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(54) **SOLID OXIDE FUEL CELL HAVING
INTERNAL ACTIVE LAYERS**

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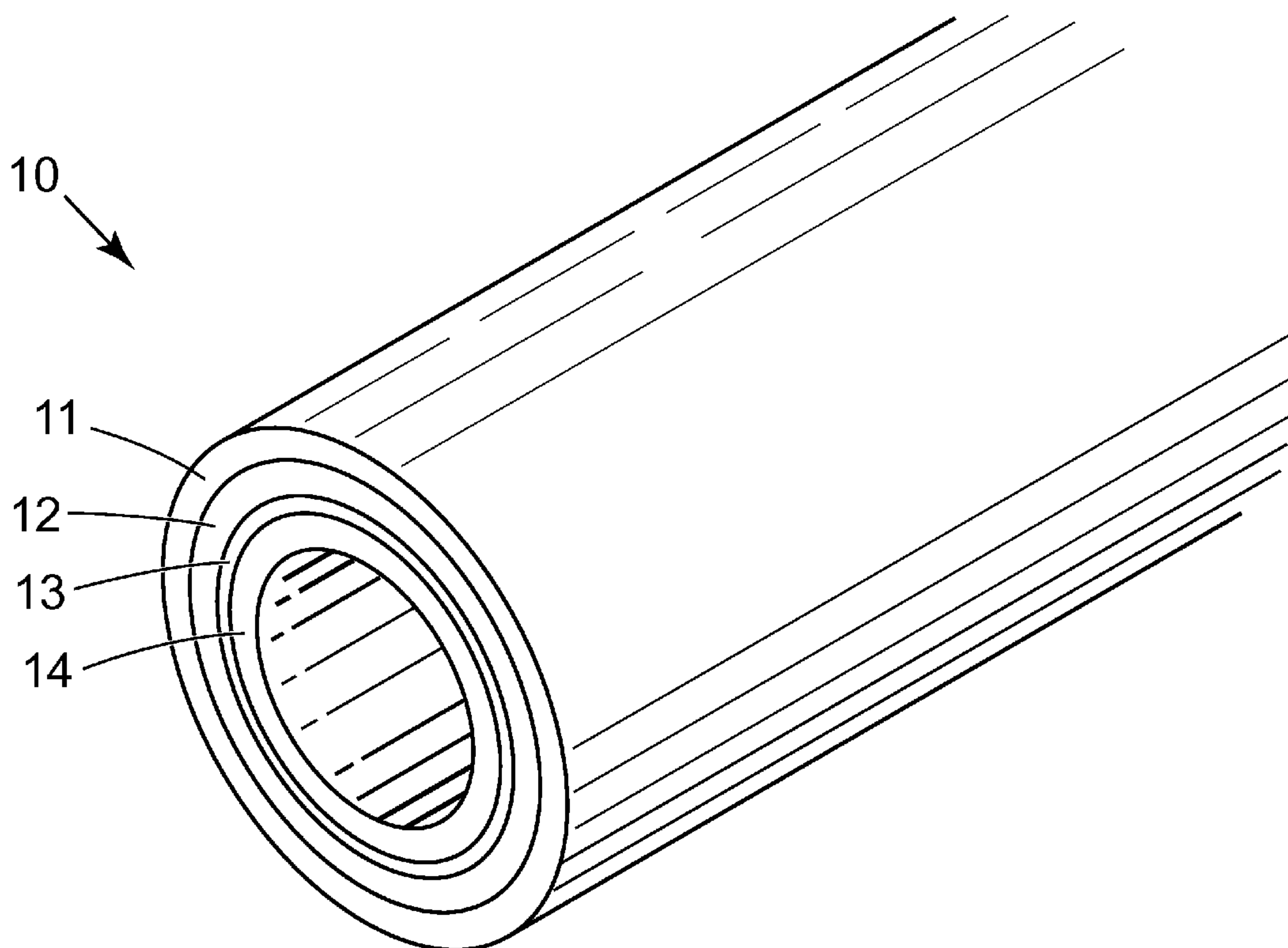
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(57) **ABSTRACT**

A solid oxide electrochemical device includes: a porous support structure having a porous outer surface and a tubular porous inner surface; a first electrode layer disposed radially inside the tubular porous inner surface and supported by the porous support structure; a dense electrolyte layer disposed radially inside and supported by the first electrode composition; and a second electrode layer disposed radially inside and supported by the dense electrolyte.



