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Quantification of the degradation of Ni-YSZ anodes upon redox cycling

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HIGHLIGHTS

- Quantification of redox damage by coupling 3D tomography, EIS and nanoindentation.
- YSZ fracture, Ni detachment and agglomeration led to irreversible mechanical damage.
- Ni nanoparticles obtained upon redox cycling improve electrochemical performance.
- Loss in TPB density estimated by model matches 3D FIB-SEM data.

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ABSTRACT

Ni-YSZ anodes for Solid Oxide Fuel Cells are vulnerable to microstructural damage during redox cycling leading to a decrease in the electrochemical performance. This study quantifies the microstructural changes as a function of redox cycles at 800 °C and associates it to the deterioration of the mechanical properties and polarisation resistance. A physically-based model is used to estimate the triple-phase boundary (TPB) length from impedance spectra, and satisfactorily matches the TPB length quantified by FIB-SEM tomography: within 20 redox cycles, the TPB density decreases from 4.63 μm^{-2} to 1.06 μm^{-2}. Although the polarisation resistance increases by an order of magnitude after 20 cycles, after each re-reduction the electrode polarisation improves consistently due to the transient generation of Ni nanoparticles around the TPBs. Nonetheless, the long-term degradation overshadows this transient improvement due to the nickel agglomeration. In addition, FIB-SEM tomography reveals fractures along YSZ grain boundaries, Ni-YSZ detachment and increased porosity in the composite that lead to irreversible mechanical damage: the elastic modulus diminishes from 36.4 GPa to 20.2 GPa and the hardness from 0.40 GPa to 0.15 GPa. These results suggest that microstructural, mechanical and electrochemical properties are strongly interdependent in determining the degradation caused by redox cycling.

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 cermets are the most commonly used SOFC anode materials, offering a combination of relatively low cost and good performance. However, the material can degrade when subject to certain operating conditions, such as redox cycling during operation [1–5].

Past work has often concentrated on Ni-YSZ microstructural evolution by annealing for long periods of time. It is commonly agreed that under these conditions the accompanying performance loss is caused by an increase in average Ni particle size and a decrease in active triple phase boundary (TPB) length per unit volume. The active TPB is the theoretical contact perimeter between percolating Ni, YSZ and pore phase, where fuel oxidation and charge transfer occur [6–8]. Ni-YSZ anodes are typically fabricated by mixing YSZ and NiO particles, which are subsequently reduced by H_2 during the fuel cell start-up. Reduction of the NiO–YSZ involves a quasi-reversible dimensional shrinkage of 41.6% by converting NiO to Ni. However, Ni is strongly sensitive to oxidising atmospheres, such as those present during operation at high fuel conversion or during emergency shut-down, which can rapidly convert Ni into its oxidised state, involving a 71.2% volume expansion. These Ni volume changes result in irreversible microstructural damage, which include bulk deformation of the microstructure, commonly leading to electrolyte cracking [1,2,9]. The size changes of Ni particles were suggested to be due to the agglomeration of metallic nickel [10] and the formation of porosity upon reduction [11]. These parameters also show a direct relationship with the change of the effective TPB length [7]. The increase in Ni particle size could lead to a corresponding drop of TPB density and growth of polarisation resistance [12], moreover, due to the potential loss of Ni–Ni contact, the electrical

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conductivity can decrease as well.

Focused ion beam (FIB)-SEM tomography [13,14] allows the microstructural change seen in Ni-YSZ electrodes after redox cycling to be quantified through ex-situ analysis, due to the good phase contrast between Ni and YSZ, and the relatively high resolution of the technique. From the 3D tomography reconstructed microstructure, parameters such as volume fractions, interfacial areas, TPB length and tortuosity factors can be quantified [9,15–19]. In terms of electrochemical performance, electrochemical impedance spectroscopy (EIS) is commonly used, as it is an effective technique to follow electrochemical changes in real time [20–22]. It has been found that after redox cycling, polarisation resistance increased due to TPB length reduction and Ni surface area decrease [5,9,19]. The relationship between electrode microstructure properties and electrochemical impedance response has been recently quantified by Bertei et al. [24], using a physically-based model [25,26].

Knowledge of the behaviour of Ni-YSZ is also important for the mechanical design of the SOFC. The mechanical properties of Ni-YSZ have been widely studied with a wide range of techniques. The Impulse Excitation Technique (IET) was used to determine parameters in thick Ni-YSZ electrodes, 300 μm or above, comparing elastic modulus with porosity, Ni content and sintering temperature [1,27–29]. The empirical relationship of porosity and elastic modulus of Ni-YSZ has been reported and validated in several studies [29,30]. A comparison of different mechanical properties determined by these experimental techniques has been undertaken [31]. The nanoindentation technique has been developed and used to study the response of the material at smaller length scales [32,33]. However, there is currently no study available on the nanoindentation characterisation of the micromechanical properties of porous Ni-YSZ films upon redox cycling.

