ABSTRACT

A novel metal supported solid oxide fuel cell has been developed, capable of operating at temperatures of 500-600°C. The rationale behind the materials used to construct this fuel cell type is given, and results presented from cell and short stack testing. This new fuel cell variant is shown to be tolerant of carbon monoxide, durable, robust to thermal and redox cycling, and capable of delivering technologically relevant power densities. These results are used as the basis for stack and system simulations, demonstrating that attractive efficiencies for systems of around 4 kWe (net AC) rating operated on natural gas can be realized using this approach.

INTRODUCTION

Ceres Power Ltd is developing a novel fuel cell type which combines ceramic materials, based around doped cerium oxide, with stainless steel to produce a robust solid oxide fuel cell capable of operating at temperatures at or below 600°C. This class of fuel cell has recently been described as a third generation (or 3G) SOFC, with advantages of lower cost and increased robustness over current systems (1). This paper reviews the rationale behind Ceres SOFC technology, and then summarises some of the technical highlights to date in terms of cell, stack and system performance.

It has been increasingly recognised by the solid oxide fuel cell (SOFC) community that, for SOFC systems not requiring integration with gas turbines, major benefits arise from a reduction in stack operating temperature, provided this does not compromise the electrode kinetics and internal resistance of the fuel cell. The lower operating temperature increases the range of materials that can be used to construct the device (including metals), increases material durability and overall product robustness, and crucially lowers cost. This has driven increasing interest in Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs) operating at temperatures at or below 800°C. Selection of the solid electrolyte for these IT-SOFCs depends on the chosen temperature of operation. To help this selection process it is useful to consider the following. Assuming that the electrolyte component should not contribute more than 0.15 Ωcm² to the total cell area specific resistance, then for an electrolyte film thickness (L) of 15 μm the associated specific ionic conductivity (σ) value of the electrolyte should exceed 10⁻² S cm⁻¹. The ionic...
conductivity of the most commonly used SOFC electrolyte, yttria stabilised zirconia (YSZ) attains this target value above 700°C, whilst the electrolyte used by Ceres Power, gadolinia doped ceria (CGO), attains this conductivity at temperatures above 500°C (2), assuming that the electrolyte is manufactured in the form of a thick film some 10–30 µm thick. Therefore, the use of a CGO electrolyte allows the cell operating temperature to be lowered to around 500°C, a temperature at which standard stainless steel can be used for many of the balance of plant components, and hence an operating condition which enables a significant cost reduction in both stack and balance of plant. A concern often expressed with regards to the use of CGO electrolytes in SOFCs is that, at elevated (>600°C) temperatures, Ce⁴⁺ ions can be reduced to Ce³⁺ under the fuel rich conditions prevailing in the anode compartment. The resulting electronic conductivity (and deleterious lattice expansion) produces an internal short circuit in the PEN structure which can significantly degrade the efficiency and performance of cells incorporating ceria based electrolytes. However Steele (3) has shown that at temperatures < 600°C the reduction of Ce⁴⁺ ions to Ce³⁺ in the anode compartment is minimized, and can be neglected under typical cell operating conditions. This therefore defines an operating temperature window for SOFCs based on CGO of around 500-600°C.

The use of thick film electrolytes requires the electrolyte to be supported on an appropriate substrate. As the substrate is the principal structural component in these cells it is necessary to optimise the conflicting requirements of mechanical strength and gaseous permeability. Most development work on planar IT-SOFC systems has involved YSZ electrolyte thick films supported on anode (Ni-YSZ) substrates which allow electrolyte powders to be densified at temperatures around 1400°C. The resultant cells and stacks operate with satisfactory power densities (0.3–0.5 W cm⁻²) in the temperature range 700-800°C using a ferritic stainless steel bi-polar plate material. However, the relatively thick porous composite anode support (1.0 +/- 0.5 mm) can introduce problems in the operation of such stacks as this structural component is relatively weak mechanically, and can have difficulty withstanding the thermal and mechanical stresses generated by rapid temperature fluctuations, or the vibrations incurred when the stack is incorporated into systems used for mobile applications. Moreover Ni/NiO redox cycling induced by air diffusing into the anode compartment during loss of fuel supply and other operational excursions can disrupt the anode micro-structure, producing a severe degradation in performance.