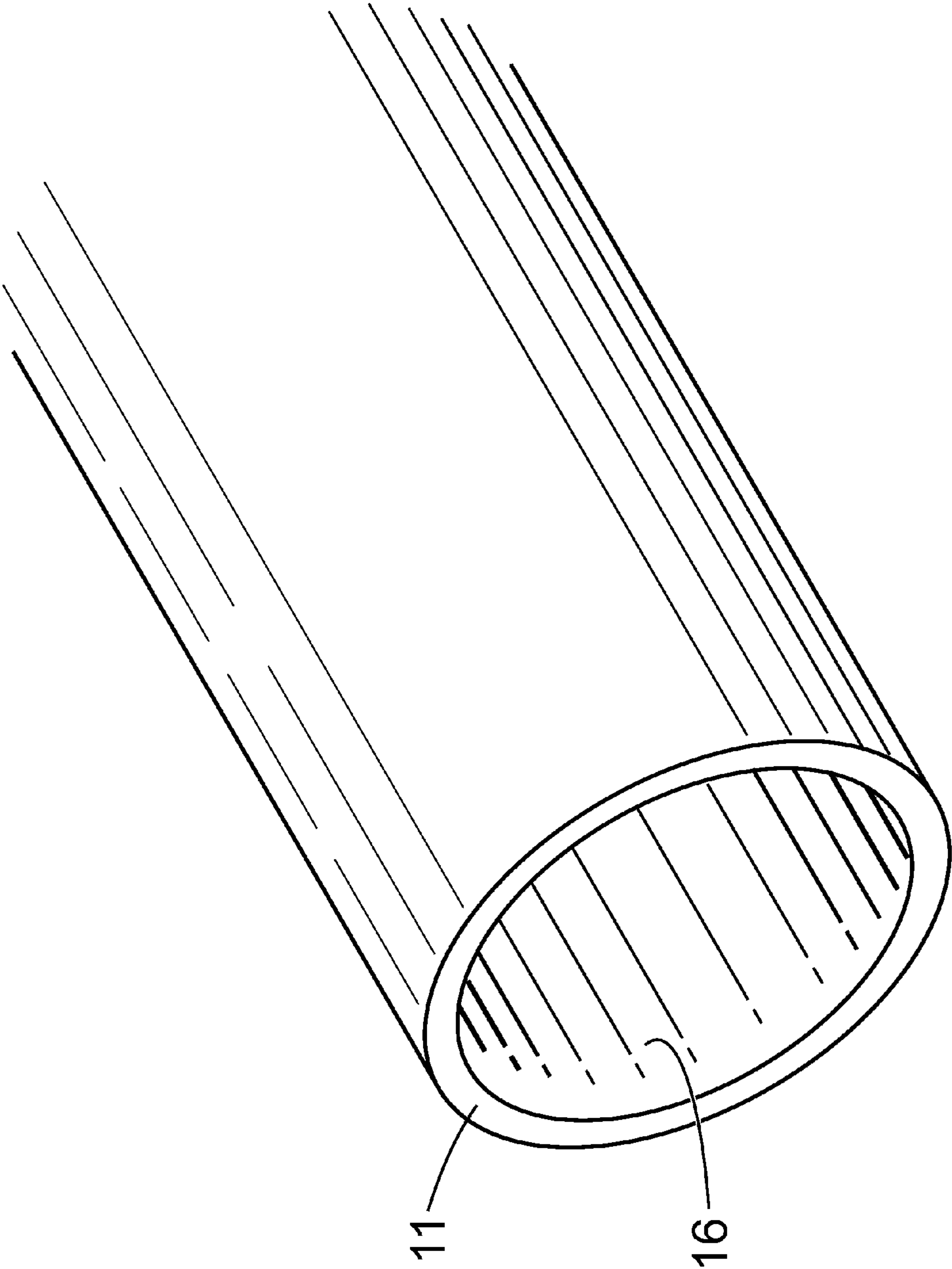


FIG. 1

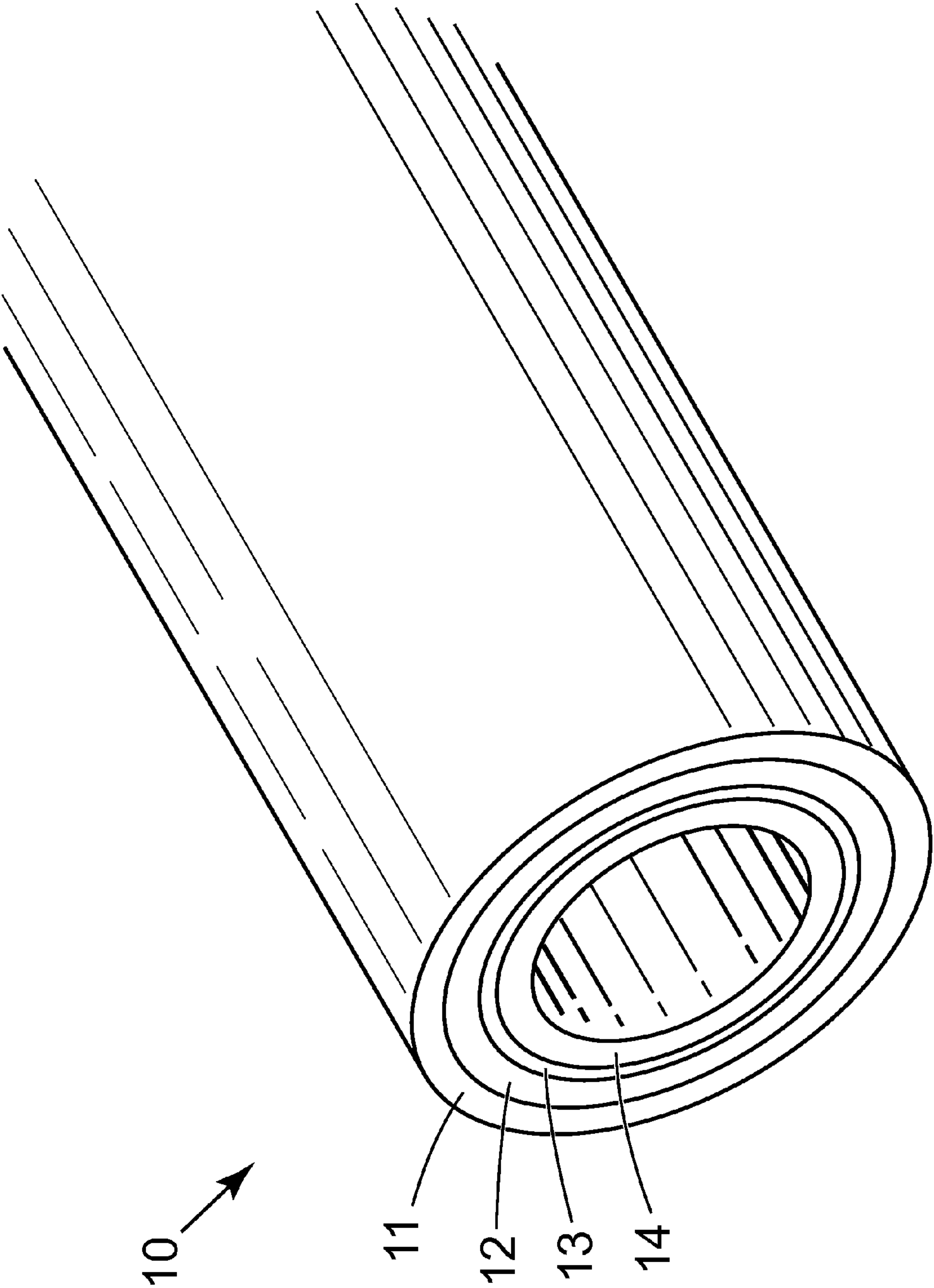


FIG. 2

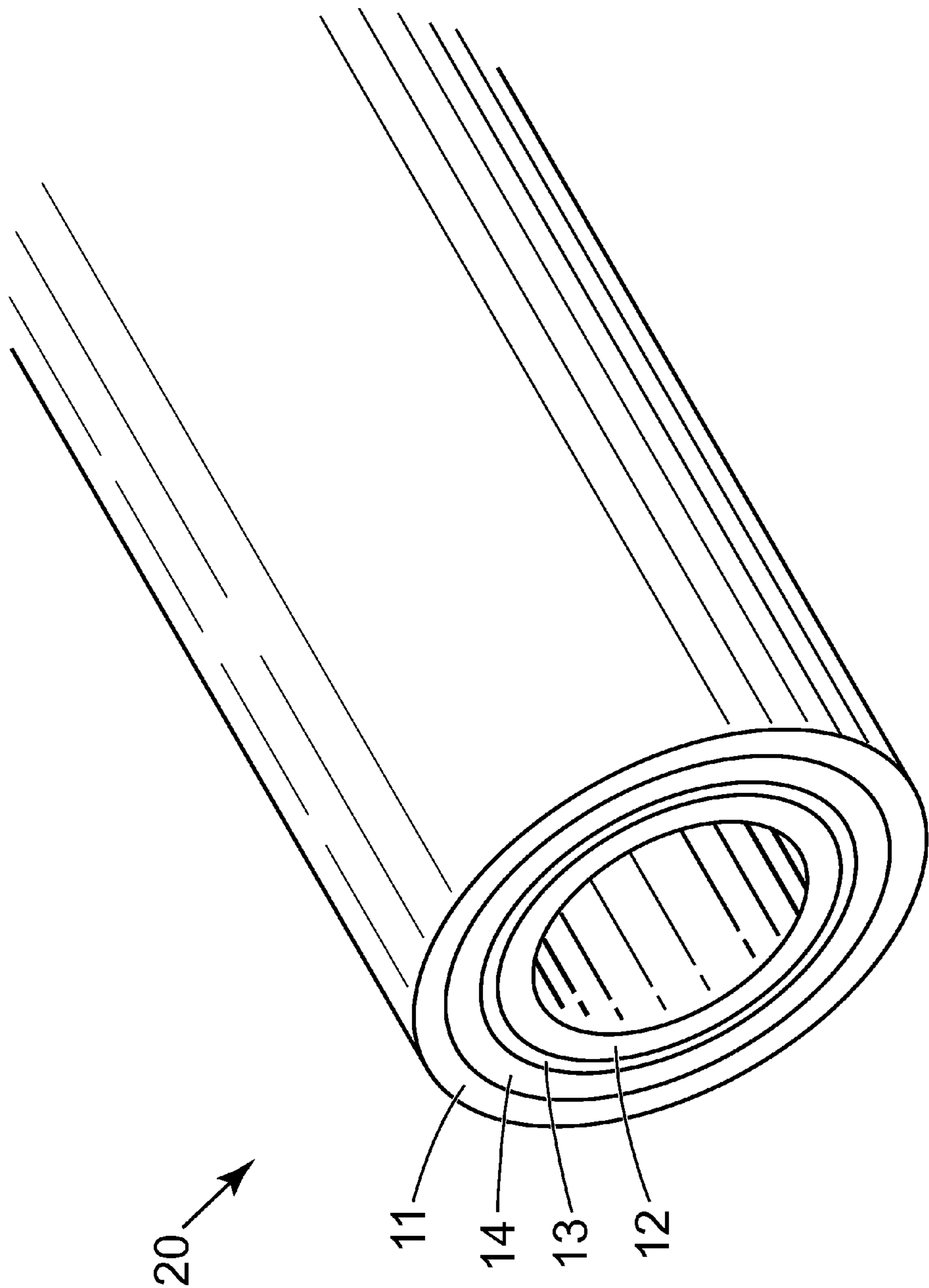


FIG. 3

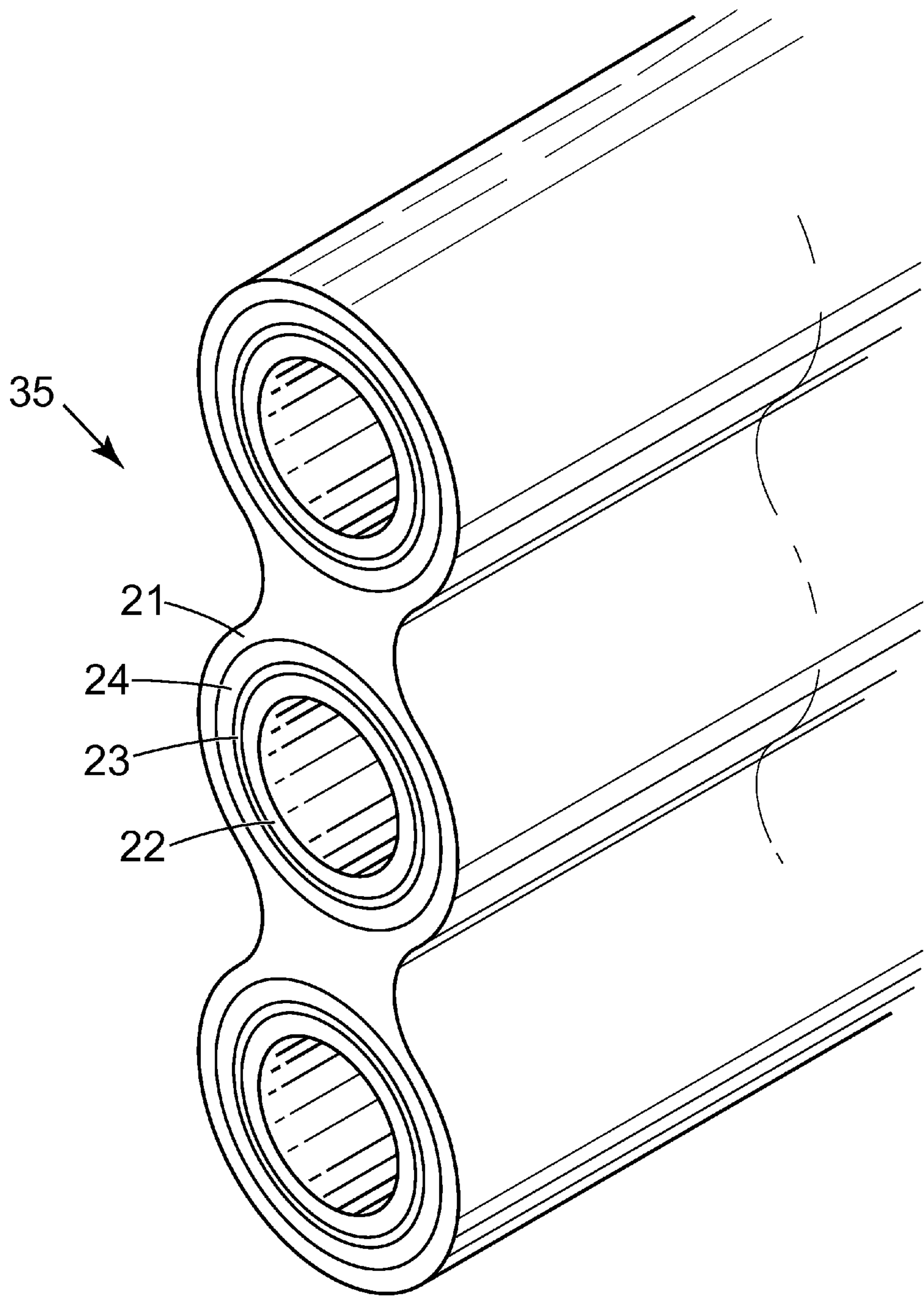


FIG. 6

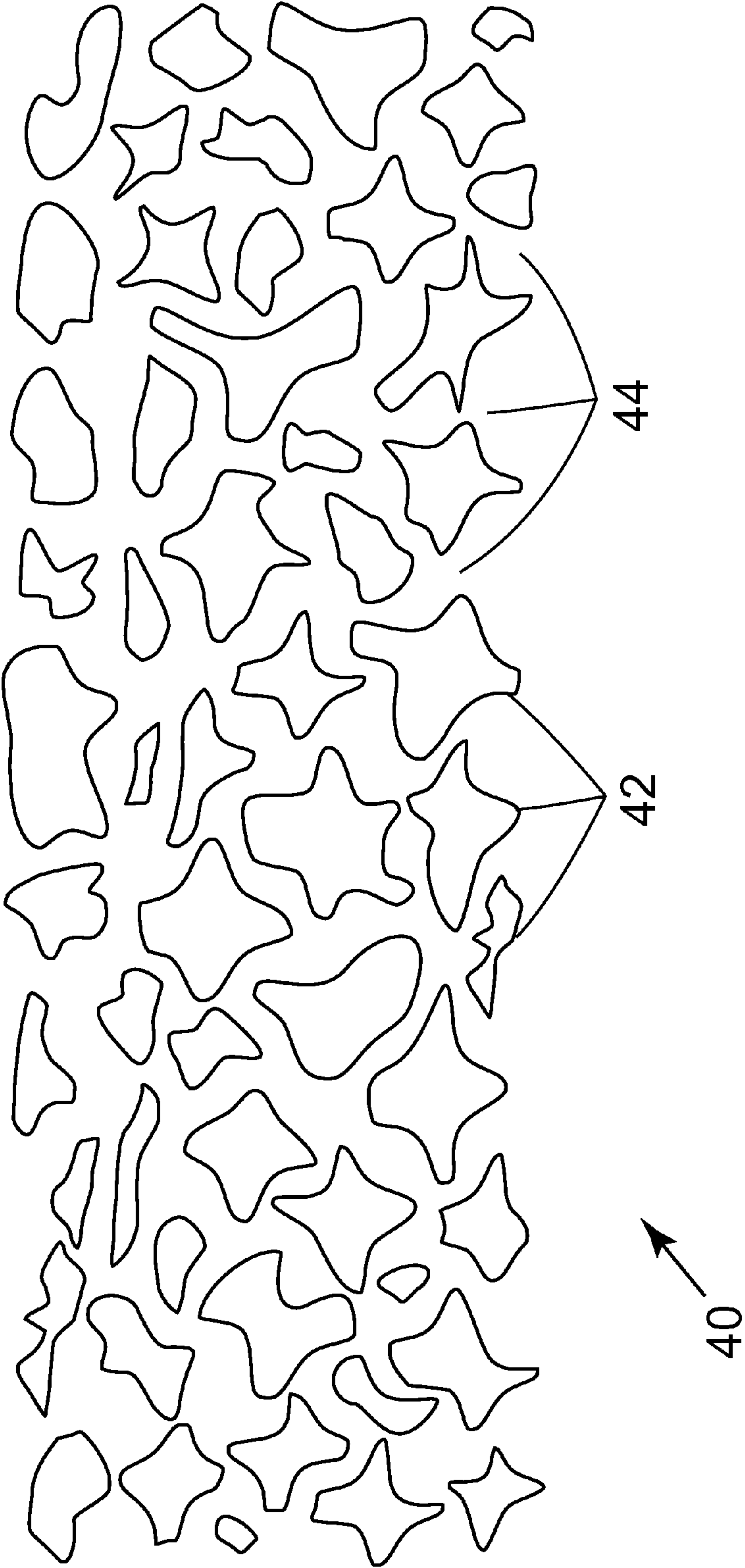


FIG. 7

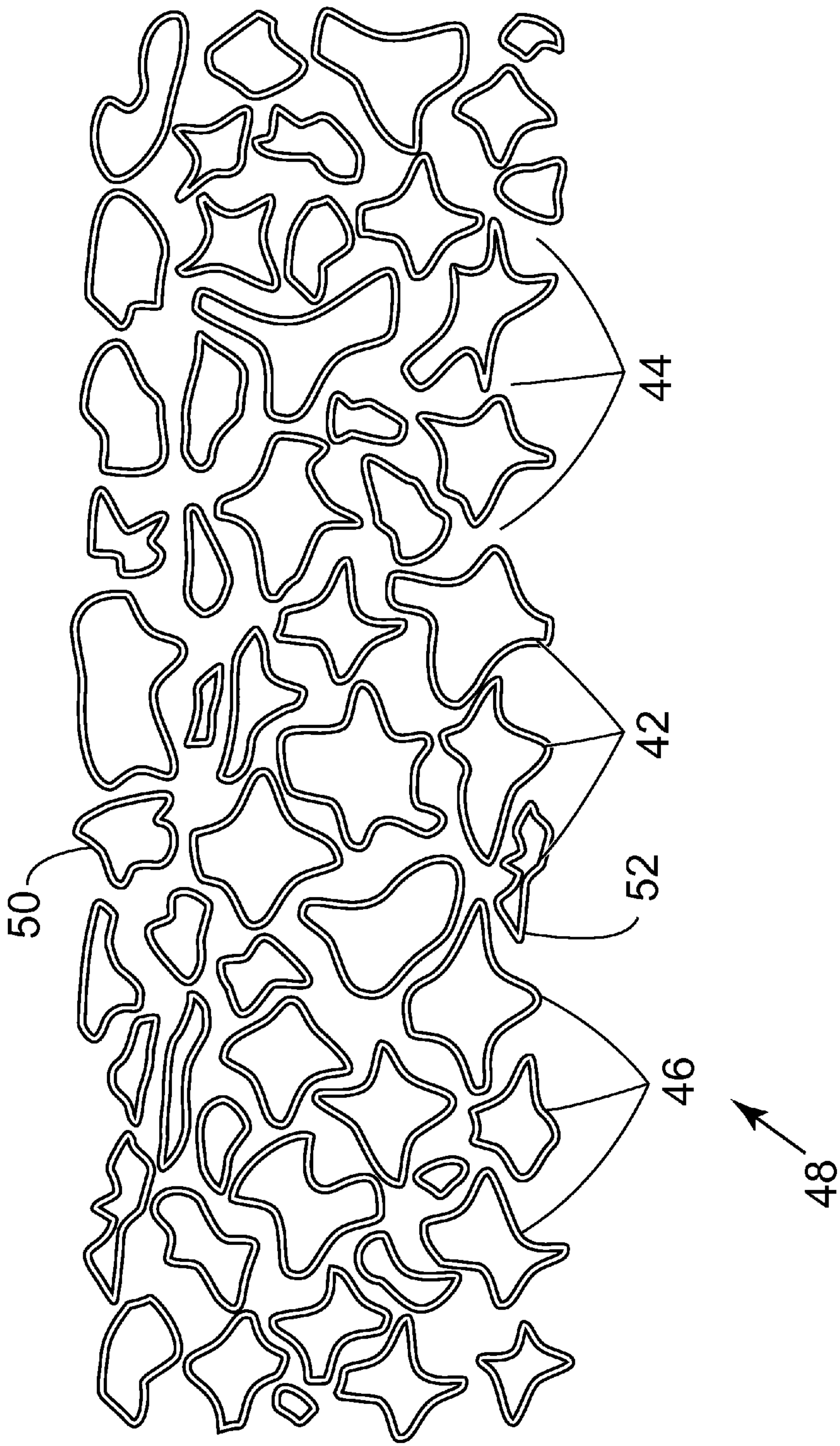


FIG. 8

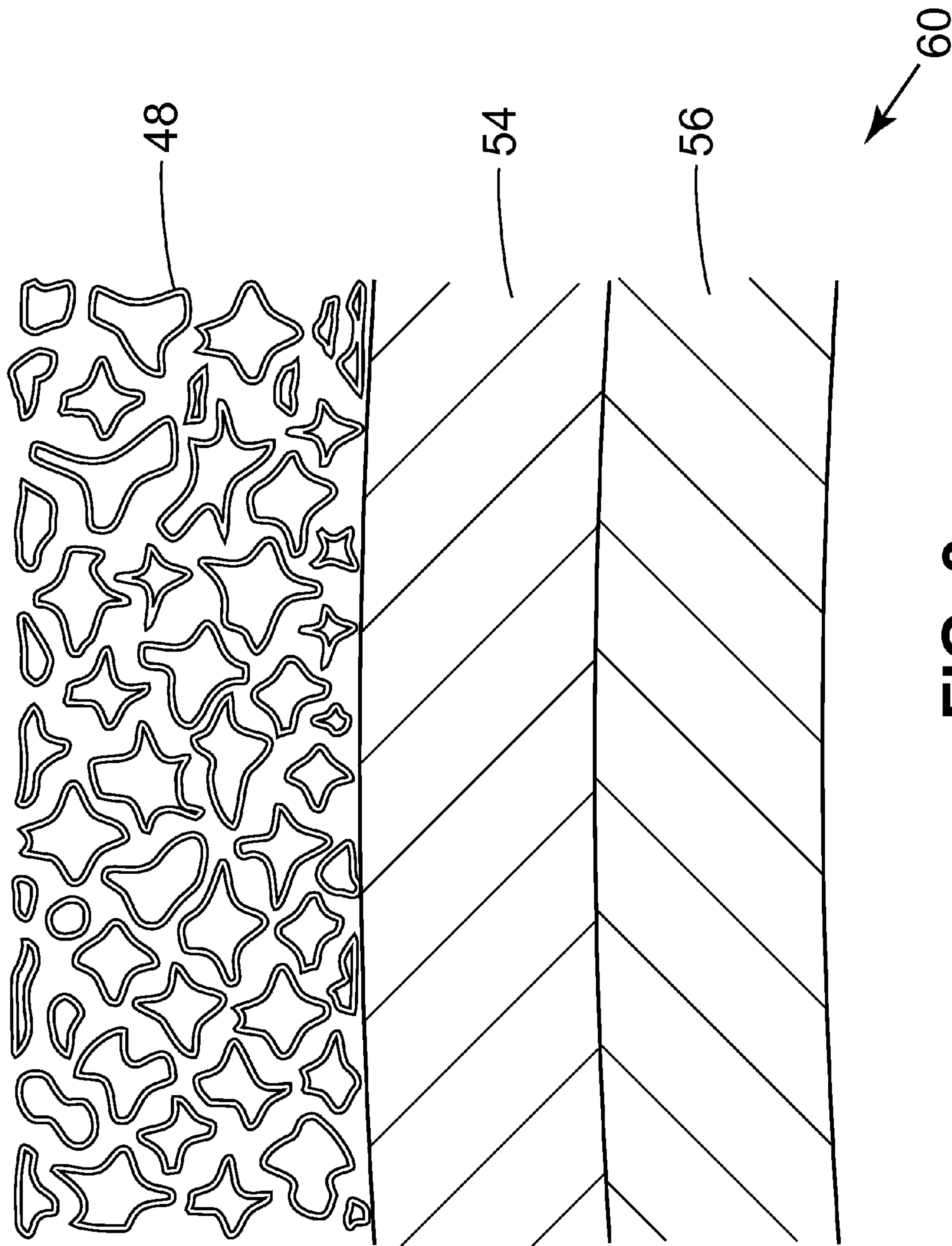


FIG. 9

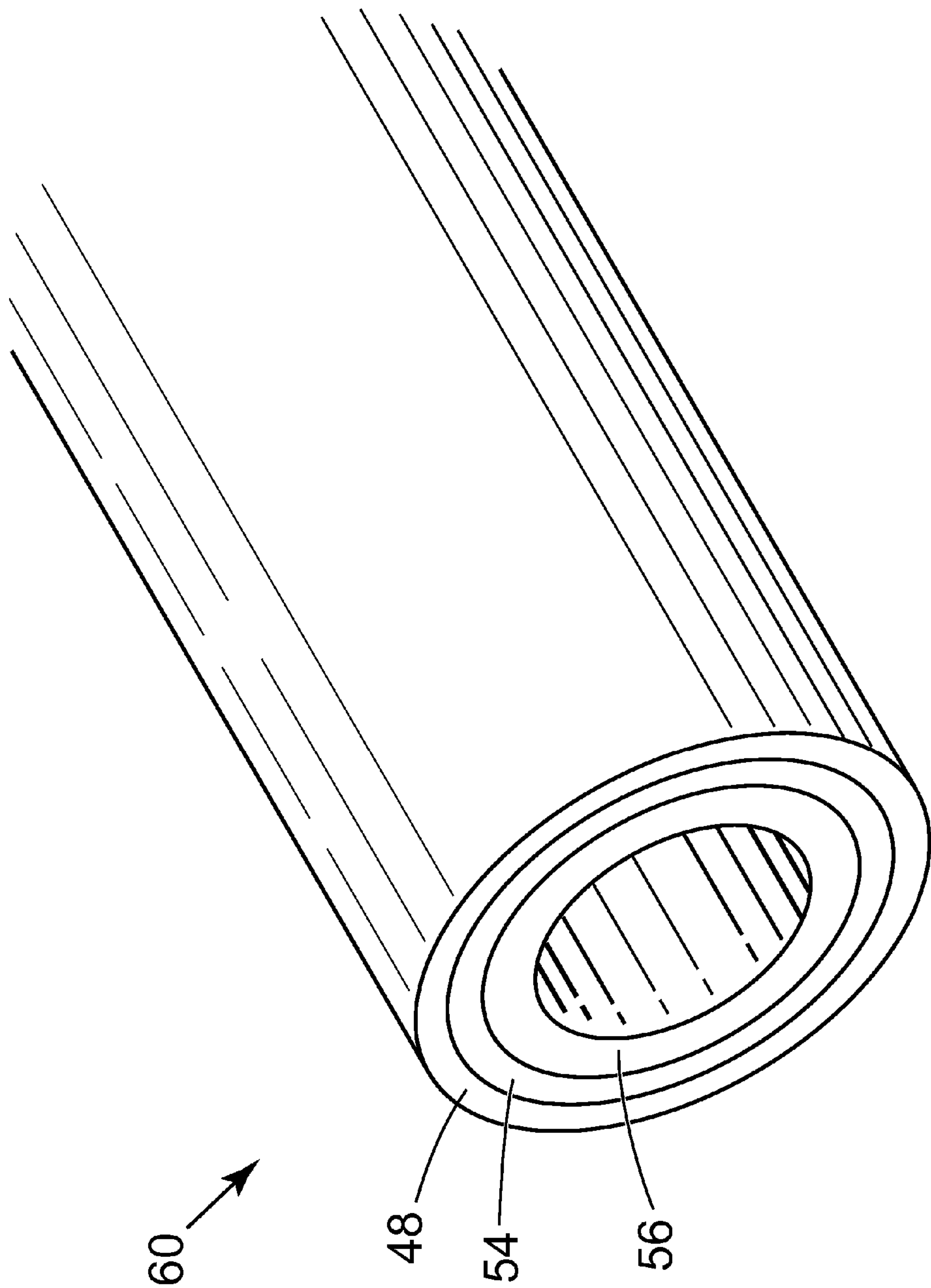


FIG. 10

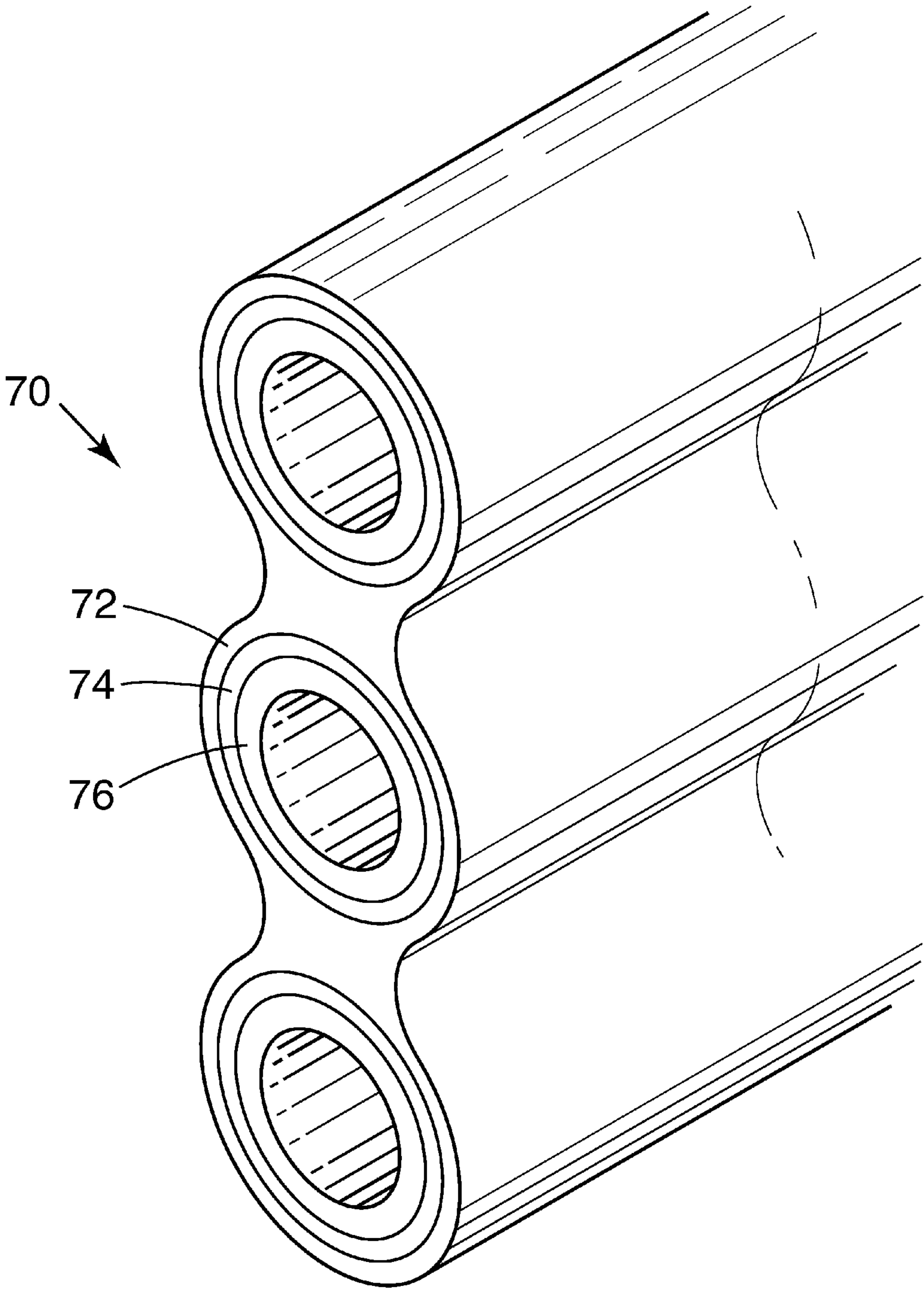


FIG. 11

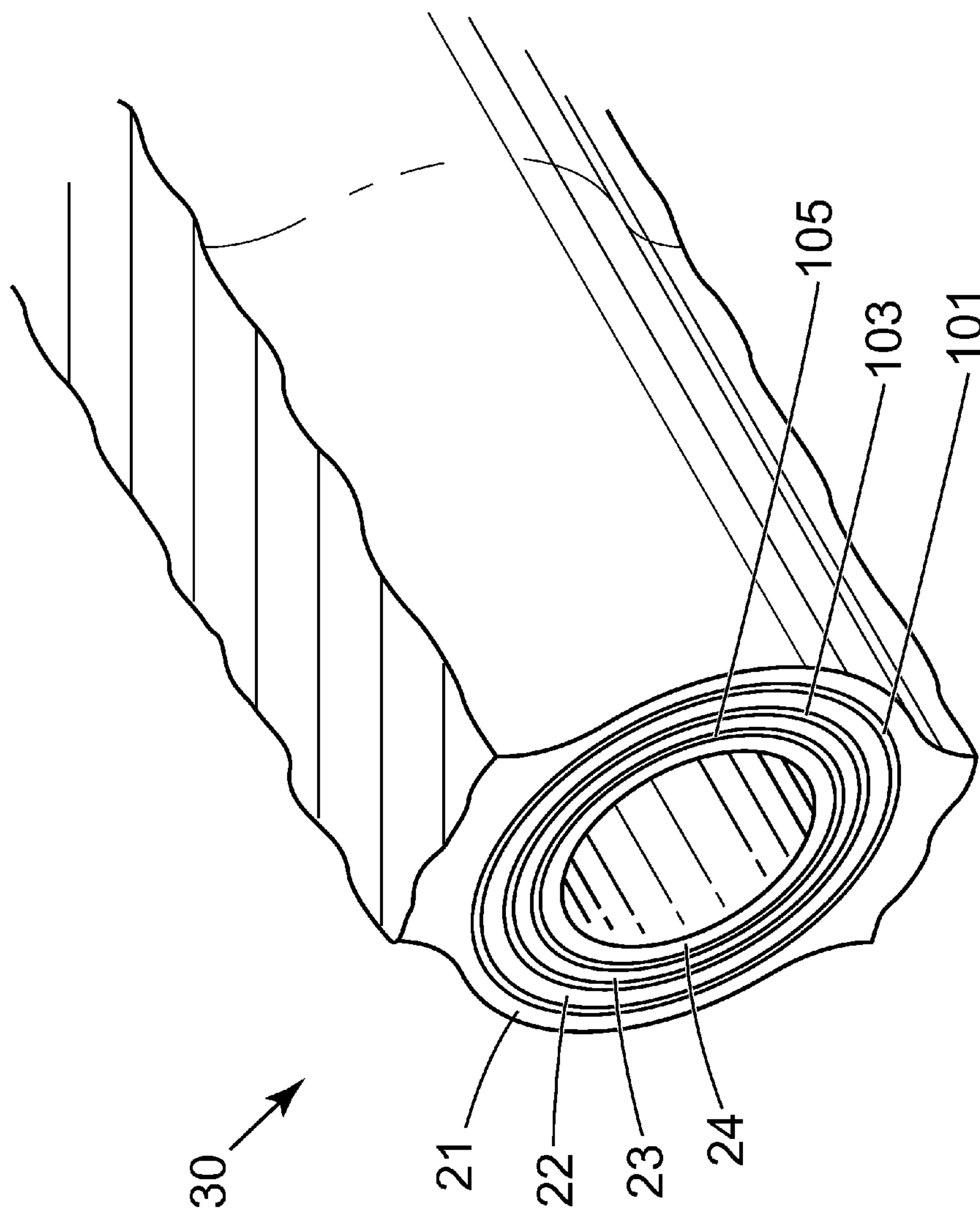


FIG. 13

SOLID OXIDE FUEL CELL HAVING INTERNAL ACTIVE LAYERS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of U.S. patent application Ser. No. 11/103,333 entitled “Stack Configurations for Tubular Solid Oxide Fuel Cells”, filed on Apr. 11, 2005, the entire disclosure of which is incorporated herein by reference.

[0002] Specifically referenced is U.S. patent application Ser. No. 11/314,111 entitled “Solid Oxide Fuel Cell and Stack Configuration”, filed on Dec. 21, 2005, the entire disclosure of which is incorporated herein by reference. Also specifically referenced is U.S. patent application Ser. No. 11/171,655 entitled “Tubular Solid Oxide Fuel Cell Current Collector”, filed on Jun. 30, 2005, the entire disclosure of which is incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0003] The United States Government has rights in this invention pursuant to contract no. DE-AC05-00OR22725 between the United States Department of Energy and UT-Battelle, LLC.

