

US 20040191601A1

(19) **United States**(12) **Patent Application Publication**
Grot(10) **Pub. No.: US 2004/0191601 A1**(43) **Pub. Date: Sep. 30, 2004**(54) **FUEL CELL ELECTRODE ASSEMBLIES**

(60) Provisional application No. 60/155,578, filed on Sep. 24, 1999.

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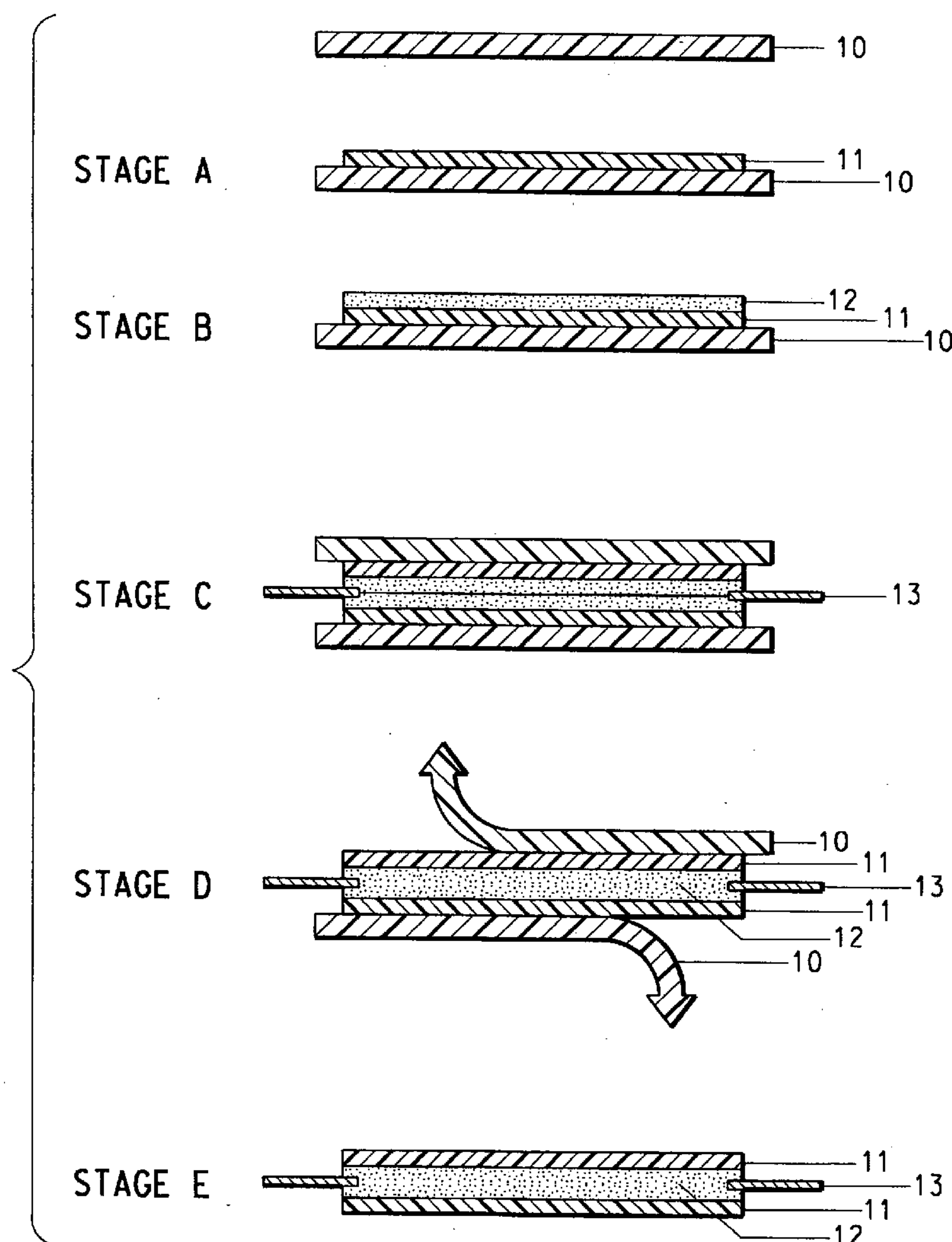
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HUNTLEY & ASSOCIATES**1105 NORTH MARKET STREET****P.O. BOX 948****WILMINGTON, DE 19899-0948 (US)****Publication Classification**(51) **Int. Cl.⁷** **H01M 8/10; H01M 2/08**(52) **U.S. Cl.** **429/30; 429/35**(21) Appl. No.: **10/701,297**(22) Filed: **Nov. 3, 2003****Related U.S. Application Data**

(63) Continuation-in-part of application No. 09/710,975, filed on Nov. 10, 2000, now Pat. No. 6,641,862, which is a continuation-in-part of application No. 09/669,623, filed on Sep. 25, 2000, now abandoned.

(57) **ABSTRACT**

Fuel cell membrane electrode assemblies having at least two solution cast films, preferably in combination with a perimeter sealing material between the solution cast films.



