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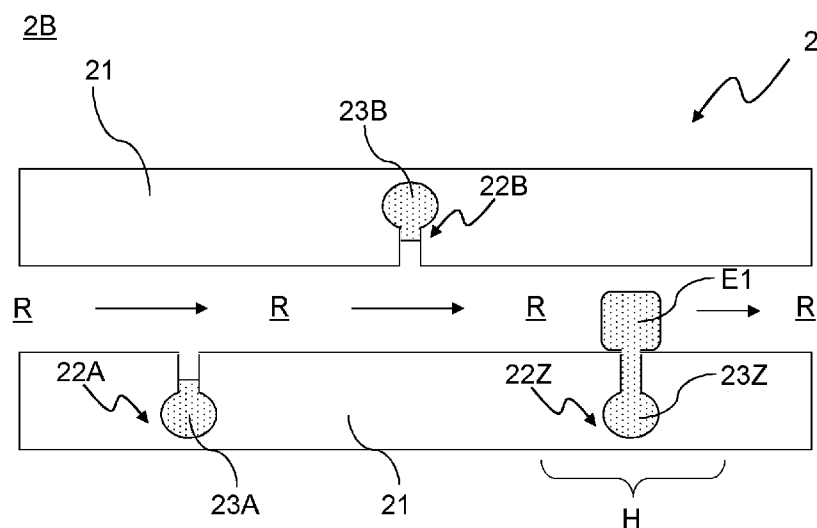


FIGURE 2B

(57) Abstract: An electrochemical energy converter, the electrochemical energy converter comprises a channel (2) for the passage of fluid (R), a thermally expansive body (23A, 23B...23Z) located to at least partially occlude the channel (2) when the thermally expansive body (23A, 23B...23Z) is exposed to or reaches a critical temperature.

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THERMAL MANAGEMENT

This invention relates generally to the thermal management of devices for energy conversion. More specifically, although not exclusively, this invention relates to devices
5 for energy conversion comprising thermal regulation means, methods of fabricating the same, and methods of thermally regulating devices for energy conversion.

The global demand for energy is ever-increasing. However, the use of large amounts of non-renewable energy sources such as fossil fuels is not sustainable, and in addition,
10 causes significant environmental pollution. Therefore, there is an urgent need for sustainable and non-polluting sources of energy, particularly for conversion to electricity, to meet present and future global energy needs.

Fuel cells are an increasingly attractive energy conversion technology. These are
15 electrochemical cells that convert chemical energy from a fuel source into electrical energy. In a hydrogen fuel cell, hydrogen reacts with oxygen to generate electricity and produce water as the waste product. This process is known to be highly efficient and has low polluting emissions.

Fuel cells comprising a proton exchange membrane (PEM), which are known as (PEMFCs), represent a promising alternative solution for energy conversion to electrically
20 power, for example, automotive vehicles and portable devices. PEMFCs have several advantages including high power density, low operating temperature, flexible power scale, and rapid start-up and shutdown. PEMFCs use a proton conducting polymer membrane, e.g. a Nafion® membrane, as an electrolyte. The PEM separates the anode and cathode
25 of the fuel cell. At the anode side, hydrogen diffuses to the anode catalyst where it dissociates into protons and electrons. The electrons move via an external circuit to the cathode. The protons transfer through the PEM to cathode where they react with electrons and oxidant, e.g. oxygen, to produce water. As the PEM is electrically insulative,
30 the electrons travel through the external circuit to generate electricity.

The extensive commercialisation of PEMFCs has been hindered thus far by several barriers. For example, it has been found that PEMFCs have poor durability. One of the main issues that has a strong influence on PEM fuel cell durability is thermal
35 management.

The favourable working temperature for the most commonly used PEM, *i.e.* Nafion®, is usually between 70 to 80°C. It is optimal for the fuel cell to be kept within this narrow temperature range during its operation. Operating temperatures higher than 80°C can result in serious degradation of the Nafion®, whereas operating temperatures lower than 70°C may result in a low fuel cell performance. The narrow range of operating temperature renders the design of a cooling system very challenging, which is required to both prevent overheating but enable the fuel cell to function at an optimal temperature.

The thermal energy in PEMFCs is mainly generated by the electrochemical reactions. These are often non-uniform throughout the entire fuel cell area due to the uneven distribution of the reactants (H₂ and O₂). In addition, the fuel cell usually contains many different components with varying thermal properties, such as different specific heat capacities, which are adjacent one another. This ensures a complex heat transfer process through the fuel cell, which can lead to localised areas of high temperature or 'hot spots', causing damage and degradation to the components of the fuel cell, and, in particular, to the membrane, *e.g.* the Nafion® membrane.

Although significant advances have been made in the research and development of thermal management strategies in past decades, it remains a challenge in practical operations to achieve a uniform and accurate temperature distribution throughout the entire fuel cell, especially throughout the cell stacks.

The focus to date has been to use active thermal management strategies, for example, using cooling coils and heat exchangers. These are cumbersome and/or complex from an engineering perspective and require a detailed map of thermal performance of the fuel cell to effectively deal with 'hot spots'.

It is therefore a first non-exclusive object of the invention to provide a means to thermally manage, *e.g.* passively and/or self-manage, an energy converter, *e.g.* a fuel cell, that provides protection from overheating, such that the components of the energy converter are not damaged by spikes in temperature and/or hot spots, whilst enabling the energy converter to function at or near its optimal operating temperature for maximum efficiency.

Accordingly, a first aspect of the invention provides an electrochemical energy converter, the electrochemical energy converter comprising a channel for the passage of fluid and a

thermally expansive body located to at least partially occlude the channel when the thermally expansive body is exposed to or reaches a pre-defined and/or critical temperature.

- 5 The thermally expansive body has a first volume below the critical temperature, and a second, larger volume at or above the critical temperature. In embodiments, the expansion of the thermally expansive body from the first volume to the second volume may be reversible.
- 10 It has been surprisingly found that the damage caused by localised increases in temperature in the channels of an electrochemical energy converter during operation may be mitigated with the provision of a thermally expansive body located within or adjacent the channel for the passage of fluid. In use, the thermally expansive body has a first, initial, volume, which expands to a second, larger volume upon exposure to a pre-defined
- 15 and/or critical temperature, to at least partially occlude the channel for the passage of fluid. In this way, the flow of fluids, e.g. reactants, through the electrochemical energy converter is at least partially or completely occluded, such that the rate of reaction is reduced thereby decreasing the amount of thermal energy generated. Once the temperature drops below the critical temperature, the thermally expansive body contracts
- 20 to its initial volume such that the channel is open, and the reaction within the electrochemical energy converter may continue at an optimum temperature. In this manner, homeostatic or self-regulating and passive temperature control is achievable.

Advantageously, this means that it is possible to significantly simplify the design of cooling

25 system, which may otherwise require complex engineering to prevent the local over-heating to avoid 'hot spots'.

The thermally expansive body may be a composite material, i.e. a material comprising two or more materials with different chemical or physical properties.

30

The thermally expansive body may be a temperature sensitive composite material (TSCM). The temperature sensitive composite material may undergo an abrupt physical change in response to a small change in local environmental temperature, for example at a critical point.

35

The thermally expansive body may exhibit a step-change expansion upon exposure to at least the critical temperature, by step-change we mean that the rate of expansion (rate of change of volume V) with respect to temperature (dV/dT) increases markedly at a certain temperature, for example at the critical temperature. This is in contrast to a thermally expansive body exhibiting a gradual or linear expansion upon exposure to increasing temperature. In embodiments, it may be preferable that the thermally expansive body has a step-change expansion upon exposure to the critical temperature such that the response time to at least partially occlude the channel within the energy converter is relatively short, e.g. less than a second, such that efficient and effective thermal management of the energy converter may be achieved.

The thermally expansive body may comprise a phase change material (PCM), that is, a material that changes phase upon exposure to a phase change temperature.

The amount of expansion undergone by the PCM may be affected by the density difference between the two phase states and the mass of the phase change material. The response time may be affected by one or more of the latent heat, thermal conductivity and heat flux from the reaction.

