

**MEMBRANES AND ELECTROCHEMICAL CELLS INCORPORATING
SUCH MEMBRANES**

Related Applications

5 [0001] The subject matter of this application is related to that of a co-owned US application no. 11/047,560 entitled "ELECTROCHEMICAL CELLS HAVING CURRENT CARRYING STRUCTURES UNDERLYING ELECTROCHEMICAL REACTION LAYERS" filed concurrently herewith and a co-owned US application
10 No. 11/047,557 entitled "ELECTROCHEMICAL CELLS FORMED ON PLEATED SUBSTRATES" filed concurrently herewith (now US Patent No. 7,201,986), both of which are hereby incorporated by reference herein. This application claims priority from United States Patent Application No. 60/567437 filed on 4 May 2004, and United States Patent Application No. 11/047558 filed on 2 February 2005 (now US Patent No. 7,378,176), both of which are hereby incorporated by reference herein.

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Field of the Invention

[0002] This invention relates to electrochemical cells, such as fuel cells, electrolysis cells and the like which incorporate ion-conducting membranes. Particular
20 embodiments of the invention provide ion-conducting membranes for use in such cells.

Background

[0003] Ion-conducting membranes, including ionomeric membranes such as Nafion™, are an important component in membrane separation processes and
25 electrochemical reactor systems including chlor-alkali cells, electrolysis cells and fuel cells. Such membranes act as ion conductors while preventing reactants from inter-mixing. In some applications, the ions conducted by such membranes are protons. The availability of materials which are solid and can conduct protons has allowed a breakthrough in the production of simple and robust fuel cell devices.

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[0004] In typical prior art fuel cells, the ion-conducting membrane is an ionomeric membrane that fulfills several functions including providing ion conductivity, providing a barrier between reactants and providing a structural spacer that withstands the clamping forces
5 necessary to seal the fuel cell.

[0005] The design of ion-conducting membranes for use in electrochemical cells typically requires balancing between two competing design objectives. Firstly, it is generally desirable to
10 maximize the conductivity of the ion-conducting membrane to minimize operational losses. This first objective tends to favor ion-conducting materials which have high water contents and therefore approach liquid form. Secondly, it is generally desirable to provide a membrane that is robust and usable as a structural material within the
15 cell to maintain integrity of the cell in the presence of differential pressures across the membrane. This second objective tends to favor ion-conducting materials which are solid and have high strength. It will be appreciated that these two design objectives often conflict with one another. Current practices for designing electrochemical cells involve
20 making compromises between these design objectives.

[0006] An example of an ion-conducting material is Nafion™, which is typically provided in the form of sheets that may be as thin as 25 microns. Figure 1 is a schematic cross-sectional view of a Nafion™
25 membrane 8. Membrane 8 is a continuous sheet of ion-conducting material. Nafion™ membranes are susceptible to mechanical failure and are difficult to work with, especially if they are very thin. Another problem with materials like Nafion™ is that they are not dimensionally stable when used to conduct protons. Variations in water content of the
30 membrane, which are inevitable during proton conduction, cause considerable shrinking and swelling. Electrochemical cells

incorporating Nafion™ membranes must be designed to accommodate such shrinking and swelling.

[0007] Gore-Select™ is a composite perfluorinated material
5 consisting of a homogeneously porous substrate filled with an ion-conducting material. US patent No. 6,613,203 describes a membrane of this type. Figure 2 schematically depicts a Gore-Select™ membrane 10 having a homogeneous substrate 12 filled with an ion-conducting material 14. Porous substrate 12 provides membrane 10 with some
10 degree of structural integrity and dimensional stability, while ion-conducting filler 14 provides proton conductivity.

[0008] There remains a need for ion-conducting membranes for use in electrochemical applications, such as fuel cells, electrolysis cells,
15 chlor-alkali plants and the like, which possess advantageous mechanical properties and desirably high ion conductivity.

Summary of the Invention

[0009] A first aspect of the invention provides an ion-conducting
20 membrane comprising an ion-conducting region. The ion-conducting region comprises a substrate having one or more ion-conducting passageways that extend through the substrate. Each passageway comprises an ion-conducting material that is relatively more ion
conductive than the substrate.

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[0010] Another aspect of the invention provides an ion-conducting membrane which comprises: a substrate penetrated by a plurality of openings in a porous region thereof; and an ion-conducting material which fills the openings to provide a plurality of ion-conducting
30 passageways through the substrate. The ion-conducting material is relatively more ion conductive than the substrate.

[0011] Another aspect of the invention provides an ion-conducting membrane, which comprises: a substrate penetrated by at least one opening; and an ion-conducting material which fills the at least one opening to provide an ion-conducting passageway through the substrate and which provides a first skin layer on a first side of the substrate, the skin layer extending transversely past a perimeter of the opening. The ion-conducting material is relatively more ion-conductive than the substrate.

10 [0012] Another aspect of the invention provides an ion-conducting membrane comprising an ion-conducting region. The ion-conducting region comprises a substrate having one or more ion-conducting passageways that extend through the substrate. The ion-conducting passageways are formed by selectively converting the substrate to a
15 relatively more ion conductive state in locations corresponding to the ion-conducting passageways.

[0013] Another aspect of the invention provides an electrochemical cell comprising an ion-conducting membrane in
20 accordance with the invention.

[0014] Another aspect of the invention provides a method for fabricating an ion-conducting membrane for use in an electrochemical cell. The method comprises: forming a plurality of openings which
25 penetrate a sheet of substrate material at selected locations to create a porous region; and, filling the openings with an ion-conducting material to create a plurality of ion-conducting passageways through the substrate material.

