Planar half-cell shaped precursor body

Esposito, Vincenzo; Linderoth, Søren

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(71) **Applicant**: **DANMARKS TEKNISKE UNIVERSITET** [DK/DK]; Anker Engelunds Vej 1, DK-2800 Kgs. Lyngby (DK).

(72) **Inventors**: **ESPOSITO, Vincenzo**; Tegelgårdsgatan 24, S-211 33 Malmö (SE). **LINDEROTH, Søren**; Egevej 47, DK-4000 Roskilde (DK).

(74) **Agent**: **ZACCO DENMARK A/S**; Arne Jacobsens Allé 15, DK-2300 Copenhagen S (DK).

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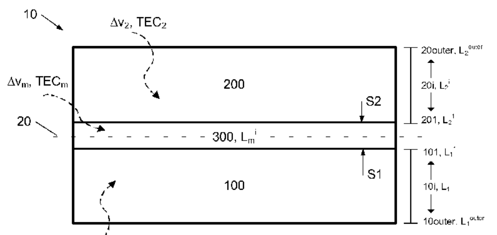

Fig. 1a

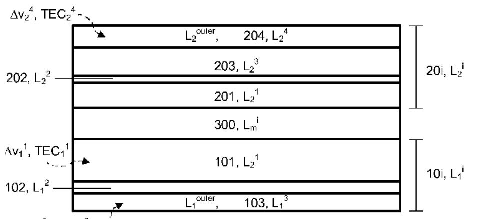

Fig. 1b

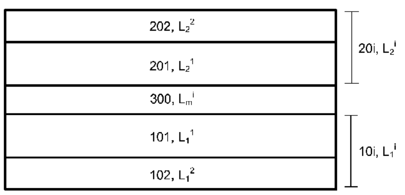

Fig. 1c

(57) **Abstract**: The invention relates to a half-cell shaped precursor body of either anode type or cathode type, the half-cell shaped precursor body being prepared to be free sintered to form a sintered or pre-sintered half-cell being adapted to be stacked in a solid oxide fuel cell stack. The obtained half-cell has an improved planar shape, which remains planar also after a sintering process and during temperature fluctuations.

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Planar half-cell shaped precursor body

The invention relates to a half-cell shaped precursor body of either anode type or cathode type, the half-cell green body being prepared to be free sintered to form a sintered or pre-sintered half-cell being adapted to be stacked in a solid oxide fuel cell stack. The obtained half-cell has an improved planar shape, which remains planar also after a sintering process and during temperature fluctuations.

Background

Solid oxide electrochemical cells (SOECs) are ceramic-based systems composed by several layers in which functional solid oxide materials are co-fired together to obtain porous and dense functional sintered layers. Processing route of such complex systems usually presents several critical aspects which can greatly compromise the final cell´s performance and durability.

Multilayer ceramic systems are of paramount importance in various technologies. Planar multilayer ceramic systems are used in electronic devices, electrochemical cells, magnetic refrigeration, electronics packaging, etc. Among these technologies, the electrochemical cells such as solid oxides fuel cells (SOFCs), gas separation membranes, sensors, etc., are usually complex arrangements of co-sintered layers assembled with different thickness, compositions and microstructures.

Particularly, SOFCs are ceramic systems arranged as functionalized layers which compose anode, electrolyte and cathode. Processing route of SOFC consists in a combination of several techniques. Tape casting, co-lamination, deposition, firing of functional ceramic materials are usually the sequential processing steps used for the production of planar anode supported half-SOFC cell.

In the planar design of the anode-supported SOFC, the anode is a porous thick CER-MET (ceramic and metallic) layer of Ni-YSZ (Nickel-Yttria-Stabilized-Zirconia). Typically, this layer will have a thickness in the order for hundreds of microns or a few millimetres. The electrolyte is a dense and “thin” stabilized-zirconia (*e.g.* Sc-YSZ) layer having a thickness in the micron-range, and the cathode is often a thick porous perovskite layer deposited on the pre-sintered anode/electrolyte half-cell. Additional ceria-gadolinium oxide (CGO) layer, called barrier layer, can be also added to the half-cell at the electrolyte/cathode interface to avoid detrimental chemical reaction between the cell components.

The sequence of the processing steps allows assembling together the different layers as organic-inorganic precursors at the *green* stage. Green-cells are then co-fired into the desired final configuration of sintered porous (electrodes) and dense ceramic layers (electrolyte and barrier layer). The number of parameters which, along the processing steps, can influence the quality of the final product is remarkably large.

At the green stage, ceramic particles size, amount of the organic component, residual solvent, presence of poreformer, relative thickness of each layer are some parameters which can influence the final shape of the assembled cell. However, shape instability and defects are usually shown after firing at high temperature. Because of the relevant stresses and strains generated at the co-firing step, use of proper thermal treatments is considered the most critical factor in the fabrication of planar multilayer cells endowed with well-formed ceramic components.

The early step of the firing, at low temperatures, is the ***drying*** of the green-cells from the volatile solvents residual in the materials. This is usually carried out in controlled conditions before the proper treatment in the firing furnace. In the successive ***de-binding*** step, at temperatures above 200 °C, the organic components in the green tapes decomposes, e.g. through softening and/or melting, and are removed as gases.

Shape instability during the de-binding process can be observed in a temperature range around 200-400 °C, depending in the organic component composition. This is due to the fact that the cell are overall thin plates combined. In particular, the edge of the cell has a micrometric distortion, which is very detrimental for the stack. It is often necessary to use laser cut to get rid of this distortion.

Increasing the temperatures, the softening and melting of the organic components in the green-cells usually lead to the release of residual stresses usually formed and “frozen” in the materials at the green-cells fabrication. Release of residual stresses can lead to a change in the shape which is directly related to the entity of the residual stress in the green-cell.

Thermal decomposition at higher temperatures leads to formation of CO, CO_2, NO_x, H_2O etc. Formation of such decompositions gas induces curling which can strain the planar cell to the typical “saddle-like” or “tube-like” shapes. In this case, shape change is attributed to both the gradients of pressure for the formation of gases and to density changes for the formation of new porosity in the materials.

The thermal decomposition reactions are driven by the amount of thermal energy in the furnace and by the oxygen/organic ratio in the materials at the green state. The decomposition phenomena result as a complex collection of chemical reactions which takes place heterogeneously in the materials, mainly at the surface which is directly exposed to the environment. As results, several parameters can control the cell shape instability. Some of them can be related to the concentration and to the chemical composition of the organics.

Other parameters are linked to the supply of oxygen at the materials´ surface and instability can depend on the air ventilation in the furnace, coverage of the material to the air supply, thickness of the cells etc.

Although the de-binding step can be relevant for the final shape and integrity of the cells, the ***sintering*** of the layers at high temperatures is surely the process step controlling final microstructures, quality, shape and composition of the ceramic cells. Sintering is a series of thermally activated processes which induces the ceramic particles to coalesce, densify, consolidate and coarsen into a continuous solid ceramic body. In the cell, each layer turns into porous or dense depending on the particles arrangement produced at the green state. The shrinkage associated to such transformation depends again on several factors. For the oxides used in SOFC, the sintering process is controlled by solid state mass diffusion phenomena, *i.e.* solid state sintering, where the driving force is the total surface energy reduction from the ceramic particles (high specific surface area) into the interconnected polycrystalline system (low specific surface area).

The total potential energy in the materials is called sintering potential energy. The overall sintering process depends mainly on the compositions of the materials but also on their microstructural features. The starting particles sinter and densify at different temperatures depending on their size and porosity. Impurities, ionic defects and stress applied can also heavily influence the solid state sintering. In solid state sintering at high temperatures, solid oxides show viscoelastic mechanical behaviour (as in creep) and, depending on the entity of the diffusive regime, the stress conditions lead mainly to viscous flow and plastic strain of the materials.

At lower temperatures, where the material presents reduced diffusive mass flow, the elastic component makes again the materials fragile and receptive to defects formation.

As consequence of these phenomena, the use of different materials and microstructures in a multilayer system introduces further additional parameters to the sintering process; typically, the ceramics used for the different cell components have different compositions and thus different diffusive regimes which are activated at different temperatures. Moreover, the formation of different microstructure, *e.g.* porous vs. dense, leads to differential shrinkage rates even for the same material composition. The overall result is thus a complex sequence of stress and strain at the different layers and at their interfaces which, at the continuum, leads to shape instability or even to formation of residual stresses and defects.

Factors which cause shape instability and mechanical failure of tape-cast multilayer ceramic systems during and after firing thus compromises the mechanical integrity and shape of planar ceramic multilayer cells. EP1768208 addresses the issue of adjusting the choice of material in a support layer in a SOFC in order to compensate for the difference in mechanical strength and thermal expansion coefficient of the different layers in SOFC, but is silent in regards to how to produce half-cells that are sufficient flat and uniform to be stacked to form a fuel cell stack.

It has been an industry and research challenge to produce fuel cells or half-cells that are sufficient flat and uniform to be stacked to form a fuel cell stack.

Countermeasures such as applying loads to the fuel cells or half-cells during preparation such as sintering and applying loads in the stack assembly have been used to remedy the deformed fuel cells. Such countermeasure are however cumbersome and requires extra resources in terms of installation and process steps.

It is an objective of this invention to overcome such challenges and drawbacks.

Description of the invention

Disclosed herein is a half-cell shaped precursor body of either anode type or cathode type, the half-cell shaped precursor body being prepared to be free sintered to form a sintered or pre-sintered half-cell being adapted to be stacked in a solid oxide fuel cell stack. By free sintered is meant that the precursor body can be sintered without necessitating the use of load.

The half-cell shaped precursor body extends in a radial direction from an axis of symmetry essentially in a plane towards an edge with an edge region. The half-cell shaped precursor body comprises a) a middle region with a middle plane including at least one middle individual layer L_m^i. By middle individual layers is also included the situation, where all the individual layers are of the same material/type or there only exists one individual middle layer.

