

Wet powder spraying of a cermet anode for a planar solid oxide fuel cell system

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Planar solid oxide fuel cell (SOFC) systems offer advantages over tubular designs especially with respect to their ease of fabrication [1]. New ceramic processing technology has enabled thin zirconia electrolyte plates to be fabricated with much lower voltage losses. The development of the SOFC cell has hinged around the cell performance and it has been shown that the Ni–yttria fully stabilized zirconia (FSZ) cermet anodes have much higher overvoltages when compared to the La(Sr)MnO₃ cathodes [2]. As such, development of the SOFC cell has concentrated on excellent electrode performance and methods of preparation and adhesion [3]. Most of these methods involve the use of expensive equipment and are very time consuming. However, the planar SOFC systems can be developed using non-vacuum techniques that enable thin, homogeneous electrodes to be adhered to the electrolyte. Techniques for adhesion of the anode onto the electrolyte have included slurry painting and wet powder spraying [4]. The work of Kawada *et al.* [5, 6] showed that the electrode characteristics were very dependent on the preparation method when using a slurry painting technique, and little control of the thickness of coating was apparent. Ruder *et al.* [7], however, used a wet spraying technique as a surface application process to produce thin electrode coatings. Wet powder spraying primarily involves spraying a powder–carrier–binder mixture onto a surface by means of an air-brush. The principal steps involved in the wet powder spraying process are mixture preparation, spraying, drying and sintering.

The NiO powder was synthesized using a standard solid state method [8]. The particle size of the powder was determined using a Malvern particle size analyser and a milling schedule was implemented to ensure particle sizes of less than 1 μm . The correct volume proportions of the NiO and the fully stabilized zirconia powder (8 mol % Y₂O₃ stabilized zirconia, provided by Tosoh, Japan) were put into a 30 ml vial with half the volume of the vial containing 95% ethanol and the FSZ grinding media. The sample was then milled for 24 h, separated from the grinding media, poured into petri dishes and heated at 90 °C until evaporation of the ethanol had occurred. The powders were then removed from the dishes and placed into platinum crucibles and fired at 1200 °C, using a slow heating and cooling rate ($\pm 5\text{ }^{\circ}\text{C min}^{-1}$), for 2 h. Each sample was then re-ground to remove any agglomerates present. The cermet was then added to methyl-ethyl ketone (as the carrier phase), sodium-free cooking spray (as the

dispersant) and poly vinyl butyral (PVB) (as the binder) and mixed for 2 h, in a sealed container, to form a semi-stable, homogeneous, dispersed slurry which had a viscosity (measured using a Brookfield viscometer, with a micro-sample adaptor) of 60 cP. Table I shows the typical composition of the “paint” for application as an anode onto an 8 mol % Y₂O₃ FSZ electrolyte, 5 cm \times 5 cm \times 150 μm thick, for fabrication into a single or multi-cellular SOFC system.

The slurry was placed into an air-spray gun (Badger air-brush system) with a continual supply of high pressure air to aid in the mixing of the cermet while spraying. The quality of the spray stream, which consequently controlled the coating thickness and uniformity, was controlled by the spray velocity, the distance and angle between the air-brush nozzle and the substrate, and the number of passes. The FSZ electrolyte was washed in ethanol and calcined at 500 °C, prior to the application of the anode coat. All electrolytes were stored in a desiccator just before they were to be fabricated into single cells. The air-brush was then used to spray an even coat of the cermet onto the electrolyte and the system was sintered at 1300 °C for 2 h (using a slow heating and cooling rate). The spraying parameters were varied to achieve a porosity of 30–50% estimated by the linear intercept method [7]. During air-brushing, the mixture should arrive at the substrate in a semi-dry condition due to the evaporation of the carrier phase. This semi-dry condition is preferable, because uncontrolled dripping and wetting can be avoided. The method was used to spray even thin layers of the cermet onto the substrate and consequently build up a layer about 50 μm in thickness. A small spray bay has been set up to provide an area for clean contamination-free spraying, using a fixed, or variable, spraying distance with excellent reproducibility. After the sintering stage had been achieved, the sample was then reduced in a N₂/H₂ (saturated with water) atmosphere tube furnace at

TABLE I Typical composition of the anode “paint” for air-brushing onto the electrolyte

Sample	Composition (wt %)
Correct NiO ^a /FSZ sample	50
PVB (binder)	2
Sodium-free cooking spray	12.5
Methyl-ethyl ketone	35.5

^aUsually NiO, although other oxides, including CeO₂, have been investigated.

900 °C for 2 h. This could be done *in situ* as a single or stacked SOFC cell, or it could be done as a single unit placed into the furnace.

Fig. 1 shows the scanning electron microscope (SEM) micrograph of NiO/FSZ cermet powder. The most apparent feature is the fine particle size distribution of the NiO. The average NiO particle size was found to be about 1 μm . This size would be effective in making good nickel to nickel contact when forming a continuous path in the electrode layer.

