ELECTRICAL CONDUCTIVITY AND MICROSTRUCTURE OF Ni-YSZ ANODE PREPARED BY LIQUID DISPERSION METHOD

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ABSTRACT

Nickel - yttria stabilized zirconia (Ni-YSZ) cermet was prepared by dispersing YSZ powder in a nonaqueous nickel nitrate solution followed by milling, drying and calcination. Concentration of nickel was varied between 10 and 60 volume percent (v/o). Samples were prepared by varying sintering temperature (1200-1350°C) and soaking time (2-6h). Hydrogen treatment was done in order to reduce nickel oxide to metallic nickel. Electrical conductivity of the samples was measured in the temperature range of ambient to 1000°C under hydrogen atmosphere. The temperature dependence of conductivity follows Arrhenius behavior. Plot of conductivity against temperature with nickel concentration gives rise to “S-shaped” curves. For each temperature a sudden rise in conductivity at around 30 v/o has been observed. The higher conductivity obtained at > 30 v/o nickel concentration is due to the percolation through interconnected Ni-chains in the YSZ matrix. A detailed microstructural investigation is also reported.

INTRODUCTION

A very common choice for anode in solid oxide fuel cells (SOFCs) is the cermet made of nickel and yttria stabilized zirconia (YSZ) (1-3). The function of YSZ is to support the nickel particles, as well as to inhibit coarsening of the particles during the fuel cell operation and also to maintain the thermal expansion coefficient comparable to those of the other cell components. On the other hand, the electrode materials are required to be highly porous so that the reactant gases can easily come in contact with the electrolyte surface and thereby allow the electron transfer reaction to occur at the electrode/electrolyte/gas triple phase boundary (4-6). At the same time, the electrodes are required to have good electronic conductivity so that ohmic loss is sufficiently small (3,4). Moreover, the material must have good stability under reducing condition at high operating temperature (7-9).

In the present investigation, the material was prepared by a different route than those normally reported and a systematic study was performed to find out the minimum possible nickel concentration required to have sufficient electrical conductivity. An
attempt has also been made to understand the process of pore formation through microstructural investigation.

EXPERIMENTAL

In this investigation, 9 mol% yttria stabilized zirconia (YSZ) powder was prepared following the same technique as used by other researchers (10,11). A mixture of ethanol and water (1:1) is used as a medium to co-precipitate hydrates of Zr and Y in required proportions from mixed solutions of zirconium oxychloride and yttrium nitrate using an ammonical solution. The precipitation was carried out at room temperature and the pH of the medium is maintained at 10 throughout the experiment. The precipitate is then thoroughly washed with double distilled water to remove chloride ion and finally rinsed with methanol to eliminate residual water. The precipitate is then dried at 80°C for 24h followed by calcination at 700°C for 4h in air. Particle size distribution of the powder is measured by Sedigraph-5100 particle size analyzer (Micromerities, USA). The average particle size (d50) is found to be ~1.3μm.

The YSZ powder thus prepared is used as a starting material for the preparation of all the compositions of Ni-YSZ cermet used in the present study. The concentration of nickel used is within 10-60 volume percent (v/o). Powders of different compositions were prepared by dispersing the YSZ powder in a nonaqueous nickel nitrate solution. The details of the preparation procedure are given elsewhere (12). The pressed pellets are sintered in air in the temperature range 1200°C-1350°C for 2h in order to convert NiO to metallic Ni. The formation of YSZ, NiO-YSZ and Ni-YSZ phases was confirmed by XRD using CuKα radiation (Phillips-PW 1730). A step scan with Δ(2θ) = 0.02° was performed with a counting time 4s per step within the interval 70°-78° (2θ). Least square profile refinement was undertaken by PRO-FIT (13) for reflection (400). Rectangular bar shaped samples of dimension 15mm x 3mm x 2mm were prepared by conventional pressing technique. Porosity of the samples was measured by water displacement method. For microstructural study a few representative specimens were examined under optical microscopy (Leitz - Ortholux Pol BK), scanning electron microscopy (Leica S440) and computerized image analyzer (Leica Q500MC). Unfluxed platinum paste was used as contacts for electrical measurement. The resistance of the specimens was measured by four probe technique using a 7-digit multimeter (HP 3458A). For each sample, the measurement was carried out at different temperatures in the range ambient to 1000°C under reducing atmosphere.

