EVALUATION OF MECHANOCHEMICALLY SYNTHESIZED NiO/SDC COMPOSITE NANOPOWDERS FOR THE DEVELOPMENT OF NANOSTRUCTURED CERMET ANODES

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ABSTRACT

Composite powders containing 35% NiO, 50% and 65% NiO/SDC have been mechanochemically synthesized. These materials were characterized as existing as 10-20 nm crystallites of NiO and SDC in 50-75 nm agglomerates. Compaction and sintering was achieved at temperatures below 1200°C, yielding composite ceramics with intermediate densities whilst maintaining crystallite sizes below 50 nm. SEM showed that the microstructure consisted of a sub-micron distribution of NiO and SDC domains which upon closer inspection had a sub-structure with 20-70 nm features. Cermet formation at 400°C by reduction in H2 was monitored by measuring the conductivity. The 60 vol% Ni cermet had the highest conductivity of 2.5 S/cm. The optimum Ni content for cermets fabricated was between 50 and 60 vol%.

INTRODUCTION

The development of intermediate temperature solid oxide fuel cells (IT-SOFC) demands a higher performance from the electrolyte and electrodes. To achieve this, strategies include employing thin, highly conductive electrolytes such as samarium-doped ceria (SDC) (1) or designing electrodes featuring highly dispersed electrocatalysts (2). Evident here is a common requirement for an ultra-fine or nano-scale grain structure. To achieve this, nano-sized ceramic precursor materials are necessary.

Mechanochemical processing is emerging as a commercially viable method for the large-scale production of highly dispersed nanoparticulate materials such as ZnO, ZrO2 and CeO2 (3). Furthermore, CeO2 has been doped with Sm (4) yielding nanoparticulate SDC, ideal for the fabrication of nanostructured electrodes and electrolytes. During mechanochemical synthesis, solid state chemical reactions are initiated between reactants during mechanical milling. The microstructure is refined due to continual deformation, welding and fracture of the powder particles leading to the formation of a nanostructured...
composite (5). Agglomeration is avoided by choosing a large volume fraction of an inert, water soluble phase, typically sodium chloride, that keeps nanoscale grains of the desired product phase(s) fully separate. Heat treatment of the as-milled powder maintains this separation during calcination and a water-washing procedure yields nanocrystalline powders of high purity.

For the purposes of constructing a highly efficient fuel cell from the starting materials, an electrolyte layer of <10 μm thick supported on a >250 μm thick, porous cermet anode is desired. While nickel receives criticism for its tendency to form carbonaceous deposits under fuel rich conditions (6), operation in the mixed fuel-air environments of single-chamber fuel cells demonstrated by Hibino (7) has shown that this aspect can be circumvented. The three steps for the development of a fuel cell anode are (i) maximization of the cermet’s conductivity, (ii) optimization of porosity, and (iii) electrochemical performance in a fuel cell. Following the characterization of the NiO/SDC nanopowder starting material, this paper discusses the first step.

For the NiO/YSZ system, most researchers use a 50:50 volume ratio of Ni to YSZ to achieve best performance, a compromise between electrical conductivity (8), anodic polarization (9) and relative thermal expansion coefficients. The NiO/SDC system is sparsely reported in the literature. Ohara and co-workers (2) report a minima in the anodic polarization at a volume ratio close to 50% Ni. More recently, the anode characteristics of a Ni/SDC cermet have been reported (10) but the scale of the microstructure tends towards the micro- rather than the nano-scale.

We report the mechanochemical synthesis and characterization of a selected number of NiO/SDC compositions. These nanoscale composite powders were compacted into pellets and sintered under conditions optimised by dilatometry. The grain structure of the sintered composites is well within the nano-regime and these crystallites appear agglomerated into micron scale pseudo-grains in the microstructure. The ceramic/metal composites (cermets) were formed by the reducing the NiO component to Ni in hydrogen at 400°C. The progress of this reaction was monitored by measuring the resistance, the maximum conductivity obtained of 2.5 S/cm from the reduced 65% NiO/SDC specimen. The mechanochemically synthesized NiO/SDC nanocomposite powders shows promise for the development of IT-SOFC supported on nanostructured cermet anodes.

