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Development of Metal Supported Solid Oxide Fuel Cells for Operation at 500-600 °C

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A novel metal-supported solid oxide fuel cell has been developed that is 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 are presented from cell testing on hydrogen and reformed natural gas, including durability trials of some 2500 h duration. 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.

Keywords CGO, metal supported, solid oxide fuel cells

1. Introduction

Ceres Power Ltd (Ceres Power, Crawley, UK) was spun-out from Imperial College London (Imperial) after more than 10 years of fundamental research, which showed that it was possible to combine ceramic materials, based around doped cerium oxide, with stainless steel to produce a robust intermediate temperature (IT) solid oxide fuel cell (SOFC) that is capable of operating at 500-600 °C. This article reviews the rationale behind the materials selection used by Ceres Power in developing its unique metal-supported SOFC technology and then summarizes some of the technical highlights to date.

2. The Ceres Power Technology Platform

To set the Ceres Power technology in context, it is first necessary to briefly consider the present state of the art in SOFC and polymer electrolyte membrane fuel cell (PEMFC) technology, which are considered by many to be the two leading fuel cell types.

PEMFCs are widely seen as the preferred technology for battery replacement applications and for fuel cell engines. This is because they are fast to start up, lightweight, and deliver a high power density. However, PEMFCs have the major disadvantage of requiring very high-purity hydrogen as a fuel (which is expensive to produce and difficult to store). Furthermore, they do not produce high-grade waste heat, inhibiting their application in the important combined heat and power (CHP) market.

In contrast, the main benefits driving the development of SOFCs are as follows:

- The elevated operating temperature of SOFCs means that carbon monoxide, always produced during the reforming of hydrocarbon fuels, is a fuel to the electrodes used within the stack, rather than a poison. This considerably simplifies the fuel-processing regimen and reduces cost.
- The high-grade waste heat produced by the SOFC is of value in CHP applications and can be used to drive the endothermic fuel-processing reactions via an integrated heat exchanger. This increases efficiency and simplifies the balance of plant requirements, saving space, weight, and cost.
- Pure hydrogen fuel is not required, although hydrogen can, of course, still be used as the fuel.

These benefits mean that SOFCs are widely seen as the leading technology for application on today's available fuels of natural gas, propane/butane, gasoline, diesel, and alcohols.

Historically, SOFC development focused solely on high-temperature (900-1000 °C) operation, with the intention of integrating SOFCs into large-scale stationary power plants. This aspect of SOFC development continues today, driven by developers such as Siemens-Westinghouse[1] and Rolls-Royce,[2] who seek to couple the SOFC with a gas turbine to produce a highly efficient stationary power generation unit. However, it is increasingly recognized by the SOFC community that for smaller SOFC stacks not requiring integration with gas turbines, the operating temperature should be lowered as far as possible without compromising 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 IT-SOFCs operating at temperatures below 800 °C.

Selection of the solid electrolyte for these IT-SOFCs depends on the chosen temperature of operation. To help this

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selection process, it is useful to consider the following. Assuming that the electrolyte component should not contribute more than 0.15 Ωcm^2 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 Scm^1 (σ = L/area specific resistance (ASR) = 0.0015/0.15). The ionic conductivity of the most commonly used SOFC electrolyte, yttria-stabilized zirconia (YSZ) attains this target value above 700 °C, while the electrolyte used by Ceres Power, ceria gadolinia oxide (CGO), attains this conductivity at temperatures above 500 °C,[3] 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 much of the balance of plant components, and, hence, creates an operating condition that enables a significant reduction in both stack and balance of plant cost. A concern often expressed with regard to the use of CGO electrolytes in SOFCs is that, at elevated (>600 °C) temperatures Ce^{4+} ions can be reduced to Ce^{3+} 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 positive electrode-electrolyte-negative electrode structure, which can significantly degrade the efficiency and performance of cells incorporating ceria-based electrolytes. However, Steele[4] has shown that at temperatures of <600 °C the reduction of Ce^{4+} ions to Ce^{3+} 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 a CGO of 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 optimize 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 in which alloy electrolyte powder is 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) introduces 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 severe vibrations incurred when the stack is incorporated into systems used for transport applications. Moreover, Ni/NiO redox cycling induced by air diffusing into the anode compartment during a loss of fuel supply and other operational excursions can disrupt the anode microstructure, producing a severe degradation in performance.

An innovative approach to overcome these challenges, and thereby to enhance the robustness of SOFCs, is the use of a metallic support, in which 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 positive electrode-electrolyte-negative electrode assemblies was first patented in 1966,[5] but little attention was paid to this configuration until some 30 years later when DLR in Germany fabricated metal-supported SOFC structures using (expensive) vacuum plasma spray techniques.[6] In contrast, work at Imperial[7] and Ceres Power[8,9] has focused on the integration of low-cost "wet" ceramic routes with metallic materials.

