Solid State Ionics 222-223 (2012) 38–46

Contents lists available at SciVerse ScienceDirect

Solid State Ionics

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

Electrical conductivity of Ni–YSZ composites: Variants and redox cycling

M.H. Pihlatie [a,b,*], A. Kaiser [a], M.B. Mogensen [a]

[a] Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, POB 46, DK-4000 Roskilde, Denmark
[b] VTT Technical Research Centre of Finland, POB 1000, FI-02044, Finland

ARTICLE INFO

Article history:
Received 12 October 2011
Received in revised form 14 May 2012
Accepted 21 June 2012
Available online 24 July 2012

Keywords:
SOFC
Ni–YSZ
Electrical conductivity
Redox stability
Ni particle growth
Master sintering curve

ABSTRACT

Short-term changes in the electrical conductivity of different Ni–YSZ composites (cermets) were measured by an in-situ 4-point DC technique. The isothermal reduction was carried out in dry, humidified or wet hydrogen at temperatures from 600 to 850 °C. The cermets reduced at 600 °C showed a stable conductivity of about 1100 S/cm, which increased to an enhanced ~2000 S/cm upon re-oxidation and subsequent re-reduction cycling at the same temperature. At 850 °C, a rapid initial conductivity loss was observed; upon re-reduction after the re-oxidation both the conductivity and its loss rate were largely the same as in the initial reduction. The presence of steam had an accelerating effect on the conductivity loss at 850 °C. In addition to cermets with a typical microstructure, different modified microstructures and compositions were tested. In the modified cermets, Al, Mg, and Ce were used as Ni dopants alongside with undoped Ni. Scanning electron microscopy of cermets reduced in different conditions showed increasing particle size and loss of metal-to-metal percolation in the samples reduced at higher temperatures, and a very fine microstructure in the high conductivity sample re-oxidised at 600 °C. Short-term conductivity changes due to microstructural changes in both the standard and modified cermets with different Ni doping were compared by re-oxidation at 600 °C and subsequent thermal excursions up to 1000 °C by normalising the conductivity to a constant temperature. Modified cermets show reduced conductivity loss on both isothermal heating and high temperature ramping. Most stable cermets were the ones with undoped NiO and modified microstructure, as well as modified microstructures using Ti and Mg, or Ce secondary oxide coatings. Master sintering curve approach was successfully implemented to analyse the conductivity loss data. The MSC analysis yielded apparent activation energies for Ni sintering within the composite of 375 kJ/mol when heated in dry H_2 and 440 kJ/mol when under wet H_2.

1. Introduction

Ceramic–metal composites (cermets) of Ni and YSZ prepared by wet ceramic processing and high temperature sintering are commonly used as structural supports and anodes in solid oxide fuel cells (SOFC). While the mean particle size of the grains embedded in such porous composites is typically in the order of 1–3 micrometres, the actual particle size distribution of both Ni and YSZ ranges from tens or hundreds of nanometres to several micrometres. It is well known that the particle size of the Ni grains increases with time under operation at high temperature [1–3]. The Ni grains need to be sufficiently connected to each other during operation so that adequate electrical conductivity for current collection can be sustained. Electrical conductivity is a good in-situ measure to monitor and quantify the microstructural changes in the cermet; particle growth of Ni leads to loss of percolation and reduces the electrical conductivity of the cermet [4,5]. The growth of the Ni grains results in decrease of the electrical conductivity through loss of inter-particle percolation; the rate of the conductivity loss depends on the temperature and humidity of operation so that increasing temperature activates the particle growth process, and humidity will additionally increase the conductivity loss at high temperatures [6,7]. A large portion of the short-term changes in the conductivity occurs fast, within a few tens of hours after the initial reduction of the cermet; at high temperatures a significant fraction of the maximum attainable conductivity of the cermets can disappear nearly instantaneously in just a few minutes [7]. In the longer term the electrical properties finally reach a plateau depending on several factors, most importantly cermet microstructure, composition and the operating conditions (temperature and humidity).

The effects of microstructure and composition of a Ni–YSZ cermet on the dimensional behaviour during cyclic reduction and re-oxidation (redox cycling) were recently reported [8]; furthermore, the same composites have also been investigated for their mechanical properties [9]. The present paper continues by electrical characterisation of these composites in redox cycling experiments. The changes in the electrical properties of the cermet were determined depending on time, temperature and the humidity using an in-situ DC conductivity measurement. The changes in the composite microstructure due to

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* Corresponding author at: VTT Technical Research Centre of Finland, POB 1000, FI-02044, Finland. Tel.: +358 400 430395; fax: +358 20 7227048.
E-mail addresses: mikko.pihlatie@vtt.fi, mikko.pihlatie@iki.fi (M.H. Pihlatie).

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doi:10.1016/j.ssi.2012.06.021

low and intermediate temperature redox cycling were examined by scanning electron microscopy.

2. Experimental

Microcomposites of Ni and YSZ were used in the experiments. The samples tested were of either a typical microstructure of anode supports for SOFC (the baseline sample), or of a modified microstructure based on the usage of powders with different particle size distributions in both YSZ and NiO. The modifications included also coating of pre-milled Ni/NiO with secondary oxides of Al, Mg, Ce or Ti. Additional information on the ceramic processing of the samples as well as results from thermal analysis experiments and mechanical tests with the same composites can be found in Refs. [8,9].

To prepare the tested samples, rectangular plates of about 6×37 mm^2 were cut from green tapes of 0.5–0.8 mm in thickness. A hole of 3 mm diameter was made in both ends of each sample before sintering at 1300–1400 °C. The naming of the samples is shown in Table 1, where also the sample naming used in Ref. [8] is given; the samples arise from the same slurry, green tape and sintering batches. The additional sample NMT is one with another modified microstructure where both Mg and Ti have been used as dopants in the cermet; Mg was used to coat the NiO whereas TiO_2 precursors were applied on both NiO and YSZ. The total porosities of the samples were determined geometrically by calculating the densities from sample dimensions and weight (a digital calliper and a Mettler Toledo gauge were used), and dividing by the known theoretical solid-phase density of the samples.

