MICROSTRUCTURAL AND ELECTRICAL PROPERTIES OF THE SOFC ANODE PRECURSOR YSZ/NiO COMPOSITE PREPARED BY A LIQUID MIXTURE TECHNIQUE

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ABSTRACT

A detailed study of the microstructural and electrical properties of the yttria-stabilized zirconia/nickel oxide (YSZ/NiO) composite was performed. This material is the precursor to the solid oxide fuel cell anode cermet YSZ/Ni. A liquid mixture technique was developed to produce the YSZ/NiO composite to fabricate high-performance SOFC anodes. This technique resulted in fine and homogeneous powders and specimens with high electrical conductivity. The combined results showed that this technique is suitable for the production of the anode cermet.

INTRODUCTION

The performance of the solid oxide fuel cell (SOFC) is closely related to the properties of its components. Thus it is necessary to carefully control the microstructural and electrical properties of each component to enhance SOFC performance. The study of yttria-stabilized zirconia/nickel oxide composites (YSZ/NiO) is motivated by a growing interest in mixed ionic and electronic conductors (MIEC). Also, this composite is the precursor to the SOFC anode cermet YSZ/Ni, which is usually obtained after heat treatment of YSZ/NiO in a reducing atmosphere (1,2). Therefore, controlling the properties of the YSZ/NiO is important for the study of the electrical transport mechanisms of the composite MIEC and a key step in the fabrication of high-performance SOFC anodes (3).

In a composite medium, the nature of the charge carriers and the dependence of electrical conductivity on the relative volume fraction, microstructure, temperature, and oxygen partial pressure are important parameters in electrochemical applications. YSZ is an ionic conductor at a wide range of temperatures and oxygen partial pressures. Transport of oxygen ions is thermally activated with activation energy $\Delta E \sim 1 \text{ eV}$ (4). The stoichiometric NiO is an insulator, though it assumes a p-type semiconductor behavior due to composition deviations where electron holes are created by Ni vacancies (5).

Several different techniques such as solid state reaction (6) and different chemical routes (7-11) have been used to produce the anode cermet precursor. We investigated the
precursor material for SOFC anodes prepared by a modified liquid mixture technique in a wide relative concentration range.

EXPERIMENTAL

A detailed study was performed on the electrical and microstructural properties of the composite \((1-v)\) \((\text{ZrO}_2:8\text{ mol\% } \text{Y}_2\text{O}_3)/v\) \(\text{NiO}\) \((\text{YSZ}/v\text{NiO})\), with \(0 \leq v\) (vol\%) \(\leq 100\), prepared by a modified liquid mixture technique \((10)\). The technique is based on the evaporation of a dispersion of \(\text{YSZ}\) (Tosoh) in a solution of nickel acetate tetrahydrate (Carlo Erba) and ethanol. The powders were calcined in air at 450°C, the minimum temperature for complete organic removal, as inferred from thermogravimetric analysis. The liquid mixture technique produced homogenous and fine powders in which the \(\text{NiO}\) nanoparticles \((d_{\text{NiO}} \sim 15\text{ nm})\) were supported by \(\text{YSZ}\) particles \((d_{\text{YSZ}} \sim 100\text{ nm})\), as observed by field emission scanning electron microscopy analysis \((10)\). Cylindrical pellets were uniaxially pressed and sintered at 1350°C for different times. Figure 1 shows the experimental sequence followed for preparing the \(\text{YSZ}/\text{NiO}\) composite samples.

The relative densities of the specimens were determined by the Archimedes' method and compared to the calculated values obtained by the mixing rule. The phase structure was evaluated using X-ray diffraction (XRD) with \(\text{Cu K}\alpha\) radiation in the 23 to 85° 2θ range.

![Flowchart for the YSZ/NiO composite sample preparation.](Image)

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Rietveld refinements were performed using GSAS software. Scanning electron microscopy (SEM) of polished surfaces was used to observe the microstructure of the samples. The electrical properties of the samples were studied by electrochemical impedance spectroscopy (EIS) measurements carried out in the temperature range 100 to 800°C and frequency range 5 Hz to 13 MHz using Ag contact pads.

RESULTS

XRD and SEM results indicate that the composite was a homogenous mixture of YSZ and NiO. The XRD data showed the diffraction peaks corresponding to YSZ and NiO. No extra peaks belonging to any additional phase were observed, as shown in Figure 2. The good quality of the Rietveld refinements are evidenced by the low values of the reliability factors $\chi^2 \sim 2.2$ and $R_{Bragg} \sim 2.6\%$. Moreover, the refined parameters indicate that the NiO concentration is less than 5% of the nominal added value, and the lattice parameters of both oxides are in good agreement with previously reported data. In addition, the XRD results indicate that the YSZ lattice parameter is independent of NiO content, as shown in the inset of Figure 2. This result suggests that no solid solution between the oxides is formed for samples sintered at 1350°C.

Figure 2. XRD pattern of YSZ/58 NiO sample showing experimental (x) and calculated profiles (solid lines) and difference plot at bottom. YSZ and NiO diffraction peaks are marked by * and +, respectively. The inset shows the YSZ lattice parameter dependence on the NiO content.