30 [0015] Another aspect of the invention provides a method for fabricating an ion-conducting membrane for use in an electrochemical

cell. The method comprises selectively converting a sheet of substrate material to a relatively more ion conductive state in a plurality of locations to create a plurality of ion-conducting passageways through the sheet and to create an ion-conducting region in the sheet.

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[0016] Another aspect of the invention provides a method for fabricating an ion-conducting membrane for use in an electrochemical cell. The method comprises: forming at least one opening which penetrates a sheet of substrate material; and, filling the at least one opening with an ion-conducting material to create an ion-conducting passageway through the substrate material; and forming a first skin layer on a first side of the substrate, the skin layer extending transversely past a perimeter of the opening.

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[0017] Further features and applications of specific embodiments of the invention are described below.

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Brief Description of the Drawings

[0018] In drawings which illustrate non-limiting embodiments of the invention:

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Figure 1 is a cross-sectional schematic view of a sheet of ion-conducting material of the type commonly employed in prior art fuel cells;

Figure 2 is a cross-sectional schematic view of a prior art composite membrane having a homogeneously porous substrate filled with ion-conducting material;

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Figure 3A is a cross-sectional schematic view of an ion-conducting membrane according to a particular embodiment of the invention;

Figure 3B is a partial transverse cross-sectional view of the ion-conducting region of the Figure 3A membrane taken along

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the line 3-3 (see Figure 3A) in accordance with a particular embodiment of the invention;

5 Figure 3C is a partial transverse cross-sectional view of the ion-conducting region of the Figure 3A membrane taken along the line 3-3 (see Figure 3A) in accordance with another embodiment of the invention;

10 Figure 4 is a perspective view of a sheet of substrate material which may be used in a membrane of the type shown in Figure 3A according to a particular embodiment of the invention;

Figure 5 is a perspective view of a sheet of substrate material which may be used in a membrane of the type shown in Figure 3A according to another embodiment of the invention;

15 Figure 6 is an exploded perspective view of a substrate made from a lamination of multiple sheets of precursor materials which may be used in a membrane of the type shown in Figure 3A according to another embodiment of the invention;

Figures 7A-7D are cross-sectional schematic views of ion-conducting membranes according to various embodiments of the invention;

20 Figures 8A-8B are cross-sectional schematic views of ion-conducting membranes in which multiple different ion-conducting materials are applied in layers to form a composite membrane structure;

25 Figures 9A and 9B schematically depict the fabrication of an ion-conducting membrane according to a particular embodiment of the invention;

Figure 9C and 9D schematically depict different cross-sectional views of an ion-conducting membrane fabricated according to another embodiment of the invention; and

Figures 10A-10C schematically depict the fabrication of an ion-conducting membrane according to another embodiment of the invention.

5 **Detailed Description**

[0019] Throughout the following description, specific details are set forth in order to provide a more thorough understanding of the invention. However, the invention may be practiced without these particulars. In other instances, well known elements have not been shown or described in
10 detail to avoid unnecessarily obscuring the invention. Accordingly, the specification and drawings are to be regarded in an illustrative, rather than a restrictive, sense.

[0020] Membranes suitable for use in electrochemical cells may
15 be fabricated by providing a sheet of substrate material and forming one or more ion-conducting passageways through the sheet of substrate material. The ion-conducting passageway(s) have an ion conductivity greater than that of the surrounding substrate material. Ion-conducting passageway(s) may be formed by creating opening(s) which penetrate
20 the substrate material and then filling the opening(s) with ion-conducting material and/or by selectively converting the substrate material to a relatively more ion conductive state in location(s) of the ion-conducting passageway(s). Mechanical and ion-conducting properties of the membranes can be made different in different regions
25 by providing the ion-conducting passageway(s) with varying sizes, shapes, densities and/or arrangements.

[0021] Figure 3A is a schematic cross-sectional depiction of an ion-conducting membrane **20** according to a particular embodiment of
30 the invention. Membrane **20** comprises one or more ion-conducting regions **33** and one or more non-ion-conducting regions **35A**, **35B**

(collectively 35). Figure 3A shows a membrane 20 having one ion-conducting region 33 bordered by a pair of non-ion-conducting regions 35A, 35B. Membrane 20 comprises a substrate 21 of substrate material 22 and optionally comprises first and/or second skins 28, 29 on
5 respective sides 32, 37 of substrate 21.

[0022] Ion-conducting region 33 of membrane 20 comprises ion-conducting passageways 27 that extend from a first side 32 of substrate 21 to a second side 37 of substrate 21. Ion-conducting passageways 27
10 comprise an ion-conducting material 26 having an ion conductivity greater than that of the surrounding material (i.e. the material outside of ion-conducting passageways 27). In some embodiments, ion-conducting material 26 is an ionomeric material. Optional skins 28, 29 may also comprise ion-conducting material 26.

15 [0023] Ion-conducting passageway(s) 27 may be formed by creating opening(s) 24 which penetrate a substrate material 22 and then filling the opening(s) 24 with ion-conducting material 26 and/or by selectively converting substrate material 22 to a relatively more ion
20 conductive state in location(s) of ion-conducting passageway(s). Both of these fabrication techniques are discussed in more detail below.

[0024] In accordance with one embodiment of the invention, membrane 20 comprises a substrate 21 made of a substrate material 22.
25 Openings 24 are formed to penetrate substrate 21 at selected locations. Openings 24 may be micro-structures. In this disclosure, a "micro-structure" is a structure capable of being revealed by a microscope having a magnification of 5 times or more. Openings 24 need not be micro-structures. In some embodiments, openings 24 are larger.

