



Enhanced mechanical stability of Ni-YSZ scaffold demonstrated by nanoindentation and Electrochemical Impedance Spectroscopy

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HIGHLIGHTS

- Quantification of redox damage by coupling 3D tomography, EIS and nanoindentation.
- Ni infiltrated YSZ scaffolds prevent structure failure during redox cycling.
- Ni agglomeration led to Ni migration observed by FIB-SEM and SEM.
- Temperature impact on YSZ scaffold sintering process has been defined.

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ABSTRACT

The electrochemical performance of Ni-YSZ SOFC anodes can quickly degrade during redox cycling. Mechanical damage at interfaces significantly decreases the number of active triple phase boundaries. This study firstly focuses on the sintering temperature impact on YSZ scaffold mechanical properties. The YSZ scaffold sintered at 1200 °C exhibited 56% porosity, 28.3 GPa elastic modulus and 0.97 GPa hardness and was selected for further redox cycling study. The Ni infiltrated YSZ scaffold operated at 550 °C had an initial stabilized polarisation resistance equal to $0.62 \Omega \text{ cm}^2$ and only degraded to $2.85 \Omega \text{ cm}^2$ after 15 redox cycles. The active triple phase boundary density was evaluated by FIB-SEM tomography, and degraded from $28.54 \mu\text{m}^{-2}$ to $19.36 \mu\text{m}^{-2}$. The YSZ scaffold structure was robust after 15 redox cycles, as there was no observation of the framework fracturing in both SEM and FIB-SEM images, which indicated that the mechanical stability of YSZ scaffold improves the anode stability during redox cycling. Nonetheless, Ni agglomeration could not be prevented within Ni-YSZ scaffolds and this needs further consideration.

1. Introduction

The solid oxide fuel cell (SOFC) is currently one of the most promising energy conversion devices, offering a high operating efficiency with minimal air pollution. Ni-YSZ cermetes are the most commonly used SOFC anode material, offering a combination of relatively low cost and good performance. However, the cermet can degrade when subject to certain operating conditions, such as redox cycling [1]. Many studies have focused on redox cycling impact on conventional Ni-YSZ, the main degradation mechanisms include: Ni-NiO volume changes, Ni agglomeration [2], YSZ framework failure [1,3–7]. The use of Ni infiltrated YSZ scaffolds minimize the degradation impact from Ni volume expansion during redox cycling [8]. The mechanical robustness and initial electrochemical performance enhancement are the key advantages of this electrode architecture compared to the conventional Ni-YSZ, which is prepared from mixtures of NiO-YSZ.

Knowledge of the mechanical properties of Ni-YSZ is fundamental for the cell design of the SOFC. The mechanical properties of conventional Ni-YSZ cermetes have been widely studied with a various range of techniques. The Impulse Excitation Technique (IET) has been used to determine mechanical parameters in thick Ni-YSZ electrodes, 300 μm or above, comparing elastic modulus with porosity, Ni content and sintering temperature [3,9–11]. Empirical relationships between the porosity and elastic modulus of conventional Ni-YSZ has been reported and validated in several studies [11,12]. A comparison of different mechanical properties determined by these experimental techniques has been undertaken [13]. The nanoindentation technique has been developed and is used to study the material indentation response and mechanical properties at nanometric scale [14,15]. Recent work has been focused on using nanoindentation to determine degradation of the mechanical properties of conventional Ni-YSZ thin films during redox cycling. The elastic modulus and hardness degradation during redox

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was caused by YSZ framework failure, which also significantly reduced activated triple phase boundary (aTPB) [1].

The Ni infiltrated YSZ scaffold is made by fabricating a ceramic porous scaffold using conventional forming techniques, such as tape casting, and then impregnating the nickel (II) nitrate ethanol solution. By adding sacrificial pore formers, the pore size, shape and volume of the scaffold structure can be modified [16]. A significant increase in the triple phase boundary (TPB) density in the electrodes is obtained after low temperature sintering [8]. It has also been shown that using YSZ scaffolds with fine grains and pores size (~200 nm each) results in a very good electrochemical performance and stability, resistance increased by only 10% after 100 h of operation [17].

This paper presents a study of the effect of sintering temperature on the mechanical properties of YSZ scaffolds using nanoindentation techniques. The tradeoff between mechanical stability and porosity is considered. The impact of redox cycling on Ni infiltrated YSZ scaffolds was studied by nanoindentation, Electrochemical Impedance Spectroscopy (EIS) and FIB-SEM tomography.

2. Experimental

2.1. Fabrication of YSZ scaffolds

The YSZ scaffolds were prepared by depositing and sintering a YSZ-carbon black slurry on top of a YSZ substrate. YSZ powder (Nexceris, USA, $11.0\text{ m}^2\text{ g}^{-1}$ surface area) and 10 wt% carbon black powder (Alfa Aesar, USA, $75.0\text{ m}^2\text{ g}^{-1}$ surface area, $80\text{--}120\text{ g L}^{-1}$ bulk density) were pre-mixed with 2-propanol (EMSURE[®] ACS) for 24 h in a roll mill. This pre-mixed powder was dried at room temperature and then mixed with terpineol, binder (Hercules ECN-7) and dispersant (Hypermer KD15). A ceramic triple-roll mill was used to homogenise the slurry and eliminate agglomerates above $5\text{ }\mu\text{m}$ in size. The slurry was deposited by tape casting on an 8YSZ electrolyte (Nexceris, USA, $\varnothing = 2\text{ cm}$, $250\text{--}300\text{ }\mu\text{m}$) and fired at 1000°C , 1100°C , 1200°C , 1300°C , 1400°C or 1500°C respectively for 2 h in air. A stage sintering process was used to avoid scaffold peeling off from substrate. The sample was firstly heated up to 500°C with 1°C/min ramping ratio, and hold for 2 h, then heated to corresponding sintering temperature. The final scaffolds had a thickness between 15 and $40\text{ }\mu\text{m}$ with a 2 cm^2 geometric area.