Preferably, the phase change material comprises a material that changes from a liquid phase to a vapour phase upon exposure to a phase change temperature. This type of phase change material is generally more expansive in comparison to materials that change from a solid phase to a liquid phase upon exposure to a phase change temperature. In other embodiments of the invention, it may be preferred to utilise a solid to liquid phase change material.

The phase change material may be responsible for a step-change expansion of the thermally expansive body upon exposure to a critical temperature. For example, if the phase change material is a liquid then a step-change expansion in volume may be observed at the boiling point of the liquid as the liquid rapidly expands to form the vapour phase. The step-change expansion in volume may be reversible such that the phase change material condenses from a vapour phase to a liquid phase at a temperature below its boiling point, i.e. the phase change temperature.

The phase change material may comprise a hydrocarbon. For example, the phase change material may comprise a hydrocarbon that is liquid at a lower temperature, for example at room temperature or at 25 °C, e.g. pentane, hexane, heptane, hexene, cyclohexene, benzene, heptene, methanol, ethanol, acetone, tetrachloromethane, ethyl acetate, and so on. The phase change material will be selected so as to exhibit a phase change at the appropriate required temperature to allow the thermally expansive body to expand at the critical temperature.

In embodiments, the phase change material may be encapsulated, e.g. microencapsulated, within a shell to form a capsule, e.g. a microcapsule.

In embodiments, the microcapsules each comprise an outer shell that is between 0.1 to 3.0 microns thick, e.g. from one of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0, and 2.5, microns thick, to any one of 3.0, 2.5, 2.0, 1.5, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2 microns thick. In embodiments, the outer shell of each microcapsule is approximately 1 micron thick.

In embodiments, the microcapsules each have a diameter of less than 10 microns, e.g. less than any one of 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0, 1.0, or 0.5 microns.

The outer shell of the microcapsules may be fabricated from and/or comprise a polymer, for example, formaldehyde, e.g. urea formaldehyde. Additionally or alternatively, the outer shell of the microcapsule may be fabricated from and/or comprise a polycarbonate, methyl methacrylate, butyl acrylate, and/or butyl methacrylate.

The phase change material may be located within a matrix material. The matrix material may comprise an elastomer, e.g. silicone rubber, latex, and/or gelatine. Any matrix material with suitable properties may be used, e.g. matrix materials that exhibit suitable flexibility, resistance to fatigue and/or degradation, and/or resistance to corrosion.

Advantageously, the matrix material, e.g. the elastomer, may be selected such that it expands with the expansion, i.e. phase change, of a phase change material, and contracts with the contraction, i.e. phase change, of the phase change material. Preferably, the matrix material exhibits a relatively high decomposing point and high

flexibility to accommodate the sudden expansion and shrink originating from the phase change material.

5 The matrix material, e.g. the elastomer, may be, and preferably is, impermeable to the phase change material. The impermeability of the matrix material to the phase change material means that the matrix material is able to seal in the phase change material, such that it cannot leak out or evaporate.

10 In embodiments, the thermally expansive body may comprise a composite material comprising a homogeneous phase of microencapsulated phase change material located within an elastomer.

The thermally expansive body may be located within a cavity formed in an inner wall of the channel. For example, the channel for the passage of fluid may comprise a rebate,
15 hollow or empty space in which the thermally expansive body is located. The channel may comprise more than one cavity each for the location of a thermally expansive body.

Advantageously, the channel may comprise multiple cavities, one or more of each comprising a thermally expansive body. By using this approach, the temperature may be
20 regulated within the electrochemical energy converter in a targeted manner such that localised temperature spikes, e.g. hot spots, that may cause localised damage to the energy converter are minimised by targeting the location within the channel that requires passive thermal management. Moreover, the locations within the energy converter that are most likely to overheat may be targeted with the provision of a greater quantity and/or
25 frequency of thermally expansive bodies, such that the temperature is controlled and damage is prevented.

Additionally or alternatively, the channel may comprise multiple points at which thermally expansive bodies are located, for example plural cavities each containing a thermally
30 expansive body. In this fashion, the channel will have a self-regulating character, insofar as only those thermally expansive bodies which are exposed to sufficient temperature will expand, whereas those exposed to insufficient temperatures will not expand. In such a way, it is not necessary to generate a comprehensive map of thermal performance of the entire channel because the activated thermally expansive bodies will self-regulate the
35 flow, and hence the reaction rate, and hence the generated thermal energy.

The cavities may be any suitable size. In an embodiment, each cavity may have a volume of 1 mm³, e.g. 1mm*1mm*1mm, to 27 mm³, e.g. 3mm*3mm*3mm. For example, each cavity may have a volume between any one of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, and 26 mm³ to any one of 27, 26, 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, or 2 mm³.

The cavities may be located at any suitable frequency within the channel. For example, the channel may comprise one cavity per 1 to 2 cm, e.g. one cavity per 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0.

Additionally or alternatively, the thermally expansive body may be located either partially or completely concentrically about the channel for the passage of fluid and/or contained within an inner wall. The inner wall may comprise one or more apertures that allow the thermally expansive body to expand into the channel upon exposure to the critical temperature such that the thermally expansive body at least partially occludes the channel.

In an embodiment, a flow volume is defined within the channel. The flow volume may be defined, at least in part, by the internal surfaces of the channel. Alternatively or additionally, the flow volume may be defined, at least in part, by the thermally expansive body, for example when the thermally expansive body is located either partially or concentrically about the channel. The flow volume preferably extends across the geometrical centre of the channel. For example, where the channel is elongate, in cross section the flow volume will encompass the geometrical centre of the channel. The thermally expansive body may, in a first non-expanded condition, be located outside of the flow volume. Advantageously, this ensures minimum disruption of the flow through the channel when the thermally-expansive body is in its first condition and/or avoids or mitigates the need to shape the channel (e.g. to widen it) to accommodate the thermally expansive body.

In embodiments, the critical temperature may be between 60 to 150 °C, e.g. between 60 to 90 °C, or between 65 to 85 °C. The critical temperature may be between any one of 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, or 145 °C to any

one of 150, 145, 140, 135, 130, 125, 120, 115, 110, 105, 100, 95, 90, 85, 80, 75, 70, or 65 °C.

Advantageously, the physical properties of the thermally expansive body (e.g. the phase
5 change temperature of the phase change material), and hence the critical temperature, may be selected depending on the optimum operating temperature of the electrochemical energy converter.

The critical temperature may be a temperature that is at, or slightly below the optimal
10 operating temperature of the energy converter. In embodiments, there may be one or more insulative materials located to separate the thermally expansive body from the local environment of the channel. For example, the thermally expansive body may be located within an insulative material for location in the channel of the energy converter, such that the temperature felt by the thermally expansive body is slightly lower than the temperature
15 of the local environment within the channel. In this case, it is preferable that the critical temperature of the thermally expansive body is slightly below the optimum operating temperature of the energy converter to allow for the effect of the insulation that is located between the thermally expansive body and the channel, which would act to prevent or delay the thermally expansive body from reaching the temperature of the local
20 environment within the channel. For example, the matrix material may be thermally insulative and thus the temperature experienced by the, e.g. phase change material may be lower than the actual temperature in the channel.

In a preferred embodiment, the critical temperature is a temperature that is close to, or
25 slightly below, the optimal operating temperature of the energy converter, such that, at a temperature above the optimal operating temperature of the energy converter, the thermally expansive body expands to at least partially occlude the channel and to restrict the flow of reactants and/or products. Therefore, passive control of the generation of thermal energy within the energy converter is achieved. This prevents the energy
30 converter from generating an excess of thermal energy and as such, the risk of the energy converter overheating is reduced, and the risk to the damage of components of the energy converter is reduced.

For example, the energy converter may be one type of fuel cell that has an optimum
35 operating temperature of 70 °C, and thus a suitable critical temperature may be 69 °C to

prevent localised overheating but to enable the fuel cell to function at its optimum temperature.

In embodiments, upon cooling, the localised temperature of the energy converter decreases below the critical temperature, which may cause the thermally expansive body to return to its original volume within the channel. In this state, the flow rate of fluid within the channel is recovered to its original rate, and the energy converter is able to continue to function at an optimum temperature.

