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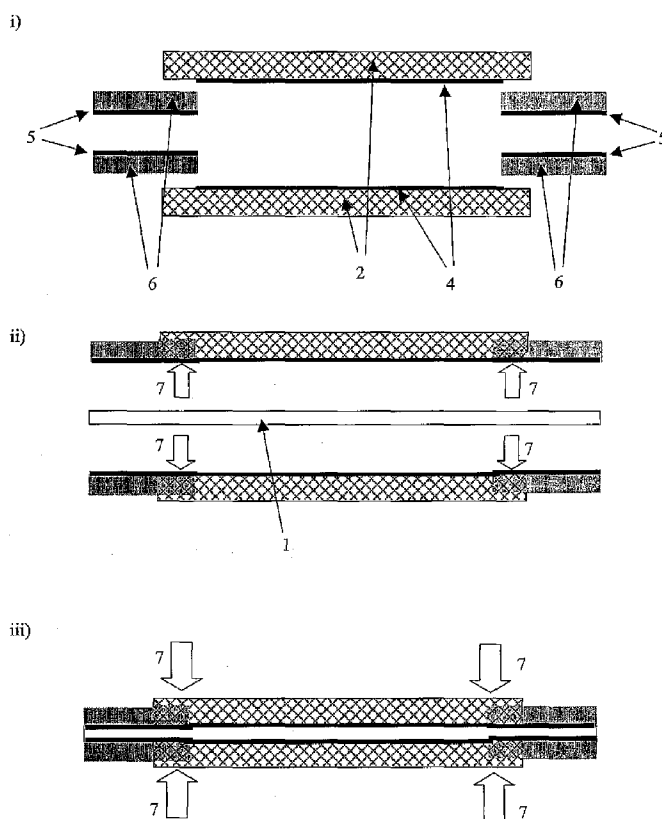
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(54) Title: MEMBRANE ELECTRODE ASSEMBLY



(57) Abstract: A membrane electrode assembly comprising an ion-conducting membrane, electrocatalyst layers disposed either side of the membrane and gas diffusion layers disposed adjacent to the electrocatalyst layers is disclosed. The membrane electrode assembly has an edge region and a central region and a film layer, optionally with an adhesive layer on one or both faces of the film layer, is positioned between the membrane and a gas diffusion layer at the edge region of the membrane electrode assembly. The film layer and/or, if present, the adhesive layer comprises an additive selected from the group consisting of oxygen scavengers, antioxidants or free radical scavengers.



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MEMBRANE ELECTRODE ASSEMBLY

The present invention relates to a membrane electrode assembly suitable for use in a proton exchange membrane fuel cell.

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A fuel cell is an electrochemical cell comprising two electrodes separated by an electrolyte. A fuel, e.g. hydrogen or methanol, is supplied to the anode and an oxidant, e.g. oxygen or air, is supplied to the cathode. Electrochemical reactions occur at the electrodes, and the chemical energy of the fuel and the oxidant is converted to electrical energy and heat. Fuel cells are a clean and efficient power source, and may replace traditional power sources such as the internal combustion engine in both stationary and automotive power applications.

In a proton exchange membrane (PEM) fuel cell, the electrolyte is a solid polymer membrane which is electronically insulating but ionically-conducting. Proton-conducting membranes based on perfluorosulphonic acid materials are typically used, and protons, produced at the anode, are transported across the membrane to the cathode, where they combine with oxygen to create water.

The principle component of a polymer electrolyte fuel cell is known as a membrane electrode assembly (MEA) and is essentially composed of five layers. The central layer is the polymer membrane. On either side of the membrane there is an electrocatalyst layer, containing an electrocatalyst, which is tailored for the different requirements at the anode and the cathode. Finally, adjacent to each electrocatalyst layer there is a gas diffusion layer. The gas diffusion layer must allow the reactants to reach the electrocatalyst layer and must conduct the electric current that is generated by the electrochemical reactions. Therefore the gas diffusion layer must be porous and electrically conducting.

