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Synthesis and properties of dense nickel and cobalt zirconia cermet anodes for solid oxide fuel cells

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Porous Ni/Zirconia cermets have been traditionally used as anodes in solid oxide fuel cell configurations. They show excellent catalytic activity towards hydrogen oxidation as well as a number of other attributes. However, they are prone to sintering during long term operation, thus causing a drop in the efficiency of the cell. This paper describes the fabrication and properties of a dense cermet which, we suggest, may act as an intermediate layer between the electrolyte and the porous anode and possibly reduce anode degradation. Co and Ni based cermet systems were investigated and a 30 vol % Co/zirconia system could be fabricated with less than 20% porosity after being sintered at 1300 °C.

1. Introduction

Nickel–yttria stabilized zirconia (YSZ) cermets are currently utilized as anode configurations for solid oxide fuel cells (SOFC). Intimate contact between Ni to Ni, Ni to YSZ and YSZ to YSZ is required [1]. The nickel and YSZ systems should form continuous electronic and ionic pathways, respectively, through the anode, and with the H_2 oxidation reaction occurring at the triple phase boundary, optimization of this contact must be considered. Hence, many authors have concentrated on optimizing the fabrication techniques to produce an anode configuration with good adherence to the electrolyte, a continuous pathway and a large number of triple points [1, 2]. However, an area that has recently received serious attention is the long term stability of the anode under the environments likely to be present [3].

Kawada *et al.* [3] and Elangovan and Khandkar [4] have suggested that control of the preparation technique is a very important factor in controlling the electrode stability and performance. It is apparent that optimization of the anode involves increasing the Ni–YSZ gas boundary which can be achieved by decreasing the size of the Ni particles. Dees *et al.* [5] and Kawada *et al.* [3] have reported a relationship between the polarisation properties of the material and the morphology. Elangovan and Khandkar [4] reported that the polarization properties can be lowered by decreasing the Ni grain size and thus reducing the sintering phenomena often observed in those systems, although this was found to have only a limited effect in the work of Kawada *et al.* [3]. Mogensen and Lindegaard [6] suggest that two partial reactions contribute to the anode polarization resistance with one being strongly dependent on P_{H_2}.

Alternative cermet systems and metal oxide based anode systems have also been reported to improve stability, reduce anodic overpotentials and possibly allow for internal reformation of, for example, methane [7].

Takahashi *et al.* [8] and Mogensen *et al.* [9] have investigated CeO_2 based systems as candidates for internal reforming anodes. Schouler and Kleitz [10] have looked at CeO_2–YSZ composite materials. Other metal-cermet systems have included Co, Ag and Mn as possible candidates for anode improvements [11, 12].

In this present paper the fabrication and properties of a dense Ni–YSZ and Co–YSZ ceramic metal composite material is investigated. It can be postulated that a dense layer can be sintered onto the zirconia electrolyte, allowing for ionic and electronic pathways to be well established. The highly dense material allows for wetting of all the nickel or cobalt particles to occur, which greatly reduces the metal particles in the anode configuration from sintering. This paper describes how a dense cermet layer can be fabricated which could be sandwiched between a non-dense cermet material and the zirconia electrolyte, possibly allowing for reduced sinterability in the porous layer.

2. Experimental methods

Ni (Riedel-deHaën, 99.9 %), yttria fully stabilized zirconia (FSZ) (Tosoh 8YSZ) and Co (Aldrich 99.8 %) electrode powders were used to synthesize the cermet materials. Ni (20–50 vol %)/FSZ and Co (20–50 vol %)/FSZ cermets were prepared by mixing the appropriate amounts of the oxide materials in a polyethylene jar containing partially stabilized zirconia (PSZ) grinding

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media in ethanol, for 24 h. 5 wt % of oleic acid was added as a pressing aid and the sample was milled for a further 15 min. After removal of the grinding media, the ethanol was evaporated and the samples were put through a 600 μm sieve. 4g of powder were die pressed in a 20 mm die at 100 kPa for 1 min. Half of the batch prepared was isostatically pressed using a CP3 Isostatic press at 400 MPa.

The pellets were dried in an oven, using a flow of N_2 and ramped up to 450 °C at 0.5 °C min^{-1}, to carefully remove the oleic acid. The samples were then placed into a high temperature furnace and fired at between 1000–1400 °C for 2 h, in an Ar atmosphere.

The porosity of the pellets was obtained using the standard Archimedes technique. X-ray diffractometry (XRD) was undertaken on the samples with a Philips APD 1700 automated powder diffractometer using Co K_α radiation. This was used to see if any spurious peaks were present, other than those for the Ni, Co or FSZ. In all the samples examined, no other phases were found. Scanning electron microscopy (SEM) was undertaken using a Hitachi Model S4000 microscope interfaced to a Kevex microanalyser system. 4-probe dc conductivity measurements were undertaken on the samples using a Hewlett Packard 34401A multimeter.

