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Comparison between anode-supported and electrolyte-supported Ni-CGO-LSCF micro-tubular solid oxide fuel cells

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Abstract

Two types of microtubular hollow fibre SOFCs (MT-HF-SOFCs) were prepared using phase inversion and sintering; electrolyte-supported, based on highly asymmetric $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO)HFs and anode-supported based on co-extruded NiO-CGO(CGO)/CGO HFs. Electroless plating was used to deposit Ni onto the inner surfaces of the electrolyte supported MT-HF-SOFCs to form Ni-CGO anodes. LSCF-CGO cathodes were deposited on the outer surface of both these MT-HF-SOFCs before their electrochemical performances were compared at similar operating conditions. The performance of the anode-supported MT-HF-SOFCs which delivered ca. 480 mW cm^{-2} at 600°C was superior to the electrolyte-supported MT-HF-SOFCs which delivered ca. 6 times lower power. The contribution of Ohmic and electrode polarisation losses of both FCs was investigated using

electrochemical impedance spectroscopy. The electrolyte-supported MT-HF-SOFCs had significantly higher Ohmic and electrode polarisation ASR values; this has been attributed to the thicker electrolyte and the difficulties associated forming quality anodes inside the small (<1 mm) lumen of the electrolyte tubes. Further development on co-extruded anode-supported MT-HF-SOFCs led to the fabrication of a thinner electrolyte layer and improved electrode microstructures which delivered a world leading 2400 mW cm^{-2} . The new-made cell was investigated at different H_2 flow rates and the effect of fuel utilization on current densities was analysed.

Keywords: micro-tubular solid oxide fuel cells (MT-HF-SOFCs), hollow fibres (HFs), electrolyte-supported, anode-supported, phase inversion, co-extrusion, Ni electroless plating.

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1 *Introduction*

Solid Oxide Fuel Cells (SOFCs) operate at high temperatures, due to their solid oxide electrolyte which becomes an oxygen ion conductor at elevated temperatures. Many different SOFC designs have made their appearances through the years [1-3]. However, compared to the other designs, the planar design has reached the stage of early market entry. A recent example of the progress made using the planar design is presented by the Bloom Energy Corporation [4] from USA and Ceramic Fuel Cells Limited (CFCL) from Australia.

However, the reduction in the high capital costs for such power units, required to break into larger market segments, remains unresolved. The main reason that planar Fuel Cells (FCs) are more developed than the other designs is because of their simple and cost effective structure. The electrodes and electrolyte layers can be fabricated and combined easily using cost-effective techniques such as tape casting. On the other hand the tubular design, which made its appearance around 1970 [1, 2], offers significant benefits. However, the technology is yet to be commercially exploited due to practical difficulties related to the cell to cell interconnection required for scaling up the current and voltage. Recently scientific interest has focused on newer tubular designs termed micro-tubular SOFCs (MT-SOFCs). These micro-sized SOFCs offer the potential of building units with high volumetric power densities, which scales inversely with tube diameter, and are less prone to the temperature inflections, minimizing the start-up time to some seconds [5]. Also tubular SOFCs are easier to seal and the cost of material used for manufacturing MT-SOFCs that could generate 1kW power, is calculated to be around 1% of the cost of Siemens-Westinghouse tubular cells [6]. The above superior characteristics of MT-SOFCs combined with the reduction of their operation temperatures down to 400-600 °C opens up the possibility of such systems being used in mobile applications [7] which has brought renewed interest in this field of research.

Currently, MT-SOFCs are categorised into 3 types; a) cathode-supported, (b) electrolyte-supported and c) anode-supported. The naming convention is usually based on the layer which is fabricated first; typically this layer is the thickest part of the cell and acts as the mechanical supporting base for the rest of the SOFC to build on. While the first tubular SOFCs were made by Siemens-Westinghouse they were built on an external support tube but very quickly the design moved to cathode-supported structures to reduce the size and the cost of the single cell units. The research on cathode-supported MT-SOFCs is currently very limited [8-11]. The reason is because the mismatch of the sintering profile [5] of the cathode

material with the sintering profile of the most electrolyte materials, which sinter at higher temperatures. Moreover, the poor mechanical strength of cathode material combined with the lower diffusion coefficient of oxygen have pushed the technology towards using alternative supporting layers.

The literatures on anode-supported and electrolyte-supported are vast and only some of the most relevant are reported here. Electrolyte-supported [1, 12-15] MT-SOFCs are the oldest design among the three. This is probably because an electrolyte supporting base such as YSZ is strong and easier to handle. Furthermore, by fabricating the electrolyte substrate followed by high temperature sintering process, a high-quality gas-tight separation layer can be achieved. The quality of electrolyte layer is important in the FC technology and is a major factor contributing to the performance of the cell. Although electrolyte supported MT-SOFCs are a more mature configuration, their performances seemed to be limited mainly due to their thick electrolyte which causes higher Ohmic losses as the oxygen ion crosses from the cathode to the anode, which reduces the power produced by the SOFCs. Furthermore, fabricating the anode inside the small micro-tubes for electrolyte-supported MT-SOFCs is impractical [1, 13] leading most of the times to low quality electrodes, which greatly increases the oxidation polarisation losses during operation. Anode-supported MT-SOFC designs [1, 16-19] gather several advantages upon the other types of tubular SOFCs. The idea of anode-supported micro-tubes was strengthened when co-extrusion/co-sintering techniques began to be applied in fuel cell technology [11]. The creation of two layers in a single step was a breakthrough step for creating a good quality anode electrode, also used as the supporting base, and at the same time a high quality electrolyte with minimum thickness. The application of the cathode layer can be achieved by dip-coating and/or paint brush based techniques [8-13], therefore reducing the cost per unit structure. Moreover, the insertion of the current collector was less of a problem since by fabricating the anode layer first this

provided a direct access to the electrode surface. However, in the case of anode-supported dual-layer fibres where anode and electrolyte are extruded simultaneously, the insertion of anodic current collection poses the same problems as the case of electrolyte-supported cells.