The MEA can be constructed by several methods. The electrocatalyst layer may be applied to the gas diffusion layer to form a gas diffusion electrode. Two gas diffusion electrodes can be placed either side of a membrane and laminated together to form the five-layer MEA. Alternatively, the electrocatalyst layer may be applied to both faces of

the membrane to form a catalyst coated membrane. Subsequently, gas diffusion layers are applied to both faces of the catalyst coated membrane. Finally, an MEA can be formed from a membrane coated on one side with an electrocatalyst layer, a gas diffusion layer adjacent to that electrocatalyst layer, and a gas diffusion electrode on the other side of the membrane.

Typically tens or hundreds of MEAs are required to provide enough power for most applications, so multiple MEAs are assembled to make up a fuel cell stack. Field flow plates are used to separate the MEAs. The plates perform several functions: supplying the reactants to the MEAs, removing products, providing electrical connections and providing physical support.

WO 2005/020356 discloses MEAs wherein film layers are positioned around the edge region of the MEA. In one embodiment, the film layers are positioned between the edges of the membrane and the gas diffusion layers. An adhesive layer is present on one or both surfaces of the film layer. The film layers reinforce the edge region of the MEA and prevent fibres from the gas diffusion layer from puncturing the membrane.

MEA failure, as demonstrated by sudden performance loss, often occurs in the edge region of the MEA and incorporation of film layers into the edge region can help to increase MEA lifetime before significant performance loss is seen. The present inventors have sought to provide an MEA wherein failure in the edge region is further decreased and serviceable lifetime is further increased before significant performance loss.

Accordingly the present invention provides a membrane electrode assembly comprising an ion-conducting membrane, electrocatalyst layers disposed either side of the membrane and gas diffusion layers disposed adjacent to the electrocatalyst layers, wherein the membrane electrode assembly has an edge region and a central region, wherein a film layer, optionally with an adhesive layer on one or both faces of the film layer, is positioned between the membrane and a gas diffusion layer at the edge region of the membrane electrode assembly, and characterised in that the film layer and/or, if

present, the adhesive layer comprises one or more additives selected from the group consisting of oxygen scavengers, antioxidants or free radical scavengers.

In one embodiment, the film layer and/or, if present, the adhesive layer comprises
5 one or more additives which is an oxygen scavenger.

In a second embodiment, the film layer and/or, if present, the adhesive layer comprises one or more additives which is an antioxidant.

10 In a third embodiment, the film layer and/or, if present, the adhesive layer comprises one or more additives which is a free radical scavenger.

Preferably the MEA comprises two film layers, wherein both film layers optionally have an adhesive layer on one or both faces of the film layer. Each film layer
15 is positioned between the membrane and one of the two gas diffusion layers at the edge regions of the MEA. Preferably each film layer, or if present the adhesive layer, comprises one or more additives selected from the group consisting of oxygen scavengers, antioxidants or free radical scavengers.

20 Incorporation of oxygen scavengers, antioxidants or free radical scavengers into the film layer or the adhesive layer is readily achieved and decreases membrane degradation in the edge region. Hydrogen peroxide formation and associated membrane degradation is minimised by decreasing the amount of oxygen that permeates through the film layer or adhesive layer. Free radical attack and associated membrane degradation is
25 minimised by scavenging free radicals that permeate through the film layer or adhesive layer.

The MEA has an edge region and a central region. It is useful to describe the dimensions of the MEA by referring to x, y and z directions. The x and y directions are
30 within the plane of the layered MEA, and the z direction is through the thickness of the MEA (this is shown in figure 1). The ion-conducting membrane, electrocatalyst layers and gas diffusion layers do not necessarily have the same dimensions in the x-y plane. The ion-conducting membrane may be larger than the electrocatalyst layers and gas

diffusion layers, so may protrude beyond these layers at the edge of the MEA. Alternatively, the gas diffusion layers may be larger than the membrane, so there may be a gap between the two gas diffusion layers at the edge of the MEA. The edge region is a region around the circumference of the MEA, encompassing the edge of the membrane, the edges of the gas diffusion layers and optionally encompassing the edges of the catalyst layers. The edge region extends inwardly from the edges of the membrane and the gas diffusion layers, suitably by at least 1mm, preferably by at least 5mm. The central region is the remaining volume of the membrane electrode assembly that is not part of the edge region.

