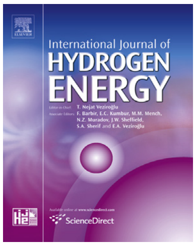
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 10833–10843

Available online at www.sciencedirect.com

ScienceDirect

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



Effects of nickel oxide impurities on the microstructure and electrical properties of a nickel–yttria-stabilized zirconia anode

Yong Guan [a], *Xiaolei Dong* [b], *Lei Zhang* [b], *Gang Liu* [a], *Zhiting Liang* [a], *Shan Chen* [a], *Liang Chen* [a], *Xiaobo Zhang* [a], *Ying Xiong* [a], *Haiqian Wang* [b,**], *Yangchao Tian* [a,*]

[a] *National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, People's Republic of China*

[b] *Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*

ARTICLE INFO

Article history:
Received 22 December 2015
Received in revised form
6 April 2016
Accepted 15 April 2016
Available online 17 May 2016

Keywords:
Solid oxide fuel cell
Nano-computed tomography
Impurity
NiO powder

ABSTRACT

Understanding the impact of raw materials on electrode microstructures is important for improving the electrical performance of fuel cells. In this study, two similar NiO powders with different amounts of impurities were used to prepare an anode support for Ni–yttria-stabilized zirconia (Ni-YSZ) anodes. The anodes fabricated with high-purity NiO and with commercial grade NiO with a high impurity concentration are denoted anode-1 and anode-2, respectively. The nano-CT technique was used to reconstruct the anode support and AFL microstructures and to calculate several structural parameters, such as the triple phase boundary, Ni and YSZ particle sizes and pore sizes. In addition, the electrical properties of the cells fabricated with anode-1 and anode-2 were measured and compared. The electrical performance of the cell fabricated with anode-1 is higher than that of the cell fabricated with anode-2 because the anode-1 microstructure is more suitable for this application. Further investigations indicate that the differences in the microstructures and electrical properties of anode-1 and anode-2 are primarily due to anode-2 over-sintering. The anode-2 sintering temperature is lower than the anode-1 sintering temperature due to MgO impurities introduced by the anode-2 raw material, which results in the observed over-sintering phenomenon. When anode-2 is sintered at a lower temperature, its microstructure and electrical performance is similar to that of anode-1.

Introduction

A solid oxide fuel cell (SOFC) is a highly efficient device for transforming the chemical energy of various fuels directly into electricity. These fuel cells exhibit fuel flexibility and have low emissions. An SOFC essentially consists of two porous electrodes separated by a dense electrolyte. The porous electrodes exhibit electrical conductivity and preferably ionic conductivity at the SOFC operating temperature.

---

* *Corresponding author.*

** *Corresponding author.*

E-mail addresses: hqwang@ustc.edu.cn (H. Wang), ychtian@ustc.edu.cn (Y. Tian).

http://dx.doi.org/10.1016/j.ijhydene.2016.04.105

One typical SOFC design, the anode-supported design, has received much attention due to its many advantages, such as low ohmic and activation polarization, high mechanical strength, a larger reaction zone and lower operating temperatures [1–5]. Nickel–yttria-stabilized zirconia (Ni–YSZ) cermet is the most widely used SOFC anode material due to its good electrocatalytic properties and low cost [6]. The anode support thickness in the anode-supported design is typically greater than 0.5 mm. During the burnout process, organic pore formers are employed to produce large additional pores that form continuous gas diffusion paths [7]. However, these large pores reduce the triple phase boundary (TPB) length of the anode. To improve the ceramic anode performance, an anode functional layer (AFL) containing fine particles is placed between the porous anode and dense electrolyte to increase the TPB length and reduce the interfacial polarization losses [8–10]. Previous studies indicated that the AFL microstructure and composition can affect the electrochemical performance of the entire anode [9,11]. The AFL and anode support have different microstructures and morphologies tuned to their specific roles in the anode. It had reported that during co-sintering process the mismatch of the shrinkage or stress between the different layers may result in serious problems such as cracks in the half-cells. Thus the introduction of AFL may lead to similar issues. Laurencin et al. investigated the interfacial interactions between the AFL and anode support during Ni-YSZ reoxidation and found that a high compressive stress is produced in the AFL layer when it is reoxidized, which might cause delamination at the AFL-anode support interface [12]. Therefore, the anode support might influence the AFL microstructure during co-firing.

