Solid State Ionics 180 (2009) 1580–1586

Contents lists available at ScienceDirect

Solid State Ionics

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

Understanding of redox behavior of Ni–YSZ cermets

Yun Zhang [a,b,c], Bin Liu [a,b,c], Baofeng Tu [a,b], Yonglai Dong [a,b], Mojie Cheng [a,b,*]

[a] Laboratory of Fuel Cell, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
[b] Dalian National Laboratory for Clean Energy, Dalian 116023, China
[c] Graduate Schools of the Chinese Academy of Sciences, Beijing, 100039, China

ARTICLE INFO

Article history:
Received 16 July 2009
Received in revised form 14 October 2009
Accepted 16 October 2009

Keywords:
SOFC
Ni–YSZ cermet
Redox
TPO
TPR
SEM

ABSTRACT

The oxidation of Ni–YSZ cermet as well the reduction of re-oxidized Ni–YSZ cermet was investigated by using temperature-programmed oxidation (TPO), temperature-programmed reduction (TPR) and scanning electron microscope (SEM). The scanning electron microscope (SEM) photographs and temperature-programmed reduction (TPR) profiles indicated that the sintering of smaller nickel oxide crystallites to larger aggregates occurred concurrently with the formation of smaller nickel oxide crystallites from the oxidation of nickel at 800 °C, and the sintering of smaller nickel oxide crystallites at 600 °C was slower than that at 800 °C. The SEM results showed that each Ni particle was separated into a lot of smaller NiO particles during oxidation. The TPO profiles showed that two kinds of nickel particles exist in the anode reduced at 800 and 600 °C, one with high activity towards oxidation for the nickel crystallites directly from reduction, and another one with low activity towards oxidation for the sintered nickel particles. The Ni–YSZ anodes reduced at higher temperature showed higher re-oxidation temperature than the one reduced at lower temperature because of the accelerated passivating and sintering of the smaller nickel particles at higher temperature. The re-oxidation profiles were almost unchanged during redox cycling at 600 °C, whereas the re-oxidation peak temperature decreased during redox cycling at 800 °C, indicating that the primary nickel grains split to smaller ones upon cyclic reduction at higher temperature.

1. Introduction

Intermediate temperature solid oxide fuel cells (IT-SOFCs) are devices which can convert the chemical energy of fuel into electrical energy cleanly and with a high electrical efficiency. Most of the state-of-the-art SOFC systems for mobile and stationary applications adopt an anode supported design because of its lower polarization losses, lower fabrication cost and sufficient mechanical properties to support the fuel cell in a reducing atmosphere. The prevalent anode materials are still fabricated from NiO–YSZ ceramic composite due to its excellent electrocatalytic activity, high conductivity and stability and good compatibility with the yttria stabilized zirconia (YSZ) electrolyte [1–11].

To achieve a high electrochemical performance, the Ni–YSZ anode should have a long triple phase boundary (TPB , where reactant gas, electrolyte and electrode meet) for electrochemical reactions, a high porosity for mass transfer and a high electrical conductivity for current collection. It is proverbial that TPB, which resulted from the reduction of NiO–YSZ ceramic, has a great influence on the cell performance [12–18]. The porosity can be partially formed after the reduction of NiO to Ni, and the electric and ionic paths are provided respectively by the Ni and YSZ networks [19].

The nickel oxide in anode is generally reduced to nickel prior to the first operation. Once exposed to air under the cell operating temperature, the Ni–YSZ cermet anode can be oxidized. It is known that redox of the anode is detrimental to the cell performance [20–31]. When startup, shutdown, leakage in seal, fuel supply interruption,

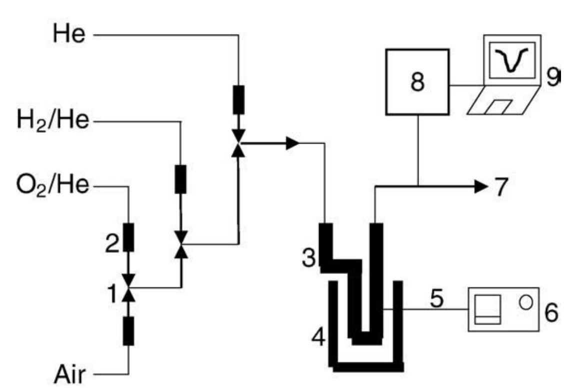

Fig. 1. TPO experimental setup. 1—Three-way valve; 2—Mass flow controller; 3—U-type quartz reactor; 4—Electric furnace; 5— Thermal couple; 6—Temperature controller; 7—Exhaust gas; 8—Mass spectrograph; 9—Recorder.

* Corresponding author. Laboratory of Fuel Cell, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.
E-mail address: mjcheng@dicp.ac.cn (M. Cheng).

