RELATIONSHIPS BETWEEN FABRICATION PROCEDURES, STRUCTURE AND CONDUCTIVITY OF Ni/YSZ CERMET ANODES

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ABSTRACT

A number of Ni/yttria stabilised zirconia (YSZ) cermet anodes for solid oxide fuel cells (SOFC) were examined to determine structural requirement, and in-plane conduction based on fabrication techniques. YSZ was prepared using 1100°C and 1400°C calcining temperatures and ball milling and centrifugal milling procedures to vary the particle size and particle distribution. Alternative paint compositions using methyl ethyl ketone (MEK) and ethanol and various binders were examined with the resulting slurries being air sprayed onto YSZ substrates. Sintering temperatures of 1250°C to 1450°C were used to determine the degree of sintering of both ceramic phases. Optical microscopy and scanning electron microscopy (SEM) were used to determine the structure of the resulting anodes. The resultant Ni/YSZ cermet anode required a relatively high density in order to obtain electronic conduction.

INTRODUCTION

The Ni/yttria stabilised zirconia (YSZ) cermet is one of the most promising anode materials for the solid oxide fuel cell (1). Intensive work concerned with the optimisation of the electrical and structural properties of this material is being carried out in many laboratories (2,3). The bulk of this work is concerned with fabrication techniques ensuring continuous Ni and YSZ networks throughout the anode structure and adequate adhesion of the anode layer to the electrolyte. There are a number of programmes dedicated to long term stability studies and the prevention of Ni agglomeration at the operating conditions of the fuel cell (4,5). It has been shown by Kawada et al. (6) that the particle size ratio of Ni/YSZ is very important for the...
performance of a cermet anode. Murakami et al. (7) suggests that a YSZ particle size of 0.5μm was suitable for maintaining electrode structure and electronic conductivity. The small particle size of the YSZ inhibited the agglomeration of the nickel particles at the operating temperature of 1000°C, thus maintaining a high nickel surface area. This gave increased nickel-nickel particle contact, and therefore increased conduction. A high surface area also reduces interfacial resistance, thus concluding that the reaction area in the anode is related to the nickel surface area, which implies that a long triple phase boundary (TPB) is essential for high performance.

Dees et al. (8) determined that increasing the YSZ particle size, while maintaining a constant nickel particle size, increased the conductivity, because as the YSZ particle size increased, the nickel-nickel particle contact becomes more intimate, the nickel phase is able to more completely cover the surface of the YSZ matrix. Bagger et al. (9) explained that by pre-calcining a certain percentage of the YSZ component, thereby changing its particle size, provided a broader particle size distribution and thus improved packing efficiency, and hence conductivity, of the anode. A range of particle sizes were also used by Murakami et al. (7) to investigate the effect of porosity on anode efficiency. Porosity values from 65% to 85% were examined, and it was concluded that the anode interface was unaffected by this variation.

Since electrochemical characteristics of the electrode are strongly affected by its morphology, it is necessary to investigate the relations between fabrication procedures and the microstructure. In the present study, Ni/YSZ cermet anodes have been fabricated to examine structural and conduction properties. Calcining temperatures, particle sizes and slurry compositions were varied in order to determine their effect on the anode microstructure and in-plane electronic conductivity.

