

The mechanical and electrical properties of Ni/YSZ anode support for solid oxide fuel cells

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Abstract

The most commonly used solid oxide fuel cell (SOFC) anode material is a two phase nickel and yttria stabilized zirconia (Ni/YSZ) cermet. And the mechanical stability of anode support layer, in anode-supported electrolyte designs, is very important for large scale applications. During the assembly of stack and normal operation, the cermet anode should withstand enough mechanical loading to prevent the cell from cracking caused by various stresses.

The electrical conductivity at ambient temperature as a function of Nickel content has a typical 'S' shape curve increasing from 0.06 S.cm^{-1} to $1178.78 \text{ S.cm}^{-1}$. The open porosity increased from 13 % to 42% with the Ni content changing from 26 wt% to 55 wt%. The open porosity as a function of Ni vol% could be expressed by equation $P=0.694X+P_0$, where P is open porosity, P_0 is initial porosity and X is Ni vol%. The density decreased with Ni content increasing both before and after reduction. The flexural strength increased with the decreasing content of Ni and has an inflexion between 60 wt% and 65 wt% of nickel before reduction. When the nickel content more than 50 wt%, the flexural strength decreased more than 25% after reduction.

Introduction

Solid oxide fuel cells (SOFC) are electrochemical devices that transform the chemical energy of fuel (hydrogen natural gas, etc.) directly to electrical energy as highly efficient and pollution-free energy sources. SOFC have been intensively studied during the past decade ^[1]. Although the reliability of SOFC depends 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 processing and service.

Present day the demonstration of SOFC use the anode to support the thin electrolyte and the cathode. The electrolyte is kept as thin as possible to decrease costs and improve performance ^[2,3]. For the construction of this component, tapes of a porous anode support with a thickness about 100~200 μ m made by tape casting easily support the thin electrolyte and the cathode of SOFC ^[4]. A cermet consisting of Ni-metal and Y₂O₃-stabilized ZrO₂ (YSZ) is widely used as an anode support material in high temperature SOFC ^[5]. This material is preferred because of its good electronic conductivity, chemical and structural stability, catalytic properties and compatibility with other materials in SOFC.

The porosity of the nickel-based anode support up to 30 vol%, enables hydrogen to diffuse through the cermet and H₂O to escape from it. The role of YSZ is mainly to support Niparticals and prevent them from sintering during service. M. Radovic and E. Iara-Curzio ^[5] determined the porosity as a function of initial porosity before reduction by equation $P=0.228+0.772P_0$ while Y. Wang et al. ^[6] reported the porosity as a function of reduced fraction of NiO by equation $P=20.4+18.0R$ and $P=26.3+17.6R$ for different specimens.

The strength of the unreduced and reduced anode-support is affected primarily by porosity and microstructural connectivity ^[6]. Selcuk and Atkinson ^[7] determined the ambient temperature biaxial strength of 187MPa for 75mol% NiO-YSZ samples of unknown porosity, while Radovic ^[8] et al. reported on decrease in the room temperature biaxial strength of NiO-YSZ with increasing porosity. Ji Haeng Yu et al. reported that the mechanical properties of Ni-YSZ cermet correlated with microstructure, which was strongly dependent on the size of starting powders. The relationship between strength, σ , and porosity, p , can be described by: $\sigma = \sigma_0 \exp(-bp)$, where σ_0 is the strength of non-porous structure and b is a pre-exponential coefficient related with pore structure ^[9]. Fine powder is beneficial to sintering and high mechanical strength while coarse powder yields desirable pore-structure. Therefore, considering the physical requirements of the anode, the composite powder was optimized at a fraction of 20% fine and 80% coarse powder ^[10].

The main goal of this work is to study the electrical and mechanical properties of the anode-support with nickel content increased.