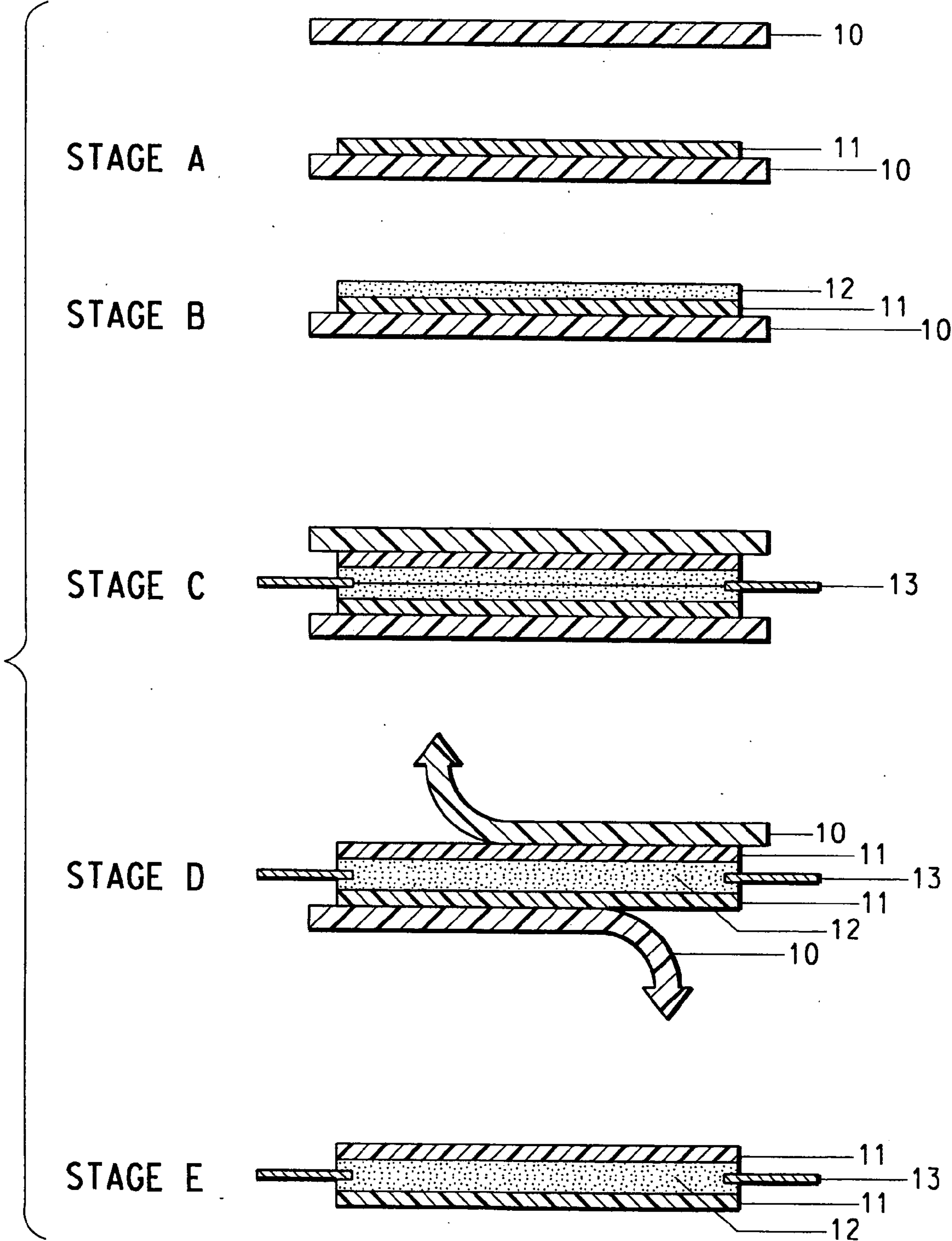


FIG. 1

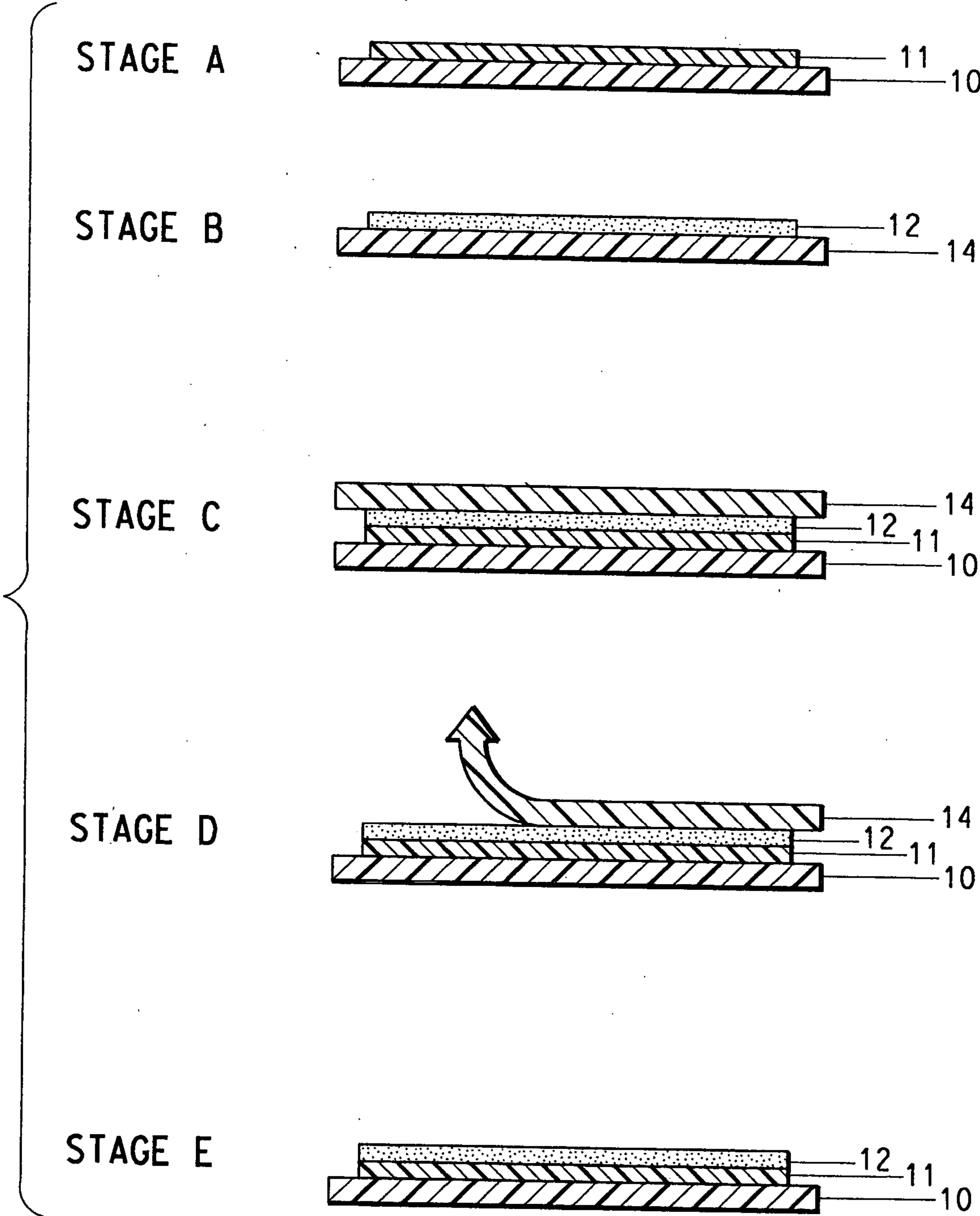