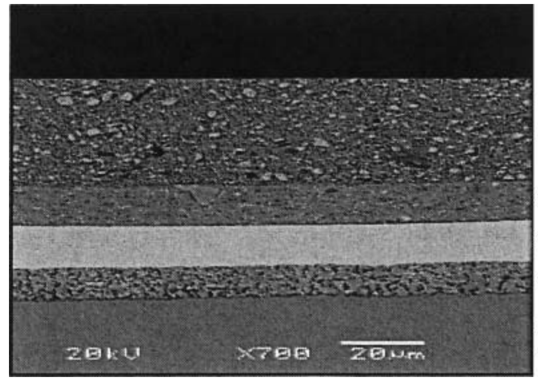

Fig. 1 Polished cross section through a metal-supported IT-SOFC, after testing on most hydrogen/air at temperatures up to 600 °C

Three suitable grades of ferritic stainless steel have so far been identified for use within the Ceres Power SOFC, and typical is our use of a Ti-Nb stabilized 17% 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 comparable, with values quoted in the range 12.5-12.8 × 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 process.[10] All of these processes are low cost and scaleable, and are used for mass manufacturing in industry today. The cell, shown in the cross section in Fig. 1, consists of a steel foil substrate, which is impermeable around the edges and porous in the center. The edges facilitate sealing, as the cell can be laser-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 CGO.

The electrolyte layer is deposited over the anode as a thick film (10-30 μm) of CGO. Ceres Power is able to fabricate fully dense CGO electrolyte films, fired at only 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/CGO composite being the present material of choice. The lanthanum ferrite/CGO composite

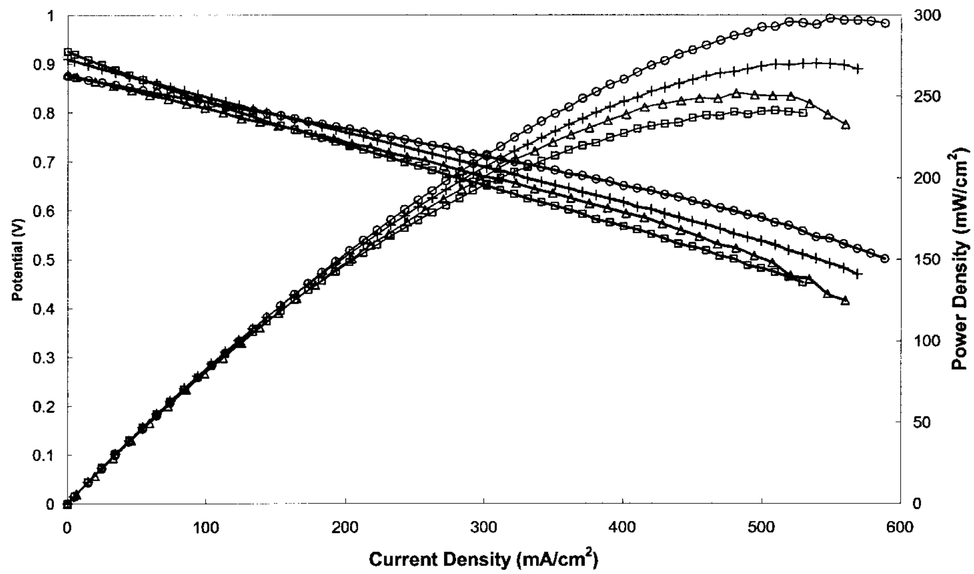

Fig. 2 Current-voltage and power curves from a 16 cm^2 cell that was tested on moist hydrogen (3% H_2O)/air at temperatures of (□) 550C, (+) 570C, (○) 600C, and (△) on emulated reformate/air at 600 °C

has been shown to have good performance at temperatures around 550 °C.[11,12] Two electrode impedance measurements in air using cathode half-cells on CGO pellets have shown that the Ceres Power embodiment of this electrode material delivers acceptable performance across the temperature range of interest, with area-specific resistance values of 0.77, 0.26, and 0.08 Ωcm^2 being measured at temperatures of 500, 550, and 600 °C, respectively.

So, to summarize, by comparison with other SOFCs, the Ceres Power approach has the following advantages:

- It uses a thick film cell supported on an inexpensive stainless steel substrate.
- Substrate foil can be easily brazed/welded to the stainless steel bipolar plate to allow flexible power scale-up via a simple array design.
- Low-cost manufacturing techniques lend themselves to mass production and, thus, to a low-cost product.
- Robust fuel cell stack manifold gaskets simplify construction and increase stack durability.
- It has a lower operating temperature than current SOFC designs (550 °C versus >750 °C).
- It has rapid start-up times compared with competing high-temperature fuel cells due to the materials used in construction and compliant stack seals.
- It has a simple, scaleable, and cost-effective modular design.
- It has a rugged, simple construction providing reliability and a long operating life.

Also, the Ceres Power approach retains the operational advantages common to all SOFCs, namely:

- High fuel efficiency and low emissions compared with heat engines, including internal combustion engine generators (operating system efficiency ≈40% for the SOFC versus 25% for the internal combustion engine).
- Near silent operation.
- Fuel type flexibility, notably the ability to run on fuels other than pure hydrogen (e.g., natural gas, LPG, methanol, and gasoline).

