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Fig. 1A

(57) Abstract: There is provided a method of manufacturing a reaction chamber for a solid-oxide fuel cell, the method comprising: extruding a dual layer hollow fibre comprising two concentric layers: an outer layer of an electrolyte precursor material and an inner layer of a first electrode precursor material; and sintering the hollow fibre such that the electrolyte precursor material forms an electrolyte.

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A Fuel Cell System

FIELD OF THE INVENTION

5 The invention relates to a method of manufacturing a reaction chamber for a solid-oxide fuel cell. The invention further relates to a solid oxide fuel cell. The invention further relates to a fuel cell system. The invention further relates to a stackable cell for a fuel cell system. The invention further relates to an arrangement of stackable cells.

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BACKGROUND

The Solid Oxide Fuel Cell (SOFC) is a reliable device for converting chemical energy into electrical energy directly and efficiently. During the last 20 years, technology has
15 made considerable improvements in the field of fuel cells. Although new materials have been tested as electrolytes, the standard materials remain YSZ (yttria-stabilized zirconia) and GDC (gadolinia-doped ceria). Nevertheless, advances have been made improving the performance of the SOFC and also reducing its overall cost. These advances have been made by: using new materials for electrodes and
20 interconnections; carefully studying the reaction kinetics and the increase of the three-phase boundary surface; establishing new fabrication techniques; and employing new geometrical designs.

Siemens–Westinghouse has developed a tubular SOFC, which has spurred great
25 interest within the realm of tubular SOFC research. However, tubular SOFCs have not yet been mass produced, due to outstanding technological and economic issues.

Embodiments of the apparatus' and methods disclosed below seek to address these issues, at least in part.

30

SUMMARY

There is provided a method of manufacturing a reaction chamber for a solid-oxide fuel cell, the method comprising: extruding a dual layer hollow fibre comprising two

concentric layers: an outer layer of an electrolyte precursor material and an inner layer of a first electrode precursor material; and sintering the hollow fibre such that the electrolyte precursor material forms an electrolyte.

- 5 The first electrode precursor material may be a material containing a metal oxide. The method may further comprising heating the dual layer hollow fibre while passing a reducing agent through the fibre, for reducing the metal oxide to a metal such that the first electrode precursor material forms a first electrode. The heating may be provided by the sintering process.

10

The method may further comprise depositing a further layer of a second electrode precursor material on an outer surface of the hollow fibre, and sintering the hollow fibre such that the second electrode precursor material forms a second electrode.

- 15 The method may further comprise heating the dual layer hollow fibre while passing a reducing agent through the fibre, for reducing the metal oxide to a metal such that the first electrode precursor material forms a first electrode. The heating may be provided by the sintering process.

- 20 The extrusion of a dual layer hollow fibre may be performed using a phase inversion process.

There is further provided a solid oxide fuel cell manufactured according to the method above.

25

There is further provided a solid oxide fuel cell comprising concentric layers of at least two electrodes separated by at least one electrolyte, wherein each layer has been sintered.

- 30 There is further provided a fuel cell system comprising a plurality of the above solid oxide fuel cells.

There is further provided a stackable cell for a fuel cell system, the stackable cell comprising electrode connections at at least one end of the stackable cell.

5 The stackable cell may further comprise a hollow fibre, the hollow fibre comprising concentric layers of at least two electrodes separated by at least one electrolyte.

The stackable cell may further comprise an inner electrode connector portion which passes through the hollow fibre for providing an electrical contact between an inner surface of the hollow fibre and at least one electrode connection.

10

An opposing pair of electrode connections may be provided at each end of the stackable cell. Each electrode connection may have a rectangular cross section.

15 Adjacent electrode connections of an opposing pair of electrode connections may be separated by an insulator.

The insulator may have has a counter bored hole having a smaller diameter part and a larger diameter part wherein the end of the hollow fibre is in the larger diameter part of the counter bore hole.

20

The smaller diameter part of the counter bored hole may have a diameter substantially the same as the inner diameter of the hollow fibre.

25 A first electrode connection may be provided as a box with a hole through which the hollow fibre is placed. A second electrode connection may be provided as a box with a hole the internal diameter of the hole being substantially the same as the inner diameter of the hollow fibre. An inner electrode connector portion may be provided which passes through the hollow fibre for providing an electrical contact between the second electrode connection and an inner surface of the hollow fibre.

30

The inner electrode connector portion may be a spring. The spring may be silver, or another material that is silver coated.

There is further provided an arrangement of the stackable cells described above, the arrangement comprising a plurality of stackable cells arranged in parallel with the like electrode connections of adjacent stackable cells in electrical contact.

- 5 The electrical contact of like electrode connections of adjacent stackable cells may be made by abutting like electrode connections of adjacent stackable cells against each other.

- The arrangement may comprise a plurality of stackable cells arranged in series with a
10 first electrode connection of a cell in electrical contact with a second electrode connection of an adjacent stackable cell.

- The electrical contact of a first electrode connection of a stackable cell with a second electrode connection of an adjacent stackable cell may be made by applying a
15 multiple layer via between adjacent cells at at least one end of the cells, the multiple layer via comprising a conducting layer in electrical connection between a first electrode connection of a first stackable cell and a second electrode connection of a second stackable cell, the conducting layer insulated from both the second electrode connection of the first stackable cell and the first electrode connection of the second
20 stackable cell.

A spacing layer may be provided between the electrodes of the adjacent stackable cells at an end of the stackable cells opposite the multiple layer via.

- 25 Equivalent connections may be made at both ends of the adjacent stackable cells.

- There is further provided a stackable unit cell for a fuel cell system, the unit cell comprising: a hollow fibre having concentric layers of at least two electrodes separated by at least one electrolyte; at least one first electrode box having a hole, and
30 wherein the tubular hollow fibre is placed through the hole, in contact with the first electrode box; at least one insulator box having a counter bored hole with a smaller diameter portion and a larger diameter portion, wherein the smaller diameter is substantially the same as an inner diameter of the tubular hollow fibre, and wherein the larger diameter portion is placed over the of an end of the hollow fibre, abutting

the first electrode box; at least one second electrode box having a hole with a diameter substantially the same as an inner diameter of the tubular hollow fibre, the second electrode box abutting against the insulator box; and a second electrode connector portion that passes through the tubular hollow fibre, providing an electrical
5 connection between an inner electrode layer of the tubular hollow fibre and the at least one second electrode box.

The first electrode box, an insulator box and a second electrode box may be provide at both ends of a tubular hollow fibre.

10

There is further provided a stackable unit cell for a fuel cell system, the unit cell comprising: a tubular hollow fibre having a first electrode layer and a second electrode layer separated by at least one electrolyte layer; first electrode connection boxes provided at either end of the tubular hollow fibre in electrical contact with the
15 first electrode layer; second electrode connection boxes provided at either end of the tubular hollow fibre in electrical contact with the second electrode layer; insulator boxes provided between the first and second electrode connection boxes at either end of the tubular hollow fibre; wherein an electrical connection between an inner electrode layer and an outer pair of electrode boxes is provided by a connection
20 element passing through the centre of the tubular hollow fibre.

BRIEF DESCRIPTION OF THE DRAWINGS

The attached figures numbered 1 to 7 illustrate, by way of example, the fuel cell and
25 fuel cell system disclosed herein.

DETAILED DESCRIPTION

30 Fabrication of Micro-tubular HF-SOFC Units

Dual-layer hollow fibres of nickel oxide / cerium-gadolinium oxide (NiO-CGO) anodes, and CGO electrolytes are extruded using a phase inversion process. This is followed by sintering to consolidate the resulting structures and to achieve gas-tight electrolyte layers. Subsequently, the lanthanum-strontium cobalt ferrite (LSCF)

cathode is deposited on the electrolyte using slurry coating techniques (combination of painting with a brush and using air-gun). The complete HF-SOFC structure is then heated to sinter the cathode and hydrogen gas used to reduce the NiO to Ni, thereby forming the anode.

