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Short communication

Quantitative analysis of micro structural and conductivity evolution of Ni-YSZ anodes during thermal cycling based on nano-computed tomography

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ABSTRACT

Understanding the mechanism of degradation in solid oxide fuel cells (SOFCs) using nickel/yttria-stabilized zirconia (Ni-YSZ) as the anode material is very important for the optimization of cell performance. In this work, the effects of thermal cycling on the microstructure of the Ni-YSZ anode are explored using the three-dimensional X-ray nano computed tomography (nano-CT) imaging technique. It is found that the average Ni particle size increased with thermal cycling, which is associated with the decreased connectivity of the Ni phase and the three-phase-boundary (TPB) length. Moreover, the conductivities of the anode samples are also reduced with the increase in thermal cycle times. The implication of these observations is discussed in terms of the relationship between the conductivity and connectivity of the Ni phase.

1. Introduction

In recent years, much attention has been paid to fuel cells because of their ability to produce clean and efficient energy by directly converting chemical energy into electricity. A solid oxide fuel cell (SOFC) uses a hard ceramic electrolyte and operates at very high temperatures, between 500 and 1000 °C, where good ionic conductivity occurs. The electrolyte is usually yttria-stabilized zirconia (YSZ), which conducts oxygen ions but not electrons. SOFC anodes also require an electronic-conducting phase, for which Ni is typically matched to YSZ. The electrodes are porous, enabling the transport of gasses along with ions and electrons. Chemical reactions take place where the ionic, electronic, and gas-conduction phases meet, which are called the triple-phase boundaries (TPBs).

Commercial applications of SOFCs for stationary power sources require their stable performance over long periods of time (>40,000 h); therefore, SOFCs must exhibit mechanical, thermal, chemical, and electrical stability during long-term high-temperature operation. Unfortunately, the electrochemical performance of SOFCs is inevitably degraded during the cell lifetime [1,2]. It is therefore of great importance to understand the degradation mechanism of SOFCs to improve the operation time and optimize the performance. Numerous degradation mechanisms for the Ni-YSZ anode have been proposed [3,4], and among them a prevailing interpretation is the rearrangement and coarsening of the Ni phase [5,6]. If the Ni phase is not stable during operation, the functions of the Ni phase, such as providing a high amount of TPBs for electrochemical reactions, can be significantly altered. It is difficult to define the effect of local conditions such as temperature on any degradation mechanisms [7]. Alternatively, high-temperature thermal-cycling experiments in conjunction with microstructural analysis on the Ni-YSZ anode provide a means of examining the changes in the Ni-YSZ anode under a defined condition. To this end, three-dimensional (3D) information regarding the full pore networks of the anode is desired because it plays a crucial role in modeling, simulating and establishing the correlation between anode microstructure and electrical properties of an SOFC. Recently, the 3D microstructure of SOFC electrodes has been directly measured by scanning electron microscopes equipped with a focused-ion beam (FIB-SEM) [8–12]. By applying these 3D

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Table 1
Summary of key parameters calculated from 3D reconstructions of anodes and conductivity measured by four-point probe.

	Non-cycle	2 Cycles	4 Cycles	6 Cycles	8 Cycles
Volume size (μm^3)	283 ± 23	391 ± 32	235 ± 23	434 ± 17	365 ± 37
Surface area of Ni (μm^{-1})	1.65 ± 0.05	1.32 ± 0.06	1.20 ± 0.05	1.15 ± 0.10	1.05 ± 0.04
Surface area of YSZ (μm^{-1})	2.53 ± 0.08	2.90 ± 0.04	2.55 ± 0.06	2.52 ± 0.16	2.21 ± 0.02
Connectivity of YSZ phase (%)	98.3 ± 0.7	98.8 ± 0.2	98.2 ± 0.1	98.8 ± 0.5	99.0 ± 0.1
Connectivity of Ni phase (%)	98.3 ± 1.0	93.9 ± 0.6	93.1 ± 0.5	92.0 ± 1.2	90.6 ± 1.3
Conductivity ($S\,cm^{-1}$)(800 °C)	611	600	550	451	396

measurements, the key microstructural parameters, such as TPB length and tortuosity factors, can be obtained.

In recent years, the development of X-ray optics has allowed the resolution of X-ray microscopy to reach the nanometer range [13,14]. This advancement, coupled with the penetrating power of X-rays, can be applied to examine the 3D volumes of SOFCs that are tens of microns in thickness with spatial resolution on the order of tens of nanometers. Compared to the FIB-SEM technique, nano-CT is a time-saving and non-destructive process for the study of SOFC microstructure. These advantages have made the nano-CT a technique of growing importance in the investigation of the shape, size, distribution and elemental composition of a wide variety of materials [15–18], particularly those used in SOFCs [19–22]. In our previous studies, we utilized X-ray absorption edge spectroscopy to identify the spatial distribution of the constituent Ni, YSZ and pore phases for a composite anode and determined some key microstructural factors that may be linked to the performance of porous composite anodes [23]. Here, the absorption edge analysis technique has been used to study the 3D structural evolutions of Ni-YSZ anodes under thermal cycling without the electrical load. The results are helpful in generating a unique understanding of the microstructure and properties of anodes during heat cycling.