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[0025] Openings 24 provide substrate 21 with one or more porous regions 30 which are relatively more porous than surrounding regions 31A, 31B. Each porous region 30 of substrate 21 comprises a plurality of openings 24 and corresponds with an ion-conducting region 33 of membrane 20. Non-porous regions 31A, 31B (collectively, 31) respectively correspond to non-ion-conducting regions 35A, 35B of membrane 20. In the Figure 3A embodiment, there are no openings 24 formed in non-porous regions 31A, 31B of substrate 21.

10 [0026] Substrate material 22 may comprise any suitable material or combination of materials that provides a substantial barrier to the reactants with which membrane 20 will be used. For example, a membrane for use in a hydrogen/air fuel cell is preferably substantially impermeable to hydrogen and oxygen gases. Substrate material 22 may
15 comprise, for example, a material selected from:

- polyamide films,
- polyimide films, such as Kapton™,
- polyethylene films,
- Teflon™ films,
- 20 • films comprising other polymers,
- a resin precursor to hydrolyzed Nafion™,
- non-polymer materials such as silicon or glass.

Substrate material 22 is selected to be suitable for the desired application. In some embodiments, it is advantageous for substrate
25 material 22 to be flexible to some degree.

[0027] In porous region(s) 30 of substrate 21, openings 24 are filled with an ion-conducting material 26 to form ion-conducting passageways 27 that extend through membrane 20 from a first side 32
30 of substrate 21 to a second side 37 of substrate 21. Ion-conducting material 26 is relatively more ion-conductive than the surrounding

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substrate material 22. In the illustrated embodiment, passageways 27 each have a path length equal to the thickness L_{core} of substrate 21. In other words, passageways 27 have tortuosity factors of 1, where tortuosity is equal to the distance that a particle must travel to pass
5 through substrate 21 divided the thickness (L_{core}) of substrate 21.

[0028] Openings 24 may be formed in substrate 21 using any suitable method. By way of non-limiting example, openings 24 may be formed through substrate 21 by:

- 10 • chemical etching;
- laser micromachining;
- laser drilling;
- mechanical drilling;
- milling;
- 15 • punching;
- calendaring;
- printed circuit board fabrication techniques;
- lithographic fabrication techniques;
- mechanical dies; and
- 20 • the like.

As noted above, passageways may also be formed without forming and filling openings 24 by selectively converting the material of substrate 21 from one state to another, for example by selectively hydrolyzing a Nafion™ precursor resin.

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[0029] The dimensions of passageways 27, the spacing between passageways 27, the shapes of passageways 27 and the arrangement of passageways 27 can be selected to suit particular applications and may be influenced by cost factors. In one particular example, passageways
30 27 are formed in the shape of slits in openings 24 made using conventional sheet conversion methods. Passageways 27 may be round

or may have other shapes, such as cross shapes, hexagonal shapes, oval-shapes, elliptical shapes or star shapes.

5 [0030] In preferred embodiments, passageways 27 are formed in ordered arrangements, as opposed to placed at random locations. Any suitable patterns may be used. For example, passageways 27 may be located at nodes of:

- a square or rectangular array;
- a triangular array;
- 10 • a hexagonal array; or,
- any other suitable arrangement.

[0031] Figure 3B is a partial cross-sectional view of ion-conducting region 33 of membrane 20 along the line 3-3 (see Figure 15 3A) in accordance with a particular embodiment of the invention. In this embodiment, ion-conducting passageways 27 are circular in transverse cross-section and are arranged in a rectangular array.

[0032] The parameter **D** is used to denote the widest transverse 20 dimension of ion-conducting passageways 27. In the Figure 3B embodiment, passageways 27 are all the same size and the parameter **D** is equal to the diameter of the openings 24 in which passageways 27 are formed. The parameter **L** denotes the center-to-center transverse spacing of the nearest adjacent ion-conducting passageways 27.

25 [0033] Figure 3C depicts a partial cross-sectional view of ion-conducting region 33 of membrane 20 along the line 3-3 (see Figure 3A) according to another embodiment of the invention. In the Figure 3C embodiment, ion-conducting passageways 27 are hexagonal in 30 transverse cross-section and are arranged in a hexagonal packing array. The parameters **D** (i.e. the widest dimension of passageways 27) and **L**

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(i.e. the center-to-center spacing between nearest adjacent passageways 27) are also illustrated in Figure 3C.

[0034] In some embodiments, the parameter **D** of passageways 27 is 200 microns or less. In other embodiments, the parameter **D** of passageways 27 is 2500 microns or less. In some embodiments, passageways 27 have cross-sectional areas not exceeding $5 \times 10^{-8} \text{ m}^2$. In other embodiments, passageways 27 have cross-sectional areas not exceeding $1 \times 10^{-5} \text{ m}^2$. In some embodiments, ion-conducting passageways 27 have a minimum transverse dimension of at least 25 microns. In other embodiments, ion-conducting passageways 27 have a minimum transverse dimension of at least 50 microns. In some embodiments, the parameter **L** of passageways 27 is 500 microns or less in at least some areas of porous region 30. In other embodiments, the parameter **L** of passageways 27 is 5000 microns or less in at least some areas of porous region 30.

[0035] For maximum conductivity through membrane 20, it is desirable for the parameter ratio **L/D** to be as close to unity as possible. In some embodiments, membranes according to the invention are constructed having a parameter ratio **L/D** not exceeding 2.5 in one or more ion-conducting regions. In other embodiments, membranes according to the invention are constructed having a parameter ratio **L/D** not exceeding 1.5.

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[0036] Another ratio parameter γ may be used to characterize conducting regions of membranes according to the invention. The ratio parameter γ may be defined as the ratio of the total transverse area of an ion-conducting region to the total transverse area of the ion-conducting passageways 27 within the ion-conducting region. In some embodiments, membranes according to the invention are constructed

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having a parameter ratio γ not exceeding 2.5 in one or more ion-conducting regions. In other embodiments, membranes according to the invention are constructed having a parameter ratio γ not exceeding 1.5.

