



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.

ARTICLE INFO

Keywords:

YSZ scaffolds
Mechanical property
Impedance
Redox cycling
Infiltration

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 cermet is 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 cermets 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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<https://doi.org/10.1016/j.jpowsour.2018.05.075>

Received 26 March 2018; Received in revised form 22 May 2018; Accepted 23 May 2018

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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

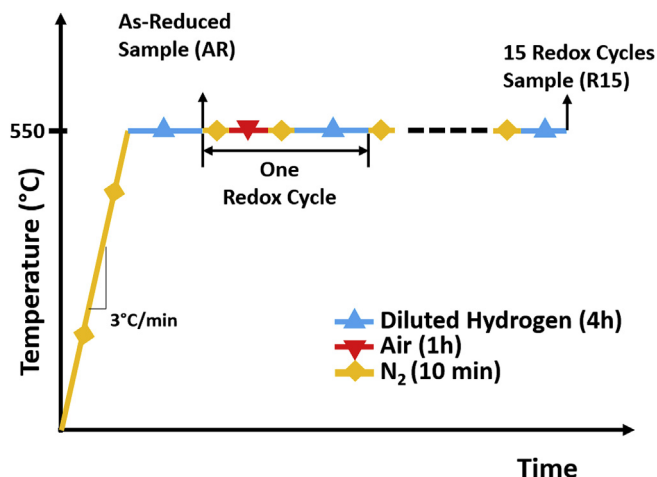


Fig. 1. Representation of redox cycling procedure. Impedance spectra were taken during each reduction process as a function of time, 4 min each measurement.

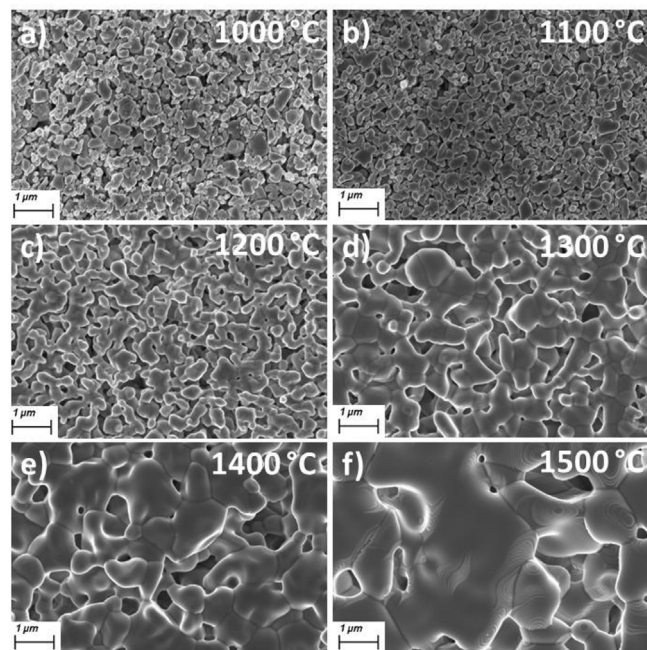


Fig. 2. SEM top views of YSZ scaffolds after 2 h of sintering under different temperature.

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:

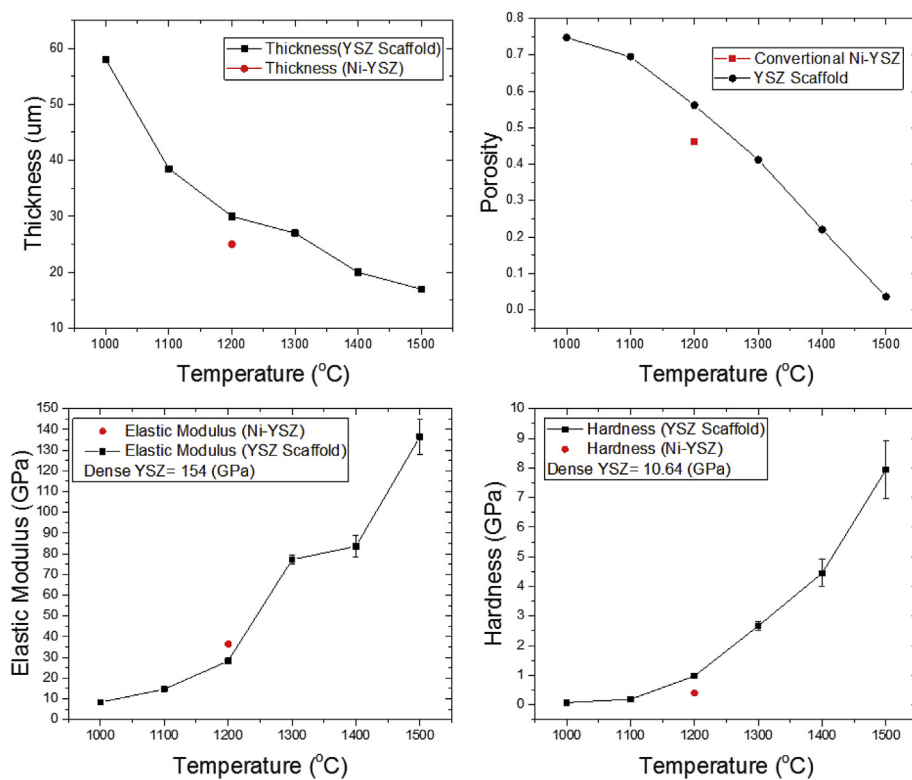


Fig. 3. YSZ thickness (measured by SEM), porosity (based on the weight gain calculation), elastic modulus and hardness of the YSZ scaffold as a function of sintering temperature, the red points represent the measurement results of tape-casted conventional Ni-YSZ sintered in 1200 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

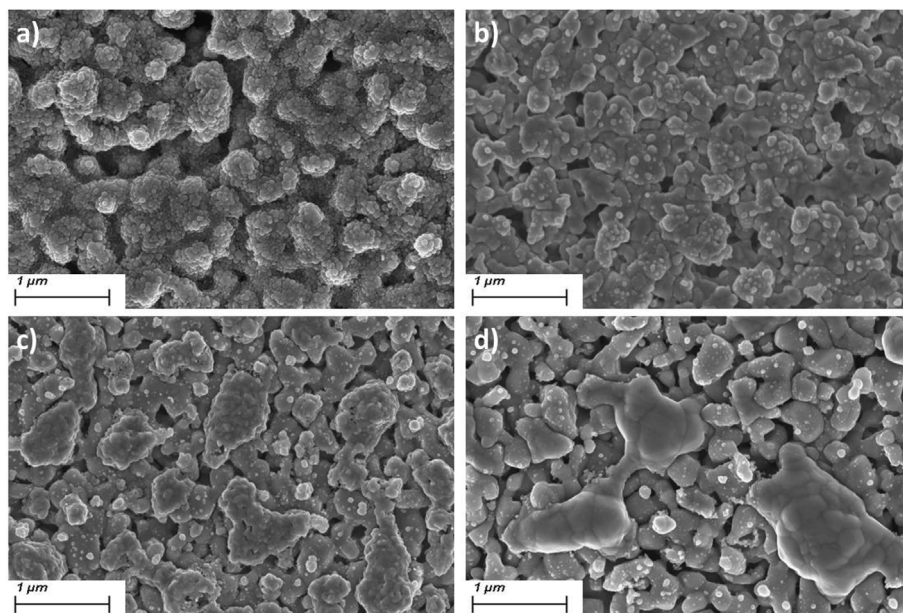


Fig. 4. Top view of YSZ scaffolds after Ni infiltration: a) As- prepared scaffold NiO-YSZ; b) As-reduced scaffold Ni-YSZ; c) Scaffold Ni-YSZ after 5 redox cycles; d) Scaffold Ni-YSZ after 15 redox cycle.