The experimental arrangement for the DC conductivity measurements was the same as in Ref. [7]. The $p(O_2)$ was measured using a sensor placed adjacent to the samples, thus observing similar conditions. The effects of redox cycling (i.e., intentional switching between reducing and oxidising gas at high temperature), temperature and humidity on the short-term (up to 100 h) conductivity changes were investigated. The test sequence was always to heat up the as-sintered sample in air to the isothermal test temperature, then flush the test chamber with nitrogen to remove oxygen, and after that to switch to the test atmosphere. Such N_2 flushing was also implemented as intermediate steps in all redox cycles. For testing under "wet" conditions, humidification was done by a small controlled flow of oxygen into the furnace so that the humidity was produced inside the tube; the exact gas composition can be calculated by using the measured $p(O_2)$ value, temperature and the $H_2 + ½O_2 \leftrightarrow H_2O$ thermodynamic equilibrium.

Three different experimental sequences are reported in the following results section:

1) Redox cycling was carried out for a typical baseline sample isothermally at 600 °C in order to compare with results on the same cermet shown for redox cycling at 850 °C in Ref. [7].
2) Isothermal redox cycle and re-oxidation at 850 °C for several composites with modified microstructures and compositions were carried out and the results were compared with the baseline cermet. The following sequence was used: i) the initial reduction took place in dry hydrogen with a hold of roughly 170 h isothermally at 850 °C, followed by a full re-oxidation in air. After this, ii) a second reduction (and a hold of about 67–100 h) was carried out isothermally at 850 °C, now in humidified H_2.
3) Ramping experiments using a constant temperature ramp rate for several composites. This sequence started after completion of step 2) above, with a complete re-oxidation of Ni at 600 °C in air, after which the composites were re-reduced at 600 °C. After this, the samples underwent ramping to 1000 °C (under a ramp rate of 3 K/min), held at 1000 °C a short while, and subsequently cooled down.

Table 1
List of the samples tested, including the details on Ni treatment, sintering, the as-sintered geometrically calculated total porosity, and comment on the microstructure of the sample.

Sample name	Sample name used in reference [*x*]	Ni treatment	Total *p* (%)	Microstructure
N0	C – baseline [8]	NiO	14[a]	Typical
N0/2	–	NiO	14	Typical
N0/3	[7]	NiO	14	Typical
N1	–	NiO	33	Modified
N2	K [8]	NiO	34	Modified
NA	I [8]	$NiO + Al_2O_3$	27	Modified
NM	J [8]	$NiO + MgO$	38	Modified
NC	M [8]	$NiO + CeO_2$	37	Modified
NMT	O [8]	$NiO + MgO + TiO_2$	23	Modified

[a] The open porosity was 12% based on Hg intrusion porosimetry.

The temperature dependency of the electrical conductivity was recorded during the cool-down. By using the measured temperature dependency of the electrical (metallic) conductivity, it was possible to normalise the measured conductivity of each sample during the ramping experiment to a selected value, in this case 850 °C. This procedure makes it possible to monitor the dynamic changes (loss) in conductivity due to Ni particle growth in the course of the ramping sequence, that is, by removing from the signal the changes in conductivity due to the temperature change.

The sinterability of the different NiO powders was studied by uniaxially pressing pellets of the different NiO powder variants, sintering them in air at 1320 °C for 12 h. The different powders investigated were: pre-milled standard 99.9% NiO powder with mean particle size of 1.5 micrometres, pre-milled NiO (1.5 micrometres mean particle size) calcined 2 h at 1100 °C in air, and the pre-milled standard NiO coated with either MgO (calcination at 1100 °C), CeO_2 (calcination at 800 °C), Al_2O_3 (calcination at 1100 °C) or TiO_2 (calcination at 800 °C). The amount of doping was 5 wt.% of dopant oxide in metallic Ni for Mg, Ce and Ti, and 10 wt.% of oxide in metallic Ni for Al. The sintering shrinkage was measured to assess the sintering activity of the powders; the theoretical density of the pellets was calculated from the composition. From weighing the samples and geometrical dimensions, total porosity of the pellets after sintering was determined. Additionally, surface microstructure of the pellets was investigated using a Jeol LVSEM.

Scanning electron microscopy (SEM) was carried out for several samples after testing. The samples were mounted in epoxy, polished and carbon coated. A field emission gun Zeiss Supra 35 SEM equipped with both a lateral and Inlens secondary electron detectors was used for the investigations. Low accelerating voltage (0.7–1 kV) was used for the electrons in order to obtain the charge contrast in the Inlens image, as described in Ref. [10]. The lateral secondary detector was used in parallel to obtain images of the uncharged microstructure. The samples for microscopy were exposed in a tube furnace to a dry mixture of H_2 (9%) and N_2 (91%) to examine the effect of exposure time and temperature on the microstructure.

3. Results

3.1. Conductivity measurements

Results from electrical conductivity measurements are presented in Fig. 1 for the baseline "N0" Ni–YSZ composite at 600 °C in wet H_2 as a function of time since the initial change of the gas to reducing. The $p(O_2)$ measured during the test is also shown. At 600 °C, the initial conductivity is 1200 S/cm and within the tested period the conductivity remains well above 1000 S/cm. The two re-oxidations in air improve the conductivity to initially about 2200–2300 S/cm; the conductivity remained in excess of 2000 S/cm during the tested periods of re-reduction and hold.