The film layer (or each film layer) is suitably a non-conducting self-supporting film material. The film layer does not impregnate the gas diffusion layers. Suitably the film layer is non-adhesive. The melting temperature of the film layer must be higher than the temperatures used when manufacturing the membrane electrode assembly (e.g. lamination temperatures), and preferably the film layer shows no appreciable softening at the manufacturing temperatures. Preferably the film layer does not shrink appreciably under the manufacturing conditions.

The film layer is suitably made of a material that does not leach contaminants into the fuel cell system, and that has low permeability to hydrogen, oxygen and water (suitably lower than the permeability of the polymer electrolyte membrane). Additionally, the material of the film layer is preferably resistant to puncture by fibres from the gas diffusion substrate.

The film layer is preferably a polymeric material such as polyethylene terephthalate (PET), polyvinylidene fluoride (PVDF), ethylene-vinyl alcohol (EVOH), biaxially-oriented polypropylene (BOPP), polytetrafluoroethylene (PTFE), ethylene tetrafluoroethylene (ETFE), polyether sulphone (PES), polyether ether ketone (PEEK), fluorinated ethylene-propylene (FEP), polyphenylene sulphide (PPS) or polyimide (PI). The backing layer could also be a metallised film, i.e. a thin layer of metal coated with polymer. The thickness of the backing layer is suitably greater than 1µm, preferably between 5µm and 50µm.

In a preferred embodiment, the film layer has an oxygen permeation rate of less than $50\text{cm}^3/\text{m}^2/\text{day}/\text{bar}$, preferably less than $10\text{cm}^3/\text{m}^2/\text{day}/\text{bar}$, and most preferably less than $1\text{cm}^3/\text{m}^2/\text{day}/\text{bar}$. Film layers that have this property include ethylene-vinyl alcohol (EVOH) ($1\text{--}5\text{cm}^3/\text{m}^2/\text{day}/\text{bar}$), metallised PET ($0.5\text{--}4\text{cm}^3/\text{m}^2/\text{day}/\text{bar}$) and amorphous silica coated PET ($0.2\text{--}0.7\text{cm}^3/\text{m}^2/\text{day}/\text{bar}$). Decreasing the oxygen permeability of the film layer improves the oxygen barrier properties of the film layer. Reducing the amount of oxygen that travels from the edge region of the cathode to the edge region of the anode should decrease degradation of the membrane in the edge region. In one embodiment of the invention, the MEA comprises two film layers, and the film layer positioned between the membrane and the cathode gas diffusion layer has a lower oxygen permeation rate than the film layer positioned between the membrane and the anode gas diffusion layer. The film layer positioned between the membrane and the cathode diffusion layer suitably has an oxygen permeation rate of less than $10\text{cm}^3/\text{m}^2/\text{day}/\text{bar}$, and preferably less than $1\text{cm}^3/\text{m}^2/\text{day}/\text{bar}$, whereas the film layer positioned between the membrane and the anode gas diffusion layer may have an oxygen permeation rate of more than $10\text{cm}^3/\text{m}^2/\text{day}/\text{bar}$.

The thickness of the film layer is suitably from $1\mu\text{m}$ to $300\mu\text{m}$, preferably from $5\mu\text{m}$ to $30\mu\text{m}$.

The adhesive layer may contain a hot-melt adhesive, a pressure-sensitive adhesive or a thermosetting adhesive. The adhesive may be a polyethylene-based or polypropylene-based adhesive. The adhesive may be a copolymer of ethylene and methacrylic acid or a copolymer of ethylene and vinyl acetate, as described in US 6,756,147. Preferably there is no softening of the adhesive layer at temperatures below 100°C . Preferably the adhesive layer does not shrink appreciably under manufacturing conditions. Suitably the adhesive layer is made of a material that does not leach contaminants into the fuel cell system.