$$E = \frac{1 - \nu^2}{\frac{1}{M} - \frac{1 - \nu_i^2}{E_i}} \quad (1)$$

$$M = \frac{\beta}{2 \left(\frac{dp}{dh} \sqrt{\frac{\pi}{A}} \right)} \quad (2)$$

$$H = \frac{P_{max}}{A} \quad (3)$$

where ν is the Poisson's ratio of the specimen, which is 0.387

approximately [29]. E_i and ν_i are the elastic modulus = 1220 GPa and Poisson's ratio = 0.07 of the diamond indenter, respectively; M is indentation modulus, β is a geometrical correction factor, which is 1.034 for a Berkovich diamond tip [30]; P_{max} is the maximum load applied and A is the contact area between indenter and material, which is, $A = 3\sqrt{3}h_c^2 \tan^2 65.3^\circ = 24.5h_c^2$ for a Berkovich indenter, where h_c is the indentation loading depth.

The selected infiltrated symmetrical cells were heated up in a protective nitrogen atmosphere to 550 °C and then reduced in-situ in the test atmosphere of humidified (3%) diluted hydrogen (a mixture of

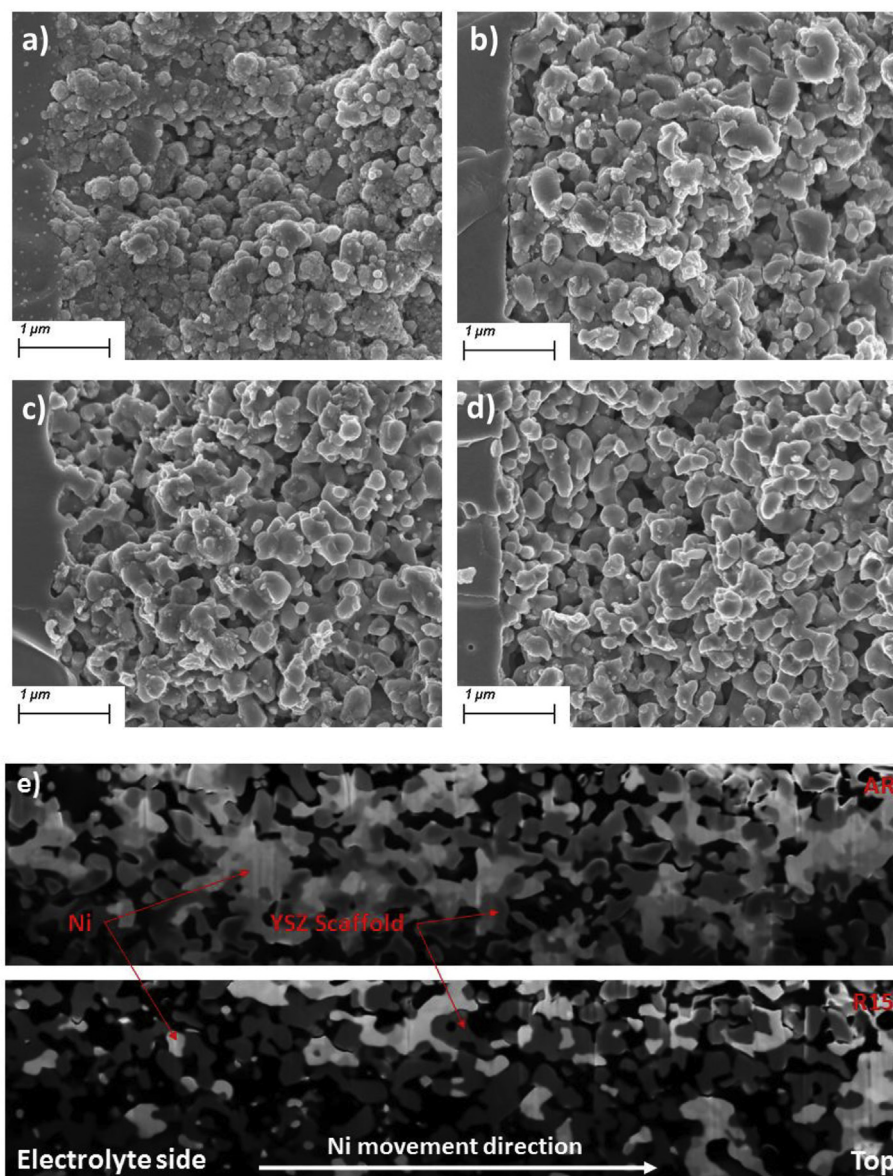


Fig. 5. Cross sectional view of YSZ scaffold after Ni infiltration, near the YSZ substrate: a) As-prepared scaffold NiO-YSZ; b) As-reduced scaffold Ni-YSZ; c) Scaffold Ni-YSZ after 5 redox cycles; d) Scaffold Ni-YSZ after 15 redox cycles; e) FIB-SEM images show the Ni movement after 15 redox cycles, the brighter colour indicate Ni, grey is YSZ, black is pore. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

5 vol % H₂ and 95 vol % N₂). A 20 mV AC amplitude was applied in the two electrode measurement set-up over the frequency range 10^6Hz – 10^{-1}Hz . Pt grids were used as current collector, 100 mesh size (aperture 149 μm) made from wire of 0.06 mm in diameter. The measurement data were fitted to an equivalent electrical circuit by using ZView3.5 (Scribner Associates Incorporated).

3. Results and discussion

