



Comprehensive understanding of the active thickness in solid oxide fuel cell anodes using experimental, numerical and semi-analytical approach



Kosuke Miyawaki^{a,*}, Masashi Kishimoto^{a,b}, Hiroshi Iwai^a, Motohiro Saito^a, Hideo Yoshida^a

^a Department of Aeronautics and Astronautics, Kyoto University, Nishikyo-ku, Kyoto 615-8540, Japan

^b Department of Earth Science and Engineering, Imperial College London, London SW7 2AZ, United Kingdom

HIGHLIGHTS

- Active thickness within SOFC electrodes are investigated through numerical simulations and experiments.
- Effect of the operating conditions and microstructural parameters on the active thickness is investigated.
- The behaviour of the active thickness predicted by numerical simulation agrees well with experimental results.
- Semi-analytical descriptions are derived to identify the dominating factor for the active thickness.

ARTICLE INFO

Article history:

Received 11 February 2014

Received in revised form

18 May 2014

Accepted 20 May 2014

Available online 4 June 2014

Keywords:

Solid oxide fuel cells

Electrochemical reaction

Active thickness

Microstructure

FIB-SEM

Ni–YSZ anode

ABSTRACT

This paper reports the evaluation of the electrochemically active region in solid oxide fuel cell (SOFC) electrodes through experimental, numerical and semi-analytical approaches. In the experiment, anodes with several different thicknesses were fabricated and their performance was measured to find its dependence on the anode thickness, microstructure and operating conditions. The three-dimensional (3D) microstructure of the anodes was imaged using focused ion beam scanning electron microscopy (FIB-SEM) and the microstructural parameters were quantified. One-dimensional (1D) and 3D numerical simulations based on the actual 3D microstructures were carried out to investigate the active thickness in the anodes. The validity of the numerical models was confirmed by comparing the results with the experiment. The active thickness, i.e., the electrochemically active region within the anode, is discussed using the verified simulation models to find its dependence on various conditions. The active thickness was found to depend on the microstructure and the operating conditions. We then attempted to find a simple expression for the active thickness useful for practical applications with semi-analytical discussion. The developed descriptions expressed the quantitative dependence of the active thickness on the effective ionic conductivity, exchange current density and area-specific current density.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Solid oxide fuel cells (SOFCs) are attracting attention for their high power generation efficiency and fuel diversity. Recently, SOFCs have been practically applied to home stationary generators and moreover, they are considered to be applicable to hybrid systems in power plants where an SOFC can be introduced into gas turbine systems. For the full-scale introduction of SOFC systems, further

research is required to improve their performance, durability and cost-effectiveness.

Ni-YSZ is commonly used as a material for SOFC porous anodes because of its low cost and high catalytic activity. The porous microstructure is composed of three phases: an electron-conductive Ni phase, an ion-conductive yttria-stabilized zirconia (YSZ) phase and a gas-diffusive pore phase. During the electrochemical reaction, various transport phenomena occur within the electrodes, i.e., ionic transport in the YSZ phase from the anode-electrolyte interface to the reaction sites, electron transport in the Ni phase from the reaction sites to the current collector and gas diffusion between the reaction sites and the electrode surface.

* Corresponding author. Tel./fax: +81 75 383 3652.

E-mail address: kosuke.miyawaki@gmail.com (K. Miyawaki).

Although the reaction sites, termed three-phase boundaries (TPBs), are distributed within the anode structure, it is widely accepted that the electrochemical reaction mostly occurs at the TPBs located in the vicinity of the anode-electrolyte interface, which is called the active reaction region or active thickness. This is because the ionic conductivity in the YSZ phase is significantly lower than the electron conductivity and gas diffusivity by several orders of magnitude. To achieve higher performance, electrodes are required to have sufficient electrochemical reaction sites in the active region as well as high conductive/diffusive flux through the three phases. Knowledge of the reaction region will therefore be significantly useful for optimizing the electrode microstructure, and hence, many researchers have attempted to identify the active thickness by both experiment and simulation [1–11].

Generally, in experimental approaches, the electrochemical performance of SOFC electrodes with several different thicknesses were evaluated by current–voltage measurement and/or electrochemical impedance spectroscopy (EIS). The reported values for the active thickness widely vary from 5 to 50 μm , which may be due to the different operating conditions and microstructures of the examined samples. In these approaches, the error caused by the individual variability of the samples is also inevitable and makes it difficult to accurately evaluate the active thickness. On the other hand, in simulation-based approaches, various methodologies have been developed to describe the porous structures and the phenomena in the electrodes. Although these approaches ensure the reproducibility of the results, few studies have discussed the validity of their models using the real electrode microstructure. To confirm the reliability of the models, results of the simulations need to be compared with experimental results.