5

Advantages of Phase Inversion / Sintering for Fabricating Micro-Tubular HF-SOFC Units

1. Extruding micro-tubes using phase inversion and sintering minimises costs of fabricating the supporting base for building fuel cells, thereby decreasing module capital costs.
2. The methods of phase inversion and sintering provide the option to control the internal structure of the micro-tube/hollow fibre in order to improve HF-SOFC performance.
3. Phase inversion and sintering enables the extrusion of micro-tubes with a range of diameters and lengths often difficult to achieve with ram extrusion.
4. Fabrication of dual-layer fibres avoids additional processing costs of fabricating electrolyte layers separately.
5. Using phase inversion and sintering to fabricate simultaneously the anode and electrolyte layers of the fuel cell minimises fabrication times and costs.
6. Extrusion of the electrolyte and anode layers simultaneously during well-controlled phase inversion and sintering enabled formation of thin, crack-free, gas-tight electrolyte layers.
7. The technique decreases the number of sintering cycles required to fabricate the fuel cell, thereby decreasing costs.
8. Deposition of the cathode using slurry coating techniques is cost effective.

25

The Design of Bundle-Stacks Using Individual HF-SOFC Units

For scaling-up, individual HF-SOFCs are bundled together in parallel to increase current output, and bundles stacked together in series to increase voltage, the numbers being matched to the current and voltage requirements of a particular application. The cost effective design enables:

30

- [a] Efficient collection of current from individual HF-SOFCs, to distribute reaction rates most uniformly, thereby maximising utilisation of electrode / electrolyte interfacial areas.

[b] Practical scale up in parallel (current) and series (voltage).

Description of the Design

Each 'unit cell' consists of:

- a micro-tubular HF-SOFC of a certain inner and outer diameter (i.e. dual-layer micro-tubular HF-SOFCs).
- a square cathode box with a hole of the same diameter as the outer diameter of the HF-SOFC.
- an insulator box with a counter bored hole. The one exit of the counter bore hole has the same diameter of the external diameter of the tubular fuel cell. The other end of the counter bore has a diameter equal to the inner diameter of the tubular cell. The tubular cell will pass through the one side of the insulator box and fit inside the insulator.
- a spring which upon expansion has a diameter equal to the inner diameter of the tubular fuel cell.
- an anode box of a diameter equal to the inner diameter of the fuel cell

The first step involves insertion of the cathode box onto the fuel cell, followed by the insulator, whereby the end of the insulator is placed in line with the end of the fuel cell. The spring is then inserted inside the insulator box throughout the tubular fuel cell. The length of the spring will be bigger than the length of the fuel cell, so that some of it extends beyond the ends of the tubular SOFC. Subsequently, the anode box is inserted on top of the spring, which extends beyond the rest of the structure. The anode box is adjusted so that its inner side is in line with the outer ends of the insulator box (Figure 1).

25

The purpose of each piece of a 'unit cell':

Cathode box: to collect the cathode current from the cathode site of the tubular fuel cell.

Insulator box: to prevent direct contact of the cathode box and the anode box, so avoiding short circuits. The counter bore structure of the insulator is needed, so a spring can pass through the insulator's smaller diameter exit (without coming into contact with the cathode box) inside the tubular fuel cell, enabling current collection from inner surfaces side of the anode of the tubular SOFCs.

Connection Element: is the current collector of the inner layer of the tubular SOFCs connected to the anode box.

Anode box: to collect the anode current from the Connection Element.

- 5 Figures 1A and 1B shows the 'unit cell' used for building the bundle, together with the exploded version of the 'unit cell'. Figure 1C shows the 'unit cell' is presented to show how the tubular fuel cell is passed through the first box and inserted inside the insulator box. The spring on the left of the main structure showing how it can pass through the anode box inside the insulator box and finally throughout the tubular cell.

10

Scale-up in series and parallel current connection:

- Each 'unit cell' can be connected easily in parallel merely by attaching the cathode, insulator and anode boxes (on each side of a 'unit cell') with the identical ones of the next (Figure 2). This creates a bundle of fuel cells of equal voltage with a current
- 15 capability proportional to number of added base units (parallel connection). Figure 2 shows a parallel connection of individual 'unit cells' to form a bundle of tubular fuel cells.

- To connect one bundle with another in series, scaling up the voltage, some different
- 20 adjustments to the main design are needed in order to avoid the short circuits.

- The series connection between the bundles is done by using some extra manufactured flat shaped rectangular anode, cathode and insulator sheets. The concept is to connect the anode boxes of one bundle with the cathode boxes of the adjacent one. To avoid direct connection between cathode-cathode or anode-anode
- 25 contacts between the bundles, extra rectangular flat insulator sheets are placed in such a way to secure the favoured (cathode-anode current collection between the bundles) connections. These can be manufactured as rectangular flat sheets, or can be merely insulating paste and electronic conductive paste painted as required.

- 30 Figures 3A and 3B show a series connection of two individual bundles. Each bundle consists of three tubular SOFCs units connected in parallel. The magnification of the side of the stack in Figure 3B shows how the anode box of the one bundle is connected to the cathode box of the second bundle. Insulating flat rectangular sheets are shown separating undesirable connections (i.e. anode-anode, or cathode-cathode).

Advantages of the 'Unit Cell'

- i) Current collector sources (anode and cathode boxes) remain outside the high temperature zone, so relaxing usually stringent material constraints.
- 5 ii) Current collector sources (anode and cathode) are on both ends of unit cells, so minimising axial ohmic potential losses.
- iii) In principles, such end boxes allow for hollow fibres of adjustable length or diameter of the unit fuel cell, apart from the insulator box, which has to be fabricated according to the thicknesses of electrolyte and cathode layers. Holes may be for e.g.
- 10 laser drilled in boxes of the chosen material post manufacture of cells to ensure optimum fit.
- iv) Insertion of a spring inside the unit cells, connecting the anode layer of the fuel cells with the anode sources outside the reaction zone, minimises anode ohmic potential losses which are predicted to be significant in such small tubes.
- 15 v) The design is based on model predictions, which highlight the detrimental effects of axial potential losses on the performance of a single HF-SOFC.
- vi) The design of the unit cell, on which the whole stack is based, can be applied easily to all types of anode-supported, electrolyte-supported or cathode-supported micro-tubular SOFCs.
- 20 vii) If the power capacity of a desired unit is pre-specified there is no need of making individual units in order to scale up the power instead the anode, insulator and cathode boxes are drilled with the requisite cell openings in series and parallel during fabrication, therefore reducing the cost and time for fabricating the stack.
- viii) The designs can easily retro-fit existing tubular SOFCs, such as those of
- 25 Siemens-Westinghouse.

Given below is a brief description of some alternatives as to how the unit cells may be constructed and stacked.

- 30 Starting with the inner most layer, a connection element of a micro-spring, of Silver or Silver coated Tungsten for example, is fabricated to the desired length, this can be done with suppliers such as (Union City Filament Corporation 1039A Hoyt Avenue | PO Box 777 | Ridgefield, NJ 07657). This expandable spring, upon expansion, has a diameter equal to the inner diameter of the spun hollow fibre. The connection

element this contacts the inner surface of the hollow fibre, making an electrical connection and thus providing a current path alternate to the anode material itself. The electrical resistance of the electrical connection is lower than the electrical resistance of the anode.

5

The length of the spring extends beyond the active length of the fibre (length coated with the cathode) and protrudes through the inner ends.

The cathode and anode end boxes may be micro-cubes fabricated with a suitable metal of high conductivity and reasonable price (e.g. Aluminium ca. \$1300 / tonne) with the holes of required diameter laser drilled into the cubes. This can be done after the fibre has been extruded to ensure good mating with the fibres and reduced contact losses.

15 The insulator box is similarly pre-fabricated with a suitable high resistivity material (ceramic or polymer) - material constraints will be minimal as these will be at room temperature. The insulator is counter bored and the holes drilled correspond to cathode outer diameter on one side and anode inner diameter on the other.