The channel for the passage of a fluid may be a microchannel, e.g. a channel with a hydraulic diameter that is less than or equal to 5 mm. The channel for the passage of a fluid may have a hydraulic diameter of between 5.0 mm to 0.1 mm, for example, between any one of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 4.5 mm to any one of 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, or 0.2 mm.

In embodiments, the fluid may be a fuel, i.e. the channel may be a passage for a fuel. The fuel may be hydrogen, e.g. hydrogen gas. Alternatively, the channel may be a passage for another, different type of reactant, e.g. oxygen gas. Additionally or alternatively, the channel may be a passage for the products, e.g. a waste product, of the energy conversion reaction, e.g. water. The channel may comprise multiple components, e.g. a mixture of unreacted reactants, and products of a fuel cell.

The energy converter may be a hydrogen fuel cell for the conversion of hydrogen and oxygen to water for the conversion of chemical energy to electrical energy.

In alternative embodiments, the energy converter may be a metal air battery, e.g. lithium air battery.

A further aspect of the invention provides a method of regulating the temperature of an electrochemical energy converter during an energy conversion reaction, the method comprising locating a thermally expansive body within a channel for the passage of fluid, such that the thermally expansive body expands from a first volume to a second larger volume to at least partially occlude the channel when the thermally expansive body is exposed to a temperature that is at or above a critical temperature, and the thermally

expansive body contracts from the second larger volume to the first volume when the thermally expansive body is exposed to a temperature that is below the critical temperature.

- 5 A yet further aspect of the invention provides a method of fabricating an energy converter having a self-regulating temperature control means, the method comprising providing a phase change material, encapsulating the phase change material in microcapsules, locating the microcapsules in a matrix material to form a thermally expansive body, and locating the thermally expansive body within a channel of the energy converter for the
10 passage of fluid.

The method may further comprise locating the thermally expansive body in a cavity within an inner wall of the channel.

- 15 The cavities may be fabricated using any technique known to the skilled person. For example, the cavities may be fabricated by machining.

The thermally expansive body may be located within a cavity by any suitable means. For example, the thermally expansive body may be located within a cavity by injection.

20

- A yet further aspect of the invention provides a method of fabricating a thermally expansive body for locating in an electrochemical energy converter, the method comprising providing a phase change material, e.g. heptane, encapsulating the phase change material, e.g. heptane in a polymer, e.g. urea formaldehyde, to form
25 microcapsules, and locating the microcapsules in a matrix material to form a thermally expansive body.

- Encapsulation of the phase change material, e.g. heptane in a polymer, e.g. urea formaldehyde, to form microcapsules, may further comprise a polymerisation process
30 comprising the use of one or more of xanthan gum and/or methyl cellulose as emulsifiers.

It has been surprisingly found that xanthan gum and/or methyl cellulose may be used as emulsifiers in a polymerisation process to encapsulate a phase change material, e.g. heptane, in a polymer, e.g. urea formaldehyde, to produce microcapsules for use in a

thermally expansive body. This is in contrast to known emulsifiers for polymerisation processes for microencapsulation.

Advantageously, the microcapsules provide a means to fabricate the thermally expansive body, according to certain embodiments of the invention. The microcapsules enable the phase change material to be located within the matrix material, e.g. the elastomer, in the method of fabricating a thermally expansive body for location within an energy converter. In use of the energy converter containing the thermally expansive body of said method, the microcapsules containing the phase change material may fracture upon expansion of the phase change material at the critical temperature, meaning that the phase change material is no longer encapsulated by the microcapsules. However, if the matrix material is impermeable then the phase change material will be sealed in and unable to leak out. In this way, the thermally expansive body may at least partially occlude a channel within the energy converter. Upon exposure to a temperature below the critical temperature, the phase change material may contract, e.g. condense, back to its original volume such that the channel will no longer be at least partially occluded. Afterwards, the thermally expansive body is then able to function in a like-manner upon exposure to the critical temperature, but without the phase change material needing to fracture the microcapsules.

Alternatively, it may be possible to provide free particles of the phase change material and locate them into a matrix material. The matrix material may then be cured or set rapidly to seal the phase change material within the matrix material.

Within the scope of this application it is expressly intended that the various aspects, embodiments, examples and alternatives set out in the preceding paragraphs, in the claims and/or in the following description and drawings, and in particular the individual features thereof, may be taken independently or in any combination. That is, all embodiments and/or features of any embodiment can be combined in any way and/or combination, unless such features are incompatible. For the avoidance of doubt, the terms “may”, “and/or”, “e.g.”, “for example” and any similar term as used herein should be interpreted as non-limiting such that any feature so-described need not be present. Indeed, any combination of optional features is expressly envisaged without departing from the scope of the invention, whether or not these are expressly claimed. The applicant reserves the right to change any originally filed claim or file any new claim

accordingly, including the right to amend any originally filed claim to depend from and/or incorporate any feature of any other claim although not originally claimed in that manner.

Embodiments of the invention will now be described by way of example only with
5 reference to the accompanying drawings in which:

Figure 1 is a PEM fuel cell of the prior art; and

Figure 2A is a cross-section of a channel located within an energy converter
comprising a thermally expansive material at an optimum operating temperature,
10 according to a first embodiment of the invention;

Figure 2B is the channel of Figure 2A showing an area of localised overheating,
according to a first embodiment of the invention;

Figure 2C is the channel of Figure 2A showing an area of localised overheating,
according to a second embodiment of the invention;

15 Figure 3A is a channel located within an energy converter comprising a thermally
expansive material at an optimum operating temperature, according to a third
embodiment of the invention;

Figure 3B is the channel of Figure 3A showing an area of localised overheating,
according to a third embodiment of the invention;

20 Figure 4 is a method of fabricating a thermally expansive material for use in a
channel of an energy converter, according to a further embodiment of the invention.

Referring now to Figure 1, there is shown a proton exchange membrane (PEM) fuel cell 1
of the prior art. The PEM fuel cell 1 comprises an anode 11, a cathode 12, a proton
25 exchange membrane 13, a fuel inlet 14A, a fuel outlet 14B, an air inlet 15A, and an air
outlet 15B, and an external circuit 16.

The proton exchange membrane 13 is located between the anode 11 and the cathode 12.
The fuel inlet 14A and the fuel outlet 14B are located adjacent the anode 11. The air inlet
30 15A and the air outlet 15B are located adjacent the cathode 12.

In this prior art example, the proton exchange membrane 13 comprises e.g. Nafion®,
which is material known to the skilled person for use in a PEM fuel cell 1.

In use, hydrogen (H_2) enters the PEM fuel cell 1 via the fuel inlet 14A. At the anode 11, the hydrogen (H_2) is catalytically split into protons (H^+) and electrons (e^-). The proton exchange membrane 13 is permeable to protons (H^+), which enables the protons (H^+) to travel from the anode 11, through the proton exchange membrane 13, to the cathode 12.

5 The proton exchange membrane 13 is electrically insulative and as such, is impermeable to electrons (e^-). The electrons (e^-) flow along an external circuit 16 to the cathode 12. Oxygen (O_2) enters the PEM fuel cell 1 via the air inlet 15A. At the cathode 12, the oxygen (O_2) reacts with the protons (H^+), which have travelled through the proton exchange membrane 13 to the cathode 12, to generate water (H_2O).

10 Therefore, energy from hydrogen (H_2) fuel is converted into electricity through the electrochemical reaction of hydrogen (H_2) with oxygen (O_2).

The reactants, i.e. hydrogen and oxygen, and the products, i.e. water, of the PEM fuel cell
15 1, may enter and exit the energy converter via microchannels.

The optimal operating temperatures of PEM fuel cells, e.g. 1, is approximately 50 to 80 °C. The proton exchange membrane 13, i.e. Nafion®, is susceptible to damage at temperatures higher than 80 °C.

20 Referring now to Figure 2A there is shown a cross-sectional view of a section of a channel 2 of an energy converter (not shown) according to a first embodiment of the invention. The channel 2 is shown in state 2A, at an optimum temperature for operation of the energy converter.

25 The energy converter (not shown) comprising the channel 2 may be a fuel cell, e.g. fuel cell 1 shown in Figure 1.

30 The channel 2 comprises a wall 21, which defines a flow path F through which the reactant R may travel. The direction of flow of the flow path F is indicated by the arrows.