The film layer may have one adhesive layer. This adhesive layer can face the gas diffusion layer, and the adhesive can impregnate into the gas diffusion layer. Alternatively, the adhesive layer can face the membrane and the adhesive can bond to the

membrane. If the film layer has two adhesive layers, the adhesive layers may contain the same or different adhesives.

The thickness of the adhesive layer is suitably from 1 μ m to 300 μ m. If the
5 adhesive layer will face the gas diffusion layer, the thickness is preferably from 20 μ m to 300 μ m. If the adhesive layer will face the membrane, the thickness of the adhesive layer is preferably from 1 μ m to 10 μ m.

The one or more additives selected from the group consisting of oxygen
10 scavengers, antioxidants or free radical scavengers is present in the film layer or, if an adhesive layer is present, may be present in the adhesive layer, or may be present in the film layer and adhesive layer if both are present. Oxygen scavenger additives will reduce the transport of oxygen across the film or adhesive layer and suitable oxygen scavengers include Amosorb® 3000 (a copolyester resin from BP Amoco), Shelfplus®
15 2500 (Ciba Speciality Chemicals) and cobalt salts such as cobalt nitrate or cobalt octoate (these are particularly effective when incorporated into Nylon MXD6 polymer).

Antioxidants can be classified as primary antioxidants, secondary antioxidants or
multifunction antioxidants. Primary antioxidants are hydrogen donors that react with
20 peroxy radicals to form hydroperoxides. This prevents the peroxy radical from reacting with a polymer backbone and causing chain scission. Examples include phenolic stabilisers (available from the Irganox® range from Ciba) and secondary aromatic amines. Secondary antioxidants decompose hydroperoxide and prevent the formation of extremely reactive hydroxy and alkoxy radicals. Examples include trivalent phosphorus
25 compounds (available from the Irgafos® range from Ciba) and thiosynergists (such as Irganox® PS 800 or 802 from Ciba). Multifunction antioxidants combine the functions of primary and second antioxidants. Examples include Irganox® 1520 or 1726 (Ciba).

Free radical scavengers can scavenge alkyl radicals but cannot scavenge alkoxy
30 and hydroxy radicals. Examples include lactones (such as substituted benzofuranone) and hydroxylamines.

The additives must be stable in the fuel cell environment and must not decompose at typical fuel cell operating temperatures (e.g. 70-100°C).

5 The film layer or the adhesive layer may comprise more than one type of additive. The film layer and the adhesive layer may both comprise additives, which may be the same or different.

The preferred amount of additive present in the film layer or adhesive layer will depend on the nature of the film or adhesive material and on the nature of the additive.
10 However, suitable levels are likely to be in the range of 0.01-1wt% (based on the weight of the film layer or the adhesive layer), preferably in the range of 0.1-0.25wt%.

Incorporating additives into a film layer or an adhesive layer may be achieved by any suitable technique known to the skilled person. Typically the additives would be
15 incorporated into the adhesive layer in a blending process. This could be done by taking adhesive resin pellets, heating and mixing with the additive, repelletising the blend and extrusion coating the blend onto the film layer. Alternatively, this could be done by mixing the additive in with the adhesive just prior to extruding the adhesive onto the film layer.

20

The ion-conducting membrane may be any type of ion-conducting membrane known to those skilled in the art. Suitably the membrane is proton-conducting. In state of the art membrane electrode assemblies, the membranes are often based on perfluorinated sulphonic acid materials such as Nafion® (DuPont), Flemion® (Asahi
25 Glass) and Aciplex® (Asahi Kasei). The membrane may be a composite membrane, containing the proton-conducting material and other materials that confer properties such as mechanical strength. For example, the membrane may comprise a proton-conducting membrane and a matrix of silica fibres, as described in EP 875 524 or the membrane may comprise an expanded PTFE substrate. The membrane is suitably less than 200µm thick,
30 preferably less than 50µm thick.