An innovative approach to overcome these challenges, and thereby enhance the robustness of SOFCs, is the use of a metallic support, where the Ni-YSZ anode support is replaced by a metal (normally stainless steel), which improves thermal shock resistance, reduces temperature gradients due to the greater thermal conductivity of the metal, and enables conventional metal joining (e.g. welding) and forming techniques to be used. The concept of using a stainless steel support for SOFC PEN assemblies was first patented in 1966 (4), but little attention was paid to this configuration until some thirty years later when DLR in Germany fabricated metal supported SOFC structures using (expensive) vacuum plasma spray techniques (5). In contrast work at Ceres Power (6-8) is focussed on the integration of low cost 'wet' ceramic routes with metallic materials.

Several grades of ferritic stainless steel have been identified, and typical is the use of a Ti-Nb stabilised 18% Cr ferritic stainless steel (European designation: 1.4509). It is important to note that operating at 600°C imposes far less severe corrosion constraints on...
the steel than sustained operation at 750-800°C, as is the case for a typical anode-supported cell stack. Also importantly, the thermal expansion of CGO10 and the selected ferritic stainless steel are well matched, with values quoted in the range (12.5-12.8) x 10^-6 K^-1 for both materials. The ceramic components of the cell are deposited as thick-films by conventional ceramic deposition technology. The electrodes are deposited by wet spraying or screen-printing. The electrolyte is deposited using an electrophoretic deposition (EPD) process. All these processes are low cost and scaleable, and are used for mass manufacturing in industry today. The cell, shown in cross section in Figure 1, consists of a steel foil substrate, typically in the range 200-300 µm thick, which is impermeable around the edges, and porous in the centre. The edges facilitate sealing, as the cell can be welded to the metallic interconnect. The anode layer is deposited over the porous section of the substrate. The anode is a nickel cermet, with the ceramic phase being gadolinia doped ceria (CGO). The electrolyte layer is deposited over the anode as a thick film (10-30 µm) of CGO. Dense CGO electrolyte films can be produced at sintering temperatures below ~1000°C. This is a major technological breakthrough, as this temperature is unusually low for ceramics processing. The low firing temperature is crucial to protect the steel substrate from excessive oxidation. The cathode layer is deposited over the fired anode and electrolyte. Various cathode materials are being investigated, with a doped lanthanum ferrite (LSCF)/CGO composite being the present material of choice (9, 10).

Figure 1. Polished cross-section through a metal supported Ceres cell, after testing on moist hydrogen/air at temperatures up to 600°C.

Cells are integrated into a stainless steel array plate by techniques such as laser welding. For the short stacks discussed in this paper, each array comprises 4 cells connected in electrical parallel. Each array is internally manifolded, and both sealed and electrically isolated by a vermiculite based gasket. Short stacks of three to ten arrays in electrical series are reported here, constructed using ferritic steel end plates with the stack held in compression by bolting. Air and fuel is fed to the stack in a co-flow arrangement.

RESULTS

Figure 2 illustrates the evolution in Ceres cell power density with time, over the period May 2003 to April 2004. All data refers to cells tested on moist hydrogen/air at a temperature of 570°C. All the cells reported in Figure 2 were fabricated using the materials set described above. Therefore, it can be seen that rapid advancements have been made in our understanding of the cell processing parameters needed to engineer improved cell microstructures, resulting in increasing levels of power density. This rapid
progress at a cell level has resulted in us taking a tiered approach to our stack development, in which a given class of cell is ‘frozen’ early in the development cycle, to ensure that manufacturing yield can be demonstrated, and reproducible cells produced, for the stack programme.

Figure 2. Historical evolution in Ceres cell power density. All data refers to cells of 16 cm² active area tested on moist hydrogen/air at 570°C.

Figure 3 illustrates the current-voltage and power density response from a recent class of single cells of 16 cm² active area, tested on moist hydrogen/air, and reformate/air, at a temperature of 550°C. A maximum power density of 320 mW cm⁻² was obtained using moist hydrogen, and 290 mW cm⁻² using reformate. Here reformate is taken to mean fuel gas mixtures emulating that produced by the steam reforming of natural gas, and in this study the reformate composition was 73.8 mol% H₂, 7.1 mol% CO, 12.1 mol% CO₂, and 7 mol% H₂O, as determined by gas chromatography measurements.

Reformate = 73.8% H₂, 7.1% CO, 12.1% CO₂, and 7% H₂O

Figure 3. Current-Voltage and Power curves from a 16 cm² cell, tested on moist hydrogen (3% H₂O)/air and reformate/air at a temperature of 550°C.