The tubular supporting base for the anode, electrolyte and cathode-supported tubular fuel cells are typically fabricated using techniques such as gel-casting [20], plasma-spraying [21], isostatic pressing [22], thermo-plastic [23], ram extrusion [24] and very recently combined phase inversion and sintering [25]. From the above techniques, phase inversion and sintering can be considered as one of the most promising techniques used in the field of MT-SOFCs as the micro-structure of the hollow fibre (HF) supporting base can be carefully controlled, which leads to the extrusion of high quality electrodes with lower polarisation losses. Currently, there is a growing interest in using phase inversion and sintering to produce HFs with controlled microstructures which leads to the increase in the performance of MT-HF-SOFCs. A number of research groups are investigating the use of phase inversion and sintering in the SOFCs technology and the power output of MT-HF-SOFCs fabricated by this technique are encouraging [12, 17-19, 26-28].

In this communication we report on the preparation of and compare the respective performances of electrolyte-supported and anode-supported dual layer MT-HF-SOFCs made by combined phase inversion and sintering. The electrolyte supported cells were based on highly asymmetric HFs, which were first introduced previously [29, 30] whereas the anode-supported dual-layer HFs were part of a research project at Imperial College, London [17]. This is the first such report to compare the electrochemical performance of two types of MT-SOFCs with similar fabrication techniques, trying to quantify the benefits and challenges in each approach.

2 Experimental

2.1 Fabrication of electrolyte and anode-supported HFs

2.1.1 CGO-based electrolyte-supported HFs

Materials employed in the fabrication of highly asymmetric cerium-gadolinium oxide (CGO) HFs were CGO powder (Nextech Materials < 1 μm particle size 35.8 m^2/g), polyethersulfone (PESf, Ameco Performance, Radel A-300), N-methyl-2-pyrrolidone (NMP) (Sigma Aldrich, HPLC grade), ethanol (VWR International Ltd, 99.7 vol. %) and polyethylene glycol (Merck Schuchardt OHG, PEG-400) with composition described in details in Table 1. CGO micro-tubes were fabricated by a phase inversion process [28], washed in tap water and heated to 600 $^{\circ}\text{C}$ at 3 $^{\circ}\text{C min}^{-1}$ for 2 hours allowing for the removal of the polymer binder. The temperature was then raised to 1000 $^{\circ}\text{C}$ at 3 $^{\circ}\text{C min}^{-1}$. CGO micro-tubes were sintered at a final temperature of 1550 $^{\circ}\text{C}$, using a heating rate of 5 $^{\circ}\text{C min}^{-1}$. After a dwell time of 5 hours the temperature was decreased to room temperature at a rate of 5 $^{\circ}\text{C min}^{-1}$.

2.1.2 NiO-CGO/CGO-based anode-supported dual-layer HFs

In the preparation of the anode-supported dual-layer HF, two ceramic suspensions were prepared separately. The suspension of the anode inner layer was composed of 60 wt.% of nickel oxide (NiO) and 40 wt.% of CGO, while the one for the electrolyte outer layer contained CGO powder only. The compositions of both suspensions are listed in Table 1.

The anode-supported dual-layer precursor HFs were prepared by a phase inversion based co-extrusion process [31]. Prior to the co-extrusion, the suspensions were degassed at room temperature, loaded into a stainless steel container and pressurized simultaneously through the triple orifice spinneret (at the extrusion rate of 0.117 cm^3s^{-1}) into a tap water coagulation bath with a 20 cm air-gap length. The internal coagulant (de-ionized water) was set to a flow

rate of $0.167 \text{ cm}^{-3}\text{s}^{-1}$. The HF precursors were then co-sintered by heating in air at 1500°C for 12 hours in a tube furnace. More details on the preparation of the ceramic suspension and the design of the spinneret can be found in [31].

2.2 Anode deposition on CGO-based HFs

Ni electroless plating was employed to deposit a Ni anode on the inner surface of the CGO micro-tubular electrolytes. The recipe of the Ni bath is reported in Table 2. Further details of the Ni electroless plating recipe can be found in [13].

The external surface was masked with PTFE tape to avoid contamination. Sensitisation and catalysing steps were carried out by dipping the micro-tube into a beaker containing the sensitisation/catalysing solution. The plating solution was contained on a beaker placed on a stirring hot plate (to provide agitation and the required heating) where the temperature and the pH were monitored with a thermometer/pH meter (Hanna Instruments HI 1295 amplified electrode Piccolo Plus). The catalysed HF was dipped into the plating solution for 1.5 hours then washed with tap water and dried at 110°C for 2 hours.

2.3 Cathode deposition

2.3.1 Cathode deposition on CGO-based HFs

On the electrolyte-supported Ni/CGO/CGO-LSCF MT-HF-SOFC, a CGO-LSCF cathode was deposited by slurry coating. CGO and LSCF ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$, Praxair) powders were employed. A first layer with composition 50 wt.% CGO and 50 wt.% LSCF was deposited and sintered at 1200°C for 6 hours. A second layer of pure LSCF acting primarily as a current collector was then deposited by slurry coating and sintered at 1200°C for 6 hours.