**EXPERIMENTAL**

The compositions of 35 wt%, 50 wt% and 65 wt% NiO/SDC (subsequently referred to as x% NiO; x=35, 50, 65) were mechanochemically synthesized from mixtures of Ni(OH)₂, SmCl₃, NaOH, Ce(OH)₄ and NaCl. The SDC recipe has been described in previous work (4). Milling was performed for 4 hours on a SPEX 8000 Mixer/Mill in a hardened steel vial using 9 mm stainless steel media at a ball to powder mass ratio of 20:1 and was loaded in a glove box. Heat treatment of the as-milled powder was performed in covered porcelain crucibles in air. Removal of the water soluble phases following heat treatment was effected by washing with de-ionised water, using an ultrasonic bath and a centrifuge. Washing cycles were performed five times, or until the supernatant had an ionic strength <10 ppm. A sample was kept for TEM analysis in a suspension of alcohol before dispersal on a holey carbon grid. The bulk was dried at 60°C for 14 hours.
Phase identification via x-ray diffraction was performed on a Siemens D5000 diffractometer with Cu-Kα radiation. WinFit (Beta Version 1.2.1) was used to extract peak widths and positions from the diffraction data, allowing the determination of crystallite size via the Scherrer equation. A Micromeritics Gemini 2360 Surface Area Analyser was used to determine the specific surface area by a five-point BET method. The equivalent spherical particle size was calculated by $D = 6S/p$, where $D$ is the diameter, $S$ is the specific surface area and $p$ is the density.

Particle morphologies and size distributions were assessed by transmission electron microscopy using a Phillips 430 at 300kV or a JEOL 2000FX at 80kV. High-resolution and energy filtered transmission electron microscopy was performed on a JEOL 3000F microscope equipped with an EDS detector and a Gatan Image Filter system. Energy filtered data was acquired and manipulated using Gatan Digital Micrograph 3. Scanning electron microscopy was performed on a JEOL 3000F (high resolution, 3kV) or a 6400 (15kV).

Dried powders were compacted into cylindrical test specimens in a 12 mm tool steel die. Dilatometry was performed on a Netzch 402EP Dilatometer. Sintered specimens were polished to 800 grit using SiC paper and the densities were determined geometrically and via the Archimedes method. Electrical contact was made on the two faces using Ag paint fired at 700°C for 30 mins or Pt ink (Engelhard A4338A) fired at 1150°C, and Pt wires. The Pt wires were soldered onto WC rods in an airtight Pyrex glass gas flow cell for study under flowing air, argon and 10% H₂/Ar. The ends of the WC protruded from the cell and electrical contact for analysis was ensured by coating the ends with Ag solder. The resistivity of the closed circuit was <33 mΩ as measured by a 4-point milliohm-meter. Current-voltage characteristics were measured using the potentiostat of an EG&G Instruments M6310A Electrochemical Impedance Analyser interfaced the 352 SoftCorr™ III program.

**RESULTS AND DISCUSSION**

**Synthesis and Characterisation of NiO/SDC Nanopowders**

Heat treatment for 2 hours at 700°C was found necessary to ensure the complete formation of a solid solution of Sm in CeO₂ (4). Following heat treatment, the washed and dried nanopowders showed x-ray diffractograms with broad reflections for NiO and SDC. Figure 1 shows the diffractogram for 50% NiO, typical in appearance for the series. Table 1 provides a summary of characterisation data for the NiO/SDC composites showing the XRD crystallite size for NiO and SDC, SDC lattice parameter and BET surface area. Given that the densities of SDC and NiO are relatively close, 7.35 and 7.45 respectively, the mean equivalent spherical particle size was calculated using the composite’s theoretical density.

The fact that the BET particle sizes are approximately twice as large as the crystallite sizes suggests that slight agglomeration is occurring, which was confirmed by TEM examination. The degree of agglomeration was also seen to increase slightly with increasing NiO content and its crystallite size. Presumably, minor inter-particle
agglomeration occurred during heat-treatment or drying. Figure 2 shows a series of energy filtered TEM elemental maps indicating separation of Ni and Ce rich regions. These regions correspond to individual NiO and SDC crystallites. The size of these nanosized crystallites correlates well with the data in Table 1. The elemental map for Sm was too noisy to be meaningful. However, previous investigations show a complete solid solution exists (4). This nanoscale dispersion of NiO and SDC crystallites was observed in the elemental maps for the three compositions studied.