This paper presents an integrated study of the impact of redox cycling on the microstructure, electrochemical performance and mechanical properties of porous Ni-YSZ cermets, using a variety of methods such as 3D tomography, nanoindentation, EIS and modelling to develop an improved understanding of the coupled nature of anode behaviour under such redox cycling conditions.

2. Experimental

2.1. Fabrication of NiO-YSZ cell

Ni-YSZ symmetrical cells were prepared with a NiO-YSZ slurry made from NiO and YSZ powder (Nexceris, USA, 60 wt% NiO, 2.45 $m^2 g^{-1}$ surface area) 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 μm. The slurry was deposited by tape casting on an 8YSZ electrolyte (Nexceris, USA, Ø = 2 cm, 250–300 μm) and fired at 1200 °C for 2 h in air. The final electrodes had a thickness of 25–30 μm and 2 cm^2 geometric surface area.

2.2. 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 800 °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 5 h, as schematically reproduced in Fig. 1. This procedure, already adopted by Shimura et al. [9], 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.

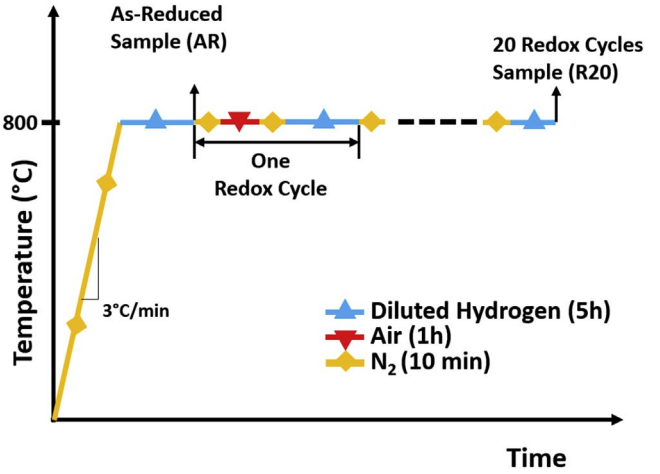

Fig. 1. Representation of redox cycling procedure. Impedance spectra were taken during each reduction process as a function of time.

2.3. Characterisation procedure

EIS measurements were performed within a frequency range of 10^6Hz-10^{-1} Hz with 20 mV AC amplitude using a potentiostat (Autolab PGSTAT302N), every 30 min during the reduction process in diluted hydrogen atmosphere. The measurement data were fitted to an equivalent electrical circuit, shown in Fig. 2, by using ZView3.5 (Scribner Associates Incorporated). The active TPB density was estimated from the intermediate-frequency polarisation resistance R_2 using a validated physically-based model [24], as follows:

$$R_2 = 2\frac{t_{an}}{k_{eff}\sigma_{io}}\frac{coth(\Gamma)}{\Gamma} \quad (1)$$

$$\Gamma = t_{an}\sqrt{\frac{F}{RT}\frac{i_0 L_{TPB}}{k_{eff}\sigma_{io}}} \quad (2)$$

where the factor 2 represents the two electrodes for the symmetric cell, t_{an} is the anode thickness, F the Faraday constant, R the gas constant, T the operating temperature in K, k_{eff} is the effective conductivity factor

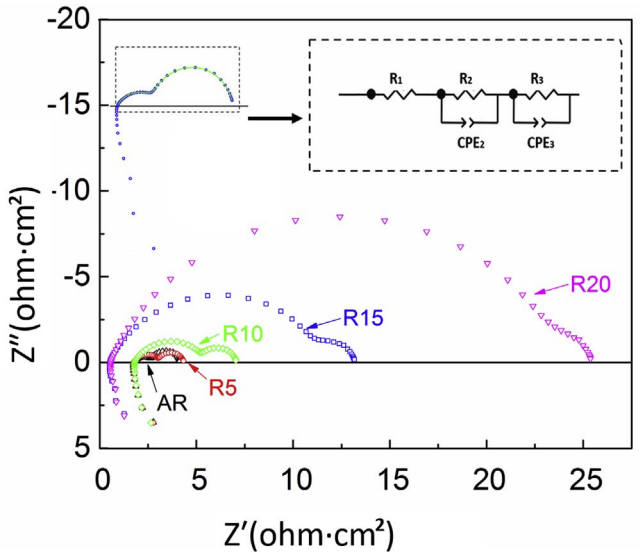

Fig. 2. Impedance spectra recorded after 0, 5, 10, 15, 20 redox cycles at 800 °C, 2 h after the introduction of wet 5 vol % H_2, AR represents as-reduced, R5 represents 5 redox cycles, R10 10 redox cycles and so on. The inset shows equivalent circuit fitting result. R_1, R_2, R_3 represent the high-frequency intercept resistance, intermediate frequency resistance and low-frequency resistance respectively; CPE_2, CPE_3 represent constant phase element for the corresponding frequency[28].