2.2. Ni infiltration

For each infiltration, $2\text{ }\mu\text{L}$ of 2 M nickel (II) nitrate ethanol solution was pipetted into the YSZ scaffold and the cell heated up to 550°C , with 5°C ramping rate, to decompose the nitrate into nickel oxide [8,18–22]. The infiltration and decomposition process was repeated 15 times until the nickel content in the electrode was about 36 wt% with respect to the scaffold as measured by weight difference.

2.3. Redox cycling

Redox cycling was carried out by sequentially exposing the cell to two different gas streams, air and diluted hydrogen (a mixture of 5 vol % H_2 and 95 vol % N_2), both humidified with 3% vol H_2O , with a flush of N_2 in between. The process was carried out at 550°C within a quartz tube furnace. For each redox cycle, the samples were kept in air for 1 h, flushed for 10 min in N_2 and then reduced in H_2 for approximately 4 h until the signal becomes stable, as schematically reproduced in Fig. 1. This procedure, already adopted by Song and Shimura [1,23], rather than mimicking any specific accidental or emergency situation, represents a benchmark scenario for reproducible redox cycling measurements around the typical working condition of an SOFC.

2.4. Characterization procedure

A scanning electron microscope (LEO, Gemini 1525 FEGSEM) was

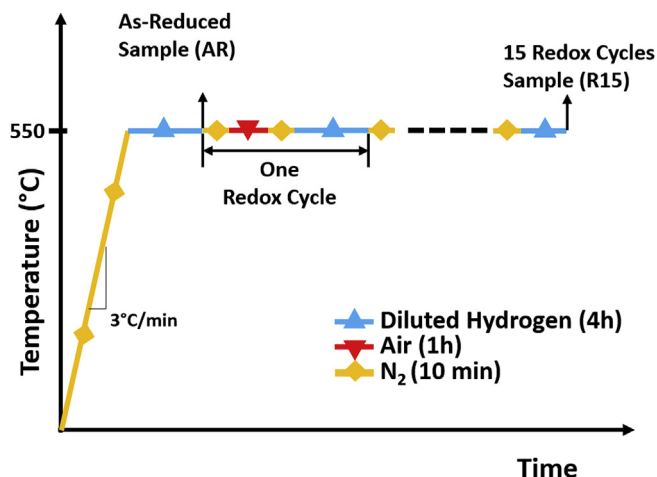


Fig. 1. Representation of redox cycling procedure. Impedance spectra were taken during each reduction process as a function of time, 4 min each measurement.

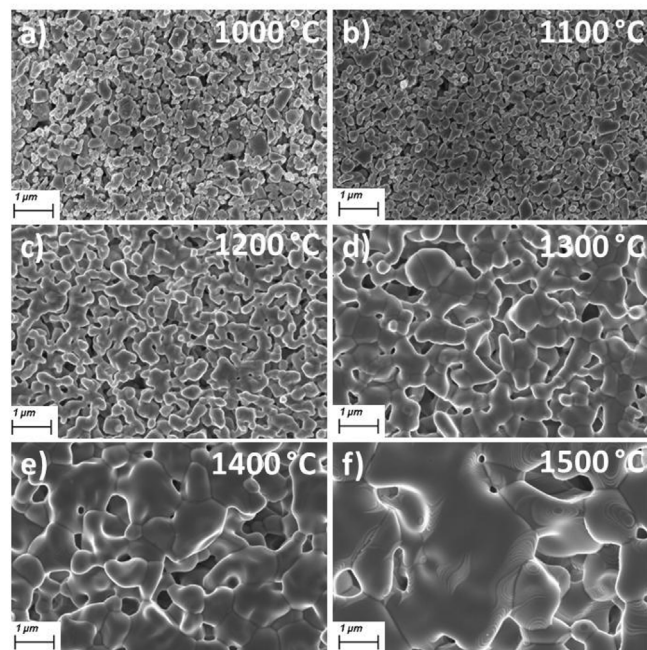


Fig. 2. SEM top views of YSZ scaffolds after 2 h of sintering under different temperature.

used to study the surface and cross-sectional microstructure of samples after coating with a 15 nm layer of Chromium. Observation and quantification of the 3D microstructure of the Ni-YSZ scaffold are facilitated by using FIB-SEM (Auriga Cross Beam, Zeiss), and the series of FIB-SEM images were processed and segmented in Avizo 9.0.0 image processing software (Visualization Science Group, Mérégnac, France) [18,24,25].

The mechanical properties of samples were measured by nanoindentation (NanoTest Platform, Micromaterial, UK) at room temperature [26–28]. Five different loading forces with 20 indentations per applied force (overall 100 indentations) were carried out with a Berkovich diamond tip with a $200\text{ }\mu\text{m}$ interval to obtain statistically representative datasets and avoid outliers due to inhomogeneities. The material response during loading and unloading was recorded.

The elastic modulus, E , and hardness, H , were calculated from the load-depth curves using Oliver–Pharr analysis:

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