A SIMPLIFIED TEST METHOD FOR PLANAR SOFCs

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ABSTRACT

Testing planar SOFCs can be expensive and time-consuming. Particular problems are sealing, manifolding, current collection and cracking of the ceramic parts. This paper describes a simplified test method which alleviates a number of these problems. A rig for testing 50 by 50 mm zirconia cells was built. The parts were all ceramic and they could be assembled and taken apart easily in a few minutes. In particular the fuel inlet was leak-proof with this new design. Single cells were electrochemically characterised at 800 °C within 30 minutes. The theory of oxygen gradient within the test cell was obtained by solving the reaction-diffusion equations. When compared to experimental results, the theory gave a good description of the diameter of the reduced nickel cermet in the fuel compartment. A range of cermet anode formulations has been tested by the new method.

INTRODUCTION

The testing of planar SOFC components suffers from the same problems experienced 60 years ago. Baur and Preis (1) made the early contributions in 1937. Thirty years later, Weissbart and Ruka (2) similarly used a pressed disc of electrolyte at the end of a ceramic tube down which oxygen passed via a feeder tube. Fuel gas mixtures were passed down an outer tube which was itself enclosed in an alumina tubular container. Platinum electrodes were deposited on the cell disc before assembly and electrical contact made with platinum wires. The whole assembly was held in a furnace between 800 and 1100 °C. In 1996, de Souza, Visco and de Jonghe (3) described a similar experimental arrangement in which a compacted disc of cermet anode was coated with a thin coating of electrolyte slurry, then dried and fired before sealing to the end of a ceramic tube and inserting in the furnace. A key difficulty with this traditional approach has been the thermal expansion mismatch of tube and cell. It was impossible to match the movements exactly for large cells; therefore cracking and...
leakage of cells often occurred, thermal ramping had to be slow, and the cells could not be removed from the melted glass seals without damage.

From the theoretical standpoint, both surfaces of the electrolyte disc have usually been treated as uniform electrodes covered by a constant concentration of gas molecules, in other words as chemical equipotential surfaces. This is approximately true when the surfaces are flooded with an excess of gas, and when the excess fuel is exhausted to atmosphere well downstream of the electrode. However, in realistic circumstances, where the fuel is depleted by oxygen transfer through the electrolyte, and where the depleted fuel meets the air a short distance from the electrode, there is a gradient of oxygen along the electrodes and this should be taken into account.

The purpose of this paper is to advance the testing procedure for planar SOFCs on two fronts; first to define a test arrangement which is simpler, more economic, faster and more scaleable; and second to establish a theory which describes realistic oxygen gradients along the cell surfaces.

PROBLEM AREAS

When larger plates of thinner zirconia became available through tape casting or calendering routes, the traditional test method was improved by using two tubes and sandwiching the planar cell between them (4,5). To make the plate demountable, gold ring seals were produced to replace the glass used previously. The tubes were pressed onto the gold rings which pushed onto the cell after heating. Electrical contacts could also be made onto the electrodes using the gold to pick up current. The main problem was that gold did not seal perfectly, especially when hydrogen was the fuel source, partly because the gold did not conform perfectly to the ceramic surfaces and partly through electrochemical leakage where the gold acted as an electrode on the zirconia (6). Also, cracking could occur on cooling.

Metal and ceramic test rigs were also developed to investigate single cells, typically the 50 by 50 mm square cells adopted as standard in Europe and Japan (7,8). A typical metal test stand pressed the cell between two Nimonic blocks which had been machined to incorporate gas channels. Fuel and oxidant gases were fed through tubes to the metal blocks and out to exhaust. Various types of seals fitted around the edges of the cell. Platinum mesh contacts pressed against the electrodes. Mechanical load was applied through springs outside the furnace to press the unit together. The snag with such apparatus was the mass and expense of these units. They tended to oxidise and distort in use.
A more academic geometry developed largely for understanding the nature of electrode-electrolyte interactions was the point contact configuration (9,10) in which metal cones were pressed onto a zirconia surface while gas was circulated on each side of the sample.