Experimental procedure

The Ni-based anode-support material examined in this study was prepared from a powder mixture of NiO and 3 mol% Y₂O₃ stabilized ZrO₂, (3YSZ) (TOSOH Corp.). Green samples with different content of NiO prepared by tape casting method were about 400 μ m thick single layers. The electrical conductivity tested at ambient temperature using a four-point probe fixture. Rectangular samples for the test were cut from tapes previously and sintered at 1350°C in air for 4h then reduced in 9% H₂ and 91%N₂ gas mixture at 1000°C for 3h. The relative porosity and density of the samples with different Nickel content before and after reduction were determined using the standard Archimedes method ^[11].

The flexural strength of the anode-support material was determined by three-point flexure fixture that carried out in an Instron machine (Model 5567) with the guidance of ASTM test method C1161^[12,13]. The standard formula for the flexural strength in three-point flexure is as follows:

$$S=3PL/2bd^2 \quad (1)$$

Where:

P = break force,

L = outer (support) span,

b = specimen width, and

d = specimen thickness.

Samples of 4×36×0.4 mm were cut by laser and polished after sintered at 1350°C in air for 4h and approximately half of the samples were also reduced in 9% H₂ and 91%N₂ gas mixture at 1000°C for 3h for the test. The number of specimens was more than 15 and the thickness of each specimen was determined by micrometer for the flexural strength testing in this study.

The microstructure of unreduced and reduced Ni-based anode-support material samples were analyzed using a field emission scanning electron microscope (FESEM) Hitachi S4800.

Experimental results and discussion

1. Electrical conductivity

The electrical conductivity of Ni/YSZ cermet is strongly depended on its nickel content. The electrical conductivity would increase with the volumetric fraction of nickel since the electrical conductivity of the cermet is determined by the percolation of the metallic nickel phase ^[1,9,14]. The electrical conductivity

of the reduced support material as a function of nickel content shows a typical S-shaped curve (Fig.1) changing from 0.058 S.cm^{-1} to $1178.78 \text{ S.cm}^{-1}$.

The conductivity of 577.87 S.cm^{-1} was obtained at the point of 40 vol%. Below 30 vol% nickel, the conductivity of the cermet is similar to that of YSZ. Above 30 vol% nickel, the conductivity is about 3 orders magnitude higher, corresponding to a change in mechanism to electronic conduction through the nickel phase ^[1].

2. The relative density and open porosity.

In addition to change in the chemical composition of Ni-based anode-support material during reduction, the porosity of the anode-support samples changed as well. If we assume that the decrease of the overall volume of anode-support material after reduction is negligible and expect the specific volume of metallic Ni is significantly smaller than that of NiO, then the following expression can be expressed for the porosity of the anode-support after reduction prepared by tape casting method without any pore formers,

$$p = p_0 + \frac{\left(\frac{M_{\text{NiO}} \cdot \rho_{\text{Ni}} \cdot V \cdot X}{M_{\text{Ni}} \cdot \rho_{\text{NiO}}} - V \cdot X \right)}{V} \quad (2)$$

Where P is the porosity of the anode-support after reduction, X is the volume percent of Nickel. P_0 is the initial porosity before reduction. M_{NiO} , ρ_{NiO} , M_{Ni} and ρ_{Ni} are molar mass, density of NiO and Ni respectively. V is total volume of the sample. For the examined anode-support material the initial porosity was $P_0 = 0$ (the porosity of the unreduced samples determined by Archimedes method was negligible). For $\rho_{\text{NiO}} = 6.67 \text{ g/cm}^3$ and $\rho_{\text{Ni}} = 8.88 \text{ g/cm}^3$ Eq.(2) yields:

$$P = 0.694X + P_0 \quad (3)$$

As demonstrated in Fig.2, The open porosity increased from 13 % to 42% with the Ni content changing from 26 wt% to 55 wt%. Equation (3) has also been plotted in Fig.2 as a solid line conforming the good agreement with the experimental results.

The minimum porosity of Ni-based anodes approximate up to 30 vol% makes it possible to enables hydrogen to diffuse through the cermet and H_2O to escape from it, while Ni metal has a vital role as a catalyst for electrochemical reactions on the anode side of YSZ and as an electrical conductor in reduced samples. So from the equation (3), we can get the conclusion the Ni vol% should be about more than 43 vol%.