The middle region has a first side and a second side, wherein the middle region on the first side has a first region including at least one first individual layer, and on the second side has a second region including at least one second individual layer. At least one individual layer is configured to form an electrode of either anode type or cathode type, at least one individual layer is configured to form an electrolyte layer, and at least one individual layer is configured to form a support of either anode type or cathode type. By at least one individual layer is meant a layer selected from the first, second or middle region.

Each individual layer of each middle, first and second region has a volume stress coefficient (Δv) component. By volume stress coefficient component is meant that each individual layer of each middle, first and second region undergoes stress conditions (σ). Such a stress has components both along the layer planes and across the layer thickness. During sintering such stress is generated mainly by shrinkage of the material. As result, the total volume strain (ε) reflects the volume instability in terms of strain and/or shrinkage primarily during a sintering process at each layer and includes contributions across the layer thickness and along the planes. However, since the layers are at the multilayer elements are mechanical connected a different strain regime at the layer can lead to additional stress components which especially develop as shearing stress at each layer interface, parallel to the layer planes. Three kinds of strain conditions at the multilayer can therefore be defined;

Longitudinal strain describes the ratio of the change in length of a body along the plane of the body compared to the original length of the body. If L is the original length and the final length is L + e under the action of a normal stress, the change in length is given by *'Longitudinal Strain = Change in length / Original length'* = e / L.

Volume Strain is the ratio of the change in volume of a body to its original volume. If **V is the original volume of a body and vol + Δvol is the volume of the body under the action of a normal stress, the change in volume is Δvol. The strain =** *'Change in volume / Original volume'* **= Δvol / vol.**

Shearing Strain is the strain resulting from the shearing stress and it is the angle through which a face originally perpendicular to the fixed face is turned. In other words, it is the ratio of the displacement of a layer to its distance from the fixed layer. As strain is a ratio, it has no units and dimensions.

For the sintered bodies, shearing strain and stress is still present at the multilayer as effect of the different thermal expansion coefficient coefficients (TECs) at the layers. Differential TECs lead to shearing stress at the interfaces and consequent elastic strain, resulting in a change of the original planar shape of the multilayer.

Each individual layer of each middle, first and second region also has an individual thermal expansion coefficient (TEC) component. The TEC mainly reflects the material volume instability in the individual layers upon changes during heating (expansion), cooling (contraction) primarily after sintering of the precursor body.

In the half-cell shaped precursor body, the middle region collectively has a TEC_m and a Δv_m. This is here intended as the resultant strain which occurs at the multilayer as effect of the collective differential TECs at the layer.

The middle region is further symmetrical about a symmetry plane. Also, the first region collectively has a TEC_1 and a Δv_1 and the second region collectively has a TEC_2 and a Δv_2 wherein TEC_1 is substantially identical to TEC_2 and Δv_1 is substantially identical to Δv_2.

By the term 'collectively' is meant the overall TEC_m / Δv_m for the specific region. The term is measurable, but not easily calculated since the final strain depends on stiffness and geometry of the layers at the multilayer. If the first region and the second region comprises the same material(s) having the same thickness and being distributed symmetrically on each sides of the middle region, it is apparent that the collective TEC_m / Δv_m will be the same. However, the same may also be true for a different construction of the first region compared to the second region.

The symmetry in regards to TEC is true for all temperatures from room temperature to 1300° C.

By 'substantially identical' is meant that the difference between TEC_1 and TEC_2 is less than 5%, or less than 3% or less than 2% or less than 1% and that the difference between Δv_1 Δv_2 is less than 5%, or less than 3% or less than 2% or less than 1%.

By the above is obtained a symmetrical precursor body, which is symmetrical in terms of TEC and Δv about a symmetrical place. The precursor body is not limited to being symmetrical in terms choice of material in the different individual layers. By the symmetrical construction in terms of TEC and Δv, a half-cell shaped precursor body is obtained, which remains nearly completely symmetrical before, during and after sintering.

It is thereby not a necessity that a mechanical load or mechanical constraint is used in order to form an essentially planar half-cell of a fuel cell for a fuel cell stack.

Further, by having a precursor body, which after sintering remain flat, allows for the generation of fuel cells and stacks of fuel cells, which retains shape and form during subsequent temperature fluctuations. This is highly advantageous since in particular temperature fluctuations has a had a tendency to make fuel cells twist and bend after stacking of these, whereby they take up to a larger amount of space.

In one or more embodiments, TEC_i and/or Δv_i is isotropic in all the directions for each individual layer before a sintering process.

In one or more embodiments, the first region comprises a first outermost layer and the second region comprises a second outermost layer, the half-cell shaped precursor body further comprising a compensation layer having a volume stress coefficient component, and an individual thermal expansion coefficient component, wherein the compensation layer covers the edge region and/or another selected portion of the first outermost layer and/or the second outermost layer.

The compensation layer has a purpose of avoiding localized distorted edges on the half-cell shaped precursor body.

In one or more embodiments, the half-cell shaped precursor body has at least one through going plane of symmetry extending from one edge region to another edge region through the axis of symmetry, the through going plane of symmetry dividing the half-cell shaped precursor body into a first section having a collectively TEC_A and a Δv_A, and a second section having a collectively TEC_B and a Δv_B, wherein the compensation layer and the individual layers comprise two or more through going channels distributed on opposite sides of the through going plane of symmetry and wherein the collective TEC_A of the first section is substantially identical to the collective TEC_B of the second section and Δv_A of the first section is substantially identical to Δv_B of the second section.

In one or more embodiments, the through going channels have different shapes and sizes.

In one or more embodiments, the individual layers in the half-cell shaped precursor body have a round shape; preferably a circular shape.

In one or more embodiments, the individual layers in the half-cell shaped precursor body have a polygonal shape such as e.g. rectangular, quadratic, pentagonal, hexagonal, octagonal, or triangular shape. The half-cell shaped precursor body may also have other polygonal shapes besides from the ones mentioned here.

In one or more embodiments, the individual layers (L_m^i, L_1^i, L_2^i) are symmetrically distributed on both sides of a middle layer (L_m^m) positioned in the middle of the middle region such that L_m^{m-1} of the middle layer is substantially identical to L_m^{m+1} of the middle layer and L_1^i of the first layer is substantially identical to L_2^i of the second layer.

In one or more embodiments, the individual layers are quasi-symmetrically distributed on both sides of a middle layer positioned in the middle of the middle region (300) such that L_m^{m-1} of the middle layer is different from L_m^{m+1} of the middle layer and/or L_1^i of the first layer is different from L_2^i of the second layer in terms of thickness, material property, TEC and/or Δv.

In one or more embodiments, the half-cell shaped precursor body further comprises a side layer extending along at least one side part of the half-cell shaped precursor body connecting the first outermost layer with the second outermost layer, wherein the side layer is an integral part of the first outermost layer and the second outermost layer thereby forming one continuously extending layer, or comprises a first side part being an integral part of the first outermost layer and a second side part being an integral part of the second outermost layer, wherein the two side parts are adjacent to each other.

The side layer has a purpose of avoiding the localized distorted edges.

Disclosed herein is also, a half-cell of anode or cathode type obtained by sintering a half-cell shaped precursor body according to the above.

In one or more embodiments, TEC_i and/or Δv_i is isotropic in all the directions for each individual layer after the sintering process.

Disclosed herein is also, a half-cell wherein the sintering process comprises steps of:

a) heating at a polymeric component decomposition temperature for a first time period in order to remove binding components;

b) heating at a poreformer component decomposition temperature for a second time period in order to completely remove poreformer components, thereby obtaining a white body;

c) heating at a first ceramic diffusion temperature for a third time period , thereby promoting necking of ceramic particles and obtaining a presintered body;

d) heating at a second ceramic diffusion temperatures for a fourth time period to promote consolidation of porous layers, densification of dense layers, and controlled grain growth;

e) consolidation of the materials in a continuum within the layers and at the interfaces thereby obtaining the sintered body, and

f) cooling to room temperature in controlled conditions to moderate the thermal stresses rising in viscous-elastic and elastic regimes of the body.

In one or more embodiments, the half-cell is planar with a flatness as the distance between the lowest and the highest data point on the sample surface of the half-cell at room temperature, and where on a half-cell

- the distance is below 6.5 mm when the half-cell experiences no load;
- the distance is below a linear decreases from 6.5 mm to 5 mm when the half-cell experiences a load from above 0 g/cm2 to 0,85 g/cm^2; or
- the distance is below 5 mm when the half-cell experiences a load above 0,85 g/cm^2.

In one or more embodiments, the half-cell is planar with a flatness as a volume per area of a half-cell at room temperature, where the volume of the half-cell is the sum of all heights of each grid-cell multiplied by the area of each grid-cell such at all grid-cells in a grid represent the area of the half-cell; and where on a half-cell

- the volume is below 110 cm^3 per 256 cm^2 when the half-cell experiences no load;
- the volume is below a linear decreases from 110 cm^3 per 256 cm^2 to 60 cm^3 per 256 cm^2 when the half-cell experiences a load from above 0 g/cm^2 to 0,85 g/cm^2; or
- the volume is below 60 cm^3 per 256 cm^2 mm when the half-cell experiences a load above 0,85 g/cm^2.

Disclosed herein is also, a fuel cell stack comprising a plurality full cells, wherein each full cell comprises at least a first half-cell according to the above, the first half-cell being of anode type and at least a second half-cell according to the above, the second half-cell being of cathode type.

Preferably the fuel cell is of the solid oxide fuel cell (SOFC) type.

Brief description of the drawings

Figures 1a-c show different embodiments of a half-cell shaped precursor body according to the invention as seen in a side view.

Figures 2a-b show prior art half-cell shaped precursor bodies not falling under the scope of this invention.

Figures 3a-b show two different embodiments of the half-cell shaped precursor body according to the invention as seen in a perspective view.