NAMES OF PARTIES TO A JOINT RESEARCH AGREEMENT

[0004] This invention arose under Work for Others Agreement No. ERD 03-2338 between UT-Battelle, LLC and Worldwide Energy, Inc.

BACKGROUND OF THE INVENTION

[0005] Devices commonly known as fuel cells comprise arrays of plates or tubes (elements) that directly convert to electricity (electric power) the energy released by oxidation of hydrogen. Simplistically, the elements comprise layers, including anodes, cathodes, and an oxygen-permeable layer therebetween. Currently available tubular solid oxide fuel cell (TSOFC) elements are limited to those having an internal support structure and external active layers such as anode, electrolyte, and cathode structures, for example. Active layers are disposed on the outer surface of the support. The term TSOFC, for purposes of describing the present invention, also includes electrolyzers.

[0006] In most cases, the internal support structure comprises a tubular, porous, ceramic cathode. Since the cathode is the support member of the device, it must be of a sufficiently thick cross-section to provide requisite strength. A layer of dense, gas-tight electrolyte—yttria-stabilized zirconia (YSZ) for example—is deposited on the external surface of the cathode, and a layer of anode—Ni—YSZ for example—is deposited on the surface of the electrolyte layer. Fabrication of currently available TSOFC is expensive in terms of resources and time.

BRIEF SUMMARY OF THE INVENTION

[0007] In accordance with one aspect of the present invention, the foregoing and other objects are achieved by a solid oxide electrochemical device that includes: a porous support structure having a porous outer surface and a tubular porous

inner surface; a first electrode layer disposed radially inside the tubular porous inner surface and supported by the porous support structure; a dense electrolyte layer disposed radially inside and supported by the first electrode composition; and a second electrode layer disposed radially inside and supported by the dense electrolyte.

[0008] In accordance with another aspect of the present invention, a solid oxide electrochemical device includes: a composite electrode including 1) a porous support structure having pores, a porous outer surface, and a tubular porous inner surface and 2) a first electrode layer disposed throughout the pores, the porous outer surface, and the tubular porous inner surface and supported by the porous support structure; a dense electrolyte layer disposed radially inside and supported by the composite electrode; and a second electrode layer disposed radially inside and supported by the dense electrolyte.