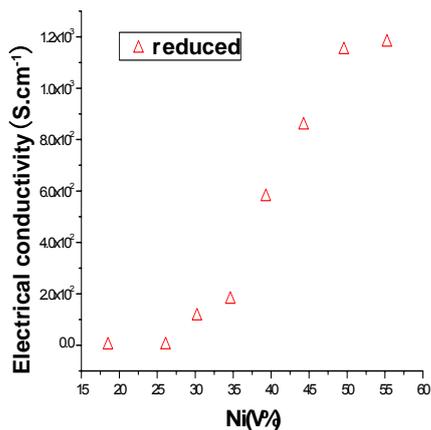


Fig. 1. Electrical conductivity as a function of nickel volume percent of total solids (Ni and YSZ) at ambient temperature in reduced samples.

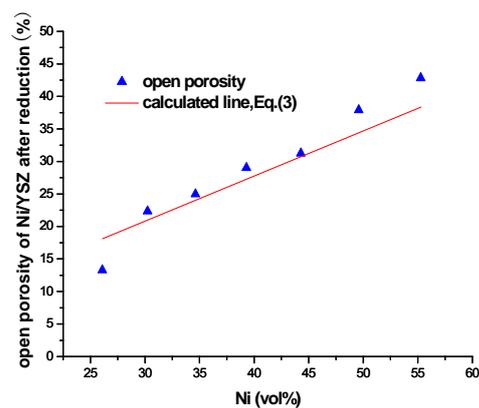


Fig. 2. Open porosity as a function of nickel volume content of total solids in reduced samples

The D_{real} versus $D_{theoretical}$ and density of the unreduced and reduced samples as a function of Ni weight percent has been shown in Fig. 3 and Fig. 4 respectively. The D_{real} versus $D_{theoretical}$ of the samples likely has linear relationship with the nickel content.

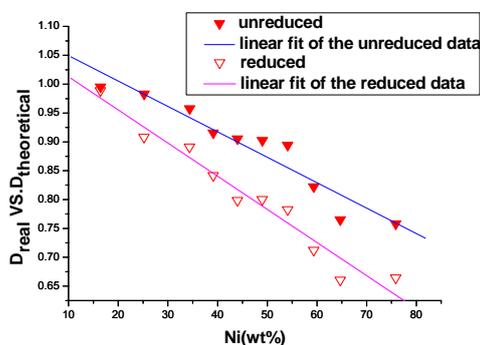


Fig. 3. D_{real} VS. $D_{theoretical}$ as a function of Ni weight percent of the samples before and after reduction

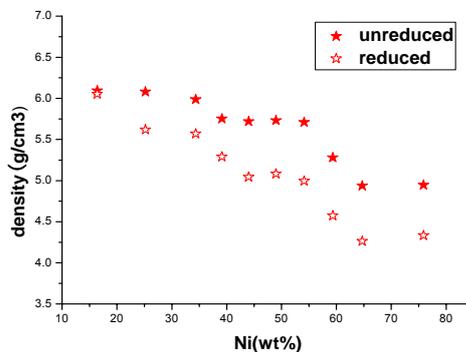


Fig. 4. Density as a function of Ni wt% in reduced and unreduced samples.

The calculated density of the anode support material should be increment by increasing Ni content. But from Fig. 3 and Fig. 4 we got both the density and the D_{real} versus $D_{theoretical}$ of the samples decreased after reduction. As discussed above, the Eq.(2) and Eq.(3) shows that the porosity enlarged with Ni content increasing and higher porosity leads to lower density. In fact the porosity is the dominant factor for decreasing the samples' density in this study, so the density and the D_{real} versus $D_{theoretical}$ of the samples decreased with nickel content increasing.

The porosity of the unreduced samples determined by Archimedes method was negligible but the density decreased which was similar to the reduced

samples (Fig.3 and Fig.4). There must be some close pores in the unreduced samples which lead to larger volume that determined by Archimedes method. So the density of the unreduced samples is smaller than the calculated values. After reduction, the closed pores connected so that the open porosity was a little higher than the calculated line (Fig.2).

