick's law:

$$J_i = -\rho D_{i,j} \frac{\partial y_i}{\partial x} \quad (7)$$

Also the area-specific mass production rates of species i (w_i) is given by the Faradaic current due to the electrochemical reaction of fuel as follow:

$$W_{H_2} = -\frac{iM_{H_2}}{2F} \quad (8)$$

$$W_{H_2O} = \frac{iM_{H_2O}}{2F} \quad (9)$$

At high temperature all the gaseous components are assumed to behave as ideal gases:

$$p = \frac{\rho RT}{M_m} = \rho RT \sum_i y_i / M_i \quad (10)$$

The transient response of fuel cell anode to harmonically varying excitation is given by:

$$\eta_{anode}(t) = \eta_{steady} + \eta_{excitation} \sin(2\pi ft) \quad (11)$$

where f is the frequency.

Simulation Procedure: In order to solve the coupled nonlinear mass transfer equation (eq. 6), electrochemical equation (eq. 5) and excitation equation (eq. 11) a code based on finite different method is developed and utilized. The initial steady state is achieved by setting the $\eta_{excitation}$ equal to zero. The obtained steady state results of the cell

are set as initial values for the transient analysis. Then the governing equations are time integrated for several periods (T= /f) to determine the transient current i(t) of the system. The computational domain is discretized by a 50 uniform grid in longitudinal directions. The grid independency of the results is examined and insured.

RESULTS AND DISCUSSION

The electrochemical impedance is calculated in the time domain using the transient numerical simulation technique. Fig. 2 depicts the Simulated impedance spectra for η_{steady}=0V and $\eta_{excitation}$= mV.

For verification purpose model parameters are chosen in order to reflect the results by Bessler [16]. The channel cross section is 1×1, the width of the channel rib is mm, the channel length is 1cm, the temperature is set to 1123 K, hydrogen inflow concentration is 99% and exchange current density is 0.483 A/cm2. In the present study, impedance is calculated for a frequency range of $10^{-4} < f < 10^4$. Here capacitive behavior in the form of an RC-type semicircle in the Nyquist diagram is shown and its characteristic frequency is 23 Hz and gas diffusion resistance (Rgas) is about 0.25 *ohm-cm*^{2}. The difference between the low-frequency and the high-frequency real part is the gas diffusion resistance . As depicted in Fig. 2 the obtained results show good agreement with the published simulation results (ref. 16, Fig 16). This arc is due to gas phase diffusion in the cell. In experimental anode characterization, these features are often referred to as gas conversion, gas diffusion or gas concentration impedance [11, 12, 14-1 6]. A parametric simulation study by changing parameters, such as supplied gas phase compositions, temperature and the cell dimensions, can be carried out. Here the effect of temperature and cell cross sectional area on electrochemical impedance spectra is investigated.

Effect of Temperature: The influence of temperature on the gas diffusion impedance is shown in Fig. 3. This fig. shows that with decreasing the temperature the cell performance gets better and the resistance decreases.

Effect of Channel Cross Section: The influence of the channel cross-sectional area on the gas diffusion impedance is shown in Fig.4. Decreasing the cross-sectional area strongly increases Rgas and this parameter has a strong influence on the gas concentration impedance. This is expected as diffusive transport between the inside of the channel and the surrounding gas chamber decreases.
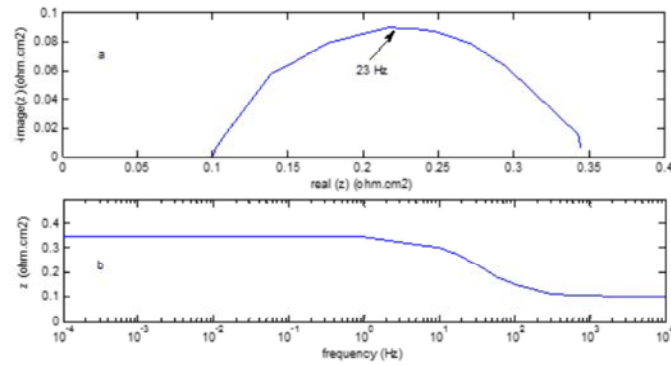
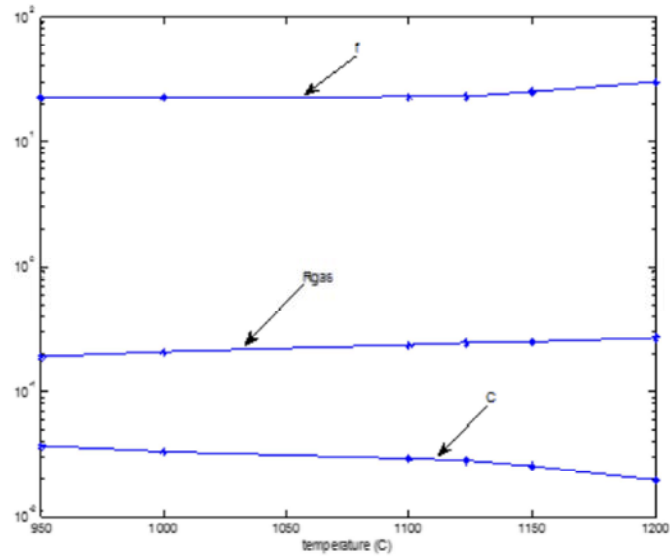Fig. 2: Simulated impedance (a) Nyquist plot (b) Bode plot

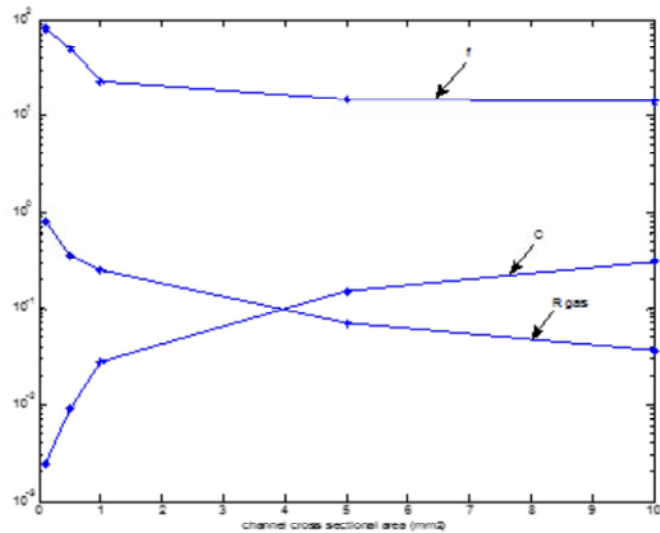Fig. 3: Effect of change in temperature on Gas diffusion resistance, capacitance, and relaxation frequency.

Fig. 4: Effect of change in cross sectional area on Gas diffusion resistance, capacitance, and relaxation frequency.

CONCLUSIONS

In this paper simulation and analyzing the electrochemical impedance spectra of a SOFC anode is considered. The obtained conclusions are as follows:

- Channel diffusion causes a capacitive behavior in the form of an RC-type semicircle in the Nyquist diagram.
- The effect of temperature on the gas diffusion impedance is investigated. The diffusion resistance decreases by decreasing the temperature and the cell performance gets better.
- The effect of cross sectional area on the gas diffusion impedance is considered. The diffusion resistance decreases by increasing the cross sectional area.

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