FIG. 2

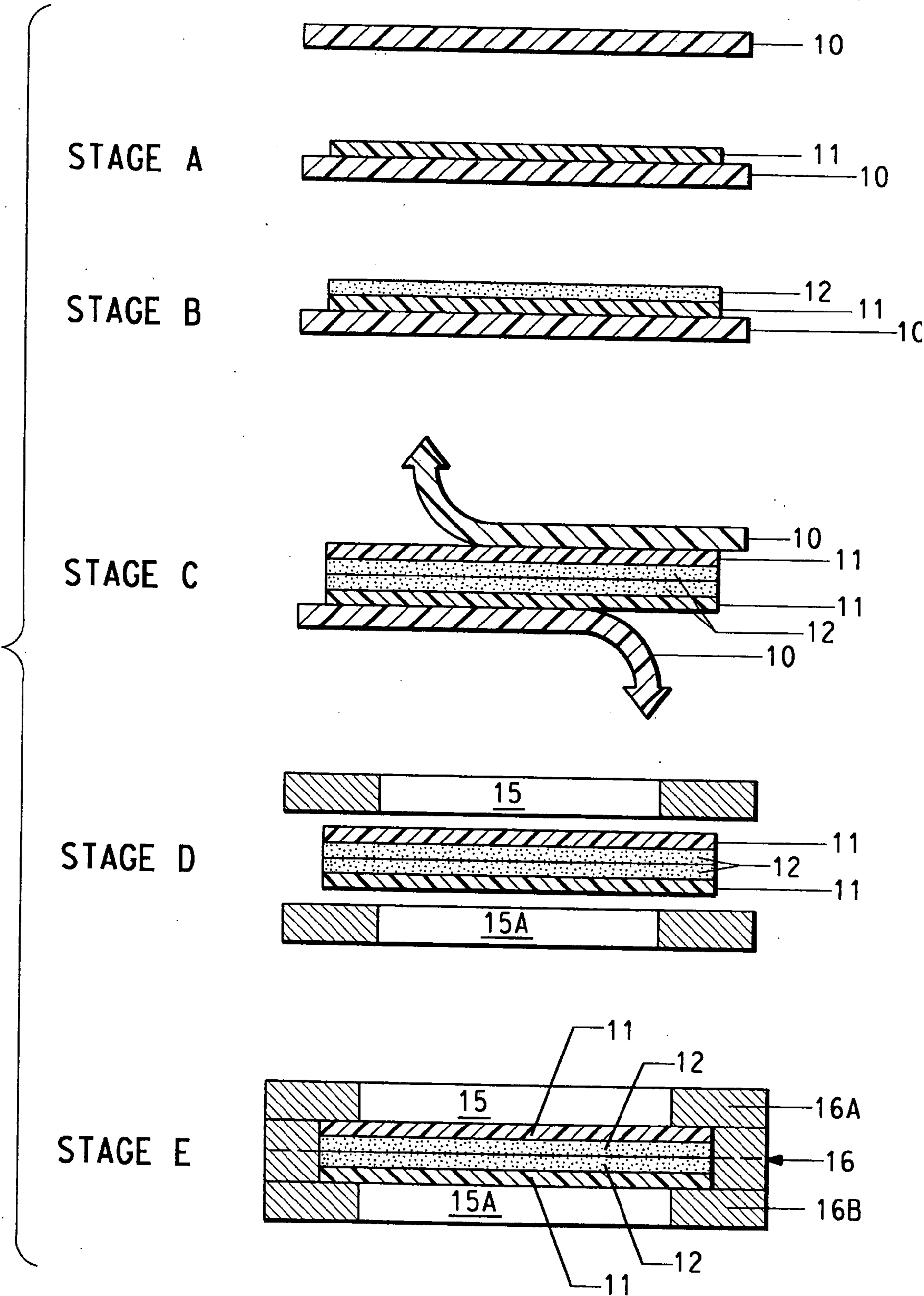


FIG 3