The electrocatalyst layers comprise an electrocatalyst which may be a finely divided metal powder (metal black), or may be a supported catalyst wherein small metal

particles are dispersed on electrically conducting particulate carbon supports. The electrocatalyst metal is suitably selected from

- (i) the platinum group metals (platinum, palladium, rhodium, ruthenium, iridium and osmium),
- 5 (ii) gold or silver,
- (iii) a base metal,

or an alloy or mixture comprising one or more of these metals or their oxides. The preferred electrocatalyst metal is platinum, which may be alloyed with other precious metals such as ruthenium, or base metals such as molybdenum or tungsten.

10 If the electrocatalyst is a supported catalyst, the loading of metal particles on the carbon support material is suitably in the range 10-100wt%, preferably 15-75wt%.

The electrocatalyst layers suitably comprise other components, such as ion-conducting polymer, which is included to improve the ionic conductivity within the
15 layer. To incorporate the layers into the membrane electrode assembly, the layers can be formed on the gas diffusion substrates, or the layers can be formed on the membrane.

The gas diffusion layers may be any suitable gas diffusion layers known to those skilled in the art. Typical gas diffusion layers include layers based on carbon paper (e.g.
20 Toray® paper available from Toray Industries, Japan or U105 or U107 paper available from Mitsubishi Rayon, Japan), woven carbon cloths (e.g. the MK series of carbon cloths available from Mitsubishi Chemicals, Japan) or non-woven carbon fibre webs (e.g. ELAT series of non-woven substrates available from E-TEK Inc, USA; H2315 series available from Freudenberg FCCT oHG, Germany; or Sigracet® series available from
25 SGL Technologies GmbH, Germany). The carbon paper, cloth or web is typically modified with a particulate material either embedded within the substrate or coated onto the planar faces, or a combination of both. The particulate material is typically a mixture of carbon black and a polymer such as polytetrafluoroethylene (PTFE). Suitably the gas diffusion substrates are between 100 and 300µm thick. Preferably there is a layer of
30 particulate material such as carbon black and PTFE on the faces of the gas diffusion substrates that contact the electrocatalyst layers.

The film layer, optionally with an adhesive layer on one or both faces of the film layer, is positioned between the membrane and a gas diffusion layer at the edge region of the MEA. In one embodiment of the invention, the electrocatalyst layer is not present in the edge region of the MEA so the film layer is not adjacent to the electrocatalyst layer.

5 In another embodiment of the invention, the electrocatalyst layer is present in the edge region of the MEA so the film layer is adjacent to a limited region of the electrocatalyst layer. Suitably the width of the electrocatalyst layer that overlaps the film layer is between 0.5 and 10mm, preferably between 1 and 5mm. The film layer is positioned between the membrane and a gas diffusion layer, and if the film layer overlaps the
10 electrocatalyst layer, the film layer can either be positioned between the membrane and the electrocatalyst layer, or can be positioned between the electrocatalyst layer and the gas diffusion layer. It is preferred that the film layer is positioned between the membrane and the electrocatalyst layer.

15 The MEAs of the invention may be prepared using the methods outlined in WO 2005/020356. The membrane, electrocatalyst layers, gas diffusion layers and film layers (with optional adhesive layers) may be combined by a combination of coating and laminating processes. For example, electrocatalyst layers may be applied to gas diffusion layers by a printing process to form gas diffusion electrodes. An assembly of
20 two gas diffusion electrodes and a membrane may be prepared, with film layers interposed between the edges of the gas diffusion electrodes and the membranes, and the components may be laminated together.

In a further aspect, the present invention provides a fuel cell comprising a
25 membrane electrode assembly according to the invention.

For a more complete understanding of the invention, reference is made to the schematic drawings wherein:

30 Fig. 1 is a schematic diagram showing a membrane electrode assembly.

Fig. 2 is a schematic diagram showing a method of producing a membrane electrode assembly according to the invention.

Fig. 3 is a schematic diagram showing a method of producing a membrane electrode assembly according to the invention.