Figures 4a-b show two different embodiments of a half-cell shaped precursor body with a side layer according to the invention as seen in a side view.

Figures 5a-e show embodiments of a half-cell shaped precursor body according to the invention, where the half-cell shaped precursor body has a compensation layer and in figures 5b-d through going channels. Figures 5a-d are seen in a side view (upper picture) and a top-down view (lower picture), whereas figure 5e is shows in a perspective view.

Figures 6a-b show the flatness of a half-cell with origin in definitions based on distance as a measure of amplitude deformation (figure 6a), on volume as a measure of magnitude deformation (figure 6b), and figure 6c show the volume and the flatness as a function of load.

Description of preferred embodiments

Figures 1a-c show different embodiments of a half-cell shaped precursor body 10 according to the invention. The half-cell shaped precursor body 10 will either have an anode layer and thus be of anode type or have a cathode layer and thus be of cathode type. As it is a half-cell, anode type and cathode type layers will not be present in the same half-cell. If the half-cell shaped precursor body 10 contains a support layer that supports layer will be of anode type if the half-cell shaped precursor body 10 contains an anode layer or of cathode type, if the half-cell shaped precursor body 10 contains a cathode layer.

The half-cell shaped precursor body 10 is prepared to be free sintered to form a sintered or pre-sintered half-cell being adapted to be stacked in a solid oxide fuel cell stack, and contains a number of layers arranged in different regions; a first region 100, a second region 200, and a middle region 300.

The middle region 300 has a middle plane including at least one middle individual layer L_m^i positioned in the middle of the body 10. The middle region 300 has a first side S1 and a second side S2, which defines the two outer sides of the middle region 300. Adjacent to the first side S1 of the middle region is the first region 100 and adjacent to the second side S2 is the second region 200.

The first region 100 includes at least one first individual layer 10i, L_1^i, where i represent the numbers 1, 2, 3, 4,.. x=outer, where x=outer represents the outermost layer number. The second region 200 likewise includes at least one second individual layer 20i, L_2^i.

The layers in the middle region 300 may be defined as L_m^i, where i represent the number of individual layers from 1 to x. The middle region 300 may have one individual layer positioned in the middle, referred to as L_m^m, where L_m^{m-1} and L_m^{m+1} define the layers adjacent on the two sides of the middle layer L_m^m.

By middle region 300 is not meant that the distance to top and bottom of the body 10 is the same, but merely that this region represents a region not including an outer layer. Normally, the middle region 300 only has one individual layer, e.g. layer 300, L_m.

In the half-cell shaped precursor body 10, at least one individual layer (L_m^i, L_1^i, L_2^i) is configured to form an electrode of either anode type or cathode type. Also, at least one individual layer (L_m^i, L_1^i, L_2^i) is configured to form an electrolyte layer, and at least one individual layer (L_m^i, L_1^i, L_2^i) is configured to form a support of either anode type or cathode type – the latter mimicking the type defined by the anode/cathode layer. Anode type and cathode type layers will not be present in the same half-cell shaped precursor body 10.

The half-cell shaped precursor body 10 extends in a radial direction from an axis of symmetry 16 essentially in a symmetry plane 20 towards an edge 12 with an edge region 14.

Each of the individual layers L_m^i, L_1^i, L_2^i in each of the middle 300, first 100 and second 200 region has a volume stress coefficient (Δv) component denoted Δv_m^i for the middle region layers L_m^i, Δv_1^i for the first region layers L_1^i, and Δv_2^i for the second region layers L_2^i. The volume stress coefficient reflects the volume strain and/or shrinkage due to densification during firing of the half-cell shaped precursor body 10.

Each of the individual layers L_m^i, L_1^i, L_2^i in each of the middle 300, first 100 and second 200 region also has an individual thermal expansion coefficient (TEC) component denoted TEC_m^i for the middle region layers L_m^i, TEC_1^i for the first region layers L_1^i, and TEC_2^i for the second region layers L_2^i. The TEC mainly reflects the materials volume instability in regards to contraction and expansion in the individual layers upon changes during heating (expansion), cooling (contraction) and/or of the half-cell in general after a sintering process. This parameter is thus primarily not effected by sintering in contrast to Δv.

The middle region 300 collectively has a TEC_m and a Δv_m and wherein the middle region is symmetrical about a symmetry plane. The first region 100 collectively has a TEC_1 and a Δv_1 and likewise for the second region 200 (TEC_2 and a Δv_2). The individual layers are chosen and position such that TEC_1 is substantially identical to TEC_2 and Δv_1 is substantially identical to Δv_2.

This ensures that the half-cell shaped precursor body 10 maintains an exceptional flatness before, during and after sintering and/or heating/cooling of the shaped precursor body 10. This in turn allows the user to assemble the half-cell bodies after sintering thereof and subsequently stacking them efficiently such that each half-cell and/or cell are in full contact with the consecutive half-cell and/or cell, respectfully.

In contrast, if an unsymmetrical build-up of the half-cell shaped precursor body 10 in terms of TEC and Δv is used, the half-cell will bend upon sintering and/or afterwards during heating and cooling of the half-cell as illustrated in figures 2a and 2b showing prior art versions of bodies.

The TEC_i and/or Δv_i will normally be isotropic in all the directions for each of the individual layers L_m^i, L_1^i, L_2^i both before, during and after a sintering process.

The individual layers L_m^i, L_1^i, L_2^i may be symmetrically distributed on both sides of the middle layer L_m^m positioned in the middle of the middle region 300 such that L_m^{m-1} is identical to L_m^{m+1} and L_1^i is identical to L_2^i. One example of this distribution is if the middle layer is an electrolyte layer which on both sides is covered by a cathode layer followed by a cathode support layer. The two cathode layers and the two support layers will in this case pair wise have the same thickness and material construction.

A quasi-symmetrical distribution on both sides of the middle layer L_m^m can also be imagined where L_m^{m-1} is different from L_m^{m+1} and/or L_1^i is different from L_2^i in terms of thickness, material property, TEC and/or Δv. The collective TEC_1 and Δv_1 of the first layer is however still substantially identical to the collective TEC_2 and Δv_2 of the second layer, respectively. An example of this setup is a body 10 having a first layer of the cathode type, a middle layer being an electrolyte and two second region layers being a cathode and a cathode support layer.

As shown in figures 3a-b, the half-cell shaped precursor body 10 may have a round shape – preferably a circular shape as shown in figure 3b – or a rectangular or quadratic shape as shown in figure 3a. The shapes are however not limited to these two shown examples. The individual layers in the half-cell shaped precursor body 10 may have a polygonal shape such as e.g. pentagonal, hexagonal, octagonal, or triangular shape. The half-cell shaped precursor body 10 may also have other polygonal shapes besides from the ones mentioned here.

The thickness of the half-cell shaped precursor body 10 is much lower than the lateral profile of the half-cell shaped precursor body 10. This gives the half-cell shaped precursor body 10 a low stiffness. Thus, the edge region 14 of the half-cell shaped precursor body 10 is particular sensible to shape distortion effects during sintering and/or subsequent thermal treatments.

The half-cell shaped precursor body 10 may therefore comprises a side layer 400 as shown in figures 4a-b, which strengthens the edge region 14 of the half-cell shaped precursor body 10. The side layer 400 extends along at least one side part 410 of the half-cell shaped precursor body 10 thereby covering the different layers in the half-cell shaped precursor body 10 on at least this side part 410. The side layer 400 connects the first outermost layer L_1^{outer} with the second outermost layer L_2^{outer}.

The side layer 400 can be constructed in at least two different embodiments. The first embodiment is shown in figure 4a, where the side layer 400 is an integral part of the first outermost layer L_1^{outer} and the second outermost layer L_2^{outer} thereby forming one continuously extending layer, When doing so, the material of the two outer layers are the same, e.g. an electrolyte layer, a cathode/anode or cathode support/anode support layer.

The a second embodiment of the side layer 400 is shown in figure 4b, where the side layer 400 comprises a first side part 401 being an integral part of the first outermost layer L_1^{outer} and a second side part 402 being an integral part of the second outermost layer L_2^{outer}. The two side parts reaches along the side part 410 and are thus adjacent to each other on this side 410. In this setup, that material of the two parts 401, 402 of the side layer 400 will normally be the same.

In some embodiments, the half-cell shaped precursor body 10 also comprises a compensation layer 600 as shown in figures 5a-d. This layer also has the purpose of strengthening the edge region 14 of the half-cell shaped precursor body 10 and can be used in combination with the side layer 400 or as an alternative thereto. The top part of each of the figures 5a, 5b, 5c, and 5d shows the body 10 seen in a side view and the bottom part of each of the figures shows a top-down view of the body 10.

The compensation layer 600 mainly covers the edge region 14 and/or another selected portion of the outermost layers L_1^{outer} and/or L_2^{outer}, and does normally not cover the entire outer layers L_1^{outer}, L_2^{outer}.

Like all the other layers, the compensation layer 600 has a volume stress coefficient (Δv_c) component, and an individual thermal expansion coefficient (TEC_c) component.

The compensation layer balances the stress at the sides of the half-cell shaped precursor body 10 both prior to sintering of the body 10 and after a subsequent sintered. It however does so in different way; during the sintering process, the compensation layer 600 compensates mainly Δv and only TEC to a minor extend, whereas in the sintered half-cell, the compensation layer 600 compensates TEC only.

A half-cell shaped precursor body 10 has a number of symmetry planes 22, 24, 26 extending from one edge region 14a to another edge region 14b through the axis of symmetry 16. The through going planes of symmetry 22, 24, 26 divides the half-cell shaped precursor body 10 into two different sections; a first section 30 and a second section 32, the two sections having collectively a TEC_A and a Δv_A (first section), and a TEC_B and a Δv_B (second section), respectively.