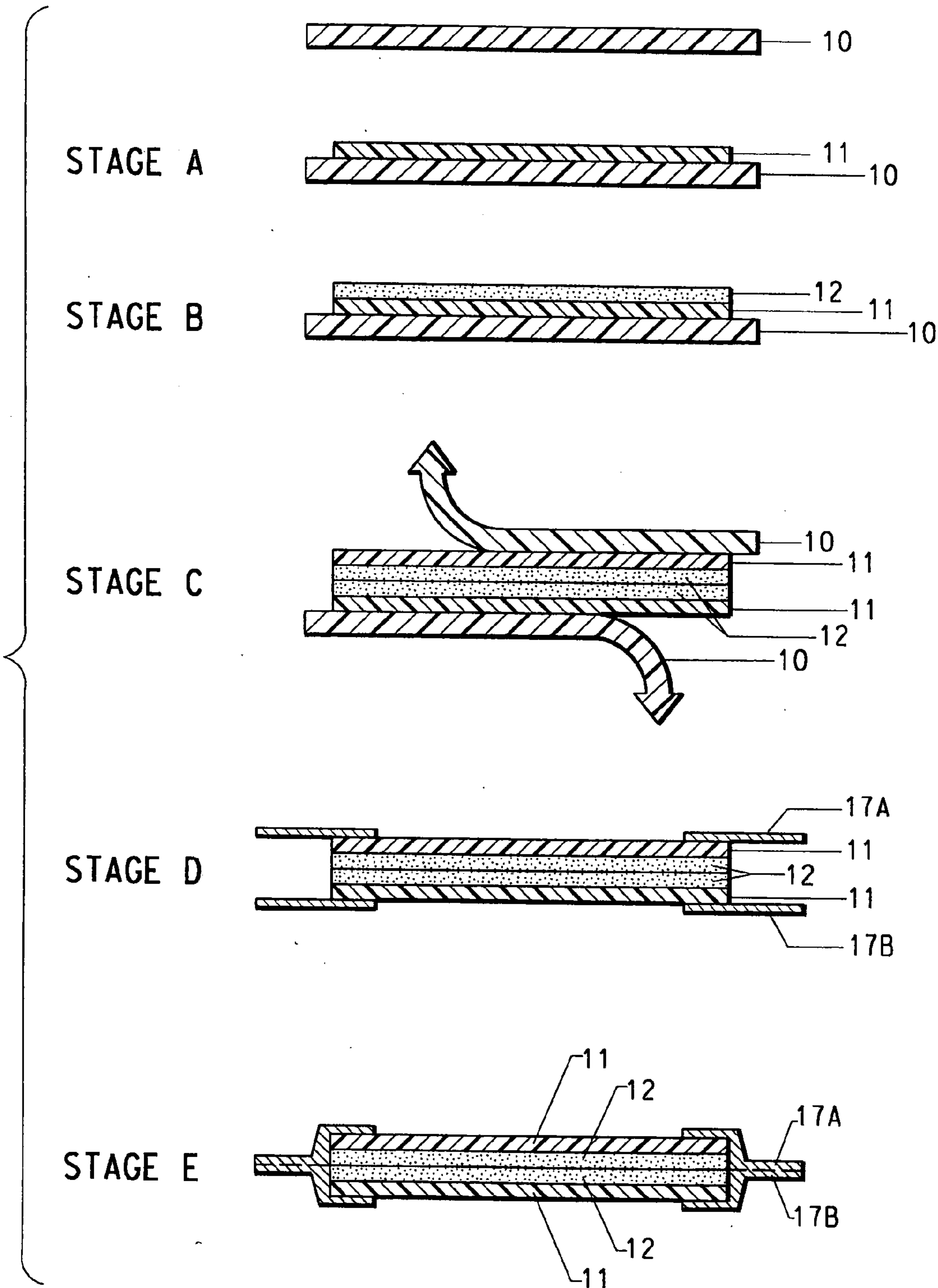
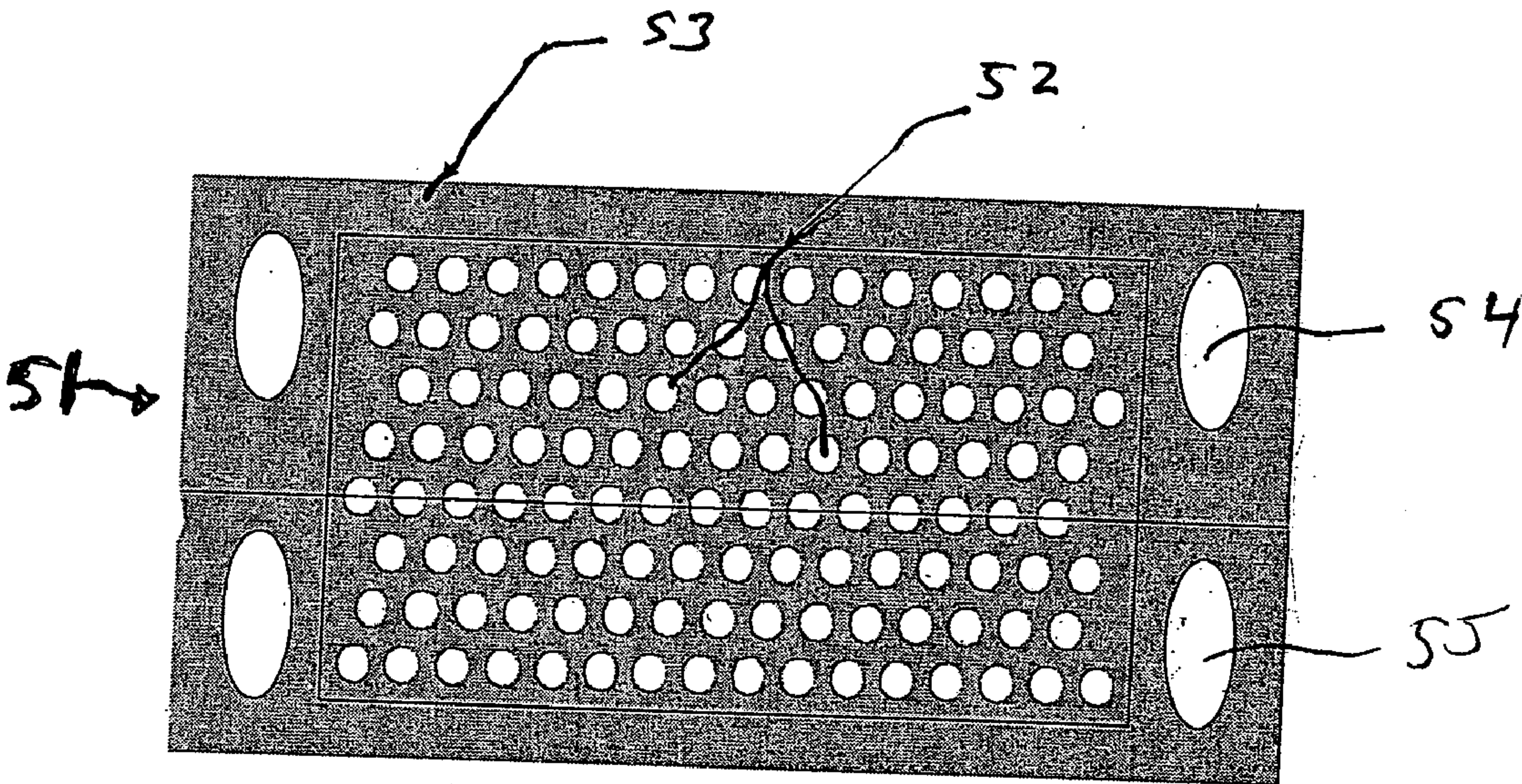