5 [0037] Substrate 21 provides structural support for ion-conducting material 26 and overall structural support for membrane 20 (see Figure 3A). The mechanical properties of substrate 21 can be selected to match the mechanical properties desired for particular applications. For example, by varying the density, size, shape and/or arrangement of
10 openings 24 in different regions of substrate 21, one can provide different mechanical properties and/or different ion-conducting properties in those different regions.

15 [0038] Figure 4 shows a planar sheet 34 of substrate material 22 according to a particular embodiment of the invention. Sheet 34 may be used as a substrate 21 of an ion-conducting membrane 20 of the type shown in Figure 3A for use in an electrochemical cell, such as a fuel cell. In the Figure 4 embodiment, sheet 34 is fabricated from a thin sheet of substrate material 22 and is divided into perimeter (non-
20 porous) seal region 31, which surrounds porous region 30. Porous region 30 has openings 24 which penetrate sheet 34. When a fuel cell having an ion-conducting membrane 20 is constructed using sheet 34 as a substrate 21, ions may be conducted through openings 24 of porous region 30, while perimeter seal region 31 provides structural strength in
25 the vicinity of the fuel cell's compressive seals.

30 [0039] It is not necessary that porous region 30 be uniformly porous. In some cases, it is advantageous to vary characteristics of openings 24 (e.g. size, shape, density and/or arrangement of openings 24) and/or the parameters associated with openings 24 (e.g. L , D , L/D and/or γ) across a porous region, such as region 30. In some cases, it is

advantageous to provide a substrate **21** with a plurality of porous regions. The characteristics of openings **24** and parameters associated with openings **24** may be different in each such porous region.

- 5 **[0040]** In regions expected to be subjected to relatively high local mechanical stresses, openings **24** may be made relatively small and/or the density of openings **24** may be made relatively low. In regions expected to be subjected to relatively high local mechanical stresses, the parameter ratio **L/D** and/or the parameter γ may be made relatively
- 10 large. For example, in such regions, the parameter ratio **L/D** and/or the parameter γ may be greater than 5. Although such regions may have relatively low proton conductivity, they may provide relatively high mechanical strength.
- 15 **[0041]** In regions expected to be subjected to relatively low mechanical stresses, openings **24** may be made relatively large and/or the density of openings **24** may be made relatively high. In regions expected to be subjected to relatively low mechanical stresses, the parameter ratio **L/D** and/or the parameter γ may be made relatively low.
- 20 For example, in such regions, the parameter ratio **L/D** and/or the parameter γ may be less than 3. Such regions may provide relatively high proton conductivity at the expense of mechanical strength. Using these techniques, it is possible tune the performance (i.e. mechanical strength and proton conductivity) over the spatial dimensions of a fuel
- 25 cell membrane.

- [0042]** Figure 5 shows a planar sheet **40** of substrate material **22** according to another example embodiment of the invention. Sheet **40** may be used as a substrate **21** of an ion-conducting membrane **20** of the
- 30 type shown in Figure 3A for use in a fuel cell. Sheet **40** is formed from a substrate material **22** and comprises: a non-porous perimeter region

- 44, a first porous region 46, a second porous region 48, and a third porous region 49. Porous regions 46, 48, and 49 each have openings 24. The characteristics of openings 24 and/or the parameters associated with openings 24 in porous regions 46, 48, 49 differ from one another.
- 5 For example, the size of their openings 24, the density of openings 24, the shape of openings 24 and/or the arrangement of openings 24 vary between porous regions 46, 48, 49. In the Figure 5 embodiment, the size and shape of openings 24 varies between porous regions 46, 48, 49.
- 10 [0043] In other embodiments (not shown), the characteristics of openings 24 (e.g. density, size, shape and/or arrangement) and/or the parameters of openings 24 (e.g. L , D , L/D and/or γ) vary smoothly over a porous region of a substrate. For example, the parameter ratio L/D and/or the parameter γ of openings 25 may vary in accordance with a
- 15 smooth function such as a bell curve. In still other embodiments (not shown), a sheet of substrate material 22 may be fabricated to have openings 24 of uniform characteristics and/or parameters over the entire sheet of substrate material 22. Openings 24 are described herein as having various characteristics, such as size, shape, density, arrangement
- 20 and various parameters, such as L , D , minimum transverse dimension, L/D and γ . Any of these characteristics and/or parameters may also be used to describe ion-conducting passageways generally.
- [0044] Each of the embodiments described above comprises a
- 25 single sheet of substrate material through which ion-conducting passageways 27 are formed to provide one or more ion-conducting regions. In some embodiments of the invention, ion-conducting membranes comprise composite substrates made of multiple layers of different materials. Some layers of a composite substrate may be
- 30 porous. For example, one or more layers of a composite substrate may comprise a mesh material. Other layers of such a composite substrate

may comprise ion-conducting regions and ion-non-conducting regions according to a suitable one of the constructions described herein. A composite substrate fabricated in this manner may have superior mechanical strength.

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[0045] Figure 6 is an exploded view of a composite substrate 50 in accordance with a particular embodiment of the invention. Composite substrate 50 comprises a first layer 52. Layer 52 may comprise a substrate layer similar to any of those described above, for example. In the illustrated embodiment, layer 52 comprises a non-porous region 31 which surrounds a porous region 30 having openings 24 formed therein. Intermediate layer 54 comprises a mesh-like structure bonded to first layer 52 to provide structural reinforcement. Optional backing layer 56 may form a lamination, so that intermediate layer 54 is encapsulated between layers 52 and 56. A composite substrate may have more than 2 or 3 layers of substrate precursor materials.