20 Connections are made as explained above with reference to the figures, with good contact ensured between a silver mesh around the cathode zone and the cathode end cubes with for example using silver wire.

This unit cell will thus provide total axial current collection for every fibre, which is important for maximising micro-tubular fuel cell performance.

25

Parallel scaling is relatively simple requiring only sufficient mechanical contact between similar electrode cubes which can be enhanced by using conductive pastes widely available in the market.

30

If the requisite number of fuel cells in parallel is known, then a long rectangular block may be laser drilled with a plurality of holes (rather than the single hole in the micro-cube used in a single unit). The required number of holes as a single parallel-scaled unit box may thereby reduce manufacturing costs.

Series scaling will require placement of such lengthy rectangular blocks one on top of the other while ensuring good electrical contact between only the cathode of one parallel stack to the anode of the other.

5

This is achieved in practice by using flat sheets of a) insulator (ceramic plates or polymer sheets) and b) anode and cathode box material i.e. Aluminium. These sheets will have the same width as the parallel unit being scaled and a small thickness required to separate layers which may, if contacted, cause short circuits. These sheets will be assembled as shown in the figures (e.g. Figure 3) to separate anode-anode and cathode-cathode contact between parallel stacks.

10

All these boxes, sheets and contacts may be repeated at both ends of the unit cell. In this way conductivity throughout the stack may be increased.

15

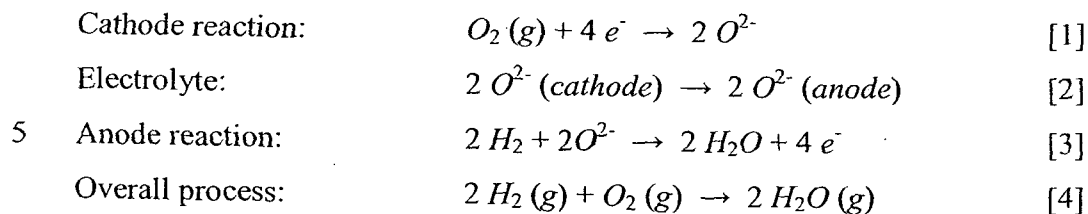
An example of the fuel cell design disclosed herein provides a novel design of SOFC which is fabricated using hollow fibres. This allows for increased specific surface area of electrodes, increased power output per unit volume/mass, facilitates sealing at high temperatures, and decreased cost of production. The supporting part of the microtubular SOFCs (the hollow fibre configuration) is fabricated firstly by a phase inversion process followed by sintering. Up to this point the anode layer and electrolyte layer are extruded in a single step. The porous sub-layers is then deposited with cathode material to produce single hollow fibre SOFCs, bundles of which may be assembled subsequently into a SOFC stack. By producing the anode layer and the electrolyte layer by a co-extrusion step this leads to a new category of fuel cells apart from the traditional anode-supported (if the supporting base is the anode) or electrolyte supported (if the supporting base is the electrolyte layer) or finally cathode supported fuel cells (if the supporting base is the cathode layer) that existed until now.

20

25

30

Yttrium-stabilised zirconia (YSZ) is used as the electrolyte. In order to decrease operating temperatures from 900 to 500-600 °C, Ce_{0.9}Gd_{0.1}O_{1.95} (CGO) electrolyte can be used. Hydrogen is used as a model fuel (H₂) at Ni anodes, coupled with oxygen reduction (O₂) at La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF) cathodes. Of course, other fuels, anode materials and cathode materials may be used.

Reactions

In fuel cells technology a fuel and an oxidant, react across a membrane and electrical current is generated in an external circuit. Their higher conversion efficiencies and therefore better utilization of fuel (which may either be fossil or renewable fuels) results not only in higher power densities but also in a much lower production of pollutants (no NOX, no SOX, no hydrocarbon emissions and no or much reduced CO₂). Further, their quiet operation makes them suitable for applications in vulnerable ecosystems and forests where human presence must be avoided. In terms of transportation, zero noise pollution and zero emission benefits from fuel cells are also important in heavily loaded city centres where the number of vehicles is dangerously increasing. High reliability and low maintenance, in addition to their modular nature are in favour of fuel cells' applicability in desert areas to which a distributed network is difficult or costly to reach. Moreover, the uninterrupted power supply and high current quality that these devices produce are considered as being trustworthy energy sources for hospitals, airports and information technology. Overall, their application ranges from being small-scale devices of high current low voltages, to forming generators big enough to produce hundreds of MW. One limitation of fuel cell technology is the overpotential losses created which increase as stack formation takes place.

The basic purpose, for which a fuel cell functions, is that in which the anode material exists on the one side of the cell, a fuel such as hydrogen is oxidised, producing electrons (and protons depending on the catalyst) which travel outside the cell in an external circuit. The external circuit is connected with the cathode where oxygen is reduced to oxide ions. Overall, oxide ions (or protons depending on the type of electrolyte) pass through the ion conducting electrolyte (which is electronically insulate), where they react to produce water. The above reaction is a continuous

circular process only if the temperature is constant and adequate reactants (fuel and oxidant) are provided.

Fuel cells are classified according to the type of the electrolyte used in the process.

- 5 An exception to this classification is the direct Methanol Fuel Cell (DMFC) because of the name of the fuel that utilizes. The reason that fuel cells are differentiated according to the electrolyte is due to the fact that the ions travelling inside the electrolyte material depend on the operating temperature of the cell. The increasing temperature provides the necessary thermal activation energy which causes the
- 10 movement of ions across the electrolyte material. Therefore, the type of the material, whether solid or liquid, acts as a regulator which operates either in low temperatures or high temperature zones. The fuel cell family may be divided into two categories. A first category of those that use low operating temperatures such as the Alkaline Fuel Cell (AFC), the Polymer Electrolyte Membrane Fuel Cell (PEMFC), the DMFC
- 15 (previous discussed) and the Phosphoric Acid Fuel Cell (PAFC). A second category is those fuel cells that operate in elevated temperatures between 500-1000 °C and are considered to be high temperature fuel cells. Examples of these are the Molten Carbonate Fuel Cell (MCFC) and the Solid Oxide Fuel Cell (SOFC). Figure 4 shows a schematic which summarises the various fuel cell types, highlighting the typical
- 20 reacting species and operating temperatures. Possibilities for fuel sources and certain pre-treatment are also indicated.

- In general, the most mature technologies of fuel cells are those of alkali and phosphoric cells. These types of cells were the first to be engineered and were
- 25 researched by NASA starting in 1960. Although their technology is more mature than all the other type of cells, there is not much that can be done to avoid the consequences of their corrosive liquid electrolyte (a phenomenon observed in the MCFC. This weakness of liquid electrolytes led to the development of the solid electrolyte. The majority of scientists in the field support the superiority of fuel cells
- 30 that utilize solid electrolytes such as in the SOFC and PEMFC. The progress in the technological breakthrough for these two types of cells is tremendous, especially for the PEMFC which is close to becoming commercialized. Despite the fact that alkaline fuel cells produce high power densities, they have a disadvantage regarding their practicality. Any trace of CO_2 in oxidant and fuel needs to be removed since it

reacts with the liquid electrolyte and forms a solid electrolyte which is non conductive. Furthermore, even though phosphoric acid fuels are comprised of electrolytes which are more resistant to CO_2 contaminations than alkaline fuel cells, they have been abandoned due to their low power density and high cost per unit.

5 Moreover, molten carbonate, although belonging to the family of high operating temperatures, comprises of a corrosive liquid electrolyte which causes problems such as the dissolution of NiO at the cathode and perspiration at the anode thus resulting in electrical losses. The DMFC is the most difficult option to make use of since a catalyst and electrolyte of an acceptable lifetime which can handle such a heavily

10 loaded fuel, has not been found yet. Overall, PEMFCs and SOFCs are fuel cells that have overcome many of their technological difficulties and have a higher chance to enter the market. Due to its low temperature operation and efficiency, the PEMFC is considered to be more practical in transportation applications. On the other hand, solid oxide fuel cells operate around 750 -1000 °C and are considered to be able to

15 operate utilizing different types of fuel which therefore makes them more suitable for stationary applications.