Figure 1. XRD Pattern of 50 wt% NiO/SDC nanocomposite, NiO peaks marked.

Table 1. Summary of BET and XRD characterisation data for NiO/SDC nanopowder.

| Composition | Theor. density, g/cm$^3$ | BET Surface Area, m$^2$/g | Mean Particle size, nm | NiO Crystallite size, nm | SDC Crystallite size, nm | SDC Lattice Parameter, Å |
|-------------|---------------------------|---------------------------|------------------------|--------------------------|--------------------------|--------------------------|
| 35% NiO     | 7.38                      | 39.32                     | 20.7                   | 12.5                     | 14.4                     | 5.4340                   |
| 50% NiO     | 7.40                      | 32.96                     | 24.6                   | 13.6                     | 11.4                     | 5.4315                   |
| 65% NiO     | 7.41                      | 27.69                     | 29.2                   | 16.2                     | 12.3                     | 5.4298                   |

Densification of NiO/SDC Compacts

The high surface area of nanoscale ceramic powders provides a large thermodynamic driving force and imparts a high sinterability. Densification of nanopowders while maintaining a nanoscale grain structure can be achieved by preventing of grain-boundary migration while enhancing grain-boundary diffusion (11). Since the SDC and NiO particles will act as interphase boundary growth inhibitors for each other, it should be possible to obtain a nanostructured composite following an appropriate sintering schedule.
Figure 3 shows the dilatometry curves for compacts pressed of the three compositions heated at 300°C/hr to 1500°C and held for 3 hrs. The temperatures corresponding to the maximum sintering rates were extracted from the derivative of shrinkage rate with respect to temperature. Table 2 presents this data together with green and sintered densities and the crystallite sizes post sintering as determined from XRD. Any strain related broadening in the diffraction patterns for NiO and SDC was insignificant. The compaction pressure was 250 MPa and the dwell time at the sintering temperature was 3 hours in all cases. These specimens were used for subsequent cermet formation and conductivity measurements.
Table 2. Sintering data for NiO/SDC compacts.

| Composition | Temp. at max. sintering rate, °C | Sintering Temp., °C | Green density, % | Sintered density, % | NiO Crystallite size, nm | SDC Crystallite size, nm |
|-------------|----------------------------------|---------------------|-----------------|-------------------|------------------------|------------------------|
| 35% NiO     | 1000                             | 1000                | 50              | 66                | 46.9                   | 34.6                   |
| 50% NiO     | 1175                             | 1200                | 48              | 86                | 41.6                   | 35.5                   |
| 65% NiO     | 1210                             | 1200                | 73              | 87                | 42.7                   | 34.8                   |

It is apparent that a range of densities appropriate for cermet are achievable and a nanoscale grain size has been maintained. Polished and unpolished specimens were examined under the SEM, shown in Figure 4. The dark and light regions on the polished surface are due to backscattered electrons collected by the secondary electron detector, such contrast is visible only because the surface is flat. As SDC has a 2.3 times the atomic weight of NiO it becomes easy to visualise the generation of a backscattered electron signal, even at the relatively low accelerating voltage (3 kV) used in the FESEM. Therefore the light regions are SDC rich and the dark regions are NiO rich.

Figure 4. Sintered 35% NiO composite pellet micrographs: (left) Polished surface, (right) fracture surface.

This microstructure was verified by the collection of a backscattered micrograph which showed identical features in Figure 5 (top-left). Thermal etching this at 1100°C for 30 mins reveals a sub-structure to these ~0.5 mm pseudo-grains in Figure 5 (top-right). The 50% NiO composite was similarly polished and thermally etched, Figure 5 (bottom) shows that the size of these sub-grains is barely resolved in the 50 nm range which is close to the XRD crystallite size. To elucidate this structural evolution and to study the interphase boundary regions, future efforts are focussed on preparing thin specimens for energy-filtered TEM.

Recalling Figure 4, it would appear that a powder consisting of agglomerates that contain chemically distinct and separate nanoparticles has evolved to a dense structure that is chemically separate on a sub-micron scale, yet maintains a nanoscale sub-grain structure. This anomaly suggests that the powder may be agglomerating into larger regions of SDC and NiO prior to compaction due to over-milling, as has been reported to occur in the mechanochemical milling of Ni (5). However, since the exact composition of the sub-
micron domains visible in Figures 4 and 5 has not been measured it is premature to draw conclusions. Future research will examine the homogeneity of the nanocomposite powders on a larger scale and investigate the microstructure of pressed compacts at various stages of sintering.