It can be seen that the performance on reformate was very similar to that on 70% hydrogen, a fuel composition of approximately the same hydrogen partial pressure as the reformate. This confirms that CO is not a poison at these reduced cell temperatures.
Rather, as hydrogen is depleted within the fuel cell stack, CO present in the fuel will undergo the water gas shift reaction to produce further hydrogen. The cell power density increased to 0.5 W cm\(^{-2}\) at 600°C, representing an excellent performance for an SOFC at this temperature range, especially when the total cell thickness of only \(\sim 300\) µm is taken into account. Note that the cell voltage of around 0.95 V is in line with that expected from a CGO based SOFC at this temperature, and with these fuel compositions.

Figure 4 shows the results of a long term durability test of a single cell on reformate/air at 570°C. Test stand interruptions resulted in fuel loss for 12 hours, and air loss for 72 hours, though neither excursion significantly impaired cell performance. It is interesting to note that Ceres cells welded into cell housings have recently completed 500 rapid thermal cycles (from ambient to 600°C then back to ambient over a ten minute period) without failure, providing further evidence of the robustness inherent to the approach.

![Figure 4. Durability test of a 16 cm\(^2\) cell, tested at 2.9 A on reformate/air at 570°C.](image)

![Figure 5. Durability data from a twenty cell, five array, short stack tested at a constant current of 5 Amp at 580°C on moist hydrogen (3% H\(_2\)O)/air.](image)
Figure 5 presents the results from a 20 cell, 5 array, short stack operated at 5 Amp. Each of the 5 arrays gave very similar performance, indicating uniformity of both gas distribution, and current collection. The low level of degradation is encouraging, particularly at this early stage of development, with the stack losing around 10 mV voltage from each array per 1000 hours on test.

Figure 6 shows the performance of a 10 layer, 40 cell stack, tested on hydrogen/air at 550, 570 and 600°C, resulting in an electrical power output of 107, 141 and 160 W respectively.

![Figure 6. VI and power curves for a 40 cell, 10 layer Ceres stack tested on moist hydrogen (3% H2O)/air.](image)

The performance of this stack under load, operating at a fuel utilisation of 35% on reformate (55% hydrogen)/air at a temperature of 585°C, is illustrated in Figure 7. The test duration was 960 hours, with minimal degradation observed over that period.

![Figure 7. Durability data for 100W_e class stack operating on reformate/air.](image)
A mathematical model of a Ceres fuel cell has been produced, described in (11). The model allows for losses within the cell in the conventional manner, but also allows for mass transport of fuel gases and, importantly, for the mixed conductivity of the CGO electrolyte. The resulting equations were solved using the gPROMS version 2.3 equation-based dynamic process simulation package. This allows sophisticated parameter-fitting which enables a set of parameters to be derived for a particular mathematical model which give the best fit to multiple sets of experimental data taken under different initial conditions. This technique was used to extract the optimum model parameters to fit a set of VI curves for a February 2004 class of fuel cell taken under a range of temperatures and fuel compositions. It has been demonstrated that this class of cell, the subject of extensive process development, can be made in large numbers with high yield and reproducibility. Figure 8 shows the good agreement between the experimental data and the model prediction, in this case at a temperature of 600°C, operating with moist hydrogen/air.

![Figure 8. Comparison of experimental and predicted VI and power curves for a Ceres cell at 600°C on moist (3% H2O) hydrogen/air (February 2004 cell class).](image)

A similar quality of fit was found across the temperature range studied (500-600°C) and with a range of fuel partial pressures. It is interesting to note that at a temperature of 600°C and a typical operating current density of 300 mAcm⁻², the predicted electronic leakage current density is only 20 mAcm⁻² or 6.3% of the total current, which means the loss of cell efficiency as a result of the mixed conductivity of the electrolyte is negligible. At lower temperatures the electronic leakage current is even lower. Dynamic modelling of a 2.5 kWe planar SOFC stack operating on a completely externally reformed hydrocarbon fuel with co-flow of the fuel and air streams has been carried out (11). This included reactant utilisation and heat generation from the electronic leakage in the electrolyte in the mass and heat balances of the stack, allowing the potential loss of efficiency resulting from the use of CGO electrolytes to be accurately simulated.

The predicted stack performance is illustrated in Table 1, again based on the February 2004 class of cell performance. Note that the lower heating value (LHV) efficiency is
based upon the energy content of the reformate fuel, not the original hydrocarbon. If the energy for reforming the hydrocarbon fuel is supplied from waste heat from the stack, the equivalent stack efficiency based upon the hydrocarbon fuel would be in excess of 40%.