FIG. 4

FIGURE 5



FUEL CELL ELECTRODE ASSEMBLIES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a Continuation-in-Part of co-pending application Ser. No. 09/710,975, filed Nov. 10, 2000, which is a Continuation-in-Part of application Ser. No. 09/669,623, filed on Sep. 25, 2000, which is based on provisional application 60/155,578 filed Sep. 24, 1999.

BACKGROUND OF THE INVENTION

[0002] The components of a Proton Exchange Membrane (PEM) fuel cell Membrane Electrode Assembly (MEA) typically include a membrane, one or more catalyst layers and a gas diffusion layer. The membrane performs a proton transport function in the cell, and provides electronic isolation between anode and cathode, thus providing a means of keeping fuel and oxidant from mixing. Typically, the membrane is between 10 and 200 microns thick, and is prepared from ionomer resin. Representative of such structures are those described in Raistrick, U.S. Pat. No. 4,876,115.

[0003] The catalyst layers are generally included on both the anode and cathode. The catalyst is typically contained in a matrix of catalyst material and binder. The binder material can be ionomer, PTFE or other material to hold the catalyst powder in place. Typically, the catalyst layers are formed by suspending the catalyst particles in a solution of binder and solvents to form a slurry. The slurry is then coated, dried and cured. Alternative catalyst structures can be created that contain large surface areas of catalyst materials. The catalyst structures are typically between 2 and 50 microns thick.