Figure 1 shows an MEA made up of a membrane (1) interposed between two gas diffusion layers (2). The x, y and z directions of the MEA are shown. The central region of the MEA is the region inside the hatched line (3) and the edge region is the remaining volume of the MEA. The electrocatalyst layers and film layer are not shown.

Step (i) of Fig. 2 shows gas diffusion electrodes comprising gas diffusion layers (2) and electrocatalyst layers (4). Film layers (5) having adhesive layers (6) are positioned on the edges of the inner faces of the gas diffusion layers (2). The film layers (5) and/or the adhesive layers (6) comprise one or more additives chosen from the group consisting of oxygen scavengers, antioxidants and free radical scavengers. In step (ii) the film layers are hot pressed (7) at the positions shown by arrows and the adhesive layers (6) impregnate into the gas diffusion layers (2). A membrane (1) is positioned between the gas diffusion layers (2). The membrane (1) extends beyond the gas diffusion layers (2). In step (iii) the gas diffusion layers (2) are laminated to the membrane (1) by hot pressing (7) at the positions shown by arrows.

Step (i) of Fig. 3 shows a membrane (1) between two gas diffusion electrodes comprising gas diffusion layers (2) and electrocatalyst layers (4). The electrocatalyst layers (4) do not contact the entire substrate area. The membrane (1) extends beyond the gas diffusion layers (2). Film layers (5), having adhesive layers (6) on both faces are positioned on the edges of the inner faces of the gas diffusion layers (2). The film layers (5) and/or the adhesive layers (6) comprise one or more additives chosen from the group consisting of oxygen scavengers, antioxidants and free radical scavengers. In step (ii) the film layers are hot pressed (7) at the positions shown by arrows. The gas diffusion electrodes are laminated to the membrane, the adhesive layers (6) impregnate into the gas diffusion layers (2) and adhere to the membrane (1). The film layers (5) extend beyond the edge of the membrane, and the region between the film layers (5) is filled by adhesive.

CLAIMS

1. A membrane electrode assembly comprising an ion-conducting membrane, electrocatalyst layers disposed either side of the membrane and gas diffusion layers
5 disposed adjacent to the electrocatalyst layers, wherein the membrane electrode assembly has an edge region and a central region, wherein a film layer, optionally with an adhesive layer on one or both faces of the film layer, is positioned between the membrane and a gas diffusion layer at the edge region of the membrane electrode assembly, and characterised in that the film layer and/or, if present, the adhesive layer comprises one or
10 more additives selected from the group consisting of oxygen scavengers, antioxidants or free radical scavengers.
2. A membrane electrode assembly according to claim 1, wherein the film layer has an adhesive layer on one or both faces of the film layer, and the adhesive layer comprises
15 one or more additives selected from the group consisting of oxygen scavengers, antioxidants or free radical scavengers.
3. A membrane electrode assembly according to claim 1 or claim 2, wherein the film layer comprises one or more additives selected from the group consisting of oxygen
20 scavengers, antioxidants or free radical scavengers.
4. A membrane electrode assembly according to any preceding claim, comprising two film layers, wherein both film layers optionally have an adhesive layer on one or both faces of the film layer, and wherein each film layer is positioned between the
25 membrane and one of the two gas diffusion layers at the edge regions of the MEA.
5. A membrane electrode assembly according to any preceding claim, wherein the film layer has an oxygen permeation rate of less than $10\text{cm}^3/\text{m}^2/\text{day}/\text{bar}$.
- 30 6. A fuel cell comprising a membrane electrode assembly according to any preceding claim.