According to the research by Kishimoto et al. [12], the active thickness is mostly determined by the balance between the oxide ion conductivity in the YSZ phase and the electrochemical reaction rate at the TPBs. Higher ionic conductivity makes it easier for ions to reach further from the electrolyte, resulting in increased active thickness. On the other hand, a higher electrochemical reaction rate enables more of the reaction to occur in the vicinity of the electrolyte, which reduces the active thickness. Since the conductivity and reaction rate are strongly affected by the electrode microstructure and operating conditions, both of them must be fully taken into account to estimate the active thickness in the electrodes.

The aim of this study is to systematically evaluate the active thickness of the anodes under various operating conditions and microstructures through both experimental and simulation-based approaches. First, the electrochemical performances of SOFC anodes are measured using anodes with various thicknesses, from which the dependence of the performance on the anode thickness is investigated. Next, the microstructural parameters are obtained through direct imaging of the anode microstructure using focused ion beam scanning electron microscopy (FIB-SEM). Subsequently, both one-dimensional (1D) and three-dimensional (3D) numerical simulations of the anodes are conducted on the basis of the actual microstructure and the results are compared with the experimental results. Finally, the active thickness is evaluated using the simulation results and then we attempt a semi-analytical approach to discover the key variables governing the active thickness.

2. Experimental

2.1. Sample preparation

In this study, Ni–YSZ cermet anodes (Ni:YSZ = 50:50 vol.%) in a button cell were examined. Fig. 1 shows a schematic picture of the prepared samples. A disk of 8 mol% YSZ (Tosoh Co., 24 mm

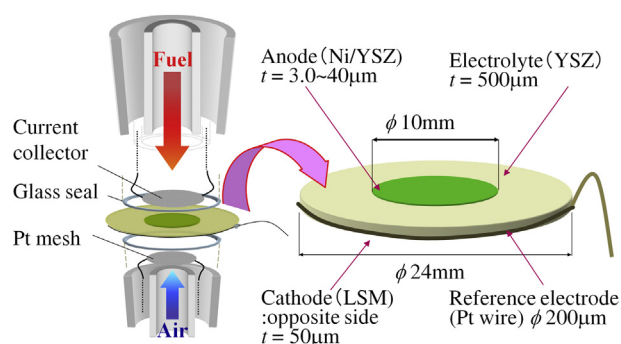


Fig. 1. Schematic picture of the single cell sample and the experimental setup.

diameter, 500 μm thickness) was used as an electrolyte. NiO powder (Wako Pure Chemical Industries, Ltd.) and YSZ powder (Tosoh Co.) were mixed and used for the anode material. The detailed procedure of the sample preparation is given in our previous works [13,14]. Here the anode material was prepared at once so as to reduce the individual difference in microstructure. In the screen printing process, several different masks were used to obtain samples with various thicknesses. Moreover, two different sintering temperatures, 1400 and 1450 $^{\circ}\text{C}$, were employed in the sintering process to obtain a series of anodes with different microstructures, which are referred hereinafter as Anode 1400 and Anode 1450, respectively. A $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.97}\text{MnO}_3$ (LSM) cathode was also fabricated on the other side of the electrolyte sintered at 1150 $^{\circ}\text{C}$ for 5 h. In addition, a platinum wire (ϕ 0.2 mm) was attached around the electrolyte disk as a reference electrode.

2.2. Power generation experiment

The electrochemical characterization of the anodes was conducted with the experimental setup used in Kishimoto et al. [14]. First, the sample cell was sandwiched between alumina tubes with a Pyrex glass seal as shown in Fig. 1, and heated to 1000 $^{\circ}\text{C}$ at a heating rate of 200 $^{\circ}\text{C h}^{-1}$. Second, the temperature was kept at 1000 $^{\circ}\text{C}$ to melt the glass seal and subsequently NiO was reduced using hydrogen. Third, power generation with a potentiostatic load was conducted for at least 12 h at a terminal voltage of 0.7 V to stabilize the performance while supplying 3% H_2O –97% H_2 and 21% O_2 –79% N_2 to the anode and cathode, respectively. The total flow rate was maintained at 100 ml min^{-1} for both electrodes during the experiment. The anodic gas was humidified by bubbling hydrogen through water at a controlled temperature. Finally, the performance of the cell was measured between the anode current collector and the reference electrode at 1000 and 800 $^{\circ}\text{C}$ while supplying 3% H_2O –97% H_2 to the anode side.

2.3. Three-dimensional imaging

Microstructural information of the tested anodes was obtained using FIB-SEM. After the electrochemical characterization, the anodes were cooled down to room temperature in a reductive atmosphere and then impregnated with epoxy resin (Specifix20, Struers) under a vacuum condition at room temperature so that the pores of the anodes could be easily distinguished from solid phases during the SEM imaging. The impregnated anodes were then cut and mechanically polished for FIB-SEM imaging. In the imaging, cross-sectional images of the anode microstructure were continuously obtained using an in-lens secondary electron detector with an acceleration voltage of ~ 2 kV. From the images, we extracted

Download English Version:

<https://daneshyari.com/en/article/1286588>

Download Persian Version:

<https://daneshyari.com/article/1286588>

[Daneshyari.com](https://daneshyari.com)