Journal of Power Sources 305 (2016) 10–16

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Simulation of the reduction process of solid oxide fuel cell composite anode based on phase field method

Zhenjun Jiao [a, b, *], Naoki Shikazono [a, b]

[a] Institute of Industrial Science, the University of Tokyo 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
[b] CREST, JST, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

HIGHLIGHTS

- A model is proposed to simulate the reduction process of NiO in SOFC anode.
- Volume change and Ni sintering determine the initial Ni microstructure.
- Phase field width can be changed to modify the sintering speed in simulation.

ARTICLE INFO

Article history:
Received 3 September 2015
Received in revised form
16 November 2015
Accepted 17 November 2015
Available online 29 November 2015

Keywords:
SOFC
Reduction
Sintering
Phase field method
Anode

ABSTRACT

It is known that the reduction process influences the initial performances and durability of nickel-yttria-stabilized zirconia composite anode of the solid oxide fuel cell. In the present study, the reduction process of nickel-yttria stabilized zirconia composite anode is simulated based on the phase field method. An three-dimensional reconstructed microstructure of nickel oxide-yttria stabilized zirconia composite obtained by focused ion beam-scanning electron microscopy is used as the initial microstructure for the simulation. Both reduction of nickel oxide and nickel sintering mechanisms are considered in the model. The reduction rates of nickel oxide at different interfaces are defined based on the literature data. Simulation results are qualitatively compared to the experimental anode microstructures with different reduction temperatures.

1. Introduction

With a high energy conversion efficiency and fuel flexibility, solid oxide fuel cell (SOFC, hereafter) has been attracting increasing attentions in recent decades [1,2], while reliability and long time stability of the electrodes remain as the main challenges. It has been reported that nickel (Ni, hereafter) agglomeration, which results in the decrease of active three phase boundary (TPB, hereafter) density and Ni network connectivity, is one of the main causes for anode degradation [3–12]. It is thus very important to optimize the microstructure which has both high initial performance and long time durability. Manufacturing processes, screen-printing, sintering and reduction etc., are of great importance to improve the microstructure of the anode. Plascencia & Utigard [13] and Utigard et al. [14] have studied the reduction process of NiO particles at different temperatures. It is shown that different initial reduction temperatures lead to totally different morphologies of Ni particles, which may influence the initial performance and durability of the composite anode. At a temperatures above 600 °C, Ni particle agglomeration and sintering were also found to take place in the reduction process. Jiao et al. [15] have investigated the effects of reduction temperature on the initial performances and short-time durability of the Ni-YSZ composite anodes. It is found that the reduction temperatures largely influence the initial anode performance and durability. Anode reduced at 500 °C showed very poor initial performance and durability, while a higher reduction temperature leads to a better anode initial performance and durability. Jeangros et al. [16,17] have observed NiO reduction process of NiO-YSZ composite anode in-situ using an environmental transmission-electron-microscopy at low temperature. It is reported that the reduction of NiO starts from at NiO-YSZ interface at 380 °C and in very low hydrogen pressure. The Ni particle

* Corresponding author. [a]Institute of Industrial Science, the University of Tokyo 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan.
E-mail address: zhenjun@iis.u-tokyo.ac.jp (Z. Jiao).

http://dx.doi.org/10.1016/j.jpowsour.2015.11.061
0378-7753/

agglomeration and sintering were also found to take place in the reduction process around a temperatures of 400 °C. Zhu et al. [18]. have reported that the initial microstructure of Ni-YSZ and the corresponding performances can be influenced by the reducing and sintering processes of NiO to Ni. The reduction process starts from grain surface or grain boundary with relatively low binding energy. Chen et al. and Jiao et al. [20,21] used phase field method (PFM, hereafter) to simulate the microstructural evolution of Ni-YSZ anode using 3D focused ion beam-scanning electron microscopy (FIB-SEM, hereafter) reconstruction microstructure of Ni-YSZ anode. Li et al. and Jiao et al. [22,23] have applied PFM to simulate both the morphological and crystal structural evolutions of Ni-YSZ anode during the sintering process. Besides phase field method, the sintering analysis of Ni phase was also conducted using Kinetic Monte Carlo simulation, which was verified by FIB-SEM reconstruction by Hara et al. [24].

Before initial operation, calcined NiO-YSZ composite is reduced to Ni-YSZ which functions as the anode. Reduced Ni is concurrently sintered during this process, which is a very complex phenomenon and its mechanism is not fully understood. In this study, a numerical model based on PFM is proposed to simulate the reduction process of composite NiO-YSZ anode to study the influences of reduction process on the initial Ni-YSZ anode microstructure right after calcination. Both volume change and sintering mechanisms are combined in the model to investigate the microstructure evolution during the reduction process.