2.3.2 Cathode deposition on NiO-CGO/CGO-based dual-layer HFs

Similar to electrolyte-supported structures, the cathode coating onto the anode-supported dual-layer HF was prepared by slurry coating techniques and brush-painted. The cathode layer deposited onto the anode-supported dual-layer HF was done in a two-step process. During the first-step, three-layers of cathode material were deposited. The first 2 layers consisted of 50 wt.% CGO (Nextech Materials < 1 μm particle size) and 50 wt.% LSCF ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$, Praxair), and the 3rd layer pure LSCF. The dual layer fibre with the deposited cathode layers were sintered at 1100°C for 3 hours. Following this a second-step consisting of another 2 layers of pure LSCF were deposited and the new samples were sintered at 1200 °C for 5 hours.

2.4 Current Collection

The current collection technique was similar for both types of fuel cells. The cathodic current was collected using silver wires (0.2 mm diameter, 99.9 % purity, Sigma-Aldrich®, UK) wrapped around the cathode; the connection between the cathode and the wire was enhanced by using platinum paste (SPI Supplies Platinum Paint, USA). The anodic current collection needed a more careful approach due to the fact that the anode was covered by the (insulator) electrolyte layer and therefore the only access to the electrode was from the lumen of the fibre. The easiest and most effective way to carry this out was to create a spring from 2 silver wires (0.25 mm diameter, 99.9 % purity, Sigma-Aldrich®, UK)) and insert the wires along with silver wool (0.05 mm diameter, 99.9 % purity, Sigma-Aldrich®, UK) into the lumen of the fibre to enhance the connection to the inner walls of the anode. Fig. 1 (A) shows how the anode current collection technique appeared for (A) only the silver wire and (B) silver wire and the silver wool. The insertion of wool into the lumen of the fibre significantly enhanced the contact between the silver wire and the inner walls of the anode without influencing H_2

flow. Fig. 1 (B) shows a complete MT-HF-SOFC with the cathode and anode current collectors.

2.5 *Single Cell Reactor Design*

Each fibre was tested separately in a single cell test reactor. The test reactor consisted of ceramic fuel feed tubes (Multilab Ceramics, UK) attached to the fibre using ceramic cement (Aremco, USA). The cement sealing became gas-tight during sintering at 200 °C for 2 hours. The fibre with the ceramic tube extensions was sealed within a quartz tube (The Technical Glass Co, UK) of diameter 30 mm OD and 430 mm length, through which air flowed to the cathode. Humidified H₂ was supplied to the anode at controlled rates. The thermocouple detector (K-type thermocouple, YC-747D-4 Channel data Logger) was also passed inside the reactor and near the fuel cell through an additional entry port on one of the cylindrical alumina parts used to accomplish the hermetic seals at the ends of the quartz tube. In order to prevent gas leakage from the reactor, silicon rubber was used to seal the cylindrical disk and associated tubing and thermocouple wire to the quartz tube. The quartz tube was inserted into a 300 mm long horizontal furnace (Carbolite, VST/HST–12/200/1200 °C). The two ends of the quartz tube extended outside of the heating zone of the furnace in order to prevent any damage occurring to the silicon connections. Fig. 2 (A) shows the ceramic parts of the reactor and Fig. 2 (B) the complete reactor before fuel cell testing.

2.6 *Fuel cell characterisation and test*

The microstructures of the two types of HFs were investigated by scanning electron microscopy (SEM, JEOL JSM-5300LV scanning microscope) and electrolyte porosity was measured with a mercury porosimeter (Micromeritics Autopore IV 9500). The mechanical strength of the HFs was measured by three-point bending strength (Instron Model 5544

tensile tester) as described elsewhere [32]. Bending strength σ_F [Pa] was calculated from the Equation (1):

$$B_F = \frac{8 N L D_o}{\pi (D_o^4 - D_i^4)} \quad (1)$$

where N [N] is the force required to fracture the micro-tube, L [m] is the length of the HF, D_o [m] the outer diameter and D_i [m] the internal diameter of the HF.

The gas-tightness of the HFs was measured by pressurising the HF with N_2 and measuring the pressure change with time. The procedure and equipment are described elsewhere [31].

Gas permeance was calculated from Equation (2):

$$P = \frac{V_c}{RT \cdot A_m t} \ln \left(\frac{p_o - p_a}{p_i - p_a} \right) \quad (2)$$

where P is the permeability of the sample [$\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$], V [m^3] is the volume of N_2 contained in the enclosing gas cylinder, R [$\text{J mol}^{-1} \text{K}^{-1}$] the gas constant, T [K] the temperature, p_o and p_i [Pa] the initial and the final pressure of the N_2 cylinder, p_a [Pa] the atmospheric pressure, t the time of the measurement [s] and A_m [m^2] the area of the micro-tube. A_m was calculated from Equation (3):

$$A_m = \frac{\pi(D_o - D_i)L}{\ln \left(\frac{D_o}{D_i} \right)} \quad (3)$$

The electrochemical characterization tests of the MT-HF-SOFCs were carried out under the continue flows of humidified H_2 (anode: ca. 15 ml min^{-1} , 97% H_2 -3% H_2O) and air (cathode: 30 ml min^{-1}). The nickel oxide of the NiO-CGO/CGO-based dual-layer HFs was reduced to

produce a Ni-CGO composite anode by flowing $5 \text{ ml min}^{-1} \text{ H}_2$ through the lumen for 150 minutes at 550°C . To control the flow rate of H_2 and air two mass flow controllers were used (Bronkhorst, UK). The controllers were monitored by a computer using Bronkhorst Software. The current collectors to the anode and cathode protruded from the fuel and air stream line, from the reactor and from the furnace and were connected to a Potentiostat / Galvanostat (Autolab PGSTAT 30, Eco Chemie, Netherlands) and a booster (Autolab, BSTR10A, Eco Chemie, Netherlands). The electrochemical characterization tests were monitored using the software Nova 1.5 (Autolab, Eco Chemie). Fig. 3 shows Connections from the fuel cells to the Potentiostat / Galvanostat.