**EXPERIMENTAL**

8mol%YSZ (Tosoh TZ8Y) pellets (30mm diameter) were pressed using an uniaxial die-press, at 7MPa and sintered at 1600°C for 6 hours, to produce a dense substrate suitable for the application of the anode system. The anode materials were modified by calcining and milling them to produce the appropriate particle sizes. The YSZ powder was in the form of 40 to 50μm porous agglomerates, which were calcined at 1100°C and 1400°C. After sintering, the YSZ was milled, using a ball mill and a centrifugal mill (Retsch) to crush the agglomerates. A 50mL milling container, with 25mL of ethanol and 10 partially stabilised zirconia (PSZ) grinding balls (10mm diameter), were used for ball milling. Various particle sizes were produced ranging from 5μm to 25μm diameter. NiO (Ajax Chemicals 99%) was crushed in the centrifugal mill to produce a large particle distribution from 0.2 μm to 1 μm. Scanning electron microscopy (Hitachi S4000) and a particle size analyser (Malvern Mastersizer) were used to determine particle size and particle distribution, respectively.
The anode powder was fabricated from YSZ and NiO with a 50vol% Ni ratio, mixed with a solvent, methyl ethyl ketone (MEK) or ethanol and a binder, polyvinyl pyrrolidone (PVP), polyvinyl butral (PVB) or Hypermer KD1™ (ICI Americas) to produce a slurry for wet powder spraying. NiO and 5wt% binder were mixed with ethanol or MEK and milled for 24 hours in a ball mill. After the first 24 hours, the YSZ powder and 5wt% binder were added to the already milled NiO and further milled for another 24 hours.

Wet powder spraying (10) was the method of choice for applying the anode to the YSZ substrate. The spraying system consisted of a Badger air powered spray gun which draws the anode slurry into the air stream, propelling it towards the target. The slurry was sprayed onto the YSZ pellets in three layers, the first being approximately 10μm in thickness, and subsequent layers were 40μm in thickness to eliminate the mudcracking-effect when only one thick layer is applied. Each layer was sintered before applying the next, and temperatures ranging from 1300°C to 1450°C were used for sintering, in order to determine the effect of sintering temperature on YSZ and NiO agglomeration.

Reduction of the NiO was performed in a 100% hydrogen atmosphere tube furnace at 700°C for 1 hour. The resulting anode layers were then prepared for optical microscopy by vacuum impregnation of epoxy resin (Struers Epofix) and subsequent polishing to a 1μm finish using a Struers diamond polishing paste. Magnification of up to 1500x was used to observe the microstructure using an Olympus BO71 optical microscope with a C-35DA-2 camera attachment.

**RESULTS AND DISCUSSION**

The YSZ agglomerates were calcined at 1100°C and 1400°C to vary the degree of sintering (11). Scanning electron micrographs of the YSZ particles showed two very different agglomerates as seen in Figs 1(a) and 1(b). The fine particles of agglomerated YSZ, calcined at 1100°C, had partially sintered together forming a porous structure, whereas the YSZ calcined at 1400°C showed a highly sintered structure with no porosity present. Each YSZ grain had sintered to the adjacent grains.

Ball milling and centrifugal milling were used to crush the YSZ agglomerates to the appropriate sizes. The YSZ calcined at 1100°C was ball milled for varying amounts of time, and particle size analysis was performed. Two individual particle sizes were present in the milled samples. These were the semi-crushed agglomerates, and the individual YSZ (0.3μm) grains. Figs 2(a) and 2(b) show the two particle size distributions obtained from each of the sintering temperatures used. The two particle sizes in each graph relate to the crushed agglomerates and the individual YSZ grains. Ball milling of the YSZ sintered at 1100°C for 10 hours produced a particle size of...
11\mu m and a particle distribution showing the two distinct sizes. Fig 3. shows the crushed particles after the milling procedure. After ball milling for 26 hours, the particle size was reduced to 5\mu m, with a very large amount of the fine YSZ grains also present. Table 1 lists the particle sizes obtained with the specified milling times using a ball milling technique. Centrifugal milling of the YSZ calcined at 1400°C produced a smaller particle size distribution. After 5 hours a particle size of 5\mu m was achieved as described in Table 2. The resulting particles produced from the centrifugal mill were very irregular in shape and thus had a large surface area, and therefore a larger reaction area in the completed anode is expected.