In embodiments, the reactant R may be, for example, hydrogen in a fuel cell, e.g. fuel cell 1 of Figure 1. In alternative embodiments, R need not be a reactant and instead may be a product, for example, water in a fuel cell, e.g. fuel cell 1 of Figure 1.

The channel 2 further comprises a plurality of cavities 22A, 22B, ...22n, which are located within recesses of the wall 21 of the channel 2. In this embodiment, there is shown three cavities 22A, 22B, and 22Z. However, it is to be understood that any number of cavities may be located within the channel 2 at any suitable spacing from one another.

5

Each cavity 22A, 22B, ...22Z contains a thermally expansive material 23A, 23B, ...23Z.

The thermally expansive material 23A, 23B, ...23Z is selected to have a critical temperature that is at, slightly below or slightly above the optimum operating temperature of the energy converter, such that, in use it expands upon exposure to the critical temperature to prevent localised overheating within the energy converter. It will be appreciated that the cavities 22A, 22B, 22n (and thus the thermally expansive material 23A, 23B,...23Z) are located away from the geometrical centre of the channel and so, in a first non-expanded state as shown, the thermally expansive material does not interfere with, or only minimally interferes with, flow of material along the channel 2.

15

For example, if the energy converter is the fuel cell 1 of Figure 1, then the optimum operating temperature may be 75°C, and consequently, a thermally expansive material may be selected that has a critical temperature of, say, 73, 74, 75, 76 or 77 °C, such that below at or above the optimum operating temperature, the rate of reaction and therefore the rate of thermal energy generation is reduced by the invention, but above, at or below the critical temperature, the fuel cell 1 may continue to function at an efficient rate.

20

Referring also to Figure 2B, there is shown the channel 2 of Figure 2A. The channel 2 is shown in state 2B, showing an area of localised overheating.

25

In state 2B, there is shown a localised area H that is at or above the critical temperature of the thermally expansive material 23Z within the wall 21 of the channel 2. The increased temperature may be caused by a localised exothermic reaction between the reactants R, which generates thermal energy at a specific location, e.g. the localised area H.

30

The thermally expansive material 23Z expands or 'swells' in response to reaching the critical temperature, which is above the normal operating temperature of the channel 2, such that the thermally expansive material 23Z comprises an expanded portion E1, which

extends into the flow path F of the channel 2, such that the diameter of the flow path F is narrowed or partially occluded.

As a consequence, the reactant R is able to travel through the channel 2 at a reduced
5 flow rate, which restricts the quantity of reactant that is able to react at a location further along the channel 2. This controls the rate of reaction and hence controls the generation of thermal energy within the energy converter to prevent overheating.

Referring also to Figure 2C, there is shown a channel 2' in state 2C, according to a
10 second embodiment of the invention. The features of channel 2' are similar to the embodiment of Figures 2A and 2B, and like references are designated with a prime (') and will not be described further.

In this embodiment, the cavity 22Z' contains a larger amount of thermally expansive
15 material 23Z' than 23Z of Figure 2A,2B.

In state 2C, there is shown a localised area H' that is at or above the critical temperature of the thermally expansive material 23Z' within the wall 21' of the channel 2'.

20 In this embodiment, the thermally expansive material 23Z' has expanded to create the expanded region E2. In contrast to the embodiment of the invention shown in Figure 2B, the expanded region E2 extends across the entire flow path F of the channel 2 such that the channel is completely occluded. The reactant R is unable to flow along the flow path F' through the channel 2.

25

In this state 2C, no further reaction with reactant R may take place beyond the expanded region E2 of the thermally expansive material 23Z' of the cavity 22' within the channel 2'. This prevents the generation of further thermal energy at the localised area H', and therefore the localised area H' cools to a temperature that is below that of the critical
30 temperature of the thermally expansive material 23Z' to prevent overheating.

Advantageously, the expansion of the thermally expansive material 23Z, 23Z' in both embodiments is reversible such that, upon cooling, the expanded region E1 or E2 retracts or 'shrinks' back into the cavity 22Z, 22Z' to enable the flow path F, F' to return to its
35 maximum capacity.

If localised overheating is experienced along the channel 2 at a different area to the localised area H, H' then the thermally expansive material 23A, 23B of Figure 2B, and 23A', 23B' of Figure 2C, and so on, may function in a similar fashion to that shown in
5 Figures 2B, 2C to restrict or completely occlude the flow path F of the channel 2, 2' at a different location.

Advantageously, the number and/or frequency and/or spacing of the cavities 22A, 22B, ...22Z, and/or 22A', 22B', ...22Z may be selected depending on the application and the
10 operating temperature of the energy converter.

Referring now to Figure 3A, there is shown a cross-sectional view of a section of a channel 3 of an energy converter (not shown) according to a second embodiment of the invention. The channel 3 is shown in state 3A, which is at or below the optimum operating
15 temperature of the energy converter.

The channel 3 comprises a wall 31, which defines a flow path F'' through which the reactant R'' may travel. The direction of flow of the flow path F'' is indicated by the arrows.

20 The channel 3 further comprises a thermally expansive material 32 and an inner wall 33. The inner wall 33 comprises a plurality of apertures 34A, 34B, ...34Z.

The thermally expansive material 32 is located on a portion of the wall 31. The thermally expansive material 32 is contained by the inner wall 33 such that it does not contact the
25 flow path F' other than at the locations provided by the plurality of apertures 34A, 34B, ...34Z.

The thermally expansive material 32 behaves in a like-manner to that described for Figures 2A to 2C.

30 In use in state 3A, at a temperature below or near the optimum operating temperature of the energy converter, i.e. below the critical temperature, the thermally expansive material 32 is contained between the wall 31 and the inner wall 33 and does not block or provide any partial occlusion of the channel 3. Indeed, the thermally expansive material 32 is

located away from the geometrical centre of the channel 3 and thus, in a first state as shown, does not or only minimally interferes with flow of material along the channel 3.

Referring also to Figure 3B, there is shown the channel 3 of Figure 3A. The channel 3 is shown in state 3B showing an area of localised overheating.

It is shown that localised area H'' has reached a temperature that is above the critical temperature of the thermally expansive material 32.

In the state 3B, the thermally expansive material 32 expands or 'swells' in response to exposure to the critical temperature such that the thermally expansive material 32 comprises an expanded portion E3, which extends into the flow path F'' of the channel 3, such that the diameter of the flow path F is completely occluded.

As a consequence, no reactant R'' is able to travel through the channel 3 and the reaction stops in this section of the energy converter. This allows the surrounding components to cool to a temperature that is below that of the critical temperature of the thermally expansive material 32, such that it contracts back into the aperture 34B the inner wall 33 to return to state 3A shown in Figure 3A. In this way, further overheating is prevented.

Upon the localised area H'' cooling to a temperature that is below that of the critical temperature of the thermally expansive material 32, the expanded region E3 of the thermally expansive material 32 contracts or 'shrinks' back into the inner wall 33 of the channel 3, to return to the state 3A, at the optimum operating temperature.

Referring now to Figure 4, there is shown a schematic diagram of the expansion of a thermally expansive material 4 at a critical temperature T_c . The thermally expansive material 4 is for use in a channel in an energy converter, according to a further embodiment of the invention.

There is shown the thermally expansive material 4 in three states: a state 4A prior to expansion; state 4B in which the thermally expansive material has expanded in response to exposure to its critical temperature; and state 4C in which the thermally expansive material has contracted from state 4B in response to exposure to a temperature below its critical temperature.

The thermally expansive material 4 comprises a plurality of microcapsules 41, which are encased in an elastomeric matrix material 42.

- 5 The microcapsules 41 contain a phase change material 43. The elastomeric matrix material 42 is impermeable to the phase change material 43, even when it is not encapsulated within the microcapsules 41.

10 In state 4A, prior to thermal expansion, the thermally expansive material 4 comprises microencapsulated phase change material in the form of the plurality of microcapsules 41, which are encased within an elastomeric matrix material 42. The volume of the thermally expansive material 4 in state 4A is V_1 .