3. Results and discussion

Fig. 1 shows the effect of sintering temperature on the porosity of the 30 vol % Ni and Co–FSZ samples. In general, as the sintering temperature was increased from 1100 °C to 1300 °C, the porosity of the samples decreased, almost linearly. The Co based cermets had less porosity than the Ni based cermets and the isopressed samples (CIP) were found to have lower porosity than the die-pressed samples. It is apparent that sintering the cermet samples to less than 10% porosity (> 90% dense) is very difficult, primarily due to the low sinterability of FSZ at temperatures below 1300 °C. A very high density may not be necessary in the dense-layer, because the increased porosity may allow for an increased triple boundary, while also acting in a way to reduce the sintering of the metal in the upper porous layer. This proposed "sandwich" electrode may prove successful if the dense layer has some porosity, increasing the overall catalytic active area. Previous work by Kawada *et al.* [3] has shown that the overriding factor in producing a stable electrode is that of preparation technique. Kawada *et al.* [13] in another publication reported no improvement in the performance of Ni–FSZ by doping with Ce and again suggested that control of the preparation technique to be the single most important factor. This point must be considered even though against the work of Miyamoto *et al.* [14] who showed that modification of the FSZ surface with, for example, Ce improved the conductivity behaviour, and improved the long term stability. Kawada *et al.* [3] have also suggested that the Ni powder source is not important towards the anode polarization, but suggested precalcination of the electrode powders prevented Ni from sintering.

What we are suggesting here is that control of the sinterability of the dense layer, by conventional cermet technology, can allow for the upper porous layer to be controlled by this dense layer.

Fig. 2 shows the effect of porosity on increasing the metal content (Ni and Co) in the cermet system. Isopressing (CIP) the material is found to be advantageous in all cases. However, in general, increasing the amount of metal, had little effect on the porosity of the cermet, with only a very slight decrease, up to 40 vol % metal. This is slightly contrary to the literature which suggests that a high Ni content increases the sinterability of the system [8]. At 50 vol % metal however, a dramatic decrease in the porosity was noted, with less than 10 vol % porosity found for the Co-cermet and approximately 12 vol % porosity found for the Ni-based systems. The high sinterability of the cermets with higher vol % metal can be

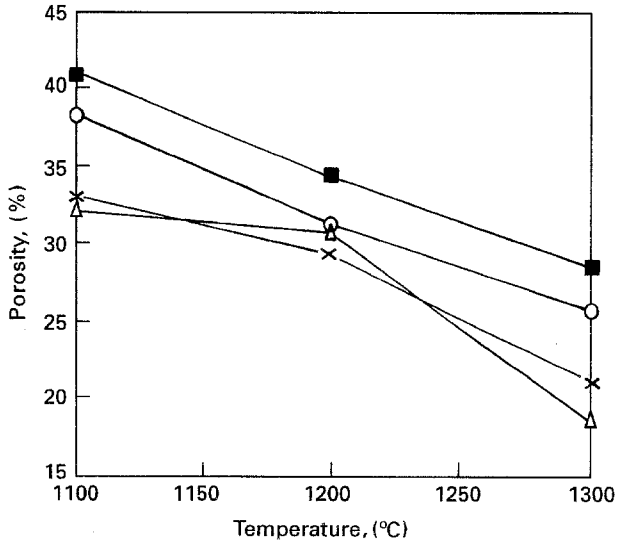

Figure 1 Percentage porosity with increasing temperature for the Ni and Co based cermet systems. (■) 30 vol % Ni, (○) 30 vol % Co, (×) 30 vol % Ni (CIP) and (Δ) 30 vol % of Co (CIP).

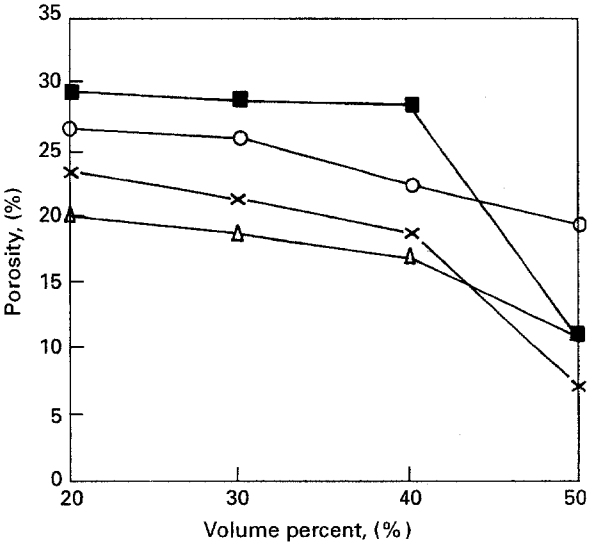

Figure 2 Percentage porosity with increasing vol % Ni and Co, in the cermet material, fired at 1300 °C. (■) Ni, (○) Co, (×) Ni (CIP) and (Δ) Co (CIP).