[0009] Solid oxide electrochemical devices include fuel cells and electrolyzers.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. 1 is an oblique, not-to-scale view of a portion of a TSOFC support tube in accordance with an embodiment of the present invention.

[0011] FIG. 2 is an oblique, not-to-scale view of a portion of a TSOFC in accordance with an embodiment of the present invention.

[0012] FIG. 3 is an oblique, not-to-scale view of a portion of a TSOFC in accordance with an embodiment of the present invention.

[0013] FIG. 4 is an oblique, not-to-scale view of a portion of a TSOFC support tube sheet in accordance with an embodiment of the present invention.

[0014] FIG. 5 is an oblique, not-to-scale view of a portion of a TSOFC tube sheet in accordance with an embodiment of the present invention.

[0015] FIG. 6 is an oblique, not-to-scale view of a portion of a TSOFC tube sheet in accordance with an embodiment of the present invention.

[0016] FIG. 7 is a magnified, two-dimensional, schematic, sectional view of a portion of a TSOFC porous support in accordance with an embodiment of the present invention.

[0017] FIG. 8 is a magnified, two-dimensional, schematic, sectional view of a portion of a TSOFC composite porous support-anode in accordance with an embodiment of the present invention.

[0018] FIG. 9 is a magnified, two-dimensional, schematic, sectional view of a portion of a TSOFC having a composite porous support-anode in accordance with an embodiment of the present invention.

[0019] FIG. 10 is an oblique, not-to-scale view of a portion of a TSOFC having a composite porous support-anode in accordance with an embodiment of the present invention.

[0020] FIG. 11 is an oblique, not-to-scale view of a portion of a TSOFC tube sheet having a composite porous support-anode in accordance with an embodiment of the present invention.

[0021] FIG. 12 is an oblique, not-to-scale view of a portion of a TSOFC tube having interlayers in accordance with an embodiment of the present invention.

[0022] FIG. 13 is an oblique, not-to-scale view of a portion of a TSOFC tube sheet having interlayers in accordance with an embodiment of the present invention.

[0023] Several elements that are essentially the same across multiple figs. are assigned like call-out numerals.

[0024] For a better understanding of the present invention, together with other and further objects, advantages and capabilities thereof, reference is made to the following disclosure and appended claims in connection with the above-described drawings.

