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Influence of temperature and atmosphere on the strength and elastic modulus of solid oxide fuel cell anode supports

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HIGHLIGHTS

- Bending test of high number of samples (~30) was performed at different conditions.
- Influence of reduction temperature on mechanical properties of Ni–YSZ was revealed.
- Temperature dependence of mechanical properties of Ni(O)–YSZ was revealed.
- Failure in Ni-YSZ is determined by YSZ; while it is determined by NiO in NiO-YSZ.

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ABSTRACT

Solid Oxide Fuel Cells are subjected to significant stresses during production and operation. The various stress-generating conditions impose strength requirements on the cell components, and thus the mechanical properties of the critical load bearing materials at relevant operational conditions need to be characterized to ensure reliable operation.

In this study, the effect of reduction temperature on microstructural stability, high temperature strength and elastic modulus of Ni–YSZ anode supports were investigated. The statistical distribution of strength was determined from a large number of samples (~30) at each condition to ensure high statistical validity. It is revealed that the microstructure and mechanical properties of the Ni–YSZ strongly depend on the reduction temperature. Further studies were conducted to investigate the temperature dependence of the strength and elastic modulus for both the unreduced and reduced Ni(O)–YSZ anode supports. With increasing temperature, the strength and elastic modulus of the reduced Ni–YSZ specimens drop almost linearly. In contrast, the strength and elastic modulus of the unreduced NiO–YSZ remain almost constant over the investigated temperature range. Compared to the NiO-YSZ, a significantly lower strength and elastic modulus of the reduced Ni-YSZ is observed; while reduction leads to a remarkable increase in failure strain of the anode support.

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are electrochemical devices that convert the chemical energy of fuel (hydrogen, natural gas, *etc.*) directly to electrical energy. They have been intensively studied due to the high efficiency and potential for low cost [1,2]. Until now, the most commonly used planar SOFCs are mechanically supported by the anode (fuel electrode) material. The most widely used anode support for SOFCs is a porous ceramic-metal composite (cermet) consisting of nickel and yttria stabilized zirconia (Ni-YSZ) [1,3]. Generally, porous Ni-based anodes and anode supports are fabricated starting with YSZ and NiO (NiO-YSZ), which is chemically reduced to Ni-YSZ through the introduction of fuel, leading to the formation of the required porosity and an electronically conducting Ni-network. Depending on temperature, reductant and water content of the reduction gas, full reduction can be achieved in time intervals spanning from a few minutes to hours, with higher temperature promoting faster reduction kinetics. The reduction process can significantly influence the microstructure of the cermet, and consequently its performance and mechanical stability [4–7].

With the implementation of the single cells into stacks and products, their reliability has received increasing attention [7,8].

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The reliability of SOFCs is dependent not only on the chemical and electrochemical stability of its components, but also on the capability of the SOFC components to withstand mechanical stresses that arise during production and operation. The stresses in a cell embedded in a stack have different origins, e.g. thermal expansion mismatch between the anode and electrolyte and between cell and interconnect, assembly forces, reduction and oxidation reactions, and intrinsic stresses arising from nonhomogeneous temperature distribution during operation [7,8]. In practical application, the integrity of the cells is crucial, since mechanical failure severely influence the performance, and could lead to overall failure of the system. Therefore, assessment of the mechanical properties of the SOFC components is important, particularly under conditions relevant for operation. This enables quantification of stresses and is required to understand reliability issues, and in developing fail safe cell- and stack-designs.

To evaluate the mechanical reliability, the stresses under operation of the SOFC stacks must be assessed together with the material resistance to failure. Typically, a statistical approach (Weibull distribution) is preferred to assess the distribution of the strength of brittle components at operational conditions; as it offers simple experiments and stress analysis [5–13]. The drawback is however that strength measurements of as many as 30 samples under the same condition are needed to get a good statistical representation and avoid large uncertainty on parameter estimates, as pointed out by Khalili and Kromp [14]. All cells will already have experienced loads (a “base load”), from various processes in the production, which will make a few cells fail. Thus, a three-parameter Weibull distribution is perhaps a better representation of the population, as the third parameter is lower limit to strength representing this base load. A three-parameter Weibull distribution does however require an even higher number of specimens (~100) [11,15].

The strength of Ni(O)-YSZ composites has received much attention as this is the main structural component in the anode supported cell design, and various effects of the processing, reduction of the Ni phase, size effects and redoxing has been investigated at room temperature. Radovic and Lara-Curzio [6] studied the dependence of strength on porosity at room temperature for both Ni-YSZ and NiO-YSZ, where the property–porosity trends were found to be in good agreement with predictions of the *minimum solid area* model. Frandsen et al. [12] showed that this was also valid even regardless of what process parameters were varied resulting in the variations in porosity.

