TRANSFER PRINTING OF THIN ELECTROLYTE LAYERS IN
SOLID OXIDE FUEL CELLS

M. Prica1, K. Kendall1 and M. Painter2

1 Centre for Inorganic Chemistry and Materials Science
   Keele University, Keele,
   U.K., ST5 5BG.
2 Cookson Matthey
   Burslem, Stoke-on-Trent,
   U.K., ST6 3AT.

ABSTRACT

A transfer printing method for depositing micron and potentially sub-micron layers on a substrate to form a solid oxide fuel cell has been developed. This method is advantageous because it is economic and applies to planar, tubular and corrugated geometries.

This paper reports the study of a 1.2 μm layer of yttria-stabilised zirconia electrolyte deposited onto a nickel/yttria-stabilised zirconia cermet tube with an outside diameter of 2.5 mm, where the cermet was either in the pre-fired or fired state. The electrolyte/cermet were fired at 1500°C for one hour. Preliminary tests carried out on the fired tube show that the electrolyte is thin and uniform.

1. INTRODUCTION

A Solid Oxide Fuel Cell (SOFC) converts chemical energy to electrical energy with the promise of a high energy conversion efficiency and a low percentage of hazardous by-products (1,2). For these reasons SOFCs are attractive because of the necessity to produce clean energy and power. However, one of the major drawbacks of SOFCs is the high operating temperature, normally around 1000°C, required for adequate oxygen-ion conductivity of the yttria-stabilised zirconia (YSZ) electrolyte (3). A way to overcome this problem is to lower the operating temperature of the SOFC by reducing the thickness of the electrolyte layer (4).

Minh and his colleagues at Allied Signal (5) have fabricated 1-10 μm electrolyte layers using a tape calendering method. Other possible techniques of depositing thin and dense electrolyte layers are electrochemical vapour deposition, slurry coating, plasma spraying, screen printing and tape casting (5). Such methods have rarely been used to deposit electrolyte layers less than 20 μm in thickness, and suffer from being too expensive or restricted to certain substrate geometries. For example, screen printing can only be used for flat surfaces. Other difficulties are the relative speed of the deposition process and the problems of mass production of SOFCs.
This paper reports a transfer printing method for depositing a thin and uniform electrolyte layer onto a tubular, corrugated or planar surface (6). It has not previously been reported for SOFC preparation. It is a potentially inexpensive and quick method of fabricating thin electrolyte layers. The method involves screen printing an electrolyte ink onto a soluble gum paper and allowing the layer to dry. Subsequently, a covercoat is screen printed over the electrolyte layer. The electrolyte layer with covercoat will be referred to as a transfer, which is released from the gum paper by immersion in water. Released transfers are draped over the appropriate substrate and fired to full density. This paper focuses on the transfer technology and its applicability to fuel cells, in particular the tubular design (7) for SOFCs.

2. EXPERIMENTAL SECTION

An electrolyte ink was prepared by triple roll milling 8% mole YSZ (54 g, Daiichi, Japan) with an organic screen printing medium (100 g). The electrolyte ink was screen printed through a 150S-X (150 apertures per linear cm) "estal mono" mesh onto a paper coated with a soluble gum. The layer of electrolyte was either allowed to air-dry or dried under an air jet and any subsequent layers could be screen printed to form a multi-layer structure over this dried layer. Each dried printed transfer was over-printed by a covercoat.†

The thickness of the electrolyte layer depends upon the number of apertures in the screen mesh, i.e. the greater the number of apertures, the thinner the screen printed electrolyte layer. The uniformity and thickness of the electrolyte layer will also greatly depend on the composition of the electrolyte ink. It was found that a 8% by volume solids content gave the best electrolyte layer.

All dried covercoated transfers were stocked until required. To release the film of electrolyte layer from its paper backing, covercoated transfers were soaked in water, and removed off the paper by applying some pressure to the transfer. During the application, the transfer retained sufficient flexibility so that the transfer could be draped onto the desired substrate. The substrate was a tube, plate or corrugated surface.

The flexible transfer sheet was wrapped around a 2.5 mm nickel oxide-YSZ cermet tube that had a wall thickness of 0.25 mm. Any water and air bubbles trapped between the transfer and tube were squeezed out using either a squeegee or by running a finger over the transfer. It was difficult to use the squeegee on a smaller diameter tube. The transfer/tube was allowed to air-dry and fired to 1500 °C for 1

† Organic medium was obtained from Cookson Matthey, Burslem, Staffs, U.K. The medium consisted 40% by wt of an acrylic resin, butyl methacrylate, in Solvesso 100 (Trademark) together with 2-5% of a plasticiser such as dioctyl phthalate.

