Understanding the thermo-mechanical behaviour of solid oxide fuel cell anodes using synchrotron X-ray diffraction

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A B S T R A C T

The formation of cermet materials *via* the addition of electrolyte ceramic to metal-based electrodes has become widely adopted in solid oxide fuel cell fabrication due to its benefits in maximizing triple-phase boundary densities, whilst mitigating bulk thermal expansion mismatch between electrode and electrolyte layers. This work improves thermo-mechanical understanding *via* examination of nickel-based anode materials using synchrotron X-ray diffraction; two cermet materials are studied: *Ni-YSZ* and *Ni-GDC*, with comparison to a ceramic-free *Ni* sample. Findings conclude that although the ceramic addition has minor effects on the cubic *Ni* structure within isothermal environments, stress induced by the different thermal properties within the cermet materials results in a shifted *Ni* thermal expansion peak on passing the Curie point. Moreover, extended cycling of the *Ni-YSZ* sample suggests that low-temperature operation (*ca.* 600 °C) may require several thermal cycles, or extended dwell times, to alleviate residual *Ni* stresses, this has potential implications for *SOFC* design and operation strategies.

1. Introduction

The high temperature operation of *SOFC*s offers advantages due to favorable kinetics [1] through the use of lower cost nickel-based catalysts and flexible fueling options with the ability to recover excess heat [2,3]. However, the desire to increase thermal ramp-rates to achieve rapid start-up and shut-down times drives concerns about thermally driven stack degradation. Whilst thermo-mechanical simulations of *SOFC*s during cycling is advancing [4–6] novel characterization and experimental methods [7–11] are still required to improve the accuracy of modeling tools and provide validation [12].

The performance of *SOFC*s can be characterized by the direct analysis of the kinetic, ohmic or diffusive properties using techniques such as electrochemical impedance spectroscopy (*EIS*) [13], or by indirect analysis using materials characterization techniques. The proliferation of tomography tools [14–16] has enabled the quantification of a range of geometrical parameters, including the triple phase boundary density (*TPB*). In order to maximize the *TPB* density and minimize the difference in thermal expansion between the neighboring electrode and electrolyte layers, the electrolyte ceramic is added to the metallic electrode forming a cermet. Nickel-based (*Ni*) anodes are commonly employed in combination with either yttria-stabilized zirconia (*YSZ*) or

gadolinium-doped ceria (*GDC*), forming *Ni-YSZ* or *Ni-GDC* cermets, respectively [17,18]. Whilst the crystallography of pure *Ni* is well-understood [19–23] the influence of such ceramic addition has been the subject of increased research in recent years [24–29].

Non-uniform thermal expansion within *SOFC*s is a known cause of unfavorable strain distribution [24,25] therefore, the location and cause of any non-linear expansion is of interest in mitigating mechanical degradation in the form of delamination and cracking, and the subsequent loss in electrochemical performance. The Curie point is the temperature that is thermodynamically sufficient to disrupt dipole alignments causing a magnetic transition from ferromagnetism to paramagnetism. This transition results in a well-documented non-linearity in the *Ni* thermal expansion coefficient (*TEC*) [19–23]; although, the temperature at which metals are able to exhibit ferromagnetism is thought to be sensitive to the level of strain which the material is subjected to [30], and correlation has also been observed between the sintering and Néel temperature [31].

Studies using macroscopic techniques such as dilatometry have suggested that bulk non-linearity is suppressed to insignificant values by the addition of the supporting ceramic backbone [32]. However, the microscopic interactions between the metal and ceramic phases (at the *TPB*) are thought to be of great thermo-mechanical importance [6] and

it has been suggested by techniques such as thermomechanometry that the non-linear expansion of the metallic phase may remain regardless of the presence of the ceramic [33].

Long-duration operation can cause undesirable agglomeration reducing *TPB* density [1,34]. *Ni* is also known to undergo thermally driven deformation (*TDD*) in the form of mechanical creep observed through lattice hysteresis during thermal cycling, thought to be attributable to temperature-triggered stress relaxation due to lattice distortions and imperfections held in residual stress within the metal [24]. Improved understanding of these mechanisms is required.

In this work, we investigate three materials: *Ni*, *Ni-YSZ* and *Ni-GDC* using *in-situ* synchrotron X-ray diffraction to explore the influence of ceramic addition on the mechanical properties of the metal during thermal cycling. For the first time known to the authors, the location of the *Ni* Curie transition temperature and lattice parameter variation during operational thermal cycling are examined, thereby improving the understanding of metal-ceramic interaction within cermet materials. This understanding of the thermo-mechanical interaction between ceramic and metal within cermet materials will ultimately lead to improved cell performance and lifetimes; knowledge that is also transferable to comparable materials where metal and ceramic interfaces prove critical to performance.

2. Materials and method

Three commonly employed *SOFC* anode materials were examined *via* synchrotron powder diffraction: *Ni* (Novamet Specialty Products Corp, Lebanon), *Ni-YSZ* (Fuel Cell Materials, OH, USA) and *Ni-GDC* (Fuel Cell Materials, OH, USA). The zirconia powder was supplied with 8 mol% yttria content, $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$, and the ceria powder was supplied with 10 mol% gadolinia doping, $Gd_{0.10}Ce_{0.90}O_2$. Both cermet materials, *Ni-YSZ* and *Ni-GDC*, were supplied with a 60:40 composition of metal to ceramic by weight, and the ceramic-free powder is supplied at 99.6% purity with the residual volume consisting of 3000 ppm oxygen, 800 ppm iron, 30 ppm carbon and 30 ppm sulphur.