2. Experimental

Cell preparation— The anode cermet powder was prepared by mechanically mixing NiO and YSZ powders (AGC Seimi Chem. Corp., Japan), where the volume ratio of NiO to YSZ was 60%:40%. The anode was then sintered at 1450 °C for 3 h. Details of the fabrication process have been introduced in Refs. [15,19].

Microstructure analysis— The porous sample was analyzed by FIB-SEM (Carl Zeiss, NVision 40) in this study. The porous sample was first infiltrated by low viscosity epoxy resin under low pressure atmosphere (ca. 15 Pa), so that the pores of the porous electrode could be easily distinguished during FIB-SEM observation. The sample was then polished by using Ar-ion beam cross-section polisher (JEOL Ltd., SM-09010). The 3D microstructure of NiO-YSZ anode then can be virtually reconstructed based on a series of 2D images by Matlab and Avizo, as shown in Fig. 1. The details of dual-beam FIB-SEM observation technique are also introduced in Refs. [15,19].

Anode reduction— Three anodes were reduced at 500 °C, 800 °C and 1000 °C for 90 min, 30 min and 10 min, respectively, to ensure a complete reduction [15]. The microstructures of anodes after reduction were then analyzed by FIB-SEM.

3. Simulation modeling

The simulation procedures are illustrated by the flow diagram shown in Fig. 2. Different phases were presented by different colors. In Step 1, the original microstructure of NiO-YSZ anode was reconstructed based on a series of FIB-SEM images. The simulation then starts by converting finite thickness of NiO phase to Ni phase at NiO-pore and NiO-YSZ interfaces, which is demonstrated as Interval 1 in Fig. 2. The corresponding time step Δt of this NiO to Ni conversion is estimated by an reduction rate kinetic model proposed by Utigard et al. [14]. The details are described below. After this NiO to Ni conversion, 40 vol% of newly generated Ni were randomly deleted and converted to pores of a characteristic size s in Interval 2 to ensure the volume decrease of NiO reduction process [1]. In Interval 3, Ni sintering simulation based on PFM is conducted for a characteristic time step Δt. Subsequently, based on the microstructure shown in Step 4, NiO of finite thickness at NiO-pore and NiO–Ni interfaces are converted to Ni phase in Interval 4, similarly as in Interval 1. Finally, Steps 3 to 5 are repeated until all NiO had been converted into Ni. In order to simplify the model, reduction rate along the Ni grain boundary is not considered in this study.

Utigard et al. [14] has proposed a reduction rate model based on chemical kinetics at the reaction front of NiO particles, which is given by the following equation,

$$\frac{dX}{dt} = k(1-X)^{\frac{2}{3}}, \tag{1}$$

where X is the volume ratio of the reduced NiO to the original NiO, and k is the reduction rate constant. Based on this equation, we can obtain an equation for the reduction time as a function of reduced

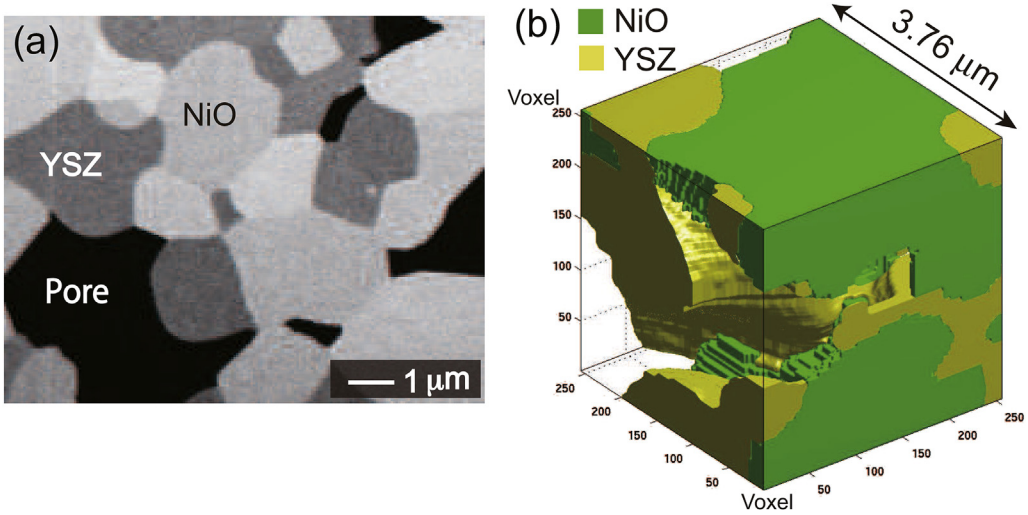

Fig. 1. (a) 2D FIB-SEM image and (b) corresponding 3D reconstruction of composite NiO-YSZ anode before reduction. (Green: NiO Gray, yellow: YSZ). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)