Figure 3 shows the SEM micrographs of the YSZ/40 NiO composite samples sintered at 1350°C for $t_s = 1$ hr (Figure 3a) and 4 hr (Figure 3b), and YSZ/58 NiO sintered at 1350°C for 1 hr (Figure 3c). The average grain size of YSZ and NiO of the samples sintered at 1350°C for 1 hr (Figures 3a and 3c) was found to be nearly independent on the relative composition, $\sim 0.8 \mu m$ and $\sim 0.7 \mu m$, respectively, increasing sintering time, $t_s$, and relative composition, $\sim 0.8 \mu m$ and $\sim 0.7 \mu m$, respectively. Increasing sintering time increased the average grain size of both phases. In addition, the micrographs of the YSZ/40 NiO specimens sintered at 1350°C for $t_s = 1$ and 4 hr shown in Fig. 3(a) and (b)
Figure 3. Backscattering scanning electron microscopy images of (a) YSZ/40 NiO composite samples sintered at 1350°C for 1 hr and (b) 4 hr, and (c) YSZ/58 NiO sintered at 1350°C for 1 hr.
indicate larger NiO intergrain separations in specimens sintered for $t_s = 4$ hr, probably due to a larger grain growth rate for YSZ. In fact, it was already reported that NiO particles may inhibit YSZ grain growth (6,11). However, possibly due to the low sintering temperature and small average grain size, we did not observe such an effect.

The electrical conductivity ($\sigma$) obtained from the impedance diagrams exhibited a strong dependence on both $t_s$ and NiO content, as shown in Figures 4 and 5. The YSZ/NiO specimens sintered at 1350°C for 1 hr had high relative densities, ~95% of theoretical values (% TD). Increasing sintering time ($t_s$) up to 6 hr resulted in increasing TD up to ~97%, as shown for the YSZ/40 NiO specimen in Figure 4. The YSZ/40 NiO sample shows a maximum $\sigma$ for $t_s = 2$ hr (Figure 4).

![Figure 4. Sintering time dependence of the electrical conductivity (■) and the theoretical relative density (●) of the YSZ / 40 NiO composite.](image)

![Figure 5. Electrical conductivity dependence on the NiO volume fraction measured at $T = 240, 350, 445, 525$, and $735 \, ^\circ C$ for the YSZ / NiO composite.](image)
The observed behavior is associated with the increase of both relative density and grain size with increasing \( t_s \). For \( t_s < 2 \) hr, the \( \sigma \) increased due to its increasing density with increasing \( t_s \). On the contrary, further increase of \( t_s \) resulted in decreasing \( \sigma \). For this relative composition, slightly above the percolation threshold, it seems that the grain growth observed for \( t_s > 2 \) hr partially disconnects the paths of the electronic charge carriers in agreement with the results in Figure 3 (a) and (b). Moreover, the \( \sigma \) (\( T = 400^\circ \text{C} \)) of YSZ/40 NiO sintered at 1350°C/2 hr is two orders of magnitude larger than the \( \sigma \) values previously reported for similar specimens prepared by a solid state mixture and sintered at 1600°C/4 hr (6). This high electrical conductivity is probably correlated with the absence of solid solution between NiO and YSZ and also the good homogeneity and high density of the samples prepared by the liquid mixture technique.

In fact, the composite samples prepared by the liquid mixture technique were found to have high electrical conductivity, as shown in Figure 5. In addition, as far as charge transport is concerned, three NiO concentration regions were observed (12). In region 1 (\( v < 20 \)), the samples showed a single activation process with activation energy close to that of YSZ (\(-1 \) eV), and the main charge carriers are thus the oxygen ions. Increasing the NiO content, the specimens exhibited a pronounced increase in electrical conductivity, and the percolation threshold was attained at NiO concentrations close to \( v \sim 23 \% \). This can be observed in the \( \sigma \) (\( T = 240^\circ \text{C} \)) data in Figure 5. In region 2 (\( 20 < v < 60 \)), the samples exhibited high electrical conductivity at low temperatures (\( T < 500^\circ \text{C} \)). Two activation processes were observed in the Arrhenius plots (not shown) with activation energies similar to those for NiO (6, 11, 12). In region 2, a mixed conduction is more likely to occur. In region 3 (\( v > 60 \)), the main charge carriers are the electron holes and YSZ particles act as insulating inclusions.

To further investigate the suitability of the liquid mixture technique to produce the anode cermet, the specimens with \( v = 40 \) and 58 \% sintered at 1350°C for 2 hr were heat-treated at 500°C for 10 hr under hydrogen flow of \( \sim 100 \) mL/min. The XRD data combined with Rietveld refinements revealed that the cermet samples were made of YSZ and \( \sim 8 \) and 45 \% Ni, respectively. Figure 6 shows the XRD data for the YSZ/45 Ni...
cermet. The Rietveld analysis indicated that ~3 wt% of residual NiO remains in the cermet. However, XRD analysis performed on both the surface and bulk of the cermet specimens showed no appreciable difference on the NiO residual content. This incomplete reduction is probably associated with the relatively low temperature used for the heat treatment.

The electrical properties of the cermet are also of interest. Electrical dc four-probe resistivity measurements of bar-cut samples were carried out in the 300°-750°C temperature range under He flow, using Ag contact pads and Pt wires. Preliminary results revealed that the cermet exhibited a metallic behavior of the electrical resistivity and high electrical conductivity $\sigma (T = 750°C) \approx 3.8 \text{ (m}\Omega \text{ cm})^{-1}$, as shown in Figure 7.

![Figure 7. Temperature dependence of electrical resistance of YSZ/45 Ni cermet.](image)

**CONCLUSIONS**

The experimental results showed that by the liquid mixture technique, YSZ/NiO sinteractive powders and samples with high electrical conductivity are produced. The electrical properties of the composite can be controlled by both the NiO content and sintering parameters. Indeed, this technique is suitable for the production of high-performance SOFC anodes.

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