The ‘active’ area used as the base for all the calculations relating to fuel cell performance was chosen to be the area of the fuel (hydrogen) electrode. In this work, the ‘active’ area of the fuel cell was found by Equation (4):

$$A_{cell} = 2r_{in}\pi L_{cell} = D_{in}\pi L_{cell} \quad (4)$$

where D_{in} [m] the inner diameter of the HF and L_{cell} [m] the active length (based on cathode deposition) of the complete fuel cell.

Current density was calculated by Equation (5):

$$j_{cell} = \frac{I}{A_{cell}} \quad (5)$$

Furthermore, the electrical power density of a fuel cell was found by calculating the cell’s true voltage and the current density produced by the cell such as Equation (6):

$$P_{d,cell} = j_{cell}U \quad (6)$$

Fuel utilization (U_f) was estimated from Equation (7):

$$U_f = \frac{I}{\nu_e F \times n_{H_2, inlet}} \times 100\% \quad (7)$$

where ν_e is the number of electrons generated per mole of hydrogen consumed in the oxidation step and F [96485.3 C mol⁻¹] is the Faraday constant.

MT-HF-SOFCs electrochemical properties were investigated using electrochemical impedance spectroscopy controlled by FRA 4.9 at 100000-0.01 Hz, 50 number of frequencies and 0.01000 V amplitude (rms).

3 Results and Discussion

3.1 Fuel cell characterisation

3.1.1 CGO-based HF's

Fig. 4 shows a scanning electron photomicrograph of the highly asymmetric CGO HF after sintering. Fig. 4 (A) shows the wall of the highly asymmetric CGO HF, where long finger-like structures are visible. These structures originate from the outer surface of the HF and extend into the structure of the highly asymmetric CGO HF. The starting points of the finger-like formation create entrances to macro-voids, as presented in Fig. 4 (B), thus improving subsequent cathode deposition. The formation of such an asymmetric structure was a result of viscous fingering phenomenon [33] due to a specific composition of the internal coagulant (i.e. 92 wt % NMP and 8 wt % water). In comparison to the highly asymmetric YSZ HF's [30], finger-like structures were less prominent and less of these macro-voids extended to the inner surface. This might be related to the higher surface area of the commercially available CGO powders, which were used to fabricate the HF's, which resulted in much higher viscosity

of the spinning suspension. Fig. 4 (C) shows the inner surface of the CGO HF. The inner surface looked dense and had a dune shape formation. The rough surface was achieved to help anode deposition.

In the literature, the bending strength of ceramic HFs for SOFC application has been reported to be in the range 100 to 407 MPa [12, 34-36]. The bending strength results of the current HFs are reported in Table 3. Since the bending strength of the prepared CGO HFs was in the range of 150-200 MPa they were considered sufficient to be employed as a support for FCs. However, this value was still slightly lower compared to YSZ HFs, which were reported to be, 210 MPa [1] and 223 MPa [3] when sintered at 1400°C–1450°C. The difference in the values of CGO and YSZ micro-tubes can be attributed to the characteristic of the material itself and also from the slight differences in terms of their macrostructure. As reported in the literature, the acceptable value for the gas-tightness property of electrolyte HF is app. 5×10^{-8} mol m⁻² s⁻¹ Pa⁻¹ and lower [34-37].

3.1.2 CGO/ Ni-CGO-based dual-layer HFs

60 wt.% NiO-40 wt.% CGO HF precursors retaining symmetric structures with a co-extruded CGO layer were initially produced by phase inversion. After sintering, these first series of experiments retained a non-uniform circular shape and the CGO layer appeared deformed; delaminations were visible with a naked eye (Fig. 5 (A)). Later, by improving parameters during fabrication, the second series of experiments showed an improved result with regards to the shape of the fibres (Fig. (B)). A circular shape was achieved and delaminations were minimised. Although the cell was not optimised yet, the cathode was deposited externally using slurry coating and several cells were electrochemically tested in single cell reactors at 550 °C. The first SOFC experiments failed due to the imperfection of the dual-layer fibre. Not only were the OCV values very low (ca. 0.5 V), but the performance of the fuel cells was

very poor. H₂ leaks were detected in the controlled area (quartz tube) of the single cell reactor. Hydrogen's direct reaction with air caused a small combustion reaction (and flame) resulting in a black spot on the quartz tube of the reactor. Post mortem tests revealed that the outer finger-like voids (Fig. 5 (B)) of the anode-support microstructure led to the delamination of the electrolyte layer. Therefore, a series of experiments were carried out to transition the microstructure from being symmetric to asymmetric to eliminate the outer finger-like voids. Furthermore, to enhance the electrical conductivity and mechanical strength of the dual-layer fibres, the anode membrane retained shorter finger-like voids on the inner side of the cell therefore increasing the volume of the sponge-like voids. The dual-layer fibre presented in the last set of experiments (Fig. (C)) retained all the main characteristics required for use in an SOFC electrochemical assessment. Fig. 5 (C) shows the SEM images of the anode-supported CGO/Ni-CGO dual-layer HF, co-sintered at 1500 °C for 12 h followed by a reduction at 550 °C for 150 minutes. The outer diameter (OD) and the inner diameter (ID) of the dual-layer HFs were measured to be of approximately 1400 and 800 µm, respectively, with the electrolyte layer on the outer surface (thickness ca. 80 µm) and anode on the inside (ca. 220 µm).