Solid Oxide Fuel Cells (Tubular design)

The process of the SOFC is based on a solid ceramic electrolyte. Thus, researchers

20 used to call these types of cells ceramic fuel cells. The electrolyte is usually either a metallic oxide, oxygen-ion conductor (YSZ being the most widely used) or a hydrogen-ion (protons) conductor. Solid oxide fuel cells with proton conductor electrolytes are limited to a small-scale single cell usually for experimental reasons. An oxygen-ion conductor allows oxygen to be reduced to oxide ions on the cathode

25 electrode by electrons taken from the external circuit. The electrolyte material acts as a conductor which drives ions to the anode electrode on the other side of the cell. The active temperature of the electrolyte varies between 600 and 1000 °C. Finally, oxygen ions reach the anode electrode surface, react with hydrogen (and/or carbon monoxide) giving up electrons, water, heat (and CO_2 when CO is included in the fuel) to the

30 external circuit. In general, five different components can usefully describe the SOFC device and these are; the electrolyte, anode, cathode and interconnections which will further be analyzed when referring to the micro-tubular design.

The results of continuous research resulted in 6 possible SOFC designs. These are: the monolithic design, flat-plate SOFCs (planar SOFC), seal-less tubular SOFCs, segmented-cell-in-series, higher power density-SOFCs (HPD-SOFC) and, microtubular SOFCs. The analysis of the different types of SOFC is beyond the
5 purview of this application and therefore emphasis will be given only to planar and tubular design.

Tubular and planar configurations are considered to be the two major SOFC configurations favoured in terms of complexity, cost and related performance. Planar
10 SOFC performance is theoretically higher (reaching up to 2 W cm^{-2} for single cells to at least 0.5 W cm^{-2} for stacks at temperatures ranging from $800\text{-}1000^{\circ}\text{C}$ than that of the tubular SOFC, because its technology leads to lower ohmic resistance losses. It is important to refer to the development of the planar anode-supported SOFC operating at $550\text{-}600^{\circ}\text{C}$ where power densities of $0.8\text{-}2 \text{ W cm}^{-2}$ were reached for single cell
15 tests. In addition, fabrication techniques like tape casting, calendaring, screen printing and other mass production techniques, (such as plasma-spraying) can easily be applied for planar SOFC production, thus making possible a substantial production cost reduction. Difficulties in successfully developing such high-temperature seals have slowed the development and use of planar-design cells for SOFC generators
20 Tubular systems have advantages, including their higher mechanical and thermal stability and simpler seal requirements. Tubular stacks only require sealing where the manifolds connect to the cells; this area can be kept outside of the active cell zone where temperatures are lower. In addition, the tubular design appears to be robust for repeated cycling under rapid changes in electrical load and in cell operating
25 temperatures. The ability to expand and contract without constraints is considered, from an engineering point of view, to be optimal, but on the other hand, this is also their main disadvantage since longer current paths are involved which cause higher resistance and therefore losses in electrical output.

30 A variety of tubular configurations was initially examined by companies such as Rolls Royce Fuel Cells, Toto Ltd (Japan) etc., but the arrangement was eventually adopted by Siemens–Westinghouse. So far, this has proved to be the most successful. This tubular design is being developed by Westinghouse Electric Corporation since the 1970s but Siemens-Westinghouse accomplished to produce $0.25\text{-}0.30 \text{ W cm}^{-2}$ on

single cell test. This 2.2 cm diameter, 180 cm length tubular cell was made by extrusion while the electrolyte and the interconnection were deposited by electrochemical vapour deposition (EVD). Using the above single cell as a power unit, Siemens was able to design and test many fully integrated power systems of successively increasing sizes. An example of the use of these tubular fibres is the world's first SOFC/gas turbine hybrid system which was delivered to Southern California Edison for operation at the University of California, Irvine's National Fuel Cell Research Centre producing an output of 220 kW. On lab 7 scale experiments, the research of Sammes at al., (University of Connecticut, USA) showed significant progress for reducing the size of tubular SOFC's to 26.4 mm diameter and 110 mm length. In addition their research focused on producing a practical-to-use stack formation and to solve the important problem of interconnection.

Methods used for fabricating tubular SOFCs

Extrusion: This process is being used in labs or mass production, for creating long objects of a fixed cross-sectional profile. A material, often in the form of a billet, is pushed or drawn through a die of the desired profile shape. Hollow sections are extruded by putting a pin or piercing the mandrel inside of the die while in some occasions, positive pressures are applied to the internal cavities throughout the pin. Extrusion is the most commonly used method for fabricating tubular and microtubular SOFCs. This method may be used for fabricating anode-supported microtubular SOFCs. The advantage of the process is the fact that it is cheap and relatively easy to fabricate, resulting in the formation of materials that have superior mechanical properties and withstand thermal shock (if high purity powders are used). This is the methods used by Siemens-Westinghouse for fabricating the cathode supporting part of their tubular SOFC.

Limitations of extrusion relate to the diameter and length of the extruded microtubes due to high temperatures rising on the materials developed by the applied high pressures.

Electrochemical vapour deposition (EVD): This process was developed by Westinghouse Electric Corporation in 1977 in order to fabricate gas-tight thin layers

of doped zirconia. EVD is the primary method available for depositing YSZ layers but also for inserting YSZ particles inside Ni anodes. This method has made the production of tubular SOFC feasible, achieving high power SOFCs densities. The EVD technique deposits a very high quality, 100% dense, uniformly thick electrolyte film. However, this technique, when used to deposit the electrolyte, is complex, capital-cost intensive, and requires vacuum equipment that makes scaling it up non cost-effective for a continuous manufacturing process for high-volume SOFC production.

EVD is expensive and a manufacturing method which itself requires a large amount of power.

Plasma spraying: Powders are injected into plasma jet and are accelerated, melted and deposited in the substrate. This specific method can be used for fabricating the whole SOFC or for fabricating small components such as the interconnections. This technique has been used several times during the past with SOFC technology. Among the latest research is the use of atmospheric plasma spraying for fabricating entirely an external supported tubular SOFC producing $0.79\text{--}0.89\text{ W cm}^{-2}$ at 1000°C . The advantages of using this method are that it is considered to be a manufacturing process that provides a fast deposition rate and is considered relatively cheap compared to EVD. The method was originally used by Siemens-Westinghouse to fabricate their tubular SOFC although later on, after the development of EVD that resulted in a better performance by the fuel cell, the method was used only for depositing the LaCrO_3 interconnection.

The problems associated with plasma spraying are that layers that are inconsistent and of poor quality are formed and are porous, thus leading to gas leakage structures or high overpotential losses.

The production cost of SOFCs is directly related to the material availability and fabrication methods. The concept of SOFC has already been proven to work, but the use of expensive materials and fabrication techniques does not allow the commercialization of the product. High temperatures preclude the use of metals which have lower fabrication costs than ceramics for the non-electrochemical

components of the cell. On the other hand, the use of metallic materials increases the potential for cracking under continued thermal cycling. Moreover, because of the high temperatures, sealing is an engineering challenge in itself, leading to the design of the sealless tubular SOFC. However, sealless tubular SOFC technology has generated yet further problems. The fabrication of a tubular design is costly and the final device produces lower power densities (because of longer current paths) and therefore the overall cost per unit is increased. The production cost of a tubular SOFC stack consisting of 20 tubular SOFC units (0.18 W cm^{-2} Siemens-Westinghouse technology), using either EVD or plasma spraying (PS) as the main fabrication method, was calculated to be 617000 yen kW^{-1} (6033.64 \$ kW^{-1}) and 293000 yen/ kW (2865.25 \$ kW^{-1}), respectively. The EVD method of fabrication is the most expensive fabrication technique. Furthermore, plasma spraying is cheaper than EVD only for producing a number of units whereas, in mass production, PS is considered to be a time consuming method and requires intensive labour; it is therefore not appropriate for larger scale applications.