0167-2738/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ssi.2009.10.011

emergency stop or other status occurs, nickel might be re-oxidized to nickel oxide. A re-oxidized cell must be reduced prior to operation. Thus, cyclic redox of the anode is likely to occur during SOFC operations. In theory, the bulk volume of a fully dense NiO sample should contract by 40.9% upon reduction and should expand by 69.2% upon oxidation, but a porous Ni–YSZ anode will not suffer such a tremendous volume change due to the existence of the pores. However, any volume change of anode, especially a large volume expansion during re-oxidation, may have an influence on the integrity of interface and lead to degradation of the cell performance, even cause some destructive changes to the thin electrolyte film. So the thermo-mechanical property as well as electrochemical performances of anode supported solid oxide fuel cell is of paramount importance [4]. It is well known that the performance and stability of Ni–YSZ cermet anodes are critically dependent on the phase distribution and microstructure of the cermets. The impact of redox cycling on the microstructural changes of Ni–YSZ and degradation of SOFC was the primary point for carrying out our investigations.

In a previous research, we investigated the redox of anode by using temperature-programmed reduction (TPR) technique, which depicted the different reduction behaviors of anodes oxidized under various conditions [2]. The present work is to investigate the different oxidation behaviors of Ni–YSZ during redox cycling. Temperature-programmed oxidation technique (TPO) in combination with TPR is applied to

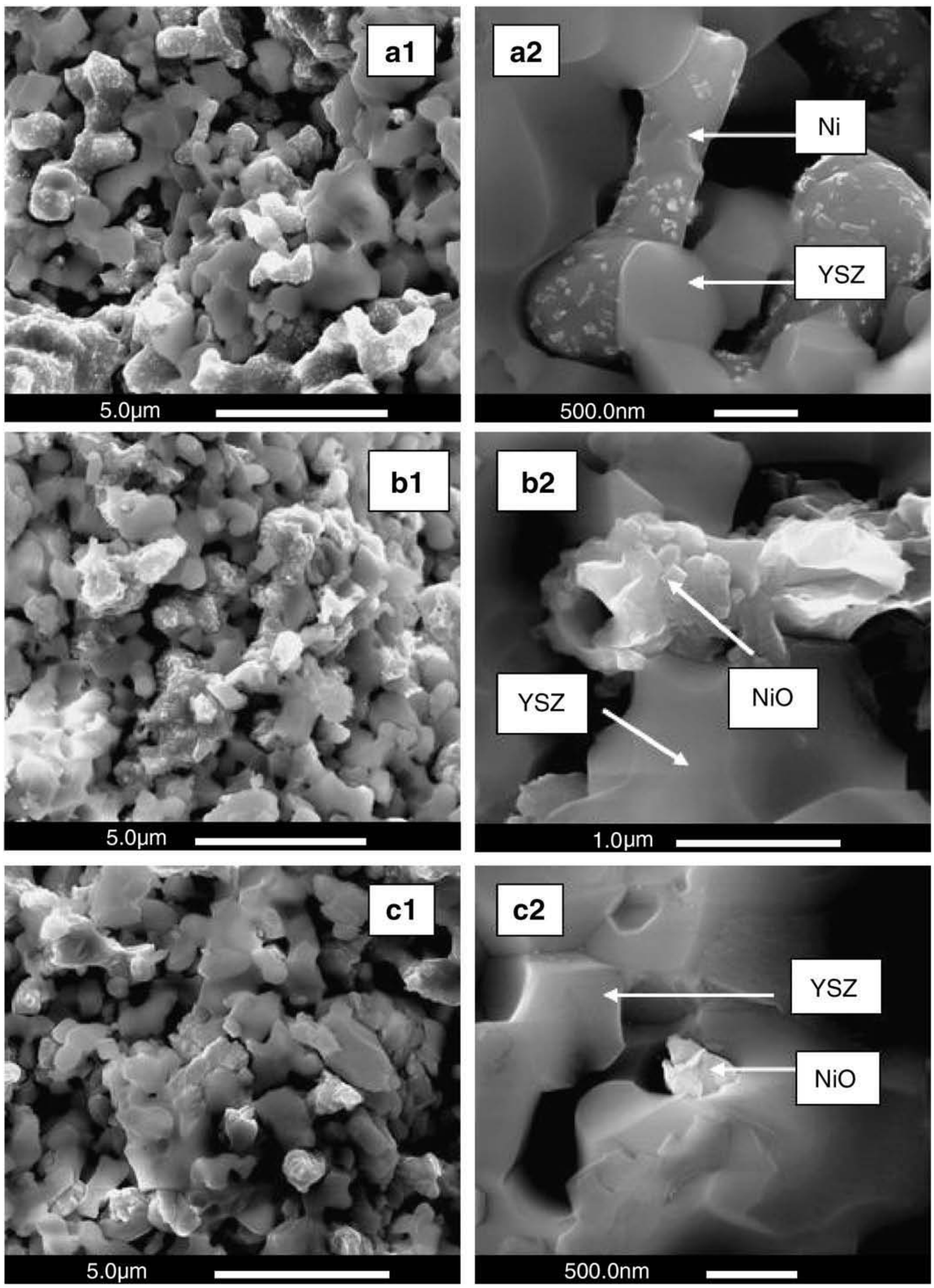

Fig. 2. SEM micrographs of the first reduced anodes (a1) (a2) and the first reduced anodes re-oxidized at 800 °C for 0.5 min (b1) (b2), 1 min (c1) (c2), 2 min (d1) (d2), 20 min (e1) (e2) (e3), and 150 min (f1) (f2).