[0004] The gas diffusion layers are included on both the anode and the cathode. Typically, the gas diffusion layers are constructed of carbon/graphite cloth, felt, paper, wire screen, or some other porous material. The diffusion layers are placed between the catalyst layers and the gas flow channels of the cell. The gas diffusion layer permits diffusion of reactant gas to the catalyst layer, and current collection from the catalyst layer. The gas diffusion layers are typically between 100 to 500 microns in thickness.

[0005] Currently, the construction of the above components into a fuel cell can be divided into two main categories, these involving attachment of the catalyst layer either to the membrane or to the gas diffusion layer. For example, Dhar, in U.S. Pat. No. 5,318,863, describes the preparation of solid polymer fuel cells having two gas diffusion electrodes, each coated on one side with a catalyst slurry and cured, followed by depositing a solution of proton conducting material on the central portion of the surface of each gas diffusion electrode and bringing the two electrodes together.

SUMMARY OF THE INVENTION

[0006] The present invention provides a membrane electrode assembly comprising at least two solution-cast components; and a catalyst layer adjacent to each side of the central layer.

[0007] The membrane electrode assemblies of the instant invention are preferably prepared by:

[0008] a. applying a catalyst slurry onto each of a first and a second removable decal;

[0009] b. drying each catalyst slurry to form a dried catalyst layer;

[0010] c. applying at least one ionomer solution layer on the resulting dried catalyst layer;

[0011] d. drying and at least partly curing each of the resulting layers of at least one ionomer solution;

[0012] e. bringing the ionomer layers on each of the first and second decal assemblies into contact to join the ionomer layers; and

[0013] f. removing the decals from the resulting assembly.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 is a schematic, cross-sectional illustration of the preparation of a membrane electrode assembly according to the present invention.

[0015] FIG. 2 is a schematic, cross-sectional illustration of an alternative preparation of an ionomer layer on the catalyst layer for use in a membrane electrode assembly according to the present invention.

[0016] FIG. 3 is a schematic, cross-sectional illustration of an alternative preparation of a membrane electrode assembly according to the present invention.

[0017] FIG. 4 is a schematic, cross-sectional illustration of still another alternative preparation of a membrane electrode assembly according to the present invention.

[0018] FIG. 5 is a plan view of a perforated reinforcing film that can be used in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0019] The process of the present invention involves fabrication of a membrane electrode assembly using a solution cast film. The membrane is formed in situ and is never a separate component. The membrane electrode assembly can be made by several ways, as schematically shown in the Figures, in which like numbers refer to like elements.

[0020] In FIG. 1, a blank decal 10 is coated with catalyst slurry 11, dried and preferably cured, to give a catalyst coated structure of Stage A. Decal materials can be selected from a wide variety of substrates. These materials can include cellulosic and polymeric materials. Generally, it is preferred that at least the decal material used to support the catalyst be porous, to permit uniform vapor release over the area coated with catalyst during the subsequent laminating steps. If polymeric films are used, those prepared from polytetrafluoroethylene (PTFE) and polyester are preferred. In general, preferred polyester materials include those prepared from biaxially oriented polyethylene terephthalate, and especially those bearing a silicone coating on at least one surface. These polyester films are particularly satisfactory as a substrate for the ionomer component of the present membrane electrode assemblies. Expanded PTFE has been found to be particularly satisfactory as a substrate for the catalyst component of the present structures.

[0021] The catalyst coated film is then further coated with ionomer solution 12 which is cured to give the structure of Stage B, which represents one half of a membrane electrode

assembly. Two such half assemblies can then be assembled by pressing them together, with either low heat or conventional hot pressing techniques. The half assemblies are preferably assembled together with perimeter sealing material **13**. This is illustrated as Stage C. As shown in this embodiment, the sealing material is partly embedded between the ionomer layers to anchor it in place. The amount of the sealing material embedded is a matter of design, varying, for example, with the material selected and the width of the perimeter seal. However, typically about 1-10% of the width of the perimeter sealing material can be beneficially embedded in the catalyst. The initial decal backing is then peeled away, as shown in Stage D, to give a finished MEA, as shown in Stage E. The resulting structure is an ionomer layer sandwiched between two catalyst layers. The solution cast ionomer layer becomes and serves the function of the membrane component of the electrode assembly. Several of the membrane electrode assemblies can be used to create an entire fuel cell.

[0022] After application of the catalyst and ionomer layers, each is dried and optionally cured at a temperature and for a time appropriate for that material. The specific times and temperatures will be known or readily determined by those skilled in the art. Curing of the ionomer can be carried out during final assembly of the MEA. An alternative fabrication sequence is illustrated in **FIG. 2**, in which catalyst layer **11** and ionomer layer **12** are applied to separate decal substrates **10** and **14**, respectively, as shown in Stages A and B in **FIG. 2**. These are then assembled, as shown in Stage C. This can be done with conventional laminating or hot press equipment. Thereafter, the decal originally bearing the ionomer is peeled away, as shown in Stage D, to give the half MEA, ready for hot pressing, as shown in Stage E.