† Covercoat was supplied by Cookson Matthey, Burslem, Staffs, U.K.. Covercoat contained an acrylic resin system of 45% butyl/methyl methacrylate co-polymer, 5% butyl benzyl phthalate in 50% Solvesso 100.
It was observed that the best furnace rates were 1°C min⁻¹ to 500°C, 3°C min⁻¹ to 1500°C and 3°C min⁻¹ to 0°C. Pre-firing the cermet tubes gave a better electrolyte layer after firing.

The fired electrolyte/nickel oxide-YSZ cermet tubes were tested electrochemically for leaks. Platinum wire was wound around the electrolyte layer and platinum paste was used to ensure good connection. A nickel wire was used to make contact with the anode electrode and the entire set-up was heated to 1000°C in a small furnace designed to test the individual fuel cells (7). Hydrogen gas as fuel, was bubbled through water and passed into the reaction cell via a rubber connector.

3. RESULTS AND DISCUSSION

A SEM micrograph of a YSZ layer deposited onto a cermet tube of 2.5 mm diameter is shown in Figure 3.1. It is evident from Figure 3.1, that the electrolyte layer is uniform and well bonded to the porous anode. The electrolyte layer is 1.2 μm thick. An open circuit voltage of 0.95 V was recorded for this tube where hydrogen and water were used as the fuel. The voltage of this cell was found to decrease with time, suggesting that the electrolyte layer is not impervious to gas and hence the electrolyte film is not fully dense. Further SEM studies confirmed these conclusions (see Figure 3.2).

One of the major problems associated with using transfers is the degree of surface roughness in the substrate (see Figure 3.2). In order for the transfer to adhere better to the substrate, the substrate must be very smooth, i.e. no steps greater than 1 μm. The cermet tubes used in this study were found to be coarse and much surface roughness was observed (see Figure 3.2). The smoothness of the extruded cermet tubes was improved by milling the zirconia and nickel oxide powders to a mean particle size of 2 μm before extrusion.

Another difficulty with applying transfers to tubes is the overlap of the transfer onto itself. At the overlap, two electrolyte layers are separated by a covercoat. This causes the upper electrolyte to delaminate after firing. This was attributed to the poor contact between the electrolyte layers before firing. The underlying electrolyte layer did not flake. Small hairline cracks were also visible in the overlap region. These factors contributed to gas leaks. Ways of improving the transfer overlap are currently being investigated.

Although the theoretical open circuit voltage was not achieved, the transfers show much potential if the rheology of the suspensions is improved. One of the limiting factors in screen printing is the low volume percent of solids used to give a thin, uniform electrolyte layer. A low volume percent of solids enables particles to form clusters and these large clusters are not healed upon sintering. Kendall (8) has shown that flocculation clustering can control the structure and strength of ceramic solids. Therefore, to improve the density of the electrolyte film, a higher percent solids is required. This poses a difficult task in the screen printing process as the suspension becomes too viscous to screen print through a fine mesh.
Figure 3.3 shows another example where the transfer technology was used to deposit a thin electrolyte layer onto a lanthanum strontium manganite plate. The composite plate was broken into tiny pieces so that a small fragment could be mounted onto a SEM stub and this caused the delamination of the electrolyte layer. The importance of this micrograph is the uniformity of the 2.1 \( \mu \text{m} \) layer. It is difficult to conclude whether the large agglomerate observed in the micrograph is due to the transfer or the underlying substrate. No electrical tests were carried out on this electrolyte layer.

4. CONCLUSIONS

The transfers are not only attractive from the point of view that thin, uniform layers can be fabricated onto curved surfaces but other electrodes and interconnect materials can also be deposited onto a substrate using this method (9). Therefore, electrolyte, electrodes and interconnects can all be screen printed and wrapped around the substrate in a single step, provided that all the materials can be fired at the same temperature. This technology enables any complicated or intricate patterns for SOFCs to be designed and delivered to any particular substrate geometry.

Transfer technology offers a cheap and practical method of depositing uniform, sub-micron layers onto planar, tubular and corrugated surfaces. It challenges us to improve ink formulations so that denser electrolyte layers can be obtained using the transfer technology.

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**Figure 3.1.** A SEM micrograph of a cross-section of a 1.2 μm yttria-stabilised zirconia layer on a nickel oxide/yttria-stabilised zirconia cermet tube.

**Figure 3.2.** SEM micrograph of the exterior surface of the 1.2 μm yttria-stabilised zirconia layer on a nickel oxide/yttria-stabilised zirconia cermet tube.
Figure 3.3. A SEM micrograph of the side view of a 2.1 μm yttria-stabilised zirconia layer on a lanthanum strontium manganite (LSM) plate.