As can be seen from Fig. 5 (C) the cross-section of the anode layer exhibited an asymmetric structure with short finger-like structures originating from the inner surface to approximately 35 % of the anode layer thickness, whereas the remaining 65 % consisted of a sponge-like structure. The anode microstructure affects cell performance by: (a) finger-like voids providing facile transport of fuel to anode sites, (b) sponge-like structures creating larger triple-phase boundary (TPB) lengths for electrochemical reactions and to provide adequate mechanical strength for fully fabricated anode-supported MT-HF-SOFCs. The cross-section of the electrolyte layer also had short finger-like structures near the outer surface and a sponge-like structure occupying the rest of the layer. The electrolyte layer was dense and

fully gas tight, preventing any mixing of fuel and air. This figure also shows that the HF had good adhesion between the inner and outer layers and that it was free from any apparent anode/electrolyte delamination. Furthermore, the electrolyte outer layer had very uniform thickness on the anode outer layer and covered the whole length of HF surface, and thus, shows another advantage of co-extrusion as a deposition technique of a thin high quality electrolyte layer on the HF support.

Fig. 6 shows SEM images from the unreduced (Fig. 6 (A)) and reduced (Fig. (B)) anode layer of the anode-supported dual layer HF. In both images it can be seen that the quality of mixing of the NiO/Ni (darker phase) and CGO (lighter phase) particles was good. Previous studies by the same group have revealed the importance of the triple phase boundary (TPB) density to MT-HF-SOFC performance [38]. In order for the oxidation to take place within the electrodes, a common surface of the electronic catalysts (such as Ni), the ionic catalyst (such as CGO) and the fuel particles (such as O_2) needs to exist. For having a high performance electrode, with fast H_2 oxidation kinetics this active area has to be as large as possible. The active surface is created during the fabrication of the electrodes. One of the most important parameters to achieve such a microstructure is the quality of mixing of the particles of different phase and uniform distribution of these particles throughout the electrode. In addition, the electrode has to retain an adequate porosity, equally distributed through the electrode, in order to allow free movement of reactant and product species to and away from the reaction sites. The above characteristics are mostly dependent on the capabilities and quality of the method used to build the electrodes. Based on imaging analysis such as Fig. 3 (B) and from the results presented in previous work [17, 32, 38, 39] it can be confirmed that phase inversion and sintering is a technique that is able to produce high quality electrodes.

The construction of complete MT-HF-SOFCs requires the fabrication of dual-layer HFs with reasonably strong mechanical properties, mainly for the deposition of the remaining components such as cathode and current collector. As presented in Table 3, the bending strength of the HF was 141.1 MPa. This value is comparable to the bending strength of the electrolyte-supported HFs. The co-extruded non-porous electrolyte layer on top of the porous anode support appreciably enhanced the mechanical strength of the dual-layer HF. Furthermore, Table 3 shows the N₂ permeability of the dual-layer HF which was $2.02 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, indicating that the produced HF was sufficiently gas tight.

3.1.3 *Electrolyte-supported Fuel Cell*

Fig. 7 shows a cross-section of the electrolyte-supported MT-HF-SOFC. Starting from the inner surface, a pure Ni layer appears to evenly cover the surface of the micro-tube. The resulting Ni deposition was expected to give good electrical conductivity but poor three phase boundary. Moving further inside the figure shows the ca. 250 μm wall of the HF. It seems that the highly asymmetric formation offered reduced thickness of the dense electrolyte layer. It appears from the images that the dense electrolyte layer was around ca. 150 μm and the rest of the CGO HF volume (ca. 100 μm) consisted of the finger-like pores which had been filled by cathode particles deposited during cathode fabrication. Furthermore, it seems that the brushed-paint cathode on top of the CGO fibre was approximately 20-30 μm thick.

3.1.4 *Anode-supported Fuel Cell*

Fig. 8 (A) displays the cross section of the anode-supported dual layer MT-HF-SOFC. Starting from the inner half of the cross sectional image, the figure shows the anode supporting layer (Ni-CGO), followed by the electrolyte layer (CGO) in the middle and lastly the external layer which represent the cathode|cathode current collector layer (LSCF-CGO|LSCF). The image was taken after the electrochemical characterisation of the FC. As

can be observed in the figure, the layers remained well adhered, consistent with the pre-test SEM showing no apparent delamination created during the test. Fig. 8 (B) shows a magnified image of the electrolyte and cathode layer. Although in reality the cathode layer consisted of 5 layers deposited in a 2-step process (explained in section 2.3.2), in the SEM analysis of the cathode highlights only two distinct layers. The reason for this is because the 3 external pure predominantly current collecting LSCF layers were indistinguishable after the high sintering temperatures, thus appearing similar in the SEM. Similarly, the other 2 mixed (CGO-LSCF) layers deposited firstly on the dual layer fibre cannot be clearly differentiated in the image. The mixed CGO-LSCF part of the cathode was ca. 25 μm thick and it consisted of CGO particles (lighter phase) and LSCF particles (darker phase). The mixed and pure cathode layers appeared well bonded creating a ca. 70 μm thick predominantly cathode current collector layer. Compared to the microstructure of the anode layer (seen in Fig. 6), it was apparent that the LSCF particles were not uniform distributed, rather tending to agglomerate creating bigger blocks. This microstructure of the functional layer appeared to be not creating high TPB surfaces for the cathode electrode and this phenomenon might have an effect upon the performance of the FC, due to reduced cathode kinetics. One possible explanation for the LSCF particle agglomeration within the functional layer is the difference in sintering profiles of the CGO and LSCF [40, 41]. Furthermore, the final layers of the cathode that consisted of the pure LSCF acting predominantly as a current collector did not retain good porosity potentially reducing the efficiency of O_2 transfer to the cathode reaction sites close to the cathode|electrolyte interface. Lastly, at some parts on the circumference of the FC some cracks were observed during visual inspection, probably caused by the 2-step sintering process that was followed.