A highly attractive potential application for SOFCs is small-scale combined heat and power (CHP). This gives the option to significantly increase the overall efficiency of power generation by recovering the waste heat, usually discharged to the environment in centralised power generation. SOFCs are particularly well suited to systems involving heat recovery, because their high operation temperature means the waste heat is of high grade. However, it is important to recognise that stack outlet temperatures of around 600°C mean that the balance of plant components can be cost effectively fabricated from commercially available steels.

**Table 1. Predicted performance of a 2.5 kWe stack.**

| Variable                        | Value | Units |
|--------------------------------|-------|-------|
| Stack external current          | 26.7  | A     |
| Stack voltage                   | 93.7  | V     |
| Mean cell voltage               | 0.670 | V     |
| Stack mean external current density | 221   | mA cm⁻² |
| Stack mean power density        | 148   | mW cm⁻² |
| Stack LHV efficiency            | 35.2  | %     |
| Air outlet temperature          | 629   | °C    |
| Fuel outlet temperature         | 630   | °C    |
| Mean electronic leakage current | 1.1   | A     |
| Mean electronic leakage current density | 9.1   | mA cm⁻² |
| Fuel flow rate                  | 5.9x10⁻⁴ | kgs⁻¹ |
| Air flow rate                   | 1.69x10⁻² | kgs⁻¹ |

A system concept has been developed based around two 2.5 kWe metal supported stacks producing a maximum electrical power output of 5.1 kWe gross, 4 kWe net after parasitic losses, operating on externally steam-reformed natural gas. Full external reforming was assumed for this analysis as this represents the minimum technical risk, allowing parallel development of the stack and fuel sub-systems. Systems analysis based on partial oxidation reforming and internal steam reforming is in progress, and will be reported separately. A process flowsheet is presented in Figure 9, and a computer model of this CHP system was written using the gPROMS version 2.3.1 dynamic process simulation package, incorporating the Ceres stack model introduced above. The predicted performance of the CHP unit at 100 and 50% power is illustrated in Table 2. The overall electrical efficiency of the system is predicted to be 33-34% based upon the lower heating value (LHV) of the fuel. One important characteristic demonstrated here is that the efficiency of the system does not vary significantly over the 50-100% power range. This constant-efficiency part-load characteristic is very attractive by comparison with CHP systems based on conventional internal combustion engines. It can be seen that the overall energy efficiency of the system is around 80% when heat recovery is included, and slightly improves at part load. It is interesting to note that the predicted electronic leakage current within the stacks is only around 4% of the total current, and therefore its effect on the cell efficiency is negligible.
Figure 9. Flowsheet of a natural gas fuelled IT-SOFC CHP system, based on full external reforming. B1 = afterburner, BPV = by-pass valve, C1 = air blower, R1 = reformer, EV1 = evaporator, P1 = pump, HX = heat exchanger.

Table 2. Predicted performance of a 4 kW (net AC) CHP system based around Ceres metal supported stack technology.

| Description                          | Value at 100% power | Value at 50% power | Units |
|--------------------------------------|---------------------|--------------------|-------|
| Stack DC power output                | 5140                | 2583               | W     |
| System AC power output               | 4000                | 2000               | W     |
| System heat output                   | 5232                | 2941               | W     |
| LHV energy input in fuel             | 11609               | 6019               | W     |
| Stoichiometric air ratio             | 5.2                 | 5.0                |       |
| Overall electrical efficiency        | 34.5                | 33.2               | %     |
| Stack efficiency                     | 44.3                | 42.9               | %     |
| Thermal efficiency                   | 45.1                | 48.9               | %     |
| Overall efficiency                   | 79.5                | 82.1               | %     |
| Fuel feed rate                       | 0.839               | 0.436              | kg.h⁻¹|
| Air feed rate                        | 49.9                | 25.1               | kg.h⁻¹|
| Specific CO₂ emissions               | 581                 | 603                | g.kWh⁻¹|
CONCLUSIONS

It has been demonstrated that metal-supported SOFCs being developed by Ceres Power can be incorporated into stacks and systems capable of delivering commercially meaningful levels of power density and efficiency. Cell and short stack durability has been demonstrated over 2500-3000 hours operation on reformate fuels, together with the ability to rapidly thermally cycle cells over 500 thermal cycles. System efficiency has been shown to be >34% at the 4kWe (net AC) scale based on today’s levels of cell performance, coupled with external steam reforming of natural gas fuels. These encouraging performance characteristics have been obtained whilst retaining the benefits of cost reduction and mechanical robustness inherent to the use of metal supports.

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