[0046] The foregoing discussion has dealt primarily with the nature and formation of substrates comprising porous regions formed in substrate material. Ion-conducting materials, such as ionomers, can be deposited into porous regions of such substrates to form ion-conducting membranes having ion-conducting passageways for use in fuel cells, electrolysis cells and the like. Ion-conducting materials may be deposited in various arrangements on such substrates to make ion-conducting membranes according to the invention.

[0047] Figures 7A, 7B, 7C and 7D show cross-sections of a number of exemplary ion-conducting membranes according to various embodiments of the invention. Ion-conducting material is arranged differently in each of the membranes depicted in Figures 7A, 7B, 7C and 7D. Figure 7A shows a membrane 60A comprising a substrate 21

formed from a substrate material 22. Substrate 21 has openings 24 formed therein. Openings 24 of membrane 60A are filled with ion-conducting material 26 to form ion-conducting passageways 27 through membrane 60A. Ion-conducting material 26 is relatively more ion-conductive than substrate material 22. In membrane 60A, the thickness of the ion-conducting material 26 and the length of ion-conducting passageways 27 are substantially similar to the thickness L_{core} of substrate 21. In other embodiments, the thickness of ion-conducting material 26 (and the ion-conducting passageways 27) differ from the thickness L_{core} of substrate 21.

[0048] Figure 7B shows a membrane 60B according to another embodiment of the invention. Membrane 60B has openings 24 filled with ion-conducting material 26 to form ion-conducting passageways 27. Membrane 60B also comprises ion-conducting skins 62, 64 which coat substrate material 22 on either side thereof. The ion-conducting material in each of skins 62, 64 may be the same or different and may be the same as or different than the ion-conducting material 26 in openings 24. The ion-conducting material in each of skins 62, 64 is relatively more ion conductive than substrate material 22. In the Figure 7B embodiment, the thickness L_{skin} of each skin 62, 64 is substantially similar. In other embodiments, the thicknesses of skins 62, 64 differ from one another.

[0049] Coating substrate 21 with skins 62, 64 is optional. The provision of skins 62, 64 may be advantageous in that skins 62, 64 can provide ion-conducting passageways between non-porous regions and porous regions of substrate 21 (i.e. between ion-conducting and non-ion-conducting regions of membrane 60B) and between non-porous regions on opposing sides of substrate 21 (i.e. between non-ion-conducting regions on either side of membrane 60B).

[0050] Figure 7C shows a membrane **60C** comprising a substrate **21** having openings **24** filled with ion-conducting material **26** to form ion-conducting passageways **27**. Substrate **21** is coated with ion-conducting skins **62**, **64**. In the Figure 7C embodiment, skins **62**, **64** extend transversely over the porous region of substrate **21** and slightly into the non-porous region of substrate **21**. In other embodiments, skins **62**, **64** extend transversely over only a part of the porous region of substrate **21**. In still other embodiments, skins **62**, **62** extend transversely over only the porous region of substrate **21** and do not extend transversely into the non-porous region of substrate **21**.

[0051] Figure 7D shows a membrane **60D** comprising a substrate material **22** having openings **24** filled with ion-conducting material **26** to form ion-conducting passageways **27** and a single ion-conducting skin **62** which coats only one side of substrate **21**. Skin **62** may have different transverse extension characteristics as described above.

[0052] Figure 8A shows an ion-conducting membrane **70A** according to another embodiment of the invention. Membrane **70A** comprises a substrate **21** made of substrate material **22** with openings **24** formed at selected locations as described above. Substrate **21** supports a plurality of ion-conducting materials of different compositions. In the Figure 8A embodiment, membrane **70A** comprises three layers of ion-conducting material including: a skin layer **62** of a first ion-conducting material **72** on a first side **73** of membrane **70A**; a mid layer of a second ion-conducting material **26** different from first material **72**; and a skin layer **64** of a third ion-conducting material **76** different from second material **26** (and optionally different from both first material **72** and second material **26**) on a second side **77** of membrane **70A**. Ion-conducting materials **72**, **26**, **76** are relatively more

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ion conductive than substrate material **22**. In the Figure 8A embodiment, skins **62**, **64** both have approximately equal thickness (L_{skin}), but this is not necessary.

5 **[0053]** Figure 8B shows an ion-conducting membrane **70B** according to another embodiment of the invention. Membrane **70B** has two ion-conducting layers **78**, **79** of different ion-conducting materials. The ion-conducting material of layers **78**, **79** is relatively more ion-conductive than substrate material **22**.

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[0054] Ion-conducting material(s) may be deposited onto and into a substrate to make an ion-conducting membrane according to the invention in any of a variety of methods including casting, dipping, printing, syringe injection and molding. Further, when one or more
15 skins are used, it is possible to fabricate a membrane by bonding a substrate having a porous region to a pre-formed sheet of ion-conducting material (i.e. a skin) or between two pre-formed sheets of ion-conducting material. A membrane may also be formed by bonding ion-conducting sheets (skins) to a liquid precursor.

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[0055] Figures 9A and 9B schematically depict the fabrication of an ion-conducting membrane according to a particular embodiment of the invention. Figure 9A depicts the formation of a substrate **80**. Substrate **80** comprises a substrate material **22** in which openings **24**
25 have been formed at selected locations as described above to provide porous region **30** and non-porous regions **31A**, **31B** on either side thereof.