The purpose of this paper is to describe a much simpler geometry for testing planar SOFCs over a wide range of sizes. The method was first used by Kendall at ICI in 1992 and has since been investigated systematically at Keele University (11,12). The main benefits are:

- all ceramic construction avoids metal corrosion and creep
- open seal arrangement gives easy assembly and dismantling
- fuel feed through a ceramic tube prevents fuel inlet leaks
- low mass gives rapid test capability, i.e. a possible 30 minute test cycle
- small size leads to simple peripherals, economic construction and easy access

The principal difference between this new test arrangement and previous designs is the non-uniformity of the fuel concentration in the anode compartment. Of course this problem applies to all fuel cell testing, but normally the electrodes are flooded and the chemical gradient is assumed to be small. Here we first describe the simplest possible planar SOFC test geometry, then produce a theoretical description of the oxygen reaction-diffusion in the anode compartment, and finally measure the chemical gradient experimentally to show that it fits the mathematical equations. The two methods used to assess the chemical gradient were visual observation of the size of the reduced nickel cermet region and measurement of electrochemical potential on the anode as a function of gas flow rate.

DESIGN OF SOFC TEST

The main components of the new design are shown in figure 1. Two zirconia foils, 50 mm by 50 mm square were prepared by calendering using the formulations described previously (13). On one of the plates, electrodes and current collecting wires were deposited. The plates were then used to sandwich a sheet of ceramic paper (Zircar felt, ZYF 100, Zircar Products). A slot was cut in the sheet to accommodate a 1.7 mm diameter zirconia tube which fed fuel gas to the centre of the sandwich. To hold the assembly together, zirconia spring clips were made (figure 1) and positioned around the perimeter of the sandwich. The whole construction was called a "lollipop".

In order to perform a test run, the lollipop was inserted in a small furnace constructed of fibre blocks containing nichrome heating wires. A thermocouple was
used to control heat input from the power supply. Fuel gas was bubbled through water, fed to the SOFC via a mass flow controller, through a rubber tube and into the cold end of the lollipop assembly which protruded from the furnace. The electrical output was monitored on a potentiostat as shown in figure 2.

Typically, the furnace attained its operating temperature in ten minutes, using 100 W of electrical heating. Then hydrogen was introduced at 100ml/min. In the first ten minutes the open circuit voltage rose to its full value as the anode was reduced. Finally, the current-voltage characteristics were determined using a passive potentiostat (built at Keele).

**THEORY FOR OXYGEN CONCENTRATION IN LOLLIPOP**

When the amount of oxygen electrochemically diffusing through the zirconia plate is small (low current) the fuel and oxygen concentrations between the two zirconia foils are dictated by the flow of fuel out from the centre, by the diffusion of oxygen inwards from the edges, and by reaction of the fuel with the oxygen. This reaction-diffusion problem has been solved previously (11) to give the theoretical equation for oxygen concentration $C_o$ at the centre.

$$C_o = 15.134\frac{(\pi D^2 h)}{(Qa^2 k) \exp(2\pi D h C/Q)}$$  \[1\]

where $D$ is the diffusion coefficient for oxygen in water vapour, $h$ is the thickness of the ceramic felt, $Q$ is flow rate of the oxidised fuel, $a$ is the radius of the zirconia plate, $k$ is the third order rate constant for the reaction between fuel and oxygen, and $C$ is the oxygen concentration at the edge of the plate.