RESULTS AND DISCUSSION

The electrical conductivity of the samples measured at 1000°C is plotted in Figure 1 as functions of nickel concentration and sintering temperature. A series of “S-shaped” curves, each corresponding to a particular sintering temperature, is obtained as predicted by the percolation theory proposed for other composite materials (15). Similar results have been reported by few other investigators (4,16). Interestingly, all these plots (as shown in Figure 1) exhibit a sudden change in conductivity at around 30 v/o of nickel,
corresponding to the electrical continuity/discontinuity transition point of the dispersed nickel phase. Electrical conductivity of Ni-YSZ samples increases with increasing nickel concentration, because metallic nickel is known to be around five orders of magnitude more than YSZ at 1000°C (16). As expected, the conductivity also increases significantly with increasing sintering temperature from 1200°C to 1350°C, due to increasing sample density and consequently improved particle-to-particle contact between the nickel particles. The overall electrical conductivity of the samples prepared with 30-60v/o nickel and sintered at 1350°C varied between $2 \times 10^2$ to $4 \times 10^3$ S/cm for a measurement temperature range 100°C-1000°C and follows a straight line behavior when plotted against increase in temperature (Figure 2). The positive slope of these plots is indicative of the predominance of metallic conductivity.

The conductivity of the cermet also depends on its microstructure. A few typical photomicrographs of hydrogen reduced samples with varied nickel concentration are shown in Figure 3. The light and black portions represent one solid phase and porosity respectively. As expected, both the nickel phase and the porosity increase with increasing nickel content. (Figure 3a-c).

Since the acceptable electrical conductivity (at 1000°C) of the anode is obtained with at least 40 v/o nickel content (as shown in Figures 1 and 2), a detailed electrical and microstructural investigation has been carried out for this composition. Other reason to choose such a composition is that upto 40v/o nickel content the thermal expansion coefficient of the composite is within the tolerable limit (1-3). Figure 4 shows the temperature dependence of electrical conductivity of such cermets prepared by varying the condition of sintering, both temperature and time. A set of parallel straight lines are obtained and in each case the conductivity decreases with increasing measurement temperature. The conductivity value obtained in case of samples sintered at 1300°C with soaking times between 2h and 6h (Figure 4a) is within the range of $9 \times 10^2$ - $5 \times 10^3$ S/cm. Similarly, the values are found to be in the range between $4 \times 10^2$ S/cm and $4 \times 10^3$ S/cm for the cermets prepared using a sintering temperature within the range of 1200°C - 1350°C for a fixed soaking time of 4h and are shown in Figure 4b. In addition, the overall conductivity also increases with increasing sintering temperature and soaking time. However, no appreciable change has been observed between the samples sintered at 1300°C and 1350°C (Figure 4b). A similar observation has been found, particularly in those samples where 2h - 4h of soaking period is used (Figure 4b). The overall change of electrical conductivity with sintering schedule used in this study is in good agreement with the corresponding variation of porosity obtained for these cermets.

Figure 5 shows the variation of porosity with sintering temperature and soaking time for samples prepared with 40 v/o of nickel. A maximum of around 55% porosity could be achieved in samples sintered at 1200°C for 2h - 6h of soaking. However, it is possible to prepare sample with porosity values ranging between 25 and 55% by suitable control of sintering parameters.

A distinct correlation between the porosity and the electrical conductivity of the cermet anode of the same composition is depicted in Figure 6. From this figure it is found that the samples with higher porosity values (> 30%) show conductivity in the range of $0.2-2.5 \times 10^3$ S/cm. The porosity of these cermets is also estimated by computerized image
analyzer and is also found to be in the same range as presented in these figures. In addition, the average pore diameter of these samples has also been estimated by the same instrument. Relatively uniform pores with average pore diameter of 0.5 μm is found. Considering these two important properties (porosity and conductivity) the sintering schedule of the cermet having 40 v/o Ni-content has been optimized. Microstructural investigation reveals an increase of porosity consequent to hydrogen reduction treatment which is evident from Figure 7. The dark portions in the micrographs represent the porosity and the white/grey spots are due to the presence of metallic nickel or YSZ in the sample. The sample used for this investigation was sintered initially in air at 1300°C for 2h (corresponding micrograph is shown in Figure 7a). On reduction the NiO phase converts to metallic nickel, there has been an increase of porosity around 10 % due to release of oxygen. A similar result was reported earlier by Dees et al. (4).