[0056] In the Figure 9A embodiment, each of non-porous regions
30 **31A**, **31B** is provided with one or more optional fabrication vias **82A**, **82B**. Fabrication vias **82A**, **82B** may be formed in the same manner as

openings 24. Fabrication vias 82A, 82B are preferably spaced apart from porous region 30. In some embodiments, fabrication vias 82 are formed at locations that are transversely spaced apart from corresponding porous region(s) 30 by a distance of at least $1\frac{1}{2}L$, where
5 L is the center to center transverse spacing between nearest adjacent openings 24 in corresponding porous region(s) 30. In other embodiments, fabrication vias 82 are formed at locations that are transversely spaced apart from corresponding porous region(s) 30 by a distance of at least 3L.

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[0057] Figure 9B depicts the addition of ion-conducting material 26 to substrate 80 to form ion-conducting membrane 84 having ion-conducting passageways 27. Ion-conducting material 26 is relatively more ion-conductive than substrate material 22. In the Figure 9B
15 embodiment, ion-conducting material 26 is applied in such a manner (e.g. by casting) that ion-conducting material 26 coats substrate 80, filling openings 24, filling optional fabrication vias 82A, 82B (as indicated at 86A, 86B) and forming ion-conducting skins 62, 64. Optional fabrication vias 82A, 82B may provide an advantage in that
20 when ion-conducting material 26 is applied it may be in a liquid form. Ion-conducting material 86A, 86B in fabrication vias 82A, 82B may act like anchors which provide ion-conducting material 26 with tensile strength, thereby tending to prevent deformation of ion-conducting material 26 during drying. In particular, fabrication vias 82A, 82B may
25 improve the uniformity of skins 62, 64. Bonds between skins 62, 64 and substrate 80 (for example, at locations 83, 85) may also add tensile strength to ion-conducting material 26 and thereby reduce deformation of ion-conducting material 26 when drying.

30 [0058] Figure 9C and 9D schematically depict different cross-sectional views of an ion-conducting membrane fabricated according to

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another embodiment of the invention. Substrate **120** comprises a substrate material **22** in which an opening **122** has been formed. Opening **122** preferably comprises a smoothly curved perimeter as shown Figure 9D to avoid stress concentrations. Non-porous region(s) **31** adjacent opening **122** may be provided with one or more optional fabrication vias **82A**, **82B** (collectively, **82**). Fabrication vias **82** may be formed in any suitable manner as described above and are preferably spaced apart from opening **122**. In some embodiments, fabrication vias **82** are formed at locations that are transversely spaced apart from corresponding opening **122** by a distance of at least 100 microns. In other embodiments, fabrication vias **82** are formed at locations that are transversely spaced apart from opening **122** by a distance of at least 200 microns.

[0059] Ion-conducting material **26** is added to substrate **120** to form ion-conducting membrane **124** having an ion-conducting passageway **27**. Ion-conducting material **26** is relatively more ion-conductive than substrate material **22**. In the Figure 9C embodiment, ion-conducting material **26** is applied in such a manner (e.g. by casting) that ion-conducting material **26** coats substrate **120**, filling opening **122**, filling optional fabrication vias **82** (as indicated at **86A**, **86B** (collectively, **86**)) and forming ion-conducting skins **62**, **64**. As discussed above, where fabrication vias **82** are present, they may act like anchors which secure ion-conducting material **26** around the edges of opening **122**. Providing such anchors can help to prevent deformation of ion-conducting material **26** during drying and makes the overall structure more rugged. Whether or not fabrication vias **82** are present, bonds between skins **62**, **64** and non-porous region(s) **31** of substrate **120** (for example, at locations **83**, **85**) may permit adhesion of ion-conducting material **26** around the edges of opening **122** that is adequate for some applications.

[0060] The membranes described above may be formed by applying an ion-conducting material 26 to a substrate 21 in which openings 24 have been formed. Ion-conducting material 26 fills openings 24 (thereby providing ion-conducting passageways 27) and optionally provides ion-conducting skins 62, 64. In some alternative embodiments, ion-conducting membranes are fabricated by providing a sheet of substrate material and selectively converting the substrate material into a relatively ion-conducting state at selected locations to form ion-conducting passageways or by providing a sheet of ion-conducting substrate material and selectively converting the ion-conducting material to a relatively non-ion-conducting state at selected locations to form ion-conducting passageways.

[0061] Figures 10A-10C schematically depict the fabrication of an ion-conducting membrane according to another embodiment of the invention. Figure 10A depicts a sheet 90 of a substrate material 92. Substrate material 92 is preferably melt processable. In one particular embodiment, substrate material 92 comprises a resin precursor to Nafion™ which may be a copolymer of tetrafluoroethylene and perfluoro-3, 6-dioxo-4-methyl-7-octenesulfonyl fluoride. Substrate material 92 is convertible in selected locations to a relatively ion-conducting state. For example, the resin precursor to Nafion™ is convertible in selected locations to Nafion™, which conducts ions.

[0062] Figure 10B depicts the conversion of substrate material 92 into a relatively ion-conducting state 94 in selected locations to form ion-conducting passageways 96. Ion-conducting passageways 96 provide ion-conduction paths through substrate sheet 90. Ion-conducting passageways 96 may be arranged in any suitable arrangement. For example, ion-conducting passageways 96 may be

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configured and arranged in any of the ways described above in relation to passageways 27. Sheet 90 may be described as having one or more ion-conducting region(s) 33 (i.e. in a vicinity of ion-conducting passageways 96) and one or more non-ion-conducting regions 35. Each
5 of ion-conducting regions 33 comprises an array of ion-conducting passageways 96. In the Figure 10B embodiment, non-ion-conducting regions 35A, 35B are located on either side of ion-conducting region 33.

10 [0063] Substrate material 92 may be converted to a relatively ion-conducting state to form ion-conducting passageways 96 using any suitable technique. By way of non-limiting example, ion-conducting passageways 96 may be formed by selectively exposing areas of substrate sheet 90 to chemicals, radiation, heat or the like. Masks may
15 be used to selectively expose areas of substrate sheet 90 to chemicals, radiation, heat or the like. Other lithographic, etching and or printed circuit board fabrication techniques may also be used.