The environmental impact of manufacturing planar and tubular solid oxide fuel cells should also be considered. EVD and PS are responsible for almost 90% of the total energy requirements for manufacturing tubular SOFCs by those methods. Once again, fabrication techniques for planar SOFC such as tape casting, slurry sintering, and screen printing prove to be cheaper than other SOFC fabrication techniques. In addition, energy inputs for sintering and treatment of Cr alloy used in interconnections (LaCrO_3) for both planar and tubular SOFCs, are considered to be relatively high when comparing the energy consumed in other fabrication techniques. In terms of expenses of the materials comprised in a tubular SOFC, air (LSM or LSCF) electrode material is costly and further cost reduction is possible if less expensive raw materials are utilized to synthesize it instead of pure lanthanum compounds. Moreover, the operation temperatures must be reduced in order for it to be possible to use other materials for electrodes and interconnections. The use of other electrolytes (except YSZ) of better performances or even more important, with active temperature zones of 500-600 °C could lead to significant economical breakthroughs.

Apart from being costly, EVD has proven to be hazardous to the environment. The above assumption was published in a research paper related to environmental issues

and the possible effects of manufacturing tubular SOFCs in mass production scale.

Beside EVD, plasma spraying, sintering and LaCrO₃ fabrication techniques (Cr leakage to the environment) are mentioned to be highly polluting methods.

Accordingly, the methods used herein such as electroless plating and slurry coating
5 methods are utilized, with the added advantage that they are also cheaper.

Performance and the diameter of tubular SOFC

The volumetric power density for this type of fuel cell is related to the micro-tubular cell radius by equation when triangular contact packing (Figures 5 and 6, equation
10 [5]):

$$P = \frac{2\pi j_{Av} U}{r\sqrt{3}} \quad \text{W m}^{-3} \quad [5]$$

Figure 5 shows a theoretical way of packing tubular SOFCs. The reason for drawing
15 this way of stacking tubular cells is only to use it from showing the volumetric power density is dependant directly from the radio of the tubular cells. Figure 6 shows the theoretical volumetric power density in relation with the tubes diameter. The graph is based on equation [5] for a theoretical triangular contact packing.

20 Since volumetric power density is related to the reciprocal of tube diameter, smaller structures should increase power densities of fuel cells and hence decrease their capital costs per kW.

Microtubular SOFCs

25 Fabrication methods used in microtubular SOFCs

1. Sintering/firing

2. Co-sintering/Co-firing

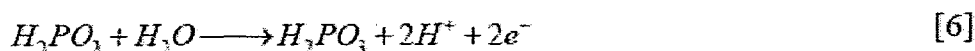
30

3. Extrusion (discussed during the description of the tubular design)
(very common method used in microtubular SOFCs technology)

4. Phase inversion and sintering (new method used in microtubular SOFCs technology). This method has been used for fabricating hollow fibre tubes with very small diameters (around 1 mm if a spinneret with orifice diameter/inner diameter of 3.0/1.5 mm respectively. The method gives the opportunity to produce very small and controlled structure formations, thus favouring this technology for making the anode or electrolyte-supported tube for microtubular SOFCs. The method has already been tested for making YSZ fibres. The method comprises:
- i) Preparation of spinning suspensions, (Mixing a dispersant and a solvent of choice, adding preconditioned particles for deflocculation and finally adding polymer binders)
 - ii) Spinning of ceramic hollow fibre precursors (The starting suspension is passed through a spinneret and the obtained precursor is dipped into the coagulant bath for the polymer precipitation)
 - iii) Sintering (Sintering at high temperatures in order to burn out the organic compounds and provide to the structure the right mechanical strength and density)
5. Slurry coating (very common method used in microtubular SOFCs technology)
- i) Dip-coating
 - ii) Painting:
 - a) By using paint brush
 - b) By using air-brush gun
- This allows for the controlling of the internal structure of the hollow fibres.
6. Electrophoretic deposition of nickel (not very common method used in microtubular SOFCs technology). It has not normally been used in microtubular SOFCs technology but this method may be used for depositing YSZ or CGO particles onto the anode-supported structures. This allows for the deposition of quality layers regardless the shape of the substrate.
7. Electroless plating (not very common method used in microtubular SOFCs technology). Electroless plating is a reduction process also called the autocatalytic process which deposits metal ions onto catalytic surfaces, regardless of the shape of the part. Deposition occurs in an aqueous solution containing metal ions, a reducing agent and a catalyst. During electroless plating, redox reactions occur, without the use of an external current flow although some electrons swap between the oxidant and

the reductant. The above process can easily be carried out by driving the reactants inside porous YSZ tubes depositing particles which will later form the anode electrode. The method has been used successfully for depositing *Ni* in electrolyte supporting microtubular SOFCs. Regarding *Ni* deposition, the most used reducing agent is sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$). When sodium hypophosphite is used as a

5 reducing agent for *Ni* deposition, the reactions are:



10 Except the nickel source and the reducing agent the electroless bath contains a series of other compounds such as stabilizers, complexing agents and buffers. The role of stabilisers is to prevent the decomposition of the bath from a) the precipitation of nickel phosphide which occurs if sodium hypophosphite is used as a reducing agent and b) after the evolution of high amounts of hydrogen. For this reason not only the

15 stabiliser is necessary but also a buffer solution has to be introduced to reduce the decrease of the pH. The aim of the complexing agent is to keep a stable pH, to avoid the formation and precipitation of nickel salts or phosphites and to reduce the concentration of Ni^{2+} ions. The effect of the pH on the process and on the microstructure of the final layer is quite important. A high pH is recommended to

20 increase the deposition rate, enhance the porosity of the layer and decrease the P content. The opposite can be achieved when working with an acid bath. The electroless deposition temperature is approximately 70°C. Higher deposition rates can be reached when increasing this value although the plating bath becomes unstable and the process collapses. Concentrations have a strong influence on the properties of

25 the deposited *Ni*. For instance, a higher *Ni* concentration and/or a lower sodium hypophosphite concentration in the plating bath gives a lower final *P* content in the *Ni* layer. With regards to the SOFC application, the *P* content of the deposited *Ni-P* alloy

raises the electric resistance and so its concentration must be lowered as much as possible. A complete investigation of these variables can be found in literature.

Microtubular SOFCs

- 5 The concept of the microtubular SOFC coincides with the creation of the first tubular cells. As above, it can be shown that power density is related to the reciprocal of tube diameter. The extrusion of 1-5mm diameter tubes is now possible. The small tubular design offers several advantages over the conventional Siemens-Westinghouse tubular SOFC and planar SOFC. One of the distinct characteristics is that the smaller design
- 10 performs better and so an increase in volumetric power density is thus expected. In theory, there is no limitation to the increase of power density as the dimensions of the tube become smaller. Furthermore, smaller tubes are less susceptible to damage caused by rapid heating. In addition, the microtubular design reduces the operating temperature of the cell since thinner structures of electrolytes and electrodes are
- 15 needed for small fuel cell structures. Moreover, microtubular SOFCs significantly reduce the start-up times for a stack, therefore accelerating the cell's entrance into transportation sector and its application in portable devices and auxiliary units for automobiles and other devices. Finally, the development of fabrication techniques such as phase inversion and sintering significantly reduce the cost per unit structure
- 20 favouring this fuel cell technology in the market.