3. Recent Technical Highlights

Recent successes in the Ceres Power technical program have included the following:

- Cell-level (16 cm^2 active area) power density of 310 mW cm^{-2} at 600 °C on moist hydrogen/air, and 250 mW cm^{-2} on emulated reformate (i.e., a gas mixture of CO, H_2, CO_2, and H_2O that is representative of that produced by the steam reforming of natural gas) at the same temperature.
- Cell-level (16 cm^2 active area) power density of 240 mW cm^{-2} at 550 °C on moist hydrogen/air.
- Rapid cell start-up from cold demonstrated (<13 min), which presently is limited by the test rig design.
- No degradation after >2500 h lifetime testing to date.
- Short (three layer) stacks of 12 cells (total active area 192 cm^2) tested, giving >80% of maximum power.
- Gas tight stack seal demonstrated using conventional compression gaskets surviving repeated thermal cycling.
- Laser welding of cells to metallic interconnect demonstrated to give gas tight seal.
- Promising results from redox and thermal cycling trials, with little degradation evident after 25 thermal cycles and 7 redox cycles to date.

Additional detail is provided by Fig. 2, which illustrates the current-voltage and power-density response from a single cell of 4 × 4 cm active area, which was tested on moist hydrogen/air at 550 °C, 570 °C, and 600 °C. A maximum power density of 310 mW cm^{-2} was obtained. This is excellent performance for

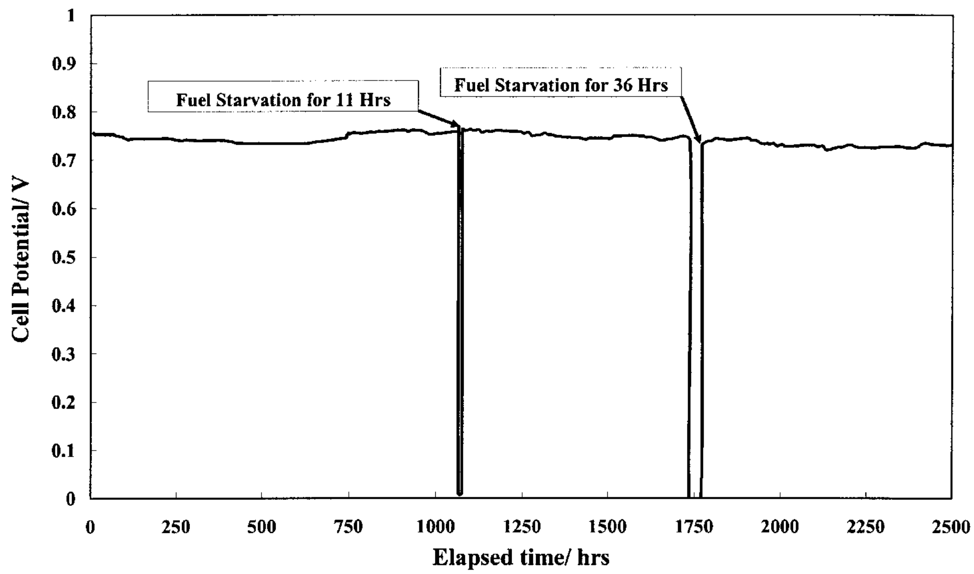

Fig. 3 Durability data from a 16 cm^2 cell that was tested at a constant current of 0.2 A cm^{-2} at 570 °C on moist hydrogen (3% H_2O)/air

an SOFC at this temperature range and represents the level needed for the commercialization of first-generation devices, especially when the total cell thickness of only 200-300 μm is taken into account. The cell voltage of around 0.91 V is in line with that expected from a CGO-based SOFC at this temperature and with this fuel composition. The cell was also tested using a fuel-gas mixture emulating that was produced by the steam reforming of natural gas (i.e., an emulated syn gas). In this case, the gas contained 73.8% H_2, 7.1% CO, 12.1% CO_2, and 7% H_2O, as determined by gas chromatography measurements. No methane could be measured in the outlet from the fuel cell, indicating that the kinetics of the thermodynamically predicted reverse methanation reaction was sufficiently slow as to be negligible. Modeling work indicates that power densities of 0.4 W cm^{-2} can be achieved at 550 °C on hydrogen/air, and 0.3 W cm^{-2} can be achieved on reformed natural gas/LPG with the present materials system, at a cell efficiency of 40-60% lower heating value (LHV), with the efficiency value depending on the actual operating point.

Figure 3 shows the results of a long-term durability test of an earlier 200 mW cm^{-2} class cell that was operated under a load of 3 A on moist hydrogen/air at 570 °C. The cell incurred a loss of fuel on two occasions due to problems with the testing infrastructure. Despite this, the cell displayed no net loss in performance after more than 2500 h of operation to date. This represents a very encouraging level of robustness, and the test is continuing.

4. Applications of Ceres Power Technology

Ceres is aiming its technology at products that are capable of generating between 1 and 25 kWe from a range of fuels, including LPG, natural gas, methanol, hydrogen, and vehicle fuels. Applications include remote power, auxiliary power units for vehicles and trucks, uninterruptible power supplies, and residential CHP.

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