Figure 8 reveals certain interesting microstructural features of these cermet samples. The porous structure is evident from the SEM fractograph (Figure 8a). However, the presence of two separate grains namely YSZ and metallic nickel is not clearly visible. On the other hand, the nickel mapping using X-ray back scattering image option available with the SEM indicates a fairly uniform distribution of metallic nickel throughout the specimen (Figure 8b). It is indicative of the fact that all the grains observed in Figure 8a are actually of YSZ with very fine dispersion of metallic nickel. This might have been possible due to the very nature of the preparation technique (liquid dispersion route) adopted in this investigation. It is believed that during sintering at elevated temperature (1300°C) NiO particles diffuse into the zirconia grains due to very fine dispersion of both the phases ending up in the formation and grain growth of NiO-YSZ composite grains. Several morphological models for the Ni-YSZ anode to explain its conduction behavior have been proposed in the literature (4-6). For example, in the model proposed by Maggio et al. (6) formation of two distinct conduction paths, one due to metallic nickel (mainly responsible for higher conductivity) and other due to zirconia (less significant in case of higher Ni-content), have been proposed. However, the metallic nickel mapping as obtained in this study could not provide any signature of metallic segregation in isolated areas of the matrix. On the other hand, the results are indicative of the formation of composite NiO-YSZ grains, which on reduction, form Ni-YSZ composite grains. Detailed X-ray profile analysis also suggests that NiO starts diffusing into the zirconia grains. Such a dissolution of Ni²⁺ caused changes of the lattice parameters of the cubic YSZ shown in Table I. The lattice parameters of YSZ and Ni-YSZ system have been determined from the profile fitting of the (400) reflection.

| Specimen | Lattice Parameter | Reliability Indices |
|----------|-------------------|---------------------|
|          | a_c (Å)           | R_p %               | R_wp %       |
| YSZ      | 5.4103 (3)        | 2.767               | 3.478        |
| Ni-YSZ   | 5.0525 (3)        | 4.042               | 5.144        |

Table I: Estimated lattice parameters of YSZ and Ni-YSZ
CONCLUSIONS

Ni-YSZ cermets have been prepared with varying concentration of nickel within the range of 10-60 v/o. A series of “S-shaped” curves is obtained while plotting the conductivity as a function of nickel content for various sintering temperatures. The electrical conductivity of the cermet exhibits a sudden change at around 30 v/o nickel. The lower value of conductivity (< 30 v/o nickel) is due to conduction through YSZ matrix and the higher value is due to continuous Ni-chain in the cermet. The desired conductivity for using the cermet as fuel electrode is obtained around 40 v/o of nickel content. The cermets (containing 40 v/o of nickel) with wide range of porosity (25% - 55%) is obtained by varying sintering temperature (1200°C-1350°C) and soaking time (2h-6h). Nickel mapping together with precise lattice parameter determination indicates partial diffusion of nickel in YSZ phase and very fine dispersion of metallic Ni within each YSZ grain instead of isolated presence of the two phases.

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Figure 1. Variation of electrical conductivity (measured at 1000°C) as a function of nickel concentration of the cermets at the indicated temperature.

Figure 2. Temperature dependence of electrical conductivity of the samples prepared with nickel concentrations in the range between 30 and 60 v/o.
Figure 3. Typical photomicrographs of the Ni-YSZ cermet anode with different concentrations (v/o) of nickel: (a) 10, (b) 30 and (c) 60 (Magnification 500X for each).
Figure 4. Temperature dependence of electrical conductivity of the 40 v/o Ni-YSZ cermet specimens sintered at different soaking time (a) and temperature (b).

Figure 5. Average porosity vs. sintering temperature for 40 v/o Ni-YSZ cermet specimens at the indicated soaking time.

Figure 6. Variation of electrical conductivity as a function of porosity for 40 v/o Ni-YSZ cermet anode.
Figure 7. Typical photomicrographs of 40 v/o Ni-YSZ cermet (a) before and (b) after reduction (Magnification 500X for both).

Figure 8. SEM fractograph (a) and distribution of nickel (b) in the 40 v/o Ni-YSZ cermet.