3.1. YSZ scaffold microstructure

The YSZ-carbon black slurry tape casts were sintered at different temperature for 2 h. Fig. 2 shows SEM images of the top surfaces of these YSZ scaffolds. As expected, with increasing sintering temperature, the YSZ grain size grew and the grain boundaries improved the connectivity with neighbouring particles. In addition to that, higher sintering temperatures also resulted in thinner thickness and less porosity. A higher porosity and large pore size is necessary for YSZ scaffold, in order to maintain space for later Ni infiltration and gas diffusion

[17,31].

The hardness and elastic modulus, Fig. 3, show an increasing trend with higher sintering temperatures, potentially due to the stronger interconnection between YSZ grains and larger grain size, along with the accompanying decrease in porosity [11]. Nevertheless, for the high sintering temperatures, the standard deviations of measured YSZ scaffolds mechanical properties were much higher, which were attributed to the much coarser surface feature after sintering at higher temperature [1]. By comparison with conventional Ni-YSZ thin films [1,3,8], the YSZ scaffolds at the same sintering temperature show a slightly higher porosity but poorer elastic modulus and greater hardness. The higher elasticity of conventional Ni-YSZ could be due to Ni content within the electrode.

It was proposed that the YSZ scaffolds could improve electrode stability during redox cycling [31]. There are several requirements that the electrode microstructure needs to satisfy, including: a mechanically strong YSZ framework that could prevent structural damage during redox cycles, maintaining a stable ionic conductivity; a sufficient porosity to ensure good gas diffusion, and a stable percolating Ni network