Figure 5. NiO/SDC micrographs: (Top-left) Back-scattered image of 35% NiO, (Top-right) thermally etched 35% NiO, (Bottom-left) thermally etched 50% NiO, (Bottom-right) close view of sub-grain structure of thermally etched 50% NiO.

Cermet Formation, Properties and Post-Reduction Examination

It was preferable to use Ag paste to achieve electrical contact as the firing temperature was below the sintering temperatures of the composites. However, it was particularly difficult to maintain adhesion between current collector and the 35% NiO composite using Ag paint, Pt ink was found necessary in this case. Ohmic contact between the collector and specimen was assured by examining the shape of the current-voltage curve, shown in Figure 6. The linearity and relative invariance of the resistance as a function of potential suggests that contact resistances are ohmic and will not be of significance during measurements.

The cermet was formed in-situ by annealing the 35% NiO pellet in 100 mL/min of 10% H2/Ar and measuring the change in resistance with time. Figure 7 shows the 35% NiO conductivity increasing to a maximum and then steadily decreasing. This is in contrast to the cermet formation in other two composites, evident as a steady increase in conductivity. The formation of Ni was verified by XRD, the typical crystallite size was 20 nm. The size of SDC crystallites was unchanged. The decrease in conductivity in the 35% NiO specimen below its maximum of 0.053 S/cm is presumably due to reduction of...
cerium oxide and possible loss of mechanical integrity associated with lattice expansion (12). This increase in resistance is of little significance when comparing the magnitude of the cermet's conductivity compared to the cermets with higher Ni contents.

Figure 6. Current-voltage characteristic of a Pt//35% NiO/SDC//Pt specimen.

Figure 7. Cermet formation via reduction of SDC/NiO composites in 10% H2/Ar at 400°C.

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The reduced 35% NiO cermet had a markedly different microstructure than the other two cermets. Figure 8 (left) shows sharp and flake-like fracture surfaces exposed from the now exceptionally fragile specimen. In contrast, the fracture surfaces obtained for the 50% NiO reduced cermet appear far more coherent, consistent with the specimen's superior strength and conductivity. The sharper edges visible in the 35% NiO specimen (left) are most likely result of repeated high temperature firings to ensure contact with the Pt ink, but may also be due to ceria reduction. The 50% NiO derived cermet (right) shows a promising sub-micron grain structure and porosity.

Figure 8. Scanning electron micrographs: (left) reduced 35% NiO cermet fracture surface, (right) reduced 50% NiO cermet fracture surface.

The conductivity measured at 400°C for the 65% NiO derived cermet, 2.5 S/cm, is 2 orders of magnitude larger than the conductivity of the SDC phase, 0.001 S/cm, so it is reasonable to assume that conduction in the cermet is occurring through a percolation network of Ni particles. Figure 9 shows a section of what for similar systems would be an "S" shaped curve. The cermets appear to be electrically conductive above 30 vol% Ni with an optimum conductivity lying between 50 and 60 vol% Ni. This value is significantly higher than the theoretical percolation limit of 16 vol% for random close packing (13), and higher than the 30 vol% Ni limit reported in the Ni/YSZ system (8) at 1000°C. The substantial conductivities of the cermets suggest that they would make ideal anode support structures for an IT-SOFC.

Figure 9. Conductivity of cermets at 400°C.
CONCLUSIONS

Mechanochemically synthesized composites consisting of highly dispersed NiO and SDC nanocrystals have been fabricated into ceramic bodies by pressing and sintering. The grain structure of these composites consisted of sub-micron pseudo grains with a nanoscale substructure visualised by SEM and confirmed by XRD. The resistance of these compacts was monitored as they were annealed in a reducing atmosphere. The highest resistance obtained was 2.5 S/cm for a cermet containing 60 vol% Ni. The optimum composition for the fabrication of porous cermets from sintered compacts of this material lies between 50 and 60 vol% Ni. Mechanochemically synthesized nanocomposites are ideal precursor materials for the fabrication of nanostructured anode supports in an IT-SOFC.

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