1/3

Fig. 1

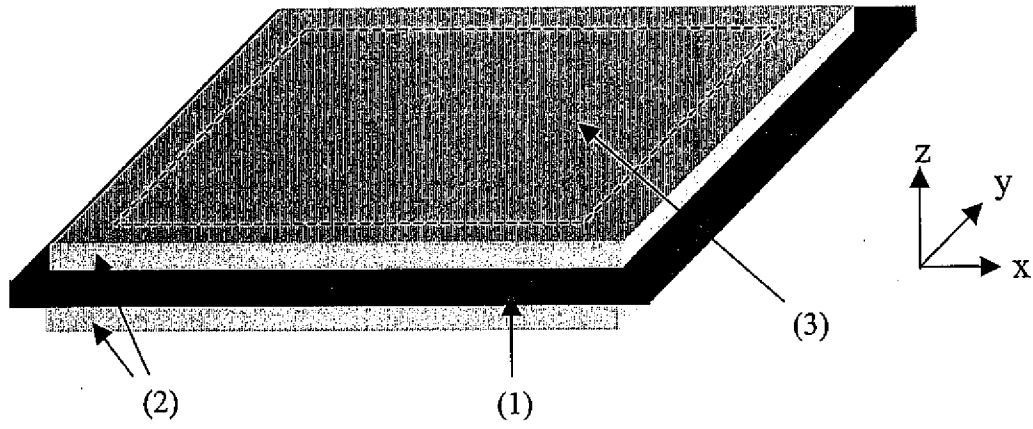
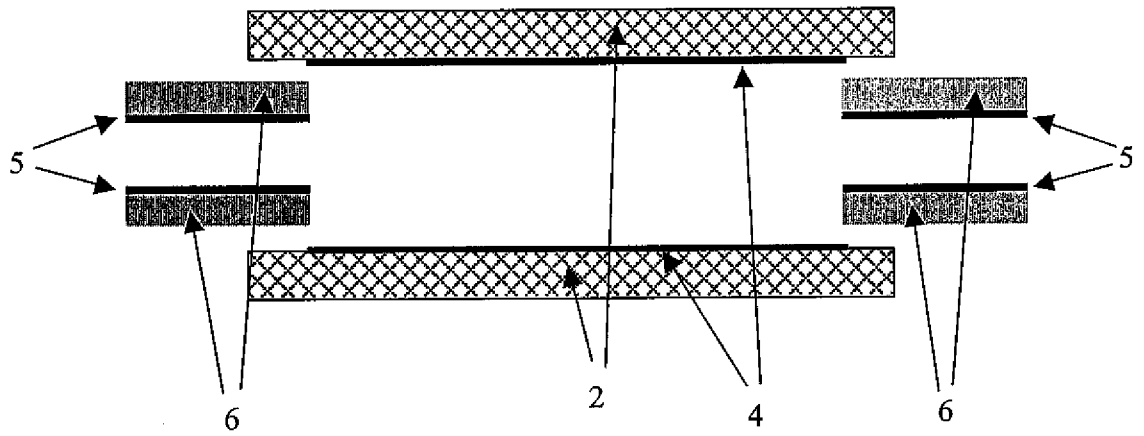
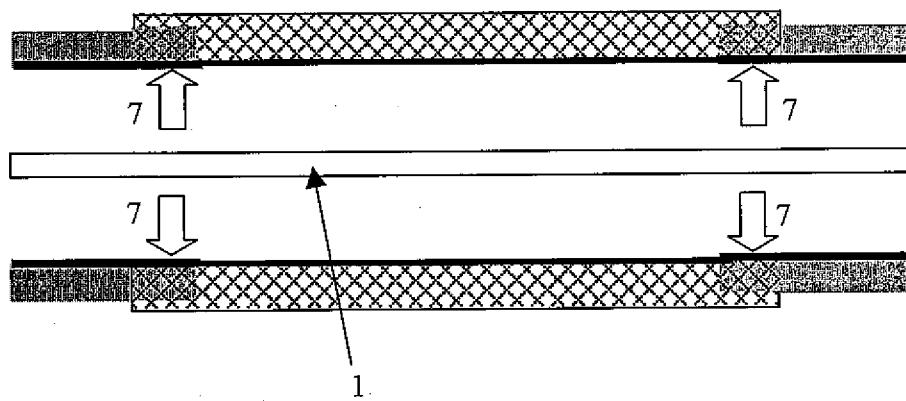


Fig. 2

i)



ii)



iii)