Fig. 2 shows the microstructure of the NiO/FSZ cermet anode coating after sintering, at 1300 °C for 2 h, onto the electrolyte. The cross-section of the sample is shown in the SEM micrograph in Fig. 3. An important feature that can be observed from these micrographs is the porosity of the coating which, according to the line-intercept estimation, is approximately 30–50 vol %. As stipulated above, the powder arrives in a semi-dry condition, thus allowing the powder particles to be “pinned” to the

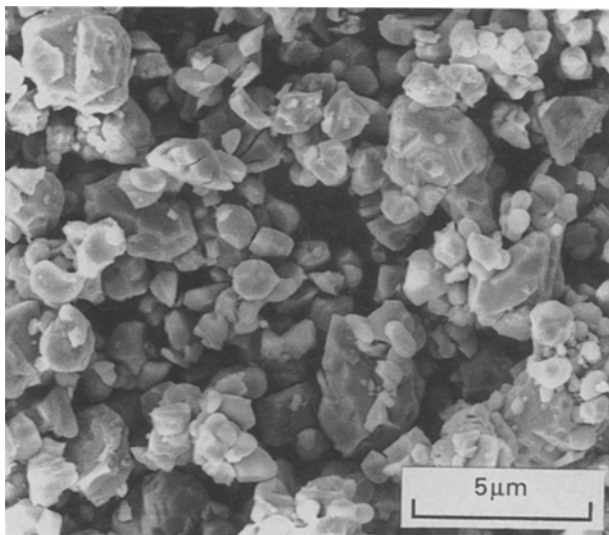


Figure 1 SEM micrograph of the NiO/FSZ cermet powder, prior to application on the electrolyte.

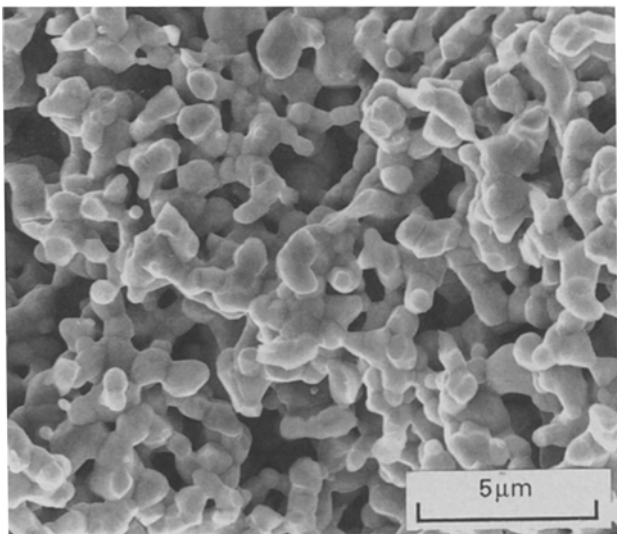


Figure 2 SEM micrograph of the NiO/FSZ cermet powder after application on the electrolyte.

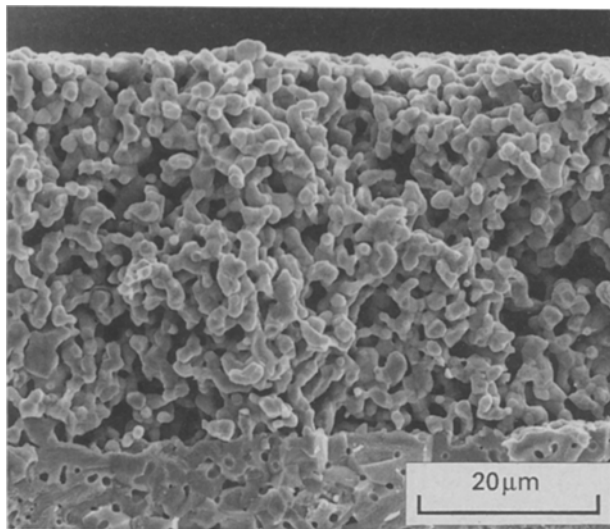


Figure 3 SEM micrograph of the cross-section of the NiO/FSZ (top) and FSZ electrolyte (bottom).

substrate and to one another at the place of impingement by the binder. Also, because there is a low fluid medium, the cermet particles are not able to migrate and rearrange to a more compact arrangement. Although densification can be obtained by prolonged sintering, this was not performed because the object of the study was to produce porous NiO/FSZ electrode coatings on the electrolyte to allow the diffusion of the fuel gas, in the SOFC system, to the triple point. Special regimes were designed to minimize densification although ensuring that particle–particle and particle–electrolyte bonding had occurred. Another important feature that can be seen in Fig. 3 is the thickness of the coating. The wet powder spraying technique enables the production of SOFC electrode coatings with uniform, controlled thickness regardless of shape and positioning of the electrolyte. Although properties such as particle size, density and solid to liquid volume ratio play a role in the deposition rate, their influence can be controlled by selecting suitable spraying conditions such as pumping power, air-brush to substrate distance and agitation efficiency.

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