The theory also gave the diameter of the transition layer where there was a sudden dramatic change in oxygen concentration. This transition layer was located where the rate of oxygen diffusing into the anode chamber was stoichiometrically equal to the rate of fuel flowing out. The diameter of the transition layer was given by

$$d = 2a \exp(-\pi D h C/Q)$$  \[2\]
EXPERIMENTAL

The first experiment was designed to show the presence of the reaction zone directly. The lollipop was assembled and hydrogen was passed through at 20 ml/min. The plates were taken apart and the anode cermet was studied. The original green nickel oxide layer had been reduced to nickel metal over a circular central region, as expected from the theory of equations [1] and [2]. The plates were assembled again and an increased flow rate of hydrogen was fed in, leading to a larger circular reduced region. After a series of such experiments the anode plates were as shown below in figure 3. The diameter of the dark reduced region was measured and plotted in figure 4 against hydrogen flow rate for comparison with equation [2]. Good agreement was obtained if the diffusion was multiplied by a mixing coefficient of 2.4.

The second experiment was designed to verify equation [1] giving the oxygen concentration at the centre of the anode chamber as a function of fuel flow rate. The initial flow rate of hydrogen was set at 100 ml/min and the potential of the cermet anode was measured. The flow rate was then decreased systematically, while measuring the anode voltage. This fell gradually as shown in figure 5. There experimental values were compared with the predictions of equation [1], giving fair agreement. As the flow rate was reduced to 13 ml/min, a large drop in anode voltage was observed. This corresponded to the transition layer contacting the nickel cermet anode, as shown by the vertical dotted line in figure 5.

ELECTRICAL TESTS

The cermet anodes were made by mixing 6 g of green nickel oxide (Alfa) with 2.86 g of yttria stabilised zirconia (FYT11, Unitec), milling in solvent and dispersing agent with zirconia media, then painting disc electrodes onto plates. Typically, electrodes were painted 50 μm thick and 13 mm diameter at the centre of the zirconia plate, then dried in an oven at 100°C. Iron was added as red ferric oxide (Fluka) at the powder mixing stage, followed by milling, painting and drying as before. The electrodes were fired at 1300°C for 1 hour. A cathode disc of lanthanum strontium manganite (LSM) was painted on the opposite side of the zirconia plate, and fired to 1300°C. Two layer cathodes were used, with an inner layer of finely milled 50/50 zirconia/LSM and an outer layer of coarser LSM (Seattle Speciality Ceramics). A current collector grid was painted onto each disc electrode using silver ink and a silver wire was pressed into electrical contact, held with polymer adhesive while assembling, then fired up in the lollipop to make the test measurements at 800°C.
Results for current against voltage are shown in figure 6 for hydrogen fuel and air oxidant. It may be seen that the cell performance increased significantly as the iron was added to the anode.

CONCLUSIONS

A new simplified test method for planar SOFCs has been demonstrated. The technique is ideal for testing 50 mm by 50 mm cells. It has the advantage that it never leaks at the fuel inlet. Also, the cell can be heated, tested and cooled within 30 minutes, then removed from the rig without damage. This allows the reduction of the anode to be studied in detail, for comparison with reaction-diffusion theory. Good agreement was obtained between theory and experimental results in that the diameter of the reduced cermet anode varied as predicted with fuel flow rate, and the voltage on the central anode spot decreased as expected as the fuel flow diminished. This geometry was ideal for studying the variation of anode performance as additives such as iron were included. The main disadvantage of this planar cell test configuration was the susceptibility to thermal shock cracking at high heating and cooling rates. To avoid this problem, it is necessary to move to dimpled plates or to small diameter tubular cells which can be heated to 800°C in seconds (13-15).

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Figure 1: Exploded view of the lollipop assembly

Figure 2: Schematic of system assembly
Figure 3  Nickel cermet anodes of cells at different hydrogen flow rates and temperatures showing reduced circular regions.

Figure 4. Diameter of transition layer as a function of hydrogen flow rate. h = 2.0mm, Plate diameter = 52mm, T = 800°C, Mixing coefficient = 2.4.
Figure 5. Open circuit voltage of 13mm diameter nickel cermet anode as a function of hydrogen flow rate compared to theory for OCV at centre, \( k = 2 \times 10^{26} \), \( T = 800 \, \text{C} \).

Figure 6. Typical current-voltage characteristics measured at 800 C of 13mm diameter electrodes with different proportions of iron in the nickel cermet anodes.