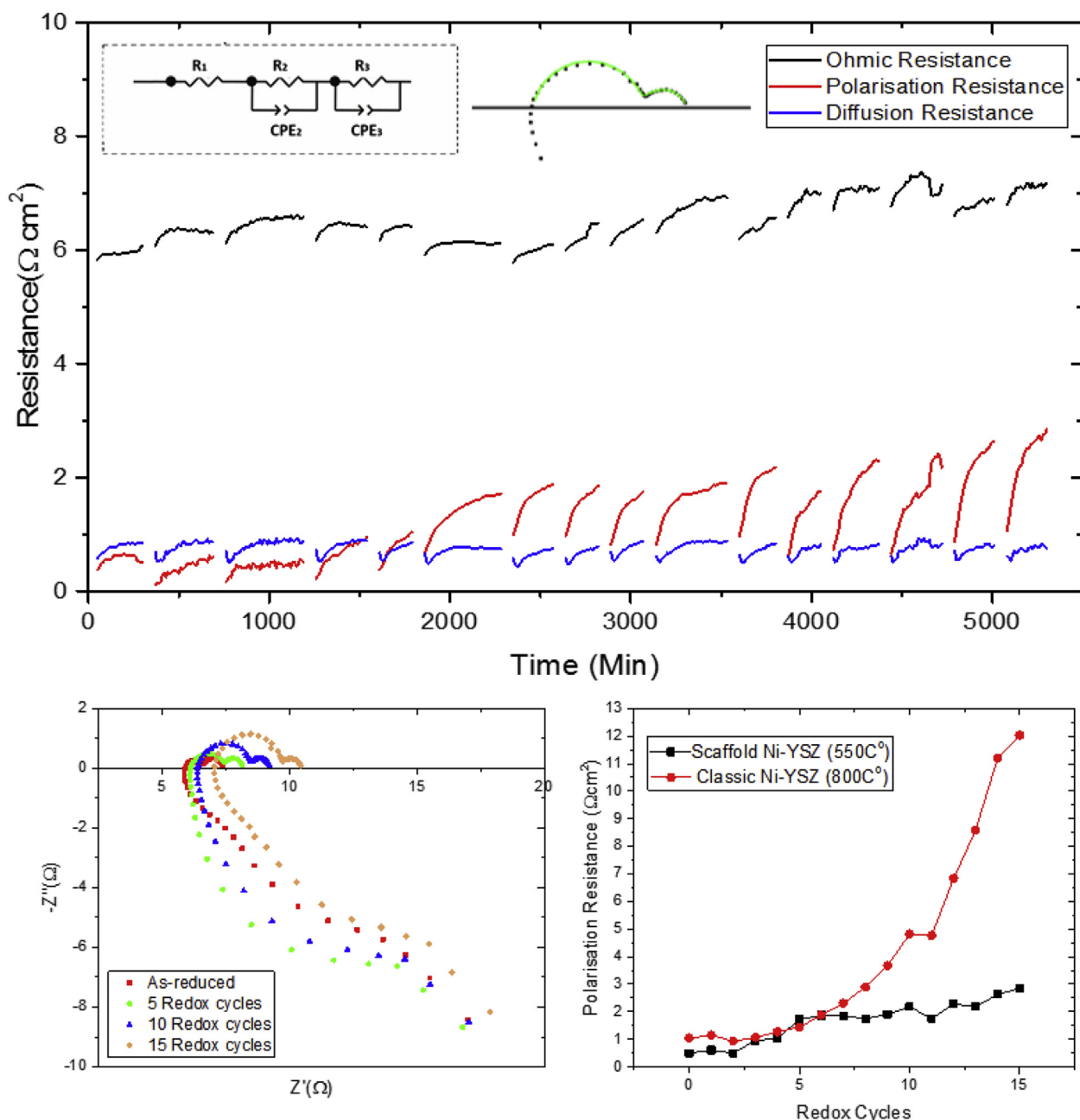


Fig. 6. Ohmic resistance, Polarisation resistance and Diffusion resistance as a function of time during the reduction process of redox cycling from EIS fitting for the Ni-YSZ scaffold. The inset shows the equivalent circuit fitting result. R_1 , R_2 , R_3 represent the high-frequency intercept resistance, intermediate frequency resistance and low-frequency resistance respectively; CPE_2 , CPE_3 represent constant phase elements for the corresponding frequency; Comparison of stabilized polarisation resistance between conventional Ni-YSZ and Ni-YSZ scaffold, measured at 800 °C and 550 °C, respectively.

for electronic transport and catalytic activity. Fig. 2 shows that YSZ scaffolds sintered below 1200 °C exhibit poor contact between YSZ grains, resulting in a low ionic conductivity and poor mechanical properties according to Fig. 3.

