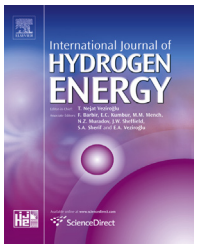
Available online at www.sciencedirect.com

ScienceDirect

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



Ni-YSZ cermets for solid oxide fuel cell anodes via two-step firing

A. Davarpanah [a], A.A. Yaremchenko [a,*], D.P. Fagg [b], J.R. Frade [a]

[a] Department of Materials and Ceramic Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
[b] TEMA-NRD, Mechanical Engineering Department, University of Aveiro, 3810-193 Aveiro, Portugal

ARTICLE INFO

Article history:
Received 28 May 2014
Received in revised form
10 July 2014
Accepted 11 July 2014
Available online 5 August 2014

Keywords:
Ni-YSZ
Composite
Cermet
SOFC anode
Electrical conductivity
Two-step sintering

ABSTRACT

The electrochemical performance and dimensional stability of Ni-YSZ cermets, conventionally used as solid oxide fuel cell anodes, depend strongly on their microstructure and therefore fabrication conditions. This work was focused on the assessment of a less common two-step firing procedure for fabrication of Ni-YSZ cermets with comparatively low nickel fraction of 30 vol.%. The impact of different firing parameters including peak temperature (1623–1723 K), heating/cooling rate (4–10 K/min), and isothermal treatment temperature (1473–1573 K) and time (2–8 h), on the porosity and electrical conductivity of cermets was assessed employing Taguchi experimental planning. The applied procedure yielded Ni-YSZ composites with porosity 26–35% and electrical conductivity ranging from 170 to 420 S/cm at 873–1173 K in 10%H_2–N_2 atmosphere. Microstructural studies indicated that the conductivity is determined mainly by Ni particle size distribution. Analysis of results suggests that, for the studied range of sintering parameters, a higher peak temperature and ramp rate are favorable for the improvement of conductivity, whereas isothermal dwell temperature and time have a rather minor effect on the conductivity level.

Introduction

Porous Ni-YSZ (yttria-stabilized zirconia) composites demonstrate high electronic conductivity, reasonable ionic conductivity and high electrocatalytic activity for hydrogen oxidation and, thus, remain benchmark anode materials for solid oxide fuel cells (as well as cathode materials for solid oxide electrolysis cells) [1–6]. In these cermets, the interconnecting Ni network acts as a catalyst for the electrochemical oxidation of hydrogen and provides a conduction path for electrons, while the interconnecting YSZ network provides a path for oxide-ions and thermal expansion coefficient compatibility of the cermet anode with the solid electrolyte. It is generally accepted that the electrochemical activity of Ni-based anodes depends strongly on the length of triple phase boundary (TPB) between the gas phase, the ionic conductor and the electronic conductor [1,2,7,8]. Conventional Ni-YSZ anodes may either be supported by the electrolyte or, inversely, support the thin-film solid electrolyte; in the latter case, the mechanical properties of the cermet are crucial for the overall mechanical durability of the cell.

The most commonly used method for the fabrication of Ni-YSZ cermets is based on sintering of a mixture of NiO and YSZ

* *Corresponding author*. Tel.: +351 234 370235; fax: +351 234 370204.
E-mail address: ayaremchenko@ua.pt (A.A. Yaremchenko).
http://dx.doi.org/10.1016/j.ijhydene.2014.07.053

powders in air at high temperatures [5,6,9–12]. Commercial NiO and YSZ powders are mixed in appropriate proportions and homogenized by milling. For better control of microstructure, the procedure may include coarsening of individual powders and/or their mixture by thermal pre-treatment to give desired particle sizes and size distribution [5,6,10]. The prepared NiO-YSZ mixture is sintered (or co-sintered with green solid electrolyte layer) in air at 1573–1773 K. After applying the cathode material to the opposite side of the electrolyte, nickel oxide phase is reduced to metallic nickel by exposure to H_2 or other fuels at the fuel cell operating temperature (≥1073 K). For a thin NiO-YSZ layer (~100 μm), it takes only minutes to complete the NiO reduction at 1273 K [3]. Sintering in air at elevated temperature results in significant growth of both the NiO and YSZ particles accompanied with some increase in porosity; the decrease of solid phase volume on NiO → Ni reduction further increases the volume fraction of pores. Traditionally, the porosity of Ni-YSZ cermets is above 30%. The pore fraction and morphology can be additionally controlled by adding pore-formers such as carbon fiber, graphite and starch. The minimum fraction of Ni required to obtain high electronic conductivity corresponds typically to ~30 vol.%, in accordance with percolation theory [1–7,13–16]. In practice, this value strongly depends on the porosity, pore size, and the particle size distribution of the anode components and their spatial distributions [5,15,16]. A typical range of conductivity for an anode support (50 wt.% Ni, ~40% porosity) operating at 1273 K is 300–400 S/cm [4,17].