DETAILED DESCRIPTION OF THE INVENTION

[0025] Referring to FIG. 1 in a basic embodiment, the invention begins with a porous support tube 11 that may, for example, comprise any porous, sinterable material selected from the group consisting of a non-noble transition metal, metal alloy, and a cermet incorporating one or more of a non-noble transition metal and a non-noble transition metal alloy, preferably a stainless steel, and more preferably a ferritic and/or austenitic stainless steel. The support tube 11 can be of any diameter or length with a wall thickness no greater than about 4 mm, preferably no greater than 1 mm. In addition, the support should have an average pore size in the range of 1 to 30 μm , preferably 1.5 to 20 μm , and more preferably 2 to 15 μm . Moreover, the support should have an average pore volume in the range of 20 to 50 volume percent and it should be electrically conductive at all operating temperatures. The support tube 11 can be formed in any suitable cross-sectional shape, including circular, elliptical, triangular, rectangular, irregular, or any other desired shape. A round shape, especially an essentially circular shape as shown in FIG. 1, accommodates uniform deposition of layers on the inner surface 16.

[0026] The porous support tube 11 may be prepared by conventional powder metallurgy techniques, such as molding, extrusion, casting, forging, isostatic compression, etc. The support tube 11 should be open on both ends.

[0027] Referring to FIG. 2, in some accordance with the present invention, active fuel cell membrane layers are deposited as layers 12, 13, 14 on the inside (inner) surface 16 of the porous support tube 11 to form an annular TSOFC 10. It can be seen that each successive layer supports the layers that are subsequently deposited thereon.

[0028] The first active fuel cell membrane layer 12 is an anode material, which can be any anode material, but is preferably comprised of a cermet composition. Examples of suitable cermet compositions include, but are not limited to Ni—YSZ, Ni—GdCeO₂, Ni—SmCeO₂, and Ag—SmCeO₂. The anode thickness should be in a range of 5-70 μm , preferably 5-60 μm , more preferably 5-50 μm , most preferably 5-40 μm . The anode should have an average pore size of 1-20 μm and pore volume of 25-40 volume percent. The anode 12 is applied to the support tube 11 by a conventional method such as sol-gel, slurry, or wash coating, for example. The anode 12 can be sintered before or after the application of subsequent layers.

[0029] The next active fuel cell membrane layer 13 is a non-porous and/or essentially fully dense O₂-permeable or H₂-permeable electrolyte composition. Examples of suitable electrolyte compositions include but are not limited to YSZ, GdCeO₂, SmCeO₂, LaSrGaMgO₃, BaCeYO₃, and La₂Mo₂O₉. The electrolyte should have a thickness in a range of 2-80 μm , preferably 2-70 μm , more preferably 2-60 μm , most preferably 2-50 μm . The electrolyte should be dense and gas tight to prevent the air and fuel from mixing. The electrolyte layer 13 may be deposited using a conventional method such as sol-gel, slurry, or wash coating, for example, and subsequently sintered.

[0030] The first two layers 12, 13 are preferably sintered simultaneously under either neutral (neutral as used herein means neither oxidizing nor reducing) or reducing conditions so that the anode maintains or attains the characteristics described hereinabove while achieving full densification of the electrolyte layer. The sintered electrolyte is preferably at least 95% dense and essentially defect-free. Sintering parameters are not critical to the invention; suggested parameters include a temperature range of 1200-1500° C., preferably about 1300° C., and a duration of 0.5 to 3 hours, preferably about 1 to 2 hours.

[0031] The final layer is the cathode 14, which is generally comprised of alkaline earth substituted lanthanum manganite, alkaline earth substituted lanthanum ferrite, lanthanum strontium iron cobaltite, or a mixed ionic-electronic conductor, but the composition of the cathode 14 is not critical to the invention. The cathode 14 thickness should be in a range of 5-70 μm , preferably 5-60 μm , more preferably 5-50 μm , most preferably 5-40 μm . The cathode 14 should have an average pore size of 1-15 μm and pore volume of 25-40 volume percent. The cathode 14 can also be deposited using a conventional method such as sol-gel, slurry, or wash coating, for example.

[0032] The final step is a sintering process that is composed of heating the entire TSOFC 10 in a neutral environment to 1000-1300° C. for 1-2 hours depending on the cathode material used. In cases where the electrolyte is H₂-permeable, BaCeYO₃ or La₂Mo₂O₉, the cathode can be metallic comprising Pt, Pd, Ag—Pd, or other metallic material, or cermet comprising Ni—BaCeYO₃ or Ni—SrCeO₃. The term neutral as used herein means neither oxidizing nor reducing.

[0033] Referring to FIG. 3, in accordance with the present invention, a TSOFC 20 can have the internal active layers deposited on the inside surface 16 of the support tube 11 in reverse order (14, 13, 12). The skilled artisan will recognize that the fuel and oxygen supplies will also need to be reversed in operation.

[0034] In some embodiments of the present invention, a TSOFC is supported by a tube sheet. Referring to FIG. 4, a simplified example of a tube sheet 21 defines an array of any number of integral openings having inner surfaces 28. The tube sheet 21 and inner surfaces 28 can be formed in any suitable cross-sectional shapes, including circular, elliptical, triangular, rectangular, irregular, or any other desired shapes. A round shape, especially an essentially circular shape as shown in FIG. 4, accommodates uniform deposition of layers on the inner surfaces 28. The tube sheet 21 can be comprised of any of the materials described hereinabove for the support tube 11. The tube sheet 21 may be prepared by

conventional powder metallurgy techniques, such as molding, extrusion, casting, forging, isostatic compression, etc. The tube sheet should be open on both ends.

[0035] Referring to FIG. 5, in some accordance with the present invention, active fuel cell membrane layers can be deposited and sintered as described hereinabove to form a SOFC tube sheet 30. Each inner surface 28 defined by the tube sheet 21 is coated on the inside thereof with a porous anode 22 such as Ni—YSZ, for example. The anode 22 is coated on the inside with a dense electrolyte 23 such as Y_2O_3 — ZrO_2 , for example. The dense electrolyte 23 is coated on the inside with a porous cathode 24 such as $LaMnO_3$, for example. It can be seen that each successive layer supports the layers that are subsequently deposited thereon.

[0036] The cross-sectional shape of the tube sheet 21 and the openings 28 defined thereby are not critical to the invention, although some shapes will be found to be more beneficial, especially those shapes which promote contact of reactive gases with respective surfaces of the tube sheet 21.

[0037] Referring to FIG. 6, in some embodiments of the present invention, a TSOFC tube sheet 35 can have the internal active layers deposited on the inside of the tube sheet 21 in reverse order (24, 23, 22). The skilled artisan will recognize that the fuel and oxygen supplies will also need to be reversed in operation.

[0038] Some embodiments of the present invention comprise a TSOFC having a composite porous support-anode. See U.S. Patent Application Publication No. US 2006/0234112 A1 to Visco, et al. published on Oct. 19, 2006.

[0039] Referring to FIG. 7, fabrication of a TSOFC in accordance with the present invention begins with a porous support 40. A network of metal 42 and pores 44 is shown schematically; open porosity of the porous support 40 is 20 to 60 vol. %, preferably 30 to 50 vol. %, more preferably 35 to 50 vol. %. The porous support 40 can be comprised of any metal, alloy, or cermet composition suitable for fuel cell construction, as described hereinabove.

[0040] The porous support 40 is wash coated with an anode-forming composition comprised of NiO/YSZ, NiO/ CeO_2 , NiO/Gd or Sm doped CeO_2 with a conventional binder such as polyethylene glycol (PEG), for example. The wash coat can be done in air or under vacuum (for a few minutes to assist coating). The coated porous support 40 is dried and sintered in Ar at 1000-1350° C. for 0.5 to 2 hrs.

[0041] Optionally, a conventional pore former comprised of a starch, for example, is included in the anode-forming composition in order to impart or enhance porosity thereof.

[0042] The resulting structure, shown in FIG. 8, is a composite porous support-anode 48 wherein the metal 42 is coated throughout, including within the pores 44 and on the external surface 50 and interior surface 52 a continuous anode layer 46 forming a three dimensional composite structure that serves as both support and anode.

[0043] FIG. 9 is a schematic magnification showing a TSOFC 60 that includes a composite porous support-anode 48 as described above and shown in FIG. 8, a dense electrolyte layer 54, and a porous cathode layer 56. FIG. 10 is an unmagnified view of the TSOFC 60 showing the

composite porous support-anode 48, dense electrolyte layer 54, and porous cathode layer 56.

[0044] FIG. 11 shows an example of a SOFC tube sheet 70 that includes a composite porous support-anode 72, a dense electrolyte layer 74, and a porous cathode layer 76.