Considering the trade-off between the mechanical stability and porosity, the YSZ scaffolds sintered at 1200 °C were used for further study, due a porosity over 55%, a pore size below 400 nm and reasonable mechanical stability compared to conventional Ni-YSZ anode.

3.2. Redox cycling of Ni infiltrated YSZ scaffolds

The ex-situ microstructural characterization was carried out with SEM image analysis. Four different samples, sintered at 1200 °C and infiltrated 15 times, were tested with various numbers of redox cycles.

In-situ electrochemical performance degradation of Ni infiltrated YSZ scaffolds was studied with EIS.

3.2.1. Microstructure changes

Fig. 4 and Fig. 5 show SEM and FIB-SEM images of the scaffold NiO/Ni-YSZ electrode top and cross-sectional views. In the as-prepared sample, the NiO was uniformly distributed on the YSZ surface and inside the scaffold after 2 h heat treatment at 550 °C. For the as-reduced sample, the NiO has fully reduced to Ni, forming isolated droplets on the YSZ surface and percolating within the YSZ framework. The detachment between Ni and YSZ scaffolds can also be observed from both SEM and FIB-SEM cross-sectional images, which was caused by the Ni volume shrinkage during the reduction process. The FIB-SEM images show Ni evenly distributed within the YSZ scaffold in the as-reduced

Table 1

Calculated microstructure parameters from the reconstructed 3D tomographic datasets of Ni-YSZ scaffold with different numbers of redox cycles. The datasets of conventional Ni-YSZ were taken from a previous study [1].

		As-reduced state		After 15 redox cycles	
		Ni-YSZ Scaffold	Conventional Ni-YSZ	Ni-YSZ Scaffold	Conventional Ni-YSZ
aTPB DENSITY (μm^{-2})		28.54	4.63	19.36	2.08
POROSITY		0.42	0.44	0.44	0.53
SURFACE	Ni	3.23	7.90	2.98	6.42
AREA PER	YSZ	7.65	3.65	7.83	3.82
TOTAL	Pore	7.45	6.19	7.68	7.54
VOLUME					
(μm^{-1})					

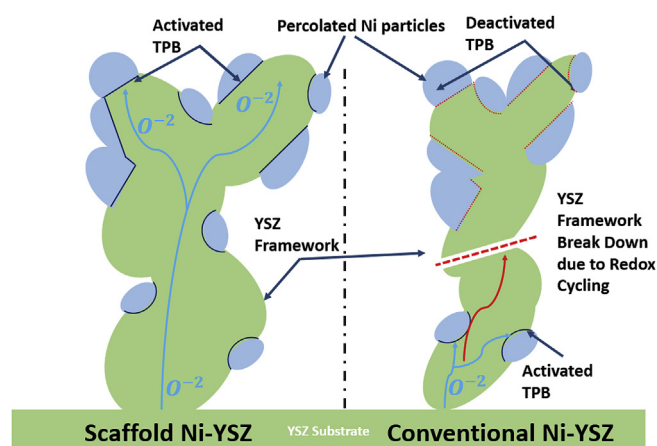


Fig. 7. Visual model the loss of aTPB led by cracking of YSZ frame. After several redox cycles, the Ni agglomeration accompanied with its volume expansion during oxidation could damage the YSZ frame for conventional Ni-YSZ (right). On the contrary, the YSZ scaffold could provide a stronger backbone framework, which could minimize impact from Ni volume change (left).

sample, Fig. 5e. The larger the number of redox cycles the bigger the Ni particles become, as can be seen on the SEM images at the uppermost part of the scaffolds (Fig. 4). Ni nano-particles were also observed after redox cycling. At the same time, Ni movement was observed from the FIB-SEM images, by comparing the as-reduced sample with the one after 15 redox cycles (Fig. 5e), this is consistent with SEM images (Fig. 4d). In conventional Ni-YSZ electrodes, YSZ framework failure can be often found from SEM images after redox cycling [1]. On the

contrary, there is no observation of YSZ framework failure in infiltrated scaffolds from both top and cross-sectional images. This can be due to the stronger mechanical ability of the YSZ scaffold to prevent its structure damage from the Ni agglomeration and volume expansion during oxidation condition, because the finer nickel particles distributed on the surface of the YSZ framework rather than within the YSZ framework as in conventional Ni-YSZ electrodes, result in less expansion and therefore less strain on the scaffold.