Electrolyte-supported structures

- Electrolyte-supported SOFCs were the first type of microtubular designs that made their appearance in the early 1990s. After it was successfully shown how to extrude
- 25 YSZ micro sized tubes which showed high ionic conductivity and gas tight characteristics, the possibility of constructing a tubular fuel cell with a very small diameter was realized. The first cells consisted of the supporting surface made by extrusion (100 – 200 mm long, 150 μm thick and 2 mm diameter); a *Ni* anode (ca. 50 μm thick, 30 mm total active length) was then deposited on the inside using a syringe;
- 30 and a lanthanum strontium manganate (LSM) cathode (ca. 100 μm thick) was deposited on the outside, usually by dip-coating. A single cell produced 0.1-0.2 W cm^{-2} at 700°C. From the development of the electrolyte-supported SOFCs it was concluded that: a) when increasing the active length of the micro cell, the power density was lowered; b) the wires, used as interconnections, of larger diameter

performed better and that silver material (compare to nickel alloys) showed less degradation during the thermal cycling tests; and c) although 3 mol of yttria provided excellent mechanical properties, this caused severe cracks under thermal cycling and resulted in poor ion conductivity; therefore, 8 mol is favoured. Moreover, apart from hydrogen, butane and natural gas were used successfully as fuels with electrolyte revealing the advantages of using the SOFC technology.

Lastly, the method of phase inversion and sintering provides the opportunity of creating porous tubes. This method has come to reveal the potential of creating electrolyte-supported cells. Although, classified as an extrusion method, major differences exist between this and the conventional method. The tubes made by phase inversion and sintering method have an asymmetric structure, forming a dense layer of YSZ in the centre and more porous (sponge type, or finger like structures) near the inner and outer surface, thus making the formation favourable for depositing the anode and cathode. The tubes have been tested, revealing sufficient mechanical strength and gas tightness. YSZ hollow fibres of 1mm diameter were produced and used as the substrate for creating microtubular electrolyte-supported SOFCs. The Ni-anode was deposited inside the cell by electroless plating while the LSCF cathode is deposited on the outside surface by dip-coating. Although the performance of the cell is still very poor, (0.018 W cm^{-2}), results show that performance can be significantly improved. One of the advantages of this method is that long tubes can be easily produced, although a restriction exists in relation to the maximum active length of such SOFCs. What differentiates the above method of extrusion of those used by Kevin Kendall et al., Suzuki et al., and Sammes et al., is that phase inversion and sintering provides the ability to the user to have a control upon the internal structure of the microtube. Electrolyte-supported SOFCs have two important disadvantages: (i) to provide mechanical support, the electrolyte has to be the thickest part of the fuel cell, leading to an increase in ohmic losses; (ii) the practical difficulty of fabricating current connections to anodes and cathodes. These have contributed to their not being commercialised, despite being subject to nearly 20 years of research and development. Anode-supported SOFCs obviate some of these problems.

Anode-supported Solid Oxide Fuel Cells

The anode-supported cells were developed initially by co-extruding Ni-YSZ cermet anode with a 30 μm thick YSZ electrolyte. This suggested that anode-supported structures could provide thinner electrolyte layers thus improved fuel cell performances. In addition, the new fabrication technique of co-extruding anode and electrolyte reduced the overall costs of fabricating a cell (reducing sintering steps, less depositing methods used, etc.). The whole anode structure was sintered at 1400°C.

Advantages of anode supported structures

These allow for fabrication of very thin, gas-tight electrolyte layers. These do not need complicated processes for deposition of an electrode inside the very small microstructure. These allow for the creation of a current collector path.

Figure 7 shows a fabrication process of a cubic micro SOFC stack using sub-millimetre tubular SOFCs.

15 Dual layer NiO-CGO/CGO Hollow fibre membrane

Despite three decades of development of solid oxide fuel cells (SOFCs) since the conception of the tubular Siemens–Westinghouse design, no practical alternatives to yttria-stabilized zirconia (YSZ) and gadolinia-doped ceria (CGO) electrolytes have been established. However, there have been considerable improvements in the performance of SOFCs, decreasing their specific overall costs, by using new materials for electrodes and interconnections, decreasing operating temperatures, understanding their reaction kinetics, increasing specific surface areas of electrode / electrolyte / reactant three-phase boundaries, establishing new fabrication techniques and employing new geometric designs. So-called micro-tubular SOFCs are one of the most promising these designs, though a misnomer, as tube diameters are normally several millimetres, significantly smaller than Siemens–Westinghouse SOFCs with 22 mm tube diameters.

A disadvantage of the tubular SOFC is that it has a relatively long current path through the cell. The long current paths in electrodes create a limitation in the performance of the cell since, due to resistance, losses are increased. Moreover, the electrical resistance of tubular SOFCs is high and specific power output (Wcm^{-2}) and volumetric power density is (Wcm^{-3}) low. These low power densities make tubular

SOFCs suitable only for stationary power generation and not very attractive for mobile applications.

5 The Siemens-Westinghouse SOFC has a major disadvantage in the requirement for the use of a EVD for depositing the electrolyte, anode electrode and interconnection. Despite being the most efficient to use, this fabrication technique is very expensive and because of the chemical nature of the technique, the selection of suitable dopants for the electrolyte and interconnection is limited. Furthermore, these cells operate around 800-1000°C in order to achieve sufficient electrolyte conductivity; only few
10 materials can resist such extreme environments and these are also more expensive. Although new materials have been used in order to achieve lower temperatures, these unfortunately do not perform as well as YSZ.

Problems with Siemens-Westinghouse tubular SOFCs technology are:

- 15 i) Long current paths of the tubular design
- ii) Low power density
- iii) Very high operation temperatures
- iv) Expensive fabrication mostly due to the inefficient and expensive EVD method which is used for depositing the electrolyte and current collectors
- 20 v) Expensive material used as current collectors due to the high operation temperatures

Microtubular SOFCs

To overcome these limitations several new designs are being researched, of which the
25 micro-tubular SOFC is one of the most promising designs. The smaller tube diameters in micro-tubular SOFCs, compared with e.g. the 22 mm diameter tubes in the Siemens design, results in increased volumetric power densities produced by the cell stack, which depends on the reciprocal of tube diameters. Reports have also shown that small diameter tubes are less susceptible to cracking induced by rapid heating at start-
30 up. Moreover, their ability to operate at lower temperatures, due to reduction of components thicknesses reducing ohmic losses and their quick start up times makes them potentially attractive for the transportation sector, in portable devices and as auxiliary units for automobiles. In addition the inexpensive slurry coating methods which are being used for depositing the electrode/electrolyte reduce the overall cost

for fabrication. Lastly, significant efforts have been made to reduce the operation temperature of these SOFCs by using different combination of materials which among them CDO electrolyte and LSCM cathode are the most promising. Because of the reduction in operation temperatures the use of inexpensive materials as current collector is possible reducing to the minimum the cost per unit structure. However, practical issues such as current collector design and stack construction with micro-tubes remains non-trivial.

Problems possible to be solved by using microtubular technology

1. Increase volumetric power densities
2. Quick start up time
3. Less susceptible to cracking
4. Reducing operation temperature
5. Reducing fabrication cost (using extruding methods in combination with slurry coating techniques)

Problems with micotubular SOFCs are:

- i) Still low power densities
- ii) Traditional extrusion limits the dimensions available for the microtubes (not very small diameters and limited on length)
- iii) Slurry coating technique for depositing the electrolyte is not suitable for achieving quality-gastight layer

Phase inversion and sintering

Phase inversion and sintering are used for the production of hollow fibre (HF) SOFC electrolytes. There are major differences between this and conventional extrusion, the advantage being that it provides control of the internal structure of the micro-tube. The number and size of the pores are decreased gradually from the outside surfaces to the centre of the fibre, so creating microstructures that can be used beneficial during electrolyte deposition (for anode-supported structures) or for depositing cathode/anode (for electrolyte supported-structures) aiming to high specific surface area three-phase boundary regions for cathode-electrolyte-reactant and anode-electrolyte-reactant. Furthermore, hollow fibres can be made with diameters, thicknesses and lengths, not achievable by conventional extrusion.

Increase power densities may be provided by minimizing the losses during the fuel cells operating (due to the control upon the internal structure of the fibres, losses caused like polarization and ohmic losses are minimized). A reduction in fabrication cost may be made by using cheaper method of extruding the supporting base.