As seen in figures 5b-d, the compensation layer 600 and the individual layers L_m^i, L_1^i, L_2^i may also have two or more through going channels 500 distributed on opposite sides of the through going plane of symmetry 22, 24, 26. Again, TEC_A of the first section 30 is substantially identical to TEC_B of the second section 32 and Δv_A of the first second is substantially identical to Δv_B of the second section thereby ensuring that the body 10 is symmetrical and remains flat before, during and after sintering.

As seen in figures 5b-d, the through going channels 500 may have different shapes and sizes – also within/on the same body 10 – as long as TEC_A is substantially identical to TEC_B and Δv_A is substantially identical to Δv_B.

Figure 5e shows an example of a half-cell shaped precursor body 10 comprising a first electrolyte layer 701, a first anode layer 702, an anode support layer 703, a second anode layer 704, and a second electrolyte layer 705. The half-cell shaped precursor body 10 shown in figure 5e has a cell size of w1 x w2 = 160 mm x 160 mm.

The first electrolyte layer 701, the first anode layer 702, and the anode support layer 703 layers may have a total thickness of T1 = 0.4 mm +/- 0.01 mm, whereas the total thickness of the second anode layer 704 and the second electrolyte layer 705 may be T2 = 0.03 mm +/- 0.001 mm. Thus, the illustration in figure 5e has been stretched significantly compared to the real dimensions of the half-cell. The width of the compensation layers 704, 705 may be w3 = w4 = 20 m, i.e. an area of 120 mm x 120 mm of the underlying anode support layer 703 is not covered by the compensation layers 704, 705.

The compensation layers 704, 705 may comprise holes extending all the way or partly through the half-cell 10.

The first electrolyte layer 701 and second electrolyte layer 705 may be a YSZ (Yttria-Stabilized-Zirconia) layer, whereas both the first and second anode layers 702, 704 and the anode support layer 703 may be Ni-YSZ (Nickel-Yttria-Stabilized-Zirconia) layers.

In figure 5e, the collective TEC/Δv of the first electrolyte layer 701 and the first anode layer 702 is substantially the same as the TEC of the second electrolyte layer 704 and the second anode layer 705.

Thus, in an embodiment of the invention, the half-cell shaped precursor body one or more of the first individual layer 701, 702 in the first region including at least a first outermost layer (L_1^{outer}), or one or more of the second individual layer 704, 705 in the second region including at least a second outermost layer (L_2^{outer}), is in the form of a compensation layer 704, 705 covering the edge region 14 and/or another selected portion of the half-cell 10.

The different half-cell shaped precursor body 10 will each be of either cathode or anode type. By sintering the half-cell shaped precursor bodies 10, half-cell of either anode or cathode type are obtained. The sintering process may proceed in the following steps:

I) heating the half-cell shaped precursor body 10 at a polymeric component decomposition temperature for a first time period in order to remove binding components;

II) heating at a poreformer component decomposition temperature for a second time period in order to completely remove poreformer components, thereby obtaining a white body;

III) heating at a first ceramic diffusion temperature for a third time period, thereby promoting necking of ceramic particles and obtaining a presintered body;

IV) heating at a second ceramic diffusion temperatures for a fourth time period to promote consolidation of porous layers, densification of dense layers, and controlled grain growth;

V) consolidation of the materials in a continuum within the layers and at the interfaces thereby obtaining the sintered body; and

VI) cooling to room temperature in controlled conditions to moderate the thermal stresses rising in viscous-elastic and elastic regimes of the body.

The half-cell obtained after the sintering process is flat and not affected by a subsequent heating and/or cooling of the half-cell due to the symmetry of the TEC on each side of a symmetry plane. Thermal expansion/contraction are relevant in the shape instability of the planar shape, especially in heating and/or cooling of the body 10 when the materials are already sintered/consolidated and are in an elastic regime. The situation illustrated in figures 2a and 2b, which will result in a bended half-cell, are thereby avoided.

During the sintering process, the body 10 further remains flat, due to the matching of the Δv on the two sides of the symmetry plane. Thus, during firing of the body transforming it from a green form to the sintered form, the change of volume attributed to loss of the organic component in the green form and annihilation of the porosity among the ceramic/metallic particles are matched symmetrically on either side of the symmetry plane. The symmetrical construction of the body 10 in regards of Δv, is especially important at high temperatures in a visco-elastic regime.

A consequence of constructing the body 10 as described above is that half-cells can be made without use of mechanical load / constraint. A load may still be used, but it is not a necessity.

The half-cell may have a flatness described as the distance 614 between the lowest 610 and the highest 612 data point on the sample surface of the half-cell, as shown in figure 6a.

The half-cell may further have a flatness described as a volume per area of a half-cell as shown in figure 6b. Herein the volume of the half-cell is the sum of all heights of each grid-cell multiplied by the area of each grid-cell such at all grid-cells in a grid represent the area of the half-cell.

Figure 6c shows graphs of the flatness of a 16 cm x 16 cm cell described by both the volume 616 and the distance 618. The 16 cm x 16 cm cell typically has a thickness in the order of 500-800 microns. Both graphs in figure 6c are plotted as a function of the load and the measurements are all conducted at room temperature.

On a half-cell, the distance 614 may be below 6.5 mm when the half-cell experiences no load. Alternatively, the distance 614 may be below a linear decreases from 6.5 mm to 5 mm when the half-cell experiences a load from above 0 g/cm2 to 0,85 g/cm^2; or yet alternatively, the distance may be below 5 mm when the half-cell experiences a load above 0,85 g/cm^2.

On a half-cell, the volume may be below 110 cm^3 per 256 cm^2 when the half-cell experiences no load. Alternatively, the volume may be below a linear decreases from 110 cm^3 per 256 cm^2 to 60 cm^3 per 256 cm^2 when the half-cell experiences a load from above 0 g/cm^2 to 0,85 g/cm^2. Yet alternatively, the volume may be below 60 cm^3 per 256 cm^2 mm when the half-cell experiences a load above 0,85 g/cm^2.

The half-cells will normally be combined in pairs of two, with one half-cell being of anode type and one being of cathode type. These pairs together form a full cell. Due to the high degree of flatness of the individual half-cells in the fuel cells – and thereby the full cells themselves – the fuel cells can be stacked easily. Also, due to the flatness, there are no problems with insufficient contact between the individual half-cells and/or fuel cells in the stack. Further, if the temperature increases or decreases, the fuel cell stack remains flat, as the individual half-cells do not bend or twist due to the symmetrical constructions in particular in regards to the TEC.

The fuel cell is preferably of the solid oxide fuel cell (SOFC) type.

References

10	half-cell shaped precursor body
12	edge
14, 14a, 14b	edge region
16	axis of symmetry
20	symmetry plane
22	symmetry plane
24	symmetry plane
26	symmetry plane
30	a first section of the half-cell shaped precursor body
32	a second section of the half-cell shaped precursor body
100	first region
10i / L_1^i	individual layer in the first region, where i = 1, 2, 3,...
101 / L_1^1	first individual layer adjacent to the first side S1 of the middle region
102 / L_1^2	second individual layer adjacent to the first individual layer L_1^1
103 / L_1^3	third individual layer adjacent to the second individual layer L_1^2
L_1^{outer}	outermost layer of the first region
200	second region
20i / L_2^i	individual layer in the second region, where i = 1, 2, 3,...
201 / L_2^1	first individual layer adjacent to the second side S2 of the middle region
202 / L_2^2	second individual layer adjacent to the first individual layer L_2^1
203 / L_2^3	third individual layer adjacent to the second individual layer L_2^2
204 / L_2^4	fourth individual layer adjacent to the third individual layer L_2^3
L_2^{outer}	outermost layer of the second region
300	middle region
L_m^i	individual layer in the middle region, where i = 1, 2, 3,...
L_m^m	middle layer of the middle region
S1	first side of the middle region
S2	second side of the middle region
400	side layer
401	first part of the side layer
402	second part of the side layer
410	side part of the half-cell shaped precursor body

500	through going channel
600	compensation layer
610	lowest data point
612	highest data point
614	distance between the highest and the lowest data point
616	flatness described by volume
618	flatness described by distance
701	first electrolyte layer
702	first anode layer 702
703	an anode support layer
704	second anode layer 704
705	second electrolyte layer
w1, w2	width of the half-cell
w3, w4	width of the compensation layer
T1	total thickness of the layers 701, 702, 703
T2	total thickness of the layers 704, 705

Claims

1. A half-cell shaped precursor body (10) of either anode type or cathode type, the half-cell shaped precursor body (10) being prepared to be free sintered to form a sintered or pre-sintered half-cell being adapted to be stacked in a solid oxide fuel cell stack, wherein the half-cell shaped precursor body (10) extends in a radial direction from an axis of symmetry (16) essentially in a plane (20) towards an edge (12) with an edge region (14), the half-cell shaped precursor body (10) comprising:
   - a middle region (300) with a middle plane including at least one middle individual layer L_m^i, the middle region (300) having a first side (S1) and a second side (S2), wherein the middle region (300):
   - on the first side (S1) has a first region (100) including at least one first individual layer (10i) L_1^i; and
   - on the second side (S2) has a second region (200) including at least one second individual layer (20i) L_2^i;

   wherein
   - at least one individual layer (L_m^i, L_1^i, L_2^i) is configured to form an electrode of either anode type or cathode type,
   - at least one individual layer (L_m^i, L_1^i, L_2^i) is configured to form an electrolyte layer, and
   - at least one individual layer (L_m^i, L_1^i, L_2^i) is configured to form a support of either anode type or cathode type;

   wherein each individual layer (L_m^i, L_1^i, L_2^i) of each middle (300), first (100) and second (200) region has:
   - a volume stress coefficient (Δv_m^i, Δv_1^i, Δv_2^i) component, and
   - an individual thermal expansion coefficient (TEC_m^i, TEC_1^i, TEC_2^i) component,

   characterised in that
   - the middle region (300) collectively has a TEC_m and a Δv_m and wherein the middle region is symmetrical about a symmetry plane, and
   - the first region (100) collectively has a TEC_1 and a Δv_1 and the second region (200) collectively has a TEC_2 and a Δv_2 wherein TEC_1 is substantially identical to TEC_2 and Δv_1 is substantially identical to Δv_2.