3. Flexural strength

The flexural strength increased with the decreasing content of Ni from 228.23MPa to 108.74MPa and from 349.88MPa to 80.75MPa before and after reduction respectively. The results were demonstrated in Fig.5. There has an inflexion between 60 wt% and 65 wt% of nickel content before reduction from 192.07MPa to 108.74MPa. When after 50 wt% the flexural strength decreased more than 25% after reduction, but before 40 wt% the flexural strength increased. With the increasing of the Ni content from 40 wt% to 50 wt%, the flexural strength changed only a little after reduction in this study and at the point of 50 wt% just from 178.97MPa to 179.55MPa.

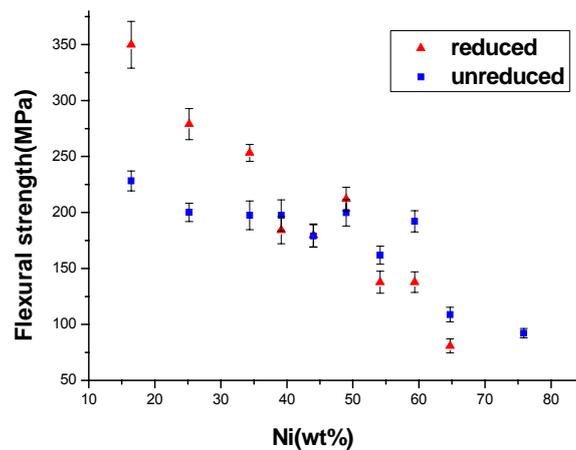


Fig.5. Flexural strength as a function of nickel weight percent both in reduced and unreduced samples. Error bars for flexural strength represent standard deviation

The samples with 20 wt% of NiO before and after reduction were analyzed using FESEM (Fig.6 and Fig.7).

We can get the conclusion from the Fig.6 and Fig.7 that the sample re-sintered after reduction and the grain of the sample increased after reduction. The surface of the sample is similar to the density electrolyte, so that the flexural strength increased after reduction.



Fig.6 FESEM micrographs of surface of 20 wt% NiO-YSZ anode support before reduction

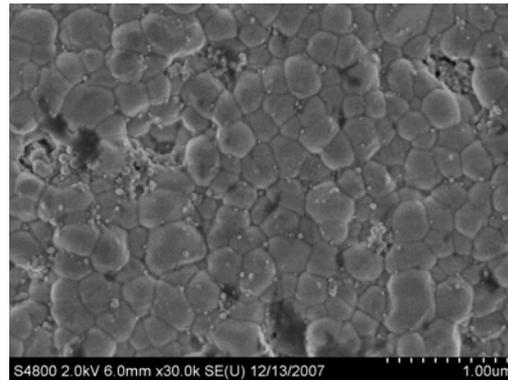


Fig.7 FESEM micrographs of surface of 20 wt% NiO-YSZ anode support after reduction.

Conclusions

In this study, the flexural strength, electrical conductivity, density and open porosity of unreduced (NiO/YSZ) and reduced (Ni/YSZ) anode support materials were studied as functions of nickel content. The electrical conductivity has a typical 'S' shape curve and obvious conductivities were obtained at the 30 vol%. The open porosity as a function of Nickel vol% could be simply expressed by equation $P=0.694X+P_0$, where P is open porosity, P_0 is the initial porosity of the samples and X is Ni vol%. The density was decreased both before and after reduction by increasing nickel content. The flexural strength both increased with the decreasing content of Ni before and after reduction and there has an inflexion between 60 wt% and 65 wt% before reduction from 192.07MPa to 108.74MPa. When the nickel content more than 50 wt%, the flexural strength of the reduced samples decreased more than 25% but before 40 wt% the flexural strength increased. With the increasing of the Ni content from 40 wt% to 50 wt%, the flexural strength changed only a little after reduction in this study and at the point of 50 wt% just from 178.97MPa to 179.55MPa. This study will be used as a guide line for anode support design and it is important to maintain a high conductivity where to increase the flexural strength for anode supported cells.

Acknowledgements

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