Often-cited disadvantages of Ni-YSZ cermets include, among others, the lack of redox tolerance and resulting microstructural instability [1–7,15]. Agglomeration and coarsening of Ni particles under prolonged operation, probably due to poor wettability of YSZ by Ni, result in a shortening of the TPB length and partial cut-off of conduction paths. Re-oxidation of nickel, which may happen during shut down procedures, or due to oxygen leaks through imperfect seals, or as a result of too high fuel utilization rising oxygen activity in a fuel/products gas mixture above Ni/NiO stability boundary, is accompanied with volume expansion that creates internal stresses in the porous anode. Redox cycling between Ni and NiO and corresponding expansion/contraction cycles eventually cause irreversible microstructural alterations, degradation of performance and, in extreme cases, fracture of the cell.

The performance of Ni-YSZ anode in terms of minimal electrode polarization losses and minimal degradation during operation depends strongly on its microstructure and, therefore, the adopted fabrication procedure. It was observed that cermets with smaller Ni particles exhibit better redox dimensional stability [4,18,19]. Finer microstructures with high surface area fabricated at lower temperatures are also desirable for improvement of TPB length and electrochemical performance [7,19,20]. On the other hand, sufficiently high firing temperature is preferred to ensure a strong YSZ network with appropriate mechanical properties and the ability to resist volume changes on NiO ↔ Ni cycling [4,21]. Thus, the optimization of fabrication/sintering conditions is critical to ensure the appropriate combination of electrical, electrochemical and mechanical properties and overall redox tolerance. Reasonably, reducing the Ni volume fraction is also expected to have a positive effect on redox dimensional stability as long as percolation is maintained to ensure high electrical conductivity and the resulting microstructures are suitable to preserve electrocatalytic activity.

The present work was focused on optimization of Ni-YSZ cermet fabrication procedure by the employment of a two-step sintering scheme. Two-step sintering was first proposed by Chen and Wang in 2000 as a method to produce nanostructured or submicron ceramics with high densification at reasonably low temperatures, due to difference in activation energy of grain growth and densification [22]. It is based on two main steps in the sintering schedule including one peak temperature and subsequent dwell at lower temperature. The first step is performed on heating at sufficiently high rate and up to a relatively high temperature in order to activate sintering by approaching the highest shrinkage rate, without significant grain growth, while the second step promotes densification with limited grain growth. The method was previously employed for the fabrication of dense ceramics such as alumina, strontium titanate, and zirconia- and ceria-based ceramic materials ([23–26] and references therein). The decrease in grain size of 2-step sintered YSZ electrolytes [26] and expected enhancement of mechanical properties suggest a similar approach for Ni/YSZ cermets, mainly if one seeks co-firing. Thus, the goal of this work was to assess the impact of different parameters (including peak temperature, time and temperature of isothermal dwell, and heating/cooling rate) during the firing of NiO-YSZ composites on the final porosity and electrical conductivity of Ni-YSZ cermets containing comparatively low nickel fraction (30 vol.% of total solid). The detailed study of this multivariable process would imply a considerable number of time-consuming experiments. In this work, the Taguchi method [27] was used to optimize the experimental plan and to minimize the number of experiments required to assess the contributions of different factors.

Experimental

Composite samples were prepared using commercial powders of YSZ ($(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$, Tosoh, crystallite size ~200–300 nm) and NiO (BDH Chemicals, crystallite size

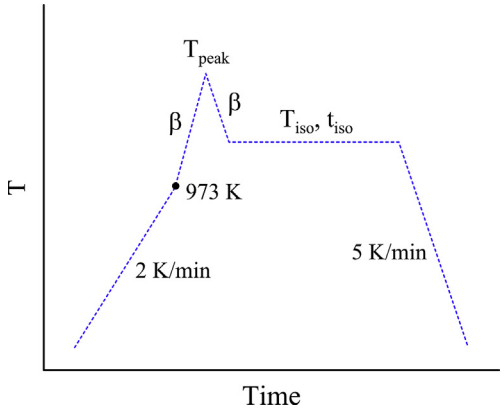


Fig. 1 – General scheme of two-step sintering procedure used in this work.