2. A half-cell shaped precursor body (10) according to claim 1, wherein TEC_i and/or Δv_i is isotropic in all the directions for each individual layer (L_m^i, L_1^i, L_2^i) before a sintering process.

3. A half-cell shaped precursor body (10) according to claim 1 or 2, wherein the first region (100) comprises a first outermost layer (L_1^{outer}) and the second region (200) comprises a second outermost layer (L_2^{outer}), the half-cell shaped precursor body (10) further comprising a compensation layer (600) having:
   - a volume stress coefficient (Δv_c^i) component, and
   - an individual thermal expansion coefficient (TEC_c) component,

wherein the compensation layer (600) covers the edge region (14) and/or another selected portion of the first outermost layer (L_1^{outer}) and/or the second outermost layer (L_2^{outer}).

4. A half-cell shaped precursor body (10) according to claim 1 or 2, wherein:
   - one or more of the first individual layer (10i) L_1^i in the first region (100), including at least a first outermost layer (L_1^{outer}), or
   - one or more of the second individual layer (20i) L_2^i in the second region (200) including at least a second outermost layer (L_2^{outer}),

is in the form of a compensation layer (704, 705) covering the edge region (14) and/or another selected portion of the half-cell.

5. A half-cell shaped precursor body (10) according to claim 3 or 4, wherein the half-cell shaped precursor body (10) has at least one through going plane of symmetry (22, 24, 26) extending from one edge region (14a) to another edge region (14b) through the axis of symmetry (16), the through going plane of symmetry (22, 24, 26) dividing the half-cell shaped precursor body (10) into
   - a first section (30) having a collectively TEC_A and a Δv_A, and
   - a second section (32) having a collectively TEC_B and a Δv_B,

wherein the compensation layer (600, 704, 705) and the individual layers (L_m^i, L_1^i, L_2^i) comprise two or more through going channels (500) distributed on opposite sides of the through going plane of symmetry (22, 24, 26) and wherein the collective TEC_A of the first section (30) is substantially identical to the collective TEC_B of the second section (32) and Δv_A of the first section (30) is substantially identical to Δv_B of the second section (32).

6. A half-cell shaped precursor body (10) according to claim 5, wherein the through going channels (500) have different shapes and sizes.

7. A half-cell shaped precursor body (10) according to any preceding claim, wherein the individual layers (L_m^i, L_1^i, L_2^i) in the half-cell shaped precursor body (10) have a round shape; preferably a circular shape.

8. A half-cell shaped precursor body (10) according to any of claims 1-6, wherein the individual layers (L_m^i, L_1^i, L_2^i) in the half-cell shaped precursor body (10) have a polygonal shape such as e.g. rectangular, quadratic, pentagonal, hexagonal, octagonal, or triangular shape.

9. A half-cell shaped precursor body (10) according to any preceding claim, wherein the individual layers (L_m^i, L_1^i, L_2^i) are symmetrically distributed on both sides of a middle layer (L_m^m) positioned in the middle of the middle region (300) such that L_m^{m-1} of the middle layer is substantially identical to L_m^{m+1} of the middle layer and L_1^i of the first layer is substantially identical to L_2^i of the second layer.

10. A half-cell shaped precursor body (10) according to any of claims 1-8, wherein the individual layers (L_m^i, L_1^i, L_2^i) are quasi-symmetrically distributed on both sides of a middle layer (L_m^m) positioned in the middle of the middle region (300) such that L_m^{m-1} of the middle layer is different from L_m^{m+1} of the middle layer and/or L_1^i of the first layer is different from L_2^i of the second layer in terms of thickness, material property, TEC and/or Δv.

11. A half-cell shaped precursor body (10) according to any of claims 1-10, wherein the half-cell shaped precursor body (10) further comprises a side layer (400) extending along at least one side part (410) of the half-cell shaped precursor body (10) connecting the first outermost layer (L_1^{outer}) with the second outermost layer (L_2^{outer}), wherein the side layer (400):

- is an integral part of the first outermost layer (L_1^{outer}) and the second outermost layer (L_2^{outer}) thereby forming one continuously extending layer, or
- comprises a first side part (401) being an integral part of the first outermost layer (L_1^{outer}) and a second side part (402) being an integral part of the second outermost layer (L_2^{outer}), wherein the two side parts are adjacent to each other.

12. A half-cell of anode or cathode type obtained by sintering a half-cell shaped precursor body (10) according to any of claims 1-11.

13. A half-cell according to claim 12 wherein the sintering process comprises steps of:
    - heating at a polymeric component decomposition temperature for a first time period in order to remove binding components;
    - heating at a poreformer component decomposition temperature for a second time period in order to completely remove poreformer components, thereby obtaining a white body;
    - heating at a first ceramic diffusion temperature for a third time period , thereby promoting necking of ceramic particles and obtaining a presintered body;
    - heating at a second ceramic diffusion temperatures for a fourth time period to promote consolidation of porous layers, densification of dense layers, and controlled grain growth;
    - consolidation of the materials in a continuum within the layers and at the interfaces thereby obtaining the sintered body, and
    - cooling to room temperature in controlled conditions to moderate the thermal stresses rising in viscous-elastic and elastic regimes of the body.

14. A half-cell according to claim 12 or 13, wherein the half-cell is planar with a flatness as the distance between the lowest and the highest data point on the sample surface of the half-cell at room temperature, and where on a half-cell
    - the distance is below 6.5 mm when the half-cell experiences no load;

- the distance is below a linear decreases from 6.5 mm to 5 mm when the half-cell experiences a load from above 0 g/cm^2 to 0,85 g/cm^2; or
- the distance is below 5 mm when the half-cell experiences a load above 0,85 g/cm^2.

15. A half-cell according to claim 12 or 13, wherein the half-cell is planar with a flatness as a volume per area of a half-cell at room temperature, where the volume of the half-cell is the sum of all heights of each grid-cell multiplied by the area of each grid-cell such at all grid-cells in a grid represent the area of the half-cell; and where on a half-cell
    - the volume is below 110 cm^3 per 256 cm^2 when the half-cell experiences no load;
    - the volume is below a linear decreases from 110 cm^3 per 256 cm^2 to 60 cm^3 per 256 cm^2 when the half-cell experiences a load from above 0 g/cm^2 to 0,85 g/cm^2; or
    - the volume is below 60 cm^3 per 256 cm^2 mm when the half-cell experiences a load above 0,85 g/cm^2.

16. A fuel cell stack comprising a plurality full cells, wherein each full cell comprises at least a first half-cell according to any of claim 12 to 15, the first half-cell being of anode type and at least a second half-cell according to any of claim 12 to 15, the second half-cell being of cathode type.