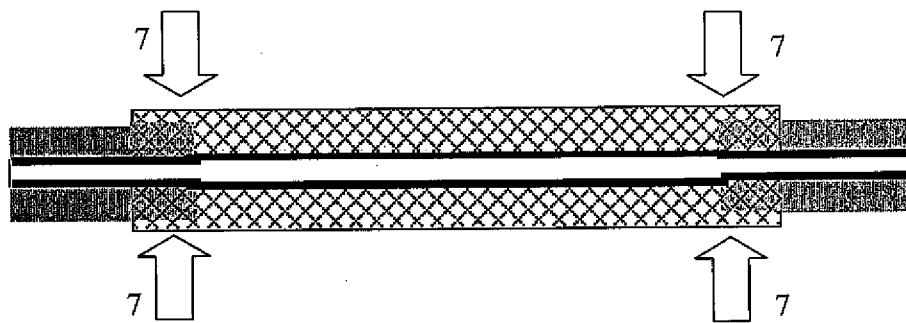
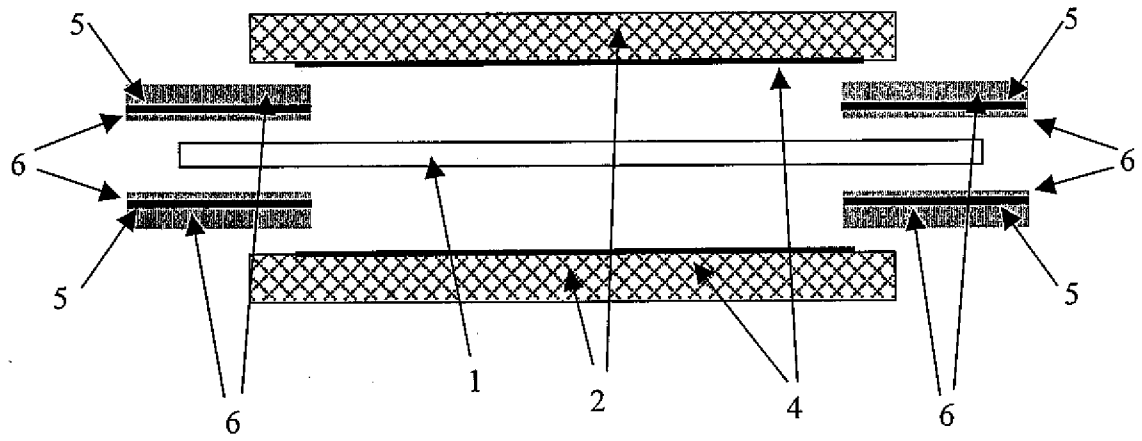
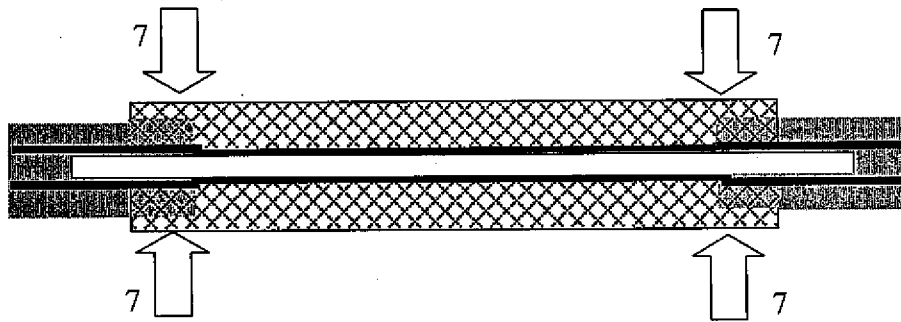


Fig. 3

i)



ii)



INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M8/02 H01M8/10

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2006/032894 A (JOHNSON MATTHEY PLC [GB]; GEN MOTORS CORP [US]; DE ROUFFIGNAC CATHERIN) 30 March 2006 (2006-03-30) page 4, line 21 - page 5, line 2 page 6, line 13 - page 7, line 6; figures 1-5	1-7
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2007/050135

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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