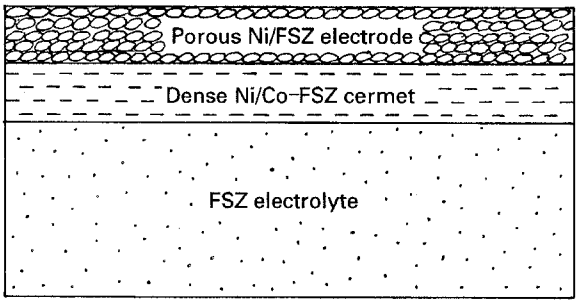

Figure 3 Pictorial representation of the anode "sandwich".

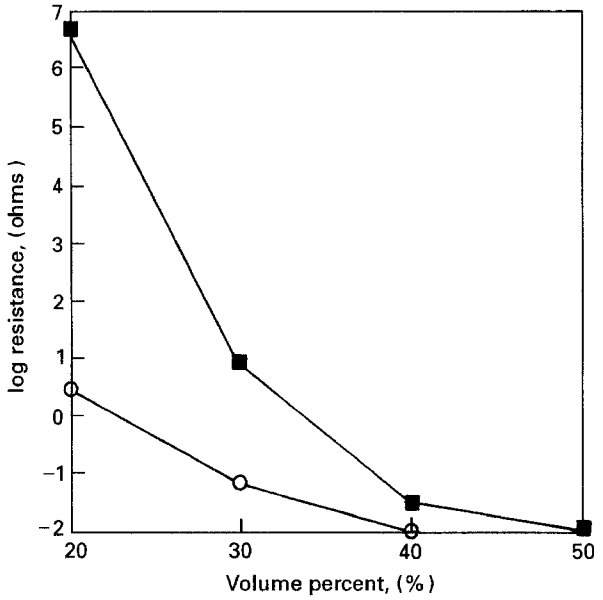

Figure 4 Resistance of the (■) Ni and (○) Co based cermets, with increasing vol % metal content (sintered at 1300 °C, isostatically pressed).

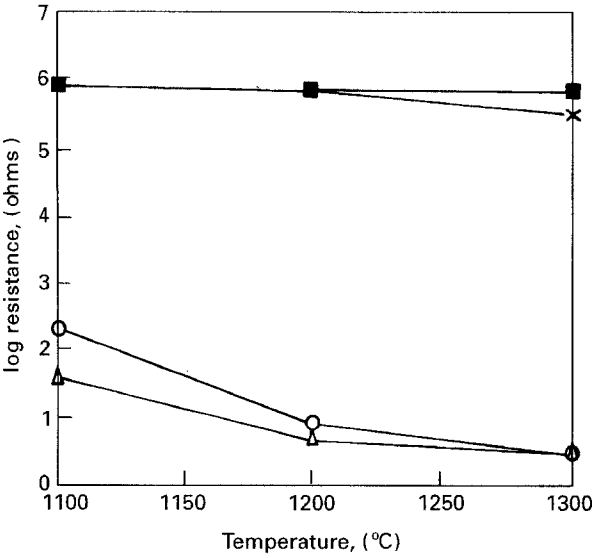

Figure 5 Resistance of the 20 vol % Ni and Co based cermets, with increasing sintering temperature. (■) 20 vol % Ni, (○) 20 vol % Co, (×) 20 vol % Ni (CIP) and (Δ) 20 vol % Co (CIP).

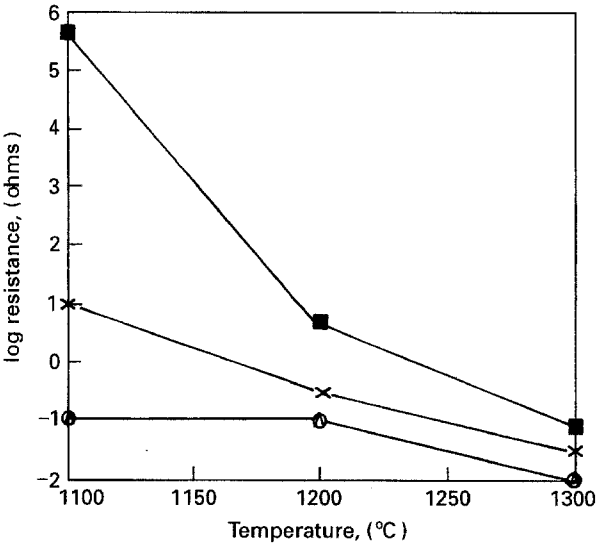

Figure 6 Resistance of the 40 vol % Ni and Co based cermets, with increasing sintering temperature. (■) 40 vol % Ni, (Δ) 40 vol % Co, (×) 40 vol % Ni (CIP) and (○) 40 vol % Co (CIP).

explained in terms of the higher sinterability of the metal versus that of the FSZ.

