ALUMINA FIBRE REINFORCED ZIRCONIA COMPOSITE SUBSTRATES
FOR PLANAR SOFCs

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ABSTRACT

A thin electrolyte layer in planar Solid Oxide Fuel Cells (SOFCs) is needed to operate at intermediate temperatures of 700 - 800°C. Screen-printing electrode inks onto thin layer is difficult. This problem can be alleviated by supporting the cell with a substrate. Ceramic matrix composites (CMCs), reinforced with ceramic fibres, are good SOFC substrate candidates because they have good physical and mechanical properties at high temperatures.

This paper discusses how fibrous substrates were made by bonding alumina fibres with colloidal zirconia dispersions and used for SOFC applications.

1. INTRODUCTION

Conventional planar solid oxide fuel cells (SOFC) use stabilised zirconia as the electrolyte with typical thicknesses of 50-300 μm (1). Cells with electrolytes of these thicknesses have to operate at temperatures of approximately 1000°C in order to obtain reasonable power densities. A high operating temperature of 1000°C leads to complex materials problems such as degradation over prolonged periods of running time (2). This problem could be overcome by running at lower temperatures (700-800°C). For efficient operation to be achieved at reduced temperatures, the ohmic losses from the electrolyte must be minimised. A way to do this is to reduce the thickness of the electrolyte layer to ≤ 10μm, but this is difficult to fabricate successfully because the electrolyte breaks when the electrodes are screen printed onto it. One possible solution is to physically support the cell by means of a substrate onto which all the cell components can be deposited without failure. Fibre reinforced ceramic matrix composites (FCMC) are good support materials because of their high physical and mechanical properties at high temperature (3). Figure 1 shows a schematic diagram of one of the several designs for a supported SOFC (4,5).
An ideal substrate for SOFCs must fulfill several criteria:

1. The substrate must be strong enough to survive the deposition of the electrodes and electrolytes onto its surface;
2. It must have a smooth surface finish to ensure even electrode layer deposition;
3. It must be sufficiently porous to allow the reaction gases to reach the electrodes;
4. It must exhibit good resistance to thermal cycling and have a high tolerance to thermal shock; and
5. It must be light weight so as to minimise the total mass of the fuel cell stack.

A material that satisfies these criteria is “Saffil” alumina mats because it is a good refractory, has high porosity and is light-weight. However, it has low physical strength and the loose fibres are readily detached from the bulk of the material during screen-printing of the electrodes, causing the undesirable blockage of pores in the mesh.

This paper describes how the physical properties of “Saffil” fibre based mats were improved. Treatments were carried out using an aqueous colloidal dispersion of zirconia. A fibre reinforced ceramic matrix composite was formed, electrodes were printed onto substrates and tested for possible applications in SOFCs.

2. EXPERIMENTAL

“Saffil” 1600S grade mats were obtained from Ash, Cheshire, UK. These mats were typically 30 x 20 x 0.2 cm in size and made up of randomly orientated alumina fibres, approximately 200 μm in length and 3 μm in diameter. The as-received mats were fired to 600°C for 1 hour in order to remove the organic binder (i.e. starch), so that the fibres were in their purest form prior to treatment with the slurry.

The zirconia powder used in the preparation of the aqueous colloidal dispersions was 8 mol% yttria stabilised zirconia (HSY-8), Daiichi, Mandoval Ltd, Surrey, UK). The as received powder had an average particle size of 10 μm as determined using laser light scattering (Mastersizer E, Malvern Instruments, Worcs, UK). The powder 60 % (g/g) was mixed with solvent and 7 % (g/g) ammonium polyelectrolyte, a deflocculant. This mixture was vibro-milled using zirconia milling beads in a polyethylene container for 4 hrs where the mean particle size was reduced to ~1μm.

This slurry was then poured over the fibrous preforms under ambient conditions until saturation occurred. The excess was removed and substrates were dried for 24 hrs at 50°C before firing the green composites between reticulated alumina foam supports to 1400°C for 1 hour in a Lenton Thermal Designs Ltd UAF 17/27 furnace.
Both the untreated and treated (fired) composites were tested for porosity using the isopropanol immersion technique. A three point bending apparatus (Lloyd Instruments LRX Materials Testing Machine) was used to determine substrate strength. All 35 samples had a geometry of 5 mm (length) x 1 mm (width) x 1.5 mm (thickness). Composite density was calculated as a function of mass and volume. Surface finish of composites was examined using scanning electron microscopy (SEM). Finally, the compatibility of the composite substrates with electrode materials was checked by applying layers of both a typical NiO/ZrO₂ anode and a LaSrMnO₃ cathode inks onto separate substrates. These were then fired to full density for 1 hr at 1300°C/hr for the anode and 1200°C in the case of the cathode.

3. RESULTS AND DISCUSSION

The untreated Saffil substrates were fragile to handle. These could not be tested in a three point bending apparatus because they failed before a load could be registered. This was attributed to the >95 % porosity found experimentally using the alcohol test. A SEM study of the untreated substrate confirmed this (see Figure 2). From the SEM micrograph, it can be seen that there was much porosity around the 3 μm thick fibres. For this reason, the untreated substrates are not suitable for SOFC applications.

These porous substrates were impregnated with a colloidal zirconia slurry, dried and fired in order to improve their strength. Figure 3 shows the Weibull plot for the strength results of the treated substrates. An average strength of 54 MPa and Weibull modulus of 5 was calculated. The improved strength of the treated substrates can be accounted for by the reduced porosity, i.e. 20-30 %. Figure 4 shows a cross section of a treated substrate. The zirconia slurry has infiltrated the substrates uniformly and coated the fibres well, removing much of the porosity. The residual porosity and the short length of the Saffil fibres has affected the surface finish of the substrates. Figure 5 shows the top surface of a substrate where a large pore and a protruding fibre are visible. These variations in surface finish may affect the uniform deposition of the electrodes. Also, the fired substrates had a final density of 3.0 g/cm³ compared with 0.3 g/cm³ for the untreated fibres. It has yet to be determined whether this value is practical.

Preliminary results show that both the anode and cathode inks adhere well to the surface of the substrates. These layers were typically 50 μm in thickness. The electrodes did not crack or peel away from the substrate upon firing. Also, no discolouration of either ink was observed after firing, suggesting that the electrodes were compatible with the substrate. This is important because migration of unwanted
species such as silica can degrade the electrochemical performance of the cell. Furthermore, the substrates survived rapid heating conditions of 1000°C min⁻¹ without failure. They were also thermally cycled 10 times successfully.

The next stage will be to put both electrodes and interconnect onto substrates, test electrochemical performance and see if the porosity of 20-30 % allows sufficient fuel and air to electrodes.

4. CONCLUSIONS

Fibre reinforced ceramic matrix composite substrates for SOFC were successfully made. A significant improvement in strength was found for the treated substrates compared to those that were not. The substrates were porous and physically strong enough to allow electrodes to be printed onto them. These treated substrates have excellent potential as physical supports for planar SOFCs.

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Figure 1 A schematic representation of a fibre reinforced composite support for a planar SOFC design.

Figure 2. A SEM image of the surface of an untreated Saffil mat.
Figure 3 Weibull plot of the strength results of treated substrates.

Figure 4 SEM micrograph of the cross section of a treated substrate.
Figure 5. SEM micrograph of treated substrate surface.