15 In state 4B, upon exposure to the critical temperature T_c of the thermally expansive material 4, the thermally expansive material 4 increases in volume to V_2 , which is larger than V_1 . Upon expansion of the phase change material 43, the microcapsules 41 fracture to release the phase change material 43 into the elastomeric matrix material 42. However, the elastomeric matrix material 42 is impermeable to the phase change material 43 such that it cannot evaporate or leak out of the elastomeric matrix material 42 and so remains
20 trapped in the starting location.

In state 4C, upon cooling to a temperature that is below the critical temperature T_c of the thermally expansive material 4, the thermally expansive material 4 reduces in volume to V_1 . The phase change material 43 remains contained and sealed within the elastomeric
25 matrix material 42.

The thermally expansive material 4 may be fabricated as follows. The phase change material 43 may be encapsulated, e.g. microencapsulated, into a capsule, e.g. a microcapsule 41, e.g. an organic shell or an inorganic shell, via an *in-situ* polymerisation
30 or a sol gel process to form the capsule or microcapsule 41.

The microcapsules 41 may then be inlaid into an elastomeric matrix material 42, e.g. an elastic film, by evaporating drops of a suspension containing the microcapsules 41.

The resulting thermally expansive material 4, which is a composite film, is temperature sensitive and will abruptly change volume at the phase change transition temperature of the phase change material 43.

5 The invention is exemplified with the following non-limiting Examples.

Example 1 - Method for the fabrication of the microcapsules containing the phase change material.

10 Heptane was used as a principal model core oil. All materials and chemicals were used as received without further purification or treatment unless specified otherwise. The following materials and chemicals were purchased from Sigma-Aldrich UK: Urea (U5128, ACS reagent grade 99.0-100.5%), formaldehyde solution (47608, for molecular biology, BioReagent, $\geq 36.0\%$ in H_2O), poly(vinyl alcohol) (PVOH) (363170, Mw 13,000~23,000,
15 87~89% hydrolyzed), xanthan gum (G1253, from *Xanthomonas campestris*), heptane (246654, anhydrous, 99%), Nile red (72485, for microscopy), and methyl cellulose (M0262, viscosity 400 cP). Ammonium chloride was purchased from Scientific Laboratory Suppliers. Resorcinol (98%) was purchased from Acros Organics.

20 The emulsifier solution was prepared by weighing the required quantity of emulsifier for 150 g water based on concentration calculation, and dissolving the weighed emulsifier in 150 g distilled water (conductivity $\leq 2.00 \mu S/cm$ monitored by a Mettler Toledo SevenCompact conductivity meter) at room temperature via ultrasonication for 10 min and magnetic stirring for 10 min respectively. For Xanthum gum, high shear homogenization
25 (4000 rpm for 10 min with a Silverson L4RT homogenizer) was used to assist and accelerate its hydration after ultrasonication. 2.500 g urea, 0.250 g resorcinol and 0.250 g ammonium chloride were weighed with a Sartorius Secura124-1S analytical balance and dissolved in the emulsifier solution prepared. The solution was ultrasonicated for 10 min and put under stirring with an IKA® RCT digital magnetic stirrer. The pH value of the
30 solution was adjusted to 3.50 ± 0.02 with HCl solutions of various concentrations, and NaOH usage was avoided whenever possible to minimize the variation of ionic strength (Mettler Toledo FiveEasy pH meter) and the stirring continued for 20 min after pH adjustment. Meanwhile the oil phase was prepared by dissolving 1 mg Nile red inside 10 mL heptane under ultrasonication for 10 min. The core solution was then injected into the
35 prepared aqueous solution via a syringe with a needle at a flow rate of 0.2 ml/s while

under homogenization at 1200 rpm for 20 min with a Silverson L4RT homogenizer. Subsequently the prepared emulsion was transferred into a 250 mL jacketed beaker. A Rushton turbine (IKA R3004 stirrer diameter $\Phi 30$ mm) blade was used to keep the emulsion under stirring for stabilization at 600 rpm (IKA Eurostar Labortechnik). 6.5 mL formaldehyde solution was added into the jacketed beaker which was then covered with Al foil. The jacketed beaker was connected with a Julabo ME-F25 water bath programed as follows: the temperature was maintained at 20 °C for 30 min, then ramped up to 55 °C at a heating rate of 1 °C/min, maintained at 55 °C for 4 h and then cooled down to 20 °C at a cooling rate of -1 °C/min. The dispersion was then centrifuged four times at 6000 rpm (relative centrifugal force (RCF) 4180) for 5 min and vacuum filtered with 5 L of water. The microcapsules harvested by centrifugation and filtration were re-dispersed back in an aqueous environment for storage and dried under ambient conditions.

Example 2 – Method for encasing the microcapsules in an elastomer.

A silicone rubber gel polymer (Sigma-Aldrich) was used as the elastomer. The microcapsules of Example 1 were used as a filler to form a composite phase change material.

- Disperse the microcapsules of Example 1 within the silicone rubber gel.
- Stir thoroughly to achieve uniform dispersion.
- Add a small amount of the catalyst gel (e.g. 5 mg) to the uniform dispersion of the microcapsules within the silicon rubber gel elastomer.
- Stir thoroughly to achieve a uniform composite gel of encased microcapsules in the silicon rubber gel elastomer.
- Place the uniform composite gel into a mould.
- Cure the uniform composite gel at 40 to 60 °C in a furnace to form the thermally expansive material (curing will take from a few hours to a few days, depending on the temperature).

Example 3 - Method for locating the thermally expansive material in the channel of a fuel cell.

- Machine a plurality of cavities (e.g. 1-10 mm²) at a frequency of 1cm apart in the side wall of a microchannel of a PEMFC.
- Add the thermally expansive material of Example 2 to the cavities.

Example 4 – Test Data

The thermally expansive member of Example 2 was used to conduct some preliminary tests to demonstrate feasibility.

- 5 5% volume fraction of PCM microcapsules was added and tested for desired expansion and the thermal expansion is >20% at 101°C.

It should be noted that the balanced pressure depends on the properties and amount of elastomer so higher expansion rate is achievable when increasing the volume fraction of
10 PCM microcapsules, while ensuring the non-breathability.

The present invention describes an adaptive and self-regulating means for adjusting the flow rate of reactants into the energy converter. This prevents overheating and ensures that the components of the energy converter are not damaged.

15 This is advantageous over approaches that require entire cooling of the energy converter. Moreover, the present invention is safer and less susceptible to break down and damage than approaches for thermal management of the prior art.

20 Advantageously, the present invention enables the energy converter to function at or near an optimum temperature.

More advantageously, the present invention does not consume additional electrical power.

25 It will be appreciated by those skilled in the art that several variations to the aforementioned embodiments are envisaged without departing from the scope of the invention. For example, the chemical nature of the phase change material, and hence the critical temperature of the phase change material and/or thermally expansive material,
30 may be selected depending on the specific requirements of the energy converter.

Different thermally expansive materials may be used at different locations within a channel and/or in different types of channel to suit the needs of the specific requirements of the energy converter. For example, the amount of phase change material within a

thermally expansive member may vary from one location to another location. In this way the flow restriction properties may be tuned to vary from location to location.

5 A different frequency and/or amount of thermally expansive material may be used depending on the application and/or the reaction that is performed within the energy converter. For example, fuel cells other than PEMFCs may have different optimal operating temperatures, as is well known to the skilled addressee, and the materials will be chosen to suit the optimal temperature range when deploying the invention.

10 The electrochemical energy converter is not limited to fuel cells. The energy converter may be a battery, e.g. a lithium air or zinc air battery.

It will also be appreciated by those skilled in the art that any number of combinations of the aforementioned features and/or those shown in the appended drawings provide clear
15 advantages over the prior art and are therefore within the scope of the invention described herein.