Overall, it seems that cathode layer needs further improvement. Optimal cathode deposition is part of a parallel research programme which aims to investigate different cathode

deposition techniques for MT-HF-SOFCs [42]. The manual mixing of different particles during the preparation of the cathode slurry and the use of paint brush for depositing the cathode layer are possibly too crude to replicate uniform structures such as in Fig. 8 (B). It is generally acceptable that low cost methods of fabricating electrodes such as the one we used for this study could result in low quality electrodes. On the other hand, if the performance of the FC is acceptable the loss in performance by using such electrodes could be compensated for by the low cost of fabrication per unit structure.

3.2 Fuel cell performance

Figure 9 and 10 show the cell voltages and power densities as functions of current density for anode-supported dual-layer MT-HF-SOFC and the electrolyte-supported MT-HF-SOFC, respectively. Active lengths were 10 mm for both MT-HF-SOFCs. The maximum power densities generated in these tests using $15 \text{ cm}^3 \text{ min}^{-1} \text{ H}_2$ flowing to the anode and $30 \text{ cm}^3 \text{ min}^{-1}$ air flowing to the cathode at 600°C , 550°C , 500°C and 450°C are reported in Table 4. By comparing the maximum power density values between the two types of MT-HF-SOFCs it can be seen that anode-supported dual layer FC performed considerably better. At high temperatures the power produced was around 5 times greater for the anode-supported structure but moving towards the lower temperature regions the difference increased to almost a factor of ten. One of the most important parameters to achieve faster kinetics in the electrodes is the magnitude of the number of active surfaces within the electrodes. Especially, at low temperatures, where kinetics is generally slower, at low fuel utilizations as in the current tests, a FC performance is generally limited by activation polarization. This phenomenon was obvious during our experiments where at 450°C the maximum power density of electrolyte-supported MT-HF-SOFC was 10 times lower compared to the anode-supported SOFC which had better electrodes characteristics with probably higher actives

surfaces (TPB).

Lower than expected equilibrium potentials or open circuit voltages (OCV) were measured for both tested fuel cells. For the anode-supported dual-layer FC OCVs were measured to be 0.88 V at 600 °C, 0.91 V at 550 °C, 0.92 V at 500 °C and 0.94 V at 450 °C and for the electrolyte-supported FC measured as 0.77 V at 600 °C, 0.79 V at 550 °C, 0.81 V at 500 °C and 0.77 V at 450 °C . In the case of electrolyte-supported FC, the lower OCV can be attributed to the three orders of magnitude higher N₂ permeability, indicating poor gas-tightness of the electrolyte. The reduced OCVs for both cells were probably due to a combination of current and gas leaks through the electrolyte layer. However, the values were within the range of values reported in an earlier work [17]. In order to increase the OCV values, a fully gas-tight electrolyte layer must be achieved during the fabrication of the HFs. Decreasing the leaks across the electrolyte will be a focus of future work.

Compared to the literature the best performed fuel cell tested in this work (anode-supported type) performed app. 2 times less compared with other MT-SOFCs of similar dimension [16]. In the case of electrolyte-supported MT-HF-SOFC the reason for low performance was a combination of Ohmic and polarization losses generated within the FC due to the existence of a very thick electrolyte layer (150 μm) and the low quality electrodes. Most importantly, the gas tightness of the electrolyte-supported structures needs to be optimised for aiming higher performances. Furthermore, the power density produced by the anode-supported dual-layer FC was limited probably due to the less developed electrodes used but also due to the relatively thick electrolyte layer (ca. 80 μm). Particularly, development needs to be done on the electrodes not only to increase the TPB surface but also to increase the electrodes' porosity and electrical conductivity. The exact magnitude of the polarization losses generated

in the cathode and anode electrode can only be measured using a 3-electrode measurement, a challenging task in the micro tubular design.

Fig. 11 shows impedance spectra for both the MT-HF-SOFCs at 600 °C. Because of the large difference in impedance diagrams between anode and electrolyte-supported MT-HF-SOFCs, the diagrams related with the values found at 550 °C, 500 °C and 450 °C are not shown. However, the Ohmic ASR values and activation ASR values calculated from the low and high frequency intercepts on the nyquist plot, at these temperatures are presented in Table 4. The big difference in size of the two diagrams, anode-supported (smaller diagram) and electrolyte-supported (bigger diagram), reiterates the differences in their performance discussed earlier. The total value found for the activation losses (anode and cathode electrode) of anode-supported structure was 6 times less than the values found for the electrolyte-supported structures. This indicates that the electrode structures of the anode-supported MT-HF-SOFCs was more developed presenting higher TPB values, and therefore faster electrode kinetics. Similar trends were observed at all temperatures with the differences in the values increasing at lower temperatures. As expected due to the thicker electrolyte, Ohmic ASR values were also higher for the electrolyte-supported MT-HF-SOFCs which compounded the poor performance.