[0023] Still another embodiment of the present invention is illustrated in **FIG. 3**. There, catalyst **11** and ionomer **12** are applied in Stages A and B, respectively. Two such half-MEAs are combined and the decals peeled away, as shown in Stage C. In Stages D and E, the laminate is assembled with diffusion media **15** and **15A**, together with perimeter seal **16**. The perimeter sealing material can be, and preferably is, applied to the edges of the gas diffusion medium in sufficient quantity to simultaneously infuse the diffusion media **15** and **15A** and fill the edge gap between them. The perimeter sealing material can be selected from a wide variety of thermoplastic and elastomeric materials, depending on the conditions for processing and expected use for the electrode assemblies. For example, to the extent that the sealing material is to be diffused into the gas diffusion media, the sealing material should be soluble or dispersible in an appropriate carrier. Specific materials, dependant on these considerations, will be evident to those skilled in the art. It is preferred that the perimeter sealing material partly infuse the diffusion media layer, as shown by shaded areas **16A** and **16B**.

[0024] A further variation of the present invention is shown in **FIG. 4**, in which the perimeter sealing material **17** is a laminate, prepared from layers **17A** and **17B**.

[0025] One advantage of the fabrication sequence shown in **FIGS. 3 and 4** is that registration and alignment of the two catalyst layers to be directly opposing each other is not needed as is the case of the embodiments shown in **FIGS. 1 & 2**. In fact the catalyst coated membrane can be formed

in a continuous process on a moving webs that are laminated together. Registration is then only required with the sealing material, as applied, for example, as element **16** in **FIG. 3** or as element **17** in **FIG. 4**. A further advantage of the embodiment shown in **FIG. 3** becomes apparent during the final assembly of a fuel cell stack. During this process normally sealing components, diffusion media, and catalyst coated membrane need to be registered and aligned with manifold holes in bipolar plates. With the fabrication sequence shown in **FIG. 3**, the seals and diffusion media are automatically registered and fixed in place. In fact, the manifold holes can be formed after the completed structure in **FIG. 3** is made by punching holes in the perimeter sealing containing region.

[0026] The advantages of the membrane electrode assembly fabrication methods used in the present invention include efficient use of expensive ionomer as well as precise application of the membrane. For example, in practicing this invention, the membrane layers can be made very thin (less than 25 microns). By creating thin membranes, the ionic resistance of the fuel cell is reduced considerably. However, when working with very thin membranes, pin hole defects are a concern and can cause premature failure of the cell. Although very thin membrane layers are created in situ, by assembling two separate halves of a membrane assembly, the chance for having a pinhole defect is substantially reduced. Any pinhole defects in the ionomer layers would have to exactly overlap in order to result in a pinhole through the entire membrane of the assembly.

[0027] Durability is another advantage over membranes made, for example, with a unitary expanded PTFE support structure. Delamination over time of the ionomer from the expanded PTFE could result in a reactant leak through the membrane component. This failure mechanism is not possible by using this invention. In addition, it may be easier to recycle the components made by the use of this invention as compared to membrane electrode assemblies made using expanded PTFE re-enforcement in the membrane. Further, substantial cost savings can be realized using the instant process, since ionomer material need not be used in the sealing region. Moreover, a different material can be used in the perimetral regions of the final assemblies which can be stronger than the ionomer.

[0028] In a preferred embodiment of the present invention, a sealing material is interposed between two solution-cast components, the sealing material having a solid perimeter and at least one perforation formed in a central portion. Preferably, a plurality of perforations are formed in the central portion. Such a reinforcing film is illustrated in **FIG. 5**, which is a plan view of a film **51**, having perforations **52** and unperforated perimetral section **53**. In this embodiment, additional apertures **54** and **55** are formed in the sealing material to allow passages of gases when the components are incorporated into a fuel cell.

[0029] The sealing material is thin, and the dimensions are generally the same as the thickness of the ionomer layer of the resulting MEA. For high power density hydrogen fed fuel cells, the thickness of the low creep sealing material is about from 10 to 30 microns.

[0030] At least one perforation is formed in the sealing material. Preferably, many perforations are formed in the sealing material, and comprise a large percentage of the

available “active area” of the MEA, so that conductive losses are minimized. When the opening size of the perforation hole is small (on the order of the ionomer layer thickness), the maximum reinforcing behavior will be achieved. The reinforcing behavior is largely a result of increasing the creep resistance of the membrane component. Other reinforcing structures introduced in the ionomer layer component, such as expanded Teflon fluoropolymer, can increase the tensile strength of the resulting membrane, however Teflon has a low creep resistance similar to that of the ionomer. Thus such fluoropolymers offer little improvements in the long term lifetime of the MEA structure since the large compressive forces found in the fuel cell result in the creep of the ionomer layer and a resulting shorting of the two opposing electrode faces. This shorting further manifests itself in holes in the structure, and ultimate MEA failure. In the preferred structure of the present invention, the compressive forces are largely borne by the areas of the active area that are protected by the interspersed reinforcing film. In this particular area, the ionomer layer will creep as in the un-reinforced structure, however, the re-enforcing film will prevent the two opposing electrode faces from touching, and further will prevent any pin-hole from forming. When the size of the perforation holes is large, the reinforcing behavior of the reinforcing film is less, however, the perimeter of the active area will have the important reinforcing benefit of the interspersed reinforcing film.