[0064] In one particular embodiment, where non-ion-conducting
20 material 92 is a resin precursor to Nafion™, conversion of non-ion-conducting material 92 into an ion-conducting material 94 in the selected locations of ion-conducting passageways 96 may comprise masking sheet 90 and selectively hydrolyzing areas of sheet 90 by exposure to water.

25 [0065] Ion-conducting membranes formed by selective conversion of a substrate material may be tailored to provide different spatial membrane regions with different ion conductivity and/or mechanical characteristics to suit particular applications. For example, ion-
30 conducting passageways 96 formed by selective conversion may be formed to have characteristics (e.g. size, shape, density and/or

arrangement) and/or parameters (e.g. L , D , L/D , γ) similar to openings 24 (and/or ion-conducting passageways 27) described above. Ion-conducting passageways 96 may have different characteristics and/or parameters in different regions of sheet 90. Such different

5 characteristics and/or parameters may vary smoothly or may vary discretely. Sheet 90 may be fabricated from a plurality of layers in accordance with the embodiments described above. One or more layers may be added to sheet 90 as described above.

10 [0066] Figure 10C depicts the application of optional skins 62, 64 of ion-conducting material to sheet 90. Skins 62, 64 may be applied using any of the techniques described above, for example.

[0067] Those skilled in the art will appreciate that there are energy

15 losses associated with the conduction of ions through the membranes described above. In some cases, it is desirable to minimize the losses associated with the conduction of ions through a membrane (or a portion of a membrane). Referring to the embodiment of Figure 7B as an example, the inventors have determined, that for a given core

20 thickness L_{core} and parameter ratio L/D , there is an optimal skin thickness L_{skin} which provides minimum losses across membrane. If the skin thickness L_{skin} is below the optimum level, then the overall membrane losses will be relatively high and will increase with further decreases in skin thickness L_{skin} below the optimum level. Conversely,

25 if the skin thickness L_{skin} is above the optimum level, then the overall membrane losses will be relatively high and will increase with further increases in skin thickness L_{skin} above the optimum level.

[0068] In some embodiments of the invention, the optimum skin

30 layer thickness L_{skin} is in a range of 5-50 microns. In some

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embodiments, the optimum skin layer thickness L_{skin} is in a range of 0.25 to 5 times the thickness of the core layer L_{core} .

[0069] The ion-conducting membranes disclosed above are
5 capable of providing desired conductivity, gas permeability and
mechanical strength characteristics that can be varied at the designer's
discretion over the spatial extent of the membrane. This affords a
designer great design flexibility and allows the local tuning of
mechanical and electrical parameters to best meet the competing needs
10 of ion conductivity and mechanical strength within a fuel cell or similar
system.

[0070] The invention may be provided in the form of
electrochemical cells of any suitable type which incorporate membranes
15 according to the invention. Some embodiments of the invention provide
fuel cells or membrane-electrode assemblies for fuel cells.

[0071] As will be apparent to those skilled in the art in the light of
the foregoing disclosure, many alterations and modifications are
20 possible in the practice of this invention without departing from the
spirit or scope thereof. Accordingly, the scope of the invention is to be
construed in accordance with the substance defined by the following
claims.

CLAIMS:

1. A membrane comprising:
a substrate comprising an ion-conducting region in which ions can pass through the substrate and a non-ion-conducting region in which the ions cannot pass through the substrate;
wherein in the ion-conducting region, the substrate having one or more ion-conducting passageways that extend through the substrate; and the passageways contain an ion-conducting material.
2. A membrane according to claim 1, wherein the ion-conducting region comprises a plurality of ion-conducting passageways.
3. A membrane according to claim 1 or 2, wherein each of the passageways penetrates the substrate substantially perpendicularly.
4. A membrane according to claim 1, 2 or 3, wherein each one of the plurality of passageways comprises a hole cleanly cut directly through the substrate.
5. A membrane according to any one of claims 1-4, wherein the substrate comprises a substantially non-porous region corresponding to the non-ion-conducting region of the membrane.
6. A membrane according to claim 5, wherein the ion-conducting region of the substrate is surrounded by the non-porous region of the substrate.
7. A membrane according to any one of the preceding claims, wherein each passageway has a maximum transverse dimension (D) that is less than or equal to about 2500 microns.
8. A membrane according to any one of the preceding claims, wherein a transverse center to center spacing between nearest neighboring passageways (L) is less than or equal to about 5000 microns.

9. A membrane according to any one of the preceding claims, wherein a maximum transverse dimension (D) of each passageway and a transverse center to center spacing between nearest neighboring passageways (L) are selected such that a parameter ratio (L/D) is less than or equal to about 2.5.
10. A membrane according to any one of the preceding claims, wherein each passageway has a transverse cross-sectional area less than or equal to about $1 \times 10^{-5} \text{ m}^2$.
11. A membrane according to any one of the preceding claims, wherein a ratio of a total transverse cross-sectional area of the ion-conducting region to a total transverse cross-sectional area of the passageways (γ) is less than or equal to 2.5.
12. A membrane according to any one of the preceding claims, wherein a minimum transverse dimension of each passageway is greater than 25 microns.
13. A membrane according to any one of the preceding claims, wherein the passageways include passageways having transverse cross-sections that include at least one of: substantially circular, substantially hexagonal, substantially rectangular and substantially slit-shaped.
14. A membrane according to any one of the preceding claims comprising a first skin layer of ion-conducting material located on a first side of the substrate, wherein the ion-conducting material of the first skin layer is in contact with the ion-conducting material of at least one of the passageways.
15. A membrane according to claim 14, comprising a second skin layer of ion-conducting material located on a second side of the substrate, wherein the ion-conducting material of the second skin layer is in contact with the ion-conducting material of at least one of the passageways.