Faes et al. [16] compared tensile uniaxial and ball-on-ring strength measurements of as-sintered NiO-YSZ anode materials. In spite of the great variation in measured strength from the two methods, the results were shown to be comparable given the strength scaling with so-called effective volume. Biswas et al. [17] also reported an influence of thickness (600–900 μm) on strength of anode supported half-cells. The strength was comparable in the oxidized condition but differed in the reduced condition, which was tentatively ascribed to an un-even reduction of the thicker sample. Moreover, the reduced half-cell structures characterized by a higher porosity presented a higher strength compared to the unreduced ones in their work, which is contrary to other results in the literature [5–7]. The reason could be that residual stresses of the tested half-cells were not considered in the characterizations. The decrease of strength and elastic modulus after reduction as observed in Refs. [5–7] is ascribed predominantly to the associated increased porosity by reduction. Moreover, it is found that the strength of the Ni-based anode materials can be influenced by reduction parameters [5]. Faes et al. [18] measured the strength of half-cells at room temperature for reduction temperatures of 600 °C and 1000 °C and enhanced strength was observed at higher reduction temperature.

In partially stabilized 3YSZ sub-critical crack growth may occur and the strength of Ni(O)-3YSZ may thus be load rate dependently, see e.g. Refs. [19,20]. Hashida et al. [21,22] also showed that plastic deformations occurred before fracture in their Ni-YSZ cermet given a sufficient slow loading rate.

The temperature dependence of the elastic modulus of both as-sintered and reduced Ni(O)–YSZ composites has been studied by Pihlatie and Biswas et al. [17,23,24]. A peaking of stiffness was observed to coincide with the Néel temperature of NiO in the as-sintered state and above this temperature, a slight decrease occurred. In the reduced state the elastic modulus decreased linearly with temperature.

The strength of Ni(O)-YSZ at high temperature has been measured at 800 °C in a few studies [7,15,21,22], and it has commonly been shown that the strength is reduced relative to room temperature. The strength at 800 °C in the oxidized state was shown to be reduced relative to room temperature by 13% and 27% in Refs. [7] and [15], respectively, and by 20% in reduced state [15]. However, only in one case [7] a high number of samples (30) were tested in the oxidized state at high temperature, allowing a reliable determination of the Weibull modulus. In the other works typically only the average strength has been supplied. This relates to the Weibull parameters via $\sigma_{av} = \sigma_0 \sqrt[m]{-\ln(0.5)}$, where m and σ_0 are the Weibull modulus and Weibull strength, respectively, but does not describe the strength distribution. The reason for this is that the conventional mechanical test approach suffers from the drawback that a considerable experimental effort is needed to characterize the needed number of samples (~30). Just recently, Frandsen et al. developed an accurate strength measurement method using a special fixture for 4-point bending, which is designed to allow efficient test of components at high temperature in controlled atmosphere [13]. This novel approach allows for testing of a high number of samples (up to 16) in one heat up, and thus significantly reduces the time needed to obtain statistically reliable data.

In this work, the influence of temperature on the strength of Ni(O)–YSZ anode supports was studied using a large number of specimens (~30) at various temperatures relevant for operation of SOFCs to investigate if the Weibull parameters varies significantly with temperature. The reduction itself, as well as the conditions for reduction can influence the defect population, size and distribution in the reduced anode materials, residual stresses and consequently the macroscopic mechanical properties. Therefore the strength distribution after reduction at different temperatures was also investigated. Furthermore, the influence of the reduction temperature was investigated for a larger range of temperatures. Also, the microstructure was studied and associated with the observed changes in mechanical properties. Based on the measurements the strength and failure strain dependency on the temperature is investigated to identify possible weakening mechanisms and what phase that determines the strength at different temperatures.

2. Experimental procedures

2.1. Materials

The anode supports tested in this study were prepared from a mixture of commercial nickel-oxide (NiO) and 3 mol% Y_2O_3 stabilized ZrO_2 (YSZ) powders using standard ceramic processing including tape casting and sintering, see e.g. Ref. [25]. The composition of the NiO-YSZ anode support was 55 wt% NiO with 45 wt% YSZ. The as-sintered anode support had dimensions of approximately 120 × 120 × 0.3 mm^3 with a porosity of around 13%. Rectangular samples of 7.3 mm by 60 mm were laser cut from the as-sintered NiO-YSZ material. In order to ensure reproducibility, the samples to be characterized were stacked and glued together with