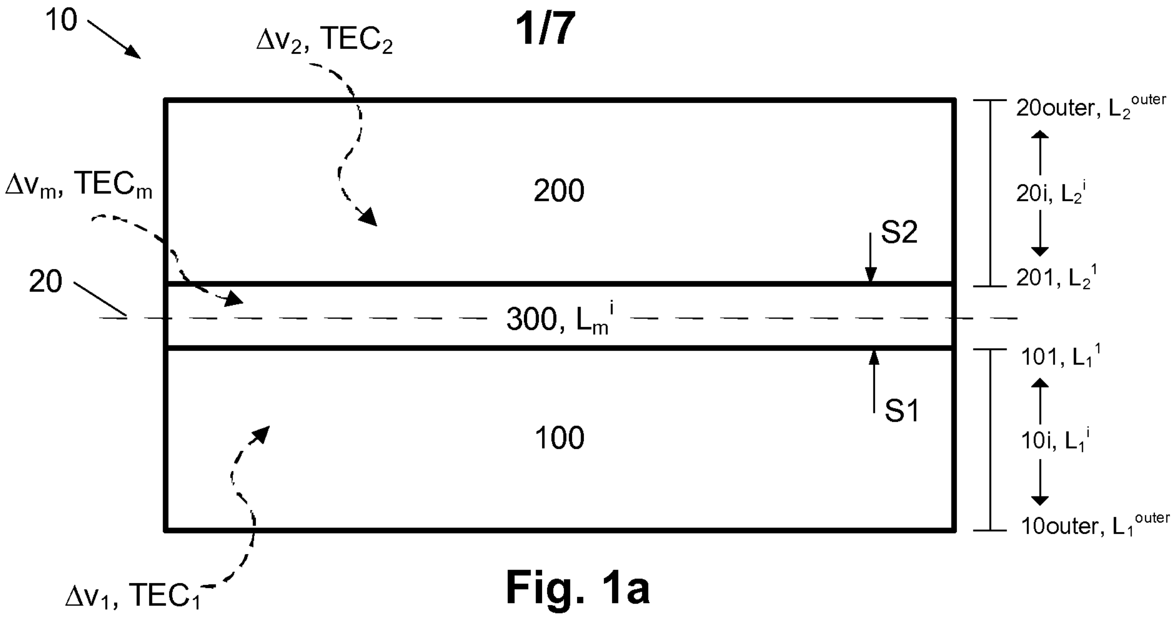


Fig. 1a

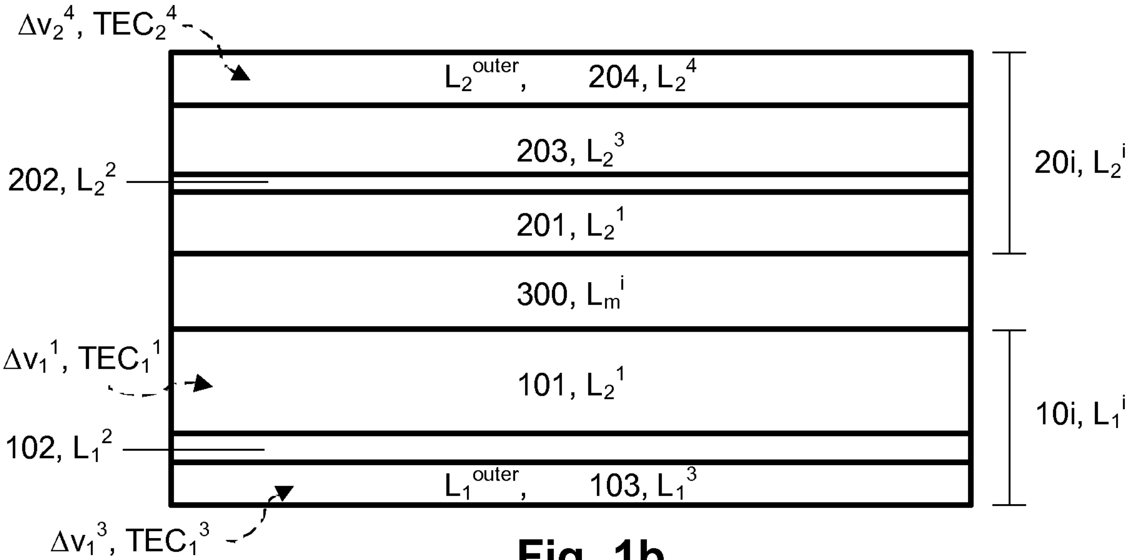


Fig. 1b

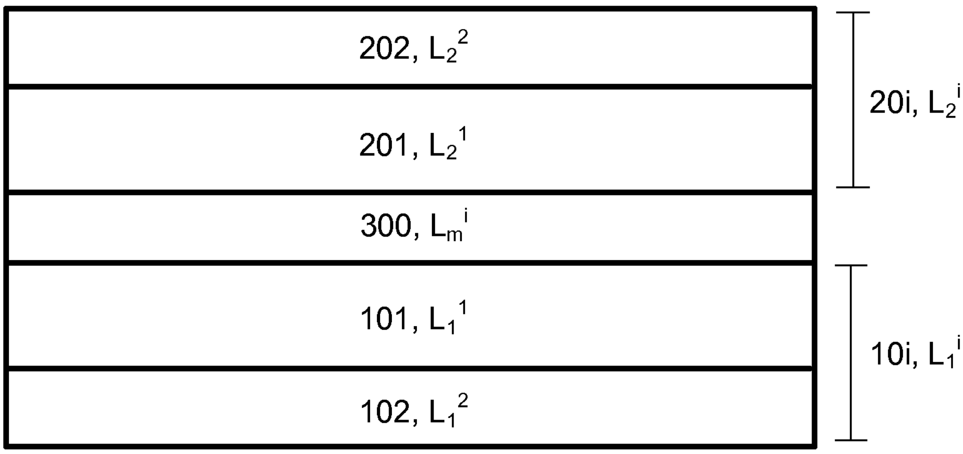


Fig. 1c

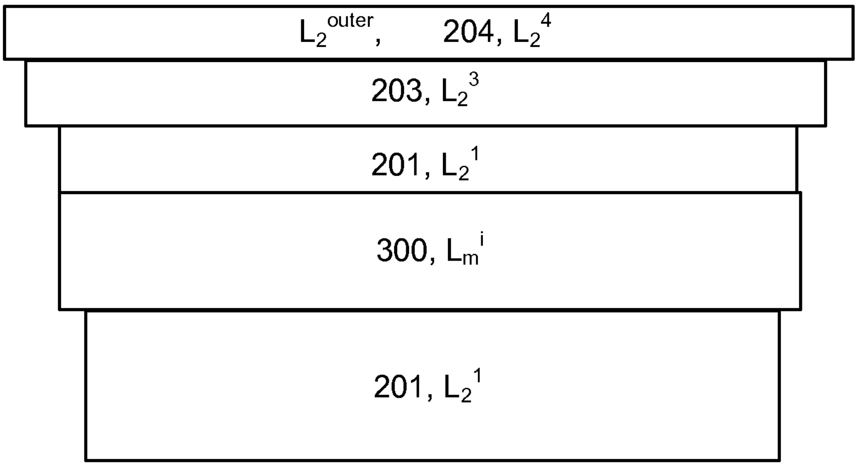


Fig. 2a – prior art

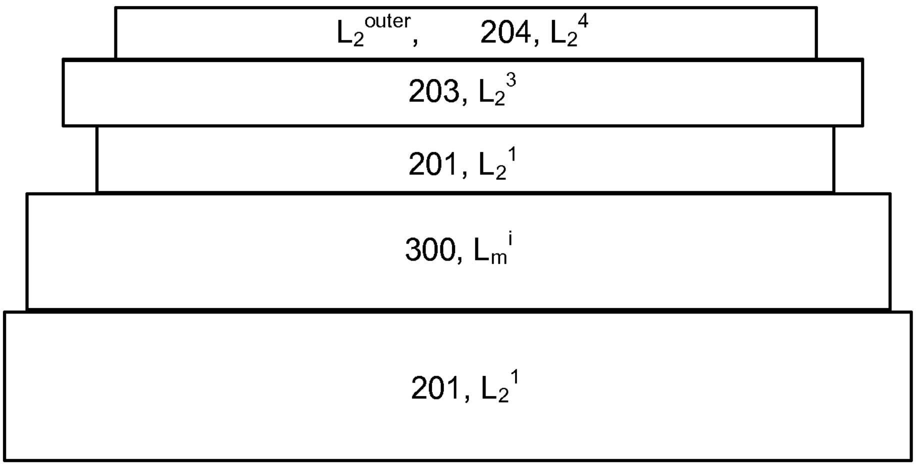


Fig. 2b – prior art

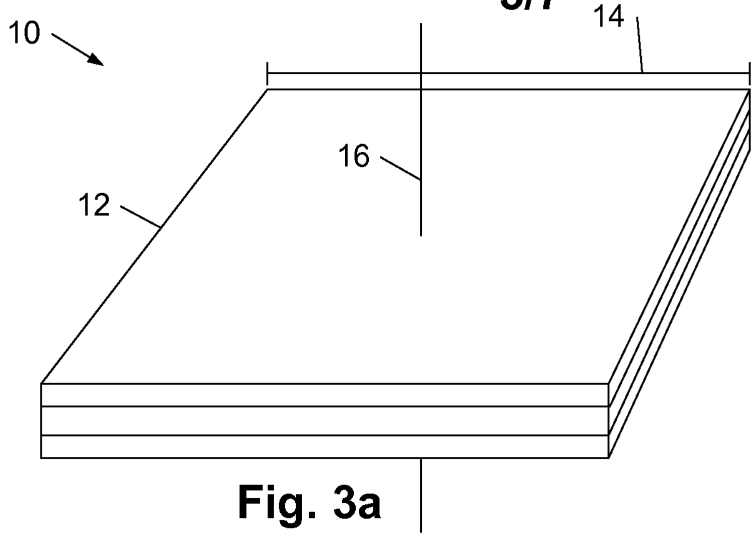


Fig. 3a

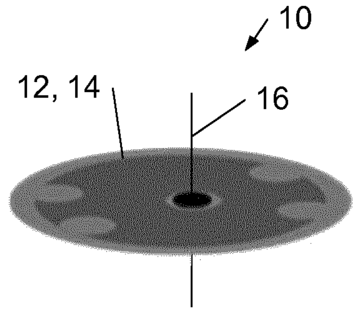


Fig. 3b

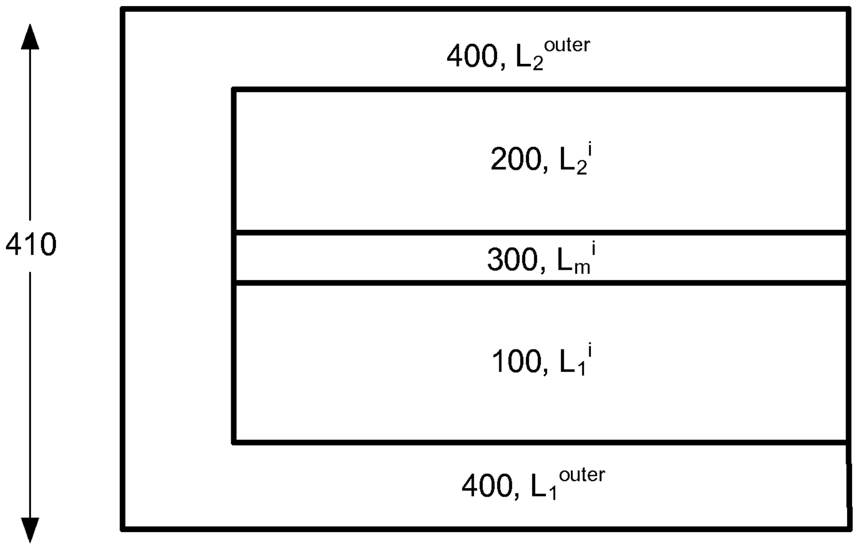


