MEMBRANES AND ELECTROCHEMICAL CELLS INCORPORATING SUCH MEMBRANES

Related Applications

[0001] The subject matter of this application is related to that of a co-owned application entitled "ELECTROCHEMICAL CELLS HAVING CURRENT CARRYING STRUCTURES UNDERLYING ELECTROCHEMICAL REACTION LAYERS" filed concurrently herewith and a co-owned application entitled "ELECTROCHEMICAL CELLS FORMED ON PLEATED SUBSTRATES" filed concurrently herewith, 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, both of which are hereby incorporated by reference herein.

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 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 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.

[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 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 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 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 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™ 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 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 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 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, 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 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.

[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 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.

[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 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 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 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.

[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.

[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.

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

Brief Description of the Drawings

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

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;

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

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

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;

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;

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;

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;

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.

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 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 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 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 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 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 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** 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**.

[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 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**. 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.

[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**.

[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 comprise, for example, a material selected from:

- polyamide films,
- polyimide films, such as Kapton™,
- polyethylene films,
- Teflon™ films,
- 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 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** of substrate **21** to a second side **37** of substrate **21**. Ion-conducting material **26** is relatively more ion-conductive than the surrounding

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 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:

- chemical etching;
- laser micromachining;
- laser drilling;
- mechanical drilling;
- milling;
- punching;
- calendaring;
- printed circuit board fabrication techniques;
- lithographic fabrication techniques;
- mechanical dies; and
- 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.

[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 **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.

[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;
- 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 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 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**.

[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 transverse cross-section and are arranged in a hexagonal packing array. The parameters **D** (i.e. the widest dimension of passageways **27**) and **L**

(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 $5x10^{-8}$ m^2. In other embodiments, passageways **27** have cross-sectional areas not exceeding 1×10^{-5} 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.

[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

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.

[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 openings **24** in different regions of substrate **21**, one can provide different mechanical properties and/or different ion-conducting properties in those different regions.

[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-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 the vicinity of the fuel cell's compressive seals.

[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.

[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 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.

[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. 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 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 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. For example, the size of their openings **24**, the density of openings **24**, the shape of openings **24** and/or the arrangement or 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**.

[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 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 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 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 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.

[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 $\mathbf{L_{core}}$ of substrate **21**. In other embodiments, the thickness of ion-conducting material **26** (and the ion-conducting passageways **27**) differ from the thickness $\mathbf{L_{core}}$ 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 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 $\mathbf{L_{skin}}$ 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

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.

[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**.

[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 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.

[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** 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 **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 1½**L**, where **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 a locations that are transversely spaced apart from corresponding porous region(s) **30** by a distance of at least 3**L**.

[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 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 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 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.

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

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 a 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 tetrafluoroethlyene and perfluoro-3, 6-dioxa-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

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 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**.

[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 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 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.

[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-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 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.

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

[0068] In some embodiments of the invention, the optimum skin layer thickness $\mathbf{L_{skin}}$ is in a range of 5-50 microns. In some

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

[0069] The ion-conducting membranes disclosed above are 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 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 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 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.

WHAT IS CLAIMED IS:

1. An ion-conducting membrane comprising an ion-conducting region, the ion-conducting region comprising a substrate having one or more ion-conducting passageways that extend through the substrate, each passageway comprising an ion-conducting material that is relatively more ion-conductive than the substrate.

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 2 wherein each passageway comprises a corresponding opening that penetrates the substrate and is filled with the ion-conducting material.

4. A membrane according to claim 3 wherein the substrate is penetrated by a plurality of openings in a porous region of the substrate, the porous region of the substrate corresponding to the ion-conducting region of the membrane.

5. A membrane according to claim 4 wherein the substrate comprises a substantially non-porous region corresponding to a non-ion conducting region of the membrane.

6. A membrane according to claim 5 wherein the porous region of the substrate is surrounded by the non-porous region of the substrate.

7. A membrane according to claim 2 wherein each passageway has a maximum transverse dimension (D) that is less than or equal to about 2500 microns.

8. A membrane according to claim 2 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 claim 2 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) that is less than or equal to about 2.5.

10. A membrane according to claim 2 wherein each passageway has a transverse cross-sectional area less than or equal to about 1×10^{-5} m^2.

11. A membrane according to claim 2 wherein a ratio of a total transverse cross-sectional area of the ion-conducting region to a total transverse cross-sectional area of the plurality of passageways (γ) is less than or equal to 2.5.

12. A membrane according to claim 2 wherein a minimum transverse dimension of each passageway is greater than 25 microns.

13. A membrane according to claim 2 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 claim 2 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 claim 4 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 the 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 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 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 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 wherein the ion-conducting material in the first skin layer and the ion-conducting material in a first portion of the passageways is different than the ion-conducting material in the second skin layer and a second portion of the passageways.

22. A membrane according to claim 15 wherein the first and second skin layers have thicknesses (L_{skin}) that are substantially the same.

23. A membrane according to claim 15 the first and second skin layers have thicknesses (L_{skin1} and L_{skin2}) that are in a range of 5-50 microns.

24. A membrane according to claim 15 wherein the first and second skin layers each comprise the same ion-conducting material.

25. A membrane according to claim 15 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.

26. A membrane according to claim 3 wherein the substrate comprises a plurality of layers.

27. A membrane according to claim 26 wherein at least one of the plurality of layers of the substrate comprises a mesh material.

28. A membrane according to claim 4 wherein the substrate is penetrated by one or more fabrication vias, the fabrication vias transversely spaced apart from the porous region of the substrate.

29. A membrane according to claim 28 wherein the fabrication vias are filled with ion-conducting material.

30. A membrane according to claim 29 wherein the ion-conducting material that fills the fabrication vias is contiguous with the ion-conducting material that fills the passageways.

31. A membrane according to claim 1 comprising 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.

32. A membrane according to claim 31 wherein the ion-conducting regions are contiguous with one another.

33. A membrane according to claim 31 wherein the ion-conducting regions are transversely spaced apart from one another.

34. A membrane according to claim 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.

35. A membrane according to claim 2 wherein the passageways are formed by converting the substrate to a relatively more ion conductive state in selected locations corresponding to the passageways.

36. A membrane according to claim 35 wherein the sheet of substantially non-ion-conducting material comprises a copolymer of tetrafluoroethlyene and perfluoro-3, 6-dioxa-4-methyl-7-octenesulfonyl fluoride.

37. A membrane according to claim 35 wherein the sheet of substantially non-ion-conducting material is converted to the relatively more ion conductive state by hydrolyzation.

38. A membrane according to claim 2 wherein the passageways are formed by converting the substrate to a relatively less ion conductive state in selected locations corresponding to locations that surround the passageways.

39. A fuel cell comprising a membrane according to claim 1.

40. An electrolysis cell comprising a membrane according to claim 1.

41. A membrane according to claim 1 wherein the ion-conducting material comprises an ionomer.

42. An ion-conducting membrane comprising:

a substrate penetrated by a plurality of openings in a porous region thereof;

an ion-conducting material which fills the openings to provide a plurality of ion-conducting passageways through the substrate, the ion-conducting material being relatively more ion conductive than the substrate.

43. An ion-conducting membrane comprising:

a substrate penetrated by at least one opening;

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;

wherein the ion-conducting material is relatively more ion-conductive than the substrate.

44. A membrane according to claim 43 wherein the substrate is penetrated by one or more fabrication vias, the fabrication vias transversely spaced apart from the at least one opening and the fabrication vias filled with ion-conducting material that is contiguous with the ion-conducting material in the first skin layer.

45. A membrane according to claim 44 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 fabrication vias.