More effort was given on improving anode-supported structures, which showed better performance. Fig. 12 (A) shows the effect of current density and Fig. 12 (B) the effect of H₂ flow rate on the cell voltage and power densities for the newly developed 10 mm long anode-supported H₂|Ni–CGO|CGO|LSCF-CGO|CGO|air MT-HF-SOFC at 600 °C. The first set of electrochemical tests was carried out at 15 ml H₂ min⁻¹ at 600 °C. As can be seen from Fig. 12 (A), the performance of the fuel cell at ca. 3000 mA cm⁻² was affected from mass transfer limitations and the performance deteriorated rapidly to ca. 4000 mA cm⁻². When the fuel cell

was tested at $30 \text{ ml H}_2 \text{ min}^{-1}$ the performance showed a remarkable increase. It seems that at current densities $>30 \text{ kA m}^{-2}$, increasing the flow rate from 15 to $30 \text{ ml H}_2 \text{ min}^{-1}$ increased cell voltages and power densities, due to a reduced contribution of anode concentration polarisation to the overall potential losses; a maximum power density of ca. 2400 mW cm^{-2} was achieved at 600°C . As the fuel flow rate was decreased from 30 to 15 ml min^{-1} , mass transfer limited current densities decreased from ca. 80 to ca. 40 kA m^{-2} , leading to sharply low voltages, caused by local decreases in partial pressure of the reactant at the triple phase boundary sites within the anode, due to diffusion limitations through the anode radial thickness. Fig. 12 (B) shows the effect of fuel utilization for 15 and $30 \text{ ml H}_2 \text{ min}^{-1}$ on the cell current densities. It seems that lower fuel utilisations, analogous to higher H_2 flow rates, improved the MT-HF-SOFC performance due to decreased anode activation and concentration polarisations which are inversely related to local H_2 partial pressures. Even though the new FC generated very high power densities at $30 \text{ ml H}_2 \text{ min}^{-1}$ the low fuel utilization results (at least ca. 85% to make a commercial case) presented in Fig. 12 (B) reveal that there is more to be done for maximising the FC's performance including the increase of the porous structure to achieve higher fuel transfer within the reaction sites of the fuel cell.

Although it is very early to make conclusions for the overall performance of this newly developed cell, the extremely high peak power density at 600°C marks a new era in the field of MT-SOFCs. This new type of anode-supported dual-layer fuel cell comprised of a different anode microstructure (65% finger-like structures compared to the 35% finger-like structures of the old version fuel cell presented in Fig. 5 (C)), more porous, that enables fuels to reach the electrode active surfaces more efficiently and thinner electrolyte layer (less than $20 \mu\text{m}$ thick) that minimized electrolyte Ohmic losses. In previous work [43] it was reported that it is likely that the distributed sponge-like pores in the anode caused mass transfer of the reactant

and product species to be dominated by diffusion. By decreasing the thickness of the anode with sponge-like structures and increasing the thickness of finger-like structures, higher anode permeabilities were achieved, consequently increasing transport limited current densities without significantly compromising the mechanical strength and axial electrical conductivity of the electrode. In addition, this newly developed fuel cell retained an improved cathode which was part of a parallel research project [42]. The newly developed cathode had better microstructure which aimed at improving the triple phase boundary sites of the electrode in order to minimize cathode activation polarizations. However, these modifications caused a decrease in the OCV of this cell at 600 °C to ca. 0.7 V which revealed some problems related to the gas tightness of the thinner electrolyte layer of the cell.

4 Conclusions

In this study, we have compared the performance of an anode-supported structure and an electrolyte-supported structure for a MT-HF-SOFC based on Ni-CGO-LSCF.

- The performance of the electrolyte supported design was poor mainly related to high Ohmic losses due to the thick dense electrolyte layer and engineering challenges involved in forming quality anode electrodes within the ca. 1 mm diameter HFs.
- Both polarisation and ohmic ASR's were ca. 30-40 times higher in the case of electrolyte supported MT-HF-SOFCs at 600 °C.
- Nickel deposition was restricted to the inner surface of the CGO and reduced the electrode's active surface. At the same time the dense nickel layer prevented the flow of hydrogen within the anode and accelerated mass transfer limitations.
- Anode-supported structures are easier to prepare and offer the opportunity to control the anode microstructure.

- The use of co-extrusion also reduces the fabrication cost and eliminates one high temperature sintering step. Also with this technique a thin gas tight electrolyte can be prepared increasing the possibilities of achieving higher performances.
- The newly developed type of anode-supported dual-layer MT-HF-SOFC generated ca. 2400 mW cm⁻² revealing the remarkable capabilities of MT-HF-SOFCs.
- Non sophisticated, cost-effective methods such as slurry coating techniques can be used for the deposition of the cathode layers however more development is needed to improve the cathode microstructure.
- One of the main problems of the MT-SOFC family is the anodic and cathodic current collection techniques. Finding a solution to the above problem will be crucial for the future of these type of fuel cells.

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Table Captions

Table 1. Electrolyte and anode-supported HFs fabrication parameters.

Table 2. Ni electroless plating recipe for Ni deposition on CGO HF.

Table 3. Bending strength and N₂ permeability for electrolyte and anode-supported HFs.

Table 4. Maximum power output and Ohmic ASR comparison between the electrolyte-supported and anode-supported Ni-CGO-LSCF MT-HF-SOFCs.

Tables

Table 1. Electrolyte and anode-supported HF's fabrication parameters.

Component	Highly asymmetric	dual-layer anode-supported HF's	
	CGO HF's	Inner layer	Outer layer
CGO	61.00 wt. %	28.00 wt. %	64.00 wt. %
NiO	-	42.00 wt. %	-
PESf	6.10 wt. %	7.00 wt. %	6.40 wt. %
Additive	0.12 wt. %	0.12 wt. %	0.12 wt. %
NMP	24.78 wt. %	-	-
DMSO	-	22.88 %	29.48 %
Ethanol	5.00 wt. %	-	-
PEG-400	3.00 wt. %	-	-
Internal coagulant	92 wt. % NMP	Water	
	8 wt. % Water		
External coagulant	Water	Water	
Spinneret i.d./o.d.	1.2 mm / 3.0 mm	1.2 mm / 2.6 mm (inner layer) / 3.5 mm (outer layer)	
Temperature	22°C	22 °C	
Air gap	0 mm	20 mm	

Table 2. Ni electroless plating recipe for Ni deposition on CGO HF.