Table 1. Table showing the reduction of particle size of YSZ sintered at 1100°C with increasing milling time using a ball milling technique.

| Time (hours) | Particle Size (\mu m) |
|--------------|-----------------------|
| 4            | 25                    |
| 6            | 20                    |
| 10           | 11                    |
| 18           | 7                     |
| 22           | 6                     |
| 26           | 5                     |

Table 2. Table showing the reduction of particle size of YSZ sintered at 1400°C with increasing milling time using a centrifugal milling technique.

| Time (mins) | Particle Size (\mu m) |
|-------------|-----------------------|
| 30          | 20                    |
| 45          | 14                    |
| 60          | 9                     |
| 180         | 7                     |
| 300         | 5                     |
| 420         | 3                     |

Different paint formulae were tested by varying the solvent and binders. Methyl ethyl ketone was mixed with Hypermer KD1™ dispersant, and the anode powder and air sprayed onto the YSZ substrate. It was discovered that the MEK evaporated
immediately after leaving the spray gun and thus the anode powder arrived at the substrate in a dry state, and therefore could not pack down sufficiently to produce a working anode. Fig 4. shows a micrograph of a sprayed anode after sintering using the MEK based paint. The paint solvent was changed to ethanol and the binder/dispersant changed to PVP which produced a slurry with no visible settling-out, in the time taken to spray an anode layer.

The anode layers were applied using the air spraying method. It was found that the thickness of the applied anode layer was critical to inhibit the baked mud-type cracking in the final sintered anode. Firstly, a thin (10µm) anode layer was applied and sintered to provide a key for the subsequent layer to adhere to. Following layers were applied to a total anode thickness of approximately 100µm.

The drying process immediately after spraying was found to be very critical. There is an optimum time to allow the anode to dry, depending on the thickness of the layer applied. There must be sufficient time for the anode powder to densify, but, if drying takes too long, the YSZ can settle before the finer NiO powder, thus forming a NiO-rich layer on the surface of the anode. The dispersion properties of the paint formula were verified with optical micrographs of anodes showing no layering effects after deposition (Fig 5.).

Three sintering temperatures were tested, these being 1300°C, 1400°C and 1450°C. At the sintering temperature of 1400°C, the NiO agglomeration was not so obvious, but, density was too low for adequate electronic conduction. The 1300°C sintering temperature was high enough to sinter the active YSZ, producing an adhering anode layer, and no agglomeration of the NiO was observed. Fig 6 shows that the particle size of the Ni after sintering and reduction has not significantly increased. Conductivity was observed for the anode sintered at 1300°C. This was due to the high density of the anode structure creating the continuous Ni phase essential for electronic conduction.

It was found that at 1450°C there was significant agglomeration of the NiO causing a very high resistance in the final anode after reduction. Fig 7(a) shows the particle size of the NiO (4-5µm) after sintering, compared to the original particle size of 0.5µm-1µm. Fig 7(b) illustrates the same anode after reduction in hydrogen. The porosity of the anode is very high, and all the fine Ni has agglomerated into 4µm particles, therefore no continuous Ni paths are present.

CONCLUSIONS

The present investigation has revealed that the particles of YSZ sintered at 1400°C were dense and consequently very hard. The resulting particles after centrifugal milling were very irregular in shape, thus had a large surface area which could give a larger
reaction area (TPB) in the completed anode. The binder and solvent used for spray painting was critical to ensure a high density electrode after sintering. There was an optimised sintering temperature of 1300°C that was high enough to sinter the active YSZ, but not too high to cause the NiO to become mobile and agglomerate. Electronic conductivity was improved with the increase in density of the anode.

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Fig 1(a). YSZ agglomerates after sintering at 1100°C showing degree of sintering.

Fig 1(b). YSZ agglomerates after sintering at 1400°C showing degree of sintering.

Fig 2(a). Particle size distribution of YSZ sintered at 1100°C and ball milled for 10 hours.

Fig 2(b). Particle size distribution of YSZ sintered at 1400°C and milled for 5 hours.
Fig 3. Micrograph of YSZ particles after ball milling showing two particle sizes.

Fig 4. Micrograph of sprayed anode layer using MEK based paint.

Fig 5. Micrograph of sprayed anode showing homogeneous microstructure.

Fig 6. Micrograph of anode sintered at 1300°C showing high density.

Fig 7(a). Micrograph of anode showing particle size of agglomerated NiO after sintering at 1450°C.

Fig 7(b). Micrograph of anode showing the individual Ni islands after reduction.