[0045] The embodiments shown and described herein are set forth as examples, and are not to be construed as limiting the scope of the invention. The physical shape and configuration of TSOFC's made in accordance with the present invention can vary widely, and are not critical to the present invention. The particular compositions used to make the SOFC dense electrolyte and porous cathode coatings described herein, and thicknesses thereof, are not critical to the present invention.

[0046] An advantage of having the metal support on the outside and ceramic materials on the inside is that as the fuel cell reaches operating temperatures, thermal expansion will cause compressive forces on the ceramic materials, which can be more easily withstood than tensile forces produced in devices with the ceramic materials on the outside of the metal tube. Other advantages provided by the present invention include: metal acts a structural backbone imparting increased strength to entire fuel cell package, increases potential for rapid start-up.

[0047] Additional advantages provided by composite porous support-anodes of the present invention include the elimination of physical interconnect material and respective constituent layer.

[0048] Arrays of the elements described herein can be used in electric power generators to power automobiles and other equipment.

[0049] Referring to FIGS. 12 and 13, one or more buffer layers (interlayers) 101, 103, 105 can be deposited between any of the active layers in any of the above described embodiments of the present invention, according to preference for a particular application. For example, if a YSZ electrolyte is used, then an interlayer of Sm doped CeO_2 can be deposited thereover to reduce interfacial polarization. Interlayers can be deposited using conventional methods such as sol-gel, slurry, or wash coating, for example. The interlayer(s) can be fully dense, i.e., essentially nonporous, about 1 μm to 5 μm thick, and conductive to oxide or hydrogen ions. Alternatively, the interlayer(s) can be porous, with pore size of <1 μm to 10 μm and thickness of 1 μm to 5 μm .

[0050] The elements described herein can be used as steam electrolyzers, i.e., high-temperature electrolysis cells. In the electrolysis configuration, an external potential, i.e., voltage, is applied to the unit via a circuit connecting the anode to the cathode. The resultant electrochemical reaction converts water to hydrogen and oxygen respectively by transport of hydrogen or oxygen ions through the electrolyte with recombination to molecular forms on exiting the electrolyte.

[0051] While there has been shown and described what are at present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications can be prepared therein without departing from the scope of the inventions defined by the appended claims.

What is claimed is:

1. A solid oxide electrochemical device comprising:
 - a. a porous support structure having a porous outer surface and a tubular porous inner surface;
 - b. a first electrode layer disposed radially inside said tubular porous inner surface and supported by said porous support structure;
 - c. a dense electrolyte layer disposed radially inside and supported by said first electrode composition; and
 - d. a second electrode layer disposed radially inside and supported by said dense electrolyte.
2. A solid oxide electrochemical device in accordance with claim 1 wherein said porous support structure comprises a structure selected from the group consisting of a tube and a tube sheet.
3. A solid oxide electrochemical device in accordance with claim 1 wherein said porous support structure comprises a composition selected from the group consisting of a non-noble transition metal, a metal alloy, and a cermet comprising at least one metallic component selected from the group consisting of a non-noble transition metal and a non-noble transition metal alloy.
4. A solid oxide electrochemical device in accordance with claim 3 wherein said composition comprises a stainless steel composition.
5. A solid oxide electrochemical device in accordance with claim 4 wherein said stainless steel composition comprises at least one stainless steel composition selected from the group consisting of a ferritic stainless steel composition and an austenitic steel composition.
6. A solid oxide electrochemical device in accordance with claim 1 wherein said first electrode layer is in contact with said porous support structure.
7. A solid oxide electrochemical device in accordance with claim 1 further comprising at least one interlayer between said first electrode layer and said porous support structure.
8. A solid oxide electrochemical device in accordance with claim 1 wherein said dense electrolyte layer is in contact with said first electrode layer.
9. A solid oxide electrochemical device in accordance with claim 1 further comprising at least one interlayer between said dense electrolyte layer and said first electrode layer.
10. A solid oxide electrochemical device in accordance with claim 1 wherein said second electrode layer is in contact with said dense electrolyte layer.
11. A solid oxide electrochemical device in accordance with claim 1 further comprising at least one interlayer between said second electrode layer and said dense electrolyte layer.
12. A solid oxide electrochemical device in accordance with claim 1 wherein said first electrode layer comprises an electrode selected from the group consisting of an anode and a cathode, and wherein said second electrode layer comprises an electrode selected from the group consisting of an anode and a cathode, said first electrode layer and said second electrode layer being dissimilar.
13. A solid oxide electrochemical device in accordance with claim 12 wherein said anode comprises a composition selected from the group consisting of Ni—YSZ, Ni—Gd—CeO₂, Ni—SmCeO₂, and Ag—SmCeO₂.

14. A solid oxide electrochemical device in accordance with claim 12 wherein said cathode comprises a composition selected from the group consisting of an alkaline earth substituted lanthanum manganite, an alkaline earth substituted lanthanum ferrite, a lanthanum strontium iron cobaltite, and a mixed ionic-electronic conductor.

15. A solid oxide electrochemical device in accordance with claim 1 wherein said solid oxide electrochemical device comprises at least one device selected from the group consisting of a fuel cell and an electrolyzer.

16. A solid oxide electrochemical device comprising:

a. a composite electrode comprising:

- 1) a porous support structure having pores, a porous outer surface, and a tubular porous inner surface; and
- 2) a first electrode layer disposed throughout said pores, said porous outer surface, and said tubular porous inner surface and supported by said porous support structure;

b. a dense electrolyte layer disposed radially inside and supported by said composite electrode; and

c. a second electrode layer disposed radially inside and supported by said dense electrolyte.

17. A solid oxide electrochemical device in accordance with claim 16 wherein said porous support structure comprises a structure selected from the group consisting of a tube and a tube sheet.

18. A solid oxide electrochemical device in accordance with claim 16 wherein said porous support structure comprises a composition selected from the group consisting of a non-noble transition metal, a metal alloy, and a cermet comprising at least one metallic component selected from the group consisting of a non-noble transition metal and a non-noble transition metal alloy.

19. A solid oxide electrochemical device in accordance with claim 18 wherein said composition comprises a stainless steel composition.

20. A solid oxide electrochemical device in accordance with claim 19 wherein said stainless steel composition comprises at least one stainless steel composition selected from the group consisting of a ferritic stainless steel composition and an austenitic steel composition.

21. A solid oxide electrochemical device in accordance with claim 16 wherein said first electrode layer is in contact with said porous support structure.

22. A solid oxide electrochemical device in accordance with claim 16 further comprising at least one interlayer between said first electrode layer and said porous support structure.

23. A solid oxide electrochemical device in accordance with claim 16 wherein said dense electrolyte layer is in contact with said first electrode layer.

24. A solid oxide electrochemical device in accordance with claim 16 further comprising at least one interlayer between said dense electrolyte layer and said first electrode layer.

25. A solid oxide electrochemical device in accordance with claim 16 wherein said second electrode layer is in contact with said dense electrolyte layer.

26. A solid oxide electrochemical device in accordance with claim 16 further comprising at least one interlayer between said second electrode layer and said dense electrolyte layer.

27. A solid oxide electrochemical device in accordance with claim 16 wherein said first electrode layer comprises an electrode selected from the group consisting of an anode and a cathode, and wherein said second electrode layer comprises an electrode selected from the group consisting of an anode and a cathode, said first electrode layer and said second electrode layer being dissimilar.

28. A solid oxide electrochemical device in accordance with claim 27 wherein said anode comprises a composition selected from the group consisting of Ni—YSZ, Ni—Gd—CeO₂, Ni—SmCeO₂, and Ag—SmCeO₂.

29. A solid oxide electrochemical device in accordance with claim 27 wherein said cathode comprises a composition selected from the group consisting of an alkaline earth substituted lanthanum manganite, an alkaline earth substituted lanthanum ferrite, a lanthanum strontium iron cobaltite, and a mixed ionic-electronic conductor.

30. A solid oxide electrochemical device in accordance with claim 16 wherein said solid oxide electrochemical device comprises at least one device selected from the group consisting of a fuel cell and an electrolyzer.

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