To further lower the high cost of SOFCs for large-scale production, industrial grade raw materials, which inevitably contain impurities, should be employed to prepare the anodes. Several studies have reported that impurities in electrodes negatively affect the electrode performance. In particular, the impurity phase can migrate to and accumulate at the anode-electrolyte interface, causing serious damage to the YSZ electrolyte [13,14]. Jensen et al. reported that NiO impurities became concentrated in the Ni-YSZ interfacial region, resulting in high resistances at the interface [15]. Oishi et al. studied the effects of impurities on SOFC cathode properties and found that the amount of impurities that could be incorporated into $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ cathodes without affecting their properties varied significantly depending on the element [16]. As mentioned previously, decreasing the cost of the raw materials will help reduce the cost of SOFCs. Therefore, to determine the optimal trade-off between the cost and performance, the effects of raw material impurities on the electrode performance must be investigated further. However, few studies have investigated this problem at the 3D microscale level.

Recently, the 3D microstructures of SOFC electrodes were studied by focused ion beam/scanning electron microscopy (FIB/SEM) [17–21] and X-ray nano-computed tomography (nano-CT) [22–32]. Currently, the spatial resolution of FIB/SEM is 10 nm [33], whereas that of transmission X-ray microscopy is 15–20 nm [34,35]. Nelson et al. used nano-CT and FIB/SEM to reconstruct the 3D microstructure of an SOFC cathode at spatial resolutions of 45 nm and 10 nm, respectively. The microstructural parameters of the cathode were quantitatively calculated from the data obtained by these two techniques. A comparison of the calculated parameters indicated that nano-CT is a viable quantitative characterization technique for investigating SOFC cathode microstructures [33]. Moreover, nano-CT is non-destructive, i.e., cross-sectional imaging can be performed without cutting the sample, is chemically and elementally sensitive and has potential for in situ studies of real samples. In other work, Cronin et al. reconstructed an entire SOFC using full-field transmission X-ray microscopy [30], and Shearing el al. studied the microstructural evolution of the cathode during heating and in situ operation using synchrotron X-ray nano-CT [36].

In this study, the effects of raw material impurities on the Ni-YSZ anode support and AFL microstructures in an anode-supported SOFC during co-firing were determined by nano-CT measurements. The 3D structural parameters of the anode support and AFL were quantitatively calculated based on 3D reconstructions. The electrochemical properties of anode-supported SOFCs fabricated from the studied anodes were also measured, and the results are discussed in terms of the microstructural changes.

Materials and methods

Sample preparation and cell tests

In this study, two different NiO powders were used to fabricate anode supports. The key properties of these NiO powders are listed in Table 1. As shown in Fig. 1, the average particle size of the NiO-1 powder is slightly smaller than that of NiO-2. Although the NiO-1 and NiO-2 powders have different particle sizes and specific surface areas, they have a similar median particle size (0.9 μm for NiO-1 vs 1 μm for NiO-2) after sintering. In addition, these NiO powders contain different amounts of impurities, which were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and are given in Table 2. The NiO-1 powder was prepared by decomposing thermally pure $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (Sinopharm Chemical Reagent Ltd., Shanghai, China) at 600 °C. NiO-2 is an industrial grade raw material containing some impurities.

The cell preparation process was described in detail in a previous report [37] and is briefly summarized in this paper. The AFL was prepared by a suspension spray method. Specifically, 8YSZ (Tosh, TZ-8Y, Japan) and fine NiO (J.T. Baker, USA) powders (YSZ:NiO = 50:50 vol.%) were mixed and ball-milled to obtain a slurry, which was then sprayed onto a polythene membrane to form a green AFL layer. The anode

Table 1 – Properties of the studied NiO powders.

Sources	Abbr.	Color	Average grain size (nm)	BET surface area ($m^2 \cdot g^{-1}$)
Sinopharm Chemical Reagent Ltd.	NiO-1	Gray–green	93	3.769
Jinchuan Ltd.	NiO-2	Gray–green	110	5.939