CLAIMS

1. An electrochemical energy converter, the electrochemical energy converter comprising a channel for the passage of fluid, a thermally expansive body located to
5 at least partially occlude the channel when the thermally expansive body is exposed to or reaches a critical temperature.
2. An electrochemical energy converter according to Claim 1, wherein the thermally expansive body has a first volume below the critical temperature, and a second,
10 larger volume at or above the critical temperature, and expansion of the thermally expansive body from the first volume to the second volume is reversible.
3. An electrochemical energy converter according to Claim 1 or 2, wherein the channel defines a flow volume for the flow of material therealong and the flow volume
15 encompasses the geometrical centre of the channel.
4. An electrochemical energy converter according to Claim 3, wherein in a first unexpanded state, the thermally expansive body is located outside of the flow volume.
20
5. An electrochemical energy converter according to any preceding Claim, wherein the thermally expansive body is a composite material.
6. An electrochemical energy converter according to any preceding Claim, wherein the
25 thermally expansive body comprises a phase change material.
7. An electrochemical energy converter according to Claim 6, wherein the phase change material comprises a hydrocarbon.
- 30 8. An electrochemical energy converter according to any of Claims 6 to 7, wherein the phase change material is encapsulated, e.g. microencapsulated, to provide capsules.

9. An electrochemical energy converter according to Claim 8, wherein the capsules each comprise an outer shell that is between 0.5 to 10 microns thick, e.g. 1 micron thick.
- 5 10. An electrochemical energy converter according to Claim 8 or 9, wherein the capsules each have a diameter of less than 10 microns.
11. An electrochemical energy converter according to Claims 8 to 10, wherein the outer shell of the capsules is fabricated from formaldehyde, e.g. urea formaldehyde.
- 10 12. An electrochemical energy converter according to any of Claims 6 to 11, wherein the phase change material is located, e.g. encased, within a matrix material.
13. An electrochemical energy converter according to Claim 12, wherein the matrix material comprises an elastomer, e.g. silicone rubber.
- 15 14. An electrochemical energy converter according to any preceding Claim, wherein the thermally expansive body comprises a composite material comprising a homogeneous phase of microencapsulated phase change material located within an elastomer.
- 20 15. An electrochemical energy converter according to any preceding Claim, wherein the thermally expansive body is located within a cavity formed within an inner wall of the channel.
- 25 16. An electrochemical energy converter according to any preceding Claim, wherein the critical temperature is between 50 to 100 °C, e.g. between 60 to 90 °C, or between 65 to 85 °C.
- 30 17. An electrochemical energy converter according to any preceding Claim, wherein the fluid is a fuel, e.g. hydrogen.
18. An electrochemical energy converter according to any preceding Claim, wherein the energy converter is a hydrogen fuel cell.
- 35

19. An electrochemical energy converter according to any of Claims 1 to 16, wherein the energy converter is a lithium air battery.
20. A method of regulating the temperature of an electrochemical energy converter during an energy conversion reaction, the method comprising locating a thermally expansive body within a channel for the passage of fluid, such that the thermally expansive body expands from a first volume to a second larger volume to at least partially occlude the channel when the thermally expansive body is at or above a critical temperature, and the thermally expansive body contracts from the second larger volume to the first volume when the thermally expansive body is below the critical temperature.
21. A method according to Claim 20, the method comprising locating the thermally expansive body outside of a flow volume through the channel, the flow volume encompassing the geometrical centre of the channel.
22. A method according to Claim 20 or 21, further comprising providing a phase change material, encapsulating the phase change material in microcapsules, locating the microcapsules in a matrix material to form the thermally expansive body.
23. A method of fabricating an electrochemical energy converter having a self-regulating temperature control means, the method comprising providing a phase change material, encapsulating the phase change material in microcapsules, locating the microcapsules in a matrix material to form a thermally expansive body, and locating the thermally expansive body within a channel of the energy converter for the passage of fluid.

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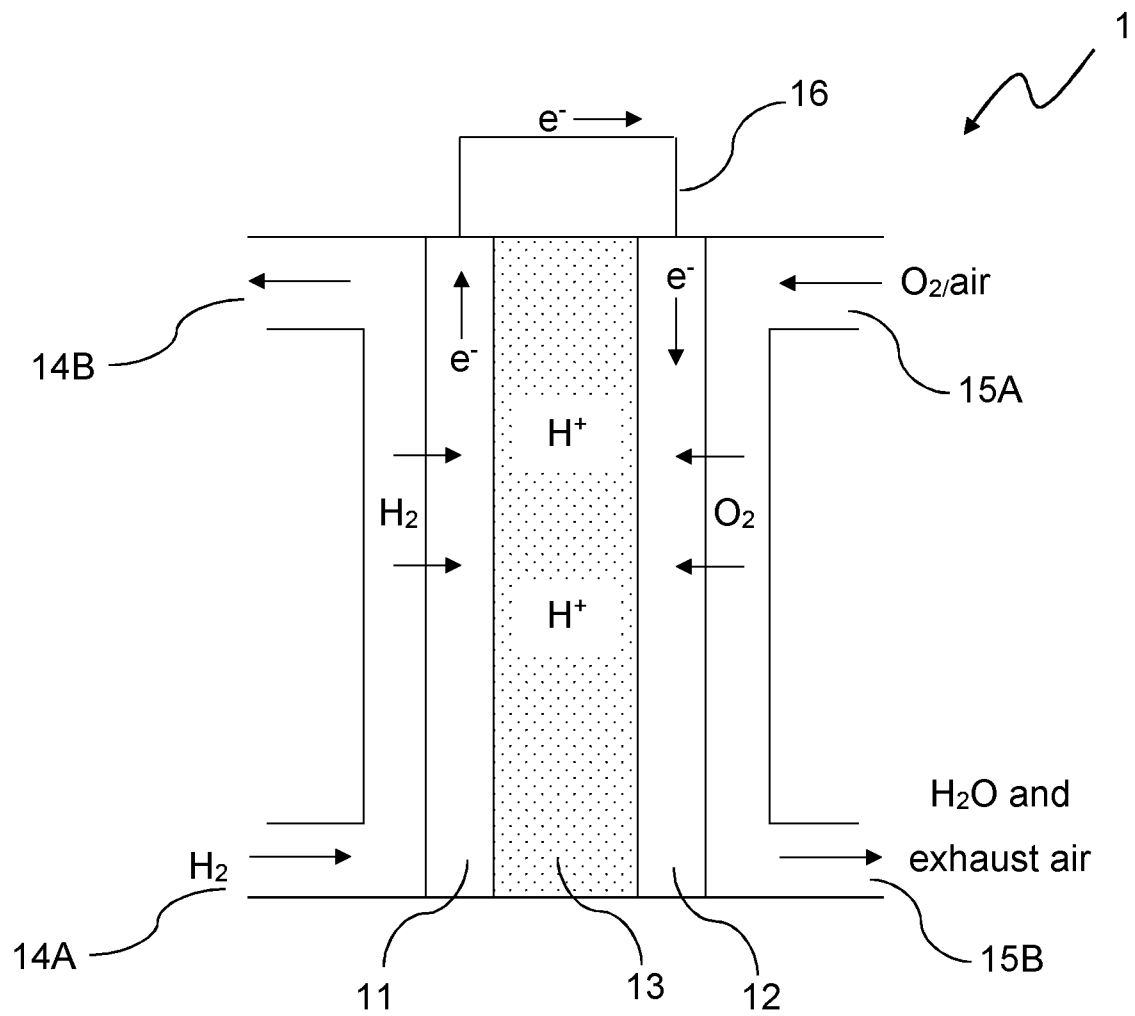