According to the method herein, phase inversion and sintering are used for producing dual layer fibre for use in SOFCs. Co-extrusion through triple orifice spinneret is used to prepare dual-layer membranes in one step. One dope is injected into the outer orifice, whereas the other is injected into the inner orifice. The internal coagulant must be injected simultaneously into the inner tube. During the spinning process, the inner dope is in contact with the internal coagulant, while the outer dope is first exposed to air and then to the external coagulant. Due to the difference in shrinkage between the two layers caused by the coagulation process, the dual layer hollow fibre may be formed. Later, by using the slurry coating technique the third layer is deposited in order to form a complete single microtubular SOFC. This time because the slurry coating method will be used only for depositing an electrode layer (and not the electrolyte layer) which doesn't have to be gas tight after sintering then less accurate method such as painting can be used without affecting the performance of the cell.

Compared to single layer hollow fibre, the dual-layer hollow fibre is more attractive for a number of reasons. The dual-layer hollow fibre retains the advantages of single layer hollow fiber membranes, they are: high active surface area to volume ratio, low resistance to gas flow, self-supporting structure, facility for fabrication and the ability to be operated at high pressure. It can save the material cost by using the cheap material as support layer material. It is one step process which can save time and decrease the risk of inducing defect. Some materials with high selectivity and permeance are impossible or very difficult to be fabricated into traditional single-layer hollow fibre membranes for various reasons such as low viscosity and brittle failure. It allows for complete fuel cell manufacture with minimum fabrication cost.

1. A method of manufacturing a reaction chamber for a solid-oxide fuel cell, the method comprising:
 - 5 extruding a dual layer hollow fibre comprising two concentric layers: an outer layer of an electrolyte precursor material and an inner layer of a first electrode precursor material; and
 - sintering the hollow fibre such that the electrolyte precursor material forms an electrolyte.
- 10 2. The method of claim 1, wherein the first electrode precursor material is a material containing a metal oxide.
3. The method of claim 2, further comprising heating the dual layer hollow fibre
- 15 while passing a reducing agent through the fibre, for reducing the metal oxide to a metal such that the first electrode precursor material forms a first electrode.
4. The method of claim 3, wherein the heating in claim 3 is provided by the sintering in claim 1.
- 20 5. The method of any preceding claim, further comprising depositing a further layer of a second electrode precursor material on an outer surface of the hollow fibre, and
- sintering the hollow fibre such that the second electrode precursor material
- 25 forms a second electrode.
6. The method of claim 5 when dependent on claim 2, further comprising heating the dual layer hollow fibre while passing a reducing agent through the fibre, for reducing the metal oxide to a metal such that the first electrode precursor material
- 30 forms a first electrode.
7. The method of claim 6, wherein the heating in claim 6 is provided by the sintering in claim 5.

8. The method of any preceding claim, wherein the extrusion of a dual layer hollow fibre is performed using a phase inversion process.
9. A solid oxide fuel cell manufactured according to the method of any preceding
5 claim.
10. A solid oxide fuel cell comprising concentric layers of at least two electrodes separated by at least one electrolyte, wherein each layer has been sintered.
- 10 11. A fuel cell system comprising a plurality of solid oxide fuel cells according to claim 9 or claim 10.
12. A stackable cell for a fuel cell system, the stackable cell comprising electrode
15 connections at at least one end of the stackable cell.
13. The stackable cell of claim 12, further comprising a hollow fibre, the hollow fibre comprising concentric layers of at least two electrodes separated by at least one electrolyte.
- 20 14. The stackable cell of claim 13, further comprising an inner electrode connector portion which passes through the hollow fibre for providing an electrical contact between an inner surface of the hollow fibre and at least one electrode connection.
- 25 15. The stackable cell of any preceding claim, wherein an opposing pair of electrode connections is provided at each end of the stackable cell.
16. The stackable cell of any preceding claim, wherein each electrode connection has a rectangular cross section.
- 30 17. The stackable cell of any preceding claim, wherein adjacent electrode connections of an opposing pair of electrode connections are separated by an insulator.

18. The stackable cell of claim 17 when dependent on claim 13, wherein the insulator has a counter bored hole having a smaller diameter part and a larger diameter part wherein the end of the hollow fibre is in the larger diameter part of the counter bore hole.
- 5
19. The stackable cell of claim 18, wherein the smaller diameter part of the counter bored hole has a diameter substantially the same as the inner diameter of the hollow fibre.
- 10
20. The stackable cell of any preceding claim when dependent on claim 13, wherein a first electrode connection is provided as a box with a hole through which the hollow fibre is placed.
21. The stackable cell of any preceding claim when dependent on claim 13,
- 15
- wherein a second electrode connection is provided as a box with a hole the internal diameter of the hole being substantially the same as the inner diameter of the hollow fibre.
22. The stackable cell of claim 21, further comprising an inner electrode connector
- 20
- portion which passes through the hollow fibre for providing an electrical contact between the second electrode connection and an inner surface of the hollow fibre.
23. An arrangement of stackable cells as claimed in any preceding claim, the arrangement comprising a plurality of stackable cells arranged in parallel with the like
- 25
- electrode connections of adjacent stackable cells in electrical contact.
24. An arrangement of stackable cells as claimed in claim 23, wherein the electrical contact of like electrode connections of adjacent stackable cells is made by abutting like electrode connections of adjacent stackable cells against each other.
- 30
25. An arrangement of stackable cells as claimed in any preceding claim, the arrangement comprising a plurality of stackable cells arranged in series with a first electrode connection of a cell in electrical contact with a second electrode connection of an adjacent stackable cell.

26. An arrangement of stackable cells as claimed in claim 25, wherein the electrical contact of a first electrode connection of a stackable cell with a second electrode connection of an adjacent stackable cell is made by applying a multiple layer via between adjacent cells at at least one end of the cells, the multiple layer via comprising a conducting layer in electrical connection between a first electrode connection of a first stackable cell and a second electrode connection of a second stackable cell, the conducting layer insulated from both the second electrode connection of the first stackable cell and the first electrode connection of the second stackable cell.

27. An arrangement of stackable cells as claimed in claim 26, wherein a spacing layer is provided between the electrodes of the adjacent stackable cells at an end of the stackable cells opposite the multiple layer via.

28. An arrangement of stackable cells as claimed in claim 26, wherein equivalent connections are made at both ends of the adjacent stackable cells.