3.2.2. Electrochemical degradation

The resistances response from the impedance data were fitted using an equivalent circuit, shown in Fig. 6. The ohmic resistance consisted of the sum of the electrolyte resistance and the anode current collection [32]. The electrolyte resistance was estimated around $5.3\ \Omega$ according to electrolyte thickness and YSZ resistivity; the anode contact resistance could be the main contribution to small ohmic resistance change during each reduction process, which is related to the Ni microstructure change during these early reduction stage. The diffusion resistance is generally constant, as it is attributed to losses by gas conversion and gas diffusion [1]. Finally, the polarisation resistance shows in general a continuous increase after redox cycling. This is mostly considered to be related to charge transfer and the activation overpotential of the fuel oxidation process at the active triple phase boundaries (aTPB). The increase in polarisation resistance could be due to the loss of aTPB length, which is due to mechanical damage at the electrochemical interfaces [10]. Fig. 6 compares the stabilized polarisation resistances of the Ni-YSZ scaffold and conventional Ni-YSZ after corresponding numbers of redox cycles. The Ni-YSZ scaffold, with less Ni content (25 wt%) and lower operation temperature ($550\ ^\circ\text{C}$), shows smaller initial polarisation resistances and relatively slow degradation compared to conventional Ni-YSZ, with 40 wt% Ni at $800\ ^\circ\text{C}$. This good initial polarisation resistance performance could due to the YSZ scaffold, which provides higher surface area and creates a large aTPB length with the infiltrated Ni. This has also been verified by using FIB-SEM tomography, as show in Table 1. While, due to the FIB-SEM resolution (20nm/Pixel), limited volume could only be scanned [33]. Also, due to the composition of the electrode, the tomography could vary for different regions within the sample. During redox cycling, several factors were considered to explain the slower degradation of Ni-YSZ scaffold compared to conventional Ni-YSZ electrode: firstly, the lower operational temperature of scaffolds ($550\ ^\circ\text{C}$ vs $800\ ^\circ\text{C}$) could result in a slower degradation rate; secondly, The relatively stronger YSZ scaffold does not degrade during redox cycles (fracture, disconnect, etc), therefore providing stable ionic transport, thus keeping the aTPB stable, as schematically shown in Fig. 7.