16. A membrane according to any one of claims 1-13 comprising a first skin layer of ion-conducting material, the first skin layer located on a first side of the substrate and extending transversely over at least a first portion of a porous region of the substrate such that the ion-conducting material of the first skin layer is in contact with the ion-conducting material of at least one of the passageways.
17. A membrane according to claim 16, comprising a second skin layer of ion-conducting material, the second skin layer located on a second side of the substrate and extending transversely over at least a second portion of the porous region of the substrate such that the ion-conducting material of the second skin layer is in contact with the ion-conducting material of at least one of the passageways.
18. A membrane according to claim 14 or 16, wherein the ion-conducting material in the first skin layer is the same as the ion-conducting material in the passageways.
19. A membrane according to claim 14 or 16, wherein the ion-conducting material in the first skin layer is different from the ion-conducting material in the passageways.
20. A membrane according to claim 15 or 17, wherein the ion-conducting material in the first skin layer is different than the ion-conducting material in the second skin layer.
21. A membrane according to claim 15 or 17, wherein the first and second skin layers have thicknesses (L_{skin}) that are substantially the same.
22. A membrane according to claim 15 or 17, wherein the first and second skin layers have thicknesses (L_{skin1} and L_{skin2}) that are in a range of 5-50 microns.
23. A membrane according to claim 15 or 17, wherein the first and second skin layers each comprises the same ion-conducting material.
24. A membrane according to claim 15 or 17, wherein the substrate has a thickness

(L_{core}), the first and second skin layers have thicknesses (L_{skin1} and L_{skin2}) and wherein a ratio of the thicknesses (L_{skin1} and L_{skin2}) of the first and second skin layers to the thickness (L_{core}) of the substrate is in a range of 0.25 to 5.

25. A membrane according to any one of the preceding claims, wherein the substrate comprises a plurality of layers.
26. A membrane according to claim 25, wherein at least one of the plurality of layers of the substrate comprises a mesh material.
27. A membrane according to any one of the preceding claims, wherein the substrate is penetrated by one or more vias, the vias transversely spaced apart from the ion-conducting region of the substrate.
28. A membrane according to claim 27, wherein the vias are filled with ion-conducting material.
29. A membrane according to claim 28, wherein the ion-conducting material that fills the vias is contiguous with the ion-conducting material that fills the passageways.
30. A membrane according to any one of the preceding claims, wherein the ion-conducting region comprises a plurality of ion-conducting regions, each ion-conducting region comprising one or more corresponding ion-conducting passageways that extend through the substrate, each ion-conducting passageway comprising the ion-conducting material.
31. A membrane according to claim 30, wherein the ion-conducting regions are transversely spaced apart from one another.
32. A membrane according to claim 30 or 31, wherein the one or more ion-conducting passageways corresponding to each ion-conducting region differ in at least one of: passageway size, passageway shape, passageway density and/or arrangement of passageways.

33. A membrane according to any one of the preceding claims, wherein the substrate comprises a copolymer of tetrafluoroethylene and perfluoro-3, 6-dioxo-4-methyl-7-octenesulfonyl fluoride.
34. A membrane according to any one of the preceding claims, wherein the substrate comprising a sheet of substantially non-ion-conducting material wherein the passageways comprise a hydrolyzed form of the substantially non-ion-conducting material that is ion-conducting.
35. A membrane according to any one of claims 1-33, wherein the passageways and substrate are formed of a material having an ion-conducting form and a non-ion-conducting form wherein the passageways comprise the ion-conducting form of the material and the substrate surrounding the passageways comprises the non-ion-conducting form of the material.
36. A membrane according to any one of the preceding claims, wherein the ion-conducting material comprises an ionomer.
37. A membrane according to any one of claims 4-33 or claim 36, wherein the ion-conducting material provides a first skin layer on a first side of the substrate, the skin layer extending transversely past a perimeter of an opening of the one or more passageways.
38. A membrane according to claim 37, wherein the substrate is penetrated by one or more vias, the vias transversely spaced apart from the at least one opening and the vias filled with ion-conducting material that is contiguous with the ion-conducting material in the first skin layer.
39. A membrane according to claim 38 comprising a second skin layer of ion-conducting material on a second side of the substrate, the ion-conducting material in the second skin layer contiguous with the ion-conducting material in the vias.

40. A membrane according to any one of claims 2-39, wherein the plurality of ion-conducting passageways are arranged to form an ordered array.
41. An electrochemical cell comprising:
 - a membrane according to any one of claims 1-40 and having first and second major surfaces, wherein, in the ion-conducting region the membrane permits ions to pass through the membrane between the first and second major surfaces, and in the non-ion-conducting region the first and second major surfaces of the membrane are not ion conducting and the membrane is substantially impermeable to ions, the passageways having an ion-conductivity that is greater than an ion-conductivity of portions of the substrate that surround the passageways, the membrane separating first and second reactant manifolds,
 - a first electrode in the first reactant manifold and a second electrode in the second reactant manifold.
42. An electrochemical cell according to claim 41, wherein the passageways are arranged in a regular array in the ion-conducting region.
43. An electrochemical cell according to claim 41 or 42, wherein the electrochemical cell comprises an electrolysis cell.
44. An electrochemical cell according to claim 41 or 42, wherein the electrochemical cell comprises a fuel cell.
45. An electrochemical cell according to claim 44, wherein the first and second reactant manifolds respectively comprise a fuel manifold and an oxidant manifold.