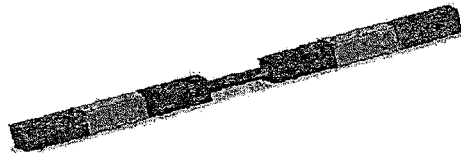


Fig. 1A



Fig. 1B

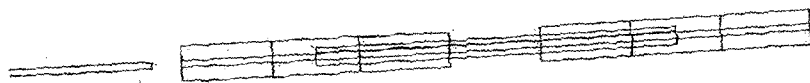


Fig. 1C

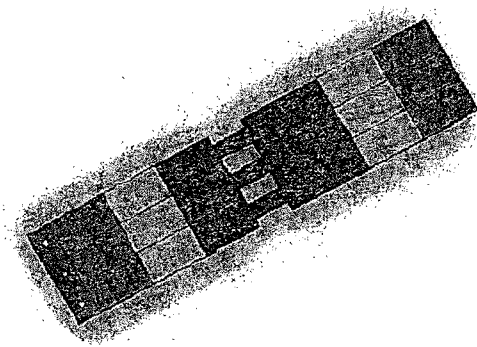


Fig. 2

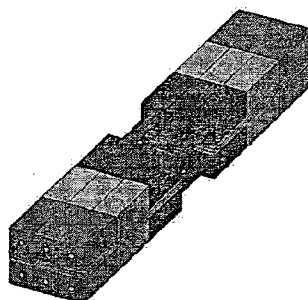


Fig. 3A

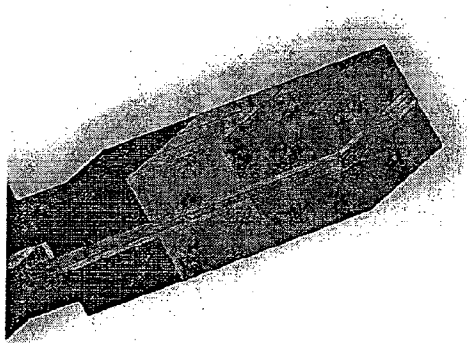


Fig. 3B

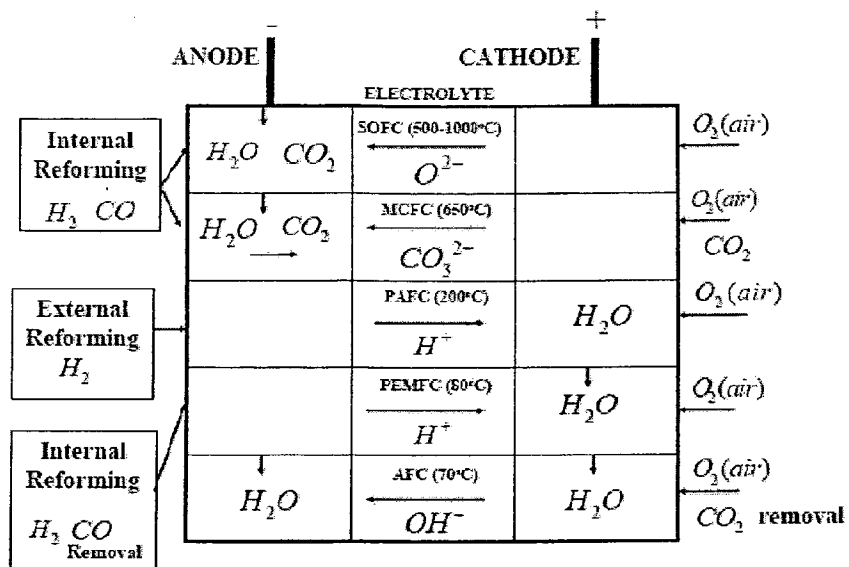


Fig. 4

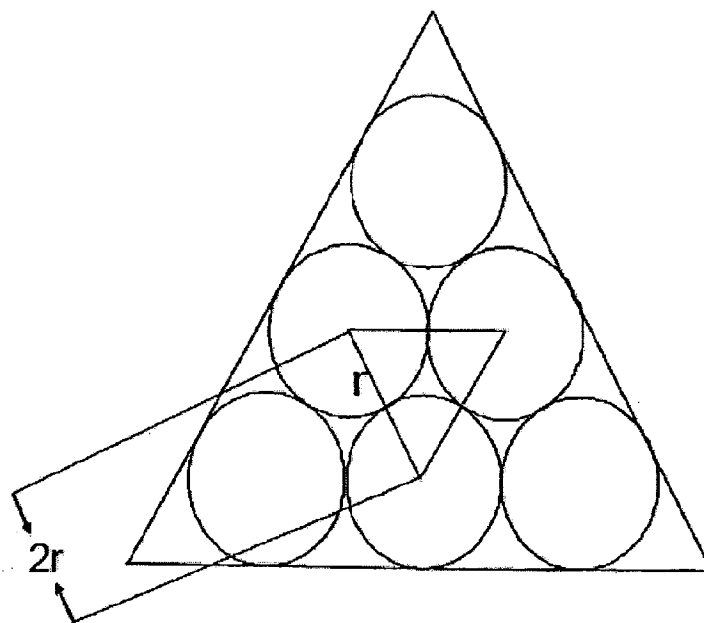


Fig. 5

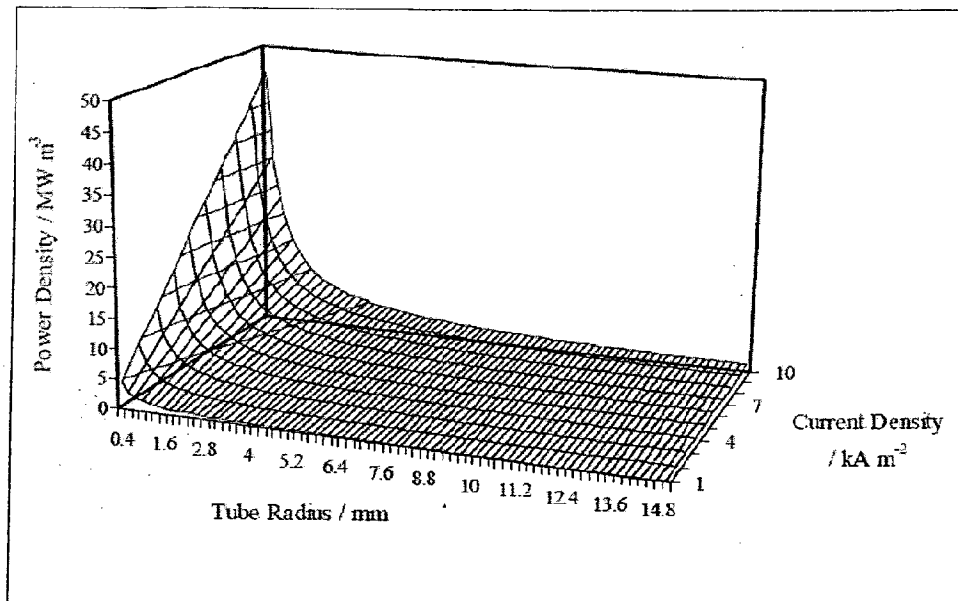


Fig. 6

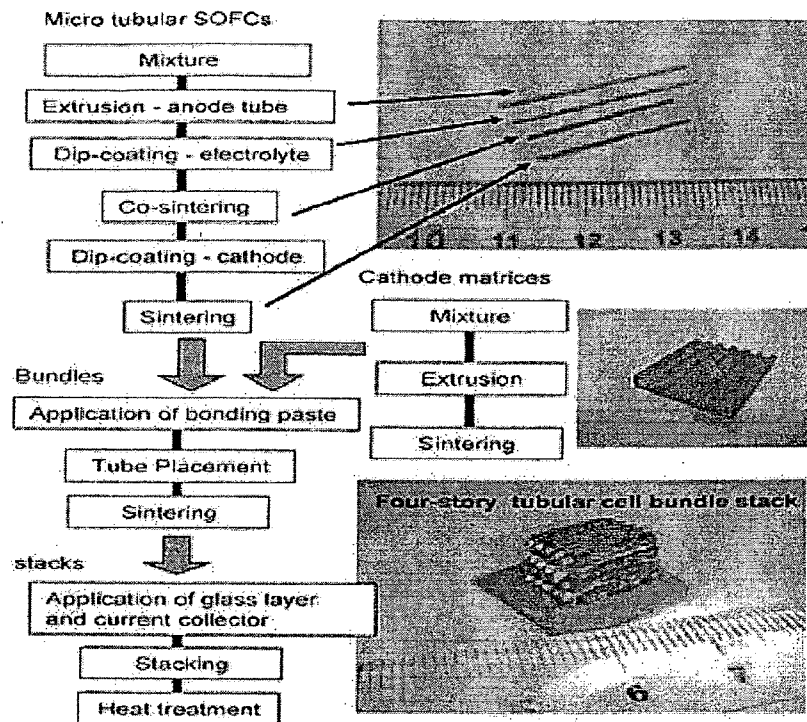


Fig. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/000424

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M8/12 H01M8/24
ADD:

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	TAN XIAO YAO ET AL.: "Preparation of electrolyte membranes for microtubular solid oxide fuel cells" SCIENCE IN CHINA SERIES B: CHEMISTRY, vol. 51, no. 9, 1 October 2008 (2008-10-01), pages 808-812, XP002586177 the whole document	1-9
X	TOSHIO SUZUKI ET AL.: "Improvement of SOFC performance using a microtubular, anode-supported SOFC" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 153, no. 5, 28 March 2006 (2006-03-28), pages A925-A928, XP002586178 the whole document	1-7, 9
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

8 June 2010

Date of mailing of the international search report

22/06/2010

Name and mailing address of the ISA/

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Authorized officer

Mercedes González

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/000424

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

International application No
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