FIGURE 1
PRIOR ART

2/5

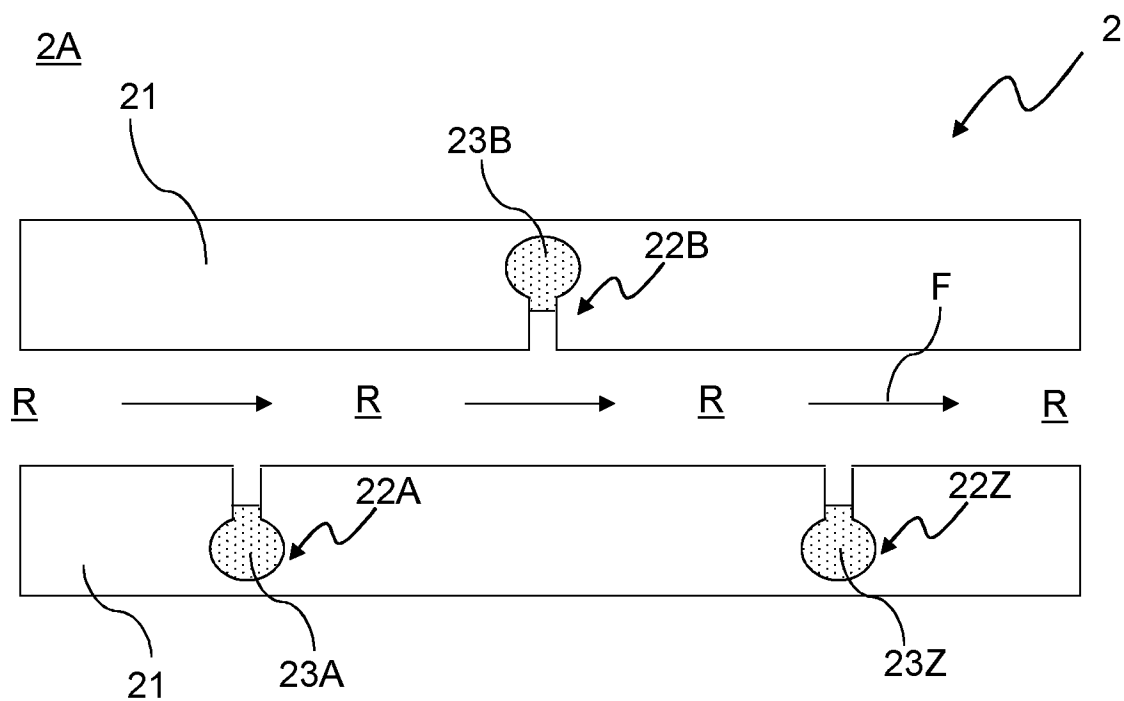


FIGURE 2A

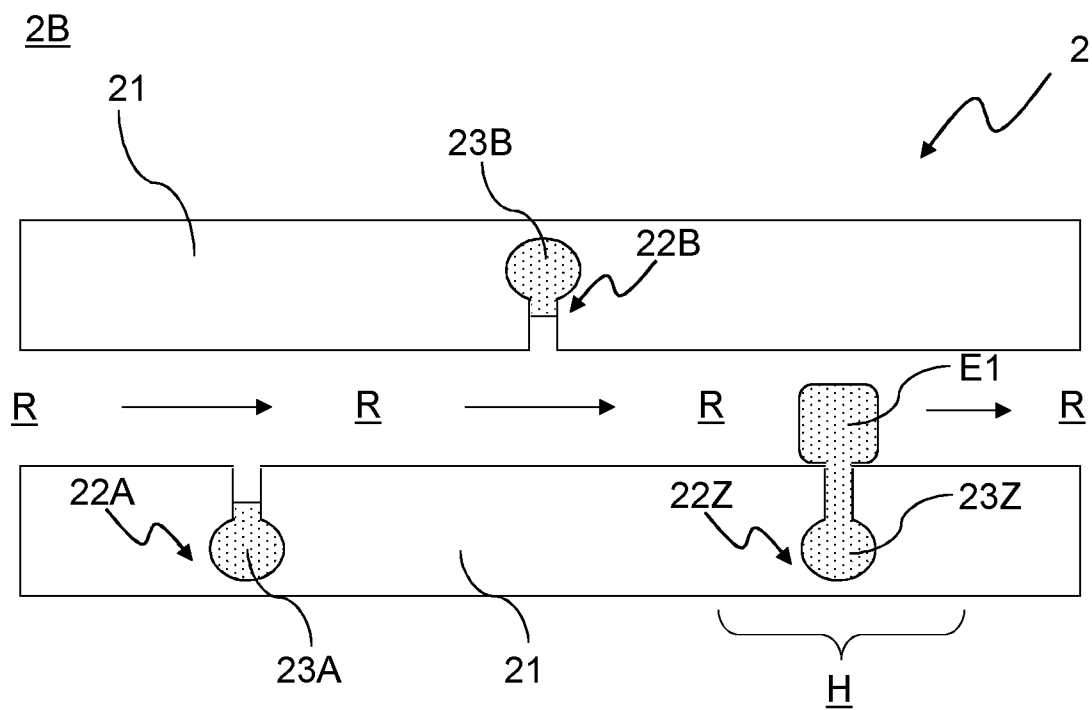


FIGURE 2B

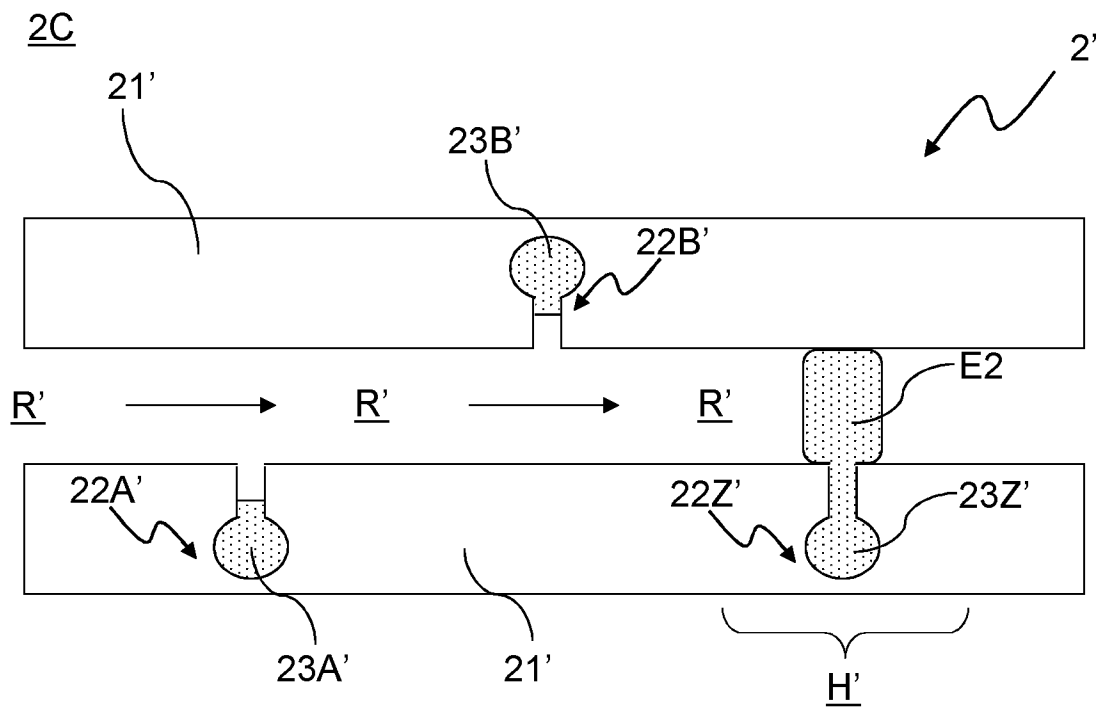


FIGURE 2C

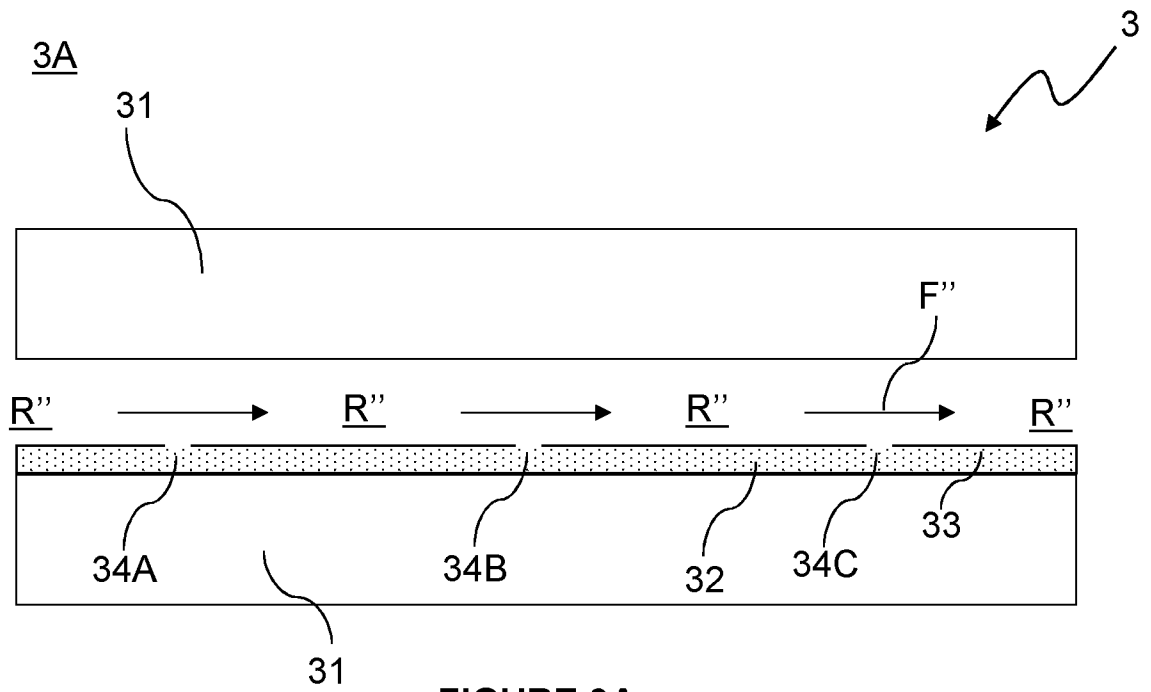


FIGURE 3A

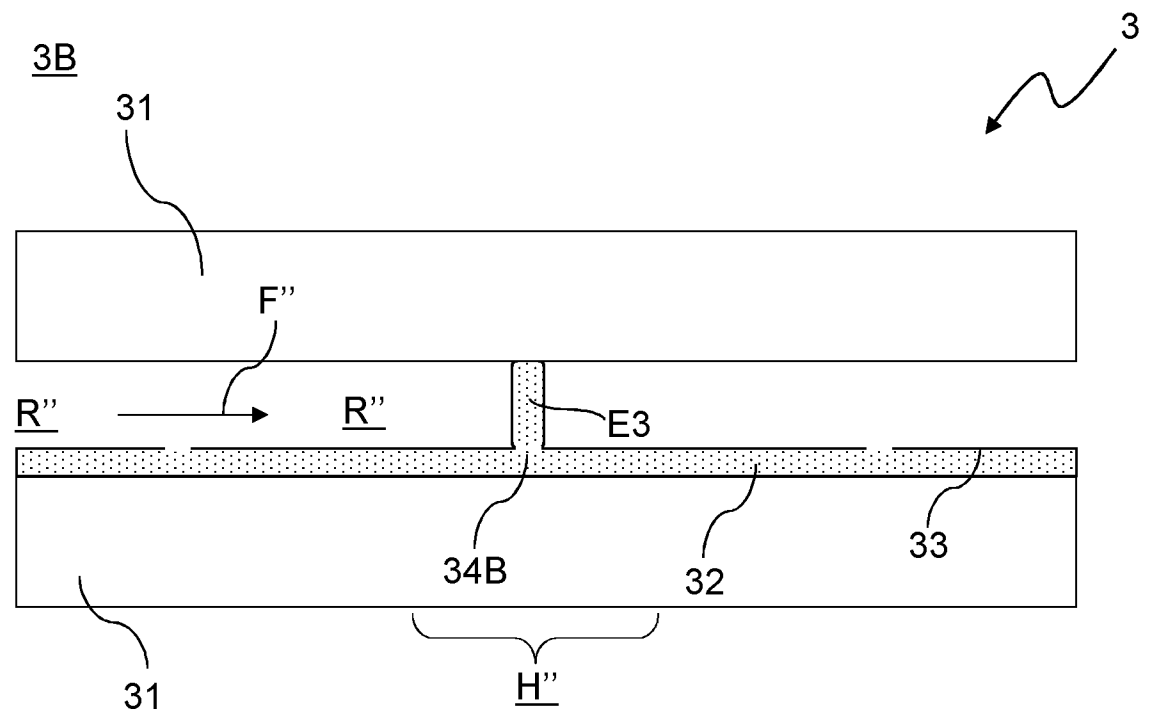


FIGURE 3B

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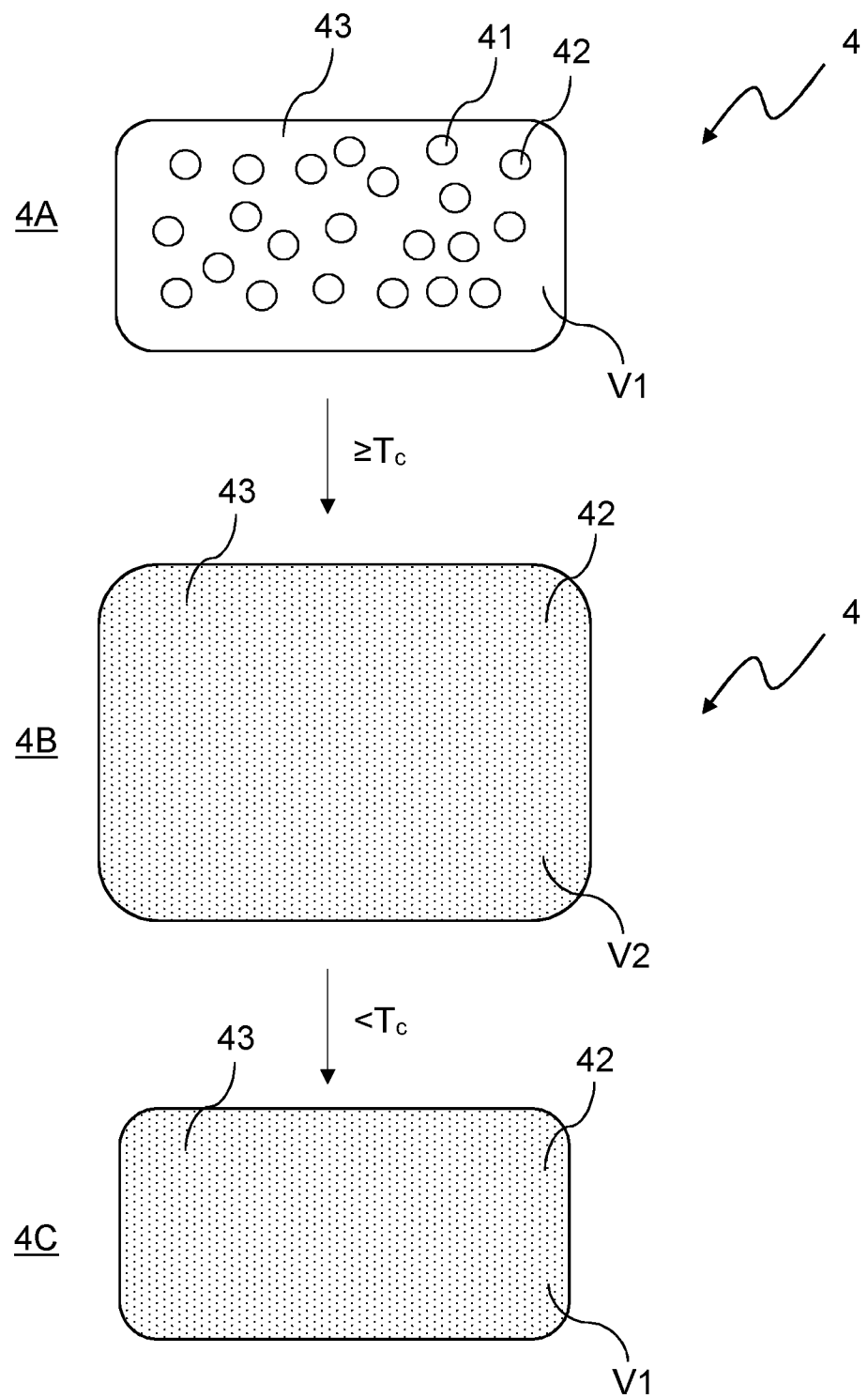


FIGURE 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2019/052964

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M8/04089
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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 2012/189934 A1 (TRAN TRONG [DE]) 26 July 2012 (2012-07-26)	1-3,5, 16-20
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Y	paragraphs [0027], [0029], [0034]; figures 3,4,10,11 ----- -/-	22,23

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

"&" document member of the same patent family

Date of the actual completion of the international search

12 December 2019

Date of mailing of the international search report

07/01/2020

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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