Fig. 4a

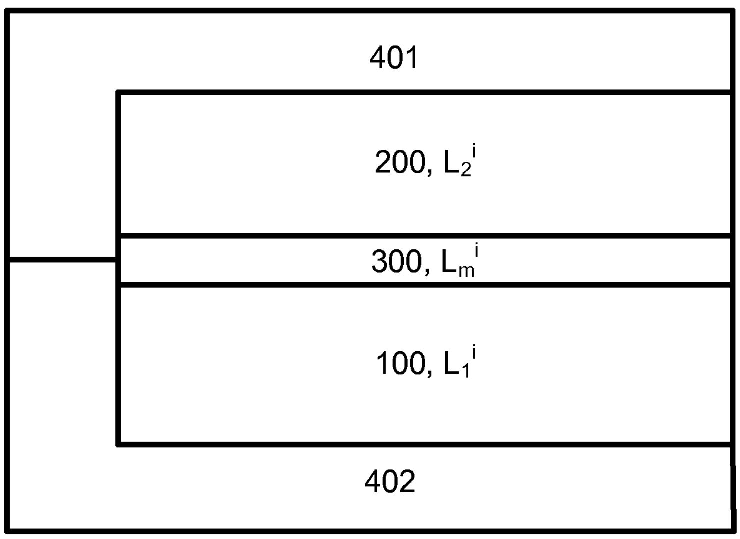
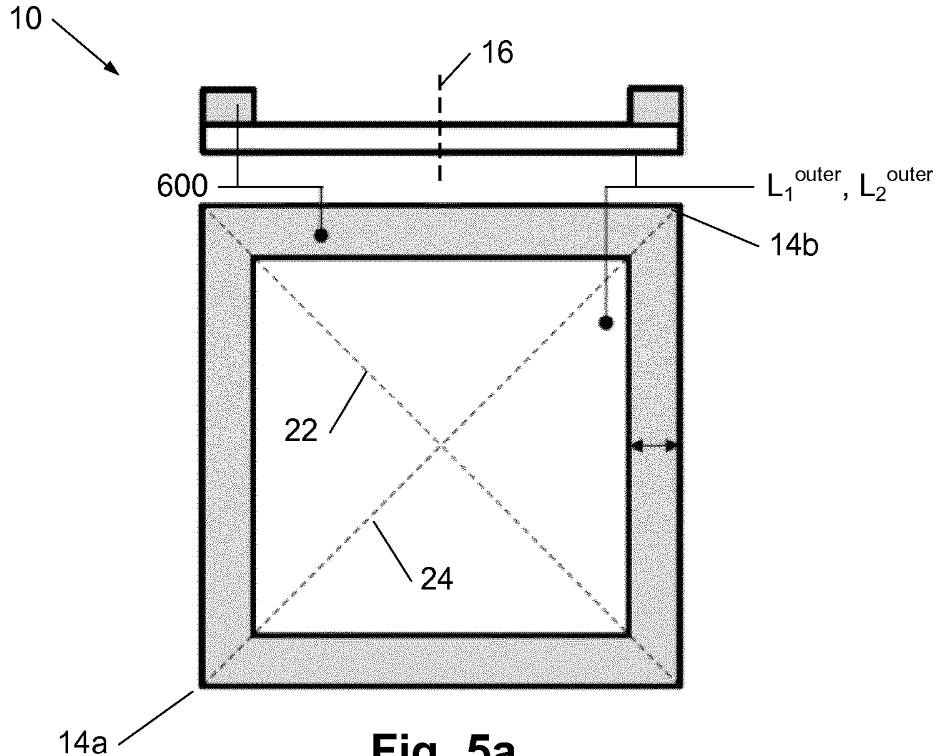
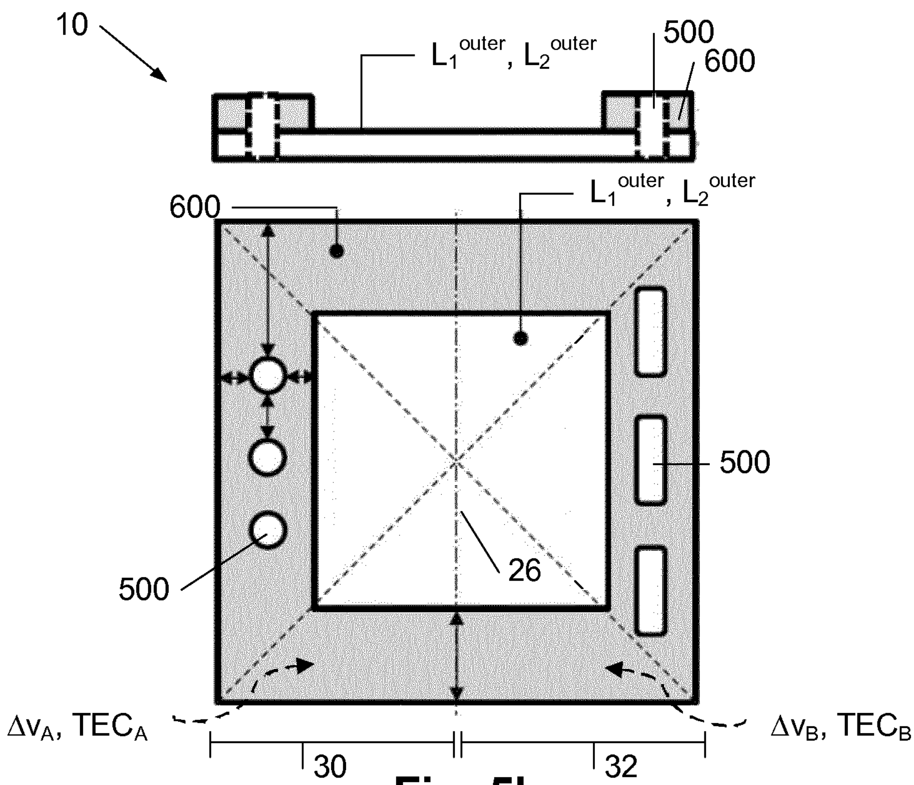


Fig. 4b



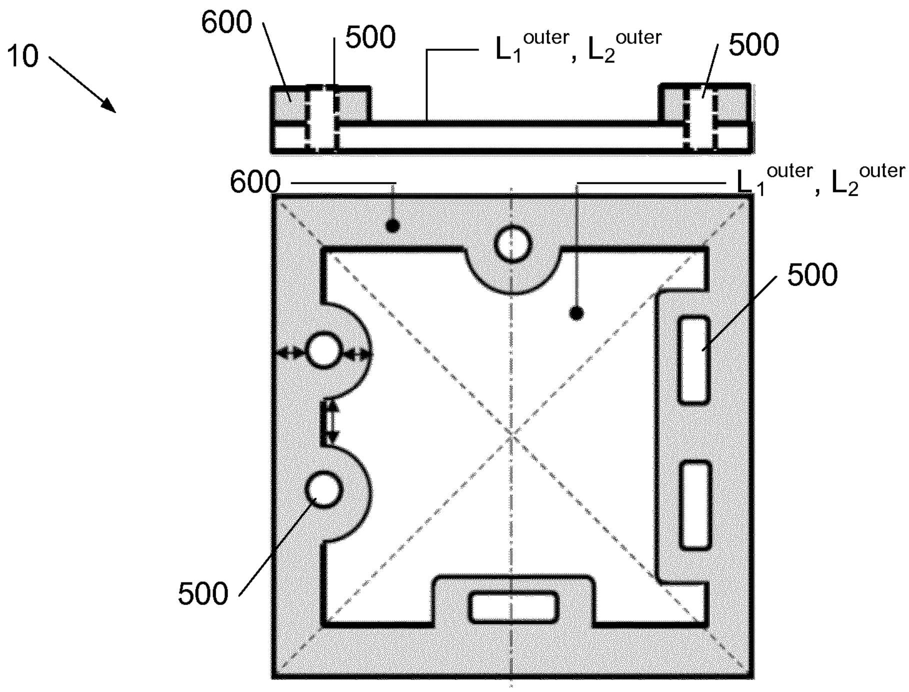
10
16
600
L_1^{outer}, L_2^{outer}
14b
22
24
14a

Fig. 5a



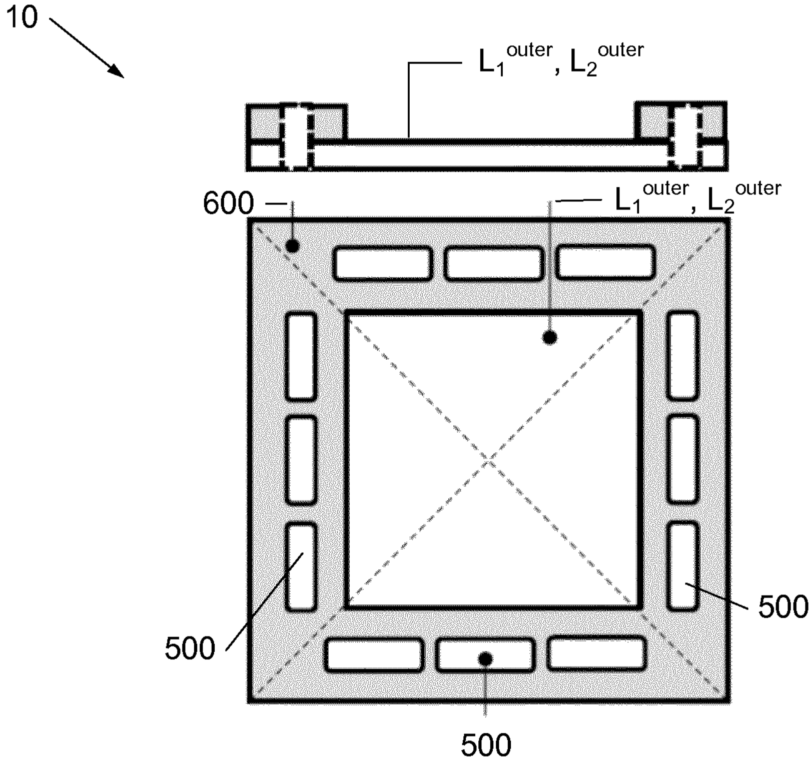
10
L_1^{outer}, L_2^{outer}
500
600
600
L_1^{outer}, L_2^{outer}
500
500
26
Δv_A, TEC_A
Δv_B, TEC_B
30
32