Step	Compound	Supplier	Concentration	Conditions
Cleaning	HCl	Sigma	10 g l ⁻¹	20°C
		Aldrich		5 min
Sensitisation	SnCl ₂	Alfa Aesar	0.2 g l ⁻¹	20°C
	HCl	Sigma	3.3 g l ⁻¹	1 min
Catalysing	PdCl ₂	Alfa Aesar	0.4 g l ⁻¹	20°C
	HCl	Sigma	3.3 g l ⁻¹	1 min
Plating	Ni (II) Acetate	Alfa Aesar	40 g l ⁻¹	85°C
		Alfa Aesar	7.5 g l ⁻¹	pH 8 - 9
	NaOH	Alfa Aesar	4 g l ⁻¹	1,5 hours
	EDTA	Alfa Aesar	20 g l ⁻¹	
	N ₂ H ₄			

Table 3: Bending strength and N₂ permeability for electrolyte and anode-supported HF.

	Electrolyte-supported	Anode-supported
Bending strength (MPa)	150-200	141.1
N ₂ permeability (mol m ⁻² s ⁻¹ Pa ⁻¹)	1 x 10 ⁻⁷	2.02 x 10 ⁻¹⁰

Table 4. Maximum power output and Ohmic ASR comparison between the electrolyte-supported and anode-supported Ni-CGO-LSCF MT-HF-SOFCs.

Temp. (°C)	Maximum Power Density (mW cm ⁻²)		Ohmic ASR (Ω cm ²)		Activation ASR (Ω cm ²)	
	Electrolyte- supported	Anode- supported	Electrolyte- supported	Anode- supported	Electrolyte- supported	Anode- supported
450	6.3	47.6	16.15	1.6	58.4	1.6
500	22.3	223.6	9.16	0.32	19.84	0.49
550	41.2	287.2	5.85	0.24	11.65	0.31
600	75.4	398.6	4.1	0.2	6.4	0.2

Figure Captions

- Fig. 1. (A) Optical microscope image of the lumen of the dual-layer fibre showing the insertion of silver wire and the insertion of both silver wire and silver wool and (B) a complete MT-HF-SOFC.
- Fig. 2. (A) The quartz tube and pieces of the alumina tubes and cylindrical parts. (B) The complete reactor with the fuel cell installed before placing it inside the furnace.
- Fig. 3. Schematic representation of the connections from the FC to the Potentiostat/Galvanostat showing a two terminal configuration. Counter electrode (CE) and reference electrode (RE) were connected to the cathode current collector which was placed on the outer surface of the MT-HF-SOFC while the working electrode (WE) and sense electrode (SE) were connected to the anode current collector coming out from the lumen of the MT-HF-SOFC.
- Fig. 4. SEM images of the asymmetric CGO HF sintered at 1550°C: (A) cross-section, (B) outer surface and (C) inner surface.
- Fig. 5. (A-C) SEM images showing the 3 series of experiments for developing the morphology of the anode-supported dual-layer MT-HF-SOFC.
- Fig. 6. SEM images of the (A) unreduced (NiO-CGO) and (B) reduced (Ni-CGO) of the anode-supported dual-layer MT-HF-SOFC.
- Fig. 7. SEM image of the cross section of the electrolyte-supported MT-HF-SOFC.
- Fig. 8. SEM images of the anode-supported dual layer MT-HF-SOFC; (A) overall view and (B) magnification of the cathode layer.
- Fig. 9. Current-voltage and power density plot of the anode-supported dual-layer MT-HF-SOFC.
- Fig. 10. Current-voltage and power density plot of the electrolyte-supported MT-HF-SOFC.

Fig. 11. Impedance spectroscopy plot (at OCV conditions) at 600 °C of anode-supported and electrolyte-supported MT-HF-SOFCs.

Fig. 12. (A) Effect of H₂ flow rate on the newly developed anode-supported dual-layer MT-HF-SOFC at 600 °C and (B) the effect of fuel utilization for 15 and 30 ml H₂ min⁻¹ on the cell current densities at 600 °C.

(A)

(B)

Anode collector

WE

Cathode collector

CE

RE

Anode collector

SE

(A)

(B)

(C)

3 μm

EHT = 10.00 kV
WD = 8.6 mm

Signal A = QBSD
Mag = 10.14 K X

Date :19 Nov 2009
Time :11:23:46

1 μm

EHT = 8.00 kV
WD = 8.1 mm

Signal A = QBSD
Mag = 10.49 K X

Date :1 Dec 2009
Time :11:30:51

Cathode

This scanning electron micrograph (SEM) shows a cross-section of a fuel cell. The image is divided into several distinct layers. On the left, a thin, dark layer is labeled 'Cathode'. To its right is a thick, textured region labeled 'Part of CGO fibre with LSCF-CGO particles'. Further right is another thick, textured region labeled 'Part of the pure CGO fibre (Electrolyte layer)'. On the far right, a dark, layered structure is labeled 'Anode'. Red arrows point from the text labels to their corresponding features in the image. A scale bar at the bottom right indicates 100 micrometers. Technical parameters at the bottom left include HV 15 kV, Mag 250 x, Spot 3, WD 12.4 mm, and Det SE.

Part of CGO fibre with
LSCF-CGO particles

Part of the pure CGO
fibre (Electrolyte layer)

Anode

HV	Mag	Spot	WD	Det
15 kV	250 x	3	12.4 mm	SE

100 μm