2. Materials and experiments

2.1. Sample preparation

The sample used in this study was taken from the anode used in the SOFC which was consisted of a thin yttria stabilized zirconia electrolyte layer sputtered onto a thick NiO-YSZ anode support by magnetron sputtering, with a composite cathode of $(La_{0.8}Sr_{0.2})_{0.95}MnO_3$ and YSZ. The porous substrate supporting the anode was fabricated using coarse NiO and YSZ powders (NiO:YSZ = 56:44 wt.%) by tape-casting. The anode was sintered in air at 1400 °C for 5 h, then cooled to 800 °C and finally reduced in an Ar/4% H_2 atmosphere to obtain the Ni/8YSZ cermets. Four samples of Ni-YSZ anode were selected for thermal cycling. The anode was first heated to 750 °C in nitrogen. Then, at the same temperature, hydrogen gas was delivered to the anode samples at 50 ml min^{-1} for 4 h. Then anode was finally cooled down to room temperature under a hydrogen atmosphere. This heating-cooling process was considered one thermal cycle. Four samples having undergone two, four, six and eight thermal cycles, respectively, were imaged; an additional Ni-YSZ anode subjected to no thermal cycling was used for comparison. After the thermal cycle testing we fetch a small part from the anode for imaging and analyzing the microstructure.

2.2. Conductivity measurement

A DC four-point probe was applied to measure the conductivities of the anodes. First, a rectangular sample obtained from the porous anode was measured by the DC four-point probe. The four probes are arranged in a linear fashion, where the two outer probes are connected to a current supply, and the inner probes to a voltage meter. As current flows between the outer probes, the voltage drop across the inner probes is measured. Then the resistance of sample can be measured directly. An expression based the co-linear four-probe (4-probe) method was applied to calculate the conductivity (σ) of samples as follow [24]:

$$\rho = \frac{KH}{L}R \tag{1}$$

$$\sigma = \frac{1}{\rho} = \frac{L}{RKH} \tag{2}$$

where L, K and H are the length, width and thickness of measured sample, respectively, ρ is the resistivity and R is the resistance measured by the DC four-point probe.

2.3. X-ray microscope

An Xradia nanoXCT-S100, full-field transmission X-ray microscope (TXM) utilizing the U7A beamline was used to carry out element-specific 3D imaging at the National Synchrotron Radiation Laboratory. This system based on a synchrotron X-ray source, uses elliptical capillary condensers coupled with zone plate optics to perform absorption contrast imaging from 7 to 11 keV. The details of the schematic experimental setup of this X-ray microscope is described elsewhere [25]. Images of samples were acquired at tilt angles ranging from −90° to +90° at an interval of 1° and then reconstructed into tomograms composed of cubic voxels with side lengths of 58.3 nm. The tomograms underwent subsequent processing for analysis, which will be described in the next section. In this paper, two different locations in each sample were selected for imaging and reconstruction. The average sizes of five samples are summarized in Table 1.

3. Results and discussion

First, each series of tomograms was segmented using simple thresholding to label the Ni, YSZ, and pore phases. This technique has been validated in a previous work, and the details are described elsewhere [23]. The same segmentation and analysis procedures developed in the previous work mentioned above were applied in this study. Some key parameters were calculated using the analysis method, the results of which were used to characterize the samples' microstructures.

From initial observation of the 2D radiographs, the Ni particles appeared to gradually agglomerate with increasing numbers of thermal cycles. When the Ni-YSZ anode sample was not treated by thermal cycling, most of the Ni phase appeared as discrete, separated particles, as shown in Fig. 1a. After six thermal cycles, the Ni particles appeared to have migrated toward each other, as observed by the formation of large, highly absorbing features (Fig. 1b). Fig. 1c and d shows 3D renderings of reconstructions before thermal cycling and after six thermal cycles, respectively, where the red label indicates the Ni phase.

The reconstruction results were further analyzed to assess the evolution of the average sizes of Ni particles. Following the Brunauer–Emmett–Teller (BET) formula $d = 6VS^{-1}$ [10], where d, V, and S are average size, volume and surface area, respectively, the mean diameter of each phase after thermal cycling for various times could be estimated as shown in Fig. 2. Clearly, the average diameter