Fig. 5b



10
600
500
L1outer, L2outer
500
600
L1outer, L2outer
500
500

Fig. 5c



10
L1outer, L2outer
600
L1outer, L2outer
500
500
500

Fig. 5d

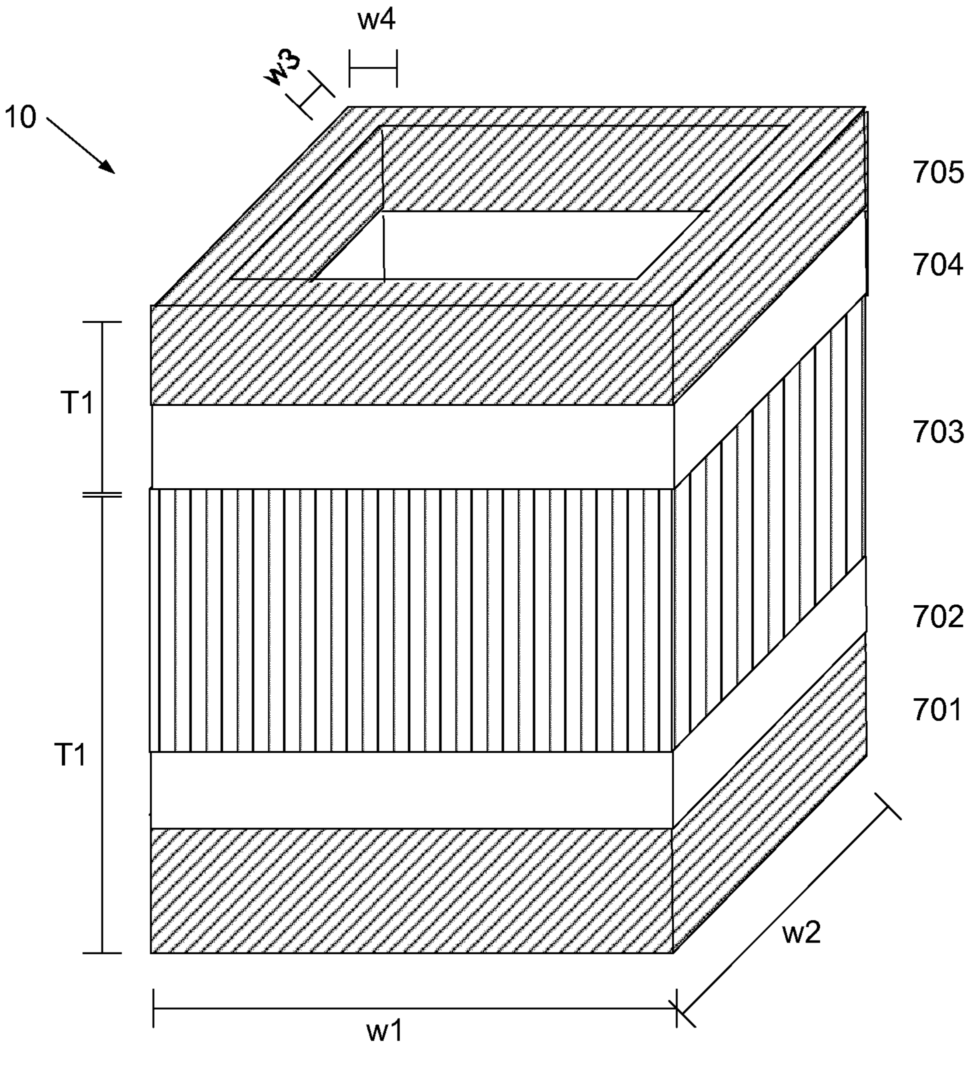


Fig. 5e

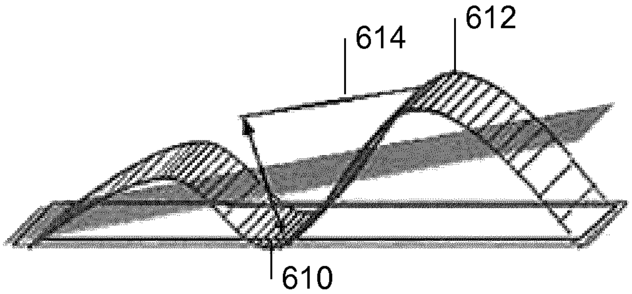


Fig. 6A

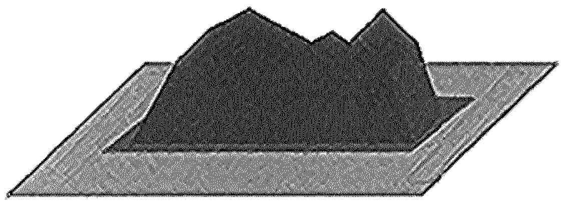


Fig. 6B

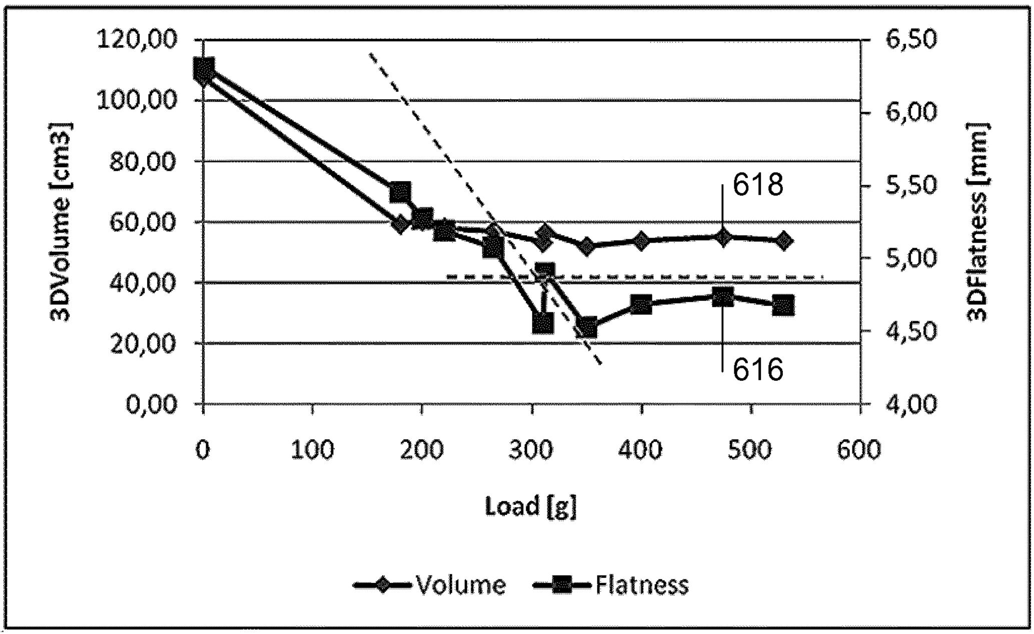


Fig. 6C

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/072599

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M8/12 H01M4/86 H01M4/88
ADD. H01M4/90

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 practicable, search terms used)

EPO-Internal, 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	EP 1 768 208 A2 (KOREA INST SCI & TECH [KR]) 28 March 2007 (2007-03-28)	1,12
Y	paragraph [0025] - paragraph [0031] -----	13
Y	EP 2 045 858 A1 (INST OF NUCLEAR ENERGY RES ATO [TW]) 8 April 2009 (2009-04-08) claim 1 -----	13
A	EP 1 928 049 A1 (UNIV DENMARK TECH DTU [DK]) 4 June 2008 (2008-06-04) paragraph [0048] - paragraph [0050] example 1 -----	1-16
A	WO 2005/122300 A2 (FORSKNINGSCT RISOE [DK]; LARSEN PETER HALVOR [DK]; MOGENSEN MOGENS BJE) 22 December 2005 (2005-12-22) example 1 -----	1-16
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 November 2014	03/12/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Fernandez Morales, N

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/072599

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 031 677 A1 (UNIV DENMARK TECH DTU [DK]) 4 March 2009 (2009-03-04) example 1 -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/072599

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 1768208	A2	28-03-2007	EP 1768208	A2	28-03-2007
			US 2007015045	A1	18-01-2007
EP 2045858	A1	08-04-2009	NONE		
EP 1928049	A1	04-06-2008	AU 2007323291	A1	29-05-2008
			CA 2669811	A1	29-05-2008
			CA 2797177	A1	29-05-2008
			CN 101563805	A	21-10-2009
			CN 103861470	A	18-06-2014
			EP 1928049	A1	04-06-2008
			EP 2084772	A2	05-08-2009
			EP 2701227	A1	26-02-2014
			JP 5219298	B2	26-06-2013
			JP 2010510635	A	02-04-2010
			KR 20090094273	A	04-09-2009
			RU 2009119261	A	27-12-2010
			US 2010062312	A1	11-03-2010
			WO 2008061782	A2	29-05-2008
WO 2005122300	A2	22-12-2005	AU 2005253203	A1	22-12-2005
			CA 2569866	A1	22-12-2005
			CN 1985397	A	20-06-2007
			CN 102013507	A	13-04-2011
			EP 1784888	A2	16-05-2007
			EP 2259373	A1	08-12-2010
			JP 5260052	B2	14-08-2013
			JP 2008502113	A	24-01-2008
			JP 2012069533	A	05-04-2012
			KR 20070038511	A	10-04-2007
			KR 20080105182	A	03-12-2008
			RU 2356132	C2	20-05-2009
			RU 2008152447	A	10-07-2010
			US 2007269701	A1	22-11-2007
			WO 2005122300	A2	22-12-2005
EP 2031677	A1	04-03-2009	AT 528812	T	15-10-2011
			AU 2008291251	A1	05-03-2009
			CA 2697467	A1	05-03-2009
			CN 101796676	A	04-08-2010
			DK 2031677	T3	12-12-2011
			EP 2031677	A1	04-03-2009
			ES 2375407	T3	29-02-2012
			JP 5430009	B2	26-02-2014
			JP 2010537390	A	02-12-2010
			KR 20100072229	A	30-06-2010
			RU 2010105243	A	10-10-2011
			US 2011198216	A1	18-08-2011
			WO 2009027100	A1	05-03-2009