Initially, powders were formed into cylindrical pellets by isostatic pressing and subsequently sintered at 1200 °C for 2.5 h in air. The pellets were then reduced in forming gas (4 %H_2 in 96 %N_2) for 2 h at 800 °C; reduction of *NiO* to *Ni* was confirmed with Raman spectroscopy,

see Fig. 1a. The reduced pellets were then ground into powders using diamond files and inserted into open-ended quartz capillary tubes, 10 cm in length with internal diameter of 580 μm, see Fig. 1b.

Crystallographic investigations were conducted at the X04SA-MS beamline [35] (Swiss Light Source, Paul Scherrer Institute, Switzerland). The samples within the capillary tubes were inserted into a goniometer head (HUBER Diffraktionstechnik GmbH & Co. KG, Germany) *via* a brass button seal, and positioned perpendicular to the X-ray beam. A hot-air blower was placed below the capillary tube, coincident with the X-ray beam, in order to collect diffraction patterns at elevated temperatures. To increase the accuracy of temperature recordings a thin, high precision thermocouple (*ca.* 250 μm in diameter) was inserted into the capillary, until coincident with the horizontal X-ray beam and vertical hot-air blower, see Fig. 1c. To prevent oxidation of the samples, premixed gas (5 %H_2 in 95 %N_2) was passed over the sample at a continuous rate of 25 mL min^{-1}. All diffraction patterns were collected at two theta angles from $-60°$ to $+60°$ at 26 keV (0.4788 Å) using a MYTHEN II (microstrip system for time-resolved experiments) detector covering 120° with over 60,000 channels on a double layer for a 0.0036° intrinsic resolution at an exposure of 60 s per detector.

For reference, diffraction patterns of the empty capillary were collected for all temperatures. A background removal was also applied to all patterns before extracting lattice parameters of interest [37]. *Ni* and *NiO* peak intensities are compared in Fig. 2a to confirm no re-oxidation of the *Ni* during thermal cycling, one thermal ramp is presented here but this was conducted for all data sets. A corrected *Ni-YSZ* pattern is displayed in Fig. 2b with *Ni* peak locations compared to a reference for several crystallographic indices displayed in Fig. 2c [24]. Very minor deviations were observed achieving a coefficient of determination close to unity ($R^2 = 0.998$).

Firstly, diffraction patterns were collected through both heating and cooling during one thermal cycle for each of the three materials: *Ni*, *Ni-YSZ* and *Ni-GDC*. Patterns were collected continuously resulting in one pattern every 2 min at a ramp-rate of *ca.* 10 °C·min^{-1} from *ca.* 100 °C to 650 °C and back to 100 °C; equating to *ca.* 2 h of data acquisition per sample. These data sets were collected to inspect hysteresis and non-linearity in the *Ni* phase. Further diffraction patterns were collected from fresh samples over an additional thermal cycle for the Curie
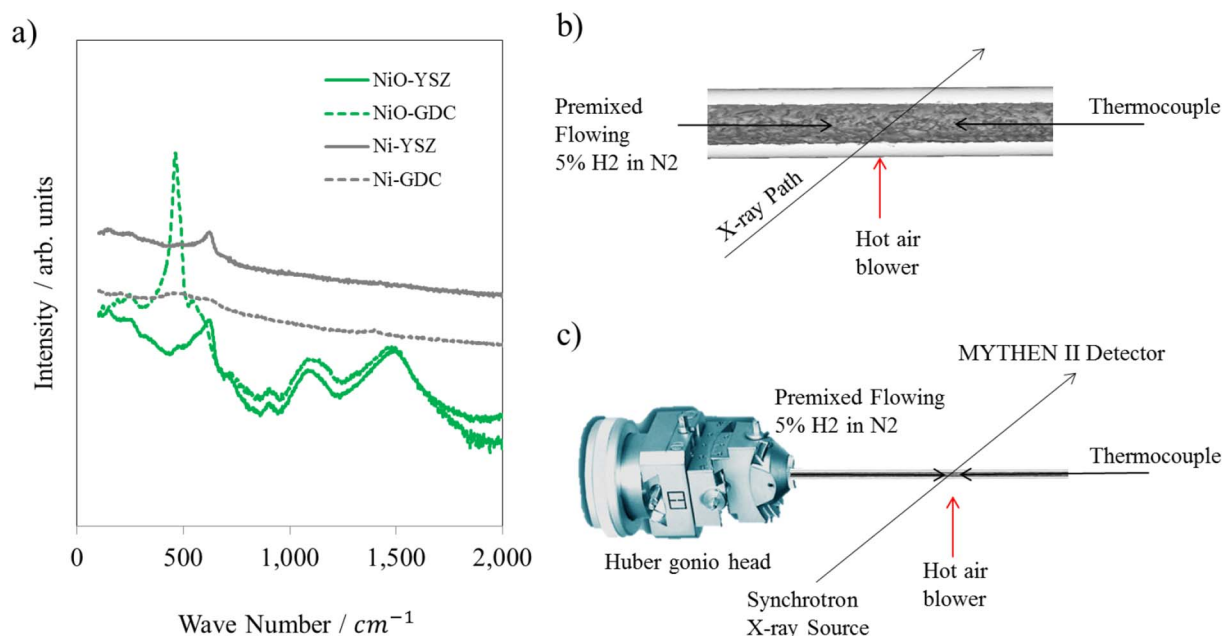

Fig. 1. Experimental set-up for diffraction collection at the X04SA-MS Beamline: (a) pre- and post-reduction Raman spectra, (b) four coincident paths of the hot-air blower, forming gas, thermocouple and X-ray beam, and (c) sample mounting *via* a quartz capillary packed with sample powder [36].