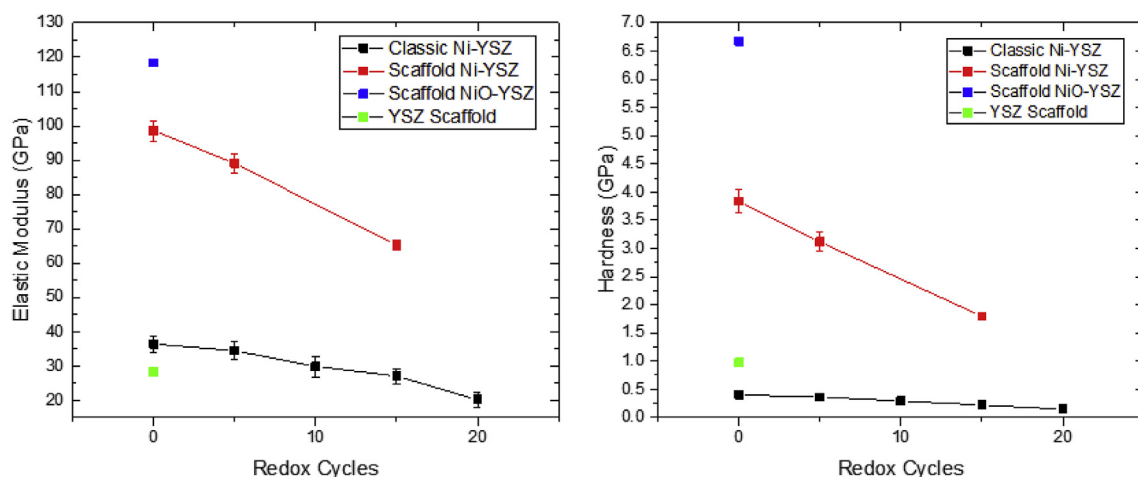


Fig. 8. Mechanical properties of Ni-YSZ anodes. The redox cycling degradation trend was compared between conventional Ni-YSZ and Ni-YSZ scaffold.

3.2.3. Mechanical properties degradation

The elastic modulus and hardness of bulk samples measured using nanoindentation are shown in Fig. 8 plotted against number of redox cycles. The green dot shows the YSZ scaffold with around 45% of porosity, which is similar to the as-reduced Ni-YSZ made from conventional Ni-YSZ. However, the hardness of YSZ scaffold is twice the value of conventional Ni-YSZ [1,11], as it is commonly agreed that YSZ is a hard material for all kinds of applications. Comparing the reduced Ni-YSZ scaffold with the conventional Ni-YSZ, the initial elastic modulus in the former was tripled, and the hardness increased by a factor of eight. These notable results can be due to the Ni infiltration which filled the pores within the YSZ scaffold. Decreasing trends against numbers of redox cycles were observed for both elastic modulus and hardness of the Ni-YSZ scaffold, dropping by 33% and 53% respectively, but still stronger than the conventional Ni-YSZ after corresponding numbers of redox cycles. As no YSZ scaffold damage was observed in the SEM images, the drop in hardness and elastic modulus could be caused by Ni agglomeration and increase in porosity due to long time operation and redox cycling.

4. Conclusion

In this study, a stable YSZ scaffold has been fabricated by using 10 wt% of carbon black as pore former with various sintering temperatures. It has been found from SEM images that different sintering temperatures have a significant influence on YSZ grain size, grain boundaries connectivity and pore formation. At sintering temperatures below 1200 °C, YSZ tends to form rather small grains, with poor YSZ grain connectivity important for ionic conductivity and mechanical stability. In the samples sintered above 1200 °C, the YSZ grains were very well connected, and grain size increased with higher sintering temperature, resulting in improved mechanical properties as high as 136.5 GPa and 7.95 GPa for elastic modulus and hardness, respectively. But the high sintering temperature also resulted in a loss in porosity and reduced pore size; this could lead to difficulty in Ni infiltration and gas phase diffusion. Considering both mechanical stability and scaffold morphology, 1200 °C was identified as the best condition for YSZ scaffold sintering.

The electrochemical and mechanical deterioration of Ni-YSZ scaffolds after up to 15 redox cycles was determined by a combination of SEM, impedance spectroscopy, nanoindentation and FIB-SEM. It has been found that, after 15 redox cycles the YSZ scaffold retained its structure well, since improved mechanical properties prevent the YSZ break down against Ni volume expansion during the oxidation cycle. That is to say, this stable YSZ framework effectively maintained considerable numbers of aTPB, that otherwise could lose effective ionic transport if there were framework damage. The infiltrated Ni-YSZ scaffold has a better initial performance, with lower Ni content (25 wt %) and lower operational temperature, compared with conventional Ni-YSZ (40 wt%) sintered under same condition.

Same as in the conventional Ni-YSZ anode, agglomeration still cannot be minimized within Ni-YSZ scaffolds, this is also the main problem for Ni-YSZ material degradation during redox cycling. The materials wetting properties between Ni and YSZ still need to be studied in future work.

Acknowledgements

This project has received funding from the China Scholarship Council (CSC), European Union's Horizon 2020 research and the EPSRC grant EP/M014045/1. Helpful discussions with Dr. Antonio Bertei and Huiwen Zha are gratefully acknowledged.

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