The anode design considered in this model has the configuration as shown in Fig. 3. The dense layer in the sandwich allows for O^{2-} and e^- mobility, via the continuous metal and FSZ phases. The boundary between the dense layer and the porous metal/FSZ cermet layer (which may have a different metal vol %) is an area of concern since it may not sinter, because of the low porosity of the dense layer. It is postulated that this will reduce the sinterability of the porous top layer, allowing for the high number of triple points, for the oxidation reaction, to remain and thus improve the long-term stability of the overall anode configuration. Some porosity in the dense layer will, however, increase the number of triple points available for reaction without being detrimental to the long term stability of the anode.

Fig. 4 shows the dc resistance of the Ni and Co cermet samples (iso-pressed) with increasing metal content, when sintered at 1300 °C. For the Ni cermet, it is apparent that below 30 vol % Ni, the electronic resistance approaches that of the FSZ material, which is in accordance with conventional percolation theory [15]. In general, most anode systems have Ni contents greater than 30 vol %. However above 30 vol % there is a greatly increased electronic conductivity. As the pellet sizes remained the same, the resistance values can be used for comparative purposes. It is also very apparent, that the Co based system at 20 vol % was far superior to that of the Ni based cermet. The 20 vol % Co/FSZ cermet showed a very low resistance, possibly due to the higher sinterability of the overall system. This may be very beneficial to the overall anode configuration if Co acted as a key for the porous electrode. Figs 5 and 6 show the effect of increased sintering temperature, on the resistance of the Ni and Co based cermets, at 20 vol % and 40 vol % metal, respectively.

It is interesting to note that increasing the sintering temperature has very little effect on the 20 vol % Ni–FSZ sample, but slightly lowers the resistance of the 20 vol % Co–FSZ sample. Cobalt is more highly sinterable and therefore, even at low vol % metal

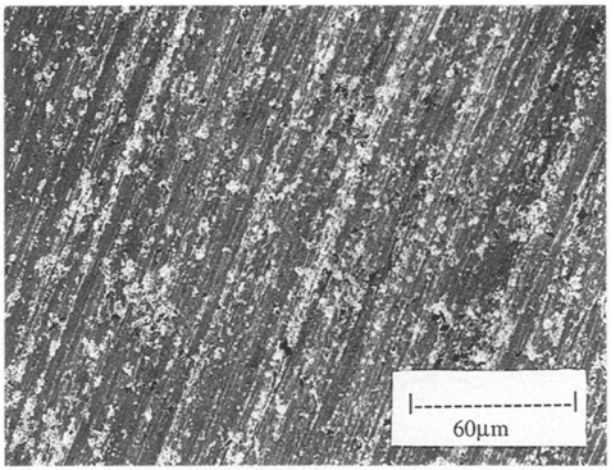

Figure 7 Scanning electron micrograph of the 30 vol % Co based cermets, fired at 1300 °C.

content, produces pathways that allow for electronic conduction to occur. Fig. 6 shows the effect of temperature on the resistance of a 40 vol % Ni–FSZ cermet sample. The increased conductivity is very apparent at temperatures below 1200 °C, particularly for the die-pressed samples. What is also apparent is that temperature has little effect on the Co based cermet systems, possibly due to their relative high-sinterability at low temperatures.

Fig. 7 shows a typical SEM micrograph of the 30 vol % Co–FSZ cermet after having been sintered at 1300 °C. What is apparent is the high density of the material and the even distribution of the 2 phases, which would allow for an anode "sandwich" to be prepared. Work is now underway to fabricate the anode described in this paper and to investigate the stability of such a system [16].

4. Conclusions

Ni and Co based cermet anodes can be synthesized with densities greater than 80 % theoretical at metal contents less than 30 vol %. The resistance of 30 vol % Co based cermets is less than $10^{-1}\,\Omega$, while for Ni based systems the resistance is less than 10 Ω. In principle a dense cermet layer can be fabricated with high conductivity and low porosity ($< 20\,\%$) which may allow for increased stability of a SOFC anode layered on top of the dense layer, which will be the subject of our next paper [16].

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