[0031] The perforations can be formed by a wide variety of known techniques. The perforations can be formed by a variety of known techniques, depending in the size and number of perforations. For a single central perforation, conventional die cutting techniques can be used. For a plurality of perforations, other techniques such as photolithography can be used to form perforations if a detailed pattern or small apertures are desired. The reinforcing film can be prepared from a variety of materials characterized by low creep behavior. Particularly satisfactory films include those consisting essentially of polyimide.

[0032] The present invention is further illustrated by the following specific examples.

EXAMPLE 1

[0033] A Membrane Electrode Assembly was prepared by first preparing the component parts and then assembling the parts.

[0034] NAFION™ WEB Formation

[0035] A coating of high viscosity NAFION™ ionomer solution was applied at a wet layer thickness of about 8 mils on a silicone coated film of biaxially oriented polyethylene terephthalate, using a knife over roll wet layer application tool. The ionomer solution was then dried and cured by passing the web under infrared lamps of about 3 kW located 1 foot away and a blower moving air over the web for cooling. The web speed was about 0.25 meter/min. The resulting NAFION™ film was 10 microns in thickness

[0036] CATALYST LAYER WEB Formation

[0037] A coating of catalyst ink was applied onto an expanded Teflon® fluoropolymer film with a reinforcing backing layer. The catalyst ink was prepared by ball milling a mixture of ionomer solution and 50 weight % of platinum supported on carbon, commercially available from Engelhard. The web was dried and cured using infrared lamps as with the NAFION ionomer web:

[0038] ACTIVE WEB Formation

[0039] The NAFION™ WEB and CATALYST LAYER WEB were then laminated together through a roll laminator at 0.3 meters/min with 50 psi on 2 four-inch diameter pistons one steel roller heated to 250° F. and one rubber roller not heated. Coupons of each material were cut out and the PET backing layer stripped off of the coupon bearing the ionomer. The coupons were assembled with the ionomer layers adjacent with a frame of polyimide film. The NAFION™ and catalyst surfaces were pressed together with solid backing plates. A pressure of about 25,000 lbs. was applied to the resulting assembly over a 9-10 square inch area to bond the inner components.

[0040] The resulting assembly was tested in a fuel cell and found to exhibit a high power density, and a durability of over 2000 hours.

EXAMPLE 2

[0041] The general procedure of Example 1 was repeated, except that a perimeter sealing layer was prepared and inserted between the two layers of ionomer. Specifically, a sheet of 0.5 mil (12 micron) thick KAPTON-14N polyimide film was coated with photolithography resist and masked to form a close-packed pattern of 2 mil (50 micron) diameter holes. After development of the photoresist, the holes were etched through completely to form the pattern of holes. These holes are formed in the central “active area” only and the perimeter area remained solid for the fuel cell stack seals to actuate upon. Two appropriately sized coupons of a laminate as prepared in Example 1 were laminated on both faces of the perforated KAPTON film, at a force of 500 psi for 3 minutes at 160° C., so that the ionomer layers were fused through the perforation hole openings. After laminating, the original backing layer was removed to reveal the finished catalyst coated reinforced membrane.

[0042] The resulting assembly is tested in a fuel cell, and is found to exhibit high power density, and a durability of over 2000 hours.

I claim:

1. A membrane electrode assembly consisting essentially of a central layer of ionomer material comprising at least two solution-cast ionomer components; and a catalyst layer adjacent to each side of the central layer.

2. A membrane electrode assembly of claim 1 wherein the assembly is prepared by

- a. applying a catalyst slurry onto each of a first and a second removable decal;
- b. drying each catalyst slurry to form a dried catalyst layer;
- c. applying at least one ionomer solution layer on each resulting dried catalyst layer;
- d. drying and at least partly curing each of the resulting layers of at least one ionomer solution;
- e. bringing the ionomer layers on each of the first and second decal assemblies into contact to join the ionomer layers; and
- f. removing the decals from the resulting assembly.

3. A membrane electrode assembly of claim 1 wherein the assembly is prepared by

- a. applying a catalyst slurry onto a first decal;
- b. drying the catalyst slurry;
- c. applying a solution of at least one ionomer to a second decal;
- d. drying and at least partly curing the resulting applied ionomer solution;
- e. joining the two decal assemblies with the ionomer and catalyst layers in contact with each other; and
- f. removing the decal from the ionomer layer to form a first membrane electrode assembly component;
- g. repeating steps (a) to (f) to form a second membrane electrode assembly component, and combining the resulting two membrane electrode components by bringing the ionomer layers of each component into contact to join the ionomer layers; and removing the decals from the resulting assembly.

4. A membrane electrode assembly of claim 1 further comprising a perimeter sealing material between the at least two solution-cast ionomer components, the sealing material having a solid perimeter and a central portion having at least one perforation formed therein.

5. A membrane electrode assembly of claim 4 wherein the sealing material consists essentially of polyimide.

6. A membrane electrode assembly of claim 4 having a plurality of perforations formed in the central portion of the sealing material.

7. A membrane electrode assembly of claim 6 wherein the perforations in the central portion of the sealing material have a diameter of about from 3 to 10 mils.

8. A membrane electrode assembly of claim 4 wherein the thickness of the sealing material is about from 10 to 30 microns.

9. A membrane electrode assembly of claim 4 wherein the perimeter sealing material has a thickness of about from 10 to 30 microns.

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